Regio- and stereo-selective additions of sodium selenides to conjugate enyne sulfones: a convenient synthesis of 4-seleno-1-sulfonylbuta-1,3-dienes

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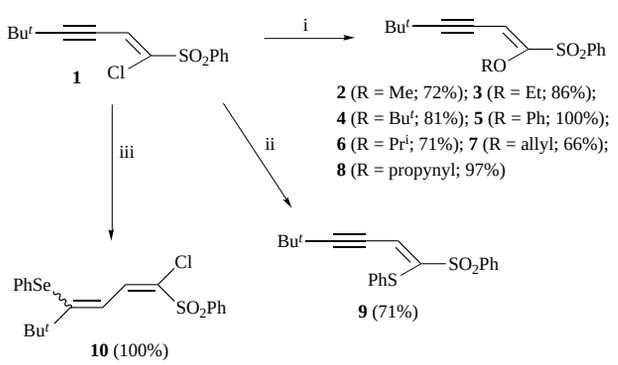
Addition of PhSeNa to the conjugate enyne sulfones 1, 11–18 occurred at the δ-position of the sulfonyl group to give the 4-phenylseleno-1-sulfonylbuta-1,3-dienes 10, 19–22, 24, 25 and 27 regio- and stereo-selectively.

Heteroatom-substituted buta-1,3-dienes have been much studied because of their marked ability to construct highly functionalized ring systems in Diels–Alder reactions.[1] In particular, dienes with two different heteroatoms, *e.g.* oxygen and sulfur,[2] or those with acylamino and sulfur[3] have received much attention because of their excellent reactivity and *endo* stereoselectivity. In contrast, there have been only limited studies of selenium-substituted dienes[4] with a second heteroatom because they are difficult to prepare. Although dienes with selenium and oxygen may be synthesized by the coupling of dienylzirconium and PhSeCl, their light- and heat-sensitivity gives rise to all four possible stereoisomers at room temperature.[5]



Scheme 1 *Reagents:* i, RONa; ii, PhSNa, THF; iii, $(PhSe)_2$, $NaBH_4$, EtOH

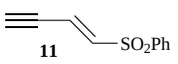
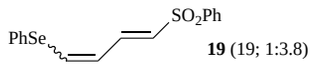
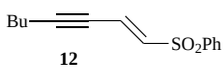
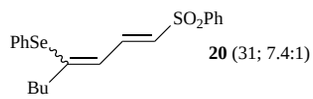
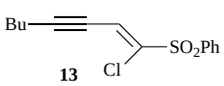
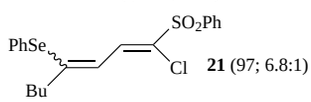
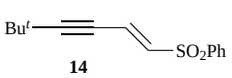
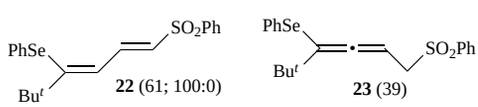
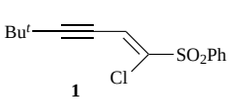
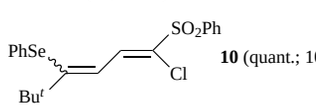
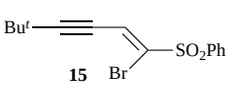
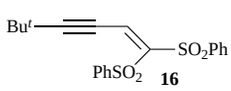
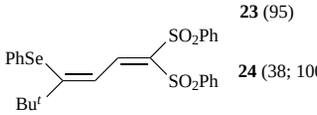
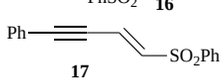
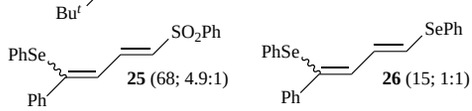
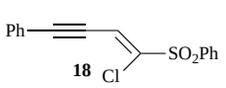
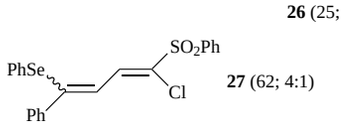
Recently, we reported the regio- and stereo-selective addition of alkoxy anions to conjugate enyne sulfones:[6] thus the α-chloro enyne sulfone **1** reacted with various alkoxides and phenoxide to give the α-alkoxy or α-phenoxy enyne sulfones **2**–**8** in high yields. The reaction of **1** and PhSNa also gave the α-phenylthio enyne sulfone **9**; however, PhSeNa [generated *in situ* from $(PhSe)_2$ and $NaBH_4$ in EtOH] attacked at the δ-position of the sulfonyl group to afford the 4-phenylseleno-1-sulfonylbuta-1,3-diene **10** quantitatively (Scheme 1). This reaction was of particular interest since, if general for conjugate enyne sulfones, it would provide a route to the simple synthesis of selenium- and sulfur-containing 1,3-dienes, compounds for which a general synthesis has not been reported earlier. Here we report such a general synthesis.

First, we examined the reaction of 1-phenylsulfonylbut-1-en-3-yne **11** with $(PhSe)_2$ and $NaBH_4$ in EtOH (Method A described above) to give (1*E*,3*E*)-4-phenylseleno-1-phenylsulfonylbuta-1,3-diene **19** (19% yield) (Table 1, entry 1). Because of the low product yield, we examined the reactions of enyne sulfones with other PhSe· species such as $B(SePh)_3$[7] and $(PhSe)_2$/*hv*;[8] however, product **19** could not be isolated. We also examined the solvent effect on this addition and found that the reaction of **19** with PhSeNa in THF–EtOH (Method B) gave satisfactory results. The stereochemistry of the major isomer (1*E*,3*E*)-**19** was determined by the coupling pattern of 3-H at δ 6.20 (ddd, *J* 15, 11 and 1). The 3-H of the minor isomer (1*E*,3*Z*)-**19** was detected at δ 6.43 (ddd, *J* 11, 9 and 1 Hz).

The butyl-substituted enyne sulfone **12** gave 4-phenylseleno-1-phenylsulfonylbuta-1,3-diene **20** quantitatively (entry 4; Method B) as colourless prisms, the IR, ^{1}H and ^{13}C NMR spectra and elemental analysis of which agreed with the assigned structure. The stereochemistry of **20** was determined as 1*E*,-3*Z* by an NOE experiment. Irradiation of the 5-methylene protons of the major isomer increased the intensity of the 3-olefinic proton (13.3%). This finding shows that product **19** resulted from an *anti*-addition of PhSeNa,[9] with (1*E*, 3*E*)-**19** being formed by the isomerization of (1*E*,3*Z*)-**19**.[5] Similarly, the *tert*-butyl derivative **14** gave (1*E*,3*Z*)-dienyl sulfone **22** stereoselectively, accompanied by the allenyl selenide **23** (entries 6 and 7). Assignment of a structure to the allenyl selenide **23** was made on the basis of IR, mass and NMR spectral evidence. Thus the IR spectrum showed the allenyl group at *ν* 1950 cm^{-1} whilst its mass spectrum showed a molecular ion peak at *m/z* 406 ($C_{20}H_{22}O_2SSe$). The ^{1}H NMR spectrum exhibited a pair of doublets at δ 3.36 (*J* 2 and 7 Hz) due to the 1-CH_2 protons and at δ 4.85 (*J* 7 and 8 Hz) due to the 2-allenic H. The ^{13}C NMR spectrum showed characteristic allenyl carbons at δ 81.94 (d), 111.52 (s) and 201.57 (s) whilst an elemental analysis was satisfactory for structure **23**. α-Chloro enyne sulfones **13**, **1** and **18** gave 1-chloro-4-seleno-1-sulfonylbuta-1,3-dienes **21**, **10** and **27** (entries 5, 8, 14, 15); however, α-bromo enyne sulfones **15** gave no adduct but, rather, a reductive product **14**, accompanied by the allenyl selenide **23** (entry 9). The 1,1-bis(sulfonyl) derivative gave the adduct **24** in low yield.

Phenyl-substituted enyne sulfones **17** and **18** gave the adducts **25** and **27** (1*E*,3*Z*)-selectively (Table 1, entries 12, 14, 15). Although the stereochemistry of the 4-phenylbuta-1,3-dienes could not be determined by NOE experiments, it was possible to assign it on the basis of ^{77}Se NMR spectral evidence (see Table 2). By comparison with the chemical shifts of dienes such as (1*E*,3*Z*)-**19**, **20**, **21**, **22**, (1*E*,3*E*)-**21**, **22** and Fryzuk's compounds[5], those of the 3*Z*-dienes were observed to be shifted to higher field than those of the 3*E*-derivatives. The ^{77}Se NMR spectrum of the 4-phenyl-substituted compound **25** exhibited two signals at δ 335.54 (1*E*,3*Z*) and 450.95 (1*E*,3*E*), a result which shows that although Ph-substituted enyne sulfones also mainly gave the (1*E*, 3*Z*)-isomer, compound **25** (3*Z*:3*E* = 4.9:1) was easily isomerized. Thus, when a solution of compound **25** in $CDCl_3$ was stored in an NMR tube for 1 week at room temperature its isomer ratio changed from 3*Z*:3*E* = 4.9:1 to 1:4.3. Isomerization of the diene **21** was also observed. (*E*)-1-Chloro-4-phenyl-1-phenylsulfonylbut-1-en-3-yne **18** gave (1*E*,3*Z*)-**27** stereoselectively (Table 1, entry 15).

Table 1 Reaction of conjugate enyne sulfones with PhSeNa

Entry	Enyne sulfone	Method	Products (% yields; 1*E*,3*Z* : 1*E*,3*E*)
1	 **11**	A	 **19** (19; 1:3.8)
2	**11**	B	**19** (53; 1:6)
3	 **12**	A	 **20** (31; 7.4:1)
4	**12**	B	**20** (quant.; 12:1)
5	 **13**	A	 **21** (97; 6.8:1)
6	 **14**	A	 **22** (61; 100:0) **23** (39)
7	**14**	B	**22** (32; 100:0) **23** (60)
8	 **1**	A	 **10** (quant.; 10:3)
9	 **15**	A	**14** (33) **23** (32)
10	**15**	B	**23** (95)
11	 **16**	A	 **24** (38; 100:0)
12	 **17**	B	 **25** (68; 4.9:1) **26** (15; 1:1)
13	**17**	C	**26** (25; 3:1)
14	 **18**	A	 **27** (62; 4:1)
15	**18**	B	**27** (83; 100:0)

Method A: 0.5 equiv. $(PhSe)_2$, $NaBH_4$, EtOH, 0 °C; Method B: 0.5 equiv. $(PhSe)_2$, $NaBH_4$, THF–EtOH, room temp., 10 min; Method C: 1.0 equiv. $(PhSe)_2$, $NaBH_4$, THF–EtOH, room temp., 1 h

Table 2 ^{77}Se NMR Chemical shifts for δ-seleno dienyl sulfones

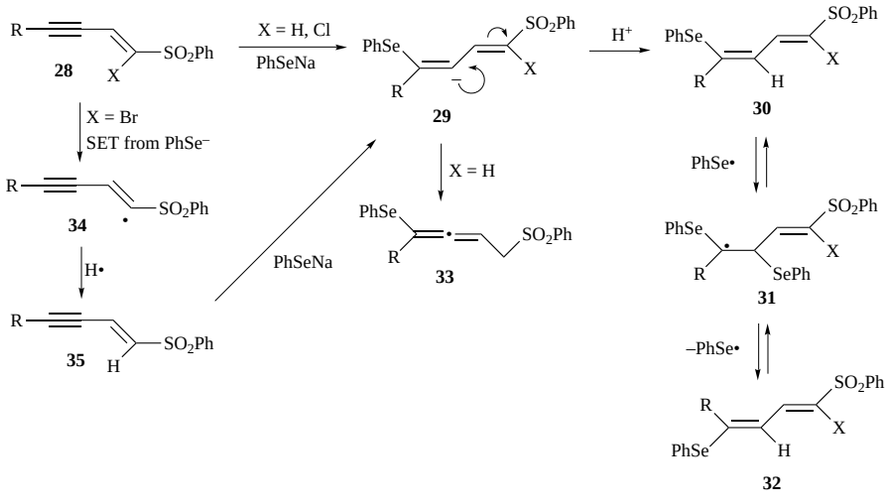
	^{77}Se δ(ppm)		
Dienyl sulfone	(1*E*,3*Z*)	(1*E*,3*E*)	Isomer ratio
19	340.02	377.25	1:6
20	333.50	—	100:0
21	346.02	430.48	6.8:1
22	265.04	—	100:0
25	335.54	450.95	4.9:1
27	346.30	—	4:1

Plausible mechanisms for these reactions are shown in Scheme 2. Addition of PhSeNa to alkynes proceeds with predominant *Z*-stereochemistry to afford the δ-selenobuta-1,3-dienes **30**; however, the dienyl selenides easily undergo thermal or photo-isomerization,[5] the mechanism of which has been discussed by Fryzuk *et al.*[5] It has been shown to be a radical chain process involving the formation and addition of PhSe radicals to the diene **30** to give the α,β-diselenenyl radical **31**. The radical **31** (R = Bu^t) affords the less hindered product **30**, not **32**, exclusively (Table 1; entry 6, 8, 11). However, **31** (R = H) easily isomerized under the reaction condition to give the more stable diene **32** described above. The isomerization of the diene **30** (R = Ph) also occurred because of the stabilization of the benzyl radical of the intermediate **31** (R = Ph). Isomerization of the butadienyl anion **29** to the sulfonyl-stabilized carbanion followed by protonation gives the allenyl selenide **33**. The SET reduction of the enyne sulfone **28** (X = Br) from $PhSe^-$ gives the enyne sulfone **35** *via* a vinyl radical **34**.[10] Substitution of the sulfonyl group was observed in entry 12 (Table 1), so that we performed the reaction of **17** under the conditions of Method C (2 mol of PhSeNa, THF, EtOH); however, 1,4-bis(phenylseleno)buta-1,3-diene in only 25% yield (entry 13) was obtained. The mechanistic details of the regioselectivity in this addition reaction of PhSeNa to the conjugate enyne sulfones could not be elucidated; however, the *δ*-addition of PhSeNa probably occurs *via* a radical intermediate.[11]

We are now examining the Diels–Alder reactions of these dienes with selenium and sulfone. These results will be reported elsewhere.

Experimental

Mps were determined on Yanagimoto micro melting point apparatus and are uncorrected. Elemental analyses were per-



Scheme 2

formed at the Microanalytical Laboratory of Gifu Pharmaceutical University. ^{1}H and ^{13}C NMR spectra were determined with a JEOL GX-270 (270 MHz) spectrometer and a Varian Gemini 2000 (200 MHz) spectrometer at the Center of Instrumentation of Gifu University. Chemical shifts (δ) are expressed in parts per million (ppm) with respect to tetramethylsilane as an internal standard. Splitting patterns are designated as follows: s = singlet, d = doublet, t = triplet, q = quartet. *J* Values are given in Hz. IR spectra of solids (KBr) and liquids (film) were recorded on a JASCO IR A-100 infrared spectrometer. EI Mass spectra (MS) were obtained using a JMS-SX102A spectrometer with a direct-insertion probe at an ionization voltage of 70 eV.

Preparation of conjugate enyne sulfones: 1, 11–18: typical procedure

(*E*)-1-Phenylsulfonylbut-1-en-3-yne 11. A benzene (50 cm^3) solution of methyl phenyl sulfone (9.64 g, 61.7 mmol) was added dropwise to a diethyl ether (50 cm^3) solution of EtMgBr [prepared from EtBr (10.1 g, 92.5 mmol) and Mg (2.25 g, 92.5 mmol)] at 0 °C. A benzene (30 cm^3) solution of propynal (5.0 g, 92.5 mmol) was then added dropwise to the reaction mixture at room temperature. After this the mixture was poured into water (500 cm^3), the organic layer was separated and the aqueous layer was extracted with diethyl ether. The organic layer and the extracts were combined, dried ($MgSO_4$) and evaporated. The residue was used without further purification. A dry CH_2Cl_2 (20 cm^3) solution of the residue and CH_3SO_2Cl (14.14 g, 123.4 mmol) and Et_3N (12.49 g, 123.4 mmol) was stirred at room temperature for 4 h after which it was poured into water. The organic layer was separated and the aqueous layer was extracted with $CHCl_3$. The organic layer and the extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by column chromatography on silica gel eluting with AcOEt–hexane (1:5) to give (*E*)-1-phenylsulfonylbut-1-en-3-yne **11** (2.82 g, 12%) as a yellow oil; ν_{max}/cm^{-1} 3250, 2100 (acetylene) and 1310 and 1140 (SO_2); δ_H(270 MHz, $CDCl_3$) 3.47 (1 H, d, *J* 2, acetylenic H), 6.74 (1 H, dd, *J* 2 and 15, olefinic H), 6.82 (1 H, d, *J* 15, olefinic H), 7.28–7.69 (3 H, m, ArH) and 7.87–7.91 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 77.55 (d), 88.61 (s), 122.16 (d), 127.90 (d × 2), 129.46 (d × 2), 133.90 (d), 139.31 (s) and 141.16 (s) (Found: M$^+$, 192.0258. $C_{10}H_8O_2S$ requires *M*, 192.0245).

(*E*)-1-Chloro-5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne 1. Yield 49%, mp 70–74 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1340, 1350 and 1160 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.28 (9 H, d, *J* 1, Bu^t), 7.12 (1 H, d, *J* 1, olefinic H), 7.26–7.68 (3 H, m, ArH) and 7.92–7.97 (2 H, m, ArH) (Found: C, 59.19; H, 5.32. $C_{14}H_{15}ClO_2S$ requires C, 59.46; H, 5.35%).

(*E*)-1-Phenylsulfonyloct-1-en-3-yne 12. Yield 70%; ν_{max}/cm^{-1} 2225 (acetylene) and 1300 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.90 (3 H, t, *J* 7, Me), 1.35–1.55 (4 H, m, CH_2CH_2), 2.37 (2 H, td, *J* 7 and 3, 5-H), 6.61 (1 H, d, *J* 15, 1-H), 6.78 (1 H, dt, *J* 15 and 3, 2-H), 7.50–7.66 (3 H, m, ArH) and 7.86–7.89 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 13.36 (q), 19.32 (t), 21.77 (t), 29.98 (t), 75.34 (d), 103.88 (s), 124.40 (d), 127.62 (d × 2), 129.25 (d × 2), 133.47 (d), 137.64 (d) and 139.89 (s) (Found: C, 67.62; H, 6.57. $C_{14}H_{16}O_2S$ requires C, 67.71; H, 6.49%).

(*E*)-1-Chloro-1-phenylsulfonyloct-1-en-3-yne 13. Yield 50%, yellow oil; ν_{max}/cm^{-1} 2200 (acetylene) and 1320 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.91 (3 H, t, *J* 7, CH_3), 1.41–1.65 (4 H, m, CH_2), 2.44 (2 H, dt, *J* 2 and 7, CH_2), 7.12 (1 H, t, *J* 2, olefinic H), 7.27–7.60 (2 H, m, ArH), 7.64–7.71 (1 H, m, ArH) and 7.92–8.01 (2 H, m, ArH) (Found: M$^+$, 282.0495. $C_{14}H_{15}ClO_2S$ requires *M*, 282.0482).

(*E*)-5,5-Dimethyl-1-phenylsulfonylhex-1-en-3-yne 14. Yield 57%, colourless prisms; mp 92–94 °C; ν_{max}/cm^{-1} 2250 (acetylene) and 1325 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.23 (9 H, s, Me), 6.59 (1 H, d, *J* 15, olefinic H), 6.78 (1 H, d, *J* 15, olefinic H) and 7.54–7.89 (5 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.39 (s), 30.33 (q × 3), 74.07 (s), 111.46 (s), 124.48 (d), 127.75 (d × 2), 129.32 (d × 2), 133.51 (d), 137.57 (d) and 140.06 (s); *m/z* 248 (M$^+$) and 91 (Found: C, 67.90; H, 6.55. $C_{14}H_{16}O_2S$ requires C, 67.71; H, 6.49%).

(*E*)-1-Bromo-5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne 15. Yield 52%, colourless prisms, mp 64–65 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1325 and 1350 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.28 (9 H, s, Me), 7.40 (1 H, s, olefinic H), 7.54–7.69 (3 H, m, ArH) and 7.93–7.95 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.8 (s), 30.3 (q × 3), 74.5 (s), 116.2 (s), 124.4 (d), 129.0 (d × 2), 129.2 (d × 2), 130.5 (s), 134.1 (d) and 137.1 (s); *m/z* 326 (M$^+$) and 241 (Found: C, 51.54; H, 4.65. $C_{14}H_{15}BrO_2S$ requires C, 51.39; H, 4.60%).

1,1-Bis(phenylsulfonyl)-5,5-dimethylhex-1-en-3-yne 16

A THF (5 cm^3) solution of bis(phenylsulfonyl)methane (2.1 g, 7.1 mmol) was added dropwise to a THF (10 cm^3) solution of LDA [prepared from diisopropylamine (1.36 g, 13.5 mmol) and BuLi (6.7 cm^3, 10.1 mmol)] at −78 °C. The reaction mixture was stirred for 10 min after which a THF (5 cm^3) solution of 4,4-dimethylpent-2-ynal (1.17 g, 10.7 mmol) was added dropwise to it. The mixture was then treated in a similar way to the procedure described above. Compound **16**: yield 73%, colourless prisms, mp 160–161 °C; ν_{max}/cm^{-1} 2200 (acetylene) and 1350 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.35 (9 H, s, CH_3 × 3), 7.27 (1 H, s, olefinic H), 7.49–7.68 (6 H, m, ArH) and 7.99–8.09 (4 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 29.4 (s), 29.8 (q × 3), 60.3 (s), 74.1 (s), 128.4 (d × 2), 128.8 (d × 2), 129.0 (d × 2), 129.0 (d × 2), 134.0 (d), 134.1 (d), 134.2 (d), 139.5 (s), 140.4 (s) and 149.6 (s); *m/z* 388 (M$^+$) and 77 (base) (Found: C, 61.72; H, 5.22. $C_{20}H_{20}O_4S_2$ requires C, 61.83; H, 5.19%).

(*E*)-4-Phenyl-1-phenylsulfonylbut-1-en-3-yne 17. Yield 25%, colourless needles, mp 71–72 °C; ν_{max}/cm^{-1} 2150 (acetylene) and 1300 and 1150 (SO_2); δ_H(270 MHz, $CDCl_3$) 6.77 (1 H, d, *J* 15, olefinic H), 7.01 (1 H, d, *J* 15, olefinic H), 7.29–7.65 (8 H, m, ArH) and 7.89–7.92 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 83.57 (s), 100.85 (s), 121.26 (s), 123.25 (s), 127.66 (d × 2), 128.41 (d × 2), 129.30 (d × 2), 129.71 (d), 131.88 (d × 2), 132.60 (d), 138.23 (d) and 139.64 (s); *m/z* 268 (M^+) and 126 (Found: C, 71.67; H, 4.57. $C_{16}H_{12}O_2S$ requires C, 71.62; H, 4.51%).

(*E*)-1-Chloro-4-phenyl-1-phenylsulfonylbut-1-en-3-yne 18. Yield 32%; mp 107–110 °C; ν_{max}/cm^{-1} 2210 (acetylene), 1320, 1340 and 1170 (SO_2); δ_H(270 MHz, $CDCl_3$) 6.61 (1 H, s, olefinic H), 7.31–7.71 (5 H, m, ArH) and 7.95–8.08 (5 H, m, ArH) (Found: C, 63.23; H, 3.72. $C_{16}H_{11}ClO_2S$ requires C, 63.47; H, 3.66%).

Reactions of α-chloro enyne sulfone 1 with alkoxides: typical procedure

A solution of MeONa (1 M NaOMe in MeOH; 1.0 mmol, 2 cm^3) was added dropwise to a MeOH (1 cm^3) solution of (*E*)-1-chloro-5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne **1** (0.14 g, 0.5 mmol) at 0 °C after which the mixture was evaporated under reduced pressure. The residue was poured into water (100 cm^3) and extracted with diethyl ether. The extracts were dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1:10) to give (*E*)-5,5-dimethyl-1-methoxy-1-phenylsulfonylhex-1-en-3-yne **2** (0.10 g, 72%) as colourless prisms; mp 76–79 °C; ν_{max}/cm^{-1} 2210 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.24 (9 H, s, Bu^t), 4.00 (3 H, s, OCH_3), 6.29 (1 H, s, olefinic H), 7.51–7.67 (3 H, m, ArH) and 7.85–7.93 (2 H, m, ArH) (Found: C, 64.53; H, 6.56. $C_{15}H_{18}O_3S$ requires C, 64.72; H, 6.52%).

(*E*)-5,5-Dimethyl-1-ethoxy-1-phenylsulfonylhex-1-en-3-yne 3. ν_{max}/cm^{-1} 2210 (acetylene) and 1340 and 1165 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.22 (3 H, t, *J* 7, CH_3), 1.24 (9 H, s, Bu^t), 4.30–4.38 (2 H, q, *J* 7, OCH_2), 6.29 (1 H, s, olefinic H), 7.50–7.66 (3 H, m, ArH) and 7.89–7.92 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 15.03 (q), 28.43 (s), 30.35 (q × 3), 70.66 (t), 71.61 (s), 99.44 (d), 110.54 (s), 128.60 (d × 2), 128.93 (d × 2), 133.64 (d), 138.15 (s) and 159.71 (s) (Found: M^+, 292.1154. $C_{16}H_{20}O_3S$ requires *M*, 292.1133).

(*E*)-5,5-Dimethyl-1-*tert*-butoxy-1-phenylsulfonylhex-1-en-3-yne 4. ν_{max}/cm^{-1} 2210 (acetylene) and 1350 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.19 (9 H, s, Bu^t), 1.48 (9 H, s, OBu^t), 6.54 (1 H, s, olefinic H), 7.42–7.54 (3 H, m, ArH) and 7.80–7.83 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.37 (s), 28.89 (q × 3), 29.60 (s), 30.35 (q × 3), 73.44 (s), 107.00 (d), 110.34 (s), 128.54 (d × 2), 128.80 (d × 2), 133.36 (d), 138.46 (s) and 157.82 (s); *m/z* 320 (small M^+) (Found: C, 66.46; H, 7.51. $C_{18}H_{24}O_3S$ requires C, 67.47; H, 7.55%).

(*E*)-5,5-Dimethyl-1-phenoxy-1-phenylsulfonylhex-1-en-3-yne 5. ν_{max}/cm^{-1} 2210 (acetylene) and 1320 and 1170 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.93 (9 H, s, Bu^t), 6.12 (1 H, s, olefinic H), 6.78–6.90 (3 H, m, ArH), 7.14–7.27 (3 H, m, ArH), 7.54–7.57 (2 H, m, ArH) and 8.01–8.05 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 27.68 (s), 29.38 (q × 3), 71.17 (s), 109.67 (s), 115.30 (d), 119.89 (d), 120.82 (d), 121.08 (d), 125.48 (d), 127.00 (d), 127.79 (d), 128.59 (d), 128.89 (d), 129.29 (d), 133.00 (d), 141.98 (s), 145.81 (s), 153.96 (s) (Found: M^+, 340.1117. $C_{20}H_{20}O_3S$ requires *M*, 340.1133).

(*Z*)-5,5-Dimethyl-1-phenoxy-1-phenylsulfonylhex-1-en-3-yne 5′. ν_{max}/cm^{-1} 2210 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 0.92 (9 H, s, Bu^t), 6.63 (1 H, s, olefinic H), 6.82–7.04 (3 H, m, ArH), 7.19–7.26 (2 H, m, ArH), 7.50–7.67 (3 H, m, ArH) and 7.96–7.97 (2 H, m, ArH) (Found: M^+, 340.1149. $C_{20}H_{20}O_3S$ requires *M*, 340.1133).

(*E*)-5,5-Dimethyl-1-isopropoxy-1-phenylsulfonylhex-1-en-3-yne 6. Mp 43–48 °C; ν_{max}/cm^{-1} 2210 (acetyene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.18 (6 H, d, *J* 6, CH_3), 1.23 (9 H, s, Bu^t), 5.04–5.13 (1 H, m, OCH), 6.29 (1 H, s, olefinic H), 7.49–7.65 (3 H, m, ArH) and 7.88–7.91 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 22.52 (q × 2), 28.79 (s), 30.77 (q × 3), 72.35 (s), 77.78 (d), 99.11 (d), 110.47 (s), 129.09 (d × 2), 129.20 (d × 2), 133.93 (d), 138.47 (s) and 158.88 (s) (Found: C, 66.46; H, 7.27. $C_{17}H_{22}O_3S$ requires C, 66.64; H, 7.24%).

(*E*)-1-Allyloxy-5,5-dimethyl-1-phenylsulfonylhex-1-en-3-yne 7. ν_{max}/cm^{-1} 2210 (acetylene) and 1340 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.24 (9 H, s, Bu^t), 4.75–4.77 (2 H, br d, *J* 6, OCH_2), 5.11–5.29 (2 H, m, olefinic H), 5.74–5.81 (1 H, m, olefinic H), 6.34 (1 H, s, olefinic H), 7.50–7.66 (3 H, m, ArH) and 7.89–7.93 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 30.41 (q × 3), 37.87 (s), 71.68 (s), 74.97 (t), 100.78 (d), 117.67 (s), 119.15 (t), 128.76 (d × 2), 129.00 (d × 2), 132.01 (d), 133.73 (d), 133.99 (s) and 159.94 (s); *m/z* 304 (small M^+). A small M^+ peak was observed but was too small for the high-resolution mass spectrum to be measured.

(*E*)-5,5-Dimethyl-1-phenylsulfonylprop-1-ynyloxyhex-1-en-3-yne 8. ν_{max}/cm^{-1} 2210 (acetylene) and 1330 and 1170 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.25 (9 H, s, Bu^t), 2.45 (1 H, t, *J* 2, acetylenic H), 4.91–4.92 (2 H, d, *J* 2, OCH_2), 6.42 (1 H, s, olefinic H), 7.50–7.56 (3 H, m, ArH) and 7.90–7.93 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.47 (s), 30.19 (q × 3), 61.25 (t), 70.11 (s), 76.52 (s), 76.67 (d), 102.10 (d), 112.32 (s), 128.71 (d × 2), 128.96 (d × 2), 133.79 (d), 137.67 (s) and 158.47 (s); *m/z* 302 (small M^+) (Found: C, 65.59; H, 6.00. $C_{17}H_{18}O_3S$ requires C, 67.52; H, 6.00%).

(*E*)-5,5-Dimethyl-1-phenylsulfonyl-1-phenylthiohex-1-en-3-yne 9. Colourless needles, mp 113–115 °C; ν_{max}/cm^{-1} 2210 (acetylene) and 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.08 (9 H, s, Bu^t), 7.04–7.32 (5 H, m, ArH), 7.45 (1 H, s, olefinic H), 7.47–7.61 (3 H, m, ArH) and 7.92–7.95 (2 H, m, ArH); δ_C(67.5 MHz, $CDCl_3$) 28.85 (s), 30.02 (q × 3), 74.76 (s), 119.70 (s), 127.03 (d), 128.77 (d × 2), 128.98 (d × 2), 129.34 (d × 2), 130.04 (d), 130.10 (d), 133.63 (d × 2) and 138.29 (s) (Found: C, 67.34; H, 5.65. $C_{20}H_{20}O_2S_2$ requires C, 67.38; H, 5.65%).

Reaction of enyne sulfones 1, 11–18 with PhSeNa: typical procedure by method A

An EtOH (3 cm^3) solution of PhSeNa [generated *in situ* from $(PhSe)_2$ (94 mg, 0.3 mmol) and $NaBH_4$ (23 mg, 0.6 mmol)] was added dropwise to an EtOH (2 cm^3) solution of 1-phenylsulfonylbut-1-en-3-yne **11** (96 mg, 0.5 mmol) at 0 °C. The reaction mixture was stirred for 10 min after which it was evaporated under reduced pressure. The residue was poured into water (100 cm^3) and extracted with diethyl ether. The extracts were combined, dried ($MgSO_4$) and evaporated under reduced pressure. The residue was purified by preparative TLC on silica gel eluting with AcOEt–hexane (1:20) to give (1*E*,3*Z*)- and (1*E*,- 3*E*)-4-phenylseleno-1-phenylsulfonylbut-1-en-3-yne **19** (34 mg, 19%) [(1*E*,3*Z*): (1*E*,3*E*) = 1:3.8] as a pale yellow oil. The isomer ratio was determined from the 1-H intensities in the ^{1}H NMR spectrum. Methods B and C were conducted as follows. An EtOH solution of PhSeNa was added dropwise to a THF (3 cm^3) solution of the enyne sulfone **11** (0.5 mmol) at 0 °C. Subsequent work-up was then almost identical with that described above; ν_{max}/cm^{-1} 1320 and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 6.13 (dd, *J* 15 and 1, 3*E*-1-H), 6.20 (ddd, *J* 15 and 11 and 1, 3*E*-3-H), 6.43 (br d, *J* 15, 3*Z*-1-H), 6.55 (ddd, *J* 11 and 9 and 1, 3*Z*-3-H), 7.22 (ddd, *J* 15 and 11 and 1, 3*E*-2-H), 7.28–7.62 (m, olefinic and ArH) and 7.82–7.90 (m, ArH) (Found: M^+, 349.9889. $C_{16}H_{14}O_2SSe$ requires *M*, 349.9879).

(1*E*,3*Z*)- and (1*E*,3*E*)-4-Phenylseleno-1-phenylsulfonylocta-1,3-diene 20. 3*Z*:3*E* = 12:1, mp 45–47 °C; ν_{max}/cm^{-1} 1320 and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 0.78 (t, *J* 7, 3*Z*-Me), 1.08–1.28 (m, alkyl H), 1.35–1.63 (m, alkyl H), 2.27 (br t, *J* 7, 3*Z*-5-CH_2), 2.57 (t, *J* 7, 3*E*-5-CH_2), 5.84 (d, *J* 9, 3*E*-3-olefinic H), 6.01 (d, *J* 14, 3*E*-1-olefinic H), 6.39 (br d, *J* 15, 3*Z*-1-olefinic H), 6.41 (br d, *J* 10, 3*Z*-3-olefinic H), 7.24–7.40 (m, ArH), 7.44–7.62 (m, ArH), 7.81 (dd, *J* 15 and 10, 3*Z*-2-olefinic H) and 7.84–7.91 (m,

ArH); δ_C of 3*Z*-isomer (50 MHz, $CDCl_3$) 13.53 (q), 21.62 (t), 30.93 (t), 38.97 (t), 126.53 (d), 127.42 (d × 2), 128.03 (d), 128.12 (d), 129.12 (d × 2), 129.24 (d), 129.48 (d), 129.60 (d), 133.08 (d), 134.23 (d), 139.66 (d), 140.77 (s) and 152.67 (s) (Found: C, 59.03; H, 5.44. $C_{20}H_{22}O_2SSe$ requires C, 59.25; H, 5.47%). The isomer ratio was determined from the intensities of 5-CH_2 in the ^{1}H NMR spectrum.

(1*E*,3*Z*)- and (1*E*,3*E*)-1-Chloro-4-phenylseleno-1-phenylsulfonylocta-1,3-diene 21. (1*E*,3*Z*):(1*E*,3*E*) = 6.8:1; ν_{max}/cm^{-1} 1330 and 1160 (SO_2); δ_H(200 MHz, $CDCl_3$) 0.79 (t, *J* 7, 3*Z*-Me), 0.94 (t, *J* 7, 3*E*-Me), 1.10–1.28 (m, alkyl H), 1.35–1.59 (m, alkyl H), 2.32 (t, *J* 7, 3*Z*-5-CH_2), 2.60 (t, *J* 7, 3*E*-5-CH_2), 6.05 (d, *J* 11, 3*E*-3-olefinic H), 6.56 (dt, *J* 10 and 1, 3*Z*-3-olefinic H), 7.27–7.40 (m, ArH), 7.47–7.69 (m, ArH), 7.87–8.00 (m, ArH) and 8.13 (d, *J* 10, 3*Z*-2-H) (Found: M^+, 440.0125. $C_{20}H_{21}ClO_2SSe$ requires *M*, 440.0116). The isomer ratio was determined from the intensities of the 3*Z*- and 3*E*-olefinic H.

(1*E*,3*Z*)-5,5-Dimethyl-4-phenylseleno-1-phenylsulfonylbuta-1,3-diene 22. Mp 119–124 °C; ν_{max}/cm^{-1} 1320 and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.25 (9 H, s, Me), 6.34 (1 H, dd, *J* 15 and 1, 1-olefinic H), 6.58 (1 H, dd, *J* 11 and 1, 3-olefinic H), 7.20–7.58 (8 H, m, ArH), 7.69 (1 H, dd, *J* 11 and 15, 2-olefinic H), 7.79–7.80 (2 H, m, ArH); *m/z* 406 (small M^+) and 265 (Found: C, 58.80; H, 5.44. $C_{20}H_{22}O_2SSe$ requires C, 59.25; H, 5.47%).

5,5-Dimethyl-4-phenylseleno-1-phenylsulfonylhexa-2,3-diene 23. Mp 47–49 °C; ν_{max}/cm^{-1} 1950 (allene), 1320, 1310, 1350 and 1340 (SO_2); δ_H(200 MHz, $CDCl_3$) 1.01 (9 H, s, Me), 3.36 (2 H, dd, *J* 2 and 7, 1-CH_2), 4.85 (1 H, dd, *J* 7 and 8, 2-H), 7.21–7.29 (3 H, m, ArH), 7.38–7.62 (5 H, m, ArH) and 7.79–7.84 (2 H, m, ArH); δ_C(50 MHz, $CDCl_3$) 29.23 (q × 3), 36.00 (s), 56.57 (t), 81.94 (d), 111.52 (s), 127.76 (d), 128.26 (d × 2), 128.93 (d × 2), 129.13 (d × 2), 130.60 (s), 133.63 (d), 134.37 (d), 135.27 (d), 138.28 (s) and 201.57 (s); *m/z* 406 (M^+), 265 (Found: C, 59.04; H, 5.44. $C_{20}H_{22}O_2SSe$ requires C, 59.25; H, 5.47%).

(1*E*,3*Z*)- and (1*E*,3*E*)-1-Chloro-5,5-dimethyl-4-phenylseleno-1-phenylsulfonylhexa-1,3-diene 10. (1*E*,3*Z*):(1*E*,3*E*) = 10:3; mp 79–83 °C; ν_{max}/cm^{-1} 1330 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.29 (s, 3*Z*-Bu^t), 1.46 (s, 3*E*-Bu^t), 5.82 (d, *J* 12, 3*E*-olefinic H), 6.75 (d, *J* 10, 3*Z*-olefinic H), 7.23–7.26 (m, ArH), 7.36–7.60 (m, ArH), 7.98 (d, *J* 12, 3*E*-olefinic H) and 8.00 (d, *J* 10, 3*Z*-olefinic H); δ_C(67.5 MHz, $CDCl_3$) 27.71 (q × 3), 38.33 (s), 98.80 (d), 106.61 (d), 115.05 (d), 115.27 (d), 120.88 (d), 121.52 (d), 125.88 (d), 126.91 (d), 128.82 (d), 129.40 (d), 129.51 (d), 129.70 (d), 151.88 (s), 157.86 (s), 164.87 (s) and 168.09 (s); *m/z* 440 (M^+) (Found: C, 54.33; H, 4.79. $C_{20}H_{21}ClO_2SSe$ requires C, 54.61; H, 4.81%). The isomer ratio was determined from the intensities of the 3*Z*- and 3*E*-3-olefinic H.

(*Z*)-1,1-Bis(phenylsulfonyl)-5,5-dimethyl-4-phenylselenohexa-1,3-diene 24. Mp 133–138 °C; ν_{max}/cm^{-1} 1340, 1320 and 1160 (SO_2); δ_H(270 MHz, $CDCl_3$) 1.35 (9 H, s, Bu^t), 6.80 (1 H, d, *J* 13, 3-olefinic H), 7.08–7.75 (11 H, m, ArH), 7.83–8.04 (4 H, m, ArH) and 8.53 (1 H, dd, *J* 13 and 1, 2-olefinic H); *m/z* 405 ($M^+ - PhSO_2$) (Found: C, 57.06; H, 4.84. $C_{26}H_{26}O_4S_2Se$ requires C, 57.24; H, 4.80%).

(1*E*,3*Z*)- and (1*E*,3*E*)-4-Phenyl-1-phenylsulfonyl-4-phenylselenobuta-1,3-diene 25. (1*E*,3*Z*):(1*E*,3*E*) = 4.9:1; mp 106–110 °C; ν_{max}/cm^{-1} 1600, 1320 and 1150 (SO_2); δ_H(200 MHz, $CDCl_3$) 6.02 (d, *J* 11, 3*E*-3-olefinic H), 6.07 (d, *J* 15, 3*E*-1-olefinic H), 6.53 (d, *J* 15, 3*Z*-1-olefinic H), 6.75 (d, *J* 11, 3*Z*-3-olefinic H), 7.02–7.70 (m, ArH), 7.74–7.91 (m, ArH) and 8.01 (dd, *J* 11 and 15, 3*Z*-2-olefinic H); δ_C of 3*Z*-isomer (50 MHz, $CDCl_3$) 127.21 (d), 127.58 (d × 2), 128.29 (d), 128.63 (d), 129.03 (d), 129.07 (d × 2), 129.07 (d × 2), 129.23 (d), 129.28 (d), 129.71 (d), 131.55 (d), 132.37 (d), 133.25 (d), 136.21 (d), 139.71 (s), 140.01 (d), 140.65 (s) and 149.18 (s) (Found: C, 61.66; H, 4.24. $C_{22}H_{18}O_2SSe$ requires C, 62.12; H, 4.26%). The isomer ratio was determined from the intensities of the 3-olefinic H in the ^{1}H NMR spectrum.

(1*E*,3*Z*)- and (1*E*,3*E*)-1,4-Bis(phenylseleno)-4-phenylbuta-1,3-diene 26. (1*E*,3*Z*):(1*E*,3*E*) = 3.0:1; a pale yellow oil; ν_{max}/cm^{-1} 1480, 1440 and 740; δ_H(200 MHz, $CDCl_3$) 4.96 (dd, *J* 10 and 1, 3*Z*-3-olefinic H), 5.38 (dd, *J* 10 and 1, 3*E*-3-olefinic H), 5.59 (dd, *J* 15 and 1, 3*Z*-1-olefinic H), 5.85 (dd, *J* 15 and 1, 3*E*-1-olefinic H), 6.23 (ddd, *J* 15 and 10 and 1, 3*Z*-2-olefinic H), 6.91–7.34 (11 H, m, ArH) and 7.47–7.53 (4 H, m, ArH); δ_C of 3*Z*-isomer (50 MHz, $CDCl_3$) 117.80 (d), 126.32 (d), 127.28 (d × 2), 128.31 (d × 2), 128.63 (d), 128.91 (d), 129.30 (d × 2), 129.42 (d × 2), 129.83 (d × 2), 134.37 (d), 135.78 (d), 135.55 (s), 136.65 (d × 2), 136.09 (s) and 153.55 (s) (Found: C, 60.29; H, 4.38. $C_{22}H_{18}Se_2$ requires C, 60.01; H, 4.12%). The isomer ratio was determined from the intensities for the 1-olefinic H in the ^{1}H NMR spectrum.

(1*E*,3*Z*)- and (1*E*,3*E*)-1-Chloro-4-phenyl-1-phenylsulfonyl-4-phenylselenobuta-1,3-diene 27. (1*E*,3*Z*):(1*E*,3*E*) = 4:1; mp 79–83 °C; ν_{max}/cm^{-1} 1600, 1580, 1320 and 1160; δ_H(200 MHz, $CDCl_3$) 6.25 (d, *J* 11, 3*E*-olefinic H), 6.91 (d, *J* 11, 3*Z*-olefinic H), 7.11–7.94 (m, ArH and 3*E*-2-olefinic H) and 8.33 (d, *J* 11, 3*Z*-2-olefinic H) (Found: C, 57.25; H, 3.78. $C_{22}H_{17}ClO_2SSe$ requires C, 57.46; H, 3.73%). The isomer ratio was determined from the intensities of the 3-olefinic H in the ^{1}H NMR spectrum.

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