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Preparation of *E*-(1,2-difluoro-1,2-ethenediyl)bis(tributylstannane)

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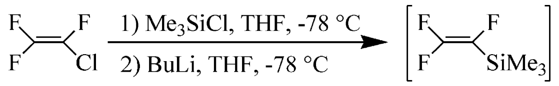
ABSTRACT

Chlorotrifluoroethene is converted *in situ* to [$F_2C{=}CFSiMe_3$]. The crude [$F_2C{=}CFSiMe_3$] solution is reduced with lithium aluminum hydride to ($HFC{=}CFSiMe_3$), which (without isolation) is converted to (*Z*)-$HFC{=}CFSnBu_3$. Subsequent metallation and trapping of the vinyllithium reagent with Bu_3SnCl gives (*E*)-$Bu_3SnCF{=}CFSnBu_3$ in 73% overall yield. Only two isolation steps are required and the use of Me_3SiCl and $F_2C{=}CFCl$ provides a cheap, economical route to this useful synthon.

1. Preparation of 1,1,2-trifluorotrimethylsilylethene[1]

A



An oven dried, 1-l, three-necked, round-bottomed flask equipped with a Teflon-coated stir bar, dry ice/isopropanol cooled cold-finger condenser,[2] low-temperature thermometer, rubber septum and nitrogen inlet (Fig. 1), was charged with 55.3 g (498 mmol) of Me_3SiCl (98% purity)[3] and 250 ml of anhydrous THF.[4] The solution was stirred and cooled to −80 °C with a liquid nitrogen/pentane bath. Then, 71 g (609 mmol) of chlorotrifluoroethene[5] was condensed into the flask using the above described cold-finger condenser, while maintaining the solution at −72 to −80 °C. Then, 208 ml (520 mmol) of a 2.5 M BuLi/hexanes[6] was added dropwise to the solution over 2.5 h *via* a syringe. After completion of the BuLi solution, the reaction mixture was stirred at −78 °C for 2 h, then warmed to RT overnight. Flash distillation (Fig. 2) of the reaction mixture yielded a colorless solution.[7] Excess $F_2C{=}CFCl$ was removed by simple distillation. The ^{19}F NMR yield of the vinylsilane was >90%[8,9] as determined by integration of an aliquot of the reaction mixture using 0.082 mmol of $C_6H_5CF_3$ as the internal standard.

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[1] Caution! This procedure involves volatile and hazardous reagents (stannanes) and should be conducted in an efficient fume hood.

[2] The temperature of the isopropanol in the cold finger was maintained at −50 to −60 °C.

[3] Me_3SiCl was purchased from the Aldrich Chemical Co. and used directly. It was transferred *via* a syringe.

[4] Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl.

[5] $F_2C{=}CFCl$ was first condensed from a commercial cylinder into a glass trap, which was cooled with dry ice. Then the liquified chlorotrifluoroethene was condensed into the reaction mixture *via* the dry ice\isopropanol cooled cold-finger condenser. The amount of $F_2C{=}CFCl$ was measured by the difference in the weight of the glass trap before and after condensation.

[6] BuLi/hexanes was purchased from the Aldrich Chemical Co. and used directly. The addition of BuLi to the reaction mixture causes an exotherm. The reaction mixture was maintained below −78 °C by carefully controlling the rate of addition over 2.5 h.

[7] The boiling point of the product, solvent and exchange product from the metallation reaction are ~70 °C – too close to separate efficiently, thus the crude $F_2C{=}CFSiMe_3$ was used directly in the next step.

[8] Procedure for calculation of the ^{19}F NMR yield of the vinylsilane (1) 0.5 ml of the reaction mixture was removed *via* a graduated syringe and transferred to an nmr tube; (2) 0.082 mmol (10 μl) of $C_6H_5CF_3$ was then added to the nmr tube *via* a microsyringe; (3) the contents of the nmr tube mixed and the ^{19}F NMR spectrum of the resultant mixture was obtained on an AC-300 NMR spectrometer; (4) *via* the integrations of the ^{19}F NMR signals, the quantity of the vinylsilane product was calculated as follows: $n = 0.082 \times 3 \times \text{In } 2/\text{In } 1$; $c = n/0.5$ (units: mmol/ml or mol/l); $N = c \times v$ (n, number of mmoles of $F_2C{=}CFSiMe_3$ in the nmr tube), In 1, integration of the ^{19}F NMR signal of $C_6H_5CF_3$; In 2, integration of one of the three peaks of $F_2C{=}CFSiMe_3$; c, the concentration of the $F_2C{=}CFSiMe_3$ in the reaction mixture; v, the total volume of the reaction mixture; N, the total number of mmoles of $F_2C{=}CFSiMe_3$ in the reaction mixture). The NMR yield of the $F_2C{=}CFSiMe_3$ was calculated as: NMR yield = $N/498$.

[9] $F_2C{=}CFSiMe_3$ gave the following ^{19}F NMR spectroscopic data: ^{19}F (282.4 Hz), $CDCl_3$, $CFCl_3$ reference): δ −88.7 ppm (dd, $^2J_{FF} = 71$ Hz, $^3J_{FF} = 25$ Hz); −117.6 (dd, $^3J_{FF} = 115$ Hz, $^2J_{FF} = 71$ Hz), −199.5 (dd, $^3J_{FF} = 115$ Hz), $^3J_{FF} = 25$ Hz).

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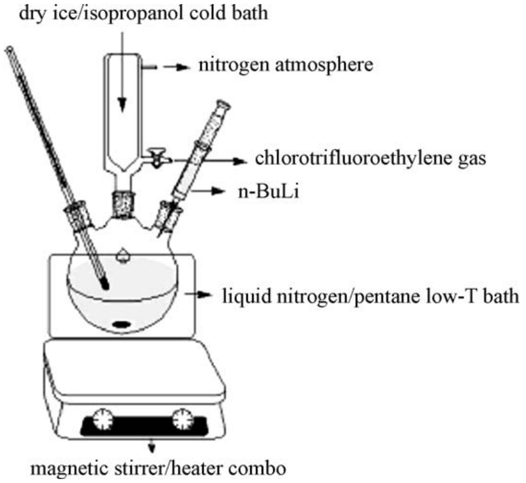
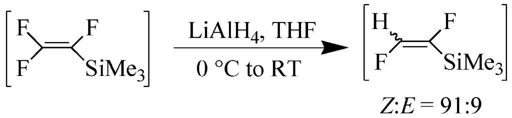


Fig. 1. Preparation of $F_2C{=}CFSiMe_3$.

2. Isomeric mixture of (*Z*)- and (*E*)-1,2-difluorotrimethylsilylethenes

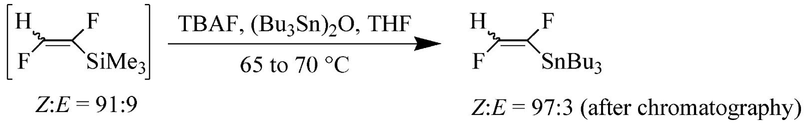
B



An oven-dried 2-l, three-necked, round-bottomed flask equipped with a Teflon-coated stir bar, cold-water condenser, thermometer, rubber septum and nitrogen inlet (Fig. 3) was charged with 15.7 g (413 mmol) of $LiAlH_4$. The flask was cooled to 0 °C and 50 ml of anhydrous THF was gradually added to the flask *via* syringe.[10] Then, the $F_2C{=}CFSiMe_3$ solution from Part A was added dropwise to the $LiAlH_4$ solution over 1 h *via* an oven-dried constant pressure addition funnel, maintaining the internal temperature of the reaction mixture below 25 °C. When the addition of the vinylsilane solution had been completed, the reaction mixture was stirred at RT for 1 h.[11] Then 100 ml of dry triglyme was added to the reaction mixture *via* a syringe.[12] Flash distillation of the solution at RT/1 mm Hg yielded a colorless solution (Note 7). ^{19}F NMR analysis of the distillate indicated the formation of (*Z*)- and (*E*)-$HFC{=}CFSiMe_3$ (*Z*:*E* = 91:9).[13]

3. (*Z*)-1,2-Difluoroethenyltributylstannane

C



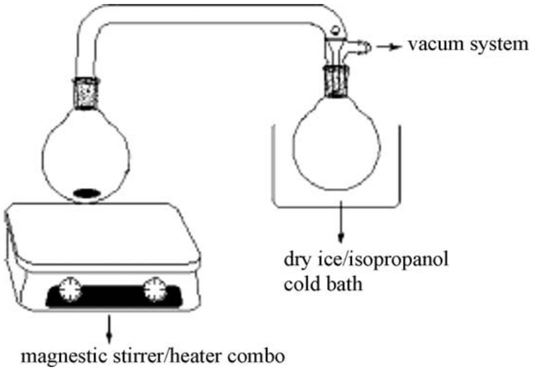
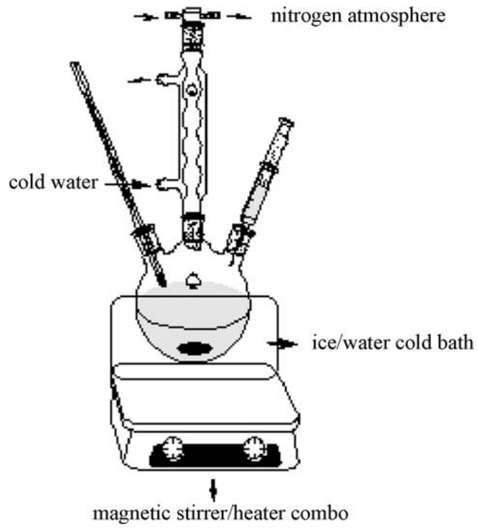


Fig. 2. Flash distillation apparatus.



Figs. 3 and 4. Preparation of (*E*)- and (*Z*)-$HFC{=}CFSiMe_3$.

An oven-dried 1-l, one-necked, round-bottomed flask equipped with a Teflon-coated stir bar, cold-water condenser, and nitrogen inlet (Fig. 4) was charged with the solution from reaction B, 124.9 g (201 mmol) of $(Bu_3Sn)_2O$ (96% purity) and 9.5 ml (9.5 mmol) of TBAF.[14] The reaction mixture was stirred at 65–70 °C for 3 h.[15] Low boiling point materials were removed by flash distillation at RT/1 mm Hg. The residue was extracted with pentane (5 × 110 ml).[16] Dark solids that are soluble in neither pentane nor water were removed *via* vacuum filtration in a well-ventilated hood. The filtrate was washed with saturated aqueous KF (5 × 100 ml) and water (4 × 200 ml) consecutively. The organic layer was separated; dried over $MgSO_4$; the $MgSO_4$ removed by gravity filtration; the majority of the solvent removed by rotary evaporation. Removal of

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[10] A solution of $LiAlH_4$ in THF could be utilized here. However, excess $LiAlH_4$ is not a problem on addition of the $F_2C{=}CFSiMe_3$ solution, since $HFC{=}CFSiMe_3$ is not reduced further under the reaction conditions employed here.

[11] At this stage, the ^{19}F NMR spectrum of the reaction mixture indicated complete consumption of $F_2C{=}CFSiMe_3$ (*Z*:*E* = 91:9). If a small amount of $F_2C{=}CFSiMe_3$ is left unreacted, it may be readily reduced to the 1,2-difluorotrimethylsilylethenes by heating the reaction mixture at 45–50 °C for 1 h. It is necessary to ensure complete conversion of the $F_2C{=}CFSiMe_3$, since $F_2C{=}CFSiMe_3$ is converted to $F_2C{=}CFSnBu_3$ in the next step; $F_2C{=}CFSnBu_3$ is difficult to separate from the anticipated products, (*Z*)- and (*E*)-1,2-difluoroethenyltributylstannanes formed in step C.

[12] Triglyme is added to the reaction mixture in order to avoid carrying the flash distillation to dryness.

[13] ^{19}F NMR yield of reaction B was calculated to be >90%.

[14] TBAF was purchased from the Aldrich Chemical Co. as a 1.0 M solution in THF containing ~5 wt% of water and was used directly.

[15] At this stage, ^{19}F NMR analysis of the reaction mixture indicated complete consumption of $HFC{=}CFSiMe_3$ and formation of $HFC{=}CFSnBu_3$ (*Z*:*E* = 91:9). The completion of the reaction was determined by estimating the NMR yield of the reaction. If the reaction stops before completion an additional aliquot of 1 ml of TBAF can be added to the reaction mixture until the ^{19}F NMR yield is ~100%.

[16] Hexanes can also be used to extract the product from the reaction mixture.

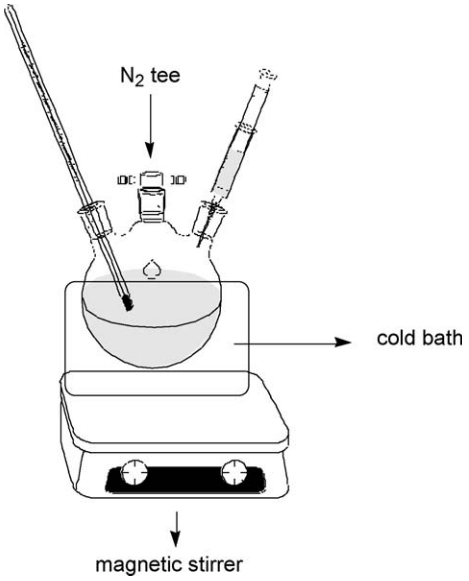


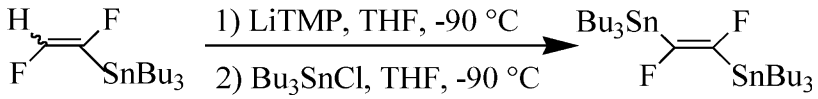
Fig. 5. Preparation of (*E*)-$Bu_3SnCF{=}CFSnBu_3$.

the remaining solvent at 20 °C/0.1 mm Hg yielded 141.5 g (98%) of a pale yellow liquid, GLPC purity 98.5% (*Z*:*E* = 92:8). This isomeric mixture was added to a silica gel column[17] and eluted with hexanes, $R_f = 0.58_{(Z)}; R_f = 0.46_{(E)}$.[18]

Fractions with similar R_f values were collected; and the majority of the solvent removed by rotary evaporation. Removal of the remaining solvent at 20 °C/0.1 mm Hg yielded 134.5 g of a colorless liquid, GLPC purity >99%; *Z*:*E* = 97:3.[19,20,21]

4. (*E*)-(1,2-Difluoro-1,2-ethenediyl)bis[tributylstannane]

D



An oven-dried 250 ml, three-necked, flask equipped with a Teflon-coated stir bar, low-temperature thermometer, rubber septum and nitrogen inlet (Fig. 5) was charged with 120 ml of anhydrous THF and 3.4 g (24 mmol, 1.2 equiv.; 99% purity) of 2,2,6,6-tetramethylpiperidine.[22] The reaction solution was cooled to −20 °C in a pentane/dry ice cooled bath. Then 10 ml (25 mmol, 2.5 M) of n-butyllithium was added dropwise to the reaction mixture over 10 min.[23] The reaction mixture temperature was maintained below −10 °C by carefully controlling the rate of addition. The light yellow solution was stirred at −5 to −10 °C for 20 min; then cooled to −90 °C *via* a pentane/liquid nitrogen cooled bath. At this temperature, 7.3 g (20.1 mmol, GLPC purity, 97%) of (*Z*)-1,2-difluoroethenyltributylstannane[24] was added dropwise *via* a syringe. The reaction mixture was maintained at −90 °C for 1 h. Then, 7.12 g (21 mmol, 1.05 equiv., 97%) of tributyltin chloride was added[25] to the reaction mixture *via* a syringe at −90 °C. The reaction mixture was maintained at −90 °C for 1 h, then warmed to room temperature (over 10 h). The solvent was removed by flash distillation, the residue was extracted with diethyl ether (4 × 100 ml), then washed consecutively with water (4 × 400 ml), saturated KF solution (3 × 75 ml)[26] and water (4 × 100 ml). The organic layer was separated and dried over anhydrous $MgSO_4$. The $MgSO_4$ was removed by gravity filtration and the remaining solvent removed by rotary evaporation. The residue was eluted with pentane through a silica gel column,[27] $R_f = 0.74$. The majority of the solvent was removed by rotary evaporation.[28] Removal of the remaining solvent at RT/1 mm Hg yielded 12.4 g (96%) of a colorless liquid.[29,30]

5. Discussion

This procedure describes the preparation of a useful organometallic reagent for the introduction of (*E*)-1,2-difluoroethenyl units. This procedure utilizes a cheap commercial fluoroolefin precursor; all other reagents are commercially available and can be

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[17] An 8 cm × 50 cm silica gel column was used. About 1.5 l of hexanes was used to wash the column.

[18] TLC was employed to monitor the elution. The TLC spots were visualized in an I_2 chamber. Thin layer chromatography was carried out using 40 mm × 80 mm Polygram SilG/$UV_{245\ \mathrm{plates}}$.

[19] Analytical GLPC was carried out on a Hewlett-Packard model 5890, equipped with a thermal conductivity detector and 3393 A integrator. The column was packed with 5% OV101 on chromosorb P. The typical conditions were set at 50 °C for 2 min, followed by a temperature increase of 20 °C/min. to the final temperature of 200 °C.

[20] (*Z*)-1,2-Difluoroethenyltributylstannane gave the following spectroscopic data: ^{19}F NMR (282.44 MHz, $CDCl_3$): δ −172.9 (dd, $^3J_{FF}$ = 119.5 Hz, $^3J_{HF}$ = 10.8 Hz), −177.60 (dd, $^3J_{FF}$ = 119.5 Hz, $^2J_{HF}$ = 83.2 Hz). ^1H NMR (300.2 MHz, $CDCl_3$): δ 7.65 (dd, 1H, $^2J_{HF}$ = 83.0 Hz, $^3J_{HF}$ = 11.0 Hz), 1.57 (m, 6H), 1.34 (m, 6H), 1.09 (t, 6H, $^3J_{HH}$ = 8.0 Hz), 0.90 (t, 9H, $^3J_{HH}$ = 7.3 Hz). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 165.9 (dd, $^1J_{CF}$ = 298.0 Hz, $^2J_{CF}$ = 78.9 Hz), 153.9 (dd, $^1J_{CF}$ = 229.8 Hz, $^2J_{CF}$ = 47.0 Hz), 29.0, 27.3, 13.7, 9.9. GC–MS, *m*/*z* (relative intensity): 296 ($M^+{-}C_4H_9$, 45). (*E*)-1,2-Difluoroethenyltributylstannane. ^{19}F NMR (282.44 MHz, $CDCl_3$): δ −142.8 (dd, $^2J_{HF}$ = 77.5 Hz, $^3J_{FF}$ = 9.5 Hz); −146.9 (dd, $^3J_{HF}$ = 25.6 Hz, $^3J_{FF}$ = 9.5 Hz). ^1H NMR (300.2 MHz), $CDCl_3$): δ 5.95 (dd, $^2J_{HF}$ = 77.2 Hz, $^3J_{HF}$ = 25.6 Hz), 1.54 (m, 6H), 1.33 (m, 6H), 1.03 (t, 6H, $^3J_{HH}$ = 8.0 Hz), 0.90 (t, 9H, $^3J_{HH}$ = 7.2 Hz). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 154.9 (dd, $^1J_{CF}$ = 313.4 Hz, $^2J_{CF}$ = 7.6 Hz), 141.7 (dd, $^1J_{CF}$ = 282.1 Hz, $^2J_{CF}$ = 7.0 Hz), 28.8, 27.2, 13.6, 9.95.

[21] For step C, the isolated yield of (*Z*)-1,2-difluoroethenyltributylstanne (97% *Z*-isomer) was 94%. The overall isolated yield of the (*Z*)-stannane, based on Me_3SiCl, was 73% (based on *Z*-isomer only).

[22] 2,2,6,6-Tetramethylpiperidine was purchased from Aldrich Chemical Co. and used directly.

[23] Caution: The addition of the n-butyllithium solution caused an exotherm.

[24] (*Z*)-1,2-Difluoroethenyltributylstannane is an isomeric mixture of 1,2-difluoroethenyltributylstannanes, *Z*:*E* = 97:3. (*E*)-1,2-Difluoroethenyltributylstannane decomposed in the reaction mixture upon lithiation.

[25] The addition took 45 min. The addition rate was adjusted to maintain the internal temperature below −90 °C. The addition of Bu_3SnCl to the reaction mixture resulted in the formation of LiCl and the reaction mixture became viscous; eventually the reaction mixture becomes homogeneous. As a consequence, Bu_3SnCl should be added dropwise.

[26] KF (aq.) reacts with Bu_3SnCl to form Bu_3SnF, which is a solid and insoluble in water and organic solvents (pentane, hexane). As a consequence, the unreacted Bu_3SnCl can be separated from the product.

[27] A 8 cm × 40 cm silica gel column was used. About 1.5 l of pentane was utilized to elute the column. TLC was employed to monitor the elution. The TLC spots were visualized in an I_2 Chamber. The termination of elution was determined by the absence of TLC spots.

[28] During rotary evaporation, the bath temperature increased from ~45 °C, while the internal pressure was gradually reduced from ambient pressure to ~15 mm Hg, maintaining the steady pace of distillation.

[29] The product showed no impurity signals *via* NMR (^1H, ^{19}F, ^{13}C). (*E*)-(1,2-Difluoroethenediyl)bis[tributylstannane] prepared by this procedure gave the following spectroscopic data: ^{19}F NMR (282.44 MHz, $CDCl_3$): δ −159.1 (s, 2F). ^1H NMR (300.2 MHz, $CDCl_3$): δ 1.53 (m, 12H), 1.32 (qt, as sextet, 12H, $^3J_{HH}$ = 7 Hz), 1.05 (t, 12H, $^3J_{HH}$ = 8 Hz), 0.90 (t, 18H, $^3J_{HH}$ = 7 Hz). ^{13}C NMR (75.48 MHz, $CDCl_3$): δ 174.5 (2nd order due to virtual coupling), 28.8, 27.1, 13.7, 10.0 (m as t). FTIR (CCl_4, cm^{-1}): 2958 (vs), 2925 (vs), 2873 (s), 2855 (s), 1465 (m), 1042 (m).

[30] (*E*)-(1,2-Difluoro-1,2-ethenediyl)bis[tributylstannane] is a stable compound. When it was stored at room temperature (without protection of an inert gas) for several months, no decomposition was observed.

used directly. Each step is accomplished in high yield and can be completed in a short period of time. The conversion of (*Z*)- and (*E*)-1,2-difluorotrimethylsilylethenes to (*Z*)- and (*E*)-1,2-difluoroethenyltributylstannanes is easily accomplished *via* our reported procedure [1] and the by-product, $Me_3SiOSIMe_3$ is readily removed from the product, (*E*)-1,2-difluoroethenyltributylstannane by flash distillation. Metallation of (*Z*)-1,2-Difluoroethenyltributylstannane is straightforward. This bisstannane can be selectively reacted with vinyl halides [2–4], aryl halides [5] to yield isomerically pure fluorinated stilbenes and polyenes [6]. Recently, this procedure has been applied for the preparation of poly(-arylenevinylenes) with fluorinated vinyl units. Bisstannane prepared with expensive triethylsilylchloride is a procedure requiring four isolation steps [6]. Thus, the titled procedure outlined here is the most economical route to the (*E*)-bisstannane. The titled bisstannane can be elaborated to (1*Z*,3*E*,5*Z*)-$Bu_3SnCF{=}CFCF{=}CFCF{=}CFSnBu_3$ in two steps and provides a useful route for the stereospecific introduction of three fluorinated ethenyl groups [2].

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