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Copper-Catalyzed Direct N-Arylation of N-Arylsulfonamides Using Diaryliodonium Salts in Water

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ABSTRACT

An efficient copper-catalyzed N-arylation of N-arylsulfonamides with diaryliodonium salts is reported. The reaction employs diaryliodonium salts and N-arylsulfonamides in water at room temperature, giving the products in moderate to excellent yields.

1. Introduction

Hypervalent iodine chemistry is currently a field of intense development. Thanks to the variety of possible derivatives, diaryliodonium salts have been used widely in organic synthesis because of their low toxicity, stability, high reactivity, and availability.[1] They have been utilized as electrophilic arylating agents in various reactions, such as nucleophilic substitution reactions with nitrogen nucleophiles,[2] carbon nucleophiles,[3] and others;[4] as well as Cu- and Pd-catalyzed coupling reactions,[5] and trapping reactions (in which they are used as benzyne precursors).[6] Despite the significant progress that has been made in this area, there is still a need for new environmentally friendly strategies.

Sulfonamides are a very important class of compounds in the pharmaceutical industry, being widely used as anticancer, anti-inflammatory and antiviral agents.[7] In addition, numerous sulfonamide derivatives have been used in preclinical development. The sulfonamide partial structure appears to belong to the so-called ‘‘privileged structures” in medicinal chemistry,[8] and it exhibits favorable pharmacokinetic properties including metabolic stability. Therefore, the further development of efficient, mild and environmentally benign procedures for synthesis of valuable sulfonamides is highly desirable and of prime synthetic value.

Although recently many efforts have been made towards the preparation of novel sulfonamides,[9] the conventional synthesis from amino compounds and sulfonyl chlorides is still the method of choice because of the reactivity and simplicity.[10] Generally, N,N-diarylsulfonamides can be synthesized from corresponding diarylamines and sulfonyl chloriedes.[10c,d,f-i] However, the starting material diarylamines were obtained via transition-metal-catalyzed C-N bond formation[11,12] which needs expensive catalysts and elevated temperature. Herein, we disclosed an efficient and simple N’N-diarylsulfonamide synthesis at room temperature in water through copper-catalyzed direct N-arylation of N-arylsulfonamides with diaryliodonium salts.

2. Results and discussion

At the outset of the study, N-phenylsulfonamide (**1a**) and dipenyliodonium triflate (**2a**) were chosen as model substrates to establish the best reaction conditions (Table 1). In the light of recent advances in this area, we treated **1a** with 1.2 equivalents **2a** using CuI as the catalyst and K_3PO_4 as the base, in toluene at room temperature for 6 h. We were pleased to find that N-arylation proceeded to give **3a** in 79% yield (Table 1, entry 2), whereas no reaction occurred in the absence of the copper catalyst (Table 1, entry 1). Modifying the nature of copper source identified CuCl and $Cu(OTf)_2$ as the most efficient catalysts, giving the desired compound **3a** in excellent yield (>99%, table 1,

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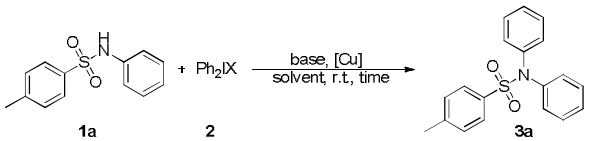
Table 1. Optimization of Cu-Catalyzed N-Arylation of N-phenylsulfonamide (**1a**)[a]



1a 2 3a

Entry	X	Base	[Cu] (mol%)	Solvent	Time (h)	Yield (%)[b]
1	OTf	K_3PO_4	--	toluene	6	N. R.
2	OTf	K_3PO_4	CuI	toluene	6	79
3	OTf	K_3PO_4	CuBr	toluene	6	81
4	OTf	K_3PO_4	CuCl	toluene	6	>99
5	OTf	K_3PO_4	$Cu(OTf)_2$	toluene	6	>99
6	OTf	K_3PO_4	CuCl	toluene	4	91
7	OTf	K_3PO_4	CuCl	DCM	6	>99
8	OTf	K_3PO_4	CuCl	1,4-dioxane	6	>99
9	OTf	K_3PO_4	CuCl	1,2-DCE	6	>99
10	OTf	K_3PO_4	CuCl	H_2O	10	>99
11	OTf	K_2CO_3	CuCl	H_2O	10	96
12	OTf	KOH	CuCl	H_2O	10	85
13	BF_4	K_3PO_4	CuCl	H_2O	10	>99
14	Br	K_3PO_4	CuCl	H_2O	10	79
15	OTs	K_3PO_4	CuCl	H_2O	10	88

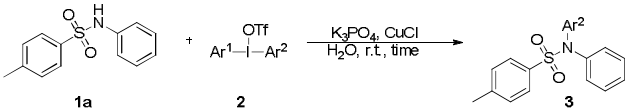
[a] Reaction conditions: N-phenylsulfonamide (0.2 mmol, 1 equiv), diphenyliodonium salt (0.24 mmol, 1.2 equiv), copper catalyst (0.04 mmol, 20 mmol%), base (0.4 mmol, 2 equiv), solvent (3 mL).

[b] Yield of isolated product.

entries 3-5). Decreasing the reaction time to 4 h had a negative impact on yield (Table 1, entry 6). The influence of solvents was examined, the results showed that the solvents of toluene, dichloromethane, dioxane and 1,2-dichloroethane were all suitable (Table 1, entries 7-9). Encouraged by the work of Olofsson group, water in combination with the mild base is ideal for environmental purpose.[13] To our delight, the desired product **3a** was obtained in excellent yield when water was used as the solvent (Table 1, entry 10). Next, a range of bases including K_3PO_4, KOH, K_2CO_3 were screened (Table 1, 10-12), and K_3PO_4 was found to be the most suitable. Furthermore, under the optimized conditions with the established model reaction of N-phenylsulfonamide and dipenyliodonium triflate, the influence of the counteranions of the diphenyliodonium salts was studied. Diphenyliodonium tetrafluoroborate furnished the desired product in excellent yield, whereas diphenyliodonium tosylate and diphenyliodonium bromide only gave the product in moderate yields (Table 1, entries 13-15), which is in accordance with the result of our previous N-arylation of carbazoles.[2g]

With the optimized conditions in hand, the reaction scope of the N-arylation of N-phenylsulfonamide by using variety of symmetrical and unsymmetrical diaryliodonium salts was explored. As shown in Table 2, substituted diaryliodonium salts with 4-Cl, 4-Br gave the corresponding products in good yields (Table 2, entries 3, 4), whereas the 4-F-substituted diaryliodonium salt afforded only 7% yield of the desired product **3ab** (Table 2, entry 2), most likely due to the low solubility of the starting materials in H_2O. The expected excellent yield of **3ab** was obtained when the solvent was changed to DCM. Excellent yields of 90 and >99% were achieved for the reactions involving electron-donating 4-Me and 4-MeO groups, respectively (Table 2, entries 6, 7), whereas the 4-^{t}Bu-substituted diaryliodonium salt

Table 2. Direct Coupling of N-phenylsulfonamide **1a** with Various Diaryliodonium Salts[a]



1a 2 3

Entry	2	Ar^1	Ar^2	Time (h)	3	Yield (%)[b]
1	**2a**	Ph	Ph	10	**3aa**	>99
2	**2b**	$4\text{-}FC_6H_4$	$4\text{-}FC_6H_4$	16	**3ab**	7 (>99[c])
3	**2c**	$4\text{-}ClC_6H_4$	$4\text{-}ClC_6H_4$	12	**3ac**	81
4	**2d**	$4\text{-}BrC_6H_4$	$4\text{-}BrC_6H_4$	12	**3ad**	74
5	**2e**	$4\text{-}^tBuC_6H_4$	$4\text{-}^tBuC_6H_4$	16	**3ae**	17 (>99[c])
6	**2f**	$4\text{-}MeC_6H_4$	$4\text{-}MeC_6H_4$	10	**3af**	90
7	**2g**	$4\text{-}MeOC_6H_4$	$4\text{-}MeOC_6H_4$	10	**3ag**	>99
8	**2h**	Mesityl	Mesityl	16	**3ah**	69
9	**2i**	Mesityl	Ph	16	**3aa**	62
10	**2j**	$4\text{-}MeOC_6H_4$	$4\text{-}NO_2C_6H_4$	16	**3ai**	60

[a] Reaction conditions: N-phenylsulfonamide (0.2 mmol, 1 equiv), iodonium salts (0.24 mmol, 1.2 equiv), CuCl (0.04 mmol, 20 mmol%), K_3PO_4(0.4 mmol, 2 equiv), H_2O (3 mL).

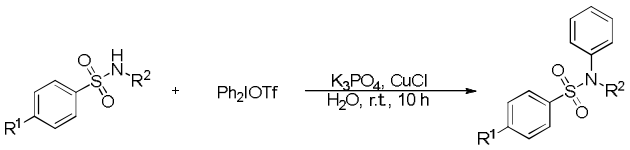
[b] Yield of isolated product.

[c] DCM as the solvent.

[d] OTs salt **2j** used.

gave 17% yield of **3ae**, and >99% yield in DCM (Table 2, entry 5). However, 2,4,6-trimethyl diphenyliodonium triflate **2h** with steric hindrance gave a decreased yield (Table 2, entry 8). It is worth mentioning that the unsymmetrical salt **2i** selectively transferred the phenyl group to the N-phenylsulfonamide in moderate yield of 62% (Table, entry 9), and the unsymmetrical salt 4-methoxy-4'-nitrodiphenyliodonium tosylate (**2j**) selectively transferred the electron-deficient *p*-nitrophenyl to the N-phenylsulfonamide in moderate yield of 60% (Table 2, entry 10).

Table 3. Direct Coupling of Diaryliodonium Salt **2a** with Various N-Arylsulfonamides[a]



1 2a 3

Entry	1	R^1	R^2	3	Yield (%)[b]
1	**1a**	Me	Ph	**3aa**	>99
2	**1b**	Me	$4\text{-}FC_6H_4$	**3ab**	97
3	**1c**	Me	$4\text{-}ClC_6H_4$	**3ac**	77
4	**1d**	Me	$4\text{-}BrC_6H_4$	**3ad**	97
5	**1e**	Me	$4\text{-}Me_2NC_6H_4$	**3ba**	64
6	**1f**	Me	$4\text{-}MeOC_6H_4$	**3ag**	>99
7	**1g**	Me	$2\text{-}MeC_6H_4$	**3ca**	>99
8	**1h**	Me	$4\text{-}NO_2C_6H_4$	**3ai**	63
9	**1i**	Me	*n*-butyl	**3da**	62 (90[c])
10	**1j**	Me	cyclohexyl	**3ea**	<5 (20[c])
11	**1k**	NO_2	$4\text{-}MeOC_6H_4$	**3fa**	23 (92[c])
12	**1l**	H	Ph	**3ga**	97

[a] Reaction conditions: N-arylsulfonamide (0.2 mmol, 1 equiv), dipenyliodonium triflate (0.24 mmol, 1.2 equiv), CuCl (0.04 mmol, 20 mmol%), K_3PO_4 (0.4 mmol, 2 equiv), H_2O (3 mL).

[b] Yield of isolated product.

[c] DCM as the solvent.

Further exploration of the scope of the reaction was conducted with various substituted N-arylsulfonamides. With **2a**, substituted N-arylsulfonamides with flouro-, chloro-, bromo-groups on the aromatic ring reacted smoothly and formed the corresponding products (Table 3, entries 2-4), among which chloro-group gave a relatively low yield (Table 3, entry 3). N-arylsulfonamides containing electron-donating substituents (4-MeO, 2-Me) also gave the excellent yields (Table 3, entries 6, 7), whereas the $-NMe_2$ afforded desired product in moderate yield (Table 3, entry 5). And the electron-withdrawing nitro-group proved to be suitable substrate (Table 3, entry 8). Additionally, N-butylsulfonamide was also viable substrate, providing desired product in 62% yield and 90% yield in DCM (Table 3, entry 9). However, N-cyclohexylsulfonamide with steric hindrance gave <5% desired product in water and 20% yield in DCM (Table 3, entry 10). Furthermore, substituted N-arylsulfonamides on the sulfonamide ring were investigated, use of **1k** as substrate gave the corresponding product in 23% yield and 92% yield in DCM (Table 3, entry 11). Meanwhile, **1l** could also give desired product with excellent yield (Table 3, entry 12).

3. Conclusion

In summary, we have developed a new protocol for the synthesis of N'N-diarylsulfonamides using diaryliodonium salts as the electrophilic coupling partners in the presence of a copper catalyst. The starting material N-arylsulfonamides can be easily prepared from corresponding arylamines and sulfonyl chlorides. The reaction is simple to perform and takes place in water under mild conditions, giving the products in moderate to excellent yields.

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Graphical Abstract

Copper-Catalyzed Direct N-Arylation of N-Arylsulfonamides Using Diaryliodonium Salts in Water

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