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Iodine-catalyzed sulfonylation of sulfonyl hydrazides with *tert*-amines: a green and efficient protocol for the synthesis of sulfonamides†

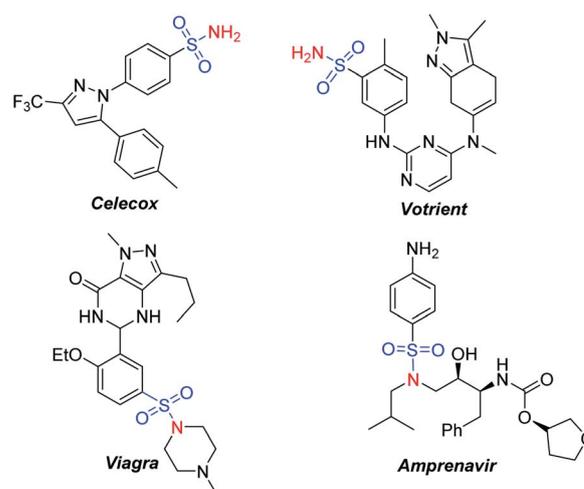
Jinyang Chen,^a Xiaoran Han,^a Lan Mei,^a Jinchuan Liu,^{*a} Kui Du,^a Tuanwu Cao^{*a} and Qiang Li^b

This study provides a direct, sustainable and eco-friendly method for the synthesis of various sulfonamides via the sulfonylation of sulfonyl hydrazides with *tert*-amines. The method utilizes sulfonyl hydrazides to oxidize and couple with tertiary amines through selective cleavage of C–N bonds. In this reaction, molecular iodine was used as the catalyst and *t*-butyl hydroperoxide was used as the oxidant.

Sulfonamides commonly serve as synthetic intermediates to produce various drugs and industrial compounds (Scheme 1).¹ They also commonly act as a *N*-sulfonyl protecting group for easy removal under mild conditions.² There have been many efforts devoted to synthesizing these compounds. Among the methods developed, nucleophilic substitution of an amine with a sulfonyl chloride or sulfonamides with organic halides in the presence of a base is frequently utilized.³ Over the past few years, transition metal catalysis has been proved a powerful tool to synthesize sulfonamides. For example, a cross-coupling reaction of primary sulfonamides with aryl halide or boronic acids,⁴ a Chan-Lam type coupling reaction of sulfonyl azides with boronic acids,⁵ or an oxidative coupling reaction of sulfinate salts with amines were developed.⁶ However, the use of non-stable, hazardous and mutagenic starting materials and toxic high boiling polar solvents in these reactions resulted in a larger amount of toxic waste. Furthermore, the use of stoichiometric amounts of bases or transition metals makes reactions with a slow reactivity and poor functional group tolerability. Therefore, a novel, sustainable, efficient, and eco-friendly method is desired to synthesize sulfonamides.

Iodine and its salts have been reported as very efficient catalysts in CDC reactions in which transition metals are used as catalysts.⁷ In recent years, many methods have been reported for synthesis of sulfonamides under metal-free conditions.⁸ As a source of sulfonyl groups, sulfonyl hydrazides are readily accessible solid. They are stable in air and under moisture

conditions, and can be easily prepared and stored. Most importantly, only water and nitrogen were obtained as by-products during the reactions using sulfonyl hydrazides as starting materials. Iodine catalyzed oxidative coupling of sulfonyl hydrazides with secondary amines have been developed (Scheme 2(a)).⁹ *Tert*-amines can donate an amine group via a C–N cleavage in place of primary or secondary amines. Compared to the high reactivity of primary or secondary amines, *tert*-amines are less nucleophilic and non-destructive for some amine-sensitive functional groups. Recently, Yuan *et al.* and Gui's have developed a new method to sulfonamides using I₂-mediated or catalyzed C–N bond cleavage of *tert*-amines (Scheme 2(b)).¹⁰ Meanwhile, Sheykhani *et al.* reported a novel electrochemical oxidative sulfonylation¹¹ of *tert*-amines (Scheme 2(c)).¹² Moreover, catalytic reactions in the aqueous



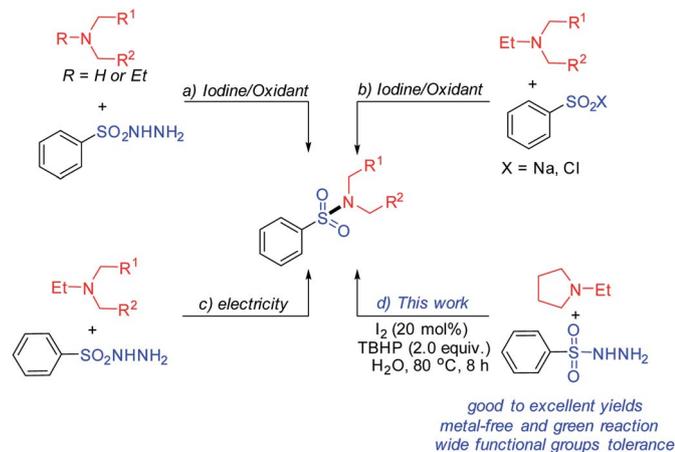
Scheme 1 Examples of important sulfonamide drugs in top 200 pharmaceuticals of 2018.

^aCollege of Chemistry and Chemical Engineering, Yangtze Normal University, Fuling, Chongqing, 408000, P. R. China. E-mail: liujinchuan123@yeah.net; caotw2013@163.com

^bInstitution of Functional Organic Molecules and Materials, School of Chemistry and Chemical Engineering, Liaocheng University, No. 1, Hunan Street, Liaocheng, Shandong, 252059, P. R. China

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Scheme 2 Methods for the synthesis of sulfonamides.

phase have also been recently developed,¹³ and sulfonylation of sulfonyl hydrazides has caused wide interest recently.¹⁴ In this study, we will report a new method to synthesize sulfonamides using iodine-catalyzed oxidative coupling of sulfonyl hydrazides with *tert*-amines (Scheme 2(d)). This approach avoids use of metal catalysts and hazardous reagents; the materials, sulfonyl hydrazides and *tert*-amines, are versatile intermediates in commercial.

Commercially available sulfonyl hydrazide **1a** was selected as a sulfonyl source to synthesize sulfonamides. When **1a** was

mixed with 1 equiv. of *N*-ethyl pyrrolidine under various solvents at 80 °C, an 80% yield of the corresponding sulfonamide **3a** was obtained after 4 hours in the aqueous phase (Table 1, entries 1–6). We found that both iodine as the catalyst and *t*-butyl hydro-peroxide (TBHP) as the oxidant are essential to convert *tert*-amines to secondary amines efficiently in this reaction (Table 1, entries 7 and 8). When TBHP was replaced by H₂O₂, oxone, or O₂, we found that the reaction was not able to be completed to produce the desired sulfonamide (Table 1, entries 9–11). The amounts of catalyst (I₂) and oxidant were also examined, and results shown that 20 mol% of I₂ and TBHP were most suitable for this reaction for giving desired product in 80% yield (Table 1, entry 3). We attempted to derive the reaction to be completed by increasing the temperature but it was not successful and there was no improvement in yield (Table 1, entry 15). Interestingly, temperature decrease has decreased the product yield rapidly (Table 1, entry 16). When iodine was replaced by tetrabutylammonium iodide (TBAI) or ammonium iodide (NH₄I) as the catalyst, only trace amount or 0% of the desired sulfonamide **3a** was achieved, respectively (Table 1, entries 17 and 18). Furthermore, the sulfonylation was affected inapparently by the atmosphere of air or nitrogen (Table 1, entry 19). After extensive screening, we were glad to find that the reaction of benzenesulfonylhydrazide (**1a**) with 1-ethylpyrrolidine (**2a**) in H₂O catalyzed by 20 mol% of I₂ and in the presence of 2.0 equiv. of TBHP provided the desired product (**3a**) with an excellent yield of 80% at 80 °C for 8 h (Table 1, entry 3). And the standard process was shown as follows (Scheme 3).

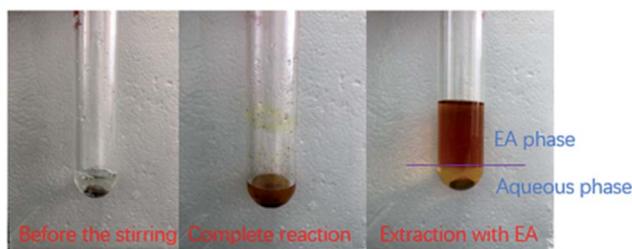
Table 1 Optimization of the reaction conditions^a

Entry	I ₂ (mol%)	Oxidant (equiv.)	Solvent	Temp. (°C)	Yields ^b (3a/4a%)
1	I ₂ (20 mol%)	TBHP (2.0 equiv.)	CH ₃ CN	80	0/50
2	I ₂ (20 mol%)	TBHP (2.0 equiv.)	THF	80	5/29
3	I₂ (20 mol%)	TBHP (2.0 equiv.)	H₂O	80	80/0
4	I ₂ (20 mol%)	TBHP (2.0 equiv.)	DMF	80	NR
5	I ₂ (20 mol%)	TBHP (2.0 equiv.)	Toluene	80	NR
6	I ₂ (20 mol%)	TBHP (2.0 equiv.)	EtOH	80	31/27
7	—	TBHP (2.0 equiv.)	H ₂ O	80	0
8	I ₂ (20 mol%)	—	H ₂ O	80	NR
9	I ₂ (20 mol%)	H ₂ O ₂ (2.0 equiv.)	H ₂ O	80	NR
10	I ₂ (20 mol%)	Oxone (2.0 equiv.)	H ₂ O	80	NR
11	I ₂ (20 mol%)	O ₂	H ₂ O	80	NR
12	I ₂ (10 mol%)	TBHP (2.0 equiv.)	H ₂ O	80	56/0
13	I ₂ (5 mol%)	TBHP (2.0 equiv.)	H ₂ O	80	43/0
14	I ₂ (20 mol%)	TBHP (1.0 equiv.)	H ₂ O	80	62/0
15	I ₂ (20 mol%)	TBHP (2.0 equiv.)	H ₂ O	100	61/0
16	I ₂ (20 mol%)	TBHP (2.0 equiv.)	H ₂ O	60	40/0
17	NH ₄ I	TBHP (2.0 equiv.)	H ₂ O	80	Trace
18	TBAI	TBHP (2.0 equiv.)	H ₂ O	80	NR
19 ^c	I ₂ (20 mol%)	TBHP (2.0 equiv.)	H ₂ O	80	80/0

^a Reaction conditions: **1a** (0.3 mmol), **2a** (0.3 mmol), I₂ (20 mol%), H₂O (3 mL), 8 h, 80 °C. TBHP: *tert*-butyl hydroperoxide, 5.0–6.0 M in decane.

^b Isolated yield. ^c The reaction was performed under nitrogen atmosphere.



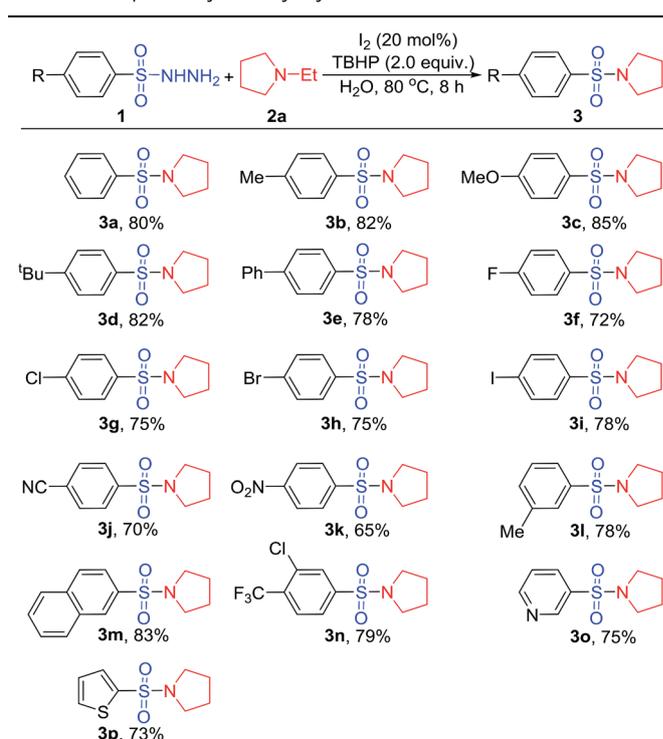


Scheme 3 The standard process of the sulfonylation reactions.

In sulfonylation of amines, it is essential to maintain the process intact by methyl, methoxy, tertiary butyl, phenyl, halo, cyan and nitro substituents presenting at the aromatic ring. In all cases, the yields of the corresponding sulfonamides **3b–3k** were in the range of 65–85%. In this series, the lowest yields were obtained for electron-deficient substituted products, which could be attributed to electron factors affecting the catalysis. Notably, arylsulfonyl hydrazides bearing substituents at the metal position could be converted to the sulfonamides in yields of 78% (**3l**). The yield of 2-naphthalene sulfonamides was 83% (**3m**). The reaction of 3-chloro-4-(trifluoromethyl)benzene-1-sulfonyl hydrazide with amine produced **3p** in a good yield, which could be leveraged for consequent coupling reaction. Because most sulfonamides with relevance for crop protection or medical application contain heterocycles, we included such substrates in our work. Fortunately, heteroaromatic sulfonyl hydrazides could be tolerated in this reaction, achieving the desired product in better yields (**3o** and **3p**). Thus, this method has been demonstrated as a practical and efficient way to synthesize sulfonamides (Table 2).

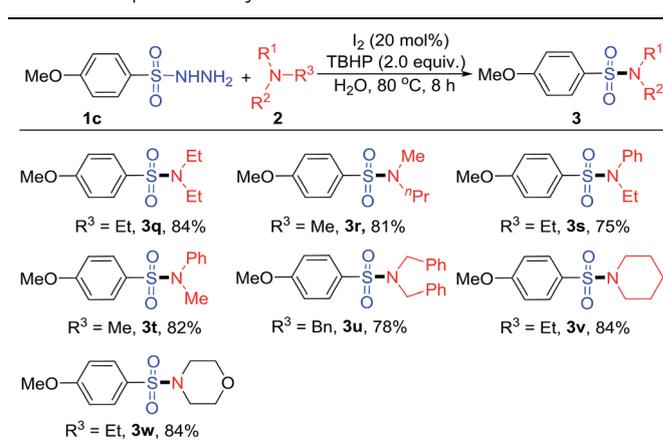
In subsequent studies, we examined the sulfonylation of sulfonyl hydrazides with various tertiary amines under the optimal conditions, and results were summarized in Table 3. Analyzing Table 3, we can see that various tertiary amines were compatible with the standard conditions, affording the corresponding sulfonamides in moderate to excellent yields. Using 4-methoxybenzenesulfonyl hydrazides (**1c**) as sulfonylating reagent, we found that both aliphatic and aromatic tertiary amines were able to react smoothly with **1c** to produce the desired products with a yield from 75% to 84%. When the tertiary amine with two different substituent groups were involved, such as *N,N*-triethylamine, *N,N*-dimethyl-*N*-propylamine, *N,N*-diethylaniline and *N,N*-dimethylaniline, the desired products were also achieved and the yield is of over 75% (**3q–3t**). It was found that tribenzylamine was able to react smoothly with **1c** to produce the target product **3u** in 78% yield. In addition, more cyclic or heterocyclic tertiary amines, such as 1-ethylpiperidine and 4-ethylmorpholine were used as the substrates, and the corresponding sulfonamides were obtained with yields of 84% (**3v** and **3w**).

The sulfonylation can also be carried out on a larger scale reaction, and the desired product (**3a**) was obtained in the yield of 80%, when 6 mmol of benzenesulfonylhydrazide (**1a**) was treated with 6 mmol of 1-ethylpyrrolidine (**2a**) under the standard conditions (Scheme 4(a)). To shed light on the mechanism

Table 2 Scope of arylsulfonyl hydrazides^{a,b}

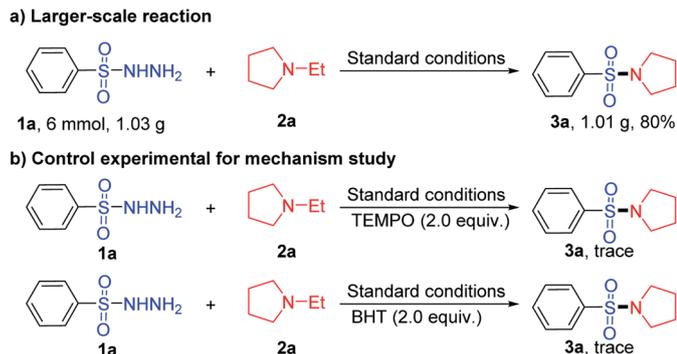
^a Conditions: **1** (0.3 mmol), **2a** (0.3 mmol), I₂ (20 mol%), H₂O (3 mL), 8 h, 80 °C. TBHP (0.6 mmol). ^b Isolated yields.

of the reaction, benzenesulfonylhydrazide (**1a**) was treated with 1-ethylpyrrolidine (**2a**) under standard conditions by using 2.0 equiv. of TEMPO or BHT as radical scavengers (Scheme 4(b)), and desired product **3a** was obtained in trace yields, suggesting that a single-electron transfer process was involved through the whole reaction.

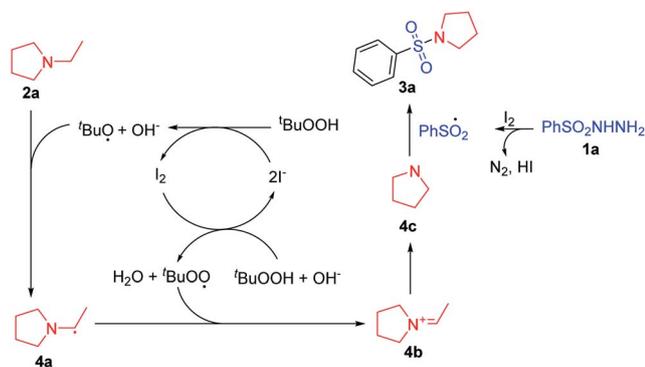
Table 3 Scope of tertiary amines^{a,b}

^a Conditions: **1c** (0.3 mmol), **2** (0.3 mmol), I₂ (20 mol%), H₂O (3 mL), 8 h, 80 °C. TBHP (0.6 mmol). ^b Isolated yields.





Scheme 4 (a) Larger-scale synthesis of **3a**. (b) Control experiments for mechanism study.



Scheme 5 Proposed mechanism of the sulfonylation.

On the basis of the above experimental results and previous works,^{9a,10b} a possible mechanism has been depicted in Scheme 5. Firstly, the transformation presumably involves an initial reaction of I_2 with TBHP to create a reactive *tert*-butoxyl or *tert*-butyl peroxy radical. Then, *tert*-butoxyl or *tert*-butyl peroxy radical abstract a hydrogen from *N*-ethyl pyrrolidine to form radical **4a**. After an electron transformation, it is converted to an intermediate aninium ion **4b**. This intermediate **4b** was then hydrolyzed by the elimination of an aldehyde to result in a secondary amine **4c**. Finally, **4c** reacts with a sulfonyl radical to generate the desired sulfonamide product **3a**.

Conclusions

In conclusion, we have developed a novel method to synthesize sulfonamides through iodine catalyzed C–N bond cleavage of tertiary amines in the aqueous phase. The method is simple and easy in operation, along with inexpensive and accessible substrates. In addition, nitrogen and acetaldehyde were the major by-products. Importantly, iodine/TBHP was first time used as the terminal oxidant in preparation of various sulfonamides from sulfonyl hydrazides and *tert*-amines.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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