Mild Silver-Mediated Geminal Difluorination of Styrenes using an Airand Moisture-Stable Fluoroiodane Reagent**

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Abstract: An air- and moisture-stable fluoroiodane in the presence of $AgBF_4$ is suitable for selective geminal difluorination of styrenes under mild reaction conditions. One of the C-F bonds is formed by transfer of electrophilic fluorine from the hypervalent iodine reagent, while the other one arises from the tetrafluoroborate counterion of silver. Deuterium-isotopelabelling experiments and rearrangement of methyl styrene substrates suggest that the reaction proceeds through a phenonium ion intermediate.

Organofluorines are very important substances in pharmaceutical and agrochemical industries and have also had an increasing role in medicinal research and diagnostics.^[1] As organofluorine compounds are specific regulator substances, inhibitors, or biomarkers, constant development of new methodologies for their selective synthesis is a very important task in synthetic chemistry. The appearance of new stable, electrophilic fluorinating reagents and methodologies allowed the extension of the new methodologies for selective synthesis of a large variety of organofluorine compounds.^[2] In recent years creation of single C-F bonds, introduction of CF₂, and trifluoromethylation reactions have received a lot of attention. Of these major areas the introduction of a CF₂ group is probably the least developed.^[3] Nevertheless, the difluoromethyl group proved to be an important motif in enzyme inhibitors.^[4] This property is probably a result of the ability of the CF₂H group to donate hydrogen bonds,^[5] and, thus serve as a bioisoster for hydroxy and thiol moieties.^[6] Furthermore, very recently CF₂ groups have found new applications in medicinal diagnostics as well. A new trend in the synthesis of trifluoromethyl-group-based PET tracers is substitution of suitable sp³ difluoromethyl groups with ¹⁸F to obtain ¹⁸FCF₂ functionalities.^[7]

The early methods for introducing difluoromethyl groups to organic molecules were mainly based on the application of highly reactive inorganic fluorinating reagents, such as DAST,^[8] Deoxofluor,^[9] and XeF₂.^[10] However, application of these reagents may lead to problems in functional-group tolerance and selectivity, and causes hazardous HF development upon contact with water. The recently reported methodologies are usually based on metal-catalyzed cross-coupling of various CF₂ carriers with aryl halides and boronates. For example the groups of Amii,^[11] Hartwig,^[12] Prakash and Olah,^[13] and Qing^[14] used a copper catalyst (or mediator), while the group of Zhang^[15] used palladium catalysis for the introduction of a CF2 group to organic substrates. Baran and co-workers have published a series of papers on C-H difluoromethylation by CF₂H radicals.^[16] Introduction of the difluoromethyl group with consecutive difluorination reactions is a less common approach compared to the abovementioned cross-coupling of CF2 units with the organic substrate. Tang and co-workers^[17] have shown that consecutive geminal difluorination of aromatic benzyl groups can be achieved by using Selectfluor as a fluorine source in combination with a silver catalyst under oxidative conditions. A similar reaction has been reported by Chen and coworkers^[18] using visible-light-promoted reactions under metal-free conditions. For both reactions a radical mechanism was postulated.

Recently, development of new fluorination reactions by application of hypervalent iodine reagents has attracted considerable attention.^[2a,b,19] As a part of our synthetic fluorochemistry program,^[20] we have studied the potential use of the hypervalent fluoroiodane $\mathbf{1}^{[19f,21]}$ as an electrophilic organofluorinating reagent [see Eq. (1)]. The fluoroiodane 1 is an air- and moisture-stable crystalline compound and structural analogue of the Togni reagent,^[2a,22] which has been one of the most successful electrophilic trifluoromethylating reagents in organic synthesis. Another attractive property is that 1 can be obtained from its chloro analogue by addition of KF.^[21b] Thus, synthesis of **1** using KF involves a simple umpolung method by changing a nucleophilic fluorine into an electrophilic one. This simple possibility for umpolung of the fluorine atom can be a useful feature for the development of new tracers for medicinal diagnostics.^[23] The first report by Legault and Prévost^[21a] on the attempts to use 1 for C-F bond-formation reactions was disappointing. In contrast to its bromo analogue, 1 was not suitable for the electrophilic halogenation of anisole. According to Stuart and co-workers^[19f] **1** reacts with 1,3-diketoesters and 1,3-diketones in the presence of TREAT-HF to give mono- and difluoro products, respectively. As far as we know, this paper by Stuart and coworkers^[19f] has been the only report on the application of 1 for creating C–F bonds.

We have now found [Eq. (1)] that mixing of equimolar amounts of the styrene **2a**, **1**, and $AgBF_4$ (**3**) results in the difluoro compound **4a** under mild reaction conditions (40 °C). The reaction was very clean and the yield of the isolated product was over 50%, thus indicating that in the geminally difluorinated product one of the fluorine atoms was derived

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from 1, while the other one originated from the BF_4^- counterion of silver. Thus, under mild reaction conditions, using air- and moisture-stable starting materials a formal F_2 addition to **2a** could be performed.



Deviation from the above mentioned [Eq. (1)] optimal reaction conditions led to either lower yields of isolated **4a** or no reaction of **2a** (Table 1). Application of catalytic amounts of AgBF₄, instead of 1 equivalent, led to a significant drop in

Table 1: Variation of the yield of the isolated product resulting from changes to the reaction conditions [see Eq. (1)].

Entry	Deviation from the reaction conditions given in Equation (1)	Yield [%]
1	10 mol% AgBF4	36
2	1 equiv AgSbF ₆	18
3	1 equiv AgOAc, AgCN and AgF	< 5
4	10 mol % AgOAc, 1 equiv Bu ₄ NBF ₄	< 5
5	10 mol % AgOAc, 1 equiv (tBu) ₃ PHBF ₄	44
6	1 equiv AgBF ₄ , 1 equiv Selectfluor instead of 1	< 5
7	$1 \text{ equiv } Zn(BF_4)_2$	46
8	1 equiv Cu(MeCN) ₄ BF ₄	32
9	$1 \text{ equiv } \text{ZnF}_2, \text{CuF}_2$	< 5
10	MeOH as solvent	< 5
11	toluene as solvent	trace

yield from 73 to 36% (entry 1). Using AgSbF₆ as a mediator and F source led to formation of 4a (entry 2) but the reaction was much slower than that with AgBF₄, as a lot of unreacted starting material (2a) remained. When AgOAc, AgCN, or AgF was applied instead of 3 the styrene 2a remained intact (entry 3). A combination of catalytic amounts of AgOAc and 1 equivalent Bu₄NBF₄ was inefficient (entry 4), but upon treatment with (tBu)₃PHBF₄, instead of Bu₄NBF₄, 4a was isolated with 44% yield (entry 5). This result and the above experiment (entry 1) with a catalytic amount of 3 indicate that the geminal difluorination reaction can be achieved with a catalytic amount of a silver salt. Thus, the source of the second fluoride [Eq. (1)] is the BF₄⁻, which must not necessarily be added as part of a silver salt. However, the yields of 4 are much higher with stoichiometric amounts of AgBF₄. Therefore, we employed one equivalent of AgBF₄ as a mediator and secondary fluorine source in additional applications (see also Table 2). When we replaced 1 with Selectfluor, fluorination of 2a was not observed (entry 6). In the case of using Zn(BF₄)₂ or Cu(MeCN)₄BF₄, instead of AgBF₄, we could observe the difluorination reaction and isolate 4a in the corresponding yields of 46 and 32%. However, particularly with a copper salt, several other byproducts were formed (entries 7 and 8).

The reaction with palladium salts was rather interesting. $[Pd(MeCN)_4(BF_4)_2]$ proved to be a rather efficient catalyst, thus affording **4a** with 50% yield [Eq. (2)]. However, when the BF₄⁻ counter ion exchanged to Cl⁻ the outcome of the



reaction was completely different. When using $[PdCl_2-(MeCN)_2]$ as the catalyst **4a** did not form at all but the reaction gave the iodofluorinated product **5**, which could be isolated with 43 % yield. Further studies indicated that in the geminal difluorination reaction with **1**, AgF, ZnF₂, or CuF₂ were not able to serve as fluoride sources (Table 1, entries 3 and 9). We employed CDCl₃ as the solvent, which allowed the careful analysis of the crude reaction mixtures by ¹H and ¹⁹F NMR spectroscopy. Change of the solvent to MeOH or THF completely hindered any transformation of **2a** (entry 10), while using toluene led to formation of only traces of **4a** (entry 11).

Subsequently, we studied the synthetic scope of the reaction (Table 2). Both α - and β -naphtyl styrenes (**2b** and 2c) underwent geminal difluorination with high yields (entries 2 and 3). Despite the use of stoichiometric amounts of AgBF₄ the bromo substituent in 2d was tolerated and 4d was formed in a clean difluorination process (entry 4). The compound 4d can be a useful intermediate for modular synthesis of difluoromethyl compounds, as the bromo functionality can easily transformed by Suzuki-Miyaura coupling.^[24] The difluorination reaction also tolerates oxygencontaining substituents, such as the ether in 2e and carboxylate in 4 f (entries 5 and 6). However, for these substrates, we obtained somewhat lower yields than those for the hydrocarbon substrates 2a-c. The parent styrene 2g reacted readily with 1 but the isolation of 4g was difficult because of its volatility. Therefore, we determined the yield of 4g by ¹H NMR spectroscopy. *meta*-Phenyl (2h) and bromo (2i) styrenes reacted readily to provide the corresponding difluorinated compounds 4h and 4i (entries 8 and 9). However, our attempts to obtain geminal difluorinated products from ortho-substituted styrenes remained fruitless. The reactions with the α -methyl styrenes **2***j*-**l** gave surprising results. We still obtained the β -difluorinated products **4***j*-**l** but the methyl group migrated from the α - to the β -position (entries 10-12). The rearrangement proceeds very cleanly, as we could not observe any other isomers of 4j-l in the crude reaction mixture.

This finding and the fact that one of the fluorines arises from an electrophilic source (from 1) and the other from a nucleophilic reagent (from a BF_4^- anion) suggests a very interesting mechanism for the geminal difluorination process. To explore the mechanism, we prepared the deutero analogue of **2a**, $[D_2]$ -**2a**. When $[D_2]$ -**2a** was reacted with 1 in the presence of AgBF₄ under the usual reaction conditions the compound $[D_2]$ -**4a** was obtained in a very clean reaction [Eq. (3)]. This outcome was a surprising result, since the shift



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Table 2: Difluorination of styrene derivatives with the iodiane 1 and ${\sf AgBF}_4.^{[a]}$



[a] Styrene **2** (0.1 mmol), **1** (0.1 mmol), and AgBF₄ (0.1 mmol) in chloroform (0.5 mL) was stirred at 40 °C for 18 h. [b] Unless otherwise stated yield is that of isolated product. [c] Yield determined by NMR spectroscopy.

of one of the deuterium atoms of $[D_2]$ -**2a** was expected. The double deuterium shift suggested a significant deuterium isotope effect. Therefore, we performed a competitive difluorination reaction between **2a** and $[D_2]$ -**2a** [Eq. (4)]. However, according to these studies the deuterium isotope effect was found to be weak (about 1.3).

The above results indicate that the hydrogen shift from the α - to the β -position of styrene is unlikely. We reasoned that the difluorination reaction probably proceeds by an α - to

 β -carbon atom exchange of the styrene derivative through a possible phenonium ion intermediate. Such types of intermediates were first suggested by Cram^[25] and subsequently observed by Olah and co-workers.^[26]

Accordingly, our plausible mechanism (Figure 1) involves silver-activated addition of the iodane to the double bond of $[D_2]$ -**2a** to give the iodonium ion **6**. Togni and co-workers^[27] studied the activation of the CF₃ analogue of **1** using zinc salts.



Figure 1. Plausible mechanism for the geminal difluorination of styrenes.

A similar metal-mediated activation is conceivable for **1** as well. As mentioned above (Table 1, entry 7) $Zn(BF_4)_2$ is also a viable mediator of the difluorination process. Moreover, suitable copper and palladium salts [Table 1, entry 8 and Eq. (2)] may have a similar activating effect. The electron deficiency of iodine in **6** can be relieved by fluorine migration to give **7**. The π donation of the aromatic ring in **7** may result in formation of the phenonium ion **8**. In this process the iodoaryl group arising from **1** serves as a leaving group. The positive charge may delocalize over five carbon atoms (for sake of clarity only one of the resonance structures is given in Figure 1).

By using the [PdCl₂(MeCN)₂] catalyst [Eq. (2)] the faith of **7** was probably different and it underwent $C(sp^2)$ -I bond fission to result in 5. The only possible source of iodine in 5 is **1**. However, in the case of $AgBF_4$ (or a few other catalysts or mediators) the fluorinated phenonium ion 8 forms (Figure 1), and may undergo a second fluorination by a nucleophilic fluorine arising from the BF_4^- . The BF_4^- anion is an unexpected but not unusual source of nucleophilic fluoride. Our recent studies^[28] have shown the BF₄⁻ from [Pd(MeCN)₄- $(BF_4)_2$] [see Eq. (2)] may serve as a fluorine source in the activation of (SiMe₃)₂ for catalytic silvlation of allyl alcohols. Gandon and co-workers^[29] have recently shown that BF₄⁻ from AgBF₄ is an excellent fluorinating reagent for organometallic compounds. The present study is probably one of the few examples demonstrating that a C-F bond can also be formed under mild reaction conditions using BF₄⁻ as a fluorine source. An additional remarkable feature of the abovepresented reaction is that the opening of the cyclopropyl ring

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of **8** is highly regioselective. We could not observe formation of α -, β -difluorinated regioisomers of **4a** in the ¹H and ¹⁹F NMR spectra of the crude reaction mixtures. Opening of the cyclopropane ring of the fluorinated carbon in **8** also easily explains the apparent migration of the methyl group in the difluorination of **2j–l** (entries 10–12 in Table 2). A further confirmation of the plausible mechanism in Figure 1 could be the analogue reactivity of phenyl iodonium acetate (PIDA) or phenyl iodonium trifluoroacetate (PIFA) with styrene derivatives. PIDA and PIFA can be considered structural analogues of **1**. Tellitu and Domínguez,^[30] and the group of Wirth^[31] also postulated that the dioxo substitution of styrenes with PIDA and PIFA probably proceeds via phenonium intermediates.

In summary, we have shown that the hypervalent iodine 1 and $AgBF_4$ (and a few other metal tetrafluoroborates) induce geminal difluorination of styrenes. These air- and moisture-stable reagents react under mild reaction conditions to perform a selective formal F₂ addition. Using equimolecular amounts of 1 and styrene derivatives resulted in yields over 50%, thus indicating that one of the C-F bonds is created by electrophilic fluorinating reagent 1, while the other one results from fluorine transfer from BF₄⁻. The deuteriumlabelling experiments indicate that the process probably proceeds via phenonium intermediates. The reaction is suitable for mild synthesis of β -difluoro aromatic compounds, which are bioisosters^[4-6] of natural compounds with benzylalcohol and thiol motifs. In addition, our method extends the scope of the fluorination reactions, including a new application of the easily accessible, stable, and safe electrophilic fluoroidane reagent 1.

Experimental Section

The iodane **1** (28.0 mg, 0.1 mmol), $AgBF_4$ **3** (19.4 mg, 0.1 mmol), and the styrene **2** (0.1 mmol, 1 equiv) were mixed in CDCl₃ (0.5 mL) and this mixture was stirred at 40 °C for 18 h. Then product **4** was isolated by chromatography.

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Communications

Hypervalent Compounds

N. O. Ilchenko, B. O. A. Tasch, K. J. Szabó* _____ **IIII-IIII**

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Phenomenal phenonium: A formal F_2 addition to styrenes was carried out by using stable and safe fluorinating

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