ELSEVIER

Journal of Fluorine Chemistry 70 (1995) 135–140

JOURNAL OF FLUORINE CHEMISTRY

Titanium-catalyzed addition of perfluoroalkyl iodides to alkenes

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Received 1 February 1994; accepted 18 March 1994

Abstract

Perfluoroalkyl iodides, in the presence of a catalytic amount of Ti^0 generated in situ, add to alkenes in dimethoxyethane solvent to afford 1-(n-perfluoroalkyl)-2-iodoalkanes in moderate to good yields. 1-Alkenes, 1-alkynes and alkenes containing bromo or ester substituents gave yields of the 1:1 addition adducts with n-perfluoroalkyl iodides. 1-Alkenes containing ketone or alcohol groups gave low yields of the 1:1 adduct. Reduction of the 1:1 adducts with Zn/CH_3CO_2H is readily accomplished, and the overall procedure is amenable to a one-flask procedure. With diallyl ether, a tetrahydrofuran derivative was obtained in good yield. The reaction is completely suppressed by *p*-dinitrobenzene and partially suppressed by galvinoxyl. A single electron transfer mechanism is proposed.

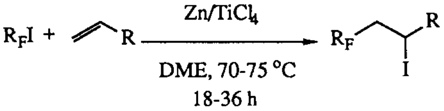
Keywords: Titanium catalyst; Addition reactions; Perfluoroalkyl iodides; Alkenes; NMR spectroscopy; IR spectroscopy; Mass spectrometry

1. Introduction

Introduction of fluorine into an organic molecule often leads to significant changes in biological activity, and organofluorine compounds have been utilized in pharmaceuticals, agrochemicals and as mechanistic probes for biochemical processes [1]. The addition of perfluoroalkyl iodides to unsaturated compounds continues to be among the most useful methods for incorporation of fluorinated groups into organic molecules. This transformation has been initiated by peroxides, heat and irradiation [2], quarternary ammonium salts [3], sodium dithionite [4,5], organophosphines [6], triethyl borane [7] and a variety of metals [8–11]. Reports of low-valent titanium in synthetic organofluorine chemistry are rare, but McMurry [12] and Mukaiyama et al. [13] have demonstrated the utility of low-valent titanium as a reducing agent in dicarbonyl couplings. These prior studies, and the ready availability of inexpensive precursors for the generation of low-valent titanium, prompted us to examine this metal as a catalytic single electron transfer initiator. We describe herein a simple procedure for the perfluoroalkylation of alkenes and alkynes.

2. Results and discussion

Perfluoroalkyl iodides, in the presence of low-valent titanium catalyst generated in situ, add to alkenes and alkynes in dimethoxyethane (DME) solvent to afford 1-(n-perfluoroalkyl)-2-iodoalkanes (Eq. (1)). The scope of this reaction has been explored by varying the perfluoroalkyliodide as well as the structural features of the alkene substrates. These results are summarized in Table 1.



(1)

Good to excellent isolated yields were obtained with $n-C_6F_{13}I$, $n-C_8F_{17}I$ and $n-C_3F_7I$ in combination with simple alkene substrates. A good yield of isomeric vinyl iodide was obtained in the reaction of $n-C_6F_{13}I$ with 1-heptyne, and 1,4-diiodooctafluorobutane adds 2 equiv. of 1-hexene. A minor amount of R_FH by-product and traces of starting material were detected by ^{19}F NMR analysis of the reaction mixtures. A modest yield of adduct was obtained in the reaction of cyclohexene and $n-C_6F_{13}I$. The reaction was tolerant of a halogen and an ester functionality, but low conversions of $n-C_6F_{13}I$ were observed in the reaction with either 5-hexen-2-one or 4-butenol. The reaction of carbonyl

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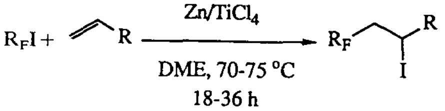
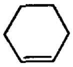
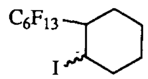
SSDI 0022-1139(94)03102-6

Table 1
Titanium-catalyzed addition of perfluoroalkyl iodides to alkenes and alkynes



Product	R_FI	R (or st. mat.)	Isolated yield (%)
1	n-$C_6F_{13}I$	$(CH_2)_3CH_3$	85
2	n-$C_6F_{13}I$	$(CH_2)_5CH_3$	82
3	n-$C_8F_{17}I$	$(CH_2)_3CH_3$	76
4	n-C_3F_7I	$(CH_2)_3CH_3$	60
5	$I(CF_2)_4I$	$(CH_2)_3CH_3$ (2 equiv.)	50[a]
6	$(CF_3)_2CFI$	$(CH_2)_3CH_3$	10
7	n-$C_6F_{13}I$	$(CH_2)_2CH_2Br$	70
8	n-$C_6F_{13}I$	$(CH_2)_3OC(O)CH_3$	53
9	n-$C_6F_{13}I$	$(CH_2)_2C(O)CH_3$	15[b]
10	n-$C_6F_{13}I$	CH_2CH_2OH	18
11	n-$C_6F_{13}I$	$HC{\equiv}C(CH_2)_4CH_3$	70[c]
12	n-$C_6F_{13}I$		45[d]

[a] Product structure, $CH_3(CH_2)_3CHICH_2(CF_2)_4CH_2CHI(CH_2)_3CH_3$.
[b] Yield determined vs. internal $PhCF_3$ standard.
[c] Product structure, n-$C_6F_{13}CH{=}CHI(CH_2)_4CH_3$ (*E*/*Z* mixture).
[d] Product structure.

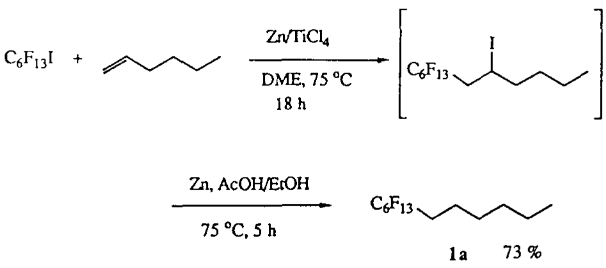


groups and alcohols (pinacols) with low-valent titanium to give reductively coupled products has been extensively studied [12,13] and it seems likely that this competitive process consumes the catalyst in these cases.

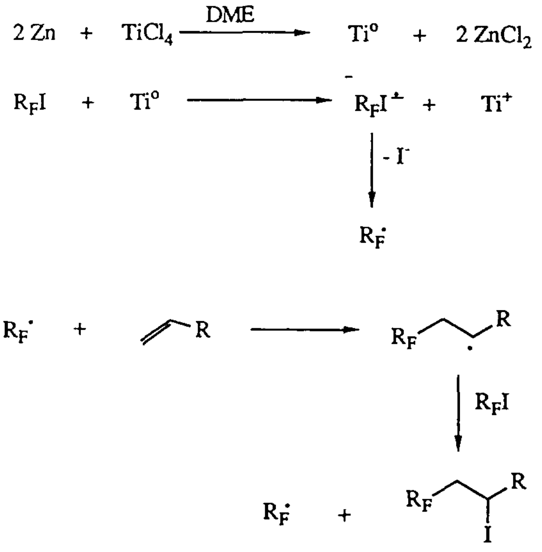
In a typical procedure, acid-washed zinc (2 equiv.) was reacted with $TiCl_4$ in DME solvent. After a brief induction period (20 min), the alkene substrate and perfluoroalkyl iodide were added, and the mixture stirred and heated at 70–75 °C for 18–30 h. The procedure is simple, utilizes inexpensive reagents and avoids the preparation and storage of easily oxidized catalysts. The reaction proceeds similarly in other glyme solvents and THF. In THF the reaction proceeds faster (2–3 h) and at room temperature; however, there is a concomitant increase in R_FH (20%–30%).

Reduction of the iodide can be carried out in a separate reaction or in a convenient one-flask procedure, by simply adding excess zinc, acetic acid and EtOH to the reaction mixture containing the unpurified iodoalkane addition product (Eq. (2)).

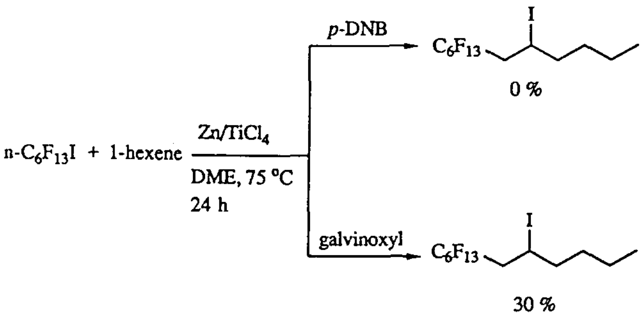
It is proposed that the addition reaction proceeds through a single electron transfer mechanism initiated by titanium (0). Complete inhibition of the reaction by *p*-dinitrobenzene (*p*-DNB), an electron scavenger



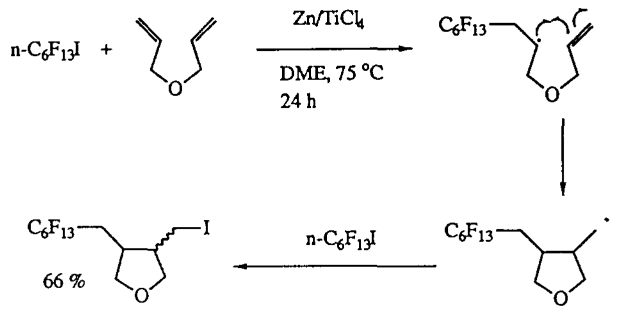
(2)



[14], and partial suppression by galvinoxyl radical is consistent with the proposed mechanism. For example, when n-$C_6F_{13}I$ was reacted with 1-hexene and 20 mol% titanium catalyst, in the presence of *p*-DNB, n-$C_6F_{13}I$ remained and no 1:1 adduct was observed on ^{19}F NMR analysis of the reaction mixture. A similar reaction in the presence of 50 mol% galvinoxyl resulted in only 30% conversion of the starting iodide as determined by ^{19}F NMR analysis.



Cyclization of the 6-hexenyl and 5-hexenyl radicals in the *exo* mode has been shown to be a useful probe for the elucidation of radical mechanisms [11,15]. Diallyl ether underwent cyclization in the presence of n-$C_6F_{13}I$ and catalytic Ti^0 to yield the isomeric (*cis*/*trans* 75:25) tetrahydrofuran derivatives in good yield.



In conclusion, we have demonstrated the utility of catalytic in situ generated low-valent titanium as a single electron transfer initiator in the addition of perfluoroalkyl iodides to unsaturated compounds. The simplicity of the procedure, good yields and the ready availability of inexpensive precursors make this an attractive method for the perfluoroalkylation of unsaturated compounds.

3. Experimental details

3.1. General

All reactions were performed in oven-dried glassware. ^{19}F NMR spectra were recorded on a JEOL FX90Q (83.81 MHz) 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. FT–IR spectra were recorded as CCl_4 solutions using a solution cell with a 0.1-cm path length. GC–MS spectra were obtained at 70 eV in the electron impact mode. GLPC analyses were carried out on a 5% OV-101 column with a thermal conductivity detector.

3.2. Materials

Perfluoroalkyl iodides were obtained from commercial sources and used without further purification. All alkenes, 1-heptyne and $TiCl_4$ were obtained from Aldrich Chemical Co. and used without further purification. Dimethoxyethane was distilled first from CaH_2 and then from Na/benzophenone ketyl. Zinc metal was washed with dilute HCl, dried under vacuum and stored under N_2 prior to use.

3.3. General procedure for the preparation of 1-(n-perfluoroalkyl)-2-iodoalkanes. Preparation of 1-(n-perfluorohexyl)-2-iodoalkane (1)

A 100 ml flask equipped with a septum port, Teflon-coated magnetic stir bar, N_2 tee and cold water condenser, was charged with 0.78 g (12 mmol) of acid-washed zinc and 30 ml of DME. To the stirred mixture was added 1.2 g (6 mmol) of $TiCl_4$ via a syringe. An exothermic reaction followed and the mixture was stirred for 20 min during which time a blue–green mixture resulted. Next, 3.1 g (36 mmol) of 1-hexene and 13.4 g (30 mmol) of n-$C_6F_{13}I$ were added via a syringe. The mixture was heated to an oil bath temperature of 75 °C and stirred for 18 h. For work-up, the mixture was cooled to room temperature, poured into 75 ml of cold water and extracted with Et_2O (3 × 75 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated by rotary evaporation. Reduced pressure distillation through a short-path apparatus gave 13.5 g (85%) of product, b.p. 80–81 °C/2 mmHg; GLPC > 99%. ^{19}F NMR δ: −81.4 (t, 3F, J=9.0 Hz); −112.2 (dm, 1F, J=265 Hz); −115.2 (dm, 1F, J=265 Hz); −122.3 (s, 2F); −123.4 (s, 2F); −124.1 (s, 2F); −126.7 (s, 2F) ppm. ^{1}H NMR δ: 0.9 (t, 3H, J=10.1 Hz); 1.3–1.6 (m, 4H); 1.8 (m, 2H); 2.9–3.1 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: 13.9, 21.4, 21.8, 31.7, 40.1, 41.9 (t, J=21.1 Hz); 105–125 (m, C_6F_{13}–) ppm. GC–MS m/z, % abundance: 403 (M^+ − I, 57.7); 91 (6.0); 83 (5.7); 69 (25.3); 55 (24.3); 47 (14.4); 43 (100.0). FT–IR (cm^{-1}): 2962 (w); 2934 (w); 2863 (w); 1241 (s); 1146 (w).

1-(n-Perfluorohexyl)-2-iodooctane (2)

In a similar manner, compound **2** was prepared from 0.78 g (12 mmol) of Zn, 30 ml of DME, 1.2 g (6 mmol) of $TiCl_4$, 4.0 g (36 mmol) of 1-octene and 13.4 g (30 mmol) of n-$C_6F_{13}I$ at 75 °C for 18 h. The purified product, 13.7 g (82%), was isolated by distillation, b.p. 112 °C/5 mmHg; GLPC 98% ^{19}F NMR δ: −81.3 (t, 3F, J=9.5 Hz); −107.0 (m, 1F); −117.3 (m, 1F); −121.5 (s, 2F); −122.6 (s, 2F); −123.0 (s, 2F); −126.1 (s, 2F) ppm. ^{1}H NMR δ: 0.9 (t, 3H, J=10.0 Hz); 1.2–1.6 (m, 6H); 1.8 (m, 2H); 2.7–3.0 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: 14.0, 20.7, 22.7, 28.4, 29.8, 31.8, 40.7, 42.2 (t, J=21.0 Hz); 105–125 (m, C_6F_{13}–) ppm. GC–MS m/z, % abundance; 431 (M^+ − I, 9.9); 389 (31.6); 71 (15.2); 69 (30.3); 57 (87.8); 55 (45.7); 43 (100.0); 41 (64.6). FT–IR (cm^{-1}): 2960 (w); 2930 (w); 2875 (w); 1239 (s); 1146 (w).

1-(n-Perfluorooctyl)-2-iodohexane (3)

In a similar manner, compound **3** was prepared from 0.4 g (6 mmol) of Zn, 30 ml of DME, 0.6 g (3 mmol) of $TiCl_4$, 1.5 g (17 mmol) of 1-hexene and 8.2 g (1 mmol) of n-$C_8F_{17}I$ at 75 °C for 24 h. The purifie product, 7.2 g (76%), was isolated by distillation, b.p 108 °C/5 mmHg; GLPC > 99%. ^{19}F NMR δ: −81.4 (t 3F, J=10.2 Hz); −112.2 (dm, 1F, J=283 Hz); −115. (dm, 1F, J=283 Hz); −122.0 (s, 2F); −122.4 (bs, 4F) −123.2 (s, 2F); −124.1 (s, 2F); −126.6 (s, 2F) ppm ^{1}H NMR δ: 0.9 (t, 3H, J=7.1 Hz); 1.3–1.5 (m, 4H 1.8 (m, 2H); 2.7–3.0 (m, 2H); 4.3 (m, 1H) ppm. ^{13}

NMR δ: 13.7, 20.7, 21.6, 31.7, 40.1 (d, $J=5.0$ Hz); 41.8 (t, $J=21.1$ Hz); 105–125 (m, $C_8F_{17}-$) ppm. GC–MS *m/z* % abundance: 503 (M^+-I, 19.6); 169 (3.5); 91 (5.6); 77 (6.3); 69 (31.3); 59 (8.6); 55 (24.0); 43 (100.0). FT–IR (cm^{-1}) 2960 (w); 2962 (w); 2932 (w); 2863 (w); 1240 (s); 1216 (s); 1147 (m); 748 (w).

1-(n-Perfluoropropyl)-2-iodohexane (4)

In a similar manner, compound **4** was prepared from 0.65 g (10 mmol) of Zn, 30 ml of DME, 0.95 g (5 mmol) of $TiCl_4$, 2.5 g (30 mmol) of 1-hexene and 7.4 g (25 mmol) of n-C_3F_7I at 70 °C for 30 h. A cold-finger/isopropyl alcohol condenser (−50 °C) was employed to prevent loss of n-C_3F_7I. The purified product, 5.7 g (60%), was isolated by distillation, b.p. 48 °C/2 mmHg; GLPC > 99%. ^{19}F NMR δ: −80.9 (t, 3F, $J=9.2$ Hz); −113.2 (dm, 1F, $J=271$ Hz); −116.3 (dm, 1F, $J=271$ Hz); −128.4 (s, 2F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=7.1$ Hz); 1.3–1.6 (m, 4H); 1.9 (m, 2H); 2.8–3.1 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: 13.9, 20.7, 21.8, 31.8, 40.2, 41.6 (t, $J=20.8$ Hz) 110–125 (m, C_3F_7-) ppm.

1-(n-Perfluoroisopropyl)-2-iodohexane (6)

In a similar manner, compound **6** was prepared from 0.5 g (7.5 mmol) of Zn, 25 ml of DME, 0.75 g (3.8 mmol) of $TiCl_4$, 2.3 g (27.5 mmol) of 1-hexene and 3.8 g (25 mmol) of $(CF_3)_2CFI$ at 70 °C for 30 h. A cold-finger/isopropyl alcohol condenser (−50 °C) was employed to prevent loss of $(CF_3)_2CFI$. The purified product, 0.95 g (10%), was isolated by distillation, b.p. 40 °C/0.1 mmHg: GLPC > 99%. ^{19}F NMR δ: −76.0 (q, 3F, $J=9$ Hz); −76.5 (q, 3F, $J=9$ Hz); −186.0 (bs, 1F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=10.0$ Hz); 1.2–1.6 (m, 4H); 1.7–1.9 (m, 2H); 2.8–3.0 (m, 2H); 4.3 (m, 1H) ppm. ^{13}C NMR δ: 13.8, 21.7, 22.9, 31.9, 39.8 (d, $J=18.3$ Hz); 41.3 (d, $J=8.0$ Hz); 92.0 (doublet of septets, $J=211.0$, 30.2 Hz); 120.5 (qd, $J=287.0$, 37.0 Hz); 121.0 (qd, $J=286.9$, 37.0 Hz) ppm. GC–MS *m/z* % abundance: 253 (M^+-I, 100.0); 77 (10.2); 69 (20.1); 65 (11.4); 55 (32.4); 43 (89.5); 42 (20.7); 41 (65.8). FT–IR (cm^{-1}) 2962 (w); 2933 (w); 2863 (w); 1288 (w); 1241 (s); 1150 (w).

1-(n-Perfluorohexyl)-2-iodo-5-bromopentane (7)

In a similar manner, compound **7** was prepared from 0.4 g (6 mmol) of Zn, 20 ml of DME, 0.6 g (3 mmol) of $TiCl_4$, 2.5 g (16.5 mmol) of 5-bromo-1-pentene and 6.7 g (15 mmol) of n-$C_6F_{13}I$ at 75 °C for 24 h. The purified product, 6.2 g (70%), was isolated by distillation, b.p. 72 °C/0.05 mmHg; GLPC > 99%. ^{19}F NMR δ: −81.1 (t, 3F, $J=9.0$ Hz); −111.8 (dm, 1F, $J=271$ Hz); −114.9 (dm, 1F, $J=271$ Hz); −122.0 (s, 2F); −123.1 (s, 2F); −124.2 (s, 2F); −126.7 (s, 2F) ppm. ^1H NMR δ: 1.9–2.3 (m, 4H); 2.7–3.1 (m, 2H); 3.5 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: 18.9, 31.2, 32.9, 38.9, 41.9 (t, $J=20.9$ Hz); 105–125 (m, $C_6F_{13}-$) ppm. GC–MS *m/z* % abundance: 470 (M^+-I, 12.6); 468 (M^+-I, 13.5); 388 (57.3); 367 (12.8); 109 (19.8); 107 (21.8); 73 (100.0); 69 (43.0). FT–IR (cm^{-1}): 2964 (w); 2932 (w); 1351 (w); 1240 (s); 1147 (w).

3.4. Preparation of 5,12-diiodo-(7,8,9,10-perfluoro)-decahexane (5)

In a similar manner, compound **5** was prepared from 0.4 g (6 mmol) of Zn, 30 ml of DME, 0.6 g (3 mmol) of $TiCl_4$, 2.8 g (33 mmol) of 1-hexene and 6.5 g (14.3 mmol) of 1,4-diiodooctafluorobutane at 75 °C for 18 h. The purified product, 4.5 g (50%), was isolated by distillation, b.p. 135 °C/0.2 mmHg; GLPC > 99%. ^{19}F NMR δ: −112.3 (dm, 2F, $J=265$ Hz); −115.3 (dm, 2F, $J=265$ Hz); −124.0 (bs, 4F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=7.1$ Hz); 1.3–1.6 (m, 4H); 1.8–1.9 (m, 2H); 2.6–3.0 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: 13.8, 21.3, 21.6, 31.6, 40.1, 41.8 (t, $J=21.2$ Hz) 110–125 (m, $-\delta_2\delta_2\delta_2\delta_2$) ppm. GC–MS *m/z* % abundance: 495 (M^+-I, 2.5); 367 (34.0); 325 (6.8); 77 (6.0); 69 (30.8); 61 (11.3); 57 (14.0); 55 (24.7). FT–IR (cm^{-1}): 2962 (m); 2934 (m); 2863 (w); 1460 (w); 1216 (m); 1172 (s); 1127 (m).

3.5. Preparation of 5-(n-perfluorohexyl)-4-iodo-pentyl acetate (8)

In a similar manner, compound **8** was prepared from 0.4 g (6 mmol) of Zn, 30 ml of DME, 0.6 g (3 mmol) of $TiCl_4$, 2.3 g (18 mmol) of 4-pentenyl acetate and 6.7 g (15 mmol) of n-$C_6F_{13}I$ at 70 °C for 20 h. The purified product, 3.5 g (53%), was isolated by distillation, b.p. 84–86 °C/0.5 mmHg; GLPC 97%. ^{19}F NMR δ: −81.0 (t, 3F); −113.0 (bs, 2F); −121.6 (s, 2F); −122.8 (s, 2F); −123.3 (s, 2F); −126.2 (s, 2F) ppm. ^1H NMR δ: 2.1 (s, 3H); 1.8–1.9 (m, 4H); 2.7–3.0 (m, 2H); 4.1 (m, 2H); 4.4 (m, 1H) ppm. GC–MS *m/z* % abundance: 447 (0.1); 387 (0.3); 127 (0.3); 73 (100.0); 69 (0.5); 61 (0.4).

*3.6. Reaction of n-$C_6F_{13}I$ and 5-hexen-2-one, Preparation of the 1:1 adduct **9***

In a similar manner to the above, the reaction was carried out using 0.13 g (2 mmol) of Zn, 10 ml of DME, 0.19 g (1 mmol) of $TiCl_4$, 0.6 g (6 mmol) of 5-hexen-2-one and 2.2 g (5 mmol) of n-$C_6F_{13}I$ at 75 °C for 24 h. ^{19}F NMR analysis of the reaction mixture indicated a 15% yield of the 1:1 adduct ***9***.

3.7. Preparation of 1-(n-perfluorohexyl)-2-iodo-4-butanol (10)

Similarly, compound **10** was prepared from 1.3 g (20 mmol) of Zn, 50 ml of DME, 1.9 g (10 mmol) of $TiCl_4$, 4.3 g (60 mmol) of 1-buten-4-ol and 22.3 g (50 mmol) of n-$C_6F_{13}I$ at 75 °C for 24 h. The product, 4.4 g (18%), was purified by silica gel chromatography (CH_2Cl_2) and obtained as a white, waxy solid, m.p. 48 °C. ^{19}F NMR δ: -81.4 (t, 3F, $J=10.2$ Hz); -112.9 (dm, 1F, $J=257$ Hz); -114.7 (dm, 1F, $J=257$ Hz); -122.2 (bs, 2F); -123.3 (bs, 2F); -124.1 (bs, 2F); -126.7 (bs, 2F) ppm. ^1H NMR δ: 2.1 (m, 3H); 2.7–3.2 (m, 2H); 3.7–3.9 (m, 2H); 4.5 (m, 1H) ppm. ^{13}C NMR δ: 16.6, 42.0 (t, $J=20.7$ Hz); 42.4, 62.5, 105–125 (m, $C_6F_{13}-$) ppm. GC–MS *m/z* % abundance: 391 (M^+-I, 0.1); 109 (21.0); 95 (35); 85 (44); 69 (73); 57 (71); 43 (77); 40 (100.0). FT–IR (cm^{-1}): 3639 (w); 2927 (w); 1239 (s); 1200 (m); 1120 (m); 1105 (w); 1050 (w).

3.8. Preparation of 1-(n-perfluorohexyl)-2-iodo-1-heptene (11)

Similarly, compound **11** was prepared from 0.4 g (6 mmol) of Zn, 20 ml of DME, 0.6 g (3 mmol) of $TiCl_4$, 1.7 g (16.5 mmol) of 1-heptyne and 6.7 g (14.9 mmol) of n-$C_6F_{13}I$ at 75 °C for 24 h. The purified product, 5.7 g (70%), was isolated by distillation as a 80:20 isomeric mixture, b.p. 56–57 °C/0.2 mmHg; GLPC 96%. ^{19}F NMR δ: -81.5 (t, 3F, $J=10.2$ Hz); -105.8 (q, 1.6F, $J=13.3$ Hz); -108.9 (q, 0.4F, $J=13.3$ Hz); -122.1 (bs, 2F); -123.3 (bs, 2F); -123.7 (m, 2F); -126.6 (m, 2F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=6.7$ Hz); 1.3 (m, 4H); 1.6 (m, 2H); 2.7 (t, 2H, $J=7.3$ Hz); 6.3 (t, 1H, $J=14.5$ Hz) ppm. ^{13}C NMR δ: major isomer: 13.75, 22.4, 30.6, 29.8, 41.2 (t, $J=2.8$ Hz); 123.0 (t, $J=5.9$ Hz); 126.6 (t, $J=23.8$ Hz) ppm. GC–MS *m/z* % abundance: 487 (4.1); 416 (4.5); 313 (5.5); 139 (8.8); 103 (18.5); 77 (12.7); 69 (22.9); 57 (18.4); 55 (100.0). FT–IR (cm^{-1}): 2961 (w); 2933 (w); 2862 (w); 1633 (w); 1238 (s); 1146 (w).

3.9 Preparation of 1-(n-perfluorohexyl)-2-iodocyclohexane (12)

Similarly, compound **12** was prepared from 1.6 g (24 mmol) of Zn, 60 ml of DME, 2.4 g (12 mmol) of $TiCl_4$, 7.4 g (90 mmol) of cyclohexene and 22.3 g (50 mmol) of n-$C_6F_{13}I$ at 75 °C for 24 h. The purified product, 12.1 g (45%), was isolated by distillation as a 60:40 isomeric mixture, b.p. 150 °C/20 mmHg; GLPC 94%. ^{19}F NMR δ: -81.5 (t, 3F, $J=8.9$ Hz); -110 (m, 0.5F); -118 (bs, 1F); -121 (m, 1F); -123 (m, 5.5F); -126.7 (bs. 2F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=10.0$ Hz); 1.2–1.6 (m, 6H); 1.8 (m, 2H); 2.7–3.0 (m, 2H); 4.4 (m, 1H) ppm. ^{13}C NMR δ: major isomer: 22.1, 22.7, 25.2, 27.3 (tm, $J=4.6$ Hz); 37.5, 44.7 (t, $J=20.4$ Hz); 110–120 (m, $C_6F_{13}-$) ppm. ^{13}C NMR δ: minor isomer: 21.4, 21.9, 22.8, 25.1 (m); 34.8, 45.2 (t, $J=19.4$); 110–125 (m, $C_6F_{13}-$) ppm. GC–MS *m/z* % abundance: 401 (M^+-I, 93.1); 381 (52.2); 361 (10.8); 131 (42.9); 127 (20.0); 119 (20.5); 81 (79.3); 59 (25.2); 41 (100). FT–IR (cm^{-1}): 2946 (w); 2861 (w); 1239 (s); 1205 (w); 1147 (w).

3.10. Reaction of n-$C_6F_{13}I$ and diallyl ether. Preparation of the tetrahydrofuran derivative 13

Similarly, the tetrahydrofuran derivative **13** was prepared from 0.26 g (4 mmol) of Zn, 25 ml of DME, 0.38 g (2 mmol) of $TiCl_4$, 1.2 g (12 mmol) of diallyl ether and 4.46 g (10 mmol) of n-$C_6F_{13}I$ at 70 °C for 36 h. The purified product, 3.6 g (66%), was isolated by silica gel chromatography (EtOAc) and obtained as a solid mixture of *cis* and *trans* isomers in a 3:1 ratio, m.p. 58 °C. ^{13}C NMR data for the isomers were in agreement with the literature data [3].

3.11. One-flask preparation of 1-(n-perfluorohexyl)-hexane (1a)

Preparation of 1-(n-perfluorohexyl)-2-iodohexane (**1**) was carried out as previously described using 0.53 g (8 mmol) of Zn, 20 ml of DME, 0.8 g (4 mmol) of $TiCl_4$, 2.5 g (30 mmol) of 1-hexene and 8.9 g (20 mmol) of n-$C_6F_{13}I$. After refluxing the mixture at 75 °C for 18 h, 1.0 g of Zn, 0.5 ml of acetic acid and 3 ml of EtOH were added to the reaction mixture. The resultant mixture was stirred at 75 °C for an additional 5 h and then cooled to room temperature. For work-up, the mixture was poured into 75 ml of cold water and extracted with Et_2O (3×75 ml). The combined extracts were dried ($MgSO_4$), filtered and concentrated by rotary evaporation. The purified product, 5.9 g (73%), was isolated by distillation, b.p. 94 °C/25 mmHg; GLPC 92%. ^{19}F NMR δ: -81.0 (t, 3F, $J=9.0$ Hz); -112.9 (bs, 2F); -121.7 (s, 2F); -122.8 (s, 2F); -123.3 (s, 2F); -126.3 (s, 2F) ppm. ^1H NMR δ: 0.9 (t, 3H, $J=10.0$ Hz); 1.2–1.5 (m, 6H); 1.6 (m, 2H); 2.0 (m, 2H) ppm. ^{13}C NMR δ: 14.0, 20.3, 22.6, 29.0, 31.1 (t, $J=22.2$ Hz); 31.6, 110–125 ($m-C_6F_{13}$) ppm. GC–MS *m/z* % abundance; 389 (M^+-CH_3, 1.8); 374 (5.3); 355 (5.4); 69 (23.0); 57 (77.9); 55 (29.6); 43 (100.0); 41 (33.3). FT–IR (cm^{-1}) 2960 (w); 2930 (w); 2860 (w); 1242 (s); 1146 (w).

Acknowledgement

We thank the National Science Foundation for support of this work.

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