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Reaction of dearomatized heterocycles with sulfur hexafluoride (SF₆) and the pentafluorosulfanyl (SF₅) group

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A Hantzsch ester and other dearomatized heterocycles undergo aromatization in the presence of sulfur hexafluoride (SF₆) upon irradiation with 390 nm LEDs, reducing SF₆ and releasing fluoride ion. Two aryl SF₅ compounds are reduced under the same conditions. No added photocatalyst is necessary for these transformations.

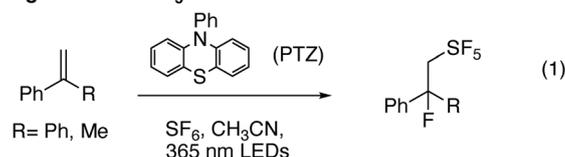
Sulfur hexafluoride (SF₆) and the pentafluorosulfanyl (SF₅) group are highly oxidized sulfur species traditionally thought of as highly unreactive. The pentafluorosulfanyl (SF₅) group is a bulky, electron-withdrawing fluorinated substituent, often described as a super-CF₃ group, similarly chemically robust, but with enhanced electronegativity, lipophilicity, and larger size.¹ While the challenging introduction of the SF₅ group has limited exploration, new introduction protocols are resulting in increasing investigation of the SF₅ group and its chemistry.² As more research groups explore SF₅ groups, unexpected reactivity patterns may emerge, and SF₅ may prove to be an attractive replacement for CF₃ in some molecules as regulatory restrictions around fluorocarbon use grows.

SF₆ is an attractive starting material for SF₅ chemistry, as it is inexpensive, and is non-toxic, compared with more commonly used SF₅ precursors such as SF₅Cl. Processes that consume SF₆ are also of special interest for environmental reasons, as it is used as a dielectric in the electrical industry, despite having a global warming potential over 23 000 times that of CO₂ per unit mass.³ Accordingly, decomposition of surplus SF₆ is of interest, even if SF₅-containing products do not result from the process. SF₆ chemistry has been challenging, despite these attractions, due to its low reactivity. A pioneering example from Beier added SF₅ to styrenes from SF₆ in the presence of TEMPO-lithium in low yield,⁴ while Hoge reported decomposition of SF₆ with weakly-coordinated phenoxides.⁵ The most prominent example of SF₆ functionalization to SF₅ are works from Wagenknecht and Rombach, where phenyl phenothiazine (PTZ) photocatalysts were used to oxidatively add SF₅ to

diphenylethylene, and methylstyrene derivatives (Scheme 1 and eqn (1)).⁶

During the course of our work, a preprint from Wang's group reported conditions using the PTZ catalyst for pentafluorosulfanylation beyond styrene derivatives.⁷ Other processes to consume SF₆ without generating organic SF₅ groups have been reported recently, predominantly using nitrogen and phosphorus compounds. Reduction of SF₆ by N-heterocyclic carbenes,⁸ diaminoethylenes and tetra aminoethylenes,⁹ in some cases stopping at the SF₅ anion have been reported by Braun, Rueping, Kirsch, and Tlili (eqn (2)). Alternatively, Dielmann's group has reported the reduction of SF₆ with electron-rich

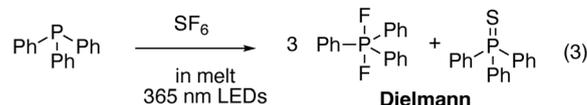
Wagenknecht's SF₅ addition



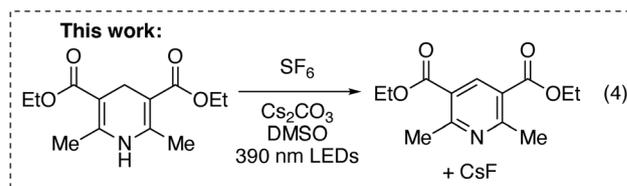
Selected light Pnictogen-compound reactivity with SF₆



Kirsch, Tlili



Dielmann


 Scheme 1 Selected chemistry of SF₆.

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phosphines and irradiated triphenylphosphine (eqn (3)).¹⁰ Our group has also showed metal phosphanides are reactive with SF₆.¹¹ Recent examples of SF₆ consumption also include a series of reactions with photocatalysts using SF₆ as a deoxyfluorination reagent.¹² Dielmann very recently showed even isopropanol can cause an autocatalytic degradation of SF₆ under energetic 280 nm light.¹³

Photoexcited Hantzsch esters and their conjugate bases have been reported as potent reductants without external photocatalysts by various groups for dehalogenations,¹⁴ radical cyclization reactions,¹⁵ and reduction of CF₃ groups.¹⁶ Being interested in SF₆ reactivity, we sought to explore if photoexcited Hantzsch esters and related compounds were reactive with SF₆. The redox potential E_{ox^*} of the photoexcited anion of Hantzsch ester **1a** has been reported by Xu and co-workers as $-3.094\text{ V vs. }Fc^+/Fc$ (Fc = ferrocene) in acetonitrile (MeCN).¹⁶ A potential of $-2.17\text{ V vs. }Fc^+/Fc$ to reduce SF₆ has been measured in MeCN by Goncalves, Magnier, and co-workers, when SF₆ was decomposed electrochemically in a cell at a constant potential of $-2.3\text{ V vs. }Fc^+/Fc$.¹⁷ These values suggest that the photoexcited Hantzsch ester anion is sufficiently reducing to transfer electrons to SF₆.

We observed that Hantzsch ester **1a** was cleanly oxidized to the corresponding pyridine **2a** by SF₆, in MeCN in the presence of base, with attendant formation of a large fluoride signal observed in the ¹⁹F NMR spectrum (Scheme 2). Product **2a** could readily be isolated by hexanes extraction and column chromatography. During the preparation of this manuscript, a pre-print from Rombach and Wagenknecht appeared, showing the pentafluorosulfanylation of alkynes from SF₆ using an iridium phenylpyridine photocatalyst with Hantzsch esters as the terminal reductant, which also leads to **2a**. However, the work reported here is distinct, as no added photocatalyst is required.¹⁸

Both MeCN (entry 1) and toluene (entry 2), gave limited yield of **2a**. Switching to DMSO, in which the Hantzsch ester has greater solubility, led to a more efficient reaction (entry 3). Cesium carbonate was the most efficient base (Entry 3), with potassium carbonate (entry 4) and sodium hydride (entry 5), giving reduced yields. Hypothesizing complete reduction of SF₆ could give as many as six fluorides per equivalent of Hantzsch

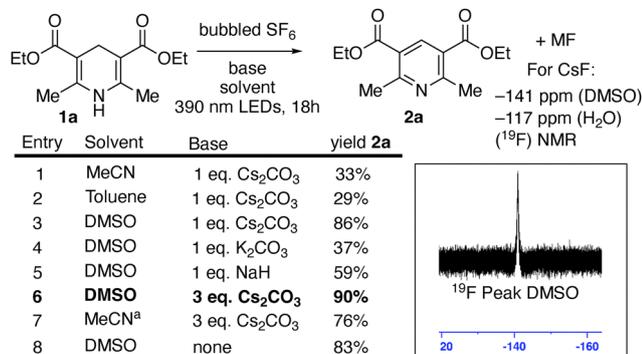
ester, an increase of the amount of base to three equivalents to provide six cesium counterions provided a slight increase in yield of **2a** (entry 6).

We speculated that the high solubility of the Hantzsch ester and moderate solubility of cesium carbonate in DMSO might explain the superiority of the optimal system. While MeCN had not been an ideal solvent in entry 1, conducting the reaction in MeCN under an increased pressure of SF₆ (80 psi), resulted in an increase of the yield of **2a** to 76% (entry 7). Interestingly, the Hantzsch ester was also oxidized by SF₆ in DMSO under irradiation in the absence of base (entry 8). A strong HF peak was observed in ¹⁹F NMR spectroscopy of that crude reaction mixture.¹⁹ The photoexcited neutral Hantzsch ester **1a** has been reported to have $E_{ox^*} = -2.375\text{ V vs. }Fc^+/Fc$ in MeCN, corroborating the feasibility of this electron transfer.¹⁶ While the isolated yield of **2a** was slightly lower than with three equivalents of cesium carbonate, it was superior to the yields obtained in entries 5 and 6, where alternate bases were explored. We explored the reaction of other dearomatized compounds (Scheme 3). More hindered and less reactive Hantzsch ester **1b** showed some aromatization to **2b**, but forcing conditions of NaH base and 80 psi SF₆ were required for good conversion. Pitre and co-workers observed that 4-substituted dihydropyridines were less reactive in reduction reactions, potentially due to steric hinderance slowing hydrogen atom transfer from the 4-position.^{14e}

Akiyama has shown that benzothiazolines can replace Hantzsch esters in reductive processes with carbonyls and imines.²⁰ We found that benzothiazolines **3a** and **3b** were also oxidized to the corresponding benzothiazoles **4a** and **4b**, upon reaction with SF₆.²¹ Reactivity both with and without cesium carbonate was observed, with cleaner and higher yielding reactions in the *absence* of base. Borylated dihydropyridines (**5a–5d**) underwent oxidation to the pyridines **6a–6d** in the presence of SF₆ in MeCN solvent with added cesium carbonate, however no productive reactivity was observed in the absence of cesium carbonate.²² Fluoride was observed bound to boron by ¹⁹F NMR in the crude reaction mixtures of these compounds. This shows the dual electron-withdrawing groups of the Hantzsch esters are unnecessary for this reactivity, and raises the possibility that someday nicotinamide (NAD-H)-dependent enzymes may be purposed to have reactivity with SF₆.²³

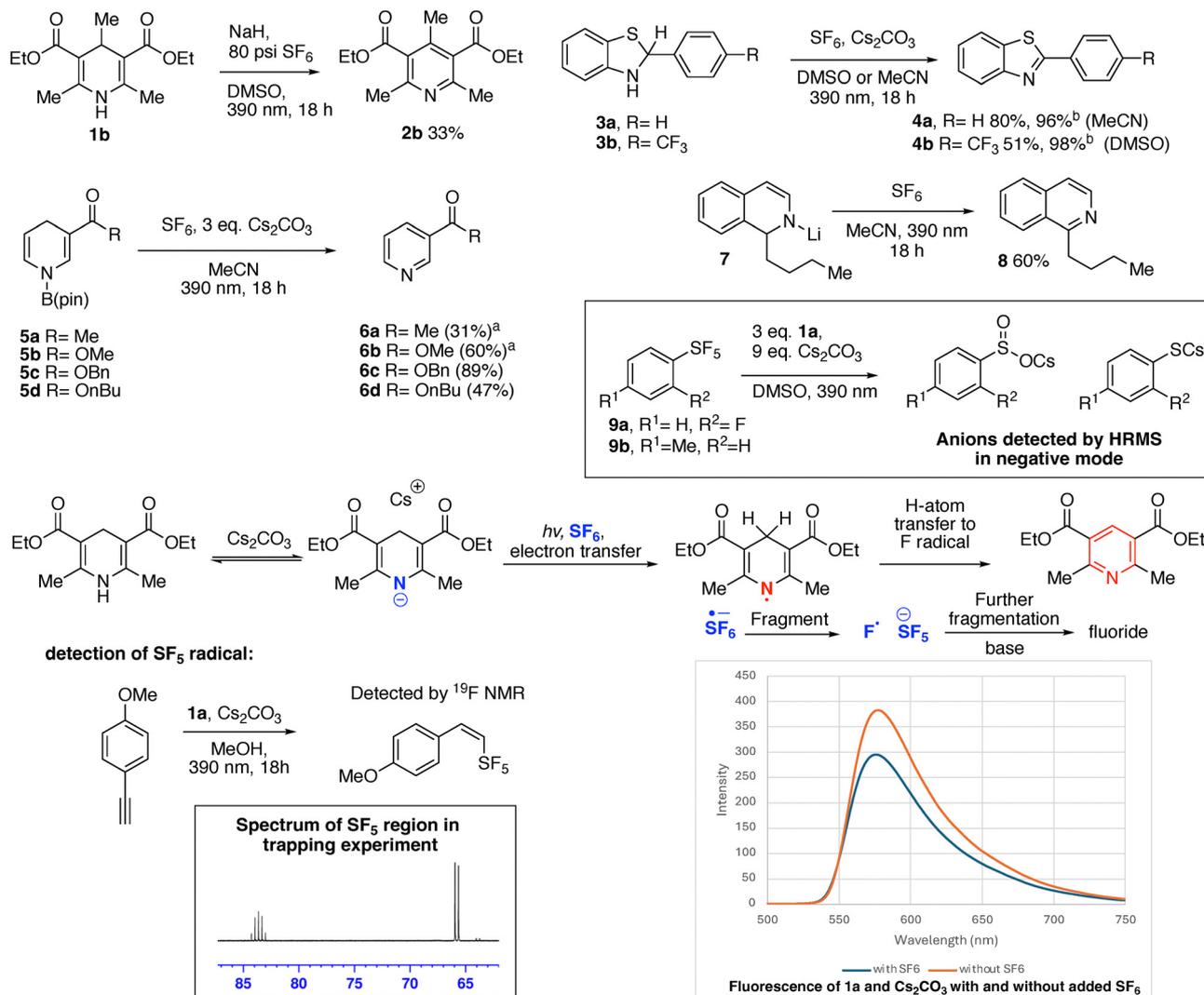
Meisenheimer intermediate **7**, prepared by addition of butyllithium to isoquinoline, is reported by Gualandi, Negri, Ceroni, and Cozzi to be a potent photoreductant (with a reported E_{ox^*} of $< -3.8\text{ V vs. SCE}$, therefore $< -4.2\text{ V vs. }Fc^+/Fc$).²⁴ Compound **7** was oxidized to the corresponding butyl-isoquinoline under SF₆ atmosphere in MeCN with 390 nm irradiation.²⁵

We extended this reactivity to the SF₅ group. Commercially available *o*-fluorophenyl **9a** and *p*-tolyl SF₅ **9b** underwent reduction using **1a** and cesium carbonate in DMSO or MeCN. Fluoride was again observed in the crude ¹⁹F NMR spectra, while the corresponding arylsulfinate and thiophenolate anions were detected by high-resolution mass-spectrometry. Only sluggish reaction between **9a** and **1a** under irradiation was observed in the absence of base, with some formation of fluoride, but the SF₅ group remained substantially intact after a



Scheme 2 Reaction of SF₆ with a Hantzsch esters (a) reaction conducted with 80 psi SF₆.





Scheme 3 Substrate scope and proposed mechanism (a) Yield determined by ¹H NMR and internal standard (b) Yield without base.

three-day irradiation, suggesting photoexcited **1a** has insufficient reducing power to reduce aryl SF₅ without deprotonation. DBU could also be used as a base rather than cesium carbonate to obtain complete decomposition of the SF₅ group with **1a** in an 18-hour irradiation. Several new SF₅-introduction reagents have recently been disclosed, which will increase the accessibility of the SF₅ group.²⁶ Our results with Hantzsch esters should be considered in the design of reductive transformations in the presence of the SF₅ group. While the SF₅ group is considered chemically robust, its decomposition has been reported in a few limited examples, including by Lewis acids and bismuth-based reductive catalysts.^{27,28} Akiyama recently reported the reduction of aryl SF₅ compounds bearing an additional electron withdrawing group to thiolates using potassium iodide *via* a charge transfer complex.²⁹ Aryl SF₅ reduction has also been reported in electrochemical devices.³⁰

Based on the catalyst-free photoreductive behavior of Hantzsch esters, and precedent from solution phase reduction of SF₆, we propose that the photoexcited anion of **1a** (or

photoexcited neutral **1a** species in reactions without base) transfers an electron to SF₆ or the pentafluorosulfanyl group under irradiation.³¹ This could be followed by fragmentation of the resulting sulfur-radical anion. Fragmentation to either fluorine radical and SF₅ anion, or to fluoride and SF₅ radical is feasible, with higher excess electron energy favouring the latter pathway.^{6a,13} Subsequent hydrogen atom transfer from the Hantzsch ester radical to the fluorine radical would aromatize the ring. The SF₅ anion is fragile without a diffuse supporting counter-cation and readily releases fluoride and SF₄.³² If the initial fragmentation to form SF₅ radical occurs, the Hantzsch system is likely also reducing enough to reduce the SF₅ radical to the SF₅ anion, with subsequent fragmentation.^{5,9b} SF₄ would likely react with base present under the reaction conditions, and we did not detect partially fluorinated intermediates such as SOF₂ (thionyl fluoride). We did detect hydrosulfite (HSO₃⁻) anion in the crude reaction mixtures by low-resolution mass-spectrometry.³³ We observed no significant change in the wavelength in the fluorescence spectrum corresponding to



the maxima of fluorescence intensity **1a** and cesium carbonate in the presence or absence of SF₆, suggesting a charge transfer complex is not formed, however a decrease in fluorescence intensity of a mixture of **1a** and cesium carbonate was observed when the mixture was sparged with SF₆.³⁴ Evidence for the formation of the SF₅ radical intermediate in a different solvent was obtained by adding ethynylanisole as a SF₅ radical trap to the reaction mixture in methanol with base, leading to the detection of a SF₅-containing product. Ethynylanisole did not form any appreciable trapping product in MeCN or DMSO, nor was any SF₅ trapping product observed in methanol in the absence of base. α -methylstyrene could also trap the SF₅ radical in MeCN, but formed a complex mixture of products. Due to the observed instability of aryl-SF₅ groups under the reaction conditions, it is unlikely this system will readily result in a preparative method for SF₅ compounds.

In conclusion, we show that photoexcited Hantzsch esters and related dearomatized compounds undergo oxidation in the presence of SF₆. Given the growing interest in SF₆ chemistry, and introduction of the SF₅ group, these findings may suggest new approaches to decomposing SF₆, or alternatively, cautionary precedent for undesirable reactions that may occur in the design of radical reactions with Hantzsch esters or related reductants in the presence of the SF₅ group.

Conflicts of interest

There are no conflicts to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: synthetic procedures, NMR Data, UV/Vis studies. See DOI: <https://doi.org/10.1039/d5cc07159c>.

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suggestions on the use and sourcing of gas-sampling bags to hold and dispense SF₆.

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