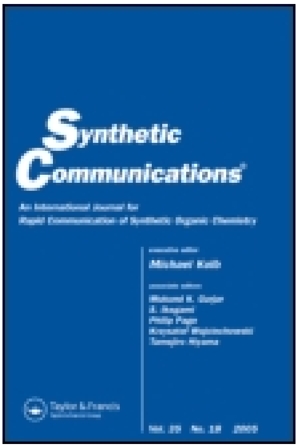

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# Stereoselective Synthesis of (Z)-Perfluoroalkyl-1-iodo-1-triisopropyl Silylalkenes: A Convenient Route to Perfluoroalkyl-Substituted Unsaturated Synthons

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# STEREOSELECTIVE SYNTHESIS OF (*Z*)-PERFLUOROALKYL-1-IODO-1-TRIISOPROPYL SILYLALKENES: A CONVENIENT ROUTE TO PERFLUOROALKYL-SUBSTITUTED UNSATURATED SYNTHONS

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***The quantitative and fully stereoselective synthesis of (Z)-perfluoroalkyl-1-iodo-1-triisopropylsilylalkenes and their easy, high-yielding transformation into the corresponding 1-iodo-2-perfluoroacetylenes and (Z)-2-perfluoroalkyl-1-iodo-1-alkenes, compounds of interest as synthons for classical organometallic chemistry or for metal-catalyzed coupling reactions, are discussed.***

***Keywords***: Perfluoroacetylenes; stereoselective synthesis; (*Z*)-1-iodoperfluoroalkenes

## INTRODUCTION

The introduction of fluorine atoms into organic compounds significantly changes the physical and chemical properties of these molecules. Partially fluorinated organic compounds, particularly those containing perfluoroalkyl groups, have widespread applications[1] as reagents for materials used in different branches of technology and in the design of medical and agricultural preparations.[2] Consequently, the development of new or improved synthetic procedures for the introduction of polyfluorinated fragments into organic molecules has recently attracted much interest.

In a previous work,[3] we described a new group of 3-perfluoroalkyl-2-propyn-1-ol acrylates, Rf(n)-C≡C-$CH_2$-OCO-CH=$CH_2$ [whereby Rf(n) is $F(CF_2)_n$], and their subsequent conversion into the corresponding polymers. The 3-perfluoroalkyl-2-propyn-1-ols were prepared via a three step-reaction procedure: first, addition of perfluoroalkyl iodide to trimethylsilylacetylene yielded a perfluoalkyl-1-iodo-1-trimethylsilylalkene; second, HI and trimethylsilyl group were simultaneously eliminated with $K^tBuO$; and last, the resulting terminal alkyne was reacted with BuLi and paraformaldehyde. The main drawback of this method is that although the addition

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of perfluoroalkyl iodide to trimethylsilylacetylene in a one-electron-transfer process affords an equimolar mixture of *Z*/*E*-isomeric alkenes in good yield, in the next step only the *Z*-isomer eliminates HI by an E2 process; in E1 conditions, both isomers disappear but the yield in acetylene is less than 50%. Consequently, despite excellent yields for the first and the third steps, the maximum possible global yield is 40%.

An alternative method[4] is the addition of perfluoroalkyl iodides to several terminal alkynes at 10 to 15 °C in aqueous acetonitrile in the presence of sodium dithionite and sodium bicarbonate in a fully regioselective process. However, this also leads to a mixture of *Z*/*E* adducts of the general formula Rf(n)-CH=CICRR′OH. The corresponding 3-perfluoroalkyl-2-propyn-1-ols are formed by subsequent elimination of HI[5] from the *Z*-isomer in basic medium. When we employed this method to form 3-perfluoroalkyl-2-propyn-1-ols starting from propargyl alcohol and perfluoroalkyl iodides with four, six, or eight carbon atoms, we obtained maximum global yields of 30%. Again, the problem is the lack of stereoselectivity in the addition step.

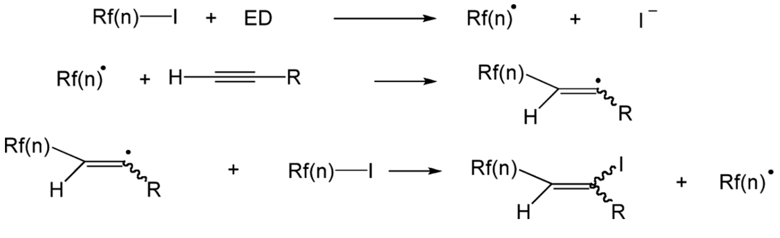
In fact, this problem was described by Brace and Van Elswyk[6] several years ago. They reported a *Z*/*E* ratio of 10:90 for the addition of 1-iodoheptafluoropropane to 1-hexyne to yield 1-perfluoropropyl-1-hexene and a *Z*/*E* ratio of 30.8:69.2 for the analogous addition to 1-heptyne.

We report here a quantitative and fully stereoselective synthesis of (*Z*)-perfluoroalkyl-1-iodo-1-triisopropylsilylalkenes. We also describe their ready transformation into unsaturated synthons for the preparation of fluorinated molecules via classical organometallic chemistry or metal-catalyzed coupling reactions.

## RESULTS AND DISCUSSION

As previously explained, the problem in the addition reaction of perfluoroalkyl iodides to alkynes is the stereoselectivity. This process consists of the direct incorporation of perfluoroalkyl radicals, generated in situ, into appropriate acetylenes by a single-electron-transfer process (Scheme 1).

We thought that the geometry of the addition compound must be controlled by the steric interaction between the perfluoroalkyl group and the R group. Thus we tried adding various perfluoroalkyl iodides to several acetylenes. This reaction has been widely studied,[7] and its radical process can been initiated photochemically,[8] by radical initiators,[9] thermally,[10] or electrochemically.[11] We chose zinc (Zn; purity ≥99%) as the electron donor[5,12] in freshly distilled methylene chloride, owing

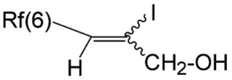
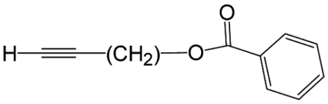
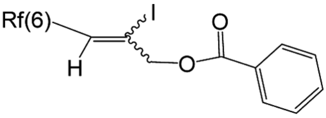
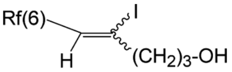
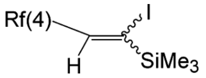
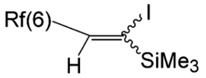
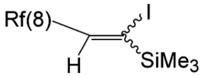
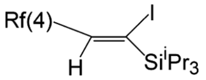
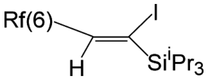
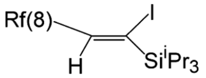


**Scheme 1.** Mechanism of the addition of perfluoroalkyl radicals to acetylenes in a one-electron-transfer reaction.

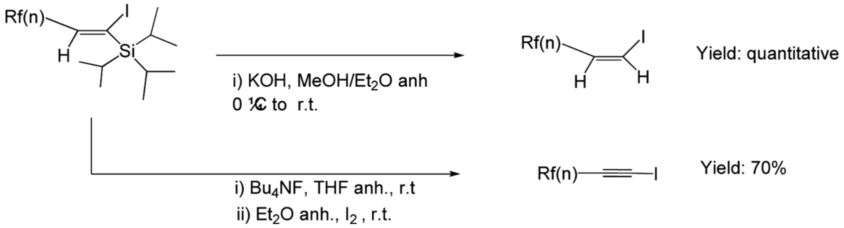
to the easy purification of the crude product: only filtration and solvent evaporation are required. The results obtained with several substituted alkynes are summarized in Table 1.

The reaction proceeded with good yield in all cases. The stereoselectivity of the process shows two opposite trends, depending on the substituent of the alkyne. When the radical is hydrocarbonated and/or oxygenated, the *E*-isomer dominates; however, with silyl derivatives, volume seems to dictate the isomeric ratio: the bulky triisopropylsilyl group led to the *Z*-isomer in practically quantitative ratio. The geometry of the isolated products was assigned by $^1$H NMR [in a one-dimensional nuclear Overhauser effect spectroscopy (1D-NOESY) experiment]: in the *Z*-isomer, the signal at 6.86 ppm corresponding to the olefinic proton shows nOe with the tertiary proton in the isopropyl groups, whereas in the *E*-isomer, this effect is not

**Table 1.** Addition of perfluorinated perfluoroalkyl iodides to terminal alkynes

| Alkyne | Product[a] | Yield (%)[b] | *Z*/*E* ratio[c] |
|---|---|---|---|
| $H{-}{\equiv}{-}CH_2\text{-}OH$ |  | 87 | 45/55 |
|  |  | 87 | 25/75 |
| $H{-}{\equiv}{-}(CH_2)_3\text{-}OH$ |  | 89 | 11/89 |
| $H{-}{\equiv}{-}SiMe_3$ |  | 93 | 50/50 |
| $H{-}{\equiv}{-}SiMe_3$ |  | 95 | 50/50 |
| $H{-}{\equiv}{-}SiMe_3$ |  | 82 | 50/50 |
| $H{-}{\equiv}{-}Si^iPr_3$ |  | 94 | Only *Z* detected |
| $H{-}{\equiv}{-}Si^iPr_3$ |  | 99 | 98/2 |
| $H{-}{\equiv}{-}Si^iPr_3$ |  | 88 | Only *Z* detected |

[a] Rf(n) = perfluorinated chain of n carbon atoms.
[b] Calculated as isolated isomer mixture.
[c] Calculated from the $^1$H or $^{19}$F NMR spectra.



**Scheme 2.** Two desilylation methods for (Z)-perfluoroalkyl-1-iodo-1-triisopropylsilylalkenes.

observed. Likewise, the $^{19}$F NMR spectra also enabled identification of each isomer: the signals at approximately $-109$ ppm and $-113$ ppm correspond to the *Z*- and *E*-isomers, respectively.

Desilylation can be achieved in two ways (Scheme 2). When a solution of silylated *Z*-alkene in anhydrous ether was added to methanolic potassium hydroxide at 0 °C and the mixture was stirred for 1 h at room temperature, only (*Z*)-2-perfluoroalkyl-1-iodoalkene was formed (based on the $^{19}$F NMR spectra) in practically quantitative yield. Silylate residue by-products had to be carefully removed by column chromatography. An average yield of 70% was obtained for the isolated products. The geometry of the pure compounds was determined based on the $^{1}$H NMR data: for the *Z*-isomer, the coupling constant $J_{\mathrm{H1\text{-}H2}}$ between the olefinic protons is 7.2 Hz, whereas for the *E*-isomer, it is 14.8 Hz. Again, $^{19}$F NMR enables identification of each isomer: the *Z*-compounds present a signal at approximately $-108$ ppm, whereas the *E*-compounds present a signal at approximately $-114$ ppm.

The pure isomers of these compounds are interesting; some of these compounds are currently only commercially available as mixtures of the *Z*- and *E*-isomers.

Treatment of the silylated *Z*-alkene with tetrabutylammonium fluoride in tetrahydrofuran (THF) for 2 h at room temperature, followed by addition of iodine after 2 more h, provided the 2-perfluoroalkyl-1-iodo-acetylene in a yield of 70%, which is twice the yield of previously described methods.[3,4,5]

Both (*Z*)-2-perfluoroalkyl-1-iodoalkenes and 2-perfluoroalkyl-1-iodo-acetylenes are very interesting as synthons for classical organometallic chemistry or for metal-catalyzed coupling reactions.

## EXPERIMENTAL

### General Methods

Infrared (IR) spectra were registered using a Perkin-Elmer Spectrum-One instrument. $^{19}$F NMR, $^{1}$H NMR, and $^{13}$C NMR spectra were recorded on a Varian Mercury-400 spectrometer with tetramethylsilane (TMS; $^{1}$H) and trifluoroacetic acid (TFA; $^{19}$F) as internal standards. The purifications of the reactions were monitored by gas chromatography/mass spectrometry (GC/MS) in a ThermoFinnigan Trace DSQ instrument coupled with a Trace GC gas chromatograph. The molecular weights of all prepared compounds were determined by MS spectrometry techniques; the MS were determined by electronic impact (EI, 70 eV) and the high-resolution MS

(HMRS) spectra have been recorded in an L/CMSD-TOF instrument (Agilent Technologies).

### General Procedure for the Addition of Iodoperfluoroalkanes to Alkynes

Zinc (5.5 g, 75.8 mmol), 1-iodoperfluoroalkane (75.5 mmol), and triisopropylsilylacetylene (17 mL, 75 mmol) were added to 20 mL of $CH_2Cl_2$. The mixture was boiled and stirred for 2 h, then filtered, and the solvent was removed under low pressure to provide (*Z*)-perfluoro-1-iodo-1-triisopropylsilyl-1-alkene (see Table 1 for yield).

**(*Z*)-3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodo-1-triisopropylsilyl-1-hexene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1660 (st C=C), 1147 (st C-F), 882 (st Si-C). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.86 (1H, t, $J_{H\text{-}F} = 13.3$ Hz, H alkene), 1.41 (3H, m, CH isopropyl), 1.14 (18H, d, $J = 7.4$ Hz, $CH_3$ isopropyl). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −84.42 (3F, t, $J = 9.4$ Hz, F6), −112.53 (2F, q, $J_{H\text{-}F} = 12.3$ Hz, F3), −127.22 (2F, m, F4), −129.20 (2F, m, F5). MS (EI): 528 (M); 485 [M -$CH(CH_3)_2$], 359 [M -$(CF_2)_2CF_3$].

**(*Z*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodo-1-triisopropylsilyl-1-octene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1661 (st C=C); 1146 (st C-F), 882 (st Si-C). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.86 (1H, t, $J_{H\text{-}F} = 12.0$ Hz, H alkene), 1.43 (3H, m, CH isopropyl), 1.14 (18H, d, $J = 8.0$ Hz, $CH_3$ isopropyl). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.35 (3F, m, F8), −111.41 (2F, q, $J_{H\text{-}F} = 12.9$ Hz, F3), −124.18 (2F, m, F4), −125.35 (4F, m, F5 and F6), −128.63 (2F, m, F7). MS (EI): 628 (M); 585 [M -$CH(CH_3)_2$], 359 [M -$(CF_2)_4CF_3$]. HRMS: 628.3261.

**(*Z*)-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iodo-1-triisopropylsilyl-1-decene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1661 (st C=C), 1151 (st C-F), 879 (st Si-C). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.86 (1H, t, $J_{H\text{-}F} = 13.3$ Hz, H2), 1.41 (3H, m, H1′), 1.14 (18H, d, $J = 7.5$ Hz, H2′). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.65 (3F, t, $J = 9.8$ Hz, F10), −111.55 (2F, q, $J_{HF} = 13.0$ Hz, F3), −124.29 (2F, m, F4), −124.77 (4F, m, F5 and F6), −125.61 (4F, m, F7 and F8), −128.98 (2F, m, F9). MS (EI) 728 (M), 685 [M-$CH(CH_3)_2$], 359 [M -$(CF_2)_6CF_3$].

### General Procedure for the Preparation of 1-Iodo-2-perfluoroacetylenes

The corresponding (*Z*)-perfluoro-1-iodo-1-triisopropylsilyl-1-alkene (23 mmol) was dissolved in anhydrous $Et_2O$ (23 mL). Under an $N_2$ atmosphere, 1 M $Bu_4NF$ (69 mL) in THF was added dropwise while the solution was maintained at 0 °C. The reaction mixture was stirred for 2 h at room temperature. Iodine (11.7 g, 46 mmol) was added, and the mixture was stirred for an additional 2 h. The mixture was then diluted with $Et_2O$ (250 mL) and washed once with $Na_2S_2O_3$ 1 M (300 mL), twice with saturated aq. NaCl. (300 mL), and once with $H_2O$ (300 mL). The organic layer was dried over anhydrous $MgSO_4$ and then filtered, and the solvent was removed under reduced pressure. The crude was purified by flash silica-gel chromatography (hexane as eluent) to obtain the corresponding 1-iodo-2-perfluoroacetylene (yield: 70 to 75%).

**3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodo-1-hexyne.** Yellow oil. IR (film, υ, $cm^{-1}$): 2196 (st C≡C), 1148 (st C-F). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.81 (3F, t, *J* = 9.5 Hz, F6), −100.22 (2F, m, F3), −125.91 (2F, m, F4), −128.28 (2F, m, F5). MS (EI): 370 (M), 351 (M -F), 201 (M $-CF_2CF_2CF_3$), 127 (I); 69 ($CF_3$).

**3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodo-1-octyne.** Yellow oil. IR (film, υ, $cm^{-1}$): 2196 (st C≡C), 1146 (st C-F). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.68 (3F, m, F8), −100.03 (2F, m, F3), −124.24 (2F, m, F4), −125.11 (2F, m, F5), −125.71 (2F, m, F6), −129.01 (2F, m, F7). MS (EI): 470 (M), 201 [M $-(CF_2)_4CF_3$], 69 ($CF_3$). HRMS: 469.8835.

**3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iodo-1-decyne.** Yellow oil. IR (film, υ, $cm^{-1}$): 2198 (st C≡C), 1151 (st C-F). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.34 (3F, t, *J* = 9.9 Hz, F10), −99.70 (2F, m, F3), −123.70 (2F, m, F4), −124.45 (4F, m, F5 and F6), −124.75 (2F, m, F7), −125.29 (2F, m, F8), −128.67 (2F, m, F9). MS (EI): 570 (M); 201 [M $-(CF_2)_6CF_3$], 69 ($CF_3$).

## General Procedure for the Preparation of (*Z*)-2-Perfluoroalkyl-1-iodo-1-alkenes

Potassium hydroxide (KOH; 779 mg, 13.1 mmol) was dissolved in MeOH (3 mL). The solution was cooled to 0 °C under an $N_2$ atmosphere, and the corresponding (*Z*)-perfluoro-1-iodo-1-triisopropylsilyl-1-alkene (4.4 mmol) in anhydrous $Et_2O$ (4 mL) was added dropwise. The reaction mixture was stirred for 1 h at room temperature, diluted with $Et_2O$ (20 mL), and washed twice with $H_2O$ (20 mL). The organic layer was dried over anhydrous $MgSO_4$ and then filtered, and the solvent was removed to afford a crude reaction mixture with silylate residue by-products. The crude was purified by silica-gel chromatography (hexane as eluent) to obtain (*Z*)-2-perfluoroalkyl-1-iodo-1-alkene (yield: 68 to 75%).

**(*Z*)-3,3,4,4,5,5,6,6,6-Nonafluoro-1-iodo-1-hexene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1559 (st C=C); 1238 (st C-F). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.42 (1H, dt, $J_{H1\text{-}F} = 2.1$ Hz, $J_{H1\text{-}H2} = 7.2$ Hz, H1), 4.51 (1H, dt, $J_{H1\text{-}H2} = 7.2$ Hz, $J_{H2\text{-}F} = 14.6$ Hz, H2). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −81.56 (3F, t, *J* = 9.7 Hz, F6), −106.72 (2F, q, *J* = 13.5 Hz, F3), −125.16 (2F, m, F4), −125.18(2F, m, F5). MS (EI): 372 (M), 303 (M $-CF_3$), 203 (M $-CF_2CF_2CF_3$), 69 ($CF_3$).

**(*Z*)-3,3,4,4,5,5,6,6,7,7,8,8,8-Tridecafluoro-1-iodo-1-octene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1558 (st C=C); 1238 (st C-F). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.39 (1H, dt, $J_{H1\text{-}F} = 2.0$ Hz, $J_{H1\text{-}H2} = 7.2$ Hz, H1), 4.49 (1H, dt, $J_{H1\text{-}H2} = 7.2$ Hz, $J_{H2\text{-}F} = 14.8$ Hz, H2). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.66 (3F, t, *J* = 9.8 Hz, F8), −108.92 (2F, q, *J* = 13.5 Hz, F3), −124.61 (2F, m, F4), −125.74 (2F, m, F5), −126.70 (2F, m, F6), −128.96 (2F, m, F7). MS (EI): 472 (M), 403 (M $-CF_3$), 203 (M $-CF_2CF_2CF_2CF_2CF_3$), 69 ($CF_3$). HRMS: 471.8995.

**3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-iodo-1-decene.** Yellow oil. IR (film, υ, $cm^{-1}$): 1560 (st C=C), 1239 (st C-F). $^1H$ NMR (400 MHz, $CDCl_3$, δ ppm): 6.39 (1H, dt, $J_{H1\text{-}F} = 2.0$ Hz, $J_{H1\text{-}H2} = 7.2$ Hz, H1), 4.48 (1H, dt, $J_{H1\text{-}H2} = 7.1$ Hz, $J_{H2\text{-}F} = 14.7$ Hz, H2). $^{19}F$ NMR (376 MHz, $CDCl_3$, δ ppm): −83.21

(3F, t, $J = 9.7$ Hz, F10), −108.50 (2F, q, $J = 13.5$ Hz, F3), −123.97 (2F, m, F4), −124.35 (2F, m, F5), −124.37 (2F, m, F6), −125.16 (2F, m, F7), 126.24 (2F, m, F8), 128.14 (2F, m, F9). MS (EI): 572 (M), 503 (M $-CF_3$), 203 (M $-CF_2CF_2CF_2CF_2CF_3$), 69 ($CF_3$).

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