

Hypervalent iodine in synthesis 67: a convenient method for the synthesis of diaryl sulfones by palladium-catalysed arylation of sodium arenesulfonates with diaryliodonium salts[†]

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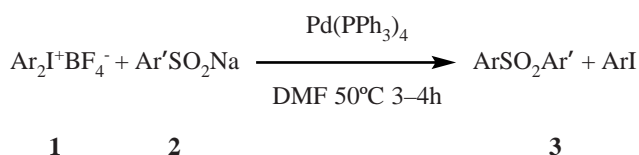
In the presence of $\text{Ph}(\text{PPh}_3)_4^+$, diaryliodonium salts react with sodium arenesulfonates to produce diaryl sulfones in reasonable yields under mild reaction conditions.

The sulfonyl group is a widely used synthon for synthetic organic chemists,¹ some sulfones have many industrial applications,² and some diaryl sulfones are known to exhibit high antifungal and antibacterial activity. There are several classic methods for preparing diaryl sulfones including the oxidation of the corresponding sulfides³ and sulfoxides,⁴ sulfonylation of arenes with arenesulfonyl halides⁵ or arenesulfonic acids⁶ in the presence of a strong acid catalyst, and the reactions of sulfonic acid derivatives with organometallic reagents.⁷ However, these methods are deficient in some respects, such as, the dependence on the availability of starting materials, difficulty of isolating the mixture of isomeric products, harsh reaction conditions, and low yields.

Some new methods have been developed for the synthesis of diaryl sulfones including the copper-assisted displacement reaction of iodoarenes with arenesulfonates,⁸ bismuth (III)-catalysed sulfonylation of arenes.⁹ However they also have their limitations.

The nucleophilic substitution reaction between haloalkanes and sulfinate anions constitutes an important synthesis of aliphatic sulfones,¹⁰ but this methodology is not suitable for the synthesis of aromatic sulfones, except in cases where highly activated haloarenes are employed as substrates.¹¹ Recently, our research into the palladium-catalysed reactions of diaryliodonium salts with some nucleophilic substrates¹² showed that diaryliodonium salts are efficient electrophilic arylation agents. This prompted us to extend the palladium-catalysed arylation to sodium arenesulfonates to provide an

efficient synthesis of aromatic sulfones. Here we wish to report the palladium-catalysed reaction of diaryliodonium salts with sodium arenesulfonates (Scheme 1).



Scheme 1

We found that the palladium-catalysed reaction of diaryliodonium salts with sodium arenesulfonates takes place smoothly, reaching completion within 3–4h at 50°C in DMF. The results are summarized in Table 1. All products gave satisfactory m.p., IR and ¹H-NMR spectra.

In order to determine the optimum reaction conditions, we examined the reaction of diphenyliodonium salt with sodium phenylsulfinate. After a series of experiments, we found that in the absence of palladium catalyst, the reaction gave diphenyl sulfone in low yield¹³ even with longer reaction time (entry 1,2). Among the solvents tested, including DMF, acetonitrile and ethyl alcohol, DMF was the best choice. Several diaryliodonium salts and sodium arenesulfonates having various substituents, such as chloro, methyl and nitro group, were successfully reacted. The reaction was found to be general and applicable to synthesis of symmetrical diaryl sulfones or unsymmetrical diaryl sulfones.

Table 1 Palladium-catalysed reaction of diaryliodonium salts and arenesulfinate^a

Entry	Ar	Ar'	T (°C)	Product	Yield (%)
1 ^b	Ph	Ph	r.t.	PhSO ₂ Ph 3a	Trace
2 ^b	Ph	Ph	75	3a	30
3	Ph	Ph	r.t.	3a	47
4	Ph	Ph	50	3a	71
5	Ph	<i>p</i> -Tol	50	PhSO ₂ Tol- <i>p</i> 3b	66
6	Ph	<i>p</i> -ClC ₆ H ₄	50	PhSO ₂ C ₆ H ₄ Cl- <i>p</i> 3c	62
7	<i>p</i> -Tol	Ph	50	3b	66
8	<i>p</i> -Tol	<i>p</i> -Tol	50	<i>p</i> -TolSO ₂ Tol- <i>p</i> 3d	67
9	<i>p</i> -Tol	<i>p</i> -ClC ₆ H ₄	50	<i>p</i> -TolSO ₂ C ₆ H ₄ Cl- <i>p</i> 3e	62
10	<i>p</i> -ClC ₆ H ₄	<i>p</i> -Tol	50	3e	60
11	<i>p</i> -ClC ₆ H ₄	<i>p</i> -ClC ₆ H ₄	50	<i>p</i> -ClC ₆ H ₄ SO ₂ C ₆ H ₄ Cl- <i>p</i> 3f	55
12	<i>m</i> -NO ₂ C ₆ H ₄	Ph	50	<i>m</i> -NO ₂ C ₆ H ₄ SO ₂ Ph 3g	48
13	<i>m</i> -NO ₂ C ₆ H ₄	<i>p</i> -Tol	50	<i>m</i> -NO ₂ C ₆ H ₄ SO ₂ Tol- <i>p</i> 3h	45

^aIsolated yields based on diaryliodonium salt.

^bPalladium catalyst was not added, the reaction time is 8h.

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

In conclusion, we have provided a simple efficient synthesis method of diaryl sulfones by palladium-catalysed reaction of diaryliodonium salts with sodium arenesulfonates. It has some advantages over the previous methods, such as a simple procedure, mild reaction conditions and reasonable yields.

Experimental

¹H NMR spectra were recorded on PMK-60 spectrometer using CCl₄ as the solvent with TMS as an internal standard. IR spectra were determined on PE-683 Infrared spectrophotometer. Melting points were not corrected.

General procedure for preparation of diaryl sulfones: A mixture of diaryliodonium salt (1 mmol), sodium arenesulfinate (1.5 mmol), Pd (PPh₃)₄ (5 mol%) and DMF (5 ml) was stirred at 50°C for 3–4h under nitrogen atmosphere. After cooling, the mixture was diluted with saturated NH₄Cl aqueous (15 ml) and extracted with diethyl ether (3 × 15 ml). The combined organic phase was washed in brine, dried over magnesium sulfate and concentrated under reduced pressure. The residue was chromatographed on silica gel plate using *c*-hexane-ethyl acetate (4:1) as eluent to give sulfone.

Diphenyl sulfone 3a: m.p. 125–127°C (lit.¹⁴ 128°C); ¹H NMR: δ_H 7.4–7.8 (m, 6H), 7.9–8.2 (m, 4H). IR (KBr, ν_{max}/cm⁻¹): 1160, 1315.

p-Methylphenyl phenyl sulfone **3b**: m.p. 122–124°C (lit.^{13(a)} 125°C); ¹H NMR: δ_H 2.4 (s, 3H), 7.2–7.8 (m, 5H), 7.85–8.2 (m, 4H); IR (KBr, ν_{max}/cm⁻¹): 1150, 1310.

p-Chlorophenyl phenyl sulfone **3c**: m.p. 92–93°C (lit.¹⁵ 93°C); ¹H NMR: δ_H 7.5–7.8 (m, 5H), 7.95–8.2 (m, 4H); IR (KBr, ν_{max}/cm⁻¹): 1160, 1320.

Bis(p-methylphenyl) sulfone 3d: m.p. 153–155°C (lit.¹⁶ 158°C); ¹H NMR: δ_H 2.37 (s, 6H), 7.18–7.5 (m, 4H), 7.7–8.05 (m, 4H); IR (KBr, ν_{max}/cm⁻¹): 1150, 1310.

p-Chlorophenyl *p*-methylphenyl sulfone **3e**: m.p. 120–122°C (lit.¹⁵ 123–123.5°C); ¹H NMR: δ_H 2.35 (s, 3H), 7.15–7.6 (m, 4H), 7.7–8.1 (m, 4H); IR (KBr, ν_{max}/cm⁻¹): 1160, 1320.

Bis(p-chlorophenyl) sulfone 3f: m.p. 144–146°C (lit.¹⁷ 147.5°C); ¹H NMR: δ_H 7.3–8.0 (m, ArH); IR (KBr, ν_{max}/cm⁻¹): 1160, 1330.

m-Nitrophenyl phenyl sulfone **3g**: m.p. 82–83°C (lit.¹⁸ 84–85°C); ¹H NMR: δ_H 7.4–8.7 (m, ArH); IR (KBr, ν_{max}/cm⁻¹): 1165, 1315, 1335, 1540.

p-Methylphenyl *m*-nitrophenyl sulfone **3h**: m.p. 130–131°C (lit.¹⁹ 131°C); ¹H NMR: δ_H 2.35 (s, 3H), 7.16–8.7 (m, 8H); IR (KBr, ν_{max}/cm⁻¹): 1155, 1310, 1330, 1540.

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