

α,β -Epoxy Sulfoxides as Useful Intermediates in Organic Synthesis. X.¹⁾
An Improved Synthesis of α,β -Unsaturated Carbonyl Compounds
from Carbonyl Compounds with Carbon Homologation
through α,β -Epoxy Sulfoxides

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Treatment of the α,β -epoxy sulfoxides derived from ketones and chloromethyl phenyl sulfoxide or 1-chloroalkyl phenyl sulfoxides with lithium perchlorate in the presence of tributylphosphine oxide in toluene at 110 °C for about 1–3 h gave α,β -unsaturated aldehydes or α,β -unsaturated ketones in high yields. In contrast to these results, the α,β -epoxy sulfoxides derived from aldehydes did not give the desired α,β -unsaturated ketones. In this case, a sequential treatment of the α,β -epoxy sulfoxides with benzenethiolate and *m*-chloroperbenzoic acid afforded α -phenylsulfinylated ketones, which were heated in toluene at 110 °C to give the desired enones in good overall yields. The oxidation of the α,β -unsaturated aldehydes obtained by this method gave α,β -unsaturated carboxylic acids in high yields. These procedures afforded a new method for the synthesis of α,β -unsaturated carbonyl compounds, including α,β -unsaturated esters, from carbonyl compounds with carbon homologation.

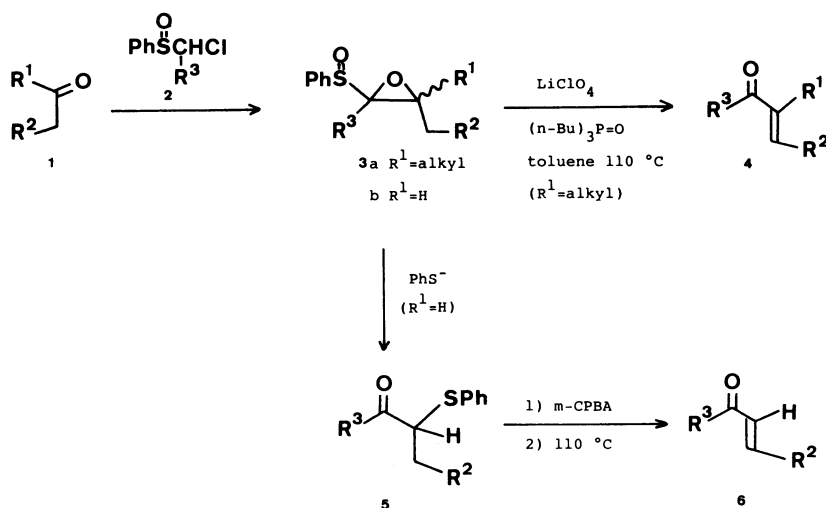
The statement made by Roberts and Caserio²⁾ ("the chemistry of carbonyl compounds is virtually the backbone of synthetic organic chemistry") clearly indicates that carbonyl compounds, including α,β -unsaturated types, are of most importance in synthetic organic chemistry. Especially, α,β -unsaturated carbonyl compounds are quite useful in various synthetic reactions such as the Diels–Alder reaction³⁾ and Michael-type reactions.⁴⁾ Almost an uncountable numbers of methods for the preparation of carbonyl compounds have already been reported; however, as a consequence of the usefulness of carbonyl compounds, the exploration of a new procedure for their syntheses from readily available precursors is always welcome.

Recently, we reported⁵⁾ a new and useful method for the syntheses of various kinds of carbonyl compounds by the homologation of carbonyl compounds through α,β -epoxy sulfoxides (**3**). In the course of our studies

on new synthetic method from carbonyl compounds **1** through α,β -epoxy sulfoxides (**3**)⁶⁾ we report here on a new and simple procedure for the synthesis of α,β -unsaturated ketones and α,β -unsaturated aldehydes from carbonyl compounds **1** with carbon homologation. These procedure are shown in Scheme 1.

Results and Discussion

A Synthesis of α,β -Unsaturated Ketones and α,β -Unsaturated Aldehydes from Ketones through α,β -Epoxy Sulfoxides. Before our first publication in 1984⁷⁾ only two kinds of synthetic methods through α,β -epoxy sulfoxides had been reported: One was a thermal reaction resulting in α,β -unsaturated carbonyl compounds,⁸⁾ and the other was a rearrangement of sulfinyl group with Lewis acids, such as $\text{BF}_3 \cdot \text{Et}_2\text{O}$, giving α -sulfinylated ketones.⁹⁾ These reactions, themselves, are quite interesting; unfortunately, the yields were not satisfactory for the

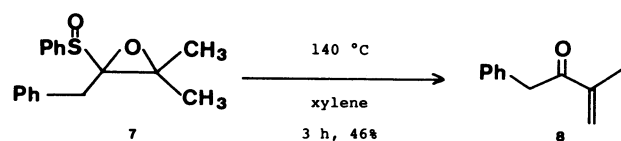


Scheme 1.

practical use in synthetic organic reactions. In fact, in our reexamination, upon heating in xylene at 140 °C for 3 h, the α,β -epoxy sulfoxide (**7**) gave a brown mixture in which the desired enone **8** was obtained in only 46% yield. On the other hand, a treatment of **7** with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CH_2Cl_2 at room temperature for 4 h gave only a complex mixture.

We thought that a treatment of α,β -epoxy sulfoxides **3** with a weak Lewis acid under heating resulted in a sulfinyl group rearrangement followed by a thermal elimination of the rearranged sulfinyl group to afford the desired α,β -unsaturated carbonyl compounds under relatively mild conditions. First of all, we started to find the appropriate weak Lewis acid under heating (a temperature around refluxing benzene) by using the α,β -epoxy sulfoxide **7** as a substrate (Table 1). As shown in Table 1, aluminum, titanium, and magnesium alkoxides were not effective for this reaction; finally, lithium perchlorate in the presence of one equivalent of tributylphosphine oxide¹⁰ was found to be quite effective for the desired reaction. This reaction was rather sluggish in refluxing benzene but in toluene at 110 °C the reaction took place quite smoothly and cleanly to afford the desired enone **8** in 74% yield. These conditions were used throughout this study.

The results of the preparation of α,β -unsaturated carbonyl compounds from ketones via α,β -epoxy sulfoxides upon a treatment with lithium perchlorate in toluene at 110 °C (the temperature of the oil bath used) are summarized in Table 2. The remarkable characteristics of the presented procedure are as



Scheme 2.

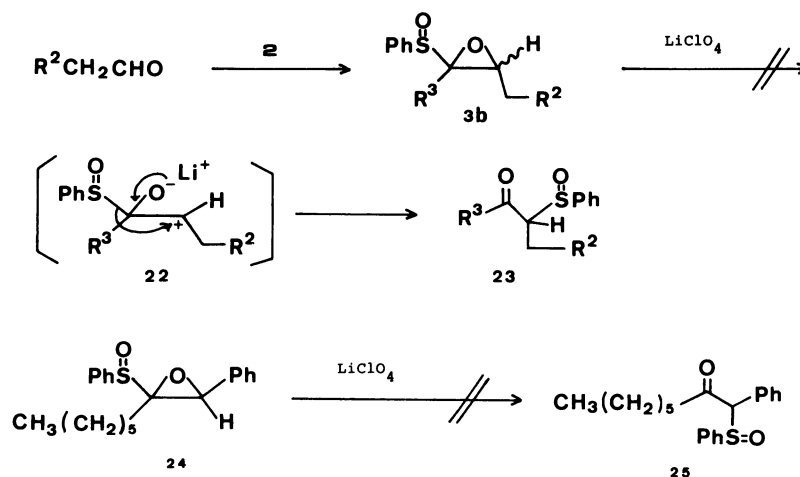
follows: a) The yields are uniformly quite good except the result in Entry 8; b) the conditions were neutral, and the temperature of the reaction was much lower than that previously reported,⁹ and the reaction time was less than 3 h; c) the reaction mixture was quite clean except the result in Entry 8; d) in Entry 8, though some by-products were observed, because of the mildness of the conditions, no double-bond migration giving conjugated divinyl ketone occurred; e) usually, but not always, the reactions giving α,β -unsaturated aldehydes tended to proceed faster than those giving α,β -unsaturated ketones (Entries 10–14).

A Synthesis of α,β -Unsaturated Ketones from Aldehydes through α,β -Epoxy Sulfoxides. In contrast to the good results mentioned above a treatment of the α,β -epoxy sulfoxides **3b**, derived from aldehydes and **2**, with lithium perchlorate under the same conditions used above, did not give any good results. The reaction was very sluggish and prolonged heating resulted in a complex mixture. The reason for this results may be interpreted as being a stability problem involving a secondary carbocation¹⁰ of the inter-

Table 1. Treatment of **7** with Weak Lewis Acid under Heating

Lewis Acid	Temp °C	Time	Enone 8 ^{a)} %
$\text{Al}(\text{OPr}^t)_3$	83 ^{b)}	8 h	20
$\text{Ti}(\text{OPr}^t)_4$	80 ^{c)}	6 d	—
$\text{Mg}(\text{OMe})_2$	80 ^{c)}	3 d	—
$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}^{\text{d)}$	80 ^{c)}	1 d	54
$\text{LiClO}_4 \cdot 3\text{H}_2\text{O}^{\text{d)}$	110 ^{e)}	2 h	74

a) Isolated purified yield after silica-gel column chromatography. b) The reaction was carried out in refluxing 2-propanol. c) The reaction was carried out in refluxing benzene. d) With tributylphosphine oxide. e) The reaction was carried out in toluene. The temperature of the oil bath used.



Scheme 3.

Table 2. Preparation of α,β -Unsaturated Carbonyl Compounds from Ketones through α,β -Epoxy Sulfoxides

Entry	Ketone 1	R ³ in 2	Time	α,β -Unsaturated carbonyl compound	Yield ^{a)} %
1	<chem>CH3COCH3</chem>	<chem>PhCH2</chem>	2 h	8	74
2		<chem>PhCH2</chem>	2.5 h	9	98
3	—	<chem>MeO-C6H4-CH2</chem>	2.5 h	10	87
4	—	<chem>CH3(CH2)5</chem>	2 h	11	89
5	—		50 min	12	83
6		<chem>CH3</chem>	3 h	13	91
7		<chem>CH3</chem>	2.5 h	14	90
8		<chem>CH2=CH-CH2</chem>	2 h	15	64
9	—	<chem>CH3</chem>	50 min	16	95
10	—	<chem>H</chem>	40 min	17	83
11		<chem>H</chem>	30 min	18^{8a)}	97
12	<chem>[CH3(CH2)3]2CO</chem>	<chem>H</chem>	1 h	19	85
13		<chem>H</chem>	50 min	20	98
14		<chem>H</chem>	2 h	21¹¹⁾	88

a) Isolated purified yield after silica-gel column chromatography.

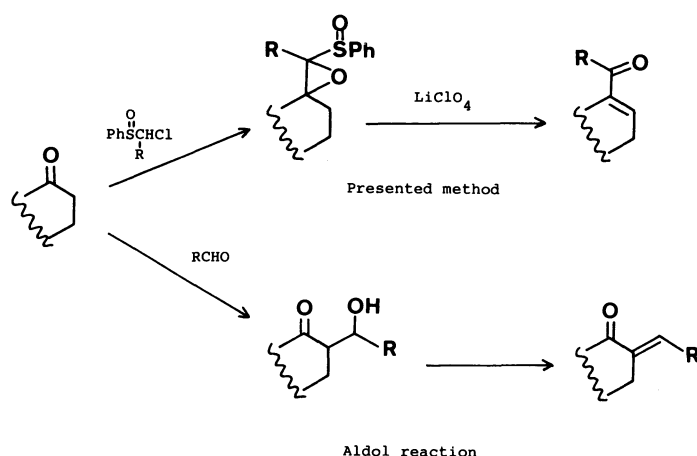
mediate (**22**). In the case of the α,β -epoxy sulfoxides derived from ketones, the cationic intermediate was tertiary, which may proceed to a rearrangement followed by a thermal elimination to afford α,β -unsaturated carbonyl compounds **4**. It is noteworthy that the α,β -epoxy sulfoxide having a phenyl group at the β position **24**, in which the carbocationic intermediate is thought to be stabilized by a phenyl ring, still did not give the rearranged product **25**.

This difficulty regarding the preparation of enones from α,β -epoxy sulfoxides could be overcome by taking another route (shown in Scheme 1). As already reported by us,^{5b)} the treatment of **3b** with benzenethiolate gave α -phenylthio ketones (**5**) in excellent yields. The sequential oxidation of **5** and the elimination of the resultant sulfoxide¹²⁾ must give the desired enone **6**.

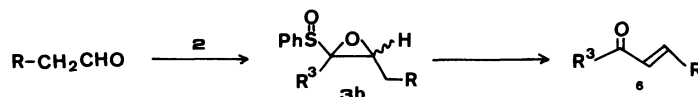
Three example are listed in Table 3. Though two more steps were required, compared to the method described above, the overall yields from α,β -epoxy sulfoxides were equally good.

Here, we should like to describe the interesting characteristic of the presented procedure. As shown in Scheme 4, the famous aldol reaction affords α,β -unsaturated carbonyl compounds from carbonyl compounds with a carbon-chain elongation at the α -position of the carbonyl group. In contrast to this, the presented procedure gives α,β -unsaturated carbonyl compounds with a carbon-chain elongation from the carbonyl carbon itself.

An Application of This Method to a Synthesis of α,β -Unsaturated Esters from Ketones by One-Carbon Homologation. α,β -Unsaturated esters have received considerable attention for a long time in synthetic



Scheme 4.

Table 3. Preparation of α,β -Unsaturated Ketones from Aldehydes through α,β -Epoxy Sulfoxides

Entry	Aldehyde	R ³ in 2	α,β -Unsaturated ketone	Yield ^{a)} %
1	CH ₃ (CH ₂) ₈ CHO	PhCH ₂	26	77
2	PhCH ₂ CH ₂ CHO	CH ₃	27	77
3	CH ₃ (CH ₂) ₄ CHO		28	88

a) Three steps overall yield from the α,β -epoxy sulfoxide. The product was purified by silica-gel column chromatography.

organic chemistry. The Michael-type conjugate addition of various kinds of nucleophiles, especially carbon nucleophiles, to α,β -unsaturated esters is one of the most useful tools for constructing a carbon framework.¹³⁾ Recently, a diastereo- and/or enantio-selective Michael addition of some enolates to α,β -unsaturated esters was also reported.¹⁴⁾ Several methods for the synthesis of saturated esters from ketones by one-carbon homologation have been reported;¹⁵⁾ however, very few methods for the synthesis of α,β -unsaturated ones from ketones by one-carbon homologation have been published.¹⁶⁾

With the new method described above in hand, it was anticipated that the desired α,β -unsaturated ester, such as **31**, could be derived from α,β -unsaturated aldehyde **20** or α,β -unsaturated methyl ketone **13** by two types of oxidations: the oxidation of aldehydes to carboxylic acids¹⁷⁾ or the haloform-type oxidation of methyl ketone **13** to carboxylic acid.¹⁸⁾

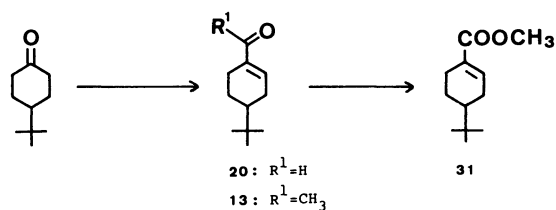
Several method for the oxidation of enals to α,β -unsaturated carboxylic acids have been reported;¹⁷⁾ we used the most recent method reported by Dalcanale

and Montanari^{17c)} with a slight modification. The enal **20** was oxidized with sodium chlorite-hydrogen peroxide in *t*-butyl alcohol followed by methylation with diazomethane to afford the desired α,β -unsaturated ester **31** in 89% yield. Parallel to this reaction, several haloform-type oxidations¹⁸⁾ of the methyl ketone **13** were carried out, but it was found that the reaction were quite sluggish and gave only complex mixtures. Table 4 shows the results of the preparation of α,β -unsaturated esters from various kinds of ketones through the α,β -unsaturated aldehydes.

Beacuse of its overall simplicity and high overall yields, we believe that the presented procedure will prove valuable in the preparation of synthetically useful α,β -unsaturated carbonyl compounds.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were measured directly on a NaCl plate or in KBr disks with a Hitachi 215 spectrometer. ¹H Nuclear magnetic resonance (NMR) spectra were measured in a CDCl₃ solution with a JOEL FX-100 spectrometer using Me₄Si as an internal standard. Ultraviolet (UV) spectra were measured in an EtOH solution 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 (Fujii-Devison) containing 2% fluorescence reagent 254 and quartz column were used for column chromatography and the products having UV absorption were detected by UV irradiation.



Scheme 5.

Table 4. Preparation of α,β -Unsaturated Esters from Ketones through α,β -Epoxy Sulfoxides and α,β -Unsaturated Aldehydes

Entry	Ketone	α,β -Unsaturated aldehyde/% ^{a)}	α,β -Unsaturated ester	Yield ^{b)} %
1		29 (91)		95
2		20		89
3		17		92
4		18		96
5		21		82

a) The isolated yields of the treatment of the α,β -epoxy sulfoxides with lithium perchlorate. b) Isolated purified yields.

α,β -Epoxy Sulfoxides. All α,β -epoxy sulfoxides, except the ones cited below, used in this study were prepared from carbonyl compounds and **2** ($R^3=H$ or alkyl) through chlorohydrins nearly quantitative yields, which were reported previously.⁵⁾ α,β -Epoxy sulfoxides in Table 2; Entry 6: Colorless oil; IR (Neat) 1090, 1055 (SO) cm^{-1} ; ^1H NMR $\delta=0.91$ (9H, s), 1.30 (3H, s), 7.4–7.7 (5H, m); MS m/z (%) 307 ($[\text{M}+\text{H}]^+$, 0.7), 181 ($[\text{M}-\text{PhSO}]^+$, 64), 43 (100). Entry 7: Colorless prisms; mp 155–157 °C (AcOEt–hexane); IR (KBr) 1055 (SO) cm^{-1} ; ^1H NMR $\delta=1.37$ (3H, s), 2.97, 3.35, 3.47, 3.97 (each 1H, d, $J=18$ Hz), 7.21 (4H, bs), 7.40–7.75 (5H, m); Found: C, 71.74; H, 5.68; S, 11.43%. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_2\text{S}$: C, 71.80; H, 5.67; S, 11.25%. Entry 9: Colorless needles; mp 164–165 °C (hexane–MeOH); IR (KBr) 1055 (SO) cm^{-1} ; ^1H NMR $\delta=0.66$ (3H, s), 0.87 (6H, d, $J=7$ Hz), 0.98 (3H, d, $J=7$ Hz), 1.01 (3H, s), 1.28 (3H, s), 7.36–7.72 (5H, m); Found: C, 78.09; H, 10.25; S, 6.12%. Calcd for $\text{C}_{35}\text{H}_{54}\text{O}_2\text{S}$: C, 78.01; H, 10.10; S, 5.95%. Entry 11: Colorless oil; IR (neat) 1085, 1.40 (SO) cm^{-1} ; ^1H NMR $\delta=1.32$ –2.24 (14H, m), 3.68 (1H, s), 7.4–7.7 (5H, m). Entry 12: Colorless oil; IR (neat) 1055 (SO) cm^{-1} ; ^1H NMR $\delta=3.60$ (1H, s), 7.3–7.8 (5H, m). Entry 13: Colorless crystals; mp 91–93 °C (recrystallized from EtOH); IR (KBr) 1050 (SO) cm^{-1} ; ^1H NMR $\delta=0.91$ (9H, s), 3.65 (1H, d, $J=1$ Hz), 7.40–7.70 (5H, m); MS m/z (%): 292 (M^+ , 0.2), 167 ($[\text{M}-\text{PhSO}]^+$, 26), 126 (83), 57 (100); Found: C, 69.77; H, 8.39; S, 10.97%. Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2\text{S}$: C, 69.82; H, 8.27; S, 10.96%. Entry 14: Colorless needles; mp 97–98 °C (recrystallized from benzene–hexane); IR (KBr): 1085, 1045, 1040 (SO) cm^{-1} ; ^1H NMR $\delta=1.10$ –2.32 (22H, m), 3.62 (1H, d, $J=1$ Hz), 7.38–7.76 (5H, m); MS m/z (%): 195 ($[\text{M}-\text{PhSO}]^+$, 26), 126 (100); Found: C, 71.40; H, 9.04; S, 10.14%. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_2\text{S}$: C, 71.21; H, 8.81; S, 10.00%.

α,β -Epoxy sulfoxides in Table 3; Entry 1: Colorless oil; IR (neat) 1090, 1055 (SO) cm^{-1} ; ^1H NMR $\delta=0.98$ (3H, bt, $J=6$ Hz), 3.00, 3.05 (each 1H, d, $J=16$ Hz, benzyl-H), 3.70 (1H, t, $J=6$ Hz), 7.00–7.24, 7.36–7.64 (each 5H, m). Entry 2: Colorless oil; IR (neat) 1085, 1045 (SO) cm^{-1} ; ^1H NMR $\delta=1.23$ (3H, s), 3.61 (1H, t, $J=7$ Hz), 7.04–7.32, 7.38–7.70 (each 5H, m). α,β -Epoxy sulfoxide in Table 4; Entry 1: Colorless oil; IR (neat) 1055 (SO) cm^{-1} ; ^1H NMR $\delta=3.65$ (1H, s), 7.40–7.72 (5H, m); MS m/z (%): 211 ($[\text{M}-\text{PhSO}]^+$, 30), 126 (100).

3-Methyl-1-phenyl-3-buten-2-one (8). A solution of **7** (69 mg; 0.24 mmol) in xylene (3 ml) was heated at reflux for 3 h under N_2 atmosphere. The mixture was diluted with benzene and washed with sat. aq NH_4Cl . The solvent was evaporated and the residue was purified by silica-gel column chromatography (hexane:AcOEt=40:1) to give 18 mg (46%) of **8** as a pale yellow oil. IR (neat) 1670 (CO) cm^{-1} ; ^1H NMR $\delta=1.87$ (3H, m), 3.98 (2H, s), 5.79 (1H, m), 6.04 (1H, m), 7.0–7.4 (5H, m); UV λ_{max} 218 nm; MS m/z (%) 160 (M^+ , 38), 91 ($[\text{M}-\text{C}_4\text{H}_5\text{O}]^+$, 59), 69 ($[\text{M}-\text{PhCH}_2]^+$, 100).

Treatment of 7 with Aluminum Isopropoxide. Aluminum isopropoxide (161 mg; 0.79 mmol) was dissolved in 2 ml of isopropyl alcohol; to this was added a solution of **7** (120 mg; 0.42 mmol) in 1 ml of isopropyl alcohol and the reaction mixture was stirred and refluxed for 8 h. The reaction mixture was diluted with AcOEt and washed with sat. aq NH_4Cl . After the usual workup, the product was purified by silica-gel column chromatography to give

14 mg (20%) of **8** as a pale yellow oil.

General Procedure for the Preparation of α,β -Unsaturated Ketones and α,β -Unsaturated Aldehydes from α,β -Epoxy Sulfoxides. A typical procedure is described for a synthesis of 1-(1-cyclohexenyl)-2-phenylethanone (**9**). To a solution of $\text{LiClO}_4 \cdot 3\text{H}_2\text{O}$ (32 mg; 0.2 mmol) and (*n*-Bu) $_3\text{PO}$ (43.6 mg; 0.2 mmol) in 3 ml of toluene was added a solution of 2'-benzyl-2'-(phenylsulfinyl)spiro[cyclohexane-1,1'-oxirane]^{5a)} (65 mg; 0.2 mmol) in 1 ml of toluene. The mixture was stirred and heated at 110 °C (the temperature of the oil bath used) under a N_2 atmosphere until all the α,β -epoxy sulfoxide was consumed (2.5 h). The solution was cooled to room temperature and diluted with benzene. The whole mixture was washed once with sat. aq NH_4Cl and dried over Na_2SO_4 . The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography (hexane:AcOEt=20:1) to give 39 mg (98%) of **9** as a colorless oil. IR (neat) 1685 (CO), 1640 (C=C) cm^{-1} ; ^1H NMR $\delta=1.60$ (4H, m), 2.23 (4H, m), 3.92 (2H, s), 6.98 (1H, m), 7.0–7.3 (5H, m); UV λ_{max} 233.5 nm; MS m/z (%): 200 (M^+ , 4), 186 ($[\text{M}-\text{CH}_2]^+$, 5), 109 ($[\text{M}-\text{PhCH}_2]^+$, 100).

1-(1-Cyclohexenyl)-2-(4-methoxyphenyl)ethanone (10). Colorless needles (AcOEt–hexane); mp 106–108 °C; IR (KBr): 1675 (CO), 1645, 1625 (C=C) cm^{-1} ; ^1H NMR $\delta=1.60$ (4H, m), 2.22 (4H, m), 3.76 (3H, s), 3.86 (2H, s), 6.98 (1H, m, vinyl-H), 6.7–7.2 (4H, m); UV λ_{max} 228.5 nm; Found: C, 78.44; H, 7.99%. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88%.

1-(1-Cyclohexenyl)-1-heptanone (11). Colorless oil; IR (neat) 1675 (CO), 1645 (C=C) cm^{-1} ; ^1H NMR $\delta=0.88$ (3H, bt, $J=7$ Hz), 2.04–2.36 (4H, m), 2.60 (2H, t, $J=8$ Hz), 6.85 (1H, m, vinyl-H); UV λ_{max} 234 nm; MS m/z (%) 194 (M^+ , 20), 124 ($[\text{M}-\text{C}_6\text{H}_{10}]^+$, 72), 109 ($[\text{M}-\text{C}_6\text{H}_{13}]^+$, 100); Found: m/z 194.1672. Calcd for $\text{C}_{13}\text{H}_{22}\text{O}$: M, 194.1669.

Cyclohexyl 1-Cyclohexenyl Ketone (12). Colorless oil; IR (neat) 1660 (CO), 1635 (C=C) cm^{-1} ; ^1H NMR $\delta=6.83$ (1H, m, vinyl-H), UV λ_{max} 234.5 nm; MS m/z (%) 192 (M^+ , 21), 163 ($[\text{M}-\text{C}_2\text{H}_5]^+$, 3), 109 ($[\text{M}-\text{C}_6\text{H}_{11}]^+$, 100); Found: m/z 192.1524. Calcd for $\text{C}_{13}\text{H}_{20}\text{O}$: M, 192.1513.

1-Acetyl-1-(4-*t*-butyl)cyclohexene (13). Colorless oil; IR (neat) 1675 (CO), 1655 (C=C) cm^{-1} ; ^1H NMR $\delta=0.89$ (9H, s), 2.27 (3H, s), 6.86 (1H, m); UV λ_{max} 233.5 nm; MS m/z (%) 180 (M^+ , 70), 165 ($[\text{M}-\text{CH}_3]^+$, 21), 123 ($[\text{M}-\text{C}_4\text{H}_9]^+$, 61), 43 (100).

2-Acetyl-1H-indene (14). Colorless crystals (Et_2O –hexane); mp 56–58 °C; IR (KBr) 1660 (CO) cm^{-1} ; ^1H NMR $\delta=2.48$ (3H, s), 3.64 (2H, d, $J=2$ Hz), 7.20–7.62 (5H, m); UV λ_{max} 233, 239.5, 301 nm; MS m/z (%) 158 (M^+ , 100), 143 ($[\text{M}-\text{CH}_3]^+$, 37), 115 ($[\text{M}-\text{CH}_3\text{CO}]^+$, 86).

3-(1-Oxo-3-butenyl)cholestene ($\Delta^{2,3}$, $\Delta^{3,4}$ -mixture) (15). Colorless oil; IR (neat) 1680 (CO), 1640 (C=C) cm^{-1} ; ^1H NMR $\delta=3.43$ (2H, m, $\text{CH}_2=\text{CH}-\text{CH}_2\text{CO}-$), 5.03 (1H, m, $\text{CH}_2=\text{CH}-$), 5.17 (1H, m, $\text{CH}_2=\text{CH}-$), 5.75–6.16 (1H, m, $\text{CH}_2=\text{CH}-$), 6.58 (bs, vinyl-H of 4-position), 6.75 (m, vinyl-H of 2-position); From these protons, the ratio of $\Delta^{2,3}$: $\Delta^{3,4}$ could be determined to be 5:6; UV λ_{max} 240 nm; MS m/z (%) 438 (M^+ , 78), 397 ($[\text{M}-\text{C}_3\text{H}_5]^+$, 100); Found: m/z 438.3869. Calcd for $\text{C}_{31}\text{H}_{50}\text{O}$: M, 438.3859.

3-Acetylcholestene ($\Delta^{2,3}$, $\Delta^{3,4}$ -mixture) (16). Colorless solid; IR (neat) 1675 (CO), 1645 (C=C) cm^{-1} ; ^1H NMR $\delta=2.27$, 2.29 (each s, CH_3CO), 6.56 (bs, vinyl-H of 4-position); From these protons the ratio of $\Delta^{2,3}$: $\Delta^{3,4}$ could

be determined to be 4:5; UV $\lambda_{\max}$ 238 nm; MS m/z (%) 412 (M^+ , 100), 397 ($[M-CH_3]^+$, 10), 369 ($[M-CH_3CO]^+$, 7); Found: m/z 412.3685. Calcd for $C_{29}H_{48}O$: M, 412.3702.

3-Formylcholestene ($\Delta^{2,3}$, $\Delta^{3,4}$ -mixture) (17). A mixture of $\Delta^{2,3}$ - and $\Delta^{3,4}$ -enal in a ratio of 2:5. Colorless solid; IR (KBr) 1680 (CO), 1655 (C=C) cm^{-1} ; 1H NMR δ =6.48 (bs, vinyl-H), 6.66 (m, vinyl-H), 9.36, 9.38 (each s, CHO); UV $\lambda_{\max}$ 233.5 nm; MS m/z (%) 398 (M^+ , 100), 383 ($[M-CH_3]^+$, 13), 315 ($[M-C_5H_7O]^+$, 25); Found: m/z 398.3553. Calcd for $C_{28}H_{46}O$: M, 398.3546.

5-Formyl-4-nonene (19). Colorless oil; IR (neat) 2730 (CHO), 1700 (CO), 1650 (C=C) cm^{-1} ; 1H NMR δ =2.00–2.48 (4H, m), 6.41 (1H, t, $J=7$ Hz, vinyl-H), 9.32 (1H, s, CHO); UV $\lambda_{\max}$ 229.5 nm; MS m/z (%) 154 (M^+ , 73), 139 ($[M-CH_3]^+$, 12), 125 ($[M-C_2H_5]^+$, 26), 111 ($[M-C_3H_7]^+$, 100).

4-*t*-Butyl-1-cyclohexene-1-carbaldehyde (20). Colorless oil; IR (neat) 1690 (CO), 1650 (C=C) cm^{-1} ; 1H NMR δ =0.91 (9H, s), 6.78 (1H, m), 9.37 (1H, s); UV $\lambda_{\max}$ 231.5 nm; MS m/z (%) 166 (M^+ , 18), 123 (21), 110 (71), 57 (100).

General Procedure for the Preparation of α,β -Unsaturated Ketones from the α,β -Epoxy Sulfoxides Derived from Aldehydes. A typical procedure is described for the synthesis of 1-phenyl-3-dodecen-2-one (26). To a solution of $NaBH_4$ (946 mg; 2.5 mmol) in 4 ml of EtOH was added diphenyl disulfide (273 mg; 1.25 mmol); the whole mixture was stirred and refluxed under a N_2 atmosphere for 30 min. The mixture was cooled to room temperature and to this was added 100 mg (0.26 mmol) of 2,3-epoxy-1-phenylsulfinyldodecane (the α,β -epoxy sulfoxide in Table 3, Entry 1); the reaction mixture was stirred at room temperature for 30 min. The reaction was quenched by adding sat. aq NH_4Cl and the EtOH was evaporated under vacuum and the residue was extracted with benzene-ether. The combined organic layer was washed once with sat. aq NH_4Cl , dried and concentrated. The residue was separated by silica-gel column chromatography to afford 98 mg (100%) of 1-phenyl-3-phenylthio-2-dodecanone as a colorless oil. IR (neat) 1705 (CO) cm^{-1} ; 1H NMR δ =0.88 (3H, bt, $J=7$ Hz), 3.67 (1H, t, $J=7$ Hz), 3.83, 3.84 (each 1H, d, $J=16$ Hz), 7.0–7.4 (10H, m). This α -phenylthio ketone (98 mg; 0.26 mmol) was dissolved in 4 ml of CH_2Cl_2 and the solution was cooled to $-50^\circ C$. To this was added *m*-CPBA (0.29 mmol) and after being stirred for 10 min, 10% aq NaOH (10 ml) was added. The whole mixture was extracted with CH_2Cl_2 and after the usual workup, the product was purified by silica-gel column chromatography to afford 99.6 mg (99%) of 1-phenyl-3-phenylsulfinyldodecanone as a colorless oil. IR (neat) 1705 (CO), 1045 (SO) cm^{-1} . This sulfoxide (57.7 mg; 0.15 mmol) was dissolved in 3 ml of toluene and the solution was refluxed under N_2 atmosphere for 15 min. The solvent was evaporated under reduced pressure and the residue was purified by silica-gel column chromatography to afford 30 mg (78%) of the desired enone 26 as a colorless oil. IR (neat) 1690, 1670 (CO), 1630 (C=C) cm^{-1} ; 1H NMR δ =0.88 (3H, bt, $J=6$ Hz), 2.00–2.32 (2H, m), 3.79 (2H, s), 6.09 (1H, dt, $J=16$, 1.5 Hz, vinyl-H), 6.88 (1H, dt, $J=16$, 7 Hz, vinyl-H), 7.04–7.40 (5H, m); UV $\lambda_{\max}$ 226.5 nm; MS m/z (%) 258 (M^+ , 6), 188 ($[M-C_5H_{10}]^+$, 6), 167 ($[M-PhCH_2]^+$, 100); Found: m/z 258.1971. Calcd for $C_{18}H_{26}O$: M, 258.1981.

5-Phenyl-3-penten-2-one (27). α -Phenylthio ketone:

Colorless oil; IR (neat) 1705 (CO) cm^{-1} ; 1H NMR δ =1.8–2.2 (2H, m), 2.24 (3H, s), 2.75 (2H, t, $J=7$ Hz), 3.55 (1H, t, $J=7$ Hz), 7.0–7.4 (10H, m); MS m/z (%) 270 (M^+ , 24), 227 ($[M-CH_3CO]^+$, 4), 166 ($[M-C_8H_8]^+$, 42), 117 ($[M-C_8H_9OS]^+$, 100); Found: m/z 270.1090. Calcd for $C_{17}H_{18}OS$: M, 270.1077. α -Phenylsulfinylated ketone: Colorless oil; IR (neat) 1710 (CO), 1085, 1050 (SO) cm^{-1} . The enone 27: Colorless oil; IR (neat) 1670 (CO), 1625 (C=C) cm^{-1} ; 1H NMR δ =2.23 (3H, s), 3.53 (2H, dd, $J=7$, 1.5 Hz), 6.03 (1H, dt, $J=16$, 1.5 Hz), 6.88 (1H, dt, $J=16$, 7 Hz), 7.0–7.4 (5H, m); UV $\lambda_{\max}$ 219 nm; MS m/z (%) 161 ($[M+H]^+$, 97), 126 (28), 117 ($[M-CH_3CO]^+$, 28), 91 ($[M-C_4H_5O]^+$, 100).

1-Cyclohexyl-2-hepten-1-one (28). α -Phenylthio ketone; see Ref. 5b. α -Phenylsulfinylated ketone: Colorless oil; IR (neat) 1700 (CO), 1085, 1050 (SO) cm^{-1} . The enone 28: Colorless oil; IR (neat) 1695, 1670 (CO), 1635 (C=C) cm^{-1} ; 1H NMR δ =0.91 (3H, bt, $J=6.5$ Hz), 2.00–2.32 (2H, m), 2.54 (1H, m), 6.10 (1H, dt, $J=15.5$, 1.5 Hz), 6.82 (1H, dt, $J=15.5$, 7 Hz); UV $\lambda_{\max}$ 228.5 nm; MS m/z (%): 194 (M^+ , 3), 137 ($[M-C_4H_9]^+$, 69), 111 ($[M-C_6H_{11}]^+$, 100); Found: m/z 194.1673. Calcd for $C_{13}H_{22}O$: M, 194.1670.

(Z)-7-Formyl-6-tridecene (29). Colorless oil; IR (neat) 1695 (CO), 1645 (C=C) cm^{-1} ; 1H NMR δ =0.90 (6H, m), 2.00–2.46 (4H, m), 6.40, (1H, t, $J=7.5$ Hz); UV $\lambda_{\max}$ 231.5 nm; MS m/z (%): 210 (M^+ , 37), 167 (25), 155 (41), 141 (51), 113 (96), 43 (100).

General Procedure for the Preparation of α,β -Unsaturated Esters from α,β -Unsaturated Aldehydes. A typical procedure is described for the synthesis of 4-*t*-butyl-1-(methoxycarbonyl)cyclohexene (31). A solution of $NaClO_2$ (85%; 48 mg; 0.45 mmol) in 0.42 ml of H_2O was added dropwise over a period of 2 h to a stirred solution of 20 (49 mg; 0.3 mmol) in *t*-BuOH (0.5 ml), 10 mg of Na_2HPO_4 in 0.12 ml of H_2O and 35 μ l of H_2O_2 (35%). The reaction mixture was vigorously stirred at room temperature for 20 h. The reaction was quenched by adding 6 mg of Na_2SO_3 ; the mixture was acidified with 10% HCl to pH 2 and the whole was extracted with ether. The combined ether layer was dried over Na_2SO_4 and the ether was evaporated. The residue, without further purification, was treated with slight excess CH_2N_2 in ether. The product was purified by silica-gel column chromatography with a mixture of hexane and AcOEt (50:1) as an eluent to give 31 (51 mg; 88%) as a colorless oil; IR (neat) 1720 (CO), 1655 (C=C), 1265 (COC) cm^{-1} ; 1H NMR δ =0.88 (9H, s), 3.70 (3H, s), 6.94 (1H, m); UV $\lambda_{\max}$ 220 nm; MS m/z (%) 196 (M^+ , 31), 181 ($[M-CH_3]^+$, 6), 153 (19), 140 ($[M-C_4H_8]^+$, 100); Found: m/z 196.1455. Calcd for $C_{12}H_{20}O_2$: M, 196.1461.

(Z)-7-Methoxycarbonyl-6-tridecene (30). Colorless oil; IR (neat) 1715 (CO), 1640 (C=C), 1275, 1250 (COC) cm^{-1} ; 1H NMR δ =0.89 (6H, m), 2.0–2.4 (4H, m), 3.71 (3H, s), 6.69 (1H, t, $J=7.5$ Hz); UV $\lambda_{\max}$ 218 nm; MS m/z (%) 240 (M^+ , 34), 209 ($[M-OCH_3]^+$, 9), 197 ($[M-C_3H_7]^+$, 13), 169 ($[M-C_5H_{11}]^+$, 100); Found: m/z 240.2092. Calcd for $C_{15}H_{28}O_2$: M, 240.2088.

The Ester 32. A mixture of $\Delta^{2,3}$ - and $\Delta^{3,4}$ -ester in a ratio of 2:5. Colorless solid; IR (KBr) 1715 (CO), 1675 (C=C), 1265, 1255, 1245 (COC); 1H NMR δ =3.72 (3H, s), 6.68 (bs, vinyl-H), 6.08 (m, vinyl-H); UV $\lambda_{\max}$ 224 nm; MS m/z (%) 428 (M^+ , 100), 413 ($[M-CH_3]^+$, 19), 315 (34); Found: m/z 428.3641. Calcd for $C_{29}H_{48}O_2$: M, 428.3651.

1-(Methoxycarbonyl)cyclooctene (33). Colorless oil; IR

(neat) 1730, 1720 (CO), 1650 (C=C), 1290, 1215 (COC); ^1H NMR δ =3.71 (3H, s), 6.95 (1H, t, J =8.5 Hz); UV λ_{max} 223 nm; MS m/z (%) 168 (M^+ , 73), 153 ($[\text{M}-\text{CH}_3]^+$, 13), 137 (35), 109 (100).

1-(Methoxycarbonyl)cyclododecene (34). Colorless oil; IR (neat) 1720 (CO), 1645 (C=C), 1285, 1220 (COC) cm^{-1} ; ^1H NMR δ =2.04–2.45 (4H, m), 3.72 (3H, s), 6.72 (1H, t, J =8 Hz); UV λ_{max} 220 nm; MS m/z (%) 224 (M^+ , 75), 193 (23), 153 (27), 95 (75), 81 (100).

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