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SYNTHESIS OF TRIFLUOROMETHYL SELENIDES

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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.

<u>Keywords:</u> 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 (SCF₃)= 1.44 vs Π_R (SCH₃)= 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 (CF₃SiMe₃) is now commercially available. In the presence of soluble fluorides (Bu₄NF, 3 H₂O (TBAF) or TASF), it forms a pentacoordinated silicon species which acts as an equivalent of a trifluoromethyl anion. Though CF₃SiMe₃ 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 (CDCl₃, CFCl₃)= - 36.60 ppm), provided that a solution of TBAF (2 equiv.) is slowly dropped to the reaction medium.

PhSeSePh + CF₃SiMe₃ + Bu₄N⁺ F
$$\frac{THF}{0 \text{ °C}}$$
 PhSeCF₃ + Me₃SiF + Bu₄N⁺ SePh (2 equiv) (2 equiv) 43 %

In contrast to the reaction of CF₃SiMe₃ 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 CF₃SiMe₃, as shown from Scheme 1. The situation is completely different when organoselenocyanates are reacted with CF₃SiMe₃. In this case, the cyanide anion is silicophilic enough to desilylate CF₃SiMe₃ and, therefore, TBAF can be used in a catalytic amount (Scheme 1).

RSeCN + CF₃SiMe₃
$$\frac{\text{TBAF (0.2 equiv)}}{\text{THF / 0 °C}}$$
 RSeCF₃ + Me₃SiCN R = n -C₈H₁₇ (75 %) R = PhCH₂ (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.

$$CF_{3}SiMe_{3} \xrightarrow{F} \begin{bmatrix} CF_{3} \\ -Si^{"III} \\ F \end{bmatrix} \xrightarrow{\Theta} \xrightarrow{PhSeSePh} PhSeCF_{3} + PhSe^{-} \\ -Me_{3}SiF \\ RSeCN \xrightarrow{RSeCF_{3}} + -CN$$

$$CF_{3}SiMe_{3} \xrightarrow{PhSe^{-}} \begin{bmatrix} CF_{3} \\ -Si^{"III} \\ SePh \end{bmatrix} \xrightarrow{\Theta} \xrightarrow{PhSeSePh} PhSeCF_{3} + PhSe^{-} \\ -Me_{3}SiF \\ RSeCN \xrightarrow{RSeCF_{3}} + -CN$$

$$CF_{3}SiMe_{3} \xrightarrow{PhSeSePh} PhSeCF_{3} + PhSe^{-} \\ -Me_{3}SiF \\ -Si^{"IIII} \xrightarrow{PhSeSePh} RSeCF_{3} + -CN$$

$$CF_{3}SiMe_{3} \xrightarrow{PhSeSePh} PhSeCF_{3} + PhSe^{-} \\ -Si^{"IIII} \xrightarrow{PhSeSePh} RSeCF_{3} + -CN$$

$$CF_{3}SiMe_{3} \xrightarrow{PhSeSePh} RSeCF_{3} + -CN$$

$$CF_{3}SiMe_{3} \xrightarrow{PhSeSePh} -Me_{3}SiCN$$

Trifluoromethyl selenides via trifluoromethaneselenosulfonates

We recently reported on the preparation of phenyl trifluoromethane-selenosulfonates CF₃SO₂SePh from easily available sodium trifluoromethanesulfinate (CF₃SO₂Na) and benzeneselenenyl chloride or diphenyl diselenide in the presence of bromine or PhI(OCOCF₃)₂.^[4] As expected, this compound can be photolytically cleaved to deliver PhSe and CF₃SO₂ radicals; the latter, known to be unstable, generates a ·CF₃ radical. Thus, recombination of PhSe and ·CF₃ would give phenyl trifluoromethylselenide PhSeCF₃. 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.

$$CF_3SO_2SePh + PhSeSePh$$
 (1 equiv) $\frac{hv / CH_2Cl_2}{40 °C / 80 min}$ $CF_3SePh + PhSeSePh$ 58 % (1 equiv)

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: PhSeCF₃ 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{hv} CF_3SO_2 + PhSe· (\longrightarrow 0.5 PhSeSePh)
 CF_3SO_2 \longrightarrow . $CF_3 + SO_2$
. $CF_3 + PhSeSePh$ \longrightarrow PhSeCF₃ + PhSe. (\longrightarrow 0.5 PhSeSePh)
SCHEME 2

$$\begin{array}{c} CF_3SO_2SePh + PhSeSePh \\ (2 \ equiv) \end{array} \xrightarrow{\begin{array}{c} CH_2Cl_2 \\ \hline 40 \ ^{\circ}C \ / \ 24 \ h \end{array}} \begin{array}{c} CF_3SePh + PhSeSePh \\ 85 \% \qquad (2 \ equiv) \end{array}$$

$$CF_3SO_2SePh + PhSeSePh \xrightarrow{\begin{array}{c} O \\ S \\ CF_3 \end{array}} \begin{array}{c} SePh \\ S \\ CF_3 \end{array} \begin{array}{c} Ph \\ SePh \end{array}$$

$$[CF_3SO_2SePh] \cdot - + [PhSeSePh] \cdot + \begin{array}{c} CF_3SO_2 \cdot + PhSeSePh + PhSeSePh + PhSeSePh + PhSeSePh \\ CF_3SO_2 \cdot \begin{array}{c} -SO_2 \\ CF_3 \end{array} \begin{array}{c} PhSeSePh \\ PhSeSePh \end{array} \begin{array}{c} PhSeSePh \\ PhSeSePh \end{array}$$

SCHEME 3

The above-mentionned process thus allowed the one-step preparation of phenyl trifluoromethylselenide from CF₃SO₂Na (2 equiv), PhSeSePh (3 equiv) and bromine (1 equiv), 2 equivalents of PhSeSePh being recovered:

$$2 \text{ CF}_3 \text{SO}_2 \text{Na} + \text{PhSeSePh} + \text{Br}_2 \qquad \frac{\text{PhSeSePh}}{\text{CH}_2 \text{Cl}_2} \\ 40 \text{ °C} \text{ / 24 h} \qquad 2 \text{ CF}_3 \text{SePh} + 2 \text{ SO}_2 + 2 \text{ NaBr} \\ 80 \% \text{ (70 \% isolated)}$$

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