Tetrahedron Letters, Vol. 34, No. 4, pp. 703-706, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

THE REACTION OF NORBORNENE WITH SELENIUM(II) AND SELENIUM(IV) FLUORIDES

Sergei A. Lermontov[*a], **Sergei I. Zavorin**[a], **Alexei N. Pushin**[a],
Anatolii N.Chekhlov[a], **Nikolai S. Zefirov**[*a], **Peter J. Stang**[b]

Institute of Physiologically Active Compounds, Russ. Acad. Sci.
142432 Chernogolovka, Moscow Region, Russia.[a]
Department of Chemistry,University of Utah, Salt Lake City,
Utah 84112, USA.[b]

Key words: phenylselenenylfluorode; phenylseleniumtrifluoride; norbornene; selenofluorination; electrophilic addition.

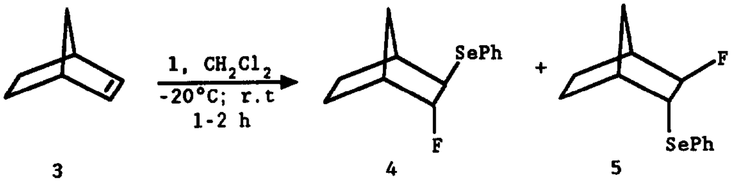
Abstract: *PhSeF adds to norbornene predominantly in a* trans-*manner to give non-rearranged 2,3-selenofluorination adducts, 4 and 5, corresponding to* exo- *and* endo-*attack. In contrast,* $PhSeF_3$ *gives mainly the products of* cis-exo-*addition, 6, along with the Wagner-Meerwein rearrangement product, 7.*

Phenylselenenylfluoride PhSeF, **1**, and its analogs were used for selenofluorination of some unsaturated compounds and appeared to be a rather convenient source of fluorine introduction into organic molecules[1]. However, phenylseleniumtrifluoride[2], $PhSeF_3$, **2**, has not been investigated as electrophilic reagent though it is isoelectronic to $PhIF_2$ and might be a potent fluorinating agent. Hence, we studied the reactions of **1** and **2** with norbornene, **3**, a standard model to study the reactivity of electrophilic reagents in Ad_E-reactions. It was also of interest to compare the stereochemistry of the additions of **1** and **2** to olefin **3** with that of sulphenyl[3a] and selenenyl halides[3b].

Phenylselenenylfluoride PhSeF, **1**, generated from diphenyldiselenide and XeF_2[1a], reacts with norbornene in CH_2Cl_2 with predominant formation of *trans*-adduct **4** (80%), diastereomeric *trans*-adduct **5** (10%) and less than 10% of several unidentified minor compounds[4,5].

$$\mathrm{Ph_2Se_2 + XeF_2 \xrightarrow[-20°C]{CH_2Cl_2,\ -Xe} 2\ PhSeF}$$

1

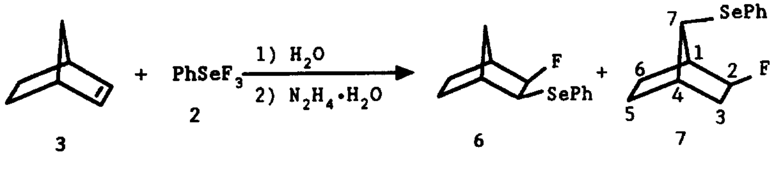


The stereochemical result of the reaction (*trans*-addition) is analogous in general to that observed in the reactions of norbornene with PhSeCl[3b] and sulphenylchlorides[3a]. However the formation of appreciable amounts of adduct **5**, due to *endo*-attack, is remarkable.

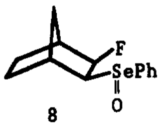
The reaction of olefin **3** with phenylseleniumtrifluoride, **2**, obtained from diphenyldiselenide and XeF_2 [6], is much slower, and sufficient amounts of products are formed only after 4-5 days at room temperature (monitored by NMR^{19}F)[7].

$$\mathrm{Ph_2Se_2 + 3XeF_2 \xrightarrow[r.t,\ 20min]{-Xe,\ CH_2Cl_2} 2\ PhSeF_3}$$

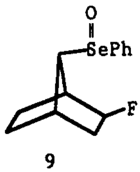
3



6 : 7 = 1.7:1



8

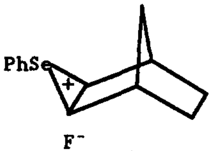


9

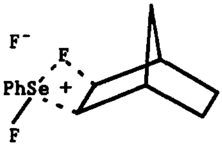
We were able to separate and to analyze the products only in the reduced form as selenides **6** and **7**. The structure of **6** was established by X-ray analysis[8], and NMR ^{1}H and ^{19}F spectra. The structure of **7** was assigned by NMR ^{1}H and ^{19}F spectra[9]. The *syn*-configuration of the

PhSe-group was confirmed by the $^{4}J_{H7-H3endo}$= 2.0 Hz (W-constant). It is worthy to mention that after hydrolysis of the reaction mixture two compounds were detected (NMR^{19}F) in approximately a 2:1 ratio. We have not been able to isolate them in pure form, but the comparison of their NMR^{19}F and mass spectra with that of selenides **6** and 7 reveals their structure as selenoxides **8** and **9**[10]. These compounds seem to originate from the primary products, namely the corresponding difluorides of type R-SeF_2Ph.

This dramatic difference between the stereochemistry of addition of **1** and **2** to norbornene can be rationalized based on different transition state structures for the two reagents.



A



B

Selenenyl fluoride **1** demonstrates classical *anti*-addition *via* episelenonium ion-pair **A** (or its *endo*-isomer) affording *trans*-adducts **4** and **5**. In the case of **2** the $PhSeF_2^+$ is likely the attacking electrophilic species (the existence of such species was discussed in Ref[2]) with a four-membered transition state of B-type, with the hard fluoride anion tightly bonded to the hard acid Se(IV) and, therefore, with more positive charge generated on carbon atom, affording after hydrolysis and reduction the *cis*-exo adduct **6** and Wagner-Meerwein rearrangement product 7.

Thus, phenylseleniumtrifluoride, **2**, is a novel reagent for selenofluorination of C=C bond, differing significantly from Se(2) fluorides in behavior. The further investigation of this interesting compound is in progress.

References and notes.

1 (a) K.Uneyama and M.Kanai, *Tetrahedron Lett.*, **31**, 3583 (1990). (b) S. Tomoda and Y. Usuki, *Chem. Lett.*, 1235, (1989). (c) J.McCarthy, D.P.Mattheus and C.L.Barney, *Tetrahedron Lett.*, **31**, 973 (1990). (d) C.Saluzzo, G.Alvernhe and D.Anker, *Tetrahedron Lett.*, **31**, 663 (1990).

2 W.M.Maxwell and K.J.Wynne, *Inorg. Chem.*, **20**, 1707 (1981).

3 (a) N.S.Zefirov, *Acc.Chem.Res.*,**12**, 282(1979); N.S.Zefirov, A.S. Koz'min, V.N.Kirin, V.V.Zhdankin and R.Caple, *J.Org.Chem.*, **46**, 5264 (1981); V.R.Kartashov, E.V.Skorobogatova, E.Yu.Grudzinskaja,

N.F.Akimkina and N.S.Zefirov, *Tetrahedron*, **41**, 5219(1985). (b) D. G. Garratt and A.Kabo, *Can. J. Chem.*, **58**, 1030 (1980).

4 The procedure was as in ^{1a}. NMR ^{19}F (188 MHz, CF_3COOH ext) for **4**: -107.82 (dd, $^2J_{H-F}$= 55, $^3J_{H-F}$= 24); for **5**: -77.95 (ddt, $^2J_{H-F}$= 56, $^3J_{H-F}$= 36, $^3J_{H-F}$= 8). The NMR ^1H (200 MHz, $CDCl_3$) of **4** is consistent with its structure. Unambiguous proof of the structure for **4** was made by X-ray analysis (Dr. A.Chehlov).

5 Satisfactory C and F elemental analysis was obtained for **4**, **6** and **7**. We failed to obtain satisfactory data for H in all cases, even for X-ray grade crystals of **4** and **6**.

6 We were unable to compare the NMR ^{19}F spectra of **2** with that reported in Ref 2 due to its extremely rapid hydrolysis in glass NMR tubes. However the chemical behavior of the reagent as well as the structures of the obtained compounds confirm its structure as **2**.

7 Procedure: 6.9 mmol of XeF_2 were added by portions to a solution of 2,3 mmol of Ph_2Se_2 in 10 ml of dry CH_2Cl_2 at r.t in 50-ml Teflon flask. After the end of gas evolution 4.6 mmol of **3** in 2 ml of dry CH_2Cl_2 were added by one portion and the mixture was stirred for 4-5 days at room temperature. 15 ml of 5% aqueous $NaHCO_3$ was added, the organic layer washed, dried and evaporated^{10}. The oily residue was dissolved in 10 ml of ethanol and reduced by equimolar amount of $N_2H_4 \cdot H_2O$ at r.t. The products were separated by column chromatography on SiO_2(hexane:$CHCl_3$, 10:1).

8 The crystal structure of **6** is monoclinic : a=10.152(2), b=10.144 (2), c= 11.570(3) Å, β= 101.50(2)°, V= 1167.6(8) Å^3, Z=4, space group $P2_1/c$. The final R= 0.071 for 1084 observed reflections was measured on a CAD-4 diffractometer (MoK_α-radiation).

9 For **6** : NMR ^{19}F -88.4 (dm, $^2J_{H-F}$= 55.6, $^3J_{H-F}$= 17.5, 8.7, $^4J_{H-F}$= 7.7. MS (70 eV): 270 (M^+). For **7** : NMR ^{19}F. -79.52 (dddt, $^2J_{H-F}$= 56, $^3J_{H-F}$= 39, 15.4, 8.8, $^4J_{H-F}$= 8.8). MS: 270 (M^+).

10 For **8**: NMR ^{19}F -84.37(dm, $^2J_{H-F}$= 54, $^3J_{H-F}$= 17, 8). MS : 286(M^+) For **9**: NMR ^{19}F -72.21(m). MS: 286(M^+). NMR ^{19}F spectrum of the reaction mixture contains minor signals of epimers of **8** and **9** (due to stereogenisity of Se) at -86.32 and -77.23 respectively.

(Received in UK 14 October 1992)