



Photoredox Catalysis

Fluoroalkylselenolation of Alkyl Silanes/Trifluoroborates under Metal-Free Visible-Light Photoredox Catalysis

Clément Ghiazza,^[a] Lhoussain Khrouz,^[b] Thierry Billard,^[a,c] Cyrille Monnereau,*^[b] and Anis Tlili*^[a]

Abstract: Herein a metal-free fluoroalkylselenolation of alkylsilanes as well as potassium alkyltrifluoroborates under visible light photocatalysis is disclosed. The developed methodologies are performed under mild conditions, room temperature in the presence of an organic photocatalyst and blue LED irradiation. Mechanistic investigations including luminescence and EPR spectroscopy allow us to shed light on both mechanisms.

Introduction

In recent years, direct incorporation of fluorinated groups has experienced widespread interest, owing to the unique physicochemical properties gained after introduction of such moieties.^[1] Trifluoromethyl-chalcogen motifs play a key role in research and development in organofluorine chemistry, as their introduction confers very high lipophilicity to the resulting molecules.^[2] Although several methodologies have been reported for the introduction of OCF₃^[3] as well as SCF₃^[4] and some compounds containing these two motifs are already commercialized, their SeCF₃ analogues are still not exploited to their full potential. A stringent bottleneck is the lack of general protocol enabling a straightforward access to trifluoromethylselenolated compounds.^[5] Although much efforts have been devoted to the formation of C(sp₂)-SeCF₃, only a handful of procedures deal with the trifluoromethylselenolation of aliphatic compounds for the C(sp₃)-SeCF₃ bond formation.^[2c,6] In this context, we decided to investigate such reaction under mild photoredox processes.^[7] Very recently we demonstrated that trifluoromethyltolueneselenosulfonate are precursor for SeCF₃ radical under visible light irradiation.^[8] Taking this finding in advantage, the generation of alkyl radical which can recombine with SeCF₃ radical could potentially drive the desired transformation. Among the known sources of alkyl radical, anionic carbon-silicon precursors have been classically investigated.^[9] In particular, alkyl trimethylsilane derivatives constitute an attractive option.[10] Al-

[a]	Institute of Chemistry and Biochemistry (ICBMS – UMR CNRS 5246),
	Univ Lyon, Université Lyon 1,
	CNRS, CPE-Lyon, INSA,
	43 Bd du 11 novembre 1918, 69622 Villeurbanne, France
	E-mail: anis.tlili@univ-lyon1.fr
[b]	Univ Lyon, ENS de LYON, CNRS UMR 5182, Université Lyon 1, Laboratoire
	de Chimie,
	69342, Lyon, France
	E-mail: cyrille.monnereau@ens-lyon.fr
[c]	CERMEP-In vivo Imaging, Groupement Hospitalier Est,
	59 Bd Pinel, 69003 Lyon, France
	Supporting information and ORCID(s) from the author(s) for this article a
D	available on the WWW under https://doi.org/10.1002/ejoc.201901063.

ternatively, several groups have explored the potential of alkyltrifluoroborates in a similar context.^[11] In both cases, synthetic access to the silane or borate precursors is well documented, and the stability of those two classes of compounds constitute very appealing features towards reaction design. In this context, we report herein two new strategies based either on desylilation or deborylation catalysed by an organic photocatalyst under blue-LED irradiation. In this range of wavelengths, it is well established that 9-Mesityl-10-methylacridinium perchlorate (Fukuzumi catalyst, **PCI**) is one of the most oxidising organic dye for photoredox processes, and we show that it can be successfully used for both transformations, although with slight mechanistic differences, which translate into subtle variations in the outcome of the reactions.^[12]

Results and Discussion

1. Desilylative Fluoroalkylselenolation

To investigate the photochemical desilvlation reaction we selected benzyl trimethylsilane 1a as model substrate in conjunction with trifluoromethyltolueneselenosulfonate in DMSO at room temperature under blue LED irradiation. The first test performed under nitrogen atmosphere with PCI as photocatalyst yielded the desired product. Although this result confirmed our initial postulate, product was only obtained in a very disappointing yield of 5 % (Table 1, entry 1). Interestingly, performing the reaction under air very positively impacts the reaction outcome since 25 % of the desired product was obtained, indicating a possible involvement of molecular oxygen in the catalytic cycle (Table 1, entry 2). Changing the PCI by other less oxidising photocatalyst including Eosin Y, Ir(ppy)₃ as well as Ru(phen)₃Cl₂ furnished the desired product in only marginal yields (up to 8 %, Table 1, entries 3 to 5). Considering the positive impact of oxygen on the reaction outcome, we thought that the addition of a sacrificial oxidant could be beneficial for the reaction. Therefore, we investigated the effect of the presence of potassium persulfate in the reaction media. A slight improvement





was indeed observed, since 30 % of the desired product was obtained (Table 1, entry 6). In a next sequence of experiments, screening of solvent conditions was undertaken. A marked increase of the yield was obtained when CH₃CN was used as solvent (42 %, Table 1 entry 7), while in contrast the use of DMF dropped down The yield to 8 % (Table 1 entry 8). A very significant yield improvement to 50 % was obtained when MeOH was used as solvent (Table 1, entry 9), which was thus selected as an optimal solvent for the rest of the study. Finally, It turned out that working at high reactant concentration strongly benefited the reaction outcome, since an impressive improvement of the vield to ca 81 % was obtained in highly concentrated media (0.8 м, Table 1, entry 12). Blank experiments were conducted either in the absence of the photocatalyst or without irradiation, demonstrating that both are mandatory components of the catalytic cycle (entries 13 and 14).

Table 1. Optimization of the reaction conditions.[a]



[a] Reaction conditions: TsSeCF₃ I (0.4 mmol), BnSiMe₃ 1a (0.4 mmol), photocatalyst (0.02 mmol), additive (0.4 mmol) and anhydrous solvent. Stirring 16 hours at r.t. under blue LED irradiation. [b] ¹⁹F NMR yield with PhOCF₃ as internal standard. [c] Performed under N₂. [d] No photocatalyst. [e] No light.

With the best conditions in hand, we turned our focuses to study the scope of the reaction. First of all, benzyl triethylsilane derivative showed lower reactivity in comparison with trimethylsilane analogues. The use of benzylsilane derivatives substituted with electron donating groups in *para, meta* as well as *ortho* positions (starting materials **1b**, **1c**, **1d** & **1e**) provided trifluoromethylselenolation from moderate yet synthetically useful yield (product **2c**, 41 %) to very good yield (product **2b**, 78 %). The presence of fluorinated benzylsilanes derivatives was also tolerated under our reaction conditions whatever the position of the fluorine in aromatic ring. The desired resulting products were obtained in moderate to good yields. Trifluoromethylselenolated biphenyl **2i** as well as naphthalene derivatives **2j**

were also obtained in very good yields. Quite expectedly, the presence of C(sp₂)-SiMe₃ as well as C(sp₃)-SiMe₃ in the same starting material provided chemoselective trifluoromethylselenolation of the benzylic position in very good yield (2k, 68 %). Secondary benzylic trimethylsilane derivatives could also be converted into their trifluoromethylselenolated derivatives with similar reactivity as primary benzylsilanes, as exemplified with compound 21. However, when a tertiary benzylsilane was engaged, namely tritylsilane, no product formation was detected due to the too high stability of the corresponding radical. Interestingly, higher fluorinated analogues (3a, 4a, 3b, 4b) could also be obtained under the same reaction conditions using their corresponding fluorinated starting materials. Finally, it should be noted that the use of TsSCF₃ allowed the trifluoromethylthiolation of the benzylic silane although with a significantly lowered yield of 30 % (Scheme 1), which could potentially, provided further improvement of the reaction conditions, pave the way to the synthesis of this class of compounds using the methodology depicted herein.



Scheme 1. Reaction conditions: TsSeR_F (0.4 mmol, 1 equiv.), alkylsilane derivative (0.4 mmol, 1 equiv.), **PCI** (0.02 mmol, 5 mol-%), K₂S₂O₈ (0.4 mmol, 1 equiv.) and anhydrous MeOH (0.5 mL). Stirring 16 hours at r.t. under blue LED irradiation. Yields shown are those of isolated products. ¹⁹F NMR yields with PhOCF₃ as internal standard are shown in parentheses.

Despite the synthetic interest of this methodology, its scope turned out to be limited to π -activated silanes. Moreover, this transformation was inoperative on silane derivatives bearing electron withdrawing substituents on the aromatic core. In this



context, we decided to turn our attention towards potassium alkyltrifluoroborates which we thought as constituting superior $C(sp_3)$ radical precursors.

2. Deborylative Fluoroalkylselenolation

In comparison with alkysilane derivatives, potassium alkyltrifluoroborates have indeed more accessible oxidation potential that could be easily reached with common photocatalysts.^[11] Moreover, trifluoroborates are commercially available or prepared from either boronic acids or esters. Potassium alkyltrifluoroborates are stable to both air and moisture and can be easily handled.^[13]

First attempts to perform this photoinduced transformation were performed following the conditions optimized on the silane series: PCI was used in combination with potassium peroxodisulfate in MeOH. Although slightly inferior to what was found in the former series, we were very glad to detect a promising yield of 53 % (Table 2, entry 1). We thus carried on investigations aiming at further improving the reaction conditions A similar efficiency could be achieved by substituting MeOH by ACN (Table 2, entry 2) while as for their silane counterparts, DMF appeared to be deleterious for the reaction outcome (Table 2, entry 3). Using DMSO instead of MeOH allowed us to reach 65 % yield (Table 2, entry 4). Here again, concentration appeared as a crucial optimization factor for the catalytic reaction. In a concentrated media (0.8 M reactant), the product was formed in 80 % yield (Table 2, entry 5). Noteworthy, removing the sacrificial oxidant only led to a marginal decrease of the yield (Table 2, entry 6). Finally, blank experiments without photocatalyst and/or light did not show any trace of the desired product revealing the requirement of both photocatalyst and light (Table 2, entries 7 and 8). Contrarily to silane derivatives, the reaction can be driven under nitrogen atmosphere with a similar outcome indicating that no oxidant is needed in this

Table 2. Optimization of the reaction conditions.^[a]



[a] Reaction conditions: TsSeCF₃ I (0.4 mmol), BnBF₃K **6a** (0.4 mmol), photocatalyst (0.02 mmol), additive (0.4 mmol) and anhydrous solvent. Stirring 16 hours at r.t. under blue LED irradiation. [b] ¹⁹F NMR yield with PhOCF₃ as internal standard. [c] No photocatalyst. [d] No light.



case, which was a first glimpse onto the subtle mechanistic differences at stake in the photocatalytic cycle.

Having determined the best conditions, we focused our efforts on evaluating the scope and limitation of this reaction (Scheme 2). Benzylic substrates were successfully converted into their trifluoromethylselenylated analogues 2a and 2m in good yields even with electron withdrawing groups. Noteworthy, substrate bearing electron withdrawing substituent on the aromatic ring could be converted into the desired product in this case. Yields turned out significantly lower for secondary substrates as highlighted for compounds 2c, 2d and 2e. Unfortunately, aliphatic starting material only gave the corresponding products 2f and 2g in marginal and low yields, which constitutes only a slight improvement as compared to the results obtained with silane precursors. This suggests that, in both case, π -system is of prior importance for the stabilization of the benzylic radical intermediate. Interestingly, higher homologs were prepared in synthetically satisfactory yields for pentafluoroethyl and heptafluoropropyl chains.



Scheme 2. Reaction conditions: TsSeR_F (0.4 mmol, 1 equiv.), potassium alkyltrifluoroborate derivative (0.4 mmol, 1 equiv.), **PCI** (0.02 mmol, 5 mol-%) and anhydrous DMSO (0.5 mL). Stirring 16 hours at r.t. under blue LED irradiation. Yields shown are those of isolated products. ¹⁹F NMR yields with PhOCF₃ as internal standard are shown in parentheses.

3. Mechanistic Studies

Reaction mechanism was then evaluated for silane derivatives by spectrofluorimetric measurements, according to the general protocol detailed in some of our previous works.^[8a,8b] Acridinium perchlorate catalyst **PCI** displayed only a weak luminescence when dissolved in methanol. It has long been established that the origin of this low fluorescence is due to charge transfer (CT) mediated quenching of the acridinium by its counterion, which is both solvent and counterion dependent.^[14] Noteworthy, luminescence intensity was only marginally affected by thorough degassing of the solution, confirming that emission



mainly occurs from a singlet excited state (fluorescence). Although weak, its intensity we tried to test whether guenching could occur upon addition of a potential electron acceptor. Attempts to characterize electron transfer (ET) in the presence of benzyltrimethylsilane 1a, in concentration conditions similar to previous reports^[10e] did not show any lowering of the luminescence, seemingly indicating that either no ET was taking place in those experimental conditions or that the initial fluorescence level was too weak to efficiently probe this process. However, during this initial series of experiments, we noticed that prolonged irradiation of an aerated methanolic solution of PCI in its main absorption band (400 nm, ca 7 mW) resulted in a fast and strong (ca 8 fold) enhancement of luminescence intensity, pointing towards a photoinduced chemical transformation of the acridinium photocatalyst $PCI \rightarrow PCI'$. Meanwhile, NMR analysis of the mixture shows a lowering of the peaks associated to the initial acridinium catalyst although no new peak is observed, in agreement with a likely radical nature of PCI'. Interestingly, contrarily to what had been observed for PCI, addition of benzyltrimethylsilane 1a on PCI' in methanol resulted in unambiguous guenching of its luminescence, thus confirming the occurrence of a photoinduced ET process between the latter and benzyltrimethylsilane as attested by a Stern Volmer Plot of the evolution. In order to understand the factors governing PCI to PCI' activation, irradiation of PCI was also investigated in the absence of oxygen. Although initial marginal increase in luminescence intensity was observed upon photoirradiation, it was soon overwhelmed with a marked decrease thereby indicating rapid stagnation and degradation of photogenerated PCI'. Similar reaction in degassed medium was thus performed in the presence of a sacrificial oxidant (K₂S₂O₈) in an otherwise degassed medium, leading this time to a weaker enhancement of luminescence intensity than in the presence of molecular oxygen, yet no degradation of the photoactivated catalyst was observed (see SI for the details of these photoactivation experiments).

We then turned our attention to the fluoroalkylselenolation of alkyltrifluoroborates, for which similar luminescence experiments were performed in DMSO. Once again, luminescence of **PCI** in DMSO was too weak to enable performing satisfactory Stern-Volmer measurements with good accuracy. Possibility of electron transfer was thus only qualitatively probed by adding excess BnBF₃K into a 10^{-5} M solution of **PCI**: in these conditions, efficient quenching of the fluorescence signal was observed, thus evidencing the occurrence of a charge transfer between the two components upon photoirradiation of **PCI**. To our surprise, in striking contrast with the observation made in methanolic solution, no increase of the fluorescence signal was observed upon prolonged irradiation of a solution of **PCI** in DMSO, seemingly indicating differences in the nature of the initial stage of the catalytic cycle.

To address the complexity of this mechanism we tested photoinduced radical generation for both type of reactions using EPR, in the presence of various radical traps.

Both reactions were tested in five different conditions using a PBN radical trap to ensure detection of the formed species: conditions I involved irradiation of the catalyst only, in solution



in either methanol or DMSO depending on the investigated reaction. In conditions II, the silane or trifluoroborate reactant was added onto a similar reaction mixture as used in conditions I, while in conditions III, the added reactant was $TsSeCF_3$. Conditions IV involved in both cases the catalyst and the two reactants, in concentrations similar to those used in the reaction scope's studies. Finally, conditions V are exclusive to silanes and reflect the addition of $K_2S_2O_8$ to reactants and **PCI**.

Irradiation of a sample of **PCI** in pure DMSO in presence of PBN (Figure 1, top) (EPR conditions I) witnessed the formation of a complex radical species (30 %, q=2.0003, $a_N=4.4G$, $a_H=3.5G$, 3.5G, 2.9G, 2.9G, 2.3G, 2.3G, 2.3G, 2.3G), incompatible with a simple PBN adduct, which signature corresponds well to previously reported radical species of the acridinium catalyst.^[15] This species coexists with two other radical species. By analogy with existing literature,^[16] and considering the absence of any other reactant in the mixture, we attributed those two species to radical adducts of DMSO, one being O centred (35 %, g=2.0037, a_N =13.56G, a_H =1.52G), the other on most likely C or S centred (35 %; g=2.0035, a_N=14.3G, a_H=2.25G). This suggests the formation of a stable radical species of the photocatalyst generated upon photoactivation of the acridinium catalyst, presumably through electron transfer with DMSO. This acridinium radical species might play an important role in the fate of the photocatalytic reaction, as it will be discussed in the following. To our surprise, this signal was completely absent when similar conditions were applied in methanol, again pointing out a distinctive initial stage in the reaction. In the meantime, a radical species was observed which we ascribed to MeO' radical $(g=2.0035 a_N=14.35G a_H=2.8G)$. The latter species has been pre-



Figure 1. EPR spin-trapping spectra under blue LED irradiation in DMSO at r.t. Blue: experimental and red: simulated. Top: cond. I: **PCI**, PBN, DMSO, blue LED. Middle: cond. II: **PCI**, **6a**, PBN, DMSO, blue LED. Bottom: cond. III: **PCI**, **1**, PBN, DMSO, blue LED.





viously reported in literature, and its features have been studied by EPR using DMPO as a radical trap; thus, we decided to alleviate the ambiguity by substituting, in our reaction mixture, PBN by DMPO: comparison of the obtained features with literature data confirmed the formation of the latter species (See SI). While the same acridinium centred radical could still be observed when similar measurements were undertaken in the presence of reactant **1a** (BF₃K) (Figure 1, middle) (EPR conditions II), it disappeared when the latter was substituted for TsSeCF₃ (Figure 1, bottom) (EPR conditions III). This strongly suggests that a redox reaction takes place between the radical evolved from **PCI** and TsSeCF₃ which leads to continuous depletion of the acridinium radical population.

In the meantime, specific signatures occur in the EPR spectra, which features [with PBN: g=2.0042, a_N =8.22G; with DMPO: g=2.0034, a_N =12.9G, a_H =13.85G, (Figure 2) (EPR conditions III')] are consistent with what we ascribed in previous papers,^[8a] to adducts of selenium centred radicals ('SeCF₃) respectively in their oxidized and native form. In other words, in the reaction with alkyltrifluoroborates, TsSeCF₃ seemingly plays the role of a sacrificial oxidant in the photocatalytic process, which restores **PCI** in its catalytically active oxidation state. This hypothesis is consistent with the fact that the reaction outcome is virtually unaltered upon removal of both potassium persulfate and oxy-

gen from the reaction medium, in contrast with what is observed with the silane derivative. This observation is further supported by the fact that a similar DMSO centred radical as mentioned with (EPR conditions I) (g=2.0035, a_N =14.3G, a_H =2.25G) is also observed in both in conditions II and III, suggesting that a similar initial electron transfer step between acridinium and DMSO can take place in the three media.

Coming back to conditions II, a radical adduct, with features consistent with a benzyl radical (g=2.0035, a_N =14.6G, a_H = 2.8G)^[16,17] was also observed in both cases. The attribution of the latter was further confirmed by substituting PBN as a radical trap by DMPO (Figure 3)(conditions II') resulting in a clear signature of a benzyl adduct (g=2.0033, a_N =14.7G, a_H =20.5G). This constitutes definitive evidence that acridinium catalyst efficiently oxidizes both reactants through electron transfer, resulting in both cases in the production of a benzyl radical, which constitutes a mandatory common intermediate towards product formation.

As a final exploration of the reaction mechanism through EPR spectroscopy, all reactants and catalyst were mixed and the resulting sample was submitted to irradiation (conditions IV and V). In both cases, EPR signals corresponding to Bn⁻ adduct fully disappeared, suggesting that the latter had been consumed in the final step of the reaction to yield the target selenolated



Figure 2. EPR spin-trapping spectra under blue LED irradiation in MeOH at r.t. Blue: experimental and red: simulated. Cond. III': PCI, I, DMPO, MeOH, blue LED.



Figure 3. EPR spin-trapping spectra under blue LED irradiation in MeOH or DMSO at r.t. Blue: experimental and red: simulated. Top: cond. II': PCI, 1a, DMPO, MeOH, blue LED. Bottom: cond. II': PCI, 6a, DMPO, DMSO, blue LED.





product 2a. For what concerns the photoconversion of the silylated compound in methanol solution, the main species present in the reaction mixture could be attributed to the aforementioned MeO', while smaller amounts of a species compatible with either Ts⁻ or 'SeCF₃ could be observed (Figure 4, left). Conversely, in the photoconversion of the trifluoroborate derivative, the dominant presence of unreacted selenium centred radicals either in their native or oxidized forms [PBN: g=2.0035, a_N = 13.7G, a_H=1.6G, 15 %; g=2.0041, a_N=8.09G, 60 %; conditions IV' with DMPO: g=2.0034, a_N=12.6G, a_H=13.95G, 50 %, (Figure 4, right)] was observed. This is consistent with our observation that a major side-reaction of the photochemical process results in the formation of dimer (SeCF₃)₂, resulting in the detrimental recombination of 'SeCF₃ radical generated in the catalytic cycle, which is then unable to further evolve towards product formation.

As a summary, while both reaction mechanisms present many analogies (electron transfer step from either the silylated or trifluoroborate reactant to the photoactivated acridinium catalyst, resulting in the formation of a benzyl radical which then evolves through reaction with a 'SeCF₃ radical), our mechanistic study also highlights some important differences. Study of the photochemical conversion of silvlated reactants in methanol point out the necessity of a sacrificial oxidant, which closes the catalytic cycle but may also participate, as an alternative mechanism A' (SI page 9) suggested by our spectrofluorometric investigations, in an activation step of the catalyst PCI to its oxidized form PCI' prior to electron transfer towards reactant **1a**. In contrast, in the conversion of the trifluoroborate reactants in DMSO, the catalytic cycle is closed through reductive decomposition of TsSeCF₃ affording 'SeCF₃ radical) which in turn impact the reaction outcome. Thus, while photoconversion of silyl-



Figure 4. EPR spin-trapping spectra under blue LED irradiation in MeOH or DMSO at r.t. Blue: experimental and red: simulated. Left: cond. V and V': **PCI**, **I**, **1a**, K₂S₂O₈, spin trap, MeOH, blue LED. Right: cond. IV and IV': **PCI**, **I**, **6a**, spin trap, DMSO, blue LED.







Scheme 3. Proposed mechanisms.

ated reactant is unable to proceed in anaerobic conditions, reaction yield is almost unaffected by oxygen removal in the case of trifluoroborate. Furthermore, while reaction proceeds with a faster kinetic for the latter (as a result of the concomitant formation of 'Bn and 'SeCF₃ throughout the catalytic cycle) it is also characterized by the production of significant amounts of (SeCF₃)₂ as a major side product of the photocatalytic reaction.

Altogether, cross-examination of the EPR and fluorimetric data leads us to propose two distinct mechanisms for the photocatalyzed reaction depending on the reactant and solvent used for the reaction. On the one hand, mechanism involved in the photoconversion of silylated reactants (Scheme 3A) is in line with previously published literature on acridinium based catalyst; it involves the various radical species observed within our different EPR tests, and is consistent with the result of our SV measurements between acridinium and benzyltrimethylsilane. On the other hand, In the light of the obtained results and existing literature,^[18] we highlight a significantly different in the case of trifluoroborate reactant where i/ a photoinduced electron transfer takes place between PCI (photoreduction) and reactant 6a (photooxidation), which eventually results in the formation of two radical species: acridinium and Bn ii/ considering a stepwise mechanism, PCI catalyst is then restored upon oxidation of the acridinium radical by electron transfer to TsSeCF₃. The reaction generates a 'SeCF₃ radical species which iii/ recombines with Bn', affording the target compound. In parallel, homorecombination of 'SeCF₃ radical into a (SeCF₃)₂ dimer (observed as the main by-product of the catalytic reaction) constitutes a dead end of the photocatalytic process. This process is favoured at low concentration, since an alternative catalytic cycle can take place by an electron transfer between DMSO and PCI, ultimately leading to the build-up of 'SeCF₃, and its evolution to SeCF₃ dimer in the absence of Bn[•] (Scheme 3B).

Worth noting, in addition to the classical (and probably dominant) mechanism depicted in Scheme 3 our spectroscopic studies suggest that another alternative is possible, where an initial acridinium photoxidation step occurs, leading to the generation of an activated oxydized form of our catalyst (**PCI**') which in turns efficiently photooxydizes BnSiMe3, as illustrated throughout Stern-Volmer experiment with the latter (See SI, S9). This step analytically translates into a progressive dramatic increase of the luminescence signal, and a concomitant lowering of the intensity of the NMR peaks attributed to the acridinium species (see SI page 9, alternative mechanism).^[19]

To confirm the stepwise nature of the photocatalytic process, as suggested in both cases by the proposed mechanism, we investigated the impact of light switch on/off experiment on the reaction outcome. In both cases, the desired compound was formed only upon irradiation of the sample after various reaction times (see SI). In parallel, we observe that the dimer is constantly formed, even in the absence of light, for trifluoroborate derivatives probably resulting from photolysis of the S-Se bond due to the slight absorption of $TsSeCF_3$ at this wavelength, in agreement with our previously published works.

Conclusions

We demonstrated herein that photochemical transformation of aliphatic radical precursors, namely alkylsilanes as well as alkyltrilfuoroborates into their corresponding fluoroalkyl selenyl products could be achieved through photoinduced electron transfer processes using Fukuzumi photocatalyst **PCI** under blue LED irradiation. The developed methodologies appeared to be complementary regarding the scope and limitations encountered. Mechanistic investigations were undertaken by spectrofluoric measurements as well as EPR spectroscopy. In the light of the obtained results, it turned out that although closely related for what concerns the photoinduced electrons transfer step; mechanisms involved in the evolution of the as-generated



benzyl radical turned out to present significant differences in their late stage depending on the substrate and solvent employed for the transformation.

Experimental Section

To a flame-dried flask equipped with a magnetic stir bar are added **I**, **II** or **III** (0.4 mmol, 1 equiv.), alkyl radical precursor **1** or **6** (0.4 mmol, 1.0 equiv.), potassium persulfate (for silane derivatives only: 0.4 mmol, 1.0 equiv.), Mesitylacridinium perchlorate **PCI** (0.02 mmol, 5 mol-%), and anhydrous solvent (0.5 mL). The reaction is stirred at 25 °C under blue LED irradiation for 16 hours. Conversion is checked by ¹⁹F NMR with PhOCF₃ as internal standard. The reaction mixture is partitioned between *n*-pentane or Et₂O and water. The aqueous layer is extracted with *n*-pentane or Et₂O and the combined organic layers are dried with MgSO₄, filtered and concentrated to dryness. The crude residue is purified by chromatography to afford the desired product **2**, **3** or **4**.

Acknowledgments

C. G. held a doctoral fellowship from la region Rhône Alpes. The authors are grateful to the CNRS, ICBMS (UMR 5246), ICL (Institut de Chimie de Lyon) for financial support. The French Fluorine Network as well as the fédération RENARD and The Département de Chimie Moléculaire, Université Grenoble Alpes, are also acknowledged for their support.

Keywords: Trifluoromethylselenolation · Acridinium · Photochemistry · Alkylsilanes · Potassium alkyltrifluoroborates · Reaction mechanisms

- P. Kirsh, Modern Fluoroorganic Chemistry: Synthesis, Reactivity, Applications, Wiley, Weinheim, 2013.
- [2] a) A. Leo, C. Hansch, D. Elkins, *Chem. Rev.* **1971**, *71*, 525–616; b) B. Linclau,
 Z. Wang, G. Compain, V. Paumelle, C. Q. Fontenelle, N. Wells, A. Weymouth-Wilson, *Angew. Chem. Int. Ed.* **2016**, *55*, 674–678; *Angew. Chem.* **2016**, *128*, 684; c) Q. Glenadel, E. Ismalaj, T. Billard, *Eur. J. Org. Chem.* **2017**, *2017*, 530–533.
- [3] a) F. R. Leroux, B. Manteau, J.-P. Vors, S. Pazenok, *Beilstein J. Org. Chem.* **2008**, 4, 13; b) A. Tilili, F. Toulgoat, T. Billard, *Angew. Chem. Int. Ed.* **2016**, 55, 11726–11735; *Angew. Chem.* **2016**, 128, 11900.
- [4] a) A. Tilili, T. Billard, Angew. Chem. Int. Ed. 2013, 52, 6818–6819; Angew. Chem. 2013, 125, 6952; b) F. Toulgoat, S. Alazet, T. Billard, Eur. J. Org. Chem. 2014, 2014, 2415–2428; c) X.-H. Xu, K. Matsuzaki, N. Shibata, Chem. Rev. 2015, 115, 731–764; d) F. Toulgoat, T. Billard in Modern Synthesis Processes and Reactivity of Fluorinated Compounds (Eds.: H. Groult, F. R. Leroux, A. Tressaud), Elsevier, 2017, pp. 141–179.
- [5] A. Tlili, E. Ismalaj, Q. Glenadel, C. Ghiazza, T. Billard, Chem. Eur. J. 2018, 24, 3659–3670.
- [6] a) C. Chen, L. Ouyang, Q. Lin, Y. Liu, C. Hou, Y. Yuan, Z. Weng, Chem. Eur. J. 2014, 20, 657–661; b) M. Rong, R. Huang, Y. You, Z. Weng, Tetrahedron



2014, *70*, 8872–8878; c) C. Ghiazza, Q. Glenadel, A. Tilii, T. Billard, *Eur. J. Org. Chem.* **2017**, *2017*, 3812–3814; d) T. Dong, J. He, Z.-H. Li, C.-P. Zhang, *ACS Sustainable Chem. Eng.* **2018**, *6*, 1327–1335; e) C. Ghiazza, A. Kataria, A. Tilii, F. Toulgoat, T. Billard, *Asian J. Org. Chem.* **2019**, *8*, 675–678; f) S. Dix, M. Jakob, M. N. Hopkinson, *Chem. Eur. J.* **2019**, *25*, 7635–7639.

- [7] a) T. P. Yoon, M. A. Ischay, J. Du, *Nat. Chem.* 2010, *2*, 527; b) D. P. Hari, B. Konig, *Chem. Commun.* 2014, *50*, 6688–6699; c) N. A. Romero, D. A. Nicewicz, *Chem. Rev.* 2016, *116*, 10075–10166; d) M. H. Shaw, J. Twilton, D. W. C. MacMillan, *J. Org. Chem.* 2016, *81*, 6898–6926; e) N. Timothy, *Photochemical processes in continuous-flow reactors: from engineering principles to chemical applications*, World Scientific, 2017; f) L. Marzo, S. K. Pagire, O. Reiser, B. König, *Angew. Chem. Int. Ed.* 2018, *57*, 10034–10072; *Angew. Chem.* 2018, *130*, 10188; g) *Visible Light Photocatalysis in Organic Chemistry* (Eds.: C. R. J. Stephenson, T. P. Yoon, D. W. C. MacMillan), Wiley, 2018; h) C. Ghiazza, T. Billard, A. Tlili, *Chem. Eur. J.* 2019, *25*, 6482–6495.
- [8] a) C. Ghiazza, V. Debrauwer, C. Monnereau, L. Khrouz, M. Médebielle, T. Billard, A. Tlili, Angew. Chem. Int. Ed. 2018, 57, 11781–11785; Angew. Chem. 2018, 130, 11955; b) C. Ghiazza, L. Khrouz, C. Monnereau, T. Billard, A. Tlili, Chem. Commun. 2018, 54, 9909–9912; c) Q. Glenadel, C. Ghiazza, A. Tlili, T. Billard, Adv. Synth. Catal. 2017, 359, 3414–3420.
- [9] a) V. Corcé, L.-M. Chamoreau, E. Derat, J.-P. Goddard, C. Ollivier, L. Fensterbank, *Angew. Chem. Int. Ed.* 2015, *54*, 11414; *Angew. Chem.* 2015, *127*, 11576–11580; b) M. Jouffroy, D. N. Primer, G. A. Molander, *J. Am. Chem. Soc.* 2016, *138*, 475–478; c) K. Lin, R. J. Wiles, C. B. Kelly, G. H. M. Davies, G. A. Molander, *ACS Catal.* 2017, *7*, 5129–5133; d) S. Zheng, D. N. Primer, G. A. Molander, *ACS Catal.* 2017, *7*, 7957–7961; e) A. Cartier, E. Levernier, V. Corcé, T. Fukuyama, A.-L. Dhimane, C. Ollivier, I. Ryu, L. Fensterbank, *Angew. Chem. Int. Ed.* 2019, *58*, 1789–1793; *Angew. Chem.* 2019, *131*, 1803.
- [10] a) K. P. Dockery, J. P. Dinnocenzo, S. Farid, J. L. Goodman, I. R. Gould, W. P. Todd, J. Am. Chem. Soc. **1997**, *119*, 1876–1883; b) T. Maruyama, Y. Mizuno, I. Shimizu, S. Suga, J.-i. Yoshida, J. Am. Chem. Soc. **2007**, *129*, 1902–1903; c) M. Silvi, C. Verrier, Y. P. Rey, L. Buzzetti, P. Melchiorre, Nat. Chem. **2017**, *9*, 868; d) N. Khatun, M. J. Kim, S. K. Woo, Org. Lett. **2018**, 20, 6239–6243; e) M. Uygur, T. Danelzik, O. García Mancheño, Chem. Commun. **2019**, *55*, 2980–2983.
- [11] J. C. Tellis, D. N. Primer, G. A. Molander, Science 2014, 345, 433-436.
- [12] a) S. Fukuzumi, H. Kotani, K. Ohkubo, S. Ogo, N. V. Tkachenko, H. Lemmetyinen, J. Am. Chem. Soc. 2004, 126, 1600–1601; b) A. C. Benniston, A. Harriman, P. Li, J. P. Rostron, H. J. van Ramesdonk, M. M. Groeneveld, H. Zhang, J. W. Verhoeven, J. Am. Chem. Soc. 2005, 127, 16054–16064; c) S. Fukuzumi, K. Ohkubo, T. Suenobu, Acc. Chem. Res. 2014, 47, 1455–1464.
- [13] A. J. J. Lennox, G. C. Lloyd-Jones, Chem. Soc. Rev. 2014, 43, 412–443.
- [14] T. G. Beaumont, K. M. C. Davis, J. Chem. Soc. B 1970, 456-459.
- [15] H. Hiratsuka, K. Sekiguchi, Y. Hatano, Y. Tanizaki, Chem. Phys. Lett. 1978, 55, 358–360.
- [16] G. R. Buettner, Free Radical Biol. Med. 1987, 3, 259-303.
- [17] E. G. Janzen, B. J. Blackburn, J. Am. Chem. Soc. 1968, 90, 5909-5910.
- [18] a) D. A. Nicewicz, T. M. Nguyen, ACS Catal. 2014, 4, 355–360; b) K. A. Margrey, D. A. Nicewicz, Acc. Chem. Res. 2016, 49, 1997–2006.
- [19] G. Fausti, F. Morlet-Savary, J. Lalevée, A.-C. Gaumont, S. Lakhdar, Chem. Eur. J. 2017, 23, 2144–2148.

Received: July 22, 2019





Photoredox Catalysis

 Fluoroalkylselenolation of Alkyl Silanes/Trifluoroborates under Metal-Free Visible-Light Photoredox Catalysis



Aliphatic trifluromethylselenolated compounds were accessed under visible-light metal free conditions. The key to success is the use of alkylsilanes or potassium alkyltrifluoroborates in conjunction with trifluoromethylselenosulfonate and acridinium as photocatalyst.

DOI: 10.1002/ejoc.201901063