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Arylselenium Trifluorides[1]

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Oxidative fluorination of diaryl diselenides, $(RSe)_2$, with silver difluoride generates the corresponding arylselenium trifluorides, $RSeF_3$, where R = C_6H_5, p-$CH_3C_6H_4$, p-FC_6H_4, o-$C_2H_5C_6H_4$, and o-$NO_2C_6H_4$. These compounds are moisture-sensitive crystalline solids. Molecular weight, infrared, and ^{19}F NMR data are presented and discussed with regard to $RSeF_3$ structures in solution and the solid state. A pseudo-trigonal-bipyramidal structure is proposed for the above compounds, except for o-$NO_2C_6H_4SeF_3$ for which a pseudo-octahedral structure is proposed. ^{19}F NMR data show that rapid fluorine exchange occurs for the arylselenium trifluorides when R = C_6H_5, p-$CH_3C_6H_4$, and p-FC_6H_4. Sterically restricted F exchange is observed for R = o-$C_2H_5C_6H_4$, while coordinatively restricted exchange is found for R = o-$NO_2C_6H_4$. Assignments of the Se–F vibrational modes are given assuming local C_s symmetry around Se. Infrared studies suggest only a limited tendency for $RSeF_3$ molecules to achieve maximum coordination in the solid state via intermolecular fluorine bridge bonding. Phenylseleninyl fluoride, C_6H_5SeOF, is found to be a product of the reaction of $C_6H_5SeF_3$ with water vapor or phenylseleninic acid.

Introduction

Although a large number of organosulfur(IV) fluorides have been prepared,[2a,b] relatively few organoselenium(IV) fluorides have been synthesized. Emeleus and Heal[3] prepared the first organoselenium(IV) fluorides, viz., trimethyl- and triphenylselenonium fluorides. More recently, the synthesis of a number of dialkyl- and diarylselenium difluorides was reported.[4,5] In addition, the synthesis of a number of (perfluoroorgano)selenium trifluorides has been described.[6,7a–c] As an extension of our work on organoselenium fluorides, we now describe the synthesis and properties of arylselenium trifluorides.

Experimental Section

General Procedures. The extreme moisture sensitivity of the compounds prepared in this study necessitated the use of a dry-nitrogen atmosphere and standard vacuum line techniques. Also, unless otherwise noted, it was necessary to minimize the contact of arylselenium trifluorides and their solutions with glass. Infrared spectra were obtained with use of a Perkin-Elmer Model 621 spectrometer. Solution IR spectra were recorded with samples in 0.5-mm polyethylene cells, while solid-state spectra were obtained on samples in Nujol mulls between polyethylene or silver chloride plates. Proton nuclear magnetic resonance (NMR) data were obtained with the use of a Perkin-Elmer Hitachi Model R-20 spectrometer, while fluorine NMR spectra were obtained by utilizing a Varian HA 100. Sampling of compounds was accomplished by use of Teflon inserts (NMR Specialties). ^{19}F NMR spectra were obtained in the presence of anhydrous NaF so as to minimize the effect of advantitious water or HF. Molecular weight data were obtained cryoscopically in dry benzene with use of a nonglass apparatus previously described.[5] Analytical data were obtained from Meade Microanalytical, Inc., Galbraith Laboratories, Inc., and Atlantic Microlab, Inc.

Materials. Freon 113 (1,1,2-trifluoroethane, Matheson Coleman and Bell) and CH_2Cl_2 were distilled from P_2O_5 onto Linde 5-Å molecular sieves. The latter were previously dried at 300 °C (10^{-3} torr) for 24 h. Chloroform was purified by shaking several times with one-half volume of water. The alcohol-free material was dried first with calcium chloride, then with P_2O_5, and finally distilled onto 5-Å molecular sieves and stored in the dark. Benzene was dried by distillation onto 5-Å molecular sieves. Silver difluoride was obtained from Ozark-Mahoning and used without further purification.

Preparation of Diaryl Diselenides.[8] Diphenyl (61%, mp 61–62 °C; lit.[9] 62 °C) and bis(o-ethylphenyl) (43%, bp 175 °C (0.10 torr)) diselenides were prepared by the Grignard route.[9] Bis(p-fluorophenyl) diselenide (46%, mp 18–21 °C), a new compound, was also prepared via this route. Anal. Calcd for $C_{12}F_2H_8Se_2$: C, 41.4; H, 2.30. Found: C, 41.3; H, 2.28. Bis(o-nitrophenyl) diselenide (75%, mp 140–142 °C; lit.[10] 142 °C) was prepared via the diazonium salt.[11]

Preparation of Arylselenium Trifluorides. Initial attempts to prepare arylselenium trifluorides in a glass reaction vessel lead to low yields of impure products. After the reaction, the glass vessel was found to be severely etched. It was subsequently found that a 500-mL narrow-mouth polypropylene bottle (Kimble) served as an ideal reaction vessel for most other operations described below.

Phenylselenium Trifluoride (I). Diphenyl diselenide (5.46 g, 0.0175 mol) was placed in a 500-mL polypropylene bottle, dry Freon 113 (200 mL) was added, and the solution was stirred magnetically until all the diselenide had dissolved. Silver difluoride (16.6 g, 0.114 mol) was added to the yellow diselenide solution. The mixture was gently refluxed (bp of Freon 113 is 47 °C) with stirring under a slow stream of dry nitrogen with the use of a glass condenser which had been tightly fitted into the mouth of the bottle. The connection between the bottle and condenser was sealed with wax. After 4 h the previously black silver difluoride had turned orange-brown, indicating reduction from the argentic to the argentous state. The reaction mixture was quickly filtered through a fritted glass filter into a polypropylene filter flask. The flask was stoppered, wrapped in a polyethylene bag, and cooled (–20 °C) for 12 h. Filtration yielded fine, white needles which were placed in a polyethylene test tube and pumped at 10^{-3} torr for 2 h (yield 2.35 g). Percent yields and other pertinent data are presented in Table I.

p-Tolylselenium Trifluoride (II). This compound was prepared in a manner similar to that described above. However, the p-tolyl derivative required 7 h of refluxing for conversion of the diselenide to the trifluoride.

(p-Fluorophenyl)selenium Trifluoride (III). The reflux time for the preparation of this compound was 7 h. Due to the greater solubility of this trifluoride, approximately 50 mL of solvent was removed by evaporation with a stream of dry N_2 before placing the polyethylene flask into the freezer.

(o-Ethylphenyl)selenium Trifluoride (IV). The reflux time required for this compound was 14 h. After being cooled at –20 °C overnight, the solution yielded an oil. Several attempts were made utilizing various solvents and solvent combinations to crystallize the oil, but none were successful. The oil was fractionally distilled in vacuo with

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Table I. General Properties and Analytical Results

Compound	%Yield[a]	Appearance	Melting Point[b]	%C		%H		%F		Cryoscopic[c] Molecular Weights
				Calcd	Found	Calcd	Found	Calcd	Found	
$C_6H_5SeF_3$(I)	32	colorless needles	78–80°	33.75	33.70	2.34	2.40	26.75	26.71	Calcd 213 Obs 197, 0.1049m 206, 0.0440m
p-$CH_3C_6H_4SeF_3$ (II)	24	colorless plates	114–116°	37.01	36.91	3.08	3.10	25.10	24.89	Calcd 227 Obs 219, 0.0445m
p-$FC_6H_4SeF_3$ (III)	51	colorless microcrystals	51–52°	31.20	31.01	1.73	1.67	32.90	32.68	Calcd 231 Obs 211, 0.0261m
o-$C_2H_5C_6H_4SeF_3$ (IV)	74	amber solid	25–27°	39.91	40.17	3.75	3.80	23.60	23.46	Calcd 241 Obs 228, 0.0365m
o-$NO_2C_6H_4SeF_3$ (V)	77	yellow irregular crystals	112–115°	27.91	28.00	1.55	1.60	22.10	21.96	Calcd 258 Obs 274, 0.0150m

[a] Based on $(ArSe)_2$. [b] Uncorrected; in sealed capillary. [c] In benzene.

the use of a Pyrez micro distillation apparatus. All connections were sealed with Kel-F polymer wax (3M Co.). The light amber trifluoride distilled between 89 and 93 °C (0.085 torr). After distillation, there was no visual evidence that this trifluoride derivative had reacted with the glass apparatus. The distillation pot which reached a temperature of 160 °C was not etched. Upon being cooled (−20 °C) overnight, the light amber oil crystallized to a dark amber solid.

(*o*-Nitrophenyl)selenium Trifluoride (V). An attempted preparation of (*o*-nitrophenyl)selenium trifluoride using the method described above was unsuccessful. Bis(*o*-nitrophenyl) diselenide is insufficiently soluble in Freon 113 to allow its conversion to the trifluoride. Although the diselenide is soluble in hot benzene, the fluorination of benzene by AgF_2 is too rapid to allow for its use as solvent. Dry, freshly distilled chloroform served well as a solvent for the conversion of bis(*o*-nitrophenyl) diselenide to the trifluoride.

Bis(*o*-nitrophenyl) diselenide (5.1 g, 0.012 mol) and AgF_2 (12.6 g, 0.085 mol) were refluxed with magnetic stirring in chloroform for 27 h. After filtration into a polypropylene flask, a stream of dry N_2 was used to reduce the volume to ca. 20 mL. Freon 113 (150 mL) was then added and the lemon-yellow solution placed at −20 °C. This solution yielded 5.0 g of product.

Preparation of Phenylseleninyl Fluoride (VI). This compound was initially obtained fortuitously as a result of storage of $C_6H_5SeF_3$ in a desiccator with the use of $CaSO_4$ as a desiccant. After storage of the trifluoride for several months, its melting point had increased to 158–162 °C. Subsequent analysis revealed that phenylselenium trifluoride had slowly reacted with the small amount of water vapor present to generate the partial hydrolysis product C_6H_5SeOF.

Phenylseleninyl fluoride was also prepared by the reaction of equimolar amounts of $C_6H_5SeF_3$ and $C_6H_5SeO_2H$. Phenylselenium trifluoride (1.45 g, 6.9 mol) and phenylseleninic acid (1.27 g, 6.8 mmol) were refluxed in $CHCl_3$ (in a polypropylene bottle) for 12 h. After the solution cooled (−20 °C) overnight, a colorless, microcrystalline solid appeared. The material was collected and recrystallized from CH_2Cl_2/Freon 113 until a constant melting point was obtained (158–162 °C). The final yield of product was 0.43 g (16% on the basis of $C_6H_5SeF_3$). Anal. Calcd for C_6FH_5OSe: C, 37.71; H, 2.62; F, 9.96. Found: C, 37.96; H, 2.93; F, 10.06.

Reaction of Phenylselenium Trifluoride with Aldehydes. Attempts were made to obtain a reaction between phenylselenium trifluoride and an aldehyde. It was expected that this reaction would provide a facile route to phenylseleninyl fluoride and would establish the usefulness of arylselenium trifluorides as reagents for conversion of an aldehyde to a difluoromethylene group. This conversion is often made with the use of SF_4, which requires high-pressure and special fluorine-resistant equipment, or with phenylsulfur trifluoride.[2]

Phenylselenium trifluoride (2.143 g, 0.01 mol) was added to a Freon 113 solution (30 mL) of benzaldehyde (1.06 g, 0.01 mol). The mixture was heated at 60 °C for 1 h in a polypropylene bottle. The trifluoride was subsequently recovered in almost quantitative yield. In another attempt, the trifluoride and *n*-butyraldehyde were heated together at 55 °C for 24 h. Again, the trifluoride was recovered unchanged.

The surprising lack of reactivity of phenylselenium trifluoride with aldehydes is in marked contrast with its sulfur analogue. Phenylsulfur trifluoride reacts exothermically with *n*-butyraldehyde and benzaldehyde to give high yields of phenylsulfinyl fluoride.[2]

Results and Discussion

Diaryl diselenides react with silver difluoride in a suitable solvent to yield arylselenium trifluorides according to eq 1,

$$R_2Se_2 + 6AgF_2 \rightarrow 2RSeF_3 + 6AgF \qquad (1)$$

where R = C_6H_5, p-$CH_3C_6H_4$, p-FC_6H_4, o-$C_2H_5C_6H_4$, and o-$NO_2C_6H_4$. Table I shows analytical data, yields, and physical properties for these compounds. ^1H and ^{19}F NMR spectra indicate the aryl groups remain intact (nonfluorinated) through the oxidative fluorination process.

The trifluorides are extremely moisture-sensitive crystalline solids, being readily hydrolyzed to seleninic acids with release of hydrogen fluoride (eq 2). Compounds I–III hydrolyze

$$RSeF_3 + 2H_2O \rightarrow RSeO_2H + 3HF \qquad (2)$$

almost instantaneously upon exposure to atmospheric moisture while (*o*-ethylphenyl)- and (*o*-nitrophenyl)selenium trifluoride hydrolyze at much slower rates. The trifluorides are soluble and nonreactive in aprotic solvents (methylene chloride, chloroform, benzene, nitromethane, and acetonitrile). Slight solubility in Freon 113 and insolubility in carbon tetrachloride and pentane is observed at ambient temperature. Solids I–III are reactive toward glass even at −20 °C. The trifluorides can be stored indefinitely by using polypropylene bottles. In solution (CH_2Cl_2 or C_6H_6) all the trifluorides react with glass rapidly and solutions become discolored. Molecular weight data (Table I) show that arylselenium trifluorides exist as monomers in benzene solution. This is in contrast with phenylselenium trichloride which undergoes limited association in this solvent.[12]

Phenylselenium trifluoride was found to undergo partial hydrolysis to give the first example of a seleninyl fluoride, VI (eq 3). Compound VI was also obtained from the reaction

$$C_5H_5SeF_3 + H_2O \rightarrow C_6H_5SeOF + 2HF \qquad (3)$$

of phenylselenium trifluoride with phenylseleninic acid in refluxing chloroform (eq 4). Both methods gave C_6H_5SeOF

$$C_6H_5SeF_3 + C_6H_5SeO_2H \rightarrow 2C_6H_5SeOF + HF \qquad (4)$$

as a colorless, microcrystalline solid. This compound is extremely moisture sensitive, immediately being converted to phenylseleninic acid when exposed to atmospheric moisture. Low solubility precluded ^1H and ^{19}F NMR studies. The

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Table II. NMR Spectral Data[a,b]

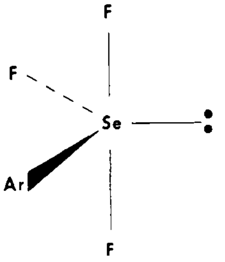
	$^1H^c$				$^{19}F^i$	
compd	ortho[d]	meta and/or para[d]				
$(C_6H_5Se)_2$	7.43	7.13				
$C_6H_5SeF_3$	7.78	7.47			240 (60 Hz[j])	
$(p\text{-}CH_3C_6H_4Se)_2$	7.29	6.81	2.20[e]			
$p\text{-}CH_3C_6H_4SeF_3$	7.98	7.33	2.41[e]		22.6 (166 Hz[j])	
$(p\text{-}FC_6H_4Se)_2$	7.44	6.87				
$p\text{-}FC_6H_4SeF_3$	8.06	7.20			25.4 (88 Hz[j])	104.5[k]
$(o\text{-}C_2H_5C_6H_4Se)_2$	7.60	6.88	2.66[f]	1.06[g]		
$o\text{-}C_2H_5C_6H_4SeF_3$	7.81	7.43	2.84[f]	1.29[g]	−6.9 (397 Hz[j])	70.5 (397 Hz[j])
$o\text{-}NO_2C_6H_4SeF_3$[h]			7.98[m]		−3.1 (doublet)[l]	70.0 (triplet)

[a] Trifluoride spectra obtained with use of Teflon inserts. [b] Diselenide spectra taken in CCl_4; trifluoride in CH_2Cl_2. [c] Shift values are ±0.01 ppm vs. internal tetramethylsilane. [d] Multiplet. [e] CH_3 singlet. [f] CH_2 quartet. [g] CH_3 triplet. [h] Diselenide insufficiently soluble for ^1H NMR data. [i] Shift values in ppm vs. $CFCl_3$. [j] Width of resonance at peak half-height. [k] $p\text{-}FC_6H_5$ resonance. [l] $J_{\text{cis-trans}} = 128.9$ Hz. [m] Ortho and meta.

infrared spectrum (Nujol mull) shows strong bands at 595 and 856 cm^{-1}. These are assigned to Se—F and Se═O stretching modes, respectively (cf. Se═O stretching at 826 cm^{-1} in $(C_6H_5)_2SeO$[13]).

NMR Data. Proton and fluorine NMR data for the diaryl diselenides and arylselenium trifluorides are presented in Table II. Where applicable, integration of peaks observed in the spectra served to confirm the stoichiometry indicated by analytical results. Chemical shifts were found to be independent of concentration and only slightly affected by varying solvent (C_6H_6, CH_2Cl_2, and CH_3NO_2).

The ^{19}F NMR spectra of I–III consist of single resonances (Figure 1). Observation of a single SeF_3 ^{19}F resonance is ascribed to rapid exchange of equatorial and apical fluorines in the assumed pseudo-trigonal-bipyramidal (TBP) structure (**1**). Lowering the temperature of solutions of I–III to −50 °C caused only a slight broadening of the resonance signal. Below −50 °C the compounds were too insoluble for study.



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At 30 °C (*o*-ethylphenyl)selenium trifluoride displays two broad resonances at −6.9 and +70.5 ppm with relative intensities of 2:1 Figure 1). At −78 °C (CH_2Cl_2) a well-resolved doublet and triplet are observed ($J_{F_{ax}-F_{eq}} = 88.4$ Hz). It is of interest to compare the chemical shift for the apical fluorines of IV (−6.9 ppm) to that of SeF_4 (−64 ppm) and $(C_6H_5)_2SeF_2$ (+65.4 ppm). From the regular trend in ^{19}F chemical shifts, it may be inferred that the Se–F bond becomes increasingly ionic with increasing aryl substitution.[14]

The presence of the *o*-ethyl group has a marked effect upon the rate of fluorine exchange. Compounds I–III undergo much more rapid exchange at 30 °C than IV. The absence of ^{77}Se–^{19}F satellites in the ^{19}F NMR spectra of I–III eliminates an intramolecular process from consideration as the rate determining step for fluorine exchange in I–III.[15] By a process of elimination, we conclude that F exchange for I–III occurs by an associative process, as was found by Sheppard for phenylsulfur trifluoride.[2] A structure for an intermediate in such a process is **2**.

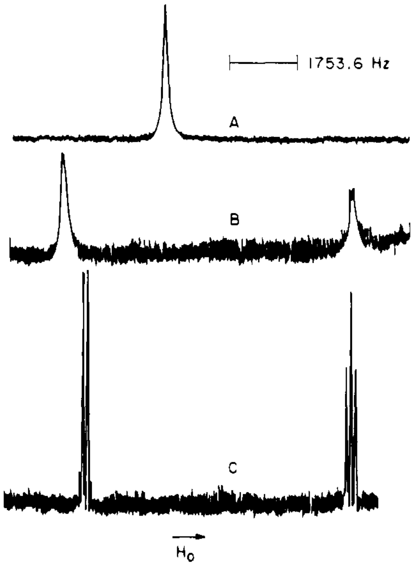
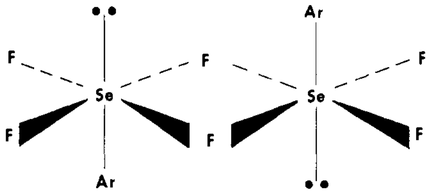


Figure 1. ^{19}F NMR spectrum (25 °C): A, phenylselenium trifluoride; B, (*o*-ethylphenyl)selenium trifluoride; C, (*o*-nitrophenyl)selenium trifluoride.



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The spectrum of IV is not concentration dependent. The width and positions of resonances at 30 °C remain unchanged in going from the neat liquid to a 1.4 M CH_2Cl_2 solution. The lack of concentration dependence of the ^{19}F NMR spectrum of IV rules out an associative mechanism as the rate-determining step for fluorine exchange. This is expected, as a molecular model of IV (**3**) demonstrates that the molecule can assume a favorable conformation in which the ethyl group projects well into the SeF_3 plane, thus sterically hindering associative fluorine exchange. Viscosity line broadening and instrument noise at low temperatures and sample decomposition at high temperatures precluded observation of ^{77}Se–^{19}F

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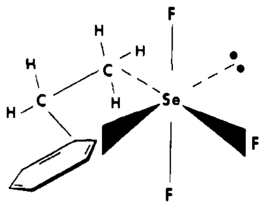

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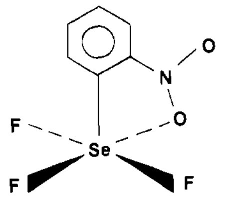
coupling. Therefore it is not possible to distinguish between dissociative and intramolecular exchange processes for IV, though we favor the former.

At 30 °C the ^{19}F NMR spectrum for (*o*-nitrophenyl)selenium trifluoride exhibits a sharp doublet and triplet in 2:1 relative intensity (Figure 1). The spectrum remains unchanged to 60 °C. Above this temperature moderate broadening occurs which is reversible only in part upon return to lower temperature. It is therefore inferred that decomposition occurs above 60 °C and that one of the products catalyzes F exchange. A pseudo-octahedral structure (**4**) rather than a pseudo-TBP structure is proposed for V based on IR data (vide infra). Examination of a saturated solution (1.1 M, CH_2Cl_2) of V revealed ^{77}Se–^{19}F satellites ($J_{\text{Se-F}_{\text{cis}}}$ = 220 Hz; $J_{\text{Se-F}_{\text{trans}}}$ = 793 Hz). The Se–F coupling constants for V indicate the trans Se–F bond has substantially more "s" character than the cis Se–F bonds.[16] The resistance of V to fluorine exchange supports *o*-nitro coordination. Such coordination would restrict association exchange via an intermediate such as **2**.



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Lewis Acid/Base Effects on Exchange. Small amounts of BF_3 (mole ratio ca. 100:1) had no effect on the room-temperature ^{19}F NMR spectrum (CH_2Cl_2) of (*o*-nitrophenyl)selenium trifluoride and had only a slight effect on (*o*-ethylphenyl)selenium trifluoride. Larger amounts of BF_3 (mole ratio ca. 10:1) caused loss of $^{19}F_{\text{cis-trans}}$ coupling for V and noticeable broadening of the ^{19}F NMR spectrum of IV.

The enhancement of the rate of exchange upon addition of BF_3 is not surprising; the presence of BF_3 allows superposition of a second-order exchange process (eq 5) on any exchange

$$ArSeF_3 + BF_3 \rightleftharpoons ArSeF_2^+ + BF_4^- \qquad (5)$$

process already occurring. What is surprising is the modest effect which BF_3 has on the rate of exchange. A pronounced acceleration of F exchange was observed upon addition of a trace of BF_3 to $(CH_3)_2SeF_2$.[14]

Experiments on the combined and separate effects of BF_3 and $(C_2H_5)_2O$ on the rate of fluorine exchange for (*o*-nitrophenyl)selenium trifluoride gave additional insight into factors effecting exchange. Diethyl ether, or for that matter CH_3CN or CH_3NO_2, have no measurable effect on the rate of fluorine exchange for V at 30 °C. Addition of an equimolar amount of $BF_3 \cdot (C_2H_5)_2O$ to a CH_2Cl_2 solution of V (0.82 *m*) resulted in a color change from yellow to intense violet over the course of 20 min. The ^{1}H NMR spectrum of the resulting solution was greatly altered compared to the parent trifluoride and indicated extensive reaction/decomposition. The ^{19}F NMR spectrum showed one sharp peak at 161 ppm. In contrast, a relatively stable solution (colorless) of V, $(C_2H_5)_2O$ and BF_3 was prepared where the mole ratio of V to BF_3 was 10:1. Although as noted above the separate presence of BF_3 or $(C_2H_5)_2O$ has no effect on fluorine exchange, the solution of V, BF_3 (10:1), and $(C_2H_5)_2O$ exhibited an ^{19}F NMR spectrum indicative of rapid exchange. An extremely broad ^{19}F peak was observed, barely distinguishable from the base line. These results may be explained by reference to eq 5–7. Diethyl ether can stabilize an $ArSeF_2^+$ cation via coordination, but in the absence of a fluoride ion-acceptor, exchange via this route (eq 6) is negligible and no effect is seen on the fluorine exchange rate. Despite the powerful fluoride acceptor ability of BF_3, in the absence of solvent stabilization for $ArSeF_2^+$, the presence of BF_3 has only a slight effect on the fluorine exchange rate. The presence of both donor and acceptor together (eq 7) results in more extensive ionization due to simultaneous coordinative stabilization of both $ArSeF_2^+$ and F^-. The result is rapid fluorine exchange which can occur via a number of processes (eq 7–9).

$$ArSeF_3 + (C_2H_5)_2O \rightleftharpoons [ArSeF_2(C_2H_5)_2O]^+ + F^- \qquad (6)$$

$$ArSeF_3 + (C_2H_5)_2OBF_3 \rightleftharpoons [ArSeF_2 \cdot (C_2H_5)_2O]^+ + BF_4^- \qquad (7)$$

$$[ArSeF_2(C_2H_5)_2O]^+ + ArSeF_3^* \rightleftharpoons ArSeFF_2^* + [ArSeF^*F(C_2H_5)_2O]^+ \qquad (8)$$

$$ArSeF_3 + BF_4^{*-} \rightleftharpoons ArSeF_2^*F + BF_3^*F^- \qquad (9)$$

Addition of 4-picoline *N*-oxide (PNO) to a 0.82 *m* CH_2Cl_2 solution of (*o*-nitrophenyl)selenium trifluoride had no effect on the ^{19}F NMR spectrum of V up to a mole ratio of V:PNO of 1:1. The invariant NMR spectrum of V in the presence of the strong Lewis base PNO demonstrates an interesting protective effect of the coordinated *o*-nitro group with respect to base coordination which could catalyze F exchange.[17]

The addition of PNO (6.4 mg) to 0.149 g of (*o*-ethylphenyl)selenium trifluoride (3.6 *m* in CH_2Cl_2, mole ratio base:trifluoride = 1:10) caused collapse of the two ^{19}F resonances and the appearance of a very broad peak at ca. 20 ppm which sharpened (22 ppm) upon addition of more base (total 10 mg). Rapid fluorine exchange is ascribed to the availability of excess IV which can coordinate with F^- and promote ionization (eq 10). It was seen above that a weak base ($(C_2H_5)_2O$) was necessary in the presence of a strong acid (BF_3) to produce rapid fluorine exchange for V. Equation 10 represents the reverse situation for IV where rapid exchange takes place in the presence of a strong base (PNO) and a weak F^- acceptor (IV). Common to both these rapid exchange situations is the presence of species which will coordinately stabilize both $ArSeF_2^+$ and F^-.

$$2o\text{-}C_2H_5C_6H_4SeF_3 + PNO \rightleftharpoons o\text{-}C_2H_5C_6H_4SeF_2PNO^+ + o\text{-}C_2H_5C_6H_4SeF_4^- \qquad (10)$$

Infrared Spectra. Initial investigation of the arylselenium trifluorides was effected via infrared spectroscopy (4000–400 cm^{-1}). In each case the trifluoride spectrum was very similar to that of its parent diselenide, except for a very strong absorption at 510–540 cm^{-1} assigned to Se–F stretching. This was the most intense band in each trifluoride spectrum, except for V which exhibited strong NO_2 absorptions as well.

Solution Infrared Spectra. Solution studies in benzene of the five arylselenium trifluorides were made between 600 and 200 cm^{-1} (Table III). Because aryl ring modes occur in this

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(17) In this connection it is noted that I–IV form isolable 1:1 adducts with PNO, while V does not: W. Maxwell, Ph.D. Thesis, University of Georgia, 1973.

Table III. Infrared Spectral Data for Organoselenium Trifluorides[a,b]

$C_6H_5SeF_3$		p-$CH_3C_6H_4SeF_3$		p-$FC_6H_4SeF_3$		o-$C_2H_5C_6H_4SeF_3$		o-$NO_2C_6H_4SeF_3$		assignment [c]
benzene	solid	benzene	solid	benzene	solid	benzene	liquid	benzene	solid	
		593m	591 m,sh	599 w,sh						aryl mode
572 s	575 m,sh	565 s	570 m,sh	572 s		567 m	572 m,sh	571 s	577 m, sh	Se-F eq stretch (A')
525 vs, br	535 vs,br	516 vs,br	530 m,sh	525 vs,br	535 vs,br	527 vs, br	538 vs, br	522 vs, br	554 m,sh 522 vs,br	Se-F apic stretch (A" + A')
479 s[d]	477 s,br[d]	490 m,sh[e]	491 m,br[e]	511 m,sh[f]	510 m[f]	508 m,sh 474 m[g]	473 w[g]	494 s[h]		phenyl "y" or related mode
472 vw,sh		465 vw,sh		475 vw 425 m				431 m	482 vs,br 433 m	aryl modes
369 m	363 m	388 m	385w	381 s[j]	383 s	369 m,sh				Se-F_{eq} bend (A')
343 s	343 m	364 s	360 w,br	365 m,sh		342 s	342 s,br	335 s	339 s	Se-F_{eq} bend (A")[i]
296 m	290 m	302 w,sh	347 w,br 310 w 303 w	310 m			304 m	296 m	326 m,sh 302 m	aryl "t" or related mode
		290 m		292 w						
275 w	269 m	272 w	269 w	271 m		265 w,sh		251 m,sh		
249 s	243 m	248 s	247 w	249 s	250 s	249 s	249 s	245 s	242 s	Se-F apic def (A')

[a] 200–600 cm^{-1}; solid-state spectra recorded on Nujol mulls. [b] Key: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad. [c] For V, apical and equatorial refer to cis and trans fluorines. [d] Occurs at 466 s in $(C_6H_5Se)_2$. Other absorptions: 304 m, 258 vw. [e] Occurs at 488 in $(p$-$CH_3C_6H_4Se)_2$. Other absorptions: 598 vw, 548 w, 314 vw, 287 vw, sh, 272 m, 245 m. [f] Occurs at 506 s in $(p$-$FC_6H_4Se)_2$. Other absorptions: 589 s, 416 m, 336 m, 272 m, 253 m, 248 m. [g] Occurs at 453 s in $(o$-$C_2H_5C_6H_4Se)_2$. Other absorptions: 570 w, 515 w, 283 s, 224 w. [h] Occurs at 478 s in $(o$-$NO_2C_6H_4Se)_2$. Other absorptions: 418 m, 320 m, 277 m, 234 w. [i] Stronger absorption assigned to A" mode. [j] Alternatively A' and A" may be degenerate at this frequency.

region, the IR spectra of corresponding diselenides were examined (see footnotes to Table III). Clear separation of aryl ring modes and related modes from Se–F frequencies facilitated assignments. The Se–F fundamental vibrational modes for I–IV are assigned by assuming a pseudo-TBP structure having local C_s symmetry around Se. The SeF vibrations for the proposed structure follow the irreducible representation 4A′ + 2A″. The frequencies and assignments of the SeF_3 modes agree well with other species containing T-shaped MF_3 groupings including $C_2F_5SeF_3$,[7b] XeF_3^+,[18] ClF_3[19] and BrF_3.[19]

Detailed assignments for I–IV are similar, and only those for I, for which Raman data are also available, are discussed in detail. Five of the six fundamental Se–F vibrational modes are observed for I. The strong absorption at 572 cm^{-1} is assigned to the symmetric equatorial Se–F stretch. In contrast, this mode occurs at 715 cm^{-1} in $C_2F_5SeF_3$.[7b] The very intense and broad band centered at 525 cm^{-1} is attributed to overlapping symmetric and asymmetric stretching of the apical fluorines. That these two stretching modes are essentially degenerate at this frequency is indicated by a Raman spectrum of I in benzene. Here, the most intense absorption is a polarized band at 523 cm^{-1}, assigned to symmetric Se–F stretching. The corresponding A′ and A″ modes in $C_2F_5SeF_3$ occur discretely at 588 and 541 cm^{-1}, respectively.[7b] The medium intensity IR band at 369 cm^{-1} and the strong band at 343 cm^{-1} are assigned to the equatorial Se–F in-plane and out-of-plane bending modes. These bending modes appear very weakly in the Raman spectrum. The strong IR absorption at 249 cm^{-1} is assigned to the apical deformation mode (A′). It also appears as a strong polarized Raman band at 246 cm^{-1}.

The remaining absorptions for I are assigned to phenyl ring or related modes as found by Whiffen.[20] Phenyl ring modes designated as "y" and "t" modes occur in this region and are assigned in Table III.

Although the spectrum of (o-nitrophenyl)selenium trifluoride is very similar to those for I–IV, the structure of V is believed to be pseudooctahedral (**4**). The suggested structure for V also displays local C_s symmetry at Se, and thus V exhibits an IR spectrum similar to those of I–IV. The major difference observed between the spectra of I–IV and V is the apparent degeneracy of the cis A′ and A″ bending modes. Alternative assignments due to coincident aryl and related modes and possible degeneracy are made for several other bands (Table III).

Solid-State Spectra. These were obtained for I–III and V but not for IV which melts close to ambient temperature.

Considering the tendency of Se and Te to achieve maximum coordination in the solid state,[21] a square-pyramidal (pseudooctahedral) structure for I–IV might be expected via formation of intermolecular fluorine bridging bonds. Higher coordination is prevented by the trans bond-lengthening effect of the aryl group.[22,24] The structures of (β-chloroethyl)tellurium trichloride[25] and TeF_4[26] show square-pyramidal coordination around tellurium generated by halogen bridge bonding. Infrared spectral data[27,28] suggest that Se in methylselenium trichloride also may be pentacoordinate. This is achieved by linking CH_3SeCl_2 units together through

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chlorine bridges in a manner similar to that found for β-$ClC_2H_4TeCl_3$.

Solid-state spectra of I–III were therefore examined in order to discern shifts indicative of fluorine bridging. In going from solution to the solid state, substantial broadening of peaks occurs for I, II, and III; aryl ring absorptions are broadened to the same extent as Se–F absorptions, however. For I–II the largest frequency shift (solid vs. solution) for an Se–F mode is 14 cm^{-1}, although most Se–F modes show much smaller shifts. For example, the modes associated with Se–F equatorial stretching for I and II shift by 3–5 cm^{-1} to higher frequency in going from solution to the solid state. A very broad absorption not observed in solution is found for I and II at 430 and 417 cm^{-1}, respectively.

The close similarity between the solid-state and solution spectra of I–II militates against pentacoordination via strong fluorine bridge bonding as found for TeF_4.[24] Our results are in contrast to the behavior of SF_4, SeF_4 and other main group fluorides[17,26,27] in which fluorine bridge bonding brings about large shifts in M-F stretching modes. However the broad weak-medium absorption for I–II at ca. 420 cm^{-1} may be an Se–F mode resulting from limited fluorine bridging. Our data do not permit an unambiguous statement in this regard.

No absorption corresponding to the Se–F equatorial stretching mode observed at 572 cm^{-1} in solution is found for III in the solid state. This corresponds to a shift to lower frequency of at least 37 cm^{-1}, assuming this absorption occurs in the vicinity of the strong, broad absorption at 535 cm^{-1}. Intermolecular fluorine bridging trans to the equatorial fluorine may be responsible for lowering this A′ mode to a position obscured by the very intense and broad absorption at 535 cm^{-1}.

Very little change occurs in the position, number, and contour of the Se–F bands of V in going from solution to solid state. In solution and solid state, the Se–F apical stretching frequency occurs at 522 cm^{-1}. The constancy of infrared frequencies observed in solution and in the solid state for V is explained by the persistence in the solid state of structure **4**. Here, the potential Se acceptor site for fluorine bridge formation is occupied through intramolecular coordination by one of the oxygens on the NO_2 group. Direct evidence for *o*-nitro coordination has been obtained through X-ray crystal structures of (*o*-nitrobenzene)selenenyl thiocyanate,[30] methyl *o*-nitrobenzenesulfenate[31] and bis(*o*-nitrophenyl) disulfide.[32] Supporting *o*-NO_2 coordination in V are the observed shifts to lower frequency of the asymmetric and symmetric NO_2 stretching modes in going from *o*-bromonitrobenzene to V. For *o*-$NO_2C_6H_4Br$ the asymmetric and symmetric frequencies are observed in the IR at 1532 and 1355 cm^{-1}, respectively. These bands are shifted to 1513 and 1323 cm^{-1}, respectively, in V.

Conclusions

The synthetic method reported here for the preparation of arylselenium trifluorides should prove generally applicable for the conversion of aryl diselenides which are soluble in Freon 113 or chloroform and which do not contain reactive functional groups.

The steric restriction of fluorine exchange observed for (*o*-ethylphenyl)selenium trifluoride and the coordinative restriction of fluorine exchange observed for (*o*-nitrophenyl)selenium trifluoride may be expected to be observed in other systems such as arylphosphoranes and -sulfuranes. Systematic study of substituted organyl main-group fluorides may thus provide an additional approach for obtaining information concerning the mechanism of F exchange and for controlling the exchange process.

Registry No. I, 76773-18-7; II, 76773-19-8; III, 76773-20-1; IV, 76773-21-2; V, 76773-22-3; VI, 76773-23-4; $(PhSe)_2$, 1666-13-3; (*p*-$CH_3C_6H_4Se)_2$, 21856-94-0; (*p*-$FC_6H_4Se)_2$, 52673-29-7; (*o*-$C_2H_5C_6H_4Se)_2$, 76773-24-5; (*o*-$NO_2C_6H_4Se)_2$, 35350-43-7; $C_6H_5SeO_2H$, 6996-92-5; AgF_2, 7783-95-1.

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Chloro Complexes in Molten Salts. 8. Potentiometric and Raman Spectroscopic Study of the Systems $NaCl-AlCl_3$, $NaCl-AlCl_3-Na_2O$, $NaCl-AlCl_3-SeCl_4$, and $NaCl-AlCl_3-SeCl_4-Na_2O$ at 175 °C

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By potentiometric measurements with chlorine/chloride electrodes the mole fraction of NaCl in a $NaCl-AlCl_3$ melt saturated with NaCl at 175 °C was found to be 0.50209 (5). Furthermore, in the pCl range of 3.885–5.034, the measured potential of the chlorine/chloride electrode at 175 °C could be rationalized by a combination of three reactions: (i) $2AlCl_4^- \rightleftarrows Al_2Cl_7^- + Cl^-$; (ii) $3Al_2Cl_7^- \rightleftarrows 2Al_3Cl_{10}^- + Cl^-$; (iii) $2Al_3Cl_{10}^- \rightleftarrows 3Al_2Cl_6 + 2Cl^-$. The p*K* values (based on the molar units) of these reactions were found to be 7.052 (7), 6.9, and 14, respectively. By potentiometric measurements combined with Raman spectroscopy it was shown that the only complex of Se(IV) formed in the $NaCl-AlCl_3-SeCl_4$ system at 175 °C in the pCl range 1.183–4.662 was $SeCl_3^+$. In the $NaCl-AlCl_3-SeCl_4-Na_2O$ system it was found that in the basic part of the system (i.e., pCl <2.58) $SeCl_3^+$ reacted with the oxide ions forming an oxochloro compound, whereas in the acidic part (i.e., pCl >2.58) the oxide ions reacted with the chloroaluminate ions (instead of the $SeCl_3^+$ ions) forming oxochloroaluminum compounds.

Introduction

The present investigation was started to find out whether analogous chloro complexes were formed in the $NaCl-AlCl_3-SeCl_4$ system as in the $KCl-AlCl_3-TeCl_4$ system, where the chloro complexes $TeCl_6^{2-}$, $TeCl_5^-$, $TeCl_4$, and $TeCl_3^+$ are formed.[2,3]

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