

Syntheses with Organoboranes. XI. Allylboration of Vinylic Epoxides with Allylic Dialkylboranes

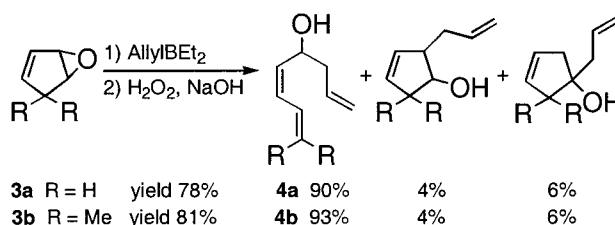
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ABSTRACT



Allylboration of representative vinylic epoxides with allyldiethylborane (1) and (2-cyclohexenyl)dicyclohexylborane (2) affords the corresponding 1,2- and 1,4-addition products. *cis*-1,2-Addition is favored in the reaction of 1 with 3,4-epoxycycloalkenes of six- to eight-membered rings. 3,4-Epoxy-cyclopentene (3a) and 5,5-dimethyl-3,4-epoxycyclopentene (3b) undergo five-membered ring opening during allylboration with 1 and 2, producing the corresponding (*Z*)-trienols (4a and 4b) with high stereoselectivity. 1,4-Addition of 1 and 2 to monoepoxides of 1,3-butadiene and isoprene is favored, producing predominantly the corresponding (*E*)-alcohols.

Vinylic epoxides are versatile synthetic building blocks, and their synthesis and reactions are extensively studied.¹ Recently, we described the kinetic resolution of vinylic epoxides with chiral dialkylboranes of high optical purity.² Earlier, we showed that the reduction of these compounds with borane and dialkylboranes proceeds with high stereoselectivity affording the corresponding allylic alcohols of (*Z*)-configuration.³

The addition of various organometallic reagents to vinylic epoxides provides an access to allylic and homoallylic alcohols.⁴ Thus, 1,2-addition products are favored by Grignard reagents,⁵ allylstannanes,⁶ and tetraallyllanthanoid complexes.⁷ 1,4-Addition predominates with organocopper reagents⁸ and copper-catalyzed reactions of organomagnesium⁹ and organozinc compounds.¹⁰ Vinylic tellurides,¹¹

organozinc,¹² and organosilicon¹³ compounds have also been used. However, mixtures of regio- and stereoisomers and rearranged products are often obtained. Clearly, new reagents are desirable.

The reactions of vinylic epoxides with organoboranes have not been extensively studied. Trialkylboranes react with 3,4-epoxy-1-butene under free radical conditions affording 1,4-addition products.¹⁴ The addition of 1-alkenylboranes in the presence of palladium and nickel complexes provides

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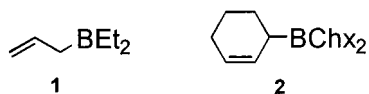
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mixtures of 1,2- and 1,4-addition products.¹⁵ Here, we wish to report the allylboration of vinylic epoxides. The reactions of allyldiethylborane (**1**) and (2-cyclohexenyl)dicyclohexylborane (**2**) with representative vinylic epoxides derived from acyclic and cyclic dienes were examined.

Allyldiethylborane was conveniently prepared in 81% yield by transmetalation of allylaluminumsesquibromide and *n*-amyl diethylborinate obtained by treatment of chlorodiethylborane with 1-pentanol.¹⁶ (2-Cyclohexenyl)dicyclohexylborane was synthesized by the hydroboration of 1,3-cyclohexadiene with dicyclohexylborane.¹⁷



3,4-Epoxy cyclopentene (**3a**) reacted readily with **1** in diethyl ether at room temperature to give one major product in good yield (Table 1). Surprisingly, it was not the expected

3-cyclopentenone formed by rearrangement of the starting epoxide, was obtained.¹⁹

In tetrahydrofuran **5a** was not formed but the amount of **6a** increased. Allylboration of 3,4-epoxy-5,5-dimethylcyclopentene²⁰ (**3b**) with **1** produced also the corresponding (*Z*)-trienol (**4b**). The reaction carried out in tetrahydrofuran was slower compared with **3a**, but the product was obtained in good purity and yield (Table 1).

Similarly, **2** reacted with **3a** to give the same type of product, (*Z*)-trienol (**7**), in moderate yield. (*Z*)-Configuration of the disubstituted double bond fixed in the ring is retained in the product.

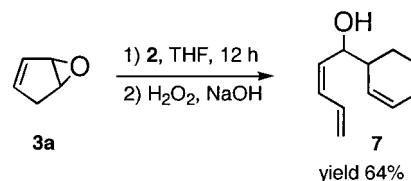
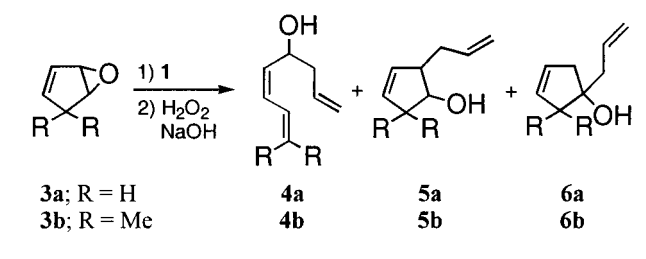


Table 1. Allylboration of **3a** and **3b** with **1** at Room Temperature



epoxide	solvent	time (h)	product composition ^a (%)			yield ^b (%)
			4	5^c	6^d	
3a ; R = H	Et ₂ O	3	90	4	6	78
3a ; R = Me	THF	4	88		12	80
3b ; R = H	Et ₂ O	24	73	12	15	77
3b ; R = Me	THF	12	93	4	3	81

^a Determined by GC analysis. ^b Isolated yields. ^c *cis/trans* mixture. Identified by hydrogenation and comparison with authentic samples of *cis*- and *trans*-2-propylcyclopentanols and 5,5-dimethyl-2-propylcyclopentanols, respectively. ^d Identified by GC comparison with authentic samples prepared by the reaction of allylmagnesium bromide with **3a** and **3b**, respectively.

1,2- or 1,4-addition product but the acyclic (*Z*)-trienol (**4a**) formed by the addition of allyl group and opening of both the epoxide and cyclopentene rings. Its structure and (*Z*)-configuration of the disubstituted internal double bond was established by 2D ¹H and ¹³C NMR analysis.¹⁸ Only 4% of the 1,2-addition product **5a** and 6% of **6a**, derived from

A stereoselective five-membered ring opening has also been observed in the hydrolysis of **3a** in water at pH ≥ 7 leading to the formation of (*Z*)-2,4-pentadienal, in addition to cyclopentanedioles and 3-cyclopentenone.²¹

The reactivity of 3,4-epoxycycloalkenes (**8a–c**) toward **1** decreases with the increasing cycloalkene ring size (Table 2). Thus, 3,4-epoxycyclohexene reacted in diethyl ether at

(17) Hydroboration of 1,3-cycloalkadienes, except 1,3-cyclopentadiene, with dialkylboranes provides preferentially the allylic borane derivatives: Brown, H. C.; Bhat, K. S.; Jadhav, P. K. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2633. The homoallylic borane derivative formed as a minor product (9%) does not interfere in the allylboration reaction.

(18) (*SZ*)-1,5,7-Octatrien-4-ol (**4a**). **Representative Procedure.** All operations were carried out under a nitrogen atmosphere. To a stirred solution of 3,4-epoxy-1-cyclopentene (**3a**) (1.23 g, 15 mmol) in diethyl ether (15 mL), was added allyldiethylborane (**1**) (1.65 g, 15 mmol) at room temperature. After 3 h, ¹¹B NMR analysis indicated no signal at δ 85 ppm corresponding to **1**. Ether was removed and THF (20 mL) was added. The mixture was cooled to 0 °C and oxidized with 3 M NaOH (6 mL) and 30% H₂O₂ (6 mL) for 4 h at room temperature. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 10 mL). The combined organic solutions were washed with brine and dried over anhydrous magnesium sulfate. The product was isolated by distillation: 1.45 g, 78% yield, bp 64–66 °C/3 mmHg. GC analysis on a capillary Supelcowax-10 column (30 m × 0.32 mm) revealed (*SZ*)-1,5,7-octatrien-4-ol (**4a**) (90%), 1-allyl-3-cyclopenten-1-ol (**6a**) (6%), and *cis/trans*-2-allyl-3-cyclopenten-1-ol (**5a**) (4%). An analytical sample of **4a** was separated by preparative GC. Anal. for C₈H₁₂O (124.18): calcd 77.38% C, 9.74% H; found 77.30% C, 9.78% H. ¹H and ¹H × ¹H COSY NMR (CDCl₃): δ 1.65 (s, 1H, OH), 2.32 (t, *J* = 6.5, 2H, CH₂), 4.64 (q, *J* = 8.5, 1H, HC–OH), 5.20 (m, 4H, C₍₁₎H₂, C₍₈₎H₂), 5.45 (t, *J* = 9.8, 1H, C₍₅₎H), 5.81 (m, 1H, C₍₂₎H), 6.08 (t, *J* = 11.1, 1H, C₍₆₎H), 6.62 (dt, *J* = 16.8, 10.6, 1H, C₍₇₎H). ¹³C NMR (CDCl₃): δ 42.02, 67.14, 118.28, 119.38, 130.72, 131.77, 133.39, 133.97. ¹H × ¹³C HETCOR NMR (CDCl₃) (correlation peaks): 2.31 (t, 2H) –41.82 (C₍₃₎H₂), 4.62 (q, 1H) –66.98 (HC₍₄₎OH), 5.20 (m, 4H) –118.01, 119.13 (C₍₁₎H₂, C₍₈₎H₂), 5.44 (t, 1H) –133.34 (C₍₅₎H), 5.80 (m, 1H) –133.87 (C₍₂₎H), 6.06 (t, 1H) –130.48 (C₍₆₎H), 6.63 (dt, 1H) –131.67 (C₍₇₎H). The ¹H and ¹³C NMR spectra were recorded on a Varian Gemini 200 instrument.

(19) For comparison, the reaction of allylmagnesium bromide with **3a** in diethyl ether at 0 °C gave *trans*-**5a** (42%), **6a** (23%), and the 1,4-addition product *trans*-4-allyl-2-cyclopenten-1-ol (35%).

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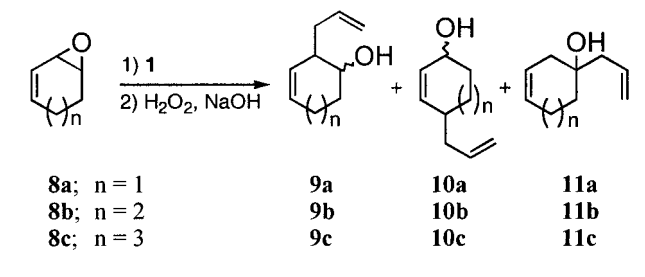
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Table 2. Allylboration of **8a–c** with **1**

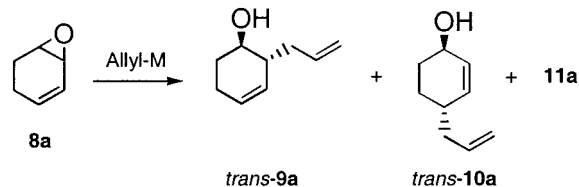
epoxide	solvent	temp (°C)	time (h)	product composition ^a (%)			yield ^b (%)
				9 (c/t) ^c	10 (c/t) ^c	11	
8a	Et ₂ O	20	5	81(72/28)	19(63/37)		82
8a	THF	20	24	82(63/37)	16(56/44)	2	69
8b	Et ₂ O	20	24	68(62/38)	32(41/59)		78
8b	THF	65	12	59(60/40)	39(43/57)	2	68
8c	neat	120	14	52(62/38)	48(52/48)		65

^a Determined by GC analysis. ^b Isolated yields. ^c The *cis/trans* ratio was established by hydrogenation to *cis/trans* 2- and 4-propyl-cyclohexanols and comparison with authentic samples by GC.

room temperature, whereas 3,4-epoxycyclooctene required prolonged heating under neat conditions.

The 1,2-addition of **1** to these epoxides is favored over 1,4-addition, and essentially no rearrangement of the epoxides to the corresponding ketones is observed under the reaction conditions used (Table 2). Noteworthy is the preferential formation of *cis*-2-allyl-3-cycloalken-1-ols.

The *cis*-1,2-addition may be rationalized assuming coordination of boron to oxygen of the vinylic epoxide and intramolecular transfer of allyl group via a six-membered transition state. In contrast, other allylmethyl reagents, e.g., derivatives of magnesium, tin, and copper, react with **8a** producing *trans*-2-allyl-3-cyclohexen-1-ol or *trans*-4-allyl-2-cyclohexen-1-ol (Table 3). Recently, a carbometalation

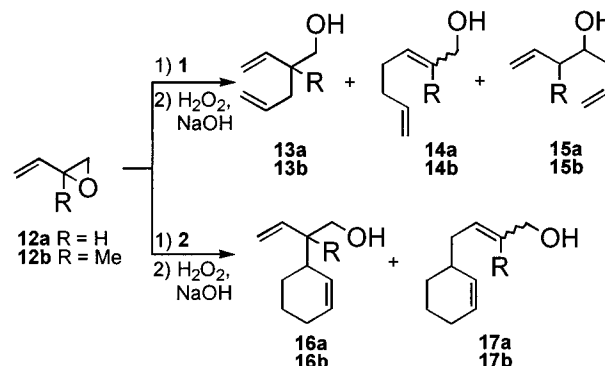
Table 3. Reaction of Allylmethyl Reagents with **8a**

allyl-M	solvent	temp (°C)	time (h)	product composition (%)	yield ^d (%)
allylMgBr	Et ₂ O	20	4	<i>trans</i> - 9a	40 ^b
allylMgBr	Et ₂ O	0	2	<i>trans</i> - 9a (77) 11a (23)	55
allylSnMe ₃	CH ₂ Cl ₂	-78	0.5	<i>trans</i> - 9a	40 ^c
allylCu(CN)Li	THF	-40 → rt	<i>d</i>	<i>trans</i> - 10a	66 ^e

^a Isolated yields. ^b Reference 5c. ^c Reference 6. ^d Not reported. ^e Reference 8c.

approach to *cis*-**9a** by allylboration of 1,3-cyclohexadiene with allyldibromoborane was reported.²²

Allylboration of epoxides **12a** and **12b** derived from acyclic 1,3-dienes was slower compared to that of **8a** and **8b** (Table 4). The reaction required several days when carried

Table 4. Allylboration of **12a** and **12b** with **1** and **2**

epoxide	reagent	temp (°C)	time (h)	product composition ^a (<i>E/Z</i>) (%)			yield ^b (%)
12a	1	20	168	13a 34	14a 66(88/12)		62
12a	1	60	24	13a 46	14a 52(80/20)	15a 2	69
12b	1	60	24	13b 30	14b 66(84/16)	15b 4	65
12a	2	60	48	16a 46	17a 54(78/22)		58
12b	2	80	72	16b 35	17b 65(77/23)		65

^a Determined by GC analysis. Products identified by ¹H and ¹³C NMR analysis and by comparison (GC, ¹H and ¹³C NMR) with authentic samples. ^b Isolated yields.

at room temperature. However, at 60 °C under neat conditions **1** reacted with **12a** in 24 h, and **2** required 48 h.

Despite the prolonged reaction time rearrangement of the epoxides is not a competing reaction since only very small amounts of rearranged products **15a** and **15b** were obtained (Table 4). 1,4-Addition predominates and the ratio of *E/Z* isomers is in the range of 80/20.

In conclusion, the allylboration of 3,4-epoxycyclopentene and its alkyl-substituted derivatives provides a convenient access to the corresponding acyclic (*Z*)-trienols in high stereoselectivity and good yields. The preferential *cis*-1,2-addition of **1** to 3,4-epoxycycloalkenes provides *cis*-2-allyl-3-cycloalken-1-ols. The stereochemistry of the addition is opposite to other allylmethyl reagents.

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Supporting Information Available: Spectroscopic data for all new products. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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