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2,2,2-Trifluoroethylation of Styrenes with Concomitant Introduction of a Hydroxyl Group from Molecular Oxygen by Photoredox Catalysis Activated by Visible Light

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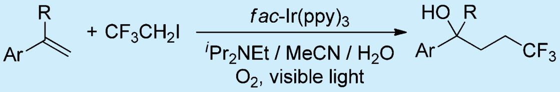
Ⓢ *Supporting Information*

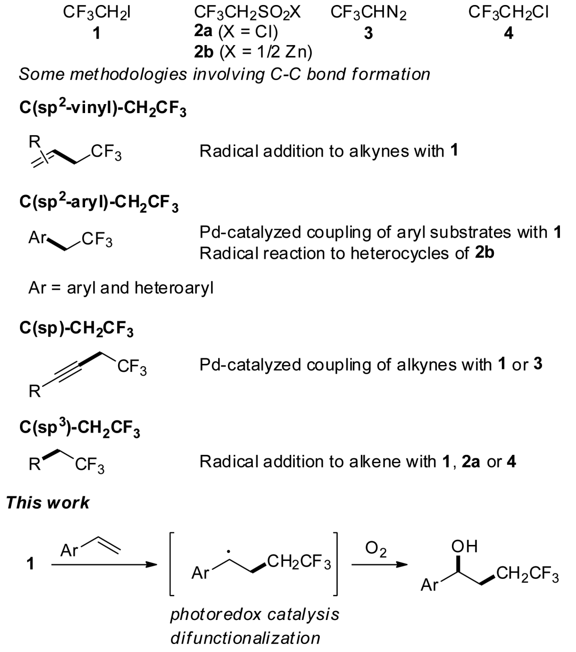
ABSTRACT: The visible-light-induced photoredox difunctionalization reactions of styrenes with 1,1,1-trifluoro-2-iodoethane under an oxygen atmosphere in the presence of water give γ-trifluoromethyl alcohols. In this radical reaction, the oxygen atom in the product originates from molecular oxygen, and water is shown to be important to promote the reaction.



Synthetic methodologies of CF_3-containing compounds have attracted attention because of the broad applications of such compounds in fluorinated agrochemicals, pharmaceuticals, and functional materials.[1] Molecules containing a 2,2,2-trifluoroethyl group can be synthesized from benzyl, allylic, and propargyl halides or trifluoroacetate,[2] and also from terminal alkenes[3] with multiple trifluoromethylation reagents, such as Chen's reagent (methyl fluorosulfonyldifluoroacetate), Ruppert−Prakash reagent ((trifluoromethyl)trimethylsilane), Togni reagent (1-(trifluoromethyl)-1,2-benziodoxol-3(1*H*)-one and trifluoromethyl 1,3-dihydro-3,3-dimethyl-1,2-benziodoxole), and Umemoto's reagent (*S*-(trifluoromethyl)dibenzothiophenium salts). The first direct 2,2,2-trifluoroethylation on iodobenzene, despite the low yield, was reported by McLoughlin and Thrower in 1969.[4] To date, the direct 2,2,2-trifluoroethylation has been categorized into C(sp^2-vinyl)−CH_2CF_3,[5] C(sp^2-aryl)−CH_2CF_3,[6] C(sp)−CH_2CF_3,[7] and C(sp^3)−CH_2CF_3 formations[5a,8] through CF_3CH_2 radical or metal-mediated cross-coupling processes (Scheme 1). The amount of research on 2,2,2-trifluoroethylation has been far less than that on trifluoromethylation.

Difunctionalization of a carbon−carbon double bond is a powerful synthetic strategy for compounds with various functional groups.[9] Dioxygen, as a clean oxygen source, has been used in the difunctionalization of a C−C double bond.[10,11] Recently, a variety of organometallic complexes, which could be activated by visible light, have been widely applied in the development of new organic reactions.[12] Owing to the electron-withdrawing ability of the fluorine atom, polyfluorinated substrates usually exhibit a higher redox potential than their nonfluorinated analogues and thus tend to be utilized in photoredox synthesis activated by visible light.[13] Among the visible-light-promoted fluoroalkylation reactions are the difunctionalization reactions.[14−22] However, to the best of our knowledge, visible-light-induced hydroxytrifluoroethylation of a double bond has never been reported.

Scheme 1. Methodologies to CF_3CH_2-Containing Molecules by Direct 2,2,2-Trifluoroethylation



Within our investigations on the organic transformation at the neighboring carbon to a CF_3 group,[23] we were interested in activating 1,1,1-trifluoro-2-iodoethane (CF_3CH_2I, **1**) to a radical

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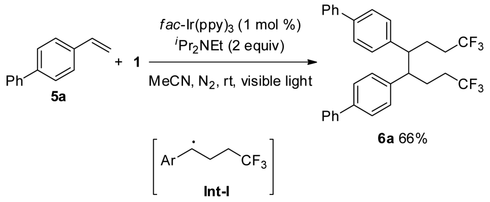
using visible-light-induced photoredox catalysis. We have already reported the sulfinatodehalogenation of **1** with alkyl-substituted alkenes and that this reaction cannot be applied to styrenes.[5a] Herein, by using a visible-light-activation system, we develop a difunctionalization method by the concomitant introduction of a hydroxyl group and a 2,2,2-trifluoroethyl group to each end of a double bond in styrenes (Scheme 1).

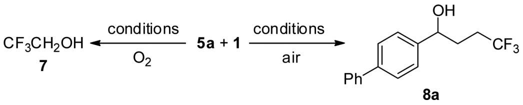
The reaction of styrene **5a** with **1** was carried out in the presence of a catalytic amount of photoredox catalyst *fac*-Ir(ppy)$_3$ and excessive *N,N*-diisopropylethylamine (Hünig's base) upon irradiation of visible light using acetonitrile as solvent under a nitrogen atmosphere at room temperature for 24 h. Although there are several new products after completion of the reaction, as identified by ^{19}F NMR spectroscopy, we were able to isolate **6a** as a major product in 66% yield. Compound **6a** is a 1:1 mixture of two diastereomers, which can be partially separated by repeat chromatography on silica gel. Other photoredox catalysts, such as Ru(bpy)$_3$(PF$_6$)$_2$, Ir(ppy)$_2$(dtbbpy), and Ir(dF(CF$_3$)ppy)$_2$(dtbbpy)PF$_6$, were examined and provided lower yields of products as determined by identification of the reaction mixtures by ^{19}F NMR spectroscopy.

We proposed that **6a** was formed from the dimerization of benzyl radical **Int I**, which resulted from the addition of the 2,2,2-trifluoroethyl radical to styrene **5a** (Scheme 2). The dimerization showed that the benzyl radical was stable and had a long lifetime. Molecular oxygen is usually used as a radical scavenger. To suppress the dimerization of the benzyl radical, we carried out the reaction under air or in an oxygen atmosphere. Unexpectedly, two special products were observed, which kindled our interest in investigating the reaction (Scheme 3). The reaction under an oxygen atmosphere gave 2,2,2-trifluoroethyl alcohol, which was identified by comparison with **7**. Further tosylation of **7** to give CF$_3$CH$_2$OTs (**7′**) confirmed the structure. In the reaction under an air atmosphere, in addition to 2,2,2-trifluoroethyl alcohol, another alcohol **8a** (about 20% determined by GC−MS) was separated and identified by multiple analytical methods. Most of the 4-phenylstyrene **5a** was recovered, and the dimerization was suppressed.

Scheme 2. Photoredox Reaction under a Nitrogen Atmosphere



Scheme 3. Photoredox Reaction under an Air or Oxygen Atmosphere[a]



[a]Conditions: **5a** (0.2 mmol), **1** (0.6 mmol), *fac*-Ir(ppy)$_3$ (0.002 mmol), and ^{i}Pr$_2$NEt (0.6 mmol) in acetonitrile (4 mL) under a molecular oxygen or air atmosphere upon irradiation of 24 W fluorescence lamp, rt, 48 h.

We proposed that the moisture in air might contribute to the difference between the two reactions. To confirm the role of water in this reaction, we examined the effect of water content on the difunctionalization in 0.2 mmol scale of **5a** in 4 mL of CH$_3$CN (Figure 1, other conditions as in Scheme 3). In an air atmosphere, the yield reached 50% in the presence of 120 μL of water. In an oxygen atmosphere, 500 μL of water was needed to enhance the yield to 77%. These experiments suggest that water can promote hydroxytrifluoroethyl difunctionalization.

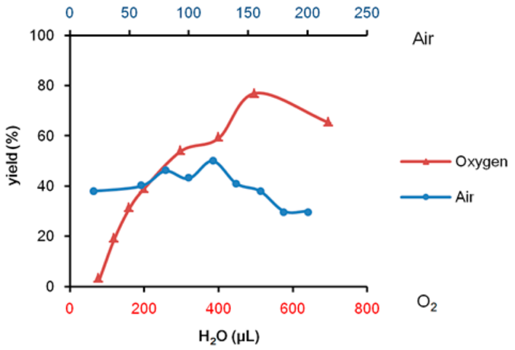
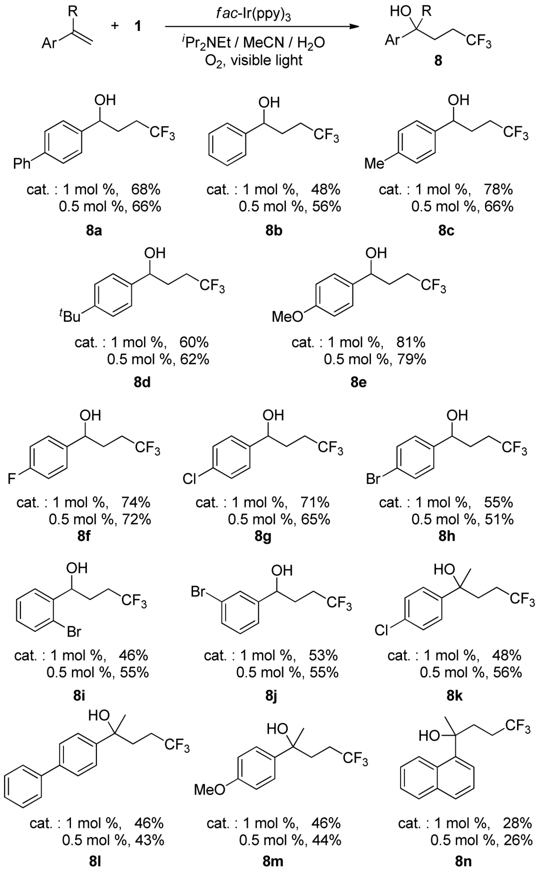


Figure 1. Effect of water content on hydroxytrifluoroethylation. (a) The yields were determined by ^{1}H NMR spectroscopy with additional CH$_2$Br$_2$ as an internal standard.

Under the optimal conditions, we investigated the scope of alkenes (Scheme 4). The presence of an electron-donating (**8c**−**e**) or halogen (**8f**−**k**) substituent on the aromatic ring was well-tolerated under the optimized conditions. For the α-CH$_3$-substituted styrene (**8k**−**n**), we could also obtain the difunctionalized products. In the reaction with **5a**, there were several sides products, and one of the side products, though in a small amount, was **6a**. In the reaction with 1-(prop-1-en-2-yl)naphthalene (**5n**), 59% of **5n** was recovered. No dimerization was found. The reaction conditions cannot be applied to aliphatic alkene and alkyne. Using this method, the hydroxyl and trifluoroethyl group can be introduced in one step, which is difficult to obtain by the conventional strategy. The hydroxyl group is widely present in physiologically active molecules, and the CF$_3$ group is known to be able to enhance lipophilicity, binding selectivity, and metabolic stability. This approach to the γ-trifluoromethyl alcohols will be useful.

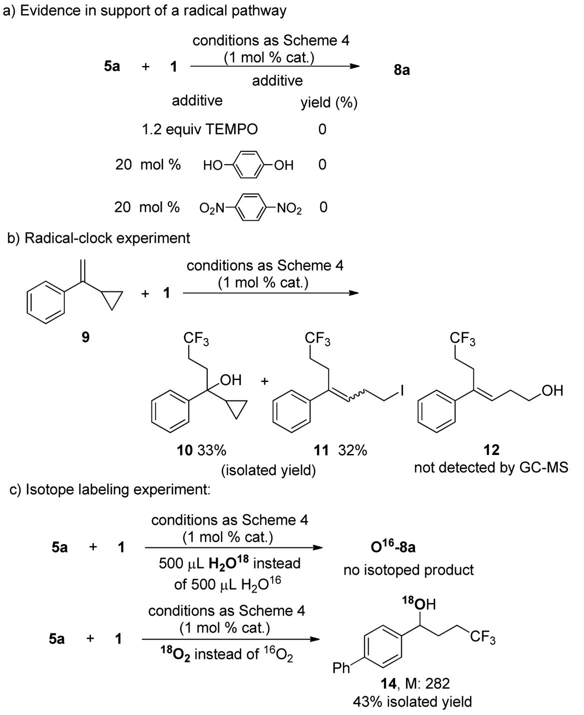
A preliminary investigation of the reaction mechanism suggested that the reaction most likely involved a 2,2,2-trifluoroethyl radical. The yield of the target product (**8a**) was reduced from 77% to 0% when the reaction was conducted under the optimized conditions in the presence of TEMPO, hydroquinone, and 1,4-dinitrobenzene (Scheme 5a). Furthermore, TEMPO−CH$_2$CF$_3$ was detected in the reaction mixture by ^{19}F NMR spectroscopy and GC−MS. These experiments prove that the reaction is an SET/radical process. A radical clock experiment was also conducted, which confirmed the existence of a trifluoroethyl radical in the reaction mixture (Scheme 5b). In the experiment, the normal product **10** was formed with a yield of isolated product of 33%. Additionally, we isolated the ring-opened product with an iodine substituent (**11**) but not with an hydroxyl group (**12**). Under the standard conditions, when we replaced H$_2$O by H$_2{}^{18}$O, we isolated the product **8a** and no ^{18}O-labeled product was detected. This means that the oxygen atom in the product **8a** does not originate from H$_2$O (Scheme 5c). We also carried out the reaction under an ^{18}O$_2$ atmosphere and

Scheme 4. Scope of Styrenes[a,b]



[a] Reaction conditions: alkenes (0.2 mmol), **1** (0.6 mmol), *fac*-Ir(ppy)$_3$ (0.001 or 0.002 mmol), ^{i}Pr$_2$NEt (0.6 mmol), MeCN (4 mL), and H_2O (0.5 mL) under a molecular oxygen atmosphere, irradiation with a 24 W fluorescence lamp, rt, 48 h. [b] Isolated yields are shown.

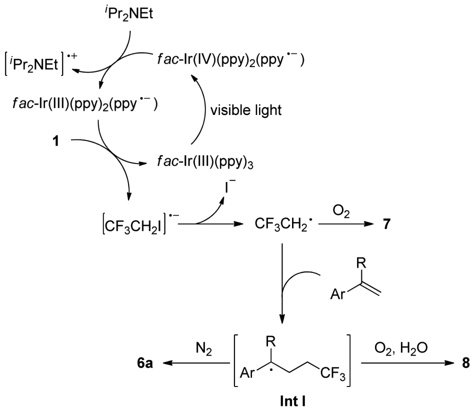
Scheme 5. Mechanistic Experiments



obtained product **14** with a mass of 282. This confirms that the oxygen atom in product **8a** originates from molecular oxygen.

Based on these experimental results, we propose that the trifluoroethyl difunctionalization of alkenes proceeds by the mechanism shown in Scheme 6. First, *fac*-Ir(III) (ppy)$_3$ undergoes metal-to-ligand charge transfer (MLCT) irradiated by visible light, producing a redox-active photoexcited state, *fac*-Ir(IV)(ppy)$_2$(ppy$^{\bullet-}$). ^{i}Pr$_2$NEt acts as a reductive quencher, and the *fac*-Ir(IV) (ppy)$_2$(ppy$^{\bullet-}$) accepts an electron from ^{i}Pr$_2$NEt to generate the *fac*-Ir(III)(ppy)$_2$(ppy$^{\bullet-}$) species, which has a high reducing ability. Single-electron reduction of CF_3CH_2I by *fac*-Ir(III)(ppy)$_2$(ppy$^{\bullet-}$) yields a radical anion and then generates a 2,2,2-trifluoroethyl radical ($CF_3CH_2^{\bullet}$). If the reaction is carried out under an O_2 atmosphere, the trifluoroethyl radical can be captured by molecular oxygen to produce CF_3CH_2OH. In another pathway, the trifluoroethyl radical can react with styrene to give benzyl radical **Int I**, which yields the hydroxyl products **8** promoted by water in the presence of molecular oxygen. If the reaction is carried out under a N_2 atmosphere, the benzyl radical **Int I** couples with itself to give the dimerization product **6a**.

Scheme 6. Proposed Mechanism



In conclusion, we have developed a visible-light-induced method for the hydroxytrifluoroethylation of styrenes under a molecular oxygen atmosphere in the presence of water. In this radical reaction, the oxygen atom in the product originates from molecular oxygen. However, the presence of H_2O is very important for the reaction. Without the presence of water, the product is 2,2,2-trifluoroethanol, and no difunctionalized product is observed. This reaction can be applied to styrenes possessing electron-donating and halogen substituents at the aryl rings and also with substituents at the β-positions of double bonds.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b02177.

Experimental procedures, characterization and NMR spectra of new compounds (PDF)

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Notes

The authors declare no competing financial interest.

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