A New Route for the Preparation of Alkylfluorovinylsilanes and Stannanes

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Methylfluorovinylsilanes and stannanes $Me_{4-x}M(CF{=}CF_2)_x$ (M = Sn, x = 1; Si, x = 1,2) can be prepared in good to excellent yields by the reaction of $CF_2{=}CFBr$ with a mixture of the corresponding $Me_{4-x}MCl_x$ and $P(NR_2)_3$ in polar solvent. Similarly, the novel silane $CF_3(SiMe_3)C{=}CF_2$ was obtained from $CF_3CBr{=}CF_2$.

Trialkyltrifluorovinyl and trifluoromethyl silanes and stannanes are useful reagents for the selective introduction of fluorovinyl and fluoroalkyl groups into carbonyl[1,2] and electrophilic fluoroorganic compounds.[3] Known methods of preparation of flurovinylsilanes are based on the reactions of trifluorovinyl magnesium[4] and lithium[5] derivatives with halosilanes. Polyfluoroalkylsilanes R_fSiR_4[6,7] and polyfluoroarylsilanes AR_fSiR_3[8] are more readily prepared in good yields by the Marchenko–Ruppert method.

We have found that the latter method may be applied for the synthesis of polyfluorovinyl silanes and stannanes. Trimethyltrifluorovinylsilane **1**, for example, was prepared in excellent yield by the reaction of commercially available trifluorobromoethylene **2** with a mixture of $P(NEt_2)_3$ **3** and chlorotrimethylsilane in benzonitrile at room temperature, reaction (1).

$$CF_2{=}CFBr\ (\mathbf{2}) + P(NEt_2)_3\ (\mathbf{3}) + ClSiMe_3 \xrightarrow[PhCN]{8\ h,\ 22\ ^\circ C} CF_2{=}CFSiMe_3\ (\mathbf{1})\quad 90\text{-}95\% \qquad (1)$$

The reaction proceeds in high yield and the crude undistilled **1** contains only traces (2–3%) of trimethylsilylfluoride as an impurity, according to GC and ^{19}F NMR. The product may be used directly for further reactions by simple vacuum distillation from the solvent.

Other phosphorous compounds such as tributylphosphine, triethyl and trimethyl phosphites are not effective in this reaction. However, the less expensive $P(NMe_2)_3$ **4**, which is reported to be less reactive than **3** for the preparation of CF_3SiMe_3[8,‡] can be substituted for **3** in the preparation of **1** (90% yield).

The same reaction conditions were applied to the tin derivative producing trimethyltrifluorovinylstannane **5** in 80% yield, reaction (2).

$$\mathbf{2} + \mathbf{4} + ClSnMe_3 \xrightarrow[PhCN]{12\ h,\ 22\ ^\circ C} CF_2{=}CFSnMe_3\ (\mathbf{5})\quad 80\% \qquad (2)$$

Bis(trifluorovinyl)dimethylsilane **6** was also prepared under similar conditions in 40% yield from the dichlorosilane, reaction (3).

$$\mathbf{22} + \mathbf{23} + Me_2SiCl_2 \xrightarrow[PhCN]{8\ h,\ 22\ ^\circ C} (CF_2{=}CF)_2SiMe_2\ (\mathbf{6})\quad 40\% \qquad (3)$$

The generality of this method was demonstrated with 2-bromopentafluoropropene **7**. Compound **7** is more active in this reaction with **3** and Me_3SiCl and the yield of 2-trimethylsilylpentafluoropropene **8** after 1 h at 22 °C was 92%, reaction (4).§

$$CF_3CBr{=}CF_2\ (\mathbf{7}) + \mathbf{3} + ClSiMe_3 \xrightarrow[PhCN]{1\ h,\ 22\ ^\circ C} CF_3(Me_3Si)C{=}CF_2\ (\mathbf{8})\quad 92\% \qquad (4)$$

It is very probable that this synthetic method can be extended to a variety of alkylvinylsilanes and stannanes and that both **3** and **4** can be employed with equal efficacy.

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‡ CF_3SiMe_3 is routinely prepared in >95% yield in our laboratories utilizing **4** in place of **3**.

§ *General Procedure for the Preparation of Fluorovinyl Compounds.* Compound **7** was prepared by a literature method. Compounds **1**[5,10,11], **5**[12] and **6**[5,11] were identified by comparison of ^1H and ^{19}F NMR, IR and mass spectral data with literature values.

In a typical experiment a 100 ml Pyrex flask was fitted with a Teflon glass valve and magnetic stir bar. Dry benzonitrile (20 ml), 30 mmol of **3** and an equimolar amount of Me_3SiCl were added to the flask. After evacuation at −196 °C, 33 mmol of **2** were added by vacuum transfer. The reaction vessel was warmed to 22 °C in 20 min and the reaction mixture was stirred at this temperature for 8 h. Vacuum distillation of the crude product through a series of cold traps (−30, −78, −196 °C) gave 30 mmol of **1** in the −78 °C trap. Compound **6** was isolated in 40% yield under similar conditions using 2 equivalents of **2** with Me_2SiCl_2. Compound **5** was isolated by vacuum distillation through −30 °C and −196 °C traps, with pure **5** collecting in the −30 °C trap in 80% yield. Compound **8** was isolated after 1 h at −22 °C in 92% yield by collecting under vacuum in a −30 °C trap, followed by washing with water and drying over Na_2SO_4.

Compound **7** was characterized as follows: b.p. 89 °C; IR (liq) ν 2969, 2910 (w), 1704 (C=C,s), 1316 (vs), 1262 (m), 1168, 1142 (m), 1030 (m), 975 (s), 852 (m), 735 (s) cm^{-1}; ^{19}F NMR $CF_3^A(Me_3Si)C{=}CF^BF^C$ A −53.40 (3F,dd), B −56.10 (1F,qd), C −67.03 (1F,pent.) ppm; J_{A-B} = 12, J_{A-C} = 11, J_{B-C} = 7 Hz; ^1H NMR 0.20 (m) ppm.