Acetamidinosulphenylation of Alkynes *via* Electrophilic Addition of 4'-Substituted Benzenesulphenanilides in Acetonitrile

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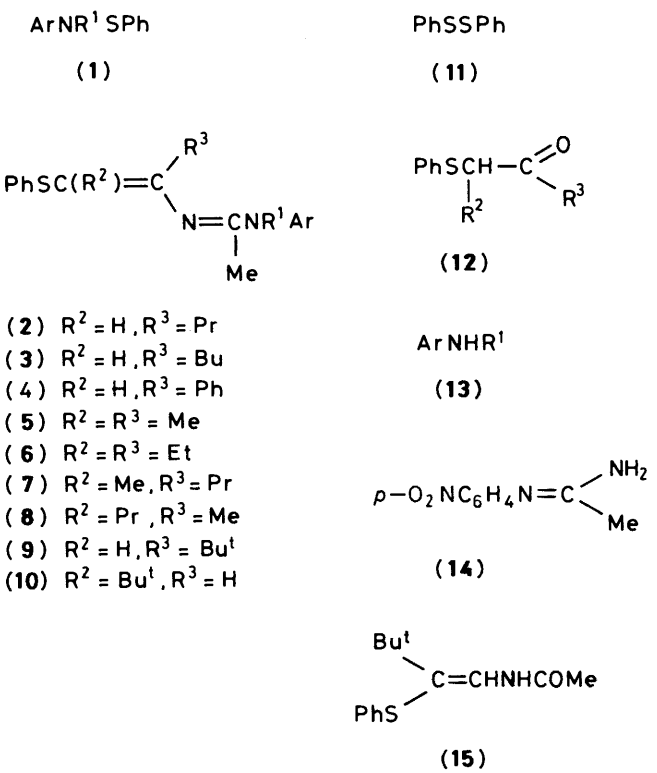
A number of 4'-substituted benzenesulphenanilides and *N*-methyl-4'-nitrobenzenesulphenanilide are shown to add to simple alkynes in acetonitrile in the presence of boron trifluoride–diethyl ether to give acetamidinovinyl sulphides in varying yields. Addition is largely favoured by dialkyl substitution on the alkyne and by electron-attracting anilide substituents. Moreover, the azasulphenylation adducts are produced with *trans*-stereospecificity and high regioselectivity (Markovnikov orientation). A likely mechanism involves nucleophilic displacement by the alkyne at the activated sulphur of the anilide complexed with boron trifluoride leading to the initial formation of a thiirenium ion intermediate. Subsequent back-side attack of acetonitrile on the thiirenium ion gives a nitrilium ion which is ultimately trapped by the liberated arylamine.

We have previously shown that benzenesulphenanilides (**1**) can smoothly undergo nucleophilic displacement at sulphur by alkenes in the presence of boron trifluoride–diethyl ether. These reactions generally lead to thiiranium ion intermediates, from which azasulphenylation products ultimately arise. In benzene solution arylamino sulphides are produced in satisfactory yields,[1] while in nitrile solvents amidino and/or amido sulphides are smoothly formed.[2] In the light of these results we were prompted to investigate related reactions of the anilides (1) with various alkynes, since to our knowledge electrophilic additions of sulphenamides to alkynes had not been previously reported.[3]

Results and Discussion

The benzenesulphenanilides (**1a**—**e**) in acetonitrile containing 1.5 equiv. of boron trifluoride–diethyl ether and a five-fold excess of the appropriate alkyne were allowed to react at room temperature for *ca.* 1 h, after which time t.l.c. showed the absence of the starting anilides (**1a**—**e**). The resulting reaction mixtures were hydrolysed with aqueous potassium carbonate and then chromatographed on silica gel.

The reaction of 4'-nitrobenzenesulphenanilide (**1a**) in the presence of acetylene gave exclusively diphenyl disulphide (**11**) (76%) and 4-nitroaniline (**13a**) (80%), which were the products expected from reaction together of two molecules of the anilide (**1a**).[1–4] Analogous reaction of the anilide (**1a**) in the presence of terminal alkynes such as pent-1-yne, hex-1-yne, and phenylacetylene gave the adducts (**2a**)—(**4a**) in moderate yields (40—54%) (Table 1) in addition to the disulphide (**11**) and the aniline (**13a**). Under the same conditions the anilide (**1a**) reacted with symmetrical alkynes such as but-2-yne and hex-3-yne to afford the enamidines (**5a**) and (**6a**) in fairly good yields, while with unsymmetrical hex-2-yne an inseparable 60:40 mixture of the regioisomeric enamidines (**7a**) and (**8a**) was obtained in 80% overall yield. (Table 1). Similar results were obtained from reaction of 4'-chlorobenzenesulphenanilide (**1b**) with but-2-yne and hex-2-yne, but a considerable decrease in the yield of the resulting enamidine (**3b**) was observed with hex-1-yne (Table 1, entries 7—9). Moreover the anilides (**1c**—**e**) reacted with hex-2-yne, hex-3-yne, and/or but-2-yne to afford the corresponding enamidines (**7c**), (**8c**), (**6c**, **d**), and (**5c**—**e**) in moderate to low yields, which became poorer with the increasing electron releasing power of the anilide substituent (Table 1, entries 11—13, 15, 16, and 18). However, these anilides (**1c**—**e**) in the presence of hex-1-yne gave no evidence of any formation of the desired adducts (**3c**—**e**). In these cases only products ascribable to reaction together of two molecules of the anilides (**1c**—**e**) could be observed[4] (see Experimental section). Structural



a ; R^1 = H, Ar = $C_6H_4NO_2$-*p* b ; R^1 = H, Ar = C_6H_4Cl-*p*
c ; R^1 = H, Ar = C_6H_5 d ; R^1 = H, Ar = C_6H_4Me-*p*
e ; R^1 = H, Ar = C_6H_4OMe-*p* f ; R^1 = Me, Ar = $C_6H_4NO_2$-*p*

Table 1. Acetamidinovinyl sulphides from BF_3-promoted reactions of benzenesulphenanilides (**1a—e**) with alkynes in acetonitrile[a]

Entry	Benzenesulphenanilide	Alkyne	Acetamidino sulphide	Yield (%)[b]
1	(**1a**)	Pent-1-yne	(**2a**)	54
2	(**1a**)	Hex-1-yne	(**3a**)	50
3	(**1a**)	Phenylacetylene	(**4a**)	40
4	(**1a**)	But-2-yne	(**5a**)	70
5	(**1a**)	Hex-3-yne	(**6a**)	72
6	(**1a**)	Hex-2-yne	(**7a**) + (**8a**)	80 (60:40)
7	(**1b**)	Hex-1-yne	(**3b**)	8
8	(**1b**)	But-2-yne	(**5b**)	64
9	(**1b**)	Hex-2-yne	(**7b**) + (**8b**)	67 (60:40)
10	(**1c**)	Hex-1-yne	(**3c**)	*c*
11	(**1c**)	But-2-yne	(**5c**)	53
12	(**1c**)	Hex-3-yne	(**6c**)	54
13	(**1c**)	Hex-2-yne	(**7c**) + (**8c**)	58 (60:40)
14	(**1d**)	Hex-1-yne	(**3d**)	*c*
15	(**1d**)	But-2-yne	(**5d**)	42
16	(**1d**)	Hex-3-yne	(**6d**)	44
17	(**1e**)	Hex-1-yne	(**3e**)	*c*
18	(**1e**)	But-2-yne	(**5e**)[d]	4

[a] Reactions were run at room temperature for *ca.* 60 min in the presence of 1.5 equiv. of BF_3–Et_2O and 5 equiv. of alkyne. [b] Isolated yields based on benzenesulphenanilide (**1**). The appropriate aniline (**13a—e**), diphenyl disulphide (**11**) and other products arising from BF_3-promoted decomposition of (**1a—e**) were also generally isolated. [c] Not detected in the reaction mixture. [d] Not isolated pure.

Table 2. Acetamidinovinyl sulphides from BF_3-promoted reaction of *N*-methyl-4′-nitrobenzenesulphenanilide (**1f**) with alkynes in acetonitrile[a]

Entry	Alkyne	Acetamidino sulphide	Yield (%)[b]	A/B Isomer ratios[c]
1	Pent-1-yne	(**2f**)	47	10:90
2	Hex-1-yne	(**3f**)	37	10:90
3	Phenylacetylene	(**4f**)	26	10:90
4	But-2-yne	(**5f**)	65	66:34
5	Hex-3-yne	(**6f**)	73	100:0
6	t-Butylacetylene	(**9f**)	28	0:100
		(**10f**)[d]	12	

[a] Reactions were run at room temperature for *ca.* 60 min in the presence of 1.5 equiv. of BF_3–Et_2O and 5 equiv. of alkyne. [b] Yields based on benzenesulphenanilide (**1f**) referring to products isolated by column chromatography. Varying mixtures of the isomeric (*E*)-(**2Af**)—(**6Af**), (**9Af**) and (*Z*)-enamidines (**2Bf**)—(**6Bf**), (**9Bf**) were obtained after chromatography on silica gel, while the (*E*)-enamidines (**2Af**)—(**6Af**), (**9Af**) were obtained essentially pure after chromatography on aluminium oxide. (see Experimental section). [c] Isomer ratios of (*E*)-(**2Af**)—(**6Af**), (**9Af**) and (*Z*)-enamidines (**2Bf**)—(**6Bf**), (**9Bf**) after prolonged heating in refluxing benzene of the (*E*)-isomers. [d] Not isolated pure (see Experimental section).

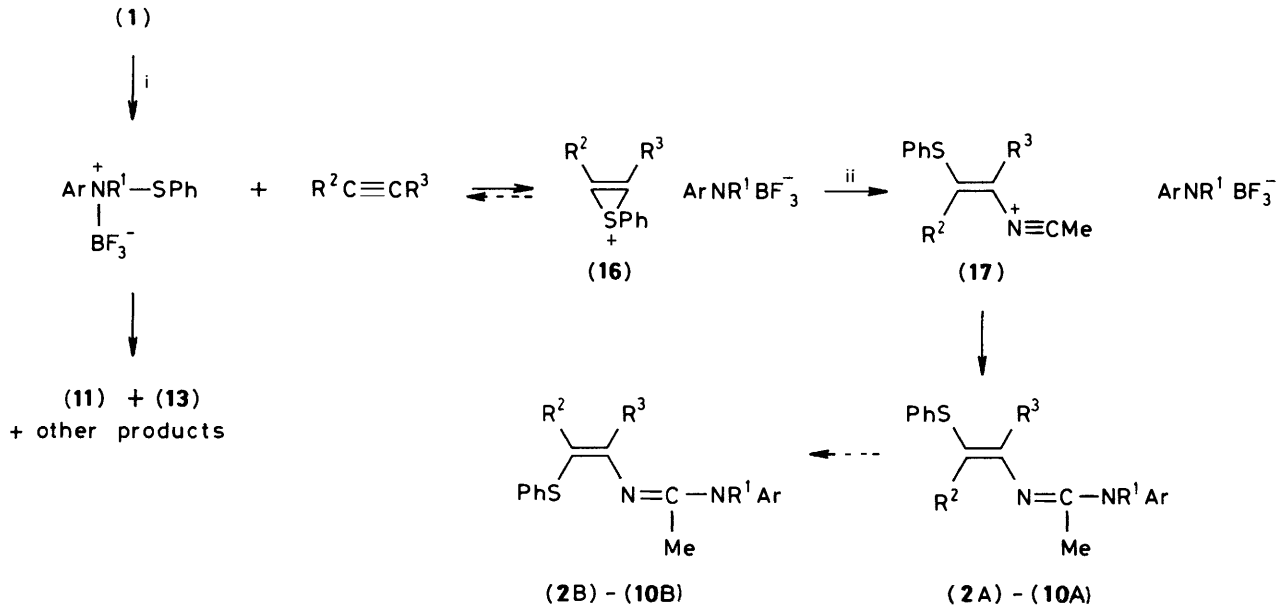
assignment of the enamidines (**2**)—(**8**) was based on ^1H n.m.r., i.r., and mass spectra data in addition to chemical evidence. In particular, the ^1H n.m.r. spectra of the compounds (**2**)—(**8**) generally showed a three-proton singlet [MeC(=N)] at δ 1.85—2.10 and a broad singlet at δ *ca.* 5—7 (NH). Moreover, the enamidines (**2**)—(**4**) showed a one-proton singlet in the vinylic region at δ 5.45—6.37. The mass spectra exhibited, in addition to the molecular ion, strong fragmentation ions ascribable to $M^+ - PhS$ and $ArNCMe^+$. Upon hydrolysis in dioxane–aqueous 4M HCl at reflux the nitro substituted enamidines (**2a**)—(**8a**) generally gave the corresponding β-keto sulphides (**12**), in addition to the acetamidine (**14**), thus offering a new synthetic route to the sulphides (**12**), which has been reported elsewhere.[5]

In particular the enamidines (**2a**)—(**4a**) afforded the keto sulphides (**12**; R^2 = H, R^3 = Pr, Bu, or Ph respectively). Furthermore, hydrolysis of the 60:40 mixture of the two regioisomers (**7a**) and (**8a**) gave the corresponding keto sulphides (**12**; R^2 = Me, R^3 = Pr) and (**12**; R^2 = Pr, R^3 = Me) in about the same ratio (85% overall yield). On this basis, the regiochemistry of the compounds [(**2a**)—(**4a**), (**7a**), and (**8a**)] could be established. As for the enamidines [(**3b**), (**7b**, **c**), and (**8b**, **c**)], their regiochemistry was assigned by spectral analogy with the corresponding nitro substituted compounds (**3a**), (**7a**), and (**8a**). In fact, our attempts to find chemical support for these assignments were unsuccessful since hydrolysis of the enamidines (**3b**), (**5b—d**), (**6c**, **d**), (**7b**, **c**), and (**8b**, **c**) generally resulted in complex mixtures of reaction products which were under study at present.

The observed formation of the enamidines (**2**)—(**8**) suggested that the anilide (**1**)–BF_3 complex should undergo nucleophilic attack at the sulphur atom by the alkyne, presumably leading to an open β-phenylthiovinyl cation or, more likely, to a bridged thiirenium ion (**16**). Subsequent capture by the nitrile solvent might give a nitrilium ion in a highly regioselective fashion (Markovnikov-type), from which the compounds (**2**)—(**8**) might be ultimately formed from attack by the $ArNHBF_3^-$ counterion. Thiirenium ions (**16**) have been suggested as intermediates in the electrophilic addition of sulphenyl chlorides, sulphonates or thiasulphonium salts to alkynes.[6] The remarkable increase in the yields of the enamidino adducts (**2**)—(**8**) with both increasing nucleophilicity of the alkyne, and the electron-attracting power of the anilide substituent, could be ascribable to the fact that the anilides themselves can act as nucleophiles and thus can compete with the alkyne present for attack at the sulphur atom of another anilide unit complexed with boron trifluoride. A similar trend had been previously evidenced with related additions of the anilides (**1**) to alkenes.[2]

However, the available spectral and chemical evidence did not allow a definite structural assignment of the enamidines (**2**)—(**8**), which can theoretically exist in a number of geometric and tautomeric forms. Thus, knowledge of the actual stereochemistry of the above reactions was not possible. We reasoned that such an aim could be more readily achieved from a study of the reaction of *N*-methyl-4′-nitrobenzenesulphenanilide (**1f**) with alkynes. In fact, replacement of the anilide hydrogen with a methyl group in the anilide (**1a**) was expected to result in the formation of the corresponding *N*-methyl substituted enamidines in which tautomerization would be prevented. Under similar conditions to those employed for the anilides (**1a—e**), the *N*-methyl substituted anilide (**1f**) reacted with pent-1-yne, hex-1-yne, and phenylacetylene to lead, after column chromatography on silica gel, to varying mixtures of the isomeric (*E*)-(**2Af**)—(**4Af**) and (*Z*)-amidines (**2Bf**)—(**4Bf**) in 20—47% overall yields, in addition to the disulphide (**11**) and the aniline (**13f**) (Table 2). In each case both isomeric compounds of the A and B series gave, upon hydrolysis, a single keto sulphide, *i.e.* (**12**; R^2 = H, R^3 = Pr, Bu, or Ph), thus indicating that the adducts (**2f**)—(**4f**) belonging to the A series are geometrical isomers of the ones belonging to the B series. Moreover, ^1H n.m.r. spectroscopy suggested that these compounds (**2f**)—(**4f**) should exhibit identical configuration within the same series (A or B). In fact, the ^1H n.m.r. spectra of the compounds (**2Af**)—(**4Af**) showed a three-proton singlet [MeC(=N)] at δ 1.98, 1.98, and 1.89, respectively, a one-proton singlet in the vinylic region at δ 5.20, 5.18, and 5.59 respectively, in addition to a three-proton singlet (NMe) and δ 3.37.

The enamidines (**2Bf**)—(**4Bf**) showed ^1H n.m.r. spectra comparable to those of the corresponding enamidines (**2Af**)—(**4Af**) but the vinylic proton was generally found to be shifted *ca.* 0.1—0.5 p.p.m. downfield, whereas a small upfield shift was generally exhibited by the amidino methyl group [MeC(=N)].



Scheme. *Reagents*: i, BF_3–Et_2O; ii, MeCN

The (*E*)- and (*Z*)-configuration at the carbon-carbon double bond could be assigned to the enamidines (**2Af**), (**4Af**) and (**2Bf**), (**4Bf**) respectively by a nuclear Overhauser enhancement (n.O.e.) study of the ^1H n.m.r. spectra. In fact, irradiation of the vinylic methylene protons of (**2Bf**) or the *ortho*-protons of the vinylic phenyl group of (**4Bf**) caused an increase in the intensity of the corresponding signal of the vinylic proton, while the intensity of the vinylic proton in the corresponding (*E*)- adducts (**2Af**) and (**4Af**) did not show any enhancement. On this basis, the (*E*)- and (*Z*)-configurations in the enamidines (**3Af**) and (**3Bf**) were assumed. Independent experiments carried out subsequently showed that the (*E*)-enamidines (**2Af**)—(**4Af**) were formed exclusive of the (*Z*)-isomers (**2Bf**)—(**4Bf**) in the reactions of the anilide (**1f**) with pent-1-yne, hex-1-yne, and phenylacetylene. This was evidenced by direct ^1H n.m.r. analysis of the resulting reaction mixtures. Column chromatography on aluminium oxide furnished the pure (*E*)-isomers (**2Af**)—(**4Af**). These compounds were found to undergo significant isomerization to the corresponding (*Z*)-isomers (**2Bf**)—(**4Bf**) upon column chromatography on silica gel. Moreover, we observed that upon prolonged heating in refluxing benzene the (*E*)-enamidines (**2Af**)—(**4Af**) led to equilibrium mixtures of the corresponding (*E*)- and (*Z*)-isomers in *ca.* 1:9 ratios.

The reaction of the anilide (**1f**) with t-butylacetylene gave, after column chromatography on aluminium oxide, the Markovnikov adduct (**9Af**) accompanied by minor amounts of the inseparable regioisomeric adduct (**10f**) (Table 2). The ^1H n.m.r. spectrum of (**9Af**) showed, in addition to two singlets at δ 1.32 and 3.37 due to the t-butyl and *N*-methyl groups, a three-proton singlet at δ 1.98 [MeC(=N)] and a one-proton singlet at δ 5.18 due to the vinylic proton. Upon adsorption onto silica gel or on heating in refluxing benzene compound (**9Af**) underwent complete isomerization to the enamidine (**9Bf**), which showed bands at δ 1.19 (Bu^t), 1.89 [MeC(=N)], 3.34 (NMe), and 5.32 (vinylic proton) in the ^1H n.m.r. spectrum.

Refluxing of the initially obtained mixture of the regioisomeric enamidines (**9Af**) and (**10f**) in dioxane–aqueous 4M HCl for *ca.* 30 min brought about complete hydrolysis of the enamidine (**10f**) leading to the enamido sulphide (**15**). Under these conditions the enamidine (**9Af**) underwent isomerization to its geometrical isomer (**9Bf**). However prolonged refluxing (*ca.* 6 h) brought about full hydrolysis of the enamidine (**9Bf**) to give the keto sulphide (**12**; R^2 = H, R^3 = Bu^t) (see Experimental section).

Definite configurational assignment of the enamidines (**9Af**) and (**9Bf**) came from an n.O.e. study of the ^1H n.m.r. spectra. Irradiation of the t-butyl signal of the (*Z*)-enamidine (**9Bf**) brought about an enhancement of the signal of the vinylic proton, whereas no enhancement of the vinylic proton was observed with the (*E*)-isomer (**9Af**). As for the regioisomeric enamidine (**10f**) and its hydrolytic product (**15**), no attempt was made to establish their actual configuration. Under the usual conditions the anilide (**1f**) reacted with but-2-yne and hex-3-yne to give the corresponding (*E*)- adducts (**5Af**) and (**6Af**) after column chromatography on aluminium oxide. The (*E*)-configuration in the adducts (**5Af**) and (**6Af**) was assumed in the light of the above results obtained with monosubstituted alkynes. The enamidines (**5Af**) and (**6Af**) were recovered unchanged after adsorption on silica gel. However, the (*E*)-enamidine (**5Af**) underwent partial isomerization upon heating in refluxing benzene to give a 66:34 mixture of the (*E*)-(**5Af**) and (*Z*)-(**5Bf**)-isomers, while the (*E*)-enamidine (**6Af**) was found to be quite stable under these conditions (Table 2). Thus, in all cases we have examined the boron trifluoride- promoted reaction of (**1f**) with alkynes was found to lead to the initial formation of (*E*)-amidinovinyl sulphides in a *trans*-stereospecific fashion. It is noteworthy that the initially formed (*E*)-adducts may undergo a ready isomerization to the corresponding (*Z*)-isomers in a manner which largely depends on the nature of both R^2 and R^3 olefinic substituents. The ready *trans*→*cis* isomerization observed with our acetamidinovinyl sulphides is in line with that previously found with vinyl sulphides bearing a halogen atom or a further two-co-ordinate sulphur atom at the β-carbon.[7] In our cases it appears that the driving force for the *trans*→*cis* isomerization is the steric hindrance between the phenylthio and the R^3 substituents; nevertheless, an increase in the bulkiness of the R^2 group would disfavour the isomerization as the result of the prevailing steric hindrance between the R^2 and R^3 substituents.

In the light of the results obtained with the *N*-methyl substituted anilide (1f) we briefly re-examined the above reactions of the anilides (**1a**—**d**) with alkynes in order to clarify

whether the previously isolated enamidines (**2a**), (**3a**, **b**), (**4a**), (**5b**—**d**), (**6c**, **d**), (**7b**, **c**), and (**8b**, **c**) actually were the first-formed reaction products. N.m.r. analyses of the mixtures resulting from the reactions of the anilides (**1a**—**d**) with the disubstituted alkynes showed the presence of the same enamidino products (**5b**—**d**), (**6c**, **d**), (**7b**, **c**), and (**8b**, **c**) as previously isolated after column chromatography on silica gel; these products could be obtained unchanged also after column chromatography on aluminium oxide. On the other hand, n.m.r. analyses of the mixtures arising from the reactions of the anilides (**1a**, **b**) with the terminal alkynes showed none of the previously isolated enamidines (**2a**), (**3a**, **b**), or (**4a**); in these cases we clearly observed the occurrence of an isomeric product which did not exhibit any signal in the vinylic region. These unknown compounds, which could be separated largely unchanged by column chromatography on aluminium oxide, were found to undergo ready isomerization to the enamidines (**2a**), (**3a**, **b**), and (**4a**) upon adsorption on silica gel or brief heating in refluxing benzene.

The bulk of the evidence provided by this work suggests that a thiirenium ion intermediate (**16**) initially results from nucleophilic displacement at the activated sulphur atom of an anilide (**1**)–BF_3 complex by the alkyne present. Subsequent back-side attack on the thiirenium ion (**16**) by acetonitrile would result in the formation of the nitrilium ion (**17**) which would be ultimately trapped by the liberated arylamino nucleophile (Scheme). Thiirenium ions are known to undergo ring opening with *trans*-stereospecificity.[6] With terminal alkynes a preference for the formation of the terminal sulphides was generally found. The high regioselectivity observed in such cases (Markovnikov orientation) suggests that nucleophilic attack of acetonitrile on the thiirenium ion intermediates (**16**) may have some S_N1 character. Such an attack is rare in thiirenium ion chemistry where anti-Markovnikov ring opening prevails, unless structural features, weak nucleophiles and/or polar solvents are involved.[6,8] Indeed, acetonitrile is a polar solvent and a weak nucleophile. It is noteworthy that in all cases we have investigated no evidence for the formation of any product ascribable to capture of the thiirenium ion (**16**) by the tetraborate counterion ($ArNRBF_3^-$) could be obtained.

On the other hand, we have previously observed that tetraborate ions are generally capable of competing with the acetonitrile solvent for attack on thiiranium ions.[2]

It is likely that the bulky $ArNRBF_3^-$ ions are not allowed to compete with acetonitrile for trapping of the thiirenium ions (**16**) owing to their high steric demand. Steric hindrance in nucleophilic attack at the ring carbons is in fact known to be comparatively higher with thiirenium than thiiranium ions.[9]

In conclusion, our study provides the first examples of electrophilic additions of benzenesulphenanilides (**1**) to alkynes, leading to regioselective and *trans*-stereospecific amidinosulphenylation of alkynes. This study furthermore offers a potential synthetic route to enamidines, a class of organic compounds of theoretical and synthetic interest, but still little explored.[10]

Experimental

The benzenesulphenanilides (**1a**—**e**)[11] and (**1f**)[12] were prepared as previously reported.

Reaction products, such as the anilines (**13a**—**f**), diphenyl disulphide (**11**), phenazine, 2,7-dichloro-,[4] 2,7-dimethyl-[4] and 2,7-dimethoxy-phenazine,[4] *N*-phenyl-[4] and *N*-(*p*-methoxyphenyl)-*N'*-phenylthio-*p*-benzoquinone di-imine,[4] and the β-keto sulphides (**12**)[5] were each identified by spectral comparison with authentic specimens independently prepared or commercially available. *N*-(*p*-Nitrophenyl)acetamidine (**14**)[13] was characterized on the basis of physical and spectral properties.

Column chromatography was generally carried out on Merck silica gel (0.040—0.063 particle size) or on Merck aluminium oxide (0.063—0.200 particle size. Brockmann activity 3) by gradual elution with light petroleum (b.p. 40—70 °C)–diethyl ether (20:80). ^1H N.m.r. spectra were recorded at 60 MHz on a Varian T60 instrument, unless otherwise stated, and are for solutions in $CDCl_3$ with Me_4Si as internal standard. ^1H N.m.r. spectra at 300 MHz were recorded on a Bruker AM300 instrument. I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer for solutions in $CHCl_3$; the absorptions are given in cm^{-1}. M.p.s are uncorrected. Mass spectra were determined by the electron impact method on a VG 7070 instrument.

Yields of the acetamidino sulphides (**2**)—(**8**) and *N*-methyl-acetamidino sulphides (**2f**)—(**6f**), (**9f**), and (**10f**) from BF_3-promoted reactions of the benzenesulphenanilides (**1a**—**e**) and *N*-methyl-4'-nitrobenzenesulphenanilide (**1f**) with alkynes in acetonitrile are given in Tables 1 and 2, respectively.

BF_3-Promoted Reaction of Benzenesulphenanilides (**1a**—**f**) *with Alkynes in Acetonitrile: General Procedure.*—To a solution of the benzenesulphenanilide (**1a**—**f**) (2 mmol) and the appropriate alkyne (10 mmol) (saturated solution in the case of acetylene) in acetonitrile (20 ml) was added boron trifluoride–diethyl ether, *ca.* 47% BF_3 (0.38 ml, 3 mmol), with vigorous stirring at room temperature. After being stirred for *ca.* 1 h the reaction mixture was treated with 10% aqueous potassium carbonate; the organic layer was then separated, the excess solvent removed, and the residue separated by column chromatography.

Reaction of 4'-Nitrobenzenesulphenanilide (**1a**).—(a) *With acetylene.* Chromatography gave diphenyl disulphide (**11**) (76%) and 4-nitroaniline (**13a**) (80%).

(b) *With pent-1-yne.* Chromatography on silica gel gave (i) diphenyl disulphide (**11**) (40%); (ii) N-(4-*nitrophenyl*)-N'-[1-(*phenylthio*)*pent*-1-*en*-2-*yl*]*acetamidine* (**2a**), m.p. 115—117 °C; $\nu_{max.}$ 3 440, 3 350br, 1 710, 1 570, and 1 330; δ_H 1.0 (3 H, t, *J* 7 Hz), 1.2—1.85 (2 H, m), 2.0 (3 H, s), 2.47 (2 H, t, *J* 7 Hz), 5.50 (1 H, s), 6.4 (1 H, br s), 7.17—7.63 (7 H, m), and 8.23 (2 H, d, *J* 9 Hz) (Found: M^+, 355.1357. $C_{19}H_{21}N_3O_2S$ requires *M*, 355.1354); *m*/*z* 246, 218, 200, and 163; and (iii) 4-nitroaniline (**13a**) (35%). Chromatography on aluminium oxide gave, together with the disulphide (**11**) and the aniline (**13a**), a yellow oily product; δ_H 1.0 (3 H, t, *J* 7 Hz), 1.2—1.9 (2 H, m), 2.05 (3 H, s), 2.53 (2 H, t, *J* 7 Hz); 6—6.7 (*ca.* 2 H, very broad signal); 7.1—7.5 (7 H, m), and 8.30 (2 H, d, *J* 9 Hz); *m*/*z* 355, 246, 218, and 163. This product afforded the acetamidine (**2a**) in quantitative yield by adsorption on silica gel or refluxing in benzene solution (*ca.* 2 h).

(c) *With hex-1-yne.* Chromatography on silica gel gave (i) diphenyl disulphide (**11**) (39%); (ii) N-(4-*nitrophenyl*)-N'-[1-(*phenylthio*)*hex*-1-*en*-2-*yl*]*acetamidine* (**3a**), m.p. 110—111 °C; $\nu_{max.}$ 3 440 and 3 370br; δ_H 0.8—1.8 (7 H, m), 2.0 (3 H, s), 2.45 (2 H, t, *J* 7 Hz), 5.50 (1 H, s), 6.7 (1 H, br s), 7.15—7.4 (5 H, m), 7.47 (2 H, d, *J* 9 Hz), and 8.20 (2 H, d, *J* 9 Hz) (Found: M^+, 369.1514. $C_{20}H_{23}N_3O_2S$ requires *M*, 369.1511); *m*/*z* 260, 163, and 117 (Found: C, 65.10; H, 6.15; N, 11.60; S, 8.85. $C_{20}H_{23}N_3O_2S$ requires C, 65.0; H, 6.25; N, 11.40; S, 8.70%); and (iii) 4-nitroaniline (**13a**) (40%). Chromatography on aluminium oxide gave, together with the disulphide (**11**) and the aniline (**13a**), a yellow oily product; δ_H 0.8—1.7 (7 H, m), 2.0 (3 H, s), 2.55 (2 H, t, *J* 7 Hz), 6.3—7.0 (*ca.* 2 H, very broad signal); 7.13—7.60 (7 H, m), and 8.30 (2 H, d, *J* 9 Hz). This product furnished the acetamidine (**3a**) by adsorption on silica gel or refluxing in benzene solution (*ca.* 2 h).

(d) *With phenylacetylene.* Chromatography on silica gel gave (i) diphenyl disulphide (**11**) (30%); (ii) N-(4-*nitrophenyl*)-N′-[1-*phenyl*-2-(*phenylthio*)*vinyl*]*acetamidine* (**4a**), as a thick yellow oil; $\nu_{max.}$ 3 440, 3 420 (sh), 1 675, 1 600, 1 340, and 1 310; δ_H 2.0 (3 H, s), 6.37 (1 H, s), 6.5 (1 H, br s), 7.25—7.80 (10 H, m), 7.80 (2 H, d, *J* 9 Hz), and 8.23 (2 H, d, *J* 9 Hz) (Found: M^+, 389.1192. $C_{22}H_{19}N_3O_2S$ requires *M*, 389.1198); *m*/*z* 280, 163, and 105 (Found: C, 67.95; H, 4.95; N, 10.65; S, 8.1. $C_{22}H_{19}N_3O_2S$ requires C, 67.85; H, 4.9; N, 10.8; S, 8.23%); and (iii) 4-nitroaniline (**13a**) (35%). Chromatography on aluminium oxide led to separation of a mixture containing the acetamidine (**4a**) and an unidentified product which showed a methyl group at δ 2.05 in the ^{1}H n.m.r. spectrum. This mixture rapidly gave pure acetamidine (**4a**) by adsorption on silica gel or refluxing in benzene solution.

(e) *With but*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (26%); (ii) N-(4-*nitrophenyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5a**), m.p. 132—133 °C; $\nu_{max.}$ 3 450, 3 430 (sh), and 1 340; δ_H 1.85 (3 H, s,), 2.05 (3 H, s), 2.20 (3 H, s), 4.7 (1 H, br s), 7.38 (5 H, m), 7.80 (2 H, d, *J* 9 Hz), and 8.32 (2 H, d, *J* 9 Hz) (Found: M^+, 341.1203. $C_{18}H_{19}N_3O_2S$ requires *M*, 341.1198); *m*/*z* 232, 204, 163, and 117; and (iii) 4-nitroaniline (**13a**) (27%).

(f) *With hex*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disuphide (**11**) (15%); (ii) a 3:2 mixture of N-(4-*nitrophenyl*)-N′-[2-(*phenylthio*)*hex*-2-*en*-3-*yl*]-*acetamidine* (**7a**) and N-(4-*nitrophenyl*)-N′-[3-(*phenylthio*)*hex*-2-*en*-2-*yl*]*acetamidine* (**8a**); $\nu_{max.}$ 3 450, 1 340, and 910; *m*/*z* 369 (M^+), 340, 260, and 163; δ_H 0.96 (3 H, t, *J* 7. Hz), 1.54 (2 H, m), 1.81 (3 H, s), 2.05 (3 H, s), 2.65 (2 H, t, *J* 7 Hz), 7.0 (1 H, br s), 7.27 (5 H, m), 7.75 (2 H br s), and 8.17 (2 H, d, *J* 9 Hz) [acetamidine (**7a**)] and 0.83 (3 H, t, *J* 7 Hz), 1.21 (2 H, m), 2.08 (3 H, s), 2.17 (3 H, s), 2.17 (2 H, t, *J* 7 Hz), 7.0 (1 H, br s), 7.27 (5 H, m), 7.75 (2 H, br s), and 8.17 (2 H, d, *J* 9 Hz) [acetamidine (**8a**)] (Found: C, 65.3; H, 6.35; N, 11.25; S, 8.55. $C_{20}H_{23}N_3O_2S$ requires C, 65.0; H, 6.25; N, 11.40; S, 8.70%); and (iii) 4-nitroaniline (**13a**) (11%).

(g) *With hex*-3-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (20%); (ii) N-(4-*nitrophenyl*)-N′-[4-(*phenylthio*)*hex*-3-*en*-3-*yl*]*acetamidine* (**6a**), m.p. 124—126 °C; $\nu_{max.}$ 3 440, 1 675, 1 600, 1 360, and 1 115; δ_H 1.01 (3 H, t, *J* 7 Hz), 1.08 (3 H, t, *J* 7 Hz), 2.26 (2 H, q, *J* 7 Hz), 2.11 (3 H, s), 2.68 (2 H, q, *J* 7 Hz), 7.0 (1 H, br s), 7.22 (5 H, m), 7.71 (2 H, d, *J* 9 Hz), and 8.30 (2 H, d, *J* 9 Hz) (Found: M^+, 369.1520. $C_{20}H_{23}N_3O_2S$ requires *M*, 369.1511); *m*/*z* 354, 260, and 163; and (iii) 4-nitroaniline (**13a**) (17%).

Reaction of 4′-*Chlorobenzenesulphenanilide* (**1b**).—(a) *With hex*-1-*yne.* Chromatography on silica gel gave (i) diphenyl disulphide (**11**) (70%); (ii) 2,7-dichlorophenazine (16%); (iii) N-(4-*chlorophenyl*)-N′-[1-(*phenylthio*)*hex*-1-*en*-2-*yl*]*acetamidine* (**3b**), as a thick oil; $\nu_{max.}$ 3 450, 1 660, 1 595, and 1 485; δ_H 0.8—1.7 (7 H, m), 1.90 (3 H, s), 2.47 (2 H, t, *J* 7 Hz), 5.45 (1 H, s), 5.9 (1 H, br s), and 7.13—7.57 (9 H, m) (Found; M^+, 358.1262. $C_{20}H_{23}N_2ClS$ requires *M*, 358.1270); *m*/*z* 317, 249, 194, and 152. The acetamidine (**3b**) was contaminated with an unknown compound which was the major component in the corresponding mixture isolated by chromatography on aluminium oxide. Upon heating or adsorption on silica gel the unknown was essentially converted into the acetamidine (**3b**); δ_H 0.8—1.7 (7 H, m), 1.93 (3 H, s), 2.52 (2 H, t, *J* 7 Hz), and 7.13—7.57 (9 H, m); and (iv) 4-chloroaniline (**13b**) (50%).

(b) *With but*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (22%); (ii) N-(4-*chlorophenyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5b**), m.p. 104—105 °C; $\nu_{max.}$ 3 460, 1 670, 1 600, 1 500, and 955; δ_H 1.83 (3 H, t, *J* 1.5 Hz), 1.95 (3 H, s), 2.15 (3 H, t, *J* 1.5 Hz), 6.0 (1 H, br s), and 7.13—7.47 (9 H, m) (Found: M^+, 330.0962. $C_{18}H_{19}N_2ClS$ requires *M*, 330.0957); *m*/*z* 221, 204, 163, and 152; and (iii) 4-chloroaniline (**13b**) (15%).

(c) *With hex*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (16%); (ii) a 3:2 mixture of N-(4-*chlorophenyl*)-N′-[2-(*phenylthio*)*hex*-2-*en*-3-*yl*]*acetamidine* (**7b**) and N-(4-*chlorophenyl*)-N′-[3-(*phenylthio*)*hex*-2-*en*-2-*yl*]*acetamidine* (**8b**); $\nu_{max.}$ 3 480, 1 680, 1 610, and 1 510; *m*/*z* 358 (M^+), 329, 249, 232, 219, and 191; δ_H 0.8—1.6 (5 H, m), 1.83 (3 H, s), 1.96 (3 H, s), 2.66 (2 H, t, *J* 7 Hz); 6.2 (1 H, br s), and 7.1—7.6 (9 H, m) [acetamidine (**7b**)] and 0.8—1.6 (5 H, m), 1.93 (3 H, s), 2.16 (3 H, s), 2.23 (2 H, t, *J* 7 Hz), 6.2 (1 H, br s), and 7.1—7.6 (9 H, m) [acetamidine (**8b**)] (Found: C, 67.5; H, 6.55; Cl, 9.8; N, 7.7; S, 8.8. $C_{20}H_{23}ClN_2S$ requires C, 66.95; H, 6.45; Cl, 9.9; N, 7.8; S, 8.95%); and (iii) 4-chloroaniline (**13b**) (10%).

Reaction of Benzenesulphenanilide (**1c**).—(a) *With hex*-1-*yne.* T.l.c. of the reaction mixture showed formation of (i) diphenyl disulphide (**11**), (ii) *N*-phenyl-*N*′-phenylthio-*p*-benzoquinone di-imine, (iii) phenazine, and (iv) aniline (**13c**); other products were not detected.

(b) *With but*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (33%); (ii) *N*-phenyl-*N*′-phenylthio-*p*-benzoquinone di-imine (4%); (iii) N-*phenyl*-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5c**), m.p. 77—79 °C; $\nu_{max.}$ 3 480, 1 680, 1 615, 1 455, and 1 340; δ_H 1.89 (3 H, s), 1.89 (3 H, t, *J* 1.5 Hz), 2.18 (3 H, t, *J* 1.5 Hz), 6.5 (1 H, br s), and 7.0—7.6 (10 H, m) (Found: M^+, 296.1351. $C_{18}H_{20}N_2S$ requires *M*, 296.1347); *m*/*z* 204, 187, 163, 148, and 118; and (iv) a mixture of aniline (**13c**) and minor amounts of unidentified products.

(c) *With hex*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (30%); (ii) *N*-phenyl-*N*′-phenylthio-*p*-benzoquinone di-imine (6%); (iii) a 60:40 mixture of N-*phenyl*-N′-[2-(*phenylthio*)*hex*-2-*en*-3-*yl*]-*acetamidine* (**7c**) and N-*phenyl*-N′-[3-(*phenylthio*)*hex*-2-*en*-2-*yl*]*acetamidine* (**8c**); $\nu_{max.}$ 3 460, 1 670, and 1 610; *m*/*z* 324 (M^+), 243, 232, 215, 118, 109, and 93; δ_H 0.8—1.7 (5 H, m), 1.87 (3 H, s), 2.05 (3 H, s), 2.65 (2 H, t, *J* 7.5 Hz), 5.3 (1 H, br s), and 6.9—7.7 (10 H, m) [acetamidine (**7c**)] and 0.8—1.7 (5 H, m), 2.05 (3 H, s), 2.17 (3 H, s), 2.23 (2 H, t, *J* 7 Hz), 5.3 (1 H, br s), and 6.7—7.7 (10 H, m) [acetamidine (**8c**)] (Found: 76.5; H, 7.7; N, 6.25; S, 9.95. $C_{20}H_{24}N_2S$ requires C, 75.9; H, 7.65; N, 6.3; S, 10.15%); and (iv) aniline (**13c**) and minor amounts of unidentified products.

(d) *With hex*-3-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (26%); (ii) N-*phenyl*-N′-[4-(*phenylthio*)*hex*-3-*en*-3-*yl*]*acetamidine* (**6c**), m.p. 109—110 °C; $\nu_{max.}$ 3 440, 1 670, 1 595, and 1 320; δ_H 1.0 (3 H, t, *J* 7.5 Hz), 1.07 (3 H, t, *J* 7.5 Hz), 2.0 (3 H, s), 2.18 (2 H, q, *J* 7.5 Hz), 2.66 (2 H, q, *J* 7.5 Hz), 5.9 (1 H, br s), and 7.0—7.5 (10 H, m) (Found: M^+, 324.1664. $C_{20}H_{24}N_2S$ requires *M*, 324.1660); *m*/*z* 309, 232, 215, and 118; and (iv) aniline (**13c**) and minor amounts of unidentified products.

Reaction of 4′-*Methylbenzenesulphenanilide* (**1d**).—(a) *With hex*-1-*yne.* T.l.c. of the reaction mixture showed formation of (i) diphenyl disulphide (**11**), (ii) *p*-toluidine (**13d**), and (iii) 2,7-dimethylphenazine; other products were not detected.

(b) *With but*-2-*yne.* Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (37%); (ii) 2,7-dimethylphenazine (4%); (iii) N-(p-*tolyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5d**), m.p. 81—83 °C; $\nu_{max.}$ 3 460, 1 665, and 1 620; δ_H 1.92 (6 H, s), 2.15 (3 H, s), 2.30 (3 H, s), 6.20 (1 H, br s), and 6.9—7.5 (9 H, m) (Found: M^+, 310.1507. $C_{19}H_{22}N_2S$ requires *M*, 310.1504); *m*/*z* 204, 202, 163, 148, and 132; and (iv) *p*-toluidine (**13d**) and minor amounts of inseparable products.

(c) *With hex*-3-*yne.* Chromatography on silica gel or

aluminium oxide gave (i) diphenyl disulphide (**11**) (26%); (ii) N-(p-*tolyl*)-N′-[4-(*phenylthio*)*hex*-3-*en*-3-*yl*]*acetamidine* (**6d**), m.p. 103—104 °C; $\nu_{max.}$ 3 450, 1 670, and 1 650; δ_H 1.0 (3 H, t, *J* 7.5 Hz), 1.07 (3 H, t, *J* 7.5 Hz), 2.0 (3 H, s), 2.18 (2 H, q, *J* 7.5 Hz), 2.32 (3 H, s), 2.66 (2 H, q, *J* 7.5 Hz), 6.0 (1 H, br s), and 6.9—7.5 (9 H, m) (Found: M^+, 388.1819. $C_{21}H_{26}N_2S$ requires *M*, 338.1817); *m*/*z* 229, 132, and 91; and (iii) *p*-toluidine (**13d**) and minor amounts of unidentified products.

Reaction of 4′-*Methoxybenzenesulphenanilide* (**1e**).—(a) *With hex*-1-*yne*. T.l.c. of the reaction mixture showed formation of (i) diphenyl disulphide (**11**), (ii) *N*-(*p*-methoxyphenyl)-*N*′-phenylthio-*p*-benzoquinone di-imine, (iii) 2,7-dimethoxyphenazine, and (iv) *p*-anisidine (**13e**); other products were not detected.

(b) *With but*-2-*yne*. Chromatography on silica gel gave (i) diphenyl disulphide (**11**) (74%); (ii) *N*-(*p*-methoxyphenyl)-*N*′-phenylthio-*p*-benzoquinone di-imine (6%); (iii) 2,7-dimethoxyphenazine (22%); (iv) *p*-anisidine (**13e**) (42%); and (v) an about equimolar mixture of 2,7-dimethoxyphenazine, *p*-anisidine (**13e**), and a product which probably was N-(4-*methoxyphenyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5e**) as indicated by spectral data. The ^{1}H n.m.r. spectrum showed, in addition to two singlets due to the methoxy groups of 2,7-dimethoxyphenazine and the aniline (**13e**), singlets at δ 1.88, 1.93, 2.17, and 4.03 ascribable to the acetamidine (**5e**). The mass spectrum showed, in addition to ions due to 2,7-dimethoxyphenazine and the aniline (**13e**), ions at *m*/*z* 326 (M^+), 204 (M^+ − ArNH) and 148 (PhSC≡CCH_2) ascribable to the acetamidine (**5e**) (Found: M^+, 326.1451. $C_{19}H_{22}N_2OS$ requires *M*, 326.1453).

Reaction of N-*Methyl*-4′-*nitrobenzenesulphenanilide* (**1f**).—(a) *With pent*-1-*yne*. Chromatography on aluminium oxide gave (i) diphenyl disulphide (**11**) (39%); (ii) *N*-methyl-4-nitroaniline (**13f**) (42%); and (iii) (E)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)*pent*-1-*en*-2-*yl*]*acetamidine* (**2Af**), as a thick yellow oil; $\nu_{max.}$ 1 640, 1 600, and 1 350; δ_H 0.96 (3 H, t, *J* 7 Hz), 1.2—1.8 (2 H, m), 1.98 (3 H, s), 2.47 (2 H, t, *J* 7 Hz), 3.37 (3 H, s), 5.20 (1 H, s), 7.0—7.4 (7 H, m), and 8.13 (2 H, d, *J* 9 Hz) (Found: M^+, 369.1514. $C_{20}H_{23}N_3O_2S$ requires *M*, 369.1511); *m*/*z* 218, 177, 163, and 135. Chromatography on silica gel furnished, in addition to products (**11**) and (**13f**), a mixture of (*E*)- and (*Z*)-acetamidines (**2Af**) and (**2Bf**) in a ratio depending on the chromatographic conditions. Prolonged refluxing (over 2 h) of a benzene solution of this mixture gave the two isomers (**2Af**) and (**2Bf**) in a 1:9 ratio. (Z)-N-*Methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)*pent*-1-*en*-2-*yl*]*acetamidine* (**2Bf**) showed bands at δ 0.97 (3 H, t, *J* 7 Hz), 1.2—1.8 (2 H, m), 1.88 (3 H, s), 2.23 (2 H, t, *J* 7 Hz), 3.30 (3 H, s), 5.32 (1 H, s), 6.9—7.4 (7 H, m), and 8.10 (2 H, d, *J* 9 Hz) in the ^{1}H n.m.r. spectrum and a mass spectrum identical to that of the (*E*)-isomer (**2Af**).

(b) *With hex*-1-*yne*. Chromatography on aluminium oxide gave (i) diphenyl disulphide (**11**) (50%); (ii) *N*-methyl-4-nitroaniline (**13f**) (55%); and (iii) (E)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)*hex*-1-*en*-2-*yl*]*acetamidine* (**3Af**), as a thick yellow oil; $\nu_{max.}$ 1 640, 1 600, and 1 350; δ_H 0.8—1.8 (7 H, m), 1.98 (3 H, s), 2.45 (2 H, t, *J* 7. Hz), 3.37 (3 H, s), 5.18 (1 H, s), 7.1—7.5 (7 H, m), and 8.2 (2 H, d, *J* 9 Hz) (Found: M^+, 383.1665. $C_{21}H_{25}N_3O_2S$ requires M^+, 383.1667); *m*/*z* 354, 274, 232, and 163 (Found: C, 66.35; H, 6.60; N, 10.75; S, 8.30. $C_{21}H_{25}N_3O_2S$ requires C, 65.75; H, 6.55; N, 10.95; S, 8.35%). Chromatography on silica gel afforded, in addition to products (**11**) and (**13f**), a mixture of (*E*)- and (*Z*)-acetamidines (**3Af**) and (**3Bf**), which were found in a 10:90 ratio after prolonged heating (over 2 h) in refluxing benzene. (Z)-N-*Methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)*hex*-1-*en*-2-*yl*]*acetamidine* (**3Bf**) had a mass spectrum identical with that of the (*E*)-isomer and showed bands at δ 0.8—1.8 (7 H, m), 1.88 (3 H, s), 2.23 (2 H, t, *J* 7 Hz), 3.34 (3 H, s), 5.32 (1 H, s), 7.0—7.5 (7 H, m), and 8.2 (2 H, d, *J* 9 Hz) in the ^{1}H n.m.r. spectrum.

(c) *With phenylacetylene*. Chromatography on aluminium oxide gave (i) diphenyl disulphide (**11**) (52%); (ii) *N*-methyl-4-nitroaniline (**13f**) (65%); and (iii) (E)-N-*methyl*-N-(4-*nitrophenyl*)-N-[1-*phenyl*-2-(*phenylthio*)*vinyl*]*acetamidine* (**4Af**) thick yellow oil; $\nu_{max.}$ 1 630, 1 600, 1 500, 1 350, and 1 330; δ_H 1.89 (3 H, s), 3.37 (3 H, s), 5.59 (1 H, s), 7.05—7.40 (10 H, m), 7.52 (2 H, d, *J* 9 Hz), and 8.11 (2 H, d, *J* 9 Hz) (Found: M^+, 403.1356. $C_{23}H_{21}N_3O_2S$ requires *M*, 403.1354); *m*/*z* 280, 252, 211, 178, and 163 (Found: C, 68.10; H, 5.30; N, 10.3; S, 8.05. $C_{23}H_{21}N_3O_2S$ requires C, 68.45; H, 5.25; N, 10.4; S, 7.95%). Chromatography on silica gel gave, in addition to products (11) and (**13f**), a mixture of (*E*)- and (*Z*)-acetamidines (**4Af**) and (**4Bf**), which were found in a 1:9 ratio after prolonged heating (over 2 h) in refluxing benzene. (Z)-N-*Methyl*-N-(4-*nitrophenyl*)-N′-[1-*phenyl*-2-(*phenylthio*)*vinyl*]*acetamidine* (**4Bf**) had a mass spectrum identical with that of the (*E*)-isomer (**4Af**) and bands at δ 1.78 (3 H, s), 3.45 (3 H, s), 6.12 (1 H, s), 7.0—7.45 (12 H, m), and 8.11 (2 H, d, *J* 9 Hz) in the ^{1}H n.m.r. spectrum.

(d) *With but*-2-*yne*. Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (**11**) (17%); (ii) *N*-methyl-4-nitroaniline (**13f**) (31%); and (iii) (E)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]*acetamidine* (**5Af**), m.p. 96—97 °C; $\nu_{max.}$ 1 640, 1 600, and 1 350; δ_H(300 MHz) 1.85 (3 H, t, *J* 1.45 Hz), 1.90 (3 H, s), 2.15 (3 H, t, *J* 1.45 Hz), 3.43 (3 H, s), 7.1—7.4 (7 H, m), and 8.27 (2 H, d, *J* 9 Hz) (Found: M^+, 355.1355. $C_{19}H_{21}N_3O_2S$ requires *M*, 355.1354); *m*/*z* 246, 204, and 163. Prolonged heating (5—6 h) of the acetamidine (**5Af**) in refluxing benzene furnished a mixture of (*E*)- and (*Z*)-isomers (**5Af**) and (**5Bf**) in a 66:34 ratio. (Z)-N-*Methyl*-N-(4-*nitrophenyl*)-N′-[3-(*phenylthio*)*but*-2-*en*-2-*yl*]-*acetamidine* (**5Bf**) showed bands at δ 1.86 (3 H, s), 1.96 (6 H, s), 3.33 (3 H, s), 7.2—7.3 (7 H, m), and 8.15 (2 H, d, *J* 9 Hz) in the ^{1}H n.m.r. spectrum.

(e) *With hex*-3-*yne*. Chromatography on silica gel or aluminium oxide gave (i) diphenyl disulphide (11) (16%); (ii) *N*-methyl-4-nitroaniline (**13f**) (14%); and (iii) (E)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[4-(*phenylthio*)*hex*-3-*en*-3-*yl*]*acetamidine* (**6Af**), m.p. 73—75 °C; δ_H 1.02 (3 H, t, *J* 7 Hz), 1.08 (3 H, t, *J* 7 Hz), 1.93 (3 H, s), 2.17 (2 H, q, *J* 7 Hz), 2.65 (2 H, q, *J* 7 Hz), 3.45 (3 H, s), 7.13—7.57 (7 H, m), and 8.3 (2 H, d, *J* 9 Hz) (Found: M^+, 383.1669. $C_{21}H_{25}N_3O_2S$ requires *M*, 383.1667); *m*/*z* 368, 232, 191, and 163. Prolonged heating (over 6 h) of the acetamidine (**6Af**) in refluxing benzene did not cause any isomerization.

(f) *With t-butylacetylene*. Chromatography on silica gel gave (i) diphenyl disulphide (11) (39%); (ii) *N*-methyl-4-nitroaniline (**13f**) (40%); and (iii) an inseparable mixture of the two regioisomeric (Z)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)-3,3-*dimethylbut*1-1-*en*-2-*yl*]*acetamidine* (**9Bf**) and N-*methyl*-N-(4-*nitrophenyl*)-N′-[2-(*phenylthio*)-3,3-*dimethylbut*-1-*enyl*]*acetamidine* (**10f**) in 7:3 ratio as determined by integration of the ^{1}H n.m.r. spectrum: δ_H 1.19 (9 H, s), 1.89 (3 H, s), 3.37 (3 H, s), 5.45 (1 H, s), 7.1—7.6 (7 H, m), and 8.20 (2 H, d, *J* 9 Hz) (**9Bf**) and 1.35 (9 H, s), 1.97 (3 H, s), 3.46 (3 H, s), 7.1—7.6 (8 H, m), and 8.23 (2 H, d, *J* 9 Hz) (**10f**); *m*/*z* 383, 232, 191, 176, and 163 (Found: C, 65.2; H, 6.7; N, 10.75; S, 8.35. $C_{21}H_{25}N_3O_2S$ requires C, 65.75; H, 6.55; N, 10.95; S, 8.35%). Hydrolysis of this mixture (see below) led to separation of the (*Z*)-acetamidine (**9Bf**), m.p. 125—127 °C; $\nu_{max.}$ 1 635, 1 590, 1 340, and 1 110 (Found: M^+, 383.1668. $C_{21}H_{25}N_3O_2S$ requires *M*, 383.1667); *m*/*z* 232, 191, 176, and 163. Chromatography on aluminium oxide afforded, in addition to products (**11**) and (**13f**), an inseparable mixture of the acetamidine (**10f**) and (E)-N-*methyl*-N-(4-*nitrophenyl*)-N′-[1-(*phenylthio*)-3,3-*dimethylbut*-1-*en*-2-*yl*]*acetamidine* (**9Af**); δ_H 1.32 (9 H, s), 1.98 (3 H, s), 3.37 (3 H, s), 5.10 (1 H, s), 7.1—7.6 (7 H, m), and 8.20 (2 H, d, *J* 9 Hz) (**9Af**). The product (**9Af**)

quantitatively gave the (*Z*)-acetamidine (**9Bf**) by adsorption on silica gel or heating in refluxing benzene (*ca.* 1 h).

Hydrolysis of the Acetamidino Sulphides (**2a**)—(**4a**), (**7a**), *and* (**8a**) *and* N-*Methylacetamidino Sulphides* (**2f**)—(**4f**), (**9f**), *and* (**10f**).—Hydrolysis of the acetamidino sulphides (**2a**)—(**8a**) was generally performed in dioxane–aqueous 4M HCl at reflux (*ca.* 30 min) as previously described,[5] and generally led to the separation of the corresponding keto sulphides (**12**) in 85—95% yield, together with 4-nitroaniline (**13a**) (10—12%), and *N*-(*p*-nitrophenyl)acetamidine (**14**) (65—70%). Similarly, hydrolysis of the *N*-methylacetamidino sulphides (**2f**)—(**4f**) furnished the keto sulphides (**12**; R^2 = H, R^3 = Pr, Bu, and Ph) in *ca.* 80% yield, in addition to *N*-methyl-4-nitroaniline (**13f**) (75—80%).

Hydrolysis of the inseparable mixture of the acetamidino sulphides (**9f**) and (**10f**) (380 mg, 1 mmol) afforded (i) 1-*phenylthio*-3,3-*dimethylbutan*-2-*one* (**12**; R^2 = H, R^3 = Bu^t) (40 mg, 19%), as an oil; δ_H 1.20 (9 H, s), 3.95 (2 H, s), 7.27—7.50 (5 H, s) (Found: M^+, 208.092 35. $C_{12}H_{16}OS$ requires *M*, 208.0922); *m*/*z* 124, 123, 110, 109, 85, 65, and 57 (100); (ii) the (*Z*)-acetamidino sulphide (**9Bf**) (180 mg, 47%); (iii) *N*-methyl-4-nitroaniline (**13f**) (65 mg, 43%); and (iv) 1-*acetamido*-2-*phenylthio*-3,3-*dimethylbut*-1-*ene* (**15**) (70 mg, 28%), m.p. 85—87 °C; $\nu_{max.}$ (CS_2) 3 380 (NH) and 1 720 (C=O); δ_H(300 MHz) 1.24 (9 H, s), 2.04 (3 H, s), 7.16—7.36 (5 H, m), 7.59 (1 H, d, *J* 10.5 Hz), and 7.88 (1 H, br d, *J* 10.5 Hz) (Found: M^+, 249.1190. $C_{14}H_{19}NOS$ requires *M*, 249.1187); *m*/*z* 220, 205 (100), 192, 170, 155, 145, 140, 85, 71, and 57.

Hydrolysis of the (*Z*)-acetamidino sulphide (**9Bf**) (180 mg, 0.47 mmol) was carried out under the usual conditions for *ca.* 6 h, after which time t.l.c. showed disappearance of (**9Bf**); column chromatography afforded the keto sulphide (**12**; R^2 = H, R^3 = Bu^t) (93 mg, 95%) and the aniline (**13f**).

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