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α,β-Epoxy Sulfoxides as Useful Intermediates in Organic Synthesis. IX.[1] A Novel Synthesis of Alkyl Vinyl Ketones and Divinyl Ketones from Carbonyl Compounds and 1-Chloro-3-phenylthiopropyl Phenyl Sulfoxide as a Three-Carbon Homologating Agent

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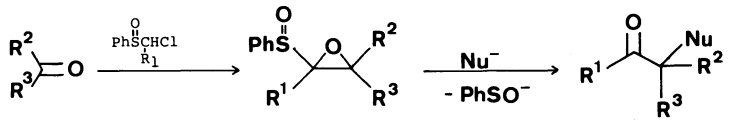
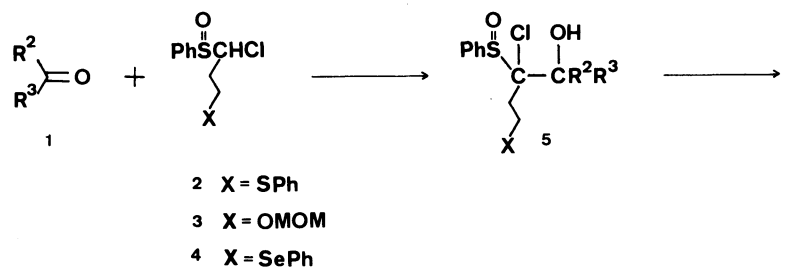
The α,β-epoxy sulfoxides easily derived from carbonyl compounds and 1-chloro-3-phenylthiopropyl phenyl sulfoxide were treated with sodium benzeneselenolate to give β-phenylthio carbonyl compounds in excellent yields. The phenylthio group was oxidized to the sulfinyl group and was then treated with a base to afford alkyl vinyl ketones in quite good yields. This reaction presents a novel method for the preparation of alkyl vinyl ketones from carbonyl compounds by three-carbon homologation. The treatment of α,β-epoxy sulfoxides mentioned above with benzenethiolate gave α,β′-bis(phenylthio) ketones. The elimination of the both thio groups afforded divinyl ketones.

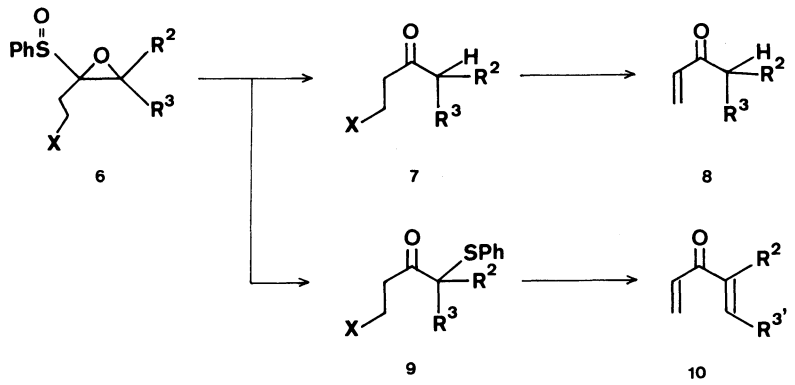
α,β-Unsaturated carbonyl compounds have received much attention for long time regarding synthetic organic reactions. They are quite useful as the dienophiles in the Diels–Alder reactions[2] and as the acceptors of Michael-type reactions.[3] Among the α,β-unsaturated carbonyl compounds, alkyl vinyl ketones and divinyl ketones are most important in the chemistry of carbon–carbon bond formation. Many methods have already been reported for the synthesis of vinyl ketones. The most widely used one is a two-carbon homologation method; one is the reaction of a vinylmetalic reagent, such as vinyllithium with carboxylic acids,[4] or with aldehydes followed by oxidation;[5] the other is a palladium-catalyzed acylation of alkenylzinc,[6] alkenyltin,[7] or alkenylcopper.[8] Another method for the synthesis of vinyl ketones is three-carbon homologation; one is the alkylation of alkyl halides or the addition of carbonyl



Scheme 1.



2 X = SPh
3 X = OMOM
4 X = SePh



Scheme 2.

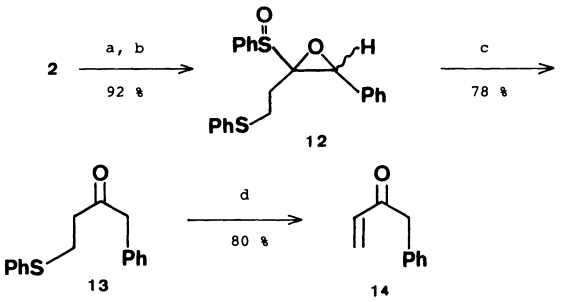
compounds with vinyl ketone anion equivalents (acyl anion equivalent)[9] and the other is a coupling of the α,β-unsaturated carboxylic acid chloride with transition-metal reagents[10] or with alkyltin[11] or alkyl iodides[12] by promotion of palladium. On the other hand, an excellent method for the synthesis of divinyl ketones was recently reported by Stille.[13]

Recently, we reported[14] a new method for the homologation of carbonyl compounds through α,β-epoxy sulfoxides upon a treatment with nucleophiles (Scheme 1). In these reactions if R_1 is to be a vinyl group or its equivalent this sequence must lead to a novel synthetic method for the preparation of alkyl vinyl ketones from carbonyl compounds by three-carbon homologation. In this paper we report a novel and versatile method for a synthesis of alkyl vinyl ketones **8** and divinyl ketones **10** from carbonyl compounds (**1**) and 1-chloro-3-phenylthiopropyl phenyl sulfoxide (**2**) as a three-carbon homologating agent through α,β-epoxy sulfoxides **6**.[15] The whole sequence is shown in Scheme 2.

Results and Discussion

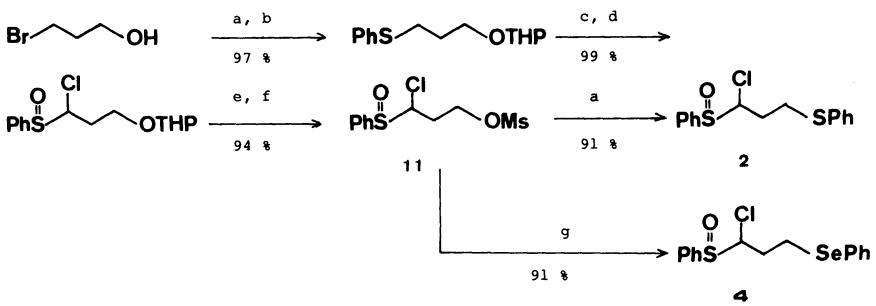
A Synthesis of Alkyl Vinyl Ketones from Carbonyl Compounds Through α,β-Epoxy Sulfoxides by the Use of 1-Chloro-3-phenylthiopropyl Phenyl Sulfoxide as Three-Carbon Homologating Agent. As the three-carbon homologating agents, we selected three kinds of 3-substituted 1-chloropropyl phenyl sulfoxides **2**—**4**. 1-Chloro-3-phenylthiopropyl phenyl sulfoxide (**2**) was synthesized from 3-bromo-1-propanol via **11** in very good overall yields as shown in Scheme 3. Addition of **2** with benzaldehyde followed by treatment with a slight excess potassium *t*-butoxide in *t*-butyl alcohol gave the desired **12** in 92% yield. A treatment of **12** with excess sodium benzeneselenolate[14a] afforded β-phenylthio ketone **13** in 78% yield without any problem. Next, the sulfur group of **13** was oxidized with one equivalent of *m*-chloroperbenzoic acid (*m*-CPBA) to give the desired sulfoxide. In this reaction, we observed some vinyl ketone **14** during the work-up stage (alkali washing of the etheral extract of the product). On the basis of this observation we established the conditions of the derivation of β-phenylthio ketone to the vinyl ketone as follows. β-Phenylthio ketone (0.2 mmol) was treated with 1.1 equivalent of *m*-CPBA in CH_2Cl_2 (2 ml) at −60 °C for 20 min. Ether (4 ml) and 10% sodium hydroxide (4 ml) was added to the reaction mixture and the whole (two phases) was vigorously stirred at room temperature. In this one-pot oxidation β-elimination sequence the β-phenylthio ketone **13** gave the desired vinyl ketone **14** in 80% overall yield. A thermal elimination of the sulfinyl group[16] was also possible; however, we found that an alkaline treatment was much more convenient owing to higher yields and a one-pot operation.

The results of the preparation of alkyl vinyl ketones from α,β-epoxy sulfoxides are summarized in Table 1. As shown in the Table, various kinds of aldehydes and ketones were converted to alkyl vinyl ketones through the α,β-epoxy sulfoxides in good overall yields. The reaction time for the elimination of the phenylsulfinyl group was dependent on the substrate varied from 15 min to 2 d. It is noteworthy that this kind of reductive three-carbon homologation has been



a) LDA then PhCHO b) t-BuOK/ t-BuOH
c) PhSeNa/ EtOH d) m-CPBA then KOH/ Et_2O

Scheme 4.



a) PhSNa/ MeOH b) Dihydropyran/ PPTS/ CH_2Cl_2
c) NCS/ CCl_4 d) m-CPBA/ CH_2Cl_2
e) PPTS/ MeOH f) MsCl/ Pyridine
g) PhSeNa/ MeOH

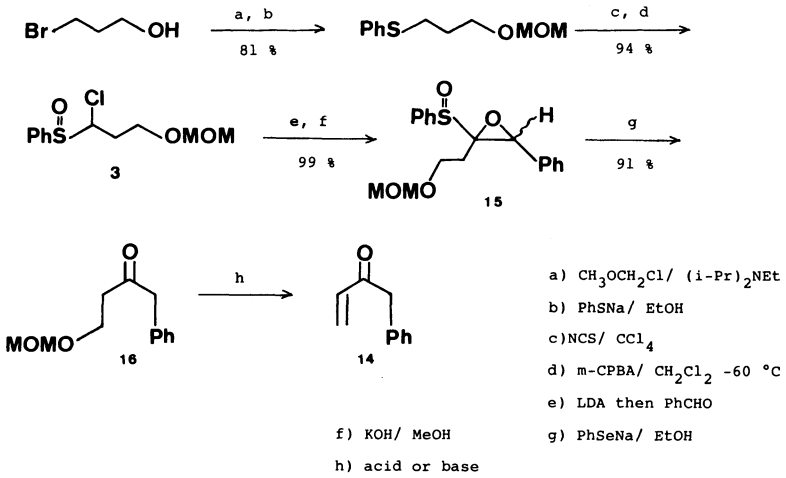
Scheme 3.

reported by Murai et al.[17] by using allylsilane chemistry; however, their procedure was reported to be useful only when unhindered aldehydes, not ketones, were used. In contrast with their results, the present method is quite useful for various kinds of aldehydes and ketones.

At the same time, we studied this vinyl ketone synthesis by using the three carbon homologating agents having a methoxymethoxy group or a phenylseleno group as the leaving group. 1-Chloro-3-(methoxymethoxy)propyl phenyl sulfoxide (**3**) was synthesized from 3-bromo-1-propanol in good overall yield (Scheme 5). The addition of **3** with benzaldehyde followed by a treatment with excess aqueous potassium hydroxide gave the α,β-epoxy sulfoxide **15** in quantitative yield; this was treated with sodium benzeneselenolate and afforded the desired ketone **16** having a leaving group at β-position.

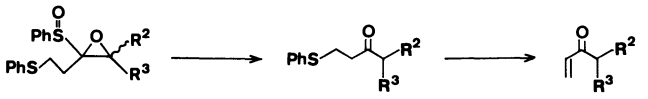
Several acidic or basic conditions for the elimination of the methoxymethoxy group of **16** were tried; however, only disappointing results were obtained. For instance, a treatment of **16** with *p*-toluenesulfonic acid in benzene at 40 °C for 2.5 h or with 10% aqueous potassium hydroxide in benzene at room temperature for 3 h gave **14** in 33 and 24% yields, respectively.

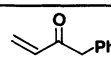
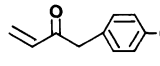
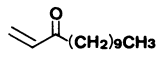
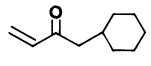
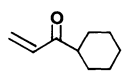
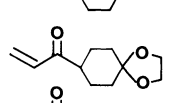
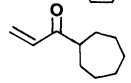
Next, 1-chloro-3-(phenylseleno)propyl phenyl sulfoxide (**4**) was synthesized from **11** (Scheme 3). The addition of **4** with 4,4-(ethylenedioxy)cyclohexanone



Scheme 5.

Table 1. Preparation of Alkyl Vinyl Ketones from α,β-Epoxy Sulfoxides through β-Phenylthio Ketones



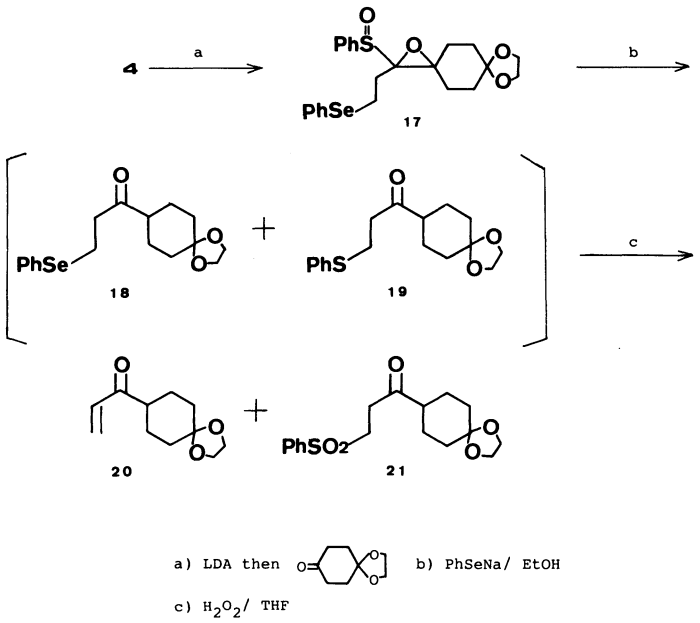
α,β-Epoxy Sulfoxide R_2	R_3		β-Phenylthio Ketone Yield/%		Time[a]	Alkyl Vinyl Ketone		Yield[b] %
H	Ph	(**12**)	78	(**13**)	1.5 h		(**14**)	80
H	Cl-C6H4-	(**22**)	86	(**28**)	1.5 h		(**34**)	74
H	$CH_3(CH_2)_8$	(**23**)	85	(**29**)	2 d		(**35**)	95
H	C6H10-	(**24**)	89	(**30**)	1 d		(**36**)	94
—$(CH_2)_5$—		(**25**)	94	(**31**)	3 h		(**37**)	74
-$(CH_2)_2$-C(O-)(O-)-$(CH_2)_2$-		(**26**)	96	(**32**)	15 min		(**20**)	85
—$(CH_2)_6$—		(**27**)	96	(**33**)	1 d		(**38**)	85

a) Reaction time for the alkaline treatment. b) Isolated purified yield.

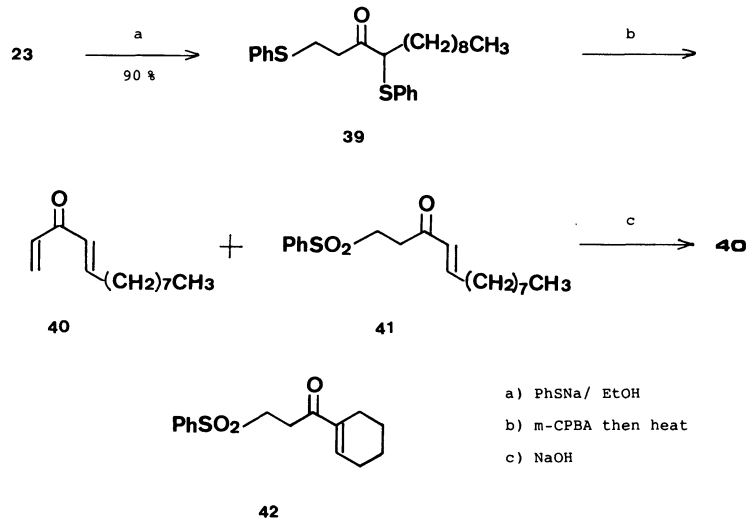
was carried out in the usual way but in this case, after the addition of **4** with ketone, an elevation of the reaction temperature from −78 °C to room temperature gave the desired **17** in 74% yield.

We came across a problem in next step. A treatment of **17** with excess sodium benzeneselenolate in refluxing ethanol for 1 h gave an unseparable mixture of the desired seleno ketone **18** and an undesired thio ketone **19**. This was confirmed from the fact that the oxidation of the mixture with hydrogen peroxide[18] gave the vinyl ketone **20** and the sulfone **21** in a ratio of about 2 to 5.

A Synthesis of Divinyl Ketones from Carbonyl Compounds with Three-Carbon Homologation. As already reported, a treatment of α,β-epoxy sulfoxides with a thiolate gave α-sulfenylated ketones in good yields.[14b] In the case of the α,β-epoxy sulfoxides **23**—**27** this reaction should afford α,β′-bis(phenylthio) ketones; these compounds must give divinyl ketones by the elimination of both phenylthio groups. First of all, a treatment of the α,β-epoxy sulfoxide **23** with sodium benzenethiolate, prepared from thiophenol and sodium hydride in ethanol, gave a rather complex mixture in which some amount of the desired bis(phenylthio) ketone **39** was observed. This complexity of this reaction was thought to be due to the strong basicity of the conditions. Based on this consideration, sodium benzenethiolate was prepared from diphenyl disulfide by the reduction with sodium borohydride in refluxing ethanol for 30 min. Treatment of **23** with thus obtained sodium benzenethiolate in this solution at 0 °C for 1 h gave the desired



Scheme 6.



Scheme 7.

bis(phenylthio) ketone **39** as a sole product in 90% yield. This method for the sulfenylation was used throughout this study. Similar kinds of differences of the two conditions as mentioned above were reported by Liotta et al.[19] in the selenolate case.

A successive oxidation followed by pyrolytic elimination was our initial plan for the conversion of **39** to the desired divinyl ketone **40**. Bis(phenylthio) ketone **39** was oxidized with two equivalents of *m*-CPBA at −40 °C. The product, bis(phenylsulfinylated) ketone, was roughly purified by silica-gel column chromatography and heated in refluxing toluene for 15 min. In this reaction the desired **40** (66%) and the unexpected sulfone **41** (26%) were obtained. Finally, this mixture was treated with a base (as described for the synthesis of alkyl vinyl ketones) to give pure divinyl detone **40** in 79% yield. The oxidant for the formation of this sulfone was not determined certainly, but was thought to be the eliminated sulfinate. In the case of the bis(phenylthio) ketone derived from the α,β-epoxy sulfoxide **25**, the yield of the sulfone **42** came up to 50%. The results of the preparation of various kinds of divinyl ketones from α,β-epoxy sulfoxides through bis(phenylthio) ketones is shown in Table 2.

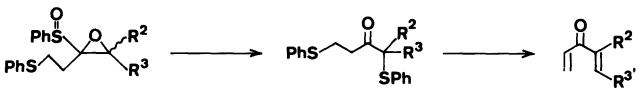
In conclusion, a novel and versatile procedure for the synthesis of vinyl and divinyl ketones from carbonyl compounds with three-carbon homologation was realized. As these unsaturated ketones are quite useful as the building blocks of compounds having a complex carbon framework, especially divinyl ketones are good precursors for cyclopentenone derivatives by Nazarov type cyclization;[20] the procedure presented in this paper contributes to the synthesis of complex natural products as well.

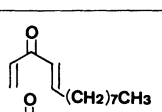
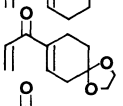
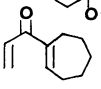
Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured directly on a NaCl plate or in KBr disks with a Hitachi 215 spectrometer. ^{1}H 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. Ultraviolet (UV) spectra were measured with a Hitachi 200 spectrometer. Electron-impact mass spectra (MS) were obtained on a Hitachi M-80 double-focusing spectrometer at 70 eV by direct insertion. Silica-gel BW-127 ZH (Fuji-Devison) containing 2% fluoresence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation.

1-Chloro-3-(methylsulfonyloxy)propyl Phenyl Sulfoxide (11). To a solution of sodium benzenethiolate (21 mmol) in MeOH (30 ml) was added 3-bromo-1-propanol (1.8 g; 20 mmol); the mixture was stirred under N_2 at room temperature for 45 min. Excess NH_4Cl was added and the MeOH was evaporated; then, the residue was extracted with ether. The product was distilled (bp 130 °C/2 mmHg (1 mmHg=133.322 Pa)) to give 3.36 g (99%) of 3-phenylthio-1-propanol as a colorless oil. IR (neat): 3350 (OH) cm^{-1}; ^{1}H NMR δ=1.89 (2H, quintet, J=7 Hz), 3.06 (2H, t, J=7 Hz), 3.78 (2H, t, J=7 Hz), 7.0—7.5 (5H, m). 3-Phenylthio-1-propanol (3.36 g; 20 mmol) was treated with dihydropyran (2.7 ml; 30 mmol) and pyridinium *p*-toluenesulfonate (PPTS) (250 mg; 1 mmol) in CH_2Cl_2 (20 ml) at room temperature for 1 h. After the workup according to Miyashita's procedure[21] the product was distilled (bp 150 °C/2 mmHg) to afford 4.9 g (97%) of 1-phenylthio-3-(tetrahydro-2-pyranyloxy)propane as a colorless oil. ^{1}H NMR δ=3.07 (2H, t, J=7 Hz), 4.58 (1H, bs). This sulfide (5.05 g; 20 mmol) was added to a suspension of NCS (21 mmol) in 40 ml of CCl_4 and the reaction mixture was stirred at room temperature for 2 h. The precipitate was filtered off and the filtrate was evaporated. The residue was dissolved in 60 ml of CH_2Cl_2 and cooled to −50 °C and *m*-CPBA (21 mmol) was added to the solution and stirred for

Table 2. Preparation of Divinyl Ketones from α,β-Epoxy Sulfoxides through Bis(phenylthio)ketones



α,β-Epoxy Sulfoxide	Bis(phenylthio) Ketone Yield/%	Conditions of the Elimination			Divinyl Ketone		Yield[c] %
		Temp[a]	Time[a]	Time[b]			
23	90	110 °C	15 min	1 d		(**40**)	79
25	94	110 °C	1 h	17 h		(**43**)	65
26	97	110 °C	1.5 h	2 h		(**44**)	76
27	94	r.t.	2 h	1 d		(**45**)	77

a) The conditions of the thermal elimination of the phenylsulfinyl group at α-position of the ketone. Refluxing in toluene. b) The time for the alkaline treatment at room temperature. c) Isolated purified yield.

1 h. The reaction mixture was diluted with 60 ml of CH_2Cl_2 and the whole was washed, successively, with 10% NaOH and sat. NH_4Cl. The usual work-up gave a crude product, which was purified by silica-gel column chromatography to afford 5.99 g (99%) of 1-chloro-3-(tetrahydro-2-pyranyloxy)-propyl phenyl sulfoxide (diastereomeric mixture) as a colorless oil. IR (neat): 1050, 1035 (SO) cm^{-1}. This product (769 mg; 2.54 mmol) was dissolved in 20 ml of MeOH and 64 mg of PPTS was added. The mixture was stirred at 50 °C for 2 h. After the usual work-up[21] 557 mg (99%) of the alcohol was obtained as a colorless oil. IR (neat): 3400 (OH), 1050 (SO) cm^{-1}. To a solution of the alcohol (3.17 g; 14.5 mmol) in 13 ml of pyridine was added methanesulfonyl chloride (2.3 ml; 29 mmol) at 0 °C and the solution was stirred for 1 h. The reaction mixture was diluted with benzene and washed, successively, with 10% HCl, sat. $NaHCO_3$, and sat. NH_4Cl. The product was purified by silica-gel column chromatography to give the desired **11** (4.06 g; 94%) as a colorless oil. IR (neat): 1360, 1180 (SO_2), 1050 (SO) cm^{-1}; ^1H NMR δ=2.0—2.9 (2H, m), 3.03, 3.07 (each s, OSO_2CH_3); MS *m/z* (%): 171 ([M−PhSO]$^+$, 21), 79 (42), 77 (57), 75 (100).

1-Chloro-3-phenylthiopropyl Phenyl Sulfoxide (2). To a solution of sodium benzenethiolate (14.4 mmol) in 21 ml of MeOH was added a solution of **11** (4.06 g; 13.7 mmol) in MeOH (5 ml). The reaction mixture was stirred at room temperature for 3 h. Excess NH_4Cl was added to the mixture and the MeOH was evaporated. The product was purified by the usual way to give 3.64 g (86%) of **2** as a colorless oil (diastereomeric mixture) and 0.24 g (6%) of recovered **11**. IR (neat): 1060 (SO) cm^{-1}; ^1H NMR δ=1.8—2.7 (2H, m), 2.8—3.4 (2H, m), 4.07 (dd, *J*=9, 4 Hz), 4.83 (dd, *J*=10, 4 Hz), 7.1—7.8 (10H, m); MS *m/z* (%): 310 (M$^+$, 8), 185 ([M−PhSO]$^+$, 28), 149 (32), 123 (100); Found: *m/z* 310.0237. Calcd for $C_{15}H_{15}ClOS_2$: M, 310.0251.

1,2-Epoxy-1-phenyl-2-phenylsulfinyl-4-phenylthiobutane (12). To a solution of LDA (2.1 mmol) in 9 ml of THF at −60 °C was added a solution of **2** (2 mmol) in 1 ml of THF dropwise with stirring. The stirring was continued for 15 min; then, 0.22 ml (2.1 mmol) of benzaldehyde was added. After 5 min the reaction was quenched by sat. aq NH_4Cl and the whole was extracted with benzene. The usual workup gave chlorohydrin-L[14a] and chlorohydrin-P[14a] in 43 and 54% yields, respectively. Chlorohydrin-L: Colorless oil; IR (neat): 3330 (OH), 1050 (SO) cm^{-1}; ^1H NMR δ=2.2—3.5 (4H, m), 5.00 (1H, s), 7.1—8.0 (15H, m); MS *m/z* (%): 290 ([M−PhSOH]$^+$, 35), 180 (27), 145 (46), 117 (77), 77 (100). Chlorohydrin-P: Colorless prisms; mp 112—114 °C (benzene-hexane); IR (KBr): 3350 (OH), 1040 (SO) cm^{-1}; ^1H NMR δ=1.6—3.1 (4H, m), 5.17 (1H, d, *J*=3 Hz), 7.0—7.8 (15H, m); MS *m/z* (%): 290 ([M−PhSOH]$^+$, 61), 180 (56), 145 (73), 117 (100); Found: C, 63.55; H, 5.04; Cl, 8.42; S, 15.53%. Calcd for $C_{22}H_{21}ClO_2S_2$: C, 63.37; H, 5.08; Cl, 8.50; S, 15.38%. To a solution of the chlorohydrin-L (1.10 g; 2.36 mmol) in 2 ml of benzene and 12 ml of *t*-BuOH was added a suspension of *t*-BuOK (234 mg; 3.03 mmol) in 2 ml of *t*-BuOH at room temperature with stirring. The reaction was quenched after 5 min by adding NH_4Cl and the solvent was evaporated. The residue was dissolved with benzene. After the usual workup, the product was purified by silica gel column chromatography to give 1.03 g (99%) of **12-L** as a colorless oil. IR (neat): 1055 (SO) cm^{-1}; ^1H NMR δ=1.5—2.1 (2H, m), 2.3—3.1 (2H, m), 4.82 (1H, s), 6.9—7.8 15H, m); MS *m/z* (%): 256 (33), 255 ([M−PhSO]$^+$, 18), 199 (38), 123 ([M-$C_{15}H_{13}O_2S$]$^+$, 100). **12-P**: Yield 92%; IR (neat): 1050 (SO) cm^{-1}; ^1H NMR δ=1.7—3.2 (4H, m), 4.53 (1H, s), 7.0—7.8 (15H, m); MS *m/z* (%): 199 (3), 125 (8), 109 ([M−$C_{16}H_{15}O_2S$]$^+$, 7), 78 (100).

1-Phenyl-4-phenylthio-2-butanone (13). To a suspension of diphenyl diselenide (1.46 g; 4.65 mmol) in 9 ml of EtOH was added $NaBH_4$ (353 mg; 9.3 mmol) by portions with stirring at room temperature. After vigorous hydrogen gas evolution ceased, the solution was cooled in an ice bath and a solution of **12** (0.93 mmol) in 0.5 ml of EtOH was added. The reaction mixture was stirred at 0 °C under N_2 for 20 min then the reaction was quenched by sat. aq NH_4Cl and then the EtOH was evaporated. The residue was extracted with benzene. After the usual workup, the product was purified by silica-gel column chromatography to give **13** in 78% yield as a colorless oil. IR (neat): 1720 (CO) cm^{-1}; ^1H NMR δ=2.7—2.9 (2H, m), 3.0—3.2 (2H, m), 3.70 (2H, s), 7.1—7.4 (10H, m); MS *m/z* (%): 256 (M$^+$, 65), 165 ([M−$PhCH_2$]$^+$, 23), 137 ([M−C_8H_7O]$^+$, 62), 123 ([M−C_9H_9O]$^+$, 100); Found: *m/z* 256.0914. Calcd for $C_{16}H_{16}OS$: M, 256.0920.

Oxidation of 13 with *m*-CPBA Followed by Treatment with Alkali. To a solution of **13** (48 mg; 0.91 mmol) in 2 ml of CH_2Cl_2 was added 44 mg (0.21 mmol) of *m*-CPBA at −60 °C with stirring. The stirring was continued for 20 min and then ether (4 ml) and 10% NaOH (4 ml) were added to the reaction mixture. This was vigorously stirred at room temperature for 1.5 h. The reaction mixture was neutralized by NH_4Cl and the whole was extracted with CH_2Cl_2, washed and dried. After the usual workup, the product was purified by silica-gel column chromatography to afford 22 mg (80%) of 1-phenyl-3-buten-2-one (**14**) as a colorless oil. IR (neat): 1690, 1670 (CO), 1615 (C=C) cm^{-1}; ^1H NMR δ=3.91 (2H, s), 5.85 (1H, dd, *J*=8, 3.5 Hz), 6.36 (1H, dd, *J*=18, 3.5 Hz), 6.45 (1H, dd, *J*=18, 8 Hz), 7.1—7.5 (5H, m); UV λ_{max}^{EtOH} 210, 256 nm; MS *m/z* (%): 146 (M$^+$, 21), 118 ([M−CO]$^+$, 13), 91 ([M−C_3H_3O]$^+$, 64), 55 (100); Found: *m/z* 146.0734. Calcd for $C_{10}H_{10}O$: M, 146.0731.

1-Chloro-3-(methoxymethoxy)propyl Phenyl Sulfoxide (3). Chloromethyl methyl ether (3.8 ml; 50 mmol) was added to a solution of 3-bromo-1-propanol (1.4 g; 10 mmol), *N,N*-diisopropylethylamine (5 ml; 29 mmol) in THF (0.5 ml) at 0 °C and the mixture was stirred at 0 °C for 30 min. The reaction mixture was poured into a mixture of ice and diluted HCl and the whole was extracted with ether. The ether extract was washed with sat. aq $NaHCO_3$, dried over Na_2SO_4 and the ether was evaporated. The residue was distilled (bp 100 °C/2 mmHg) to give 1.63 g (88%) of 1-bromo-3-(methoxy)methoxypropane as a colorless oil. ^1H NMR δ=2.10 (2H, quintet, *J*=6 Hz), 3.30 (3H, s), 3.45, 3.60 (each 2H, t, *J*=6 Hz), 4.55 (2H, s). This bromide (1 g; 5.5 mmol) was added to a solution of sodium benzenethiolate (6 mmol) in 6 ml of dry EtOH and the mixture was stirred at room temperature for 1.5 h under an N_2 atmosphere. The reaction mixture was neutralized by NH_4Cl and the EtOH was evaporated. The residue was dissolved with benzene and washed, successively, with 5% NaOH and sat. NH_4Cl. The product was distilled (bp 130 °C/2 mmHg) to give 1.07 g (92%) of 1-(methoxy)methoxy-3-phenylthiopropane as a colorless oil. ^1H NMR δ=1.95

(2H, quintet, J=6 Hz), 3.00 (2H, t, J=6 Hz), 3.31 (3H, s), 3.60 (2H, t, J=6 Hz), 4.55 (2H, s), 7.0—7.5 (5H, m). This product (1.07 g; 5 mmol) was chlorinated then oxidized according to the procedure described for the synthesis of **11** to afford 1.25 g (94%) of **3** as a colorless oil (diastereomeric mixture). IR (neat): 1050 (SO) cm^{-1}; ^1H NMR δ=3.28, 3.30 (each s, CH_3), 3.72 (m), 4.53, 4.55 (each s, $-OCH_2O-$).

1,2-Epoxy-4-(methoxymethoxy)-1-phenyl-2-phenylsulfinylbutane (15). Addition of **3** with benzaldehyde according to the procedure described for the synthesis of **12** gave two chlorohydrins. Chlorohydrin-L: Yield 40%, colorless prisms (benzene-hexane) mp 116—118 °C; IR (KBr): 3220 (OH), 1035, 1025 (SO) cm^{-1}; ^1H NMR δ=3.35 (3H, s), 4.60 (2H, s), 5.00 (1H, s), 7.25 (5H, s), 7.4—8.0 (5H, m). Chlorohydrin-P: Yield 60%, colorless prisms (AcOEt-hexane) mp 85 °C (decomp); IR (KBr): 3310 (OH), 1065, 1035, 1015 (SO) cm^{-1}; ^1H NMR δ=3.29 (3H, s), 4.47 (2H, s), 5.20 (1H, s), 7.2—7.8 (10H, m). **15-L**: Yield 99%, colorless oil, IR (neat): 1050 (SO) cm^{-1}; ^1H NMR δ=1.24—2.05 (2H, m), 3.29 (3H, s), 3.45 (2H, m), 4.49 (2H, s), 4.91 (1H, s), 7.10—7.94 (10H, m); MS m/z (%): 271 ([M−$C_2H_5O_2$]$^+$, 0.1), 207 ([M−PhSO]$^+$, 0.4), 125 (5), 91 (9), 45 (100). **15-P**: Yield 98%, colorless oil, IR (neat): 1050 (SO) cm^{-1}; ^1H NMR δ= 1.58—1.90 (1H, m), 2.47—2.78 (1H, m), 3.34 (3H, s), 3.56 (2H, t, J=6 Hz), 4.56 (2H, s), 4.61 (1H, s), 7.24—7.75 (10H, m); MS m/z (%): 271 ([M−$C_2H_5O_2$]$^+$, 0.1), 207 ([M−PhSO]$^+$, 0.4), 125 (3), 45 (100).

4-(Methoxymethoxy)-1-phenyl-2-butanone (16). The α,β-epoxy sulfoxide **15** was treated with sodium benzeneselenolate as described above to give **16** in 91% yield as a colorless oil. IR (neat): 1720, 1715 (CO) cm^{-1}; ^1H NMR δ=2.71 (2H, t, J=6 Hz), 3.33 (3H, s), 3.72 (2H, s), 3.76 (2H, t, J=6 Hz), 4.56 (2H, s), 7.0—7.4 (5H, m); MS m/z (%): 208 (M^+, 0.3), 177 ([M-CH_3O]$^+$, 2), 117 ([M−$PhCH_2$]$^+$, 16), 91 (51), 45 (100); Found: m/z 208.1092. Calcd for $C_{12}H_{16}O_3$: M, 208.1098.

Treatment of 16 with Acid or Base. Acidic conditions: A solution of **16** (35 mg) and p-TsOH·$2H_2O$ (3.2 mg) in 1.7 ml of benzene was stirred at 40 °C under N_2 for 2.5 h. The mixture was passed through a short pad of Na_2CO_3 and the product was purified by silica-gel column chromatography to give 8 mg (33%) of **14** as a colorless oil. Basic conditions: A mixture of **16** (42 mg) in 2 ml of benzene and 1.5 ml of 10% KOH was vigorously stirred at room temperature for 3 h to give 7 mg (24%) of **14** and several by-products.

1-Chloro-3-phenylselenopropyl Phenyl Sulfoxide (4). To a suspension of diphenyl diselenide (815 mg; 2.61 mmol) in 15 ml of MeOH was added $NaBH_4$ (200 mg; 5.23 mmol) by portions with stirring. After vigorous hydrogen gas evolution ceased, a solution of **11** (1.41 g; 4.75 mmol) in 2 ml of MeOH was added and the reaction mixture was stirred at room temperature for 2 h. Excess NH_4Cl was added and the MeOH was evaporated. After the usual work-up, the product was purified by silica-gel column chromatography to give 1.54 g (91%) of **4** as a colorless oil (diastereomeric mixture). IR (neat): 1055 (SO) cm^{-1}; ^1H NMR δ=2.0—2.7 (2H, m), 2.8—3.4 (2H, m), 4.69, 4.82 (each dd, J=9, 4 Hz), 7.1—7.8 (5H, m); MS m/z (%): 358 (M^+, 13), 233 ([M−PhSO]$^+$, 30), 201 ([M−PhSe]$^+$, 25), 171 (54), 101 (95), 77 (100).

2″-Phenylsulfinyl-2″-(2-phenylseleno)ethyldispiro[1,3-dioxolane-2,1′-cyclohexane-4′,1″-oxirane] (17). To a LDA (3.5 mmol) solution in THF (30 ml) at −78 °C was added a solution of **4** (118 g; 3.3 mmol) in 2 ml of THF dropwise with stirring. The stirring was continued for 30 min then a solution of 4,4-(ethylenedioxy)cyclohexanone (0.77 g; 5 mmol) in THF was added. After 5 min the cooling bath was removed and the mixture was stirred at room temperature for 1 h. Sat. aq NH_4Cl was added to the reaction mixture and the whole was extracted with benzene. After the usual work-up, the product was purified by silica-gel column chromatography to give 1.17 g (74%) of **17** as a colorless oil. In this reaction 0.28 g (24%) of **4** was recovered. IR (neat): 1145, 1100, 1090 (COC), 1050 (SO) cm^{-1}; ^1H NMR δ=1.1—2.9 (12H, m), 4.00 (4H, s), 7.1—7.7 (10H, m); MS m/z (%): 352 ([M−PhSO]$^+$, 27), 297 (25), 157 (34), 99 (100).

8-(1-Oxo-2-propenyl)-1,4-dioxaspiro[4.5]decane (20) and 8-(1-Oxo-3-phenylsulfonylpropyl)-1,4-dioxaspiro[4.5]decane (21). To a solution of sodium benzeneselenolate (5 mmol) in 9 ml of EtOH was added a solution of **17** (238 mg; 0.5 mmol) in 1 ml of EtOH and the mixture was refluxed for 1 h under N_2. Excess NH_4Cl was added and the EtOH was evaporated. The residue was extracted with benzene. After the usual work-up, te products were purified by silica-gel column chromatography to give 146 mg of unseparable mixture of **18** and **19**. IR (neat): 1715 (CO) cm^{-1}; MS m/z (%): 354 (M^+; $C_{17}H_{22}O_3Se$; 3), 306 (M^+; $C_{17}H_{22}O_3S$; 26), 99 (100). To a solution of the mixture (53 mg) in 1.5 ml of THF was added 35% H_2O_2 (0.5 ml) and the mixture was stirred at room temperature for 30 min. The whole was extracted with ether and washed, dried over Na_2SO_4. The products were separated by silica-gel column chromatography to afford 9 mg of **20** and 39 mg of **21**. **20**: Colorless oil; IR (neat): 1705, 1685 (CO), 1625 (C=C) cm^{-1}; UV λ_{max}^{EtOH} 214 nm; ^1H NMR δ=1.4—2.0 (8H, m), 2.5—2.8 (1H, m), 3.97 (4H, s), 5.77 (1H, dd, J=9, 3 Hz), 6.32 (1H, dd, J=18, 3 Hz), 6.50 (1H, dd, J=18, 9 Hz); MS m/z (%): 196 (M^+, 0.5), 168 ([M−C_2H_4]$^+$, 4), 141 ([M−C_3H_3O]$^+$, 4) 99 (100). **21**: Colorless prisms (benzene-hexane); mp 102—104.5 °C; IR (KBr): 1715 (CO), 1310 (SO_2) cm^{-1}; ^1H NMR δ=1.4—2.0 (8H, m), 2.2—2.6 (1H, m), 2.9—3.1 (2H, m), 3.3—3.5 (2H, m), 3.96 (4H, s), 7.4—8.0 (5H, m); MS m/z (%): 338 (M^+, trace), 197 ([M−$PhSO_2$]$^+$, 18), 141 ([M−$C_9H_9O_3S$]$^+$, 11), 99 (100); Found: C, 60.54; H, 6.53; S, 9.41%. Calcd for $C_{17}H_{22}O_5S$: C, 60.34; H, 6.55; S, 9.47%.

α,β-Epoxy Sulfoxides 22—27. All α,β-epoxy sulfoxides **22—27** were synthesized from **2** and carbonyl compounds as described for **12**.

1,2-Epoxy-1-(4-chlorophenyl)-2-phenylsulfinyl-4-phenylthiobutane (22). Chlorohydrin-L: Colorless oil; yield 42%; IR (neat): 3330 (OH), 1050 (SO) cm^{-1}; ^1H NMR δ=2.0—3.5 (4H, m), 4.91 (1H, s), 7.0—8.9 (14H, m), Chlorohydrin-P: Colorless powder: yield 42%; IR (KBr): 3490 (OH), 1050 (SO) cm^{-1}; ^1H NMR δ=1.6—3.1 (4H, m), 5.18 (1H, s), 7.0—7.7 (14H, m), **22-L**: Colorless oil; yield 86%; IR (neat): 1090, 1050 (SO) cm^{-1}; ^1H NMR δ=1.3—3.1 (4H, m), 4.72 (1H, s), 6.9—7.7 (14H, m); MS m/z (%): 414 (M^+, trace), 398 ([M−O]$^+$, 1.6), 341 (0.7), 289 (47), 233 (75), 125 (100). **22-P**: Colorless oil; yield 89%; IR (neat): 1090, 1050 (SO) cm^{-1}; ^1H NMR δ=1.6—3.1 (4H, m), 4.45 (1H, s), 7.0—7.7 (14H, m); MS m/z (%): 288 ([M−C_6H_6SO]$^+$, 12), 233 (100).

3,4-Epoxy-3-phenylsulfinyl-1-phenylthiotridecane (23). Chlorohydrin: Diastereomeric mixture; colorless oil; IR (neat): 3350 (OH), 1045 (SO) cm^{-1}; ^1H NMR δ=0.88, 0.90 (each t, J=7 Hz), 7.2—7.9 (10H, m); MS m/z (%): 340

([M−PhSOH]$^+$, 23), 230 (23), 284 (23), 110 (100). Less polar **23**: Colorless oil; yield 36%; IR (neat): 1055 (SO) cm^{-1}; ^{1}H NMR δ=0.90 (3H, bt, J=6 Hz), 1.0—3.1 (20H, m), 3.32 (1H, t, J=7 Hz), 7.1—7.8 (10H, m); MS m/z (%): 304 ([M−PhSOH]$^+$, 5), 249 (34), 218 (25), 186 (31), 125 (100). More polar **23**: Colorless oil; yield 45%; IR (neat): 1045 (SO) cm^{-1}; ^{1}H NMR δ=0.90 (3H, bt, J=6 Hz), 1.0—3.1 (20H, m), 3.67 (1H, m), 7.1—7.7 (10H, m); MS m/z (%): 305 ([M−PhSO]$^+$, 52), 249 (69), 123 (100).

1-Cyclohexyl-1,2-epoxy-2-phenylsulfinyl-4-phenylthiobutane (24). Chlorohydrin: Diastereomeric mixture; colorless oil; yield 95%; IR (neat): 3370 (OH), 1055 (SO) cm^{-1}; MS m/z (%): 296 ([M−PhSOH]$^+$, 15), 126 (53), 110 (100). Less polar **24**: Colorless oil; yield 38%; IR (neat): 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.0—3.0 (15H, m), 3.04 (1H, d, J=8 Hz), 7.1—7.8 (10H, m); MS m/z (%): 386 (M$^+$, 0.2), 261 (23), 205 (31), 123 (100). More polar **24**: Colorless oil; yield 32%; IR (neat): 1055 (SO) cm^{-1}; ^{1}H NMR δ=0.8—3.4 (15H, m), 3.44 (1H, d, J=8 Hz), 7.1—8.0 (10H, m); MS m/z (%): 386 (M$^+$, trace), 261 (11), 185 (19), 123 (100).

2′-Phenylsulfinyl-2′-(2-phenylthioethyl)spiro[cyclohexane-1,1′-oxirane] (25). Chlorohydrin: Colorless plate; mp 100—102 °C (benzene-hexane); yield 77%; IR (KBr): 3210 (OH), 1030 (SO) cm^{-1}; ^{1}H NMR δ=0.8—3.2 (14H, m), 7.1—7.8 (10H, m); MS m/z (%): 282 ([M−PhSOH]$^+$, 28), 126 (31), 110 (100); Found: C, 61.65; H, 6.09; Cl, 8.60; S, 15.59%. Calcd for $C_{21}H_{25}ClO_2S_2$: C, 61.67; H, 6.16; Cl, 8.67; S, 15.68%. Epoxy sulfoxide **25**: Colorless prisms; mp 86—87 °C (benzene-hexane); yield 93%; IR (KBr): 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.3—2.9 (14H, m), 7.1—7.7 (10H, m); MS m/z (%): 372 (M$^+$, trace), 247 ([M−PhSO]$^+$, 43), 123 (100); Found: C, 67.87; H, 6.46; S, 17.30% m/z 372.1191. Calcd for $C_{21}H_{24}O_2S_2$: C, 67.70; H, 6.49; S, 17.21% M, 372.1216.

2″-Phenylsulfinyl-2″-(2-phenylthioethyl)dispiro[1,3-dioxrane-2,1′-cyclohexane-4′,1″-oxirane] (26). Chlorohydrin: Colorless oil; yield 94%; IR (neat): 3400 (OH), 1040 (SO) cm^{-1}; ^{1}H NMR δ=1.4—3.2 (12H, m), 3.98 (4H, s), 7.1—7.8 (10H, m); MS m/z (%): 340 ([M−PhSOH]$^+$, 26), 203 (22), 99 (100). Epoxy sulfoxide **26**: Colorless oil; yield 99%; IR (neat): 1100 (COC), 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.2—3.0 (12H, m), 4.02 (4H, s), 7.1—7.7 (10H, m); MS m/z (%): 414 ([M−O]$^+$, 0.2), 305 ([M−PhS]$^+$, 54), 249 (73), 99 (100).

2′-Phenylsulfinyl-2′-(2-phenylthio)ethylspiro[cycloheptane-1,1′-oxirane] (27). Chlorohydrin: Colorless oil; yield 97%; IR (neat): 3410 (OH), 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.2—3.1 (16H, m), 7.1—7.8 (10H, m); MS m/z (%): 296 ([M−PhSOH]$^+$, 19), 278 (4), 234 (17), 186 (34), 149 (19), 125 (100). Epoxy sulfoxide **27**: Colorless oil; yield 68%; IR (neat): 1090, 1050 (SO) cm^{-1}; ^{1}H NMR δ=1.3—3.0 (16H, m), 7.0—7.7 (10H, m); MS m/z (%): 261 ([M−PhSO]$^+$, 17), 205 (100).

1-(4-Chlorophenyl)-4-phenylthio-2-butanone (28). Colorless crystals (EtOH-hexane); mp 52—55 °C; IR (KBr): 1720 (CO) cm^{-1}; ^{1}H NMR δ=1.64—1.85 (2H, m), 3.00—3.20 (2H, m), 3.62 (2H, s), 6.95—7.32 (9H, m); MS m/z (%): 290 (M$^+$, 38), 165 (25), 137 (64), 123 (100); Found: m/z 290.0526. Calcd for $C_{16}H_{15}OClS$: M, 290.0530.

1-Phenylthio-3-tridecanone (29). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; ^{1}H NMR δ=0.89 (3H, bt, J=7 Hz), 1.1—1.7 (16H, m), 2.40 (2H, t, J=8 Hz), 2.75 (2H, m), 3.18 (2H, m), 7.2—7.4 (5H, m); MS m/z (%): 306 (M$^+$, 58), 165 (22), 137 (65), 123 (100).

1-Cyclohexyl-4-phenylthio-2-butanone (30). Colorless oil; IR (neat): 1720 (CO) cm^{-1}; ^{1}H NMR δ=0.5—2.1 (11H, m), 2.18 (2H, d, J=7 Hz), 2.72 (2H, m), 3.16 (2H, m), 7.1—7.4 (5H, m); MS m/z (%): 262 (M$^+$, 57), 137 (41), 125 (72), 109 (35), 97 (60), 55 (100).

1-Cyclohexyl-3-phenylthio-1-propanone (31). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; ^{1}H NMR δ=0.8—2.0 (10H, m), 2.1—2.3 (1H, m), 2.6—2.9 (2H, m), 3.0—3.3 (2H, m), 7.1—7.6 (5H, m); MS m/z (%): 248 (M$^+$, 77), 191 (14), 165 (17), 137 (49), 123 (51), 109 (42), 83 (100); Found: m/z 248.1221. Calcd for $C_{15}H_{20}OS$: M, 248.1233.

8-(1-Oxo-3-phenylthiopropyl)-1,4-dioxaspiro[4.5]decane (32). Colorless oil; IR (neat): 1715 (CO) cm^{-1}; ^{1}H NMR δ=1.3—2.0 (8H, m), 2.1—2.5 (1H, m), 2.7—2.9 (2H, m), 3.0—3.3 (2H, m), 3.96 (4H, s), 7.1—7.4 (5H, m); MS m/z (%): 306 (M$^+$, 30), 192 (12), 169 (6), 137 (7), 123 (14), 99 (100); Found m/z 306.1291. Calcd for $C_{17}H_{22}O_3S$: M, 306.1288.

1-Cycloheptyl-3-phenylthio-1-propanone (33). Colorless oil; IR (neat): 1710 (CO) cm^{-1}; ^{1}H NMR δ=1.2—2.0 (12H, m), 2.3—2.6 (1H, m), 2.6—2.9 (2H, m), 3.0—3.2 (2H, m), 7.0—7.6 (5H, m); MS m/z (%): 262 (M$^+$, 95), 180 (6), 165 (23), 137 (58), 123 (70), 97 (87), 55 (100); Found: m/z 262.1372. Calcd for $C_{16}H_{22}OS$: M, 262.1389.

1-(4-Chlorophenyl)-3-buten-2-one (34). Colorless oil; IR (neat): 1690 (CO), 1620 (C=C) cm^{-1}; ^{1}H NMR δ=3.83 (2H, s), 5.85 (1H, dd, J=8, 3.5 Hz), 6.28 (1H, dd, J=17.5, 3.5 Hz), 6.37 (1H, dd, J=17.5, 8 Hz), UV λ_{max}^{EtOH} 218.5 nm; MS m/z (%): 180 (M$^+$, 24), 125 ([M−C_3H_3O]$^+$, 43), 55 ([M−C_7H_6Cl]$^+$, 100); Found: m/z 180.0333. Calcd for $C_{10}H_9OCl$: M, 180.0341.

1-Tridecen-3-one (35). Colorless oil; IR (neat): 1705, 1690 (CO), 1620 (C=C) cm^{-1}; ^{1}H NMR δ=0.89 (3H, t, J=7 Hz), 1.0—1.8 (16H, m), 2.61 (2H, t, J=7 Hz), 5.83 (1H, dd, J=9, 3 Hz), 6.26 (1H, dd, J=17.5, 3 Hz), 6.40 (1H, dd, J=17.5, 9 Hz); UV λ_{max}^{EtOH} 212 nm, MS m/z (%): 196 (M$^+$, 2), 167 ([M−C_2H_5]$^+$, 11), 139 ([M−C_4H_9]$^+$, 12), 70 ([M−C_9H_{18}]$^+$, 100); Found: m/z 196.1820. Calcd for $C_{13}H_{24}O$: M, 196.1825.

1-Cyclohexyl-3-buten-2-one (36). Colorless oil; IR (neat): 1700, 1685 (CO), 1620 (C=C) cm^{-1}; ^{1}H NMR δ=0.6—2.1 (11H, m), 2.47 (2H, d, J=7 Hz), 5.83 (1H, dd, J=9, 3 Hz), 6.23 (1H, dd, J=17.5, 3 Hz), 6.40 (1H, dd, J=17.5, 9 Hz); UV λ_{max}^{EtOH} 213 nm; MS m/z (%): 152 (M$^+$, 17), 134 ([M$^+$−H_2O]$^+$, 4), 109 ([M−C_3H_3O]$^+$, 18), 70 (100); Found: m/z 152.1182. Calcd for $C_{10}H_{16}O$: M, 152.1200.

1-Cyclohexyl-2-propen-1-one (37). Colorless oil; IR (neat): 1700, 1680 (CO), 1620 (C=C) cm^{-1}; ^{1}H NMR δ=1.0—2.0 (10H, m), 2.4—2.8 (1H, m), 5.77 (1H, dd, J=9, 3 Hz), 6.36 (1H, dd, J=18, 3 Hz), 6.45 (1H, dd, J=18, 9 Hz); UV λ_{max}^{EtOH} 212 nm.

1-Cycolheptyl-2-propen-1-one (38). Colorless oil; IR (neat): 1700, 1680 (CO), 1615 (C=C) cm^{-1}; ^{1}H NMR δ=1.1—2.1 (12H, m), 2.6—2.9 (1H, m), 5.71 (1H, dd, J=9, 3 Hz), 6.22 (1H, dd, J=18, 3 Hz), 6.38 (1H, dd, J=18, 9 Hz); UV λ_{max}^{EtOH} 212.5 nm; MS m/z (%): 152 (M$^+$, 7), 123 (10), 97 ([M−C_3H_3O]$^+$, 26), 55 ([M−C_7H_{13}]$^+$, 100).

General Procedure for the Preparation of Divinyl Ketones from α,β-Epoxy Sulfoxides Through Bis(phenylthio) Ketones. A synthesis of (*E*)-1,4-tridecadien-3-one (**40**) is described. A solution of diphenyl disulfide (660 mg; 3 mmol) and $NaBH_4$ (230 mg; 6 mmol) in 11 ml of dry EtOH was refluxed under N_2 for 30 min. This solution was cooled in an ice bath and a solution of **23** (260 mg; 0.6 mmol) in 1 ml of EtOH was added. The whole mixture was stirred at 0 °C for 1 h. The reaction was quenched by adding NH_4Cl

and the EtOH was evaporated. The residue was extracted with benzene and the organic layer was washed with sat. aq NH_4Cl and dried over Na_2SO_4. The product was purified by slilca-gel column chromatography to afford 226 mg (90%) of **39** as a colorless oil. IR (neat): 1710 (CO) cm^{-1}; ^1H NMR δ=0.88 (3H, bt, J=7 Hz), 1.0—2.0 (16H, m), 2.8—3.3 (4H, m), 3.62 (1H, t, J=7 Hz), 7.1—7.4 (10H, m); MS m/z (%): 414 (M^+, 6), 304 ([M−PhSH]$^+$, 10), 249 ([M−C_9H_9OS]$^+$, 100). To a solution of **39** (66 mg; 0.16 mmol) in 3 ml of CH_2Cl_2 at −40 °C was added *m*-CPBA (0.35 mmol) and the mixture was stirred for 5 min. The whole mixture was treated with short silica-gel column chromatography to remove the excess *m*-CPBA and *m*-chlorobenzoic acid. The crude product was heated in refluxing toluene (6 ml) for 15 min. The reaction mixture was cooled to room temperature and ether (6 ml) and 10% NaOH (3 ml) were added. The whole mixture (two phases) was vigorously stirred at room temperature for 1 d. The product was extracted with benzene and after the usual workup and silica-gel column chromatography, 24.5 mg (79%) of **40** was obtained as a colorless oil. IR (neat): 1670 (CO), 1640, 1620 (C=C) cm^{-1}; ^1H NMR δ=0.89 (3H, bt, J=7 Hz), 1.0—1.8 (12H, m), 2.1—2.4 (2H, m), 5.83 (1H, dd, J=10, 2 Hz), 6.32 (1H, dd, J=17.5, 2 Hz), 6.37 (1H, dt, J=16, 1.5 Hz), 6.70 (1H, dd, J=17.5, 10 Hz), 6.99 (1H, dt, J=16, 6.5 Hz); MS m/z (%): 194 (M^+, 2), 167 ([M−C_2H_4]$^+$, 9), 124 (16), 109 (32), 83 (63), 55 ([M−$C_{10}H_{19}$]$^+$, 100); Found: m/z 194.1641. Calcd for $C_{13}H_{22}O$: M, 194.1668.

(*E*)-1-Phenylsulfonyl-4-tridecen-3-one (41). Colorless oil; IR (neat): 1680 (CO), 1635 (C=C), 1310, 1155 (SO_2) cm^{-1}; ^1H NMR δ=0.89 (3H, bt, J=6.5 Hz), 1.0—1.7 (12H, m), 2.0—2.4 (2H, m), 2.96—3.20 (2H, m), 3.36—3.56 (2H, m), 6.09 (1H, dt, J=16, 1.5 Hz), 6.82 (1H, dt, J=16, 7 Hz), 7.4—8.1 (5H, m).

1-(1-Cyclohexenyl)-3-phenylsulfonyl-1-propanone (42). Colorless oil; IR (neat): 1665 (CO), 1305, 1150 (SO_2) cm^{-1}; ^1H NMR δ=1.40—1.80 (4H, m), 1.90—2.40 (4H, m), 2.96—3.25 (2H, m), 3.26—3.55 (2H, m), 6.90 (1H, m), 7.35—8.05 (5H, m); MS m/z (%): 278 (M^+, 14), 136 ([M−$PhSO_2H$]$^+$, 100), 109 (94).

1-(1-Cyclohexenyl)-2-propen-1-one (43). α,β′-Bis(phenylthio) ketone: Colorless oil; IR (neat): 1695 (CO) cm^{-1}; ^1H NMR δ=1.0—2.0 (10H, m), 3.12 (4H, m), 7.0—7.4 (10H, m); MS m/z (%): 356 (M^+, 6), 248 (6), 191 ([M−C_9H_9OS]$^+$, 86), 110 ([M−$C_{15}H_{18}OS$]$^+$, 100). **43**: Colorless oil; IR (neat): 1660 (CO), 1635, 1610 (C=C) cm^{-1}; ^1H NMR δ=1.64 (4H, m), 2.25 (4H, m), 5.65 (1H, dd, J=10.5, 2 Hz), 6.20 (1H, dd, J=17, 2 Hz), 6.90 (1H, m), 6.91 (1H, dd, J=17, 10.5 Hz); UV λ_{max}^{EtOH} 248.5 nm; MS m/z (%): 136 (M^+, 67), 108 ([M−C_2H_2]$^+$, 53), 81 ([M−C_3H_3O]$^+$, 100).

8-(1-Oxo-2-propenyl)-1,4-dioxaspiro[4.5]dec-7-ene (44). α,β′-Bis(phenylthio) ketone: Colorless oil; IR (neat): 1690 (CO), 1090 (COC) cm^{-1}; ^1H NMR δ=1.2—2.2 (8H, m), 2.9—3.4 (4H, m), 3.96 (4H, bs), 7.1—7.5 (10H, m); MS m/z (%): 414 (M^+, 13), 249 ([M−C_9H_9OS]$^+$, 100). **44**: Colorless oil; IR (neat): 1665 (CO), 1645, 1610 (C=C) cm^{-1}; ^1H NMR δ=1.82 (2H, bt, J=6 Hz), 2.4—2.7 (4H, m), 4.04 (4H, s), 5.73 (1H, dd, J=10.5, 2 Hz), 6.26 (1H, dd, J=17, 2 Hz), 6.83 (1H, m), 6.96 (1H, dd, J=17, 10.5 Hz); UV λ_{max}^{EtOH} 248.5 nm; MS m/z (%): 194 (M^+, 16), 86 ([M−C_7H_8O]$^+$, 100), Found: m/z 194.0940. Calcd for $C_{11}H_{14}O_3$: M, 194.0941.

1-(1-Cycloheptenyl)-2-propen-1-one (45). α,β′-Bis(phenylthio) ketone: Colorless oil; IR (neat): 1700 (CO) cm^{-1}; ^1H NMR δ=1.2—2.2 (12H, m), 3.0—3.4 (4H, m), 7.1—7.5 (10H, m); MS m/z (%): 370 (M^+, 5), 262 (44), 205 ([M−C_9H_9OS]$^+$, 100). To a solution of this bis(phenylthio) ketone (66 mg; 0.18 mmol) in 4 ml of CH_2Cl_2 at −70 °C was added *m*-CPBA (0.38 mmol) and stirred for 5 min. The cooling bath was removed and the mixture was stirred at room temperature for 2 h. To the reaction mixture was added ether (5 ml) and 10% NaOH (4 ml) and the whole (two phases) was vigorously stirred under N_2 for 1 d. The usual work-up and purification by silica-gel column chromatography gave **45** (20.6 mg; 77%) as a colorless oil. IR (neat): 1660 (CO), 1635, 1610 (C=C) cm^{-1}; ^1H NMR δ=1.3—2.0 (6H, m), 2.2—2.7 (4H, m), 5.72 (1H, dd, J=10, 2 Hz), 6.23 (1H, dd, J=17, 2 Hz), 6.95 (1H, dd, J=17, 10 Hz), 7.10 (1H, t, J=6 Hz); UV λ_{max}^{EtOH} 255 nm; MS m/z (%): 150 (M^+, 60), 135 (27), 95 (100); Found: m/z 150.1030. Calcd for $C_{10}H_{14}O$: M, 150.1043.

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