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FULL PAPER

Photoredox catalytic activation of sulfur hexafluoride for pentafluorosulfanylation of α-methyl and α-phenyl styrene

David Rombach,[a] and Hans-Achim Wagenknecht*[a]

Abstract Sulfur hexafluoride is inert, non-toxic, and cannot simply be applied as pentasulfanylation reagent. We present the first photoredox catalytic way to convert it into pentafluorosulfanylated α-methyl and α-phenyl styrenes simply by using light. The work tackles the challenges of precise activation of sulfur hexafluoride by a photoredox catalyst with designed consecutive electron transfer cycles that styrenes trap the generated pentafluorosulfanyl radical. The method overcomes the highly problematic access to vinylic and allylic pentafluorosulfanyl styrenes and combines it with the disposal of the most potent greenhouse gas. Together with the use of light as energy source, an exceptionally high level of sustainability is gained.

Introduction

Fluorinated compounds play not only an important role in pharmaceutical chemistry,[1-3] but also in agrochemicals,[4] and in materials for e.g. optoelectronics, because fluorine helps to design unique properties by its significant electronic influence. The most common fluorinated substituent is the trifluoromethyl (CF_3) group.[5] However, the search for even more effective and more stable fluorinated groups is an important task. In contrast to the extensively applied CF_3 group, the pentafluorosulfanyl (SF_5) group is a relatively new fluorinated substituent and one of the most underexplored ones; therefore often designated as "forgotten functional group".[6] This is surprising with respect to the proposed, highly beneficial properties of the SF_5 group, especially as bioisosteric replacement in pharmaceutically active compounds,[7] but also for the design of polymerization catalysts.[8] In contrast to the weakness of the CF_3 group, namely its sensitivity towards hydrolytic activation, the SF_5 group is both thermally and chemically stable and not prone to hydrolysis under physiological conditions, is highly electronegative, and is lipophilic.[9] This renders the SF_5-compounds as prospective alternatives to common CF_3-compounds in drugs, and does not simply represent a more expensive perfluorinated group. So far, the exploration and the use of the SF_5 group are dramatically limited by its very difficult synthetic accessibility[10,11] due to the extraordinary toxicity and availability of the reagents that the very few available methods are based on, such as the dangerous mixed sulfur fluorides SF_5Cl and SF_5Br as well as the highly toxic S_2F_{10}. The extraordinary toxicity of these compounds makes the usage in a standard research laboratory as well as broad industrial use of these methodologies nearly impossible. In recent work, there was progress by the chlorofluorination of dibenzyl sulfides to SF_4Cl-compounds. However, these reactions are also highly dangerous to handle due to the use of chlorine gas and subsequent fluorination by HF or ZnF_2[12,13] and do not transfer the final functional group but require the preinstallation of a thiofunction in earlier synthetic steps. The accessibility of SF_5-alkyl compounds is even more restricted due to the lackage of any methodology which is not based on the use of mixed or low sulfur fluorides today.[7] In contrast to the high reactivity and toxicity of the mixed sulfur fluorides there is the notorious inertness of sulfur hexafluoride (SF_6) which renders this inexpensive gas as a promising pentafluorosulfanylation reagent for organic synthesis. However, SF_6 cannot yet simply be applied as chemical pentasulfanylation reagent for organic compounds. Due to its susceptibility to infrared light excitation SF_6 is the strongest greenhouse gas known to humankind today. It displays a 22,800-fold higher greenhouse potential than carbon dioxide and has a mean lifetime in the atmosphere of about 3,200 years.[14] SF_6 is still indispensable in many applications, especially in the context of high voltage switchgears, and needs finally to be destroyed after usage, but should be better reused for chemical transformations in order to significantly gain more sustainability. We follow this idea and present herein a completely new photocatalytic method that applies SF_6 as substrate, precisely activates it by LED light at 365 nm for chemical transformations, and transfers it to organic compounds modified with SF_5 groups. By this new photochemical method, a new access to potentially valuable SF_5-modified α-methyl and α-phenyl styrenes for further transformations is gained while the highly potent greenhouse gas SF_6 is destroyed. The method is designed as a highly clean reaction regarding the formation of fluorinated side products.

Results and Discussion

The conventional photochemical activation of SF_6 requires highly energetic UV light (185 nm≙650 kJ/mol) in the presence of styrene and yields only SF_4 and sulfur as products.[15] The main challenge in photoactivation of SF_6 is to establish a single electron reduction step and stabilize the resulting reactive SF_5 radical after dissociation of the fluoride anion in order to form a carbon-SF_5 bond. This is a very difficult task due to the energetics of the bond enthalpies of the consecutively reducible S-F-bonds in SF_6, which means that the subsequent reduction step yields the stable molecule SF_4 after fragmentation of the resulting SF_5^- anion.[16] However, it was also shown by nanocalorimetric studies that the fragmentation channel of the radical anion $SF_6^{\bullet-}$ is highly dependent on the excess energy that is brought into by the

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Supporting information for this article is given via a link at the end of the document.

reducing electron.[17] This is the most critical issue for SF_6 activation by photoredox catalysis. In general, photoredox catalysis emerged over the last few years and applies visible light as energy source for organic reactions.[18-24] Recently, Jamison *et al.* developed a method to activate SF_6 by the widely used and standard $Ir(ppy)_2(dtbppy)PF_6$ using highly reducing conditions by addition of a sacrificial reductant. They used it for allylic deoxyfluorinations.[25] This approach, however, does not allow the introduction of SF_5 groups to organic compounds. This is not surprising since at such low electron excess energies, the fragmentation of photoactivated radical anion $SF_6^{\cdot-}$ yields only reactive fluoride radicals, lower sulfur fluorides and non-reactive SF_5 anions.[17] Photoredox catalysis is, however, a tool to precisely control electron transfer processes by both the intensity of the irradiation power and the excess energy of the transferred electron that is tuned by the photophysical properties of the excited state of the chosen photoredox catalyst. Thus, we focused our work on a photoredox catalytic approach that avoids an excess of reducing agents and carefully controls the local "reductivity" of the reaction medium. Since early reports showed that alkali metals in the presence of polyarenes are suited to overcome kinetic barriers to reduce SF_6 to sulfide and fluoride[26] we anticipated to cut off the kinetically favoured channel of consecutive reductions by a carefully designed photoredox catalytic cycle in combination with a two-photon absorption.[27] Accordingly, a photocatalyst with a strongly reducing excited state is needed. N-Phenylphenothiazines are some of the most strongly reducing photoredox catalysts known today[28] because the excited state potentials of -2.1-2.5 V are getting close to the reduction potential of -2.7 V of solid sodium.

Our photoredox catalytic approach consisted of 5 mol% N-phenyl-phenothiazine (**1**, for electrochemical charaterization see Supplementary Information (SI)) as photoredox catalyst, 1,1-diphenylethylene (**2**) as substrate (0.1 M) in acetonitrile as solvent due to its large electrochemical window avoiding undesired reductive side reactions (Figure 1). The irradiation was performed by 365 nm LEDs (λ_{max}=368 nm) and 525 nm LEDs (λ_{max}=512 nm, for LED spectra see SI), additionally (*vide infra*). The successful and selective activation of SF_6 was indicated by the formation of a SF_5-modified carbon species, probably the solvent acetonitrile according to NMR spectroscopy. This issue was related to the high reactivity and hydrogen abstraction ability of the generated SF_5 radical. This makes the SF_5-radical too short-lived for the desired selective chemical reaction with **2**. An increase of the substrate concentration was not successful due to undesired side reactions. Copper(II) salts are known to stabilize the similarly behaving CF_3 radical and manage to bind to both generated radicals and mediate the bond formation.[29,30] Thereby, the coordination of copper(II) to radicals can drastically enhance the lifetime of short-lived radicals and enable selective reactions using even very short-lived transient radicals. In our chemistry, $Cu(acac)_2$ showed the best performance of enabling addition of SF_6 to substrate **2**. In fact, the selectivity for the desired product **3** was dramatically enhanced to the almost complete suppression of dimerization using a low substrate concentration of 0.05 M as well as 30 mol% of catalyst in the reaction mixture however the yield dropped significantly due to overreduction of the generated radical and the resulting quenching of to the key intermediates. Finally we found optimized reaction conditions to get the product in up to 63% by addition of a low amount (10 mol%) of $Cu(acac)_2$ together with 5 mol% **1** in the reaction mixture (Figure 2) and irradation with second LED (522 nm, vide infra). The fluoride of product can be eliminated by treatment with the Lewis acid BF_3 in order to form **4** that carries the SF_5 group in the vinylic position in more than 95% yield. This type of photoreaction works also well with α-methyl styrene (0.05 M) (**5**) to the addition product **6** (see SI). BF_3-induced eliminations of **3** and **6** yield **4** and **7**, respectively, that carry the SF_5 group (see SI) in the vinylic or allylic position and thereby nicely complements this photoredox catalytic approach (*vide infra*).

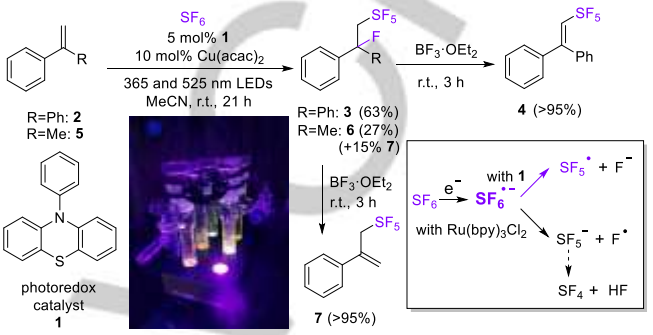

Figure 1. Photoredox catalytic activation of SF_6 using N-phenyl-phenothiazine (**1**) as photoredox catalyst and pentafluorosulfanylation of 1,1-diphenylethylene (**2**) and α-methyl styrene (**5**) to **3** and **6**, and subsequently the products with vinylic SF_5 group **4** and allylic SF_5 group **7**. The inset shows the different fragmentation channels of the photoredox catalytically formed $SF_6^{\cdot-}$ depending on the excess energy that is high in case of **1** and low in case of standard $Ru(bpy)_3Cl_2$. The image shows the irradiation setup using LEDs (see SI).

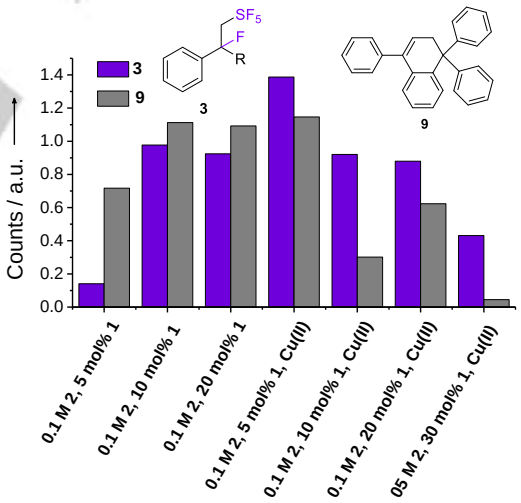

Figure 2. Relative ratio of pentafluorosulfanylation product **3** and substrate dimerization product **9** after irradiation of substrate **2** at 365 nm in the presence of different amounts of photoredox catalyst **1** and 10 mol% $Cu(acac)_2$ according to GC/MS-EI analysis.

In order to gain mechanistic insights (Figure 3), detailed optical-spectroscopic quenching studies gave important hints. The photoredox catalyst **1** was stable under irradiation in absence of a quencher molecule. After addition of SF_6 no reaction was observed at all in the dark. After irradiation of the sample solution for 1 min at 365 nm a red color was observed, which was shown to be persistent in the absence of light. The intermediate species that results from charge separation between photoexcited **1** and

SF_6 (in the presence of **2**) was identified by spectroelectrochemistry (for spectrum see SI), especially by its absorbance bands at 274 nm and 514 nm, as the radical cation $\mathbf{1}^{\cdot+}$ of the photoredox catalyst. This initial electron transfer yields the radical anion $SF_6^{\cdot-}$ as transient species. The radical cation $\mathbf{1}^{\cdot+}$ is not able to oxidize **2** and regenerate the photoredox catalyst into the ground state, because this back electron transfer is about 100 kJ/mol endergonic which was also shown in theoretical calculations of reduction potentials by DFT. Only the irradiation of $\mathbf{1}^{\cdot+}$ at 365 nm or 530 nm reduced its concentration due to oxidation of **2**. This second electron transfer is the key activation step for **2**. According to the Rehm-Weller equation (without the Coulomb energy), the driving force for this step is estimated by $\Delta G = E_{ox}(\mathbf{2}^{\cdot+}/\mathbf{2}) - E_{red}(\mathbf{1}^{\cdot+}/\mathbf{1}) - E_{00}$. Using $E_{ox}(\mathbf{2}^{\cdot+}/\mathbf{2})$=1.7 V,[31] $E_{red}(\mathbf{1}^{\cdot+}/\mathbf{1})$=0.7-0.8 V (for cyclic voltagrams see SI)[32] and E_{00}=2.4 eV (514 nm), this electron transfer step is clearly exergonic (ΔG=-1.4--1.5 eV). To study this reaction more precisely, the radical cation $\mathbf{1}^{\cdot+}$ was chemically synthesized by oxidation of **1** with $NOPF_6$.[33] The red solid could be isolated and is stable at room temperature under inert conditions. The radical cation $\mathbf{1}^{\cdot+}$ reacted very slowly with **2** in the dark under inert conditions by the loss of <2% absorbance at 711 nm over 20 h (Figure 3 left. This result was further supported by ^{1}H NMR studies that showed that the concentration of **2** in the reaction mixture stayed constant over a period of 11.5 h in the dark, even in presence of the chemically formed radical cation $\mathbf{1}^{\cdot+}$ (for ^{1}H spectra see SI). These results ruled out a significant reactivity of $\mathbf{1}^{\cdot+}$ with **2** which is in agreement with the results of Moutet.[34] In contrast, the radical cation $\mathbf{1}^{\cdot+}$ reacts by irradiation at 525 nm in the absence of **2** and the spectroscopic signature at 711 nm vanishes over 5 h (Figure 3 left). The careful analysis of these UV/Vis absorption spectra indicated a complex between **2** and $\mathbf{1}^{\cdot+}$ that enables the second excitation and electron transfer under non-diffusion controlled conditions.

The addition of the SF_5 radical, subsequent back electron transfer to radical cation $\mathbf{1}^{\cdot+}$ and finally the reaction with the fluoride anion would represent a simpler alternative mechanism. However, we observe a substrate dimerization product **9** that can only be formed by the sustrate radical cation $\mathbf{2}^{\cdot+}$. Taken together with the observations that we do not find any H-abstraction SF_5-alkyl product and that the yield is increased from 32% to 49% under comparable conditions by irradiation both at 368 nm where **1** absorbs and 522 nm where $\mathbf{1}^{\cdot+}$ absorbs, our studies imply the following extended photoredox catalytic cycle (Figure 3). After excitation of **1**, the excited electron is selectively transferred to SF_6 that dissociates into the reactive SF_5 radical and the fluoride anion. An interesting feature of the usage of **1** is that both the photocatalyst itself and its radical cation $\mathbf{1}^{\cdot+}$ absorbs at light at 365 nm (for UV/Vis absorption spectrum see SI). That means that the second excitation of $\mathbf{1}^{\cdot+}$ in the presence of substrate **2** yields the substrate radical cation $\mathbf{2}^{\cdot+}$ after a second electron transfer that regenerates **1** and closes the extended photoredox catalytic cycle. The radical cation $\mathbf{2}^{\cdot+}$ allows for addition of the SF_5 radical generating the SF_5-substituted 1,1-diphenylethyl cation **8**, which is consecutively trapped by the generated fluoride ion into the product **3**. In this mechanistic scenario, it can be assumed that copper(I) stabilizes the SF_5 radical and $\mathbf{2}^{\cdot+}$ enabling their reaction to product cation **8**[29]. This is the second key chemical step in the whole mechanism since it forms the C-SF_5 bond. Therefore, the global electrophilicity index of the SF_5 radical was calculated by means of DFT using the method developed by Parr[35] correlating the chemical hardness and the chemical potential, which are both easily accessible by DFT calculations (for details see SI). The calculated value of 3.7 for the reactivity parameter gives highly electrophilic character which is expected for such a highly electron deficient radical. The regioselective addition of the SF_5 radical to the less substituted position of the electron deficient radical $\mathbf{2}^{\cdot+}$ was assumed based on the stabilized character of the generated cation **8** and further supported by the calculation of spin densities that showed substantial character of localisation at C-1 (Figure 3 right). This explains nicely the radical attack of the SF_5 radical at this position. Finally, we isolated the products **3** and **6** and verified their structure by means of NMR spectroscopy. A detailed structure analysis was carried out using ^{13}C-^{1}H as well as ^{19}F-^{1}H and ^{19}F-^{13}C correlation spectroscopy which proved the regioselective addition of the SF_5 radical and fluoride anion in products **3** and **6** (for NMR spectra see SI).

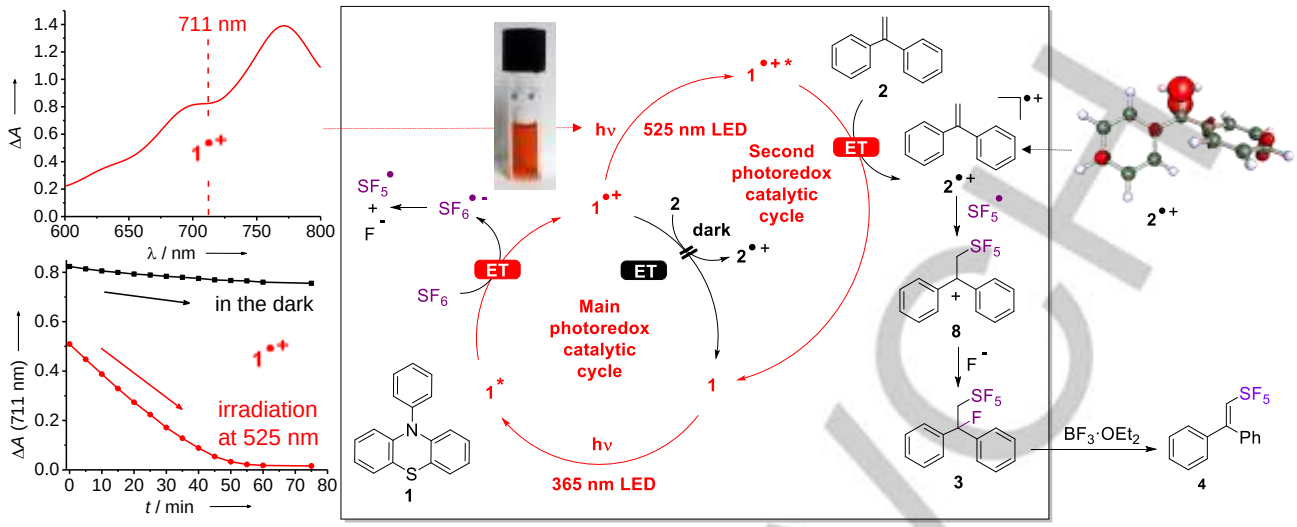

Figure 3. Mechanistic proposal for the photoredox catalytic cycle of **1** (box) that converts the substrate **2** into product **3**. The spectra (left) show the spectroscopic signature of the intermediate radical cation **1**$^{\bullet+}$ after the first photoinduced electron transfer from the photoredox catalyst **1** to SF_6 (top) and its conversion by the second photoinduced electron transfer and oxidation of the substrate **2** to its radical cation **2**$^{\bullet+}$ (bottom). The calculated spin density of the substrate radical cation **2**$^{\bullet+}$ (right) rationalizes the regioselectivity of the subsequent reactions to product **3**.

The detailed reaction conditions were further developed to support not only the proposed reaction mechanism but to improve the yield. If it is assumed that the quenching reaction of the excited photocatalyst **1*** by SF_6 is a bimolecular reaction it should be dependent on the concentration of SF_6 and **1**. Increasing the SF_6 pressure from 2 up to 6 atm (for determination of the SF6 pressure see SI) has not a reasonable impact on the yield of **3** (ca. 10%). Although the solubility of SF_6 in acetonitrile as solvent should be describable by Henry's law suggesting a linear increase in concentration with pressure, the sensitivity of this parameter is quite low. This concludes that the formation of $SF_6^{\bullet-}$ is not the rate limiting step and the first electron transfer is probably fast. The raise of catalyst concentration from 5 mol% to 10 mol% reduces the yield due to unproductive overreduction of the generated SF_5 radical. The experimental results show a strong dependence of product formation on the two operating catalytic cycles which have to be connected precisely by controlling the rate of forming the SF_5 radical and the photoredox catalyst cation **1**$^{\bullet+}$. Slowed down trapping of **1**$^{\bullet+}$ decreases the amount of formed desired SF_5-modified product **2** and favours the formation of the substrate dimer (Figure 2).

For the elimination of the vicinal fluorine substituent in **3** to generate exclusively SF_5-substituted alkene **4** as final product all attempts to abstract the acidified proton in α-position of the strongly electronegative SF_5 group by Et_3N or carbonates failed. This is likely because the resonance energy that is liberated by the elimination of HF does not compensate for the loss in energy due to the cleavage of the strong C-F bond. However, we could show that the addition of 38 eq. $BF_3{\cdot}Et_2O$ as Lewis acid yielded the elimination product **4** after stirring the reaction mixture under air for 3 h at room temperature in almost quantitative yield. The enthalpy gain using the Lewis acid assisted elimination seems to overcompensate for the C-F bond enthalpy and therefore allows for clean elimination of the fluoride anion, followed by deprotonation. The similar procedure using **5** delivers **7**. There is an interesting side result by this reaction: While CF_3 groups are sensitive towards abstraction of fluoride anion, the SF_5 group stayed completely stable during the attack by this strong Lewis acid. This is an important feature of the SF_5 group that it makes it very attractive as stated in the introduction.

Conclusions

We found the first selective activation of SF_6, which generates the transient SF_5 radical that reacts with carbon to form exclusively SF_5-substituted organic products, in particular pentafluorosulfanylated α-methyl and α-styrene products. The formation of the SF_5 radical instead of the fluoride radical is likely due to the precisely matching excess electron energy of the excited electron. Based on the newly gained knowledge of the solution behaviour of the initially formed radical anion $SF_6^{\bullet-}$ which was so far only studied in the gas phase, our results confirm the strong dependence of the fragmentation channel on the electron excess energy of the transferred electron in solution. Since electron excess energies of less than 2 eV yield the anion SF_5^- (that decomposes to SF_4 and fluoride anions) N-phenyl phenothiazine **1** is the right choice to turn SF_6 into a precious pentafluorosulfanylation reagent by means of photoredox catalysis. This chromophore provides electrons with a sufficiently high electron excess to allow fragmentation of $SF_6^{\bullet-}$ into the desired reactive SF_5 radical and fluoride anions. It is important to note that further increase of electron energies is not productive because it yields the lower fluorine species SF_4^-, SF_3^-, SF_2 and F_2^-.[1-3] The electron affinity of SF_6 generating $SF_6^{\bullet-}$ is still under debate[17] but the threshold for electron attachment generating SF_6^- was determined to be about 0 V in various experimental studies.[36] This is in very good agreement with our results since the estimated excited state potential of **1** is E_{red}(**1**$^{\bullet+}$/**1***)=-2.1V and

the electron attachement energy of 0 V yields an electron excess energy of about 2.1 V which corresponds to the fragmentation channel into the SF_5 radical. Common $Ru(bpy)_3Cl_2$ as photoredox catalyst has an estimated excited state reduction potential of $E_{red}(Ru^{3+}/Ru^{2+*})$=-0.88V that gives an excess electron energy of about 0.8 V, which serves the SF_5^- anion generating channel, which is in good agreement with the observed lower sulfur intermediates.[25] In our approach, the SF_5 radical can be trapped by activated styrenes, represented by **2** and **5**, as substrates yielding SF_5-substituted organic products in yields of up to 63%. Furthermore, we developed a method to abstract the vicinal fluoride anion and prepare the vinyl- and allylpentafluorosulfanyl compounds **4** and **7**, respectively. These are valuable precursors for further chemical transformations comparable to the trifluoromethylthiolated styrenes by Glorius *et al.*,[37] the styrene addition products by Nicewicz *et al.*,[38] and as polymerization precursors.[39] Furthermore, vinylic and allylic SF_5 compounds allow for a wide variety of functionalization to prepare small SF_5-containing building blocks. Our approach is not yet a routinely applicable protocol for the pentafluorosulfanylation of any organic compound but we could show for the first time, that one can turn SF_6 in a precious pentafluorosulfanylation agent by addressing the correct fragmentation channel in solution. We believe that this is a milestone in understanding the chemical properties of the reduction of SF_6 which opens up a new era in organofluorine chemistry. The impact of SF_5 substituents in pharmacology, agrochemistry, modern optoelectronic functional materials and other fields will be speeded up by this facile and synthetically useful access of SF_5-modified organic compounds. Our methodology avoids the highly toxic and often not even commercially available precursor molecules SF_5Cl, SF_5Br and S_2F_{10} to SF_5-alkenes[11] and uses instead the inert and non-toxic SF_6 as valuable precursor molecule for such transformations by comparable yields. As side effect, the usage of SF_6 as a chemical resource reduces its climate change and greenhouse effect. Our vision is not to only destroy SF_6[40] after its usage in industrial applications but to connect SF_6 with chemical synthesis to generate a symbiosis and facilitate the disposal of SF_6 by generation of valuable molecules. We showed that the combination of photoredox catalysis and SF_6 chemistry is a powerful tool in the synthesis of SF_5-containing α-methyl and α-phenyl styrenes Together with the use of light as energy source, an exceptionally high level of sustainability is gained.

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Experimental Section

Supplementary Information gives the complete experimental methods.

Synthesis of N-Phenylphenothiazine (1). N-Phenylphenothiazine was synthesized similar to the reported procedure.[41] 810 mg Phenothiazine (4.06 mmol, 1.00 eq.) were dissolved in 8.0 mL anhydrous toluene. Then 780 mg (520 µL, 4.98 mmol, 1.23 eq.) bromobenzene, 587 mg (5.23 mmol, 1.29 eq.) KOtBu as well as 71 mg (0.489 mmol, 12 mol%) $(t\text{-Bu})_3PHBF_4$ was added. Then 112 mg Pd_2dba_3 (0.122 mmol, 24 mol% Pd) added. The reaction mixture was degasses using three freeze-pump-thaw cycles and was finally refluxed for The reaction mixture was let come to room temperature and 100 mL EtOAc and 50 mL water was added. The reaction mixture was extracted with EtOAc (3 x 100 mL). The combined organic phases were dried over Na_2SO_4. The solvent was evaporated and the crude product was purified by column chormatography (SiO_2, Cyclohexane, R_f = 0.3). The product was gotten as colorless solid (1.082 g, 3.93 mmol, 97 %). ^{1}H NMR (400 MHz, Acetonitrile-d_3) δ 7.70 – 7.60 (m, 2H), 7.60 – 7.46 (m, 1H), 7.45 – 7.30 (m, 2H), 7.05 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.91 (ddd, *J* = 8.1, 7.3, 1.7 Hz, 2H), 6.84 (td, *J* = 7.4, 1.4 Hz, 2H), 6.22 (dd, *J* = 8.1, 1.4 Hz, 2H). ^{13}C{^{1}H} -NMR (126 MHz, Acetonitrile-d_3) δ 145.1, 141.9, 131.9, 131.4, 129.3, 128.1, 127.6, 123.6, 120.9, 117.17. HR-EI-MS m/z (calcd.) = 275.0769 [M$^{\bullet+}$]; m/z (found) = 275.0767 [M$^{\bullet+}$].

General procedure of adding SF_6 to styrenes. Under inert gas atmosphere in a Young-type Schlenk tube 0.1 mmol of the substrate as well as 5 mol% of **1** and 10 mol% $Cu(acac)_2$. was dissolved in 1 mL MeCN. The reaction was subjected to three freeze-pump-thaw cycles. Then the reaction mixture was frozen to -196°C, the vessel was evacuated and the atmosphere was exchanged against SF_6 (70 mL) using a gas dosage glass apparatus. After complete transfer of the gas volume to the reaction vessel the vessel was sealed and SF_6 was resublimed to the gas phase while letting come the reaction mixture to room temperature. The reaction was irradiated at 365 respective 525 nm at 20°C for 21 h carried out by ^{19}F-NMR spectroscopy after addition of standard to the crude reaction mixture and dilution with 300 µL $CDCl_3$.

Pentafluoro-(2-fluoro-2,2-diphenylethyl)-λ^6-sulfane (3). The compound was prepared according to the general procedure using 17.6 µL (18.0 mg, 0.100 mmol) **2**, 1.4 mg **1** and 2.6 mg $Cu(acac)_2$ in metal organic grade solvent using two wavelength irradiation for 21 h at 20°C. The product was determined by ^{19}F-NMR (64% yield). Purification of the material was carried out by removing the solvent under reduced pressure and column chromatography (SiO_2, hexanes) using a micro column (R_f = 0.2). ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.29 (m, 10H), 4.49 (dp, J_{HF} = 21.4, 7.9 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ 140.65, 140.42, 128.78, 128.63, 125.11, 125.03, 119.12, 115.78, 97.53, 95.66, 76.55, 76.43, 76.32, 76.20, 76.08. ^{19}F-NMR (471 MHz, Chloroform-*d*) δ 86.48 – 78.62 (m), 70.95 (ddt, J = 147.9, 9.2, 8.7 Hz), -155.43 (tp, *J* = 21.9, 11.8 Hz). HR-EI-MS m/z (calcd.) = 326.0564 [M$^{\bullet+}$]; m/z (found) = 326.0565 [M$^{\bullet+}$] $C_{14}H_{12}F_6{}^{32}S$.

Pentafluoro(2-fluoro-2-phenylpropyl)-λ^6-sulfane (6). The compound was prepared using the general procedure using 6.50 µL (5.92 mg, 0.050 mmol) **5**, 0.70 mg **1** and 1.30 mg $Cu(acac)_2$ using filtered Sureseal solvent (*Aldrich*). The reaction mixture was subjected to irradiation for 21h at 20°C using a 365 nm LED. The product yield was determined by ^{19}F-NMR (27%). There was a product distribution that also yielded the elimation product yielding molecule in significant yield (15%). Purification of the adduct was carried out using column chromatography (SiO_2, n-pentane) using a pipet column. The product is highly volatile and could not be seen after spotting on TLC at room temperature. The TLC therefore was g precooled before spottinby dipping it into liquid nitrogen for some seconds. Immediate staining with $KMnO_4$ staining reagent indicated the product as yellowish spot0 (R_f = 0.3). The solvent could not be completely removed for characterization due to the higher boiling point of pentanes compared to the product. Complete evaporation of the solvent was tried but yielded residual pentanes in NMR. Structural characterisation was therefore carried out in the presence of pentanes. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.48

– 7.32 (m, 5H), 4.06 (ddp, J = 29.9, 22.7, 7.3 Hz, 2H), 1.86 (d, J = 21.6 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 142.01, 128.88, 128.87, 128.48, 124.20, 124.11, 119.30, 115.96, 78.02 - 79.00 (m), 27.94, 27.08. ^{19}F NMR (471 MHz, Chloroform-d) δ 84.10 – 81.99 (m), 70.59 (ddt, *J* = 147.5, 9.2 Hz), -152.43 – -152.71 (m). HR-EI-MS m/z (calcd.) = 264.0407 [M$^{\bullet+}$]; m/z (found) = 264.0408 [M$^{\bullet+}$].

General procedure for elimination of the vicinal fluoride. Under air the vicinal fluorinated sulfur pentafluoride (12.6 mM) was dissolved in $CDCl_3$. Then $BF_3{\cdot}Et_2O$ (473 mM, 37.6 eq.) was added and the mixture immediately turned slightly redish. The mixture was stirred for 3 h at room temperature. Then the progress was checked by ^{1}H-NMR. No other SF_5 species was formed during reaction. The mixture was quenched by addition of 1 mL $NaHCO_3$ solution and was extracted with $CHCl_3$ (3 x 5 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed carefully under reduced pressure and was subjected to column chromatography.

(2,2-Diphenylvinyl)-pentafluoro-λ^6-sulfane (4). In a screw-cap vial 4.11 mg **3** were dissolved in 1 mL of $CDCl_3$ and $BF_3{\cdot}Et_2O$ was added and the mixture was stirred at room temperature for 3h. The starting material was cleanly converted to the product. The yield was determined by ^{1}H-NMR spectroscopy (>95%). The crude oily product was purified by column chromatography (SiO_2; 2% acetone in hexanes). The product was gotten as highly volatile oil. Therefore to characterize the compound the solution was not completely taken to dryness but characterized in presence of some pentanes. ^{1}H NMR (300 MHz, Chloroform-d) δ 7.43 – 7.28 (m, 6H), 7.25 – 7.19 (m, 4H), 6.87 (p, J = 8.4 Hz, 1H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 147.64 (q, J = 5.7 Hz), 139.03, 137.55 (q, J = 18.3 Hz), 137.32, 128.58 (q, J = 1.8 Hz), 128.31, 128.14, 128.06. ^{19}F NMR (471 MHz, Chloroform-d) δ 86.19 – 81.57 (m), 68.57 (dd, J = 152.4, 8.5 Hz). HR-ESI**-MS** m/z (calc.) = 306.0500 [M$^{\bullet+}$]; m/z (found) = 306.0502 [M$^{\bullet+}$].

Pentafluoro-(2-phenylallyl)-λ^6-sulfane (7). In a NMR tube 1.33 mg **6** were dissolved in 0.4 mL of $CDCl_3$. Then 20 µL $BF_3{\cdot}Et_2O$ was added and the mixture was stirred at room temperature for 3h. The crude NMR only showed product and starting material was completely consumed. The mixture was quenched by addition of 1 mL $NaHCO_3$ solution and was extracted with $CHCl_3$(3 x 5 mL) and the combined organic phases were dried over Na_2SO_4. The solvent was removed carefully under reduced pressure. The yield was determined by ^{19}F-NMR spectroscopy (>95%). The resulting crude oil was purified by column chromatography (SiO_2; 2% acetone in hexanes). The product was gotten as highly volatile oil. The product was not taken to high vacuum due to its high volatility and was characterized in the presence of some residual hexanes. ^{1}H NMR (400 MHz, Chloroform-d) δ 7.50 – 7.29 (m, 5H), 5.77 (s, 1H), 5.56 (s, 1H), 4.71 (p, J = 7.6 Hz, 2H). ^{13}C{^{1}H} NMR (101 MHz, Chloroform-d) δ 139.17 , 138.55 , 128.75 , 128.50 , 126.17 , 123.97, 75.36 (p, J = 13.4 Hz). ^{19}F NMR (471 MHz, Chloroform-d) δ 83.69 – 79.98 (m, 1F), 64.65 (dt, J = 145.5, 7.7 Hz, 4F). EI-MS m/z (ber.) = 244.0 [M$^{\bullet+}$]; m/z (gef.) = 243.9 [M$^{\bullet+}$].

Preparation of PTA radical cation (1$^{\bullet+}$). In a Schlenk tube 55.5 mg (0.202 mmol) **1** was dissolved in 1 mL anhydrous acetonitrile. Then the mixture was cooled to -78°C and 34 mg (0.194 mmol, 0.96 eq.) $NOPF_6$ was slowly added to the mixture. The mixture turned deep red immediately and was stirred for further 5 min. The mixture was cooled to -196°C and was freeze-pump-thawed for three cycles to remove the generated NO. Then the mixture was let come to room temperature and then 2 mL hexanes was added. A red solid precipitated. The red solid was washed with hexanes three times to remove excess of PTA. Then the solid was dried under reduced pressure and characterized by absorption spectroscopy.

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The green and sustainable way: Using designed photoredox catalysis it is possible to transfer the SF_5 group from inert SF_6 to organic substrate.

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