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Regiochemical Control of the Ring Opening of 1,2-Epoxides by Means of Chelating Processes. 4.[1] Synthesis and Reactions of the *cis*- and *trans*-Oxides Derived from 3-[(Benzyloxy)methyl]cyclohexene

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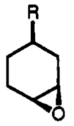
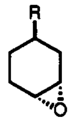
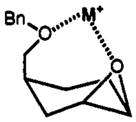
The synthesis and nucleophilic addition reactions of diastereoisomeric title epoxides *cis*-7 and *trans*-8 were studied. While the ring-opening reactions of trans epoxide 8 are rationalized by means of steric, stereoelectronic, and conformational arguments, the analogous reactions of cis epoxide 7 indicate the ability of this isomer to react through chelated intermediates when metal salt catalyst is used. In 7 chelation reaction conditions led to a significant increase of nucleophilic attack on the C-1 oxirane carbon; the lack of reversal of the regiochemistry of the ring opening on passing from nonchelating to chelating reaction conditions suggests that cis epoxide 7 reacts through its more stable conformation in both of the two different operating conditions.

Remote polar heterofunctionality has been shown to be useful in controlling the regiochemistry of the addition of epoxides by chelating processes.[2-4] The presence of a C-4 benzyloxy group in a 1,2-epoxycyclohexane system leads to excellent regiocontrol in the addition reactions of the cis isomer (1) by metal-assisted chelating or nonchelating processes.[3,4] We also studied epoxides 3 and 4[5] which can be considered homologues of 1 and 2. Cis epoxide 3 exhibits a much lower tendency than cis epoxide 1 to react through chelated intermediates.[5] This may be due both to the larger steric hindrance of the CH_2OBn group of 3 compared with that of the OBn group in 1 and to the entropically disfavored seven-membered ring present in the bidentate chelating structure 5 derived from epoxide 3,[5] compared with the six-membered ring present in bidentate chelating structure 6 deriving from epoxide 1.[3,4]

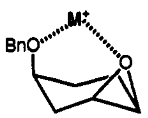




R = OBn 1 2
R = CH₂OBn 3 4



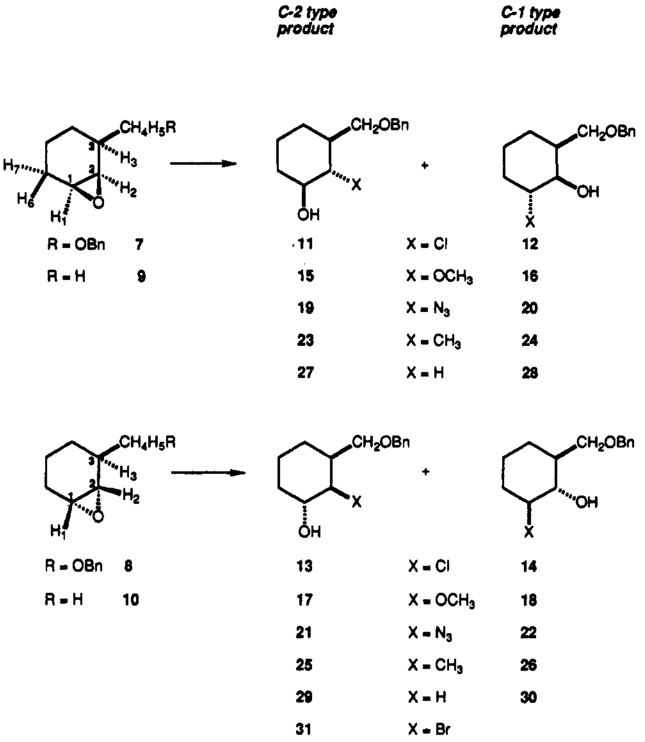
5 (*from epoxide* 3)



6 (*from epoxide* 1)

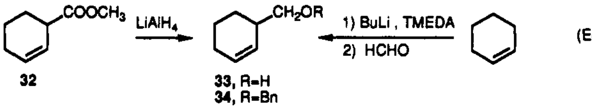
Now we report the results obtained with *cis*- and *trans*-3-[(benzyloxy)methyl]-1,2-epoxycyclohexane 7 and 8 (Scheme I) which contain structural similarities to epoxides 1,2 and epoxides 3,4. In the cis isomer 7 chelating processes of the type shown for epoxide 1[3,4] are possible both in the more stable (7a) and in the less stable conformation (7b) (vide infra), contrary to epoxide 1 in which such chelation is allowed only in its less stable conformation.[4] In the trans isomer 8 chelation is always impossible as in 2.[3,4]

Scheme I

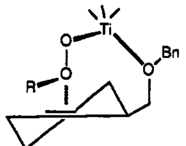


Results and Discussion

The synthesis of olefin 34, precursor of epoxides 7 and 8, was accomplished by benzylation of the alcohol 33[6] initially obtained by $LiAlH_4$ reduction of the known ester 32[7] (eq 1). Alcohol 33 was obtained more coveniently by



(Eq. 1)



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(1) Preceding paper in this series: Chini, M.; Crotti, P.; Flippin, L. A.; Macchia, F. *J. Org. Chem.* 1991, *56*, 7043.

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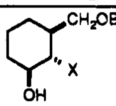
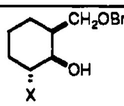
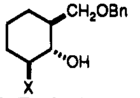
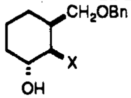
Table I. Regioselectivity (%) of the Ring-Opening Reactions of Cis Epoxide 7

entry	reagents	reactn cond[a]	reactn time		
1	$HCl/CHCl_3$	A	30 min	11[b]	89[c]
2	$TiCl_4$/TBHP	B	40 min	4[b]	96[c]
3	H^+/MeOH	C	1 h	8[d]	92[e]
4	$LiClO_4$/MeOH	D	20 h	2[d]	98[e]
5	NaN_3/NH_4Cl	E	20 h	14[f]	86[g]
6	$NaN_3/LiClO_4$	F	20 h	5[f]	95[g]
7	$LiAlH_4$/pentane	G	2 h	<1[h]	>99[i]
8	$LiAlH_4$/crown, pentane	H	3 h	<1[h]	>99[i]
9	$(CH_3)_2CuLi/Et_2O$	I	2 h	<1[j]	>99[k]
10	$Al(CH_3)_3$/BuLi	J	5 h	<1[j]	>99[k]
11	$Al(CH_3)_3$/BuLi/crown	K	4 h	<1[j]	>99[k]

[a] Conditions: A, 36% aqueous HCl in $CHCl_3$, rt; B, CH_2Cl_2 solution, −78 °C; C, 0.2 N H_2SO_4, rt; D, 17 M $LiClO_4$ in anhydrous MeOH, refluxing temperature; E, $MeOH/H_2O$ 8:1, 80 °C, see ref 12; F, MeCN, 80 °C, see ref 13; G, epoxide:$LiAlH_4$ = 1:2; H, $LiAlH_4$ (2.0 mmol) and 12-crown-4 (2.2 mmol) in the solvent are stirred 15 h at rt and then the epoxide (1.0 mmol) is added, see ref 4; I, 30 min at −15 °C and then 1.5 h at −2 °C; J, epoxide:$Al(CH_3)_3$:BuLi = 1:2.4:0.24 at −50 °C, then 5 h at 0 °C, see ref 3; K, epoxide:$Al(CH_3)_3$:BuLi:crown = 1:3:0.32:3.1, at rt, see ref 3. [b] Chlorohydrin **11**, X = Cl. [c] Chlorohydrin **12**, X = Cl. [d] Methoxy alcohol **15**, X = OMe, see ref 18. [e] Methoxy alcohol **16**, X = OMe. [f] Azido alcohol **19**, X = N_3. [g] Azido alcohol **20**, X = N_3. [h] Alcohol **27**, X = H. [i] Alcohol **28**, X = H. [j] Methyl alcohol **23**, X = Me, see ref 18. [k] Methyl alcohol **24**, X = Me.

Table II. Regioselectivity (%) of the Ring-Opening Reactions of Trans Epoxide 8

entry	reagents	reactn cond[a]	reactn time		
1	$HCl/CHCl_3$	A	30 min	38[b]	62[c]
2	$TiCl_4$/TBHP	B	40 min	53[b]	47[c]
3	H^+/MeOH	C	1 h	65[d]	35[e]
4	$LiClO_4$/MeOH	D	20 h	75[d]	25[e]
5	NaN_3/NH_4Cl	E	20 h	46[f]	54[g]
6	$NaN_3/LiClO_4$	F	20 h	42[f]	58[g]
7	$LiAlH_4$/pentane	G	2 h	28[h]	72[i]
8	$(CH_3)_2CuLi/Et_2O$	H	20 h	10[j]	90[k]

[a] Conditions: A–G see footnote a, Table I; H, 20 h at 0 °C. [b] Chlorohydrin **14**, X = Cl. [c] Chlorohydrin **13**, X = Cl. [d] Methoxy alcohol **18**, X = OMe. [e] Methoxy alcohol **17**, X = OMe. [f] Azido alcohol **22**, X = N_3. [g] Azido alcohol **21**, X = N_3. [h] Alcohol **30**, X = H. [i] Alcohol **29**, X = H. [j] Methyl alcohol **26**, X = Me, see ref 18. [k] Methyl alcohol **25**, X = Me.

allylic metalation[8] of cyclohexene with butyllithium in the presence of tetramethylethylenediamine (TMEDA) followed by treatment with paraformaldehyde. Epoxidation of **34** with *m*-CPBA yielded a 54:46 mixture of epoxides **7** and **8**, which could not be cleanly separated. In an attempt to obtain a more selective synthesis of **7** and **8**, we investigated the $TiCl_4$-catalyzed Sharpless chlorohydroxylation of olefin **34**, followed by oxirane ring closure of the crude chlorohydrin mixture.[9] This reaction, in fact, had turned out to be useful in the selective synthesis of cis epoxide **1**.[3,4] In the present case the reaction of **34** with *tert*-butyl hydroperoxide (TBHP) in the presence of $TiCl_4$[9] afforded a reaction mixture consisting mainly (90%) of chlorohydrin **12** arising from cis epoxide **7**, accompanied by small amounts (10%) of chlorohydrins **13** and **14** arising from trans epoxide **8**. No trace of chlorohydrin **11** was revealed. Chlorohydrin **12** is a solid and was purified by crystallization: treatment of pure **12** with *t*-BuOK afforded pure cis epoxide **7**. The reaction of olefin **34** with *N*-bromoacetamide (NBA) in aqueous THF afforded a mixture of intermediate bromohydrins [bromohydrin **31** is the main product (90%, GC and ^1H NMR)], whose base-catalyzed cyclization afforded a 9:1 mixture of **8** and **7**. Bromohydrin **31** may be purified by flash chromatography then cyclized under basic conditions to give pure trans epoxide **8**. The high selectivity observed in the Sharpless chlorohydroxylation[9] of **34** is in accordance with an initial coordination of the oxidant with the oxygen of the benzyloxy group of **34**, very likely in its more stable conformation (structure **35**), followed by preferential attack of the oxidant on the syn side, to yield cis epoxide **7**.[4,9] The preferential attack of Cl^- on C-1 carbon of the intermediate epoxide **7** affords chlorohydrin **12**. On the other hand, the attack of Cl^- on the intermediate trans epoxide **8** affords a mixture of **13** and **14** (vide infra). The high regio- and stereoselectivity observed in the reaction of olefin **34** with aqueous NBA is in accordance with an analogous selectivity previously observed in a similar reaction (aqueous NBS) of 3-methylcyclohexene.[10]

We tested the reactivity and the regioselectivity of epoxides **7** and **8** under the same series of reaction conditions already used with epoxides **1**–**4**.[3–5] The results are summarized in Tables I and II.

The reaction of cis epoxide **7** with HCl in $CHCl_3$ afforded a mixture of the two chlorohydrins **11** and **12** in which the latter (*C-1-type product*,[11] Scheme I) largely (89%) prevailed (entry 1, Table I). However, when epoxide

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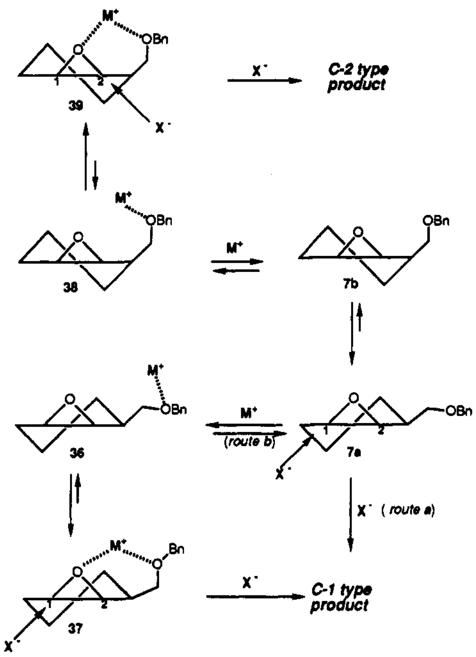
(11) The *C-1-* and *C-2-type product* nomenclature refers to the attacking site of the nucleophile (i.e., at the C-1 or C-2 oxirane carbon of both **7** and **8**), in accordance with the numbering scheme shown in Scheme I.

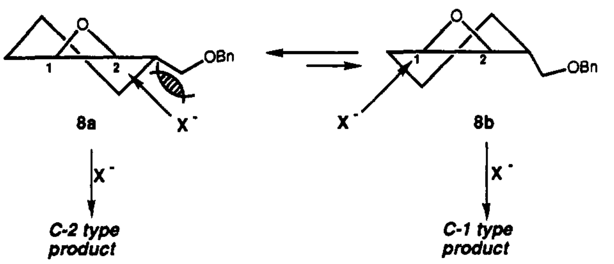
Scheme II



7 was allowed to react with $TiCl_4$ under the Sharpless chlorohydroxylation conditions,[9] the expected reversal of the regioselectivity, as found with 1,[4] was not observed; on the contrary, the selectivity of the attack of the nucleophile for the C-1 carbon of 7 increased (96% of chlorohydrin **12** was obtained in these conditions, entry 2, Table I). The same trend was observed in the other reactions examined (methanolysis, azidolysis, entries 3–6, Table I): under nonchelating conditions (proton-catalyzed methanolysis and azidolysis with sodium azide in aqueous methanol in the presence of NH_4Cl[12]), a large preference for nucleophilic attack on C-1 is observed, which significantly increases when chelating conditions are operating (Li^+-catalyzed methanolysis[4] and Li^+-catalyzed azidolysis in the presence of NaN_3[13]). The $LiAlH_4$ reductions and the methylating ring opening of 7 are the only exceptions, an exclusive formation of C-1-type product being observed both in chelating and in nonchelating conditions (entries 7–11, Table I).[2-4]

The results obtained in the reaction of cis epoxide 7 under nonchelating conditions are comparable to previously reported reactions of *cis*-3-methylcyclohexene oxide (**9**) with hydrogen halides[10b] and with $LiAlH_4$.[14] Thus, the highly preferential attack of the nucleophile on the C-1 carbon can be explained assuming that ring opening of 7 occurs through its more stable conformation **7a** in a diaxial fashion according to the Fürst–Plattner rule[15] (Scheme II, route *a*). The small but significative increase of nucleophilic attack on the C-1 oxirane carbon observed when the opening reactions of cis epoxide 7 are carried out under metal ion-chelating procedures could be explained by initial complexation (Scheme II, route *b*) of the metal ion with the oxygen of the benzyloxy group of 7, very likely in its more stable conformation **7a**, to give structure **36** followed by entropically favored coordination with the oxirane oxygen to give the bidentate structure **37**. Attack of the nucleophile on the C-1 oxirane carbon of **37** to give C-1-type product will be favored in the present case not only on the basis of the Fürst–Plattner rule,[15] but also on the stereoelectronic factors implicated in the chelation-controlled ring opening of 3,4-epoxy-1-alkanol derivatives.[2] The same factors[2] should disfavor the formation of *C-2-type products*[11] by an analogous pathway starting from the less stable conformation **7b** (**7b** → **38** → **39** sequence, Scheme II). This type of chelation cannot be directly observed in those reactions of 7 [$LiAlH_4$ reduction and methylation with $(CH_3)_2CuLi$ and $Al(CH_3)_3$-BuLi] which are completely regioselective, even when nonchelating conditions (presence of 12-crown-4, a crown ether specific for Li^+) are used[4] (entries 8 and 11, Table I).

Scheme III



Marked amounts of both the possible regioisomers are observed in the reactions of trans epoxide 8 (Table II). The regioselectivity depends both on the reaction type and on the reaction conditions. Whereas in the methanolysis (H^+ or Li^+ catalyzed), C-1-type product predominates (entries 3 and 4, Table II) in the $LiAlH_4$ reduction and in the ring opening under methylating conditions (entries 7 and 8, Table II), the opposite regioisomer (C-2-type product) is found as the main product. A less marked regioselectivity is observed in the formation of chlorohydrins and in the azidolysis (entries 1, 2, 5, 6, Table II).

Keeping in mind that no chelating ring-opening processes are possible with trans epoxide 8, we may rationalize the results of the ring opening of this epoxide on the same basis as previously done for HBr addition and $LiAlH_4$ reduction of *trans*-3-methylcyclohexene oxide (**10**)[10b,14] which afforded regiochemical outcomes quite similar to those observed in the present case. Accordingly, if the ring opening of 8 occurs in a diaxial mode by its more stable conformation **8a** with the side chain pseudoequatorial, the attack of the nucleophile on the C-2 oxirane carbon is subjected to steric hindrance by the 3-[(benzyloxy)methyl] substitutent (Scheme III). On the other hand, the stereoelectronic favored diaxial ring opening[15] of 8 can occur also by the less favored conformation **8b** with attack of the nucleophile on the C-1 oxirane carbon affording C-1-type products. Changing the nucleophile and/or the reaction conditions can influence the relative rate of the two reaction pathways which lead to C-1- and C-2-type products, thus modifying the regioselectivity of the reaction. These variations are not easy to rationalize. However, the impressively high C-2 selection in the reaction of 8 with Me_2CuLi could be explained by means of a directing effect of the CH_2OBn group exerted by its coordination with the organometallic reagent.

Recently, it was found[16] that the reactions of epoxides 1 and 2 with $(CH_3)_2CuLi$ differ markedly in rate: cis epoxide 1 reacts much faster (ca. 10 times) than trans isomer 2; this result can be attributed to the ability of cis isomer 1 to react through a chelate-activated intermediate of type

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[12] Caron, M.; Sharpless, K. B. *J. Org. Chem.* **1985**, *50*, 1557.

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[16] Preliminary results from this laboratory: work in progress.

Table III. Spectroscopic Data for Chlorohydrins 11–14, Methoxy Alcohols 16–18, Azido Alcohols 19–22, Methyl Alcohols 24 and 25, Alcohols 27–30, and Bromohydrin 31

	^1H NMR[a] δ ($W_{1/2}$, Hz)		IR (CCl_4) (OH stretching) cm^{-1}		
compd	C*H*OH	C*H*X	1,2-OH···X	1,3-OH···O	OH_{free}
11	3.54 (23.5)	3.78 (20.1)[b]	3590		
12	4.01 (8.4)	4.14 (6.3)[b]	3588[g]	3502[h]	
13	4.01 (9.6)	4.25 (9.6)[b]	3590[g]		3622
14	3.50 (26.0)	3.79 (26.0)[b]	3594[h]	3514[g]	
16	3.95 (9.9)	3.31 (13.1)[c]	3586[g]	3520[h]	
17	3.67 (13.0)	3.14 (13.0)[c]	3592[h]		3632[g]
18	3.56 (22.1)	3.16 (25.6)[c]	3594[h]	3522[g]	
19	3.46 (26.0)	3.22 (20.8)[d]	3598[h]		3624[g]
20	2.85 (10.7)	3.68[d,e]		3510[h]	
21	3.85 (11.2)	3.73 (10.5)[d]	3598[i]		3626[h]
22	3.41 (19.4)	3.26 (26.0)[d]	3598[g]	3518[h]	
24	3.75 (18.0)			3526[h]	
25	3.64 (15.5)				3626
27	3.60 (21.6)				3622
28	4.10 (8.0)			3530[h]	3630[g]
29	4.34 (9.0)				3626
30	3.51 (23.0)			3530[h]	3630[g]
31	4.04 (7.5)	4.40 (8.8)[f]	3578[g]		3622[h]

[a] All the spectra were recorded in $CDCl_3$ (200 MHz). All the signals are multiplets. [b] X = Cl. [c] X = OMe. [d] X = N_3. [e] The signal is overlapped with the signal of CH_2OBn. [f] X = Br. [g] Weak band. [h] Strong band. [i] Shoulder.

6. In accordance with these data we reasoned that this difference in reactivity might also be observable in the corresponding reaction of epoxides of type 7 and 8. When an equimolar mixture of 7 and 8 was left in contact with $(CH_3)_2CuLi$ at −15 °C for 10 min, cis epoxide 7 reacted completely, while trans isomer 8 could be recovered almost completely unchanged. We calculate that cis epoxide 7 reacts almost 150 times faster than trans epoxide 8 in these conditions.[16]

The difference in rate observed in the reactions of the epoxides 7 and 8 with $(CH_3)_2CuLi$ is markedly larger than that found between the related epoxides *cis*-9 and *trans*-10 in their reaction with HCl, cis isomer 9 being ca. 2.3 times faster than trans isomer 10.[10b] In this case, the difference in reaction rate was justified on the basis of steric, conformational and stereoelectronic factors.[10b] However, the significantly larger difference in rate observed in the reaction of 7 and 8 with $(CH_3)_2CuLi$ may lend strong support to a metal-assisted chelating pathway in the case of 7.

Structures and Configurations

The distinction of the C-1- and C-2-type products was based, where possible, on the presence or absence of 1,2- and/or 1,3-OH···X interactions in the IR spectra (OH stretching) in diluted CCl_4 solutions (Table III). In some cases, independent syntheses or appropriate chemical transformations were also needed. The ^1H NMR spectra of all the isolated opening products are completely consistent with the structures and configurations assigned (Table III). A more detailed discussion about the structural assignments, is given in the Supplementary Material.

Experimental Section

For general experimental information, see ref 4. Alcohols 27 and 29 were prepared as previously described.[5]

2-Cyclohexenemethanol (33). (a) TMEDA (93 mL, 0.64 mol) was slowly added to a stirred 1.6 M butyllithium (400 mL), under nitrogen. Cyclohexene (518 mL, 5.12 mol) was then added, and the resulting reaction mixture was stirred for 16 h at rt. Paraformaldehyde (25.5 g, 0.85 mol) was added in 2 h, keeping the reaction temperature under 30 °C, and then the reaction mixture was stirred for 3 h. Water (200 mL) was added; evaporation of the washed (10% aqueous HCl and saturated aqueous NaCl) ether extracts afforded a crude liquid product (44.0 g) mostly consisting of alcohol 33 (GC and ^1H NMR) which was distilled to give 1-pentanol (10.5 g) and pure 33 (30.5 g) as a liquid, bp 96 °C (20 mmHg) [lit.[6] bp 51–54 °C (1.3 mmHg)].

(b) A solution of ester 32[7] (8.30 g, 59.3 mmol) in anhydrous ether (50 mL) was slowly added to a stirred suspension of $LiAlH_4$ (2.25 g, 59.3 mmol) in anhydrous ether (200 mL). The resulting reaction mixture was refluxed for 3 h and then cooled. Usual workup yielded a liquid product (6.0 g) consisting of alcohol 33[6] (5.6 g).

3-[(Benzyloxy)methyl]cyclohexene (34). Following a previously described procedure,[17] reaction of alcohol 33 (11.2 g, 0.10 mol) in anhydrous THF (85 mL) with benzyl bromide (14.1 mL, 0.115 mol) in the presence of NaH (5.52 g of an 80% dispersion in mineral oil, 0.184 mol) afforded a crude liquid reaction product (25.5 g) consisting of ether 34 (^1H NMR and GC) which was distilled to give pure 34 as a liquid, bp 95 °C (0.5 mmHg): ^1H NMR δ 7.26–7.37 (m, 5 H), 5.80 (m, 1 H), 5.61 (2 m, 1 H), 4.54 (s, 2 H), 3.35–3.38 (m, 2 H). Anal. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.04; H, 8.72.

Chlorohydroxylation of Olefin 34. Following the Sharpless procedure,[9] reaction of olefin 34 (6.9 g, 34.0 mmol) in anhydrous CH_2Cl_2 (400 mL) with 3 M TBHP in 2,2,4-trimethylpentane (13.6 mL) and $TiCl_4$ (4.49 mL, 41.0 mmol) in anhydrous CH_2Cl_2 (25 mL) at −78 °C afforded a crude solid reaction product (8.6 g) consisting of a 90:6:4 mixture of chlorohydrins 12–14 (GC). Recrystallization from hexane afforded pure *c*-**2-[(benzyloxy)methyl]-*t*-6-chloro-*r*-1-cyclohexanol (12)** (3.6 g) as a solid: mp 40–41 °C; IR, see Table III; ^1H NMR δ 7.26–7.36 (m, 5 H), 4.55 and 4.48 (ABdd, 2 H, J = 12.6 Hz), 3.61–3.65 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52. Found: C, 65.96; H, 7.48.

***c*-3-[(Benzyloxy)methyl]-*r*-1,2-epoxycyclohexane (7).** Following a standard procedure,[4] treatment of chlorohydrin 12 (3.0 g, 11.8 mmol) in anhydrous benzene (250 mL) with *t*-BuOK (2×1.67 g, 2×14.9 mmol) afforded a crude liquid reaction product (2.1 g) consisting of practically pure 7: ^1H NMR δ 7.25–7.38 (m, 5 H), 4.59 and 4.52 (ABdd, 2 H, J = 12.0 Hz), 3.60 (dd, 1 H, $J_{4,5}$ = 9.0 and $J_{3,4}$ = 7.8 Hz, H_4), 3.43 (dd, 1 H, $J_{4,5}$ = 9.0 and $J_{3,5}$ = 6.6 Hz, H_5), 3.25 (dd, 1 H, $J_{2,3}$ = 2.5 and $J_{1,2}$ = 4.0 Hz, H_2), 3.19 (m, 1 H, $J_{1,2}$ = 4.0, $J_{1,6}$ = 3.8, and $J_{1,7}$ = 1.7 Hz, H_1). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.96; H, 8.19.

Analogous treatment with *t*-BuOK (0.36 g × 2) of the crude chlorohydroxylation reaction product of olefin 34 (0.8 g) afforded a crude liquid product consisting of a 9:1 mixture of epoxides 7 and 8 (GC).

Reaction of Olefin 34 with NBA. A solution of olefin 34 (5.0 g, 24.7 mmol) in a 3:1 THF/H_2O mixture (200 mL) was treated with NBA (3.8 g, 27.2 mmol), and the reaction mixture was left in the dark for 4 h at rt. Usual workup afforded a crude oily product (6.44 g) mostly consisting (90%) of bromohydrin 31 which was subjected to flash chromatography with a 85:15 hexane/diisopropyl ether as the eluant, to give pure ***t*-3-[(benzyloxy)methyl]-*t*-2-bromo-*r*-1-cyclohexanol (31)** as a liquid (4.32 g): IR, see Table III; ^1H NMR δ 7.25–7.35 (m, 5 H), 4.51 and 4.50 (ABdd, 2 H, J = 11.8 Hz), 3.45 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}BrO_2$: C, 56.20; H, 6.40. Found: C, 56.05; H, 6.31.

***t*-3-[(Benzyloxy)methyl]-*r*-1,2-epoxycyclohexane (8).** Proceeding as usual, treatment of bromohydrin 31 (3.0 g, 10.0 mmol) in anhydrous benzene (200 mL) with *t*-BuOK (1.26 g × 2, 10.0 mmol × 2) afforded a crude liquid reaction product (1.75 g) consisting of practically pure trans epoxide 8: ^1H NMR δ 7.26–7.37 (m, 5 H), 4.55 and 4.54 (ABdd, 2 H, J = 11.0 Hz), 3.50 (dd, 1 H, $J_{4,5}$ = 9.1 and $J_{3,4}$ = 5.7 Hz, H_4), 3.45 (dd, 1 H, $J_{4,5}$ = 9.1 and $J_{3,5}$ = 6.7 Hz, H_5), 3.17 (m, 1 H, $J_{1,2}$ = 3.9 Hz, H_1), and 3.09 (dd, 1 H, $J_{1,2}$ = 3.9 and $J_{2,3}$ < 0.5 Hz, H_2). Anal. Calcd for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 76.90; H, 8.25.

Analogous treatment with *t*-BuOK (2 × 0.24 g) of the crude reaction product of olefin 34 with NBA (0.64 g) afforded a 9:1 mixture of epoxides 8 and 7 (GC).

Reaction of Epoxide 7 with HCl/CHCl$_3$. The reaction[4] of epoxide 7 (0.50 g, 2.3 mmol) in $CHCl_3$ (45 mL) with 36% aqueous

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HCl (23 mL) afforded after 30 min a crude oily product (0.56 g) consisting of a 89:11 mixture of chlorohydrins **12** and **11** (entry 1, Table I) which was subjected to preparative TLC with 7:3 hexane/ether as the eluant. Extraction of the two most intense bands afforded pure **12** (0.35 g) and ***c*-3-[(benzyloxy)methyl]-*t*-2-chloro-*r*-1-cyclohexanol (11)** as a liquid (0.020 g): IR, see Table III; ^{1}H NMR δ 7.25–7.67 (m, 5 H), 4.51 (s, 2 H), 3.61 (d, 2 H, J = 3.8 Hz), and see Table III. Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52. Found: C, 65.86; H, 7.32.

The same experimental result was obtained when the reaction was carried out with a gaseous HCl saturated $CHCl_3$ solution.

Chlorohydroxylation Reaction of Epoxide 7. The reaction[4] of epoxide **7** (0.10 g, 0.46 mmol) in anhydrous CH_2Cl_2 (7 mL) at −78 °C with 3 M TBHP in 2,2,4-trimethylpentane (0.2 mL) and $TiCl_4$ (0.06 mL, 0.55 mmol) afforded a crude oily product consisting of a 4:96 mixture of chlorohydrins **11** and **12** (GC, entry 2, Table I).

Reaction of Epoxide 8 with $HCl/CHCl_3$. The reaction[4] of epoxide **8** (0.66 g, 3.0 mmol) in $CHCl_3$ (60 mL) with 36% aqueous HCl (30 mL) (or with a gaseous HCl saturated $CHCl_3$) afforded a crude reaction product (0.74 g) consisting of a 62:38 mixture of chlorohydrins **13** and **14** which was subjected to preparative TLC with 8:2 petroleum ether/ether as the eluant. Extraction of the two most intense bands afforded pure **13** (0.20 g) and **14** (0.15 g).

***t*-3-[(Benzyloxy)methyl]-*t*-2-chloro-*r*-1-cyclohexanol (13)**: liquid; IR, see Table III; ^{1}H NMR δ 7.26–7.36 (m, 5 H), 4.55 and 4.48 (ABdd, 2 H, J = 11.2 Hz), 3.38–3.60 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52. Found: C, 65.78; H, 7.44.

***t*-2-[(Benzyloxy)methyl]-*t*-6-chloro-*r*-1-cyclohexanol (14)**: solid, mp 71–72 °C; IR, see Table III; ^{1}H NMR δ 7.27–7.41 (m, 5 H), 4.54 (s, 2 H), 3.61 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}ClO_2$: C, 66.00; H, 7.52. Found: C, 65.85; H, 7.39.

Chlorohydroxylation Reaction of Epoxide 8. The reaction[4] of epoxide **8** (0.10 g, 0.46 mmol) with TBHP and $TiCl_4$ as above described for **7** afforded a crude oily product consisting of a 47:53 mixture of chlorohydrins **13** and **14** (GC, entry 2, Table II).

Reaction of Epoxide 7 with 0.2 N H_2SO_4 in Anhydrous MeOH. Following a previously described procedure,[4] treatment of epoxide **7** (0.20 g, 0.92 mmol) with 0.2 N H_2SO_4 in anhydrous MeOH (20 mL) afforded, after 1 h at rt, a crude oily product (0.205 g) consisting of a 92:8 mixture of methoxy alcohols **16** and **15**[18] (GC, entry 3, Table I), which was subjected to semipreparative TLC with 8:2 petroleum ether/AcOEt as the eluant. Extraction of the most intense band afforded pure ***c*-2-[(benzyloxy)methyl]-*t*-6-methoxy-*r*-1-cyclohexanol (16)** (0.14 g) as a solid: mp 58–59 °C; IR, see Table III; ^{1}H NMR δ 7.26–7.36 (m, 5 H), 4.52 and 4.51 (ABdd, 2 H, J = 11.1 Hz), 3.63 (d, 2 H, J = 4.7 Hz), 3.35 (s, 3 H), and see Table III. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.82; H, 8.73.

Methanolysis of Epoxide 7 in the Presence of $LiClO_4$. Following a previously described procedure,[4] treatment of epoxide **7** (0.050 g, 0.23 mmol) with 17 M $LiClO_4$ in anhydrous MeOH (2 mL), at refluxing temperature for 20 h, afforded a crude liquid reaction product consisting of a 98:2 mixture of methoxy alcohols **16** and **15** (GC, entry 4, Table I).

Reaction of Epoxide 8 with 0.2 N H_2SO_4 in Anhydrous MeOH. Treatment[4] of epoxide **8** (0.18 g, 0.84 mmol) with 0.2 N H_2SO_4 in anhydrous MeOH (16 mL) for 1 h at rt afforded a crude oily product (0.18 g) consisting of a 35:65 mixture of methoxy alcohols **17** and **18** (GC) which was subjected to semipreparative TLC with 7:2:1 petroleum ether/CH_2Cl_2/AcOEt as the eluant. Extraction of the two most intense bands afforded pure **17** (0.050 g) and **18** (0.086 g).

***t*-3-[(Benzyloxy)methyl]-*t*-2-methoxy-*r*-1-cyclohexanol (17)**: liquid; IR, see Table III; ^{1}H NMR δ 7.24–7.33 (m, 5 H), 4.51 and 4.48 (ABdd, 2 H, J = 15.0 Hz), 3.39 (m, 2 H), 3.35 (s, 3 H), and see Table III. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.77; H, 8.80.

***t*-2-[(Benzyloxy)methyl]-*t*-6-methoxy-*r*-1-cyclohexanol (18)**: liquid; IR, see Table III; ^{1}H NMR δ 7.26–7.34 (m, 5 H), 4.53 (s, 2 H), 3.42 (s, 3 H), 3.36 (m, 2 H) and see Table III. Anal. Calcd for $C_{15}H_{22}O_3$: C, 71.97; H, 8.86. Found: C, 71.85; H, 8.71.

Methanolysis of Epoxide 8 in the Presence of $LiClO_4$. Treatment[4] of epoxide **8** (0.050 g, 0.23 mmol) with 17 M $LiClO_4$ in anhydrous MeOH (2 mL), at the refluxing temperature, afforded after 20 h a crude oily product consisting of a 25:75 mixture of methoxy alcohols **17** and **18** (GC, entry 4, Table II).

Reaction of Epoxide 7 with NaN_3/NH_4Cl. Following a previously described procedure,[12] treatment of epoxide **7** (0.20 g, 0.92 mmol) in a 8:1 MeOH/H_2O mixture (4.5 mL) with NH_4Cl (0.108 g, 2.02 mmol) and NaN_3 (0.30 g, 4.61 mmol) at 80 °C for 20 h afforded a crude oily product (0.24 g) consisting of a 14:86 mixture of azido alcohols **19** and **20** (entry 5, Table I) which was subjected to semipreparative TLC with 85:15 hexane/diisopropyl ether as the eluant. Extraction of the two most intense bands afforded pure **19** (0.020 g) and **20** (0.14 g).

***t*-2-Azido-*c*-3-[(benzyloxy)methyl]-*r*-1-cyclohexanol (19)**: liquid; IR, see Table III; ^{1}H NMR δ 7.26–7.36 (m, 5 H), 4.53 and 4.52 (ABdd, 2 H, J = 14.0 Hz), 3.61 (dd, 1 H, $J_{4,5}$ = 9.1 and $J_{3,4}$ = 4.4 Hz, H_4), 3.52 (dd, 1 H, $J_{4,5}$ = 9.1 and $J_{3,5}$ = 2.3 Hz, H_5), and see Table III. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.21; H, 7.38; N, 16.10.

***t*-2-Azido-*c*-6-[(benzyloxy)methyl]-*r*-1-cyclohexanol (20)**: solid, mp 46–47 °C; IR, see Table III; ^{1}H NMR δ 7.26–7.39 (m, 5 H), 4.55 and 4.47 (ABdd, 2 H, J = 12.0 Hz), 3.63 (d, 2 H, J = 4.7 Hz, H_4 and H_5) and see Table III. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.40; H, 7.21; N, 15.85.

Azidolysis of Epoxide 7 with NaN_3 in the Presence of $LiClO_4$. A solution of epoxide **7** (0.050 g, 0.23 mmol) in CH_3CN (2 mL) was treated with $LiClO_4$ (0.13 g, 1.22 mmol) and NaN_3 (0.020 g, 0.31 mmol), and the resulting reaction mixture was stirred at 80 °C for 20 h. Usual workup[1] afforded a crude oily residue consisting of a 5:95 mixture of azido alcohols **19** and **20** (GC, entry 6, Table I).

Reaction of Epoxide 8 with NaN_3/NH_4Cl. Treatment[12] of epoxide **8** (0.20 g, 0.92 mmol) with NaN_3 and NH_4Cl as previously described for epoxide **7** afforded a crude reaction product (0.23 g) consisting of a 54:46 mixture of azido alcohols **21** and **22** which was subjected to semipreparative TLC with 85:15 hexane/diisopropyl ether as the eluant. Extraction of the two most intense bands afforded pure **21** (0.070 g) and **22** (0.060 g).

***t*-2-Azido-*t*-3-[(benzyloxy)methyl]-*r*-1-cyclohexanol (21)**: liquid; IR, see Table III; ^{1}H NMR δ 7.25–7.37 (m, 5 H), 4.52 and 4.50 (ABdd, 2 H, J = 12.1 Hz), 3.35–3.52 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.18; H, 7.08; N, 15.87.

***t*-2-Azido-*t*-6-[(benzyloxy)methyl]-*r*-1-cyclohexanol (22)**, liquid; IR, see Table III; ^{1}H NMR δ 7.26–7.39 (m, 5 H), 4.53 (s, 2 H), 3.46–3.65 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{19}N_3O_2$: C, 64.35; H, 7.33; N, 16.08. Found: C, 64.09; H, 7.12; N, 15.79.

Azidolysis of Epoxide 8 with NaN_3 in the Presence of $LiClO_4$. Proceeding as previously described for the corresponding reaction of epoxide **7**, treatment of epoxide **8** (0.050 g, 0.23 mmol) in CH_3CN (2 mL) with $LiClO_4$ (0.13 g) and NaN_3 (0.020 g) afforded a crude oily reaction product consisting of a 58:42 mixture of azido alcohols **21** and **22** (GC, entry 6, Table II).

Reaction of Epoxide 7 with $(CH_3)_2CuLi$. A solution of epoxide **7** (0.218 g, 1.0 mmol) in anhydrous ether (5 mL) was added in 10 min to a stirred suspension of $(CH_3)_2CuLi$ [from 1.6 M CH_3Li (3.75 mL) and CuI (0.57 g, 3.0 mmol)] at −15 °C. The reaction mixture was kept at −15 °C for 30 min and then allowed to warm up to −2 °C in about 90 min. Saturated aqueous NH_4Cl was then added: evaporation of the washed (water) ether extracts afforded a crude liquid residue (0.22 g) consisting of **24**[18] (^{1}H NMR and GC) which was subjected to semipreparative TLC with 85:15 hexane/diisopropyl ether as the eluant. Extraction of the most intense band afforded pure ***c*-2-[(benzyloxy)methyl]-*t*-6-methyl-*r*-1-cyclohexanol (24)** as a liquid (0.18 g): IR, see Table III; ^{1}H NMR δ 7.26–7.35 (m, 5 H), 4.52 (s, 2 H), 3.54 (m, 2 H), 2.12 (m, 1 H, $W^1/_2$ = 18.0 Hz), 0.98 (d, 3 H, J = 7.7 Hz), and see Table III. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.65; H, 9.31.

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[18] Methoxy alcohol **15** and methyl alcohols **23** and **26** were not isolated pure due to insufficient amount present (**15** and **26**) or because not present (**23**) in the ring-opening reactions of epoxides **7** and **8**. However, in the case of **15** and **26** their presence was substantiated by GC and ^{1}H NMR analysis of the crude reaction products (Tables I and II).

Reaction of Epoxide 7 with $Al(CH_3)_3$–BuLi. Proceeding as previously described,[3] a solution of epoxide 7 (0.20 g, 0.9 mmol) in pentane (8 mL) was cooled at −50 °C then treated under N_2 with 2 M $Al(CH_3)_3$ in hexane (1.08 mL) and with 1.6 M BuLi in hexane (0.16 mL). The reaction mixture was then stirred at 0 °C for 5 h. Evaporation of the washed (water) ether extracts afforded an oily residue (0.205 g) consisting of practically pure **24** (^1H NMR and GC, entry 10, Table I).

Reaction of Epoxide 7 with $Al(CH_3)_3$–BuLi in the Presence of 12-Crown-4. Proceeding as previously described,[3] treatment of epoxide 7 (0.10 g, 0.46 mmol) with $Al(CH_3)_3$–BuLi [from 2 M $Al(CH_3)_3$ (1.5 mL) and 1.6 M BuLi (0.2 mL)] in the presence of 12-crown-4 (3.1 mmol), afforded after 4 h at rt a crude reaction product consisting of practically pure methyl alcohol **24** (GC, ^1H NMR, entry 11, Table I).

Reaction of Epoxide 8 with $(CH_3)_2CuLi$. As previously described for the corresponding reaction of epoxide 7, treatment of epoxide 8 (0.218 g, 1.0 mmol) with $(CH_3)_2CuLi$ (3.0 mmol) in anhydrous ether (5 mL) at 0 °C for 20 h afforded a crude oily reaction product (0.22 g) consisting of a 90:10 mixture of methyl alcohols **25** and **26**[18] (GC, entry 8, Table II) which was subjected to semipreparative TLC with 85:15 petroleum ether/diisopropyl ether as the eluant. Extraction of the most intense band afforded pure ***t*-3-[(benzyloxy)methyl]-*t*-2-methyl-*r*-1-cyclohexanol (25)** (0.12 g) as a liquid: IR, see Table III; ^1H NMR δ 7.22–7.35 (m, 5 H), 4.49 (s, 2 H), 3.35 (m, 2 H), 2.20 (m, 1 H, $W^1/_2 = 23.8$ Hz), 0.87 (d, 3 H, $J = 7.2$ Hz), and see Table III. Anal. Calcd for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 76.65; H, 9.31.

LAH Reduction of Epoxide 7. Following previously described procedures,[4] reduction of epoxide 7 (0.218 g, 1.0 mmol) in pentane (10 mL) with $LiAlH_4$ (0.078 g, 2 mmol) afforded a crude oily product (0.19 g) consisting of alcohol practically pure **28** (GC and ^1H NMR, entry 7, Table I), which was subjected to semipreparative TLC with 8:2:0.1 petroleum ether/AcOEt/MeOH as the eluant. Extraction of the most intense band afforded pure ***cis*-2-[(benzyloxy)methyl]cyclohexanol (28)** (0.16 g) as a liquid: IR, see Table III; ^1H NMR δ 7.26–7.35 (m, 5 H), 4.53 and 4.52 (ABdd, 2 H, $J = 12.5$ Hz), 3.57 (m, 2 H). Anal. Calcd for $C_{14}H_{20}O_2$: C, 85.66; H, 10.27. Found: C, 85.70; H, 10.32.

LAH Reduction of Epoxide 7 in the Presence of 12-Crown-4. Following a previously described procedure,[4] treatment of a solution of epoxide 7 (0.218 g, 1.0 mmol) in pentane (10 mL) with a suspension of $LiAlH_4$ (0.078 g, 2.0 mmol) previously left in contact with 12-crown-4 (0.36 mL, 2.2 mmol) for 15 h at rt, afforded after 3 h at rt a crude oily product consisting of alcohol **28** practically pure (GC and ^1H NMR, entry 8, Table I).

LAH Reduction of Epoxide 8. As above described for 7, treatment of epoxide 8 (0.218 g, 1.0 mmol) in pentane (10 mL) with $LiAlH_4$ (0.078 g, 2.0 mmol) afforded a crude oily product (0.21 g) consisting of a 72:28 mixture of alcohols **29** and **30** which was subjected to semipreparative TLC with 8:2:0.1 petroleum ether/AcOEt/MeOH as the eluant. Extraction of the two most intense bands afforded pure **29**[5] (0.12 g) and ***trans*-2-[(benzyloxy)methyl]cyclohexanol (30)** (0.030 g) as a liquid: IR, see Table III; ^1H NMR δ 7.26–7.35 (m, 5 H), 4.54 (s, 2 H), 3.50 (m, 2 H), and see Table III. Anal. Calcd for $C_{14}H_{20}O_2$: C, 85.66; H, 10.27. Found: C, 85.49; H, 10.32.

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Supplementary Material Available: Determination of the structure, configuration, and conformational analysis of epoxides 7 and 8 and of all the ring-opening products 11–31 (9 pages). Ordering information is given on any current masthead page.

Reactions of 2-Halovinyl Aryl Sulfoxides with Organometallic Reagents

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(*E*)- and (*Z*)-2-halovinyl aryl sulfoxides 1–4 were subjected to reactions with organocopper, organomagnesium, or organolithium reagents. The organometallic reagents gave different products: diorganocuprates led to formation of carbon–carbon bond, with production of alkenyl sulfoxides 5–10, whereas formation of carbon–sulfur bond and production of diaryl or aryl alkyl sulfoxides 11–13 were observed in the reaction with the other organometallics. Possible mechanisms for the two observed processes are briefly discussed.

In a series of papers,[1] we have described the stereospecific cross-coupling reaction of (*E*)- or (*Z*)-2-bromovinyl phenyl sulfide[1b,g,2] with Grignard reagents in the presence of nickel or palladium complexes as catalyst. We have also reported a variety of syntheses which shows that the method represents a convenient stereospecific route to alkenes and dienes.[3] In earlier studies,[4] we had investigated the synthetic, mechanistic, and stereochemical aspects of the cross-coupling process between (*E*)- or (*Z*)-2-halovinyl phenyl sulfones and diorganocuprates. A similar investigation of the reactions of the corresponding sulfoxides appeared essential. In particular, a versatile route to

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