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PREPARATION OF PERFLUOROORGANOSELENIDES FROM PERFLUOROALKENES AND SELENIUM OR DISELENIUMDICHLORIDE

A. HAAS*, C. LIMBERG and S.R. STERLIN**

Lehrstuhl für Anorganische Chemie II der Ruhr-Universität Bochum, Postfach 102 148, D-4630 Bochum (F.R.G).

SUMMARY

Hexafluoropropene reacts with selenium in dimethylformamide in the presence of CsF at 45-55°C to form tetrakis(trifluoromethyl)-1.3-diselenetane in 50% yield. With SbF_5 the diselenetane forms a dark blue selenium-centered radical-cation. Under mild conditions Se_2Cl_2 reacts with $CF_2{=}CF_2$ or $CF_3CF{=}CF_2$ in $HOSO_2F$ to yield $[FSO_2OCF_2CFX]_2Se_2$ as a major and $FSO_2OCF_2CFXSeCl$ (X = F, CF_3) as a minor product. In the presence of CsF at 8-10°C, **$[FSO_2OCF_2CF(CF_3)]_2Se_2$ reacts with methanol to give $[CH_3OC(O_2)CF(CF_3)]_2Se_2$.**

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* To whom correspondence should be addressed.

** Visiting scientist; on leave from Academy of Science of USSR, Nesmeyanov **Institute of** Organoelement Compounds; Laboratory of Organofluorine Compounds; ul. Vavilova 28, V-334 Moscow 117813, USSR.

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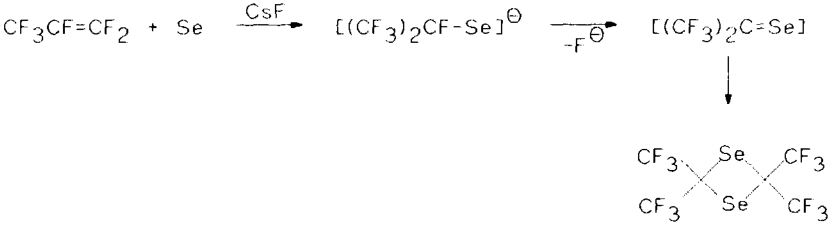
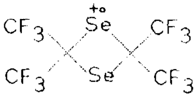
INTRODUCTION

The interaction of hexafluoropropene with sulfur in the presence of alkali metal fluorides in aprotic polar solvents is a convenient method for the preparation of tetrakis(trifluoromethyl)-1,3-dithiethanes [1-3]. Up to now the reaction of hexafluoroacetone with Ph_3PSe was the only preparative method for the synthesis of the analogous selenium compound [4]. It might be assumed that $CF_3CF{=}CF_2$ and selenium under similar reaction conditions form tetrakis(trifluoromethyl)-1,3-diselenetane (1). When $CF_3CF{=}CF_2$ and selenium are reacted in the presence of CsF in anhydrous DMF at 45-55°C 1 is obtained in 50% yield according to



1

In addition a complex mixture of other fluoroaliphatic derivatives of selenium -among them, according to GLC-data, perfluorodiisopropyldiselenide- is formed. It should be noted that contrary to the analogous reaction of $CF_3CF{=}CF_2$ with sulfur [2] the ratio of products obtained does not depend on the ratio of reagents. The yield of 1 is independent of the amounts of CsF used. While investigating some properties of 1 it was shown that on heating 1 with SbF_5 to 50-55°C (1-1,5 min) the formation of a dark-blue solution was observed. An unresolved strong broad ($W_{1/2}$ = 30 G) signal was identified by ESR-spectroscopy with a g factor (g = 2,01515) differing significantly from the value of a free electron. It can be supposed that the observed ESR-signal refers to the following selenium centered radical-cation.

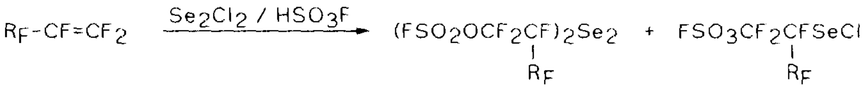


A less strong unresolved signal (g = 2,0128) was also observed in a solution of tetrakis(trifluoromethyl)-1,3-dithietane in SbF_5 after heating to 80-85°C for 3-4 min [5].

RESULTS AND DISCUSSION

Electrophilic methods for the synthesis of fluoroaliphatic derivatives of divalent selenium are of more theoretical than of preparative interest. The reaction of hexafluoropropene with selenium in the presence of SbF_5 [6] is carried out under extreme reaction conditions and provides complex product mixtures. This process can scarcely be considered as a convenient synthetic route for the preparation of fluoroalkylselenides.

It was found that Se_2Cl_2 under mild reaction conditions readily interacts with tetrafluoroethylene or hexafluoropropene in $HOSO_2F$ forming predominantly bis(fluorosulfatoperfluoroalkyl)diselenide (2a,b) and - as minor products - fluorosulfatoperfluoroalkylselenylchloride (3a,b) according to



$$R_F\text{-}CF{=}CF_2 \xrightarrow{Se_2Cl_2\ /\ HSO_3F} (FSO_2OCF_2\underset{R_F}{\underset{|}{C}}F)_2Se_2 + FSO_3CF_2\underset{R_F}{\underset{|}{C}}FSeCl$$

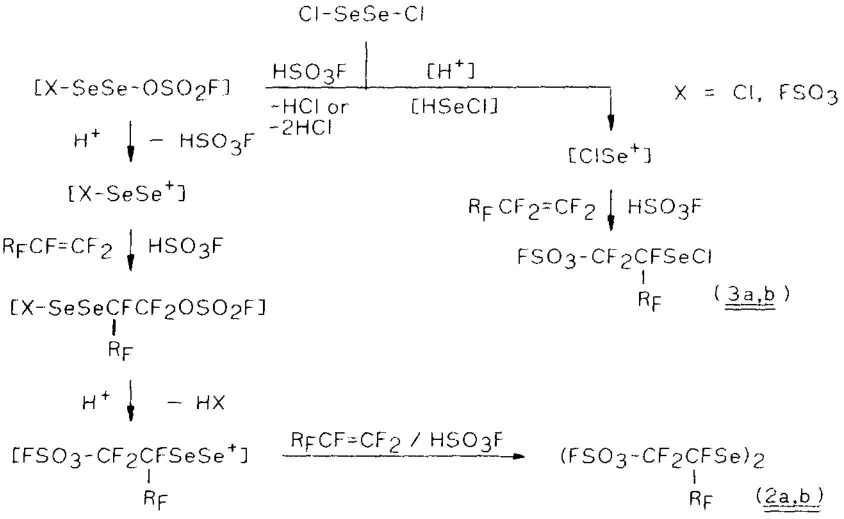
(2a,b) (3a,b)

R_F = F (2a-3a) ; CF_3 (2b-3b)

Since Se_2Cl_2 reacts vigorously with HSO_3F, it is reasonable to assume formation of fluorosulfate derivatives of selenium such as $ClSeSeOSO_2F$ or $Se_2(OSO_2F)_2$ as intermediates. In HSO_3F solution those add electrophilically to fluoroolefines forming the corresponding diselenides.

For the formation of selenylchlorides an alternative route, protonation of Se_2Cl_2 at the chlorine atom to generate a $ClSe^+$-cation, has to be considered.

The following reaction scheme could explain the formation of the final products.

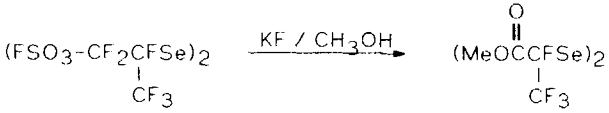


(3a,b)

(2a,b)

It should be noted that the main products of the reaction of hexafluoropropene with S_2Cl_2 in HSO_3F [7] are 2-chlorodithiohexafluoropropylfluorosulfate and bis(fluorosulfatohexafluoropropyl)trisulfide. Only traces of the corresponding disulfide are formed in the course of the reaction. Possibly such a distinct difference in product formation as observed in the reactions of $CF_3CF{=}CF_2$ with S_2Cl_2 or Se_2Cl_2 is due to the more "metallic" character of selenium and - as a consequence - easier generation of a fluorosulfatoperfluoropropyldiselenyl cation as compared with its disulfur analogue.

Bis-(α-methoxycarbonyltetrafluoroethyl)diselenide (4) was obtained by the reaction of 2b with methanol in the presence of KF.



$$(FSO_3\text{-}CF_2\underset{\displaystyle CF_3}{\underset{|}{C}}FSe)_2 \xrightarrow{KF\ /\ CH_3OH} (MeO\overset{\displaystyle O}{\overset{\|}{C}}\underset{\displaystyle CF_3}{\underset{|}{C}}FSe)_2$$

2b

(4)

The analogous reaction of 2a with CH_3OH/KF leads to the mineralization of all fluorine atoms and elimination of elemental selenium; the only organic product found in the reaction mixture was dimethyl oxalate.

EXPERIMENTAL

NMR-spectra were obtained on either a Bruker WM 250 or WP 80 PFT-spectrometer with chemical shifts relative to $CFCl_3$ (^{19}F), TMS (^{13}C) and CH_3SeCH_3 (^{77}Se) as external standards. A positive sign of chemical shift means a shift to lower field and a negative sign a shift to higher field relative to the standards.

Preparation of 2,2,4,4-Tetrakis(trifluoromethyl)-1,3-diselenetane (1)

A stream of hexafluoropropene is bubbled through a mixture of 12 g (0,152 mol) selenium, 2 g (0,013 mol) CsF and 50 ml of dry DMF at 45-48°C at a speed allowing a complete consumption of the gas. A weakly exothermic reaction occurs and after the complete dissolution of selenium the reaction mixture is quenched by water. The organic layer is separated and distilled from concentrated H_2SO_4. The distillate is cooled to -30°C and the solid filtered and washed with cold pentane. 17 g (0,037 mol) of pure 1 are obtained (yield: 48,8%). The liquid part of the reaction products (14 g) contains mainly 5 compounds. Two of them are $[(CF_3)CF]Se$ and $[(CF_3)CF]Se_2$ as their ^{19}F-NMR-spectra were identical with literature data [6].

NMR-data of 1:

^{19}F-NMR: δ(CF_3) = -68,8 (s) Lit. [4]: δ = -70,5

^{77}Se-NMR: δ(Se) = 666,6 (m)

^{13}C-NMR: δ(CF_3) = 123,1 (qu) ^1J(C-F) = 280,5 Hz

δ[C-$(CF_3)_2$] = 14,8 (sept) ^2J(C-F) = 36,0 Hz

m.p.: 59°C. The other analytical data are **equivalent** with those, found by Raasch [4].

Preparation of Bis(2-fluorosulfatotetrafluoroethyl)diselenide (2a) and 2-Fluorosulfatotetrafluoroethyl selenylchloride (3a)

A slow stream of tetrafluoroethylene is bubbled at 30-40°C through a mixture of 40 g (0,4 mol) HSO_3F and 23 g (0,1 mol) Se_2Cl_2, after the intensive evolution of HCl ceased. When the consumption of CF_2=CF_2 stops , the reaction mixture is poured into crushed ice, the organic layer is separated, washed with conc. H_2SO_4 and distilled in vacuo (yield: 40 g). The mixture contains 87% 2a, 10% 3a and 3% of an unidentified product by NMR. Analytically pure samples of 2a and 3a are obtained by additional fractionation.

$(FSO_3CF_2CF_2Se)_2$ (2a) is a straw yellow liquid with a penetrating smell. Yield: 29.9 g (53,5 %), b.p. 77-81°C/1,5 torr; ^{19}F-NMR: δ(OCF_2) = -82,0; δ(FSO_3) = 47,9; δ(CF_2Se) = -86.8.

$C_4F_{10}O_6S_2Se_2$ (556.1) calc. C: 8,64; F 34,17; found C 8.63; F 34,14.

$FSO_3CF_2CF_2SeCl$ (3a) is a deep red coloured liquid with a penetrating odour. Yield: 2,5 g (4,0 %), b.p. 48-50 °C/65 torr; ^{19}F-NMR: δ(OCF_2) = -82,0; δ(FSO_3) = 47,9; δ(CF_2Se) = -91.9.

$C_2ClF_5O_3SSe$ (313,5) calc. C: 8,64; F 34,17; found C 7,54; F 34,14.

Preparation of Bis(2-fluorosulfatohexafluoroisopropyl)diselenide (2b) and 2-Fluorosulfatohexafluoroisopropylselenylchloride (3b)

29 g (0,13 mol) of Se_2Cl_2 are added dropwise to 70 g (0,7 mol) HSO_3F. Evolution of HCl begins immediately. The mixture is stirred for 2h in a stream of argon, heated up to 60°C for 1h and then stirred in an atmosphere of hexafluoropropene for 7d. After that the reaction mixture is poured into crushed ice and the organic layer is separated. After distillation from conc. H_2SO_4, 27,4 g (32 .1%) of 2b are obtained as a straw yellow liquid.

b.p. 68-70° C/0,03 torr; ^{19}F-NMR: $\delta(FSO_3)$ = 50,1; $\delta(CF_3)$ = -74,3; $\delta(CF_2)$ = -76,7; $\delta(CF)$ = -161,0; ^{3}J $(C\underline{F}_3\text{-}C\underline{F})$ = 9,5 Hz.

$C_6F_{14}O_6S_2Se_2$ (656,1) calc. C 10,98; found C 10,9.

The other fraction gave 2,7 g (5,7 %) of 3b as a deep red liquid. b.p. 110-115° C; ^{19}F-NMR: $\delta(FSO_3)$ = 50,5; $\delta(CF_3)$ = -72,0; $\delta(CF_2)$ = -75,0; $\delta(CF)$ = -163,0 (all signals are broad singlets).

$C_3ClF_7O_3SSe$ (363,5) calc. C 9,91; Cl 9,75; found C 10,3; Cl 11.1

Preparation of Bis(α-methoxycarbonyltetrafluoroethyl)diselenide (4)

To the stirred suspension of 70 ml CH_3OH and 6 g (0,10 mol) dry KF 26,4 g (0,04 mol) of 2b are added at 8-10°C. After stirring for 40 min. the mixture is quenched by water, extracted with ether and dried over $CaCl_2$. The solvent is evaporated and the residue fractionated.

Yield: 17,5 g (92 %), b.p. 85-87°C/0,03 torr, mixture of diastereomers ; ^{19}F-NMR: $\delta(CF_3)$ = -74,5 (d); $\delta(CF)$ = -152,2 (q): ^{3}J (F–F) =10,2 Hz; $\delta(CF_3)$ = -74,6 (d); $\delta(CF)$ = -153,1 (q); ^{3}J (F-F) = 10,5 Hz;

$C_8H_6F_8O_4Se_2$ (476,1) calc. C 20,18; found C 19,7 .

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