Pyridine-promoted dediazoniation of aryldiazonium tetrafluoroborates: Application to the synthesis of SF₅-substituted phenylboronic esters and iodobenzenes

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Abstract
Pyridine promotes dediazoniation of aryldiazonium tetrafluoroborates. The formed aryl radicals were trapped with B₂pin₂, iodine, or tetrahydrofuran to afford boronic esters, iodobenzenes and benzenes, respectively. The application to the synthesis of (pentafluorosulfanyl)phenylboronic esters, iodo(pentafluorosulfanyl)benzenes and (pentafluorosulfanyl)benzene is shown.

Introduction
Pentafluorosulfanyl-containing compounds have been known for more than half a century [1-4]; however, for a long time they remained a relatively underdeveloped class of compounds [5,6]. The main reason for the slow development of the chemistry of SF₅-containing compounds was the lack of availability of key building blocks. However, in recent years, the scientific community has been witnessing a renewed interest in this functional group. Synthetic methods towards aliphatic SF₅-containing compounds are based on free radical addition of SF₅Cl or SF₅Br to unsaturated compounds [7-9], whereas aromatic derivatives are available either by the Umemoto’s two-step synthesis from diaryl disulfides or benzenethiols [10-12], or by the reaction of nitrophenyl disulfides with elemental fluorine [13-16]. Aromatic and heteroaromatic SF₅ compounds are mostly prepared by the derivatization of commercial nitro-pentafluorosulfanyl)benzenes [14,17-27] and approaches from SF₅-aliphatics have also been studied [28-30]. The unique combination of properties the SF₅ group imparts includes high chemical, thermal, and metabolic stability, strong electron-acceptor property, and high lipophilicity. Furthermore, applications of SF₅ compounds in catalysis [31,32], life-science [6,18,33-38], and material sciences [5,19,38,39] are emerging.

Arylboronic acids and aryloborates represent versatile building blocks in organic synthesis [40]. They have found wide applications in transition metal-catalyzed cross-coupling reactions [41,42]. These boron compounds are accessed mainly by the reactions of arylmagnesium or aryllithium species with trialkyl-
boronates [43,44], Pd- or Cu-catalyzed borylations of aryl halides using B₂P̃IN₂, H-Bpin [45-50] or R₂N-BH₂ [51], direct borylations via aromatic C–H bond activations [52-58], Lewis acid catalyzed electrophilic borylations of electron-rich arenes [59-62], and Sandmeyer-type borylation of alylamines or diazonium salts with B₂P̃IN₂ [63-67], B₂(OH)₄ [68] or R₂N-BH₂ [69]. Several attempts were made to synthesize the SF₅-phenylboronates. Patent literature describes the synthesis of 3- or 4-(pentafluorosulfanyl)phenylboronates or boronic acids from SF₅-bromobenzenes via lithiation or magnesiation. These approaches suffer from low yields and other drawbacks [70,71]. For lithiation of the aryl bromide, t-BuLi had to be used and the formation of Grignard reagents is inefficient. On the other hand, Shibata and co-workers have recently reported the synthesis of 3,5-bis(pentafluorosulfanyl)phenylboronic acid from the corresponding aryl bromide, trimethyl borate and iPrMgBr [32].

Finally, Joliton and Carreira have recently shown efficient Ir-catalyzed C–H borylation of several 1-substituted-3-(pentafluorosulfanyl)benzenes and applied the products of borylation to the Pd-catalyzed Suzuki–Miyaura reaction with aryl bromides or iodides. However, the reaction is limited to borylation in position five of 1-substituted-3-(pentafluorosulfanyl)benzenes [72].

Straightforward access to SF₅-phenylboronic acids or boronates would be highly desirable since it would allow easy installation of the SF₅-phenyl group by the subsequent Suzuki–Miyaura reaction. Nitro-(pentafluorosulfanyl)benzenes are the primary industrial SF₅-aromatics, therefore the easiest access to SF₅-phenylboronates appears to be starting from readily available SF₅-substituted anilines or diazonium salts rather than SF₅-containing halobenzenes. Herein, we report a new protocol for efficient borylation, iodination and hydrodediazoniation of SF₅-phenyl/diazonium tetrafluoroborates in the presence of pyridine. The generality of the borylation and iodination reactions was demonstrated on several examples.

**Results and Discussion**

At the onset of our investigation, Sandmeyer-type borylation of 3- and 4-(pentafluorosulfanyl)anilines (1a and 1b, respectively) to pinacolboronates 2a and 2b according to Wang and co-workers was studied [64,65] (Table 1). The borylation of 1a took place in a reasonable yield in the presence of catalytic amounts of benzylic peroxide (BPO, Table 1, entry 1), while for 1b, heating without any additives was preferable; however, the yield of 2b was only moderate (Table 1, entry 3).

For a detailed investigation of the borylation reaction, the diazonium tetrafluoroborates 3a and 3b were prepared and isolated according to Doyle conditions [73]. High yields (above 90%) of both isomers of the diazonium tetrafluoroborates 3a and 3b were obtained on 0.3–6 g scale (Table 2). Crystal structures of 3a (CCDC 1009848) and 3b (CCDC 1009849) were determined confirming the nature of the products. During the course of our studies, Okazaki and co-workers reported the synthesis of 3b in 84% yield under similar conditions and have shown its reactivity in various cross-coupling reactions with varied degree of success. The most efficient cross-coupling reactions were the Heck reactions with alkenes, a biaryl homocoupling reaction, an azo coupling to electron-rich arenes, and a dediazoniation with TMSN₃ in an ionic liquid medium [74,75].

An efficient borylation of aryl diazonium tetrafluoroborates with NHC-Pd catalysts was reported recently [63]. When applied to 3a and 3b using Pd(OAc)₂ and NH₄ iodide precursors 1, the borylated products 2a and 2b were isolated in only moderate yields (Table 2, entries 1 and 2). However, it was found that the Pd catalyst was not required for an efficient reaction. Alkali metal acetates are known to facilitate decomposition of aryl diazonium salts by the formation of diazoacetates and diazo anhydrides, which decompose to aryl radicals [76]. These additives were used in Meerwein arylation of isopropenyl acetate [77]. In our case, two-fold excess of sodium acetate in acetonitrile afforded 2a and 2b in good and moderate yields, respectively (Table 2, entries 3 and 4). The conditions reported by Yu and co-workers [66] (Table 2, entry 5) provided a mixture with starting 3b as the major component. While the diazonium salts 3a and 3b were found to be stable in acetonitrile, we observed slow decomposition in methanol and in the presence of B₂P̃IN₂ under strictly Pd-free conditions (new Teflon stirring bar and glassware), the borylation took place with low conversion (Table 2, entry 6) [78]. In pyridine, however, the decomposition of 3b was very fast and a vigorous evolution of nitrogen was observed affording the borylated product in a moderate yield together with a mixture of SF₅-pyridines in ca. 10% GC–MS yield (Table 2, entry 7). Finally, the use of a

| Entry | Additive | Temp. (°C) | 2. Yield (%)* |
|-------|----------|------------|---------------|
| 1     | 1a, 3-SF₅ | BPO        | rt            | 2a, 70       |
| 2     | 1b, 4-SF₅ | BPO        | rt            | 2b, traces   |
| 3     | 1b, 4-SF₅ | —          | 80            | 2b, 55c     |

*Reaction conditions: 1 (1 mmol), t-BuONO (1.5 mmol), B₂P̃IN₂ (1.1 mmol), additive (2 mol %), MeCN (4 mL). *Isolated yield. *82% purity.
4-fold excess of pyridine in acetonitrile was found to be optimal. Conducting the reaction on a gram scale proceeded without a notable loss of efficiency and the reaction can be performed in air (Table 2, entries 8–10).

Pyridine is known to induce decomposition of aryldiazonium salts. Zollinger and Abramovitch studied the interaction of pyridine with aryldiazonium tetrafluoroborates and suggested the formation of diazopyridinium salts which homolytically decompose to aryl radicals, nitrogen and a pyridinium tetrafluoroborate radical [79,80]. Tanaka and co-workers have used the combination of PhN$_2^+$BF$_4^-$ and pyridine for arylations of silylenol ethers [81]. They have observed the formation of large amounts of phenylpyridines. In our case, we detected SF$_5$-phenylpyridines in trace amounts only during borylation using pyridine as a solvent. The major products in the borylation reaction apart from 2a and 2b were found to be F-Bpin and pyridine BF$_3$ complexes. Both compounds are easily hydrolyzable but they were observed by NMR of the crude reaction mixture and compared to the synthetized authentic samples. On the other hand, we were not able to observe a pyridine-B$_2$pin$_2$ complex by $^{13}$B NMR in CD$_2$CN or CDC$_3$. The borylation was extended to several other aryldiazonium tetrafluoroborates showing that both electron-donor and electron-acceptor substituted phenyldiazonium tetrafluoroborates undergo efficient borylation with an equimolar amount of B$_2$pin$_2$ (Scheme 1); however, ortho-substituted phenyldiazonium salts were found to be either not efficient substrates (3f) or completely unreactive (3g), presumably due to a large steric demand of B$_2$pin$_2$.

The mechanism of this borylation reaction remains to be elucidated. Based on experimental results and literature precedent, we propose the following free-radical mechanism (Scheme 2). Aryldiazonium salt 3 reacts with pyridine to form aryldiazopyridinium 4 which decomposes to an aryl radical, a pyridinium tetrafluoroborate radical and nitrogen. The aryl radical reacts with pyridine·BF$_3$ and the Bpin radical. Products pyridine·BF$_3$ and F-Bpin are formed by the reaction of the diazopyridinium radical (likely to be stabilized by pyridine) [82]. The byproducts pyridine·BF$_3$ and F-Bpin are formed by the reaction of the pyridinium tetrafluoroborate radical and the Bpin radical.

Subjecting the diazonium salt 3i to the borylation conditions gave further indirect evidence for the formation of aryl radicals (Scheme 3). Full conversion of 3i was observed affording a mixture of products 2i, 2i', 5i (two isomers of unknown configuration) and 6i in 16:31:28:25 GC–MS ratio. The presence of these products can be explained only by the formation of the substituted SF$_5$-phenyl radical which undergoes borylation to 2i, hydrogen atom transfer followed by borylation to 2i', intramolecular cyclization to 5i or hydrogen abstraction to 6i.

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**Table 2: Synthesis of diazonium tetrafluoroborates 3a and boronates 2b.**

| Entry | 3 (mmol) | Reagents (equiv), solvent | Temp. (°C) | Time (h) | 2, Yield (%)$^c$ |
|-------|----------|---------------------------|-----------|---------|-----------------
| 1     | 3a (1)   | Pd(OAc)$_2$ (0.01), L (0.02), THF | rt        | 18      | 2a, 43         |
| 2     | 3b (1)   | Pd(OAc)$_2$ (0.01), L (0.02), THF | rt        | 18      | 2b, 57         |
| 3     | 3a (1)   | NaOAc (2), MeCN            | −50 to rt | 3       | 2a, 73         |
| 4     | 3b (1)   | NaOAc (2), MeCN            | −50 to rt | 3       | 2b, 49         |
| 5     | 3b (1)   | CuBr (0.05), MeCN/H$_2$O (3:1) | rt        | 330     | 2b, 23         |
| 6     | 3a (1)   | —, MeOH                    | rt        | 24      | 2a, 32         |
| 7     | 3b (1)   | —, pyridine$_d$            | −30 to rt | 2       | 2b, 55         |
| 8     | 3b (1)   | pyridine (4), MeCN$_d$      | −30 to rt | 2       | 2b, 77         |
| 9     | 3b (3)   | pyridine (4), MeCN$_d$      | −30 to rt | 2       | 2b, 77         |
| 10    | 3b (2)   | pyridine (4), MeCN$_d$      | −30 to rt | 2       | 2a, 80         |

$^a$Reaction conditions: 1 (1–28 mmol), BF$_3$OEt$_2$ (2.1 equiv), t-BuONO (1 equiv), CH$_2$Cl$_2$ or Et$_2$O (3 mL/1 mmol of 1), 30 min. $^b$Reaction conditions: 3 (1–3 mmol), B$_2$pin$_2$ (1 equiv), reagents, solvent (2 mL/1 mmol of 3) under N$_2$. $^c$Isolated yield. $^d$The reaction was conducted under air.
Starting from aniline derivative 1b, a one-pot diazotization–borylation sequence using different acids afforded the corresponding borylated product 2b in good yields (Table 3).

Suzuki–Miyaura cross-coupling reactions of boronates 2a and 2b with aryl iodides using a simple system without any optimization proceeded in satisfactory yields considering the electron-deficient character of the boronates and consequently less efficient transmetallation step (Scheme 4).

Transformation to SF₅-phenylboronic acid 8b and potassium trifluoroborates 9 was straightforward under standard conditions (Scheme 5). Similar potassium SF₅-phenyltrifluoroborates were found to be highly reactive with a variety of aryl bromides and iodides in the presence of catalytic amounts of
Scheme 4: Suzuki–Miyaura reaction of boronates 2a and 2b with aryl iodides. Reaction conditions: 2 (1 mmol), ArI (1.1 mmol), Pd(PPh$_3$)$_4$ (5 mol %), LiOH·H$_2$O (4 mmol), 1,4-dioxane (2 mL), water (1 mL), 3.5 h.

Scheme 5: Synthesis of boronic acid 8b and trifluoroborates 9. Reaction conditions for the synthesis of 8b: 2 (2 mmol), NaIO$_4$ (8 mmol), THF (8 mL), H$_2$O (2 mL), rt, 1 h. Reaction conditions for the synthesis of 9: 2 (2 mmol), KHF$_2$ (10 mmol), MeOH (8 mL), H$_2$O (3.6 mL), rt, 20 min.

PdCl$_2$(dppf)·CH$_2$Cl$_2$ or Pd(OAc)$_2$ [72]. The recently published synthesis of arylboronic acids from anilines or aryldiazonium tetrafluoroborates using B$_2$(OH)$_4$ [68] applied to 3b provided 8b in only 25% $^{19}$F NMR yield.

To extend the synthetic utility of the pyridine-mediated derivatization of aryldiazonium tetrafluoroborates we investigated the reaction with iodobenzene and iodine as efficient scavengers of aryl radicals [83,84]. A competitive experiment starting from 3a and equimolar amounts of B$_2$pin$_2$ and iodobenzene in the presence of pyridine (4 equiv) in MeCN afforded a mixture of 2a (72% yield) and 1-iodo-3-(pentafluorosulfanyl)benzene (10a, 23% yield). Additionally, a reaction of 3b with PhI (4 equiv) in the absence of B$_2$pin$_2$ gave 1-iodo-4-(pentafluorosulfanyl)benzene (10b) in 35% yield. Both experiments point to the formation of aryl radicals during the reaction and suggest a possibility to conduct practical aromatic iodination. Indeed, the iodination reaction with I$_2$ proved to be more efficient than with PhI (Scheme 6). In contrast to borylation, iodination with I$_2$ shows a higher sensitivity to electronic properties of substituents on the aromatic ring. Electron-acceptor substituted aryldiazonium compounds are excellent substrates while those with electron-
donor groups react much less efficiently. The substitution of pyridine with collidine (2,4,6-trimethylpyridine) gave similar yields. Unlike borylations, the iodination reactions were not sensitive to ortho substitutions. In the case of 3i, compound 10i was the sole product; no product of hydrogen atom transfer or cyclization was observed, demonstrating that the reaction with I2 is much faster than with B3pin2. Importantly, the yields of SF5-phenyl iodides 10a and 10b using our two-step diazotization–iodination method significantly exceed those obtained by classical Sandmeyer reaction (ca. 80% yield over two steps compared to 63% for 10a and 50% for 10b by one-pot Sandmeyer procedure requiring 10 fold excess of KI) [14]. The side-product in the iodination of 3 was bis(pyridine)iodonium tetrafluoroborate, which can be easily isolated from the reaction mixture by precipitation upon addition of diethyl ether. This iodonium salt was first synthesized by Barluenga [85] and later used for mild iodination of alkenes, alkynes and aromatics [85-87]. Its formation can be explained by the reaction of the pyridinium tetrafluoroborate radical (Scheme 2), pyridine and I2 or iodine radical. Bromination of 3b with Br2 was attempted under conditions similar to iodination but the reaction was slow and inefficient resulting in a mixture of products with expected 1-bromo-4-(pentafluorosulfanyl)benzene as a minor product. With equimolar NBS instead of bromine, the reaction is much cleaner but slow; after overnight at ambient temperature the bromo product was isolated in 35% yield.

Finally, hydrodediazoniation using tributyltin hydride or THF was tested and THF proved to be a more efficient hydrogen atom donor. The addition of excess pyridine to MeCN/THF solution of diazonium tetrafluoroborates 3a or 3b led to an efficient hydrodediazoniation and the formation of (pentafluorosulfanyl)benzene (6). Deuteration experiments established that the hydrogen atom in the product comes exclusively from THF and not from pyridine or MeCN (Table 4). The observed deuterium enrichment using THF-d8 was around 80%. Thermal decomposition of aryldiazonium salts prepared from immobilized triazene precursors and the formation of deuterated aromatics using THF-d8 was reported [88]. We explain the reduced yield of 6-D (48% yield) and the formation of tar products by hydrogen atom abstraction from 3 or 6 and subsequent polymerization. No significant amounts of double deuterated products were detected. The kinetic isotope effect was determined from intermolecular competition experiment using 3b and a 1:1 mixture of THF and THF-d8 giving KIE = 5.5 (6-6-D ratio determined by GC–MS) and combined yield of 62%. This means that the hydrogen abstraction is much faster than the deuterium abstraction and suggests the C-H(D) bond formation as the rate-limiting step. For unambiguous identification of the rate-limiting step, individual rate constants $k_{D1}$ and $k_{D2}$ in two parallel reactions would have to be determined [89]. Dihydrofuran (11) and pyridinium tetrafluoroborate were identified as byproducts of the dediazoniation reactions. Similarly to the previous processes, we presume the formation of aryldiazopyridinium 4 and its decomposition to an aryl radical and the pyridinium tetrafluoroborate radical. The aryl radical abstracts a hydrogen atom from THF forming 6 and a THF radical. The THF radical then transfers the hydrogen atom to the pyridinium tetrafluoroborate radical giving dihydrofuran (11) and pyridinium salt.

**Conclusion**

In conclusion, a novel dediazoniation–borylation methodology was developed based on the reaction of aryldiazonium tetrafluoroborates with pyridine and B3pin2 to give arylpinacolborates. Particular emphasis was on the synthesis of SF5-phenylboronates where our methodology represents a considerable improvement in reaction efficiency compared to previously published syntheses. Furthermore, no transition metals are needed and mild reaction conditions are used. The borylation is applicable to a variety of aryldiazonium tetrafluoroborates with electron-donor or acceptor groups while ortho-substituted substrates are less reactive. A mechanism involving aryl radicals is suggested. The Suzuki–Miyaura reaction of SF5-phenylboronates with aryl iodides provided the cross-coupling biaryl products. In analogy to the borylation reaction, iodination of aryldiazonium tetrafluoroborates with pyridine and iodine resulted in aryl iodides. An efficient reaction was observed with electron-acceptor substituted aromatic compounds even with ortho-substituted derivatives. In the case of SF5-substituted

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**Table 4: Hydrodediazoniation of 3a and 3b with THF**

| Entry | 3 (mmol) | D source | D enrichment | 6, Yield (%) |
|-------|----------|----------|--------------|--------------|
| 1     | 3a (0.5) | —        | n/a          | 6, 75        |
| 2     | 3b (0.5) | —        | n/a          | 6, 70        |
| 3     | 3b (0.5) | THF-d8   | 0.5 mL       | 6-D, 48      |
| 4     | 3b (0.25)| C5D5N    | (4 mmol)     | 0            | 6, 70        |
| 5     | 3b (0.25)| CD3CN    | (0.75 mL)    | 0            | 6, 67        |

Reactions conditions: 3 (0.25–0.5 mmol), pyridine (4 equiv), THF (1 mL/1 mmol of 3), MeCN (3–4 mL/1 mmol of 3); 2 h. Based on GC–MS. Based on 19F NMR using 1-nitro-4-(pentafluorosulfonyl)-benzene as an internal standard.
iodobenzenes, the method is much more efficient than the classical Sandmeyer reaction starting from SF₅-containing aniline derivatives. Finally, hydrodediazoniation of SF₅-phenylidazonium tetrafluoroborates by hydrogen atom abstraction from THF in the presence of pyridine provided (pentafluorosulfanyl)-benzene.

Supporting Information

Synthesis and characterization of all products, copies of ¹H, ¹³C, and ¹⁹F NMR spectra of newly synthesized products, and X-ray crystallographic files of the compounds 3a and 3b.

Supporting Information File 1

Experimental part.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-11-162-S1.pdf]

Supporting Information File 2

Crystal structure of compound 3a.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-11-162-S2.cif]

Supporting Information File 3

Crystal structure of compound 3b.
[http://www.beilstein-journals.org/bjoc/content/supplementary/1860-5397-11-162-S3.cif]

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