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Fluoroselenenylation of Alkenes

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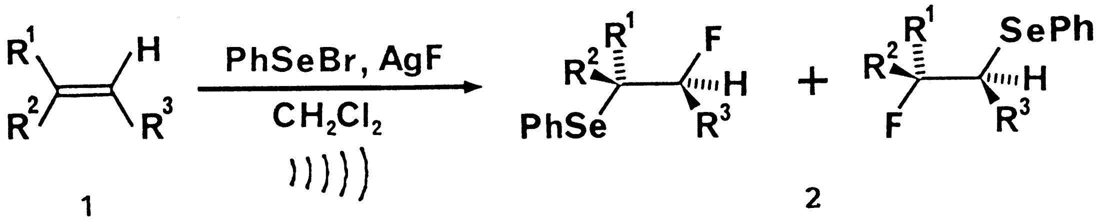
Treatment of alkenes with the reagent generated by the reaction of silver(I) fluoride with benzeneselenenyl bromide under ultrasound irradiation afforded 2-fluoroalkyl selenides in decent yields.

Although a number of methods for the introduction of fluorine into organic substrates have been developed and successfully utilized for the synthesis of fluorocarbons, polymers and chemotherapeutically important compounds,[1)] simple methods for direct introduction of fluorine atom into carbon-carbon double bonds are quite few:[2)] most of these employ hazardous reagents, such as molecular fluorine, hydrogen fluoride(HF),[2b)] HF-pyridine complex,[2c)] and acetyl hypofluorite,[2e)] the handling of which needs some caution. Very recently, a highly efficient procedure of introducing fluorine into alkenes using dimethyl(methylthio)sulfonium fluoroborate and HF-triethylamine complex has been reported.[3)] As an extension of our work on organic synthesis based on organoselenium methodology,[4)]we now describe a simple and safe method for fluorination of carbon-carbon double bond.



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In a typical procedure, a mixture of silver(I) fluoride(1.1 mmol) and benzeneselenenyl bromide (1.0 mmol) in dichloromethane (2.5 mL) was irradiated with ultrasound[5)] for 1 h at 5-10 °C under nitrogen atmosphere. After dropwise addition of a solution of alkene (1.0 mmol) in dichloromethane (3.5 mL), the mixture was further mixed with ultrasonic cleaner for 2 h at the same temperature. The residual oil, obtained by usual extractive workup with dichloromethane, was purified by reversed phase liquid chromatography to give 2-fluoroalkyl selenides (**2**).[6)]

Table 1 summarizes the results of the reaction along with pertinent spectral data of the products (**2**). The structures of **2** were confirmed by high-resolution mass spectra, ^{1}H, ^{13}C, ^{19}F, ^{77}Se NMR and IR spectral data. Each symmetrical alkene afforded a single adduct, indicating that the reaction is most likely to be a stereospecific trans-addition(entries **c** and **d**) as most addition reactions involving electrophilic selenium reagents. Entries **e**, **f**, and **g** show that Markovnikov products are the major regioisomers in all cases.

Table 1. Synthesis of 2-Fluoroalkylselenides (**2**) by the Reaction between Alkenes and the Reagent Generated by Mixing Benzeneselenenyl Bromide and Silver Fluoride[a]

Entry	Alkenes (**1**)	Yields/% of **2**	Molecular formula of **2**	MS(HEI)[b] (calcd)	^{19}F-NMR[c]	^{77}Se-NMR[d]
a	cyclohexene	57	$C_{12}H_{15}FSe$	258.0354 (258.0323)	-166.6 (br s)	368.6
b	cyclopentene	62	$C_{11}H_{13}FSe$	244.0107 (244.0166)	-161.6 (m)	345.0
c	<u>trans</u>-2-butene	38	$C_{10}H_{13}FSe$	232.0161 (232.0166)	-172.5 (m)	377.4
d	<u>cis</u>-2-butene	49	$C_{10}H_{13}FSe$	232.0134 (232.0166)	-168.7 (m)	361.4
e	2-methyl-2-butene	46	$C_{11}H_{15}FSe$	246.0239 (246.0323)	-133.7 (m)	381.8
f	2-ethyl-1-hexene	45	$C_{14}H_{21}FSe$	288.0806 (288.0792)	-148.0 (m)	246.0
g	1-hexene	59[e] major	$C_{12}H_{17}FSe$	260.0487 (260.0479)	-173.8 (m)	262.5
		minor		260.0504 (260.0479)	-207.0 (m)	-

Conditions: **1**(1.0 mmol), benezeneselenenyl bromide(1.0 mmol), silver(I) fluoride (1.1 mmol), dichloromethane(6 mL), irradiation with ultrasound, 3 h.
a) The 2-hydroxyalkyl selenides (**3**) were formed in 10 to 20% in all cases.
b) High-resolution mass spectra obtained with a JEOL JMS-D300. c) Obtained at 84.26 MHz in chloroform-d_1 with trichlorofluoromethane as an internal standard.
d) Obtained at 17.04 MHz in chloroform-d_1 with dimethylselenide as an external standard. e) Major: Markovnikov adduct(51%); minor: anti-Markovnikov adduct(8%).

Application of the present procedure to other substrates is now in progress and will be reported in due course.

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5) A Branson ultrasonic cleaner(Model B-1200, 30 W, frequency 45 kHz) was employed.

6) Since 2-fluoroalkyl selenides (**2**) were not stable under the usual chromatographic conditions using silica gel, they were separated by reversed phase liquid chromatography(TOSOH ODS-120T, acetonitrile).

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