α,β-Epoxy Sulfoxides as Useful Intermediates in Organic Synthesis. II.[1] A Novel Synthesis of α-Sulfenylated Ketones and α-Sulfenylated Aldehydes from α,β-Epoxy Sulfoxides

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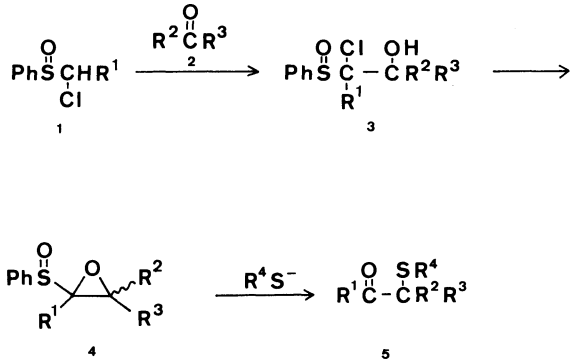
Treatment of α,β-epoxy sulfoxides, prepared from 1-chloroalkyl phenyl sulfoxides and carbonyl compounds, with various kinds of alkane- or arenethiolates afforded α-sulfenylated ketones in good yields. This method also offered a novel procedure for a synthesis of α-sulfenylated aldehydes.

Since the pioneering work of Trost and others, it is recognized that α-sulfenylated carbonyl compounds, including α-sulfinylated and α-sulfonylated carbonyl compounds, are useful and versatile compounds in synthetic organic chemistry.[2] The synthetic methods of α-sulfenylated carbonyl compounds are classified into two categories. One is the S_N2 displacement of α-halo ketones with alkanethiolates[3] and the other is the sulfenylation of carbanions (ketone enolate anions) with dialkyl disulfides or other electrophilic sulfenylating reagents.[4] These methods are widely used in the synthesis of α-sulfenylated carbonyl compounds but they have some drawbacks. The former method is useful only when regio-selectively halogenated carbonyl compounds are easily available. The latter has four fundamental problems. The first is a regioselectivity. Especially when simple unsymmetrical ketones are sulfenylated; it is very difficult to obtain regioselectively sulfenylated ketones exclusively by this method. The second one is the feasibility for bis-sulfenylation. The third one is the availability of dialkyl disulfide or other electrophilic sulfenylating reagents. The last one is the applicability of these methods to a synthesis of α-sulfenylated aldehydes.

In previous papers,[1,5] we have reported a method for the preparation of dialkyl ketones, aldehydes, and α-sulfenylated ketones from α,β-epoxy sulfoxides. In this paper we describe, in detail, a simple and useful method for a synthesis of α-sulfenylated ketones and α-sulfenylated aldehydes through the reaction of α,β-epoxy sulfoxides (**4**) with sodium alkanethiolates or sodium arenethiolates according to Scheme 1.

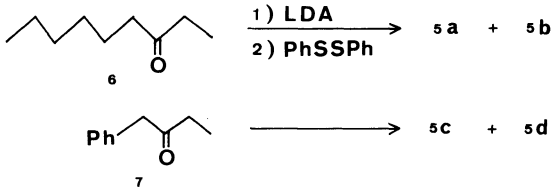


Scheme 1.

Results and Discussion

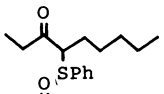
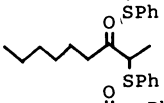
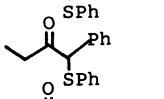
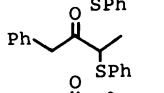
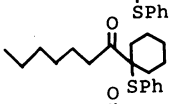
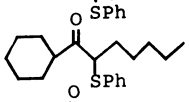
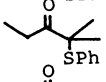
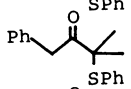
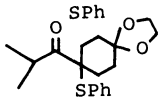
α,β-Epoxy sulfoxides (**4**) were initially reported by Durst in 1969.[6] They are easily prepared from chloromethyl phenyl sulfoxide (**1**; R^1=H) or 1-chloroalkyl phenyl sulfoxides (**1**; R^1=alkyl)[7] and carbonyl compounds (**2**) *via* chlorohydrins (**3**) in good overall yields. A few synthetic methods have already been reported[8] by using α,β-epoxy sulfoxides (**4**) but these interesting compounds have scarcely been used in organic synthesis. We have found that the β carbon of α,β-epoxy sulfoxides is highly reactive to various kinds of thiolates to afford α-sulfenylated ketones in good to excellent yields.[5]

The results of the reaction of α,β-epoxy sulfoxides (**4a—i**) with sodium benzenethiolate are summarized in Table 1. As shown in Table 1, various kinds of α-phenylsulfenylated ketones (**5a—i**) were synthesized through this method in good yields. More notable is the regiochemistry of the products. Treatment of 3,4-epoxy-3-phenylsulfinylnonane (**4a**) and 2,3-epoxy-3-phenylsulfinylnonane (**4b**) with two equivalents of sodium benzenethiolate in ethanol gave 4-phenylthio-3-nonanone (**5a**) and 2-phenylthio-3-nonanone (**5b**) in 87 and 80% yields, respectively, without any contamination by their regioisomers as shown in Table 1. Similarly, the epoxy sulfoxides (**4c**) and (**4d**) afforded single phenylsulfenylated ketones (**5c**) and (**5d**) in good yields without their regioisomers. As described above, the sulfenylation of ketones through the reaction of ketone enolate anions with electrophilic sulfenylating reagents possess a big problem, that is, the regioselectivity. Actually, the sulfenylation of 3-nonanone (**6**) and 1-phenyl-2-butanone (**7**) according to Trost's procedure[4e] gave a mixture of **5a** and **5b** (ratio 3:4),[9] a mixture of **5c** and **5d** (ratio 16:1)[9] in moderate



Scheme 2.

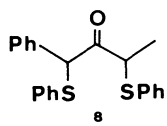
TABLE 1. SYNTHESIS OF α-PHENYLTHIO KETONES FROM α,β-EPOXY SULFOXIDES (4) AND SODIUM BENZENETHIOLATE

	α,β-Epoxy sulfoxide (4) R_1	R_2	R_3	PhSNa equiv.	Conditions	Ketone 5	Yield[a] %
4a	CH_3CH_2	$CH_3(CH_2)_4$	H	2	r.t. 45 min		**5a** 87
4b	$CH_3(CH_2)_5$	CH_3	H	2	0°C, 30 min		**5b** 80
4c	CH_3CH_2	Ph	H	2	r.t. 1 h		**5c** 74
4d	$PhCH_2$	CH_3	H	3	0°C, 2.5 h		**5d**[1] 92
4e	$CH_3(CH_2)_5$	$-(CH_2)_5-$		7	reflux 2.5 h		**5e** 96
4f		$CH_3(CH_2)_4$	H	3	0°C, 6 h		**5f** 93
4g	CH_3CH_2	CH_3	CH_3	7	50°C, 2.5 h		**5g** 91
4h	$PhCH_2$	CH_3	CH_3	7	r.t. 3 h		**5h** 91
4i	CH_3 CH_3 >CH	$-(CH_2)_2-C(O_2)-(CH_2)_2-$		10	reflux 24 h		**5i** 66 (92)[b]

a) Isolated yields after silica-gel column chromatography. b) Calculated from consumed starting material.

yields as shown in Scheme 2. Both sulfenylated ketones **5a** and **5b**, **5c** and **5d** have the same R_f values on silica-gel thin-layer chromatography and they are hardly separable by the usual techniques. From these results, it can be understood that the present method is one of the best ways for the preparation of relatively simple sulfenylated ketones. The synthesis of α-phenylsulfenylated ketones (**5e**) and (**5f**) is another example of the preparation of regioselectively sulfenylated isomers.

Attention should be called to the reaction of **4d** and **4h** with sodium benzenethiolate. Treatment of **4d** with three equivalents of sodium benzenethiolate in ethanol at room temperature for 20 min gave the desired **5d** and bis-sulfenylated ketone (**8**) in 47 and 52% yields, respectively. Similary, treatment of **4h** with three equivalents of sodium benzenethiolate at room temperature for 6 h gave a sulfenylated ketone (**5h**) and a bis-sulfenylated ketone (**9**) in 54 and 30% yields, respectively. The formation of these bis-sulfenylated ketones may be interpreted as shown in Scheme 3. The reaction of **4d** and **4h** with sodium benzenethiolate gives α-sulfenylated ketones **5d** and **5h** along with sodium benzenesulfenate. This sulfenate oxidizes thiophenol to give diphenyl disulfide. On the other hand, the hydrogen on the benzyl carbon of **5d** and **5h**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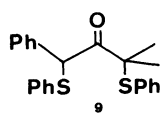
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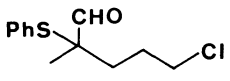
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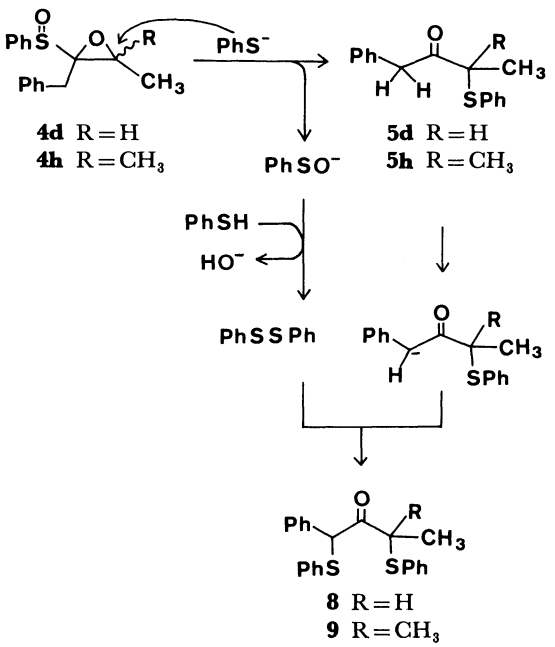
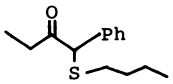
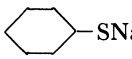
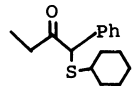
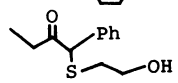
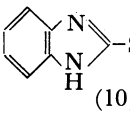
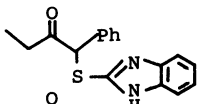
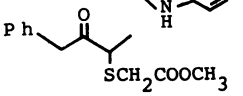


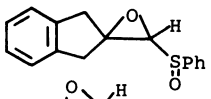
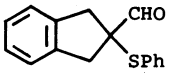
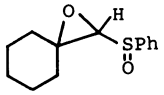
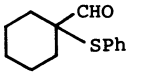
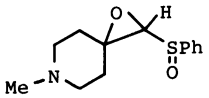
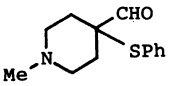
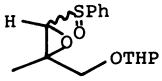
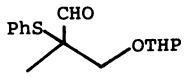
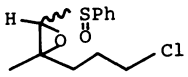
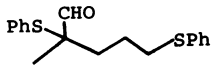
Scheme 3.

TABLE 2. SYNTHESIS OF α-SULFENYLATED KETONES FROM α,β-EPOXY SULFOXIDES (4) AND THIOLATES OTHER THAN BENZENETHIOLATE

	α,β-Epoxy sulfoxide (4) R1	R2	R3	Thiolate equiv.	Conditions	Ketone 5		Yield[a] %
4c	CH_3CH_2	Ph	H	$CH_3(CH_2)_3SNa$ (10)	0°C, 2h		5j	73
4c	CH_3CH_2	Ph	H	 (10)	r.t. 30min		5k	73
4c	CH_3CH_2	Ph	H	$HO(CH_2)_2SNa$ (10)	0°C, 30min		5l	53
4c	CH_3CH_2	Ph	H	 (10)	r.t. 20min		5m	82
4d	$PhCH_2$	CH_3	H	$NaOCOCH_2SNa$ (5)	r.t. 20min		5n	95[b]

a) Isolated yields after silica-gel column chromatography. b) Isolated as a methyl ester.

TABLE 3. SYNTHESIS OF α-PHENYLTHIO ALDEHYDES FROM α,β-EPOXY SULFOXIDES (4) AND SODIUM BENZENETHIOLATE

	α,β-Epoxy sulfoxide (4)	PhSNa equiv.	Conditions	Aldehyde 5		Yield[a] %
4k		2	r.t. 40min		5o	83
4l		2	40°C, 2h		5p	79
4m		2	r.t. 4h		5q	55
4n		2	r.t. 1h		5r	64
4o		5	40°C, 1h		5s	59

a) Isolated yields after silica-gel column chromatography.

(these hydrogens are very acidic because of adjacent carbonyl group and phenyl ring) is deprotonated by sodium benzenethiolate giving a carbanion, which attacks the diphenyl disulfide[10] to afford the bis-sulfenylated ketones (**8**) and (**9**). The formation of these bis-sulfenylated ketones were simply prevented by using a large excess of benzenethiolate at a lower reaction temperature as shown in Table 1.

The present method also permits thiolates other than benzenethiolate to be easily introduced at the β-carbon of α,β-epoxy sulfoxides (**4**) to afford α-sulfenylated carbonyl compounds in good yields under very mild conditions, as is shown in Table 2. As mentioned above, only limited numbers of dialkyl or diaryl disulfides, or electrophilic sulfenylating reagents are available, these sulfenylated ketones in Table 2 (**5j—n**) are not easily obtained by the reaction of ketone enolate anions with electrophilic sulfenylating reagents. To prevent the formation of by-products, such as phenylsulfenylated compounds[11] or products deriving from the desired sulfenylated ketones, excess (five to ten-fold excess) thiolate and low temperature (0°C to room temperature) were found to be suitable for obtaining the desired α-sulfenylated ketones.

As mentioned above, direct sulfenylation of aldehydes through the reaction of enolate anion of aldehyde with sulfenylating reagents is difficult and no good methods have been reported to make α-sulfenylated aldehydes. From the equation in Scheme 1, one would expect that the reaction of **4** having hydrogen as R^1 with thiolates may give α-sulenylated aldehydes (**5**; R^1=H).

The α,β-epoxy sulfoxide (**4k**), prepared from 2-indanone and chloromethyl phenyl sulfoxide in good overall yield, on treatment with two equivalents of sodium benzenethiolate in ethanol at room temperature for 40 min gave α-phenylsulfenylated aldehyde (**5o**) in 83% yield. Other results are summarized in Table 3. All the epoxy sulfoxides in Table 3 reacted with sodium benzenethiolate under mild conditions to afford the desired aldehydes in moderate to good yields. When **4o** was treated with benzenethiolate under room temperature, some chloro aldehyde (**10**) was obtained along with **5s**. This implies that the rate of opening of the epoxide of **4o** by thiolate is slightly faster than that of the substitution of chloro substituent.

In conclusion a novel and versatile procedure for a synthesis of α-sulfenylated ketones and α-sulfenylated aldehydes has been developed from chloromethyl phenyl sulfoxide and carbonyl compounds through the reaction of α,β-epoxy sulfoxides with various kinds of thiolates. The commercial availability of starting materials and ease of handling, mildness of the reaction conditions, and high yields of the products, the present method offers a simple and useful approach to a synthesis of relatively simple α-sulfenylated carbonyl compounds.

Experimental

General. All melting points and boiling points are uncorrected. A Shibata GTO-250 glass tube oven was used for bulb-to-bulb distillation and boiling points are given as the temperature of the heating bath. The isomeric ratio of the products was determined by gas-liquid phase chromatography (GLC) using a Shimadzu GC-6AM (OV-101, 20 m) instrument. Infrared (IR) spectra were measured directly on an NaCl plate or in KBr disks with a Hitachi 215 spectrometer. ^{1}H-NMR spectra were measured in $CDCl_3$ solution with a JEOL FX-100 pulse Fourier-transform 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. For TLC analysis throughout this work, Merck precoated TLC plates (Kieselgel 60 F_{254}, 0.25 mm) were used. Silica gel BW-127 ZH (Fuji-Davison) containing 2% fluorescence 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation. In experiments requiring dry solvent, THF was distilled from benzophenone ketyl; ethanol was dried by sodium metal and distilled.

General Procedure for the Preparation of α,β-Epoxy Sulfoxides (4): A synthesis of 3,4-epoxy-3-phenylsulfinylnonanone (**4a**) is described. To a solution of lithium diisopropylamide (3 mmol) in dry THF (8 ml) at -60 °C under N_2 was added a solution of 1-chloropropyl phenyl sulfoxide[7] (2.5 mmol) in 2 ml of dry THF dropwise with stirring and the solution was stirred for 15 min. Hexanal (3.75 mmol) was added to the reaction mixture through a syringe and the reaction was immediately quenched by aq NH_4Cl. The whole was extracted with ether–benzene and the organic layer was washed with sat. aq NH_4Cl. After the usual work-up, the crude products were purified by silica-gel column chromatography to give chlorohydrins (**3a-L**)[12] and (**3a-P**).[12] **3a-L** (30% yield): Colorless oil; IR (neat): 3250 (OH), 1030, 1020 (SO) cm^{-1}; NMR: δ=0.83 (3H, t, J=6.5 Hz), 1.36 (3H, t, J=7 Hz), 1.9—2.5, 2.5—3.0 (each 1H, m), 3.80 (1H, m), 7.4—7.9 (5H, m); MS m/z (%): 126 ([M−$C_9H_{17}ClO$]$^+$, 100), 105 (15), 78(31). **3a-P** (37% yield): Colorless oil; IR (neat): 3380 (OH), 1080, 1040 (SO) cm^{-1}; NMR: δ=0.89 (3H, t, J=6.5 Hz), 1.19 (3H, t, J=7 Hz), 2.10 (2H, m), 3.74 (1H, dd, J=9, 2 Hz), 7.4—7.8 (5H, m); MS m/z (%): 126 ([M−$C_9H_{17}ClO$]$^+$, 100), 105(78), 78(31).

To a solution of **3a-L** (1 mmol) in 12 ml of MeOH was added 30% aq KOH (2.5 ml) dropwise with stirring and the mixture was stirred at room temperature for 1 h. The reaction mixture was neutralized by NH_4Cl and the MeOH was evaporated. The residue was extracted with benzene and the organic layer washed with sat. aq NH_4Cl. After the usual work-up, the product was purified by silica-gel column chromatography to afford 89% yield of **4a-L**.[13] Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.82 (3H, t, J=7 Hz), 0.88 (3H, t, J=6.5 Hz), 3.64 (1H, t, J=6 Hz), 7.4—7.8 (5H, m); MS m/z (%): 266 (M$^+$, trace), 126(10), 77(10), 57(100); Found: m/z 266.1321. Calcd for $C_{15}H_{22}O_2S$: M, 266.1338. The epoxy sulfoxide (**4a-P**)[13] was synthesized from **3a-P** as similar procedure described above in 90% yield as a colorless oil. IR (neat): 1090, 1050 (SO) cm^{-1}; NMR: δ=0.70 (3H, t, J=7 Hz), 0.94 (3H, t, J=6.5 Hz), 3.25 (1H, t, J=6 Hz), 7.4—7.7 (5H, m); MS m/z (%): 266 (M$^+$, trace), 126(8), 77(6), 57(100); Found: m/z 266.1333. Calcd for $C_{15}H_{22}O_2S$: M, 266.1339.

1,2-Epoxy-1-phenyl-2-phenylsulfinylbutane (4c). Chlorohydrin **3c-L** (45% yield): Colorless prisms; mp 140—142 °C; IR (KBr): 3210 (OH), 1035 (SO) cm^{-1}; NMR: δ=1.29 (3H, t, J=7 Hz), 2.02 (1H, dq, J=15, 7 Hz), 2.97 (1H, dq, J=15, 7 Hz), 4.93 (1H, s), 7.23 (5H, s), 7.5—8.0 (5H, m); MS m/z (%): 309 ([M+1]$^+$, trace), 126(100), 105(40), 91(47); Found: C, 62.45; H, 5.52; Cl, 11.65; S, 10.44%. Calcd for $C_{16}H_{17}ClO_2S$: C, 62.23; H, 5.55; Cl, 11.48; S, 10.38%. **3c-P** (52% yield): Colorless prisms; mp 110 °C (dec); IR (KBr): 3370 (OH), 1035 (SO) cm^{-1}; NMR: δ=0.94 (3H, t, J=7 Hz), 1.3—2.3 (2H, m), 5.31 (1H, s), 7.2—7.9 (10H, m); MS m/z (%): 182(11), 147(27), 126(100), 105(38); Found: C, 62.30; H, 5.49; Cl, 11.62; S, 10.58%. Calcd for $C_{16}H_{17}ClO_2S$: C, 62.23; H, 5.55, Cl, 11.48; S, 10.38%. Epoxy sulfoxide **4c-L** (99% yield): Colorless oil; IR (neat): 1045, (SO) cm^{-1}; NMR: δ=0.76 (3H, t, J=7 Hz), 1.1—2.0 (2H, m), 4.77 (1H, s), 7.1—7.9 (10H, m); MS m/z (%): 272 (M$^+$, 0.6), 147 ([M−PhSO]$^+$, 47), 91(100); Found m/z 272.0846. Calcd for $C_{16}H_{16}O_2S$: M, 272.0869. **4c-P** (99% yield): Colorless oil; IR (neat): 1045 (SO) cm^{-1}; NMR: δ=0.85 (3H, t, J=7 Hz), 1.4—1.8 (1H, m), 2.37 (1H, sextet, J=7 Hz), 4.42 (1H, s), 7.2—7.8 (10H, m); MS m/z (%): 272 (M$^+$, trace), 147 ([M−PhSO]$^+$, 35), 91(100); Found m/z 272.0909. Calcd for $C_{16}H_{16}O_2S$: M, 272.0870.

1,2-Epoxy-1-cyclohexyl-1-phenylsulfinylheptane (4f). Chlorohydrin **3f-L** (46% yield): IR (neat): 3375 (OH), 1040 (SO) cm^{-1}; NMR: δ=0.80 (3H, t, J=6 Hz), 3.95 (1H, t, J=6 Hz), 7.4—7.9 (5H, m). **3f-P** (47% yield): Colorless oil; IR (neat): 3410 (OH), 1085, 1060, 1030, (SO) cm^{-1}; NMR: δ=0.89 (3H, t, J=6 Hz), 3.70 (1H, bd, J=8 Hz), 7.3—7.8 (5H, m). Epoxy sulfoxide **4f-L** (85% yield): Colorless oil; IR (neat): 1095, 1060 (SO) cm^{-1}; NMR: δ=0.91 (3H, t, J=7 Hz), 3.55 (1H, dd, J=7, 5 Hz), 7.4—7.7 (5H, m); MS m/z (%): 320 (M$^+$, 0.3), 304 (0.7), 195 ([M−PhSO]$^+$, 8), 126(7), 111(24),

83(100); Found: *m/z* 320.1829. Calcd for $C_{19}H_{28}O_2S$: M, 320.1809. **4f-P** (93% yield): Colorless oil; IR (neat): 1090, 1050 (SO) cm^{-1}; NMR: δ=0.95 (3H, t, *J*=6 Hz), 3.26 (1H, t, *J*=6 Hz), 7.4—7.8 (5H, m).

2,3-Epoxy-2-methyl-3-phenylsulfinylpentane (4g). Chlorohydrin **3g** (99% yield): Colorless prisms; mp 76—77 °C; IR (KBr): 3350 (OH), 1035 (SO) cm^{-1}; NMR: δ=0.93 (3H, t, *J*=7 Hz), 1.43, 1.67 (each 3H, s), 1.99 (2H, m), 7.3—7.8 (5H, m); MS *m/z* (%): 162 ([M−$C_6H_{11}ClO$]$^+$, 86), 78 (32), 43 (100); Found: C, 55.10; H, 7.31; Cl, 13.67; S, 12.33%. Calcd for $C_{12}H_{17}ClO_2S$: C, 55.27; H, 6.57; Cl, 13.59; S, 12.30%. Epoxy sulfoxide **4g** (75% yield): Colorless oil; IR (neat): 1075, 1040 (SO) cm^{-1}; NMR:δ=0.50 (3H, t, *J*=7 Hz), 1.41, 1.83 (5H, m); MS *m/z* (%): 224 (M$^+$, trace), 126(48), 99 ([M−PhSO]$^+$, 79), 43 (100).

α,β-Epoxy Sulfoxide (4m). Chlorohydrin **3m** (85% yield): Colorless prisms; mp 165 °C (dec); IR (KBr): 3400 (OH), 1085, 1040 (SO) cm^{-1}; MS *m/z* (%): 287 (M$^+$, 0.4), 272 ([M−CH_3]$^+$, 40), 270(99), 126(58), 70(83), 42(100). Epoxy sulfoxide **4m** (95% yield): Colorless oil; IR (neat): 1090, 1050 (SO) cm^{-1}; NMR: δ=2.37 (3H, s), 4.76 (1H, s), 7.5—7.8 (5H, m); MS *m/z* (%): 251 (M$^+$, 1.8), 234(46), 126(32), 96(26), 83 (100); Found: *m/z* 251.1003. Calcd for $C_{13}H_{17}NO_2S$: M, 251.0979.

1,2-Epoxy-5-chloro-2-methyl-1-phenylsulfinylpentane (4o). Chlorohydrin **3o** (97% yield): Diastereomeric mixture; colorless needles; mp 138—145 °C; IR (KBr): 3360 (OH), 1045 (SO) cm^{-1}; MS *m/z* (%): 126 ([M−$C_6H_{10}Cl_2O$]$^+$, 100), 78(37), 43(50). Epoxy sulfoxide **4o** (12% yield): Colorless oil; IR (neat): 1085, 1045 (SO) cm^{-1}; NMR: δ=1.44 (3H, s), 3.72 (1H, s), 4.04 (1H, t, *J*=6 Hz), 7.5—7.9 (5H, m); MS *m/z* (%): 258 (M$^+$, 0.1), 133 ([M−PhSO]$^+$, 41), 126(100); Found: *m/z* 258.0457. Calcd for $C_{12}H_{15}ClO_2S$: M, 258.0479.

All other α,β-epoxy sulfoxides (**4**) are reported in Ref. 1.

General Procedure for the Preparation of α-Sulfenylated Ketones and α-Sulfenylated Aldehydes: A synthesis of 4-phenylthio-3-nonanone (**5a**) is described. To 2 ml of dry EtOH NaH (60% oil suspension; 20 mg; 0.5 matom) was added followed by thiophenol (52 μl; 0.5 mmol) at 0 °C under N_2 atmosphere. A solution of 3,4-epoxy-3-phenylsulfinylnonane (**4a**) (68 mg; 0.25 mmol) in 0.5 ml of EtOH was added to the benzenethiolate solution and the reaction mixture was stirred at room temperature under N_2 atmosphere for 45 min. The reaction mixture was neutralized by adding NH_4Cl and the EtOH evaporated. The residue was extracted with benzene and the organic layer was washed with sat. aq NH_4Cl, dried and concentrated. The crude product was purified by silica-gel column chromatography to afford 54.5 mg (87%) of 4-phenylthio-3-nonanone (**5a**) as a colorless oil. IR (neat): 1705 (CO) cm^{-1}; NMR: δ=0.88 (3H, t, *J*=7 Hz), 1.03 (3H, t, *J*=7 Hz), 3.58, 3.59 (each 1H, q, *J*=7 Hz), 3.63 (1H, t, *J*=7 Hz), 7.1—7.5 (5H, m); MS *m/z* (%): 250 (M$^+$, 24), 193 ([M−C_2H_5CO]$^+$, 100), 123(73), 109(18), 83(29); Found: *m/z* 250.1384. Calcd for $C_{15}H_{22}OS$: M, 250.1389.

2-Phenylthio-3-nonanone (5b). Colorless oil; IR (neat): 1710 (CO) cm^{-1}; NMR: δ=0.87 (3H, t, *J*=7 Hz), 1.40 (3H, d, *J*=7 Hz), 2.60 (2H, m), 3.76 (1H, q, *J*=7 Hz), 7.1—7.4 (5H, m); MS *m/z* (%): 250 (M$^+$, 10), 137 ([M−$C_6H_{13}CO$]$^+$, 100), 109 (16); Found: *m/z* 250.1363. Calcd for $C_{15}H_{22}OS$: M, 250.1389.

1-Phenyl-1-phenylthio-2-butanone (5c). Colorless prisms; mp 35—36 °C (sublimation); IR (neat): 1710 (CO) cm^{-1}; NMR: δ=0.98 (3H, t, *J*=7 Hz), 2.44, 2.64 (each 1H, dq, *J*=18, 7 Hz), 4.95 (1H, s), 7.1—7.4 (10H, m); MS *m/z* (%): 256 (M$^+$, 5), 200 (16), 199 ([M−C_2H_5CO]$^+$, 100), 165 (10), 91(16); Found: *m/z* 256.0907. Calcd for $C_{16}H_{16}OS$: M, 256.0920.

1-Phenyl-1,3-bis(phenylthio)-2-butanone (8). Diastereomeric mixture; colorless oil; IR (neat): 1720 (CO) cm^{-1}; NMR: δ=1.26, 1.30 (each d, *J*=7 Hz), 3.71, 3.94 (each q, *J*=7 Hz), 5.32, 5.46 (each s), 7.0—7.5 (m); MS *m/z* (%): 364 (M$^+$, 9), 255 ([M−PhS]$^+$, 14), 227 (11), 199 ([M−C_9H_9OS]$^+$, 100).

1-(1-Phenylthiocyclohexyl)-1-heptanone (5e). Colorless oil; IR (neat): 1705 (CO) cm^{-1}; NMR: δ=0.90 (3H, t, *J*=7 Hz), 2.74 (2H, t, *J*=7 Hz), 7.26 (5H, s); MS *m/z* (%): 304 (M$^+$, 2), 191 ([M−$C_7H_{13}O$]$^+$, 100); Found: *m/z* 304.1839. Calcd for $C_{19}H_{28}OS$: 304.1858.

1-Cyclohexyl-2-phenylthio-1-heptanone (5f). Colorless oil; IR (neat): 1710 (CO) cm^{-1}; NMR: δ=0.87 (3H, t, *J*=7 Hz), 2.68 (1H, m), 3.68 (1H, dd, *J*=8, 7 Hz), 7.1—7.4 (5H, m); MS *m/z* (%): 304 (M$^+$, 13), 193 ([M−$C_7H_{11}O$]$^+$, 100), 123 (38); Found: *m/z* 304.1857. Calcd for $C_{19}H_{28}OS$: M, 304.1859.

2-Methyl-2-phenylthio-3-pentanone (5g). Colorless oil; IR (neat): 1695 (CO) cm^{-1}; NMR: δ=1.10 (3H, t, *J*=7 Hz), 1.41 (6H, s), 2.79 (2H, q, *J*=7 Hz), 7.27 (5H, s); MS *m/z* (%): 208 (M$^+$, 7), 191 (3), 151 ([M−C_2H_5CO]$^+$, 100), 109 (13); Found: *m/z* 208.0911. Calcd for $C_{12}H_{16}OS$: M, 208.0920.

3-Methyl-1-phenyl-3-phenylthio-2-butanone (5h). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; NMR: δ=1.44 (6H, s), 4.07 (2H, s), 7.1—7.3 (10H, m); MS *m/z* (%): 270 (M$^+$, 4), 151 ([M−$PhCH_2CO$]$^+$, 100); Found: *m/z* 270.1083. Calcd for $C_{17}H_{18}OS$: M, 270.1078.

3-Methyl-1-phenyl-1,3-bis(phenylthio)-2-butanone (9). Colorless crystals; mp 97—98 °C; IR (KBr): 1695 (CO) cm^{-1}; NMR: δ=1.25, 1.42 (each 3H, s), 5.60 (1H, s), 7.0—7.4 (15H, m); MS *m/z* (%): 378 (M$^+$, 4), 269(5), 199(36), 151 ([M−$C_{14}H_{11}OS$]$^+$, 100); Found: *m/z* 378.1084. Calcd for $C_{23}H_{22}OS_2$: M, 378.1111.

2-Methyl-1-(4,4-ethylenedioxy-1-phenylthiocyclohexyl)-1-propanone (5i). Colorless oil; IR (neat): 1700 (CO) cm^{-1}; NMR: δ=1.20 (6H, d, *J*=7 Hz), 3.40 (1H, septet, *J*=7 Hz), 3.92 (4H, bs), 7.26 (5H, bs); MS *m/z* (%): 320 (M$^+$, 4), 249 ([M−C_4H_7O]$^+$, 90), 205(8), 187(26), 99(100); Found: *m/z* 320.1457. Calcd for $C_{18}H_{24}O_3S$: M, 320.1444.

1-Butylthio-1-phenyl-2-butanone (5j). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; NMR: δ=0.87 (3H, t, *J*=7 Hz), 1.00 (3H, t, *J*=7 Hz), 2.3—2.7 (4H, m), 4.61 (1H, s), 7.1—7.4 (5H, m); MS *m/z* (%): 236 (M$^+$, 2), 199(11), 179 ([M−C_2H_5CO]$^+$, 100), 123(43), 91(38); Found: *m/z* 236.1214. Calcd for $C_{14}H_{20}OS$: M, 236.1233.

1-Cyclohexylthio-1-phenyl-2-butanone (5k). Colorless oil; bp 170 °C/ 5 mmHg[†]; IR (neat): 1720 (CO) cm^{-1}; NMR : δ=0.99 (3H, t, *J*=7 Hz), 2.4—2.8 (3H, m), 4.68 (1H, s), 7.1—7.4 (5H, m); MS *m/z* (%): 262 (M$^+$, 1), 205 ([M−C_2H_5CO]$^+$, 69), 199(4), 123(100); Found: *m/z* 262.1387. Calcd for $C_{16}H_{22}OS$: M, 262.1390.

1-(2-Hydroxyethylthio)-1-phenyl-2-butanone (5l). Colorless oil; IR (neat): 3400 (OH), 1710 (CO) cm^{-1}; NMR: δ= 1.01 (3H, t, *J*=7 Hz), 2.3—2.7 (2H, m), 2.63 (2H, t, *J*=6 Hz), 3.67 (2H, bt, *J*=6 Hz), 4.73 (1H, s), 7.32 (5H, bs); MS *m/z* (%): 224 (M$^+$, 1), 167 ([M−C_2H_5CO]$^+$, 100), 150(10), 123 (12), 91 (54); Found: *m/z* 224.0861. Calcd for $C_{12}H_{16}O_2S$: M, 224.0870.

1-(Benzimidazol-2-ylthio)-1-phenyl-2-butanone (5m). Colorless powder; mp 141—142 °C; IR (KBr): 1725 (CO)

[†] 1 mmHg≈133.322 Pa.

cm^{-1}; NMR: δ=0.99, 1.12 (each t, J=7 Hz), 2.0—2.7 (2H, m), 5.34, 5.84 (each s), 6.9—7.8 (m); The complexity of the signals is thought to be due to the restricted rotation of the imidazolylthio group; MS m/z (%): 296 (M^+, 33), 240 (100), 239 ([M−C_2H_5CO]$^+$, 56), 207 (40); Found: C, 68.89; H, 5.35; N, 9.42; S, 10.83%; M^+ 296.0987. Calcd for $C_{17}H_{16}N_2OS$: C, 68.89; H, 5.44; N, 9.45; S, 10.82%; M, 296.0983.

*3-Methoxycarbonylmethylthio-1-phenyl-2-butanone (**5n**).* Colorless oil; IR (neat): 1745, 1715 (CO) cm^{-1}; NMR: δ= 1.39 (3H, d, J=7 Hz), 3.18 (2H, s), 3.61 (1H, q, J=7 Hz), 3.69 (3H, s), 3.91, 3.96 (each 1H, d, J=15 Hz), 7.23 (5H, m); MS m/z (%): 252 (M^+, 20), 193 ([M−$C_2H_3O_2$]$^+$, 3), 133 ([M−$PhCH_2CO$]$^+$, 78), 91 (100); Found: m/z 252.0791. Calcd for $C_{13}H_{16}O_3S$: M, 252.0818.

*2-Phenylthio-2-indancarbaldehyde (**5o**).* Colorless oil; IR (neat); 2725 (CHO), 1730, 1725 (CO) cm^{-1}; NMR: δ=3.13, 3.47 (each 2H, d, J=16 Hz), 7.21 (4H, s), 7.2—7.5 (5H, m), 9.57 (1H, s); MS m/z (%): 220 (M^+, 17), 191 ([M−CHO]$^+$, 81), 123 (28), 110 (40), 109 (26), 81 (100).

*1-Phenylthio-1-cyclohexanecarbaldehyde (**5p**).* Colorless oil; IR (neat): 2720 (CHO), 1720 (CO) cm^{-1}; NMR: δ=1.1— 2.0 (10H, m), 7.1—7.5 (5H, m), 9.29 (1H, s); MS m/z (%): 254 (M^+, 13), 225 ([M−CHO]$^+$, 33), 145 ([M−PhS]$^+$, 27), 116 (49), 115 (100).

*4-Formyl-N-methyl-4-phenylthiopiperidine (**5q**).* Colorless oil; IR (neat): 1710 (CO) cm^{-1}; NMR: δ=1.8—2.3 (6H, m), 2.29 (3H, s), 2.6—2.9 (2H, m), 7.2—7.5 (5H, m), 9.30 (1H, s); MS m/z (%): 235 (M^+, 11), 207 ([M−CO]$^+$, 17), 174 (3), 126 ([M−PhS]$^+$, 79), 109(13), 96(44), 83(100); Found: m/z 235.1020. Calcd for $C_{13}H_{17}NOS$: M, 235.1030.

*2-Methyl-2-phenylthio-3-tetrahydropyranyloxypropanal (**5r**).* Diastereomeric mixture; colorless oil; IR (neat): 1730 (CO), 1020 (COC) cm^{-1}; NMR: δ=1.34, 1.38 (each s), 3.49, 3.64, 3.93, 4.05 (each d, J=10 Hz), 4.62 (1H, bs), 7.2—7.6 (m), 9.46, 9.47 (each s); MS m/z (%): 280 (M^+, 2), 179 ([M− THPO]$^+$, 8), 166(51), 140(34), 109(29), 85(100).

*2-Methyl-2,5-bis(phenylthio)pentanal (**5s**).* Colorless oil; IR (neat): 2720 (CHO), 1720 (CO) cm^{-1}; NMR: δ=1.24 (3H, s), 2.93 (2H, t, J=7 Hz), 7.1—7.4 (10H, m), 9.35 (1H, s); MS m/z (%) 316 (M^+, 30), 287 ([M−CHO]$^+$, 8), 207 ([M−PhS]$^+$, 39), 177(64), 150(42), 123(58), 109(100); Found: m/z 316.0943. Calcd for $C_{18}H_{20}OS_2$: M, 316.0954.

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11) When this reaction was carried out with less than three equivalents of alkane- or arenethiolate, some amounts of α-phenylthio ketone was observed. The source of benzenethiolate is thought to be the liberated benzenesulfenate from α,β-epoxy sulfoxide.[1)]

12) The diastereomers of the chlorohydrin (**3**) are expressed as **L** or **P**, in which **3-L** is the chlorohydrin having large R_f value (less polar chlorohydrin).

13) The diastereomers of the α,β-epoxy sulfoxide (**4**) are expressed as **L** or **P**. **4-L** and **4-P** are epoxy sulfoxides derived from the chlorohydrins **3-L** and **3-P**, respectively.