Reaction of Perfluoroalkanesulfinates with Allyl and Propargyl Halides. A Convenient Synthesis of 3-(Perfluoroalkyl)prop-1-enes and 3-(Perfluoroalkyl)allenes

Chang-Ming Hu,* Feng-Ling Qing, and Wei-Yuan Huang

Shanghai Institute of Organic Chemistry, Academia Sinica, 345 Lingling Lu, Shanghai 200032, China

Received June 5, 1990

The reaction of perfluoroalkanesulfinates, RrCF₂SO₂Na, with allyl and propargyl halides, in the presence of (NH4)2S2O8, gave 3-(perfluoroalkyl)prop-1-enes (RCH2CH=CH2) and 3-(perfluoroalkyl)allenes (RCH=C=CH2), respectively, in good yield. Evidence is presented for a radical addition-elimination mechanism for the reaction. The reaction represents a synthetically viable and convenient route to such compounds.

Introduction

The development of methods for the introduction of perfluoroalkyl groups into organic molecules is the object of active and continuing research.¹ Both 3-(perfluoroalkyl)prop-1-enes $(R_f CH_2 CH=CH_2)$ and 3-(perfluoroalkyl)allenes ($R_fCH=C=CH_2$), with reactive $CH_2CH=C$ - H_2 or CH=C=CH₂ groups, are useful building blocks for organofluorine systems. Therefore, it is of value to develop a convenient synthesis of such compounds.

Usually, 3-(perfluoroalkyl)prop-1-enes are prepared by the reaction of perfluoroalkyl metallic reagents with allyl halides²⁻⁴ (eqs 1 and 2) or by the reaction of perfluoroalkyl iodides with allyltrimethylsilane (eq 3).^{5,6}

$$R_{f}X + RCH = CHCH_{2}Br \xrightarrow{Zn/Pd(II)}$$

X = I, Br $R_{f}(R)CHCH = CH_{2}$ (1)

$$(\text{RO})_{2}\text{P(O)CF}_{2}\text{MBr} + \text{XCH}_{2}\text{C(R)} = \text{CH}_{2} \xrightarrow{\text{CuBr}} M = \text{Cd}, \text{Zn} \qquad X = \text{Br}, \text{Cl} \\ (\text{RO})_{2}\text{P(O)CF}_{2}\text{CH}_{2}\text{CR} = \text{CH}_{2} (2)$$

$$R_{f}\text{I} + \text{CH}_{2} = \text{CHCH}_{2}\text{SiMe}_{3} \xrightarrow{\text{Fe}_{3}(\text{CO})_{12}}_{\text{or Cu}} R_{f}\text{CH}_{2}\text{CH} = \text{CH}_{2} (3)$$

However, (perfluoroalkyl)allenes, R_rCH=C=CH₂, have never been isolated from reaction mixtures containing perfluoroalkyl metallic reagents and propargyl halides because, in some cases, the reaction mixtures decomposed violently on attempted distillation.^{3,4,7}

We now report that perfluoroalkanesulfinates react smoothly with allyl or propargyl halides, in the presence of an oxidant, to yield 3-(perfluoroalkyl)prop-1-enes or 3-(perfluoroalkyl)allenes, respectively, in good yield. The reaction constitutes a synthetically viable and convenient route to these compounds.

Results and Discussion

Perfluoroalkanesulfinates ($R_f CF_2 SO_2 Na$) are readily available by sulfinate-dehalogenation of perfluoroalkyl halides ($R_f X$, X = I, Br, CCl₃).⁸⁻¹¹

- (5) Fuchikami, T.; Ojima, I. Tetrahedron Lett. 1984, 25, 307.
 (6) Yang, Z.-Y. Ph.D. Dissertation, Shanghai Institute of Organic Chemistry, 1986.
 - (7) Coe, P. L.; Milner, N. E. J. Organomet. Chem. 1974, 70, 147.

Table I. Reaction of 1a with Allyl Bromide in the Presence of an Oxidant

. . . .

$$Cl(CF_2)_8OCF_2CF_2SO_2Na + CH_2 = CHCH_2Br \xrightarrow{\text{oxidant}} 1a$$

$$Cl(CF_2)_8OCF_2CF_2CF_2CH_2CH = CH_2 + Cl(CF_2)_8OCF_2COOH$$
2a
3a

		product composition,ª %	
entry no.	oxidant	2a	3a
1	UV, 0, ^b	55	45
2	$(NH_4)_2S_2O_8^c$	90	10
3	$Ce(SO_4)_2^c$	60	40

^a The product composition was estimated by ¹⁹F NMR. ^b The reaction mixture, in a quartz reaction tube, was irradiated at room temperature for 5 h with a 500-W high-pressure mercury lamp. Air was bubbled through the reaction mixture during irradiation. ^c An equimolar mixture of 1a, allyl bromide, and either $(NH_4)_2S_2O_8$ or $Ce(SO_4)_2$, in DMF, was stirred at 40 °C for 4 h.

Because sulfinates are well-known electron donors,¹²⁻¹⁴ a suitable electron acceptor (oxidant) should initiate electron transfer from R_fCF₂SO₂Na to generate R_fCF₂SO₂• and, subsequently, $R_f CF_2$ radicals (eq 4). That such an

$$R_{f}CF_{2}SO_{2}^{-} + Ox \rightarrow R_{f}CF_{2}SO_{2}^{*} + Ox^{*}$$
$$R_{f}CF_{2}SO_{2}^{*} \rightarrow R_{f}CF_{2}^{*} + SO_{2}$$
(4)

assumption is reasonable was supported by the observation that the photooxidation of RrCF2SO2Na gave the corresponding perfluorocarboxylic acid.¹⁵ The intermediate

$$R_{f}CF_{2}SO_{2}Na \xrightarrow{UV \text{ light}} R_{f}CF_{2} \rightarrow R_{f}COOH$$

 $R_{f}CF_{2}$ radical could be trapped by t-BuNO and was identified from the EPR spectrum of the nitroxide radical so formed.¹⁶

- (8) Huang, W.-Y.; Huang, B.-N.; Hu, C.-M. J. Fluorine Chem. 1983. 23, 193.
- (9) Huang, W.-Y.; Huang, B.-N.; Wang, Y. Acta Chim. Sin. 1983, 41, 1193.
- (10) Huang, B.-N.; Wang, B.-H.; Wang, W.; Huang, W.-Y. Acta Chim. Sin. 1985, 43, 1167. (11) Huang, W.-Y.; Huang, B.-N.; Chen, J. L. Acta Chim. Sin. 1984,
- 42, 1114.
- (12) Huang, W.-Y.; Chen, J.-L. Acta Chim. Sin. 1988, 46, 669.
 (13) Huang, W.-Y.; Hu, L.-Q.; Xie, Y. Acta Chim. Sin. (Engl. Ed.)
- 1989, 190.
 (14) Feiring, A. E. J. Org. Chem. 1985, 50, 3269.
 (15) Hu, C.-M.; Xu, Z.-Q.; Huang, W.-Y. J. Fluorine Chem. 1989, 42, 145.
- (16) Hu, C.-M.; Xu, Z.-Q.; Qing, F.-L. Tetrahedron Lett. 1989, 30, 7617.

^{(1) (}a) Knunyants, I. L.; Yakobson, G. G. Synthesis of Fluoroorganic Compounds; Springer: Berlin, 1985. (b) Gerstenberger, M. R. C.; Haas, A. Angew. Chem., Int. Ed. Engl. 1981, 20, 647. (c) Welch, J. T. Tetrahedron 1987, 43, 3123. (d) Rozen, S. Acc. Chem. Res. 1988, 21, 307.

Kitazume, T.; Ishikama, N. J. Am. Chem. Soc. 1985, 107, 5186.
 Burton, D. J.; Sprague, L. G. J. Org. Chem. 1989, 54, 613.
 Chambers, R. D.; Jaouhari, R.; Ohagan, D. J. Fluorine Chem. 1989,

^{44, 275.}





From these observations, it was hypothesized that the reaction of $R_f CF_2 SO_2 Na$ and an oxidant, in the presence of allyl or propargyl halides, would lead to perfluoroalkylation of the halides by way of a perfluoroalkyl radical. In fact, $Cl(CF_2)_8OCF_2CF_2SO_2Na$ (1a) did react readily with allyl bromides, in the presence of an oxidant, to give Cl- $(CF_2)_8OCF_2CF_2CH_2CH=CH_2$. The results are summarized in Table I.

Because it was obvious from Table I that $(NH_4)_2S_2O_8$ was an effective oxidant for initiating the perfluoroalkylation of allyl bromide, $(NH_4)_2S_2O_8$ was adopted as the oxidant of choice for the reaction of $R_f CF_2 SO_2 Na$ with allyl and propargyl halides.

Synthesis of 3-(Perfluoroalkyl)prop-1-enes. Perfluoroalkanesulfinates reacted readily with allyl halides, in the presence of $(NH_4)_2S_2O_8$, to give 3-(perfluoroalkyl)prop-1-enes. The byproducts were perfluoroalkanecarboxylic acids 3. Some $Cl(CF_2)_2Br$ (4c) was also formed in one case (Table II, entry 4). The results are summarized in Table II.

No 3-(perfluoroalkyl)prop-1-yl halide, the product of addition of perfluoroalkyl radical to the carbon-carbon double bond of the allyl halide, was formed in these reactions. Allyl bromide gave higher product yields than allyl chloride.

A perfluoroalkanedisulfinate also reacted readily with allyl bromide, to form 2i. In contrast, allyl acetate and

$$(CF_{2})_{8}(SO_{2}Na)_{2} + CH_{2} = CHCH_{2}Br \xrightarrow{(NH_{4})_{2}S_{2}O_{8}}{DMF, 40 \circ C}$$

$$(CF_{2})_{8}(CH_{2}CH = CH_{2})_{2} + (CF_{2})_{6}(COOH)_{2}$$

$$2i, 55\% \qquad 3i, 17\%$$

$$CF_{3}(CF_{2})_{5}SO_{2}Na + CH_{2} = CHCH_{2}Y \xrightarrow{(NH_{4})_{2}S_{2}O_{8}}{DMF, 40 \circ C}$$

$$1g \qquad Y = CH_{3}COO \\ Y = (CH_{3})_{3}Si$$

$$CF_{3}(CF_{2})_{5}CH_{2}CH_{2}CH_{2}Y + CF_{3}(CF_{2})_{4}COOH$$

5, Y = CH₃COO, 63% 3g, 24%
6, Y = (CH₃)_{3}Si, 74% 3g, 13%

allyltrimethylsilane reacted with 1g to yield only the addition products 5 and 6.

Synthesis of 3-(Perfluoroalkyl)allenes. Propargyl halides reacted readily with 1, in the presence of (N- $H_4)_2S_2O_8$, to yield the allenes 7c-h (Table III). The main byproduct was the corresponding perfluoroalkanecarboxylic acid 3.

The fluorinated allenes so obtained could be isolated by distillation. Possible alkyne byproducts could not be detected. The composition of 7 was determined by mass spectrometry and elemental analysis. the ¹H NMR spectra showed the presence of olefinic protons and the absence of acetylenic protons. The infrared spectra showed strong

Table II. Synthesis of 3-(Perfluoroalkyl)prop-1-enes

 $\begin{array}{c} R_{f}CF_{2}SO_{2}Na + CH_{2} = CHCH_{2}X \xrightarrow{(NH_{2})_{2}S_{2}O_{6}} \\ 1 \\ R_{f}CF_{2}CH_{2}CH = CH_{2} + R_{f}COOH + R_{f}CF_{2}Br \\ 4 \end{array}$

	4			J	-
<u> </u>			products (isolated,yields, %)		
entry no.	$R_{f}CF_{2}$	Х	2	3	4
1	Cl(CF ₂) ₈ OCF ₂ CF ₂ (1a)	Br	2a (75)	3a (10)	
2	$Cl(CF_2)_8OCF_2CF_2$ (1a)	Cl	2a (34)	3a (16)	
3	CF_3CCl_2 (1b)	Br	2b (46)	3b (33)	
4	$Cl(CF_2)_2$ (1c)	Br	2c (53)	3c (14)	4c (22)
5	$Cl(CF_2)_4$ (1d)	Br	2d (62)	3d (10)	
6	$Cl(CF_{2})_{4}$ (1d)	Cl	2d (28)	3d (15)	
7	$Cl(CF_2)_6$ (1e)	Br	2e (65)	3e (18)	
8	$Cl(CF_2)_6$ (1e)	Cl	2e (40)	3e (16)	
9	$CF_{3}(CF_{2})_{3}$ (1f)	Br	2f (72)	3f (10)	
10	$CF_{3}(CF_{2})_{5}$ (1g)	Br	2g (67)	3g (12)	
11	$CF_3(CF_2)_7$ (1h)	Br	2h (74)	3h (15)	
12	$CF_{3}(CF_{2})_{7}$ (1h)	Cl	2h (32)	3h (17)	

Table III. Synthesis of 3-(Perfluoroalkyl)allenes

D CE SO No + CH-C	(NH4)2S2O8		
$r_{1} Cr_{2} SO_{2} Na + C \Pi = C$	Br Cl DMF, 40 °C		
\mathbf{I} $\mathbf{X} = \mathbf{I}$	RCF.CH=C=CH.	+ R.COOH	+ R.CF.Br
	7	3	4

entry no.	R _f CF ₂	X	products	(isolated	yields, %)
1	$ClCF_2CF_2$ (1c)	Br	7c (32)	3c (12)	4c (30)
2	$Cl(CF_2)_4$ (1d)	Br	7d (46)	3d (20)	
3	$Cl(CF_2)_4$ (1d)	Cl	73 (27)	3d (30)	
4	$Cl(CF_2)_6$ (1e)	Br	7e (47)	3e (15)	
5	$CF_3(CF_2)_3$ (1f)	Br	7f (42)	3f (10)	
6	$CF_3(CF_2)_5$ (1g)	Br	7g (54)	3g (17)	
7	$CF_3(CF_2)_7$ (1h)	Br	7h (50)	3h (25)	

absorptions at 1955 and 1975 cm⁻¹, characteristic of allenes. Compound li also reacted readily with propargyl bromide to yield 7i. It was noteworthy that $R_f CF_2 H$, which

$$(CF_{2})_{8}(SO_{2}Na)_{2} + CH \equiv CCH_{2}Br \xrightarrow{(NH_{2})_{2}S_{2}O_{8}} \xrightarrow{(NH_{2})_{2}S_{2}O_{8}} \xrightarrow{(CF_{2})_{8}(CH = C = CH_{2})_{2} + (CF_{2})_{6}(COOH)_{2}} \xrightarrow{(CF_{2})_{8}(CH = C = CH_{2})_{8}} \xrightarrow{(CF_{2})_{8}(CH = C} \xrightarrow{(CF_{2})_{8}} \xrightarrow{(CF_{2})_{8}(CH = C} \xrightarrow{(CF_{2})_{8}} \xrightarrow{(CF_{2})_{8}(CH = C} \xrightarrow{(CF_{2})_{8}} \xrightarrow{(CF_{2})_{8}} \xrightarrow{(CF_{2})_{8}(CH = C} \xrightarrow{(CF_{2})_{8}} \xrightarrow{($$

could have been formed by hydrogen abstraction by the $R_{f}CF_{2}$ radical, was not detected.

The experimental results can be explained by invoking a radical addition-elimination mechanism for the reaction (Scheme I).¹⁷ Thus, the oxidizing agent ammonium persulfate decomposes spontaneously to produce SO4 --. 18

⁽¹⁷⁾ Poutsma, M. L. In Free Radicals; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, 113.
 (18) Kberhardt, M. K. J. Am. Chem. Soc. 1981, 103, 3876.

⁽¹⁹⁾ Aldrich Catalog, 1988-1989, No. 30,203-1, p 1474.

The radical anion then receives an electron from $R_{f}CF_{2}SO_{2}Na$ to generate the $R_{f}CF_{2}$ radical. The $R_{f}CF_{2}$ radical then adds to allyl or propargyl bromide to form the radical intermediate RrCF2CH2C*HCH2Br or RrCH2CH= C'CH₂Br. These eliminate bromine atom Br' to give $R_f CF_2 CH_2 CH = CH_2$ or $R_f CF_2 CH = C = CH_2$. Bromine atom may then combine with $R_r CF_2$ to form $R_r CF_2 Br$.

It is unlikely that the reaction proceeds by a radical $S_N 2$ process.¹⁷ If this were the case, 3-(perfluoroalkyl)prop-1ynes would have been formed in the reaction of 1g with propargyl bromide. Also, the reaction of 1g with benzyl bromide, which would be expected to show reactivity similar to that of allyl bromide toward radical displacement, should have produced RrCF2CH2C6H5 or RrCF2Br. However, only RrCOOH was detected in the reaction mixture by ¹⁹F NMR.

In conclusion, a convenient synthesis of a variety of 3-(perfluoroalkyl)prop-1-enes and 3-(perfluoroalkyl)allenes is described. The reaction is believed to proceed by radical addition-elimination.

Experimental Section

General Comments. Boiling points and melting points are uncorrected. ¹H NMR spectra were recorded with a Varian EM-60 instrument at 60 MHz, with external TMS reference. $\rm ^{19}F$ NMR spectra were recorded with a Varian EM-60 instrument at 56.4 MHz, with external CF₃COOH reference. Infrared (IR) spectra were recorded with a Shimadzu IR-440 instrument. Mass spectra were recorded with a Finnegan GC-MS-4021 mass spectrometer.

All chemicals were of analytical grade and were used without further purification.

Preparation of Perfluoroalkanesulfinates 1a-i. General **Procedure.** A mixture of 0.1 mol of $R_f X$ (X = I, SO₂F, or CCl₃), 0.12 mol of $Na_2S_2O_4$, 0.1 mol of $NaHCO_3$, 30 mL of H_2O , and 15 mL of CH₃CN was stirred at 25-70 °C for 2-6 h. Then the mixture was poured into 70 mL of ethyl acetate, and the organic layer was separated. The organic layer was washed with brine and dried (Na_2SO_4) . After removal of solvent, the solid residue was crystallized (iPrOH) to give the pure perfluoroalkanesulfinate.

Sodium 3-oxa-11-chloro-1,1,2,2,4,4,5,5,6,6,7,7,8,8,9,9,10,-10,11,11-eicosafluoroundecanesulfinate (1a):⁹ from Cl(C- F_2)₈OCF₂CF₂SO₂F; reaction temperature 70 °C; reaction time 7 h; yield 78%; ¹⁹F NMR (iPrOH) -9.0 (2 F, s, CF₂Cl), 4.7 (4 F, s, CF_2OCF_2), 42.5–47.3 (12 F, m, 6 × CF_2), 55.4 (2 F, s, CF_2SO_2Na).

Sodium 1,1-dichloro-2,2,2-trifluoroethanesulfinate (1b):¹¹ from CF₃CCl₃; reaction temperature 25 °C; reaction time 6 h; yield 60%; ¹⁹F NMR (AcOEt) -4.8 (s).

Sodium 2-chloro-1,1,2,2-tetrafluoroethanesulfinate (1c):¹⁰ from ClCF₂CF₂I; reaction temperature 30 °C; reaction time 4 h; yield 55%; ¹⁹F NMR (AcOEt) -11.0 (2 F, s, CF₂Cl), 51.5 (2 F, s, CF₂SO₂Na).

Sodium 4-chloro-1,1,2,2,3,3,4,4-octafluorobutanesulfinate (1d):¹⁰ from $Cl(CF_2)_4I$; reaction temperature 45 °C; reaction time 2 h; yield 85%; ¹⁹F NMR (AcOEt) -8.6 (2 F, s, CF₂Cl), 43.2 (2 F, s, CF₂), 45.7 (2 F, s, CF₂), 54.2 (2 F, s, CF₂SO₂Na).

Sodium 6-chloro-1,1,2,2,3,3,4,4,5,5,6,6-dodecafluorohexanesulfinate (1e):¹⁰ from $Cl(CF_2)_6I$; reaction temperature 45 °C; reaction time 2 h; yield 82%; ¹⁹F NMR (AcOEt) -9.4 (2 F, s, CF₂Cl), 42.2 (2 F, s, CF₂), 44.2 (6 F, s, $3 \times CF_2$), 53.8 (2 F, s, CF₂SO₂Na).

Sodium perfluorobutanesulfinate (1f):¹⁰ from $CF_3(CF_2)_3I$; reaction temperature 45 °C; reaction time 3 h; yield 75%; ¹⁹F NMR (AcOEt) 5.7 (3 F, s, CF₃), 48.0 (4 F, s, $2 \times CF_2$), 55.5 (2 F, s, CF_2SO_2Na).

Sodium perfluorohexanesulfinate (1g):¹⁰ from $CF_3(CF_2)_5I$; reaction temperature 55 °C; reaction time 4 h; yield 83%; ¹⁹F

NMR (AcOEt) 4.3 (3 F, s, CF₃), 45.6 (6 F, s, $3 \times CF_2$), 49.5 (2 F, s, CF₂). 54.2 (2 F, s, CF₂SO₂Na).

Sodium perfluorooctanesulfinate (1h):¹⁰ from CF₃(CF₂)₇I; reaction temperature 60 °C; reaction time 5 h; yield 72%; ¹⁹F NMR (AcOEt) 5.2 (3 F, s, CF₃), 45.9 (10 F, s, $5 \times CF_2$), 55.4 (2 F, s, CF_2SO_2Na).

Sodium perfluorooctane-1,8-disulfinate (1i):10 from I(C-F₂)₈I; reaction temperature 70 °C; reaction time 5 h; yield 55%; ¹⁹F NMR (AcOEt) 44.5 (12 F, s, $6 \times CF_2$), 53.2 (4 F, s, $2 \times$ $CF_2SO_2Na)$

Synthesis of 3-(Perfluoroalkyl)prop-1-enes 2a-i. General **Procedure.** A mixture of sodium perfluoroalkanesulfinate (1) (10 mmol), allyl halide (10 mmol), $(NH_4)_2S_2O_8$ (2.7 g, 10 mmol), and 30 mL of DMF was stirred at 40 °C for 4 h. The cooled mixture was poured into 40 mL of H_2O and was extracted with ether $(3 \times 100 \text{ mL})$. The combined ether extracts were neutralized with aqueous NaHCO₃ and washed with H_2O . The water layers were combined and were evaporated to dryness. To the residue, which was mainly the sodium salt of the fluorinated carboxylic acid, was added 10 mL of concentrated H_2SO_4 . Distillation of the mixture gave the fluoro carboxylic acid $\bar{3}$. The ether extracts were then dried (Na_2SO_4) . After evaporation of ether, distillation under reduced pressure gave 2 and 4.

6-Oxa-14-chloro-4,4,5,5,7,7,8,8,9,9,10,10,11,11,12,12,13,13,-14,14-eicosafluoro-1-tetradecene (2a): bp 96-97 °C (5 mmHg); ¹⁹F NMR (neat) -8.7 (2 F, s, CF_2Cl), 7.0 (2 F, s, CF_2O), 10.7 (2 F, s, CF₂O), 41.0 (2 F, t, J = 16 Hz, CF₂CH₂), 44.0 (2 F, s, CF₂), 45.3 (8 F, s, 4 × CF₂), 49.0 (2 F, s, CF₂); ¹H MMR (neat) 2.90 (2 H, td, ${}^{3}J_{F,H} = 16$ Hz, ${}^{3}J_{H,H} = 6$ Hz, CF₂CH₂CH₂CH₂CH₂), 5.10–6.20 (3 H, m, vinylic H); IR (neat) 1650 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (100, C₃H₅), 91 (97.96, CF₂CH₂CH= CH₂), 592 (1.28, M).

Anal. Calcd for C₁₃H₅ClF₂₀O: C, 26.32; H, 0.84; F, 64.13. Found: C, 26.37; H, 0.79; F, 63.98.

4,4-Dichloro-5,5,5-trifluoro-1-pentene (2b): bp 85-87 °C; ¹⁹F NMR (neat) 2.7 (s); ¹H NMR (neat) 2.65 (2 H, d, ${}^{3}J_{H,H} = 6$ Hz, CCl₂CH₂CH=CH₂), 5.20-6.10 (3 H, m, vinylic H); IR 1648 (C=C) cm¹⁻; mass spectrum m/z (relative intensity) 41 (45.15, CH₂CH=CH₂), 157 (100.00, M - Cl), 192 (2.62, M).

Anal. Calcd for C₅H₅F₃Cl₂: C, 31.25; H, 2.60; F, 29.69. Found: C, 31.75; H, 2.85; F, 27.38.

5-Chloro-4,4,5,5-tetrafluoro-1-pentene (2c): bp 49-51 °C; ¹⁹F NMR (neat) -5.7 (2 F, s, CF₂Cl), 37.3 (2 F, t, J = 16 Hz, CF_2CH_2 ; ¹H NMR (neat) 2.90 (2 H, td, ³ $J_{F,H}$ = 16 Hz, ³ $J_{H,H}$ = 6 Hz, CF₂CH₂CH=CH₂), 5.10-6.00 (3 H, m, vinylic H); IR 1650 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (100.00, CH₂CH=CH₂), 85 (17.52, CF₂Cl), 91 (88.66, CF₂CH₂CH=CH₂), 176 (25.23, M).

Anal. Calcd for C₅H₅F₄Cl: C, 34.09; H, 2.84; F, 43.18. Found: C, 34.23; H, 2.94; F, 42.08.

1-Bromo-2-chloro-1,1,2,2-tetrafluoroethane (4c): ¹⁹F NMR (neat) -11.7 (2 F, s, CF₂Br), -7.6 (2 F, s, CF₂CL); mass spectrum m/z (relative intensity) 85 (24.15, CF₂Cl), 135 (100.00, M - Br), 179 (8.39, M - Cl), 214 (1.27, M).

7-Chloro-4,4,5,5,6,6,7,7-octafluoro-1-heptene (2d): bp 90-91 °C; ¹⁹F NMR (neat) -7.3 (2 F, s, CF₂Cl), 38.3 (2 F, t, J = 16 Hz, CF₂CH₂), 44.6 (2 F, s, CF₂), 49.0 (2 F, s, CF₂); ¹H NMR (neat) 2.90 (2 H, td, ${}^{3}J_{F,H} = 16$ Hz, ${}^{3}J_{H,H} = 6$ Hz, $CF_{2}CH_{2}CH=CH_{2}$), 5.10-6.20 (3 H, m, vinylic H); IR 1658 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (35.25, CH₂CH=CH₂), 85 (48.63, CF₂Cl), 91 (100.00, CF₂CH₂CH₂=CH₂), 276 (3.58, M).

Anal. Calcd for C₇H₅F₈Cl: 30.43; H, 1.81; F, 55.07. Found: C, 31.20; H, 1.90; F, 54.48

9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1-nonene (2e): bp 118-119 °C; ¹⁹F NMR (neat) -8.0 (2 F, s, CF₂Cl), 36.7 (2 F, t, J = 16 Hz, CF_2CH_2), 45.3 (6 F, s, 3 × CF_2), 47.3 (2 F, s, CF_2); ¹H NMR (neat) 2.65 (2 H, td, ${}^{3}J_{F,H} = 16$ Hz, ${}^{3}J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.20-5.80 (3 H, m, vinylic H); IR 1647 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (40.65, CH2CH=CH2), 85 (27.25, CF2CL), 91 (100.00, CF2CH2CH=CH2), 376 (4.71, M).

Anal. Calcd for C₉H₅F₁₂Cl: C, 28.68; H, 1.32; F, 60.56. Found: C, 28.65; H, 1.29; F, 61.20.

4,4,5,5,6,6,7,7,7-Nonafluoro-1-heptene (2f): bp 82-85 °C; ¹⁹F NMR (neat) 5.7 (3 F, s, CF_3), 38.4 (2 F, t, J = 16 Hz, CF_2CH_2), 45.3 (2 F, s, CF₂), 49.4 (2 F, s, CF₂); ¹H NMR (neat) 2.95 (2 H,

⁽²⁰⁾ Swarts, F. Bull. Soc. Chim. Fr. 1906, 42.
(21) Chen, Q.-Y.; Qiu, Z.-M. Acta Chim. Sin. 1988, 46, 38.
(22) Aldrich Catalog, 1990–1991, No. 15,739-2, p 686.
(23) Ulimanns Encyklopaedie der Technischen Chemie, 5th ed.; Band

A-11, p 371-32.

⁽²⁴⁾ Aldrich Catalog, 1990-1991, No. 17,146-8, p 1011.

td, ${}^{3}J_{H,F} = 16$ Hz, ${}^{3}J_{H,H} = 6$ Hz, $CF_{2}CH_{2}CH_{--}CH_{2}$), 5.05-6.15 (3 H, m, vinylic H); IR 1655 (C--C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (45.65, $CH_{2}CH_{--}CH_{2}$), 69 (100.00, CF_{3}), 91 (73.68, $CF_{2}CH_{2}CH_{--}CH_{2}$), 260 (10.32, M).

Anal. Calcd for C₇H₆F₉: C, 32.31; H, 1.92; F, 65.77. Found: C, 33.08; H, 2.05; F, 64.63.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-nonene (2g): bp 109-112 °C; ¹⁹F NMR (neat) 6.0 (3 F, s, CF₃), 38.3 (2 F, t, J =16 Hz, CF₂CH₂), 48.0 (6 F, s, $3 \times CF_2$), 51.0 (2 F, s, CF₂); ¹H NMR (neat) 2.65 (2 H, td, ³J_{F,H} = 16 Hz, ³J_{H,H} = 6 Hz, CF₂CH₂CH= CH₂), 5.20-5.80 (3 H, m, vinylic H); IR 1645 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (100.00, CH₂CH=CH₂), 69 (22.35, CF₃), 91 (46.70, CF₂CH₂CH=CH₂), 360 (35.98, M).

Anal. Calcd for $C_9H_5F_{13}$: C, 30.00; H, 1.39; F, 68.61. Found: C, 29.52; H, 1.40; F, 68.32.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1-undecene (2h): bp 124-127 °C; ¹⁹F NMR (neat) 6.0 (3 F, s, CF₃), 38.3 (2 F, t, J = 16 Hz, CF₂CH₂), 46.3 (10 F, s, 5 × CF₂), 50.6 (2 F, s, CF₂); ¹H NMR (neat) 2.75 (2 H, td, ³J_{F,H} = 16 Hz, ³J_{H,H} = 6 Hz, CF₂CH₂CH=CH₂), 5.30-5.95 (3 H, m, vinylic H); IR 1650 (C=C) cm⁻¹; mass spectrum m/z (relative intensity) 41 (29.63, CH₂CH=CH₂), 69 (100.00, CF₃), 91 (73.46, CF₂CH₂CH=CH₂), 460 (3.85, M).

Anal. Calcd for $C_{11}H_5F_{17}$: C, 28.69; H, 1.08; F, 70.22. Found: C, 29.08; H, 1.13; F, 68.96.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Hexadecafluoro-1,13-tetradecadiene (2i): bp 75–76 °C (2 mmHg); ¹⁹F NMR (neat) 37.3 (4 F, t, J = 16 Hz, $2 \times CF_2CH_2$), 45.0 (8 F, s, $4 \times CF_2$); 46.7 (4 F, s, $2 \times CF_2$); ¹H NMR (neat) 2.75 (2 H, $t \times d$, ³ $J_{F,H} = 16$ Hz, ³ $J_{H,H} = 6$ Hz, $CF_2CH_2CH=CH_2$), 5.30–5.95 (3 H, m, vinylic H); IR 1655 (C=C) cm⁻¹; mass spectrum $m/_z$ (relative intensity) 41 (87.2, CH₂CH=CH₂), 91 (100.00, $CF_2CH_2CH=CH_2$), 482 (17.17, M).

Anal. Calcd for $C_{14}H_{10}F_{16}$: C, 34.85; H, 2.07; F, 63.07. Found: C, 34.65; H, 1.99; F, 64.17.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluorononyl acetate (5): bp 86-88 °C (2 mmHg); ¹⁹F NMR (neat) 6.0 (3 F, s, CF₃), 38.5 (2 F, t, J = 16 Hz, CF₂CH₂), 48.5 (6 F, s, 3 × CF₂), 51.5 (2 F, s, CF₂); ¹H NMR (neat) 2.17 (s, 3 H, CH₃CO), 2.22-2.85 (m, 4 H, CH₂CH₂CF₂), 4.40 (t, 2 H, J = 4 Hz, CH₂O); IR 1750 (s, C=O) cm⁻¹; mass spectrum m/z (relative intensity) 59 (100.00, CH₃COO), 92 (43.56, CF₂CH₂CH₂CH₂CH₂), 420 (5.38, M).

Anal. Calcd for $C_{11}H_{9}F_{13}O_{2}$: C, 34.43; H, 2.14; F, 58.81. Found: C, 35.01; H, 2.35; F, 59.62.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1-(trimethylsilyl)nonane (6): bp 125–128 (5 mmHg); ¹⁹F NMR (neat) 5.8 (3 F, s, CF₃), 37.8 (2 F, t, J = 16 Hz, CF₂CH₂), 48.0 (6 F, s, $3 \times$ CF₂), 51.0 (2 F, s, CF₂); ¹H NMR (neat) 0.00 (s, 9 H, Si(CH₃)₃), 0.65–0.85 (m, 2 H, CH₂Si), 1.65–2.85 (m, 4 H, CF₂CH₂CH₂CH₂); mass spectrum m/z(relative intensity) 161 (100, CF₂CH₂CH₂CH₂Si(CH₃)₃), 430 (3.42, M).

Anal. Calcd for $C_{12}H_{15}F_{13}Si: C, 33.49; H, 3.49; F, 57.44$. Found: C, 34.30; H, 3.52; F, 57.01.

Synthesis of 3-(Perfluoroalkyl)allenes. General Procedure. A mixture of sodium perfluoroalkanesulfinate (10 mmol), propargyl halide (10 mmol), and $(NH_4)_2S_2O_8$ (2.7 g, 10 mmol) in 30 mL of DMF was stirred at 40 °C for 4 h. The usual workup gave the products.

5-Chloro-4,4,5,5-tetrafluoro-1,2-pentadiene (7c): bp 58–60 °C; ¹⁹F NMR (neat) -4.0 (2 F, s, CF₂Cl), 32.7 (2 F, d, ³ $J_{H,F}$ = 11.5 Hz, CF₂CH=); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm⁻¹; mass spectrum m/z (relative intensity) 85 (57.00, CF₂Cl), 89 (100.00, CF₂CH=C=CH₂). Anal. Calcd for $C_{5}H_{3}F_{4}Cl: C, 20.69; H, 1.72; F, 43.68.$ Found: C, 21.45; H, 1.80; F, 45.78.

7-Chloro-4,4,5,5,6,6,7,7-octafluoro-1,2-heptadiene (7d): bp 85–87 °C; ¹⁹F NMR (neat) –7.3 (2 F, s, CF₂Cl), 32.7 (2 F, d, ${}^{3}J_{HF}$ = 11.5 Hz, CF₂CH=), 43.7 (2 F, s, CF₂), 46.3 (2 F, s, CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm⁻¹; mass spectrum m/z (relative intensity) 85 (100.00, CF₂Cl), 89 (61.63, CF₂CH=C=CH₂), 139 (14.94, CF₂CF₂CH=C=CH₂), 255 (3.66, M - F).

Anal. Calcd for C₇H₃F₈Cl: C, 30.66; H, 1.09; F, 55.47. Found: C, 31.42; H, 1.20; F, 54.68.

4,4,5,5,6,6,7,7,7-Nonafluoro-1,2-heptadiene (7f): bp 64–67 °C; ¹⁹F NMR (neat) 6.0 (3 F, s, CF₃), 33.5 (2 F, d, ${}^{3}J_{H,F} = 11.5$ Hz, CF₂CH—), 46.8 (2 F, s, CF₂), 49.6 (2 F, s, CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C—C—C) cm⁻¹; mass spectrum m/z (relative intensity) 69 (100.00, CF₃), 89 (63.54, CF₂CH—C—CH₂), 139 (18.30, CF₂CF₂CH—C—CH₂), 239 (6.48, M – F).

Anal. Calcd for $C_7H_3F_9$: C, 32.56; H, 1.66; F, 66.28. Found: C, 32.98; H, 1.28; F, 65.93.

4,4,5,5,6,6,7,7,8,8,9,9,9-Tridecafluoro-1,2-nonadiene (7g): bp 113-114 °C; ¹⁹F NMR (neat) 5.6 (3 F, s, CF₃), 33.0 (2 F, d, ${}^{3}J_{H,F}$ = 11.5 Hz, CF₂CH=), 47.3 (6 F, s, 3 × CF₂), 50.7 (2 F, s, CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C= C=C) cm⁻¹; mass spectrum m/z (relative intensity) 69 (100.00, CF₃), 89 (98.76, CF₂CH=C=CH₂), 139 (17.50, CF₂CF₂CH=C= CH₂), 339 (26.02, M - F).

Anal. Calcd for $C_9H_3F_{13}$: C, 30.17; H, 0.84; F, 68.99. Found: C, 31.22; H, 0.98; F, 68.63.

9-Chloro-4,4,5,5,6,6,7,7,8,8,9,9-dodecafluoro-1,2-nonadiene (7e): bp 126-128 °C; ¹⁹F NMR (neat) -7.4 (2 F, s, CF₂Cl), 32.7 (2 F, d, ${}^{3}J_{H,F} = 11.5$ Hz, CF₂CH=), 47.5 (6 F, s, 3 × CF₂), 50.6 (2 F, s, CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm⁻¹; mass spectrum m/z (relative intensity) 85 (87.45, CF₂Cl), 89 (100.00, CF₂CH=C=CH₂), 139 (11.59, CF₂CF₂CH=C=CH₂), 355 (7.80, M - F).

Anal. Calcd for $C_9H_3F_{12}Cl$: C, 28.88; H, 0.80; F, 60.96. Found: C, 29.12; H, 0.96; F, 59.03.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-Heptadecafluoro-1,2-undecadiene (7h): bp 63–64 °C (3 mmHg); ¹⁹F NMR (neat) 6.0 (3 F, s, CF₃), 33.3 (2 F, d, ${}^{3}J_{H,F} = 11.5$ Hz, CF₂CH—), 46.0 (10 F, s, 5 × CF₂), 51.0 (2 F, s, CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C—C—C) cm⁻¹; mass spectrum m/z (relative intensity) 69 (49.80, CF₃), 89 (100.00, CF₂CH—C—CH₂), 139 (8.20, CF₂CF₂CH—C—CH₂), 439 (6.45, M – F).

Anal. Calcd for $C_{11}H_3F_{17}$: C, 28.82; H, 0.66; F, 70.52. Found: C, 29.23; H, 0.78; F, 69.42.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11-Hexadecafluoro-1,2,12,13tetradecatetraene (7i): bp 75–77 °C (3 mmHg); ¹⁹F NMR (neat) 31.0 (4 F, d, ${}^{3}J_{HF} = 11.5$ Hz, 2 × CF₂CH=), 45.0 (8 F, s, 4 × CF₂), 47.3 (4 F, s, 2 × CF₂); ¹H NMR (neat) 5.40, 5.30, 5.20 (vinylic H); IR 1975, 1995 (C=C=C) cm⁻¹; mass spectrum m/z (relative intensity) 89 (100.00, CF₂CH=C=CH₂), 139 (10.73, CF₂CF₂CH=C=CH₂), 459 (6.58, M – F).

Anal. Calcd for $C_{14}H_6F_{16}$: C, 35.15; H, 1.26; F, 63.59. Found: C, 35.45; H, 1.31; F, 62.96.

Acknowledgment. We thank Hoechst AG for providing perfluoroalkyl iodides.

Supplementary Material Available: Experimental results (bp, mp, ¹H NMR, and ¹⁹F NMR) for compounds **3a-i** (1 page). Ordering information is given on any current masthead page.