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

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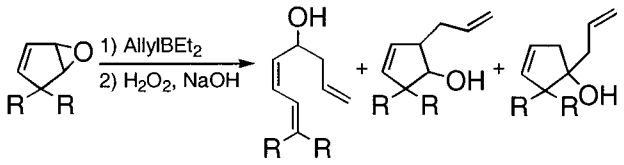
ABSTRACT



3a	R = H	yield 78%	**4a** 90%	4%	6%
3b	R = Me	yield 81%	**4b** 93%	4%	6%

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-Epoxycyclopentene (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 regents,[5] allylstannanes,[6] and tetraallyllanthanoid complexes.[7] 1,4-Addition predominates with organocopper reagents[8] and copper-catalyzed reactions of organomagnesium[9] and organozinc compounds.[10] Vinylic tellurides,[11] organozinc,[12] and organosilicon[13] 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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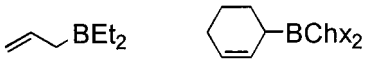
mixtures of 1,2- and 1,4-addition products.[15] Here, we wish to report the allylboration of vinylic epoxides. The reactions of allyldiethylborane (**1**) and (2-cyclohexenyl)dicyclohexylborane (**2**) with representative vinylic epoxides derived from acyclic and cyclic dienes were examined.

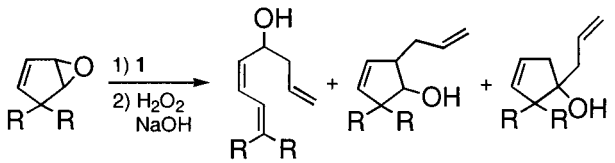
Allyldiethylborane was conveniently prepared in 81% yield by transmetalation of allylaluminumsesquibromide and *n*-amyl diethylborinate obtained by treatment of chlorodiethylborane with 1-pentanol.[16] (2-Cyclohexenyl)dicyclohexylborane was synthesized by the hydroboration of 1,3-cyclohexadiene with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



1 **2**

3,4-Epoxycyclopentene (**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 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 ^{1}H and ^{13}C NMR analysis.[18] Only 4% of the 1,2-addition product **5a** and 6% of **6a**, derived from 3-cyclopentenone formed by rearrangement of the starting epoxide, was obtained.[19]

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



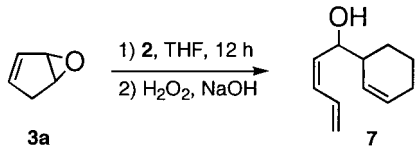
3a; R = H **3b**; R = Me **4a** **4b** **5a** **5b** **6a** **6b**

epoxide	solvent	time (h)	product composition[a] (%) **4**	**5**[c]	**6**[d]	yield[b] (%)
3a	Et_2O	3	90	4	6	78
3a	THF	4	88		12	80
3b	Et_2O	24	73	12	15	77
3b	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-propylcyclo-pentanols, respectively. [d] Identified by GC comparison with authentic samples prepared by the reaction of allylmagnesium bromide with **3a** and **3b**, respectively.

In tetrahydrofuran **5a** was not formed but the amount of **6a** increased. Allylboration of 3,4-epoxy-5,5-dimethylcyclopentene[20] (**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.



3a **7**
yield 64%

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 cyclopentanediols 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

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(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) **(5*Z*)-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, ^{11}B 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% H_2O_2 (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 (*5Z*)-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 $C_8H_{12}O$ (124.18): calcd 77.38% C, 9.74% H; found 77.30% C, 9.78% H. ^{1}H and ^{1}H × ^{1}H COSY NMR ($CDCl_3$): δ 1.65 (s, 1H, OH), 2.32 (t, J = 6.5, 2H, CH_2), 4.64 (q, J = 8.5, 1H, *H*C−OH), 5.20 (m, 4H, $C_{(1)}H_2$, $C_{(8)}H_2$), 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, $C_{(7)}H$). ^{13}C NMR ($CDCl_3$): δ 42.02, 67.14, 118.28, 119.38, 130.72, 131.77, 133.39, 133.97. ^{1}H × ^{13}C HETCOR NMR ($CDCl_3$) (correlation peaks): 2.31 (t, 2H) −41.82 ($C_{(3)}H_2$), 4.62 (q, 1H) −66.98 ($HC_{(4)}OH$), 5.20 (m, 4H) −118.01, 119.13 ($C_{(1)}H_2$, $C_{(8)}H_2$), 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 ^{1}H and ^{13}C 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%).

(20) Compound **3b** was synthesized by epoxidation of 5,5-dimethyl-1,3-cyclopentadiene. (a) Crandall, J. K.; Banks, D. B.; Colyer, R. A. *J. Org. Chem.* **1968**, *33*, 423. (b) Smith, W. T.; McLeod, G. L. *Organic Syntheses*; Schreiber, R. S., Ed.; J. Wiley: New York, 1951; Vol. 31, p 40. (c) Holder, R. W.; Daub, J. P.; Baker, W. E.; Gilbert, R. H., III; Graf, N. A. *J. Org. Chem.* **1982**, *47*, 1445.

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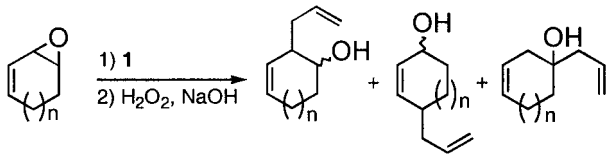
Table 2. Allylboration of **8a**−**c** with **1**



8a; n = 1 **9a** **10a** **11a**
8b; n = 2 **9b** **10b** **11b**
8c; n = 3 **9c** **10c** **11c**

epoxide	solvent	temp (°C)	time (h)	product composition[a] (%) **9** (c/t)[c]	**10** (c/t)[c]	**11**	yield[b] (%)
8a	Et_2O	20	5	81(72/28)	19(63/37)		82
8a	THF	20	24	82(63/37)	16(56/44)	2	69
8b	Et_2O	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

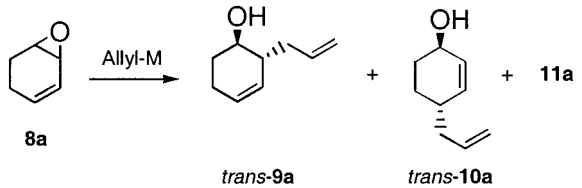
[a] Determined by GC analysis. [b] Isolated yields. [c] The *cis*/*trans* ratio was established by hydrogenation to *cis*/*trans* 2- and 4-propyl-cyclohexanols and comparison with authentic samples by GC.

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 allylmetal 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 Allylmetal Reagents with **8a**



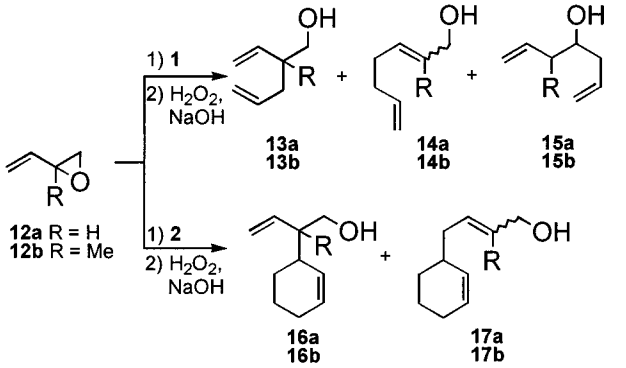
allyl-M	solvent	temp (°C)	time (h)	product composition (%)	yield[a] (%)
allylMgBr	Et_2O	20	4	*trans*-**9a**	40[b]
allylMgBr	Et_2O	0	2	*trans*-**9a** (77) **11a** (23)	55
$allylSnMe_3$	CH_2Cl_2	−78	0.5	*trans*-**9a**	40[c]
allylCu(CN)Li	THF	−40 → rt	*d*	*trans*-**10a**	66[e]

[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 tothat 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] (*E*/*Z*) (%)			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 ^{13}C NMR analysis and by comparison (GC, ^1H and ^{13}C 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 allylmetal 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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