



Fluoroalcohols: versatile solvents in hypervalent iodine chemistry and syntheses of diaryliodonium(III) salts

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ABSTRACT

We first introduced 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and 2,2,2-trifluoroethanol (TFE) as unique solvents for reactions involving hypervalent iodine-mediated phenolic oxidations in the 1980s, in which the fluoroalcohols have been successfully utilized as stabilizing solvents of the reactive cationic intermediates, generated *in situ* by the action of phenyliodine(III) diacetate (PIDA) and phenyliodine bis(trifluoroacetate) (PIFA). This pioneering study produced a breakthrough in hypervalent iodine chemistry, and many synthetic applications that enable a variety of transformations have appeared utilizing this unique medium. For example, the single-electron-transfer (SET) oxidation ability of PIFA toward phenyl ethers has been discovered for the first time in HFIP and TFE, taking advantage of the unique acid-like behaviors to stabilize the aromatic cation radicals. More recently, the catalytic strategy of hypervalent iodine reagents has found extensive applications with the aid of the fluoroalcohols to produce highly reactive catalytic species under mild conditions. The fluoroalcohols are now widely used as versatile solvents not only in hypervalent iodine chemistry, but also in other organic syntheses. This manuscript for the Special Issue deals with the background of the hypervalent iodine chemistry and a new topic concerning the utility of fluoroalcohols for the synthesis of diaryliodonium(III) salts.

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1. Introduction

Most chemical transformations known to date in organic synthesis were carried out in the solution phase using solvents. The solvents employed would work to break the self-association between the molecules and dissolve the reactants and reagents, allowing the opportunity for all components to react on a molecular level in one flask. In exothermic processes, the heat transport ability of the medium is particularly important, and reactions would often result in proceeding disorderly, and sometimes even explosively, in the absence of solvents. Many other properties of solvents have been summarized as macroscopic physical parameters and constants, such as the boiling point, density, dipole moment, hydrogen-bond donor and acceptor capability, etc., by which the solvent effect on organic reactions would be now quantitatively estimated.¹ 'A reaction cannot be separated from the medium in which it is performed',² and no one can neglect this long-live theme when performing the reactions.

For this objective, the selection of an appropriate solvent is indispensable for enhancing the efficiency of most chemical processes. Even recently, progress regarding a new solvent foundation

is active and the number of available solvents is increasing. In particular, the use of fluorous liquids,³ ionic liquids,⁴ and supercritical fluids⁵ as solvents is actively being promoted with the growing impetus of greener synthetic processes.

The fluoroalcohols, i.e., 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) and 2,2,2-trifluoroethanol (TFE), appear as a group of solvents with unique properties (Fig. 1). These are significantly different from classic alcohols, and the presence of the fluoroalkyl groups provides many specific properties that no other solvents show. The highly polar [$E_T(30)=69.3$ for HFIP, 59.8 for TFE],^{6a} but low nucleophilic [$N=-4.23$ (HFIP), -2.78 (TFE)]⁷ fluoroalcohols are unique solvents that exhibits a high ionizing power [$Y=3.8$ (HFIP), 1.8 (TFE)]⁷ with a pK_a higher [9.3 (HFIP), 12.4 (TFE)]^{6b} than that of acetic acid [$pK_a=5.2$]. In addition, HFIP, and TFE have quite excellent hydrogen-bond donor abilities [$\alpha=1.96$ (HFIP), 1.51 (TFE)].^{6c} Due to these

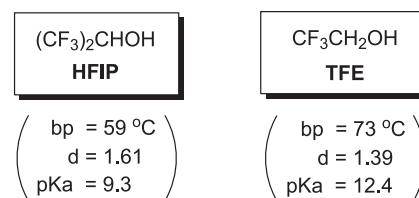


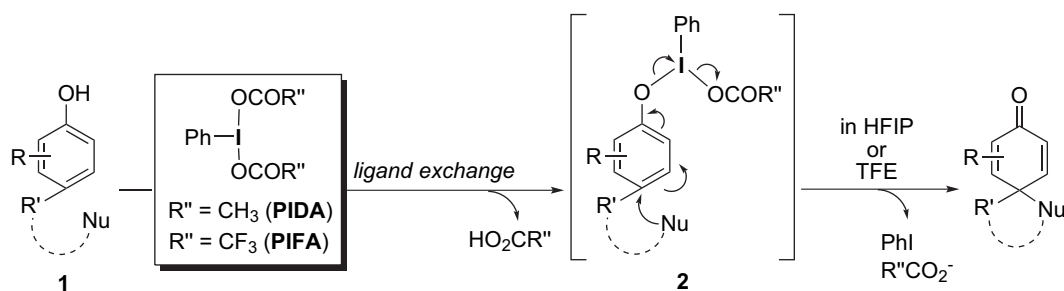
Figure 1. Fluorinated alcohols as solvents in organic synthesis.

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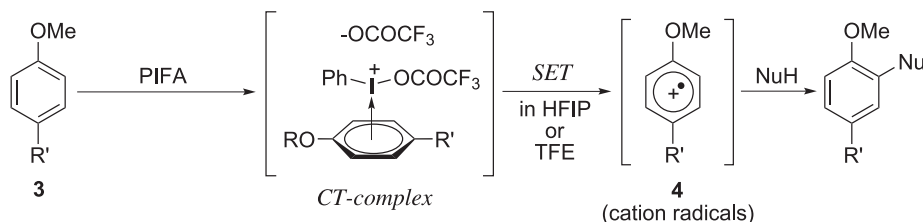
unique properties, the fluoroalcohols sometimes dramatically direct the course of reactions as the solvent. That is, the synthetic potential of fluoroalcohols as an attractive and unique alternative to ordinary commercially available solvents has been growing in interest in modern organic synthesis.⁸

Although the solvents show the characteristic properties, the reports that applied the unique solvents were relatively sporadic in organic synthesis until recently. In the 1980s, the authors introduced for the first time these alcohols as polar, but less nucleophilic solvents, in hypervalent iodine chemistry to perform the oxidation of phenols for the purpose of synthesizing spirodienones,⁹ and applied the reaction to the synthesis of natural products having the spirodienone moiety.¹⁰ Thereafter, the ability to stabilize aromatic cation radicals was first established for HFIP and TFE during our continuing study of the single-electron-transfer (SET) oxidations of aromatic compounds using hypervalent iodine reagents.¹¹ These two cases are good examples that the fluoroalcohols directed the reactive intermediates and the course of the reactions as solvents.

For the oxidation of phenols **1** using hypervalent iodine reagents, i.e., PIDA and PIFA, the reactions are typically explained by the two-electron-transfer processes that involve the initial ligand exchange at the iodine centers (Scheme 1).¹² Thus, the iodine(III) centers of PIDA and PIFA would react with phenolic oxygens to give the phenoxyiodine(III) intermediates **2**. The excellent leaving ability of the high-valent iodine atoms may smoothly generate the phenoxenium ions in the solvents, HFIP and TFE,¹³ which were trapped by various concomitant types of nucleophiles,⁹ thus



Scheme 1. Hypervalent iodine(III)-mediated oxidations of phenols in HFIP and TFE.



Scheme 2. Aromatic cation radical generation in HFIP and TFE in the hypervalent iodine-induced SET processes.

completing the oxidations. Based on the combination of the versatility of the reactions with the excellent features of the reagents as safe and low-toxic alternatives to heavy metal oxidizers, such as lead, mercury, cadmium, and thallium-based agents,¹⁴ the oxidation of phenols basis of the umpolung of aromatic rings using hypervalent iodine reagents is recognized, for natural product synthesis, as the most practical and important biomimetic dearomatization process.^{15–17}

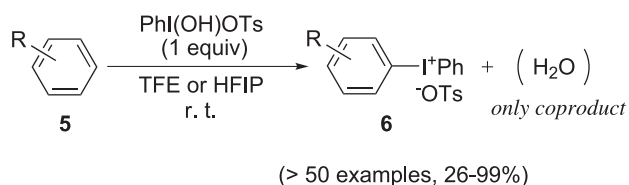
On the other hand, the hypervalent iodine(III) reagents also act as excellent SET oxidizing agents in the fluoroalcohol solvents. In 1991, we reported the aromatic azidation of phenyl ethers by the treatment of PIFA in HFIP in the presence of TMSN₃.^{11a} Interestingly, the novel aromatic azidation only proceeded in the fluoroalcohol solvents. For the novel aromatic substitution process, therefore,

a new mechanism should apparently be involved. A few years later, we determined the generation of aromatic cation radicals **4** produced by the SET oxidation through the charge-transfer (CT)-complex of phenyl ethers **3** and PIFA (Scheme 2), based on detailed UV and ESR spectroscopic measurements.^{11b} This is the first strong evidence that clarified the SET oxidation ability of hypervalent iodine reagents toward aromatic rings, the success of which has found further applications for the synthesis as the method of C–H functionalization to directly introduce a wide range of nucleophiles (AcO, ArS, SCN, CN, β-dicarbonyl compounds, etc.)^{11b–g} into aromatic compounds and for the oxidative biaryl couplings.¹⁸ Applications of HFIP as a solvent for the spectroscopic studies of cation radicals have now become the reasonable choice.^{8b}

The pioneering works including ours have triggered a recent rapid promotion of their use as solvent in hypervalent iodine chemistry as well as in the vast field of organic synthesis, and the utility seems to go beyond the initial perspective as new unique outcomes are revealed.

Recently, during our study of hypervalent iodine chemistry, we found a remarkable rate enhancement caused by the addition of fluoroalcohols for the condensation of aromatic compounds and hypervalent iodine reagents.¹⁹ This finding has given rise to the opportunity for realizing a highly efficient dehydrative approach for diaryliodonium(III) salts. Notably, the fluoroalcohols were indispensable for the success of each reaction, while other typical solvents were unsatisfactory in terms of the reaction rate and yield of the products, which seems to support involvement of the Wheland type of cationic σ-complexes suggested in the related

studies of diaryliodonium(III) synthesis.²⁰ In the following sections, we discuss the versatility of our new dehydrative approach to diaryliodonium(III) salts in fluoroalcohol solvents (Scheme 3). The method is very clean, only producing water as the sole coproduct.



Scheme 3. Direct dehydrative approach to diaryliodonium(III) salts in fluoroalcohol solvents, TFE and HFIP.

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