AN EFFICIENT SYNTHETIC ROUTE TO γ,δ-UNSATURATED SEVEN-MEMBERED LACTONES †

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Abstract- Treatment of the diazomalonates (**9a-d**) of 2-phenylthio-3-butenol derivatives with catalytic rhodium acetate resulted in the [2,3]sigmatropic rearrangement of six-membered allylsulfonium ylides to provide γ,δ-unsaturated seven-membered lactones (**10a-d**) in good yields.

Lactone function is found as a structural unit in many classes of natural products.[1] Considerable attention for the synthesis of natural products possessing this unit has been attracted not only from chemical, but also from biological point of view, leading to development of a variety of general synthetic methods for lactones.[2]

We have been studying the chemistry of the [2,3]sigmatropic rearrangement of cyclic allylsulfonium ylides, and recently reported a highly efficient synthetic route to functionalized five- and six-membered lactones from acyclic diazomalonates having terminal allylic sulfide function (Scheme 1, **1** → **3**).[3] We wish to report herein an efficient synthetic route to seven-membered lactones in connection with our program dealing with use of the rearrangement of cyclic allylsulfonium ylides toward the lactone synthesis.[4]

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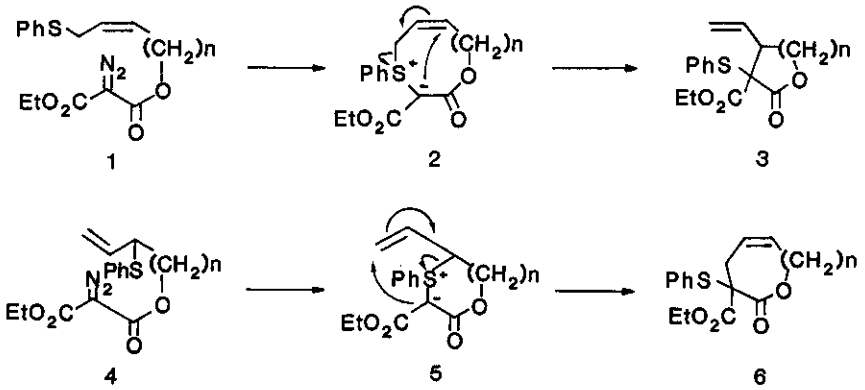
† Dedicated to Professor Masatomo Hamana at the occasion of his 75th birthday.

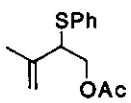


Scheme 1

As seen in Scheme 1, five- (n = 1) and six-membered lactones (**3**, n = 2) are formed <u>via</u> eight- and nine-membered cyclic allylsulfonium ylides (**2**) in the transition state, respectively. To prepare seven or more larger sized lactones by use of this methodology, larger cyclic intermediates than nine-membered cyclic ylide are required, so that the reaction would be governed not only by reaction conditions wherein high dilution conditions are necessary for intramolecular reaction, but also by conformation of the cyclic sulfonium ylides generated.

Thus, we designed the reaction of diazomalonates (**4**), isomeric to **1** in the allyl sulfide function, wherein diazomalonates (**4**, n = 1) of 2-phenylthio-3-butenol derivatives provide the desired seven-membered γ,δ-unsaturated lactones (**6**) through a six-membered sulfonium ylide intermediate (**5**). This synthetic plan may be utilizable for the preparation of medium ring-sized lactones such as eight-membered ones.

The starting materials, 2-phenylthio-3-butenol derivatives, employed in this study are shown in Table 1. Acyclic alcohols (**7a**) and (**7b**) were readily prepared from the known homoallyl acetate (**11**)[5] and vinyl ester



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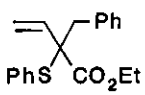

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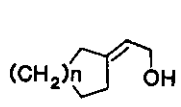
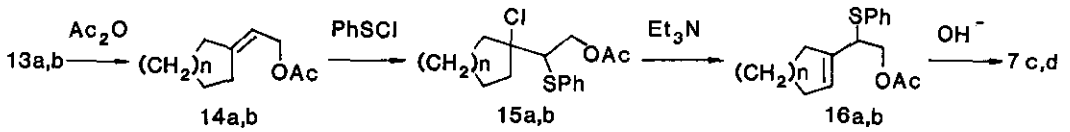


13a, n=2
13b, n=1

(12)[6] by alkaline hydrolysis for the former and by lithium aluminium hydride reduction for the latter, respectively. On the other hand, 2-(1-cycloalkenyl)-2-phenylthioethanol (**7c**) and (**7d**) were derived from the known 2-cycloalkylideneethanols (**13a**)[7] and (**13b**)[7] in 53 and 49% overall yields, respectively, as shown in Scheme 2: Acetylation of **13a** followed by regioselective addition of benzenesulfenyl chloride[5,8] to the resultant acetate (**14a**) gave chloro sulfide (**15a**) in high yield. Dehydrochlorination of crude **15a** with triethylamine in dimethylformamide proceeded regioselectively to furnish cyclohexenyl acetate (**16a**) in a high yield. Subsequent hydrolysis of the latter with K_2CO_3 in methanol provided the desired alcohol (**7c**). Similarly, alcohol (**7d**) was prepared from **13b**.

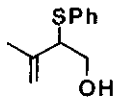
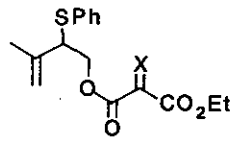
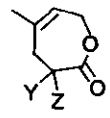
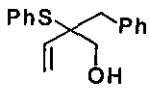
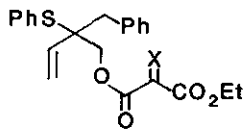
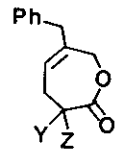
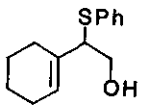
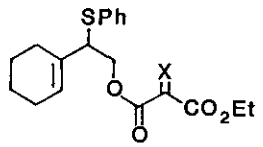
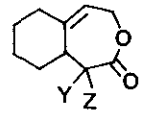
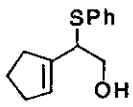
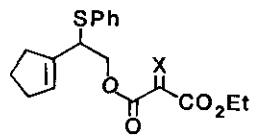
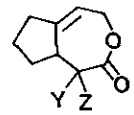
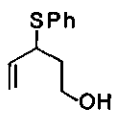
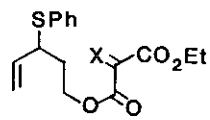
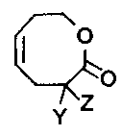


Scheme 2

The alcohols (**7a-d**) were subjected to esterification with malonic acid monoethyl ester in CH_2Cl_2, wherein additives of dicyclohexylcarbodiimide as the condensing agent and 4-dimethylaminopyridine promoted the reactions to produce malonates (**8a-d**) in high to excellent yields (Table 1). Finally, the requisite diazomalonates (**9a-d**) were prepared from **8a-d** by diazotization with tosyl azide in acetonitrile containing triethylamine in almost quantitative yields.

Construction of the seven-membered lactone ring from **9a-d** was carried out under our standard reaction conditions. Diazomalonates (**9a-d**) were gently refluxed with a catalytic amount of rhodium acetate (0.02 mol% of the substrate) in benzene to give γ,δ-unsaturated seven-membered lactones (**10a-d**) in good to high yields (entries 1-4) via the [2,3]sigmatropic rearrangement of six-membered cyclic sulfonium intermediates (5, n = 1 in Scheme 1). The lactones (**10c**) and (**10d**) were single epimers from ^1H nmr and tlc analyses though their stereostructures could not be assigned.

Table 1. Alcohols (7a-e), Malonates (8a-e and 9a-e), and Lactones (10a-e).

entry	alcohol	yield (%) malonates	lactone
1			
	7a	**8a**, X=H_2 (76) **9a**, X=N_2 (quant)	**10a** (53)
2			
	7b	**8b**, X=H_2 (95) **9b**, X=N_2 (quant)	**10b** (49)
3			
	7c	**8c**, X=H_2 (88) **9c**, X=N_2 (quant)	**10c** (64)
4			
	7d	**8d**, X=H_2 (89) **9d**, X=N_2 (quant)	**10d** (81)
5			
	7e	**8e**, X=H_2 (90) **9e**, X=N_2 (quant)	**10e** (19)

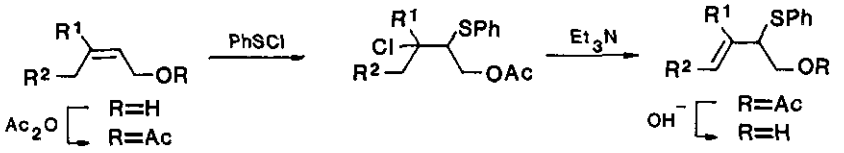
Y,Z = SPh, CO_2Et

This synthetic approach was then extended to the preparation of eight-membered lactones. The starting material, 3-phenylthio-4-pentenol (**7e**), was obtained by a reaction of the lithium salt of allyl phenyl sulfide and ethylene oxide. Transformation of **7e** to the diazomalonate (**9e**) was accomplished according to the procedures employed for preparation of **9a-d** via malonate (**8e**). Diazomalonate (**9e**) was then subjected to our rearrangement

reaction, giving the expected unsaturated lactone (**10e**) albeit in low yield (entry 5).

The main features of this methodology are as follows:

(1) The starting acyclic and cyclic homoallyl alcohols having a phenylthio group can be obtained generally from allyl alcohols through a four-step sequence, as shown below.



(2) Seven-membered lactone formation occurs smoothly only on refluxing the diazomalonates with catalytic rhodium acetate in benzene.

(3) In view of the fact that a Baeyer-Villiger oxidation of cyclohexanones is now the most widely employed method for the preparation of seven-membered lactones, our synthetic route may be useful because of its simplicity, reliability, and applicability.

EXPERIMENTAL

^{1}H nmr spectra were recorded at 90 MHz. All reactions were carried out under dry N_2 or Ar atmosphere. Extracts obtained by aqueous workup of the reaction mixtures were washed successively with water and brine and dried over $MgSO_4$, unless otherwise stated. Column chromatography was performed on 70-230 mesh silica gel (Merck). Solvents for elution are shown in parentheses.

3-Methyl-2-phenylthio-3-butenol (**7a**). A mixture of 4-acetoxy-2-methyl-3-phenylthio-1-butene (**11**)[5] (804 mg, 3.4 mmol), K_2CO_3 (2.35 g, 17 mmol), and methanol (15 ml) was stirred at room temperature for 1.5 h, and diluted with water. Extraction with CH_2Cl_2 followed by concentration left an oily residue, which was chromatographed on silica gel (hexane-AcOEt, 2:1) to give **7a** (529 mg, 80%) as an oil: ir($CHCl_3$) 3500, 3080, 1645, 1590, 1025, 905 cm^{-1}; ^{1}H nmr($CDCl_3$) 1.87 (s, 3 H, =C-CH_3), 2.1 (br s, 1 H, OH), 3.5-3.8 (m, 3 H in total, S-CH and O-CH_2), 4.80 and 4.93 (s, 1 H each, =CH_2),

7.30 (br m, 5 H, Ph). Anal. Calcd for $C_{11}H_{14}OS$: C, 67.99; H, 7.20; S, 16.50. Found: C, 68.28; H, 7.28; S, 16.78.

2-Benzyl-2-phenylthio-3-butenol (7b). To a stirred suspension of lithium aluminium hydride (152 mg, 4.0 mmol) in ether (8 ml) was added dropwise at 0 °C a solution of ethyl 2-benzyl-2-phenylthio-3-butenoate (**12**)[6] (840 mg, 2.69 mmol) in ether (5 ml), and stirring was continued at 0 °C for 15 min, then at room temperature for 1 h. The reaction mixture was quenched by addition of wet ether followed by a little amount of water, and filtered. The solid was washed with ether, and the combined filtrate and washing were dried. Evaporation followed by purification of an oily residue by chromatography on silica gel (hexane-AcOEt, 9:1) gave **7b** (651 mg, 90%) as an oil: ir($CHCl_3$) 3500, 3080, 1640, 1610, 1580, 1050, 910 cm^{-1}; ^1H nmr($CDCl_3$) 2.38 (br t, J=5.0 Hz, 1H, OH), 2.98 and 3.10 (d, J=14 Hz each, 2 H in total, $PhCH_2$), 3.45 and 3.51 (d, J=13 Hz each, 2 H in total, CH_2-OH), 4.52 (d, J=18.0 Hz, 1 H, CH=CHH), 5.03 (d, J=10.8 Hz, 1 H, CH=CHH), 5.95 (dd, J=18.0. 10.8 Hz, 1 H, $CH=CH_2$), 7.3-7.6 (m, 10 H, 2 Ph). Anal. Calcd for $C_{17}H_{18}OS$: C, 75.51; H, 6.71; S, 11.86. Found: C, 75.73; H, 6.92; S, 11.75.

2-(1-Cyclohexenyl)-2-phenylthioethanol (7c). According to the standard procedure, cyclohexylideneethanol (**13a**)[7] (1.55 g, 12.26 mmol) was acetylated with acetic anhydride (3.75 g, 36.76 mmol) and 4-dimethylaminopyridine (1.65 g, 13.48 mmol) in CH_2Cl_2 (20 ml) to give acetate (**14a**) (1.92 g, 93%) as an oil.

To a stirred solution of **14a** (1.89 g, 11.22 mmol) in CH_2Cl_2 (30 ml) was added dropwise at -20 °C a solution of benzenesulfenyl chloride[5] (1.62 g, 11.22 mmol). After brief stirring for 15 min, the solvent was removed under reduced pressure to give crude chloro sulfide (**15a**) (3.20 g) as an oil: ^1H nmr($CDCl_3$) 1.3-2.4 (m, 10 H), 1.89 (s, 3 H, $COCH_3$), 3.49 (dd, J=7.2, 5.4 Hz, 1 H, S-CH), 4.43 (dd, J=10.8, 7.2 Hz, 1 H, O-CHH), 4.78 (dd, J=10.8, 5.4 Hz, 1 H, O-CHH), 7.2-7.6 (m, 5 H, Ph). The oil was used for

the next reaction without purification.

A solution of **15a** obtained above and triethylamine (3.29 g, 33.65 mmol) in dimethylformamide (30 ml) was heated at 70 °C for 1 d and cooled to room temperature. Water was added and the product was extracted with CH_2Cl_2. The combined extracts were washed successively with 1 M HCl, water, and brine, and dried. Evaporation followed by chromatography of an oily residue on silica gel gave homoallyl acetate (**16a**) (1.85 g, 60%) as an oil: ir(film) 1740, 1210, 1010 cm^{-1}; ^1H nmr($CDCl_3$) 1.1-2.1 (m, 8 H), 2.01 (s, 3 H, $COCH_3$), 3.90 (t, J=6.8 Hz, S-CH), 4.28 (m, 2 H, O-CH_2), 5.47 (br s, 1 H, =CH), 7.2-7.5 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_2S$: C, 69.25; H, 7.29; S, 11.60. Found: C, 69.47; H, 7.66; S, 11.14.

A mixture of **16a** (1.08 g, 3.89 mmol) and K_2CO_3 (2.69 g, 19.5 mmol) in methanol (15 ml) was stirred at room temperature for 1.5 h. Workup gave an oil which was purified by chromatography on silica gel (hexane-AcOEt, 7:1) to give **7c** (858 mg, 94%) as an oil: ir(film) 3500, 1590, 1040, 1010 cm^{-1}; ^1H nmr($CDCl_3$) 1.2-2.4 (m, 9 H), 3.6-3.8 (m, 3H, O-CH_2, S-CH), 5.53 (br s, 1 H, =CH), 7.2-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{14}H_{18}OS$: C, 71.75; H, 7.74; S, 13.68. Found: C, 71.75; H, 7.40; S, 13.34.

2-(1-Cyclopentenyl)-2-phenylthioethanol (7d). The alcohol (**7d**) was prepared according to the procedures for preparation of **7c**. Allyl acetate (**14b**) (3.25 g, 21 mmol), obtained from acetylation of 2-cyclopentylideneethanol (**13b**)[7], was reacted with benzenesulfenyl chloride (3.05 g, 21 mmol) in CH_2Cl_2 (50 ml) to give chloro sulfide (**15b**) (6.3 g); ^1H nmr($CDCl_3$) 1.4-2.4 (m, 8 H), 1.95 (s, 3 H, $COCH_3$), 3.50 (t, J=7.3 Hz, 1 H, S-CH), 4.2-4.8 (m, 2 H, O-CH_2), 7.2-7.6 (m, 5 H, Ph).

Treatment of **15b** obtained above with triethylamine (6.37 g) in dimethylformamide (60 ml) afforded **16b** (3.3 g, 60%) as an oil: ir(film) 1740, 1220, 1020 cm^{-1}; ^1H nmr($CDCl_3$) 1.5-2.5 (m, 6 H), 2.08 (s, 3 H, $COCH_3$), 3.0-3.4 (m, 3 H, O-CH_2, S-CH), 5.50 (br s, 1 H, =CH), 7.2-7.5 (m, 5 H, Ph). Anal. Calcd for $C_{15}H_{18}O_2S$: C, 68.66; H, 6.91; S, 12.22. Found: C, 68.42; H,

7.18; S, 11.77.

Hydrolysis of **16b** (1.40 g, 5.34 mmol) with K_2CO_3 (3.69 g, 26.7 mmol) in methanol (20 ml) provided **7d** (1.05 g, 89%) as an oil: ir(film) 3500, 1595, 1050, 1010 cm^{-1}; ^1H nmr($CDCl_3$) 1.6-2.6 (m, 7 H), 3.6-4.0 (m, 3 H, O-CH_2, S-CH), 5.52 (br s, 1 H, =CH), 7.2-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{13}H_{16}OS$: C, 70.86; H, 7.32; S, 14.55. Found: C, 70.96; H, 7.61; S, 14.95.

3-Phenylthio-4-pentenol (7e). To a stirred solution of allyl phenyl sulfide (2.39 g, 15.93 mmol) and HMPA (6.85 g, 19.12 mmol) in THF (40 ml) was added dropwise at -78 °C a solution of 1.49 M BuLi in hexane (12.8 ml, 19.12 mmol), and stirring was continued for an additional 1 h. To this solution was added at -78 °C ethylene oxide (3.2 ml, 64 mmol) precooled at 0 °C. After brief stirring for 1 h, the reaction was quenched by addition of aqueous NH_4Cl followed by water, and the product was extracted with CH_2Cl_2. Evaporation followed by chromatography of an oily residue on silica gel (hexane-AcOEt, 3:1) gave **7e** (1.79 g, 58%) as an oil: ^1H nmr($CDCl_3$) 1.6-2.2 (m, 2 H), 3.6-4.0 (m, 3 H, S-CH, O-CH_2), 4.8-5.0 (m, 2 H, CH=C$\underline{H}_2$), 5.6-6.0 (m, 1 H, C$\underline{H}$=CH_2), 7.2-7.5 (m, 5 H, Ph).

Ethyl 3-methyl-2-phenylthio-3-butenyl malonate (8a) (Representative procedure). To a stirred solution of ethyl hydrogen malonate (727 mg, 5.50 mmol) in CH_2Cl_2 (6 ml) was added at 0 °C a solution of **7a** (356 mg, 1.83 mmol) and 4-dimethylaminopyridine (23 mg, 0.18 mmol) in CH_2Cl_2 (6 ml), followed by a solution of dicyclohexylcarbodiimide (944 mg, 4.57 mmol) in CH_2Cl_2 (6 ml). After brief stirring for 30 min, an ice bath was removed and stirring was continued for an additional 2 h at room temperature. The reaction mixture was diluted with ether and the precipitate was filtered. The filtrate was washed successively with 1 M HCl, aqueous $NaHCO_3$, water and brine, and dried. Removal of the solvent left an oil which was chromatographed on silica gel (hexane-AcOEt, 4:1) to give **8a** (412 mg, 76%) as an oil: ir(film) 1755, 1735 cm^{-1}; ^1H nmr($CDCl_3$) 1.28 (t, $\underline{J}$=7.2 Hz, 3 H, C$\underline{H}_3$$CH_2$), 1.86 (s, 3 H, =C-$CH_3$), 3.34 (s, 2 H, $COCH_2CO$), 3.90 (t, $\underline{J}$=7 Hz, S-

CH), 4.0-4.4 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 4.47 and 4.90 (s with fine splittings, 1 H each, $=CH_2$), 7.2-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.53; S, 10.49. Found: C, 62.06; H, 6.75; S, 10.28.

Ethyl 2-benzyl-2-phenylthio-3-butenyl malonate (8b). An oil; 95% yield from **7b**; ir(film) 1750, 1725 cm^{-1}; ^1H nmr($CDCl_3$) 1.32 (t, $\underline{J}$=7.0 Hz, 3 H, $C\underline{H}_3CH_2$), 3.18 (s, 2 H, $PhC\underline{H}_2$), 3.48 (s, 2 H, $COCH_2CO$), 4.03 and 4.18 (d, $\underline{J}$= 11 Hz each, 2 H in total, O-CH_2), 4.30 (q, $\underline{J}$=7.0 Hz, 2 H, $CH_3C\underline{H}_2$), 4.55 (d, $\underline{J}$=17.0 Hz, 1 H, CH=C$\underline{H}$H), 5.00 (d, $\underline{J}$=10.8 Hz, 1 H, CH=CH$\underline{H}$), 5.83 (dd, $\underline{J}$=17.0, 10.8 Hz, C$\underline{H}$=CH_2), 7.2-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.53; S, 10.39. Found: C, 62.06; H, 6.75; S, 10.28.

Ethyl 2-(1-cyclohexenyl)-2-phenylthioethyl malonate (8c). An oil; 88% yield from **7c**; ir(film) 1750, 1730 cm^{-1}; ^1H nmr($CDCl_3$) 1.28 (t, $\underline{J}$=7.0 Hz, 3 H, $C\underline{H}_3CH_2$), 1.4-2.2 (m, 8 H), 3.32 (s, 2 H, $COCH_2CO$), 3.78 (br t, $\underline{J}$=7 Hz, 1 H, S-CH), 4.1-4.4 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 5.44 (br s, 1 H, =CH), 7.2-7.5 (m, 5 H, Ph). Anal. Calcd for $C_{19}H_{24}O_4S$: C, 65.49; H, 6.94; S, 9.20. Found: C, 65.16; H, 7.17; S, 8.89.

Ethyl 2-(1-cyclopentenyl)-2-phenylthioethyl malonate (8d). An oil; 89% yield from **7d**; ir(film) 1750, 1735 cm^{-1}; ^1H nmr($CDCl_3$) 1.29 (t, $\underline{J}$=7.0 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.6 (m, 6 H), 3.33 (s, 2 H, $COCH_2CO$), 4.0-4.4 (m, 5 H, $CH_3C\underline{H}_2$, O-SH, O-CH_2), 5.48(br s, 1 H, =CH), 7.2-7.5 (m, 5 H, Ph). Anal. Calcd for $C_{18}H_{22}O_4S$; C, 64.64; H, 6.63; S, 9.59. Found: C, 64.41; H, 6.78; S, 9.45.

Ethyl 3-phenylthio-4-pentenyl malonate (8e). An oil; 90% yield from **7e**; ir(film) 1750, 1730 cm^{-1}; ^1H nmr($CDCl_3$) 1.30 (t, $\underline{J}$=7.0 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.0 (m, 2 H), 3.38 (s, 2 H, $COCH_2CO$), 3.75 (m, 1 H, S-CH), 4.1-4.4 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 4.8-5.1 (m, 2 H, CH=C$\underline{H}_2$), 5.5-6.0 (m, 1 H, C$\underline{H}$=CH_2), 7.2-7.5 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{20}O_4S$: C, 62.31; H, 6.54; S, 10.39. Found: C, 62.03; H, 6.26; S, 9.98.

Diazotization of malonates (8a-e) with tosyl azide (General procedure). A

solution of the malonate (1.0 mmol) in acetonitrile (4 ml) was added to a solution of tosyl azide (1.1 mmol) and triethylamine (4.0 mmol) in acetonitrile (4 ml), and the resulting solution was warmed at 45 °C for 1-2 d with stirring. After the reaction completed, ether was added and the solution was washed successively with 10% K_2CO_3, water and brine, and dried. Evaporation of the solvent left an oil which was purified by filtration through a short silica gel column (hexane-AcOEt, 4:1) to give the oily diazomalonate in almost quantitative yield.

9a. ir(film) 2150, 1750 cm^{-1}; ^1H nmr($CDCl_3$) 1.30 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 1.80 (s, 3 H, =C-CH_3), 3.88 (t, J=7 Hz, 1 H, S-CH), 4.1-4.5 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2) 4.75 and 4.83 (s, 1 H each, =CH_2), 7.2-7.5 (m, 5 H, Ph).

9b. ir(film) 2150, 1750, 1680 cm^{-1}; ^1H nmr($CDCl_3$) 1.35 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 3.10 (s, 2 H, Ph$C\underline{H}_2$), 4.1-4.2 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 4.58 (d, J=18.0 Hz, 1 H, CH=C$\underline{H}$H), 5.02 (d, J=10.8 Hz, 1 H, CH=CH$\underline{H}$), 5.85 (dd, J=18.0, 10.8 Hz, 1 H, C$\underline{H}$=CH_2), 7.2-7.6 (m, 5 H, Ph).

9c. ir(film) 2150, 1755, 1690 cm^{-1}; ^1H nmr($CDCl_3$) 1.30 (t, J=7.0 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.2 (m, 8 H), 3.85 (t, J=7.2 Hz, 1 H, S-CH), 4.1-4.5 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 5.50 (br s, 1 H, =CH), 7.2-7.5 (m, 5 H,).

9d. ir(film) 2150, 1755, 1730, 1690 cm^{-1}; ^1H nmr($CDCl_3$) 1.35 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.6 (m, 6 H), 4.0-4.5 (m, 5 H, $CH_3C\underline{H}_2$, O-CH_2, S-CH), 5.52 (br s, 1 H, =CH), 7.2-7.5 (m, 5 H, Ph).

9e. ir(film) 2140, 1750, 1720, 1685 cm^{-1}; ^1H nmr($CDCl_3$) 1.32 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.2 (m, 2 H), 3.7 (m, 1 H, S-CH), 4.1-4.5 (m, 4 H, $CH_3C\underline{H}_2$, O-CH_2), 4.8-5.1 (m, 2 H, CH=C$\underline{H}_2$), 5.6-6.0 (m, 1 H, C$\underline{H}$=CH_2), 7.2-7.5 (m, 5 H, Ph).

2-Ethoxycarbonyl-4-methyl-2-phenylthio-4-hexen-6-olide (10a) (Representative procedure). A solution of **9a** (125 mg, 0.37 mmol) and rhodium acetate (1.7 mg, 0.007 mmol, 0.02 equiv.) in benzene (5 ml) was stirred at room temperature for 2 h, whereupon the pale purple color was produced. The reaction mixture was then gently refluxed for 2 h, cooled to room tempera-

ture, and passed through a short silica gel column. Concentration followed by chromatography of an oily residue on silica gel (hexane-AcOEt, 2:1) gave **10a** (61 mg, 53%) as an oil: ir($CHCl_3$) 1720 cm^{-1}; ^1H nmr($CDCl_3$) 1.08 (t, J=7 Hz, 3 H, $C\underline{H}_3CH_2$), 1.64 (s, 3 H, =C-CH_3), 2.64 (br s, 2 H, =C-CH_2-C), 4.03 (q, J=7 Hz, 2 H, $CH_3C\underline{H}_2$), 4.3-4.6 (m, 2 H, O-CH_2), 5.40 (br s, 1 H, =CH), 7.0-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.74; H. 5.58; S, 10.46. Found: C, 62.77; H, 5.97; S, 10.61.

5-Benzyl-2-ethoxycarbonyl-2-phenylthio-4-hexen-6-olide (10b). An oil, 49% yield from **9b**; ir(film) 1730 cm^{-1}; ^1H nmr($CDCl_3$) 1.14 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 2.84 (br s, 2 H, =C-CH_2-C), 3.32 (s, 2 H, Ph$C\underline{H}_2$), 4.10 (q, J=7.2 Hz, 2 H, $CH_3C\underline{H}_2$), 4.28 (d, J=14.4 Hz, 1 H, O-C<u>H</u>H), 4.60 (br d, J=14.4 Hz, 1 H, O-CH<u>H</u>), 5.56 (br s, 1 H, =CH), 7.0-7.6 (m, 10 H, 2 Ph). Anal. Calcd for $C_{22}H_{22}O_4S$: C, 69.08; H, 5.80; S, 8.38. Found: C, 69.36; H, 6.01; S, 8.30.

2-Ethoxycarbonyl-2-phenylthio-4-oxabicyclo[5.4.0]undec-6-en-3-one (10c). An oil, 64% yield from **9c**; ir(film) 1730 cm^{-1}; ^1H nmr($CDCl_3$) 1.20 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 1.2-2.8 (m, 9 H), 4.08 (q, J=7.2 Hz, 2 H, $CH_3C\underline{H}_2$), 4.36 (dd, J=16.5, 7.2 Hz, 1 H, O-C<u>H</u>H), 4.72 (dd, 16.5, 3.5 Hz, 1 H, O-CH<u>H</u>), 5.36 (dd, J=7.2, 3.5 Hz, 1 H, =CH), 7.0-7.6 (m, 5 H, Ph). Anal. Calcd for $C_{19}H_{22}O_4S$: C, 65.87; H, 6.40; S, 9.23. Found: C, 65.61; H, 6.48; S, 8.93.

2-Ethoxycarbonyl-2-phenylthio-4-oxabicyclo[5.3.0]dec-6-en-3-one (10d). An oil, 81% yield from **9d**; ir(film) 1730(sh), 1720 cm^{-1}; ^1H nmr($CDCl_3$) 1.16 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 1.5-2.6 (m, 7 H), 4.12 (m, 2 H, $CH_3C\underline{H}_2$), 4.68 (d with fine splittings, J=16.2 Hz, 1 H, O-C<u>H</u>H), 5.12 (d with fine splittings, J=16.2 Hz, 1 H, O-CH<u>H</u>), 5.64 (br s, 1 H, =CH), 7.2-7.7 (m, 5 H, Ph). Anal. Calcd for $C_{18}H_{20}O_4S$: C, 65.03; H, 6.06; S, 9.64. Found: C, 65.15; H, 6.04; S, 9.94.

2-Ethoxycarbonyl-2-phenylthio-4-hepten-7-olide (10e). An oil, 19% yield from **9e**; ir(film) 1730 cm^{-1}; ^1H nmr($CDCl_3$) 1.16 (t, J=7.2 Hz, 3 H, $C\underline{H}_3CH_2$), 2.0-3.5 (m, 4 H, 2 =C-CH_2), 4.0-4.3 (m, 3 H, $CH_3C\underline{H}_2$, O-C<u>H</u>H), 4.60 (td, J=10.8, 2.8 Hz, 1 H, O-CH<u>H</u>), 5.96 (m, 2 H, CH=CH), 7.2-7.7 (m, 5 H, Ph).

Anal. Calcd for $C_{16}H_{18}O_4S$: C, 62.72; H, 5.92; S, 10.46. Found: C, 62.47; H, 5.93; S, 10.27.

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