Tetrahedron Letters,Vol.22,No.52,pp 5289-5292,1981 0040-4039/81/525289-04$02.00/0
Printed in Great Britain

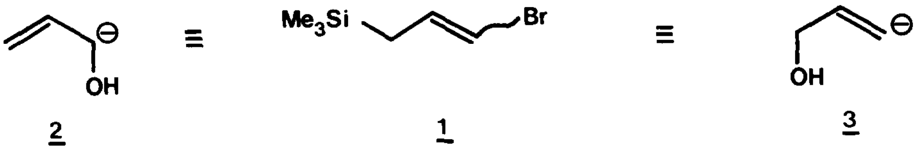
PREPARATION AND SYNTHETIC APPLICATION OF 3-BROMOALLYLTRIMETHYLSILANE AS HYDROXYPROPENYL SYNTHONS

Hisao Nishiyama, Shinzo Narimatsu, and Kenji Itoh*

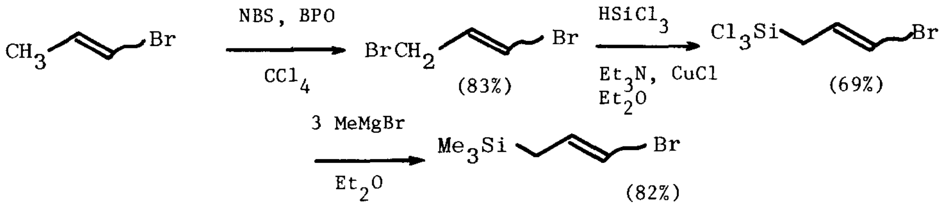
School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi, 440 Japan

Abstract: 3-Trimethylsilylpropen-1-yl group, as hydroxypropenyl synthons, was easily introduced to several epoxides with the corresponding Grignard reagent derived from 3-bromoallyltrimethylsilane. The introduced skeleton of allyltrimethylsilane was regiospecifically converted to 3-hydroxypropen-3-yl or 3-hydroxypropen-1-yl group.

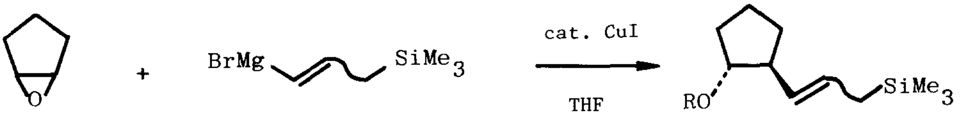
The preceding paper describes a regiospecific displacement of allylsilanes with phenylselenenyl cation providing a new route for the effective transformation of allylsilanes to allylic alcohols.[1] Alternatively, transformation via allylsulfides gave regio-isomeric allylic alcohols from allylsilanes.[1,2] We wish to describe here a new method for the introduction of two allylic alcohols skeletons (hydroxypropenyl groups) into several epoxides with 3-bromoallyltrimethylsilane 1 followed by the regiospecific reactions via allylselenides or allylsulfides. These methods provide the utility of 3-bromoallyltrimethylsilane 1 as a 3-hydroxypropen-3-yl synthon 2 or a 3-hydroxypropen-1-yl synthon 3.[3]



3-Bromoallyltrimethylsilane 1 was readily prepared in three steps according to the following scheme from commercially available 1-bromo-1-propene.[4] This process can be performed on large scale.[5]



Treatment of several epoxides 4 with 3-trimethylsilylpropen-1-yl Grignard reagent[6] generated from 1 in tetrahydrofuran in the presence of a catalytic amount of cuprous iodide[7] gave hydroxy allylsilanes 5 in good yields (Table 1). The hydroxy allylsilanes were readily acetylated with acetic anhydride in pyridine.

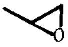
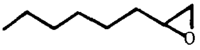
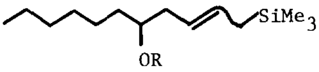
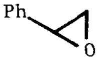
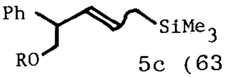
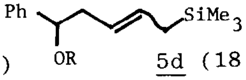
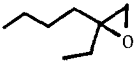
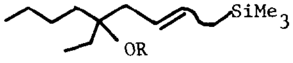
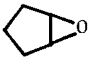
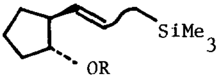
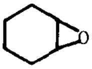
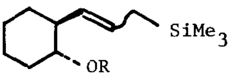


4e

5f (R= H)

6f (R= Ac)

Table 1 Reaction of Epoxides with 3-Trimethylsilylpropen-1-yl Grignard Reagent[a] and Acetylation of 5.

Entry	Epoxide 4		Hydroxy Allylsilane	5 (yield,%)[b]	6 (yield,%)[b]
				R= H	R= Ac
1		4a		5a (97)	6a (83)
2		4b		5b (88)	6b (96)
3		4c	 5c (63)  5d (18)		6c (97) 6d (94)
4		4d		5e (69)	6e (33)[c]
5		4e		5f (74)	6f (92)
6		4f		5g (57)	6g (96)

a. The Grignard reagent(1.5 equiv. of 4), CuI(10 mol % of 4), THF, -20°C(1 hr) then 0 °C(2 hr). For this reaction condition in detail, see ref. 7. b. Isolated yield. c. 4-Dimethylaminopyridine was used, but many side reactions were observed.

These allylsilanes 6 were next subjected to reaction with phenylseleneyl chloride and following treatment with anhydrous tin(II) chloride to give allylselenides 7 (Table 2). Subsequent oxidation of 7 with hydrogen peroxide and pyridine afforded regiospecifically secondary allylic alcohols 8 in good yields.

This transformation of allylsilanes to allylic alcohols was demonstrated for a interesting utility of 3-bromoallyltrimethylsilane 1 as a synthetic equivalent of the 3-hydroxypropen-3-yl anion 2.

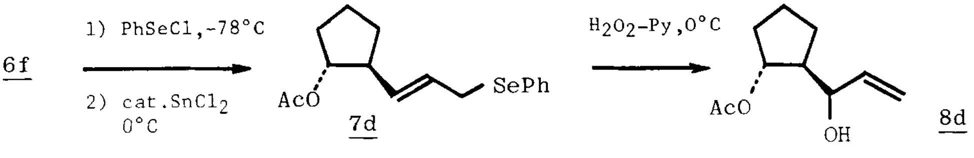
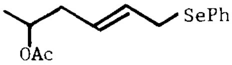
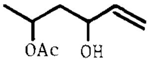
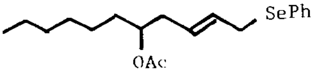
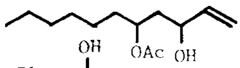
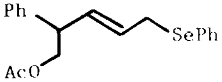
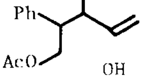
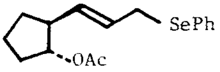
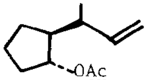
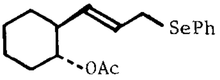
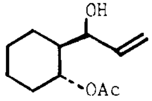


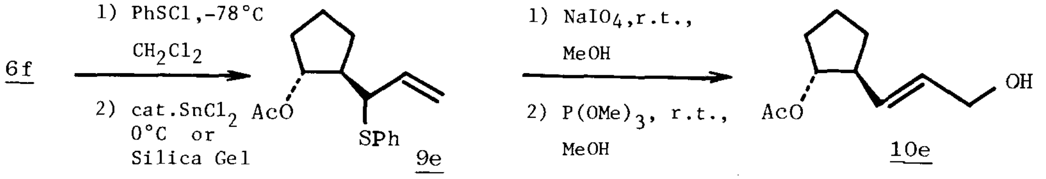
Table 2 Transformation of Allylsilanes 6 to Allylic Alcohols 8.[a]

Entry	Allylsilane 6	Allylselenide 7(yield,%)[b]		Allylic Alcohol 8(yield,%)[c]	
1	6a		7a(91)		8a(85)
2	6b		7b(88)		8b(82)
3	6c		7c(86)		8c(81)
4	6f		7d(81)		8d(78)
5	6g		7e(78)		8e(90)

a. PhSeCl(1.3-1.5 equiv. of 6), $SnCl_2$(0.3-0.5 equiv. of 6). The other reaction condition and the work up were the same as previously reported (ref. 1). b. Isolated yield after purification by florisil column chromatography(ether-hexane). c. Isolated yield.

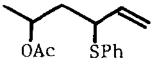
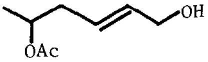
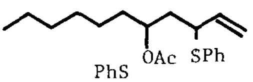
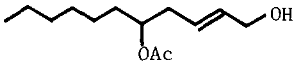
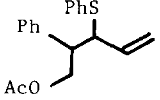
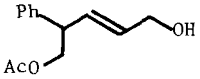
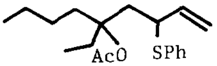
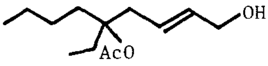
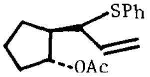
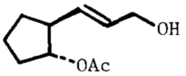
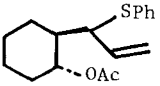
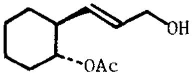
In contrast, the allylsilanes 6 were converted to the regio-isomeric allylic alcohols 10 by reaction with phenylsulfenyl chloride and by following oxidation process (Table 3).[1,2] The reaction of 6 with phenylsulfenyl chloride in dichloromethane at -78 °C gave the corresponding adducts, which were easily transformed to allylsulfides 9 by treatment with tin(II) chloride at room temperature for 6 hours or by passing through silica gel column several times.[8] The allylsulfides 9 were readily converted to allylic alcohols 10 by well known oxidative rearrangement with sodium metaperiodate in methanol at room temperature for 1 day and with trimethylphosphite.[3b,3c]

This regio-retentive transformation of allylsilanes to allylic alcohols provides a useful application of 1 as a synthetic equivalent of the 3-hydroxypropen-1-yl anion 3.



6f 9e 10e

Table 3 Transformation of Allylsilanes 6 to Allylic Alcohols 10.[a]

Entry	Allylsilane 6	Allylsulfide 9	(yield,%)[b]	Allylic Alcohol	10(yield,%)[b]
1	6a		9a (80)		10a (82)
2	6b		9b (87)		10b (73)
3	6c		9c (96)		10c (71)
4	6e		9d (67)		10d (69)
5	6f		9e (95)		10e (81)
6	6g		9f (85)		10f (71)

a. PhSCl(1.1 equiv. of 6), $SnCl_2$(0.2 equiv. of 6). b. Isolated yield after purification by silica gel column chromatography(ether-hexane). c. Isolated yield. $NaIO_4$(1.2 equiv. of 9), $P(OMe)_3$(1.0 equiv. of 9). See ref. 3b and 3c in detail.

References and Notes

1. H. Nishiyama, K. Itagaki, K. Sakuta, and K. Itoh, Tetrahedron Lett., preceding paper.
2. B. -W. Au-Yeung and I. Fleming, J. Chem. Soc., Chem. Comm., 79 (1977).
3. (a). E.J. Corey, B. Erickson, and R. Noyori, J. Am. Chem. Soc., 93, 1724 (1971).
(b). D.A. Evans, G.C. Andrews, T.T. Fujimoto, and D. Wells, Tetrahedron Lett., 1385, (1973). (c). Idem., ibid., 1389 (1973).
4. From Aldrich Chem. Co., No. B7820-3.
5. $BrCH=CHCH_2Br$, b.p. 59-64 °C/17 mmHg; $Cl_3SiCH_2CH=CHBr$, b.p. 85-91 °C/29 mmHg; $Me_3SiCH_2CH=CHBr$, b.p. 56-58 °C/19 mmHg. For this process, refer,N. Furuya and T. Sukawa, J. Organomet. Chem., 96(1975) C1-C3.
6. The formation of the Grignard reagent from 1 was fairly slow(ca. 2-3 hours at 50 °C). Sufficient activation of magnesium was necessary to initiate the reaction. 3-Chloroallyltrimethylsilane gave the corresponding Grignard reagent in a poor yield. See, M. Ochiai and E. Fujita, Tetrahedron Lett., 4369 (1980).
7. C. Huynh, F. Derguini-Boumechal , and G. Linstrumelle, Tetrahedron Lett., 1503 (1979).
8. See ref.1, note 7.

(Received in Japan 10 August 1981)