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

Kohei Matsuzaki,[†] Kenta Okuyama,[†] Etsuko Tokunaga,[†] Norimichi Saito,[‡] Motoo Shiro,[§] and Norio Shibata*[,†]

[†]Department of Nanopharmaceutical Sciences, Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan

[‡]Pharmaceutical Division, Ube Industries, Ltd., Seavans North Building 1-2-1 Shibaura, Minato-ku, Tokyo 105-8449, Japan

[§]Rigaku Corporation, 3-9-12 Mastubara-cho, Akishima, Tokyo 196-8666, Japan

Supporting Information

ABSTRACT: Novel reagents for the electrophilic introduction of pentafluorosulfanyl (SF_5) arenes into target molecules are disclosed. Unsymmetrical diaryliodonium salts **1** having SF_5-arenes were synthesized by a one-pot process from iodo-SF_5-benzenes **2** in good yields. The SF_5-aryliodonium salts **1** were found to be efficient for the electrophilic SF_5-arylation of carbon and heterocentered nucleophiles to furnish the corresponding substituted SF_5-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 (CF_3-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 CF_3-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 (SF_5-Ar) have recently emerged as prospective drug units due to the chemical similarity of CF_3 and SF_5.[5] The SF_5 moiety is thermally stable (>300 °C) and also more stable under acidic and basic hydrolysis than a CF_3 group.[6] Electrostatic potential maps of CF_3-Ph and SF_5-Ph clearly indicate their three-dimensional resemblance of charge distributions and molecular size (Figure 1a).[7] However, the SF_5 group has a much higher impact on the benzene ring attached to CF_3 since it is more electronegative (Hammett substituent constants: for SF_5 $\sigma_I = 0.55$, for CF_3 $\sigma_I = 0.39$),[6] has higher intrinsic lipophilicity (Hansch hydrophobicity constants: for SF_5 $\pi = 1.51$, for CF_3 $\pi = 1.09$),[8] bulkier size of van der Waals volume (Å^3) for SF_5Ph 152.9, for CF_3Ph 129.0, for HPh 96.6),[7] and higher chemical and thermal stability.[6] Thus, replacement of the CF_3-Ar moiety in a drug or drug candidate by SF_5-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 SF_5 analogues of

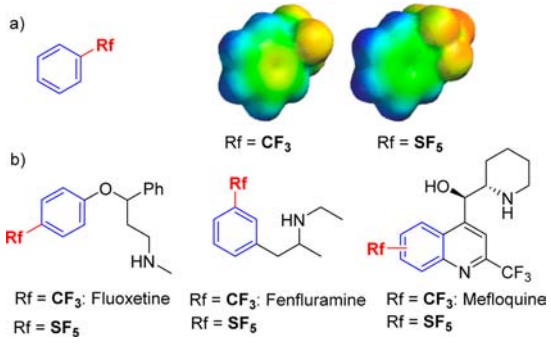

Figure 1. (a) Electrostatic potential maps of CF_3-Ph and SF_5-Ph. (b) Drug-containing CF_3-arenes and their SF_5 analogues.

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, SF_5-arenes have attracted considerable interest as a potential unit of functional materials.[11]

While many synthetic routes toward CF_3-arene compounds have been explored,[12] only a handful of synthetic methods for SF_5-arenes have been reported,[13] and the chemistry of SF_5-arenes is somewhat under-investigated. The direct construction of an SF_5 unit on benzene rings is possible from aryl disulfides using HF/Cl_2, AgF_2, or F_2 methodology.[13] However, the methods are limited to simple SF_5-arenes, and more effective and convenient methods are required. By virtue of the fact that simple SF_5-arenes are now commercially available,[14] it is hoped

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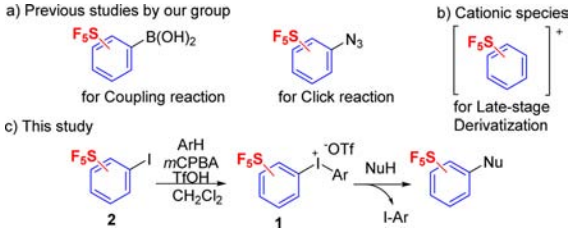
that direct functionalization of simple SF_5-arenes at all positions of the benzene ring could allow for the synthesis of more complex SF_5-arenes.[15] Recently, we reported two valuable building blocks, 3,5-bis(SF_5)phenylboronic acid[16] for the Suzuki−Miyaura coupling reaction and bis(SF_5)-5-azido-1,3-phenylene[17] as a tool for click chemistry, which furnish functional dyes and antitumor compounds, respectively (Scheme 1a). We envisaged

Scheme 1. (a) SF_5-arenes for Coupling and Click Reactions; (b) Cationic Species for Late-Stage Derivatization; (c) SF_5-Arylaryliodonium Salts 1 for SF_5-Arylations

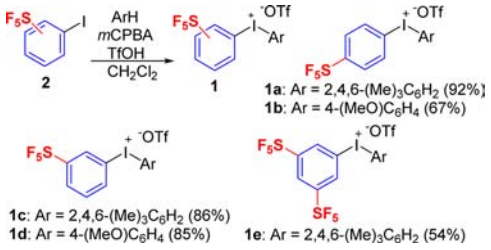


that if cationic species represented by $[SF_5\text{-Ar}]^+$ are generated (Scheme 1b), the late-stage derivatization of target molecules to SF_5-aryl compounds would be realized. As part of our ongoing research program committed to the development of late-stage fluorinated functionalized reagents,[18] herein we disclose the synthesis of unsymmetrical diaryl-λ^3-iodanes **1**, diaryliodonium salts having SF_5-arenes, and their wide utility as electrophilic regents for pentafluorosulfanylarylation (SF_5-arylation) reactions. 1,3-Dicarbonyl compounds smoothly react with SF_5-arylaryl-λ^3-iodanes **1** to provide SF_5-arylation products having a quaternary carbon center in good to high yields. The SF_5-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 SF_5-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 SF_5-arylation since half of the "expensive" SF_5-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 SF_5-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 SF_5-arylaryliodonium salts **1** were easily synthesized in a one-pot process from iodo-SF_5-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 SF_5-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 SF_5-Arylaryliodonium Salts 1



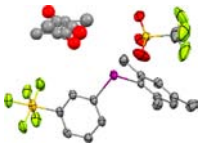
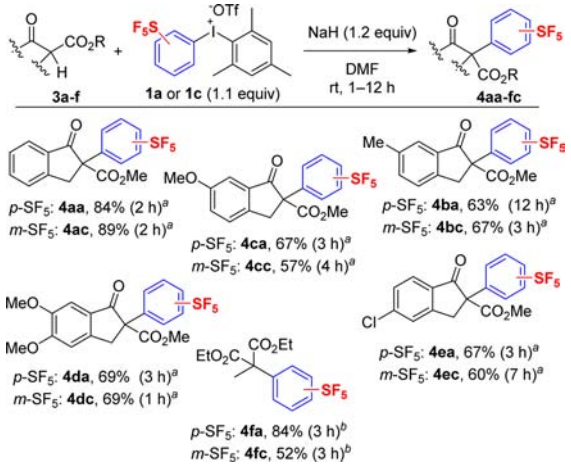


Figure 2. X-ray crystallographic structure of **1c** (CCDC 1062829).

Scheme 3. SF_5-Arylation of 1,3-Dicarbonyl Compounds 3 with Reagents 1a and 1c



[a]The 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. [b]The 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 SF_5-arylation by **1a** providing corresponding products with an SF_5-arene on the quaternary carbon center in good to high yields (**4aa**−**dc**). Less reactive malonate **3f** also reacted with **1a**,**c** to furnish SF_5-arylation products **4fa** and **4fc** in 84% and 52% yield, respectively, under the same conditions.

Phenols and alcohols were next examined in the SF_5-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 $NaOH/H_2O$ conditions (Table S1, Supporting Information). A clear advantage is that the SF_5-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 SF_5-

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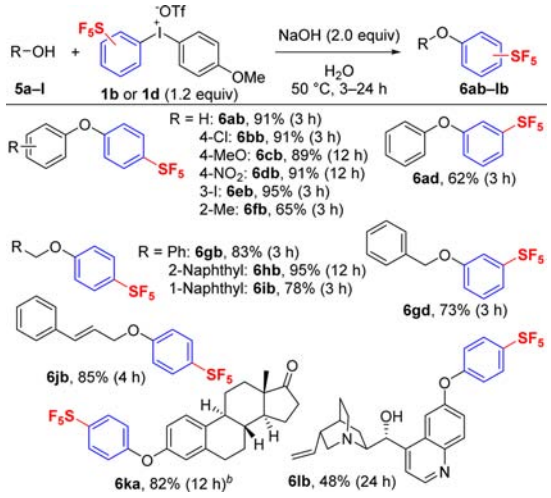
Scheme 4. SF_5-Arylation of Phenols and Alcohols 5 with 1[a]

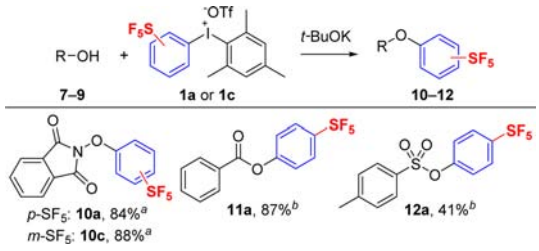


[a]The reaction of **5** (0.20 mmol) with reagent **1b** or **1d** (0.22 mmol) was carried out in the presence of NaOH (0.40 mmol) in H_2O (1.0 mL) at 50 °C, unless noted otherwise. [b]Reagent **1a** (0.22 mmol) was employed instead of **1b**.

arylation of the druglike estrone derivative progressed nicely to give **6ka** in 82% yield. Chemoselective SF_5-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 SF_5-arylation products **10**–**12** in good to high yields (Scheme 5).[19o,r,s]

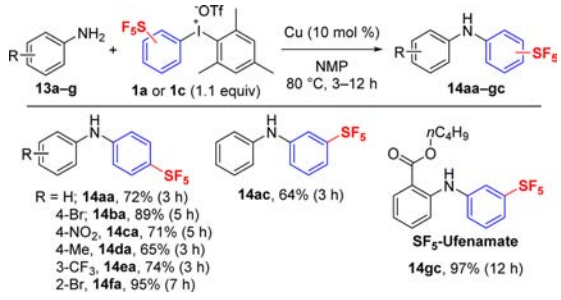
Scheme 5. SF_5-Arylations of *N*-Hydroxyphthalimide, Carboxylic Acid, and Sulfonic Acid[a]



[a]The 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. [b]The 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 SF_5-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 SF_5-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, NO_2, CF_3) groups on the aniline were accepted, and the position of their substituents, including the sterically

Scheme 6. SF_5-Arylation of Anilines 13 with 1a or 1c[a]

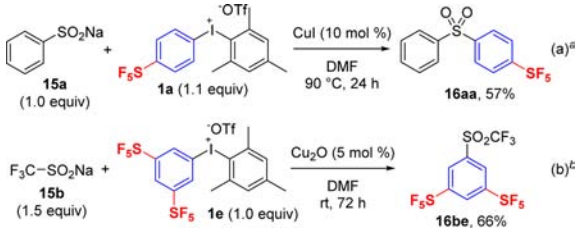


[a]The reaction of **13** (0.20 mmol) with reagent **1a** or **1c** (0.22 mmol) was carried out in the presence of Cu (0) (0.020 mmol) in NMP (0.4 mL) at 80 °C.

demanding ortho position, had no effect on yields. We succeeded in synthesizing a medicinally attractive SF_5-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. SF_5-Arylation of Sulfinates 15 with 1a and 1e



[a]The 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. [b]The reaction of **15b** (0.45 mmol) with reagent **1e** (0.30 mmol) was carried out in the presence of Cu_2O (0.015 mmol) in DMF (1.5 mL) at rt.

found to be necessary to obtain good yields of SF_5-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 SF_5-arylaryl-λ^3-iodanes **1** are effective reagents for the electrophilic SF_5-arylation of 1,3-dicarbonyl compounds, phenols, alcohols, *N*-hydroxyphthalimide, carboxylic acid, sulfonic acid, anilines, and sulfinates. A wide variety of SF_5-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 medicinally attractive molecules. This should be a nice application of established arylations using iodonium salts for the synthesis of SF_5-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, ^{13}C, and ^{19}F NMR spectra, and X-ray data (CIF). The Supporting Information is available free of

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AUTHOR INFORMATION

Corresponding Author

*E-mail: nozshiba@nitech.ac.jp.

Notes

The authors declare no competing financial interest.

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