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Article

Facile Synthesis of Sulfonyl Chlorides/Bromides from Sulfonyl Hydrazides

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Abstract: A simple and rapid method for efficient synthesis of sulfonyl chlorides/bromides from sulfonyl hydrazide with NXS (X = Cl or Br) and late-stage conversion to several other functional groups has been described. A variety of nucleophiles could be engaged in this transformation thus permitting the synthesis of complex sulfonamides, sulfonates. In most cases, these reactions are highly selective, simple, and clean, affording products in excellent yields.

Keywords: Sulfonyl chlorides; sulfonyl bromides; sulfonyl hydrazides; NCS; NBS

1. Introduction

Organic sulfur compounds are ubiquitous structural elements in numerous natural products and widely used as various artificial chemicals [1-3]. In particular, sulfonyl chlorides are the most prevalent reagents for the installation of the sulfonyl protecting group [4], which could be converted into numerous different sulfonyl derivatives [5-9], undergo diverse desulfitative cross-couplings [10,11] or serve as arylating agents [12-16]. In addition, they have been widely used as important building blocks for manufacture of elastomers, pharmaceuticals, dyes, detergents, ion exchange resins, herbicides [17-19]. Given the importance in various fields, there is strong interest in developing efficient synthetic methods for preparing them. Oxidative chlorination of thiols was frequently applied synthetic pathway using several combinations of oxidants and chloride sources [20-27]. In addition, chlorination with different sulfur compounds [28-31] or Grignard reactions [32] have been developed as efficient methods for the synthesis of sulfonyl chlorides. However, in the reported methods, toxic and highly corrosive reagents were required, the formation of some side products, tedious workup procedures for isolation of the pure products. Therefore, development of a milder and practical method for the synthesis of sulfonyl chlorides is highly desirable. In 2017, Montelongo's group has developed an elegant strategy for the synthesis of sulfonyl chlorides and bromides by the oxidation of thiols using NCS/NBS - iPrOH as an oxyhalogenation reagent (Scheme 1a) [33]. Recently, Cornella reported highly selective conversion reactions of primary sulfonamides to the corresponding sulfonyl chlorides and fluorides by using pyrylium salt as activating reagent (Scheme 1b) [34]. It is well known that sulfonyl chlorides could react with hydrazine hydrate to synthesize various sulfonyl hydrazide [35]. To the best of our knowledge, the approach to sulfonyl chlorides/bromides from widely available sulfonyl hydrazide under metal-free conditions is rare. Magnotta reported a simple strategy for the synthesis of sulfonyl bromides from sulfonyl hydrazides with bromine (Scheme 1c) [36]. This elegant strategy represents a highly valuable synthetic tool but leaves ample opportunities to develop more green and gentle reaction system to construct sulfonyl chlorides/bromides. Herein, we describe that the sulfonyl hydrazides react with NCS/NBS under mild reaction

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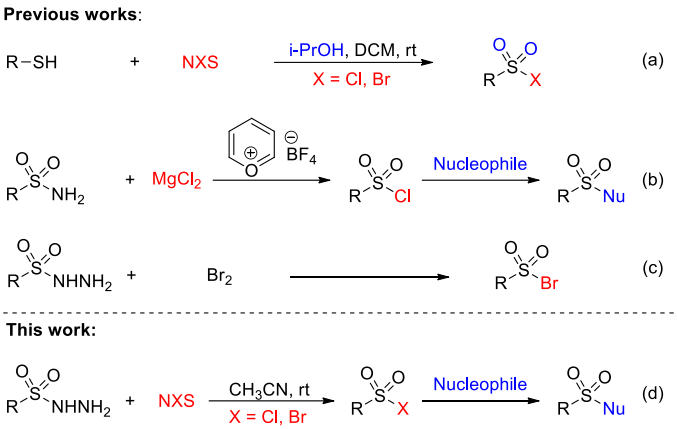
conditions, providing convenient and efficient access to sulfonyl chlorides/bromides. (Scheme 1d).



Scheme 1. Synthesis of sulfonyl halides.

2. Results

We commenced our study by investigating 4-methylbenzenesulfonhydrazide (**1a**) and halogen source (**2**). Inspired by the work of Cornella, we first evaluated the reaction using $MgCl_2$ as the halogen source in CH_3CN at room temperature without any catalysts or additives, however, no appreciable formation of the target product **3a** was detected in the reaction mixture (Table 1, entry 1). Subsequent screening of a large panel of chlorides found the use of CuCl resulted in the generation of **3a** in 38% yield (Table 1, entries 2-7). We further investigated the reactivity of organic chlorides and the results suggested that NCS (*N*-chlorosuccinimide) was optimal to give a comparable 99% yield (Table 1, entries 8-10). Furthermore, the replacement of CH_3CN by other solvents hampered product formation in various degree (Table 1, entries 11−16). Furthermore, the replacement of NCS by NBS (*N*-bromosuccinimide) also smoothly gave the target product sulfonyl bromide **4a** in 87% yield (Table 1, entry 17). However, when using NIS (*N*-iodosuccinimide) as the substrate, corresponding product **5a** was not formed (Table 1, entry 18).

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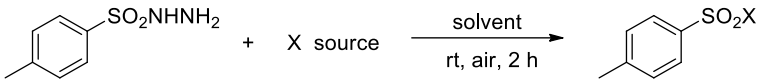
Table 1. Optimization of reaction conditions. [a]



1a **2** **3a-6a**

Entry	X source	Solvent	Product	Yield (%)[b]
1	$MgCl_2$	CH_3CN	**3a**	N.R.
2	NaCl	CH_3CN	**3a**	N.R.
3	$CaCl_2$	CH_3CN	**3a**	N.R.
4	$ZnCl_2$	CH_3CN	**3a**	N.R.
5	HCl	CH_3CN	**3a**	N.R.
6	CuCl	CH_3CN	**3a**	38
7	$FeCl_3$	CH_3CN	**3a**	8
8	$SOCl_2$	CH_3CN	**3a**	trace
9	PCl_5	CH_3CN	**3a**	65
10	**NCS**	**CH_3CN**	**3a**	**99**
11	NCS	CH_2Cl_2	**3a**	91
12	NCS	EtOAc	**3a**	94
13	NCS	DME	**3a**	87
14	NCS	THF	**3a**	56
15	NCS	DCE	**3a**	58
16	NCS	Dioxane	**3a**	75
17	**NBS**	**CH_3CN**	**4a**	**87**
18	NIS	CH_3CN	**5a**	N.R.

[a]Unless noted otherwise, reactions were performed with **1a** (0.3 mmol), **X source** (0.6 mmol, 2 equiv), in 2 mL solvent, room temperature, under open air, 2 h. [b] Isolated yield. N.R. = no reaction. NCS = *N*-chlorosuccinimide. NBS = *N*-bromosuccinimide. NIS = *N*-iodosuccinimide.

3. Discussion

With the optimized reaction conditions in hand, we explored the substrate scope. As shown in Scheme 2, various ortho-, meta-, and parasubstituted arylsulfonyl hydrazides, including the aryl and alkyl substitution, underwent smoothly in this sulfonyl chlorides formation reaction to deliver the desired products in good to excellent yields (**3a**-**3u**). The substitution in the aromatic ring of sulfonyl hydrazides, regardless of the electron-donating or electron-withdrawing groups, hardly affected the reactivity of the reaction. To our delight, the naphthyl and heterocyclic sulfonyl hydrazides, such as thiophene, also afforded the corresponding products in satisfactory yields (**3p**-**3r**). In addition, both benzylsulfonyl hydrazide and alkylsulfonyl hydrazides could undergo this process smoothly to afford the corresponding products (**3s**–**3u**) in moderate to high yields. On the other hand, NBS was subjected to the reaction under the same reaction conditions. In contrast with NCS, NBS showed relatively weak reactivity and the corresponding sulfonyl bromide products could also be obtained in moderate to good yields (**4a**-**4u**). Unfortunately, benzylsulfonyl hydrazide was not suitable for this transformation (**4s**).

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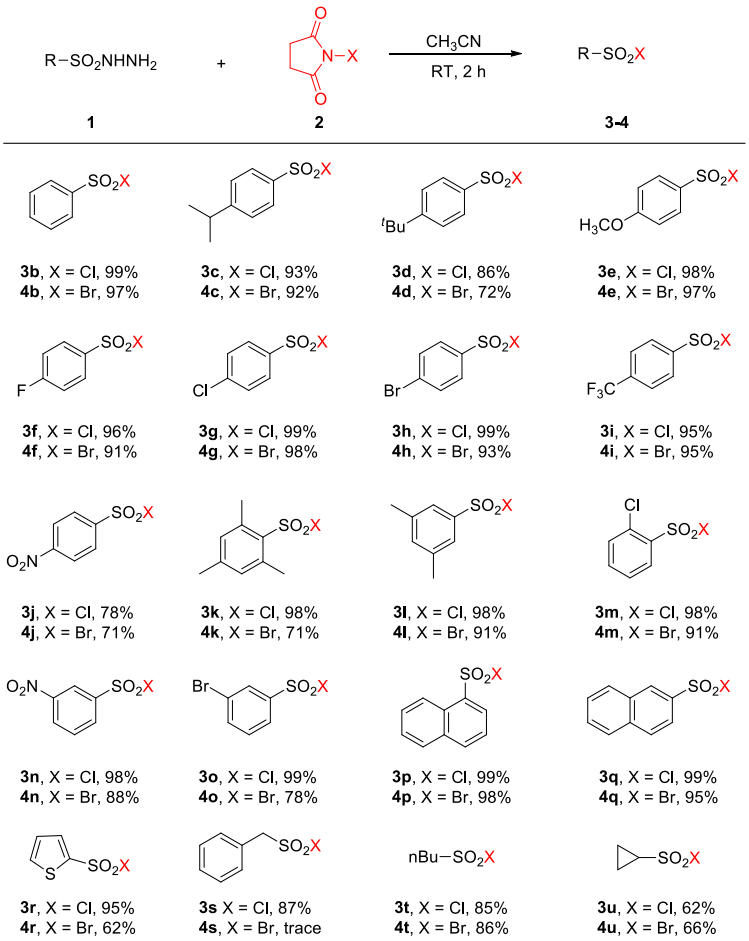

Scheme 2. Scope of the conversion of sulfonyl hydrazides to sulfonyl chlorides and sulfonyl bromides. Conditions: **1** (0.3 mmol), **2** (0.6 mmol) and CH_3CN (2.0 mL), rt, for 2 h, under air.

Having established a protocol for synthesizing highly versatile sulfonyl chlorides and considering that the importance of complex sulfonamide and sulfonates in drug discovery, we next assessed the scope of the reaction between different nucleophiles in presence of base in one pot. As listed in Scheme 3, both aromatic and aliphatic primary amines reacted smoothly with **1a** and **2a** under air, giving the corresponding sulfonamides in moderate to excellent yields (**7a**-**7i**). It was discovered that secondary alkyl amines were suitable participants (**7j**-**7l**), as well as ammonia (**7m**). Phenol was amenable to furnish corresponding sulfonate **7p** in good yield. In addition, we turned our attention to biologically active compounds bearing various functional groups embedded in their structure. Paroxetine was successfully applied in this transformation and afforded 87% yield of the corresponding sulfonamides over two steps (**7o**). As we predicted, ethynyl estradiol was also compatible in sulfonate formation via a simple two-step process (**7q**).

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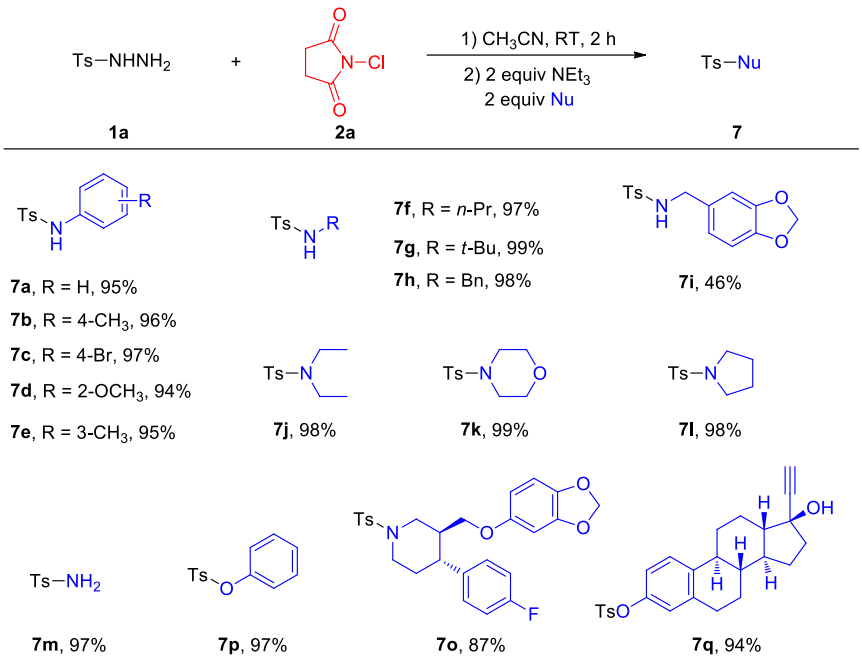
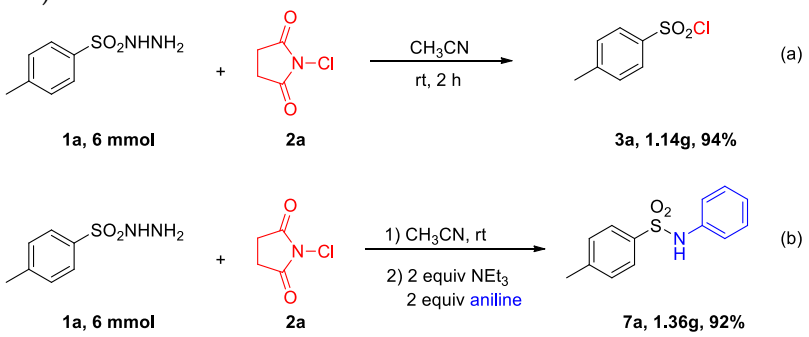


Scheme 3. Synthesis of sulfonamides or sulfonates under the optimum conditions. Conditions:1) **1a** (0.3 mmol), **2a** (0.6 mmol) and CH_3CN (2.0 mL), rt, for 2 h, under air. 2) NEt_3 (0.6 mmol), nucleophile (0.6 mmol), rt, for 2 h, under air.

To further illustrate the robustness of the protocol, we scaled-up this sulfonyl chloride synthesis. Without modification of the original protocol, 6 mmol of 1a could successfully be converted to **3a** in 94% yield (Scheme 4a). Adding aniline to the above reaction system without any separation, sulfonamide 7a could be obtained with a yield of 92% (Scheme 4b).



Scheme 4. Formation of the sulfonyl chloride and sulfonamide at gram-scale.

To gain insights into the reaction mechanism, several control experiments were designed to understand the mechanism of this process. We performed experiments with the addition of the radical inhibitor TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) or BHT (butylated hydroxytoluene), however, the reaction was not suppressed enough (Scheme 5a). These results suggested that a radical process might not be involved in this transformation. Next, we tried to react NCS with sodium benzenesulfinate **8** instead of **1a** in our conditions. As desired, the product **3b** was isolated in 86% yield (Scheme 5b), which suggested that it may serve as key intermediates in this transformation.

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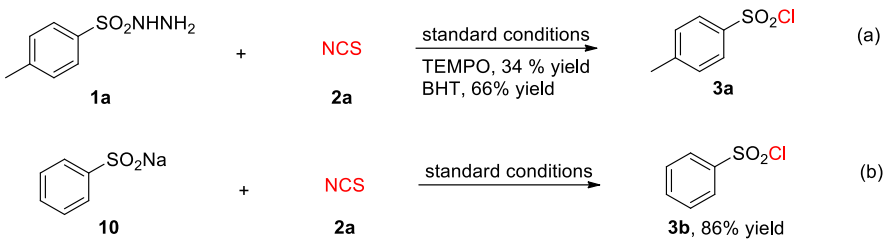
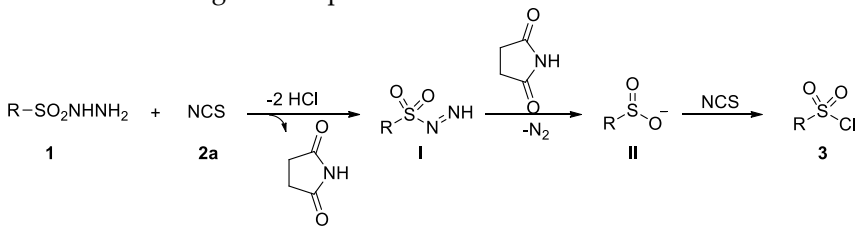


Scheme 5. Preliminary research mechanism.

Based upon the above results and literatures, a plausible mechanism was proposed, as shown in Scheme 6. Initially, sulfonyl hydrazides **1** reacts with NCS to give intermediate **I** [37], which is converted to sulfinate **II** with the release of N_2. Then, the final product **3** was formed through electrophilic substitution with NCS.



Scheme 6. Proposed Reaction Mechanism.

4. Materials and Methods

4.1 General Information

NMR data were obtained for ^{1}H at 400 MHz, and for ^{13}C at 100 MHz. Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution. Column chromatography was performed on silica gel (300-400 mesh) eluting with ethyl acetate/petroleum ether. TLC was performed on glass-backed silica plates. UV light and I_2 were used to visualize products. All chemicals were used without purification as commercially available unless otherwise noted.

*4.2 General procedure for synthesis of sulfonyl chloride **3** or sulfonyl bromide **4**.*

N-Chlorosuccinimide **2a** or N-bromosuccinimide **2b** (0.6 mmol, 2.0 equiv) was added to a solution of sulfonyl hydrazide **1** (0.3 mmol) in CH_3CN (2 mL) in one portion. The mixture was stirred at room temperature for 2 h. The solvent was removed and the residue was purified by flash column chromatography (petroleum ether/ethyl acetate) to provide the corresponding sulfonyl chloride **3** or sulfonyl bromide **4**.

*4.3 Large-scale reaction for the synthesis of sulfonyl chloride **3a**.*

N-Chlorosuccinimide **2a** (12 mmol, 2.0 equiv, 1.6 g) was added to a solution of 4-methylbenzenesulfonhydrazide **1a** (6 mmol, 1.12 g) in CH_3CN (10 mL) in one portion. The mixture was stirred at room temperature for 2 h. The solvent was removed and the residue was purified by flash column chromatography (PE/EA =20:1) to provide the corresponding p-toluenesulfonyl chloride **3a** (1.14g, 94%).

4.4 General procedure for one-port reaction with nucleophile.

N-Chlorosuccinimide **2a** (0.6 mmol, 2.0 equiv) was added to a solution of 4-methylbenzenesulfonhydrazide **1a** (0.3 mmol) in CH_3CN (2 mL) in one portion. The mixture was stirred at room temperature for 2 h. Then Et_3N (0.6 mmol, 2.0 equiv) and nucleophile (0.6 mmol, 2.0 equiv) were added to the above reaction system and the mixture was stirred at room temperature for 2 h. The solvent was removed and the residue was purified by flash column chromatography (PE/EA) to provide the corresponding sulfonamides and sulfonates **7**.

4.5 Large-scale reaction for the synthesis of ***7a****.*

N-Chlorosuccinimide **2a** (12 mmol, 2.0 equiv) was added to a solution of 4-methylbenzenesulfonhydrazide **1a** (6 mmol, 1.12 g) in CH_3CN (10 mL) in one portion. The mixture was stirred at room temperature for 2 h. Then Et_3N (12 mmol, 2.0 equiv) and aniline (12 mmol, 2.0 equiv) were added to the above reaction system and the mixture was stirred at room temperature for 2 h. The solvent was removed and the residue was purified by flash column chromatography (PE/EA) to provide the corresponding sulfonamide **7a** (1.39g, 94%).

5. Conclusions

In conclusion, we have successfully developed an efficient, simple, practical approach for the construction of sulfonyl chlorides/bromides from sulfonyl hydrazide. This methodology allows a wide substrate scope, utilizes readily available starting materials, and provides operational simplicity. Efforts to develop more direct applications in the chemical community are in progress in our laboratory.

Supplementary Materials: Characterization of products, ^{1}H and ^{13}C-NMR spectra are available online at http://www.mdpi.com

Author Contributions: R.X. Chen, F.M. Shen, C. Xu, K.K. Wang and Z.Y. Wang participated in the purification and characterization of the compounds. S.H. Xu and L.L. Liu participated in the interpretation of spectroscopy of compounds and the review of the manuscript. S.H. Xu and L.L. Liu participated in the interpretation of the results, writing, revision and correspondence to the journal of molecules until the manuscript was accepted. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples of the compounds are available from the authors.

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