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On the reaction of 4-substituted trimethyltin aromatics with perchlorylfluoride

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Abstract

To evaluate the suitability of [^{18}F]perchorylfluoride [^{18}F]$FClO_3$ as an electrophilic fluorination agent for the preparation of radiopharmaceuticals, the reactivity non-radioactive $FClO_3$ towards 4-substituted trimethyltin aromatic compounds was studied. Contrary to the expectation, an electrophilic fluorination of the aromatic nucleus did not occur. The reaction of perchlorylfluoride with aromatic trimethylstannyl compounds resulted in the formation of trimethyltin fluoride and the respective destannylated aromatics in variable yields.

Keywords: Aryl stannanes; Perchlorylfluoride; Fluorination; Electrophilic substitution

1. Introduction

Trialkyltin substituted aromatic compounds are versatile precursors for a variety of electrophilic substitution reactions in particular for radiochemical syntheses. The destannylation procedure has been used as a routine method for many years to label specific molecules with radioactive nuclides such as $^{123/131}$I, very recently summarized in [1], ^{18}F [2] and ^{211}At [3]. Numerous precursors are commercially available as trimethyltin or tributyltin aromatics for such applications. Due to their high regioselectivity, (radio)fluorodemetallation reactions are a very efficient method to obtain fluorinated substances and ^{18}F labelled radioligands in good (radiochemical) yields [4], for instance to synthesize 6-[^{18}F]fluoro-L-DOPA [5].

Tracer compounds radiolabelled with the positron emitter fluorine-18 play a pivotal role in functional molecular imaging with positron emission tomography (PET) and thus, ^{18}F labelled compounds are important for non invasive medical diagnostics and biomedical research with PET. Radiolabelling methods starting with [^{18}F]F_2 and the derived electrophilic fluorinating agents (EFAs) have two major disadvantages: (1) The radiochemical yield is ab initio limited to 50%. (2) The radiotracer is diluted by high amounts of isotopic carrier compound ^{19}F (carrier added, c.a.). The importance of n.c.a. (no carrier added) ^{18}F-labelled EFAs is based on the need for radiolabelling nucleophilic moieties of molecules.

Perchlorylfluoride ($FClO_3$) is a mild and selective gaseous EFA [6,7], which has been previously applied for fluorination of various organic substances [8,9]. It was later replaced by more reactive and more easily to handle EFAs such as acetyl hypofluorite (AcOF) and Selectfluor™ [10]. For the synthesis of radiofluorinated EFAs, [^{18}F]$FClO_3$ was identified as the only substance within the scope of our search, which can be generated in principle on an n.c.a. level starting from [^{18}F]fluoride [11]. [^{18}F]fluoride is produced in a cyclotron by proton irradiation of ^{18}O-enriched water and is obtained as aqueous solution with high specific activity.

Ehrenkaufer and MacGregor [12] reported the synthesis of ^{18}F labelled aryl fluorides by the reaction of substituted aryl lithiums with [^{18}F]$FClO_3$, the latter obtained however from [^{18}F]F_2 with $KClO_3$. First experiments in our laboratory to synthesize [^{18}F]$FClO_3$ starting from n.c.a. [^{18}F]fluoride were successful. [^{18}F]$FClO_3$ therefore should be a potential candidate for an n.c.a. [^{18}F]EFA. Coenen and

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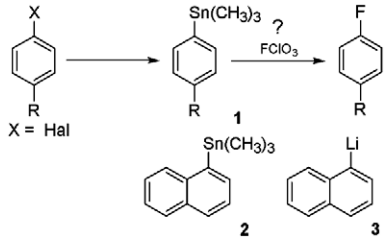
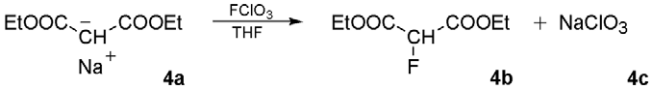
Moerlein [2] investigated the reactions of ^{18}F labelled fluorine and acetyl hypofluorite based on $[^{18}F]F_2$ (see above) with a series of 4-substituted trimethyltin aromatics and found this approach to be a promising preparative radiolabelling method. This encouraged us to study the reactivity of non-radioactive $FClO_3$ on 4-substituted aromatic trimethyltin compounds (**1**) for possible radiochemical applications to prepare n.c.a. ^{18}F labelled radiotracers. Compounds **1**, which comprise both electron deficient and electron rich aromatic systems (see Table 1) were used as model substrates expecting an $SnMe_3$ for F exchange (Scheme 1) and an increasing sensitivity to an electrophilic attack in this direction. For comparison, trimethyl-naphthalen-1-yl-stannane (**2**), naphthalen-1-yl-lithium (**3**), and sodium diethyl malonate (**4a**, see Scheme 2) were included in this study.



Scheme 1.



Scheme 2.

2. Results and discussion

All experiments were performed in micro scale with the main goal to identify fluorinated products.

2.1. Preparation of aromatic trimethyltin compounds

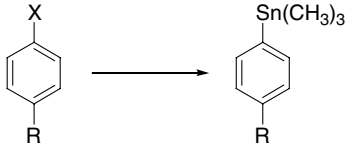
The precursor compounds were prepared as shown in Table 1 mainly referring to procedures reported in the literature. The reaction of an aromatic iodine compound with hexamethyl-distannane (Sn_2Me_6) in the presence of tetrakis(triphenylphosphine)palladium(0) $[Pd(PPh_3)_4]$ as catalyst proved to be the best synthetic approach for the trimethyltin precursors in most cases. Compound **1b** is cited without detailed description [13b]. Both the reaction of (4-bromo-phenyl)-carbamic acid *tert*-butyl ester with *n*-BuLi in THF and trimethyltin chloride and the Pd-catalyzed reaction of the corresponding iodine derivative with hexamethyltin afforded **1b** in good yields.

All trimethyltin aromatic compounds were characterized by ^1H NMR spectra.

2.2. Reactions with perchlorylfluoride

$FClO_3$ was obtained by the reaction of $KClO_4$ with fluorosulfonic acid at elevated temperature [9]. Two methods for the reaction of the trimethyltin compound with $FClO_3$ were used. Method A: addition of $FClO_3$ at about −60 °C followed by gradual warming to 60 °C in a closed vial ("closed system"), method B: introduction of $FClO_3$ at about 0 °C, further reaction at room temperature and at about 60 °C in an open vessel ("open conditions"). The reactions were monitored at various temperatures by

Table 1
Synthesis scheme of 4-substituted aromatic trimethyltin compounds and trimethyl-naphthalen-1-yl-stannane (**2**)



Entry	Starting compound		Method	Separation/purification	Yield (%)	Reference
	X	R				
1a	Iodo	NO_2	A	Recryst., CC PE/EtOAc 3:1	70	[13a]
1b	Bromo	NHBoc	C	CC PE/EtOAc 10:1	81	–
	Iodo		B	CC PE/DEE 5:1	81	–
1c	Bromo	OCH_3	C	CC PE/DEE 3:1	70	[13c, modified]
	Iodo		B	CC PE/EtOAc 10:1	85	[13d]
1d	Bromo	NH_2	B	CC PE/EtOAc 4:1	46[a]	[13e, modified]
1e	Bromo	$N(CH_3)_2$	D	CC PE/EtOAc 10:1	42[a]	[13f]
2	Bromo	Naphthyl	C	Crude product	88[b]	[13g, modified]; [14]

Method. A: Sn_2Me_6; π-allyl $PdCl_2$; B: Sn_2Me_6, $[Pd(PPh_3)_4]$; C: *n*-BuLi, Me_3SnCl; D: Li, Me_3SnCl CC: column chromatography silica gel 60; PE: petroleum ether; EtOAc: ethyl acetate; DEE: diethyl ether.

[a] Tends to decompose (destannylate) upon column chromatography complicating the separation of pure product.

[b] Contains ~8% naphthalene judged by ^1H NMR analysis, TLC: not distinguishable.

TLC. For most reactions anhydrous THF was used as solvent [9]. All reactions with compounds **1a**–**e**, **2** were conducted several times showing good reproducibility.

2.2.1. Reaction of sodium diethyl malonate (*4a*) and naphthalen-1-yl-lithium (*3*) with $FClO_3$

Molecules with carbanionic structures such as **4a** and some functionalized aryllithiums can be fluorinated in moderate yield with $FClO_3$ [8] and [^{18}F]$FClO_3$ [12]. We adopted the first reaction and obtained 2-fluoro-malonic acid diethyl ester in high yield. The precipitated solid was separated and characterized by anion chromatography to consist mainly of (sodium) chlorate (**4c**, see Scheme 2). Fluoride as well as traces of acetate and formiate were identified as by-products.

In a further experiment, we prepared naphthalen-1-yl-lithium (**3**) and tried to react it with $FClO_3$. **3** is a reactive and rather instable compound [14] and was characterized as adduct with diethyl ether by ^{1}H NMR. Contrary to the results obtained with naphthalen-2-yl-lithium [8], no fluorinated product was formed even under varying reaction conditions in agreement with Schuetz et al. [15].

2.2.2. Reaction of substituted aromatic trimethyltin compounds with $FClO_3$

In order to test the behaviour and reactivity of **1a**–**e**, these substances were reacted according to their increasing nucleophilicity with $FClO_3$ (cf. Scheme 1).

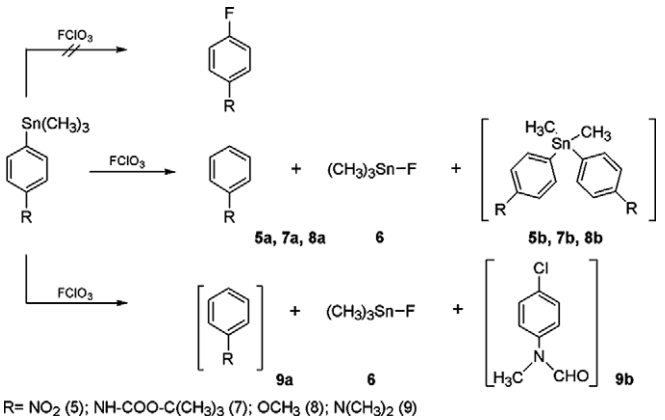
The nitro compound **1a** was reacted according to method A. At 60 °C and prolonged reaction time (60 min) only small amounts of a white solid precipitated. TLC analysis of the product mixture revealed the formation of three new trace compounds. Two reaction products could be isolated by semi-preparative TLC and identified as nitrobenzene (**5a**) and dimethyl-bis-(4-nitro-phenyl)-stannane (**5b**), a yellow solid. The expected product 4-fluoro-1-nitrobenzene could not be detected. We conclude that the reactivity of $FClO_3$ is insufficient to achieve the electrophilic fluorination of the deactivated aromatic moiety.

The electron rich aromatics **1b** and **1c** should be more reactive for electrophilic fluorination with $FClO_3$. The BOC (*tert*-butoxycarbonyl) group in **1b** however, both reduces the electron donating effect of the amino group and resonance-stabilizes the free electron pair at nitrogen. Compounds **1b**, **1c** were reacted according to methods A and B. In both cases three reaction products were observed at 60 °C. The contemporaneous precipitation of a white solid was promoted by the addition of petroleum ether. This solid substance, soluble only in polar solvents like MeOH or DMSO, shows a very high melting point and could be identified as trimethyl tinfluoride (**6**). This compound has a chain-like polymer structure $[Me_3SnF]_n$ with fluorine bridges [16]. Phenyl-carbamic acid *tert*-butyl ester (**7a**) and methoxy-benzene (**8a**) were separated from the reaction mixture by chromatographic procedures and identified as other major products, respectively. 1-Fluoro-4-methoxy-benzene was only formed in trace amounts, (4-fluoro-phenyl)-carbamic acid *tert*-butyl ester could not be detected in the product mixture. $FClO_3$ did not react with **1b**, **1c** in dichloromethane and petroleum ether as solvent.

Perchlorylfluoride reacts with **1b**, **1c** by cleavage of the $SnMe_3$ group but with fluorinating the functional group rather than the aromatic ring (Scheme 3). The formation of the C–F bond is apparently prevented by the low electrophilic power of $FClO_3$ and the only less polarized C–Sn bond due to the probably weak −I, +M effect of the $SnMe_3$ group [17]. Contrary to trimethyltin aromatics, *ortho*-lithiated anisole and phenyl-carbamic acid *tert*-butyl ester are converted into 2-fluoro derivatives in moderate yield [12]. The formation of a stable delocalized anion is supposed to promote the reaction of organolithium reagents with $FClO_3$ [15,18] but this mechanism does not explain some successful fluorinations [8]. For comparison, it was also not possible to fluorinate 1-(4-tributylstannanyl-phenyl)-1*H*-pyrazole, a non-deactivated aromatic system [21]. The behaviour of $FClO_3$ significantly differs from those of the more reactive [^{18}F]AcOF [2] where the formation of 4-fluoro compounds is the main reaction. For the formation of **5a**, **7a**, **8a** from $FClO_3$ and **1a**–**c** a hydrogen atom must be abstracted, presumably from the solvent (THF). We did not find aromatic perchloryl compounds available from $FClO_3$ and aromatics in the presence of aluminium chloride as Friedel-Crafts catalyst [19,20], even though Sn(IV) may act as a weak Lewis acid.

The by-products bis-[4-(*tert*-butoxycarbonyl-amino)-phenyl]-dimethyl-stannane (**7b**) and bis-(4-methoxy-phenyl)-dimethyl-stannane (**8b**) (given in square bracket in Scheme 3) could be isolated with semi-preparative TLC in small amounts. The reaction mechanism for the formation of **5b**, **7b**, **8b** is not quite evident. Intermediate species like $ArSnMe_2F$ come into question but could neither be isolated nor detected in the crude reaction mixture (e.g. ^{19}F NMR).

The reaction of the precursors containing amino groups **1d**, **1e** showed a different behaviour. Reactions of **1d** with $FClO_3$ according to method A and B resulted in a violet coloured solution. Several new compounds were detected



Scheme 3.

by TLC. 4-Fluoroaniline could not be verified by ESI-MS in the reaction mixture. The *N*,*N*-dimethylamino compound **1e** revealed a similar behaviour. During passing a stream of $FClO_3$ in nitrogen through the reaction mixture the solution turned violet and three new reaction products occurred at low and ambient temperature. Warming at elevated temperature led to at least 6 compounds. Again a relative large amount of **6** was isolated. (4-Fluoro-phenyl)-dimethyl-amine and dimethyl-phenyl-amine (**9a**) were detected as trace products by NMR. In particular, two strongly polar components were formed. One could be separated and identified as *N*-(4-chloro-phenyl)-*N*-methyl-formamide (**9b**) (Scheme 3). In contrast to the reactions described above, starting compound was not present in the reaction mixture. Table 2 summarizes the relative product distribution for the reaction of **1a–c** and **1e** with $FClO_3$.

The oxidizing properties of $FClO_3$ are responsible for the formation of a broad variety of by-products and the sensitive amino function will undergo numerous subsequent reactions that prevent the fluorination of the aromatic ring. Formation of **9b** can be explained with both the substitution of the $SnMe_3$ moiety by chlorine and the oxidation of one *N*-methyl group. The reaction of $FClO_3$ with amines results in the formation of N–F compounds and oxidation products which are often unstable [22]. The fluorination of phenylamine and dimethyl-phenyl-amine with $CsSO_4F$ failed as well [23]. Some N-containing and amino-substituted heterocycles afforded corresponding N-fluoro-derivatives under mild conditions [24].

Finally, compound **2** was tested according to method A and B, and with petroleum ether as solvent. The major portion of **2** did not react, a small amount of **6** was separated and three trace components were found but not further investigated. 1-Fluoro-naphthalene could not be verified.

3. Conclusions

$FClO_3$ as a weak EFA is not a suitable agent for the fluorination or radiofluorination of trimethyltin compounds to produce radiopharmaceuticals. The reactivity of $FClO_3$ is not sufficient for the electrophilic fluorination of the substituted aromatic trimethyltin compounds **1a–e**. Even compounds with high nucleophilicity show a very low $SnMe_3$ for F exchange. A series of substituted diphenyl dimethyltin compounds were recorded as trace components. Accordingly, ^{18}F-labelled $FClO_3$ is of minor interest for the labelling of aromatic substances with ^{18}F, even if it can be synthesized directly from n.c.a. [^{18}F]HF.

4. Experimental

4.1. General

Chemical reagents were purchased from standard commercial suppliers and were used without further purification. For column chromatography Merck silica gel 60 was used. Melting points were determined with a Büchi B-545 apparatus. ^1H NMR (300 or 400 MHz), ^{19}F NMR (282 MHz) and ^{119}Sn NMR (150 MHz) spectra were obtained on either a Varian Gemini or Bruker DRX-400 spectrometer, respectively and referenced to residual solvent signals or to the Ξ scale with reference to $SnMe_4$ (^{119}Sn). Thin-layer chromatography (TLC) was performed on silica gel 60_{F254} precoated plates, and spots were visualized under UV light or in a iodine chamber in the case of malonate derivatives. IR spectra were measured on KBr cards using a Perkin Elmer FT-IR spectralphotometer system 2000. ESI-, EI- and FAB-mass spectra were obtained with a Bruker APEXII (7 Tesla, in dichloromethane/methanol), Thermo Electron MAT 95 (70, 16 eV) and VG ZAB-HSQ (matrix 3-nitrobenzyl alcohol) instrument, respectively.

When products formed could not be isolated, yields were estimated from % conversion judged by ^1H NMR analysis.

4.2. Preparation of precursor substances

4.2.1. Trimethyl-(4-nitro-phenyl)-stannane (*1a*)

m.p. 51–53 °C; ^1H NMR ($CDCl_3$) δ 0.37 (9H, s, CH_3), 7.68 (2H, d, $J = 8.2$ Hz, H_{ar}), 8.15 (2H, d, H_{ar}). ^{119}Sn NMR ($CDCl_3$) δ −21 (s, Sn–CH_3, ^1H decoupled).

4.2.2. (4-Trimethylstannanyl-phenyl)-carbamic acid tert-butyl ester (*1b*)

A solution of *n*-BuLi in *n*-hexane (1.3 mL, 2 mmol) was added dropwise to a stirred solution of (4-bromo-phenyl)-carbamic acid *tert*-butyl ester (272 mg, 1 mmol) in anhydrous THF (8 mL) at −78 °C under nitrogen followed by dropwise addition of trimethyltin chloride (397 mg, 2 mmol) in THF (4 mL). The solution was

Table 2
Overview of the relative product distribution for the reaction of **1a–c** and **1e** with $FClO_3$

$SnMe_3$ compound	Number of spots (TLC)	Starting compound	Yield F-aromatic	Yield Me_3SnF (**6**) (%)	Yield destannylated compound (%)	Isolated by-product
1a	4	++	n.d.	17	11 (**5a**)	Diarylstannane (**5b**)
1b	4	+	n.d.	40	52 (**7a**)	Diarylstannane (**7b**)
1c	4(5)	+	Traces	40	34 (**8a**)	Diarylstannane (**8b**)
1e	⩾6	n.d.	Traces	52	12 (**9a**)	(**9b**)

++ detectable, + detectable, n.d. not detectable.

stirred for 30 min gradually warmed up to −40 °C, and further 1.5 h with gradual warming up to room temperature. After addition of saturated aqueous NH_4Cl (~70 mL), the mixture was extracted with diethyl ether (3 × 15 mL). The combined organic layers were washed with water, dried and concentrated resulting in an oily residue. The crude product was purified over column chromatography (Kieselgel 60; ϕ: 30, h: 145 mm) using *n*-hexane/ethyl acetate 10:1 for elution. After evaporation of the solvent nearly pure **1b** was isolated (290 mg, 81%).

A mixture of (4-iodo-phenyl)-carbamic acid *tert*-butyl ester (319 mg, 1 mmol), hexamethyl-distannane (240 μL, 1.15 mmol) and tetrakis(triphenylphosphine) palladium(0) (15 mg, 13 μmol) in dry toluene (5 mL) was stirred under nitrogen and heated to 100 °C. The solution was cooled to ambient temperature after 15 min, filtered over Celite, and the solvent was evaporated under reduced pressure. The crude product was purified over column chromatography (Kieselgel 60; ϕ: 32 mm, h: 130 mm) using petroleum ether/diethylether 5:1 for elution. The evaporation of solvents from the appropriate fractions, checked by TLC, afforded **1b** as white needles (289 mg, 81%).

m.p. 85–86 °C; ^{1}H NMR ($CDCl_3$) δ 0.26 (9H, s, CH_3), 1.51 (9H, s, *tert*-Bu), 6.43 (1H, s, NH), 7.33 (2H, d, $J = 8.4$ Hz, H_{ar}), 7.40 (2H, d, H_{ar}). ^{119}Sn NMR ($CDCl_3$) δ −27 (s, Sn–CH_3, ^{1}H decoupled). Anal Calc.: ($C_{14}H_{23}NO_2Sn$) C, 47.23; H, 6.51; N, 3.93. Found: C, 47.60; H, 6.53; N, 3.76.

4.2.3. (4-Methoxy-phenyl)-trimethyl-stannane (**1c**)

^{1}H NMR ($CDCl_3$) δ 0.26 (9H, s, CH_3), 3.81 (3H, s, OCH_3), 6.92 (2H, d, $J = 8.4$ Hz, H_{ar}), 7.41 (2H, d, H_{ar}).

4.2.4. 4-Trimethylstannanyl-phenylamine (**1d**)

^{1}H NMR ($CDCl_3$) δ 0.23 (9H, s, CH_3), 3.65 (2H, s, NH_2), 6.70 (2H, d, $J = 8.1$ Hz, H_{ar}), 7.27 (2H, d, H_{ar}).

4.2.5. Dimethyl-(4-trimethylstannanyl-phenyl)-amine (**1e**)

m.p. 38–39 °C; ^{1}H NMR ($CDCl_3$) δ 0.25 (9H, s, CH_3), 2.95 (6H, s, NCH_3), 6.77 (2H, d, $J = 8.7$ Hz, H_{ar}), 7.37 (2H, d, H_{ar}).

4.2.6. Trimethyl-naphthalen-1-yl-stannane (**2**)

^{1}H NMR ($CDCl_3$) δ 0.44 (9H, s, $J_{Sn–H} = 54$ Hz, CH_3), 7.47 (3H, m, H_{ar}), 7.65 (1H, d, H_{ar}), 7.84 (3H, m, H_{ar}).

4.2.7. Naphthalen-1-yl-lithium (**3**)

^{1}H NMR (C_6D_6/THF-d8 3:1) δ H_{ar}: 7.48 (1H, t), 7.60 (2H, m), 7.83 (1H, d), 7.95 (1H, d), 8.53 (1H, d), 8.66 (1H, d); – coordinated with 2 molecules diethyl ether: CH_3 1.13 (3H, t), OCH_2 3.31 (2H, q).

(THF-d_8/cyclohexane-d_{12} 1:2) δ H_{ar}: 7.14 (2H, m), 7.22 (1H, t), 7.35 (1H, d), 7.58 (1H, d), 8.17 (1H, d), 8.21 (1H, d); – coordinated with 2 molecules diethyl ether: CH_3 1.13 (3H, t), OCH_2 3.39 (2H, q).

4.3. Preparation of and reactions with perchlorylfluoride

Perchlorylfluoride according to [9], slightly modified.

A mixture of potassium perchlorate (usually 50 mg, 0.36 mmol) in fluorosulfonic acid (220 μL, 3.8 mmol) was charged into a 8 mL glass vial and stirred under gradual warming up to ~95 °C. $FClO_3$ was flushed with moderate N_2 flow, purified through a column filled with solid sodium thiosulfate and ascarite® (10–35 mesh) and transferred into the precursor solution.

4.3.1. General protocol for fluorination experiments with $FClO_3$

Method A. About 150–300 μmol of the aromatic trimethyltin precursor dissolved in dry THF (⩽1 mL) was cooled at −60 °C. The $FClO_3/N_2$ mixture was passed through the precursor solution for approx. 35 min. After sealing the vial, the solution was warmed up to ambient temperature under stirring and stirred at approx. 60 °C for further 20 min (''closed'' conditions).

Method B. The same procedure as described above but with the introduction of $FClO_3$ at ~0 °C, further reaction at room temp. and approx. 60 °C under ''open'' conditions.

4.3.2. 2-Fluoro-malonic acid diethyl ester (**4b**)

According to B. After separation of the white solid identified as sodium chlorate (**4c**) the isolated organics consisted of **4b** (84%) and 2,2-difluoro-malonic acid diethyl ester (16%) according to ^{1}H and ^{19}F NMR.

4.3.3. Reaction of **1a** with $FClO_3$ (200 μmol)

Nitro-benzene (**5a**). 3 mg, yield 11%; ^{1}H NMR spectroscopic data agree with published ones.

Trimethyltin fluoride (**6**). 6.1 mg, yield 17%; m.p. >330 °C; RFA: 25.27 keV (Sn, Kα), 28.48 keV (Sn, Kβ); IR (KBr); ν 2855, 2928, 1186, 555 cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 0.35 (3H, s, $J_{Sn-H} = 67.8$ Hz, Sn–CH_3), ^{1}H NMR (CD_3OD): δ 0.46 (3H, s, CH_3). ^{19}F NMR (DMSO-d_6): δ −162, ^{19}F NMR (CD_3OD): δ −168. ^{119}Sn NMR (CD_3OD): δ 47 (d, $J_{Sn–F} = 1773$ Hz, ^{1}H decoupled). Anal. Calc. for C_3H_9FSn: C, 19.71; H, 4.96. Found: C, 20.09; H, 5.10.

Dimethyl-bis-(4-nitro-phenyl)-stannane (**5b**). 4.5 mg; yellow solid; R_f 0.30 (petroleum ether/ethyl acetate 10:1).

IR: ν 3033, 2854–2955, 1574, 1346, 1595, 1514, 1188, 522 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 0.67 (3H, s, $J_{Sn-H} = 56.4$ Hz, Sn–CH_3), 7.67 (2H, d, H_{ar}), 8.19 (2H; d, $J = 7.8$ Hz). ^{119}Sn NMR ($CDCl_3$): −51 (s, ^{1}H decoupled).

EI-MS m/z: 386 $[M]^+$, 371 $[M - CH_3]^+$, 264 $[M - C_6H_4NO_2]^+$.

4.3.4. Reaction of **1b** with $FClO_3$ (150 μmol)

Phenyl-carbamic acid tert-butyl ester (**7a**). 15 mg, yield 52%; m.p. and ^{1}H NMR spectroscopic data accord with the literature data. Anal. Calc. for $C_{11}H_{15}NO_2$: C, 68.37; H, 7.82; N, 7.25. Found: C, 68.45; H, 8.03; N, 7.43.

*Trimethyltin fluoride (**6**)*. 11.5 mg, yield 40%, analytical data see above.

*Bis-[4-(tert-butoxycarbonyl-amino)-phenyl]-dimethyl-stannane (**7b**)*. 4 mg; white solid; R_f 0.27 (petroleum ether/ethyl acetate 10:1).

IR: ν 3330, 3015, 2856–2978, 1703, 1589, 1515, 515 cm^{-1}. ^1H NMR ($CDCl_3$) δ 0.45 (3H, s, J_{Sn-H} = 54.3 Hz, Sn–CH_3), 1,51 (9H, s, *tert*-Bu), 6.43 (1H, s, NH), 7.33 (2H, d, H_{ar}), 7.40 (2H, d, H_{ar}). ^{119}Sn NMR ($CDCl_3$): δ −56 (s, ^1H decoupled).

ESI-MS *m/z*: 535 $[M]^+$ $C_{24}H_{35}N_2O_4{}^{120}Sn$ det., 557 $[M + Na]^+$, 1067 $[2M]^+$.

*4.3.5. Reaction of **1c** with $FClO_3$ (300 μmol)*

*Methoxy-benzene (**8a**)*. 11 mg, yield 34%. ^1H NMR spectroscopic data are identical with published ones.

*Trimethyltin fluoride (**6**)*. 22 mg, yield 40%, analytical data see above.

*Bis-(4-methoxy-phenyl)-dimethyl-stannane (**8b**)*. 3.5 mg; semisolid substance; R_f 0.54 (petroleum ether/ethyl acetate 10:1).

^1H NMR ($CDCl_3$) δ 0.46 (3H, s, J_{Sn-H} = 54.6 Hz, Sn–CH_3), 3.81 (3H, s, OCH_3), 6.93 (2H, d, J = 8.4 Hz, H_{ar}), 7.43 (2H, d, H_{ar}).

FAB-MS *m/z*: 356 $[M]^+$, 341 $[M - CH_3]^+$, 249 $[M - C_6H_4OCH_3]^+$; EI-MS *m/z*: 341 $[M - CH_3]^+$.

*4.3.6. Reaction of **1e** with $FClO_3$ (200 μmol)*

*Dimethyl-phenyl-amine (**9a**)*. 3 mg, yield 12%. ^1H NMR spectroscopic data agree with published ones.

*Trimethyltin fluoride (**6**)*. 19 mg, yield 52%, analytical data see above.

*N-(4-Chloro-phenyl)-N-methyl-formamide (**9b**)*. 4 mg; R_f 0.56 (petroleum ether/ethyl acetate 1:1).

IR; ν 3030, 2976, 2924, 2854, 1682, 1597, 1497, 1116 cm^{-1}.

^1H NMR ($CDCl_3$) 2 rotamers ~2:1, δ 3.33/3.30 (3H, s, N-CH_3), 7.18/7.11 (2H, d, H_{ar}), 7.43/7.38 (2H, d, H_{ar}), 8.48/8.45 (1H, s, CHO).

EI-MS *m/z*: 169 $[M]^+$, 140 $[M - CHO]^+$, 134 $[M - Cl]^+$, 77 $[C_6H_5]^+$.

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