

Stereospecific Desulfinylation of α,β -Epoxy Sulfoxides with Butyllithium. A New Synthesis of Epoxides and Allylic Alcohols from Carbonyl Compounds¹⁾

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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 condensation⁷⁾ including sulfur ylides⁸⁾ 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)}

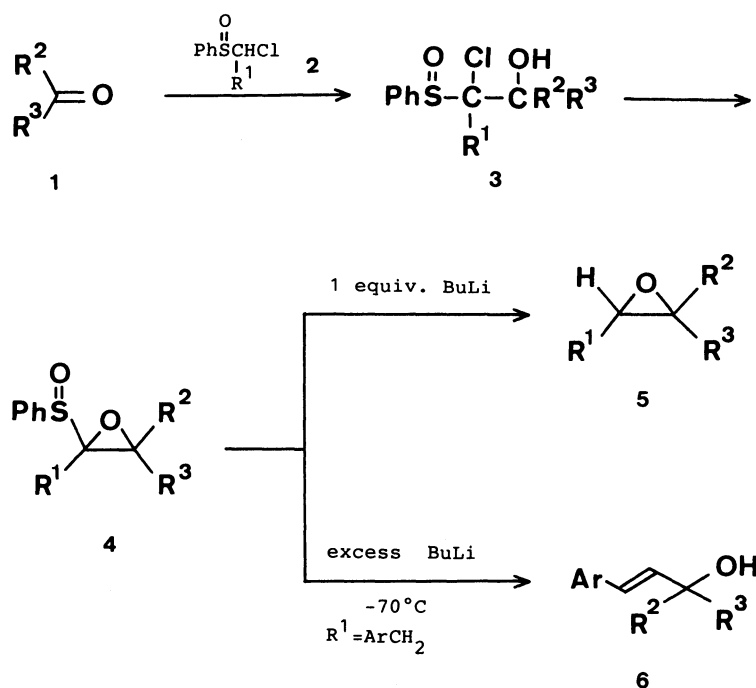
α -sulfenylated ketones,^{11b)} α -amino ketones,^{11c)} and α -acetoxy ketones,^{11d)} respectively, in good yields.

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.

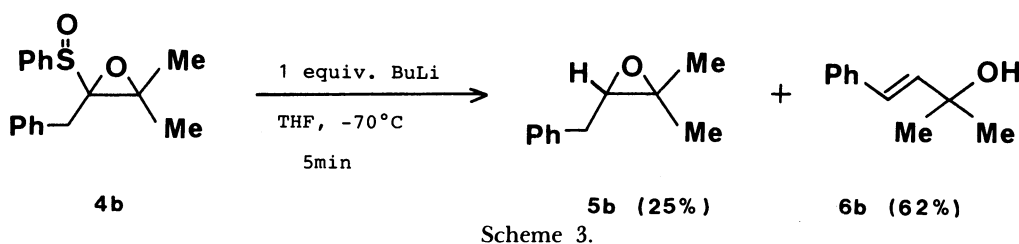
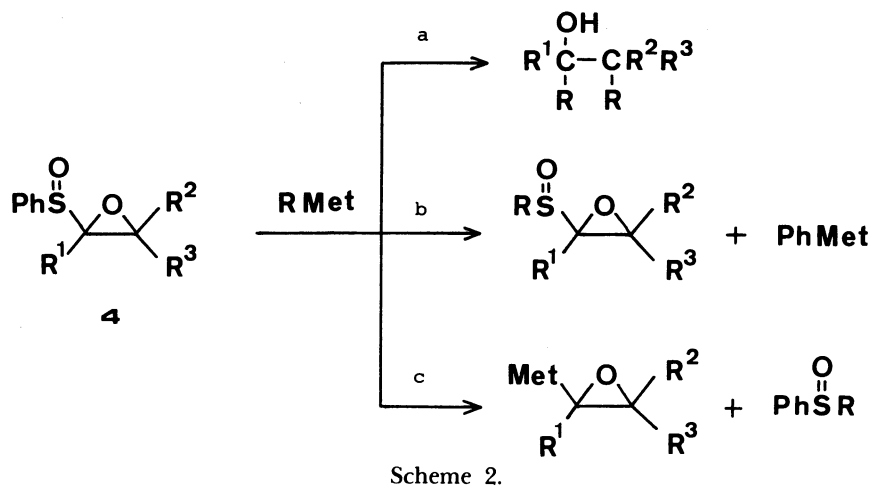
In this paper we describe details and the mechanistic aspects of these reactions.

Results and Discussion

A Synthesis of Epoxides from Carbonyl Compounds



Scheme 1.



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-

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)/%
<i>n</i> -BuLi	89	0
CH_3Li	43	30 ^{a)}
<i>t</i> -BuLi	28	Trace ^{a)}
EtMgBr	Trace	47 ^{a)}
LDA	0	88

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

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**).

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 Butyllithium¹⁹⁾

Entry	α,β -Epoxy sulfoxide (4)			Temp °C	Epoxide (5)	Yield ^{a)} %	
	R ¹	R ²	R ³				
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)}	−70		86	
			(4c-P) ^{b)}	−70		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	MeO--CH ₂	CH ₃	CH ₃ (4f)	−100		(5f) 69	
8	MeO--CH ₂	— (CH ₂) ₅ —	(4g)	−100		(5g) 78	
9	-CH ₂	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 shift¹⁵⁾ of their NMR spectra using tris[(heptafluorobutanoyl)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 ($\Delta\delta$) 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 R¹ (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

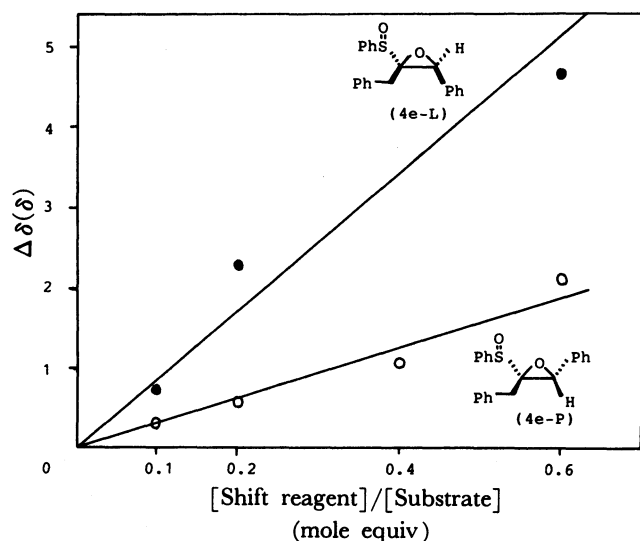
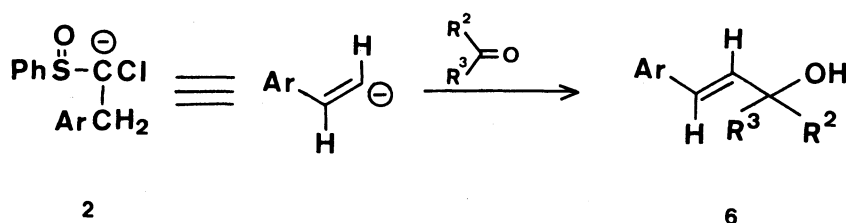
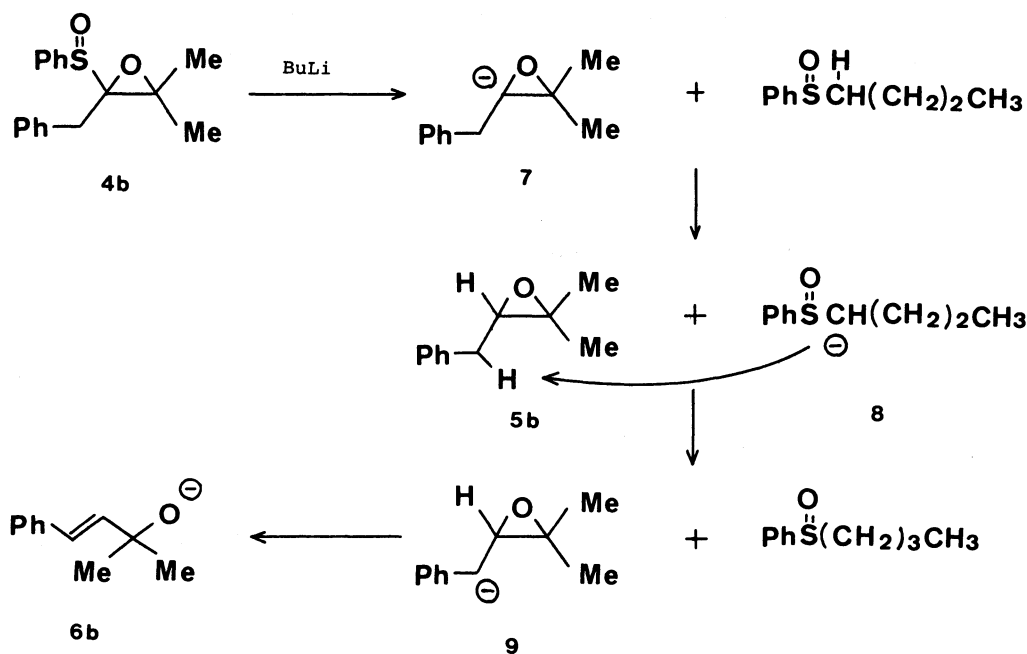


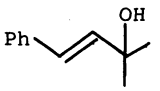
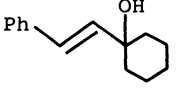
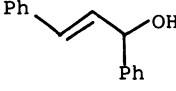
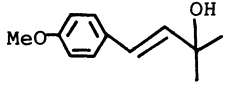
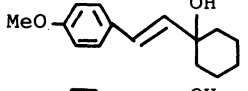
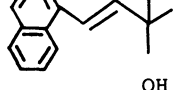
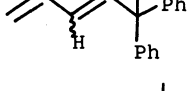
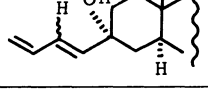
Fig. 1.

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 -Epoxy Sulfoxides and Excess Butyllithium at $-70^\circ\text{C}^{19)}$

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**; $\text{R}^1=\text{CH}_2\text{Ar}$) 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-

Devoson) 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 11a 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 $\delta=2.76$ (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 ($[\text{M}-\text{PhSO}]^+$, 100), 178 ($[\text{M}-\text{PhSOH}]^+$, 84), 134 (43), 121 (26). 1-Chloro-2-(1-naphthyl)ethyl phenyl sulfoxide: Diastereomeric mixture; colorless crystals; mp $127\text{--}129^\circ\text{C}$ (AcOEt-hexane); 40% yield; IR (KBr): 1085, 1040 (SO) cm^{-1} ; ^1H NMR $\delta=3.06$ (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; ¹H 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-C₄H₄Cl]⁺, 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 N₂ 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 NH₄Cl 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; ¹H 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 NH₄Cl 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; ¹H 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 C₁₈H₂₀O₃S: 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; ¹H 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; ¹H 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; ¹H 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; ¹H 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; ¹H 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 C₂₃H₂₀O₂S: 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; ¹H 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-H₂O); IR (KBr): 1095, 1060 (SO) cm⁻¹; ¹H 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 C₃₇H₅₆O₂S: 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 N₂ 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 NH₄Cl and the whole was extracted with ethyl acetate. The organic layer was washed with sat. aq NH₄Cl and dried over Na₂SO₄. 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; ¹H 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; ¹H 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-CH₃]⁺, 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; ¹H 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 C₁₃H₂₄O: M, 196.1825. **5c-P:** Colorless oil; IR (neat): 2970, 2940, 2870, 1470, 1450, 925, 900, 890, 875 cm⁻¹; ¹H 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 C₁₃H₂₄O: M, 196.1826.

3'-Benzylspiro[cyclohexane-1,2'-oxirane] (5d). Colorless oil; IR (neat): 3040, 2940, 2860, 1610, 1495, 1450, 740, 695 cm⁻¹; ¹H 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 C₁₄H₁₈O: M, 202.1355.

2,3-Epoxy-1-(4-methoxyphenyl)-3-methylbutane (5f). Colorless oil; IR (neat): 1255, 1040 cm⁻¹; ¹H 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-CH₃]⁺, 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[5 α -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 $-70^\circ C$ 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 $^\circ C$ (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 $^\circ C$ (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 $^\circ C$ (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.

3 β -(1,3-Butadienyl)-5 α -cholestan-3 α -ol (6j). Mp 84—86 $^\circ C$ (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 $-70^\circ C$. 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 $-70^\circ C$ 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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References

- 1) α,β -Epoxy sulfoxides as useful intermediates in organic synthesis VIII. Part VII. T. Satoh, S. Motohashi, and K. Yamakawa, *Tetrahedron Lett.*, **27**, 2889 (1986).
- 2) a) H. O. House "Modern Synthetic Reactions," W. A. Benjamin, Inc. Menlo Park, California (1982), pp. 292—352; b) K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta*, **12**, 63 (1979); c) T. Katsuki and K. B. Sharpless, *J. Am. Chem. Soc.*, **102**, 5974 (1980).
- 3) C. H. Behrens and K. B. Sharpless, *Aldrichimica Acta*, **16**, 67 (1983); J. G. Smith, *Synthesis*, **1983**, 629.
- 4) Y. Kishi, *Aldrichimica Acta*, **13**, 23 (1980); S. Masamune and W. Choy, *ibid.*, **15**, 47 (1982).
- 5) D. Swern, *Org. React.*, **7**, 378 (1953).
- 6) J. P. Pizey "Synthetic Reagents," John Wiley & Sons, Inc., 2, pp. 1—66 (1974).
- 7) M. S. Newmann and B. J. Mogerlein, *Org. React.*, **5**, 413 (1949); M. Ballester, *Chem. Rev.*, **55**, 283 (1955).
- 8) E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, **87**, 1353 (1965); B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides," Academic Press, New York (1975).
- 9) W. C. Still and V. J. Novack, *J. Am. Chem. Soc.*, **103**, 1283 (1981).
- 10) T. Durst, *J. Am. Chem. Soc.*, **91**, 1034 (1969); T. Durst, K.-C. Tin, F. de Reinach-Hirtzbach, J. M. Decesare, and M. D. Ryan, *Can. J. Chem.*, **57**, 258 (1979).
- 11) a) T. Satoh, Y. Kaneko, T. Izawa, K. Sakata, and K. Yamakawa, *Bull. Chem. Soc. Jpn.*, **58**, 1983 (1985); b) T. Satoh, T. Kumagawa, and K. Yamakawa, *ibid.*, **58**, 2849 (1985); c) T. Satoh, Y. Kaneko, K. Sakata, and K. Yamakawa, *ibid.*, **59**, 457 (1986); d) T. Satoh, S. Motohashi, and K. Yamakawa, *ibid.*, **59**, 946 (1986).
- 12) J. P. Lockard, C. W. Schroeck, and C. R. Johnson, *Synthesis*, **1973**, 485; T. Durst, M. J. LeBelle, R. Van den Elzen, and K.-C. Tin, *Can. J. Chem.*, **52**, 761 (1974); K. Ogura, K. Arai, and G. Tsuchihashi, *Bull. Chem. Soc. Jpn.*, **55**, 3669 (1982).

- 13) The diastereomers of the α,β -epoxy sulfoxides (**4**) are expressed as L- and P-, respectively. Details see references 11a and 11b.
- 14) Y. Tamura, S. M. Bayomi, K. Sumoto, and M. Ikeda, *Synthesis*, **1977**, 693.
- 15) A. Gaudemer, M. Golfier, A. Mandelbaum, and R. Parthasarathy "Stereochemistry Fundamentals and Methods" H. B. Kagan, Ed., Georg Thieme Publishers Stuttgart, Vol. 1, pp. 51—53 (1977).
- 16) A. C. Cope and J. K. Heeren, *J. Am. Chem. Soc.*, **87**, 3125 (1965); H. Nozaki, T. Mori, and R. Noyori, *Tetrahedron*, **22**, 1207 (1966).
- 17) J. D. Ballantine and P. J. Sykes, *J. Chem. Soc., (C)* **1970**, 731; C. Fleischmann and E. Zbiral, *Tetrahedron*, **34**, 317 (1978).
- 18) H. Neumann and D. Seebach, *Chem. Ber.*, **111**, 2785 (1978).
- 19) In the preliminary communication (T. Satoh, Y. Kaneko, and K. Yamakawa, *Tetrahedron Lett.*, **27**, 2379 (1986)) of this study, the configuration of 3-position of cholestanone derivatives (**4j**, **4k**, **5j**, **5k**, and **6j**) were erroneously described as β -epoxides and β -hydroxy compound.
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