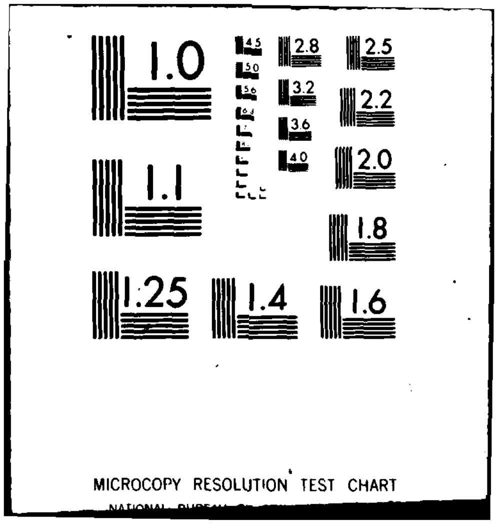
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Synthesis of Fluorinated Acetylenes

by

Kurt Baum, Clifford D. Bedford and Ronald J. Hunadi

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Fluorochem, Inc.
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New routes to fluorinated acetylenes were developed based on additions of iodofluorocarbons to silylacetylenes. Free radical addition of , -diiodoperfluoroalkanes to trimethylsilylacetylene gave the iodotrimethylsilylolefins, $Me_3SiIC{=}Ch(CF_2)_nCH{=}CISiMe_3$, which reacted with potassium t-butoxide or DBU to give the trimethylsilylacetylenes, and with an excess of the base, the free diacetylenes. Perfluoroalkyl iodides similarly gave perfluoroalkyl acetylenes.

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The addition of perfluoroheptyl iodide to phenylacetylene, followed by treatment with potassium t-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 trimethylsilylacetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated based on addition of perfluoroiodo compounds to ethylene, dehydroiodination, bromination and elimination.

Synthesis of Fluorinated Acetylenes[1]

Kurt Baum,* Clifford D. Bedford and Ronald J. Hunadi

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Abstract

New routes to fluorinated acetylenes were developed based on additions of iodofluorocarbons to silylacetylenes. Free radical addition of α,ω-diiodoperfluoroalkanes to trimethylsilylacetylene gave the iodotrimethylsilylolefins, $Me_3SiIC{=}CH(CF_2)_nCH{=}CISiMe_3$, which reacted with potassium *t*-butoxide or DBU to give the trimethylsilylacetylenes, 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 *t*-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 trimethylsilylacetylenes, which were desilylated with potassium fluoride. A route to diacetylenes was investigated based on 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%). Perfluoroethylacetylene 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 1). More recently,[6] this approach was used to prepare the perfluorobutyl, perfluorohexyl and perfluorooctyl analogs.

Scheme 1

$$CF_3CH{=}CH_2 \xrightarrow{Br_2} CF_3CHBrCH_2Br \xrightarrow{KOH} CF_3CBr{=}CH_2$$

$$\xrightarrow{Br_2} CF_3CBr_2CH_2Br \xrightarrow{KOH} CF_3CBr{=}CHBr \xrightarrow{Zn} CF_3C{\equiv}CH$$

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 2). 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% yield. 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 2

$$I(CF_2)_nI + CH_2{=}CH_2 \longrightarrow ICH_2CH_2(CF_2)_nCH_2CH_2I$$

$$\xrightarrow{KOH} CH_2{=}CH(CF_2)_nCH{=}CH_2 \xrightarrow{Br_2} BrCH_2CHBr(CF_2)_nCHBrCH_2Br \qquad n = 4,\ 6$$

$$BrCH_2CHBr(CF_2)_4CHBrCH_2Br \xrightarrow{KOH} CH_2{=}CBr(CF_2)_4CBr{=}CH_2$$

$$\xrightarrow{Br_2} BrCH_2CBr_2(CF_2)_4CBr_2CH_2Br \xrightarrow{KOH} BrCH{=}CBr(CF_2)_4CBr{=}CHBr$$

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

We undertook the synthesis of fluorocarbon acetylenes by the free radical addition of iodofluorocarbons to trimethylsilylacetylene.

Treatment of 1,6-diiodoperfluorohexane with an excess of trimethylsilylacetylene in the presence of di-t-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(trimethylsil 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, based on 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.

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

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

$$CF_3(CF_2)_6I \;+\; HC{\equiv}CSiMe_3 \longrightarrow CF_3(CF_2)_6CH{=}CI(SiMe_3)$$

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 analogs.[11] The vinyl proton of (E)-1-iodo-1-trimethylsilylhexene appears at δ7.1 (t, J_{HH} = 8 Hz) and that of the (Z) isomer, at δ6.1 (t, J_{HH} = 6 Hz). The respective values for the fluorinated compounds are δ7.1 (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 111-113 ppm.

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 $ICH{=}CH(CF_2)_6CH{=}CHI$, and attempts to dehydroiodinate this olefin were unsuccessful. The most satisfactory reagents to effect elimination to the silyl acetylene were potassium t-butoxide in methylene chloride at -20°C and DBU in tetrahydrofuran at -25°C. An excess 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, 45 to 72%. The analogous dodecadiyne, tetradecadiyne and hexadecadiyne were prepared from the mixture of the iodo silyl olefins described above, and pentadecafluorononyne was prepared similarly.

$$(Me_3Si)IC{=}CH(CF_2)_nCH{=}CI(SiMe_3) \xrightarrow[\text{DBU/THF}]{\text{KO-}\underline{\text{t}}\text{-Bu/CH}_2\text{Cl}_2\text{ or}} Me_3SiC{\equiv}C(CF_2)_nC{\equiv}CSiMe_3$$

$$\longrightarrow HC{\equiv}C(CF_2)_nC{\equiv}CH \qquad n = 6,\ 8,\ 10,\ 12$$

$$CF_3(CF_2)_6CH{=}CI(SiMe_3) \longrightarrow CF_3(CF_2)_6C{\equiv}CH$$

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 t-butoxide in methylene chloride gave a 78% yield of the acetylene. Several adducts of fluorocarbon iodides with aliphatic acetylenes have been reported recently.[12]

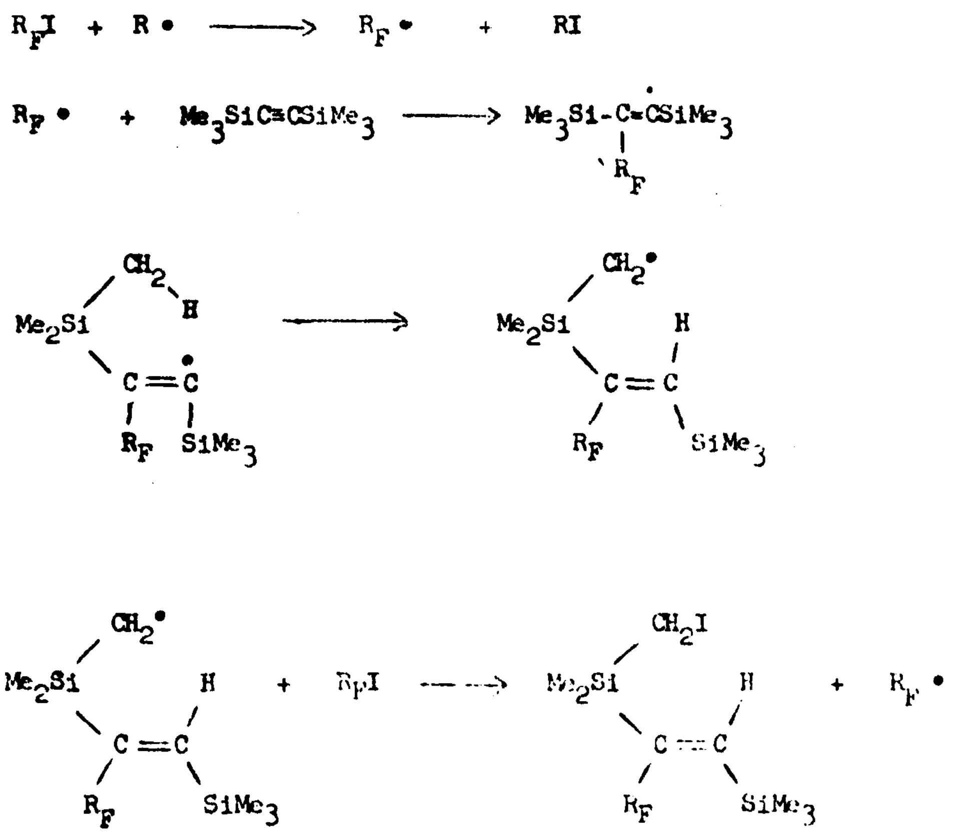
$$C_6H_5C{\equiv}CH + I(CF_2)_6CF_3 \xrightarrow[120^\circ C]{\underline{t}\text{-Bu-O-O-}\underline{t}\text{-Bu}} C_6H_5IC{=}CH(CF_2)_6CF_3 \xrightarrow{\text{KO-}\underline{t}\text{-Bu}} C_6H_5C{\equiv}C(CF_2)_6CF_3$$

Bis(trimethylsilyl)acetylene Additions. In the formation of acetylenes from the adducts of fluorinated iodides with trimethylsilylacetylene, 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-t-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 3.

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]

Scheme 3



$R_F = -(CF_2)_6-,\ CF_3(CF_2)_2-,\ CF_3(CF_2)_6-$

It was reasoned that this intramolecular hydrogen transfer might be averted if a better source of iodine 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. Thus, the initial adduct spontaneously eliminated trimethylsilyl iodide to give the silylated acetylene

$$I(CF_2)_8I + Me_3SiC{\equiv}CSiMe_3 \longrightarrow \left[(Me_3Si)IC{=}C(SiMe_3)(CF_2)_8(SiMe_3)C{=}CI(SiMe_3)\right]$$

$$\longrightarrow ISiMe_3 + Me_3SiC{\equiv}C(CF_2)_8C{\equiv}CSiMe_3$$

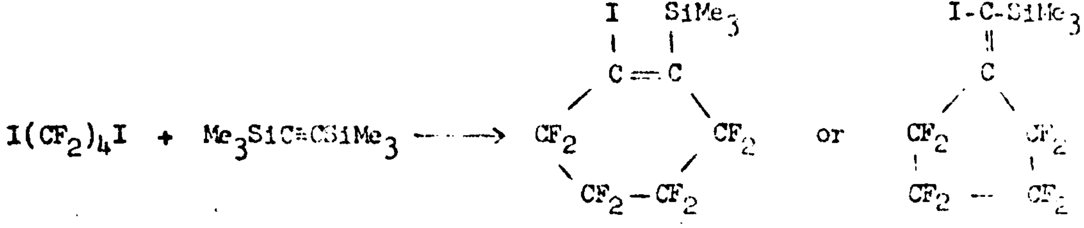
Monofunctional perfluoroalkyl iodides reacted similarly; 1-trimethylsilylperfluorononyne was isolated in 65% yield from perfluoroheptyl iodide, whereas 1-trimethylsilylperfluorooctyne, 1-trimethylsilylperfluorodecyne and 1-trimethylsilylperfluorododecyne were obtained from a commercial mixture of perfluoroalkyl iodides.

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

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

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

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 elemental analysis consistent with 1-iodo-2-(trimethylsilyl)perfluorocyclohexene, or its isomer, iodo(trimethylsilyl)-methylenecyclopentane.



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 trimethylsilylacetylene and with bis(trimethylsilyl)acetylene. Trimerization and polymerization studies with these acetylenes will be reported elsewhere.

Experimental Section

A Varian 920 chromatograph with a 10 ft x 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 recrystallized from methanol: mp 89-91°C; '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 ppm (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-diiodododecane. The above procedure using 1,6 diiodoperfluorohexane gave a 76% yield of white solid, mp 69-71°C: 'H NMR ($CDCl_3$) δ 2.60 (m, 4 H, CH_2), 3.16 (m, 4 H, CH_2I); ^{19}F NMR ($CDCl_3$) 0 116.4 (m, 4 F, CF_2), 124.8 (m, 4 F, CF_2), 123.2 ppm (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°, distilled from the reaction mixture as it was formed. An analytical sample was isolated by GC: 'H NMR ($CDCl_3$) δ 5.6-5.9 (m, 6 H, CH_2=CH); ^{19}F NMR ($CDCl_3$) 0 115.7 (m, 4 F, CF_2), 124.8 ppm (t, 4 F, J=11.3 Hz, CF_2).

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

<u>3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,9-decadiene</u>. The above procedure using 1,10-diiodo-3,3,4,4,5,5,6,6,7,7,8,8-dodecafluorodecane gave an 87% 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 ppm (m, 4 F, CF_2).

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

<u>3,3,4,4,5,5,6,6-Octafluoro-1,2,7,8-tetrabromooctane</u>. 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 ppm (m, 4 F, CF_2).

<u>Anal.</u> Calcd for $C_8H_6F_6Br_4$: C, 16.75; H, 1.05; Br, 55.71; Found: C 16.76; H, 0.99: Br, 55.40.

<u>3,3,4,4,5,5,6,6,7,7,8,8-Dodecafluoro-1,2,9,10-tetrabromodecane.</u> 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 ppm (m, 4 F, CF_2).

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

<u>2,7-Dibromo-3,3,4,4,5,5,6,6-octafluoro-1,7-octadiene</u>. 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-octa-

fluoro-1,2,7,8-tetrabromooctane in 15 mL of methanol was heated with stirring for 1 h at 60°C. The product was diluted with 50 mL of methylene chloride, washed with 2-50 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: 'H NMR ($CDCl_3$) δ 6.16 (m, 2 H, $J_{H,H}$= 3.0 Hz, $C\genfrac{}{}{0pt}{}{H}{\underline{H}}$) 6.42 (d, 2 H, $J_{H,H}$= 3.0 Hz, $C\genfrac{}{}{0pt}{}{\underline{H}}{H}$); ^{19}F NMR ($CDCl_3$) 0 110.8 (t, 4 F, $J_{F,F}$= 11.3 Hz, CF_2), 122.0 ppm (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, 23.6[illegible]; 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 2-10 mL portions of 1 N sodium thiosulfate, dried over magnesium sulfate and stripped of solvent under vacuum 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. 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: 'H NMR ($CDCl_3$) δ 7.45 ppm (br s. CH); ^{19}F NMR ($CDCl_3$) 0 108.0 (t, 4 F, CF_2), 121.2 ppm (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 trimethylsilylacetylene and 0.5 mL of di-*t*-butyl peroxide was heated in a sealed glass tube under nitrogen for 85 hrs at 120°. 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: proton NMR $CDCl_3$ δ 7.23 (t, J_{HF}= 15 Hz, =CH-, E isomers), δ 6.60 (t, J_{HF}= 13 Hz, =CH-, Z isomers) 0.35 (t, CH_3Si, E isomers) and 0.25 ppm (s, CH_3Si, Z isomers); ^{19}F NMR ($CDCl_3$) ϕ 108.4 (m, =CH-CF_2-, E isomers), 111.6 (m, =CH-CF_2 , Z isomers), 123.2 (m, CF_2 internal) and 124.4 ppm (m, =CH-CF_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-trimethylsilyloctene. 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 'H NMR ($CDCl_3$) δ 7.15 (t, 1 H, $J_{H,F}$= 14 Hz, CH), 0.35 ppm (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), 111.2 (m, 2 F, CF_2). 122.8 (m, 4 F, CF_2), 124.4 ppm (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 'H NMR ($CDCl_3$) δ 6.70 (t, 1 H, $J_{H,F}$= 13 Hz, CH), 0.25 ppm (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 ppm (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 moles) of a mixture of 1,8-diiodoperfluorooctane, 1,10-diiodoperfluorodecane and 1,12-diiodoperfluorododecane with 5 g of trimethylsilylacetylene and 2.5 mL of di-*t*-butyl peroxide by the above procedure yielded, after 48 hrs 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) and 0.27 ppm (s, 18 H, $SiCH_3$, Z isomer); ^{19}F NMR ($CDCl_3$) ϕ 108.4 (m, 4 F, $CH-CF_2$, E isomer) 111.6 (m, 4 F, $CHCF_2$, Z isomer), 123.2 (m, CF_2 internal) and 124.2 ppm (m, $=CH-CF_2-\underline{CF_2}$).

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 trimethylsilylacetylene and 0.5 mL of di-*t*-butyl peroxide was sealed in a glass tube under nitrogen and heated at 120°C for 48 hrs. The product was dissolved in methylene chloride, and dried over magnesium sulfate. Removal of 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

E isomer proton NMR ($CDCl_3$): δ 7.10 (t, 1 H, J_{HF}= 15 Hz, =CH), 0.33 ppm (t, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, 3 F, CF_3), 108.4 (q, 2 F, =CH-$\underline{CF_2}$), 124 (m, 8 F, CF_2) and 127.6 ppm (m, 2 F, =$CHCF_2\underline{CF_2}$-); Z isomer proton NMR ($CDCl_3$) δ 6.58 (t, J_{HF}= 12 Hz, 1 H, =CH), 0.25 ppm (s, 9 H, $SiCH_3$); ^{19}F NMR ($CDCl_3$) ϕ 85.2 (t, 3 F, CF_3), 111.8 (q, 2 F, =$CH\underline{CF_2}$), 124 (m, 8 F, CF_2) and 127.6 ppm (m, 2 F, =$CHCF_2\underline{CF_2}$).

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 Trimethylsilylacetylene. A mixture of 1.4 g (3.0 mmol) of 1,4-diiodoperfluorobutane, 0.90 g (9.2 mmol) of trimethylsilylacetylene and 0.2 g (1.4 mmol) of di-t-butyl peroxide was heated in a sealed tube for 6 days at 120°C. GC analysis (150-185°C) showed 7 components, 12%, 23%, 20%, 13%, 6%, 22% and 3% of the sample, respectively. The first component consisted of 1,4-diiodoperfluorobutane and trimethylsilylacetylene. 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: ^1H NMR ($CDCl_3$), δ 7.12 (t, J_{HF}= 15 Hz, 1 H, $\underline{H}$C=C), 0.35 ppm (t, J = 1.5 Hz 9 H, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 64.8 (t, 2 F, -$\underline{CF_2}$I), 108.2 (q, 2 F, -$\underline{CF_2}$-C(H)=C), 114.8 (m, 2 F, CF_2), 123.4 ppm (t, 2 F, $\underline{CF_2}$).

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: ^1H NMR ($CDCl_3$) δ 6.60 (t, $J_{H,F}$= 12 Hz, 1 H, C=$\underline{CH}$), 0.22 ppm (s, 9 H, -CH_3); ^{19}F NMR ($CDCl_3$)

ϕ 64.8 (t, 2 F, $-C\underline{F_2}I$), 112.0 (q, 2 F, $-C\underline{F_2}-C(H)=C$), 114.8 (m, 2 F, $C\underline{F_2}$), 123.4 (t, 2 F, $C\underline{F_2}$). The sixth component was an (E/E)/(Z/Z)/(E/Z) mixture of 3,3,4,4,5,5,6,6-octafluoro-1,8-diioda-1,8-bis(trimethylsilyl)-1,7-octadiene: ^{19}F NMR ($CDCl_3$) ϕ 116.9 (m, 2 F, $-C\underline{F_2}-C(H)=C$, E-isomer), 117.9 (m, 2 F, $-CF_2-C(H)=C$, Z-isomer), 120.0 (m, 2 F, CF_2), 132.1 (m, 2 F, CF_2), 134.0 ppm (m, 2 F, CF_2); IR (film) 3005 (Si CH_3), 2950 (Si CH_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 Trimethylsilylacetylene. A mixture of 0.106 g (0.30 mmol) of tetrafluoro-1,2-diiodoethane, 0.088 g (0.90 mmol) of trimethylsilylacetylene and 0.007 g (0.05 mmol) of di-*t*-butyl peroxide was heated in a sealed tube for 36 h at 120°C and 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 (t of t, J = 14.5 and 1 Hz, 1 H, $CF_2C(\underline{H})=C$), 0.36 ppm (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 ppm (m, 2 F, $ICF_2C\underline{F_2}-$); (Z) isomer ^{1}H NMR ($CDCl_3$) δ 6.79 (t of t, J = 12 and 1 Hz, 1 H, $CF_2C(\underline{H})=C$, 0.31 ppm (s, 9 H, $-SiC\underline{H_3}$); ^{19}F NMR ($CDCl_3$) ϕ 66.8 (t, J_{FF}= 10 Hz, 2 F, $IC\underline{F_2}-$), 107.0 ppm (m, 2 F, $ICF_2C\underline{F_2}-$).

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-diiodo-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 2-50 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 ppm (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 ppm (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 *t*-butoxide and 250 mL of methylene chloride was stirred under nitrogen at -20°C and 12.8 g (0.017 mole) 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 hr at -20° and for 4 hrs at 0°, and then 100 ml of 3 *N* hydrochloric 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° (15-20 mm): ^{1}H NMR ($CDCl_3$) δ 2.93 ppm (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) and 124.4 ppm (m, 4 F, β-CF_2); IR 3350 (CH), 2200 ($C{\equiv}C$) and 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 to 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 t-butoxide in 40 mL of methylene chloride was stirred under nitrogen at -20°C while 8.2 g of a solution of $(CH_3)_3SiIC=CH(CF_2)_8CH=CISi(CH_3)_3$, $(CH_3)_3SiIC=CH(CF_2)_{10}CH=CISi(CH_3)_3$, and $(CH_3)_3SiIC=CH(CF_2)_{12}CH=CISi(CH_3)_3$ 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 t-butanol 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: proton NMR ($CDCl_3$) δ 2.94 ppm (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) and 124 ppm (m, 4 F, β-CF_2); IR 3355 (CH), 2195 ($C\equiv C$) and 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: ^1H NMR ($CDCl_3$) δ 2.94 ppm (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) and 124.2 ppm (m, 4 F, β-CF_2); IR 3355 (CH), 2200 ($C\equiv C$) and 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°: ^1H 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) and 124.2 ppm (m, 4 F, β-CF_2); IR 3355 (CH), 2200 ($C\equiv C$) and 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 biproducts (bp 120-155°C). An analytical sample was isolated by GC (78°C): ^1H NMR ($CDCl_3$) δ 2.93 (t, J = 6 Hz, $\equiv CH$); ^{19}F NMR ($CDCl_3$) ϕ 85.1 (t, J = 10 Hz, 3 F, CF_3) 102.4 (m, 2 F, $\equiv C$-CF_2), 113.4

(m, 2 F, CF_2), 124.2 (m, 6 F, CF_2), 128.0 ppm (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-t-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; ^1H NMR ($CDCl_3$) δ 7.20 (s, 5 H, C_6H_5), 6.51 ppm (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 ppm (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-pentadecafluoro-1-iodo-1-phenylnonene in 20 mL of dry methylene chloride was added dropwise to a stirred suspension of 1.1 g of potassium t-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: ^1H NMR ($CDCl_3$) δ 7.33 ppm (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 ppm (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(iodomethyldimethylsilyl)-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-*t*-butyl peroxide was sealed under vacuum in a heavy-walled glass tube and the tube heated at 120°C for 48 h. The mixture was dissolved in 50 mL of methylene chloride, washed with 3-50 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 ppm (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 ppm (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-trimethylsilylpentene. 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-*t*-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 ppm (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 ppm (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-trimethylsilylnonene. 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-*t*-butyl peroxide gave 0.56 g (85%) of the title compound. An analytical sample was isolated by GC: ^1H 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 ppm (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 ppm (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 to 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: ^1H NMR ($CDCl_3$, CH_2Cl_2) δ 0.37 ppm (s, $-SiCH_3$); ^{19}F NMR ($CDCl_3$, $CFCl_3$) ϕ 100.8 (m, 4 F, $-\underline{CF_2}$ C≡C), 123.2 (m, 8 F, CF_2), 124.3 ppm (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.

<u>3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-Hexadecafluoro-1,11-dodecadiyne</u>. 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); 'H NMR ($CDCl_3$) δ 2.94 ppm (t, J_{HF} = 4.5 Hz, $C\equiv C\text{-}H$); ^{19}F NMR ($CDCl_3$) ϕ 102.0 (m, 4 F, $CF_2C\equiv$), 122.8 (m, 8 F, $\equiv CF_2\underline{CF_2}$), 124.0 ppm (m, 4 F, $\equiv CCF_2CF_2CF_2\underline{CF_2}$); IR (film) 3355 (C-H), 2195 ($C\equiv C$), 1190 cm^{-1} (CF_2).

<u>Anal</u>. 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.

<u>1-Trimethylsilylperfluorononyne</u>. A mixture of 11.8 g (0.079 mmol) of bis(trimethylsilyl)acetylene, 30.0 g (0.060 mol) of perfluoroheptyl iodide and 0.022 g (0.00009 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-trimethylsilylnonyne, bp 39-40°C (0.27 0.37 mm): 'H NMR ($CDCl_3$, CH_2Cl_2) δ 0.15 ppm (s, 9 H, $Si\underline{CH_3}$); ^{19}F NMR ($CDCl_3$) ϕ 85.6 (t, J = 10 Hz, 3 F, $\underline{CF_3}$), 101.2 (t, J = 8 Hz, 2 F, $\text{-}CF_2C\equiv$), 122.8 (m, 2 F, CF_2), 124.0 (m, 6 F, CF_2), 127.6 ppm (m, 2 F, CF_2); IR (film) 3000 ($SiCH_3$), 2940 ($SiCH_3$), 2230 ($C\equiv C$), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

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

<u>1-Trimethylsilylperfluorooctyne, 1-Trimethylsilylperfluorodecyne and 1-Trimethylsilylperfluorododecyne</u>. 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 trimethylsilylacetylenes. Samples of the three major components were isolated by preparative GC at 80°C. 1-Trimethylsilylperfluorooctyne was a colorless liquid: 'H NMR ($CDCl_3$) δ 0.44 ppm (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, $C\underline{F_2}CF_2C\equiv$), 125.6 (m, 4 F, $CF_3CF_2C\underline{F_2}C\underline{F_2}$-), 129.0 ppm (m, 2 F, $CF_3C\underline{F_2}$-); IR (film) 3000 (C-H), 2230 (C≡C), 1200 (CF_2), 860 cm^{-1} ($SiCH_3$).

<u>Anal</u>. 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-Trimethylsilylperfluorodecyne was a colorless liquid: 'H NMR ($CDCl_3$) δ 0.35 ppm (s, CH_3); ^{19}F NMR ($CDCl_3$) ϕ 86.2 (t, J = 10 Hz, 3 F, $-C\underline{F_3}$), 102.2 (t, J = 11 Hz, 2 F, $-C\underline{F_2}C\equiv$), 125.2 (m, 10 F, $CF_3CF_2(CF_2)_5$), 129.2 ppm (m, 2 F, $CF_3C\underline{F_2}$): IR (film) 3010 (C-H), 2250 (C≡C), 1200 (CF_2) 860 cm^{-1} ($SiCH_3$).

<u>Anal</u>. 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-Trimethylsilylperfluorododecyne was a colorless liquid: 'H NMR ($CDCl_3$) δ 0.40 ppm (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 ppm (m, 2 F,

$-\underline{CF_2}CF_3$); 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 (10%). 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: ^1H NMR ($CDCl_3$) δ 6.31 (d t, J_{HH} = 7.2 Hz, J_{HF} = 1.8 Hz, 1 H, $C{=}C\underline{H}OMe$), 4.44 (d t, J_{HH} = 7.2 Hz, J_{HF} = 15 Hz, 1 H, $CF_2C\underline{H}{=}$), 3.77 ppm (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: ^1H NMR ($CDCl_3$) δ 4.76 (t, J = 6 Hz, 1 H, $CH_2C\underline{H}(OMe)_2$), 3.39 (s, 6 H, OCH_3), 2.40 ppm (m, 2 H, $CF_2\underline{CH_2}$); ^{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 ppm (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 (0.00044 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): 'H NMR ($CDCl_3$ δ0.50 ppm (t, J_{HF} = 1 Hz, 9 H, $SiC\underline{H}_3$), ^{19}F NMR ($CDCl_3$) 104.4 (m, 2 F, CF_2), 113.6 (m, 2 F, CF_2), 135.2 (m, 2 F, CF_2), 136.8 ppm (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 g (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: 'H NMR ($CDCl_3$) δ0.55 ppm (t, J = 1 Hz, $-Si(C\underline{H}_3)_3$); ^{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 ppm (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 ppm (s, 18 H, $-SiC\underline{H}_3$); ^{19}F NMR ($CDCl_3$) ϕ 101.3 (m, 4 F, $-C{\equiv}C-C\underline{F}_2$), 123.4 (m, 4 F, CF_2), 124.8 ppm (m, 4 F, CF_2); IR (film) 3000 ($SiMe_3$), 2940 ($SiMe_3$), 2220 ($C{\equiv}C$), 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.

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