SHORT PAPER

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Synthesis of sulfones from arenesulfonyl chlorides and alkyl halides using the Sm/$HgCl_2$ bimetallic system

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A simple and convenient procedure for the synthesis of sulfones from arenesulfonyl chlorides and alkyl halides using the Sm/$HgCl_2$ bimetallic system in tetrahydrofuran is presented.

Keywords: sulfones, arenesulfonyl chlorides, alkyl halides

Organosulfones are a class of important synthetic reagents and intermediates in organic synthesis. Their carbanions which are stabilised by sulfonyl groups may react with various electrophiles to give α-substituted sulfones. The substituted sulfones can be converted conveniently into the corresponding sulfur-free compounds by elimination of the sulfonyl groups.[1] The most commonly used procedures for the preparation of sulfones involve oxidation of the corresponding sulfides or displacement reactions of alkyl halides with the sodium benzenesulfinate as nucleophile.[2-5] These two methods have some weaknesses such as long reaction times, various side reactions and the very unpleasant odour of the sulfides. Huang[6] and Suzuki and co-workers[7] reported that arenesulfonyl chlorides could be transformed into the corresponding sulfones *via* the telluride ion-mediated coupling reaction with alkyl halides. The reactions need air sensitive tellurium compounds as mediators. The formation of sulfones from arenesulfonyl chlorides and alkyl halides can also be promoted by active Ni[*8] or metallic indium in aqueous media.[9] Recently, samarium metal has been employed as a useful reagent or catalyst in organic synthesis.[10] Metallic samarium is stable in the air and its strong reducing power (Sm^{3+}/Sm= –2.41 V) is similar to that of magnesium (Mg^{2+}/Mg = –2.37 V), and superior to that of zinc (Zn^{2+}/Zn = –0.71 V). In order to improve the activity of samarium metal, some additives were used, such as $HgCl_2$, NH_4Cl (aq.), or TMSCl, *etc*. Our group has applied Sm/$HgCl_2$ system to induce the reduction of ArSeSeAr,[11] pinacolic coupling of aromatic aldehydes and ketones.[12] We now try to apply this system to the synthesis of sulfones. Here we present our report on this simple and convenient method for the synthesis of sulfones by the reaction of alkyl halides with arenesulfonyl chlorides in the presence of the Sm/$HgCl_2$ system in THF (as shown in Scheme 1).

$$\underset{1}{RX} + \underset{2}{ArSO_2X} \xrightarrow[THF]{Sm/HgCl_2} \underset{3}{ArSO_2R}$$

Scheme 1

The results are listed in Table 1. From Table 1 it can been seen that the Sm/$HgCl_2$ system mediated coupling reactions of arenesulfonyl chlorides and active alkyl halides such as allyl bromide, 2-bromoacetophenone, ethyl bromoacetate, cinnamyl bromide, methyl iodide and 2,4′-dibromoacetophenone proceed smoothly to give the corresponding organosulfones in satisfactory yields. When RX is *p*-$NO_2C_6H_4CH_2Br$, the yield is much lower (entry g). Unfortunately, ethanesulfonyl chloride gives too little product to be isolated (entry o). Moreover, when the alkyl halide is less active, such as *n*-butyl bromide or allyl chloride, no product was isolated (entry q and p). The mechanism is not yet clear, but may involve the reduction of $HgCl_2$ by metallic samarium, implicating Sm(Hg) amalgam as the promoter of the reactions.

Table 1 Formation of sulfones from arenesulfonyl chlorides and alkyl halides.

Entry	Ar	RX	Time/ h	Temp/ °C	Yield %[a]
a	C_6H_5	$C_6H_5CH_2Br$	2.5	50	75
b	C_6H_5	$BrCH_2CO_2C_2H_5$	2.5	50	69
c	C_6H_5	$C_6H_5COCH_2Br$	2.5	50	72
d	C_6H_5	CH_2=$CHCH_2Br$	2.5	50	64
e	C_6H_5	*p*-$BrC_6H_4COCH_2Br$	2.5	60	57
f	C_6H_5	C_6H_5CH=$CHCH_2Br$	2.5	60	57
g	C_6H_5	*p*-$NO_2C_6H_4CH_2Br$	2.5	60	44
h	*p*-$CH_3C_6H_4$	$C_6H_5CH_2Br$	2.5	50	71
i	*p*-$CH_3C_6H_4$	$BrCH_2CO_2C_2H5_5$	2.5	50	66
j	*p*-$CH_3C_6H_4$	$C_6H_5COCH_2Br$	2.5	50	73
k	*p*-$CH_3C_6H_4$	CH_2=$CHCH_2Br$	2.5	50	69
l	*p*-$CH_3C_6H_4$	*p*-$BrC_6H_4COCH_2Br$	2.5	60	61
m	*p*-$CH_3C_6H_4$	C_6H_5CH=$CHCH_2Br$	2.5	60	57
n	*p*-$CH_3C_6H_4$	CH_3I	2.5	50	51
o	C_2H_5	CH_2=$CHCH_2Br$	10	50	-
p	C_6H_5	CH_2=$CHCH_2Cl$	10	50	-
q	C_6H_5	$CH_3CH_2CH_2CH_2Br$	10	50	-

[a]Isolated yields based on arenesulfonyl chlorides.

In summary, a new and facile method for the preparation of sulfones through a Sm/$HgCl_2$ mediated reaction between arenesulfonyl chlorides and active alkyl halides is reported. The notable advantages of this methodology are the mild conditions, short reaction times, simple operation and satisfactory chemical yields. This is a new application of the Sm/$HgCl_2$ bimetallic system in the synthesis of organic sulfur compounds.

Experimental

Tetrahydrofuran (THF) was distilled from sodium-benzophenone immediately prior to use. All reactions were conducted under a nitrogen atmosphere. Melting points were uncorrected. Infrared spectra were recorded on an IR-408 spectrometer in KBr with absorptions in cm^{-1}. ^1H NMR spectra were recorded on a Bruker AC–80 spectrometer as $CDCl_3$ solutions. *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal tetramethylsilane. Mass

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spectra were recorded on a HP 5989B MS spectrometer. Microanalysis was carried out on a Carlo-Erba 1106 instrument.

General procedure: To a mixture of Sm powder (1 mmol) and $HgCl_2$ (1 mmol) was added THF (10 ml), then alkyl halide (1.2 mmol) and arenesulfonyl chloride (1 mmol) were added under nitrogen atmosphere at room temperature. Reactions were heated to the stated temperature and for the given time (Table 1, the reaction was monitored by TLC), then quenched by addition of water (5 ml). The organic layer was separated, and the water layer was extracted with ether (3×20 ml). The combined extracts were washed with a saturated solution of $Na_2S_2O_3$ (15 ml) and brine (15 ml), then dried over anhydrous Na_2SO_4. After evaporating the solvent under reduced pressure, the crude product was purified by preparative thick layer chromatography using ethyl acetate and cyclohexane (1:4) as eluant.

For the significance of the letter after the compound number see the Table.

Compound **3a**: m.p. 146–147°C (lit.[13], 146–146.5°C) ; ν_{max} 3065, 1598, 1310, 1155cm^{-1}; ^{1}H NMR δ4.28 (2 H, s), 7.10–8.10 (10H, m) ppm.

Compound **3b**: m.p. 40–42°C (lit.[14], 42–43°C); ν_{max} 3080, 1750, 1610 1330, 1275, 1150cm^{-1}, ^{1}H NMR δ1.13 (3 H, t), 3.90–4.45 (4 H, m), 7.20–7.85 (5H, m) ppm.

Compound **3c**: m.p. 94–95°C (lit.[15], 93–95°C); ν_{max} 3100, 1690, 1340, 1150 cm^{-1}; ^{1}H NMR δ4.72 (2 H, s), 7.30 – 8.10 (10 H, m) ppm.

Compound **3d**: oil (lit.[16]) ν_{max} 3090, 1605, 1325, 1150 cm^{-1}; ^{1}H NMR δ3.61 (2 H, d, *J*=6.4 Hz), 5.21–6.05 (3 H, m), 7.20–7.90 (5 H, m) ppm.

Compound **3e**: m.p. 138–140°C (lit.[17], 138.5–139.5°C); ν_{max} 3100, 1700, 1330, 1145 cm^{-1}; ^{1}H NMR δ4.72 (2 H, s), 7.20–8.10 (9 H, m) ppm.

Compound **3f**: m.p. 109–110°C (lit.[18], 110°C); ν_{max} 3110, 1590, 1330, 1135 cm^{-1}; ^{1}H NMR δ4.22 (2 H, d, *J*=5.0 Hz), 6.20–6.57 (1 H, m), 6.70 (1 H, d, *J*= 16.4 Hz), 7.06–7.88 (10 H, m) ppm.

Compound **3g**: m.p. 208–210°C (lit.[8], 209–211°C); ν_{max} 2950, 1520, 1340, 1290, 1145 cm^{-1}; ^{1}H NMR δ4.88 (2 H, s), 8.10–8.95 (9 H, m) ppm.

Compound **3h**: m.p. 144–145°C (lit.[19], 143–145°C); ν_{max} 3080, 1580, 1330, 1140 cm^{-1}; ^{1}H NMR δ2.36 (3 H, s), 4.24 (2 H, s), 7.00–7.60 (9 H, m) ppm.

Compound **3i**: m.p. 34–35°C (lit.[19], 34–35°C); ν_{max} 3090, 1755, 1600, 1340, 1280, 1145 cm^{-1}; ^{1}H NMR δ1.15 (3 H, t), 2.40 (3 H, s), 3.95–4.55 (4 H, m), 7.25–7.90 (4 H, m) ppm.

Compound **3j**: m.p. 109–110°C (lit.[20], 108–109.5°C); ν_{max} 3100, 1680, 1330, 1210, 1145 cm^{-1}; ^{1}H NMR δ2.42 (3 H, s), 4.70 (2 H, s), 7.26–8.05 (9 H, m) ppm.

Compound **3k**: m.p. 51–52°C (lit.[20], 50–52°C); ν_{max} 3060, 1593, 1325, 1280, 1150 cm^{-1}; ^{1}H NMR δ2.40 (3 H, s), 3.67 (2 H, d, *J*=6.4 Hz), 5.30–6.00(3 H, m), 7.17–7.80 (4 H, m) ppm.

Compound **3l**: m.p. 146–147°C (lit.[21], 145–147°C); ν_{max} 3090, 1695, 1325, 1290, 1130 cm^{-1}; ^{1}H NMR, δ2.43 (3 H, s), 4.67 (2 H, s), 7.20–8.00 (8 H, m) ppm.

Compound **3m**: m.p. 115–117°C (lit.[22], 116–118°C); ν_{max} 3090, 1590, 1340, 1280 cm^{-1}; ^{1}H NMR δ2.40 (3 H, s), 4.22 (2 H, d, *J*=6.2 Hz), 6.15–6.52 (1 H, m), 6.69 (1 H, d, *J*=15.7 Hz), 7.05–7.86 (9 H, m) ppm.

Compound **3n**: m.p. 86–87°C (lit.[23], 86.5–87.5°C); ν_{max} 3070, 1580, 1310, 1145 cm^{-1}; ^{1}H NMR δ2.40 (3 H, s), 3.05 (3 H, s), 7.10–7.80 (4 H, m) ppm.

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