Fluorination

International Edition: DOI: 10.1002/anie.201503308
German Edition: DOI: 10.1002/ange.201503308

Diphenyliodonium-Catalyzed Fluorination of Arynes: Synthesis of *ortho*-Fluoroiodoarenes**

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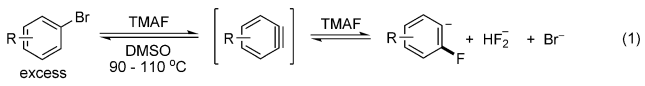
Abstract: *Described is a one-pot vicinal fluorination-iodination of arynes at room temperature. The diphenyliodonium salt proved to be a privileged catalyst for this nucleophilic fluorination process using CsF as a fluorine source, and a subsequent facile electrophilic iodination with C_4F_9I was also found to be crucial to ensure the efficient fluorination. This new synthetic protocol has a broad substrate scope under mild reaction conditions.*

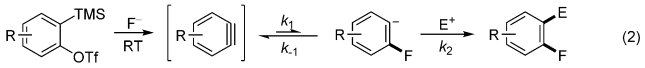
Aryl fluorides (ArF) have found an increasing number of applications in pharmaceuticals, agrochemicals, and materials science, as well as in positron emission tomography (PET).[1] Currently, the formation of Ar–F bonds can be achieved by either transition-metal-free or transition-metal-assisted fluorination processes using F^-/F^+ reagents.[2–4] However, Ar–F bond-formation reactions by nucleophilic fluorination with F^- reagents are usually performed at elevated temperatures, typically higher than 80 °C.[3a–c] Therefore, new routes for nucleophilic fluorination to form Ar–F bonds under mild reaction conditions have been highly sought after [Eq. (2); Tf = trifluoromethanesulfonyl, TMS = trimethylsilyl].

Previous work (harsh conditions and low yields)



(1)

This work (empowered by electrophilic quenching under mild conditions)



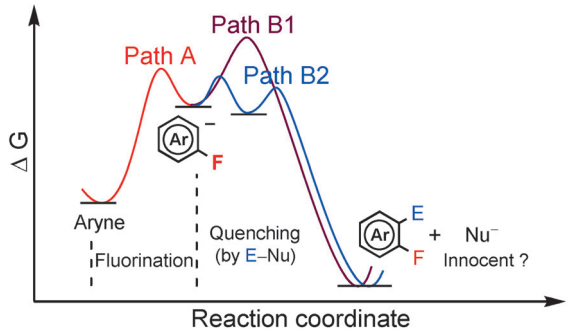
(2)

Arynes, with their unique structure and extraordinary reactivity, are particularly attractive in organic synthesis[5] and for theoretical studies.[6] From a synthetic point of view, the nucleophilic addition of fluoride anions (F^-) to arynes would be a straightforward strategy to synthesize aryl fluorides, and this process may proceed at ambient temperature or even lower temperatures. However, among the rich chemistry of arynes, direct nucleophilic fluorination of an aryne with F^- still remains a challenging task.[7] Indeed, aryne intermediates are often generated by their *o*-(trimethylsilyl)aryl triflate precursors in the presence of excessive amounts of F^-, but only in few cases were aryl fluorides detected as byproducts.[8] In 2008, Grushin et al. found that ArBr could be transformed into ArF through aryne intermediates [Eq. (1); DMSO = dimethylsulfoxide, TMAF = tetramethylammonium fluoride].[9] However, this reaction is impractical owing to the harsh reaction conditions (90–110 °C), poor conversion of ArX, and inseparability of the product from starting materials.

We have recently reported silver-mediated perfluoroalkylations of arynes.[10] As a continuing research effort, we sought to develop a mild nucleophilic fluorination of arynes.

We reasoned that the previous failures in developing efficient nucleophilic fluorination of arynes may be attributed to the following reasons: a) arynes are "soft" species[5a] and reluctant to react with the "hard" F^-,[1c] and the kinetically unfavorable fluorination step possesses a much higher energy barrier (Scheme 1, path A) compared to other pathways. Actually, in the absence of productive pathways, the highly reactive aryne intermediates could even react with inert solvent molecules rather than F^-.[11] b) *ortho*-Fluoroaryl anion intermediates are thermodynamically unstable above −50 °C and have been used as excellent aryne precursors since 1940 (Scheme 1, retro-path A).[12]

To solve these problems, we envisioned that this both kinetically and thermodynamically unfavorable fluorination step might be achieved by combining a facile electrophilic quenching step (Scheme 1, paths B) to give stable *ortho*-functionalized aryl fluorides [Eq. (2)]. Thus, a wide range of electrophiles were screened to see whether fluorination of benzyne would take place (Table 1). However, the consistent failures when using many electrophiles, such as C^+ (entries 1–5), N^+ (entries 6 and 7), S^+ (entries 8 and 9), and X^+



Scheme 1. Reaction coordinate diagram for the fluorination of aryne.

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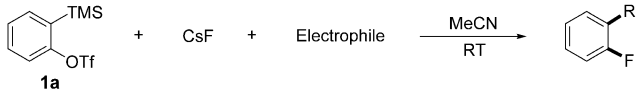
[**] This work was supported by the National Basic Research Program of China (2015CB931900, 2012CB821600), the National Natural Science Foundation of China (21372246, 21421002), Shanghai Science and Technology program (13QH1402400 and 15XD1504400), and the Chinese Academy of Sciences.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201503308.

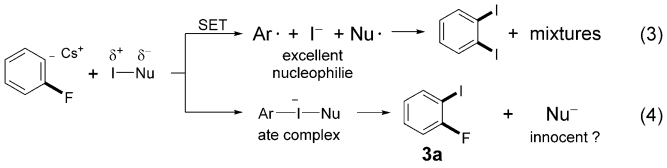
Table 1: Fluorination of benzyne in the presence of electrophilies.



Entry[a]	Electrophile	R	Yield [%][b]
1	epoxypropane	$CH_2CH(OH)CH_3$	0
2	PhCHO	CH(OH)Ph	0
3	PhCOF	COPh	0
4	$Et_3O^+BF_4^-$	Et	0
5	Togni reagent	CF_3	0
6	$NO_2^+BF_4^-$	NO_2	0
7	$NO^+BF_4^-$	NO	0
8	PhSSPh	SPh	0
9	$FSO_2CH_2CH_2SO_2F$	SO_2R'	0
10	Selectfluor	F	0
11	NCS	Cl	0
12	NBS	Br	0
13	NIS	I	0
14	PhC≡C–I	I	7
15	CF_3I	I	32
16	*n*-C_4F_9I	I	36

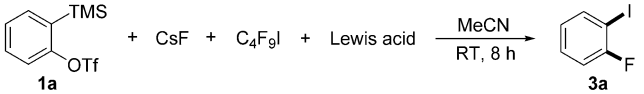
[a] Reaction conditions: **1a** (0.1 mmol), CsF (0.4 mmol), electrophile (0.2 mmol), MeCN (4 mL). [b] Yields were determined by ^{19}F NMR spectroscopy using $PhOCF_3$ as an internal standard. NBS = *N*-bromosuccinimide, NCS = *N*-chlorosuccinimide, NIS = *N*-iodosuccinimide.

(entries 10–12) reagents, reminded us that our simple picture of electrophilic quenching was incomplete. These E^+ reagents either exhibited insufficient reactivity (Scheme 1, path B1) or showed incompatibility with the reaction system. Thereafter, we realized that several requirements should be met to give the desired quenching product. On one hand, the energy barrier of the quenching step should be lower than that of retro-fluorination step to prevent the degradation of the *ortho*-fluoroaryl anion intermediate (Scheme 1, path B2 and retro-path A). On the other hand, the added electrophile E^+ should not undergo side reactions in the reaction system. Furthermore, the newly formed Nu^- (resulting from electrophilic species E-Nu; see Scheme 1) should be an innocent nucleophile, since the desired fluorination process would not proceed in the presence of another nucleophile (Nu^-) which possesses higher nucleophilicity than F^-. With these considerations in mind, we chose I^+ reagents (Table 1, entries 13–16) as electrophiles because an iodination process such as metal–iodine exchange may proceed smoothly, even at −100 °C,[13] thus indicating a low activation energy barrier (Scheme 1, path B2). However, it was found that the highly active iodination reagents such as *N*-iodosuccinimide (NIS) and 1-iodophenylacetylene (Table 1, entries 13 and 14) were prone to undergoing single-electron transfer (SET) processes [Eq. (3)] rather than the desired metal–iodine exchange [Eq. (4)]. The SET pathway was supported by our experimental observation of *ortho*-diiodobenzene in a large quantity (compared with desired product; determined by GC-MS), which was derived from a nucleophilic addition of benzyne by I^- followed by an electrophilic iodination step. We reasoned that using a milder iodination reagent could diminish the tendency of SET during the iodination step. This turned out to be the case when CF_3I and C_4F_9I were employed as I^+ reagents, and *ortho*-fluoroiodobenzene was formed in 32% and 36% yields, respectively, without *ortho*-diiodobenzene being observed (entries 15 and 16). In addition, in all cases, no PhF was observed, and further supports our hypothesis that a facile quenching process is the precondition for the nucleophilic fluorination of arynes.



Inspired by these results, we then turned our attention to enhancing the efficiency of this fluorination-iodination process. However, simple alteration of the reaction parameters such as reactants (F^- source and R_fI), temperature, solvent, and reactant ratio proved to be unfruitful. Then, we analyzed the reaction mixture and found that R_fH was formed in a comparable yield with the product **3a**, thus indicating a proton abstraction process between the ate complex [Ar-I-R_f]$^-$ and proton sources. Furthermore, deuterium-labeling experiments revealed that both MeCN and residual H_2O are responsible for this protonation process.[14] Thus, the poor reaction yields can be attributed to the interference from ^-OH and $^-CH_2CN$ as nucleophiles.[15,16] To minimize the influence of these anions, we reasoned that adding 1 equivalent of a Lewis acid may deactivate these anions by forming donor–acceptor adducts. A series of Lewis acids were then screened and some of the results are summarized in Table 2. Metal fluorides or triflates were preferred here because these

Table 2: Fluorination-iodination of benzyne in the presence of a Lewis acid.



Entry[a]	Lewis acid	Yield [%][b]
1	BF_3·THF	40
2	MgF_2	42
3	$Zn(OTf)_2$	0
4	AlF_3	44
5	$Fe(OTf)_2$	0
6	TiF_4	12
7	SbF_3	23
8	MnF_3	40
9	$In(OTf)_3$	0
10	SnF_2	29
11	CuOTf	0
12	AgOTf	0
13	$Ph_2I^+OTf^-$ (**2a**)	81
14	(*p*-F-Ph)$_2I^+OTf^-$ (**2b**)	84
15	$Mes_2I^+OTf^-$ (**2c**)	79
16	**2a**[c]	83

[a] Reaction conditions: **1a** (0.1 mmol), CsF (0.4 mmol), C_4F_9I (0.2 mmol), Lewis acid (0.1 mmol), MeCN (4 mL). [b] Yields were determined by ^{19}F NMR spectroscopy using PhF as an internal standard. [c] 10 mol% of **2a**. THF = tetrahydrofuran.

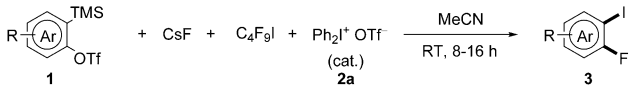
salts do not introduce new nucleophiles. After a quick screening, we found that common metal-based Lewis acids did not give improved results (entries 1–12). The reasons are complicated, and probably include: 1) poor solubility of metal fluorides (MF_n); 2) undesired side reactions;[17] 3) formation of stable ate complexes. Gratifyingly, $Ph_2I^+OTf^-$ (**2a**), a non-metal-based Lewis acid, was found to be a privileged promoter which afforded the product in 81% yield (entry 13). This finding is intriguing because although $Ar_2I^+OTf^-$ is known as an electrophilic arylating agent as well as an oxidant,[18] its role as a Lewis acid promoter has rarely been recognized and utilized.[19] We then tuned the structure of $Ar_2I^+OTf^-$ but did not achieve improved results (entries 14 and 15). However, we noticed that when the fluorine-labeled **2b** was used as a promoter (entry 14), its structure remained intact during the course of reaction (>98% by ^{19}F NMR spectroscopy), thus indicating that **2b** might be a catalyst.[20] Intrigued by this observation, we conducted a reaction using a catalytic amount of **2a** (10 mol%), and were delighted to find that the reaction efficiency was unaffected (entry 16), and it further demonstrated that $Ph_2I^+OTf^-$ acted as a catalyst (rather than an scavenger of undesired anions such as ^-OH and $^-CH_2CN$) for fluorination process.

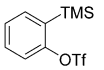
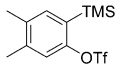
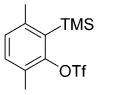
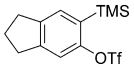
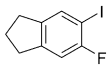
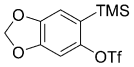
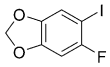
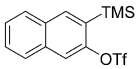
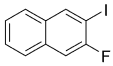
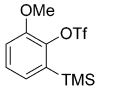
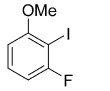
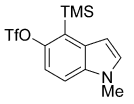
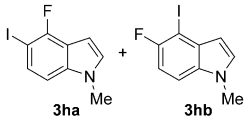
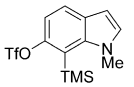
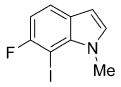
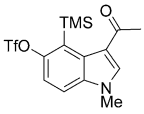
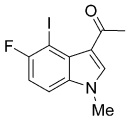
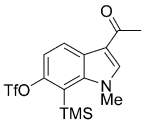
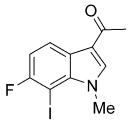
The application of this method to various structurally diverse arynes illustrates its synthetic scope (Table 3). Both symmetrical (entries 1–6) and unsymmetrical arynes (entries 7–11) are amenable to this reaction, thus affording the corresponding products in moderate to good yields. Remarkably, in most cases of unsymmetrical arynes, complete regioselectivities were observed (entries 7 and 9–11). Sterically hindered 3,6-dimethylbenzyne also works well in this transformation. Functional groups such as acetal, ether, and ketone are all well-tolerated in this reaction (entries 5, 7, 10, and 11). Additionally, heteroarynes such as indolynes[21] are also good substrates for this reaction (entries 8–11). It is worth noting that although the indole heterocycle motif is present in numerous natural products and medicinal agents, methods to access benzenoid-substituted iodoles remain limited.[22] Moreover, our method could not only introduce fluorine into the benzenoid ring of indoles, but also offer an excellent handle (the iodine atom) for further functionalization (such as cross-coupling reactions).

To gain more insight into the role of $Ph_2I^+OTf^-$, we carried out preliminary mechanistic studies. Initially, we envisaged that the Lewis acidity of diphenyliodonium might be responsible for its unique performance. To verify this hypothesis, we studied the interaction between Ph_2I^+ and all possible anions. First, we investigated whether Ph_2IAr or Ph_2ICH_2CN was involved as a key intermediate in the formation of desired product. However, such a possibility was ruled out by control experiments[14] in which these intermediates were found to be unstable. These observations are in line with previous studies which showed that triorganoiodines are prone to undergoing reductive elimination to give PhI and PhAr, or undergoing homolysis to give free radicals, even at low temperatures.[23]

We next explored the interaction between Ph_2I^+ and F^-. Various amounts of CsF were added into the CD_3CN solution of $Ph_2I^+OTf^-$. These mixtures were then monitored by ^1H NMR spectroscopy (Figure 1). In the absence of CsF, the ^1H NMR peaks for all aromatic protons exhibited significant downfield shifts owing to the influence of the highly electron-deficient iodonium species (Figure 1a). However, upon the treatment of 0.5 equivalents of CsF, each signal for the phenyl groups shifted upfield (Figure 1b), and at the same time, the insoluble CsF dissolved quickly to afford a homogeneous solution. Moreover, when the ratio of CsF to $Ph_2I^+OTf^-$ was increased to 1:1, the signals continued moving upfield (Figure 1c). However, in this case, a small portion of undissolved CsF was found at the bottom of the solution even after vigorous stirring for 30 minutes, thus indicating that the

Table 3: Scope of fluorination-iodination of arynes.



Entry[a]	Substrate (**1**)	Product (**3**)	Yield [%][b]
1			78[c]
2			71
3			70
4			67
5			72
6			50[e]
7			73
8			**3ha**: 6 **3hb**: 57
9			68[d]
10			88[d]
11			57[e]

[a] Reaction conditions: **1** (0.5 mmol), CsF (2 mmol), C_4F_9I (1 mmol), **2a** (10 mol%) in MeCN (20 mL). [b] Yield of isolated product. [c] Yield determined by ^{19}F NMR spectroscopy. [d] **2a** (30 mol%). [e] **2a** (50 mol%).

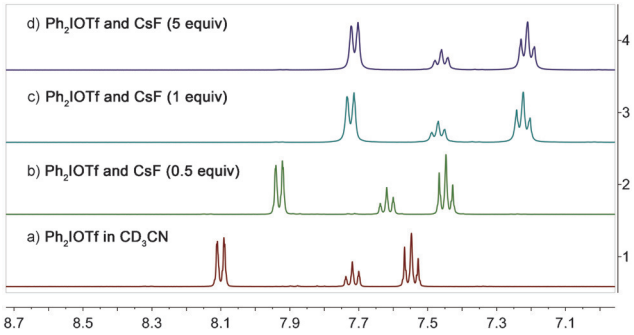


Figure 1. ^{1}H NMR monitoring of the interaction between $Ph_2I^+OTf^-$ and CsF in CD_3CN at room temperature.

$Ph_2I^+OTf^-$ solution was saturated with F^- and the adduct **4** was formed. This outcome is surprising because it indicates that the newly formed **4** is not the neutral species Ph_2IF[24] but a positively charged ion[25] [Eq. (5)]. Indeed, adding an excess of CsF (4 equiv) into this saturated solution did not change its ^{1}H NMR spectrum (Figure 1 d). Moreover, the fact that only one set of signals were observed in the spectrum of an unsaturated solution (Figure 1 b) led us to conclude that free Ph_2I^+ species are in a fast equilibrium (on the NMR time scale) with **4** [Eq. (6)], thus all the Ph groups were equivalent in the spectrum (Figure 1 b).[26] Additionally, DOSY (diffusion ordered spectroscopy) experiments have demonstrated that the phenyl groups in the $Ph_2I^+OTf^-$/CsF (excess) system possesses a higher degree of aggregation than those in the fluoride-free $Ph_2I^+OTf^-$ system.[14]

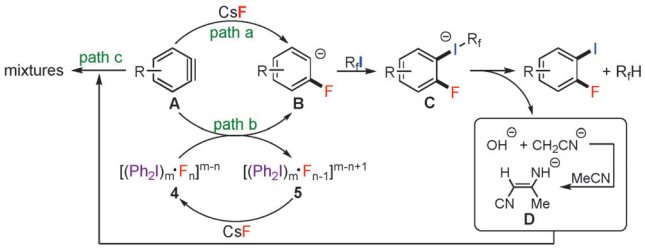
$$m\ Ph_2IOTf + n\ CsF \xrightarrow[(m > n)]{MeCN} \underset{\mathbf{4}}{[(Ph_2I)_m{\cdot}F_n]^{m-n}} + n\ Cs^+ + m\ OTf^- \quad (5)$$

$$\underset{\mathbf{4}}{[(Ph_2I)_m{\cdot}F_n]^{m-n}} + (Ph_2I)^+ \underset{}{\overset{fast}{\rightleftharpoons}} \underset{\mathbf{4}}{[(Ph_2I)(Ph_2I)_{m-1}{\cdot}F_n]^{m-n}} + (Ph_2I)^+ \quad (6)$$

$$\underset{6\ equiv}{Ph_2IOTf} + \underset{4\ equiv}{CsF} \xrightarrow{MeCN} \underset{excess}{(Ph_2I)^+} + \underset{\mathbf{4}}{[(Ph_2I)_m{\cdot}F_n]^{m-n}} \xrightarrow[RT,\ 8\ h]{\text{benzyne precursor \& } C_4F_9I} \underset{\mathbf{3a},\ 81\ \%}{\text{  }} \quad (7)$$

Although the exact structure of **4** is not clear at present, we assume that this complex may play a crucial role in the fluorination of arynes. It was found that when the benzyne precursor and C_4F_9I (2 equiv) were added into an unsaturated solution (4 equiv of CsF in 6 equiv of $Ph_2I^+OTf^-$, thus indicating there was no free CsF) and stirred at room temperature, **3a** was formed in 81 % yield [Eq. (7)]. Therefore, this novel adduct shows promising fluorinating ability in both aryne generation and Ar–F bond formation.

With these results in hand, we propose a plausible reaction mechanism for this unprecedented and very intriguing diphenyliodonium-catalyzed fluorination reaction (Scheme 2). The in situ generated aryne intermediate **A** reacts with either CsF (path a) or **4** (path b) to afford an *ortho*-fluoroaryl anion **B**, which is quickly captured by R_fI to give the iodine ate complex **C**.[13,27] Meanwhile, **4** is readily regenerated from the adduct **5** and CsF. Subsequent proton abstraction of **C** from adventitious water or solvent (MeCN) produces the desired product, byproduct R_fH, and corresponding anions (^-OH and $^-CH_2CN$). In a noncatalytic process, these anions, as well as their derivative **D**,[15] react with an aryne to generate byproducts (reaction rate: path c > path a). However, in the presence of $Ph_2I^+OTf^-$, the fluoride anion coordinates with the soft iodine atom in Ph_2I^+ to afford **4**. The adduct **4** works as a new nucleophilic fluorinating agent, which possesses higher reactivity toward arynes than other nucleophiles (reaction rate: path b > path c). Another beneficial effect may stem from the increased concentration of fluoride sources in the solution, which is also brought about by coordination with $Ph_2I^+OTf^-$.



Scheme 2. Proposed mechanism for diphenyliodonium-catalyzed fluorination of arynes.

In conclusion, a novel diphenyliodonium-catalyzed and iodination-promoted nucleophilic fluorination of arynes under mild reaction conditions has been accomplished. This process provides a powerful synthetic tool for the one-pot synthesis of *ortho*-iodinated aryl fluorides, which are highly useful compounds for organic synthesis. Diphenyliodonium plays a crucial catalytic role in the fluorination process by forming an adduct with CsF. Moreover, the intriguingly new reactivity exhibited by this new adduct provides a basis for the further development of other new fluorination processes, which is currently underway in our laboratory.

Keywords: arynes · fluorine · hypervalent compounds · Lewis acids · synthetic methods

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 10773–10777
Angew. Chem. **2015**, *127*, 10923–10927

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Received: April 12, 2015
Revised: May 13, 2015
Published online: July 23, 2015

