Preparation of 2,6-Dialkoxy-3,5-dialkyl-1,4-oxaselenane 4,4-Dichlorides and Structure Determination of 2,6-Dimethoxy-3,5-dimethyl-1,4-oxaselenane

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A variety of aliphatic aldehydes reacted with SeO_2 in alcohols containing aqueous HCl, yielding 2,6-dialkoxy-3,5-dialkyl-1,4-oxaselenane 4,4-dichlorides, as unstable, nicely crystalline compounds. The corresponding Cl-stripped compounds are much more stable (distillable). The structure of one member in the series, 2,6-dimethoxy-3,5-dimethyl-1,4-oxaselenane, has been determined by single-crystal X-ray diffraction techniques.

The oxidation of a CH_2 group α to a carbonyl in ketones and, to a lesser extent, aldehydes with SeO_2 is a well-established[1-3] procedure for the synthesis of 1,2-dicarbonyl compounds (Scheme 1, eqn. 1). It is likely that this type of oxidation is initiated by an electrophilic attack by a Se(IV) species, thus creating a C−Se bond α to the carbonyl group.[4,5] In the presence of aqueous HCl (in methanol), such Se(IV) compounds (eqn. 2) can often be isolated.[6-9]

Interaction of aldehydes with SeO_2 in aqueous HCl has been studied extensively by Futekov et al.[10,11] in the area of analytical chemistry, particularly for specific separation of selenium by sol-
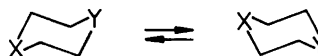

Fig. 1.

vent extraction. The results of the Bulgarian workers clearly indicate the formation of defined (albeit unstable) extractable species. Bergman and Laitalainen[12] have recently established that these species are 2,6-dialkoxy-3,5-dialkyl-1,4-oxaselenane 4,4-dichlorides (eqn. 3). In this paper, we report further experiments in this area including X-ray, NMR and MS studies.

Results and discussion

It has been demonstrated[12] that aliphatic aldehydes, in the presence of selenium dioxide, aqueous HCl and ethanol or methanol, readily form 2,6-dialkoxy-3,5-dialkyl-1,4-oxaselenane 4,4-dichlorides (*1*), which are usually obtained directly from the reaction mixtures as highly, albeit unstable, crystalline solids. The parent compound, (*1a*), in the series can not be prepared due to rapid decomposition and the simplest member, (*1b*), after preparation, must be stored in the re-

Scheme 1.

Scheme 2.

$(HCOCH_2)_2SeX_2$

$$HCOCH_3 + SeX_4$$
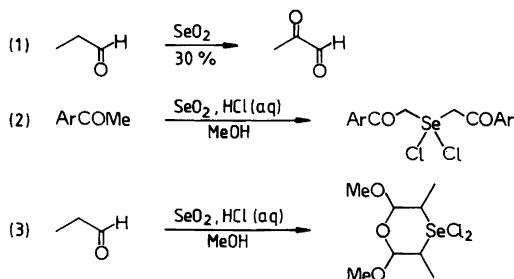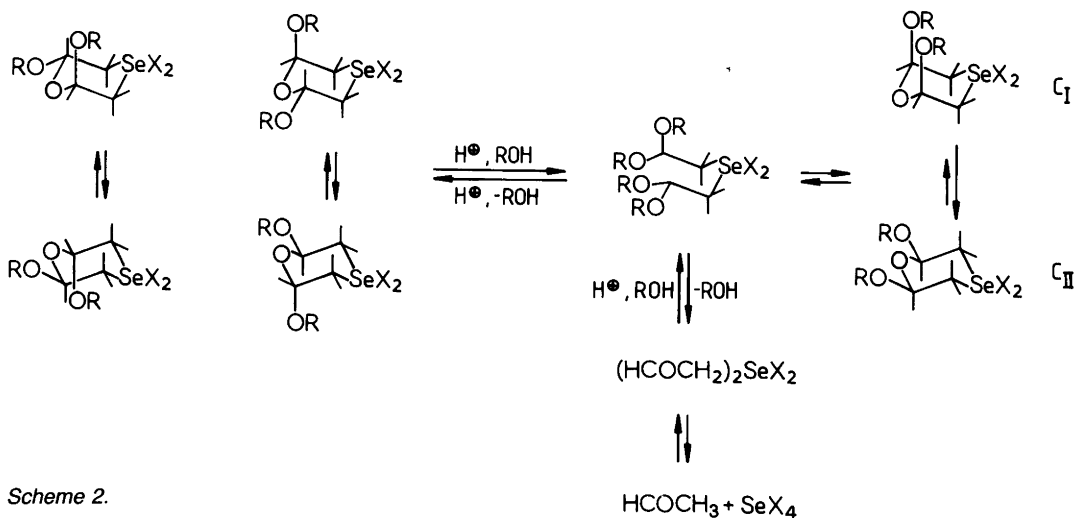
frigerator, otherwise, it will decompose within 24 h. Some of the higher members (e.g. *1f*) can be stored at room temperature without protection for several weeks. Reduction of compound *1* with sulfite or with zinc in alcohol gives the corresponding selenides (*2*), which are much more stable. Compound *2b* for instance, is a low-melting

1 *a* $R_1=CH_3, R_2=H$
   b $R_1=R_2=CH_3$
   c $R_1=CH_3, R_2=C_2H_5$
   d $R_1=R_2=C_2H_5$
   e $R_1=CH_3, R_2=C_4H_9$
   f $R_1=C_2H_5, R_2=C_4H_9$
   g $R_1=CH_3, R_2=C_6H_5$
   h $R_1=C_2H_5, R_2=CH_2C_6H_5$

2 *a* $R_1=CH_3, R_2=H$
   b $R_1=R_2=CH_3$

3

4

5 *a* $R=OC_2H_5$
   b $R=Cl$

(47–48 °C), distillable, (86–88 °C, 10 mm Hg) solid that readily sublimes even at room temperature. The divalent 1,4-oxaselenanes can, when completely pure, be stored for long periods (so far, 18 months) without decomposition. Attempts to convert *2b* into *3* failed, which was somewhat surprising as *3* had previously[13] been prepared by dehydrochlorination of the adduct (*4*) made from diallyl ether and $SeOCl_2$.

Unsubstituted six-membered 1,4-heterocycles (Fig. 1, where X, Y = O, S, CH_2 or NH) have been reported[14-16] to exist in rapid equilibrium between two identical chair conformers. In the 2,6-disubstituted 1,4-oxaselenanes, the picture is more complicated even for the simplest possible cases (*1a* and *2a*) since an equilibrium mixture of *trans* and *cis* isomers should be possible. All *trans* conformers have one alkoxy group in the equatorial and one alkoxy group in the axial position. The pair of conformers of the *cis* isomer (C_I = aa, C_{II} = ee, Scheme 2) are different. However, under the necessary reaction conditions for the formation of the 1,4-oxaselenanes from simple aldehydes, interconversion should be expected to occur via the ring-opened intermediate as indicated in Scheme 2 and, finally, the thermodynamically most stable conformer would predominate (see Ref. 17). The prediction from this Scheme would be a preference for the e,e conformer C_{II}. With substituents in 3 and 5 positions, the preference for the conformer with all substituents in equatorial positions should be even
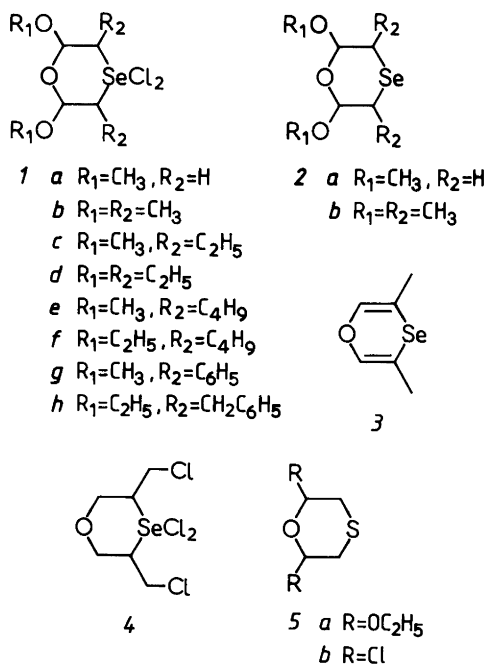
Table 1. ¹H NMR data[a] for the compound *2b*.

Proton	Multi-plicity	$_{H}(CDCl_3)$	(C_6D_6) H		$^3J_{HH}$
CH₃	d	1.22	1.18	0.04	6.90
OCH₃	s	3.52	3.24	0.28	–
3 and 5	dq	3.16	3.27	−0.11	6.90. 8.30
2 and 6	d	4.44	4.29	0.15	9.30

[a]The chemical shifts are given in ppm from Me₄Si, and coupling constants in Hz.

Table 3. ⁷⁷Se NMR data[a] for the compound *2b*.

Proton/carbon	$^nJ_{SeH}$	$^nJ_{SeC}$	n
3 and 5	–	56.9	1
3 and 5	3.1	–	2
CH₃	–	22.0	2
CH₃	18.0	–	3
2 and 6	1.1	–	3

[a]The chemical shift in ppm relative to external dimethyl selenide, and coupling constants in Hz. The ⁷⁷Se chemical shift was 256 ppm.

stronger. An X-ray analysis established indeed that compound *2b* crystallizes as this conformer.

According to Barnes,[16] 1,4-oxaselenane undergoes rapid ring inversion at room temperature. Lowering the temperature produces coalescence phenomena, and the vicinal coupling constants in a fixed chair conformation can be obtained: $J_{eq}(O)$,, ax(Se)=2.8 Hz, $J_{ax}(O)$, eq(Se)=1.7 Hz and $J_{ax}(O)$,ax(Se)=12.3 Hz. At room temperature, the averaged coupling constants were; J_{trans}=7.22 Hz and J_{cis}=2.74 Hz. The observed vicinal coupling constant of *2b*(Tables 1–3) was, J_{H2H3}=8.30 Hz, which indicates that there is a rapid ring inversion at room temperature. We also suggest on the basis of the above coupling information, that the 4,4-dichloride *1b* undergoes similar ring inversions, because the value of the coupling constant was 8.4 Hz. The readiness of these compound to undergo ring inversion, in spite of the unfavourable 1,3-diaxial interactions, may be due to the likewise unfavourable dipole-dipole interactions of the three coplanar dipoles.

The assignments of the signals in the ¹H NMR and ¹³C NMR spectra are based on the correlation data and signal multiplicity. The analysis of

Table 2. ¹³C NMR data[a] for the compound *2b*.

Carbon	C	$^1J_{CH}$	$^2J_{CH}$	$^3J_{CH}$
CH₃	14.95	128.3	2.8 (3,5)	1.2 (2,6)
OCH₃	56.15	142.7	–	4.0 (2,6)
2 and 6	107.34	159.3	–	–
3 and 5	34.25	145.7	2.1 (2,6); 4.6 (CH₃)	–

[a]The chemical shifts are given in ppm from Me₄Si, and the coupling constants in Hz.

coupled ¹³C and ⁷⁷Se spectra were confirmed by a series of selective irradiation experiments. The ¹H NMR chemical shifts were larger in CDCl₃ than in C₆D₆ except those for the protons 3 and 5.

The ⁷⁷Se−¹³C coupling constant, $^1J_{SeC}$ of value 56.9 ± 0.2 Hz is in the range found[18] for sp^3 hybridized carbon atoms. The value of $^3J_{SeH(Me)}$ (18.0 Hz) was significantly larger than $^3J_{SeH2}$ (1.1 Hz). This might indicate the dependence of the magnitude of the coupling constants on the orientation of lone pair electrons at selenium with respect to the coupling nuclei as suggested earlier.[19]

A few compounds in the sulfur series related to *2* (no tellurium isologs are known) have previously been studied. Thus, it has been known[20,21] at least since 1909 that S(CH₂CHO)₂ upon treatment with HCl in ethanol yields the 1,4-oxathiane (*5a*). No conformational analysis of this compound has been published but it is predicted that it will crystallize as the 2e,6e conformer. Demaster[22] studied the reactions outlined in Scheme 3. The pair of isomeric sulfones formed was separated by fractional crystallization. The ¹H NMR spectrum of cis-2,6-diethoxy-1,4-oxathiane 4,4-dioxide (m.p. 103–105 °C) had, according to Demaster, $J_{a,a}$ = 8 Hz and $J_{a,e}$ = 2 Hz, which was interpreted to indicate that the *cis* isomer had a preferred e,e conformation. However, in view of the data from *1b* and *2b*, this conclusion is questionable. The *trans* isomer of 2,6-diethoxy-1,4-oxathiane 4,4-dioxide (m.p. 136–137 °C) gave an averaged coupling constant indicating rapid chair-chair interconversions.[22] More recently, Schoufs, Meijer and Brandsma[23] as well as Spoormaker and de Bie[24] have studied the 1,4-oxathiane *5b* (mixture of *trans* and *cis* isomers) and concluded that the *cis* isomer in the liquid phase is predominantly in the e,e form.

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Mass spectral studies. The fragmentation patterns of 2,6-dimethoxy-3,5-dimethyl-1,4-oxaselenane (*2b*) and the three 4,4-dichlorides (*1c, 1d,* and *1g*) fit well to the proposed structures as presented in Scheme 4 and Table 4. In summary, two series of ions were produced on the electron impact: those containing one chlorine atom and those containing none. Intensities in the former series were higher except for 4-membered[25,26] ions for which only weak signals (rel. int. <0.5 %) were observed. The suggested genesis of secondary ions is based mainly on analogy with fragmentation of 2,6-dimethoxy-3,5-dimethyl-1,4-oxaselenane (*2b*).

Although weak signals are sometimes (especially in the rear of direct inlet run) observed at *m/z* values corresponding to molecular ions, isotopic pattern analysis and high resolution measurements reveal that they originate from diselenide species produced by heat in the specimen tube. This kind of behavior has been reported.[27] Also, Kulkarni *et al.*[26] were unable to find molecular ions for oxaselenane dichlorides.

Isotopic pattern analysis[28] makes it easy to distinguish between selenium (mono and di) and chloroselenium species. This analysis also indicates that loss of chlorine is, to some extent (5–20 %), accompanied by loss of hydrogen chloride.

Crystal structure of 2b. A view of the molecule *2b* with the atom numbering scheme is shown in Fig.

Table 4. Mass spectral data[a] of compounds *2b, 1c, 1d* and *1q. m/z* (rel. int. %). HRMS, Form., Calc. Found.

| Ion	2b	1c	1d	1q
a		303 (3) M–Cl $C_{10}H_{20}ClO_3Se$ 297.0326 297.0347	331 (3) M–Cl $C_{12}H_{24}ClO_3Se$ 331.0579 331.0607	387 (17) M–Cl $C_{16}H_{32}ClO_3Se$ 387.1206 387.1223
b	240 (6)$^+$ $C_8H_{16}O_3Se$ 240.0263 240.0241	268 (2) $C_{10}H_{20}O_3Se$ 268.0578 268.0607	296 (2) $C_{12}H_{24}O_3Se$ 296.0889 296.0864	352 (4) $C_{16}H_{32}O_3Se$ 352.1516 352.1489
c	72 (53)[b] C_4H_8O 72.0575 72.0599	86 (94)[b] $C_5H_{10}O$ 86.0732 86.0747	100 (100) $C_6H_{12}O$ 100.0888 100.0864	128 (100) $C_8H_{16}O$ 128.1201 128.1173
d		201 (17) $C_5H_{10}ClOSe$ 200.9585 200.9589	215 (6) $C_6H_{12}ClOSe$ 214.9741 214.9735	243 (28) $C_8H_{16}ClOSe$ 243.0053 243.0037
e	180 (5) $C_6H_{12}OSe$ 180.0054 180.0470	208 (20) $C_8H_{16}OSe$ 208.0367 208.0366	222 (5) $C_9H_{18}OSe$ 222.0522 222.0517	278 (5) $C_{10}H_{20}OSe$ 278.1149 278.1152
f	151 (14) C_4H_7OSe 150.9662 150.9691	165 (3) C_5H_9OSe 164.9819 164.9790	179 (4) $C_6H_{11}OSe$ 178.9975 178.9984	207 (6) $C_8H_{15}OSe$ 207.0288 207.0298
q	209 (1) $C_7H_{13}O_2Se$ 209.0080 209.0115	237 (5) $C_9H_{17}O_2Se$ 237.0393 237.0389	251 (1) $C_{10}H_{19}O_2Se$ 251.0550 251.0525	307 (2) $C_{14}H_{27}O_2Se$ 307.1175 307.1192

[a]74 eV, 30–40 °C. [b]Base peak for methoxy derivatives is *m/z* = 71.

Scheme 3.

58% 5%
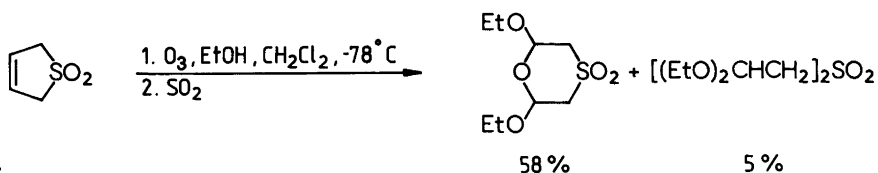
2, and a view of the molecular packing in Fig. 3. Tables 5–8 present atomic coordinates, bond lengths and angles, deviations of atoms from the selected planes and torsional angles. The crystal structure consists of discrete molecules. A crystallographic mirror plane bisects the molecule through atoms Se and O1. The asymmetric unit of the structure thus consists of the atoms Se, O1, O2, C1, C2, C3 and C4 plus the corresponding hydrogen atoms. Due to the symmetry the four ring-carbon atoms are ideally coplanar.

Figure 2 shows that the six-membered ring of the 1,4-oxaselenane derivative 2b adopts a chair conformation and the C2−O2 and C1−C3 bonds are oriented equatorially. Thus all ring-hydrogen atoms are axially oriented. The chair conformation has also been found in some solid 1,4-oxaselenane complexes studied by X-ray analysis.[29,30] The Se−C bonds in 2b, both of length 1.952(8) Å, are comparable to the Se−C bond lengths of 1.93(3) and 1.98(3) Å in the iodine complex of 1,4-oxaselenane.[29] There are no significant differ-
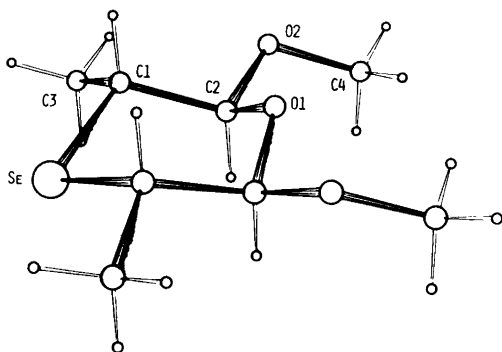

Scheme 4.

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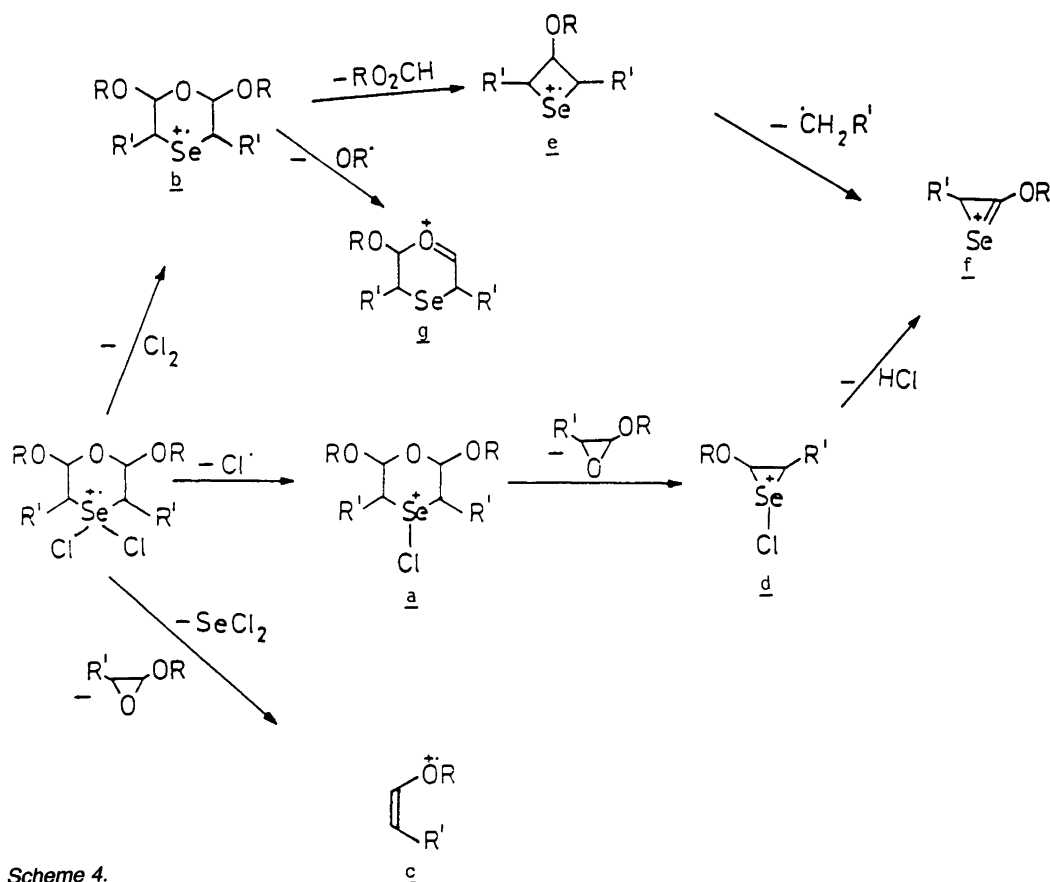
Fig. 2. One molecular unit of the compound 2b with atom labelling. The positions of the other atoms of the molecule are obtained through the symmetry operation x, y, 3/2-z.

ences in other bond lengths, nor in the endocyclic bond angles, between the two compounds. In the direction of the a axis (see Fig. 3), in which the molecule is quite flat, the interatomic distances between corresponding atoms are ca. 4.4 Å. No short interatomic distances were found in other directions either; the intermolecular forces are thus very weak.

Experimental

The ¹H, ¹³C and ⁷⁷Se NMR spectra were recorded on a Jeol FX-100 spectrometer. Proton noise-decoupled ¹³C NMR spectra were produced with a pulse angle of 25° and a repetition time of 3 sec. Proton noise-decoupled ¹³C NMR spectra used for the determination of J_{SeC} were produced with

16500 pulses. The J_{SeC} coupling constants were obtained from fully coupled ⁷⁷Se spectra. ¹H NMR spectra were obtained from 0.06 M CDCl₃ and C₆D₆ solutions, ¹³C and ⁷⁷Se NMR spectra from 0.85 M CDCl₃ solutions. ⁷⁷Se chemical shifts were measured relative to external dimethyl selenide.

The mass spectra were registered with a Jeol–JMS–OISG–2 mass spectrometer as direct inlet runs, electron energy 75 eV and sample temperature 30–40 °C. Only the most intense peaks in each pattern are reported.

All aldehydes used were freshly distilled.

2,6-Dimethoxy-3,5-dimethyl-1,4-oxaselenane 4,4-dichloride (1b). Propionaldehyde (5.8 g, 0.1 mol) was added in portions to a stirred solution (30 °C) of SeO₂ (11.0 g, 0.1 mol) in methanol (35 ml) and concentrated aqueous HCl (15 ml). Within 10 min, the product commenced to separate as an oil (or sometimes directly as crystals) that soon solidified. After 2 h at 30 °C, the reaction mixture was quenched by addition of water (200 ml) and the product collected and recrystallized from methanol/water. Yield, 11.5 g (68 %); m.p. 130–132 °C. ¹H NMR (CDCl₃): δ 5.10 (d, 2H, 3–CH, J=8.4 Hz), 4.25 (m, 2H, 2–CH, 3.60 (s, 6H, OCH₃), 1.73 (d, 6H, CH₃, J=6.8 Hz).

The following compounds were similarly prepared:

Compound 1c: yield 70 %; m.p. 148–150 °C (dec). MS m/z (rel. int. %) 303(3), M–Cl, 268(2), 237(5), 208(20), 201(17), 165(3), 150(6), 127(32), 120(35), 103(6), 86(94), 71(100), 57(12). ¹H NMR (CDCl₃): δ 5.05 (d, 2H, 3–CH, J=8.4), 4.23 (m, 2H, 2–CH), 3.52 (s, 6H, OCH₃), 2.22
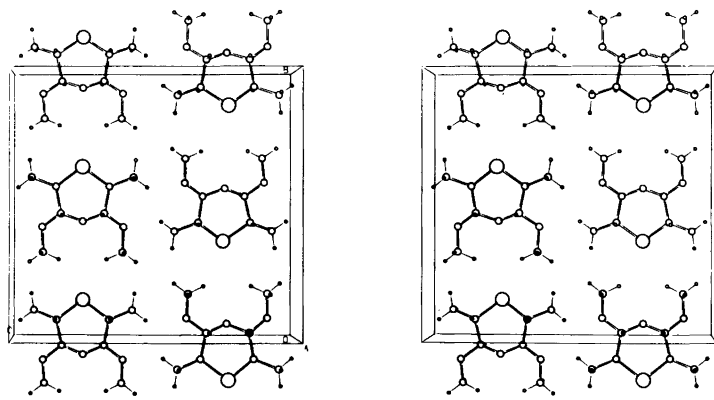

Fig. 3. Stereoscopic view along the a axis.

Table 5. Final atomic coordinates (×10⁴) with e.s.d.s in parentheses. The equivalent isotropic thermal parameters (×10³) have been calculated by $U_{eq} = \frac{1}{3}(U_{11} + U_{22} + U_{33})$.

	x	y	z	U_{eq}(Å²)
Se	1539(3)	1381(1)	7500	50(1)
O1	3757(20)	−614(5)	7500	45(5)
O2	3548(18)	−822(4)	6089(4)	61(4)
C1	3132(21)	669(5)	6573(5)	45(5)
C2	2335(19)	−320(6)	6750(5)	44(5)
C3	1851(26)	1002(6)	5748(6)	62(7)
C4	2537(30)	−1742(7)	6126(7)	79(9)

(m, 4H, CH₂, J=6.8), 1.25 (t, 6H, CH₃). ¹³C (CDCl₃): 11.98 (q), 21.00 (t), 56.85 (q), 75.83 (d), 102.21 (d).

Compound *1d*: yield 64%; m.p. 145°C (dec). MS: m/z (rel. int. %) 331(3) M−Cl, 296(2), 251(1), 222(5), 215(6), 179(4), 134(8), 103(1), 100(100), 85(54), 72(69), 57(47).

Compound *1e*: yield 68%; m.p. 140°C (dec).

Compound *1f*: yield 70%; m.p. 78–80°C. MS: m/z (rel. int. %) 387 (17) M−Cl, 352(4), 307(2), 278(5), 243(28), 207(6), 128(100), 103(10), 99(23), 85(76), 57(21).

¹³C (CDCl₃): 13.75 (q), 15.06 (q), 22.53 (t), 27.17 (t), 29.40 (t), 65.46 (t), 73.94 (d), 100.85 (d).

Compound *1g*: yield 85%; m.p. 230°C (dec). ¹³C (DMSO−d₆): 44.74 (d), 55.45 (q), 104.64 (d), 127.38 (d), 128.17 (d), 128.49 (d), 136.69 (s).

Compound *1h*: yield 60%; m.p. 128–130°C. ¹³C (CDCl₃): 15.10 (q), 33.55 (t), 65.58 (t), 75.57 (d), 100.86 (d), 127.65 (d), 128.75 (d), 129.43 (d), 134.69 (s).

2,6-Dimethoxy-3,5-dimethyl-1,4-oxaselenane
(2b). 2,6-Dimethoxy-3,5-dimethyl-1,4-oxaselenane 4,4-dichloride (*1b*, 3.11 g, 10 mmol) was added to a well stirred mixture of dichloromethane (35 ml) and Na₂S₂O₅ (aq., 15%, 30 ml) at ~20°C. After ~2 h, no solid material was left and the organic phase was separated, washed with water, dried (Na₂SO₄) and evaporated. The residue was distilled (86–88°C, 10 mm). Yield 2.05 g (85%); m.p. 47–48°C. The sample used for the X-ray determination was recrystallized from methanol/water and then from diisopropyl ether. MS: m/e (rel. int. %) 240(6) M⁺, 209(1), 180(5), 151(14), 113(30), 108(29), 99(42), 71(100), 57(88).

The crystal selected for the data collection had approximate dimensions 0.25×0.25×0.35 mm. Because the crystal showed a marked tendency to decompose in air or under X-ray radiation, it was sealed into a 2-component epoxy glue. Lattice parameters were obtained from least-squares refinement of 20 well-centered reflections measured on a Nicolet *P3* diffractometer using graphite-monochromatized MoKα radiation (λ = 0.7107).

Intensity data were collected at room temperature using the ω-scan technique (5° < 2θ < 50°) with a scan rate varying from 3 to 30° min⁻¹, depending upon the peak intensity. The intensities of check reflections showed only statistical fluctuations. Of 966 independent reflections measured, 632 had $F^o < 4\sigma(F^o)$ and were used in the structure determination. The data were corrected for Lorentz and polarization factors. An empirical absorption correction was done as well as dispersion corrections for Se (−0.178 and 2.223).

The orthorhombic space group *Pbcm* (No. 57) was indicated from the systematic absence and structure analysis. The structure was solved primarily by MULTAN 78[31] technique and the final refinements were carried out by the program system X-Ray 76[32]. The hydrogen atoms were placed in the calculated positions with the bond length 1.0 Å. The final R value was 0.054 (R_w = 0.056, unit weights). The atomic scattering factors were from the program system X-Ray 76.

The crystal data are as follows: C₈H₁₆O₃Se, FW = 239.17; space group *Pbcm* (No. 57); a = 4.421(3), b = 14.966(7) and c = 15.937(7) Å; Z = 4; $D_{calc.}$ = 1.51 g cm⁻³; λ(MoKα) = 0.7107 Å; μ(MoKα) = 38.0 cm⁻¹.

Table 6. Bond lengths (Å) and angles (°).

Se−C1	1.953(8)	C1−Se−C1ᵃ	98.3(3)
O1−C2	1.420(9)	Se−C1−C2	107.6(5)
O2−C2	1.401(11)	Se−C1−C3	110.0(6)
O2−C4	1.449(12)	C2−C1−C3	112.8(7)
C1−C2	1.547(12)	O1−C2−O2	107.3(7)
C1−C3	1.516(13)	O1−C2−C1	110.4(7)
		O1−C2−C1	106.8(7)
		C2−O1−C2ᵃ	114.6(7)
		C2−O2−C4	111.2(7)

ᵃDenotes symmetry operation x, y, 3/2-z.

Table 7. Deviations (Å) of atoms from crystallographic planes.

Plane 1. Plane through C1, C2, C1^i and C2^i					
Atom	Se	O1	O2	C3	C4
Dev.	−0.93(1)	0.71(1)	0.70(1)	−0.67(2)	0.58(2)

Plane 2. Plane through C1, Se and C1^i					
Atom	O1	O2	C2	C3	C4
Dev.	−0.83(1)	−1.08(2)	−1.11(1)	−0.20(2)	−2.21(2)

Plane 3. Plane through C2, O1 and C2^i					
Atom	Se	O2	C1	C3	C4
Dev.	1.88(2)	−0.31(2)	1.42(2)	1.50(2)	−1.69(2)

Angle between planes *1* and *2* is 46.9(4)°
Angle between planes *1* and *3* is 68.4(7)°

Table 8. Torsion angles (°).

C1^i−Se−C1−C2 = 48.8(6)	C3−C1−C2−O1 = 176.0(8)
Se−C1−C2−O1 = −62.5(8)	C3−C1−C2−O2 = 59.7(10)
C1−C2−O1−C2^i = 77.3(9)	C1−C2−O2−C4 = −171.2(8)
C1^i−Se−C1−C3 = 172.0(6)	C4−O2−C2−O1 = 70.3(10)

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