[Chem. Pharm. Bull. 36(5)1727—1737(1988)]

Palladium-Catalyzed Allylic Sulfinate–Sulfone Rearrangements

KUNIO HIROI* and KUNITAKA MAKINO

Department of Synthetic Organic Chemistry, Tohoku College of Pharmacy, 4–4–1 Komatsushima, Sendai, Miyagi 983, Japan

(Received October 27, 1987)

Upon treatment with a zero-valent palladium catalyst, tetrakis(triphenylphosphine)palladium, in tetrahydrofuran under mild conditions allylic *p*-toluenesulfinates underwent α- or γ-rearrangements of the sulfonyl group *via* ionic intermediates to give allylic sulfones. The regiochemistry of the rearrangements depends on the character of the intermediary allylic cationic carbons generated and the steric hindrance involved therein.

Keywords——allylic sulfinate; allylic sulfone; palladium catalyst; sulfinate–sulfone rearrangment; regiochemistry; tetrakis(triphenylphosphine)palladium

Thermal sulfinate–sulfone rearrangements are well known[1] and have been widely used, usually under solvolytic conditions. Hitherto much attention has been devoted by many investigators to the mechanistic pathway for the rearrangements,[2] but no report has appeared on the stereochemistry of the rearrangements.

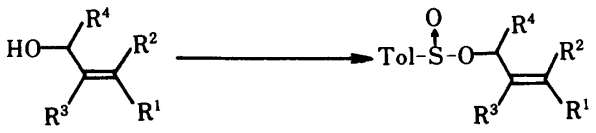
Recently we have disclosed the stereochemistry of thermal allylic sulfinate–sulfone rearrangements, using chiral allylic sulfinates possessing chirality on the sulfur atoms.[3] We have also continued our attempts to develop a new method for facile transformation of allylic sulfinates into sulfones by activation with metal catalysts. Finally, quite recently we have found palladium-catalyzed allylic sulfinate–sulfone rearrangements: allylic sulfinates were smoothly converted into allylic sulfones under mild conditions assisted by a zero-valent palladium catalyst.[4]

Many studies have been reported on palladium-catalyzed reactions of allylic systems[5] such as allylic acetates,[6] carbonates,[5i] carbamates,[7] phosphates,[8] amines,[9] nitro compounds,[10] and sulfones,[11] but no paper has been published on palladium-catalyzed reactions of allylic sulfinates. We wish to describe herein the details of the palladium-catalyzed rearrangements of allylic sulfinates into sulfones.

In general, allylic sulfinates **2a**—**o** were easily prepared in good yields by reacting allylic alcohols **1a**—**o** with *p*-toluenesulfinyl chloride in tetrahydrofuran (THF) at 0 °C in the presence of pyridine.

Treatment of allylic sulfinates thus obtained with a zero-valent palladium catalyst afforded allylic sulfones with various degrees of regioselectivity, depending on the stereochemical properties of the substituents involved in the allylic moieties.

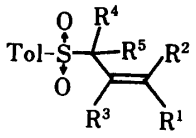
The palladium-catalyzed rearrangement of (*E*)-2-butenyl *p*-toluenesulfinate (**2a**) was carried out by treating **2a** with 0.15 eq of tetrakis(triphenylphosphine)palladium in the presence of 0.66 eq of triphenylphosphine in THF at 0, 50, or 60 °C to afford allylic sulfones, as a 20 : 80 mixture of (*E*)-2-butenyl *p*-tolyl sulfone (**3a**) and 1-buten-3-yl *p*-tolyl sulfone (**3c**), in 86, 93, or 94% yield, respectively. Rearrangement of (*Z*)-2-butenyl *p*-toluenesulfinate (**2b**) under the same conditions at 0 °C, room temperature, or 50 °C gave the corresponding allylic sulfones in 92, 79, or 65% yields with the same ratio of (*E*)- and (*Z*)-2-butenyl *p*-tolyl sulfone (**3a**) and (**3b**) [**3a** : **3b** = 2 : 3, 1 : 1, or 3 : 2] to **3c** as described above, respectively. The



1a—o **2a—o**

a:	$R^1=CH_3$	$R^2=H$	$R^3=H$	$R^4=H$
b:	$R^1=H$	$R^2=CH_3$	$R^3=H$	$R^4=H$
c:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_3$
d:	$R^1=CH_3$	$R^2=CH_3$	$R^3=H$	$R^4=H$
e:	$R^1=CH_3$	$R^2=H$	$R^3=CH_3$	$R^4=H$
f:	$R^1=CH_3$	$R^2=H$	$R^3=C_2H_5$	$R^4=H$
g:	$R^1=n\text{-}C_3H_7$	$R^2=H$	$R^3=H$	$R^4=H$
h:	$R^1=H$	$R^2=n\text{-}C_3H_7$	$R^3=H$	$R^4=H$
i:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=n\text{-}C_3H_7$
j:	$R^1=n\text{-}C_5H_{11}$	$R^2=H$	$R^3=H$	$R^4=H$
k:	$R^1=H$	$R^2=n\text{-}C_5H_{11}$	$R^3=H$	$R^4=H$
l:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=n\text{-}C_5H_{11}$
m:	$R^1=CH_2CH_2CH=C(CH_3)_2$	$R^2=CH_3$	$R^3=H$	$R^4=H$
n:	$R^1=H$	$R^2=CH_2OTHP$	$R^3=H$	$R^4=H$
o:	$R^1=CH_2CH_2COCH_2CO_2CH_3$	$R^2=H$	$R^3=H$	$R^4=H$

Chart 1

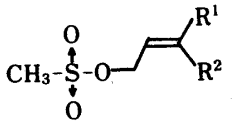


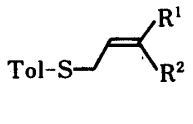
3

3a:	$R^1=CH_3$	$R^2=H$	$R^3=H$	$R^4=H$	$R^5=H$
3b:	$R^1=H$	$R^2=CH_3$	$R^3=H$	$R^4=H$	$R^5=H$
3c:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_3$	$R^5=H$
3d:	$R^1=CH_3$	$R^2=CH_3$	$R^3=H$	$R^4=H$	$R^5=H$
3e:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_3$	$R^5=CH_3$
3f:	$R^1=CH_3$	$R^2=H$	$R^3=CH_3$	$R^4=H$	$R^5=H$
3g:	$R^1=H$	$R^2=H$	$R^3=CH_3$	$R^4=CH_3$	$R^5=H$
3h:	$R^1=CH_3$	$R^2=H$	$R^3=C_2H_5$	$R^4=H$	$R^5=H$
3i:	$R^1=H$	$R^2=H$	$R^3=C_2H_5$	$R^4=CH_3$	$R^5=H$
3j:	$R^1=n\text{-}C_3H_7$	$R^2=H$	$R^3=H$	$R^4=H$	$R^5=H$
3k:	$R^1=H$	$R^2=n\text{-}C_3H_7$	$R^3=H$	$R^4=H$	$R^5=H$
3l:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=n\text{-}C_3H_7$	$R^5=H$
3m:	$R^1=n\text{-}C_5H_{11}$	$R^2=H$	$R^3=H$	$R^4=H$	$R^5=H$
3n:	$R^1=H$	$R^2=n\text{-}C_5H_{11}$	$R^3=H$	$R^4=H$	$R^5=H$
3o:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=n\text{-}C_5H_{11}$	$R^5=H$
3p:	$R^1=CH_2CH_2CH=C(CH_3)_2$	$R^2=CH_3$	$R^3=H$	$R^4=H$	$R^5=H$
3q:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_2CH_2CH=C(CH_3)_2$	$R^5=CH_3$
3r:	$R^1=CH_2OTHP$	$R^2=H$	$R^3=H$	$R^4=H$	$R^5=H$
3s:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_2OTHP$	$R^5=H$
3t:	$R^1=H$	$R^2=H$	$R^3=H$	$R^4=CH_2CH_2COCH_2CO_2CH_3$	$R^5=H$

Chart 2

stereochemistry in the olefinic part was partially retained in this case. The degree of retention of (*Z*)-configuration was greater in the catalysis at lower reaction temperature. The stereochemistry of the olefin in the produced 2-butenyl *p*-tolyl sulfone was determined by comparison of the nuclear magnetic resonance (NMR) spectra with those of authentic samples prepared from (*E*)- and (*Z*)-2-butenyl alcohols (**1a** and **1b**) by mesylation of the





	4a—f	5a—f
a:	$R^1=CH_3$	$R^2=H$
b:	$R^1=H$	$R^2=CH_3$
c:	$R^1=n\text{-}C_3H_7$	$R^2=H$
d:	$R^1=H$	$R^2=n\text{-}C_3H_7$
e:	$R^1=n\text{-}C_5H_{11}$	$R^2=H$
f:	$R^1=H$	$R^2=n\text{-}C_5H_{11}$

Chart 3

alcohols, followed by substitution of the mesylates **4a**, **b** with sodium *p*-toluenethiolate and subsequent oxidation of the produced sulfides **5a**, **b** with sodium metaperiodate. The ratio of the olefinic isomers was determined by high-performance liquid chromatography (HPLC).

Similarly, palladium-catalyzed rearrangement of 1-buten-3-yl *p*-toluenesulfinate (**2c**) under the same conditions at 0 °C, room temperature, or 50 °C led to the smooth formation of allylic sulfones **3a** (17%) and **3c** (83%) in 82, 71, or 85% yield.

Thus, it should be concluded that in the catalysis of α- or γ-methylated-allyl *p*-toluenesulfinates **2a—c**, the more -α-substituted allylic sulfone **3c** was preferentially formed, regardless of stereochemistry of the olefin and of the α- or γ-position of the methyl substituent, in a 4 : 1 ratio of **3c** to **3a**, and in the case of **2b** the (*Z*)-configuration was partially retained with various degrees of stereoselectivity, depending on the reaction conditions used.

Treatment of (*E*)-2-hexenyl *p*-toluenesulfinate (**2g**) with tetrakis(triphenylphosphine)-palladium in THF at −78, 0 °C, room temperature, or 50 °C gave a 60 : 40 mixture of (*E*)-2-hexenyl *p*-tolyl sulfone (**3j**) and 1-hexen-3-yl *p*-tolyl sulfone (**3l**) in 82, 96, 90, or 78% yield, respectively. Palladium catalysis of (*Z*)-2-hexenyl *p*-toluenesulfinate (**2h**) at 0 °C, room temperature, or 50 °C provided a 40 : 60 mixture of **3l** and **3j**, **k** [**3j** : **3k** = 7 : 3, 4 : 1, or 5 : 1], with partial retention of the (*Z*)-configuration, in 86, 69, or 68% yield, respectively. The ratios of **3j** to **3k** were determined by HPLC analysis. Rearrangement of 1-hexen-3-yl *p*-toluenesulfinate (**2i**) under the same conditions at 0 °C provided a 60 : 40 mixture of **3j** and **3l** in 98% yeild.

Similar results were obtained in octenyl sulfinate systems: palladium-catalyzed rearrangement of (*E*)-2-octenyl and 1-octen-3-yl *p*-toluenesulfinate (**2j**) and (**2l**) at 0—50 °C produced allylic sulfones as a 70 : 30 mixture of 2-octenyl *p*-tolyl sulfone (**3m**) and 1-octen-3-yl *p*-tolyl sulfone (**3o**) in 64 and 83—96% yields, respectively. In the rearrangement of (*Z*)-2-octenyl *p*-toluenesulfinate (**2k**) the predominant product was the more stable (*E*)-isomer **3m** [**3m** : **3n** = 4 : 1 (at 0 °C), 5 : 1 (at room temperature), and 6 : 1 (at 50 °C)], produced by partial isomerization of the carbon–carbon double bond *via* a carbonium ion intermediate assisted by the palladium catalyst.

Thus, the palladium-catalyzed rearrangement of the α- or γ-methyl-substituted allyl sulfinates produced preferentially the more-α-substituted allylic sulfone (**3c**) with high regioselectivity, while greater steric bulkiness of the substituents in allylic sulfinates resulted in a preference for less-α-substituted allylic sulfones, presumably because of the steric hindrance involved.

γ,γ-Dimethylated-allyl sulfinate underwent γ-rearrangement with complete regioselectivity, in preference to α-rearrangement in the palladium-catalyzed reaction. Upon treatment of 3-methyl-2-butenyl *p*-toluenesulfinate (**2d**) with tetrakis(triphenylphosphine)palladium in THF at 0 °C, room temperature, or 50 °C, 3-methyl-1-buten-3-yl *p*-tolyl sulfone (**3e**) was prepared as the only isolatable product in a quantitative yield; the α-rearranged sulfone **3d** was not detected.

However, increase of steric bulkiness of the γ-substituents in γ,γ-disubstituted-allyl sulfinates decreased the ratios of γ-rearranged products to α-ones. Palladium catalysis of

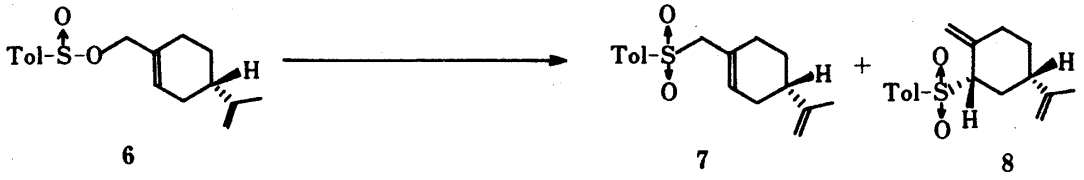
geranyl *p*-toluenesulfinate (**2m**) under the same conditions as described earlier at 0 °C, room temperature, or 50 °C afforded γ- and α-rearranged allylic sulfones (94, 91, or 89% yield) in an 80 : 20 ratio of **3q** to **3p**, respectively.

Palladium catalysis of (*Z*)-4-(tetrahydro-2-pyranyloxy)-2-butenyl *p*-toluenesulfinate (**2n**) gave **3r** (86%) [the (*E*)-configuration was determined by NMR analysis] and **3s** (14%) through preferential α-rearrangement for steric reasons. On the other hand, catalysis of (*Z*)-7-methoxycarbonyl-6-oxo-2-heptenyl *p*-toluenesulfinate (**2o**) by palladium provided the γ-

TABLE I. Palladium-Catalyzed Rearrangements of Allylic Sulfinates into Sulfones

2	Reaction conditions[a]		Yields of 3 (%)	Ratio of α to γ[b]
	Reaction temp. (°C)	Reaction time (h)		α : γ
2a	66	10.0	94	20 80
2a	50	10.0	93	20 80
2a	0	1.0	86	20 80
2b	66	10.0	65	20 80
2b	50	10.0	65	20 80
2b	r.t.	15.0	79	20 80
2b	0	20.0	92	20 80
2c	50	4.5	85	83 17
2c	r.t.	18.0	71	83 17
2c	0	24.5	82	83 17
2d	50	7.0	92	0 100
2d	r.t.	8.0	69	0 100
2d	0	24.5	75	0 100
2e	50	6.0	80	0 100
2e	r.t.	19.0	78	0 100
2e	0	24.0	83	0 100
2f	50	6.0	88	0 100
2f	r.t.	18.0	83	0 100
2f	0	24.0	85	0 100
2g	50	8.0	78	60 40
2g	r.t.	13.5	90	60 40
2g	0	16.5	96	60 40
2g	−78	6.0	82	60 40
2h	50	10.0	68	60 40
2h	r.t.	20.5	69	60 40
2h	0	24.0	86	60 40
2i	50	1.0	85	59 41
2i	r.t.	3.5	89	62 38
2i	0	8.0	98	60 40
2j	r.t.	15.5	64	70 30
2k	50	10.0	63	70 30
2k	r.t.	17.0	69	70 30
2k	0	23.0	72	70 30
2l	50	1.0	83	30 70
2l	r.t.	2.5	91	30 70
2l	0	7.0	96	30 70
2m	50	10.0	89	20 80
2m	r.t.	17.0	91	20 80
2m	0	26.0	94	20 80
2n[c]	r.t.	16.0	90	86 14
2o[c]	0	1.0	66	0 100

a) Each reaction was carried out in THF in the presence of 0.15 eq of tetrakis(triphenylphosphine)palladium and 0.66 eq of triphenylphosphine. *b*) The ratios of α- to γ-attack of a sulfonyl group in allylic systems are listed. *c*) Tetrakis-(triphenylphosphine)palladium (0.10 eq) and triphenylphosphine (0.44 eq) were used. r.t. = room temperature.



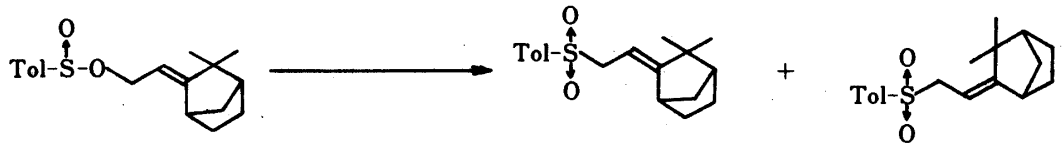
6 7 8

Chart 4

TABLE II. Palladium-Catalyzed Rearrangement of **6**[a]

Reaction temp. (°C)	Reaction time (h)	Yields of **7** and **8** (%)	Ratio of **7** to **8** **7**:**8**
50	10.0	99	48 52
r.t.	20.5	88	45 55
0	24.0	97	48 52

a) Each reaction was carried out in THF in the presence of 0.15 eq of tetrakis(triphenylphosphine)palladium and 0.66 eq of triphenylphosphine. r.t. = room temperature.



9 10a 10b

Chart 5

TABLE III. Palladium-Catalyzed Rearrangement of **9**[a]

Reaction temp. (°C)	Reaction time (h)	Yields of **10**	Ratio of **10a** to **10b** **10a**:**10b**
50	10.0	68	50 50
r.t.	19.0	59	65 35
0	26.0	79	56 44

a) Each reaction was carried out in THF in the presence of 0.15 eq of tetrakis(triphenylphosphine)palladium and 0.66 eq of triphenylphosphine. r.t. = room temperature.

rearranged allylic sulfone **3t**, in spite of steric hindrance at the γ-position of the system, without any detectable formation of the α-rearranged sulfone.

β-Substitution in crotyl sulfinates promoted formation of γ-rearranged allylic sulfones in the palladium catalysis. Upon treatment of 2-methyl-2-butenyl and 2-ethyl-2-butenyl *p*-toluenesulfinate (**2e**) and (**2f**) with tetrakis(triphenylphosphine)palladium in THF, γ-rearranged allylic sulfones, 2-methyl-1-buten-3-yl and 2-ethyl-1-buten-3-yl *p*-tolyl sulfone (**3g**) and (**3i**), were prepared with high regioselectivity and no α-rearranged product (**3f** or **3h**) was detected.

All of the results obtained above are summarized in Table I.

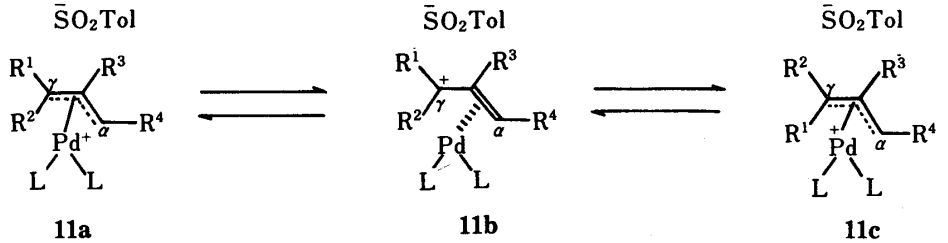
Next, palladium-catalyzed rearrangements of cyclic allylic sulfinates were examined. In the case of the *endo*-cyclic allylic sulfinate **6**, prepared from commercially available (*S*)-perillyl alcohol, both α- and γ-rearrangements occurred to afford **7** (45—48%) and **8** (52—55%) in extremely high total yield, as listed in Table II.

Palladium-catalyzed rearrangement of the *exo*-cyclic allylic sulfinate **9**, prepared from commercially available patchenol, provided only the α-rearranged product **10** with a 50—65 : 35—50 ratio of the (*E*)-olefinic isomer **10a** to the (*Z*)-isomer **10b**, and no γ-rearrangement occurred because of the steric hindrance in the cyclic system. The results obtained are listed in Table III.

These results can be rationalized in terms of an ionic intermediary mechanism as follows. Previously we have suggested a cyclic transition state mechanism such as a [2, 3] sigmatropic rearrangement for thermal chiral allylic sulfinate–sulfone rearrangement on the basis of the observations of complete preference for γ-rearranged allylic sulfones and extremely high retention of optical activity on the sulfur atoms of chiral sulfinates in the thermolysis.[3] In contrast to this thermolysis, formation of both α- and γ-rearranged allylic sulfones was observed in the palladium catalysis of allylic sulfinates, as mentioned earlier. Therefore, a mechanistic pathway *via* ionic intermediates mediated by the palladium catalyst seems plausible for this transformation. The dissociated sulfonyl anion reacts with the electron deficient allylic carbons generated from the allylic sulfinates by the palladium catalyst. The regiochemistry in the attack of the sulfonyl group depends on the chemical properties of the carbocations generated and the steric environment in the allylic moieties. In the palladium-catalyzed rearrangement of the allylic sulfinates **2a**, **2b**, and **2c** possessing a methyl substituent at the α- or γ-position of the allyl moiety, the sulfonyl group reacted at the most stable cationic center C_γ in **11**, yielding the more-substituted allylic sulfone **3c** as the main product. The stereochemistry of the (*Z*)-olefin in **2b** was partially retained owing to incomplete equilibration between **11a** and **11c**, depending on the reaction conditions employed in this catalysis. However, allylic sulfinates **2g**—**l** having bulkier substituents than a methyl group underwent a rearrangement of the sufonyl group to sterically less-hindered allylic sites (C_α in **11**) to furnish mainly less-substituted allylic sulfones. In the rearrangements of **2h** and **2k**, the more stable (*E*)-allylic sulfones were formed predominantly by isomerization of the carbon–carbon double bonds during equilibration between **11a** and **11c**.

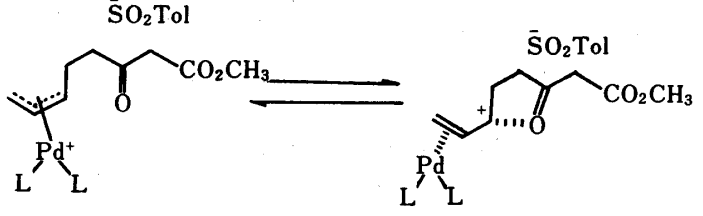
Exceptionally, palladium-catalyzed rearrangement of **2o** provided the more-substituted allylic sulfone **3t**, by reaction of the sulfonyl group with a γ-cationic carbon presumably stabilized by coordination of the carbonyl oxygen (**12b**).

In conclusion, allylic sulfinate–sulfone rearrangements were smoothly accomplished under extremely mild conditions with the assistance with a zero-valent palladium catalyst.



11a **11b** **11c**

Chart 6



12a **12b**

Chart 7

Experimental

Melting points were determined on a Yanagimoto melting point apparatus and are uncorrected. Thin-layer or preparative thick layer plates were made of Merck Silica gel 60PF-254 activated by drying at 140 °C for 3.5 h. The column for flash chromatography was made of Merck Silica gel 60. Infrared (IR) spectra were obtained in the indicated state with a Hitachi 215 spectrometer. NMR spectra were determined in the indicated solvent with a Hitachi R-24B high-resolution NMR spectrometer (60 MHz); chemical shifts are given in ppm from tetramethylsilane. Splitting patterns are designated as s, singlet; br s, broad singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra (MS) were taken on a Hitachi M-52G or JEOL TMS-01 SG-2 spectrometer and a JEOL JMA-DA-5000 JMS-DX-303 spectrometer. HPLC was conducted with HLC-803A (Toyo Soda) and UV-8 model II (Toyo, Soda), apparatus, using ODS-80TM (Toyo Soda) (acetonitrile–H_2O).

Allylic alcohols **1a**, **c**, **d**, **g**, **h**, **i**, **l**, **m**, (*S*)-perillyl alcohol, and patchenol are commercially available. Allylic alcohols **1b**,[12] **e**,[13] **f**,[14] **j**,[15] and **k**[15] were prepared according to the procedures reported.

(*Z*)-4-(Tetrahydro-2-pyranyloxy)-2-buten-1-ol (1n)——Two drops of phosphorus oxychloride were added by syringe to a mixture of 2.00 g (22.73 mmol) of (*Z*)-2-butene-1,4-diol and 2.44 ml (27.27 mmol) of dihydropyran in 30 ml of THF cooled to 0 °C. The reaction mixture was stirred at 0 °C for 1.5 h and then diluted with ether.

The solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to flash column chromatography over silica gel (ether–hexane, 2 : 1) to give 1.95 g (50% yield) of **1n**. IR ν_{max}^{film} cm^{-1}: 3400 (OH), 1650 (C=C). NMR (CCl_4) δ: 1.16—2.06 (6H, m, $(CH_2)_3$), 3.30—3.90 (2H, m, O–$CH_2(CH_2)_3$), 3.90—4.21 (2H, m, THPOCH_2), 4.21—4.46 (2H, m, CH_2OH), 4.46—4.73 (1H, m, O–CH–O), 5.23—5.96 (2H, m, CH=CH). MS *m/z*: 172 (M^+). Exact mass determination: 172.0990 (Calcd for $C_9H_{16}O_3$: 172.1099).

Synthesis of (*Z*)-Methyl 8-Hydroxy-3-oxo-6-octenoate (1o)——A solution of 1.56 g (13.60 mmol) of methanesulfonyl chloride was added to a mixture of 1.95 g (11.34 mmol) of **1n** and 4.76 ml (34.01 mmol) of triethylamine in 40 ml of THF cooled to 0 °C. The reaction mixture was stirred at 0 °C for 3 h and then diluted with ether. The ethereal solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The crude product was subjected to flash column chromatography over silica gel (ether–hexane, 5 : 1) to give 2.44 g (86% yield) of (*Z*)-4-(tetrahydro-2-pyranyloxy)-2-butenyl methanesulfonate. IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1350, 1170 (sulfonate). NMR (CCl_4) δ: 1.23—1.93 (6H, m, $(CH_2)_3$), 2.93 (3H, s, SO_3CH_3), 3.35—3.90 (2H, m, $OCH_2(CH_2)_3$), 4.00—4.23 (2H, m, THPOCH_2), 4.55—4.65 (1H, m, O–CH–O), 4.75 (2H, d, J=6 Hz, SO_3–CH_2), 5.49—6.00 (2H, m, CH=CH).

A 1.5 N hexane solution of butyllithium (13.70 ml, 21.47 mmol) was added to a solution of 3.00 ml (21.47 mmol) of diisopropylamine in 30 ml of THF at 0 °C. After 30 min, a solution of 1.05 ml (9.76 mmol) of methyl acetoacetate in 5 ml of THF was added dropwise to the above solution at 0 °C. The whole was stirred at 0 °C for 1 h, then a solution of 2.44 g (9.76 mmol) of (*Z*)-4-(tetrahydro-2-pyranyloxy)-2-butenyl methanesulfonate, obtained above, was added to the above mixture at 0 °C.

The reaction mixture was stirred at 0 °C for 2 h and then quenched with 10% aqueous HCl. The mixture was extracted with ether. The ethereal layers were combined, washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to preparative TLC (ether–hexane, 2 : 1) to give 2.24 g (85% yield) of (*Z*)-methyl 8-(tetrahydro-2-pyranyloxy)-3-oxo-6-octenoate. IR ν_{max}^{film} cm^{-1}: 1735 (ester), 1710 (ketone), 1650 (C=C). NMR (CCl_4) δ: 1.15—1.93 (6H, m, $(CH_2)_3$), 2.13—2.70 (4H, m, $C=C(CH_2)_2CO$), 3.30 (2H, s, $COCH_2CO$), 3.40—3.90 (2H, m, O–$CH_2(CH_2)_3$), 3.63 (3H, s, CO_2CH_3), 3.90—4.16 (2H, m, THPOCH_2), 4.41—4.65 (1H, m, O–CH–O), 5.26—5.65 (2H, m, CH=CH).

A solution of 2.24 g (8.30 mmol) of (*Z*)-methyl 8-(tetrahydro-2-pyranyloxy)-3-oxo-6-octenoate, obtained above, in 25 ml of methanol was stirred at room temperature for 2 h in the presence of a catalytic amount of *p*-toluenesulfonic acid. The solution was concentrated *in vacuo* and the residue was dissolved in ether. The ether solution was washed with saturated aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over Na_2SO_4, and concentrated *in vacuo*. The residual oil was subjected to preparative TLC (ether–hexane, 2 : 1) to give 1.28 g (83% yield) of **1o**. IR ν_{max}^{film} cm^{-1}: 3400 (OH), 1730 (ester), 1710 (ketone), 1650 (C=C). NMR (CCl_4) δ: 2.00—2.80 (4H, m, $C=C(CH_2)_2CO$), 3.39 (2H, s, $COCH_2CO$), 3.56 (3H, s, CO_2CH_3), 4.13 (2H, d, J=5 Hz, O–CH_2), 5.06—5.76 (2H, m, CH=CH). MS *m/z*: 186 (M^+). Exact mass determination: 186.1061 (Calcd for $C_9H_{14}O_4$: 186.0892).

Synthesis of Allylic Sulfinates 2a—o——General Procedure: *p*-Toluenesulfinyl chloride (1.45 g, 8.33 mmol) in 5 ml of THF was added to a solution of an allylic alcohol **1a—o** (6.94 mmol) and pyridine (1.12 ml, 13.89 mmol) in 10 ml of THF at 0 °C. The reaction mixture was stirred at 0 °C for 4 h and then diluted with ether. The ether solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, then dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to preparative TLC (ether–hexane, 1 : 2) to give the corresponding allylic sulfinate **2a—o** (quantitative yield). The spectral data of **2a**, **b**, **g**, **h**, **j**, and **k** were identical with those reported for samples prepared by other methods.[3]

1-Buten-3-yl *p*-Toluenesulfinate (**2c**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1145 (sulfinate). NMR (CCl_4) δ: 1.20, 1.27 (3H, dd, J=7, 7 Hz, $CHCH_3$), 2.35 (3H, s, $C_6H_4CH_3$), 4.50—6.12 (4H, m, CH–CH=CH_2), 6.96—7.63

(4H, m, C_6H_4). MS *m/z*: 210 (M^+). Exact mass determination: 210.0725 (Calcd for $C_{11}H_{14}O_2S$: 210.0713).

3-Methyl-2-butenyl *p*-Toluenesulfinate (**2d**): IR ν_{max}^{film} cm^{-1}: 1670 (C=C), 1600 (aromatic). NMR (CCl_4) δ: 1.55, 1.66 (6H, s, s, $C(CH_3)_2$), 2.36 (3H, s, $C_6H_4CH_3$), 3.53—4.53 (2H, m, O-CH_2), 4.96—5.36 (1H, m, CH=C), 7.03—7.66 (4H, m, C_6H_4). MS *m/z*: 224 (M^+). Exact mass determination: 224.0881 (Calcd for $C_{12}H_{16}O_2S$: 224.0871).

(*E*)-2-Methyl-2-butenyl *p*-Toluenesulfinate (**2e**): IR ν_{max}^{film} cm^{-1}: 1670 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 1.46—1.66 (6H, m, $CH_3C=CCH_3$), 2.33 (3H, s, $C_6H_4CH_3$), 3.53—4.33 (2H, m, O-CH_2), 5.00—5.46 (1H, m, CH_3-CH=C), 6.86—7.45 (4H, m, C_6H_4). MS *m/z*: 224 (M^+). Exact mass determination: 224.0941 (Calcd for $C_{12}H_{16}O_2S$: 224.0871).

(*E*)-2-Ethyl-2-butenyl *p*-Toluenesulfinate (**2f**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 0.91 (3H, t, J=7 Hz, CH_2CH_3), 1.57 (3H, d, J=7 Hz, $C=CCH_3$), 2.03 (2H, q, J=7, 7 Hz, CH_2CH_3), 2.40 (3H, s, $C_6H_4CH_3$), 3.53—4.43 (2H, m, O-CH_2), 5.10—5.53 (1H, m, CH_3CH=C), 6.99—7.55 (4H, m, C_6H_4). MS *m/z*: 238 (M^+). Exact mass determination: 238.1075 (Calcd for $C_{13}H_{18}O_2S$: 238.1028).

1-Hexen-3-yl *p*-Toluenesulfinate (**2i**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1140 (sulfinate). NMR (CCl_4) δ: 0.50—1.03 (3H, m, CH_2CH_3), 1.06—1.80 (4H, m, CH_2CH_2), 2.35 (3H, s, $C_6H_4CH_3$), 4.36—4.83 (1H, m, O-CH), 4.90—6.10 (3H, m, $CH=CH_2$), 7.06—7.60 (4H, m, C_6H_4). MS *m/z*: 238 (M^+). Exact mass determination: 238.0846 (Calcd for $C_{13}H_{18}O_2S$: 238.1027).

1-Octen-3-yl *p*-Toluenesulfinate (**2l**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1140 (sulfinate). NMR (CCl_4) δ: 0.61—1.08 (3H, m, CH_2CH_3), 1.12—1.82 (8H, m, $(CH_2)_4CH_3$), 2.35 (3H, s, $C_6H_4CH_3$), 4.38—4.85 (1H, m, O-CH), 4.92—6.00 (3H, m, $CH=CH_2$), 7.03—7.60 (4H, m, C_6H_4). MS *m/z*: 266 (M^+). Exact mass determination: 266.1333 (Calcd for $C_{15}H_{22}O_2S$: 266.1341).

Geranyl *p*-Toluenesulfinate (**2m**): IR ν_{max}^{film} cm^{-1}: 1670 (C=C), 1600 (aromatic), 1140 (sulfinate). NMR (CCl_4) δ: 1.55 (6H, s, $C(CH_3)_2$), 1.63 (3H, s, $C=CCH_3$), 1.89—2.12 (4H, m, CH_2CH_2), 2.40 (3H, s, $C_6H_4CH_3$), 3.20—4.49 (2H, m, O-CH_2), 4.76—5.40 (2H, m, $CH=CCH_2CH_2CH$), 7.09—7.56 (4H, m, C_6H_4). MS *m/z*: 292 (M^+). Exact mass determination: 292.1492 (Calcd for $C_{17}H_{24}O_2S$: 292.1496).

(*Z*)-4-(Tetrahydro-2-pyranyloxy)-2-butenyl *p*-Toluenesulfinate (**2n**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 1.25—1.90 (6H, m, $(CH_2)_3$), 2.40 (3H, s, $C_6H_4CH_3$), 3.12—4.30 (6H, m, $(O-CH_2)_3$), 4.36—4.68 (1H, m, O-CH), 5.35—5.83 (2H, m, CH=CH), 7.10—7.70 (4H, m, C_6H_4). MS *m/z*: 310 (M^+). Exact mass determination: 310.1211 (Calcd for $C_{16}H_{22}O_4S$: 310.1239).

(*Z*)-8-Methoxycarbonyl-6-oxo-2-octenyl *p*-Toluenesulfinate (**2o**): IR ν_{max}^{film} cm^{-1}: 1750 (ester), 1720 (ketone), 1655 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 2.13—2.76 (4H, m, $C=CCH_2CH_2$), 2.38 (3H, s, $C_6H_4CH_3$), 3.40 (2H, s, $COCH_2CO$), 3.66 (3H, s, CO_2CH_3), 3.93—4.73 (2H, m, O-CH_2), 5.30—5.70 (2H, m, CH=CH), 7.15—7.70 (4H, m, C_6H_4). MS *m/z*: 324 (M^+). Exact mass determination: 324.0949 (Calcd for $C_{16}H_{20}O_5S$: 324.1031).

Sulfinylation of (*S*)-perillyl alcohol and patchenol was carried out in the same way as described above.

(*S*)-Perillyl *p*-Toluenesulfinate (**6**): 85% yield. IR ν_{max}^{film} cm^{-1}: 1645 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 1.66 (3H, s, $C=CCH_3$), 1.82—2.20 (7H, m, $CH_2CH_2CHCH_2$), 2.37 (3H, s, $C_6H_4CH_3$), 3.56—4.36 (2H, m, O-CH_2), 4.60 (2H, s, $C=CH_2$), 5.66 (1H, br s, C=CH), 7.05—7.60 (4H, m, C_6H_4). MS *m/z*: 290 (M^+). Exact mass determination: 290.1402 (Calcd for $C_{17}H_{22}O_2S$: 290.1340).

Patchenyl *p*-Toluenesulfinate (**9**): 97% yield. IR ν_{max}^{film} cm^{-1}: 1675 (C=C), 1600 (aromatic), 1135 (sulfinate). NMR (CCl_4) δ: 0.76—2.05 (8H, m, CH_2CHCH_2-CH_2CH), 0.95, 1.00 (6H, s, s, $C(CH_3)_2$), 2.49 (3H, s, $C_6H_4CH_3$), 3.70—4.56 (2H, m, OCH_2), 4.76—5.10 (1H, m, C=CH), 7.05—7.60 (4H, m, C_6H_4). MS *m/z*: 304 (M^+). Exact mass determination: 304.1248 (Calcd for $C_{18}H_{20}O_2S$: 304.1101).

Palladium-Catalyzed Transformation of Allylic Sulfinates into Sulfones——General Procedure: A dry 25 ml two-necked flask equipped with a septum inlet and a magnetic stirring bar, and containing 41 mg (0.04 mmol) of tetrakis(triphenylphosphine)palladium, was flushed with nitrogen, and maintained under a positive pressure of nitrogen. THF (1 ml) was added to the flask. A solution of 41 mg (0.16 mmol) of triphenylphosphine in 1 ml of THF was added to the mixture, followed by dropwise addition of a solution of an allylic sulfinate **2a**—**o** (0.24 mmol) in 2 ml of THF, and the reaction mixture was stirred at the temperature and for the time shown in Table I.

The reaction mixture was diluted with ether, washed with saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo*. The residue was subjected to preparative TLC (ether–hexane, 1:2) to give the corresponding allylic sulfone **3**. The yields are listed in Table I.

The spectral data of **3c**, **1**, and **o** were identical with those reported for samples prepared by other methods.[3]

(*E*)-2-Butenyl *p*-Tolyl Sulfone (**3a**): IR ν_{max}^{film} cm^{-1}: 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.60 (3H, d, J=4 Hz, C=C-CH_3), 2.35 (3H, s, $C_6H_4CH_3$), 3.56 (2H, d, J=6 Hz, O-CH_2), 5.10—5.57 (2H, m, CH=CH), 7.00—7.70 (4H, m, C_6H_4). MS *m/z*: 210 (M^+). Exact mass determination: 210.0749 (Calcd for $C_{11}H_{14}O_2S$: 210.0713).

(*Z*)-2-Butenyl *p*-Tolyl Sulfone (**3b**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.43 (3H, d, J=6 Hz, C=C-CH_3), 2.39 (3H, s, $C_6H_4CH_3$), 3.69 (2H, d, J=8 Hz, O-CH_2), 5.10—5.93 (2H, m, CH=CH), 7.00—7.79 (4H, m, C_6H_4). MS *m/z*: 210 (M^+). Exact mass determination: 210.0730 (Calcd for $C_{11}H_{14}O_2S$: 210.0714).

3-Methyl-1-buten-3-yl *p*-Tolyl Sulfone (**3e**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1590 (aromatic), 1300, 1120 (sulfone). NMR (CCl_4) δ: 1.35 (6H, s, $C(CH_3)_2$), 2.40 (3H, s, $C_6H_4CH_3$), 4.70—6.23 (3H, m, $CH=CH_2$), 7.03—7.66 (4H, m, C_6H_4). MS *m/z*: 224 (M^+). Exact mass determination: 224.0876 (Calcd for $C_{12}H_{16}O_2$: 224.0871).

2-Methyl-1-buten-3-yl *p*-Tolyl Sulfone (**3g**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.40 (3H, d, J=7 Hz, CH_3–CH–S), 1.79 (3H, s, CH_3–C=C), 2.40 (3H, s, $C_6H_4CH_3$), 3.42—3.64 (1H, m, S–CH), 4.58, 4.86 (2H, br s, $C=CH_2$), 7.08—7.72 (4H, m, C_6H_4). MS *m/z*: 224 (M^+). Exact mass determination: 224.0879 (Calcd for $C_{12}H_{16}O_2S$: 224.0871).

2-Ethyl-1-buten-3-yl *p*-Tolyl Sulfone (**3i**): IR ν_{max}^{film} cm^{-1}: 1620 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.00 (3H, t, J=7 Hz, CH_2CH_3), 1.45 (3H, d, J=7 Hz, $CHCH_3$), 2.07 (2H, q, J=7, 10 Hz, CH_2CH_3), 2.36 (3H, s, $C_6H_4CH_3$), 3.56—3.70 (1H, m, S–CH), 4.70—5.19 (2H, m, $C=CH_2$), 7.10—7.90 (4H, m, C_6H_4). MS *m/z*: 238 (M^+). Exact mass determination: 238.1028 (Calcd for $C_{13}H_{18}O_2S$: 238.1028).

(*E*)-2-Hexenyl *p*-Tolyl Sulfone (**3j**): IR ν_{max}^{film} cm^{-1}: 1660 (C=C), 1595 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 0.89 (3H, t, J=6 Hz, CH_2CH_3), 0.95—1.60 (2H, m, CH_2CH_3), 1.66—2.13 (2H, m, C=C–CH_2), 2.36 (3H, s, $C_6H_4CH_3$), 3.56 (2H, d, J=6 Hz, O–CH_2), 5.06—5.53 (2H, m, CH=CH), 7.03—7.70 (4H, m, C_6H_4). MS *m/z*: 238 (M^+). Exact mass determination: 238.1070 (Calcd for $C_{13}H_{18}O_2S$: 238.1028).

(*Z*)-2-Hexenyl *p*-Tolyl Sulfone (**3k**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1595 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 0.79 (3H, t, J=6 Hz, CH_2CH_3), 1.00—1.48 (2H, m, CH_2CH_3), 1.53—2.13 (2H, m, C=C–CH_2), 2.50 (3H, s, $C_6H_4CH_3$), 3.80 (2H, d, J=8 Hz, O–CH_2), 5.20—5.97 (2H, m, CH=CH), 7.30—8.09 (4H, m, C_6H_4). MS *m/z*: 238 (M^+). Exact mass determination: 238.1102 (Calcd for $C_{13}H_{18}O_2S$: 238.1028).

(*E*)-2-Octenyl *p*-Tolyl Sulfone (**3m**): IR ν_{max}^{film} cm^{-1}: 1660 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 0.85 (3H, t, J=5 Hz, CH_2CH_3), 1.02—1.49 (6H, m, $(CH_2)_3CH_3$), 1.66—2.13 (2H, m, C=C–CH_2), 2.39 (3H, s, $C_6H_4CH_3$), 3.59 (2H, d, J=6 Hz, O–CH_2), 5.13—5.50 (2H, m, CH=CH), 7.03—7.73 (4H, m, C_6H_4). MS *m/z*: 266 (M^+). Exact mass determination: 266.1066 (Calcd for $C_{15}H_{22}O_2S$: 266.1340).

(*Z*)-2-Octenyl *p*-Tolyl Sulfone (**3n**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 0.83 (3H, t, J=5 Hz, CH_2CH_3), 1.03—1.50 (6H, m, $(CH_2)_3CH_3$), 1.58—2.13 (2H, m, C=C–CH_2), 2.50 (3H, s, $C_6H_4CH_3$), 3.80 (2H, d, J=8 Hz, O–CH_2), 5.29—5.96 (2H, m, CH=CH), 7.26—8.01 (4H, m, C_6H_4). MS *m/z*: 266 (M^+). Exact mass determination: 266.1287 (Calcd for $C_{15}H_{22}O_2S$: 266.1341).

Geranyl *p*-Tolyl Sulfone (**3p**): IR ν_{max}^{film} cm^{-1}: 1665 (C=C), 1600 (aromatic), 1300, 1150 (sulfone). NMR (CCl_4) δ: 1.38 (3H, s, $C=CCH_3$), 1.53, 1.66 (6H, s, s, $C(CH_3)_2$), 1.91—2.09 (4H, m, CH_2CH_2), 2.42 (3H, s, $C_6H_4CH_3$), 3.56 (2H, d, J=7 Hz, S–CH_2), 4.85—5.15 (2H, m, $(CH=C)_2$), 7.06—7.75 (4H, m, C_6H_4). MS *m/z*: 292 (M^+). Exact mass determination: 292.1449 (Calcd for $C_{17}H_{24}O_2S$: 292.1496).

Linalyl *p*-Tolyl Sulfone (**3q**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.38 (3H, s, S–C–CH_3), 1.56, 1.66 (6H, s, s, $C(CH_3)_2$), 2.40 (3H, s, $C_6H_4CH_3$), 4.69—6.10 (4H, m, $CH_2=CHC(CH_2)_2CH=C$), 7.02—7.62 (4H, m, C_6H_4). MS *m/z*: 292 (M^+). Exact mass determination: 292.1492 (Calcd for $C_{17}H_{24}O_2S$: 292.1496).

(*Z*)-4-(Tetrahydro-2-pyranyloxy)-2-butenyl *p*-Tolyl Sulfone (**3r**): IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1590 (aromatic), 1300, 1135 (sulfone). NMR (CCl_4) δ: 1.33—1.73 (6H, m, $(CH_2)_3$), 2.41 (3H, s, $C_6H_4CH_3$), 3.20—4.03 (6H, m, S–CH_2, (O–$CH_2)_2$), 4.30—4.56 (1H, m, O–CH), 5.43—5.72 (2H, m, CH=CH), 7.07—7.78 (4H, m, C_6H_4). MS *m/z*: 310 (M^+). Exact mass determination: 310.1198 (Calcd for $C_{16}H_{22}O_4S$: 310.1238).

4-(Tetrahydro-2-pyranyloxy)-1-buten-3-yl *p*-Tolyl Sulfone (**3s**): IR ν_{max}^{film} cm^{-1}: 1640 (C=C), 1590 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.13—1.80 (6H, m, $(CH_2)_3$), 2.40 (3H, s, $C_6H_4CH_3$), 3.13—4.16 (5H, m, O–CH_2, OCH_2–CH–S), 4.43—4.56 (1H, m, O–CH–O), 4.80—5.93 (3H, m, $CH=CH_2$), 7.03—7.70 (4H, m, C_6H_4). MS *m/z*: 310 (M^+). Exact mass determination: 310.1307 (Calcd for $C_{16}H_{22}O_4S$: 310.1238).

Methyl 3-Oxo-6-*p*-toluenesulfonyl-7-octenoate (**3t**): IR ν_{max}^{film} cm^{-1}: 1740 (ester), 1720 (ketone), 1640 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 1.73—2.86 (4H, m, $C=C(CH_2)_2CO$), 2.40 (3H, s, $C_6H_4CH_3$), 3.40 (2H, s, $COCH_2CO$), 3.56—3.96 (1H, m, S–CH), 3.68 (3H, s, CO_2CH_3), 4.83—5.86 (3H, m, $CH=CH_2$), 7.16—7.86 (4H, m, C_6H_4). MS *m/z*: 324 (M^+). Exact mass determination: 324.0743 (Calcd for $C_{16}H_{20}O_5S$: 324.1031).

Palladium-catalyzed transformations of **6** and **9** into **7**, **8**, **10a**, and **10b** were carried out according to the general procedures described above.

(*S*)-Perillyl *p*-Tolyl Sulfone (**7**): IR ν_{max}^{film} cm^{-1}: 1645 (C=C), 1600 (aromatic), 1300, 1150 (sulfone). NMR (CCl_4) δ: 1.68 (3H, s, $C=CCH_3$), 1.83—2.31 (7H, m, $CH_2CH_2CHCH_2$), 2.40 (3H, s, $C_6H_4CH_3$), 3.50 (2H, s, S–CH_2), 4.60 (2H, s, $C=CH_2$), 5.13—5.46 (1H, m, C=CH), 7.03—7.80 (4H, m, C_6H_4). MS *m/z*: 290 (M^+). Exact mass determination: 290.1377 (Calcd for $C_{17}H_{22}O_2S$: 290.1341).

(5*S*)-Isopropenyl-2-methylenecyclohexyl *p*-Tolyl Sulfone (**8**): Colorless needles of mp 104—105 °C (recryst. from hexane). IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1600 (aromatic), 1300, 1145 (sulfone). NMR (CCl_4) δ: 1.00—3.07 (7H, m, $CH_2CH_2CHCH_2$), 1.72 (3H, s, $C=CCH_3$), 2.35 (3H, s, $C_6H_4CH_3$), 3.38—3.78 (1H, m, S–CH), 4.23, 4.75 (2H, s, s, S–CHC=CH_2), 4.62 (2H, s, $C=CH_2$), 6.95—7.75 (4H, m, C_6H_4). MS *m/z*: 290 (M^+). Exact mass determination: 290.1241 (Calcd for $C_{17}H_{22}O_2S$: 290.1340).

(*E*)-Perillyl *p*-Tolyl Sulfone (**10a**): IR ν_{max}^{film} cm^{-1}: 1680 (C=C), 1600 (aromatic), 1300, 1140 (sulfone). NMR (CCl_4) δ: 0.71—1.90 (8H, m, $CH_2CHCH_2CH_2CH$), 0.96, 1.02 (6H, s, s, $C(CH_3)_2$), 2.23 (3H, s, $C_6H_4CH_3$), 3.52—4.03

(2H, d, J=5 Hz, S–CH_2), 4.70—5.20 (1H, m, CH=C), 7.10—7.70 (4H, m, C_6H_4). MS m/z: 304 (M^+). Exact mass determination: 304.1551 (Calcd for $C_{18}H_{24}O_2S$: 304.1497).

(*Z*)-Perillyl *p*-Tolyl Sulfone (**10b**): IR ν_{max}^{film} cm^{-1}: 1675 (C=C), 1600 (aromatic), 1300, 1150 (sulfone). NMR (CCl_4) δ: 0.73—1.83 (8H, m, $CH_2CHCH_2CH_2CH$), 0.93, 1.00 (6H, s, s, $C(CH_3)_2$), 2.43 (3H, s, $C_6H_4CH_3$), 3.55—4.05 (2H, d, J=7 Hz, S–CH_2), 4.66—4.93 (1H, m, C=CH), 7.06—7.66 (4H, m, C_6H_4). MS m/z: 304 (M^+). Exact mass determination: 304.1506 (Calcd for $C_{18}H_{24}O_2S$: 304.1496).

Synthesis of Authentic (*E*)- and (*Z*)-Allylic Sulfones——General Procedures: A solution of 0.50 ml (6.50 mmol) of methanesulfonyl chloride in 3 ml of THF was added to an ice-cooled mixture of an allylic alcohol **1a**, **b**, **g**, **h**, **j**, or **k** (5.42 mmol) and 2.27 ml (16.25 mmol) of triethylamine in 2 ml of THF. The reaction mixture was stirred at 0 °C for 3 h and then diluted with ether. The ethereal solution was washed with 10% aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl, dried over anhydrous Na_2SO_4, and concentrated *in vacuo* to give the mesylate **4a**—**f** of the corresponding allylic alcohol as a yellowish oil quantitatively.

(*E*)-2-Butenyl Methanesulfonate (**4a**): 89% yield. IR ν_{max}^{film} cm^{-1}: 1680 (C=C), 1360, 1180 (sulfonate). NMR (CCl_4) δ: 1.80 (3H, d, J=6 Hz, C=C–CH_3), 3.03 (3H, s, SO_3CH_3), 4.75 (2H, d, J=6 Hz, O–CH_2), 5.56—6.23 (2H, m, CH=CH).

(*Z*)-2-Butenyl Methanesulfonate (**4b**): 89% yield. IR ν_{max}^{film} cm^{-1}: 1650 (C=C), 1360, 1170 (sulfonate). NMR (CCl_4) δ: 1.68 (3H, d, J=6 Hz, C=C–CH_3), 3.00 (3H, s, SO_3CH_3), 4.86 (2H, d, J=6 Hz, O–CH_2), 5.50—6.23 (2H, m, CH=CH).

(*E*)-2-Hexenyl Methanesulfonate (**4c**): 99% yield. IR ν_{max}^{film} cm^{-1}: 1670 (C=C), 1350, 1170 (sulfonate). NMR (CCl_4) δ: 0.95 (3H, t, J=6 Hz, CH_2CH_3), 1.15—1.75 (2H, m, CH_2CH_3), 1.89—2.38 (2H, m, C=C–CH_2), 3.00 (3H, s, SO_3CH_3), 4.73 (2H, d, J=6 Hz, O–CH_2), 5.45—6.38 (2H, m, CH=CH).

(*Z*)-2-Hexenyl Methanesulfonate (**4d**): 97% yield. IR ν_{max}^{film} cm^{-1}: 1660 (C=C), 1350, 1170 (sulfonate). NMR (CCl_4) δ: 0.98 (3H, t, J=6 Hz, CH_2CH_3), 1.30—1.80 (2H, m, CH_2CH_3), 1.90—2.45 (2H, m, C=C–CH_2), 3.03 (3H, s, SO_3CH_3), 4.85 (2H, d, J=6 Hz, O–CH_2), 5.50—6.23 (2H, m, CH=CH).

(*E*)-2-Octenyl Methanesulfonate (**4e**): 85% yield. IR ν_{max}^{film} cm^{-1}: 1675 (C=C), 1360, 1170 (sulfonate). NMR (CCl_4) δ: 1.00 (3H, t, J=5 Hz, CH_2CH_3), 1.15—1.75 (6H, m, $(CH_2)_3CH_3$), 1.99—2.61 (2H, m, C=C–CH_2), 3.03 (3H, s, SO_3CH_3), 4.75 (2H, d, J=6 Hz, O–CH_2), 5.48—6.25 (2H, m, CH=CH).

(*Z*)-2-Octenyl Methanesulfonate (**4f**): 92% yield. IR ν_{max}^{film} cm^{-1}: 1660 (C=C), 1360, 1180 (sulfonate). NMR (CCl_4) δ: 0.95 (3H, t, J=5 Hz, CH_2CH_3), 1.13—1.78 (6H, m, $(CH_2)_3CH_3$), 1.93—2.50 (2H, m, C=C–CH_2), 3.03 (3H, s, SO_3CH_3), 4.88 (2H, d, J=6 Hz, O–CH_2), 5.53—6.21 (2H, m, CH=CH).

One of the mesylates **4a**—**f** (4.78 mmol), obtained above, in 5 ml of absolute ethanol was added to a suspension of sodium *p*-toluenethiolate, prepared from *p*-toluenethiol (1.78 g, 14.35 mmol) and sodium hydride (50% oily washed with hexane, 688 mg, 14.35 mmol) (at 0 °C for 1 h), in 25 ml of absolute ethanol. The reaction mixture was stirred at 0 °C for 16 h, then concentrated *in vacuo*, and diluted with ether. The solution was washed with 10% aqueous NaOH and saturated aqueous NaCl, dried over anhydrous Na_2SO_4 and concentrated *in vacuo*. The residual oil was subjected to preparative TLC (ether–hexane, 1:8) to give the corresponding allylic sulfide **5a**—**f**.

(*E*)-2-Butenyl *p*-Tolyl Sulfide (**5a**): 87% yield. IR ν_{max}^{film} cm^{-1}: 1670 (C=C). NMR (CCl_4) δ: 1.61 (3H, d, J=5 Hz, C=C–CH_3), 2.26 (3H, s, $C_6H_4CH_3$), 3.42 (2H, d, J=6 Hz, S–CH_2), 5.43—5.76 (2H, m, CH=CH), 7.01—7.53 (4H, m, C_6H_4). MS m/z: 178 (M^+). Exact mass determination: 178.0747 (Calcd for $C_{11}H_{14}S$: 178.0817).

(*Z*)-2-Butenyl *p*-Tolyl Sulfide (**5b**): 87% yield. IR ν_{max}^{film} cm^{-1}: 1650 (C=C). NMR (CCl_4) δ: 1.49 (3H, d, J=5 Hz, C=C–CH_3), 2.23 (3H, s, $C_6H_4CH_3$), 3.46 (2H, d, J=6 Hz, S–CH_2), 5.10—5.63 (2H, m, CH=CH), 6.73—7.80 (4H, m, C_6H_4). MS m/z: 178 (M^+). Exact mass determination: 178.0757 (Calcd for $C_{11}H_{14}S$: 178.0816).

(*E*)-2-Hexenyl *p*-Tolyl Sulfide (**5c**): 98% yield. IR ν_{max}^{film} cm^{-1}: 1650 (C=C). NMR (CCl_4) δ: 0.83 (3H, t, J=6 Hz, CH_2CH_3), 1.03—1.60 (2H, m, CH_2CH_3), 1.73—2.17 (2H, m, C=C–CH_2), 2.30 (3H, s, $C_6H_4CH_3$), 3.43 (2H, d, J=6 Hz, S–CH_2), 5.41—5.70 (2H, m, CH=CH), 7.00—7.60 (4H, m, C_6H_4). MS m/z: 206 (M^+). Exact mass determination: 206.1031 (Calcd for $C_{13}H_{18}S$: 206.1129).

(*Z*)-2-Hexenyl *p*-Tolyl Sulfide (**5d**): 78% yield. IR ν_{max}^{film} cm^{-1}: 1660 (C=C). NMR (CCl_4) δ: 0.88 (3H, t, J=6 Hz, CH_2CH_3), 1.10—1.68 (2H, m, CH_2CH_3), 1.70—2.16 (2H, m, C=C–CH_2), 2.23 (3H, s, $C_6H_4CH_3$), 3.53 (2H, d, J=6 Hz, S–CH_2), 5.40—5.73 (2H, m, CH=CH), 7.03—7.53 (4H, m, C_6H_4). MS m/z: 206 (M^+). Exact mass determination: 206.0836 (Calcd for $C_{13}H_{18}S$: 206.1130).

(*E*)-2-Octenyl *p*-Tolyl Sulfide (**5e**): 81% yield. IR ν_{max}^{film} cm^{-1}: 1665 (C=C). NMR (CCl_4) δ: 0.83 (3H, t, J=5 Hz, CH_2CH_3), 1.05—1.48 (6H, m, $(CH_2)_3CH_3$), 1.62—2.18 (2H, m, C=C–CH_2), 2.30 (3H, s, $C_6H_4CH_3$), 3.41 (2H, d, J=6 Hz, S–CH_2), 5.40—5.73 (2H, m, CH=CH), 7.01—7.58 (4H, m, C_6H_4). MS m/z: 234 (M^+). Exact mass determination: 234.1450 (Calcd for $C_{15}H_{22}S$: 234.1443).

(*Z*)-2-Octenyl *p*-Tolyl Sulfide (**5f**): 96% yield. IR ν_{max}^{film} cm^{-1}: 1650 (C=C). NMR (CCl_4) δ: 0.90 (3H, t, J=5 Hz, CH_2CH_3), 1.10—1.55 (6H, m, $(CH_2)_3CH_3$), 1.70—2.20 (2H, m, C=C–CH_2), 2.45 (3H, s, $C_6H_4CH_3$), 3.53 (2H, d, J=6 Hz, S–CH_2), 5.76—5.79 (2H, m, CH=CH), 7.00—7.66 (4H, m, C_6H_4). MS m/z: 234 (M^+). Exact mass determination: 234.1454 (Calcd for $C_{15}H_{22}S$: 234.1442).

A mixture of one of the allylic sulfides **5a**—**f** (4.72 mmol), $NaIO_4$ (2.52 g, 11.79 mmol), H_2O (3 ml) and methanol (30 ml) was heated under reflux for 18 h. The solution was concentrated *in vacuo*, diluted with chloroform, and

filtered. The filtrate was concentrated to dryness under reduced pressure and the residue was subjected to preparative TLC (ether–hexane, 1 : 2) to give the corresponding allylic sulfone **3a** (83% yield), **3b** (83% yield), **3j** (88% yield), **3k** (91% yield), **3m** (80% yield) or **3n** (79% yield). The IR and NMR spectra of these authentic allylic sulfones obtained above were identical with those of the samples prepared by rearrangement of allylic sulfinates as described earlier.

References and Notes

1) *a*) C. L. Arcus, M. P. Balfe, and J. Kenyon, *J. Chem. Soc.*, **1938**, 485; *b*) K. Hiroi, S. Sato, and R. Kitayama, *Tohoku Yakka Daigaku Kenkyu Nempo*, **30**, 1 (1983) and references cited therein.
2) *a*) A. C. Cope, D. E. Morrison, and I. Field, *J. Am. Chem. Soc.*, **72**, 59 (1950); *b*) A. H. Wragg, J. S. McFadyen, and T. S. Stevens, *J. Chem. Soc.*, **1958**, 3603; *c*) D. Darwish and R. A. McLaren, *Tetrahedron Lett.*, **1962**, 1231; *d*) D. Darwish and E. A. Preston, *ibid.*, **1964**, 113; *e*) E. Ciuffarin, M. Isola, and A. Fava, *J. Am. Chem. Soc.*, **90**, 3594 (1968); *f*) S. Braverman, *Int. J. Sulfur Chem., Part C*, **6**, 149 (1971).
3) K. Hiroi, R. Kitayama, and S. Sato, *J. Chem. Soc., Chem. Commun.*, **1983**, 1470; *idem, Chem. Pharm. Bull.*, **32**, 2628 (1984).
4) K. Hiroi, R. Kitayama, and S. Sato, *J. Chem. Soc., Chem. Commun.*, **1984**, 303.
5) *a*) J. Tsuji, *Acc. Chem. Res.*, **2**, 144 (1969); *b*) *Idem, ibid.*, **6**, 8 (1973); *c*) B. M. Trost, *Tetrahedron*, **33**, 2615 (1977); *d*) *Idem, Acc. Chem. Res.*, **13**, 385 (1980); *e*) *Idem, Pure Appl. Chem.*, **53**, 2357 (1981); *f*) B. M. Trost and T. R. Verhoeven, *Compreh. Organometal. Chem.*, **8**, 799 (1982); *g*) J. Tsuji, *Pure Appl. Chem.*, **54**, 197 (1982); *h*) *Idem, ibid.*, **58**, 869 (1986); *i*) *Idem, Tetrahedron*, **42**, 4361 (1986).
6) G. Hada, K. Takahashi, and A. Miyake, *J. Chem. Soc., Chem. Commun.*, **1970**, 1392; *idem, Bull. Chem. Soc., Jpn.*, **45**, 230 (1972); K. E. Atkins, W. E. Walker, and R. M. Manyik, *Tetrahedron Lett.*, **1970**, 3821.
7) J. Tsuji, I. Shimizu, I. Minami, and Y. Ohashi, *Tetrahedron Lett.*, **1982**, 4809; J. Tsuji, I. Shimizu, I. Minami, Y. Ohashi, T. Sugiura, and K. Takahashi, *J. Org. Chem.*, **50**, 1523 (1985); I. Minami, Y. Ohashi, I. Shimizu, and J. Tsuji, *Tetrahedron Lett.*, **1985**, 2449.
8) Y. Tanigawa, K. Nishimura, A. Kawasaki, and S. Murahashi, *Tetrahedron Lett.*, **1982**, 5549.
9) T. Hirao, N. Yamada, Y. Oshiro, and Y. Agawa, *J. Organomet. Chem.*, **236**, 409 (1982).
10) R. Tamura and L. S. Hegedus, *J. Am. Chem. Soc.*, **104**, 3727 (1982); N. Ono, I. Hamamoto, and A. Kaji, *J. Chem. Soc., Chem. Commun.*, **1982**, 821.
11) B. M. Trost, N. R. Schmuff, and M. J. Miller, *J. Am. Chem. Soc.*, **102**, 5979 (1980).
12) L. F. Hatch and S. S. Nesbitt, *J. Am. Chem. Soc.*, **72**, 727 (1950).
13) R. S. Lenox and J. A. Katzenellenbogen, *J. Am. Chem. Soc.*, **95**, 957 (1973).
14) B. Jousseaume and J. G. Duboudin, *J. Organomet. Chem.*, **91**, C1 (1975).
15) A. C. Cope, L. J. Fleckenstein, S. Moon, and H. E. Petree, *J. Am. Chem. Soc.*, **85**, 3752 (1963).