Isolation, Structure and Reaction of Selenobenzophenones. X-Ray Molecular Structure of 4,4'-Dimethoxyselenobenzophenone and of 4,4-Diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene

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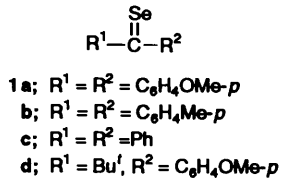
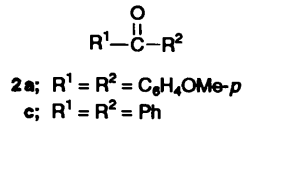
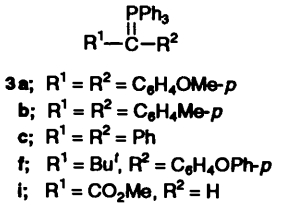
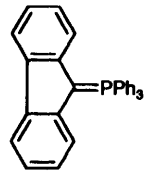
4,4'-Dimethoxy- **1a** and 4,4'-dimethyl-selenobenzophenone **1b** could be isolated in moderate yields by the reaction of the corresponding ylides **3** with elemental selenium in benzene at 80 °C. Their spectral data are described. Attempted isolation of unsubstituted selenobenzophenone afforded only its dimer **5**. Compound **1a** crystallizes in space group $P2_1/n$ with unit-cell parameters a = 7.191(3), b = 7.505(4), c = 24.856(4) Å, β = 90.32(1)°, Z = 4, R = 0.055. The oxidation and thiation of 4,4'-dimethoxyselenobenzophenone **1a** afforded the corresponding benzophenone and thiobenzophenone in good yields. The reaction of compound **1** with cyclopentadiene afforded the corresponding cycloadducts **7** (3,3-diaryl-2-selenabicyclo[2.2.1]hept-5-enes), whereas bicyclic diselenides **8** (4,4-diaryl-2,3-diselenabicyclo[3.3.0]oct-7-enes) were obtained by using an excess of selenium and a higher temperature. Oxidation of compound **8c** gave the corresponding diol **12**, aldehyde **13**, and diphenylfulvene **11**. The reaction of compound **1a** with benzenediazonium carboxylate afforded 2,2-bis-(4-methoxyphenyl)-4*H*-3,1-benzooxaselenin-4-one **17**.

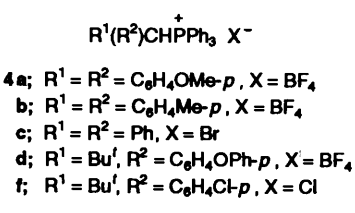
In recent years, a number of research groups have demonstrated the generation and trapping reactions of selones **1**.[1,2] Thiobenzophenones **2** had already been prepared in pure form by the reaction of phosphorus ylides **3** with elemental sulfur in 1919.[3] Application of this methodology to the synthesis of selones **1** has only recently been reported. Erker's and our group independently found that selenocarbonyl compounds (selenoaldehydes and selenoketones) were formed by the reaction of phosphonium salts **4** with bases followed by the addition of elemental selenium.[4] However, there are a few reports on the synthesis of stable selenocarbonyl compounds, **1**, which contain bulky groups or electron-donating groups on the selenocarbonyl α-carbons.[5] Recently, Erker *et al.* reported the reaction of diphenylmethylenetriphenylphosphorane **3c** with elemental selenium.[6] They isolated selenobenzophenone dimer **5c** as yellowish green crystals, whose structure was confirmed by X-ray crystallographic analysis. We have also published papers on the isolation of 4,4'-dimethoxyselenobenzophenone **1a** and 4,4'-dimethylselenobenzophenone **1b**.[7] In this paper, we report full details of the isolation, structure, and some reactions of compounds **1a** and **1b**.

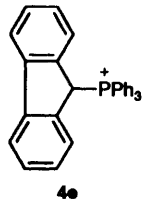


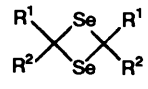




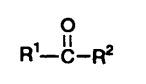








5c; $R^1 = R^2$ = Ph
d; $R^1 = R^2 = C_6H_4OPh\text{-}p$, R^2 = But



6a; $R^1 = R^2 = C_6H_4OMe\text{-}p$
b; $R^1 = R^2 = C_6H_4Me\text{-}p$
c; $R^1 = R^2$ = Ph

Results and Discussion

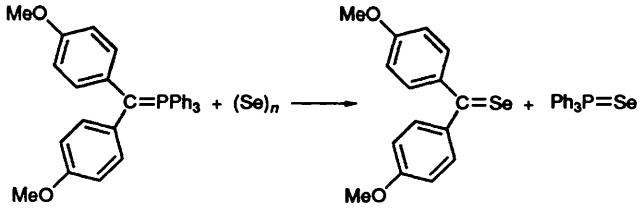
Isolation of Selenobenzophenones.—Treatment of diarylmethylenetriphenylphosphorane **3a** with elemental selenium in refluxing benzene resulted in the formation of selone **1a** in moderate yields (Scheme 1). 4,4'-Dimethoxyselenobenzophenone **1a** is a green, stable compound under nitrogen, and can be stored in a refrigerator (−15 °C) for more than 2 years. However, on exposure to the air, this compound decomposed to give the corresponding benzophenone **6a** and selenium after 15 h. The whole work-up must, therefore, be done under nitrogen.

Isolation of 4,4'-dimethylselenobenzophenone **1b** was also attempted. This compound was also characterized in solution by its ^{13}C NMR spectrum and exact mass spectroscopy. By careful work-up, this compound was isolated in 38% yield. It is less stable than compound **1a** and changed to the corresponding 4,4'-dimethylbenzophenone **6b** and selenium upon storage at room temperature within 1 h. The spectral data of compound **1a** and **1b** were shown in Table 1.

Isolation of unsubstituted selenobenzophenone **1c** was also attempted. In solution, this compound was generated by the reaction of diphenylmethylenetriphenylphosporane **3c** with

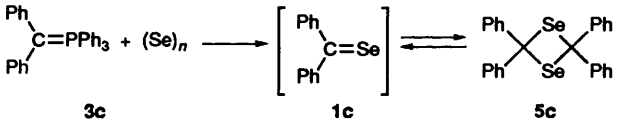
Table 1 Spectral data of compound **1a** and **1b**

Compound	^{1}H NMR (δ $CDCl_3$)	^{13}C NMR (δ $CDCl_3$)	UV-VIS (λ_{max}/nm(ε))
1a	3.87 (6 H, s)	55.6, 113.7,	360 (21 500)
	6.82 (4 H, d)	131.2, 148.0,	386 sh (11 300)
	7.79 (4 H, d)	162.9, 240.1 (C=Se)	744 (335)
1b	2.23 (6 H, s)	21.9, 128.7,	340 (15 300)
	7.10 (4 H, d)	129.2, 142.4,	368 (11 900)
	7.69 (4 H, d)	152.7, 244.4 (C=Se)	750 (240)



3a **1a**

Scheme 1



3c **1c** **5c**

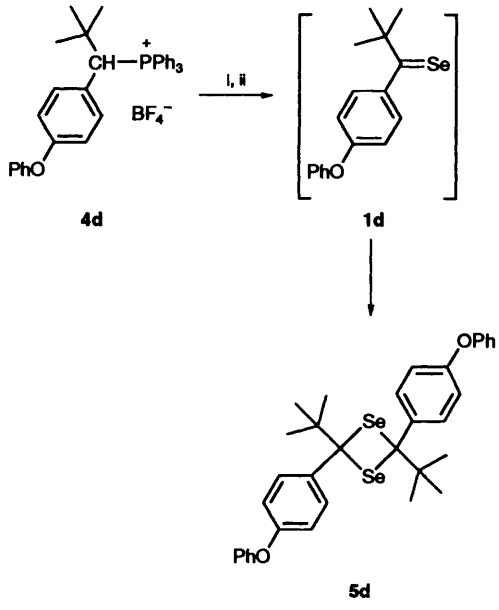
Scheme 2

elemental selenium and its formation was confirmed by its ^{13}C NMR spectrum. A green solution of compound **1c** turned to pale greenish yellow crystals of dimer **5c** on evaporation of the solvent as stated by Erker *et al.* (Scheme 2).[6]

Since there is no report of the isolation of alkyl aryl selenoketones, the reaction of [2,2-dimethyl-1-(*p*-phenoxyphenyl)propyl]triphenylphosphonium tetrafluoroboranide **4d** with elemental selenium was carried out. However, the isolated product was only the dimer of *tert*-butyl *p*-phenoxyphenyl selenoketone, compound **5d** (Scheme 3). Recently, Nakayama and co-workers reported the synthesis of alkyl aryl selenoketones by the reaction of hydrazones with diselenium dichloride in the presence of tributylamine.[8] The present result is quite different from theirs.

Since Krafft and Meinke stated that no detectable colours of selenoketones (selenobenzophenone and selenofluorenone) were observed by the reaction of the corresponding selenocyanate with triethylamine, the reaction of fluorenylidenetriphenylphosphorane **3e** with elemental selenium was carried out to isolate selenofluorenone.[2a] The obtained products were only 9,9'-bifluorenylidene and triphenylphosphine selenide. During this experiment, there is no characteristic green colour attributed to selenofluorenone **1e**, indicating the high reactivity of selenofluorenone.

X-Ray Crystallographic Analysis.—The only reported crystal structure of a stable selenoketone is that of 1,5-dimethyl-3,7-dithiabicyclo[3.3.1]nonane-9-selone **1f**. It is interesting to compare compound **1f** with other selenocarbonyl compounds; however, there are few reports of X-ray crystallographic analyses concerning this type of compound.[1,9] Since the selenobenzophenone **1a** sometimes affords a beautiful deep-green single crystal and might be the least sterically congested selenoketone which have been previously isolated, the molecular structure of compound **1a** in the solid state was determined by X-ray crystallography. Compound **1a** crystallizes in space group $P2_1/n$ with unit-cell parameters a = 7.191(3), b = 7.505(4), c = 24.856(4) Å, β = 90.32(1)°. The



Scheme 3 *Reagents:* i, BuLi; ii, $(Se)_n$

structure was refined to R = 0.055, R_w = 0.068. The ORTEP representation of the molecular structure of compound **1a** is depicted in Fig. 1. The positional parameters and the bond lengths and angles have been deposited as supplementary material.*

The length of the carbon–selenium double bond is 1.790(4) Å. The reported length of that of selenobenzaldehyde–tungsten complex is 1.864 Å. Thus, the free C=Se bond is shorter than that in the metal complex.[2g] However, in the isolable, sterically hindered selenoketone **1f**, a distance of 1.774(6) Å is found for the C=Se double bond. A theoretical approach to the length of the C=Se double bond in selenoformaldehyde arrived at a value of 1.739 Å (see Collins *et al.*)[10] These results suggested that aromatic groups of selenobenzophenones **1** allow the C=Se bond length to be greater than those of normal selenocarbonyl compounds. The C=S bond length in diphenylcyclopropenethione has been found to be 1.630 Å by X-ray crystallography.[11] The C=O bond of 4,4'-dimethoxybenzophenone **6a** has been found to be 1.280 Å.[12] The length of the C=Se double bond has been found to be much longer than those of C=S and C=O bonds. The dihedral angles between the C=Se plane and the two benzene rings are 136.8(1)°, 158.5(5) and the dihedral angle between the two benzene rings is 57.9(1)°.

Oxidation and Thiation.—The reaction of compound **1a** with 3-chloroperbenzoic acid (MCPBA) gave the corresponding benzophenone **6a** in 88% yield, as expected. The reaction of compound **1a** with elemental sulfur afforded 4,4'-dimethoxythiobenzophenone **2a** in nearly quantitative yield. We presume

* See Instructions for Authors, in the January issue.

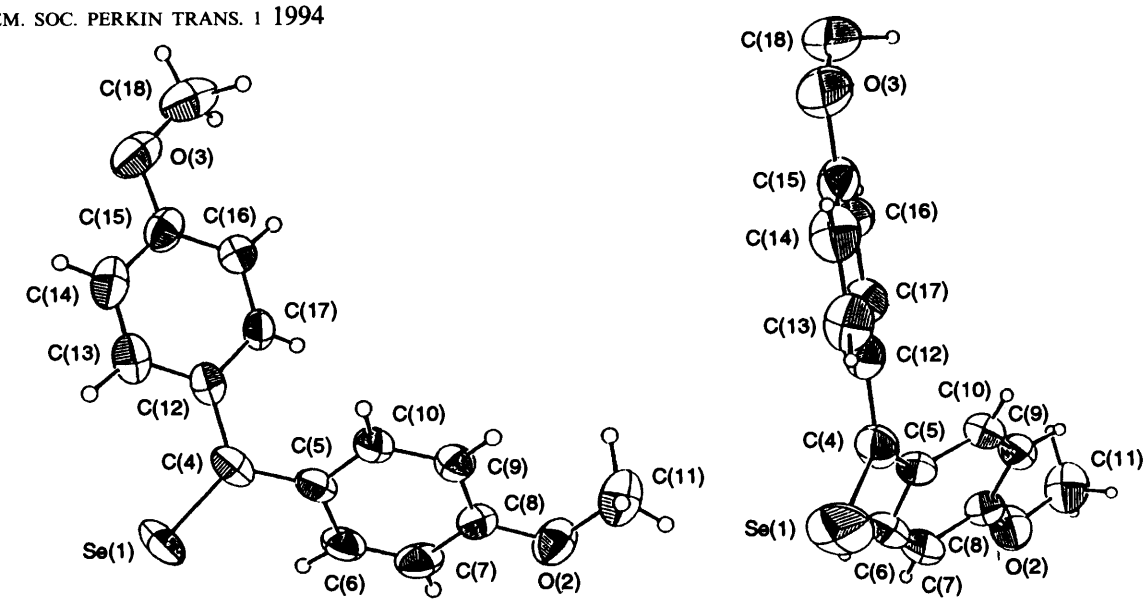
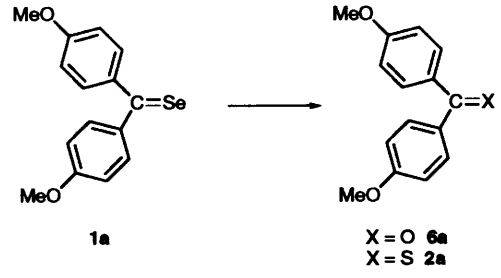
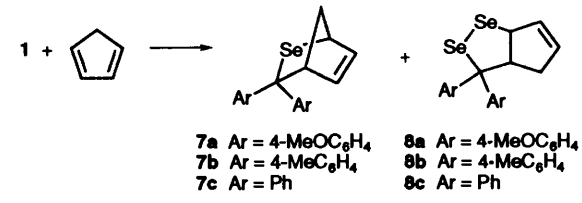


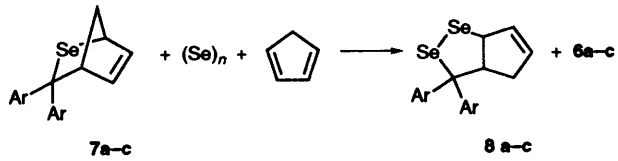
Fig. 1 X-Ray molecular structure of 4,4'-dimethoxyselenobenzophenone **1a**



Scheme 4 *Reagents and conditions:* [O] or S_8



Scheme 5



Scheme 6

that selone **1a** reacted with elemental sulfur to give the corresponding thioselenine (selone *Se*-sulfide:=C=Se=S) and selenathiirane intermediate, which decomposed to give thione **2a** (Scheme 4).[13]

Reaction with Cyclopentadiene.—It is well known that selenocarbonyl compounds react with cyclopentadiene to afford the corresponding cycloadducts.[2] We therefore investigated the reaction of isolated selenobenzophenones **1** with cyclopentadienes. Treatment of compound **1a** with cyclopentadiene afforded 3,3-bis-(4-methoxyphenyl)-2-selenabicyclo[2.2.1]-hept-5-ene **7a** in 45% at room temperature. Since compound **1a** is more stable than its analogues **1b** and **1c**, the reactivity of compounds **1b** and **1c** with cyclopentadiene is greater than that of compound **1a**. The yields of the corresponding cycloadducts (**7b**, **7c**) were 55 and 65%, as expected. In the course of an attempt to improve the yields of these cycloadducts, small amounts of side-products were obtained along with triphenylphosphine selenide when the reaction was carried out at elevated temperature and prolonged reaction time. These minor products were found to be the bicyclic diselenides **8a–c** (4,4-diaryl-2,3-diselenabicyclo[3.3.0]oct-7-enes) (Scheme 5).

Excess of elemental selenium might further react with selenides **7** to give diselenides **8**. To confirm this assumption, the reaction of compounds **7** with selenium was investigated. When 3,3-diphenyl-2-selenabicyclo[2.2.1]hept-5-ene **7c** was treated with elemental selenium in refluxing toluene, 4,4-diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene **8c** was obtained in 34% yield. Small amounts of benzophenone **6c** was also obtained along with recovered substrate **7c** (24%). Other selenides **7** were successfully converted into diselenides **8** in moderate yields (Table 2). The reaction is regioselective; only one isomer of **8a–c** was obtained in this reaction (Scheme 6).

Table 2 Reaction of selenides **7** with elemental selenium

Compound 7 Ar	Conditions		Products (yield/%)[a]	
	Temperature	Solvent	**8**	**6**
7a 4-$MeOC_6H_4$	reflux	toluene	**8a** 31	**6a** 4
7b 4-MeC_6H_4	reflux	toluene	**8b** 38	**6b** 4
7c Ph	reflux	benzene	**8c** 34	**6c** 8
7c Ph	reflux	toluene	**8c** 38	**6c** 4

[a] Starting material **7** was recovered to the extent of ~ 30%.

Regiochemistry was determined by ^1H and ^{13}C NMR spectroscopy. Additionally, X-ray crystallographic analysis was performed in the case of compound **8c**. The ORTEP representation of compound **8c** is depicted in Fig. 2.

Since selenides **7** were prepared by the reaction of phosphonium ylides **3** with selenium and cyclopentadiene,[4a] we further investigated this reaction in the presence of an excess of elemental selenium. Treatment of diphenylmethylenetriphenylphosphorane **3c** with elemental selenium (4 mol equiv.) afforded a bright green solution of selenobenzophenone **1c**. After treating this solution with 4 mol equiv. of cyclopentadiene for 18 h at 90 °C, we obtained reddish orange crystals of bicyclic diselenide **8c** and triphenylphosphine selenide in 52 and 88% yield, respectively. The reaction of other substituted phosphoranes **3** with elemental selenium is summarized in Table 3 (Scheme 7).

When the reaction was carried out by using a mixture of

Table 3 Reaction of phosphoranes 3 with selenium and cyclopentadienes

Ylide 3			Conditions		Products (Isolated yield/%)		
R	R'	Diene	Temperature	Solvent	8		Ph_3P=Se
4-MeC_6H_4	4-MeC_6H_4	Cp[a]	90 °C	toluene	**8b**	71	80
Ph	Ph	Cp	reflux	benzene	**8c**	42	75
Ph	Ph	Cp	90 °C	toluene	**8c**	52	88
4-FC_6H_4	4-FC_6H_4	Cp	90 °C	toluene	**8e**	75	82
4-ClC_6H_4	4-ClC_6H_4	Cp	90 °C	toluene	**8f**	62	78
Ph	Ph	MeCp[a]	90 °C	toluene	**8g, 8h**	63	76
H	CO_2Et	Cp	reflux	toluene	**8i**	35	68

[a] Cp = cyclopentadiene, MeCp = a mixture of methylcyclopentadienes.

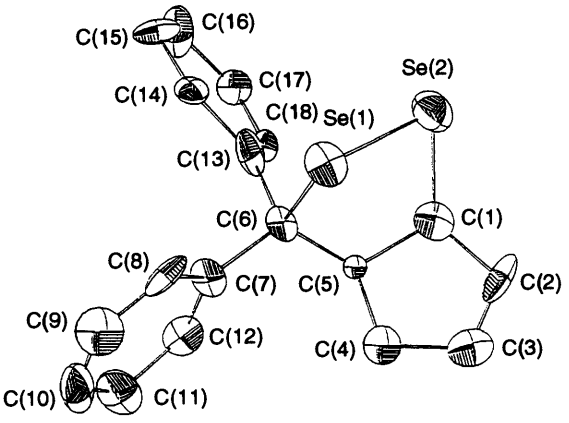
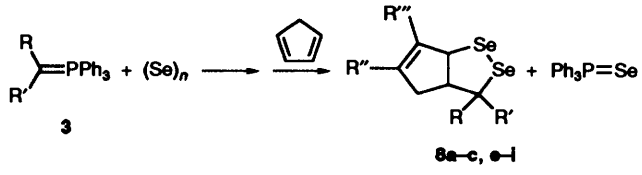


Fig. 2 X-ray molecular structure of compound **8c**. Selected distances (Å) and angles (°): Se(1)–Se(2) 2.322(2), Se(1)–C(6) 2.121(2), Se(2)–C(1) 2.201(13), C(1)–C(2) 1.513(19), C(1)–C(5) 1.529(17), C(2)–C(3) 1.335(20), C(3)–C(4) 1.464(20), C(4)–C(5) 1.542(18), C(5)–C(6) 1.476(16); C(6)–Se(1)–Se(2) 89.2(3), Se(1)–Se(2)–C(1) 90.5(3)



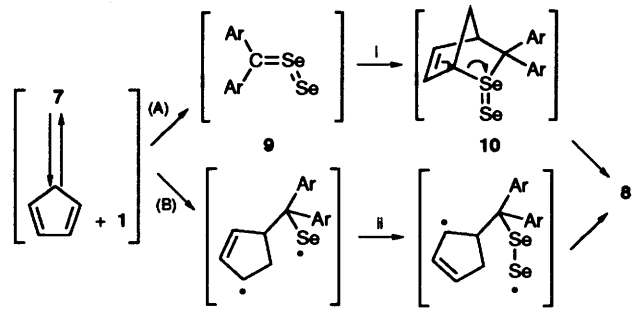
8 e; R = R' = C_6H_4F-*p*, R'' = R''' = H
f; R = R' = C_6H_4Cl-*p*, R'' = R''' = H
g; R = R' = Ph, R'' = H, R''' = Me
h; R = R' = Ph, R'' = Me, R''' = H
i; R = CO_2Et,, R' = R'' = R''' = H

Scheme 7

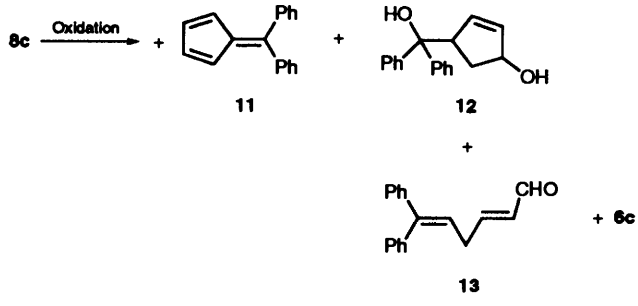
methylcyclopentadienes instead of cyclopentadiene, a mixture of 4,4-diphenyl-2,3-diselena-8-methylbicyclo[3.3.0]oct-7-ene **8g** and 4,4-diphenyl-2,3-diselena-7-methylbicyclo[3.3.0]oct-7-ene **8h** was obtained in a 4:1 ratio.

There are two possible mechanisms to explain the formation of diselenides **8**. First, selenide **7** decomposed to give selone **1** *via* a retro-Diels–Alder reaction, which further reacted with elemental selenium to afford diarylselenoselenine (selone *Se*-selenide) **9**. Compound **9** then reacts with cyclopentadiene to give *endo*-selenoselenide **10** which rearranges to bicyclic diselenide **8** (Route A). Block *et al.* reported that a bicyclic oxathiane was formed *via* an *endo* oxo-sulfide intermediate.[14] A radical mechanism is another explanation for the formation of bicyclic diselenides **8**. The adducts **7** homolytically decomposed to biradicals which further react with selenium followed by recombination to afford the bicyclic diselenide **8** (Route B) (Scheme 8).

To confirm which mechanism is operative, we then tried an



Scheme 8 *Reagents:* i, cyclopentadiene; ii, $(Se)_8$



Scheme 9

electron paramagnetic resonance (EPR) study of this reaction. When compound **3a** was treated with elemental selenium, followed by the addition of cyclopentadiene in toluene at 100 °C, a broad signal was observed in its EPR spectrum (*G*-value; 2.00). This result suggests that the reaction proceeds through a radical intermediate. Thus, Route B is a reasonable mechanism in this reaction. While many methods have been reported for the preparation of diselenides, there are only a few reports on the synthesis of cyclic diselenides.[4a] Only one example includes the cycloaddition of selenofluorenone **1e**, which acted not only as a dipolarophile but also a dipole.[2a] The present reaction is the first convenient synthesis of cyclic diselenides.

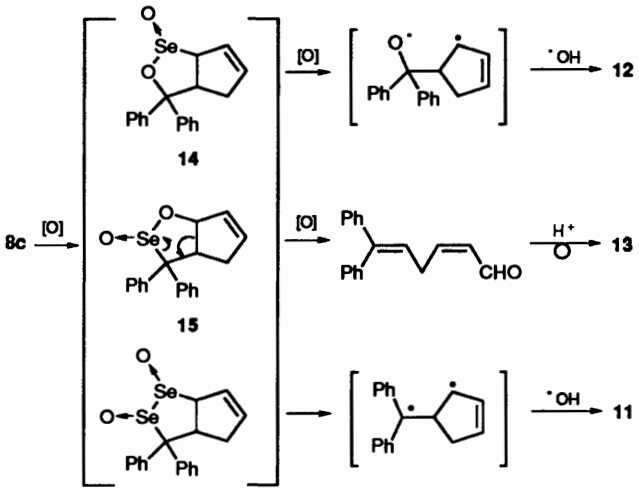
Oxidation of Diselenides **8**.—We also investigated the oxidation of compound **8c**. Treatment of diselenide **8c** with MCPBA afforded diphenylfulvene **11**, 4-(hydroxydiphenylmethyl)cyclopent-2-en-1-ol **12**, 6,6-diphenylhexa-2,5-dienal **13**, and benzophenone **6c** (Scheme 9 and Table 4).

The reaction might proceed as follows: diselenide **8c** is oxidized to give cyclic seleninate **14**, which decomposes to afford diol **12**. Another seleninate **15** decomposes to afford aldehyde **13**. Diphenylfulvene **11** might be produced *via* a radical reaction, because diselenide **8c** is converted into compound **11** in refluxing toluene for 24 h in 15% yield along with benzophenone **6c** (18%) and selenide **7c** (30%) (Scheme 10).

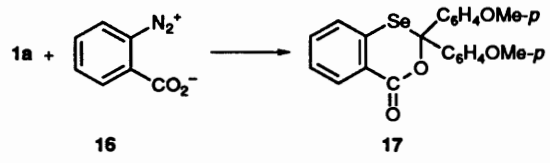
Table 4 Oxidation of diselenide **8c**

Oxidant	Conditions		Products (yield/%)			
	Solvent	Temp.[a]	**11**	**12**	**13**	**6c**
MCPBA (2 mol equiv.)	CH_2Cl_2	RT	22	23	0	5
MCPBA (5 mol equiv.)	CH_2Cl_2	RT	4	41	8	5
H_2O_2 (5 mol equiv.)	acetone	RT	27	35	3	6

[a] RT = room temperature.

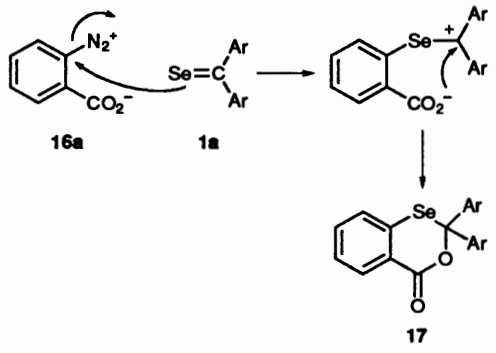


Scheme 10



16 **17**

Scheme 11 *Conditions:* reflux in CH_2Cl_2



Scheme 12

Reaction with Benzenediazonium 2-Carboxylate.—Benzenediazonium-2-carboxylate **16** is a well known benzyne precursor. However, thiobenzophenone **2c** reacted with this compound to give a 4*H*-3,1-benzoxathian-4-one.[15] We studied the reaction of compound **1a** with benzenediazonium-2-carboxylate. Treatment of compound **1a** with this inner salt in refluxing dichloromethane afforded the corresponding 2,2-bis(4-methoxyphenyl)-3,1-benzoxaseleninone **17** in 61% yield (Scheme 11). When diphenyliodonium-2-carboxylate monohydrate was used instead of compound **16**, compound **17** was obtained in 25% yield.

Thus, these reagents did not act as benzyne precursors. The following mechanism is reasonable: the selenocarbonyl selenium intercepts a radicaloid or cationic intermediate and then cyclizes to give the final product **17** (Scheme 12).

Experimental

All reactions were carried out under nitrogen. NMR spectra were measured on a JEOL GSX-400 (400 MHz for ^1H, 100 MHz for ^{13}C spectrometer). *J* Values are given in Hz. M.p.s were measured on a YANACO MPS-3 and are uncorrected. UV–VIS spectra were recorded on a JASCO UVDEC-505 spectrometer. The EPR spectrum was measured on a JEOL JES-RE1A spectrometer.

Materials.—Phosphonium salts **4b**, **4c**, **4e** and **4f** were prepared by the reaction of triphenylphosphine with the corresponding halides by the procedure described by Tokunaga *et al.*[3b] [Bis(4-methoxyphenyl)methyl]triphenylphosphonium tetrafluoroboramide **4a** was prepared by the reaction of triphenylphosphonium tetrafluoroboramide with bis(4-methoxyphenyl)methanol and had m.p. 211–212 °C (Found: C, 69.0; H, 5.3. Calc. for $C_{33}H_{30}BF_4O_2P$: C, 68.8; H, 5.3%). Salt **4d** was prepared in a similar manner: m.p. 197.5–198.5 °C (Found: C, 71.7; H, 6.1. Calc. for $C_{35}H_{34}BF_4OP$: C, 71.5; H, 6.1%).

Preparation of 4,4'-Dimethoxyselenobenzophenone **1a**.—To a degassed solution of [bis(4-methoxyphenyl)methyl]triphenylphosphonium tetrafluoroboramide **4a** (1.15 g, 2.0 mmol) in benzene (40 cm^3) was added butyllithium (1.6 mol dm^{-3} in hexane; 1.41 cm^3, 2.2 mmol) at room temperature. After the mixture has been stirred for 30 min, selenium powder (0.47 g, 6.0 mmol) was added portionwise and the mixture was refluxed for 30 min. The resulting suspension was filtered to give a green solution, which was evaporated to give a green solid. This solid was chromatographed over silica gel by elution with pentane–dichloromethane (4:1) to give crude compound **1a** (0.354 g, 58%) as green crystals, which was recrystallized from pentane to afford pure green needles of compound **1a**, m.p. 98–99 °C; ^{77}Se NMR ($CDCl_3$; PhSeSePh was used as standard; 480 ppm) δ 1926 (Found: C, 59.1; H, 4.6. Calc. for $C_{15}H_{14}O_2Se$: C, 59.0; H, 4.6%. Found: M^+, 306.0101. Calc. for $C_{15}H_{14}O_2{}^{80}Se$: *M*, 306.0159).

X-Ray Crystal Structure Determination of Compound **1a**.—*Data collection and structure solution.* Molecular formula $C_{15}H_{14}O_2Se$, relative molecular mass 305.2, crystal colour deep green, crystal size 0.50 × 0.50 × 0.90 mm mounted in a glass capillary with its long axis roughly parallel to the Φ axis of the goniometer. Preliminary examination and data collection were performed with Mo-Kα radiation (λ = 0.710 73 Å) on an Enraf–Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochrometer. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the set angles of 25 reflections in the range $11 < \theta < 15°$, measured by the computer-controlled diagonal-slit method of centering. The monoclinic cell parameters and calculated volume are: a = 7.191(3), b = 7.505(4), c = 24.856(4) Å, β = 90.32(3), V = 1341.4 Å^3. For

$Z = 4$, the calculated density is 1.51 g cm^{-3}. From the systematic absence of: $h0l: h + l = 2n: 0k0: k = 2n$ and from subsequent least-squares refinement, the space group was determined to be $P2_1/n$. The structure was solved by direct methods, and H-atom positions were calculated and fixed in the final least-squares refinement, $R = 0.055$, $R_w = 0.068$.

Preparation of 4,4'-*Dimethylselenobenzophenone* **1b**.—To a degassed solution of [di(*p*-tolyl)methyl]triphenylphosphonium tetrafluoroboramide **4b** (1.09 g, 2.0 mmol) in benzene (40 cm^3) was added butyllithium (1.41 cm^3, 1.6 mol dm^{-3} in hexane; 1.41 cm^3, 2.2 mmol). After the mixture had been stirred for 30 min, selenium powder (0.47 g, 6.0 mmol) was added portionwise to this suspension and the mixture was refluxed for 30 min. The resulting suspension was filtered to give a green solution, which was evaporated to give a green solid. This solid was chromatographed over silica gel by elution with pentane to afford crude compound **1b** (0.21 g, 38%) as green crystals, which was recrystallized from pentane to give pure compound **1b** as green needles, m.p. 74–75.5 °C (Found: C, 66.2; H, 5.0. Calc. for $C_{15}H_{14}Se$: C, 65.9; H, 5.1%. Found: M^+, 274.0302. Calc. for $C_{15}H_{14}{}^{80}Se$: *M*, 274.0261).

Attempted Preparation of Selenobenzophenone **1c**.—To a degassed solution of (diphenylmethyl)triphenylphosphonium bromide **4c** (1.02 g, 2.0 mmol) in benzene (40 cm^3) was added a solution of butyllithium (1.6 mol dm^{-3} in hexane; 1.4 cm^3, 2.2 mmol) in hexane. After the mixture had been stirred for 30 min at room temperature, elemental selenium (0.47 g, 6.0 mmol) was added in one portion. The resulting red suspension was refluxed for 30 min to afford a bright green suspension of selenobenzophenone **1c**. The reaction mixture was filtered and evaporated to give greenish yellow crystals. The resulting solid was chromatographed over silica gel by elution with pentane and on recrystallization from pentane gave a dimer of selenobenzophenone, compound **5c** (0.294 g, 30%), m.p. 105–107 °C (lit.,[6] 109 °C). Spectral data of **5c** are identical with those reported (Found: M^+, 245.9950. Calc. for $C_{13}H_{10}{}^{80}Se$: *M*, 245.9947).

Attempted Preparation of tert-*Butyl p-phenoxyphenyl Selenoketone* **1d**.—To a suspension of [2,2-dimethyl-1-(*p*-phenoxyphenyl)methyl]triphenylphosphonium tetrafluoroboranide **4d** (0.588 g, 1.0 mmol) in benzene (30 cm^3) was added a solution of butyllithium (1.6 mol dm^{-3} in hexane; 0.7 cm^3, 1.1 mmol) in hexane at room temperature. After the mixture had been stirred for 30 min, elemental selenium (0.24 g, 3.0 mmol) was added in one portion. After the resulting red suspension had been refluxed for 30 min, a bright green solution of a mixture of *tert*-butyl phenoxyphenyl selenoketone **1d** and its dimer **5d** was obtained. The reaction mixture was filtered and evaporated to give a greenish solid. The resulting mixture was chromatographed over silica gel by elution with pentane to afford greenish crystals of dimer **5d**, which were recrystallized from pentane to afford greenish yellow crystals (0.15 g, 47%), m.p. 164.5–166 °C; δ_H(400 MHz; $CDCl_3$) 1.03 (18 H, s, Bu^t), 6.67 (4 H, d, ArH), 6.87 (4 H, d, ArH), 7.06 (2 H, t, ArH), 7.33 (4 H, t, ArH) and 7.59 (4 H, d, ArH); δ_C(100 MHz; $CDCl_3$) 26.88 (Bu^t), 39.49, 40.30, 115.70, 118.44, 122.89, 129.75, 132.87, 139.99, 154.25, 154.25 and 157.65 (Found: C, 64.5; H, 5.5. Calc. for $C_{34}H_{36}O_2Se_2$: C, 64.4; H, 5.7%).

Reaction of Fluorenylidenetriphenylphosphorane **3e** *with Elemental Selenium*.—To a solution of fluorenylidenetriphenylphosphorane **3e** [3a] (0.153 g, 0.5 mmol) in toluene (30 cm^3) was added elemental selenium (0.12 g, 1.5 mmol) in one portion. After being stirred for 6 h at 90 °C, the reaction mixture turned reddish orange in colour. The resulting suspension was filtered and evaporated to give reddish brown crystals, which were chromatographed over silica gel by elution with dichloromethane–hexane (1:1) to afford 9,9'-bifluorenylidene (0.130 g, 79%) and triphenylphosphine selenide (0.153 g, 90%). 9,9'-Bifluorenylidene was identical with that reported, m.p. 183–184 °C (lit.,[16] 182–183 °C).

Oxidation of Compound **1a**.—To a solution of compound **1a** (0.153 g, 0.5 mmol) in benzene (10 cm^3) was added a solution of MCPBA (0.173 g, 1 mmol) in benzene (10 cm^3). Immediately, red selenium was precipitated. After stirring of the mixture for 6 h, 3-chlorobenzoic acid had also precipitated. These substances were filtered off. The filtrate was washed with 5% aq. sodium carbonate, dried over magnesium sulfate, and evaporated to give the crude 4,4'-dimethoxybenzophenone **6a** in nearly quantitative yield (0.235 g, 97%). Recrystallization from methanol afforded pure ketone **6a** (0.106 g, 0.44 mmol, 88%), m.p. 112–114 °C (lit.,[17] 116–118 °C).

Thiation of Compound **1a**.—To a solution of compound **1a** (0.153 g, 0.5 mmol) in benzene (10 cm^3) was added a solution of elemental sulfur (0.017 g, 0.53 mmol) in benzene (10 cm^3). The reaction mixture was refluxed for 30 min, and red selenium was precipitated, which was filtered off. The filtrate was evaporated to give 4,4'-dimethoxythiobenzophenone **2a** in almost quantitative yield (0.118 g, 97%), m.p. 113–115 °C (lit.,[18] 116–118 °C).

Reaction of Compound **1a** *with Cyclopentadiene*.—To a solution of compound **1a** (0.460 g, 1.5 mmol) in benzene (15 cm^3) was added a solution of cyclopentadiene (0.50 g, 7.5 mmol) in benzene (15 cm^3). After being stirred for 6 h, the bright green solution turned to pale brown, and was evaporated to give a brown oil. The reaction mixture was chromatographed over silica gel by elution with dichloromethane–hexane (1:1) to afford the corresponding adduct **7a** (0.251 g, 45%) as a pale green oil, δ_H(400 MHz; $CDCl_3$) 2.12 (1 H, dt, *J* 9.8, 2.4 and 2.4, CH*H*), 2.31 (1 H, d, *J* 9.8, CH*H*), 3.68 (1 H, br s, CH), 3.76 (6 H, d, *J* 9.2, OMe), 4.55 (1 H, br s, CH), 5.44 (1 H, dd, *J* 3.1 and 5.5, =CH), 6.43 (1 H, dd, *J* 2.5 and 3.1, =CH), 6.70 (2 H, d, *J* 9.2, ArH), 6.78 (2 H, d, *J* 9.2, ArH), 7.22 (2 H, d, *J* 9.2, ArH) and 7.28 (2 H, d, *J* 9.2, ArH); δ_C(100 MHz; $CDCl_3$) 51.34 (CH), 52.84 (CH_2), 55.73 (CH), 55.80 (Me), 55.90 (Me), 76.47, 113.45, 113.98, 129.91, 131.15, 133.44 (=CH), 139.05 (*C*OMe), 139.51 (=CH), 142.07 (*C*OMe), 158.03 (*ipso*-C) and 158.29 (*ipso*-C) (Found: C. 64.8; H, 5.3. Calc. for $C_{20}H_{20}O_2Se$: C, 64.7; H, 5.4%).

3,3-(*p*-Ditolyl)-2-selenabicyclo[2.2.1]hept-5-ene **7b** was prepared in a similar manner by using compound **1b** (0.137 g, 0.50 mmol) and cyclopentadiene (0.132 g, 2.0 mmol). Compound **7b** (0.098 g, 55%) had m.p. 114 °C (decomp.); δ_H(400 MHz; $CDCl_3$) 2.00–2.37 (2 H, m, CH_2), 2.27 (6 H, s, Me), 3.74 (1 H, br s, CH), 4.50 (1 H, br s, CH), 5.37–5.47 (1 H, m, =CH), 6.35–6.45 (1 H, m, =CH) and 6.90–7.30 (8 H, m, ArH) (Found: C, 70.7; H, 5.9. Calc. for $C_{20}H_{20}Se$: C, 70.8; H, 5.9%).

3,3-*Diphenyl-2-selenabicyclo*[2.2.1]*hept-5-ene* **7c** was prepared in a similar manner by using the crude dimer of compound **1c** (0.123 g, 0.50 mmol) and cyclopentadiene (0.132 g, 2.0 mmol) to give compound **7c** (0.101 g, 65%), m.p. 139–141 °C; δ_H(400 MHz; $CDCl_3$) 2.27 (1 H, m, C*H*H), 2.37 (1 H, d, CH*H*), 3.80 (1 H, br s, CH), 4.57 (1 H, br s, CH), 5.47 (1 H, dd, CH), 6.43 (1 H, dd, =CH) and 7.09–7.60 (10 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 50.98, 52.50, 55.31, 126.39, 127.96, 128.34, 128.72, 129.96, 132.73, 133.05, 139.39, 146.22 and 149.25; ν_{max}(KBr)/cm^{-1} 3045, 3015, 2990, 1595, 1483, 1440, 1337, 1075, 1035, 1017, 972, 905, 850, 785, 760, 730 and 700 (Found: C, 69.4; H, 5.1. Calc. for $C_{18}H_{16}Se$: C, 69.5; H, 5.2%).

Reaction of Adducts **7** *with Elemental Selenium.*—To a solution of adduct **7b** (0.170 g, 0.50 mmol) and cyclopentadiene (0.066 g, 1.0 mmol) in toluene (20 cm^3) was added elemental selenium (0.16 g, 2.0 mmol) in one portion. After being refluxed for 16 h, the reaction mixture was filtered and evaporated to give reddish orange crystals, which were chromatographed over silica gel by elution with hexane–dichloromethane (5:1) to give 4,4-di-(*p*-tolyl)-2,3-diselenabicyclo[3.3.0]oct-7-ene **8b** (0.079 g, 38%), m.p. 118–119 °C, δ_H(400 MHz; $CDCl_3$) 2.18–2.26 (1 H, m, CH*H*), 2.29 (6 H, s, Me), 2.32–2.44 (1 H, m, CH*H*), 4.59–4.65 (1 H, q, *J* 6.6 and 14.7, CH), 5.04–5.05 (1 H, br d, *J* 6.6, CH), 5.70 (1 H, br d, *J* 5.9, =CH), 5.88–5.91 (1 H, m, =CH) and 7.04–7.45 (8 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 20.90 (Me), 31.01 (Me), 40.25, 56.95, 59.31, 82.99, 127.94, 127.98, 128.16, 128.99, 136.28, 136.50, 142.19 and 143.84 (Found: C, 57.7; H, 4.8. Calc. for $C_{20}H_{20}Se_2$: C, 57.4; H, 4.8%). 4,4′-Dimethylbenzophenone **6b** (0.006 g, 6%) was also obtained along with recovered substrate **7b** (0.038 g, 22%).

4,4′-Bis(*p*-methoxyphenyl)-2,3-diselenabicyclo[3.3.0]oct-7-ene **8a** (0.067 g, 31%) was prepared in a similar manner as an orange oil; δ_H(400 MHz; $CDCl_3$) 2.18–2.25 (1 H, m, CH*H*), 2.34–2.25 (1 H, m, C*H*H), 3.77 (6 H, s, Me), 4.54 (1 H, br dd, *J* 8.6 and 6.4, CH), 5.04–5.05 (1 H, m, CH), 5.71–5.72 (1 H, m, =CH), 5.89–5.91 (1 H, m, =CH), 6.78 (4 H, d, *J* 8.5, ArH), 7.17 (2 H, d, *J* 8.5, ArH) and 7.42 (2 H, d, *J* 8.5, ArH); δ_C(100 MHz; $CDCl_3$) 40.19 (CH_2), 55.11 (Me), 55.20 (Me), 57.38 (CH), 59.44 (CH), 82.32 (CAr_2), 112.63, 113.50, 128.44, 128.55, 129.07, 129.16, 130.83 (=CH), 131.54 (=CH), 137.39, 138.98, 157.98 (*ipso*-C) and 158.13 (*ipso*-C) (Found: M^+, 451.9807. Calc. for $C_{20}H_{20}O_2{}^{80}Se_2$: *M*, 451.9792). 4,4′-Dimethoxybenzophenone **6a** (0.015 g, 12%) was isolated along with recovered substrate **7a** (0.036 g, 20%).

4,4′-Diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene **8c** (0.086 g, 38%) was prepared in a similar manner by using compound **7c** (0.225 g, 0.58 mmol) and elemental selenium (0.150 g, 1.9 mmol). Benzophenone **6c** (0.009 g, 9%) and substrate **7c** (0.044 g, 24% recovery) were also obtained. Compound **8c** had m.p. 158–160 °C, δ_H(400 MHz; $CDCl_3$) 2.18–2.24 (1 H, m, 6-H), 2.33–2.39 (1 H, m, 6-H′), 4.62–4.68 (1 H, q, *J* 7.0, 5-H), 5.05–5.07 (1 H, m, 1-H), 5.70 (1 H, m, 7-H), 5.89 (1 H, m, 8-H) and 7.15–7.52 (10 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 40.18 (C-6), 56.88 (C-5), 59.06 (C-1), 83.05 (C-4), 126.66, 126.84, 127.34, 128.19, 128.30, 130.31 (C-8), 132.85 (C-7), 144.92 (*ipso*-C) and 146.54 (*ipso*-C) (Found: C, 55.7; H, 3.9. Calc. for $C_{18}H_{16}Se_2$: C, 55.4; H, 4.1%). Crystal data of compound **8c**: space group $Pna2_1$, a = 10.694(1), b = 9.289(1), c = 15.340(2) Å, V = 1523.8 $Å^3$, Z = 4, D_{calc} = 1.70 g cm^{-3}. Data collected at 25 °C on Rigaku AFC-III diffractometer with Mo-Kα radiation, μ = 47.9 cm^{-1}, $15 < \theta < 25°$, 182 variables refined with 1076 unique reflections $F_o > 3\sigma(F_o)$ to R = 0.067 (R_w = 0.034).

Reaction of Phosphorus Ylides **3** *with Elemental Selenium followed by the Addition of Cyclopentadiene.*—To a suspension of compound **4c** (2.55 g, 5 mmol) in toluene (50 cm^3) was added a solution of butyllithium (1.6 mol dm^{-3} in hexane; 3.8 cm^3, 6 mmol) in hexane by using a dropping funnel at 0 °C. After the mixture had been stirred for 1 h at 0 °C, elemental selenium (1.58 g, 20 mmol) was added in one portion to this suspension. This red suspension, heated for 15 min at 90 °C, afforded a bright green solution of selenobenzophenone **6c**. After this mixture had been stirred for 30 min at this temperature, cyclopentadiene (1.32 g, 20 mmol) was added to this suspension. After being refluxed for 15 h, the reaction mixture was filtered and evaporated to give reddish orange crystals, which were chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give compound **8c** (0.92 g, 52%), compound **7c** (0.25 g, 16%), diphenylfulvene **11** (0.021 g, 2%) and triphenylphosphine selenide (1.51 g, 88%).

4,4-Bis(4-fluorophenyl)-2,3-diselenabicyclo[3.3.0]oct-7-ene **8e** was obtained in a similar manner, m.p. 119–120 °C; δ_H(400 MHz; $CDCl_3$) 2.16–2.24 (1 H, m, 6-H), 2.30–2.37 (1 H, m, 6-H′), 4.51–4.57 (1 H, q, *J* 6.5, 5-H), 5.03 (1 H, br d, *J* 6.5, 1-H), 5.71 (1 H, br d, 7-H), 5.88–5.91 (1 H, m, 8-H), 6.91–6.98 (ArH), 7.21–7.25 (ArH) and 7.44–7.48 (ArH); δ_C(100 MHz; $CDCl_3$) 40.23 (C-6), 57.44 (C-5), 59.25 (C-1), 81.24 (C-4), 114.19, 114.39, 115.18, 115.40, 129.64, 129.70, 129.77 (Ar), 130.38 (C-8), 132.81 (C-7), 140.64, 142.35, 160.11, 160.20, 162.56 and 162.67 (Ar) (Found: C, 50.8; H, 3.3. Calc. for $C_{18}H_{14}F_2Se_2$: C, 50.7; H, 3.3%).

4,4-Bis(4-chlorophenyl)-2,3-diselenabicyclo[3.3.0]oct-7-ene **8f** was obtained in a similar manner by using [bis(4-chlorophenyl)methyl]triphenylphosphonium chloride **4f** (1.60 g, 3.0 mmol), butyllithium (1.6 mol dm^{-3} in hexane; 2 cm^3, 3.2 mmol), elemental selenium (0.95 g, 12 mmol) and cyclopentadiene (0.79 g, 12 mmol). Compound **8f** (0.233 g, 62%) had m.p. 121–122 °C; δ_H(400 MHz; $CDCl_3$) 2.23–2.25 (1 H, m, 6-H), 2.29–2.31 (1 H, m, 6-H′), 4.51–4.56 (1 H, q, *J* 6.6, 5-H), 5.03 (1 H, br d, *J* 6.6, 1-H), 5.72 (1 H, br d, 7-H), 5.89–5.91 (1 H, m, 8-H) and 7.17–7.26 and 7.40–7.42 (8 H, m, ArH); δ_C(100 MHz; $CDCl_3$) 40.22 (C-6), 57.02 (C-5), 59.18 (C-1), 81.15 (C-4), 127.65, 128.60, 129.48 (Ar), 130.40 (C-8), 132.77 (C-7), 143.02 (*ipso*-C) and 144.92 (*ipso*-C) (Found: C. 47.4; H, 3.3. Calc. for $C_{18}H_{14}Cl_2Se_2$: C, 47.1; H, 3.1%).

8-Methyl-4,4-diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene **8g** and 7-methyl-4,4-diphenyl-2,3-diselenabicyclo[3.3.0]oct-7-ene **8h** were prepared in a similar manner by using diphenylmethylenetriphenylphosphorane **3c** (1.28 g, 3.0 mmol), elemental selenium (0.71 g, 9.0 mmol), and a mixture of methylcyclopentadienes (0.96 g, 12 mmol). A mixture of products **8g** and **8h** was obtained (4:1 ratio; 0.77 g, 63%). Separation was carried out on silica gel chromatography by elution with hexane–dichloromethane (5:1) followed by recrystallization (hexane–dichloromethane). Compound **8g** (0.35 g, 29%) had m.p. 143–144 °C; δ_H(400 MHz; $CDCl_3$) 1.83 (3 H, s, Me), 2.11 (1 H, m, 6-H), 2.28 (1 H, m, 6-H′), 4.68–4.73 (1 H, dd, *J* 6.9 and 7.3, 5-H), 4.87 (1 H, br d, *J* 5.9, 1-H), 5.40 (1 H, br s, 7-H), 7.16–7.27 (8 H, m, Ph) and 7.53 (2 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 16.14 (Me), 40.38 (C-6), 57.89 (C-5), 64.44 (C-1), 82.92 (C-4), 125.79 (C-7), 126.72, 126.90, 127.41, 128.16, 128.19 and 128.37 (Ar), 141.03 (C-8), 144.54 (*ipso*-C) and 146.61 (*ipso*-C) (Found: C, 56.2; H, 4.45. Calc. for $C_{19}H_{18}Se_2$: C, 56.5; H, 4.5%). Compound **8h** (0.080 g, 6.3%) had m.p. 141–142 °C; δ_H(400 MHz; $CDCl_3$) 1.70 (3 H, s, Me), 2.04–2.11 (1 H, m, 6-H), 2.35–2.39 (1 H, m, 6-H′), 4.67–4.72 (1 H, q, *J* 6.6 and 8.1, 5-H), 5.07 (1 H, br d, *J* 6.6, 1-H), 5.52 (1 H, br s, 8-H), 7.14–7.28 (8 H, m, Ph) and 7.50–7.52 (2 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 16.51 (Me), 44.15 (C-6), 57.74 (C-5), 60.19 (C-1), 82.81 (C-4), 126.63 and 126.83 (Ph), 127.14 (C-8), 127.34, 128.14, 128.24 and 128.31 (Ph), 141.13 (C-7), 145.04 (*ipso*-C) and 146.56 (*ipso*-C) (Found: C, 56.6; H, 4.2%).

Methyl 2,3-*Diselenabicyclo*[3.3.0]*oct-7-ene-4-carboxylate* **8i**.—To a solution of (methoxycarbonylmethylene)triphenylphosphorane **3i** (1.67 g, 5.0 mmol) and cyclopentadiene (1.32 g, 20 mmol) in toluene (30 cm^3) was added elemental selenium (1.18 g, 15 mmol). After being refluxed for 23 h, the resulting mixture was filtered and evaporated to give reddish orange oily crystals. The resulting mixture was roughly chromatographed over silica gel by elution with hexane–dichloromethane (1:1) to give isomeric products **8i** (*cis*) and **8i′** (*trans*) as a mixture (0.52 g, 35%, ~9:4 determined by ^1H NMR spectroscopy). This mixture was further chromatographed over silica gel by elution with hexane–dichloromethane (5:2) to afford the *cis* isomer of methyl 2,3-diselenabicyclo[3.3.0]oct-7-ene-4-carboxylate **8i** as a reddish orange oil, δ_H(400 MHz; $CDCl_3$) 2.27–2.35 (1 H, m, 6-H), 2.69–2.77 (1 H, m, 6-H′), 3.76 (3 H, s, OMe), 4.07–4.13

(1 H, q, 5-H), 4.41 (1 H, s, 4-H), 5.23–5.29 (1 H, br d, 1-H), 5.73–5.75 (1 H, br d, 7-H) and 5.80–5.83 (1 H, m, 8-H); δ_C(100 MHz; $CDCl_3$) 37.44 (C-6), 50.05 (C-5), 52.85 (OMe), 57.68 (C-4), 63.06 (C-1), 131.11 (C-7), 132.57 (C-8) and 170.23 (C=O) (Found: M^+, 297.9008. Calc. for $C_8H_{10}O_2{}^{80}Se_2$: *M*, 297.9004).

Reaction of Compound **8c** *with MCPBA*.—To a solution of compound **8c** (0.393 g, 1.0 mmol) in dichloromethane (10 cm^3) was added dropwise a solution of MCPBA (0.345 g, 2.0 mmol) in dichloromethane (10 cm^3). After being stirred for 30 min, the resulting suspension was filtered, washed with 10% aq. $NaHCO_3$ (10 cm^3), dried over magnesium sulfate, and evaporated to give a pale brown oil. This oil was chromatographed over silica gel by elution with hexane, hexane–dichloromethane, dichloromethane, and ethyl acetate to afford diphenylfulvene **11**, benzophenone **6c** and 4-(hydroxydiphenylmethyl)cyclopent-2-en-1-ol **12**. Diphenylfulvene **11** (0.051 g, 22%) had m.p. 81–82 °C and was identical with an authentic sample purchased from Aldrich (m.p. 81.5–83 °C). Benzophenone **6c** (0.009 g, 5%). Diol **12** (0.061 g, 23%) had δ_H(400 MHz; $CDCl_3$) 1.64 (1 H, d, *J* 14.7, CH*H*), 2.24 (1 H, m, CH*H*), 2.37 (1 H, br s, OH), 2.95 (1 H, br s, OH), 3.94 (1 H, dq, *J* 6.7 and 1.8, CH), 4.68 (1 H, br s, C*H*OH), 5.68 (1 H, dd, *J* 3.7 and 2.4, =CH), 6.04 (1 H, dt, *J* 6.1 and 1.0) and 7.18–7.52 (10 H, m, Ph); δ_C(100 MHz; $CDCl_3$) 35.71 (CH_2), 53.52 (CH), 75.56 (CHOH), 77.93 (Ph_2COH), 125.76, 125.87, 126.67, 126.86, 128.23 and 134.66 (=CH), 136.73 (=CH) and 146.60 (*ipso*-C) (Found: C, 81.1; H, 6.8. Calc. for $C_{18}H_{18}O_2$: C, 81.2; H, 6.8%).

When 5 mol equiv. of MCPBA (0.862 g, 5 mmol) were used, 6,6-diphenylhexa-2,5-dienal **13** was obtained in 8% yield along with compounds **11** (0.009 g, 4%) and **12** (0.108 g, 41%). The aldehyde **13** was an oil (0.020 g, 8%), δ_H(400 MHz; $CDCl_3$) 3.15 (2 H, m, CH_2), 6.09 (1 H, t, *J* 14.7 and 7.3, 5-H), 6.18 (1 H, dd, *J* 8.1 and 8.0, 2-H), 6.87 (1 H, *J* 15.4 and 8.1, 3-H), 7.15–7.45 (10 H, m, Ph) and 9.54 (1 H, d, *J* 8.1, CHO); δ_C(100 MHz; $CDCl_3$) 33.06 (CH_2), 127.32, 127.55, 128.24, 128.45, 129.56, 133.12 (C-2), 156.44 (C-3) and 193.84 (C-1) (Found: M^+, 248.1200. Calc. for $C_{18}H_{16}O$: *M*, 248.1201).

Reaction of Compound **1a** *with Benzenediazonium-2-carboxylate* **16**.—To a solution of benzenediazonium-2-carboxylate hydrochloride (23 mg, 0.15 mmol) in dichloromethane (10 cm^3) was added 4,4′-dimethoxyselenobenzophenone **1a** (40 mg, 0.13 mmol) in one portion and the mixture was refluxed for 1 h. The green solution turned yellow. After removal of the solvent, the residual oil was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1). 2,2-Bis(4-methoxyphenyl)-4*H*-3,1-benzoxaselenenin-4-one **17** was obtained in 61% yield (34 mg, 0.080 mmol), m.p. 131–132 °C; δ_H(400 MHz; $CDCl_3$) 3.76 (6 H, s, OMe), 6.79 (4 H, s, ArH), 7.17 (1 H, t, Ph), 7.34 (1 H, q, Ph), 7.39 (1 H, d, Ph), 7.48 (4 H, d, ArH) and 8.03 (1 H, dd, Ph); δ_C(100 MHz; $CDCl_3$) 55.24 (OMe), 92.73 ($SeCOAr_2$), 113.56 (Ar), 126.65 (Ph), 126.91 (Ph), 128.90 (Ar), 129.56 (Ph), 132.74 (Ph), 133.55 (Ph), 134.61 (Ar), 159.64 (Ar) and 165.44 (CO_2) (Found: M^+, 424.0379. Calc. for $C_{22}H_{18}O_4{}^{78}Se$; *M*, 424.0379).

The reaction of diphenyliodonium-2-carboxylate monohydrate with compound **1a** was also investigated. A mixture of diphenyliodonium-2-carboxylate (0.172 g, 0.50 mmol) and compound **1a** (0.152 g, 0.50 mmol) in *p*-dichlorobenzene (15 cm^3) was refluxed for 1 h. The resulting mixture was evaporated, and the residue was chromatographed over silica gel by elution with hexane–dichloromethane (1 : 1) to afford compound **17** (0.053 g, 25%).

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