FLUORIDE-CATALYZED NUCLEOPHILIC PERFLUOROALKYLATIONS OF ACETYLENIC KETONES OR ALDEHYDES

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Received April 15, 2002
Accepted June 5, 2002

Dedicated to the memory of Professor Miloš Hudlický – one of fluorine chemistry's finest gentlemen.

Reactions of 4-phenylbut-3-yn-2-one (**1a**) and phenylpropynal (**1b**) with trimethyl(perfluoroalkyl)silanes (Me_3SiR_f) (R_f = CF_3, C_2F_5, n-C_6F_{13}, n-C_7F_{15}, n-C_8F_{17}) in the presence of catalytic amounts of cesium fluoride (CsF) have been studied. Compounds **1a**, **1b** were reacted with 0.5 equivalent excess of Me_3SiR_f in ethylene glycol dimethyl ether (monoglyme) at 25 °C for R_f = CF_3, C_2F_5 and at 50 °C for R_f = n-C_6F_{13}, n-C_7F_{15}, n-C_8F_{17} to give the corresponding perfluoroalkylated alcohols in good yields after acid hydrolysis. The new compounds were characterized by IR, NMR (^1H, ^{19}F, ^{13}C), MS and elemental analysis. In these reactions, tetrabutylammonium fluoride (TBAF) is also effective as the fluoride catalyst. The alcohols with CF_3 or C_2F_5 are viscous liquids whereas those with n-C_6F_{13}, n-C_7F_{15} or n-C_8F_{17} are solids. They are soluble in common organic solvents and stable to air and moisture.

Keywords: Fluoride; Nucleophilic additions; Perfluoroakylations; Ketones; Aldehydes; Alkynes; Trimethyl(perfluoroalkyl)silanes.

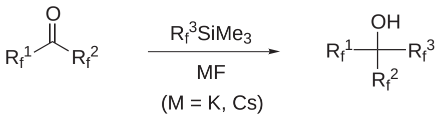
The perfluoroalkyl group is a highly important substituent in the field of organofluorine compounds. The introduction of a fluorine atom or fluorinated group into an organic compound can bring about some remarkable changes in the physical, chemical and biological properties that result in new compounds/materials suitable for diverse applications in the areas of materials science, agrochemistry and industry[1–5]. The powerful electron-withdrawing ability and relatively small size of the fluorine atom lead to significant changes in the chemistry of substituted compounds when compared with their nonfluorinated analogues. The influence of a perfluoroalkyl group in biologically active molecules is often associated with the increased lipophilicity[6] that gives active pharmaceutical and agrochemical compounds with improved transport characteristics. Among other things, this property facilitates lower dose rates. While other methods have been

doi:10.1135/cccc20021296

developed for the introduction of perfluoroalkyl groups into organic compounds[7], the utilization of trimethyl(perfluoroalkyl)silanes (Me_3SiR_f) as nucleophilic perfluoroalkylating reagent is rapidly becoming the method of choice[8]. Recently, we and others have reported the reactions of keto compounds with Me_3SiCF_3 in the presence of fluoride ions[8]. However, little effort has been devoted to the transfer of longer perfluoroalkyl groups into a nonactivated carbonyl system. We became interested in the nucleophilic perfluoroalkylation reactions of carbonyl compounds while examining various fluoride ion sources as catalysts. Here we report the fluoride-catalyzed perfluoroalkylations of 4-phenylbut-3-yn-2-one and phenylpropynal with trimethyl(perfluoroalkyl)silane. To our knowledge, this is the first report of the transfer of the higher perfluoroalkyl groups into a simple acetylenic ketones or aldehydes system utilizing fluoride ion catalysis.

RESULTS AND DISCUSSION

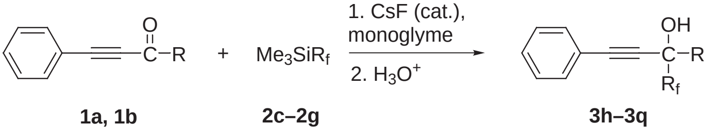
Nucleophilic transformation of the longer perfluoroalkyl groups with simple carbonyl compounds using fluoride ion catalysis is unknown. Nearly a decade ago reactions were reported that involved trimethyl(perfluoroalkyl)silane and highly activated carbonyl compounds with very strong electron-withdrawing perfluoroalkyl groups, catalyzed by cesium fluoride or potassium fluoride[9] (Scheme 1). Recently, we have carried out a large variety of fluoride catalyzed reactions[8]. Here we report our study of the nucleophilic perfluoroalkylations of acetylenic ketones or aldehydes, with trifluoromethyl and higher perfluoroalkyl homologues. The details of the chemistry are described below.



R_f^1	R_f^2	R_f^3
n-C_8F_{13}	CF_3	*n*-C_6F_{13}
$(CF_3)_2CHO(CF_2)_4$	CF_3	*n*-C_6F_{13}

SCHEME 1

Reactions of trimethyl(trifluoromethyl)silane (**2c**) with 4-phenylbut-3-yn-2-one (**1a**) and phenylpropynal (**1b**) in the presence of a catalytic amount of cesium fluoride in monoglyme proceeded smoothly at 25 °C to give the corresponding (trifluoromethyl)silyl ether derivatives in quantitative yields. Hydrolysis of the silyl ether intermediates with aqueous hydrochloric acid formed the (phenylethynyl)(trifluoromethyl)methanols **3h**, **3i** in 88% isolated yields. Under similar reaction conditions, when trimethyl(pentafluoroethyl)silane (**2d**) was reacted with **1a** and **1b**, (pentafluoroethyl)(phenylethynyl)methanols **3j**, **3k** were obtained in >80% isolated yield. These reactions are not surprising, and gave a simple route to the trifluoromethyl and pentafluoroethyl compounds in very good yields. When **1a** was reacted with **2e** in monoglyme at 25 °C in the presence of a catalytic amount of CsF, or TBAF after 24 h, the reaction was found to be incomplete with *ca* 25% of **1a** remaining unreacted. Heating the reaction mixture at 50 °C for 15 h completed the conversion of **1a**. Hydrolysis with aqueous HCl produced **3l** in 60% isolated yield. Under similar reaction conditions, **1b** reacted with **2e** to yield **3m** in 55% isolated yield (Scheme 2). Thus, the reaction of **1a**, **1b** with **2f**, **2g** produced **3n**–**3q** in good isolated yields after acid hydrolysis (Table I).



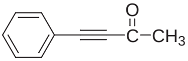
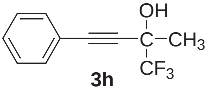
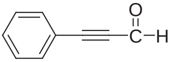
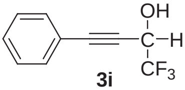
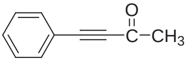
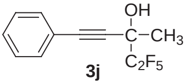
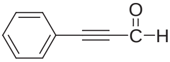
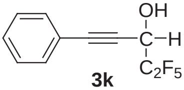
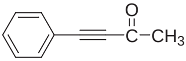
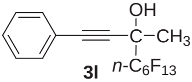
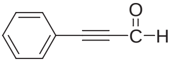
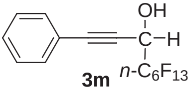
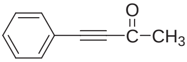
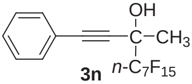
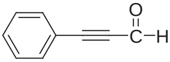
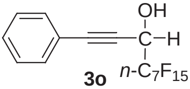
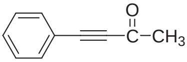
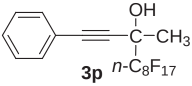
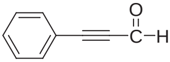
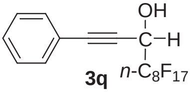
SCHEME 2

In all these reactions, TBAF was also found to be a suitable fluoride ion catalyst to produce the final products in comparable yields. For Me_3SiCF_3 and $Me_3SiC_2F_5$, the corresponding silyl ether intermediate was found to be stable while for Me_3SiR_f (R_f = n-C_6F_{13}, n-C_7F_{15}, n-C_8F_{17}) the corresponding silyl ether intermediates were unstable and were not isolated. Tetrahydrofuran was also found to be a suitable solvent for the above chemistry.

The nucleophilic reaction mechanisms for trifluoromethylation and pentafluoroethylation of acetylenic ketones or aldehydes with Me_3SiR_f (R_f = CF_3, C_2F_5) are assumed to be the same as that reported for ketones and aldehydes[10]. The reaction was initiated by fluoride ion to form perfluoroalkylated oxyanions which catalyze subsequent reaction.

With the exception of **3h**–**3k** that are viscous liquids, the new (perfluoroalkyl)(phenylethynyl)methanols (Table I) are solids. They are soluble in common organic solvents (dichloromethane, chloroform, acetone, diethyl ether, monoglyme, *etc.*) and have poor solubility in pentane and hexane. They all are stable to moisture and air. The solid compounds **3l**–**3q** are crystallizable in a mixture of pentane/dichloromethane at –15 °C. The infrared spectra of all the compounds have a broad peak in the region 3 200–3 400 cm^{-1} assigned to ν(OH) and a sharp peak in the region 2 200–2 300 cm^{-1}

TABLE I
Nucleophilic perfluoroalkylation of acetylenic ketone/aldehyde[a]

Acetylenic ketone/aldehyde	Me_3SiR_f R_f	Product	Yield, %
 **1a**	CF_3 **2c**	 **3h**	88
 **1b**	CF_3 **2c**	 **3i**	90
 **1a**	C_2F_5 **2d**	 **3j**	85
 **1b**	C_2F_5 **2d**	 **3k**	83
 **1a**	n-C_6F_{13} **2e**	 **3l**	60
 **1b**	n-C_6F_{13} **2e**	 **3m**	55
 **1a**	n-C_7F_{15} **2f**	 **3n**	62
 **1b**	n-C_7F_{15} **2f**	 **3o**	53
 **1a**	n-C_8F_{17} **2g**	 **3p**	62, 60[c]
 **1b**	n-C_8F_{17} **2g**	 **3q**	58

[a] All reactions were carried out with 2 mmol of acetylenic ketone/aldehyde and 2.5 mmol of Me_3SiR_f in 3 ml of monoglyme. [b] Isolated. [c] Using a catalytic amount of TBAF in THF.

assigned to ν(C≡C). In the ^{19}F NMR spectra, a peak due to the CF_3 moiety appeared in the range of –70 to –80 ppm. The CF_2 groups appeared as a multiplet in the region of –119 to –127 ppm. The ^{1}H NMR spectra of all the products clearly show the presence of protons of hydroxy groups. This resonance disappeared upon treating with D_2O. In the ^{13}C NMR spectra, the peak assigned to the carbonyl carbon that appeared at about 190 ppm in the starting materials **1a**, **1b**, shifted upfield to *ca* 60–70 ppm. This shift resulted from introduction of the perfluoroalkyl group and hydroxy group on the same carbon.

In conclusion, we have described a useful method to prepare longer chain (perfluoroalkyl)(phenylpropynyl)methanols in good yields by fluoride-catalyzed reactions of 4-phenylbut-3-yn-2-one and phenylpropynal with trimethyl(perfluoroalkyl)silane.

EXPERIMENTAL

All the reactions were performed under dry nitrogen. The (perfluoroalkyl)trimethylsilanes were prepared by published procedures[11]. Cesium fluoride was maintained at 200 °C and repeatedly ground until it remained as a finely divided powder. Once this stage is reached, it can be stored at this temperature in its finely divided state and used indefinitely. The 4-phenylbut-3-yn-2-one and phenylpropynal (Aldrich) were used as received. Ethylene glycol dimethyl ether (monoglyme) of high purity (Aldrich) was used as solvent. ^{1}H, ^{19}F, and ^{13}C NMR spectra were recorded in $CDCl_3$ on a spectrometer operating at 300, 282, and 75 MHz, respectively. Chemical shifts are reported in ppm (δ-scale) relative to the appropriate standard, $CFCl_3$ for ^{19}F, and TMS for ^{1}H and ^{13}C NMR spectra. Coupling constants (J) are given in Hz. IR spectra (wavenumbers in cm^{-1}) were recorded using NaCl plates. Mass spectra were measured on an electron-impact 70 eV spectrometer. Elemental analyses were performed at the Shanghai Institute of Organic Chemistry, China.

General Procedure for Perfluoroalkylation of Phenylpropynal (**1a**) and 4-Phenylbut-3-yn-2-one (**1b**) with Trimethyl(trifluoromethyl)silane (**2c**) and Trimethyl(pentafluoroethyl)silane (**2d**)

In a typical experiment, **1a** or **1b** (2 mmol) and **2c** or **2d** (2.5 mmol) were dissolved in monoglyme (3 ml). A catalytic amount of cesium fluoride/tetrabutylammonium fluoride (0.1 mmol) was added at 25 °C. Reaction occurred with the generation of heat and color change to dark brown. Progress of the reaction was monitored by GC-MS. Glyme and excess Me_3SiR_f were removed at reduced pressure and THF (2 ml) was added to the residue followed by 4 M HCl (8 ml). Volatile materials were removed under reduced pressure and the product was extracted with methylene chloride. Purification was accomplished *via* thin layer chromatography using methylene chloride/pentane mixtures (1 : 1) to yield **3h**–**3k** in good to excellent yields.

1,1,1-Trifluoro-2-methyl-4-phenylbut-3-yn-2-ol[12] (**3h**). Yield 88%; yellowish viscous liquid. IR (NaCl film): 3 412, 2 958, 2 240, 1 491, 1 708, 1 491, 1 445, 1 296, 1 261, 1 188, 1 154, 1 105, 958, 905, 756, 690. ^{1}H NMR ($CDCl_3$): 1.68 (s, 3 H); 2.87 (s, 1 H);7.2–7.4 (m, 5 H). ^{19}F NMR

(CDCl$_3$): –82.67 (s, 3 F). ^{13}C NMR (CDCl$_3$): 23.49, 69.52 (q, $J_{C\text{-}C\text{-}F}$ = 33, COHCF$_3$); 85.12, 86.64, 121.6, 124.5 (q, $J_{C\text{-}F}$ = 278, CF$_3$); 128.8, 129.7, 132.3. MS (EI), *m/z* (species, rel. int.): 214 (M$^+$, 25), 197 (M$^+$ – OH, 31), 145 (M$^+$ – CF$_3$, 79), 129 [M$^+$ – (CF$_3$ + CH$_3$ + H), 94], 115 (PhCCCH$_2^+$, 51), 102 (PhCCH, 22), 77 (Ph$^+$, 20), 69 (CF$_3^+$, 14), 43 (CH$_3$CO$^+$, 100).

1,1,1-Trifluoro-4-phenylbut-3-yn-2-ol[13] (**3i**). Yield 90%; yellowish viscous liquid. IR (NaCl film): 3 379, 3 063, 2 241, 1 678, 1 599, 1 491, 1 445, 1 353, 1 272, 1 186, 1 140, 1 073, 981, 838, 756, 690. ^{1}H NMR (CDCl$_3$): 2.93 (s, 1 H); 4.86 (q, 1 H, *J* = 5.7); 7.1–7.4 (m, 5 H). ^{19}F NMR (CDCl$_3$): –79.78 (d, 3 F, *J* = 5.3). ^{13}C NMR (CDCl$_3$): 63.3 (q, $J_{C\text{-}C\text{-}F}$ = 36, COHCF$_3$); 80.9, 88.3, 121.4, 123.3 (q, $J_{C\text{-}F}$ = 279, CF$_3$); 128.9, 129.9, 132.5. MS (CI), *m/z* (species, rel. int.): 201 (M$^+$ + H, 100), 200 (M$^+$, 13), 183 (M$^+$ – OH, 4), 131 (M$^+$ – CF$_3$, 18).

4,4,5,5,5-Pentafluoro-3-methyl-1-phenylpent-1-yn-3-ol (**3j**). Yield 85%; yellowish viscous liquid. IR (NaCl film): 3 423, 3 061, 3 009, 2 243, 1 491, 1 445, 1 342, 1 273, 1 215, 1 197, 1 117, 1 089, 1 010, 956, 889, 756. ^{1}H NMR (CDCl$_3$): 1.75 (s, 3 H); 2.46 (s, 1 H); 7.23–7.45 (m, 5 H). ^{19}F NMR (CDCl$_3$): –78.4 (s, 3 F); –123.6 (d, 1 F, *J* = 270); –125.3 (d, 1 F, *J* = 270). ^{13}C NMR (CDCl$_3$): 23.65 (m); 69.25 (t, *J* = 26.9, COHCF$_2$CF$_3$); 84.58 (m); 87.1 (t, *J* = 0.6); 113.15 (t of q, *J* = 262.8, CF$_2$CF$_3$, *J* = 0.37); 119.38 (q of t, *J* = 289, CF$_2$CF$_3$, *J* = 35.9); 121.1, 128.393, 129.3, 131.8. MS (EI), *m/z* (species, rel. int.): 264 (M$^+$, 17), 247 (M$^+$ – OH, 84), 145 (M$^+$ – CF$_2$CF$_3$, 100), 129 [M$^+$ – (C$_2$F$_5$ + CH$_3$ + H), 60], 115 (CCCOCHCF$_2^+$, 29), 102 (PhCCH, 13), 77 (Ph$^+$, 8), 43 (CH$_3$CO$^+$, 60). For C$_{12}$H$_9$F$_5$O (264.2) calculated: 54.56% C, 3.43% H; found: 54.47% C, 4.87% H.

4,4,5,5,5-Pentafluoro-1-phenylpent-1-yn-3-ol (**3k**). Yield 83%; yellowish viscous liquid. IR (NaCl film): 3 392, 2 240, 1 659, 1 598, 1 491, 1 445, 1 193, 1 140, 1 078, 953, 804, 757. ^{1}H NMR (CDCl$_3$): 2.54 (d, 1 H, *J* = 8.6); 4.97 (m, 1 H); 7.28–7.6 (m, 5 H). ^{19}F NMR (CDCl$_3$): –81.5 (s, 3 F); –123.2 (dd, 1 F, *J* = 270, *J* = 8.0); –128.02 (dd, 1 F, *J* = 270, *J* = 13). ^{13}C NMR (CDCl$_3$): 62.7 (t, $J_{C\text{-}C\text{-}F}$ = 26.0, COHCF$_2$CF$_3$); 80.3, 89.4, 113.50 (t of q, *J* = 258, CF$_2$CF$_3$, *J* = 35.5); 120.0 (q of t, *J* = 286.5, CF$_2$CF$_3$, *J* = 35.5); 121.3, 128.9, 130.0, 132.4. MS (EI), *m/z* (species, rel. int.): 250 (M$^+$, 23), 233 (M$^+$ – OH, 35), 131 (M$^+$ – CF$_2$CF$_3$, 100), 114 [M$^+$ – (OH + CF$_2$CF$_3$), 12], 77 (C$_6$H$_5$, 22), 69 (CF$_3$, 2).

General Procedure for Perfluoroalkylation of 4-Phenylbut-3-yn-2-one (**1a**) and Phenylpropynal (**1b**) with Me$_3$SiR$_\mathrm{f}$ (R$_\mathrm{f}$ = n-C$_6$F$_{13}$, n-C$_7$F$_{15}$, n-C$_8$F$_{17}$) (**2e**–**2f**)

Reactions were carried out under similar conditions as reported for **3h**–**3k** except in the present case the reaction mixture was heated at 50 °C for 15 h.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-3-methyl-1-phenylnon-1-yn-3-ol (**3l**). Yield 60%; very light viscous liquid. IR (NaCl film): 3 433, 2 243, 1 491, 1 445, 1 357, 1 238, 1 205, 1 145, 959, 831, 754. ^{1}H NMR (CDCl$_3$): 1.74 (s, 3 H); 2.74 (s, 1 H); 7.19–7.41 (m, 5 H). ^{19}F NMR (CDCl$_3$): –81.35 (t, 3 F, *J* = 9.8); –119.0 to –126.75 (m, 10 F). ^{13}C NMR (CDCl$_3$): 23.9, 77 (t, $J_{C\text{-}C\text{-}F}$ = 30, COHCF$_2$); 85.0, 87.7, 106.2–121 (m); 121.2, 128.4, 129.4, 131.8. MS (CI), *m/z* (species, rel. int.): 465 (M$^+$ + H, 2), 447 (M$^+$ – OH, 58), 145 (M$^+$ – C$_6$F$_{13}$, 100), 129 [M$^+$ – (C$_6$F$_{13}$ + CH$_3$ + H), 23], 43 (CH$_3$CO$^+$, 24). For C$_{16}$H$_9$F$_{13}$O (464.2) calculated: 41.40% C, 1.95% H; found: 41.39% C, 2.22% H.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-phenylnon-1-yn-3-ol (**3m**). Yield 55%; yellowish solid, m.p. 34 °C. IR (KBr film): 3 389, 2 235, 1 666, 1 600, 1 493, 1 446, 1 359, 1 145, 1 070, 894, 755. ^{1}H NMR (CDCl$_3$): 2.66 (d, 1 H, *J* = 8.8); 5.05 (t of d, 1 H, *J* = 8.5, 3.5); 7.28–7.44 (m, 5 H). ^{19}F NMR (CDCl$_3$): –81.35 (t, 3 F, *J* = 8.6); –121.6 to –126.8 (m, 10 F). ^{13}C NMR (CDCl$_3$): 63.2 (t, $J_{C\text{-}C\text{-}F}$ = 27, COHCF$_2$); 80.4, 89.4, 105.0–120 (m); 121.3, 128.8, 129.9, 132.4.

MS (CI), *m/z* (species, rel. int.): 451 (M^+ + H, 1), 450 (M^+, 6), 433 (M^+ – OH, 4), 131 (M^+ – C_6F_{13}, 100), 103 (PhCHCH, 40), 102 (PhCCH, 23), 77 ($C_6H_5^+$, 45), 69 (CF_3^+, 16). For $C_{15}H_7F_{13}O$ (450.2) calculated: 40.02% C, 1.57% H; found: 40.22% C, 1.79% H.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-3-methyl-1-phenyldec-1-yn-3-ol (**3n**). Yield 62%; very light yellowish solid, m.p. 35 °C. IR (KBr film): 3 428, 3 062, 3 009, 2 954, 2 243, 1 953, 1 884, 1 806, 1 757, 1 668, 1 598, 1 492, 1 445, 1 350, 1 245, 1 006, 957, 899, 864, 824, 754. ^{1}H NMR ($CDCl_3$): 1.78 (s, 3 H); 2.66 (s, 1 H); 7.25–7.50 (m, 5 H). ^{19}F NMR ($CDCl_3$): –81.10 (t, 3 F, J = 9.5); –126.48 to –117.26 (m, 12 F). ^{13}C NMR ($CDCl_3$): 24.1, 70.5 (t, $J_{C\text{-}C\text{-}F}$ = 30.16, $COHCF_2$); 84.9, 87.6, 107.0–199.3 (m); 121.4, 128.6, 129.6, 132.1. MS (CI), *m/z* (species, rel. int.): 515 (M^+ + H, 1), 498 (M^+ + H – OH, 8), 497 (M^+ – OH, 41), 178 [M^+ – (C_6F_{13} + OH), 15], 146 (M^+ + H – C_7F_{15}, 14), 145 (M^+ – C_7H_{15}, 100), 129 ($PhCCCO^+$, 23), 69 (CF_3^+, 4), 43 (CH_3CO^+, 47). For $C_{17}H_9F_{15}O$ (514.2) calculated: 39.71% C, 1.76% H; found: 39.78% C, 1.90% H.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Pentadecafluoro-1-phenyldec-1-yn-3-ol (**3o**). Yield 53%; yellowish solid, m.p. 38 °C. IR (KBr film): 3 369, 3 065, 2 932, 2 243, 1 660, 1 600, 1 490, 1 442, 1 351, 1 240, 1 207, 1 135, 1 072, 1 017, 972, 836, 882, 796, 754, 690. ^{1}H NMR ($CDCl_3$): 2.75 (d, 1 H, J = 8.8); 5.09 (m, 1 H); 7.23–7.48 (m, 5 H). ^{19}F NMR ($CDCl_3$): –81.09 (t, 3 F, J = 9.7); –126.4 to –119.2 (m, 12 F). ^{13}C NMR ($CDCl_3$): 63.2 (t, $J_{C\text{-}C\text{-}F}$ = 22.6, $COHCF_2$); 80.4, 89.4, 105–119 (m); 121.3, 128.8, 130.4, 132.4. MS (CI), *m/z* (species, rel. int.): 501 (M^+ + H, 11), 500 (M^+, 3), 483 (M^+ – OH, 14), 182 [M^+ – (C_6F_{13} + H), 4], 181 [M^+ – (C_6F_{13} + 2 H), 3], 164 ($C_6H_5CCCHCF_2^+$, 24), 132 (M^+ + H – C_7F_{15}, 11), 131 (M^+ – C_7F_{15}, 100), 103 ($PhC_2H_2^+$, 31), 102 (PhC_2H^+, 13), 77 ($C_6H_5^+$, 16), 69 (CF_3^+, 4). For $C_{16}H_7F_{15}O$ (500.2) calculated: 38.42% C, 1.41% H; found: 38.47% C, 1.56% H.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-3-methyl-1-phenylundec-1-yn-3-ol (**3p**). Yield 62%; very light yellowish solid, m.p. 33 °C. IR (KBr film): 3 433, 2 243, 1 492, 1 445, 1 351, 1 240, 1 209, 1 150, 958, 892, 754. ^{1}H NMR ($CDCl_3$): 1.73 (s, 3 H); 2.64 (s, 1 H); 7.24–7.41 (m, 5 H). ^{19}F NMR ($CDCl_3$): –81.66 (t, 3 F, J = 11.28); –119.19 to –126.95 (m, 14 F). ^{13}C NMR ($CDCl_3$): 24.1, 70.72 (t, $^2J_{C\text{-}C\text{-}F}$ = 27, $COHCF_2$); 84.9, 87.6, 117–118 (m); 121.6, 128.7, 129.7, 132.2. MS (CI), *m/z* (species, rel. int.): 565 (M^+ + H, 1), 548 (M^+ + H – OH, 5), 547 (M^+ – OH, 23), 146 (M^+ + H – C_8F_{17}, 14), 145 (M^+ – C_8F_{17}, 100), 129 [M^+ – (C_8F_{17} + CH_3 + H), 17], 102 (PhC_2H^+, 2), 69 (CF_3^+, 3), 43 (CH_3CO^+, 31). For $C_{18}H_9F_{17}O$ (564.2) calculated: 38.32% C, 1.61% H; found: 38.41% C, 1.66% H.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1-phenylundec-1-yn-3-ol (**3q**). Yield 58%; white solid, m.p. 43 °C. IR (KBr film): 3 382, 2 212, 1 655, 1 491, 1 445, 1 147, 1 080, 999, 949, 756. ^{1}H NMR ($CDCl_3$): 2.64 (d, 1 H, J = 8.8); 5.05 (t of d, 1 H, J = 8.5, 3.5); 7.20–7.50 (m, 5 H). ^{19}F NMR ($CDCl_3$): –80.98 (t, 3 F, J = 9.8); –119.0 to –126.5 (m, 14 F). ^{13}C NMR ($CDCl_3$): 63.2 (t, $^2J_{C\text{-}C\text{-}F}$ = 30.1, $COHCF_2$); 80.5, 89.4, 105.0–122.0 (m); 121.3, 128.8, 129.1, 132.4. MS (EI), *m/z* (species, rel. int.): 551 (M^+ + H, 24), 164 [M^+ – (OH + C_7F_{15}), 21], 131 (M^+ – C_8F_{17}, 100), 105 ($PhC_2H_4^+$, 34), 104 ($PhC_2H_3^+$, 2), 103 ($PhC_2H_2^+$, 20), 102 (PhC_2H^+, 7), 77 ($C_6H_5^+$, 3), 69 (CF_3^+, 1). For $C_{17}H_7F_{17}O$ (550.2) calculated: 37.11% C, 1.28% H; found: 37.29% C, 1.41% H.

This work was supported by National Science Foundation (Grant No. CHE-9720365) and donors of the American Chemical Society Petroleum Research Fund. We thank Dr A. Blumenfeld for NMR measurements.

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