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# Formation of 2-phenylselenenylenones and 2-haloenones from enones. Mechanistic and synthetic aspects, X-ray crystal structures of intermediates

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## Abstract

The structure of *trans*-3-chloro-2-phenylselenenylcyclohexanone (**1**) was determined by X-ray diffraction. Although this and similar compounds were readily dehydrohalogenated to give vinylic selenides, they were ruled out as intermediates in the synthesis of 2-phenylselenenylenones from enones and the 1 : 1 complex of PhSeCl and pyridine.

2-Phenylselenenylenones were halogenated by treatment with $SO_2Cl_2$ or $Br_2$ to give unstable products of 1,2-addition to the double bond. The structure of *trans*-2,3-dichloro-2-phenylselenenylcyclohexanone (**5**) was determined by X-ray diffraction. Since this compound does not readily lose a molecule of PhSeCl in solution, it was considered to be unlikely as an intermediate in the PhSeCl · pyridine induced conversion of 2-cyclohexenone to 2-chloro-2-cyclohexenone. However, upon treatment of phenylselenenylenones with $SO_2Cl_2$ in the presence of pyridine, rapid formation of the corresponding $\alpha$-chloroenone was observed under mild conditions.

## Introduction

In 1979 Liotta and coworkers [1] reported the conversion of enones to 2-phenylselenenylenones by treatment with a stoichiometric amount of the 1 : 1 complex of phenylselenenyl chloride and pyridine (eq. 1). A few years later Ley [2] observed the formation of 2-haloenones when enones were heated in methylene chloride with three equivalents of similar reagents (eq. 2). 2-Phenylselenenylenones were shown to be intermediates in this transformation. As suggested by the authors, several mechanistic alternatives are possible for both reactions, none of which has yet been firmly established. Our recent finding [3] that phenylselenenyl chloride gives an unstable, but isolable, addition compound **1** with 2-cyclohexenone, prompted us to

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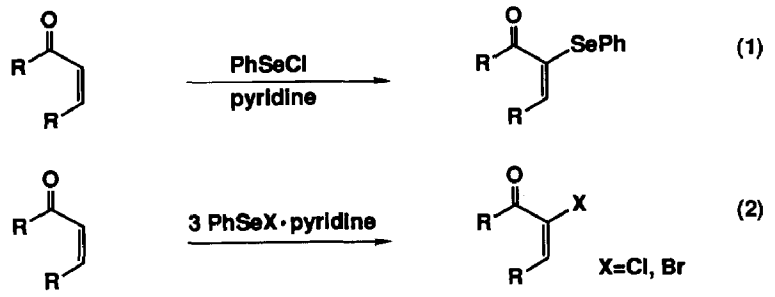
see whether such materials could have any application in the phenylselenenylenone and chloroenone syntheses.



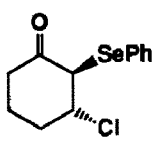

## Results

Enones generally form $\alpha'$-phenylselenenylated enones when treated with PhSeCl [4]. This is evident from the ready conversion of the products into cross conjugated enones upon oxidation/selenoxide elimination. However, examples are known in which the elements of chlorine and selenium add across the double bond instead [5–7]. The regiochemistry of this process is highly substrate-dependent. We recently isolated an addition product **1** (83% yield) when phenylselenenyl chloride was stirred in dry ether with 2-cyclohexenone [3]. The stereo- and regiochemistry of addition were revealed by determining the molecular structure of the product by an X-ray diffraction study at low temperature. As shown in Fig. 1a, the chloro and phenylselenenyl groups are located *trans* to each other, with selenium bonded to the 2-position.

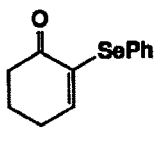
In order to investigate the possible intermediacy of compound **1** in the synthesis of 2-phenylselenenyl-2-cyclohexenone (**2**) according to eq. 1, the original experiment [1] (1.0 equiv. PhSeCl, 1.05 equiv. pyridine and 0.95 equiv. 2-cyclohexenone) was repeated in an NMR tube. The conversion to product, as determined by integration, was monitored at intervals during 144 h and compared with that observed in a parallel experiment with compound **1** (1.0 equiv. together with pyridine 1.05 equiv.). The degree of conversion of 2-cyclohexenone into compound **2** increased gradually during the first 22 h (60% conversion) but then remained constant, and no formation of compound **1** was ever detected. In contrast, the extent of conversion of compound **1** to enone **2** increased steadily (though more slowly) throughout (40% after 22 h; 85% after 144 h). This suggests that addition compounds similar to **1** are not involved in the reaction shown in eq. 1.

In order to facilitate the elimination of HCl from compound **1**, triethylamine, a stronger base than pyridine, was tried. When a slight excess of the amine was used the reaction was complete within 3 h at ambient temperature. The addition of PhSeCl and the triethylamine-induced elimination could, indeed, be performed consecutively in one pot, to provide a highly competitive route to certain 2-phenylselenenylenones from enones [8*]. Thus, compounds **2**, **3** and **4** were obtained in 85, 73, and 53% yields, respectively, from the corresponding cyclic enones.

* Reference number with asterisk indicates a note in the list of references.



1



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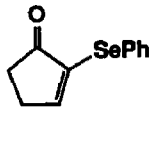

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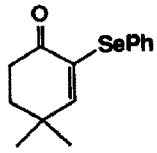
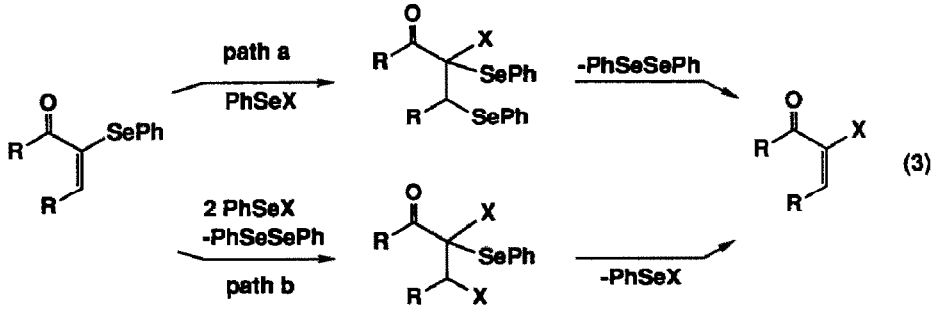


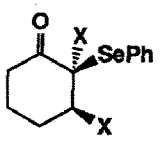
4

The phenylselenenyl halide induced conversion of 2-phenylselenenylenones into 2-haloenones (eq. 2) has been suggested to involve the addition of PhSeX to the double bond followed by elimination of diphenyl diselenide (eq. 3, path a) [2]. It occurred to us that this transformation might occur by halogenation (via selenium) of the double bond followed by elimination of PhSeX (eq. 3, path b). Phenyl-

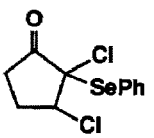



(3)

selenenyl chloride is known to act as a chlorinating agent towards selenides with formation of diphenyl diselenide [3,9]. In order to examine this possibility, selenide **2** was treated in chloroform with 1 equiv. of sulfuryl chloride to give an unstable chlorination product **5**, which was isolated in 98% yield after chromatography. The highly crystalline material rapidly decomposed in air at room temperature, but in a freezer ($-20\,^{\circ}C$) the material remained unchanged for several months. The molecular structure of compound **5** was determined by X-ray crystallography at low temperature. As shown in Fig. 1b the two chlorine atoms are oriented *trans* to each other. Compound **3** similarly gave the dichloride **7** in 63% yield. However, the dibromide **6**, prepared from selenide **2** and bromine, decomposed during chromatography (loss of PhSeBr), and only a minute amount of the pure material was recovered and characterized. The phenylselenenylated enal **8** was rapidly converted into the corresponding chloroenal **9** (96% yield) when treated with $SO_2Cl_2$ in $CHCl_3$ at $0\,^{\circ}C$ for 1 h.



5 X=Cl
6 X=Br



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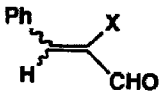


8 X=SePh
9 X=Cl

Thus, the ease of formation of haloenones (via loss of PhSeX) from halogenated phenylselenenyl-enones and -enals seems to be highly substrate-dependent. It was found that stability of the halogenation products in solution was generally greater than that in the solid state. When compound **2** was treated with one equivalent of

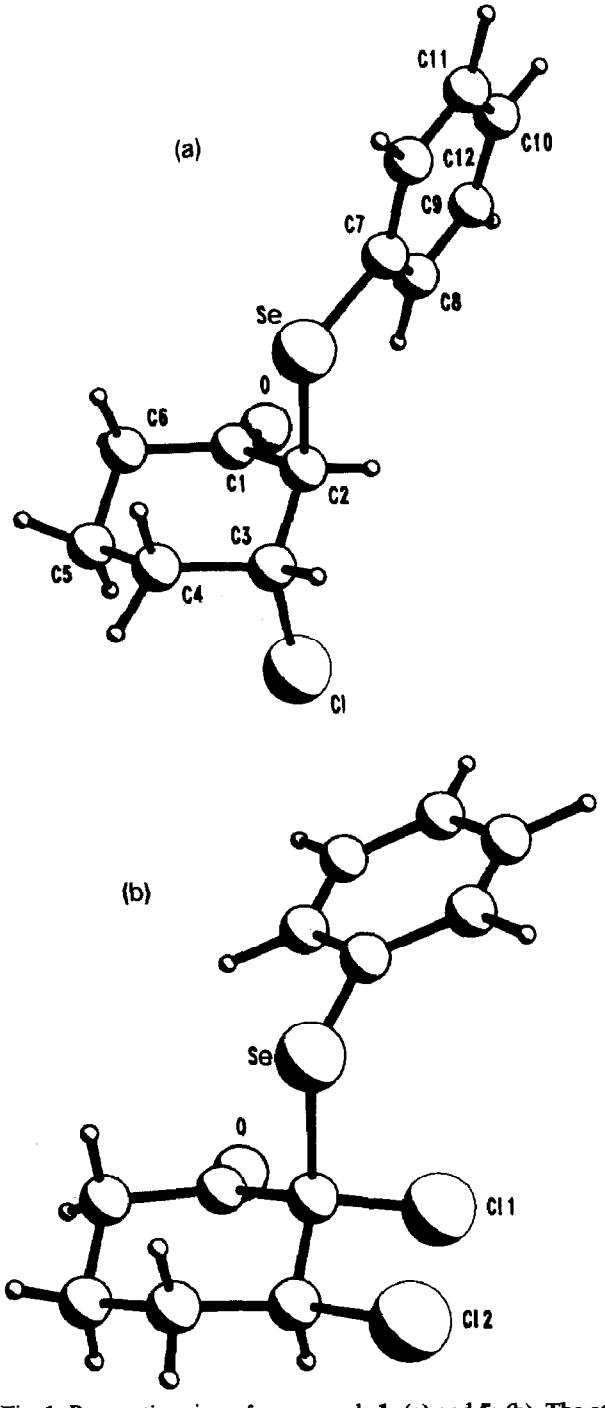
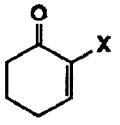


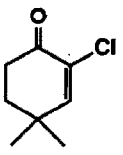

Fig. 1. Perspective view of compounds **1**; (a) and **5**; (b). The atomic numbering omitted in (b) is identical to (a).

bromine in chloroform, 2-bromo-2-cyclohexenone (**10**) was isolated in 67% yield after 30 h at ambient temperature. Selenide **4** similarly afforded chloroenone **12** upon treatment with sulfuryl chloride (51% yield). However, loss of a molecule of

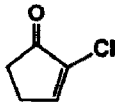
phenylselenenyl chloride from the chlorinated selenide **5** required much more forcing reaction conditions. Refluxing of a chloroform solution of compound **5** and two equivalents of pyridine for 22 h gave chloroenone **11** in 59% yield. A similar yield (58%) of chloroenone was obtained by treatment of vinylic selenide **2** with two equivalents of sulfuryl chloride at ambient temperature for 2 h. However, an equally mild but higher-yield conversion of 2-phenylselenenylenones to 2-chloroenones occurred when a mixture of the selenide and two equivalents of pyridine was treated dropwise with one equivalent of sulfuryl chloride. This procedure gave chloroenones **11**, **12** and **13** in 62, 76 and 62% isolated yields, respectively, from the corresponding phenylselenenylated enones.




**10** X=Br
**11** X=Cl




**12**




**13**

All attempts to replace the vinylic phenylselenenyl group of compound **2** by iodine were unsuccessful.

In order to decide between the two mechanisms shown in eq. 3, the conversions of selenides **2**, **5** and 2-cyclohexenone into chloroenone **11** were studied under a variety of conditions: When selenide **2** was treated in an NMR tube ($CDCl_3$) with 2 equivalents of PhSeCl, the dichloride **5** was rapidly formed (ratio **2**/**5** = 1/2 after 1 h 15 min). However, when the reaction was carried out in the presence of pyridine (vinylic selenide added to 2 equivalents of preformed 1 : 1 complex of PhSeCl and pyridine) a slow conversion of compound **2** into the vinylic chloride **11** was observed (63% conversion after 5 h; 85% conversion after 120 h), and only trace amounts of selenide **5** were present. Compound **5** did not show any tendency to lose PhSeCl during 30 min refluxing of its solution in $CDCl_3$ containing pyridine (2 equivalents). With PhSeCl (1 equivalent) and/or diphenyl diselenide (1 equivalent) present, only a trace amount of compound **11** was formed. On the other hand, selenide **2** was converted into a 27/64 mixture of compounds **5** and **11** under similar reaction conditions (2 equivalents of PhSeCl · pyr.; 9% unreacted **2**). Continued heating at reflux resulted in the slow conversion of compound **5** into compound **11** (ratio **11**/**5** = 82/18 after 5.5 h). When the original experiment (1 equivalent 2-cyclohexenone; 3 equivalents PhSeCl · pyridine) was performed in $CD_2Cl_2$ at reflux temperature, only a trace of compound **5** was present as indicated by $^1H$ NMR spectroscopy (spectrum recorded at intervals during 4.5 h). After ca. 30 min all the 2-cyclohexenone was consumed and several new, still unidentified, peaks appeared in the spectrum. These peaks gradually disappeared to give a clean 85/15 mixture of compounds **11** and **2** after 4.5 h.

The reluctance of compound **5** to lose PhSeCl and the failure to detect substantial amounts of the material in the original experiment seem to indicate that the dichloride **5** is not involved in the conversion of 2-cyclohexenone into 2-chloro-2-cyclohexenone according to eq. 2.

Table 1

Fractional atomic coordinates for compound **1**, estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Se | 0.02586(5) | 0.00000(0) | 0.16621(5) |
| Cl | 0.3818(2) | −0.2261(3) | 0.0194(2) |
| O | 0.3360(6) | −0.3232(10) | 0.3736(5) |
| C(1) | 0.3072(6) | −0.1537(12) | 0.3028(6) |
| C(2) | 0.1961(6) | −0.1609(11) | 0.1597(6) |
| C(3) | 0.2474(7) | −0.0452(11) | 0.0491(6) |
| C(4) | 0.3081(7) | 0.1874(12) | 0.0941(7) |
| C(5) | 0.4259(7) | 0.1835(12) | 0.2348(8) |
| C(6) | 0.3751(7) | 0.0732(13) | 0.3476(7) |
| C(7) | −0.0581(6) | −0.2175(12) | 0.2584(6) |
| C(8) | 0.0047(7) | −0.4180(13) | 0.3120(6) |
| C(9) | −0.0682(7) | −0.5648(12) | 0.3762(6) |
| C(10) | −0.2001(7) | −0.5095(18) | 0.3846(6) |
| C(11) | −0.2605(8) | −0.3029(14) | 0.3312(7) |
| C(12) | −0.1891(7) | −0.1552(13) | 0.2678(7) |

*Crystallographic results*

The cyclohexanone ring adopts the expected chair conformation in both structures **1** and **5**, with no unusual bond lengths (Tables 2 and 4). Comparison of the structure of **5** with that of **1** shows that the presence of a chlorine atom in position C(2) of compound **5** primarily affects the conformation of the phenylselenenyl group. The dihedral angle between a least-squares plane in the cyclohexanone group and a least-squares plane of the phenyl ring is 77.8(2)° in structure **1**, whereas the corresponding angle in structure **5** is 19.0(2)°. Furthermore, the presence of Cl(1) increases the torsion angle C(3)–C(2)–Se–C(7) by 6.1(5)° relative to that in compound **1**. The distance between Cl(1) and Cl(2) in structure **5** is 3.261(3) Å, which is less than the expected sum of the Van der Waals radii, 3.60 Å. This is probably the cause of the minor differences in the angles within the cyclohexanone ring. The C(2)–Se and Se–C(7) distances differ in the two structures, but as the

Table 2

Selected bond distances (Å) and angles (°) for compound **1**, estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Se–C(2) | 1.969(6) | C(2)–Se–C(7) | 101.7(3) |
| Se–C(7) | 1.928(7) | O–C(1)–C(6) | 123.9(6) |
| Cl–C(3) | 1.815(7) | O–C(1)–C(2) | 120.3(6) |
| O–C(1) | 1.214(9) | C(2)–C(1)–C(6) | 115.8(5) |
| C(1)–C(2) | 1.524(7) | Se–C(2)–C(1) | 109.8(4) |
| C(1)–C(6) | 1.511(10) | C(1)–C(2)–C(3) | 111.6(5) |
| C(2)–C(3) | 1.528(10) | Se–C(2)–C(3) | 107.3(4) |
| C(3)–C(4) | 1.518(9) | Cl–C(3)–C(2) | 106.8(4) |
| C(4)–C(5) | 1.537(9) | C(2)–C(3)–C(4) | 112.5(5) |
| C(5)–C(6) | 1.529(11) | Cl–C(3)–C(4) | 109.8(5) |
| | | C(3)–C(4)–C(5) | 112.5(6) |
| | | C(4)–C(5)–C(6) | 110.9(6) |
| | | C(1)–C(6)–C(5) | 112.4(6) |

Table 3

Fractional atomic coordinates for compound **5**, estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Se | 0.51512(7) | 0.25887(4) | 0.22874(5) |
| Cl(1) | 0.7155(2) | 0.0641(1) | 0.2052(1) |
| Cl(2) | 0.3956(2) | 0.0646(1) | 0.3869(1) |
| O | 0.5969(5) | 0.1045(3) | −0.0235(3) |
| C(1) | 0.4823(6) | 0.1222(3) | 0.0442(4) |
| C(2) | 0.5139(6) | 0.1212(3) | 0.1746(4) |
| C(3) | 0.3682(7) | 0.0649(4) | 0.2338(4) |
| C(4) | 0.1901(6) | 0.1046(4) | 0.2034(5) |
| C(5) | 0.1630(7) | 0.0970(4) | 0.0723(5) |
| C(6) | 0.3029(8) | 0.1510(5) | 0.0069(5) |
| C(7) | 0.7324(6) | 0.3024(3) | 0.1704(4) |
| C(8) | 0.8615(7) | 0.3228(4) | 0.2510(4) |
| C(9) | 1.0172(7) | 0.3611(4) | 0.2145(5) |
| C(10) | 1.0444(8) | 0.3795(4) | 0.0984(6) |
| C(11) | 0.9174(9) | 0.3592(4) | 0.0194(5) |
| C(12) | 0.7594(8) | 0.3199(4) | 0.0552(4) |

Table 4

Selected bond distances (Å) and angles (°) for compound **5**, estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Se–C(2) | 1.982(5) | C(2)–Se–C(7) | 100.6(2) |
| Se–C(7) | 1.911(5) | O–C(1)–C(6) | 122.8(4) |
| Cl(1)–C(2) | 1.778(5) | O–C(1)–C(2) | 121.7(4) |
| Cl(2)–C(3) | 1.789(5) | C(2)–C(1)–C(6) | 115.4(4) |
| O–C(1) | 1.213(6) | Cl(1)–C(2)–C(1) | 109.7(3) |
| C(1)–C(2) | 1.532(6) | Se–C(2)–C(1) | 107.8(3) |
| C(1)–C(6) | 1.505(8) | Se–C(2)–Cl(1) | 110.4(2) |
| C(2)–C(3) | 1.531(7) | C(1)–C(2)–C(3) | 109.6(4) |
| C(3)–C(4) | 1.521(7) | Cl(1)–C(2)–C(3) | 109.7(3) |
| C(4)–C(5) | 1.539(8) | Se–C(2)–C(3) | 109.6(3) |
| C(5)–C(6) | 1.517(8) | Cl(2)–C(3)–C(2) | 111.3(3) |
| | | C(2)–C(3)–C(4) | 112.7(4) |
| | | Cl(2)–C(3)–C(4) | 109.5(3) |
| | | C(3)–C(4)–C(5) | 108.9(4) |
| | | C(4)–C(5)–C(6) | 111.7(5) |
| | | C(1)–C(6)–C(5) | 112.9(5) |

difference between the sums of the two distances is only 0.004 Å, this is not a real effect. Refinement of the coordinates for the other enantiomer of structure **1** gave an *R*-value higher by 0.45 and 0.64% for $R_w$, indicating that the choice of enantiomer is correct. Neither structures show any intermolecular contacts below the sum of the Van der Waals radii. Atomic coordinates for structures **1** and **5** are given in Tables 1 and 3, respectively.

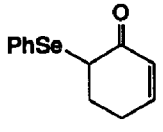
## Discussion

One of the mechanisms suggested by Liotta for phenylselenenylenone formation from enones involved formation of the addition compound **1** (with loss of HCl) [1].

However, this pathway was ruled out because PhSeCl and 2-cyclohexenone, in the absence of pyridine in chlorocarbon solvent, gave a compound formulated as 6-phenylselenenyl-2-cyclohexenone (**14**) [10*]. The slow pyridine-induced elimination of compound **1** to give 2-phenylselenenyl-2-cyclohexenone, and its absence in the original preparation of compound **2**, seem to indicate that it is not relevant to the reaction. The mechanism adopted by Liotta involved 1,4-addition of pyridine followed by phenylselenenylation of the resulting enolate and loss of a pyridinium ion to give the observed product. Similar mechanisms were proposed for the reactions of phenylselenenyl amides with enones [11] and enals [12] and for the lithium diisopropyl amide-assisted 2-phenylselenenylation of $\alpha,\beta$-unsaturated esters [13].

Alkenes bearing electron-withdrawing substituents are known to add phenylselenenyl halides in a 1,2-fashion with rather poor regiocontrol [6,7]. However, upon treatment with base only the isomer bearing the phenylselenenyl group next to the electron-withdrawing group undergoes elimination of hydrogen halide [6]. The one-pot syntheses of compounds **2**, **3** and **4** from the corresponding enones provide additional examples of this reaction which up to now has been applied only to acyclic enones.

Little is known about the halogenation of vinylic selenides. Hölzle and Jenny [14] observed the formation of a vinylic bromide **15** when selenide **16** was treated with $Br_2$. This reaction is likely to involve halogenation of the double bond followed by loss of an arylselenenyl bromide (although the authors did not consider this possibility). Upon bromination and aqueous work-up, the acrylic acid derivative **17** was decarboxylated, with loss of HBr to afford a vinylic selenide **18** [15]. To our knowledge, compounds **5**–**7** are the first isolated and characterized products of 1,2-addition of halogen to the double bond of a vinyl selenide. Owing to the reluctance of some of these compounds to eliminate a molecule of PhSeX, they were considered unlikely to be intermediates in the PhSeX · pyridine induced conversion of enones to haloenones [16*]. The unstable 1,2-arrangement of phenylselenenyl groups suggested by Ley for the transformation (eq. 3; path a) has been discussed by others [5,17,18], but to the best of our knowledge no such compounds have ever been isolated.

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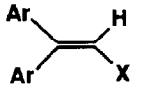
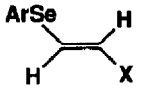


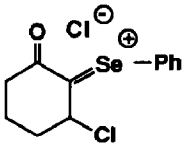

15 X=Br
16 X=2-nitro-phenylselenenyl



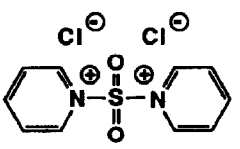

17 X=COOH
18 X=Br

As can be seen from Fig. 1b the phenylselenenyl group of compound **5** is located *cis* to the chlorine atom in the 3-position. This does not necessarily mean that the elimination of PhSeCl is a *syn* process, since inversion of configuration at carbon C(2) could occur via a selenonium ion **19**. The ease of elimination of phenylselenenyl halides from halogenated phenylselenenylenones and phenylselenenylenals is highly substrate-dependent, with the chlorinated compounds the less reactive. The mild $SO_2Cl_2$-induced conversion of selenides **2**–**4** to their corresponding chloroenones, in the presence of pyridine, is therefore remarkable. Since compound **5** does

not decompose in solution in the presence of pyridine, addition of chlorine to the double bond is unlikely to occur in the reaction. Instead, the sulfuryl chloride seems to react preferentially with the pyridine present to form a reagent capable of converting phenylselenenylenones to chloroenones. In support of this view, the preformed 2:1 complex of pyridine and $SO_2Cl_2$ was shown to convert selenide **2** rapidly into chloroenone **11** at ambient temperature with elimination of PhSeCl. The 2:1 complex of pyridine and sulfuryl chloride has been formulated as an addition compound **20** [19]. However, we can see no obvious pathway whereby this reagent would yield chloroenones from phenylselenenylenones.




**19**




**20**

Since phenylselenenylenones are readily available from enones by several routes [1,20], their conversion, via halogenation and elimination of PhSeX, to 2-haloenones could offer a useful and less expensive (when account is taken of the high cost of phenylselenenyl halides) alternative to the selenium-assisted one-pot synthesis from enones.

## Experimental

All melting points are uncorrected. NMR spectra ($\delta$ (ppm)) were recorded on Bruker AM 400 and WP 200 instruments, operating at 400 and 200 MHz, respectively, and were recorded with $CDCl_3$ solutions containing tetramethylsilane as the internal standard. Chloroform was washed several times with water to remove ethanol and was dried over $CaCl_2$. Pyridine was dried over KOH, distilled, and kept over molecular sieves (4Å). Diethyl ether was dried over sodium. Sulfuryl chloride was freshly distilled before use. *trans*-3-Chloro-2-phenylselenenylcyclohexanone [3] and 2-phenylselenenyl-3-phenyl-2-propenal [1] were prepared as previously described. Crystals of compound **1** suitable for X-ray crystallography were obtained by recrystallization from $CH_2Cl_2$/hexane. All enones were obtained from commercial suppliers.

*2-Phenylselenenyl-2-cyclohexenone (2)*

A mixture of phenylselenenyl chloride (1.0 g, 5.2 mmol), 2-cyclohexenone (0.50 g, 5.2 mmol), and dry diethyl ether (10 ml) was stirred at 0 °C for 2 h. Triethylamine (0.63 g, 6.2 mmol) was then added and the mixture stirred for 3 h at ambient temperature, then treated with 10% aqueous hydrochloric acid. The organic phase was separated, dried, and evaporated and the residue purified by flash chromatography ($SiO_2$; $CH_2Cl_2$/hexanes = 1/1) to give 1.11 g (85%) of compound **2**, m.p. 67 °C (lit. [20] 49.5–51 °C). The $^1H$ and $^{13}C$ NMR spectra were in good agreement with published data [20].

2-Phenylselenenyl-2-cyclopentenone (**3**), m.p. 42 °C (lit. [20] 35–37 °C) and 4,4-dimethyl-2-phenylselenenyl-2-cyclohexenone (**4**), m.p. 79–81 °C, were similarly pre-

pared (reaction time at 0 °C 1.5 h) in 73 and 53% yield, respectively. $^{13}C$ NMR for compound **4**: $\delta_C$ 27.53, 34.49, 35.32, 35.95, 127.24, 128.40, 129.47, 132.40, 135.95, 155.53, 195.61.

*trans-2,3-Dichloro-2-phenylselenenylcyclohexanone (5)*

To a stirred solution of 2-phenylselenenyl-2-cyclohexenone (0.50 g, 2.0 mmol) in chloroform (5 ml) at 0 °C was added sulfuryl chloride (0.27 g, 2.0 mmol). After a few minutes the solvent was evaporated off and the residue purified by flash chromatography ($SiO_2$; $CH_2Cl_2$/hexanes = 1/1) to give 0.63 g (98%) of compound **5**, m.p. 112–114 °C (dec.). Crystals suitable for X-ray crystallography were obtained by recrystallization from $CH_2Cl_2$/hexanes. $\nu_{max}$ (KBr) 1709 $cm^{-1}$. $\delta_H$ 1.74 (m, 1 H), 2.15 (m, 1 H), 2.42–2.48 (several peaks, 2 H), 2.61 (m, 1 H), 3.07 (ddd, 1 H, *J* 6.0, 11.3 and 14.8 Hz), 4.35 (m, 1 H), 7.34–7.37 (m, 2 H), 7.44 (m, 1 H), 7.66 (m, 2 H). $\delta_C$ 21.95, 32.81, 36.08, 68.31, 82.86, 124.76, 129.26, 130.23, 137.42, 195.76.

2,3-Dichloro-2-phenylselenenylcyclopentanone (**7**) was similarly prepared in 63% yield, m.p. 65–67 °C (dec.). This material could be kept only for a few days in the freezer (−20 °C) before it started to decompose. $\delta_H$ 2.41 (m, 1 H), 2.54–2.61 (several peaks, 2 H), 2.86 (m, 1 H), 4.49 (m, 1 H), 7.34–7.38 (m, 2 H), 7.47 (m, 1 H), 7.60 (m, 2 H). $\delta_C$ 29.27, 33.12, 66.50, 124.40, 129.21, 130.49, 137.91, 197.25.

2,3-Dibromo-2-phenylselenenylcyclohexanone (**6**), similarly prepared from bromine and selenide **2**, decomposed during chromatography (loss of PhSeBr). A small amount (ca. 5%) of the compound passed through the column unchanged. $\delta_H$ 1.86 (m, 1 H), 2.29 (m, 1 H), 2.44 (m, 1 H), 2.59 (m, 1 H), 2.89–3.00 (several peaks, 2 H), 4.57 (m, 1 H), 7.30–7.49 (several peaks, 3 H), 7.77 (m, 2 H). $\delta_C$ 22.86, 32.65, 35.42, 61.06, 77.34, 125.93, 129.17, 130.24, 137.56, 196.58.

*2-Chloro-3-phenyl-2-propenal (9)*

Sulfuryl chloride (0.19 g, 1.4 mmol) was added to a stirred solution of a 68/32 mixture [21*] (0.40 g) of 2-phenylselenenyl-3-phenyl-2-propenal (**8**) and 2-chloro-3-phenyl-2-propenal in $CHCl_3$ (5 ml) at 0 °C. After a few minutes the solution began to turn orange-red owing to the formation of phenylselenenyl chloride. Evaporation of the solvent after 1 h and flash chromatography ($SiO_2$; $CHCl_2$/hexanes = 1/1) afforded 0.26 g (96% based on compound **8**) of compound **9**. The $^{13}C$ NMR spectrum of the material was in good agreement with that assigned to the *Z*-isomer of compound **9** [22].

*2-Bromo-2-cyclohexenone (10)*

A solution of 2-phenylselenenyl-2-cyclohexenone (0.30 g, 1.2 mmol) and bromine (0.20 g, 1.2 mmol) in $CHCl_3$ (15 ml) was stirred for 30 h. Evaporation and flash chromatography ($SiO_2$; $CH_2Cl_2$/hexanes = 1/1) afforded 0.14 g (67%) of compound **10**, m.p. 75–76 °C (lit. [2] 75–76 °C).

4,4-Dimethyl-2-phenylselenenyl-2-cyclohexenone (**4**) was similarly converted into 2-chloro-4,4-dimethyl-2-cyclohexenone (**12**), m.p. 34 °C (lit. [23] ca. 15 °C), by treatment with $SO_2Cl_2$ for 20 h (51% isolated yield). $\delta_C$ 27.64, 34.73, 35.40, 35.75, 130.06, 155.32, 191.14.

*2-Chloro-2-cyclohexenone (11)*

To a solution of 2-phenylselenenyl-2-cyclohexenone (0.25 g, 1.0 mmol) and pyridine (0.16 g, 2.0 mmol) in $CHCl_3$ (10 ml) was added sulfuryl chloride (0.14 g,

1.0 mmol). The orange-red colour of phenylselenenyl chloride started to develop within a few minutes. Hydrolysis (10% HCl aq.) after 3 h and flash chromatography ($SiO_2$; $CH_2Cl_2$/hexanes = 1/1) afforded 0.080 g (62%) of compound **11**, m.p. 71–72 °C (lit. [2] 71–72 °C).

By a similar procedure, 2-chloro-4,4-dimethyl-2-cyclohexenone (**12**) and 2-chloro-2-cyclopentenone (**13**) were obtained in 76 and 62% yield, respectively, from the phenylselenenylated enones **4** and **3**. The $^1H$ NMR data for compound **13** were in good agreement with those previously reported [20].

2-Chloro-2-cyclohexenone (**11**) was also obtained from 2-phenylselenenyl-2-cyclohexenone (**2**) by to the following procedures:

(a) Sulfuryl chloride (0.16 g, 1.2 mmol) was added to a solution of compound **2** (0.30 g, 1.2 mmol) in $CHCl_3$ (15 ml). After 15 min pyridine (0.19 g, 2.4 mmol) was added and the mixture heated under reflux for 22 h. Workup as above afforded 0.092 g (59%) of compound **11**.

(b) Sulfuryl chloride (0.32 g, 2.4 mmol) was added to a stirred solution of compound **2** (0.30 g, 1.2 mmol) in $CHCl_3$ (15 ml). After 2 h at ambient temperature the solvent was evaporated off and the residue purified by flash chromatography to give 0.090 g (58%) of compound **11**.

*Reactions in an NMR tube*

*2-Phenylselenenyl-2-cyclohexenone formation from 2-cyclohexenone [1]*

Pyridine (6.7 μl) and PhSeCl (0.015 g) were mixed in $CDCl_3$ (1 ml). After 15 min 2-cyclohexenone (7.4 μl) was added and the NMR spectrum recorded at intervals during 144 h. The following 2-cyclohexenone/**2** ratios were obtained by integration of the peaks at 6.02 ppm (enone) and 6.46 ppm (phenylselenenylated enone): 97/3 (3 h), 84/16 (5 h), 40/60 (22 h), 38/62 (46 h), 40/60 (144 h).

*2-Phenylselenenyl-2-cyclohexenone formation from compound 1*

Pyridine (6.7 μl) and compound **1** (0.0225 g) were mixed in $CDCl_3$ (1 ml) and the NMR spectrum recorded at intervals. The following **1**/**2** ratios were obtained by integration of the peaks at 4.84 ppm (compound **1**) and 6.46 ppm (compound **2**): 91/9 (3 h), 60/40 (22 h), 41/59 (48 h), 15/85 (144 h).

*2-Chloro-2-cyclohexenone (11) formation from compound 2*

Pyridine (6.7 μl) and PhSeCl (0.015 g) were mixed in $CDCl_3$ (1 ml). After 15 min compound **2** (0.010 g) was added and the NMR spectrum recorded at intervals. The following **11**/**2** ratios were obtained by integration of the peaks at 7.14 ppm (compound **11**) and 6.46 ppm (compound **2**): 30/70 (3/4 h), 63/57 (5 h), 80/20 (26 h), 85/15 (120 h).

A solution of pyridine (32 μl), PhSeCl (0.076 g), and compound **2** (0.050 g) in $CDCl_3$ (2 ml) was heated under reflux for 30 min. The integrated NMR spectrum showed the presence of compounds **2**, **5** and **11** in a ratio of 9/27/64. After a further 4 h refluxing only compounds **11** and **5** remained, in a ratio of 82/18.

*2-Chloro-2-cyclohexenone (11) formation from 2-cyclohexenone*

A solution of pyridine (0.125 g), PhSeCl (0.30 g) and 2-cyclohexenone (0.050 g) in $CD_2Cl_2$ (3.5 ml) was heated under reflux and the NMR spectrum was recorded at

intervals during 5.5 h. After 30 min the signals from the enone had disappeared. New peaks appeared at 7.20, 7.00, 6.10, 5.41 and 3.12 ppm. The new peaks gradually disappeared to give a clean 85/15 mixture of compounds **11** and **2** after 5.5 h.

*Crystal data*

Compound **1**. $C_{12}H_{13}ClOSe$, $M = 287.65$, Monoclinic space group, $P2_1$, $a$ 9.998(3), $b$ 5.928(2), $c$ 10.088(3) Å, $\beta$ 108.09(3)°, $V$ 568.35(3) Å$^3$, least-squares refinement of 22 centred reflections, $16.56 \leq 2\theta \leq 39.69°$, $\lambda$ 0.71073 Å, $Z = 2$, $D_c$ 1.681 g cm$^{-3}$. Colourless transparent crystals which decay within minutes at ambient temperature to give a yellow compound. Crystal specimen, flat prism, 0.08 × 0.20 × 0.45 mm, $\mu$ 34.75 cm$^{-1}$, $F(000) = 278$.

Compound **5**. $C_{12}H_{12}Cl_2OSe$, $M = 322.09$, Monoclinic space group $P2_1/c$, $a$ 7.739(3), $b$ 13.653(4), $c$ 11.614(4) Å, $\beta$ 90.31(5)°, $V$ 1227.1(7) Å$^3$, least-squares refinement of 24 centred reflections, $25.38 \leq 2\theta \leq 36.41°$, $\lambda$ 0.71073 Å, $Z = 4$, $D_c$ 1.743 g cm$^{-3}$. Colourless transparent crystals which decay within hours at ambient temperature to give a pale yellow compound. Crystal specimen, rhombic, 0.30 × 0.30 × 0.50 mm, $\mu$ 34.42 cm$^{-1}$, $F(000) = 640$.

*Data collection and processing*

Compound **1**. STOE AED-2 diffractometer, $\omega/2\theta$ scan mode, scan width 1.40–1.60°, scan speed 1.20–4.80 deg min$^{-1}$, graphite monochromated Mo-$K_\alpha$ radiation, 1809 unique reflections collected, $2.12 \leq \theta \leq 29.90°$, $T$ 153 K. Three standard reflections indicated no significant decay. No absorption correction was applied.

Compound **5**. STOE AED-2 diffractometer, $\omega/2\theta$ scan mode, scan width 1.05–1.26°, scan speed 0.90–3.60 deg min$^{-1}$, graphite monochromated Mo-$K_\alpha$ radiation 3104 reflections collected, $1.49 \leq \theta \leq 29.96°$, $T$ 153 K, crystal decay within 2% for 3 monitored reflections. No absorption correction was applied.

*Structure analysis and refinement*

Structures were solved by SHELXS-86 [24], full-matrix least squares refinement, minimizing $\Sigma w(\Delta F)^2$, with SHELX-76 [25], all non-hydrogen atoms anisotropic, H-atoms in cyclohexanone ring isotropically refined with common temperature factor and group refinement of C–H distances, refined to 1.01 Å, compound **1** and 0.95 Å for compound **5**. H-atoms in phenyl ring were geometrically fixed with common temperature factor.

Structure **1**: 177 parameters refined using 1660 reflections, $|F| \geq 4\sigma(F)$, $R = 0.062$, $R_w = 0.076$, $w = 1/(\sigma^2 F + 0.002F^2)$, max $\Delta/\sigma$ for any parameter 0.030, max and min electron density in final $\Delta p$ map 2.93 and −2.24 eÅ$^{-3}$, in close vicinity of Se atom.

Structure **5**: 184 parameters refined using 2599 reflections, $|F| \geq 4\sigma(F)$, $R = 0.066$, $R_w = 0.090$, $w = 5.1274/(\sigma^2 F + 0.001F^2)$, max $\Delta/\sigma$ for any parameter 0.001, max and min electron density in final $\Delta p$ map 3.42 and −1.31 e Å$^{-3}$, in close vicinity of Se atom.

Atomic scattering parameters were from International Tables for X-ray Crystallography [26]. Geometrical calculations were made with PARST [27] and figures drawn with PLUTO [28].

**Acknowledgement**

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*Supplementary material available.* Complete lists of atom coordinates, thermal parameters, bond lengths, angles, least squares planes, and structure factors tables for compounds **1** and **5** are available from the authors.

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