Tetrahedron Letters,Vol.23,No.12,pp 1267-1270,1982 0040-4039/82/121267-04$03.00/0
Printed in Great Britain

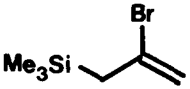
PREPARATION AND SYNTHETIC APPLICATION OF 2-BROMOALLYLTRIMETHYLSILANE AS A 1-HYDROXYMETHYLVINYL ANION EQUIVALENT

Hisao Nishiyama, Hiroshi Yokoyama, Shinzo Narimatsu, and Kenji Itoh*

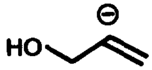
School of Materials Science, Toyohashi University of Technology,
Tempaku-cho, Toyohashi, 440 Japan

Abstract: The 1-trimethylsilylmethylvinyl group, as a 1-hydroxymethylvinyl equivalent, was readily introduced to epoxides with the corresponding Grignard reagent derived from 2-bromoallyltrimethylsilane. Obtained 2-(2-hydroxyethyl)-allylsilanes were converted to α-methylene-γ-lactones via diols.

Allylsilane has been recognized not only as a versatile reagent for a new type of carbon-carbon bond formation but also as a readily convertible functional group by reaction with a variety of electrophiles.[1] We wish to describe here a new method for the introduction of 1-trimethylsilylmethylvinyl group to several epoxides. This method and subsequent desilylative oxidation provide the utility of 2-bromoallyltrimethylsilane 1 as a 1-hydroxymethylvinyl anion equivalent 2, which serves to construct α-methylene-γ-lactone skeleton.

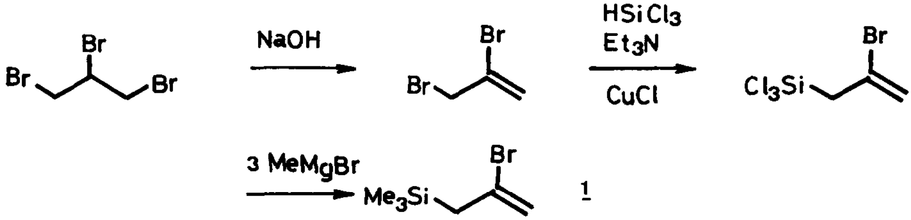


1



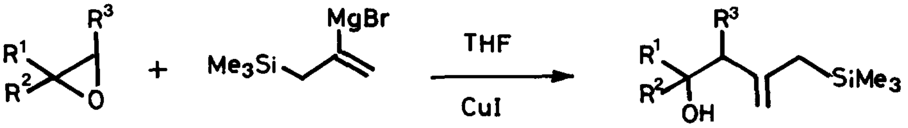
2

2-Bromoallyltrimethylsilane 1 was prepared in three steps from commercially available 1,2,3-tribromopropane[2]. The process of this sequence can be performed on a large scale. According to the reported method[3] 1,2,3-tribromopropane was converted to 2,3-dibromopropene by the action of sodium hydroxide. Treatment of 2,3-dibromopropene with trichlorosilane and triethylamine in the presence of a catalytic amount of cuprous chloride to give 2-bromoallyltrichlorosilane.[4] For large scale manipulation, there is no need to purify the trichloroallylsilane. The crude trichlorosilane can be directly added to an ether solution of methyl Grignard reagent to give 1 (63% yield from 2,3-dibromopropene).[5]



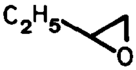
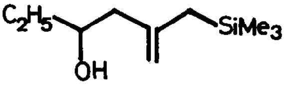
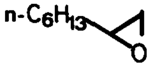
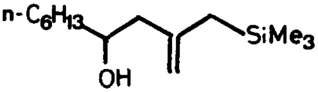
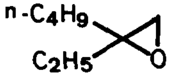
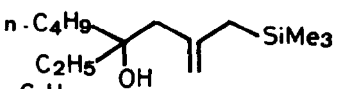
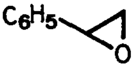
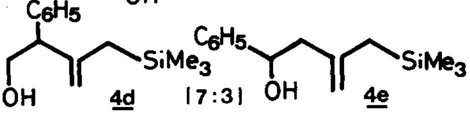
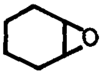
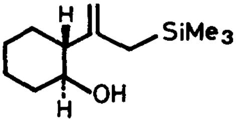
1

Several epoxides 3 were subjected to react with the 1-trimethylsilylmethylvinyl Grignard reagent generated from 1 in tetrahydrofuran in the presence of cuprous iodide to 2-(2-hydroxyethyl)allylsilanes 4 in good yields (Table 1).[6]



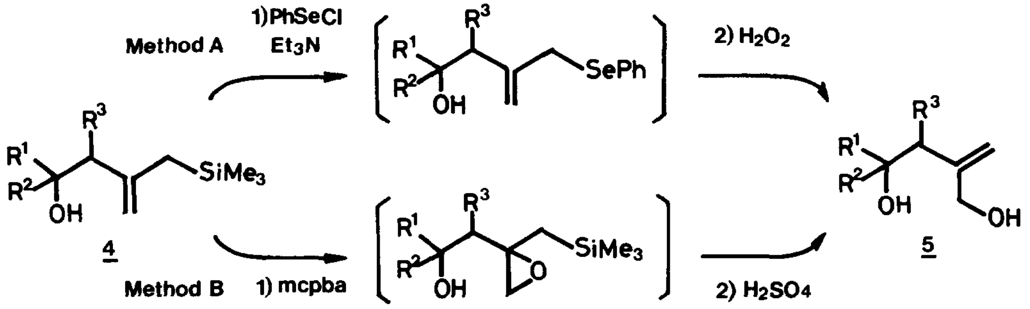
4

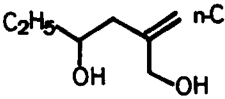
Table 1 Reaction of Epoxides and 1-Trimethylsilylmethylvinyl Grignard Reagent.[a]

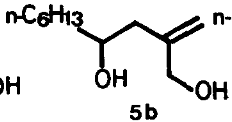
Entry	Epoxide 3	2-(2-Hydroxyethyl)allylsilane 4	Yield[b] (%)
1	 3a	 4a	83
2	 3b	 4b	82
3	 3c	 4c	93
4	 3d	 4d [7:3] 4e	95
5	 3e	 4f	85

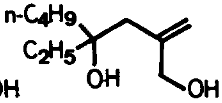
a. The Grignard reagent (1.6 equiv. to 3), CuI (10 mol% to 3), THF, -30 °C (1 hr) then 0 °C (ca. 2 hr). b. Isolated yield; after purification by silica gel column chromatography with ether-hexane as eluent.

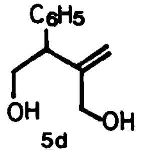
The 2-(2-hydroxyethyl)allylsilane 4 was treated with m-chloroperbenzoic acid (1.4 equiv. to 4) and sodium bicarbonate (2 equiv. to 4) in dichloromethane (0 °C, 1.0-1.5 hr), followed by a solution of aqueous sulfuric acid (0.3 N, 0.8 equiv. to 4) and tetrahydrofuran (volume ratio, 1:3) to afford diol 5. The diols were also obtained by treatment of 4 with phenylselenenyl chloride (2-3 equiv. to 4) and triethylamine (1 equiv.) in dichloromethane (-78 °C, 15 min), followed by oxidation with hydrogen peroxide (0 °C, 30 min). These transformation are shown in the following scheme.

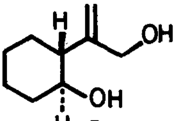



5a


5b

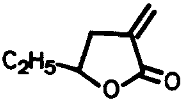

5c

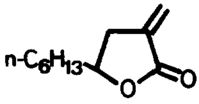

5d

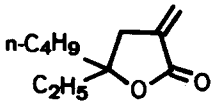

H 5e

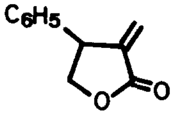
		5a	5b	5c	5d	5e
Method	A	–	69%	64%	–	53%
	B	80%	66%	53%	51%	–

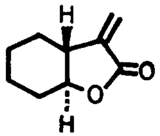
These results have shown that 2-bromoallyltrimethylsilane served as a synthetically useful 1-hydroxymethylvinyl anion.[7] Further application is described as follows. The diols 5 thus obtained are useful precursors to α-methylene-γ-lactones.[8] The diols (5a-5d) were treated with active manganese dioxide (15-30 weight fold of 5) in dichloromethane to give the corresponding lactones (6a-6d) by way of hemiacetals.[9] The diol 5e gave


6a (65%)

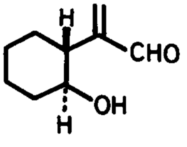

6b (71%)


6c (86%)

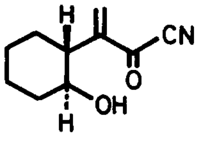

6d (77%)


6e (68% from 7)

the aldehyde 7 in 67% yield. The lactone 6e could be obtained by treatment of the aldehyde 7 with active manganese dioxide (20 weight fold), potassium cyanide (5 equiv.), and 18-crown-6 (ca. 10 mol% of 7) in terahydrofuran for 1 day.[10] This reaction may proceed via hydroxy cyanoketone 8 as in Corey's oxidation procedure of α,β-unsaturated aldehyde.[11]



7 (67% from 5e)



8

References and Notes

1. (a) A. Hosomi and H. Sakurai, Tetrahedron Lett., 1976, 1295.
   (b) A. Hosomi and H. Sakurai, J. Am. Chem. Soc., 99, 1673 (1977).
   (c) A. Hosomi, H.Hashimoto, and H. Sakurai, Tetrahedron Lett., 1980, 951.
   (d) As review: T.H. Chan and I. Fleming, Synthesis, 1979, 761.
2. Tokyo Kasei, T 0355.
3. R. Lespieau and M. Bourguel, Organic Syntheses, Coll. Vol. I, 209 (1956).
4. 2-Bromoallyltrichlorosilane: b.p. 98 °C/38 mmHg; ^{1}H-NMR(CDCl$_3$, TMS)δ 2.94 (s, 2H, SiCH$_2$), 5.6-5.9(m, 2H, C=CH$_2$) ppm.
5. 1: b.p. 64-65 °C/38-39 mmHg; ^{1}H-NMR(CDCl$_3$, TMS)δ 0.13(s, 9H, SiCH$_3$), 2.13 (s, 2H, SiCH$_2$), 5.1-5.4(m, 2H, C=CH$_2$)ppm.For this procedure in detail, see N. Furuya and T. Sukawa, J. Organomet. Chem., 96,C1-C3 (1975).
6. C. Huynh, F. Derguini-Boumechal, and G. Linstrummelle, Tetrahedron Lett., 1979, 1503.
7. E.J. Corey and G.N. Widiger, J. Org. Chem., 40, 2975 (1975).
8. (a) J.A. Marshall and R.H. Ellison, J. Am. Chem. Soc., 98, 4312 (1976).
   (b) R.M. Carlson, Tetrahedron Lett., 1978, 111.
9. ^{1}H-NMR (CDCl$_3$, TMS)δ ppm: 6a, 1.1(t,3H), 1.7(m,2H),2.2-3.3(m,2H), 4.57(m, 1H), 5.7(t,1H,J=2 Hz),6.27(dd,1H, J=2 Hz, 6Hz); 6b, 0.9-2.0(11H), 2.8(m, 2H), 4.49(dt,1H), 5.55(t,1H, J=2.6Hz), 6.13(t,1H, J=2.6Hz); 6c, 0.9-2.0 (11H), 2.73(t,2H,J=2.6Hz), 5.54(t,1H,J=2.6Hz),6.15(t,1H,J=2.6Hz); 6d, 4.73 (t,1H), 4.85(m,2H),5.43(d,1H,J=3Hz),6.37(d,1H,J=3Hz),7.3(bs,5H); IR (liquid film)ν cm^{-1}; 6a,1765, 1669; 6b, 1770, 1672; 6c, 1764, 1667; 6d, 1772, 1674.
10. 6e:^{1}H-NMR(CDCl$_3$,TMS)δ ppm, 1.0-2.7(9H),3.70(dt,1H,J=3.6Hz, 10.2 Hz), 5.33 (d,1H,J=3.2Hz), 5.69(d,1H,J=3.2Hz); IR(liquid film) ν cm^{-1}, 1771, 1668.
11. E.J. Corey, N.W. Gilman, and B.E. Ganem, J. Am. Chem. Soc., 90, 5616 (1968).

(Received in Japan 17 December 1981)