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Cs_2CO_3 promoted direct C–H bond sulfenylation of imidazo[1,2-*a*]pyridines and related heteroarenes in ionic liquid†

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An efficient and novel method was developed for the synthesis of 3-sulfenyl imidazo[1,2-*a*]pyridines in good to excellent yields *via* a Cs_2CO_3 promoted direct sulfenylation of imidazo[1,2-*a*]pyridines. The reaction proceeds smoothly with a wide range of structurally diverse heteroarenes and disulfides. This protocol is environmentally friendly because it is free of transition-metal catalysts and utilizes aryl-substituted imidazolium-based ionic liquid rather than volatile organic solvents.

Introduction

Sulfur-containing substances are an important class of compounds, which exist in a variety of natural products and synthetic drugs and play a significant role in medicinal chemistry for their biological activities.[1] Sulfenyl aza-aromatics are especially valued due to their comprehensive therapeutic value against a variety of diseases, such as tubulin polymerization, human breast cancer and other tumors,[2,3] and vascular[4] and respiratory disorders.[5]

Imidazopyridine and its derivatives exist in a variety of natural products and have attracted much attention due to their important biological activities and broad utilization in the pharmaceutical industry. Generally, the pharmacological profile is mainly dependent on the nature of the substitutional groups and introduction of sulfenyl groups on the aza-aromatic rings could impart markedly biological properties to the compounds, for example, 3-sulfenyl indoles, 3-sulfenyl pyrroles and 3-sulfenyl imidazopyridines are of considerable therapeutic value against a variety of diseases.[6]

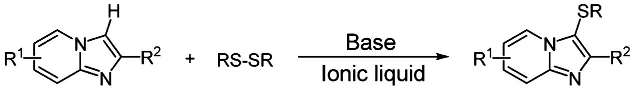
Since the discovery of the important applications of sulfur-containing agent, many strategies for the construction of carbon–sulfur bond have been developed in recent years.

Research on copper-catalyzed Ullmann-type carbon–sulfur couplings have made great progresses in recent years.[7] Chan–Evans–Lam-type reactions are also very efficient for C–S bond formation.[8] Base-promoted procedure *via* reductive coupling of tosylhydrazones with thiols under metal-free conditions has been reported recently.[9] As an important and attractive method, Friedel–Crafts reaction combined with selective C–H bond activation strategy has also been used for the selective C–S bond formation.[10] In view of the synthetic strategies as indicated above, a number of procedures have been devised for sulfenylation of electron-rich aza-aromatics with transition-metal catalysts,[11] new sulfur reagents[12] and stoichiometric amounts of promoters.[13]

In recent years, rare earth metal catalysts were extensively used in organic synthesis.[14] Cerium(III) chloride has emerged as a cheap, nontoxic, water-tolerant and very useful Lewis acid catalyst, which can promote the reactions of electron-rich aza-aromatics with several electrophiles to form carbon–sulfur, carbon–nitrogen, carbon–oxygen, and carbon–carbon bonds.[15]

In compliance to green chemistry principles, "ionic liquids" (ILs) constitute an attractive alternate in the field of organic synthesis, electrochemistry and separation process due to catalyst recycling, improve selectivity and ease in product isolation. Henceforth, imidazolium based ILs have been utilized widely in current organic chemistry.[16]

Although a number of synthetic protocols have been developed for the sulfenylation of electron-rich aza-aromatics, it is still desirable to explore new methods avoid using metal catalyst and complex sulfur-containing reagent under environmentally friendly reaction condition. Towards research in developing new methods for the carbon–heteroatom bond forming reactions, an efficient and simple base promoted direct C–H bond sulfenylation of imidazo[1,2-*a*]pyridines and related heteroarenes with disulfides in aryl-substituted imidazolium-based ionic liquid has been developed (Scheme 1).



Scheme 1 Base promoted 3-sulfenylation of imidazo[1,2-*a*]pyridines in ionic liquid.

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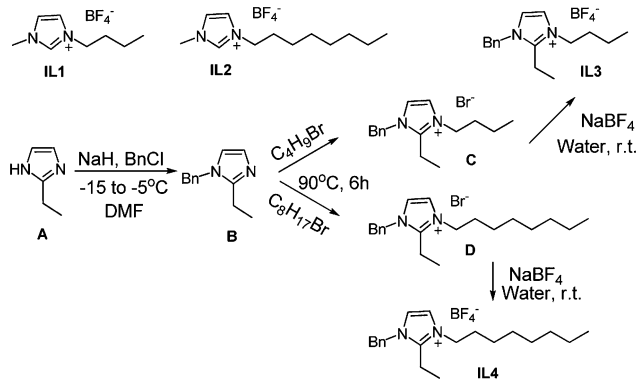
Results and discussion

Inspired by the outcomes of recent reports on base promoted direct C–H bond sulfenylation in volatile organic solvents[17] and the decisive role of ionic liquids in organic synthesis,[18] we designed aryl-substituted 2-ethyl-imidazolium-based ionic liquid 1-benzyl-3-butyl 2-ethyl-imidazolium tetrafluoroborate ([BnEBIm]BF_4) and 1-benzyl-3-octyl 2-ethyl-imidazolium tetrafluoroborate ([BnEOIm]BF_4) and investigated their solvent effect for the present reaction (Scheme 2).[16g]

We started our studies by reacting phenyl disulfide with 2-phenylimidazo[1,2-*a*]pyridine in the presence of 2 equivalents of Cs_2CO_3 in DMSO at 80 °C under an air atmosphere. However, only 32% yield of product was detected after 15 hours reaction. Encouraged by this result, the reaction was optimized and the results are summarized in Table 1.

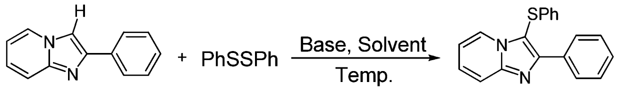
At first, several kinds of bases were tested and it was found that other bases such as K_2CO_3, $KHCO_3$, KF, NaOH and *t*BuOK were less effective compared to Cs_2CO_3 due to their higher or lower pK_a value (Table 1, entries 1–6). Subsequently, several solvents such as DMSO, EtOH, CH_3CN, DMC, toluene and ionic liquids were tested for the reaction (Table 1, entries 7–14). Results show that ionic liquids can give moderate to excellent yield of the desired product and the highest yield was obtained in IL4, which may because the aryl and alkyl substituted groups of ionic liquids increased the interaction and solubility of reactants. However, when IL3 was used as the solvent, work-up manipulation is easier than IL4 because the melting point of IL4 is about 60 °C. Reducing the dosage of base from 2 equivalents to 1.5 and 1.0 equivalent led to decrease of the yield of **3a** from 89% to 77% and 53% (Table 1, entries 15–16). When the reaction was carried out at 50 °C instead of 80 °C, the yield of **3a** decreased from 89% to 20% (Table 1, entries 17–18). Blank experiment show that the reaction cannot proceed without the use of base (Table 1, entry 19).

In order to extend the scope of this methodology, a variety of imidazo[1,2-*a*]pyridines were allowed to reacted with disulfides under optimized conditions. As can be seen from Table 2, the direct C–H bond sulfenylation reactions of imidazo[1,2-*a*]pyridines with disulfides generated the corresponding products in good to excellent yields.



Scheme 2 Simple routes for the synthesis of aryl-substituted imidazolium-based ionic liquids.

Table 1 Optimization of reaction conditions for sulfenylation of imidazo[1,2-*a*]pyridines[a]



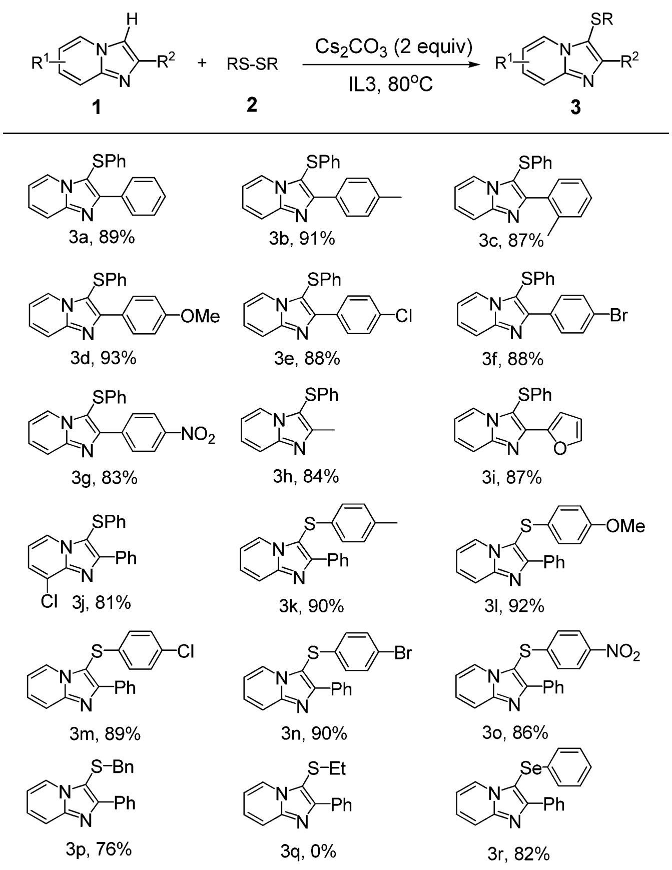
1a **2a** **3a**

Entry	Base	Solvent	Temp (°C)	Yield[b] (%)
1	Cs_2CO_3	DMSO	80	32
2	K_2CO_3	DMSO	80	11
3	$KHCO_3$	DMSO	80	0
4	KF	DMSO	80	0
5	NaOH	DMSO	80	23
6	*t*BuOK	DMSO	80	15
7	Cs_2CO_3	EtOH	80	36
8	Cs_2CO_3	CH_3CN	80	31
9	Cs_2CO_3	DMC	80	Trace
10	Cs_2CO_3	Toluene	80	Trace
11	Cs_2CO_3	IL1	80	56
12	Cs_2CO_3	IL2	80	68
13	Cs_2CO_3	IL3	80	89
14	Cs_2CO_3	IL4	80	91
15[c]	Cs_2CO_3	IL3	80	77
16[d]	Cs_2CO_3	IL3	80	53
17	Cs_2CO_3	IL3	100	89
18	Cs_2CO_3	IL3	50	20
19	—	IL3	80	0

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), base (1 mmol), solvent (1 mL), 15 h, 80 °C in a 25 mL flask. [b] Yield of isolated product after column chromatography. [c] 1.5 equivalent of base was used. [d] 1.0 equivalent of base was used.

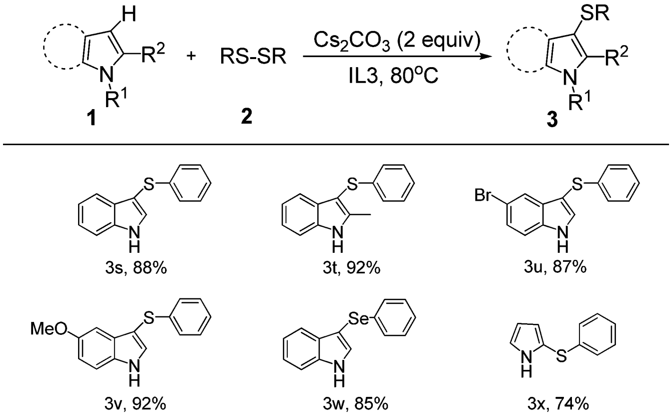
Electron-donating and electron-withdrawing groups on the benzene rings of imidazo[1,2-*a*]pyridines were tolerated. Benzene rings of imidazo[1,2-*a*]pyridines with electron-donating groups (Table 2, entries **3b–d**), such as CH_3 and OCH_3, gave a slightly higher yield than those bearing electron-withdrawing groups, such as Cl, Br and NO_2 (Table 2, entries **3e–g**). Benzene rings of imidazo[1,2-*a*]pyridines bearing CH_3 group at the *ortho*-position of the benzene ring afforded the corresponding product in 87% yield, compared with the yield of 91%, when the CH_3 group was located at the *para*-position of the benzene ring (Table 2, entries **3b–c**). The result represented a slight *ortho*-position effect of imidazo[1,2-*a*]pyridines. Under the present reaction conditions, imidazo[1,2-*a*]pyridines bearing furan group can be easily converted to the desired product **3i** in 87% yield (Table 2, entry **3i**). To our delight, imidazo[1,2-*a*]pyridines bearing alkyl group can also be transformed to the desired product **3h** in 84% yield (Table 2, entry **3h**). On another hand, various disulfides used for the direct C–H bond sulfenylation reaction were also investigated. Disulfides bearing electron-donating groups on **R** (Table 2, entries **3k–l**) gave better yields than those bearing electron-withdrawing groups (Table 2, entries **3m–o**). It was worth noting that dibenzyl disulfide could also be converted to the corresponding product **3r** in 82% under the presence reaction condition (Table 2, entry **3r**). However, alkyl disulfides could not afford the

Table 2 The scope of imidazo[1,2-*a*]pyridines and disulfides for the synthesis of 3-sulfenyl imidazopyridines under the optimum conditions[a,b]



[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), Cs_2CO_3 (1 mmol), IL3 (1 mL), 15 h, 80 °C in a 25 mL flask. [b] Yield of isolated product after column chromatography.

Table 3 The scope of other electron-rich heterocycles and disulfides for direct C–H bond sulfenylation reaction[a,b]



[a] Reaction conditions: **1a** (0.5 mmol), **2a** (0.5 mmol), Cs_2CO_3 (1 mmol), IL3 (1 mL), 15 h, 80 °C in a 25 mL flask. [b] Yield of isolated product after column chromatography.

desired product under the optimized reaction conditions (Table 2, entry **3q**).

Other electron-rich heterocycles such as indoles and pyrroles were also tested under the present optimized reaction condition. To our delight, they can both transformed to the desired products in good to excellent yield after simple work-up manipulation steps and the results was listed in Table 3. Under the present reaction condition, diphenyl diselenide can also react with 1-*H* indole to form the desired product in 85%.

With respect to the reaction mechanism we assume that deprotonation of the heterocycle afforded an anion was a key reaction step. Then the anion reacted with disulfide by nucleophilic attack, resulting in C–S bond formation.[17,18]

Conclusions

In conclusion, we have developed an efficient and environmentally friendly Cs_2CO_3 promoted direct C–H bond sulfenylation of imidazopyridines, indoles, and pyrroles with disulfides in aryl-substituted imidazolium-based ionic liquid rather than volatile organic solvents. Further more, this protocol is free of transition-metal catalyst and ionic liquid designed above can be reused *via* an easy work-up manipulation. A wide range of heterocycles with both electron-releasing and electron-withdrawing groups were tested and the corresponding sulfenyl heterocycles were obtained in good to excellent yields.

Experimental

All chemicals (AR grade) were obtained from commercial sources and were used without further purification. Petroleum ether (PE) refers to the fraction boiling in the 60–90 °C range. The progress of the reactions was monitored by TLC (silica gel, Polygram SILG/UV 254 plates). Column chromatography was performed on Silicycle silica gel (200–300 mesh). Melting points were obtained using a Yamato melting point apparatus Model MP-21 and are uncorrected. IR spectra were recorded on a Shimadzu spectrophotometer using KBr discs. ^1H and ^{13}C NMR spectra were obtained using a Bruker DRX 500 (500 MHz) spectrometer in $CDCl_3$ or DMSO-d_6 with TMS as the internal standard. All the products are known compounds and they were identified by comparison of their physical and spectral data with those reported in the literature.

General procedure for the synthesis of aryl-substituted imidazolium-based ionic liquid

(1) Sodium hydride (60% suspension, 40 mmol) was placed in a two-necked flask and 2-ethyl imidazole (20 mmol) in DMF (20 mL) was added under nitrogen atmosphere at −15 °C. The reaction mixture was stirred for another 30 min at −15 °C, and then benzyl chloride (20 mmol) was added. The temperature of the reaction was raised to −5 °C and the reaction mixture was stirred for another 3 hours under N_2. After completion, reaction was quenched with methanol (5 mL) and solvent was evaporated to give the crude product which was purified using silica gel column chromatography to obtain B in 92% yield.

(2) Alkyl bromide (25 mmol) was added to B (20 mmol) in THF (20 mL) and the reaction was stirred for 4–6 hours at 80 °C. The reaction mixture was dried under reduced pressure and column chromatography over silica gel provided the desired compounds C and D in the yield of 91% and 90%.

(3) To the solutions of the imdazolium halides C and D (20 mmol) in water (20 mL) was added $NaBF_4$ (21 mmol) and the reaction mixture was stirred for 1.5 h at room temperature. Reaction mixture was extracted with dichloromethane (3 × 10 mL) and purified by column chromatography to obtain ionic liquid IL3 and IL4 in the yield of 95% and 94%.

General procedure for sulfenylation of heterocycles with disulfides

A mixture of heterocycle (0.5 mmol), disulfide (0.5 mmol) and Cs_2CO_3 (1 mmol) were added in IL3 (1 mL) at 80 °C in a flask. The reaction was carried out under an air atmosphere for about 15 h until complete consumption of starting material as monitored by TLC. The solution was extracted with ethyl ether (3 × 10 mL). And then the organic layer was separated and concentrated under vacuum and the crude product was purified by column chromatography (PE : EtOAc, 15 : 1) or recrystallization (PE : EtOAc, 5 : 1) to provide the analytically pure product. The ionic liquid layer was washed with water (2 × 2 mL) and separated *via* simple work-up manipulation. And the ionic liquid can be easily recycled after drying under vacuum.

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