

Synthesis and structure of 1-methyl-2,6-bis(electron-withdrawing group)-substituted selenabenzenes

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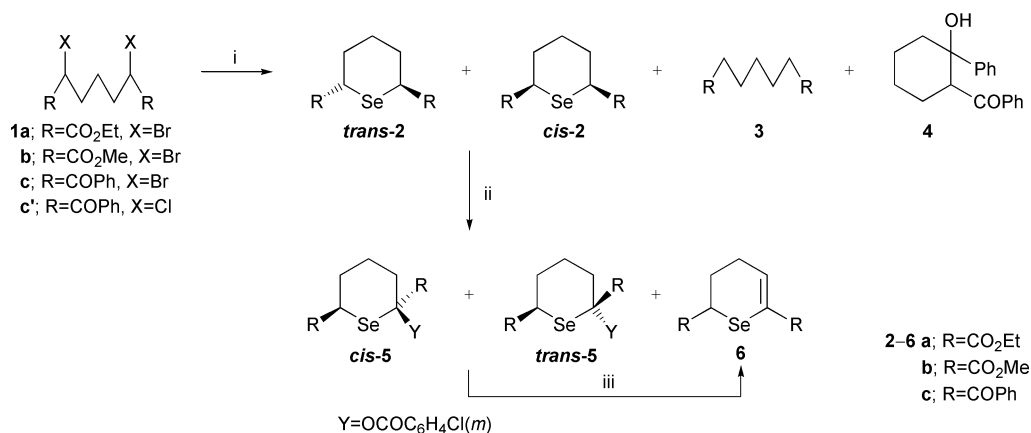
Selenabenzenes **12a–c** with two electron-withdrawing groups (EWGs) at the 2- and 6-positions were synthesized from dihalides **1a**, **1b** and **1c'** via seven steps and isolated as stable compounds at room temperature. According to X-ray structural analysis of the dibenzoyl derivative **12c**, the six-membered ring containing a selenium atom is almost planar and the structure of the selenium atom is tetrahedral with four sp³ hybridized orbitals.

The chemistry of heterobenzenes is one of the interesting research fields in heterocyclic chemistry and has recently been the focus of attention. Heterobenzenes containing a group 15 element have been widely studied and well documented,¹ and very recently, silabenzenes containing a group 14 element were prepared by Tokitoh *et al.*² Thiabenzenes have been studied for a long time and many papers reporting these studies have been published.³ In contrast, selenabenzenes were generated by proton-abstraction of the selenonium salts in the 1970s.⁴ After more than fifteen years cyano-stabilized selenanaphthalenes were synthesized⁵ and their reactions were studied. Successful synthesis of monocyclic selenabenzenes was required before their intrinsic properties would be studied. Monocyclic selenabenzene derivatives with one electron-withdrawing group (EWG) could not be isolated as stable compounds at room temperature but their generation was confirmed at –30 °C by NMR spectroscopy,⁶ whereas the corresponding thiabenzenes have been isolated as stable crystals.⁷ We recently succeeded in the isolation of monocyclic selenabenzene derivatives stabilized by two EWGs at the 2- and 6-positions.⁸ This paper describes the details of the synthesis and structure of monocyclic selenabenzenes having two EWGs such as ester or benzoyl groups.

which are key starting materials for the synthesis of selenabenzenes, were synthesized by ring closure reaction of dihalides **1a–c** and **1c'** with metal selenides (Scheme 1, Table 1).

The reaction of dibromides **1a,b** with sodium selenide⁹ at room temperature gave the desired cyclic compounds **2a,b**. The reaction of dibromide **1b** with sodium selenide under gentle reflux in ethanol gave only dehalogenated compound **3b** (78%), which would be formed by single electron reduction with sodium selenide or by the nucleophilic attack of sodium selenide on a halogen atom¹⁰ (entry 3). In the case of the benzoyl derivatives the reduction product **3c** was formed even from the reactions of both the bromide **1c** and the chloride **1c'** at 0 °C (entries 4 and 5). Therefore, lithium selenide,¹¹ having a higher oxidation–reduction potential than sodium selenide, was used. Although the reaction of the bromide **1c** with lithium selenide at room temperature formed **3c** in 54% yield, the reaction of the chloride **1c'** at 0 °C afforded selenane **2c** in moderate yield and by-products **3c** and **4** in low yields (entries 6 and 7).

Selenanes **2a–c** consisted of two isomers, *cis*-**2a–c** and *trans*-**2a–c**, and the isomers could be separated by PTLC on silica gel. The stereostructure of **2a** was determined by ¹H-NMR spectroscopy (Fig. 1). Two coupling constants, 2 and 12 Hz, due to H(2,6) of *cis*-**2a** are typical axial–equatorial and axial–axial coupling constants, respectively. Therefore, the two EWGs at the 2- and 6-positions are located in equatorial positions and the *cis* isomer takes the chair form shown in Fig. 1. On the other hand, if *trans*-**2a** takes a chair form or a boat form, the two protons at the 2- and 6-positions are not equivalent and should



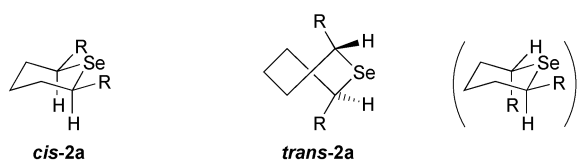
Scheme 1 Reagents and conditions: (i), Na₂Se or Li₂Se (1 equiv.), EtOH, 0.5 h; (ii), MCPBA (1.1 equiv.), CH₂Cl₂, 3 h; (iii), PPSE, ClCH₂CH₂Cl, reflux, 20 h.

Table 1 Cyclization of halides **1a–c** with metal selenides (see Scheme 1)

Entry	Dihalide	M ₂ Se	Temp.	Products (% yield)
1	1a	Na ₂ Se	rt	<i>trans</i> - 2a (31), <i>cis</i> - 2a (23)
2	1b	Na ₂ Se	rt	<i>trans</i> - 2b (35), <i>cis</i> - 2b (36)
3	1b	Na ₂ Se	reflux	3b (78)
4	1c	Na ₂ Se	0 °C	3c (58), 4 (10)
5	1c'	Na ₂ Se	0 °C	3c (29), 4 (2)
6	1c	Li ₂ Se	rt	3c (54), 4 (40)
7	1c'	Li ₂ Se	0 °C	<i>trans</i> - 2c (24), <i>cis</i> - 2c (25), 3c (14), 4 (19)

Table 2 Reactions of selenanes **2a–c** with MCPBA (see Scheme 1)

Entry	2	Temp.	Products (% yield)
1	<i>trans</i> - 2a	0 °C	5a (14), 6a (7)
2	<i>trans</i> - 2a	reflux	5a (70), 6a (16)
3	<i>cis</i> - 2a	0 °C	5a (35), 6a (16)
4	<i>cis</i> - 2a	reflux	5a (70), 6a (25)
5	<i>trans</i> - 2a + <i>cis</i> - 2a	reflux	5a (64), 6a (23)
6	<i>trans</i> - 2b + <i>cis</i> - 2b	reflux	5b (46), 6b (29)
7	<i>cis</i> - 2c	0 °C	<i>trans</i> - 5c (18), <i>cis</i> - 5c (24), 6c (39)
8	<i>trans</i> - 2c	0 °C	<i>trans</i> - 5c (13), <i>cis</i> - 5c (23), 6c (5)
9	<i>trans</i> - 2c	reflux	<i>trans</i> - 5c (7), <i>cis</i> - 5c (12), 6c (41)



$\delta_{\text{H}}(2,6)$ 3.87 (dd, *J* 2, 12)

$\delta_{\text{H}}(2,6)$ 3.87 (dd, *J* 4, 7)

Fig. 1 Conformation of **2a**.

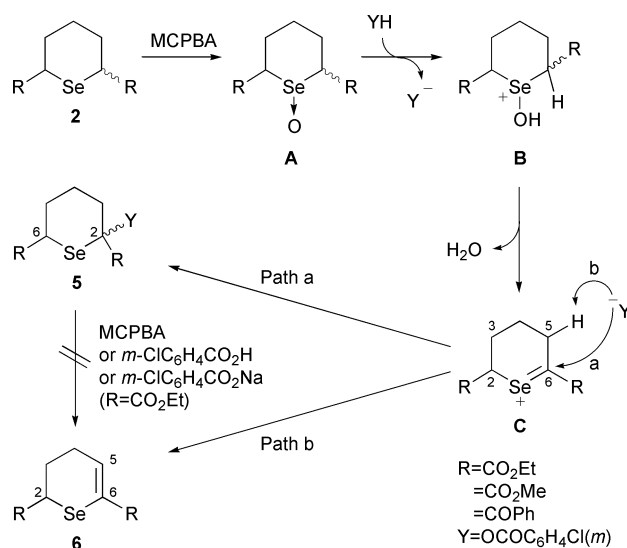
show complex signals. They were equivalent in a 400 MHz ¹H NMR spectrum with coupling constants of 4 and 7 Hz. This indicates that the twist conformation is adopted by *trans*-**2a**.

In order to construct a C=C bond between the 2- and 3-positions of the selenane ring, we used the method developed by our group,⁶ *i.e.* the peracid oxidation of selenanes **2a–c** and successive Pummerer reaction of the resulting selenoxides as shown in Scheme 1. Reactions of selenanes **2a–c** with *m*-chloroperbenzoic acid (MCPBA) gave benzoates **5a–c** and the desired products, dihydro-2*H*-selenines **6a–c** (Table 2).

Reactions of ethyl ester **2a** under reflux in dichloromethane gave **5a** and **6a** in better yields than those at 0 °C (entries 1, 2, 3 and 4). Both *cis* and *trans* isomers reacted similarly with MCPBA under reflux in dichloromethane (entries 2 and 4). Reaction of the *trans*-benzoyl derivative *trans*-**2c** under reflux in dichloromethane gave dihydroselenine **6c** in better yield than that at 0 °C (entries 8 and 9), whereas the reaction of *cis*-**2c** proceeded even at 0 °C to give **5c** and **6c** in good yields (combined yield of **5c** and **6c**: 81%) (entry 7).

Benzoates **5** and dihydroselenines **6** are formed *via* the pathways shown in Scheme 2. First, MCPBA oxidises the selenium atom to give selenoxide **A** and *m*-chlorobenzoic acid. The benzoic acid protonates the oxygen atom of selenoxide **A** to give selenonium ion **B**. The concurrent *m*-chlorobenzoate anion abstracts the α -proton of **B** to form intermediate **C** with dehydration. *m*-Chlorobenzoate anion nucleophilically attacks at the 6-position of **C** to give benzoates **5a–c** (path a) or deprotonates a hydrogen at the 5-position to give dihydroselenines **6a–c** (path b). Since benzoate **5a** did not react with MCPBA, *m*-chlorobenzoic acid, or *m*-chlorobenzoate anion, conversion of benzoates **5a–c** to dihydroselenines **6a–c** during the reactions was ruled out.

The benzoates **5a–c** are mixtures of two isomers, *cis*-**5a–c** and *trans*-**5a–c**, and the *cis*:*trans* isomer ratios of *ca.* 3 for **5a**, **5b** and 1.3–1.8 for **5c** were determined by comparison with the

**Scheme 2** Mechanism of the reactions of selenanes **2** with MCPBA.

signal intensities of H(6) at δ 4.06 (*trans*-**5a**) and H(6) at δ 3.77 and one of CH₂CH₃ at δ 3.74 (*cis*-**5a**) (overlapped), and H(6) at δ 4.07–4.09 (*trans*-**5b**) and OMe at δ 3.38 (*cis*-**5b**) in the ¹H NMR spectra. This *cis*-predominant selectivity can be explained by attack of *m*-chlorobenzoate anion on the carbon atom at the 6-position of **C** from the opposite side of the EWG at the 2-position, avoiding its steric hindrance. In the case of the benzoyl derivative, dihydroselenine **6c** was produced in preference to benzoate **5c**. This is attributed to an assumption that steric hindrance of the benzoyl group at the 6-position of **C** prevented the *m*-chlorobenzoate anion from attacking the carbon atom at the 6-position and deprotonation of 5-H was predominantly brought about.

Benzoates **5a–c** have two isomers, *trans*-**5a–c** and *cis*-**5a–c**, as shown in Fig. 2. These conformations are explained by a discussion similar to that for selenanes **2a–c**. Two coupling constants, 3 and 12 Hz, due to H(6) of one isomer of **5a** are typical axial–equatorial and axial–axial coupling constants, respectively. Therefore, this isomer takes a chair form and the EWG at the 6-position occupies an equatorial position. The chemical shift of H(6) appeared at δ 4.06, lower than that of the other isomer at δ 3.77. This lower-field shift is attributed to the anisotropic effect of the axial carbonyl (ethyl ester) group β to the H(6). From these ¹H NMR data the isomer was identified as *trans*-**5a** bearing a 6-equatorial ethyl ester group, a 2-equatorial chlorobenzyloxy group and a 2-axial ethyl ester group. On the other hand, the other isomer, *cis*-**5a**, showed an H(6) signal at δ 3.77 as a triplet (*J* 5 Hz). This indicates that the methylene protons at the 5-position affect H(6) equivalently and the selenane ring adopts a twist conformation. In this conformation H(6) is apart from the ethyl ester group at the 2-position and therefore the down-field shift of H(6) was not observed.

In order to convert undesired benzoates **5a–c** to the desired dihydroselenines **6a–c**, we treated **5a–c** with polyphosphoric acid trimethylsilyl ester (PPSE)¹² which is usually used as a good reagent for dehydration under neutral conditions and is

Table 3 Reactions of dihydroselenines **6a–c** with MCPBA (see Scheme 3)

Entry	6	Temp.	Time	Products (% yield) ^a
1	6a	0 °C	3 h	7a (52), 8a (trace)
2	6a	reflux	3 h	7a (50), 8a (trace)
3	6b	0 °C	3 h	7b (71), 8b (9)
4	6c	0 °C	3 h	7c (31), 8c (trace)
5	6c	reflux	3 h	7c (39), 8c (31)
6	6c	reflux	15 min	7c (32), 8c (54) ^b

^a Isolated yield. ^b Based on the signal intensities of H(5) of **7c** and H(3,5) of **8c** in a ¹H NMR spectrum.

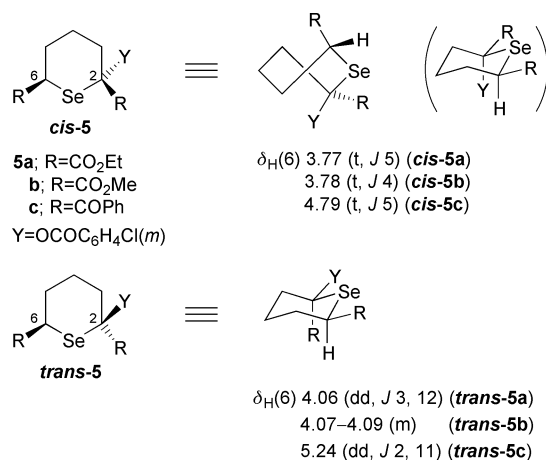
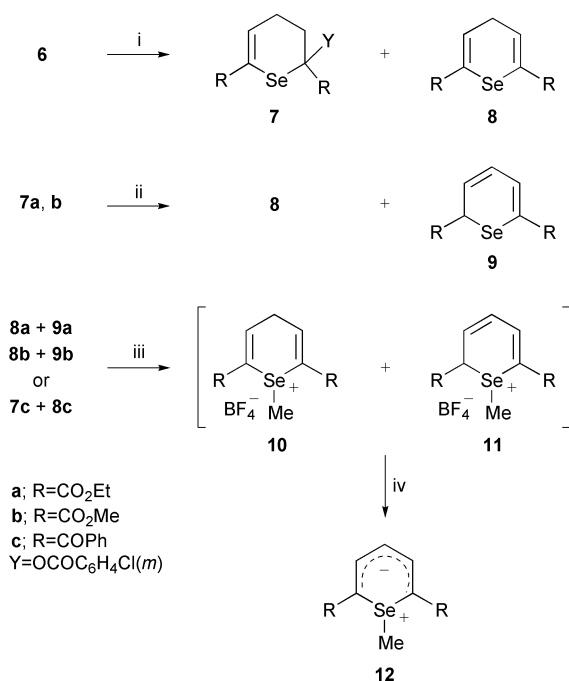


Fig. 2 Conformation of **5a–c**.

prepared from hexamethyldisiloxane and phosphorus pentoxide in a variety of organic solvents (Scheme 1).

The benzoates **5a–c** were not converted into **6a–c** by refluxing with PPSE in dichloromethane, but were converted by refluxing in dichloroethane in high yield (85–99%).

Treatment of **6a–c** with MCPBA one more time gave the benzoates **7a–c** and 4*H*-selenines **8a–c** (Scheme 3, Table 3).



Scheme 3 Reagents and conditions: (i), MCPBA (1.1 equiv.), CH₂Cl₂; (ii), PPSE, toluene, reflux, 20 h; (iii), MeI (6 equiv.), AgBF₄ (1.5 equiv.), CH₂Cl₂, 0 °C, 2 h; (iv), Et₃N (3 equiv.), EtOH, 0 °C, 5 h.

Ester derivatives **6a,b** produced benzoates **7a,b** in good yields accompanied by a small amount of 4*H*-selenines **8a,b** (entries 2, 3), and benzoyl derivative **6c** gave benzoate **7c** and 4*H*-selenine

8c in moderate yields. The reaction of **6c** under reflux in dichloromethane for 15 min (entry 6) gave a better result than those at 0 °C and under reflux for 3 h in entries 4 and 5.

Since the reactions with PPSE in dichloroethane did not proceed and starting materials **7a,b** were recovered, **7a,b** were treated with PPSE in refluxing toluene to give 4*H*-selenines **8a,b** and the double bond regio-isomers **9a,b**. The reaction of **7c** with PPSE in dichloroethane at 0 °C gave a complex mixture.

Methylation of mixtures of **8a,b** and **9a,b** with MeI–AgBF₄ and successive deprotonation with triethylamine afforded selenabenzenes **12a,b**.⁸ The 4*H*-selenine **8c** was too unstable to be isolated and a mixture of **7c** and **8c** obtained from the reactions in Table 3 was used for the preparation of selenabenzene **12c**. The selenabenzenes **12a–c** thus prepared were stable in the atmosphere at room temperature and could be purified by silica-gel PTLC (Scheme 3).

The structures of selenium salts¹³ **10a, 11a** and selenabenzenes⁸ **12a–c** based on the ¹H and ¹³C NMR and IR spectral data have been described in previous papers. The molecular structure of **12c** was unequivocally established by crystal structure analysis and is discussed on the basis of the X-ray analytical data in this paper.

X-Ray analysis

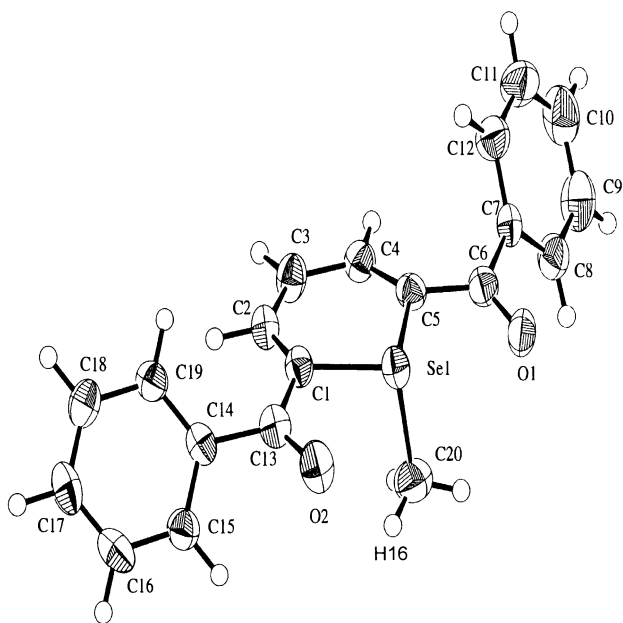
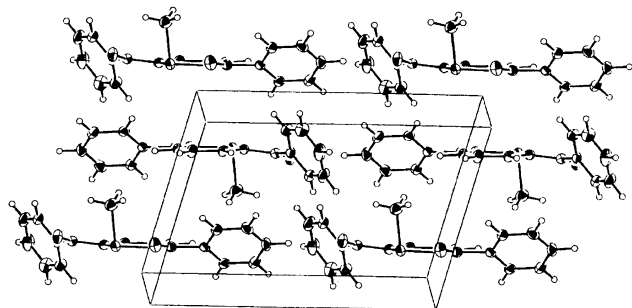
The ORTEP drawing of **12c** and characteristic crystal data are shown in Fig. 3 and in Table 4, respectively. Two torsion angles (C1–C2–C3–C4 and C2–C3–C4–C5) show that the carbon chain composed of C1, C2, C3, C4 and C5 is planar. The dihedral angle between the plane and another plane involving C1, Se1, and C5 was found to be *ca.* 5°, the selenium atom deviating slightly from the planar structure. The bond lengths of the four C–C bonds of the C1–C5 chain are in the range 1.357–1.390 Å, which corresponds well to the C–C bond length of benzene (1.397 Å). On the other hand, the lengths of the two Se–C bonds in the selenabenzene (1.915 and 1.918 Å) and that of the Se1–C20 bond (1.970 Å) are in good agreement with those of C(sp²)–Se (1.91 Å)^{14,15} and C(sp³)–Se (1.98 Å)^{14,15} bonds, respectively, suggesting that these three bonds are single bonds (*cf.* 1.67 Å for C=Se).¹⁵ Furthermore, two kinds of coupling constant, 33 Hz for C2– or C6–Se1 and 39 Hz for C20–Se1 in the ¹³C NMR spectrum, also indicates that the bonds of the selenium atom are sp³ hybridized.¹⁶ Furthermore, this was supported by calculation of the simplified molecule, 2,6-diformyl-1-methylselenabenzene by MOPAC-PM3. The bond orders of the three C–Se bonds are 0.964 (Se1–C1), 0.963 (Se1–C5), and 0.841 (Se1–C20) indicating that these bonds are single bonds.

The ORTEP drawing in Fig. 3 shows that the two carbonyl groups face the selenium and the phenyl groups are directed to C2–H and C4–H in the solid state. The distances between Se1...O2 and Se1...O1 are 2.723 and 2.873 Å, respectively and are significantly less than the sum of their van der Waals radii (*ca.* 3.40 Å). An NOE enhancement between H(3, 5) and protons of the phenyl group (11%) was observed in the ¹H NMR spectrum. This observation indicates that the phenyl groups are located in the direction of C2–H and C4–H in a CDCl₃ solution as well. The arrangement of the benzoyl groups is attributed to the electrostatic interaction between the benzoyl oxygen and the positively charged selenium atoms.

The intermolecular distances between one of the Se-methyl hydrogen atoms and the six carbons of the benzene ring of the benzoyl group are 2.89 (H16–C14), 3.02 (H16–C15), 3.09 (H16–C18) and 2.93 (H16–C19) Å. These values are very close to the sum of the van der Waals radii of H and C (*ca.* 2.90 Å), and show the presence of a CH–π interaction¹⁷ between them. However, π–π interactions between two intermolecular benzene rings of the benzoyl groups do not occur because the angle between them is unfavorable according to the packing diagram (Fig. 4).

Table 4 Selected data of **12c**

Torsion angle/°		Bond length/Å		Angle/°	
C1–C2–C3–C4	1(1)	C1–C2	1.370(7)	C1–Se1–C5	97.0(2)
C2–C3–C4–C5	0(1)	C2–C3	1.375(8)	C1–Se1–C20	99.4(3)
Se1–C1–C2–C3	–6.2(9)	C3–C4	1.390(7)	C5–Se1–C20	99.9(3)
Se1–C5–C4–C3	2.1(9)	C4–C5	1.357(7)		
C1–Se1–C5–C4	–4.9(5)	Se1–C1	1.915(5)		
C2–C1–Se1–C5	6.7(5)	C5–Se1	1.918(5)		
Se1–C1–C13–O2	–1.3(7)	C20–Se1	1.970(7)		
Se1–C5–C6–O1	6.0(7)				

**Fig. 3** ORTEP drawing for **12c**.**Fig. 4** Packing diagram for **12c**.

Conclusion

We have succeeded in synthesising monocyclic selenabenzene having two EWGs, ethyl ester, methyl ester, and benzoyl groups, at the 2- and 6-positions. They were stable at room temperature and against moisture. According to X-ray analysis of selenabenzene **12c**, its bond lengths and angles show a tetragonal structure arising from sp^3 hybridization of the selenium atom.

Experimental

General

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. IR spectra of solids (KBr) and liquids (NaCl) were recorded on a JASCO FT/IR-230 spectrophotometer. The 1H , ^{13}C , and ^{77}Se NMR spectra were measured at 400, 100, and 76 MHz, respectively, with a JEOL EX-400 spectrometer. The 1H , ^{13}C and ^{77}Se chemical shifts are given in ppm relative to those of internal tetramethyl-

silane, $CDCl_3$ or CD_3CN as solvent, and external dimethyl selenide, respectively. The J values are given in Hz. Mass spectra were recorded on a JEOL JMS-SX 102A spectrometer with a direct-insertion probe at 70 eV. Elemental analyses of new compounds were performed on a Yanaco CHN Corder MT-5. All chromatographic isolations were accomplished with either Kieselgel 60 (Merck) or BW-127ZH (Fuji Silysia) for column chromatography or Kieselgel 60 PF254 containing gypsum (Merck) for PTLC. The recycling preparative HPLC was performed by LC-918 liquid chromatography (Japan Analytical Industry Co. Ltd.) equipped with JAIGEL-1H and -2H columns (polystyrene gels).

Synthesis of diethyl 2,6-dibromoheptanedioate **1a**

Title compound 1a (52 g, 90%) was synthesised from heptanedioic acid (25 g, 156 mmol) according to the procedure used previously for the synthesis of diethyl 2,5-dibromohexenedioate from hexanedioic acid.¹⁸ Brown oil, $\nu_{max}(\text{film})/cm^{-1}$ 1730 (ester C=O); δ_H (270 MHz; $CDCl_3$) 1.30 (6 H, t, J 7, CH_2CH_3), 1.48–1.70 (2 H, m, 4-H), 2.00–2.34 (4 H, m, 3- and 5-H), 4.20–4.27 (6 H, m, 2-, 6-H and CH_2CH_3); m/z (EI) 372 (M^+ , ^{79}Br , 3%), 247 (100).

Dimethyl 2,6-dibromoheptanedioate **1b**

Title compound 1b (45 g, 81%) was similarly prepared from heptanedioic acid (26 g, 160 mmol). Yellow oil; $\nu_{max}(\text{film})/cm^{-1}$ 1740 (ester C=O); δ_H (400 MHz; $CDCl_3$) 1.40–1.77 (2 H, m, 4-H), 1.97–2.17 (4 H, m, 3- and 5-H), 3.79 (6 H, s, $OMe \times 2$), 4.24 (2 H, t, J 6, 2- and 6-H); m/z (EI) 344 (M^+ , 1%), 233 (100). The 1H NMR signals of this compound were identical with those of an authentic sample in the literature.¹⁹

Synthesis of 1,5-dibenzoylpentane **3c**

Title compound 3c (218 g, 86%) was synthesised from heptanedioic acid (144 g, 0.9 mol) according to the procedure used previously for the synthesis of 1,4-dibenzoylbutane starting from hexanedioic acid.²⁰ White needles, mp 64–65 °C (from benzene); $\nu_{max}(\text{KBr})/cm^{-1}$ 1670 (C=O); δ_H (400 MHz; $CDCl_3$) 1.49 (2 H, quintet, J 8, 3-H), 1.81 (4 H, quintet, J 8, 2- and 4-H), 3.00 (4 H, t, J 8, 1- and 5-H), 7.46 (4 H, t, J 8, aromatic), 7.55 (2 H, t, J 8, aromatic), 7.96 (4 H, d, J 8, aromatic); δ_C (100 MHz; $CDCl_3$) 24.0 (t $\times 2$), 28.9 (t), 38.3 (t $\times 2$), 128.0 (d $\times 4$), 128.5 (d $\times 4$), 132.9 (d $\times 2$), 137.0 (s $\times 2$), 200.3 (s $\times 2$).

Synthesis of 1,5-dibenzoyl-1,5-dibromopentane **1c**

Title compound 1c (194 g, 89%) was synthesised from heptanedioic acid (140 g, 0.5 mol) according to the procedure used previously for the synthesis of α -bromoacetophenone starting from acetophenone.²¹ Yellow oil; $\nu_{max}(\text{film})/cm^{-1}$ 1685 (C=O); δ_H (400 MHz; $CDCl_3$) 1.69 (2 H, quintet, J 8, 3-H), 2.22–2.27 (4 H, m, 2- and 4-H), 5.15 (2 H, t, J 7, 1- and 5-H), 7.47 (4 H, t, J 8, aromatic), 7.59 (2 H, t, J 8, aromatic), 8.00 (4 H, d, J 8, aromatic); δ_C (100 MHz; $CDCl_3$) 25.5 (t), 32.7 (t $\times 2$), 46.4 (d $\times 2$), 128.76 (d $\times 4$), 128.81 (d $\times 4$), 133.7 (d $\times 2$), 134.2 (s $\times 2$), 192.9 (s $\times 2$). The 1H NMR signals of this compound

were identical with those of an authentic sample in the literature.²²

Synthesis of 1,5-dibenzoyl-1,5-dichloropentane 1c'

A solution of sulfonyl chloride (297 mg, 2.2 mmol) in tetrachloromethane (3 cm³) was added to a solution of 1,5-dibenzoylpentane (280 mg, 1 mmol) in tetrachloromethane (5 cm³) with stirring at 0 °C. The mixture was stirred for 1 day at room temperature, and then a saturated sodium hydrogen carbonate solution was added to it. The organic layer was separated and the aqueous layer was extracted with dichloromethane. The organic layer and the extracts were combined, washed with water, dried (MgSO₄), and concentrated to dryness. The residue was purified by PTLC on silica gel using hexane–ethyl acetate (3:1) to give *title compound 1c'* (321 mg, 92%). Yellow oil, $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1690 (C=O); δ_{H} (400 MHz; CDCl₃) 1.59–1.89 (2 H, m, 3-H), 2.02–2.25 (4 H, m, 2- and 4-H), 5.12 (2 H, dd, *J* 6 and 7, 1- and 5-H), 7.44–7.51 (4 H, m, aromatic), 7.56–7.61 (2 H, m, aromatic), 7.95–8.00 (4 H, m, aromatic); δ_{C} (100 MHz; CDCl₃) 23.1 (t), 32.8 (t), 32.9 (t), 57.0 (d × 2), 128.8 (d × 4), 128.9 (d × 4), 133.9 (d × 2), 134.3 (s × 2), 193.2 (s × 2); *m/z* (EI) 351 (M⁺ – ³⁵Cl, 2%), 105 (100).

Synthesis of selenane 2a

NaBH₄ (250 mg, 6.5 mmol) was gradually added to a suspension of selenium powder (158 mg, 2 mmol) in ethanol (4 cm³). After the reaction mixture turned colorless, it was cooled to rt. A solution of diethyl 2,6-dibromoheptanedioate **1a** (748 mg, 2 mmol) in ethanol (4 cm³) degassed by an aspirator was added dropwise to the solution of sodium selenide and the mixture was stirred for 0.5 h at rt. Air was bubbled into the mixture and then water was added to it. The whole was extracted with dichloromethane. The extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was fractionated by PTLC on silica gel using hexane–ethyl acetate (4:1) to give diethyl *trans*-selenane-2,6-dicarboxylate, *trans*-**2a** (182 mg, 31%) and *cis*-isomer *cis*-**2a** (135 mg, 23%).

Diethyl trans-selenane-2,6-dicarboxylate trans-2a. Yellow oil (Found: C, 44.9; H, 6.2; C₁₁H₁₈O₄Se requires C, 45.1; H, 6.2%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1720 (ester C=O); δ_{H} (400 MHz; CDCl₃) 1.28 (6 H, t, *J* 7, CH₂CH₃), 1.92–2.17 (6 H, m, 3-, 4- and 5-H), 3.87 (2 H, dd, *J* 4 and 7, 2- and 6-H), 4.18 (4 H, q, *J* 7, CH₂CH₃); δ_{C} (100 MHz; CDCl₃) 14.0 (q × 2), 22.0 (t), 28.7 (t × 2), 34.0 (d × 2), 61.1 (t × 2), 172.8 (s × 2); δ_{Se} (76 MHz; CDCl₃) 353; *m/z* (EI) 294 (M⁺, 25%), 248 (100).

Diethyl cis-selenane-2,6-dicarboxylate cis-2a. Yellow oil; $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1720 (ester C=O); δ_{H} (400 MHz; CDCl₃) 1.27 (6 H, t, *J* 7, CH₂CH₃), 1.30–2.39 (6 H, m, 3-, 4- and 5-H), 3.87 (2 H, dd, *J* 2 and 12, 2- and 6-H), 4.18 (4 H, q, *J* 7, CH₂CH₃); δ_{C} (100 MHz; CDCl₃) 14.1 (q × 2), 26.0 (t), 29.7 (t × 2), 37.6 (d × 2), 61.5 (t × 2), 171.6 (s × 2); δ_{Se} (76 MHz; CDCl₃) 357; *m/z* (EI) 294.0355 (C₁₁H₁₈O₄Se requires 294.0370), 294 (M⁺, 50%), 147 (100).

Synthesis of selenane 2b

Similar preparation of dimethyl 2,6-dibromoheptanedioate **1b** (692 mg, 2 mmol) gave dimethyl *trans*-selenane-2,6-dicarboxylate, *trans*-**2b** (186 mg, 35%) and *cis*-isomer *cis*-**2b** (191 mg, 36%).

Dimethyl trans-selenane-2,6-dicarboxylate trans-2b. Pale yellow oil (Found: C, 41.1; H, 5.3; C₉H₁₄O₄Se requires C, 40.8; H, 5.3%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1731 (ester C=O); δ_{H} (400 MHz; CDCl₃) 1.94–2.11 (6 H, m, 3-, 4- and 5-H), 3.73 (6 H, s, OMe × 2), 3.89 (2 H, dd, *J* 4 and 7, 2- and 6-H); δ_{C} (100 MHz; CDCl₃) 22.0 (t),

28.6 (t × 2), 33.7 (d × 2), 52.3 (q × 2), 173.3 (s × 2); δ_{Se} (76 MHz; CDCl₃) 346; *m/z* (EI) 266 (M⁺, 34%), 234 (100).

Dimethyl cis-selenane-2,6-dicarboxylate cis-2b. Pale yellow plates, mp 41–43 °C (from hexane–ethyl acetate) (Found: C, 40.5; H, 5.3; C₉H₁₄O₄Se requires C, 40.8; H, 5.3%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1731 (ester C=O); δ_{H} (400 MHz; CDCl₃) 1.25–1.42 (1 H, m, 3-, 4- or 5-H), 1.82–1.94 (2 H, m, 3-, 4- or 5-H), 2.05–2.15 (1 H, m, 3-, 4- or 5-H), 2.25–2.40 (2 H, m, 3-, 4- or 5-H), 3.73 (6 H, s, OMe × 2), 3.87 (2 H, dd, *J* 3 and 11, 2- and 6-H); δ_{C} (100 MHz; CDCl₃) 25.5 (t), 29.5 (t × 2), 37.1 (d × 2), 52.4 (q × 2), 172.0 (s × 2); δ_{Se} (76 MHz; CDCl₃) 348; *m/z* (EI) 266 (M⁺, 50%), 147 (100).

Synthesis of selenane 2c

A solution of 1,5-dibenzoyl-1,5-dichloropentane **1c'** (349 mg, 1 mmol) in THF (2.5 cm³) was added to a solution of lithium selenide in THF (2.5 cm³) prepared from selenium powder (79 mg, 1 mmol), Super-Hydride® in a THF solution (1.0 M) (2.1 cm³, 2.1 mmol) and *tert*-butyl alcohol (0.15 cm³) at 0 °C under an argon atmosphere. The reaction mixture was stirred at 0 °C for 0.5 h under an argon atmosphere. The reaction mixture was similarly worked up and purified to give 1,5-dibenzoylpentane **3c** (38 mg, 14%), *trans*-2,6-dibenzoylselenane, *trans*-**2c** (85 mg, 24%), *cis*-2,6-dibenzoylselenane, *cis*-**2c** (89 mg, 25%), and 1-benzoyl-2-hydroxy-2-phenylcyclohexane **4** (48 mg, 19%).

trans-2,6-Dibenzoylselenane trans-2c. Pale yellow oil (Found: C, 63.7; H, 5.15; C₁₉H₁₈O₂Se requires C, 63.9; H, 5.1%); $\nu_{\max}(\text{film})/\text{cm}^{-1}$ 1680 (C=O); δ_{H} (400 MHz; CDCl₃) 2.20–2.26 (6 H, m, 3-, 4- and 5-H), 4.81–4.83 (2 H, m, 2- and 6-H), 7.44 (4 H, t, *J* 7, aromatic), 7.54 (2 H, t, *J* 7, aromatic), 7.94 (4 H, dd, *J* 1 and 7, aromatic); δ_{C} (100 MHz; CDCl₃) 22.7 (t), 28.5 (t × 2), 37.7 (d × 2), 128.5 (d × 4), 128.6 (d × 4), 133.1 (d × 2), 135.2 (s × 2), 198.3 (s × 2); δ_{Se} (76 MHz; CDCl₃) 355; *m/z* (EI) 358 (M⁺, 8%), 105 (100).

cis-2,6-Dibenzoylselenane cis-2c. White needles, mp 97 °C (from ethyl acetate–hexane) (Found: C, 63.7; H, 5.1; C₁₉H₁₈O₂Se requires C, 63.9; H, 5.1%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1660 (C=O); δ_{H} (400 MHz; CDCl₃) 1.67 (1 H, tt, *J* 3 and 14, 3-, 4- or 5-H), 2.15 (2 H, dq, *J* 3 and 13, 3-, 4- or 5-H), 2.25–2.32 (1 H, m, 3-, 4- or 5-H), 2.35–2.41 (2 H, m, 3-, 4- or 5-H), 4.97 (2 H, dd, *J* 2 and 11, 2- and 6-H), 7.47 (4 H, t, *J* 7, aromatic), 7.57 (2 H, t, *J* 7, aromatic), 8.03 (4 H, d, *J* 7, aromatic); δ_{C} (100 MHz; CDCl₃) 26.6 (t), 29.8 (t × 2), 42.8 (d × 2), 128.66 (d × 4), 128.72 (d × 4), 133.4 (d × 2), 135.1 (s × 2), 197.6 (s × 2); δ_{Se} (76 MHz; CDCl₃) 389; *m/z* (EI) 358 (M⁺, 23%), 105 (100).

1-Benzoyl-2-hydroxy-2-phenylcyclohexane 4. Colourless needles, mp 128 °C (from acetone–hexane) (Found: C, 81.5; H, 7.3; C₁₉H₂₀O₂ requires C, 81.4; H, 7.2%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1650 (C=O), 3425 (OH); δ_{H} (400 MHz; CDCl₃) 1.50–1.56 (1 H, m, 3-, 4-, 5- or 6-H), 1.65–1.72 (2 H, m, 3-, 4-, 5- or 6-H), 1.86–2.09 (5 H, m, 3-, 4-, 5- or 6-H), 3.99 (1 H, dd, *J* 3 and 12, 1-H), 5.14 (1 H, d, *J* 2, OH), 7.09 (1 H, t, *J* 7, aromatic), 7.21 (2 H, t, *J* 7, aromatic), 7.39 (2 H, t, *J* 7, aromatic), 7.47 (2 H, d, *J* 7, aromatic), 7.51 (1 H, t, *J* 7, aromatic), 7.81 (2 H, d, *J* 8, aromatic); δ_{C} (100 MHz; CDCl₃) 21.6 (t), 25.5 (t), 27.1 (t), 40.5 (t), 50.7 (d), 74.4 (s), 124.4 (d × 2), 126.4 (d), 128.1 (d × 4), 128.6 (d × 2), 133.5 (d), 136.1 (s), 148.4 (s), 206.4 (s); *m/z* (EI) 280 (M⁺, 5%), 105 (100).

Oxidation of diethyl selenane-2,6-dicarboxylate 2a with MCPBA

MCPBA (75%) (253 mg, 1.1 mmol) was added to a solution of **2a** (293 mg, 1 mmol) in dichloromethane (10 cm³) at 0 °C with stirring. The reaction mixture was stirred for 3 h under reflux, and then a saturated sodium hydrogen carbonate solution was

added to the cooled reaction mixture. The whole was extracted with dichloromethane. The extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by PTLC on silica gel using hexane–ethyl acetate (5:1) to give a mixture of the diethyl selenane-2,6-dicarboxylate **5a** (313 mg, 70%) and diethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **6a** (47 mg, 16%). Diethyl *cis*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate, *cis*-**5a** was isolated from a mixture of *trans*-**5a** and *cis*-**5a** by recrystallisation (hexane–ethyl acetate).

Diethyl *cis*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate *cis*-5a. Colourless prisms, mp 75 °C (from hexane–ethyl acetate) (Found: C, 48.2; H, 4.8; C₁₈H₂₁ClO₆Se requires C, 48.3; H, 4.7%); ν_{\max} (KBr)/cm⁻¹ 1720 (ethyl ester); δ_{H} (400 MHz; CDCl₃) 1.05 (3 H, t, *J* 7, CH₂CH₃), 1.27 (3 H, t, *J* 7, CH₂CH₃), 1.84–1.94 (1 H, m, 3-H), 2.04–2.12 (1 H, m, 5-H), 2.28–2.54 (4 H, m, 3-, 4- and 5-H), 3.74 (1 H, dq, *J* 11 and 7, CH₂CH₃), 3.77 (1 H, t, *J* 5, 6-H), 3.93 (1 H, dq, *J* 11 and 7, CH₂CH₃), 4.26 (2 H, q, *J* 7, CH₂CH₃), 7.41 (1 H, t, *J* 8, aromatic), 7.56 (1 H, d, *J* 9, aromatic), 7.94 (1 H, d, *J* 8, aromatic), 8.03 (1 H, s, aromatic); δ_{C} (100 MHz; CDCl₃) 13.8 (q), 13.9 (q), 19.0 (t), 27.1 (t), 34.6 (d), 35.5 (t), 61.1 (t), 62.5 (t), 79.6 (s), 128.1 (d), 129.7 (d), 130.0 (d), 131.0 (s), 133.5 (d), 134.6 (s), 163.4 (s), 169.7 (s), 172.7 (s); δ_{Se} (76 MHz; CDCl₃) 466; *m/z* (EI) 448 (M⁺, 5%), 139 (100).

Diethyl *trans*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate *trans*-5a. δ_{H} (400 MHz; CDCl₃) 4.06 (1 H, dd, *J* 3 and 12, 6-H); δ_{C} (100 MHz; CDCl₃) 13.9 (q), 14.0 (q), 22.4 (t), 29.4 (t), 35.5 (t), 37.5 (d), 61.6 (t), 62.6 (t), 80.9 (s), 127.9 (d), 129.7 (d), 129.8 (d), 131.1 (s), 133.5 (d), 134.6 (s), 163.1 (s), 169.3 (s), 171.2 (s); δ_{Se} (76 MHz; CDCl₃) 461. These signals were picked up from the mixture of *trans*-**5a** and *cis*-**5a** and other signals were overlapped with the signals of *cis*-**5a**.

Diethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate 6a. Red oil; ν_{\max} (film)/cm⁻¹ 1720 (ester C=O); δ_{H} (400 MHz; CDCl₃) 1.28 (3 H, t, *J* 7, CH₂CH₃), 1.31 (3 H, t, *J* 7, CH₂CH₃), 2.06–2.16 (2 H, m, 3- or 4-H), 2.34 (1 H, ddt, *J* 19, 8 and 4, 3- or 4-H), 2.66 (1 H, ddt, *J* 19, 7 and 5, 4-H), 3.98 (1 H, dd, *J* 3 and 8, 2-H), 4.20 (2 H, dq, *J* 3 and 7, CH₂CH₃), 4.24 (2 H, q, *J* 7, CH₂CH₃), 7.33 (1 H, t, *J* 5, 5-H); δ_{C} (100 MHz; CDCl₃) 14.0 (q), 14.1 (q), 23.5 (t), 25.2 (t), 34.1 (d), 61.4 (t), 61.5 (t), 121.4 (s), 136.3 (d), 164.5 (s), 172.0 (s); δ_{Se} (76 MHz; CDCl₃) 301; *m/z* (EI) 292.0220 (C₁₁H₁₆O₄Se requires 292.0213), 292 (M⁺, 56%), 246 (100).

Oxidation of dimethyl selenane-2,6-dicarboxylate **2b** with MCPBA

The MCPBA oxidation of dimethyl selenane-2,6-dicarboxylate **2b** (265 mg, 1 mmol) gave a mixture of dimethyl *trans*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate, *trans*-**5b** and *cis*-isomer *cis*-**5b** (194 mg, 46%), and dimethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **6b** (76 mg, 29%).

Dimethyl *cis*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate *cis*-5b. Colourless prisms, mp 98 °C (from hexane–ethyl acetate) (Found: C, 45.75; H, 4.15; C₁₆H₁₇ClO₆Se requires C, 45.8; H, 4.1%); ν_{\max} (KBr)/cm⁻¹ 1740 (ester); δ_{H} (400 MHz; CDCl₃) 1.85–1.94 (1 H, m, 3-, 4- or 5-H), 2.03–2.12 (1 H, m, 3-, 4- or 5-H), 2.27–2.57 (4 H, m, 3-, 4- or 5-H), 3.38 (3 H, s, OMe), 3.78 (1 H, t, *J* 4, 6-H), 3.80 (3 H, s, OMe), 7.42 (1 H, t, *J* 8, aromatic), 7.57 (1 H, d, *J* 8, aromatic), 7.94 (1 H, d, *J* 8, aromatic), 8.02 (1 H, s, aromatic); δ_{C} (100 MHz; CDCl₃) 18.8 (t), 27.1 (t), 34.3 (d), 35.5 (t), 52.2 (q), 53.3 (q), 79.4 (s), 128.1 (d), 129.7 (d), 130.0 (d), 130.8 (s), 133.6 (d), 134.6 (s), 163.3 (s), 170.2 (s), 173.0 (s); δ_{Se} (76 MHz; CDCl₃) 468; *m/z* (EI) 420 (M⁺, 6%), 139 (100).

Dimethyl *trans*-2-(*m*-chlorobenzoyloxy)selenane-2,6-dicarboxylate *trans*-5b. δ_{H} (400 MHz; CDCl₃) 3.70 (3 H, s, OMe), 3.80

(3 H, s, OMe), 4.07–4.09 (1 H, m, 6-H); δ_{C} (100 MHz; CDCl₃) 22.3 (t), 29.3 (t), 35.4 (d), 37.2 (t), 52.5 (q), 53.3 (q), 80.5 (s), 127.8 (d), 129.6 (d), 130.7 (d), 130.8 (s), 133.6 (d), 134.6 (s), 163.0 (s), 169.7 (s), 171.6 (s); δ_{Se} (76 MHz; CDCl₃) 464. These signals were picked up from the mixture of *trans*-**5b** and *cis*-**5b** and other signals were overlapped with the signals of *cis*-**5b**.

Dimethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate 6b. Red oil (Found: C, 41.3; H, 4.6; C₉H₁₂O₄Se requires C, 41.1; H, 4.6%); ν_{\max} (film)/cm⁻¹ 1720 (ester C=O); δ_{H} (400 MHz; CDCl₃) 2.05–2.19 (2 H, m, 3- or 4-H), 2.35 (1 H, ddt, *J* 20, 8 and 5, 3- or 4-H), 2.67 (1 H, ddt, *J* 20, 7 and 5, 3- or 4-H), 3.75 (3 H, s, OMe), 3.79 (3 H, s, OMe), 4.00 (1 H, dd, *J* 4 and 7, 2-H), 7.34 (1 H, t, *J* 5, 5-H); δ_{C} (100 MHz; CDCl₃) 23.4 (t), 25.0 (t), 33.7 (d), 52.4 (q × 2), 120.9 (s), 136.7 (d), 164.9 (s), 172.4 (s); δ_{Se} (76 MHz; CDCl₃) 303; *m/z* (EI) 264 (M⁺, 33%), 145 (100).

Oxidation of 2,6-dibenzoylselenane **2c** with MCPBA

The MCPBA oxidation of 2,6-dibenzoylselenane **2c** (357 mg, 1 mmol) and purification by recycling preparative HPLC, eluting with chloroform, gave *trans*-2,6-dibenzoyl-2-(*m*-chlorobenzoyloxy)selenane, *trans*-**5c** (90 mg, 18%), *cis*-isomer *cis*-**5c** (123 mg, 24%) and 2,6-dibenzoyl-3,4-dihydro-2*H*-selenine **6c** (137 mg, 39%).

***cis*-2,6-Dibenzoyl-2-(*m*-chlorobenzoyloxy)selenane *cis*-5c.** White prisms, mp 135 °C (from ether) (Found: C, 61.1; H, 4.2; C₂₆H₂₁O₄ClSe requires C, 61.0; H, 4.1%); ν_{\max} (film)/cm⁻¹ 1680 (C=O), 1730 (ester C=O); δ_{H} (400 MHz; CDCl₃) 2.05–2.11 (1 H, m, 3-, 4- or 5-H), 2.23–2.27 (1 H, m, 3-, 4- or 5-H), 2.51–2.55 (1 H, m, 3-, 4- or 5-H), 2.66–2.78 (3 H, m, 3-, 4- or 5-H), 4.79 (1 H, t, *J* 5, 6-H), 7.29 (2 H, t, *J* 7, aromatic), 7.35 (2 H, t, *J* 8, aromatic), 7.39 (1 H, t, *J* 8, aromatic), 7.42 (1 H, t, *J* 7, aromatic), 7.49 (1 H, t, *J* 7, aromatic), 7.57 (1 H, d, *J* 8, aromatic), 7.70 (2 H, d, *J* 8, aromatic), 7.82 (1 H, d, *J* 7, aromatic), 7.91 (1 H, s, aromatic), 8.02 (2 H, d, *J* 8, aromatic); δ_{C} (100 MHz; CDCl₃) 19.8 (t), 26.7 (t), 34.5 (t), 38.5 (d), 87.6 (s), 128.1 (d), 128.3 (d × 2), 128.48 (d × 2), 128.52 (d × 2), 128.8 (d × 2), 129.8 (d), 130.0 (d), 130.5 (s), 133.0 (d × 2), 133.2 (s), 133.7 (d), 134.6 (s), 135.2 (s), 163.5 (s), 194.4 (s), 197.9 (s); δ_{Se} (76 MHz; CDCl₃) 476; *m/z* (EI) 512 (M⁺, >1%), 105 (100).

***trans*-2,6-Dibenzoyl-2-(*m*-chlorobenzoyloxy)selenane *trans*-5c.** White needles, mp 148–149 °C (from ether) (Found: C, 61.1; H, 4.2; C₂₆H₂₁ClO₄Se requires C, 61.0; H, 4.1%); ν_{\max} (KBr)/cm⁻¹ 1680 (C=O), 1730 (ester C=O); δ_{H} (400 MHz; CDCl₃) 2.13–2.33 (3 H, m, 3-, 4- or 5-H), 2.48 (1 H, dq, *J* 14 and 3, 3-, 4- or 5-H), 2.59 (1 H, ddd, *J* 3, 13 and 15, 3-, 4- or 5-H), 2.98 (1 H, dt, *J* 15 and 3, 3-, 4- or 5-H), 5.24 (1 H, dd, *J* 2 and 11, 6-H), 7.36 (2 H, t, *J* 8, aromatic), 7.42 (2 H, t, *J* 8, aromatic), 7.46 (2 H, t, *J* 8, aromatic), 7.56 (1 H, t, *J* 7, aromatic), 7.61 (1 H, ddd, *J* 1, 2 and 8, aromatic), 7.92 (2 H, dd, *J* 1 and 7, aromatic), 7.98 (1 H, dt, *J* 7 and 1, aromatic), 8.06 (1 H, t, *J* 2, aromatic), 8.13 (2 H, dd, *J* 1 and 7, aromatic); δ_{C} (100 MHz; CDCl₃) 22.8 (t), 29.5 (t), 34.8 (t), 42.9 (d), 88.9 (s), 127.8 (d), 128.5 (d × 2), 128.6 (d × 2), 128.7 (d × 2), 128.9 (d × 2), 129.7 (d), 130.2 (d), 130.8 (s), 133.2 (d), 133.3 (s), 133.6 (d), 133.9 (d), 134.9 (s), 135.0 (s), 163.4 (s), 194.1 (s), 197.5 (s); δ_{Se} (76 MHz; CDCl₃) 512; *m/z* (EI) 512 (M⁺, >1%), 105 (100).

2,6-Dibenzoyl-3,4-dihydro-2*H*-selenine 6c. Brown oil (Found: C, 64.3; H, 4.7; C₁₉H₁₆O₂Se requires C, 64.2; H, 4.5%); ν_{\max} (film)/cm⁻¹ 1640, 1680 (C=O); δ_{H} (400 MHz; CDCl₃) 2.22–2.26 (1 H, m, 3- or 4-H), 2.32–2.41 (1 H, m, 3- or 4-H), 2.51 (1 H, ddt, *J* 20, 8 and 4, 3- or 4-H), 2.92 (1 H, ddt, *J* 20, 7 and 5, 3- or 4-H), 4.96 (1 H, dd, *J* 4 and 7, 2-H), 7.08 (1 H, t, *J* 5, 5-H), 7.43 (2 H, t, *J* 8, aromatic), 7.48 (2 H, t, *J* 8, aromatic), 7.52 (1 H, t, *J* 8, aromatic), 7.58 (1 H, t, *J* 7, aromatic), 7.62 (2 H, d, *J* 7, aromatic), 7.99 (2 H, d, *J* 7, aromatic); δ_{C} (100 MHz;

CDCl₃) 23.1 (t), 26.1 (t), 36.6 (d), 128.2 (d × 2), 128.4 (d × 2), 128.7 (d × 2), 129.0 (d × 2), 131.8 (d), 132.4 (s), 133.4 (d), 135.4 (s), 136.9 (s), 142.4 (d), 194.3 (s), 196.8 (s); δ_{Se} (76 MHz; CDCl₃) 310; *m/z* (EI) 356 (M⁺, 25%), 105 (100).

Reaction of 2-(*m*-chlorobenzoyloxy)selenane derivatives **5a–c** with PPSE

Hexamethyldisiloxane (1.7 cm³, 10 mmol) was added to a suspension of phosphorus pentoxide (850 mg, 10 mmol) in dry 1,2-dichloroethane (3.3 cm³) under an argon atmosphere and the mixture was refluxed for 1 h. A solution of **5a** (365 mg, 0.8 mmol) in dry 1,2-dichloroethane (5 cm³) was added to the PPSE solution under an argon atmosphere and the mixture was refluxed for 20 h. Water was added to the cooled reaction mixture, and the whole was extracted with dichloromethane. The extracts were washed with a saturated hydrogen carbonate solution, dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by silica gel column chromatography using hexane–ethyl acetate (5 : 1) to give diethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **6a** (198 mg, 85%).

Selenane **5b** (21.43 g, 51 mmol) gave dihydroselenine **6b** (13.32 g, 99%).

Selenane **5c** (480 mg, 0.9 mmol) gave dihydroselenine **6c** (290 mg, 96%).

Oxidation of diethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **6a** with MCPBA

Oxidation of **6a** (291 mg, 1 mmol) with MCPBA gave diethyl 2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **7a** (232 mg, 52%) and diethyl 4*H*-selenine-2,6-dicarboxylate **8a** (trace).

Diethyl 2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **7a.** Red oil; ν_{max}(film)/cm⁻¹ 1720 (ester); δ_H (400 MHz; CDCl₃) 1.28 (3 H, t, *J* 7, CH₂CH₃), 1.30 (3 H, t, *J* 7, CH₂CH₃), 2.24–2.32 (1 H, m, 3- or 4-H), 2.55–2.71 (3 H, m, 3- and 4-H), 4.25 (2 H, q, *J* 7, CH₂CH₃), 4.29 (2 H, q, *J* 7, CH₂CH₃), 7.38–7.42 (2 H, m, 5-H and aromatic), 7.57 (1 H, dt, *J* 8 and 1, aromatic), 7.91 (1 H, d, *J* 8, aromatic), 7.98 (1 H, s, aromatic); δ_C (100 MHz; CDCl₃) 13.9 (q), 14.0 (q), 23.1 (t), 30.2 (t), 61.7 (t), 62.7 (t), 81.0 (s), 122.8 (s), 127.9 (d), 129.7 (d), 129.8 (d), 130.7 (s), 133.6 (d), 134.6 (s), 134.8 (d), 163.9 (s), 164.1 (s), 169.2 (s); δ_{Se} (76 MHz; CDCl₃) 459; *m/z* (EI) 446.0031 (C₁₈H₁₉ClO₆Se requires 446.0035), 446 (M⁺, 2%), 139 (100).

Diethyl 4*H*-selenine-2,6-dicarboxylate **8a.** Red oil, ν_{max}(film)/cm⁻¹ 1720 (ester C=O); δ_H (400 MHz; CDCl₃) 1.32 (6 H, t, *J* 7, CH₂CH₃), 3.18 (2 H, t, *J* 5, 4-H), 4.27 (4 H, q, *J* 7, CH₂CH₃), 6.99 (2 H, t, *J* 5, 3- and 5-H); δ_C (100 MHz; CDCl₃) 14.1 (q × 2), 31.0 (t), 61.8 (t × 2), 125.2 (s × 2), 131.6 (d × 2), 163.8 (s × 2); δ_{Se} (76 MHz; CDCl₃) 294; *m/z* (EI) 290.0049 (C₁₁H₁₄O₄Se requires 290.0057), 290 (M⁺, 58%), 217 (100).

Oxidation of dimethyl 3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **6b** with MCPBA

The MCPBA oxidation of **6b** (263 mg, 1 mmol) gave dimethyl 2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **7b** (297 mg, 71%) and dimethyl 4*H*-selenine-2,6-dicarboxylate **8b** (24 mg, 9%).

Dimethyl 2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine-2,6-dicarboxylate **7b.** Red oil; ν_{max}(film)/cm⁻¹ 1730 (ester C=O); δ_H (400 MHz; CDCl₃) 2.27–2.31 (1 H, m, 3- or 4-H), 2.61–2.65 (3 H, m, 3- and 4-H), 3.79 (3 H, s, OMe), 3.83 (3 H, s, OMe), 7.39–7.43 (2 H, m, 5-H and aromatic), 7.56 (1 H, d, *J* 8, aromatic), 7.91 (1 H, d, *J* 8, aromatic), 7.97 (1 H, s, aromatic); δ_C (100 MHz; CDCl₃) 23.0 (t), 30.2 (t), 52.4 (q), 53.4 (q), 80.7

(s), 122.3 (s), 127.8 (d), 129.6 (d), 129.8 (d), 130.5 (s), 133.6 (d), 134.5 (s), 135.2 (d), 163.8 (s), 164.3 (s), 169.6 (s); δ_{Se} (76 MHz; CDCl₃) 460; *m/z* (EI) 417.9715 (C₁₆H₁₅ClO₆Se requires 417.9722), 418 (M⁺, 4%), 139 (100).

Dimethyl 4*H*-selenine-2,6-dicarboxylate **8b.** Colourless needles, mp 81 °C (from hexane–ether) (Found: C, 41.3; H, 3.8; C₉H₁₀O₄Se requires C, 41.4; H, 3.9%); ν_{max}(KBr)/cm⁻¹ 1700, 1730 (ester C=O); δ_H (400 MHz; CDCl₃) 3.18 (2 H, t, *J* 5, 4-H), 3.808 (3 H, s, OMe), 3.812 (3 H, s, OMe), 7.00 (2 H, t, *J* 5, 3- and 5-H); δ_C (100 MHz; CDCl₃) 31.0 (t), 52.6 (q × 2), 124.9 (s × 2), 131.9 (d × 2), 164.2 (s × 2); δ_{Se} (76 MHz; CDCl₃) 298; *m/z* (EI) 262 (M⁺, 25%), 203 (100).

Oxidation of 2,6-dibenzoyl-3,4-dihydro-2*H*-selenine **6c** with MCPBA

The MCPBA oxidation of **6c** (263 mg, 1 mmol) and purification by recycling preparative HPLC, eluting with chloroform, gave 2,6-dibenzoyl-2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine **7c** (199 mg, 39%) and 2,6-dibenzoyl-4*H*-selenine **8c** (110 mg, 31%).

2,6-Dibenzoyl-2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine **7c.** White needles, mp 60 °C (from ethyl acetate–hexane) (Found: C, 61.1; H, 3.8; C₂₆H₁₉ClO₄Se requires C, 61.25; H, 3.8%); ν_{max}(KBr)/cm⁻¹ 1640, 1680 (C=O), 1720 (ester C=O); δ_H (400 MHz; CDCl₃) 2.51–2.61 (1 H, m, 3- or 4-H), 2.67–2.81 (2 H, m, 3- or 4-H), 2.93–3.01 (1 H, m, 3- or 4-H), 7.19 (1 H, dd, *J* 3 and 6, 5-H), 7.37 (2 H, t, *J* 8, aromatic), 7.39 (2 H, t, *J* 8, aromatic), 7.47 (2 H, t, *J* 8, aromatic), 7.50 (1 H, t, *J* 8, aromatic), 7.55 (1 H, d, *J* 8, aromatic), 7.68 (2 H, d, *J* 8, aromatic), 7.88 (1 H, d, *J* 8, aromatic), 7.96 (1 H, s, aromatic), 8.20 (2 H, d, *J* 8, aromatic); δ_C (100 MHz; CDCl₃) 23.7 (t), 28.8 (t), 87.5 (s), 128.0 (d), 128.4 (d × 2), 128.7 (d × 2), 128.8 (d × 2), 129.2 (d × 2), 129.8 (d), 130.0 (d), 130.5 (s × 2), 132.2 (d), 133.4 (d), 133.6 (s), 133.9 (d), 134.8 (s), 136.7 (s), 141.3 (d), 164.0 (s), 192.9 (s), 193.9 (s); δ_{Se} (76 MHz; CDCl₃) 468; *m/z* (EI): 510 (M⁺, 3%), 105 (100).

2,6-Dibenzoyl-4*H*-selenine **8c.** Green powder, mp 70–72 °C (dec.) (from CHCl₃–ether) (Found: C, 64.7; H, 4.0; C₁₉H₁₄O₂Se requires C, 64.6; H, 4.0%); ν_{max}(KBr)/cm⁻¹ 1600, 1620 (C=O); δ_H (400 MHz; CDCl₃) 3.24 (2 H, t, *J* 5, 4-H), 6.76 (2 H, t, *J* 5, 3- and 5-H), 7.46 (4 H, t, *J* 7, aromatic), 7.56 (2 H, t, *J* 7, aromatic), 7.70 (4 H, dd, *J* 1 and 7, aromatic); δ_C (100 MHz; CDCl₃) 32.3 (t), 128.4 (d × 4), 129.2 (d × 4), 132.3 (d × 2), 135.5 (d × 2), 136.4 (s × 2), 137.4 (s × 2), 192.8 (s × 2); δ_{Se} (76 MHz; CDCl₃) 317; *m/z* (EI) 353 (M⁺, 15%), 105 (100).

Reaction of 2-(*m*-chlorobenzoyloxy)-3,4-dihydro-2*H*-selenine derivatives **7a,b** with PPSE

The reaction of dihydroselenine **7a** (446 mg, 1 mmol) with PPSE in toluene gave a mixture of diethyl 4*H*-selenine-2,6-dicarboxylate **8a** and diethyl 2*H*-selenine-2,6-dicarboxylate **9a** (192 mg, 66%).

Diethyl 2*H*-selenine-2,6-dicarboxylate **9a.** δ_H (400 MHz; CDCl₃) 5.77 (1 H, dd, *J* 6 and 10, 3-H), 6.26 (1 H, ddd, *J* 1, 7 and 10, 4-H), 7.31 (1 H, d, *J* 7, 5-H); δ_{Se} (76 MHz; CDCl₃) 248.

These signals were picked up from the ¹H and ¹³C NMR spectra of the mixture of diethyl 4*H*-selenine-2,6-dicarboxylate **8a** and diethyl 2*H*-selenine-2,6-dicarboxylate **9a**.

The reaction of dihydroselenine **7b** (418 mg, 1 mmol) similarly gave a mixture of dimethyl 4*H*-selenine-2,6-dicarboxylate **8b** and dimethyl 2*H*-selenine-2,6-dicarboxylate **9b** (260 mg, 44%).

Dimethyl 2*H*-selenine-2,6-dicarboxylate 9b. δ_{H} (400 MHz; CDCl₃) 3.75 (3 H, s, OMe), 3.81 (3 H, s, OMe), † 4.35 (1 H, dd, *J* 1 and 6, 2-H), 5.78 (1 H, dd, *J* 6 and 10, 3-H), 6.28 (1 H, ddd, *J* 1, 6 and 10, 4-H), 7.33 (1 H, d, *J* 6, 5-H); δ_{C} (100 MHz; CDCl₃) 33.1 (d), 52.5 (q), 53.0 (q), 120.1 (d), 123.7 (s), 128.6 (d), 130.6 (d), 164.1 ‡ (s), 165.2 (s); δ_{Se} (76 MHz; CDCl₃) 251.

These signals were picked up from the ¹H and ¹³C NMR spectra of the mixture of dimethyl 4*H*-selenine-2,6-dicarboxylate **8b** and dimethyl 2*H*-selenine-2,6-dicarboxylate **9b**.

Synthesis of diethyl 1-methyl-1 λ^4 -selenabenzene-2,6-dicarboxylate **12a**

The synthetic procedure and data of dimethyl 1-methyl-1 λ^4 -selenabenzene-2,6-dicarboxylate **12b** were described in a previous report.⁸ A mixture of selenines **8a** and **9a** (**8a**:**9a** = 5:1; 291 mg, 1 mmol) gave *title compound 12a* (292 mg, 96%) [purification by PTLC on silica gel using hexane–ethyl acetate (5:1)], red powder, mp 35 °C (from ethyl acetate–hexane) (Found: C, 47.3; H, 5.3; C₁₂H₁₆O₄Se requires C, 47.5; H, 5.3%); ν_{max} (KBr)/cm⁻¹ 1640 (ethyl ester); δ_{H} (400 MHz; CDCl₃) 1.32 (6 H, t, *J* 7, CH₂CH₃ × 2), 2.13 (3 H, s, SeMe), 4.26 (2 H, q, *J* 7, CH₂CH₃), 4.27 (2 H, q, *J* 7, CH₂CH₃), 5.21 (1 H, t, *J* 9, 4-H), 7.40 (2 H, t, *J* 9, 3- and 5-H); δ_{C} (100 MHz; CDCl₃) 14.5 (q × 2), 26.6 (q), 60.8 (t × 2), 83.9 (s × 2), 100.7 (d), 139.1 (d × 2), 165.4 (s × 2); δ_{Se} (76 MHz; CDCl₃) 311; *m/z* (EI) 304 (M⁺, 65%), 231 (100).

Synthesis of 2,6-dibenzoyl-1-methyl-1 λ^4 -selenabenzene **12c**

MCPBA (75%) (759 mg, 3.3 mmol) was added to a solution of dihydroselenine **6c** (1.065 g, 3 mmol) in dichloromethane (30 cm³) at 0 °C with stirring. The reaction mixture was stirred for 15 min under reflux, followed by addition of a saturated sodium hydrogen carbonate solution. The whole was extracted with dichloromethane. The extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue and iodomethane (1.2 cm³, 9 mmol) were dissolved in dry dichloromethane (30 cm³). Silver tetrafluoroborate (975 mg, 4.5 mmol) was added to this solution at 0 °C. The reaction mixture was stirred for 10 min, and then the precipitate was filtered off and washed with a small amount of dry dichloromethane. The filtrate and the washings were combined. Triethylamine (1.7 cm³, 12 mmol) was added to this solution at 0 °C with stirring. The reaction mixture was stirred for 15 min at 0 °C and then water was added to it. The whole was extracted with dichloromethane. The extracts were dried (MgSO₄) and concentrated under reduced pressure. The residue was purified by recycling preparative HPLC, eluting with chloroform, to give *title compound 12c* (212 mg, 19%), dark green plates, mp 165 °C (from benzene) (Found: C, 65.7; H, 4.5; C₂₀H₁₆O₂Se requires C, 65.4; H, 4.4%); ν_{max} (KBr)/cm⁻¹ 1540 (C=O); δ_{H} (400 MHz; CDCl₃) 2.55 (3 H, s, SeMe), 5.18 (1 H, t, *J* 9, 4-H), 7.20 (2 H, d, *J* 9, 3- and 5-H), 7.44–7.51 (6 H, m, aromatic), 7.63 (4 H, d, *J* 7, aromatic); δ_{C} (100 MHz; CDCl₃) 26.8 (q), 102.3 (s × 2), 103.1 (d), 128.3 (d × 4), 128.7 (d × 4), 131.1 (d × 2), 137.5 (s × 2), 141.8 (d × 2), 189.3 (s × 2); δ_{Se} (76 MHz; CDCl₃) 289; *m/z* (EI) 353 (M⁺, 85%), 105 (100).

† This signal was overlapped with the OMe signal of **8b**.

‡ This signal was overlapped with the C=O signal of **8b**.

This compound was also purified by column chromatography on silica gel using hexane–ethyl acetate (5:1).

Crystal structure analysis of 12c. § Crystal data for C₂₀H₁₆O₂Se: *M* = 367.3, triclinic, *a* = 8.658(2), *b* = 13.031(3), *c* = 7.875(2) Å, *a* = 103.77(2), *β* = 98.21(2), *γ* = 105.39(2)°, *V* = 811.6(4) Å³, *T* = 293 K. Space group *P* $\bar{1}$ (No. 2), *Z* = 2, μ (Mo–K α) = 2.32 mm⁻¹, 3976 reflections measured, 3727 unique (*R*_{int} = 0.038) which were used in all calculations. The final *R*-factor was 0.042 and the *wR*-factor was 0.048 (all data).

§ CCDC reference number 152309. See <http://www.rsc.org/suppdata/p1/b0/b008562f/> for crystallographic files in .cif format.

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