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Phosphorus, Sulfur, and Silicon and the Related Elements

Publication details, including instructions for authors and subscription information: http://www.informaworld.com/smpp/title~content=t713618290

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To cite this Article Ama, Kenji Uney , Asai, Hideki , Dan-Oh, Yasufumi and Funatsuki, Hiroshi(1997) 'Electrochemical Fluoro-Chalcogenation', Phosphorus, Sulfur, and Silicon and the Related Elements, 120: 1, 395 - 396

To link to this Article: DOI: 10.1080/10426509708545565 URL: http://dx.doi.org/10.1080/10426509708545565

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Electrochemical Fluoro-Chalcogenation

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Electrochemical fluoro-chalcogenation (S, Se) of alkenes and alkynes, and recycle use of *in situ* generated PhSeF for allylic fluorination are discussed.

Introduction of fluorine-functionality into organic molecules is a subject of current interests in synthetic fluorine chemistry. Organo-chalcogenes such as sulfur and selenium have potentially versatile reactivities and thus should promote transformations of fluorinated organic molecules. Here, we report a new electrochemical method for introduction of both fluorine and chalcogen functionalities into olefins and further transformations of the products by the use of characteristic reactivities of chalcogene atoms.

Benzene selencnyl and sulfenyl halides (PhMX, M: Se, S, X = Cl, Br) are well known. However, the corresponding fluorides PhSeF or PhSF have not yet been studied in details. In particular, PhSeF must be a very strong selenenylating reagent. Generation of the active reagents has been proposed by several groups, which consists of systems such as AgF-PhSeBr, AgF-R₂NSePh and XeF₂-(PhSe)₂.

$$(PhSe)_{2} \xrightarrow{-e} [(PhSe)_{2}]^{+ \cdot} \xrightarrow{Et_{3}N \cdot 3HF} [PhSeF]$$

$$1$$

$$R_{1} \xrightarrow{R_{2}} R_{2} \xrightarrow{R_{2}} \begin{bmatrix} PhSeF \end{bmatrix}$$

$$R_{1} \xrightarrow{F} R_{2} \xrightarrow{F} R_{2}$$

Electrochemical oxidation of (PhSe)₂ can generate an electron-deficient intermediate [(PhSe)₂]⁺ which reacts with HF leading to [PhSeF]. Likewise, a combination of (PhS)₂ and Et₃N•3HF would give [PhSF].

Electrochemical reaction was conducted in a CH₂Cl₂-Et₃N•3HF-olefin system in an undivided cell using Pt-Pt (2×3cm²)as electrodes. A constant current of 0.03A was passed at 0°C until (PhSe)₂ was consumed (4 F/mol). The result of the reaction is summarized in Table 1. The yields were dependent on the types of the substates. For example, both cyclic and cyclic aliphatic olefins reacted smoothly to give 2 in good yields. However, olefins such as ethyl 4-pentenoate and aryl allyl ether provided mainly the corresponding alcohols. Formation of 2 from methyl acrylate was failed because of the less reactivity of the electron-deficient olefin.

The addition of 1 to alkynes also gives the corresponding (E)-olefins 3 exclusively.

$$R_1$$
 or R_1 R_2 R_2 R_3 R_4 R_4 R_5 R

Table 1 Fluoro-selenenylation of alkenes and alkynes

Entry	R ₁	R ₂	Yield (%) of product ^a	
			2	3
1	— (CI	— (CH ₂) ₃ —		
2	— (CI	— (CH ₂) ₄ —		
3	— (CH ₂) ₆ —		78 ^{b.c}	
4	— (CI	— (CH ₂) ₁₀ —		
5	Н	Bu	.63 ^d	
6	Н	(CH ₂) ₅ CH ₃	65 ^e	
7	Н	(CH ₂) ₉ CH ₃	50 ^f	
8	$CH_3(CH_2)_4$	(CH2)4CH3		70 ^b
9	Ph	Bu		51 ^b
10	Ph	Me		35 ^b
11	Ph	Ph		10 ^b
12	Ph	Н		10 ^b

^a For entries 1~6, yields were obtained by ¹⁹F NMR. For entries 7~12, isolated yields based on (PhSe)₂ ^b trans- Isomer was a major product. ^c 6 eq. of olefin was used. ^d Regioisomer (2-F:1-F) = 94:6 ^f Regioisomer (2-F:1-F) = 93:7