Boron Trifluoride-promoted Reaction of 4'-Nitrobenzenesulphenanilide with Alkynes. Formal Addition of Benzenesulphenyl Fluoride to Carbon–Carbon Triple Bonds

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The BF_3-promoted reaction of 4'-nitrobenzenesulphenanilide with simple alkyl- and aryl-alkynes at 80 °C in the presence of tetrabutylammonium tetrafluoroborate provides a one-pot synthetic route to β-fluorovinyl sulphides *via* a formal regioselective and *trans*-stereospecific addition of benzenesulphenyl fluoride towards carbon–carbon triple bonds.

In a previous paper [1] we showed that, at room temperature, the BF_3-promoted reaction of 4'-nitrobenzenesulphenanilide (NBSA) with aryl-substituted alkynes in non-nucleophilic solvents generally led to the bis-sulphides (**2**) and sulphimides (**6**) in addition to the disulphide (**3**) and the aniline (**4**). With alkyl-substituted alkynes this reaction afforded, besides compounds (**3**) and (**4**), (*E*)-β-fluorovinyl sulphides (**1**) in low yield, along with minor amounts of compounds (**2**) and (**6**). The occurrence of compounds (**1**), (**2**), and (**6**) was ascribed to thiirenium ions intermediates (**5**), produced by phenylthio transfer from an NBSA·BF_3 complex to the alkyne triple bond. Capture of thiirenium ions (**5**) by the disulphide (**3**) and NBSA would give the adducts (**2**) and (**6**), respectively, whereas attack of a fluorine atom of the fluoroborate counterion [$O_2NC_6H_4NHBF_3^-$] would lead to the (*E*)-fluorovinyl sulphides (**1**) (Scheme). The different reactivity encountered with alkyl- and aryl-thiirenium ions was attributed to a lower steric hindrance for nucleophilic attack at an aryl-substituted ring carbon with respect to an alkyl-substituted one. Thus, aryl-substituted thiirenium ions showed a definite preference for reaction with sulphur nucleophiles, whereas the alkyl-substituted analogues showed a tendency to attack a smaller, though weaker, nucleophile such as a fluoroborate fluorine atom.

These findings prompted us to undertake a study of the reaction of NBSA with simple alkynes under various experimental conditions, in the hope of providing a practicable synthetic route for the fluorosulphenylation of alkynes. The addition of the elements of sulphenyl fluorides to alkynes has not yet been reported, in sharp contrast with the addition of sulphenyl chlorides, leading to β-chlorovinyl sulphides, which has been extensively studied.[2] To our knowledge, β-fluorovinyl sulphides represent a class of organic compounds which is virtually unknown,[3] but of potential synthetic interest, particularly as possible synthons of vinyl fluorides and keto fluorides.[4,5]

In this paper we show that fluorosulphenylation of alkynes can be conveniently achieved by suitable reaction of NBSA with alkynes in the presence of tetrabutylammonium tetrafluoroborate (ATFB).

Results and Discussion

We reasoned that fluorovinyl sulphide formation should have been limited essentially by (i) self-reaction of NBSA to afford diphenyl disulphide (**3**) and 4-nitroaniline (**4**)[6] (such unwanted reaction might have been discouraged by decreasing NBSA concentration and/or increasing alkyne concentration); and (ii) the reaction of the sulphur nucleophiles present [NBSA and (**3**)] with the intermediate ions (**5**) at the expense of attack by the more weakly nucleophilic fluorine atom of the fluoroborate counterion. This latter reaction might have been favoured by increasing fluoroborate ion concentration and/or decreasing NBSA concentration, as well as by using a very weakly polar solvent and a higher reaction temperature, which should bring about a 'levelling' effect on the strength of the competing nucleophiles. On this basis, we initially examined the above variables by investigating the reaction of BNSA with hex-1-yne under various conditions. Results are collected in Table 1.

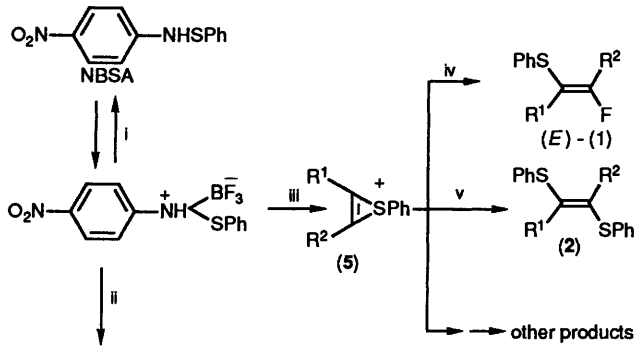
The reaction of NBSA with an excess of alkyne (8.7 mol equiv.), carried out at room temperature in chlorobenzene in the presence of BF_3·Et_2O (2 mol equiv.), gave a poor yield of fluoro sulphide (*E*)-(**1b**), in addition to the disulphide (**3**), the aniline (**4**), and small amounts of the bis-sulphide (**2b**), in agreement with previous results [1] (entry 2). No formation of the adduct (**1b**) was observed when the same reaction was carried out in nitromethane (entry 1). In such a polar solvent the disulphide (**3**) and the aniline (**4**) were the only identifiable products, thus suggesting that under these conditions the intermediate thiirenium ion (**5b**), if formed at all, is not capable of undergoing nucleophilic attack at the ring carbons. However, when NBSA was allowed to react with hex-1-yne in chlorobenzene in the presence of an excess of ATFB (2–5 mol equiv.), an increase in the yield of the adduct (*E*)-(**1b**) was observed (entries 3, 4). As expected, the same reaction carried out at a higher temperature (80 °C) in the presence or in the absence of ATFB led to a remarkable enhancement of the yield of the sulphide (*E*)-(**1b**) (entries 2, 5 and 3, 6). Finally, a satisfactory yield of compound (*E*)-(**1b**) could be achieved when NBSA was allowed to react in the presence of a large excess of the alkyne and boron trifluoride; which was accomplished by slow addition of NBSA to a chlorobenzene solution of hex-1-yne and BF_3·Et_2O (entry 7). A further increase in the concentration of the alkyne or boron trifluoride (entries 8, 9) did not bring about any significant effect.

In the light of these results, NBSA was allowed to react with a number of alkyl- and aryl-alkynes in chlorobenzene at 80 °C in the presence of ATFB by use of a method analogous to that reported in Table 1, entry 7 (see Experimental section). Results are shown in Table 2. Terminal alkynes, such as pent-1-yne, hex-1-yne, 3-methylbut-1-yne, and t-butylacetylene, gave the corresponding β-fluorovinyl sulphides (*E*)-(**1a,b,d,** and **e**) in moderate yield (35–55%), together with the disulphide (**3**), the aniline (**4**), and small amounts of the bis-sulphides (**2a,b,d,** and **e**) (entries 1, 2, 4, and 5). Symmetrical alkynes, such as but-2-yne, hex-3-yne, oct-4-yne, and dec-5-yne, afforded the desired

Table 1. Yields (%)[a] of (*E*)-2-fluoro-1-phenylthiohex-1-ene (**1b**) obtained from the BF_3-promoted reaction of NBSA (1 mmol) with hex-1-yne under various conditions.

Entry	Hex-1-yne (mol equiv.)	BF_3·Et_2O (mol equiv.)	ATFB (mol equiv.)	Solvent	Procedure[b]	Sulphide (*E*)-(**1b**)
1	8.7	2	0	$MeNO_2$	A	0
2	8.7	2	0	PhCl	A	12
3	8.7	2	2	PhCl	A	19
4	8.7	2	5	PhCl	A	19
5	8.7	2	0	PhCl	B	24
6	8.7	2	2	PhCl	B	34
7	8.7	2	2	PhCl	C	53
8	17.4	2	2	PhCl	C	57
9	8.7	4	2	PhCl	C	51

[a] Yields based on 1 mmol of NBSA giving 1 mmol of the sulphide (*E*)-(**1b**) and determined by HPLC analysis. The disulphide (**3**), the aniline (**4**), and small amounts of the bis-sulphide (**2b**) were generally produced in yields which were not determined. [b] Procedure A: a solution of the appropriate reagents in nitromethane or chlorobenzene (10 ml) was stirred for *ca.* 45 min at room temperature, then neutralised with 10% aqueous sodium carbonate. The organic layer was separated, diluted with acetonitrile, and analysed by HPLC; procedure B: a solution of the appropriate reagents in chlorobenzene (10 ml) was heated at 80 °C for *ca.* 20 min. in a sealed tube and then worked-up as described in procedure A; procedure C: to a solution of hex-1-yne, BF_3·ET_2O, and ATFB in chlorobenzene (10 ml), heated at 80 °C in a sealed tube, was slowly added (*ca.* 45 min) a solution of NBSA in benzene (5 ml). After being heated at 80 °C for further 10 min, the reaction mixture was worked up as described in procedure A.



PhSSPh + O_2N–C$_6$H$_4$–NH_2

(3) (4)

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

Scheme. *Reagents:* i, BF_3·Et_2O; ii, NBSA; iii, $R^1C{\equiv}CR^2$; iv, BF_4^- and/or $O_2NC_6H_4NHBF_3^-$; v, NBSA and/or disulphide (**3**).

adducts (*E*)-(**1f–i**) in fairly good yield (65–87%) (entries 6–9), while with unsymmetrical hex-2-yne an inseparable 55:45 mixture of the regioisomeric vinyl sulphides (*E*)-(**1n**) and (*E*)-(**1o**) was obtained in 76% overall yield (entry 14). However, no fluorovinyl sulphide adduct (**1j**) could be obtained with di-t-butylacetylene; in such a case the disulphide (**3**) and the aniline (**4**) were the main products, which were accompanied by small amounts of an unknown compound (entry 10). The aryl-substituted alkynes such as phenylacetylene, 1-phenylpropyne, 1-phenylbut-1-yne, and diphenylacetylene generally gave rather low yields (6–33%) of the desired adducts (*E*)-(**1c,k–m**). These were accompanied by remarkable amounts of the bis-sulphides (**2c,k–m**) (entries 3, 11–13).

With unsymmetrical alkyl-substituted and aryl-substituted alkynes the addition reaction was found to occur in a highly regioselective fashion, leading exclusively to the Markovnikov products (**1a–e,k,l**). The observed regioselectivity is consistent with previous evidence provided by related additions of NBSA (and other benzenesulphenanilides) to alkynes at room temperature in the presence of various nucleophiles.[1,7,8] It appears that nucleophilic attack of a fluoroborate fluorine atom at the thiirenium ring carbons can proceed with some S_N1 character even under the thermal conditions employed in the present work. In all cases examined, β-fluorovinyl sulphide formation occurred in a *trans*-stereospecific fashion, which was expected for the intermediacy of thiirenium ions (**5**). The fluorovinyl sulphides (*E*)-(**1a,e,f,g,h**, and **m**) had been previously reported.[1] The observed values of the coupling constant between the vinyl proton and the fluorine atom (*J* 17–20 Hz) in the ^{1}H NMR spectra allowed us to establish the *trans*-configuration for the new sulphides (*E*)-(**1b,c**, and **d**).[1,9] For the remaining cases, the (*E*)-configuration in the adducts (**1**) was assumed.

It is noteworthy that the terminal vinyl sulphides (*E*)-(**1a–c,e**) were largely converted into the corresponding (*Z*)-isomers upon prolonged heating in benzene at 170 °C (Table 2, entries 1–3, 5). Under the same conditions, the dialkyl- and arylalkyl-vinyl sulphides (*E*)-(**1f–h,k**, and **l**) remained largely unchanged (Table 2, entries 6–8, 11, and 12). The values of the coupling constant between the vinylic proton and the fluorine atom were found to be *J* 34 and *J* 35 Hz for (*Z*)-(**1b**) and (*Z*)-(**1c**), respectively, in agreement with those previously observed for the sulphides (*Z*)-(**1a** and **e**).[1] Moreover, the values of the coupling constant between the vinylic methylene or methyl protons and fluorine were found to be generally higher in the (*E*)-isomers (**1f–h,k**, and **l**) than in the corresponding (*Z*)-isomers (Table 3).

Vinyl sulphides carrying a β-substituent with a lone pair are known to undergo ready *trans* ⟶ *cis* isomerisation.[7,8,10] Such a process would be favoured by a ready availability of the β-substituent lone pair[11] as well as by steric hindrance between the RS group and the R^2 substituent, but discouraged by steric repulsion between the R^1 and R^2 substituents in the (*Z*)-isomer.[7] The observed low tendency of the (*E*)-fluorovinyl sulphides (**1**) to convert into the (*Z*)-isomers might be attributed to the scarce availability of the lone pair of the fluorine atom.

The general evidence provided by the present study indicates that the BF_3-promoted reaction of NBSA with alkynes can offer a useful one-pot method for the *trans*-stereospecific and

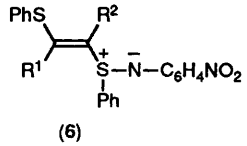
Table 2. Product yields[a] (%) for the BF_3-promoted reaction of NBSA with alkynes in the presence of ATFB[b]

Entry	Alkyne	β-Fluorovinyl sulphide	Bis-sulphide	Disulphide (3)	(*E*)-(1):(*Z*)-(1) isomer ratios[i]
1	Pent-1-yne	(*E*)-(**1a**), 56	(**2a**), 3	26	60:40
2	Hex-1-yne	(*E*)-(**1b**), 54	(**2b**), 2	28	43:57
3	Phenylacetylene[c]	(*E*)-(**1c**), 33[c]	(**2c**), 16	18	8:92
4	3-Methylbut-1-yne	(*E*)-(**1d**), 34	(**2d**), 4	42	
5	t-Butylacetylene	(*E*)-(**1e**), 37	(**2e**), 4	40	25:75
6	But-2-yne	(*E*)-(**1f**), 65	(**2f**), 2	20	90:10
7	Hex-3-yne	(*E*)-(**1g**), 76		19	93:7[j]
8	Oct-4-yne	(*E*)-(**1h**), 77		16	99:1[j]
9	Dec-5-yne	(*E*)-(**1i**), 87		9	
10	Di-t-butylacetylene			75[e]	
11	1-Phenylpropyne	(*E*)-(**1k**), 25	(**2k**), 36	23	80:20
12	1-Phenylbut-1-yne	(*E*)-(**1l**), 30	(**2l**), 16	18	85:15
13	Diphenylacetylene[f]	(*E*)-(**1m**), 6	(**2m**), 63	*g*	
14	Hex-2-yne	(*E*)-(**1n**) + (*E*)-(**1o**), 76[h]		12	

[a] Yields isolated by column chromatography. Yields of the sulphides (**1**) are based on 1 mol of NBSA giving 1 mol of each of the products. Yields of the bis-sulphides (**2**) and diphenyl disulphide (**3**) are based on 2 mol of NBSA giving 1 mol of each of the product. The aniline (**4**) (85–95%) and small amounts of unidentified products were also generally isolated. [b] For reaction conditions, see Experimental section. [c] An oily product, which probably was α-(chlorophenyl)-β-(phenylthio)styrene (**7**) was also separated in *ca.* 6% yield; δ (60 MHz) 6.88 (1 H, s) and 7.2–7.6 (14 H, m); *m/z* 322 (M^+, 100). [d] Small amounts (*ca.* 2%) of the (*Z*)-isomer were also separated. [e] Contaminated with minor amounts of an inseparable, unknown product, which had *m/z* 246, 171, 169, 121, 113, 77, and 57 (100), as determined by GLC–MS analysis. [f] 2,3-Diphenylbenzothiophene (**8**) was also separated in *ca.* 4% yield. [g] Yield not determined. [h] Inseparable mixture of the regioisomeric sulphides (*E*)-(**1n**) and (*E*)-(**1o**) in a *ca.* 55:45 ratio, as determined by ^1H NMR spectroscopy and GLC–MS analysis. [i] After a benzene solution of (*E*)-(**1**) had been heated at 170 °C for 48 h. The relative yields of the (*E*)-(**1**) and (*Z*)-(**1**) isomers refer to products isolated by column chromatography unless otherwise stated. [j] Relative yields determined by GLC–MS analysis.

X = F, Cl, SR, OCOMe, N =C (Me) $C_6H_4NO_2$

regioselective synthesis of β-fluorovinyl sulphides (*E*)-(**1**). This method appears attractive with alkyl-, and particularly dialkylacetylenes, unless bulky substituents are present. In fact, no fluoro sulphide formation could be observed with di-t-butylacetylene, but the actual reasons for this are unclear at present. It is possible that a thiirenium ion (**5j**) was initially formed, but that it underwent preferential nucleophilic attack at the sulphur rather than at the strongly sterically hindered ring carbons.[2] With aryl-substituted acetylenes, rather poor yields of fluorovinyl sulphide product can be obtained, the concomitant occurrence of bis-sulphide by-product being a serious limitation to the method in these cases. This would be especially true for a diaryl-substituted acetylene, as suggested by the fact that diphenylacetylene gave little of the fluoro sulphide (*E*)-(**1m**), leading mainly to the bis-sulphide (**2m**). In such a case small amounts of 2,3-diphenylbenzothiophene (**8**),resulting from the thiirenium ion (**5m**) by intramolecular nucleophilic attack of the *S*-phenyl ring at a ring carbon,[1] were also formed.



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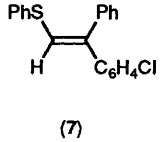

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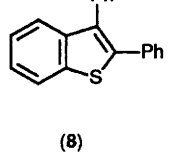

(8)

Finally, the peculiar high reactivity of the 2-phenyl-substituted thiirenium ion (**5c**) towards aromatic nucleophiles, which was first uncovered in our earlier study,[1] was substantiated in the present work. In fact, the reaction of NBSA with phenylacetylene in chlorobenzene gave, besides the fluoro sulphide (*E*)-(**1c**) and the bis-sulphide (**2c**), significant amounts of the adduct (**7**), arising from attack of the very poorly nucleophilic aromatic solvent on the phenyl-substituted ring carbon of intermediate (**5c**) (Table 2, entry 3).

Experimental

4′-Nitrobenzenesulphenanilide (NBSA) was prepared as previously reported.[6] All the alkynes employed in this work were commercially available, except di-t-butylacetylene, which was prepared according to the literature method.[12] Reaction products such as diphenyl disulphide (**3**), 4-nitroaniline (**4**), and 2,3-diphenylbenzothiophene (**8**)[13] were identified by spectral comparison with authentic specimens. The β-fluorovinyl sulphides (*E*)-(**1a,e,f,g,h,** and **m**) and (*Z*)-(**1e**), and the bis-sulphides (**2a,c,e,f,k,l,** and **m**) had physical and spectral properties consistent with those previously reported.[1] All new β-fluorovinyl sulphides (*E*)-(**1b,c,d,i,k,l,n,** and **o**) and (*Z*)-(**1a,b,c,f,k,** and **l**), annd the bis-sulphides (**2b** and **d**) were characterised on the basis of their MS and/or ^1H NMR spectra; the homogeneity of these compounds was confirmed by TLC analysis. ^1H NMR spectra were measured on a Varian T 60 (60 MHz) or a Varian Gemini 200 (200 MHz) instrument, and are for solutions in $CDCl_3$ with Me_4Si as internal standard. HPLC analyses were performed on a Varian LC 5000 instrument, using a C-18 column. Column chromatography was carried out with Merck silica gel (0.040–0.063 mm particle size).

BF_3-Promoted Reaction of NBSA with Alkynes. General Procedure.—To a solution of the appropriate alkyne (20 mmol), ATBF (1.33 g, 4 mmol), and boron trifluoride–diethyl ether complex (*ca.* 47% BF_3; 0.50 ml, 4 mmol) in chlorobenzene (20 ml), stirred at 80 °C in a sealed tube, was slowly added (*ca.* 45 min) a solution of NBSA (492 mg, 2 mmol) in chlorobenzene (10 ml). The resulting mixture was heated at 80 °C for a further 10 min and was then neutralised with 10% aqueous sodium carbonate. The organic layer was separated, the excess of solvent and alkyne removed under reduced pressure (in the case of diphenylacetylene, the alkyne was separated by subsequent

Table 3. ^{1}H NMR and mass spectral data of β-fluorovinyl sulphides (**1**)

Compound	δ(ppm)[a]			*m/z*[b]
	Vinylic proton	Allylic protons in the R^2 group	Other protons	
(*E*)(**1a**)	5.90 (1 H, d, *J* 17 Hz)	2.53 (2 H, dt, J_d 23, J_t 7 Hz)	0.95 (3 H, t, *J* 7 Hz), 1.40–1.92 (2 H, m), 7.33 (5 H, m)[c]	
(*Z*)-**1a**)	5.38 (1 H, d, *J* 33 Hz)	2.30 (2 H, dt, J_d 17, J_t 7 Hz)	0.97 (3 H, t, *J* 7 Hz), 1.30–1.9 (2 H, m), 7.33 (5 H, m)	
(*E*)-(**1b**)	5.80 (1 H, d, *J* 17 Hz)	2.50 (2 H, dt, J_d 23, J_t 7 Hz)	0.90 (3 H, t, *J* 7 Hz), 1.20–1.7 (4 H, m), 7.3 (5 H, m)[d]	210.0874 (M^+, 100)($C_{12}H_{15}FS$ requires *M*, 210.0878), 167 (60), 147 (22), 134 (36), 110 (18), and 77 (14)
(*Z*)-(**1b**)	5.35 (1 H, d, *J* 34 Hz)	2.30 (2 H, dt, J_d 17, J_t 7 Hz)	0.90 (3 H, t, *J* 7 Hz), 1.10–1.6 (4 H, m), 7.3 (5 H, m)	
(*E*)-(**1c**)	6.25 (1 H, d, *J* 20 Hz)		7.1–8.0 (10 H, m)	230.0562 (M^+, 100) ($C_{14}H_{11}FS$ requires *M*, 230.0565), 205 (20), 196 (25), 185 (25), and 121 (30)
(*Z*)-(**1c**)	6.25 (1 H, d, *J* 35 Hz)		7.27–7.7 (10 H, m)	
(*E*)-(**1d**)	5.75 (1 H, d, *J* 17 Hz)	3.27 (1 H, dm, J_d 17 Hz)	1.17 (6 H, d, *J* 7 Hz), 7.33 (5 H, m)	196.0725 (M^+, 100)($C_{11}H_{13}FS$ requires *M*, 196.0722), 181 (62), 110 (17), 109 (17), and 103 (15)
(*E*)-(**1e**)	5.75 (1 H, d, *J* 24 Hz)		1.32 (9 H, d, *J* 1.7 Hz), 7.2 (5 H, m)[c]	
(*Z*)-(**1e**)	5.43 (1 H, d, *J* 35 Hz)		1.13 (9 H, s), 7.17–7.33 (5 H, m)[c]	
	Allylic protons in the R^1 group			
(*E*)-(**1f**)	1.97 (3 H, dq, J_d 2.2 J_q 1.5 Hz)	2.18 (3 H, dq, J_d 18, J_q 1.5 Hz)	7.27 (5 H, m)[d]	
(*Z*)-(**1f**)	1.80 (3 H, dq, $J_d = J_q = 1$ Hz)	2.07 (3 H, dq, J_d 17, $J_q = 1$ Hz)	7.15–7.40 (5 H, m)[d]	
(*E*)-(**1g**)	2.33 (2 H, dq, J_d 3 J_q 7.5 Hz)	2.68 (2 H, dq, J_d 23, J_q 7.5 Hz)	1.08 (3 H, t, *J* 7.5 Hz), 1.18 (3 H, t, *J* 7.5 Hz), 7.25 (5 H, m)[d]	
(*E*)-(**1h**)	2.24 (2 H, dt, J_d 3.2 J_t 7.5 Hz)	2.61 (2 H, dt, J_d 21, J_t 7.5 Hz)	0.85 (3 H, t, *J* 7.5 Hz), 0.95 (3 H, t, *J* 7.5 Hz), 1.4–1.7 (4 H, m), 7.25 (5 H, m)[d]	
(*E*)-(**1i**)	2.35 (2 H, dt, J_d 3.0, J_t 7.5 Hz)	2.72 (2 H, dt, J_d 24, J_t 7.5 Hz)	0.90 (3 H, t, *J* 7 Hz), 0.98 (3 H, t, *J* 7 Hz), 1.25–1.70 (8 H, m), 7.1–7.4 (5 H, m)[d]	266.1507 (M^+, 100)($C_{16}H_{23}FS$ requires *M*, 266.1504), 223 (30), 168 (22), and 110 (28)
(*E*)-(**1k**)	2.10 (3 H, d, *J* 4.2 Hz)		7.1–7.9 (10 H, m)	244.0719 (M^+, 100)($C_{15}H_{13}FS$ requires *M*, 244.0722), 218 (10), 185 (15), and 133 (10)
(*Z*)-(**1k**)	1.98 (3 H, d, *J* 3.4 Hz)		7.1–7.9 (10 H, m)	
(*E*)-(**1l**)	2.82 (2 H, dq, J_d 4.8, J_q 7.2 Hz)		1.13 (3 H, t, *J* 7.2 Hz), 7.10–7.90 (10 H, m)[d]	258.0882 (M^+, 100)($C_{16}H_{15}FS$ requires *M*, 258.0878), 229 (15), 185 (20), and 133 (22)
(*Z*)-(**1l**)	2.27 (2 H, dq, J_d 1.6, J_q 7.2 Hz)		1.08 (3 H, t, *J* 7.2 Hz), 7.2–7.6 (10 H, m)	
(*E*)-(**1m**)			7.10–7.53 (11 H, m), 7.6–7.8 (4 H, m)	
(*E*)-(**1n**)	1.91 (3 H, d, *J* 3.7 Hz)	2.61 (2 H, dt, J_d 23, J_t 7.2 Hz)	0.95 (3 H, t, *J* 7 Hz), 1.4–1.7 (2 H, m), 7.1–7.35 (5 H m)[d]	210 (M^+, 75), 181 (37), 161 (45), 135 (45), 109 (25), and 59 (100)
(*E*)-(**1o**)	2.25 (2 H, dt, J_d 3.3, J_t 7.4 Hz)	2.21 (3 H, d, J_d 17 Hz)	0.85 (3 H, t, *J* 7 Hz), 1.4–1.7 (2 H, m), 7.1–7.35 (5 H, m)[d]	210 (M^+, 100), 167 (44), 135 (54), 110 (64), 77 (48), 65 (40), and 51 (62)[e]

[a] At 60 MHz, unless otherwise stated. [b] Determined on a VG 7070 instrument by the electron-impact method, unless otherwise stated. [c] From ref. 1. [d] At 200 MHz. [e] Determined with a GC-MS workstation HP 59970.

column chromatography, and the residue was chromatographed on a silica gel column (*h* 50 cm). Elution with light petroleum (b.p. 40–70 °C) gave: (i) the appropriate fluorovinyl sulphide (*E*)-(**1a,b,d–i,n,** and **o**); (ii) the disulphide (**3**); and (iii) the appropriate bis-sulphide (**2a–f,k–m**). [The fluorovinyl sulphides (*E*)-(**1c,k–m**) were eluted after the disulphide (**3**).] Further elution with diethyl ether gave: (iv) small amounts of mixtures of unidentified products and (v) the aniline (**4**). Yields of all the identified products thus obtained are given in Table 2. The ^{1}H NMR and mass spectral data of the new β-fluorovinyl sulphides (*E*)-(**1b,c,d,i,k,l,n,** and **o**) are given in Table 3. All these compounds were obtained as oily products. The ^{1}H NMR spectral data of the previously known sulphides (*E*)-(**1a,e,f,g,h,** and **m**) are also reported in Table 3 for comparison. The following new bis-sulphides (**2**) were obtained as oily products: (i) 1,2-*bis*(*phenylthio*)*hex*-1-*ene* (**2b**); δ_H (60 MHz) 0.87 (3 H, t, *J* 7 Hz), 1.17–1.67 (4 H, m), 2.43 (2 H, t, *J* 7 Hz), 6.38 (1 H, s), and 7.1–7.6 (10 H, m) (Found: M^+, 300.1012. $C_{18}H_{20}S_2$ requires *M*, 300.1006); *m*/*z* 186, 167, 147, 135, 109, and 91; and (ii) 3-*methyl*-1,2-*bis*(*phenylthio*)*but*-1-*ene* (**2d**); δ_H (200 MHz) 1.15 (6 H, d, *J* 6.8 Hz), 3.27 (1 H, septet, *J* 6.8 Hz), 6.08 (1 H, s), ahd 7.1–7.5 (10 H, m) (Found: M^+ 286.0844. $C_{17}H_{18}S_2$ requires *M*, 286.0850); *m*/*z* 264, 251, 177, 167, 161, 135, and 109.

Thermal Isomerisation of the (E)-*Fluorovinyl Sulphides* (E)-(**1a–c,e–h, k,** *and* **l**).—A solution of the appropriate sulphide (*E*)-(**1a–c,e–h,k,** or **l**) (200 mg) in benzene (5 ml) was heated at 170 °C in a sealed tube for *ca.* 48 h, after which time the solvent was evaporated off. In the case of the sulphides (*E*)-(**1a,b,c,e,f,k,** and **l**) the resulting residue was chromatographed on silica gel to give the unchanged (*E*)-isomers followed by the corresponding (*Z*)-isomers (*Z*)-(**1a,b,c,e,f,k,** and **l**), which were all obtained as oily compounds. The resultant (*E*):(*Z*) ratios are reported in Table 2. The ^{1}H NMR spectral data of the isolated (*Z*)-isomers are given in Table 3. In the case of the sulphides (*E*)-(**1g**) and (*E*)-(**1h**), the resulting residue was analysed by GLC-MS. Ratios of (*E*)-(**1g** and **h**) to (*Z*)-(**1g** and **h**) thus determined are given in Table 2.

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