

Synthesis of Diaryliodonium Salts Having Pentafluorosulfanylarenes and Their Application to Electrophilic Pentafluorosulfanylation of C-, O-, N-, and S-Nucleophiles

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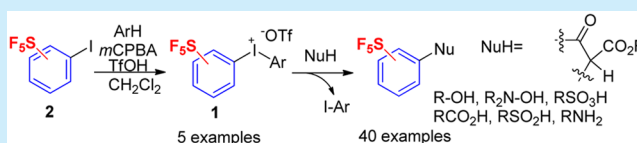
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S Supporting Information

ABSTRACT: Novel reagents for the electrophilic introduction of pentafluorosulfanyl (SF₅) arenes into target molecules are disclosed. Unsymmetrical diaryliodonium salts **1** having SF₅-arenes were synthesized by a one-pot process from iodo-SF₅-benzenes **2** in good yields. The SF₅-aryliodonium salts **1** were found to be efficient for the electrophilic SF₅-arylation of carbon and heterocentered nucleophiles to furnish the corresponding substituted SF₅-arenes in good to high yields.



Aromatic molecules bearing fluorinated functional groups are prevalent in a variety of pharmaceuticals and agrochemicals.¹ Drug candidates in the developmental pipeline also highly likely contain fluorinated aromatics in their structures. In particular, trifluoromethylated arene (CF₃-Ar)-containing compounds are one of the major families on the drug market;² examples include aprepitant (antiemetic) and travoprost (for glaucoma). Thus, the incorporation of a CF₃-Ar unit into an organic compound could form the basis for the development of new drugs. On the other hand, the pharmaceutical industry has faced difficulties in bringing new drugs onto the market in recent years.³ One of the reasons is that rational drug designs to improve challenging human life-threatening diseases have still not been found, even in the 21st century.⁴ Pentafluorosulfanyl arenes (SF₅-Ar) have recently emerged as prospective drug units due to the chemical similarity of CF₃ and SF₅.⁵ The SF₅ moiety is thermally stable (>300 °C) and also more stable under acidic and basic hydrolysis than a CF₃ group.⁶ Electrostatic potential maps of CF₃-Ph and SF₅-Ph clearly indicate their three-dimensional resemblance of charge distributions and molecular size (Figure 1a).⁷ However, the SF₅ group has a much higher impact on the benzene ring attached to CF₃ since it is more electronegative (Hammett substituent constants: for SF₅ σ_1 = 0.55, for CF₃ σ_1 = 0.39),⁶ has higher intrinsic lipophilicity (Hansch hydrophobicity constants: for SF₅ π = 1.51, for CF₃ π = 1.09),⁸ bulkier size of van der Waals volume (Å³) for SF₅Ph 152.9, for CF₃Ph 129.0, for HPh 96.6),⁷ and higher chemical and thermal stability.⁶ Thus, replacement of the CF₃-Ar moiety in a drug or drug candidate by SF₅-Ar could become an alternative fine-tuning mechanism for drug design and might result in an improvement of the physiological and/or biological properties compared to the parent drugs.⁹ In addition, both sulfur and fluorine are among the most used elements in marketed drugs.^{4b} The SF₅ analogues of

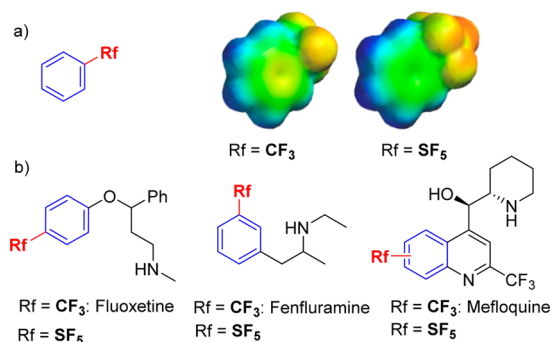


Figure 1. (a) Electrostatic potential maps of CF₃-Ph and SF₅-Ph. (b) Drug-containing CF₃-arenes and their SF₅ analogues.

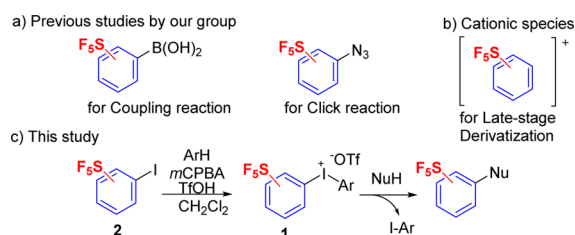
the antidepressant drug fluoxetine, the antiobesity drug fenfluramine, and the antimalaria drug mefloquine are three representative examples (Figure 1b) that have recently been prepared.¹⁰ Moreover, SF₅-arenes have attracted considerable interest as a potential unit of functional materials.¹¹

While many synthetic routes toward CF₃-arene compounds have been explored,¹² only a handful of synthetic methods for SF₅-arenes have been reported,¹³ and the chemistry of SF₅-arenes is somewhat under-investigated. The direct construction of an SF₅ unit on benzene rings is possible from aryl disulfides using HF/Cl₂, AgF₂, or F₂ methodology.¹³ However, the methods are limited to simple SF₅-arenes, and more effective and convenient methods are required. By virtue of the fact that simple SF₅-arenes are now commercially available,¹⁴ it is hoped

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that direct functionalization of simple SF₅-arenes at all positions of the benzene ring could allow for the synthesis of more complex SF₅-arenes.¹⁵ Recently, we reported two valuable building blocks, 3,5-bis(SF₅)phenylboronic acid¹⁶ for the Suzuki–Miyaura coupling reaction and bis(SF₅)-5-azido-1,3-phenylene¹⁷ as a tool for click chemistry, which furnish functional dyes and antitumor compounds, respectively (Scheme 1a). We envisaged

Scheme 1. (a) SF₅-arenes for Coupling and Click Reactions; (b) Cationic Species for Late-Stage Derivatization; (c) SF₅-Arylaryliodonium Salts **1** for SF₅-Arylations



that if cationic species represented by [SF₅-Ar]⁺ are generated (Scheme 1b), the late-stage derivatization of target molecules to SF₅-aryl compounds would be realized. As part of our ongoing research program committed to the development of late-stage fluorinated functionalized reagents,¹⁸ herein we disclose the synthesis of unsymmetrical diaryl-λ³-iodanes **1**, diaryliodonium salts having SF₅-arenes, and their wide utility as electrophilic reagents for pentafluorosulfanylation (SF₅-arylation) reactions. 1,3-Dicarbonyl compounds smoothly react with SF₅-aryliodonium salts **1** to provide SF₅-arylation products having a quaternary carbon center in good to high yields. The SF₅-arylation by **1** was also found to be effective for a wide variety of heterocentered nucleophiles (Scheme 1c). The application of this method for the late-stage derivatization of biologically important molecules, affording SF₅-arene analogues, is also described.

Diaryliodonium salts have gained attention as arylation agents with a variety of nucleophiles under metal-free or metal-catalyzed conditions.¹⁹ An ideal transformation can be obtained using symmetrical diaryliodonium salts; however, the symmetrical diaryliodonium salts are not suitable for SF₅-arylation since half of the “expensive” SF₅-aryl must be sacrificed to achieve a desired reaction. On the other hand, unsymmetrical diaryliodonium salts sometimes encounter poor regioselectivity for arylation.²⁰ On the basis of the vast number of investigations on the chemistry of diaryliodonium salts,¹⁹ regioselectivity for arylation could be controlled by the balance of electronic differences of the two independent aryl groups and their steric factors, and the electron-deficient aryl moiety tends to be preferably transferred.²⁰ Fortunately, the SF₅-aryls are fundamentally electron-deficient; thus, electron-rich aryl groups with or without steric hindrance could be considered as dummy aryl ligands, i.e., the mesitylene or anisole group. Designed SF₅-aryliodonium salts **1** were easily synthesized in a one-pot process from iodo-SF₅-aryls with mesitylene or anisole using *m*-CPBA and trifluoromethanesulfonic acid at room temperature (Scheme 2).^{19c,d} The iodonium salts **1** were characterized by spectroscopic analysis and X-ray crystallography in the case of **1c** (Figure 2).

With the reagents **1** in hand, we first attempted the electrophilic SF₅-arylation of cyclic β-keto esters **3** with **1** in the presence of NaH in DMF (Scheme 3).^{19j} Compared to the iodonium salt **1b** with anisole in the dummy part of the ligand,

Scheme 2. Synthesis of SF₅-Arylaryliodonium Salts **1**

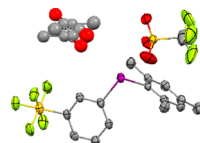
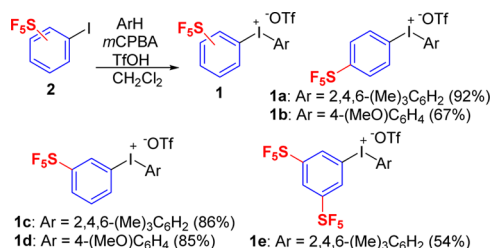
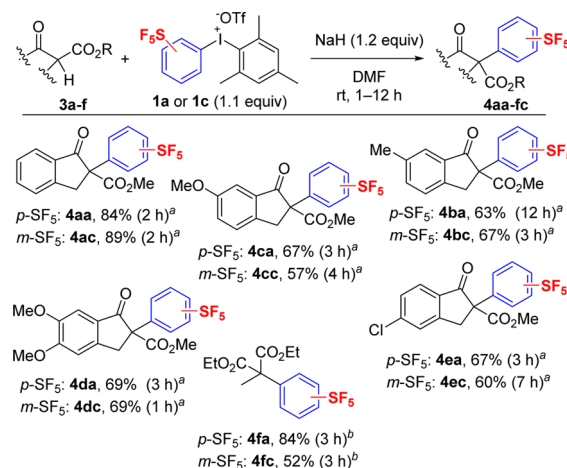


Figure 2. X-ray crystallographic structure of **1c** (CCDC 1062829).

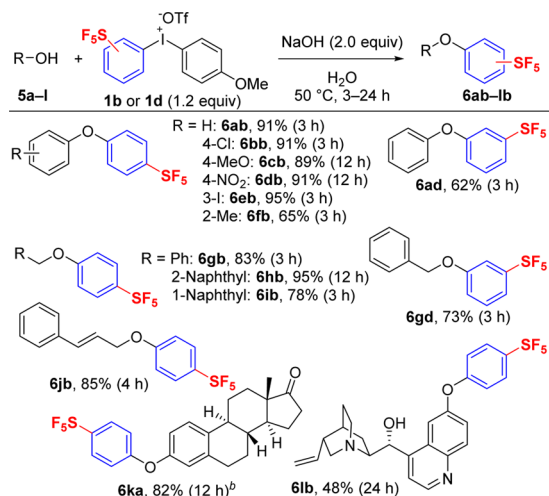
Scheme 3. SF₅-Arylation of 1,3-Dicarbonyl Compounds **3** with Reagents **1a** and **1c**



^aThe reaction of **3** (0.10 mmol) with reagent **1a** or **1c** (0.11 mmol) was carried out in the presence of NaH (0.12 mmol) in DMF (1.0 mL) at rt. ^bThe reaction was carried out with malonate **3f** (0.30 mmol), reagent **1a** (0.39 mmol), and NaH (0.39 mmol) in DMF (1.17 mL).

the reagent **1a**, having a steric mesityl group, was found to be preferred, giving the desired **4aa** in better yield (64% by **1b** vs 84% by **1a**).²⁰ Both electron-donating (OMe, Me) and electron-withdrawing (Cl) functional groups on substrates **3** were acceptable for electrophilic SF₅-arylation by **1a** providing corresponding products with an SF₅-arene on the quaternary carbon center in good to high yields (**4aa–dc**). Less reactive malonate **3f** also reacted with **1a,c** to furnish SF₅-arylation products **4fa** and **4fc** in 84% and 52% yield, respectively, under the same conditions.

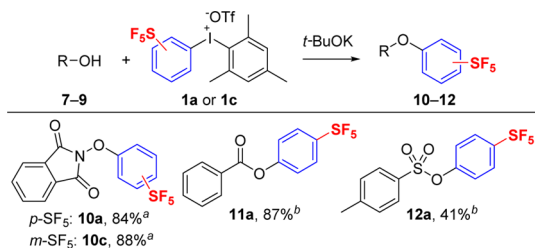
Phenols and alcohols were next examined in the SF₅-arylation with **1** (Scheme 4).^{19p} It should be noted that reagent **1b** with anisole as a dummy ligand gave considerably better yields in most cases than **1a** under NaOH/H₂O conditions (Table S1, Supporting Information). A clear advantage is that the SF₅-arylation of less reactive nitrophenol by **1b** furnished **6db** in 91% yield, while only a 24% yield of **6db** was isolated using **1a**. The reaction proceeded smoothly not only for phenols but also other oxygen nucleophiles such as naphthylmethanols, benzyl alcohol, and cinnamyl alcohol using **1b** and **1d**. It is noteworthy that SF₅-

Scheme 4. SF₅-Arylation of Phenols and Alcohols **5** with **1**^a

^aThe reaction of **5** (0.20 mmol) with reagent **1b** or **1d** (0.22 mmol) was carried out in the presence of NaOH (0.40 mmol) in H₂O (1.0 mL) at 50 °C, unless noted otherwise. ^bReagent **1a** (0.22 mmol) was employed instead of **1b**.

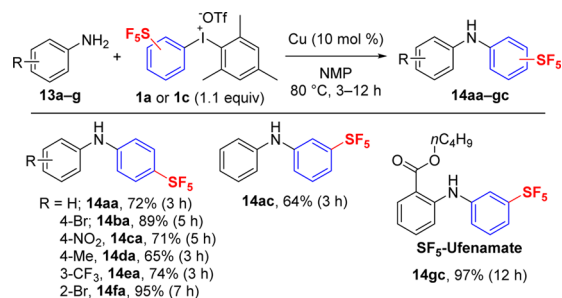
arylation of the druglike estrone derivative progressed nicely to give **6ka** in 82% yield. Chemoselective SF₅-arylation of C6'-OH cinchona alkaloid derivative was observed by **1b** to furnish **6lb** in 48% yield with a secondary alcohol moiety untouched under these conditions.

The iodonium salts **1** were reacted with other oxygen nucleophiles such as *N*-hydroxyphthalimide (**7**), carboxylic acid **8**, and sulfonic acid **9** under slightly different conditions in the presence of *t*-BuOK in DMF or toluene to provide the corresponding SF₅-arylation products **10–12** in good to high yields (Scheme 5).^{19o,r,s}

Scheme 5. SF₅-Arylations of *N*-Hydroxyphthalimide, Carboxylic Acid, and Sulfonic Acid^a

^aThe reaction of *N*-hydroxyphthalimide (**7**, 0.20 mmol) with reagent **1a** or **1c** (0.22 mmol) was carried out in the presence of *t*-BuOK (0.22 mmol) in DMF (0.8 mL) at 60 °C for 1.5 h. ^bThe reaction of benzoic acid or sulfonic acid (**11** or **12**, 0.10 mmol) with **1a** (0.11 mmol) was carried out in the presence of *t*-BuOK (0.11 mmol) in toluene (0.6 mL) at reflux for 3 h.

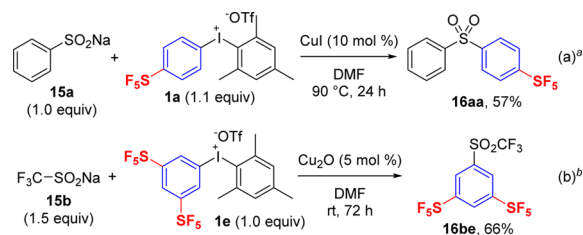
We further expanded the scope of these reagents **1** for SF₅-arylation of aromatic amines **13**.^{19j–m} After considerable optimization of the reaction conditions (Table S2), it was found that 10 mol % of Cu(0) at 80 °C in NMP allowed for the SF₅-arylation of **13** with **1**, providing good yields of **14**. The scope of substrate under the optimized conditions is shown in Scheme 6. Both electron-donating (Me) and electron-withdrawing (Br, NO₂, CF₃) groups on the aniline were accepted, and the position of their substituents, including the sterically

Scheme 6. SF₅-Arylation of Anilines **13** with **1a** or **1c**^a

^aThe reaction of **13** (0.20 mmol) with reagent **1a** or **1c** (0.22 mmol) was carried out in the presence of Cu(0) (0.020 mmol) in NMP (0.4 mL) at 80 °C.

demanding ortho position, had no effect on yields. We succeeded in synthesizing a medically attractive SF₅-analogue of the anti-inflammatory agent ufenamate in 97% yield under the same conditions (Scheme 6).

Sodium sulfinates as sulfur nucleophiles were finally examined for the reaction with **1** (Scheme 7).^{19v,w} Copper(I) salts were

Scheme 7. SF₅-Arylation of Sulfinates **15** with **1a** and **1e**

^aThe reaction of **15a** (0.20 mmol) with reagent **1a** (0.22 mmol) was carried out in the presence of CuI (0.020 mmol) in DMF (0.4 mL) at 90 °C. ^bThe reaction of **15b** (0.45 mmol) with reagent **1e** (0.30 mmol) was carried out in the presence of Cu₂O (0.015 mmol) in DMF (1.5 mL) at rt.

found to be necessary to obtain good yields of SF₅-arylated sulfones **16**. It is noteworthy that highly electron-deficient benzene derivative **16be** was synthesized by this method, and its potential utility as a nonexplosive alternative to trinitrobenzene will be examined.^{15d}

In conclusion, this study has revealed that SF₅-arylaryl-λ³-iodanes **1** are effective reagents for the electrophilic SF₅-arylation of 1,3-dicarbonyl compounds, phenols, alcohols, *N*-hydroxyphthalimide, carboxylic acid, sulfonic acid, anilines, and sulfinates. A wide variety of SF₅-arylated compounds can be obtained in the presence of a base or copper catalyst under mild conditions in good to high yields. The reagents **1** are applicable for the late-stage functionalization of medically attractive molecules. This should be a nice application of established arylations using iodonium salts for the synthesis of SF₅-aryl compounds, which have not been easy to obtain. Further studies on the potential of **1** are now under investigation.

■ ASSOCIATED CONTENT

Supporting Information

Scheme S1, Table S1, experimental details, analytical data (HRMS), copies of ¹H, ¹³C, and ¹⁹F NMR spectra, and X-ray data (CIF). The Supporting Information is available free of

charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b01323.

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Notes

The authors declare no competing financial interest.

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