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Fluorination of olefins with $PhSeF_3$, $PhSeF_5$ and $PhTeF_5$

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Abstract

Phenyselenium trifluoride, $PhSeF_3$ (PSTF) either oxidatively difluorinates or selenofluorinates olefins, depending on their structures. The pentafluorides $PhSeF_5$ and $PhTeF_5$ appear to be effective difluorinating reagents, affording 1,2-difluoroalkanes from olefins. © 1998 Elsevier Science S.A.

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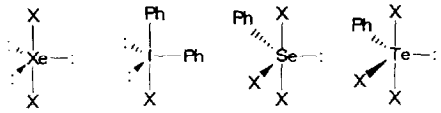
1. Introduction

Fluorinated compounds are of considerable interest [1–4] in inorganic, organic, polymer, industrial and medicinal [5,6] chemistry. Particularly valuable are mild and selective fluorinating agents and methods for the ready fluorination of organic and bioorganic compounds [5–7]. Currently known fluorinating methods can be conveniently classified [7] into three broad categories: (a) nucleophilic displacement of an appropriate leaving group by fluoride; (b) oxidative substitution of aromatic substrates; (c) electrophilic addition to carbon=carbon double bonds. The great majority of fluorinating agents are nucleophilic with relatively few sources of electrophilic fluorine having been used [1–7]. This is understandable since as the most electronegative element it is very difficult to induce fluorine to behave as an electrophile.

Progress has been made in the past 30 years however through the development of reagents effectively delivering F^+. Commonly employed electrophilic fluorinating agents include F_2 itself [8–10], XeF_2 [11–13], $PhIF_2$ [14–16], acetyl hypofluorite, MeCOOF [17–20] and N–fluoroamines and amides [21–24]. Unfortunately, these reagents have various drawbacks and limitations such as hazardous handling (F_2, RCOOF), lack of selectivity (XeF_2) or weak fluorinating ability ($PhIF_2$). Therefore, new electrophilic fluorinating agents that allow the ready introduction of fluorine under mild conditions into electron rich substrates such as olefins are highly desirable and useful. In this communication we report power variable electrophilic fluorinating agents, based upon polyvalent Se and Te and capable of addition to olefins.

Dicoordinate Xe(II), tricoordinate iodine(III), tetracoordinate Se(IV) and Te(IV), are all isoelectronic 10-electron members of the family of polycoordinated nonmetallic main group species [25]. Members of the iodine family [26,27] have been known since 1886 when Willgerodt first reported $PhICl_2$.



The renaissance in polyvalent iodine chemistry [26–31] and the similarity of the isoelectronic series prompted us to investigate the fluorinating properties of $PhSeF_3$, $PhTeF_3$, and the related hexavalent fluorides $PhSeF_5$, $PhTeF_5$.

2. Results

2.1. The reaction of $PhSeF_3$ (PSTF) with stilbenes, indene and acenaphthylene

Phenylselenium trifluoride, PSTF, was prepared by the reaction of diphenyl diselenide with three equivalents of XeF_2 according to Eq. (1), and used directly without isolation (it

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should be noted that the reaction of equimolar amounts of Ph_2Se_2 and XeF_2 affords PhSeF [32]).

$$Ph_2Se_2 + 3\ XeF_2 \xrightarrow[-Xe,\ 15\ min]{CH_2Cl_2,\ rt} 2PhSeF_3 \quad (1)$$
PSTF

PSTF reacts smoothly with *trans*- and *cis*-stilbenes in methylene chloride at ambient temperature affording good yields (70%) of mixtures of *erythro*- and *threo*-1,2-difluorides, **1**, with predominance of the *erythro*-isomer in both cases (Eq. (2)).

$$PhCH=CHPh \xrightarrow[rt,\ 5–7\ h]{PSTF/CH_2Cl_2} \underset{1}{PhCHF–CHFPh} \quad (2)$$

Trans- *erythro*:*threo* = 9:1 *cis*- *erythro*:*threo* = 2:1

Both diastereomeric difluorides of **1** were isolated pure by column chromatography on silica gel. Diphenyl diselenide (Ph_2Se_2) was the only selenium containing by-product isolated. X-ray grade crystals were obtained for *erythro*-**1** and its structure was confirmed by X-ray crystallographic analysis [33]. The ^{19}F NMR spectra of both diastereomers comprised characteristic AA'XX' spin systems at −109 ppm (*erythro*-**1**) and −106 ppm (*threo*-**1**) (relative to external CF_3-COOH).

Our attempts to establish the structures of difluorides **1** by dehydrofluorination into fluorostilbenes **2** using potassium *tert*-butoxide were unsuccessful (Eq. (3)).

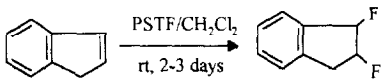
$$\underset{1}{PhCHF–CHFPh} \xrightarrow{t\text{-}BuOK/t\text{-}BuOH} \underset{2}{PhCH=CFPh} \quad (3)$$

Earlier, this procedure was used for the determination of diastereomeric composition of 1,2-difluoro-1,2-diphenylethanes, **1**, [34–36] assuming that only *anti*-elimination takes place and hence, only *cis*-(*E*)-fluorostilbene **2** is formed from *erythro*-**1** and *trans*-(*Z*)-**2**– from *threo*-**1** (the resulting fluoroolefins can be easily identified by ^{19}F NMR). We performed the dehydrofluorination as in Refs. [34–36] and found that in all cases the *trans*-(*Z*)-isomer of **2** was formed as the main product (see Table 1). Moreover, it was shown earlier that)CHF–CHF(groups in some cyclic polyfluorides undergo both *anti*- and *syn*-elimination (the review can be seen in Ref. [37]) and thus, the estimation of diastereomeric content by potassium *tert*-butoxide dehydrofluorination of 1,2-difluorides cannot be considered reliable.

Table 1
Results of dehydrofluorination of difluorides **1** by *t*-BuOK

Diastereomeric content in difluorides **1** (%)		Fluorostilbenes **2** (%)	
erythro-	*threo*-	*cis*-(*E*)	*trans*-(*Z*)
100	0	32	68
67	33	33	67
0	100	0	100

Indene reacts with PSTF under similar conditions affording a mixture of *cis*- and *trans*-difluorides **3** in 45% isolated yield (Eq. (4)).



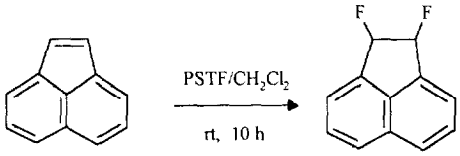
(4)

3

cis : *trans* = 1:4

The isomeric ratio in **3** was determined using a ^{19}F NMR procedure as in Ref. [38].

Fluorination of acenaphthylene, a tricyclic analogue of *cis*-stilbene, proceeds in a similar manner to afford *trans*- (8% yield) and *cis*-difluoride **4** (2% yield) (Eq. (5)):

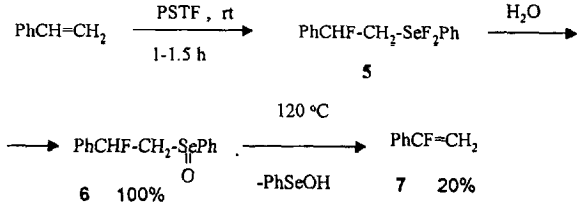


(5)

4 *cis* : *trans* = 1 : 4

2.2. The reaction of PSTF with styrene, cyclohexene and norbornene

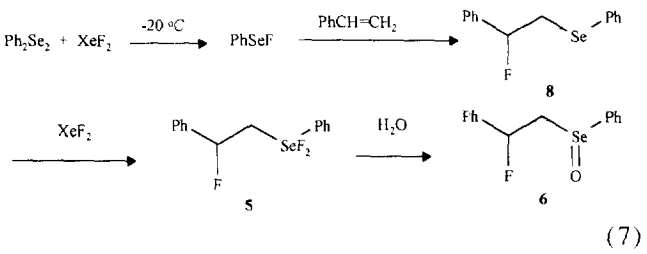
These olefins react with PSTF in a different way, giving no difluorides but affording the products of selenofluorination. Thus, styrene reacts with PSTF forming the addition product **5**, which can be transformed into other fluorine containing compounds **6** and **7** (Eq. (6)).



(6)

We could not isolate **5** due to its extreme hydrolytic instability. Its ^{19}F NMR spectrum shows three separate groups of signals in a 1:1:1 ratio: at −93.4 ppm, m, (PhCHF); 7.2 ppm, d, $^2J(F–F) = 150$ Hz and −3.5 ppm, d, $^2J(F–F) = 150$ Hz ($PhSeF_2$). These data are consistent with those published earlier for R_2SeF_2 [39] but show at least one peculiarity—strong difference between two fluorine atoms attached to selenium. After treatment with aqueous $NaHCO_3$ or just on silica gel during attempted purification **5** converts quantitatively into selenoxide **6** which is rather stable and can be stored in a refrigerator at least for some days. Selenoxide **6** is a viscous oil which we were unable to purify to analytical grade. On heating in vacuo **6** eliminates phenylselenenic acid affording α-fluorostyrene, **7**.

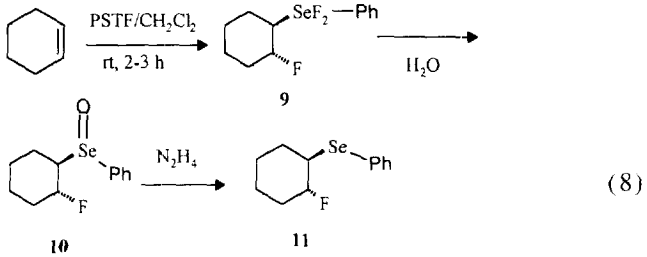
To confirm the structures of **5** and **6**, we prepared them in an independent way, using PhSeF (Eq. (7)), a reagent recently synthesised by Japanese investigators [32].



(7)

Fluorinated alkylaryl selenide **8**, prepared from PhSeF and styrene, was oxidised further by XeF_2 into **5** which in turn was hydrolysed into oxide **6**.

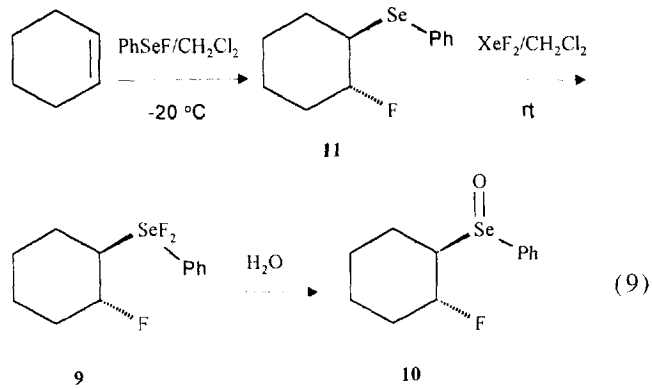
Cyclohexene reacts with PSTF analogously and appropriate products can be either detected by ^{19}F NMR spectroscopy (**9**) or isolated in individual state (**10**, **11**) (Eq. (8)).



(8)

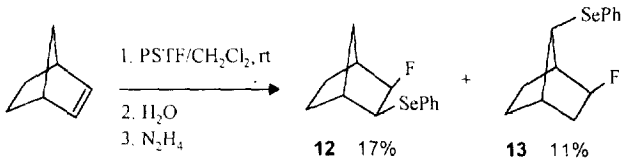
The *trans*-structures of **10** and **11** were established by the comparison of their ^1H NMR spectra with those published for **11** in Ref. [32] (10.5 Hz and 8.5 Hz coupling constants ^3J(H–H) were obtained for **10** and **11** respectively indicating the *trans*-configuration). Hence, the *trans*-structure was assigned to the primary product **9**. The ^{19}F NMR spectrum of **9** contains three groups of signals in a 1:1:1 ratio at −1 ppm (d, ^2J(F–F) = 158 Hz), −22 ppm (d, ^2J(F–F) = 158 Hz), and at −90.5 ppm (d, ^2J(F–H) = 49 Hz) which were attributed to CHF and $PhSeF_2$ units respectively (compare with the ^{19}F NMR spectrum of **5**). It is worth mentioning that selenoxide **10** exists as a mixture of two diastereomers in approximately 2:1 ratio (as shown by ^1H and ^{19}F NMR spectroscopy) due to the chirality of the >Se=O fragment. This diastereomerism disappears after the reduction of **10** to selenide **11**.

To confirm the structures of **9**, **10** and **11** we used PhSeF and got the same products (Eq. (9)).



(9)

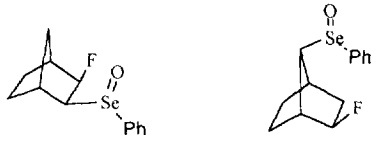
Surprisingly, norbornene reacts with PSTF very slowly, the reaction being completed only in 4–5 days at room temperature (as monitored by ^{19}F NMR). We were able to separate and to analyse the products only in the reduced form as selenides **12** and **13** (Eq. (10)).



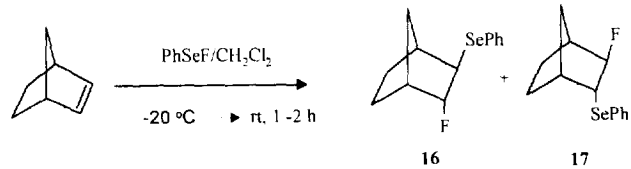
(10)

Pure selenides **12** and **13** were isolated by column chromatography on silica gel. The structure of **12** was established by X-ray analysis revealing the *exo*-, *cis*-configuration for the initial product of addition of PSTF to norbornene [40,41]. The structure of the Wagner–Meerwein rearrangement product **13** was assigned by ^1H, ^{19}F NMR and mass-spectroscopy. The *syn*-configuration of the PhSe-substituent was confirmed by the NMR data (^4J(H7–H3 *endo*) = 2.0 Hz (W-constant) [42,43]).

After the hydrolysis of the original reaction mixture two compounds were detected by ^{19}F NMR in a 2:1 ratio. We have not been able to isolate them in a pure form, but comparison of their ^{19}F NMR and mass-spectra with those of selenides **12** and **13** has enabled them to be identified as selenoxides **14** and **15**. These compounds, existing as diastereomeric pairs, seem to originate from the primary products, namely the corresponding selenium difluorides of the type R–SeF_2–Ph.

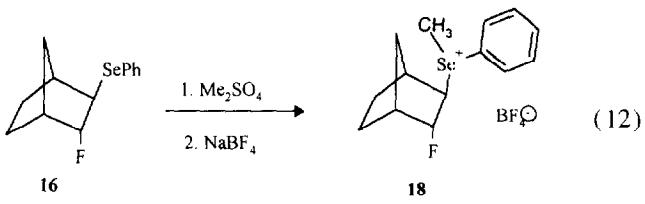


Our attempts to prepare fluoroselenides **12** and **13** by an independent procedure using the reaction of norbornene with phenylselenenyl fluoride PhSeF were unsuccessful because the course of this reaction differed from that of the reaction of PSTF with norbornene. PhSeF adds to norbornene with predominant formation of the *trans*-adduct **16** (80%), diastereomeric *trans*-adduct **17** (10%) and less than 10% of several unidentified minor compounds [40,41] (Eq. (11)).



(11)

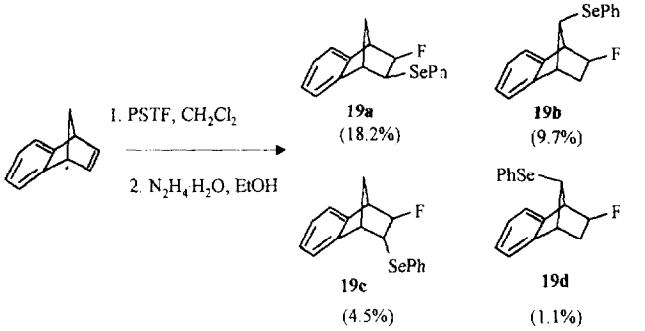
Individual compounds **16** (yield 65%) and **17** were isolated by column chromatography on silica gel. We managed to prepare X-ray grade crystals of the methylselenonium fluoroborate **18** from **16** and hence, to establish its structure unambiguously [44] (Eq. (12)). The structure of **17** was established by ^{19}F NMR.



16 18 (12)

The stereochemical result of the reaction of PhSeF with norbornene (*trans*-addition) is analogous in general to that observed in the reaction of norbornene with PhSeCl [45] and ArSCl [46]. However the formation of appreciable amounts of the adduct **17**, due to the *endo*-attack, is remarkable.

PSTF attacks benzonorbornadiene to give, after aqueous reductive work-up, products **19a–d**, the fluorine atom being in the *exo*-2 position in each compound (Eq. (13)).



(13)

Our attempts to perform the fluorination of olefins by $PhTeF_3$ failed. In the cases of *trans*-stilbene, styrene, indene and cyclohexene no organic fluorides were detected by means of ^{19}F NMR spectroscopy.

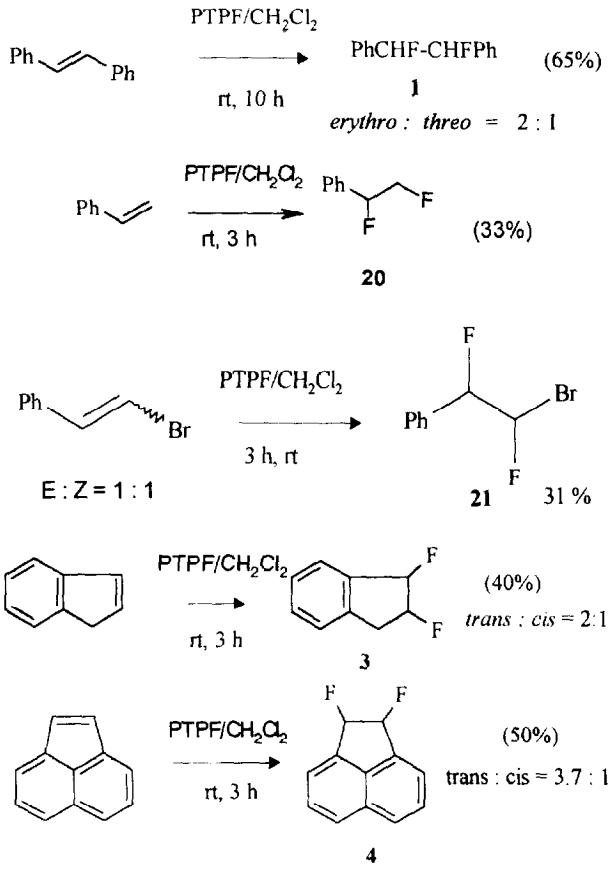
2.3. Fluorination of olefins by $PhTeF_5$ (PTPF) and $PhSeF_5$ (PSPF)

To increase the electrophilic power of the reagents we prepared and investigated the appropriate derivatives of hexavalent Te and Se—namely $PhTeF_5$ (PTPF) and $PhSeF_5$ (PSPF). PTPF has been described in the literature, although only the nucleophilic displacement of its fluorine was investigated [47,48]; we were unable to find any data concerning PSPF. We prepared them using the reaction of diphenyl diselenide or ditelluride with five equivalents of XeF_2 (Eq. (14)):

$$Ph_2X_2 + 5XeF_2 \xrightarrow{CH_2Cl_2,\ -Xe} \underset{\substack{\text{PTSF X = Te,}\\ \text{PSPF X = Se.}}}{2\ PhXF_5} \qquad (14)$$

The conversion of Ph_2Se_2 needs 3–4 h but Ph_2Te_2 reacts faster (5–10 min). The reactions were monitored by Xe evolution (gas burette, usually 95–100 vol.% of Xe evolved). Both reagents were used without isolation.

Phenyltellurium pentafluoride (PTPF) reacts smoothly with olefins affording the corresponding 1,2-difluorides as the principal products (Scheme 1). In the case of styrene the only fluorine-containing product was difluoro derivative **20**,



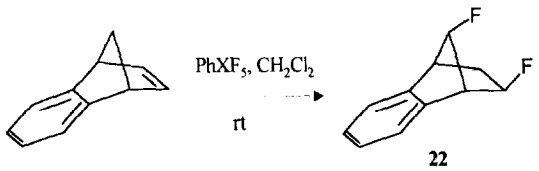
Scheme 1.

whereas not even traces of **20** could be found when PSTF was used as the fluorinating agent.

In general, phenylselenium pentafluoride, PSPF, reacts with olefins in the same manner, also affording 1,2-difluorides, as shown in Scheme 2.

It is worth mentioning that in the case of styrene the reaction mixture contains an equimolar amount of selenofluoride **5**, which we prepared independently from styrene and PSTF as well as from styrene, PhSeF and XeF_2 (see Section 2.2).

Benzonorbornadiene reacted with PTPF and PSPF giving 5-*exo*-7-*syn*-difluorobenzonorbornene, **22**, the product known to result from fluorination of benzonorbornadiene by XeF_2 [38] (Eq. (15)):

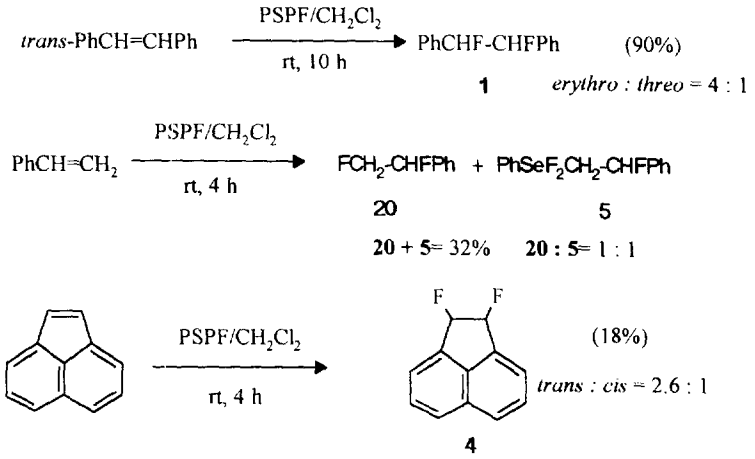


(15)

PTPF Yield 58%
PSPF Yield 61%
XeF_2 Yield 68% [38]

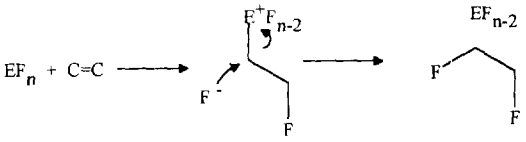
3. Discussion

An electrophilic reagent EF_n capable of introduction of two fluorine atoms into an olefinic molecule must (i) be



Scheme 2.

electrophilic enough for the addition to a C=C bond and (ii) the EF_{n-1} or $(EF_{n-2})^+$ moiety must possess a high leaving capacity to be substituted by such a weak nucleophile as the fluoride anion F^-.



Fluorinating reagents, investigated in this work, can be divided into three separate groups.

(1) PhSeF: This molecule is moderately electrophilic (no skeletal rearrangements in the case of norbornene) and the resulting $PhSe^-$ group is a very strong nucleophile and cannot be substituted by the fluoride anion to give difluorination products. Our results and earlier work [32] reveal that PhSeF can be used only for the selenofluorination of olefins and, after appropriate workup, for the preparation of monofluorinated olefins.

(2) Phenylselenium trifluoride (PSTF) appears to be a potent electrophilic agent. It reacts quickly with stilbenes and the presence of appreciable amount of Wagner–Meerwein rearrangement product in the case of norbornene reveals that a strong carbocationic center forms on carbon atoms in the transition state.

The leaving capacity of the resulting $PhSeF_2^-$ group is much greater than that of $PhSe^-$ group and hence, difluorination can be achieved in some cases. It is easy to notice that 1,2-difluorides are formed only in cases where the $PhSeF_2^-$ group (which is to be substituted by the fluoride anion) can occupy a benzylic position (Ph–C–Se), which is activated towards nucleophilic displacement according to general rules of S_N reactions (stilbenes, indene, acenaphthylene). In other cases (styrene, cyclohexene and norbornene) nucleophilic displacement does not take place and the reaction stops at the selenofluorination products **5**, **9**, **12**, **13**.

(3) $PhTeF_5$, (PTPF) and $PhSeF_5$ (PSPF): These reagents possess high electrophilic power (due to the formal +6 oxidation state of the central atom) and the resulting $ArXF_4^-$ moiety (X = Te, Se) is a good leaving group. In accordance with above principles, both PTPF and PSPF should be powerful difluorinating reagents. In fact, all investigated olefins (even styrene and benzonorbornadiene) are transformed into appropriate difluorides by PTPF and PSPF. The contaminating selenofluoride **5** in the case of styrene and $PhSeF_5$, is undoubtedly formed from styrene and $PhSeF_3$ which is a by-product in the reaction of styrene and PSPF. The absence of contaminating tellurofluorination in the reaction of phenyltellurium pentafluoride, PTPF, with styrene is explained by the low reactivity of the resulting Te(IV) fluoride towards the C=C bond.

We may conclude that fluorides of polyvalent selenium and tellurium can serve as source of 'electrophilic fluorine' in the reactions with olefins.

4. Experimental

^1H and ^{19}F NMR spectra were recorded using a Bruker CXP-200 spectrometer. Chemical shifts are reported in δ units downfield from external TMS and CF_3COOH respectively. Mass-spectra were recorded on a Finnigan GC/MS-4021 spectrometer.

4.1. Reaction of olefins with phenylselenium trifluoride, PSTF: general procedure

All reactions were performed in Teflon or quartz reactors. In a typical experiment 1.8×10^{-3} mol of XeF_2 were added by portions to a solution of 6×10^{-4} mol of Ph_2Se_2 in 5–10 ml of thoroughly dried CH_2Cl_2 at ambient temperature. After gas evolution ceased (gas burette, approximately 100% of Xe evolved) 1.2×10^{-3} mol of an olefin were added in one portion. After appropriate stirring the solvent was carefully evaporated in vacuo, the reaction mixture was dissolved in $CDCl_3$ or d_6-acetone (0.3–0.4 ml) and an exact quantity of C_6F_6 was added as an internal standard for integration. For products isolation the reaction mixture was washed with 5%-$NaHCO_3$, dried over $MgSO_4$, CH_2Cl_2 was removed and prod-

Table 2
Reaction of olefins with PSTF, PTPF and PSPF

Olefin	Products	Yields from reagents			NMR data ($CDCl_3$)		
		$PhSeF_3$ (PSTF)	$PhTeF_5$ (PTPF)	$PhSeF_5$ (PSPF)	δF	^2J(F–H)	^3J(F–H, F–F)
Styrene	**20**	0	33	16	−108.9, m. −145.3 t.t.	48.5, 48.	15., 21., 32.
	5	72	0	16	−94.3, 7.2, −3.5	46.5	16.5, 30.8
trans-stilbene	*threo*-**1**	8	24	18	−104.2	AA'XX'	AA'XX'
	erytro-**1**	57	41	72	−108.2	AA'XX'	AA'XX'
cis-stilbene	*threo*-**1**	23	–	–	−104.2	AA'XX'	AA'XX'
	erytro-**1**	46	–	–	−108.2	AA'XX'	AA'XX'
Acenaphthylene	**4**	8	77	13	−97.9	53.	20.
	4	2	21	5	−113.1	46.	13.
Indene	**3**	36	27	–	−99.6, −111.0		
	3	9	13	–	−114.0, −124.3		
Cyclohexene	**9**				−90.5, −22, 1	49	
Benzonorborna diene	**22**[a]	–	58	61	−99.6 d, −100.8 m	56	10
	19	33.5					

[a]The compound was shown to be identical with the sample we synthesized via the known procedure from benzonorbornadiene and XeF_2 [38].

ucts were isolated by chromatography on silica gel. NMR spectral data and the yields of products are given in Table 2.

We were unable to compare the ^{19}F NMR spectra of PSTF with that reported in Ref. [49] due to its extremely rapid hydrolysis in glass NMR tubes. However the chemical behavior of the reagent (mild hydrolysis to PhSe(O)OH, mp 110°C, lit. data 121°C [50]) as well as the structures of the compounds obtained confirm its structure as PSTF.

*4.1.1. erythro- and threo-1,2-Difluoro-1,2-diphenylethane, **1***

The reaction of PSTF with *trans*- and *cis*-stilbene needs 5–7 h for completion. The evaporated reaction mixtures (see Section 4.1) were analysed by ^{19}F NMR. The products were separated by column chromatography on SiO_2 100/160 μ (eluent-hexane: $CHCl_3$ = 4:1).

The *erythro*-isomer was isolated as a crystalline solid (yield 57%), mp 100–102.5°C (CH_3OH) (lit. [34] mp 99–100°C). Mass spectrum (calc. for $C_{14}H_{12}F_2$ 218): 218 (M^+, 10), 178 (M–2HF, 1), 109 (Ph–CHF, 100). Unambiguous proof of the structure for *erythro*-**1** was made by X-ray analysis (see Ref. [33]). ^{19}F NMR data can be seen in Table 2.

The *threo*-isomer was isolated as a viscous oil (yield 8%). Mass spectrum (calc. for $C_{14}H_{12}F_2$ 218): 218 (M^+, 15), 178 (M–2HF, 2), 109 (Ph–CHF, 100).

*4.1.2. Dehydrofluorination of erythro- and threo-isomers of **1***

The individual isomers of **1** or their mixture (1 equiv.) were dissolved in 3–5 ml of *tert*-butyl alcohol and 1.5 equiv. of potassium-*tert*-butoxide was added. The reaction mixture was stirred for 18 h at room temperature and 4 h at 50–60°C, then cooled, mixed with water, and extracted with CH_2Cl_2. The extract was washed with dilute acid and water, dried over $MgSO_4$, filtered, and evaporated and the residue was analysed by ^{19}F NMR spectroscopy (see Table 1).

*4.1.3. cis- and trans-1,2-Difluoroindane, **3***

The reaction of PSTF with indene needs 2–3 days for completion. The mixed title compounds were isolated as a viscous oil after column chromatography on SiO_2 100/160 μ (eluent hexane: $CHCl_3$ = 4:1). Mass spectrum: 154 (M^+, 100), 153 (69), 134 (29), 133 (43), 127 (9), 115 (6), 107 (9). Lit. data [38]: 154 (M^+, 100), 153 (61), 134 (34), 133 (59), 127 (11), 115 (11), 107 (11). ^{19}F NMR data can be seen in Table 2.

*4.1.4. cis- and trans-9,10-Difluoroacenaphthenes, **4***

The reaction with acenaphthylene needs 10 h for completion. The title compounds were characterized by their ^{19}F NMR spectra which were similar to those reported in Ref. [38]. Column chromatography afforded the pure *trans* isomer. ^{19}F NMR data can be seen in Table 2.

4.2. The reaction of styrene with PSTF

*4.2.1. (2-Fluoro-2-phenylethyl)phenylselenodifluoride, **5***

The reaction of styrene with PSTF needs 1–1.5 h for completion giving **5** as an unstable oil. Mass spectrum (calc. for $C_{14}H_{13}F_3Se$ 317): 299 (M–F+H, 5), 280 (M–2F, 30), 123 (PhCHF–CH_2, 97), 77 (Ph, 100).

*4.2.2. (2-Fluoro-2-phenylethyl)phenylselenoxide, **6***

Selenodifluoride **5** in methylene chloride was hydrolyzed by 5% aqueous $NaHCO_3$, the reaction mixture extracted with ether and dried over $MgSO_4$. Evaporation left **6** as a viscous oil quantitatively. The ^{19}F NMR spectrum reveals two signals at −93.8 ppm and −93.3 ppm, which were attributed to two

diastereomers of **6**, both having the same spin–spin constant set: ^2J(F–H) = 47.5 Hz, ^3J(F–H) = 41 Hz, 11.4 Hz.

4.2.3. 1-Fluoro-1-phenylethene, 7

Selenoxide **6** was heated at 110–120°C in vacuo during 5 h. In the liquid nitrogen cooled trap **7** as an oily liquid was found (20% yield). ^{19}F NMR: −30.67 ppm, ^3J(F–H) = 51 Hz, 17 Hz. ^{1}H NMR: 6.8–7.1 ppm, 5 H; 4.55 ppm, 1 H, dd ^3J(F–H) = 50.5 Hz, ^2J(H–H) = 3 Hz; 4.37 ppm, 1 H, dd ^3J(F–H) = 17 Hz, ^2J(H–H) = 3 Hz. Lit. data: ^{19}F −31.4 ppm, ^{1}H 4.72 ppm, 4.98 ppm [51].

4.2.4. (2-Fluoro-2-phenylethyl)phenylselenide, 8

The title compound **8** was prepared as in Ref. [32] from styrene and PhSeF. ^{19}F NMR: −89.3 ppm, ^2J(F–H) = 42.5 Hz, ^3J(F–H) = 23.8 Hz, 17.5 Hz. Oxidation of **8** by equimolar amount of XeF_2 in CH_2Cl_2 during 10 min at ambient temperature afforded **5** and, after hydrolysis, **6**. Their ^{19}F NMR spectra were similar to those described above.

4.3. The reaction of PSTF with cyclohexene

The reaction of cyclohexene with PSTF needs 2–3 h for completion.

4.3.1. (trans-2-Fluorocyclohexyl)phenylselenodifluoride, 9

^{19}F NMR data for **9** are given in Table 2. Mass spectrum (calc. for $C_{12}H_{15}F_3Se$ 295): 277 (M–F, 1), 258 (M–2F, 30).

4.3.2. (trans-2-Fluorocyclohexyl)phenylselenoxide, 10

The title compound was obtained after washing of the solution of **9** by water, drying of the reaction mixture over $CaCl_2$ and column chromatography on SiO_2 as an oily mixture of two diastereomers (yield 65%). ^{19}F NMR: −90.55 (d, ^2J(H–F) = 49 Hz), −90.95 (d, ^2J(H–F) = 49 Hz) (the ratio of signals was 2:1). ^{1}H NMR (for CHF fragment): 4.2 (dm, ^2J(F–H) = 48.71 Hz), 4.75 (dm, ^2J(F–H) = 48.7 Hz, ^3J(H–H) = 10.5 Hz, 5 Hz). The ratio of these signals was 2:1. Anal. calc. for $C_{12}H_{15}FOSe$: C, 52.76; F, 6.95. Found: C, 52.74; F, 7.10.

4.3.3. (trans-2-Fluorocyclohexyl)phenylselenide, 11

The alcoholic solution of **10** was treated with an equimolar amount of hydrazine hydrate during 1–2 h at room temperature. The reaction mixture was evaporated in vacuo, extracted by ether, the organic solution was dried over $MgSO_4$ and the solvent was removed to leave an oil (70% yield). ^{19}F NMR: −88.8 ppm, ^2J(F–H) = 45 Hz. The same compound was obtained from cyclohexene and PhSeF, as in Ref. [32]. Oxidation of **11** by equimolar amount of XeF_2 in CH_2Cl_2 during 10 min at ambient temperature afforded **9** and, after hydrolysis, **10**. Their ^{19}F NMR spectra were similar to those described above.

4.4. The reaction of norbornene with PSTF

The reaction of norbornene with PSTF needs 4–5 days for completion. After usual work-up (see Section 4.1) the crude material was analysed by ^{19}F NMR and mass-spectroscopy with subsequent reduction by equimolar amount of N_2H_4 in EtOH during 0.5 h. Evaporation of the solvent left a viscous oil which was subjected to column chromatography (silica gel, hexane: $CHCl_3$ = 4:1) to give 2-*exo*-fluoro-3-*exo*-(phenylseleno)norbornane, **12**, (yield 17%) and 2-*exo*-fluoro-7-*syn*-(phenylseleno)norbornane, **13**, (yield 11%).

4.4.1. Fluoro-(phenylselenoxido)norbornanes 14 and 15

The previous reaction mixture in methylene chloride was hydrolyzed by 5% aqueous $NaHCO_3$ and dried over $MgSO_4$. Evaporation left a viscous oily mixture of **14** (as a pair of diastereomers in 4:1 ratio) and **15** (as a pair of diastereomers in 5:1 ratio).

4.4.2. 2-exo-Fluoro-3-exo-(phenylseleno)norbornane, 12

Mp 64–65°C (hexane). Calc. for $C_{13}H_{15}FSe$: C, 58.0; F, 7.06 Found: C, 58.21; F, 7.10.

4.4.3. 2-exo-Fluoro-7-syn-(phenylseleno)norbornane, 13

Oil. Anal. calc. for $C_{13}H_{15}FSe$: C, 58.0; F, 7.06. Found: C, 57.99; F, 6.73.

4.4.4. Fluoro-(phenylseleno)norbornanes 16 and 17

The title compounds were synthesised according to the literature procedure [32] and obtained pure after repeated preparative column chromatography on SiO_2 (hexane: $CHCl_3$ = 4:1). **16**: oil (yield 65%). Anal. calc. for $C_{13}H_{15}FSe$: C, 58.0; Found: C, 58.42. **17**: oil (yield 7%). NMR spectra of compounds **12–17** are presented in Tables 3 and 4.

4.5. Reaction of benzonorbornadiene with PSTF

The reaction needs 2–3 h at room temperature for the completion The solvent was removed in vacuo, the residue was reduced with alcoholic $N_2H_4 \cdot H_2O$, extracted with ether and washed with water, the organic layer was dried over $MgSO_4$ and purified from tar by passing through silica gel. After evaporation of the solvent components **19a** and **19b** were isolated in an individual form by column chromatography on silica gel (pentane: CH_2Cl_2 = 5:1). Selenofluorides **19c** and **19c** were characterized only by NMR spectra.

4.5.1. 5-exo-Fluoro-6-exo-phenylseleno-2-benzonorbornene, 19a

The title compound was obtained as an oil. Anal. calc. for $C_{17}H_{15}FSe$: C, 64.36, H, 4.77, F, 5.99. Found: C, 64.30, H, 4.63, F, 6.34.

Table 3
^{19}F NMR and mass-spectral data (Molecular Ions) for compounds **12–17**

Compound	Chemical shifts, δ, ppm	Coupling constants, Hz	Mass-spectra, m/z
12	−88.4 (dm)	^2J(H2–F) = 55.6, ^3J(F–H3) = 17.5, ^4J(F–H6 *exo*) = 7.7	270 (M^+)
13	−79.52 (dddt)	^2J(F–H2) = 56, ^3J(F–H1) = 8.8, ^3J(F–H3 *exo*) = 39, ^3J(F–H3 *endo*) = 15.4, ^4J(F–H6 *exo*) = 8.8	270 (M^+)
14	−84.37 (dm)	^2J(F–H2) = 54, ^3J(F–H) = 8, ^3J(F–H) = 17	286 (M^+)
	−86.32 (m)	–	
15	−72.21 (m)	–	286 (M^+)
	−77.23 (m)	–	
16	−107.82 (dd)	^2J(F–H2) = 55, ^3J(F–H3) = 24	–
17	−77.95 (ddt)	^2J(F–H2) = 56, ^3J(F–H) = 36, ^3J(F–H) = 8	–

Table 4
^{1}H NMR data for compounds **12**, **13**, **16**

Comp.	Protons chemical shifts, δ, ppm							
	$H_{(1)}$	$H_{(2exo)}$	$H_{(2endo)}$	$H_{(3exo)}$	$H_{(3endo)}$	$H_{(4)}$	$H_{(7syn)}$	$H_{(7anti)}$
12	2.43	–	4.65	–	3.35	2.28	1.97	1.18
13	2.67	–	4.70	2.32	1.85	2.46	–	3.20
16	2.40	4.82	–	–	3.04	2.16		
Comp.	^{1}H–^{1}H Coupling constants, Hz							
12	*J*(1–2) = 0.8, *J*(2–3) = 6.1, *J*(2–7 *anti*) = 1.5, *J*(3–4) < 1, *J*(3–7 *anti*) = 2.4, *J*(7 *syn*-7 *anti*) = 10.2, *J*(7 *syn*-6 *endo*) = 2, *J*(7 *syn*-6 *exo*) = 2							
13	*J*(1–2) < 1, *J*(1–6 *exo*) = 5.1, *J*(2–3 *exo*) < 2, *J*(2–3 *endo*) = 6.6, *J*(3 *exo*-3 *endo*) = 13.4, *J*(3 *endo*-7 *anti*) = 2							
16	*J*(1–2) = 4.4, *J*(1–6 *exo*) = 4, *J*(2–3) = 2–2.6, *J*(3–4) < 1, *J*(3–7 *anti* or 5 *endo*) = 2.8–3.3							

Table 5
NMR spectra of compounds **19a–d**

^{19}F NMR spectra

Comp.	δF, ppm	^2J(F–H), Hz	^3J(F–H3 *exo*), Hz	^3J(F–H3 *endo*), Hz	^3J(F–H1), Hz	^3J(F–Se), Hz
19a	−94.30	56.3	–	15.5	6.	0.
19b	−91.41	55.46	32.33	14.25	7.	124.
19c	−87.04	54.0	30.25	–	6.5	118.
19d	−95.60	56.6	32.6	15.4	9.6	0.

^{1}H NMR Spectra, ^{1}H Chemical Shifts, ppm

Comp.	δH(1)	δH(2*endo*)	δH(3*exo*)	δH(3*endo*)	δH(4)	δH(7*syn*)	δH(7*anti*)
19a	3.6	4.88	–	3.6	3.36	2.04	2.55
19b	3.66	4.7	2.8	1.76	3.77	–	3.28
19c	3.5	4.80	3.72	–	3.5	2.25	2.15

^{1}H NMR Spectra, ^{1}H–^{1}H Coupling Constants, Hz

Comp.	1, 2 *endo*	2 *endo*, 3 *exo*	2 *endo*, 3 *endo*	2 *endo*, 7 *anti*	3 *exo*, 3 *endo*	3 *exo*, 4	3 *exo*, 7 *anti*	3 *endo*, 7 *anti*	7 *syn*, 7 *anti*	Unknown
19a	1.	–	6.1	1.	–	–	–	2.2	9.75	
19b	>1.	>1.	6.6		13.5	2.	4.		–	
19c	1.44			2.65					10.	4. (3*exo*), 3. (7*syn*)

4.5.2. 5-exo-Fluoro-7-anti-phenylseleno-2-benzonorbornene, **19b**

The title compound was obtained as an oil. Anal. calc. for $C_{17}H_{15}FSe$: C, 64.36, H, 4.77, F, 5.99. Found: C, 64.95, H, 4.56, F, 6.42. Spectral data of the compounds **19** can be seen in Table 5.

4.6. Pentafluorides PTPF and PSPF

Phenyltellurium pentafluoride, PTPF, was prepared by the addition of five equivalents of XeF_2 to the solution of $(PhTe)_2$ in methylene chloride at room temperature followed by stirring of the reaction mixture until the gas evolution ceased (five equivalents of xenon were produced within 5–10 min). ^{19}F NMR spectrum revealed the presence of phenyltellurium pentafluoride. $\delta F_1 = 41$ ppm, quintet; $\delta F_2 = 23$ ppm, doublet, $J(F–F) = 152$ Hz [47,48]. Phenylselenium pentafluoride, PSPF, was prepared in the same manner. It was not described in the literature earlier and we used it without further investigation.

4.7. Fluorination by phenylselenium pentafluoride, PSPF, and phenyltellurium pentafluoride, PTPF

4.7.1. General procedure

About 2 mmol of an olefin were added in one portion to the solution of 2 mmol of appropriate pentafluoride. After stirring overnight the solvent was removed in vacuo, the residue dissolved in $CDCl_3$ and exact quantity of C_6F_6 was added (internal standard for integration) and analysed by ^{19}F NMR.

The reaction products were separated from parent olefins by column chromatography on silica gel with hexane–dichloromethane 9:1 mixture as eluent. Spectral data and yields are given in Table 2.

4.8. Fluorination of β-bromostyrene

β-Bromostyrene (a 1:1 mixture of *cis*- and *trans*-isomers) being fluorinated with $PhTeF_5$ gave the 55:45 mixture of *threo*- and *erythro*-1,2-difluoro-2-phenylbromoethanes, **21**, with total yield 31%. ^{19}F NMR −69.2 ppm (ddd, $^2J(F–H) = 50$ Hz, $^3J(F–F, F–H) = 12.5$ Hz, 27 Hz), −71 ppm (m), −100.21 (ddd, $^2J(F–H) = 45$ Hz, $^3J(F–F, F–H) = 11$ Hz, 19 Hz), −103.64 ppm (ddd, $^2J(F–H) = 47$ Hz, $^3J(F–F, F–H) = 12$ Hz, 26 Hz).

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