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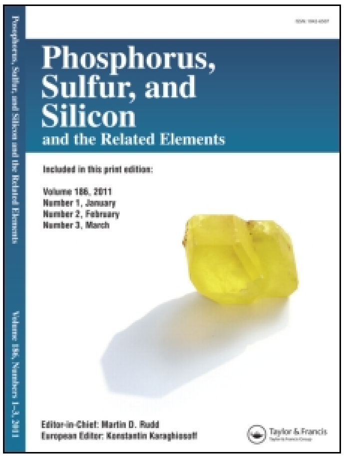

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DESULFONYLATION OF ARYLMETHANESULFONYL CHLORIDES CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

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DESULFONYLATION OF ARYLMETHANESULFONYL CHLORIDES CATALYZED BY DICHLOROTRIS(TRIPHENYLPHOSPHINE)-RUTHENIUM(II)

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Reactions of arylmethanesulfonyl chlorides catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) (**1**) have been studied. Desulfonylation occurred when arylmethanesulfonyl chlorides were treated with catalytic amounts of the ruthenium(II) catalyst to give chloromethylarene in high yields. No addition of the sulfonyl chloride to olefin was observed when the reaction was carried out in the presence of an equimolar amount of an olefin such as styrene. However, the rate of disappearance of the sulfonyl chloride was accelerated by addition of an olefin. The desulfonylation is assumed to proceed by a redox transfer promoted homolytic mechanism in the coordination sphere of the catalyst. In the presence of large excess of styrenes, arylmethanesulfonyl chlorides added to the olefins to give 1 : 1 adducts competitively with the desulfonylation yielding chloromethylarenes.

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Recently, considerable attention has been focused on the radical reactions brought about by the interaction of a transition metal salt or complex with organic halides.[1] For example, ruthenium(II)-triphenylphosphine complexes have been shown to catalyze the radical addition reactions of carbontetrachloride and chloroform to olefins.[2] Previously, we have reported the reaction of sulfonyl chlorides with olefins to give 1 : 1 adducts in high yield in the presence of a ruthenium(II) catalyst.[3] We wish to report here the desulfonylation of arylmethanesulfonyl chlorides catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) (**1**) under mild conditions.

When benzylsulfonyl chloride was allowed to react with an equimolar amount of styrene catalyzed by (**1**) at 80°C, no addition of the sulfonyl chloride to olefin was observed, and only the desulfonylation occurred to give benzyl chloride. The desulfonylation was also observed in the absence of styrene, however, in this case the yield of benzyl chloride was low (71% yield after 72 hours at 80°C) compared with the yield in the presence of an equimolar amount of styrene (94% yield after 40 hours at 80°C).

$$\mathrm{PhCH_2SO_2Cl} \quad + \quad \mathrm{PhCH{=}CH_2} \xrightarrow{\mathrm{RuCl_2(PPh_3)_3}\quad (\mathbf{1})} \mathrm{PhCH_2Cl} \quad + \quad \mathrm{SO_2}$$

The rate of disappearance of benzylsulfonyl chloride catalyzed by (**1**) was determined in the presence or absence of styrene, and it was found that the rate was

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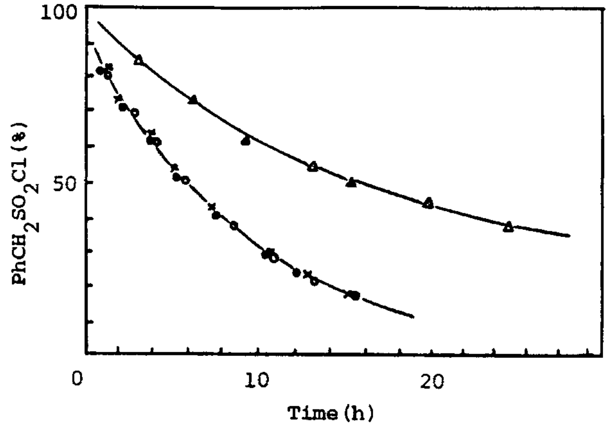

FIGURE 1 Time course of disappearance of benzylsulfonyl chloride catalyzed by (**1**) at 80°C: —△—in the absence of styrene; —○—0.2 equivalent of styrene was added; —●—1.1 equivalent of styrene was added; —×—3.0 equivalent of styrene was added.

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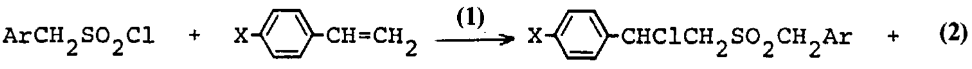
accelerated by addition of styrene. However, the degree of acceleration did not depend on the amount of styrene added as shown in Figure 1. At present it is not clear why the rate of disappearance is accelerated in the presence of an olefin.

When the reaction of benzylsulfonyl chloride was carried out in the presence of a radical inhibitor such as galvinoxyl, the formation of benzyl chloride was suppressed to 1% (after 6 hours at 80°C) from 50% (Table I). This finding suggests that the desulfonylation proceed via a homolytic mechanism. Desulfonylations of some other arylmethanesulfonyl chlorides in the presence of styrene catalyzed by (**1**) were carried out under similar conditions to give chloromethylarenes (**2**) in high yields. The results are summarized in Table I. It is of interest that the desulfonylation of arylmethanesulfonyl chlorides catalyzed by a ruthenium(II) complex occurs under mild conditions in contrast to the desulfonylation of arenesulfonyl chlorides which were observed at 240°C.[4]

$$\mathrm{ArCH_2SO_2Cl} \xrightarrow{(\mathbf{1})} \underset{(\mathbf{2})}{\mathrm{ArCH_2Cl}} + \mathrm{SO_2}$$

The reaction of arylmethanesulfonyl chlorides with large excess of styrenes catalyzed by (**1**) was carried out. In this case 1 : 1 adducts (**3**) were isolated along with desulfonylation products (**2**). The results are summarized in Table II.



(**3**)

These findings suggest that ruthenium(II) catalyzed reactions of arylmethanesulfonyl chlorides proceed competitively by two routes, namely, desulfonylation and addition

TABLE I

Desulfonylation of arylmethanesulfonyl chloride catalyzed by dichlorotris(triphenylphosphine)ruthenium(II)[a]

Ar in $ArCH_2SO_2Cl$	Olefin (mmol)	Temp. (°C)	Time (h)	Yield (%)[b] of $ArCH_2Cl$
Ph	—	60	20	26
Ph	—	60	41	43
Ph	—	60	90	63
Ph	—	80	72	71
Ph	Styrene 2.2	80	6	50
Ph	Styrene 2.2	80	6	1[c]
Ph	Styrene 2.2	80	16	73
Ph	Styrene 2.2	80	40	94
Ph	1-Octene 2.2	80	44	91
p-$CH_3C_6H_4$	Styrene 2.2	80	40	98
p-ClC_6H_4	Styrene 2.2	80	40	96
p-$NO_2C_6H_4$	Styrene 2.2	80	45	72

[a] The reaction was carried out in a degassed sealed tube containing arylmethanesulfonyl chloride (2.0 mmol) and ruthenium catalyst (0.02 mmol) in 4.0 ml of benzene in the presence or absence of olefin.

[b] The yield was determined by GLC.

[c] Galvinoxyl (0.2 mmol) was added.

TABLE II

The reaction of arylmethanesulfonyl chloride with styrenes catalyzed by ruthenium(II) complex[a]

Ar in $ArCH_2SO_2Cl$	X in p-$XC_6H_4CH{=}CH_2$	Temp. (°C)	Time (h)	Yields (%)[b]	
a. Ph	H	60	120	(**2a**) 33	(**3a**) 46
b. Ph	H	80	40	(**2a**) 25	(**3a**) 57
b. Ph	CH_3	80	40	(**2a**) 38	(**3b**) 52
c. Ph	Cl	80	40	(**2a**) 23	(**3c**) 66
d. p-$CH_3C_6H_4$	H	80	72	(**2d**) 60	(**3d**) 31
e. p-ClC_6H_4	H	80	72	(**2e**) 52	(**3e**) 21
f. p-$NO_2C_6H_4$	H	80	72	(**2f**) 34	(**3f**) 9

[a] The reaction was carried out in a degassed sealed tube containing arylmethanesulfonyl chloride (2.0 mmol), ruthenium(II) catalyst (0.02 mmol), and olefin (3.6 g).

[b] The yield based on the arylmethanesulfonyl chloride used.

to olefin. The reaction seems to proceed by a redox transfer homolytic mechanism as shown in Scheme 1.

The failure to detect a desulfonylated adduct such as (**4**) indicates that the arylmethyl radical (**6**), formed by extrusion of sulfur dioxide from arylmethanesulfonyl radical (**5**), has no ability to add to the carbon–carbon double bond of styrene and only abstracts the chlorine atom from Ru^{III}–Cl. It is known that benzyl radical formed by thermal decomposition adds to olefins,[5] but the arylmethyl radical (**6**) formed by the present method will be confined in the coordination sphere of the ruthenium(II) catalyst, and so the reactivity of (**6**) is decreased. Therefore, the reaction of (**6**) with Ru^{III}–Cl affording (**2**) occurs to the exclusion of addition of (**6**)

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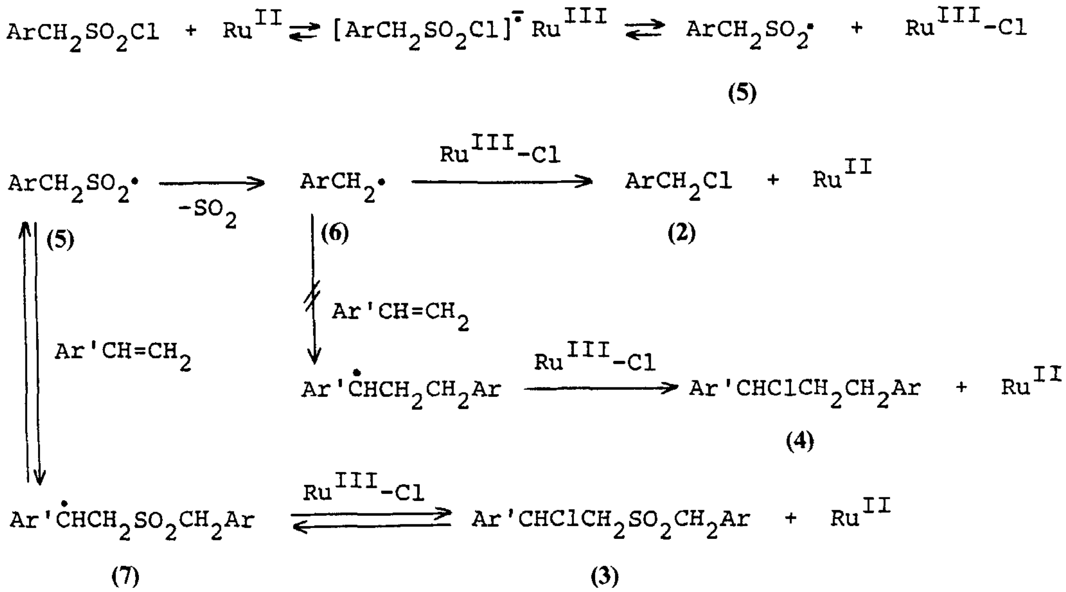
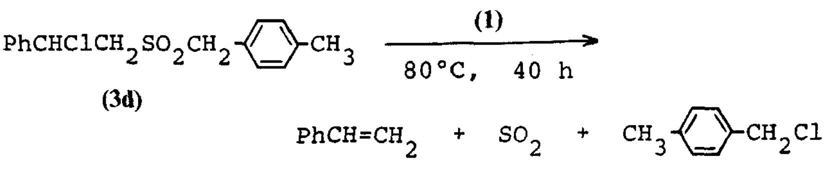


SCHEME 1

to olefin. Arylmethanesulfonyl radical (**5**) adds to olefin competitively with the extrusion of sulfur dioxide affording radical intermediate (**7**), which abstracts the chlorine atom from Ru^{III}–Cl to give the adduct (**3**).

No adduct was observed in the reaction of arylmethanesulfonyl chlorides with an equimolar amount of styrene. This fact may be explained by the assumption that the processes (**5**) to (**7**) and (**7**) to (**3**) are both reversible and a small amount of (**3**) once formed regenerates styrene and radical (**5**) which dissociates sulfur dioxide to give chloromethylarene (**2**) via the radical (**6**). When pure 1-chloro-1-phenyl-2-(*p*-methylbenzyl)sulfonylethane (**3d**) was heated in benezene in the presence of ruthenium(II) catalyst at 80°C for 40 hours, styrene and *p*-methylbenzyl chloride were isolated in 52 and 54% yield, respectively. This finding supports the reversible nature of the reaction (**5**) ⇄ (**7**) ⇄ (**3**) in Scheme 1.



EXPERIMENTAL

All melting points are uncorrected. The infrared absorption spectra were determined on a Hitachi Model EPI-G2 spectrophotometer using samples as either neat liquid or in KBr disks. The proton magnetic spectra were recorded at 60 MHz using a Hitachi R-20B spectrometer with tetramethylsilane as an internal standard in deuteriochloroform. Mass spectra were determined with a Jeol JMS-07 mass spectrometer at an ionizing voltage of 15–30 eV. Gas chromatography was carried out with a Hitachi 163 gas chromatograph with a 1-m column packed with 10% SE-30. Iatroscan was used on a IATROSCAN Lab. Model TH-10 on silica gel rod using hexane–benzene as the eluent. Dichlorotris(triphenyl-

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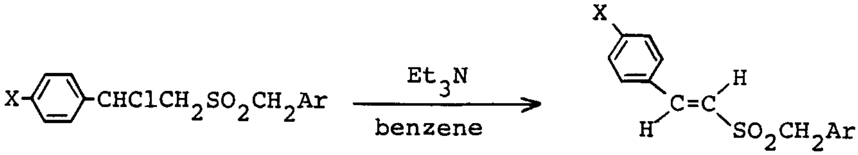
phosphine)ruthenium(II) was prepared by the methods described in the literature.[6] Arylmethanesulfonyl chlorides were prepared by the methods described in the literature;[7] benzylsulfonyl chloride: 89% yield, mp 92–93°C (91–92°C); *p*-methylbenzylsulfonyl chloride: 74% yield, mp 82–83°C; *p*-chlorobenzylsulfonyl chloride, 88% yield, mp 95–96°C; *p*-nitrobenzylsulfonyl chloride, 83% yield, mp 92–93°C (92–93°C).

General Procedure for the Reaction of Arylmethanesulfonyl Chloride Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II). A solution containing 2.0 mmol of benzylsulfonyl chloride and 0.02 mmol of dichlorotris(triphenylphosphine)ruthenium(II) in 4.0 ml of benzene in the presence or absence of olefin (2.2 mmol) was degassed and heated in a sealded tube at 60–80°C for 6–90 hours. The crude reaction mixture was chromatographed to remove the catalyst on a short column of silica gel (Wako gel C-200) using benzene as an eluent. Chloromethylarenes formed were determined by GLC using mesitylene as an internal standard. The results are summarized in the Table I.

Determination of the Rate of Disappearance of Benzylsulfonyl Chloride Catalyzed by Ru(II) Complex. A solution containing 2.0 mmol of benzylsulfonyl chloride and ruthenium(II) catalyst (0.02 mmol) in 4.0 ml of benzene in the presence or absence of styrene was degassed and heated in a sealed tube at 80°C. After an adequate time interval, the remaining benzylsulfonyl chloride was determined by IATROSCAN using *p*-methoxybiphenyl as an internal standard.

General Procedure for the Reaction of Arylmethanesulfonyl Chloride with Styrenes Catalyzed by Dichlorotris(triphenylphosphine)ruthenium(II). A solution containing 2.0 mmol of arylmethanesulfonyl chloride, 3.6 g of substituted styrene, and 0.02 mmol of the ruthenium(II) catalyst was degassed and heated in a sealed tube at 60–80°C for 40–120 hours. The crude reaction mixture was subjected to elution chromatography on silica gel (Wako gel C-200) using hexane and then benzene as the eluent. Chloromethylarene was obtained from the hexane eluate and determined by GLC using phenethyl chloride as the internal standard. 1-Aryl-1-chloro-2-(arylmethanesulfonyl) ethane (**3**) was isolated from the benzene eluate. The structure of (**3**) was confirmed by converting it to (*E*)-arylmethanesulfonyl ethene (**8**) by treating it with triethylamine in benzene at room temperature.



(**3**)

(**8**)

The physical and spectral data of the compounds (**3**) and (**8**) are as follows:

(**3a**): IR (KBr) 1325, 1305, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 3.30–3.95 (2 H, m), 4.12 (2 H, s), 5.46 (1 H, t, *J* = 7.2 Hz), 7.36 (5 H, s), and 7.38 (5 H, s). (**8a**): mp 151–152°C (from EtOH); IR (KBr) 1310, 1295, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 4.26 (2 H, s), 6.64 (1 H, d, *J* = 15.6 Hz), 7.30 (5 H, s), 7.32 (1 H, d, *J* = 15.6 Hz), and 7.34 (5 H, s); Mass (20 eV) m/z 258 (M^+); Anal. Calcd. for $C_{15}H_{14}O_2S$: C, 69.74; H. 5.46. Found: C, 69.66; H, 5.41.

(**3b**): IR (KBr) 1330, 1310, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 2.32 (3 H, s), 3.32–3.90 (2 H, m), 4.08 (2 H, s), 6.40 (1 H, t, *J* = 7.2 Hz), 7.10–7.40 (4 H, m), and 7.35 (5 H, s). (**8b**): mp 132–133°C (from EtOH); IR (KBr) 1315 and 1130 cm^{-1}; NMR ($CDCl_3$) δ 2.39 (3 H, s), 4.34 (2 H, s), 6.64 (1 H, d, *J* = 15.6 Hz), 7.29 (4 H, s), 7.39 (5 H, s), and 7.44 (1 H, d, *J* = 15.6 Hz); Mass (20 eV) m/z 272 (M^+); Anal. Calcd. for $C_{16}H_{16}O_2S$: C, 70.56; H, 5.92. Found: C, 70.55; H, 5.93.

(**3c**): IR (KBr) 1330, 1310, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 3.20–4.02 (2 H, m), 4.20 (2 H, s), 5.40 (1 H, t, *J* = 7.2 Hz), 7.30 (4 H, s), and 7.36 (5 H, s). (**8c**): mp 167–168°C (from EtOH); IR (KBr) 1310 and 1140 cm^{-1}; NMR ($CDCl_3$) δ 4.32 (2 H, s), 6.73 (1 H, d, *J* = 15.6 Hz), 7.33 (4 H, s), 7.36 (5 H, s), and 7.37 (1 H, d, *J* = 15.6 Hz); Mass (20 eV) m/z 294 and 292 (M^+); Anal. Calcd. for $C_{15}H_{13}O_2SCl$: C, 61.53; H, 4.48. Found: C, 61.57; H, 4.50.

(**3d**): IR (KBr) 1330, 1305, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 2.34 (3 H, s), 3.30–3.92 (2 H, m), 4.08 (2 H, s), 5.43 (1 H, t, *J* = 7.2 Hz), 7.18 (4 H, s), and 7.66 (5 H, s); Mass (15 eV) m/z 308 (M^+); Anal. Calcd. for $C_{16}H_{17}O_2SCl$: C, 62.22; H, 5.55. Found: C, 62.24; H, 5.59.

(**3e**): IR (KBr) 1325, 1305, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 3.34– 3.92 (2 H, m), 4.08 (2 H, s), 5.44 (1 H, t, *J* = 7.2 Hz), 7.20–7.48 (4 H, m), and 7.40 (5 H, s): Mass (20 eV) m/z 330 and 328 (M^+); Anal. Calcd. for $C_{15}H_{14}O_2SCl$: C, 54.72; H, 4.29. Found: C, 54.67; H, 4.30.

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(**3f**): IR (KBr) 1530, 1360, 1325, 1310, and 1140 cm^{-1}; NMR ($CDCl_3$) δ 3.38–3.40 (2 H, m), 4.08 (2 H, d, J = 6.6 Hz), 5.44 (1 H, t, J = 6.6 Hz), 7.40 (5 H, s), 7.74 (2 H, d, J = 8.4 Hz), and 8.36 (2 H, d, J = 8.4 Hz); Mass (15 eV) m/z 341 and 339 (M^+); Anal. Calcd. for $C_{15}H_{14}O_2NSCl$: C, 53.02; H, 4.15. Found: C, 52.96; H, 4.12.

The Reaction of 1-*Phenyl*-2-(*p-methylbenzyl*)*sulfonylethane* (**3d**) *Catalyzed by* (**1**). A solution of 90 mg (0.29 mmol) of (**3d**) and 10 mg of (**1**) in 4.0 ml of benzene was degassed and heated at 80°C in a sealed tube for 40 hours. The reaction mixture was subjected to a short column of Wako gel C-200 using hexane and then benzene as the eluent. The hexane fraction was analyzed by GLC to determine the yield of *p*-chloromethyltoluene and styrene as 54 and 52%, respectively. From the benzene fraction 22 mg (28%) of (**3d**) was recovered.

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