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Crystal Structure of 2,3-Epoxy-5-(1-hydroxy-2,3-epoxy-5-phenylselenocyclopent-1-yl)cyclopent-1-one

CHRISTIAN RØMMING and PER EGIL HANSEN

Department of Chemistry, University of Oslo, Oslo 3, Norway

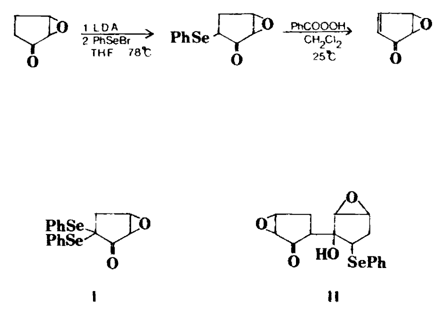
The crystal structure of the title compound ($C_{16}H_{16}O_4Se$) has been determined by X-ray diffraction methods using 2201 reflections collected by counter methods at −160 °C. The crystals are monoclinic, space group $P2_1/c$, with unit cell dimensions $a = 14.689(5)$ Å; $b = 6.591(2)$ Å; $c = 15.913(4)$ Å; $\beta = 106.41(2)°$. The structure was solved by the Patterson method and refined to a conventional R-factor of 0.07.

The phenyl ring attached to selenium is disordered in the crystal; it was found to occupy two positions with about equal probability. Estimated standard deviations in bond lengths and angles in this part of the molecule are 0.03 Å and 2°, respectively, whereas in the main part of the molecule the corresponding figures are 0.01 Å and 0.5°.

The torsional angle for the bond between the cyclopentane rings is fixed by an *intra*-molecular hydrogen bond.

In the course of an investigation of the valence isomers of 1-substituted 3-oxidopyridinium and 3-oxidopyrylium a mild method to introduce a carbon-carbon double bond in the ring was sought.[1,2] The selenoxide method appeared to fulfil this requirement.[3–5] The outline of the synthesis is shown in Scheme 1. The reaction gave some unexpected results, however. The enolate anion reacted very fast with the added benzeneselenenyl bromide at −78 °C, and after quenching the reaction mixture with 10 % hydrochloric acid and work-up it was possible to isolate two products. The minor product was found to be the α-disubstituted phenylselenoketone(I).[6,7]

The constitution and structure of the major product has been determined by X-ray crystallographic methods as described in the present paper.



Scheme 1.

EXPERIMENTAL

Crystals were formed by recrystallization from ethanol. The specimen used in the X-ray experiment was cut from a larger crystal to the approximate dimensions 0.15 × 0.2 × 0.3 mm. Data were collected first at room temperature; the subsequent structure determination revealed a partial disorder, however, and the data collection was repeated with a temperature at the crystal site of −160 °C. Unit cell dimensions were calculated from diffractometer measurements of 15 general reflections using Mo*K*α-radiation ($\lambda = 0.71069$ Å). Intensity data were recorded using a SYNTEX P$\bar{1}$ diffractometer with graphite crystal monochromated Mo*K*α-radiation. The $\theta/2\theta$ scanning mode was used with a scan speed (2θ) of 2–4 °/min depending on the peak intensity; three standard reflections were measured for every 50 reflections; they showed a decrease of about 2 % during the data collection and the data were accordingly adjusted. 2201 reflections with $\sin\theta/\lambda < 0.8$ Å^{-1} were found to have net intensities larger than $3\sigma(I)$ and were used for the structure determination. They were corrected for Lorentz and polarization effects, but not for absorption and

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secondary extinction. The standard deviation of the intensities were taken as $\sigma(I)=(C_T+(0.02C_N)^2)^{\frac{1}{2}}$, where C_T is the total number of counts and C_N is the scan count minus background count. The full-matrix least-squares program employed minimizes the function $\sum w(F_o-F_c)^2$, where w is the inverse of the variance of the observed structure factor. A brief description of the computer programs employed is given in Ref. 8. The atomic form factors used were those of Doyle and Turner[9] for selenium, oxygen and carbon, and of Stewart *et al.*[10] for hydrogen.

CRYSTAL DATA

2,3-Epoxy-5-(1-hydroxy-2,3-epoxy-5-phenylselenocyclopent-1-yl)cyclopentan-1-one, $C_{16}H_{16}O_4Se$, monolinic. $t=18$ °C: $a=14.839(7)$ Å; $b=6.624(2)$ Å; $c=15.995(5)$ Å; $\beta=105.02(3)°$; $V=1514.5$ Å^3. $D_x=1.540$ g cm^{-3}. $t=-160$ °C: $a=14.689(5)$ Å; $b=6.591(2)$ Å; $c=15.913(4)$ Å; $\beta=106.41(2)°$; $V=1477.8$ Å^3 $D_x=1.579$ g cm^{-3}. $M=351.26$; $F(000)=712$; $Z=4$. Absent reflections: ($0k0$) for k odd, ($h0l$) for l odd. Space group $P2_1/c$. (No. 14).

Table 1. Fractional atomic coordinates and thermal parameters. The anisotropic temperature factor is given by $\exp-2\pi^2(U_{11}a^{*2}h^2+\ldots+2U_{12}a^*b^*hk+\ldots)$.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Se	.6830(1)	.6690(1)	.4464(1)	.024(1)	.016(0)	.048(5)	−.001(0)	.019(0)	−.003(0)
O1	.8836(3)	.7298(7)	.4816(3)	.023(3)	.016(2)	.021(2)	.002(2)	.010(2)	.003(2)
O2	.8411(4)	1.1848(7)	.3465(3)	.042(3)	.008(2)	.031(3)	−.001(2)	.001(2)	.006(2)
O3	1.0069(4)	.5798(7)	.3962(4)	.032(3)	.018(2)	.034(3)	.006(2)	.013(3)	−.004(2)
O4	.8918(5)	.5076(8)	.1821(4)	.072(5)	.017(2)	.033(3)	−.003(3)	.027(3)	−.007(2)
C1	.7417(5)	.8936(10)	.3989(5)	.030(4)	.012(3)	.033(4)	.001(3)	.012(3)	−.001(3)
C2	.7539(6)	1.0923(10)	.4515(6)	.038(5)	.016(3)	.050(5)	.013(3)	.012(4)	−.007(3)
C3	.8397(5)	1.1860(11)	.4370(5)	.032(4)	.009(3)	.036(4)	.004(3)	.001(3)	−.002(3)
C4	.8941(5)	1.0311(9)	.4057(5)	.027(4)	.011(3)	.022(4)	.002(3)	.003(3)	.004(3)
C5	.8425(4)	.8296(11)	.4002(4)	.016(3)	.012(3)	.021(3)	.004(3)	.006(3)	.000(3)
C6	.8456(5)	.5876(10)	.3234(4)	.028(4)	.010(3)	.014(3)	−.003(3)	.006(3)	−.001(3)
C7	.8063(6)	.7839(10)	.2313(5)	.034(5)	.021(3)	.016(4)	−.005(3)	.006(3)	.003(3)
C8	.8763(7)	.7229(11)	.1813(5)	.054(6)	.020(3)	.027(4)	−.007(3)	.017(4)	−.007(3)
C9	.9628(6)	.6361(10)	.2403(5)	.045(5)	.020(4)	.034(4)	−.002(3)	.026(4)	−.005(3)
C10	.9479(5)	.6263(9)	.3305(5)	.038(4)	.008(3)	.025(4)	−.004(3)	.017(3)	−.005(3)
C121	.516(1)	.903(2)	.331(1)	.018(9)	.023(6)	.040(9)	.004(6)	.015(7)	.010(6)
C132	.417(1)	.928(2)	.296(1)	.021(9)	.033(7)	.032(9)	.008(6)	.008(7)	.013(7)
C151	.388(1)	.645(2)	.376(1)	.027(9)	.039(7)	.038(9)	−.003(7)	.017(7)	.010(7)
C161	.485(1)	.618(2)	.410(1)	.025(10)	.029(7)	.025(8)	−.013(6)	.000(7)	.008(6)
C122	.513(1)	.880(2)	.450(1)	.020(9)	.030(8)	.038(8)	−.004(7)	.012(7)	−.001(6)
C132	.419(4)	.923(3)	.415(1)	.035(10)	.037(9)	.049(10)	.004(8)	.028(9)	.004(9)
C152	.405(2)	.705(3)	.292(2)	.071(12)	.044(10)	.051(11)	−.017(10)	−.005(10)	−.008(11)
C162	.500(1)	.652(3)	.325(1)	.028(10)	.031(9)	.066(10)	−.001(8)	.006(10)	−.026(10)

Atom	x	y	z	B	Atom	x	y	z	B
C111	.550(2)	.741(4)	.388(1)	2.3(4)	C141	.355(2)	.796(3)	.314(1)	2.3(8)
C112	558(2)	.741(4)	.405(1)	2.3(5)	C142	.363(1)	.837(3)	.339(1)	2.3(4)
HC1	.698	.918	.337	1.5	H1C2	.763	1.064	.516	1.5
H2C2	.698	1.186	.431	1.5	HC3	.856	1.292	.486	1.5
HC4	.963	.983	.420	1.5	HC6	.802	.575	.327	1.5
H1C7	.801	.934	.235	1.5	H2C7	.742	.726	.201	1.5
HC8	.861	.838	.135	2.0	HC9	1.033	.658	.254	2.0
H121	.557	.991	.304	2.3	H131	.393	1.060	.264	2.3
H141	.282	.822	.284	2.3	H151	.344	.547	.393	2.3
H161	.512	.501	.453	2.3	H122	.552	.943	.506	2.3
H132	.388	1.028	.446	2.3	H142	.294	.859	.320	2.3
H152	.364	.627	.237	2.3	H162	.536	.565	.292	2.3
HO1	.927	.678	.452	1.1					

STRUCTURE DETERMINATION

The structure was solved using the room temperature data set by Patterson methods and refined by successive Fourier syntheses. It turned out that whereas the peaks corresponding to bicyclopentyl and the selenium and oxygen atoms attached to it were clearly indicated in the Fourier maps, the phenyl ring bonded to the selenium atom was only vaguely indicated in two alternative positions. A low temperature data set was collected, and the refinements were carried out using these data.

The disorder comprises the phenylseleno moiety, which seems to be situated in two positions with approximately equal probability, one with the phenyl plane *in* the C–Se–C plane, the other nearly normal to it.

The least-squares refinements proceeded with variation of all positional parameters of the heavy atoms. The hydrogen atomic positions were calculated from stereochemical considerations but excluded from the refinement. The "half" carbon atoms bonded to selenium and those in *para* positions were given isotropic thermal parameters as were the hydrogen atoms; all other atoms were refined anisotropically.

The refinements converged to a conventional R-factor of 0.070, $R_w=0.066$ and a goodness of fit $(S=(\sum w\Delta^2/n-m)^{\frac{1}{2}})$ of 2.2 for the 1492 reflections with $\sin\theta/\lambda \geq 0.4$ Å^{-1}. The corresponding parameters are listed in Table 1. The structure factor list may be obtained from the authors.

Structural data for the molecule are given in Table 2. Estimated standard deviations are calculated from the correlation matrix.

DISCUSSION

A drawing of the molecule is presented in Fig. 1 where the numbering of the atoms is also given.

The X-ray analysis proves the main reaction product of the synthesis outlined in Scheme 1 to be the dimer (II).

The central cyclopentane ring (C1–C5) has the envelope conformation, the C1 atom being displaced by 0.48 Å out of the plane through the four other atoms. The other cyclopentane ring (C6–C10) has a somewhat flattened half chair conformation with C6 and C7 0.10 and 0.16 Å, respectively, out of the plane through C8, C9 and C10.

The epoxy rings display the usual structural features with a short C–C bond (1.47 Å) and a long C–O bond (1.45 Å).[11]

A moderately strong *intra*-molecular hydrogen bond (2.74 Å) is found between the hydroxyl oxygen atom of the central cyclopentane ring and the keto oxygen atom of the other.

Because of the disorder the accuracy in the structural data found for the phenylseleno part of the molecule is rather poor. The "half" carbon atoms C111 and C112 are situated close together as are C141 and C142, and the shifts in positional parameters from the pairs are strongly correlated. The angle between the least-squares planes of the two phenyl rings is 92°. The disorder may also include the selenium atom; the accuracy of bond lengths and angles including this atom may therefore be less than that indicated by the estimated standard deviations given in Table 2.

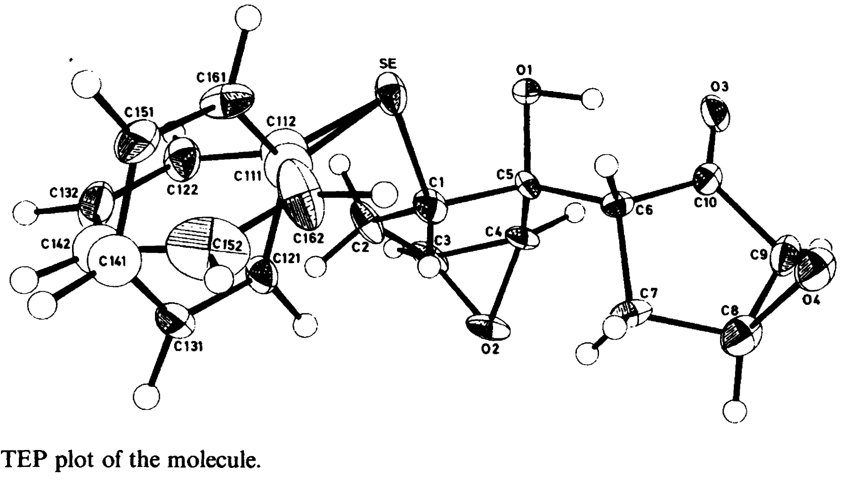

Fig. 1. ORTEP plot of the molecule.

Table 2. Structural data.

Distance	Å	Distance	Å	Distance	Å
Se-C1	1.97(1)	Se-C111	1.97(2)	Se-C112	1.83(2)
C1-C2	1.54(1)	C2-C3	1.48(1)	C3-C4	1.47(1)
C3-O2	1.45(1)	O2-C4	1.45(1)	C4-C5	1.52(1)
C5-O1	1.43(1)	C5-C1	1.53(1)	C5-C6	1.55(1)
C6-C7	1.55(1)	C6-C10	1.53(1)	C7-C8	1.52(1)
C8-C9	1.47(1)	C8-O4	1.44(1)	O4-C9	1.45(1)
C9-C10	1.51(1)	C10-O3	1.19(1)	C111-C121	1.41(3)
C121-C131	1.41(2)	C131-C141	1.34(3)	C141-C151	1.40(2)
C151-C161	1.38(2)	C161-C111	1.38(3)	C112-C122	1.43(2)
C122-C132	1.37(3)	C132-C142	1.38(3)	C142-C152	1.39(3)
C152-C162	1.39(3)	C162-C112	1.44(3)	O1-O3	2.74(1)

Angle	°	Angle	°
Se-C1-C2	115.3(5)	Se-C1-C5	108.3(4)
O5-C1-C2	105.3(6)	C1-C2-C3	104.1(6)
C2-C3-C4	109.4(6)	C3-C4-C5	108.5(6)
C4-C5-C1	102.9(5)	O2-C3-C4	59.8(4)
C3-O2-C4	60.9(4)	O2-C4-C3	59.4(4)
C2-C3-O2	113.9(6)	O2-C4-C5	113.9(6)
C4-C5-O1	105.9(5)	O1-C5-C1	107.4(5)
O1-C5-C6	109.8(5)	C4-C5-C6	116.6(5)
C1-C5-C6	113.5(5)	C5-C6-C10	110.4(5)
C5-C6-C7	114.3(5)	C10-C6-C7	105.9(5)
C6-C7-C8	105.1(6)	C7-C8-C9	111.1(6)
C8-C9-C10	107.0(6)	C9-C10-C6	108.7(6)
C9-C8-O4	60.1(5)	C9-O4-C8	60.9(5)
C8-C9-O4	58.9(5)	C9-C10-O3	125.3(7)
C6-C10-O3	125.9(6)	C111-Se-C1	97.0(7)
C112-Se-C1	99.7(7)		

Torsion angle	°	Torsion angle	°
Se-C1-C2-C3	149.5(5)	Se-C1-C5-C4	-153.8(4)
Se-C1-C5-O1	-42.3(6)	Se-C1-C5-C6	79.2(6)
C1-C2-C3-C4	-18.5(8)	C2-C3-C4-C5	-0.4(8)
C3-C4-C5-C1	19.0(7)	C4-C5-C1-C2	-30.0(7)
C5-C1-C2-C3	30.1(7)	C1-C2-C3-O2	46.2(8)
C2-C3-O2-C4	-99.3(6)	C3-O2-C4-C5	98.1(7)
O2-C4-C5-C1	-45.0(7)	O2-C4-C5-O1	-157.5(5)
O2-C4-C5-C6	80.0(7)	C4-C5-C6-C7	-57.2(8)
C4-C5-C6-C10	62.0(7)	O1-C5-C6-C7	-177.7(5)
O1-C5-C6-C10	-58.4(6)	C1-C5-C6-C7	62.2(7)
C1-C5-C6-C10	-178.6(5)	C5-C6-C7-C8	136.7(6)
C6-C7-C8-C9	-11.7(7)	C7-C8-C9-C10	3.6(8)
C8-C9-C10-C6	6.2(7)	C9-C10-C6-C7	-13.3(7)
C9-C10-C6-C5	-137.5(5)	C6-C7-C8-O4	53.6(8)
C7-C8-O4-C9	-102.1(7)	C8-O4-C9-C10	99.4(7)
O4-C9-C10-O3	124.6(7)	C8-C9-C10-O3	-173.3(6)
C5-C6-C10-O3	42.0(8)	C7-C6-C10-O3	166.2(6)
C10-C6-C7-C8	14.9(7)		

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