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# BENZENESELENENYL FLUORIDE EQUIVALENT IN SITU GENERATED WITH $XeF_2$-$(PhSe)_2$ IN $CH_2Cl_2$ FOR FLUOROSELENENYLATION OF OLEFINS

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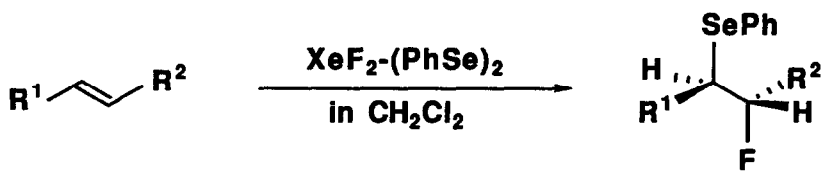
Summary; Benzeneselenenyl fluoride equivalent has been generated by the reaction of diphenyl diselenide with xenon difluoride in $CH_2Cl_2$ at -20 °C employed for fluoroselenenylation of olefins.

Organofluorine compounds have been accepting increasing attention because of their unique nature for material science and biological activities.[1] Monofluorinations of olefins have been performed by addition of alkyl and acetylhypofluorite,[2] bromofluoride,[3] iodofluoride,[3] hydrogen fluoride,[4] xenon difluoride,[5] and N-fluoropyridinium salt.[6]

One of the promising approach to allylfluoride from olefins would be fluoroselenenylation followed by oxidative deselenenylation. Benzeneselenenyl fluoride has not yet been characterized although both PhSeCl and PhSeBr have been widely empolyed.[7] Recently, Tomoda[8] and McCarthy[9] demonstrated a fluoroselenenylation of olefins by AgF-PhSeBr-ultrasound system and AgF-PhSeCl-MeCN system, respectively where an exchange of bromine with fluorine would involve in the initially formed haloselenenyl adducts and Saluzzo fluoroselenenylated olefins with an N-phenylselenophthalimide-Py-HF system.[10] No report on generation and reaction of PhSeF equivalent has been known so far.

Here, we describe a generation of PhSeF equivalent by the action of $(PhSe)_2$ with $XeF_2$[11] in $CH_2Cl_2$ and its reaction with olefins.




Reaction of $XeF_2$ with $(PhSe)_2$ takes place violently in dry $CH_2Cl_2$ at -20 °C. Gas evolution was observed and the $CH_2Cl_2$ solution turned dark brown. So, after addition of $XeF_2$ in $CDCl_3$ solution of $(PhSe)_2$ at -20 °C, $^1$H-NMR shows a new set of phenyl protons at 7.96-8.03 ppm (m, 2H) and 7.62-7.75 ppm (m, 3H) which are

down field by about 0.4 ppm from those of $(PhSe)_2$ and would correspond to ortho, meta, and para protons of PhSeF equivalent.[12] $^1$H-NMR of PhSeF equivalent, PhSeCl and PhSeBr in $CDCl_3$ demonstrates a similarity of the NMR patterns among these benzeneselenenyl halides and a regular down field shift of the chemical shifts dependent on the stronger electronegativity of the halogen atoms, suggesting fluorination occurs on selenium rather than phenyl ring. The $^1$H-NMR signals of PhSeF equivalent are considerably broadened within 15 min, revealing instability of the reagent at around 20 °C. In fact, the yield of fluoroselenenylation of 1,4-dicyano-2-butene decreased in the order of 72%, 51%, and 19% with the fluoroseleno-reagent stored at room temperature for 0 min, 20 min, and 60 min, respectively. The $^1$H-NMR signals of PhSeF equivalent disappeared soon after addition of an excess amount of cyclohexene to the $CDCl_3$ solution in an NMR tube and the new signals corresponding to -CHF- and PhSe-CH- moiety appeared.

Olefin was added to PhSeF equivalent generated at -20 °C in $CH_2Cl_2$ and allowed to react (temp. -20 °C~20 °C) for an appropriate time depending on the reactivity of an olefin (5~30 min.). The product fluoroselenides are in general unstable and are partially hydrolyzed to the corresponding hydroxyselenides in a silica gel chromatography. Especially, the reaction with styrene gave no desired fluoroselenide and exclusively the hydroxyselenide after chromatography although $^1$H-NMR of the extracted reaction mixture reveals the formation of the corresponding fluoroselenide. Benzeneselenenyl fluoride equivalent is an electrophile where PhSe moiety acts as an electrophilic center to react with olefins smoothly, providing preferentially Markownikoff type adducts.

The trans-addition was confirmed by the detailed NMR analysis of **2g**.[13] Benzeneselenenyl fluoride equivalent was found to be more reactive than PhSeCl and PhSeBr since it reacts even with an electron-deficient olefin, methyl acrylate and 2,5-dihydrothiophene-1,1-dioxide while PhSeCl-AgF-MeCN system failed.[9][14] This result clearly suggests the selenium-fluorine bond is more polarized than those of Se-Cl and Se-Br and thus PhSe moiety bears more positive charge and thus more electrophilic as supported by the lower field chemical shifts of phenyl protons of benzeneselenenyl fluoride equivalent.

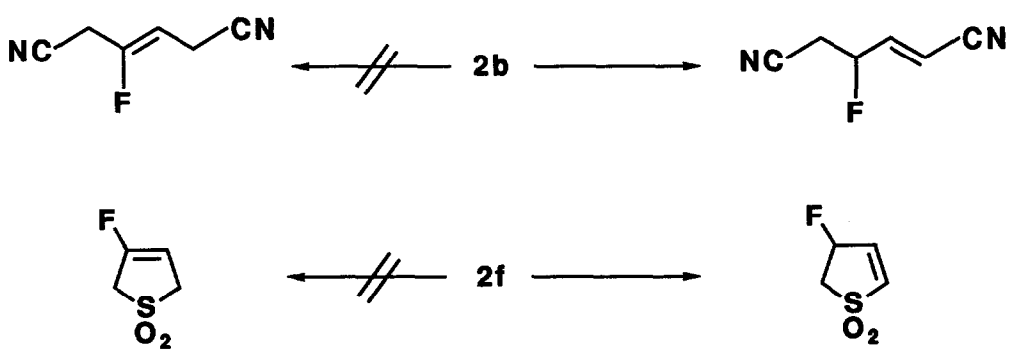
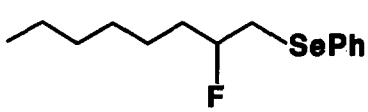
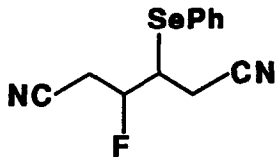


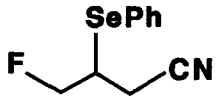
**Table Fluoroselenation of Olefins** [a), b)]



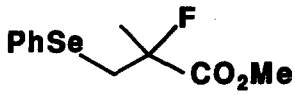

**2a (63%) [8%]**



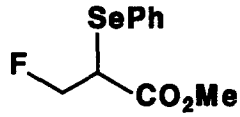

**2b (72%)**



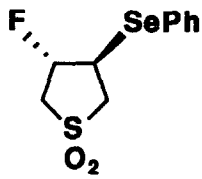

**2c (82%)** [c)]



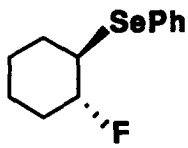

**2d (34%)**



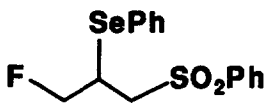

**2e (9%)**




**2f (43%) [22%]**




**2g (73%) [5%]**




**2h (71%) [22%]** [d)]

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a) $XeF_2$ (0.2 mmol) + $(PhSe)_2$ (0.21 mmol) + Olefin (0.42 mmol) + $CH_2Cl_2$ (1 ml) After 10 min stirring of $XeF_2$ and $(PhSe)_2$ in $CH_2Cl_2$ at -20 °C, an olefin was added and the mixture was stirred for 5 min ~ 30 min depending on the reactivity of olefins.

b) (Yield) and [Yield] represent isolated yields of **2** and the corresponding hydroxyselenide, respectively.

c) **2c** ; regioisomer (4-F : 3-F) = 63% : 19%

d) **2h** ; regioisomer (2-F : 3-F) = 25% : 75%

Oxidative deselenenylation of the fluoroselenides proceeds cleanly by the conventional hydrogen peroxide oxidation, affording the allylic fluoride exclusively rather than vinylic fluoride.[15] For example **2b** and **2f** were converted to 3-fluoro-1-buten-1,4-dinitrile (geometry of olefin, E:Z=90:10) and 4-fluoro-4,5-dihydrothiophene-1,1-dioxide in 88 % and 82%, respectively.

References and Notes


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11) Xenon difluoride adds C-C double[a] and triple bonds,[b] triphenylphosphine[c] and diphenyl sulfide.[d] a) T. C. Shieh, N. C. Yang, and C. L. Chernick, J. Am. Chem. Soc., **86**, 5021 (1964). b) M. Zupan and A. Pollak, J. Org. Chem., **39**, 2646 (1974). c) J. A. Gibson, R. K. Mart, and A. F. Janzen, Can. J. Chem., **53**, 3044 (1975). d) M. Zupan and B. Zajc, J. C. S. Perkin I., 965 (1978).
12) NMR of $PhSeF_3$ prepared by the action of $AgF_2$ with $(PhSe)_2$ was reported. W. M. Maxwell and K. J. Wynne, Inorg. Chem., **20**, 1707 (1981).
The structure of the present fluoroseleno reagent prepared from $(PhSe)_2$-$XeF_2$ is not clear at this moment. From the stoichiometry of $XeF_2$, the reagent behaves as PhSeF rather than $PhSeF_3$ since yield of **2c** (82%) is obtained on the basis of $XeF_2$. [ $(PhSe)_2 + XeF_2 \longrightarrow 2PhSeF$ ]
13) The coupling constant between both methyne protons of **2g** is J = 8.6 Hz.
14) No evidence for the formation of PhSeF equivalent was given in PhSeCl-AgF-MeCN[10] and PhSeBr-AgF-$CH_2Cl_2$-ultrasound systems.[8] The former case requires a prolonged reaction time (18h) at room temperature, and the latter case activates the reagent by ultrasound irradiation.
15) Similarly, oxidative deselenenylation of ß-hydroxyselenides occurs away from hydroxylated carbon, affording allylic alcohols. K. B. Shapless and R. F. Lauer, J. Am. Chem. Soc., **95**, 2697 (1973).


16) The authors are grateful to the Ministry of Education, Culture, and Science of Japan (a Grant-in-Aid, No 63303009 and No 01550675) and CIBA-GEICY Foundation for the financial support and the SC-NMR Laboratory of Okayama University for 500 MHz NMR analysis.

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