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Tetrahedron Letters xxx (xxxx) xxx





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A general and practical sulfonylation of benzylic ammonium salts with sulfonyl hydrazides for the synthesis of sulfones

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Introduction

The formation of C-S bonds has emerged as of great interest over the years in organic synthesis due to their prevalence in many biologically active compounds including pharmaceuticals and organic materials [1]. As types of these species, sulfone-containing compounds often show different biological activities and provide important functions in applications in the pharmaceutical industry [2]. Tremendous efforts have been devoted to develop novel and efficient methodologies to construct sulfones during past decades [3], such as the oxidation of the corresponding sulfides [4], the electrophilic aromatic substitution of arenes [5], the coupling reaction of arylboronic acids [6]. With the development of organic synthesis, rapid progress has been witnessed with the insertion of sulfur dioxide by using inorganic sulfites or the sulfur dioxide surrogate of 1,4-diazabicyclo[2.2.2]octane-sulfur dioxide [DABSO: DABCO-bis(sulfur dioxide)] as the source [7]. Our group have also reported N-heterocyclic carbene metal-catalyzed sulfonylations towards the synthesis of sulfones from boronic acids with various electrophiles under mild conditions, such as alkyl halides and diaryliodonium salts [8]. However, fewer synthetic steps, less toxic waste, high selectivity and milder conditions in the formation of sulfone increasingly become a research hotspot in the future organic synthesis.

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ABSTRACT

A practical and efficient approach adopting transition-metal-free cross-coupling of sulfonyl hydrazides with benzyl ammonium salts has been developed to synthesize benzyl sulfones using Cs_2CO_3 as base under mild conditions. The protocol employs stable and easy to handle coupling partners, and is endowed with good substrate compatibility, leading to functional benzyl sulfones in good yields.

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In recent years, the readily available arylsulfonyl hydrazides have attracted considerable attention in organic synthesis as powerful sulfonyl source [9] and arylation reagents [10] via S—N bond cleavage in the transition-metal catalyzed reactions [11]. Compared to other sulfenylation/sulfonation agents [12], arylsulfonyl hydrazides are insensitive to air and moisture due to stability and easy preparation, more significantly, H_2O and N_2 are the only byproducts. However, the noble and toxic transition-metals residue which difficult to separate from the system, greatly restricts the practicality of these approaches (Scheme 1a).

Remarkably, few examples include the transition metal-free mediated sulfonylation in the presence of equivalent of oxidant and elemental iodine (Scheme 1b, 1c), which violate the concept of green chemistry [13]. Therefore, it remains highly desirable to develop more general and straightforward methods for the facile preparation of sulfones, without transition-metal catalysts or oxidants.

Due to the higher C—N reactivity and convenient preparation, the quaternary ammonium salts have represented types of novel electrophilic reagents and attracted lots of attention in organic synthesis [14], especially in the construction of C—C and C—S bonds catalyzed by transition-metal with various nucleophilic reagents [15,16]. However, leveraging recent remarkable achievements in uncovering practical synthetic reactions that relied on transition-metal-free approaches [17], it is particularly appealing to explore the potential applications in designing and identifying useful alternatives to constructed various of C-X bonds. To the best of our knowledge, the C—S bond formation through S—N and C—N cleavage by using benzylic ammonium salts and arylsulfonyl

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H. Zhu et al./Tetrahedron Letters xxx (xxxx) xxx

Table 1

Optimization of reaction conditions.^a

a) Cu-catalyzed cross-coupling of arylboronic acids, aryl halides

$$R^{1} \xrightarrow{[I]}{K} NHNH_{2} + R^{2} \xrightarrow{[I]}{K} X \xrightarrow{[Cu]} R^{1} \xrightarrow{[Cu]} R^{2}$$

b) I2-mediated cross-coupling of pyridine/quinoline N-oxides



c) Cu or I2-mediated cross-coupling of alkenes



Present work:

d) Transition-metal-free sulfonylation of Benzylic Ammonium



Scheme 1. Various synthetic routes to sulfonyl-containing compounds.

hydrazides has not been explored so far. Herein, we would like to explore the possibility of direct sulfonylation of benzylic ammonium salts to build arylsulfones promoted by cesium carbonate under transition-metal-free conditions (Scheme 1d).

Results and discussion

With *p*-toluenesulfonyl hydrazide (**1a**) and benzylic ammonium iodides (2a) as the model substrates, we started the optimization using K₂CO₃ as base in N,N-dimethylformamide (DMF) at 120 °C for 24 h, To our delight, this reaction takes place in the absence of any transition metal catalyst, product **3a** could be isolated in 77% yield (Table 1, entry 1). Similar outcome was obtained when Na₂CO₃ was applied (Table 1, entry 2). No further enhancement was found when other bases (including strong base tBuOK, K₃PO₄, and CsF) were used instead (Table 1, entries 3, 4 and 5). Delightedly the yield was improved to 80% when Cs₂CO₃ was used (Table 1, entry 6). Remarkably, When the reaction was performed in the absence of Cs_2CO_3 , only 32% yield was found. (Table 1, entry 7). Merely trace yield was found when dichloroethane (DCE) was used (Table 1, entry 8) as the solvent of this coupling, and the inferior yields were found when dioxane, dimethyl sulfoxide (DMSO) and N,N-dimethylacetamide (DMAc) (Table 1, entries 9, 10 and 11) were used. After intensive optimization of the other solvents and bases (for more information see the ESI, Table S1), good result was found when N-methylpyrrolidone (NMP) and Cs₂CO₃ were utilized, and product **3a** was formed in 82% yield (Table 1, entry 12), probably due to better solubility of substrates in amide solvents. In order to further investigate the effects of this approach, the reaction temperature and molar ratio were also considered (for more information see the ESI, Table S2). Finally, a yield of 82% was provided when using 1.5 equiv of Cs₂CO₃, 2.0 equiv of p-toluenesulfonyl hydrazide (1a) and 1.0 equiv of benzylic ammonium iodide (2a) in 2 mL NMP at 120 °C under an atmosphere of N₂ for 24 h. In addition, the nature of the counterion had negative influence on the reaction, and variable yields were obtained (for more information see the ESI, Table S3).

Upon the identification of optimal reaction conditions, a series of alkyl sulfones was obtained in moderate to good yields from arylsulfonyl hydrazides with a variety of substituted benzylic

$SO_2NHNH_2 + U + I = Base, Solvent + 120 °C, 24 h + 3a$			
Entry	Base	Solvent	3a (%) ^b
1	K ₂ CO ₃	DMF	77
2	Na ₂ CO ₃	DMF	76
3	<i>t</i> BuOK	DMF	56
4	K ₃ PO ₃	DMF	56
5	CsF	DMF	52
6	Cs ₂ CO ₃	DMF	80
7	1	DMF	32
8	Cs ₂ CO ₃	DCE	trace
9	Cs_2CO_3	Dioxane	68
10	Cs ₂ CO ₃	DMSO	66
11	Cs ₂ CO ₃	DMAc	75
12 ^c	Cs ₂ CO ₃	NMP	82

 $^a\,$ Reaction conditions: 1a (0.4 mmol), 2a (0.2 mmol, 1.0 equiv), base (1.0 equiv) in 2 mL solvent at 120 °C under an atmosphere of N_2 for 24 h.

^b Isolated yield.

^c 1.5 equiv of Cs₂CO₃ was used.

ammonium iodides as depicted in Table 2. Both benzylic ammonium iodides with electron-withdrawing and electron-donating groups attached on the phenyl ring were compatible in this process (**3b-3g**). The relative position of methyl located on the aromatic ring of benzylic ammonium iodides had slightly influence on the efficiency of the transformation, and considerable yields were obtained with *ortho*-, and *meta*-substituents (**3b-3c**), only 48% product **3d** was detected when *para*-isomer was used as coupling partner. Unexpectedly, steric hindered substrate, such as bulky 1naphthylbenzylic ammonium salt and 2-naphthylbenzylic ammo-

Table 2

Reaction of arylsulfonyl hydrazides (1) with various benzylic ammonium iodides (2).^a



^a Reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol, 1.0 equiv), Cs_2CO_3 (1.5 equiv) in 2 mL NMP at 120 °C under an atmosphere of N_2 for 24 h. ^b Isolated yield.

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nium gave out the excellent result in this reaction (31 and 3n, 82 and 79%, respectively), and the ideal yields were observed when p-trifluoromethyl benzene sulfonyhydrazide instead of benzenesulfonyl hydrazide (**3m** and **3o**, 92 and 96%, respectively). Similar outcome was obtained when a range of ortho-substitutes even with strong electron-donating and electron-withdrawing were used on the coupling process, up to 82% yields were afforded (3k, **3s**, and **3h-3i**). The process works well for substrates displaying (hetero)aryl ammonium salt, and good results were observed with the couplings of 2-furyl and 2-thienyl benzylic ammoniums as substrates (**3p**, **3q**), which clearly indicated the protocol efficiency.

Based on the optimization study, the scope of the arylsulfonyl hydrazides was also studied, the results are summarized in Table 3. To our delight, arylsulfonyl hydrazides bearing strong electrondonating and strong electron-withdrawing substituents on the aromatic ring were all tolerated (4a-41). The arvlsulfonvl hvdrazides with strong electron donor groups including *tert*-butyl and methoxy had well compatibilities, and good yields were produced in synthetically (4b and 4c, 76 and 67%, respectively). Unexpectedly, the reaction with electron-poor sulfinate was well tolerated, 84% and 92% yields of products 4e and 4f were obtained even with strong electron-withdrawing groups (trifluoromethyl), and the lower results were shown in 4g and 4h when the sensitive functional groups including chloro and bromo were used. The steric effect of arylsulfonyl hydrazides had a certain effect on the efficiency of this transformation. Only acceptable yields were observed when the large steric effect arylsulfonyl hydrazides were applied (4d and 4j). Notably, 2,3-dihydrobenzofuransulfonyl hydrazide could work well in the reaction to provide the corresponding heterocyclic products 4k and 4m in 56% and 73% yields.

In order to stress the practicality of this protocol, a gram-scale reaction between p-toluenesulfonyl hydrazide (1a) and benzylic ammonium iodides (2a) was carried out (Scheme 2). When 8.0 mmol of 2a reacted with TsNHNH₂ under the optimal conditions, the reaction also proceeded well to give the corresponding

,0 SO₂NHNH ₩R `NMe₃ Cs₂CO₃, NMP R¹-۰. 120 °C, 24 h R 4a-4n^[b] 0 0,, *,*0 ,0 Ő, ,0 4a: 84% 4b: 76% 4c: 67% 0 ,0 0 E₂C 4d: 48% 84% (R = H) **4g**: 48% (X = Cl) 4f: 92% (R = Me) 4h: 33% (X = Br 0 0 .О **4i**: 48% 4k: 56% 4i: 82% 0, 0 E₂CC 4m 73% 4n: 60% **4I**: 46%

^a Reaction conditions: 1 (0.4 mmol), 2 (0.2 mmol, 1.0 equiv), Cs2CO3 (1.5 equiv) in 2 mL NMP at 120 °C under an atmosphere of N2 for 24 h. ^b Isolated vield.

product **3a** with a satisfactory yield of 78%, demonstrated the high efficiency of the newly developed sulfones protocol.

To gain an insight into the reaction mechanism, the following control experiments were conducted to better understand the possible mechanism of this coupling reaction (Scheme 3). When the radical inhibitor TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) was added to the reaction under optimized reaction conditions, and 67% of desired product **3a** was obtained (Scheme 3, eq 1), indicating that a radical reaction might not be involved in the reaction. Furthermore, no radical intermediate was trapped when 1,1diphenylethylene was employed in the reaction, and 75% of 3a was gained (Scheme 3, eq 2). 3a could also be obtained in 56% yield when *p*-toluenesulfinate (7a) was used as the substrate instead of 1a under the standard conditions (Scheme 3, eq 3). However, TEMPO was found to have little influence on this reaction. We observed that reaction of 2a with Cs_2CO_3 in the presence of NMP at 120 °C generates benzvl iodide 7b in 52% isolated vield (Scheme 3, eq 4). The results implied that aryl sulfinate and benzyl iodide maybe intermediates in this process.

On the basis of these results and previous works [13], a possible mechanism for the cross-coupling reaction is proposed in Scheme 4. The sulfonyl nucleophile intermediate A was generated from base-accelerated decomposition of benzenesulfonohydrazide [12a]. Then benzyl iodide **B** was produced by heating benzylic ammonium iodide releasing a molecule of trimethylamine simultaneously [18]. Lastly, nucleophilic substitution takes place in solvent between sulfonyl nucleophile and benzyl iodide to afford the desired product. More detailed mechanistic studies of this reaction are ongoing in our laboratory.

Conclusions

In summary, for the first time, the sulfonylaiton of benzylic ammonium salts using arylsulfonyl hydrazides as sulfonylation reagents in absence of transition-metal has been developed for



Scheme 3. Control experiments for the reaction mechanism

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Reaction of benzylic ammonium iodide (2) with various arylsulfonyl hydrazides (1).^a

Table 3

H. Zhu et al./Tetrahedron Letters xxx (xxxx) xxx



Scheme 4. Proposed reaction mechanisms.

the synthesis of sulfones. This general and efficient synthetic process works well with a wide range of benzylic ammonium salts and various functional arylsulfonyl hydrazides. The features such as generality, high efficiency and easy to handle reaction conditions make the present method an attractive alternative for the preparation of aryl-benzyl sulfones.

Experimental section

General

All commercial reagents were used directly without further purification, unless otherwise stated. dioxane, tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone, Acetonitrile (MeCN), 1,2-dichloroethane (DCE) and dimethylsulfoxide (DMSO) was distilled from calcium hydride prior to use. N,Ndimethylformamide (DMF), N,N-dimethylacetamide (DMAc) and 1-methyl-2-pyrrolidinone (NMP) were purchased from J & K chemical, stored over 4 Å molecular sieves and handled under N₂, *t*BuOK and CDCl₃ was purchased from Shanghai aladdin Biochemical Technology Co., Ltd. All Schlenk tubes and sealed vessels (50 mL) were purchased from Beijing Synthware Glass. The following abbreviations were used to describe NMR signals: s = singlet, d = doublet, t = triplet, m = mulitplet, dd = doublet of doublets, q = quartet.

General procedure for the transition metal-free approach

To a 50 mL Schlenk tube containing benzylic ammonium salts (0.2 mmol), p-toluenesulfonyl hydrazide (0.4 mmol), Cs₂CO₃ (1.5 mmol), and the tube was purged with N₂ for 3 times, followed by 2 mL of NMP. The resulted reaction mixture was allowed to stir for 24 h at 120 °C under the atmosphere of nitrogen. After cooling to room temperature, the mixture was partitioned between water (15 mL) and ethyl acetate (15 mL). The phases were separated and the aqueous phase extracted with further ethyl acetate $(3 \times 15 \text{ mL})$. The organic phases were dried over sodium sulfate. Filtration of the drying agent, and removal of all volatiles in vacuo gave a residue. Directly purified by flash chromatography to give the desired product.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tetlet.2020.151975.

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