Regioselective Preparation of Allylic Sulfones by Palladium-Catalyzed Reactions of Allylic Nitro Compounds with Sodium Benzenesulfinate

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Treatment of allylic nitro compounds with sodium benzenesulfinate in the presence of 5 mol% of $Pd(PPh_3)_4$ in *N,N*-dimethylformamide (DMF) at 20—70 °C for 1—10 h resulted in the formation of allylic sulfones with predominance of kinetically controlled products. The product distribution is mainly controlled by the electronic nature of substituents of an allyl unit, and the isomerization to the thermodynamically-stable isomers is negligible. On the other hand, the palladium-catalyzed sulfonylation of allylic acetates with sodium benzenesulfinate is accompanied by the isomerization to give the thermodynamically-controlled products selectively. These results can be explained by assuming that allylic nitro compounds are more reactive to the palladium catalyst than allylic acetates and sulfones.

Allylic sulfones are useful synthetic intermediates because of ability of the sulfonyl group as an activating group for generation of an adjacent carbanion[1] and as a leaving group in substitution reactions[2] and elimination reactions.[3] Allylic sulfones have been prepared so far by following four methods as described in the recent paper,[1] method A: The displacement of allylic halides with sodium benzenesulfinate, method B: The oxidation of the corresponding allylic sulfides, method C: The replacement of an allylic hydroxyl group with sulfone with sodium benzenesulfinate,[4] method D: Oxidation of allyl sulfoxides formed via rearrangement of allyl sulfenates. We now wish to report a new method for the preparation of allylic sulfones.

Recently we have reported that allylic nitro compounds can serve as allylic electrophiles in the palladium-catalyzed allylic alkylation or amination,[5,6] and in the substitution reactions with dialkylcuprates[7] or sodium benzenethiolate.[8] In our previous communications, we reported that allylic nitro compounds were converted into allylic sulfones on treatment with sodium benzenesulfinate in the presence of 5 mol% of $Pd(PPh_3)_4$.[8,9] This provides a useful addition to the above four methods, for some kinds of allylic nitro compounds are more readily available than other conventional allylic electrophiles and the reaction gives the kinetically-controlled products.[8,9] In this paper we wish to report additional experimental data for this reaction which further extend its synthetic utility.

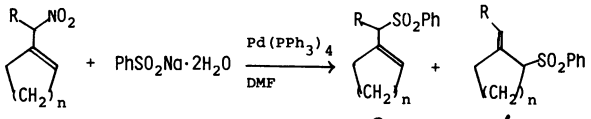
Results and Discussion

Cyclic allylic nitro compounds (**1**), which were readily prepared by the amine-catalyzed reaction of nitroalkanes with cycloalkanones,[10] reacted with sodium benzenesulfinate in the presence of 5 mol% of $Pd(PPh_3)_4$ to give the corresponding sulfones (**2** and **2′**) with predominance of the endo isomer. The results are summarized in Table 1.

Table 1. Preparation of Cyclic Allylic Sulfones (**2**)[a]

Run	R	*n*	Temp/°C	Time/h	Product,	Yield/%
1	H	2	20	10	**2a**,	70[b]
2	H	3	70	1	**2b**,	85[b]
3	H	3	20	10	**2b**,	70
4	Me	3	20	15	**2c**,	75
5	H	4	70	1	**2d**,	92
6	H	5	70	1	**2e**,	76

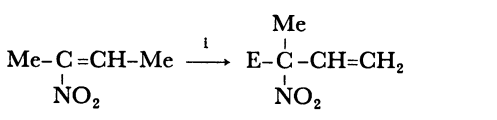
a) The reaction was carried out in DMF in the presence of $Pd(PPh_3)_4$ (5 mol%). b) The regio-isomer (**2′**) was also formed in 2—3% yield.



1 **2** **2′** (1)

DMF = *N,N*-Dimethylformamide

Acyclic allylic nitro compounds are also readily prepared in the same way using carbonyl compounds and nitroalkanes as cyclic cases.[10] α-Nitro olefins, which are prepared by dehydration of β-nitro alcohols[11] or nitration of olefins,[12] can be used as allylic nitro compounds because α-nitro olefins are readily isomerized on treatment with bases. A series of acyclic allylic nitro compounds (**3**) were prepared either by the base-catalyzed isomerization of 2-nitro-2-butene or by the introduction of a vinyl group into secondary nitroalkanes via the Michael addition of nitroalkanes to phenyl vinyl sulfoxide and the subsequent thermolysis.[5,6]



(2)

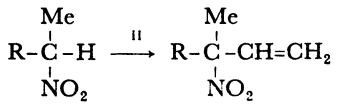
3

i) Et_3N (0.1 equiv), CH_3CN, E (H^+, HCHO, CH_2=CH-COOMe, CH_2=CH-C(=O)-Me)

Table 2. Preparation of Acyclic Allylic Sulfones (**4**, **5**)

Run	R	3	Temp/°C	Time/h	Product,	Yield/%	4/5
7	Me	**3a**	20	10	**4a**,	75	100/0
8	n-C_6H_{13}	**3b**	20	15	**4b**,	96	95/5
9	CH_2CH_2COOMe	**3c**	20	10	**4c**,	79	95/5
10	$CH_2CH_2C(=O)Me$	**3d**	20	15	**4d**,	80	95/5
11	Ph	**3e**	20	15	**4e**+**5e**	76	53/47
12	CH_2OAc	**3f**	20	15	**4f**+**5f**	95	51/49
13	COOEt	**3g**	20	15	**5g**,	87	0/100
14	H	**3h**	20	15	**4h**+**5h**	60	25/75

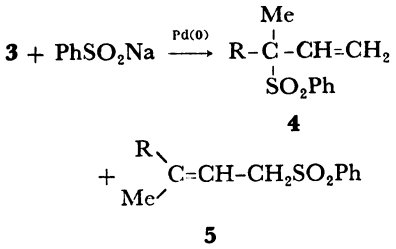
The reaction was carried out by stirring a mixture of **3** (1 mmol), $PhSO_2Na \cdot 2H_2O$ (2 mmol), and $Pd(PPh_3)_4$ (0.05 mmol) in DMF (10 ml).



3 (3)

ii) $CH_2=CH-SOPh$, DBU, CH_3CN, 25 °C, 24 h, then thermolysis

Allylic nitro compounds (**3**) underwent the palladium-catalyzed denitro-sulfonylation with sodium benzenesulfinate in the similar way as in the reaction of **1** to give allylic sulfones, **4** and **5**, in good yields. The results are summarized in Table 2.

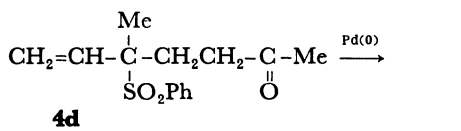


4

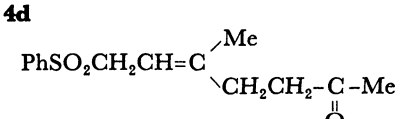
5 (4)

The product distribution was mainly controlled by the nature of substituents (R) in **3** and was a little affected by the reaction conditions. When R was an electron-donating group such as alkyl groups, the substitution reaction took place at the more hindered site to give the thermodynamically less stable isomer, **4**, regioselectively. When R was an electron-withdrawing group, the reverse regioselectivity was observed and **5** was obtained selectively.

Allylic sulfones are readily isomerized to the thermodynamically more stable isomers by the palladium catalyst.[4] In fact, stirring a mixture of **4d** and $Pd(PPh_3)_4$ (5 mol%) in DMF at room temperature resulted in clean isomerization to **5d**.

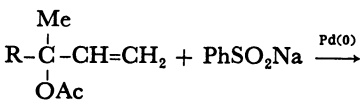


4d

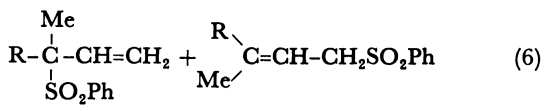


5d, 91% (5)

Nevertheless, **4d** was selectively obtained by the reaction of **3d** with sodium benzenesulfinate in the presence of $Pd(PPh_3)_4$. On the other hand, the palladium-catalyzed sulfonylation of allylic acetates was accompanied by the isomerization to give the thermodynamically-controlled products selectively. For example, treatment of linaryl acetate (**6**) with sodium benzenesulfinate in DMF at 70 °C in the same way as the reaction of **3** resulted in the exclusive formation of **5i**. This fact indicates that sodium nitrite which is liberated during the reaction suppresses the isomerization of the product, **4**. So the reaction was carried out in the presence of sodium nitrite (1 equiv). The results are summarized in Tables 3 and 4. Thus, addition of sodium nitrite is very effective to suppress the isomerization of the product in the sulfonylation of allylic nitro compounds and allylic acetates.



6



4i **5i** (6)

$R = Me_2C=CH-CH_2CH_2$

The sulfonylation of allylic nitro compounds (**3**) gives the kinetically-controlled product essentially when the isomerization can be ignored. However, the isomerization may occur to some extent during the sulfonylation of **3**. If the isomerization of **4** to **5** competes with the sulfonylation of **3**, the ratio of **4**/**5** may be affected by various factors. So the reaction of **3** with sodium benzenesulfinate was carried out under various conditions. The results are summarized in Tables 2 and 4. Concentration, temperature, and the nature of catalyst affect the ratio of **4**/**5** slightly. However, the reaction time does not affect the ratio of **4**/**5** (Run 19, 20). Namely, the isomerization occurrs at the initial stage of the reaction. As the reaction

Table 3. Sulfonylation of Linaryl Acetate (**6**)

Run	Catalyst	Temp/°C	Time/h	Yield/%	Ratio of **4i**/**5i**
15	$Pd(PPh_3)_4$	70	3	**5i**, 76	0/100
16	$Pd(PPh_3)_4$+$NaNO_2$	70	3	**4i**+**5i**, 72	80/20

Table 4. Effects of Reaction Conditions on the Ratio of **4**/**5**[a]

Run	**3**	DMF, ml	Additive	Temp/°C	Time/h	Yield/%	**4**/**5**[b]
8	**3b** (1 mmol)	10	NONE	20	15	96	95/5
17	**3b** (1 mmol)	10	Ph_3P (0.04 mmol)	20	15	79	88/12
18	**3b** (1 mmol)	10	dppe[c] (0.04 mmol)	20	15	70	77/23
9	**3c** (1 mmol)	10	NONE	20	10	79	95/5
19	**3c** (1 mmol)	2	NONE	25	21	d	82/18
20	**3c** (1 mmol)	2	NONE	25	168	64	82/18
21	**3c** (1 mmol)	2	$NaNO_2$ (1 mmol)	25	21	79	100/0
22	**3d** (1 mmol)	2	NONE	25	24	d	78/22
23	**3d** (1 mmol)	5	NONE	25	24	d	85/15
10	**3d** (1 mmol)	10	NONE	20	15	80	95/5
24	**3d** (1 mmol)	2	NONE	70	1	91	75/25
25	**3d** (1 mmol)	2	$NaNO_2$ (1 mmol)	25	21	83	75/25

a) The reaction was carried out under Ar in the presence of $Pd(PPh_3)_4$ (5 mol%). b) The ratio of **4**/**5** was determined by GLC and NMR. c) $Ph_2PCH_2CH_2PPh_2$. d) Yields were not determined.

proceeds, sodium nitrite is liberated, which deactivates the palladium catalyst to generate a new palladium catalyst which catalyzes the sulfonylation of **3** but is inert to the isomerization of **4**.[13] Consequently, when the reaction was carried out in the presence of sodium nitrite (1 equiv), the isomerization could be completely suppressed to give **4** as a sole product. When the reaction was carried out at higher temperature (Run 24) or in a highly concentrated solution (Run 22, 23), it proceeds fast and the selectivity between the sulfonylation and the isomerization becomes low.

Thus, kinetically-controlled products are readily prepared from the reaction of allylic nitro compounds and thermodynamically-controlled products are obtained from the reaction of allylic acetates. It is rather difficult to get the kinetically-controlled products by the palladium-catalyzed sulfonylation of allylic acetates as shown in Table 3. It might be expected that pure **4i** might be obtained if the reaction is carried out at low temperature in the presence of sodium nitrite. However, allylic acetates were less reactive than allylic nitro compounds, and the reaction did not proceed well in the presence of sodium nitrite at low temperature.

All these facts strongly suggest that allylic nitro compounds are more reactive toward the palladium catalyst than allylic acetates or allylic sulfones. To confirm this hypothesis, the competition reaction of **7** (X=NO_2, OAc, tosyl) was carried out. The mixture of the allylic nitro compound and another electrophile was treated with sodium benzenesulfinate in the presence of $Pd(PPh_3)_4$ and the relative reactivity was estimated by measuring the amount of **7** using ^1H-NMR. The approximate order of relative reactivity of **7** is summarized in Table 5. Thus, higher reactivity of

Table 5. Relative Reactivity of Allylic Electrophiles (**7**)

X	Rel. Rate
NO_2	1
OAc	0.5
Ts	0.3

allylic nitro compounds than other allylic electrophiles was verified.

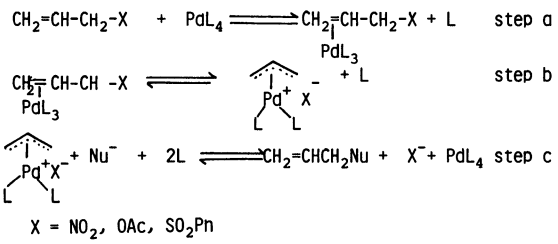
$$Me_2C(X)-CH=CH_2 + PhSO_2Na \xrightarrow{Pd(0)} \mathbf{4} + \mathbf{5} \qquad (7)$$

7 (X = NO_2, OAc, Ts)

Another type of competition reaction was carried out; 4-acetoxy-2-methyl-1-nitro-2-butene (**8**) was treated with sodium benzenesulfinate in the presence of $Pd(PPh_3)_4$ in DMF or tetrahydrofuran (THF)-MeOH. The results are summarized in Eq. 8. When the reaction was carried out in THF-MeOH, the acetoxyl group was selectively displaced to give **9** in 52% yield. When the reaction was carried out in DMF, both groups were displaced to give **10**. Namely, the acetoxyl group is more readily displaced than the nitro group in the reaction of Eq. 8.

$$O_2N-CH_2-C(Me)=CHCH_2OAc + PhSO_2Na \xrightarrow[\text{THF-MeOH}]{} O_2N-CH_2-C(Me)=CH-CH_2SO_2Ph \quad \mathbf{9}$$
$$PhSO_2Na \xrightarrow[\text{DMF}]{} PhSO_2CH_2-C(Me)=CH-CH_2SO_2Ph \quad \mathbf{10} \qquad (8)$$

The regiochemistry of the present sulfonylation can be explained by the mechanism shown in Scheme 1, which has been proposed by Tsuji and Trost for the palladium-catalyzed allylic alkylation of allylic acetates or related reactions.[14] Three key-steps are involved there, step a: π-complexation of double bonds with PdLn, step b: elimination of X from this complex to form π-allylpalladium complex, step c: nucleophilic attack to this π-allyl complex.

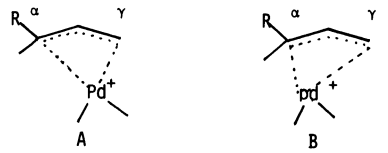


Scheme 1. The Mechanism of Palladium-Catalyzed Allylation

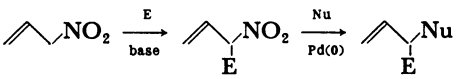
As the nitro group is a stronger electron-accepting group than the acetoxyl and sulfonyl groups, allylic nitro compounds are more reactive than other allylic electrophiles at step a. On the other hand, the acetoxyl group is a better leaving group than other allylic electrophiles at step b. The palladium catalyst may be used preferably for the sulfonylation of allylic nitro compounds rather than for the isomerization of allylic sulfones until the reaction is complete. As the palladium catalyst is deactivated by sodium nitrite when the reaction is complete, the sulfonylation of allylic nitro compounds gives the kinetically-controlled product selectively.

When allylic electrophiles have both the nitro and acetoxyl groups at the allylic positions as compound **8**, the regiochemistry of the leaving group is determined only at step b, and the acetoxyl group is more readily displaced by nucleophiles than the nitro group.

Product distribution is intrinsically controlled by the nature of substituents of an allyl unit. Although the steric effect plays an important role for the control of the regiochemistry of the palladium-catalyzed allylic alkylation,[15] the steric effect is a minor factor in the present sulfonylation as shown in Table 2. The regiochemical results are understood in terms of the electronic effects of the substituents of **3**. The palladium atom in the reaction intermediates may be unsymmetrically bonded to the allylic system depending on the substituents. When R is an electron-donating group, palladium lies close to the γ-carbon (intermediate A), and when R is an electron-withdrawing group, palladium lies close to the α-carbon (intermediate B).[16] The former intermediates causes the external nucleophilic attack to occur at the more weakly bonded α-carbon and the latter do it at the γ-position.[4] Hegedus and his co-workers have proposed that some kinds of palladium-assisted allylic aminations and alkylations may proceed via the σ-allyl complex rather than the cationic π-allyl complex. The regiochemical data of the present sulfonylation can also be explained by assuming that the reaction proceeds via the σ-allyl complex.[17] However, it is very difficult to distinguish these mechanisms at the present stage by the regiochemical data only.



Although the utility of the present method is well demonstrated in Tables 1 and 2, it should be emphasized that allylic nitro compounds can be used both as nucleophiles and electrophiles. Namely, electrophiles (E) and nucleophiles (Nu) can be introduced stepwise as shown in Eq. 9. The regiochemistry of both steps is well-controlled as discussed here. Considering these merits, the present method provides a useful addition to the exisiting methods for the preparation of allylic sulfones.[1]



(9)

E = Electrophiles Nu = Nucleophiles

Experimental

Preparation of Allylic Nitro Compounds. Cyclic allylic nitro compounds were prepared by heating a solution of cycloalkanones, nitroalkanes, and amines in benzene at 80 °C according to the literature.[10] Acyclic allylic nitro compounds, **3a**,[18] **3b**, **3e**, and **3g**,[6] were prepared by the Michael addition of the corresponding nitro compounds to phenyl vinyl sulfoxide and the subsequent thermolysis. **3b**: IR (neat) 1340, 1540 cm^{-1}, ^1H NMR ($CDCl_3$) δ=0.92 (3H,m), 1.3 (8H, m), 1.62 (3H, s), 2.0 (2H, m), 5.24 (1H, d, J=17 Hz), 5.28 (1H, d, J=10 Hz), 6.20 (1H, dd, J=17 and 10 Hz). **3e**: IR (neat) 1360, 1540 cm^{-1}, ^1H NMR ($CDCl_3$) δ=2.04 (3H, s), 5.26 (1H, d, J=17 Hz), 5.48 (1H, d, J=10 Hz), 6.60 (1H, dd, J=17 and 10 Hz), 7.4 (5H, m). Other allylic nitro compounds, **3c**,[6] **3d**, and **3f** were prepared by the isomerization of 2-nitro-2-butene. **3d**: IR (neat) 1700, 1530, 1350 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.61 (3H, s), 2.08 (3H, s), 2.12—2.48 (4H, m), 5.12 (1H, d, J=10 Hz), 5.22 (1H, d, J=17 Hz), 6.12 (1H, dd, J=17 and 10 Hz). All these compounds were prepared in 70—80% yields according to the literatures.[6,18] Compound **3f** was prepared as follows: A solution of 2-nitro-2-butene (3.03 g, 30 mmol), 35%-HCHO (5.14 g, 60 mmol), and triethylamine (0.303 g, 3 mmol) in 20 ml of acetonitrile was kept at room temperature for 24 h. The reaction mixture was poured into water and extracted with diethyl ether. The usual work-up followed by distillation with Kugelrohr gave 2-methyl-2-nitro-3-buten-1-ol, 3.15 g (80%), bp 110 °C/1 mmHg (1 mmHg=133.322 Pa). This alcohol (0.74 g, 5.65 mmol) was dissolved in 10 ml of benzene and to this solution was added acetic anhydride (0.58 g, 5.65 mmol), 3 ml of pyridine and 4-

(dimethylamino)pyridine (70 mg) and the resulting mixture was stirred at room temperature for 15 h. The usual work-up followed by column chromatography (silica gel/benzene–hexane) gave **3f**, 0.86 g (88%). IR (neat) 1730, 1540, 1370 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.72 (3H, s), 2.01 (3H, s), 5.48 (2H, q, J=10 Hz), 5.52 (1H, d, J=10 Hz), 5.54 (1H, d, J=17 Hz), 6.10 (1H, dd, J=10 and 17 Hz). Found: C, 45.74; H, 6.84; N, 10.38. Calcd for $C_5H_9NO_4$ (alcohol): C, 45.79; H, 6.92; N, 10.68.

Preparation of 1-(Phenylsulfonylmethyl)cyclopentene (2a). A mixture of 1-(nitromethyl)cyclopentene (0.381 g, 3 mmol), sodium benzenesulfinate dihydrate (0.60 g, 3 mmol), and $Pd(PPh_3)_4$ (20 mg) in 11 ml of DMF was stirred at 20 °C under Ar for 10 h and then poured into water. The product was extracted with diethyl ether and the organic layer was washed with brine and water, dried with anhydrous magnesium sulfate. After the solvent was evaporated, the residue was subjected to column chromatography (silica gel/hexane–ethyl acetate) to give **2a**, 0.466 g (70%), mp (from benzene–hexane) 95—96 °C. IR ($CHCl_3$) 1313, 1152 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.86 (2H, m), 2.28 (2H, m), 2.37 (2H, m), 3.92 (2H, s), 5.50 (1H, br), 7.50—7.90 (m, 5H). Found: C, 64.70; H, 6.32. Calcd for $C_{12}H_{14}O_2S$: C, 64.84; H, 6.35. Following compounds were prepared by this procedure.

2b: Mp 63—65 °C. IR ($CHCl_3$) 1315, 1155 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.38—1.58 (4H, m), 1.86 (2H, m), 2.00 (2H, m), 3.61 (2H, s), 5.33 (1H, br), 7.44—7.83 (5H, m). Found: C, 65.92; H, 6.84. Calcd for $C_{13}H_{16}O_2S$: C, 66.07; H, 6.82.

2c: IR (neat)1310, 1155 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.44 (3H, d, J=7 Hz), 1.4—2.2 (8H, m), 3.60 (1H, q, J=7 Hz), 5.34 (1H, br), 7.40—7.82 (5H, m). MS, found; M^+, 250.1047. Calcd for $C_{14}H_{18}O_2S$: M^+, 250.1056.

2d: Mp 48—49.5 °C. IR ($CHCl_3$) 1657, 1310, 1155 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.41 (2H, m), 1.53 (2H, m), 1.80 (2H, m), 2.02 (2H, m), 2.25 (2H, m), 3.73 (2H, s), 5.50 (1H, t, J=6.5 Hz), 7.52—7.92 (5H, m). Found: C, 67.12; H, 7.19. Calcd for $C_{14}H_{18}O_2S$: C, 67.17; H, 7.25.

2e: Mp 64—65.5 °C. IR ($CHCl_3$) 1658, 1316, 1151 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.2—1.71 (8H, m), 1.84—2.40 (4H, m), 3.72 (2H, s), 5.42 (1H, t, J=8.2 Hz), 7.40—7.97 (5H, m). Found: C, 68.52; H, 7.60. Calcd for $C_{15}H_{20}O_2S$: C, 68.15; H, 7.62.

Preparation of 3-Phenylsulfonyl-3-methyl-1-butene (4a). A mixture of 3-methyl-3-nitro-1-butene (**3a**, 0.115 g, 1 mmol), sodium benzenesulfinate dihydrate (0.24 g, 1.2 mmol), and $Pd(PPh_3)_4$ (40 mg) in 10 ml of DMF was stirred at 20 °C under Ar for 10 h. The usual work-up followed by column chromatography (silica gel/hexane–ethyl acetate) gave **4a**, 0.157 g (75%). IR (neat) 1300, 1135 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.68 (3H, s), 5.08 (1H, d, J=17 Hz), 5.26 (1H, d, J=10 Hz), 6.01 (1H, dd, J=17 and 10 Hz), 7.42—7.86 (5H, m). The spectra of **5a** was also detected slightly. The ratio of **4a**/**5a** was determined by GLC to be 98/2. Following acyclic allylic sulfones (**4** or **5**) were prepared by this procedure.

4b: IR (neat) 1300, 1150 cm^{-1}, ^1H NMR ($CDCl_3$) δ=0.88 (3H, t, J=7 Hz), 1.32 (3H, s), 1.0—1.4 (8H, m), 1.8—2.04 (2H, m), 5.00 (1H, d, J=16 Hz), 5.31 (1H, d, J=10 Hz), 5.90 (1H, dd, J=16 and 10 Hz), 7.36—7.86 (5H, m). The ratio of **4b**/**5b** was determined by NMR and GLC to be 95/5. Found: C, 68.44; H, 8.64. Calcd for $C_{16}H_{24}O_2S$: C, 68.53; H, 8.63.

4c: Mp 72—75 °C. IR ($CHCl_3$) 1735, 1298, 1147 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.35 (3H, s), 2.22—2.39 (4H, m), 3.66 (3H, s), 5.08 (1H, d, J=17 Hz), 5.38 (1H, d, J=11 Hz), 5.91 (1H, dd, J=17 and 11 Hz), 7.38—7.99 (5H, m). Found: C, 59.90; H, 6.65. Calcd for $C_{14}H_{18}O_4S$: C, 59.55; H, 6.43.

4d: Mp 82—84 °C. IR ($CHCl_3$) 1715, 1302, 1148 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.34 (3H, s), 2.13 (3H, s), 2.20 (2H, m), 2.48 (2H, m), 5.06 (1H, d, J=17 Hz), 5.35 (1H, d, J=11 Hz), 5.91 (1H, dd, J=17 and 11 Hz), 7.95—7.35 (5H, m). Found: C, 62.84; H, 6.73. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81.

4e, **5e**: Treatment of **3e** (0.16 g, 0.9 mmol) in the same way as the preparation of **4a** gave the mixture of **4e** and **5e** (the ratio of **4e**/**5e**=53/47), 0.177 g (72%). Mp 117—120 °C. IR ($CHCl_3$) 1310, 1155 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.64 (Me of **5e**, s), 1.82 (Me of **4e**, s), 3.96 (CH_2 of **5e**, d, J=8 Hz), 5.32 (CH=C of **4e**, m), 5.64 (C=CH, of **5e**, t, J=8 Hz), 6.65 (C=CH of **4e**), 7.08—7.84 (10H, m). Found: C, 70.23; H, 5.91. Calcd for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92.

4f, **5f**: Treatment of **3f** (0.173 g, 1 mmol) gave the mixture of **4f** and **5f** (**4f**/**5f**=51/49), 0.254 g (95%). IR (neat) 1740, 1310, 1060 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.36 (s, Me of **5f**), 1.44 (s, Me of **4f**), 1.98 (s, Ac of **4f**), 2.01 (s, Ac of **5f**), 3.90 (m, CH_2 of **5f**), 4.3—4.5 (m, CH_2O- of **4f**, **5f**), 5.22 (1H, d, J=17 Hz), 5.40 (1H, d, J=10 Hz), 5.3—5.5 (CH=C of **5f**), 5.94 (1H, dd, J=17 and 10 Hz). MS, found: M^+ 268.0736. Calcd for $C_{13}H_{16}SO_4$: 268.0767.

5g: Treatment of **3g** (0.173 g, 1 mmol) in the same way as the preparation of **4a** gave **5g**, 0.234 g (87%). No **4g** was detected in GLC and NMR. *E*/*Z* ratio was determined by GLC and NMR to be 97/3. IR (neat) 1730, 1290, 1170 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.28 (3H, t, J=7 Hz), 1.60 (3H, s), 4.01 (2H, d, J=7 Hz), 4.22 (2H, q, J=7 Hz), 6.66 (1H, t, J=8 Hz), 7.44—7.96 (5H, m). MS, found: M^+ 268.0747. Calcd for $C_{13}H_{16}SO_4$: 268.0767.

4h, **5h**: A mixture of 2-nitro-2-butene (0.101 g, 1 mmol), sodium benzensulfinate dihydrate (0.4 g, 2 mmol), $Pd(PPh_3)_4$ (58 mg), dppe (20 mg), and triethylamine (0.101 g, 1 mmol) in 4 ml of DMF was stirred at 70 °C under Ar for 2 h. The usual work-up followed by column chromatography (silica gel/benzene–hexane) gave the mixture of **4h** and **5h** (**4h**/**5h**=25/75), 0.117 g (60%). IR (neat) 1305, 1150 cm^{-1}. The GLC analysis showed that the products consists of **5h** consisted of two isomers, (*E*)-**5h** and (*Z*)-**5h**, (*E*/*Z*=75/25). ^1H NMR ($CDCl_3$) δ=1.34 (Me of (*Z*)-**5h**, d, J=7 Hz), 1.42 (Me of **4h**, d, J=7 Hz), 1.65 (Me of (*E*)-**5h**), 3.7—3.9 (CH-SO_2Ph or CH_2SO_2Ph of **4h** or **5h**), 5.06—6.0 (CH=C of **4h** and **5h**), 7.4—7.9 (5H, m). The spectral data of this mixture are in good agreement with those of the literature where this sulfone was prepared by the reaction of crotyl chloride with sodium benzenesulfinate.[1] MS, found: M^+ 196.0546. Calcd for $C_{10}H_{12}O_2S$: 196.0548.

Palladium-Catalyzed Isomerization of 4d to 5d. A mixture of **4d** (0.133 g, 0.5 mmol) and $Pd(PPh_3)_4$ (0.029 g) in 2 ml of DMF was stirred at 25 °C under Ar for 30 h and poured into water. After the usual work-up, the crude product was subjected to column chromatography (silica gel/hexane–ethyl acetate) to give *E*-**5d**, 0.097 g (73%) and *Z*-**5d**, 0.024 g (18%). (*E*)-**5d**: Mp 79—81 °C, IR ($CHCl_3$) 1714, 1311, 1149 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.35 (3H, s), 2.16 (3H, s), 2.27 (2H, t, J=7 Hz), 2.51 (2H, t, J=7 Hz), 3.80 (2H, d, J=8 Hz), 5.19 (1H, t q, J=2 and 8 Hz), 7.52—7.90 (5H, m). Found: C, 63.06; H, 6.83. Calcd for $C_{14}H_{18}O_3S$: C, 63.13; H, 6.81. (*Z*)-**5d**: colorless oil, ^1H NMR ($CDCl_3$) δ=1.25 (3H, s), 2.16 (2H, t, J=8 Hz), 2.18 (3H, s), 2.42 (2H, t, J=8 Hz), 3.90 (2H, d, J=8 Hz), 5.28 (1H, t, J=8 Hz), 7.53—7.95 (5H, m).

Sulfonylation of Linaryl Acetate (6). A mixture of linaryl acetate (0.196 g, 1 mmol), $PhSO_2Na \cdot 2H_2O$ (0.22 g,

1.1 mmol), and $Pd(PPh_3)_4$ (58 mg) in 3 ml of DMF was stirred at 70 °C under Ar for 3 h. The usual work-up followed by column chromatography (silica gel/hexane–ethyl acetate) gave **5i**,[4] 0.211 g (76%). The *E*/*Z* ratio was determined by GLC to be 74/26. IR (neat) 1310, 1150 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.30 (3H, s), 1.58 (3H, s), 1.65 (3H, s), 1.98 (4H, m), 3.82 (2H, d, *J*=8 Hz), 5.1 (2H, m), 7.5—7.9 (5H, m). The same reaction was carried out in the presence of $NaNO_2$ (0.069 g, 1 mmol) under the same reaction conditions as above. The mixture of **4i** and **5i**, 0.203 g (73%), was obtained. The ratio of **4i**/**5i** was determined by GLC to be 80/20.

Effects of Reaction Conditions on the Ratio 4/5 A mixture of **3** (1 mmol), $PhSO_2Na \cdot 2H_2O$ (1.2 mmol), and $Pd(PPh_3)_4$ (0.059 g) in DMF (2—10 ml) was stirred under various conditions as in Table 4. The product, which was isolated by the procedures described in the preparation of **4a**, was analyzed by GLC and NMR. The yields are in the range of 70—90% in every case. The results are summarized in Table 4.

Effects of Ligands on the Ratio of 4/5. A mixture of **3b** (0.185 g, 1 mmol), $PhSO_2Na \cdot 2H_2O$ (0.24 g, 1.2 mmol), $Pd(PPh_3)_4$ (0.059 g), and dppe (0.035 g) in 5 ml of DMF was stirred at 20 °C for 15 h under Ar. The usual work-up followed by column chromatography gave the mixture of **4b** and **5b**, 0.196 g (70%). The reaction in the presence of Ph_3P (0.090 g) was carried out in the same way. The product was analyzed by GLC and NMR.

Preparation of 4c and 4d by the Reaction of 3c and 3d in the Presence of Sodium Nitrite. A mixture of $Pd(PPh_3)_4$ (0.058 g, 0.05 mmol) and sodium nitrite (0.069 g, 1.0 mmol) in DMF (4 ml) was stirred at 25 °C under Ar for 30 min. To the resulting mixture was added $PhSO_2Na \cdot 2H_2O$ (0.22 g, 1.1 mmol) and **3c** (0.188 g, 1 mmol) and stirred at 25 °C for 21 h and then poured into water. The usual work-up followed by column chromatography (silica gel/hexane–ethyl acetate) gave **4c**, 0.22 g (79%), mp 72—75 °C. The same procedure using **3d** (0.172 g, 1 mmol) gave **4d**, 0.22 g (83%), mp 82—84 °C.

Competition Reaction of Allylic Electrophiles (7). To a mixture of **7** (X=NO_2, 1 mmol) and **7** (X=OAc, 1 mmol) in 5 ml of DMF was added $PhSO_2Na \cdot 2H_2O$ (1 mmol) and $Pd(PPh_3)_4$ (58 mg) and the resulting mixture was stirred at 20 °C. After 3 h and 6 h, a portion of the reaction mixture was poured into water and extracted with diethyl ether and the organic components were analyzed by NMR. The same reaction was carried out by using **7** (X=NO_2) and **7** (X=Ts). The reactivity was estimated by the peak at δ 1.60 (Me, X=NO_2), 2.02 (OAc, X=OAc), and 2.30 (Me, X=Ts). The results are summarized in Table 5.

Sulfonylation of 4-Acetoxy-2-methyl-1-nitro-2-butene (8).[19] A mixture of **8** (0.52 g, 3 mmol), $PhSO_2Na \cdot 2H_2O$ (0.60 g, 3 mmol), and $Pd(PPh_3)_4$ (70 mg) in 10 ml of THF and 2 ml of MeOH was stirred at 20 °C under Ar for 20 h. The usual work-up followed by column chromatography (silica gel/hexane–ethyl acetate) gave **9**, 0.52 g (52%). Mp 50—52 °C. IR ($CHCl_3$) 1550, 1357, 1305, 1150 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.42 (3H, s), 3.92 (2H, d, *J*=8 Hz), 4.83 (2H, s), 5.64 (1H, br t, *J*=8 Hz), 7.40—7.88 (5H, m). Found: C, 51.66; H, 4.90; N, 5.36. Calcd for $C_{11}H_{13}NO_4S$: C, 51.75; H, 5.13; N, 5.49. The same reaction was carried out in 12 ml of DMF to give **10**, 0.53 g, (42%). Mp 136—138 °C. IR ($CHCl_3$) 1310, 1150 cm^{-1}, ^1H NMR ($CDCl_3$) δ=1.55 (3H, s), 3.82 (4H, d, *J*=8 Hz), 5.30 (1H, br t, *J*=8 Hz), 7.44—7.96 (10H, m). Found: C, 58.13; H, 5.10. Calcd for $C_{17}H_{18}O_4S_2$: C, 58.26; H, 5.18.

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