

Hydrogen-Bond Activation Enables Aziridination of Unactivated Olefins with Simple Iminoiodinanes

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Abstract

Iminoiodinanes comprise a class of hypervalent iodine reagents that is often encountered in nitrogen-group transfer (NGT) catalysis. In general, transition metal catalysts are required to effect efficient NGT to unactivated olefins because iminoiodinanes are insufficiently electrophilic to engage in direct aziridination chemistry. Here, we demonstrate that 1,1,1,3,3,3-hexafluoroisopropanol (HFIP) activates *N*-arylsulfonamide-derived iminoiodinanes for the metal-free aziridination of unactivated olefins. ¹H NMR and cyclic voltammetry (CV) studies indicate that hydrogen-bonding between HFIP and the iminoiodinane generates an oxidant capable of direct NGT to unactivated olefins. Stereochemical scrambling during aziridination of 1,2-disubstituted olefins is observed and interpreted as evidence that aziridination proceeds via a carbocation intermediate that subsequently cyclizes. These results demonstrate a simple method for activating iminoiodinane reagents, provide analysis

of the extent of activation achieved by H-bonding, and indicate the potential for chemical non-innocence of fluorinated alcohol solvents in NGT catalysis.

Keywords

Hypervalent iodine; aziridination; H-bond activation; electrochemistry; nitrene transfer

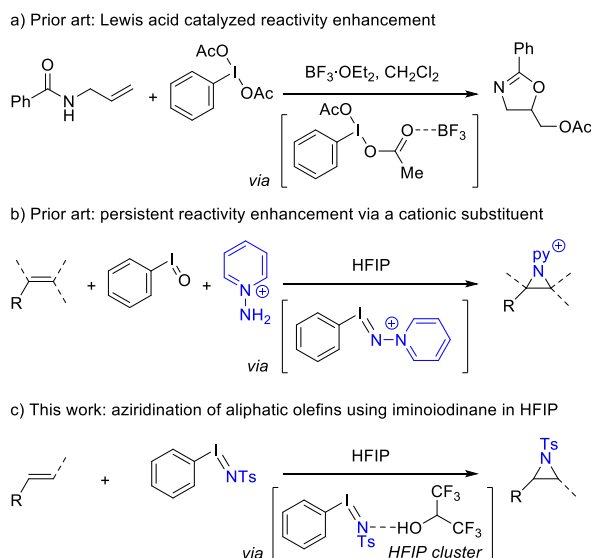
Introduction

Hypervalent iodine reagents find widespread application in selective oxidation chemistry due to the combination of synthetically tunable iodine-centered electrophilicity and the diversity of substrate functionalization mechanisms that can be accessed [1,2]. Large families of iodine(III)- and iodine(V)-based reagents have been developed — including iodobenzene diacetate ($\text{PhI}(\text{OAc})_2$, PIDA), Koser's reagent ($\text{PhI}(\text{OH})\text{Ots}$), Zhdankin's reagent ($\text{C}_6\text{H}_4(o\text{-COO})\text{IN}_3$, ABX), and Dess–Martin periodinane (DMP) — and find application in an array of synthetically important transformations including olefin difunctionalization, carbonyl desaturation, alcohol oxidation, and C–H functionalization [3,4]. Iminoiodinanes ($\text{ArI}=\text{NR}$) are a subclass of hypervalent iodine reagents that function as nitrene equivalents in synthesis [5,6]. The direct reaction of iminoiodinanes with olefins, which could be envisioned to give rise to aziridines directly, is typically not observed and thus families of transition metal catalysts or photochemical procedures have been developed to enable this transformation [7-9].

The reactivity of hypervalent iodine reagents can be enhanced via Lewis acid catalysis [10]. For example, PIDA becomes a stronger oxidant upon coordination of BF_3oEt_2 , enabling chemistry that was not available in the absence of Lewis acid activation

(Scheme 1a) [11,12]. A variety of Lewis acid activators have been reported [13-22] in an array of group-transfer reactions, including trifluoromethylation, cyanation, and fluorination. Brønsted acid activation has also been described in some group-transfer schemes [23-25], and in particular, fluorinated alcohol solvents, such as 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), have been reported to enhance hypervalent iodine reactivity by providing a H-bonding solvent cluster that enhances the electrophilicity of the iodine center [26,27]. Despite the prevalence of acid-activation in promoting carbon [28], oxygen [29,30], sulfur [31], chlorine [32], and fluorine [33], transfer reactions of hypervalent iodine compounds, these strategies have not been applied to activation of iminoiodinanes for nitrene transfer chemistry.

We recently developed a metal-free aziridination of unactivated olefins via the intermediacy of an *N*-pyridinium iminoiodinane (Scheme 1b) [34]. We rationalized the enhanced reactivity towards olefin aziridination as a result of charge-enhanced iodine-centered electrophilicity arising from the cationic *N*-pyridinium substituent. Based on those observations, we reasoned that similarly enhanced reactivity might be accessed by Lewis acid or H-bonding iminoiodinanes. Here, we describe the HFIP-promoted aziridination of unactivated olefins with *N*-sulfonyl iminoiodinane reagents, which are among the most frequently encountered iminoiodinanes in NGT catalysis (Scheme 1c). This simple procedure afforded the formal transfer of various nitrogen groups, including those derived from complex amines, and is complementary to other metal-free aziridinations of unactivated olefins [35-39].



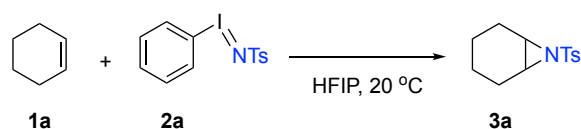
Scheme 1: a) Lewis acid activation of hypervalent iodine reagents can enhance the reactivity of these reagents. b) Charge-tagged iminoiodinanes display enhanced reactivity in aziridination reactions with unactivated olefins (ref. 34). c) Here, we demonstrate that H-bonding between fluorinated alcohol solvents and iminoiodinanes can enable direct metal-free aziridination of unactivated olefins with simple iminoiodinanes.

Results and Discussion

Treatment of cyclohexene (**1a**) with a stoichiometric amount of simple iminoiodinane such as PhINTs (**2a**) in CH_2Cl_2 resulted in <10% conversion to the corresponding *N*-sulfonyl aziridine (**3a**), which is consistent with the previously reported need for transition metal catalysts to promote nitrene transfer catalysis (Table 1, entry 1) [40,41]. In contrast, combination of PhINTs (2.0 equiv) with **1a** in HFIP afforded **3a** in 67% NMR yield (entry 2). Lowering the loading of iminoiodinane **2a** to 1.5 or 1.0 equivalents decreased the reaction yield to 28% and 22%, respectively (entries 3 and 4). Increasing the reaction temperature negatively affected the efficiency of aziridination: Reactions performed at 30 or 50 °C afforded **3a** in 50% and 43% yield,

respectively (entries 5 and 6). Replacing HFIP with 2,2,2-trifluoroethanol (TFE), which is also a commonly encountered fluorinated alcohol solvent, resulted in a 16% yield of **3a** (entry 7). Performing aziridination with 10 equivalents of HFIP in CH₂Cl₂ resulted in a 38% yield (entry 8). The aziridine product **3a** was not observed when other Lewis or Bronsted acids, such as BF₃·Et₂O, TfOH, or Zn(OTf)₂, were employed in CH₂Cl₂ (entry 9). Attempts to generate **2a** *in situ* using 1 equivalent of TsNH₂ (**4**) in combination with 1 or 2 equivalents of PhIO (**5**) resulted in aziridination yields of 19% and 27%, respectively (entries 10 and 11). Finally, exclusion of ambient light had no impact of the aziridination of **1a** with PhINTs (entry 12) [42,43].

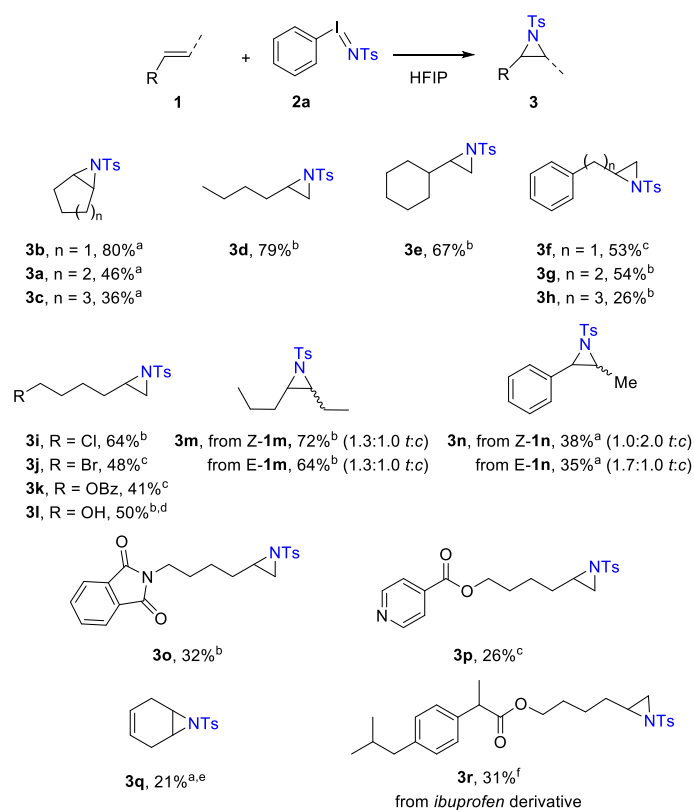
Table 1: Optimization of HFIP-promoted aziridination of cyclohexene (**1a**). Conditions: 0.20 mmol **1a**, 0.40 mmol PhINTs **2a**, 1.0 mL HFIP, N₂ atmosphere, 20 °C, 16 h. Yield was determined via ¹H NMR using triethyl 1,3,5-benzenetricarboxylate as internal standard.



Entry	Deviation from Standard Condition	Yield (%)
1	CH ₂ Cl ₂	<10%
2	none	67
3	1.5 equiv. PhINTs	28
4	1.0 equiv. PhINTs	22
5	30 °C	50
6	50 °C	43
7	TFE	16
8	10 equiv. HFIP in CH ₂ Cl ₂	38
9	5 equiv. BF ₃ ·Et ₂ O, TfOH, or Zn(OTf) ₂ in CH ₂ Cl ₂ ,	0
10	1 equiv. 4 and 1 equiv. 5 instead of 2a	19
11	1 equiv. 4 and 2 equiv. 5 instead of 2a	27
12	no ambient light	64

With metal-free aziridination conditions in hand, we explored the scope and limitations of the HFIP-promoted aziridination of unactivated olefins (Scheme 2). For cyclic substrates, aziridination of cyclopentene, cyclohexene, and cycloheptene afforded the corresponding aziridines in modest to high isolated yields: **3b** (80%), **3a** (46%), and **3c** (36%), respectively. Acyclic olefin 1-hexene underwent aziridination to **3d** in 79% yield (reaction performed at 50 °C); aziridination of vinylcyclohexane proceeded in 67% yield of **3e**. Allyl benzene engages in aziridination to deliver **3f** in 53% yield, while homoallylbenzene and pent-4-en-1-ylbenzene undergo aziridination in yields of 54% (**3g**) and 26% (**3h**), respectively. The procedure was compatible with various commonly encountered functional groups, such as chloride (**3i**), bromide (**3j**), and benzoyl (**3k**). Noticeably, an unprotected alcohol is tolerated in our procedure, with product **3l** delivered at 50% NMR yield; **3l** is sensitive to column chromatography, and thus aziridine-opening to a cyclic ether was observed (31% isolated yield) during purification. Aziridination of *cis*- or *trans*-4-octene afforded aziridine **3m** as a 1.3:1.0 *trans*:*cis* mixture in 72% and 64% yield, respectively. While many styrene derivatives polymerize in HFIP [44], 1,2-disubstituted styrene derivatives were sufficiently stable to engage in the developed aziridination reaction, with *cis*- or *trans*- β -methylstyrene **1n** furnishing aziridine **3n** as diastereomeric mixtures with comparable yields of 38% (1.0:2.0 *trans*:*cis*, from *cis*-**1n**) and 35% (1.7:1.0 *trans*:*cis*, from *trans*-**1n**). Olefins containing *N*-heteroaromatics such as phthalimide and pyridine undergo aziridination to give **3o** (32% yield) and **3p** (26% yield). Similarly, 1,4-cyclohexadiene was compatible in this procedure, giving product **3q** in 21% yield (see Figure S1 for other challenging substrates). Finally, ibuprofen-derived olefin **1r** underwent aziridination to afford **3r** in 31% yield. Overall, these results highlight the efficacy of a simple activation

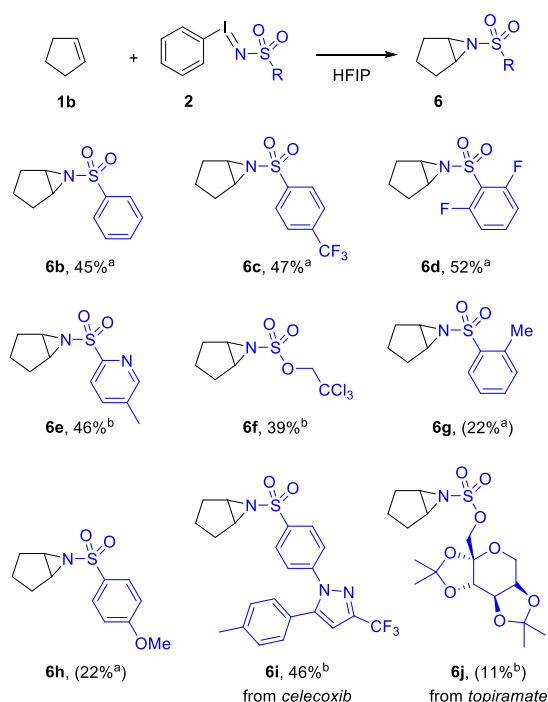
protocol and the generality of H-bond activation of iminoiodinanes for direct aziridination, albeit with modest efficiency for some substrates.



Scheme 2: Scope and limitations of HFIP-promoted direct aziridination with iminoiodinane reagents. Conditions: 0.20 mmol **1**, 0.40 mmol **2a**, 1.0 mL HFIP, N₂ atmosphere. a) 20 °C for 16 h, b) 50 °C for 16 h, c) 50 °C for 48 h, d) NMR yield, e) 1.2 equiv. PhINTs was used, and f) 4.0 equiv. of PhINTs at 20 °C for 48 h.

The impact of iminoiodinane structure on the efficiency of HFIP-promoted direct aziridination was next investigated (Scheme 3). For this purpose, cyclopentene was selected as it underwent efficient aziridination with PhINTs. A family of iminoiodinanes (**2**) was synthesized from PIDA and the corresponding sulfonamide derivative. Reaction of phenylsulfonamide-derived iminoiodinane with cyclopentene afforded *N*-phenylsulfonyl aziridine **6b** in 45% yield, while *N*-*p*-trifluoromethylsulfonyl aziridine **6c** was furnished in 47% yield. Similarly, 2,6-difluorosulfonyl substituted iminoiodinane **2d**

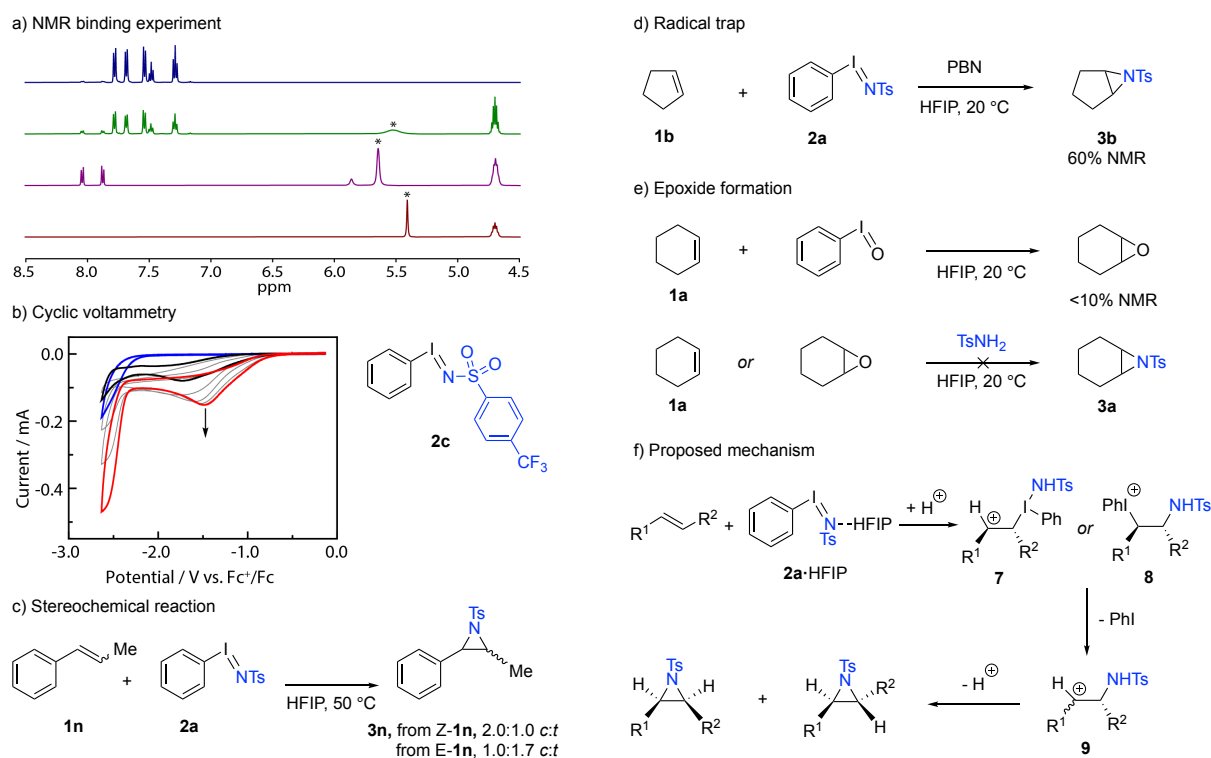
afforded aziridine **6d** in 52% yield. The aziridination procedure was tolerant of heterocyclic substituents on the iminoiodinane *N*-5-methylpyridin-2-ylsulfonyl aziridine **6e** could be obtained in 46% yield. The *N*-Tces group (Tces = trichloroethylsulfamate) could also be transferred to afford **6f** in 39% yield. Finally, the iminoiodinane derived from celecoxib (**2i**) could be used to transfer this drug moiety to furnish aziridine **6i** in 46% yield. In general, the efficiency of aziridination correlates with the stability of the relevant iminoiodinane reagent, with higher yields attributed to more electron rich sulfonamide substitution such as **2a**. Relatively electron deficient iminoiodinanes are less efficient but are also more prone to decomposition (see Figure S2 for challenging iminoiodinanes). *In situ* preparation of the iminoiodinane intermediates is possible, and for those reagents that undergo facile decomposition, aziridination is more efficient using these conditions (yields for *in situ* generated iminoiodinanes are in parentheses in Scheme 3, with *N*-*o*-methyl (**6g**) and *N*-*p*-methoxysulfonyl (**6h**) aziridines obtained each in 22% yield; the drug topiramate could also be transferred to furnish aziridine **6j** in 11% yield).



Scheme 3: Scope of nitrogen group transfer in the aziridination of aliphatic olefins. Condition using synthesized iminoiodinane: 0.20 mmol cyclopentene **1b**, 0.40 mmol iminoiodinane **2**, 1.0 mL HFIP, N₂ atmosphere. Condition using *in situ* generated iminoiodinane: 0.20 mmol cyclopentene **1b**, 0.20 mmol sulfonamide, 0.40 mmol iodosylbenzene (PhIO), 1.0 mL HFIP, N₂ atmosphere. a) 20 °C for 16 h, b) 40 °C for 16 h.

We carried out a series of experiments to clarify the origin of the observed reactivity enhancement of *N*-arylsulfonyl iminoiodinanes in the presence of HFIP (Scheme 4a). First, ¹H NMR was employed to examine the interaction between HFIP and iminoiodinane **2c** in CD₃CN (compound **2c** was chosen over **2a** due to its increased solubility in nonprotic solvents). In a sample of **2c** with 4 equivalents of HFIP, a broad signal for O–H proton of HFIP was observed at 5.52 ppm with a FWHM = 56.6 Hz (Scheme 4a). This resonance was broader and more downfield than that of free HFIP in CD₃CN (5.41 ppm with FWHM = 5.0 Hz), suggesting a hydrogen bonding interaction between HFIP and **2c**, and similar observations were also reported for the hydrogen bonding between HFIP and PIDA [30,33]. During this experiment, a small amount of hydrolysis product 4-(trifluoromethyl)benzenesulfonamide was also observed (1.2 mM, signals at 8.0, 7.9, and 5.86 ppm), but this compound did not greatly contribute to the broadening of O–H proton signal of HFIP as a separate 4.0 mM sample of the sulfonamide resulted in O–H proton signal of HFIP being at 5.64 ppm with FWHM = 11.3 Hz. Second, to evaluate the impact of HFIP on the redox chemistry of PhINTs, we collected cyclic voltammograms (CVs) of iminoiodinane **2c** in MeCN in the presence of varying HFIP increments (Scheme 4b). The CV of 25 μL HFIP in MeCN showed no electrochemical events between –2.0–0 V. The CV of **2c** in the absence of HFIP showed a reductive current (*i*_p = –0.80 mA) at peak potential (*E*_{pr}) of –1.72 V vs.

Fc^+/Fc . Upon addition of 5.0 μL of HFIP (1.2 equiv. with respect to **2c**), the current increased to -1.22 mA , signaling the binding of HFIP to **2c** enhanced the electron transfer kinetics between the hypervalent iodine reagent and the electrode [45]. Further additions of HFIP further increased the current response and shifted the peak potential, with 10 μL and 15 μL of HFIP showing responses with E_{pr} at -1.55 V and -1.52 V , respectively. The titration showed a saturation point at 25 μL of HFIP (6.0 equiv. with respect to **2c**), at which the CV of **2c** showed an $E_{\text{pr}} = -1.47\text{ V}$ and -1.52 mA current. Overall, the addition of HFIP results in a 250 mV shift in the reduction of **2c**. The increased facileness of reduction is consistent with H-bonding between HFIP and **2c**, which results in a more potent oxidant and gives rise to the observed HFIP-promoted olefin aziridination chemistry.



Scheme 4: a) The broadening of the hydroxide proton (denoted by asterisk *) of HFIP in the presence of iminoiodinane **2c** suggesting hydrogen bonding observed in ^1H NMR spectra (CD_3CN) of: 8.0 mM **2c** with no HFIP (blue line —), 8.0 mM **2c** with 32 mM

HFIP (green line —), 4.0 mM of 4-(trifluoromethyl)benzenesulfonamide with 32 mM HFIP (purple line —), only 32 mM HFIP (red line —). b) Cyclic voltammogram of iminoiodinane **2c** (8.0 mM) with varying amounts of HFIP in 5.0 mL solution of MeCN (0.10 M TBABF₄) under N₂ atmosphere: **2c** with no HFIP (black line —); **2c** with 5, 10, 15 μ L HFIP (grey line —); **2c** with 25 μ L HFIP (red line —); only 25 μ L (blue line —). c) Diastereomeric mixtures of aziridines are obtained from aziridination reactions of *cis*- or *trans*- β -methylstyrene, suggesting aziridine formation likely to operate via a step-wise pathway. d) Aziridination is not impacted by the presence of potential radical traps. e) PhIO, potentially generated by PhINTs hydrolysis, can give rise to epoxidation products. Epoxides are not on-path to the observed aziridines. f) Proposed reaction mechanism.

A number of observations are relevant to the mechanism by which unactivated olefin aziridination is accomplished by the HFIP-activated iminoiodinanes: First, the reaction of PhINTs with either *cis*- or *trans*- β -methylstyrene (**1n**) in HFIP afforded aziridine **3n** as a mixture of 2.0:1.0 *cis:trans* (from *cis*-**1n**) and 1.0:1.7 *cis:trans* (from *trans*-**1n**) (Scheme 4c). The formation of diastereomeric mixtures suggests that aziridination proceeds in a stepwise fashion. The dissimilarity of the diastereomeric ratios from *cis*- and *trans*- starting materials indicates that the potential intermediate is too short lived for complete ablation of the starting material stereochemistry. Second, the aziridination of cyclopentene by PhINTs in the presence of a radical trap *N*-*tert*-butyl- α -phenylnitrone (PBN) afforded the aziridine product **3b** in 60% NMR yield (Scheme 4d), suggesting a radical pathway was unlikely to be operative.

An ¹H NMR experiment was carried out to probe the speciation of **2a** in HFIP, and we observed that **2a** underwent reversible ligand exchange with alcohol solvent to afford ArI(OR)₂ and TsNH₂ (Figure S3); similar solvolysis of PhIO in HFIP has been reported

[10]. Reaction between cyclohexene and PhIO (2 equiv.) in HFIP delivered <10% of cyclohexene oxide; meanwhile, both cyclohexene and cyclohexene oxide were shown to be unreactive towards sulfonamide (Scheme 4e), suggesting that epoxidation is not on path to the observed aziridines. For discussion of side-products and reaction mass balance, see Figure S4. Based on these observations, we favor a mechanism in which Brønsted-acid activated iminoiodinane reacts directly with the olefin to generate a short-lived alkyl-bound iodine **7** or iodonium species **8** (Scheme 4f). Ligand coupling from **7** or extrusion of iodobenzene from **8** would furnish a carbocation intermediate (**9**) which could undergo C–C bond rotation prior to ring closure to form the aziridine product. Such a process would account for the simultaneous stereochemical scrambling observed and the lack of radical trapping noted.

Conclusion

In conclusion, we describe the activation of simple iminoiodinane reagents by fluorinated alcohols, such as HFIP. While most iminoiodinane reagents do not engage aliphatic olefins in the absence of transition metal catalysts, the addition of HFIP enables direct aziridination to be observed. The enhanced reactivity is rationalized as resulting from H-bonding between HFIP and the nitrogen center of the iminoiodinane reagents. ¹H NMR data are consistent with such an association and electrochemical data collected in the presence of increasing HFIP concentrations are consistent with H-bonding affording an increasingly strong oxidant. These results demonstrate a simple method for activating iminoiodinane reagents and indicate the potential for chemical non-innocence of fluorinated alcohol solvents in NGT catalysis.

Supporting Information (if any)

Experimental procedures and characterization data. Original spectra of new compounds. Optimization details.

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