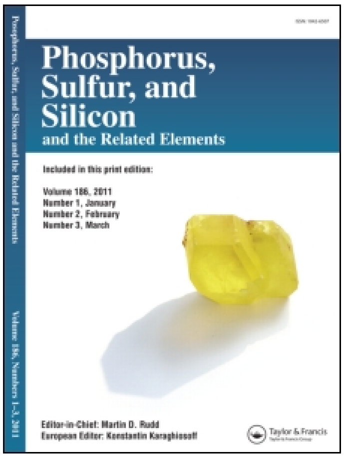

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ADDITION OF SULFONYL CHLORIDES TO OLEFINS IN THE PRESENCE OF CATALYTIC AMOUNTS OF DICHLOROTRIS-(TRIPHENYLPHOSPHINE)RUTHENIUM(II)

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Reactions of sulfonyl chlorides with olefins catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) have been studied. Methanesulfonyl and arenesulfonyl chlorides added to 1-alkenes to give 1 : 1 adducts in high yields. Telomer formation is not observed, therefore the present reaction provides a general and convenient method for synthesis of β-chlorosulfones. A radical-chain mechanism is proposed for the reaction.

Considerable interest has been recently focused on the radical reactions brought about by the interaction of a transition metal salt or complex with organic halides.[1] For example, the addition of polyhaloalkanes to a variety of olefins is known to be initiated by metal halides[2] and metal carbonyls.[3] The transition metal-phosphine complexes which are often utilized for homogeneous hydrogenation catalysts[4] might also be expected to activate organic halides and, in fact, ruthenium(II)-triphenylphosphine complexes have been known to catalyze the radical addition reactions of carbon tetrachloride and chloroform to olefins.[5] We wish to report here our finding that dichlorotris(triphenylphosphine)ruthenium(II) (**1**) catalyzed effectively the addition of sulfonyl chlorides to 1-alkenes.

In the presence of a catalytic amount of (**1**), the reaction of methanesulfonyl and arenesulfonyl chlorides with 1-alkenes proceeded smoothly under mild conditions to give corresponding 1 : 1 adducts in high yields. The results of the addition reactions are summarized in Tables I and II.

$$\mathrm{RSO_2Cl} \quad + \quad \mathrm{R'CH{=}CH_2} \quad \xrightarrow{\mathrm{RuCl_2(PPh_3)_3} \quad (\underset{\sim}{1})} \quad \mathrm{R'CHClCH_2SO_2R}$$

$\mathrm{R{=}CH_3}$ or aryl

Although it has been known that such alkylsulfonyl chlorides as methanesulfonyl or chloromethanesulfonyl chloride add to 1-alkenes in the presence of catalysts such as peroxides, light, or metal salts, the yields of the adducts are low and always accompanied by telomerized by-products.[6] In contrast, the present reaction system has significant advantages in affording β-halosulfones in high yields without formation of any by-products.

TABLE I

Reactions of methanesulfonyl chloride with 1-alkenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II)[a]

1-Alkene	Reaction time (h)	Product[b]		mp (°C)	Yield (%)[c]
$PhCH{=}CH_2$	26	$PhCHClCH_2SO_2CH_3$	**(2)**	104–105	99
$PhCH{=}CH_2$[d]	26	$PhCHClCH_2SO_2CH_3$	**(2)**	104–105	43
$p\text{-}CH_3C_6H_4CH{=}CH_2$	26	$p\text{-}CH_3C_6H_4CHClCH_2SO_2CH_3$	**(3)**	107–108	96
$p\text{-}ClC_6H_4CH{=}CH_2$	26	$p\text{-}ClC_6H_4CHClCH_2SO_2CH_3$	**(4)**	92.5–93.5	98
$m\text{-}NO_2C_6H_4CH{=}CH_2$	40	$m\text{-}NO_2C_6H_4CHClCH_2SO_2CH_3$	**(5)**	149.5–150.5	87
$CH_3(CH_2)_4CH{=}CH_2$	26	$CH_3(CH_2)_4CHClCH_2SO_2CH_3$	**(6)**	31–32	84
$CH_3(CH_2)_6CH{=}CH_2$	42	$CH_3(CH_2)_6CHClCH_2SO_2CH_3$	**(7)**	48–49	87
$CH_3(CH_2)_7CH{=}CH_2$	39	$CH_3(CH_2)_7CHClCH_2SO_2CH_3$	**(8)**	44–45	86
$CH_3COCH{=}CH_2$	40	$CH_3COCHClCH_2SO_2CH_3$	**(9)**	51–52	80
$CH_3CO_2CH{=}CH_2$	40	$CH_3CO_2CHClCH_2SO_2CH_3$	**(10)**	64–65	71

[a] Reactions were carried out at 100°C in a degassed sealed tube containing 2.0 mmol of methanesulfonyl chloride, 2.0 mmol of 1-alkene, and 0.02 mmol of the catalyst in 3.0 ml of benzene.

[b] All products were identified by their IR, ^1H NMR, and mass spectra, and elemental analyses.

[c] The yields refer to pure isolated products.

[d] *p*-Quinone (0.02 mmol) was added.

TABLE II

Reactions of arenesulfonyl chlorides with styrenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II)[a]

X in $X{-}C_6H_4SO_2Cl$	Y in $Y{-}C_6H_4CH{=}CH_2$	Product[b]		mp (°C)	Yield (%)[c]
$p\text{-}CH_3O$	H	$PhCHClCH_2SO_2C_6H_4OCH_3\text{-}p$	**(11)**	82–83	98
$p\text{-}CH_3$	H	$PhCHClCH_2SO_2C_6H_4CH_3\text{-}p$	**(12)**	85–86	92
$p\text{-}CH_3$	H[d]	$PhCHClCH_2SO_2C_6H_4CH_3\text{-}p$	**(12)**	85–86	21
$p\text{-}CH_3$	$p\text{-}CH_3$	$p\text{-}CH_3C_6H_4CHClCH_2SO_2C_6H_4CH_3\text{-}p$	**(13)**	83–84	94
$p\text{-}CH_3$	$p\text{-}Cl$	$p\text{-}ClC_6H_4CHClCH_2SO_2C_6H_4CH_3\text{-}p$	**(14)**	118–119	98
H	H	$PhCHClCH_2SO_2C_6H_5$	**(15)**	89.5–90.5	98
$p\text{-}Cl$	H	$PhCHClCH_2SO_2C_6H_4Cl\text{-}p$	**(16)**	86–87	92

[a] The reactions were carried out at 120°C for 40 hours in a degassed sealed tube containing 2.0 mmol of arenesulfonyl chloride, 2.2 mmol of styrene, and 0.02 mmol of the catalyst in 4.0 ml of benzene.

[b] All products were identified by their IR, ^1H NMR, and mass spectra.

[c] The yields refer to pure isolated products.

[d] Galvinoxyl 84.3 mg (0.02 mmol) was added.

The reaction of trichloromethanesulfonyl chloride with 1-alkenes catalyzed by (**1**) afforded 1 : 1 adducts in good yields with extrusion of sulfur dioxide. The results are summarized in Table III.

$$CCl_3SO_2Cl \quad + \quad R'CH{=}CH_2 \quad \xrightarrow{(\underline{1})} \quad R'CHClCH_2CCl_3 \quad + \quad SO_2$$

The reaction of methanesulfonyl chloride with styrene catalyzed by (**1**) was considerably suppressed by addition of p-benzoquinone as shown in Table I. The effect of the radical reaction inhibitor suggests that the ruthenium(II) catalyzed reaction of sulfonyl chlorides involves a radical mechanism. By analogy with the

TABLE III

Reactions of trichloromethanesulfonyl chloride with 1-alkenes in the presence of dichlorotris(triphenylphosphine)ruthenium(II)[a]

1-Alkene	Conditions	Product[b]		Yield (%)[c]
$PhCH{=}CH_2$	100°C, 18 h	$PhCHClCH_2CCl_3$	**(17)**	86
$p\text{-}CH_3C_6H_4CH{=}CH_2$	100°C, 24 h	$p\text{-}CH_3C_6H_4CHClCH_2CCl_3$	**(18)**	55
$p\text{-}ClC_6H_4CH{=}CH_2$	100°C, 22 h	$p\text{-}ClC_6H_4CHClCH_2CCl_3$	**(19)**	87
$m\text{-}NO_2C_6H_4CH{=}CH_2$	100°C, 40 h	$m\text{-}NO_2C_6H_4CHClCH_2CCl_3$	**(20)**	89
$CH_3(CH_2)_3CH{=}CH_2$	140°C, 36 h	$CH_3(CH_2)_3CHClCH_2CCl_3$	**(21)**	61
$CH_3(CH_2)_4CH{=}CH_2$	140°C, 38 h	$CH_3(CH_2)_4CHClCH_2CCl_3$	**(22)**	52
$CH_3(CH_2)_5CH{=}CH_2$	140°C, 36 h	$CH_3(CH_2)_5CHClCH_2CCl_3$	**(23)**	87
$CH_3(CH_2)_6CH{=}CH_2$	140°C, 36 h	$CH_3(CH_2)_6CHClCH_2CCl_3$	**(24)**	64
$CH_3(CH_2)_7CH{=}CH_2$	140°C, 36 h	$CH_3(CH_2)_7CHClCH_2CCl_3$	**(25)**	65

[a] The reactions were carried out in a degassed sealed tube containing 2.0 mmol of trichloromethanesulfonyl chloride, 2.0 mmol of 1-alkene, and 0.02 mmol of the catalyst in 2.0 ml of benzene.

[b] The structural assignment for these products was based on a comparison of their IR and NMR spectra with those of authentic samples.

[c] The yields refer to pure isolated products.

previously proposed mechanism for the ruthenium(II) catalyzed reaction of carbon tetrachloride with olefins,[5] our results are likely to be accounted for in terms of the following redox chain reactions,

$$RSO_2Cl \quad + \quad Ru^{II} \longrightarrow RSO_2\bullet \quad + \quad Ru^{III}\text{-}Cl$$

when R = CH_3 or aryl

$$RSO_2\bullet \quad + \quad R'CH{=}CH_2 \longrightarrow R'\dot{C}HCH_2SO_2R$$

$$R'\dot{C}HCH_2SO_2R \quad + \quad Ru^{III}\text{-}Cl \longrightarrow R'CHClCH_2SO_2R \quad + \quad Ru^{II}$$

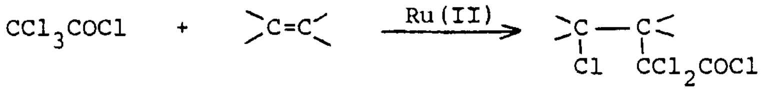
when R = CCl_3

$$RSO_2\bullet \longrightarrow R\bullet \quad + \quad SO_2$$

$$R\bullet \quad + \quad R'CH{=}CH_2 \longrightarrow R'\dot{C}HCH_2R$$

$$R'\dot{C}HCH_2R \quad + \quad Ru^{III}\text{-}Cl \longrightarrow R'CHClCH_2R \quad + \quad Ru^{II}$$

Nagai *et al.* have reported that ruthenium(II) complex catalyzed reactions of trichloroacetyl chloride with olefins gave 1 : 1 adducts, α,α,γ-trichloroalkanoyl chlorides, and no formation of such a product as $\underset{Cl}{>\!C}-\underset{COCCl_3}{C\!<}$ was observed.



$$CCl_3COCl \quad + \quad >\!C{=}C\!< \xrightarrow{Ru(II)} \underset{Cl}{>\!C}-\underset{CCl_2COCl}{C\!<}$$

In this case a chlorine atom was abstracted only from the trichloromethyl group by the catalyst to give the radical $\dot{C}Cl_2COCl$ and Ru^{III}—Cl even though $CCl_3\dot{C}O$ could have been formed by abstraction of chlorine from the acyl group. In contrast, in the present reaction the chlorine atom is abstracted only from the sulfonyl group, and no formation of such a product as $R'CHClCH_2CCl_2SO_2Cl$ was observed. The trichloromethanesulfonyl radical once formed will be unstable even under mild conditions and lose sulfur dioxide to give the trichloromethyl radical which adds to olefins in a similar way to the reactions of carbon tetrachloride with olefins.[5]

EXPERIMENTAL

All melting points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model EPI-G2 spectrophotometer using samples as either neat liquids or in KBr disks. The proton magnetic spectra were recorded at 60 MHz 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 using a Perkin-Elmer 240 elemental analyzer. Dichlorotris(triphenylphosphine)ruthenium(II) (**1**) was prepared by the methods described in the literature.[7]

General Procedure for the Reaction of Sulfonyl Chlorides with Olefins Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II). A solution containing 2.0 mmol of sulfonyl chloride, 2.0 mmol of olefin, and 0.02 mmol of dichlorotris(triphenylphosphine)ruthenium(II) in 3.0 ml of benzene was degassed and heated in a sealed tube at 100–140°C for 18–40 hours. The crude reaction mixture was chromatographed on a short column of silica gel using benzene as an eluent to give pure addition product. The yields of the products are summarized in Tables I–III. The physical and spectral data, and analyses of these compounds are as follows:

(**2**): mp 104–105°C (70.5–72°C);[8] IR(KBr) 1310, 1290, and 1130 cm^{-1}; NMR($CDCl_3$) δ 2.79 (3 H, s), 3.78 (1 H, d, J = 7.2 Hz), 3.84 (1 H, d, J = 7.2 Hz), 5.49 (1 H, t, J = 7.2 Hz), and 7.53 (5 H, s); Mass (15 eV) m/e 183, 140, 138, 104, 103, and 77; Anal. Calcd for $C_9H_{11}ClO_2S$: C, 49.42; H, 5.07. Found: C, 49.30; H, 5.03.

(**3**): mp 107–108°C; IR(KBr) 1300 and 1140 cm^{-1}; NMR($CDCl_3$) δ 2.35 (3 H, s), 2.72 (3 H, s), 3.68 (1 H, d, J = 7.2 Hz), 3.73 (1 H, d, J = 7.2 Hz), 5.32 (1 H, t, J = 7.2 Hz), and 7.10–7.40 (4 H, m).

(**4**): mp 92.5–93.5°C: IR(KBr) 1310 and 1150 cm^{-1} NMR($CDCl_3$) δ 2.89 (3 H, s), 3.77 (1 H, d, J = 7.2 Hz), 3.85 (1 H, d, J = 7.2 Hz), 5.45 (1 H, t, J = 7.2 Hz), and 7.42 (4 H, s); Mass (15 eV) m/e 254, 218, 216, 174, 172, 140, and 138; Anal. Calcd for $C_9H_{10}Cl_2O_2S$: C, 42.70; H, 3.98. Found: C, 42.65; H, 3.95.

(**5**): mp 149.5–150.5°C; IR(KBr) 1540, 1360, 1300, and 1140 cm^{-1}; NMR($CDCl_3$) δ 3.00 (3 H, s), 4.09 (1 H, d, J = 7.2 Hz), 4.15 (1 H, d, J = 7.2 Hz), 5.70 (1 H, t, J = 7.2 Hz), and 7.62–8.48 (4 H, m).

(**6**): mp 31–32°C (28–30°C);[6c] IR(KBr) 1310 and 1130 cm^{-1}; NMR ($CDCl_3$) δ 0.81–2.00 (11 H, m), 3.11 (3 H, s), 3.43 (1 H, d, J = 6.0 Hz); 3.52 (1 H, d, J = 6.0 Hz), and 4.26–4.59 (1 H, m); Mass (15 eV) m/e 213, 177, 97, and 81.

(**7**): mp 48–49°C; IR(KBr) 1295 and 1125 cm^{-1}; NMR($CDCl_3$) δ 0.80–2.05 (15 H, m), 3.10 (3 H, s), 3.30–3.60 (2 H, m), and 4.23–4.60 (1 H, m); Anal. Calcd for $C_{10}H_{21}ClO_2S$: C, 49.88; H, 8.79; Found: C, 49.89; H, 8.71.

(**8**): mp 44–45°C; IR(KBr) 1300 and 1125 cm^{-1}; NMR($CDCl_3$) δ 0.83–2.05 (17 H, m), 3.11 (3 H, s), 3.35–3.65 (2 H, m), and 4.21–4.69 (1 H, m); Anal. Calcd for $C_{11}H_{23}ClO_2S$: C, 51.84; H, 9.10. Found: C, 51.83; H, 9.15.

(**9**): mp 51–52°C; IR(KBr) 1335, 1320, and 1150 cm^{-1}; NMR($CDCl_3$) δ 2.45 (3 H, s), 3.09 (3 H, s), 3.64 (1 H, d, J = 6.6 Hz), 3.89 (1 H, d, J = 6.6 Hz), and 4.88 (1 H, t, J = 6.6 Hz); Anal. Calcd for $C_5H_9ClO_3S$: C, 32.53; H, 4.91. Found: C, 32.47; H, 4.90.

(**10**): mp 64–65°C (60–61°C);[6d] IR(KBr) 1310 and 1140 cm^{-1}; NMR($CDCl_3$) δ 3.11 (3 H, s), 3.76 (1 H, d, J = 7.2 Hz), 3.84 (1 H, d, J = 7.2 Hz), 3.92 (3 H, s), and 4.89 (1 H, t, J = 7.2 Hz).

(**11**): mp 82–83°C (from EtOH); IR(KBr) 1325, 1310, and 1140 cm^{-1}; NMR($CDCl_3$) δ 3.84 (3 H, s), 3.84–3.97 (2 H, m), 5.36 (1 H, t, J = 7.2 Hz), 6.90 (2 H, d, J = 9.0 Hz), 7.25 (5 H, s), and 7.70 (2 H, d, J = 9.0 Hz); Mass (30 eV) m/e 310 (M^+).

(**12**): mp 85–86°C (from EtOH); IR(KBr) 1320, 1305, and 1140 cm^{-1}; NMR($CDCl_3$) δ 2.40 (3 H, s), 3.87–3.99 (2 H, m), 5.39 (1 H, t, J = 7.2 Hz), 7.36 (5 H, s), 7.28 (2 H, d, J = 9.0 Hz), and 7.69 (2 H, d, J = 9.0 Hz); Mass (30 eV) m/e 294 (M^+).

(**13**): mp 83–84°C (from EtOH); IR(KBr) 1320, 1305, and 1145 cm^{-1}; NMR($CDCl_3$) δ 2.21 (3 H, s), 2.28 (3 H, s), 2.81 (2 H, d, J = 6.6 Hz), 5.23 (1 H, d, J = 6.6 Hz), and 6.9–7.5 (8 H, m); Mass m/e 308 (M^+).

(**14**): mp 118–119°C (from EtOH); IR(KBr) 1310, 1300, and 1140 cm^{-1}; NMR($CDCl_3$) δ 2.44 (3 H, s); 4.82–4.96 (2 H, m), 5.32 (1 H, t, J = 7.2 Hz), 7.20 (4 H, s) 7.24 (2 H, d, J = 9.0 Hz), and 7.62 (2 H, d, J = 9.0 Hz). Mass (30 eV) m/e 328 (M^+).

(**15**): mp 89.5–90.5°C (from EtOH); IR(KBr) 1320, 1305, and 1145 cm^{-1}; NMR($CDCl_3$) δ 3.90–4.02 (2 H, m), 5.41 (1 H, t, J = 7.2 Hz), 7.29 (5 H, s), and 7.44–7.91 (5 H, m); Mass (30 eV) m/e 280 (M^+).

(**16**): mp 86–87°C (from EtOH); IR(KBr) 1325 and 1140 cm^{-1}; NMR($CDCl_3$) δ 3.88–4.01 (2 H, m), 5.38 (1 H, t, J = 7.2 Hz), 7.28 (5 H, s), 7.39 (2 H, d, J = 9.0 Hz), and 7.70 (2 H, d, J = 9.0 Hz); Mass (30 eV) m/e 314 (M^+).

(**17**): IR(neat) 3215, 3175, 3140, 1600, 1490, 1440, 1400, 1310, 1175, 1160, 1140, 1120, 995, 930, 875, and 790 cm^{-1}; NMR($CDCl_3$) δ 3.49–3.60 (2 H, m), 5.26 (1 H, t, J = 6.0 Hz), and 7.32 (5 H, s).

(**18**): IR(neat) 3030, 2920, 1610, 1510, 970, and 820 cm^{-1}; NMR($CDCl_3$) δ 2.28 (3 H, s), 3.47 (2 H, d, J = 6.0 Hz), 5.18 (1 H, t, J = 6.0 Hz), and 6.90–7.30 (4 H, m).

(**19**): IR(neat) 3210, 3100, 1610, 1500, 1415, 1195, 1175, 1070, 1040, 990, 820, 800, 780, 760, 700, 680, and 600 cm^{-1}; NMR($CDCl_3$) δ 3.45–3.57 (2 H, m), 5.25 (1 H, t, J = 6.0 Hz), and 7.28 (4 H, s).

(**20**): IR(neat) 1530 and 1350 cm^{-1}; NMR($CDCl_3$) δ 3.47 (2 H, d, J = 6.0 Hz), 5.28 (1 H, t, J = 6.0 Hz), and 7.31–8.20 (4 H, m).

(**21**): IR(neat) 3120, 3035, 2980, 2950, 1470, 1420, 1375, 1315, 1235, 1190, 1095, 1010, 980, 930, 895, 755, and 670 cm^{-1}; NMR(CCl_4) δ 0.82–2.03 (9 H, m), 3.17 (2 H, q, J = 2.4 Hz), 4.03–4.32 (1 H, m).

(**22**): IR(neat) 3150, 3075, 2970, 1450, 1410, 1360, 1235, 1180, 1140, 1075, 957, 895, 790, 770, and 650 cm^{-1}; NMR(CCl_4) δ 0.85–2.11 (11 H, m), 3.23 (2 H, q, J = 2.4 Hz), 4.09–4.38 (1 H, m).

(**23**): IR(neat) 3055, 3010, 2930, 1455, 1400, 1355, 1175, 1150, 1080, 1010, 950, 730, and 650 cm^{-1}; NMR(CCl_4) δ 0.80–2.09 (13 H, m), 3.20 (2 H, q, 2.4 Hz), and 4.08–4.37 (1 H, m).

(**24**): IR(neat) 2950, 2910, 2845, 1475, 1460, 1430, 1390, 1215, 1130, 1055, 965, 800, and 710 cm^{-1}; NMR(CCl_4) δ 0.78–1.98 (15 H, m), 3.18 (2 H, q, J = 2.4 Hz), and 4.05–4.33 (1 H, m).

(**25**): IR(neat) 3100, 3055, 2955, 1460, 1190, 1080, 1015, 920, 740, and 660 cm^{-1}; NMR(CCl_4) δ 0.80–2.01 (17 H, m), 3.19 (2 H, q, J = 2.4 Hz), and 4.09–4.46 (1 H, m).

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