Tetrahedron Vol 46, Nos 13/14, pp 4887–4906, 1990
Printed in Great Britain

0040-4020/90 $3.00 + .00

STEREOSELECTIVITY IN THE SIGMATROPIC REARRANGEMENT OF EIGHT- AND NINE-MEMBERED CYCLIC ALLYLSULFONIUM YLIDES. SYNTHESIS OF VINYL-SUBSTITUTED BUTYRO- AND VALEROLACTONES†

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(*Received in UK* 13 *March* 1990)

Abstract - The rhodium(II) acetate-catalyzed [2,3]sigmatropic rearrangement of the diazo malonates of (Z)-4-phenylthio-2-buten-1-ol derivatives **6** afforded vinyl-substituted butyrolactones **10** in a highly stereoselective manner, while the rearrangement of the diazo malonates of homologues, (Z)-5-phenylthio-3-penten-1-ol derivatives **9**, yielded vinyl-substituted valerolactones **13** and **14** in the predominance of the formers. A stereochemically fixed substituent R in **9** was found to be an important factor resulting to high stereoselectivity in the latter rearrangement as shown by using diazo malonate **20b** as substrate.

Since excellent works of the groups of Corey[1] and Franzen,[2] sulfonium ylides have been recognized as highly useful species in organic synthesis. Usually sulfonium ylides can be generated by alkylation of sulfides followed by proton abstraction with base or more efficiently by the reaction of sulfides with carbenes generated from diazo compounds photochemically, thermally, or catalytically.[3] For the catalytic generation of carbenes from diazo compounds, copper catalysts have traditionally been employed for many years, while recently rhodium compounds such as rhodium(II) acetate were reported to be more efficient catalysts, in particular for the generation of sulfonium ylides.[4]

The symmetry-allowed [2,3]sigmatropic rearrangement of allylic sulfonium ylides is a facile and predominant reaction, and over the past two decades it has been developed as a remarkably useful tool for bond reorganization in organic synthesis,[3,5] and a number of works have been published on the transpositional migration of allylic groups.[3,5] When a sulfide substrate has a cyclic structure (A), the rearrangement of its sulfonium ylide (B) results to formation of ring expanded product (C) as shown in eq. 1, and this ring expansion reaction has also elegantly been applied to the

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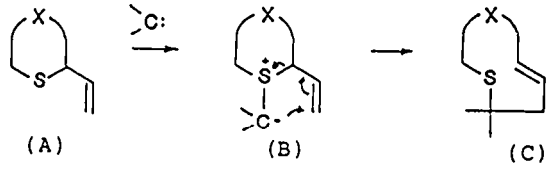
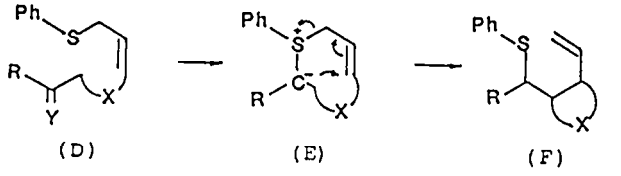
† Dedicated to Professor David Ollis at the occasion of his 65th birthday.

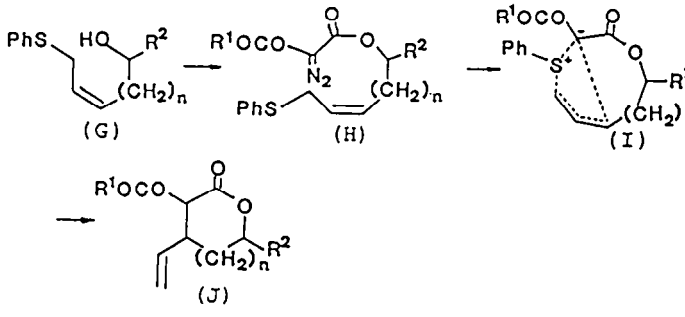
synthesis of cyclic natural compounds.[6] On the other hand, when an acyclic substrate (D) has both sulfide group such as the phenylthio group and carbene generating group (>C=Y in D) such as the diazo group in the same molecule, the presumable intermediate cyclic sulfonium ylide (E) can be expected to give cyclic product (F) via transannular reaction as shown in eq. 2.



eq. 1



eq. 2

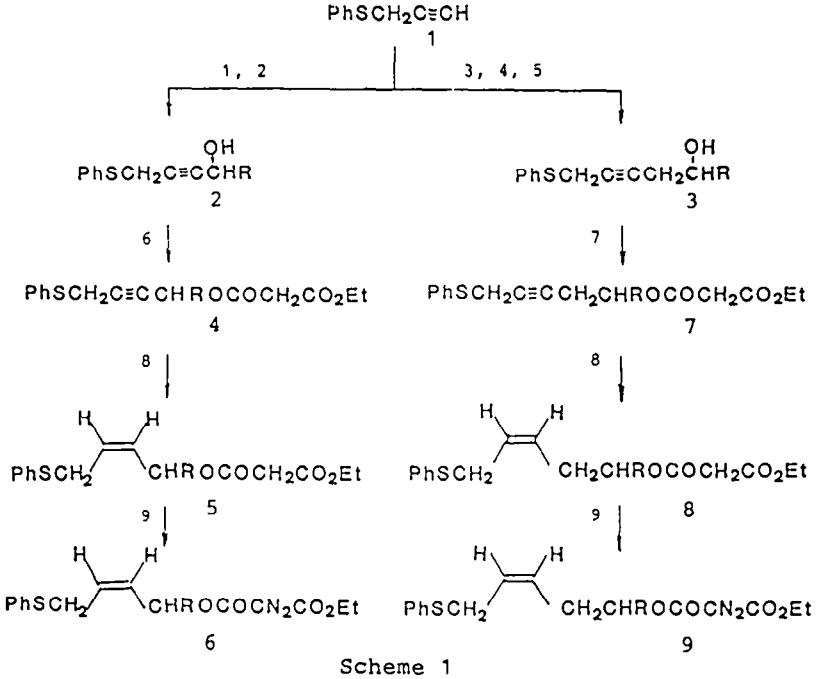


eq. 3

To our knowledge, however, there appears to be no precedent of such a ring forming reaction through this rearrangement hitherto.

We were interested in this ring forming reaction from both standpoints of synthetic utilization and the stereochemical course of reaction, and examined the reaction by employing the diazo malonates (H) of alcohols (G) having the allylic sulfide function. In this protocol, we selected Z-olefinic alcohols (G), because it was surmised that stereochemical requirements in presumptive cyclic transition state (I) would readily be satisfied

with the Z-olefin structure.[7] It was reported that five- to seven-membered sulfonium ylides of the non-allylic system were stable and isolated, while larger cyclic sulfonium ylides could not be prepared from homologous substrates since the C-H bond insertion predominated in the rhodium(II) acetate-catalyzed decomposition of 2-diazo-3-oxo-ω-(phenylthio)carboxylates to form cyclopentane derivatives in place of the expected eight- and ten-membered cyclic sulfonium ylides.[8] As in our case the transition state (I) is required to take an eight- (n=0) or nine-membered (n=1) cyclic sulfonium ylide structure, our interest also lay in examining the possibility of formation of such medium-sized cyclic sulfonium ylide intermediates. In



Scheme 1

Reagents and conditions: 1) EtMgBr, THF, 0 °C; RCHO, 0 °C; 3) BuLi, THF, -30 - -35 °C; 4) R–⟨O⟩; 5) $BF_3 \cdot Et_2O$, -70 °C; 6) $ClCOCH_2CO_2Et$, pyridine, THF, 0 °C; 7) $HOCOCH_2CO_2Et$, dicyclohexylcarbodiimide, CH_2Cl_2, 0-30 °C; 8) H_2(6 kg/cm^2), Pd-$BaSO_4$, EtOH; 9) p-$MeC_6H_4SO_2N_3$, Et_3N, MeCN.

this paper, we describe the detail of some of our recent results in this area.[9]

Table 1. Synthesis of Alcohols 2 and 3, Malonates 4 and 7, and Olefins 5 and 8

entry	alcohol (% yield[a])	malonate (% yield)	Z-olefin (% yield)
1	$PhSCH_2C{\equiv}C(HOCHMe)$ **2a** (94)	$PhSCH_2C{\equiv}C(CHMe)(EtOCOCH_2CO_2)$ **4a** (89)	$PhSCH_2$ / $EtOCOCH_2CO_2CHMe$ **5a** (89)
2	$PhSCH_2C{\equiv}C(HOCHPr)$ **2b** (87)	$PhSCH_2C{\equiv}C(CHPr)(EtOCOCH_2CO_2)$ **4b** (96)	$PhSCH_2$ / $EtOCOCH_2CO_2CHPr$ **5b** (83)
3	$PhSCH_2C{\equiv}C(HOCH\text{-}i\text{-}Pr)$ **2c** (93)	$PhSCH_2C{\equiv}C(CH\text{-}i\text{-}Pr)(EtOCOCH_2CO_2)$ **4c** (78)	$PhSCH_2$ / $EtOCOCH_2COCH\text{-}i\text{-}Pr$ **5c** (81)
4	$PhSCH_2C{\equiv}C(HOCHBu)$ **2d** (80)	$PhSCH_2C{\equiv}C(CHBu)(EtOCOCH_2CO_2)$ **4d** (80)	$PhSCH_2$ / $EtOCOCH_2CO_2CHBu$ **5d** (82)
5	$PhSCH_2C{\equiv}C(HOCHCH_2Ph)$ **2e** (63)	$PhSCH_2C{\equiv}C(CHCH_2Ph)(EtOCOCH_2CO_2)$ **4e** (82)	$PhSCH_2$ / $EtOCOCH_2CO_2CH(CH_2Ph)$ **5e** (78)
6	$PhSCH_2C{\equiv}CCH_2(HOCHMe)$ **3a** (93)	$PhSCH_2C{\equiv}CCH_2(EtOCOCH_2CO_2CHMe)$ **7a** (83)	$PhSCH_2$ / $EtOCOCH_2CO_2CHMeCH_2$ **8a** (80)
7	$PhSCH_2C{\equiv}CCH_2(HOCHBu)$ **3b** (81)	$PhSCH_2C{\equiv}CCH_2(EtOCOCH_2CO_2CHBu)$ **7b** (95)	$PhSCH_2$ / $EtOCOCH_2CO_2CHBuCH_2$ **8b** (77)
8	$PhSCH_2C{\equiv}CCH_2(HOCHCH_2OPh)$ **3c** (91)	$PhSCH_2C{\equiv}CCH_2(EtOCOCH_2CO_2CHCH_2OPh)$ **7c** (90)	$PhSCH_2$ / $EtOCOCH_2CO_2CHCH_2CH_2OPh$ **8c** (81)

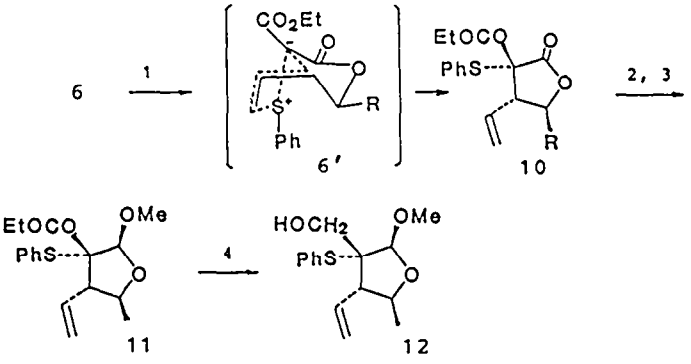
a) Based on 1.

Results and Discussion

Required substrates **6** and **9** were prepared according to Scheme 1. For the preparation of alcohol **2**, phenyl propargyl sulfide (**1**), readily available from propargyl bromide and benzenethiol under phase transfer condi-

tions,[10] was treated with ethylmagnesium bromide and then submitted to the reaction with aldehyde. A variety of secondary alcohols **2** were obtained as shown in Table 1 (entries 1-5). Homologous alcohols **3** (entries 6-8) were prepared from the lithium salt of **1** by the boron trifluoride-promoted reaction with terminal epoxides. In this reaction, it was alleged that a presumed alkynylborane was first formed by adding boron trifluoride to lithium acetylide and gave alcohol **3** by successive addition of epoxide.[11] In contrast to the suggested procedure, addition of boron trifluoride prior to epoxide, however, turned out low yield of **3**. Addition of boron trifluoride to a mixture of the lithium salt of **1** and an epoxide at low temperature was essential to obtain high yield.

After an unsuccessful attempt in partial hydrogenation of **2** leading to a Z-olefinic alcohol, we postponed the formation of Z-olefinic bond to a later stage. The alcohols **2** and **3** were esterified with ethyl malonyl chloride and pyridine[12] (Table 1, entries 1-5) or monoethyl malonate and dicyclohexylcarbodiimide[13] (entries 6-8) to give malonates **4** and **7**, respectively. Partial hydrogenation of these malonates over 5% palladium on barium sulfate provided good results in formation of the corresponding Z-olefins **5** and **8**. Yields of the malonates **4** and **7** and of Z-olefins **5** and **8**



Scheme 2

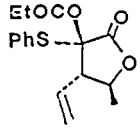
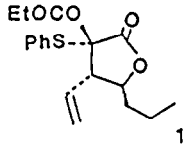
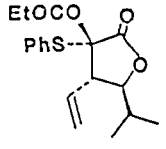
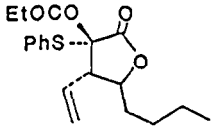
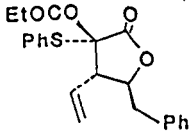
Reagents and conditions: 1) $Rh_2(OAc)_4$, benzene, reflux; 2) i-Bu_2AlH, THF, -78 °C then dilute HCl; 3) $(MeO)_3CH$, pyridinium p-toluenesulfonate, THF, 0 °C; 4) $LiAlH_4$, Et_2O, 0 °C.

were summarized in Table 1. These Z-olefins were then diazotized with

toluenesulfonyl azide under basic conditions to give diazo malonates **6** and **9**, respectively.

As the required substrates **6** and **9** were thus secured, we examined generation of sulfur ylides from these diazo malonates using rhodium(II) acetate as catalyst. When **6** was treated in boiling benzene with rhodium-(II) acetate freshly prepared from rhodium(III) chloride,[14] the rearrangement stereoselectively proceeded as expected, giving rise to formation of ring formed product, butyrolactones **10**, as evidenced by their IR absorptions at 1770-1780 cm^{-1} (Scheme 2). Formation of neither insertion nor fragmentation product was observed. A variety of butyrolactones were thus

Table 2. Rearrangement of the Diazo Derivatives of Olefins 5 to Butyrolactones 10

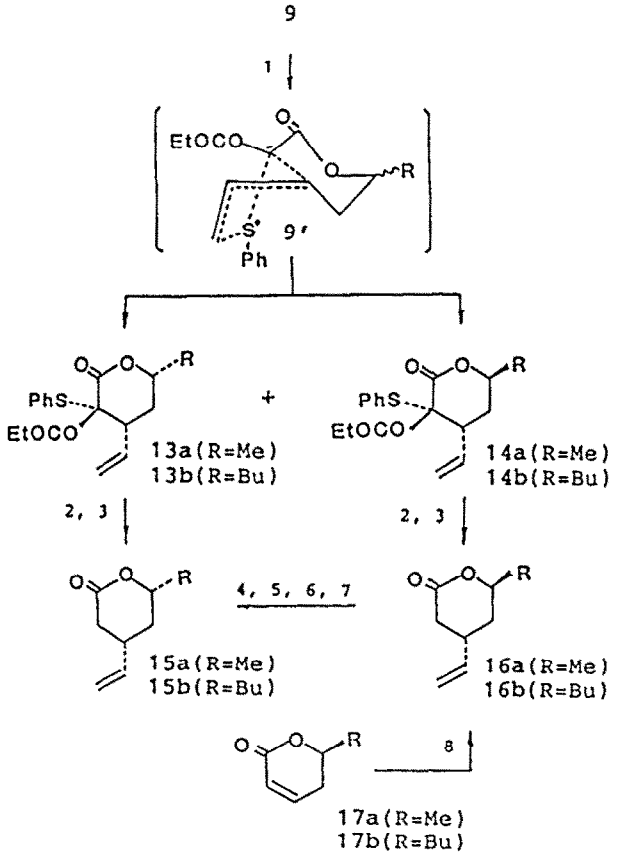
Z-olefin	rearranged product	overall yield (%)[a]
5a	 10a	52
5b	 10b	65
5c	 10c	68
5d	 10d	65
5e	 10e	61

a) From 5.

obtained stereoselectively (Table 2). In the transition state of this rearrangement, the bicyclic sulfonium ylide structure **6'**, wherein two five-

membered rings fused together, was surmisable. The energetically most favorable conformation would be as depicted and this predicts the stereochemistry of product to be as shown with **10**. This presumption on the stereochemistry of substituents on the five-membered lactone ring was actually proved by the following experiment using **10a** as a model.

The lactone **10a** was reduced with diisobutylaluminum hydride and the



Scheme 3

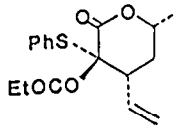
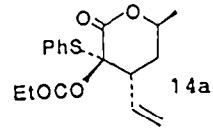
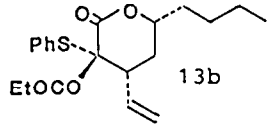
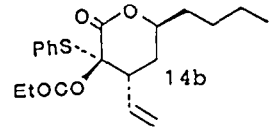
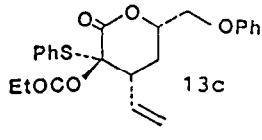
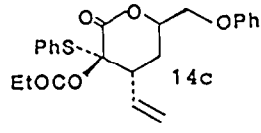
Reagents and conditions: 1) $Rh_2(OAc)_4$, benzene, reflux; 2) Zn, AcOH, 60 °C; 3) NaCl, dimethyl sulfoxide, 150 °C; 4) K_2CO_3, MeOH, room temp.; 5) Ph_3P, $PhCO_2H$, diethyl azodicarboxylate, THF, 0 °C-room temp.; 6) KOH, MeOH, reflux; 7) dilute HCl; 8) CH_2=CHMgBr, CuI, THF, -45 °C.

resulting epimeric mixture of lactols was methylated with trimethyl ortho-

formate using pyridinium p-toluenesulfonate[15] as catalyst to give single acetal **11**. The acetal **11** was further reduced with lithium aluminum hydride to provide alcohol **12**. The stereochemistry of substituents on the furan ring was determined by N.O.E. experiments of **12** using 500 MHz NMR. Irradiation on two hydroxymethylene protons (δ 3.74 and 3.88) showed N.O.E. (5.0 and 3.3%) at an allylic proton (δ 2.98), respectively, while irradiation on secondary methyl protons (δ 1.33) also showed a large N.O.E. (16.3%) at the same allylic proton, these results demonstrating the allylic proton to be syn to both hydroxymethyl and secondary methyl groups. The above irradiations gave no effect on acetal proton (δ 4.66). This outcome allowed us to assign the depicted stereochemistry to **12** and accordingly **10** (R=Me) to the rearranged product.

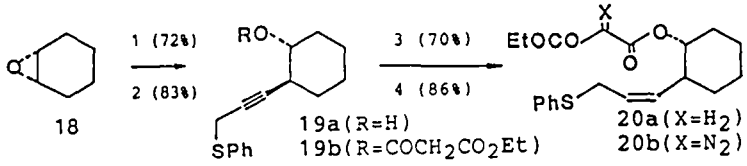
Our continuing interest was to extend the rearrangement to homologous substrates **9** for exploring its stereochemical course. In a similar procedure, i.e. treatment of **9** with rhodium(II) acetate in boiling benzene, diastereomeric valerolactones **13** and **14**, whose ring sizes were evidenced by

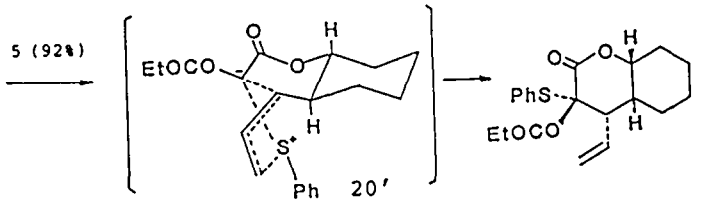
Table 3. Rearrangement of the Diazo Derivatives of Olefins 8 to Valerolactones 13 and 14

Z-olefin	rearranged product		combined overall yield (%)	ratio[a]
8a	 13a	 14a	65	79:21
8b	 13b	 14b	71	74:26
8c	 13c	 14c	74	74:26

a) Based on the separated diastreomers.

IR absorptions at 1740-1750 cm^{-1}, were produced as mixtures in which the former lactones predominated in approximate ratios of 4:1 to 3:1 (Scheme 3, Table 3). Again, neither insertion nor fragmentation product was formed in this case. The stereochemical relationship of these isomers was established by the following chemical correlation using **13a** and **14a** as models. The phenylthio and ester groups of these diastereomers were removed by reduction with zinc in acetic acid followed by treatment with sodium chloride in hot dimethyl sulfoxide[16] to give lactones **15a** and **16a**, respectively (Scheme 3). The latter lactone **16a** derived from the minor rearranged product **14a** could be converted to **15a** by a sequence of successive reactions involving the Mitsunobu inversion,[17] i.e. 1) hydrolysis with potassium carbonate, 2) treatment of the resulting hydroxy ester with triphenylphosphine, benzoic acid, and diethyl azodicarboxylate, 3) hydrolysis of the





Scheme 4

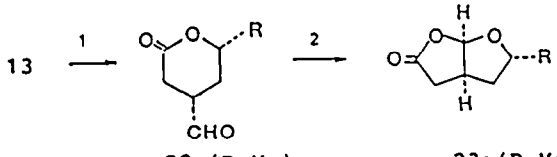
Reagents and conditions: 1) $PhSCH_2C{\equiv}CLi$, THF, -30 - -35 °C then $BF_3{\cdot}Et_2O$, -70 °C; 2) $EtOCOCH_2CO_2H$, 4-(dimethylamino)pyridine, dicyclohexylcarbodiimide, CH_2Cl_2, 0 °C; 3) H_2(6 kg/cm^2), Pd-$BaSO_4$, EtOH, room temp.; 4) p-$MeC_6H_4SO_2N_3$, Et_3N, MeCN, 45 °C; 5) $Rh_2(OAc)_4$, benzene, reflux.

inverted product, a benzoate, with potassium hydroxide, and 4) relactonization of the resulting hydroxy acid with mineral acid. This result confirmed a diastereomeric relationship between **15a** and **16a**. The relative stereochemistry of lactones **15a** and **16a** was determined by an alternative and unequivocal synthesis. In the conjugate addition of Grignard reagents to unsaturated lactones such as **17a**, the reaction has been known to proceed

in a trans selective manner.[18] The reaction of **17a** with vinylmagnesium bromide selectively yielded an addition product that was identical with **16a**. Thus the configurations of the rearranged products **13a** and **14a** could totally be assigned except for their phenylthio and ester groups, whose stereochemistry has tentatively been assigned as depicted by assuming the sterically favorable transition state **9'**. A similar stereochemical correlation was also made with lactones **13b** and **14b**.

Formation of the minor rearranged product **14** implies that nine-membered cyclic allylsulfonium ylides rearranged through stereochemically less restricted transition state **9'** than **6'** through which eight-membered ylides passed in the rearrangement of lower analogues **6**, that is, the substituent R played poor steric control in the case of **9** although its equatorial configuration is predominant in the transition state **9'**.

This outcome stimulated us to examine diastereomer distribution in the rearrangement of a substrate possessing a sterically fixed R substituent. To that end, we selected a trans-substituted cyclohexane derivative **20b** as substrate, which was readily obtained from epoxycyclohexane **18** by the standard procedure described for the diazo malonates **9** (Scheme 4). Alcohol **19a** obtained from the epoxide **18** on the boron trifluoride-promoted reaction with the lithium salt of phenyl propargyl sulfide was malonylated to give **19b**, which was hydrogenated to **20a** and then diazotized to lead to the expected substrate **20b**. Heating of **20b** in benzene in the presence of rhodium(II) acetate provided valerolactone **21** as the sole rearranged pro-



Scheme 5

Reagents and conditions: 1) O_3, CH_2Cl_2, -78 °C then Me_2S; 2) p-toluenesulfonic acid, THF, room temp.

duct without formation of its epimer. Obviously this result demonstrated that the rearrangement proceeded through the transition state **20'** in which alkyl substituent R is fixed as a trans-fused cyclohexane bond, resulting in the observed stereoselective formation of valerolactone **21**.

To illustrate the validity of this sigmatropic rearrangement in natur-

al product synthesis, we attempted the synthesis of the furo[2,3-b]furan ring system that has frequently been found in bioactive natural compounds. The rearranged products **13a** and **13b** were submitted to ozonization and the resulting ozonides were reduced with dimethyl sulfide to give aldehydes **22a** and **22b**, respectively (Scheme 5). When these aldehydes were treated with mineral acid, furofuranones **23a** and **23b** were obtained in good overall yields.

In conclusion, eight- and nine-membered cyclic allylsulfonium ylides intramolecularly generated from the diazo malonates of allylic and homoallylic alcohols having the Z-phenylthiomethyl group at their termini suffered smooth and stereoselective rearrangement to give ring formed products, vinyl-substituted five- and six-membered lactones, respectively.

Acknowledgment. We are indebted to Prof. K. Ogasawara (this University) for 500MHz NMR measurements. This work was supported in part by a Grant-in-Aid for Special Project Research.

Experimental

General Remarks. Melting points are uncorrected. IR and ^{1}H NMR spectra were recorded on a JASCO A-3 spectrophotometer and a JEOL FX-90Q (90 MHz) spectrometer, respectively. Spectral data are described with frequency (cm^{-1}) for the former spectra and chemical shift (δ) referred to tetramethylsilane (δ, 0) for the latter ones. These IR spectra were taken with chloroform solutions and ^{1}H NMR spectra with deuterochloroform solutions. Coupling constants (J) are given in herz. Kieselgel 60 (70-230 mesh) was employed for usual and flash column chromatography. Kieselgel GF_{254} was used for preparative thin-layer chromatography (TLC). High performance liquid chromatography (HPLC) was carried out on a Kusano Kagaku Kikai Model Si-10. Anhydrous magnesium sulfate was used for drying extracts. Elution solvents used in chromatography were shown in parentheses.

Phenyl propargyl sulfide (1). To a stirred mixture of NaOH (0.8 g, 20 mmol) in water (15 mL), benzenethiol (1.65 g, 5 mmol) in benzene (15 mL), and 10% tetrabutylammonium fluoride (0.3 mL) was added dropwise propargyl bromide (1.19 g, 10 mmol) at 0 °C. After being stirred for 30 min at 0 °C, the mixture was allowed to warm to room temperature and then was stirred for an additional 2 h at the same temperature. The resulting mixture was diluted with ether and the organic layer was washed with water and saturated brine, and dried. Removal of the solvent afforded an oil, which was purified by column chromatography (dichloromethane-hexane, 3:7) to give **1** (1.45 g, quantitative yield). IR 3300; NMR 2.24 (t, 1H, J, 3.0), 3.62 (d, 2H, J 3.0), 7.0-7.6 (m, 6H). Anal. Calcd for C_9H_8S: C, 72.93; H, 5.44; S,

21.63. Found: C, 72.71; H, 5.50; S, 21.43%.

General Synthetic Procedure for the Alcohols 2. To a solution of **1** (20 mmol) in tetrahydrofuran (50 mL) was added dropwise a tetrahydrofuran solution of ethylmagnesium bromide (20 mmol) at 0 °C. After stirring had been continued for an additional 1 h, an aldehyde (24 mmol) in tetrahydrofuran (5 mL) was added, and the mixture was stirred for 1.5 h at the same temperature. The resulting mixture was treated with saturated NH_4Cl and then 3M HCl, and extracted with dichloromethane. The extract was washed with water and brine, and dried. Removal of the solvent provided an oil, which was purified by column chromatography (hexane-EtOAc, 2:1-5:1) to give **2**.

2a: IR 3600; NMR 1.35 (d, 3H, J 7.2), 3.64 (d, 2H, J 1.8), 4.48 (q, 1H, J 7.2). Anal. Calcd for $C_{11}H_{12}OS$; C, 67.83; H, 6.21; S, 16.12. Found: C, 68.48; H, 6.39; S, 16.50%.

2b: IR 3600; NMR 0.88 (t, 3H, J 5.4), 1.1-1.8 (m, 6H), 3.62 (d, 2H, J 1.8), 4.30 (t, 1H, J 7.2), 7.1-7.5 (m, 5H). Anal. Calcd for $C_{13}H_{16}OS$; C, 70.87; H, 7.32; S, 14.55. Found: C, 70.78; H, 7.32; S, 14.30%.

2c: IR 3600; NMR 0.88 (d, 6H, J 7.2), 1.78 (sep, 1H, J 7.2), 3.63 (d, 2H, J 1.8), 4.10 (d, 1H, J 7.2), 7.10-7.50 (m, 5H). Anal. Calcd for $C_{13}H_{16}OS$; C, 70.87; H, 7.32; S, 14.55. Found: C, 70.79; H, 7.36; S, 14.43.

2d: IR 3600; NMR 0.88 (t, 3H, J 5.4), 3.64 (d, 2H, J 1.8), 4.35 (m, 1H), 7.1-7.6 (m, 5H). Anal. Calcd for $C_{15}H_{20}OS$; C, 72.54; H, 8.12; S, 12.91. Found: C, 72.28; H, 8.01; S, 12.71%.

2e: IR 3580; NMR 2.92 (d, 2H, J 7.2), 3.62 (d, 2H, J 1.8), 4.94 (q, 1H, J 7.2), 7.0-7.5 (m, 10H). Anal. Calcd for $C_{17}H_{16}OS$; C, 76.08; H, 6.01; S, 11.95. Found: C, 76.15; H, 6.27; S, 11.67%.

General Synthetic Procedure for the Alcohols 3.. To a tetrahydrofuran solution of the lithium salt of **1**, prepared from **1** (6 mmol) and BuLi (6 mmol) in tetrahydrofuran at -30 - -35 °C, was added dropwise a solution of an epoxide (5 mmol) in tetrahydrofuran (14 mL). The mixture was cooled to -70 °C and $BF_3 \cdot Et_2O$ (0.74 mL) was immediately added. After being stirred for 15 min at the same temperature, the mixture was diluted with water and extracted with dichloromethane. The extract was washed with water and brine, and dried. Removal of the solvent provided **3**, which was purified by HPLC (hexane-EtOAc, 2:1-5:1) to give pure **3**.

3a: IR 3550, 1570; NMR 1.16 (d, 3H, J 6.1), 1.80 (br s, 1H), 3.64 (t, 2H, J 2.8), 3.83 (q, 1H, J 6.1), 6.92-7.52 (m, 5H). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S 15.54. Found: C, 70.02; H 6.96; S, 15.42%.

3b: IR 3560; NMR 0.88 (t, 3H, J 5.4), 3.64 (t, 2H, J 2.8), 7.00-7.60 (m, 5H). Anal. Calcd for $C_{15}H_{20}OS$; C, 72.53; H, 8.12; S, 12.91. Found: C, 72.63; H, 8.34; S, 12.52%.

3c: IR 3560, 1600, 1588; NMR 2.48 (m, 2H), 3.66 (t, 2H, J 2.2), 3.96 (m, 3H), 6.76-7.52 (m, 10H). Anal. Calcd for $C_{18}H_{18}O_2S$; C, 72.45; H, 6.08; S, 10.74. Found; C, 72.25; H, 6.25; S, 10.51%.

19a: IR 3550, 1580; NMR 3.28 (m, 1H), 3.64 (d, 2H, J 2.1), 7.08-7.60 (m, 5H). Anal. Calcd for $C_{15}H_{18}OS$; C, 73.13; H, 7.36; S, 13.02. Found: C, 73.41; H, 7.31; S, 12.85%.

General Synthetic Procedure for the Malonates 4 and 5. a) To a stirred solution of **2** (20 mmol) and pyridine (33 mmol) in dry tetrahydrofuran (80 mL) was added dropwise ethyl malonyl chloride (4.51 g, 30 mmol) at 0 °C and the mixture was stirred for 2 h at the same temperature. The mixture was diluted with ether, and the organic layer was washed with 10% aqueous $CuSO_4$ solution, water, and brine. After drying, evaporation of the solvent left an oil, which was purified by column chromatography (hexane-EtOAc, 2:1-5:1) to give **4**.

4a: IR 1740; NMR 1.32 (t, 3H, J 7.2), 1.45 (d, 3H, J 7.2), 3.36 (s, 2H), 3.63 (d, 2H, J 1.8), 4.22 (q, 2H, J 7.2), 5.44 (dt, 1H, J 7.2 and 1.8), 7.00-7.50 (m, 5H). Anal. Calcd for $C_{16}H_{18}O_4S$; C, 62.73; H, 5.92; S, 10.46. Found: C, 62.89; H, 6.15; S, 10.14%.

4b: IR 1750, 1730; NMR 0.88 (t, 3H, J 7.2), 1.25 (t, 3H, 7.2), 3.36 (d, 2H, J 1.8), 4.18 (q, 2H, J 7.2), 5.2-5.5 (m, 1H), 7.1-7.5 (m, 5H). Anal. Calcd for $C_{18}H_{22}O_4S$; C, 64.65; H, 6.63; S, 9.59. Found: C, 64.56; H, 6.32; S, 9.42%.

4c: IR 1740; NMR 0.88 (dd, 6H, J 7.2 and 1.8), 1.28 (t, 3H, J 7.2), 1.94 (q, 1H, J 7.2), 3.36 (s, 2H), 3.64 (d, 2H, J 1.8), 4.20 (q, 2H, J 7.2), 5.22 (dt, 1H, J 5.4 and 1.8), 7.2-7.6 (m, 5H). Anal. Calcd for $C_{18}H_{22}O_4S$; C, 64.65; H, 6.63; S, 9.59. Found: C, 64.34; H, 6.35; S, 9.42%.

4d: IR 1745, 1720; NMR 0.88 (t, 3H, J 5.0), 1.32 (t, 3H, J 7.2), 3.36 (s, 2H), 3.62 (d, 2H, J 1.8), 4.20 (q, 2H, J 7.2), 5.38 (tt, 1H, J 6.1 and 1.8), 7.00-7.50 (m, 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.27; H, 7.23; S, 8.84. Found: C, 65.92; H, 7.08; S, 8.28%.

4e: IR 1740; NMR 1.26 (t, 3H, J 7.2), 3.02 (d, 2H, J 7.2), 3.35 (s, 2H), 3.62 (d, 2H, J 2.0), 4.20 (q, 2H, J 7.2), 5.56 (tt, 1H, J 7.2 and 1.8), 7.00-7.50 (m, 5H). Anal. Calcd for $C_{22}H_{22}O_4S$; C, 69.09; H, 5.80; S, 8.38. Found: C, 68.83; H, 5.99; S, 8.14%.

b) To a stirred solution of 3 (2.5 mmol), malonic acid monoethyl ester (991 mg, 7.5 mmol) and 4-(dimethylamino)pyridine (30 mg, 0.25 mmol) in dichloromethane (30 mL) was added dropwise a solution of dicyclohexylcarbodiimide (1.289 g, 6.25 mmol) in dichloromethane (5 mL) at 0 °C, and the mixture was then stirred for 4 h at 30 °C. Water was added and the mixture was acidified with 6M HCl. After removal of precipitates by filtration, the filtrate was extracted with dichloromethane. The extract was

washed with water, and dried. Removal of the solvent provided an oil, which was purified by HPLC (hexane-EtOAc, 2:1-5:1) to give pure **7**.

7a: IR 1750, 1730, 1590; NMR 1.22 (d, 3H, J 6.2), 1.30 (t, 3H, J 7.2), 2.42 (m, 2H), 3.32 (s, 2H), 3.60 (t, 2H, J 2.8), 4.19 (q, 2H, J 7.2), 4.96 (sex, 1H, J 6.2), 7.12-7.48 (m, 5H). Anal. Calcd for $C_{17}H_{20}O_4S$; C, 63.73; H, 6.29; S, 10.00. Found: C, 63.47; H, 6.24; S 9.77%.

7b: IR 1750, 1730; NMR 0.88 (t, 3H, J 5.4), 1.26 (t, 3H, J 7.2), 4.18 (q, 2H, J 7.2), 4.88 (q, 1H, J 5.4), 7.32 (m, 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.27; H, 7.23; S, 8.84. Found: C, 65.90; H, 6.92; S, 9.23%.

7c: IR 1755, 1735, 1601, 1590; NMR 1.24 (t, 3H, J 7.2), 2.67 (dt, 2H, J 7.2 and 2.8), 3.36 (s, 2H), 3.60 (t, 2H, J 2.2), 4.04 (d, 2H, J 5.0), 4.18 (q, 2H, J 7.2), 5.22 (q, 1H, J 5.4), 6.72-7.48 (m. 5H). Anal. Calcd for $C_{23}H_{24}O_5S$; C, 66.97; H, 5.86; S 7.77. Found: C, 66.68; H, 5.90; S, 7.88%.

19b: IR 1750, 1730, 1590; NMR 1.26 (t, 3H, J 7.2), 3.30 (s, 2H), 3.60 (d, 2H, J 2.1), 4.20 (q, 2H, J 7.2), 4.76 (m, 1H), 7.04-7.56 (m, 5H). Anal. Calcd for $C_{20}H_{24}O_4S$; C, 66.63; H, 6.71; S, 8.90. Found: C, 66.39; H, 6.97; S, 8.76%.

General Synthetic Procedure for the Olefins 5 and 8. A solution of **4** (2 mmol) in ethanol (10 mL) was hydrogenated over 5% Pd-$BaSO_4$ (540 mg) under a slight pressure (6 kg/cm^2) at room temperature until uptake of hydrogen ceased. Filtration of the mixture followed by evaporation afforded an oil, which was purified by TLC (hexane-EtOAc, 2:1-5:1) to give **5**.

5a: IR 1740, 1720; NMR 1.16 (d, 3H, J 7.2), 1.30 (t, 3H, J 7.2), 3.34 (s, 2H), 3.54 (dd, 1H, J 14.4 and 7.2), 3.83 (dd, 1H, J 14.4 and 7.9), 4.22 (q, 2H, J 7.2), 5.3-5.9 (m, 3H), 7.10-7.50 (m, 5H). Anal. Calcd for $C_{16}H_{20}O_4S$; C, 62.32; H, 6.54; S, 10.40. Found: C, 62.08; H, 6.70; S, 10.34%.

5b: IR 1740, 1725; NMR 0.88 (t, 3H, J 5.4), 1.27 (t, 3H, J 7.2), 3.32 (s, 2H), 3.54 (dd, 1H, J 13.0 and 7.2), 3.82 (dd, 1H, J 7.2 and 7.9), 4.19 (q, 2H, J 7.2), 5.2-5.9 (m, 3H), 7.10-7.50 (m, 5H). Anal. Calcd for $C_{18}H_{24}O_4S$: C, 64.26; H, 7.19; S, 9.53. Found: C, 64.00; H, 7.24; S, 9.74%.

5c: IR 1740, 1730; NMR 0.84 (d, 3H, J 6.4), 0.92 (d, 3H, J 6.4), 1.30 (t, 3H, J 7.2), 1.76 (sep, 1H, J 7.0), 3.36 (s, 2H), 3.62 (dd, 1H, J 14.4 and 7.2), 3.84 (dd, 1H, J 14.4 and 7.2), 4.22 (q, 2H, J 7.2), 5.2-6.0 (m, 3H), 7.10-7.50 (m, 5H). Anal. Calcd for $C_{18}H_{24}O_4S$; C, 64.26; H, 7.19; S, 9.53. Found: C, 63.97; H, 7.33; S, 9.50%.

5d: IR 1725, 1710; NMR 0.88 (t, 3H, J 5.4), 3.30 (s, 2H), 3.54 (dd, 1H, J 14.4 and 7.2), 3.82 (dd, 1H, J 14.4 and 7.2), 4.20 (q, 2H, J 7.2), 5.2-5.9 (m, 3H), 7.10-7.50 (m, 5H). Anal. Calcd for $C_{20}H_{20}O_4S$; C, 65.90; H, 7.74; S,8.80. Found: C, 66.05; H, 7.94; S, 9.07%.

5e: IR 1750, 1735; NMR 1.25 (t, 3H, J 7.2), 2.65 (dd, 1H, J=14.4 and 7.2), 2.90 (dd, 1H, J 14.4 and 7.2), 3.30 (s, 2H), 4.16 (q, 2H, J 7.2), 5.2-5.8 (m, 3H), 7.00-7.50 (m, 5H). Anal. Calcd for $C_{22}H_{24}O_4S$; C, 68.73; H, 6.29; S, 8.34. Found: C, 68.44; H,6.73; S,8.48%.

8a: IR 1745, 1725, 1580; NMR 1.20 (d, 3H, J 7.0), 1.25 (t, 3H, J 7.2), 2.25 ((m, 2H), 3.35 (s, 2H), 3.55 (d, 2H, J 7.0), 4.20 (q, 2H, J 7.2), 4.90 (q, 1H, J 7.0), 5.56 (m, 2H), 7.12-7.52 (m, 5H). Anal. Calcd for $C_{17}H_{22}O_4S$; C, 63.33; H, 6.88; S, 9.94. Found: C, 63.60; H, 7.01; S 9.57%.

8b: IR 1750, 1730, 1580; NMR 0.88 (t, 3H, J 5.4), 2.24 (t, 2H, J 6.5), 3.34 (s, 2H), 3.54 (d, 2H, J 6.5), 4.87 (quin, 1H, J 5.4), 5.54 (m, 2H), 7.04-7.44 (m, 5H). Anal. Calcd for $C_{20}H_{28}O_4S$; C, 65.90; H, 7.23; S, 8.80. Found: C, 66.35; H, 7.93; S, 8.53%.

8c: IR 1752, 1735, 1601, 1592; NMR 2.46 (t, 2H, J 6.1), 3.36 (s, 2H), 3.54 (d, 1H, J 6.8), 3.96 (d, 1H, J 5.0), 5.14 (m, 1H), 5.58 (m, 2H), 6.76-7.60 (m, 10H). Anal. Calcd for $C_{23}H_{26}O_5S$; C, 66.64; H, 6.33 ; S, 7.73. Found. C, 66.78; H, 6.37; S, 7.75%.

20a: IR 1745, 1725, 1583; NMR 1.24 (t, 3H, J 7.2), 3.30 (s, 2H), 3.58 (t, 2H, J 6.8), 4.20 (q, 2H, J 7.2), 4.58 (m, 1H), 5.40 (m, 2H), 7.08-7.52 (m, 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.27 ; H, 7.23; S, 8.84. Found: C, 66.24; H, 7.24; S, 8.52%.

General Synthetic Procedure for the Lactones 10, 13, and 14. To a stirred solution of **6** (1 mmol) and p-toluenesulfonyl azide (217 mg, 1.1 mmol) in dry acetonitrile (8 mL) was added triethylamine (253 mg, 2.5 mmol), and the mixture was stirred at 45 °C for 48 h. The mixture was diluted with dichloromethane and washed with 3% aqueous KOH solution, water, and brine. Removal of the solvent afforded an oil, which was purified by HPLC (hexane-EtOAc, 2:1-5:1) to give the diazo malonate **6** (or **9**) in 96-98% yield. After a solution of the diazo malonate (1 mmol) and $Rh_2(OAc)_4$ (0.001 mmol) in dry benzene (10 mL) had been stirred for 10 min at room temperature, the mixture was refluxed for 30 min. The reaction mixture was passed through a short silica gel column with the aid of dichloromethane-ether (2:1) and removal of the solvent afforded crude **10** (or **13** and **14**), which was purified by HPLC (hexane-EtOAc, 2:1-5:1).

10a: IR 1770, 1740; NMR 1.29 (t, 3H, J 6.5), 1.46 (d, 3H, J 6.5), 3.36 (dd, 1H, J 10 and 8), 4.28 (q, 2H, J 6.5), 4.73 (dq, 1H, J 10 and 6.5), 5.34 (dd, 1H, J 18 and 1), 5.42 (dd, 1H, J 10.8 and 1), 5.95 (ddd, 1H, J 18, 10.8 and 8), 7.20-7.70 (m, 5H). Anal. Calcd for $C_{16}H_{18}O_4S$; C, 62.73; H, 5.92; S, 10.46. Found: C, 62.50; H, 6.08; S, 10.52%.

10b: IR 1770, 1720; NMR 0.96 (t, 3H, J 5), 1.26 (t, 3H, J 6.5), 3.40 (dd, 1H, J 10.8 and 8), 4.26 (q, 2H, J 6.5), 4.57 (ddd, 1H, J 10, 7.2 and 3.6), 5.30 (dd, 1H, J 17 and 2), 5.39 (d, 1H, J 10.8), 5.90 (ddd, 1H, J 17,

10.8 and 8), 7.20-7.74 (m, 5H). Anal. Calcd for $C_{18}H_{22}O_4S$; C, 64.65; H, 6.63; S, 9.59. Found: C, 64.62; H, 6.58; S, 9.63%.

10c: IR 1779, 1730; NMR 1.04, 1.01 (d, 3H, J 6 each), 1.26 (t, 3H, J 6.5), 1.94 (m, 1H), 3.56 (dd, 1H, J 10 and 8), 4.21 (q, 2H, J 6.5), 4.46 (dd, 1H, J 10 and 5), 5.30 (dd, 1H, J 18 and 2), 5.37 (d, 1H, J 10.8), 5.96 (ddd, 1H, J 18, 10.8 and 8), 7.20-7.68 (m, 5H). Anal. Calcd for $C_{18}H_{22}O_4S$; C, 64.55; H, 6.63; S, 9.59. Found: C, 64.81; H, 6.83; S, 9.37%.

10d: IR 1770, 1710; NMR 0.90 (t, 3H, J 6.5), 1.25 (t, 3H, J 6.5), 3.40 (dd, 1H, J 10 and 8), 4.24 (q, 2H, J 6.5), 4.56 (m, 1H), 5.30 (dd, 1H, J 10.8 and 2), 5.39 (d, 1H, J 10.8), 5.96 (ddd, 1H, J 18, 10.8 and 8), 7.20-7.72 (m, 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.27; H, 7.23; S, 8.84. Found: C, 66.49; H, 7.16; S, 8.99%.

10e: IR 1780, 1743; NMR 1.20 (t, 3H, J 6.5), 3.02 (m, 2H), 3.46 (dd, 1H, J 10.8 and 8), 4.20 (q, 2H, J 6.5), 4.82 (ddd, 1H, J 10, 7 and 4), 5.30 (dd, 1H, J 18 and 2), 5.46 (d, 1H, J 10.8), 5.97 (ddd, 1H, J 18, 10.8 and 8), 7.20-7.68 (m, 10H). Anal. Calcd for $C_{22}H_{22}O_4S$; C, 69.09; H, 5.80; S, 8.38. Found: C, 68.83; H, 6.00; S, 8.04%.

13a: IR 1726, 1740; NMR 1.20 (t, 3H, J 7.2), 1.40 (d, 3H, J 6.1), 3.46 (br q, 1H, J 7.2), 3.86-4.66 (m, 3H), 5.08-6.05 (ABX, 3H), 7.20-7.72 (m, 5H). Anal. Calcd for $C_{17}H_{20}O_4S$; C, 63.73; H, 6.29; S, 10.00. Found: C, 64.08; H, 6.35; S, 10.14%.

14a: IR 1740, 1730; NMR 1.18 (t, 3H, J 7.2), 1.40 (d, 3H, J 6.1), 3.40 (br q, 1H, J 6.2), 4.12 (dq, 2H, J 7.2 and 3.6), 4.92 (m, 1H), 5.16-6.12 (ABX, 3H), 7.16-7.76 (m, 5H). Anal. Calcd for $C_{17}H_{20}O_4S$; C, 63.73; H, 6.29; S, 10.00. Found: C, 63.67; H, 6.29 ; S, 9.76%.

13b: IR 1750, 1725, 1640, 935; NMR 0.92 (t, 3H, J 5,4), 3.48 (br q, 1H, J 7.9), 5.08-6.06 (ABX, 3H), 7.08-7.76 (m. 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.26; H, 7.23; S, 8.85. Found: C, 66.32; H, 7.03; S, 9.02%.

14b: IR 1725, 935; NMR 0.90 (t, 3H, J 5.4), 3.42 (br q, 1H, J 5.4), 4.76 (m, 1H), 5.08-6.12 (ABX, 3H), 7.08-7.76 (m, 5H). Anal. Calcd for $C_{20}H_{26}O_4S$; C, 66.26; H, 7.23; S, 8.85. Found: C, 66.24; H, 7.37; S, 9.02%.

13c: IR 1750, 1735, 935; NMR 3.54 (m, 1H), 4.12 (m, 4H), 4.72 (dq, 1H, J 11.1 and 3.6), 5.12-6.08 (ABX, 3H), 6.80-7.76 (m, 10H). Anal. Calcd for $C_{23}H_{24}O_5S$; C, 66.97; H, 5.87; S, 7.77. Found: C, 66.87; H, 5.94; S, 8.04%.

14c: IR 1742, 1730, 935; NMR 2.24 (t, 2H. J 6.8), 3.56 (q, 1H, J 7.2), 4.12 (q, 4H, J 7.2), 5.08 (m, 1H), 5.20-6.12 (ABX, 3H), 6.76-7.80 (m, 10H). Anal. Calcd for $C_{23}H_{24}O_5S$; C, 66.97; H, 5.87; S, 7.77. Found: C, 67.11; H, 6.01; S, 7.69%.

21: IR 1755, 1730, 1645, 1590, 1580; NMR 1.12 (t, 3H, J 7.2), 3.12 (t, 1H, J 10.0), 5.04-6.00 (ABX, 3H). Anal. Calcd for $C_{20}H_{24}O_4S$; C, 66.63; H, 6.71; S, 8.90, 7.08-7.84 (m, 5H). Found: C, 66.87; H, 6.84; S, 9.26%.

Conversion of the Rearranged Product 6a to the Lactone 12. After a toluene solution of diisobutylaluminum hydride (1.1 mmol) had been added dropwise to a stirred solution of **6a** (135 mg, 0.44 mmol) in tetrahydrofuran (2 mL) at -78 °C, the mixture was further stirred at the same temperature for an additional 1 h. A saturated NH_4Cl solution was added, and the mixture was then acidified with 6M HCl and extracted with dichloromethane. The extract was washed with water and brine, and then dried. Evaporation of the solvent left a diastereomeric mixture of lactols (73 mg). A solution of the lactols (72 mg), trimethyl orthoformate (0.2 mL) and pyridinium p-toluenesulfonate[15] (14 mg) in tetrahydrofuran (2 mL) was stirred at 0 °C for 4 h and diluted with dichloromethane. The mixture was washed with aqueous K_2CO_3 solution, water, and brine, and then dried. Evaporation of the solvent provided an oil, which was purified by TLC (hexane-AcOEt, 4:1) to give **11** (63 mg) as homogeneous product as evidenced by its ^1H NMR spectrum. A solution of **11** (32 mg) in ether (1 mL) was added dropwise to a suspension of $LiAlH_4$ (7.6 mg) in ether (1 mL) at 0 °C and the mixture was stirred for 30 min at the same temperature. Wet ethyl acetate was added to quench excess $LiAlH_4$, and the organic layer was decanted and then dried. Evaporation of the solvent left an oil, which was purified by TLC (hexane-AcOEt, 4:1) to afford **12** (12 mg); IR 3500; NMR 1.33 (d, 3H J 6.1), 2.98 (d, 1H, J 7.9), 3.17 (dd, 1H, J 9.8 and 9.1), 3.24 (s, 3H), 3.74 (dd, 1H, J 12.2 and 7.9), 3.88 (d, 1H, J 12.2), 4.43 (dq, 1H, J 9.1 and 6.1), 4.66 (s, 1H), 5.28-5.34 (m, 2H), 5.90 (ddd, 1H, J 17.1, 9.8 and 8.5), 7.26-7.60 (m, 5H).

Reductive Desulfurization and Deethoxycaronylation of the Rearranged Product 13 Leading to the Lactone 15. The mixture of **13** (0.6 mmol) and zinc powder (190 mg, 3.0 mmol atom) in acetic acid (7 mL) was heated at 60 °C for 2 h with stirring. The reaction mixture was diluted with dichloromethane and washed with 10% aqueous K_2CO_3 solution and water, and dried. Removal of the solvent afforded an oil, which was purified by column chromatography (dichloromethane) to give desulfurized product. A solution of the product and NaCl (34 mg) in dimethyl sulfoxide (3 mL) containing water (0.035 mL) was heated at 156-160 °C for 2 h. The reaction mixture was diluted with water and extracted with dichloromethane. The extract was washed with water and brine. After drying, removal of the solvent provided an oil, which was purified by HPLC (hexane-EtOAc, 5:1) to give **15** (48 mg) in 75-80% yields.

15a: IR 1726, 1645, 924; NMR 1.40 (d, 3H, J 6.1), 4.48 (m, 1H), 5.00-5.96 (ABX, 3H). Anal. Calcd for $C_8H_{12}O_2$; C, 68.54; H, 8.63. Found: C, 68.69; H, 8.83%.

15b: IR 1740; NMR 1.36 (d, 3H, J 6.1), 4.54 (sex, 1H, J 6.1), 4.96-

6.02 (ABX, 3H). Anal. Calcd for $C_8H_{12}O_2$; C, 68.54; H, 8.63. Found: C, 68.31; H, 8.71%.

16a: IR 1720, 925; NMR 0.90 (t, 3H, J 5.4), 4.30 (m, 1H), 4.96-5.92 (ABX, 3H). Anal. Calcd for $C_{11}H_{18}O_2$; H, 72.73; H, 9.52. Found. C, 72.55; H, 9.97%.

16b: IR 1725, 926; NMR 0.90 (t, 3H, J 5.4), 4.32 (m, 1H), 4.96-6.04 (ABX, 3H). Anal. Calcd for $C_{11}H_{18}O_2$; C, 72.73; H, 9.52. Found: C, 72.49; H, 9.79%.

Conjugate Addition of Vinylmagnesium Bromide to the Lactone 17. To a slurry of CuI (95 mg, 0.49 mmol) and a tetrahydrofuran solution (7.8 mL) of vinylmagnesium bromide (2.5 mmol) was added dropwise a solution of **17** (0.98 mmol) in tetrahydrofuran (3 mL) at -45 °C over 45 min. After being stirred for 90 min at the same temperature, aqueous NH_4Cl solution was added, and the mixture was diluted with ether. After removal of precipitates by filtration, the filtrate was washed with water, and dried. Removal of the solvent afforded an oil, which was purified by column chromatography (hexane-AcOEt, 4:1) to give **16** (74-81% yields). These products **16a** and **16b** were proved to be identical with those derived from **14a** and **14b** on spectroscopic comparison.

Conversion of the Lactone 16 to Its Epimer 15. A solution of K_2CO_3 (2 g, 14.5 mmol) and **16** (4.21 mmol) in methanol (7 mL) was vigorously stirred at room temperature for 2 h, and the mixture was diluted with water and acidified with dilute HCl. Extraction of the product with ether followed by working up in a standard manner gave a hydroxy ester (575 mg). A solution of diethyl azodicarboxylate (0.32 mL, 2.03 mmol) in tetrahydrofuran (2 mL) was added dropwise to a stirred solution of the hydroxy acid (160 mg 0.93 mmol), triphenylphosphine (565 mg, 2.15 mmol), and benzoic acid (260 mg, 2.13 mmol) in tetrahydrofuran (8 mL) at 0 °C and then stirred at room temperature overnight. The reaction mixture was diluted with water and extracted with ether. After drying, the extract was evaporated to leave a benzoate (250 mg). A mixture of the benzoate (239 mg, 0.86 mmol) in methanol (3 mL) and 2.5M aqueous KOH solution (6 mL) was refluxed for 6 h. After being concentrated to a half volume, the reaction mixture was acidified with 6M HCl and then extracted with dichloromethane. The extract was washed with brine and dried. Removal of the solvent afforded crude product, which was purified by column chromatography (hexane-AcOEt, 5:1) to give pure **15** (51-64% yield from **16**).

These products **15a** and **15b** were proved to be identical with those derived from **13a** and **13b** on spectroscopic comparison.

Conversion of the Lactone 13 to the Furofuranone 23. Ozone was bubbled through a solution of **13** (0.53 mmol) in dichloromethane (10 mL) at -78

^{o}C until slight blue coloration developed. An excess of ozone was purged with argon, and then dimethyl sulfide (0.1 mL) was added. After evaporation of the solvent, the residue was dissolved in tetrahydrofuran (3 mL), and a catalytic amount of p-toluenesulfonic acid was added. The mixture was stirred at room temperature overnight. Removal of the solvent provided an oil, which was purified by column chromatography to give **23** in 79-80% yield.

23a: IR 1790; NMR 1.33 (d, 1H, J 5), 2.42 and 2.90 (q, 1H, J 18 each), 4.30 (m, 1H), 6.10 (d, 1H, J 4). Anal. Calcd for $C_7H_{10}O_3$; C, 59.14; H, 7.09. Found: C, 59.23; H, 7.32%.

23b: IR, 1790; NMR 4.1 (m, 1H), 6.08 (d, 1H, J 5). Anal. Calcd for $C_{10}H_{16}O_3$; C, 65.19; H, 8.75. Found: C, 65.04; H, 8.94%.

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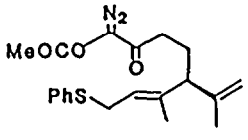
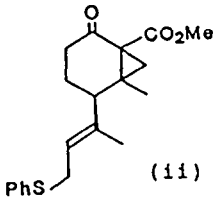


(i)



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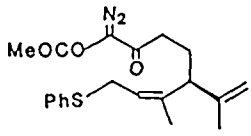

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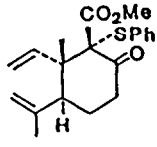

(iv)

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