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Journal of Fluorine Chemistry 126 (2005) 797–801

JOURNAL OF FLUORINE CHEMISTRY
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Fluorinated stannanes
Part 2. The stereospecific synthesis of fluorinated stannanes via a Barbier-type reaction between fluorinated halides and tributyltin chloride mediated by zinc or cadmium[☆]

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Received 15 December 2004; received in revised form 22 February 2005; accepted 23 February 2005
Available online 13 April 2005

Abstract

Fluorinated stannanes are valuable synthons in synthetic organofluorine chemistry. Fluorinated vinyl, alkyl and aryl halides reacted efficiently with tri-*n*-butyltin chloride in the presence of zinc or cadmium to yield the corresponding stannanes in good yields. In some cases, yield of the stannanes showed a dramatic improvement over the transmetalation method. In all other cases, comparable yields were obtained.
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Keywords: Fluorinated vinyl; Aryl and alkyl stannanes; Tri-*n*-butyltin chloride; Barbier reactions; ^{119}Sn NMR spectra

1. Introduction

The stereospecific synthesis of fluorinated stannanes via a novel transmetalation of the corresponding zinc or cadmium reagents was described in an earlier report [1]. Traditional syntheses as well as utility of these reagents were also discussed.

The transmetalation method consists of first generating the fluorinated zinc or cadmium reagent, then adding tri-*n*-butyltin chloride to get the corresponding stannane. This method has an advantage over traditional methods due to the relatively stable nature of the intermediates involved—fluorinated zinc and cadmium reagents show exceptional thermal stability relative to the corresponding lithium or Grignard reagents. However, the zinc or cadmium reagents still need to be stored under complete absence of moisture or oxygen. Secondly, in the case of perfluoroalkyl systems, as the chain length increases, the yield of the corresponding cadmium reagent decreases [2].

In 1899, Philippe Barbier started his work in the area of organomagnesium chemistry, and in doing so, discovered the one-step reaction that was to be named after him: The Barbier Reaction. Barbier prepared a tertiary alcohol from a ketone and alkyl iodide in the presence of elemental magnesium with diethyl ether as the solvent followed by acid work-up [3]. Earlier, it was Frankland who first introduced the "in situ procedure". He completely bypassed the preparation of the alkyl zinc reagent when he mixed iodoethane, ethyl oxalate and zinc amalgam to obtain the tertiary alcohol [4]. The Barbier reaction involves mixing a carbonyl compound with an alkyl halide in the presence of a metal such as magnesium, zinc or cadmium. Ethereal solvents are generally used.

In an earlier report from this group, a novel Barbier-type reaction of fluorinated vinyl and aryl iodides with aldehydes in the presence of zinc to stereospecifically yield partially fluorinated alcohols was discussed [5]. Mechanistic details as well as scope of the reaction were also elucidated [5].

[☆] Presented in part at the 13th Winter Fluorine Conference, St. Pete Beach, FL, 1999, abstract # P44.

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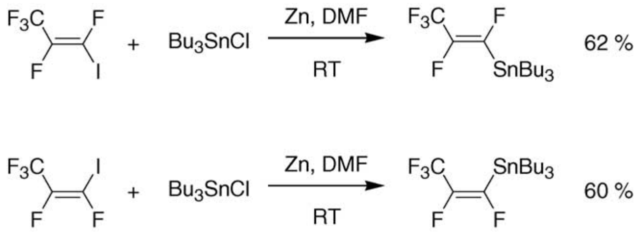
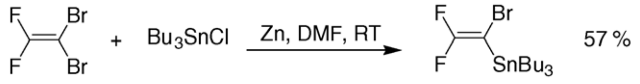
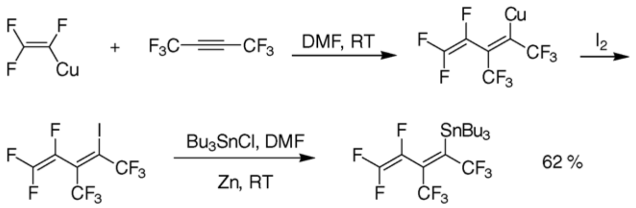
doi:10.1016/j.jfluchem.2005.02.015



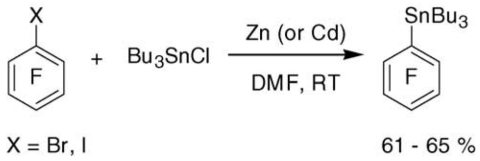
Scheme 1. Stereospecific syntheses of fluorinated propenyl stannanes.



Scheme 2. Synthesis of 1-bromo-2,2-difluoro-1-tri-*n*-butylstannylethylene.



Scheme 3. Synthesis of the pentadienyl stannane.



Scheme 4. Synthesis of pentafluorophenyl stannane.

$R_FI + Bu_3SnCl \xrightarrow{\text{Zn, DMF, RT}} R_FSnBu_3$

$R_F = n\text{-}C_3F_7$, 65 %
$n\text{-}C_4F_9$, 52 %
$n\text{-}C_6F_{13}$, 35 %

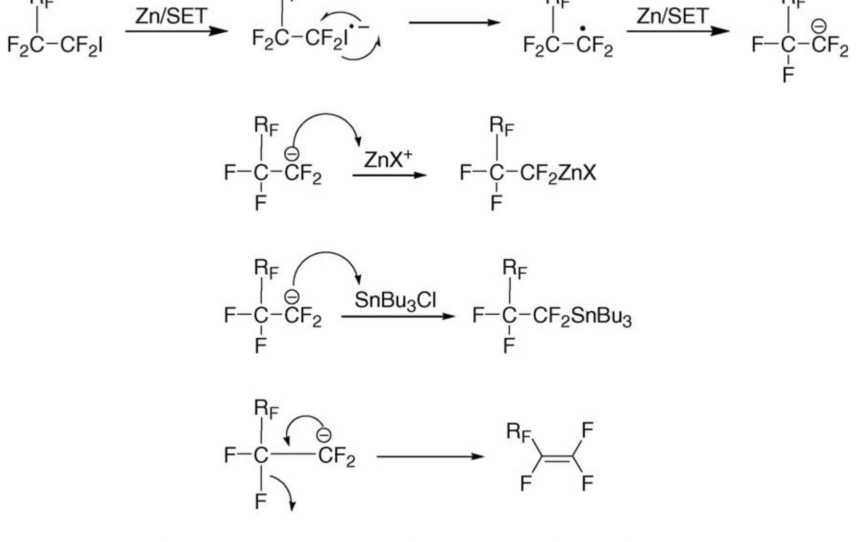
Scheme 5. Synthesis of perfluoroalkyl stannanes.

In this report, we present the stereospecific synthesis of fluorinated stannanes via a Barbier-type reaction of the corresponding fluorinated halides with tri-*n*-butyltin chloride in the presence of zinc.

2. Results and discussion

As part of a mechanistic study of the Barbier reaction, the methodology was extended to the synthesis of fluorinated stannanes [5]. (*Z*)-1-iodo-1,2,3,3,3-pentafluoropropene reacted efficiently with tri-*n*-butyltin chloride in the presence of zinc to stereospecifically yield the corresponding stannane in good yields (Scheme 1). Not surprisingly, the corresponding (*E*) isomer also reacted smoothly and stereospecifically to yield the stannane, again in good yields (Scheme 1). In either case, no isomerization about the double bond was detected by ^{19}F NMR analysis. This result was not surprising, because the mechanistic pathway of the Barbier reaction involves no change in the stereocenters. The advantage of the Barbier reaction became evident when the zinc reagent of (*E*)-1-iodo-1,2,3,3,3-pentafluoropropene failed to react with tri-*n*-butyltin chloride.

The zinc reagent of 1,1,-dibromo-2,2-difluoroethene reacted sluggishly with tri-*n*-butyltin chloride even at elevated temperatures. However, under the Barbier conditions, 1,1-dibromo-2,2-difluoroethene reacted readily with



Scheme 6. Generation and three possible pathways of the perfluoroalkyl anion.

tri-*n*-butyltin chloride to yield the corresponding stannane. This stannane was found to decompose readily even at low temperatures (Scheme 2).

The iodide obtained from the stereospecific *syn* addition of trifluorovinyl copper to 1,1,1,4,4,4-hexafluorobutyne reacted readily with tri-*n*-butyltin chloride under the Barbier conditions to yield the corresponding stannane in good yields [6] (Scheme 3).

This methodology could be extended to the pentafluorophenyl systems also. Both, iodo- and bromo-pentafluorobenzene reacted readily with tri-*n*-butyltin chloride in the presence of activated zinc (or cadmium) to yield the corresponding stannane in greater than 60% isolated yield (Scheme 4). In these systems, both the transmetalation as well as the Barbier methods gave similar results.

It is in the syntheses of perfluoroalkyl stannanes that the Barbier methodology proved its value. The zinc reagent of perfluoropropyl iodide failed to react with tri-*n*-butyltin chloride, while yields of the higher homologs decreased as the chain length increased. On the other hand, under the Barbier conditions, the yields of the stannanes increased dramatically (Scheme 5).

It has been shown that the yield-determining step of the reaction is the initial metalation [2]. The zinc reagent is formed via a series of single electron transfer reactions forming the perfluoroalkyl anion intermediate. This anion has three possible pathways:

- react with $Zn^{+}X$ to form the zinc reagent;
- react with Bu_3SnCl to form the stannane;
- eliminate to form the olefin.

Tin, being a stronger electrophile, would be preferentially attacked. On the other hand, with increase in chain length, it has been proposed that elimination would be favored [2] (Scheme 6). Hence, in the case of perfluorohexyl systems, though the yield of the stannane nearly doubled on going from the transmetalation to the Barbier method, the stannane could be isolated only in 35% yields (Table 1).

Table 1
Synthesis of fluorinated stannanes

No.	Halide	Metal	Yield (%)[a]
1	(*Z*)-$CF_3CF{=}CFI$	Zn	65
2	$CF_2{=}CBr_2$	Zn	55
3	(*Z*)-$CF_2{=}CFC(CF_3){=}C(CF_3)I$	Zn	62
4	(*E*)-$CF_3CF{=}CFI$	Zn	60
5	C_6F_5Br	Zn	65
6	C_6F_5Br	Cd	63
7	C_6F_5I	Zn	66
8	C_6F_5I	Cd	61
9	C_4F_9I	Cd	50
10	C_4F_9I	Zn	51
11	C_3F_7I	Zn	65
12	$C_6F_{13}I$	Zn	35

[a] Isolated yields based on the starting halide.

3. Conclusions

An efficient and stereospecific method for the synthesis of fluorinated stannanes is described. This methodology makes use of cheap and readily available starting materials and reagents. This is a ‘one-pot’ reaction and no unstable intermediates are involved. No major reaction set up is required. Work-up, isolation and characterization protocols are straightforward.

4. Experimental

4.1. General

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen. DMF was dried by stirring over calcium hydride followed by distillation under reduced pressure. Zinc and cadmium activated by the following method: 50 g of the metal was stirred with 500 mL of distilled water. To this slurry was added concentrated HCl drop wise until the metal began to coagulate (about 10 mL). The slurry was stirred for about 20 min and decanted. The metal was washed repeatedly with water (3 × 500 mL), acetone (3 × 250 mL) and ether (3 × 100 mL). The metal was finally dried under full vacuum for at least 8 h.

Most of the starting materials were commercial samples and were used as received, with the following exceptions: 1-iodoperfluorobutane and 1,1-dibromo-2,2-difluoroethene were distilled before use. The pentadienyl iodide as well as (*Z*)- and (*E*)-1-iodo-1,2,3,3,3-pentafluoropropene were prepared by the literature procedure [6–8]. Tri-*n*-butyltin chloride was used as received.

^{19}F NMR spectra were recorded on a Bruker AC-300 spectrometer operating at 282.41 MHz. The spectra of reaction mixtures were recorded in the reaction solvent, while those of isolated products in $CDCl_3$. All chemical shifts are reported in ppm relative to either chlorotrifluoromethane ($CFCl_3$) $\delta = 0$ ppm or benzotrifluoride ($PhCF_3$) $\delta = 63.2$ ppm. Hydrogen-decoupled fluorine NMR spectra were obtained when hydrogens were present in the olefinic system that could couple with fluorine. ^{1}H NMR spectra were recorded either on a Bruker AC-300 spectrometer operating at 300.17 MHz or a Bruker WM-360 spectrometer operating at 360.14 MHz or a Bruker DRX-400 spectrometer operating at 400.13 MHz. $CDCl_3$ was the lock solvent used in all cases. Chemical shifts are reported in ppm relative to internal TMS or the solvent itself. ^{13}C NMR spectra were recorded either on a Bruker AC-300 spectrometer operating at 75.49 MHz or a Bruker WM-360 spectrometer operating at 90.57 MHz or a Bruker DRX-400 spectrometer operating at 100.62 MHz. $CDCl_3$ was the lock solvent used in all cases. Chemical shifts are reported in ppm relative to internal TMS or the solvent itself. ^{119}Sn NMR spectra were recorded on a Bruker WM-360 spectrometer operating at 134.29 MHz. The spectra were obtained either in DMF or neat. Chemical shifts are reported in ppm relative to standard tetramethyltin, which was placed in a capillary inside the NMR sample tube. It was found that tetramethyltin underwent exchange with fluorinated tributyltin, which resulted in complicated spectra.

Mass spectra were obtained either on a TRIO-1 or a Varian GC–MS Spectrometer, both operating at 70 eV in the electron impact mode.

4.2. Barbier reaction of fluorinated halides with tri-n-butyltin chloride—a representative procedure

A 25 mL single necked round bottomed flask equipped with a side arm, Teflon® coated magnetic stir bar and cold water condenser attached to a nitrogen-T was charged with acid washed zinc and dry DMF. To this slurry was charged tri-*n*-butyltin chloride and the mixture stirred at room temperature. To this stirred reaction mixture was added (*Z*)-1-iodo-1,2,3,3,3-pentafluoropropene slowly via a syringe. The reaction was instantaneous, as indicated by an exotherm. The reaction mixture was stirred at room temperature for about 2 h. The reaction mixture was then washed with water and extracted with ether. The ether extracts were combined and washed with a saturated aqueous solution of potassium fluoride. The organic layer was washed again with water, dried over anhydrous magnesium sulfate and isolated by column chromatography, using hexanes as the eluant, unless otherwise indicated. Generally, R_F values of the stannanes were high (greater than 0.65).

4.2.1. (Z)-1-Tri-n-butylstannyl-1,2,3,3,3-pentafluoropropene

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.29 g (5 mmol) of (*Z*)-1-iodo-1,2,3,3,3-pentafluoropropene gave 1.37 g (65%) of the product. All spectroscopic data match with the reported values [1].

4.2.2. 1-Bromo-2,2-difluoro-1-tri-n-butylstannylethene

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 1.6 g (5 mmol) of tri-*n*-butyltin chloride and 1.1 g (5 mmol) of 1,1-dibromo-2,2-difluoroethene gave 1.18 g (55%) of the product. This product decomposed quickly to a white solid, possibly tri-*n*-butyltin fluoride even at low temperatures, so all the spectroscopic data could not be obtained.

^{19}F NMR ($CDCl_3$): δ −63.2 (d, $^2J_{FF} = 43.6$ Hz, 1F, $C\mathit{F}_2{=}CBrSnBu_3$); −81.0 (d, $^2J_{FF} = 43.6$ Hz, 1F, $C\mathit{F}_2{=}CBrCBrSnBu_3$).

On adding a crystal of iodine to an aliquot from the reaction mixture, the vinyl stannane was readily converted to 1-bromo-1-iodo-2,2-difluoroethylene.

^{19}F NMR ($CDCl_3$): δ −73.4 (d, $^2J_{FF} = 30.0$ Hz, 1F, $C\mathit{F}_2{=}CBrI$); −76.7 (d, $^2J_{FF} = 28.0$ Hz, 1F, $C\mathit{F}_2{=}CBrI$) [9].

4.2.3. (Z)-1,1,2,5,5,5-Pentafluoro-4-tri-n-butylstannyl-3-trifluoromethyl-1,3-pentadiene

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 1.63 g (5 mmol) of tri-*n*-butyltin chloride and 1.85 g (5 mmol) of (*Z*)-1,1,2,5,5,5-pentafluoro-4-iodo-3-trifluoromethylpentadiene gave 1.28 g (62%) of the product. This product decomposed quickly to a white solid, possibly tri-*n*-butyltin fluoride, so all the spectroscopic data could not be obtained.

^{19}F NMR ($CDCl_3$): δ −55.1 (qd, 13.7 Hz, $^5J_{FF} = 4.0$, 3F, $(C\mathit{F_3})C(SnBu_3){=}C(CF_3)CF{=}CF_2$); −61.1 (qm, $^5J_{FF} = 14.7$ Hz, 3F, $(CF_3)C(SnBu_3){=}C(C\mathit{F_3})CF{=}CF_2$); −96.2 (dd, $^2J_{FF} = 62.6$ Hz, $^3J_{FF(cis)} = 31.2$ Hz, 1F, $(CF_3)C(SnBu_3){=}C(CF_3)CF{=}C\mathit{F_2}$); −112.6 (dd, $^3J_{FF(trans)} = 121.0$ Hz, $^2J_{FF} = 61.2$ Hz, 1F, $(CF_3)C(SnBu_3){=}C(CF_3)CF{=}C\mathit{F_2}$); −158.6 (ddm, $^3J_{FF(trans)} = 119.6$ Hz, $^3J_{FF(cis)} = 31.2$ Hz, 1F, $(CF_3)C(SnBu_3){=}C(CF_3)C\mathit{F}{=}CF_2$).

^{1}H NMR ($CDCl_3$): δ 0.9 (tm, $^3J_{FF} = 5.0$ Hz, 9H, R_F Sn ($CH_2\ CH_2\ CH_2\ C\mathit{H_3})_3$); 1.1 (m, 6H, R_F Sn ($C\mathit{H_2}\ CH_2\ CH_2\ CH_3)_3$); 1.4 (m, 6H, R_F Sn ($CH_2\ C\mathit{H_2}\ CH_2\ CH_3)_3$); 1.5 (m, 6H, R_F Sn ($CH_2\ CH_2\ C\mathit{H_2}\ CH_3)_3$).

4.2.4. (E)-1-Tri-n-Butylstannyl-1,2,3,3,3-pentafluorpropene

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.29 g (5 mmol) of (*E*)-1-iodo-1,2,3,3,3-pentafluoropropene gave 1.3 g (60%) of the product.

^{19}F NMR ($CDCl_3$): δ −68.9 (m, 3F, $(C\mathit{F_3})C(F){=}C(F)SnC(F)SnBu_3$); −132.2 (m, 1F, $^3J_{SnF} = 147.0$ Hz, $(CF_3)C(\mathit{F}){=}C(F)SnBu_3$); −142.7 (brq, $^4J_{FF} = 14.0$ Hz, 1F, $(CF_3)C(F){=}C(\mathit{F})SnBu_3$).

^{1}H NMR ($CDCl_3$): δ 0.92 (t, $^3J_{HH} = 7.2$ Hz, 9H, R_F Sn ($CH_2\ CH_2\ CH_2\ C\mathit{H_3})_3$); 1.2 (m, 6H, R_F Sn ($C\mathit{H_2}\ CH_2\ CH_2\ CH_3)_3$); 1.4 (m, 6H, R_F Sn ($CH_2\ C\mathit{H_2}\ CH_2\ CH_3)_3$); 1.5 (m, 6H, R_F Sn ($CH_2\ CH_2\ C\mathit{H_2}\ CH_3)_3$).

^{13}C NMR ($CDCl_3$): δ 11.3 (s, R_F Sn ($CH_2\ CH_2\ CH_2\ \mathit{C}H_3)_3$); 13.7 (s, R_F Sn ($CH_2\ CH_2\ C\mathit{H_2}\ CH_3)_3$); 27.5 (s, $^2J_{SnC} = 63.5$ Hz, R_F Sn ($\mathit{C}H_2\ CH_2\ CH_2\ CH_3)_3$); 28.9 (s, $^3J_{SnC} = 22.7$ Hz, R_F Sn ($CH_2\ \mathit{C}H_2\ CH_2\ CH_3)_3$); 162.7 (dqd, $^1J_{CF} = 321.1$ Hz, $^2J_{CF} = 23.9$ Hz, $^3J_{CF} = 7.5$ Hz, $(CF_3)C(F){=}\mathit{C}(F)SnBu_3$); 144.8 (dqd, $^1J_{CF} = 275.7$ Hz, $^2J_{CF} = 37.7$ Hz, 15.6 Hz, $(CF_3)\mathit{C}(F){=}C(F)SnBu_3$); 120.4 (qdd, $^1J_{CF} = 270.1$ Hz, $^2J_{CF} = 61.7$ Hz, $^3J_{FF} = 7.5$ Hz, $(\mathit{C}F_3)C(F){=}C(F)SnBu_3$).

^{119}Sn NMR (Neat): δ −25.3 (dd, $^2J_{SnF} = 152.6$ Hz, $^3J_{SnF} = 12.4$ Hz).

GC–MS: 365 (M^+—57, 59); 309 (M^+—114, 100); 250 (M^+—171, 36); 57 (*n*-Bu, 67) [10].

4.2.5. Pentafluorophenyl tri-n-butylstannane from bromopentafluorobenzene mediated by zinc

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.24 g (5.02 mmol) of bromopentafluorobenzene gave 1.48 g (65%) of the product. All spectroscopic data match with the reported values [1]. Similar results were obtained when iodopentafluorobenzene was used; as also when the reaction was promoted by cadmium.

4.2.6. *n-Perfluoropropyl tri-n-butylstannane*

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.48 g (5 mmol) of 1-iodoperfluoropropane gave 1.19 g (65%) of the product.

^{19}F NMR ($CDCl_3$): δ -80.0 (t, $^4J_{FF} = 9.7$ Hz, 3F, $CF_3\,CF_2\,CF_2\,SnBu_3$); -118.6 (bq, 2F, $^2J_{FF} = 187.1$ Hz, $CF_3\,CF_2\,CF_2\,SnBu_3$); -122.9 (s, 2F, $CF_3\,CF_2\,CF_2\,SnBu_3$).

^1H NMR ($CDCl_3$): δ 0.9 (t, $^3J_{FF} = 7.1$ Hz, 3H, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 1.3 ($R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$), 1.4 (m, 4H, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 1.6 (m, 2H, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$).

^{13}C NMR ($CDCl_3$): δ 10.8 (s, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 13.7 (s, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 27.6 (s, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 28.8 (s, $R_F\,Sn\,(CH_2\,CH_2\,CH_2\,CH_3)_3$); 107–134 (m, $CF_3\,CF_2\,CF_2\,SnBu_3$).

^{119}Sn NMR ($CDCl_3$): δ -6.5 (t, $^2J_{SnF} = 196.1$ Hz).

GC–MS: 403 (M^+—57, 10) [11].

4.2.7. *n-Perfluorobutyl tri-n-butylstannane*

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.73 g (5 mmol) of 1-iodoperfluorobutane gave 0.99 g (52%) of the product. This product decomposed quickly, even at low temperatures, so complete spectroscopic data could not be obtained. It was also observed that this stannane reacted sluggishly with iodine even at elevated temperatures. All spectroscopic data match with reported values [1,12].

4.2.8. *n-Perfluorohexyl tri-n-butylstannane*

Similarly, the reaction of 0.65 g (10 mmol) of acid washed zinc, 5.0 mL of dry DMF, 3.25 g (10 mmol) of tri-*n*-butyltin chloride and 1.23 g (5 mmol) of 1-iodoperfluorohexane gave 1.23 g (35%) of the product. This product decomposed quickly, even at low temperatures, so complete spectroscopic data could not be obtained. It was also observed that this stannane reacted sluggishly with iodine even at elevated temperatures.

^{19}F NMR ($CDCl_3$): δ -81.4 (m, 3F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$); -117.8 (m, 2F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$); -118.2 (m, 2F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$); -122.5 (m, 2F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$); -123.4 (m, 2F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$); -126.7 (m, 2F, $CF_3\,CF_2\,CF_2\,CF_2\,CF_2\,CF_2\,SnBu_3$).

^{119}Sn NMR ($CDCl_3$): δ 9.9 (bm).

Acknowledgement

We thank the National Science Foundation for financial support of this work.

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