The application of trimethylvinylsilane as a convenient synthetic precursor of perfluoroalkyl ethenes: an unusual fluoride-induced elimination-desilylation coupled reaction.

Zoltán Szlávik, Gábor Tárkányi[†], Ágnes Gömöry[‡] and József Rábai*

Department of Organic Chemistry, Eötvös University, P.O. Box 32, H-1518 Budapest 112, Hungary

Supporting Information:
^{1}H-, ^{13}C-, ^{19}F-NMR, MS (EI, 70 eV), FT-IR data.

General experimental conditions: All structures were verified by one- and two-dimensional NMR experiments using recent assignment strategies that allowed a so called *ab initio* structure determination. Two-dimensional experiments involved both homo- (^{19}F-^{19}F) and hetero-nuclear (^{1}H-^{13}C, ^{19}F-^{13}C) correlations based on the GMQFCOPS and inverse ^{1}H and/or ^{19}F detected GHSQC, GHMQC sequences employing broadband adiabatic ^{13}C-decoupling. The ^{1}H-, ^{13}C- and ^{19}F-NMR measurements were carried out at 30°C in $CDCl_3$ and CD_3COCD_3 on a Varian INOVA-500 spectrometer (operating at 500 MHz for ^{1}H) equipped with a waveform generator, using a ^{1}H{^{13}C,^{15}N} PFG-triple resonance 5mm probe tunable for ^{19}F. Samples were prepared and measured in ca. 40-60 mmol/L concentrations. ^{1}H and ^{19}F chemical shifts are given relative to δ_{TMS}=0.00 ppm, δ_{CFCl3}=0.00 ppm, where TMS and $CFCl_3$ were used as internal standards. ^{13}C chemical shifts are reported by recording broadband ^{1}H or ^{19}F decoupled spectra and are referenced relative to the solvent ^{13}C-shifts δ_{CDCl3}=77.00 ppm and $\delta_{CD3COCD3}$=29.92 ppm. The reported homo- ^{19}F-^{19}F and heteronuclear ^{1}H-^{19}F scalar coupling constants were verified from bandselective decoupled ^{19}F spectra. Both broadband ^{19}F- and ^{13}C-decoupling and bandselective ^{19}F decoupling was performed by adiabatic decoupling using the WURST[1] decoupling sequence. Asterisk (*) denotes interchangeable assignments.

The FT-IR measurements were carried out on a BRUKER IFS 55 spectrometer. Mass spectra were determined on a VG ZAB2-SEQ tandem mass spectrometer using electron impact (70 eV) for ionization.

1. F-$(CF_2)_4$-CH_2-CHI-$SiMe_3$ **1**
^{1}H-NMR($CDCl_3$): 0.20 s (9H) [$SiMe_3$]; 2.53-2.80 m (2H) [H-2]; 3.21 dd (1H) ($^{3}J_{(H,H)}$=10.0Hz, $^{3}J_{(H,H)}$=3.5Hz) [H-1].
^{13}C-NMR($CDCl_3$): -2.5 [$SiMe_3$]; 0.5 [C-1]; 35.4 ($^{2}J_{(C,F)}$=21.1Hz) [C-2]; 108.8 [C-5]; 110.5 [C-4]; 117.4 [C-6]; 117.8 [C-3].
^{19}F-NMR($CDCl_3$): -81.6 (3F) [F-6]; -114.8 d (1F) ($^{2}J_{(F,F)}$ = 268.8Hz) and –116.1 d (1F) ($^{2}J_{(F,F)}$ = 268.8Hz) [F-3_x and F-3_y]; -125.0 (2F) [F-4]; -126.4 (2F) [F-5].
MS: (m/z, I, M-X) 446, <0.1, M; 354, 33, M-F$Si(CH_3)_3$; 335, 8.5, M-$F_2Si(CH_3)_3$; 227, 47, M-I$Si(CH_3)_3$; 207, 29, M-$IF_2Si(CH_3)_3$; 189, 19; 185, 19; 139, 13; 77, 77, $CF_2CH{=}CH_2$; 73, 100, $Si(CH_3)_3$.
FT-IR: (liquid film) υ (cm^{-1}): 2959.2 (CH_{as}); 2902.7 (CH_s); 1254.3, 1221.6 (CF).

2. F-$(CF_2)_6$-CH_2-CHI-$SiMe_3$ **2**
^{1}H-NMR($CDCl_3$): 0.20 s (9H) [$SiMe_3$]; 2.53-2.80 m (2H) [H-2]; 3.21 dd (1H) ($^{3}J_{(H,H)}$=10.0Hz, $^{3}J_{(H,H)}$=3.0Hz) [H-1].
^{13}C-NMR($CDCl_3$): -2.5 [$SiMe_3$]; 0.6 [C-1]; 35.5 ($^{2}J_{(C,F)}$=20.9Hz) [C-2]; 108.5 [C-7]; 110.3 [C-6]; 111.0 [C-4]; 111.1 [C-5]; 117.2 [C-8]; 117.9 [C-3].
^{19}F-NMR($CDCl_3$): -81.3 (3F) [F-8]; -114.6 d (1F) ($^{2}J_{(F,F)}$ = 268.0Hz) and -115.8 d (1F) ($^{2}J_{(F,F)}$ = 268.0Hz) [F-3_x and F-3_y]; -122.2 (2F) [F-5]; -123.3 (2F) [F-6]; -124.1 (2F) [F-4]; -126.6 (2F) [F-7].
MS: (m/z, I, M-X) 546, <0.1, M; 454, 24, M-F$Si(CH_3)_3$; 435, 9.0, M-$F_2Si(CH_3)_3$; 327, 46, M-I$Si(CH_3)_3$; 307, 14, M-$IF_2Si(CH_3)_3$; 189, 15; 185, 17; 139, 20; 77, 75, $CF_2CH{=}CH_2$; 73, 100, $Si(CH_3)_3$.
FT-IR: (liquid film) υ (cm^{-1}): 2959.6 (CH_{as}); 2902.9 (CH_s); 1239.8, 1208.1 (CF).

3. F-$(CF_2)_8$-CH_2-CHI-$SiMe_3$ **3**
^{1}H-NMR(Acetone): 0.24 s (9H) [$SiMe_3$]; 2.67-2.81 m (1H) and 2.89-3.00 m (1H) [H-2_x and H-2_y]; 3.40 dd (1H) ($^{3}J_{(H,H)}$=10.5Hz, $^{3}J_{(H,H)}$=2.5Hz) [H-1].
^{13}C-NMR(Acetone): -2.4 [$SiMe_3$]; 1.8 [C-1]; 36.1 ($^{2}J_{(C,F)}$=21.8Hz) [C-2]; 109.6 [C-9]; 111.4 [C-8]; 111.9 and 112.0 [C-6 and C-7]*; 112.2 [C-4]; 112.4 [C-5]; 118.2 [C-10]; 119.5 [C-3].
^{19}F-NMR(Acetone): -80.7 (3F) [F-10]; -112.9 d (1F) ($^{2}J_{(F,F)}$ = 267.9Hz) and -114.7 d (1F) ($^{2}J_{(F,F)}$ = 267.9Hz) [F-3_x and F-3_y]; -120.9 (2F) [F-5]; -121.2 (4F) [F-6 and F-7]; -122.1 (2F) [F-8]; -122.9 (2F) [F-4]; -125.6 (2F) [F-9].
MS: (m/z, I, M-X) 646, <0.1, M; 554, 18, M-F$Si(CH_3)_3$; 535, 10, M-$F_2Si(CH_3)_3$; 427, 41, M-I$Si(CH_3)_3$; 407, 8.8, M-$IF_2Si(CH_3)_3$; 189, 13; 185, 15; 139, 21; 77, 69, $CF_2CH{=}CH_2$; 73, 100, $Si(CH_3)_3$.
FT-IR: (liquid film) υ (cm^{-1}): 2961.5 (CH_{as}); 2906.5 (CH_s); 1225.0 (CF).

4. F-$(CF_2)_{10}$-CH_2-CHI-$SiMe_3$ **4**

^{1}H-NMR(Acetone): 0.24 s (9H) [$SiMe_3$]; 2.68-2.83 m (1H) and 2.90-3.03 m (1H) [H-2_x and H-2_y]; 3.42 dd (1H) ($^3J_{(H,H)}$=10.5Hz, $^3J_{(H,H)}$=2.5Hz) [H-1].

^{13}C-NMR(Acetone): -2.4 [$SiMe_3$]; 1.9 [C-1]; 36.0 ($^2J_{(C,F)}$=21.9Hz) [C-2]; 109.5 [C-11]; 111.3 [C-10]; 111.8 and 111.9 [C-6 and C-9]*; 112.0 [C-7 and C-8]; 112.2 [C-4]; 112.4 [C-5]; 118.2 [C-12]; 119.4 [C-3].

^{19}F-NMR(Acetone): -80.5 (3F) [F-12]; -112.7 d (1F) ($^2J_{(F,F)}$ = 267.4Hz) and -114.6 d (1F) ($^2J_{(F,F)}$ = 267.4Hz) [F-3_x and F-3_y]; -120.8 (2F) [F-5]; -120.9 (4F) [F-7 and F8]; -121.1 (4F) [F-6 and F-9]; -121.9 (2F) [F-10]; -122.8 (2F) [F-4]; -125.4 (2F) [F-11].

MS: (m/z, I, M-X) 746, <0.1, M; 654, 22, M-$FSi(CH_3)_3$; 635, 18, M-$F_2Si(CH_3)_3$; 527, 55, M-$IFSi(CH_3)_3$; 507, 10, M-$IF_2Si(CH_3)_3$; 189, 20; 185, 20; 139, 32; 77, 78, $CF_2CH{=}CH_2$; 73, 100, $Si(CH_3)_3$.

FT-IR: (KBr) υ (cm^{-1}): 2957.1 (CH_{as}); 2900.4 (CH_s); 1240.2, 1207.2 (CF).

5. F-$(CF_2)_4$-$CH{=}CH_2$ **5**

^{1}H-NMR($CDCl_3$): 5.75-5.85 m (1H) [H-1C]; 5.91-6.05 m (2H) [H-2A and H-1B].

^{13}C-NMR($CDCl_3$): 108.9 [C-5]; 110.5 [C-4]; 114.2 ($^2J_{(C,H)}$=12.8Hz, $^3J_{(C,H)}$=6.3Hz) [C-3]; 117.6 [C-6]; 125.3 ($^2J_{(C,F)}$=23.6Hz) [C-2]; 125.5 ($^3J_{(C,F)}$=9.5Hz) [C-1].

^{19}F-NMR($CDCl_3$): -81.8 (3F) ($^3J_{(F,F)}$=3.3 Hz, $^4J_{(F,F)}$=9.9Hz) [F-6]; -114.6 (2F) [F-3]; -125.0 (2F) [F-4]; -126.3 (2F) [F-5].

MS: (m/z, I, M-X) 246, <0.1, M; 227, 3.5, M-F; 181, 3.6, M-F-($FCH{=}CH_2$); 157, 3.6, M-F-(HCF_3); 181, 3.6, C_4F_7; 169, <1, C_3F_7; 131, 3.0, C_3F_5; 119, 3.4, C_2F_5; 100, 4.9, $CF_2{=}CF_2$; 77, 100, $CF_2CH{=}CH_2$; 69, 15, CF_3; 51, 24, HCF_2; 31, 6.3, CF.

FT-IR: (liquid film) υ (cm^{-1}): 2962.1 (CH_{as}); 2904.2 (CH_s); 1237.2 (CF).

6. F-$(CF_2)_6$-$CH{=}CH_2$ **6**

^{1}H-NMR($CDCl_3$): 5.75-5.85 m (1H) [H-1C]; 5.90-6.04 m (2H) [H-2A and H-1B].

^{13}C-NMR($CDCl_3$): 108.7 [C-7]; 110.5 [C-6]; 111.0 [C-4]; 111.2 [C-5]; 114.3 [C-3]; 117.4 [C-8]; 125.6 ($^3J_{(C,F)}$=9.5Hz) [C-1]; 125.2 ($^2J_{(C,F)}$=23.9Hz) [C-2].

^{19}F-NMR($CDCl_3$): -81.5 (3F) [F-8]; -114.4 (2F) [F-3]; -122.1 (2F) [F-5]; -123.4 (2F) [F-6]; -124.1 (2F) [F-4]; -126.7 (2F) [F-7].

MS: (m/z, I, M-X) 346, <0.1, M; 327, 4.1, M-F; 281, 2.3, M-F-($FCH{=}CH_2$); 257, 2.3, M-F-(HCF_3); 181, <1, C_4F_7; 169, 1.5, C_3F_7; 131, 7.4, C_3F_5; 119, 4.3, C_2F_5; 100, 4.8, $CF_2{=}CF_2$; 77, 100, $CF_2CH{=}CH_2$; 69, 16, CF_3; 51, 21, HCF_2; 31, 3.8, CF.

FT-IR: (liquid film) υ (cm^{-1}): 2963.0 (CH_{as}); 1245.0, 1202.4 (CF).

7. F-$(CF_2)_8$-$CH{=}CH_2$ **7**

^{1}H-NMR($CDCl_3$):5.74-5.84 m (1H) [H-1C]; 5.90-6.05 m (2H) [H-2A and H-1B].

^{13}C-NMR($CDCl_3$):108.6 [C-9]; 110.4 [C-8]; 110.9 [C-6 and C-7]; 111.0 [C-4]; 111.3 [C-5]; 114.3 [C-3]; 117.3 [C-10]; 125.5 ($^3J_{(C,F)}$=9.5Hz) [C-1]; 125.3 ($^2J_{(C,F)}$=23.6Hz) [C-2].

^{19}F-NMR($CDCl_3$):-81.6 (3F) [F-10]; -114.5 (2F) [F-3]; -121.9 (2F) [C-5]; -122.4 (4F) [C-6 and C-7]; -123.2 (2F) [C-8]; -124.1 (2F) [F-4]; 126.7 (2F) [C-9].

MS: (m/z, I, M-X) 446, <0.1, M; 427, 3.2, M-F; 381, 1.1, M-F-($FCH{=}CH_2$); 357, 1.0, M-F-(HCF_3); 181, 1.4, C_4F_7; 169, 2.0, C_3F_7; 131, 8.0, C_3F_5; 119, 5.3, C_2F_5; 100, 4.3, $CF_2{=}CF_2$; 77, 100, $CF_2CH{=}CH_2$; 69, 15, CF_3; 51, 15, HCF_2; 31, 7.5, CF.

FT-IR: (liquid film) υ (cm^{-1}): 2964.3 (CH_{as}); 1225.0 (CF).

8. F-$(CF_2)_{10}$-$CH{=}CH_2$ **8**

^{1}H-NMR(Acetone): 5.99 d ($^3J_{(H,H)}$=11.0Hz) (1H) [H-1C]; 6.05 dt ($^3J_{(H,H)}$=17.0Hz, $^4J_{(H,F)}$=2.5Hz) (1H) [H-1B]; 6.19 dq ($^3J_{(H,H)}$=17.0Hz, $^3J_{(H,H)}$=11.0Hz, $^4J_{(H,F)}$=11.5Hz) (1H) [H-2A].

^{13}C-NMR(Acetone): 109.4 [C-11]; 111.2 [C-10]; 111.7 [C-6]*; 111.8 [C-8]*; 111.9 [C-9]*; 111.9 [C-7]*; 111.9 [C-4]; 112.2 [C-5]; 115.5 [C-3]; 118.1 [C-12]; 125.7 ($^2J_{(C,F)}$=23.6Hz) [C-2]; 127.3 ($^3J_{(C,F)}$=9.6Hz) [C-1].

^{19}F-NMR(Acetone): -81.0 (3F) [F-12]; -113.3 (2F) [F-3]; -121.1 (2F) [F-5]; -121.4 (4F) [F-7 and F-8]; -121.5 (4F) [F-6 and F-9]; -122.4 (2F) [F-10]; -123.3 (2F) [F-4]; -125.9 (2F) [F-11].

MS: (m/z, I, M-X) 546, <0.1, M; 527, 12, M-F; 481, 1.6, M-F-($FCH{=}CH_2$); 457, 2.0, M-F-(HCF_3); 181, 3.9, C_4F_7; 169, 5.5, C_3F_7; 131, 16, C_3F_5; 119, 11, C_2F_5; 100, 7.3, $CF_2{=}CF_2$; 77, 100, $CF_2CH{=}CH_2$; 69, 25, CF_3; 51, 23, HCF_2; 31, 2.2, CF.

FT-IR: (liquid film) υ (cm^{-1}): 2964.7 (CH_{as}); 1245.2, 1202.7 (CF).

9. MeOOC-$(CF_2)_8$-CH_2-CHI-$SiMe_3$ **9**

^{1}H-NMR(Acetone): 0.24 s (9H) [$SiMe_3$]; 2.67-2.81 m (1H) and 2.89-3.02 m (1H) [H-2_x and H-2_y]; 3.41 dd (1H) ($^3J_{(H,H)}$=10.5Hz, $^3J_{(H,H)}$=2.5Hz) [H-1]; 4.08 s (3H) [COOMe].

^{13}C-NMR(Acetone): -2.4 [$SiMe_3$]; 1.9 [C-1]; 36.1 ($^2J_{(C,F)}$=21.9Hz) [C-2]; 55.9 [OMe]; 109.2 [C-10]; 111.5 [C-9]; 111.9 [C-6, C-7 and C-8]; 112.1 [C-4]; 112.3 [C-5]; 119.3 [C-3]; 159.3 [C=O].

^{19}F-NMR(Acetone): -112.8 d (1F) ($^{2}J_{(F,F)}$ = 267.4Hz) and -114.7 (1F) ($^{2}J_{(F,F)}$ = 267.4Hz) [F-3_x and F-3_y]; -118.0 (2F) [F-10]; -120.8 (2F) [F-5]; -121.0 (2F) [F-8]; -121.1 (4F) [F-6 and F-7]; -122.2 (2F) [F-9]; -122.8 (2F) [F-4].
MS: (m/z, I, M-X) 686, 0.1, M; 586, 1.1; M-C_2F_4; 567, 0.3, M-C_2F_5; 527, 0.2, M-C_2F_4COOMe; 459, 2.2, M-C_2F_4I; 59, 20, COOMe; 31, 100, CF.
FT-IR: (liquid film) υ (cm^{-1}): 2965.1 (CH_{as}); 1784.4 (CO); 1212.0, 1150.3 (CF).

10. HO-CH_2-$(CF_2)_8$-CH_2-CHI-$SiMe_3$ **10**
^{1}H-NMR(Acetone): 0.24 s (9H) [$SiMe_3$]; 2.67-2.81 m (1H) and 2.89-3.02 m (1H) [H-2_x and H-2_y]; 3.41 dd (1H) ($^{3}J_{(H,H)}$=10.5Hz, $^{3}J_{(H,H)}$=2.5Hz) [H-1]; 4.13 t (2H) ($^{3}J_{(H,F)}$=14.5Hz) [H-11]; 3.10-3.90 s,br (1H) [OH].
^{13}C-NMR(Acetone): -2.4 [$SiMe_3$]; 1.9 [C-1]; 36.1 ($^{2}J_{(C,F)}$=21.9Hz) [C-2]; 60.6 ($^{2}J_{(C,F)}$=25.3Hz) [C-11]; 112.0 [C-6 and C-7]; 112.1 [C-4]; 112.2 [C-8]; 112.3 [C-5]; 112.6 [C-9]; 117.3 [C-10]; 119.3 [C-3].
^{19}F-NMR(Acetone): -112.7 d (1F) ($^{2}J_{(F,F)}$ = 267.1Hz) and -114.6 d (1F) ($^{2}J_{(F,F)}$ = 267.1Hz) [F-3_x and F-3_y]; -120.8 (2F) [F-5]; -121.0 (2F) [F-10]; -121.1 (4F) [F-6 and F-7]; -121.3 (2F) [F-8]; -122.7 [F-9]; -122.8 [F-4].
MS: (m/z, I, M-X) 658, 19, M; 566, 11, M-FSi$(CH_3)_3$; 547, 8.1, M-F_2Si$(CH_3)_3$; 439, 31, M-IFSi$(CH_3)_3$; 420, 5.9; 189, 20; 185, 23; 139, 37; 77, 73, $CF_2CH{=}CH_2$; 73, 100, Si$(CH_3)_3$; 31, 45, CF.
FT-IR: (liquid film) υ (cm^{-1}): 3384.2 (OH); 2958.9 (CH_{as}); 2900.5 (CH_s); 1775.3 (CO); 1210.7, 1149.7 (CF).

11. HO-CH_2-$(CF_2)_8$-$CH{=}CH_2$ **11**
^{1}H-NMR(Acetone): 4.15 dt (2H) ($^{3}J_{(H,F)}$=14.0Hz, $^{3}J_{(H,H)}$=6.5Hz) [H-11]; 5.12 t (1H) ($^{3}J_{(H,H)}$=6.5Hz) [OH]; 6.00 d (1H) ($^{3}J_{(H,H)}$=11.0Hz) [H-1C]; 6.07 dt (1H) ($^{3}J_{(H,H)}$=17.0Hz, $^{4}J_{(H,F)}$=2.0Hz) [H-1B]; 6.22 dq (1H) ($^{3}J_{(H,H)}$=17.0Hz, $^{3}J_{(H,H)}$=11.0Hz, $^{3}J_{(H,F)}$=11.5Hz) [H-2A].
^{13}C-NMR(Acetone): 60.9 ($^{2}J_{(C,F)}$=25.2Hz) [C-11]; 112.2 [C-4, C-6 and C-7]; 112.3 [C-8]; 112.4 [C-5]; 112.7 [C-9]; 115.7 [C-3]; 117.4 [C-10]; 125.9 ($^{2}J_{(C,F)}$=23.6Hz) [C-2]; 127.4 ($^{3}J_{(C,F)}$=21.9Hz) [C-1].
^{19}F-NMR(Acetone): -113.1 (2F) [F-3]; -120.9 (2F) [F-5]; -121.3 (2F) [F-10]; -121.4 (4F) [F-6 and F-7]; -121.5 (2F) [F-8]; -123.0 (2F) [F-9]; -123.2 (2F) [F-4].
MS: (m/z, I, M-X) 458, <0.1, M; 439, 3.5, M-F; 438, 1.8, M-HF; 419, 1.4, M-HF_2; 408, 4.8, M-CF_4; 207, 1.0; 181, 1.4; 157, 3.6; 139, 3.2; 131, 15, C_3F_5; 77, 100, $CF_2CH{=}CH_2$; 51, 16, CF_2H; 31, 72, CF.
FT-IR: (liquid film) υ (cm^{-1}): 3372.5 (OH); 2999.1, 2959.2 (CH_{as}); 2899.3 (CH_s); 1210.2, 1149.8 (CF).

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†Chemical Works of Gedeon Richter, Spectroscopic Research Division, Budapest, Hungary.
‡Institute of Chemistry, Chemical Research Center, Hungarian Academy of Sciences, Budapest, Hungary
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