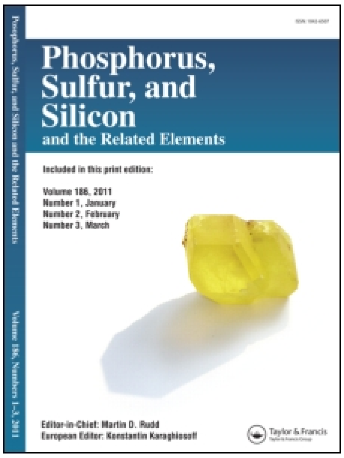


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Synthesis of Trifluoromethyl Selenides

Thierry Billard; Bernard R. Langlois; Sylvie Large

To cite this Article Billard, Thierry , Langlois, Bernard R. and Large, Sylvie(1998) 'Synthesis of Trifluoromethyl Selenides', Phosphorus, Sulfur, and Silicon and the Related Elements, 136: 1, 521 — 524
To link to this Article: DOI: 10.1080/10426509808545987
URL: http://dx.doi.org/10.1080/10426509808545987

Phosphorus Sulphur and Silicon
Vols. 136, 137 & 138 pp. 521–524
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF TRIFLUOROMETHYL SELENIDES

THIERRY BILLARD, BERNARD R. LANGLOIS* and SYLVIE LARGE
Université de Lyon I, Laboratoire de Chimie Organique 3 (UMR CNRS 5622), 43 Bd du 11 Novembre 1918, Villeurbanne, France

Alkyl and aryl trifluoromethylselenides are easily obtained from trifluoromethyl trimethylsilane and diselenides or selenocyanates as well as from sodium trifluoromethanesulfinate and diselenides or selenenyl chlorides, *via* trifluoromethaneselenosulfonates.

Keywords: trifluoromethyl selenides; trifluoromethyl trimethylsilane; trifluoromethaneselenosulfonates

INTRODUCTION

Growing interest is paid to bioactive organic trifluoromethyl sulfides because of the lipophilicity brought by the trifluoromethylthio moiety which is the most lipophilic one known until now (Hansch's constants Π_R (SCF_3)= 1.44 vs Π_R (SCH_3)= 0.61).[1] It is suspected that trifluoromethyl selenides are more lipophilic than their thio-analogs. However, very few accesses to these compounds have been described at the moment, except the reaction of benzeneselenenyl chloride with the "Ruppert's reagent" generated *in situ* from bromotrifluoromethane and tris-(diethylamino)phosphine.[2] Nevertheless, the preparation of the "Ruppert's reagent" needs special equipements so that new syntheses of trifluoromethylselenides have to be found.

RESULTS AND DISCUSSION

Trifluoromethyl selenides from trifluoromethyl trimethylsilane

Trifluoromethyl trimethylsilane (CF_3SiMe_3) is now commercially available. In the presence of soluble fluorides (Bu_4NF, 3 H_2O (TBAF) or TASF), it forms a pentacoordinated silicon species which acts as an equivalent of a trifluoromethyl anion. Though CF_3SiMe_3 has been extensively used to prepare α-trifluoromethyl silylethers from ketones and aldehydes, through an anionic chain process promoted by catalytic amounts of TBAF,[3] no reaction has been studied from sulfur- or selenium-containing substrates.

According to the fact that diselenides can behave as electrophiles, we observed, indeed, that diphenyl diselenide reacts at 0°C with CF_3SiMe_3 (2 equiv.) to deliver phenyl trifluoromethylselenide (43 %; ^{19}F NMR δ ($CDCl_3$, $CFCl_3$)= - 36.60 ppm), provided that a solution of TBAF (2 equiv.) is slowly dropped to the reaction medium.

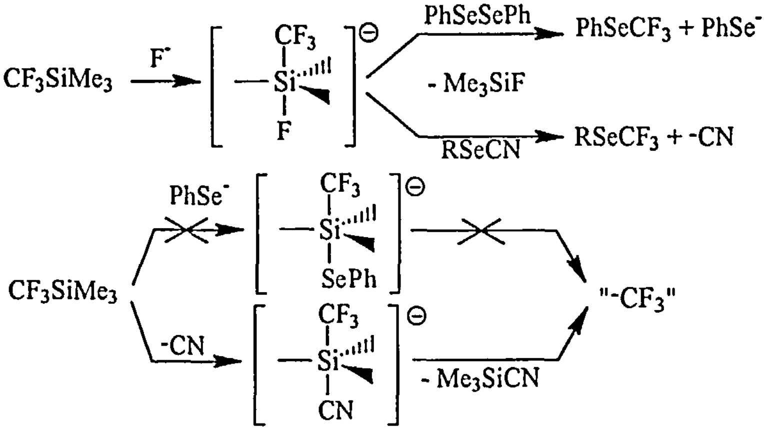
$$\mathrm{PhSeSePh} + \underset{(2\ \mathrm{equiv})}{\mathrm{CF_3SiMe_3}} + \underset{(2\ \mathrm{equiv})}{\mathrm{Bu_4N^+\,F^-}} \xrightarrow[0\ °\mathrm{C}]{\mathrm{THF}} \underset{43\ \%}{\mathrm{PhSeCF_3}} + \mathrm{Me_3SiF} + \mathrm{Bu_4N^+\,{}^-SePh}$$

In contrast to the reaction of CF_3SiMe_3 with carbonyl groups, an excess of TBAF is necessary in the present case since, because of the poor silicophilicity of selenium, the resulting selenophenate is not able to desilylate CF_3SiMe_3, as shown from Scheme 1. The situation is completely different when organoselenocyanates are reacted with CF_3SiMe_3. In this case, the cyanide anion is silicophilic enough to desilylate CF_3SiMe_3 and, therefore, TBAF can be used in a catalytic amount (Scheme 1).

$$\mathrm{RSeCN} + \underset{(2\ \mathrm{equiv})}{\mathrm{CF_3SiMe_3}} \xrightarrow[\mathrm{THF}\ /\ 0\ °\mathrm{C}]{\mathrm{TBAF}\ (0.2\ \mathrm{equiv})} \mathrm{RSeCF_3} + \mathrm{Me_3SiCN}$$

$R = n\text{-}C_8H_{17}$ (75 %)
$R = PhCH_2$ (70 %)
$R = Ph$ (60 %)

This technique provides a very good access to trifluoromethyl selenides since selenocyanates are readily prepared from organic halides, for instance, and cheap potassium selenocyanate.



SCHEME 1

Trifluoromethyl selenides *via* trifluoromethaneselenosulfonates

We recently reported on the preparation of phenyl trifluoromethaneselenosulfonates CF_3SO_2SePh from easily available sodium trifluoromethanesulfinate (CF_3SO_2Na) and benzeneselenenyl chloride or diphenyl diselenide in the presence of bromine or $PhI(OCOCF_3)_2$.[4] As expected, this compound can be photolytically cleaved to deliver PhSe•and CF_3SO_2•radicals; the latter, known to be unstable, generates a •CF_3 radical. Thus, recombination of PhSe• and •CF_3 would give phenyl trifluoromethylselenide $PhSeCF_3$. However, under these conditions, the yield did not exceed 25%. Nevertheless, in the presence of 1 equivalent of diphenyl diselenide, this yield raised up to 58 % and, moreover, the added diselenide was quite completely recovered.

$$\underset{\phantom{(1\ \text{equiv})}}{CF_3SO_2SePh} + \underset{(1\ \text{equiv})}{PhSeSePh} \xrightarrow[40\ °C\ /\ 80\ \text{min}]{h\nu\ /\ CH_2Cl_2} \underset{58\ \%}{CF_3SePh} + \underset{(1\ \text{equiv})}{PhSeSePh}$$

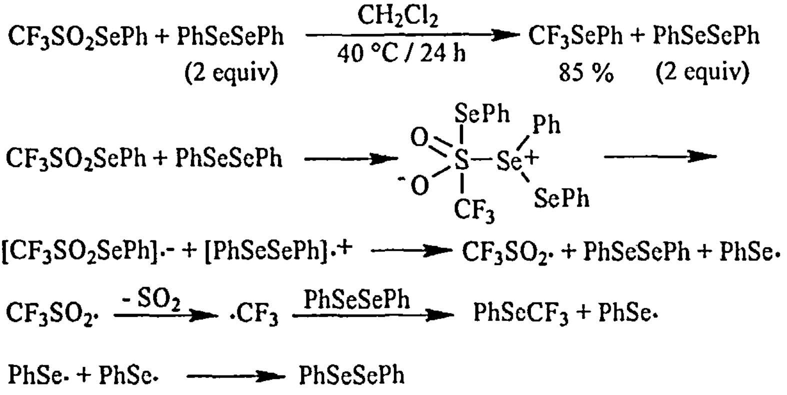
To account for these phenomena, a S_H2 mechanism can be proposed (Scheme 2). It has been also observed that, provided that 2 equivalents of PhSeSePh was added, irradiation was not necessary : $PhSeCF_3$ was obtained in a better yield (85 %) and, again, the added diphenyl diselenide was recovered. Such a process could involve the dissociation of a charge transfer complex between CF_3SO_2SePh, acting as an oxidant, and PhSeSePh, acting as a reducer (Scheme 3).

$$CF_3SO_2SePh \xrightarrow{h\nu} CF_3SO_2\cdot + PhSe\cdot\ (\longrightarrow 0.5\ PhSeSePh)$$

$$CF_3SO_2\cdot \longrightarrow \cdot CF_3 + SO_2$$

$$\cdot CF_3 + PhSeSePh \longrightarrow PhSeCF_3 + PhSe.\ (\longrightarrow 0.5\ PhSeSePh)$$

SCHEME 2



$$\underset{(2\text{ equiv})}{CF_3SO_2SePh + PhSeSePh} \xrightarrow[40\ °C\ /\ 24\ h]{CH_2Cl_2} \underset{85\ \%}{CF_3SePh} + \underset{(2\text{ equiv})}{PhSeSePh}$$

$$CF_3SO_2SePh + PhSeSePh \longrightarrow \longrightarrow$$

$$[CF_3SO_2SePh]\cdot^- + [PhSeSePh]\cdot^+ \longrightarrow CF_3SO_2\cdot + PhSeSePh + PhSe\cdot$$

$$CF_3SO_2\cdot \xrightarrow{-SO_2} \cdot CF_3 \xrightarrow{PhSeSePh} PhSeCF_3 + PhSe\cdot$$

$$PhSe\cdot + PhSe\cdot \longrightarrow PhSeSePh$$

SCHEME 3

The above-mentionned process thus allowed the one-step preparation of phenyl trifluoromethylselenide from CF_3SO_2Na (2 equiv), PhSeSePh (3 equiv) and bromine (1 equiv), 2 equivalents of PhSeSePh being recovered :

$$2\ CF_3SO_2Na + PhSeSePh + Br_2 \xrightarrow[\substack{CH_2Cl_2 \\ 40\ °C\ /\ 24\ h}]{PhSeSePh} 2\ CF_3SePh + 2\ SO_2 + 2\ NaBr \quad 80\ \%\ (70\ \%\ \text{isolated})$$

References

[1.] C. Hansch and A. Leo, *Substituent Constants for Correlation Analysis in Chemistry and Biology* (Wiley, New York, 1979).

[2.] I. Ruppert *et al.*, *J. Fluorine Chem.*, 29, 89 and 98 (1985); *J. Organomet. Chem.*, 316, 41 (1986).

[3.] G.K. Surya Prakash and A.K. Yudin, *Chem. Rev.*, 97, 757 (1997).

[4.] B.R. Langlois *et al.*, *J. Org. Chem.*, 61, 7545 (1996) and *J. Fluorine Chem.*, in press.