Synthesis and thermolysis of novel spiroselenuranes bearing two oxaselenetane rings: double oxirane formation reactions from 1,5-dioxa-4λ^4-selenaspiro[3.3]heptanes†

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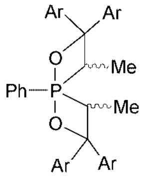
Received (in Cambridge, UK) 6th December 2000, Accepted 29th January 2001
First published as an Advance Article on the web 14th February 2001

The first stable spiroselenuranes bearing two oxaselenetane rings have been synthesized, chracterized by X-ray crystallographic analysis, and shown to be thermally reactive giving two molar equivalents of the corresponding oxirane with elimination of elemental selenium, in sharp contrast to the behavior of the phosphorus and silicon analogues.

In the course of our study on oxetanes containing high-coordinate main group elements at the position adjacent to the oxygen atom,[1] we have reported the syntheses and isolation of intermediates of Wittig- and Peterson-type olefin formation reactions.[2,3] For the purpose of elucidating the influence of ring size of the spiro-ring system on the reactivity of the hetera-cyclobutanes, we have investigated the synthesis and reactivity of compounds **1** and **2**, which have two oxaphosphetane and oxasiletane rings, respectively, and found that **1** undergoes double olefin extrusion,[4] while **2** undergoes homo-Brook rearrangement to give the corresponding alcohol.[5] On the other hand, we have recently found that the oxirane formation reactions from pentacoordinate 1,2λ^6-oxathietanes **3a**,**b** or tetracoordinate 1,2λ^4-oxaselenetanes **4a**,**b** proceed with retention of configuration,[6] which is the first example for the oxirane formation without backside attack of oxide anion on the carbon attached to the chalcogen atom, in sharp contrast to the Corey–Chaykovsky reaction.[7] These results prompted us to study tetracoordinate 1,5-dioxa-4λ^4-selenaspiro[3.3]heptanes, a novel type of a spiroselenurane bearing two oxaselenetane rings. We now report, for the first time, their synthesis and unique thermal behavior.



Ar= p-ClC$_6$H$_4$

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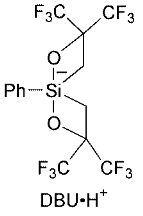

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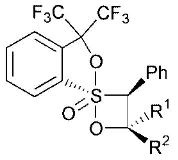

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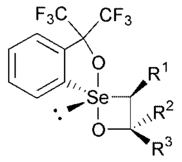
a: R^1= CF$_3$; R^2= Ph
b: R^1= Ph; R^2= CF$_3$



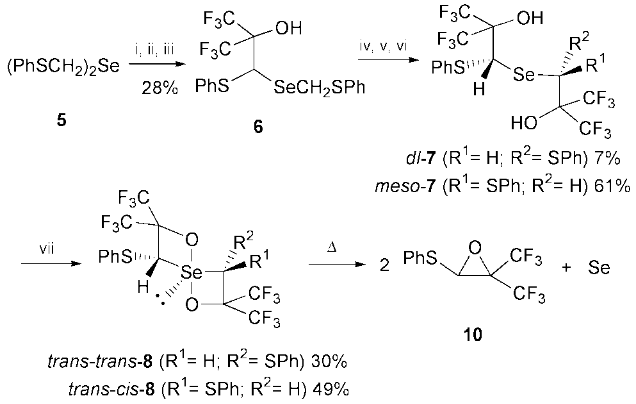
4

a: R^1= Ph; R^2= CF$_3$; R^3= Ph
b: R^1= Ph; R^2= Ph; R^3= CF$_3$
c: R^1= H; R^2=R^3= Ph

Sequential treatment of (PhSCH$_2$)$_2$Se **5** with 1.1 equiv. of lithium diisopropylamide (LDA), with 2.0 equiv. of freshly generated hexafluoroacetone (HFA), and then with aqueous NH$_4$Cl gave mono(β-hydroxyalkyl) selenide **6** (28%) (Scheme 1). A diastereomer mixture of bis(β-hydroxyalkyl) selenides **7** was obtained from **6** by repetition of the same procedure as the addition of HFA to **5** (2.0 equiv. of LDA and 3.0 equiv. of HFA). Separation by flash column chromatography (SiO$_2$) gave *dl*-**7** (7%) and *meso*-**7** (61%). Oxidative cyclization of *dl*-**7** and *meso*-**7** with Br$_2$ in the presence of Et$_3$N afforded the corresponding tetracoordinate 1,5-dioxa-4λ^4-selenaspiro[3.3]heptanes *trans-trans*-**8** (30%) and *trans-cis*-**8** (49%), respectively. Recrystallization of *trans-trans*-**8** and *trans-cis*-**8** from hexane–diethyl ether gave colorless plates which melted at 93.5–108.4 and 105.0–106.2 °C with decomposition, respectively.§

In the ^{1}H, ^{13}C and ^{19}F NMR spectra of *trans-trans*-**8**, the two oxetane rings were observed equivalently, whereas those of *trans-cis*-**8** were non-equivalent. Downfield shifts from *dl*-**7** (δ_H 4.98, δ_C 52.31) to *trans-trans*-**8** (δ_H 6.35, δ_C 88.07) were observed for the proton and carbon of the methine adjacent to the central selenium, which is a common spectral feature for tetracoordinate 1,2-oxachalcogenetanes.[1,6] In the ^{77}Se NMR spectra of *trans-trans*-**8** (δ_{Se} 835.3) and *trans-cis*-**8** (δ_{Se} 882.0) were observed multiplets due to the long-range coupling with ^{19}F nuclei. The large downfield shifts in δ_{Se} from **7** [δ_{Se} 521.1 (*dl*), 521.7 (*meso*)] to **8** and their similar chemical shifts to compounds **4** (**4a**: δ_{Se} 781; **4b**: δ_{Se} 793; **4c**: δ_{Se} 840.8) strongly support the selenurane structure for **8**. We have also synthesized *trans-trans*-**9** with two phenyl groups instead of two phenylthio groups of *trans-trans*-**8**.¶

X-Ray crystallographic analysis indicated that the asymmetric unit of a crystal of *trans-trans*-**9** contains one and a half molecules, A and B, the latter of which is disordered in two different orientations on the crystallographic inversion center.‖ Both molecules have a distorted pseudo-trigonal bipyramidal (TBP) structure with two oxygen atoms at apical positions and two carbon atoms and a lone pair at equatorial positions. The



dl-**7** (R^1= H; R^2= SPh) 7%
meso-**7** (R^1= SPh; R^2= H) 61%

trans-trans-**8** (R^1= H; R^2= SPh) 30%
trans-cis-**8** (R^1= SPh; R^2= H) 49%

Scheme 1 *Reagents and conditions*: i, 1.1 equiv. of LDA, THF, −78 °C, 10 min; ii, 2.0 equiv. of (CF$_3$)$_2$C=O, –78 °C, 30 min; iii, aqueous NH$_4$Cl; iv, 2.0 equiv. of LDA, THF, –78 °C, 10 min; v, 3.0 equiv. of (CF$_3$)$_2$C=O, –78 °C, 30 min; vi, 1.1 eq Br$_2$, 8.3 equiv. of Et$_3$N, CCl$_4$, 0 °C, 30 min.

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† Electronic supplementary information (ESI) available: full experimental details and spectroscopic data. See http://www.rsc.org/suppdata/cc/b0/b009789f

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DOI: 10.1039/b009789f

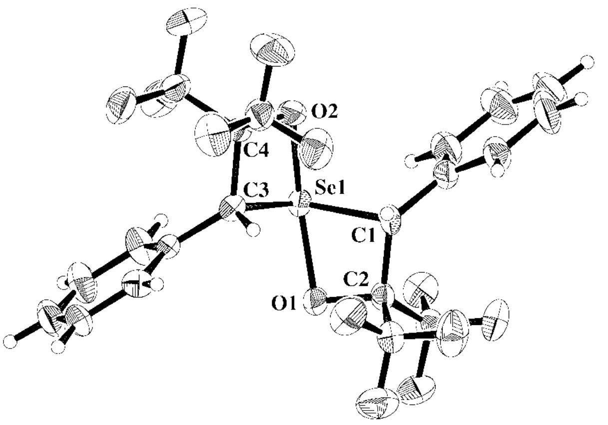
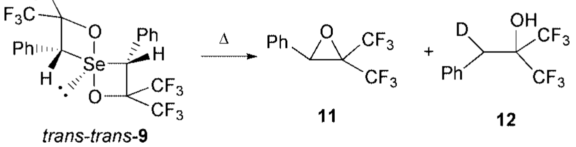


Fig. 1 ORTEP drawing of *trans-trans*-**9** with thermal ellipsoid plot (30% probability for all non-hydrogen atoms). Selected bond lengths (Å), bond angles (°) and torsion angles (°): Se1–O1 1.971(4), Se1–O2 1.955(4), Se1–C1 1.979(6), Se1–C3 1.978(6), C1–C2 1.532(8), C2–O1 1.388(6), C3–C4 1.531(8), O2–C4 1.392(7); O1–Se1–O2 155.26(18), C1–Se1–O1 71.1(2), Se1–C1–C2 90.0(4), C1–C2–O1 103.7(5), Se1–O1–C2 94.7(3), C1–Se1–C3 109.2(3), O2–Se1–C3 71.9(2), O2–C4–C3 104.3(5), Se1–C3–C4 89.1(4); Se1–C1–C2–O1 −5.9(5), Se1–C3–C4–O2 −6.1(5).

ORTEP drawing of molecule A (Fig. 1) shows that both the phenyl groups at the 3- and 3′-positions are *cis* to the lone pair of selenium and *trans* to the Se–C bond of another four-membered ring. The apical Se–O bonds are bent away from the lone pair leading to the deviation of the O–Se–O angle by 22.74(18)° from linearity, which is a common structural feature of the hypervalent species containing a four-membered ring.[1,4,6a] The apical Se–O bond lengths [1.971(4) and 1.955(4) Å)] are between those [1.977(4) and 1.902(4) Å] of selenurane **4c**.[1b] The two oxaselenetane rings of *trans-trans*-**9** are almost planar [Se–C–C–O; −6.2195(10)° and −6.5439(10)°] similar to **4c** [Se–C–C–O 4.7(4)°].[1b]

Thermolyses of *trans-trans*-**8** (C_6D_6, 120 °C, 11 h) and *trans-cis*-**8** (C_6D_6, 60 °C, 19 h) in a degassed sealed tube gave oxirane **10** in 72 and 83% yields,** respectively, with black precipitates and minor unidentified products, indicating that both compounds underwent double oxirane extrusion reaction. The formation of elemental selenium (black precipitates) was confirmed by observation of the signal due to tris(dimethylamino)phosphine selenide (δ_P 84.9) after treatment of the reaction mixture with tris(dimethylamino)phosphine (δ_P 121.5). On the other hand, the thermolysis of *trans-trans*-**9** ($CD_3C_6D_5$, 200 °C, 12 d) gave a somewhat complicated mixture containing oxirane **11** (31%) and deuterated alcohol **12** (19%). (Scheme 2)** The formation of **12** indicates that radical species were generated by homolytic bond cleavage, probably because drastic conditions were necessary for the thermolysis.



Scheme 2

Although oxetanes containing a pentacoordinate group 14 or 15 element give rise to olefins,[1a] spiro oxachalcogenetanes yielded oxiranes, regardless of the ring size (five- or four-membered ring). This indicates that the thermal reactivity mainly depends on the bond energy of the oxygen and the central atom. Investigation of the stereochemistry of the oxirane formation is now in progress.

This work was partially supported by Grants-in-Aid for Scientific Research on Priority Areas No. 09239101 and General Scientific Research (B) No. 10440212 (T. K.) from the Ministry of Education, Science, Sports and Culture, Japan. We are grateful to Professor N. Tokitoh of Kyoto University for the determination of the X-ray structure of *trans-trans*-**9**. We also thank Central Glass, Shin-etsu Chemical, and Toso Akzo Co. Ltd. for the gifts of organofluorine compounds, trialkylsilanes and alkyllithiums, respectively.

Notes and references

§ *Selected data*: for *trans-trans*-**8**: colorless plates (hexane–Et_2O); mp 93.5–108.4 °C (decomp.); ^1H NMR (C_6D_6, 500 MHz) δ 6.35 (s, 2H, SeCH), 6.86–6.95 (m, 6H), 7.43–7.46 (m, 4H); ^{19}F NMR (C_6D_6, 254 MHz) δ –74.0 (q, $^4J_{FF}$ = 8.3 Hz, 6F), −78.7 (q, $^4J_{FF}$ 8.3 Hz, 6F); ^{77}Se NMR ($CDCl_3$, 51.5 MHz) δ 835.3 (m). HRMS (70 eV): *m/z* calc. for $C_{20}H_{12}F_{12}O_2S_2{}^{80}Se$ 655.9252, found 655.9263. For *trans-trans*-**9**: colorless plates (hexane–Et_2O); mp 178.2–179.8 °C (decomp.); ^1H NMR ($CDCl_3$, 500 MHz) δ 6.86 (s, 2H, SeCH), 7.40 (d, ^3J 7.2 Hz, 4H), 7.45–7.53 (m, 6H); ^{19}F NMR ($CDCl_3$, 254 MHz) δ −73.4 (q, $^4J_{FF}$ 9.0 Hz, 6F), –78.2 (q, $^4J_{FF}$ 9.0 Hz, 6F); ^{77}Se NMR ($CDCl_3$, 51.5 MHz) δ 723.1 (s). HRMS (70 eV): *m/z* calc. for $C_{20}H_{12}F_{12}O_2{}^{80}Se$ 591.9811, found 591.9816. Satisfactory ^{13}C NMR spectra were obtained for both *trans-trans*-**8** and *trans-trans*-**9**.

¶ Synthesis of *trans-trans*-**9** is described in the supporting information (ESI†).

‖ Crystal data for *trans-trans*-**9**: $C_{20}H_{12}F_{12}O_2Se$, M = 591.25, monoclinic, space group $P2_1/n$, a = 9.621(2), b = 22.144(3), c = 16.221(2) Å, β = 106.209(4)°, U = 3318.3(9) Å^3, T = 298 K, Z = 6, μ(Mo-Kα) = 18.14 cm^{-1}, 8261 refelections measured, 7812 (R_{int} = 0.075) which were used in all calculations. The final w$R(F^2)$ was 0.221 (all data). CCDC 154648. See http://www.rsc.org/suppdata/cc/b0/b009789f/ for crystallographic data in .cif or other electronic format.

** The yields were calculated assuming that 1 mol of **8** or **9** gives 2 mol of products.

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