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A Facile Perfluoroallylation of Olefins

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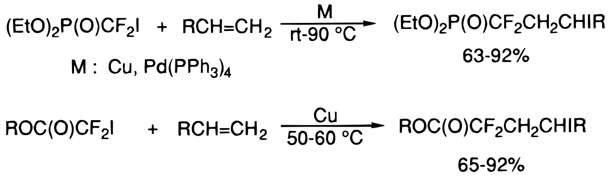
The addition of *F*-allyl iodide to terminal alkenes is induced by a catalytic amount of copper powder in the absence of solvent at room temperature to 50 °C to give the corresponding 1:1 adducts in good yields. A variety of functional groups such as trimethylsilyl, alkyl, epoxy, ester, hydroxyl, bromo, ether, and phosphonate are tolerated in the addition reaction. This reaction also worked well with internal olefins such as cyclohexene, cyclopentene, and 4-octene. Reaction with dienes gives the corresponding linear adduct and cyclization adduct depending on the chain length of the dienes. With 1,7-octadiene, a bis(perfluoroallyl) product is formed, while a tetrahydrofuran derivative is obtained with diallyl ether. Reduction of the adducts with zinc in the presence of nickel dichloride in moist THF or zinc in moist DMF affords the perfluoroallyl derivatives. The adduct reacts with zinc in DMF to form a zinc reagent which couples with organic electrophiles in the presence of CuBr.

Introduction

Organofluorine compounds and their synthesis have attracted much attention in the fields of biologically active compounds and materials science.[1] Although perfluoroalkylation of organic molecules has been extensively investigated with perfluoroalkyl iodides,[2] few reports of perfluoroallylation have been documented. Recently, Burton and co-workers generated perfluoroallylcadmium reagents from *F*-allyl iodide and cadmium.[3] Metathesis of this cadmium reagent with cuprous halide at low temperature gave the perfluoroallylcopper reagent. These cadmium or copper reagents reacted readily with allyl halides to form fluorinated dienes, but they did not react with less reactive organic halides due to low thermal stability. More recently, success achieved in the addition of iododifluoroacetates[4] and iododifluoromethylphosphonate[5] to functionalized alkenes initiated by metals prompted us to examine the metal-initiated addition of *F*-allyl iodide to alkenes as a general route to perfluoroallylated products.

In a preliminary report,[6] we briefly described the addition of *F*-allyl iodide to alkenes in the presence of copper and the reduction of the adduct products with Zn/NiCl$_2$·6H$_2$O. This methodology provides a convenient approach to perfluoroallyl compounds in good yields. We now report the detailed methodology as well as a new method for iodide reduction. We also report the formation of a zinc reagent from the addition product and its reaction with electrophiles.



Results and Discussion

Addition of *F*-Allyl Iodide to Olefins. Addition of perfluoroalkyl iodide to olefins can be readily achieved by initiation with a variety of metals or metal complexes.[2e−k] Among the metals, copper has been the most widely used due to its low cost, reasonable reactivity, and ease of purification of the final products.[2m] We found that *F*-allyl iodide reacted readily with terminal alkenes in the presence of a catalytic amount of copper powder, at room temperature to 50 °C to give the corresponding adducts in good yields as shown in Scheme 1. Although the reaction could be carried out in solvent, the absence of solvent greatly simplified isolation and purification of the products. A variety of functionalized groups including bromo, trimethylsilyl, ester, epoxy, phenoxy, hydroxyl, and phosphonate are tolerated under the reaction conditions. For example, the addition of *F*-allyl iodide to 1-hexene in the presence of Cu(0) at 50 °C in 4 h produced 1,1,2,3,3-pentafluoro-5-iodo-1-nonene (**1**) in 80% isolated yield. Similarly, reaction of *F*-allyl iodide with 4-penten-1-yl acetate, 1,2-epoxy-5-hexene, and diethyl allylphosphonate gives 6,6,7,8,8-pentafluoro-4-iodo-7-octen-1-yl acetate (**13**), 7,7,8,9,9-pentafluoro-1,2-epoxy-5-iodo-8-nonene (**15**), and diethyl 4,4,5,6,6-pentafluoro-2-iodo-5-hexenylphosphonate (**14**) in 82%, 79%, and 79% yield, respectively. All examples of the addition reactions

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(1) (a) Hudlicky, M. *Chemistry of Organofluorine Compounds*, 2nd ed.; Ellis, Horwood: Chichester, England, 1976. (b) Welch, J. T. *Tetrahedron* **1987**, *43*, 3123.

(2) Addition of perfluoroalkyl iodides to alkenes initiated by heating, photolysis, radical initiators, and metals: (a) Low, H. C.; Tedder, J. M.; Walton, J. C. *J. Chem. Soc. Faraday Trans. 1* **1976**, *72*, 1300. (b) Brace, N. O.; Van Elswyk, J. E. *J. Org Chem.* **1976**, *41*, 766. (c) Tordeux, M.; Wakselman, C. *Tetrahedron* **1981**, *37*, 315. (d) Baum, K.; Bedford, C. D.; Hunadi, R. J. *J. Org. Chem.* **1982**, *47*, 2251. (e) Chen, Q. Y.; Yang, Z. Y. *J. Chem. Soc., Chem. Commun.* **1986**, 498. (f) Chen, Q. Y.; Yang, Z. Y. *J. Fluorine Chem.* **1985**, *28*, 399. (g) Chen, Q. Y.; Yang, Z. Y. *Acta Chim. Sin.* **1986**, *44*, 265. (h) Von Werner, K. *J. Fluorine Chem.* **1985**, *28*, 299. (i) Fuchikami, T.; Ojima, I. *Tetrahedron Lett.* **1984**, *25*, 303. (j) Chen, Q. Y.; Yang, Z. Y.; Zhao, C. X.; Qiu, Z. M. *J. Chem. Soc. Perkin Trans. 1* **1988**, 563. (k) Chen, Q. Y.; Yang, Z. Y.; Qiu, Z. M. *Kexue Tongbao* **1987**, 593. (l) Lu, X.; Ma, S.; Zhu, J. *Tetrahedron Lett.* **1988**, *29*, 5129. (m) Chen, Q. Y.; Yang, Z. Y. *J. Fluorine Chem.* **1985**, *28*, 399.

(3) Burton, D. J.; Tarumi, Y.; Heinze, P. L. *J. Fluorine Chem.* **1990**, *50*, 257.

(4) (a) Yang, Z. Y.; Burton, D. J. *J. Fluorine Chem.* **1989**, *45*, 435. (b) Yang, Z. Y.; Burton, D. J. *J. Org. Chem.* **1991**, *56*, 5125.

(5) Yang, Z. Y.; Burton, D. J. *Tetrahedron Lett.* **1991**, *32*, 1019.

(6) Yang, Z. Y.; Nguyen, B. V.; Burton, D. J. *Synlett* **1992**, *2*, 141.

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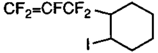
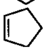
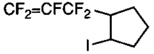
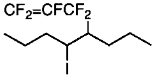
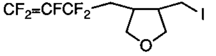
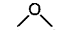
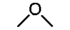
Table 1. Perfluoroallylation of Alkenes

$$CF_2{=}CFCF_2I + CH_2{=}CHR \xrightarrow[\text{rt-50 °C}]{\text{Cu}} CF_2{=}CFCF_2CH_2CHIR$$

Entry*	Alkenes	Product*	Yield%[a]
1	$CH_2{=}CH(CH_2)_3CH_3$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_3CH_3$	80
2	$CH_2{=}CH(CH_2)_4CH_3$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_4CH_3$	67
3	$CH_2{=}CH(CH_2)_{11}CH_3$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_{11}CH_3$	89
4	$CH_2{=}CH(CH_2)_4CH{=}CH_2$	$(CF_2{=}CFCF_2CH_2CHICH_2CH_2)_2$	70
5	$CH_2{=}CHCH_2C_6H_5$	$CF_2{=}CFCF_2CH_2CHICH_2C_6H_5$	73
6	$CH_2{=}CH(CH_2)_5CH_2Br$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_5CH_2Br$	80
7			47-73
8			69
9			65
10	$(CH_2{=}CHCH_2)_2O$		55
11	$CH_2{=}CHSiMe_3$	$CF_2{=}CFCF_2CH_2CHISiMe_3$	78
12	$CH_2{=}CHCH_2OAc$	$CF_2{=}CFCF_2CH_2CHICH_2OAc$	54
13	$CH_2{=}CH(CH_2)_3OAc$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_3OAc$	82
14	$CH_2{=}CHCH_2PO(OEt)_2$	$CF_2{=}CFCF_2CH_2CHICH_2PO(OEt)_2$	79
15	 $CH_2{=}CH(CH_2)_2\overset{O}{CH{-}CH_2}$	 $CF_2{=}CFCF_2CH_2CHI(CH_2)_2\overset{O}{CH{-}CH_2}$	79
16	$CH_2{=}CHCH_2OC_6H_5$	$CF_2{=}CFCF_2CH_2CHICH_2OC_6H_5$	78
17	$CH_2{=}CHCH_2OH$	$CF_2{=}CFCF_2CH_2CHICH_2OH$	80
18	$CH_2{=}CH(CH_2)_2CH(OH)CH_2OH$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_2CH(OH)CH_2OH$	90
19	$CH_2{=}CH(CH_2)_4CH(OH)CH_2OH$	$CF_2{=}CFCF_2CH_2CHI(CH_2)_4CH(OH)CH_2OH$	87

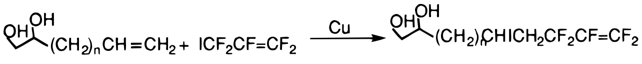
* The entry number is the product number. [a] Isolated yields are based on alkenes.

Scheme 1

$$H_2C{=}CHR + CF_2{=}CFCF_2I \xrightarrow[\substack{\text{rt-50°C}\\ \text{4-7 hrs}}]{\text{Cu(0)}} CF_2{=}CFCF_2CH_2CHIR \quad \text{47-90\%}$$

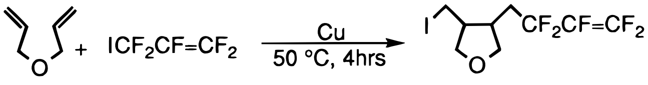
are summarized in Table 1. However, with styrene, *F*-allyl iodide only gave polymers under similar conditions. In all cases no 1,5-perfluorohexadiene, via Wurtz coupling, was detected. Copper powder, freshly prepared via reaction of copper(II) sulfate and zinc in water, exhibits higher reactivity than aged copper powder. The reaction of *F*-allyl iodide and terminal alkenes occurs at room temperature with freshly prepared copper (entries 4 and 18). However, the reaction required heating to 50 °C to initiate the reaction with aged copper powder.

Alcohols usually react with perfluoroolefins, particularly in the presence of base. However, *F*-allyl iodide smoothly added to olefins containing hydroxy groups in the presence of copper. No side reactions, such as reaction of the hydroxy group with *F*-allyl iodide or the addition product, were observed. For example, when neat 5-hexen-1,2-diol was treated with *F*-allyl iodide in the presence of copper at room temperature, the addition adduct (**18**) was isolated in 90% yield by silica gel chromatography. ^{19}F NMR spectroscopy indicated that the adduct was a mixture of diastereomers. Similarly, 7-octen-1,2-diol gave the addition adduct (**19**) in 87% isolated yield.



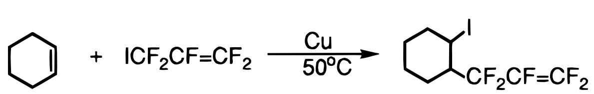
n = 2 (**18**) 90%
n = 4 (**19**) 87%

Addition of *F*-allyl iodide to dienes affords linear bis-adducts or cyclized adducts, depending on the chain length of the dienes. When 1,7-octadiene reacted with 2.1 equiv of *F*-allyl iodide and copper powder at 50 °C, the bis-adduct was isolated in 70% yield. On the other hand, reaction of *F*-allyl iodide with diallyl ether and copper under the same conditions afforded the cyclization product **10** in 55% yield, which indicated that radical intermediates are most likely involved in the addition reaction. With divinyl ether, the reaction occurs rapidly and exothermically at room temperature and produces polymers which were not structurally characterized.



55% **10**

Copper powder also initiated the addition of *F*-allyl iodide to internal olefins such as 4-octene, cyclohexene, and cyclopentene. Upon reaction of *F*-allyl iodide with 1 equiv of cyclohexene in the presence of 33 mol % of copper powder at 50 °C, the addition adduct **7** was obtained in 73% yield as a 1:2 mixture of cis and trans isomers as characterized by ^{19}F NMR and GC−MS analysis.



7

Reduction of the Adducts. Organic iodides have been reduced by numerous methods including transition-metal catalysts[7] and mixtures of metal hydrides and metal salts, such as $CoCl_2$,[8] $NiCl_2$,[9] CuCl,[10] $CeCl_3$,[11] $RhCl_3$,[12] $TiCl_3$,[13] and Zn/acid.[14] These reagents not only reduce the carbon−halogen bond, they are also capable of reducing other functionalities. Radical dehalogenation with tributyltin hydrides[15] gives high yields and excellent selectivity. However, traces of tributyltin iodide are often difficult to remove from the reduced product.[16] Recently we reported that $NiCl_2{\cdot}6H_2O$/Zn could reduce α,α-difluoro-γ-iodo esters[4] and 1,1-difluoro-3-iodoalkylphosphonates[5] to the corresponding α,α-difluoro esters and 1,1-difluoro phosphonates in good yields.

$$R'CHICH_2CF_2CO_2R \xrightarrow[\text{THF, rt}]{\text{Zn/NiCl}_2\cdot 6H_2O} R'CH_2CH_2CF_2CO_2R \quad \text{71-88\%}$$

$$RCHICH_2CF_2PO(OEt)_2 \xrightarrow[\text{THF, rt}]{\text{Zn/NiCl}_2\cdot 6H_2O} RCH_2CH_2CF_2PO(OEt)_2 \quad \text{52-84\%}$$

When the adducts were treated with $Zn/NiCl_2{\cdot}6H_2O$ in moist THF, reaction occurs rapidly and exothermically

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(7) Pinder, A. R. *Synthesis* **1980**, 425.

(8) (a) Satoh, T.; Suzuki, S.; Suzuki, Y.; Miyaji, Y.; Imai, Z. *Tetrahedron Lett.* **1969**, 4555. (b) Chung, S. K.; Han, G. *Synth. Commun.* **1982**, *12*, 903.

(9) (a) Lin, S. T.; Roth, J. A. *J. Org. Chem.* **1979**, *44*, 309. (b) Back, T. G.; Birass, V. I.; Edwards, V. I.; Krishna, M. V. *J. Org. Chem.* **1988**, *53*, 3815.

(10) Narisada, M.; Horibe, I.; Watanabe, F.; Takeda, K. *J. Org. Chem.* **1989**, *54*, 5308.

(11) (a) Luche, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 2226. (b) Rucker, G.; Horster, H.; Gajewski, W. *Synth. Commun.* **1980**, *10*, 623.

(12) Nishiki, M.; Miyataka, H.; Niino, Y.; Mitsuo, N.; Satoh, T. *Tetrahedron Lett.* **1982**, *23*, 193.

(13) Ashby, E. C.; Lin, J. J. *J. Org. Chem.* **1978**, *43*, 1263.

(14) Levene, P. A. *Organic Syntheses;* Wiley: New York, 1943; Collect. Vol. 2, p 320.

(15) Newmam, W. P. *Synthesis* **1987**, 665.

(16) Yang, Z. Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 4676.

Scheme 2

$$CF_2{=}CFCF_2CH_2CHIR \xrightarrow[\text{THF}]{\text{Zn/NiCl}_2\cdot 6H_2O} F_2C{=}CFCF_2CH_2CH_2R$$

$$F_2C{=}CFCF_2CH{=}CHR'$$

Scheme 3

$$CF_2{=}CFCF_2CH_2CHICH_2R \xrightarrow[H_2O/DMF]{\text{Zn}} CF_2{=}CFCF_2CH_2CH_2CH_2R$$

to produce reduced products with a significant amount of dehydroiodination products (10−20%), as shown in Scheme 2. Separation of these two products by simple distillation was difficult. The formation of the dehydroiodination product is probably due to β-hydride elimination from an intermediate nickel complex, particularly at elevated temperature. Fortunately, the elimination side reaction could be minimized by addition of Et_2O to the reaction mixture and careful control of the reaction temperature at 25 °C. When the adduct was treated with $Zn/NiCl_2\cdot 6H_2O$ in moist THF/ether at 25 °C, the reduction product was isolated in 92% yield without detectable amounts of the elimination product. Although the exact mechanism of the effect of ether is not clear, the ether probably plays two roles in the nickel-catalyzed reaction. First, ether may reduce the rate of oxidative addition of the adducts to nickel due to its lower polarity than THF. Second, ether may also inhibit reductive elimination of the nickel complex intermediate. In fact, the reduction reaction in THF/ether proceeded much more smoothly than that in THF, and no exothermic reaction occurred in THF/ether.

Since group VIII metals usually cause β-hydride elimination from alkyl halides, the formation of the elimination product could be avoided if the adducts were reacted with zinc in the absence of nickel under appropriate conditions. In fact, Knochel investigated the reaction of alkyl halides with zinc to make the corresponding zinc reagents without formation of the elimination product.[17] We found that the adduct was readily reduced by treatment with zinc in moist DMF at room temperature as illustrated in Scheme 3. The reaction was conveniently monitored by ^{19}F NMR. The AB quartet of multiplets around −100.5 ppm (J_{F-F} = 275.0 Hz), the ^{19}F signal for the CF_2 adjacent to the CH_2, became a multiplet at ca. −102.0 ppm when the reaction was complete. Although the reduction of an adduct with zinc in moist DMF occurs slower than with $Zn/NiCl_2\cdot 6H_2O$ in THF, no elimination product was detected. Various functional groups were tolerated under the reduction conditions as shown in Table 2.

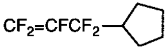
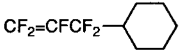
However, β-elimination occurred upon reduction of an adduct containing a leaving group in the β-position of the iodide. For example, adduct **16** gave a 37% yield of the reduction product **26a** and a 23% yield of the elimination product **26b**.

$$\underset{\textbf{16}}{CF_2{=}CFCF_2CH_2CHICH_2OC_6H_5} \xrightarrow[H_2O,\ rt]{Zn\ /\ DMF} \underset{\textbf{26a}\ (37\%)}{CF_2{=}CFCF_2(CH_2)_2CH_2OC_6H_5}$$

$$\underset{\textbf{26b}\ (23\%)}{CF_2{=}CFCF_2CH_2CH{=}CH_2}$$

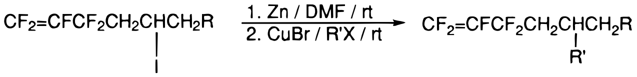
Table 2. Reduction of Addition Products

$$CF_2{=}CFCF_2CH_2CHIR \xrightarrow[\text{or Zn / DMF / }H_2O\text{ / rt}]{\text{Zn /NiCl}_2\cdot 6H_2O \quad \text{THF / }H_2O\text{ / rt}} CF_2{=}CFCF_2CH_2CH_2R$$

Entry*	Adduct	Product*	Yield %[a]
20	3	$CF_2{=}CFCF_2(CH_2)_{13}CH_3$	73[c]
21	8		60[c]
22	7		58[c]
23	5	$CF_2{=}CFCF_2(CH_2)_3C_6H_5$	92[b]
24	6	$CF_2{=}CFCF_2(CH_2)_7CH_2Br$	74[c]
25	11	$CF_2{=}CFCF_2(CH_2)_2SiMe_3$	64[c]
26a	16	$CF_2{=}CFCF_2(CH_2)_3OC_6H_5$	37[c]
26b		$CF_2{=}CFCF_2CH_2CH{=}CH_2$	23
27	18	$CF_2{=}CFCF_2(CH_2)_4CH(OH)CH_2OH$	81[b]

* The entry number is the product number. [a] Isolated yields are based on the 1:1 addition product. [b] $Zn/NiCl_2\cdot 6H_2O$ in moist THF/ether was used as the reducing reagent. [c] $Zn/DMF/H_2O$ was used as the reducing reagent.

Scheme 4



$$CF_2{=}CFCF_2CH_2\underset{I}{C}HCH_2R \xrightarrow[\text{2. CuBr / R'X / rt}]{\text{1. Zn / DMF / rt}} CF_2{=}CFCF_2CH_2\underset{R'}{C}HCH_2R$$

28,29

	28	29
R	$(CH_2)_3CH_3$	C_6H_5
R'X	$C_6H_5C(O)Cl$	$CH_2{=}CHCH_2Cl$
Yield	80%	69%

Zinc Reagents from the Adducts. Reduction of an adduct with zinc in moist DMF involves hydrolysis of an organozinc intermediate. Knochel reported that alkyl zinc reagents underwent metathesis with CuCN to form intermediate copper−zinc reagents which react with organic electrophiles to produce cross-coupled products. If the zinc reagent was formed when the adduct reacted with zinc in DMF, it would react with electrophiles in the presence of CuBr. We found that the adduct could couple with electrophiles on treatment with zinc and CuBr. For example, upon reaction of the adduct with acid-washed Zn in dry DMF at room temperature for 15 min, the adduct was completely consumed, as determined by ^{19}F NMR analysis. After addition of CuBr and electrophiles, such as benzoyl chloride or allyl halide, the resulting mixture was stirred at room temperature for 2 h to give high yields of the coupled products as illustrated in Scheme 4.

Conclusion

The addition of F-allyl iodide to alkenes is initiated by copper metal under mild conditions to give high yields of the corresponding addition products. Reaction with dienes give the corresponding linear adduct or cyclization adduct depending on the chain length of the diene. With 1,7-octadiene, a bis(perfluoroallyl) product is formed, while a tetrahydrofuran derivative is obtained with diallyl ether. Reduction of the adducts with zinc in the presence of nickel dichloride in moist THF or with zinc in moist DMF affords the perfluoroallyl derivatives. We also found that the adduct reacts with zinc in DMF to form a zinc reagent which couples with organic electrophiles in the presence of CuBr. The mild reaction conditions, readily available starting materials and catalysts, and simple procedure provides a convenient and

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(17) (a) Knochel, P.; Yeh, M. C. P.; Berk, S. C.; Talbert, J. *J. Org. Chem.* **1988**, *53*, 2390. (b) Berk, S. C.; Knochel, P.; Yeh, M. C. P. *J. Org. Chem.* **1988**, *53*, 5789.

practical method for the preparation of interesting and important compounds.

Experimental Section

General Materials. *F*-allyl iodide[19] and copper[20] were prepared according to literature methods. All alkenes were purchased from Aldrich Chemical Co. All reactions were monitored by ^{19}F NMR analysis of the reaction mixtures on a 90-MHz spectrometer. The ^{1}H, ^{19}F, and ^{13}C NMR spectra of final products were obtained on a 300-MHz spectrometer (CDCl$_3$, CFCl$_3$, or TMS internal references). FT-IR were recorded as CCl$_4$ solutions in a 0.1 cm path length cell. Low-resolution mass spectra analyses were performed at 70 eV in the electron-impact mode on a single quadrapole instrument interfaced to a gas chromatograph fitted with an OV-101 column. High-resolution mass spectra analyses were performed by the University of Iowa High Resolution Mass Spectroscopy Facility at 70 eV in the electron impact mode. GLPC analysis were performed on a 5% OV-101 column and thermal conductivity detector.

Preparation of 1,1,2,3,3-Pentafluoro-5-iodo-1-nonene (1). In a typical experimental procedure, a 50-mL, two-necked, round-bottomed flask, equipped with a septum, a Teflon-coated magnetic stir-bar, and a water condenser topped with an argon inlet, was charged with 8.9 g (30 mmol) of *F*-allyl iodide, 3.4 g (40 mmol) of 1-hexene, and 0.6 g (10 mmol) of copper. The reaction mixture was stirred at 50 °C under an argon atmosphere for 4 h. The volatile components were removed under reduced pressure, and the residue was introduced into a silica gel column and eluted with hexane to give 9.1 g (80%) of **1**: GLPC purity >99%; ^{19}F NMR (δ) −94.5 (dd, J = 61.6, 36.2 Hz, 1F), −100.9 (AB qm, J = 274.5 Hz, 2F), −108.7 (ddt, J = 115.3, 59.5, 28.6 Hz, 1F), −186.7 (ddt, J = 115.1, 35.9, 14.5 Hz, 1F); ^{1}H NMR (δ) 4.2 (m, 1H), 3.0−2.7 (m, 2H), 1.8−1.7 (m, 2H), 1.6−1.3 (m, 4H), 0.9 (t, J = 7.1 Hz, 3H); ^{13}C NMR (δ) 153.9 (tdm, J = 291.0, 42.0 Hz), 124.4 (ddtd, J = 237.4, 43.4, 36.1, 20.3 Hz), 117.2 (tdm, J = 244.8, 29.3 Hz), 45.7 (t, J = 24.7 Hz), 40.3 (s), 31.6 (s), 22.1 (s), 21.7 (s), 13.6 (s); FT-IR (cm^{-1}) 1785.7 (s); GC−MS (*m/z*) 342 (M$^+$, 1.8), 215 (0.6), 195 (32.5), 175 (26.1), 167 (11.8), 155 (21.3), 153 (18.0), 149 (8.2), 139 (55.3), 131 (100.0), 127 (39.1), 121 (9.4), 113 (9.6), 109 (11.7), 95 (11.5).

Preparation of 1,1,2,3,3-Pentafluoro-5-iodo-6-phenoxy-1-hexene (16). Similarly, **16** was prepared from 6.5 g (25 mmol) of *F*-allyl iodide, 2.7 g (20 mmol) of allyl phenyl ether, and 0.4 g (6 mmol) of Cu at 50 °C. Usual workup gave 6.2 g (78%) of **16**: GLPC purity >99%; ^{19}F NMR (δ) −94.0 (ddm, J = 60.8, 35.9 Hz, 1F), −101.1 (AB qm, J = 273.4 Hz, 2F), −108.2 (ddt, J = 116.9, 59.0, 28.8 Hz, 1F), −186.7 (ddt, J = 115.2, 35.9, 15.5 Hz, 1F); ^{1}H NMR (δ) 7.3 (m. 2H), 7.0 (m, 1H), 6.9 (m, 2H), 4.4 (m, 1H), 4.2 (dm, J = 5.1 Hz, 2H), 3.2−2.7 (m, 2H); ^{13}C NMR (δ) 157.7 (s), 153.7 (tdm, J = 289.8, 41.8 Hz), 129.5 (s), 124.1 (ddtd, J = 238.0, 43.7, 35.8, 19.8 Hz), 121.6 (s), 116.9 (tdt, J = 244.4, 29.2, 4.5 Hz), 114.8 (s), 72.6 (s), 41.3 (t, J = 25.2 Hz), 14.8 (s); FT-IR (cm^{-1}) 1786.2 (s); GC−MS (*m/z*) 392 (M$^+$, 11.3), 393 (M$^+$ + 1, 1.4), 299 (1.3), 279 (1.9), 235 (4.0), 220 (33.9), 173 (7.1), 171 (23.5), 152 (15.6), 131 (22.3), 108 (9.5), 94 (100.0), 93 (80.4), 77 (33.4), 65 (57.0); HRMS calcd for C$_{12}$H$_{10}$OF$_5$I 391.9696, obsd 391.9679.

Preparation of 1,1,2,3,3-Pentafluoro-1-heptadecene (20). A two-necked, round-bottom flask, equipped with an argon inlet, a Teflon-coated stir-bar, and a septum port, was charged with 0.6 g (10 mmol) of Zn, 10 mL of DMF, 0.5 mL of water, and 2.3 g (5 mmol) of **3**. The reaction mixture was stirred at room temperature for 1 h. Then the reaction mixture was introduced onto a silica gel column and eluted with hexane. After removal of the solvent, 1.2 g (73%) of **20** was obtained: GLPC purity 95%; ^{19}F NMR (δ) −96.3 (dd, J = 65.1, 35.9 Hz, 1F), −101.9 (m, 2F), −110.2 (ddt, J = 114.9, 65.3, 27.2 Hz, 1F), −187.6 (ddt, J = 114.9, 36.0, 14.1 Hz, 1F); ^{1}H NMR (δ) 2.0 (m, 2H), 1.5−1.3 (m, 24H), 0.9 (t, J = 6.7 Hz, 3H); ^{13}C NMR (δ) 154.3 (tdm, J = 290.0, 42.7 Hz), 125.4 (ddtd, J = 238.1, 43.9, 36.6, 19.5 Hz), 118.5 (tdt, J = 241.5, 28.9, 4.2 Hz), 35.2 (t, J = 24.5 Hz), 32.4 (s), 30.1 (s), 30.0 (s), 29.8 (s), 29.7 (s), 29.6 (s), 29.5 (s), 23.1 (s), 21.0 (t, J = 3.6 Hz), 14.2 (s); FT-IR (cm^{-1}) 1785.7 (m); GC−MS (*m/z*) 258 (M$^+$ − C$_5$H$_{10}$, 0.4), 257 (0.6), 244 (1.0), 243 (1.4), 229 (1.8), 228 (2.5), 216 (2.8), 21.5 (3.9), 202 (4.1), 131 (5.7), 111 (4.7), 97 (12.8), 84 (23.0), 70 (45.6), 57 (100.0).

Preparation of 1,1,2,3,3-Pentafluoro-6-phenyl-1-hexene (23). Similarly, **23** was prepared from 3.8 g (10 mmol) of **5**, 0.6 g (10 mmol) of zinc, 0.1 g (0.4 mmol) of NiCl$_2$·6H$_2$O, in 10 mL THF, 10 mL of Et$_2$O, and 0.5 mL of water at room temperature. Usual workup gave 2.3 g (92%) of **23**: GLPC purity >99%; ^{19}F NMR (δ) −96.0 (ddm, J = 64.2, 36.0 Hz, 1F), −101.9 (m, 2F), −109.8 (ddt, J = 115.2, 64.0, 26.8 Hz, 1F), −187.7 (ddt, J = 115.0, 36.0, 14.2 Hz, 1F); ^{1}H NMR (δ) 7.3 (m, 2H), 7.2 (m, 3H), 2.7 (t, J = 7.6 Hz, 2H), 2.0−2.2 (m, 2H), 1.8−1.9 (m, 2H); ^{13}C NMR (δ) 154.6 (tdm, J = 291.1, 42.1 Hz), 141.5 (s), 129.1 (s), 128.9 (s), 126.8 (s), 125.7 (ddtd, J = 238.6, 44.0, 36.4, 19.5 Hz), 118.8 (tdt, J = 214.6, 29.0, 4.2 Hz), 35.5 (s), 34.7 (t, J = 24.6 Hz), 23.8 (t, J = 3.8 Hz); FT-IR (cm^{-1}) 1785.5 (s); GC−MS (*m/z*) 251 (M$^+$ + 1, 1.5), 250 (12.4), 230 (0.2), 199 (0.2), 131 (2.5), 117 (35.7), 103 (3.0), 91 (100.0), 77 (5.7); HRMS calcd for C$_{12}$H$_{11}$F$_5$ 250.0781, obsd 250.0778.

Preparation of 1,1,2,3,3-Pentafluoro-6-phenoxy-1-hexene (26a). Similarly, **26** was prepared from 1.9 g (5 mmol) of **16**, 0.6 g (10 mmol) of zinc in 10 mL of DMF, and 0.5 mL of water at room temperature. Usual workup gave 0.5 g (37%) of **26**: GLPC purity 93%; ^{19}F NMR (δ) −95.6 (dd, J = 63.7, 36.3 Hz, 1F), −102.2 (m, 2F), −109.5 (ddt, J = 115.7, 63.6, 26.1 Hz, 1F), −187.7 (ddt, J = 115.1, 36.1, 13.7 Hz, 1F); ^{1}H NMR (δ) 7.3 (m, 2H), 7.0−6.9 (m, 3H), 4.0 (t, J = 6.0 Hz, 2H), 2.4−2.2 (m, 2H), 2.1−2.0 (m, 2H). ^{13}C NMR (δ) 158.8 (s), 154.2 (tdm, J = 290.4, 41.8 Hz), 129.5 (s), 125.0 (ddtd, J = 238.2, 44.0, 36.7, 19.8 Hz), 120.9 (s), 118.1 (tdt, J = 241.5, 28.4, 4.6 Hz), 114.1 (s), 66.2 (s), 31.7 (t, J = 24.9 Hz), 21.7 (t, J = 4.0 Hz); FT-IR (cm^{-1}) 1772.7 (s); GC−MS (*m/z*) 266 (M$^+$, 23.9), 267 (M$^+$ + 1, 3.0), 173 (0.2), 153 (1.5), 145 (0.5), 131 (8.9), 94 (100.0), 77 (11.5), 65 (11.2); HRMS calcd for C$_{12}$H$_{11}$F$_5$O 266.0730, obsd 266.0720.

1,1,2,3,3-Pentafluoro-1,5-hexadiene (26b). The yield of **26b** was 0.2 g (23%): GLPC purity >99%, bp 55 °C; ^{19}F NMR (δ) −96.2 (ddm, J = 63.8, 36.1 Hz, 1F), −101.7 (m, 2F), −109.9 (ddt, J = 114.8, 64.2, 27.4 Hz, 1F), −188.0 (ddt, J = 114.8, 36.7, 14.0 Hz, 1F); ^{1}H NMR (δ) 5.8−5.7 (m, 1H), 5.3 (m, 2H), 2.8 (td, J = 15.7, 7.0 Hz, 2H); ^{13}C NMR (δ) 154.4 (tdm, J = 290.0, 42.6 Hz), 127.2 (t, J = 5.3 Hz), 125.1 (dm, J = 250.0 Hz), 122.2 (s), 117.4 (tdm, J = 242.8, 29.1 Hz), 39.8 (t, J = 25.6 Hz); FT-IR (cm^{-1}) 1786.4 (s); GC−MS (*m/z*) 172 (M$^+$, 0.6), 157 (0.5), 152 (2.5), 144 (1.1), 139 (1.3), 131 (100.0), 103 (59.4).

Preparation of 1,1,2,3,3-pentafluoro-5-benzoyl-1-decene (28). A dry, 50-mL, two-necked, round-bottomed flask, equipped with an argon inlet, a Teflon-coated stir-bar, and septum, was charged with 1.3 g (3.5 mmol) of **2**, 0.3 g (5 mmol) of acid-washed Zn, and 10 mL of dry DMF. After stirring for 15 min at room temperature, **2** had been completely consumed, as determined by ^{19}F NMR analysis. To the flask was added 0.7 g (5 mmol) of CuBr and 1.0 g (7 mmol) of benzoyl chloride, and the reaction mixture was stirred at room temperature for 2 h. The reaction mixture was introduced onto a silica gel column and eluted with hexane/CH$_2$Cl$_2$ (6/4) to give 0.95 g (80%) of **28**: ^{19}F NMR (δ) −95.4 (ddm, J = 63.1, 35.9 Hz, 1F), −100.9 (AB qm, J = 271.6 Hz, 2F), −108.9 (ddt, J = 115.1, 62.7, 26.6 Hz, 1F), −187.1 (ddt, J = 115.7, 36.1, 14.5 Hz, 1F); ^{1}H NMR (δ) 7.9 (m, 2H), 7.6 (m, 1H), 7.5 (m, 2H), 3.8 (m, 1H), 3.0−2.9 (m, 1H), 2.3−2.1 (m, 1H), 1.8−1.5 (m, 2H), 1.3−1.2 (m, 6H), 0.8 (m, 3H); ^{13}C NMR (δ) 201.2 (s), 153.5 (tdm, J = 290.7, 42.4 Hz), 136.5 (s), 133.0 (s), 128.6 (s), 128.1 (s), 124.8 (ddtd, J = 238.2, 43.9, 36.5, 19.5 Hz), 117.4 (tdt, J = 242.4, 28.8, 4.5 Hz), 38.9 (s), 36.0 (t, J = 24.3 Hz), 33.4 (s), 31.5 (s), 26.5 (s), 22.2 (s), 13.5 (s); FT-IR (cm^{-1}) 1766.9 (s); GC−MS (*m/z*) 334 (M$^+$, 1.3), 315 (0.1), 294 (1.5), 264 (5.5), 133 (2.7),

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[18] Yang, Z. Y.; Burton, D. J. *J. Org. Chem.* **1992**, *57*, 5144.

[19] Miller, W. T., Jr.; Fainberg, A. H. *J. Am. Chem. Soc.* **1957**, *79*, 4164.

[20] Brewster, R. Q.; Groening, T. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 446.

131 (1.1), 105 (100.0), 77 (23.9); HRMS calcd for $C_{17}H_{19}F_5O$ 334.1356, obsd 334.1351.

Preparation of 1,1,2,3,3-Pentafluoro-5-benzyl-1,7-octadiene (29). Similarly, **29** was prepared from 1.9 g (5 mmol) of **5**, 0.6 g (10 mmol) of Zn, 10 mL of DMF, 1.0 g (7 mmol) of CuBr, and 0.8 g (10 mmol) of allyl chloride at room temperature for 2 h. Usual workup gave 1.0 g of **29** (69%); ^{19}F NMR (δ) −96.0 (ddm, J = 64.6, 36.3 Hz, 1F), −99.9 (m, 2F), −109.6 (ddt, J = 115.0, 64.1, 27.7 Hz, 1F), −186.6 (ddt, J = 115.0, 35.9, 14.3 Hz, 1F); ^{1}H NMR (δ) 7.3−7.1 (m, 5H), 5.8−5.7 (m, 1H), 5.1−5.0 (m, 2H), 2.7−2.6 (m, 2H), 2.1−2.0 (m, 5H); ^{13}C NMR (δ) 153.7 (tdm, J = 311.7, 42.6 Hz), 139.7 (s), 135.3 (s), 129.3 (s), 128.4 (s), 126.3 (s), 125.2 (ddtd, J = 246.4, 43.8, 36.6, 19.5 Hz), 118.5 (tdm, J = 242.9, 28.5 Hz), 117.7 (s), 40.3 (s), 37.7 (s), 37.2 (t, J = 23.7 Hz), 33.9 (s); FT-IR (cm^{-1}) 1298.2(s); GC−MS (m/z) 290 (M$^+$, 1.9), 275 (6.3), 248 (20.6), 209 (2.0), 171 (9.1), 131 (3.6), 117 (25.5), 91 (100.0), 77 (3.8), 65 (9.5); HRMS calcd for $C_{15}H_{15}F_5$ 290.1094, obsd 290.1098.

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Supporting Information Available: ^{13}C NMR spectra for all compounds and experimental data for compounds **2**−**15**, **17**−**19**, **21**, **22**, **24**, **25**, and **27** (38 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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