***SHORT PAPER***

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# Ionic liquid-accelerated arylation of sodium arenesulfinates with diaryliodonium salts used for the synthesis of diaryl sulfones

**Feng-Yan Wang [b], Zhen-Chu Chen[a,b]* and Qin-Guo Zheng[c]**

[a]*Ningbo Institute of Technology, Zhejiang University, Ningbo, 315104, P.R.China*

[b]*Department of Chemistry, Zhejiang University (Xixi campus), Hangzhou, 310028, P.R.China*

[c]*Pharmaceutical Sciences Research Institute, Aston University, Aston Triangle, Birmingham B4 7ET, UK*

Arylation of sodium arenesulfinates with diaryliodonium salts can be performed with good yields in the room-temperature ionic liquid, 1-butyl-3-methylimidazolium tetrafluoroborate ([BMim]$BF_4$), which provides an efficient method for the synthesis of diaryl sulfones; the ionic liquid can be recycled and reused.

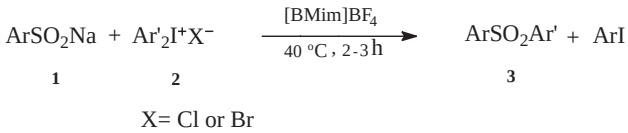
**Keywords:** ionic liquid, sodium arenesulfinates, diaryliodonium salts, diaryl sulfones

The sulfonyl group is widely used in synthons for organic synthesis.[1] Some sulfones have many industrial applications,[2] and some diaryl sulfones exhibit high antifungal and antibacterial activity. The nucleophilic substitution reaction between haloalkanes and sulfinate anions constitutes an important synthesis of aliphatic sulfones,[3] but this methodology is not suitable for the synthesis of aromatic sulfones, except in cases where highly activated haloarenes are employed as substrates.[4]

Diaryliodonium salts show superior reactivity compared to aryl halides. These iodonium salts have been used to arylate a wide variety of nucleophilic substrates.[5] Beringer and co-workers[6] originally reported the formation of aromatic sulfones by the reaction of diphenyliodonium salts with metal sulfinates. However, this reaction was run in ethanol–water solution at long reflux, and gave generally low yields. Recently, we reported a mild palladium-catalysed method for the arylation of sodium arenesulfinates with diaryliodonium salts, which gave a reasonable yield of diaryl sulfones.[7] But the drawback to this approach is the necessary use of an expensive palladium catalyst.

More recently, room-temperature ionic liquids (RTILs), consisting of 1,3-dialkylimidazolium cations and their counterions have attracted growing interest.[8] Desirable properties, such as thermal stability, lack of vapour pressure, and good solubility for a wide range of organic and inorganic materials, have promoted these ionic liquids as a promising alternative to conventional solvents for chemical synthesis and transition-metal catalysed reactions, *e.g.*, Friedel–Crafts alkylation,[9] hydrogenation,[10] the Heck reaction[11] and the Suzuki cross-coupling reaction,[12] *etc.* In this respect, the use of ionic liquids may be advantageous to the nucleophilic displacement process. As part of a programme to investigate the range of organic reactions possible in ionic liquids, we examined the reaction of sodium arenesulfinates with diaryliodonium salts in the ionic liquid 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ([BMim]$BF_4$)[13] to provide an efficient method for the synthesis of diaryl sulfones.

Here we report the ionic liquid-accelerated arylation of sodium arenesulfinates with diaryliodonium salts (Scheme 1).




**Scheme 1**

We found that the reaction of sodium arenesulfinates **1** with diaryliodonium salts **2** in [BMim]$BF_4$ occurred readily, reaching completion within 2–3h at 40°C, and gave the corresponding diaryl sulfones **3** in good yields. The results are summarised in Table 1. All products gave satisfactory m.p., IR and $^1$H NMR spectra.

As can be seen in Table 1, several sodium arenesulfinates and diaryliodonium salts having various substituents, such as chloro, methyl and nitro group, were successfully reacted and the reaction was found to be general and applicable to synthesis of symmetrical diaryl sulfones or unsymmetrical diaryl sulfones. The ionic liquid [BMim]$BF_4$ can be compared with classical molecular solvents, and has the advantage of rate acceleration and increase of yield. For example, using the classical molecular solvents, such as DMF or ethanol, the preparation of diaryl sulfone (**3a** or **3b**) needs heating for longer times to give low yields (Entries 14 and 15) but the same reaction was successful in [BMim]$BF_4$ at 40°C and gave a higher yield (Entries 1 and 4) in only two hours. Also in comparison with our previous reported method, [7] the present method avoids the use of the expensive palladium catalyst and is simple, rapid and gives a higher yield. The compared results are also summarised in Table 1.

The ionic liquid [BMim]$BF_4$ can typically be recovered by extracting the isolation product and filtering to remove insoluble sodium chloride or bromide, followed by vacuum drying. The recovered solvent can be reused with no appreciable decrease in yield (Entry 5). Further studies indicate that the related ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate [BMim]$PF_6$ and 1-butylpyridinium tetrafluoroborate [BPy]$BF_4$ are also efficient solvents for arylation of sodium benzenesulfinate with diphenyliodonium chloride (Entries 2 and 3).

As shown in Scheme 1, an iodoarene was another product in the reaction. However, it was easily converted into diaryliodonium salts in sufficient yield as described in our previous paper.[14]

In conclusion, we have demonstrated that arylation of sodium arenesulfinates with diaryliodonium salts can be effectively performed in the room-temperature ionic liquid ([BMim]$BF_4$)

* To receive any correspondence.

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

**Table 1** Arylation of sodium arenesulfinates with diaryliodonium salts in [BMim]$BF_4$

| Entry | Ar | Ar′ | $X^-$ | Product | Yield[a]/% | |
|---|---|---|---|---|---|---|
| | | | | | This work | (lit.) |
| 1 | Ph | Ph | Cl | $PhSO_2Ph$ **3a** | 73 | (71)[e] |
| 2 | Ph | Ph | Cl | **3a** | 73[b] | |
| 3 | Ph | Ph | Cl | **3a** | 71[c] | |
| 4 | *p*-Tol | Ph | Br | $PhSO_2$Tol-*p* **3b** | 75 | (66)[e] |
| 5 | *p*-Tol | Ph | Br | **3b** | 75[d] | |
| 6 | *p*-$ClC_6H_4$ | Ph | Cl | $PhSO_2C_6H_4$Cl-*p* **3c** | 66 | (62)[e] |
| 7 | Ph | *p*-Tol | Br | **3b** | 75 | (66)[e] |
| 8 | *p*-Tol | *p*-Tol | Br | *p*-Tol$SO_2$Tol-*p* **3d** | 74 | (67)[e] |
| 9 | *p*-$ClC_6H_4$ | *p*-Tol | Br | *p*-Tol$SO_2C_6H_4$Cl-*p* **3e** | 70 | (62)[e] |
| 10 | *p*-Tol | *p*-$ClC_6H_4$ | Br | **3e** | 69 | (60)[e] |
| 11 | *p*-$ClC_6H_4$ | *p*-$ClC_6H_4$ | Br | *p*-$ClC_6H_4SO_2C_6H_4$Cl-*p* **3f** | 62 | (55)[e] |
| 12 | Ph | *m*-$NO_2C_6H_4$ | Cl | *m*-$NO_2C_6H_4SO_2Ph$ **3g** | 56 | (48)[e] |
| 13 | *p*-Tol | *m*-$NO_2C_6H_4$ | Cl | *m*-$NO_2C_6H_4SO_2$Tol-*p* **3h** | 54 | (45)[e] |
| 14 | Ph | Ph | $BF_4$ | **3a** | | (30)[f] |
| 15 | *p*-Tol | Ph | Br | **3b** | | (56)[g] |

[a]Isolated yield based on diaryliodonium salts. [b] Using [BMim]$PF_6$. [c] Using [bpy]$BF_4$. [d] Using recovered [BMim]$BF_4$. [e] Our previous reported palladium-catalysed method, data from ref. 7. [f] Reaction in DMF at 80°C for 8h. [g] Data from ref. 6 (reaction in EtOH, refluxing for 4h).

and provides a simple, efficient method for the synthesis of diaryl sulfones. The present method has many obvious advantages including being environmentally more benign, with simplicity of methodology, ease of product isolation, higher yield and the potential for recycling the ionic liquid.

## Experimental

$^1$H NMR spectra were recorded on a PMK-60 spectrometer using $CCl_4$ as the solvent with TMS as an internal standard. IR spectra were determined on a PE-683 Infrared spectrophotometer. Melting points were not corrected. Some liquids were dried *in vacuo* at 60°C for 15–20 hours.

*General procedure for preparation of diaryl sulfones:* Sodium arenesulfinate **1** (1.5mmol) was dissolved in [BMim]$BF_4$ (4ml) and then diaryliodonium salt **2** (1mmol) was added slowly with stirring. The mixture was stirred at 40°C for 2–3h. The resulting solution was cooled to room temperature and extracted with diethyl ether (15ml×6). The combined extracts were concentrated on a rotary evaporator to give a solid residue, which was recrystallised from dichloromethane/pentane to afford pure product **3** as white crystals. After filtering off the salt byproduct, the cleaned ionic liquid was obtained and reused.

*Physical and spectroscopic data*

*Diphenyl sulfone* **3a**: m.p. 125–127°C (lit.[15]128°C); $^1$H NMR $\delta_H$ 7.4–7.8 (m, 6H), 7.9–8.2 (m, 4H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1160, 1315.

*p-Methylphenyl phenyl sulfone* **3b**: m.p. 122–124°C (lit.[16] 125°C); $^1$H NMR $\delta_H$ 2.4 (s, 3H), 7.2–7.8 (m, 5H), 7.85–8.2 (m, 4H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1150, 1310.

*p-Chlorophenyl phenyl sulfone* **3c**: m.p. 92°C (lit.[16] 93°C); $^1$H NMR $\delta_H$ 7.5–7.8 (m, 5H), 7.95–8.2 (m, 4H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1160, 1320.

*Bis(p-methylphenyl)sulfone* **3d**: m.p. 153–155°C (lit.[17] 158°C); $^1$H NMR $\delta_H$ 2.37 (s, 6H), 7.18–7.5 (m, 4H), 7.7–8.05 (m, 4H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1150, 1310.

*p-Chlorophenyl p-methylphenyl sulfone* **3e**: m.p.120–122°C (lit.[16] 123–123.5°C); $^1$H NMR $\delta_H$ 2.35(s, 3H), 7.15–7.6 (m, 4H), 7.7–8.1(m, 4H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1160, 1320.

*Bis(p-chlorophenyl) sulfone* **3f**: m.p. 144–146°C (lit.[18] 147.5°C); $^1$H NMR $\delta_H$ 7.3–8.0 (m, ArH); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1160, 1330.

*m-Nitrophenyl phenyl sulfone* **3g**: m.p. 82–83°C (lit.[19] 84–85°C); $^1$H NMR $\delta_H$ 7.4–8.7 (m, ArH); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1165, 1315, 1335, 1540.

*p-Methylphenyl m-nitrophenyl sulfone* **3h**: m.p. 130–131°C (lit.[20] 131°C); $^1$H NMR $\delta_H$ 2.35 (s, 3H), 7.16–8.7 (m, 8H); IR (KBr, $\nu_{max}$/cm$^{-1}$) 1155, 1310, 1330, 1540.

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