α,β-Epoxy Sulfoxides as Useful Intermediates in Organic Synthesis. I. A Novel Synthesis of Dialkyl Ketones and a Synthesis of Aldehydes from Ketones by One Carbon Elongation

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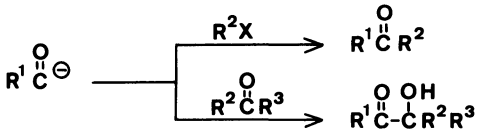
Treatment of α,β-epoxy sulfoxides, prepared from 1-chloroalkyl phenyl sulfoxides with ketones or aldehydes, with sodium benzeneselenolate gives dialkyl ketones or aldehydes in good yields under mild conditions. The mechanism of this reaction and an application of this process to a formal total synthesis of dihydrojasmone are described.

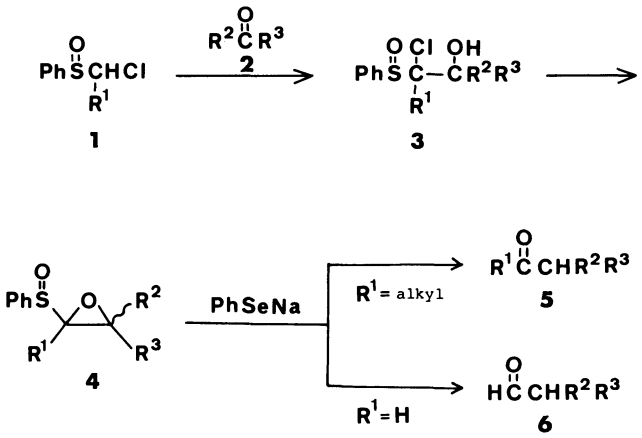
Carbonyl compounds are obviously of most important in synthetic organic chemistry. In the synthesis of ketones with the construction of carbon skeleton, reactions of carboxylic acid or acid halide with organometallic compounds[1] or acid halide with organocopper reagents[2] have extensively been used. Recent years, methods by using organotransition metal catalyst such as palladium are also actively studied.[3] On the other hand, reaction of the "umpolung" reagents involving sulfur compounds acting acyl anion equivalent with alkyl halides or carbonyl compounds is another good method for preparation of carbonyl compounds (Scheme 1).[4] This process, however, has some drawbacks. For example, this reaction usually gives good yields only when primary alkyl halides or active alkyl halides, such as benzyl or allyl halides, are used.

α,β-Epoxy sulfoxides (**4**) were initially reported by Durst in 1969.[5] They are very easily prepared from 1-chloroalkyl phenyl sulfoxide (**1**)[6] and carbonyl compounds (**2**) *via* chlorohydrin (**3**). A few studies on the synthesis of α,β-unsaturated ketones or aldehydes from α,β-epoxy sulfoxides are reported[7] but these interesting compounds have received a scant attention. On the other hand, synthetic methods for a synthesis of α-substituted ketones or aldehydes *via* α,β-epoxy sulfones were reported by Durst[8] and Watt.[9]

Recently, we have found that the β-carbon of α,β-epoxy sulfoxides (**4**) is very reactive to benzeneselenolate to give dialkyl ketones (**5**) or aldehydes (**6**) in excellent yields as shown in Scheme 2.[10] In this paper we describe, in detail, the synthesis of dialkyl ketones and the synthesis of aldehydes from ketones by one carbon elongation through the reaction of α,β-epoxy sulfoxides with sodium benzeneselenolate and an application of this method to a formal total synthesis of dihydrojasmone.



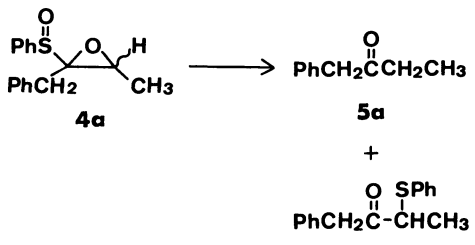
Scheme 1.



Scheme 2.

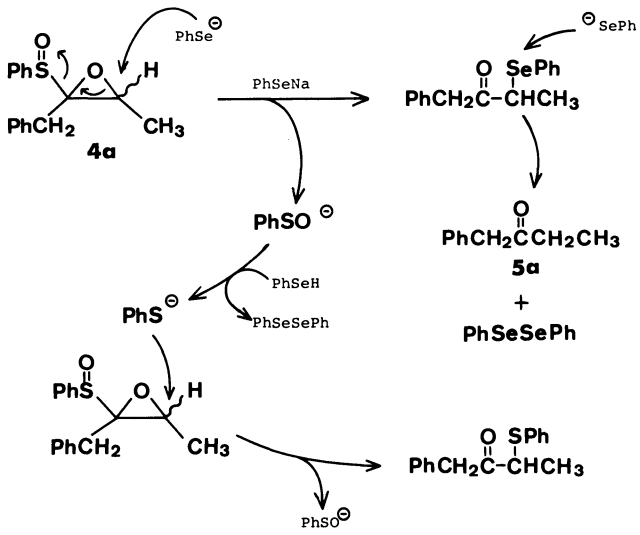
Results and Discussion

A Synthesis of Dialkyl Ketones from α,β-Epoxy Sulfoxides. The α,β-epoxy sulfoxide (**4a**) prepared from 1-chloro-2-phenylethyl phenyl sulfoxide and acetaldehyde was treated with three mol equivalents[11] of sodium benzeneselenolate[12] in ethanol under nitrogen for 20 min to give two ketones, 1-phenyl-2-butanone (**5a**) and 1-phenyl-3-phenylthio-2-butanone, in 73 and 18% yields, respectively. The



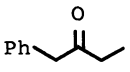
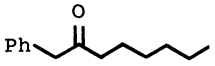
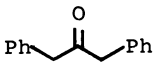
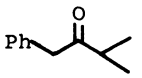
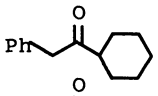
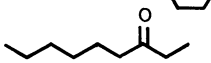
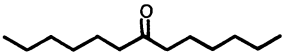
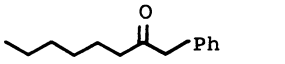
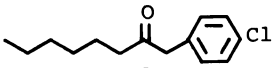
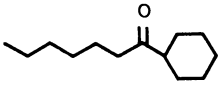
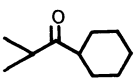
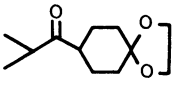
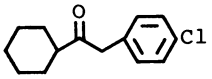
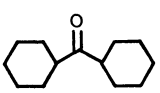
Scheme 3.

mechanism of this reaction is of some interest. The observation that the α,β-epoxy sulfoxide (**4a**) rapidly yields α-sulfenylated carbonyl compounds (1-phenyl-3-phenylthio-2-butanone) along with the desired 1-phenyl-2-butanone (**5a**) implies that the reaction takes place on the pathway as shown in Scheme 4. Benzeneselenolate attacks the β-carbon of **4a** to give 1-phenyl-3-phenylseleno-2-butanone and benzenesulfenate. The α-phenylseleno ketone was attacked by benzeneselenolate to afford 1-phenyl-2-butanone (**5a**) and diphenyl diselenide.[13] On the other hand, the liberated benzenesulfenate is reduced with benzeneselenol to afford benzenethiolate, which attacks the β-carbon of **4a** competitively with benzeneselenolate to give 1-phenyl-3-phenylthio-2-butanone. As the nucleophilicity of selenolate is known to be higher than that of thiolate and the generated thiolate is less than one equivalent, it is thought that the excess



Scheme 4.

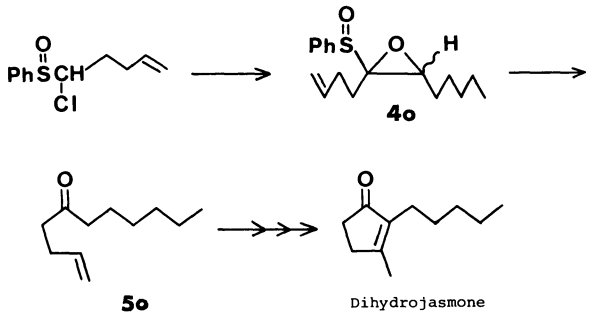
TABLE 1. PREPARATION OF DIALKYL KETONES FROM α,β-EPOXY SULFOXIDES AND SODIUM BENZENESELENOLATE

	α,β-Epoxy sulfoxide (**4**) R_1	R_2	R_3	NaSePh mol equiv	Conditions	Ketone **5**		Yield[a] %
4a	$PhCH_2$	CH_3	H	6	r.t. 20 min		**5a**[16]	92
4b	$PhCH_2$	$CH_3(CH_2)_4$	H	6	r.t. 20 min		**5b**[17]	92
4c	$PhCH_2$	Ph	H	6	r.t. 3 h		**5c**[16]	80
4d	$PhCH_2$	CH_3	CH_3	10	r.t. 3 h		**5d**[18]	86
4e	$PhCH_2$	——$(CH_2)_5$——		12	60 °C, 2 h		**5e**[19]	90
4f	$CH_3(CH_2)_5$	CH_3	H	6	r.t. 5 min		**5f**[20]	80
4g	$CH_3(CH_2)_5$	$CH_3(CH_2)_4$	H	6	r.t. 5 min		**5g**[16]	89
4h	$CH_3(CH_2)_5$	Ph	H	10	r.t. 20 min		**5h**[17]	94
4i	$CH_3(CH_2)_5$	Cl-C$_6$H$_4$-	H	6	r.t. 20 min		**5i**	85
4j	$CH_3(CH_2)_5$	——$(CH_2)_5$——		14	70 °C, 2 h		**5j**[21]	83
4k	$(CH_3)_2CH$	——$(CH_2)_5$——		12	reflux 19 h		**5k**[22]	84
4l	$(CH_3)_2CH$	$-(CH_2)_2-C(O)(O)-(CH_2)_2-$		12	reflux 16 h		**5l**	89
4m	C$_6$H$_5$-	Cl-C$_6$H$_4$-	H	12	r.t. 50 min		**5m**	98
4n	C$_6$H$_5$-	——$(CH_2)_5$——		12	reflux 16 h		**5n**[22]	75

a) Isolated yield after silica-gel column chromatography.

benzeneselenolate exclusively gives the desired ketone with little sulfenylated carbonyl compound. Actually treatment of **4a** with six mol equivalents of sodium benzeneselenolate gave 92% yield of 1-phenyl-2-butanone (**5a**) along with almost no sulfenylated carbonyl compound.

The results of the reaction of various α,β-epoxy sulfoxides (**4**) with excess sodium benzeneselenolate are summarized in Table 1. As shown in Table 1, various kinds of dialkyl ketones were synthesized in good yields under mild conditions. Di-(secondary alkyl) ketones were also synthesized with no problem though at a higher temperature, a larger amount of sodium benzeneselenolate, and a longer period of reaction time were required. It is worth noting that the unreacted sodium benzeneselenolate is recovered as diphenyl diselenide, which was given by oxidation of benzeneselenolate by air, in nearly quantitative yield.



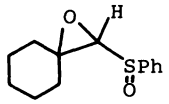
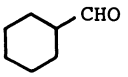
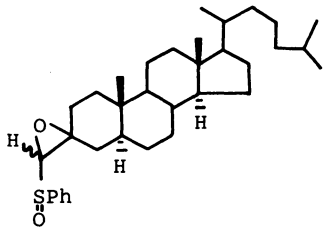
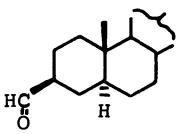
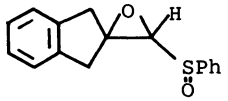
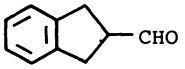
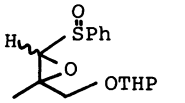
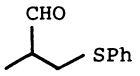
Scheme 5.

This procedure was applied to a formal total synthesis of dihydrojasmone as shown in Scheme 5. Alkylation of chloromethyl phenyl sulfoxide with 4-bromo-1-butene gave 1-chloro-4-pentenyl phenyl sulfoxide in 61% yield. Treatment of this chloride with lithium diisopropylamide followed by hexanal afforded chlorohydrin in 89% yield, which was treated with aqueous potassium hydroxide in methanol to give α,β-epoxy sulfoxide (**4o**) in good yield. The epoxy sulfoxide (**4o**) was treated with six mol equivalents of sodium benzeneselenolate in ethanol at room temperature for 10 min to afford 1-undecen-5-one (**5o**)[14] in 91% yield. This ketone was already converted to dihydrojasmone.[14]

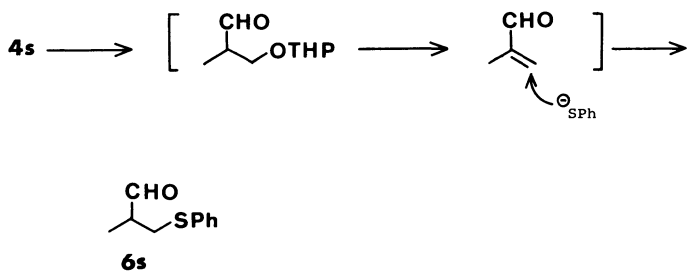
Synthesis of Aldehydes from Ketones by One Carbon Elongation. Many synthetic methods for aldehydes from ketones by one carbon homologation have already been known[15] but they have some advantages and at the same time disadvantages. We have found that the α,β-epoxy sulfoxides (**4**) having hydrogen for R^1 gave aldehydes in excellent yields by the present method. This result means a synthesis of aldehydes (**6**) from ketones (**2**) by one carbon elongation (see Scheme 2). The results of the reaction of α,β-epoxy sulfoxides (**4p—4s**) with sodium benzeneselenolate are summarized in Table 2.

The reaction of **4s** with sodium benzeneselenolate gave 2-methyl-3-phenylthiopropanal (**6s**). This fact may be interpreted as shown in Scheme 6: The α,β-

Table 2. Preparation of aldehydes from ketones via α,β-epoxy sulfoxides

α,β-Epoxy sulfoxide (**4**)		NaSePh mol equiv.	Conditions	Aldehyde (**6**)		Yield[a] %
4p		12	50 °C, 15 min		**6p**[16]	80
4q		16	60 °C, 1.5 h		**6q**	96
4r		10	r.t. 1 h		**6r**[23]	90
4s		10	r.t. 70 min		**6s**	75[b]

a) Isolated yield after silica-gel column chromatography. b) Contamination of a trace of 2-methyl-3-phenylselenopropanal is observed by NMR and mass spectrum.



Scheme 6.

epoxy sulfoxide (**4s**) initially gave the aldehyde having tetrahydropyranyloxyl group, which underwent β elimination to afford an enal. Michael addition of benzenethiolate generated from benzenesulfenate (see Scheme 4) to the enal gave the aldehyde having phenylthio group (**6s**).

In conclusion, a novel and versatile procedure for a synthesis of dialkyl ketones and aldehydes has been developed from α,β-epoxy sulfoxides. In regard to the accessibility of the starting material, the simplicity and mildness of the operation, and high yield of the products, the present procedure offers a simple and useful approach to ketones and aldehydes.

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. 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 puls 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. Wako silica gel c-200 containing 2% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by ultraviolet irradiation. In experiments requiring dry solvent, THF or ether was distilled from benzophenone ketyl and amines were from calcium hydride.

Preparation of 1-Chloroalkyl Phenyl Sulfoxide. Method A: Alkylation of chloromethyl phenyl sulfoxide with primary alkyl halides (benzyl bromide and 1-iodohexane) was carried out according to Wemple's procedure[6a] to give almost quantitative yield of 1-chloro-2-phenylethyl phenyl sulfoxide [diastereomeric mixture; colorless oil; NMR: δ=2.74 (dd, J=10, 14 Hz), 3.18 (dd, J=10, 14 Hz), 3.58 (dd, J=3, 14 Hz), 3.63 (dd, J=5, 14 Hz), 4.53 (dd, J=3, 10 Hz), 4.67 (dd, J=5, 10 Hz), 7.23 (s), 7.1—7.8 (m)] and 1-chloroheptyl phenyl sulfoxide [diastereomeric mixture; bp 185 °C/1 mmHg†; NMR: δ=0.87 (t, J=6 Hz), 4.39 (dd, J=3.5, 9 Hz), 4.51 (dd, J=3.5, 9 Hz), 7.4—7.8 (m)]. *Method B*: As the alkylation of chloromethyl phenyl sulfoxide with 2-iodopropane or cyclohexyl iodide gave almost no product 1-chloro-2-methylpropyl phenyl sulfoxide and 1-chloro-1-cyclohexylmethyl phenyl sulfoxide were prepared as follows: To a solution of EtONa (55 mmol) in 30 ml of dry EtOH was added thiophenol (50 mmol) followed by isobutyl bromide or cyclohexylmethyl bromide (50 mmol) and the mixture was stirred at room temperature for 3 h. The EtOH was evaporated and the residue was extracted with benzene. The product was distilled to give isobutyl phenyl sulfide (bp 110—114 °C/19 mmHg; 94%) or cyclohexylmethyl phenyl sulfide (bp 117 °C/2 mmHg; 92%). Isobutyl phenyl sulfide (10 mmol) was added to a suspension of *N*-chlorosuccinimide (10.5 mmol) in 30 ml of CCl_4 and the reaction mixture was stirred at room temperature for 2.5 h. The reaction mixture was filtered and the CCl_4 was evaporated. The residue was dissolved with 20 ml of CH_2Cl_2 and cooled to −60 °C. To this solution was added *m*-chloroperbenzoic acid (10 mmol) and the temperature of the reaction mixture was allowed to warm to −40 °C. The reaction mixture was diluted with CH_2Cl_2 and was washed with 10% NaOH followed by sat. aq NH_4Cl. The sulfoxides were separated by flash column chromatography to give 1-chloro-2-methylpropyl phenyl sulfoxide as two diastereomers. Main isomer (a colorless oil; 60%): IR (neat): 1055 (SO) cm^{-1}; NMR: δ=1.14, 1.20 (each 3H, d, J=7 Hz), 2.88 (1H, double septet, J=2, 7 Hz), 4.30 (d, J=2 Hz), 7.4-7.8 (5H, m). Minor isomer (a colorless oil; 25%): IR (neat): 1060 (SO) cm^{-1}; NMR: δ=1.20, 1.24 (each 3H, d, J=7 Hz), 2.40 (1H, octet, J=7 Hz), 4.24 (d, J=7 Hz), 7.4—7.7 (5H, m). Cyclohexylchloromethyl phenyl sulfoxide was synthesized from cyclohexylmethyl phenyl sulfide as similar procedure described above. Main isomer (70% yield): Colorless prisms; mp 86—87 °C; IR (KBr): 1055 (SO) cm^{-1}; NMR: δ=1.0—2.7 (11H, m), 4.31 (1H, d, J=3 Hz), 7.5—7.9 (5H, m). Minor isomer (22% yield): Colorless needles; mp 127—128 °C; IR (KBr): 1060, 1055 (SO) cm^{-1}; NMR: δ=1.0—2.3 (11H, m), 4.24 (1H, d, J=7 Hz), 7.5—7.7 (5H, m). The main isomers were used in this study.

General Procedure for the Preparation of α,β-Epoxy Sulfoxide (4): A synthesis of 2,3-epoxy-1-phenyl-2-phenylsulfinylbutane (**4a**) is described. To a solution of lithium diisopropylamide (3.45 mmol) in dry THF (8 ml) at −70 °C under N_2 was added a solution of 1-chloro-2-phenylethyl phenyl sulfoxide (3 mmol) in 2 ml of dry THF dropwise with stirring. The solution was stirred at −70 °C for 20 min and then acetaldehyde (6 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 ether. The products were separated by silica-gel column chromatography (hexane: AcOEt=5:1) to give chlorohydrins (**3a-L**)[24] and (**3a-P**).[24] **3a-L** (40% yield): mp 89—91 °C; IR (KBr): 3360 (OH), 1030 (SO) cm^{-1}; NMR: δ=1.26 (3H, d, J=7 Hz), 3.41, 4.18 (each 1H, d, J=15 Hz), 4.17 (1H, q, J=7 Hz), 7.2—7.8 (5H, m); MS m/z (%): 182 ([M−PhSOH]$^+$, 7), 165 (14), 147 (29), 126 (100), 91 (81). **3a-P** (54% yield): mp 113-115 °C; IR (KBr): 3375 (OH), 1025 (SO) cm^{-1}; NMR: δ=1.40 (3H, d, J=6 Hz), 3.29, 3.42 (each 1H, d, J=15 Hz), 3.83 (1H, q, J=15 Hz), 3.83 (1H, q, J=6 Hz), 7.2—7.8 (5H, m); MS m/z (%): 182 ([M−PhSOH]$^+$, 20), 147 (55), 126 (100), 91 (79); Found: C, 62.21; H, 5.48; S, 10.37; Cl, 11.24%. Calcd for $C_{16}H_{17}SO_2Cl$: C, 62.23; H, 5.55; S,

† 1 mmHg=133.322 Pa.

10.38; Cl, 11.48%. 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 solution was neutralized by adding NH_4Cl and the MeOH was evaporated. The residue was extracted with ether and the product was purified by silica-gel column chromatography to give 2,3-epoxy-1-phenyl-2-phenylsulfinylbutane (**4a-L**)[25] as colorless oil in 95% yield. IR (neat): 1095, 1055 (SO) cm^{-1}; NMR: δ=1.34 (3H, d, J=6 Hz), 3.05, 3.10 (each 1H, d, J=16 Hz), 3.79 (1H, q, J=6 Hz), 6.9—7.7 (10H, m); MS m/z (%): 272 (M^+, 2), 147 ([M−PhSO]$^+$, 18), 126 (39), 105 (38), 91 (100). Epoxy sulfoxide (**4a-P**)[25] was synthesized from **3a-P** by the similar procedure described above in 98% yield. **4a-P**: IR (neat): 1095, 1055 (SO) cm^{-1}; NMR: δ=1.62 (3H, d, J=6 Hz), 2.45, 3.55 (each 1H, d, J=15 Hz), 2.75 (1H, q, J=6 Hz), 6.9—7.8 (10H, m); MS m/z (%): 272 (M^+, 1.5), 147 ([M−PhSO]$^+$, 20), 126 (49), 105 (40), 91, (100).

2,3-Epoxy-1-phenyl-2-phenylsulfinyloctane (4b). Chlorohydrin **3b-L** (37% yield): Colorless oil; IR (neat): 3375 (OH), 1075, 1020 (SO) cm^{-1}; NMR: δ=0.83 (3H, t, J=6 Hz), 3.38, 4.14 (each 1H, d, J=15 Hz), 3.90 (1H, m), 7.2—7.8 (10H, m). **3b-P** (47% yield): Colorless oil; IR (neat): 3390 (OH), 1075, 1040 (SO) cm^{-1}; NMR: δ=0.87 (3H, t, J=6 Hz), 3.36, 3.50 (each 1H, d, J=14 Hz), 3.52 (1H, m), 7.2—7.9 (10H, m). Epoxy sulfoxide **4b-L** (65% yield): Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.86 (3H, t, J=6 Hz), 1.0—1.7 (8H, m), 3.00, 3.05 (each 1H, d, J=16 Hz), 3.71 (1H, t, J=6 Hz), 7.0—7.7 (10H, m); MS m/z (%): 328 (M^+, trace), 203 (7), 126 (11), 91 (100). **4b-P** (69% yield): Colorless oil; IR (neat): 1090, 1050 (SO) cm^{-1}. NMR: δ=0.89 (3H, t, J=6 Hz), 1.1—2.1 (8H, m), 1.96 (2H, m), 2.54, 3.54 (each 1H, d, J=14 Hz), 2.63 (1H, t, J=6 Hz), 6.8—7.8 (10H, m); MS m/z (%): 328 (M^+, trace), 203 (7), 126 (11), 91 (100).

1,2-Epoxy-1,3-diphenyl-2-phenylsulfinylpropane (4c). Chlorohydrin **3c-L** (37% yield): mp 158—160 °C; IR (KBr): 3320 (OH), 1015 (SO) cm^{-1}; NMR: δ=3.16 4.40 (each 1H, d, J=15 Hz), 5.07 (1H, s), 7.2—8.0 (15H, m); MS m/z (%): 250 (1), 241 (1), 233 (3), 207 (3), 126 (100). **3c-P** (45% yield): Colorless oil; IR (neat): 3350 (OH), 1040 (SO) cm^{-1}; NMR: δ=2.55, 3.30 (each 1H, d, J=15 Hz), 5.41 (1H, s), 7.2—7.8 (15H, m); MS m/z (%): 244 ([M−PhSO]$^+$, 13), 209 (29), 186 (17), 125 (86), 77 (100). Epoxy sulfoxide **4c-L** (50% yield): mp 135.5—136 °C; IR (KBr): 1060 (SO) cm^{-1}; NMR: δ=2.76 (2H, s), 4.87 (1H, s), 7.0—7.7 (15H, m); MS m/z (%): 209 ([M−OhSO]$^+$, 18), 181 (25), 91 (100). **4c-P** (71% yield): mp 112—113 °C; IR (KBr): 1040 (SO) cm^{-1}; NMR: δ=2.66, 3.71 (each 1H, d, J=15 Hz), 3.79 (1H, s), 7.0—7.8 (15H, m); MS m/z (%): 209 ([M−PhSO]$^+$, 19), 181 (28), 91 (100); Found: C, 75.45; H, 5.26; S, 9.69%. Calcd for $C_{21}H_{18}O_2S$: C, 75.42; H, 5.42; S, 9.59%.

2,3-Epoxy-3-methyl-1-phenyl-2-phenylsulfinylbutane (4d). Chlorohydrin **3d** (95% yield): Colorless oil; IR (neat): 3420 (OH), 1090, 1060 (SO) cm^{-1}; NMR: δ=1.25, 1.55 (each 3H, s), 3.30, 3.46 (each 1H, d, J=15 Hz), 7.2—7.8 (10H, m); MS m/z (%): 196 ([M−PhSO]$^+$, 37), 183 (34), 181 (100). Epoxy sulfoxide **4d** (89% yield): mp 81—82 °C; IR (KBr): 1095, 1050 (SO) cm^{-1}; NMR: δ=1.26, 1.83 (each 3H, s), 3.25 (2H, s), 6.6—7.8 (10H, m) MS m/z (%): 286 (M^+, 0.04), 161 (26), 126 (30), 91 (100); Found: C, 71.00; H, 6.30; S, 11.15%; M^+, 286.0997. Calcd for $C_{17}H_{18}O_2S$: C, 71.30; H, 6.34; S, 11.19%; M, 286.1026.

2'-Benzyl-2'-phenylsulfinylspiro[cyclohexane-1,1'-oxirane] (4e). Chlorohydrin **3e** (82% yield): Colorless oil; IR (neat): 3410 (OH), 1090, 1045 (SO) cm^{-1}; NMR: δ=1.0—2.4 (10H, m), 3.35, 3.43 (each 1H, d, J=15 Hz), 7.1—7.8 (10H, m); MS m/z (%): 236 ([M−PhSO]$^+$, 38), 179 (100). Epoxy sulfoxide **4e** (86% yield): mp 61—62 °C; IR (KBr): 1055 (SO) cm^{-1}; NMR: δ=1.2—2.3 (10H, m), 3.24 (2H, s), 6.7—7.7 (10H, m); MS m/z (%): 201 ([M−PhSO]$^+$, 18), 91 (100); Found: C, 73.37; H, 6,76; S, 9.92%. Calcd for $C_{20}H_{22}O_2S$: C, 73.58; H, 6.79; S, 9.82%.

2,3-Epoxy-3-phenylsulfinylnonane (4f). Chlorohydrin **3f-L** (37% yield): mp 62—64 °C; IR (KBr): 3375 (OH), 1085, 1025 (SO) cm^{-1}; NMR: δ=0.93 (3H, t, J=6 Hz), 1.19 (3H, d, J=6 Hz), 1.1—3.0 (10H, m), 4.08 (1H, q, J=6 Hz), 7.5—7.9 (5H, m); MS m/z (%): 250 (2), 126 (100). **3f-P** (52% yield): mp 67—69 °C; IR (KBr): 3360 (OH), 1080, 1035, 1020 (SO) cm^{-1}; NMR: δ=0.89 (3H, t, J=6 Hz), 1.1—2.2 (10H, m), 1.37 (3H, d, J=6 Hz), 4.10 (1H, q, J=6 Hz), 7.4—7.8 (5H, m); MS m/z (%): 241 (1), 126 (100). Epoxy sulfoxide **4f-L** (90% yield): Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.83 (3H, t, J=6 Hz), 0.9—2.0 (10H, m), 1.37 (3H, d, J=6 Hz), 3.73 (1H, q, J=6 Hz), 7.4-7.7 (5H, m); MS m/z (%): 266 (M^+, 4), 141 (12), 126 (29), 57 (100); Found: m/z 266.1353. Calcd for $C_{15}H_{22}O_2S$: M, 266.1339. **4f-P** (92% yield): Colorless oil; IR (neat): 1090, 1050 (SO) cm^{-1}; NMR: δ=0.81 (3H, t, J=6 Hz), 0.9—2.3 (10H, m), 1.77 (3H, d, J=6 Hz), 3.39 (1H, q,J=6 Hz), 7.4—7.7 (5H, m); MS m/z (%): 266 (M^+, 3), 141 (10), 126 (23), 57 (100); Found: m/z 266.1325. Calcd for $C_{15}H_{22}O_2S$: M, 266.1339.

6,7-Epoxy-7-phenylsulfinyltridecane (4g). Chlorohydrin **3g-L** (39% yield): Colorless oil; IR (neat): 3350 (OH), 1075, 1035 (SO) cm^{-1}; NMR: δ=0.83, 0.93 (each 3H, t, J=6 Hz), 3.82 (1H, dd, J=4, 8 Hz), 7.4—7.9 (5H, m); MS m/z (%): 306 (1), 233 (9), 161 (34), 126 (100). **3g-P** (61% yield): Colorless oil; IR (neat): 3375 (OH), 1075, 1035 (SO) cm^{-1}; NMR: δ=0.95 (6H, t, J=6 Hz), 3.70 (1H, dd, J=2, 9 Hz), 7.4-7.8 (5H, m); MS m/z (%): 306 (1), 197 (7), 161 (62), 41 (100). Epoxy sulfoxide **4g-L** (93% yield): Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.84, 0.88 (each 3H, t, J=6 Hz), 3.63 (1H, t, J=6 Hz), 7.4—7.7 (5H, m); MS m/z (%): 322 (M^+, 0.5), 197 (12), 113 (77), 43 (100). **4g-P** (87% yield): Colorless oil; IR (neat): 1090, 1050 (SO) cm^{-1}; NMR: δ=0.81, 0.94 (each 3H, t, J=6 Hz), 3.25 (1H, t, J=6 Hz), 7.4—7.7 (5H, m); MS m/z (%): 322 (M^+, 0.5), 197 (16), 113 (100).

1,2-Epoxy-1-phenyl-2-phenylsulfinyloctane (4h). Chlorohydrin **3h-L** (45% yield): mp 133—134 °C; IR (KBr): 3325 (OH), 1035 (SO) cm^{-1}; NMR: δ=0.89 (3H, t, J=6 Hz), 1.1—2.1 (10H, m), 4.92 (1H, s), 7.24 (5H, s), 7.5—8.0 (5H, m); MS m/z (%)+ 238 ([M−PhSOH]$^+$, 9), 203 (17), 126 (69), 105 (100). **3h-P** (34% yield): mp 99—100 °C; IR (KBr): 3350 (OH), 1035 (SO) cm^{-1}; NMR: δ=0.83 (3H, t, J=6 Hz), 0.9—2.0 (10H, m), 5.29 (1H, s), 7.2—7.9 (10H, m); MS m/z (%): 238 ([M−PhSOH]$^+$, 11), 203 (25), 133 (22), 126 (33), 107 (100). Epoxy sulfoxide **4h-L** (99% yield): mp 55—56 °C; IR (KBr): 1085 1055 (SO) cm^{-1}; NMR: δ=0.80 (3H, t, J=6 Hz), 0.8—1.7 (10H, m), 4.78 (1H, s), 7.1—7.8 (10H, m); MS m/z (%): 328 (M^+, 0.4), 203 ([M−PhSO]$^+$, 14), 91 (100); Found: C, 73.02; H, 7.36; S, 10.00%; M^+, 328.1500. Calcd for $C_{20}H_{24}O_2S$: C, 73.13; H, 7.36; S, 9.76%; M, 328.1496. **4h-P** (95% yield): mp 38—39 °C; IR (KBr): 1085, 1045 (SO) cm^{-1}; NMR: δ=0.84 (3H, t, J=6 Hz), 1.0—2.4 (10H, m), 4.41 (1H, s), 7.3—7.8 (10H, m); MS m/z (%): 328 (M^+, trace), 203 ([M−

PhSO]$^+$, 15), 91 (100); Found: *m/z* 328.1507. Calcd for $C_{20}H_{24}O_2S$: M, 328.1495.

*1,2-Epoxy-1-(4-chlorophenyl)-2-phenylsulfinyloctane (**4i**).* Chlorohydrin **3i-L** (41% yield): mp 67—69 °C; IR (KBr): 3230, 1040 (SO) cm^{-1}; NMR: δ=0.90 (3H, t, J=6 Hz), 4.93 (1H, s), 7.28 (4H, s), 7.6—8.0 (5H, m); MS *m/z* (%): 398 (M$^+$, trace), 272 (5), 237 (7), 141 (33), 139 (31), 126 (100). **3i-P** (49% yield): Colorless crystals; mp 114—115 °C; IR (KBr): 3330 (OH), 1045 (SO) cm^{-1}; NMR: δ=0.85 (3H, t, J=6 Hz), 5.43 (1H, d, J=2.5 Hz), 7.2—7.9 (9H, m); MS *m/z* (%): 272 ([M−PhSOH]$^+$, 16), 237 (36), 167 (42), 141 (100). Epoxy sulfoxide **4i-L** (93% yield): Colorless oil; IR (neat): 1090, 1060 (SO) cm^{-1}; NMR: δ=0.81 (3H, t, J=6 Hz), 4.74 (1H, s), 7.0—7.8 (9H, m); MS *m/z* (%): 362 (M$^+$, trace), 237 (14), 125 (100). **4i-P** (90% yield): Colorless crystals; mp 76—77 °C; IR (KBr): 1090, 1050 (SO) cm^{-1} ; NMR: δ=0.84 (3H, t, J=6 Hz), 4.38 (1H, s), 7.3—7.8 (9H, m); MS *m/z* (%): 362 (M$^+$, trace), 237 ([M−PhSO]$^+$, 18), 125 (100); Found: C, 66.13; H, 6.32; Cl, 9.89; S, 8.81%. Calcd for $C_{20}H_{23}ClO_2S$: C, 66.19; H, 6.39, Cl, 9.77; S, 9.08%.

*2'-Hexyl-2'-phenylsulfinylspiro[cyclohexane-1,1'-oxirane] (**4j**).* Chlorohydrin **3j** (99% yield): Colorless crystrals; mp 73—74 °C; IR (neat): 3345 (OH), 1035 (SO) cm^{-1}; NMR: δ=0.84 (3H, t, J=6 Hz), 7.3—7.8 (5H, m). Epoxy sulfoxide **4j** (76% yield): Colorless oil; IR (neat): 1080, 1045 (SO) cm^{-1}; NMR: δ=0.78 (3H, t, J=6 Hz), 7.4—7.7 (5H, m); MS *m/z* (%): 195 ([M−PhSO]$^+$, 57), 126 (10), 113 (100).

*2'-Isopropyl-2'-phenylsulfinylspiro[cyclohexane-1,1'-oxirane] (**4k**).* Colorless crystals; mp 84—85 °C; 94% yield from 1-chloro-2-methylethyl phenyl sulfoxide *via* chlorohydrin (**3k**); IR (KBr): 1050 (SO) cm^{-1}; NMR: δ=0.59, 1.17 (each 3H, d, J=7 Hz), 1.4—2.3 (10H, m), 2.66 (1H, septet, J=7 Hz), 7.3—7.7 (5H, m); MS *m/z* (%): 278 (M$^+$, trace), 262 (1.2), 218 (8), 191 (16), 43 (100); Found: C, 68.89; H, 8.02; S, 11.57%. Calcd for $C_{16}H_{22}O_2S$: C, 69.03; H, 7.97; S, 11.52%.

*2''-Isopropyl-2''-phenylsulfinyldispiro[1,3-dioxolane-2,1'-cyclohexane-4',1''-oxirane] (**4l**).* Chlorohydrin **3l** (97% yield): Colorless oil; IR (neat): 3400 (OH), 1040 (SO) cm^{-1}; NMR: δ=1.37, 1.42 (each 3H, d, J=6 Hz), 3.88 (4H, s), 7.3—7.8 (5H, m). Epoxy sulfoxide **4l** (92% yield): Colorless crystals; mp 73—76 °C; IR (KBr): 1090, 1050, 1040 (SO) cm^{-1}; NMR: δ=0.59, 1.16 (3H, d, J=7 Hz), 1.6—2.5 (4H, m), 2.68 (1H, septet, J=7 Hz), 4.01 (4H, s), 7.4—7.7 (5H, m); MS *m/z* (%): 336 (M$^+$, trace), 249 (trace), 211 (55), 99 (100); Found: C, 64.27; H, 7.26; S, 9.60%; M$^+$, 336.1383. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53%; M, 336.1393.

*1,2-Epoxy-2-(4-chlorophenyl)-1-cyclohexyl-1-phenylsulfinylethane (**4m**).* Chlorohydrin **3m-L** (46% yield): Colorless crystals; mp 165—167 °C; IR (KBr): 3350 (OH), 1045 (SO) cm^{-1}; NMR: δ=1.0—2.9 (11H, m), 5.17 (1H, s), 7.2—8.1 (9H, m); MS *m/z* (%): 270 (4), 139 (100). **3m-P** (51% yield): Colorless crystals; mp 164—166 °C; IR (KBr): 3175 (OH), 1015 (SO) cm^{-1}; NMR: δ=0.9—2.6 (11H, m), 5.78 (1H, s), 7.3—7.8 (9H, m); MS *m/z* (%): 270 (10), 252 (15), 217 (63), 78 (100). Epoxy sulfoxide **4m-L** (95% yield): Colorless crystals; mp 131—132 °C; IR (KBr): 1090, 1050 (SO) cm^{-1}; NMR: δ=0.6—1.9 (11H, m), 4.63 (1H, s), 7.2—7.5 (4H, m), 7.5—8.0 (5H, m); MS *m/z* (%): 360 (M$^+$, 0.6), 344 (2), 125 (88), 83 (100); Found: C, 66.43; H, 5.70; Cl, 9.89; S, 8.98%. Calcd for $C_{20}H_{21}ClO_2S$: C, 66.56; H, 5.86; Cl, 9.82; S, 8.88%. **4m-P** (80% yield): Colorless crystals; mp 137—138 °C; IR (KBr): 1090, 1040 (SO) cm^{-1}; NMR: δ=0.6—2.4 (11H, m), 4.42 (1H, s), 7.44 (4H, m), 7.4—7.8 (5H, m); MS *m/z* (%): 344 (trace), 235 (14), 207 (4), 125 (100).

*2'-Cyclohexyl-2'-phenylsulfinylspiro[cyclohexane-1,1'-oxirane] (**4n**).* 32% overall yiels from 1-chloro-1-cyclohexylmethyl phenyl sulfoxide and cyclohexanone *via* chlorohydrin (**3n**): Colorless crystals; mp 104—105.5 °C; IR (KBr): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.5—2.5 (methylene-H), 7.3—7.8 (5H, m); MS *m/z* (%): 193 ([M−PhSO]$^+$, 29), 126 (11), 111 (41), 83 (100); Found: C, 71.40; H, 8.15%. Calcd for $C_{19}H_{26}O_2S$: C, 71.66; H, 8.23%.

*2'-Phenylsulfinylspiro[5α-cholestane-3,1'-oxirane] (**4q**).* Chlorohydrin **3q-L** (55% yield): Colorless oil; IR (neat): 3430 (OH), 1060 (SO) cm^{-1}; NMR: δ=0.66 (3H, s), 0.89 (6H, d, J=7 Hz), 0.91 (3H, d, J=7 Hz), 0.99 (3H, s), 4.79 (1H, s), 7.62 (5H, s). **3q-P** (39% yield): Colorless oil; IR (neat): 3400 (OH), 1050 (SO) cm^{-1}; NMR: δ=0.66 (3H, s), 0.88 (6H, d, J=7 Hz), 0.91 (3H, d, J=7 Hz), 1.01 (3H, s), 4.30 (1H, s), 7.60 (5H, m). Epoxy sulfoxide **4q-L** (96% yield): Colorless crystals; mp 142—143 °C; IR (KBr): 1050 (SO) cm^{-1}; NMR: δ=0.67 (3H, s), 0.88 (6H, d, J=7 Hz), 0.92 (3H, d, J=7 Hz), 1.04 (3H, s), 3.68 (1H, s), 7.5—7.9 (5H, m); Found: C, 78.03; H, 10.07%. Calcd for $C_{34}H_{52}O_2S$: C, 77.81; H, 9.99%. **4q-P** (94% yield): Colorless crystals; mp 137—140 °C; IR (KBr): 1055 (SO) cm^{-1}; NMR: δ=0.67 (3H, s), 0.89 (6H, d, J=7 Hz), 0.92 (3H, d, J=7 Hz), 1.02 (3H, s), 3.74 (1H, s), 7.5—7.9 (5H, m); Found: C, 77.87; H, 10.03%. Calcd for $C_{34}H_{52}O_2S$: C, 77.81; H, 9.99%.

*2'-Phenylsulfinylspiro[indan-2,1'-oxirane] (**4r**).* Chlorohydrin **3r** (86% yield): Colorless crystals; mp 193—195 °C; IR (KBr): 3420 (OH), 1050 (SO) cm^{-1}. Epoxy sulfoxide **4r** (85% yield): Colorless crystals; mp 77—78 °C; IR (KBr): 1060 (SO) cm^{-1}; NMR: δ=3.07, 3.36, 3.52, 3.94 (each 1H, d, J=18 Hz), 4.08 (1H, s), 7.28 (4H, m), 7.5—7.9 (5H, m); MS *m/z* (%): 193 ([M−C_6H_5]$^+$, 0.3), 145 (10), 117 (100); Found: C, 70.93; H, 5.17%. Calcd for $C_{16}H_{14}O_2S$: C, 71.08; H, 5.22%.

*1,2-Epoxy-2-methyl-1-phenylsulfinyl-3-(tetrahydropyranyloxy)propane (**4s**).* Chlorohydrin **3s** (99% yield): Colorless oil (about 2:1 diastereomeric mixture); IR (neat); 3340 (OH), 1040 (SO) cm^{-1}. Epoxy sulfoxide **4s** (94% yield): Colorless oil (diastereomeric mixture); IR (neat): 1020 (SO) cm^{-1}; NMR: δ=1.51, 1.76 (s, CH_3).

*General Procedure for the Preparation of Dialkyl Ketones (**5**) or Aldehydes (**6**) from α,β-Epoxy Sulfoxides (**4**):* A synthesis of 1-phenyl-2-butanone (**5a**) is described. Note that both isomers of the α,β-epoxy sulfoxides (**4**) shows almost the same reactivity toward benzeneselenolate. $NaBH_4$(34 mg; 0.9 mmol) was added to a suspension of diphenyl diselenide (140 mg; 0.45 mmol) in 2 ml of EtOH by portions with stirring. After vigorous hydrogen gas evolution ceased, a solution of **4a** (41 mg; 0.15 mmol) in small amount of EtOH was added to the selenolate solution through a syringe under nitrogen. The reaction mixture was stirred at room temperature for 20 min. The reaction mixture was neutralized by NH_4Cl and the EtOH was evaporated. The residue was extracted with ether and, after usual work-up, the product was purified by silica-gel column chromatography followed by bulb-to-bulb distillation (150 °C/15 mmHg) to give 20.5 mg (92%) of 1-phenyl-2-butanone (**5a**). When this reaction was carried out with 3 mol equivalents of sodium benzeneselenolate, 1-phenyl-3-phenylthio-2-butanone (18%) was obtained with 73% of **5a**. 1-Phenyl-3-phenylthio-2-butanone: Colorless oil; IR (neat): 1720 (CO) cm^{-1}; NMR: δ=1.37 (3H, d, J=7 Hz), 3.83 (1H, q, J=7 Hz), 3.92 (2H, s), 7.0—7.5 (10H, m); MS *m/z* (%): 256

(M+, 18), 147 (19), 137 (100); Found: *m/z* 256.0922. Calcd for $C_{16}H_{16}OS$: M, 256.0921.

1-Phenyl-2-octanone (5b). Colorless oil; IR (neat): 1710 (CO) cm^{-1}; NMR: δ=0.85 (3H, t, J=6 Hz), 2.43 (2H, t, J=6.5 Hz), 3.66 (2H, s), 7.24 (5H, m); MS *m/z* (%): 204 (M+, 2), 113 (100), 91 (49); Found: *m/z* 204.1512. Calcd for $C_{14}H_{20}O$: M, 204.1513.

1-Cyclohexyl-2-phenylethanone (5e). Bp 135 °C/2.5 mmHg; IR (neat): 1720 (CO) cm^{-1}; NMR: δ=1.0—2.0 (10H, m), 2.44 (1H, m), 3.72 (2H, s), 7.22 (5H, m).

1-(4-Chlorophenyl)-2-octanone (5i). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; NMR; δ=0.86 (3H, t, J=6 Hz), 1.1—1.7 (8H, m), 2.44 (2H, t, J=7 Hz), 3.64 (2H, s), 7.0—7.3 (4H, m); MS *m/z* (%): 238 (M+, 3), 125 (29), 113 (100); Found: *m/z* 238.1111. Calcd for $C_{14}H_{19}ClO$: M, 238.1122.

1-(4,4-Ethylenedioxycyclohexyl)-2-methyl-1-propanone (5l). Bp 115 °C/3 mmHg; IR (neat): 1715 (CO) cm^{-1}; NMR: δ=1.09 (6H, d, J=7 Hz), 2.50 (1H, m), 2.79 (1H, septet, J=7 Hz), 3.95 (4H, s); MS *m/z* (%): 212 (M+, 12), 169 (3), 141 (15), 99 (100), 86 (66); Found: *m/z* 212.1387. Calcd for $C_{12}H_{20}O_3$: M, 212.1400.

2-(4-Chlorophenyl)-1-cyclohexylethanone (5m). Mp 97—98 °C; IR (KBr): 1700 (CO) cm^{-1}; NMR: δ=1.0—2.0 (10H, m), 2.42 (1H, m), 3.69 (2H, s), 6.98—7.32 (4H, m); MS *m/z* (%): 236 (M+, 2), 125 (16), 111 (32), 83 (100); Found: *m/z* 236.0954. Calcd for $C_{14}H_{17}ClO$: M, 236.0967.

3-Formyl-5α-cholestane (6q). Colorless oil; IR (neat): 2720 (CHO), 1740 (CO) cm^{-1}; NMR: δ=0.64 (3H, s), 0.87 (6H, d, J=7 Hz), 0.90 (3H, d, J=7 Hz), 0.96 (3H, s), 9.67 (1H, d, J=2 Hz); MS *m/z* (%): 400 (M+, 61), 385 (31), 382 (61), 245 (100).

2-Methyl-3-phenylthiopropanal (6s). Colorless oil; IR (neat): 2740 (CHO), 1735 (CO) cm^{-1}; NMR: δ=1.24 (3H, d, J=7 Hz), 2.63 (1H, m), 2.93, 3.33 (each 1H, dd, J=7, 14 Hz), 7.33 (5H, m), 9.71 (1H, d, J=1 Hz); MS *m/z* (%): 180 (M+, 16), 158 (16), 123 (13), 110 ([M−C_4H_6O]+, 100).

A Formal Total Synthesis of Dihydrojasmone: Alkylation of chloromethyl phenyl sulfoxide with 4-bromo-1-butene in the Method A afforded 61% yield of 1-chloro-4-pentenyl phenyl sulfoxide as an oil; IR (neat): 1640 (C=C), 1085, 1055 (SO) cm^{-1}; NMR: δ=1.6—2.5 (4H, m), 4.50 (dd, J=3, 14 Hz), 4.59 (dd, J=3, 10 Hz), 4.98—5.21 (2H, m), 5.55—5.97 (1H, m), 7.4—7.9 (5H, m); MS *m/z* (%): 228 (M+, 1), 126 (100). This was treated with LDA in THF at −50 °C for 15 min followed by slight excess hexanal to give chlorohydrins (**3o-L**) and (**3o-P**) in 60 and 29% yield, respectively. **3o-L**: Colorless oil; IR (neat): 3350 (OH), 1080, 1040 (SO) cm^{-1}; NMR: δ=0.83 (3H, t, J=6 Hz), 3.88 (1H, dd, J=3, 7.5 Hz), 4.97—5.24 (2H, m), 5.84 (1H, ddt, J=6, 10, 17 Hz), 7.4—7.9 (5H, m); MS *m/z* (%): 259 ([M−C_4H_9]+, 3), 203 (6), 126 (100). **3o-P**: Colorless oil; IR (neat): 3380 (OH), 1080, 1050 (SO) cm^{-1}; NMR: δ=0.88 (3H, t, J=6 Hz), 3.67 (1H, dd, J=2.5, 9 Hz), 4.88—5.16 (2H, m), 5.74 (1H, ddt, J=6, 10, 17 Hz), 7.4—7.8 (5H, m); MS *m/z* (%): 259 ([M−C_4H_9]+, 1), 203 (5), 126 (100).

These chlorohydrins were treated with aq KOH in MeOH at room temperature for 2 h to give α,β-epoxy sulfoxide (**4o-L**) and (**4o-P**) in 56 and 99% yield, respectively. **4o-L**: Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.89 (3H, t, J=6 Hz), 3.68 (1H, t, J=6 Hz), 4.8—5.0 (2H, m), 5.62 (1H, ddt, J=6, 10, 17 Hz), 7.5—7.8 (5H, m); MS *m/z* (%): 292 (M+, trace), 167 (5), 126 (11), 83 (48), 55 (100). **4o-P**: Colorless oil; IR (neat): 1090, 1055 (SO) cm^{-1}; NMR: δ=0.94 (3H, t, J=6 Hz), 3.27 (1H, t, J=6 Hz), 4.74—5.02 (2H, m), 5.58 (1H, ddt, J=6, 10, 17 Hz), 7.4—7.7 (5H, m); MS *m/z* (%): 292 (M+, trace), 167 (4), 126 (11), 83 (55), 55 (100).

The α,β-epoxy sulfoxide (**4o-P**) or (**4o-L**) was treated with 6 mol equivalents of sodium benzeneselenolate in EtOH at room temperature for 10 min. The reaction mixture was neutralized by NH_4Cl and the EtOH was evaporated. After usual work-up, the product was purified by silica-gel column chromatography to give 91% yield of 1-undecene-5-one as an oil. Bp 95 °C/16 mmHg; IR (neat): 1715 (CO), 1645 (C=C) cm^{-1}; NMR: δ=0.88 (3H, t, J=6 Hz), 4.84—5.12 (2H, m), 5.56—6.00 (1H, m); MS *m/z* (%): 168 (M+, 6), 113 ([M−C_4H_7]+, 86), 83 ([M−C_6H_{13}]+, 50), 43 (100).

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24) We express the diastereomers of the chlorohydrin (**3**) as **L** and **P**. **3-L** is the chlorohydrin having large Rf value (less polar product) on silica gel TLC (hexane-AcOEt mixture as a developing solvent) and **P** means that it is polar chlorohydrin.

25) We express the diastereomers of the α,β-epoxy sulfoxide (**4**) as **L** and **P**. **4-L** and **4-P** are the epoxy sulfoxides derived from the chlorohydrin **3-L** and **3-P**, respectively.