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Tri- and di-fluoroethylation of alkenes by visible light photoredox catalysis†

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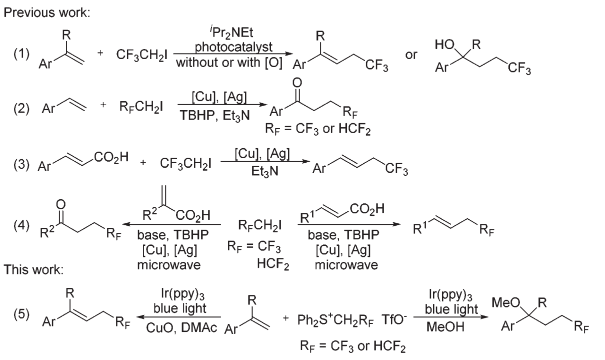
The tri- and di-fluoroethylation of alkenes with sulfonium salts, ($Ph_2S^+CH_2R_F$ TfO^-) (R_F = CF_3 or HCF_2), by visible light photoredox catalysis to give tri-/di-fluoroethyl alkenes or methoxytri-/di-fluoroethylation products are described. It was found that varying the reaction solvent led to changes in the reaction path.

Since both trifluoromethyl (CF_3) and difluoromethyl (HCF_2) substituents have emerged as valuable functionalities for modulating the physicochemical properties of pharmaceuticals and agrochemicals,[1] significant efforts have been directed towards the development of efficient methods for the incorporation of these two groups into organic molecules. Although both tri-/di-fluoromethylation[2] and tri-/di-fluoroethylation are efficient approaches for CF_3 or HCF_2 incorporation, tri-/di-fluoroethylation (only 2,2,2-trifluoroethylation and 2,2-difluoroethylation, respectively, are under discussion here) has been far less explored compared with tri-/di-fluoromethylation. In particular, only limited examples have been disclosed for difluoroethylation.[3] Various trifluoroethylation reagents including CF_3CH_2I,[4] CF_3CH_2OTs,[5] CF_3CHN_2,[6] CF_3CHCl_2,[7] $(CF_3CH_2SO_2)_2Zn$,[8] CF_3CO_2H[9] and ($CF_3CH_2I^+Ar$ TfO^-)[10] have been developed, but most of them are volatile, explosive (CF_3CHN_2) or water sensitive ($CF_3CH_2I^+Ar$ TfO^-).[11] The only difluoroethylation reagent so far is HCF_2CH_2I, which is a volatile liquid (bp: 87 °C) and thus could lead to practical inconvenience. Apparently, the development of operationally convenient tri- and di-fluoroethylation reagents is highly desirable.

Tri- and di-fluoroethylation of alkenes are straightforward approaches for CF_3 and HCF_2 incorporation. In 2013, Carreira and coworkers described the photocatalytic trifluoroethylation of styrenes to give trifluoroethyl alkenes (Scheme 1, eqn (1)).[12] Shortly afterwards, the group of Guo found that oxytrifluoroethylation occurred under photocatalytic conditions in the presence of an oxygen source (eqn (1)).[13] Xiang *et al.* disclosed a copper/silver-cocatalyzed oxidative coupling to give β-CF_3/HCF_2-substituted ketones (eqn (2)).[3b] Decarboxylation of cinnamic acids catalyzed by copper could also afford trifluoroethyl alkenes using the silver complex as an oxidizing reagent (eqn (3)).[14] Wang and coworkers found that microwave conditions could accelerate this process and the varied positions of the CO_2H substituent would result in different products (eqn (4)).[3c] All of these reactions are efficient and attractive, but the use of a volatile reagent (CF_3CH_2I or HCF_2CH_2I) is required.

We have previously shown that tri- and difluoroethyl sulfonium salts, ($Ph_2S^+CH_2R_F$ TfO^-) (R_F = CF_3 or HCF_2), could act as valuable sulfonium ylide reagents and fluorinated carbene precursors.[15] As visible light photoredox catalysis has proven to be a valuable synthetic tool for the generation of radical species from electrophilic reagents,[16] we speculated that reactive fluorinated radicals ($CF_3CH_2^\bullet$ or $HCF_2CH_2^\bullet$) may be produced from these sulfonium salts by visible light photoredox catalysis. In continuation of our research interest in the chemistry of fluorinated organic salts,[15,17] we have now investigated



Scheme 1 Tri- and di-fluoroethylation of alkenes.

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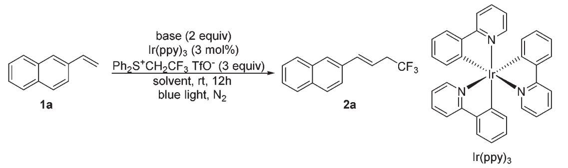
the use of these sulfonium salts as reagents for visible light photoredox catalyzed tri- and -di-fluoroethylation of alkenes. Like other fluorinated sulfonium salts,[18] these sulfonium salts show sufficient oxidizing power and therefore could enable tri- and di-fluoroethylation. Interestingly, we found that varying reaction solvents led to changes in the reaction process (Scheme 1, eqn (5)). Tri- and di-fluoroethylation occurred to give alkenes in DMAc, while difunctionalization was observed in MeOH.

Our initial attempts at the trifluoroethylation of alkene **1a** with trifluoroethylsulfonium salt, [$Ph_2S^+CH_2CF_3$ TfO^-] (reagent **I**), were successful to afford the desired product **2a** albeit in a low yield (Table 1, entry 1). The examination of the reaction solvent (entries 1–4) indicated that dimethylacetamide (DMAc) was a suitable solvent (entry 4). A brief survey of the photocatalyst revealed that only Ir(ppy)$_3$ was capable of catalyzing this reaction (entry 4 *vs.* entries 5–7) probably due to a high reduction potential of Ir(ppy)$_3$ in the excited state ($E_{1/2}^{IV/*III}$ = −1.73 V *vs.* SCE).[16a] The concentration had slight effect on the reaction, and increasing the concentration led to an increase in the yield to 62% (entry 8 *vs.* entries 4 and 9). Increasing the loading of reagent **I** (entry 10) or prolonging the reaction time (entry 11) did not increase the yield. This reaction should be accompanied by a deprotonation process, and thus the presence of a base may be favorable. Various organic and inorganic bases were investigated (entries 12–17) and it was found that the use of CuO gave the product in 75% yield (entry 16). The photocatalyst was essential for this transformation, and no product was observed without using the photocatalyst (entry 18).

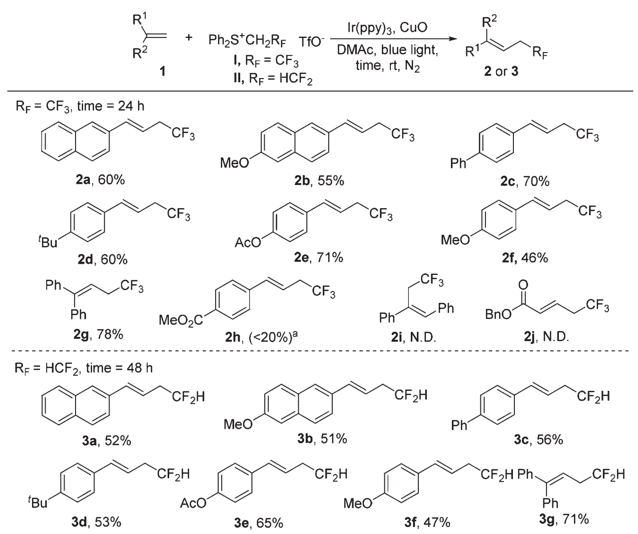
With the optimal conditions (Table 1, entry 16) in hand, we explored the substrate scope of tri- and di-fluoroethylation of alkenes to give CF_3CH_2- and HCF_2CH_2-substituted alkenes (Scheme 2). Various aryl alkenes were converted smoothly into the desired trifluoroethylation products (**2a**–**2g**), and a good reactivity was observed even for sterically hindered 1,1-disubstituted alkene (**2g**). The reaction was apparently affected by electronic effects of substituents. A strong electron donating group (**2f**) or an electron withdrawing group (**2h**) would suppress the desired conversion. A Cl or CN substituent present in the phenyl group in styrene also resulted in low yields (<30%). The internal alkene was inert towards trifluoroethylation under these conditions, probably due to strong steric effects (**2i**). No desired product was observed for the transformation of α,β-unsaturated alkene (**2j**). In the case of alkyl alkenes such as 4-phenyl-1-butene, complex mixtures were obtained partially because deprotonation can occur at two different positions to give regioisomers. Compared with trifluoroethyl sulfonium salt **I**, difluoroethyl sulfonium salt **II** shows lower reactivity and therefore a longer reaction time (48 h) was required (**3a**–**3g**). Moderate yields were obtained for trifluoroethylation. All the products obtained above (except **2g** and **3g**) were *E*-isomers, as indicated by the ^1H NMR coupling constant of around 16.0 Hz for the two H atoms in the C═C bond and by comparing the NMR data with the reported literature values (see the ESI†).

Table 1 Screening reaction conditions for trifluoroethylation[a]



Entry	Solvent	Base	Yield[b]
1	MeCN (2 mL)	—	7
2	DMF (2 mL)	—	44
3	DMSO (2 mL)	—	35
4	DMAc (2 mL)	—	52
5[c]	DMAc (2 mL)	—	0
6[d]	DMAc (2 mL)	—	0
7[e]	DMAc (2 mL)	—	0
8	DMAc (1.5 mL)	—	62
9	DMAc (2.5 mL)	—	49
10[f]	DMAc (1.5 mL)	—	62
11[g]	DMAc (1.5 mL)	—	60
12	DMAc (1.5 mL)	$^iPr_2NEt$	14
13	DMAc (1.5 mL)	Et_3N	15
14	DMAc (1.5 mL)	$NaHCO_3$	30
15	DMAc (1.5 mL)	$KHCO_3$	25
16	DMAc (1.5 mL)	CuO	75
17	DMAc (1.5 mL)	ZnO	48
18[h]	DMAc (1.5 mL)	—	0

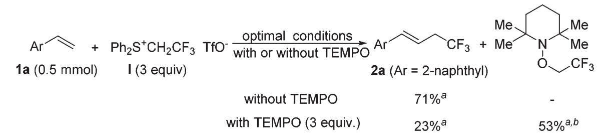
[a] Reaction conditions: Substrate **1a** (0.2 mmol), ($Ph_2S^+CH_2CF_3$ TfO^-) (3 equiv.), Ir(ppy)$_3$ (3 mol%) and base (2 equiv.) in solvent irradiated with blue LEDs at room temperature for 12 h. [b] The yields were determined by ^{19}F NMR spectroscopy. [c] [Ir(ppy)$_2$(dtbbpy)]PF$_6$ was used as the photocatalyst instead of Ir(ppy)$_3$. [d] [Ru(bpy)$_3$](PF$_6$)$_2$ was used as the photocatalyst instead of Ir(ppy)$_3$. [e] [Ru(phen)$_3$](PF$_6$)$_2$ was used as the photocatalyst instead of Ir(ppy)$_3$. [f] 4 equivalents of reagent **I** were used. [g] The reaction time was 18 h. [h] No photocatalyst was used.



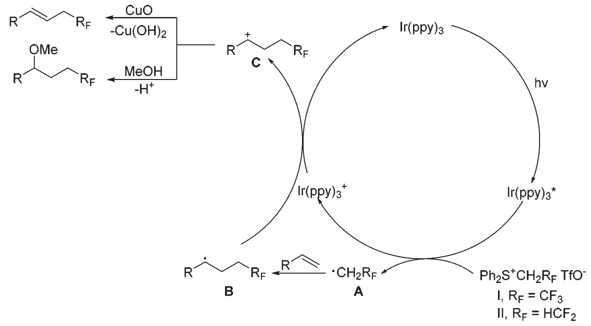
Scheme 2 Tri- and di-fluoroethylation to give alkenes. Isolated yields. Reaction conditions: Substrate **1a** (0.5 mmol), reagent **I** or **II** (3 equiv.), Ir(ppy)$_3$ (3 mol%) and CuO (2 equiv.) in DMAc (3 mL) irradiated with blue LEDs at room temperature for 24 h or 48 h. [a] The yield was determined by ^{19}F NMR spectroscopy.

Interestingly, we found that subtle changes in reaction solvents resulted in a different reaction process. The use of methanol as the solvent for trifluoroethylation of the substrate **1a** gave the methoxytrifluoroethylation product **4a** in 77% ^{19}F NMR yield. Low solubility of sulfonium salt **I** (completely soluble in DMAc) in MeOH could lead to a decrease in the efficiency of light absorption, meaning that the yield may be increased by reducing the loading of salt **I**. Indeed, the ^{19}F NMR yield was slightly increased to 82% without the presence of CuO even by reducing the loading of salt **I** to 2 equiv. The substrate scope of methoxytrifluoroethylation of alkenes was investigated by using 2 equiv. of sulfonium reagents (Scheme 3). Various aryl alkenes were reactive towards methoxytrifluoroethylation and moderate yields were obtained (**4a**–**4e**). The use of ethanol instead of methanol as the reaction solvent gave the ethoxytrifluoroethylation product in a low yield. Gratifyingly, 57% yield could be obtained (**4f**) in the presence of a cosolvent, DMAc. Methoxydifluoroethylation was found to be quite sluggish using methanol as the single solvent. To our delight, the MeOH/DMAc cosolvent could afford the desired products in moderate yields by prolonging the reaction time (**5a**–**5e**).

The redox potentials of trifluoroethylsulfonium salt and difluoroethylsulfonium salt measured by cyclic voltammetry were −1.517 V *vs.* SCE and −1.237 V *vs.* SCE, respectively (see the ESI†) (for comparison, the reduction potential of CF_3CH_2I is −1.70 V),[19] indicating that these two sulfonium salts may be reduced by reducing the intermediate, photoexcited complex $[Ir(ppy)_3{}^*]$ ($E_{1/2}^{IV/*III}$ = −1.73 V *vs.* SCE),[16a] to generate radical species ($CF_3CH_2{}^\bullet$ and $HCF_2CH_2{}^\bullet$), thus allowing for the above tri- and di-fluoroethylation reactions. Indeed, we found that trifluoroethylation of alkene **1a** was dramatically suppressed in the presence of a radical scavenger, TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) (Scheme 4). Moreover, TEMPO-CH_2CF_3 was obtained in 53% yield, indicating the generation of $CF_3CH_2{}^\bullet$ radicals in this process.

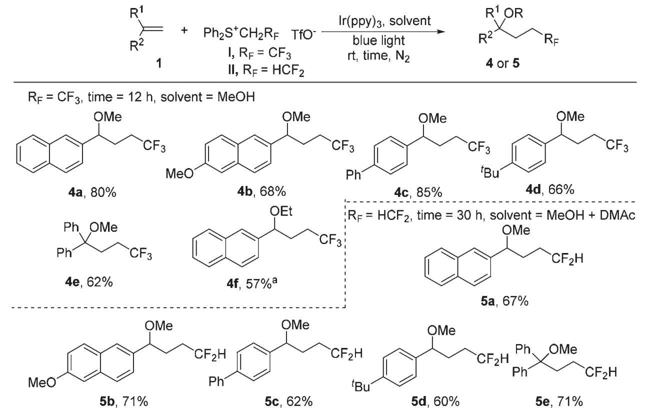


Scheme 4 Evidence for the radical process. ^{a} The yield was determined by ^{19}F NMR spectroscopy; ^{b} the yield was calculated based on TEMPO as the limiting reagent.



Scheme 5 The proposed reaction mechanism.

On the basis of the above results, the reaction mechanism is proposed as shown in Scheme 5. Upon irradiation with visible light, $Ir(ppy)_3$ undergoes photoexcitation to give an excited species $Ir(ppy)_3{}^*$, which is a strong reductant ($E_{1/2}^{IV/*III}$ = −1.73 V *vs.* SCE)[16a] and capable of donating an electron to sulfonium salts to generate an oxidized catalyst $Ir(ppy)_3{}^+$ and radical species **A**, $R_FCH_2{}^\bullet$ (R_F = CF_3 or HCF_2). The radical species **A** is readily trapped by alkenes to produce the radical intermediate **B**, oxidation of which with $Ir(ppy)_3{}^+$ releases the photocatalyst and affords the cation intermediate **C**. Deprotonation of the intermediate **C** furnishes alkenes, and the nucleophilic attack of methanol gives methoxytri-/di-fluoroethylation products.



Scheme 3 Methoxytri- and methoxydi-fluoroethylation of alkenes. Isolated yields. Reaction conditions: Substrate **1a** (0.5 mmol), reagent **I** or **II** (2 equiv.) and $Ir(ppy)_3$ (2 mol%) in DMAc (3 mL) or DMAc/MeOH (v/v = 2 mL/1 mL) irradiated with blue LEDs at room temperature for 12 h or 30 h. ^{a} EtOH/DMAc (v/v = 1 mL/2 mL) was used as the solvent instead of MeOH to obtain product **4f**.

Conclusions

In summary, we have described tri- and di-fluoroethylation of alkenes with sulfonium salts, ($Ph_2S^+CH_2R_F$ TfO^-) (R_F = CF_3 or HCF_2), by visible light photoredox catalysis to give tri-/di-fluoroethyl alkenes or methoxytri-/di-fluoroethylation products. It is interesting that varying the reaction solvent led to changes in the reaction process, and difunctionalization of alkenes was observed in the presence of methanol. This work represents the first protocol for the use of convenient sulfonium reagents in the solvent-dependent tri-/di-fluoroethylation reactions. Sulfonium salts, ($Ph_2S^+CH_2R_F$ TfO^-) (R_F = CF_3 or HCF_2), may become attractive tri-/di-fluoromethylation reagents because of their stability, facile accessibility, and ease of handling.

Conflicts of interest

The authors declare no competing financial interest.

Acknowledgements

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