# Electrophilic Addition of 4'-Nitrobenzenesulphenanilide to Alkynes in Acetic Acid. A Synthesis of β-Acetoxyvinyl Sulphides

**Luisa Benati, Daniele Casarini, and Pier Carlo Montevecchi** *
*Dipartimento di Chimica Organica dell'Università, Viale Risorgimento 4, 40136 Bologna, Italy*
**Piero Spagnolo**
*Istituto Chimico dell'Università della Basilicata, Via N. Sauro 85, 85100 Potenza, Italy*

4'-Nitrobenzenesulphenanilide reacts at room temperature with simple alkyl- and aryl-alkynes in acetic acid in the presence of boron trifluoride–diethyl ether to afford products of acetoxysulphenylation in moderate to good yields. The addition products are generally produced with *trans*-stereospecificity and in a regioselective fashion (Markovnikov orientation). The findings are consistent with a mechanism involving intermediacy of thiirenium ions which would result from alkyne attack at the sulphur atom of the anilide complexed with boron trifluoride.

In previous papers[1,2] we have shown that 4'-substituted benzenesulphenanilides are capable of undergoing electrophilic addition to simple alkynes in the presence of boron trifluoride. In acetonitrile these reactions lead to the formation of β-acetamidinovinyl sulphides with *trans*-stereospecificity and high regioselectivity (Markovnikov orientation) in yields which largely increase with increasing electron-withdrawing power of the anilido substituent. Satisfactory yields as azasulphenylation adducts can be generally obtained with 4'-nitrobenzenesulphenanilide (BSA). Thiirenium ion intermediates, arising from phenylthio transfer from an anilide–$BF_3$ complex to the alkyne triple bond, are probably involved. These would be captured by the nitrile solvent to give eventually the enamidino products. We now report our results obtained from a study of the $BF_3$-promoted reaction of BSA with a number of simple alkynes (**1a**—**l**) in acetic acid. This study was undertaken in order to investigate further the mechanism of these electrophilic additions and to explore their potential utility in the synthesis of β-acetoxyvinyl sulphides (**2**), which are useful intermediates in organic synthesis, particularly as masked β-keto sulphides.[2,3] Earlier studies have provided evidence that thiirenium ions, occurring as reaction intermediates in the solvolysis of β-arylthiovinyl sulphonates, can afford products of acetoxysulphenylation.[4,5] However, a systematic study has not been performed and this method appears to be somewhat limited by the fact that the arylthiovinyl sulphenate precursors are prepared by addition of a rather unstable and expensive sulphenyl sulphonate to alkynes.[6]

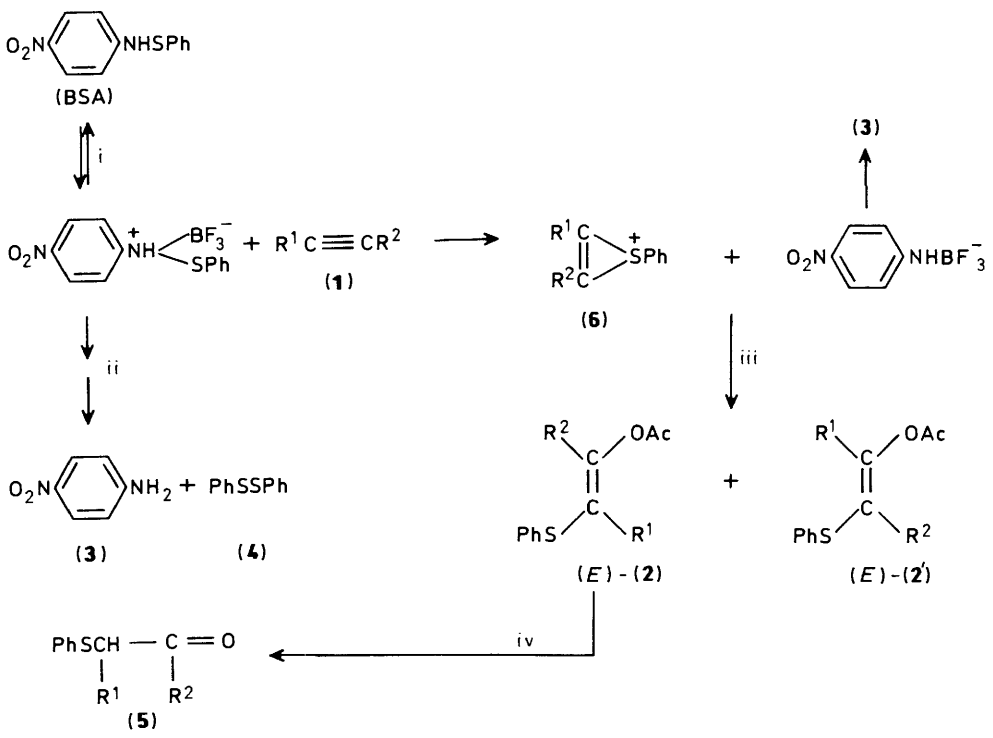
## Results and Discussion

A solution of BSA in acetic acid was added to a solution of the appropriate alkyne (**1a**—**l**) (5 mol equiv.) and boron trifluoride–diethyl ether (1.5 mol equiv.) in acetic acid. The resulting reaction mixture was stirred at room temperature for 1—2 h, and then hydrolysed with aqueous potassium carbonate. Column chromatography led generally to isolation of the β-acetoxyvinyl sulphides (**2a**—**l**) and (**2'a**—**e**) in variable yields, in addition to 4-nitroaniline (**3**) and diphenyl disulphide (**4**) (Table 1). The disulphide (**4**) and the aniline (**3**), at least in part, were the products expected from self-reaction of BSA.[1,7] As can be seen in Table 1, terminal alkynes led to the sulphides (**2**) and (**2'**) in moderate yields (30—57%) (entries 1—4, 9), while the disubstituted ones gave the corresponding adducts (**2'**) and/or (**2**) in fair to good yields (72—90%) (entries 4—8, 10, 11), except diphenylacetylene (**1l**) which gave the acetoxy disulphide (**2l**) in low yield (entry 12). With unsymmetrical alkynes the addition reaction was found to proceed in a regioselective fashion. In fact the alkyl-substituted alkynes (**1a**, **c**, and **d**) gave predominantly the Markovnikov adducts (**2a**, **c**, and **d**) along with minor amounts of the anti-Markovnikov adducts (**2'a**, **c**, and **d**), but with t-butylacetylene (**1b**) the anti-Markovnikov product (**2'b**) was the main product. Moreover, exclusive formation of the Markovnikov products (**2i**—**k**) was observed with the aryl-substituted alkynes (**1i**—**k**). However, the dialkyl-substituted alkyne (**1e**) gave an inseparable mixture of the two regioisomeric sulphides (**2e**) and (**2'e**) in the ratio 55:45. The sulphide (**2l**) had been previously reported.[5d] Structural assignment of the new compounds (**2a**—**k**) and (**2'a**—**e**) was accomplished on the basis of $^1H$ n.m.r. and mass spectral data in addition to chemical evidence. In particular, the n.m.r. spectra of the sulphides (**2a**—**d**) exhibited a signal for the vinylic proton at δ 5.8—5.95, whereas such a proton resonated at lower field (δ 7.5—7.65) with the regioisomeric sulphides (**2'a**—**d**). Upon hydrolysis in dioxane–5M-hydrochloric acid at reflux the compounds (**2a**, **c**, **d**, **f**—**k**) were converted into the corresponding β-keto sulphides (**5**) in almost quantitative yield.[2] Analogous hydrolysis of the 55:45 mixture of the regioisomers (**2e**) and (**2'e**) gave the keto sulphides (**5e**) and (**5**; $R^1$ = Pr, $R^2$ = Me) respectively in about the same ratio.

**Table 1.** (*E*)-Acetoxyvinyl sulphides prepared *via* $BF_3$-promoted reaction of BSA with alkynes in acetic acid[a]

| Entry | Alkyne | (*E*)-Acetoxyvinyl sulphide | Yield (%)[b] | (**2**):(**2'**) ratio |
|---|---|---|---|---|
| 1 | Propyne (**1a**) | (**2a**) + (**2'a**) | 30 | 73:27 |
| 2 | t-Butylacetylene (**1b**) | (**2b**) + (**2'b**) | 35 | 14:86 |
| 3 | Pent-1-yne (**1c**) | (**2c**) + (**2'c**) | 54 | 80:20 |
| 4 | Hex-1-yne (**1d**) | (**2d**) + (**2'd**) | 54 | 80:20 |
| 5 | Hex-2-yne (**1e**) | (**2e**) + (**2'e**) | 80 | 55:45 |
| 6 | But-2-yne (**1f**) | (**2f**) | 73 | |
| 7 | Hex-3-yne (**1g**) | (**2g**) | 90 | |
| 8 | Oct-4-yne (**1h**) | (**2h**) | 90 | |
| 9 | Phenylacetylene (**1i**) | (**2i**)[c] | 57 | 100:0 |
| 10 | 1-Phenylpropyne (**1j**) | (**2j**) | 72 | 100:0 |
| 11 | 1-Phenylbut-1-yne (**1k**) | (**2k**) | 84 | 100:0 |
| 12 | Diphenylacetylene (**1l**) | (**2l**) | 35 | |

[a] Reactions were run at room temperature in the presence of $BF_3{\cdot}Et_2O$ (1.5 mol equiv.) and alkyne (5 mol equiv.) [b] Isolated yields based on starting BSA. The aniline (**3**) (90—95%) and diphenyl disulphide (**4**) (10—60%) were also generally isolated. [c] Mixture of (*E*)- and (*Z*)-isomer in *ca.* 87:13 ratio.




**a**; $R^1$ = H, $R^2$ = Me
**b**; $R^1$ = H, $R^2$ = Bu$^t$
**c**; $R^1$ = H, $R^2$ = Pr
**d**; $R^1$ = H, $R^2$ = Bu
**e**; $R^1$ = Me, $R^2$ = Pr
**f**; $R^1$ = $R^2$ = Me
**g**; $R^1$ = $R^2$ = Et
**h**; $R^1$ = $R^2$ = Pr
**i**; $R^1$ = H, $R^2$ = Ph
**j**; $R^1$ = Me, $R^2$ = Ph
**k**; $R^1$ = Et, $R^2$ = Ph
**l**; $R^1$ = $R^2$ = Ph

**Scheme.** *Reagents:* i, $BF_3$·$Et_2O$; ii, BSA; iii, AcOH; iv, dioxane–5M-HCl

In all cases we have examined the acetoxy sulphides (**2**) and (**2'**) were found to occur exclusively in the (*E*)-configuration. Only in the case of phenylacetylene was the resulting (*E*)-adduct accompanied by minor amounts of the (*Z*)-isomer (Table 1, entry 9). The (*E*)-configuration in compounds (**2a** and **d**) and (**2'b**) was established by nuclear Overhauser enhancement (n.O.e.) measurements on the (*E*)- and (*Z*)-derivatives. These latter were in turn produced by photolytic isomerisation of the (*E*)-isomers (see Experimental section). Irradiation of the methyl protons of (*Z*)-(**2a**) or the vinylic methylene protons of (*Z*)-(**2d**) caused a *ca.* 10% increase in the intensity of the corresponding signal of the vinylic proton, while the intensity of the vinylic proton in the (*E*)-adducts (*E*)-(**2a** and **d**) showed a smaller enhancement (*ca.* 2%). Moreover, upon irradiation of the t-butyl signal of (*Z*)-and (*E*)-(**2'b**) the intensity of the corresponding vinylic proton showed a 26 and 8% increase respectively. For the remaining cases, the (*E*)-configuration in the adducts (**2**) and (**2'**) was assumed.

The *trans*-stereospecificity of the above reactions points to the involvement of thiirenium ion intermediates (**6**),[4] which would result from nucleophilic attack at the sulphur atom of the BSA–$BF_3$ complex by the alkyne; subsequent trapping of the intermediates (**6**) by the solvent acetic acid would lead to the (*E*)-adducts (**2**) and (**2'**) (Scheme). The probable intermediacy of the thiirenium ions (**6**) is consistent with our previous evidence.[1] The observed increase in the extent of the addition products (**2**) and (**2'**) with alkyl substitution on the alkyne is in line with our previous findings [1] that an enhancement of the nucleophilicity of the alkyne strongly favours electrophilic attack by the BSA–$BF_3$ complex at the expense of self-reaction of BSA leading to the disulphide (**4**) [and the aniline (**3**)]. The reason why phenylacetylene (**1i**) does not undergo addition in a *trans*-stereospecific fashion remains somewhat unclear at this stage. Control experiments showed that no isomerization of the resulting sulphides (*E*)- and (*Z*)-(**2i**) occurred under the reaction conditions, thus suggesting that these products are produced under conditions of kinetic control. Possibly in such a case the intermediate thiirenium ion (**6i**) is in equilibrium to some extent with the corresponding vinyl cation (PhSCH=$\overset{+}{C}$Ph).

Our observation that the addition products to nonsymmetrical alkyl- and aryl-alkynes are preferentially or exclusively those with Markovnikov orientation would suggest that the product-determining transition state for nucleophilic attack of acetic acid at the thiirenium-ring carbons occurs with some $S_N1$ character, thus suggesting that substituent polar effects are prevailing over steric effects, unless a very bulky substituent such as the t-butyl group is present. Exclusive Markovnikov ring-opening was previously shown to occur in the reaction of acetonitrile with thiirenium ions.[1] The lower regioselectivity exhibited by acetic acid might be attributed to the fact that attack by this nucleophile proceeds with a lesser degree of $S_N1$ character. This would be the consequence of both the greater nucleophilicity and the larger size of acetic acid compared with acetonitrile. In fact, steric hindrance between the entering nucleophile and the substituent on the thiirenium ion is expected to be particularly relevant.[8] Our suggestion is in line with earlier general evidence that attack on thiirenium ions by chloride ion (which is a fairly strong and bulky nucleophile) occurs through an $S_N1$-like transition state leading to preferential formation of anti-Markovnikov adducts.[4,8–10] No evidence of formation of any product resulting from trapping of the thiirenium ion (**6**) by the tetraborate counterion [$O_2NC_6H_4NHBF_3^-$] could be obtained in any case we have examined. Analogous results were obtained from related additions of benzenesulphenanilides to alkynes in acetonitrile.[1] As we have previously suggested,[1] the lack of attack at the ring

**Table 2.** Yields of the acetoxyvinyl sulphides (**2c** and **g**) and (**2′c**) obtained from $BF_3$-promoted reaction of BSA with the alkynes (**1c** and **g**) in the presence of varying amounts of acetic acid[a]

| Alkyne | [AcOH]/M | Yields (%) of acetoxyvinyl sulphide (**2**)[b] |
|---|---|---|
| (**1c**) | 0.17 | 30 (**2c**)[c] |
| (**1c**) | 0.68 | 44 (**2c**)[c] |
| (**1c**) | 1.75 | 49 (**2c**)[c] |
| (**1c**) | 3.5 | 52 (**2c**)[c] |
| (**1c**) | 17.5[d] | 54 (**2c**)[c] |
| (**1g**) | 0.17 | 55 (**2g**) |
| (**1g**) | 0.42 | 62 (**2g**) |
| (**1g**) | 0.87 | 71 (**2g**) |
| (**1g**) | 1.75 | 75 (**2g**) |
| (**1g**) | 3.5 | 80 (**2g**) |
| (**1g**) | 17.5[d] | 90 (**2g**) |

[a] Reactions were run at room temperature in dichloromethane in the presence of $BF_3{\cdot}Et_2O$ (1.5 mol equiv.) and the alkyne (**1c** or **g**) (5 mol equiv.). [b] Yields determined by h.p.l.c. [c] Mixtures of (**2**) and (**2′**) isomers. [d] Neat solvent.

carbons of the thiirenium ions (**6**) by the counterion is probably ascribable to its high steric demand. However, the counterion might attack the sulphur atom of (**6**) to give back the starting alkyne (**1**) and BSA. In fact, nucleophilic attack at the thiirenium sulphur is well documented.[4] In order to test this possibility we have briefly investigated the effect of varying the concentration of acetic acid in the addition of BSA to pent-1-yne (**1c**) and hex-3-yne (**1g**). Results are collected in Table 2.

As can be seen in Table 2, the yields of the resulting adducts (**2c** and **g**) and (**2′c**) increase with increasing concentration of acetic acid over the range of concentrations 0.17—3.5M, but they remain largely unchanged at acetic acid concentrations >3.5M. On this basis, it may be inferred that electrophilic addition of BSA to the alkynes (**1c**) and (**1g**) should be essentially irreversible at acetic acid concentration >3.5M. Thus, at least at such acetic acid concentrations, attack of the tetraborate counterion on the sulphur of (**6c** and **g**) does not occur.

In summary, we have shown that electrophilic addition of 4′-nitrobenzenesulphenanilide to simple alkynes in acetic acid provides a useful 'one-step' method for the *trans*-stereospecific and regioselective synthesis of acetoxyvinyl sulphides. Our procedure is easy, convenient, and employs BSA, a quite stable and readily available precursor.[7]

## Experimental

4′-Nitrobenzenesulphenanilide (BSA) was prepared as previously reported.[7] The alkynes (**1a** and **l**), 4-nitroaniline (**3**), and diphenyl disulphide (**4**) were commercially available. The β-acetoxyvinyl sulphide (**2l**) was identified by comparison of its physical and spectral data with those reported in the literature.[5d] All new β-acetoxyvinyl sulphides (**2a**—**k**) and (**2′a**—**e**) were characterized on the basis of their n.m.r. and m.s. spectra; the homogeneity of these compounds was confirmed by t.l.c. and/or h.p.l.c. analysis. Only ions of >10% of base peak are given for mass spectra, except where a less intense ion is of importance for structure establishment. $^1H$ N.m.r. spectra were measured on a Varian T60 (60 MHz) or a Brucker AM300 (300 MHz) instrument, and are for solutions in $CDCl_3$ with $Me_4Si$ as internal standard. The nuclear Overhauser enhancement (n.O.e.) measurements were performed at 300 MHz on degassed $CDCl_3$ solutions of the (*E*)- and (*Z*)-acetoxyvinyl sulphides (**2a** and **d**) and (**2′b**). Mass spectra were determined by the electron-impact method on a VG 7070 instrument. H.p.l.c. analyses were performed on a Varian LC 5000 instrument using a reverse-phase C-18 column. Column chromatography was carried out on Merck silica gel (0.040—0.063 particle size).

*$BF_3$-Promoted Reaction of BSA with Alkynes* (**1a**—**l**) *in Acetic Acid. General Procedure.*—A solution of BSA (486 mg, 2 mmol) in acetic acid (10 ml) was added to a stirred solution of the appropriate alkyne (**1a**—**l**) [10 mmol; saturated solution in the case of propyne (**1a**)] and boron trifluoride–diethyl ether (*ca.* 47% $BF_3$) (0.04 ml, 3 mmol) in acetic acid (10 ml). The reaction mixture was stirred at room temperature for *ca.* 1 h [*ca.* 2 h in the case of the terminal alkynes (**1a**—**d** and **i**)] and then neutralized by treatment with 10% aqueous potassium carbonate. The organic layer was extracted with diethyl ether, the excess of solvent removed, and the residue was chromatographed. Elution with light petroleum (b.p. 40—70 °C) gave variable amounts of the disulphide (**4**) (10—60%); elution with light petroleum–diethyl ether (9:1) gave the appropriate (*E*)-acetoxyvinyl sulphide(s) (**2**) and (**2′**) (yields are given in Table 1). Further elution with diethyl ether gave the aniline (**3**) (85—95%).

The following new (*E*)-acetoxyvinyl sulphides (**2**) and (**2′**) were obtained as oily products: (i) (E)-2-*Acetoxy*-1-*phenylthiopropene* (**2a**); $\delta_H$(300 MHz) 2.07 (3 H, s), 2.15 (3 H, s), 5.95 (1 H, s), and 7.28 (5 H, m) (Found: $M^+$, 208.055 95. $C_{11}H_{12}O_2S$ requires *M*, 208.055 80); *m/z* 208 (21), 166 (67), 137 (17), 123 (100), 109 (31), 91 (20), 77 (30), 51 (25), and 43 (100); (ii) (E)-1-*acetoxy*-2-*phenylthiopropene* (**2′a**); $\delta_H$(60 MHz) 1.95 (3 H, t, *J* 1.5 Hz), 2.21 (3 H, s), 7.3—7.45 (5 H, m), and 7.65 (1 H, t, *J* 1.5 Hz) (Found: $M^+$, 208.055 68); *m/z* 208 (25), 166 (100), 137 (30), 109 (30), 105 (25), 78 (30), 77 (22), 59 (50), and 43 (63); (iii) (E)-1-*acetoxy*-3,3-*dimethyl*-2-*phenylthiobut*-1-*ene* (**2′b**); $\delta_H$(300 MHz) 1.20 (9 H, s), 2.20 (3 H, s), 7.15—7.40 (5 H, m), and 7.55 (1 H, s) (Found: $M^+$, 250.102 90. $C_{14}H_{18}O_2S$ requires *M*, 250.102 75); *m/z* 250 (30), 208 (100), 193 (45), 175 (63), 109 (18), 87 (14), 77 (15), 69 (20), 57 (30), and 43 (50); (iv) (E)-2-*acetoxy*-3,3-*dimethyl*-1-*phenylthiobut*-1-*ene* (**2b**), contaminated with some of its regioisomer (**2′b**); $\delta_H$(300 MHz) 1.28 (9 H, s), 2.17 (3 H, s), 5.80 (1 H, s), and 7.15—7.40 (5 H, m) (Found: C, 67.7; H, 7.2; S, 12.7. $C_{14}H_{18}O_2S$ requires C, 67.15; H, 7.25; S, 12.8%); (v) (E)-2-*acetoxy*-1-*phenylthiopent*-1-*ene* (**2c**); $\delta_H$(60 MHz) 0.95 (3 H, t, *J* 7 Hz), 1.18—1.82 (2 H, m), 2.17 (3 H, s), 2.50 (2 H, t, *J* 7 Hz), 5.93 (1 H, s), and 7.0—7.4 (5 H, m) (Found: $M^+$, 236.086 90. $C_{13}H_{16}O_2S$ requires *M*, 236.087 10); *m/z* 236 (58), 194 (90), 165 (10), 123 (100), 71 (56), and 43 (18); (vi) (E)-1-*acetoxy*-2-*phentylthiopent*-1-*ene* (**2′c**); $\delta_H$(60 MHz) 0.8—1.8 (5 H, m), 2.15 (3 H, s), 2.22 (2 H, t, *J* 7 Hz), 7.0—7.4 (5 H, m), and 7.48 (1 H, s) (Found: $M^+$, 236.086 94); *m/z* 236 (45), 194 (100), 165 (6), 147 (22), 135 (22), 110 (15), 109 (15), 91 (25), 87 (36), 77 (16), 71 (15), 57 (28), and 43 (30); (vii) (E)-2-*acetoxy*-1-*phenylthiohex*-1-*ene* (**2d**); $\delta_H$(300 MHz) 0.90 (3 H, t, *J* 7 Hz), 1.28—1.55 (4 H, m), 2.16 (3 H, s), 2.49 (2 H, t, *J* 7 Hz), 5.94 (1 H, s), and 7.2—7.4 (5 H, m) (Found: $M^+$, 250.102 88. $C_{14}H_{18}O_2S$ requires *M*, 250.102 75); *m/z* 250 (34), 208 (100), 123 (77), 121 (50), 91 (34), 85 (84), 77 (36), 69 (36), and 43 (52); (viii) (E)-1-*acetoxy*-2-*phenylthiohex*-1-*ene* (**2′d**); $\delta_H$(300 MHz) 0.85 (3 H, t, *J* 7 Hz), 1.20—1.53 (4 H, m), 2.10 (3 H, s), 2.25 (2 H, t, *J* 7 Hz), 7.2—7.4 (5 H, m), and 7.50 (1 H, s) (Found: $M^+$, 250.102 90); *m/z* 250 (25), 208 (100), 147 (27), 135 (35), 123 (15), 110 (22), 109 (30), 91 (34), 77 (23), and 43 (60); (ix) an inseparable 55:45 mixture of (*E*)-3-acetoxy-2- phenylthiohex-2-ene (**2e**), $\delta_H$(60 MHz) 0.91 (3 H, t, *J* 7 Hz), 1.20—1.63 (2 H, m), 1.80 (3 H, s), 2.18 (3 H, s), 2.60 (2 H, t, *J* 7 Hz), and 7.0—7.33 (5 H, m), and (*E*)-2-acetoxy-3-phenylthiohex-2-ene (**2′e**); $\delta_H$(60 MHz) 0.90 (3 H, t, *J* 7 Hz), 1.20—1.63 (2 H, m), 2.18 (6 H, s), 2.10 (2 H, t, *J* 7 Hz), and 7.0—7.33 (5 H, m); *m/z* 250 (23), 208 (100), 179 (16), 165 (14), 137 (42), 109 (23), 91 (26), 77 (16), 59 (33), and 43 (95) (Found: C, 67.6; H, 7.15; S, 12.9. $C_{14}H_{18}O_2S$ requires C, 67.15; H, 7.25; S, 12.8%); (x) (E)-2-

*acetoxy*-3-*phenylthiobut*-2-*ene* (**2f**); $\delta_H$(300 MHz) 1.82 (3 H, q, *J* 1.5 Hz), 2.18 (3 H, q, *J* 1.5 Hz), 2.18 (3 H, s), and 7.17—7.33 (5 H, m) (Found: $M^+$, 222.071 25. $C_{12}H_{14}O_2S$ requires *M*, 222.071 45); *m*/*z* 222 (8), 180 (30), 137 (30), 109 (16), 91 (12), 77 (17), 59 (52), and 43 (100); (xi) (E)-3-*acetoxy*-4-*phenylthiohex*-3-*ene* (**2g**); $\delta_H$(60 MHz) 0.98 (3 H, t, *J* 7 Hz), 1.02 (3 H, t, *J* 7 Hz), 2.13 (2 H, q, *J* 7 Hz), 2.18 (3 H, s), 2.65 (2 H, q, *J* 7 Hz), and 7.0—7.5 (5 H, m) (Found: $M^+$, 250.102 60. $C_{14}H_{18}O_2S$ requires *M*, 250.102 75); *m*/*z* 250 (36), 208 (86), 151 (100), 110 (12), 109 (22), 91 (19), and 73 (54); (xii) (E)-4-*acetoxy*-5-*phenylthio*-*oct*-4-*ene* (**2h**); $\delta_H$(60 MHz) 0.92 (6 H, t, *J* 7 Hz), 1.17—1.77 (4 H, m), 2.10 (2 H, t, *J* 7 Hz), 2.18 (3 H, s), 2.66 (2 H, t, *J* 7 Hz), and 7.0—7.5 (5 H, m) (Found: $M^+$, 278.134 30. $C_{16}H_{22}O_2S$ requires *M*, 278.135); *m*/*z* 278 (16), 236 (100), 207 (10), 165 (15), 123 (10), 91 (10), 71 (13), 55 (15), and 43 (30); (xiii) an inseparable mixture of (*E*)- and (*Z*)-α-*acetoxy*-β-*phenylthiostyrene* (**2i**), in *ca.* 87:13 ratio, as shown by $^1$H n.m.r. spectroscopy; $\delta_H$[(*E*)-isomer] (300 MHz) 2.21 (3 H, s), 6.30 (1 H, s), and 7.15—7.7 (10 H, m); $\delta_H$[(*Z*)-isomer] (300 MHz) 2.34 (3 H, s), 6.62 (1 H, s), and 7.15—7.7 (10 H, m) (Found: $M^+$, 270.071 64. $C_{16}H_{14}O_2S$ requires *M*, 270.071 45); *m*/*z* 270 (13), 228 (40), 105 (100), 91 (12), 85 (22), 77 (28), 71 (30), 57 (44), and 43 (44) (Found: C, 71.6; H, 5.2; S, 11.8. $C_{16}H_{14}O_2S$ requires C, 71.1; H, 5.22; S, 11.85%); (xiv) (E)-1-*acetoxy*-1-*phenyl*-2-*phenylthiopropene* (**2j**); $\delta_H$(60 MHz) 1.98 (3 H, s), 2.18 (3 H, s), and 7.0—7.5 (10 H, m) (Found: $M^+$, 284.086 87. $C_{17}H_{16}O_2S$ requires *M*, 284.087 10); *m*/*z* 284 (21), 242 (100), 175 (10), 137 (43), 105 (85), 91 (13), 77 (58), 59 (23), 51 (14), and 43 (22); and (xv) (E)-1-*acetoxy*-1-*phenyl*-2-*phenylthiobut*-1-*ene* (**2k**); $\delta_H$(60 MHz) 1.08 (3 H, t, *J* 7 Hz), 2.11 (3 H, s), 2.27 (2 H, q, *J* 7 Hz), and 7.0—7.6 (10 H, m) (Found: $M^+$, 298.103 00. $C_{18}H_{18}O_2S$ requires *M*, 298.102 75); *m*/*z* 298 (12), 256 (63), 189 (12), 157 (32), 148 (62), 133 (57), 105 (100), 91 (13), 77 (60), 55 (27), 51 (22), and 43 (37).

$BF_3$-*Promoted Reaction of BSA with Alkynes* (**1c** *and* **g**) *in Dichloromethane*.—To a 1.0M dichloromethane solution (1 ml) of the alkyne (**1c** or **g**) containing varying amounts of acetic acid (20, 80, 200, and 400 μl or 20, 50, 100, 200, and 400 μl, respectively) and boron trifluoride–diethyl ether (*ca.* 47% $BF_3$) (40 μl, 0.3 mmol) was added a 0.2M solution (1 ml) of BSA in dichloromethane and the reaction mixtures were stirred at room temperature for *ca.* 1 h [*ca.* 2 h in the case of pent-1-yne (**1c**)]. Aliquot parts (100 μl) of the resulting reaction mixtures were then diluted with acetonitrile (20 ml) and the yields of the acetoxyvinyl sulphides (**2c** or **g**) and (**2′c**) were determined by quantitative h.p.l.c. analysis using the corresponding reactions carried out in neat acetic acid as standards. Yields of the compounds (**2c** and **g**) and (**2′c**) thus obtained are given in Table 2.

*Isomerization of the* (E)-*Acetoxyvinyl Sulphides* (E)-(**2a** *and* **d**) *and* (E)-(**2′b**). A $CDCl_3$ solution of the appropriate (*E*)-sulphide (**2a** or **d**) or (**2′b**) was irradiated at room temperature with a high-pressure mercury lamp (360—420 nm) for *ca.* 20 min. In each case an inseparable mixture of the (*Z*)- and (*E*)-isomer in *ca.* 2:1 ratio was obtained as indicated by $^1$H n.m.r. spectroscopy. The mass spectra of these isomeric mixtures were found to be virtually identical with those exhibited by the pure (*E*)-isomers. The $^1$H n.m.r. spectral data for the (*Z*)-isomers were as follows: (i) (*Z*)-2-acetoxy-1-phenylthiopropene (**2a**), $\delta_H$(300 MHz) 2.05 (3 H, s), 2.20 (3 H, s), 5.81 (1 H, s), and 7.17—7.37 (5 H, m); (ii) (*Z*)-1-acetoxy-2-phenylthio-3,3-dimethylbut-1-ene (**2′b**), $\delta_H$(300 MHz) 1.25 (9 H, s), 1.78 (3 H, s), 7.17—7.40 (5 H, m), and 7.53 (1 H, s); and (iii) (*Z*)-2-acetoxy-1-phenylthiohex-2-ene (**2d**), $\delta_H$(300 MHz) 0.90 (3 H, t, *J* 7 Hz), 1.28—1.55 (4 H, m), 2.18 (3 H, s), 2.31 (2 H, t, *J* 7 Hz), 5.81 (1 H, s), and 7.2—7.4 (5 H, m).

*Hydrolysis of the* (E)-*Acetoxy Sulphides* (**2**).—A solution of the appropriate sulphide (**2a**, **c**, **d**, **f**—**h**, **j** and **k**) (0.5 mmol) in 5M-hydrochloric acid–dioxane (1:2) (10 ml) was refluxed for *ca.* 20 min, then cooled to room temperature, treated with 10% aqueous potassium carbonate, and extracted with diethyl ether. Evaporation of the solvent gave the corresponding β-keto sulphide (**5**)[2,11] in *ca.* 90—95% yield. Similar hydrolysis of the 87:13 mixture of (*E*)- and (*Z*)-α-acetoxy-β-phenylthiostyrene (**2i**) gave the β-keto sulphide (**5i**). Similar hydrolysis of the 55:45 mixture of the regioisomeric sulphides (**2e**) and (**2′e**) gave the corresponding β-keto sulphides (**5e**)[2] and (**5**; $R^1$ = Pr, $R^2$ = Me) in about the same ratio and in *ca.* 90% yield.

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