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Thiourea dioxide as a source of sulfonyl groups: photoredox generation of sulfones and sulfonamides from heteroaryl/aryl halides†

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Thiourea dioxide as the source of sulfonyl groups for the efficient synthesis of heteroaryl sulfones and sulfonamides from heteroaryl halides under visible light irradiation is reported. This transformation proceeds smoothly *via* heteroaryl sulfinate intermediates, which can be trapped *in situ* by various electrophiles. A broad reaction scope is demonstrated, especially for the electron-deficient heteroaryl halides. Mechanistic studies show that the radical coupling of the heteroaryl radical and sulfur dioxide radical anion may be the key step during the reaction process, as supported by EPR spectroscopy and DFT calculations.

It is well-known that the applications of sulfonyl-containing compounds in pharmaceuticals,[1] agrochemicals,[2] and materials[3] have been demonstrated. Additionally, heteroaryl sulfones and sulfonamides have displayed excellent biological activities.[4] The traditional method for the preparation of sulfones is through the sulfonylation of arenes or oxidation of sulfides.[5] The general route to sulfonamides is from the condensation of sulfonyl chlorides and amines.[6] Thus, odorous thiol compounds and chlorosulfonic acid are often required, and the substrate scope is limited due to the harsh reaction conditions. Considering the importance of sulfonyl-containing compounds, it is highly desirable to provide a general and simple method for the formation of sulfones and sulfonamides under mild conditions.

Recently, the insertion of sulfur dioxide into organic molecules for the synthesis of sulfonyl compounds has attracted much attention. The bench-stable $\mathrm{DABCO{\cdot}(SO_2)_2}$[7,8*a*] and inorganic sulfites[8*b*] have been applied successfully as the sulfur dioxide surrogates avoiding the use of gaseous sulfur dioxide. The transformations could proceed under transition metal catalysis or through radical processes. So far, aryl halides,[8] arylboronic acids,[9] aryl nonaflates,[10] and aryl triethoxysilanes[11] have been proven to be good partners in the metal-catalyzed reactions with the insertion of sulfur dioxide. Additionally, aryl or heteroaryl halides with a stoichiometric amount of metal could be converted to the corresponding organometallic reagents, which would act as a nucleophile to react with sulfur dioxide giving rise to sulfinates.[12] The metal sulfinates would subsequently undergo electrophilic reaction to afford sulfonyl compounds. Interestingly, the carbon radicals formed *in situ* from different precursors[13–19] would be captured by sulfur dioxide, leading to the corresponding sulfonyl radicals. These sulfonyl radicals would further react with unsaturated bonds or metal intermediates providing various sulfonyl compounds.

Although significant progress for the synthesis of sulfonyl compounds from sulfur dioxide has been witnessed,[20] there are few reports on the sulfonation of electron-deficient heterocycles *via* insertion of sulfur dioxide.[11*d*,21] To our knowledge, it is hard for a carbon radical with a heteroatom in its 2-position to capture sulfur dioxide, thus providing a sulfonyl radical.[22] Recently, we described the sulfonylation of (hetero)aryl iodides by using sodium dithionite as the sulfonyl source.[21*b*] We conceived that the sulfonyl source might be broadened to others, and it would be attractive and challenging to develop a route for access to sulfonated heterocyclic compounds through radical coupling procedures.

Thiourea dioxide has been widely used as a strong reducing agent in various transformations.[23] In the presence of hydroxide, thiourea dioxide would be converted to sulfur dioxide anions and urea (Scheme 1, eqn (a)). We envisioned that under suitable conditions, sulfur dioxide anions would undergo a single electron transfer (SET) thus providing the source of the sulfonyl group. Herein, we report that for the first time, the cheap and commercially available thiourea dioxide is unprecedently applied as the source of sulfonyl groups for the efficient synthesis of heteroaryl

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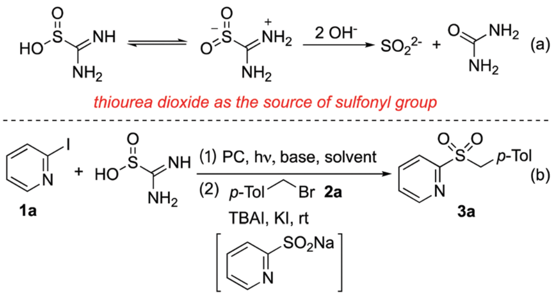
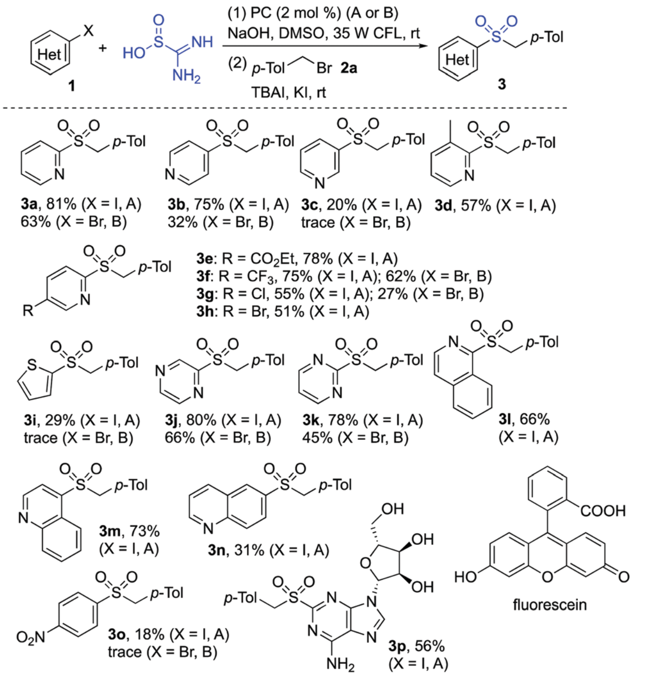


Scheme 1 Initial studies for the reaction of 2-iodopyridine **1a**, thiourea dioxide and 1-(bromomethyl)-4-methylbenzene **2a**.

sulfones and sulfonamides from heteroaryl halides under visible light irradiation. This transformation proceeds smoothly *via* heteroaryl sulfinate intermediates, which can be trapped *in situ* by various electrophiles. A broad reaction scope is demonstrated, especially for the electron-deficient heteroaryl halides. Mechanistic studies show that the radical coupling of heteroaryl radicals and sulfur dioxide radical anions may be the key step during the reaction process.

Since thiourea dioxide would be converted to sulfur dioxide anions in the presence of hydroxide, heteroaryl halides were selected as substrates for reaction development. We expected that sulfur dioxide anions would be transferred to sulfur dioxide radical anions under suitable conditions, which would react with heteroaryl halides *via* a single electron transfer (SET) to produce heteroaryl sulfinates. To test the above hypothesis, a reaction of 2-iodopyridine **1a** and thiourea dioxide was selected as the model for initial studies (Scheme 1, eqn (b). For details, please see the ESI†). As mentioned above, thiourea dioxide showed reducibility in alkaline conditions, so at the outset the reaction was performed at room temperature in several solvents in the presence of NaOH (Table S1, entries 1–6, ESI†). Gratifyingly, the formation of sodium 2-pyridinesulfinate was observed when the reaction occurred in DMF, DMA or DMSO. Subsequently, TBAI, KI and 1-(bromomethyl)-4-methylbenzene **2a** were added in these reactions. It was found that the expected product **3a** could be afforded in 42% isolated yield in DMSO (Table S1, entry 6, ESI†). The yield of product **3a** was increased to 80% when the reaction was stirred under visible-light irradiation with Ir(ppy)$_3$ (Table S1, entry 8, ESI†). After screening other photocatalysts (Table S1, entries 9–13, ESI†), we found that the cheap fluorescein could replace the expensive iridium catalyst with comparative yield (Table S1, entry 13, ESI†). No better results were obtained when other bases were used in the reaction (Table S1, entries 14–17, ESI†). Changing the amount of thiourea dioxide or NaOH could not improve the final outcome (Table S1, entries 18 and 19, ESI†).

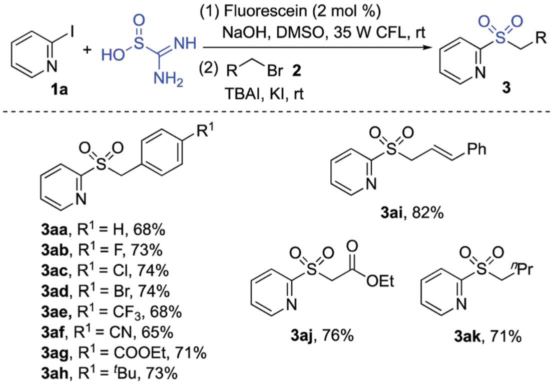
The scope of the reaction of heteroaryl halides **1**, thiourea dioxide, and 1-(bromomethyl)-4-methylbenzene **2a** was then explored. As shown in Scheme 2, a range of heteroaryl iodides **1** were suitable substrates under these conditions. Since the less active heteroaryl-bromides are much cheaper than heteroaryl-iodides, we further examined the reaction of heteroaryl/aryl bromides. Although only a trace amount of product was detected when 2-bromopyridine was used as the substrate under the standard conditions, product **3a** could be obtained in 63% yield when Ir(ppy)$_3$ was used as the photocatalyst instead of fluorescein. Many functional groups including ester, trifluoromethyl, chloro, bromo, amino, and hydroxy were tolerated. Reactions of other heteroaryl halides as substrates were further explored. It showed that examples of pyrazine, pyrimidine, quinoline, isoquinoline and thiophene ring systems were all proven to be applicable, and the corresponding sulfones were produced as expected. However, the result was not satisfactory when 1-iodo-4-nitrobenzene was employed in the reaction. We postulated that the aryl radical generated *in situ* would be hydrogenated easily.[24] To verify the usefulness of this sulfonation method, the reaction of thiourea dioxide and 1-(bromomethyl)-4-methylbenzene **2a** was scaled up by using 1.0 gram of 2-iodopyridine **1a**. The procedure proceeded smoothly, affording the desired product **3a** in 78% yield.



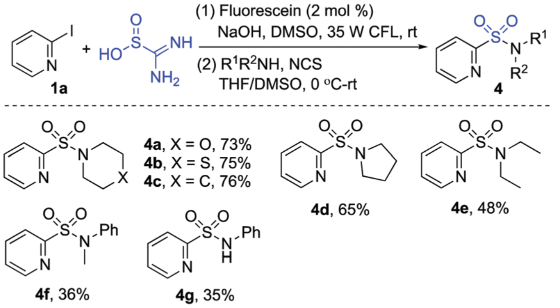
Scheme 2 Reactions of heteroaryl/aryl iodides **1**, thiourea dioxide and 1-(bromomethyl)-4-methylbenzene **2a**. (Isolated yield based on heteroaryl/aryl iodide **1**. A: fluorescein; B: Ir(ppy)$_3$).

Next, we examined the reactions by using other alkyl bromides as electrophilic substrates in the reaction of 2-iodopyridine **1a** with thiourea dioxide. The result is shown in Scheme 3. As expected, all reactions worked well to provide the corresponding products.

We further applied this method in the preparation of heteroaryl sulfonamides (Scheme 4). Several aliphatic amines were added in the reaction instead of alkyl bromides in the presence of *N*-chlorosuccinimide, and the corresponding heterocyclic sulfonamides were obtained in good yields. Additionally, aromatic amines were also compatible in this transformation, although the yields were not satisfactory. We reasoned that the less nucleophilic anilines could not convert smoothly into the corresponding amine chloride during the reaction process.



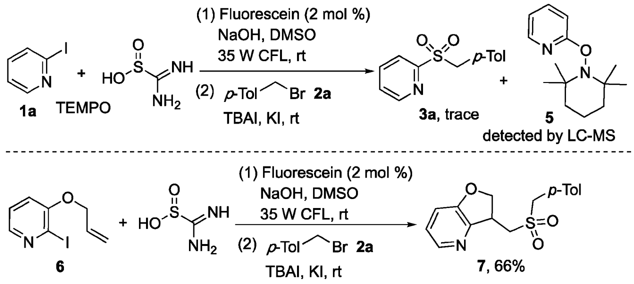
Scheme 3 Reactions of 2-iodopyridine **1a**, thiourea dioxide and other alkyl bromides **2** (isolated yield based on 2-iodopyridine **1a**).



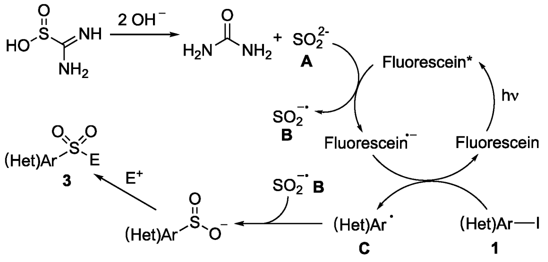
Scheme 4 Synthesis of heteroaryl sulfonamides (isolated yield based on 2-iodopyridine **1a**).

In order to understand the mechanism of this photoinduced reaction, a preliminary mechanistic investigation was carried out. The reaction was hampered when 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added in the reaction of 2-iodopyridine **1a**, thiourea dioxide, and 1-(bromomethyl)-4-methylbenzene **2a**, and the formation of 2-(TEMPO) pyridine **5** was detected by LC-MS (Scheme 5). Meanwhile, compound **7** was obtained in 66% yield when 3-(allyloxy)-2-iodopyridine **6** was employed in the reaction of thiourea dioxide with 1-(bromomethyl)-4-methylbenzene **2a** (Scheme 5). These results demonstrated that a heteroaryl radical might be involved in the reaction process.

Additionally, a series of control experiments were conducted by using electron paramagnetic resonance (EPR) spectroscopy and a fluorescence spectrophotometer, as shown in the ESI.†



Scheme 5 Control experiments.



Scheme 6 Plausible mechanism.

The results also demonstrated the radical process of this transformation. Thus, a plausible mechanism of this visible-light induced sulfonylation reaction was proposed, as illustrated in Scheme 6. We reasoned that sulfur dioxide anion **A** would be generated from the reaction of thiourea dioxide with sodium hydroxide. Subsequently, the excited state of fluorescein would react with sulfur dioxide anion **A** giving rise to sulfur dioxide radical anion **B**, along with the formation of a fluorescein radical anion. Then, the fluorescein radical anion would undergo a single electron transfer (SET) with heteroaryl iodide, leading to a heteroaryl radical and an iodide anion. Finally, the heteroaryl sulfinate intermediate would be formed *via* a radical coupling between sulfur dioxide radical anion **B** and heteroaryl radical **C**. This key step in the transformation was supported by DFT calculations in the meantime (see the ESI†).

In conclusion, we have reported that the cheap and commercially available thiourea dioxide is applied as the source of sulfonyl groups for the efficient synthesis of heteroaryl sulfones and sulfonamides from heteroaryl halides under visible light irradiation. This transformation proceeds smoothly *via* heteroaryl sulfinate intermediates, which can be trapped *in situ* by various electrophiles. A broad reaction scope is demonstrated, especially for the electron-deficient heteroaryl halides. Mechanistic studies show that the radical coupling of heteroaryl radicals and sulfur dioxide radical anions may be the key step during the reaction process, as supported by EPR spectroscopy and DFT calculations.

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Conflicts of interest

There are no conflicts to declare.

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