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Synthesis of Heteroaryl Iodanes(III) via *ipso*-Substitution Reactions Using Iodine Triacetate Assisted by HFIP

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Abstract: The synthesis of monoaryl- λ^3 -iodanes generally requires the oxidation of iodoarenes, but the functional group compatibility is often problematic when using oxidizable substrates such as heteroaromatic compounds. Although electrophilic aromatic substitution or *ipso*-substitution reactions using iodine tricarboxylates have been studied as an alternative synthetic route to dicarboxyiodoarenes, several common heteroaromatic substrates such as indoles, quinolines, (benzo)furans, and (benzo)thiophenes have not been investigated to date. Here, we report that *ipso*-substitution reactions of heteroaromatic stannanes using $\text{I}(\text{OAc})_3$ in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP) effectively provide diacetoxyiodoarenes, which can be converted into the corresponding iodonium ylides or be directly used in an one-pot iodoarylation reaction.

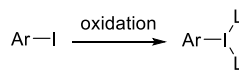
Monoaryl- λ^3 -iodanes, i.e., hypervalent iodine(III) species bearing one aromatic substituent (ArIX_2), have found widespread applications in organic synthesis.^[1] These compounds can serve as safe and less toxic oxidants and/or terminal co-oxidants in most reported transformations, in which the aryl group is not involved in the products. However, an investigation into monoaryl- λ^3 -iodanes as electrophilic aryl group donors has disclosed a unique sigmatropic rearrangement reaction pathway leading to the introduction of a 2-iodoaryl group in nucleophiles without cleavage of the carbon–iodine bond.^[2–4] In addition, monoaryl iodonium ylides with a Meldrum's acid backbone, which are readily obtained from monoaryl- λ^3 -iodanes, are efficient precursors for ^{18}F positron emission tomography (PET) probes.^[5,6] In order to further extend their applications as arylating agents, the development of broadly applicable synthetic routes to mono- λ^3 -aryliodanes is of great importance.

The oxidation of aryl iodides is the most straightforward and thus well-documented protocol providing access to monoaryl- λ^3 -iodanes (Scheme 1a).^[7–13] The functional group compatibility is, however, of great concern when applied to oxidizable substrates. To avoid an additional oxidation step, the direct introduction of a trivalent iodine moiety ($-\text{IX}_2$) in aromatic rings using $[\text{I}(\text{OCOCF}_3)_3]_2(\text{OCOCF}_3)(\text{NO})$ (ITT) or $\text{I}(\text{OAc})_3$ has been investigated (Scheme 1b).^[14–16] Electrophilic aromatic substitution reactions using ITT were reported by Maletina in 1974^[14] and by Kurosawa in 1987.^[15] A recent report by Wirth demonstrated the potential of such electrophilic substitution reactions with iodine tricarboxylates as an alternative route to

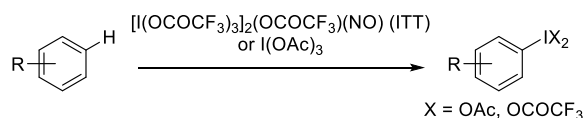
monoaryl- λ^3 -iodanes, thus circumventing said additional oxidation step.^[16]

We have reported that arylgermanes, arylstannanes, and arylsilanes undergo selective *ipso*-substitution reactions with ITT to afford bis(trifluoroacetoxy)iodoarenes under mild reaction conditions (Scheme 1c).^[17] Such *ipso*-substitution reactions with stable organometallic precursors enable reactions at low temperatures, thus improving the functional-group compatibility. Although several oxidizable functional groups were tolerated in our previous protocol, we encountered difficulties in expanding the scope to some common heteroaromatic compounds such as indoles and quinolines. We speculated that such limitations may be due to the high electrophilicity of ITT and the instability of the resulting bis(trifluoroacetoxy)iodoarenes. This assumption prompted us to investigate similar *ipso*-substitution reactions using the less electrophilic $\text{I}(\text{OAc})_3$, which should afford more stable diacetoxyiodoarenes. Herein, we report selective *ipso*-substitution reactions of heteroaryl stannanes using $\text{I}(\text{OAc})_3$ to afford diacetoxyiodoarenes, which can be converted into the corresponding iodonium ylides or be directly used for an one-pot iodoarylation reaction.

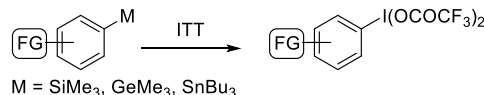
(a) Oxidation of aryl iodides



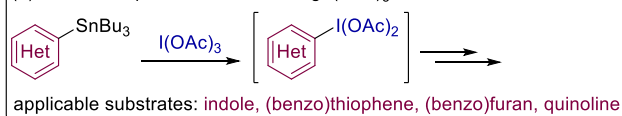
(b) Electrophilic aromatic substitution using iodine tricarboxylates



(c) Our previous work: *ipso*-substitution using ITT



(d) This work: *ipso*-substitution using $\text{I}(\text{OAc})_3$



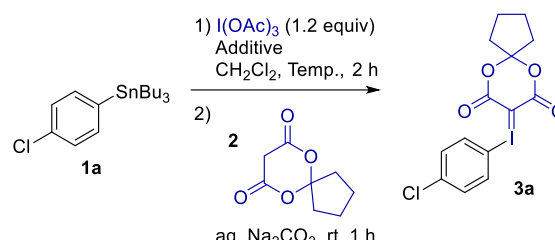
Scheme 1. Synthetic routes to monoaryl- λ^3 -iodanes.

Prior to investigating the aforementioned challenging heteroaromatic substrates, we optimized the reaction conditions using tributyl(4-chlorophenyl)stannane (**1a**) as a model substrate (Table 1). We decided to use arylstannanes expecting that their high reactivity in *ipso*-substitution reactions^[18] would compensate for the attenuated electrophilicity of I(OAc)₃ compared to that of ITT. We initially treated **1a** with I(OAc)₃ in CH₂Cl₂ at 0 °C, followed by a treatment with a basic aqueous solution of Meldrum's acid derivative **2** to convert the product into **3a** for analysis. However, **3a** was obtained only in 19% yield together with large amounts of unreacted/recovered **1a** (entry 1). To improve the reactivity, we subsequently screened several acidic additives to activate I(OAc)₃ (entries 2–8). Although the addition of strong acids such as Tf₂O, TMSOTf, BF₃·OEt₂, and B(C₆F₅)₃ resulted in complete consumption of **1a**, **3a** was not obtained (entries 2–5). In these cases, an ESI-MS analysis of the crude mixtures indicated the formation of the corresponding diaryliodonium salt, probably due to a further *ipso*-substitution reaction of **1a** with the resulting diacetoxyiodoarene promoted by such strong acids.^[19–21] On the other hand, mild acidic additives were effective to selectively promote a single *ipso*-substitution to afford **3a** in moderate to good yield (entries 6–8). Accordingly, we selected 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP)^[22] as the optimal additive (entry 8) for further examination upon considering both the reactivity and the functional group compatibility. The *ipso*-substitution reaction proceeded in moderate yield even at –20 °C in the presence of HFIP (entry 9). Increasing the amount of HFIP improved the yield (entries 10 and 11) and **1a** was fully converted in the presence of a large excess of HFIP (entry 11). Under these optimized conditions, iodonium ylide **3a** was readily isolated in 73% yield by a single recrystallization of the crude material without chromatographic purification.

Subsequently, we investigated the *ipso*-substitution of indolylstannane **1b** (Scheme 2). Treatment of **1b** with I(OAc)₃ and HFIP at –40 °C successfully provided the corresponding diacetoxyiodoindole intermediate, which was then converted into iodonium ylide **3b** in 88% yield. In addition, the *in-situ*-generated diacetoxyiodoindole was subjected to a cyanomethylation reaction using **4**, following the report by Wang and Peng.^[3g] Even though the use of TMSOTf, which was used in the original report, led to a complex mixture, we found that the use of TFAA as the activator facilitated the desired reaction, providing an isomeric mixture of **5b** and **5b'** in moderate yield and selectivity.

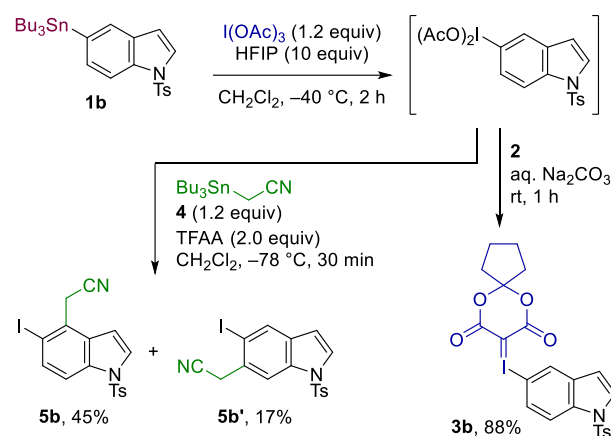
We also examined *ipso*-substitution reactions of indole derivatives **1b** and **6b** using ITT instead of I(OAc)₃ (Table 2). Under most reaction conditions, only complex mixtures were obtained, which we tentatively attributed to undesired electrophilic aromatic substitution or oxidation reactions at the C2 or C3 position of the indole (entries 1–6). When we used indolylstannane **1b** as the substrate and EtCN as the solvent, **3b** was obtained in moderate yield, but many unidentified byproducts were also formed. These results demonstrate the limitations of using ITT in combination with oxidizable heteroaromatic substrates.

Table 1. Optimization of the *ipso*-Substitution of Arylstannane **1a** Using I(OAc)₃^[a]



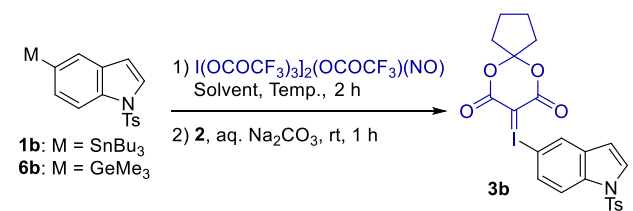
Entry	Additive (equiv)	Temp. [°C]	Yield ^[b] [%]
1	none	0	19
2	Tf ₂ O (1.3)	0	0
3	TMSOTf (1.3)	0	0
4	BF ₃ ·OEt ₂ (1.3)	0	0
5	B(C ₆ F ₅) ₃ (1.3)	0	0
6	TFA (1.3)	0	39
7	TFAA (1.3)	0	78
8	HFIP (1.3)	0	73
9	HFIP (1.3)	–20	62
10	HFIP (3.0)	–20	77
11	HFIP (10)	–20	97 (73) ^[c]

[a] Reaction conditions: 1) **1a** (0.050 mmol), I(OAc)₃ (0.060 mmol), and the corresponding additive in CH₂Cl₂ (0.50 mL) for 2 h at the indicated temperature; 2) **2** (0.10 mmol), aq. Na₂CO₃ (0.30 mL; 10% w/v) for 1 h at room temperature. [b] Determined by ¹H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard. [c] Isolated yield after recrystallization from CH₂Cl₂/hexane on a 0.30 mmol scale. TFA = trifluoroacetic acid. TFAA = trifluoroacetic anhydride.



Scheme 2. *ipso*-Substitution of indolylstannane **1b** and subsequent one-pot transformations.

Table 2. Control Experiments: *ipso*-Substitution of Indole Derivatives Using ITT.^[a]

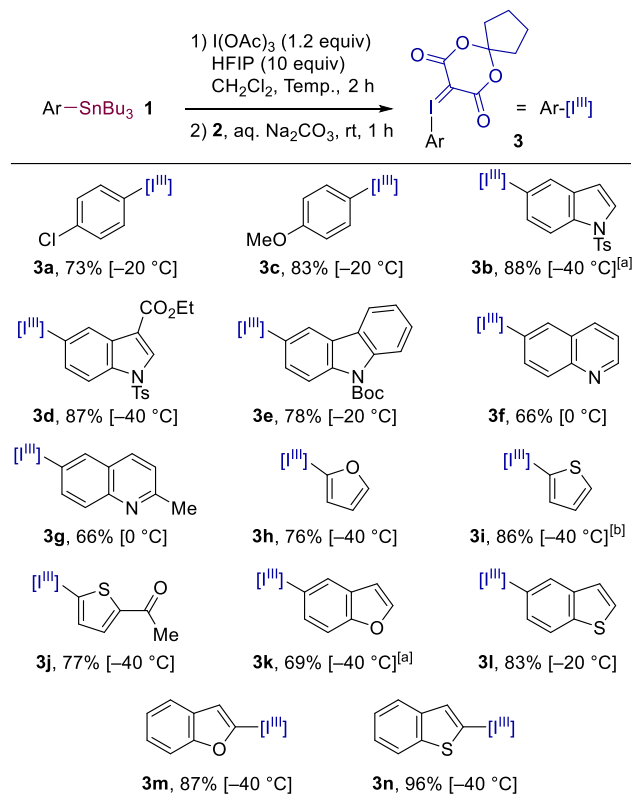


Entry	Substrate (M)	Solvent	Temp. [°C]	Result
1	6b (GeMe ₃)	CH ₂ Cl ₂	−20	Complex mixture
2	6b (GeMe ₃)	EtCN	−20	Complex mixture
3	6b (GeMe ₃)	CH ₂ Cl ₂	−40	Complex mixture
4	6b (GeMe ₃)	EtCN	−40	Complex mixture
5	1b (SnBu ₃)	CH ₂ Cl ₂	−40	Complex mixture
6	1b (SnBu ₃)	EtCN	−40	44% ^[b] + byproducts

[a] Reaction conditions: 1) **1b** or **6b** (0.050 mmol), I(OCOCF₃)₃(OCOCF₃)(NO) (0.030 mmol), and the corresponding additive in the indicated solvent (0.50 mL) for 2 h at the indicated temperature; 2) **2** (0.05 mmol), aq. Na₂CO₃ (0.15 mL; 10% w/v) for 1 h at room temperature. [b] Determined by ¹H NMR analysis of the crude mixture using 1,1,2,2-tetrachloroethane as the internal standard.

Applying the optimized reaction conditions using I(OAc)₃ to a variety of (hetero)arylstannanes (**1**) provided the corresponding (hetero)aryl iodonium ylides (**3**) in moderate to excellent yield (Scheme 3). It is noteworthy that iodonium ylides **3**, which are efficient precursors for ¹⁸F PET probes,^[5] were in most cases readily isolated by a direct recrystallization of the crude reaction mixtures. In addition to electron-rich nitrogen-containing heterocyclic substrates (**1b,d,e**), electron-deficient quinolinylstannanes (**1f,g**) also underwent this *ipso*-substitution in good yield upon increasing the reaction temperature to 0 °C (**3f,g**). We also investigated furan-, thiophene-, benzofuran-, and benzothiophene-derived stannanes, all of which efficiently provided the corresponding iodonium ylides (**3h–n**) at −20 or −40 °C.

In summary, *ipso*-substitution reactions of various electron-rich and electron-deficient heteroaromatic arylstannanes using I(OAc)₃ in the presence of HFIP effectively generates the corresponding diacetoxyiodoarenes in moderate to excellent yield. The present method enables the otherwise difficult synthesis of hypervalent iodine(III) compounds, thus facilitating the investigation of the fundamental properties, reactivity, and synthetic applications of such species.



Scheme 3. Substrate scope of the *ipso*-substitution reactions of (hetero)arylstannanes **1** using I(OAc)₃. Reaction conditions: 1) **1** (0.30 mmol), I(OAc)₃ (0.36 mmol), and HFIP (3.0 mmol) in CH₂Cl₂ (3.0 mL) for 2 h at the indicated temperature; 2) **2** (0.60 mmol), aq. Na₂CO₃ (10% w/v, 1.8 mL) for 1 h at room temperature. The isolated yield after a recrystallization is shown unless otherwise stated. [a] Isolated yield after column chromatography on silica gel. [b] The reaction was carried out using I(OAc)₃ (0.30 mmol, 1.0 equiv).

Acknowledgements

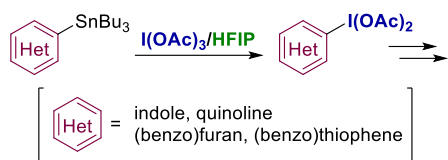
This work was supported in part by JSPS KAKENHI Grant Number JP15H05802 in Precisely Designed Catalysts with Customized Scaffolding and The Assistance Program for Kakenhi from Hokkaido University. We thank the Open Facility, Global Facility Center, Creative Research Institution, Hokkaido University for the high-resolution mass spectrometry analysis.

Keywords: hypervalent iodine • iodonium ylide • *ipso*-substitution • iodine triacetate • stannane

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Heteroaryl iodonium ylides were prepared via *ipso*-substitution reactions of heteroaryl stannanes using I(OAc)₃ in the presence of 1,1,1,3,3,3-hexafluoro-2-propanol (HFIP). Both electron-rich and electron-deficient heteroaryl stannanes were applicable substrates, and the corresponding iodonium ylides were synthesized in a one-pot fashion. The present method thus enables the otherwise difficult synthesis of hypervalent iodine(III) compounds.