November, 1991] © 1991 The Chemical Society of Japan NOTES *Bull. Chem. Soc. Jpn.*, ***64***, *3479—3481 (1991)* 3479

$\mathrm{S_H}2'$ Type Reactions of Arenesulfonyl Chlorides with Allylic Compounds Catalyzed by a Ruthenium(II) Complex

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(Received June 6, 1991)

Synopsis. In the presence of a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II), the reactions of arenesulfonyl chlorides with allyl phenyl sulfide and allyl phenyl selenide proceeded smoothly to give allyl phenyl sulfone in high yield as well as the corresponding diphenyl disulfide or diphenyl diselenide. An $\mathrm{S_H}2'$-type mechanism involving the arenesulfonyl radical is proposed.

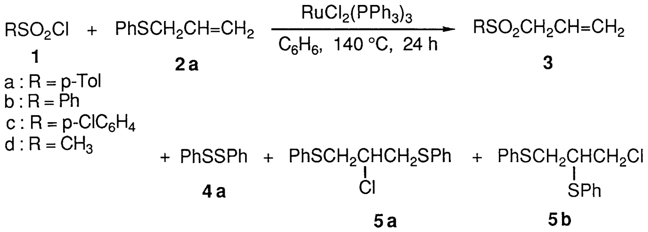
We previously reported that the reactions of alkane- and arenesulfonyl chlorides with olefins in the presence of a catalytic amount of ruthenium(II) phosphine complex gave the corresponding 1:1 adducts in high yields. A radical mechanism in the coordination sphere of the metal complex is proposed since the reactions were suppressed by the addition of radical inhibitors, such as galvinoxyl, *p*-benzoquinone or DPPH.[1] However, there was no further experimental evidence for the radical process; i.e. we failed to detect the radical intermediates by ESR and CIDNP methods. By the way, Kosugi and Migita first reported the $\mathrm{S_H}2'$-type reactions of the allyl sulfides and halides as being characteristic free radical reactions.[2] We have thus studied the ruthenium(II)-catalyzed reactions of arenesulfonyl chlorides with allyl sulfide and selenide, expecting to obtain the $\mathrm{S_H}2'$-type reaction products; the results should provide good evidence to support the radical mechanism previously proposed by us.

When a solution of tosyl chloride (**1**) (2.0 mmol), allyl phenyl sulfide (**2a**) (4.0 mmol), and a catalytic amount of dichlorotris(triphenylphosphine)ruthenium(II) in benzene was degassed and heated at 140 °C for 24 h, the reaction proceeded smoothly, yielding allyl *p*-tolyl sulfone (**3a**) (89%), diphenyl disulfide (**4a**) (5%), 2-chloro-1,3-bis(phenylthio)propane (**5a**) (51%), and 1-chloro-2,3-bis(phenylthio)propane (**5b**) (17%). No such 1:1 adduct as 2-chloro-3-phenylthio-1-tosylpropane was detected in the reaction products. Similarly, the reactions of benzene-, *p*-chlorobenzene-, and methanesulfonyl chlorides with **2a** in the presence of ruthenium(II) catalyst were also carried out. The results are summarized in Table 1.

Table 1. Reaction of Arene- and Methanesulfonyl Chlorides with Allyl Aryl Sulfide

R in RSO_2Cl	Products, yields[a)]/%			
	3	4a	5a	5b
1a *p*-$CH_3C_6H_4$	**3a** 89	5	51	17
1b Ph	**3b** 71	2	54	18
1c *p*-ClC_6H_4	**3c** 71	3	55	18
1d CH_3	**3d** 68	2	48	16

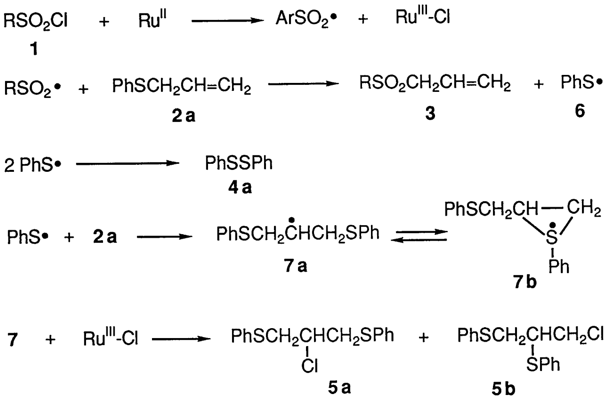
a) Yields were determined by GC based on **1** used.



The formation of these reaction products can be accounted for by the radical mechanism shown in Scheme 1. The $\mathrm{S_H}2'$ reaction of the arenesulfonyl radical, formed by the interaction of arenesulfonyl chloride with the ruthenium(II) catalyst, with allyl phenyl sulfide gives allyl aryl sulfone (**3**) and phenylthiyl radical (**6**). Although the dimerization of radical **6** affords diphenyl disulfide (**4a**), this represents a minor reaction course. Alternatively, phenylthiyl radical (**6**) adds to excess allyl phenyl sulfide (**2a**), coexisting in the reaction media, to give carbon radical (**7a**) which is considered to lie in equilibrium with radical (**7b**).[3] The transformation of the chlorine atom from the ruthenium(III)–Cl species to radical intermediate **7** gives products **5a** and **5b**.

The reaction of tosyl chloride (**1a**) with allyl phenyl selenide (**2b**) in the presence of the ruthenium(II) catalyst was also studied under similar conditions. In this case, allyl *p*-tolyl sulfone (**3a**), diphenyl diselenide (**4b**), and allyl chloride (**8**) were obtained in high yields. Similarly, the reactions of benzene- and *p*-chlorobenzenesulfonyl chloride (**1b** and **1c**) with **2b** under the ruthenium(II) catalyst were also studied. The results are summarized in Table 2.

The formation of product **3** is accounted for by a $\mathrm{S_H}2'$ reaction of the arenesulfonyl radical with allyl phenyl selenide (**2b**). The dimerization of the phenylseleno



Scheme 1.

Table 2. Reaction of Arenesulfonyl Chlorides with Allyl Aryl Selenide

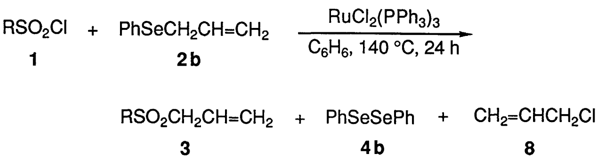
R in RSO_2Cl	Products, yields[a)]/%		
	3	4b	8
1a *p*-$CH_3C_6H_4$	**3a** 78	98	67
1b Ph	**3b** 75	73	60
1c *p*-ClC_6H_4	**3c** 72	83	62

a) Yields were determined by GC based on **1** used.

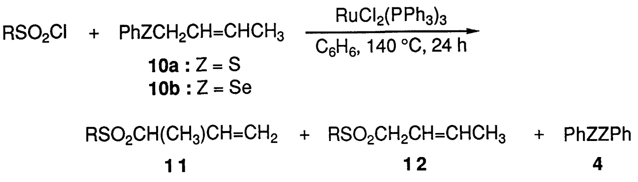
Table 3. Reaction of Arenesulfonyl Chlorides with Aryl (*E*)-2-Butenyl Sulfide and Selenide

R in RSO_2Cl	Z in **10**	Products, yields[a)]/%		
1a *p*-$CH_3C_6H_4$	**10a** S	**11a** 22	**12a** 7	**4a** 14
1b *p*-ClH_6H_4	**10a** S	**11b** 34	**12b** 13	**4a** 22
1a *p*-$CH_3C_6H_4$	**10b** Se	**11a** 29	**12a** 28	**4b** 77
1b *p*-ClC_6H_4	**10b** Se	**11b** 41	**12b** 28	**4b** 84

a) Yields were determined by GC based on **1** used.



$$\underset{\mathbf{1}}{RSO_2Cl} + \underset{\mathbf{2b}}{PhSeCH_2CH{=}CH_2} \xrightarrow[C_6H_6,\ 140\ ^\circ C,\ 24\ h]{RuCl_2(PPh_3)_3} \underset{\mathbf{3}}{RSO_2CH_2CH{=}CH_2} + \underset{\mathbf{4b}}{PhSeSePh} + \underset{\mathbf{8}}{CH_2{=}CHCH_2Cl}$$

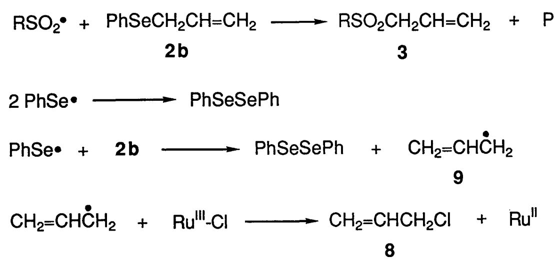


$$RSO_2Cl + PhZCH_2CH{=}CHCH_3 \xrightarrow[C_6H_6,\ 140\ ^\circ C,\ 24\ h]{RuCl_2(PPh_3)_3} \underset{\mathbf{11}}{RSO_2CH(CH_3)CH{=}CH_2} + \underset{\mathbf{12}}{RSO_2CH_2CH{=}CHCH_3} + \underset{\mathbf{4}}{PhZZPh}$$

10a : Z = S
10b : Z = Se

radical to afford diphenyl diselenide (**4b**) is a minor course. In this case, the phenylseleno radical attacks on the selenium atom of excess allyl phenyl selenide coexisting in the reaction media gives diphenyl diselenide (**4b**) and allyl radical (**9**). The allyl radical abstracts the chlorine atom from the Ru(III)–Cl to afford allyl chloride and regenerate Ru(II) (Sheme 2).

The reason why the phenylseleno radical attacks the selenium atom of allyl selenide (**2b**), whereas the phenylthiyl radical reacts with the carbon–carbon double bond of allyl phenyl sufide (**2a**), is accounted for as follows. Although a soft phenylseleno radical reacts selectively with the soft atom (selenium atom) of **2b**, a hard phenylthiyl radical attacks the hard atom (carbon atom) of **2a**.



$$RSO_2^{\bullet} + \underset{\mathbf{2b}}{PhSeCH_2CH{=}CH_2} \longrightarrow \underset{\mathbf{3}}{RSO_2CH_2CH{=}CH_2} + PhSe^{\bullet}$$

$$2\,PhSe^{\bullet} \longrightarrow PhSeSePh$$

$$PhSe^{\bullet} + \mathbf{2b} \longrightarrow PhSeSePh + \underset{\mathbf{9}}{CH_2{=}CH\dot{C}H_2}$$

$$CH_2{=}CH\dot{C}H_2 + Ru^{III}\text{-}Cl \longrightarrow \underset{\mathbf{8}}{CH_2{=}CHCH_2Cl} + Ru^{II}$$

Scheme 2.

In order to obtain further evidence for the S_H2' reaction, the reactions of arenesulfonyl chlorides with (*E*)-2-butenyl phenyl sulfide (**10a**) or (*E*)-2-butenyl phenyl selenide (**10b**) catalyzed by the ruthenium(II) complex were studied. As shown in Table 3, aryl 1-methyl-2-propenyl sulfones (**11**) were formed together with aryl (*E*)-2-butenyl sulfones (**12**). The formation of **11** can be accounted for by the S_H2' reaction. Product **12** is considered to be formed by a secondary reaction of the arenesulfonyl radical with aryl 1-methyl-2-propenyl sulfone (**11**), once formed.

In any case, the fact that the S_H2' reaction products were obtained in high yields strongly supports the radical mechanism in the ruthenium(II)-catalyzed reaction of sulfonyl chloride with olefins, as we proposed previously.

Experimental

Measurement. The melting points were determined on a Yamato MP-21 apparatus and are uncorrected. The infrared absorption spectra were determined on a Hitachi Model 260-10 spectrophotometer with samples as either neat liquids or KBr disks. The proton magnetic resonance spectra were taken with JEOL-PMX 60SI (60 MHz) and Varian XL-200 (200 MHz) spectrometers. The mass spectra were determined with a JEOL JMS-DX 300 mass spectrometer with a JEOL JMA 5000 Mass Data System at an ionizing voltage of 20—70 eV. Gas chromatography was performed using a Hitachi 263-30 gas chromatograph with a SE-30 (10%) 1 m stainless-steel column. Gel-permeation chromatography was performed using a JAI LC-08 liquid chromatograph with two JAIGEL-1H columns (20 mm×600 mm) with chloroform as the eluent.

Materials. Allyl phenyl sulfide (**2a**) (bp 73 °C/4 mmHg, 1 mmHg=133.322 Pa) and allyl phenyl selenide (**2b**) (bp 71 °C/3 mmHg) were prepared by the reaction of allyl bromide with sodium benzenethiolate and sodium benzeneselenolate, respectively. (*E*)-2-Butenyl phenyl sulfide (**10a**) (bp 88 °C/4 mmHg) and (*E*)-2-butenyl phenyl selenide (**10b**) (bp 88 °C/3 mmHg) were prepared by the treatment of (*E*)-2-butenyl bromide with sodium benzenethiolate and sodium benzeneselenolate, respectively. Distillation was performed using a precission-distillation apparatus (Kyowa VI-DL Concentric-Tube Fractionator); the regioisomers formed as the by-products, 1-methyl-2-propenyl phenyl sulfide and 1-methyl-2-propenyl phenyl selenide, were completely removed, respectively. Methanesulfonyl chloride and benzenesulfonyl chloride of Tokyo Kasei Chemicals were purified by distillation under nitrogen prior to use. *p*-Toluenesulfonyl chloride (Tokyo Kasei Chemicals) and *p*-chlorobenzenesulfonyl chloride (Wako Chemicals) were recrystallized prior to use. Dichlorotris(triphenylphosphine)ruthenium(II) was prepared by the method described in the literature.[4)]

General Procedure for the Reaction of Sulfonyl Chlorides with Allyl Sulfide or Selenide. A solution containing arenesulfonyl chloride (2.0 mmol), allyl phenyl sulfide (4.0 mmol) or allyl phenyl selenide (6.0 mmol), and dichlorotris(triphenylphosphine)ruthenium(II) (0.1 mmol) in 4.0 cm^3 of benzene was degassed by a freeze-pump-thaw cycle, sealed in an ampoule, and heated at 140 °C for 24 h. The reaction mixture was subjected to short-column chromatography on Florisil with ethyl acetate to remove the metal complex. The products were isolated from the reaction mixture by the use of gel-permeation chromatography and/or column chromatography over silica gel (Wakogel C-60), and were identified by IR, NMR, and MS. The yields of the products were determined by GC with eicosane as an internal standard. The physical and spectral data of allyl aryl sulfones (**3a**—**3c**) and allyl methyl sulfone (**3d**) were identical to authentic samples. 2-Chloro-1,3-bis(phenylthio)propane (**5a**) IR (neat) 3050, 1480, 1275, 918, and 740 cm^{-1}; ^{1}H NMR (CDCl$_3$; 200 MHz) δ=3.32 (2H, dd, J=3.75 and 1.92 Hz), 3.47 (2H, dd, J=3.75 and 1.98 Hz), 4.05 (1H, quint, J=1.92 Hz), and 7.13—7.56 (10H, m); MS m/z 294 (M$^+$), 185, 149, 109, and 77.

1-Chloro-2,3-bis(phenylthio)propane (5b): IR (neat) 3050, 1480, 1275, 920, and 720 cm^{-1}; ^{1}H NMR (CDCl$_3$; 200 MHz) δ=3.14—3.58 (3H, m), 3.86 (1H, dd, J=3.03 and 1.80 Hz), 4.02 (1H, dd, J=3.03 and 1.17 Hz), and 7.13—7.56 (10H, m); MS m/z 294 (M$^+$), 185, 149, 135, 123, 116, 109, and 77.

3-Methyl-3-tosylpropene (11a): Mp 63 °C, IR (KBr) 2980, 2260, 1640, 1598, 1315, 1145, and 1085 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.41 (3H, d, J=6.6 Hz), 2.41 (3H, s), 3.42—3.90 (1H, m), 4.84—6.11 (3H, m), and 7.26 and 7.63 (4H, ABq, J=8.4 Hz), MS m/z 210 (M$^+$), 156, 140, and 91.

3-(*p*-Chlorophenylsulfonyl)-1-butene (11b): IR (neat) 3100, 2090, 1645, 1585, 1315, 1145, and 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.42 (3H, d, J=7.2 Hz), 3.45—3.94 (1H, m), 4.85—6.12 (3H, m), and 7.46 and 7.72 (4H, ABq, J=9.0 Hz); MS m/z 230 (M$^+$), 175, 160, 144, and 112.

1-Tosyl-2-butene (12a): IR (neat) 2920, 1735, 1665, 1585, 1320, 1130, and 1085 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.69 (3H, d, J=4.2 Hz), 2.43 (3H, s), 3.71 (2H, d, J=5.4 Hz), 5.35—5.60 (2H, m) and 7.32 and 7.70 (4H, ABq, J=8.4 Hz); MS m/z 210 (M$^+$), 156, 135, and 92.

1-(*p*-Chlorophenylsulfonyl)-2-butene (12b): IR (neat) 3080, 2910, 1690, 1665, 1585, 1320, 1145, and 1090 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ=1.68 (3H, d, J=4.2 Hz), 3.70 (2H, d, J=6.0 Hz), 5.25—5.63 (2H, m), and 7.47 and 7.73 (4H, ABq, J=8.4 Hz); MS m/z 230 (M$^+$), 197, 175, and 112.

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