Perfluoroalkyl-Chalcogenation of Alkynes

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Perfluoroalkyl-telluration of alkynes has been performed by a $(PhTe)_2$–$NaBH_4$–RfX system at a low temperature (−40, −80, or −100 °C) to give 2-(perfluoroalkyl)vinyl tellurides. Meanwhile, perfluoroalkyl-sulfenylation and perfluoroalkyl-selenation were less effective. The perfluoroalkyl-telluration proceeds mainly via both $S_{RN}1$ process and photochemical addition of the in situ formed perfluoroalkyl phenyl telluride (RfTePh). The efficiency of the chalcogenolate anions for perfluoroalkyl-chalcogenation was found to be the order of $PhS^- < PhSe^- < PhTe^-$.

Recently, we have reported perfluoroalkyl-chalcogenations (sulfenylation, selenation, telluration) of olefins which proceed by a single electron transfer (SET) from sodium chalcogenolates to perfluoroalkyl halides (RfX) followed by the radical chain reaction of $S_{RN}1$ mechanism.[1,2] Here, we describe perfluoroalkyl-chalcogenation of alkynes.

Perfluoroalkyl-halogenations[3—7] and hydroperfluoroalkylations[8] along with perfluoroalkyl carbonylations[9] can introduce both perfluoroalkyl (Rf) and other functional groups into a carbon–carbon triple bond of alkynes via perfluoroalkyl radicals. In particular, perfluoroalkyl-halogenation of alkynes is quite common and has been accomplished by the photolytic,[3] thermal,[4] electrochemical,[5] radical-initiated,[6] and metal-catalyzed reactions.[7] To our knowledge, however, the direct introduction of a Rf group and a heteroatom moiety into alkynes has been performed by only perfluoroalkyl-halogenation. There is no report on the direct introduction of a Rf group and a chalcogen moiety into a carbon–carbon triple bond of alkynes.

Results and Discussion

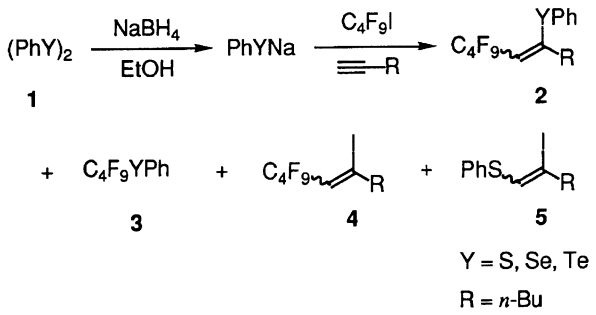
Perfluorobutyl-chalcogenations of 1-hexyne with a PhYNa–C_4F_9I system (Y=S, Se, Te) were examined, and the results were shown in Table 1. The reaction was regioselective and the desired products **2** were obtained. Perfluorobutyl-telluration occurred smoothly even at a low temperature (−40 °C) to give **2a** in a high yield (81%). In contrast, perfluorobutyl-selenation gave perfluorobutyl phenyl selenide **3b** (71%) as major product and the desired adduct **2b** (19%) as a minor product at room temperature. Perfluorobutyl-sulfenylation proceeded so slowly even on refluxing in ether for 2 h that a large amount of the starting material **1c**[10] (67%) was recovered and the yield of **2c** was very low (6%). The sulfide **3c** (14%), the perfluorobutyl-iodo adduct **4** (18%), and 2-iodo-1-hexenyl phenyl sulfide (**5**) (12%) were produced (Scheme 1). Perfluorobutyl-chalcogenation reaction would proceed by a single electron transfer (SET) from sodium chalcogenolate to perfluorobutyl iodide (C_4F_9I) followed by the radical chain reaction of $S_{RN}1$ mechanism as proposed for perfluoroalkyl-chalcogenations of olefins.[1,2] In fact, when nitrobenzene[11] as a radical trapping agent was added in a 1-hexyne–PhTeNa–C_4F_9I system, an inhibition of the reaction was observed, and the yield of **2a** (10%) markedly decreased and **1a** was recovered in 49% yield. On the other hand, the yield of **3a** increased from 5 to 39%.

The question to be solved is why the tellurolate provides **2a** exclusively, on the other hand, the selenolate gave **3b** preferentially. Benzeneselenolate mediates the perfluoroalkyl-selenation of olefins[1] by the $S_{RN}1$ process. However, the perfluoroalkyl radicals react competitively both with alkynes and the selenolate or the seleno radical (PhSe·), and the latter reaction pathway would predominate because of the less reactivity of alkynes to perfluoroalkyl radicals than that of alkenes. Accordingly, the telluride **3a** would be preferentially formed when the telluration is conducted in the dark. In fact, perfluorobutyl-telluration of 1-hexyne with a PhTeNa–C_4F_9I system in the dark[12] gave **2a** (29%), **3a** (46%),

Table 1. Perfluorobutyl-Chalcogenation of 1-Hexyne with a PhYNa–C_4F_9I System[a]

Y	Yield[e] (%)							
	2[f]		**3**[f]		**4**[g]	**5**	**1**	
Te[b]	**2a**	81	**3a**	8	5	—	**1a**	—
Se[c]	**2b**	19	**3b**	71	15	—	**1b**	2
S[d]	**2c**	6	**3c**	14	18	12	**1c**	67

a) Reaction time (2 h). Temperature: b) −40 °C→r.t. c) r.t. d) Refluxing in ether. e) Yield based on PhYNa. f) ^1H NMR yields. g) Yield based on C_4F_9I.



Scheme 1.

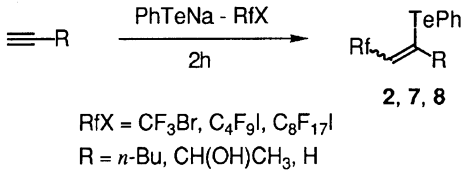
4 (5%), and recovery of **1a** (8%).

It is well-known that the homolytic cleavage of carbon–tellurium bond takes place by the photolytic, thermal, and radical-initiated reactions of organotellurium compounds to generate radicals which are trapped with carbon–carbon multiple bonds.[13] Therefore, the in situ formed **3a** may react with 1-hexyne, affording **2a** under the same conditions. The reaction of **3a** under the photolytic conditions for 2 h provided 42% of **2a**, a trace of **1a**, and a recovery of **3a** (51%). On the other hand, no **2a** was detected in the dark.[12] In contrast, no reaction of the corresponding selenide **3b** occurred even under the photolytic conditions.

Judging from the formation of **4**, the addition–elimination process to the adduct **4** with the tellurolate ($PhTe^-$) is one of the plausible process. Then, the adduct **4** was subjected to react with the tellurolate under the same reaction conditions for the perfluorobutyl-telluration. This experiment revealed that only 12% of **2a** was formed and 60% of **4** was recovered.

These results suggest that perfluoroalkyl-telluration proceeds mainly via both pathes A and B, and partially via path C. In particular, path B occurs only in the telluration and never in the selenation and sulfenylation. The thiolate reacts very slowly with RfX, instead attacks 1-hexyne to generate the thiolated vinyl anion, which transfers an electron to C_4F_9I and then abstracts iodine, leading to the sulfide **5** (Scheme 3).

Based on the effective perfluorobutyl-telluration, the perfluoroalkyl-telluration of some alkynes with a PhTeNa–RfX (CF_3Br, C_4F_9I, $C_8F_{17}I$) system was examined. These results were listed in Table 2. When



Scheme 2.

Table 2. Perfluoroalkyl-Telluration of Alkynes with a PhTeNa–RfX System

≡—R	Yield (%)[a] of **2**, **7**, and **8** (E/Z)[b]		
	C_4F_9I	$C_8F_{17}I$	CF_3Br[c]
≡—Bu-*n*	**2a** 81 (75/25)[d]	**2d** 57 (57/43)	**2e** 50 (67/33)
≡—CH(OH)CH3	**7a** 43 (12/88)	**7b** 28 (14/86)	**7c** Trace
HC≡CH	**8a** 28 (83/17)[e]	**8b** 6 (82/18)[e]	**8c** 37 (80/20)[f]

a) Yield based on PhTeNa. b) The ratio of E/Z-isomers was determined by ^1H NMR except for **7**. c) Reaction started at −100 °C under CF_3Br atmosphere. d) ^1H NMR yields. e) Acetylene was transformed to lithium acetylide and then the reaction was conducted at −80 °C for 4 h. f) Acetylene bubbling.

1-hexyne was employed, the desired products **2** were obtained in moderate to good yields. It is noteworthy that trifluoromethyl-telluration which starts at a very low temperature (−100 °C) proceeds smoothly. Meanwhile, in the cases of 3-butyn-2-ol and acetylene, the compounds **7** and **8** were obtained in moderate to low yields (Scheme 2).

Experimental

Infrared spectra were taken on a Hitachi 270-30 spectrometer. The ^1H and ^{19}F NMR spectra were measured on a Varian VXR-200 using TMS for ^1H NMR and C_6F_6 for ^{19}F NMR as internal standards and $CDCl_3$ as the solvent. Because ^{19}F NMR spectra of the perfluorinated compounds **2a—d**, **7a**, **7b**, **8a**, and **8b** provided broadning or multiple signals, the center of those signals was indicated. Boiling points are uncorrected and are indicated by a temperature of a glass tube oven (°C/mmHg, 1 mmHg≈133.322 Pa).

Perfluorobutyl-Telluration of 1-Hexyne. Sodium benzenetellurolate was prepared from $(PhTe)_2$ (122.8 mg, 0.3 mmol) and $NaBH_4$ (68.1 mg, 1.8 mmol) dissolved in EtOH (0.5 ml) and benzene (0.5 ml) at 0 °C for 20 min. After the mixture was cooled at −40 °C, 1-hexyne (0.69 ml, 6.0 mmol) and C_4F_9I (0.21 ml, 1.2 mmol) were added to the tellurolate solution under N_2. The temperature of the reaction mixture was allowed to rise up to room temperature for 2 h under constant stirring and then the organic products were extracted with ether several times. The combined extracts were washed with brine and dried over Na_2SO_4. After evaporation of the solvent, the residue was chromatographed through silica gel using hexane to give a mixture of **2a** ($E:Z=75:25$, 246.6 mg, 81%) and **3a** (20.7 mg, 8%) together with **4** (13.2 mg, 5%).

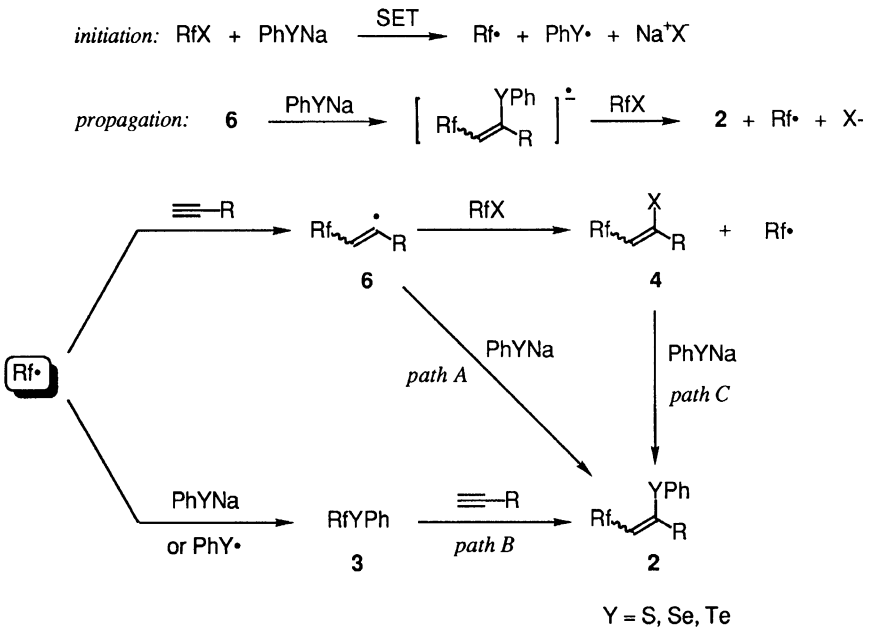
1-Butyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexenyl Phenyl Telluride (2a). Anal. Calcd for $C_{16}H_{15}F_9Te$: C, 37.99; H, 2.99%. Found: C, 37.65; H, 3.02%.

***E*-Isomer:** A yellow green oil; IR (neat) 1622 (C=C) cm^{-1}; ^1H NMR $\delta=0.89$ (3H, t, $J=7.2$ Hz, CH_3), 1.33 (2H, sex, $J=7.2$ Hz, $C\underline{H}_2CH_3$), 1.44—1.63 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.48—2.60 (2H, m, =(CTePh)$C\underline{H}_2$), 5.49 (1H, t, $J_{H-F}=15.1$ Hz, C_4F_9CH=), 7.22—7.48 (3H, m, ArH), 7.78—7.88 (2H, m, ArH); ^{19}F NMR $\delta=35.8$ (2F), 37.2 (2F), 57.0 (2F), 80.5 (3F).

***Z*-Isomer:** A yellow green oil; IR (neat) 1616 (C=C) cm^{-1}; ^1H NMR $\delta=0.71$ (3H, t, $J=7.2$ Hz, CH_3), 1.04 (2H, sex, $J=7.2$ Hz, $C\underline{H}_2CH_3$), 1.24—1.43 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.10—2.23 (2H, m, =C(TePh)$C\underline{H}_2$), 6.14 (1H, t, $J_{H-F}=15.4$ Hz, C_4F_9CH=), 7.23—7.48 (3H, m, ArH), 7.88—7.98 (2H, m, ArH); ^{19}F NMR $\delta=36.0$ (2F), 37.6 (2F), 54.4 (2F), 80.8 (3F).

1,1,2,2,3,3,4,4,4-Nonafluorobutyl Phenyl Telluride (3a). A yellow green oil; bp 50—60 °C (2 mmHg); IR (neat) 1576, 1236, 1000, 734 cm^{-1}; ^1H NMR $\delta=7.30$—7.40 (2H, m, ArH), 7.45—7.55 (1H, m, ArH), 7.98—8.08 (2H, m, ArH); ^{19}F NMR $\delta=36.1$ (2F), 45.6 (2F), 76.4 (2F), 80.5 (3F). Anal. Calcd for $C_{10}H_5F_9Te$: C, 28.35; H, 1.19%. Found: C, 28.23; H, 1.37%.

1-Butyl-3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluoro-1-decenyl Phenyl Telluride (2d). Anal. Calcd for $C_{20}H_{15}F_{17}Te$: C, 34.03; H, 2.14%. Found: C, 34.26; H, 2.32%.



Scheme 3.

***E*-Isomer:** A yellow green oil; IR (neat) 1622 (C=C) cm^{-1}; ^1H NMR δ=0.89 (3H, t, J=7.2 Hz, CH_3), 1.32 (2H, sex, J=7.2 Hz, $C\underline{H}_2CH_3$), 1.46—1.62 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.48—2.62 (2H, m, =C(TePh)$C\underline{H}_2$), 5.48 (1H, t, J_{H-F}=15.1 Hz, $C_8F_{17}CH$=), 7.23—7.47 (3H, m, ArH), 7.78—7.87 (2H, m, ArH); ^{19}F NMR δ=35.6 (2F), 38.2 (2F), 38.9 (2F), 39.7 (4F), 40.2 (2F), 57.2 (2F), 81.0 (3F).

***Z*-Isomer:** A yellow green oil; IR (neat) 1616 (C=C) cm^{-1}; ^1H NMR δ=0.70 (3H, t, J=7.3 Hz, CH_3), 1.03 (2H, sex, J=7.3 Hz, $C\underline{H}_2CH_3$), 1.24—1.41 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.10—2.23 (2H, m, =C(TePh)$C\underline{H}_2$), 6.14 (1H, t, J_{H-F}=15.2 Hz, $C_8F_{17}CH$=), 7.23—7.48 (3H, m, ArH), 7.88—7.98 (2H, m, ArH); ^{19}F NMR δ=35.6 (2F), 38.4 (2F), 39.0 (2F), 39.8 (4F), 40.2 (2F), 54.5 (2F), 81.0 (3F).

5,5,6,6,7,7,8,8,8-Nonafluoro-3-phenyltelluro-3-octen-2-ol (7a). Anal. Calcd for $C_{14}H_{11}OF_9Te$: C, 34.05; H, 2.25%. Found: C, 34.24; H, 2.44%.

***E*-Isomer:** A white solid; IR ($CDCl_3$) 3672 (OH), 1622 (C=C) cm^{-1}; ^1H NMR δ=1.48 (3H, d, J=6.2 Hz, CH_3), 2.37—2.46 (1H, m, OH), 4.89—5.02 (1H, br, C$\underline{H}$OH), 5.07 (1H, t, J_{H-F}=15.9 Hz, C_4F_9CH=), 7.25—7.49 (3H, m, ArH), 7.77—7.87 (2H, m, ArH); ^{19}F NMR δ=35.9 (2F), 37.2 (2F), 57.3 (2F), 80.8 (3F).

***Z*-Isomer:** A yellow green oil; IR (neat) 3352 (OH), 1622 (C=C) cm^{-1}; ^1H NMR δ=1.27 (3H, d, J=6.4 Hz, CH_3), 1.76—1.90 (1H, br, OH), 4.16 (1H, m, C$\underline{H}$OH), 6.66 (1H, t, J_{H-F}=15.8 Hz, C_4H_9CH=), 7.23—7.36 (2H, m, ArH), 7.38—7.48 (1H, m, ArH), 7.87—7.96 (2H, m, ArH); ^{19}F NMR δ= 36.0 (2F), 37.6 (2F), 55.2 (2F), 80.7 (3F).

5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,12-Heptadecafluoro-3-phenyltelluro-3-dodecen-2-ol (7b). Anal. Calcd for $C_{18}H_{11}OF_{17}Te$: C, 31.16; H, 1.60%. Found: C, 31.41; H, 1.82%.

***E*-Isomer:** A white solid; IR ($CDCl_3$) 3688 (OH), 1622 (C=C) cm^{-1}; ^1H NMR δ=1.48 (3H, d, J=6.2 Hz, CH_3), 2.30—2.37 (1H, m, OH), 4.89—5.04 (1H, m, C$\underline{H}$OH), 5.07 (1H, t, J_{H-F}=16.8 Hz, $C_8F_{17}CH$=), 7.25—7.49 (3H, m, ArH), 7.77—7.87 (2H, m, ArH); ^{19}F NMR δ=35.6 (2F), 38.0 (2F), 38.9 (2F), 39.7 (4F), 40.2 (2F), 57.4 (2F), 81.0 (3F).

***Z*-Isomer:** A white solid; IR ($CDCl_3$) 3460 (OH), 1620 (C=C) cm^{-1}; ^1H NMR δ=1.27 (3H, d, J=6.3 Hz, CH_3), 1.67—1.85 (1H, br, OH), 4.07—4.22 (1H, m, C$\underline{H}$OH), 6.66 (1H, t, J_{H-F}=15.6 Hz, $C_8F_{17}CH$=), 7.23—7.34 (2H, m, ArH), 7.36—7.47 (1H, m, ArH), 7.86—7.94 (2H, m, ArH); ^{19}F NMR δ=35.6 (2F), 38.5 (2F), 39.0 (2F), 39.8 (4F), 40.4 (2F), 55.5 (2F), 81.0 (3F).

1-Butyl-3,3,3-trifluoro-1-propenyl Phenyl Telluride (2e). After the preparation of the tellurolate as described above, the mixture was cooled at −100 °C and then 1-hexyne (6.0 mmol) was added to the tellurolate solution under N_2. A rubber balloon filled with CF_3Br gas was settled with a reaction flask and then under CF_3Br atmosphere, the mixture was stirred and the reaction temperature was allowed to rise up to room temperature for 2 h. After quenching the reaction with water, the organic products were extracted with ether several times. Chromatography of the crude products afforded **2e** (E:Z=67:33, 217.8 mg, 50%).

Anal. Calcd for $C_{13}H_{15}F_3Te$: C, 43.88; H, 4.25%. Found: C, 43.99; H, 4.32%.

***E*-Isomer:** A yellow green oil; IR (neat) 1626 (C=C) cm^{-1}; ^1H NMR δ=0.89 (3H, t, J=7.2 Hz, CH_3), 1.33 (2H, sex, J=7.2 Hz, $C\underline{H}_2CH_3$), 1.46—1.62 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.45—2.58 (2H, m, =C(TePh)CH_2), 5.63 (1H, q, J_{H-F}=8.3 Hz, CF_3CH=), 7.24—7.47 (3H, m, ArH), 7.79—7.89 (2H, m, ArH); ^{19}F NMR δ=104.8 (3F, d, J_{H-F}= 8.3 Hz, CF_3).

***Z*-Isomer:** A yellow green oil; IR (neat) 1626 (C=C) cm^{-1}; ^1H NMR δ=0.71 (3H, t, J=7.2 Hz, CH_3), 1.06 (2H, sex, J=7.2 Hz, $C\underline{H}_2CH_3$), 1.23—1.43 (2H, m, $C\underline{H}_2CH_2CH_3$), 2.06—2.19 (2H, m, =C(TePh)CH_2), 6.18 (1H, tq, J_{H-F}=8.3 Hz, J=1.2 Hz, CF_3CH=), 7.22—7.48 (3H, m, ArH), 7.85—7.95 (2H, m, ArH); ^{19}F NMR δ=102.5 (3F, d, J_{H-F}=8.3 Hz, CF_3).

3,3,4,4,5,5,6,6,6-Nonafluoro-1-hexenyl Phenyl Telluride (8a). Acetylene was bubbled in THF (3.0 ml) at

−80 °C for 10 min. *n*-BuLi (0.48 ml of 2.5 M in hexane, 1.2 mmol, M=mol dm^{-3}) was added to the acetylene–THF mixture and the mixture was stirred for 50 min. The lithium acetylide solution and C_4F_9I (1.2 mmol) were added to the tellurolate solution in EtOH (0.5 ml) and DMF (0.5 ml) at −80 °C. The mixture was stirred and the reaction temperature was allowed to rise up to room temperature for 4 h. After quenching the reaction with water, the organic products were extracted with ether several times. Usual workup provided **2e** (*E*: *Z*=83 : 17, 75.9 mg, 28%).

An inseparable mixture of *E*: *Z*-isomers; a yellow green oil; IR (neat) 1606 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_7F_9Te$: C, 32.05; H, 1.57%. Found: C, 31.86; H, 1.70%.

***E*-Isomer:** ^{1}H NMR δ=5.88 (1H, dt, J=16.6 Hz, J_{H-F}=11.4 Hz, C_4F_9CH=), 7.28—7.49 (3H, m, ArH), 7.74—7.87 (2H, m, ArH), 7.94 (1H, dt, J_1=16.6 Hz, J_2=2.2 Hz, =C<u>H</u>TePh); ^{19}F NMR δ=35.8 (2F), 37.5 (2F), 50.8 (2F), 80.6 (3F).

***Z*-Isomer:** ^{1}H NMR δ=6.57 (1H, dt, J=11.7 Hz, J_{H-F}= 14.5 Hz, C_4F_9CH=), 7.28—7.49 (3H, m, ArH), 7.74—7.87 (3H, m, =CHTePh); ^{19}F NMR δ=35.8 (2F), 37.0 (2F), 49.9 (2F), 80.6 (3F).

3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-Heptadecafluoro-1-decenyl Phenyl Telluride (8b). An inseparable mixture of *E*: *Z*-isomers; a pale orange oil; IR (neat) 1614 (C=C) cm^{-1}. Anal. Calcd for $C_{16}H_7F_{17}Te$: C, 29.57; H, 1.09%. Found: C, 29.69; H, 1.36%.

***E*-Isomer:** ^{1}H NMR δ=5.89 (1H, dt, J=16.5 Hz, J_{H-F}= 11.5 Hz, $C_8F_{17}CH$=), 7.28—7.50 (3H, m, ArH), 7.75—7.88 (2H, m, ArH), 7.95 (1H, d, J=16.5 Hz, =C<u>H</u>TePh); ^{19}F NMR δ=35.5 (2F), 38.0 (2F), 38.4 (2F), 38.9 (4F), 40.1 (2F), 51.0 (2F), 80.9 (3F).

***Z*-Isomer:** ^{1}H NMR δ=6.59 (1H, dt, J=11.3 Hz, J_{H-F}= 14.5 Hz, $C_8F_{17}CH$=), 7.28—7.50 (3H, m, ArH), 7.75—7.88 (3H, m, =CHTePh); ^{19}F NMR δ=35.5 (2F), 38.0 (2F), 38.4 (2F), 38.9 (4F), 40.1 (2F), 50.4 (2F), 80.9 (3F).

Phenyl 3,3,3-Trifluoro-1-propenyl Telluride (8c). The tellurolate solution dissolved in EtOH (0.5 ml), THF (1.8 ml), and DMF (0.6 ml) was cooled at −100 °C and then, acetylene was bubbled in the reaction flask. A rubber balloon filled with CF_3Br gas was settled on the reaction flask and then under CF_3Br atmosphere, the mixture was stirred and the temperature was allowed to rise up to room temperature for 2 h. After quenching the reaction with water, the organic products were extracted with ether several times. Usual workup gave **8c** (*E*: *Z*=80 : 20, 67.0 mg, 37%).

An inseparable mixture of *E*: *Z*-isomers; a yellow green oil; IR (neat) 1606 (C=C) cm^{-1}. Anal. Calcd for $C_9H_7F_3Te$: C, 36.06; H, 2.35%. Found: C, 36.20; H, 2.64%.

***E*-Isomer:** ^{1}H NMR δ=5.87 (1H, dq, J=16.6 Hz, J_{H-F}=6.3 Hz, CF_3CH=), 7.20—7.47 (3H, m, ArH), 7.78—7.91 (3H, m, =CHTePh); ^{19}F NMR δ=97.6 (3F, d, J_{H-F}=5.9 Hz, CF_3).

***Z*-Isomer:** ^{1}H NMR δ=6.57 (1H, dq, J=11.2 Hz, J_{H-F}= 7.7 Hz, CF_3CH=), 7.20—7.47 (3H, m, ArH), 7.61 (1H, d, J=11.2 Hz, =C<u>H</u>TePh), 7.78—7.82 (2H, m, ArH); ^{19}F NMR δ=98.8 (3F, d, J_{H-F}=7.8 Hz, CF_3).

Perfluorobutyl-Selenation of 1-Hexyne. Sodium benzeneselenolate was prepared from $(PhSe)_2$ (0.3 mmol) in EtOH (0.5 ml) as described above (0 °C for 15 min). 1-Hexyne (6.0 mmol) and C_4F_9I (1.2 mmol) were added to the selenolate solution under N_2. The reaction mixture was stirred at room temperature for 2 h and extracted with ether several times. Usual workup afforded a mixture of **2b** (*E*: *Z*=83 : 17, 95.8 mg, 19%) and **3b** (159.7 mg, 71%) together with **4** (78.4 mg, 15%).

1-Butyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexenyl Phenyl Selenide (2b). Bp 90—100 °C (1 mmHg). Anal. Calcd for $C_{16}H_{15}F_9Se$: C, 42.03; H, 3.31%. Found: C, 42.22; H, 3.40%.

***E*-Isomer:** A colorless oil; IR (neat) 1634 (C=C) cm^{-1}; ^{1}H NMR δ=0.91 (3H, t, J=7.2 Hz, CH_3), 1.36 (2H, sex, J=7.2 Hz, C<u>H</u>$_2$CH$_3$), 1.53—1.70 (2H, m, C<u>H</u>$_2$CH$_2$CH$_3$), 2.48—2.61 (2H, m, =C(SePh)C<u>H</u>$_2$), 5.12 (1H, t, J_{H-F}=15.6 Hz, C_4F_9CH=), 7.32—7.45 (3H, m, ArH), 7.54—7.63 (2H, m, ArH); ^{19}F NMR δ=35.9 (2F), 37.3 (2F), 57.2 (2F), 80.6 (3F).

***Z*-Isomer:** A colorless oil; IR (neat) 1624 (C=C) cm^{-1}; ^{1}H NMR δ=0.72 (3H, t, J=7.2 Hz, CH_3), 1.10 (2H, sex, J=7.2 Hz, C<u>H</u>$_2$CH$_3$), 1.27—1.45 (2H, m, C<u>H</u>$_2$CH$_2$CH$_3$), 2.06—2.20 (2H, m, =C(SePh)C<u>H</u>$_2$), 5.80 (1H, t, J_{H-F}=15.6 Hz, C_4F_9CH=), 7.25—7.44 (3H, m, ArH), 7.56—7.65 (2H, m, ArH); ^{19}F NMR δ=36.0 (2F), 37.6 (2F), 56.3 (2F), 80.8 (3F).

Perfluorobutyl-Sulfenylation of 1-Hexyne. Into the sodium benzenethiolate solution dissolved in EtOH (0.5 ml) and ether (1.2 ml), 1-hexyne (6.0 mmol) and C_4F_9I (1.2 mmol) were added under N_2. The reaction mixture was refluxed for 2 h and extracted with ether several times. Usual workup provided a mixture of **2c** (13.7 mg, 6%) and **3c** (27.4 mg, 14%) along with **4** (89.9 mg, 18%) and **5** (22.9 mg, 12%) after chromatography.

***E*-1-Butyl-3,3,4,4,5,5,6,6,6-nonafluoro-1-hexenyl Phenyl Sulfide (2c).** A colorless oil; bp 80—90 °C (1 mmHg); IR (neat) 1632 (C=C) cm^{-1}; ^{1}H NMR δ=0.93 (3H, t, J=7.2 Hz, CH_3), 1.39 (2H, sex, J=7.2 Hz, C<u>H</u>$_2$CH$_3$), 1.58—1.73 (2H, m, C<u>H</u>$_2$CH$_2$CH$_3$), 2.42—2.54 (2H, m, =C(SPh)C<u>H</u>$_2$), 4.77 (1H, t, J_{H-F}=15.6 Hz, C_4F_9CH=), 7.38—7.52 (5H, m, ArH); ^{19}F NMR δ=36.0 (2F), 37.3 (2F), 57.9 (2F), 80.7 (3F). Anal. Calcd for $C_{16}H_{15}F_9S$: C, 46.83; H, 3.68%. Found: C, 46.93; H, 3.79%.

2-Iodo-1-hexenyl Phenyl Sulfide (5). A mixture of *E*: *Z*-isomers; a colorless oil; IR (CCl_4) 1604 (C=C) cm^{-1}. Anal. Calcd for $C_{12}H_{15}IS$: C, 45.29; H, 4.75%. Found: C, 45.40; H, 5.02%.

***E*-Isomer:** ^{1}H NMR δ=0.94 (3H, t, J=7.1 Hz, CH_3), 1.27—1.60 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 2.59 (2H, t, J=7.1 Hz, =C(I)CH$_2$), 6.78 (1H, s, PhSC<u>H</u>=), 7.22—7.35 (5H, m, ArH).

***Z*-Isomer:** ^{1}H NMR δ=0.90 (3H, t, J=7.0 Hz, CH_3), 1.27—1.60 (4H, m, C<u>H</u>$_2$C<u>H</u>$_2$CH$_3$), 2.35 (2H, t, J=7.0 Hz, =C(I)CH$_2$), 7.22—7.35 (6H, m, PhSCH=).

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