

Photo-Induced Selenothio Esterification of Olefins: Radical Addition to Vinylsilanes

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Irradiation of terminal olefins or cycloalkenes with *Se*-phenyl (selenothioperoxy)benzoate (**1**) gave regioselective addition products in high yield. Vinyllic silanes also gave the adducts regioselectively. The stabilization effect of the α -silyl group on the alkyl radical is discussed for photolyses in carbon tetrachloride solution. The adducts obtained from vinylsilanes were efficiently converted into vinylic selenides by action of fluoride ion. The preparation of *S*-allyl thiobenzoate from allylsilane is also described.

As part of an ongoing programme aimed at the development of efficient methods for the introduction of seleno functionality,¹ we have been investigating selenenylation with concomitant thio esterification of olefins *via* a free-radical pathway,[†] which we call selenothio esterification. We have recently reported an efficient method for the selenothio esterification of various olefins *via* a free-radical process by heating an olefin and *Se*-phenyl (selenothioperoxy)benzoate (**1**) in the presence of azoisobutyronitrile (AIBN).³ This reaction offers a useful and efficient method for introducing a phenylseleno and thiobenzyloxy group regioselectively into a molecule. Furthermore, oxidation-elimination of the phenylseleno group from the addition products obtained comprises a new preparative method for vinylic and/or allylic thiobenzoates. We now report a more efficient, photo-induced selenothio esterification of olefins and its application to the synthesis of alkenyl phenyl selenides from vinylsilanes.

Results and Discussion

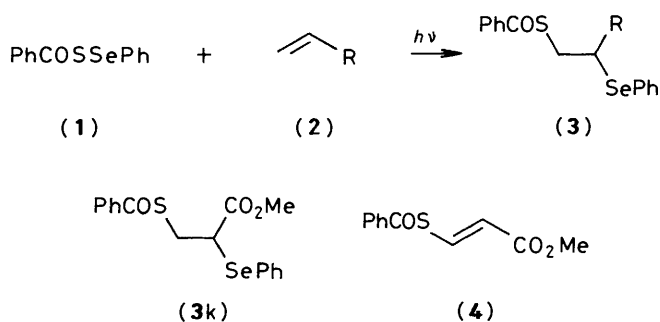
A solution of a slight excess (1.2 equiv.) of *Se*-phenyl (selenothioperoxy)benzoate⁴ (**1**) and an olefin (**2**) in benzene was irradiated by a high-pressure mercury lamp. The addition proceeded regioselectively to give the products in high yield. The results are summarized in Table 1. We found that the photo-induced selenothio esterification of olefins (**2a–g**) under the conditions employed proceeded much more efficiently than the thermal reaction; *e.g.* irradiation of dec-1-ene with a 1.2-fold excess of the (selenothioperoxy)benzoate (**1**) for 3 h gave the selenothio ester (**3a**) in 95% yield, whereas refluxing a benzene solution of dec-1-ene and a 1.2-fold excess of the (selenothioperoxy)benzoate (**1**) for 10 h in the presence of AIBN gave the addition product (**3a**) in 70% yield. The advantage of the photochemical reaction over the thermal reaction was also shown in the reaction of cycloalkenes (**2h–j**). The photochemical reaction of cyclohexene (**2h**) or cyclopentene (**2i**) with (**1**) was complete within 3 h and gave the product in high yield, while the thermal reaction required a much longer reaction period for completion.[‡] The reactivity of norbornene (**2j**) was such that it gave the product in high yield within 1 h in both

Table 1. Irradiation of olefins (**2**) with *Se*-phenyl (selenothioperoxy)benzoate (**1**)^a

Olefin	Reaction time (h)	Product	Yield (%)
CH ₂ =CH(CH ₂) ₇ Me	(2a) 3	(3a)	95
CH ₂ =CHCH ₂ OH	(2b) 7	(3b)	93
CH ₂ =CHCH ₂ OAc	(2c) 3	(3c)	86
CH ₂ =CHCH ₂ NHAc	(2d) 3	(3d)	78
CH ₂ =CHCH ₂ CN	(2e) 3	(3e)	89
CH ₂ =CHCH ₂ CO ₂ Me	(2f) 3	(3f)	86
CH ₂ =CHCH ₂ Ph	(2g) 4	(3g)	89
Cyclohexene	(2h) 3	(3h) ^b	92
Cyclopentene	(2i) 3	(3i) ^b	88
8,9,10-Trinorbornene	(2j) 1	(3j) ^b	98
CH ₂ =CHCO ₂ Me	(2k) 4	(3k)	41

^a All the reactions were carried out with 1.2 mol equiv. of (**1**), see Experimental section. ^b The *trans*:*cis* ratios were 88:12 for (**3h**), 92:8 for (**3i**), and 30:70 for (**3j**).

photochemical and thermal reactions. The ratios of the *cis* and *trans* isomers of these products (**3h–j**) were almost the same as



Scheme 1.

those obtained in the thermal reaction.² Methyl acrylate§ (**2k**) also gave the corresponding adduct, methyl 2-phenylseleno-3-thiobenzyloxypropionate (**3k**) in moderate yield. The regiochemistry of (**3k**) was determined by the spectral data and further confirmed by the oxidation-elimination of the phenylseleno group to give methyl (*E*)-3-thiobenzyloxyacrylate (**4**) in 94% yield.

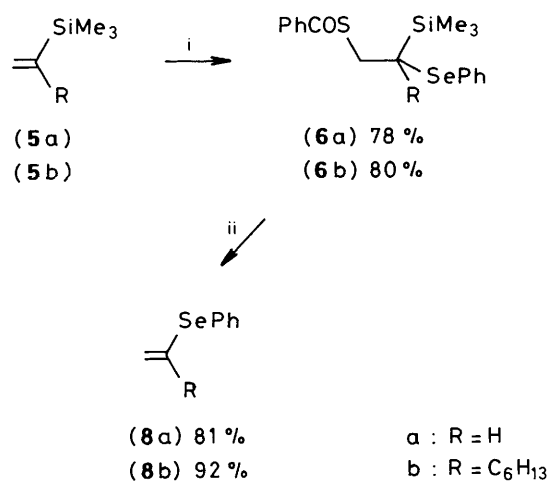
The (selenothioperoxy)benzoate (**1**) reacted with electron deficient methyl acrylate (**2k**). We next examined the radical addition reaction of vinylic silanes (**5a**) and (**5b**),¶ the silyl group

[†] The introduction of a seleno group together with another function *via* a free-radical pathway, selenosulphonation, has been reported.²

[‡] Thermal reaction of (**1**) with a 3-fold excess of cyclohexene or cyclopentene required 17 or 12 h, respectively, for completion, whereas that with 8,9,10-trinorbornene required 1 h; see ref.3.

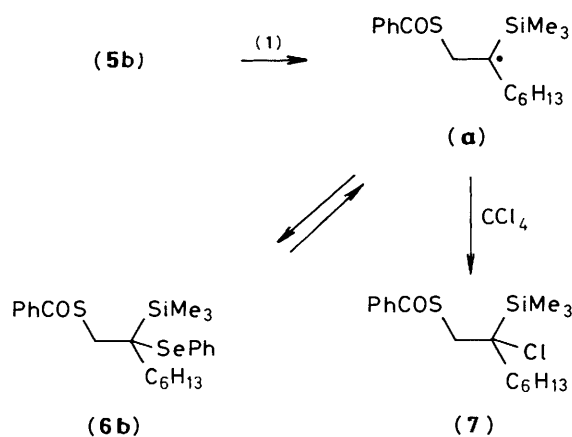
§ Methyl acrylate is often used for trapping electron-rich carbon radicals.⁵

¶ Addition reaction of silyl radical to vinylsilane had been reported.⁶



Scheme 2. Reagents and conditions: i, PhCOSSePh, *hν*, C₆H₆, 2h; ii, Bu₄NF, THF

of which is known to be slightly electron withdrawing.* Irradiation of a benzene solution of (1) and the vinylic silanes (5a) and (5b) in benzene was also successful, giving rise to *S*-2-trimethylsilyl-2-(phenylseleno)alkyl thiobenzoates (6a) and (6b) in 78 and 80% yield, respectively. The thiobenzoates (6a) and (6b) had the same regio-orientation as in the adducts obtained from terminal olefins, *i.e.* the thyl radical, PhCOS·, added to the terminal carbon and the resulting carbon radical α to the silyl group was trapped by the phenylseleno group. We found an interesting reaction feature in the reaction of the (selenothio-peroxy)benzoate (1) and vinylsilane (5b). When irradiation of (5b) with (1) was carried out in carbon tetrachloride, a



Scheme 3.

significant amount (21% yield) of the chloro adduct (7) was formed in addition to the adduct (6a) (19% yield). On irradiation of dec-1-ene with (1) in carbon tetrachloride no formation of such a chloro adduct was observed. Furthermore, the chloro adduct (7) was formed when the selenothioester (6b) was irradiated in carbon tetrachloride. These facts suggest that the chloro adduct (7) can be reversibly formed through α-silyl radical (a) from selenothioester (6b). α-Chloro- or α-bromo-silanes compared with their carbon analogues such as 1-chloro- or 1-bromo-pentane are strongly activated towards halogen abstraction by tributyltin hydride.⁸ This apparent stabilization effect of the α-silyl group on the radical could be attributed to reversibility between the radical (a) and (6b), *i.e.* to the formation of the chloro adduct (7). The yield of the chloro adduct (7) depends on the wavelength used for irradiation as shown in Table 2. Photolysis through a coloured glass filter

Table 2. Irradiation of a carbon tetrachloride solution of 2-trimethylsilyl-dec-1-ene (5b) and *S*-phenyl (selenothio-peroxy)benzoate (1)

Irradiation		Reaction Time ^c (h)	Yields (%)	
Lamp ^a	Filter(λ _{max} , nm) ^b		(6b)	(7)
H.P.Hg		3	19	21
S.H.P.Hg	IRA-10 (> 350)	3	44	21
S.H.P.Hg	UVD-35 (365)	6	47	8
Xe	KL-40 (400)	9	58	5
Xe	KL-40 (400)	9 ^d	77	
Xe	KL-50 (500)	6	No reaction	

^a H.P.Hg: a high pressure mercury lamp (Toshiba H-400P; 400 W). S.H.P.Hg: a super high-pressure mercury lamp (Ushio USH-500D; 500 W). Xe: a xenon lamp (UXL-500-0; 500 W). ^b Toshiba coloured glass filters, IRA-10 and UVD-35, and Toshiba silver interference filters, KL-40 and KL-50, were used. ^c All the reactions were carried out with 1.2 mol equiv. of (1) otherwise noted. ^d The reaction was carried out with 3.0 mol equiv. of (1).

(IRA-10, > 350 nm) with a super high-pressure mercury lamp gave (7) in 21% yield together with (6b) in 44% yield, while the reaction through UVD-35 (λ_{max}, 365 nm) resulted in a decrease in the formation of the chloro adduct (7). Irradiation through KL-40 (λ_{max}, 400 nm) with a xenon lamp afforded (6b) and (7) in 58 and 5% yield, respectively. Formation of (7) was suppressed when irradiated with a 500 W xenon lamp through KL-40, giving (6b) in 77% yield.

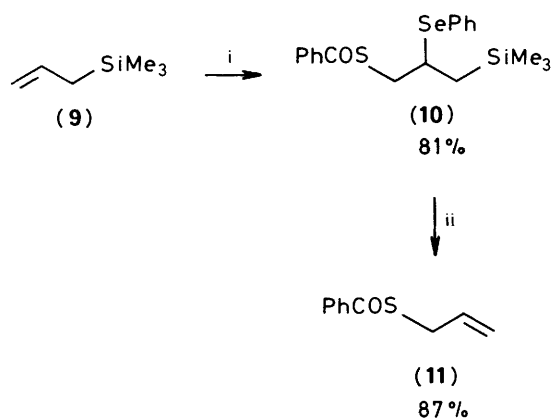
The exclusive and high-yield formation of *S*-2-trimethylsilyl-2-(phenylseleno)alkyl thiobenzoates (6a) and (6b) in the photolysis of a mixture of (1) and vinylsilanes (5a) and (5b) led to an efficient preparative method for alkanyl selenides which have recently attracted interest as synthetic intermediates.⁹ Tetrabutylammonium fluoride was chosen to bring about the chemoselective removal of trimethylsilyl and thiobenzoxy groups from among three functional groups including a phenylseleno group. Thus, treatment of the thiobenzoates (6a) and (6b) with tetrabutylammonium fluoride at room temperature resulted in elimination of the trimethylsilyl group together with the vicinal thiobenzoxy group to yield vinyl selenide (8a) and oct-1-en-2-yl selenide (8b) in 81 and 92% yield, respectively. This remarkable regioselectivity is noteworthy, reflecting as it does a characteristic, regioselective feature of free-radical addition of (1) to olefins. Thus the ionic selenylation of terminal olefins with benzeneselenenyl halides has been reported to give an equilibrated mixture of the adducts which affords, by subsequent elimination of hydrogen halide, a vinyl selenide but with inevitable contamination of the regioisomer.† The above reaction serves as an alternative method for the preparation of vinyl and alk-1-en-2-yl selenides.

Irradiation of a benzene solution of (1) and allylsilane (9) afforded the selenothio esterified product (10) in 81% yield. The thiobenzoate (10) was then treated with tetrabutylammonium fluoride to give *S*-allyl thiobenzoate (11) in 87% yield, as a result of the elimination of the vicinal selenide together with the silyl group. No formation of cyclopropyl phenyl selenide, derived from the elimination of both thiobenzoxy and silyl groups, was observed in this reaction.

The present photo-induced selenothio esterification of olefins,

* The energy levels of the HOMO and LUMO of vinylsilane (5a) have been reported to be lower than those of the corresponding alkene, 3,3-dimethylbut-1-ene.⁷

† A mixture of oct-1-en-2-yl phenyl selenide and oct-1-en-1-yl phenyl selenide in the ratio 9:1 is formed after dehydrobromination (Bu⁺OK) of the adduct obtained in the reaction of oct-1-ene with benzeneselenenyl bromide at -78 °C.¹⁰



Scheme 4. Reagents and conditions: i, PhCOSSePh, *hν*, C₆H₆, 2 h; ii, Bu₄NF, THF

complementing the thermal reaction, offers a practical method for introducing both a phenylseleno and a thiobenzoyloxy group simultaneously into a molecule. Furthermore, this reaction is useful in that it leads to alk-1-en-2-yl selenides and allyl thiobenzoate.

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 Me₄Si 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 Material Science and Engineering, Nagoya Institute of Technology. All reactions were performed under argon. Column chromatography was carried out using a Michael Miler column packed with Fuji Davison silica 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.

Addition of Se-Phenyl (Selenothioperoxy)benzoate (1) to Alkenes (2): General Procedure.—A 1M benzene solution of the alkene (2) with a 1.2-fold excess of the (selenothioperoxy)benzoate (1) contained in a glass tube was irradiated externally by a 400W high-pressure mercury lamp (Toshiba H-400P) at a distance of 10 cm. After irradiation the solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography. The yields are shown in Table 1. For the spectral data for the products, (3a–f) and (3h–j), see ref. 3b.

S-3-Phenyl-2-(phenylseleno)propyl thiobenzoate (3g). Purification by flash column chromatography (5:95, benzene–hexane) afforded compound (3g); v_{\max} (film) 1 665 cm⁻¹; δ_{H} (CCl₄) 2.67–3.23 (2 H, m), 3.23–3.87 (3 H, m), and 6.87–8.06 (10 H, m); m/z 412 (M^+ , ⁸⁰Se, 2%), 275 (4), 255 (21), 157 (3), 137 (10), and 105 (100) (Found: C, 64.5; H, 4.9. C₂₂H₂₀OSSe requires C, 64.23; H, 4.88%).

Methyl 2-Phenylseleno-3-thiobenzoyloxypropionate (3k).—A solution of the (selenothioperoxy)benzoate (1) (200 mg, 0.68 mmol) and methyl acrylate (2k) (49 mg, 0.57 mmol) in benzene (0.6 ml) was irradiated for 4 h in the manner described above. The crude product was purified by column chromatography [silica gel, ethyl acetate–hexane (3:97)] to give compound (3k) (88 mg, 41%) as well as unchanged reactant (1) (83 mg, 41%

recovery). Compound (3k): v_{\max} (film) 3 050, 1 725, and 1 660 cm⁻¹; δ_{H} (CCl₄) 2.95–3.90 (3 H, m), 3.65 (3 H, s), and 7.17–8.07 (10 H, m); m/z 380 (M^+ , ⁸⁰Se, 1%), 243 (9), 223 (2), and 105 (100) (Found: C, 53.7; H, 4.3. C₁₇H₁₆O₃SSe requires C, 53.83; H, 4.25%).

Methyl 3-Thiobenzoyloxyacrylate (4).—To a solution of the adduct (3k) (46 mg, 0.12 mmol) in dichloromethane (0.5 ml) was added a solution of *m*-chloroperbenzoic acid (80% purity; 29 mg, 0.13 mmol) in dichloromethane (0.3 ml) at –60 °C; the mixture was then stirred at –30 °C for 30 min. After this pyridine (38 mg, 39 μl, 0.49 mmol) was added to the mixture and the cooling bath was removed. The reaction mixture was stirred at room temperature for 30 min after which it was evaporated under reduced pressure. The residue was purified by column chromatography [silica gel, ethyl acetate–hexane (5:95)] to give compound (4) (26 mg, 94%); m.p. 87–89 °C (hexane); v_{\max} (KBr) 3 050, 1 710, and 1 680 cm⁻¹; δ_{H} (CCl₄) 3.75 (3 H, s), 6.18 (1 H, d, *J* 16 Hz), 7.28–8.10 (5 H, m), and 8.28 (1 H, d, *J* 16 Hz); m/z 222 (M^+ , 2%), 191 (3), and 105 (100) (Found: C, 59.4; H, 4.6. C₁₁H₁₀O₃S requires C, 59.44; H, 4.53%).

S-2-Trimethylsilyl-2-(phenylseleno)ethyl Thiobenzoate (6a).—A solution of trimethylvinylsilane (5a) (110 mg, 1.1 mmol) and (selenothioperoxy)benzoate (1) (320 mg, 1.1 mmol) in benzene (1.1 ml) was irradiated for 2 h in a similar manner to that described in the general procedure. The crude product was purified by column chromatography [silica gel, benzene–hexane (5:95 and then 20:80)] to give thiobenzoate (6a) (336 mg, 78%); v_{\max} (film) 3 060 and 1 655 cm⁻¹; δ_{H} (CCl₄) 0.19 (9 H, s), 2.67 (1 H, dd, *J* 8.7, 5.9 Hz), 3.35 (1 H, dd, *J* 13.8, 8.7 Hz), 3.65 (1 H, dd, *J* 13.8, 5.9 Hz), and 7.11–7.98 (10 H, m); δ_{C} (CDCl₃) 33.56, 35.35, 128.93, 129.12, 130.25, 130.73, 132.57, 134.96, 135.37, 135.46, 138.90, and 193.58; m/z 394 (M^+ , ⁸⁰Se, 4%), 379 (2), 256 (11), 237 (3), 184 (4), 157 (3), 105 (98), 77 (59), and 73 (100) (Found: C, 54.9; H, 5.4. C₁₈H₂₂OSSeSi requires C, 54.95; H, 5.64%).

S-2-Trimethylsilyl-2-(phenylseleno)octyl Thiobenzoate (6b).—2-(Trimethylsilyl)oct-2-ene (5b) was prepared from oct-1-yne according to a literature procedure.¹¹ A solution of (5b) (35 mg, 0.19 mmol) and the (selenothioperoxy)benzoate (1) (56 mg, 0.19 mmol) in benzene (0.19 ml) was irradiated for 2 h as above. The solvent was then removed under reduced pressure to leave an oil which was purified by column chromatography [silica gel, benzene–hexane (5:95 and then 10:90)] to afford compound (6b) (72 mg, 80%); v_{\max} (film) 3 050 and 1 665 cm⁻¹; δ_{H} (CCl₄) 0.18 (9 H, s), 0.73–1.06 (3 H, m), 1.06–1.79 (10 H, m), 3.37–3.64 (2 H, m), and 6.73–8.07 (10 H, m); m/z 478 (M^+ , ⁸⁰Se, 1%), 463 (3), 341 (29), 321 (78), 268 (3), 157 (3), and 105 (100) (Found: C, 60.4; H, 7.3. C₂₄H₃₄OSSeSi requires C, 60.35; H, 7.17%).

S-2-Chloro-2-(trimethylsilyl)octyl Thiobenzoate (7).—A solution of 2-(trimethylsilyl)oct-2-ene (5b) and the (selenothioperoxy)benzoate (1) in carbon tetrachloride was irradiated under the conditions shown in Table 1. The results are summarized in the Table. Purification of the reaction mixture as above afforded compound (7); v_{\max} (film) 3 060 and 1 660 cm⁻¹; δ_{H} (CCl₄) 0.21 (9 H, s), 0.70–1.03 (3 H, m), 1.03–2.08 (10 H, m), 3.57–3.67 (2 H, m), and 7.16–8.20 (5 H, m); m/z 358 (M^+ , ³⁷Cl, 0.2%), 356 (M^+ , ³⁵Cl, 0.7), 341 (1), 321 (12), 306 (1), 248 (1), 184 (2), and 105 (100) (Found: C, 60.6; H, 8.1. C₁₈H₂₉ClOSSI requires C, 60.55; H, 8.19%).

Phenyl Vinyl Selenide (8a).—To a solution of thiobenzoate (6a) (58 mg, 0.15 mmol) in tetrahydrofuran (THF) (0.3 ml) was added a solution of tetrabutylammonium fluoride trihydrate (93 mg, 0.29 mmol) in THF (0.5 ml) at room temperature. T.l.c. showed that immediately after the addition starting compound

(6a) disappeared. The solution was then diluted with ether (20 ml), washed with water and brine, dried (MgSO_4), and evaporated under reduced pressure. The residual oil was purified by column chromatography [silica gel, light petroleum (b.p. 30–40 °C)] to give compound (8a)¹² (22 mg, 81%).

Oct-1-en-2-yl Phenyl Selenide (8b).—The thiobenzoate (6b) (64 mg, 0.13 mmol) was treated with tetrabutylammonium fluoride trihydrate (85 mg, 0.27 mmol) in THF in a similar manner to that described above. Purification by column chromatography (silica gel, hexane) afforded compound (8b)¹² (33 mg, 92%).

S-3-Trimethylsilyl-2-(phenylseleno)propyl Thiobenzoate (10).—A solution of compound (1) (236 mg, 0.81 mmol) and allyltrimethylsilane (9) (92 mg, 0.81 mmol) in benzene (0.8 ml) was irradiated for 2 h. The crude product was purified by column chromatography [silica gel, benzene–hexane (5:95, 10:90, and then 15:85)] to give compound (10) (265 mg, 81%); ν_{max} (film) 3 050 and 1 660 cm^{-1} ; $\delta_{\text{H}}(\text{CCl}_4)$ 0.11 (9 H, m), 0.67–1.53 (2 H, m), 2.97–3.77 (3 H, m), and 7.07–8.07 (10 H, m); m/z 408 (M^+ , ^{80}Se , 1%), 393 (1), 251 (21), 157 (2), 105 (100), 77 (31), and 73 (68) (Found: C, 55.9; H, 6.0. $\text{C}_{19}\text{H}_{24}\text{OSSeSi}$ requires C, 56.00; H, 5.94%).

S-Allyl Thiobenzoate (11).—A solution of the thiobenzoate (10) (62 mg, 0.15 mmol) in THF (0.5 ml) was treated with a 1M THF solution of tetrabutylammonium fluoride (0.30 ml, 0.30 mmol) as above. Purification by column chromatography [silica gel, benzene–hexane (5:95)] gave compound (11)¹³ (23 mg, 87%).

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