SHORT PAPER

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Magnesium perchlorate : an efficient catalyst for selective sulfonylation of arenes under neutral conditions†

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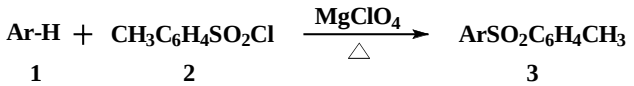
Magnesium perchlorate is found to be an extremely efficient catalyst for the sulfonylation of activated, unactivated and heterocyclic aromatics under almost neutral conditions.

Keywords: catalyst, magnesium perchlorate, sulfonylation, selectivity

Sulfonylation reactions are one of the most important groups of aromatic electrophilic substitutions.[1] The sulfonyl group is widely used synthon for synthetic organic chemists.[2] and sulfones have many industrial applications.[3] In Friedel–Crafts acylation and sulfonylation, a consequence of the complexation of the Lewis acid with the reaction product implies that a stoichiometric amount of the activator is often required. However, some metal halides such as iron(III) chloride, Bronsted acids, for example polyphosporic acid[4] or trifluoroacetic acid,[5] zeolites,[6,7] and Fe(III) exchange montmorillonite[8] have been reported to catalyse the sulfonylation of arenes. Very recently, bismuth(III) triflate[9] and indium(III) triflate[10] have been reported to catalyse sulfonylation of activated and unactivated aromatics. The former is not commercially available and has to be prepared from triphenylbismuth and triflic acid. Although several methods are reported for the preparation of sulfones under acidic conditions,[1–10] the synthesis of sulfones under neutral conditions has not been reported so far. Therefore, in order to expand the versatility of diaryl sulfones, a catalytic method for the synthesis of diaryl sulfones using neutral reaction conditions is highly desirable and needs to be developed. In this paper we highlight our results on catalytic sulfonylation of activated, unactivated and heterocyclic aromatics under almost neutral conditions (Scheme 1).



Scheme 1

After screening different catalysts, we found that magnesium perchlorate worked remarkably well (Table 1, entry 2). The sulfonylation using lithium perchlorate, sodium perchlorate and sodium periodate as catalysts also worked equally well (Table 1, entries 3–5) whereas there was no sulfonylation with sodium perborate as a catalyst even after heating the reaction mixture for longer period of time (Table 1, entry 1). Therefore, for further study of sulfonylation, it was decided to use magnesium perchlorate as a preferred catalyst.

The catalytic activity of the magnesium perchlorate was then investigated with respect to the loadings. After many studies on sulfonylation of anisole (10 ml) with *p*-toluenesulfonyl chloride (5 mmol) under reflux conditions, we found that when less than 20 mol% of magnesium perchlorate was applied, it resulted in low yields of the corresponding product (Table 2, entries 2–4) whereas use of more than 20 mol% did not improve the yield (Table 2, entries 6–7). When attempts were made to carry out sulfonylation of anisole (10 ml) with *p*-toluenesulfonyl chloride (5 mmol) in the absence of catalyst, (magnesium perchlorate), it resulted in almost quantitative recovery of the substrate (Table 2, entry 1). The sulfonylation of anisole in presence of 20 mol% of magnesium perchlorate under mild conditions (25°C) failed even after stirring the reaction mixture for a longer period of time (15 h.).

Table 1 Sulfonylation of anisole (10 ml) with *p*-toluenesulfonyl chloride (5 mmol) using various catalysts 20 mol% at reflux temperature

Entry	Catalyst	Time/h	Yield/%
1	$NaBO_3$	10	—
2	$MgClO_4$	1.5	94
3	$LiClO_4$	2.5	90
4	$NaClO_4$	3	91
5	NaIO4	3	89

Table 2 A catalytic study of $MgClO_4$ during sulfonylation of anisole (10 ml) with *p*-toluenesulfonyl chloride (5 mmol) at reflux temperature

Entry	$MgClO_4$/mol%	Time/h	Yield/%
1	—	1.5	—
2	5	1.5	60
3	10	1.5	65
4	15	1.5	80
5	20	1.5	94
6	25	1.5	92
7	30	1.5	92

The sulfonylation of various aromatics were carried out and the results are summarised in Table 3. It was observed that for the sulfonylation of activated aromatics less reaction time is required (Table 3, entries a–e) as compared to the unactivated and heterocyclic aromatics (Table 3, entries f–m). It is important to note that selectivity of the reaction is impressive in the reported examples wherein exclusively *para*-isomers of diaryl sulfones are obtained in good yields. The detection or isolation of ortho/meta isomers was less than 1% of the total yield of the product. On the other hand recently reported indium(III) triflate[10] catalysed sulfonylation of activated aromatics (e.g. anisole, toluene) yields a mixture of isomers with the composition *ortho:meta:para* = 38:0:62. Also aluminium chloride[11] gives mixture of isomers (e.g. ditolyl sulfones) with the composition of *ortho:meta:para* = 29:7:65 and it generates enormous amount of solid waste. Similarly bismuth(III) triflate[9] gives mixture of isomers (e.g. ditolyl sulfones) with the composition of *ortho:meta:para* = 29:5:66. In this regard the present method is superior because it gives selectively *para*-ditolyl sulfones

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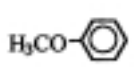
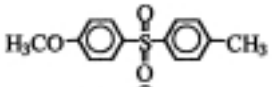
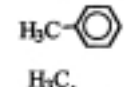
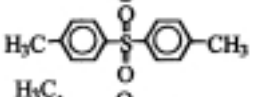
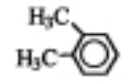
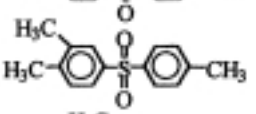
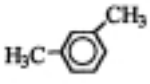
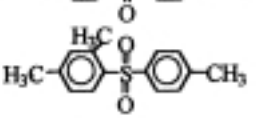
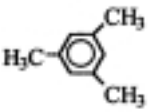
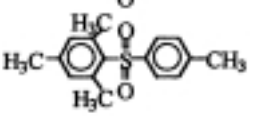
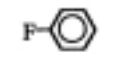
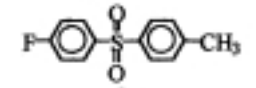
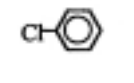
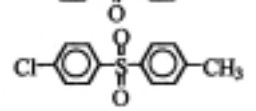
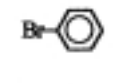
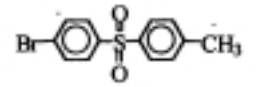
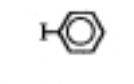
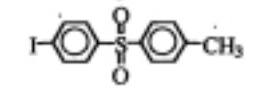
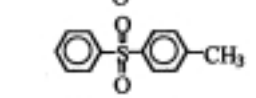
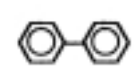
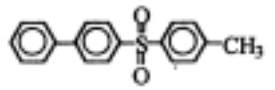
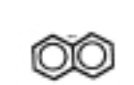
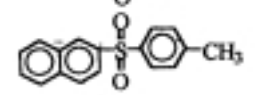
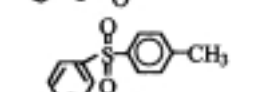
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 3 MgClO4 catalysed sulfonylation of armatics

Entry	Arene	Product	Time /h	Yield[a,b] /%
a			1.5	94
b			3	88
c			3	90
d			2.5	88
e			2.5	87
f			4.5	86
g			4	88
h			4	85
i			4	84
j			5	79
k			5	80
l			6	84
m			6	87

[a] Yields are of pure isolated products.
[b] Products are characterised by their physical constants and spectral analysis.

only in good yield (Table 3, entry b). Further, an improvement in regioselectivity is also observed using magnesium perchlorate in the sulfonylation of naphthalene with *para*-toluenesulfonyl chloride giving only β-isomer without formation of the α-isomer in trace amount. On the other hand, sulfonylation of naphthalene using Fe(III)-exchanged montmorillonite[8] catalyst gave a mixture of α- and β-isomers.

In conclusion, present results demonstrate the efficiency of magnesium perchlorate as a catalyst for sulfonylation of activated, unactivated and heterocyclic aromatics under almost neutral conditions and constitutes a useful alternative to the commonly accepted sulfonylation procedures. The effectiveness of this protocol is manifested in its selectivity.

Experimental

Melting points are uncorrected. IR spectra were recorded on a Bomem FT-IR MB-104 spectrophotometer with zinc selenide optics. ^{1}H NMR were recorded on a Brucker AC-300 spectrometer (300 MHz) in $CDCl_3$ using TMS as an internal standard. Mass spectra were recorded on a Fining MAT 1020 mass spectrometer operating at 70 eV. CHN analysis were recorded on a Vario-EL analyser. TLC was monitored on 0.25mm E. Merck precoated silica gel plates (60 F–254). $MgClO_4$ used for the reactions was purchased from Aldrich and was used without purification.

Typical experimental procedure: A mixture of anisole (10 ml), *p*-toluenesulfonyl chloride (5 mmol) and magnesium perchlorate (1mmol) was refluxed for 1.5 h. On completion of the reaction (TLC), the reaction mixture was cooled and anisole was removed under reduced pressure. To the residue, chloroform (10 ml) and water (10 ml) where added. The aqueous layer was washed with chloroform (3 × 5 ml). The combined organic layer was dried with anhydrous Na_2SO_4 and removal of the solvent under vacuum furnished crude product which was further purified by column chromatography (petroleum ether : ethyl acetate = 8:2). In case of solid substrates, nitrobenzene (10 ml) was used as a solvent.

(4-Methoxyphenyl)-p-tolyl sulfone (**3a**): m.p.=105°C; (lit. 104°C)[12]. IR (KBr, cm^{-1}): 683, 838, 1007, 1360, 1599, 2910, 3300; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.95 (d, 2H, *J*=7.2 Hz, Ar–H), 7.91 (d, 2H, *J*=7.2 Hz, Ar–H), 7.15(d, 2H, *J*=8.8 Hz, Ar–H), 8.14 (d, 2H, *J*=8.8 Hz, Ar–H).

Di-p-tolyl sulfone (**3b**): m.p.=156°C; (lit. 156°C)[12]. IR (KBr, cm^{-1}): 630, 765, 816, 990, 1035, 1100, 1180, 1360, 1460, 1500, 1600, 3421; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.39 (s, 6H, 2 × Ar–CH_3), 7.27 (d, 4H, *J* = 5 Hz, 4 × Ar–H), 7.80 (d, 4H, *J* = 5 Hz, 4 × Ar–H).

(3,4-Dimethylphenyl)-p-tolyl sulfone (**3c**): m.p.=55°C. IR(KBr, cm^{-1}) : 1017, 1123, 1342, 1447, 1515, 1603; ^{1}H NMR(300 MHz, $CDCl_3$): δ 2.3(s, 3H, Ar–CH_3), 2.36 (s, 3H, Ar–CH_3) 2.43 (s, 3H, Ar–CH_3), 7.1 (d, 1H, *J*=7.5 Hz, Ar–H), 7.8 (d, 1H, *J*=1.5 Hz, Ar–H), 8.0(dd, 1H, *J*=1.5 Hz, 7.5 Hz, Ar–H) 7.5(d, 2H, *J*=8.6 Hz, Ar–H), 8.1 (d, 2H, *J*=8.6 Hz, Ar–H) 7.5 (d, 2H, *J*=8.6 Hz, Ar–H).

(2,4-Dimethylphenyl)-p-tolyl sulfone (**3d**): m.p. = 49°C (lit 48–49°C)[12]. IR(KBr, cm^{-1}): 1028, 1110, 1175, 1355, 1455, 1505, 1610; ^{1}H NMR(300 MHz, $CDCl_3$): δ 2.34(s, 3H, $ArCH_3$), 2.38 (s, 3H, Ar–CH_3) 2.41 (s, 3H, Ar–CH_3), 7.01 (d, 1H, *J*=1.7 Hz, Ar–H), 7.16 (dd, 1H, *J*=1.7 Hz, 7.7 Hz, Ar–H), 7.25 (d, 2H, *J* = 8.8 Hz, Ar–H), 7.77 (d, 2H, *J*=8.8 Hz, Ar–H), 8.08(d, 1H, *J*=7.7 Hz, Ar–H).

(2,4,6-Trimethylphenyl)-p-tolyl sulfone (**3e**): m.p.=122°C (lit.123 °C).[12]. IR(KBr, cm^{-1}):810, 1011, 1150, 1350, 1460, 1522, 1611; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.32(s, 3H, Ar–CH_3), 2.35(s, 3H, Ar–CH_3), 2.45(s, 6H, 2 × Ar–CH_3), 7.03(s, 2H, Ar–H), 7.62(d, 2H, *J*=8.4Hz, Ar–H), 8.2 (d, 2H, *J*=8.4 Hz, Ar–H).

(4-Fluorophenyl)-p-tolyl-sulfone (**3f**): m.p.=93°C (lit. 95°C)[13]. IR (KBr, cm^{-1}):629, 775, 816, 880, 1050, 1110, 1175, 1355, 1590, 3390,; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.42 (s, 3H, Ar–CH_3), 7.20 (m, 2H, Ar–H), 7.35 (d, 2H, *J*=8.4 Hz, Ar–H) 7.85 (d, 2H, *J* =8.4 Hz, Ar–H), 7.91–7.98 (m, 2H, Ar–H).

(4-Chlorophenyl)-p-tolyl sulfone (**3g**): m.p. = 124°C (lit. 123°C)[12]. IR (KBr, cm^{-1}): 626, 772, 885, 816, 990, 1040, 1100, 1175, 1353, 1599, 3397; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.38 (s, 3H, Ar–CH_3), 7.34 (d, 2H, *J*=7.7 Hz, Ar–H), 7.43-7.52 (m, 2H, Ar–H), 7.82 (d, 2H, *J*= 9.0 Hz, Ar–H), 7.86–7.92 (m, 2H, Ar–H).

(4-Bromophenyl)-p-tolyl sulfone (**3h**): m.p.=136–137°C (lit. 135–136 °C)[13]. IR (KBr, cm^{-1}) : 626, 772, 816, 895, 1030, 1120, 1175, 1360, 1580, 3410; ^{1}H NMR (300 MHz, $CDCl_3$) : δ 2.49 (s, 3H, Ar–CH_3), 7.48 (d, 2H, *J*=8.5 Hz, Ar–H), 7.76-7.91 (m, 4H, 4 ? Ar–H), 7.98 (d, 2H, *J* = 8.5 Hz, Ar–H).

(4-Iodophenyl)-p-tolyl sulfone (**3i**): m.p.=140°C. IR(KBr, cm^{-1}): 621, 778, 801, 904, 1050, 1107, 1160, 1355, 1518, 1600; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.4(s, 3H, Ar–CH_3), 7.76(d, 2H, *J*=7.7 Hz, Ar–H), 7.72(d, 2H, *J*=8.4Hz, Ar–H), 8.1 (d, 2H, *J*=8.4 Hz, Ar–H), 8.21 (d, 2H, *J*=7.7 Hz, Ar–H).

(Phenyl)-p-tolyl sulfone (**3j**): m.p.=126°C (lit. 127°C);[12]. IR (KBr, cm^{-1}): 1153, 1303, 1500, 1604; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.4 (s, 3H, Ar–CH_3), 7.2(d, 2H, *J*=7.8 Hz, Ar–H), 7.4–7.8(m, 5H, Ar–H), 8.01(d, 2H, *J*=7.8 Hz, Ar–H).

(Bisphenyl)-p-tolyl sulfone (**3k**): m.p. = 155°C. IR (KBr, cm^{-1}): 1160, 1312, 1512, 1601; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.36 (s, 3H, Ar–CH_3), 7.11–7.24 (m, 5H, Ar–H), 7.75 (d, 2H, *J*=8.2 Hz, Ar–H), 7.89(d, 2H, *J*=7.9 Hz, Ar–H), 8.1(d, 2H, *J*=7.9 Hz, Ar–H), 8.3 (d, 2H, *J*=8.2 Hz, Ar–H).

(β-Naphthyl)-p-tolyl sulfone (**3l**): m.p.=164°C. IR (KBr, cm^{-1}) : 1155, 1305, 1509, 1607; ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.33 (s, 3H, Ar–CH_3) 7.06–7.15(m, 4H, Ar–H), 7.7(d, 2H, *J*=7.7 Hz, Ar–H), 7.8(d, 1H, *J*=8.1Hz, Ar–H), 8.1(dd, 1H, *J*=1.3Hz, 8.1 Hz, Ar–H), 8.2(d, 1H, *J*=1.3Hz, Ar–H), 8.3 (d, 2H, *J*=7.7 Hz, Ar–H)

(Thiophene)-3-p-tolylsulfone (**3m**): m.p. = 110°C. IR (KBr, cm^{-1}): 1160, 1310, 1500, 1610; ^{1}H, NMR (300 MHz, $CDCl_3$): δ 7.8 (d, 2H, *J*=8.1 Hz, Ar–H), 8.02(d, 2H, *J*=8.1 Hz, Ar–H), 8.12-8.3 (m, 3H, Ar–H).

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