

coupling reactions.

Letter

One-Pot Synthesis of Pentafluorophenyl Sulfonic Esters via Copper-Catalyzed Reaction of Aryl Diazonium Salts, DABSO, and Pentafluorophenol

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S ulfonyl-bearing organic compounds are among the most important building blocks used for the synthesis of organic functional molecules such as drugs.¹ For example, sulfone, sulfonamide, sulfonyl ester, and sulfonyl hydrazine moieties are present in a variety of bioactive molecules and drugs.² Thus, numerous synthetic methods for accessing sulfonyl-containing compounds have been developed to date.³ The oxidation of sulfides to sulfones is one such reliable method; however, sulfide preparation often entails multistep processes, wherein thiols are used as starting materials. In addition, direct oxidation of thiols to sulfonyl chlorides has been developed and employed for the synthesis of sulfonyl derivatives. However, the use of thiols as starting materials presents several drawbacks, such as strong unpleasant odors.⁴

The use of sulfonyl chlorides as electrophiles in reactions with a variety of nucleophiles is the most straightforward approach because sulfonyl chloride derivatives are commercially available and highly reactive.⁵ However, their high reactivity suffers from disadvantages such as narrow functional group tolerance, diminished stability, and complicated storage and handling.

To address these issues, several sulfonyl chloride surrogates have been developed. Among them, pentafluorophenyl (PFP) sulfonic esters have been used as an alternative to sulfonyl electrophiles due to their stability and versatility.⁶

The Caddick group reported the first synthesis of PFP vinylsulfonate via the reaction of sulfonyl chloride and pentafluorophenol (PFPOH) (Scheme 1a).⁷ In 2004, the same group developed a general tool for the synthesis of PFP sulfonic esters from sulfonic acid (Scheme 1b). This methodology initially entailed a two-step process, and was subsequently modified to a one-pot reaction.⁸ Furthermore, 2,4,6-trichlorophenol (TCP) sulfonic esters have also been

Scheme 1. Synthesis of Pentafluorosulfonic Esters



d) This work: Directly from Aryl diazonium salt

γ cheap Cu catalystγ good functional group toleranceγ one-step reactionγ gram-scale synthesis

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developed as sulfonyl chloride surrogates by the same group.⁹ However, the drawback of these approaches is the necessity to prepare sulfonyl derivatives using expensive materials.

Willis and co-workers developed Pd/Cu and Ni/Cucatalyzed sequential reactions for the synthesis of PFP sulfonic esters from aryl boronic acids, DABSO (DABCO· $(SO_2)_2$), and PFPOH in 2018 (Scheme 1c).¹⁰ However, the protocol involves a sequential two-step process employing an expensive palladium catalyst, with only one example being reported for the Ni/Cu catalytic system. Therefore, the development of a general synthetic method for accessing sulfonyl derivatives is imperative.

Recently, reactions involving DABSO have garnered considerable attention, as this reagent can be employed as a surrogate for SO_2 , which is a toxic gas, whereas DABSO is a commercially available air-stable solid. The use of sulfinate salts as intermediates readily provides a variety of sulfonyl compounds, such as sulfonyl fluorides, sulfones, sulfonamides, and sulfonic esters.¹¹

The transition-metal-catalyzed sulfination of aryl substrates, such as aryl halides and boronic acids, has been developed, entailing the use of DABSO as a sulfur dioxide surrogate to access the corresponding arene sulfinate salts.¹²

Aryl diazonium salts have been widely utilized as starting materials for the synthesis of aryl derivatives, as they are readily prepared from a plethora of commercially available aryl amines.¹³ Han and co-workers reported that copper-catalyzed reactions of aryl diazonium salts, DABSO, and alkyl alcohols provide the corresponding sulfonic esters. However, they failed to obtain the corresponding aryl sulfonic esters from aromatic alcohols.¹⁴

We envisaged that the use of aryl diazonium salts and DABSO would be an efficient system for the synthesis of PFP sulfonic esters. Herein, we report the copper-catalyzed synthesis of diverse PFP sulfonic esters entailing a multicomponent reaction of aryl diazonium salts, DABSO, and pentafluorophenol. This method employs an inexpensive Cu catalyst in a single-step operation.

After extensive screening of the reaction parameters, the optimized conditions for the reaction of 1a and HOPFP were established as follows: CuI (20 mol %) in CH₃CN in the presence of DABSO in air at 85 °C for 12 h afforded the desired product 2a in 98% yield (Table 1, entry 1). Modification of the reaction parameters provided the following results. No product was formed in the absence of copper catalyst (entry 2). In addition to copper(I), copper(II) likewise provided 2a, albeit in lower yields (entries 2-6). When inorganic sulfur dioxide surrogates, such as $Na_2S_2O_5$ and $K_2S_2O_5$, were employed, no product was formed (entries 7 and 8). Conducting the reaction in 1,4-dioxane or DMF afforded a trace amount of product (entries 9 and 10). When DMSO or toluene was employed as the solvent, the product was obtained in 35% and 30% yield, respectively (entries 11 and 12). Reducing the amount of catalyst and decreasing the reaction temperature provided inferior results (entries 13 and 14). However, shortening the reaction time to 6 h did not significantly affect the yield (entry 15). No product was formed in the presence of CF₃CO₂H, employed as a promoter in CuBr₂-catalyzed syntheses of sulfonic esters from alkyl alcohols (entries 16 and 17).

With the optimized conditions in hand, we next investigated the substrate scope with respect to aryl diazonium salts. Aryl diazonium salts bearing substituents of varying electronic and Table 1. Optimization of Conditions for the Synthesis of PFP Sulfonic Esters^a

la la	$\frac{1}{2}BF_4 + O_2S + HO + HO + F + O_2S + HO + HO + F + S^{CUl}(20 \text{ mol }\%)$	
Entry	Change from the standard conditions	Yield (%)
1	No changes	98
2	No CuI	0
3	CuCl instead of CuI	67
4	CuBr instead of CuI	86
5	CuCl ₂ instead of CuI	50
6	CuBr ₂ instead of CuI	55
7	Na ₂ S ₂ O ₅ instead of DABSO	0
8	K ₂ S ₂ O ₅ instead of DABSO	0
9	1,4-Dioxane instead of MeCN	trace
10	DMF instead of MeCN	trace
11	DMSO instead of MeCN	35
12	Toluene instead of MeCN	30
13	10 mol % CuI instead of 20 mol %	60
14	50 °C instead of 85 °C	45
15	6 h instead of 12 h	96
16	In the presence of CF_3CO_2H (1 equiv)	trace
17	In the presence of CF_3CO_2H (0.1 equiv)	trace
18	Under N ₂ atmosphere	0
~		

^aReaction conditions: 1a (0.15 mmol), DABSO (0.2 mmol), HOPFP (0.1 mmol), and CuI (0.02 mmol) were reacted in MeCN (1.0 mL) under air at 85 $^{\circ}$ C for 12 h.

steric properties were well-tolerated. Phenyl diazonium provided a 98% isolated yield of 2a. Aryl diazonium salts bearing alkyl substituents on the phenyl ring delivered excellent yields of the corresponding products (2b, 2c, and 2d; Scheme 2). Halide substitutions with chloride, bromide, iodide, and fluoride were well-tolerated, and moderate to good yields of the corresponding products 2e-2j were obtained. Aryl diazonium salts disubstituted with methyl and iodide as well as methyl and bromide groups also reacted well to produce 2k, 2l, and 2m in 53%, 98% and 48% yield, respectively. 2-Naphthyl- and 2-phenoxyphenyl diazonium salts gave 2n and 2o, respectively, in good yields; however, 2-biphenyl diazonium provided a low yield due to the steric hindrance of the ortho-substituted phenyl group. Alkoxy-, thiomethyl-, and amine-substituted aryl diazonium salts afforded the corresponding products 2q, 2r, 2s, 2t, and 2u in moderate to excellent yields. 3-Pyridyl-, 3-acetyl-, and 3-ethyl ester-substituted aryl diazonium salts produced 2v, 2w, and 2x in 45%, 77%, and 98% yields, respectively. In the case of aryl diazonium salts containing electron-withdrawing groups at the para-position, such as a cyano or nitro, the corresponding products (2y, 2z, and 2ab) were also isolated in moderate yields (45%-53%). It is noteworthy that no desired sulfonic esters were formed when phenol and methanol were employed instead of HOPFP (see Scheme S1 in the Supporting Information).

Next, we evaluated the efficiency of this method for largescale reactions, and the applicability of the generated PFP sulfonic esters in further transformations. Products 2i and 2t were chosen for gram scale preparation and as substrates in further transformations. As shown in Scheme 3, 2i and 2t were successfully obtained in 92% and 63% yield, respectively.





"Reaction conditions: 1 (1.5 mmol), DABSO (2.0 mmol), HOPFP (1.0 mmol), and CuI (0.2 mmol) were reacted in MeCN (8.0 mL) under air at 85 $^\circ$ C for 12 h.

Scheme 3. Gram Scale Synthesis of PFP Sulfonic Esters



We then investigated the suitability of PFP sulfonic esters in several reactions, as shown in Scheme 4. PFP sulfonic ester 2i was employed as a coupling partner in palladium-catalyzed cross-coupling reactions. In the case of Sonogashira coupling, the reaction of 2i and phenyl acetylene afforded the coupled product in 72% yield. When phenyl propiolic acid was employed in the reaction with 2i under decarboxylative coupling conditions, the desired product was formed in 61% yield. In addition, Suzuki coupling of 2i with phenylboronic acid provided 4 in 88% yield. The PFP sulfonic ester bearing an amine group displayed good activity in the Chan–Evans–Lam reaction¹⁵ providing 5 in 67% yield, and *N*-acylation proceeded smoothly to afford the corresponding product 6 in 91% yield.

To study the reaction pathway, the standard reaction was conducted in the presence of radical trapping reagents

Scheme 4. Transformation of PFP Sulfonic Esters



TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy), BHT (2,6-ditert-4-methylphenol), and DPE (1,1-diphenylethylene). As shown in Scheme 5, no product was formed in the presence

Scheme 5. Control Experiments

() () () () () () () () () () () () () (DABSO + HOPFP	Cu Ado C 8	I (20 mol %) litive (3 equiv) ∺H ₃ CN, Air 5 °C, 12 h		Ρ
			Additive	Yield of 2a (%)	
			TEMPO	0	
			BHT	0	
		_	DPE	20	

of TEMPO or BHT. When the standard reaction was performed in the presence of DPE, **2a** was formed in 20% yield and the arylsulfonyl-bearing alkene byproduct was obtained in 44% yield.¹⁶

Based on the results from the control experiments and previous reports, a plausible reaction mechanism is outlined in Scheme 6. The aryldiazonium salt generates the aryl radical, and it reacts with DABSO to provide the corresponding arylsulfonyl radical and a DABCO radical cation, which in turn

Scheme 6. Proposed Mechanism



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oxidizes Cu(I) to Cu(II). In addition, it is suggested that molecular oxygen may be involved in the oxidation of Cu(I) to Cu(II) because the reaction fails under a nitrogen atmosphere. PFPOH reacts with Cu(II) to produce the corresponding alkoxy copper complex, which subsequently reacts with the arylsulfonyl radical to generate the Cu(III) intermediate. Finally, reductive elimination produces the corresponding PFP sulfonyl ester and regenerates the Cu(I) species.

In summary, we have developed a copper-catalyzed synthesis of PFP sulfonyl esters via a multicomponent one-pot reaction of aryl diazonium tetrafluoroborates, DABSO, and PFPOH. CuI was found to be the optimal copper catalyst source and CH₃CN was the best solvent. The protocol exhibits a broad substrate scope, providing the corresponding PFP sulfonyl esters in good yields. PFP 4-iodobenzenesulfonate (2i) successfully participated in Sonogashira, Suzuki, and decarboxylative coupling reactions. In addition, PFP 4-aminobenzenesulfonate (2t) participated in Chan-Evans-Lam reaction.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.1c01056.

Experimental procedures and spectral data for the products (PDF)

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Notes

The authors declare no competing financial interest.

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(16) (2-(Phenylsulfonyl)ethene-1,1-diyl)dibenzene and ethene-1,1,-2-triyltribenzene were formed in 44% and 9% yields, respectively. See Scheme S2 in the Supporting Information.