Reaction of Tetrafluoroethylene with $Se_8(AsF_6)_2$ and $Se_8(Sb_2F_{11})_2$. Preparation of Bis(pentafluoroethyl) Triselenide and Perfluoroethyldiselenylperfluoroacetyl Fluoride

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Solid $Se_8(AsF_6)_2$ reacts with C_2F_4 at room temperature to form $(C_2F_5)_2Se_x$ (x = 2 or 3). $Se_8(Sb_2F_{11})_2$ gives similar products on reaction with C_2F_4 at 100 °C. In SO_2 solution $Se_8(AsF_6)_2$ and C_2F_4 give mainly $(C_2F_5)_2Se_2$ and $C_2F_5Se_2CF_2C[O]F$; the latter was characterised by its ^{19}F n.m.r. and mass spectrum.

VARIOUS polycations of Group VI have been prepared and characterized [1] and the structure of these and related compounds discussed.[1–3] However, their chemical properties have not been systematically investigated. As part of such a study,[4] solid $S_8(AsF_6)_2$ was allowed to react with tetrafluoroethylene at ambient pressure and temperature to yield $(C_2F_5)_2S_x$ ($x = 2$—6).[5] A reaction intermediate with C_2F_4 interacting with the weak *trans*-ring sulphur–sulphur bond in S_8^{2+}, was suggested.[6] The structure [7] of Se_8^{2+} is very much like that of S_8^{2+}, and it was of interest to determine whether a similar reaction yielding the corresponding bis(perfluoroethyl)polyselenides would occur. The selenium system is probably simpler in that Se_8^{2+} in the solid state, and in solution, is diamagnetic,[7,8] and that a species analogous to S_4^{+}, which exists in equilibrium with S_8^{2+} in solution,[9–11] has not been observed. The results reported herein involve the reaction of tetrafluoroethylene with $Se_8(AsF_6)_2$ and $Se_8(Sb_2F_{11})_2$.

EXPERIMENTAL

Apparatus.—All volatile compounds were manipulated in a Pyrex glass vacuum line fitted with ' Rotaflo ' valves or in a Monel vacuum line equipped with Whitey 1KS4 valves and Swagelok fittings. Mass spectra were obtained on a Hitachi–Perkin-Elmer RMU 6D mass spectrometer, with an ionizing voltage of 70 eV except where confirmation of molecular ions required reduced voltage. ^{19}F N.m.r. spectra were obtained on a Varian HA 100 (94·08 MHz) or on a Varian HA 60 (56·4 MHz) spectrometer. Vapour-phase chromatography analyses were obtained using ¼ in by 10 ft stainless-steel tubing filled with 10% Silicone Oil DC200/12,500 CS on 45/60 mesh Chromosorb W, NAW. V.p.c. preparative work was carried out by use of a 2465T Dohrmann Envirotech gas chromatograph equipped with a manual preparative collection unit. Programs were run isothermally at 80 °C with a helium gas flow-rate of about 33 ml min^{-1}. Retention times for $(C_2F_5)_2Se_2$, $C_2F_5Se_2CF_2C(O)F$, and $(C_2F_5)_2Se_3$ were 2·0, 4·1, and 12·8 min, with a 1 µl sample. I.r. spectra were recorded on a Perkin-Elmer 457 i.r. spectrometer using a 10 cm stainless-steel gas cell equipped with AgCl windows. High-pressure reactions were carried out in Monel vessels (40 ml) whose closure was made leak tight by use of a Teflon ' O ' ring, fitted with Whitey 1KS4 valves. Low-pressure reactions were carried out in vessels made from Kel F tubing (0·5 in o.d., 5/16 in i.d.) connected to the

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[8] J. Barr, R. J. Gillespie, R. Kapoor and K. C. Malhotra, *Canad. J. Chem.*, 1968, **46**, 149.

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vacuum line *via* a valve and a brass reducing Swagelok junction.

Reagents.—Tetrafluoroethylene (Columbia Organic Chemicals), sulphuryl fluoride (Chemicals Procurement Laboratories), selenium (Fisher Scientific Co.), and elemental fluorine (Matheson Co.) were all used without further purification. Sulphur dioxide and anhydrous hydrogen fluoride (Matheson Co.) were dried over calcium hydride and K_2NiF_6, respectively, and redistilled before use. Arsenic pentafluoride was prepared by fluorination of arsenic trifluoride (Ozark–Mahoning). Purity of gases was checked by i.r. spectroscopy. $Se_8(AsF_6)_2$ and $Se_8(Sb_2F_{11})_2$ were prepared by modifications of the methods reported by Gillespie and Ummat.[12]

Reaction of Solid $Se_8(AsF_6)_2$ *with* C_2F_4.—In a typical experiment $Se_8(AsF_6)_2$ (7·48 g, 7·41 mmol) was treated with an excess of C_2F_4 (*ca.* 20 atm) in a Monel reaction vessel for 2 days at room temperature. The volatile products contained C_2F_4, C_2F_6, a yellow liquid (7·74 g), and AsF_3 (1·73 g, 89% of the arsenic). The yellow liquid was separated by freezing out the AsF_3 and decanting off the liquid polyselenides into an isolatable side-arm. Arsenic trifluoride was unambiguously identified by its physical properties and i.r. spectrum. A mass spectrum of the yellow liquid showed (Table 1) the presence of bis(perfluoroethyl) diselenide and traces of bis(perfluoroethyl) triselenide. The high-resolution ^{19}F n.m.r. (Table 2) and i.r. spectrum (1330s, 1290wsh, 1225s, 1160m, 1115s, 930s, 750m, 620w, 545w cm^{-1}) were in substantial agreement with those reported.[13] A v.p.c. analysis showed the distribution of products to be >99% $(C_2F_5)_2Se_2$, <1% $(C_2F_5)_2Se_3$. Assuming the product to be the ' diselenide ', the yellow liquid incorporates 85% of the available fluorine from AsF_6^- (*i.e.* 3 fluorine atoms per AsF_6^-) and 66% of the available selenium. A greyish solid (2·5 g) was also obtained, which was partially soluble in SO_2 to give a mixture of crystalline products.

TABLE 1

Mass spectra of $C_2F_5Se_2C_2F_5$ based on isotope ^{80}Se

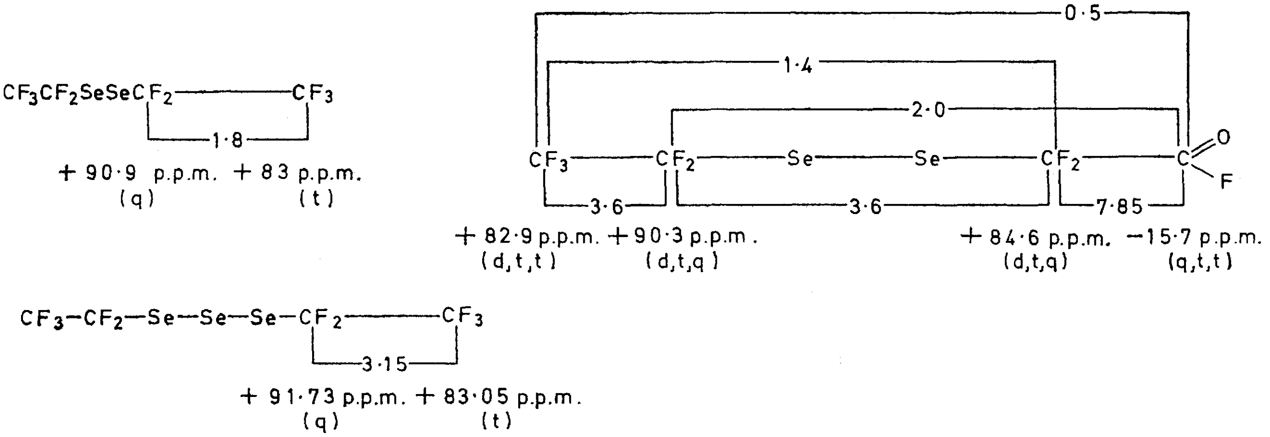
$(C_2F_5)_2Se_2$: 398 $C_2F_5Se_2C_2F_5$ (26), 379 $C_3F_4Se_2C_2F_5$ (1), 329 $CF_2Se_2C_2F_5$ (<1), 279 $C_2F_5Se_2$ (36), 260 $C_2F_4Se_2$ (8), 241 $CF{-}CF_2Se$ (<1), 210 CF_2Se_2 (<1), 199 C_2F_5Se (5), 191 $CFSe_2$ (<1), 180 C_2F_4Se(7), 172 Se_2C (<1), 160 Se_2 (39), 149 (CF_3Se (2), 142 $C{-}CF_2{-}Se$ (<1), 130 CF_2Se (8), 119 C_2F_5 (37), 111 SeCF (17), 100 C_2F_4 (23), 92 Se–C (1), 80 Se (9), 69 CF_3 (100,) 50 CF_2 (8), 31 CF (24)

The reaction was also carried out at 100 °C. In a typical reaction 6·1 mmoles $Se_8(AsF_6)_2$ (6·1 g) was reacted with excess of C_2F_4 (*ca.* 20 atm) in a Monel vessel at 100 °C for 3 days. The volatile products were removed and consisted of C_2F_4, C_2F_6, AsF_3 (1·37 g, 83·5% of the arsenic), and a yellow liquid (6·15 g). The mass spectrum showed the presence of $(C_2F_5)_2Se_2$, $(C_2F_5)_2Se_3$, and traces of $(C_4F_9)_2Se_2$, $C_4F_9Se_2C_2F_5$, and $C_4F_9Se_3C_2F_5$. V.p.c. analysis showed the distribution of products to be 95% $(C_2F_5)_2Se_2$, 4·5% $(C_2F_5)_2Se_3$, and traces of other material presumed to be the C_4F_9 derivatives found in the mass spectrum. 85·3% of available fluorine and 64·2% of available selenium were incorporated into the polyselenides. A greyish solid (1·24 g) remained which contained traces of SO_2 soluble products. An *X*-ray diffraction powder photograph of this solid was identical to that of elemental selenium (grey). This solid product contained 31·6% of the available selenium

The mixture of polyselenides was distilled under vacuum (10^{-3} mmHg) at room temperature. The residue contained a mixture of bis(pentafluoroethyl) di- and tri-selenides in about equal proportions. A sample of triselenide was obtained from this mixture by preparative scale v.p.c. A v.p.c. analysis of this product showed that it contained 75% $(C_2F_5)_2Se_3$, 15% $C_2F_5Se_3C_4F_9$, 8% $(C_2F_5)_2Se_2$, and *ca.* 2% of unidentified material. The mass spectrum showed peaks attributable to the molecular ion 476 $(C_2F_5)_2Se_3$ (74·72) and various fragments containing three selenium atoms [457 $C_2F_4Se_3C_2F_5$ (7·12), 357 $Se_3C_2F_5$ (100), 338 $Se_3C_2F_4$ (8·79)] as well as peaks attributable to $C_4F_9Se_3C_2F_5$ and $(C_2F_5)_2Se_2$. The distribution of peaks in the $(C_2F_5)_2Se_3$ molecular ion is compared to the calculated distribution, and the corresponding pattern found and calculated for the ' diselenide' (Table 3). The high-resolution ^{19}F n.m.r. spectrum (Table 2) was consistent with the presence of C_2F_5 and was differens from the diselenide. The ' triselenide ' was much lest

TABLE 2

Schematic representation of the ^{19}F n.m.r. spectra † of $(C_2F_5)_2Se_2$, $CF_3CF_2Se_2CF_2C[O]F$, and $(C_2F_5)_2Se_3$



† CCl_3F Internal standard.

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stable than the bisperfluoroethyl diselenide and reacted immediately with moisture and deposited elemental selenium in the vacuum line on transfer under vacuum.

Reaction of $Se_8(AsF_6)_2$ *with* C_2F_4 *in the Presence of* O_2SF_2.—In a typical reaction $Se_8(AsF_6)_2$ (10·7 mmol, 10·8 g) was treated with excess of C_2F_4 (*ca.* 20 atm) in the presence of O_2SF_2 (7 g) in a Monel vessel at 100 °C for 3 days. The products were C_2F_4, C_2F_6, an unidentified reddish brown solid (2·55 g), AsF_3 (1·41 g), and a yellow liquid (6·2 g). The yellow liquid was shown by v.p.c. to contain *ca.* 99% $(C_2F_5)_2Se_2$ and $<1\%$ $(C_2F_5)_2Se_3$, as well as small traces of other material. Molecular ions attributable to $(C_2F_5)_2Se_2$, $(C_2F_5)_2Se_3$, $C_2F_5Se_2C_4F_9$, $C_2F_5Se_3C_4F_9$, and $(C_4F_9)_2Se_2$ were observed in the mass spectrum. 48·5% of available fluoride and 36·4% of available selenium were incorporated into the polyselenides.

A reaction also occurred at room temperature. $Se_8(AsF_6)_2$ (11·2 g) was treated with excess of C_2F_4 (*ca.* 20 atm) and O_2SF_2 (7 g) for 3 days to give a yellow liquid (1·8 g) and an unidentified reddish solid (10·95 g). 13·6% of available fluoride ion and 10·2% of available selenium were incorporated into the polyselenides.

Reaction of Solid $Se_8(Sb_2F_{11})_2$ *and* C_2F_4.—$Se_8(Sb_2F_{11})_2$ (1·26 mmol, 1·95 g) was reacted with C_2F_4 (10 atm) in a Monel vessel for 3 days. The products were C_2F_4 and a white-green solid (3·64 g) which was partly soluble in SO_2. The soluble portion was identified as $Se_8(Sb_2F_{11})_2$ and the insoluble portion was found to be a Teflon-like amorphous white solid, which was insoluble in strong acids and bases.

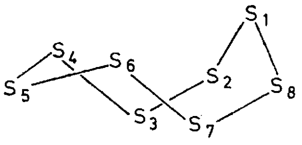
$Se_8(Sb_2F_{11})_2$ (0·75 mmol, 1·16 g) was allowed to react with C_2F_4 (*ca.* 10 atm) at 100 °C for 3 days. The volatile products contained C_2F_4, C_2F_6, and a yellow liquid (0·58 g) which was shown by mass spectrometry to contain largely $(C_2F_5)_2Se_2$ with traces of $(C_2F_5)_2Se_3$ and $C_4F_9Se_2C_2F_5$. A v.p.c. analysis showed that the product contained $>99\%$ $(C_2F_5)_2Se_2$ as well as traces of other material. An unidentified brown solid (2·15 g) was obtained. Its i.r. spectrum showed the presence of fluorine attached to antimony(V), and C–F bonds. 42·5% of the available fluoride ion and 32% of available selenium were incorporated into the polyselenides.

Reaction of $Se_8(AsF_6)_2$ *with* C_2F_4 *in* SO_2.—$Se_8(AsF_6)_2$ (2·15 mmol) was dissolved in liquid SO_2 and treated with C_2F_4 in a glass vessel equipped with a 'Rotaflo' valve. The partial pressure of C_2F_4 above the solution was maintained at *ca.* 3 atm for 2 days. The solution turned from green to wine-red and *ca.* 11 mmol of C_2F_4 (1·1 g) were consumed. The volatile products were C_2F_4, C_2F_6, SO_2, OSF_2, traces of a noncondensable gas thought to be carbon monoxide, AsF_3 (0·5 g), and a yellow liquid (2·33 g): a yellowish brown unidentified SO_2-soluble solid (0·35 g) remained. V.p.c. analysis of the yellow liquid showed it to contain 60% $(C_2F_5)_2Se_2$, 36% $C_4F_8OSe_2$, 2% $C_2F_5Se_2CF_3$, and traces of $(CF_3)_2Se_2$ and $(C_2F_5)_2Se_3$; 91% of available fluoride ion and 68% of available selenium were incorporated into the polyselenides. The mass spectrum of the product showed molecular ions corresponding to all species. The sample was distilled at 100 °C and 115 mmHg pressure. The residue was shown (v.p.c.) to contain 85·3% $C_4F_8OSe_2$, 10% $(C_2F_5)_2Se_2$, and 4·7% of other species. An i.r. spectrum of this mixture had a strong absorption at 1870 cm^{-1}; the ^{19}F n.m.r. spectrum contained peaks attributable to $C_2F_5Se_2CF_2C[O]F$ (Table 2). The mass spectrum included peaks attributable to 398 $(C_2F_5)_2Se_2$ (imp) (1·5), 376 $C_2F_5Se_2CF_2C[O]F$ (16·1), 329 $C_2F_5Se_2CF_2$ (1·0), 279 $C_2F_5Se_2$ (23·2), 260 $C_2F_4Se_2$ (3·6), 257 $Se_2CF_2C[O]F$ (9·8), 238 $Se_2CF_2C[O]$ (2·7), 97 $CF_2C[O]F$ (3·6), and 47 C[O]F (33·0) (CF_3 = 100). The rest of the spectrum was similar to that observed for $(C_2F_5)_2Se_2$. $C_2F_5Se_2CF_2C[O]F$ reacted readily with moisture and Apiezon N grease.

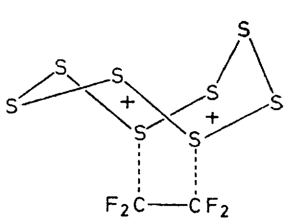
RESULTS AND DISCUSSION

$Se_8(AsF_6)_2$ reacts with tetrafluoroethylene at room temperature at moderate pressures to yield bis(pentafluoroethyl) diselenide, arsenic trifluoride, and small amounts of bis(pentafluoroethyl) triselenide. Increased yields are obtained at 100 °C. Similar results are obtained in the presence of SO_2F_2 in which $Se_8(AsF_6)_2$ is not detectably soluble at 0 °C. $Se_8(Sb_2F_{11})_2$ causes polymerization of tetrafluoroethylene at room temperature, but at 100 °C it reacts to give bis(pentafluoroethyl) diselenide and traces of bis(pentafluoroethyl) triselenide. Very small traces of C_4F_9 derivatives were detected as products in the reactions carried out at 100 °C.

Octasulphur bishexafluoroarsenate reacts with tetrafluoroethylene at ambient pressures and temperatures to give $(C_2F_5)_2S_x$ (x = 2—6).[5] It was suggested that this reaction proceeds by addition of C_2F_4 across the *trans*-ring S(3)–S(7) bond in S_8^{2+} (1) [4] to form the intermediate (2). The selenium reaction may proceed by an analogous mechanism. The structure [7] of Se_8^{2+} is similar to that of S_8^{2+}, although the Se–Se bond corresponding to S(3)–S(7) is relatively shorter [S(3)–S(7) 2·86, *cf.* S–S in S_8 [14] 2·048; Se(3)–Se(7) 2·84, *cf.* Se–Se in α- and β-selenium [15,16] 2·30—2·36 Å]. It is possible then that S(3)–S(7) is weaker than Se(3)–Se(7). Sulphur–carbon bonds are stronger than selenium–carbon [17] bonds and it would be expected therefore that $S_8C_2F_4^{2+}$ would be more readily formed than $Se_8C_2F_4^{2+}$. Experimentally it is observed that the reaction of C_2F_4 with solid $Se_8(AsF_6)_2$ requires higher pressures of C_2F_4, or higher temperatures, to proceed at a comparable rate to that of the S_8^{2+} reaction. Formation of bis(perfluoroethyl) selenides may then proceed by fluoride-ion transfer from the anion to the intermediate followed by fluorination and cleavage of selenium–selenium bonds by the pentafluoride and addition of C_2F_4 across Se–F bonds.



(1)



(2)

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Intermediates of the type $^{+}Se_xC_2F_5$ may react with C_2F_4 and abstract fluoride from AsF_6^- to form $C_2F_5Se_xC_2F_5$ ($x = 2$, 3). Arsenic(v) hexafluoride anion donates fluoride ion more readily than $Sb_2F_{11}^-$, and presumably, at room temperature $Se_8C_2F_4^{2+}$ accompanied by the anion $Sb_2F_{11}^-$, acts as a polymerization initiator, rather than accepting fluoride ion from the anion. The tendency for fluoride-ion donation increases with increase in temperature, and at 100 °C $Se_8(Sb_2F_{11})_2$ reacts with C_2F_4 to give largely bis(perfluoroethyl) diselenide.

Perfluoroalkyl selenides have been previously prepared by the reaction of perfluoroalkyl iodide and selenium at 260 °C and by the reaction of $R_FC[O]OAg$ with selenium at 280 °C.[18,19] These reactions lead to monoselenides and lesser amounts of diselenides. Emeléus[20] and co-workers suggested that bis(perfluoromethyl) triselenide was produced in the reaction of CF_3I and selenium at 260—285 °C, on the basis of a molecular-weight determination. However, unambiguous evidence was not given. The reaction of $Se_8(AsF_6)_2$ with C_2F_4 under mild conditions gave mostly bis(perfluoroethyl) diselenide and small amounts of bis(perfluoroethyl) triselenide, characterized by its mass spectrum and ^{19}F n.m.r. (Tables 2 and 3). Bis(perfluoroethyl) diselenide has been prepared and characterized.[13]

TABLE 3

Molecular-ion isotopic distribution

	m/e	Isotopic distribution (calc.)[a]	Mass spectra distribution (obs.)[a,b]
(a) $(C_2F_5)_2Se_3$			
	468	1·38	1·6
	470	4·69	5·1
	472	11·78	12·2
	474	20·56	20·6
	476	26·75	26·5
	478	23·66	23·2
	480	9·24	9·0
	482	1·57	1·8
(b) $(C_6F_5)_2Se_2$			
	390	1·42	1·8
	392	6·61	7·1
	394	17·07	17·6
	396	29·18	29·4
	398	33·89	33·0
	400	10·65	10·2
	402	0·98	0·9

[a] Only even mass numbers included. [b] For molecular ion.

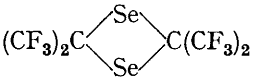
$Se_8(AsF_6)_2$ reacts with C_2F_4 in the presence of sulphur dioxide to give $(C_2F_5)_2Se_2$, $C_2F_5Se_2CF_2C[O]F$, and small amounts of $C_2F_5Se_2CF_3$, $(CF_3)_2Se_2$, and $(C_2F_5)_2Se_3$. $C_2F_5Se_2CF_2C[O]F$ has a strong peak in the i.r. spectrum at 1870 cm^{-1} in a similar region to the C=O stretch in $CF_3C[O]F$ (1890 cm^{-1}).[21] The mass spectrum has a molecular ion corresponding to $C_4F_8OSe_2$ and fragments which support the formulation $C_2F_5Se_2CF_2C[O]F$. ^{19}F N.m.r. spectra provide conclusive evidence for the suggested structure (Table 2). It is observed that all the fluorines are spin-coupled and that the coupling is first-order. Coupling between fluorines separated by six atoms is observed. Not dissimilar coupling constants are found for 3-fluoroxyperfluoropropionyl fluoride.[22,23] It would appear that perfluoroethyldiselenylperfluoroacetyl fluoride is the first compound of this type to be unambiguously identified. Evidence for the related[5] sulphur compounds $C_2F_5S_xCF_2C[O]F$ ($x = 2$ or 3) has been obtained from the analogous reaction of $S_8(AsF_6)_2$ with C_2F_4 in SO_2. The nature of the solids produced in the various reactions of tetrafluoroethylene and salts of Se_8^{2+} are unknown, and are still under investigation.

The mechanism of the reaction of $Se_8(AsF_6)_2$ and C_2F_4 in sulphur dioxide solution may be similar to that of the neat reaction except that intermediate (2), or a species similar to it may react according to equations (1) and (2).

$$(1)\quad Se_8C_2F_4^{2+} + SO_2 \longrightarrow {}^{+}Se_8CF_2CF_2O\overset{+}{S}O$$

$$(2)\quad {}^{+}Se_8CF_2CF_2OSO + AsF_6^- \longrightarrow {}^{+}Se_8CF_2C[O]F + OSF_2 + AsF_5$$

$^{+}Se_8CF_2C[O]F$ may further react with C_2F_4 and AsF_6^- to form $C_2F_5Se_2CF_2C[O]F$. This and OSF_2 were both observed as reaction products. Olah[24] *et al.* have shown that sulphur dioxide reacts with very acidic carbonium ions. $C_2F_5Se_2CF_2C[O]F$ may decarbonylate in the presence of arsenic pentafluoride to give the observed $C_2F_5Se_2CF_3$, and CO. Carbon monoxide and $C_2F_5Se_2CF_3$ were both formed on reaction of $C_2F_5Se_2CF_2C[O]F$ and AsF_5.[25]

While this work was in progress Knunyants[26] *et al.* reported the reaction of perfluoropropylene with elemental selenium and antimony pentafluoride in sulphur dioxide solution at 120 °C. Se_4^{2+} was suggested as an intermediate and $(CF_3)_2CFSeCF(CF_3)_2$, $(CF_3)_2CFSe_2CF(CF_3)_2$, and  were detected as products. A similar reaction using tetrafluoroethylene gave a small amount of bisperfluoroethyl diselenide. Compounds analogous to perfluoroethyldiselenylperfluoroacetyl fluoride were not observed.

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