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Copper-mediated sulfonylation of aryl iodides and bromides with arylsulfonyl hydrazides in PEG-400

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The sulfonylation from stable and readily available arylsulfonyl hydrazides and aryl iodides or bromides mediated by cupric acetate has been achieved. Using polyethylene glycol (PEG-400) as eco-friendly medium, the coupling reaction could afford a series of unsymmetrical diaryl sulfones in moderate to good yields without the presence of additional ligand and base.

Introduction

Aryl sulfone moieties are ubiquitous in many biologically and pharmaceutically active molecules which present potential antifungal, antibacterial, or antitumor activities, and moreover, they also constitute versatile building blocks in materials science and organic synthesis.¹ Conventional routes to aryl sulfones mainly comprises the reaction of organometallic reagents with sulfonate esters,² the oxidation of corresponding sulfides,³ the sulfonylation of suitable arenes in the presence of strong acid with arylsulfonic acids or arylsulfonyl halides,⁴ as well as the nucleophilic substitution of alkyl halides with arylsulfinate salts.⁵ Every last the aforementioned strategy has its own merit, however, disadvantages such as the limited availability of precursors, the formation of mixtures of isomeric, low compatibility of some functional groups and harsh reaction conditions are usually supervened in the most cases.

Over the past few decades, palladium or coppercatalyzed coupling of arylsulfinic acid salts or arylsulfonyl chlorides with aryl halides and triflates as well as arylboronic acids to synthesize aryl sulfones, especially for unsymmetrical diaryl sulfones, were developed as milder and more applicable alternatives to

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these above-mentioned methods.⁶ Advantageously, a transition metal-free synthesis of diaryl sulfones from arylsulfinic acid salts and diaryliodonium salts was also described.⁷ Furthermore, in the recent years, transition metal-catalyzed direct sulfonylation via C-H bonds of heteroaromatic compounds with sodium arylsulfinates or arylsulfonyl chlorides were explored, possessing its fascinating synthesis prospects.⁸

Nevertheless, the high cost of palladium catalyst obviously restricts the practical utilization, and various bases or relevant additives are often required in a stoichiometric excess in most transition metal complexes-catalyzed cases, which inevitably generate a certain amount of wasteful byproducts that complicate the isolation of desired products. In addition, the use of air or moisture-sensitive sulfonylating reagents is usually not avoidable or additional prefunctionalization of the starting material like diaryliodonium salts is concluded in the metal-free protocol. And most of all, it is noteworthy that environmentally unfriendly solvents such as DMF, DMSO or toluene are indispensability in the above-mentioned works, which have a negative impact on the environment under a larger scale process. Undoubtedly, due to the extensive use of arylsulfones and related scaffolds, improved methods catalyzed or promoted by inexpensive and non-toxic copper complexes under environmentally benign solvents for the access to diaryl sulfones is still in demand.

Compared to conventional organic solvents, owing to the traits of negligible vapour pressure, thermally

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stability, biodegradability non-toxicity, and polyethylene glycols (PEG) and their derivatives have emerged as perfect medium for environmentally friendly and secure chemical reactions indisputably.⁹ On the other hand, it is well known that sulforyl hydrazides which exist as stable solids and being readily available as sulfonylation reagent theoretically produce only N₂ as byproduct.¹⁰ Therefore, based on our previous report about the copper-mediated coupling reaction between aryl boronic acids and aryl sulfonyl hydrazides using EtOH as solvent ¹¹, and considering that aryl iodides and bromides are readily accessible, low cost and compatible with numerous functional groups, and especially, the impendency of the pursuit for the environmentally benign media, herein, we wish to report a mild and efficient route to diaryl sulfones from arylsulfonyl hydrazides and aryl iodides or bromides using cupric acetate as promoter and polyethylene glycol as an eco-friendly medium.

Results and discussion

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Initially, a model reaction between commercially available *p*-toluenesulfonyl hydrazide and *p*-iodoanisole was investigated using 10 mol% of $Cu(OAc)_2 \cdot H_2O$ as catalyst in combination with PEG-400 as solvent under air at room temperature. However, almost no desired cross-coupling product was detected. Further. stoichiometric quantity of $Cu(OAc)_2 \cdot H_2O$ (1.0 equiv.) as reaction promoter was also unsuccessful. To our delight, when the latter process was conducted at 60°C, a certain amount of the target product and trace amount of bis-p-tolyl sulfone derived from the undesired homocoupling of *p*-toluenesulfonyl hydrazide were determined by GC-MS analysis (Table 1, entry 1), indeed, without the presence of *p*-iodoanisole, only bis*p*-tolyl sulfone was observed under the same conditions. Raising the temperature to 100°C, the reaction proceeded smoothly and the desired product was isolated in 75% yield after 12 h (entry 2).

Based on the result, the influence of PEG with different chain lengths was examined in the presence of 1.0 equiv. of $Cu(OAc)_2 \cdot H_2O$ at 100°C. The results revealed that PEG with longer or shorter chain lengths such as PEG-600, PEG-800 and PEG-200 did not remarkably change the yields (entries 3-6), however, the

smaller alcohols such as ethyl alcohol, glycol and glycerol give less satisfactory results (entries 7-9).

Next, comparison of different copper sources indicated that Cu(OAc)₂·H₂O promoted the reaction effectively and provided a higher yield compared to the other Cu(II) compounds tested, such as Cu(NO₃)₂· $5H_2O_3$, CuSO₄·5H₂O, CuCl₂·2H₂O, CuBr₂ and CuO (entries 10-14). In addition, Cu(I) sources were also checked, and they could give relatively lower yields under the same conditions (entries 15-17). However, almost no anticipated product was observed when the other metal salts like Ni(OAc)₂, Co(OAc)₂ or FeCl₃ was substituted for copper salts (entries 18-20). Furthermore, with regard to the quantity of $Cu(OAc)_2 \cdot H_2O$, 1.0 equiv. was found to be optimal as no significant increase in the yield of desired product was observed with the use of more than 1.0 equiv of $Cu(OAc)_2 \cdot H_2O$ and it resulted in somewhat lower yield when less than 1.0 equiv. was adopted (entries 21 and 22). A certain amount of unsymmetrical diaryl sulfide. definitely. pmethoxyphenyl-p-tolyl sulfide, was obtained when decreasing the stoichiometric amount of Cu(OAc)₂·H₂O to 0.1 equiv.. Control experiment carried out in the absence of Cu(OAc)₂·H₂O completely failed and the starting materials were isolated intact from the reaction mixtures (entry 23). Generally, an external base was found to be necessary or crucial for the preparation of aryl sulfones in most previous examples, however, the addition of bases like KOH, K₂CO₃ and Cs₂CO₃, did not enhance the reaction efficiency in this protocol (entries 24-26). Moreover, the change from air to nitrogen atmosphere did not increase the conversion, which consequently makes it be manipulatively simple and convenient. Raising the temperature to 120°C almost gave no improvement of the expected product. Therefore, 1.0 equiv. Cu(OAc)₂·H₂O in PEG-400 at 100 °C under air for 12 h served as the optimal conditions for the synthesis of *p*-methoxyphenyl-*p*-tolyl sulfone from *p*-toluenesulfonyl hydrazide and *p*-iodoanisole.

Table 1 Optimization of reaction conditions^a



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Entry	Additive(1 eq.)	Solvent	Yield(%) ^b
1 ^c	$Cu(OAc)_2 \cdot H_2O$	PEG-400	40
2	$Cu(OAc)_2 \cdot H_2O$	PEG-400	75
3	$Cu(OAc)_2 \cdot H_2O$	PEG-200	70
4	$Cu(OAc)_2 \cdot H_2O$	PEG-600	75
5	$Cu(OAc)_2 \cdot H_2O$	PEG-800	74
6	$Cu(OAc)_2 \cdot H_2O$	PEG-1000	72
7	$Cu(OAc)_2 \cdot H_2O$	EtOH	50
8	$Cu(OAc)_2 \cdot H_2O$	glycol	65
9	$Cu(OAc)_2 \cdot H_2O$	glycerol	68
10	$Cu(NO_3)_2 \cdot 5H_2O$	PEG-400	25
11	$CuSO_4 \cdot 5H_2O$	PEG-400	30
12	$CuCl_2{\cdot}2H_2O$	PEG-400	28
13	CuBr ₂	PEG-400	25
14	CuO	PEG-400	10
15	CuCl	PEG-400	17
16	CuBr	PEG-400	18
17	CuI	PEG-400	20
18	Ni(OAc) ₂	PEG-400	/
19	Co(OAc) ₂	PEG-400	/
20	FeCl ₃	PEG-400	/
21 ^d	$Cu(OAc)_2 \cdot H_2O$	PEG-400	76
22 ^e	$Cu(OAc)_2 \cdot H_2O$	PEG-400	60
23	/	PEG-400	/
$24^{\rm f}$	$Cu(OAc)_2 \cdot H_2O$	PEG-400	75
25 ^g	$Cu(OAc)_2 \cdot H_2O$	PEG-400	75
26 ^h	$Cu(OAc)_2 \cdot H_2O$	PEG-400	76

^aReaction conditions: 1.2 mmol *p*-iodoanisole; 1.0 mmol *p*-toluenesulfonyl hydrazide; 2.0 ml solvent; 100 °C, 12h, in air. ^bIsolated yield. ^c60 °C ^dCu(OAc)₂·H₂O (1.5eq.) ^eCu(OAc)₂·H₂O (0.5eq.) ^fKOH ${}^{g}K_{2}CO_{3}$ ^hCs₂CO₃ View Article Online DOI: 10.1039/C8NJ00075A ARTICLE

Using the established optimal conditions, a series of
diaryl sulfones was obtained in moderate to good yields
from p-toluenesulfonyl hydrazide with a variety of
substituted aryl iodides as depicted in Table 2. It is
noteworthy that substrates having different electron-
donating and electron-withdrawing substituents such as
methyl, methoxy, methylthio, fluoro, chloro, bromo and
amino groups at para, meta or ortho position were all
efficiently coupled to afford the corresponding products
(3aa-3ar). In general, aryl iodides bearing electron-
withdrawing substituents produce the corresponding
products in good yields (egF, Cl and Br), whereas the
use of aryl iodides containing electron-donating
substituents led to a slight decrease in the yield (eg
Me, -OMe, -SCH $_3$ and NH $_2$). Moreover, the same group
at ortho position affording in a modest yield illustrated
that this coupling reaction should be sensitive to
sterichindrance (3ad, 3ah, 3an, and 3ar). A heteroatom-
containing aryl iodides like 2-iodopyridine and 2-
iodothiophene also provided 65% and 55% isolated
yields for the corresponding diaryl sulfones (3as and
3at). Remarkably, bromo, chloro and fluoro substituent
on the phenyl ring of aryl iodides remained intact under
the standard reaction conditions, which could offer the
opportunity for further synthetic manipulations (3aj-
3aq).

To gain more insight into the substrate scope of this coupling reaction, several substitued arylsulfonyl hydrazides with iodobeneze were further evaluated under the optimal reaction conditions. It was shown that no matter if the arylsulfonyl hydrazides possessing electron-donating or electron-withdrawing functional groups, they were all good coupling partners in this transformation and afforded the desired products in moderate to good yields (3ba-3bd). Similar to the aforementioned results, the sulfonylhydrazide group represented exclusive chemoselectivity over halide group on the phenyl ring as leaving groups, demonstrating the potential access to highly functionalized targets by stepwise coupling.

Further experiments show that bromobenzen was inappropriate as materials for the present aryl sulfone synthesis, however, aryl bromides with electron-withdrawing substituents can be utilized for this transformation, like *p*-fluorobromobenzen and *p*-chlorobromobenzen, although gave still somewhat low

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Table 2 Synthesis of diaryl sulfones from various aryl iodides with arylsulfonyl hydrazide a,b,12



^a Reaction conditions: 1.2 mmol aryl iodides; 1.0 mmol arylsulfonyl hydrazide; 1.0 mmol Cu(OAc)₂·H₂O; 2.0 ml PEG-400; 100 °C, 12h, in air. ^bIsolated yield.

Table 3 Synthesis of diaryl sulfones from various aryl bromides with *p*-toluenesulfonyl hydrazide ^{a,b,12}



^aReaction conditions: 1.2 mmol aryl bromides; 1.0 mmol arylsulfonyl hydrazide; 1.0 mmol Cu(OAc)₂·H₂O; 2.0 ml PEG-400; 100 °C, 12h, in air. ^bIsolated yield. ^c120 °C (in parentheses)

yield (Table 3, **3aa**, **3aj**, and **3al**). As for *p*bromoiodobenzen, except for the former desired product (**3ap**), trace amount of *p*-iodophenyl-*p*-tolyl sulfone was detected by GC-MS analysis. Furthermore, elevating the reaction temperature to 120° C significantly improved the reaction, thus affording the desired products in acceptable yields (data in parentheses).

Due to the fact that free radical reactions mediated by sulfonyl radicals have been reported by several groups^{10c-e,g,h}, a radical trapping experiment was conducted. When radical inhibitor, such as 2,2,6,6tetramethylpiperidine-N-oxide (TEMPO, 2 equiv. based *p*-toluenesulfonyl hydrazide) or butylated on hydroxytoluene (BHT) was added into the reaction system of *p*-toluenesulfonyl hydrazide and piodoanisole, the efficiency of the transformation was almost not affected, which suggested that a radical process for this reaction might be ruled out. On the basis of our experimental results and the previous literatures¹³, a plausible reaction pathway for this sulfonylation of arylsulfonyl hydrazides and aryl iodides or bromides is illustrated in Scheme 1 although the precise mechanism is still not clear currently.





Conclusions In summary, protocol for

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In summary, we have developed an efficient and facile protocol for copper-mediated coupling of arylsulfonyl hydrazides and aryl iodides or bromides. It is worth noting that the reaction can proceeds smoothly with the use of polyethylene glycol as an eco-friendly medium under neutral conditions and exhibits good functional group tolerance and, hence, this method represents an indispensable complement to current synthetic methodologies.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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12 General procedure

Aryl halide (1.2 mmol), arylsulfonyl hydrazide (1.0 mmol), cupric acetate (1.0 mmol), and PEG-400 (2.0 ml) were taken in a 25 ml sealed tube. The reaction mixture was stirred at 100 °C for 12 hours in air. Water (10 ml) was added and then the mixture was extracted with EtOAc (4×10 ml). The extracts were combined and washed by brine (3×15 ml), dried over MgSO₄, filtered, and evaporated, and purified by chromatography on silica gel to obtain the desired products with ethyl acetate/hexane (v/v=1:3~1:0). The products were characterized by their spectral and analytical data and compared with those of the known compounds.

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Copper-mediated sulfonylation of aryl iodides and bromides with arylsulfonyl hydrazides in PEG-400

Xiangmei Wu* and Yan Wang

Abstract: The sulfonylation from aryl iodides or bromides and arylsulfonyl hydrazides mediated by cupric acetate with polyethylene glycol (PEG-400) as eco-friendly medium is successful.

