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The Stereoselective Preparation of *cis* and *trans*-1,2-Difluoroethylene Synthons

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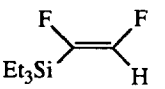
Abstract: Isomerization of *(Z)*-HFC=CFSiEt3 with ultraviolet light and catalytic phenyl disulfide has resulted in a high yield, stereoselective preparation of *cis*-1,2-difluorotriethylsilylethylene, *(E)*-HFC=CFSiEt3. *(E)*-HFC=CFSiEt3 has been converted to *(Z)*-F(Bu3Sn)C=CFSiEt3, *(Z)*-IFC=CFSiEt3, *(Z)*-BrFC=CFSiEt3, *(Z)*-Me3SiFC=CFSiEt3, and *(Z)*-IFC=CFI. *(E)*-IFC=CFI has been prepared from *(Z)*-HFC=CFSiEt3.

INTRODUCTION

The role of fluorinated alkenes and perfluoroalkenyl organometallics in the preparation of fluorine-containing organic molecules is well documented[1] and recent work in our laboratories has described the synthetic utility of perfluoroalkenyl zinc, cadmium, and copper reagents.[1,2,3] These thermally stable metal reagents provide a convenient and generalized method for introduction of perfluoroalkenyl groups, including the trifluorovinyl, *(E)* and *(Z)*-pentafluoropropenyl, and pentafluoropropen-2-yl groups. In contrast, methodology for stereoselective incorporation of 1,2-difluoroethylene units is not well developed, particularly for the *cis*-1,2-difluoroethylene system. This paucity of methodology for *cis* analogues has been due to the difficulties in the stereoselective preparation of suitable vinyl iodo, bromo, silyl, or hydro precursors, although such precursors and their organometallic reagents would be invaluable building blocks in the design of fluorine-containing bioactive natural products, pharmaceuticals, polymers, and agrochemicals.[4,5] We report herein the preparation of *cis*-1,2-difluorotriethylsilyethylene, **3**, and its conversion to a variety of key *cis*-1,2-difluoroethylene synthons.



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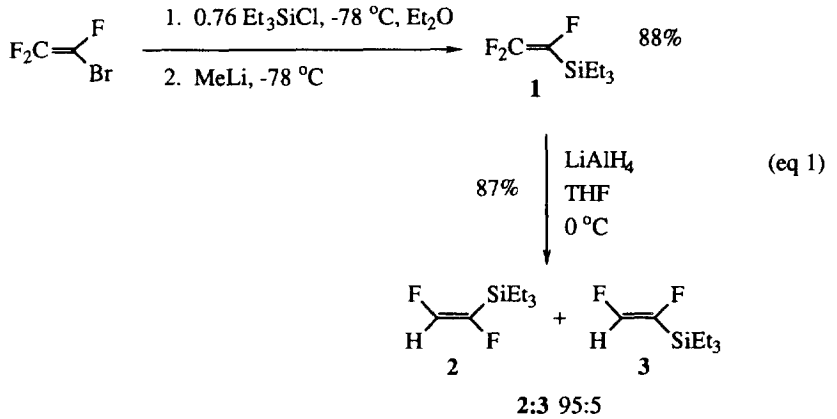
RESULTS AND DISCUSSION

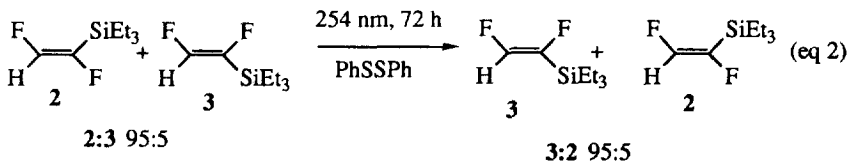
Except for the report of Leroy,[6] literature reports of *cis*-1,2-difluoroethylene compounds have been mainly limited to examples in which the *cis* isomer has been observed as the minor component of a *trans/cis* mixture and reports of isomerization of *trans*-1,2-difluoro compounds are rare. An exception is the isomerization-bromination of $(CH_3)FC{=}CFCO_2Et$ (*E*:Z 1:1)which has been reported to give *(Z)*-$(BrCH_2)FC{=}CFCO_2Et$ as the sole product.[7] Several *trans*-α,β-difluoro-α,β-unsaturated ketones have also been reported to undergo isomerization to *cis*-α,β-difluoro-α,β-unsaturated ketones upon treatment with Me_3SiI or HCl[8] and bromodesilylation of *(Z)*-$(n\text{-}C_7H_{15})FC{=}CFSiMe_3$ affords predominately the *cis*-1,2-difluoro isomer of $(n\text{-}C_7H_{15})FC{=}CFBr$ (E:Z 90:10).[9] This bromodesilylation, however, has not been extended to other *n*-alkyl substituted olefins.

We have prepared silane **3** in three steps from commercially available bromotrifluoroethylene, utilizing literature procedures for the first two steps (eq 1).[10,11,12] In a modification of Hiyama's procedure,[10] $F_2C{=}CFSiEt_3$ was prepared utilizing MeLi (Et_2O solution) and $F_2C{=}CFBr$, whereas Hiyama employed *n*-BuLi (hexane solution) and $F_2C{=}CFCl$. Use of MeLi (Et_2O) and Et_3SiCl simplifies purification of the trifluorovinyltrialkylsilane.

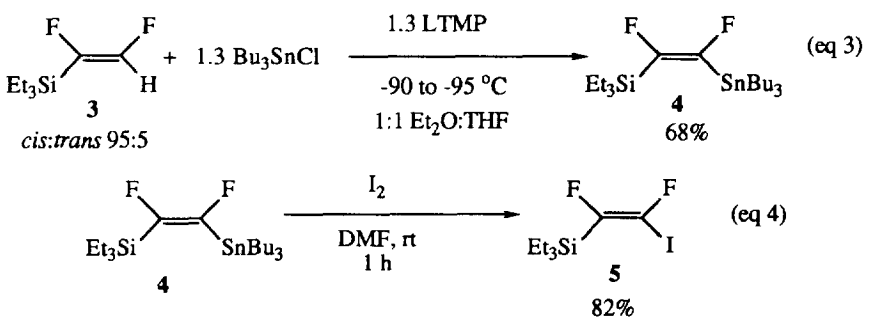


Treatment of F_2C=CFSiEt$_3$ with $LiAlH_4$ results in predominantly the *trans*-1,2-difluoro isomer (*trans*:*cis* 95:5).[11,12] Both reactions are easily carried out on a molar scale.

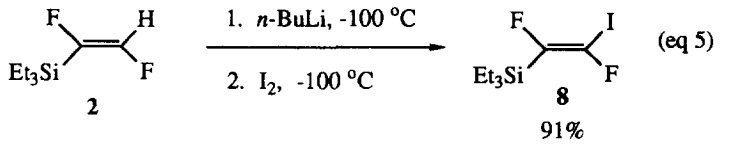
In a key transformation, neat *trans*-1,2-difluorotriethylsilylethylene, **2** (in a mixture with *cis*-**3**), undergoes isomerization in the presence of ultraviolet light (254 nm) and catalytic (3 mol %) phenyl disulfide (eq 2).



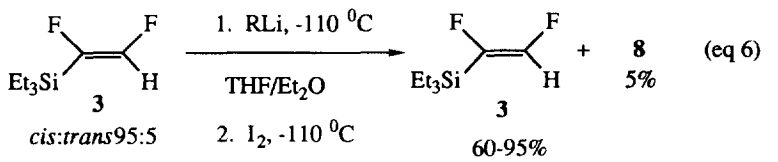
The stereochemistry of the vicinal fluorines was unambiguously determined given the large difference in ^{19}F NMR coupling constants ($J_{F\text{-}F\ cis}$ = 0 - 40 Hz, $J_{F\text{-}F\ trans}$ = 110 -140 Hz).[13] Silane **3** was converted to the *cis* vinyl stannane **4** in good yield (eq 3) and subsequent cleavage of the tin moiety with iodine resulted in *cis*-1,2-difluoroiodotriethylsilylethylene, **5** (eq 4). The *cis* vinyl stannane **4** was readily separated from the minor *trans* isomer by column chromatography.



It should be noted that **5** could not be directly prepared from **3**. In contrast, preparation of the corresponding **8** has been reported by low temperature iodination of the pregenerated *trans* vinyl lithium reagent (trans:cis > 95:5);[12] under these conditions, the minor *cis* product **5** is not observed (eq 5).

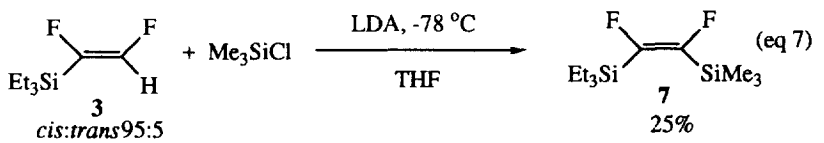


All attempts to pregenerate the *cis* vinyl lithium reagent from **3** followed by iodination or metathesis with $ZnCl_2$ resulted in varying amounts (60-95%) of recovered starting material, in addition to a minor amount of *trans* iodide **8** (eq 6). The approach suffers from two problems: 1) recovery of **3** suggests that the vinyl hydrogen in **3** is less acidic than the vinyl hydrogen of **2** and 2) the resultant vinyl lithium reagent of **3**, if formed, decomposes prior to iodination.

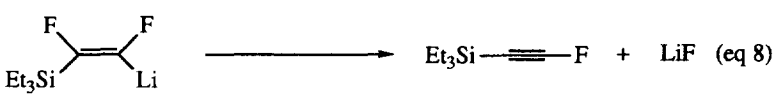


R = *n*-Bu, *t*-Bu, Me

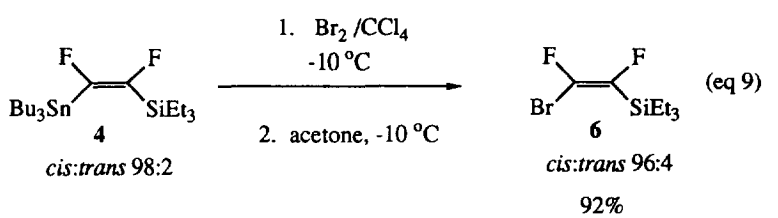
Attempts to metallate **3** at -78 °C with *n*-BuLi, MeLi, or *t*-BuLi, in the presence of Me_3SiCl also resulted in incomplete metallation, decomposition of the vinyl lithium reagent, and reaction of the alkyl lithium reagents with Me_3SiCl. When LDA was employed, however, silane **7** was obtained in low yield and starting material was not recovered (eq 7).



In the conversion of **3** to **4** the vinyl lithium reagent was generated at low temperature with the hindered base, lithium-2,2,6,6-tetramethylpiperidide (LTMP), and trapped *in situ* with the more reactive electrophile Bu_3SnCl. The reaction proceeds with retention of the stereochemistry and in good yield only when carried out at temperatures less than -90 °C. Similar reaction at -78 °C resulted in lower yield and preferential decomposition of the *cis* isomer (*cis*:*trans* 80:20, 49%), presumably through a facile *anti* β-elimination pathway unavailable to the *trans* lithium reagent of **2** (eq 8).

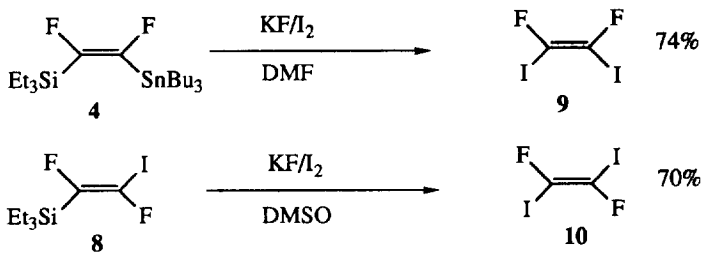


Bromodestannation of **4** resulted in a high yield preparation of *cis*-1,2-difluorobromosilane **6** (eq 9).



Retention of stereochemistry was dependent on 1) low reaction temperature and 2) addition of acetone at -10 °C. Exploratory reactions carried out at room temperature resulted in isomerization, the extent of which depended on the reaction time. Although reaction at -10 °C initially resulted in retention of stereochemistry, significant isomerization occurred when the reaction mixture was warmed to room temperature. Suppression of the isomerization was achieved by addition of acetone at low temperature. The mechanistic details of this isomerization have not yet been thoroughly studied.

Treatment of stannane **4** and silane **8** with KF/I_2 resulted in the stereospecific preparation of diiodides **9** and **10**, which have recently been utilized in the photochemical preparation of difluoroethyne.[14]



CONCLUSION

In conclusion, we have described a high yield stereoselective preparation of *cis* and *trans*-1,2-difluoroethylenes. These novel synthons should find application in the design of bioactive natural products, pharmaceuticals, polymers, and agrochemicals. Future work will describe their synthetic utility.

EXPERIMENTAL

General. All reactions were performed in oven-dried glassware. ^{19}F NMR spectra were recorded on a JEOL FX90Q (83.81MHz) spectrometer or a Bruker 300 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 MHz spectrometer. Unless otherwise indicated, all NMR spectra were recorded in $CDCl_3$. All chemical shifts are reported in parts per million downfield (positive) of the standard. ^{19}F NMR spectra are referenced against internal $CFCl_3$, ^{1}H and ^{13}C against internal tetramethylsilane. FTIR spectra were recorded as CCl_4 solutions using a solution cell with 0.1 cm path length. GC/MS spectra were obtained at 70 *eV*, in the electron impact mode. High resolution mass spectral analyses were performed with a VG ZAB-HF spectrometer operating at 70 *eV* in the electron impact mode. GLPC analyses were carried out on a 5% OV-101 column with a thermal conductivity detector. Column chromatography was carried out utilizing 200-425 mesh silica gel.

Materials. All alkyl lithium reagents, Et_3SiCl, Me_3SiCl, anhydrous diethyl ether, 2,2,6,6-tetramethylpiperidine, diisopropylamine, phenyl disulfide, bromotrifluoroethylene, $LiAlH_4$, and Bu_3SnCl were obtained from commercial sources and used without further purification. DMSO and DMF were distilled form CaH_2. THF was distilled from sodium benzophenone ketyl or $LiAlH_4$.

Preparation of 1,1,2-trifluorotriethylsilylethylene, F_2C=CF$SiEt_3$, (1). Preparation of F_2C=CF$SiEt_3$ was carried out according to the literature procedure,[10] with the following modifications. A three-neck 2L flask equipped with a low temperature thermometer adapter, magnetic stir bar, N_2 tee, and a dry ice/isopropanol condenser, was charged with 500 mL anhydrous diethyl ether, 54.3 g (0.36 mol) triethylsilyl chloride, and cooled to -78 °C *via* dry ice/isopropanol bath. Next, bromotrifluoroethylene (75.0 g, 0.47 mol) was condensed into the cooled solution. MeLi (336 mL, 1.4 M in Et_2O, 0.47 mol) was slowly added over 2-2.5 h *via* 50 mL syringe (clogging of the stopcock opening by precipitation of MeLi occurred when a pressure-equalized addition funnel was used). During addition, the reaction mixture was maintained at ≤ -70 °C. After addition was complete, the reaction mixture was stirred at -78 °C for 4 h and then allowed to warm to room temperature with stirring overnight. For workup, the mixture was quenched slowly at room temperature with

3N HCl until pH 5-6. The aqueous phase was separated and the organic layer was washed with 5% aqueous $NaHCO_3$ solution. The combined aqueous phases were extracted with 200 mL ether. The combined organic layers were dried ($MgSO_4$), filtered, and the majority of the solvent was removed by rotary evaporation. The crude residue was fractionated through a 6 cm Vigreux column to yield 62.2 g (88%, based on Et_3SiCl) vinyl silane product: bp 144 °C; lit.[10] bp 144 °C; GLPC ≥ 99%.

Preparation of *trans*-1,2-Difluorotriethylsilylethylene, *(Z)*-HFC=CFSiEt$_3$, (2). Preparation of *(Z)*-HFC=CFSiEt$_3$ was carried out according to the literature procedure,[11,12] with the following modifications. A three-necked, 1L flask equipped with a low temperature thermometer adapter, magnetic stir bar, pressure-equalized addition funnel, N_2 source, and cold water condenser, was charged with 15.2 g (0.4 mol) $LiAlH_4$, 150 mL dry THF, and cooled to -10 °C with a dry ice/isopropanol bath. A solution of 63.0 g (0.32 mol) F_2C=CFSiEt$_3$ in 100 mL dry THF was added dropwise *via* the addition funnel, maintaining the temperature at 0 °C. The resultant solution was then stirred at room temperature for 3 h. The solution was cooled to -20 °C and quenched *cautiously* by dropwise addition of 150 mL 2N HCl. After addition of the acid was complete, the solution was allowed to slowly warm to room temperature and the liquid fraction was decanted from the solids. The solids were rinsed several times (2 x 250 mL, 1 x 150 mL) with diethyl ether and any remaining solid in the organic layer was filtered by water aspiration. The ether fractions were combined and washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and the majority of the solvent was removed by rotary evaporation. The remaining residue was distilled through a 6 cm Vigreux column to give 49.25 g (87%) of product: bp 145 °C; GLPC ≥ 99 %; Z:E 95:5, lit.[12] bp 146-148 °C; ^{1}H NMR 0.8 (q, 6H, $J_{H,H}$ = 6 Hz), 1.0 (t, 9H, $J_{H,H}$ = 6 Hz), 7.5 (dd, 1H, $^2J_{H,F}$ = 79 Hz, $^3J_{H,F}$ = 12 Hz); ^{19}F NMR -174.7 (dd, 1F, $^3J_{F,F}$ = 129 Hz, $^2J_{F,H}$ = 79 Hz), -182.8 (dd, 1F, $^3J_{F,F}$ = 129 Hz, $^3J_{F,H}$ = 12 Hz); GC/MS *m/e* 178 (M^+), 159, 149, 121, 115.

Preparation of *cis*-1,2-Difluorotriethylsilylethylene, *(E)*-HFC=CFSiEt$_3$, (3). A quartz tube equipped with a small magnetic stir bar and rubber septum was charged with phenyl disulfide (0.8 g, 3.6 mmol, 3 mol %) and 21.5 g (0.120 mol) *trans*-1,2-difluorotriethylsilylethylene **2** (Z:E 95:5). With stirring, the solution was irradiated at 254 nm for 72 h in a Rayonet photochemical reactor and then flash distilled into a liquid N_2 cooled receiver and 21.1 g (98%) product was collected (E:Z 95:5): ^{19}F NMR -146.4 (t, 1F, $^3J_{F,F}$ = $^3J_{F,H}$ = 21 Hz), -157.7 (dd, 1F, $^2J_{F,H}$ = 75 Hz, $^3J_{F,F}$ = 21 Hz); ^{1}H NMR 0.7 (q, 6H, $J_{H,H}$ = 8 Hz), 1.0 (t, 9H, $J_{H,H}$ = 8 Hz), 6.2 (dd, 1H, $^2J_{H,F}$ = 75 Hz, $^3J_{H,F}$ = 21 Hz); ^{13}C NMR 2.0, 6.9, 143.3 (dd, $^1J_{C,F}$ = 276 Hz, $^2J_{C,F}$ =10 Hz), 151.7 (dd, $^1J_{C,F}$ = 277 Hz, $^2J_{C,F}$ = 5 Hz); HRMS calcd for $C_8H_{16}F_2Si$ 178.0989; obsd, 178.1002; FTIR 2959 (m), 2879 (m), 1656 (m), 1566 (s), 1458 (w), 1113 (m), 1006 (w) cm^{-1}.

Preparation of *cis*-1,2-Difluoro-1-tributylstannyl-2-triethylsilylethylene, *(Z)*-F(Bu$_3$Sn)C=CFSiEt$_3$, (4). A 250 mL three-neck flask equipped with magnetic stir bar, low temperature thermometer adapter, N_2 source, and rubber septum, was charged with 7.52 g (42.2 mmol) *(E)*-HFC=CFSiEt$_3$, **3**, 16.5 g (50.7 mmol) Bu_3SnCl, and 60 mL 1:1 THF:Et_2O. The solution was cooled to -90 to -95 °C *via* liquid N_2/pentane bath. In a separate flask, a solution of Li-2,2,6,6-tetramethylpiperidide base was prepared from 7.06 g (50.0 mmol) 2,2,6,6-tetramethylpiperidine, 50 mL 1:1 THF:Et_2O, and 50 mmol *n*-BuLi (2.5 M, hexanes). The LTMP base solution was then added dropwise to the cooled solution, maintaining the temperature at -90 to -95 °C. After addition was complete, the solution was stirred at -90 to -95 °C for 1 h and then allowed to warm to room temperature. The reaction mixture was poured into 100 mL H_2O and extracted (4 x 100 mL) with Et_2O. The combined Et_2O layers were dried ($MgSO_4$), filtered and the solvent was removed by rotary evaporation. The *cis*-vinylstannane product, 13.4 g (68%), was isolated by silica gel chromatography as a pale yellow liquid (hexane, R_f 0.4, 5% phosphomolybdic acid in EtOH used for visualization): ^{19}F NMR -120.6 (bs, 1F), -120.6 (d, $^2J_{F,Sn}$ =221 Hz, 0.16 F, due to natural abundances of 8.6 and 7.3% for ^{119}Sn and ^{117}Sn isotopomers, respectively), -132.4 (bs, 1F); ^{1}H NMR 0.7 (q, 6H, $J_{H,H}$ = 8 Hz), 0.9 (t, 9H, $J_{H,H}$ = 7 Hz), 1.0 (t , 9H, $J_{H,H}$ = 8 Hz), 1.1 (m, 6H), 1.3 (sextet, 6H, $J_{H,H}$ = 7 Hz), 1.5 (m, 6H); ^{13}C NMR 2.7, 7.1, 11.2 (s), 11.2 (d, $^1J_{C,Sn}$ = 354 Hz), 13.5, 27.2 (s), 27.2 (d, $^2J_{C,Sn}$ = 63 Hz), 28.8 (s), 28.8 (d, $^3J_{C,Sn}$ = 19 Hz), 160.3 (d, $^1J_{C,F}$ = 289 Hz), 166.1 (d, $^1J_{C,F}$ = 321 Hz); ^{119}Sn NMR {^{1}H} ($CDCl_3$, referenced vs. internal Bu_4Sn) 32.4 (dd, $^2J_{Sn,F}$ = 221 Hz, $^3J_{Sn,F}$ = 16 Hz); ^{29}Si NMR (neat, referenced vs. external $(CH_3)_4Si$) 0.55 (dd, $^2J_{Si,F}$ = 31 Hz, $^3J_{Si,F}$ = 6 Hz); FTIR 2958 (s), 2922 (s), 2875 (s), 2856 (w), 1577 (w), 1464 (m), 1416 (w), 1358 (w), 1070 (m), 1305 (m) cm^{-1}; HRMS calcd for $C_{16}H_{33}F_2Si^{120}Sn$ (M^+-C_4H_9) 411.1342, obsd 411.0134.

Preparation of cis-1,2-Difluoroiodotriethylsilylethylene, (Z)-IFC=CFSiEt$_3$, (5). A 100 mL flask equipped with a cold water condenser, N_2 source, magnetic stir bar, and septum port, was charged with I_2 (10.9 g, 42.8 mmol, 1.6 eq) and 30 mL dry DMF. Next, 12.5 g (26.8 mmol) (Z) -F(Bu$_3$Sn)C=CFSiEt$_3$ was added via syringe in one portion. A mild exotherm (ca. 40 °C) occurred and the solution was stirred for an additional 45 min. at room temperature. For workup, the mixture was diluted with 75 mL aq. $NaHSO_3$ to remove I_2 and then extracted (3 x 100 mL) with 1:1 pentane:Et_2O. The pentane:Et_2O fractions were then dried ($MgSO_4$), filtered, and the solvent was removed by rotary evaporation. The crude residue containing the vinyl iodide product, Bu$_3$SnI (bp 172 °C, 10 mm Hg), and a small amount of DMF, was fractionated through a 6 cm Vigreux column to yield 6.7 g (82%) vinyl iodide product: bp 105 °C (10 mm Hg); GLPC ≥ 99 %; *Z:E* 98:2; ^{19}F NMR -82.2 (bs, 1F), -120.0 (bs, 1F); ^{1}H NMR 0.8 (q, 6H, $J_{H,H}$ = 8 Hz), 1.0 (t, 9H, $J_{H,H}$ = 8 Hz); ^{13}C NMR 2.9, 7.0, 106.5 (dd, $^1J_{C,F}$ = 349 Hz, $^2J_{C,F}$ = 26 Hz), 153.4 (dd, $^1J_{C,F}$ = 287 Hz, $^2J_{C,F}$ = 5 Hz); FTIR 2959 (s), 2878 (s), 1606 (s), 1458 (m), 1380 (w), 1084 (s), 1238 (w), 876 (m) cm^{-1}; HRMS calcd for $C_8H_{15}F_2SiI$ 303.9956, obsd 303.9952.

Preparation of *cis*-1,2-Difluorobromotriethylsilylethylene, *(Z)*-BrFC=CFSiEt$_3$, (6). Into a 50 mL three-neck flask equipped with a low temperature thermometer adapter, magnetic stir bar, N_2 source, and rubber septum, was placed 4.29 g (9.18 mmol) *(Z)*-F(Bu$_3$Sn)C=CFSiEt$_3$ and 30 mL CCl_4. The solution was cooled to -10 to -15 °C *via* dry ice/ IPA bath. Next, a solution of Br_2 (1.5 g, 9.2 mmol) in 5 mL CCl_4 was added dropwise so as to maintain the reaction mixture at -10 °C. Complete consumption of substrate was indicated when a slight yellow-red coloration persisted in the reaction mixture. Next, 2 mL of acetone was added at -10 °C. The mixture was then allowed to warm to room temperature. The solvent was removed by rotary evaporation and the residue contained Bu$_3$SnBr (bp 120 °C, 2 mm Hg) and *(Z)*-BrFC=CFSiEt$_3$. The product, 2.23 g (92%), was purified by distillation at reduced pressure through a 6 cm Vigreux column: *Z:E* > 96:4; bp 85 °C (10 mm Hg); GLPC > 98%; ^{19}F NMR -82.9 (d, 1F, $^3J_{F,F}$ = 4 Hz), -135.4 (d, 1F, $^3J_{F,F}$ = 4 Hz); ^{1}H NMR 0.8 (q, 6H, $J_{H,H}$ = 8 Hz), 1.0 (t, 9H, $J_{H,H}$ = 8 Hz); ^{13}C NMR 2.5, 7.0, 136.2 (dd, $^1J_{C,F}$ =339 Hz, $^2J_{C,F}$ =21 Hz), 148.9 (dd, $^1J_{C,F}$ = 282 Hz, $^2J_{C,F}$ = 4 Hz); GC/MS *m/e* 258 (M$^+$, 1.4), 256 (M$^+$, 1.4), 227 (2.4), 229 (2.3), 171 (3.7), 173 (2.6), 155 (5.4), 157 (5.1), 127 (3.4), 129 (3.5), 119 (8.2), 105 (100.0), 77 (61.6), 53 (25.0); HRMS calcd. for $C_8H_{15}{}^{79}BrF_2Si$ 256.0095, obs. 256.0089; FTIR 2961 (s), 2879 (s), 1629 (s), 1458 (m), 1416 (w), 1100 (s), 1095 (s), 1005 (m), 897 (s). ^{19}F NMR for *trans* isomer -115.8 (d, 1F, $^3J_{F,F}$ = 137 Hz), -151.8 (d, 1F, $^3J_{F,F}$ = 137 Hz).

Preparation of *cis*-1,2-Difluoro-1-triethylsilyl-2-trimethylsilylethylene, *(Z)*-Me$_3$SiFC=CFSiEt$_3$, (7). A 25 mL three-neck flask equipped with a magnetic stir bar, addition funnel, low temperature thermometer adapter, and N_2 inlet, was charged with 0.89 g (5.0 mmol) **3**, 0.60 g (5.5 mmol) Me_3SiCl, and 7 mL THF. The solution was cooled to -78 °C *via* dry ice/isopropanol bath. Next, a solution of LDA (1 M in THF, 6.0 mmol) was added *via* syringe, maintaining the temperature at -78 °C. After addition of LDA was complete, the solution was stirred at -78 °C for 1 h and then warmed to room temperature. The reaction mixture was quenched with 3 mL 1 N HCl and extracted with diethyl ether (2 x 15 mL). The ether extracts were washed with aqueous $NaHCO_3$, dried ($MgSO_4$), and concentrated by rotary evaporation. Fractional distillation yielded 0.297 g (25%) of **7**: bp 145 °C (2 mm Hg); ^{19}F NMR -131.0 (d, $^3J_{F,F}$ = 12 Hz), -131.7 (d, $^3J_{F,F}$ = 12 Hz); ^{1}H NMR 0.18 (s, 9H), 0.66 (q, 6H, $J_{H,H}$ = 8 Hz), 0.93 (t, 9H, $J_{H,H}$ = 8 Hz), ^{13}C NMR 1.0, 3.2, 7.2, 160.7 (dd, $^1J_{C,F}$ = 159 Hz, $^2J_{C,F}$ = 4 Hz), 164.5 (dd, $^1J_{C,F}$ = 158 Hz, $^2J_{C,F}$ = 4 Hz); GC/MS *m/e* 250 (M$^+$, 1.4), 129 (13.9), 115 (4.8), 101 (22.7), 87 (22.1), 73 (100.0); HRMS calcd for $C_{11}H_{24}F_2Si_2$ 250.1385, obsd 250.1390.

Preparation of *trans*-1,2-Difluoroiodotriethylsilylethylene,[12] *(E)*-IFC=CFSiEt$_3$, (8). A three-neck 1.0 L flask equipped with a magnetic stir bar, low temperature thermometer adapter, septum port, and N_2 inlet, was charged with 230 mL THF, 140 mL diethyl ether, and 25.0 g (0.14 mol) **2**. The solution was cooled to -100 to -110 °C *via* pentane-liquid N_2 bath. *n*-BuLi was slowly added to the solution *via* syringe (2.5 M in hexanes, 0.16 mol, 64.0 mL), carefully maintaining the reaction mixture at -95 to -100 °C. After addition of *n*-BuLi was complete, the solution was stirred at -95 to -100 °C for an additional 45 minutes. Next, a solution of I_2 (45.7 g, 0.18 mol in 140 mL THF) was added slowly *via* pressure equalized addition funnel, maintaining the reaction mixture at -95 to -100 °C. After I_2 addition was complete, the reaction mixture was stirred an additional 45 min. at -90 to -100 °C. Dilute HCl (3 N) was added at -30 to -40 °C until pH 5-6. Excess I_2 was

then removed by addition of aqueous $NaHSO_3$ until the reaction mixture turned from brown to yellow. The resultant mixture was extracted with ether, and the ether extracts were washed with aqueous $NaHCO_3$ and water. The extracts were dried ($MgSO_4$), and concentrated by rotary evaporation. The residue was distilled through a 10 cm Vigreux column to give 39.0 g (91%) of **8** (*E* isomer only): bp 96-97 °C (15 mm Hg); GLPC > 99%, lit.[12] bp 96 °C (15 mm Hg); ^{19}F NMR -117.2 (d, 1F, $^3J_{F,F}$ = 145 Hz), -139.5 (d, 1F, $^3J_{F,F}$ = 145 Hz); ^1H NMR 0.75 (q, 6H, $J_{H,H}$ = 8 Hz), 1.0 (t, 9H, $J_{H,H}$ = 8 Hz); GC/MS *m/e* 304 (M^+), 247, 219, 127, 119.

Preparation of *trans*-1,2-Difluorodiiodoethylene, *(E)*-IFC=CFI, (10). A 50 mL two-neck flask equipped with a magnetic stir bar, septum port, and N_2 inlet, was charged with 1.74 g (30.0 mmol) dry KF, 6.35 g (25.0 mmol) iodine, and 15 mL DMSO. Then, 6.38 g (21.0 mmol) **8** was added *via* syringe in one portion. The mixture was stirred 1 h at room temperature and then quenched by addition of aqueous $NaHSO_3$. The mixture was extracted with ether (3 x 25 mL) and the ether fractions were washed with water and dried ($MgSO_4$). Purification by fractional distillation yielded 4.64 g (70%) **10**: bp 87-88 °C (132 mm Hg); GLPC 98%; ^{19}F NMR (90 MHz) -105.5 (s); ^{13}C NMR 96.4 (m); FTIR[14] (gas phase) 1182 (s), 685 (s) cm^{-1}; GC/MS *m/e* 316 (M^+), 189, 170, 158, 127.

Preparation of *cis*-1,2-Difluorodiiodoethylene, *(Z)*-IFC=CFI, (9). A 25 mL two-neck flask equipped with a magnetic stir bar, rubber septum, and N_2 inlet, was charged with 2.54 g (10 mmol) I_2, 0.53 g KF (9.2 mmol), and 10 mL DMF. To the stirred mixture was added 1.86 g (4.0 mmol) **4** dropwise *via* syringe. The mixture was allowed to stir 45 minutes at room temperature and then filtered through a short column of silica gel (hexane eluent) to give a mixture of **9** and Et_3SiF. Fractional distillation through a short path apparatus yielded 0.95 g (74%) of **9**: bp 158 °C; GLPC 96%; ^{19}F NMR -83.7 (s); ^{13}C NMR 108.3 (dd, $^1J_{C,F}$ = 337 Hz, $^2J_{C,F}$ = 25 Hz); GC/MS *m/e* 316 (M^+, 100.0), 317 (M^++1, 2.2), 189 (26.9), 170 (13.2), 127 (72.7); FTIR[14] (gas phase) 1631 (m), 1129 (m), 1105 (s), 863 (s) cm^{-1}.

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REFERENCES

1 Burton, D. J.; Yang, Z. Y.; Morken, P. A. *Tetrahedron*, **1994**, *50*, 2993.

2. Burton, D. J. In *Synthetic Fluorine Chemistry*; Olah, G. A.; Chambers, R. D.; Prakash, G. K.S., Eds.; Wiley-Interscience, New York, NY, 1992, 205-226.

3. Liebman, J. F.; Greenberg, A.; Dolbier, Jr., W. R., Eds.; *Fluorine-Containing Molecules*; VCH Publishers, New York, NY, 1988.

4. Filler, R.; Kobayashi, Y., Eds.; *Biomedical Aspects of Fluorine Chemistry*; Kodasha/Elsevier, New York, NY, 1982. *Organofluorine Chemicals and Their Industrial Applications*; Banks, R. E., Ed.; Ellis Horwood Ltd., Chichester, 1979.

5. Banks, R. E.; Smart, B. E.; Tatlow, J. C., Eds.; *Organofluorine Chemistry, Principles and Chemical Applications*, Plenum Press, New York, NY 1994.

6. Leroy, J. *J. Org. Chem.*, **1981**, *46*, 206.

7. Asato, A.; Liu, R. *Tetrahedron Lett.*, **1986**, *27*, 3337.

8. Martinet, P.; Sauvetre, R.; Normant, J. F. *Bull. Soc. Chim. Fr.*, **1990**, *127*, 86.

9. Gouyon, T.; Sauvetre, R.; Normant, J. F. *J. Organomet. Chem.*, **1990**, *394*, 37.

10. Hiyama T.; Nishide, K.; Obayashi, M. *Chem. Lett.*, **1984**, *10*, 1765.

11. Fujita, M.; Obayashi, M.; Hiyama, T. *Tetrahedron*, **1988**, *44*, 4135.

12. Martinet, P.; Suavetre, R.; Normant, J. F. *J. Organomet. Chem.*, **1989**, *367*, 1.
13. Hudlicky, M., *Chemistry of Organic Fluorine Compounds*; Ellis Horwood Ltd., Chichester, 1976.
14. Friedrich, H. B.; Tardy, D. C.; Burton, D. J. *J. Fluorine Chem.*, **1993**, *65*, 53.

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