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One-step Oxidative Monofluorination of Electron-deficient Sulfoxides to Access Highly Lewis Acidic Sulfur(VI) Cations

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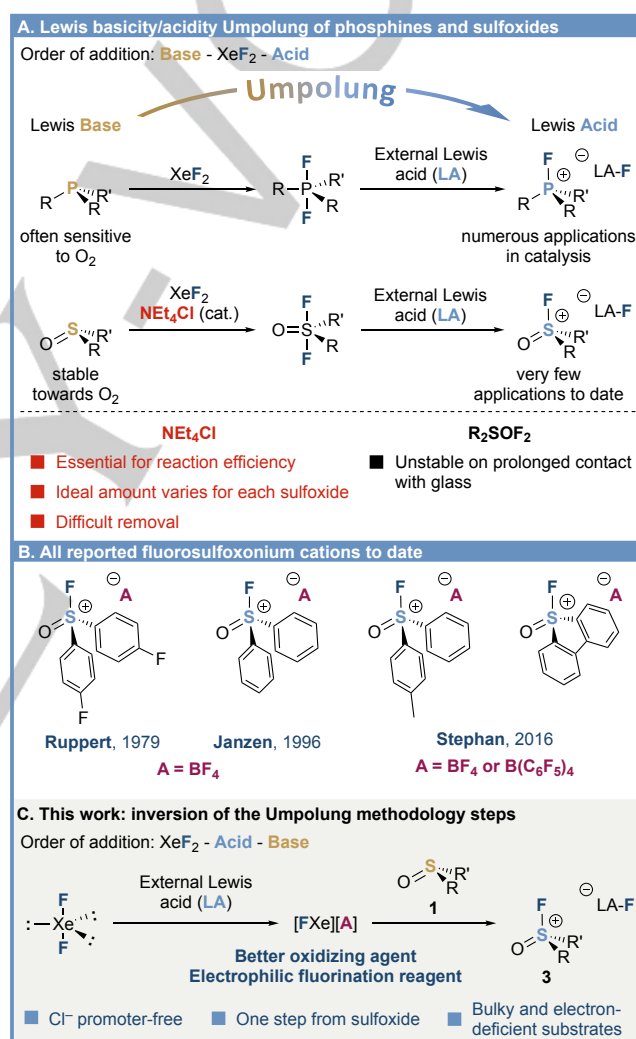
Abstract: The strongly oxidizing, powerful electrophilic fluorination reagent $[\text{FXe}][\text{OTf}]$ is shown to effect direct oxidative monofluorination of sulfoxides. This one-step, chloride promoter-free methodology provides access to so far inaccessible, yet highly desirable strongly Lewis acidic fluorosulfoxonium cations from electron-deficient and/or sterically demanding sulfoxides that are shown to be practically unreactive towards the previously reported $\text{XeF}_2/\text{NEt}_4\text{Cl}$ system. Experimental and density functional theory studies have been conducted to assess the Lewis acidities of the prepared sulfur(VI) cations. Preliminary results obtained with chiral sulfoxides provide early insights into the mechanism of these fluorination reactions.

Introduction

Since the advent of Frustrated Lewis Pairs (FLP),^[1] much attention has been drawn to the development of non-metallic highly electron-deficient species, mainly based on boron, but group 14 Lewis acids based on carbon or silicon also continue to garner much attention.^[2]

In the last decade, Stephan and coworkers shed light on the potential of organophosphorus compounds to act as Lewis acids after inversion of their traditional Lewis basic behavior. To this end, they described the oxidative difluorination of phosphines using XeF_2 , followed by fluoride abstraction from the resulting R_3PF_2 by an external Lewis acid such as $[\text{Et}_3\text{Si}\cdot\text{C}_7\text{H}_8][\text{B}(\text{C}_6\text{F}_5)_4]$, to afford the fluorophosphonium cations R_3PF^+ (Scheme 1A).^[3] These species have since emerged as powerful Lewis acidic organocatalysts for many applications, including the challenging hydrodefluorination of fluoroalkanes.^[4] Since Stephan's pioneering work, several reports have described alternative strategies to access fluorophosphonium cations,^[5,6] and more generally, extensive research has been dedicated to the synthesis of highly Lewis acidic phosphorus cations^[7]. This methodology represents a formal "Umpolung" of the Lewis basic character of the phosphorus atom in phosphines, that eventually exhibits Lewis acidic character and unique reactivity.^[4b]

The same Umpolung strategy can be applied to Lewis basic sulfoxides **1** to access sulfur(VI) Lewis acidic cations. In 1979, Ruppert described the reaction of sulfoxides R_2SO with F_2 ,^[8] but they also react with XeF_2 in the presence of chloride ions to give the corresponding difluorosulfurane oxides R_2SOF_2 **2**.^[9] Subsequent fluoride abstraction with an external Lewis acid affords the desired fluorosulfoxonium cations R_2SOF^+ **3**, which were used by Stephan and co-workers ($\text{R} = \text{Ph}$, **3a**) as efficient Lewis acid catalysts for the hydroarylation and hydrothiolation of alkenes or the polymerization of THF.^[10]



Scheme 1. Our strategy to access sulfur(VI) cations and its scientific context.

In fact, only our own recent contribution on the use of the fluorosulfoxonium salt $[\text{Ph}_2\text{SOF}][\text{B}(\text{C}_6\text{F}_5)_4]$ **3a** $[\text{B}(\text{C}_6\text{F}_5)_4]$ for the annulation of strained cycloalkanes^[11] has appeared since Stephan's pioneering work in 2016 (Scheme 1B).^[12] In the present report, we would like to expose and address the reasons why we believe fluorosulfoxonium cations have been granted little interest compared to their phosphorus counterpart. These reasons include a) the necessary use of a catalytic amount of chloride ions as promoters for the reaction of sulfoxides with

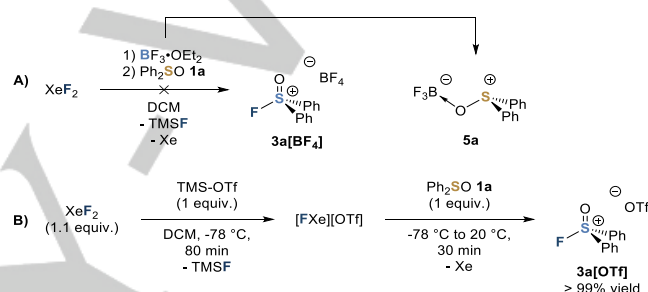
XeF₂ to proceed smoothly, b) the necessity of fine-tuning the amount of chloride promoter required for each new sulfoxide and the yield-affecting removal of this promoter at the end of the sequence, c) the degradation of the R₂SOF₂ intermediate on prolonged contact with glass (**Scheme 1 A**). Herein, the inversion of the steps of the previously described Umpolung methodology is shown to avoid the sensitive R₂SOF₂ intermediate and to afford the direct mono-fluorination of sulfoxides in a chloride promoter-free manner, *via* their reaction with an *in situ* generated fluoroxenonium cation.

Results and Discussion

In parallel with our recent study uncovering further reactivity of the salt [Ph₂SO][B(C₆F₅)₄],^[11] we were interested in the preparation of fluorosulfoxonium cations based on electron-deficient sulfoxides and their study as conceivably stronger Lewis acid catalysts. Whereas the reaction of Ph₂SO with XeF₂ is greatly facilitated by the addition of substoichiometric NEt₄Cl,^[9–10] we found that the conversion of the sulfoxide **1g** bearing bis(3,5-trifluoromethyl)phenyl groups was much less straightforward. Indeed, only about 10% was converted to the desired difluorosulfurane oxide after 49 h without significant change in the next 70 h when using 5 mol% NEt₄Cl (see SI for details). Drastically increasing the chloride mediator loading to 50 mol% afforded 69% of **2g** after 15 h, and further addition of XeF₂ led to a satisfying 93% conversion after a total of 22 h. Similarly, at least 15 mol% NEt₄Cl and 3 h were required to quantitatively transform the axially chiral biphenyl sulfoxide **1m**^[13] into the corresponding difluorosulfurane oxide. While the next reaction of the R₂SOF₂ products with BF₃·OEt₂ or [Et₃Si·C₇H₈][B(C₆F₅)₄] did not seem to be influenced by the nature of the starting sulfoxide, the purification of the R₂SOF₂ or [R₂SOF][A] (A = anion) products also proved difficult, as traces of the ammonium chloride promoter can only be removed by several rounds of recrystallisation, rendering this process even more tedious when a higher loading was used. We therefore sought an alternative strategy to access fluorosulfoxonium cations from electron-deficient and/or bulkier sulfoxides.

The structural similarity between difluorosulfurane oxides R₂SOF₂ and XeF₂ —i.e., their trigonal bipyramid geometry with the fluorine ligands occupying the apical positions— prompted us to explore the reaction of the latter with fluoride ion acceptors i.e., Lewis acids, in a similar logic to the previously described Umpolung methodology. The reaction of XeF₂ with Brønsted or Lewis acids has first been studied more than 50 years ago,^[14] and would lead to the polarization of the Xe-F bond, up to the point of complete dissociation and formation of the fluoroxenonium cation XeF⁺.^[15] The reactivity of fluoroxenonium salts has been studied for the functionalization of alkenes or the access to hypervalent iodine reagents, among others.^[16] Notably, the fluoroxenonium salts [FXe][AsF₆] and [FXe][SbF₆] have been used for the direct fluorination of alkylsulfides and 1,3-dithietanes to deliver the corresponding fluorosulfonium salts.^[17] This strategy failed to afford the direct fluorination of DMSO or its perfluorinated analog (F₃C)₂SO.^[18] We were nevertheless interested in the potential of fluoroxenonium salts as strong oxidants and electrophilic fluorination reagents for the direct conversion of sulfoxides into fluorosulfoxonium salts.

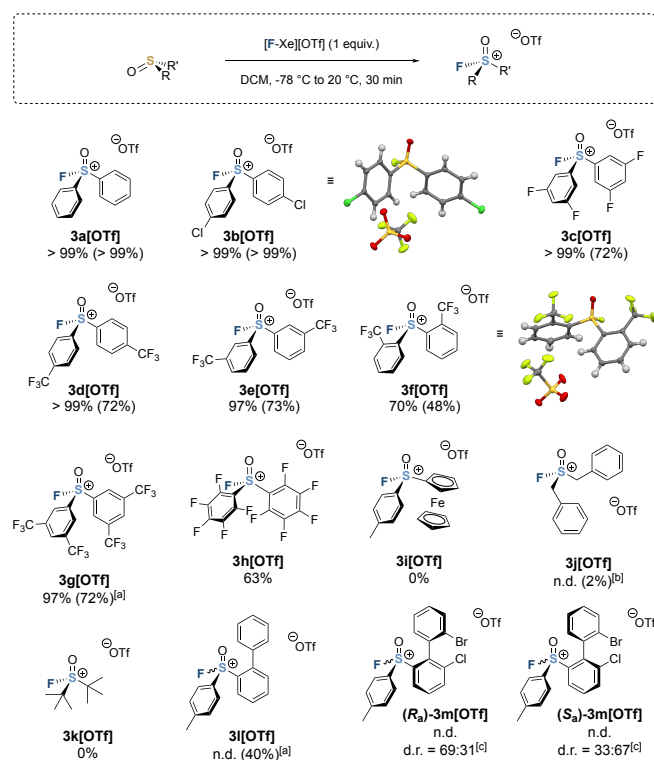
Treatment of XeF₂ with one equivalent BF₃·OEt₂ and subsequent reaction with Ph₂SO **1a** invariably afforded a coordination complex between BF₃ and the Lewis basic sulfoxide (**Scheme 2A**), with no evidence for oxidation of the latter (neither the fluorosulfoxonium cation nor its hydrolysis product Ph₂SO₂ could be detected). We attributed this lack of reactivity with BF₃·OEt₂ to the unfavored dissociation of XeF₂ under our reaction conditions.^[19] To our delight, however, the addition of one equivalent TMS-OTf to a cold suspension of XeF₂ smoothly generated the fluoroxenonium salt [FXe][OTf], as demonstrated by the ensuing reaction with **1a**, which gave **3a[OTf]** as the major product. Rapid optimization of the reaction (see Supporting Information for details) led us to generate [FXe][OTf] by reacting a small excess XeF₂ (1.1 equiv.) with TMS-OTf (1 equiv.) in -78 °C cold DCM for 80 min, before adding the resulting mixture to a solution of the sulfoxide (**Scheme 2B**). This gave the pure fluorosulfoxonium salt **3a[OTf]** quantitatively by simple evaporation of the solvent.



Scheme 2. A) Reaction of XeF₂ with BF₃·OEt₂ and Ph₂SO **1a**, leading to the exclusive formation of coordination complex **5a**. B) Optimized reaction conditions for the formation of [FXe][OTf] and subsequent reaction with **1a**, affording **[3a][OTf]** quantitatively.

Since the nature of the counterion can have a dramatic impact on the reactivity of p-block cations in catalysis,^[20] we have shown that **3a[OTf]** can be transformed into **3a[B(C₆F₅)₄]** via simple anion metathesis with excellent yield (see Supporting Information).

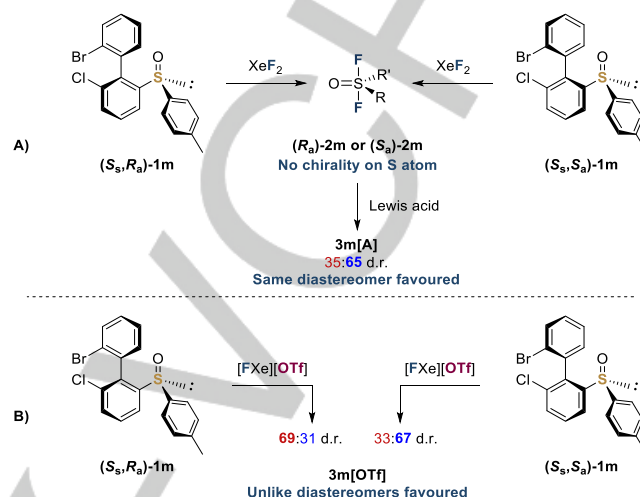
Next, we investigated the scope of sulfoxides in this electrophilic fluorination strategy. Symmetrical diaryl sulfoxides bearing 4-chloro, 3,5-difluoro, 3- or 4-trifluoromethyl groups on the arene rings (**1b–1e**) were quantitatively converted, and the desired fluorosulfoxonium triflates were isolated with good to excellent yields (72–99%). Sulfoxide **1f** possessing 2-trifluoromethylphenyl groups could not be fully converted, as reflected in the lower 48% isolated yield of salt **3f[OTf]**. This could be explained by the high steric hindrance around the sulfur center, considerably slowing down the process. Even the highly electron-deficient sulfoxide **1g** carrying 3,5-bis(trifluoromethyl)phenyl groups was almost fully converted, giving **3g[OTf]** with 72% isolated yield. Bis(pentafluorophenyl) sulfoxide **1h** instantaneously gave a colorless precipitate which gradually turned into a brown oil upon removal of the solvent under vacuum or after repeated washings with DCM. ¹⁹F-NMR analysis of this poorly soluble solid revealed the presence of a quintet at +48.4 ppm (*J* = 33.5 Hz) along with the expected signals for the pentafluorophenyl groups.^[21] Nevertheless, this new compound **3h[OTf]** is of particular interest because of its high (computed) Lewis acidity, as reported by Stephan et al.^[22]



Scheme 3. Conversion of sulfoxides into fluorosulfoxonium triflates using [F-Xe][OTf]. Isolated yields are given in parentheses when applicable. [a] 2.5/1 mixture with the corresponding sulfone. [b] NMR yield determined using *p*-TolSO₂F as internal standard. [c] Determined by ¹H and ¹⁹F NMR. See Supporting Information for details about the obtained crystallographic structures.^[30]

Ferrocenyl *p*-tolyl sulfoxide **1i** reacted quantitatively, giving a dark green mixture of intractable products, which we attribute to a chemoselective Fe(II) to Fe(III) oxidation.^[23] Similar results were obtained when reacting **1i** with XeF₂. Dibenzyl sulfoxide **1j** gave a complicated mixture of products as well, which could potentially be attributed to a fluoro-Pummerer rearrangement known to occur with sulfoxides bearing α -hydrogens.^[24] Nevertheless, a small triplet at +50.9 ppm ($J = 3.4$ Hz) was observed in the ¹⁹F-NMR spectrum, presumably corresponding to the desired salt **3j[OTf]**. Di-*tert*-butyl sulfoxide **1k**, although quantitatively converted under these conditions, gave no trace of any detectable fluorosulfoxonium product. Biphenyl-2-yl *p*-tolyl sulfoxide **1l**, as well as the two diastereomers of axially chiral sulfoxide **1m** gave mixtures that were difficult to analyze. Nevertheless, we noted the formation of a mixture of diastereomers in the case of diastereopure **1m**. This is to be expected when the classical Umpolung strategy is used, as the chirality of the sulfur center is lost upon difluorination and passage through a trigonal bipyramid geometry; subsequent monodefluorination would result in the same diastereomer (respectively its enantiomer) of **3m** being favored, independently of the initial configuration of the starting sulfoxide (**Scheme 4A**). In our case, however, as the sulfoxide with axial (*R*)

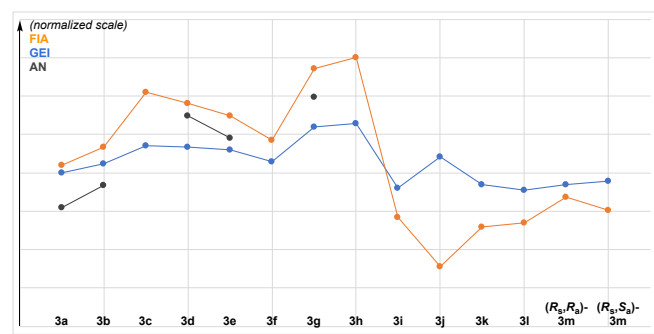
configuration and the one with axial (*S*) configuration led to unidentical relative configurations of the respective major diastereomers of the fluorosulfoxonium, with practically identical d.r., the diastereomeric preference is clearly dictated by the initial relative configuration of **1m**, thus indicating a certain degree of substrate control over the final stereochemistry (**Scheme 4B**).



Scheme 4. A) Conversion of each diastereomer of sulfoxide **1m** into **3m** using the previously described Umpolung method, giving the same diastereomeric preference because of passage through enantiomeric **2m**, which is non-stereogenic at sulfur. B) Direct conversion of each diastereomer of sulfoxide **1m** into **3m** using the method described herein, favoring opposite sets of diastereomers of **3m**.

To assess the Lewis acidity of the newly prepared fluorosulfoxonium cations bearing electron-withdrawing groups, their fluoride ion affinities (FIAs)^[25] and global electrophilicity indexes (GEIs)^[26] were computed at the MP2/def2-TZVPP/BP86/def2/TZVP level of theory (Table 1). The values obtained for both the FIA and the GEI are generally well correlated and increase in an expected trend for Lewis acids bearing increasingly electron-withdrawing groups (see Supporting Information).

To further probe the strength of these Lewis acids, the Gutmann-Beckett method was employed (Table 1).^[27] In some cases, the expected downfield shift of the Et₃PO resonance in ³¹P-NMR was observed, but in most instances, a fluorine/oxygen exchange was observed when mixing the fluorosulfoxonium salts with about 0.3 to 1 equivalent Et₃PO. This reactivity has already been observed by Stephan and coworkers for fluorosulfoxonium^[10] or fluorophosphonium cations.^[28] The low solubility of most of the fluorinated fluorosulfoxonium salts prevented an accurate description of the system, thus greatly increasing the uncertainty over the obtained numbers. Even though satisfying results could be obtained in certain cases, this is an additional support of previous claims that the Gutmann-Beckett method is not generally suitable to provide accurate Lewis acidities for highly electrophilic fluoro-onium salts.^[29]

Table 1. FIA, GEI and Gutmann-Beckett data for fluorosulfoxonium cations.

Entry	Compound	FIA (kJ/mol)	GEI (eV)	AN ^[a]
1	3a	630.0	3.067	80.9
2	3b	646.8	3.223	86.7
3	3c	679.2	3.697	— ^[b]
4	3d	676.9	3.601	104.9
5	3e	671.6	3.495	99.0
6	3f	650.9	3.283	— ^[b]
7	3g	713.3	3.905	109.8
8	3h	719.5	4.004	— ^[b]
9	3i	602.0	2.612	— ^[c]
10	3j	658.6	2.187	— ^[c]
11	3k	608.9	2.528	— ^[c]
12	3l	598.2	2.566	— ^[c]
13	(R_s,R_a)-3m	608.9	2.787	— ^[c]
14	(R_s,S_a)-3m	614.3	2.672	— ^[c]

[a] The AN was determined on triflate salts **3[OTf]** of fluorosulfoxonium cations. [b] A consistent value could not be obtained due to the low solubility of the Lewis acid. [c] Unavailable data, due to unsuccessful preparation of the product.

Conclusion

In conclusion, we demonstrated the use of the highly reactive [FXe][OTf] reagent to access a variety of fluorosulfoxonium salts from electron-deficient and/or sterically demanding sulfoxides that were shown to be practically unreactive towards the previously reported XeF₂/NEt₄Cl system, in a one-step, chloride promoter-free fashion. This method is expected to unlock the use of strongly Lewis acidic fluorosulfoxonium cations in catalysis. Further investigations into the stereoselectivity and the mechanism of this oxidative monofluorination reaction, catalytic application of the newly prepared sulfur(VI) Lewis acids as well as application of this reversed Umpolung strategy to other Lewis bases are currently ongoing in our laboratory.

Experimental Section

General procedure (GP) for the *in situ* preparation of fluoroxenonium triflate [FXe][OTf] and fluorination of sulfoxides

In an argon-filled glovebox, XeF₂ (1.0 eq., 53 mg, 0.32 mmol) was dissolved in DCM (1.0 mL) in a Schlenk tube. Outside the glovebox, the colourless solution was cooled to -78 °C and TMS-OTf (1.0 eq., 0.050 mL, 0.28 mmol) was added dropwise. The resulting mixture was stirred at -78 °C for 80 min. The freshly prepared fluoroxenonium triflate solution was added *via* cannula to a -78 °C pre-cooled solution of the sulfoxide (1.0 eq., 0.28 mmol) in DCM (0.50 mL). The cooling bath was subsequently removed, and the mixture was stirred at 20 °C for 30–45 min. The volatiles were removed under reduced pressure. Conversions were determined by ¹H NMR at this stage, according to the integration of remaining sulfoxide signals vs product (and possible sulfone) signals. Except for the removal of solvent under reduced pressure, all work-up procedures were carried out in an argon-filled glovebox, and details are given for the isolation of each product. All NMR samples were prepared in J. Young NMR tubes in the glovebox.

Acknowledgements

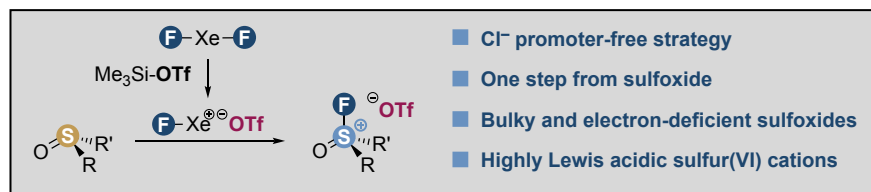
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Keywords: electrophilic fluorination • Lewis acids • sulfoxides • sulfur • Umpolung

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Highly Lewis acidic fluorosulfoxonium cations can be prepared in a one-step, chloride promoter-free fashion from electron-deficient sulfoxides using $[\text{FXe}][\text{OTf}]$. The latter is prepared by reaction of XeF_2 with TMS-OTf , thus representing an inversion of the previously described Umpolung strategy, which failed to convert the same sulfoxides efficiently. The Lewis acidities of the obtained cations have been probed experimentally and computationally.

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