and guidance and also Kathryn Linhardt for typing this paper.

Registry No. **1a**, 81505-79-5; **1b**, 81505-80-8; **1c**, 81505-81-9; (–)-**1c**, 81505-82-0; **1d**, 81505-83-1; **1e**, 81505-84-2; **1f**, 71530-87-5; **1g**, 81505-85-3; **2a**, 71491-85-5; **2b**, 81505-86-4; **2c**, 81505-87-5; (–)-**2c**, 81505-88-6; **2d**, 13137-24-1; (4-chlorophenyl)phenylacetyl-3-chlorobenzoyl peroxide, 81505-89-7; (4-nitrophenyl)phenylacetyl-3-chlorobenzoyl peroxide, 81505-90-0; (4-nitrophenyl)phenylacetyl-4-nitrobenzoyl peroxide, 81505-91-1; bis(4-nitrophenyl)acetyl-4-nitrobenzoyl peroxide, 81505-92-2; diphenylacetyl *tert*-butyl perester, 13144-32-6; benzoyl peroxide, 94-36-0.

Supplementary Material Available: Complete procedures for the preparation and spectral data for (4-nitrophenyl)phenylacetic acid, (4-nitrophenyl)phenylacetyl chloride, 4-chlorobenzhydryl 4-nitrobenzoic carbonic anhydride, and 4-methylbenzhydryl 4-nitrobenzoic carbonic anhydride are available (4 pages). Ordering information is given on any current masthead page.

Synthesis of Fluorinated Acetylenes[1]

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New routes to fluorinated acetylenes were developed on the basis of additions of iodofluorocarbons to silylacetylenes. Free radical addition of α,ω-diiodoperfluoroalkanes to (trimethylsilyl)acetylene gave the iodotrimethylsilyl olefins $Me_3SiIC{=}CH(CF_2)_nCH{=}CISiMe_3$, which reacted with potassium *tert*-butoxide or DBU to give the (trimethylsilyl)acetylenes and, with an excess of the base, the free diacetylenes. Perfluoroalkyl iodides similarly gave (perfluoroalkyl)acetylenes. The addition of perfluoroheptyl iodide to phenylacetylene, followed by treatment with potassium *tert*-butoxide gave 1-phenylperfluorononyne. The peroxide-catalyzed reaction of perfluoroalkyl iodides and bis(trimethylsilyl)acetylene gave 1:1 adducts, $R_F(Me_2SiCH_2I)C{=}CHSiMe_3$, resulting from intramolecular hydrogen abstraction by the initially formed vinyl radical. However, the thermal reaction of perfluoroalkyl iodides and diiodides with bis(trimethylsilyl)acetylene in the presence of free iodine gave the (trimethylsilyl)acetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated on the basis of addition of perfluoroiodo compounds to ethylene, dehydroiodination, brominations, and eliminations.

Although perfluoroalkyl-substituted primary acetylenes have been known for three decades, (perfluoroalkylene)diacetylenes, $HC{\equiv}C(CF_2)_nC{\equiv}CH$, have not been reported. Haszeldine[2,3] originally prepared 3,3,3-trifluoropropyne by the addition of trifluoromethyl iodide to acetylene (70–80%) followed by dehydrohalogenation (75%). (Perfluoroethyl)acetylene was prepared similarly.[4] Henne and Nager[5] developed a high-yield multistep route to 3,3,3-trifluoropropyne that avoided the use of acetylene under pressure; bromination of 3,3,3-trifluoropropene was followed by dehydrohalogenation, another bromination, dehydrohalogenation, and dehalogenation (Scheme I). More recently,[6] this approach was used to prepare the perfluorobutyl, perfluorohexyl, and perfluorooctyl analogues.

Using α,ω-diiodoperfluoroalkanes as starting materials, available from the telomerization of tetrafluoroethylene with iodine,[7] we approached the synthesis of α,ω-diacetylenes using Henne's sequence (Scheme II). Reactions of ethylene with 1,4-diiodoperfluorobutane and 1,6-diiodoperfluorohexane, followed by dehydrohalogenations, have been reported to give the corresponding α,ω-diolefins.[8] Bromine adducts of these olefins were obtained in 74–91% yields. The reaction of 3,3,4,4,5,5,6,6-octafluoro-1,2,7,8-tetrabromooctane with potassium hydroxide in methanol gave 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Another bromination followed by reaction with methanolic potassium hydroxide gave a complex product mixture, the major component of which was isolated by GC and identified as the desired 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. Although moderately good yields were obtained for each step of the sequence, overall yields were poor. Therefore, this approach to diacetylenes was abandoned.

Scheme I

$$CF_3CH{=}CH_2 \xrightarrow{Br_2} CF_3CHBrCH_2Br \xrightarrow{KOH} CF_3CHBr{=}CH_2$$
$$\xrightarrow{Br_2} CF_3CBr_2CH_2Br \xrightarrow{KOH} CF_3CBr{=}CHBr \xrightarrow{Zn} CF_3C{\equiv}CH$$

Scheme II[a]

$$I(CF_2)_nI + CH_2{=}CH_2 \longrightarrow ICH_2CH_2(CF_2)_nCH_2CH_2I \xrightarrow{KOH}$$
$$CH_2{=}CH(CF_2)_nCH{=}CH_2 \xrightarrow{Br_2}$$
$$BrCH_2CHBr(CF_2)_nCHBrCH_2Br$$
$$BrCH_2CHBr(CF_2)_4CHBrCH_2Br \xrightarrow{KOH}$$
$$CH_2{=}CBr(CF_2)_4CBr{=}CH_2 \xrightarrow{Br_2} BrCH_2CBr_2(CF_2)_4CBr_2CH_2Br$$
$$\xrightarrow{KOH} BrCH{=}CBr(CF_2)_4CBr{=}CHBr$$

[a] $n = 4$ or 6.

(Trimethylsilyl)acetylene Additions. The trimethylsilyl group is a convenient blocking group for the synthesis of acetylenes. The synthesis of arylacetylenes has recently been accomplished by using a paladium-catalyzed coupling of aromatic halides with (trimethylsilyl)-acetylene, followed by desilylation of the resulting arylacetylene derivatives with nucleophiles.[9,10]

(1) This work was supported by the Office of Naval Research.
(2) Haszeldine, R. N. *J. Chem. Soc.* **1950**, 3037.
(3) Haszeldine, R. N. *J. Chem. Soc.* **1951**, 588.
(4) Haszeldine, R. N.; Leedham, K. *J. Chem. Soc.* **1952**, 3483.
(5) Henne, A. L.; Nager, M. *J. Am. Chem. Soc.* **1951**, *73*, 1042.
(6) LeBlanc, M.; Santini, G.; Jeanneaux, F.; Riess, J. G. *J. Fluorine Chem.* **1976**, *7*, 525.
(7) Bedford, C. D.; Baum, K. *J. Org. Chem.* **1980**, *45*, 347.
(8) Knunyants, I. L.; Khriakvan, S. P.; Zeifman, Y. V.; Shokina, V. V. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1964**, 384.
(9) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.

0022-3263/82/1947-2251$01.25/0

We undertook the synthesis of fluorocarbon acetylenes by the free-radical addition of iodofluorocarbons to (trimethylsilyl)acetylene. Treatment of 1,6-diiodoperfluorohexane with an excess of (trimethylsilyl)acetylene in the presence of di-*tert*-butyl peroxide at 120 °C for 85 h gave a 92% yield of the diadduct 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene. With a reaction time of 47 h, a 73% yield was obtained of the corresponding product in which only one iodine of the 1,6-diiodoperfluorohexane was involved. A mixture of 1,8-diiodoperfluorooctane, 1,10-diiodoperfluorodecane, and 1,12-diiodoperfluorododecane, readily obtained from the iodine–tetrafluoroethylene reaction, gave a 95% yield of the diadducts. Lower diiodides, however, did not readily give diadducts. Thus 1,4-diiodoperfluorobutane gave a complex mixture containing 33% of the monoadduct and 22% of the diadduct, on the basis of GC analysis. Only the monoadduct was isolated from 1,2-diiodoperfluoroethane. A monofunctional starting material, perfluoroheptyl iodide, gave a 92% yield of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene (eq 1 and 2).

$$I(CF_2)_nI + HC{\equiv}CSiMe_3 \rightarrow (Me_3Si)IC{=}CH(CF_2)_nCH{=}CI(SiMe_3) \quad (1)$$

$$n = 6, 8, 10, 12$$

$$CF_3(CF_2)_6I + HC{\equiv}CSiMe_3 \rightarrow CF_3(CF_2)_6CH{=}CI(SiMe_3) \quad (2)$$

These trimethylsilyl iodo olefins were obtained as a mixture of *E* and *Z* isomers, separable by GC. Isomer assignments were based on NMR comparison with the hydrocarbon analogues.[11] The vinyl proton of (*E*)-1-iodo-1-(trimethylsilyl)hexene appears at δ 7.1 (t, J_{HH} = 8 Hz) and that of the *Z* isomer at δ 6.1 (t, J_{HH} = 6 Hz). The respective values for the fluorinated compounds are δ 7.1 (t, J_{HF} = 14–16 Hz) and 6.8 (J_{HF} = 10–13 Hz). The silyl methyls for the *E* isomers appear as triplets whereas those of the *Z* isomers appear as singlets. The α-CF_2 groups of the *E* isomers appear at ϕ 107–109 and those of the *Z* isomers at ϕ 111–113.

Dehydroiodination of these 1-iodo-1-(trimethylsilyl) olefins was quite sensitive to the types of basic reagents that were employed. The reaction of $(Me_3Si)IC{=}CH(CF_2)_6CH{=}CI(SiMe_3)$ with methanolic potassium hydroxide at room temperature gave a 56.5% yield of $IC{=}CH(CF_2)_6CH{=}CHI$, and attempts to dehydroiodinate this olefin were unsuccessful. The most satisfactory reagents to effect elimination to the silyl acetylene were potassium *tert*-butoxide in methylene chloride at −20 °C and DBU in tetrahydrofuran at −25 °C (eq 3). An excess

$$(Me_3Si)IC{=}CH(CF_2)_nCH{=}CI(SiMe_3) \xrightarrow[\text{or DBU/THF}]{\text{KO-}t\text{-Bu/}CH_2Cl_2} Me_3SiC{\equiv}C(CF_2)_nC{\equiv}CSiMe_3 \rightarrow HC{\equiv}C(CF_2)_nC{\equiv}CH \quad (3)$$

$$n = 6, 8, 10, 12$$

$$CF_3(CF_2)_6CH{=}CI(SiMe_3) \rightarrow CF_3(CF_2)_6C{\equiv}CH \quad (4)$$

of the reagents gave the free acetylene under the same conditions, or potassium fluoride could be used for the desilylation. The former reagent gave a 32.5% yield of $HC{\equiv}C(CF_2)_6C{\equiv}CH$ from the iodo silyl olefin and the latter a 45–72% yield. The analogous dodecadiyne, tetradecadiyne, and hexadecadiyne were prepared from the mixture of the iodo silyl olefins described above, and pentadecafluorononyne was prepared similarly.

Another terminal acetylene that underwent free-radical addition of an iodofluorocarbon was phenylacetylene. An adduct with perfluoroheptyl iodide was obtained in 89% yield, and its reaction with potassium *tert*-butoxide in methylene chloride gave a 78% yield of the acetylene (eq 5). Several adducts of fluorocarbon iodides with aliphatic acetylenes have been reported recently.[12]

$$C_6H_5C{\equiv}CH + I(CF_2)_6CF_3 \xrightarrow[120\ °C]{t\text{-BuOO-}t\text{-Bu}} C_6H_5IC{=}CH(CF_2)_6CF_3 \xrightarrow{\text{KO-}t\text{-Bu}} C_6H_5C{\equiv}C(CF_2)_6CF_3 \quad (5)$$

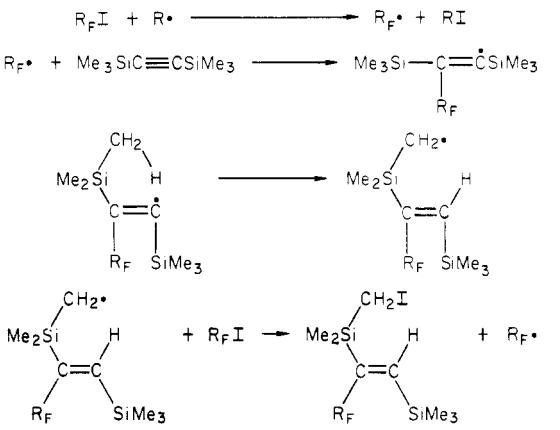
Bis(trimethylsilyl)acetylene Additions. In the formation of acetylenes from the adducts of fluorinated iodides with (trimethylsilyl)acetylene, the ability of iodine to function as a leaving group is evidently enhanced by the adjacent silyl group. Accordingly, adducts of bis(trimethylsilyl)acetylene would be expected to provide acetylenes readily.

Iodofluorocarbons were found to react with bis(trimethylsilyl)acetylene at 120 °C, in the presence of di-*tert*-butyl peroxide, to give high yields of products that were shown to be 1:1 adducts by elemental analysis. Adducts were obtained from 1,6-diiodoperfluorohexane, perfluoropropyl iodide, and perfluoroheptyl iodide in 75–85% yield. The NMR spectra, however, showed an olefinic hydrogen and two silyl hydrogens shifted to δ 2.05–2.08. Evidently, free-radical hydrogen transfer took place, as shown in Scheme III.

Generally in free-radical-catalyzed iodide additions, a radical derived from the catalyst abstracts an iodine atom from the alkyl iodide, and the resulting free radical adds to the unsaturated substrate. The new radical thus formed would normally abstract an iodine atom from the starting material to propagate the chain mechanism. In this case, however, the trimethylsilyl hydrogens are favorably situated for intramolecular hydrogen abstraction to give a silylmethylene radical. Abstraction of iodine from the starting material gives the observed product and regenerates a fluorocarbon radical. Intramolecular hydrogen abstractions of this type are well-known in other systems.[13]

It was reasoned that this intramolecular hydrogen transfer might be averted if a better source of iodine

Scheme III



[a] R_F = $(CF_2)_6$, $CF_3(CF_2)_2$, or $CF_3(CF_2)_6$.

(10) Austin, W. B.; Bilow, N.; Kelleghan, W. J.; Law, K. S. Y. *J. Org. Chem.* **1981**, *46*, 2280.
(11) Zweifel, G.; Murray, R. E.; On, H. P. *J. Org. Chem.* **1981**, *46*, 1292.
(12) Brace, N. O.; Van Elswyk, J. E. *J. Org. Chem.* **1976**, *41*, 766.
(13) Freidlina, R. K.; Terent'ev, A. B. *Acc. Chem. Res.* **1977**, *10*, 9. Piccardi, P.; Massardo, P.; Modena, M.; Santoro, E. *J. Chem. Soc., Perkin Trans. 1* **1974**, 1848.

radicals were available to trap the initially formed vinyl radicals. The desired reaction took place in the presence of a catalytic amount of elemental iodine at 200 °C. Under these conditions, 1,8-diiodoperfluorooctane gave an 86% yield of 1,12-bis(trimethylsilyl)perfluoro-1,11-dodecadiyne (eq 6). Thus, the initial adduct spontaneously eliminated

$$I(CF_2)_8I + Me_3SiC{\equiv}CSiMe_3 \rightarrow [(Me_3Si)IC{=}C(SiMe_3)(CF_2)_8(SiMe_3)C{=}CI(SiMe_3)] \rightarrow ISiMe_3 + Me_3SiC{\equiv}C(CF_2)_8C{\equiv}CSiMe_3 \quad (6)$$

trimethylsilyl iodide to give the silylated acetylene. Monofunctional perfluoroalkyl iodides reacted similarly; 1-(trimethylsilyl)perfluorononyne was isolated in 65% yield from perfluoroheptyl iodide, whereas 1-(trimethylsilyl)-perfluorooctyne, 1-(trimethylsilyl)perfluorodecyne, and 1-(trimethylsilyl)perfluorododecyne were obtained from a commercial mixture of perfluoroalkyl iodides.

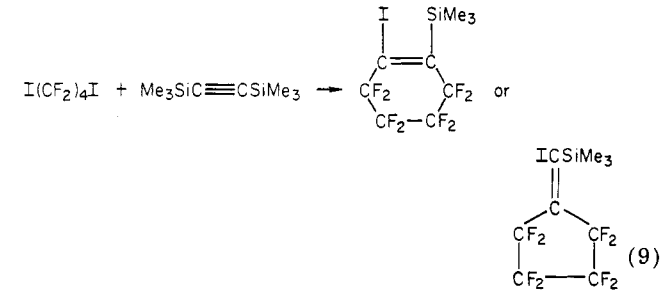
1,12-Bis(trimethylsilyl)perfluoro-1,11-dodecadiyne was desilylated with potassium fluoride dihydrate to give a 79% yield of the free diacetylene (eq 7). Potassium

$$Me_3SiC{\equiv}C(CF_2)_8C{\equiv}CSiMe_3 \xrightarrow[MeOH]{KF{\cdot}2H_2O} HC{\equiv}C(CF_2)_8C{\equiv}CH \quad (7)$$

$$R_FC{\equiv}CSiMe_3 \xrightarrow[MeOH]{K_2CO_3} R_FCH_2CH(OMe)_2 + R_FCH{=}CHOMe \quad (8)$$

carbonate in methanol, the desilylation reagent of choice for arylsilylacetylenes,[10] could not be used because of the susceptibility of the fluorinated acetylenes to nucleophilic additions (eq 8). Thus, 1-(trimethylsilyl)perfluorononyne and methanol–potassium carbonate at room temperature gave a 73% yield of 1,1-dimethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononane and an 11% yield of the 1-methoxynonene. The reaction of trifluoropropyne with sodium alkoxides to give 3,3,3-trifluoro-1-alkoxypropenes has been reported.[14]

Reactions of lower diiodides with bis(trimethylsilyl)-acetylene were complicated by the formation of cyclic products by the involvement of both iodine functions with the same acetylene molecule. The 1,4-diiodoperfluorobutane gave an 81% yield of a product with an elemental analysis consistent with 1-iodo-2-(trimethylsilyl)perfluorocyclohexene or its isomer iodo(trimethylsilyl)-methylenecyclopentane (eq 9).



(9)

The corresponding cyclic adduct, as well as 1,10-bis-(trimethylsilyl)perfluoro-1,9-decadiyne, was obtained from 1,6-diiodoperfluorohexane. The ratio of these products was a function of the amount of bis(trimethylsilyl)acetylene used. The ratio of acetylenic product to cyclic olefin varied from 0.3 for equimolar amounts of the starting materials to 7.5 for a fourfold excess of bis(trimethylsilyl)acetylene. As is the case for the above example, the spectral evidence does not clearly differentiate between the exocyclic and endocyclic olefin structures for the cyclic adduct.

Thus, (perfluoroalkyl)acetylenes as well as (α,ω-perfluoroalkylene)diacetylenes are available from iodofluorocarbon reactions with (trimethylsilyl)acetylene and with bis(trimethylsilyl)acetylene. Polymerization studies with these acetylenes will be reported elsewhere.

Experimental Section

A Varian 920 chromatograph with a 10 ft $\times^3/_8$ in. column of 10% QF-1 on acid-washed Chromosorb W was used for both analytical and preparative gas chromatography. NMR spectra were obtained with a Varian T-60 spectrometer and IR spectra with a Perkin-Elmer 700 spectrometer.

3,3,4,4,5,5,6,6-Octafluoro-1,8-diiodooctane. Ethylene (0.050 mol) was condensed at −130 °C (*n*-pentane–liquid nitrogen bath) into a 75-mL Monel cylinder containing 11.4 g (0.025 mol) of 1,4-diiodoperfluorobutane and 0.2 mL of dibutyl peroxide. The cylinder was sealed and heated for 22 h at 130 °C. The product was extracted with two 50-mL portions of methylene chloride, and the solution was washed with two 25-mL portions of 0.1 N sodium thiosulfate and dried over magnesium sulfate. Removal of the solvent gave 10.4 g (82%) of white solid. An analytical sample was recyrstallized from methanol: mp 89–91 °C; ^{1}H NMR ($CDCl_3$) δ 2.58 (m, 4 H, CH_2), 3.16 (m, 4 H, CH_2I); ^{19}F NMR ($CDCl_3$) ϕ 118.0 (t, 4 F, J = 11.3 Hz, CF_2), 126.0 (t, 4 F, J = 11.3 Hz, CF_2).

Anal. Calcd for $C_8H_8F_8I_2$: C, 18.84; H, 1.58. Found: C, 18.70; H, 1.65.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiododecane. The above procedure with 1,6-diiodoperfluorohexane gave a 76% yield of white solid: mp 69–71 °C; ^{1}H NMR ($CDCl_3$) δ 2.60 (m, 4 H, CH_2), 3.16 (m, 4 H, CH_2I); ^{19}F NMR ($CDCl_3$) ϕ 116.4 (m, 4 F, CF_2), 124.8 (m, 4 F, CF_2), 123.2 (m, 4 F, CF_2).

3,3,4,4,5,5,6,6-Octafluoro-1,7-octadiene. A solution of 20 g (0.039 mol) of 3,3,4,4,5,5,6,6-octafluoro-1,8-diiodooctane and 4.5 g of potassium hydroxide in 15 mL of ethylene glycol was heated with stirring at 140 °C. The product, (7.25 g (73%) of colorless oil; bp 82–87 °C), distilled from the reaction mixture as it was formed. An analytical sample was isolated by GC: ^{1}H NMR ($CDCl_3$) δ 5.6–5.9 (m, 6 H, $CH_2{=}CH$); ^{19}F NMR ($CDCl_3$) ϕ 115.7 (m, 4 F, CF_2), 124.8 (t, 4 F, J = 11.3 Hz, CF_2).

Anal. Calcd for $C_8H_6F_8$: C, 37.81; H, 2.38. Found: C, 37.55; H, 2.10.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiene. The above procedure with 1,10-diiodo-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane gave an 82% yield of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene: bp 135–137 °C; ^{1}H NMR ($CDCl_3$) δ 5.5–5.8 (m, 6 H, $CH_2{=}CH$); ^{19}F NMR ($CDCl_3$) ϕ 116.8 (m, 4 F, CF_2), 126.4 (m, 4 F, CF_2), 124.1 (m, 4 F, CF_2).

Anal. Calcd for $C_{10}H_6F_{12}$: C, 33.92; H, 1.71. Found: C, 33.66; H, 1.80.

3,3,4,4,5,5,6,6-Octafluoro-1,2,7,8-tetrabromooctane. A solution of 6.0 g (0.023 mol) of 3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene and 2.56 mL (0.046 mol) of bromine in 10 mL of chloroform was irradiated with a Par lamp for 1 h. Methylene chloride (20 mL) was added, and the solution was washed with two 10-mL portions of 1 N sodium thiosulfate and dried over magnesium sulfate. Removal of solvent under vacuum gave 10.05 g (74%) of a white solid. Recrystallization from methanol afforded an analytical sample: mp 32–34 °C; ^{1}H NMR ($CDCl_3$) δ 3.72 (m, 4 H, CH_2Br), 4.24 (m, 2 H, CHBr); ^{19}F NMR ($CDCl_3$) ϕ 114.7 (m, 4 F, CF_2) 121.6 (m, 4 F, CF_2).

Anal. Calcd for $C_8H_6F_8Br_4$: C, 16.75; H, 1.05; Br, 55.71. Found: C, 16.76; H, 0.99; Br, 55.40.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,2,9,10-tetrabromodecane. Bromination of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene by the above method gave a 91% yield of the solid product: mp 43–45 °C; ^{1}H NMR ($CDCl_3$) δ 3.59 (m, 4 H, CH_2Br), 4.20 (m, 2 H, CHBr); ^{19}F NMR ($CDCl_3$) ϕ 114.8 (m, 4 F, CF_2), 121.7 (m, 4 F, CF_2), 124.4 (m, 4 F, CF_2).

Anal. Calcd for $C_{10}H_6F_{12}Br_4$: C, 17.83; H, 0.90. Found: C, 18.01; H, 0.98.

2,7-Dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. A solution of 1.5 g of potassium hydroxide and 7.0 g (0.012 mol) of 3,3,4,4,5,5,6,6-octafluoro-1,2,7,8-tetrabromooctane in 15 mL of

(14) Haszeldine, R. N. *J. Chem. Soc.* **1952**, 3496.

methanol was heated with stirring for 1 h at 60 °C. The product was diluted with 50 mL of methylene chloride, washed with two 50-mL portions of water, dried over sodium sulfate, and stripped of solvent under vacuum to give 3.8 g (75%) of a colorless oil. An analytical sample was isolated by GC: ^{1}H NMR ($CDCl_3$) δ 6.16 (m, 2 H, $J_{H,H}$ = 3.0 Hz, HC**H**) 6.42 (d, 2 H, $J_{H,H}$ = 3.0 Hz, **H**CH); ^{19}F NMR ($CDCl_3$) ϕ 110.8 (t, 4 F, $J_{F,F}$ = 11.3 Hz, CF_2), 122.0 (t, 4 F, $J_{F,F}$ = 11.3 Hz, CF_2).

Anal. Calcd for $C_8H_4F_8Br_2$: C, 23.33; H, 0.98. Found: C, 23.62; H, 0.91.

1,2,7,8-Tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene. A solution of 2.4 g (0.0058 mol) of 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene and 1.86 g (0.0106 mol) of bromine in 15 mL of chloroform was irradiated with a Par lamp for 1 h. The mixture was diluted with 20 mL of methylene chloride, washed with two 10-mL portions of 1 N sodium thiosulfate, dried over magnesium sulfate, and stripped of solvent under vaccum to give 2.9 g of white solid. This solid was stirred for 1 h with a solution of 0.5 g of potassium hydroxide in 15 mL of methanol. The mixture was added to 25 mL of water and the product extracted with 35 mL of methylene chloride. The methylene chloride solution was washed with 50 mL of water and dried. The solvent was removed to give 1.2 g of an oil. GC showed a complex mixture from which the major component was trapped and identified as 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene: ^{1}H NMR ($CDCl_3$) δ 7.45 (br s, CH); ^{19}F NMR ($CDCl_3$) ϕ 108.0 (t, 4 F, CF_2), 121.2 (t, 4 F, CF_2).

Anal. Calcd for $C_8H_2F_8Br_4$: C, 16.87; H, 0.35. Found: C, 17.09; H, 0.50.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene. A mixture of 3.3 g (6.0 mmol) of 1,6-diiodoperfluorohexane, 1.5 g of (trimethylsilyl)acetylene, and 0.5 mL of di-*tert*-butyl peroxide was heated in a sealed glass tube under nitrogen for 85 h at 120 °C. The product was dissolved in 50 mL of methylene chloride, dried over magnesium sulfate and stripped of solvent under vacuum to give 4.2 g (92%) of the title compound as a mixture of *E*/*E*, *Z*/*Z*, and *E*/*Z* isomers, analytically pure without further treatment: ^{1}H NMR ($CDCl_3$) δ 7.23 (t, J_{HF} = 15 Hz, =CH, *E* isomers), 6.60 (t, J_{HF} = 13 Hz, =CH, *Z* isomers), 0.35 (t, CH_3Si, *E* isomers), 0.25 (s, CH_3Si, *Z* isomers); ^{19}F NMR ($CDCl_3$) ϕ 108.4 (m, =$CHCF_2$, *E* isomers), 111.6 (m, =$CHCF_2$, *Z* isomers), 123.2 (m, CF_2 internal), 124.4 (m, =$CHCF_2CF_2$).

Anal. Calcd for $C_{16}H_{20}F_{12}I_2Si_2$: C, 25.61; H, 2.69; F, 30.39; I, 33.83. Found: C, 25.52; H, 2.60; F, 30.15; I, 33.67.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,8-diiodo-1-(trimethylsilyl)octene. When a heating period of only 47 h at 120 °C was used with the above reactants, a 72% yield of the monoadduct was obtained as a 70:30 mixture of *E* and *Z* isomers. The isomers were separated by GC.

E isomer: ^{1}H NMR ($CDCl_3$) δ 7.15 (t, 1 H, $J_{H,F}$ = 14 Hz, CH), 0.35 (t, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 65.6 (t, 2 F, CF_2I), 108.4 (q, 2 F, CF_2), 115.2 (m, 2 F, CF_2), 122.8 (m, 4 F, CF_2), 124.4 (m, 2 F, CF_2).

Anal. Calcd for $C_{11}H_{10}F_{12}I_2Si$: C,20.26; H, 1.55; F, 34.96; I, 38.92. Found: C, 20.25; H, 1.57; F, 34.76; I, 38.66.

Z isomer: ^{1}H NMR ($CDCl_3$) δ 6.70 (t, 1 H, $J_{H,F}$ = 13 Hz, CH), 0.25 (s, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 65.6 (t, 2 F, CF_2I), 111.6 (q, 2 F, CF_2), 115.2 (m, 2 F, CF_2), 122.8 (m, 4 F, CF_2), 124.4 (m, 2 F, CF_2).

Anal. Calcd for $C_{11}H_{10}F_{12}I_2Si$: C, 20.26; H, 1.55; F, 34.96; I, 38.92. Found: C, 20.21; H, 1.52; F, 34.69; I, 38.85.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,12-diiodo-1,12-bis(trimethylsilyl)-1,11-dodecadiene, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Eicosafluoro-1,14-diiodo-1,14-bis(trimethylsilyl)-1,13-tetradecadiene, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-Tetraeicosafluoro-1,16-diiodo-1,16-bis(trimethylsilyl)-1,15-hexadecadiene. Treatment of 16.35 g (0.025 mol) of a mixture of 1,8-diiodoperfluorooctane, 1,10-diiodoperfluorodecane, and 1,12-diiodoperfluorododecane with 5 g of (trimethylsilyl)acetylene and 2.5 mL of di-*tert*-butyl peroxide by the above procedure yielded, after 48 h of heating, 16.1 g (95%) of a mixture of the title compounds as an equal mixture of *E* and *Z* isomers: ^{1}H NMR ($CDCl_3$) δ 7.25 (t, 2 H, J_{HF} = 15 Hz, =CH, *E* isomer), 6.70 (t, 2 H, J_{HF} = 13 Hz, =CH, *Z* isomer), 0.33 (t, 18 H, $SiCH_3$, *E* isomer), 0.27 (s, 18 H, $SiCH_3$, *Z* isomer); ^{19}F NMR ($CDCl_3$) ϕ 108.4 (m, 4 F, $CHCF_2$, *E* isomer), 111.6 (m, 4 F, $CHCF_2$, *Z* isomer), 123.2 (m, CF_2 internal), 124.2 (m, =$CHCF_2CF_2$).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene. A mixture of 3.0 g (6.0 mmol) of perfluoroheptyl iodide, 0.60 g (6.0 mmol) of (trimethylsilyl)acetylene, and 0.5 mL of di-*tert*-butyl peroxide was sealed in a glass tube under nitrogen and heated at 120 °C for 48 h. The product was dissolved in methylene chloride and dried over magnesium sulfate. Removal of the solvent under vacuum gave 3.31 g (92%) of a colorless oil, which proved to be an equal mixture of *E* and *Z* isomers of the title compound. The isomers were separated by GC.

E isomer: ^{1}H NMR ($CDCl_3$) δ 7.10 (t, 1 H, J_{HF} = 15 Hz, =CH), 0.33 (t, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, 3 F, CF_3), 108.4 (q, 2 F, =$CHCF_2$), 124 (m, 8 F, CF_2), 127.6 (m, 2 F, =$CHCF_2CF_2$).

Z isomer: ^{1}H NMR ($CDCl_3$) δ 6.58 (t, J_{HF} = 12 Hz, 1 H, =CH), 0.25 (s, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, 3 F, CF_3), 111.8 (q, 2 F, =$CHCF_2$), 124 (m, 8 F, CF_2), 127.6 (m, 2 F, =$CHCF_2CF_2$).

Anal. Calcd for $C_{12}H_{13}F_{15}ISi$: C, 24.14; H, 2.19; F, 47.72; I, 21.25. Found: C, 23.93; H, 1.99; F, 47.60; I, 21.57.

Reaction of 1,4-Diiodoperfluorobutane with (Trimethylsilyl)acetylene. A mixture of 1.4 g (3.0 mmol) of 1,4-diiodoperfluorobutane, 0.90 g (9.2 mmol) of (trimethylsilyl)-acetylene, and 0.2 g (1.4 mmol) of di-*tert*-butyl peroxide was heated in a sealed tube for 6 days at 120 °C. GC analysis (150–185 °C) showed seven components, 12%, 23%, 20%, 13%, 6%, 22%, and 3% of the sample, respectively. The first component consisted of 1,4-diiodoperfluorobutane and (trimethylsilyl)acetylene. The second, fifth, and last components were not identified. The third component identified as (*E*)-1,6-diiodo-1-(trimethylsilyl)-3,3,4,4,5,5,6,6-octafluorohexene: ^{1}H NMR ($CDCl_3$) δ 7.12 (t, J_{HF} = 15 Hz, 1 H, HC=C), 0.35 (t, J = 1.5 Hz, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 64.8 (t, 2 F, CF_2I), 108.2 (q, 2 F, CF_2CH=C), 114.8 (m, 2 F, CF_2), 123.4 (t, 2 F, CF_2).

Anal. Calcd for $C_9H_{10}F_8I_2Si$: C, 19.58; H, 1.83; F, 27.53; I, 45.98. Found: C, 19.70; H, 1.76; F, 27.39; I, 45.70.

The fourth fraction consisted of a 1:1.5 *E*/*Z* isomer mixture of the above compound. Assignments for the *Z* isomer are as follows: ^{1}H NMR ($CDCl_3$) δ 6.60 (t, $J_{H,F}$ = 12 Hz, 1 H, C=CH), 0.22 (s, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 64.8 (t, 2 F, CF_2I), 112.0 (q, 2 F, CF_2CH=C), 114.8 (m, 2 F, CF_2), 123.4 (t, 2 F, CF_2). The sixth component was an (*E*/*E*)/(*Z*/*Z*)/(*E*/*Z*) mixture of 3,3,4,4,5,5,6,6-octafluoro-1,8-diiodo-1,8-bis(trimethylsilyl)-1,7-octadiene ^{19}F NMR ($CDCl_3$) ϕ 116.9 (m, 2 F, CF_2CH=C, *E* isomer), 117.9 (m, 2 F, CF_2CH=C, *Z* isomer), 120.0 (m, 2 F, CF_2), 132.1 (m, 2 F, CF_2), 134.0 (m, 2 F, CF_2); IR (film) 3005 ($SiCH_3$), 2950 ($SiCH_3$), 1585 cm^{-1} (C=CH).

Anal. Calcd for $C_{14}H_{20}F_8I_2Si_2$: C, 25.86; H, 3.10; F, 23.37. Found: C, 26.17; H, 3.01; F, 23.81.

Reaction of Tetrafluoro-1,2-diiodoethane with (Trimethylsilyl)acetylene. A mixture of 0.106 g (0.30 mmol) of tetrafluoro-1,2-diiodoethane, 0.088 g (0.90 mmol) of (trimethylsilyl)acetylene, and 0.007 g (0.05 mmol) of di-*tert*-butyl peroxide was heated in a sealed tube for 36 h at 120 °C and for 25 h at 150 °C. GC (130 °C) showed that the major product was (*E*)- and (*Z*)-3,3,4,4-tetrafluoro-1,4-diiodo-1-trimethylsilylbutene.

E isomer: ^{1}H NMR ($CDCl_3$) δ 7.31 (tt, J = 14.5, 1 Hz, 1 H, CF_2CH=C), 0.36 (t, J = 1 Hz, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 66.2 (t, J_{FF} = 8 Hz, 2 F, ICF_2), 102.8 (m, 2 F, ICF_2CF_2).

Z isomer: ^{1}H NMR ($CDCl_3$) δ 6.79 (tt, J = 12, 1 Hz, 1 H, CF_2CH=C), 0.31 (s, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 66.8 (t, J_{FF} = 10 Hz, 2 F, ICF_2), 107.0 (m, 2 F, ICF_2CF_2).

Anal. Calcd for $C_7H_{10}F_4I_2Si$: C, 18.60; H,2.23. Found: C, 18.65; H, 2.05.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,10-diido-1,9-decadiene. A solution of 0.5 g of potassium hydroxide and 1.0 g (1.3 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene in 20 mL of methanol was allowed to stand for 18 h. The solution was diluted with 100 mL of water, and the product was extracted with two 50-mL portions of methylene chloride, washed with water, dried over magnesium sulfate, and stripped of solvent to give 0.46 g (56.5%) of a pale yellow oil that solidified on standing. An analytical sample was obtained by GC: mp 42–44 °C; ^{1}H NMR ($CDCl_3$) δ 7.22 (2 H, J_{HH} = 16 Hz, J_{HF} = 1 Hz, CHI), 6.60 (2 H, J_{HH} = 16 Hz, J_{HF} =

12 Hz, CH); ^{19}F NMR ($CDCl_3$) ϕ 113.6 (m, 4 F, CF_2), 122.8 (m, 4 F, CF_2), 124.4 (m, 4 F, CF_2).

Anal. Calcd for $C_{10}H_4F_{12}I_2$: C, 19.82; H, 0.66; F, 37.62; I, 41.89. Found: C, 19.93; H, 0.72; F, 37.40; I, 41.78.

3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiyne. A mixture of 15 g of potassium *tert*-butoxide and 250 mL of methylene chloride was stirred under nitrogen at −20 °C, and 12.8 g (0.017 mol) of 1,10-diiodo-1,10-bis(trimethylsilyl)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene was added dropwise. The slurry was stirred for 1 h at −20 °C and for 4 h at 0 °C, and the 100 mL of 3 N hydrochloride acid was added. The mixture was stirred for 1 h, and the organic layer was washed with water, dried, and distilled to give 1.92 g (32.5%) of the title compound: bp 55–59 °C (15–20 mm); ^{1}H NMR ($CDCl_3$) δ 2.93 (t, 2 H, J_{HF} = 4.5 Hz, CH); ^{19}F NMR ($CDCl_3$) ϕ 102 (m, 4 F, α-CF_2), 123.0 (m, 4 F, γ-CF_2), 124.4 (m, 4 F, β-CF_2); IR 3350 (CH), 2200 (C≡C), 1165 cm^{-1} (CF_2).

Anal. Calcd for $C_{10}H_2F_{12}$: C, 34.31; H, 0.57. Found: C, 34.08; H, 0.56.

Alternatively, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was used for the elimination. To a solution of 20.0 g (0.0256 mol), of 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene in 160 mL of freshly distilled tetrahydrofuran at −25 °C under nitrogen was added, over a 10-min period, 8.8 mL (0.08 mol) of DBU. The mixture was stirred for 1.5 h at −25 °C and was filtered. The precipitate was washed with pentane, and the combined solutions were washed with saturated sodium chloride solution and filtered through a short column of basic alumina. Distillation gave the diacetylene in 45–72% yield.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,11-dodecadiyne, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-Eicosafluoro-1,13-tetradecadiyne, and 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-Tetraeicosafluoro-1,15-hexadecadiyne. A slurry of 3 g (26 mmol) of potassium *tert*-butoxide in 40 mL of methylene chloride was stirred under nitrogen at −20 °C while 8.2 g of a solution of $(CH_3)_3SiC{\equiv}CH(CF_2)_8CH{=}CHSi(CH_3)_3$, $(CH_3)_3SiC{\equiv}CH(CF_2)_{10}CH{=}CHSi(CH_3)_3$, and $(CH_3)_3SiC{\equiv}CH(CF_2)_{12}CH{=}CHSi(CH_3)_3$ in 20 mL of methylene chloride was added dropwise. The reaction mixture was stirred for 1 h at −20 °C and for 3 h at 0 °C. Potassium fluoride (1.5 g) and 25 mL of *tert*-butyl alcohol were then added, and the mixture was stirred for 3 h at ambient temperature. Methylene chloride (100 mL) was added, and the solution was washed with five 100-mL portions of water, dried over magnesium sulfate, and stripped of solvent. The residue, analyzed by GC, was shown to contain 1.3 g of $HC{\equiv}C(CF_2)_8C{\equiv}CH$, 0.73 g of $HC{\equiv}C(CF_2)_{10}C{\equiv}CH$, and 0.22 g of $HC{\equiv}C(CF_2)_{12}C{\equiv}CH$ (total yield 50%). Analytical samples were isolated by GC.

Hexadecafluoro-1,11-dodecadiyne [$HC{\equiv}C(CF_2)_8C{\equiv}CH$] was a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 2.94 (t, J_{HF} = 4.5 Hz, CH); ^{19}F NMR ($CDCl_3$) ϕ 102 (m, 4 F, α-CF_2), 122.8 (m, 8 F, internal fluorines), 124 (m, 4 F, β-CF_2); IR 3355 (CH), 2195 (C≡C), 1190 cm^{-1} (CF_2).

Anal. Calcd for $C_{12}H_2F_{16}$: C, 32.02; H, 0.45. Found: C, 32.44; H, 0.55.

Eicosafluoro-1,13-tetradecadiyne [$HC{\equiv}C(CF_2)_{10}C{\equiv}CH$] was a colorless oil: ^{1}H NMR ($CDCl_3$) δ 2.94 (t, J_{HF} = 4.5 Hz, CH); ^{19}F NMR ($CDCl_3$) ϕ 102 (m, 4 F, α-CF_2), 122.8 (m, 12 F, internal F), 124.2 (m, 4 F, β-CF_2); IR 3355 (CH), 2200 (C≡C), 1195 cm^{-1} (CF_2).

Anal. Calcd for $C_{14}H_2F_{20}$: C, 30.57; H, 0.37; F, 69.07. Found: C, 30.27; H, 0.38; F, 68.84.

Tetraeicosafluoro-1,15-hexadecadiyne [$HC{\equiv}C(CF_2)_{12}C{\equiv}CH$] was a white solid: mp 54–56 °C; ^{1}H NMR ($CDCl_3$) δ 2.94 (t, J_{HF} = 4.5 Hz, CH); ^{19}F NMR ($CDCl_3$) ϕ 102 (m, 4 F, α-CF_2), 122.8 (m, 16 F, internal F), 124.2 (m, 4 F, β-CF_2); IR 3355 (CH), 2200 (C≡C), 1190 cm^{-1} (CF_2).

Anal. Calcd for $C_{16}H_2F_{24}$: C, 29.56; H, 0.31; F, 70.13. Found: C, 29.30; H, 0.31; F, 70.23.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluorononyne. To 10.0 g (0.0168 mol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene in 60 mL of tetrahydrofuran at −25 °C was added, over a period of 10 min, 5.6 mL (0.0505 mol) of DBU. The mixture was stirred at −25 °C for 2 h and was then filtered. The precipitate was washed with cold pentane. The combined organic solutions were washed with brine, filtered through basic alumina, and distilled to give 3.25 g (39%) of 80% pure (by GC) 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononyne contaminated with silane byproducts (bp 120–155 °C). An analytical sample was isolated by GC (78 °C): ^{1}H NMR ($CDCl_3$) δ 2.93 (t, J = 6 Hz, ≡CH); ^{19}F NMR ($CDCl_3$) ϕ 85.1 (t, J = 10 Hz, 3 F, CF_3) 102.4 (m, 2 F, ≡CCF_2), 113.4 (m, 2 F, CF_2), 124.2 (m, 6 F, CF_2), 128.0 (m, 2 F, CF_2).

Anal. Calcd for C_9HF_{15}: C, 27.43; H, 0.26. Found: C, 27.51; H, 0.28.

(*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-1-iodo-1-phenylnonene. A mixture of 3.0 g (6.0 mmol) of perfluoroheptyl iodide, 0.60 g (6.0 mmol) of phenylacetylene, and 0.5 mL of di-*tert*-butyl peroxide was sealed in a glass tube under vacuum and was heated for 48 h at 120 °C. The product was dissolved in methylene chloride, dried over magnesium sulfate, and stripped of solvent to give 3.24 g (89%) of essentially pure (*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-phenylnonene. An analytical sample was isolated by GC: mp 49–51 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (s, 5 H, C_6H_5), 6.51 (t, $J_{H,F}$ = 12 Hz, 1 H, CH); ^{19}F NMR ($CDCl_3$) ϕ 85.6 (t, 3 F, CF_3), 108.0 (q, 2 F, CF_2), 123.6 (m, 2 F, CF_2), 124.4 (m, 6 F, CF_2), 128.0 (m, 2 F, CF_2).

Anal. Calcd for $C_{15}H_6F_{15}I$: C, 30.12; H, 1.01; F, 47.65; I, 21.22. Found: C, 30.18; H, 1.22; F, 47.30; I, 21.10.

1-Phenylperfluorononyne. A solution of 3.0 g (5.04 mmol) of 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentafluoro-1-iodo-1-phenylnonene in 20 mL of dry methylene chloride was added dropwise to a stirred suspension of 1.1 g of potassium *tert*-butoxide in 40 mL of dry methylene chloride at −20 °C. The mixture was stirred for 1 h at −20 °C and for 2 h at 0 °C. The mixture was stirred for 1 h with 20 mL of 3 N hydrochloric acid. The organic layer was washed with water and dried over magnesium sulfate. Solvent was removed to give 1.84 g (78%) of essentially pure 1-phenylperfluorononyne. An analytical sample was obtained by GC: ^{1}H NMR ($CDCl_3$) δ 7.33 (m, 5 H, C_6H_5); ^{19}F NMR ($CDCl_3$) ϕ 84.8 (t, 3 F, CF_3), 100 (t, 2 F, CF_2), 122.8 (m, 2 F, CF_2), 124.0 (m, 6 F, CF_2), 127.6 (m, 2 F, CF_2).

Anal. Calcd for $C_{15}H_5F_{15}$: C, 38.32; H, 1.07; F, 60.61. Found: C, 37.85; H, 1.14; F, 59.37.

(*E*,*E*)-3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-2,9-bis[(iodomethyl)dimethylsilyl]-1,10-bis(trimethylsilyl)-1,9-decadiene. A mixture of 3.7 g (0.0066 mol) of 1,6-diiodoperfluorohexane, 2.3 g (0.0133 mol) of bis(trimethylsilyl)acetylene, and 0.5 mL of di-*tert*-butyl peroxide was sealed under vacuum in a heavy-walled glass tube, and the tube was heated at 120 °C for 48 h. The mixture was dissolved in 50 mL of methylene chloride, washed with three 50-mL portions of water, dried over magnesium sulfate, and stripped of solvent with a rotary evaporator to give 4.5 g (75%) of essentially pure product (NMR) as an off-white solid, mp 62–68 °C. Recrystallization from methanol CH_3OH afforded an analytical sample: mp 68–70 °C; ^{1}H NMR ($CDCl_3$) δ 6.83 (br s, 2 H, CH), 2.08 (s, 4 H, CH_2I), 0.35 (s, 12 H, CH_3), 0.17 (s, 18 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 104.4 (m, 4 F, CF_2), 120.4 (m, 4 F, CF_2), 123.2 (m, 4 F, CF_2).

Anal. Calcd for $C_{22}H_{36}F_{12}I_2Si_4$: C, 29.54; H, 4.06; I, 28.37. Found: C, 29.38; H, 4.37; I, 27.99.

(*E*)-3,3,4,4,5,5,5-Heptafluoro-2-[(iodomethyl)dimethylsilyl]-1-(trimethylsilyl)pentene. By the above procedure, 0.300 g (0.001 mol) of perfluoropropyl iodide, 0.170 g (0.001 mol) of bis(trimethylsilyl)acetylene, and 0.25 mL of di-*tert*-butyl peroxide gave 0.40 g (84%) of the title compound. An analytical sample was isolated by GC: ^{1}H NMR ($CDCl_3$) δ 6.65 (br s, 1 H, CH), 2.07 (s, 2 H, CH_2I), 0.37 (s, 6 H, CH_3), 0.18 (s, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 84.8 (t, 3 F, CF_3), 105.2 (d, 2 F, CF_2), 124.8 (s, 2 F, CF_2).

Anal. Calcd for $C_{11}H_{18}F_7ISi_2$: C, 28.33; H, 3.89; F, 28.52; I, 27.21. Found: C, 28.12; H, 3.77; F, 28.52; I, 27.45.

(*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-Pentadecafluoro-2-[(iodomethyl)dimethylsilyl]-1-(trimethylsilyl)nonene. By the above procedure, 0.50 g (0.001 mol) of perfluoroheptyl iodide, 0.170 g (0.001 mol) of bis(trimethylsilyl)acetylene, and 0.25 mL of di-*tert*-butyl peroxide gave 0.56 g (85%) of the title compound. An analytical sample was isolated by GC: ^{1}H NMR ($CDCl_3$) δ 6.71 (br s, 1 H, CH), 2.05 (s, 2 H, CH_2I), 0.33 (s, 6 H, CH_3), 0.18 (s, 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, 3 F, CF_3), 104.4 (m, 2 F, CF_2), 120.4 (m, 2 F, CF_2), 123.6 (m, 6 F, CF_2), 127.6 (m, 2 F, CF_2); IR (film) 3010 (CH_3), 1200 cm^{-1} (CF_2).

Anal. Calcd for $C_{12}H_{18}F_{15}ISi_2$: C, 27.04; H, 2.72; F, 42.77; I, 19.04. Found: C, 27.14; H, 2.78; F, 42.54; I, 18.91.

1,12-Bis(trimethylsilyl)perfluoro-1,11-dodecadiyne. A heavy-walled silylated glass tube, loaded with 4.2 g (0.025 mol) of bis(trimethylsilyl)acetylene, 5.0 g (0.00765 mol) of 1,8-diiodoperfluorooctane, and 0.024 g (0.0001 mol) of iodine, was evacuated at −78 °C, filled with nitrogen, and sealed. The tube was heated at 200 °C for 57 h. Bulb-to-bulb distillation at 90–110 °C (0.02–0.05 mm) gave 3.91 g (86%) of 1,12-bis(trimethylsilyl)perfluorododeca-1,11-diyne as a pink liquid (>97% pure by GC). An analytical sample was obtained by preparative GC at 125 °C; ^{1}H NMR ($CDCl_3$, CH_2Cl_2) δ 0.37 (s, $SiCH_3$); ^{19}F NMR ($CDCl_3$, $CFCl_3$) ϕ 100.8 (m, 4 F, $CF_2C{\equiv}C$), 123.2 (m, 8 F, CF_2), 124.3 (m, 4 F, CF_2); IR (film) 3000 ($SiMe_3$), 2940 ($SiMe_3$), 2230 (C≡C), 1200 cm^{-1} (CF_2).

Anal. Calcd for $C_{12}H_{18}F_{16}Si_2$: C, 36.37; H, 3.05; F, 51.13. Found: C, 36.18; H, 3.00; F, 50.90.

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,11-dodecadiyne. A mixture of 38.4 g (0.0646 mol) of 1,12-bis(trimethylsilyl)perfluoro-1,11-dodecadiyne, 60.7 g (0.646 mol) of potassium fluoride dihydrate, and 150 mL of methanol was stirred at room temperature for 20 h. Saturated sodium chloride solution and ether were added, and the phases were separated. The aqueous phase was extracted several times with ether, and the combined ether solutions were washed with brine, dried over magnesium sulfate, and distilled to give 23.0 g (79%) of the diacetylene as a pale pink liquid: bp 85–90 °C (30 mm); ^{1}H NMR ($CDCl_3$) δ 2.94 (t, J_{HF} = 4.5 Hz, C≡CH); ^{19}F NMR ($CDCl_3$) ϕ 102.0 (m, 4 F, $CF_2C{\equiv}$), 122.8 (m, 8 F, $\equiv CCF_2CF_2$), 124.0 (m, 4 F, $\equiv CCF_2CF_2CF_2CF_2$); IR (film) 3355 (CH), 2195 (C≡C), 1190 cm^{-1} (CF_2).

Anal. Calcd for $C_{12}H_2F_{16}$: C, 32.02; H, 0.45; F, 67.53. Found: C, 32.44; H, 0.55; F, 65.56.

1-(Trimethylsilyl)perfluorononyne. A mixture of 11.8 g (0.070 mmol) of bis(trimethylsilyl)acetylene, 30.0 g (0.060 mol) of perfluoroheptyl iodide, and 0.022 g (0.000 09 mol) of iodine was heated for 71 h at 200 °C in a Monel bomb. The product was dissolved in methylene chloride, washed with sodium thiosulfate solution, dried, and distilled to give 18.4 g (65%) of 1-(trimethylsilyl)nonyne: bp 39–40 °C (0.27–0.37 mm); ^{1}H NMR ($CDCl_3$, CH_2Cl_2) δ 0.15 (s, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 85.6 (t, J = 10 Hz, 3 F, CF_3), 101.2 (t, J = 8 Hz, 2 F, $CF_2C{\equiv}$), 122.8 (m, 2 F, CF_2), 124.0 (m, 6 F, CF_2), 127.6 (m, 2 F, CF_2); IR (film) 3000 ($SiCH_3$), 2940 ($SiCH_3$), 2230 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

Anal. Calcd for $C_{12}H_9F_{15}Si$: C, 30.91; H, 1.94. Found: C, 30.98; H, 1.68.

1-(Trimethylsilyl)perfluorooctyne, 1-(Trimethylsilyl)-perfluorodecyne, and 1-(Trimethylsilyl)perfluorododecyne. A commercial mixture of perfluoroalkyl iodides (CF_3CF_2-$(CF_2CF_2)_{2-5}$ I, Hoechst perfluoroalkyljodid 25) was subjected to the above reaction. Thus, 26.7 g of the mixture was heated with 10.0 g of bis(trimethylsilyl)acetylene and 0.12 g of iodine for 66 h at 200 °C. Kugelrohr distillation [25–75 °C (0.1–0.02 mm)] gave 21.7 g of a mixture of the (trimethylsilyl)acetylenes. Samples of the three major components were isolated by preparative GC at 80 °C. 1-(Trimethylsilyl)perfluorooctyne was a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.44 (s, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 86.1 (m, 3 F, CF_3), 102.1 (t, J = 11 Hz, 2 F, $CF_2C{\equiv}$), 124.4 (m, 2 F, $CF_2CF_2C{\equiv}$), 125.6 (m, 4 F, $CF_3CF_2CF_2CF_2$), 129.0 (m, 2 F, CF_3CF_2); IR (film) 3000 (CH), 2230 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

Anal. Calcd for $C_{11}H_9F_{13}Si$: C, 31.74; H, 2.18; F, 59.33. Found: C, 31.60; H, 2.22; F, 59.12.

1-(Trimethylsilyl)perfluorodecyne was a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.35 (s, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 86.2 (t, J = 10 Hz, 3 F, CF_3), 102.2 (t, J = 11 Hz, 2 F, $CF_2C{\equiv}$), 125.2 (m, 10 F, $CF_3CF_2(CF_2)_5$), 129.2 (m, 2 F, CF_3CF_2): IR (film) 3010 (CH), 2250 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

Anal. Calcd for $C_{13}H_9F_{17}Si$: C, 30.24; H, 1.76; F, 62.56. Found: C, 30.13; H, 1.77; F, 62.80.

1-(Trimethylsilyl)perfluorododecyne was a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 0.40 (s, CH_3); ^{19}F NMR ($CDCl_3$, $CFCl_3$) ϕ 86.0 (t, J = 10 Hz, 3 F, CF_3), 102.0 (m, 2 F, $CF_2C{\equiv}$), 124.8 (m, 14 F, CF_2), 128.9 (m, 2 F, CF_2CF_3); IR (film) 3020 (CH), 2250 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

Anal. Calcd for $C_{15}H_9F_{21}Si$: C, 29.23; H, 1.47; F, 64.74. Found: C, 28.59; H, 1.53; F, 63.71.

Reaction of 1-(Trimethylsilyl)perfluorononyne with Methanol. A mixture of 0.40 g (0.86 mmol) of 1-(trimethylsilyl)perfluorononyne, 0.6 g (4.3 mmol) of anhydrous potassium carbonate, and 1.5 mL of methanol was stirred at room temperature under nitrogen for 15 h. Water was added, and the product was extracted into ether. The ether solution was washed with water, dried over magnesium sulfate, and stripped of solvent to give 0.33 g of a 7.3:1 mixture (by GC) of 1,1-dimethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononane (73%) and 1-methoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononene (11%). The mixture was separated by preparative GC at 60 °C. The olefin consisted of a 5.8:1 mixture of Z and E isomers; an analytical sample of the major isomer was isolated as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 6.31 (d t, J_{HH} = 7.2 Hz, J_{HF} = 1.8 Hz, 1 H, C=CHOMe), 4.44 (d t, J_{HH} = 7.2 Hz, J_{HF} = 15 Hz, 1 H, $CF_2CH{=}$), 3.77 (s, 3 H, OCH_3); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, J = 10 Hz, 3 F, CF_3), 108.8 (q, J = 23 Hz, 2 F, $CF_2CH{=}$), 124.2 (m, 6 F, CF_2), 125.6 (m, 2 F, CF_2), 128.0 (m, 2 F, CF_2).

Anal. Calcd for $C_{10}H_5F_{15}O$: C, 28.19; H, 1.18. Found: C, 28.29; H, 1.15.

The dimethoxy compound was isolated as a colorless liquid: ^{1}H NMR ($CDCl_3$) δ 4.76 (t, J = 6 Hz, 1 H, $CH_2CH(OMe)_2$), 3.39 (s, 6 H, OCH_3), 2.40 (m, 2 H, CF_2CH_2); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, J = 10 Hz, 3 F, CF_3), 124.2 (m, 10 F, CF_2), 128.0 (m, 2 F, CF_2).

Anal. Calcd for $C_{11}H_9F_{15}O_2$: C, 28.84; H, 1.98; F, 62.20. Found: C, 28.62; H, 1.86; F, 62.39.

Reaction of 1,4-Diiodoperfluorobutane with Bis(trimethylsilyl)acetylene. A mixture of 41 g (0.024 mol) of bis(trimethylsilyl)acetylene, 10.0 g (0.022 mol) of 1,4-diiodoperfluorobutane, and 0.11 g (0.000 44 mol) of iodine was heated by the above procedure for 70 h at 200 °C. Bulb-to-bulb distillation [30–50 °C (0.12 mm), −78 °C receiver] gave 7.6 g (81%) of the cyclic adduct as a purple liquid. An analytical sample was isolated by preparative GC (115 °C): ^{1}H NMR ($CDCl_3$) δ 0.50 (t, J_{HF} = 1 Hz, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 104.4 (m, 2 F, CF_2), 113.6 (m, 2 F, CF_2), 135.2 (m, 2 F, CF_2), 136.8 (m, 2 F, CF_2); IR (film) 3000 ($SiMe_3$), 2940 ($SiMe_3$), 1590 cm^{-1} (C=C).

Anal. Calcd for $C_9H_9F_8ISi$: C, 25.49; H, 2.14; F, 35.82; I, 29.92. Found: C, 25.27; H, 2.11; F, 36.02; I, 30.27.

Reaction of 1,6-Diiodoperfluorohexane with Bis(trimethylsilyl)acetylene. A mixture of 1.24 g (0.0073 mol) of bis(trimethylsilyl)acetylene, 2.0 g (0.0036 mol) of 1,6-diiodoperfluorohexane, and 0.12 (0.0005 mol) of iodine was heated by the above procedure for 24 h at 200 °C. Bulb-to-bulb distillation of the product [70–84 °C (0.02–0.03 mm)] gave 1.09 g of liquid shown by GC to contain 0.65 g (36%) of 1,10-bis(trimethylsilyl)perfluoro-1,9-decadiyne and 0.22 g (12%) of the cyclic adduct (see discussion). Analytical samples were isolated by GC at 105 °C. The latter was isolated as a pale orange liquid: ^{1}H NMR ($CDCl_3$) δ 0.55 (t, J = 1 Hz, $Si(CH_3)_3$); ^{19}F NMR ($CDCl_3$) ϕ 97.6 (m, 2 F, $CF_2C{=}C$, 105.4 (m, 2 F, $CF_2C{=}C$), 124.2 (m, 2 F, CF_2), 126.5 (m, 2 F, CF_2), 129.6 (m, 2 F, CF_2), 130.4 (m, 2 F, CF_2); IR (film) 3000 ($SiMe_3$), 2940 ($SiMe_3$), 1550 cm^{-1} (C=C).

Anal. Calcd for $C_{11}H_9F_{12}ISi$: C, 25.20; H, 1.73; F, 43.49; I, 24.21. Found: C, 24.97; H, 1.70; F, 43.62; I, 24.38.

1,10-Bis(trimethylsilyl)perfluoro-1,9-decadiyne was isolated as a pale pink liquid: ^{1}H NMR (CDCl) δ 0.27 (s, 18 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 101.3 (m, 4 F, $C{\equiv}CF_2$), 123.4 (m, 4 F, CF_2), 124.8 (m, 4 F, CF_2); IR (film) 3000 ($SiMe_3$), 2940 ($SiMe_3$), 2220 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiMe_3$).

Anal. Calcd for $C_{16}H_{18}F_{12}Si_2$: C, 38.86; H, 3.67; F, 46.11. Found: C, 38.72; H, 3.67; F, 46.25.

Registry No. 3,3,4,4,5,5,6,6-Octafluoro-1,8-diiodooctane, 2681-00-7; ethylene, 74-85-1; 1,4-diiodoperfluorobutane, 375-50-8; 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiododecane, 1813-83-8; 1,6-diiodoperfluorohexane, 375-80-4; 3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene, 678-65-9; 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiene, 1800-91-5; 3,3,4,4,5,5,6,6-octafluoro-1,2,7,8-tetrabromooctane, 81388-07-0; 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,2,9,10-tetrabromodecane, 81388-08-1; 2,7-dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene, 81388-09-2; 1,2,7,8-tetrabromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene, 81388-10-5; (trimethylsilyl)acetylene, 1066-54-2; (*E*,*E*)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene, 81388-11-6; (*Z*,*Z*)-3,3,4,4,5,5,6,6,7,7,8,8-dodeca-

fluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene, 81388-12-7; (*E,Z*)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,10-bis(trimethylsilyl)-1,9-decadiene, 81388-13-8; (*E*)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,8-diiodo-1-(trimethylsilyl)octene, 81388-14-9; (*Z*)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,8-diiodo-1-(trimethylsilyl)octene, 81388-15-0; (*E,E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-diiodo-1,12-bis(trimethylsilyl)-1,11-dodecadiene, 81388-16-1; (*Z,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-diiodo-1,12-bis(trimethylsilyl)-1,11-dodecadiene, 81388-17-2; (*E,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,12-diiodo-1,12-bis(trimethylsilyl)-1,11-dodecadiene, 81388-18-3; (*E,E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-eicosafluoro-1,14-diiodo-1,14-bis(trimethylsilyl)-1,13-tetradecadiene, 81388-19-4; (*Z,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-eicosafluoro-1,14-diiodo-1,14-bis(trimethylsilyl)-1,13-tetradecadiene, 81388-20-7; (*E,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-eicosafluoro-1,14-diiodo-1,14-bis(trimethylsilyl)-1,13-tetradecadiene, 81388-21-8; (*E,E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-tetraeicosafluoro-1,16-diiodo-1,16-bis(trimethylsilyl)-1,15-hexadecadiene, 81388-22-9; (*Z,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-tetraeicosafluoro-1,16-diiodo-1,16-bis(trimethylsilyl)-1,15-hexadecadiene, 81388-23-0; (*E,Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14-tetraeicosafluoro-1,16-diiodo-1,16-bis(trimethylsilyl)-1,15-hexadecadiene, 81388-24-1; 1,8-diiodoperfluorooctane, 335-70-6; 1,10-diiodoperfluorodecane, 65975-18-0; 1,12-diiodoperfluorododecane, 72049-11-7; (*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)nonene, 81388-25-2; (*Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-(trimethylsilyl)-nonene, 81388-26-3; perfluoroheptyl iodide, 335-58-0; (*E*)-1,6-diiodo-1-(trimethylsilyl)-3,3,4,4,5,5,6,6-octafluorohexene, 81388-27-4; (*Z*)-1,6-diiodo-1-(trimethylsilyl)-3,3,4,4,5,5,6,6-octafluorohexene, 81388-28-5; (*E,E*)-3,3,4,4,5,5,6,6-octafluoro-1,8-diiodo-1,8-bis(trimethylsilyl)-1,7-octadiene, 81388-29-6; (*Z,Z*)-3,3,4,4,5,5,6,6-octafluoro-1,8-diiodo-1,8-bis(trimethylsilyl)-1,7-octadiene, 81388-30-9; (*E,Z*)-3,3,4,4,5,5,6,6-octafluoro-1,8-diiodo-1,8-bis(trimethylsilyl)-1,7-octadiene, 81388-31-0; tetrafluoro-1,2-diiodoethane, 354-65-4; (*E*)-3,3,4,4-tetrafluoro-1,4-diiodo-1-(trimethylsilyl)butene, 81388-32-1; (*Z*)-3,3,4,4-tetrafluoro-1,4-diiodo-1-(trimethylsilyl)butene, 81388-33-2; 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,10-diiodo-1,9-decadiene, 81388-34-3; 3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-1,9-decadiyne, 81388-35-4; 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-hexadecafluoro-1,11-dodecadiyne, 81388-36-5; 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12-eicosafluoro-1,13-tetradecadiyne, 81388-37-6; 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,11-,11,12,12,13,13,14,14-tetraeicosafluoro-1,15-hexadecadiyne, 81388-38-7; 3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononyne, 81388-39-8; phenylacetylene, 536-74-3; (*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-1-iodo-1-phenylnonene, 81388-40-1; 1-phenylperfluorononyne, 52717-10-9; bis(trimethylsilyl)acetylene, 14630-40-1; (*E,E*)-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluoro-2,9-bis[(iodomethyl)dimethylsilyl]-1,10-bis(trimethylsilyl)-1,9-decadiene, 81388-41-2; (*E*)-3,3,4,4,5,5,5-heptafluoro-2-[(iodomethyl)dimethylsilyl]-1-(trimethylsilyl)pentene, 81388-42-3; perfluoropropyl iodide, 754-34-7; (*E*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluoro-2-[(iodomethyl)dimethylsilyl]-1-(trimethylsilyl)nonene, 81388-43-4; 1,12-bis(trimethylsilyl)perfluoro-1,11-dodecadiyne, 81388-44-5; 1-(trimethylsilyl)perfluorononyne, 81388-45-6; 1-(trimethylsilyl)perfluorooctyne, 81388-46-7; 1-(trimethylsilyl)perfluorodecyne, 81388-47-8; 1-(trimethylsilyl)perfluorododecyne, 81388-48-9; perfluorohexyl iodide, 355-43-1; perfluorooctyl iodide, 507-63-1; perfluorodecyl iodide, 423-62-1; 1,1-dimethoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononane, 81388-49-0; (*E*)-1-methoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononene, 81388-50-3; (*Z*)-1-methoxy-3,3,4,4,5,5,6,6,7,7,8,8,9,9,9-pentadecafluorononene, 81388-51-4; 1,10-bis(trimethylsilyl)perfluoro-1,9-decadiyne, 81388-52-5.

On the Mechanism of the Conversion of Dethiobiotin to Biotin in *E. coli*. Studies with Deuterated Precursors Using Tandem Mass Spectroscopic (MS-MS) Techniques

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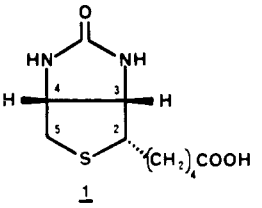
The last step of the biosynthesis of biotin (1), i.e., the conversion of dethiobiotin (2) into biotin has been studied in *E. coli* by starting from specifically deuterated precursors: [3-$^2H_{0;1}$,4-$^2H_{1;0}$]-, [5,5,5-$^2H_3$]-, and [6,6-$^2H_2$]-*dl*-dethiobiotins. Deuterium has been localized in the biosynthesized biotin by using MS–MS techniques. In each case, it is possible to conclude to the absence of deuterium migration: the two C–S bonds of biotin are formed with removal of only one hydrogen from C-2 and C-5 and without involvement of the adjacent positions.

Deuterium is now widely used instead of tritium for biosynthetic experiments, its localization by NMR avoiding degradation experiments. However, when very low amounts of material are produced, ^2H NMR is not sensitive enough. Isotope determination by mass spectrometry requires a highly purified product, not always easily available with small quantities. This problem can now be overcome by using MS–MS techniques,[2] which allow the localization of deuterium even on very small amounts of an impure sample.

We report here some studies on biotin biosynthesis which illustrate the advantages of this method.

The last step of the biosynthesis of biotin (1), i.e., the conversion of dethiobiotin (2) to biotin[3] has been intensively studied by using specifically tritiated dethiobiotins.



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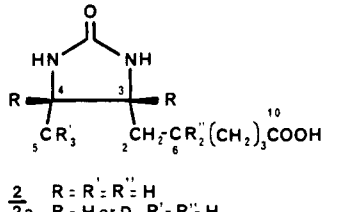

2 R = R' = R'' = H
2a R = H or D, R' = R'' = H
2b R' = D, R = R'' = H
2c R'' = D, R = R' = H

In our first investigation,[4] we have shown, using doubly labeled samples, that [10-^{14}C,3,4-$^3H_2$]dethiobiotin was converted into biotin by *E. coli*, with complete tritium retention. The same results have been obtained by Parry[5] with *Aspergillus niger* as the microorganism. In the same

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(2) F. W. Mc Lafferty, *Acc. Chem. Res.*, **13**, 33 (1980).
(3) M. A. Eisenberg, *Adv. Enzymol.*, **38**, 317 (1973).
(4) G. Guillerm, F. Frappier, M. Gaudry, and A. Marquet, *Biochimie*, **59**, 119, (1977).
(5) R. J. Parry and M. G. Kunitani, *J. Am. Chem. Soc.*, **98**, 4024 (1976).

0022-3263/82/1947-2257$01.25/0