COMMUNICATION

Photoredox-Catalyzed Preparation of Sulfones Using *Bis*-Piperidine Sulfur Dioxide – An Underutilized Reagent for SO_2 Transfer

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Abstract: Sulfonyl groups are widely observed in biologically relevant molecules and consequently, SO_2 capture is an increasingly attractive method to prepare these sulfonyl-containing compounds given the range of SO_2-surrogates now available as alternatives to using the neat gas. This, along with the advent of photoredox catalysis, has enabled mild radical capture of SO_2 to emerge as an effective route to sulfonyl compounds. Here we report a photoredox-catalyzed cross-electrophile sulfonylation of aryl and alkyl bromides making use of a previously under-used amine-SO_2 surrogate; *bis*(piperidine) sulfur dioxide (PIPSO). A broad selection of alkyl and aryl bromides were photocatalytically converted to their corresponding sulfinates and then trapped with various electrophiles in a one-pot multistep procedure to prepare sulfones and sulfonamides.

Introduction

The prevalence of sulfur in functional materials, agrochemicals and pharmaceuticals is a testament to the wide range available of stable sulfur-containing groups including sulfides, sulfoxides, sulfones and sulfonamides (Figure 1).[1] The versatile nature of sulfur makes it more common than fluorine and phosphorus in approved drug molecules.[2] As a result, many methods to incorporate sulfur into organic molecules have been explored, including *via* various sources of SO_2; either neat (as a gas or in solution) or as a surrogate. Despite the abundance of technologies now available to handle reactive gases in synthesis,[3] the use of SO_2 gas on a laboratory scale is typically avoided due to its notable toxicity and pungent odour.[4] In response to this, cheap, convenient and stable SO_2 surrogates have been developed and play an impressive role in sulfur-based organic synthesis research.[5]

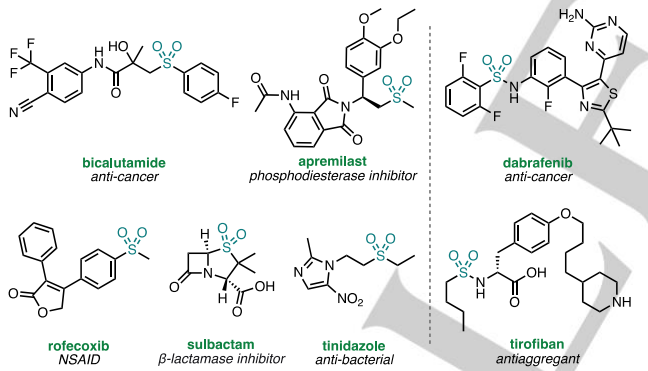


Figure 1. Organosulfur pharmaceuticals – examples containing sulfonyl motifs.

Directly preparable by bubbling or condensing SO_2 gas with the appropriate amine, amine-SO_2 adducts have been studied for over 100 years, with the most notable and useful example being 1,4-diazabicyclo[2.2.2]octane *bis*(sulfur dioxide), abbreviated as DABSO.[6] DABSO has emerged in synthesis as a commercially available and convenient source of SO_2 in the last decade, and as such, has found many uses in synthesis to incorporate SO_2 moieties into target compounds, including metal sulfonates, sulfinates, sulfonyl fluorides, sulfonamides, sulfonohydrazides, sulfonate esters, thiosulfonate esters and sulfones.[6] Despite the isolation and characterisation of several other stable amine-SO_2 adducts over the years, many others exhibit practical challenges regarding thermal stability and moisture sensitivity such as the commercially available 1-methylpyrrolidine sulfur dioxide (TIMSO).

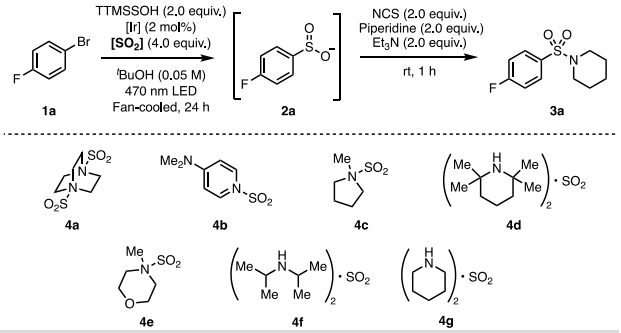
Perhaps the most widely used approach to incorporate SO_2 into a molecule is *via* metal sulfinates. Indeed, sulfinates are versatile intermediates to a range of organosulfur functional groups. They can be prepared from a suitable organometallic reagent or catalyst-activated substrate and a source of SO_2,[7] such as DABSO,[8,9] and subsequently converted *in-situ*. As an alternative to the harsh conditions of organometallic approaches to incorporate SO_2, radical methods have gained attention in recent years[10–13] with the emergence photoredox catalysis, as a range of highly reactive species can be generated under mild conditions by the use of light and a photocatalyst.[14,15] Although several photochemical strategies to incorporate aryl (and other sp^2) radicals into SO_2 sources have been developed,[16–25][26,27] there are somewhat fewer examples of alkyl radicals being trapped by SO_2,[28–35] and fewer still, established general methods that allows the incorporation of both substituents.[36–39] Those that do have limited scope due to the required use of UV light irradiation in their preparation. The exception to this is the recent use of photocatalytic strategies with thianthrenium salts,[40] which has made the preparation of sulfones from aryl and alkyl radicals possible and has the advantage of tolerating a wider range of functional groups than previous UV light procedures. Our group has previously worked on photoredox-catalyzed methods to prepare sulfonyl compounds making use of sulfone tetrazoles as precursors to sulfonyl radicals.[41] Following on from this, we sought to develop a general route to sulfonyl compounds *via* both alkyl and aryl sulfinate intermediates, themselves generated using a photoredox-catalyzed C(sp^2 & sp^3)-S bond-forming reaction. To incorporate both alkyl and aryl substrates using a single radical method, we took inspiration from previous work pertaining to halogen atom transfer (XAT) due to the availability of a wide range of both C(sp^2)-Br and C(sp^3)-Br compounds and the photoredox-mediated strategies available to form their respective carbon radicals.[42] The use of silanes to perform halogen abstraction is well-established and can facilitate the activation of a range of C-X bonds.[43–45] Indeed, MacMillan and co-workers recently reported the application of silane-mediated XAT as a method to prepare alkyl sulfonyl compounds.[35] Disclosed herein is the application of a previously underutilised piperidine-SO_2 complex to a general photoredox-mediated sulfinate forming reaction using a silane reductant and a range of alkyl and aryl halides.

Results and Discussion

Our investigation began by first irradiating a mixture of 4-fluorobromobenzene (**1a**), DABSO (**4a**), *Tris*(trimethylsilyl)silanol and (Ir[dF(CF_3)ppy]$_2$(dtbpy)PF_6 in ^{t}BuOH with ~10 W 470 nm LEDs for 24 hours at room temperature (**Table 1**). The reaction proceeded and indeed formed sulfinate (**2a**) by ^{1}H and ^{19}F NMR. Initially, the sulfinate was quenched *in-situ* using NCS and piperidine to give sulfonamide **3a** in a modest 28% yield by NMR (entry 1). Switching out ^{t}BuOH for other solvents failed to deliver any substantial quantity of the product. *Tris*(trimethylsilyl)silanol proved to be the best XAT reagent, outperforming both *tris*(trimethylsilyl)silane (TTMSS, entry 2) and *N*-adamantyl aminosupersilane (entry entry 3). With these established, SO_2 sources were then investigated. A balloon of SO_2 gas, aqueous SO_2, rongalite and sodium thiosulfate gave no improvement in yield (entries 4-7). With a promising result obtained by DABSO, we then set about preparing a selection of other amine-SO_2 adducts to investigate their suitability in

this reaction. Amine-SO_2 adducts are easily preparable for laboratory use by exposing a solution of the appropriate amine to SO_2 gas (bought as a canister or generated *in-situ*).[46] A selection of adducts were prepared, including those from *N*,*N*-dimethylpyridin-4-amine (**4b**) tetramethylpiperidine (**4d**), *N*-methylmorpholine (**4e**), diisopropylamine (**4f**) and piperidine (**4g**). We then examined their performance, along with commercially available amine-SO_2 adducts **4a** and **4c**, as sources of SO_2 in the radical reaction. They produced **3a** in a range of conversions (entries 8-13), however *bis*(piperidine) sulfur dioxide (**4g**) proved the best, producing **3a** in 72% yield (entry 13).

Table 1. Finding a suitable SO_2 source.

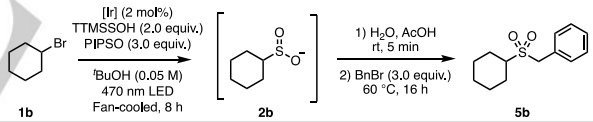


Entry	SO_2 source	Yield **3a** (%)[a]
1	**4a** (DABSO)	28
2	**4a**	1[b]
3	**4a**	14[c]
4	SO_2 balloon	10
5	Aq. SO_2	3
6	Rongalite	7
7	$Na_2S_2O_3$	9
8	**4b**	23
9	**4c** (TIMSO)	24[d]
10	**4d**	46
11	**4e**	30
12	**4f**	45
13	**4g** (PIPSO)	72[e]

[a] Yield determined by ^{19}F NMR with respect to a trifluorotoluene internal standard. [b] *Tris*(trimethylsilyl)silane used instead of TTMSSOH. [c] *N*-adamantyl aminosupersilane used instead of TTMSSOH. [d] Large quantity of starting material observed by ^{19}F NMR. [e] Isolated yield.

Towards the goal of a general method for the preparation of sulfonyl compounds *via* sulfinates, a simple method to quench sulfinate **2a** with carbon electrophiles such as benzyl bromide was developed. To the resultant photochemical reaction solution, H_2O and AcOH were added to protonate the residual piperidine, followed by BnBr and the resultant solution stirred at 60 °C for 16 hours to form sulfone **5a** in 70% yield by NMR. With the ability to manipulate the sulfinate solution to form either sulfonamides or sulfones, sulfones were subsequently pursued due to the wide range of possible carbon electrophiles able to react with sulfinates.[7] Wanting to engage both aryl and alkyl sulfinates, bromocyclohexane (**1b**) was then trialled against the most successful SO_2 surrogates found for 1-bromo-4-fluorobenzene. Interestingly, *only bis*(piperidine) sulfur dioxide (noted from here as PIPSO) delivered sulfone **5b** after quenching with BnBr in any substantial quantity and was subsequently isolated in 90% yield. It is worth noting here that PIPSO is an oxygen stable, white flocculent solid, preparable on multigram scale with ease, that is also hygroscopic (for details on how PIPSO was prepared and handled, see the SI). We found that it could be stored either in ^{t}BuOH in the fridge for days to weeks or as a solid under N_2 in the freezer for months and remain effective for the transformation. In terms of the cost of SO_2 sources, PIPSO offers an advantage due to the affordability of piperidine compared to DABCO for example. With PIPSO established as an effective source of SO_2 for this reaction, the reaction conditions were further investigated towards the synthesis of sulfones (**Table 2**). Controlling the irradiation time carefully enabled a 99% conversion to sulfone **5b**, which was then isolated in 96% yield after the subsequent quench with benzyl bromide (entry 1). While a photocatalyst was essential (entry 2), other photocatalysts were able to deliver the product, but only in inferior yields (entries 3 and 4). 1.1 equivalents of TTMSSOH proved sufficient to give the product in excellent yield (entry 5). The reaction was also able to tolerate air well, delivering sulfone **5b** in only a slightly diminished yield (entry 6). Altering the reaction concentration made little effect on the yield (entries 7 and 8). Surprisingly, irradiating the reaction mixture for over 10 hours led to the observation of thiosulfonate ester by-product **6b** (see SI for details), presumably by generation of sulfur through over-reduction under the reaction conditions (entry 9). This effect was seen generally across the alkyl bromides, but not for the aryl halides. As a result, the alkyl bromides were irradiated for a limit of 8 hours on 0.2 mmol scale using the standardized reaction set-up (see SI).

Table 2. Reaction Optimization.

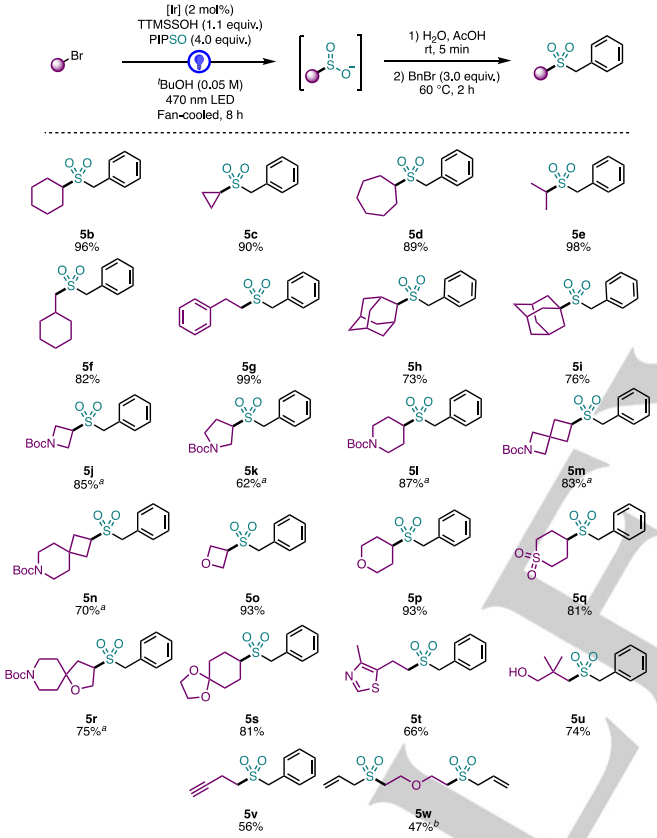


Entry	Deviation from conditions	Yield **5b** (%)[a]
1	none	99 (96)
2	No photocatalyst	0
3	[Ir]-2	93[b]
4	4CzIPN	45[c]
5	1.1 equiv. TTMSSOH	99
6	Air	97
7	0.1 M	90
8	0.025 M	95
9	16 h irradiation time	23[d]

[a] Yield determined by ^1H NMR with respect to a 1,3,5-trimethoxybenzene internal standard. [b] Trace **1b** unreacted [c] Only 50% conversion of **1b** achieved. [d] 75% conversion to thiosulfonate ester by-product **6b**. See SI for details.

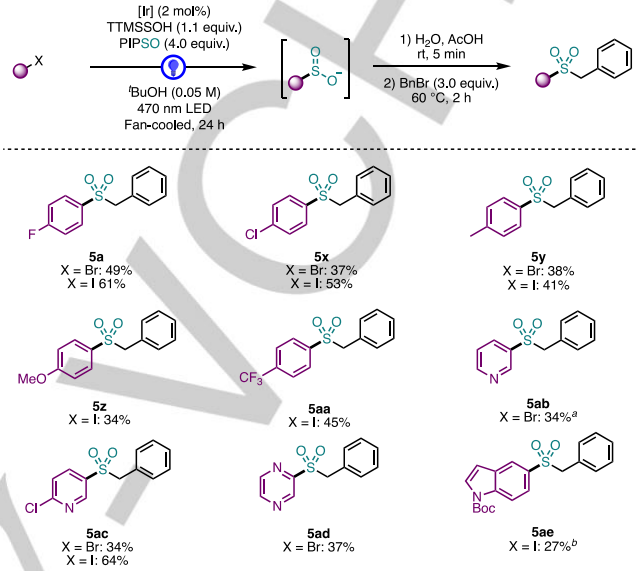
With new reaction conditions established, we set about evaluating the suitability of a range of alkyl bromides (**Scheme 1**). Small and medium cycloalkyl ring bromides produced their respective sulfones in excellent yields (**5b**-**d**), as did aliphatic bromides (**5e** and **5f**). Primary bromides also proved fruitful substrates, giving sulfones **5f** and **5g** in excellent yields. Sterically hindered and tertiary 1- and 2-adamantyl bromides

also afforded their respective sulfones, **5h** and **5i** respectively, in good yields. Aliphatic heterocycles also worked well, producing the respective benzyl sulfones of azetidine, pyrrolidine and piperidine in good to excellent yields (**5j-l**). Bromo-azaheterospirocycles were also well tolerated (**5m** and **5n**). Chalcogen-containing heterocycles were excellent substrates, producing oxetane **5o**, tetrahydropyran **5p** and *bis*-sulfone **5q** in excellent yields. *N*-heterospirocyclic tetrahydrofuran sulfone **5r** was prepared in very good yield also. The acetal protecting group was carried through to give sulfone **5s** in very good yield. Other functional groups including thiazole (**5t**) alcohol (**5u**) and alkyne (**5v**) were transformed to benzyl sulfone products in good yields. *Bis*(2-bromoethyl)ether was successfully converted to *bis*-sulfone **5w** with the use of allyl bromide as the electrophile in the second step.



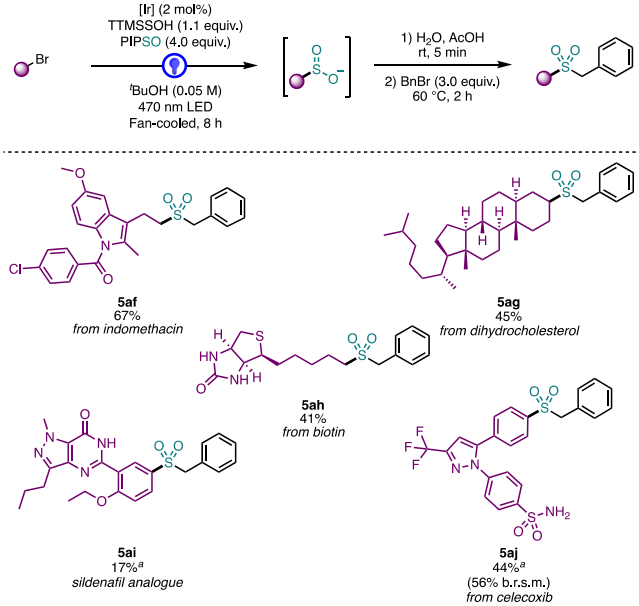
Scheme 1. Alkyl sulfones prepared from alkyl bromides. [a]10 hour irradiation time in the first step. [b]0.1 mmol of alkyl dibromide used and 3 equiv. allyl bromide used as the electrophile in the second step.

With a range of alkyl sulfones prepared, we next investigated the preparation of aryl sulfones (**Scheme 2**). Applying them to the reaction conditions afforded the corresponding sulfone products, albeit in poor yield (<30%). A brief investigation of the reaction conditions found that for the aryl bromides, conversion of the starting material was not proceeding significantly beyond 6 hours of irradiation and so the reaction conditions were modified. A modest increase in reducing agent stoichiometry and increased irradiation time improved the conversion of the starting material such that the products were isolable in reasonable yields. We then found that switching out the aryl bromide for the corresponding aryl iodide enabled the starting material to be fully converted under the reaction conditions. The major by-product observed for these substrates were the dehalogenated product, presumably obtained by HAT of the generated aryl radical. No HAT by-products were observed from the alkyl bromide substrates. Nonetheless, a range of aryl sulfones were prepared in modest to good yields including aryl halides **5a** and **5x**, electron rich arenes **5y** and **5z** and electron deficient arene **5aa**. Heterocyclic sulfones were also successfully prepared, albeit in modest yields, including pyridines **5ab** and **5ac**, pyrazine **5ad** and indole **5ae**.



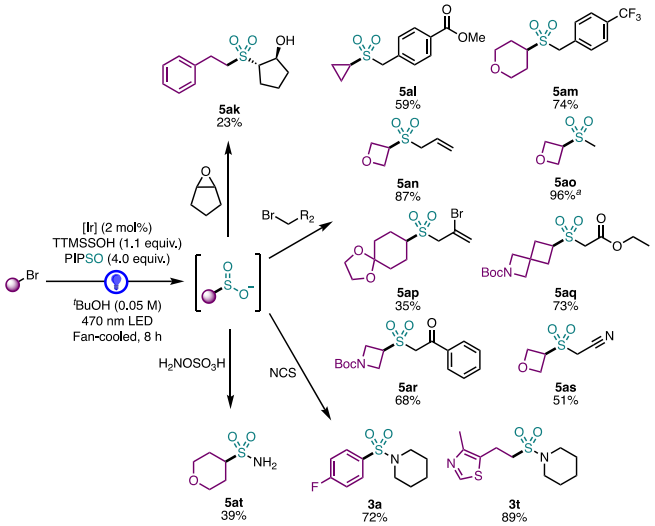
Scheme 2. Aryl sulfones prepared from aryl bromides and iodides. [a]Approximately 17% of pyridine *N*-benzylated product was observed by ^{1}H NMR. [b]Partial Boc deprotection of the product was observed during the second step.

With a selection of alkyl and aryl sulfones prepared, we set about demonstrating the application of the reaction to synthesising API derivatives and analogues (**Scheme 3**). Indomethacin analogue **5af** was prepared from its corresponding alkyl bromide in good yield, demonstrating the tolerance of indole and amide moieties in the reaction. Dihydrocholesterol was derivatised to sulfone **5ag** in moderate yield. Likewise, Biotin derivative **5ah** was prepared in moderate yield, showing possibilities to prepare biotin-sulfone linkers using this method and also the tolerance of the reaction towards thioethers and ureas.



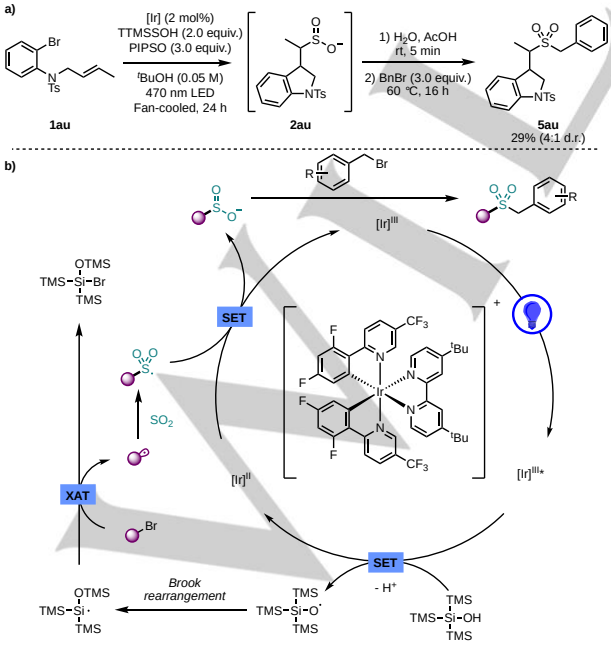
Scheme 3. Sulfone derivatives of APIs, drugs and natural products. [a]Reaction irradiated for 24 hours in the first step.

Sildenafil analogue **5ai** was prepared in low yield from its corresponding aryl bromide. Finally, celecoxib derivative **5aj** was isolated in good yield, thus also showing a tolerance of sulfonamide and pyrazole moieties.



Scheme 4. Alternative electrophiles in the right-hand side.

Having established a series of possible substrates from which to prepare sulfones, alternative electrophiles to couple with the generated sulfinates were assessed using a one-pot procedure (**Scheme 4**). Epoxides are well established electrophiles for ring opening by sulfinates and worked well as part of a one-pot procedure to generate β-hydroxysulfone **5ak**. Electron-deficient benzyl bromides were also converted in moderate to good yields producing sulfones **5al** and **5am**. Moving to other C-X electrophiles, allyl sulfone **5an** was synthesised in excellent yield from 3-bromooxetane as was methyl sulfone **5ao**. Vinyl bromide **5ap** was preparable in modest yield from the dibromide starting material. α-Sulfonyl ester **5aq** was prepared in good yield, as was α-sulfonyl ketone **5ar**. Nitrile **5as** was also prepared in moderate yield. Next, using NCS as a chlorinating agent, piperidine sulfonamides **3a** and **3t** were isolated in very good and excellent yields respectively. Finally, treating the sulfinate with the aminating agent hydroxylamine-*O*-sulfonic acid successfully delivered primary sulfonamide **3at**, albeit in modest yield.



Scheme 5. a) Radical trap control experiment and b) Proposed mechanism for the synthesis of sulfones.

A control experiment was conducted by employing aryl bromide **1au** as a substrate (**Scheme 5a**). As is consistent with a radical mechanistic pathway, cyclisation of the *o*-*N*-crotyl substitutent led to the isolation of sulfone **5au** after treatment with benzyl bromide. We therefore propose a radical mechanism (**Scheme 5b**) that is related to that proposed by Singh and co-workers.[47]

In summary, we have developed a general procedure for the construction of alkyl and aryl sulfones *via* sulfinate intermediates with the use of a previously unused source of SO_2. In doing so, a method for the convenient preparation of PIPSO on laboratory scale has been developed, demonstrated its use for radical capture, and also shown how the sulfinate intermediates in such a reaction can be trapped to form a variety of sulfones and sulfonamides. The reaction shows the possibility of preparing sulfones from a variety of alkyl and aryl halides including a range of functional groups, medicinally relevant fragments and API derivatives.

Acknowledgements

‡O.M.G. and H.A.E. contributed equally. O.M.G. was supported by the EPSRC (EP/S024220/1) SynTech Automated Centre for Chemical Synthesis, Centre for Doctoral Training in Cambridge, United Kingdom. H.A.E. was funded by Pfizer Inc. for a postdoctoral fellowship (Jan 2021 – Jan 2022). S.V.L. was supported by the American Chemical Society through receipt of the Arthur C. Cope Award.

Keywords: SO_2 surrogate • sulfinates • sulfones • sulfonamides • photoredox catalysis

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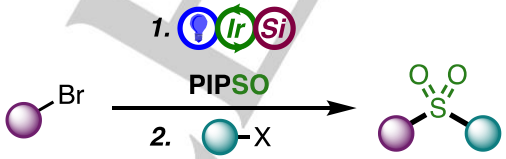

A photoredox-catalyzed one-pot sulfone preparation is reported from alkyl bromides activated by silane-mediated halogen atom transfer. In the process, a previously unutilized SO_2 adduct *bis*(piperidine) sulfur dioxide – or PIPSO – was found to be the best source of SO_2 for radical capture under the reaction conditions. Alkyl and aryl sulfones were prepared as well as sulfonylated APIs.