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Reactions of Arenesulfonyl Chlorides with Olefins Catalyzed by a Ruthenium(II) Complex

Nobumasa Kamigata,* Hideo Sawada, and Michio Kobayashi

Department of Chemistry, Tokyo Metropolitan University, Fukazawa, Setagaya-ku, Tokyo 158, Japan

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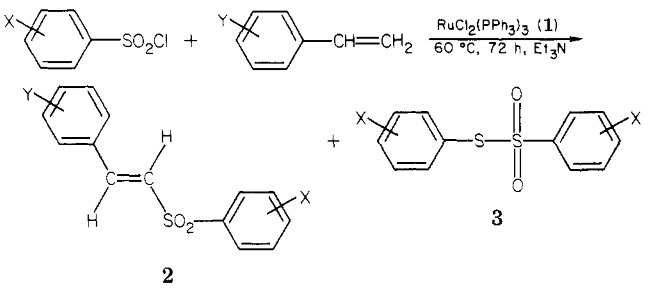
Arenesulfonyl chlorides react with vinylarenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II) catalyst and 1 molar equiv of a tertiary amine to form α,β-unsaturated sulfones **2**. Only the *E* isomers of the sulfones are formed. In reactions of arenesulfonyl chlorides containing an electron-withdrawing Cl or NO_2 substituent with α-methylstyrenes, 2-aryl-3-(arylsulfonyl)propenes (**5**) are also formed. Mechanisms for these reactions are proposed.

Reactions of arenesulfonyl halides with olefins catalyzed by transition metals have been studied extensively. Asscher[1] and Amiel[2] have reported the copper-catalyzed addition of sulfonyl halides to olefins[1] and acetylenes[2] to give, respectively, β-chloro sulfones and β-chlorovinyl sulfones, with no formation of telomers, and they proposed a free-radical, redox-transfer chain mechanism. Blum found that arenesulfonyl halides undergo desulfonylation in the presence of various transition-metal complexes to give aryl halides.[3] The formation of biaryls by the extrusion of sulfur dioxide from sodium arenesulfinates in the presence of a palladium catalyst has been reported,[4] and the formation of *trans*-*p*-methylstilbene in high yield from the reaction of sodium *p*-toluenesulfinate with styrene in the presence of a palladium catalyst has been observed.[5] Tamaru and Yoshida studied the reaction of sodium sulfinates with diolefins in the presence of a stoichiometric amount of palladium chloride and isolated yellow, chloro-bridged palladium(II) complexes.[6]

In a preliminary paper we reported that *p*-toluenesulfonyl chloride reacts with styrene, α-methylstyrene, or 1,1-diphenylethylene under mild conditions in the presence of $RuCl_2(PPh_3)_3$ (**1**) as a catalyst to give (*E*)-β-tosylstyrenes in high yields without extrusion of sulfur dioxide.[7] We here report additional results on ruthenium(II) complex **1** catalyzed vinylsulfonylations of olefins with arenesulfonyl halides and discuss possible mechanisms for these reactions.

Results and Discussion

The reactions of arenesulfonyl chlorides with olefins were carried out in benzene, using ruthenium(II) complex **1** as a catalyst, by heating the reaction mixtures at 60 °C for 72 h in degassed sealed tubes. In the absence of the ruthenium(II) catalyst, no reaction was observed between *p*-toluenesulfonyl chloride and styrene, and all the starting materials were recovered unreacted. In the presence of 1 mol % of **1** there was some reaction, but the conversion of tosyl chloride was low, and (*E*)-β-tosylstyrene (**2b**) was isolated in only very low yield. However, when an equimolar amount of a tertiary amine such as triethylamine or tri-*n*-butylamine was also added to the reaction system, the conversion of tosyl chloride became quantitative, and product **2b** was isolated in high yield. A trace amount of thiolsulfonate **3** (X = *p*-CH_3) was also detected. Thiolsulfonates have also been found as byproducts in the desulfonylation of arenesulfonyl halides or sodium-*p*-toluenesulfinates catalyzed by transition-metal catalysts.[4,5]



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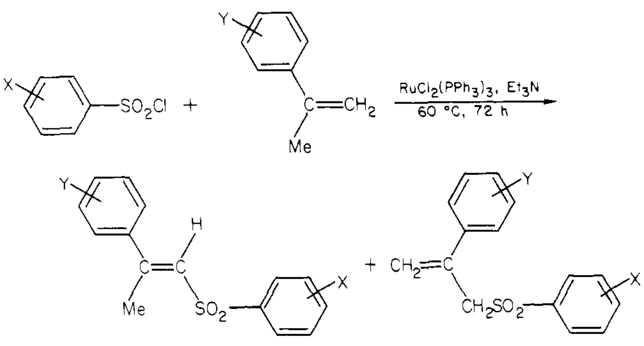
Reactions of other arenesulfonyl chlorides with styrenes in the presence of **1** and a tertiary amine were carried out in a similar manner, and the effect of substituents on the consumption of arenesulfonyl chloride and product yields was determined. The results are summarized in Tables I and II. Arenesulfonyl chlorides possessing electron-donating groups such as methoxy and methyl reacted completely, and the yields of reaction products were high, but arenesulfonyl chlorides with electron-withdrawing substituents showed less than complete consumption of the arenesulfonyl halide and lower product yields (entries 1, 4, and 6–13). However, substituents in the styrene nucleus had no significant effect on the reaction (entries 5, 10, 14, and 15).

The reaction with styrenes and α-methylstyrenes formed only the (*E*)-β-(arylsulfonyl)styrenes and (*E*)-α-methyl-β-(arylsulfonyl)styrenes. The formation of *Z* isomers was not observed.

In the reaction of *p*-chlorobenzenesulfonyl chloride with *p*-chloro-α-methylstyrene, 2-(*p*-chlorophenyl)-3-[(*p*-chlorophenyl)sulfonyl]propene (**5a**) was formed (13%) in addition to the expected product **4f** (41%). The unusual products **5** were formed only in reactions where both the arenesulfonyl chloride and the α-methylstyrene possessed electron-withdrawing substituents (entries 24–26).



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The reaction of arenesulfonyl chlorides with 1,1-diphenylethylene in the presence of **1** gave 1,1-diphenyl-

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Table I. Reactions of Arenesulfonyl Chlorides with Styrenes in the Presence of $RuCl_2(PPh_3)_3$ in Benzene at 60 °C for 72 h[a]

entry	X in $XC_6H_4SO_2Cl$	Y in $YC_6H_4CH{=}CH_2$	amine	product[b]	mp, °C	yield, % (conv, %)[c]
1	*p*-OMe	H	Et_3N	2a	88-89	90 (100)
2	*p*-Me	H	Et_3N	2b	124-125	80 (100)
3	*p*-Me	H	Bu_3N	2b	124-125	86 (100)
4	H	H	Bu_3N	2c	77.0-77.5	71 (75)
5	*p*-Cl	H	Et_3N	2d	87.5-88.0	65 (72)
6	*m*-NO_2	H	Et_3N	2e	109-110	52 (57)
7	*p*-OMe	*p*-Cl	Et_3N	2f	139.5-140.0	91 (100)
8	*p*-Me	*p*-Cl	Et_3N	2g	158-159	76 (90)
9	H	*p*-Cl	Bu_3N	2h	133-134	95 (100)
10	*p*-Cl	*p*-Cl	Et_3N	2i	169-170	77 (86)
11	*m*-NO_2	*p*-Cl	Et_3N	2j	140.0-140.5	27 (53)
12	*p*-Me	*p*-Me	Et_3N	2k	155.5-157.0	86 (91)
13	*p*-Me	*m*-NO_2	Et_3N	2l	145-146	65 (96)
14	H	*p*-Me	Bu_3N	2m	140.5-141.0	72 (73)
15	*p*-Cl	*p*-Me	Et_3N	2n	126.0-126.5	77 (93)

[a] A small amount (1-5%) of thiolsulfonate ($XC_6H_4SSO_2C_6H_4X$) was formed in each case. [b] Satisfactory elemental analyses of the products were submitted to the editor. [c] Yields were determined by isolation. Conversions were determined on the basis of the amount of arenesulfonyl chloride consumed.

Table II. Reactions of Arenesulfonyl Chlorides with α-Methylstyrene and 1,1-Diphenylethylene in the Presence of $RuCl_2(PPh_3)_3$ in Benzene at 60 °C for 72 h[a]

entry	X in $XC_6H_4SO_2Cl$	Y and R in $YC_6H_4(R)C{=}CH_2$: Y	R	amine	product[b]	mp, °C	yield, % (conv, %)[c]
16	*p*-Me	H	Me	Et_3N	4a	101-102	68 (79)
17	*p*-Me	H	Me	Bu_3N	4a	102-103	77 (88)
18	*p*-Me	*p*-Cl	Me	Et_3N	4b	91-92	63 (72)
19	H	H	Me	Bu_3N	4c	78-79	51 (65)
20	H	*p*-Cl	Me	Bu_3N	4d	105.0-105.5	46 (59)
21	*p*-Cl	H	Me	Et_3N	4e	74.5-75.5	51 (71)
22	*p*-Cl	*p*-Cl	Me	Et_3N	4f 5a	92-93 140-141	41 13 (88)
23	*m*-NO_2	H	Me	Et_3N	4g 5b	77.5-78.0 110-111	19 25 (68)
24	*m*-NO_2	*p*-Cl	Me	Et_3N	4h 5c	103-104 147.0-147.5	15 26 (51)
25	*p*-Me	H	Ph	Et_3N	4i	106	29 (78)
26	H	H	Ph	Bu_3N	4j	116-117	27 (29)
27	*p*-Cl	H	Ph	Et_3N	4k	127-128	22 (79)

[a] A small amount (1-5%) of thiolsulfonate ($XC_6H_4SSO_2C_6H_4X$) was formed in each case. [b] Satisfactory elemental analyses of the products were submitted to the editor. [c] Yields were determined by isolation. Conversions were determined on the basis of the amount of the arenesulfonyl chloride consumed.

2-(arylsulfonyl)ethylenes (**4i–k**), but in only 22–29% yields. The low yields may be due to steric hindrance.

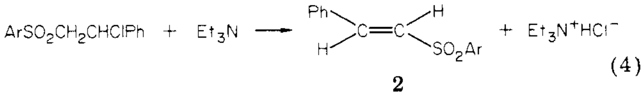
One plausible reaction mechanism for the ruthenium(II)-catalyzed reaction involves a free-radical, redox-transfer chain process (Scheme I). A second possible mechanism involves oxidative addition of the arenesuflonyl halide to form ruthenium complex **10** and subsequent reductive elimination of the ruthenium complex hydrochloride **12** (Scheme II). Considerations outlined below lead us to prefer the mechanism in Scheme I.

Scheme I

$$ArSO_2Cl + Ru^{II} \rightleftarrows \underset{\mathbf{6}}{ArSO_2\cdot} + \underset{\mathbf{7}}{Ru^{III}Cl} \quad (1)$$

$$ArSO_2\cdot + PhCH{=}CH_2 \rightleftarrows \underset{\mathbf{8}}{ArSO_2CH_2\dot{C}HPh} \quad (2)$$

$$ArSO_2CH_2\dot{C}HPh + Ru^{III}Cl \rightleftarrows \underset{\mathbf{9}}{ArSO_2CH_2CHClPh} + Ru^{II} \quad (3)$$

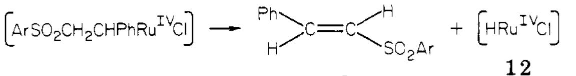


2 (4)

Scheme II

$$ArSO_2Cl + Ru^{II} \rightarrow \underset{\mathbf{10}}{[ArSO_2Ru^{IV}Cl]} \quad (5)$$

$$[ArSO_2Ru^{IV}Cl] + PhCH{=}CH_2 \rightarrow [ArSO_2CH_2CHPhRu^{IV}Cl] \quad (6)$$



2 **12** (7)

$$[HRu^{IV}Cl] + Et_3N \rightarrow Ru^{II} + Et_3N^+HCl^- \quad (8)$$

In Scheme I the ruthenium catalyst **1** first abstracts a chlorine atom from the arenesulfonyl chloride to give an arenesulfonyl radical (**6**) and the Ru(III) species **7** (eq 1). Chlorine atom abstraction by **1** from carbon tetrachloride is known.[8] In the second step (eq 2) the sulfonyl radical

Table III. Effects of Triethylamine and Free Radical Inhibitors in the Ru(II)-Catalyzed Reaction of *p*-Methoxybenzenesulfonyl Chloride with Styrene[a]

mmol of Et_3N	radical inhibitor (mmol)	conv,[b] %	yield,[c] %
0		5	trace
0.2		25	21
1.0		58	52
2.0		100	90
2.0	*p*-benzoquinone (0.20)	100	85
2.0	galvinoxyl (0.01)	95	87
2.0	galvinoxyl (0.20)	60	57

[a] All reactions carried out at 60 °C for 72 h. [b] Based on *p*-methoxybenzenesulfonyl chloride consumed. [c] Isolated yield of product 2a.

6 attacks the double bond of the styrene to give an intermediate radical, **8**, which then abstracts the chlorine atom from **7** to give the adduct **9** and regenerate the ruthenium(II) catalyst (eq 3). All three steps are considered to be equilibriums, and the overall equilibrium must lie far to the left because no adduct **9** is found in the reaction mixture when the reaction of tosyl chloride with the olefin is carried out in the absence of a tertiary amine. The role of the tertiary amine is to promote the dehydrohalogenation of **9** to **2**; the resulting triethylamine hydrochloride precipitates, shifting the equilibrium toward the final produts (**2** and $Et_3NH^+Cl^-$). This assumption is supported by the finding that the yield of **2b** was increased in proportion to the amount of triethylamine added to the reaction medium (see Table III), the yield of **2b** being almost quantitative when an equimolar amount of triethylamine to *p*-methoxybenzenesulfonyl chloride was used. The dehydrochlorination of the adduct **9** by a tertiary amine is known to give only the (*E*)-vinyl sulfones.[9]

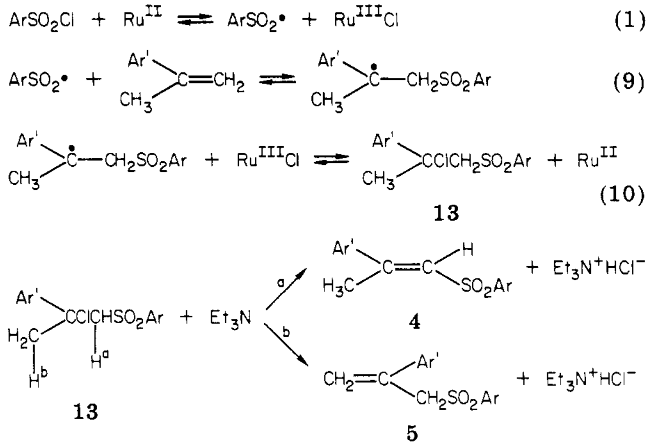
The effect of free-radical inhibitors was also studied. As shown in Table III, the yield of **2b** was affected to only a small extent when 0.2 mmol of *p*-benzoquinone or 0.01 mmol of galvinoxyl was added. However, addition of 0.2 mmol of galvinoxyl led to a definite reduction in the yield of **2a**. This finding supports the free-radical mechanism of Scheme I.

The alternative reaction mechanism shown in Scheme II requires the conversion of Ru(II) to Ru(IV), and since it is our belief that the formation of Ru(IV) from Ru(II) should be very difficult, we consider this mechanism to be much less likely than the one shown in Scheme I.

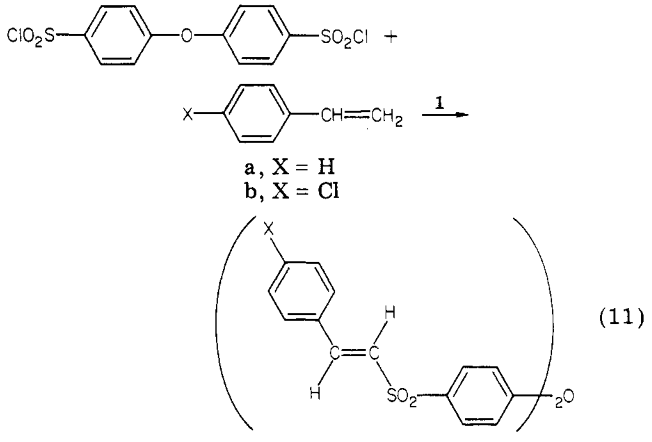
The formation of the unusual products **5** in the reaction of *p*-chloro- and *m*-nitrobenzenesulfonyl chloride with α-methylstyrene or *p*-chloro-α-methylstyrene can be explained by the reaction mechanism shown in Scheme III. The elimination of hydrogen chloride from the adduct **13** by triethylamine may occur in two ways. However, it is not clear why **5** is formed only when Ar and Ar′ groups possess electron-withdrawing groups.

p-Toluenesulfonyl fluoride did not react with styrene, even at 100 °C, or with *p*-chlorostyrene, both in the presence of **1** and triethylamine. *p*-Toluenesulfonyl bromide gave lower yields than the chloride: **2b**, 53% vs. 80%; **2i**, 36% vs. 77%.

Scheme III



The reaction of bifunctional arenesulfonyl chlorides with styrene and *p*-chlorostyrene in the presence of **1** were also examined. Bis[*p*-(chlorosulfonyl)phenyl] ether underwent **1**-catalyzed reaction with styrene or *p*-chlorostyrene to give (*E*)-bis[*p*-(styrylsulfonyl)phenyl] ether (**14a**) and (*E*)-bis[[*p*-(*p*-chlorostyryl)sulfonyl]phenyl] ether (**14b**) (eq 11) in 51% and 29% isolated yields, respectively. However, *m*-benzenedisulfonyl dichloride did not react with styrene under our reaction conditions.



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Reactions of tosyl and *p*-methoxybenzenesulfonyl chloride with methyl acrylate and ethyl vinyl ether catalyzed by **1** gave vinyl sulfones were in yields of 23–27%.

Other transition-metal catalysts such as chlorotris(triphenylphosphine)rhodium(I), palladium chloride, palladium acetate, and tetrakis(triphenylphosphine)palladium(0) were examined in the reaction of arenesulfonyl chlorides with olefins, but they showed only a small catalytic effect in various solvents under similar reaction conditions.

Experimental Section

Measurements. Melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model EPI-G2 spectrophotometer with samples as either neat liquids or in KBr disks. The proton magnetic spectra were recorded at 60 MHz by using a Hitachi R-20B spectrometer with Me_4Si as an internal standard in $CDCl_3$. Mass spectra were determined with a JEOL JMS-07 mass spectrometer at an ionizing voltage of 20–75 eV. Elemental analyses were carried out by using a Perkin-Elmer 240 elemental analyzer. Gas chromatography was carried out with a Hitachi K-53 gas chromatograph with a 1-m column packed with 10% SE-30.

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Materials. Ruthenium trichloride, palladium chloride, palladium acetate, and rhodium chloride (Wako Chemicals) were used without further purification. Dichlorotris(triphenylphosphine)ruthenium(II)[10] (1), chlorotris(triphenylphosphine)rhodium(I),[11] and tetrakis(triphenylphosphine)palladium(0)[12] were prepared by the methods described in the literature. *p*-Toluenesulfonyl chloride, *p*-chlorobenzenesulfonyl chloride, and *m*-nitrobenzenesulfonyl chloride (Tokyo Kasei Chemicals) were recrystallized prior to use. *p*-Toluenesulfonyl fluoride, *cis*-stilbene, and *m*-nitrostyrene (Aldrich Chemical) and *trans*-stilbene (Wako Chemicals) were used without further purification. Styrene, *p*-chlorostyrene, *p*-methylstyrene, α-methylstyrene, and *p*-chloro-α-methylstyrene (Tokyo Kasei Chemicals) and benzenesufonyl chloride (Wako Chemicals) were purified by distillation under nitrogen prior to use. *p*-Toluenesulfonyl bromide,[13] 1,1-diphenylethylene,[14] *p*-methoxybenzenesulfonyl chloride,[15] bis[(*p*-(chlorosulfonyl)phenyl] ether,[16] and *m*-benzenedisulfonyl dichloride[17] were prepared by published procedures.

General Procedure for the Reaction of Arenesulfonyl Halides with Olefins. A solution containing 2.0 mmol of arenesulfonyl halide, 2.0 mmol of olefin, 0.02 mmol of dichlorotris(triphenylphosphine)ruthenium(II) (1), and 2.0 mmol of triethylamine (or tri-*n*-butylamine) in 3.0 mL of benzene was degassed and heated in a sealed tube at 60 °C for 72 h. The amount of unreacted arenesulfonyl halide was determined by GLC with benzenesulfonyl chloride or *p*-toluenesulfonyl chloride as an internal standard. The reaction mixture was chromatographed on Florisil by using benzene as the eluent. The results are summarized in Tables I and II.

Reaction of *p*-Methoxybenzenesulfonyl Chloride with Styrene Catalyzed by 1 in the Presence of Galvinoxyl. A solution of 208 mg (2.0 mmol) of styrene, 413 mg (2.0 mmol) of *p*-methoxybenzenesulfonyl chloride, 202 mg (2.0 mmol) of triethylamine, 19 mg (0.02 mmol) of 1, and 4 mg (0.01 mmol) of galvinoxyl in 3.0 mL of benzene was heated at 60 °C in a degassed sealed tube for 72 h. The unreacted *p*-methoxybenzenesulfonyl chloride (5%) was determined by GLC. The reaction product **2a** was isolated by chromatography on Florisil by using benzene as the eluent; yield 470 mg (87%).

Reactions of Bis[*p*-(chlorosulfonyl)phenyl] Ether with Styrene (or *p*-Chlorostyrene). A solution of 734 mg (2.0 mmol) of bis[*p*-(chlorosulfonyl)phenyl] ether, 417 mg (4.0 mmol) of styrene (or 554 mg, 4.0 mmol, of *p*-chlorostyrene), 405 mg (4.0 mmol) of triethylamine, and 38 mg (0.04 mmol) of 1 in 3.0 mL of benzene was heated in a degassed sealed tube at 60 °C for 72 h. The reaction mixture was chromatographed on Florisil by using benzene as the eluent. The major reaction products were identified as bis[(*E*)-*p*-(styrylsulfonyl)phenyl] ether (**14a**; 510 mg, 51% yield), and bis[(*E*)-*p*-[(*p*-chlorostyryl)sulfonyl]phenyl] ether (**14b**; 334 mg, 29% yield), respectively, from the following data. **14a**: mp 155 °C (from CH_2Cl_2–EtOH); IR (KBr) 1140, 1295, 1310 cm^{-1}; NMR ($CDCl_3$) δ 6.91 (2 H, d, J = 15.0 Hz), 7.16 (4 H, d, J = 9.0 Hz), 7.42 (10 H, s), 7.71 (2 H, d, J = 15.0 Hz), 7.98 (4 H, d, J = 9.0 Hz). Anal. Calcd for $C_{28}H_{22}O_5S_2$: C, 66.91; H, 4.41. Found: C, 66.61; H, 4.62. **14b**: mp 216 °C (from CH_2Cl_2–EtOH); IR (KBr) 1145, 1305 cm^{-1}; NMR ($CDCl_3$) δ 6.84 (2 H, d, J = 15.6 Hz), 7.16 (4 H, d, J = 9.0 Hz), 7.40 (8 H, s), 7.65 (2 H, d, J = 15.6 Hz), 7.97 (4 H, d, J = 9.0 Hz). Anal. Calcd for $C_{28}H_{20}Cl_2O_5S_2$: C, 58.84; H, 3.53. Found: C, 58.65; H, 3.51.

Reaction of *p*-Toluenesufonyl Chloride (or *p*-Methoxybenzenesulfonyl Chloride) with Methyl Acrylate. A solution of 381 mg (2.0 mmol) of *p*-toluenesulfonyl chloride (or 413 mg, 2.0 mmol, of *p*-methoxybenzenesulfonyl chloride), 172 mg (2.0 mmol) of methyl acrylate, 202 mg (2.0 mmol) of triethylamine, and 19 mg (0.02 mmol) of 1 in 3.0 mL of benzene was heated at 40 °C for 72 h. The reaction mixture was chromatographed on Florisil by using benzene as the eluent, giving two colorless solid products which were identified as methyl *trans*-3-tosyl-2-propenoate (**15a**) and methyl *trans*-3-[(*p*-methoxyphenyl)sulfonyl]-2-propenoate (**15b**) from the following data. **15a**: mp 124–125 °C (from EtOH); IR (KBr) 1130, 1295, 1725 cm^{-1}; NMR ($CDCl_3$) δ 2.46 (3 H, s), 3.81 (3 H, s), 6.79 (1 H, d, J = 15.0 Hz), 7.37 (2 H, d, J = 9.6 Hz), 7.38 (1 H, d, J = 15.0 Hz), 7.81 (2 H, d, J = 9.6 Hz); mass spectrum, (20 eV), m/e 240 (M^+). Anal. Calcd for $C_{11}H_{12}O_4S$: C, 54.98; H, 5.03. Found: C, 55.18; H, 5.04. **15b**: mp 91.0–91.5 °C (from EtOH); IR (KBr) 1135, 1295, 1730 cm^{-1}; NMR ($CDCl_3$) δ 3.82 (3 H, s), 3.92 (3 H, s), 6.75 (1 H, d, J = 15.6 Hz), 7.04 (2 H, d, J = 9.0 Hz), 7.36 (1 H, d, J = 15.6 Hz), 7.85 (2 H, d, J = 9.0 Hz); mass spectrum (20 eV), m/e 256 (M^+). Anal. Calcd for $C_{11}H_{12}O_5S$: C, 51.55; H, 4.72. Found: C, 51.72; H, 4.80.

Reaction of *p*-Methoxybenzenesulfonyl Chloride with Ethyl Vinyl Ether. A solution of 413 mg (2.0 mmol) of ethyl vinyl ether, 405 mg (4.0 mmol) of triethylamine, and 38 mg (0.04 mmol) of 1 in 5.0 mL of benzene was degassed and heated in a sealed tube at 60 °C for 72 h. The reaction mixture was chromatographed on Florisil by using benzene as the eluent. The colorless solid isolated was identified as *trans*-1-ethoxy-2-[(*p*-methoxyphenyl)sulfonyl]ethylene (**15c**): 129 mg (27%); mp 67–68 °C (from EtOH); IR (KBr) 1130, 1310 cm^{-1}; NMR ($CDCl_3$) δ 1.35 (3 H, t, J = 7.2 Hz), 3.88 (3 H, s), 3.91 (2 H, q, J = 7.2 Hz), 5.68 (1 H, d, J = 12.6 Hz), 6.98 (2 H, d, J = 9.0 Hz), 7.55 (1 H, d, J = 12.6 Hz), 7.80 (2 H, d, J = 9.0 Hz); mass spectrum (20 eV), m/e 242 (M^+). Anal. Calcd for $C_{11}H_{14}O_4S$: C, 54.53; H, 5.82. Found: C, 54.57; H, 5.81.

Registry No. 2a, 68668-00-8; **2b**, 16212-08-1; **2c**, 16212-06-9; **2d**, 16215-12-6; **2e**, 86971-40-6; **2f**, 76859-81-9; **2g**, 40807-08-7; **2h**, 34101-22-9; **2i**, 6178-26-3; **2j**, 86971-41-7; **2k**, 86971-42-8; **2l**, 40807-09-8; **2m**, 30166-88-2; **2n**, 86971-43-9; **4a**, 70312-73-1; **4b**, 86971-44-0; **4c**, 64329-88-0; **4d**, 86971-45-1; **4e**, 86971-46-2; **4f**, 86971-47-3; **4g**, 86971-48-4; **4h**, 86971-49-5; **4i**, 70312-74-2; **4j**, 26189-62-8; **4k**, 86971-50-8; **5a**, 86971-51-9; **5b**, 86971-52-0; **5c**, 86971-53-1; **14a**, 86971-54-2; **14b**, 86971-55-3; **15a**, 64326-53-0; **15b**, 86971-56-4; MeO-*p*-$C_6H_4SO_2Cl$, 98-68-0; Me-*p*-$C_6H_4SO_2Cl$, 98-59-9; $C_6H_5SO_2Cl$, 98-09-9; Cl-*p*-$C_6H_4SO_2Cl$, 98-60-2; O_2N-*m*-$C_6H_4SO_2Cl$, 121-51-7; $C_6H_5CH{=}CH_2$, 100-42-5; Cl-*p*-$C_6H_4CH{=}CH_2$, 1073-67-2; Me-*p*-$C_6H_4CH{=}CH_2$, 622-97-9; O_2N-*m*-$C_6H_4CH{=}CH_2$, 586-39-0; $C_6H_5(Me)C{=}CH_2$, 98-83-9; Cl-*p*-$C_6H_4(Me)C{=}CH_2$, 1712-70-5; $C_6H_5(Ph)C{=}CH_2$, 530-48-3; $RuCl_2(PPh_3)_3$, 15529-49-4; bis[*p*-(chlorosulfonyl)phenyl] ether, 121-63-1; methyl acrylate, 96-33-3; ethyl vinyl ether, 109-92-2; *trans*-1-ethoxy-2-[(*p*-methoxyphenyl)sulfonyl]ethylene, 86971-57-5.

Supplementary Material Available: IR and ^{1}NMR spectral data for compounds **2a–n**, **4a–k**, and **5a–c** (1 page). Ordering information is given on any current masthead page.

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