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A Novel Stereospecific Route to E and Z-2-Substituted-1,2-Difluoroethenylstannanes

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Abstract: *A series of E and Z-2-substituted-1,2-difluoroethenylstannanes are readily obtained in good yield (69-92%) by the reaction of the corresponding fluorinated alkenyl silanes with tributylstannyl chloride and potassium fluoride in DMF under mild conditions.*

Unsaturated organostannanes are widely utilized for the construction of carbon-carbon bonds *via* palladium-catalyzed coupling with organic halides and sulfonates (Stille Reaction).[1] However, fluorinated analogs have received little attention in this transformation, in part due to limited synthetic methodology for the preparation of fluorinated alkenylstannanes. Trifluorovinylstannanes (CF_2=$CFSnR_3$) have been prepared from the corresponding trifluorovinylmagnesium[2] or trifluorovinyllithium[3] reagents and trialkylstannyl halides, and have been successfully employed in the Stille reaction.[4,5] The stereospecific preparation of E- and Z-α-fluorovinylstannanes *via* the radical reaction of the corresponding α-fluorovinylsulfones with tributyltin hydride has been reported by McCarthy.[6] Recently, ethyl-3-fluoro-3-(tributylstannyl)-2-methoxyacrylate was prepared from ethyl trifluoropyruvate in several steps and used in the Stille reaction for the synthesis of β-fluoro-α-keto acid derivatives.[7]

Our recent interest in the development of difluoroethenyl synthons[8] prompted our attention to the preparation of E- and Z-2-substituted-1,2-difluoroethenylstannanes, R'CF=$CFSnR_3$ (where R' = alkyl, aryl, H, I). Based on analogous silane chemistry,[9] an addition-elimination reaction between R'Li (R' = alkyl, aryl) and trifluorovinylstannanes would appear to be a reasonable route to the title compounds. However, in contrast to the facile formation of 2-substituted-1,2-difluoroethenylsilanes, the trifluorovinylstannanes gave **only** the exchange product (CF_2 = CFLi) with R'Li[3,10] and none of the addition-elimination product. Similarly, reduction of trifluorovinylsilanes with $LiAlH_4$ gave excellent yields of Z-CHF=$CFSiR_3$,[8] whereas reduction of the analogous trifluorovinylstannanes gave **only** trifluoroethylene[11] and no CHF=$CFSnR_3$. Curiously, radical reduction (Me_3SnH) of trifluoroethenylstannane gives the 1,2-

difluoroethenylstannanes; however, the reduction is not stereospecific.[12] Consequently, it was necessary to develop a new, stereospecific route to these synthons.

Here we report a new, general method for the stereospecific preparation of 2-substituted-1,2-difluoroethenylstannanes ($RCF=CFSnBu_3$, R = H, I, Ph, alkyl, $F_2C=CF$) from the corresponding silanes, which are readily synthesized *via* a modified literature procedure.[9] Either E or Z-1,2-difluoroethenylsilanes reacted with tributylstannyl chloride in the presence of dry potassium fluoride in DMF at RT-80°C to stereospecifically afford the corresponding stannanes in good yields. **Table 1** summarizes our preliminary results. Although Buchwald[13] recently reported the conversion of trimethylsilylated acetylenes to the corresponding stannanes using TBAF and bis(tributyltin)oxide, to our knowledge this work is the first report of the stereospecific conversion of a vinylsilane to the corresponding vinylstannane.

In all cases, the configuration of the double bond was unchanged and trialkylsilyl fluoride was formed as the major byproduct. When R was iodine, phenyl, or trifluorovinyl, the conversion occurred readily at room temperature. The conversion proceeded slowly at room temperature when R = H, and no reaction was observed at room temperature when R = alkyl. However, at 70-80°C the conversion of the ethenylsilane to ethenylstannane occurred readily regardless of the nature of the R-group. The trimethylsilyl derivatives were more reactive than the corresponding triethylsilyl derivative (Entries 8,9), presumably due to more facile attack by fluoride ion on the smaller trimethylsilyl group.

In a typical experimental procedure, a round bottom flask equipped with a nitrogen tee, Teflon coated magnetic stir bar, and rubber septum, was charged with dry DMF (20 mL), anhydrous potassium fluoride (1.33 g. 22.9 mmol), and E-1,2-difluoro-2-iodoethenyltriethylsilane (4.95 g., 16.3 mmol). Tributyltin chloride (5.32 g, 16.3 mmol) was added *via* syringe and the reaction mixture was stirred at room temperature overnight. Analysis by ^{19}F NMR indicated the absence of the vinylsilane. The reaction mixture was extracted with ether and washed with water. Evaporation of solvent followed by chromatography on silica gel using hexane as eluant gave 6.5 g of E-1,2-difluoro-2-iodoethenyltributylstannane in 83% yield. ^{19}F NMR ($CDCl_3$): -122.8 (d, J = 137.3 Hz, 1F), -133.7 (d, J = 137.3 Hz, 1F) ppm; ^1H NMR ($CDCl_3$): 0.91 (t, J = 7.3 Hz, 9H), 1.23 (m, 6H), 1.34 (m, 6H), 1.55 (m, 6H) ppm; ^{13}C NMR ($CDCl_3$): 166.9 (dd, J = 313.1, 84.2 Hz), 108.0 (dd, J = 300.9, 55.9 Hz), 28.65 (s), 27.05 (s), 13.56 (s), 10.58 (t, J = 1.5 Hz) ppm; GC-MS (EI): 423 (M^+-C_4H_9, 22.66), 253 (100); FTIR: 1606.0 (C=C) cm^{-1}.

In conclusion, this reaction provides a novel, efficient, and stereospecific method for the synthesis of a variety of E and Z-2-substituted-1,2-difluoroethenylstannanes from the corresponding silanes. These alkenylstannanes are potentially useful synthons for the stereospecific introduction of the fluorinated ethylene unit into organic compounds, and the

palladium-catalyzed coupling reactions of these stannanes with aryl and vinyl halides is in progress.

Table I. The Reaction of Vinylsilanes with Bu_3SnCl in the Presence of KF

$$RCF{=}CFSiR'_3 \xrightarrow[RT\ to\ 80°C]{KF,\ DMF,\ Bu_3SnCl} RCF{=}CFSnBu_3$$

E or Z E or Z

Entry	R	SiR'_3	Configuration	Reaction Conditions	Yield (%)[a]
1	I	$SiEt_3$	E	RT, overnight	83
2[b]	I	$SiEt_3$	Z	RT, overnight	82[b]
3[c]	H	$SiEt_3$	Z	70°C, overnight	80[c]
4[d]	H	$SiEt_3$	E	70°C, overnight	74[d]
5	F	$SiEt_3$	--	RT, overnight	92
6	Ph	$SiMe_3$	Z	RT, overnight	70
7	n-Bu	$SiMe_3$	Z	RT, overnight	NR
8	n-Bu	$SiMe_3$	Z	80°C, 10 hours	78
9	n-Bu	$SiEt_3$	Z	80°C, 24 hours	72
10	sec-Bu	$SiMe_3$	Z	80°C, 10 hours	87
11	tert-Bu	$SiMe_3$	Z	80°C, 24 hours	79
12	CF_2=CF	$SiEt_3$	Z	RT, 24 hours	82
13	CF_2=CF	$SiMe_2Ph$	Z	RT, 24 hours	69

[a]Isolated yield based on the vinylsilane, all compounds gave satisfactory ^{19}F, ^1H, and ^{13}C NMR, IR, and GC-MS data; [b]Z:E = 95:5; [c]Z:E - 95:5; [d]E:Z - 95:5.

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