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Palladium-Catalyzed Intramolecular Metallo-Ene Reactions Using Allylic Sulfones as Enophiles

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Palladium-catalyzed intramolecular metallo-ene reactions were studied using allylic sulfones as enophiles. Palladium-catalyzed reactions of allylic acetates and methyl carbonates bearing allylic sulfones at appropriate sites were carried out in acetic acid at 80 °C to give cyclized products, cyclohexane derivatives, with extremely high diastereoselectivity. The stereochemistry of these reactions was examined under various reaction conditions using several model compounds.

Keywords palladium catalyst; metallo-ene reaction; allylic acetate; allylic sulfone; sulfinate–sulfone rearrangement; stereoselectivity

Ene reactions have received much attention owing to their high diastereo- and enantioselectivity in carbon–carbon bond formations.[1] In particular, intramolecular ene reaction should be a useful tool for stereoselective construction of cyclic compounds.[2]

Transition metal-promoted carbon–carbon bond formation reactions also offer high stereoselectivity and stereospecificity in organic synthesis.[3] Many reports have been published on reactivity and the stereochemistry of π-allylpalladium complexes.[4] In general, π-allylpalladium complexes react readily with carbonucleophiles to form new carbon–carbon bonds. However, π-allylic palladium complexes sometimes undergo metallo-ene reactions with olefins as enophiles.[5,6] We report here diastereoselective cyclizations by means of intramolecular metallo-ene reactions using allylic sulfones as enophiles.[7]

Synthesis of Model Compounds Model compounds for intramolecular metallo-ene reactions were prepared as follows. Dimethyl (4-acetoxy-2(*Z*)-butenyl)propanedioate (**1a**) was obtained in 72% yield by the reaction of dimethyl malonate sodium enolate with 4-acetoxy-2(*Z*)-butenyl bromides which was prepared *in situ* by bromination of 4-acetoxy-2(*Z*)-butenol with *N*-bromosuccinimide (NBS)–triphenylphosphine (PPh_3). Alkylation of **1a** with 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z*)-butenyl bromide was carried out in tetrahydrofuran (THF) at 0 °C for 1 h in the presence of sodium hydride to give dimethyl (4-acetoxy-2(*Z*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z*)-butenyl]propanedioate (**2a**) in 72% yield. Treatment of **2a** with pyridinium *p*-toluenesulfonate (PPTS) in methanol at room temperature for 12 h gave dimethyl (4-acetoxy-2(*Z*)-butenyl)(4-hydroxy-2(*Z*)-butenyl)propanedioate (**3a**) in 85% yield. Sulfinylation of **3a** with *p*-toluenesulfinyl chloride was carried out in THF at 0 °C for 0.5 h in the presence of triethylamine to give dimethyl (4-acetoxy-2(*Z*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*Z*)-butenyl)propanedioate (**4a**) in 85% yield.

The reaction of **1a** with 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*E*)-butenyl bromide followed by treatment of the malonate derivative **6a** produced with PPTS and the sulfinylation of the resulting alcohol **7a** with *p*-toluenesulfinyl chloride gave a sulfinate, **8a**.

The methoxycarbonyloxy compound **1b** was obtained by the reaction of dimethyl malonate sodium enolate with 4-methoxycarbonyloxy-2(*Z*)-butenyl bromide. The reaction of **1b** with 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl bromide was carried out in THF at 0 °C for 1 h using sodium hydride as a base to give **2b** or **6b** in 80 or 70% yield, respectively. The same reaction sequences of **2b** and **6b** as described above gave **4b** and **8b**.

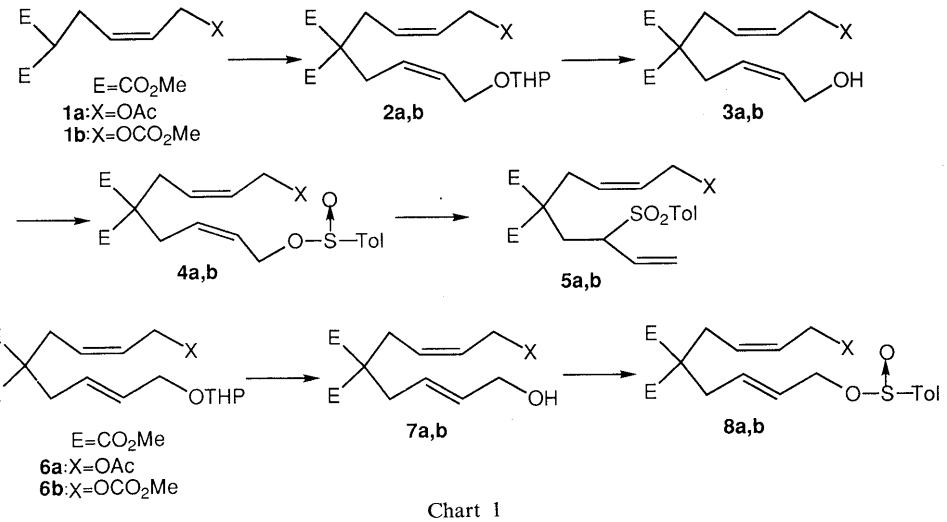

Chart 1

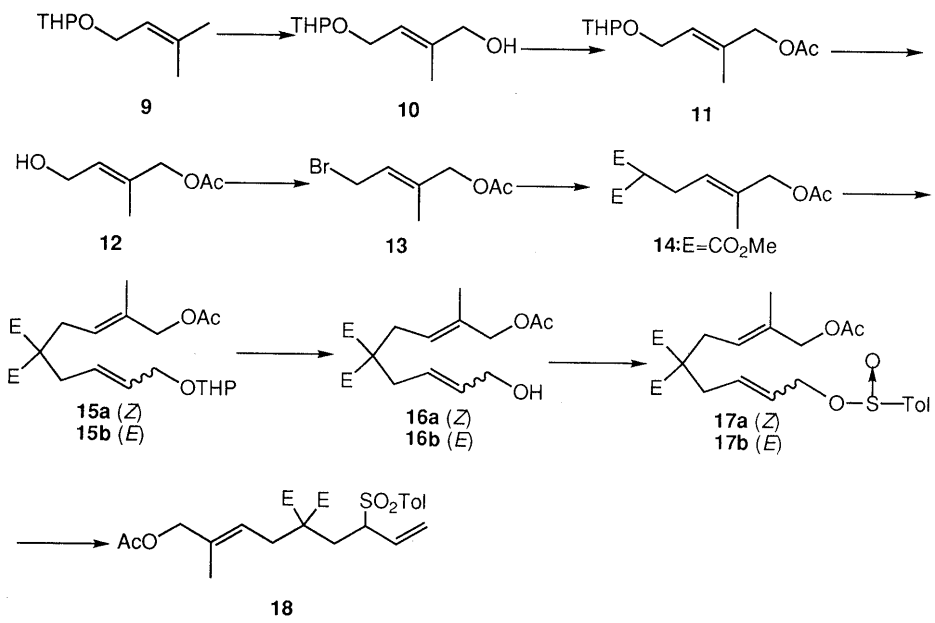

Chart 2

Upon heating at 115 or 125 °C in *N*,*N*-dimethylformamide (DMF), the sulfinates **4a** and **8a**, or **4b** and **8b** underwent sulfinate-sulfone rearrangements to afford dimethyl (4-acetoxy or methoxycarbonyloxy-2(*Z*)-butenyl)(2-*p*-toluenesulfonyl-3-butenyl)propanedioate (**5a, b**) in 79—91% yields. A much higher reaction temperature (125 °C) was required for the rearrangement of the (*Z*)-allylic sulfinates **4a, b**.

The model compound, dimethyl (4-acetoxy-3-methyl-2(*E*)-butenyl)(2-*p*-toluenesulfonyl-3-butenyl)propanedioate (**18**), was prepared as follows. Regioselective allylic oxidation[8] of 1-(tetrahydro-2*H*-pyran-2-yl)oxy-3-methyl-2-butene (**9**) with selenium dioxide and *tert*-butyl perhydroxide (in dichloromethane, at room temperature, for 12 h, 45% yield) followed by acetylation of the resulting alcohol **10** with acetic anhydride afforded 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2-methyl-2(*E*)-butenyl acetate (**11**). Deprotection of the tetrahydropyranyl group with PPTS followed by bromination of the alcohol **12** with NBS–PPh_3 gave 4-acetoxy-3-methyl-2(*E*)-butenyl bromide (**13**). Alkylation of dimethyl malonate sodium enolate with the bromide **13** (in THF, at 0 °C, for 1 h) produced dimethyl (4-acetoxy-3-methyl-2(*E*)-butenyl)propanedioate (**14**) in 89% yield. The reaction of **14** with 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl bromide was carried out in THF at 0 °C for 1 h using sodium hydride as a base to give dimethyl (4-acetoxy-3-methyl-2(*E*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl]propanedioate (**15a, b**) in 84 or 90% yield, respectively. The same reaction sequences of **15a, b** as described earlier gave the sulfinates **17a, b**. Heating of **17a, b** at 115 and 125 °C in DMF gave **18** in 93 and 90% yields, respectively.

Intramolecular Metallo-Ene Reactions The allylic sulfone **5a** underwent an intramolecular metallo-ene reaction to give dimethyl *cis*- and *trans*-4-methylene-3-*p*-toluenesulfonyl-5-vinyl-1,1-cyclohexanedicarboxylate (**19a, b**), upon heating at 80 °C in acetic acid for 4 h in the presence of a palladium catalyst, bis(dibenzylideneacetone)palladium [$Pd(dba)_2$] or tetrakis(triphenylphosphine)palladium [$Pd(PPh_3)_4$], with or without a phosphine ligand (PPh_3). The results are summarized in Table I.

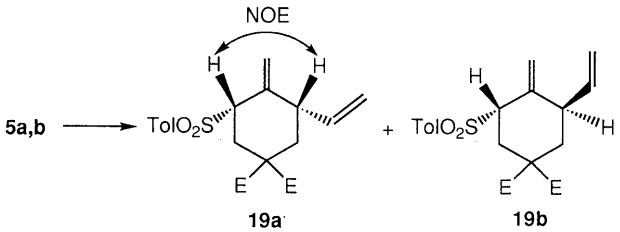

Chart 3

TABLE I. Stereochemical Studies on Palladium-Catalyzed Cyclizations of Allylic Sulfones **8a, b**[a]

8	Catalyst (mol%)	PPh_3 (mol%)	Yield (%)[b] of **19a, b**	Ratio of **19a** to **19b**
8a	$Pd(dba)_2$ (5)	15	24 (66)	83:17
8a	$Pd(dba)_2$ (10)	30	26 (36)	63:37
8a	$Pd(PPh_3)_4$ (10)	—	12 (47)	82:18
8b	$Pd(dba)_2$ (5)	15	25 (32)	80:20
8b	$Pd(dba)_2$ (10)	30	17 (67)	67:33
8b	$Pd(PPh_3)_4$ (5)	—	22 (82)	83:17
8b	$Pd(PPh_3)_4$ (10)	—	19 (22)	81:19

a) The palladium-catalyzed reactions of **8a, b** were carried out in AcOH at 80 °C for 4 h. *b*) The corrected yields based on the recovered starting material are given in parentheses.

The stereochemistry of the products **19a, b** was determined on the basis of the NMR spectral data. A nuclear Overhauser effect (NOE) was observed between the hydrogen atoms at the C_3 and C_5 positions in the NMR spectrum of **19a**, whereas such NOE was not observed in that of **19b**. The ratio of the two products (**19a, b**), determined by high performance liquid chromatographic (HPLC) analysis, was dependent on the reaction conditions employed, the species of the catalyst and the molar amount of the catalyst and the ligand. The *cis* isomer **19a** was preferentially (63—83%) formed under the reaction conditions examined. Similar results were ob-

tained with the acetoxy **5a** and the methoxycarbonyloxy compound **5b**.

In the palladium-catalyzed reaction of **18**, high stereoselectivity was observed. The allylic sulfone **18** was treated with a catalytic amount of a palladium catalyst, $Pd(dba)_2$ or $Pd(PPh_3)_4$, in acetic acid at 80 °C for 4 h to give dimethyl *cis*- and *trans*-5-isopropenyl-4-methylene-3-*p*-toluenesulfonyl-1,1-cyclohexanedicarboxylate (**20a, b**) with extremely high diastereoselectivity (88—96% diastereomeric excess). The ratios of the products **20a, b** were determined by HPLC analysis. The results obtained under various reaction conditions are summarized in Table II.

Table II. Stereochemical Studies on Palladium-Catalyzed Cyclizations of Allylic Sulfone **18**[a]

Catalyst (mol%)	PPh_3 (mol%)	Yield (%)[b] of **20a, b**	Ratio of **20a** to **20b**
$Pd(dba)_2$ (5)	15	31 (75)	95:5
$Pd(dba)_2$ (10)	30	29 (84)	94:6
$Pd(PPh_3)_4$ (5)	—	21 (59)	96:4
$Pd(PPh_3)_4$ (10)	—	25 (51)	98:2

a) The palladium-catalyzed reactions of **18** were carried out in AcOH at 80 °C for 4 h. *b*) The corrected yields based on the recovered starting material are given in parentheses.

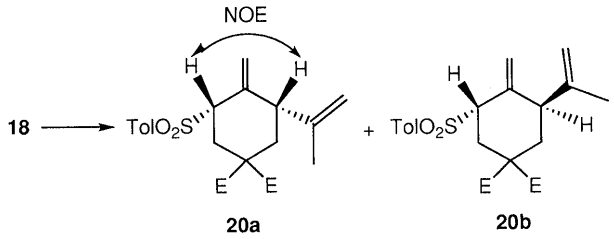

Chart 4

Similarly, the stereochemistry of the products **20a, b** was determined by NMR spectral analysis; NOE was observed between the hydrogen atoms at the C_3 and C_5 positions in the NMR spectrum of **20a**, but not in that of **20b**. In contrast to the afore-mentioned cyclization of **5a, b**, the methyl group of the isopropenyl substituent is highly effective for obtaining high diastereoselectivity.

Stereochemistry of Palladium-Catalyzed Cyclizations of Allylic Sulfones Palladium catalysts were reacted with allylic systems (**5a, b** and **18**) at the reactive allylic sites (allylic acetates and methyl carbonate) to form π-allylpalladium complexes. In the six-membered transition states **22a—c** for the metallo-ene cyclization, the transition state **22c** with an axial *p*-toluenesulfonyl group suffers extremely severe steric hindrance, particularly between the *p*-toluenesulfonyl group and the ester. Therefore, the palladium complexes were reacted with intramolecular olefins and underwent metallo-ene cyclizations preferentially *via* the six-membered transition states **22a, b** having equatorially orientated bulky groups (*p*-toluenesulfonyl), giving **24a, b** through reductive elimination of palladium in **23a, b**. Since the conformer **22b** has rather severe steric hindrance due to the *cis* confusion, the metallo-ene reaction would occur preferentially *via* **22a** to give **24a** as a major product. In particular, extremely high diastereoselectivity was observed in the case of **21** (R = CH_3), owing to the steric effects of the sterically bulky isopropenyl group in **22b**.

Thus, the products formed were controlled by the stereochemical environment in the transition states (**22a, b**) for cyclization without any equilibration between **24a** and **24b** in the presence of the palladium catalysts *via* π-allylpalladium complexes of the allylic sulfonyl parts,

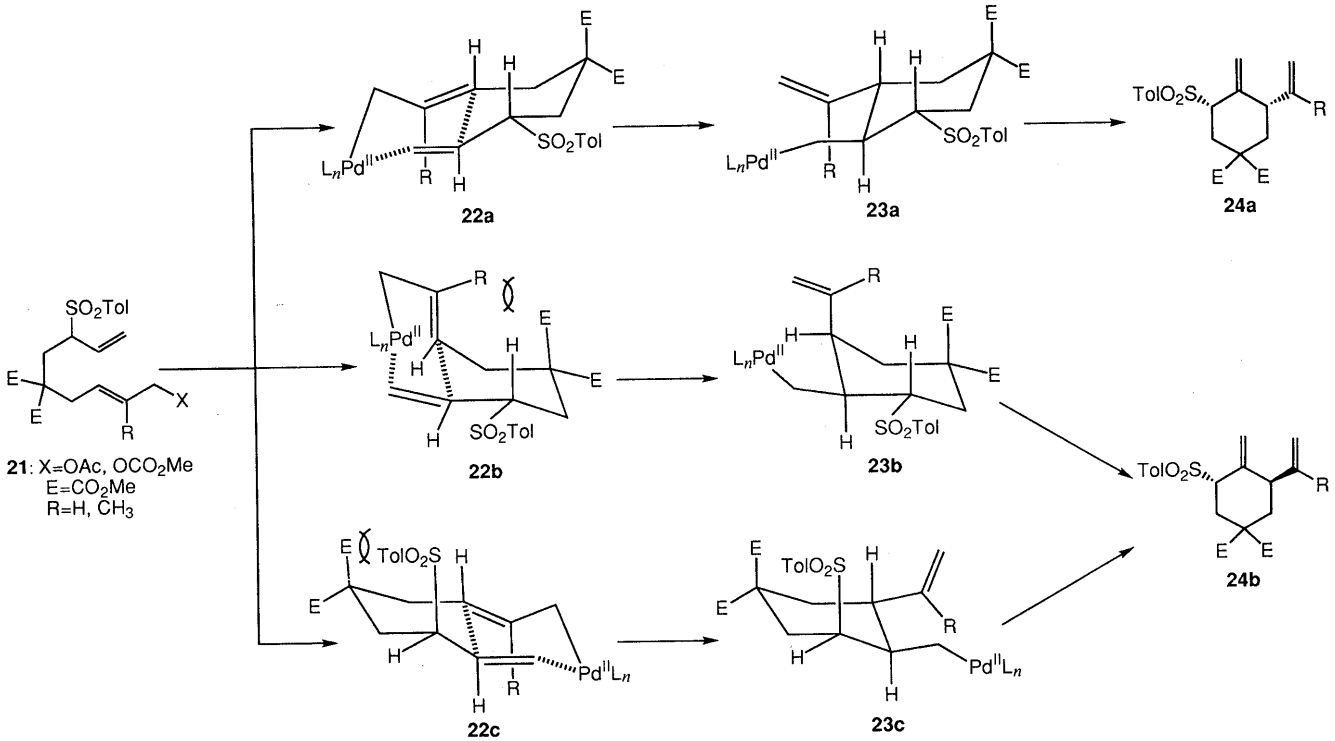

Chart 5

because no isomerization of the unstable isomer **24b** into the stable one **24a** was observed under the palladium-catalyzed reaction conditions in acetic acid at 80 °C (upon treatment with $Pd(PPh_3)_4$ in acetic acid at 80 °C for 4 h, **19a, b** (**19a** : **19b** = 81 : 19 and 69 : 31) was recovered without any change of the ratios).

In conclusion, these allylic systems bearing allylic sulfones at appropriate sites undergo metallo-ene cyclizations with the allylic sulfones as enophiles upon treatment with palladium catalysts in acetic acid to give cyclohexane derivatives having allylic sulfonyl groups, with extremely high diastereoselectivity.

Experimental

Infrared (IR) spectra were obtained in the indicated state with a JASCO DR-81 Fourier-transform infrared spectrometer. NMR spectra were determined in an indicated solvent with a JEOL GSX-400 (^{1}H-NMR, 400 MHz), EX-270 (^{1}H-NMR, 270 MHz), or JNM PMX-60SI (60 MHz) high resolution NMR spectrometer; chemical shifts are given in ppm from tetramethylsilane as an internal standard. Splitting patterns are designated as s, singlet; ss, singlet singlet; d, doublet; dd, doublet doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were taken on a JEOL JMS-DX303/JMA-DA5000 system. High performance liquid chromatographic data (HPLC) were obtained with a Tosoh UV-8010 CCPM (column, Tosoh TSK-gel ODS-80TM). Flash column chromatography was performed with Merck Silica gel 60 (230—400 mesh). Thin or thick layer plates dried at 140 °C for 3.5 h were used.

Dimethyl (4-Acetoxy-2(*Z*)-butenyl)propanedioate (1a) A dry 200 ml two-necked flask equipped with a septum inlet and a magnetic stirring, containing sodium hydride (NaH) (60% oil dispersion, 799 mg, 16.6 mmol), was flushed with nitrogen, and maintained under a positive pressure of nitrogen. Anhydrous (THF) (100 ml) was added to the flask. A solution of dimethyl malonate (2.98 g, 22.7 mmol) in anhydrous THF (10 ml) was added to the above solution at 0 °C and the mixture was stirred at 0 °C for 30 min. A solution of 4-acetoxy-2(*Z*)-butenyl bromide (2.9 g, 15.1 mmol) in anhydrous THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual colorless oil was isolated by column chromatography on silica gel with ether–hexane (1 : 4) to give **1a** (2.65 g, 72% yield). IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40—3.00 (2H, m, $C\underline{H}_2CH(CO_2Me)_2$), 3.20—3.50 (1H, m, $CH(CO_2Me)_2$), 3.70 (6H, s, $CH(CO_2C\underline{H}_3)_2$), 4.40—4.70 (2H, m, $AcOC\underline{H}_2$), 5.30—5.80 (2H, m, CH=CH). MS *m/z*: 244 (M^+). Exact mass determination: 244.0844 (Calcd for $C_{11}H_{16}O_6$: 244.0942).

Dimethyl (4-Methoxycarbonyloxy-2(*Z*)-butenyl)propanedioate (1b) The alkylation of dimethyl malonate (3.0 g, 22.7 mmol) with 4-methoxycarbonyloxy-2(*Z*)-butenyl bromide (3.3 g, 15.1 mmol) was carried out in the same manner as described in the preparation of **1a**. The crude colorless oil was subjected to column chromatography on silica gel (ether–hexane, 1 : 4) to give **1b** (2.8 g, 72% yield). IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.40—2.90 (2H, m, $C\underline{H}_2CH(CO_2Me)_2$), 3.20—3.50 (1H, m, $CH(CO_2Me)_2$), 3.70 (9H, s, $CH(CO_2C\underline{H}_3)_2$, CH_3O_2CO), 4.40—4.80 (2H, m, MeO_2COCH_2), 5.30—5.90(2H, m, CH=CH). MS *m/z*: 260 (M^+). Exact mass determination: 260.0903 (Calcd for $C_{11}H_{16}O_7$: 260.0896).

Dimethyl (4-Acetoxy-2(*Z*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z*)-butenyl]propanedioate (2a) A mixture of NaH (60% oil dispersion, 541 mg, 9.02 mmol) and **1a** (2.0 g, 8.2 mmol) in anhydrous THF (60 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z*)-butenyl bromide (2.1 g, 9.02 mmol) in anhydrous THF (10 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h. The reaction solution was diluted with ether, and washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 4) to give **2a** (2.35 g, 72% yield). IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40—4.70 (2H, m, $AcOCH_2$), 5.00—5.90 (4H, m, 2CH=CH). MS *m/z*: 398 (M^+). Exact mass determination: 398.1975 (Calcd for $C_{20}H_{30}O_8$: 398.1941).

Dimethyl (4-methoxycarbonyloxy-2(*Z*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z*)-butenyl]propanedioate (**2b**), dimethyl (4-acetoxy-2(*Z*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*E*)-butenyl]-propanedioate (**6a**) and dimethyl (4-methoxycarbonyloxy-2(*Z*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*E*)-butenyl]propanedioate (**6b**) were similarly prepared from **1a, b** and 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl bromide.

2b: 80% yield. IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40—4.80 (2H, m, MeO_2COCH_2), 5.00—5.90 (4H, m, 2CH=CH). MS *m/z*: 414 (M^+). Exact mass determination: 414.2038 (Calcd for $C_{20}H_{30}O_9$: 414.1890).

6a: 71% yield. IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40—4.70 (2H, m, $AcOCH_2$), 5.30—6.00 (2H, m, $AcOCH_2C\underline{H}=C\underline{H}$), 5.60—5.90 (2H, m, $THPOCH_2C\underline{H}=C\underline{H}$). MS *m/z*: 398 ($M^+$). Exact mass determination: 398.1975 (Calcd for $C_{20}H_{30}O_8$: 398.1941).

6b: 70% yield. IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40—4.80 (2H, m, MeO_2COCH_2), 5.60—5.90 (2H, m, $THPOCH_2C\underline{H}=C\underline{H}$), 5.80—6.10 (2H, m, $MeO_2COCH_2C\underline{H}=C\underline{H}$). MS *m/z*: 414 ($M^+$). Exact mass determination: 414.2038 (Calcd for $C_{20}H_{30}O_9$: 414.1890).

Dimethyl (4-Acetoxy-2(*Z*)-butenyl)(4-hydroxy-2(*Z*)-butenyl)propanedioate (3a) PPTS (6.3 mg, 0.025 mmol) was added to a solution of **2a** (200 mg, 0.50 mmol) in methanol (1.5 ml). The mixture was stirred at room temperature for 12 h and then concentrated to dryness. The residue was diluted with ether, and the solution was washed with saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 1) to give **3a** (134 mg, 85% yield). IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (3H, m, $HOCH_2$), 4.40—4.70 (2H, m, $AcOCH_2$), 5.10—6.00 (4H, m, 2CH=CH). MS *m/z*: 314 (M^+). Exact mass determination: 314.1354 (Calcd for $C_{15}H_{22}O_7$: 314.1366).

Dimethyl (4-hydroxy-2(*Z*)-butenyl)(4-methoxycarbonyloxy-2(*Z*)-butenyl)propanedioate (**3b**), dimethyl (4-acetoxy-2(*Z*)-butenyl)(4-hydroxy-2(*E*)-butenyl)propanedioate (**7a**) and dimethyl (4-hydroxy-2(*E*)-butenyl)(4-methoxycarbonyloxy-2(*Z*)-butenyl)propanedioate (**7b**) were similarly prepared from **2b** and **6a, b**.

3b: 93% yield. IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.90—4.21 (3H, m, $HOCH_2$), 4.40—4.80 (2H, m, MeO_2COCH_2), 5.10—6.00 (4H, m, 2CH=CH). MS *m/z*: 330 (M^+). Exact mass determination: 330.1295 (Calcd for $C_{15}H_{22}O_7$: 330.1315).

7a: 82% yield. IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (3H, m, $HOCH_2$), 4.40—4.70 (2H, m, $AcOCH_2$), 5.30—6.00 (2H, m, $AcOCH_2C\underline{H}=C\underline{H}$), 5.50—5.80 (2H, m, $HOCH_2C\underline{H}=C\underline{H}$). MS *m/z*: 314 ($M^+$). Exact mass determination: 314.1354 (Calcd for $C_{15}H_{22}O_7$: 314.1366).

7b: 88% yield. IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.90—4.21 (3H, m, $HOCH_2$), 4.40—4.80 (2H, m, MeO_2COCH_2), 5.50—5.80 (2H, m, $HOCH_2C\underline{H}=C\underline{H}$), 5.80—6.10 (2H, m, $MeO_2COCH_2C\underline{H}=C\underline{H}$). MS *m/z*: 330 ($M^+$). Exact mass determination: 330.1295 (Calcd for $C_{15}H_{22}O_7$: 330.1315).

Dimethyl (4-Acetoxy-2(*Z*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*Z*)-

butenyl)propanedioate (4a) A solution of *p*-toluenesulfinyl chloride (67 mg, 0.38 mmol) in anhydrous THF (1 ml) was added to a solution of **3a** (100 mg, 0.32 mmol) and triethylamine (Et_3N) (48 mg, 0.48 mmol) in anhydrous THF (6 ml) at 0 °C. The reaction mixture was stirred at 0 °C for 30 min, then diluted with ether, and the suspension was filtered through Celite. The filtrate was concentrated *in vacuo*. The residual yellow oil was subjected to preparative TLC (ether–hexane, 2 : 1) to give **4a** (123 mg, 85% yield). IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.80—4.80 (4H, m, $2OCH_2$), 5.00—5.90 (4H, m, 2CH=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 452 (M^+). Exact mass determination: 452.1390 (Calcd for $C_{22}H_{28}O_8S$: 452.1505).

Dimethyl (4-methoxycarbonyloxy-2(*Z*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*Z*)-butenyl)propanedioate (**4b**), dimethyl (4-acetoxy-2(*Z*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*E*)-butenyl)propanedioate (**8a**) and dimethyl (4-methoxycarbonyloxy-2(*Z*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*E*)-butenyl)propanedioate (**8b**) were similarly prepared from **3b** and **7a, b**.

4b: 85% yield. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.80—4.80 (4H, m, $2OCH_2$), 5.00—5.90 (4H, m, 2CH=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 468 (M^+). Exact mass determination: 468.1253 (Calcd for $C_{22}H_{28}O_9S$: 468.2454).

8a: 93% yield. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $CH_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.80—4.80 (4H, m, $2OCH_2$), 5.30—5.50 (2H, m, $AcOCH_2C\underline{H}=C\underline{H}$), 5.50—5.80 (2H, m, $Tol(O)SOCH_2C\underline{H}=C\underline{H}$), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 452 (M^+). Exact mass determination: 452.1390 (Calcd for $C_{22}H_{28}O_8S$: 452.1505).

8b: 74% yield. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C) 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (9H, s, $C(CO_2CH_3)_2$, CH_3O_2CO), 3.80—4.80 (4H, m, $2OCH_2$), 5.30—5.60 (2H, m, $MeO_2COCH_2C\underline{H}=C\underline{H}$), 5.60—5.90 (2H, m, $Tol(O)SOCH_2C\underline{H}=C\underline{H}$), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 468 (M^+). Exact mass determination: 468.1253 (Calcd for $C_{22}H_{28}O_9S$: 468.2454).

Dimethyl (4-Acetoxy-2(*Z*)-butenyl)(2-*p*-toluenesulfonyl-3-butenyl)propanedioate (5a) A solution of **4a** (100 mg, 0.22 mmol) in anhydrous DMF (2 ml) was stirred at 125 °C for 24 h and then concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 3 : 2) to give **5a** (91 mg, 91% yield). IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ^{1}H-NMR ($CDCl_3$) δ: 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.20—2.90 (4H, m, $(CH_2)_2C(CO_2Me)_2$), 3.60—3.80 (7H, m, $C(CO_2CH_3)_2$, CHS), 4.50—4.70 (2H, m, $AcOCH_2$), 4.90—5.30 (5H, dd, $CH_2=CH$), 5.35—5.60 (1H, m, $CH_2=C\underline{H}$), 5.30—5.80 (2H, m, CH=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 452 (M^+). Exact mass determination: 452.1501 (Calcd for $C_{22}H_{28}O_8S$: 452.1505).

Dimethyl (4-Methoxycarbonyloxy-2(*Z*)-butenyl)(2-*p*-toluenesulfonyl-3-butenyl)propanedioate (5b) The rearrangement of **4b** (100 mg, 0.21 mmol) into **5b** was carried out in the same manner as described in the preparation of **5a**. The crude product was subjected to preparative TLC (ether–hexane, 3 : 2) to give **5b** (91 mg, 91% yield). IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, $C\underline{H}_3C_6H_4$), 2.20—2.90 (4H, m, $(CH_2)_2C(CO_2Me)_2$), 3.60—3.80 (10H, m, $C(CO_2CH_3)_2$, CHS, CH_3O_2CO), 4.50—4.70 (2H, m, $AcOCH_2$), 4.90—5.30 (5H, dd, $C\underline{H}_2=CH$), 5.35—5.60 (1H, m, $CH_2=C\underline{H}$), 5.30—5.80 (2H, m, CH=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 468 (M^+). Exact mass determination: 468.1454 (Calcd for $C_{22}H_{28}O_9S$: 468.1454).

The thermal rearrangement of **8a, b** was carried out at 115 °C in the same manner as described above, to give **5a, b** in 86 and 85% yields.

2-Methyl-4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*E*)-buten-1-ol (10) Selenium dioxide (130.4 mg, 1.18 mmol) was added to a solution of 3-methyl-1-(tetrahydro-2*H*-pyran-2-yl)oxy-2-butene (**9**) (1000 mg, 5.88 mmol) in dichloromethane (21 ml) and 70% aqueous *tert*-butyl hydroperoxide (9.8 ml, 6.17 mmol). The reaction mixture was stirred at room temperature for 3 h and then concentrated to dryness. The residue was diluted with ether. The organic layer was washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 3) to give **10** (495 mg, 45% yield). IR ν_{max}^{film} cm^{-1}: 3400 (OH), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 1.70 (3H, s, $CH_3C=$), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 3.90—4.40 (3H, s, $HOCH_2$), 5.30—5.70 (1H, t, C=CH). MS *m/z*: 186 (M^+). Exact mass determination: 186.9854 (Calcd for $C_{10}H_{18}O_3$: 186.1256).

2-Methyl-4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*E*)-butenyl Acetate (11) A catalytic amount of 4-(dimethylamino)pyridine was added to a solution of **10** (1.59 g, 8.53 mmol) and Et_3N (1.6 ml, 12.8 mmol) in anhydrous dichloromethane (35 ml). A solution of acetic anhydride (957 mg, 9.37 mmol) in anhydrous dichloromethane (5 ml) was added to the above solution. The reaction mixture was stirred at room temperature for 1 h, diluted with dichloromethane, and washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 3) to give **11** (1.94 g, 100% yield). IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 3.30—3.90 (2H, m, $CHOC\underline{H}_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40—4.50 (2H, s, $AcOCH_2$), 5.40—5.70 (1H, t, C=CH). MS *m/z*: 228 (M^+). Exact mass determination: 228.1328 (Calcd for $C_{12}H_{20}O_4$: 228.1362).

4-Acetoxy-2-methyl-2-buten-1-ol (12) PPTS (111 mg, 0.54 mmol) was added to a solution of **11** (2.0 g, 8.77 mmol) in methanol (18 ml). The reaction mixture was stirred at room temperature for 3 h and then concentrated to dryness. The residue was diluted with ether. The solution was washed with saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 1) to give **12** (889 mg, 71% yield). IR ν_{max}^{film} cm^{-1}: 3400 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 3.90—4.30 (3H, m, $HOCH_2$), 4.40 (2H, s, $AcOCH_2$), 5.40—5.70 (1H, t, C=CH). MS *m/z*: 144 (M^+). Exact mass determination: 144.0786 (Calcd for $C_7H_{12}O_3$: 144.0786).

Dimethyl (4-Acetoxy-3-methyl-2(*E*)-butenyl)propanedioate (14) A solution of NBS (1.32 g, 7.4 mmol) in anhydrous THF (15 ml) was added to a mixture of triphenylphosphine (PPh_3) (1.95 g, 7.4 mmol) and **12** (889 mg, 6.17 mmol) in anhydrous THF (45 ml), and the reaction mixture was stirred at room temperature for 1 h under a nitrogen atmosphere, diluted with ether, and washed with 10% aqueous NaOH and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to column chromatography (ether–hexane, 1 : 6) to give 4-acetoxy-3-methyl-2(*E*)-butenyl bromide (**13**) (1.11 g, 87% yield) [IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 3.80—4.10 (2H, d, $BrCH_2$), 4.40 (2H, s, $AcOCH_2$), 5.60—6.00 (1H, t, C=CH)]. A mixture of NaH (60% oil dispersion, 288 mg, 4.81 mmol) and dimethyl malonate (865 mg, 6.55 mmol) in anhydrous THF (45 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of **13** (900 mg, 4.37 mmol) obtained above in anhydrous THF (5 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h, then diluted with ether, and washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, then dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography (ether–hexane, 1 : 4) to give **14** (1.0 g, 89% yield). IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.30—2.80 (2H, m, $C\underline{H}_2CH(CO_2Me)_2$), 3.10—3.40 (1H, m, $CH(CO_2Me)_2$), 3.70 (6H, s, $CH(CO_2C\underline{H}_3)_2$), 4.40 (2H, s, $AcOCH_2$), 5.10—5.50 (1H, t, C=CH). MS *m/z*: 258 (M^+). Exact mass determination: 258.1063 (Calcd for $C_{12}H_{18}O_6$: 258.1104).

Dimethyl (4-Acetoxy-3-methyl-2(*E*)-butenyl)[4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl]propanedioate (15a, b) A mixture of NaH (60% oil dispersion, 256 mg, 3.88 mmol) and **14** (1.0 g, 3.88 mmol) in anhydrous THF (45 ml) was stirred at 0 °C for 30 min under a nitrogen atmosphere. A solution of 4-(tetrahydro-2*H*-pyran-2-yl)oxy-2(*Z* or *E*)-butenyl bromide (1.0 g, 4.26 mmol) in anhydrous THF (5 ml) was added and the reaction mixture was further stirred at 0 °C for 2 h, diluted with ether, and washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual colorless oil was subjected to column chromatography

(ether–hexane, 1:4) to give **15a** (1.35 g, 84% yield) or **15b** (1.44 g, 90% yield), respectively.

15a: IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOCH_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40 (2H, s, $AcOCH_2$), 5.10—5.50 (1H, t, C=CH), 5.50—5.90 (2H, m, CH=CH). MS *m/z*: 412 (M^+). Exact mass determination: 412.2115 (Calcd for $C_{21}H_{32}O_8$: 412.2097).

15b: IR ν_{max}^{film} cm^{-1}: 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.40—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.30—3.90 (2H, m, $CHOCH_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.90—4.21 (2H, m, $THPOCH_2$), 4.21—4.40 (1H, m, OCHO), 4.40 (2H, s, $AcOCH_2$), 5.10—5.50 (1H, t, C=CH), 5.60—5.80 (2H, m, CH=CH). MS *m/z*: 412 (M^+). Exact mass determination: 412.2115 (Calcd for $C_{21}H_{32}O_8$: 412.2097).

Dimethyl (4-Acetoxy-3-methyl-2(*E*)-butenyl)(4-hydroxy-2(*Z* or *E*)-butenyl)propanedioate (16a, b) PPTS (41 mg, 0.16 mmol) was added to a solution of **15a, b** (1.35 g, 3.26 mmol) in methanol (6.5 ml). The reaction mixture was stirred at room temperature for 12 h and then concentrated to dryness under reduced pressure. The residue was diluted with ether. The solution was washed with saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to column chromatography (ether–hexane, 1:1) to give **16a, b** (788 mg, 74% yield).

16a: IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.50—2.80 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 4.00—4.30 (3H, m, $HOCH_2$), 4.40 (2H, s, $AcOCH_2$), 5.10—5.50 (1H, t, C=CH), 5.40—6.00 (2H, m, CH=CH). MS *m/z*: 328 (M^+). Exact mass determination: 328.1827 (Calcd for $C_{16}H_{24}O_7$: 328.1522).

16b: IR ν_{max}^{film} cm^{-1}: 3470 (OH), 1750 (C=O), 1650 (C=C). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.50—2.80 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 4.00—4.30 (3H, m, $HOCH_2$), 4.40 (2H, s, $AcOCH_2$), 5.10—5.50 (1H, t, C=CH), 5.50—5.80 (2H, m, CH=CH). MS *m/z*: 412 (M^+). Exact mass determination: 412.2115 (Calcd for $C_{21}H_{32}O_8$: 412.2097).

Dimethyl (4-Acetoxy-3-methyl-2(*E*)-butenyl)(4-*p*-toluenesulfinyloxy-2(*Z* or *E*)-butenyl)propanedioate (17a, b) A solution of *p*-toluenesulfinyl chloride (192 mg, 1.10 mmol) in anhydrous THF (3 ml) was added to a mixture of **16a, b** (300 mg, 0.91 mmol) and Et_3N (0.19 ml, 1.37 mmol) in anhydrous THF (17 ml). The reaction mixture was stirred at 0 °C for 30 min. The reaction solution was diluted with ether, and the suspension was filtered through Celite. The filtrate was concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 2:1) to give **17a, b** (336 mg, 79% yield).

17a: IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $CH_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.80—4.80 (4H, m, $2OCH_2$), 5.00—5.90 (3H, m, CH=CH, C=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 466 (M^+). Exact mass determination: 466.1522 (Calcd for $C_{23}H_{30}O_8S$: 466.1661).

17b: IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1140 (sulfinate). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $CH_3C_6H_4$), 2.20—2.90 (4H, d, $(CH_2)_2C(CO_2Me)_2$), 3.70 (6H, s, $C(CO_2CH_3)_2$), 3.80—4.80 (4H, m, $2OCH_2$), 5.00—5.50 (1H, m, C=CH), 5.50—5.70 (2H, m, CH=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 466 (M^+). Exact mass determination: 466.1522 (Calcd for $C_{23}H_{30}O_8S$: 466.1661).

Dimethyl (4-Acetoxy-3-methyl-2(*E*)-butenyl)(2-*p*-toluenesulfonyl-3-butenyl)propanedioate (18) A solution of **17a, b** (100 mg, 0.21 mmol) in anhydrous DMF (2 ml) was stirred at 125 °C or 115 °C for 24 h and then concentrated under reduced pressure. The crude product was subjected to preparative TLC (ether–hexane, 3:2) to give **18** (93 mg, 93% yield or 90 mg, 90% yield, respectively). IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.00 (3H, s, CH_3CO_2), 2.40 (3H, s, $CH_3C_6H_4$), 2.20—2.90 (4H, m, $(CH_2)_2C(CO_2Me)_2$), 3.60—3.80 (7H, m, $C(CO_2CH_3)_2$, CHS), 4.40 (2H, s, $AcOCH_2$), 4.90—5.30 (2H, dd, $CH_2=CH$), 5.35—5.60 (1H, m, $CH_2=CH$), 5.30—5.80 (1H, m, C=CH), 7.20—7.80 (4H, m, C_6H_4). MS *m/z*: 466 (M^+). Exact mass determination: 466.1834 (Calcd for $C_{23}H_{30}O_8S$: 466.1661).

Dimethyl 4-Methylene-3-*p*-toluenesulfonyl-5-vinyl-1,1-cyclohexanedicarboxylate (19) A mixture of $Pd(dba)_2$ (3.1 mg, 0.005 mmol) and PPh_3 (4.3 mg, 0.016 mmol) in anhydrous AcOH (1 ml) was stirred at room temperature for 5 min under a nitrogen atmosphere. A solution of **5a** (50 mg, 0.11 mmol) in anhydrous AcOH (1 ml) was added and the mixture was stirred at 80 °C for 4 h. The mixture was filtered through Celite and the filtrate was concentrated to dryness under reduced pressure. The residue was diluted with dichloromethane, and the solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl. The organic layers were combined, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to preparative TLC (ether–hexane, 3:2) to give **19** (10 mg, 24% yield). The results obtained with **5a, b** under other reaction conditions are listed in Table I. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ^{1}H-NMR ($CDCl_3$) δ: 2.40 (3H, s, $CH_3C_6H_4$), 1.80—2.80 (5H, m, $CH_2=CHCH$, $(CH_2)_2C(CO_2Me)_2$), 3.60—3.80 (6H, m, $C(CO_2CH_3)_2$), 3.80—4.00 (1H, m, CHS), 4.90—5.10 (1H, m, $CH_2=CH$), 5.00—5.20 (2H, dd, $CH_2=CH$), 5.20—5.70 (2H, ss, $CH_2=C$), 7.20—7.90 (4H, m, C_6H_4). MS *m/z*: 392 (M^+). Exact mass determination: 392.1271 (Calcd for $C_{20}H_{24}O_6S$: 392.1294).

Dimethyl 5-Isopropenyl-4-methylene-3-*p*-toluenesulfonyl-1,1-cyclohexanedicarboxylate (20) The palladium-catalyzed cyclization of **18** (50 mg, 0.11 mmol) was carried out in the same manner as described in the preparation of **19**. The crude product was subjected to preparative TLC (ether–hexane, 3:2) to give **20** (14 mg, 31% yield). The results obtained under other reaction conditions are listed in Table II. IR ν_{max}^{film} cm^{-1}: 1740 (C=O), 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). ^{1}H-NMR ($CDCl_3$) δ: 1.70 (3H, s, $CH_3C=$), 2.40 (3H, s, $CH_3C_6H_4$), 1.80—2.80 (5H, m, $CH_2=CCH_3CH$, $(CH_2)_2C(CO_2Me)_2$), 3.60—3.80 (6H, m, $C(CO_2CH_3)_2$), 3.90—4.00 (1H, m, CHS), 4.80—5.10 (2H, ss, $CH_2=CCH_3$), 5.10—5.70 (2H, ss, $CH_2=C$), 7.20—7.90 (4H, m, C_6H_4). MS *m/z*: 406 (M^+). Exact mass determination: 406.1481 (Calcd for $C_{21}H_{26}O_6S$: 406.1450).

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