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A New Synthesis of (E)-1-Alkyl-1-trimethylsilylpropenes via Hydroboration of 3-Chloro-1-trimethylsilylpropyne with Dialkylboranes

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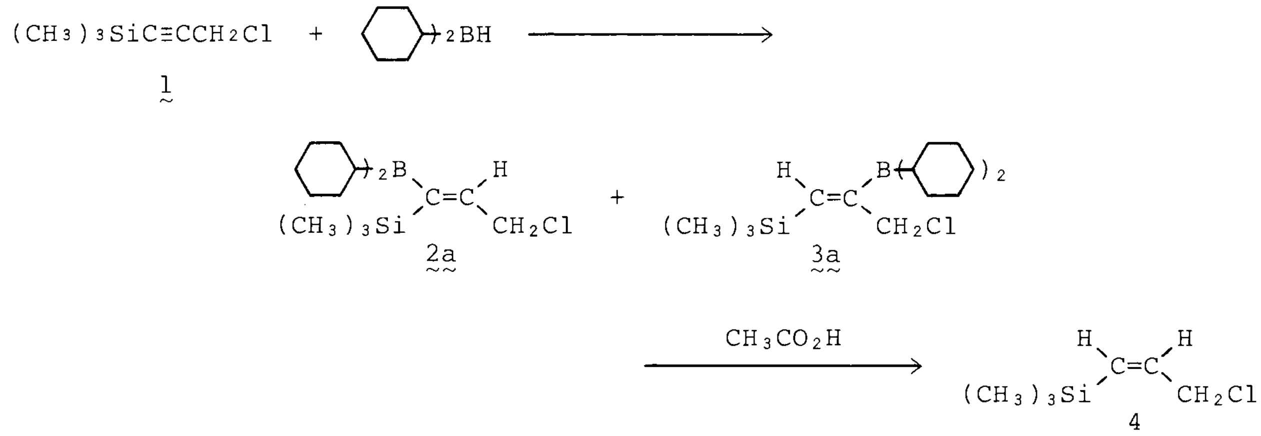
The successive treatment of 3-chloro-1-trimethylsilylpropyne with dialkylboranes and aqueous sodium hydroxide provided (E)-1-alkyl-1-trimethylsilylpropenes whose alkyl groups were derived from a terminal or internal alkene via dialkylboranes.

Alkenylboranes have attracted much attention as versatile intermediates in organic synthesis.1) In the course of our study of functionally substituted alkenylboranes,2) we became interested in monohydroboration of 3-chloro-1-trimethylsilylpropyne (**1**) with dialkylboranes. The monohydroboration product, expected to be provided, has three functional groups in addition to a carbon-carbon double bond, both a dialkylboryl group and a trimethylsilyl group on the double bond, and a chlorine atom on the allylic carbon atom. Thus, the product has a possibility to provide versatile compounds by applying reactions characteristic of the respective functional groups. We wish to report a synthesis of (E)-1-alkyl-1-trimethylsilylpropenes (**6**) via the monohydroboration of compound **1** with dialkylboranes followed by reaction with aqueous sodium hydroxide.

A stoichiometric hydroboration of compound **1** with dicyclohexylborane, prepared by reaction of cyclohexene with BH_3 in tetrahydrofuran (THF), was carried out at 0 °C for 2 h. The hydroboration mixture was protonolyzed with acetic acid to give (Z)-3-chloro-1-trimethylsilylpropene (**4**)3) in a quantitative yield (Scheme 1). Both complete monohydroboration of compound **1** and complete cis-addition of the dicyclohexylboryl group and the hydrogen atom were thus confirmed by the above result.4)

The hydroboration mixture was treated with an excess amount of aqueous sodium hydroxide at 0 °C for 1 h. By column chromatography of the work-up reaction mixture, highly pure (E)-1-cyclohexyl-1-trimethylsilylpropene (**6a**)5) was obtained in 70% yield based on starting amount of **1** (entry 1).



Scheme 1.

Treatment of product 6a with hydroiodic acid, a method for conversion of the carbon-silicon bond of alkenyltrimethylsilanes into a carbon-hydrogen bond with retention of configuration,[6] afforded (Z)-1-cyclohexylpropene[7] with a high stereoselectivity. The configuration of product 6a was thus assigned on the basis of the above result. The synthesis of compounds 6 was also applicable to such dialkylboranes as derived from terminal or sterically unhindered internal alkenes (entries 3-7). For example, when bis-(2-phenylpropyl)borane derived from 2-phenylpropene by a modified hydroboration procedure[8] was used as the monohydroborating agent for compound 1, a similar treatment[9] of the hydroboration mixture provided (E)-5-phenyl-3-trimethylsilyl-2-hexene (6e) in 90% yield. These results are summarized in Table 1.

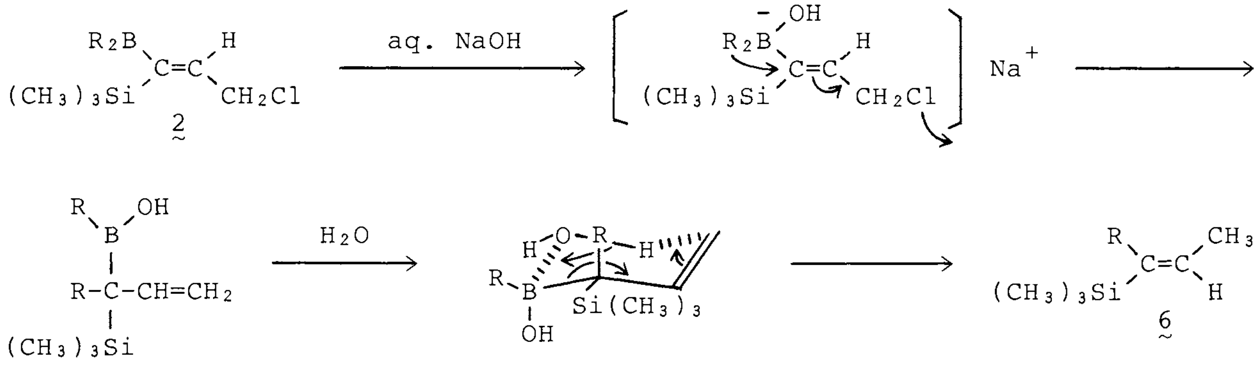
The formation of compounds 6 is speculated as follows. Treatment of

Table 1. Successive Reaction of Compound 1 with Dialkylboranes and Aqueous Sodium Hydroxide

Entry	R of R_2BH	Product	Yield/%[a]
1	$c\text{-}C_6H_{11}$	6a	70
2	$(CH_3)_2CHCH(CH_3)$	6b	31
3[b]	$n\text{-}C_6H_{13}$	6c	57
4[b]	$n\text{-}C_3H_7CH(CH_3)CH_2$	6d	69
5[b]	$C_6H_5CH(CH_3)CH_2$	6e	90
6[b]	$c\text{-}C_5H_9$	6f	73
7[b]	$exo\text{-}C_7H_{11}$[c]	6g	60

a) Isolated yield and based on starting amount of 1 used.
b) Ref. 8. c) exo-Norbornyl.

(E)-(3-chloro-1-trimethylsilylpropenyl)dialkylborane (2) in the hydroboration mixture with aqueous sodium hydroxide results in a concomitant migration of an alkyl group from the boron atom to the α-alkenyl carbon atom and an elimination of the allylic chlorine atom via a borate complex to give the corresponding allylborane (5). Intermediate 5 is hydrolyzed through a cyclic transition state, where the less hindered hydroxyl group on the boron atom occupies an axial position and the trimethylsilyl group occupies an equatorial position because of an affinity of silicon atom for oxygen atom (Scheme 2). A similar migration-elimination reaction occurs in the case of alkenylboranes having a chloromethyl group on the β-alkenyl carbon atom.[2c,10)]



2

5

6

Scheme 2.

Vinylsilanes are useful intermediates in organic synthesis and various reactions have been proposed for their synthesis.[11)] In some reports, reactions including hydroboration procedure, via monohydroboration of 1-trimethylsilyl-1-alkynes with dicyclohexylborane[12)] and a trialkylalkynylborate process,[13)] have been recomended for regio- and stereoselective synthesis of alkenyltrimethylsilanes. In the former reaction, the dicyclohexylboryl group is used merely as an intermediary substituent. In the latter reaction, one of three alkyl groups on the boron atom is introduced into the β-alkenyl carbon atom of the resulting alkenyltrimethylsilanes. The present reaction provides a new synthesis of alkenyltrimethylsilanes in which the alkyl group derived from an alkene is introduced into the trimethylsilylated alkenyl carbon atom in an excellently stereoselective manner.

References

1) For example: A. Pelter, K. Smith, and H. C. Brown, "Borane Reagents," Academic Press, London (1988), Part 4.
2) For example: a) M. Hoshi, Y. Masuda, and A. Arase, J. Chem. Soc., Chem.

Commun., 1985, 714; b) M. Hoshi, Y. Masuda, and A. Arase, Bull. Chem. Soc. Jpn., 59, 659 (1986); c) A. Arase and M. Hoshi, J. Chem. Soc., Chem. Commun., 1987, 531; d) M. Hoshi, Y. Masuda, and A. Arase, Bull. Chem. Soc. Jpn., 63, 447 (1990).

3) **4**: ^{1}H NMR ($CDCl_3$) δ=0.16 (s, 9H), 4.08 (d, J=7.8 Hz, 2H), 5.78 (d, J=13.7 Hz, 1H), and 6.39 (dt, J=13.7 and 7.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=0.31 (CH_3- x 3), 44.20 (-CH_2-), 135.36 (-CH=), and 142.52 (-CH=); IR (film) 2950, 2920, 2845, 1600, 1450, 1250, 850, 835, and 770 cm^{-1}; MS m/z 148 and 150 (M^{+}).

4) Detail study on the regioselectivity of the hydroboration will be reported elsewhere.

5) **6a**: ^{1}H NMR ($CDCl_3$) δ=0.08 (s, 9H), 0.90-2.00 (m, 10H), 1.69 (d, J=6.8 Hz, 3H), 2.30-2.70 (m, 1H), and 5.80 (q, J=6.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ=1.22 (CH_3- x 3), 14.86 (CH_3-), 26.56 (-CH_2-), 27.31 (-CH_2- x 2), 32.91 (-CH_2- x 2), 41.42 (>CH-), 133.93 (-CH=), and 147.55 (>C=); IR (film) 3010, 2920, 2840, 1590, 1440, 1255, 1245, 955, 885, 845, 830, 750, and 675 cm^{-1}; MS m/z 196 (M^{+}).

6) K. Utimoto, M. Kitai, and H. Nozaki, Tetrahedron Lett., 1975, 2825.

7) ^{1}H NMR ($CDCl_3$) δ=0.80-2.00 (m, 10H), 1.61 (dd, J=6.4 and 1 Hz, 3H), 2.10-2.40 (m, 1H), and 5.00-5.50 (m, 2H); ^{13}C NMR ($CDCl_3$) δ=12.89 (CH_3-), 26.02 (-CH_2- x 2), 26.10 (-CH_2-), 33.13 (-CH_2- x 2), 35.87 (>CH-), 121.77 (-CH=), and 136.95 (-CH=); IR (film) 3000, 2920, 2840, 1735, 1655, 1440, 1400, 1370, 955, 885, 835, and 705 cm^{-1}; MS m/z 124 (M^{+}).

8) The alkene was hydroborated with monobromoborane-dimethyl sulfide complex (25 °C, 1 h) and the resulting dialkylbromoborane was treated with an equimolar amount of diisobutylaluminium hydride (added at -78 °C, then 0 °C, 3 h and r.t., 2 h) to give the desired dialkylborane.

9) In this case the hydroboration mixture was added to a mixture of aqueous sodium hydroxide, hexamethylphosphoric triamide (HMPT), and THF at -15 °C.

10) G. Zweifel and A. Horng, Synthesis, 1973, 672.

11) For example: E. W. Colvin, "The Chemistry of the Metal-Carbon Bond," ed by F. R. Hartley, John Wiley & Sons, Chichester (1987), Vol. 4, Chap. 6.

12) R. B. Miller and T. Reichenbach, Tetrahedron Lett., 1974, 543; K. Uchida, K. Utimoto, and H. Nozaki, J. Org. Chem., 41, 2941 (1976); K. Uchida, K. Utimoto, and H. Nozaki, Tetrahedron, 33, 2987 (1977).

13) P. Binger and R. Köster, Synthesis, 1973, 309; K. Utimoto, M. Kitai, M. Naruse, and H. Nozaki, Tetrahedron Lett., 1975, 4233; R. Köster and L. A. Hagelee, Synthesis, 1976, 118.

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