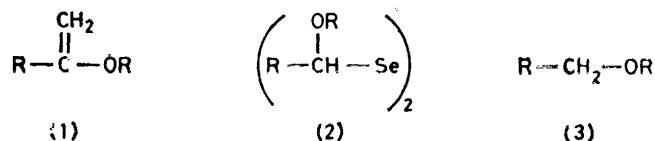


## Chemistry of *O*-Alkyl Selenoesters. Reaction with Triethylphosphine

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The reactions between triethylphosphine and a number of aliphatic and aromatic selenoesters under oxygen-free conditions have been investigated. The purple intermediate formed in the reaction with the aliphatic selenoesters was quenched with atmospheric oxygen and gave the corresponding esters, whereas quenching with methyl iodide gave the corresponding 1-alkoxy-1-iodoalkyltriethylphosphonium iodides (13)–(16). The 1-alkoxy-1-iodoalkyltriethylphosphonium iodides gave the 1-alkoxyalkyltriethylphosphonium iodides (17)–(20) upon treatment with methanol, and treatment with benzaldehyde at  $-70^{\circ}\text{C}$  gave  $\alpha$ -alkoxyalkyl phenyl ketones (22)–(25). The reaction between the selenobenzoates and triethylphosphine gave  $\alpha$ -dialkoxy-stilbenes and -dibenzyls. When the reaction was carried out in cyclohexene 7-alkoxy-7-phenylbicyclo[4.1.0]heptanes were formed. The presence of benzaldehyde in the reaction mixture led to  $\alpha$ -alkoxystilbenes. An explanation for these different reactions is presented.

ONLY a few reactions involving *O*-alkyl selenoesters have been investigated. The transformation of aliphatic *O*-alkyl selenoesters into selenoamides using primary alkylamidomagnesium bromides or secondary amines is a known reaction.<sup>1</sup> In contrast to certain esters<sup>2-4</sup> and

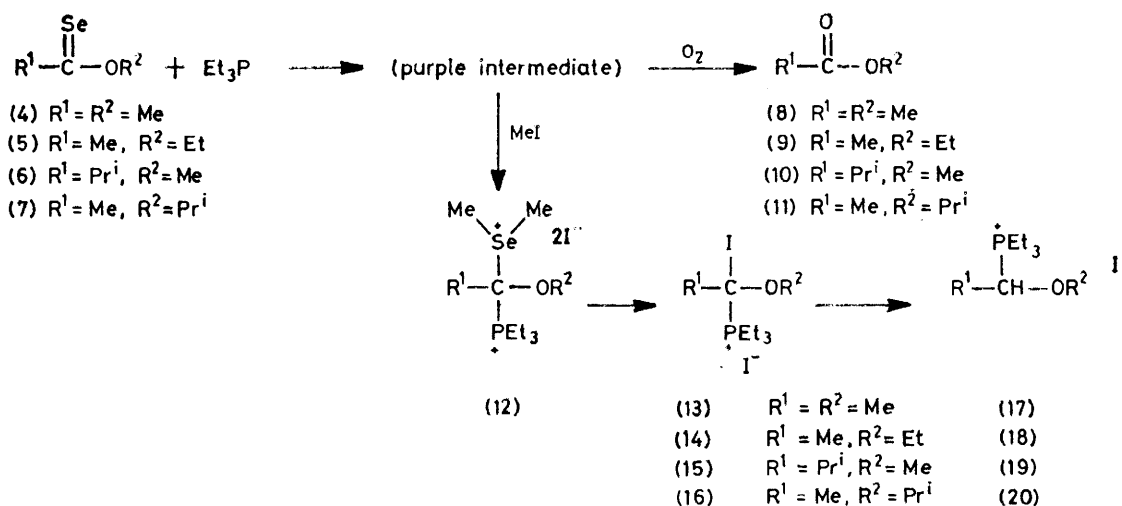


*S*-alkyl thioesters,<sup>5</sup> the *O*-alkyl selenoesters reacted with methylenetriphenylphosphorane and gave the corresponding vinyl ethers (1).<sup>6</sup> The reaction of aliphatic

the reduction was carried out in ethanolic sodium borohydride–triethylphosphine the corresponding ethers (3) were formed. During this investigation it was established that the *O*-alkyl selenoesters reacted with triethylphosphine, but the products were not characterised.

### RESULTS AND DISCUSSION

*Aliphatic Selenoesters.*—When the selenoesters (4)–(7), dissolved in benzene, were treated with triethylphosphine at  $50^{\circ}\text{C}$  in the presence of atmospheric oxygen, it was possible to isolate, after 5 h, triethylphosphine selenide and the corresponding esters (8)–(11). Duplication of this experiment under anaerobic



SCHEME 1

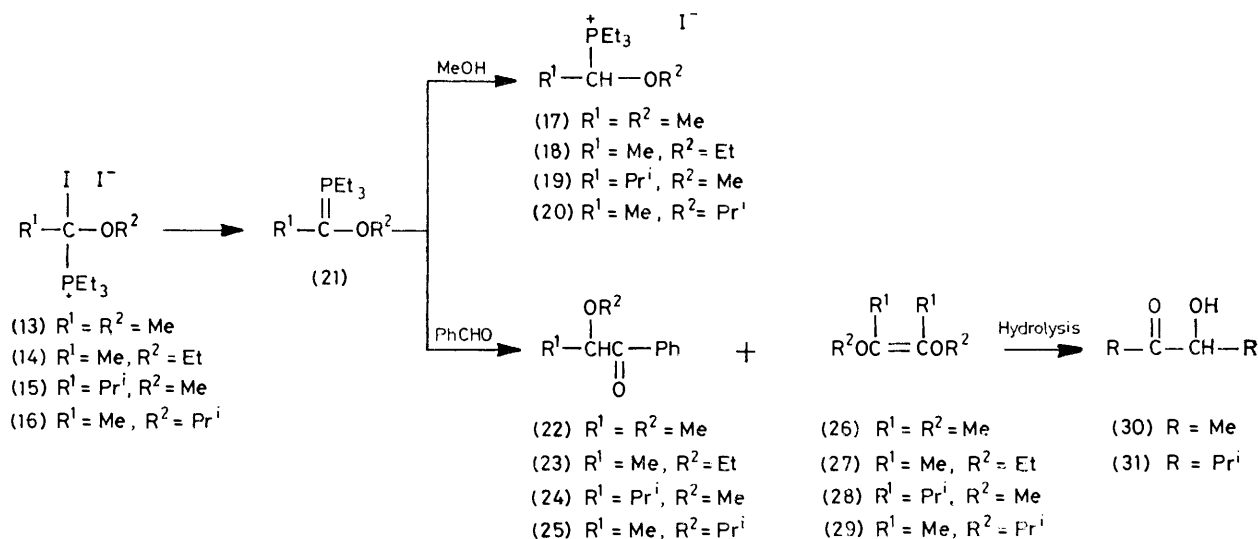
*O*-alkyl selenoesters in strongly basic media and their behaviour towards reducing agents such as sodium borohydride and Raney nickel have also been investigated.<sup>6</sup> It was established that if the reduction was carried out in ethanolic sodium borohydride, the bis-(alkoxyalkyl) diselenides (2) were formed. If, however,

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conditions resulted, however, in a deep purple solution, which upon exposure to atmospheric oxygen decolourised rapidly, and from which triethylphosphine selenide and the corresponding esters (8)–(11) could be isolated. The purple solution was stable if oxygen was rigorously excluded; it could be stored for several days, and heating at  $110^{\circ}\text{C}$  in a sealed tube for several hours resulted in no visible change; and the two above-mentioned pro-

ducts could again be isolated after exposure to atmospheric oxygen. Similar results were obtained when the reaction was performed in cyclohexane and triethylphosphine, or when benzaldehyde and triethylphosphine, or when benzaldehyde, acetone, benzyldimethylsilane, or triethyl orthoformate was added prior to exposure to atmospheric oxygen. Addition of methyl

methanol gave the phosphonium iodides (17)–(20) as the only products. Treatment of a methanol solution of the 1-iodoalkylphosphonium iodides (13)–(16) with aqueous potassium iodide–starch solution produced an intense blue solution, thus indicating the presence of iodine. In another experiment the 1-iodoalkylphos-



SCHEME 2

iodide resulted, however, in rapid decolourisation, and from the reaction mixture the phosphonium iodides (17)–(20) and dimethyl selenide could be isolated (Scheme 1). Evaporation of excess of triethylphosphine prior to addition of methyl iodide produced a compound which gave a different  $^{31}\text{P}$  n.m.r. spectrum from those of the corresponding phosphonium iodides (17)–(20). It would therefore appear that the phosphonium iodides

(13)–(16) were suspended in tetrahydrofuran at  $-70^\circ\text{C}$ , in which they slowly dissolved producing a red solution. Addition of benzaldehyde then resulted in the formation of the 1-alkoxyalkyl phenyl ketones (22)–(25) and triethylphosphine (Scheme 2). Trace amounts of a third product could also be detected by  $^1\text{H}$  n.m.r. spectroscopy, which suggested that these volatile fractions were the 1,2-dialkoxy-

TABLE I  
N.m.r. data for the aliphatic selenoesters <sup>a</sup>

	$^{31}\text{P}$		$^1\text{H}^b$	
	Se $\text{R}^1-\text{C}-\text{OR}^2/\text{PET}_3$	$+\text{PET}_3 \text{I}^-$ $\text{R}^1-\text{CH}-\text{OR}^2$	$+\text{PET}_3 \text{I}^-$ $\text{R}^1-\text{CH}-\text{OR}^2$	$+\text{PET}_3 \text{I}^-$ $\text{R}^1-\text{CH}-\text{OR}^2$
$\text{R}^1 = \text{Me}, \text{R}^2 = \text{Me}$	60.13	60.09	5.26 (1 H, m), 3.75 (3 H, s)	4.25 (3 H, s)
$\text{R}^1 = \text{Me}, \text{R}^2 = \text{Et}$	59.89	59.81	5.23 (1 H, m), 3.76 (2 H, q)	4.31 (2 H, q)
$\text{R}^1 = \text{Pr}^i, \text{R}^2 = \text{Me}$	58.93	58.99	5.18 (1 H, m), 3.70 (3 H, s)	4.22 (3 H, s)
$\text{R}^1 = \text{Me}, \text{R}^2 = \text{Pr}^i$	59.37	59.35	5.28 (1 H, m), 3.97 (1 H, sept)	4.53 (1 H, sept)

<sup>a</sup>  $^{31}\text{P}$  Shifts in p.p.m. downfield from triethylphosphine;  $^1\text{H}$  shifts in p.p.m. downfield from  $\text{SiMe}_4$ . The spectra were recorded in  $\text{CDCl}_3$ . <sup>b</sup> The spectra also showed unresolved signals in the region 2.90–1.00.

(17)–(20) were produced from the initially formed products during the work-up procedure. Based on the following experiments, these products were assigned the 1-iodoalkylphosphonium iodide structures (13)–(16), which are very labile compounds and could not be isolated in the pure state. The  $^1\text{H}$  n.m.r. spectra of these compounds at  $-50^\circ\text{C}$  suggested that these molecules have a similar structure to the stable phosphonium iodides (17)–(20). The main difference was the absence of the methine proton at  $\delta$  5.0. A solution of the 1-iodoalkylphosphonium iodides (13)–(16) in methanol rapidly turned brown, and evaporation of the

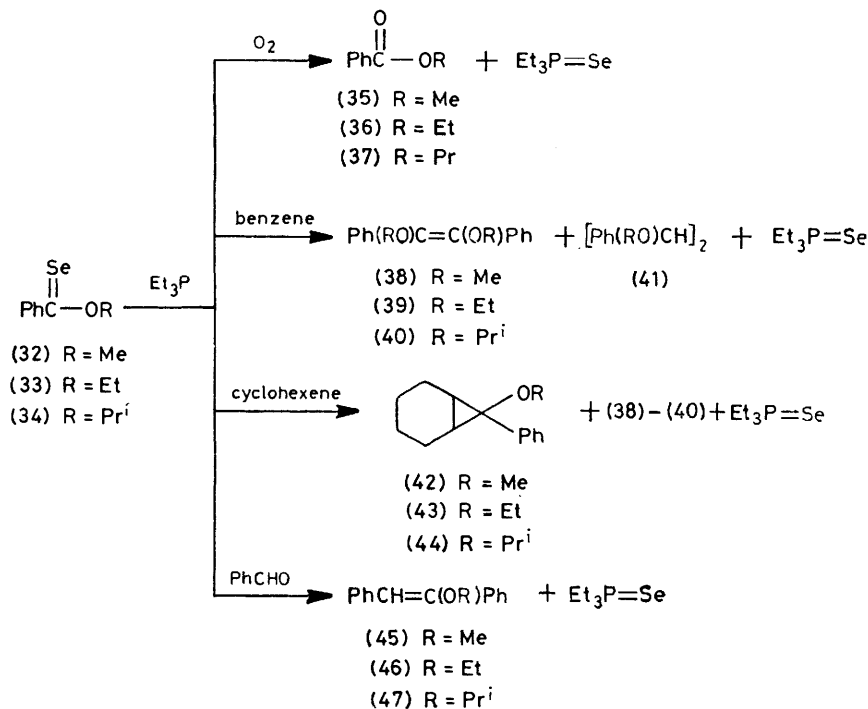
1,2-dialkylethylenes (26)–(29). These products hydrolysed to the corresponding acetoin (30) and (31) during the purification procedure, *i.e.* on the silica gel plates.

Wittig-type ylids generated from 1-alkoxyalkyl-triphenylphosphonium iodides are known to react with benzaldehyde in a similar manner.<sup>7,8</sup> The intermediacy of the ylid (21) in the reaction between the 1-iodoalkylphosphonium iodides (13)–(16) and methanol or benzaldehyde seems therefore to be a reasonable assumption. The ylid (21) can be formed by attack of the iodide ion on the phosphonium iodides (see Scheme 2).

The  $^{31}\text{P}$  n.m.r. spectra (Table I) of the purple inter-

mediates shows that only one type of phosphorus atom is present. The chemical shift of these phosphorus atoms are almost identical to those of the phosphonium iodides (17)—(20), thus indicating that the phosphorus atoms in the purple intermediates and the phosphonium iodides (17)—(20) are in similar electronic environments. This eliminates the phosphorane (21) as a possible structure for the purple intermediate, since in this case

ation of triethylphosphine selenide and the corresponding benzoates (35)—(37). The reaction in the absence of oxygen gave a colourless solution, from which triethylphosphine selenide and the stilbenes (38)—(40) could be isolated after exposure to atmospheric oxygen. The dibenzyl (41) was only formed for R = Pr<sup>i</sup>. The *cis* : *trans* ratio for the stilbenes was determined chromatographically; it could also be determined from the <sup>1</sup>H



SCHEME 3

the signal corresponding to the phosphorus atom in triethylphosphine selenide ( $\delta$  63.28) would have been detected. The e.s.r. spectra of the purple intermediates also gave negative results, *i.e.* no radicals were present. The e.s.r. spectra were recorded in such a way that both singlet and triplet radicals would have been detected.

TABLE 2  
Data for reactions of selenobenzoates with triethylphosphine

	<i>cis</i> : <i>trans</i> ratio *	Total yield (%)	<i>meso</i> : $\pm$ ratio *	Total yield (%)
R = Me (35)	48 : 52 (45 : 55)	87	not formed	
R = Et (36)	37 : 63 (40 : 60)	82	not formed	
R = Pr <sup>i</sup> (37)	0 : 100 (0 : 100)	57	49 : 51 (52 : 48)	23

\* Ratio determined by <sup>1</sup>H n.m.r. in parentheses.

**Aromatic Selenoesters.**—The selenobenzoates (32)—(34) appeared to be more reactive towards triethylphosphine than the aliphatic selenoesters. The reaction with triethylphosphine was completed in 4 h at room temperature, both in the presence and absence of oxygen. As was the case with the aliphatic selenoesters, the presence of atmospheric oxygen resulted in the form-

n.m.r. spectra, by integration of the  $\alpha$ -alkoxy-proton signals (Table 2). Similar results were obtained when the reaction was carried out in solvents such as toluene, tetrahydrofuran, and triethylphosphine.

The product composition changed when the reaction was performed in cyclohexene. The major products were the two epimers of the norcaranes (42)—(44) and triethylphosphine selenide, in addition to a small amount of the stilbenes (38)—(40). The dibenzyl (41) was not formed under these conditions. The two norcarane epimers were identified by their <sup>1</sup>H n.m.r. spectra and their hydrolysis product, cyclohexyl phenyl ketone. The ratio between the two epimers was determined by <sup>1</sup>H n.m.r. spectroscopy, based on the integration of the protons  $\alpha$  to the oxygen atom (Table 3). It has been shown that the shielding effect of the cyclopropyl ring can only affect the  $\alpha$ -alkoxy-protons in the *exo*-epimer,<sup>9,10</sup> in which the alkoxy-group is *anti* with respect to the cyclohexyl ring. The high-field resonance is therefore assigned to the *exo*-epimer.

When the reaction with triethylphosphine in benzene was performed in the presence of benzaldehyde (1 equiv.) the  $\alpha$ -alkoxy-stilbenes (45)—(47) and triethylphosphine selenide were formed; neither the stilbenes

(38)—(40) nor the dibenzyl (41) were formed under these conditions. The *cis:trans* ratio of the  $\alpha$ -alkoxy-stilbenes (45)—(47) was determined both from the  $^1\text{H}$  n.m.r. spectra<sup>11</sup> and chromatographically. The reactions of the selenobenzoates are summarised in Scheme 3.

These experiments point to a mechanism in which both a carbene and a Wittig-type ylid are involved. The  $^{31}\text{P}$  n.m.r. spectra of the reaction between the selenobenzoates and triethylphosphine at 40 °C showed

(Scheme 4).  $\alpha$ -Alkoxy-ylids are known to be very reactive compounds.<sup>7,8</sup> In the absence of a suitable reactant these ylids will fragment into  $\alpha$ -alkoxy-carbenes and trisubstituted phosphines.<sup>8</sup> Formation of the stilbenes (38)—(40) may be due either to a reaction between the ylids (49) and the selenobenzoates (a Wittig reaction<sup>6</sup>), or between the  $\alpha$ -alkoxy-carbenes (50) and the ylids (49).<sup>8</sup> If the Wittig reaction is responsible for the formation of the stilbenes (38)—(40), it appeared unreasonable that only one Wittig product was formed

TABLE 3  
Data of products from the reactions of selenobenzoates (38)—(40) with triethylphosphine in cyclohexane

Starting material	Norcorane			Total yield of norcorane	Analysis (%)		Hydrolysis product <sup>c</sup>	Yield of PhC(OR)=C(OR)Ph (%)
	$^1\text{H}$ n.m.r. <sup>a</sup>		<i>exo:endo</i> ratio		Found (Required)			
	<i>exo</i>	<i>endo</i>			C	H		
(38) R = Me <sup>c</sup>	2.94 (OMe)	3.11 (OMe)	60 : 40	73	83.35 (83.12)	8.8 (8.97)	253 mg (92%)	15
(39) R = Et	3.09 (OCH <sub>2</sub> )	3.39 (OCH <sub>2</sub> )	54 : 46	79	83.5 (83.28)	9.15 (9.32)	267 mg (91%)	12
(40) R = Pr <sup>i</sup>	3.31 (OCH)	3.64 (OCH)	68 : 32	83	83.3 (83.42)	9.45 (9.63)	289 mg (93%)	6

<sup>a</sup> In addition the spectra showed a complex aromatic pattern at  $\delta$  7.7—6.7 and a broad multiplet at  $\delta$  2.3—0.4; the spectra were recorded in  $\text{CDCl}_3$  with  $\text{SiMe}_4$  as internal standard. <sup>b</sup> Cyclohexyl phenyl ketone. <sup>c</sup> D. B. Ledlie and E. A. Nelson, *Tetrahedron Letters*, 1969, 1175.

four different phosphorus signals, two of which disappeared as time progressed (Table 4). The remaining signals were unequivocally assigned to triethylphosphine ( $\delta$  0) and triethylphosphine selenide ( $\delta$  63.28) on the basis

TABLE 4  
 $^{31}\text{P}$  N.m.r. data for the reaction of the selenobenzoates Ph-C-OR with triethylphosphine\*

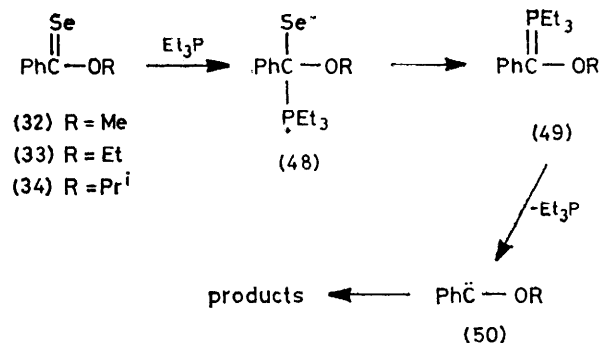
R	$\delta_{\text{H}}$	
	After 90 min	After 240 min
R = Me	0, 54.12,	0, 63.28
	57.19, 63.28	
R = Et	0, 54.37,	0, 63.35
	57.82, 63.35	
R = Pr <sup>i</sup>	0, 16.40,	0, 16.40,
	54.81, 56.82,	63.12

\* In p.p.m. downfield from triethylphosphine.

of blank runs. In the case of the isopropyl selenobenzoate (34) a fifth phosphorus signal at  $\delta$  16.4 was detected, which could not be assigned to any of the isolated phosphorus-containing compounds. Upon exposure to air this signal disappeared and a new signal appeared at  $\delta$  69.83. It therefore seems that the reaction starts with a nucleophilic attack by triethylphosphine on the selenocarbonyl carbon atom. Both selenocarbonyl and thiocarbonyl esters are known to undergo attack at the carbonyl carbon atom by certain nucleophiles.<sup>6,12,13</sup> The resulting tetrahedral intermediate (48) has a tendency to expel selenium, since the carbon atom bonded to selenium can delocalise a negative charge into the phenyl group by resonance-stabilisation. The tetrahedral intermediate (48) can therefore fragment by ejecting the selenium atom giving the ylid (49)

when benzaldehyde (1 equiv.) as a competing reactant was added. Highly reactive Wittig ylids react very quickly with the selenobenzoates at room temperature,<sup>6,14</sup> and consequently both the mono- and the di-alkoxy-stilbenes should have been formed when benzaldehyde was added. The logical conclusion is that the selenobenzoates are already completely transformed into the tetrahedral intermediates (48) by the time the ylids (49) are formed in the reaction mixture. Therefore the reaction between the ylids (49) and the  $\alpha$ -alkoxy-carbenes (50) must be responsible for the formation of the stilbenes (38)—(40).

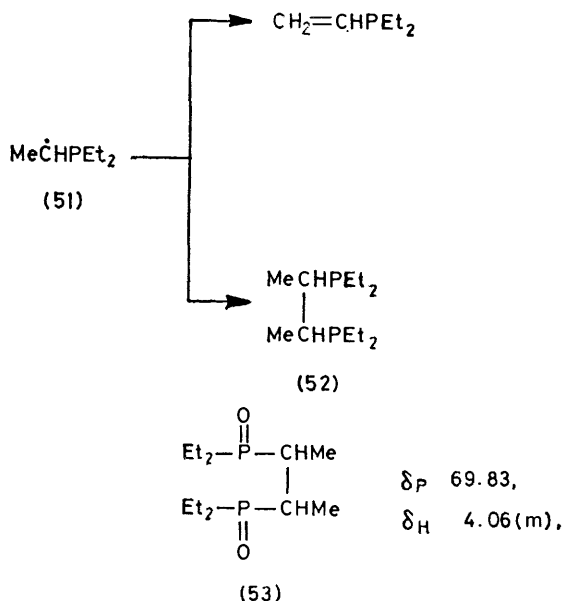
Formation of the bibenzyl (41) can also be explained by a reaction of the  $\alpha$ -alkoxy-carbene (50). The bibenzyl is only formed when R = Pr<sup>i</sup>; this is probably



SCHEME 4

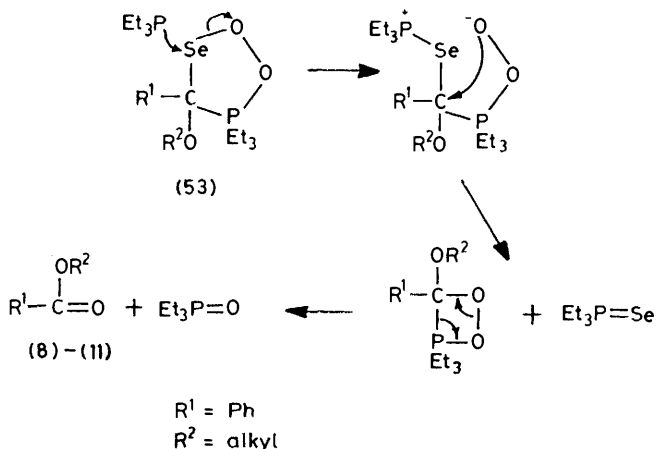
due to steric hindrance caused by the isopropyl group, which will make the attack of the  $\alpha$ -alkoxy-carbene at the ylid more difficult, and hence any other reaction pathways for the  $\alpha$ -alkoxy-carbene will be enhanced.

Hydrocarbon formation in the desulphurisation of thioketones by trialkylphosphines has been explained by the intermediacy of a carbene, which in turn abstracts a hydrogen radical from the trialkylphosphine and dimerises.<sup>15</sup> This mechanism in this reaction would create a trialkylphosphine radical such as (51), which



SCHEME 5

could react further either by dimerisation or by eliminating  $\text{H}^+$  (Scheme 5). In both cases a trisubstituted phosphine is formed, which might be the unknown phosphorus-containing compound in the reaction when the bibenzyl (41) is formed. Unfortunately it was not possible to isolate this compound in a pure state, but



SCHEME 6

only as a mixture with triethylphosphine selenide. Based on the  $^{31}\text{P}$  and  $^1\text{H}$  n.m.r. spectra of this mixture the dimer (52) seems to be a reasonable candidate. The two time-dependent phosphorus signals are tentatively assigned to the  $\alpha$ -alkoxy-ylid (49) ( $\delta$  57.20) and the tetrahedral intermediate (48) ( $\delta$  54.10).

Formation of the benzoates (35)–(37) when the

reaction was performed in the presence of atmospheric oxygen can be explained by the ability of molecular oxygen to add to a dipolar molecule, e.g. (48), creating a cyclic intermediate (53), which can fragment to the esters (35)–(37) with the aid of a second molecule of triethylphosphine (Scheme 6).

## EXPERIMENTAL

M.p.s were determined with a Reichert hot-stage apparatus. I.r. spectra were recorded with a Perkin-Elmer 257 spectrometer and u.v. spectra with a Unicam SP 800 spectrometer.  $^1\text{H}$  N.m.r. spectra were determined with a Varian T60 instrument for solutions in  $\text{CDCl}_3$ , with tetramethylsilane as internal standard.  $^{13}\text{C}$  N.m.r. spectra were determined with a JEOL FX-60 instrument at 15.4 MHz for solutions in  $\text{CDCl}_3$  with tetramethylsilane as internal standard.  $^{31}\text{P}$  N.m.r. spectra were determined with a Varian XL-100 instrument at 40.5 MHz for solutions in  $\text{CDCl}_3$  with triethylphosphine as internal standard. Mass spectra were recorded with an A.E.I. MS9 instrument. G.l.c. was performed on a Hewlett-Packard 5700A instrument, using a 20% SE-52 on Chrom W column. Preparative t.l.c. used  $20 \times 20$  cm plates coated with 2 mm of Merck silica gel 60 PF-254, and activated in an oven at  $120^\circ\text{C}$  for 2 h. 'Light petroleum' refers to the fraction of b.p.  $40\text{--}50^\circ\text{C}$ , and 'petroleum' to the fraction of b.p.  $60\text{--}80^\circ\text{C}$ . Florisil (100–200 mesh) was dried *in vacuo* at  $130^\circ\text{C}$  for 24 h prior to use. All reactions involving triethylphosphine were conducted under oxygen-free conditions unless otherwise stated.

*Preparation of Selenoesters.*—The selenoesters (4), (7), and (35)–(37) were prepared as previously described.<sup>6,16</sup> *O*-Ethyl selenoacetate (5) and *O*-methyl selenoisobutyrate (6) were prepared from *N*-acetyl- and *N*-isobutyryl-piperidine, respectively, using the standard procedure.<sup>6</sup> *O*-Ethyl selenoacetate (5), b.p.  $127\text{--}129^\circ\text{C}$  at 767 mmHg, was a yellow oil (82%);  $\nu_{\text{max}}$  (film) 2985m, 1455m, 1385m, 1315m, 1245s, 1205s, 1015m, 1090m, and 1015m  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 272 and 443 nm ( $\epsilon$  7200 and 50);  $\delta$  4.60 (2 H, q,  $J$  7.0 Hz), 2.36 (3 H, s), and 1.45 (3 H, t,  $J$  7.0 Hz);  $m/e$  152 ( $M^+$ ), 124, 107, and 43 (Found: C, 31.65; H, 5.40.  $\text{C}_4\text{H}_8\text{OSe}$  requires C, 31.80; H, 5.34%). *O*-Methyl selenoisobutyrate (6), b.p.  $58\text{--}59^\circ\text{C}$  at 35 mmHg, was a yellow oil (79%);  $\nu_{\text{max}}$  (film) 3010w, 2985w, 1460m, 1365m, 1335m, 1215s, 1200s, 1155m, and 1060m  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 271 and 443 nm ( $\epsilon$  7300 and 50);  $\delta$  4.18 (3 H, s), 2.99 (1 H, sept,  $J$  6.5 Hz), and 1.28 (6 H, d,  $J$  6.5 Hz);  $m/e$  166 ( $M^+$ ), 135, and 59 (Found: C, 36.3; H, 6.25.  $\text{C}_5\text{H}_{10}\text{OSe}$  requires C, 36.37; H, 6.10%).

*Reaction of the Aliphatic Selenoesters (4)–(7) with Triethylphosphine in the Presence of Atmospheric Oxygen.*—The selenoester (2 mmol) in benzene (5 ml) was heated at  $50^\circ\text{C}$  for 5 h with triethylphosphine (0.994 g, 8 mmol), the purple mixture was then exposed to the atmosphere until the colour had disappeared, and methyl iodide (6 ml) was then added. The mixture was filtered, the residue was washed with light petroleum (10 ml), and evaporation of the combined solutions *in vacuo* and trapping of the distillate at liquid-nitrogen temperature gave a solution from which the esters (8)–(11) were identified (preparative and comparative g.l.c. analysis with authentic samples). Chromatography of the non-volatile residue on alumina (grade III) gave triethylphosphine selenide, eluted with petroleum-ethyl acetate (10:1); yield from *O*-methyl selenoacetate

(4) 366 mg (93%); from *O*-ethyl selenoacetate (5) 358 mg (91%); from *O*-methyl selenoisobutyrate (6) 374 mg (95%); and from *O*-isopropyl selenoacetate (7) 366 mg (93%), in each case identical with an authentic specimen.

*Reaction of the Aliphatic Selenoesters (4)–(7) with Triethylphosphine and Methyl Iodide.*—The selenoester (2 mmol) in benzene (10 ml) was heated at 50 °C for 5 h with triethylphosphine (0.994 g, 8 mmol). Benzene and triethylphosphine were then evaporated *in vacuo*, and the purple reaction mixture was cooled in ice-water. Addition of an oxygen-free solution of methyl iodide (1 ml) in tetrahydrofuran (15 ml) gave a colourless suspension. After 15 min, 1 equiv. of sodium iodide was added and the reaction mixture was evaporated *in vacuo* and the distillate was trapped at liquid-nitrogen temperature. This gave a tetrahydrofuran solution containing dimethyl selenide [isolated as trimethylselenonium iodide, m.p. 143–144 °C (lit.,<sup>17</sup> m.p. 150–151 °C)]. Chromatography of the residue [1-alkoxy-1-iodoalkyltriethylphosphonium iodides (13)–(16)] on alumina (grade III) (eluant methanol) gave the 1-alkoxyalkyltriethylphosphonium iodides (17)–(20); *O*-methyl selenoacetate (4) gave (1-methoxyethyl)triethylphosphonium iodide (17) (551 mg, 91%); *O*-ethyl selenoacetate (5) gave (1-ethoxyethyl)triethylphosphonium iodide (18) (557 mg, 88%); *O*-methyl selenoisobutyrate (6) gave (1-methoxy-2-methylpropyl)triethylphosphonium iodide (19) (489 mg, 74%); and *O*-isopropyl selenoacetate (7) gave [1-(1-methylethoxy)ethyl]triethylphosphonium iodide (20) (543 mg, 82%); compounds (17)–(20) were identical with independently prepared specimens. Trimethylselenonium iodide was isolated in yields ranging from 59 to 71%.

*Preparation of 1-Chloroalkyl Alkyl Ethers.*—1-Chloro-1-methoxyethane, 1-chloro-1-ethoxyethane, and 1-chloro-1-(1-methylethoxy)ethane were prepared according to the general procedure by Grummit *et al.*,<sup>18</sup> and 1-chloro-1-methoxy-2-methylpropane was prepared according to Kwart and Silver.<sup>19</sup>

*Preparation of (1-Alkoxyalkyl)triethylphosphonium Iodides (17)–(20).*—To a stirred solution of the 1-chloroalkyl alkyl ether (50 mmol) in benzene (30 ml) was added triethylphosphine (5.9 g, 50 mmol), in benzene (10 ml) at 0 °C, and after 2 h the precipitated salt was collected and redissolved in acetone (50 ml). Addition of sodium iodide (1 equiv.) in acetone (10 ml) gave, after filtration, evaporation, and drying *in vacuo*, the (1-alkoxyalkyl)triethylphosphonium iodides (17)–(20); (1-methoxyethyl)triethylphosphonium iodide (17) (11.09 g, 73%) had m.p. 78–80 °C (decomp.) (Found: C, 35.4; H, 7.5. C<sub>9</sub>H<sub>22</sub>IOP requires C, 35.54; H, 7.29%); (1-ethoxyethyl)triethylphosphonium iodide (18) (11.00 g, 69%) had m.p. 93–95 °C (decomp.) (Found: C 37.5; H, 7.85. C<sub>10</sub>H<sub>24</sub>IOP requires C, 37.75; H, 7.60%); (1-methoxy-2-methylpropyl)triethylphosphonium iodide (19) (12.30 g, 74%) had m.p. 77–79 °C (decomp.) (Found: C, 39, 65; H, 8.01. C<sub>11</sub>H<sub>26</sub>IOP requires C, 39.77; H, 7.89%); and [1-(1-methylethoxy)ethyl]triethylphosphonium iodide (20) (14.20 g, 86%) had m.p. 70 °C (decomp.) (Found: C, 39.65; H, 8.0. C<sub>11</sub>H<sub>26</sub>IOP requires C, 39.77; H, 7.89%). The <sup>1</sup>H n.m.r. data of these compounds are given in Table I.

*Reaction of the (1-Alkoxy-1-iodoalkyl)triethylphosphonium Iodides (13)–(16) with Methanol.*—The crude (1-alkoxy-1-iodoalkyl)triethylphosphonium iodide (1 mmol) was dissolved in methanol (25 ml) and stirred at room temperature for 30 min, sodium iodide (1 equiv.) was then added and the

mixture was evaporated. Chromatography of the residue on alumina (grade III) (eluant methanol) gave the (1-alkoxyalkyl)triethylphosphonium iodides (13)–(16). The <sup>1</sup>H n.m.r. spectra of the crude products showed that no chemical transformation had taken place during the chromatographic purification. (1-Methoxy-1-iodoethyl)triethylphosphonium iodide (13) gave (1-methoxyethyl)triethylphosphonium iodide (17) (206 mg, 68%); (1-ethoxy-1-iodoethyl)triethylphosphonium iodide (14) gave (1-ethoxyethyl)triethylphosphonium iodide (18) (242 mg, 76%); (1-methoxy-1-iodo-2-methylpropyl)triethylphosphonium iodide (15) gave (1-methoxy-2-methylpropyl)triethylphosphonium iodide (19) (236 mg, 71%); and [1-(1-methylethoxy)-1-iodoethyl]triethylphosphonium iodide (16) gave [1-(1-methylethoxy)ethyl]triethylphosphonium iodide (20) (272 mg, 83%); all were identical with independently prepared specimens.

*Reaction of the (1-Alkyl-1-iodoalkyl)triethylphosphonium Iodides (13)–(16) with Benzaldehyde.*—A suspension of crude (1-alkoxy-1-iodoalkyl)triethylphosphonium iodide (2 mmol) in tetrahydrofuran (20 ml) was stirred under an atmosphere of argon at –70 °C for 1 h. The resulting red homogeneous solution was then treated with benzaldehyde (212 mg, 2 mmol) at –70 °C, and after 15 min methyl iodide (1 ml) was added to the cold reaction mixture, and the solvent was evaporated *in vacuo*. The oily residue was distilled at 100 °C and 0.01 mmHg and the distillate was trapped at liquid-nitrogen temperature. This left a residue from which triethylmethylphosphonium iodide was isolated. The distillate was subjected to preparative t.l.c.; elution with petroleum–diethyl ether (4:1) gave the ketones (22)–(25) as the less polar band and the acetoin (30) and (31) as the more polar band. (1-Methoxy-1-iodoethyl)triethylphosphonium iodide (13) gave 1-phenyl-2-methoxypropan-1-one (22) (242 mg, 74%) as a colourless oil, identified by comparison with published data,<sup>8</sup> the acetoin (30) (14 mg, 16%), identical with an authentic specimen, and triethylmethylphosphonium iodide (343 mg, 66%), m.p. 298–301 °C (lit.,<sup>20</sup> m.p. 300–302 °C). (1-Ethoxy-1-iodoethyl)triethylphosphonium iodide (14) gave 1-phenyl-2-ethoxypropan-1-one<sup>21</sup> (23) (236 mg, 72%) as a colourless oil;  $\delta$  8.01–7.14 (5 H, m), 4.84 (1 H, q, *J* 6.5 Hz), 3.47 (2 H, q, *J* 7.0 Hz), 1.45 (3 H, d, *J* 6.5 Hz), and 1.18 (3 H, t, *J* 7.0 Hz);  $\nu_{\text{max}}$  (film) 1 695s, 1 680s, 1 605s, 1 225s, 1 130s, and 695s cm<sup>-1</sup>; *m/e* 178 (*M*<sup>+</sup>), 163, 150, 105, 77, and 51 (Found: C, 74.0; H, 8.0. C<sub>11</sub>H<sub>14</sub>O<sub>2</sub> requires C, 74.13; H, 7.92%); the acetoin (30) (18 mg, 20%); and triethylmethylphosphonium iodide (374 mg, 72%). (1-Methoxy-1-iodo-2-methylpropyl)triethylphosphonium iodide (15) gave 1-phenyl-2-methoxy-3-methylbutan-1-one (24) (261 mg, 68%) as a colourless oil;  $\delta$  8.12–6.99 (5 H, m), 4.56 (1 H, d, *J* 7.0 Hz), 3.31 (3 H, s), 2.73 (1 H, m), and 1.07 (6 H, d, *J* 7.0 Hz);  $\nu_{\text{max}}$  (film) 1 690s, 1 615s, 1 235s, 1 135s, and 685s cm<sup>-1</sup>; *m/e* 192 (*M*<sup>+</sup>), 177, 150, 149, 105, 77, and 51 (Found: C, 74.8; H, 8.45. C<sub>12</sub>H<sub>16</sub>O<sub>2</sub> requires C, 74.96; H, 8.39%); 4-hydroxy-2,5-diethylhexan-3-one (23) (37 mg, 26%), identified by comparison with published data,<sup>22</sup> and triethylmethylphosphonium iodide (332 mg, 64%). [1-(1-Methylethoxy)-1-iodoethyl]triethylphosphonium iodide (16) gave 1-phenyl-2-(1-methylethoxy)propan-3-one (25) (295 mg, 77%) as a colourless oil;  $\delta$  8.06–7.10 (5 H, m), 4.83 (1 H, q, *J* 7.0 Hz), 3.63 (1 H, sept, *J* 7.0 Hz), 1.41 (3 H, d, *J* 7.0 Hz), and 1.13 (6 H, d, *J* 7.0 Hz);  $\nu_{\text{max}}$  (film) 1 685s, 1 680s, 1 610s, 1 230s, 1 130s, and 690s cm<sup>-1</sup>; *m/e* 192 (*M*<sup>+</sup>), 177, 162, 105, 77, and 51 (Found:

C, 74.85; H, 8.5.  $C_{12}H_{16}O_2$  requires C, 74.96; H, 8.39%): the acetoin (30) (15 mg, 17%); and triethylmethylphosphonium iodide (421 mg, 81%).

*Reaction of the Selenobenzoates (32)–(34) with Triethylphosphine in the Presence of Atmospheric Oxygen.*—The selenobenzoate (1 mmol) was treated with triethylphosphine (0.497 g, 4 mmol) in benzene (10 ml) for 4 h at room temperature. Methyl iodide (6 ml) was then added, the mixture was filtered, and the residue was washed with light petroleum. Evaporation of the combined solutions and chromatography of the residue on alumina (grade III) [elution with petroleum–ethyl acetate (10 : 1)] gave the benzoates (35)–(37) and triethylphosphine selenide, identical with authentic samples. *O*-Methyl selenobenzoate (32) gave methyl benzoate (35) (123 mg, 91%); *O*-ethyl selenobenzoate (33) gave ethyl benzoate (36) (133 mg, 89%); and *O*-isopropyl selenobenzoate (34) gave isopropyl benzoate (37) (152 mg, 93%). Triethylphosphine selenide was isolated in yields ranging from 87 to 94%.

*Reaction of the Selenobenzoates (32)–(34) with Triethylphosphine in the Absence of Oxygen.*—The selenobenzoate (2 mmol) in benzene (15 ml) was treated with triethylphosphine (0.994 g, 8 mmol) for 4 h at room temperature. Evaporation of the reaction mixture *in vacuo* at 80 °C left a residue which was chromatographed on a dehydrated Florisil column. Elution with petroleum–diethyl ether (95 : 1) gave two fractions. The first fraction, containing triethylphosphine selenide, the tetrasubstituted ethane (41) (when present), and the phosphine oxide (53), was subjected to preparative t.l.c. Elution with petroleum–diethyl ether (50 : 1) gave the disubstituted ethane (41) (when present) as the more polar band and triethylphosphine selenide and the phosphine oxide (53) as the less polar band. Separation of the diastereoisomeric ethane mixture was performed on a neutral alumina (grade I) column (elution with benzene). Evaporation of the second fraction *in vacuo* gave a *cis*–*trans* mixture of the stilbenes (38)–(40). Separation of the *cis*- and *trans*-isomers was accomplished using a neutral alumina (grade III) column [elution with benzene–hexane (1 : 3)]. *O*-Methyl selenobenzoate (32) gave *cis*- $\alpha,\alpha$ -dimethoxystilbene (38) (100 mg, 42%), from methanol, m.p. 124–125 °C (lit.,<sup>23</sup> m.p. 123 °C), identified by comparison with published data,<sup>23</sup> *trans*- $\alpha,\alpha$ -dimethoxystilbene (38) (108 mg, 45%), from methanol, m.p. 87–88 °C (lit.,<sup>23</sup> m.p. 88 °C), identified by comparison with published data,<sup>23</sup> and triethylphosphine selenide (369 mg, 93%). *O*-Ethyl selenobenzoate (33) gave *cis*- $\alpha,\alpha$ -diethoxystilbene (39) (81 mg, 30%), from methanol, m.p. 73–74 °C;  $\delta$  7.02–6.91 (10 H, m), 3.64 (4 H, q, *J* 6.5 Hz), and 0.97 (6 H, t, *J* 6.5 Hz);  $\nu_{\max}$  (Nujol) 1 260s, 1 125s, 1 061s, 780s, and 700s  $cm^{-1}$ ; *m/e* 268 ( $M^+$ ), 253, 211, 194, 165, 120, 105, and 77 (Found: C, 80.75; H, 7.45.  $C_{18}H_{20}O_2$  requires C, 80.56; H, 7.51%); *trans*- $\alpha,\alpha$ -diethoxystilbene (39) (138 mg, 51%), from methanol, m.p. 52–53 °C;  $\delta$  7.11–6.83 (10 H, m), 3.39 (4 H, q, *J* 6.5 Hz), and 1.05 (6 H, t, *J* 6.5 Hz);  $\nu_{\max}$  (Nujol) 1 250s, 1 125s, 1 065s, 775s, and 695s  $cm^{-1}$ ; *m/e* 268 ( $M^+$ ), 253, 211, 194, 165, 120, 105, and 77 (Found: C, 80.8; H, 7.55.  $C_{18}H_{20}O_2$  requires C, 80.56; H, 7.51%); and triethylphosphine selenide (352 mg, 89%). *O*-Isopropyl selenobenzoate (34) gave *trans*- $\alpha,\alpha$ -di-isopropoxystilbene (40) (168 mg, 57%), from methanol, m.p. 93–94 °C;  $\delta$  7.09–6.87 (10 H, m), 3.75 (2 H, sept, *J* 6.0 Hz), and 1.10 (12 H, d, *J* 6.0 Hz);  $\nu_{\max}$  (Nujol) 1 245s, 1 135s, 1 045s, 785s, and 690s  $cm^{-1}$ ; *m/e* 296 ( $M^+$ ), 281, 225, 194, 165, 120, 105, and 77 (Found: C, 81.25; H, 8.3.  $C_{20}H_{24}O_2$

requires C, 81.04; H, 8.16%): *meso*- $\alpha,\alpha$ -di-isopropoxybibenzyl (41) (68 mg, 11%), from methanol, m.p. 82–84 °C (lit.,<sup>24</sup> m.p. 83.0–83.5 °C), identified by comparison with published data:<sup>24</sup> DL- $\alpha,\alpha$ -di-isopropoxybibenzyl (41) (71 mg, 12%), from methanol, m.p. 34–36 °C (lit.,<sup>25</sup> m.p. 35–37 °C), identified by comparison with published data:<sup>24</sup> and triethylphosphine selenide (372 mg, 94%).

*Reaction of the Selenobenzoates (32)–(34) with Triethylphosphine in Cyclohexene.* The selenobenzoate (2 mmol) was treated with triethylphosphine in cyclohexene (15 ml) as described in the preceding section. Chromatography of the residue on a dehydrated Florisil column, eluting with petroleum–diethyl ether (20 : 1), gave triethylphosphine selenide, a *cis*–*trans* mixture of the stilbenes (38)–(40), and an *exo*–*endo* mixture of the norcaranes (42)–(44). The results are shown in Table 3. Triethylphosphine selenide was isolated in yields ranging from 86 to 94%.

*Hydrolysis of the Norcaranes (42)–(44).*—The norcarane (1 mmol) was dissolved in ethanol (10 ml) and 2M aqueous sulphuric acid (1 ml) was added. After 30 min at room temperature water (10 ml) was added, and the reaction mixture was neutralised with sodium hydrogencarbonate. Extraction with dichloromethane and evaporation gave a residue which was chromatographed on alumina (grade III). Elution with petroleum–diethyl ether (10 : 1) gave phenyl cyclohexyl ketone, identical with an authentic specimen. The results are shown in Table 3.

*Reaction of the Selenobenzoates (32)–(34) with Triethylphosphine in the Presence of Benzaldehyde.*—The selenobenzoate (2 mmol) was treated with triethylphosphine in the presence of benzaldehyde (212 mg, 2 mmol) as in the preceding section. Evaporation of the reaction mixture *in vacuo* at 80 °C left a residue which was chromatographed on a dehydrated Florisil column. Elution with petroleum–diethyl ether (95 : 1) yielded triethylphosphine selenide and a *cis*–*trans* mixture of the stilbenes (45)–(47). Separation of the *cis*–*trans* mixture was accomplished on an alumina (grade III) column [elution with benzene–hexane (1 : 5)]. *O*-Methyl selenobenzoate (32) gave *trans*- $\alpha$ -methoxystilbene (45) (172 mg, 41%), from pentane, m.p. 47–49 °C (lit.,<sup>8</sup> m.p. 48–50 °C), identified by comparison with published data;<sup>8</sup> *cis*- $\alpha$ -methoxystilbene (45) (185 mg, 44%), as a colourless oil, identified by comparison with published data;<sup>8</sup> and triethylphosphine selenide (352 mg, 89%). *O*-Ethyl selenobenzoate (33) gave *trans*- $\alpha$ -ethoxystilbene (46)<sup>26</sup> (174 mg, 39%) as a colourless oil;  $\delta$  7.03–7.40 (10 H, m), 6.03 (1 H, s), 3.76 (2 H, q, *J* 6.5 Hz), and 1.24 (3 H, t, *J* 6.5 Hz);  $\nu_{\max}$  (film) 1 685s, 1 630s, 1 590s, 1 215s, and 1 055s  $cm^{-1}$ ; *m/e* 224 ( $M^+$ ), 209, 196, 180, 179, 165, 152, and 105 (Found: C, 85.5; H, 7.25.  $C_{16}H_{16}O$  requires C, 85.68; H, 7.19%); *cis*- $\alpha$ -ethoxystilbene (46)<sup>26</sup> (193 mg, 43%) as a colourless oil;  $\delta$  7.05–7.75 (5 H, m), 6.95 (5 H, s), 5.75 (1 H, s), 3.81 (2 H, q, *J* 6.5 Hz), and 1.27 (3 H, t, *J* 6.5 Hz);  $\nu_{\max}$  (film) 1 680s, 1 640s, 1 605s, 1 205s, and 1 060s  $cm^{-1}$ ; *m/e* 224 ( $M^+$ ), 209, 196, 180, 179, 165, 152, and 105 (Found: C, 85.55; H, 7.3.  $C_{16}H_{16}O$  requires C, 85.68; H, 7.19%); and triethylphosphine selenide (360 mg, 91%). *O*-Isopropyl selenobenzoate (34) gave *trans*- $\alpha$ -isopropoxystilbene (47) (176 mg, 37%) as a colourless oil;  $\delta$  7.10–7.45 (10 H, m), 6.15 (1 H, s), 3.92 (1 H, sept, *J* 7.5 Hz), and 1.15 (6 H, d, *J* 7.5 Hz);  $\nu_{\max}$  (film) 1 675s, 1 635s, 1 605s, 1 225s, and 1 045s  $cm^{-1}$ ; *m/e* 238 ( $M^+$ ), 223, 182, 180, 179, 165, 152, and 105 (Found: C, 85.5; H, 7.75.  $C_{17}H_{18}O$  requires C, 85.67; H, 7.61%); *cis*- $\alpha$ -isopropoxystilbene (47)<sup>27</sup> (214 mg, 45%) as a colourless oil;  $\delta$  7.01–

7.70 (5 H, m), 6.90 (5 H, s), 5.93 (1 H, s), 4.02 (1 H, sept,  $J$  7.5 Hz), and 1.20 (6 H, d,  $J$  7.5 Hz);  $\nu_{\max}$  (film) 1 670s, 1 625s, 1 595s, 1 215s, and 1 040s  $\text{cm}^{-1}$ ;  $m/e$  238 ( $M^+$ ), 223, 182, 180, 179, 165, 152, and 105 (Found: C, 85.4; H, 7.8.  $\text{C}_{17}\text{H}_{18}\text{O}$  requires C, 85.67; H, 7.61%): and triethylphosphine selenide (321 mg, 81%).

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