CHEMISTRY LETTERS, pp. 1507-1510, 1992.

Fluoroselenenylation of Alkynes

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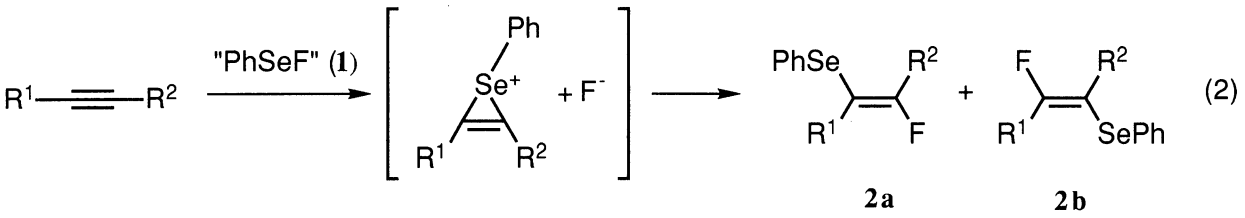
Benzeneselenenyl fluoride equivalent was generated *in situ* by the reaction of silver(I) fluoride with benzeneselenenyl bromide in dichloromethane under ultrasound irradiation. Treatment of internal alkynes with this reagent afforded 2-fluoro-1-alkenyl phenyl selenides in moderate yields.

Selective fluorination of organic substrates have received considerable attention because of potential utilities of fluorine-containing compounds as medicinal agents and as probes for positron emission tomography(PET).[1] Very few methods, however, involve addition reaction of fluorine across carbon-carbon triple bonds and they usually require hazardous reagents such as gaseous fluorine,[2a] halogen monofluorides,[2b] and pyridinium poly(hydrogen fluoride) $(HF)_x \cdot Pyr.$[2c] We expected that it would be more efficient to use electrophilic selenium reagents. In the previous paper,[3] we reported a new fluorination method of carbon-carbon double bond, which involve benzeneselenenyl fluoride equivalent generated from benzeneselenenyl bromide and silver(I) fluoride under ultrasonic conditions(Eq. 1). Herein we report an extension of this method to the substrates containing the carbon-carbon triple bond.

Benzeneselenenyl fluoride equivalent (**1**) was generated by the reaction of finely powdered silver(I) fluoride with benzeneselenenyl bromide in dichloromethane at 5-10 °C for 10 minutes under ultrasound irradiation (Eq. 1). Since attempts to isolate **1** were unsuccessful, it was employed *in situ*. Subsequent addition of a solution of an alkyne in

dichloromethane resulted in electrophilic 1,2-addition to produce the 2-fluoro-1-alkenyl phenyl selenide (**2**) in moderate yields (Eq.2). The results are summarized in Table 1 along with pertinent spectral data of the products **2**.

$$\mathrm{PhSeBr} + \mathrm{AgF} \xrightarrow[\textit{Sonication}]{} \underset{\mathbf{1}}{\text{"PhSeF"}} + \mathrm{AgBr} \qquad (1)$$

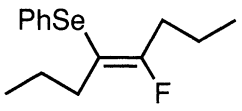
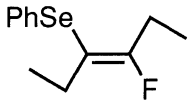
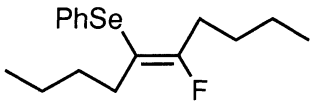
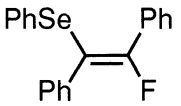
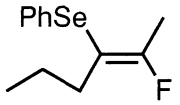
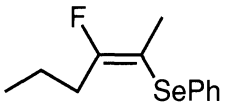
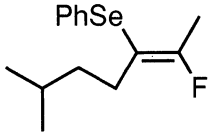
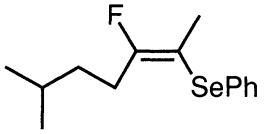
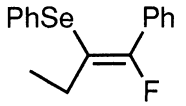


2a **2b** (2)

The synthesis of (E)-5-fluoro-4-phenylseleno-4-octene (**2a**) is outlined as follows: A suspension of finely powdered silver fluoride (140 mg, 1.1 mmol) and benzeneselenenyl bromide (241 mg, 1.0 mmol) in dry dichloromethane (2.5 mL) was irradiated with ultrasound at 5-10 ^{o}C for 10 minutes under nitrogen atmosphere. Pale yellow precipitates were formed and the dichloromethane solution turned pale yellow. After dropwise addition of a solution of 4-octyne (110 mg) in dry dichloromethane (3.5 mL), the mixture was further sonicated for 2 h at the same temperature. The residual oil, obtained by the usual extractive workup with chloroform, was purified by reversed phase liquid chromatography (TOSOH ODS-120T, acetonitrile as an eluent) to give **2a** as pale yellow oil(130 mg, 45.6%). ^{1}H-NMR (90 MHz, $CDCl_3$/TMS) δ 0.85 (3H, t), 0.93 (3H, t), 1.25-1.80 (4H, m), 2.32 (2H, dt, J=2.7, 7.8 Hz), 2.67 (2H, dt, J=22.5, 7.5 Hz), 7.08-7.42 (5H,m). ^{19}F-NMR (89.26 MHz, $CDCl_3/CFCl_3$) δ -92.1(m). ^{77}Se-NMR (17.04 MHz, $CDCl_3$; Me_2Se as an external reference) δ 336.7; HRMS Calcd. for $C_{14}H_{19}FSe$: 286.0636, Found: 286.0606.

The addition of **1** to alkynes produced exclusively the corresponding (E)-adducts **2**. The stereochemical assignments were based on the coupling constants between the two allylic methylene hydrogens and fluorine (for example, $^{4}J_{HF}$=2.7 Hz (cis), $^{3}J_{HF}$=22.5 Hz (geminal) for **2a**). Preferential *anti*-addition suggests the formation of the selenirenium cation as an intermediate as shown in Eq.2.[4] Unsymmetrical internal alkynes (entries **e** and

Table 1. Synthesis of 2-Fluoro-1-Alkenyl Phenyl Selenides

Alkynes	Product(s)	Yield/%	^{19}F-NMR[a)]	^{77}Se-NMR[b)]
a. 4-Octyne		45.6	-92.1	336.7
b. 3-Hexyne		24.5	-95.0	332.5
c. 5-Decyne		77.8	-92.4	337.5
d. Diphenylacetylene		69.8	-80.9	418.5
e. 2-Hexyne		16.7	-84.2	342.2
			-92.1	379.7
f. 6-Methyl-2-heptyne		49.4	-84.3	345.0
			-91.9	380.8
g. 1-Phenyl-1-butyne		41.6	-85.3	353.3

a) Obtained at 84.26 MHz in chloroform-d_1 with trichlorofluoromethane as an internal standard.
b) Obtained at 17.04 MHz in chloroform-d_1 with dimethylselenide as an external standard.

f) afforded in each case a 1:1 mixture of the two regioisomers,[5] indicating that the regioselectivity of the addition is not high. However 1-phenyl-substituted alkyne (entry **g**) gave only 1-fluorinated product. On the other hand, terminal alkynes do not afforded the desired fluorinated adducts to give only the corresponding alkynyl phenyl selenides.[6]

The reaction described herein provides exclusively (E)-2-fluoro-1-alkenyl phenyl selenides, which are considered as versatile intermediates in the synthesis of fluorinated organic compounds.

We thank the Ministry of Education, Culture and Science for continuous financial support through Grants-in-Aid in the Priority Area for Scientific Research (Nos.03233204 and 03453026).

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4) G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, **1975**, 3991.

5) The ratio was determined by ^{19}F-NMR spectroscopy.

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(Received May 21, 1992)