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Sulfones Bearing Perfluorinated Pyridine Group: Synthesis and Photocatalytic Reaction with α-(Trifluoromethyl)styrenes

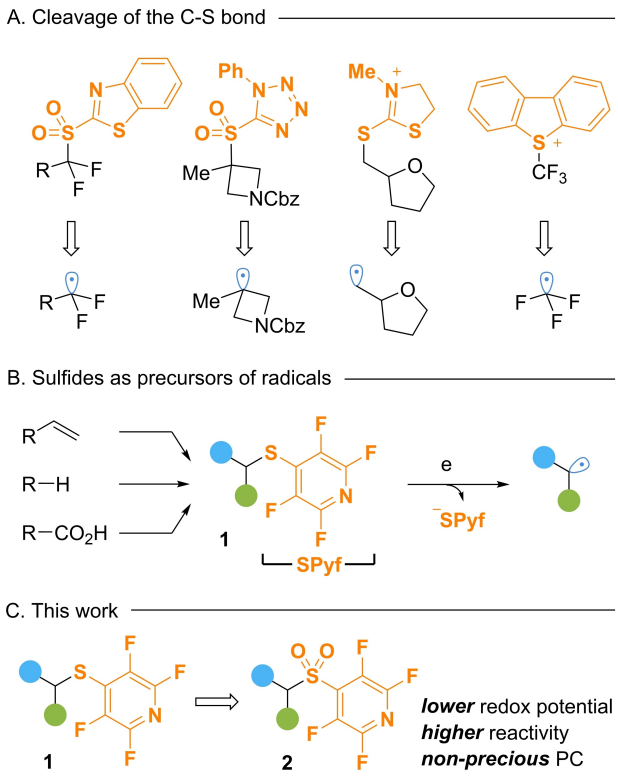
Artem G. Savchenko,[a, b] Mikhail O. Zubkov,[a] Vladimir A. Kokorekin,[a] Jinbo Hu,[c] and Alexander D. Dilman*[a]

A photocatalytic protocol for the reductive coupling of tetrafluoropyridyl-substituted sulfones with α-(trifluoromethyl)styrenes in the presence of zinc and sodium iodide is reported. Sulfones were obtained by oxidation of the corresponding sulfides catalyzed by molybdenum or ruthenium salts. A combination of sulfonyl fragment and electron depleting fluorinated pyridyl group is a key feature determined properties of these sulfones. Their propensity to undergo single electron reduction and to form electron donor-acceptor complexes with *N*-arylamines were evaluated. Plausible pathways of fragmentation of radical anion generated after single electron reduction of sulfones were analyzed, and the pathway leading to the formation of the alkyl radical and the sulfinate anion was found preferable.

Introduction

In recent decades, there has been an explosive growth in the number of new radical processes. Particular attention was focused on photocatalytic mode of radical generation[1] as it circumvents harsh conditions and toxic reagents.[2] Across the plethora of radical precursors, sulfur derivatives occupy a special place.[3] Generation of the alkyl radicals may proceed through single electron oxidation of various anionic substrates such as sulfinates,[4] sulfinamides,[5] thiolates,[6] or xanthogenates.[7] Alternatively, radicals may be formed as a result of reduction of sulfonyl chlorides,[8] sulfones,[9,10] mercaptothiazolinium,[11] and sulfonium[12,13] salts. Sulfones bearing at sulfur a fluoroalkyl and an aromatic (or heteroaromatic) groups selectively generate fluoroalkyl radicals[10] (Scheme 1A). Thus, reductive cleavage of the C–S bond is achieved by utilizing electron deficient nature of the SO_2 or sulfonium-type fragments.

Conventional sulfides are neutral molecules and, as a result, they usually require strong reducing species with potentials, which are beyond the typical photoredox catalysts. Recently, we reported that sulfides **1** derived from pentafluoropyridine can behave as sources of radicals under reductive photoredox conditions (Scheme 1B).[14] The ability of sulfides **1** to undergo single electron reduction is apparently associated with the effect of four fluorine atoms. Indeed, both alkyl and fluoroalkyl radicals were generated by the reduction of these sulfides under photoredox conditions, and the radicals were involved in various reactions. In addition, an important advantage of sulfides **1** is their availability from various feedstocks such as



Scheme 1. Sulfur-based precursors of alkyl radicals.

[a] *A. G. Savchenko, M. O. Zubkov, Dr. V. A. Kokorekin, Prof. Dr. A. D. Dilman*
N. D. Zelinsky Institute of Organic Chemistry
119991 Moscow, Leninsky prosp. 47 (Russian Federation)
E-mail: adil25@mail.ru
[b] *A. G. Savchenko*
Department of Chemistry
Moscow State University
119991 Moscow, Leninskie Gory 1–3 (Russian Federation)
[c] *Prof. Dr. J. Hu*
Key Laboratory of Organofluorine Chemistry, Center for Excellence in Molecular Synthesis
Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences
200032 Shanghai, 345 Ling-Ling Road (China)

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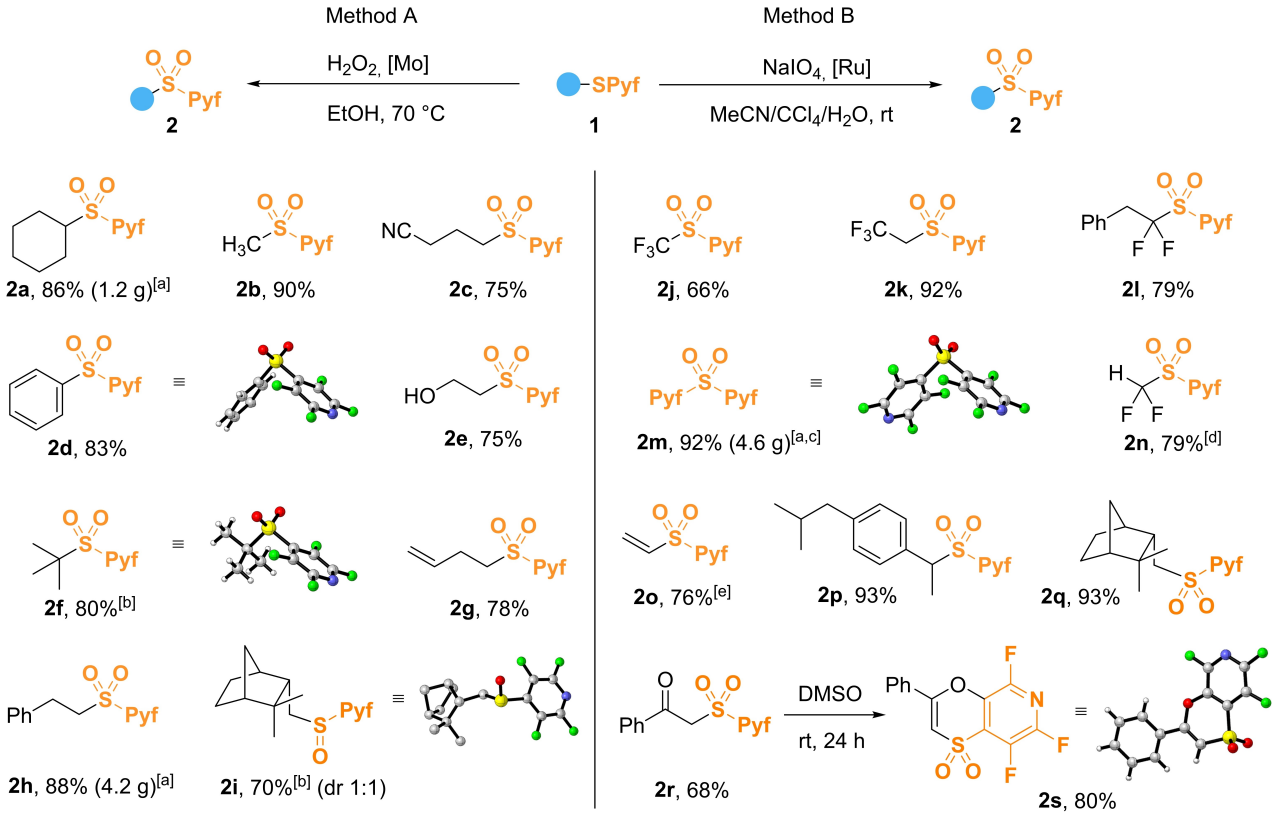
alkenes,[14a] alkanes,[14b] and carboxylic acids.[14f] Nevertheless, activity of these sulfides is not sufficient for performing some processes. For this reason, we decided to investigate corresponding sulfones **2**, which are expected to have lower reduction potential compared to that of sulfides **1** (Scheme 1C). The latter circumstance would also allow to use as photocatalysts more readily available organic dyes compared to precious iridium complexes.

α-(Trifluoromethyl)styrenes are known to serve as efficient acceptors of radicals under photocatalytic conditions.[15,16] However, our attempts to involve sulfides **1** in reaction with these substrates were unsuccessful. Herein, we report that sulfones **2** can be used as efficient reagent in photocatalytic coupling reactions using α-(trifluoromethyl)styrenes as radical traps.

Results and Discussion

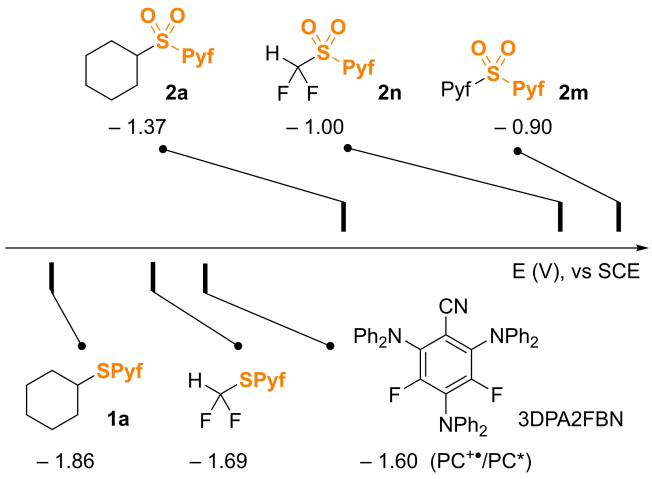
First, oxidation of sulfides **1** to sulfones **2** was investigated (Scheme 2). Alkyl sulfides **1** were readily oxidized with hydrogen peroxide and ammonium heptamolybdate as catalyst[17] (Method A). The reaction proceeds in ethanol for 3 hours at 70 °C and tolerates various functionalities such as nitrile (**2c**) and hydroxyl (**2e**) groups, as well as double bond (**2g**). The reaction of *tert*-butyl-substituted sulfide **1f** under standard conditions gave low yield of the product, presumably due to its decomposition. Fortunately, the desired product **2f** was successfully obtained at room temperature after over two days. Fluoroalkyl sulfides required stronger oxidation conditions involving sodium periodate and ruthenium (III) chloride as a catalyst[18] (Method B). Compound **2p** from the sulfide originating from Ibuprofen was also prepared in good yield. Structures of **2d**, **2f**, and **2m** were supported by X-ray diffraction analysis. Finally, sulfones **2a**, **2h**, **2m** were obtained on a gram scale and isolated by simple recrystallization. Camphene derived sulfide **1i** reacted at room temperature by Method A affording sulfoxide **2i** in 70% yield as a mixture of isomers, but the corresponding sulfone **2q** was synthesized in good yield by Method B. Another curious observation is a relative instability of sulfone **2r**, derived from α-bromoacetophenone. Although it is stable for days in chloroform, dichloromethane, and ethyl acetate, it undergoes S_NAr cyclization to compound **2s** without any additives in dimethylsulfoxide for 1 day at room temperature. Alternatively, this cyclization proceeds in the presence of triethylamine in dichloromethane. Overall, this sequence of transformations provides access to the formal annulation of α-bromoacetophenone leading to the oxidized thiaflavone core.

Next, we evaluated the reduction potentials of the sulfones **2** and compared them with previously reported data for sulfides **1**.[14b,c] Cyclic voltammetric studies revealed a strong increase in reduction potential from S(II) compounds to their S(VI) counter-



Scheme 2. Synthesis of sulfones **2**. Reaction conditions: Method A, **1** (2 mmol), aq. H_2O_2 (8 mmol), $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (0.5 mol%), and EtOH (1 mL) at 70 °C for 3 h; Method B, **1** (2 mmol), $NaIO_4$ (5 mmol), $RuCl_3$ (1.0 mol%), and $CH_3CN/CCl_4/H_2O$ (1 : 1 : 2, 4 mL) at 25 °C for 3 h. [a] Gram-scale reaction. [b] 2 days, 25 °C. [c] 30 h, 60 °C. [d] From fluoroalkylsilane Me_3SiCF_2SPyf. [e] From $ClCH_2CH_2SPyf$; 15 h, then K_2CO_3 was added.

parts (Scheme 3). For instance, the reduction potential of Cy-SO_2Pyf **2a** (−1.37 V vs SCE, DMSO) is 0.5 V higher than the potential of Cy-SPyf **1a** (−1.86 V vs SCE, DMSO). In the case of difluoromethyl derivatives, the potential of the sulfone (−1.00 V vs SCE, DMSO) is even 0.7 V higher than the potential of the corresponding sulfide (−1.69 V vs SCE, DMSO). Diarylated sulfone **2m** demonstrated an exceptionally low reduction potential of −0.9 V vs SCE (in DMSO) comparable with some cationic compounds such as Katrizky salts.[2a] Considering 3DPA2FBN as a typical organic photocatalyst[19] it may be expected that the single electron transfer (SET) between the excited state photocatalyst and alkyl sulfone **2a** would be highly favorable.



Scheme 3. Redox potentials.

To evaluate the reactivity of sulfones **2**, we performed the photoredox reaction with α-(trifluoromethyl)styrenes **3**. Compounds **2a** and **3a** were selected as model substrates and their coupling was performed using 3DPA2FBN as a photocatalyst (Table 1). Zinc dust was used as a stoichiometric reductant in combination with sodium iodide in acetonitrile, and the reaction was irradiated with 60 W blue light-emitting diodes (LEDs) at room temperature, and these conditions provided difluorostyrene **4a** in 25% yield (entry 1). The iodide additive serves as activator of zinc surface,[20] and it turned out to be critical for the reaction to proceed (entry 2). Screening of photocatalysts (entries 3–5), reductants (entries 6–8), and iodide sources (entries 9–10) suggested that 3DPA2FBN, zinc, and sodium iodide are optimal reagents. Subsequent solvent optimization revealed that DMSO is required for the reaction efficiency (entries 11–14). Finally, switching to sulfone excess and decreasing its concentration provided **4a** in 65% isolated yield (entry 17). In accordance with our preliminary observations, sulfide **1a** remains unreactive under optimal conditions (entry 18). When the reaction was set up in the air atmosphere with further irradiation in a closed test tube, there was no deleterious effect to the product yield (entry 19). However, the presence of water reduced the yield of **4a** to 56% (entry 20).

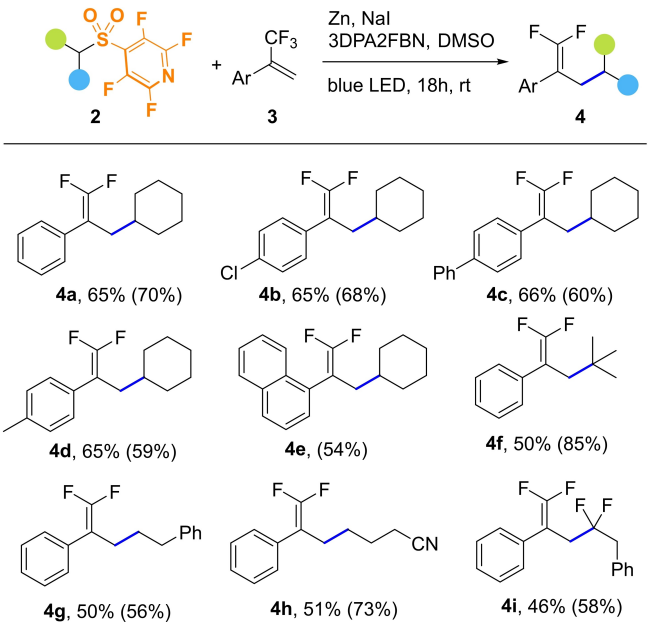
Under the optimized conditions, we explored the scope of the reaction (Scheme 4). Products bearing chloride (**4b**), phenyl (**4c**), and methyl (**4d**) groups were successfully obtained. In reaction of *ortho*-substituted α-naphthyl styrene **3e**, incomplete conversion was observed affording product **4e** in 54%

Table 1. Optimization studies.

2a **3a** (1.2 equiv) **4a**

Entry	Deviation	Yield [%][a]
1	None	25
2	without NaI	0
3	*fac*-Ir(ppy)$_3$ as photocatalyst	10
4	4CzIPN as photocatalyst	14
5	Benzophenothiazine as photocatalyst	10
6	DIPEA instead of Zn/NaI	0
7	Hantzsch ester instead of Zn/NaI	9
8	Mn instead of Zn	0
9	LiI instead of NaI	4
10	TBAI instead of NaI	0
11	DMF as solvent	22
12	DMA as solvent	11
13	DMSO as solvent	34
14	$PhCF_3$ as solvent	0
15	**2a** (3 equiv), Zn/NaI (6 equiv), DMSO (1 mL)	31
16	**2a** (3 equiv), Zn/NaI (6 equiv), DMSO (2 mL)	53
17	**2a** (2.5 equiv), Zn/NaI (5 equiv), DMSO (10 mL)	70 (65)[b]
18	Entry 17, **1a** instead of **2a**	6
19	Entry 17, without degasing	70
20	Entry 17, with H_2O (10 equiv)	56

[a] Determined by ^{19}F NMR using $PhCF_3$ as internal standard. [b] Isolated yield.



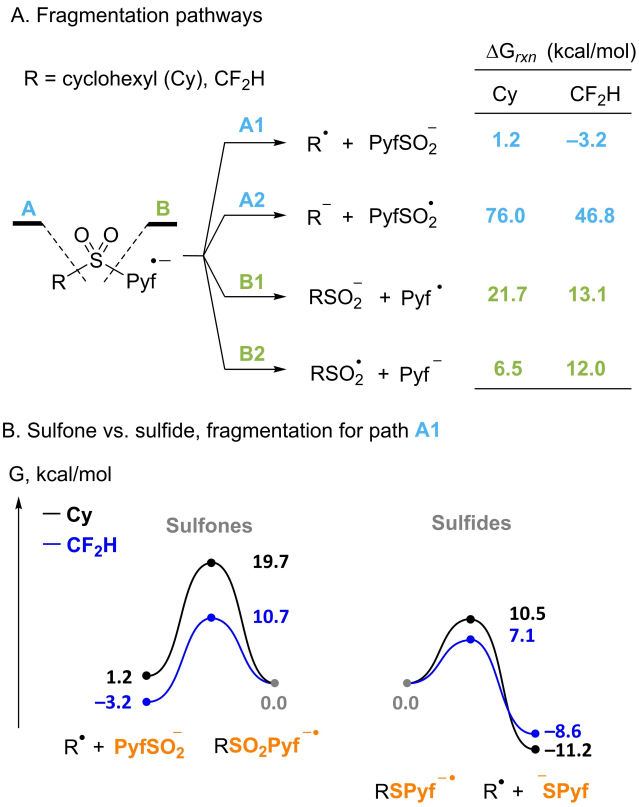
Scheme 4. Reaction of sulfones **2**. Reaction conditions: **2** (0.75 mmol), **3** (0.3 mmol), zinc (1.5 mmol), NaI (1.5 mmol), 3DPA2FBN (1.0 mol%), DMSO (10 mL), 20 °C, 18 h, 60 W blue LEDs (λ_{max} = 455 nm). Isolated yields are given; in parenthesis yields determined by ^{19}F NMR using $PhCF_3$ as internal standard.

determined by NMR spectroscopy. The reaction works well for sulfones generating primary, secondary and tertiary radicals. Furthermore, *gem*-difluorinated alkyl radical can be successfully generated from the corresponding sulfone affording product **4i**.

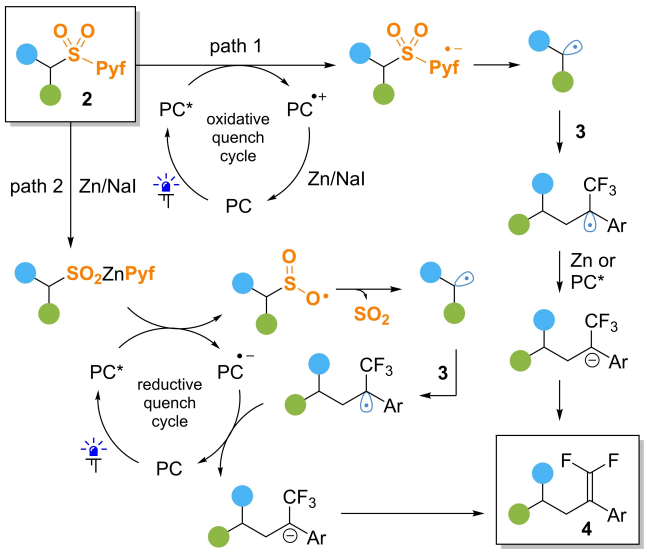
To investigate the energetics of the fragmentation of the radical anion intermediate, we performed DFT calculations for a model sulfone at the ωB97XD/def2TZVP-PCM(DMSO) level of theory. Four possible directions for breaking the C–S bond were considered (Scheme 5A). We found that mesolytic cleavage to alkyl radical and sulfinate anion (path A1) is the most favourable. Apparently, the high electron deficiency of sulfones, which causes their low reduction potentials, also leads to the relative stability of the radical anion itself. Nevertheless, fragmentation of radical anion of **2a** (R = Cy) to sulfinate radical and aryl carbanion (path B2) has free energy of only +6.5 kcal/mol, and still may be operative through subsequent stabilization due to organozinc formation. Other fragmentation pathways have been ruled out as too endergonic. For path A1, transition state free energies for difluoromethyl and cyclohexyl sulfones were calculated, and they were compared with those for ananlogous sulfides (Scheme 5B). These data suggest that fluoroalkyl radical is formed faster than secondary alkyl radical. This may be associated with a combination of factors often referred to as "fluorine effect",[21] reflecting electron accepting character of the fluorine atom and destabilizing interactions of the lone pairs. The radical anions from sulfones are less reactive than those from sulfides, probably due to greater stabilization of negative charge in sulfones and steric repulsion in the corresponding transition states. Apperently, the observed decreased reactivity of the sulfides is associated with ineffective step of their single electron reduction.

Based on these calculations, two reaction pathways can be proposed (Scheme 6). The first mechanistic scenario (path 1) involves the oxidative quench of the photocatalyst excited state ($E_{1/2}(PC^{+\bullet}/PC^*) = -1.60$ V vs SCE) by the sulfone **2**. It should be noted that zinc or iodide anion can be oxidized by the photocatalyst, generating a more reducing species ($E_{1/2}(PC/PC^{-\bullet}) = -1.92$ V vs SCE).[19] However, the inactivity of TBAI in the reaction (Table 1, entry 10) suggests that the role of iodide is not in the quenching, but in the activation of metallic zinc.[20] Then, the sulfone anion radical would undergo mesolytic cleavage to form alkyl radical and sulfinate anion. The resulting radical could be trapped by α-(trifluoromethyl)styrene **3** to form benzyl radical, which undergoes reduction (by zinc or photocatalyst) with subsequent β-elimination of the fluoride anion. Despite the fact that zinc is a weaker reducing agent ($E_{1/2}(Zn^{2+}/Zn) = -1.00$ V vs SCE)[22] than the excited photocatalyst, direct formation of organozinc reagent from the sulfones can be assumed (path 2).[23] In this case, further transformation can be considered as electro-neutral interaction of alkylsulfinate and α-(trifluoromethyl)styrene via photocatalytic cycle involving oxidative quenching of the photocatalyst.[24] While oxidation of the sulfinate salts is a facile process,[4b,c] the efficiency of subsequent SO_2 release depends on the nature of the alkyl group and is favored for fluorinated fragments,[25] though the metal counterion may also affect the efficiency of radical generation.[4b]

To shed more light on the reaction mechanism, we followed the fate of the sulfinate anion formed during the reduction of the sulfone. To our surprise, 2,3,5,6-tetrafluoropyridine was clearly detected by ^{19}F NMR as the main fluorinated by-product in the reaction mixture. Indeed, the amount of tetrafluoropyridine after reaction was always greater than the amount of the



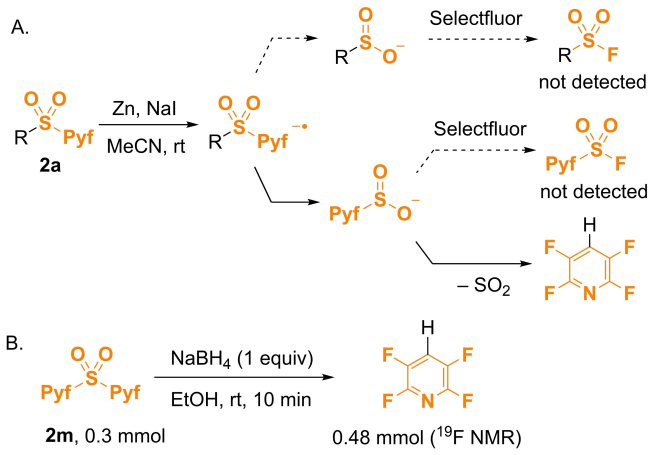
Scheme 5. Calculations of fragmentation step.



Scheme 6. Proposed mechanism.

target product and it was a significant part of the sulfone conversion.

From another experiment, we found that sulfone **2a** slightly converted to tetrafluoropyridine even with zinc and sodium iodide as the only reagents (Scheme 7A). However, an attempt to detect any sulfinates in the reaction by treating the filtrate with excess of Selectfluor failed (no signals in 40–80 ppm area of ^{19}F NMR spectrum for the expected sulfonyl fluoride). Finally, the reaction of diaryl sulfone **2m** (0.3 mmol) with sodium borohydride in ethanol provided 0.48 mmol of tetrafluoropyridine (Scheme 7B).[26] We believe that these observations indicate the instability of the perfluorinated sulfinate anion and the release of sulfur dioxide,[27] similar to perfluorobenzoate protodecarboxylation.[28] On the other hand, tetrafluoropyridine can be formed by protonation of the organozinc reagent. Thus, at the present stage, we cannot to definitively conclude which of these two pathways are operative.

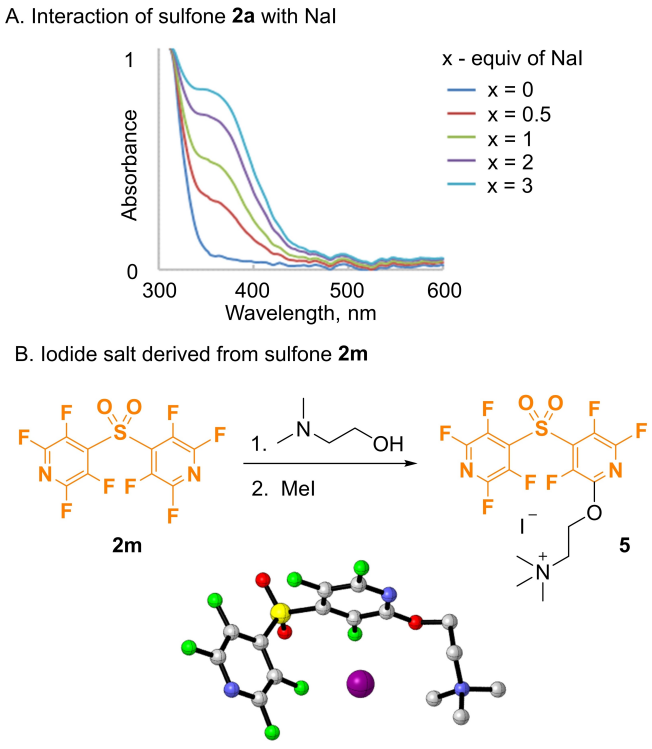


Scheme 7. Sulfinate detection studies.

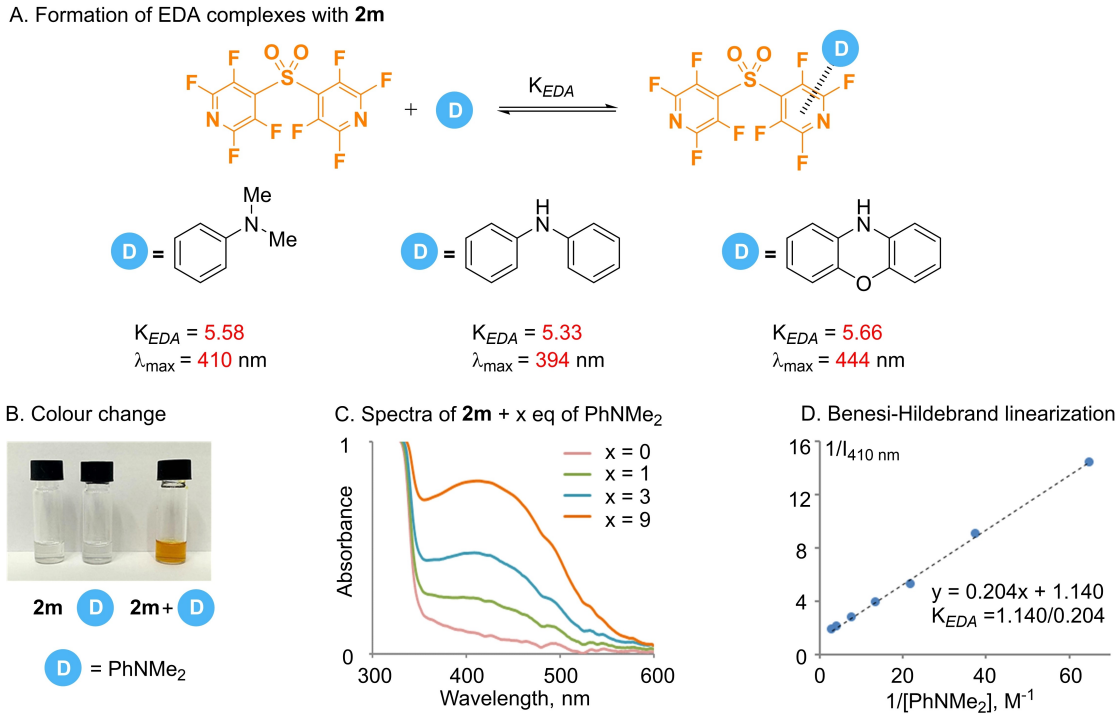
The presence of electron donor-acceptor (EDA) complexes with iodide anion in the reaction could be hypothesized.[29] Indeed, cyclohexyl sulfone **2a** gave a slight yellow color with sodium iodide, clearly detectable spectrophotometrically (Scheme 8A). Such interaction often accompanies light-promoted iodination reactions.[30] To clarify this possibility, we tried to carry out the reaction of the sulfonyl/iodide exchange in **2a** under blue light irradiation, but no traces of cyclohexyl iodide were detected.

Recently, we studied the EDA complex in SPyf-containing ammonium salt with iodide counterion.[30b] X-Ray diffraction indicated a presence of a weak binding between sulfur atom and iodide anion. We were interested in whether iodide anion has short contacts with sulfone **2**, as direct sulfur/iodide contact is hindered. For this purpose, we synthesized iodide salt **5** derived from sulfone **2m** to observe intermolecular interactions in solid state (Scheme 8B). However, X-ray diffraction analysis showed no short contacts between the iodide and other non-hydrogen atoms. For instance, the shortest distances were 3.65 Å, 3.77 Å, and 3.77 Å (for I…F, I…N, and I…C, respectively), which are longer than the corresponding sums of van der Waals radii (3.45 Å, 3.53 Å, and 3.68 Å, respectively).[31] Nevertheless, this does not exclude EDA formation in solution, as is evident from the yellow color of solutions of salt **5**.

In addition to EDA complexes with iodide, complexes between sulfones and photocatalyst can be assumed. However, the study of such complexes with 3DPA2FBN by spectrophotometry is hindered due to its poor solubility and strong coloring. Instead, we employed amines (such as diphenylamine) having a donor fragment of this cyanoarene catalyst. To avoid overlapping of absorption bands (see Scheme 8A), we also chose more electron deficient diaryl sulfone **2m** instead of **2a** as the acceptor component (Scheme 9A). Indeed, donor-acceptor complexes were formed when **2m** was combined with various aromatic amines, as follows from the instant coloration when colorless solutions are mixed (Scheme 9B). The color varies from yellow to red depending on the nature of the amine. Three EDA complexes with *N*,*N*-dimethylaniline, diphenylamine, and phenoxazine were experimentally quantified. All of these interactions are favorable with $K_a = 5–6\ M^{-1}$ according to the Benesi-Hildebrand method (Scheme 9C–D), which corresponds to the Gibbs free energy of −1.0 kcal/mol. Although we have not been able to grow a cocrystal for these complexes, we can assume that this interaction has a stacking origin with slip-stacked geometry, as reported earlier.[32] Such interaction may also contribute to the SET event with photocatalyst 3DPA2FBN, which structure contains diphenylamino fragment.



Scheme 8. EDA complexes with iodide anion.



Scheme 9. Observation of EDA complexes.

Conclusion

In summary, the first efficient protocol for the catalytic defluorinative coupling of alkyl sulfones and α-(trifluoromethyl)styrenes under visible light conditions is described. This was realized with the aid of sulfonyl fragment bearing strongly electron deficient tetrafluoropyridine group. The conversion of sulfides to sulfones results in significant decrease of reduction potential, thereby increasing the reactivity under photoredox conditions and allowing to apply available organic photocatalyst. Theoretical treatment suggested the preferred pathway of fragmentation of the radical anion formed after single electron reduction of the sulfones. The electron depleting nature of the tetrafluoropyridine fragment led to the observation of EDA complexes of the sulfones with a series of amines.

Experimental Section

Synthesis of sulfones (Method A, General Procedure I)

Sulfide **1** (1.0 equiv., 2.0 mmol), ammonium heptamolybdate tetrahydrate (0.5 mol.%, 12.4 mg), ethanol (1 mL), and 30% hydrogen peroxide (4.0 equiv., 8 mmol, 0.82 mL) were successively added into a 5 mL tube containing a stirring bar under air atmosphere. The tube was closed with a screw-cap and placed in a preheated oil bath (70 °C) and stirred for 3 hours (or 48 hours at room temperature for **2f**). The reaction mixture was cooled to room temperature, diluted with water (10 mL) and extracted with dichloromethane (3×10 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel.

Synthesis of sulfones (Method B, General Procedure II)

Sulfide **1** (1.0 equiv., 2.0 mmol), sodium periodate (2.5 equiv., 5.0 mmol, 1.07 g) and ruthenium trichloride hydrate (1 mol.%, 4.5 mg) were successively added into a 10 mL flask containing a mixture of acetonitrile (1 mL), tetrachloromethane (1 mL) and water (2 mL). The solution was vigorously stirred for 3 hours at room temperature and then extracted with dichloromethane (3×15 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel.

Photoredox reaction of sulfones (General procedure III)

A 20 mL test tube containing a stirring bar, dry sodium iodide (5.0 equiv., 1.5 mmol, 225 mg), zinc (5.0 equiv., 1.5 mmol, 98 mg), sulfone **2** (2.5 equiv., 0.75 mmol) and 3DPA2FBN (1 mol%, 1.9 mg) was evacuated and filled with argon. Then, dimethyl sulfoxide (10 mL) and α-(trifluoromethyl)-styrene **3** (1.0 equiv., 0.3 mmol) were added. The tube was closed and irradiated with 455 nm LED chip (60 W) for 18 hours at 20 °C. For the work-up, the mixture was diluted with water (30 mL) and 1 M HCl (10 mL) and extracted with dichloromethane (3×10 mL). The combined organic layers were filtered through Na_2SO_4, concentrated under reduced pressure, and the residue was purified by column chromatography on silica gel.

X-ray crystallography

Deposition Numbers 2253695 (**2d**), 2253700 (**2f**), 2253702 (**2i**), 2253703 (**2m**), 2253704 (**2s**) and 2253701 (**5**) contain the supplementary crystallographic data for this paper. Access Structures service.

Acknowledgements

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Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: fluorine · photocatalysis · radicals · sulfones · visible light

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