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Synthesis, multinuclear NMR (^1H, $^{13}C\{^1H\}$, ^{19}F, $^{77}Se\{^1H\}$) and properties of alkyl-2,2,2-trifluoroethyl selenides and some of their derivatives*

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Abstract

Alkyl-2,2,2-trifluoroethyl selenides, $RSeCH_2CF_3$ ($R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, s-C_4H_9, t-C_4H_9) have been prepared in good yields by reacting alkyl selenolate anions RSe^-, generated by the reduction of dialkyl diselenides with metallic sodium in liquid ammonia, with 1-iodo-2,2,2-trifluoroethane. Some of these bivalent selenides have been oxidized to their corresponding tetravalent selenium compounds, viz. $CF_3CH_2(R)SeX_2$ ($X = Cl$ or Br) with halogens. The compounds have been characterized by elemental analysis, IR, ^1H, $^{13}C\{^1H\}$, ^{19}F and $^{77}Se\{^1H\}$ NMR and mass spectral studies.

Introduction

The chemistry of organoselenium compounds is of interest from the viewpoint of organic synthesis, biochemistry and polymer chemistry and has been well studied [1–4]. Compared to the chemistry of perfluoroalkyl derivatives [5, 6], partially fluorinated derivatives of selenium and tellurium are a little studied class among organochalcogen compounds. Alkyl- and aryl-2,2,2-trifluoroethyl sulphides as well as selenides have been used successfully to synthesize alkyl- and arylthioynamines and -selenoynamines, respectively [7, 8]. We have recently reported the synthesis and characterization of a number of aryl-2,2,2-trifluoroethyl tellurides [9, 10]. In continuation of our studies on the chemistry of organoselenium and tellurium compounds [11, 12], we report in this paper the preparation and characterization of some previously unknown alkyl-2,2,2-trifluoroethyl selenides and some of their derivatives.

Results and discussion

Alkylmercaptans are known to react with 2,2,2-trifluoroethyl tosylate and give moderate yields of alkyl-2,2,2-trifluoroethyl sulphides [7].

$$RSH + CF_3CH_2OTs \xrightarrow[DMSO]{KOH} RSCH_2CF_3 + KOTs$$

However, attempts to prepare the corresponding selenides by using alkylselenols were not encouraging because alkylselenols are difficult to handle and readily undergo oxidation to dialkyl diselenides even when oxygen is present in traces.

A route for the preparation of the title compounds similar to that adopted for the synthesis of phenyl-2,2,2-trifluoroethyl selenides [8] by reacting alkyl selenolate anions, RSe^-, with 1-iodo-2,2,2-trifluoroethane in the presence of HMPA in refluxing THF gave very low yields (~10%).

In an effort to develop a high-yield method for the preparation of these compounds, the cleavage of dialkyl diselenides with sodium was carried out in anhydrous liquid ammonia at −38 °C. The resulting colourless solution of the alkyl selenolate ion, RSe^-, on alkylation with CF_3CH_2I and slow removal of ammonia gave the desired selenides in excellent yields. The reaction proceeds very rapidly with moderate evolution of heat. The reaction is clean and side-products were formed in negligible amounts.

$$1/2R_2Se_2 + Na \xrightarrow{liq.\ NH_3} RSeNa$$

$$RSeNa + CF_3CH_2I \longrightarrow \underset{\mathbf{(1\text{–}6)}}{RSeCH_2CF_3} + NaI$$

$$(R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9,\ s\text{-}C_4H_9,\ t\text{-}C_4H_9)$$

The alkyl-2,2,2-trifluoroethyl selenides thus obtained are golden yellow low-boiling, volatile liquids with obnoxious odours. The composition of these selenides has

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*Dedicated to Professor R.D. Verma on his 60th birthday.

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TABLE 1. Physical and analytical data for alkyl-2,2,2-trifluoroethyl selenides

Compound	B.p (°C/Torr)	Yield (%)	Mol. wt.	Analytical data [%Found/(Reqd.)]		
				C	H	Se
$CF_3CH_2SeCH_3$ (**1**)	52/760	90	177	20.34 (20.33)	2.80 (2.82)	44.88 (44.63)
$CF_3CH_2SeCH_2CH_3$ (**2**)	90/760	90	191	25.25 (25.13)	3.62 (3.66)	40.95 (41.36)
$CF_3CH_2SeCH_2CH_2CH_3$ (**3**)	123/760	95	205	28.96 (29.27)	4.36 (4.39)	38.55 (38.53)
$CF_3CH_2SeCH_2CH_2CH_2CH_3$ (**4**)	75/4	91	219	32.79 (32.87)	5.05 (5.02)	36.98 (36.07)
$CF_3CH_2SeCH(CH_3)CH_2CH_3$ (**5**)	85/4	79	219	32.92 (32.87)	5.01 (5.02)	36.10 (36.07)
$CF_3CH_2SeC(CH_3)_3$ (**6**)	45/2	60	219	32.85 (32.87)	5.01 (5.02)	36.15 (36.07)

been established by elemental analysis (Table 1) and by ^1H, $^{13}C\{^1H\}$, ^{19}F and $^{77}Se\{^1H\}$ NMR spectral studies.

The ^1H NMR spectra exhibit a quartet in the δ 3.05–3.18 ppm region which is due to the methylene protons of the CF_3CH_2 group. This quartet overlaps with the proton signals due to the methylene protons, $Se-CH_2R$, in compounds **2**–**4**, and with the methine proton, $SeCH(CH_3)R$, in compound **5**. All other protons in the alkyl chain exhibit the usual chemical shifts. The ^{19}F NMR spectra show a triplet resonating in the region δ -64.0 to -65.0 ppm due to the CF_3 group in compounds **1**–**6**.

The $^{13}C\{^1H\}$ NMR spectra of compounds **1**–**4** (Table 2) exhibited interesting features. The signal due to the carbon atom bearing three fluorine atoms was deshielded and appeared as a widely spaced quartet in the δ 126.61 ppm region due to ^{13}C–^{19}F coupling. The $^1J_{C,F}$ coupling constants were found to be of the order of -273.5 Hz. The carbon atom (CF_3CH_2) bonded to CF_3 was observed as a narrowly spaced quartet in the δ 23.54–25.49 ppm region. The geminal coupling constants [$^2J_{C,F}$] were found to be 32.85 Hz for these compounds. Higher order couplings were not observed in these compounds. The chemical shifts of the carbon atoms in the alkyl chain are close to the values quoted in the literature for related compounds [13].

$^{77}Se\{^1H\}$ NMR spectroscopy is the most useful technique for studying the chemical environment of a selenium atom within a molecule [2]. Chemical shifts are found over the range δ 0–2000 ppm with respect to dimethyl selenide as a standard for organoselenides and diselenides. $^{77}Se\{^1H\}$ NMR spectra of compounds **1**–**4** (Table 2) were recorded using dimethyl selenide as an external reference resonating at δ 0 ppm. In

TABLE 2. ^{13}C and ^{77}Se NMR data for alkyl-2,2,2-trifluoroethyl selenides (δ ppm)

Compound	δ_C values						δ_{Se} values
	C(β')	C(α')	C(α)	C(β)	C(γ)	C(δ)	
CF_3CH_2I	123.63 (q) [$^1J_{C,F} = -273.32$][a]	-5.24 (q) [$^2J_{C,F} = 36.50$]	–	–	–	–	–
$CF_3CH_2SeCH_3$ (**1**)	126.61 (q) [$^1J_{C,F} = -273.70$]	25.49 (q) [$^2J_{C,F} = 32.84$]	5.91	–	–	–	68.14
$CF_3CH_2SeCH_2CH_3$ (**2**)	126.47 (q) [$^1J_{C,F} = -274.15$]	23.54 (q) [$^2J_{C,F} = 32.84$]	19.18	14.96	–	–	176.72
$CF_3CH_2SeCH_2CH_2CH_3$ (**3**)	126.49 (q) [$^1J_{C,F} = -273.48$]	23.87 (q) [$^2J_{C,F} = 32.84$]	23.35	28.18	14.04	–	140.86
$\overset{\beta'}{CF_3}\overset{\alpha'}{CH_2}Se\overset{\alpha}{CH_2}\overset{\beta}{CH_2}\overset{\gamma}{CH_2}\overset{\delta}{CH_3}$ (**4**)	126.50 (q) [$^1J_{C,F} = -273.56$]	24.08 (q) [$^2J_{C,F} = 32.84$]	22.92	32.29	25.79	13.50	144.45

[a] Coupling constants are in Hz.

compound **1**, the selenium signal was observed at δ 68.14 ppm whereas in **2** it resonated at δ 176.72 ppm, so that the change in the chemical shift due to the replacement of a proton by a methyl group is δ 108.58 ppm. In compounds **3** and **4**, the selenium signals resonated at δ 140.86 and 144.45 ppm, respectively, demonstrating that β- and γ-substitution by a methyl group has virtually no effect on the selenium environment. In fact, shift change parameters and additivity for β- and γ-alkyl substitutions in selenium have not been demonstrated [14]. The mass spectra of these selenides could be recorded because of the extreme volatility of these compounds.

Diorganyl selenium(IV) halides are among the most widely studied class of tetravalent selenium compounds [1, 2]. Perfluoroalkyl selenides [15], $(R_f)_2Se$, have been found to be resistant towards chlorination even under rigorous conditions. However, the alkyl-2,2,2-trifluoroethyl selenides **1**–**4** reacted readily with elemental chlorine or bromine in tetrachloromethane and diethyl ether, respectively, at 0 °C to afford alkyl-2,2,2-trifluoroethyl selenium(IV) chlorides or bromides, respectively, in quantitative yield.

$$RSeCH_2CF_3 + X_2 \longrightarrow \underset{\mathbf{(7\text{–}14)}}{CF_3CH_2(R)SeX_2}$$

$R = CH_3,\ C_2H_5,\ n\text{-}C_3H_7,\ n\text{-}C_4H_9)$

These compounds are low melting, hygroscopic and thermally unstable, being soluble in polar solvents. They decompose at room temperature within a few hours, although they are stable at low temperatures ($\sim$0 °C) under an inert atmosphere of dry N_2. The composition of derivatives **7**–**14** has been established by elemental analysis (Table 3), IR, ^1H and ^{19}F NMR spectroscopy, and by mass spectral studies.

The presence of several stable isotopes of naturally occurring selenium [16] leads to a highly characteristic pattern in the mass spectra of these compounds consisting of a group of peaks for selenium-containing fragments. The major fragments observed are listed in the Experimental section based on ^1H, ^{12}C, ^{19}F, ^{35}Cl, ^{80}Se and ^{80}Br isotopes. Peaks corresponding to the M^+ ion were not observed for these tetravalent derivatives however, with peaks corresponding to $[M-X]^+$ being observed at the highest m/z species. This is attributed to the weakness of Se−X bond in these compounds. The other most prominent cluster of peaks corresponded to $[M-X_2]^+$ ions which confirms the formation of the parent alkyl-2,2,2-trifluoroethyl selenides whose mass spectra were not obtained. Other major fragments were m/z 163 $[CF_3CH_2Se]^+$, 83 $[CF_3CH_2]^+$ and 69 $[CF_3]^+$, including $[RSe]^+$.

The preparation of alkyl-2,2,2-trifluoroethyl selenides described here constitutes an efficient, high-yield procedure which is advantageous since it is simple, strictly reproducible and one-step.

Experimental

N.B. All manipulations were carried out under a dry nitrogen atmosphere to prevent oxidation of the oxygen-sensitive selenium intermediates.

Materials and methods

Dialkyl diselenides [17] and 1-iodo-2,2,2-trifluoroethane [18] were prepared by literature methods. Liquid ammonia was dried over sodium metal and distilled prior to use. All other chemicals were of reagent grade and used as such.

^1H and ^{19}F NMR spectra were recorded on a Varian model EM390 spectrometer using TMS as an internal and $CFCl_3$ as an external reference, respectively. $^{13}C\{^1H\}$ NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer operating at 22.49 MHz using 30° pulse width, 4500 Hz sweep width and $CDCl_3$ as a solvent and as an internal lock. $^{77}Se\{^1H\}$ NMR spectra were recorded on a JEOL FX 90Q FT NMR spectrometer using dimethyl selenide as an external reference in $CDCl_3$. The IR spectra were recorded either as neat liquids or as Nujol/HCB mulls between KBr plates on a Perkin-Elmer model 1430 spectrophotometer. The EI mass spectra were obtained on a VG70S, 11-250J mass spectrometer at 70 eV. All boiling and melting points are uncorrected. Selenium, chlorine and bromine were determined by standard methods [19]. Carbon and hydrogen were determined microanalytically on a Perkin-Elmer 2400CHN elemental analyzer.

Preparation of alkyl-2,2,2-trifluoroethyl selenides. General procedure

In a typical preparation, a clean, dry two-necked round-bottomed flask equipped with a Dry Ice condenser and a gas inlet valve was charged with dialkyl diselenide (13 mmol). Anhydrous ammonia (100 ml) is condensed into the flask and pieces of sodium metal (0.60 g, 26 mmol) were then added slowly over a period of 30 min to the vigorously stirred yellowish reaction mixture. During this addition a fast reaction occurred with completion of the reduction being indicated by complete decolourization of the liquid ammonia solution. 1-Iodo-2,2,2-trifluoroethane (5.4 g, 2.56 ml, 26 mmol) was then added dropwise through a syringe with stirring over a period of 30 min. Stirring was continued and the liquid ammonia was allowed to evaporate slowly overnight. The light yellow residue obtained was hydrolyzed with deoxygenated water (25 ml) and extracted with dichloromethane (3×25 ml). The combined organic layers were washed with water and dried over anhydrous

TABLE 3. Physical and analytical data for diorganyl selenium(IV) halides

Compound	Colour	M.p. (°C)	Mol. wt.	Analytical data [%Found (Reqd.)]			
				C	H	Se	Cl/Br
$CF_3CH_2(CH_3)SeCl_2$ (**7**)	greenish yellow	60	248	14.62 (14.52)	2.03 (2.02)	31.80 (31.85)	28.55 (28.63)
$CF_3CH_2(CH_3CH_2)SeCl_2$ (**8**)	green	33–34	262	18.30 (18.32)	2.65 (2.67)	30.22 (30.15)	27.01 (27.10)
$CF_3CH_2(CH_3CH_2CH_2)SeCl_2$ (**9**)	white	38–40	276	21.66 (21.74)	3.25 (3.26)	28.71 (28.62)	25.55 (25.72)
$CF_3CH_2(CH_3CH_2CH_2CH_2)SeCl_2$ (**10**)	white	70	290	24.85 (24.83)	3.80 (3.79)	27.35 (27.24)	24.54 (24.48)
$CF_3CH_2(CH_3)SeBr_2$ (**11**)	yellow	65	337	10.55 (10.68)	1.47 (1.48)	23.10 (23.44)	47.80 (47.74)
$CF_3CH_2(CH_3CH_2)SeBr_2$ (**12**)	yellowish orange	38	351	13.85 (13.67)	1.95 (1.99)	22.65 (22.50)	45.40 (45.58)
$CF_3CH_2(CH_3CH_2CH_2)SeBr_2$ (**13**)	light yellow	57–58	365	16.50 (16.43)	2.42 (2.47)	21.77 (21.64)	43.95 (44.11)
$CF_3CH_2(CH_3CH_2CH_2CH_2)SeBr_2$ (**14**)	orange	62–63	379	18.90 (18.99)	2.92 (2.90)	20.91 (20.84)	42.32 (42.21)

sodium sulphate for 6 h. The solvent was stripped off and the residue distilled to afford the analytically pure alkyl-2,2,2-trifluoroethyl selenides **1**–**6**.

$CF_3CH_2SeCH_3$ (**1**): IR (liquid film) (cm^{-1}): 2980 (w); 2890 (w); 1460 (s); 1420 (s); 1398 (s); 1300 (s); 1265 (s); 1230 (s); 1110 (s); 910 (w); 730 (w); 620 (s). ^1H NMR (CCl_4) δ: 2.24 (s, $SeCH_3$); 3.05 (q, $SeCH_2CF_3$) ppm. ^{19}F NMR (CCl_4) δ: −64.50 (t, CH_2CF_3) ppm.

$CF_3CH_2SeCH_2CH_3$ (**2**): IR (liquid film) (cm^{-1}): 2990 (s); 2950 (s); 2885 (s); 1460 (s); 1420 (s); 1385 (s); 1305 (s); 1270 (s); 1225 (s); 1115 (s); 970 (s); 750 (s); 705 (s); 635 (s). ^1H NMR (CCl_4) δ: 2.80 (q, CH_2CH_3); 3.06 (q, CH_2CF_3); 1.48 (t, CH_2CH_3) ppm. ^{19}F NMR (CCl_4) δ: −64.50 (t, CH_2CF_3) ppm.

$CF_3CH_2SeCH_2CH_2CH_3$ (**3**): IR (liquid film) (cm^{-1}): 2985 (s); 2955 (s); 2895 (s); 1470 (s); 1420 (s); 1385 (s); 900 (w); 890 (w); 795 (w); 770 (s); 710 (s); 638 (s). ^1H NMR (CCl_4) δ: 2.74 (t, $CH_2CH_2CH_3$); 3.06 (q, CH_2CF_3); 1.75 (m, $CH_2CH_2CH_3$); 1.10 (t, CH_3) ppm. ^{19}F NMR (CCl_4) δ: −64.00 (t, CH_2CF_3) ppm.

$CF_3CH_2SeCH_2CH_2CH_2CH_3$ (**4**): IR (liquid film) (cm^{-1}): 2980 (s); 2880 (s); 2850 (s); 1470 (s); 1420 (s); 1385 (s); 1300 (s); 1275 (s); 1235 (s); 1210 (sh); 1115 (s); 910 (w); 740 (w); 715 (s); 635 (s). ^1H NMR (CCl_4) δ: 2.69 (t, $CH_2CH_2CH_2CH_3$); 3.09 (q, CH_2CF_3); 1.63 (m, $CH_2CH_2CH_2CH_3$); 1.03 (t, CH_3) ppm. ^{19}F NMR (CCl_4) δ: −65.00 (t, CH_2CF_3) ppm.

$CF_3CH_2SeCH(CH_3)CH_2CF_3$ (**5**): IR (liquid film) (cm^{-1}): 2985 (s); 2945 (s); 2895 (s); 1460 (s); 1420 (s); 1385 (s); 1300 (s); 1265 (s); 1232 (s); 1208 (s); 1115 (s); 980 (s); 798 (w); 705 (s); 638 (s). ^1H NMR (CCl_4) δ: 3.18 (m, $CF_3CH_2SeCH(CH_3)-$); 1.62 (m, $SeCH(CH_3)CH_2CH_3$); 1.00 (t, CH_3) ppm. ^{19}F NMR (CCl_4) δ: −65.00 (t, CH_2CF_3) ppm.

$CF_3CH_2SeC(CH_3)$ (**6**): IR (liquid film) (cm^{-1}): 2980 (s); 2958 (sh); 2910 (s); 2880 (s); 1470 (s); 1420 (s); 1375 (s); 1298 (s); 1265 (s); 1230 (s); 1220 (s); 1110 (s); 705 (w); 635 (s). ^1H NMR (CCl_4) δ: 3.05 (q, CH_2CF_3); 1.45 (s, $C(CH_3)_3$) ppm. ^{19}F NMR (CCl_4) δ: −63.0 (t, CH_2CF_3) ppm.

Preparation of alkyl-2,2,2-trifluoroethyl selenium(IV) chlorides

Elemental chlorine was bubbled through a well-stirred solution of alkyl-2,2,2-trifluoroethyl selenide (10 mmol) in 25 ml of tetrachloromethane over a period of 10 min at 0–5 °C. The contents were subsequently stirred at room temperature for 30 min. Removal of the solvent under vacuum left behind a residual mass which on recrystallization from chloroform/petroleum ether (5:1) afforded pure crystalline alkyl-2,2,2-trifluoroethyl selenium(IV) chloride in excellent yield.

$CF_3CH_2(CH_3)SeCl_2$ (**7**): IR (Nujol and HCB mulls) (cm^{-1}): 2980 (s); 2960 (sh); 1490 (w); 1410 (s); 1385 (s); 1300 (s); 1270 (s); 1230 (s); 1145 (s); 1125 (s); 1070 (s); 980 (w); 775 (w); 730 (s); 648 (s); 580 (w). ^1H NMR ($CDCl_3$) δ: 3.85 (s, CH_3); 4.50 (q, CH_2CF_3) ppm. ^{19}F NMR ($CDCl_3$) δ: −59.50 (t, CH_2CF_3) ppm. MS(EI) *m/z* (%rel. int.): 214 (7.1) $CF_3CH_2(CH_3)SeCl^+$; 198 (11.8) $CF_3CH_2SeCl^+$; 178 (50.2) $CF_3CH_2SeCH_3{}^+$; 163 (42.5) $CF_3CH_2Se^+$; 159 (11.6) $CF_2CH_2SeCH_3{}^+$; 158 (16.3) $CH_3SeCHCF_2{}^+$; 143 (49.5) $SeCHCF_2{}^+$; 140 (12.0) $CH_3SeCH_2CF^+$; 131 (7.8) CH_3SeCl^+; 109 (30.4) $CH_3SeCH_2{}^+$; 95 (51.7) CH_3Se^+; 93 (100.0) $SeCH^+$;

83 (13.9) $CF_3CH_2^+$; 80 (48.8) Se^+; 69 (51.9) CF_3^+; 64 (99.1) $CF_2CH_2^+$.

$CF_3CH_2(CH_3CH_2)SeCl_2$ (**8**): IR (Nujol and HCB mulls) (cm^{-1}): 2980 (s); 2950 (sh); 2890 (s); 1495 (s); 1410 (s); 1385 (s); 1295 (s); 1275 (s); 1250 (w); 1228 (s); 1140 (s); 1075 (b); 970 (w); 728 (s); 685 (s); 645 (s); 535 (w). ^1H NMR ($CDCl_3$) δ: 4.18 (q, $C\mathit{H}_2CH_3$); 4.45 (q, $C\mathit{H}_2CF_3$); 1.88 (t, $CH_2C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.50 (t, $CH_2C\mathit{F}_3$) ppm. MS(EI) *m/z*: 227 (7.8) $CF_3CH_2(CH_3CH_2)SeCl^+$; 198 (10.4) $CF_3CH_2SeCl^+$; 192 (26.3) $CF_3CH_2SeCH_2CH_3^+$; 177 (24.4) $CF_3CH_2SeCH_2^+$; 163 (40.1) $CF_3CH_2Se^+$; 109 (19.1) $CH_3CH_2Se^+$; 95 (19.3) CH_2SeH^+; 93 (49.2) $SeCH^+$; 83 (14.3) $CF_3CH_2^+$; 80 (25.8) Se^+; 69 (50.4) CF_3^+.

$CF_3CH_2(CH_3CH_2CH_2)SeCl_2$ (**9**): IR (Nujol and HCB mulls) (cm^{-1}): 2980 (s); 2955 (sh); 2898 (s); 1465 (s); 1410 (s); 1385 (s); 1295 (s); 1270 (s); 1230 (s); 1135 (s); 1090 (s); 1070 (s); 900 (w); 790 (s); 725 (s); 680 (s); 645 (s); 615 (s). ^1H NMR ($CDCl_3$) δ: 4.11 (t, $C\mathit{H}_2CH_2CH_3$); 4.42 (q, $C\mathit{H}_2CF_3$); 2.88 (m, $CH_2C\mathit{H}_2CH_3$); 1.17 (t, $CH_2CH_2C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.50 (t, $CH_2C\mathit{F}_3$) ppm. MS(EI) *m/z*: 241 (5.5) $CF_3CH_2(CH_3CH_2CH_2)SeCl^+$; 206 (100.0) $CF_3CH_2SeCH_2CH_2CH_3^+$; 191 (4.0) $CF_3CH_2SeCH_2CH_2^+$; 177 (16.8) $CF_3CH_2SeCH_2^+$; 163 (12.2) $CF_3CH_2Se^+$; 158 (4.6) $CF_3CH_2SeCl^+$; 123 (8.3) $CH_3CH_2CH_2Se^+$; 93 (35.3) $SeCH^+$; 83 (7.1) $CF_3CH_2^+$; 80 (13.2) Se^+; 69 (13.3) CF_3^+; 64 (11.2) $CF_2CH_2^+$.

$CF_3CH_2(CH_3CH_2CH_2CH_2)SeCl_2$ (**10**): IR (Nujol and HCB mulls) (cm^{-1}): 3000 (w); 2950 (m); 2850 (w); 1460 (m); 1400 (m); 1385 (s); 1280 (s); 1250 (s); 1205 (s); 1110 (s); 1060 (s); 900 (w); 630 (w). ^1H NMR ($CDCl_3$) δ: 4.16 (t, $C\mathit{H}_2CH_2CH_2CH_3$); 4.49 (q, $C\mathit{H}_2CF_3$); 2.16 (m, $CH_2C\mathit{H}_2CH_2CH_3$); 1.59 (m, $CH_2CH_2C\mathit{H}_2CH_3$); 1.03 (t, $C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.90 (t, $CH_2C\mathit{F}_3$) ppm. MS(EI) *m/z*: 255 (3.2) $CF_3CH_2(CH_3CH_2CH_2CH_2)SeCl^+$; 220 (23.8) $CF_3CH_2(CH_3CH_2CH_2CH_2)Se^+$; 205 (3.2) $CF_3CH_2SeCH_2CH_2CH_2^+$; 198 (9.2) $CF_3CH_2SeCl^+$; 191 (13.1) $CF_3CH_2SeCH_2CH_2^+$; 177 (16.5) $CF_3CH_2SeCH_2^+$; 163 (11.7) $CF_3CH_2Se^+$; 137 (7.7) $CH_3CH_2CH_2CH_2Se^+$; 93 (100.0) $CHSe^+$; 83 (11.3) $CF_3CH_2^+$; 80 (5.4) Se^+; 69 (13.3) CF_3^+; 64 (10.2) $CF_2CH_2^+$.

Preparation of alkyl-2,2,2-trifluoroethyl selenium(IV) bromides

Over a period of 15 min, elemental bromine (1.6 g, 0.51 ml, 10 mmol) in 10 ml of diethyl ether was added dropwise to a well-stirred solution of alkyl-2,2,2-trifluoroethyl selenide (10 mmol) in 25 ml of diethyl ether at a temperature of 0–5 °C. The contents were stirred for a further 30 min and the solvent was then removed under vacuum. The yellow solid left was recrystallized from chloroform/petroleum ether (5:1) to afford pure alkyl-2,2,2-trifluoroethyl selenium(IV) bromide in nearly quantitative yield.

$CF_3CH_2(CH_3)SeBr_2$ (**11**): IR (Nujol and HCB mulls) (cm^{-1}): 2990 (s); 2820 (s); 1460 (s); 1410 (s); 1385 (s); 1298 (s); 1260 (s); 1220 (s); 1152 (s); 1140 (s); 980 (w); 725 (s); 690 (w); 640 (s). ^1H NMR ($CDCl_3$) δ: 4.50 (q, $C\mathit{H}_2CF_3$); 3.82 (s, $C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.50 (t, $CH_2C\mathit{F}_3$) ppm.

$CF_3CH_2(CH_3CH_2)SeBr_2$ (**12**): IR (Nujol and HCB mulls) (cm^{-1}): 2990 (s); 2880 (s); 1460 (s); 1410 (s); 1385 (w); 1295 (s); 1270 (s); 1230 (s); 1140 (s); 1070 (s); 1050 (s); 970 (s); 760 (s); 725 (s); 680 (s); 645 (s). ^1H NMR ($CDCl_3$) δ: 4.45 (q, $C\mathit{H}_2CF_3$); 4.15 (q, $C\mathit{H}_2CH_3$); 1.85 (t, $CH_2C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −58.00 (t, $CH_2C\mathit{F}_3$) ppm.

$CF_3CH_2(CH_3CH_2CH_2)SeBr_2$ (**13**): IR (Nujol and HCB mulls) (cm^{-1}): 3000 (s); 2975 (s); 2800 (w); 1465 (s); 1420 (w); 1390 (w); 1290 (s); 1260 (s); 1230 (s); 1160 (s); 1140 (s); 1070 (s); 980 (br); 725 (s); 680 (s); 645 (s); 610 (s). ^1H NMR ($CDCl_3$) δ: 4.40 (q, $C\mathit{H}_2CF_3$); 4.02 (t, $C\mathit{H}_2CH_2CH_3$); 2.22 (m, $CH_2C\mathit{H}_2CH_3$); 1.19 (t, $CH_2CH_2C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −57.80 (t, $CH_2C\mathit{F}_3$) ppm.

$CF_3CH_2(CH_3CH_2CH_2CH_2)SeBr_2$ (**14**): IR (Nujol and HCB mulls) (cm^{-1}): 3020 (w); 2960 (m); 2875 (m); 1470 (w); 1420 (m); 1370 (w); 1300 (s); 1265 (w); 1222 (m); 1122 (s); 1080 (s); 1042 (m); 920 (w); 740 (w); 705 (w); 640 (w). ^1H NMR ($CDCl_3$) δ: 4.49 (q, $C\mathit{H}_2CF_3$); 4.29 (t, $C\mathit{H}_2CH_2CH_2CH_3$); 2.19 (m, $CH_2C\mathit{H}_2CH_2CH_3$); 1.54 (m, $CH_2CH_2C\mathit{H}_2CH_3$); 1.06 (t, $CH_2CH_2CH_2C\mathit{H}_3$) ppm. ^{19}F NMR ($CDCl_3$) δ: −56.25 (t, $CH_2C\mathit{F}_3$) ppm.

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