Thio- and Seleno-lactonizations of Alkynoic Acids

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Regio- and stereo-specific thio- and seleno-lactonizations of hept-4-ynoic acid (**1a**), hex-4-ynoic acid (**1b**), and pent-4-ynoic acid (**1c**) can be achieved by treatment of benzenesulphenyl chloride and benzeneselenenyl chloride using a hydrogen chloride capture such as triethylamine or a better capture in most cases, 3,4-dihydro-2*H*-pyrido[1,2*a*]pyrimidin-2-one. *N*-Phenylselenophthalimide is also effective for the selenolactonization, although *E* and *Z* lactones (*E*)-(**2c**; X = Se) and (*Z*)-(**2c**; X = Se) are formed from (**1c**). Cleavage reactions of γ-alkylidene-γ-butyrolactones afford a new preparative method for 4-oxoalkanoic acid derivatives.

Phenylsulphenium or phenylselenenium ion-induced cyclofunctionalization using benzenesulphenyl halides, benzeneselenenyl halides, or *N*-phenylselenophthalimide (N-PSP) is an important synthetic method, since phenylthio and phenylseleno groups introduced simultaneously with cyclization have great versatility in synthesis owing to their ease of manipulation.[1] To date, compounds reported for this thio- or seleno-cyclization are alkenes possessing internal nucleophilic centres such as oxygen,[2] sulphur,[3] nitrogen,[4] and carbon.[5] Recently attempts have been made to utilize alkynes carrying a hydroxy group in reaction with benzeneselenenyl chloride (PhSeCl), in order to provide only 1,2-addition products in which the selenocyclization was absent.[6] In addition, there have been reported many naturally occurring γ-alkylidene-γ-butyrolactones,[7] the biological profiles of which have not been well defined. Several synthetic methods for γ-alkylidene-γ-butyrolactones from alkynoic acids have been reported by the use of metal catalysts such as mercuric salts,[8] palladium,[9] and also by use of *N*-halosuccinimide.[10] We have reported the preliminary results on selenolactonization of alkynoic acids with N-PSP.[11] We now report successful thio- and seleno-lactonizations of alkynoic acids into phenyl-thio and -seleno substituted γ-alkylidene-γ-butyrolactones and their use as synthetic precursors for the preparation of 4-oxoalkanoic acid derivatives in detail.

Table 1. Thio- and seleno-lactonization of alkynoic acids

Alkynoic Acid	X	Reagent[a]	HCl Capture	Product and yield (%) (2)	(3) + (4)	[(3):(4)][b]
(**1a**)	S	A	Et_3N	78	20	(40:60)
(**1a**)	S	A[c]	Et_3N	70	19	(42:58)
(**1a**)	S	A[d]	Et_3N	70	23	(40:60)
(**1a**)	S	A[e]	Et_3N	45	43	(40:60)
(**1a**)	S	A	(**5**)	99	Trace	
(**1a**)	Se	B	Et_3N	51	32	(45:55)
(**1a**)	Se	B	(**5**)	83	6	(32:68)
(**1a**)	Se	C		76		
(**1b**)	S	A	(**5**)	92	Trace	
(**1b**)	Se	B	(**5**)	77	5	(35:65)
(**1b**)	Se	C		76		
(**1c**)	S	A	Et_3N	32	40	(10:90)
(**1c**)	Se	B	(**5**)	20	12	[(**4**) only]
(**1c**)	Se	C		63[f]		

[a] A = PhSCl, B = PhSeCl, C = N-PSP. CH_2Cl_2 as the solvent unless otherwise stated. [b] The ratio determined by h.p.l.c. of the corresponding methyl esters. [c] CCl_4 as the solvent. [d] Benzene as the solvent. [e] Ether as the solvent. [f] Composed of (*E*)-(**2c**; X = Se) (50%) and (*Z*)-(**2c**; X = Se) (13%).

Results and Discussion

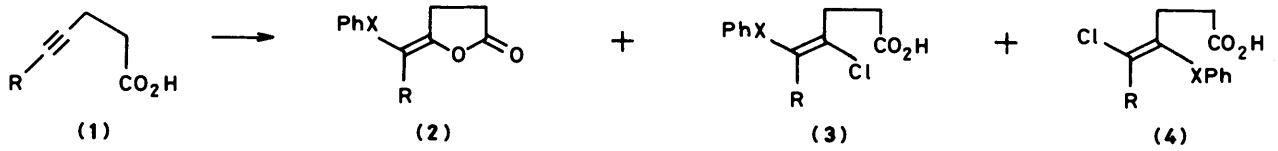
Thio- and Seleno-lactonizations.—It has been reported that benzenesulphenyl chloride (PhSCl) can add to enol ethers in the presence of triethylamine, to give a new method for the preparation of allyl phenyl sulphides.[12] This is in contrast to PhSeCl which cannot act as an electrophile to a double bond in the presence of triethylamine.[13] Thus, initially, we examined the addition of PhSCl to hept-4-ynoic acid (**1a**) in CH_2Cl_2 at −78 °C in the presence of triethylamine.† After purification by flash chromatography[14]‡ 4-(1-phenylthiopropylidene)butan-4-olide (**2a**; X = S) was obtained in 78% yield as well as the addition products (**3a**; X = S) and (**4a**; X = S) in 20% yield. No formation of pentenolactone, *endo*-cyclization product, was observed in this reaction. The ratio of (**3a**; X = S) to (**4a**; X = S) was determined by h.p.l.c. of the corresponding methyl ester which was obtained by treatment of the mixture of the acids (**3a**; X = S) and (**4a**; X = S) with diazomethane. The ratio (**3a**; X = S):(**4a**; X = S) was in good accord with that obtained from the addition reaction of methyl hex-4-ynoate with PhSCl. In order to improve the yield of thiolactonization, several conditions were examined. The results are summarized in Table 1. The yield of compound (**2a**; X = S) was not significantly changed in CCl_4 or benzene but was lowered in ether at certain temperatures. The yield of the cyclization dramatically increased when 3,4-dihydro-2*H*-pyrido[1,2-*a*]pyrimidin-2-one (**5**), a reagent developed by Mukaiyama for a neutral HCl acceptor,[15] was used, to give the lactone (**2a**; X = S) almost quantitatively. It should be noted that the dihydropyridopyrimidinone (**5**) should be added after the addition of PhSCl, because PhSCl forms a complex with (**5**) which does not react with alkynoic acids even at elevated temperatures.

The use of the pyridopyrimidinone (**5**) as a hydrogen chloride captor was also advantageous in selenolactonization. Thus, hept-4-ynoic acid (**1a**) was treated with PhSeCl in CH_2Cl_2 at −78 °C, followed by the addition of triethylamine,§ to give

† The reaction in the absence of triethylamine resulted in the exclusive formation of the addition products (**3a**; X = S) and (**4a**; X = S) in 80% yield.

‡ Purification by the normal pressure silica gel chromatography gave (**2a**; X = S) in low yield, probably because of its unstable nature towards hydrolysis on silica gel.

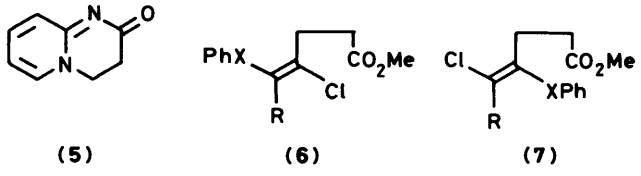
§ Phenylselenothiolactonization did not occur when PhSeCl was added in the presence of triethylamine, see also ref. 13.



(1) (2) (3) (4)

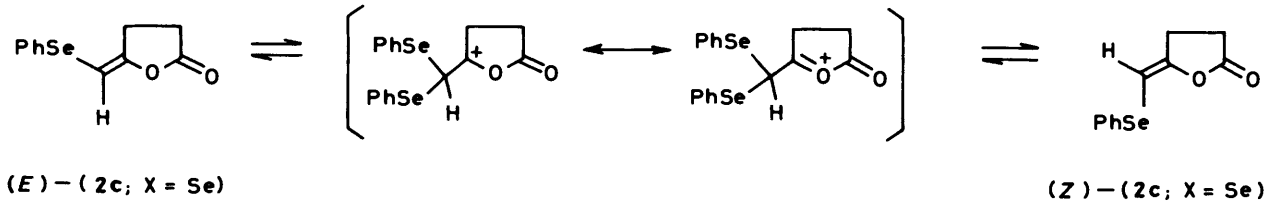
a; R = Et
b; R = Me, X = S, SO, Se
c; R = H

Scheme 1.



(5) (6) (7)

(*E*)-(**2c**; X = Se) and (*Z*)-(**2c**; X = Se), whereas the reaction of hept-4-ynoic acid (**1a**) or hex-4-ynoic acid (**1b**) resulted in the exclusive formation of the *E*-isomer (**2a**; X = Se) or (**2b**; X = Se). Treatment of the separated *E*- and *Z*-isomers (*E*)-(**2c**; X = Se) and (*Z*)-(**2c**; X = Se) with 0.1 equiv. of N-PSP in CH_2Cl_2 gave an equilibrium mixture of (*E*)-(**2c**; X = Se) and (*Z*)-(**2c**; X = Se) in the ratio 3:2 after 190 h from the *E*-isomer (*E*)-(**2c**;



(*E*)-(**2c**; X = Se) (*Z*)-(**2c**; X = Se)

Scheme 2.

4-(1-phenylselenopropylidene)butan-4-olide (**2a**; X = Se) along with PhSeCl addition products (**3a**; X = Se) and (**4a**; X = Se) in 51 and 32% yield, respectively, whereas the yield of the butan-4-olide (**2a**; X = Se) increased to 83% when the pyridopyrimidinone (**5**) was added instead of triethylamine. These results encouraged us to examine the cyclization of other alkynoic acids. The cyclization of hex-4-ynoic acid (**1b**) with PhSCl or PhSeCl also proceeded smoothly to afford the butan-4-olide (**2b**; X = S) or (**2b**; X = Se) in high yield when (**5**) was used. On the other hand, thiolactonization of pent-4-ynoic acid (**1c**) in the presence of triethylamine gave lactone (**2c**; X = S) in 37% yield as well as the addition products (**3c**; X = S) and (**4c**; X = S) in 43% yield. The pyridopyrimidinone (**5**) did not improve thiolactonization at all in this case. Selenolactonization of (**1c**) using (**5**) also gave lactone (**2c**; X = Se) in rather poor yield.

In the former reaction the ratio of PhSCl adducts (**3c**; X = S):(**4c**; X = S) was found to be 10:90 on the basis of the methyl esters, and in the latter, exclusive formation of PhSeCl adduct (**4c**; X = Se) was observed. These facts are in good accord with the results reported in the literature[16] concerning the reaction of terminal acetylenes with PhSCl or PhSeCl. We obtained similar results; the reaction of methyl pentynoate with PhSCl gave 4-chloro-5-phenylthiopent-4-enoate (**6a**; X = S) and 5-chloro-4-phenylthiopent-4-enoate (**7a**; X = S) in a ratio of 5:95, whereas the reaction with PhSeCl gave only 5-chloro-4-phenylselenopent-4-enoate (**7a**; X = Se). The regioselectivity in the reaction of pent-4-ynoic acid (**1c**) with PhSCl or PhSeCl, possibly as in the case of methyl pent-4-ynoate, disfavours the *exo-digonal* cyclization[17] to 4-methylenebutan-4-olide (**2c**; X = S) or (**2c**; X = Se), thus accounting for its low yield. The yield of selenolactonization of pent-4-ynoic acid (**1c**) was improved by use of N-PSP as shown in Table 1.[11] The reaction was carried out at room temperature, giving a mixture of *E* and *Z* isomers X = Se) and after 24 h from the *Z*-isomer (*Z*)-(**2c**; X = Se). These results clearly suggest that the formation of the *Z*-isomer resulted from the isomerization of the *E*-isomer initially formed by the action of N-PSP as shown in Scheme 2.

That the phenylthiolactonization of (**1a**) proceeded in an *anti* manner was shown by the n.m.r. study of the sulphoxide (**2a**; X = SO) which was prepared by the oxidation of phenylthiobutan-4-olide (**2a**; X = S) with *m*-chloroperbenzoic acid (*m*CPBA). The data are summarized in Table 2. The well-

Table 2. ^{1}H N.m.r. spectroscopic data of (**2a**; X = S), (**6a**; X = S), and (**7a**; X = S), and their sulphoxides (**2a**; X = SO), (**6a**; X = SO), and (**7a**; X = SO)[a]

Compd.	Protons	$\delta_{X=S}$	$\delta_{X=SO}$
$MeCH_2C(X)=CCH_2CH_2COO$ (**2a**)	a	2.73, 2.76	2.85
	b	3.06, 3.11	3.35, 3.57
	c	2.40	2.15, 2.30
	d	1.06	0.76
$MeCH_2C(Cl)=CCH_2CH_2CO_2Me$ (**6a**)	a	2.63	2.80
	b	3.17	3.25, 3.47
	c	2.42	2.24, 2.44
	d	1.05	0.74
$MeCH_2C(X)=CCH_2CH_2CO_2Me$ (**7a**)	a	2.55	1.98, 2.50
	b	2.75	2.52, 2.74
	c	2.85	3.05
	d	1.16	1.34

[a] Chemical shifts (p.p.m.) relative to Me_4Si.

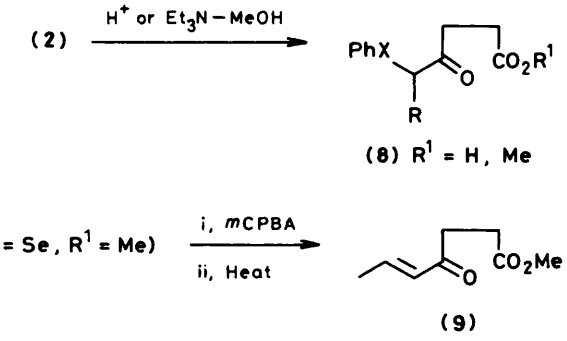


Table 3. Treatment of the butan-4-olides (**2**) with methanol in the presence of triethylamine

Butan-4-olide	Reaction temp. (°C)	Reaction time (h)	Product	Yield (%)
(**2a**)	−50	0.5	(**8a**;X = S, R′ = Me)	97
(**2c**)	−65→−15	3	(**8c**;X = S, R′ = Me)	99
(**2a**)	−50→−15	1.5	(**8a**; X = Se, R′ = Me)	90
(*E*)-(**2c**)	−40	0.25	(**8c**; X = Se, R′ = Me)	100
(*Z*)-(**2c**)	−40	0.25	(**8c**; X = Se, R′ = Me)	99

known downfield shift[18] was observed in the methylene protons *syn* to the phenylsulphinyl group, which appeared separately at 3.35 and 3.57 p.p.m., whereas the corresponding protons of the parent sulphide (**2a**; X = S) appeared at 3.06 and 3.11 p.p.m. The similar downfield shifts in the methylene protons *syn* to the phenylsulphenyl group in comparison with those *syn* to the phenylsulphinyl group were observed in the series of adducts (**6a**; X = S) and (**7a**; X = S). It should be noted that the protons of the ethyl group geminal to the phenylsulphinyl group appeared at a field higher by 0.25 and 0.10 p.p.m. for methylene and 0.30 p.p.m. for methyl protons than those of the sulphide (**2a**; X = S) possibly due to the anisotropy of the benzene ring. This upfield shift was also observed in the n.m.r. spectra of the sulphoxide (**6a**; X = SO) and (**7a**; X = SO) of PhSCl adducts (**3a**; X = S) and (**4a**; X = S)).

Transformation of the Butan-4-olide (**2**) *to 4-Oxo-5-phenylthio- and 5-Phenylseleno-alkanoic Acid Derivatives* (**8**; X = S) *and* (**8**; X = Se).—Phenylthio and phenylseleno substituted 4-alkylidenebutan-4-olides (**2**) are useful precursors to 4-oxoalkanoic acid derivatives. Thus, the thiolactone (**2a**; X = S) was treated with 5% aqueous HCl in THF at room temperature, to give 4-oxo-5-phenylthioheptanoic acid (**8**; X = S, R′ = H). Treatment of the butan-4-olides (**2**) with triethylamine in methanol gave 5-phenylthio- and 5-phenylseleno-substituted 4-oxoalkanoic acid methyl esters (**8**) in almost quantitative yield as shown in Table 3. Both the *E* and *Z* isomers (*E*)-(**2c**; X = Se) and (*Z*)-(**2c**; X = Se) were converted into the same selenopentenoate (**8c**; X = Se, R′ = Me). Oxidative elimination of the phenylseleno group of (**8c**; X = Se, R′ = Me) gave (**9**) in 74% yield.

Finally, the following aspects characteristic of the present reactions should be pointed out. It is known that the addition of PhSCl and PhSeCl to disubstituted acetylenes is non-regiospecific.[16] We also confirmed the reaction of methylhept-4-ynoate with PhSCl and PhSeCl which gave the adducts in ratios of (**6a**):(**7a**) 42:58 (X = S) and 40:60 (X = Se). Higher regioselectivity was obtained in the reaction of methylpent-4-ynoate possessing a terminal acetylene, as mentioned above, with predominant formation of 5-chloro-4-phenylthiopent-4-enoate (**7c**; X = S) and exclusive formation of 5-chloro-4-phenylselenopent-4-enoate (**7c**; X = Se). In contrast to these regioselectivities in the addition reactions, phenylthio- and phenylseleno-lactonizations of alkynoic acids (**1**) proceeded exclusively in an *exo-digonal* fashion according to Baldwin's rules[17] to give 5-phenylthio- and 5-phenylseleno-butan-4-olides (**2**) which in turn were transformed to the 4-oxo-5-phenylthio- and 4-oxo-5-phenylseleno-alkanoate derivatives (**8**) and (**9**). It is of great interest that this overall regiospecific transformation of an acetylene unit in an alkynoic acid (**1**), in the anti-Markownikoff manner, into the α-phenylthio(seleno)carbonyl moiety could be achieved by the action of the remote carboxylic acid *via* the regiospecific thio(seleno)lactonization and its ring opening.

Experimental

M.p.s were recorded on a Yanagimoto hot plate apparatus and are uncorrected. I.r. spectra were recorded with a JASCO-102 spectrophotometer. ^{1}H N.m.r. spectra were recorded on a Varian XL-200 (200 MHz) or JEOL JNM-PMX60si (60 MHz) instruments. Chemical shifts are reported on the δ scale relative to Me_4Si as the internal standard. ^{13}C N.m.r. spectra were obtained on a Varian XL-200 spectrometer for solutions in deuteriochloroform. Microanalyses were performed by the Institute of Microanalyses, University of Kyoto. All reactions were carried out under an argon atmosphere. Column chromatography was performed with Fuji Davison silica gel adsorbant BW-820MH. Flash chromatography was performed using a Michael Miler column packed with Fuji Davison silica gel BW-200, equipped with FMI LAB Pump RP-G150 and FMI Pulse Damper PD-60LF, normally at a pressure of 1—2 kg cm^{-2}. H.p.l.c. was performed on an ERMA ERC-8710 with a column (4.6 × 150 mm) packed with Cosmosil 5SL. Ether refers to diethyl ether.

Reaction of 4-*Alkynoic Acid* (**1**) *with* PhSCl *in the Presence of Triethylamine*.—To a solution of hept-4-ynoic acid (**1a**) (50 mg, 0.40 mmol) in CH_2Cl_2 (1.7 ml) was added triethylamine (44 mg, 0.44 mmol) at room temperature and the mixture was stirred for 30 min. Then to the cooled mixture (−78 °C) was added dropwise PhSCl (4.8M solution in CH_2Cl_2; 114 μl, 0.55 mmol) over a period of 5 min, during which the yellow colour of PhSCl disappeared immediately after the addition. After the reaction had been stirred for 30 min, ether (10 ml) was added and the organic solution was washed with ice–water and brine, dried ($MgSO_4$), and evaporated under reduced pressure. The residual oil was purified by flash chromatography [silica gel (6 g); hexane–ethyl acetate (99:1; 100 ml) and then (95:5; 200 ml)] to give (E)-4-(1-*phenylthiopropylidene*)*butan-4-olide* (**2a**; X = S) (72 mg, 78%), $\nu_{max.}$(film) 3 050, 1 810, 1 660, and 1 580 cm^{-1}; $\delta_H(CDCl_3)$ 7.28 (5 H, m), 3.11 (1 H, dd, *J* 10.6 and 0.2 Hz), 3.06 (1 H, dd, *J* 9.4 and 0.2 Hz), 2.76 (1 H, dd, *J* 9.4 and 0.2 Hz), 2.73 (1 H, dd, *J* 10.6 and 0.2 Hz), 2.40 (2 H, q, *J* 7.5 Hz), and 1.06 (3 H, t, *J* 7.5 Hz); $\delta_C(CDCl_3)$ 172.0, 154.5, 141.6, 130.3, 128.7, 127.0, 28.0, 25.5, 24.5, and 12.8; *m/z* 234 (M^+, 100%), 218 (23), 206 (15), and 125 (32) (Found: C, 66.7; H, 6.0. $C_{13}H_{14}O_2S$ requires C, 66.64; H, 6.02%). Further elution [hexane–ethyl acetate (1:1); 50 ml] gave a mixture of (*E*)-4-chloro-5-phenylthiohept-4-enoic acid (**3a**; X = S) and (*E*)-5-chloro-4-phenylthiohept-4-enoic acid (**4a**; X = S) (21 mg, 20%), $\nu_{max.}$(film) 3 300—2 500 and 1 715 cm^{-1}; $\delta(CCl_4)$ 11.40 (1 H, s), 7.13 (5 H, s), 3.5—2.0 (6 H, m), and 1.17 (3 H, m); *m/z* 270 (M^+, 29%), 253 (4), 235 (5), 161 (22), and 109 (100). This mixture was treated with diazomethane

in ether to transform the acids to their methyl esters (**6a**; X = S) and (**7a**; X = S). The ratio of (**6a**; X = S):(**7a**; X = S) was found to be 40:60 by h.p.l.c. analysis, R_t 17 min for (**6a**; X = S) and 20 min for (**7a**; X = S). The peaks had been assigned after the isolation of each compound. The mixture of the esters (110 mg) was chromatographed [silica gel (30 g); hexane:benzene (99:1)] to give (*E*)-methyl 4-chloro-5-phenylthiohept-4-enoate (**6a**; X = S) (16 mg) and (*E*)-methyl 5-chloro-4-phenylthiohept-4-enoate (**7a**; X = S) (16 mg) as well as a mixture of the two (71 mg). The ratio obtained above was in good accord with that obtained for the addition products as follows. To a solution of methyl hept-4-ynoate (50 mg, 0.36 mmol) in CH_2Cl_2 (1.5 ml) was added dropwise PhSCl (10M in CH_2Cl_2; 54 μl, 0.54 mmol) at −78 °C and the mixture was stirred for 30 min. Work-up as above gave a mixture of (**6a**; X = S) and (**7a**; X = S) (81 mg, 80%), whose ratio as determined by h.p.l.c. analysis was 42:58. Compound (**6a**; X = S) showed $\nu_{max.}$(film) 1 730 cm^{-1}; δ($CDCl_3$) 7.30 (5 H, m), 3.70 (3 H, s), 3.17 (2 H, t, *J* 7.2 Hz), 2.63 (2 H, t, *J* 7.2 Hz), 2.42 (H, q, *J* 7.4 Hz), and 1.05 (3 H, t, *J* 7.4 Hz) (Found: C, 59.2; H, 6.2. $C_{14}H_{17}ClO_2S$ requires C, 59.04; H, 6.02%); (**7a**; X = S) showed $\nu_{max.}$(film) 1 725 cm^{-1}; δ($CDCl_3$) 7.28 (5 H, m), 3.65 (3 H, s), 2.85 (2 H, q, *J* 7.2 Hz), 2.75 (2 H, m), 2.55 (2 H, m), and 1.16 (3 H, t, *J* 7.2 Hz) (Found: C, 58.95; H, 5.9. $C_{14}H_{17}ClO_2S$ requires C, 59.04; H, 6.02%). The structures of (**2a**; X = S), (**6a**; X = S), and (**7a**; X = S) were further confirmed by oxidation to the corresponding sulphoxides.

A similar reaction was carried out at −25 °C using compound (**1a**) (30 mg, 0.24 mmol), triethylamine (26 mg, 0.26 mmol), and PhSCl (0.26 mmol) in CCl_4 (1 ml) which gave compound (**2a**; X = S) (39 mg, 70%) and a mixture of compounds (**3a**; X = S) and (**4a**; X = S) (12 mg, 19%).

Similarly, the reaction of compound (**1a**) (30 mg, 0.24 mmol) in benzene (1 ml) at 10 °C gave (**2a**; X = S) (39 mg, 70%) and a mixture of (**3a**; X = S) and (**4a**; X = S) (15 mg, 23%).

The reaction of compound (**1a**) (30 mg, 0.24 mg) in ether (1 ml) at −78 °C gave (**2a**; X = S) (25 mg, 45%) and a mixture of (**3a**; X = S) and (**4a**; X = S) (28 mg, 43%).

The treatment of compound (**1c**) (30 mg, 0.31 mmol) and PhSCl (0.34 mmol) in the presence of triethylamine (0.34 mmol) in CH_2Cl_2 gave (**2c**; X = S) (20 mg, 32%), $\nu_{max.}$($CHCl_3$) 3 005, 1 799, 1 650, and 1 579 cm^{-1}; δ(CCl_4) 7.20 (5 H, s), 6.28 (1 H, t, *J* 2 Hz), and 2.70—2.50 (4 H, m); *m/z* 206 (M^+, 100%), 134 (12), 122 (88), and 109 (18) (Found: C, 64.0; H, 5.05. $C_{11}H_{10}O_2S$ requires C, 64.06; H, 4.89%), and a mixture of (**3c**; X = S) and (**4c**; X = S) (30 mg, 40%), $\nu_{max.}$(KBr) 3 350—2 500, 1 690, 1 600, and 1 579 cm^{-1}; δ(CCl_4) 11.45 (1 H, br s), 7.22 (5 H, s), 6.39 (1 H, t, *J* 2 Hz), and 2.58 (4 H, m); *m/z* 242 (M^+, 12%), 207 (12), 162 (10), 148 (75), 98 (22), and 55 (100). A mixture of the methyl esters (**6c**; X = S) and (**7c**; X = S) were obtained, $\nu_{max.}$(film) 3 050, 3 000, 1 725, and 1 575 cm^{-1}; δ(CCl_4) 7.27 (5 H, s), 6.30 (1 H, t, *J* 2 Hz), 3.60 (3 H, s), and (4 H, m).

Oxidation of (E)-4-(1-*Phenylthiopropylidene*)*butan*-4-*olide* (**2a**; X = S).—To a solution of (**2a**; X = S) (86 mg, 0.37 mmol) in CH_2Cl_2 (1.5 ml) was added dropwise a solution of *m*CPBA (82 mg, 0.38 mmol) in CH_2Cl_2 (1 ml) at −30 °C and the mixture was stirred for 30 min and followed by the addition of ether (20 ml). The mixture was then washed successively with aqueous $NaHCO_3$, water, and brine, before being dried ($MgSO_4$) and evaporated under reduced pressure. Flash chromatography [silica gel (5 g); hexane–ethyl acetate (8:2; 100 ml) and then (6:4; 200 ml)] afforded (*E*)-4-(1-phenylsulphinylpropylidene)buten-4-olide (**2a**; X = SO) 64.5 mg, 70%), $\nu_{max.}$(film) 3 050, 1 805, and 1 660 cm^{-1}; δ($CDCl_3$) 7.64 (5 H, m), 3.57 (1 H, dt, *J* 8.0 and 16.0 Hz), 3.35 (1 H, dq, *J* 8.0 and 16.0 Hz), 2.85 (2 H, t, *J* 8.0 Hz), 2.30 (1 H, dq, *J* 7.0 and 14.0 Hz), 2.15 (1 H, dq, *J* 7.0 and 14.0 Hz), and 0.76 (3 H, t, *J* 7.0 Hz); δ_C($CDCl_3$) 174.6, 156.8, 143.6, 132.0, 130.4, 125.4, 123.2, 27.2, 25.2, 16.4, and 13.8; *m/z* 250 (M^+, 24%), 234 (100), 206 (9), and 125 (21) (Found: C, 62.25; H, 5.85. $C_{13}H_{14}O_3S$ requires C, 62.38; H, 5.64%).

Oxidation of (E)-*Methyl* 4-*Chloro*-5-*phenylthiohept*-4-*enoate* (**6a**; X = S) *and* (E)-*Methyl* 5-*Chloro*-4-*phenylthiohept*-4-*enoate* (**7a**; X = S).—To a solution of compound (**6a**; X = S) (16 mg, 0.056 mmol) in CH_2Cl_2 (0.7 ml) was added dropwise a solution of *m*CPBA (80% purity; 13 mg, 0.062 mmol) in CH_2Cl_2 (0.9 ml) at −30 °C. After the reaction had been stirred for 40 min and work-up as above, flash chromatography [silica gel (3 g); hexane–ethyl acetate (9:1; 100 ml) and then (1:1; 100 ml)] afforded methyl (*E*)-4-chloro-5-phenylsulphinylhept-4-enoate (**6a**; X = SO) (12 mg, 71%), $\nu_{max.}$(film) 3 050 and 1 730 cm^{-1}; δ($CDCl_3$) 7.59 (5 H, m), 3.78 (3 H, s), 3.47 (1 H, ddd, *J* 15.5, 7.5 and 7.5 Hz), 3.25 (1 H, ddd, *J* 15.5, 7.5, and 7.5 Hz), 2.80 (2 H, t, *J* 7.5 Hz), 2.44 (1 H, dq, *J* 15.0 and 7.5 Hz), 2.24 (1 H, dq, *J* 15.0 and 7.5 Hz), and 0.74 (3 H, t, *J* 7.5 Hz); *m/z* 300 (M^+, 3%), 284 (30), 269 (19), 175 (51), and 79 (100) (Found: C, 55.95; H, 5.65. $C_{14}H_{17}ClO_3S$ requires C, 55.90; H, 5.70%).

Similarly, compound (**7a**; X = S) (16 mg, 0.056 mmol) furnished (*E*)-methyl 5-chloro-4-phenylsulphinylhept-4-enoate (**7a**; X = SO) (12 mg, 71%), $\nu_{max.}$($CDCl_3$) 3 000 and 1 725 cm^{-1}; δ($CDCl_3$) 7.58 (5 H, m), 3.64 (3 H, s), 3.05 (2 H, q, *J* 7.2 Hz), 2.74 (1 H, ddd, *J* 12.0, 10.2, and 4.6 Hz), 2.52 (1 H, ddd, *J* 12.0, 8.8, and 4.6 Hz), 2.50 (1 H, ddd, *J* 17.9. 10.2, and 4.6 Hz), 1.98 (1 H, ddd, *J* 17.9, 8.8, and 4.6 Hz), and 1.34 (3 H, t, *J* 7.2 Hz); *m/z* 300 (M^+, 5%), 284 (12), 269 (25), 225 (25), and 175 (100) (Found: C, 55.8; H, 5.8. $C_{14}H_{17}ClO_3S$ requires C, 55.90; H, 5.70%).

Reaction of Alkyn-4-*oic acid* (**1**) *with* PhSCl *and* 3,4-*Dihydro*-2H-*pyridopyrimidin*-2-*one* (**5**).—To a solution of compound (**1a**) (50 mg, 0.40 mmol) in CH_2Cl_2 (1.7 ml) was added dropwise a solution of PhSCl (4.8M CH_2Cl_2 solution; 91 μl, 0.44 mmol) over a period of 5 min at −78 °C. After the reaction had been stirred for 30 min at the same temperature, the solid dihydropyridopyrimidinone (**5**) (65 mg, 0.44 mmol) was added all at once and stirred for further 10 min. Hexane (10 ml) was added and the resultant precipitate was filtered off. Evaporation under reduced pressure gave an oily residue which was purified by flash chromatography as above, to give compound (**2a**; X = S) (92 mg, 99%) and a mixture of (**3a**; X = S) and (**4a**; X = S) (0.6 mg, 0.6%).

Similarly, from compound (**1b**) (30 mg, 0.27 mmol) was obtained (**2b**; X = S) (54 mg, 92%), $\nu_{max.}$(film) 3 050, 1 804, 1 673, and 1 590 cm^{-1}; δ(CCl_4) 7.10 (5 H, s, 3.30—2.40 (4 H, m), and 1.97 (3 H, t, *J* 1 Hz); *m/z* 220 (M^+, 100%), 136 (40), and 111 (6) (Found: C, 65.55; H, 5.4. $C_{12}H_{12}O_2S$ requires C, 65.43; H, 5.49%).

Reaction of Alk-4-*ynoic acid* (**1**) *with* PhSeCl *and* 3,4-*Dihydro*-2H-*pyridopyrimidin*-2-*one* (**5**).—To a solution of (**1a**) (50 mg, 0.40 mmol) in CH_2Cl_2 (1.7 ml) was added dropwise a solution of PhSeCl (84 mg, 0.44 mmol) in CH_2Cl_2 (1 ml) at −78 °C during 5 min. After the reaction had been stirred for 30 min the dihydropyridopyrimidinone (**5**) (65 mg, 0.44 mmol) was added and stirring was continued for a further 10 min. Hexane (10 ml) was added and the resultant precipitate was filtered off. Evaporation under reduced pressure gave an oily residue which was purified by flash chromatography [silica gel (5 g); hexane–ethyl acetate (99:1; 300 ml) (98:2; 200 ml), and then (80:20; 100 ml)] to give (*E*)-4-(1-phenylselenopropylidene)butan-4-olide (**2a**; X = Se) (92 mg, 83%), $\nu_{max.}$(film) 3 050, 1 800, 1 660, and 1 570 cm^{-1}; δ(CCl_4) 7.21 (5 H, m), 3.25—2.20 (6 H, m), and 1.06 (3 H, t, *J* 7 Hz); *m/z* 282 (M^+, 20%), 198 (8), and 77 (100) (Found: C, 55.9; H, 5.07. $C_{13}H_{14}O_2Se$ requires C, 55.52; H, 5.02%), and a mixture of (*E*)-4-chloro-5-phenylselenohept-4-enoic acid (**3a**; X = Se) and (*E*)-5-chloro-4-phenylselenohept-4-enoic acid (**4a**; X = Se) (8 mg, 6%), $\nu_{max.}$($CHCl_3$) 3 400—2 500, 1 700, 1 605,

and 1 570 cm^{-1}; δ(CCl_4) 9.20 (1 H, s), 7.20 (5 H, m), 3.2—2.1 (6 H, m), and 1.14 (3 H, t, *J* 7 Hz); *m/z* 318 (M^+, 40), 283 (9), and 157 (100). This mixture was converted into a mixture of methyl ethers by treatment with diazomethane (**6a**; X = Se) and (**7a**; X = Se), $\nu_{max.}$(film) 1 725 cm^{-1}; δ(CCl_4) 7.50—7.11 (5 H, m), 3.56 (3 H, s), 2.90—2.25 (6 H, m), and 1.18 (3 H, t, *J* 7 Hz). H.p.l.c. analysis showed the ratio of (**6a**; X = Se):(**7a**; X = Se) to be 32:68, while the ratio of the adducts, obtained from the reaction of methyl hept-4-ynoate and PhSeCl, was 40:60. The structure of the shorter retention time component (15 min) was tentatively assigned as (**6a**; X = Se) and the longer retention time component (17 min) as (**7a**; X = Se), by comparison with the relative retention times of authentic PhSCl adducts (**6a**; X = S) and (**7a**; X = S).

The following compounds were prepared as above.

(E)-4-(1-*Phenylselenoethylidene*)*butan*-4-*olide* (**2b**; X = Se), $\nu_{max.}$ 3 050, 1 800, 1 670, and 1 578 cm^{-1}; δ(CCl_4) 7.20 (5 H, m), 3 40—2.41 (4 H, m), and 2.10 (3 H, t, *J* 2 Hz); *m/z* 269 (M^+, 15%), 184 (6), 157 (4), and 77 (100) (Found: C, 53.95; H, 4.45. $C_{12}H_{12}O_2Se$ requires C, 53.87; H, 4.52%).

(E)-4-(*Phenylselenomethylene*)*butan*-4-*olide* (*E*)-(**2c**; X = Se), m.p. 47—48 °C, $\nu_{max.}$(KBr) 3 050, 1 799, 1 640, and 1 570 cm^{-1}; δ(CCl_4) 7.15 (5 H, m), 6.04 (1 H, t, *J* 2 Hz), 3.20—2.75 (2 H, m), 2.75—2.35 (2 H, m); *m/z* 254 (M^+, 100%), 174 (95), and 149 (35) (Found: C, 52.15; H, 4.0. $C_{11}H_{10}O_2Se$ requires C, 52.17; H, 3.98%).

(E)-5-*Chloro*-4-*phenylselenopent*-4-*enoic acid* (**4c**; X = Se), $\nu_{max.}$(film) 3 500—2 500, and 1 705 cm^{-1}; δ(CCl_4) 10.20 (1 H, br s), 7.60—7.10 (5 H, m), 6.41 (1 H, t, *J* 2 Hz), and 2.95—2.10 (4 H, m); *m/z* 290 (M^+, 39%), 254 (17), and 157 (100).

(E) *Methyl* 5-*chloro*-4-*phenylselenopent*-4-*enoate* (**7c**; X = Se), ν_{max} (film) 1 725 cm^{-1}; δ(CCl_4) 7.84—7.04 (5 H, m), 6.35 (1 H, s), 3.59 (3 H, s), and 2.94—2.21 (4 H, m); *m/z* 304 (M^+, 90%), 273 (7), 157 (41), and 147 (100) (Found: C, 47.5; H, 4.2. $C_{12}H_{13}ClO_2Se$ requires C, 47.41; H, 4.31%).

Reaction of Hept-4-*ynoic Acid* (**1a**) *with* PhSeCl *and Triethylamine*.—To a solution of (**1a**) (30 mg, 0.24 mmol) in CH_2Cl_2 (0.6 ml) was added dropwise a solution of PhSeCl (46 mg, 0.24 mmol) in CH_2Cl_2 (0.6 ml) at −40 °C and the mixture was stirred for 30 min. Triethylamine (26 mg, 0.26 mmol) was then added and the reaction was stirred at −40 °C for 10 min. After removal of the cooling bath, ether (20 ml) was added and the solution was washed successively with ice–water (5 ml) and brine (5 ml). The dried ($MgSO_4$) solution was evaporated under reduced pressure and the residue was purified by flash chromatography [silica gel (5 g); hexane–ethyl acetate (99:1; 100 ml), (98:2; 300 ml), and then (1:1; 100 ml)] to give compound (**2a**; X = Se) (34 mg, 51%) and a mixture of (**3a**; X = Se) and (**4a**; X = Se) (24 mg, 32%).

Reaction of Alk-4-*ynoic Acid* (**1**) *with* N-PSP.—To a solution of N-PSP (302 mg, 1.0 mmol) in CH_2Cl_2 (2 ml) was added a solution of hept-4-ynoic acid (**1a**) (100 mg, 0.79 mmol) in CH_2Cl_2 (1 ml) at 0 °C. After having been stirred at this temperature for 10 min, the mixture was further stirred at room temperature for 4 h. Hexane (10 ml) was then added and the resultant precipitate was filtered off. The solvent was evaporated under reduced pressure to give a residual oil which was purified by flash chromatography [silica gel (9 g); hexane–ethyl acetate (99:1; 100 ml) and then (95:5, 300 ml)] to afford (**2a**; X = Se) (170 mg, 76%).

Similarly, the reaction of hex-4-ynoic acid (**1b**) (30 mg, 0.27 mmol) and N-PSP (98 mg, 0.32 mmol) in CH_2Cl_2 (1 ml) at room temperature for 160 h gave (**2b**; X = Se) (54 mg, 76%) after purification by flash chromatography.

The reaction of pent-4-ynoic acid (**1c**) (30 mg, 0.31 mmol) and N-PSP (138 mg, 0.46 mmol) in CH_2Cl_2 (1.5 ml) at room temperature for 22 h gave the less polar (*E*)-(**2c**; X = Se) (39 mg, 50%) and the more polar (*Z*)-(**2c**; X = Se) (10 mg, 13%), $\nu_{max.}$(film) 3 070, 3 010, 1 809, 1 660, and 1 578 cm^{-1}; δ(CCl_4) 7.60—7.10 (5 H, m), 5.41 (1 H, t, *J* 2 Hz), 3.00—2.75 (2 H, m,), and 2.75—2.33 (2 H, m); *m/z* 254 (M^+, 100%), 174 (67), 157 (90), and 97 (28) (Found: C, 52.05; H, 4.05. $C_{11}H_{10}O_2Se$ requires C, 52.17; H, 3.98%), after purification by flash chromatography [silica gel (4 g); hexane–ethyl acetate (99:1; 100 ml), (97:3; 100 ml), and then (95:5; 200 ml)]. The *E*:*Z* ratio for this reaction was found to be time-dependent. Monitoring by h.p.l.c. showed equilibration of the products after 8 days, ratio 53:47. When a mixture of (*E*)-(**2c**; X = Se) (20 mg, 0.079 mmol) and N-PSP (2.4 mg, 0.0078 mol) in CH_2Cl_2 (0.3 ml) was stirred for 190 h, the ratio of (*E*)-(**2c**; X = Se):(*Z*)-(**2c**; X = Se) was 60:40. A similar experiment showed that equilibrium was reached after 24 h in the isomerization of (*Z*)-(**2c**; X = Se).

Acid Hydrolysis of (E)-4-(1-*Phenylthiopropylidene*)*butan*-4-*olide* (**2a**; X = S).—A mixture of (**2a**; X = S) (30 mg, 0.13 mmol), tetrahydrofuran (0.5 ml), and 5% aqueous HCl (0.5 ml) was stirred at room temperature for 10 h. Brine (5 ml) was added and the mixture was extracted with ethyl acetate (15 ml). The organic solution was washed with brine (5 ml), dried ($MgSO_4$) and evaporated under reduced pressure to give an oil which was chromatographed [silica gel (3 g); hexane–ethyl acetate (9:1; 150 ml) and then (8:2; 100 ml)] to give 4-oxo-5-phenylthioheptanoic acid (**8a**; X = S, R′ = H) (27 mg, 84%), $\nu_{max.}$(film) 1 715 and 1 705 cm^{-1}; δ(CCl_4) 10.40 (1 H, br s), 7.23 (5 H, s), 3.50 (1 H, t, *J* 7 Hz), 3.20—2.35 (4 H, m), 2.30—1.50 (2 H, m), and 1.03 (3 H, t, *J* 7 Hz); *m/z* 252 (M^+, 32%), 235 (30), and 151 (100) (Found: C, 61.8; H, 6.3. $C_{13}H_{16}O_3S$ requires C, 61.88; H, 6.39%).

Methanolysis of the Lactone (**2**).—(*E*)-4-(1-Phenylthiopropylidene)butan-4-olide (**2a**; X = S) (14.5 mg, 0.062 mmol) was treated with methanol (0.2 ml) containing triethylamine (10 μl, 0.074 mmol) at −45 °C. After 30 min the methanol was evaporated off under reduced pressure and the residue was chromatographed [silica gel (1 g), hexane–benzene (1:1; 60 ml) and then (2:8; 60 ml)] to give methyl 4-oxo-5-phenylthioheptanoate (**8a**; X = S, R′ = Me) (16 mg, 97%), $\nu_{max.}$(film) 3 050, 1 734, 1 705, and 1 580 cm^{-1}; δ(CCl_4) 7.21 (5 H, m), 3.59 (3 H, s), 3.30 (1 H, t, *J* 7 Hz), 3.09—2.65 (2 H, m), 2.65—2.28 (2 H, m), 2.00—1.50 (2 H, m), and 1.01 (3 H, t, *J* 7 Hz); *m/z* 266 (M^+, 22%), 151 (100), 123 (27), 15 (34), and 109 (42) (Found: C, 63.15; H, 6.8. $C_{14}H_{18}O_3S$ requires C, 63.16; H, 6.67%).

(*E*)-4-(1-Phenylselenopropylidene)butan-4-olide (**2a**; X = Se) (37 mg, 0.13 mmol) was treated as above to give methyl 4-oxo-5-phenylselenoheptanoate (**8a**; X = Se, R′ = Me) (37 mg, 90%), $\nu_{max.}$(film) 1 734 and 1 698 cm^{-1}; δ(CCl_4) 7.60—7.10 (5 H, m), 3.59 (3 H, s), 3.32 (1 H, m), 3.0—2.1 (4 H, m), 2.0—1.5 (2 H, m), and 0.98 (3 H, t, *J* 7 Hz); *m/z* 314 (M^+, 31%), 283 (12), 157 (72), and 105 (100) (Found: C, 55.65; H, 5.75. $C_{14}H_{18}O_3Se$ requires C, 53.62; H, 5.79%).

(*E*)-4-(Phenylthiomethylene)butan-4-olide (**2c**; X = S) (14 mg, 0.068 mmol) was subjected to methanolysis at −65 °C for 1.5 h to give methyl 4-oxo-5-phenylthiopentanoate (**8c**; X = S, R′ = Me) (16 mg, 99%), $\nu_{max.}$($CHCl_3$) 3 005, 1 728, and 1 710 cm^{-1}; δ(CCl_4) 7.16 (5 H, s), 3.57 (5 H, s), and 2.9—2.3 (4 H, m); *m/z* 238 (M^+, 73%), 207 (45), 179 (8), and 114 (100) (Found: C, 60.45; H, 5.95. $C_{12}H_{14}O_3S$ requires C, 60.48; H, 5.92%).

Methanolysis of (*E*)-4-(phenylselenomethylene)butan-4-olide (*E*)-(**2c**; X = Se) (30 mg, 0.12 mmol) at −40 °C for 15 min gave methyl 4-oxo-5-phenylselenopentanoate (**8c**; X = Se, R′ = Me) (34 mg, 100%), $\nu_{max.}$ 3 050, 1 730, 1 695, and 1 575 cm^{-1}; δ(CCl_4) 7.57—7.07 (5 H, m), 3.58 (3 H, s), 3.53 (2 H, s), and 2.95—2.30 (4 H, m); *m/z* 286 (M^+, 13%), 255 (4), 171 (10), 157

(14), 129 (3), and 115 (100) (Found: C, 50.8; H, 5.05. $C_{12}H_{14}O_3Se$ requires C, 50.54; H, 4.95%).

Methanolysis of (*Z*)-4-(phenylselenomethylene)butan-4-olide (*Z*)-(**2c**; X = Se) (9 mg, 0.036 mmol) at −40 °C for 15 min gave (**8c**; X = Se, R′ = Me) (10 mg, 99%).

Preparation of Methyl 4-Oxohept-5-enoate (**9**).—To a solution of (**8a**; X = Se, Me) (13.5 mg, 0.043 mmol) in CH_2Cl_2 (1 ml) was added dropwise a solution of *m*CPBA (10 mg, 0.046 mmol) in CH_2Cl_2 (1 ml) at −40 °C and the mixture was stirred for 30 min. Pyridine (14 mg, 0.18 mmol) was then added, the cooling bath was removed and the reaction was stirred at room temperature for a further 21 h. Ether (15 ml) was added and the organic solution was washed successively with 0.1M-HCl (3 ml), aqueous $NaHCO_3$ (3 ml), aqueous NH_4Cl (3 ml), and brine (3 ml). The dried ($MgSO_4$) solution was evaporated under reduced pressure and the residual oil was purified by flash chromatography [silica gel (3 g); hexane–ethyl acetate (95:5; 100 ml) and then (9:1; 100 ml)] to give (**9**)[19] (5 mg, 74%), $\nu_{max.}$(film) 3 010, 1 728, 1 718, 1 669, and 1 630 cm^{-1}; $\delta(CCl_4)$ 6.83 (1 H, dq, *J* 16 and 6 Hz), 6.07 (1 H, dq, *J* 16 and 1 Hz), 3.60 (3 H, s), 2.97—2.33 (4 H, m), and 1.93 (3 H, dd, *J* 7 and 1 Hz); *m/z* 156 (M^+, 100%), 141 (90), and 110 (54).

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