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Monobromoborane–Dimethyl Sulfide—a Highly Promising Reagent for the Regio- and Chemoselective Brominative Cleavage of Terminal Epoxides into Vicinal Bromohydrins*

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Monobromoborane–dimethyl sulfide (BH_2Br–SMe_2) is a highly regio- and chemoselective reagent useful for the brominative cleavage of the epoxy moiety into bromohydrins in the presence of alkenes, alkynes, ethers, acetals, ketals, and acetonides at 0°C, besides being an excellent hydroborating reagent. Several reactive functional groups, such as chloride, ketones, esters, nitriles, nitros, and thioethers, have been accommodated during such transformations. Although the reduction of acetophenone was completely suppressed at −25°C, 4-chlorobenzaldehyde still underwent 12–13% reduction of an aldehydic group.

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Introduction

Vicinal halohydrins have proven to be versatile intermediates in synthetic organic chemistry, mainly owing to their utility in marine natural products (laurenyne, aplysiapyranoid A, and 2-bromo-β-chamigrene)[1] and pharmaceuticals (immunosuppressant-ISP 1, thienamycin, and halohydrins of cryptophycin 1 and epothilone),[2] as well as in functional group transformations.[3] Epoxides are very important building blocks in organic synthesis owing to their high reactivity[4] (due to ring strain) with a variety of nucleophiles and also availability in enantiomerically enriched forms.[5] Although halohydrins have been prepared by the halohydroxylation of alkenes[6a–6c] and the reduction of α-haloketones,[6d–6g] the most facile and versatile route to 1,2-halohydrins appears to be the halogenative cleavage of epoxides with halide nucleophiles.[6h] Therefore, there is a continued interest in developing new procedures to effect regioselective ring opening of epoxides to vicinal halohydrins. Although a significant effort has been made in the past decade to develop simple and mild procedures to achieve such transformations, most of them are not always fully satisfactory and suffer from certain disadvantages, such as handling and in situ preparation of the reagents, high stochiometric ratio of the reagents, acidity, hygroscopicity, harsh reaction conditions, longer reaction times, low chemical yields, by-product formation, low regioselectivity, and negative solvent effects (no reaction in certain solvents).[7]

Boron halides are excellent reagents for the cleavage of aliphatic and aromatic ethers.[8,9] Several structurally modified *B*-haloorganoboranes have shown to cleave epoxides to halohydrins.[10,11] Also, α-pinene-based *B*-haloorganoboranes, $^{d}Ipc_2BX$ (X = Cl, Br, I), as well as structurally modified Ter_2BX have been used in the asymmetric cleavage of *meso*-epoxides to chiral halohydrins.[12] Bovicelli and co-workers reported the synthetic utility of BH_2Cl–SMe_2 in the regiocontrolled opening of terminal epoxides without hydroborating the alkene.[13] In conjunction with ongoing research on the topic of developing simple, convenient, and efficient methodologies for the regio-, chemo-, and enantioselective ring opening of epoxides, we reported our preliminary results on the regioselective cleavage of terminal epoxides and cyclic ethers using BH_2X–SMe_2, BHX_2–SMe_2 and $(MeO)_2BX$ (X = Cl, Br).[14,15] The commercially available reagent BH_2Br–SMe_2 (Aldrich) has two nucleophilic sites, the bromine and the hydrogen atoms; therefore, it is of great interest to explore the chemoselective reactions of these two reagents. Although we demonstrated the ability of BH_2Br–SMe_2 to chemoselectively cleave the epoxy group in the presence of a terminal alkene and the phenyl ether,[14] there has been no systematic study on the chemoselective transformation of epoxy groups into vicinal bromohydrins using this commercially available reagent, monobromoborane–dimethyl sulfide (BH_2Br–SMe_2). We herein report a systematic study on the regio- and chemoselective ring opening of terminal epoxides into bromohydrins using BH_2Br–SMe_2.

Results and Discussion

First, we decided to optimize the reaction conditions by re-examining the cleavage of a few typical symmetrical epoxides. A careful examination of the reaction revealed that BH_2Br–SMe_2

* This paper is dedicated to the memory of my mentor, the late Professor Herbert C. Brown (1912–2004). The work described herein was carried out at Purdue University during my stay as a post-doctoral research associate (1995–2001).

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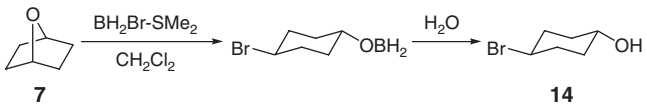
very efficiently cleaved *meso*-epoxides **1**–**7** into the corresponding *trans*-bromohydrins **8**–**14** at 0°C in 15 min in excellent chemical yield and isomeric purity. The cleavage of 5-membered ether, 7-oxanorbornane **7**, was observed to be slow at 0°C and required a relatively longer reaction time (12–16 h) even at room temperature to yield *trans*-4-bromocyclohexan-1-ol **14** (Scheme 1, Table 1).

Next, we investigated the regioselective ring opening of some terminal epoxides **15**–**24** with BH_2Br–SMe_2. Except for styrene oxide **17**, BH_2Br–SMe_2 readily cleaved the epoxy group into vicinal bromohydrins, by the regioselective bromine transfer at the less-hindered carbon (terminal), by a borderline S_N2-type mechanism, in CH_2Cl_2 solvent at 0°C in 0.25 h (Scheme 2, Table 2).[16] 1,2-Epoxydodecane **15** did not show any appreciable improvements in regioselectivity at lower temperatures (0°C (91:9); −25°C (92:8); −78°C (92:8)). In the case of styrene epoxide **17**, a benzylic epoxide, the cleavage proceeds following an apparent S_N1-type mechanism (the bromine appearing at the benzylic position). Arylglycidyl ethers have been found to be very useful organic intermediates in the synthesis of amino alcohols.[17] These amino alcohols have shown significant biological activities as adrenergic β-blockers and as muscle relaxants.[18] Bromohydrins can also very easily be converted into the corresponding amino alcohols.[19] Consequently, we undertook the study of the regioselective ring opening of few arylglycidyl ethers **20**–**24** with BH_2Br–SMe_2. Arylglycidyl



Scheme 1. Ring opening of 7-oxanorbornane **7** with BH_2Br–SMe_2.

ethers also reacted smoothly to produce bromohydrins, without affecting the aryl ether bonds. In the cases of 2-(naphthalen-2-yloxymethyl)oxirane **20** and 2-*o*-tolyloxymethyloxirane **24**, the formation of the minor isomer was greatly suppressed (<2%) when the reaction was conducted at −78°C for 2 h.

After examining the regioselectivity, we focussed on the chemoselective halogenative cleavage of a representative epoxide, 1,2-epoxydodecane **15**, in the presence of a variety of compounds bearing reactive functional groups **35**–**49**. Monobromoborane–dimethyl sulfide complex is well known as an excellent hydroborating agent.[20] Therefore, it is of considerable interest to examine the chemoselective ring opening of an oxirane in the presence of alkenes and alkynes. We had observed[14] the partial hydroboration of 1,2-epoxyoct-7-ene, a terminal alkene, at room temperature as well as at 0°C. Later, the hydroboration was suppressed by performing the reaction at −35°C. Although, the cleavage reaction was usually complete within an hour at −35°C, 90% conversion was observed without any significant hydroboration of the terminal olefin, even after longer reaction time (16 h). The reagent, BH_2Br–SMe_2, successfully cleaved the epoxy group at −25°C, without hydroborating the double bonds, in the cases of allyl phenyl ether **35** and nopol benzyl ether **37** (Scheme 3, Table 3). The olefinic moiety of vinyl phenyl sulfone **36** and 6-methylcoumarin **38** survived even at 0°C. The terminal alkyne **39** was also observed to be significantly non-reactive towards this reagent at 0°C (89% recovery of the 2-but-3-ynyloxytetrahydropyran **39**). It is also worth noting that dodecyloxytetrahydropyran underwent selective reductive opening of the endocyclic C–O bond of THP ether to form monoetherate diol, at low temperature (−30°C) with BH_2Cl–SMe_2.[13] Even the more Lewis acid sensitive structure, such as 1,2:3,5-di-*O*-isopropylidene-D-xylofuranose **40**, remains intact during the transformation at 0°C (Scheme 4).

Table 1. Ring opening of symmetrical epoxides with BH_2Br–SMe_2 in CH_2Cl_2 solvent

Epoxide no.	Epoxide	Reaction conditions[A]	Bromohydrin no.	Bromohydrin	Yield[B] [%]
1		CH_2Cl_2/0°C/0.25 h	**8**		88 (85)
2		CH_2Cl_2/0°C/0.25 h	**9**		92 (87)
3		CH_2Cl_2/0°C/0.25 h	**10**		96 (92)
4		CH_2Cl_2/0°C/0.25 h	**11**		90 (85)
5		CH_2Cl_2/0°C/0.25 h	**12**		91 (87)
6		CH_2Cl_2/0°C/0.25 h	**13**		89 (85)
7		CH_2Cl_2/room temp./24 h	**14**		92 (89)

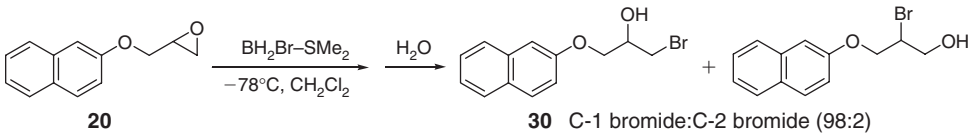
[A] 1.10 equiv of BH_2Br–SMe_2 used.

[B] All products formed have been identified by ^1H and ^{13}C NMR spectroscopic data. Each yield was determined by ^1H NMR analysis (300 MHz) using biphenyl as an internal standard. Values in parentheses are isolated yields of purified product.

In order to further explore the functional group tolerance of this reagent, the ring-opening reactions of 1,2-epoxydodecane **15** were carried out in the presence of equivalent amounts of compounds bearing reducible functional groups such as aldehyde, ketone, ester, nitrile, and chloride (Scheme 5, Table 3). In the cases of 4-chlorobenzaldehyde **43**, acetophenone **44**, and 4-cyanoacetophenone **45**, considerable amounts of reduction took place at 0°C. At −25°C, the reduction of acetophenone **44** was completely suppressed, but 4-chlorobenzaldehyde **43** still underwent 12–13% reduction of the aldehydic group. Other functional groups, such as esters **47** and **48**, nitro and thioether **49** were found to be unaffected even at room temperature.

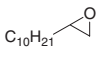
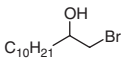
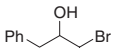
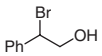
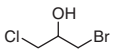
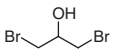
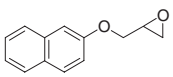
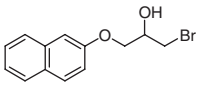
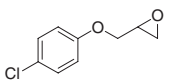
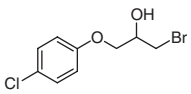
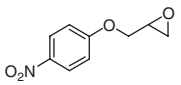
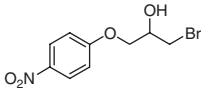
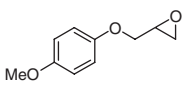
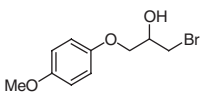
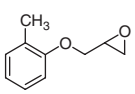
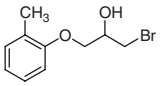
Conclusions

We have demonstrated the successful application of BH_2Br–SMe_2 as a highly promising regio- and chemoselective reagent for the halogenative cleavage of epoxides. Several unsaturated structures, e.g. alkenes and alkynes that are highly susceptible to hydroboration, have been accommodated. Many Lewis acid sensitive functional groups, such as ethers, pyranylacetals, and ketals, remain intact during these transformations. It is interesting to note that several reducible functional groups, such as ketones, chloro, nitro, esters, and thioethers, remain unaffected during the ring-opening process. In the case of 4-chlorobenzaldehyde, the reduction of the aldehydic group was suppressed (only 13% reduction) considerably at −25°C. We believe that the present method offers considerable advantages over currently available methodologies in terms of mildness, simplicity, efficiency, and high regio- and chemoselectivity. In addition, the advantages, such as the commercial availability and convenient handling of the reagent, shorter reaction time, scalability, and simple workup, should make this reagent valuable and useful in organic synthesis.



Scheme 2. Regioselective ring opening of 2-(naphthalen-2-yloxymethyl)oxirane with BH_2Br–SMe_2.

Table 2. Regioselective cleavage of unsymmetrical terminal epoxides with BH_2Br–SMe_2 in CH_2Cl_2

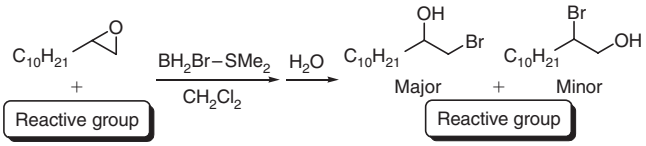
Epoxide no.	Epoxide	Reaction conditions[A]	Bromohydrin no.	Major bromohydrin	Regioisomeric ratios[B]	Bromohydrin yield[B] [%]
15		Room temp./0.25 h	**25**		90:10	93 (79)
16		Room temp./0.25 h	**26**		94:06	93 (80)
17		Room temp./0.25 h	**27**		10:90	86 (75)
18		Room temp./0.25 h	**28**		95:05	99 (87)
19		Room temp./0.25 h	**29**		96:04	94 (89)
20		0°C/1 h	**30**		95:05	92 (84)
21		0°C/1 h	**31**		95:05	92 (82)
22		0°C/1 h	**32**		95:05	89 (80)
23		0°C/1 h	**33**		95:05	91 (83)
24		0°C/1 h	**34**		95:05	90 (82)

[A] 1.10 equiv of BH_2Br–SMe_2 used.

[B] All products formed have been identified by ^1H and ^{13}C NMR spectroscopic data. Each yield was determined by ^1H NMR analysis (300 MHz) using biphenyl as an internal standard. Values in parentheses are isolated yields of purified product (major).

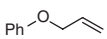
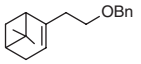
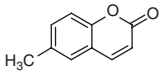
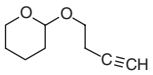
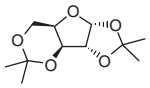
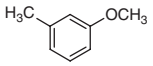
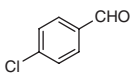
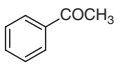
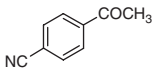
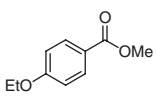
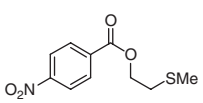
Experimental

Manipulations and reactions with air-sensitive compounds were carried out under a nitrogen atmosphere. Glassware was oven-dried, assembled while hot, and cooled in a stream of dry nitrogen gas. ^{1}H, ^{13}C, and ^{11}B NMR spectra were recorded on Varian-Gemini 300 MHz multinuclear NMR spectrometer. The ^{11}B NMR chemical shifts are in δ relative to $BF_3{\cdot}OEt_2$. All the epoxides and other reducible substrates were purchased from Aldrich and used as received. Dichloromethane (CH_2Cl_2) was distilled over P_2O_5 and stored under nitrogen. All other solvents for chromatography and extraction were technical grade and purified according to literature procedures. Column chromatography was performed using 230–400 mesh silica gel.



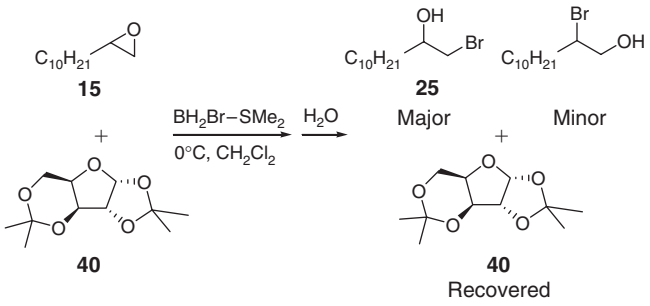
Scheme 3. Chemoselective ring opening of 1,2-epoxydodecane **15** with BH_2Br–SMe_2 in the presence of various reactive functional groups **35**–**49**.

Table 3. Chemoselective cleavage of 1,2-epoxydodecane 15 with BH_2Br–SMe_2 in CH_2Cl_2 solvent

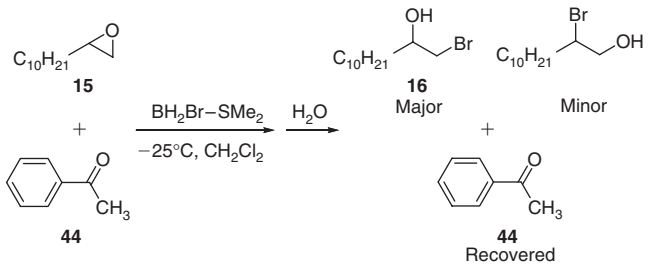
Reactive compound no.	Reactive compound	Reaction conditions[A]	Regioisomeric bromohydrins [%][B]	Recovered reactive compound [%][B]
35		CH_2Cl_2/−25°C/0.5 h	89	97
36		CH_2Cl_2/0°C/0.5 h	95	93
37		CH_2Cl_2/−25°C/0.5 h	88	99
38		CH_2Cl_2/0°C/0.5 h	95	99
39		CH_2Cl_2/0°C/0.5 h	95	89
40		CH_2Cl_2/0°C/0.25 h	90	98
41		CH_2Cl_2/0°C/0.5 h	95	99
42		CH_2Cl_2/room temp./0.25 h	95	95
43		CH_2Cl_2/−25°C/1.5 h	87	87
44		CH_2Cl_2/−25°C/1.5 h	95	99
45		CH_2Cl_2/0°C/0.5 h	95	75
46		CH_2Cl_2/−25°C/1.5 h	87	96
47		CH_2Cl_2/room temp./0.25 h	98	99
48		CH_2Cl_2/room temp./0.25 h	90	98
49		CH_2Cl_2/room temp./0.25 h	98	99

[A] 1.10 equiv of BH_2Br–SMe_2 used.

[B] Yields of bromohydrins and the recovery of added reactive compounds were determined by ^{1}H NMR analysis (300 MHz) using biphenyl as an internal standard. All products are known compounds and have been characterized by 300 MHz ^{1}H NMR spectroscopy.



Scheme 4. Chemoselective ring opening of 1,2-epoxydodecane **15** with BH_2Br–SMe_2 in the presence of 1,2:3,5-di-*O*-isopropylidene-D-xylofuranose **40**.



Scheme 5. Chemoselective ring opening of 1,2-epoxydodecane **15** with BH_2Br–SMe_2 in the presence of acetophenone **44**.

*Stereoselective Cleavage of Symmetrical Epoxides **1**–**7**: General Procedure*

To a stirred solution of a symmetrical epoxide **1**–**6** (2.0 mmol) in anhydrous CH_2Cl_2 (5 mL), under nitrogen atmosphere at room temperature, was slowly added BH_2Br–SMe_2 (2.2 mmol, 2.2 mL, 1.0 M in CH_2Cl_2) by syringe. After the addition was complete, the reaction mixture was stirred for 0.25 h. After 0.25 h, the reaction mixture was quenched with water (5–10 mL) and the organic materials were extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were dried (anhydrous $MgSO_4$), filtered, and evaporated under vacuum to give the product bromohydrin. The percent chemical conversion was determined by ^{1}H NMR analysis of the crude product using biphenyl as an internal standard. In all cases, the crude product was found to be spectroscopically pure. The product bromohydrin was purified on silica gel column and characterized by ^{1}H and ^{13}C NMR spectroscopic data. Most of the bromohydrins are well characterized in the literature: 2-bromocyclopentan-1-ol **8**,[7q] *trans*-4-bromocyclohexan-1-ol **14**,[11] 3-bromobutan-2-ol **13**,[12b] 2-bromocyclohexan-1-ol **9**,[21d] 2-bromo-1,2-diphenylethan-1-ol **12**,[21e] 2-bromocycloheptan-1-ol **10**,[21f] and 2-bromocyclooctan-1-ol **11**.[21f]

*Regioselective Cleavage of Terminal Epoxides **15**–**24**: General Procedure*

To a stirred solution of an epoxide **15**–**24** (2.0 mmol) in anhydrous CH_2Cl_2 (5 mL), under nitrogen atmosphere at room temperature, was slowly added BH_2Br–SMe_2 (2.2 mmol, 2.2 mL, 1.0 M in CH_2Cl_2) by syringe. After the addition was complete, the reaction mixture was stirred for 0.25 h. After 0.25 h, the reaction mixture was quenched with water (5–10 mL) and extracted with CH_2Cl_2 (3×30 mL). The combined organic extracts were dried (anhydrous $MgSO_4$), filtered, and evaporated under vacuum to give the product bromohydrins. The chemical yields of the product bromohydrins were determined by ^{1}H NMR analysis of the crude product using biphenyl as an internal standard. The regioselectivities of various reaction product mixtures were calculated by comparing the integrations of the protons attached with either −Br or −OH groups. The product bromohydrins were also purified on a silica gel column, and characterized by ^{1}H and ^{13}C NMR spectroscopic data. Most of the products are well characterized in the literature: 1-bromododecan-2-ol **25**,[7r] 1-bromo-3-phenylpropan-2-ol **26**,[3l] 2-bromo-2-phenyl-ethanol **27**,[7c] 1-bromo-3-chloropropan-2-ol **28**,[7e] 1,3-dibromopropan-2-ol **29**,[7c] 1-bromo-3-(naphthalen-2-yloxy)propan-2-ol **30**,[19b] 1-bromo-3-(4-chlorophenoxy)propan-2-ol **31**,[7e] 1-bromo-3-(4-nitrophenoxy)propan-2-ol **32**,[7s] 1-bromo-3-(4-methoxyphenoxy)propan-2-ol **33**,[7s] and 1-bromo-3-(2-methylphenoxy) propan-2-ol **34**.

1-Bromododecan-2-ol **25**[7r]: δ_H ($CDCl_3$) 3.70 (m, 1H, -C*H*OH), 3.50 (dd, 1H, -CH_2Br), 3.35 (dd, 1H, -CH_2Br), 2.10 (d, 1H, -CHO*H*), 1.60–1.10 (m, 18H, -CH_2-), 0.88 (m, 3H, -CH_3).

1-Bromo-3-chloropropan-2-ol **28**[7e]: δ_H ($CDCl_3$) 4.05 (m, 1H, -C*H*OH), 3.71 (dd, 2H, -CH_2Br), 3.57 (d, 2H, -CH_2Cl), 2.48 (d, 1H, -CHO*H*). δ_C ($CDCl_3$) 70.4, 46.5, 34.8.

1-Bromo-3-(naphthalen-2-yloxy)propan-2-ol **30**[19b]: δ_H ($CDCl_3$) 7.78 (m, 3H, ArH), 7.50–7.30 (m, 2H, ArH), 7.14 (m, 2H, ArH), 4.30–4.10 (m, 3H, -C*H*OH and ArOCH_2-), 3.65 (m, 2H, -CH_2Br), 2.55 (d, 1H, -CHO*H*). δ_C ($CDCl_3$) 156.1, 134.3, 129.6, 128.7, 127.6, 126.1, 125.5, 121.5, 118.5, 107.1, 69.5, 69.1, 35.1.

1-Bromo-3-(4-nitrophenoxy)propan-2-ol **32**[7s]: δ_H ($CDCl_3$) 8.20 (d, 2H, ArH), 7.00 (d, 2H, ArH), 4.30–4.00 (m, 3H, -C*H*OH and ArOCH_2-), 3.65 (m, 2H, -CH_2Br), 2.55 (d, 1H, -CHO*H*). δ_C ($CDCl_3$) 163.1, 142.0, 126.0, 117.0, 68.3, 68.1, 34.3.

1-Bromo-3-(4-methoxyphenoxy)propan-2-ol **33**[7s]: δ_H ($CDCl_3$) 6.85 (m, 4H, ArH), 4.20 (m, 1H, -C*H*OH), 4.06 (m, 2H, -ArOCH_2-), 3.77 (s, 3H, ArOCH_3), 3.65 (m, 2H, -CH_2Br), 2.55 (d, 1H, -CHO*H*). δ_C ($CDCl_3$) 154.3, 152.3, 69.9, 69.6, 55.7, 35.1.

1-Bromo-3-(2-methylphenoxy)propan-2-ol **34**: δ_H ($CDCl_3$) 7.30–6.70 (m, 4H, ArH), 4.20 (m, 1H, -C*H*OH), 4.05 (m, 2H, ArOCH_2-), 3.75 (m, 2H, -CH_2Br), 2.60 (d, 1H, -CHO*H*), 2.22 (s, 3H, Ar-CH_3). δ_C ($CDCl_3$) 156.2, 130.8, 126.9, 126.8, 121.1, 111.2, 69.9, 68.4, 46.1, 16.1.

1-Bromooct-7-en-2-ol[14a]: δ_H ($CDCl_3$) 5.80 (m, 1H, CH_2=C*H*-), 5.00 (m, 2H, CH_2=CH-), 3.80 (m, 1H, -C*H*OH), 3.55 (dd, 1H, -CH_2Br), 3.40 (dd, 1H, -CH_2Br), 2.20 (m, 3H, -CH_2- and -CHO*H*), 1.70–1.20 (m, 6H, -CH_2-). δ_C ($CDCl_3$) 138.6, 114.5, 71.0, 40.6, 34.9, 33.5, 28.7, 25.0.

2-Bromooct-7-en-1-ol[14a]: δ_H ($CDCl_3$) 5.80 (m, 1H, CH_2=C*H*-), 5.00 (m, 2H, CH_2=CH-), 4.15 (m, 1H, -CHBr), 3.80 (m, 2H, -CH_2OH), 2.10–1.40 (m, 9H, -CH_2- and CHO*H*). δ_C ($CDCl_3$) 138.5, 114.7, 67.2, 59.9, 34.7, 33.4, 28.2, 26.9.

*Chemoselective Ring Opening of 1,2-Epoxydodecane **15**: General Procedure*

The cooled reagent, BH_2Br–SMe_2 (2.0 mmol, 1.0 M in CH_2Cl_2), was added slowly to a stirred solution of 1,2-epoxydodecane **15** (2.0 mmol) and the reactive compound **35**–**49** (2.0 mmol) in CH_2Cl_2 (10 mL), cooled to −25°C (or the reaction conditions given in Table 3) under nitrogen. The reaction mixture was allowed to stir for the given time. The intermediate boron species was treated with water (10 mL) at −25°C (or 0°C or room temperature) and the reaction mixture was allowed to slowly warm up to room temperature (0.25 h). The resulting

bromohydrins were extracted with CH_2Cl_2 (3 × 35 mL), and the combined organic layers dried (anhydrous $MgSO_4$) and concentrated in vacuum. The percentage chemical transformation of bromohydrins and the recovered reactive compounds were determined by ^1H NMR spectroscopy using biphenyl (0.25 mmol) as an internal standard.

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