Reaction of Olefins with *Se*-Phenyl (Selenothioperoxy)benzoate: A New Anti-Markownikoff Benzeneselenenylation

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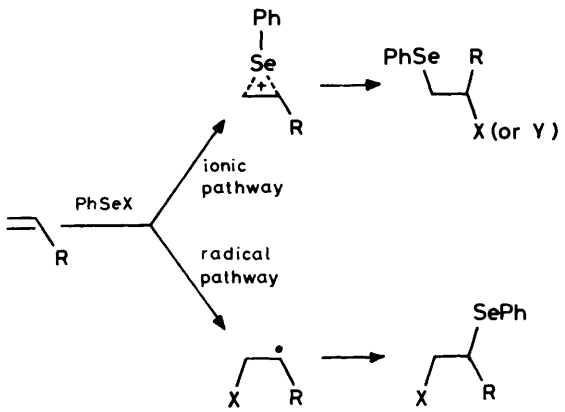
A novel free radical addition of *Se*-phenyl (selenothioperoxy)benzoate (**1**) to a variety of olefins is described. The addition of selenosulphide (**1**) to terminal olefins proceeds regiospecifically to give the anti-Markownikoff benzeneselenenylated adducts. The addition to cycloalkenes gives a mixture of *cis* and *trans* isomers. These reactions provide a useful method for simultaneous introduction of phenylseleno and thiobenzoyloxy groups into a molecule. Oxidation–elimination of the phenylseleno group of the adducts gives vinyl thiobenzoates and/or allyl thiobenzoates.

In recent years, oganoselenium chemistry has become important in organic synthesis because of the ease of manipulation of the seleno group.[1] There are numerous methods for simultaneous introduction of a phenylseleno group and a functional group (X or Y in Scheme 1) such as halide,[2]

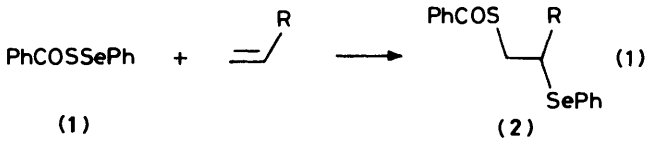


Scheme 1.

CN,[3] NO_2,[4] SCN,[5] NMe_2,[6] OCOR,[7] OR,[8] or HNCOR.[9] These methods, however, constitute an electrophilic addition of the phenylseleno group to an unsaturated bond *via* an ionic pathway, providing Markownikoff benzeneselenenylated products. It would be important, from the synthetic viewpoint, to be able to reverse the regiochemistry of the selenenylation. We envisaged that a free-radical pathway could be a method of choice to this end, and that anti-Markownikoff selenenylation using PhSeX would be realized, when radical X is electrophilic[10] and the carbon radical generated during the addition of X to an olefin is captured by PhSe. The selenosulphonation recently reported[11] is an excellent method along these lines. We chose *Se*-phenyl (selenothioperoxy)benzoate for PhSeX, which we found can be easily prepared,[12] and preliminary experiments showed such addition to be feasible.[13] We here describe a novel anti-Markownikoff benzeneselenenylation with concomitant thioesterification *via* the free-radical addition of *Se*-phenyl (selenothioperoxy)benzoate to a variety of olefins as well as subsequent oxidation–elimination of the phenylseleno group.

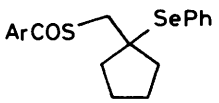
Results and Discussion

Addition Reaction of Se-*Phenyl (selenothioperoxy)benzoate* (**1**) *to Olefins.*—Compound (**1**) was prepared according to our recently developed method by treatment of thiobenzoic acid with *N*-(phenylseleno)phthalimide.[12] We first examined the addition reaction of compound (**1**) with terminal olefins. Thus, a 1M benzene solution of (**1**) was heated under reflux with a 3-fold excess of dec-1-ene in the presence of 10 mol% azoisobutyronitrile (AIBN), to give the addition product (**2a**) in 99% yield as shown in equation (1). The addition reaction, selenothioesterification, proceeded regiospecifically leading to the exclusive formation of *S*-2-(phenylseleno)decyl thiobenzoate

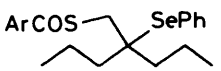


(**1**) (**2**)

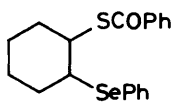
(**2a**) R = $[CH_2]_7Me$
(**2b**) Ph
(**2c**) CH_2OH
(**2d**) CH_2OAc
(**2e**) CH_2NHAc
(**2f**) CH_2CO_2Me
(**2g**) CH_2CN



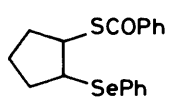
(**2h**) Ar = Ph
(**2i**) Ar = $3\text{-}O_2NC_6H_4$



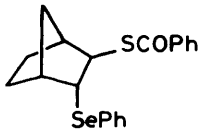
(**2j**) Ar = Ph
(**2k**) Ar = $3\text{-}O_2NC_6H_4$



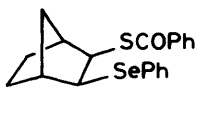
(**2l**)



(**2m**)



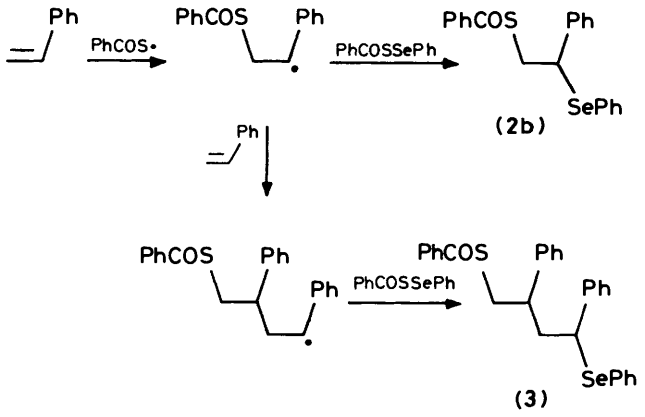
trans-(**2n**)



exo-cis-(**2n**)

(**2a**), the ^1H and ^{13}C n.m.r. spectra of which showed no indication of the signals expected for the regioisomer. Selenothioesterification using an equimolar amount of dec-1-ene resulted in a lower yield of adduct (**2a**); 65% yield after 3 h refluxing and 67% after 20 h with recovery of (**1**) in 30 and 27% yield, respectively. The yield of adduct (**2a**) was also greatly influenced by the concentration of the reaction mixture; the reaction in a 0.3M benzene solution of (**1**) with a 3-fold excess of dec-1-ene gave adduct (**2a**) in only 11% yield after 40 h refluxing.

The reaction of (**1**) with 3 mol equiv. of styrene gave adduct (**2b**) in only 44% yield, accompanied by 1:2-adduct (**3**) isolated in 30% yield. The reaction using 1.2 mol equiv. of styrene resulted in no improvement in the yield of (**2b**). Considerable formation of 1:2-adduct (**3**) showed that the carbon radical formed during the reaction reacted competitively with either styrene or compound (**1**) as shown in Scheme 2 (see below for



Scheme 2.

the free-radical mechanism). In order to minimize the formation of compound (**3**) six portions of 0.2 mol equiv. of styrene were added portionwise (one every 5 min) to an initial 2M solution of (**1**) in refluxing benzene, to give a 75% yield of adduct (**2b**) without significant formation of 1:2-adduct (**3**) but with 19% recovery of (**1**). On the other hand, heating allyl alcohol in a 2M solution of (**1**) for 4 h resulted in the formation of adduct (**2c**) in 81% yield, whereas the reaction in a 1M solution gave (**2c**) in 47% yield after 22 h refluxing, as well as unchanged reactant (**1**) (21% recovery).

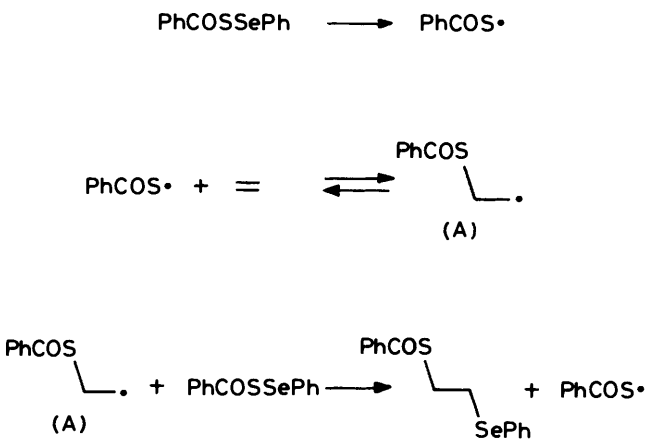
All the selenothioesterifications other than those mentioned above were performed in a 1M benzene solution of (**1**). The allyl reactants gave adducts (**2d**), (**2e**), (**2f**), and (**2g**) in high yields. Methylenecyclopentane reacted very rapidly to give adduct (**2h**) in 96% yield, whereas 2-propylpent-1-ene was rather less reactive; hence, formation of adduct (**2j**) in 61% yield required 10 h reflux. These data are summarized in Table 1.

It is noteworthy that all the reactions proceeded regiospecifically in an anti-Markownikoff manner. These reaction features are consistent with a free-radical chain process,[10c,d] which involves the formation of a sufficiently electrophilic thiyl radical bearing an electron-withdrawing benzoyl group, followed by attack of the thiyl radical on the electron-rich terminal carbon. We have previously shown [13] that the reaction of compound (**1**) and dec-1-ene was almost completely suppressed by the addition of hydroquinone, supporting the free-radical chain pathway as shown in Scheme 3 (see also Table 1). Reversibility of the second step in this process was suggested by the fact that treatment of adduct (**2a**) with tri-n-butyltin hydride in the presence of AIBN did not give thiobenzoate with the phenylseleno group reductively removed, but instead afforded dec-1-ene with the thiobenzoyloxyl radical eliminated from the carbon radical intermediate (A).

Table 1. Addition of *Se*-phenyl (selenothioperoxy)benzoate (**1**) to olefins[a]

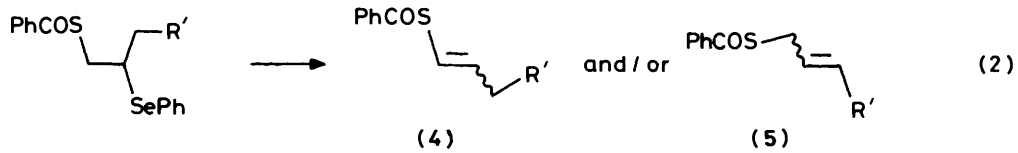
Olefin	Reaction time (h)	Product	Isolated yield[i] (%)
Dec-1-ene	3	(**2a**)	99
Dec-1-ene	30[b]	(**2a**)	30[j]
Dec-1-ene	30[c]	(**2a**)	2[k]
Dec-1-ene	30[d]	(**2a**)	3[l]
Dec-1-ene	20[e]	(**2a**)	67[m]
Styrene	1	(**2b**)	44[n]
Styrene	1.5[f]	(**2b**)	44[o]
Styrene	0.5[g]	(**2b**)	75[p]
Allyl alcohol	4	(**2c**)	81
Allyl acetate	4	(**2d**)	94
N-Allylacetamide	19	(**2e**)	85
Methyl but-3-enoate	7	(**2f**)	79
Allyl cyanide	3	(**2g**)	81
Methylenecyclopentane	1	(**2h**)	96
Methylenecyclopentane	1[h]	(**2i**)	81
2-Propylpent-1-ene	10	(**2j**)	61
2-Propylpent-1-ene	6[h]	(*2k*)	58
Cyclohexene	17	*trans*-(**2l**)	54
		cis-(**2l**)	10
Cyclopentene	12	*trans*-(**2m**)	76
		cis-(**2m**)	7
8,9,10-Trinorbornene	1	*trans*-(**2n**)	30
		exo-cis-(**2n**)	68

[a] For a typical procedure, see Experimental section. [b] Heated without AIBN. [c] Heated in the presence of AIBN and hydroquinone (10 mol%). [d] Heated in the presence of hydroquinone (10 mol%). [e] An equimolar amount of dec-1-ene was used. [f] A slight excess (1.2 mol equiv.) of styrene was used. [g] To a refluxing mixture of (**1**) and styrene (0.2 mol equiv.) in benzene were added six portions of styrene (0.2 mol equiv.), one every 5 min. [h] *Se*-Phenyl 3-nitro(selenothioperoxy)benzoate was used instead of (**1**). [i] The yield is based on the original amount of (selenothioperoxy)benzoate. [j–m] Selenosulphide (**1**) recovery was 46 (*j*), 90 (*k*), 87 (*l*), and 27% (*m*). [n–p] 1:2-Adduct (**3**) was obtained in 30 (*n*), 33 (*o*), and 1% (*p*) yield.



Scheme 3.

Since selenothioesterification of various terminal olefins was found to be regiospecific, the stereoselectivity was next examined in the addition of (**1**) to cycloalkenes. The reaction of (**1**) with cyclohexene gave *cis*-adduct *cis*-(**2l**) as well as *trans*-adduct *trans*-(**2l**) in 10 and 54% yield, respectively. Cyclopentene also gave both *trans*- and *cis*-adducts *trans*-(**2m**) and *cis*-(**2m**) in 76 and 7% yield. The formation of substantial amount of *cis*-adducts *cis*-(**2l**) and *cis*-(**2m**) shows that the reaction proceeded *via* the carbon radical intermediate (A) (Scheme 3) rather than *via* a bridged-type intermediate such as episulphonium,



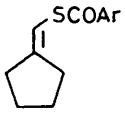
(2)

(4) CH_2R'

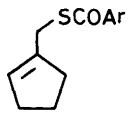
a; $[CH_2]_7Me$
b; Ph
c; CH_2OH
d; CH_2OAc
e; CH_2NHAc

(5)

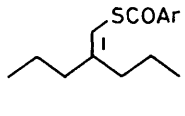
a; $R' = [CH_2]_6Me$
f; $R' = CO_2Me$
g; $R' = CN$



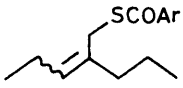
(4h) Ar = Ph
(4i) Ar = $3\text{-}O_2NC_6H_4$



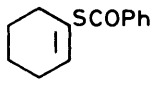
(5h) Ar = Ph
(5i) Ar = $3\text{-}O_2NC_6H_4$



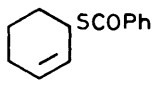
(4j) Ar = Ph
(4k) Ar = $3\text{-}O_2NC_6H_4$



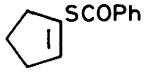
(5j) Ar = Ph
(5k) Ar = $3\text{-}O_2NC_6H_4$



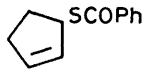
(4l)



(5l)



(4m)



(5m)

(4n)

episelenenium ion, or epithiyl radical intermediate. It contrasts with photoinitiated phenylselenosulphonation of cyclohexene which proceeds highly stereoselectively to give the *trans*-adduct as the sole product.[11b,*] This difference in stereoselectivity of both reactions may be ascribed to the phenylselenosulphide (**1**) being less reactive than the corresponding phenylselenosulphone towards the carbon radical intermediate (A). Thus, the carbon radical (A) must have enough time to equilibrate conformationally *via* a ring flip prior to the chain transfer forming the *cis*-adduct.[14] The addition of compound (**1**) to 8,9,10-trinorbornene was much more rapid than that to cyclohexene or cyclopentene, and gave adducts *exo-cis*-(**2n**) and *trans*-(**2n**) in 68 and 30% yield, respectively. Predominant formation of *exo-cis*-(**2n**) and no indication of the Wagner–Meerwein type of rearrangement, which is characteristic of ionic additions,[15] can be explained by an attack of thiobenzoyloxyl radical from the less crowded *exo*-side to form a carbon radical such as (A), followed by preferential approach of the selenosulphide (**1**) from the *exo*-side for chain transfer.

* On the other hand, thermal addition of a selenosulphonates, $PhSeSO_2Ar$, to acyclic alkenes is not stereoselective, and gives *erythro* and *threo* isomers from both (*E*)- and (*Z*)-alkenes; see ref. 11*a*.

Oxidation–Elimination of Phenylseleno Group of Adduct (**2**).—The addition products (**2**) of compound (**1**) to olefins were treated with *m*-chloroperbenzoic acid (MCPBA) in dichloromethane at between −20 and −50 °C. Fortunately, the phenylseleno group was selectively oxidized to the selenoxide under these conditions without oxidation of the thiocarboxy sulphur [equation (2) and Table 2]. Successful selective oxidation in our case is apparently due to the electron-withdrawing benzoyl group on the sulphur, since it is known that the selective oxidation of a selenide containing a dithioacetal group is rather difficult.[16] The selective oxidation allowed the elimination reaction of the phenylseleno group to be realized in adducts (**2**) with a thiobenzoyloxy group at the β-position. Pyridine was added to the reaction mixture, which was then warmed up to room temperature in most cases or heated under reflux in the case of the compounds from which elimination did not easily occur. The mixture gradually turned yellow as the reaction proceeded, possibly due to formation of benzeneselenenic acid and/or diphenyl diselenide during the reaction. The elimination from (**2a**) afforded a mixture of the vinyl thiobenzoate (**4a**) and the allyl thiobenzoate (**5a**) in the ratio 9:1 in 91% yield, both of which had the *E*-isomer as the major component (by ^1H n.m.r. spectroscopy). This result

Table 2. Oxidation–elimination of phenylseleno group from adducts (2)[a]

Adduct	Yield (%)	Product ratio[b] (4) (E)-(4)	(Z)-(4)	(5) (E)-(5)	(Z)-(5)
(2a)	98	72	18	8	2
(2b)	82	100			
(2c)	82	80	20		
(2d)	94	79	21		
(2e)	89	82	18		
(2f)	94			100	
(2g)	88			46	54
(2h)	84		25	75	
(2i)	61		33	67	
(2j)	92		87	13[c]	
(2k)	57		90	10[c]	
trans-(21)	73		90	10	
cis-(2l)	77			100	
trans-(2m)	97		80	20	
cis-(2m)	86			100	
trans-(2n)	83		100		
exo-cis-(2n)	*d*				

[a] For a typical procedure, see Experimental section. [b] Product ratio determined by n.m.r. integration. [c] Obtained as a mixture of *E* and *Z* isomers, the ratio of which was not determined. [d] The starting *exo-cis*-(2n) was recovered.

shows the preference of the elimination of PhSeOH towards the carbon bearing the thiobenzoyloxy group and it is in sharp contrast with those in the elimination of PhSeOH in compounds bearing an oxygen atom of the β-carbon, which show a great preference for elimination in the direction away from the oxygen-containing group such as OH, OAc, OMe, *etc.*[17]

Adduct (**2b**) gave only (*E*)-styryl thiobenzoate (*E*)-(**4b**). Adduct (**2c**), (**2d**), or (**2e**) carrying respectively an OH, OAc, or NHAc group at the β-position to the phenylseleno group afforded the vinyl thiobenzoate (**4c**), (**4d**), or (**4e**) free from the product derived by elimination of PhSeOH towards the carbon attached to the OH, OAc, or NHAc group. These vinyl thiobenzoates each consisted of similar ratios (*ca.* 8:2) of the *E* and *Z* isomers. Adduct (**2f**) or (**2g**) carrying a methyl carboxylate or a cyano group eliminated PhSeOH selectively towards the carbon away from the thiocarboxy group. Exclusive formation of the *E* isomer from adduct (**2f**) and formation of a considerable amount of the *Z* isomer from adduct (**2g**) were observed. A significant amount of the *Z* isomers was obtained in the PhSeOH-elimination reaction of most adducts, while adducts (**2b**) and (**2f**) gave only the *E* isomers. We also examined the oxidation of (**2a**) with 30% H_2O_2 at room temperature in tetrahydrofuran and subsequently stirred to effect elimination, giving similar ratios of the stereoisomers to those obtained in the above reaction. The formation of *Z* isomers of not only vinyl (**4**) but also allyl thiobenzoates (**5**) seems to be consistent with the elimination of selenides bearing alkyl group at both β-positions.[18] It is, however, in contrast to the exclusive or highly predominant formation[19] of *E* isomers from phenyl selenides carrying a functional groups such as CN, SO_2, SCN, NO_2, OH, OAc, or NHAc at the β-position.

The PhSeOH-elimination reaction with adducts (**2a**), (**2c**), (**2d**), and (**2e**) clearly showed a preference for elimination towards the carbon attached to the thiobenzoyloxy group (Table 2). This preference was also observed in cyclic systems. Cyclohexane derivative *trans*-(**2l**) gave the vinyl (**4l**) and the allyl thiobenzoate (**5l**) in the ratio 9:1, and cyclopentane derivative *trans*-(**2m**) similarly gave compounds (**4m**) and (**5m**) in the ratio 8:2. The well known *syn*-elimination[18] of PhSeOH was probably the cause of the exclusive formation of the allyl thiobenzoates (**5l**) and (**5m**) from *cis*-(**2l**) and from *cis*-(**2m**), respectively. Similar treatment of bicyclo[2.2.1]heptane derivative *trans*-(**2n**) gave the vinyl thiobenzoate (**4n**) without formation of a bridgehead olefin, while heating of the selenoxide of *cis*-(**2n**) gave the starting selenide *cis*-(**2n**) with loss of the selenoxide oxygen.

The PhSeOH-elimination reaction from (**2h**) led to the predominant formation of endocyclic olefin (**5h**) over exocyclic olefin (**4h**) in the ratio 3:1. On the expectation of an increase in the formation of the exocyclic olefin, the elimination of PhSeOH from the addition product (**2i**), which could be prepared from methylenecyclopentane and *Se*-phenyl 3-nitro(selenothioperoxy)benzoate, was examined and was found to give a slight increase in formation of the vinyl benzoate (**4i**) compared with the case for (**2h**) ⟶ (**4h**). In (**2j**) there was a strong preference for elimination giving the vinyl thiobenzoate (**4j**). Heating of nitrobenzoyl derivative (**2k**) did not lead to a sharp increase in formation of (**4k**) but showed similar preference for elimination to (**4k**) as did (**2j**) ⟶ (**4j**).

The effective use of *Se*-phenyl (selenothioperoxy)benzoate (**1**) described in the present work constitutes a new selenofunctionalization procedure which offers a new method for the simultaneous introduction of phenylseleno and thiobenzoyloxy groups to an olefin in an anti-Markownikoff manner, followed by elimination of PhSeOH to give the vinyl and allyl thiobenzoate derivatives. Thus, depending on the substituent at the β-position to the phenylseleno group, one can obtain (substituted) vinyl or allyl thiobenzoates exclusively or predominantly, and there could be precursors of vinyl hydrosulphides, *i.e.* thioaldehydes, or allyl hydrosulphides.

Experimental

I.r. spectra were recorded on a JASCO A-102 spectrometer. N.m.r. spectra were obtained on either JEOL JNM-PMX60Si (60 MHz) or Varian XL-200 (200 MHz) spectrometers. N.m.r. spectra are reported in p.p.m. downfield from Me_4Si as internal standard. Mass spectra were recorded on a ESCO EMD-05B spectrometer. Elemental analyses were performed by the Laboratory for Organic Elemental Microanalysis, Faculty of Pharmaceutical Sciences, Kyoto University, and also by the laboratory at the Department of Applied Chemistry, Faculty of Engineering, Nagoya University. M.p.s were recorded on a Yanagimoto hot-plate apparatus and are uncorrected. All reactions were performed under argon. Flash chromatography was carried out using a Michael Miler column packed with Fuji Davison solica gel BW-200, equipped with FMI LAB Pump RPG150 and a FMI Pulse Damper PD-60LF, normally at a pressure of 1—2 kg cm^{-2}. Dichloromethane was distilled from calcium chloride. Benzene was distilled under argon from calcium hydride and stored over 4 Å molecular sieves. All other materials were commercially available.

Addition of Se-*Phenyl* (*Selenothioperoxy*)*benzoate* (**1**) *to Alkenes* (*see Table 1*). *Typical Procedure.*—S-2-(*Phenylseleno*)*decyl thiobenzoate* (**2a**). A mixture of *Se*-phenyl (selenothioperoxy)benzoate[12] (**1**) (50 mg, 0.17 mmol), dec-1-ene (71 mg, 0.51 mmol), and AIBN (3 mg, 0.02 mmol) was refluxed for 4 h in benzene (0.2 ml). The solvent was then evaporated off under reduced pressure, and the residue was purified by flash chromatography (2:98, benzene–hexane) to afford unchanged dec-1-ene (39 mg), and compound (**2a**) (73 mg, 99%) as an *oil*, $\nu_{max.}$(film) 1 660, 1 205, 910, and 690 cm^{-1}; $\delta_H(CCl_4)$ 0.60—1.05 (3 H, m), 1.05—2.04 (14 H, m), 3.02—3.65 (3 H, m), and 6.98—

8.06 (10 H, m); $\delta_C(CDCl_3)$ 14.1, 22.7, 27.7, 29.2, 29.3, 29.4, 31.9, 34.0, 35.3, 44.7, 127.3, 120.8, 128.3, 128.6, 129.1, 133.3, 135.3, 137.0, and 191.3; *m/z* 434 (M^+, ^{80}Se, 2%), 297 (5), 277 (21), 189 (4), 157 (8), and 105 (100) (Found: C, 63.9; H, 6.8. $C_{23}H_{30}OSSe$ requires C, 63.72; H, 6.98%).

S-β-(*Phenylseleno*)*phenethyl thiobenzoate* (**2b**). To a refluxing mixture of compound (**1**) (50 mg, 0.17 mmol), styrene (3.5 mg, 0.03 mmol), and AIBN (3 mg, 0.02 mmol) in benzene (0.1 ml) were added six portions of a solution of styrene (3.5 mg, 0.03 mmol) in benzene (0.04 ml) (one every 5 min). After the addition the mixture was refluxed for a further 5 min and was then cooled to room temperature. The solvent was evaporated off under reduced pressure and the residue was purified by flash chromatography (1:99, diethyl ether–hexane) to afford 1:1-adduct (**2b**) (51 mg, 75%) and a small amount of 1:2-adduct (**3**) (1 mg, 1%) in addition to recovered seleno compound (**1**) (10 mg). *Compound* (**2b**) showed m.p. 98.5—99.0 °C (from hexane); $\nu_{max.}$(KBr) 1 660, 1 200, 910, and 680 cm^{-1}; $\delta_H(CCl_4)$ 3.58 (1 H, dd, *J* 13 and 10 Hz), 3.89 (1 H, dd, *J* 13 and 15 Hz), 4.52 (1 H, d, *J* 6 and 10 Hz), and 6.92—8.03 (15 H); *m/z* 398 (M^+, ^{80}Se, 1%), 314 (1), 240 (27), 157 (9), 137 (8), and 105 (100) (Found: C, 63.6; H, 4.4. $C_{20}H_{18}OSSe$ requires C, 63.47; H, 4.57%).

Compound (**3**) showed $\nu_{max.}$(film) 1 660, 1 205, 910, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.86—2.92 (3 H, m), 3.04—3.36 (2 H, m), 3.57—4.21 (1 H, m), and 6.63—7.99 (20 H, m); *m/z* 502 (M^+, ^{80}Se, 1.5%), 345 (49), 240 (5), 208 (6), and 105 (100) (Found: C, 69.4; H, 5.4. $C_{29}H_{26}OSSe$ requires C, 69.45; H, 5.23%).

The following compounds were prepared in the same manner as (**2a**) under the conditions and in the yields shown in Table 1.

S-3-*Hydroxy*-2-(*phenylseleno*)*propyl thiobenzoate* (**2c**). Purification by flash chromatography (5:95, ethyl acetate–hexane) afforded *compound* (**2c**); $\nu_{max.}$(film) 3 420, 1 660, 1 205, 910, and 685 cm^{-1}; $\delta_H(CCl_4)$ 2.63 (1 H, br s, exchangeable with D_2O), 3.08—3.80 (5 H, m), and 6.93—8.07 (10 H, m); *m/z* 352 (M^+, ^{80}Se, 1%), 247 (1), 215 (2), 195 (2), 157 (4), and 105 (100) (Found: C, 54.6; H, 4.8. $C_{16}H_{16}O_2SSe$ requires C, 54.70; H, 4.59%).

3-*Benzoylthio*-2-(*phenylseleno*)*propyl acetate* (**2d**). Purification by flash chromatography (10:90, ethyl acetate–hexane) afforded *compound* (**2d**), m.p. 44—45 °C (from hexane–dichloromethane); $\nu_{max.}$(film) 1 737, 1 660, 1 230, 1 205, 910, and 685 cm^{-1}; $\delta_H(CDCl_3)$ 2.03 (3 H, s), 3.09—3.84 (3 H, m), 4.04—4.64 (2 H, m), and 6.89—8.08 (10 H, m); *m/z* 394 (M^+, ^{80}Se, 1%), 289 (1), 257 (5), 237 (4), 178 (6), 157 (8), and 105 (100) (Found: C, 55.1; H, 4.65. $C_{18}H_{18}O_3SSe$ requires C, 54.96; H, 4.61%).

S-3-*Acetamido*-2-(*phenylseleno*)*propyl thiobenzoate* (**2e**). Purification by flash chromatography afforded *compound* (**2e**); $\nu_{max.}$(film) 1 650, 1 205, 910, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.90 (3 H, s), 3.10—3.73 (5 H, m), 6.73 (1 H, br s), and 7.10—8.10 (10 H, m); *m/z* 393 (M^+, ^{80}Se, 1%), 256 (4), 236 (4), 157 (4), 137 (6), and 105 (100) (Found: C, 55.2; H, 5.1; N, 3.3. $C_{18}H_{19}NO_2$ requires C, 55.10; H, 4.88; N, 3.57%).

Methyl 4-*benzoylthio*-3-*phenylselenobutyrate* (**2f**). Purification by flash chromatography (5:95, benzene–hexane) afforded *compound* (**2f**); $\nu_{max.}$(film) 1 735, 1 670, 1 200, 910, 780, and 685 cm^{-1}; $\delta_H(CCl_4)$ 2.46—2.83 (2 H, m), 3.06—3.76 (3 H, m), 3.56 (3 H, s), and 7.00—8.03 (10 H, m); *m/z* 394 (M^+, ^{80}Se, 3%), 257 (11), 237 (10), 157 (7), and 105 (100) (Found: C, 55.1; H, 4.5. $C_{18}H_{18}O_3SSe$ requires C, 54.96; H, 4.61%).

S-3-*Cyano*-2-(*phenylseleno*)*propyl thiobenzoate* (**2g**). Purification by flash chromatography (5:95, ethyl acetate–hexane) afforded *compound* (**2g**); $\nu_{max.}$(film) 2 240, 1 660, 1 205, 1 170, 905, and 685 cm^{-1}; $\delta_H(CCl_4)$ 2.50—2.93 (2 H, m), 3.06—3.75 (3 H, m), and 7.03—8.06 (10 H, m); *m/z* 361 (M^+, ^{80}Se, 3%), 224 (9), 204 (5), 157 (8), and 105 (100) (Found: C, 56.4; H, 4.2: N, 3.7. $C_{17}H_{15}NOSSe$ requires C, 56.67; H, 4.20; N, 3.89%).

S-[1-(*Phenylseleno*)*cyclopentyl*]*methyl thiobenzoate* (**2h**). Purification by flash chromatography (5:95, benzene–hexane) afforded *compound* (**2h**); $\nu_{max.}$(film) 1 660, 1 200, 907, 780, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.17—2.20 (8 H, m), 3.47 (2 H, s), and 7.10—8.12 (10 H, m); *m/z* 376 (M^+, ^{80}Se, 1%), 239 (1), 219 (39), 157 (10), and 105 (100) (Found: C, 60.7; H, 5.4. $C_{19}H_{20}OSSe$ requires C, 60.79; H, 5.27%).

S-[1-(*Phenylseleno*)*cyclopentyl*]*methyl* 3-*nitro*(*thiobenzoate*) (**2i**). Purification by flash chromatography (5:95, benzene–hexane) afforded *compound* (**2i**); $\nu_{max.}$(film) 1 660, 1 530, 1 345, 1 200, 740, and 680 cm^{-1}; $\delta_H(CCl_4)$ 1.51—2.07 (8 H, m), 3.52 (2 H, s), and 6.97—8.79 (9 H, m); *m/z* 421 (M^+, ^{80}Se, 0.2%), 264 (7), 157 (53), and 105 (100) (Found: C, 54.5; H, 4.6. $C_{19}H_{19}NO_3SSe$ requires C, 54.29; H, 4.56%).

S-2-*Phenylseleno*-2-*propylpentyl thiobenzoate* (**2j**). Purification by flash chromatography (2:98, benzene–hexane) afforded *compound* (**2j**); $\nu_{max.}$(film) 1 660, 1 200, 907, 780, and 685 cm^{-1}; $\delta_H(CCl_4)$ 0.65—1.17 (6 H, m), 1.17—1.82 (8 H, m), 3.32 (2 H, s), and 7.07—8.13 (10 H, m); *m/z* 406 (M^+, ^{80}Se, 0.1%), 267 (0.2), 249 (18), 157 (3), and 105 (100) (Found: C, 62.2; H, 6.4. $C_{21}H_{26}OSSe$ requires C, 62.21; H, 6.46%).

S-2-*Phenylseleno*-2-*propylpentyl* 3-*nitro*(*thiobenzoate*) (**2k**). Purification by flash chromatography (5.95, benzene–hexane) afforded *compound* (**2k**); $\nu_{max.}$(film) 1 660, 1 535, 1 350, 1 205, 790, 760, and 740 cm^{-1}; $\delta_H(CCl_4)$ 0.71—1.16 (6 H, m), 1.16—1.78 (8 H, m), 3.41 (2 H, s), and 7.08—8.82 (9 H, m); *m/z* 294 (M^+ – PhSe, 34%), 269 (2), 157 (14), 150 (100), 144 (7), and 112 (97) (Found: C, 56.0; H, 5.65. $C_{21}H_{25}NO_3SSe$ requires C, 55.99; H, 5.59%).

S-2-(*Phenylseleno*)*cyclohexyl thiobenzoate* (**2l**). Two products were isolated by flash chromatography (1:99, diethyl ether–hexane). *Compound* trans-(**2l**) showed $\nu_{max.}$(film) 1 650, 1 200, 910, 730, and 680 cm^{-1}; $\delta_H(CDCl_3)$ 1.08—1.90 (6 H, m), 2.05—2.26 (1 H, m), 2.26—2.47 (1 H, m), 3.49 (1 H, ddd, *J* 8.0, 8.0, and 3.8 Hz), 4.02 (1 H, ddd, *J* 8.0, 8.0, and 3.8 Hz), and 7.00—8.13 (10 H, m); *m/z* 376 (M^+, ^{80}Se, 2%), 239 (6), 219 (16), 157 (8), and 105 (100) (Found: C, 60.8; H, 5.3. $C_{19}H_{20}OSSe$ requires C, 60.74; H, 5.37%). *Compound* cis-(**2l**) showed $\nu_{max.}$(film) 1 650, 1 200, 910, 730, and 680 cm^{-1}; $\delta_H(CCl_4)$ 1.18—1.90 (6 H, m), 2.05—2.25 (1 H, m), 2.25—2.44 (1 H, m), 3.48 (1 H, m), 4.02 (1 H, m), and 7.14—8.12 (10 H, m); *m/z* 376 (M^+, ^{80}Se, 4%), 239 (3), 219 (5), 157 (4), and 105 (100) (Found: C, 60.65; H, 5.4%).

S-2-(*Phenylseleno*)*cyclopentyl thiobenzoate* (**2m**). Two isomers were isolated by flash chromatography (1:99, diethyl ether–hexane). *Compound* trans-(**2m**) showed $\nu_{max.}$(film) 1 660, 1 205, 910, 785, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.35—2.75 (6 H, m), 3.58 (1 H, m), 3.93 (1 H, m), and 6.98—8.07 (10 H, m); *m/z* 362 (M^+, ^{80}Se, 1%), 225 (3), 205 (4), 157 (7), and 105 (100) (Found: C, 59.9; H, 4.9. $C_{18}H_{18}OSSe$ requires C, 59.83; H, 5.02%). *Compound* cis-(**2m**) showed $\nu_{max.}$(film) 1 660, 1 205, 910, 785, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.35—2.75 (6 H, m), 3.30—4.40 (2 H, m), and 6.95—8.08 (10 H, m); *m/z* 362 (M^+, ^{80}Se, 3%), 225 (4), 205 (3), 157 (100), 137 (13), and 105 (57) (Found: C, 59.7; H, 4.85%).

S-3-(*Phenylseleno*)*bicyclo*[2.2.1]*heptan*-2-*yl thiobenzoate* (**2n**). *Trans* and *cis* isomers were isolated by flash chromatography (1:99, diethyl ether–hexane). *Compound* trans-(**2n**) showed $\nu_{max.}$(film) 1 660, 1 210, 910, 900, 730, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.15—2.20 (6 H, m), 2.20—2.50 (2 H, m), 3.40 (2 H, m), and 7.00—8.05 (10 H, m); *m/z* 388 (M^+, ^{80}Se, 2%), 249 (13), 231 (3), 157 (3), and 105 (100) (Found: C, 62.0; H, 5.3. $C_{20}H_{20}OSSe$ requires C, 62.01; H, 5.20%). *Compound* exo-cis-(**2n**) showed $\nu_{max.}$(film) 1 660, 1 210, 910, 900, 730, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.05—2.10 (6 H, m), 2.20—2.35 (2 H, m), 3.67 (1 H, dd, *J* 8.0 and 1.8 Hz), 4.01 (1 H, dd, *J* 8.0 and 1.8 Hz), and 7.00—8.10 (10 H, m); *m/z* 388 (M^+, ^{80}Se, 6%), 249 (2), 231 (7), and 105 (100) (Found: C, 61.8; H, 5.3%).

Oxidation–Elimination of Phenylseleno Group. Typical Procedure.—S-*Dec*-1-*enyl thiobenzoate* (**4a**) *and* S-*Dec*-2-*enyl thiobenzoate* (**5a**). To a solution of *S*-2-(phenylseleno)decyl

thiobenzoate (**2a**) (85.5 mg, 0.2 mmol) in dichloromethane (0.5 ml) at −30 °C was added dropwise during 2 min a solution of MCPBA (47.5 mg, 0.22 mmol) in dichloromethane (1.5 ml). Immediately after the addition of MCPBA, t.l.c. analysis (silica gel, Merck 0.25 mm thick plates) showed disappearance of compound (**2a**) and a new spot with higher polarity. After pyridine (63 mg, 0.8 mmol) had been added to the mixture at −30 °C, the cooling bath was removed and the mixture was stirred for a further 30 min, washed successively with aqueous $NaHCO_3$ and saturated aqueous NaCl, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash chromatography (1:99, and then 3:97, benzene–hexane) to afford a 90:10 (n.m.r.) mixture of compounds (**4a**) and (**5a**) (53 mg, 98%); $\nu_{max.}$(film) 1 667, 1 205, 910, and 690 cm^{-1}; $\delta_H(CDCl_3)$ 0.89 (3 H, t, *J* 7.0 Hz), 1.16—1.70 (12 H, m), 2.12—2.40 [1.8 H, m, =CHCH_2 of (*E*)-(**4a**) and (*Z*)-(**4a**)], 3.71 [0.16 H, d, *J* 7.0 Hz, CH_2S of (*E*)-(**5a**)], 3.77 [0.04 H, d, *J* 7.0 Hz, CH_2S of (*Z*)-(**4a**)], 5.52 [0.08 H, dtt, *J* 15.0, 7.0, and 1.5 Hz, SCH_2CH= of (*E*)-(**5a**)], 5.77 [0.08 H, dtt, *J* 15.0, 7.0, and 1.5 Hz, SCH_2CH=C*H* of (*E*)-(**5a**)], 5.98 [0.18 H, dt, *J* 10.0 and 7.0 Hz, SCH=C*H* of (*Z*)-(**4a**)], 6.04 [0.72 H, dt, *J* 16.0 and 7.0 Hz, SCH=C*H* of (*E*)-(**4a**)], 6.64 [0.72 H, dt, *J* 16.0 and 1.5 Hz, SCH= of (*E*)-(**4a**)], 6.77 [0.18 H, dt, *J* 10.0 and 1.5 Hz, SCH= of (*Z*)-(**4a**)], 7.42—7.74 (3 H, m), and 7.93—8.20 (2 H, m); *m/z* 276 (M^+) (Found: C, 73.6; H, 8.7. $C_{17}H_{24}OS$ requires C, 73.86; H, 8.75%).

The following alkenes were similarly prepared from the corresponding selenide (**2**).

S-(E)-*Styryl thiobenzoate* (**4b**) had $\nu_{max.}$(KBr) 1 665, 1 205, 905, and 683 cm^{-1}; $\delta_H(CCl_4)$ 6.74 (1 H, d, *J* 16 Hz) and 6.94—8.06 (11 H, m); *m/z* 240 (M^+, 4%), 135 (4), and 105 (100) (Found: C, 74.9; H, 5.1. $C_{15}H_{12}OS$ requires C, 74.97; H, 5.08%).

S-3-*Hydroxyprop*-1-*enyl thiobenzoate* (**4c**) had $\nu_{max.}$(film) 1 665, 1 210, 910, and 690 cm^{-1}; $\delta_H(CCl_4)$ 2.25 (1 H, br s), 4.31 [1.56 H, dd, *J* 5.5 and 1.7 Hz, CH_2 of (*E*)-(**4c**)], 4.34 [0.44 H, m, CH_2 of (*E*)-(**4c**)], 6.16 [0.22 H, dt, *J* 10.0 and 6.2 Hz, SCH=C*H* of (*Z*)-(**4c**)], 6.22 [0.78 H, dt, *J* 16.0 and 5.5 Hz, SCH=C*H* of (*E*)-(**4c**)], 6.97 [0.22 H, dt, *J* 10.0 and 1.5 Hz, SC*H*=CH of (*Z*)-(**4c**)], 7.00 [0.78 H, dt, *J* 16.0 and 1.7 Hz, SC*H*=CH of (*E*)-(**4c**)], and 7.42—8.10 (5 H, m); *m/z* 194 (M^+, 1.5%) and 105 (100) (Found: C, 61.8; H, 5.25. $C_{10}H_{10}O_2S$ requires C, 61.83; H, 5.19%).

(E)-3-*Thiobenzoylallyl acetate* (E)-(**4d**) had $\nu_{max.}$(film) 1 735, 1 665, 1 230, 1 205, 900, and 685 cm^{-1}; $\delta_H(CCl_4)$ 2.02 (3 H, s), 4.62 (2 H, dd, *J* 6.0 and 1.2 Hz), 5.99 (1 H, dt, *J* 15.6 and 6.0 Hz), 7.01 (1 H, dt, *J* 15.6 and 1.2 Hz), and 7.25—8.06 (5 H, m); *m/z* 236 (M^+, 7%), 177 (2), and 105 (100) (Found: C, 61.0; H, 5.2. $C_{12}H_{12}O_3S$ requires C, 61.00; H, 5.12%).

(Z)-3-*Thiobenzoylallyl acetate* (Z)-(**4d**) had $\nu_{max.}$(film) 1 735, 1 665, 1 230, 1 205, 900, and 685 cm^{-1}; $\delta_H(CCl_4)$ 2.00 (3 H, s), 4.59 (2 H, dd, *J* 6.0 and 1.2 Hz), 5.95 (1 H, dt, *J* 10.0 and 6.0 Hz), 6.98 (1 H, dt, *J* 10.0 and 1.2 Hz), and 7.18—8.16 (5 H, m); *m/z* 236 (M^+, 3%), 177 (2), and 105 (100) (Found: C, 60.9; H, 5.1%).

S-3-*Acetamidoprop*-2-*enyl thiobenzoate* (**4e**). The *products* were obtained as an 82:18 (n.m.r.) mixture of compounds (*E*)-(**4e**) and (*Z*)-(**4e**); $\nu_{max.}$(KBr) 1 660, 1 620, 1 210, 900, and 680 cm^{-1}; $\delta_H(CDCl_3)$ 2.03 [0.54 H, s, Me of (*Z*)-(**4e**)], 2.05 [2.46 H, s, Me of (*E*)-(**4e**)], 4.06 (2 H, m, CH_2N), 5.93 (1 H, br s, NH), 6.00 [0.18 H, dt, *J* 9.6 and 5.8 Hz, SCH=C*H* of (*Z*)-(**4e**)], 6.06 [0.82 H, dt, *J* 15.8 and 6.0 Hz, SCH=C*H* of (*E*)-(**4e**)], 6.90 [0.82 H, dt, *J* 15.8 and 1.6 Hz, SC*H*=CH of (*E*)-(**4e**)], 6.96 [0.18 H, dt, *J* 9.6 and 1.5 Hz, SC*H*=CH of (*Z*)-(**4e**)], and 7.45—8.06 (5 H, m); *m/z* 235 (M^+, 2%), 130 (6), and 105 (100) (Found: C, 61.4; H, 5.6; N, 5.8. $C_{12}H_{13}NO_2S$ requires C, 61.25; H, 5.57; N, 5.95%).

Methyl (E)-4-*thiobenzoylbut*-2-*enoate* (**5f**) had $\nu_{max.}$(film) 1 720, 1 660, 1 320, 1 270, 1 205, 910, and 690 cm^{-1}; $\delta_H(CCl_4)$ 3.63 (3 H, s), 3.75 (2 H, dd, *J* 6.5 and 1.2 Hz), 5.97 (1 H, dt, *J* 15.0 and 1.2 Hz), 6.82 (1 H, dt, *J* 15.0 and 6.5 Hz), and 7.28—8.08 (5 H, m); *m/z* 236 (M^+, 4%), 203 (2), and 105 (100) (Found: C, 60.8; H, 5.0. $C_{12}H_{12}O_3S$ requires C, 61.00; H, 5.12%).

S-3-*Cyanoprop*-2-*enyl thiobenzoate* (**5g**). The *products* were obtained as a 46:54 (n.m.r.) mixture of compounds (*E*)-(**5g**) and (*Z*)-(**5g**); $\nu_{max.}$(film) 2 220, 1 665, 1 210, 910, and 685 cm^{-1}; $\delta_H(CCl_4)$ 3.79 [0.92 H, d, *J* 7.0 Hz, SCH_2 of (*E*)-(**5g**)], 3.99 [1.08 H, d, *J* 7.5 Hz, SCH_2 of (*Z*)-(**5g**)], 5.43 [0.54 H, d, *J* 10.5 Hz, =CHCN of (*Z*)-(**5g**)], 5.63 [0.46 H, d, *J* 16.0 Hz, =CHCN of (*E*)-(**5g**)], 6.34 [0.54 H, dt, 10.5 and 7.5 Hz, C*H*=CHCN of (*Z*)-(**5g**)], 6.70 [0.46 H, dt, *J* 16.0 and 7.0 Hz, C*H*=CHCN of (*E*)-(**5g**)], and 7.30—8.18 (5 H, m); *m/z* 203 (M^+, 7%) and 105 (100) (Found: C, 65.3; H, 4.6; N, 6.75. $C_{11}H_9NOS$ requires C, 65.00; H, 4.46; N, 6.89%).

S-*Cyclopentylidenemethyl thiobenzoate* (**4h**) *and* S-(*Cyclopent*-1-*enyl*)*methyl thiobenzoate* (**5h**). The *products* were obtained as a 27:75 (n.m.r.) mixture of isomers (**4h**) and (**5h**); $\nu_{max.}$(film) 1 660, 1 220, 1 170, 917, 770, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.55—2.65 [6.5 H, m, $4CH_2$ of (**4h**)], 3.75 [1.5 H, s, CH_2S of (**5h**)], 5.58 [0.75 H, m, CH= of (**5h**)], 6.44 [0.25 H, m, SCH= of (**4h**)], and 7.16—8.07 (5 H, m); *m/z* 218 (M^+) (Found: C, 71.8; H, 6.5. $C_{13}H_{14}OS$ requires C, 71.52; H, 6.46%).

S-*Cyclopentylidenemethyl* 3-*nitro*(*thiobenzoate*) (**4i**) *and* S-(*Cyclopent*-1-*enyl*)*methyl*3-*nitro*(*thiobenzoate*) (**5i**). The *products* were obtained as a 30:70 (n.m.r.) mixture of compounds (**4i**) and (**5i**); $\nu_{max.}$(film) 1 665, 1 535, 1 205, 1 080, 980, 945, 865, 745, 720, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.60—2.68 (8 H, m), 3.83 [1.4 H, m, CH_2S of (**5i**)], 5.65 [0.7 H, m, CH= of (**5i**)], 6.41 [0.3 H, m, CH of (**4i**)], and 7.43—8.82 (4 H, m); *m/z* 263 (M^+) (Found: C, 59.15; H, 5.1. $C_{13}H_{13}NO_3S$ requires C, 59.30; H, 4.98%).

S-2-*Propylpent*-1-*enyl thiobenzoate* (**4j**) *and* S-2-*Propylpent*-2-*enyl thiobenzoate* (**5j**). The *products* were obtained as an 87:13 (n.m.r.) mixture of compounds (**4j**) and (**5j**); $\nu_{max.}$(film) 1 655, 1 205, 1 175, 910, 770, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.76—2.50 [13.7 H, m, Me and CH_2 of (**4j**) and (**5j**)], 3.50—3.74 [0.26 H, m, CH_2S of (**5j**)], 5.40 [0.13 H, m, CH= of (**5j**)], 6.36 [0.87 H, m, CH= of (**4j**)], and 7.14—8.09 (5 H, m); *m/z* 248 (M^+) (Found: C, 72.4; H, 8.25. $C_{15}H_{20}OS$ requires C, 72.54; H, 8.12%).

S-2-*Propylpent*-1-*enyl* 3-*nitro*(*thiobenzoate*) (**4k**) *and* S-2-*Propylpent*-2-*enyl* 3-*nitro*(*thiobenzoate*) (**5k**). The *products* were obtained as a 90:10 (n.m.r.) mixture of compounds (**4k**) and (**5k**); $\nu_{max.}$(film) 1 665, 1 535, 1 350, 1 205, 980, 945, 865, 745, 720, and 685 cm^{-1}; $\delta_H(CCl_4)$ 0.73—1.17 (6 H, m), 1.17—2.47 (7.8 H, m, CH_2), 3.77 [0.2 H, m, CH_2S of (**5k**)], 5.40 [0.1 H, m, CH= of (**5k**)], 6.36 [0.9 H, m, CHS of (**4k**)], and 7.10—8.80 (4 H, m); *m/z* 293 (M^+) (Found: C, 61.35; H, 6.65. $C_{15}H_{19}NO_3S$ requires C, 61.41; H, 6.53%).

S-*Cyclohex*-1-*enyl thiobenzoate* (**4l**) *and* S-*Cyclohex*-2-*enyl thiobenzoate* (**5l**). A mixture of compounds (**4l**) and (**5l**) showed $\nu_{max.}$(film) 1 655, 1 205, 905, 785, 770, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.42—2.50 [7.8 H, m, CH_2 of (**4l**) and (**5l**)], 4.27 [0.1 H, m, C*H*SCOPh of (**5l**)], 5.65 [0.2 H, m, CH=CH of (**5l**)], 6.03 ([0.9 H, m, CH= of (**4l**)], and 7.18—8.17 (5 H, m); *m/z* 218 (M^+). The PhSeOH–elimination reaction of compound *cis*-(**2l**) gave only *compound* (**5l**); $\nu_{max.}$(film) 1 660, 1 200, 905, 785, 770, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.52—2.27 (6 H, m), 4.27 (1 H, m), 5.65 (2 H, m), and 7.18—8.17 (5 H, m); *m/z* 218 (M^+, 90%), 137 (76), 113 (33), and 105 (100) (Found: C, 71.4; H, 6.55. $C_{13}H_{14}OS$ requires C, 71.52; H, 6.46%).

S-*Cyclopent*-1-*enyl thiobenzoate* (**4m**) *and* S-*Cyclopent*-2-*enyl thiobenzoate* (**5m**). The PhSeOH–elimination reaction of compound *trans*-(**2m**) gave a mixture of *products* (**4m**) and (**5m**); $\nu_{max.}$(film) 1 665, 1 445, 1 205, 1 175, 905, 775, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.60—2.90 [5.6 H, m, CH_2 of (**4m**) and (**5m**)], 4.65 [0.2 H, m, C*H*SCOPh of (**5m**)], 5.80 [0.4 H, m, CH=CH of (**5m**)], 6.07 [0.8 H, m, CH= of (**4m**)], and 7.10—8.07 (5 H, m); *m/z* 204 (M^+). The PhSeOH-elimination reaction of *cis*-(**2m**) gave *compound* (**5m**); $\nu_{max.}$(film) 1 660, 1 445, 1 205, 1 175, 915, 905, and 690 cm^{-1}; $\delta_H(CCl_4)$ 1.60—2.7 (4 H, m), 4.65 (1 H, m),

5.80 (2 H, m), and 7.10—8.07 (5 H, m); *m/z* 204 (M^+, 34%), 137 (44), 105 (100), and 99 (21) (Found: C, 70.7; H, 6.0. $C_{12}H_{12}OS$ requires C, 70.55; H, 5.92%).

S-*Bicyclo*[2.2.1]*hept-2-en-2-yl thiobenzoate* (**4n**) had $\nu_{max.}$(film) 1 655, 1 445, 1 305, 1 205, 900, and 685 cm^{-1}; $\delta_H(CCl_4)$ 1.03—1.91 (6 H, m), 3.03 (2 H, m), 6.25 (1 H, d, 3.2 Hz), and 7.12—8.02 (5 H, m); *m/z* 230 (M^+, 15%), 125 (66), and 105 (100) (Found: C, 73.1; H, 6.1. $C_{14}H_{14}OS$ requires C, 73.01; H, 6.13%).

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