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An Useful Synthetic Method for 3-Substituted δ-Lactones. Synthesis of (±)-Secocrispiolide

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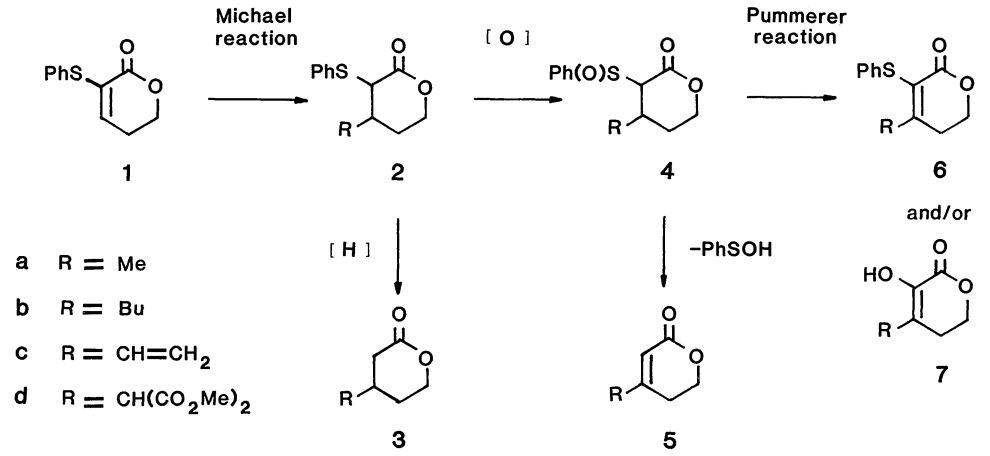
2-Phenylthio-2-penten-5-olide (**1**) acted as a reactive Michael acceptor toward some typical carbon neucleophiles to give 3-substituted 2-phenylthio-5-pentanolides (**2**) which were convertible both to 3-substituted 5-pentanolides by reductive desulfurization and to 3-substituted 2-penten-5-olides by sulfenic acid *syn* elimination of the sulfoxides **4** derived from **2**. The Pummerer rearrangement of **4** provided 3-substituted 2-phenylthio-2-penten-5-olides and/or 2-hydroxy-2-penten-5-olides. (±)-Secocrispiolide was synthesized via the adduct obtained by the Michael reaction of **1** with the Grignard reagent prepared from 2,6-dimethylbenzyl bromide and magnesium.

Lactone function is found as a structural subunit in many classes of natural product.[1] Up to date, considerable attention for the syntheses of natural products having this group has been attracted especially in connection with investigation of their biological activities.[2] Although a variety of efficient methods for construction of γ-lactones have been developed,[3] comparatively a few are general methods for the syntheses of δ-lactones. In the course of our synthetic study on a natural product, we required an efficient preparation of 3-substituted 2-penten-5-olides. However, methodologies for the syntheses of these useful compounds were, to our knowledge, not well defined. We wish to report here a versatile synthetic method for 3-substituted 5-pentanolides and 2-penten-5-olides, starting with 2-phenylthio-2-penten-5-olide (**1**) which acts as a common building block upon this purpose.[4]

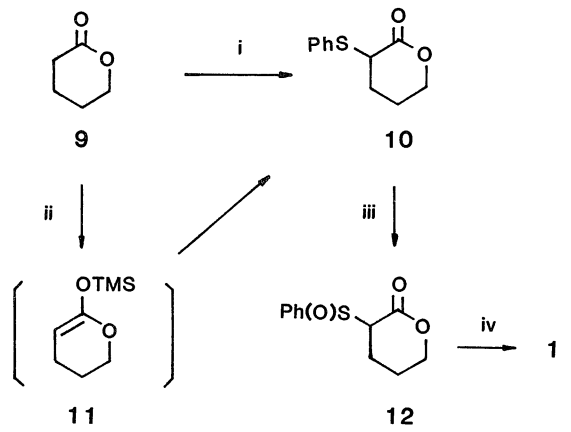
Our contributions to this objective are illustrated in Scheme 1. In contrast to 2-penten-5-olide (**8**), 2-phenylthio-2-penten-5-olide (**1**) was deemed most favorable as a starting material in that the phenylthio group would not only serve as an activator for the Michael reaction,[5] but also subsequently act as a key substituent for introduction of a double bond in the adduct. A series of reactions used in this study is as follows; (i) reactions of **1** with some carbon nucleophiles would proceed exclusively in 1,4 addition fashion to give the required 3-substituted 2-phenylthio-5-pentanolides (**2**) which are convertible to 3-substituted 5-pentanolides (**3**) in reductive cleavage of the phenylthio group, (ii) thermolysis of the sulfoxides **4** derived from **2** provides 3-substituted 2-penten-5-olides (**5**), and (iii) exposure of **4** to the conditions of the Pummerer rearrangement leads to 3-substituted 2-phenylthio-2-penten-5-olides (**6**), which would keep the capacity to act as a reactive Michael acceptor toward 3,3-disubstituted 5-pentanolide synthesis. This strategy has mostly proven to be successful as described below.

Results and Discussion

We started our synthesis with preparation of 2-phenylthio-5-pentanolide (**10**) (Scheme 2). Treatment of freshly distilled δ-valerolactone (**9**) with lithium diisopropylamide (LDA) followed by addition of diphenyl disulfide provided **10** in moderate yield. On this occasion, an attempt to improve the yield of **10** by sulfenylation with *S*-phenyl benzenethiosulfonate[6] was fruitless. Furthermore, sulfenylation of the silyl enol ether **11**, prepared



Scheme 1.



Scheme 2. (i) LDA, THF, HMPA, then Ph_2S_2, −78°C—r.t. (53%): (ii) LDA, Me_3SiCl, THF, then PhSCl, −78°C—r.t. (44%): (iii) *m*CPBA (1.0 equiv), CH_2Cl_2, −15°C: (iv) $(CF_3CO)_2O$, CH_2Cl_2, r.t. (98% from **10**).

Table 1. Yields (%)[a] of 3-Substituted 5-Pentanolides **2**—**4** and 2-Penten-5-olides **5**

Compound	2	3	4	5
a R=Me	91	74	100	72
b R=Bu	80	76	100	79
c R=CH=CH$_2$	82	42	100	73
d R=CH(CO$_2$Me)$_2$	73	56	100	80

a) Isolated yield.

from **9** by treatment with LDA (1 equiv) followed by chlorotrimethylsilane, with benzenesulfenyl chloride provided disappointing 44% yield of **10**. The substrate **10** was converted by oxidation with equimolar *m*-chloroperbenzoic acid (*m*CPBA) to the sulfoxide **12** which on exposure to trifluoroacetic anhydride led to **1** in 52% overall yield from **9**.

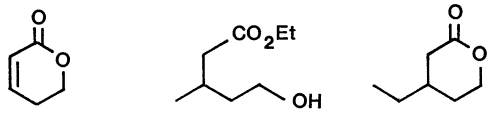
We turned our attention to conjugate addition of **1** with representative carbon nucleophiles. The nucleophiles used in this study were lithium dimethylcuprate (**i**), lithium dibutylcuprate (**ii**), vinylmagnesium bromide–copper(I) iodide 1:1-complex (**iii**), and dimethyl sodiomalonate (**iv**). Reactions of **1** with eqimolar cuprates, **i** and **ii**, proceeded smoothly, to our expectations, to give the 1,4-addition products, 3-substituted 2-phenylthio-5-pentanolides, **2a** and **2b**, in excellent yields (Scheme 1 and Table 1). On the other hand, on reaction with the reagents, **iii** and **iv**, 2.0 equivalent amount of the reagents was required to maximize yields of the adducts, **2c** and **2d**. While the pentanolides obtained were inseparable diastereomeric mixtures, it would be reasonable to estimate that the thermodynamically stable *trans*-isomers are in large quantities, although relatively small vicinal coupling constants (6.4—6.5 Hz, PhS–CH–CH) were observed in their ^{1}H NMR spectra. In order to verify the effect of the phenylthio group used as an activator, the Michael reactions of 2-penten-5-olide (**8**)

Table 2. The Pummerer Rearrangement of Sulfoxides **4**

Run	4	Conditions	Product, yield (%)[a]		
			6	**7**	**5c**
1	**a** R=Me	3d[b]	52	18	—
2	**a** R=Me	1h[c]	14	59	—
3	**b** R=Bu	2d[b]	49	Trace	—
4	**c** R=CH=CH$_2$	3d[b]	10	—	74
5	**d** R=CH(CO$_2$Me)$_2$	1d[b]	—	34	—

a) Isolated yield. b) Room temperature. d; day. c) 0°C, then quenched with aqueous sodium hydrogencarbonate. h; hour.

with the nucleophiles, **ii** and **iii**, were examined for comparison, giving 3-butyl-[7] and 3-vinyl-5-pentanolides, (**3b**) and (**3c**), in such poor yields as 45 and 13%, respectively. After all, it was demonstrated that 2-phenylthio-2-penten-5-olide (**1**) has highly electrophilic reactivity enough to act as a common Michael acceptor.

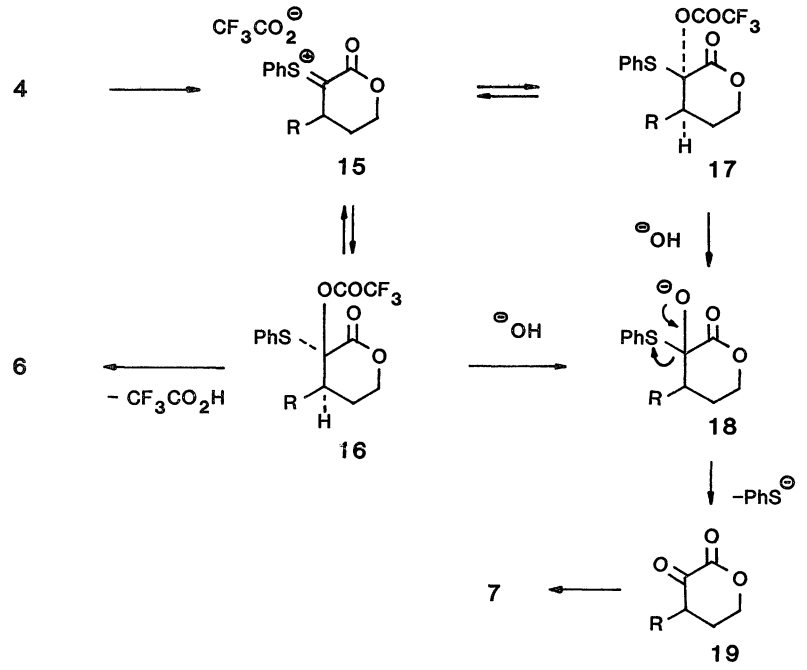


8 13 14

Desulfurization of **2** was next examined (Scheme 1 and Table 1). Reaction of **2b** with W-4 Raney nickel in ethanol proceeded smoothly to give 3-butyl-5-pentanolide (**3b**)[7] in good yield, whereas desulfurization of **2a** and **2c** under the similar reaction conditions produced hydroxy ester **13** and 3-ethyl-5-pentanolide (**14**),[8] respectively, as the result of concomitant ethanolysis for the former and hydrogenation of the vinyl group for the latter. These unexpected results were suppressed as follows. Replacement of ethanol into acetone resulted in good formation of **3a** from **2a**. On the other hand, **3c** was obtained on reduction of **2c** with Raney nickel deactivated with acetone. Finally, **2d** was desulfurized in acetone to afford **3d** in good yield.

Synthesis of 3-substituted 2-penten-5-olides **5a**—**d**[9] was accomplished readily by oxidation of **2a**—**d** with equimolar *m*CPBA followed by refluxing the resulting sulfoxides **4a**—**d** in benzene containing catalytic amount of pyridine, wherein the oxidation and thermal elimination of sulfenic acid proceeded in quantitative and in good yield, respectively, (Scheme 1 and Table 1).

Table 2 details the result obtained by the Pummerer reaction of sulfoxides **4a**—**d**. Contrary to our expectations, the reactions of **4a**—**c** with trifluoroacetic anhydride proceeded considerably slowly to produce unexpected 2-hydroxy-2-penten-5-olides (**7**) as well as the desired 2-phenylthio-2-penten-5-olides (**6**) (Scheme 1), so that this type of reactions showed marked dependence on reaction conditions employed and/or on type of the substituent at C(3) of **4**. Treatment of **4a** with trifluoroacetic anhydride at room temperature afforded a mixture of **6a**[10] and 2-hydroxy-2-penten-5-olide (**7a**),

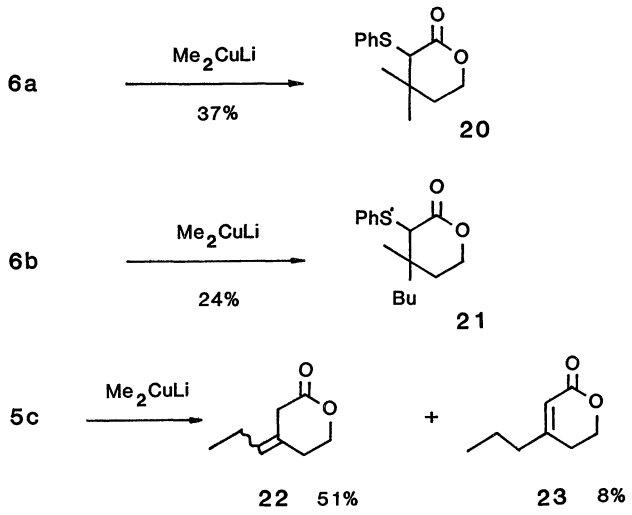


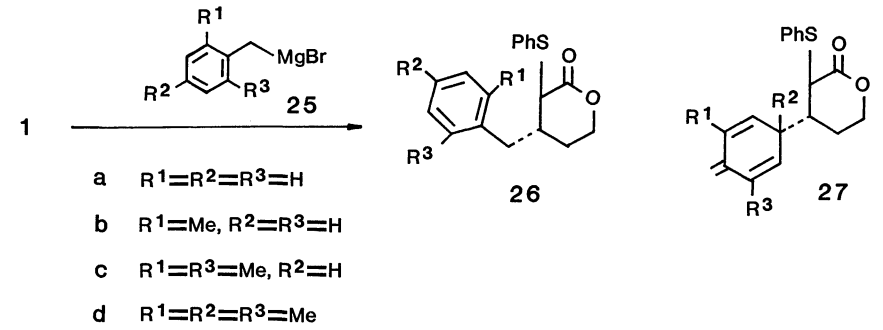
Scheme 3.

in which the former predominated (Run 1). On the contrary, **7a** was obtained predominantly when the reaction was carried out at low temperature, followed by quenching with aqueous sodium hydrogencarbonate (Run 2). Compound **6b** was derived in fair yield from **4b** along with a trace of 2-hydroxy-2-penten-5-olide (**7b**) which was detectable by the TLC analysis (Run 3). On the other hand, the pummerer reaction of **4c** provided low yield of **6c**, and in this case, the major product isolated in 74% yield was unexpected **5c** (Run 4). In the case of **4d**, the only product obtained in low yield was **7d** (Run 5).

The following mechanism would be surmised to account for the formation of **6** and **7** (Scheme 3). Exposure of the sulfoxide **4** to trifluoroacetic anhydride leads to the Pummerer intermediate **15**. On reacting with a trifluoroacetate anion, **15** provides two kinds of trifluoroacetates, **16** with cis relationship between the trifluoroacetoxy group and the substituent (R), and **17** with trans relationship between the two. These trifluroacetates would exist as comparatively stable intermediates in equilibrium. 2-Penten-5-olide **6** is derived only from **16** in trans elimination fashion of trifluoroacetic acid. On the other hand, hydrolysis of **16** and **17** on hydrolytic workup using aqueous sodium hydrogencarbonate leads to the alkoxide **18**, which spontaneously eliminates the phenylthio group to give α-keto lactone **19**. Subsequent tautomerization of **19** affords 2-hydroxy-2-penten-5-olide (**7**). In the case of **4d** which has a bulky bis(methoxycarbonyl)methyl group as a substituent (R), **17d** whose R and trifluoroacetoxy groups are in a trans relationship is formed exclusively to provide **7d** on hydrolytic workup. Formation of **5c** (Table 2, Run 4) would be rationalized by surmising that, because of high acidity of the allylic β-hydrogen in **4c**, *syn* elimination of sulfenic acid readily occurs, before the Pummerer rearrangement initiates.

A parallel study on the conjugate addition to 3-substituted 2-phenylthio-2-penten-5-olides obtained reproduced the important role of the phenylthio group as the activator: Reactions of **6a** and **6b** with lithium dimethylcuprate provided 3,3-disubstituted δ-lactones, **20**, and **21**, respectively, albeit in low yields, whereas 3-methyl- and 3-butyl-2-penten-5-olides, (**5a**) and (**5b**), were recovered unchanged on treatment with this cuprate reagent. It is noteworthy that reaction of 3-vinyl-2-penten-5-olide (**5c**) with lithium dimethylcuprate underwent regioselective conjugate addition to give a mixture of 1,6-addition products, **22** and **23**.





Scheme 4.

Table 3. Conjugate Addition of **1** with Benzylic Grignard Reagents **25**

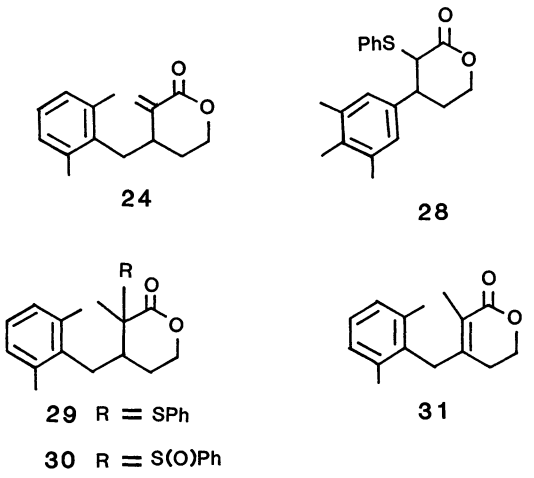
Run		25			Product		Recoverd **1**, (%)[a]
		R^1	R^2	R^3	**26**, yield (%)[a]	**27**, yield (%)[a]	
1	**a**	H	H	H	82	—	16
2	**b**	Me	H	H	62	—	16
3	**c**	Me	H	Me	34	65	—
4	**d**	Me	Me	Me	6[b]	10[b]	75

a) Isolated yield. b) Calculated from the integral ratio in the ^{1}H NMR of the mixture.

In an effort to extend the scope of this methodology, conjugate addition of **1** with a few benzylic Grignard reagents was examined for the purpose of the synthesis of secocrispiolide **24**,[11] a seco-sesquiterpene lactone isolated from *Plicaria crispa* Sch. Bip. The Grignard reagents **25** used in this study and the results thereby obtained are shown in Scheme 4 and Table 3, respectively.

It is known that condensation of the benzylic Grignard reagent with carbon dioxide or some aldehydes occasionally provides an abnormal product resulting from the so-called allylic rearragement of the reagent.[12] While exposure of **1** to benzyl- and 2-methylbenzylmagnesium bromides, (**25a**) and (**25b**), gave diastereomeric mixtures of the normal adducts, **26a** and **26b**, respectively, (Table 3, Run 1, 2), the abnormal adduct **27c** was produced together with the normal **26c** in a ratio of ca. 2:1, when **1** was treated with 2,6-dimethylbenzylmagnesium bromide (**25c**) (Run 3). These results indicated that the steric bulk at the benzyl face would impose the allylic rearrangement on the ortho-disubstituted benzylic Grignard reagents to give the para addition products. **27c** was an unstable oil and, to our surprise, the structure possessing a cross-conjugate methylenecyclohexadiene skeleton was clarified as follows. Two resonances [δ=5.59 (2H, br s) and 2.28 (6H, d, J= 1 Hz)] in the ^{1}H NMR and those [δ=125.1 (d) and 19.9 (q)] in the ^{13}C NMR showed the presence of two trisubstituted double bonds possessing a methyl group. In addition, resonances due to an *exo*-methylene group appeared at δ=5.04 (2H, br s) in the ^{1}H NMR and δ= 107.7 (t) and 128.2 (s) in the ^{13}C NMR. In fact, aromatization of **27c** with catalytic *p*-toluenesulfonic acid readily occured to give a stable compound **28**. An analogous trend was observed on reaction of **1** with 2,4,6-trimethylbenzylmagnesium bromide (**25d**) (Run 4).

The procurement of the synthetic intermediate **26c** prompted us to complete the synthesis of secocrispiolide (**24**). The lithium enolate obtained from treatment of **26c** with LDA was submitted to methylation with methyl iodide in the presence of hexamethylphosphoric triamide (HMPA), providing 2-methyl-δ-lactone (**29**) as an inseparable 3:1 mixture of diastereomers. Oxidation of **29** with equimolar *m*CPBA followed by elimination of sulfenic acid from the resulting sulfoxide **30** afforded (±)-secocrispiolide (**24**) and an *endo*-olefin regioisomer **31** in 23 and 69% yields, respectively. The spectra (IR, ^{1}H NMR and MS) of the synthetic **24** were identical with those of the natural product.[13]



In conclusion, we have developed an useful method for the synthesis of a variety of 3-substituted δ-lactones starting with 2-phenylthio-2-penten-5-olide (**1**), and (±)-secocrispiolide (**24**) was synthesized via the Michael adduct **26c**.

Experimental

Melting points are uncorrected. IR spectra were obtained with a JASCO A-3 infrared spectrophtometer. ^{1}H NMR spectra were recorded on a JEOL FX90Q spectrometer in deuterochloroform with tetramethylsilane as internal standard. High resolution mass spectra were obtained by a JEOL JMS-DX 300 spectrometer. δ-Valerolactone was purchased from Aldrich Chemical Co. Dry tetrahydrofuran (THF) and diethyl ether were obtained by distillation over sodium benzophenone ketyl. Other organic solvents were purified and dried by using standard procedures. All reactions were carried out under N_2 or Ar atmosphere with use of standard procedures for the exclusion of moisture. Column chromatography was performed by using silica gel (Merck, Kieselgel 60, 70—230 mesh). Kieselgel GF_{254} was employed for preparative thin-layer chromatography (TLC) and a mixed solvent (hexane–ether, 1:2) was used for elution, unless otherwise stated. Na_2SO_4 was employed for the drying of extracts.

2-Phenylthio-5-pentanolide (10). (a) To a stirred solution of diisopropylamine (5.133 g, 50.8 mmol) in THF (50 ml) at −78 °C was added dropwise a 1.5 M solution (1 M=1 mol dm^{-3}) of butyllithium in hexane (30.0 ml, 46.91 mmol). The bath was replaced by an ice bath and the mixture was stirred for 10 min, then recooled at −78 °C. A solution of freshly distilled δ-valerolactone (**9**) (1.959 g, 19.5 mmol) in THF (15 ml) was added dropwise and stirring was continued for 30 min. To the reaction mixture, a solution of diphenyl disulfide (8.535 g, 39.1 mmol) in HMPA (40 ml) and THF (50 ml) was added and the temperature was gradually raised to room temperature over 10 h. The reaction was quenched by addition of saturated aqueous ammonium chloride (30 ml) and the phases were separated. The aqueous phase was extracted with ether. The combined organic solutions were washed with 0.1 M HCl and brine, and dried. Evaporation of the solvent left an oil, which was chromatographed on 50 g of silica gel with ether–hexane (1:3) as the eluant to give **10** (2.139 g, 53%) as a colorless oil: IR (film) 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ= 1.6—2.6 [4H, m, $(CH_2)_2$], 3.92 (1H, t, J=6.5 Hz, SCH), 4.4 (2H, m, CH_2O), and 7.2—7.7 (5H, m, Ph).

Found: C, 63.50; H, 5.85%. Calcd for $C_{11}H_{12}O_2S$: C, 63.45; H, 5.81%.

(b) A solution of lithium diisopropylamide in THF was prepared from a 1.5 M solution of buthyllithium in hexane (35.1 ml, 54.9 mmol) and diisopropylamine (6.05 g, 59.9 mmol) in THF (30 ml), and a solution of **9** (5.00 g, 59.9 mmol) in THF (15 ml) was added dropwise with stirring at −78 °C. After being stirred for 40 min, chlorotrimethylsilane (6.51 g, 59.9 mmol) was added. Two hours later, a solution of benzenesulfenyl chloride (10.83 g, 74.9 mmol) in THF (15 ml) was added and the reaction was warmed to room temperature and stirred for 20 h, then quenched with aqueous ammonium chloride. The mixture was extracted with ether and the combined extracts were washed with brine and dried. Evaporation followed by purification of a residue with column chromatography on silica gel using ether–hexane (1:1) as the eluant gave **10** (4.57 g, 44%) and recovered **9** (1.29 g, 26%).

2-Phenylthio-2-penten-5-olide (1). To a stirred solution of **10** (1.614 g, 7.76 mmol) in CH_2Cl_2 (50 ml) at −16 °C, was added dropwise over 30 min a solution of *m*CPBA (80% purity 1.673 g, 7.76 mmol) in CH_2Cl_2 (20 ml). After stirring for 30 min, the reaction mixture was washed with aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine, and dried. Evaporation of the solvent afforded practically pure sulfoxide **12** (1.617 g) as an oil: IR (film) 1720 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.5—2.6 [4H, m, $(CH_2)_2$], 3.6 (1H, t, J=7.5 Hz, SCH), 4.4 (2H, m, CH_2O), and 7.55 (5H, m, Ph). To a solution of **12** in CH_2Cl_2 (10 ml) precooled at −15 °C, trifluoroacetic anhydride (10 ml) was added. The mixture was stirred for 12 h and allowed to warm gradually to room temperature. The mixture was diluted with CH_2Cl_2 and washed with aqueous sodium hydrogencarbonate and brine, and dried. Filtration followed by evaporation left an oil, which was passed through a short silica-gel column with ether to provide **1** (1.644 g, 98%) as an oli: IR (film) 1710 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=2.48 (2H, m, CH_2C=C), 4.41 (2H, t, J=5.4 Hz, CH_2O), 6.25 (1H, t, J=5.5 Hz, C=CH), and 7.40 (5H, m, Ph).

Found: m/z 206.0398. Calcd for $C_{11}H_{10}O_2S$: M, 206.0401.

3-Methyl-2-phenylthio-5-pentanolide (2a). To a stirred mixture of copper(I) iodide (51 mg, 0.27 mmol), dimethyl sulfide (0.5 ml), and ether (3 ml) at −35 °C was added dropwise 1.6 M methyllithium in ether (0.33 ml, 0.53 mmol). After stirring for 50 min at −35 °C, a solution of **1** (50.2 mg, 0.24 mmol) in THF (2 ml) was added, and stirring was continued for an additional 30 min at the range of −35 to −18 °C. The reaction was quenched by addition of aqueous ammonium chloride followed by 25% aqueous ammonia, and the product was extracted with CH_2Cl_2. The combined extracts were washed with brine, and dried. Evaporation of the solvent left an oil which was purified by TLC to give **2a** (49.3 mg, 91%) as a colorless oil: IR (film) 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.25 (3H, d, J=7.2 Hz, Me), 1.4—2.3 (3H, m), 3.41 and 3.85 (1H in total, d, J=6.5 and 6.3 Hz, each, 9:1 ratio by integration, SCH), 4.2—4.5 (2H, m, CH_2O), 7.2—7.6 (5H, m, Ph).

Found: m/z 222.0702. Calcd for $C_{12}H_{14}O_2S$: M, 222.0714.

3-Butyl-2-phenylthio-5-pentanolide (2b). According to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (48.6 mg, 0.26 mmol) with 1.5 M butyllithium in hexane (0.32 ml, 0.51 mmol), followed by addition of **1** (49.8 mg, 0.24 mmol) provided **2b** (51.0 mg, 80%) as a colorless oil: IR (film) 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=0.90 (3H, br t, Me), 1.1—2.3 (9H, m), 3.51 and 3.92 (1H, in total, d, J=6.4 and 5.4 Hz each, 9:1 ratio by integration, SCH), 4.2—4.6 (2H, m, CH_2O), and 7.2—7.6 (5H, m, Ph).

Found: m/z 264.1182. Calcd for $C_{15}H_{20}O_2S$: M, 264.1183.

2-Phenylthio-3-vinyl-5-pentanolide (2c). According to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (388 mg, 2.04 mmol) with 1.09 M vinylmagnesium bromide (1.79 ml, 1.94 mmol) at −55 °C, followed by addition of **1** (200 mg, 0.97 mmol) gave **2c** (185 mg, 82%) as a colorless oil: IR (film) 1730 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.5—2.8 (3H, m), 3.61 and 3.85 (1H in total, d, J=6.4 and 5.0 Hz, 7:1 ratio by integration, SCH), 4.3—4.7 (2H, m, CH_2O), 5.1—5.38 (2H, m, $C\underline{H}_2$=CH), 5.7—6.1 (1H, m, CH_2=$C\underline{H}$), and 7.2—7.6 (5H, m, Ph).

Found: m/z 234.0722. Calcd for $C_{13}H_{14}O_2S$: M, 234.0714.

3-[Bis(methoxycarbonyl)methyl]-2-phenylthio-5-pentanolide (2d). To a stirred suspension of 60% sodium hydride in min-

eral oil (20 mg, 0.49 mmol) in ether (4 ml) was added dimethyl malonate (64.2 μl, 0.53 mmol). After stirring for 25 min, a solution of **1** (50 mg, 0.24 mmol) in THF (2 ml) was added at 0 °C and stirring was continued for an additional 1.5 h at 0 °C. The mixture was poured into aqueous ammonium chloride and extracted with CH_2Cl_2. The combined extracts were washed with brine, and dried. Evaporation of the solvent followed by purification of a residue by TLC afforded **2d** (60 mg, 73%) as a colorless oil: IR (film) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.6—2.2 (3H, m), 2.7 (1H, m), 3.76 and 3.78 (3H, s each, Me), 3.8 (1H, s, SCH), 4.2—4.5 (2H, m, CH_2O), and 7.3—7.6 (5H, m, Ph).

Found: *m/z* 338.0848. Calcd for $C_{16}H_{18}O_6S$: M, 338.0823.

3-Methyl-5-pentanolide (3a). A mixture of **2a** (36 mg), W-4 Raney nickel (500 mg) and acetone (3 ml) was stirred at room temperature for 3.5 h, and filtered through a short celite column. The filtrate was evaporated to leave an oil, whose purification by TLC afforded **3a** (14 mg, 74%) as an oil: IR (film) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.02 (3H, d, *J*=6.0 Hz, Me), 1.1—2.8 (5H, m), and 4.1—4.5 (2H, m, CH_2O).

3-Butyl-5-pentanolide (3b). (a) According to the procedure described for the preparation of **3a**, treatment of **2b** (60 mg) with W-4 Raney nickel (1 g) in ethanol (10 ml) afforded **3b** (26 mg, 76%) as an oil: IR (film) 1740 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.90 (3H, br t, Me), 1.1—2.8 (11H, m), 4.1—4.6 (2H, m, CH_2O).

(b) According to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (94 mg, 0.49 mmol) with 1.5 M butyllithium in hexane (0.62 ml, 0.98 mmol) at −40 °C, followed by addition of **8** (40 mg, 0.41 mmol) afforded **3b** (29 mg, 45%).

3-Vinyl-5-pentanolide (3c). (a) According to the procedure described for the preparation of **3a**, desulfurization of **2c** (47 mg) in acetone (3 ml) with W-4 Raney nickel (500 mg) deactivated with refluxing acetone provided **3c** (11 mg, 42%) as a colorless oil: ^1H NMR ($CDCl_3$) δ=1.2—2.9 (5H, m), 4.1—4.6 (2H, m, CH_2O), 4.9—5.2 (2H, m, $C\underline{H}_2$=CH), and 5.6—6.0 (1H, m, CH_2=C$\underline{H}$).

Found: *m/z* 126.0679. Calcd for $C_7H_{16}O_2$: M, 126.0680.

(b) According to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (117 mg, 0.61 mmol) with 1.09 M vinylmagnesium bromide (0.52 ml, 0.56 mmol) at −50 °C, followed by addition of **8** (51 mg, 0.52 mmol) gave **3c** (9 mg, 17%).

3-[Bis(methoxycarbonyl)methyl]-5-pentanolide (3d). According to the procedure described for the preparation of **3a**, reaction of **2d** (31 mg) with W-4 Raney nickel (500 mg) in acetone (3 ml) gave **3d** (12 mg, 56%) as an oil: ^1H NMR ($CDCl_3$) δ=1.3—2.8 (5H, m), 3.3 (1H, br d, COCHCO), 3.75 and 3.81 (6H in total, s each, Me_2), and 4.2—4.5 (2H, m, CH_2O).

Found: *m/z* 230.0793. Calcd for $C_{10}H_{14}O_6$: M, 230.0790.

Ethyl 5-Hydroxy-3-methylpentanoate (13) and 3-Ethyl-5-pentanolide (14). A mixture of **2a** (42 mg), W-4 Raney nickel (500 mg) and ethanol (5 ml) was stirred for 4 h. Workup according to the procedure described for the preparation of **3a** followed by purification of a residue by TLC gave **13** (23 mg, 75%) as a colorless oil: IR (film) 3300 (OH) and 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.98 (3H, d, *J*=6.0 Hz, CH$\underline{Me}$), 1.28 (3H, t, *J*=7.0 Hz, $CH_2\underline{Me}$), 1.6 (2H, m), 2.0 (1H, m, C$\underline{H}$Me), 2.25 (2H, m, CH_2CO), 3.65 (2H, t, *J*=6.0 Hz, $C\underline{H}_2OH$), and 4.17 (2H, q, *J*=6.0 Hz, $MeC\underline{H}_2$).

By the similar procedure, reaction of **2c** (31 mg) with W-4 Raney nickel (500 mg) in ethanol (5 ml) afforded **14** (14 mg, 86%) as an oil: IR (film) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.1—2.8 (10H, m), 4.1—4.6 (2H, m, CH_2O).

Found: *m/z* 128.0830. Calcd for $C_7H_{12}O_2$: M, 128.0837.

General Procedure for the Preparation of 3-Substituted 2-penten-5-olide (5). To a stirred solution of **2** (0.3 mmol) in CH_2Cl_2 (15 ml) at −10 °C for **2a**, **b**, **d** and at −50 °C for **2c**, was added dropwise over 30 min a solution of *m*CPBA (0.3 mmol) in CH_2Cl_2 (10 ml). After addition was complete, stirring was continued for an additional 10 min at −10 °C for **2a**, **b**, **d** and at −20 °C for **2c**, and the mixture was washed with aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate, and brine, and dried. Evaporation gave practically pure and oily sulfoxide **4** in quantitative yield. To a solution of **4** in benzene (10 ml) was added pyridine (100 μl) and the mixture was gently refluxed for 1.5 h. After cooling, the mixture was diluted with benzene and washed with aqueous sodium hydrogencarbonate, aqueous copper(II) sulfate and brine, and dried. Evaporation of the solvent followed by purification of a residue by TLC afforded **5** as a colorless oil.

3-Methyl-2-phenylsulfinyl-5-pentanolide (4a). ^1H NMR ($CDCl_3$) δ=0.75 and 1.30 (3H in total, both d, *J*=6.8 Hz, 1:9 ratio by integration, Me), 1.2—2.4 (3H, m), 3.38 and 3.85 (1H in total, d, *J*=5.4 and 5.7 Hz each, 9:1 ratio by integration, SOCH), 4.1—4.5 (2H, m, CH_2O), and 7.4—8.0 (5H, m, Ph).

3-Butyl-2-phenylsulfinyl-5-pentanolide (4b). ^1H NMR ($CDCl_3$) δ=0.8—2.6 (12H, m), 3.38 and 3.82 (1H in total, d, *J*=4.3 and 5.4 Hz each, 9:1 ratio by integration, SOCH) 4.2—4.7 (2H, m, CH_2O), and 7.4—8.0 (5H, m, Ph).

2-Phenylsulfinyl-3-vinyl-5-pentanolide (4c). ^1H NMR ($CDCl_3$) δ=1.5—2.8 (3H, m), 3.82 and 4.02 (1H in total, both d, *J*=5.4 Hz, 7:1 ratio by integration, SOCH), 4.4 (2H, m, CH_2O), 5.1—5.3 (2H, m, $C\underline{H}_2$=CH), 5.7—6.2 (1H, m, CH_2=C$\underline{H}$), and 7.3—8.0 (5H, m, Ph).

3-[Bis(methoxycarbonyl)methyl]-2-phenylsulfinyl-5-pentanolide (4d). ^1H NMR ($CDCl_3$) δ=1.6—2.4 (2H, m), 2.84—3.5 (2H, m), 3.6—4.0 (7H, m), 4.3—4.7 (2H, m, CH_2O), and 7.3—8.0 (5H, m, Ph).

3-Methyl-2-penten-5-olide (5a). 72% yield from **2a**; IR (film) 1720 (C=O) and 1645 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.0 (3H, d, *J*=1.6 Hz, Me), 2.40 (2H, t, *J*=5.8 Hz, C=CCH_2), 4.38 (2H, t, *J*=6.1 Hz, CH_2O), and 5.80 (1H, q, *J*=1.6 Hz, C=CH).

Found: *m/z* 112.0519. Calcd for $C_6H_8O_2$: M, 112.0524.

3-Butyl-2-penten-5-olide (5b). 79% yield from **2b**; ^1H NMR ($CDCl_3$) δ=0.95 (3H, br t, Me), 1.1—1.8 (4H, m), 2.1—2.5 (4H, m, C=CCH_2), 4.38 (2H, t, *J*=6.1 Hz, CH_2O), and 5.80 (1H, s with fine splittings, C=CH).

Found: *m/z* 154.1009. Calcd for $C_9H_{14}O_2$: M, 154.0994.

3-Vinyl-2-penten-5-olide (5c). 73% yield from **2c**; IR (film) 1720 (C=O), 1630 (C=C), and 1590 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.58 (2H, t, *J*=6.4 Hz, C=CCH_2), 4.44 (2H, t, *J*=6.4 Hz, CH_2O), 5.58 (1H, d, *J*=10.5 Hz, $C\underline{H}_aH_b$=CH), 5.65 (1H, d, *J*=17.3 Hz, $CH_a\underline{H}_b$=CH), 5.92 (1H, s, C=CHCO), and 6.56 (1H, dd, *J*=17.3, 10.5 Hz, CH_2=C$\underline{H}$).

3-[Bis(methoxycarbonyl)methyl]-2-penten-5-olide (5d). 80% yield from **2d**; IR (film) 1730 (C=O) and 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.63 (2H, t with fine splittings, *J*=5.8 Hz, C=CCH_2), 3.80 (6H, s, Me_2), 4.3—4.5 (3H, m, CH_2O, COCHCO), and 6.0 (1H, s with fine splittings, C=CHCO).

Found: *m/z* 228.0669. Calcd for $C_{10}H_{12}O_6$: M, 228.0633.

General Procedure for the Pummerer Reaction of 4. The sulfoxide **4** was prepared by oxidation of **2** with equimolar *m*CPBA according to the aforementioned procedure. Trifluoroacetic anhydride was added to **4** at −60 °C and the

resulting mixture was stirred, and allowed to warm gradually to room temperature. The reaction mixture was diluted with CH_2Cl_2 and washed with aqueous sodium hydrogencarbonate and brine, and dried. Filtration followed by removal of the solvent left an oil, which was purified by TLC to give **6** and/or **7**.

3-Methyl-2-(phenylthio)-2-penten-5-olide (6a) and 2-Hydroxy-3-methyl-2-penten-5-olide (7a). (a) A solution of **4a** (190 mg) prepared from **2a** (183 mg, 0.82 mmol) and trifluoroacetic anhydride (4 ml) was stirred for 3d to give **6a** (94 mg, 52% from **2a**) and **7a** (19 mg, 18% from **2a**).

6a: an oil; IR (film) 1720 (C=O) and 1605 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=2.28 (3H, s, Me), 2.65 (2H, t, *J*=5.7 Hz, $C=CCH_2$), 4.40 (2H, t, *J*=5.7 Hz, CH_2O), and 7.18 (5H, br s, Ph).

Found: *m/z* 220.0548. Calcd for $C_{12}H_{12}O_2S$: M, 220.0557.

7a: an oil; IR (film) 3350 (OH), 1700 (C=O), and 1580 cm^{-1}; ^1H NMR ($CDCl_3$) δ=1.91 (3H, t, *J*=1.3 Hz, Me), 2.47 (2H, tt, *J*=5.3, 1.3 Hz, $C=CCH_2$), 4.39 (2H, t, *J*=6.3 Hz, CH_2O), and 5.59 (1H, s, OH).

Found: *m/z* 128.0470. Calcd for $C_6H_8O_3$: M, 128.0473.

(b) **4a** (47 mg) prepared from **2a** (42 mg, 0.19 mmol) was treated with trifluoroacetic anhydride (3 ml) and the temperature was gradually raised to 0 °C over 3 h. The reaction mixture was diluted with CH_2Cl_2 and poured into ice-cooled aqueous sodium hydrogencarbonate. Workup gave **6a** (5 mg, 14% from **2a**) and **7a** (14 mg, 59% from **2a**).

3-Butyl-2-phenylthio-2-penten-5-olide (6b). A solution of **4b** (71 mg) prepared from **2b** (63 mg, 0.24 mmol) and trifluoroacetic anhydride (2 ml) was stirred for 2d to give **6b** (31 mg, 49% from **2b**) as an oil: IR (film) 1720 (C=O) and 1600 cm^{-1}; ^1H NMR ($CDCl_3$) δ=0.95 (3H, t, Me), 1.1—1.8 (4H, m), 2.5—2.8 (4H, m, $C=CCH_2\times2$), 4.40 (2H, t, *J*=6.7 Hz, CH_2O), and 7.22 (5H, m, Ph).

Found: *m/z* 262.1036. Calcd for $C_{15}H_{18}O_2S$: M, 262.1027.

2-Phenylthio-3-vinyl-2-penten-5-olide (6c). A solution of **4c** (39 mg) prepared from **2c** (33 mg, 0.14 mmol) and trifluoroacetic anhydride (2 ml) was stirred for 3d to give **6c** (4 mg, 10% from **2c**) and **5c** (13 mg, 74% from **2c**).

6c: a colorless oil; ^1H NMR ($CDCl_3$) δ=2.64 (2H, t, *J*=6.1 Hz, $C=CCH_2$), 4.48 (2H, t, *J*=6.1 Hz, CH_2O), 5.45 (1H, d, *J*=10.4 Hz, $C\underline{H}_aH_b=CH$), 5.52 (1H, d, *J*=18.0 Hz, $CH_aH_b=CH$), and 6.95 (1H, dd, *J*=10.4, 18.0 Hz, $CH_2=C\underline{H}$).

2-Hydroxy-3-[bis(methoxycarbonyl)methyl]-2-penten-5-olide (7d). A solution of **4d** (54 mg) prepared from **2d** (50 mg, 0.15 mmol) and trifluoroacetic anhydride (2 ml) was stirred for 2d to give **7d** (12 mg, 34% from **2d**): IR (film) 3350 (OH) and 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=2.70 (2H, t, *J*=6.4 Hz, $C=CCH_2$), 3.81 (6H, s, Me), 4.47 (2H, t, *J*=6.4 Hz, CH_2O), 4.92 (1H, s, COCHCO), and 6.0 (1H, br, OH).

3,3-Dimethyl-2-phenylthio-5-pentanolide (20). Acoording to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (19 mg, 0.10 mmol) with 1.25 M methyllithium in ether (160 μl, 0.18 mmol) at −13 °C, followed by addition of **6a** (18 mg, 0.08 mmol) gave **20** (6 mg, 32%): ^1H NMR ($CDCl_3$) δ=1.24 (6H, s, Me_2), 1.4—2.1 (4H, m), 3.43 (1H, br s, SCH), 4.4 (2H, m, CH_2O), and 7.2—7.7 (5H, m, Ph).

Found: *m/z* 236.0867. Calcd for $C_{13}H_{16}O_2S$: M, 236.0870.

3-Butyl-3-methyl-2-phenylthio-5-pentanolide (21). Acoording to the procedure for the preparation of **2a**, treatment of copper(I) iodide (16 mg, 0.08 mmol) with 1.22 M methyllithium in ether (0.13 ml, 0.16 mmol) at −25 °C, followed by addition of **6b** (18 mg, 0.07 mmol) gave **21** (5 mg, 24%). ^1H NMR ($CDCl_3$) δ=0.9 (3H, br t, Me), 1.1—2.23 (11H, m), 3.52 (1H, br s, SCH), 4.1—4.6 (2H, m, CH_2O), and 7.2—7.7 (5H, m, Ph).

Found: *m/z* 278.1347. Calcd for $C_{16}H_{22}O_2S$: M, 278.1340.

Reaction of 5c with Lithium Dimethylcuprate. Acoording to the procedure described for the preparation of **2a**, treatment of copper(I) iodide (102 mg, 0.54 mmol) with 1.6 M methyllithium in ether (0.67 ml, 1.07 mmol) at −30 °C, followed by addition of **5c** (61 mg, 0.49 mmol) gave **22** (35 mg, 51%) and **23** (6 mg, 8%).

22: IR (film) 1750 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=0.95 (3H, t, *J*=7.1 Hz, Me), 2.0 and 2.5 (2H, m each, $C\underline{H}_2CH_2O$ and $C=CC\underline{H}_2Me$), 3.3 (2H, m, CH_2CO), 4.2—4.42 (2H, m, CH_2O), and 5.35 (1H, br t, C=CH).

Found: *m/z* 140.0841. Calcd for $C_8H_{12}O_2$: M, 140.0837.

23: IR (film) 1710 (C=O) and 1640 cm^{-1} (C=C); ^1H NMR ($CDCl_3$) δ=0.98 (3H, t, *J*=7.0 Hz, Me), 1.1—2.1 (4H, m), 2.42 (2H, m, $C\underline{H}_2CH_2O$), 4.2—4.5 (2H, m, CH_2O), and 6.0 (1H, s, with fine splittings, C=CH).

Found: *m/z* 140.0829. Calcd for $C_8H_{12}O_2$: M, 140.0837.

General Procedure for the Reaction of 1 with Benzylic Grignard Reagents 25. Benzyl or substituted benzyl bromide (3 equiv) was added to a mixture of finely powdered magnesium (30 equiv) and a catalytic amount of 1,2-dibromoethane in ether. The resulting suspension was stirred at room temperature for 30 min, and then with refluxing for an additional 10 min, and cooled at −12 °C. A solution of **1** (1.0 equiv) in THF (1—2 ml) was added with stirring and stirring was continued for an additional 20—30 min. The reaction was quenched by addition of aqueous ammonium chloride, and the product was extracted with CH_2Cl_2, washed with brine, and dried. Removal of the solvent left an oil which was purified by TLC to give **26** and/or **27**, along with recovered **1** on the reactions with the Grignard reagents **25a**, **b**, **d**.

3-Benzyl-2-phenylthio-5-pentanolide (26a). Reaction of **1** (49 mg, 0.24 mmol) with the Grignard reagent **25a**, prepared from magnesium (175 mg, 7.29 mmol) and benzyl bromide (125 mg, 0.23 mmol) in ether (3 ml), gave **26a** (58 mg, 82%) and **1** (8 mg, 16%). **26a**: a colorless oil; IR (film) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.2—2.8 (3H, m), 3.2 (2H, m, $C\underline{H}_2Ph$), 3.58 and 3.75 (1H in total, d, *J*=5.7 and 3.6 Hz each, 9:1 ratio by integration, SCH), 4.2—4.4 (2H, m, CH_2O), and 7.1—7.6 (10H, m, Ph).

Found: *m/z* 298.1026. Calcd for $C_{18}H_{18}O_2S$: M, 298.1027.

3-(2-Methylbenzyl)-2-phenylthio-5-pentanolide (26b). Reaction of **1** (50 mg, 0.24 mmol) with the Grignard reagent **25b** prepared from magnesium (176 mg, 7.33 mmol) and 2-methylbenzyl bromide (139 mg, 0.73 mmol) in ether (4 ml), provided **26b** (47 mg, 62%) and **1** (8 mg, 16%). **26b**: a colorless oil; IR (film) 1730 cm^{-1} (C=O); ^1H NMR ($CDCl_3$) δ=1.3—2.8 (5H, m), 2.26 (3H, s, Me), 3.57 and 3.80 (1H in total, d, *J*=6.1 and 4.7 Hz each, 9:1 ratio by integration, SCH), 4.1—4.5 (2H, m, CH_2O), and 7.0—7.6 (9H, m, Ph, Ar$\underline{H}$).

Found: *m/z* 312.1193. Calcd for $C_{19}H_{20}O_2S$: M 312.1183.

3-(2,6-Dimethylbenzyl)-2-phenylthio-5-pentanolide (26c) and 3-(3,5-Dimethyl-4-methylene-2,5-cyclohexadienyl)-2-phenylthio-5-pentanolide (27c).[4b] Reaction of **1** (105 mg, 0.51 mmol) with the Grignard reagent **25c**, prepared from magnesium (350 mg, 14.59 mmol) and 2,6-dimethylbenzyl bromide (195 mg, 1.48 mmol) in ether (4 ml), afforded **26c** (58 mg, 34%) and **27c** (108 mg, 65%).

26: Found: *m/z* 326.1339. Calcd for $C_{20}H_{22}O_2S$: M 326.1340.

27: Found: *m/z* 326.1340. Calcd for $C_{20}H_{22}O_2S$: M 326.1340.

3-(2,4,6-Trimethylbenzyl)-2-phenylthio-5-pentanolide (26d) and 3-(1,3,5-Trimethyl-4-methylene-2,5-cyclohexadienyl)-2-phenylthio-5-pentanolide (27d).[4b] Reaction of **1** (50 mg, 0.4 mmol) with the Grignard reagent **25d**, prepared from magnesium (175 mg, 7.29 mmol) and 2,4,6-trimethylbenzyl bromide (155 mg, 0.72 mmol) in ether (3 ml), gave a mixture of **26d** and **27d** (14 mg in total, 6 and 10%, respectively) and recoverd **1** (37 mg, 75%). The yields of **26d** and **27d** were calculated from the integral ratio of the aromatic and aliphatic methyls in **26d** and **27d**, respectively, in the ^{1}H NMR spectrum of the mixture.

2-Phenylthio-3-(2,4,6-trimethylphenyl)-5-pentanolide (28).[4b] A mixture of **27** (40 mg) and a catalytic amount of *p*-toluenesulfonic acid in anhydrous benzene (1 ml) was allowed to stir at room temperature for 10 h. After removal of the solvent, an oily residue was purified by TLC (CH_2Cl_2) to give **28** (39 mg, 98%) as colorless crystals, mp 107—108 °C.

Found: C, 73.58; H, 6.70%. Calcd for $C_{20}H_{22}O_2S$: C, 73.60; H, 6.79%.

3-(2,6-Dimethylbenzyl)-2-methyl-2-phenylthio-5-pentanolide (29). According to the procedure described for the preparation of **10**, lithium diisopropylamide was prepared from diisopropylamine (62 mg, 0.61 mmol) and 1.5 M butyllithium in hexane (0.37 ml, 0.58 mmol) in THF (5 ml). A solution of **26c** (181 mg, 0.54 mmol) in THF (5 ml) was added to the above solution at −70 °C with rapid stirring, and stirring was continued for an additional 30 min. To this mixture, HMPA (1 ml) followed by methyl iodide (91 mg, 0.64 mmol) was added and the temperature was gradually raised to −10 °C over 3.5 h. The reaction was quenched by addition of aqueous ammonium chloride, and the product was extracted with CH_2Cl_2. The combined extracts were washed with brine and dried. Evaporation followed by purification of a residue by TLC gave a mixture of diastereomers **29** (135 mg, 72%) as an oil; IR (film) 1720 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.59 (3H, s, Me), 1.7 (2H, m, C$\underline{H_2}$CH$_2$O), 2.35 (6H, s, Ar$\underline{Me}$), 2.2—3.3 (3H, m, PhC$\underline{H_2}$C$\underline{H}$), 4.2—4.5 (2H, m, CH$_2$O), 7.0 (3H, br s, Ar$\underline{H}$), and 7.2—7.7 (5H, m, Ph).

Found: *m/z* 340.1498. Calcd for $C_{21}H_{24}O_2S$: M 340.1496.

(±)-Secocrispiolide (24) and 3-(2,6-Dimethylbenzyl)-2-methyl-2-penten-5-olide (31). To a stirred solution of **29** (91 mg, 0.27 mmol) in CH_2Cl_2 (10 ml) at −20 °C was added a solution of 80% *m*CPBA (58 mg, 0.27 mmol) in CH_2Cl_2 (8 ml) over 30 min. The mixture was stirred for 30 min, diluted with CH_2Cl_2, and washed with aqueous sodium thiosulfate, aqueous sodium hydrogencarbonate and brine, and dried. Evaporation of the solvent gave the sulfoxide **30** (94 mg, quantitative), which was dissolved in benzene (5 ml). The resulting solution was gently refluxed for 30 min and cooled to room temperature. Removal of the solvent followed by purification of a residue with TLC gave a mixture of (±)-secocrispiolide (**24**) and **31** in 1:3 ratio (57 mg in total). Separation of the mixture by HPLC (Waters Associates, column 25 cm/0.46 (i.d.), silica gel, 9:2 hexane–chloroform) provided pure **24** and **31**. The spectra (IR, ^{1}H NMR and MS) of the synthetic **24** were identical with those of the natural material.[12]

24: a colorless oil; IR ($CHCl_3$) 1730 (C=O) and 1625 cm^{-1} (C=C); ^{1}H NMR ($CDCl_3$) δ=1.9—2.1 (2H, m, C$\underline{H_2}$CH$_2$O), 2.30 (6H, br s, Me$_2$), 2.7—3.1 (3H, m, ArC$\underline{H_2}$C$\underline{H}$), 4.1—4.3 (2H, m, CH$_2$O), 5.38 (1H, br s, C$\underline{H_a}$H$_b$=C), 6.42 (1H, br s, CH$_a\underline{H_b}$=C), and 7.04 (3H, s, ArH).

Found: *m/z* 230.1304. Calcd for $C_{15}H_{18}O_2$: M 230.1306.

31: a colorless oil; IR (film) 1710 cm^{-1} (C=O); ^{1}H NMR ($CDCl_3$) δ=1.8—2.1 (2H, m, C$\underline{H_2}$CH$_2$O), 2.08 (3H, s, C=CMe), 2.25 (6H, s, Ar$\underline{Me}$), 3.50 (2H, br s, PhC$\underline{H_2}$), 4.18 (2H, br t, *J*=5 Hz, CH$_2$O), and 7.05 (3H, br s, Ph).

Found: *m/z* 230.1296. Calcd for $C_{15}H_{18}O_2$: M 230.1306.

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