Stereospecific Desulfinylation of α,β-Epoxy Sulfoxides with Butyllithium. A New Synthesis of Epoxides and Allylic Alcohols from Carbonyl Compounds[1)]

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Desulfinylation of α,β-epoxy sulfoxides, easily prepared from carbonyl compounds and 1-chloroalkyl phenyl sulfoxide, with 1 equivalent of butyllithium at low temperature gave epoxides in good yields. The similar α,β-epoxy sulfoxides having an arylmethyl group at the α-position gave 3-aryl-allylic alcohols upon treatment with excess butyllithium at −70 °C. These reactions offer a simple and useful approach to the synthesis of epoxides and 3-aryl-allylic alcohols from a carbonyl compound.

Epoxides have received considerable attention in recent years with interest concerning their synthesis, including asymmetric synthesis,[2)] their use as versatile intermediates in organic synthesis,[3)] and their use in the total synthesis of complex natural products.[4)] The preparation of epoxides are usually classified into two categories. One is the oxidation of a double bond with peroxy acids[2a,5)] or peroxides[2b)] or with NBS in the presence of water followed by a treatment with an alkali.[6)] The other is the method from ketones *via* Darzens-type condensation[7)] including sulfur ylides[8)] or arsonium ylides.[9)] The most important characteristic of the latter method is that the reaction gives epoxides with carbon–carbon bond formation.

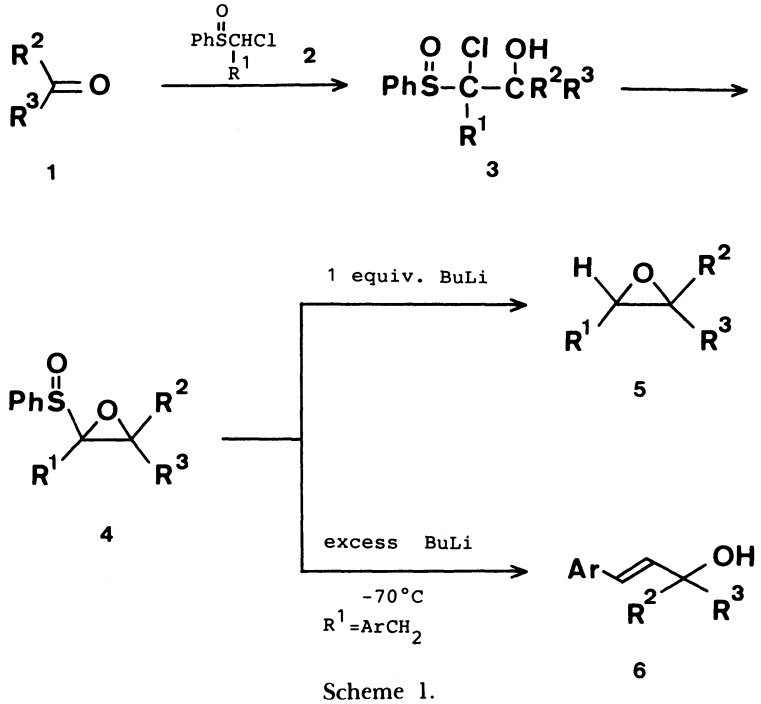
α,β-Epoxy sulfoxides (**4**) are very easily prepared in high yields and on a large scale from carbonyl compounds (**1**) and 1-chloroalkyl phenyl sulfoxide (**2**) by the Darzens-type condensation.[10)] We have reported that the β-carbon of α,β-epoxy sulfoxides (**4**) is highly reactive toward nucleophiles such as selenolates, thiolates, amines, and acetate giving dialkyl ketones,[11a)] α-sulfenylated ketones,[11b)] α-amino ketones,[11c)] and α-acetoxy ketones,[11d)] respectively, in good yields.

In the course of studies on the new synthetic methods from carbonyl compounds through α,β-epoxy sulfoxides, we found that the phenylsulfinyl group of the α,β-epoxy sulfoxides (**4**) could be easily cleaved with butyllithium (*n*-BuLi), even at −100 °C, to give epoxides (**5**) in quite good yields. This reaction leads to a novel synthetic method for the synthesis of epoxides from carbonyl compounds via α,β-epoxy sulfoxides. We also found that the α,β-epoxy sulfoxides (**4**) having an arylmethyl group at the α-position afforded 3-aryl-allylic alcohols (**6**) upon treatment with excess *n*-BuLi at −70 °C. These procedures are given in Scheme 1.

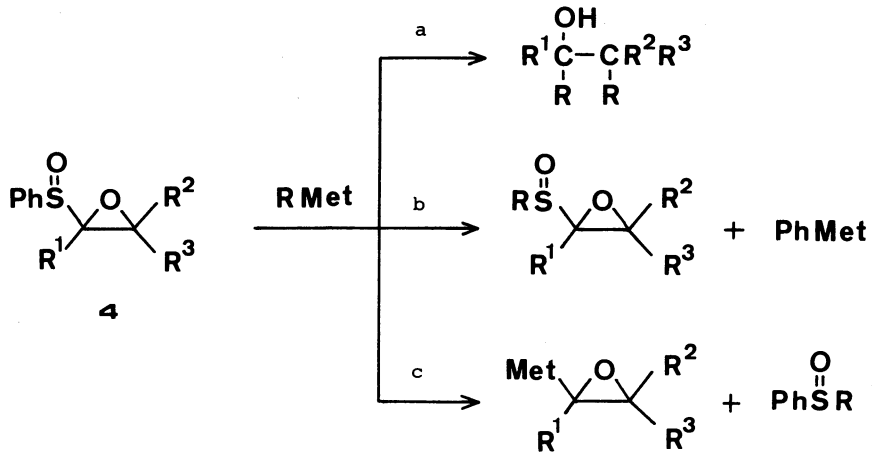
In this paper we describe details and the mechanistic aspects of these reactions.

Results and Discussion

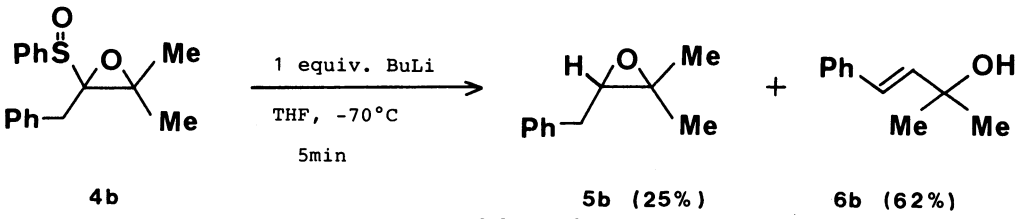
A Synthesis of Epoxides from Carbonyl Compounds



Scheme 1.



Scheme 2.



Scheme 3.

Through α,β-Epoxy Sulfoxides. If the phenylsulfinyl group of the α,β-epoxy sulfoxides (**4**) can be easily exchanged with hydrogen; this reaction offers a novel method for the epoxidation of carbonyl compounds. It has been reported that a treatment of sulfoxides with alkylmetal takes place carbon–sulfur bond cleavage.[12] In the treatment of α,β-epoxy sulfoxides (**4**) with alkylmetal, three types of reactions could be expected to take place: 1) A nucleophilic attack of a carbanion to the β-carbon of α,β-epoxy sulfoxides (**4**) (route a in Scheme 2); 2) the addition of a carbanion to the sulfinyl group leading to phenyl-alkyl exchange (route b); and 3) the addition of a carbanion to the sulfinyl group leading to the cleavage of the bond between sulfur and epoxide (route c). On the basis of this consideration α,β-epoxy sulfoxide (**4a**) was treated with 1 equivalent of *n*-BuLi in THF at −70°C. In this reaction all the starting materials disappeared within 5 min, and an 89% yield of the epoxide (**5a**) along with trace amounts of by-products and reasonable amount (about 50%) of butyl phenyl sulfoxide were obtained. This result clearly indicates that the reaction proceeded along route c shown in Scheme 2.

A search was made to find the most effective alkylmetal for this reaction. Table 1 shows the results for a treatment of α,β-epoxy sulfoxide (**4a**) with various alkylmetals, including lithium diisopropylamide (LDA) in THF at −70°C for 5 min. From these results, we decided to use *n*-BuLi throughout the study.

Next, α,β-epoxy sulfoxide (**4b**) was treated with 1 equivalent of *n*-BuLi under the same conditions as above. In this reaction a 62% yield of unexpected 3-phenyl-allylic alcohol (**6b**) along with the expected epoxide (**5b**) (25% yield) was obtained as shown in Scheme 3. The allylic alcohol (**6b**) was thought to form from the epoxide (**5b**) by isomerization with bases. When the reaction was carried out at −100°C for 5 min it was found that the desired epoxide (**5b**) was obtained in 71% yield with almost no allylic alcohol (**6b**).

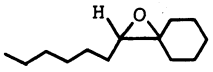
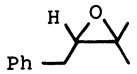
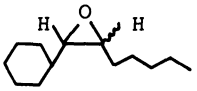
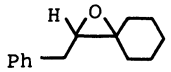
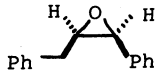
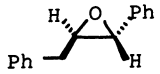
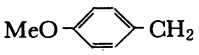
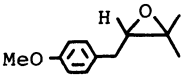
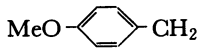
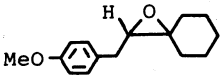
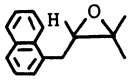
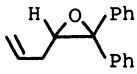
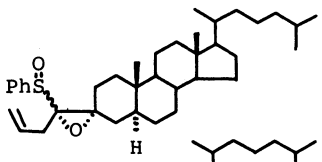
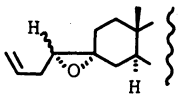
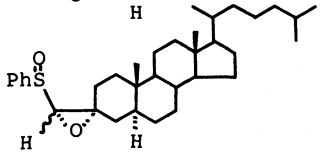
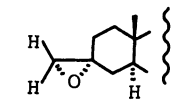
Table 1. Treatment of the α,β-Epoxy Sulfoxide (**4a**) with 1 Equivalent of Alkylmetal (RMet) in THF at −70°C for 5 min

RMet	**5a** (%)	Recovered (**4a**)/%
n-BuLi	89	0
CH_3Li	43	30[a]
t-BuLi	28	Trace[a]
EtMgBr	Trace	47[a]
LDA	0	88

a) The product other than **5a** was a complex mixture.

Representative results of the treatment of α,β-epoxy sulfoxides (**4**) with 1 equivalent of *n*-BuLi are listed in Table 2. As shown in Table 2, quite good results were obtained, except for Entry 12. It should be noted that in Entries 5 and 6, diastereomers (**4e-L**) and (**4e-P**)[13] afforded (*Z*)-epoxide (**5e-L**) and (*E*)-epoxide (**5e-P**),[14] respectively, without any contamination of their isomers. In previous studies the configuration of the diastereomers of the α,β-epoxy sulfoxides (**4**) was not determined but in this study, in order to clarify the stereochemistry of this reaction, we needed to determine the configuration of **4e**.

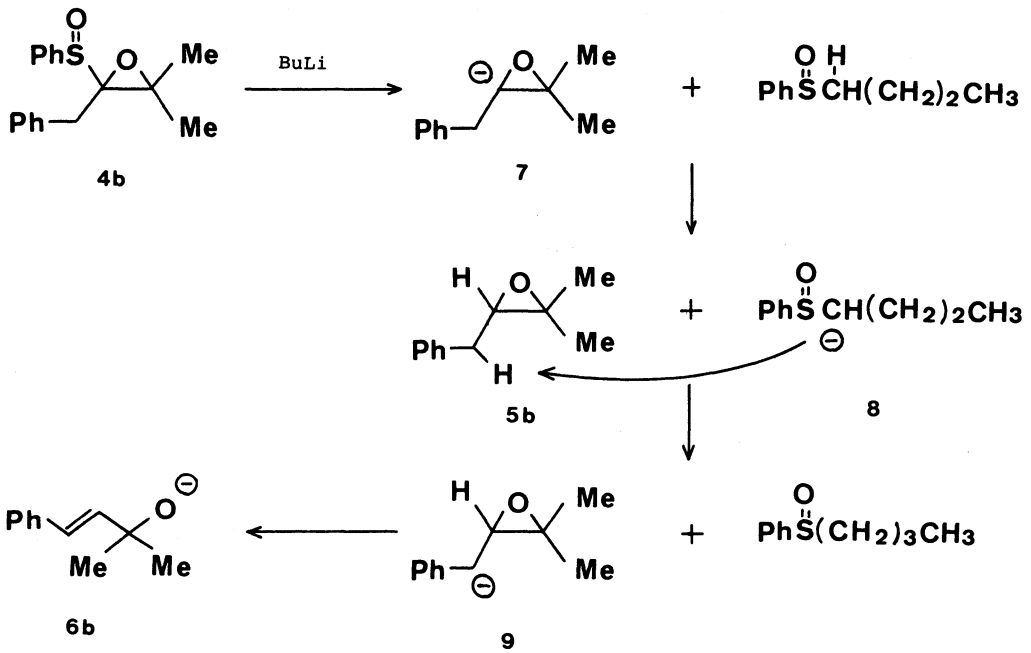
Table 2. Synthesis of Epoxides from α,β-Epoxy Sulfoxides and 1 Equivalent of Butyllithium[19]

Entry	α,β-Epoxy sulfoxide (4)				Temp	Epoxide (5)		Yield[a]
	R^1	R^2	R^3		°C			%
1	$CH_3(CH_2)_5$	— $(CH_2)_5$ —		(4a)	−70		(5a)	89
2	$PhCH_2$	CH_3	CH_3	(4b)	−100		(5b)	71
3		$CH_3(CH_2)_4$ or H		(4c-L)[b] (4c-P)[b]	−70 −70		(5c-L)[b] (5c-P)[b]	86 97
4	$PhCH_2$	— $(CH_2)_5$ —		(4d)	−100		(5d)	65(91)
5	$PhCH_2$	H	Ph	(4e-L)[c]	−100		(5e-L)	79
6	$PhCH_2$	Ph	H	(4e-P)[c]	−100		(5e-P)	90
7		CH_3	CH_3	(4f)	−100		(5f)	69
8		— $(CH_2)_5$ —		(4g)	−100		(5g)	78
9		CH_3	CH_3	(4h)	−100		(5h)	49(62)
10	CH_2=$CHCH_2$	Ph	Ph	(4i)	−100		(5i)	85
11				(4j)[b]	−100		(5j)[b]	83
12				(4k)[b]	−100		(5k)[17]	27

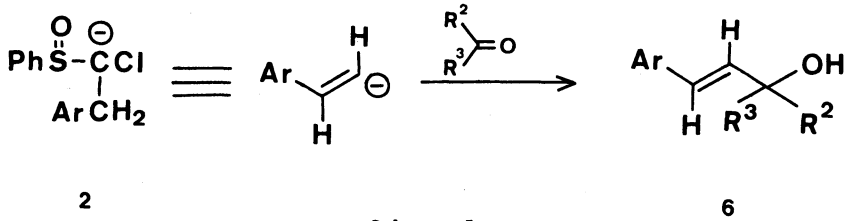
a) Isolated yields after silica-gel column chromatography. The yields in parenthesis are calculated from consumed starting material. b) The configuration was not determined. c) The configuration see Fig. 1.

The structures of these α,β-epoxy sulfoxides (**4e-L**) and (**4e-P**) were determined by the lanthanoid-induced shift[15] of their NMR spectra using tris[(heptafuluorobutanoyl)pivaloylmetanato]europium as a NMR shift reagent. Figure 1 shows the shift curves of the hydrogen on the β-carbon of the α,β-epoxy sulfoxides (**4e**), in which the differences of the chemical shift between original ones (**4e-L**:δ 4.87, **4e-P**:δ 3.79) and shifted ones (Δδ) are scaled on a vertical line and amounts (mole equivalents) of the shift reagent added are scaled on a horizontal line. From the results shown in Fig. 1, the structure of **4e-L** and **4e-P** were unambiguously determined as *E*- and *Z*-configurations, respectively. As already described, **4e-L** (*E*) and **4e-P** (*Z*) gave *Z*-epoxide (**5e-L**) and *E*-epoxide (**5e-P**); this reaction is stereospecific and the configuration of the carbon bearing the sulfinyl group was retained.

A Synthesis of 3-Aryl- and 3-Vinyl-Allylic Alcohols from Carbonyl Compounds Through α,β-Epoxy Sulfoxides. As mentioned above, a treatment of α,β-epoxy sulfoxide having a benzyl group as R^1 (**4b**) with 1 equivalent of *n*-BuLi gave 3-phenyl-allylic alcohol (**6b**) along with the epoxide (**5b**). The supposed mechanism of this reaction is shown in Scheme 4. The attack



Scheme 4.



Scheme 5.

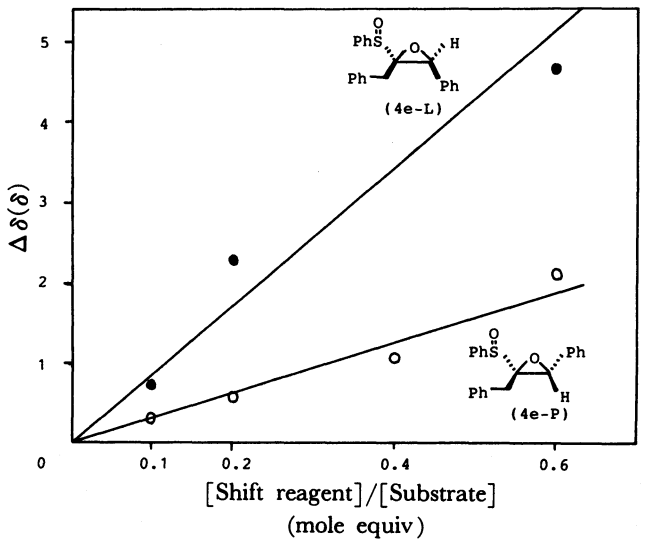
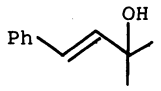
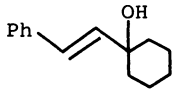
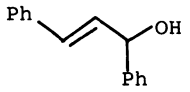
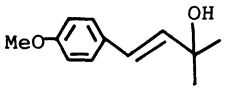
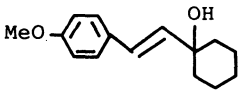
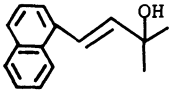
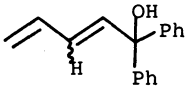
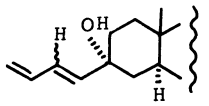


Fig. 1.

of *n*-BuLi on the sulfinyl group of **4b** leads to a carbon–sulfur bond cleavage, giving the carbanion (**7**) and butyl phenyl sulfoxide. Then, a proton transfer from the sulfoxide to **7** takes place to afford **5b** and the α-carbanion of butyl phenyl sulfoxide (**8**). As **5b** has acidic hydrogens on benzyl methylene carbon, the hydrogen is eliminated by the carbanion (**8**) giving **9**. This is isomerized to the allylic alcohol (**6b**). To make sure that the carbanion (**8**) acted as a base to isomerize the epoxide (**5**) into the allylic alcohol (**6**), the following experiment was carried out by using **5e-P** as an epoxide. To a solution of **5e-P** in THF at −70°C was added a solution of 1 equivalent of the carbanion (**8**), prepared from butyl phenyl sulfoxide and LDA. The reaction mixture was stirred for 5 min. After the usual work-up, the allylic alcohol (**6e**) and the starting material (**5e-P**) were obtained in 25 and 75% yields, respectively. From these facts it was predicted that excess bases and the higher temperature cause an acceleration of the epoxide-allylic alcohol isomerization. In fact, a treatment of **4b** with 3 equivalents of *n*-BuLi at −70°C for 5 min gave the allylic alcohol (**6b**) in 76% yield without the epoxide (**5b**).

Table 3 shows the results of the treatment of α,β-epoxy sulfoxides with excess *n*-BuLi (3—5 equivalents) in THF at −70°C for 5 min. All α,β-epoxy sulfoxides having an arylmethyl group, including an allyl group at the α-position, afforded 3-aryl-allylic alcohols (**6**) in good yields (except Entry 3). In this reaction the α,β-epoxy sulfoxides having a simple alkyl group as R^1 gave only epoxides (**5**) and no allylic alcohol was observed. The configuration of the double bond of **6** was confirmed as E by the NMR spectra.[16] It is

Table 3. Synthesis of Allylic Alcohols from α,β-Eoxy Sulfoxides and Excess Butyllithium at −70 °C[19]

Entry	α,β-Epoxy sulfoxide (4)	BuLi (eq)	Allylic alcohol (6)		Yield[a] %
1	**4b**	3		(**6b**)	76
2	**4d**	3		(**6d**)	87
3	**4e-L**	3		(**6e**)[18]	16
4	**4e-P**	3	**6e**		58
5	**4f**	3		(**6f**)	72
6	**4g**	3		(**6g**)	71
7	**4h**	3		(**6h**)	69
8	**4i**	5		(**6i**)[b]	85
9	**4j**	3		(**6j**)[b]	68

a) Isolated yields after silica-gel column chromatography. b) The product is single isomer. The configuration of the double bond is not determined.

noteworthy that in this reaction the carbanion of 1-chloroalkyl phenyl sulfoxide (**2**; $R^1=CH_2Ar$) acted as a β-arylvinyl carbanion equivalent as shown in Scheme 5.

In conclusion, a novel and versatile procedure for the synthesis of epoxides and 3-aryl-allylic alcohols has been developed from carbonyl compounds with carbon–carbon bond formation through α,β-epoxy sulfoxides. In regard to the accessibility of the starting materials, the simplicity and mildness of the operation, and high overall yields, the present procedure offers a simple and useful approach to the synthesis of epoxides and 3-aryl-allylic alcohols from carbonyl compounds.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured directly on a NaCl plate or in KBr disks with a Hitachi 215 spectrometer. ^1H Nuclear magnetic resonance (NMR) spectra were measured in a $CDCl_3$ solution with a JEOL FX-100 spectrometer using Me_4Si as an internal standard. Electron-impact mass spectra (MS) were obtained on a Hitachi M-80 double-focusing spectrometer at 70 eV by direct insertion. Silica gel BW-127ZH (Fuji-Devison) containing 2% fluorescence reagent 254 and quartz column were used for column chromatography and the products having ultraviolet (UV) absorption were detected by UV irradiation.

Materials. All α,β-epoxy sulfoxides (**4**) except **4f—j** were reported in the references IIa and 11b.

Preparation of 1-Chloro-2-(4-methoxyphenyl)ethyl Phenyl Sulfoxide, 1-Chloro-2-(1-naphthyl)ethyl Phenyl Sulfoxide, and 1-Chloro-3-butenyl Phenyl Sulfoxide. These sulfoxides were prepared from chloromethyl phenyl sulfoxide with 4-methoxybenzyl chloride, 1-(chloromethyl)naphthalene, and allyl bromide according to the procedure reported previously.[11a] 1-Chloro-2-(4-methoxyphenyl)ethyl phenyl sulfoxide: Diastereomeric mixture; colorless oil; 87% yield; IR (neat): 1090, 1040 (SO) cm^{-1}; ^1H NMR δ=2.76 (dd, *J*=9, 14 Hz), 3.18 (dd, *J*=9.5, 14.5 Hz), 3.53 (dd, *J*=3, 14.5 Hz), 3.58 (dd, *J*=5, 14 Hz), 3.79 (s), 4.55 (dd, *J*=3, 9 Hz), 4.67 (dd, *J*=5, 9 Hz), 6.8—7.3 (m), 7.5—7.9 (m); MS *m/z* (%): 179 ($[M-PhSO]^+$, 100), 178 ($[M-PhSOH]^+$, 84), 134 (43), 121 (26). 1-Chloro-2-(1-naphthyl)ethyl phenyl sulfoxide: Diastereomeric mixture; colorless crystals; mp 127—129 °C (AcOEt–hexane); 40% yield; IR (KBr): 1085, 1040 (SO) cm^{-1}; ^1H NMR δ=3.06 (dd, *J*=9, 14.5 Hz), 3.36 (dd, *J*=11, 15 Hz), 4.27 (dd, *J*=4.5, 15 Hz), 4.34 (dd, *J*=2, 14.5 Hz), 4.70 (dd, *J*=2, 11 Hz), 4.93 (dd, *J*=4.5, 9 Hz), 7.3—8.1 (m); MS *m/z* (%): 314 (M^+, trace),

188 ([M−PhSOH]$^+$, 23), 153 (100). 1-Chloro-3-butenyl phenyl sulfoxide: Diastereomeric mixture; colorless oil; 72% yield; IR (neat): 1090, 1050 (SO) cm^{-1}; ^{1}H NMR δ=2.1—2.5 (m), 2.6—3.2 (m), 4.48 (dd, J=4, 8 Hz), 4.60 (dd, J=4.5, 8.5 Hz), 5.1—5.3 (m), 5.6—6.1 (m), 7.5—7.9 (m); MS m/z (%): 214 (M$^+$, 2), 126 ([M−C_4H_4Cl]$^+$, 100), 89 ([M−PhSO]$^+$, 26), 78 (79).

General Procedure for the Preparation of α,β-Epoxy Sulfoxide (4): The synthesis of 2,3-epoxy-1-(4-methoxyphenyl)-3-methyl-2-(phenylsulfinyl)butane (**4f**) is described. To a solution of LDA (2.2 mmol) in dry THF (3 ml) at −70°C under N_2 was added a solution of 1-chloro-2-(4-methoxyphenyl)-ethyl phenyl sulfoxide (2 mmol) in 2 ml of dry THF dropwise through a syringe with stirring. The solution was stirred at −40°C for 20 min and then acetone (3 mmol) was added through a syringe and the reaction mixture was stirred for additional 10 min. The reaction was quenched with sat. aq NH_4Cl and the whole was extracted with ethyl acetate. The product was separated by silica-gel column chromatography to give chlorohydrin (**3**) and recovered starting material in 49 and 37% yield, respectively. Chlorohydrin: Mp 103—105°C (AcOEt-hexane); IR (KBr): 3400 (OH), 1035 (SO) cm^{-1}; ^{1}H NMR δ=1.26, 1.58 (each 3H, s), 3.30, 3.48 (each 1H, d, J=15 Hz), 3.83 (3H, s), 6.88, 7.30 (each 2H, d, J=9 Hz), 7.4—7.8 (5H, m); MS m/z (%): 226 ([M−PhSOH]$^+$, 29), 211 (67), 125 (40), 78 (76), 43 (100).

To a solution of the chlorohydrin (1.47 mmol) in 7 ml of MeOH and 4 ml of THF was added 30% aq KOH (6 ml) dropwise with stirring and the mixture was stirred at room temperature for 2 h. The reaction mixture was neutralized by adding NH_4Cl and the MeOH was evaporated. The residue was extracted with ethyl acetate and the product was purified by silica-gel column chromatography to give **4f** in quantitative yield. Mp 70—72°C (AcOEt-hexane); IR (KBr): 1080, 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.29, 1.83 (each 3H, s), 3.23 (2H, s), 3.73 (3H, s), 6.64, 6.72 (each 2H, d, J=10 Hz), 7.4—7.8 (5H, m); MS m/z (%): 316 (M$^+$, trace), 191 ([M−PhSO]$^+$, 31), 163 (8), 121 (100); Found: C, 68.22; H, 6.37; S, 9.95%. Calcd for $C_{18}H_{20}O_3S$: C, 68.33; H, 6.37; S, 10.13%.

3′-(4-methoxybenzyl)-3′-(phenylsulfinyl)spiro[cyclohexane-1,2′-oxirane] (4g). Chlorohydrin (**3**); colorless oil; 65% yield; IR (neat): 3400 (OH), 1080, 1035 (SO) cm^{-1}; ^{1}H NMR δ=1.0—2.4 (10H, m), 3.32, 3.44 (each 1H, d, J=15 Hz), 3.82 (3H, s), 6.7—7.0 (2H, m), 7.2—7.4 (2H, m), 7.4—7.8 (5H, m); MS m/z (%): 266 ([M−PhSOH]$^+$, 22), 209 (40), 126 (57), 78 (100). Epoxy sulfoxide (**4g**); 88% yield; colorless oil; IR (neat): 1080, 1050, 1035 (SO) cm^{-1}; ^{1}H NMR δ=1.3—2.3 (10H, m), 3.21 (2H, s), 3.73 (3H, s), 6.64, 6.77 (each 2H, d, J=10 Hz), 7.4—7.8 (5H, m); MS m/z (%): 231 ([M−PhSO]$^+$, 11), 202 (2), 121 (100).

2,3-Epoxy-3-methyl-1-(1-naphthyl)-2-(phenylsulfinyl)butane (4h). Chlorohydrin (**3**); mp 101—103°C (AcOEt-hexane); 52% yield; IR (KBr): 3380 (OH), 1080, 1040, 1020 (SO) cm^{-1}; ^{1}H NMR δ=1.45, 1.60 (each, 3H, s), 4.02, 4.40 (each 1H, d, J=15 Hz), 7.3—8.3 (12H, m); MS m/z (%): 246 ([M−PhSOH]$^+$, 68), 231 (18), 213 (80), 141 (28), 110 (87), 43 (100). Epoxy sulfoxide (**4h**); 93% yield; colorless oil; IR (neat): 1090, 1055, 1045 (SO) cm^{-1}; ^{1}H NMR δ=1.07, 1.89 (each 3H, s), 3.50, 3.87 (each 1H, d, J=17 Hz), 7.2—7.9 (12H, m); MS m/z (%): 336 (M$^+$, trace), 211 ([M−PhSO]$^+$, 22), 169 (68), 141 (100).

5,5-Diphenyl-4,5-epoxy-4-phenylsulfinyl-1-pentene (4i). In this case alkylation of 1-chloro-3-butenyl phenyl sulfoxide with benzophenone directly gave the α,β-epoxy sulfoxide (**4i**) in 92% yield. Mp 121—123°C (AcOEt-hexane); IR (KBr): 1640 (C=C), 1085, 1045 (SO) cm^{-1}; ^{1}H NMR δ=2.20, 2.90 (each 1H, dddd, J=1.2, 1.2, 6.5, 16 Hz), 4.36 (1H, m, $W/2$=20 Hz), 4.62 (1H, m, $W/2$=11 Hz), 4.96 (1H, dddd, J=6.5, 6.5, 10, 17 Hz), 7.2—7.8 (15 H, m); MS m/z (%): 234 ([M−PhSOH]$^+$, 41), 194 (46), 167 (71), 165 (100), 129 (80); Found: C, 75.95; H, 5.50; S, 8.90%. Calcd for $C_{23}H_{20}O_2S$: C, 76.64; H, 5.59; S, 8.89%.

3′-Allyl-3′-(phenylsulfinyl)spiro[5α-cholestane-3,2′-oxirane] (4j). Chlorohydrin (**3**); mp 107—108°C (AcOEt-hexane); 88% yield; IR (KBr): 3450 (OH), 1085, 1060, 1025 (SO) cm^{-1}; ^{1}H NMR δ=0.65 (3H, s), 0.87 (6H, d, J=7 Hz), 0.91 (3H, d, J=7 Hz), 0.97 (3H, s), 2.66 (2H, d, J=6.5 Hz), 5.08—5.50 (1H, m), 5.71—6.13 (1H, m), 6.44—6.94 (1H, m), 7.3—7.9 (5H, m); MS m/z (%): 474 ([M−PhSOH]$^+$, trace), 456 (4), 438 (9), 421 (5), 43 (100). Epoxy sulfoxide (**4j**); 88% yield; mp 114—116°C (MeOH-H_2O); IR (KBr): 1095, 1060 (SO) cm^{-1}; ^{1}H NMR δ=0.68 (3H, s), 0.88 (6H, d, J=7 Hz), 0.92 (3H, d, J=7 Hz), 1.03 (3H, s), 4.60—5.50 (3H, m), 7.4—7.8 (5H, m); MS m/z (%): 438 ([M−PhSOH]$^+$, 100), 397 (44), 369 (9); Found: C, 78.70; H, 9.93; S, 5.62%. Calcd for $C_{37}H_{56}O_2S$: C, 78.67; H, 9.99; S, 5.68%.

General Procedure for the Preparation of Epoxide (5) from α,β-Epoxy Sulfoxide (4): The synthesis of 3′-hexylspiro[cyclohexane-1,2′-oxirane] (**5a**) is described. To a solution of *n*-BuLi (0.1 mmol) in 0.2 ml of dry THF at −70°C under N_2 was added a solution of **4a** (0.1 mmol) in 0.2 ml of dry THF through a syringe with stirring. The reaction mixture was stirred for 5 min, then the reaction was quenched by adding sat. aq NH_4Cl and the whole was extracted with ethyl acetate. The organic layer was washed with sat. aq NH_4Cl and dried over Na_2SO_4. The product was purified by silica-gel column chromatography to give **5a** as a colorless oil in 89% yield. IR (neat): 2970, 2940, 2860, 1470, 1445, 910 cm^{-1}; ^{1}H NMR δ=0.90 (3H, t, J=6 Hz), 1.0—2.2 (20H, m), 2.73 (1H, t, J=6 Hz); MS m/z (%): 196 (M$^+$, 1), 153 (4), 125 (19), 98 (100).

2,3-Epoxy-3-methyl-1-phenylbutane (5b). Colorless oil; IR (neat): 1260, 1035 cm^{-1}; ^{1}H NMR δ=1.34, 1.41 (each 3H, s), 2.92 (3H, m), 7.30 (5H, m); MS m/z (%): 162 (M$^+$, 6), 147 ([M−CH_3]$^+$, 35), 119 (52), 91 (100).

1-Cyclohexyl-1,2-epoxyheptane (5c). 5c-L: Colorless oil; IR (neat): 2960, 2940, 2870, 1470, 1450, 1390, 1260, 885, 855, 830, 820, 790 cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, J=6 Hz), 1.0—2.1 (19H, m), 2.64 (1H, m, $W/2$=13 Hz) 2.93 (1H, m, $W/2$=12 Hz); MS m/z (%): 196 (M$^+$, 2), 113 (44), 95 (58), 81 (100); Found: m/z 196.1818. Calcd for $C_{13}H_{24}O$: M, 196.1825. **5c-P:** Colorless oil; IR (neat): 2970, 2940, 2870, 1470, 1450, 925, 900, 890, 875 cm^{-1}; ^{1}H NMR δ=0.90 (3H, t, J=6 Hz), 1.2—2.0 (19H, m), 2.47 (1H, m, $W/2$=10 Hz), 2.75 (1H, m, $W/2$=10 Hz); MS m/z (%): 196 (M$^+$, 2), 113 (44), 95 (58), 81 (100); Found: m/z 196.1831. Calcd for $C_{13}H_{24}O$: M, 196.1826.

3′-Benzylspiro[cyclohexane-1,2′-oxirane] (5d). Colorless oil; IR (neat): 3040, 2940, 2860, 1610, 1495, 1450, 740, 695 cm^{-1}; ^{1}H NMR δ=1.2—1.9 (10H, m), 2.94 (3H, m, $W/2$=14 Hz), 7.31 (5H, m, $W/2$=3 Hz); MS m/z (%): 202 (M$^+$, 7), 173 (20), 159 (35), 105 (100), 91 (73); Found: m/z 202.1345. Calcd for $C_{14}H_{18}O$: M, 202.1355.

2,3-Epoxy-1-(4-methoxyphenyl)-3-methylbutane (5f). Colorless oil; IR (neat): 1255, 1040 cm^{-1}; ^{1}H NMR δ=1.33, 1.40 (each 3H, s), 2.85 (3H, m), 3.82 (3H, s), 6.88, 7.18 (each 2H, d, J=9 Hz); MS m/z (%): 192 (M$^+$, 43), 177 ([M−CH_3]$^+$, 8),

163 (32), 149 (77), 121 (100); Found: *m/z* 192.1130. Calcd for $C_{12}H_{16}O_2$: M, 192.1149.

3′-(4-Methoxybenzyl)spiro[cyclohexane-1,2′-oxirane] (5g). Colorless oil; IR (neat): 1250, 1040 cm^{-1}; ^1H NMR δ=1.3—1.9 (10H, m), 2.88 (3H, m), 3.83 (3H, s), 6.88, 7.20 (each 2H, d, J=8 Hz); MS *m/z* (%): 232 (M^+, 20), 203 (23), 189 (34), 121 (100); Found: *m/z* 232.1463. Calcd for $C_{15}H_{20}O_2$: M, 232.1462.

2,3-Epoxy-3-methyl-1-(1-naphthyl)butane (5h). Colorless oil; IR (neat): 1260, 1030 cm^{-1}; ^1H NMR δ=1.36, 1.48 (each 3H, s), 3.06—3.56 (3H, m), 7.4—8.2 (7H, m); MS *m/z* (%): 212 (M^+, 33), 197 ([M−CH_3]$^+$, 7), 183 (17), 153 (83), 141 (100); Found: *m/z* 212.1196. Calcd for $C_{15}H_{16}O$: M, 212.1199.

5,5-Diphenyl-4,5-epoxy-1-pentene (5i). Colorless oil; IR (neat): 1270, 1030 cm^{-1}; ^1H NMR δ=2.16 (2H, bt, J=6.5 Hz), 3.51 (1H, t, J=6.5 Hz), 5.06 (1H, m, $W/2$=9 Hz), 5.19 (1H, m, $W/2$=6 Hz), 5.77—6.08 (1H, m), 7.2—7.6 (10H, m); MS *m/z* (%): 236 (M^+, 7), 207 (7), 194 (34), 165 (100); Found: *m/z* 236.1203. Calcd for $C_{17}H_{16}O$: M, 236.1200.

3′-Allylspiro[5α-cholestane-3,2′-oxirane] (5j). Colorless oil; IR (neat): 1650, 1265 cm^{-1}; ^1H NMR δ=0.67 (3H, s), 0.87 (6H, d, J=7 Hz), 0.92 (3H, d, J=7 Hz), 1.00 (3H, s), 2.2—2.4 (2H, m), 2.85 (1H, t, J=6 Hz), 5.0—5.3 (2H, m), 5.88 (1H, dddd, J=6.5, 6.5, 10, 17.5 Hz); MS *m/z* (%): 440 (M^+, 6), 400 (83), 381 (41), 55 (100), 43 (100); Found: *m/z* 440.4009. Calcd for $C_{31}H_{52}O$: M, 440.4014.

General Procedure for the Preparation of Allylic Alcohols (6) from α,β-Epoxy Sulfoxides (4): The synthesis of (*E*)-2-methyl-4-phenyl-3-buten-2-ol (**6b**) is described. To a solution of *n*-BuLi (0.6 mmol) in 0.3 ml of dry THF at −70 °C under N_2 was added a solution of epoxy sulfoxide (**4b**) (0.2 mmol) in 0.3 ml of dry THF with stirring. The reaction mixture was stirred for 5 min; then the reaction was quenched by adding sat. aq NH_4Cl. The whole was extracted with ethyl acetate and after the usual work-up, the product was purified by silica-gel column chromatography to give **6b** as a colorless oil in 76% yield. IR (neat): 3360 (OH) cm^{-1}; ^1H NMR δ=1.44 (6H, s), 6.37 (1H, d, J=16 Hz), 6.62 (1H, d, J=16 Hz), 7.2—7.5 (5H, m); MS *m/z* (%): 161 ([M−H]$^+$, 30), 126 (32), 91 (100).

(*E*)-1-Styryl-1-cyclohexanol (6d). Mp 65—66 °C (hexane); IR (KBr): 3400 (OH) cm^{-1}; ^1H NMR δ=1.1—2.0 (10H, m), 6.36 (1H, d, J=16 Hz), 6.67 (1H, d, J=16 Hz), 7.1—7.6 (5H, m); MS *m/z* (%): 202 (M^+, 69), 184 ([M−H_2O]$^+$, 24), 159 (100); Found: C, 83.09; H, 9.00%; *m/z* 202.1353. Calcd for $C_{14}H_{18}O$: C, 83.12; H, 8.79%; M, 202.1356.

(*E*)-4-(4-Methoxyphenyl)-2-methyl-3-buten-2-ol (6f). Mp 57—59 °C (hexane); IR (KBr): 3370 (OH) cm^{-1}; ^1H NMR δ=1.42 (6H, s), 3.83 (3H, s), 6.24 (1H, d, J=16.5 Hz), 6.54 (1H, d, J=16.5 Hz), 6.88, 7.33 (each 2H, d, J=8 Hz) MS *m/z* (%): 192 (M^+, 42), 177 ([M−CH_3]$^+$, 100), 159 (24), 121 (90); Found: C, 75.07; H, 8.28%. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39%.

(*E*)-1-(4-Methoxystyryl)-1-cyclohexanol (6g). Colorless oil; IR (neat): 3400 (OH) cm^{-1}; ^1H NMR δ=1.0—1.8 (10H, m), 3.82 (3H, s), 6.22 (1H, d, J=16 Hz), 6.58 (1H, d, J=16 Hz), 6.87, 7.33 (each 2H, d, J=9 Hz); MS *m/z* (%): 232 (M^+, 46), 214 ([M−H_2O]$^+$, 7), 189 (54), 121 (100); Found: *m/z* 232.1466. Calcd for $C_{15}H_{20}O_2$: M, 232.1462.

(*E*)-2-Methyl-4-(1-naphthyl)-3-buten-2-ol (6h). Colorless oil; IR (neat): 3370 (OH) cm^{-1}; ^1H NMR δ=1.49 (6H, s), 6.40 (1H, d, J=16 Hz), 7.2—8.2 (8H, m); MS *m/z* (%): 212 (M^+, 52), 197 ([M−CH_3]$^+$, 26), 179 (77), 152 (34), 141 (100); Found: *m/z* 212.1204. Calcd for $C_{15}H_{16}O$: M, 212.1200.

1,1-Diphenyl-2,5-pentadien-1-ol (6i). Mp 52—54 °C (MeOH-H_2O); IR (KBr): 3380 (OH) cm^{-1}; ^1H NMR δ= 5.08—5.37 (2H, m), 6.23—6.68 (3H, m), 7.1—7.5 (10H, m); MS *m/z* (%): 236 (M^+, 8), 218 ([M−H_2O]$^+$, 1), 183 (5), 165 (4), 105 (100); Found: *m/z* 236.1192. Calcd for $C_{17}H_{16}O$: M, 236.1200.

3β-(1,3-Butadienyl)-5α-cholestan-3α-ol (6j). Mp 84—86 °C (MeOH-H_2O); IR (KBr): 3500 (OH) cm^{-1}; ^1H NMR δ=0.66 (3H, s), 0.87 (6H, d, J=6.5 Hz), 0.90 (3H, d, J=6.5 Hz), 0.99 (3H, s), 5.0—5.4 (2H, m), 5.7—6.0 (1H, m), 6.1—6.6 (2H, m); MS *m/z* (%): 440 (M^+, 12), 422 ([M−H_2O]$^+$, 16), 407 (10), 43 (100); Found: *m/z* 440.3999. Calcd for $C_{31}H_{52}O$: M, 440.4014.

Isomerization of the Epoxide (5e-P) into Allylic Alcohol (6e). To a solution of LDA (0.2 mmol) in 0.2 ml of dry THF was added a solution of butyl phenyl sulfoxide (0.2 mmol) in 0.2 ml of dry THF under N_2 at −70 °C. After 10 min, a solution of **5e-P** (0.2 mmol) in 0.4 ml of dry THF was added to the mixture and stirred at −70 °C for 5 min. The reaction was quenched with sat. aq NH_4Cl. After the usual work-up, the allylic alcohol (**6e**) and the starting material (**5e-P**) were obtained in 25 and 75% yield, respectively.

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