

Reactions of *O*-Silyl Selenocarboxylates; IR and NMR Spectra of Heteroatom-substituted Selenocarboxylates

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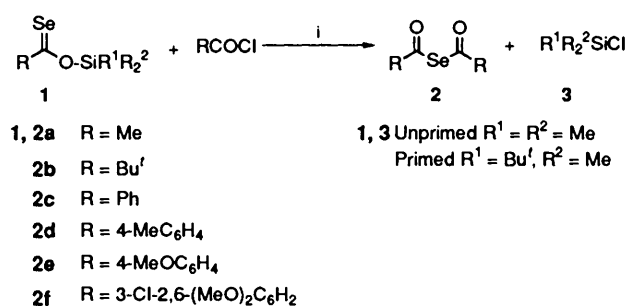
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O-Silyl selenocarboxylates **1** react readily with acyl chlorides to give selenoanhydrides. Attempts to synthesize unsymmetrical selenoanhydrides selectively gave mixtures of the desired products with *symmetrical* selenoanhydrides. Ph_3GeCl , Ph_3SnCl , Ph_3PbCl , Ph_2PCl and Ph_2AsCl were treated with **1** to give the corresponding selenocarboxylates containing a Se-heteroatom bond. Reactions with ArSCl , PhSeBr and PhTeI afforded the corresponding arenechalcogenyl selenocarboxylates. The C=O stretch of these derivatives showed a shift to lower frequency in moving from lighter to heavier atoms within a group of the Periodic Table. This may partly be due to the delocalization of an electron lone pair on selenium to form a diene type of conjugated system involving the C=O and Se-heteroatom bonds. A downfield shift in the signals in the ^{77}Se NMR spectra was observed in going from group 14 to group 16 elements; in contrast, the ^{13}C NMR signals of the C=O moiety were almost independent of the heteroatom attached to Se.

In contrast to *O*-alkyl or -aryl thiocarboxylates (RCSOR'),¹ much less is known about the chemistry of *O*-alkyl or -aryl selenocarboxylates (RCSeOR').² Previously, we have reported the preparation of *O*-silyl thio- ($\text{RCSOSiR}'_3$)³ and selenocarboxylates ($\text{RCSeOSiR}'_3$)⁴ from silyl chlorides with potassium thiocarboxylates and sodium selenocarboxylates, respectively. High reactivity for these compounds might be expected since they easily undergo hydrolysis. In this paper, we report the details of the reaction of *O*-silyl selenocarboxylates **1** with various carbon electrophiles, heteroatom substituted chlorides containing group 14, 15 and 16 elements, and the spectral properties of the heteroatom substituted selenocarboxylates obtained.

Results and Discussion

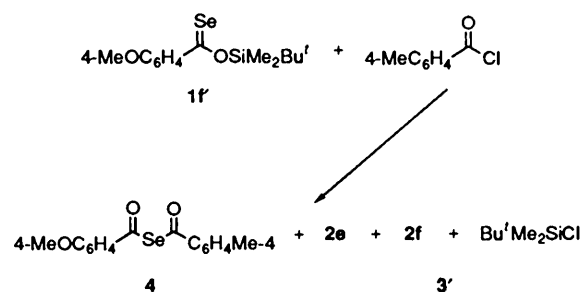
Reactions.—Initially, the reactivity of *O*-silyl selenocarboxylates towards carbon electrophiles was examined. Although the treatment of **1** with methyl iodide gave the *Se*-methyl selenocarboxylates only in low yields, the reaction of **1** with acyl chlorides took place smoothly at room temperature to afford the selenoanhydrides **2**⁵ in 60–95% yield together with the corresponding silyl chloride **3** (Scheme 1, Table 1). The reaction



Scheme 1 Conditions: i, CH₂Cl₂, room temp., 2–5 h

with aliphatic *O*-silyl selenocarboxylates (**1**, R = alkyl) proceeded more quickly than with aromatic ones. It is noted that even with the bulky *O*-trimethylsilyl 2,2-dimethylpropane-selenoate **1b**, the reaction proceeded smoothly to give bis(2,2-dimethylpropanoic) selenoanhydride **2b** in high yield. The reaction was monitored by the change in colour of the reaction

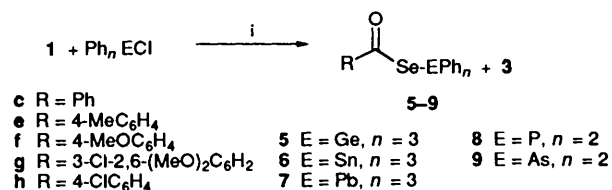
mixture from purple to pale yellow. In all cases, acylation took place on the selenium atom of **1**. In order to prepare unsymmetrical selenoanhydrides such as **4** (see Scheme 2), the reaction of *O*-silyl selenocarboxylate **1f'** with 4-methylbenzoyl chloride was carried out under various conditions. However, the formation of symmetrical selenoanhydrides accompanied the desired reaction (Scheme 2). A number of attempts to isolate



Scheme 2

4 by fractional crystallization and by thin layer or column chromatography failed because of its disproportionation to symmetrically substituted acid anhydrides and selenoanhydrides.⁶

The reaction of **1** with heteroatom substituted chlorides involving group 14 or 15 elements was also carried out (Scheme 3). Of the group 14 examples Ph_3GeCl , Ph_3SnCl and Ph_3PbCl ,



Scheme 3 Reagents and conditions: i, tetrahydrofuran, room temp., 2–15 h

the first two required longer reaction times. The reactions with Ph_2PCl and Ph_2AsCl proceeded at 20 °C to give the corresponding selenocarboxylates **8** and **9** in 70–90% yields. The structures of **5–9** were confirmed by comparison of their IR and ^1H and ^{13}C NMR spectra with those of authentic samples prepared from the reaction using the corresponding sodium

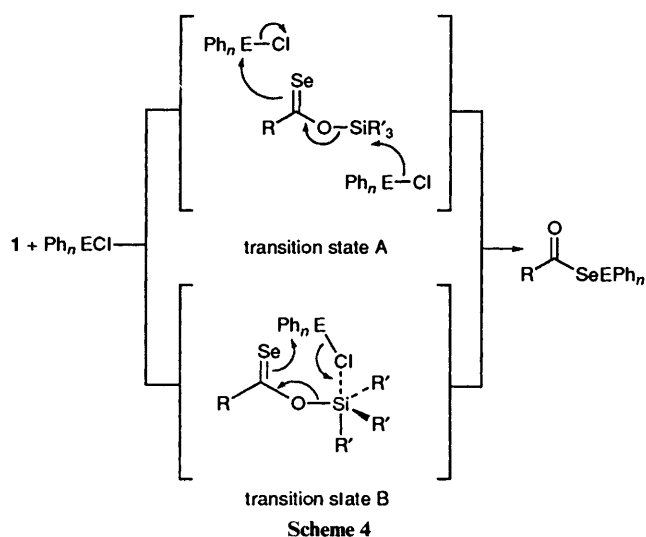
Table 1 Yields of heteroatom substituted selenocarboxylates

R	2	5	6	7	8	9	10	11	12
a	58	—	—	—	—	—	—	—	—
b	86	—	—	—	—	—	—	—	—
c	26 (91 ^a)	80	59	94	90	—	54	35 (89 ^a)	74
d	—	—	—	—	—	—	—	22 (94 ^a)	56
e	89	60	60	80	72	88	52	56 (93 ^a)	64
f	86	68	65	84	—	—	71 (88 ^b)	33 (93 ^a)	84
g	86	61	87	76	—	—	—	—	—
h	—	63	67	72	—	—	49	39 (97 ^a)	94

^a Crude yield. ^b RC(O)SeSC₆H₃(NO₂)₂-2,4.

selenocarboxylates.⁷⁻¹⁰ In a similar way to the reactions with acyl chlorides, products in which the heteroatom was attached to oxygen were not detected.

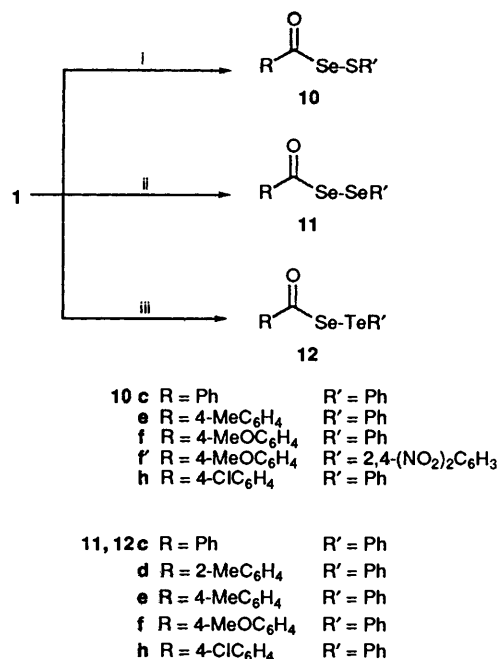
The reaction described above can be classified as S_E2'. There are two possible mechanisms for the electrophilic addition of the heteroatom substituted chlorides to the selenium atom of **1** (Scheme 4). One of them is *via* the three-molecule transition



state **A** in which the addition of a heteroatom to selenium and the nucleophilic attack of the chlorine atom of another molecule of chloride take place simultaneously. Alternatively, the reaction may proceed *via* a six-membered ring transition state **B**. Although, at the present stage, no spectroscopic experiment to support either one or other mechanisms has been obtained, transition state **B** is preferred since the product yields and reaction times are unaffected by substituents adjacent to the selenocarbonyl group which would cause steric congestion when the heteroatom-substituted chloride approaches **1** in transition state **A**.

Finally, the treatment of **1** with ArSCl, PhSeBr and PhTeI at room temperature yielded the expected *S*(Se)-aryl seleno(thio)perbenzoates **10**, *Se*(Se)-aryl diselenoperbenzoates **11**, and the hitherto unknown *Te*(Se)aryl seleno(telluro)perbenzoates **12** in 50–94% yields (Scheme 5). It is noted that the attempted syntheses of compounds **10**, **11** and **12** using alkali metal selenocarboxylates gave exclusively selenoperoxyacid anhydrides and diaryl dichalcogenides. The *Te*(Se)-aryl seleno(telluro)perbenzoates **12** were obtained as yellow–orange crystals and are relatively stable towards oxygen and water. For example, when exposed to air at room temperature for 2 h, no appreciable decomposition of *Te*(Se)-phenyl seleno(telluro)perbenzoate was observed.

Spectra of Heteroatom Substituted Selenocarboxylates 5–12.—The C=O stretching frequencies for compounds **5c–12c**,



Scheme 5 Reagents and conditions: i, R'SCl, Et₂O, 20 °C, 0.5 h; ii, R'SeBr, Et₂O, 18 °C, 0.5 h; iii, R'TeI, hexane, 20 °C, 0.5 h

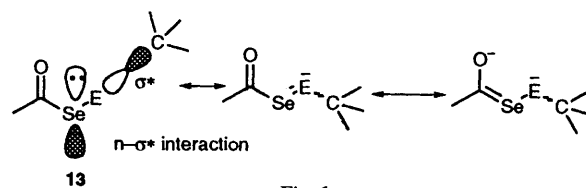


Fig. 1

summarized in Table 2, all occur at *ca.* 1660 cm⁻¹. In a given group of the Periodic Table, a shift to lower frequency is observed in moving from lighter to heavier atoms. This may partly be due to the low-lying σ^* orbital of **13** (Fig. 1). Delocalization of the lone pair electrons on Se into the σ^* orbital may allow the C=O group to conjugate with the partial double bond between Se and heteroatom. This may weaken the C=O bond of **13**. Intramolecular coordination of the carbonyl O to the heteroatom attached to Se may also affect the frequency of the C=O stretch in frequency.^{8,9} ⁷⁷Se NMR spectra signals for heteroatom substituted selenocarboxylates are shown in Table 3. Downfield shifting of the signals is observed in going from group 14 to group 16 derivatives. This can be easily understood by the difference in the electron density on Se in each compound. When a more electronegative heteroatom is attached to Se, signals for the latter are more electronically deshielded and this results in a downfield shift in the ⁷⁷Se NMR spectrum. In contrast, the ¹³C NMR signals of the C=O group are observed in a similar region regardless of the heteroatom attached to Se (Table 4).

Table 2 Carbonyl stretching frequencies of heteroatom substituted selenocarboxylates

PhC(O)SeEPh ₃ E	$\nu_{\max}/\text{cm}^{-1}$ C=O	PhC(O)SeEPh ₂ E	$\nu_{\max}/\text{cm}^{-1}$ C=O	PhC(O)SeEPh E	$\nu_{\max}/\text{cm}^{-1}$ C=O
C	1675 ^a	N	—	O	—
Si	—	P	1682	S	1689
Ge	1665	As	1684	Se	1684
Sn	1640	Sb	1633	Te	1675
Pb	1642	Bi	—	Po	—

^a PhC(O)SeMe.**Table 3** ⁷⁷Se NMR spectra of heteroatom substituted selenocarboxylates

PhC(O)SeEPh ₃ E	δ_{Se}	PhC(O)SeEPh ₂ E	δ_{Se}	PhC(O)SeEPh E	δ_{Se}
C	445.0 ^a	N	—	O	—
Si	—	P	582.7	S	772.9
Ge	356.5	As	586.1	Se	745.8
Sn	347.2	Sb	490.6	Te	616.6
Pb	419.0	Bi	—	Po	—

^a PhC(O)SeMe.¹⁶**Table 4** ¹³C NMR spectra of the C=O groups of heteroatom substituted selenocarboxylates

PhC(O)SeEPh ₃ E	δ_{C}	PhC(O)SeEPh ₂ E	δ_{C}	PhC(O)SeEPh E	δ_{C}
C	194.7 ^a	N	—	O	—
Si	200.7 ^b	P	189.6	S	191.0
Ge	192.8	As	192.7	Se	189.1
Sn	195.5	Sb	194.7	Te	187.4
Pb	196.1	Bi	—	Po	—

^a PhC(O)SeMe. ^b 2-MeOC₆H₄C(O)SeSiMe₂Bu.⁴

Conclusion.—*O*-Trimethylsilyl selenocarboxylates **1** act as effective selenocarboxylating reagents. The present selenocarboxylation using **1** has several advantages compared with that using alkali metal selenocarboxylates: (a) the progress of the reaction can be readily monitored by a change in the colour of the reaction mixture (purple→pale yellow); (b) trimethylsilyl chloride as a by-product can be easily removed together with a solvent; (c) aprotic nonpolar solvents such as hexane can be used; (d) the yields are high; (e) the method is particularly effective for the preparation of S(*Se*)-aryl seleno(thio)perbenzoates **10** and Te(*Se*)-aryl seleno(telluro)perbenzoates **12**. Whereas a significant heteroatom effect was observed in the ⁷⁷Se NMR spectrum, there was practically no effect on the C=O signals in the ¹³C NMR spectrum. The change in the C=O stretching frequency can be understood in terms of formation of a conjugated system including the C=O group and the Se-heteroatom bond.

Experimental*

M.p.s were determined with a Yanagimoto micromelting point apparatus, and are uncorrected. IR spectra were recorded on a Perkin Elmer FT-IR 1640 spectrophotometer and a JASCO grating IR spectrophotometer IR-G. ¹H NMR, ¹³C NMR and ⁷⁷Se NMR were recorded on a JEOL JNM-GX-270 instrument at 270, 67.8 and 51.4 MHz, respectively. CDCl₃ was employed as the solvent with tetramethylsilane as internal standard for ¹H NMR, CDCl₃ for ¹³C NMR as internal standard and with

dimethyl selenide for ⁷⁷Se NMR as external standard. Mass spectra were obtained on Shimadzu GCMS-QP-1000 and GCMS-9020-DF high-resolution mass spectrometer. Elemental analyses were performed by the Elemental Analyses Centre of Kyoto University.

Materials.—*O*-Trimethylsilyl and *O*-*tert*-butyldimethylsilyl selenocarboxylates,⁴ benzenesulfonyl chloride,¹¹ benzeneselenenyl bromide,¹² benzenetellurenyl iodide¹³ and diphenylarsenic chloride¹⁴ were prepared according to the literature. 2,4-Dinitrobenzenesulfonyl, triphenylstannyl, triphenylgermyl, triphenylplumbyl and diphenylphosphinoyl chlorides, were commercial grade and used without further purification. Acyl chlorides were commercial grade and distilled before use. The following solvents were purified under nitrogen or argon and dried as indicated: light petroleum (b.p. < 40 °C), hexane, diethyl ether and tetrahydrofuran (THF), all refluxed with sodium metal using benzophenone as indicator and distilled before use; dichloromethane, distilled over phosphorus pentoxide, after refluxing for 5 h. These solvents were degassed before use. Chromatography was carried out on BW-820 MH of Fuji Davison Chemical Co. Ltd.

The preparations of compounds **2a**, **2c**, **5c**, **6c**, **7c**, **8c**, **9e**, **10c**, **11c** and **12c** are described in detail as typical procedures for the preparation of **2**, **5**–**12**, respectively. All manipulations were carried out under argon.

Reaction with Acyl Chlorides.—Except for the 3-chloro-2,6-dimethoxy derivative **2g**, the symmetrically substituted selenoanhydrides were identified by comparison of their IR spectra with those of authentic samples prepared from the reaction of

* Non-SI unit employed: 1 Torr = 133.322 Pa.

acyl chlorides with sodium selenide^{5c} or by deselenation of the corresponding diselenoacid anhydride with triphenylphosphine.^{5b} Some ¹³C NMR spectral data have been added.

Acetic selenoanhydride 2a. Acetyl chloride (0.245 g, 3.12 mmol) in diethyl ether (50 cm³) was added to *O*-*tert*-butyldimethylsilyl selenoacetate **1a'** (0.370 g, 1.56 mmol), and the mixture was stirred at 20 °C for 2 h. The solvent, excess of acetyl chloride and the *tert*-butyldimethylsilyl chloride formed were distilled off under reduced pressure. Vacuum distillation of the resulting residue yielded the title compound **2a** as a slightly yellow liquid (0.148 g, 58%), b.p. 40 °C/1 Torr (lit.,^{5c} 38 °C/1 Torr); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1740 (C=O) and 1720 (C=O).

Bis(2,2-dimethylpropanoic) selenoanhydride 2b. A slightly yellow liquid (86%), b.p. 74–78 °C/0.5 Torr (lit.,^{5c} 76 °C/0.6 Torr); $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1770 (C=O), 1740 (C=O), 1720 (C=O) and 1690 (C=O).

Benzoic selenoanhydride 2c. A solution of benzoyl chloride (0.287 g, 2.04 mmol) in diethyl ether (1 cm³) was added to *O*-*tert*-butyldimethylsilyl selenobenzoate **1c'** (0.304 g, 1.02 mmol) and the mixture was stirred at 20 °C for 5 h. Evaporation under reduced pressure of the solvent and the *tert*-butyldimethylsilyl chloride formed in the reaction gave crude compound **2c** as yellow oil (0.268 g, 91%). Crystallization of this from CH₂Cl₂–hexane (1:10) at –20 °C afforded, after 20 h, the title compound **2c** as slightly yellow crystals (0.077 g, 26%), m.p. 61–63 °C (decomp.) (lit.,^{5b} 61–62 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1714 (C=O); $\delta_{\text{C}}(\text{CDCl}_3)$ 128.0, 128.3, 129.0, 134.4 (Ar) and 188.4 (C=O).

Bis(4-methylbenzoic) selenoanhydride 2e. Slightly yellow needles (89%), m.p. 92–93 °C (decomp.) (lit.,^{5b} 91–94 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1722 (C=O) and 1700 (C=O); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.7 (CH₃), 128.6, 129.6, 136.2, 145.6 (Ar) and 190.4 (C=O).

Bis(4-methoxybenzoic) selenoanhydride 2f. Slightly yellow needles (86%), m.p. 77–79 °C (decomp.) (lit.,^{5b} 77.8–80.2 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1735 (C=O) and 1700 (C=O); $\delta_{\text{C}}(\text{CDCl}_3)$ 55.5 (CH₃O), 114.1, 130.9, 141.1, 164.6 (Ar) and 189.4 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 601.9.

Bis(3-chloro-2,6-dimethoxybenzoic) selenoanhydride 2g. Slightly yellow needles (86%), m.p. 104–105 °C (decomp.) (Found: C, 45.2; H, 3.3. C₁₈H₁₆Cl₂O₆Se requires C, 45.21; H, 3.37%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3025, 2975, 2950, 2850, 1730 (C=O), 1685 (C=O), 1570, 1450, 1425, 1395, 1230, 1220, 1115, 1130, 1070, 990, 910, 880, 800, 770, 725, 700, 680, 625, 570, 545, 520 and 500; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.79 (6 H, s, CH₃O), 3.87 (6 H, s, CH₃O) and 6.6–7.2 (4 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 56.1 (CH₃O), 62.2 (CH₃O), 108.0, 119.3, 132.5, 136.0, 152.0, 154.9 (Ar) and 189.3 (C=O).

Reaction of *O*-*tert*-Butyldimethylsilyl 4-Methoxyselenobenzoate 1f' with 4-Methylbenzoyl Chloride.—In a similar fashion to **2c**, *O*-*tert*-butyldimethylsilyl 4-methoxyselenobenzoate **1f'** (0.320 g, 0.97 mmol) and 4-methylbenzoyl chloride (0.154 g, 1.00 mmol) were stirred in diethyl ether (5 cm³) at 10 °C for 5 h. The slightly yellow, microfine crystals (0.41 g), were filtered off m.p. 60–86 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1775 (C=O), 1730 (C=O), 1710 (C=O) and 1680 (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.40 (CH₃) and 3.84 (CH₃O); $\delta_{\text{C}}(\text{CDCl}_3)$ 20.5 (CH₃), 55.5 (CH₃O), 184.4 (C=O), 187.7 (C=O) and 188.8 (C=O); m/z (CI) 351 [(CH₃OC₆H₄COSeCOC₆H₄OCH₃ + 1)⁺, 3.2%], 335 [(CH₃C₆H₄COSeCOC₆H₄OCH₃ + 1)⁺, 1.2], 319 [(CH₃C₆H₄COSeCOC₆H₄CH₃ + 1)⁺, 2.3], 135 [(CH₃OC₆H₄CO)⁺, 95] and 119 [(CH₃C₆H₄CO)⁺, 100]. Fractional crystallization of these mixed crystals from ether–hexane and CH₂Cl₂–hexane failed to isolate the unsymmetrical selenoanhydride **4**.

Reaction of Sodium 4-Methylselenobenzoate 3 with Benzoyl Chloride.—A solution of benzoyl chloride (0.67 g, 4.77 mmol) in diethyl ether (7 cm³) was added dropwise to a suspension of sodium 4-methylselenobenzoate **3** (1.12 g, 5.07 mmol) in the

same solvent (3 cm³) during 30 min and the mixture was stirred for 1 h. Filtration and evaporation under reduced pressure gave yellow oils, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 1780 (C=O) and 1710 (C=O); $\delta_{\text{C}}(\text{CDCl}_3)$ 182.8 (C=O), 184.4 (C=O) and 188.8 (C=O); m/z (CI) 319 [(CH₃C₆H₄COSeCOC₆H₄CH₃ + 1)⁺, 2.7%], 305 [(CH₃C₆H₄COSeCOC₆H₅ + 1)⁺, 1.5], 291 [(C₆H₅COSeCOC₆H₅ + 1)⁺, 3.3], 119 [(CH₃C₆H₄CO)⁺, 96] and 105 [(C₆H₅CO)⁺, 100].

Reaction with Triphenyl-germyl, -stannyl and -plumbyl Chlorides.—**Se-Triphenylgermyl selenobenzoate 5c.** A solution of Ph₃GeCl (0.398 g, 1.17 mmol) in THF (1 cm³) was added to the selenobenzoate **1c** (0.302 g, 1.17 mmol) and the mixture was stirred at 25 °C for 15 h. The solvent and the trimethylsilyl chloride formed were distilled off under reduced pressure, to leave the title compound **5c** as a purple oil (0.46 g, 80%) contaminated with Ph₃GeCl. Crystallization of the oil from CH₂Cl₂–hexane (1:5, 2 cm³) at –20 °C afforded, after 20 h, the chemically pure compound **5c** as pale yellow crystals (0.326 g, 59%), m.p. 107–110 °C (lit.,⁷ 126–131 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1665 (C=O). The IR spectrum of **5c** was consistent with that of an authentic sample.

Se-Triphenylgermyl 4-methylselenobenzoate 5e. Pale yellow crystals (60%), m.p. 132–138 °C (lit.,⁷ 123–125 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1775 (C=O) and 1653 (C=O).

Se-Triphenylgermyl 4-methoxyselenobenzoate 5f. Pale yellow crystals (68%), m.p. 115–117 °C (lit.,⁷ 115–117 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1660 (C=O) and 1638 (C=O).

Se-Triphenylgermyl 3-chloro-2,6-dimethoxyselenobenzoate 5g. Pale yellow crystals (61%), m.p. 118–119 °C (lit.,⁷ 116–119 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1690 (C=O).

Se-Triphenylgermyl 4-chloroselenobenzoate 5h. Pale yellow crystals (63%), m.p. 100–102 °C (lit.,⁷ 101–104 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1670 (C=O).

Se-Triphenylstannyl selenobenzoate 6c. A solution of Ph₃SnCl (1.44 g, 3.74 mmol) in THF (3 cm³) was added to the selenobenzoate **1c** (0.963 g, 3.74 mmol) and the mixture was stirred at 20 °C for 15 h. The solvent and the trimethylsilyl chloride formed were distilled off under reduced pressure to give the crude title compound **6c** as a red oil. Crystallization of this from CH₂Cl₂–hexane (1:5, 2 cm³) at –20 °C afforded, after 20 h, chemically pure **6c** as pale yellow crystals (1.18 g, 59%), m.p. 105–106 °C (lit.,⁸ 106–108 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1640 (C=O). The IR spectrum was consistent with that of an authentic sample prepared from the reaction of potassium selenobenzoate with triphenylstannyl chloride.

Se-Triphenylstannyl 4-methylselenobenzoate 6e. Pale yellow crystals (60%), m.p. 112–115 °C (lit.,⁸ 113–116 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1638 (C=O).

Se-Triphenylstannyl 4-methoxyselenobenzoate 6f. Pale yellow crystals (65%), m.p. 101–104 °C (lit.,⁸ 102–104 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1638 (C=O).

Se-Triphenylstannyl 3-chloro-2,6-dimethoxyselenobenzoate 6g. Pale yellow crystals (87%), m.p. 123.5–124.5 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3025, 2950, 2925, 2850, 1650 (C=O), 1560, 1522, 1449, 1437, 1408, 1385, 1270, 1209, 1168, 1150, 1120, 1072, 1051, 977, 916, 882, 780, 760, 710, 678, 630, 608 and 420; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.68 (3 H, s, CH₃O), 3.77 (3 H, s, CH₃O) and 6.6–7.7 (17 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 56.2 (CH₃O), 62.1 (CH₃O), 108.1, 119.5, 128.7, 129.1, 129.6, 132.2, 136.0, 136.5, 154.2 (Ar) and 193.4 (C=O).

Se-Triphenylstannyl 4-chloroselenobenzoate 6h. Pale yellow crystals (67%), m.p. 97–99 °C (lit.,⁸ 96–97 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1648 (C=O).

Se-Triphenylplumbyl selenobenzoate 7c. To a solution of the selenobenzoate **1c** (0.430 g, 1.67 mmol) in THF (10 cm³), Ph₃PbCl (0.792 g, 1.67 mmol) was added, and the mixture was stirred at 20 °C for 2.5 h. The solvent was removed under reduced pressure and the residue washed with diethyl ether–

hexane (1:5; 6 cm³), and then recrystallized from diethyl ether-hexane (3:7) to yield the title compound **7c** as white crystals (0.977 g, 94%) with an IR spectrum identical with that of an authentic sample prepared from the reaction of sodium selenobenzoate with triphenylplumbyl chloride; m.p. 97–98 °C (decomp.) (lit.,⁹ 95–97 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1642 (C=O); m/z (CI) 625 (MH⁺, 0.8%).

Se-Triphenylplumbyl 4-methylselenobenzoate 7e. White crystals (80%), m.p. 100–103 °C (decomp.) (lit.,⁹ 108–110 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1640 (C=O).

Se-Triphenylplumbyl 4-methoxyselenobenzoate 7f. White crystals (84%), m.p. 92–97 °C (decomp.) (lit.,⁹ 99–100 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1630 (C=O).

Se-Triphenylplumbyl 3-chloro-2,6-dimethoxyselenobenzoate 7g. White microfine crystals (76%), m.p. 138–141 °C (decomp.); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1640 (C=O), 1580, 1565, 1470, 1430, 1290, 1230, 1180, 1090, 1015, 995, 940, 800, 735, 725, 690 and 435; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.75 (6 H, s, CH₃O) and 7.22–8.01 (17 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 56.3 (CH₃O), 62.2 (CH₃O), 108.1, 119.6, 129.2, 129.9, 130.5, 136.3, 137.1, 152.3 (Ar) and 197.5 (C=O).

Se-Triphenylplumbyl 4-chloroselenobenzoate 7h. White crystals (72%), m.p. 90–93 °C (decomp.) (lit.,⁹ 86–88 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1650 (C=O).

Reactions with Diphenyl-phosphinous and -arsinous Chlorides.—**Benzoic diphenylphosphinous selenoanhydride 8c.** A solution of Ph₂PCl (0.236 g, 1.07 mmol) in diethyl ether-hexane (2:5, 7 cm³) was added to the selenobenzoate **1c** (0.276 g, 1.07 mmol) and the mixture was stirred at 20 °C for 30 min. Evaporation of the solvent and the trimethylsilyl chloride formed left the title compound **8c** as a yellow oil (0.356 g, 90%) with an IR spectrum identical with that of an authentic sample prepared by the reaction of sodium selenobenzoate with diphenylphosphinous chloride, $\nu_{\max}(\text{neat})/\text{cm}^{-1}$ 3055, 3040, 1682 (C=O), 1578, 1478, 1442, 1436, 1308, 1196, 1173, 1083, 998, 862, 760, 748, 738, 692, 677 and 660; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.37–8.08 (15 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 128.1–137.6 (Ar) and 189.6 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 582.7 (d, J_{SeP} 207); m/z (CI) 451 (MH⁺).

4-Methylbenzoic diphenylphosphinous selenoanhydride 8e. Colourless needles (72%), m.p. 124–126 °C (decomp.) (Found: C, 67.8; H, 4.1. C₂₀H₁₇OPSe requires C, 67.67; H, 4.47%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3050, 1670 (C=O), 1645 (C=O), 1600, 1480, 1430, 1405, 1302, 1202, 1175, 1160, 880, 820, 783, 735, 640, 615, 610, 505, 480 and 460; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.33 (3 H, s, CH₃) and 7.1–7.8 (14 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.6 (CH₃), 128.2–144.8 (Ar) and 191.4 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 577.8 (d, J_{SeP} 209); m/z (CI) 385 (MH⁺).

4-Methylbenzoic diphenylarsinous selenoanhydride 9e. A solution of Ph₂AsCl (0.293 g, 1.11 mmol) in diethyl ether (10 cm³) was added to *O*-trimethylsilyl 4-methylselenobenzoate **1e** (0.300 g, 1.11 mmol) and the mixture was stirred at 20 °C for 3 h. Evaporation of the solvent and trimethylsilyl chloride under reduced pressure followed by recrystallization of the residue from CH₂Cl₂-hexane (1:7) gave the title compound **9e** as pale yellow crystals (0.42 g, 88%), m.p. 104–106 °C (decomp.) (Found: C, 56.3; H, 4.07. C₂₀H₁₇AsOSe requires C, 56.22; H, 4.02%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3025, 1660 (C=O), 1636 (C=O), 1592, 1560, 1470, 1420, 1298, 1169, 1150, 1070, 1062, 902, 876, 812, 776, 724, 682, 610, 602, 455 and 422; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.28 (3 H, s, CH₃) and 7.2–7.8 (14 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.6 (CH₃), 127–144.6 (Ar) and 192.5 (C=O); m/z (CI) 428 (M⁺).

Reaction with Arene-sulfonyl, -selenenyl and -tellurenyl Halides.—**S(Se)-Phenyl seleno(thio)perbenzoate 10c.** To a solution of the selenobenzoate **1c** (0.514 g, 2.00 mmol) in diethyl ether (5 cm³), a solution of PhSeCl (0.289 g, 2.00 mmol) in diethyl ether (5 cm³) was added, and the mixture was stirred at 20 °C for 30 min. Removal of the solvent under reduced pressure and crystallization of the resulting orange oil from diethyl ether-

hexane (1:2, 1.5 cm³) at –20 °C for 6 h yielded the title compound **10c** as slightly yellow crystals (0.316 g, 54%) whose IR spectrum was identical with that of an authentic sample prepared from the reaction of triphenylplumbyl selenobenzoate with benzenesulfonyl chloride, m.p. 33–35 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1740, 1685, 1596, 1580, 1470, 1449, 1439, 1300, 1200, 1170, 1090, 1060, 1020, 990, 868, 765, 751, 688, 668, 614 and 482; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.24 (3 H, d, Ar), 7.44 (2 H, t, Ar), 7.59 (3 H, t, Ar) and 7.87 (2 H, d, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 127.5, 128.1, 128.9, 129.1, 131.7, 134.3 (Ar) and 191.0 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 772.9; m/z (CI) 295 (MH⁺, 44) and 105 (100).

S(Se)-Phenyl 4-methyl(seleno)thioperbenzoate 10e. Slightly yellow crystals (52%), m.p. 80–82 °C (Found: C, 54.6; H, 3.9. C₁₄H₁₂OSe requires C, 54.73; H, 3.94%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1750, 1700, 1610, 1578, 1490, 1476, 1440, 1410, 1310, 1220, 1204, 1174, 1160, 1126, 1023, 870, 810, 783, 751, 702, 689, 620, 610, 490 and 460; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.40 (3 H, s, CH₃), 7.23 (2 H, m, Ar), 7.47 (1 H, t, Ar), 7.54 (4 H, d, Ar) and 7.61 (2 H, d, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.7 (CH₃), 127.7, 128.0, 128.9, 129.1, 129.8, 130.4, 131.6, 136.1 (Ar) and 190.0 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 767.1; m/z (CI) 309 (MH⁺, 58) and 119 (100).

S(Se)-Phenyl 4-methoxy(seleno)thioperbenzoate 10f. Slightly yellow crystals (71%), m.p. 50–52 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1742, 1683, 1598, 1572, 1504, 1465, 1440, 1420, 1325, 1306, 1270, 1207, 1166, 1120, 1070, 1030, 876, 834, 780, 745, 700, 688, 644, 610 and 470; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.83 (3 H, s, CH₃), 6.92 (2 H, d, Ar), 7.23 (3 H, d, Ar), 7.58 (2 H, d, Ar) and 7.86 (2 H, d, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 55.6 (CH₃), 114.4, 127.9, 128.9, 130.0, 131.5, 164.6 (Ar) and 188.7 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 758.6; m/z (CI) 325 (MH⁺, 16%) and 135 (CH₃OC₆H₄CO⁺, 100).

S(Se)-2,4-Dinitrophenyl 4-methoxy(seleno)thioperbenzoate 10f'. Orange needles (88%), m.p. 133–135 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 3000, 2800, 1746, 1702, 1590, 1516, 1456, 1443, 1350, 1321, 1315, 1303, 1270, 1241, 1210, 1158, 1131, 1120, 1082, 1041, 1021, 914, 864, 836, 830, 782, 749, 739, 698, 675, 620, 60 and 530; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.92 (3 H, s, CH₃), 7.45 (4 H, d, Ar), 8.00 (1 H, d, Ar), 8.31 (1 H, d, Ar) and 9.07 (1 H, d, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 55.8 (CH₃), 114.8, 121.2, 127.2, 128.3, 130.7, 132.0, 165.4 (Ar) and 185.2 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 675.0.

S(Se)-Phenyl 4-chloro(seleno)thioperbenzoate 10h. Slightly yellow crystals (49%), m.p. 93–96 °C; $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1733, 1690, 1586, 1570, 1482, 1440, 1400, 1310, 1200, 1170, 1095, 1027, 1015, 1007, 917, 870, 850, 840, 826, 741, 722, 712, 700, 688, 628, 612, 559, 489 and 469; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.25 (2 H, d, Ar), 7.42 (3 H, t, Ar), 7.60 (2 H, d, Ar) and 7.87 (2 H, d, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 128.3, 128.8, 129.1, 129.0, 129.3, 129.5, 132.0 (Ar) and 190.0 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 775.5; m/z (CI) 329 (MH⁺, 36%) and 140 (100).

Se(Se)-Phenyl diselenoperbenzoate 11c. To a solution of the perbenzoate **1c** (0.519 g, 2.02 mmol) in diethyl ether (10 cm³), PhSeBr (0.476 g, 2.02 mmol) was added, and the mixture was stirred at 20 °C for 15 min. Removal of the solvent under reduced pressure gave crude title compound **11c** as an orange oil (0.612 g, 89%). Crystallization of this from CH₂Cl₂-hexane (1:3, 2 cm³) at –20 °C for 6 h yielded slightly yellow crystals (0.240 g, 35%) whose IR spectrum was consistent with that of an authentic sample of compound **11c**, m.p. 41–43 °C (lit.,⁷ 40–42 °C); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1684 (C=O), 1575, 1440, 1310, 1190, 1170, 1070, 1020, 1000, 870, 760, 740, 680, 660 and 620; $\delta_{\text{C}}(\text{CDCl}_3)$ 128.0, 128.4, 129.1, 129.2, 136.4, 154.5 (Ar) and 189.1 (C=O); $\delta_{\text{Se}}(\text{CDCl}_3)$ 745.8 (SeCO) and 382.6 (SePh); m/z (CI) 343 (MH⁺, 86.5).

Se(Se)-Phenyl 2-methyl(diseleno)perbenzoate 11d. Orange oil (94%), yellow crystals (22%), m.p. 30–35 °C (Found: C, 47.4; H, 3.5. C₁₄H₁₂OSe₂ requires C, 47.48; H, 3.42%); $\nu_{\max}(\text{KBr})/\text{cm}^{-1}$ 1700 (C=O), 1595, 1565, 1470, 1450, 1430, 1380, 1280, 1200, 1175, 1120, 1020, 855, 750, 725, 710, 650 and 620; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.47 (3 H, s, CH₃) and 7.1–8.3 (9 H, m, Ar);

$\delta_{\text{C}}(\text{CDCl}_3)$ 20.5 (CH₃), 126.2, 129.0, 130.1, 131.3, 131.9, 132.7, 135.7, 161.0 (Ar) and 190.6 (C=O); m/z (CI) 357 (MH⁺).

Se(Se)-Phenyl 4-methyl(diseleno)perbenzoate **11e**. Orange oil (93%), yellow crystals (56%), m.p. 83–85 °C (lit.,¹⁵ 85–86 °C); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1690 (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 2.30 (3 H, s, CH₃) and 7.15–7.82 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.7 (CH₃), 128.1, 129.1, 129.7, 130.4, 133.2, 136.4, 145.3, 154.6 (Ar) and 188.3 (C=O); m/z (CI) 357 (MH⁺, 0.7%).

Se(Se)-Phenyl 4-methoxy(diseleno)perbenzoate **11f**. Orange oil (93%), yellow crystals (33%), m.p. 42–44 °C (lit.,¹⁵ 43–44 °C); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1685 (C=O); $\delta_{\text{H}}(\text{CDCl}_3)$ 3.77 (3 H, s, CH₃O) and 6.83–7.85 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 55.6 (CH₃O), 128.2, 129.1, 130.4, 133.1, 136.4, 154.5, 164.5 (Ar) and 186.9 (C=O); m/z (CI) 373 (MH⁺, 15.0%).

Se(Se)-Phenyl 4-chlorodiseleno)perbenzoate **11h**. Orange oil (97%), yellow crystals (39%), m.p. 75–77 °C (decomp.) (lit.,¹⁵ 76–78 °C); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1675 (C=O), 1580, 1565, 1470, 1440, 1395, 1190, 1170, 1080, 1010, 860, 730, 710, 680, 610 and 550; $\delta_{\text{C}}(\text{CDCl}_3)$ 127.9, 128.9, 130.0, 131.5, 137.0, 146.7, 164.6 (Ar) and 188.7 (C=O); m/z (CI) 377 (MH⁺, 21.1%).

Te(Se)-Phenyl seleno(telluro)perbenzoate **12c**. To a solution of the selenobenzoate **1c** (0.547 g, 2.13 mmol) in hexane (10 cm³), PhTeI (0.707 g, 2.13 mmol) was added and the mixture was stirred at 20 °C for 2.5 h. Crystallization of the residue from CH₂Cl₂–hexane (3 : 7, 2 cm³) at –20 °C for 6 h yielded the title compound **12c** as orange crystals (0.619 g, 74%), m.p. 82–90 °C (Found: C, 40.25; H, 2.5. C₁₃H₁₀OSeTe requires C, 40.16; H, 2.59%); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1675 (C=O), 1575, 1440, 1310, 1195, 1170, 1000, 865, 730, 680, 660 and 450; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.21–8.03 (10 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 128.2, 128.9, 129.2, 134.4 (Ar) and 187.4 (C=O); $\delta_{\text{S}}(\text{CDCl}_3)$ 616.6; m/z (EI) 392 (M⁺, 13%), 207 (C₆H₅Te⁺, 90), 105 (C₆H₅CO⁺, 100), 77 (C₆H₅⁺, 85).

Te(Se)-Phenyl 2-methyl(seleno)telluroperbenzoate **12d**. Orange crystals (56%), m.p. 50–58 °C (Found: M⁺, 405.9116. C₁₄H₁₂O₂SeTe requires M, 405.9115); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1710 (C=O), 1570, 1480, 1440, 1190, 1125, 1060, 1000, 860, 740, 690, 665 and 450; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.49 (3 H, s, CH₃) and 7.2–8.1 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 20.6 (CH₃), 126.2, 129.4, 130.4, 131.4, 131.8, 135.7, 163.0 (Ar) and 189.0 (C=O); m/z (EI) 406 (M⁺, 1.0%), 119 (CH₃C₆H₄CO⁺, 100) and 91 (CH₃C₆H₄⁺, 53).

Te(Se)-Phenyl 4-methyl(seleno)telluroperbenzoate **12e**. Orange crystals (56%), m.p. 123–124 °C (Found: M⁺, 405.9118. C₁₄H₁₂O₂SeTe requires M, 405.9115); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3050, 1680 (C=O), 1595, 1430, 1195, 1170, 870, 820, 775, 730, 682, 610 and 452; $\delta_{\text{H}}(\text{CDCl}_3)$ 2.39 (3 H, s, CH₃) and 7.2–7.9 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 21.7 (CH₃), 113.6–145.1 (Ar) and 186.9 (C=O); m/z (CI) 407 (M⁺ + 1).

Te(Se)-Phenyl 4-methoxy(seleno)telluroperbenzoate **12f**. Orange crystals (84%), m.p. 68–72 °C (Found: M⁺, 421.9089. C₁₄H₁₂O₂SeTe requires M, 421.9064); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 3050, 1670 (C=O), 1590, 1565, 1498, 1430, 1416, 1316, 1215, 1260, 1160, 1025, 870, 830, 770, 722, 680, 620, 600 and 400; $\delta_{\text{H}}(\text{CDCl}_3)$ 3.74 (3 H, s, CH₃O) and 6.8–7.9 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 55.6 (CH₃O), 114.6–164.5 (Ar) and 185.4 (C=O); m/z (CI) 423 (MH⁺).

Te(Se)-Phenyl 4-chloro(seleno)telluroperbenzoate **12h**. Orange crystals (94%), m.p. 110–112 °C (Found: M⁺, 425.8576. C₁₃H₉ClOSeTe requires M, 425.8569); $\nu_{\text{max}}(\text{KBr})/\text{cm}^{-1}$ 1670 (C=O), 1580, 1565, 1470, 1430, 1395, 1190, 1170, 1090, 860, 730,

685, 610 and 555; $\delta_{\text{H}}(\text{CDCl}_3)$ 7.2–8.0 (9 H, m, Ar); $\delta_{\text{C}}(\text{CDCl}_3)$ 128.7, 129.0, 129.3, 129.4, 129.6, 130.1, 138.4, 141.0 (Ar) and 189.7 (C=O); m/z (EI) 426 (M⁺, 6.4%), 207 (C₆H₅Te⁺, 31), 139 (ClC₆H₄CO⁺, 100), 111 (ClC₆H₄⁺, 65) and 77 (C₆H₅⁺, 70).

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