SHORT PAPER

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An efficient and convenient method for the synthesis of aromatic sulfones catalysed by $ZrO_2/S_2O_8^{2-}$solid superacid[†]

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A manipulatively simple and rapid procedure for the synthesis of diaryl sulfones from arylsulfonyl chlorides with aromatic compounds is described; the reaction is conducted under Friedel–Crafts conditions in the absence of solvent using $ZrO_2/S_2O_8^{2-}$ as catalyst in 78–93% yields.

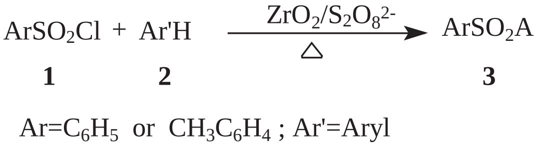
Keywords: diaryl sulfones, arylsulfonyl chlorides, aromatic compounds, Friedel–Crafts

Organosulfones are very important intermediates in organic synthesis[1] and industrial application.[2] Especially, diaryl sulfones deserve much attention as they are intermediates in the drug industry. For example, diphenyl sulfone is used as an intermediate for DAPSONE (4,4'-diamino-diphenyl sulfone, effective for leprosy treatment).[3] Sulfones are usually prepared by oxidation of the corresponding sulfides and sulfoxides or by a displacement reaction of sodium arenesulfinate with an appropriate alkyl halide.[4] Some catalysts such as metal halides,[1a] zeolites,[5] Bronsted acids,[6] lithium perchlorate[7] and $Bi(OTf)_3$[8] have been reported to catalyse the sulfonylation of aromatics. More recently, Fe(III) exchanged montmorillonite clay,[9] indium triflate[10] and $BiCl_3$-triflic acid[11] have been successfully used for catalytic sulfonylation of aromatics. Each of the above methods has its own merit, but some methods have not been entirely satisfactory with drawbacks such as low yield, long reaction time, emerging problems of corrosiveness, tedious workup and a requirement for special techniques. Consequently, it is desirable to develop improved methods for the synthesis of diaryl sulfones under good and environmental friendly conditions.

Solid superacids have received considerable attention as powerful reaction media for effecting various transformations. In addition, solid superacids are attractive because they are stable, reusable, 'green' and cheap. Recently, we have developed efficient and convenient procedures for the preparation of some organic compounds catalysed by ZrO_2/SO_4^{2-} or TiO_2/SO_4^{2-} solid superacid.[12-18] As a part of ongoing work on solid superacid catalysis, we now describe a simple and practical method for the sulfonylation of aromatic compounds in the presence of $ZrO_2/S_2O_8^{2-}$ affording diaryl sulfones in 78–93% yields (Scheme 1).

To the best of our knowledge, this technique for the preparation of aromatic sulfones using solid superacid is completely novel and has not been reported in the literature and so we report in this paper for the first time the arylsulfonylation of aromatics catalysed by $ZrO_2/S_2O_8^{2-}$ solid superacid. The process in its entirety involves a simple mixing of arylsulfonyl chlorides **1** and aromatic compounds **2** in the presence of $ZrO_2/S_2O_8^{2-}$ under heating conditions for the time and temperature specified in Table 1. The purities of products **3** were established by ^{1}H NMR, IR and melting point determination.

It should be noted that in the absence of catalyst no product was observed even with a prolonged heating time. The lowering of reaction temperature was detrimental to the reaction. For example, for entry 2, at 100°C for 2.5 hours only 35% yield of product was obtained, whereas 85% yield was obtained at 140°C for 0.5 hour. Substituent effects have been studied in these reactions. According to the data listed in the Table 1, it is clear that electron-donating groups have increased the reaction speed as well as reaction yields (Table 1**,** entries 2–9, 15–21). On the other hand, electron-withdrawing groups have decreased yields and increased reaction time (Table 1, 11–13, 22 and 23). When one strong electron-withdrawing group is on the aromatic hydrocarbon **2**, the reaction does not take place at all (Table 1, entries 24,25). This may be due to the strongly electron-withdrawing NO_2 or CN that will reduce the reactivity of the aromatic ring. The yields and reaction conditions of our method have been compared with actual figures for other methods. We only use 0.5 hour obtaining 85% yield product in the *p*-toluenesulfonylation of toluene by $ZrO_2/S_2O_8^{2-}$ solid superacid catalyst in our experiment, compared to other reported catalysts such as InX_3 (lit.[10] 2.0 hours, 80% yield) and zeolite beta (lit.[11] 24 hours, 53% yield). So the $ZrO_2/S_2O_8^{2-}$ solid superacid is a better catalyst to this kind of reaction.



$$\underset{\mathbf{1}}{ArSO_2Cl} + \underset{\mathbf{2}}{Ar'H} \xrightarrow[\triangle]{ZrO_2/S_2O_8^{2-}} \underset{\mathbf{3}}{ArSO_2Ar'}$$

$$Ar{=}C_6H_5 \text{ or } CH_3C_6H_4\text{ ; } Ar'{=}Aryl$$

Scheme 1

In conclusion, we have developed a practical and efficient method for the synthesis of aromatic sulfones under solvent-free conditions using aromatic compounds and arylsulfonyl chlorides in the presence of $ZrO_2/S_2O_8^{2-}$.This method is superior from the view of operation simplicity, higher yields, short reaction times, non-corrosion, and friendliness to the environment than previously reported methods.

Experimental

Melting points are uncorrected.^{1}H NMR spectra were determined on a Varian VXR-300S (300 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. IR spectra were determined on an FTS-175C spectrometer. All the liquid parent materials were freshly distilled. The products were also characterised by comparison of their melting points with literature values. The catalyst $ZrO_2/S_2O_8^{2-}$ solid superacid was prepared as follows. $Zr(OH)_4$ was infused in $(NH_4)_2S_2O_8$ (1 mol/l) for 4 hours, then filtered off, dried at 110°C for 2 hours, crushed to below 150 mesh, calcined in a furnace at 600°C for 4 hours and finally stored in a desiccator until used.

General procedure for the preparation of aromatic sulfones: A mixture of arylsulfonyl chloride **1** (2.00 mmol), aromatic compound **2** (8.00 mmol) and $ZrO_2/S_2O_8^{2-}$ (200 mg) was stirred at a suitable temperature for the corresponding time shown in the Table 1. The progress of the reaction was monitored with TLC. After completion

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

Table 1 Arylsulfonylation of aromatics in the presence of $ZrO_2/S_2O_8^{2-}$

Entry	Ar	Ar′H	Product	Time /h	Temp. /°C	Yield /%[a]	M.P./ °C Found	Reported
1	$4\text{-}CH_3C_6H_4$	C_6H_6	$4\text{-}CH_3C_6H_4SO_2C_6H_5$	1.0	140	83	117–118	125[19]
2	$4\text{-}CH_3C_6H_4$	$CH_3C_6H_5$	$4\text{-}CH_3C_6H_4SO_2C_6H_4CH_3\text{-}4$	0.5	140	85	154–156	156[19]
3	$4\text{-}CH_3C_6H_4$	$1,2\text{-}(CH_3)_2C_6H_4$	$4\text{-}CH_3C_6H_4SO_2C_6H_3(CH_3)_2\text{-}3,4$	1.0	150	85	128–130	127–129[20]
4	$4\text{-}CH_3C_6H_4$	$1,3\text{-}(CH_3)_2C_6H_4$	$4\text{-}CH_3C_6H_4SO_2C_6H_3(CH_3)_2\text{-}2,4$	0.5	150	89	47–48	48–49[10]
5	$4\text{-}CH_3C_6H_4$	$1,4\text{-}(CH_3)_2C_6H_4$	$4\text{-}CH_3C_6H_4SO_2C_6H_3(CH_3)_2\text{-}2,5$	1.0	150	81	104–105	108–110[21]
6	$4\text{-}CH_3C_6H_4$	$1,3,5\text{-}(CH_3)_3C_6H_3$	$4\text{-}CH_3C_6H_4SO_2C_6H_2(CH_3)_3\text{-}2,4,6$	0.5	150	88	123	117[19]
7	$4\text{-}CH_3C_6H_4$	$C_6H_5C_6H_5$	$4\text{-}CH_3C_6H_4SO_2C_6H_4Ph\text{-}4$	0.5	140	83	198–200	198–203[20]
8	$4\text{-}CH_3C_6H_4$	$CH_3CH_2C_6H_5$	$4\text{-}CH_3C_6H_4SO_2C_6H_4C_2H_5\text{-}4$	1.0	150	85	106–108	104–106[20]
9	$4\text{-}CH_3C_6H_4$	$CH_3OC_6H_5$	$4\text{-}CH_3C_6H_4SO_2C_6H_4OCH_3\text{-}4$	0.5	150	93	148–149	149[7]
10	$4\text{-}CH_3C_6H_4$	$C_{10}H_8$	$4\text{-}CH_3C_6H_4SO_2C_{10}H_7\text{-}\beta$	1.5	140	89	116	121[19]
11	$4\text{-}CH_3C_6H_4$	FC_6H_5	$4\text{-}CH_3C_6H_4SO_2C_6H_4F\text{-}4$	1.0	150	81	93–94	95[11]
12	$4\text{-}CH_3C_6H_4$	ClC_6H_5	$4\text{-}CH_3C_6H_4SO_2C_6H_4Cl\text{-}4$	1.0	160	81	121–122	123[8b]
13	$4\text{-}CH_3C_6H_4$	BrC_6H_5	$4\text{-}CH_3C_6H_4SO_2C_6H_4Br\text{-}4$	1.0	160	87	134–135	135–136[4]
14	C_6H_5	C_6H_6	$C_6H_5SO_2C_6H_5$	1.0	140	83	117–118	124[11]
15	C_6H_5	$CH_3C_6H_5$	$4\text{-}CH_3C_6H_4SO_2C_6H_5$	0.5	140	83	117–118	125[19]
16	C_6H_5	$1,2\text{-}(CH_3)_2C_6H_4$	$3,4\text{-}(CH_3)_2C_6H_3SO_2C_6H_5$	1.0	150	84	108–110	108–112[19]
17	C_6H_5	$1,3\text{-}(CH_3)_2C_6H_4$	$2,4\text{-}(CH_3)_2C_6H_3SO_2C_6H_5$	0.5	150	89	84–85	86[11]
18	C_6H_5	$1,4\text{-}(CH_3)_2C_6H_4$	$2,5\text{-}(CH_3)_2C_6H_3SO_2C_6H_5$	1.0	150	78	106–108	107–110[21]
19	C_6H_5	$1,3,5\text{-}(CH_3)_3C_6H_3$	$2,4,6\text{-}(CH_3)_3C_6H_2SO_2C_6H_5$	0.5	150	85	78–79	80[22]
20	C_6H_5	$C_6H_5C_6H_5$	$4\text{-}PhC_6H_4SO_2C_6H_5$	0.5	140	80	146–148	143–146[20]
21	C_6H_5	$CH_3CH_2C_6H_5$	$4\text{-}C_2H_5C_6H_4SO_2C_6H_5$	1.0	150	83	88–90	88–91[20]
22	C_6H_5	ClC_6H_5	$4\text{-}ClC_6H_4SO_2C_6H_5$	1.0	160	79	118–119	119–120[10]
23	C_6H_5	BrC_6H_5	$4\text{-}BrC_6H_4SO_2C_6H_5$	1.0	160	83	102–104	98–103[20]
24	$4\text{-}CH_3C_6H_4$	$NO_2C_6H_5$		3.5	160	0		
25	$4\text{-}CH_3C_6H_4$	NCC_6H_5		3.5	160	0		

[a] Isolated yield.

of the reaction, the mixture was cooled and extracted with ether (10 ml × 3). Evaporation of the solvent under reduced pressure afforded the crude product. The crude product was purified by column chromatography on silica gel using hexane/ethylacetate (9:1) as eluent. Selected spectral data of some of the products are given below:

p-Tolyl phenyl sulfone (Table 1, entry **1** or **15**): IR 1153, 1307 cm^{-1}; δ_H 2.40 (s, 3H, CH_3), 7.30 (d, 2H, *J*=8.3Hz, Ar-H), 7.48–7.55 (m, 3H, Ar-H), 7.85(d, 2H, *J*=8.3Hz, Ar-H), 7.90–7.95 (m. 2H, Ar-H).

Di(*p*-tolyl) sulfone (Table 1, entry **2**): IR 1161, 1310 cm^{-1}; δ_H 2.39 (s, 6H, CH_3), 7.27 (d, 4H, *J*=9.0Hz, Ar-H), 7.80 (d, 4 H, *J*=9.0 Hz, Ar-H).

(2,4-Dimethylphenyl) *p*-tolyl sulfone (Table 1, entry **4**): IR 1153, 1310 cm^{-1}; δ_H 2.36 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.40 (s, 3H, CH_3), 6.99 (s, 1H, Ar-H), 7.13 (d, 1H, *J*=7.8Hz, Ar-H), 7.23 (d, 2H, *J*=8.8Hz, Ar-H), 7.70 (d, 2H, *J*=8.8Hz, Ar-H), 8.03 (d, 1H, *J*=7.8Hz, Ar-H).

(2,5-Dimethylphenyl) *p*-tolyl sulfone (Table 1, entry **5**): IR 1146, 1300 cm^{-1}; δ_H 2.36 (s, 3H, CH_3), 2.41 (s, 6H, CH_3), 7.06 (d, 1H, *J*=7.8Hz, Ar-H), 7.21 (d, 1H, *J*=7.8Hz, Ar-H), 7.26 (d, 2H, *J*=8.8Hz, Ar-H), 7.72 (d, 2H, *J*=8.8Hz, Ar-H), 7.98 (s, 1H, Ar-H).

(2,4,6-Trimethylphenyl) *p*-tolyl sulfone (Table 1, entry **6**): IR 1149, 1309 cm^{-1}; δ_H 2.62 (s, 3H, CH_3), 2.72 (s, 3H, CH_3), 2.92 (s, 6H, CH_3), 7.59 (d, 2H, *J*=8Hz, CH_3), 7.59 (s, 2H, Ar-H), 8.00 (d, 2H, *J*=8Hz, Ar-H).

(4-Methoxyphenyl) *p*-tolyl sulfone (Table 1, entry **9**): IR 638, 834, 1007, 1360, 1599, 2910, 3300 cm^{-1}; δ_H 2.36 (s, 3H, CH_3), 3.81 (s, 3H, OCH_3), 6.95 (d, 2H, *J*=8.3Hz, Ar-H), 7.31 (d, 2H, *J*=7.4Hz, Ar-H), 7.85 (d, 2H, *J*=8.3Hz, Ar-H), 7.90 (d, 2H, *J*=7.4Hz, Ar-H).

β-Naphthyl *p*-tolyl sulfone (Table 1, entry **10**): IR 1152, 1312 cm^{-1}; δ_H 2.38 (s, 3H, CH_3), 7.27(d, 2H, Ar-H), 7.59 (m, 2H, Ar-H), 7.78 (d, 1H, Ar-H), 7.83 (d, 2H), 7.87 (m, 1H, Ar-H), 7.93 (d, 1H, Ar-H), 7.97 (d, 1H, Ar-H), 8.52 (s, 1H, Ar-H).

(4-Fluorophenyl) *p*-tolyl sulfone (Table 1, entry **11**): IR 1155, 1316 cm^{-1}; δ_H 2.40 (s, 3H, CH_3), 7.16 (m, 2H, Ar-H), 7.31(d, 2H, *J*=8.0Hz, Ar-H), 7.81(d, 2H, *J*=8.0Hz, Ar-H), 7.90–7.95 (m, 2H, Ar-H).

(4-Chlorophenyl) *p*-tolyl sulfone (Table 1, entry **12**): IR 1153, 1315 cm^{-1}; δ_H 2.40 (s, 3H, CH_3), 7.31 (d, 2H, *J*=7.8Hz, Ar-H), 7.40–7.50 (m, 2H, Ar-H), 7.80 (d, 2H, *J*=12.0Hz, Ar-H), 7.85–7.90 (m, 2H, Ar-H).

(4-Bromophenyl) *p*-tolyl sulfone (Table 1, entry **13**): IR 1152, 1314 cm^{-1}; δ_H 2.54 (s, 3H, CH_3), 7.45 (d, 2H, *J*=8.6Hz, Ar-H), 7.77–7.92 (m, 4H, Ar-H), 7.95 (d, 2H, *J*=8.6Hz, Ar-H).

Diphenyl sulfone (Table 1, entry **14**): IR 1148, 1287 cm^{-1}; δ_H 7.50 (m, 6H, CH_3), 7.88 (m, 4H, Ar-H).

(2,4-Dimethylphenyl) phenyl sulfone (Table 1, entry **17**): IR 1151, 1306 cm^{-1}; δ_H 2.32 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.99 (s, 1H, Ar-H), 7.16 (d, 1H, *J*=7.8Hz, Ar-H), 7.46 (m, 3H, Ar-H), 7.81 (d, 2H, *J*=8.8Hz, Ar-H), 8.07 (d, 1H, *J*=7.8Hz, Ar-H).

(2,4,6-Trimethylphenyl) phenyl sulfone (Table 1, entry **19**): IR 1148, 1306 cm^{-1}; δ_H 2.30 (s, 3H, CH_3), 2.59 (s, 6H, CH_3), 6.94 (s, 2H, Ar-H), 7.49–7.79 (m, 5H, Ar-H).

(4-Chlorophenyl) phenyl sulfone (Table 1, entry **22**): IR 1152, 1318 cm^{-1}; δ_H 7.50–7.59 (m, 5H, Ar-H), 7.82–7.93 (m, 4H, Ar-H).

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