

A MILD AND PRACTICAL PREPARATION OF TRIFLUOROMETHANESELENENYL CHLORIDE

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Received March 19, 2002

Accepted June 6, 2002

Dedicated to the memory of Professor Miloš Hudlický.

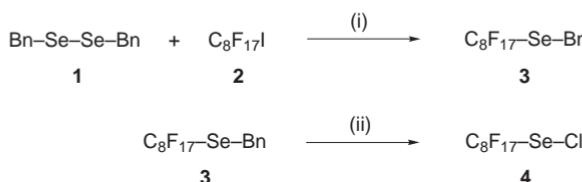
Trifluoromethaneselenenyl chloride is prepared by a two-step procedure with an 85% overall yield. Benzyl trifluoromethyl selenide is formed from dibenzyl diselenide and trifluoromethyl iodide in the presence of sodium hydroxymethanesulfinate. The benzyl–selenium bond is then cleaved with sulfuryl chloride to give the corresponding selenenyl chloride.

Keywords: Selenium; Fluorine; Radical ions; Electron transfer; Cleavage reactions.

Trifluoromethaneselenenyl chloride, CF_3SeCl , is a useful synthon for the introduction of the trifluoromethylseleno group into organic molecules^{1,2}. This chloride is classically obtained by reaction of a limited amount of chlorine with bis(trifluoromethyl) diselenide³, $\text{CF}_3\text{SeSeCF}_3$. The latter is formed, as a mixture with bis(trifluoromethyl) selenide, CF_3SeCF_3 , by treatment of trifluoromethyl iodide with selenium under pressure at 260–280 °C³. Following this method, the yield of the diselenide is limited to 10–15%. Alternatively, this compound is formed when a glass tube containing mercuric or silver trifluoroacetate and selenium is gradually heated in an open flame. In this case, yields are 16 and 28%, respectively⁴. Obviously, these harsh conditions and poor yields have limited the use of this fluorinated diselenide and consequently of its selenenyl chloride derivative.

Recently, we reported that perfluorooctaneselenenyl chloride, $\text{C}_8\text{F}_{17}\text{SeCl}$, can be obtained in a two-step procedure: formation of benzyl perfluoroctyl selenide from dibenzyl diselenide and perfluoroctyl iodide in the presence of sodium hydroxymethanesulfinate (Rongalite), followed by cleavage of the benzyl–selenium bond with chlorine or sulfuryl chloride (Scheme 1)⁵. Initially, application of this method to the preparation of

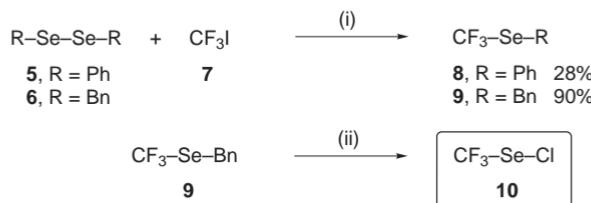
CF_3SeCl did not appear to be viable given that the yield in a similar reaction between trifluoromethyl iodide and diphenyl diselenide was rather limited (Scheme 2).



(i) $\text{HOCH}_2\text{SO}_2\text{Na}$, DMF, H_2O , rt, 80%; (ii) Cl_2 , CCl_4 , 0°C or SO_2Cl_2 , 0°C , 95%

SCHEME 1

However, we have observed very recently that the same reaction performed with the more reactive dibenzyl diselenide gives a much better yield. This mild transformation opens the way to an easy access to the very first member of the perfluoroalkylselenenyl chloride series (Scheme 2). Our method, previously described, has allowed us to produce the benzyl trifluoromethyl selenide (**9**) in 90% yield in a straightforward manner. The compound is obtained pure without any purification⁶. Such fluorinated selenides are also available by fluoride-catalysed nucleophilic trifluoromethylation of alkyl- or arylselenocyanate with trimethyl(trifluoromethyl) silane (Ruppert's reagent)^{7,8}. To facilitate the isolation of CF_3SeCl which has a very low boiling point (b.p. 22°C), the second step was performed without any solvent. Cleavage of the benzyl-selenium bond was accomplished by sulfuryl chloride. The desired compound was directly distilled and isolated in an almost quantitative yield (>95%). NMR data of compounds **9** and **10** were in total accordance with the literature^{7,9}.

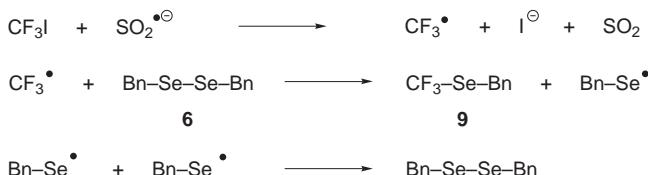


(i) $\text{HOCH}_2\text{SO}_2\text{Na}$, DMF, H_2O , rt; (ii) SO_2Cl_2 , rt, 95%

SCHEME 2

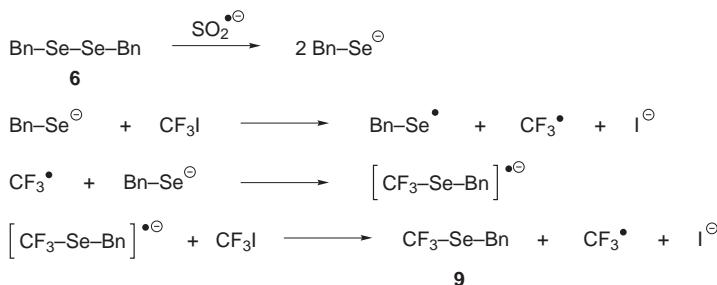
Several mechanisms can be considered for the formation of the benzyl trifluoromethyl selenide. It is known that hydroxymethanesulfinate salts can behave as a source of the sulfoxylate radical anion SO_2^\cdot ^{10,11}. The latter

is able to transfer an electron to trifluoromethyl iodide and to generate a trifluoromethyl radical^{11,12} (Scheme 3). Owing to the susceptibility of the weak selenium–selenium bond in diselenide to radical attack¹³, benzyl trifluoromethyl selenide can be produced from dibenzyl diselenide. This mechanism is similar to that proposed for the reaction of disulfides^{14,15}.



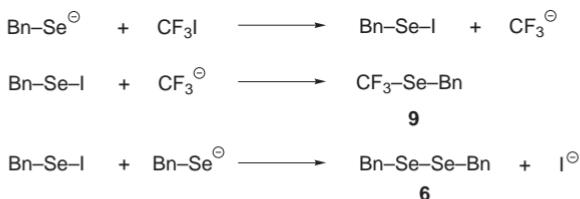
SCHEME 3

However, the reduction of diphenyl diselenide with sodium hydroxymethanesulfinate in alkaline ethanol has been described¹⁶. A selenide anion, which can also be formed, in small quantity, in the aqueous DMF medium employed¹⁷, can react with trifluoromethyl iodide by two different mechanisms¹⁸: an SRN1 process involving a radical chain reaction (Scheme 4)

SCHEME 4
SRN1 process

or a halogenophilic process occurring by intermediate formation of a trifluoromethyl carbanion¹⁹ (Scheme 5). However, the presence of this carbanion in the medium is highly improbable. It should react with water to form trifluoromethane or decompose quickly to difluorocarbene. Perhaps, the formation of the corresponding ate-complex²⁰ $[\text{BnSe-I-}\text{CF}_3]^{\bullet\ominus}\text{Na}^+$ could stabilize partially the carbanion and could be responsible for the benzyl trifluoromethyl selenide formation²¹. This anionic pathway appears rather unlikely. Evidence has been presented in support of the occurrence of a one-electron transfer from the selenide anion to perfluoroalkyl halides²². Nevertheless, in both mechanisms, the formation of dibenzyl diselenide

can occur, analogously with the behaviour of aliphatic thiolates²³ (Schemes 3, 5). The diselenide so produced is recycled and can react further to give benzyl trifluoromethyl selenide (Scheme 3). Consequently, formation of this selenide from trifluoromethyl iodide and dibenzyl diselenide in the presence of sodium hydroxymethanesulfinate can be the result of a competition of several processes (Schemes 3, 4, 5). We assume that the first one (Scheme 3) is probably the predominant one.



SCHEME 5
Halogenophilic process

In conclusion, we have developed an efficient and mild preparation of CF_3SeCl in two steps starting from a commercial product and with 85% overall yield.

EXPERIMENTAL

NMR spectra were recorded in CDCl_3 solutions, on a Bruker AC-300 spectrometer. Reported coupling constants (J , Hz) and chemicals shifts (δ , ppm) were based on a first-order analysis. Internal reference was the residual peak of CHCl_3 (7.27 ppm) for ^1H NMR spectra (300 MHz), central peak of CDCl_3 (77 ppm) for ^{13}C NMR spectra (75 MHz), internal CFCl_3 (0 ppm) for ^{19}F NMR spectra (282 MHz) and external Me_2Se (0 ppm) for ^{77}Se NMR spectra (57 MHz).

CAUTION: All experiments with CF_3SeCl must be carried out in well ventilated fume-hood with safety precautions. As CF_3SCl is known to be extremely toxic²⁴, it must be anticipated that CF_3SeCl is at least as toxic. This compound is stable and can be kept pure or in solution in the fridge.

Benzyl Trifluoromethyl Selenide (9)

Dibenzyl diselenide (5.13 g, 15.08 mmol) was dissolved in DMF (65 ml) under argon. Then, trifluoromethyl iodide CF_3I (9 g, 45.24 mmol) was bubbled into the solution. Lastly, water (1.2 ml) was introduced into the medium and sodium hydroxymethanesulfinate (7.00 g, 45.24 mmol) was added in portions over 4 h. The solution was stirred at room temperature for 16 h. The mixture was extracted three times with Et_2O , the organic layer washed with NaHCO_3 (5% in H_2O) and water, then dried over MgSO_4 , and concentrated under reduced pressure. The product **9** (6.50 g; 90%) was obtained pure without further purification as a pale yellow liquid. ^1H NMR: 7.36 m, 5 H (aromatic); 4.28 s, 2 H (benzylic). ^{19}F NMR: -34.0 s, 3 F. ^{13}C NMR: 136.2 ($\text{C}_{\text{Ar}}\text{H}$); 129.1 (2 $\text{C}_{\text{Ar}}\text{H}$); 128.9 (2 $\text{C}_{\text{Ar}}\text{H}$); 127.8 (C_{Ar}); 123.0 q (CF_3 , $J = 331$); 29.2 (CH_2).

Trifluoromethaneselenenyl Chloride **10**

Benzyl trifluoromethyl selenide (**9**; 2.00 g, 8.36 mmol) was placed in a two-necked round-bottomed flask, equipped with a magnetic stirring bar, a septum and a bridge connected to a series of two round bottomed flasks cooled with liquid nitrogen. Sulfuryl chloride (0.69 ml, 8.36 mmol) was added slowly with a syringe at ambient temperature. After 10 min, a flush of argon was applied. Trifluoromethaneselenenyl chloride (**10**; 1.75 g; 95%) was isolated in the two first traps (mainly in the first one) as an intensively red liquid. ^{19}F NMR: -41.6 s, 3 F. ^{13}C NMR: 121.1 q (CF_3 , $J = 335.7$). ^{77}Se NMR: 1 076.4 s.

This work was supported by the CNRS. The authors thank E. Vit who began this work.

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