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The First Structure of a Vicinal (*E*)-Fluoroselenoolefin: (*E*)-(5-Fluoro-4-octen-4-yl)dimethylselenonium Picrate

Helmut Poleschner[a] and Uwe Schilde[b]

[a]*Universität Potsdam, WIP-Forschungsgruppe Naturstoffe, Stahnsdorfer Damm 81, D-14532 Kleinmachnow, Germany, and* [b]*Universität Potsdam, Institut für Anorganische Chemie und Didaktik der Chemie, Postfach 601553, Am Neuen Palais 10, D-14415 Potsdam, Germany. E-mail: us@serv.chem.uni-potsdam.de*

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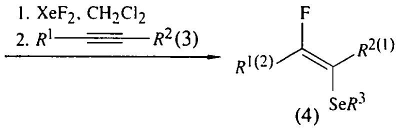
Abstract

The structure of the title compound, $C_{10}H_{20}FSe^+.C_6H_2N_3O_7^-$, synthesized from (*E*)-4-methylseleno-5-fluoro-4-octene with trimethyloxonium tetrafluoroborate, followed by anion exchange with sodium picrate, proves the *trans* addition of *R*SeF equivalents in the fluoroselenenylation of acetylenes with XeF_2–R_2Se_2 and XeF_2–$PhSeSiR_3$ reagents [dihedral angle Se—C4—C5—F −178.7 (1)°].

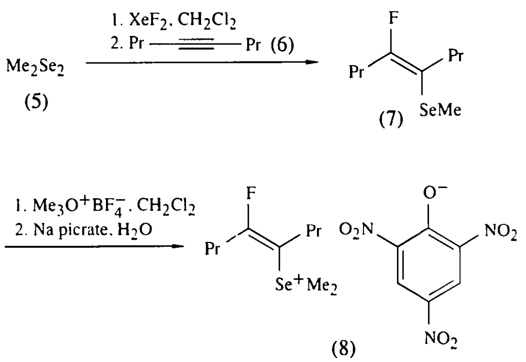
Comment

Recently we have found that the reagents XeF_2–R^3SeX [(1), (2)] react with acetylenes (3) as selenenyl fluoride equivalents, R^3SeF, by diastereoselective addition to form the fluoroselenoolefins (4). Suitable selenium precursors in this reaction are diselenides (1) and silylselenides (2).



(1) $X = SeR^3$
(2) $X = SiMe_3, SiMe^t_2Bu$

The ^{1}H NMR spectra from products of terminal acetylenes gave first indications as to the stereochemistry of the reaction, characteristic of *trans* addition (Poleschner, Heydenreich, Spindler & Haufe, 1994). X-ray crystal structure analysis of the title selenonium picrate, (8), allows a significant stereochemical characterization of these compounds. The synthesis of this crystalline salt was necessary because most of the compounds of type (4) are oily liquids. The adduct from XeF_2–Me_2Se_2 and 4-octyne, (6), was methylated with trimethyloxonium tetrafluoroborate and then transformed with sodium picrate to (8).



With compound (8), we present the first structure determination of a vicinal fluoroselenoolefin (Fig. 1). The few known monofluoroalkene reference structures are: 10-fluoro-all-*trans*-α-retinal (Ratnapala & Seff, 1988), 2-cyclohexylidene-2-fluoroacetic acid (Abraham, Ellison, Schonholzer & Thomas, 1986) and (*E*)-1-fluoro-2-bromovinyl phenyl sulfone (Shainyan & Belskii, 1991). Moreover, the following difluoroalkene structures have been described: zinc *trans*-1,2-difluoroethenediyldiphosphonate (Su *et al.*, 1990), potassium hydrogen difluoromaleate and potassium hydrogen difluorofumarate (Mattes & Göhler, 1980), and 1,2-difluoro-2-(pentafluorosulfanyl)vinyltrimethylphosphonium tetrafluoroborate (Wessolowski *et al.*, 1992).

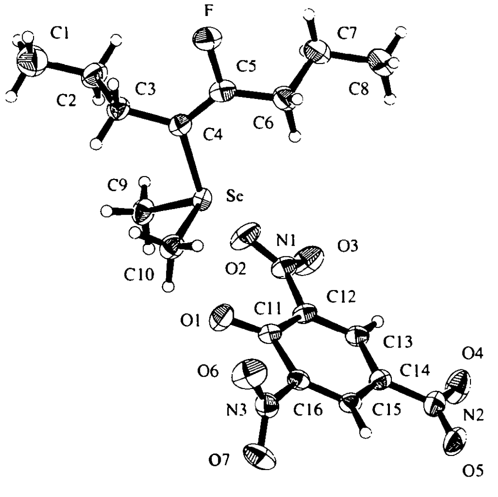


Fig. 1. Molecular structure of (8), showing 50% probability displacement ellipsoids for non-H atoms.

The C5—F bond length in (8) corresponds well with that in 10-fluoro-all-*trans*-α-retinal (1.381 Å; Ratnapala & Seff, 1988) and in 2-cyclohexylidene-2-fluoroacetic acid (1.369 Å; Abraham *et al.*, 1986). Thus, it is somewhat longer than in potassium hydrogen difluoromaleate and potassium hydrogen difluorofumarate (1.342 and 1.338 Å, respectively; Mattes & Göhler, 1980) or (*E*)-1-fluoro-2-bromovinyl phenyl sulfone (1.301 Å; Shainyan & Belskii, 1991). The fluorovinyl double bond, C4═C5, is somewhat longer than the corresponding bond in 10-fluoro-all-*trans*-α-retinal (1.322 Å; Ratnapala & Seff, 1988) and potassium hydrogen difluorofumarate (1.307 Å; Mattes & Göhler, 1980). However, it is significantly longer than in the above-mentioned difluoroethenediyl diphosphonate (1.289 Å; Su *et al.*, 1990) and (*E*)-1-fluoro-2-bromovinyl phenyl sulfone (1.301 Å; Shainyan & Belskii, 1991). The F—C5—C4 and especially the F—C5—C6 bond angles are smaller than 120°, whereas the C4—C5—C6 bond angle is considerably widened. This corresponds to the situation in other fluoroolefins, *e.g.* 10-fluoro-all-*trans*-α-retinal (117.4, 110.7, 131.9°; Ratnapala & Seff, 1988), potassium hydrogen difluoromaleate (116.8, 111.9, 131.4°; Mattes & Göhler, 1980) and 2-cyclohexylidene-2-fluoroacetic acid (118.9, 110.1, 130.1°; Abraham *et al.*, 1986).

Known reference structures for the selenonium part of (8) are $Me_3Se^+.I^-$ (Hope, 1966), $Me_3Se^+.MeAlCl_3^-$ (Sangokoya, Pennington & Robinson, 1990), $Ph_3Se^+.Cl^-.H_2O$ (Mitcham, Lee, Mertes & Ziolo, 1979), $Ph_3Se^+.SCN^-$ (Ash, Lee, Titus, Mertes & Ziolo, 1977), a selenonium ylide (Kamigata *et al.*, 1992) and a phenylseleniranium ion (Borodkin *et al.*, 1990). The C—Se distances in (8) (average value 1.930 Å) are more similar to those in $Ph_3Se^+.Cl^-.H_2O$ (1.932 Å; Mitcham *et al.*, 1979) or $Ph_3Se^+.SCN^-$ (1.923 Å; Ash *et al.*, 1977) than those in $Me_3Se^+.I^-$ (1.951 Å; Hope, 1966). The C—Se—C bond angles in (8) (average value 99.0°), $Me_3Se^+.I^-$ (98.5°; Hope, 1966), $Me_3Se^+.MeAlCl_3^-$ (99.1°; Sangokoya *et al.*, 1990), $Ph_3Se^+.Cl^-.H_2O$ (100.8°; Mitcham *et al.*, 1979) and $Ph_3Se^+.SCN^-$ (100.9°; Ash *et al.*, 1977) are of nearly equal size.

The dihedral angles Se—C4—C5—F [−178.7 (1)°] and C3—C4—C5—C6 [176.7 (2)°], the key parameters of the investigated problem, prove the (*E*) configuration at the C4═C5 double bond. The dihedral angles C2—C3—C4—C5 and C4—C5—C6—C7 [87.5 (3)° and 126.5 (3)°, respectively] indicate a *gauche* conformation to the double-bond plane. The torsion angles C1—C2—C3—C4 and C5—C6—C7—C8 [−179.8 (2) and −178.4 (2)°, respectively] correspond to a fully eclipsed conformation.

Characteristic of the picrate ion in (8) is the marked rotation of the NO_2 group at C16 out of the aromatic plane [−55.6 (3)°]; the NO_2 group at C12 is slightly rotated [18.6 (3)°], whereas the NO_2 group in the *para* position is approximately coplanar with the ring [−3.2 (2)°]. Reference structures for (8) are caesium picrate (Schouten, Kanters & Poonia, 1990), potassium picrate and ammonium picrate (Martmann-Moe, 1969). Caesium picrate shows a somewhat smaller rotation of one NO_2 group in an *ortho* position (42.0°) and a nearly planar arrangement of the NO_2 group in the other *ortho* position (4.8°), whereas the torsion in the *para* position is quite strong (16.4°) (Schouten *et al.*, 1990). In potassium and ammonium picrate, however, both NO_2 groups in *ortho* positions are equally rotated (25–27°), whereas that in the *para* position is planar.

The Se···O1 distance (2.95 Å) is smaller than the sum of the van der Waals radii of selenium and oxygen [1.65 + 2.15 = 3.8 Å] (Allinger, 1976). This indicates an ionic interaction between the phenolate O atom and the selenonium center. Analogous interactions, so-called secondary bonds, are deduced from the structures of $Me_3Se^+.I^-$ (Hope, 1966), $Ph_3Se^+.Cl^-.H_2O$ (Mitcham *et al.*, 1979) and $Ph_3Se^+.SCN^-$ (Ash *et al.*, 1977).

Experimental

The title compound was synthesized from (*E*)-4-methylseleno-5-fluoro-4-octene with trimethyloxonium tetrafluoroborate, followed by anion exchange with sodium picrate. Recrystallization from toluene gave the product as yellow crystals suitable for X-ray analysis.

Crystal data

$C_{10}H_{20}FSe^+.C_6H_2N_3O_7^-$
$M_r = 466.33$
Triclinic
$P\overline{1}$
$a = 8.236\,(1)$ Å
$b = 11.260\,(3)$ Å
$c = 11.608\,(3)$ Å
$\alpha = 90.30\,(2)°$
$\beta = 101.98\,(1)°$
$\gamma = 110.44\,(2)°$
$V = 983.2\,(4)$ Å^3
$Z = 2$
$D_x = 1.575$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 24 reflections
$\theta = 15.1–19.6°$
$\mu = 1.88$ mm^{-1}
$T = 210\,(2)$ K
Prism
0.46 × 0.42 × 0.19 mm
Yellow

Data collection

Stoe Stadi-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Matthews, 1968)
$T_{min} = 0.417$, $T_{max} = 0.626$
4451 measured reflections
4189 independent reflections

3685 observed reflections [$I > 2\sigma(I)$]
$R_{int} = 0.0221$
$\theta_{max} = 30°$
$h = 0 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -12 \rightarrow 12$
2 standard reflections
frequency: 120 min
intensity decay: 6.2%

Refinement

Refinement on F^2
$R(F) = 0.0299$
$wR(F^2) = 0.0762$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.825$ e Å^{-3}
$\Delta\rho_{min} = -0.838$ e Å^{-3}

$S = 1.030$
4188 reflections
248 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2 + 0.4977P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Se	0.29328 (2)	0.19220 (2)	0.83897 (2)	0.02618 (8)
F	0.3102 (2)	0.55471 (15)	0.85890 (13)	0.0439 (4)
O1	0.2972 (2)	−0.0623 (2)	0.78116 (14)	0.0376 (4)
O2	−0.0164 (2)	−0.0409 (2)	0.6728 (2)	0.0482 (5)
O3	−0.1526 (2)	−0.1582 (2)	0.5104 (2)	0.0476 (5)
O4	0.1540 (2)	−0.2690 (2)	0.2560 (2)	0.0504 (5)
O5	0.4276 (3)	−0.2537 (2)	0.3172 (2)	0.0477 (5)
O6	0.6659 (2)	0.0000 (2)	0.8009 (2)	0.0560 (5)
O7	0.6469 (3)	−0.1919 (2)	0.7627 (2)	0.0548 (5)
N1	−0.0176 (2)	−0.1071 (2)	0.5884 (2)	0.0321 (4)
N2	0.2919 (3)	−0.2397 (2)	0.3326 (2)	0.0348 (4)
N3	0.5958 (2)	−0.1029 (2)	0.7440 (2)	0.0343 (4)
C1	0.0616 (4)	0.3676 (3)	1.1546 (3)	0.0570 (7)
C2	0.0712 (3)	0.3450 (3)	1.0274 (2)	0.0408 (6)
C3	0.2632 (3)	0.3711 (2)	1.0181 (2)	0.0326 (5)
C4	0.2872 (3)	0.3517 (2)	0.8948 (2)	0.0278 (4)
C5	0.3108 (3)	0.4405 (2)	0.8187 (2)	0.0328 (5)
C6	0.3447 (3)	0.4456 (2)	0.6979 (2)	0.0363 (5)
C7	0.2138 (3)	0.4857 (3)	0.6086 (2)	0.0405 (6)
C8	0.2515 (4)	0.4857 (3)	0.4860 (2)	0.0520 (7)
C9	0.1273 (3)	0.0777 (2)	0.9192 (2)	0.0340 (5)
C10	0.5105 (3)	0.1942 (2)	0.9439 (2)	0.0351 (5)
C11	0.2935 (3)	−0.0966 (2)	0.6790 (2)	0.0274 (4)
C12	0.1454 (3)	−0.1239 (2)	0.5768 (2)	0.0274 (4)
C13	0.1468 (3)	−0.1686 (2)	0.4667 (2)	0.0287 (4)
C14	0.2949 (3)	−0.1889 (2)	0.4474 (2)	0.0277 (4)
C15	0.4454 (3)	−0.1666 (2)	0.5392 (2)	0.0280 (4)
C16	0.4408 (3)	−0.1220 (2)	0.6471 (2)	0.0268 (4)

Table 2. *Selected geometric parameters (Å, °)*

Se—C9	1.926 (2)	C2—C1	1.520 (4)
Se—C4	1.927 (2)	C2—C3	1.531 (3)
Se—C10	1.937 (2)	C3—C4	1.509 (3)
F—C5	1.368 (3)	C4—C5	1.328 (3)
O1—C11	1.236 (3)	C5—C6	1.483 (3)
O2—N1	1.224 (3)	C6—C7	1.524 (3)
O3—N1	1.231 (2)	C7—C8	1.519 (4)
O4—N2	1.227 (3)	C11—C16	1.455 (3)
O5—N2	1.230 (3)	C11—C12	1.457 (3)
O6—N3	1.216 (3)	C12—C13	1.374 (3)
O7—N3	1.220 (3)	C13—C14	1.378 (3)
N1—C12	1.452 (3)	C14—C15	1.402 (3)
N2—C14	1.440 (3)	C15—C16	1.359 (3)
N3—C16	1.466 (3)	Se···O1	2.95
C9—Se—C4	99.61 (10)	C4—C5—F	115.1 (2)
C9—Se—C10	97.95 (11)	C4—C5—C6	133.8 (2)
C4—Se—C10	99.55 (10)	F—C5—C6	111.0 (2)
O2—N1—O3	122.0 (2)	C5—C6—C7	113.6 (2)
O2—N1—C12	119.7 (2)	C8—C7—C6	111.3 (2)
O4—N2—O5	123.3 (2)	O1—C11—C16	122.5 (2)
O4—N2—C14	118.7 (2)	O1—C11—C12	127.0 (2)
O6—N3—O7	123.8 (2)	C13—C12—N1	115.9 (2)
O6—N3—C16	118.5 (2)	N1—C12—C11	120.1 (2)
C1—C2—C3	111.0 (2)	C13—C14—N2	119.4 (2)
C4—C3—C2	115.1 (2)	C15—C14—N2	119.4 (2)
C5—C4—C3	124.3 (2)	C15—C16—N3	117.5 (2)
C5—C4—Se	114.9 (2)	C11—C16—N3	115.7 (2)
C3—C4—Se	120.7 (2)		
C1—C2—C3—C4	−179.8 (2)	C5—C6—C7—C8	−178.4 (2)
C2—C3—C4—C5	87.5 (3)	O2—N1—C12—C11	18.6 (3)
C9—Se—C4—C5	−147.7 (2)	O1—C11—C12—N1	2.3 (4)
C10—Se—C4—C5	112.5 (2)	O4—N2—C14—C13	−3.2 (3)
Se—C4—C5—F	−178.72 (14)	O1—C11—C16—N3	−0.6 (3)
C3—C4—C5—C6	176.7 (2)	O6—N3—C16—C11	−55.6 (3)
C4—C5—C6—C7	126.5 (3)		

The structure was solved by direct methods and successive difference Fourier syntheses. All of the H atoms were placed in calculated positions and refined as riding atoms. Full-matrix least-squares anisotropic refinement was carried out for all atoms except the H atoms, which were refined isotropically.

Data collection: *Stadi*-4 *Diffractometer Control Program* (Stoe, 1995*a*). Cell refinement: *Stadi*-4 *Diffractometer Control Program*. Data reduction: *XRED* (Stoe, 1995*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1970).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: JZ1086). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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1,8-Dichloroanthracene

María del Rosario Benites, Andrew W. Maverick and Frank R. Fronczek*

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA. E-mail: fronz@chxray.dnet.lsu.edu

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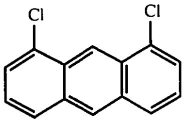
Abstract

The C—Cl distances in the title compound, $C_{14}H_8Cl_2$, average 1.751 (3) Å. The C atoms of the anthracene ring system exhibit a maximum deviation of 0.016 (5) Å from coplanarity and the Cl atoms are slightly displaced on opposite sides of the anthracene plane by −0.045 (1) and 0.035 (1) Å.

Comment

The structure of the title compound, (1), has been determined as part of our continuing work on the activation of 1,8-disubstituted anthracenes towards nucleophilic substitution. The unit-cell dimensions and space group of (1) have been previously reported by Desvergne, Chekpo & Bouas-Laurent (1978) to be a = 15.25, b = 18.90 and c = 4.00 Å, and $Pnma$ (with Z = 4). The crystals were described as needles and measurements were made from Weissenberg photographs. As these authors apparently did not measure intensities and do not report coordinates, their space-group determination is ambiguous and space group $Pna2_1$ cannot be ruled out. Although the a and c dimensions match the present determination to approximately 1%, the b axial length is 4.5% longer than the c dimension here. While we cannot rule out the possibility of polymorphism, we note that a likely typographical error (18.09 *versus* 18.90) would account for the difference. We strongly suspect that the two crystal phases are identical.



(1)

The C—Cl distances in compound (1) [1.745 (4) and 1.756 (4) Å] agree well with the value of 1.749 Å reported for 1,8-dichloro-10-methylanthracene (Desvergne, Gaultier & Hauw, 1970) and are marginally longer than that of 1,8-dichloro-9-methylanthracene [1.726 (7) Å; Dellaca, Penfold & Robinson, 1969]. The molecular plane normal is inclined by 28.4 (1)° to the b-axis direction and the interplanar distance is 3.477 (1) Å. This stack of molecules forms a dihedral angle of 56.8 (2)° with that related to it by the a glide.

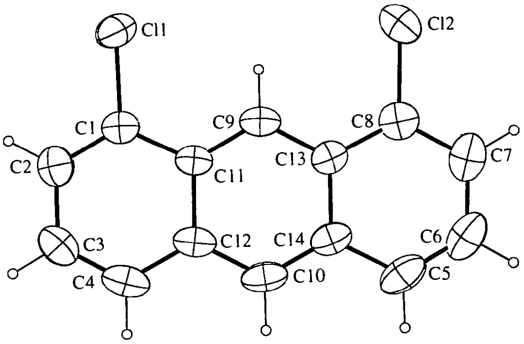


Fig. 1. The molecular structure of (1) showing 40% probability ellipsoids. H atoms are represented by spheres of arbitrary radii.

Experimental

The title compound was prepared according to the procedure of Collman *et al.* (1992) and crystallized from 2-propanol by slow evaporation.

Crystal data

$C_{14}H_8Cl_2$
M_r = 247.13
Orthorhombic
$Pna2_1$
a = 15.410 (3) Å
b = 3.953 (1) Å
c = 18.081 (6) Å
V = 1101.4 (9) Å^3
Z = 4
D_x = 1.490 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 10–13°
μ = 0.554 mm^{-1}
T = 295 K
Lath
0.60 × 0.40 × 0.12 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scans (North, Phillips & Mathews, 1968)
$T_{\min}$ = 0.949, $T_{\max}$ = 0.999
1952 measured reflections
1664 independent reflections
1358 observed reflections [$I > \sigma(I)$]
$\theta_{\max}$ = 30°
$h = 0 \rightarrow 21$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 25$
3 standard reflections
frequency: 120 min
intensity decay: <1%

Refinement

Refinement on F
R = 0.057
$\Delta\rho_{\max}$ = 0.49 e Å^{-3}
$\Delta\rho_{\min}$ = −0.35 e Å^{-3}