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SYNTHESIS OF FLUORINATED VINYL SULFIDES AND SELENIDES

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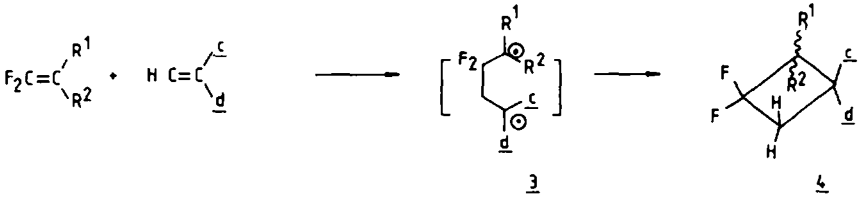
ABSTRACT : The reaction between fluoroolefins **1** and **10e** and benzenesulfenyl or selenenyl halides **6** is found to be solvent-dependent and gives in most cases predominantly the regioisomer **8**. The structure of adducts **8** and **9** are ascertained by ^{1}H, ^{19}F and ^{77}Se NMR spectroscopy. Compounds **8** are easily halogenated and treatment of the products with magnesium or zinc leads to the desired polyfluorovinyl sulfides and selenides **10**. A second route of synthesis of these reagents results from the reaction of fluorovinyllithio-derivatives **11** with benzenesulfenyl or selenenyl halides. Olefin **10e** is also obtained from the selenoacetal **8t** of trifluoroacetaldehyde.

INTRODUCTION

For more than 40 years, fluorinated olefins 1 have been of interest in organic chemistry (1) especially because of their industrial applications and their particular reactivity. The classical work of Bartlett has demonstrated the radical character of the thermal [2+2] cycloaddition reactions between fluorinated olefins and olefins or dienes (2). Recently, we showed that capto-dative olefins 2, favouring radical intermediates 3, react easily with various known 1 and new fluoroolefins 10 to afford substituted cyclobutanes 4 in good to high yields (3). Furthermore, some of these new reagents can be considered as potential synthetic equivalents of the highly unstable difluoroketene 5 (4).



$\underline{c}$ = capto (electron withdrawing) group

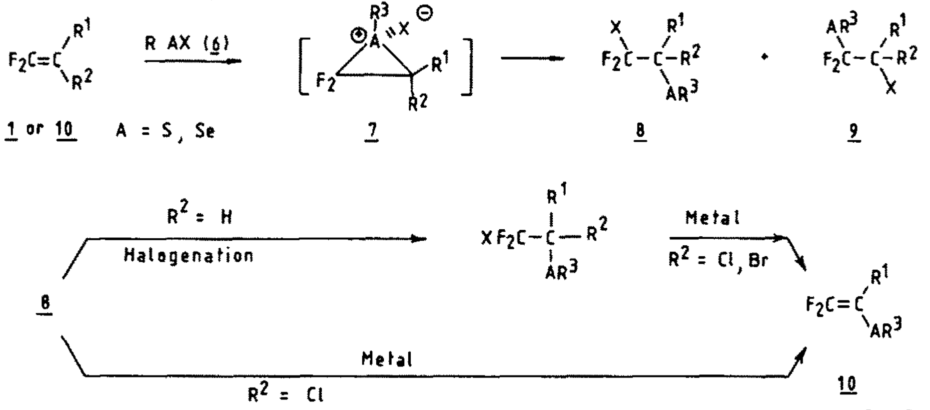
$\underline{d}$ = dative (electron donating) group

R^1 = H, F, Cl, SC_2H_5 ; R^2 = SC_2H_5, SC_6H_5, SeC_6H_5

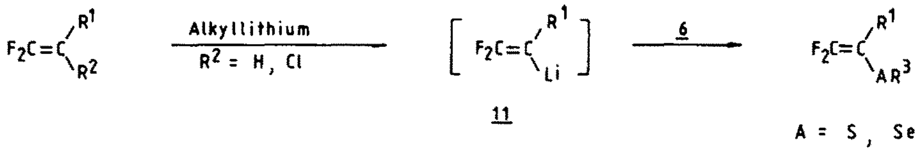
$$2\ \underset{\underline{5}}{\left[F_2C{=}C{=}O\right]} \xrightarrow{\Delta} F_2C{=}CF_2 + 2\,CO$$

RESULTS AND DISCUSSION

We wish to report herein the synthesis of some new fluorinated vinylsulfides and selenides **10** via two distinct ways. The first route investigated involves the addition of benzenesulfenyl or selenenyl halides **6** to fluoroolefins **1** and **10e** followed in some cases by mono- or dihalogenation of the CH or CH_2 moieties. The polyhaloderivatives **8** are then subjected to dehalogenation by the use of magnesium or zinc to give the desired olefins **10**. The second route involves the reaction between the fluorinated vinyllithium reagents **11** and benzenesulfenyl or selenenyl halides **6**.



Route A



Route B

TABLE I : Reaction conditions, yields and ratios of regioisomers **8** and **9** (Route A)

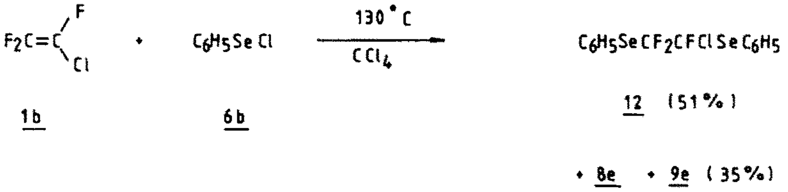
entry	starting olefin	R^1	R^2	R^3A	X	Solv. T° (°C) time (hrs)	Adducts		Yield (%)
							8	**9**	
a	**1a**	H	H	C_6H_5S	Cl	CH_2Cl_2,60(15)	85(**8a**)	15(**9a**)	80(Ref.9d)
b	**1a**	H	H	C_6H_5Se	Cl	CH_2Cl_2,40(15)	100(**8b**)	0(**9b**)	90(Ref.5a)
c	**1a**	H	H	C_6H_5Se	Br	CH_2Cl_2,40(15)	100(**8c**)	0(**9c**)	91(Ref.5a)
d	**1b**	F	Cl	C_6H_5S	Cl	CCl_4,130(15)	75(**8d**)	25(**9d**)	64
e	**1b**	F	Cl	C_6H_5Se	Cl	CH_3CN,60(15)	100(**8e**)	0(**9e**)	92
f	**1b**	F	Cl	C_6H_5Se	Cl	CCl_4,130(18)	94(**8e**)	6(**9e**)	35[a]
g	**1b**	F	Cl	C_6H_5Se	Br	CH_3CN,60(15)	100(**8f**)	0(**9f**)	95
h	**1b**	F	Cl	C_6H_5Se	Br	CCl_4,100(15)	100(**8f**)	0(**9f**)	89
i	**1c**	Cl	Cl	C_6H_5Se	Cl	CH_3CN,85(15)	100(**8g**)	0(**9g**)	92
j	**1c**	Cl	Cl	C_6H_5Se	Br	CH_3CN,85(15)	100(**8h**)	0(**9h**)	94
k	**10e**	H	SeC_6H_5	C_6H_5Se	Cl	CH_3CN,25(24)	32(**8i**)	68(**9i**)	94
l	**10e**	H	SeC_6H_5	C_6H_5Se	Cl	CCl_4,80(72)	55(**8i**)	45(**9i**)	85
m	**10e**	H	SeC_6H_5	C_6H_5Se	Br	CH_3CN,25(24)	15(**8j**)	85(**9j**)	96
n	**10e**	H	SeC_6H_5	C_6H_5Se	Br	CCl_4,80(72)	90(**8j**)	10(**9j**)	86

(a) Compound **12** was also isolated in 51% yield (see text)

Route A

Methylene chloride solutions of 1,1-difluoroethylene **1a** are known to react with sulfenyl or selenenyl halides **6** to give predominantly or exclusively the regioisomer **8**(5a) We observed the same tendency in carbon-tetrachloride solution. Reactions between olefins **1b**, **1c** and **10e** and **6** are conducted in solvents of different polarity. According to the usually proposed mechanism(5) (i.e. involvement of episulfonium or episelenonium ions **7**), the addition is favored in acetonitrile compared to carbon tetrachloride (see Table I).

Compound **12** is formed in 51% yield in the reaction between olefin **1b** and benzeneselenenyl chloride **6b** in CCl_4(6). Reaction between olefin **1c** and **6b** in CCl_4 proceeds only at 140°C and led to intractable mixture.



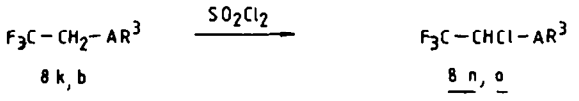
The observed regioselectivity leading to the isomer **8** can be rationalised considering polar and steric effects in the transition state for the ring opening of intermediate **7**. Whereas the relative stabilisation of a positive charge on a $^{+}CF_2R$ group compared to $^{+}CFClR$ and $^{+}CCl_2R$ is not clearly established (7a,b), a difluoromethyl substituent certainly destabilises more than CFClR or CCl_2R a cation on the carbon in α-position. The observed direction of ring opening is also in agreement with steric arguments for the attack of X^-. In the case of the intermediate **7** formed from 1,1-difluoroethylene **1a** the positive charge is clearly better stabilised in $^{+}CF_2CH_2R$ than in $^{+}CH_2CF_2R$(7b-d).

Steric effects also favor the formation of isomer **8**. It is noteworthy that, in the case of olefin **10e**, the selectivity is reversed when passing from acetonitrile to carbon tetrachloride (see Table I entries m and n). Furthermore halide substitutents on olefins **1** clearly slow down the addition rate of sulfenyl and selenenylhalides as compared to ethylene(8). Based on our results, the following qualitative scale of reactivity of ethylene and olefins **1** toward **6** is proposed :

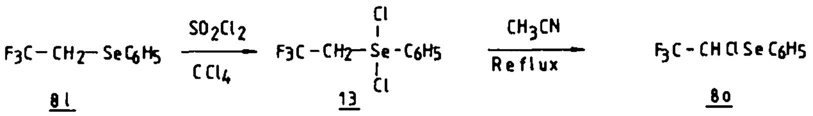
$$H_2C=CH_2 \quad \gg \quad F_2C=CH_2 \quad > \quad F_2C=CFCl \quad \gg \quad F_2C=CCl_2$$

The structure of the adducts and their regiochemistry are assigned by means of ^{19}F and ^{77}Se NMR spectroscopy. For example, the ^{19}F-NMR spectra of regioisomers **8e** and **8f** shows ABX patterns due to the presence of asymmetric centers. The corresponding proton-decoupled ^{77}Se-NMR spectra shows patterns having a 2x2x2 multiplicity resulting from the coupling between the selenium atom and the three different fluorines [one two-bonds coupling (^2J=50Hz) and two three-bonds couplings (^3J=10Hz and ^3J=6-8Hz)]. Product **8g** was also compared to an authentic sample obtained by chlorination of adduct **8b** (see below). In the case of the adducts of the olefin **10e**, all ^1H, ^{19}F and ^{77}Se NMR spectra show the presence (**9i**,**9j**) or the absence (**8i**,**8j**) of an asymmetric center.

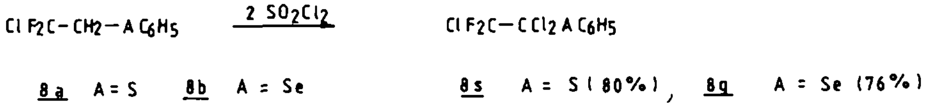
Adduct **8a** as well as the trifluoromethylcompounds **8k**, **8l** and **8m** are halogenated in fair to good yield by using either sulfuryl chloride, N-chloro or N-bromosuccinimide (NCS and NBS) (Table II). When a carbon tetrachloride solution of compound **8l** was reacted with sulfuryl chloride at 0°C a quantitative yield of the selenurane **13** is isolated as colorless crystals. Refluxing **13** in CCl_4 or CH_3CN for 28hrs led to product **8o**. Adducts **8a** and **8b** were also dichlorinated to **8s** and **8g** in good yields by using 2 equivalents of sulfuryl chloride.



$$F_3C-CH_2-AR^3 \xrightarrow{SO_2Cl_2} F_3C-CHCl-AR^3$$



$$F_3C-CH_2-SeC_6H_5 \xrightarrow[CCl_4]{SO_2Cl_2} F_3C-CH_2-SeCl_2-C_6H_5 \xrightarrow[Reflux]{CH_3CN} F_3C-CHClSeC_6H_5$$



$$ClF_2C-CH_2-AC_6H_5 \xrightarrow{2\ SO_2Cl_2} ClF_2C-CCl_2AC_6H_5$$

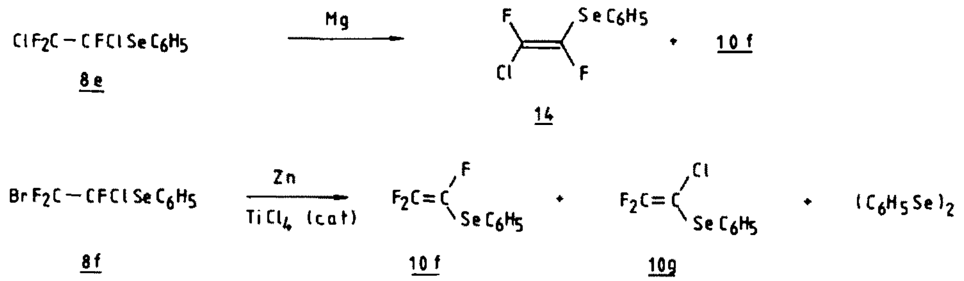
TABLE II : Halogenation of compounds **8**

Compound	Product (yield %)	R^1	R^2	R^3A	X	Halog. Agent
8k	**8n** (95)	H	Cl	C_6H_5S	F	SO_2Cl_2
8l	**8o** (52)	H	Cl	C_6H_5Se	F	SO_2Cl_2
8l	**8o** (53)	H	Cl	C_6H_5Se	F	NCS
8l	**8p** (69)	H	Br	C_6H_5Se	F	NBS
8a	**8q** (93)	H	Cl	C_6H_5S	Cl	SO_2Cl_2
8m	**8r** (88)	C_2H_5S	Cl	C_2H_5S	F	SO_2Cl_2

Thiocompounds **8d,n,q,r** and **s** were subjected to dehalogenation by using magnesium to furnish the desired fluorovinylsulfides **10a-10d** in good yields (Table III). However, when selenenyl adducts **8f** or **8g** were reacted with magnesium, only complex mixtures of products were obtained[10]. Adduct **8e** afforded in this reaction trans-1,2-difluoro-2-chlorovinyl phenyl selenide **14** in 41% yield beside diphenyldiselenide, a small amount of olefin **10f** and other unidentified compounds. Reaction between adduct **8f** and zinc in the presence of catalytic amount of titanium tetrachloride(11) furnished olefins **10f** and **10g** in 48 and 16% yield along with diphenyl diselenide in 19% yield.

TABLE III : Synthesis of olefins **10** by dehalogenation of compounds **8** (A=S, R^2=Cl)

Reagent	R^1	R^3	X	Yield (%)
8n	H	C_6H_5	F	78 (**10a**)
8q	H	C_6H_5	Cl	82 (**10a**)
8d	F	C_6H_5	Cl	75 (**10b**)
8s	Cl	C_6H_5	Cl	65 (**10c**)
8r	C_2H_5S	C_2H_5	F	70 (**10d**)



Route B

Fluoroolefins **1** are metallated with alkyllithium compounds at low temperature to afford **11** either via direct deprotonation [**1a**[12]] or via halogen-metal exchange [**1b**,**1c**[13].] The quenching of **11** with carbonyl compounds gave the expected allylic alcohols(11,12). When lithioderivatives **11** were reacted with benzenesulfenyl chloride **6a** or benzeneselenenyl bromide **6c**, the corresponding fluorovinyl sulfide **10a** or selenides **10e**,**g** were obtained, albeit in low to fair yields (Table IV)(14).

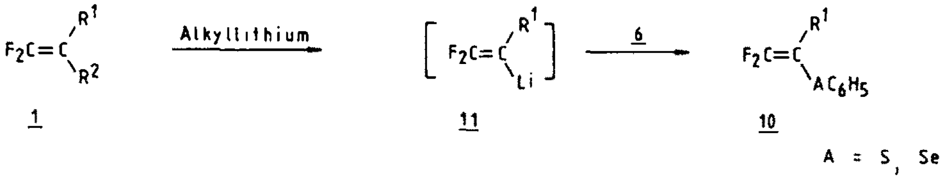
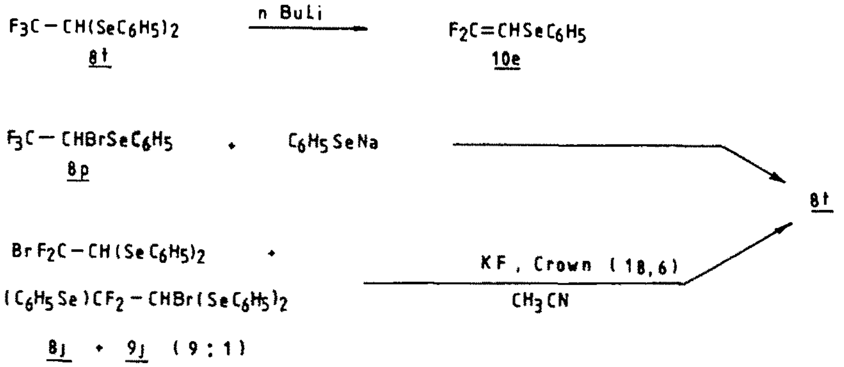


TABLE IV : Yields of olefins **10** synthesized from vinyllithium intermediates **11**

11	R^1	R^2	C_6H_5AX	Yield (%)
a	H	H	C_6H_5SCl	30 (**10a**)
a	H	H	C_6H_5SeBr	55 (**10e**)
b	F	Cl	C_6H_5SeBr	17 (**10f**)
c	Cl	Cl	C_6H_5SeBr	9 (**10g**)

2,2-Difluorovinylphenyl selenide **10e** is also obtained in 74% yield from the reaction between the selenoacetal of fluoral **8t** and n-butyllithium at -110°C. The starting **8t** is synthesized from bromoderivative **8p** and sodium phenylselenolate in 64% yield and from the reaction between the 9:1 mixture of adducts **8j** and **9j** and potassium fluoride in 61% yield. Attempts to obtain diselenoacetal **8t** by established procedures(15) failed (sulfuric acid method) or gave only the hemiselenoacetal **15** in 81% yield (zinc chloride procedure).



The use of these new fluorolefins as synthetic equivalents of the difluoroketene **5** is under study now.

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EXPERIMENTAL

Boiling points are uncorrected; melting points were measured on a Leitz-Wetzlar HM-Lux apparatus and are uncorrected. ^{1}H, ^{19}F and ^{77}Se-NMR spectra were recorded in $CDCl_3$ solutions using TMS, $FCCl_3$ or CH_3SeCH_3 as internal references on Varian XL-200 spectrometer. ^{13}C-NMR spectra were recorded in $CDCl_3$ solution on Varian CFT-20 and XL-200 spectrometers (multiplicity due to one-bond coupling : S= singlet, D = doublet, T = triplet, Q = quadruplet, M = multiplet; long-range couplings : s,d,t,q,m). Infrared spectra were recorded on a Perkin-Elmer 297 infrared spectrometer. Mass spectra were recorded on a Varian MAT-44S spectrometer and are given for the 80-Se isotope. Benzenesulfenyl chloride and benzeneselenenyl halides were synthetized as described in literature^{16}. Chromatography of the products was achieved on silicagel. Microanalyses were performed by the Microanalyses Laboratory of the University of Wien.

Addition of benzenesulfenyl or selenenylhalides to olefins 1 or 10e : General procedure:

Fluoroolefin $^{(17)}$ (**1b** : 20 mmoles; **1c** and **1d** : 10 mmoles), benzenesulfenyl or selenenylhalide (5 mmoles) and the appropriate solvent (8 ml see Table I) were placed into a Glass tube which was cooled, degassed, sealed and heated to the temperature given in Table I. The tube was then cooled down, opened and the volatiles were evaporated. Purification was achieved as indicated below. The isomeric compounds **8** and **9** have not been separated and identified by NMR.

1,2-dichloro-1,2,2-trifluoroethyl phenyl sulfide 8d and 2,2-dichloro-1,1,2-trifluoroethyl phenyl sulfide 9d : Purified by chromatography (eluent : petroleum ether) and distillation b.p.: 50-53°C/0.1 Torr. ^{1}H-NMR : δ = 7.4-7.7(5H,m). ^{19}F-NMR = **8d** : δ = -63.6(d), -90.9(1F,t), ^{3}J(F-F) = ^{3}J'(F-F) = 13.8 Hz; **9d** : δ = -69.27(1F,t), -83.7(d), ^{3}J(F-F) = 12.4 Hz. IR(film) : ν = 3070, 1580, 1475, 1445, 1310, 1190, 1170, 1070, 1020, 960, 790, 750, 705, 690, 640 cm^{-1}. MS(EI) : **262**(m/e); 225, 175, 109. Found : C = 36.75, H = 2.09, S = 12.29, Cl = 26.77%. Requires: C = 36.80, H = 1.93, S = 12.27, Cl = 27.15%.

1,2-dichloro-1,2,2-trifluoroethyl phenyl selenide 8e : Isolated as a colorless liquid by chromatography (eluent : petroleum ether) and distillation, b.p.: 60-68°C/0.2 Torr. ^{1}H-NMR : δ = 7.43(3H,m), 7.77(2H,m); ^{19}F-NMR : δ = -62.8(1F,m), -63.8(1F,m), -95.7(1F,m); ^{2}J(F-F) = 165Hz ^{3}J(F-F) = ^{3}J'(F-F) = 15.2 Hz; ^{77}Se-NMR : δ = 781.3[Se,Ddd; ^{2}J(Se-F) = 50 Hz, ^{3}J(Se-F) = 10 Hz, ^{3}J(Se-F) = 8.4 Hz]. IR(film) : ν = 3070, 1580, 1470, 1435, 1190, 1150, 1060, 1020, 850, 760, 740, 690 cm^{-1}. MS(EI) : **308**(m/e); 273, 254, 157, 77. Found : C = 31.37, H = 1.68, Cl = 22.93%. Requires: C = 31.20, H = 1.64, Cl = 23.02%.

1-chloro-1,2,2-trifluoro-1,2-bis(phenylselenenyl)ethane 12$^{(18)}$: When the reaction was carried out in CCl_4, direct distillation gave adduct **8e** followed by compound **12** as a yellow oil, b.p.: 100-120°C/0.002 Torr. ^{1}H-NMR : δ = 7.4(6H,m), 7.8(4H,m). ^{19}F-NMR : δ = -76.2(1F,m), -77.6(1F,m), -90.6(1F,m), ^{2}J(F-F) = 207 Hz; ^{3}J(F-F) = ^{3}J'(F-F) = 21 Hz. ^{77}Se-NMR : δ = 564(Se2, ddd), 650.2 (Se1,ddd); ^{2}J(Se1-F2) = 8 Hz, ^{3}J(Se1-F) = 7.6 Hz, ^{2}J(Se2-F) = 50.3 Hz, ^{3}J(Se2-F1) = 9.8 Hz, ^{3}J(Se2-F2) = 4.9 Hz. ^{13}C-NMR : δ = 109.9[CFCl,Dt,^{1}J(C-F) = 303.2 Hz, ^{2}J(C-F) = 32.4 Hz], 123.1[CF_2,Td,^{1}J(C-F) = 308.4 Hz, ^{2}J(C-F) = 30.0 Hz], 123.3[ipso Se2,Sm], 125.5[ipso Se1,Sm], 129.2[ortho Se1 and Se2,Dm], 130.0 and 130.3[para Se1 and Se2,Dt], 137.7 and 137.9[meta Se1 and Se2,Dm]. IR(film) : ν = 3070, 1580, 1475, 1440, 1160, 1100, 1060, 850, 740, 690 cm^{-1} MS(EI): **430**(m/e); 411, 395, 314, 273, 157, 77, 51.

1-chloro-2-bromo-1,2,2-trifluoroethyl phenyl selenide 8f : Isolated by chromatography using petroleum ether as eluent and distillation; a colorless liquid, b.p.: 65-66°C/0.4 Torr. ^{1}H-NMR: δ= 7.2(3H,m), 7.51(2H,m). ^{19}F-NMR : δ = -58.2(1F,m), -59.8(1F,m), -92.73(1F,m); ^{2}J(F-F) = 166Hz ^{3}J(F-F) = 18.9 Hz, ^{3}J'(F-F) = 17.1 Hz. ^{77}Se-NMR : δ = 783.7[Se,ddd, ^{2}J(Se-F) = 50.2 Hz ^{3}J(Se-F) =

10.6 Hz, ^{3}J'(Se-F) = 6.8 Hz]. ^{13}C-NMR (proton decoupled) : δ = 108.5[CFCl,Dt,^{1}J(C-F) = 346 Hz, ^{2}J(C-F) = 34 Hz)], 119.6[CF$_2$,Td, ^{1}J(C-F) = 312 Hz, ^{2}J(C-F) = 38 Hz], 125.4[ipso], 129.3[ortho], 130.7[para], 138.0[meta]. IR(film) : ν = 3070, 1580, 1475, 1440, 1190, 1160, 1060, 1000, 855, 740, 720, 690 cm^{-1}. MS(EI) : **354** and **352**(m/e); 319 and 317, 273, 223, 197, 157, 77. Found : C = 27.32, H = 1.45, Cl = 10.13%. Requires : C = 27.26, H = 1.43, Cl = 10.06%.

1,1,2-trichloro-2,2-difluoroethyl phenyl selenide 8g : Chromatography (eluent : petroleum-ether) and distillation gave **8g** as a colorless liquid, b.p.: 55-57°C/0.02 Torr. ^{1}H-NMR : δ = 7.4-7.55(3H,m), 7.82(2H,m). ^{19}F-NMR : δ = -58.9(2F,s); (CD$_3$CN) : δ = -56.5(2F,s). IR(film) : ν = 3095, 3080, 2975, 2945, 2865, 1580, 1480, 1440, 1240, 1170, 1010, 820, 740, 690cm^{-1}. MS(EI) : **324**(m/e); 289, 157, 77, 51.

1,1-dichloro-2-bromo-2,2-difluoroethyl phenyl selenide 8h : Isolation as for **8g** led to a colorless liquid, b.p.: 70-73°C/0.02 Torr. ^{1}H-NMR : δ = 7.61(3H,m), 7.90(2H,m). ^{19}F-NMR(CD$_3$CN) : δ = -50.1 (2F,s). IR(film) : ν = 3070, 1580, 1480, 1440, 1150, 990, 745, 690 cm^{-1}. MS(EI) : **370** and **368**(m/e); 351 and 349, 157, 77, 51.

1-phenylselenyl-2-chloro-2,2-difluoroethyl phenyl selenide 8i and 1-chloro-2-phenylselenenyl-2,2-difluoroethyl phenyl selenide 9i(18) : The excess of 2,2-difluorovinyl phenyl selenide **9e** was distilled and the crude product was subjected to a rapid chromatography (eluent : cyclohexane/ ethylacetate (95/5) and kept as a carbon tetrachloride solution at -20°C (the pure mixture of adducts decomposed at room temperature within a few days); a yellow oil. ^{1}H-NMR : **8i** : δ = 4.65 [1H,t,^{3}J(H-F) = 10.5 Hz], 7.2-7.4(10H,m). **9i** : δ = 5.36[1H,dd,^{3}J(H-F) = 13 Hz, ^{3}J(H-F) = 9.7 Hz] 7.15-7.3(5H,m), 7.4(3H,m), 7.66(2H,m). ^{19}F-NMR : **8i** : δ = -48.7[2F,d]; **9i** : δ = -70.2(1F,Dd), -72.9(1F*,Dd); ^{2}J(F-F*) = 200 Hz. ^{77}Se-NMR : **8i** : δ = 454.9(2Se,s); **9i** : δ = 516[Se-CFCl,t, ^{3}J(Se-F) = 5 Hz], 578.6[Se-CF$_2$,dd, ^{2}J(Se-F1) = 7 Hz, ^{2}J(Se-F2) = 25 Hz]. IR(film) : ν = 3075, 3060, 1580, 1475, 1440, 1235, 1180, 1150, 945, 740, 690 cm^{-1}. MS(EI) : **412**(m/e); 393, 377, 255, 157, 77.

1-phenylselenenyl-2-bromo-2,2-difluoroethyl phenyl selenide 8j and 1-bromo-2-phenylselenenyl-2,2-difluoroethylphenyl selenide 9j(18) : Isolated as above as a rather unstable yellow oil which was kept at -20°C in carbon tetrachloride solution. ^{1}H-NMR : **8j** : δ = 4.68[1H,t,^{3}J(H-F) = 11.5 Hz], 7.2-7.4(10H,m); **9j** : δ = 5.30[1H,dd,^{3}J(H-F) = 9.3Hz, ^{3}J(H-F*) = 11.1Hz], 7.2-7.6(10H,m). ^{19}F-NMR : **8j** : δ = -41.9[2F,d]; **9j** : δ = -46.2(1F,Dd), -47.7(1F*,Dd); ^{2}J(F-F*) = 196 Hz. ^{77}Se-NMR : **8j** : δ = 461.9(s). IR(film) : ν = 3075, 3060, 1580, 1480, 1440, 1230, 1180, 1135, 940, 740, 690 cm^{-1}. MS(CI/IB) : **459** and **457**(M+H)$^{+}$; 301 and 299, 221 and 219, 157, 77, 51.

2,2,2-trifluoroethyl phenyl selenide dichloride 13 : Sulfuryl chloride (0.27 g, 2 mmoles) was added dropwise to a carbon tetrachloride solution (10 ml) of 2,2,2-trifluoroethyl phenyl selenide **8l**(19) (0.478 g, 2 mmoles) at 0°C and stirring was continued for 1 hour. Evaporation of the solvent gave colorless crystals, m.p. : 86°C (diethylether). ^{1}H-NMR : δ = 4.7[2H,q,^{3}J(H-F) = 8.7 Hz], 7.4(3H,m), 7.83(2H,m). ^{19}F-NMR : δ = -58.4(d). IR(CH$_2$Cl$_2$) : ν = 3040, 2980, 1580, 1480, 1445, 1400, 1285, 1260, 1220, 1135, 1065 cm^{-1}. MS(EI) : **310**(m/e); 275, 240, 192, 157, 77. Found : C = 30.99, H = 2.30%. Requires : C = 30.99, H = 2.28%.

1-chloro-2,2,2-trifluoroethyl phenyl selenide 8o : A carbon tetrachloride solution (10 ml) of selenide dichloride **13** (0.622 g, 2 mmoles) was refluxed for 28 hours. Evaporation of the solvent gave an oil which was purified by chromatography (eluent : petroleum ether) and distilled as a colorless liquid. b.p. : 48-50°C/0.3 Torr. ^{1}H-NMR : δ = 5.27[1H,q,^{3}J(H-F) = 7.2 Hz], 7.4(3H,m), 7.77(2H,m). ^{19}F-NMR : δ = -71.8[3F,d,^{3}J(F-H) = 7.3 Hz]. IR(film) : ν = 3075, 2980, 1580, 1480, 1445, 1300, 1255, 1120, 1100, 770, 745, 690 cm^{-1}. MS(EI) : **274**(m/e); 239, 157, 77. Found : C = 35.25, H = 2.30%. Requires : C = 35.13, H = 2.21%. The same selenide **8o** was also prepared by irradiation of a carbon tetrachloride solution (15 ml) of 2,2,2-trifluoroethyl phenyl selenide **8l**

(1.4 g, 5.86 mmoles), N-chlorosuccinimide (0.865 g, 6.48 mmoles) and 5 mg of azobisisobutyronitrile with a 100 watts high-pressure lamp for 4 hours. Filtration of succinimide and evaporation of the solvent gave the crude product which was purified as above.

1-bromo-2,2,2-trifluoroethyl phenyl selenide 8p : By using the same selenide **8l** and N-bromosuccinimide, the above procedure permitted to get product **8p** as a colorless liquid, b.p. : 45-47°C/0.3 Torr. ^{1}H-NMR : δ = 5.14[1H,q,^{3}J(H-F) = 8.8 Hz], 7.4(3H,m), 7.70(2H,m). ^{19}F-NMR : δ = -69.7(d). ^{77}Se-NMR : δ = 513.3[q,^{3}J(Se-F) = 4 Hz]. IR(film) : ν = 3070, 2980, 1580, 1475, 1440, 1285, 1250, 1170, 1100, 745, 690 cm^{-1}. MS(EI) : **320** and **318**(m/e); 239, 219, 157, 77. Found : C = 30.43, H = 2.22%. Requires : C = 30.02, H = 1.90%.

Chlorination of thiocompounds 8k, 8a and 8m : General procedure : Sulfurylchloride (0.3 g, 2.3 mmoles) in methylene chloride (**8k**$^{(20)}$, **8a**$^{(9d)}$) or carbon tetrachloride (**8m**$^{(21)}$) was added dropwise to a solution of the appropriate thiocompound (2.3 mmoles) in the same solvent at 0°C. Stirring was continued for 2 hours at room temperature and the resulting mixture was then poured in water (50 ml) which was extracted with methylene chloride (3x10 ml). The extract was washed with a saturated sodium hydrogenocarbonate solution, then with brine and dried over magnesium sulfate. Evaporation of the solvent gave a residue which was purified by chromatography using petroleum ether as eluent, and distillation.

1-chloro-2,2,2-trifluoroethyl phenyl sulfide 8n : A colorless liquid, b.p. : 93-95°C/17 Torr. ^{1}H-NMR: δ = 5.26[1H,q,^{3}J(H-F) = 6.6 Hz], 7.4(3H,m), 7.62(2H,m). ^{19}F-NMR : δ = -76.4 (d). IR(CCl_4) : ν = 3030, 2970, 1575, 1480, 1440, 1300, 1250, 1170, 1120, 1080, 1025, 1000, 920, 865, 730, 690, 670 cm^{-1}. MS(EI) : **226**(m/e); 191, 157, 109. Found : C = 42.37, H = 2.62, S = 14.08, Cl = 15.72% Requires : C = 42.29, H = 2.66, S = 14.14, Cl = 15.64%.

1,2-dichloro-2,2-difluoroethyl phenyl sulfide 8q : A colorless liquid, b.p. : 60-62°C/0.1 Torr. ^{1}H-NMR : δ = 5.30[1H,t,^{3}J(H-F) = 7.4 Hz], 7.7(5H,m). ^{19}F-NMR : δ = -57.4(2F,d). IR(film) : ν = 3070, 2970, 1580, 1480, 1445, 1265, 1195, 1145, 1110, 1080, 1020, 970, 820, 775, 740, 720, 690 cm^{-1}. MS(EI) : **242**(m/e); 207, 191, 143, 109, 51.

1-chloro-1,1-bis ethylsulfenyl -2,2,2-trifluoroethane 8r : A colorless liquid, b.p. : 42-44°C/0.05 Torr ^{1}H-NMR : δ = 1.22(6H,t), 2.83(4H,q). ^{19}F-NMR : δ = -73.4(s). MS(EI) : **238**(m/e); 203.

Double Chlorination of compounds 8a and 8b : Sulfuryl chloride (1.19 g, 8.8 mmoles) in methylene chloride **8a** or carbon tetrachloride **8b** (5 ml) was added dropwise at room temperature to a solution (5 ml) of 2-chloro-2,2-difluoro-ethylphenyl sulfide **8a**$^{(9d)}$ or a solution (5 ml) of the selenoanalog **8b** in the same solvent. The solutions were then refluxed for two hours and the product **8s** and **8g** were isolated as for the monochlorinated compounds **8n**, **8q** and **8r**.

1,1,2-trichloro-2,2-difluoroethyl phenyl sulfide 8s : A colorless liquid, b.p. : 59-61°C/0.2 Torr. ^{1}H-NMR : δ = 7.49(3H,m), 7.52(2H,m). ^{19}F-NMR : δ = -59.26(s). IR(film) : ν = 3060, 1575, 1475, 1445, 1380, 1310, 1160, 1070, 1010, 925, 870, 830, 760, 745, 710, 690 cm^{-1}. MS(EI) : **276**(m/e); 241, 191, 143, 109, 51. Found : C = 34.59, H = 2.10, S = 11.64, Cl = 38.05%. Requires : C = 34.62, H = 1.81, S = 11.55, Cl = 38.32%.

1,1,2-trichloro-2,2-difluoroethyl phenyl selenide 8g : See physical and spectral data above.

Dehalogenation of compounds 8d, 8n, 8r and 8s : General procedure : Magnesium (84 mg, 3.5 mg at) were placed in THF (1 ml) and catalytic amounts of iodine and 1,2-dibromoethane were added. After discoloration, the solution was cooled to 0°C(**8n**, **8d**, **8s**) or to -10°C(**8q**, **8r**). A THF solution (5 ml) of **8** (3,2 mmoles) was then added dropwise and stirring was continued overnight at room temperature. The mixture was poured in cooled 5% sulfuric acid (100 ml) and extracted with diethylether (3x20 ml). The organic layers were washed with a saturated sodium hydrogenocarbonate solution (50 ml) and dried over magnesium sulfate. Evaporation of the solvent gave the crude product which was purified by distillation.

2,2-difluorovinyl phenyl sulfide 10a : A colorless liquid, b.p. : 58-60°C/15 Torr (litt$^{(22)}$: 68-69°C/11 Torr). ^{1}H-NMR : δ = 5.4[1H,dd,^3J(H-F$_{cis}$) = 0.5 Hz, ^3J(H-F$_{trans}$) = 21 Hz], 7.2-7.6(5H,m). ^{19}F-NMR: δ = -76.1(1F,dd), -79.6(1F*,dd); ^2J(F-F*) = 19.2 Hz. IR(CH$_2$Cl$_2$) : ν = 3070, 1705, 1655, 1585, 1540, 1480, 1445, 1315, 1265, 1175, 1090, 1025, 960, 785, 735, 705, 690 cm^{-1}.

1,2,2-trifluorovinyl phenyl sulfide 10b : A colorless liquid, b.p. : 57-60°C/17 Torr. ^{1}H-NMR : δ = 7.2(5H,m). ^{19}F-NMR : δ = -88.4(1F,dd,trans to S-phenyl), -106.7(1F,dd,cis to S-phenyl), -149.6 ppm(1F,dd,C-1 fluorine); ^2J = 44.4 Hz, ^3J(trans) = 123.9 Hz, ^3J(cis) = 34.8 Hz. IR(CH$_2$Cl$_2$) : ν = 3050, 3000, 1740, 1590, 1480, 1310, 1140, 1050, 1030, 1000 cm^{-1}. MS(EI) : **190**(m/e); 109.

1-chloro-2,2-difluorovinyl phenyl sulfide 10c : A colorless liquid, b.p. : 88-90°C/17 Torr. ^{1}H-NMR: δ = 7.30-7.4(5H,m). ^{19}F-NMR : δ = -73.95(1F,d), -80.0(1F,d); J_{gem} = 10.1 Hz. IR(CCl$_4$) : ν = 3060, 1695, 1585, 1475, 1440, 1295, 1020, 945, 685 cm^{-1}. MS(EI) : **206**(m/e); 156, 128, 109, 77.

1-ethylthio-2,2-difluorovinyl ethyl sulfide 10d : A colorless liquid, b.p. : 70-72°C/17 Torr (lit$^{(21)}$: 85-87°C/45 Torr). ^{1}H-NMR : δ = 1.27(6H,t), 2.70(4H,q). ^{19}F-NMR : δ = -72.0(s) IR(CHCl$_3$) : ν = 2995, 2940, 2870, 1670, 1450, 1380, 1270, 1160, 1120, 1005, 975, 720 cm^{-1}.

E-1,2-difluoro-2-chlorovinyl phenyl selenide 14 : Following the above procedure, the reaction between adduct **8e** and magnesium afforded compound **14** as a colorless liquid, b.p. : 60-65°C/0.3 Torr. ^{1}H-NMR : δ = 7.3(3H,m), 7.56(2H,m). ^{19}F-NMR : δ = -104.3(1F,d), -123.0(1F,d); ^3J(F-F) = 145 Hz. IR(film) : ν = 3060, 1660, 1580, 1480, 1440, 1180, 805 cm^{-1}. MS(EI) : **254**(m/e); 219, 157, 77, 51.

Reaction between 1-chloro-2-bromo-1,2,2-trifluoroethyl phenyl selenide 8f and zinc in the presence of TiCl$_4$: 3 Drops of TiCl$_4$ were added to a mixture of 1-chloro-2-bromo-1,2,2-trifluoroethyl phenyl selenide **8f** (0.705 g, 2 mmoles) and powdered zinc (0.4g, 6 mg-at.) in dry THF (16 ml) at -100°C (diethylether, dry ice, liquid nitrogen). The mixture was then warmed up to room temperature and poured in water (100 ml) followed by extraction with methylene chloride (3x20 ml). The organic layer was washed with brine (50 ml) and dried over magnesium sulfate. Evaporation of the solvent gave the crude product which was distilled to give a 3:1 mixture of **101** : **10g**. They were separated by gas-chromatography using SE30 column (5%Chrom. WAW/DMCS 80/100 or 40/60).

Reactions between lithiated reagents 11 and benzene seleneyl bromide 6c : General procedure : A cooled (0°C) ethereal solution (100 ml) of C$_6$H$_5$SeBr (7.08 g, 30 mmoles) was added dropwise to a solution of **11a, 11b** or **11c** [30 mmoles, prepared according to refs (12), (13a) and (13b,c)] at -100°C, -110°C and -125°C, respectively. Stirring was continued at the same temperature for 15 minutes after the addition was completed and the solution was then allowed to reach the room temperature. The mixture was poured in water (100 ml) and extracted with diethylether (3x50 ml). The organic layer was washed with brine (100 ml) and dried over magnesium sulfate. Chromatography using petroleum ether as eluent and distillation afforded olefins **10e, 10f** of **10g**.

2,2-difluorovinyl phenyl selenide 10e : A colorless liquid, b.p. : 40-45°C/0.6 Torr (litt$^{(5a)}$: 35-36°C/0.5 Torr). ^{1}H-NMR : δ = 5.2[1H,dd, ^3J(H-F$_{cis}$) = 2.4 Hz, ^3J(H-F$_{trans}$) = 24.6 Hz], 7.3(5H,m). ^{19}F-NMR : δ = -75.4(1F,dd), -77.6(1F,dd); ^2J = 24 Hz. IR(film) : ν = 3075, 1695, 1580, 1475, 1440, 1290, 1150, 945, 735, 690 cm^{-1}. MS(EI) : **220**(m/e); 157, 77.

1,2,2-trifluorovinyl phenyl selenide 10f : A colorless liquid, b.p. : 66-68°C/17 Torr. ^{1}H-NMR : δ = 7.25(m,5H). ^{19}F-NMR : δ = -89.9(1F,dd,C-1 fluorine), -107.3[1F,dd,C-2 fluorine (Z-relationship with the SeC$_6$H$_5$ substituent)], -151.3[1F,dd,C-2 fluorine (E-relationship with the SeC$_6$H$_5$ substituent)]; ^{2}J = 49 Hz, $^{3}J_{trans}$ = 130 Hz, $^{3}J_{cis}$ = 38 Hz. IR(CH$_2$Cl$_2$) : ν = 3090, 3060, 1735, 1580, 1480, 1440, 1300, 1130, 1015, 690 cm^{-1}. MS(EI) : **238**(m/e); 219, 157, 77.

1-chloro-2,2-difluorovinyl phenyl selenide 10g : A colorless liquid, b.p. : 70-72°C/17 Torr. ^{1}H-NMR : δ = 7.20(m,5H). ^{19}F-NMR : δ = -75.09(1F,d), -78.3(1F,d); ^{2}J = 15.6 Hz. IR(film) : ν = 3090, 3060, 1700, 1580, 1480, 1440, 1265, 1010, 690 cm^{-1}. MS(EI) : **254**(m/e); 235, 219, 200, 157, 77, 51. Found : C = 37,89, H = 2.38%. Requires : C = 37.90, H = 1.99%

1-phenylselenenyl-2,2,2-trifluoroethanol 15 : Phenylselenol (3.14 g, 20 mmoles) was added at room temperature to a suspension of zinc chloride (0.681 g, 5 mmoles) in carbon tetrachloride (10 ml), followed by gaseous trifluoroacetaldehyde$^{(23)}$ (1.96 g, 20 mmoles). The resulting mixture was stirred overnight and poured in 5% aqueous hydrochloric acid (20 ml). The aqueous phase was extracted once with ether (15 ml) and the extract was washed with 10% sodium hydrogenocarbonate (15 ml) with water (15 ml) and dried over magnesium sulfate. Evaporation of the solvent and distillation gave first the unreacted phenylselenol and then compound **15** as a colorless oil which crystallized upon standing, b.p. : 60°C/0.01 Torr, m.p. : 32°C. ^{1}H-NMR : δ = 2.65(1H,d), 5.3(1H,m), 7.32(3H,m), 7.64(2H,m). ^{19}F-NMR : δ = -76.36(3F,d,J = 7.1 Hz). IR (CH$_2$Cl$_2$) : ν = 3550, 3080, 2980, 1580, 1480, 1440, 1390, 1310, 1250, 1180, 1110, 1070, 850, 690 cm^{-1} MS(CI/IB) : **313**(M+57)$^{+}$; 257(M+1)$^{+}$; 236, 157, 77.

1-phenylselenenyl-2,2,2-trifluoroethyl phenyl selenide 8t : A 50% aqueous sodium hydroxide solution (0.34 ml, 5.22 mmoles) was added at room temperature in a benzene solution (10 ml) of phenylselenol (0.82 g, 0.53 ml, 5.22 mmoles) and the resulting mixture was stirred for 5 minutes and then cooled down to 0°C. A tetrahydrofuran solution (10 ml) of 1-bromo-2,2,2-trifluoro-ethylphenyl selenide **8p** (1.66 g, 5.22 mmoles) was added dropwise and stirring was continued at 0°C for four hours. The mixture was poured in water (60 ml) and extracted with methylene chloride (3x25 ml). The combined organic layers were washed with brine (100 ml) and dried over magnesium sulfate. Evaporation of the solvents, chromatography (eluent : petroleum ether) and distillation afforded **8t** as a pale yellow oil, b.p. : 98-100°C/0.005 Torr. ^{1}H-NMR : δ = 4.48(1H,q), 7.32(6H,m), 7.6(4H,m). ^{19}F-NMR : δ = -65.6[3F,d, ^{3}J(F-H) = 8.4 Hz]. IR(film) : ν = 3065, 1580, 1475, 1440, 1280, 1240, 1150, 1090, 740, 690 cm^{-1}. MS(EI) : **396**(m/e); 239, 219, 157, 77. Found : C = 42.73, H = 3.05%. Requires : C = 42.66, H = 2.81%. The same compound was also obtained by refluxing for 22 hours an acetonitrile solution (8 ml) of potassium fluoride (0.87 g, 1.5 mmole) and a 9:1 mixture of adducts **8j** : **9j** (0.758 g, 1.5 mmole of **8j**). The same work-up and purification as above led to compound **8t**.

Treatment of selenoacetal 8t with n-butyllithium : A solution of 1-phenylselenenyl-2,2,2-trifluoroethyl phenylselenide (0.4 g, 1.02 mmole) in 10 ml of a 5:3:3 mixture of tetrahydrofuran, diethylether and pentane was cooled down to -110°C (pentane, dry ice and liquid nitrogen) and a solution of 1.56 N n-butyllithium in hexane (1.58 ml, 1.02 mmole) in 10 ml of the same 5:3:3 mixture of THF/Et$_2$O/ pentane was then added dropwise. Stirring was continued for 15 minutes at -110°C and the mixture was warmed up to room temperature, washed with a 10% aqueous sulfuric acid solution (20 ml), water (20 ml) and 10% aqueous sodium hydrogenocarbonate solution (20 ml) and dried over magnesium sulfate. Evaporation of the solvent and distillation gave fluoroolefin **10e**.

References and Footnotes :

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