Boron Trifluoride-Promoted Reaction of Benzenesulphenanilides with Alkenes in Acetonitrile and Benzonitrile: Amidino- and Amido-sulphenylation of Alkenes

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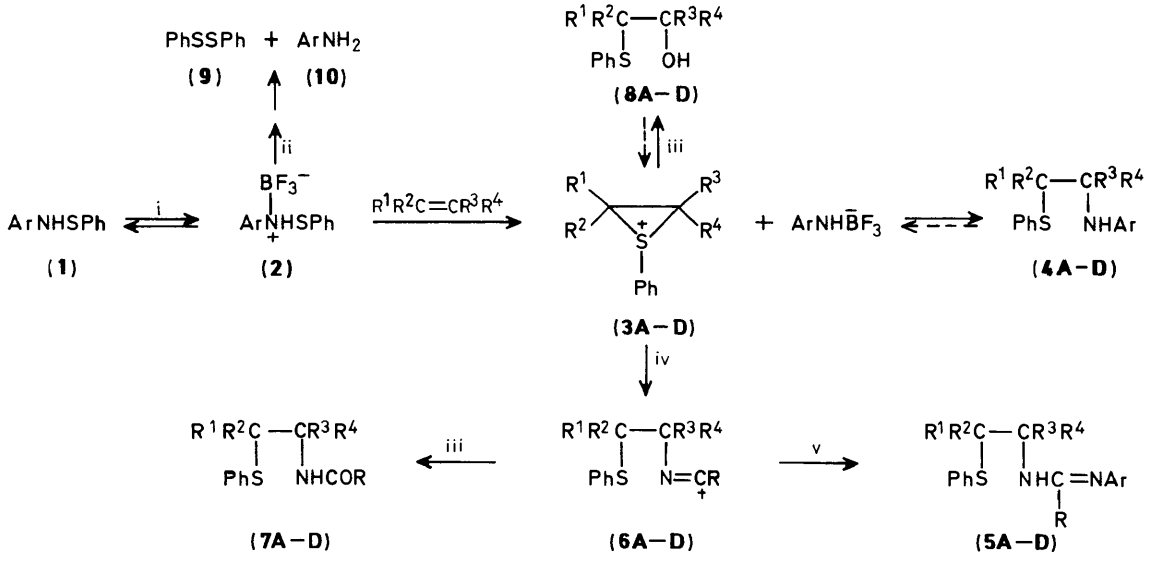
Benzenesulphenanilides (**1**) react at room temperature with alkenes in acetonitrile or benzonitrile in the presence of boron trifluoride–diethyl ether to give amidino sulphides (**5**; R = Me, Ph) in fair to good yields together with varying amounts of amido sulphides (**7**; R = Me, Ph) and arylamino sulphides (**4**), whereas at 100 °C and in the presence of water 4′-nitrobenzenesulphenanilide affords amido sulphides (**7**; R = Me, Ph) as the main products. With cyclohexene a high selectivity for *trans*-addition is observed. With terminal alkenes the terminal sulphides are produced with high regioselectivity. The findings are consistent with a mechanism involving intermediacy of episulphonium ions (**3**) which result from alkene attack at the sulphur atom of an anilide–BF_3 complex.

In the course of our previous studies on the chemistry of benzenesulphenanilides (**1**)[1] we have shown that boron trifluoride transforms these compounds into highly reactive electrophilic species, presumably $PhSNHAr^+BF_3^-$ (**2**), which readily undergo nucleophilic displacement at sulphur. In fact, nucleophilic displacement by another sulphenanilide unit affords, in addition to diphenyl disulphide (**9**) and anilines (**10**), *N*-aryl bis(benzenesulphen)amides [$ArN(SPh)_2$] or products arising from sulphenylation of the *N*-aryl ring,[1c] whereas nucleophilic attack by thiols leads to the formation of disulphides in high yields, thus providing an effective route to symmetrical and unsymmetrical disulphides.[1d] Moreover, we have shown that the boron trifluoride-promoted reaction of benzenesulphenanilides (**1**) with alkenes in benzene solution generally affords arylamino sulphides in fair to good yields. Possible intermediacy of episulphonium-borate ion-pairs, arising from nucleophilic attack at the sulphur atom of (**2**) by an alkene, was postulated in these addition reactions.[1b,e]

The considerable interest recently devoted to regioselective 1,2-difunctionalization of alkenes,[1e,2-4] led us to extend our study to the investigation of the BF_3-promoted reaction of the anilides (**1**) with alkenes in acetonitrile and benzonitrile as a possible synthetic route to amidino and amido sulphides (**5**) and (**7**). Earlier studies have given evidence that episulphonium ions, produced in acetonitrile by reaction of sulphenyl halides with alkenes in the presence of silver salts[2] or by electrochemical oxidation of disulphides in the presence of alkenes,[3] can afford products of acetamidosulphenylation. Moreover, amidino sulphides have been recently reported to be formed in good yields by reaction of *N*-alkyl- and *N*,*N*-dialkylbenzenesulphenamides with alkenes in nitrile solvents in the presence of trifluoromethanesulphonic acid.[4]

Results and Discussion

The benzenesulphenanilides (**1a—d**) in acetonitrile containing a suitable excess of cyclohexene were treated with boron trifluoride–diethyl ether (1.5—2.5 equiv.) at room temperature.



A; $R^1 = R^3 = H$, R^2, $R^4 = [CH_2]_4$ **B**; $R^1 = R^2 = R^3 = H$, $R^4 = n\text{-}C_4H_9$ **C**; $R^1 = R^2 = H$, $R^3 = R^4 = Me$ **D**; $R^1 = R^2 = R^3 = H$, $R^4 = Ph$
a; $Ar = C_6H_4NO_2\text{-}p$ **b**; Ar = Ph **c**; $Ar = C_6H_4Me\text{-}p$ **d**; $Ar = C_6H_4OMe\text{-}p$

Scheme. *Reagents:* i, $BF_3{\cdot}Et_2O$; ii, +(**1**); iii, H_2O; iv, RCN, R = Me or Ph; v, $ArNHBF_3^-$ and/or $ArNH_2$

Table 1. BF_3-Promoted reaction of benzenesulphenanilides (**1a—d**) with alkenes in acetonitrile and benzonitrile

Entry	Benzene-sulphenanilide	Alkene (molar equiv.)	RCN R	Procedure[b]	Products[c] Amido sulphide	Amido sulphide	Arylamino sulphide
1	(**1a**)	Cyclohexene (2)	Me	A	85 (**5Aa**)		6 (**4Aa**)
2	(**1c**)	Cyclohexene (20)	Me	A	88 (**5Ac**)		6 (**4Ac**)
3	(**1b**)	Cyclohexene (20)	Me	A	65 (**5Ab**)	12 (**7A**)	10 (**4Ab**)
4	(**1b**)	Cyclohexene (20)	Me	B	82 (**5Ab**)	8 (**7A**)	5 (**4Ab**)
5	(**1d**)	Cyclohexene (40)	Me	B	63 (**5Ad**)	3 (**7A**)	10 (**4Ad**)
6	(**1a**)	Cyclohexene (2)	Ph	B	75 (**5Aa**)	12 (**7A**)	6 (**4Aa**)
7	(**1b**)	Cyclohexene (20)	Ph	B	60 (**5Ab**)	15 (**7A**)	8 (**4Ab**)
8	(**1a**)	Hex-1-ene (2)	Me	B	70 (**5Ba**)	20 (**7B**)	
9	(**1c**)	2-Methylpropene (*a*)	Me	B	63 (**5Cc**)	18 (**7C**)	
10	(**1b**)	2-Methylpropene (*a*)	Me	B	62 (**5Cb**)	9 (**7C**)	8 (**4Cb**)
11	(**1a**)	Styrene (1)	Me	B			78 (**4Da**)
12	(**1a**)	Styrene (1)	Me	C	60 (**5Da**)	10 (**7D**)	

[a] Saturated acetonitrile solution. [b] See Experimental section. [c] Isolated yields based on benzenesulphenanilide (%). Diphenyl disulphide (**9**) and the appropriate arylamine (**10**) were also generally isolated in variable yields.

Smooth reaction of the starting anilide took place within 10—15 min. The resulting reaction mixtures were hydrolysed with aqueous potassium carbonate or alternatively first treated with the appropriate arylamine (**10**) (2 equiv.) and then hydrolysed [procedure (A) or (B), respectively]. Column chromatography led to the isolation of the *trans*-acetamidino sulphides (**5Aa—d**; R = Me) in fair to good yield in addition to varying amounts of the *trans*-arylamino sulphides (**4Aa—d**),[1a] the *trans*-acetamido sulphide (**7A**),[3a] diphenyl disulphide (**9**),[1e] and the corresponding anilines (**10a—d**).[1e] (Table 1, entries 1—5.) The *trans*- stereochemical assignment to the acetamidino sulphides (**5Aa—d**; R = Me) is based on ^{1}H n.m.r. spectral evidence. ^{1}H N.m.r. spectra of the compounds (**5Aa—d**; R = Me) generally exhibit signals at δ 3.0—3.1 and 3.6—4.2 ascribable to the methine protons. The latter signal is coupled to the amidino proton, which occurs at δ 4.6—5.5. The *trans*-stereochemistry is clearly defined by observation of couplings of 10 and 4 Hz for the methine proton at δ 3.0—3.1.

On the basis of ^{1}H n.m.r. spectral evidence it may also be inferred that these *N,N*-disubstituted acetamidines prefer to exist in the form (**5A**; R = Me) rather than in the tautomeric form bearing the amidino hydrogen on the nitrogen attached to the aryl group. This is in agreement with earlier related findings.[5] In the light of previous studies[2—4] the reaction products (**5Aa—d**; R = Me), (**4Aa—d**), and (**7A**) can be reasonably explained by assuming intermediacy of the episulphonium ion (**3A**) resulting from cyclohexene attack at the sulphur atom of the activated anilide (**2a—d**). Back-side attack on the episulphonium ion (**3A**) by the solvent acetonitrile would give the nitrilium ion (**6A**; R = Me) and by the liberated arylamine the *trans*-arylamino sulphide (**4Aa—d**). Subsequent capture of the nitrilium ion (**6A**; R = Me) by the arylamino nucleophile would eventually give the *trans*-acetamidino sulphide (**5Aa—d**; R = Me), whereas trapping by water during aqueous work-up would afford the *trans*-acetamido sulphide (**7A**; R = Me) (Scheme).

As shown in Table 1, 4′-nitrobenzenesulphenanilide (**1a**) smoothly gave the amidinosulphenylation adduct (**5Aa**; R = Me) in the presence of a slight excess of cyclohexene (2 equiv.) and boron trifluoride (1.5 equiv.) (Table 1, entry 1). However, with the anilides (**1b**) and (**1c**) and, particularly, with the strongly nucleophilic 4′-methoxybenzenesulphenanilide (**1d**) satisfactory yields of the desired adducts (**5Ab—d**) could be obtained by using a large excess of cyclohexene in order to allow the alkene to compete favourably with unchanged anilide (**1b—d**) for attack at the BF_3-anilide complex (**2b—d**).[1e] Moreover, as shown in Table 1 (entries 3 and 4), the yield of the amidino sulphide (**5Ab**) can be somewhat enhanced at the expense of the by-products (**4Ab**) and (**7A**) by allowing the anilide (**1b**) to react in the presence of a larger excess of BF_3·Et_2O (2.5 in place of 1.5 equiv.) and finally treating the reaction mixture with aniline (**10b**) (2 equiv.) before aqueous work-up [procedure (B)].

Evidently, an increase in the concentration of the acid favours capture of the intermediate episulphonium ion (**3A**) by acetonitrile at the expense of the strongly basic arylamino nucleophile. On the other hand, eventual quenching of the reaction mixture with aniline (**10b**) can ensure essential trapping of the nitrilium ion (**6A**; R = Me) by the aniline itself, thus minimizing hydrolysis during aqueous work-up. Such a procedure (B) has been found to be more suitable than procedure (A) both in the case of the anilide (**1d**) and generally in the remaining cases we have examined in this work (*vide infra*).

In line with the findings obtained in acetonitrile, the anilides (**1a**) and (**1b**) reacted with cyclohexene in benzonitrile solution to give the corresponding *trans*-benzamidino sulphides (**5Aa** and **b**; R = Ph) (Table 1, entries 6 and 7). Since benzonitrile is comparatively less nucleophilic than acetonitrile, it can compete less successfully with the arylamine nucleophile for the episulphonium ion (**3A**). In fact, control experiments showed that the occurrence of the arylamino sulphide (**4Aa—b**) is significant, unless a somewhat large excess of boron trifluoride is employed. In both cases, satisfactory yields of the amidines (**5Aa** and **b**; R = Ph) could be achieved by employing 4 equiv. of the acid.

The reaction of the anilide (**1a**) with hex-1-ene in acetonitrile exclusively gave the terminal sulphide (**5Ba**) together with minor amounts of the terminal sulphide (**7B**) in a high regioselective fashion (Table 1, entry 8). Similarly, the anilides (**1b**) and (**1c**) reacted with 2-methylpropene in acetonitrile to give only the Markownikoff-type adducts (**5Cb**) and (**5Cc**), and (**7C**) (Table 1, entries 9, 10). In the presence of styrene, the anilide (**1a**) in acetonitrile at room temperature afforded only the arylamino sulphide (**4Da**) (Table 1, entry 11). Thus, at room temperature, the intermediate episulphonium ion (**3D**) is trapped by the stronger arylamino nucleophile rather than acetonitrile.

In another experiment the reaction mixture was kept at room temperature for several minutes and then heated at 100 °C for *ca.* 1 h. After this time, complete disappearance of the initially formed arylamino sulphide (**4Da**) was observed with formation

Table 2. BF_3-Promoted reaction of 4′-nitrobenzenesulphenanilide (**1a**) with alkenes in acetonitrile or benzonitrile containing 1% water

Entry	Alkene (molar equiv.)	RCN R	Procedure[b]	Products[c] Amido sulphide	Amidino sulphide	Hydroxy sulphide
1	Cyclohexene (2)	Me	A	58 (**7A**)	10 (**5Aa**)	28 (**8A**)
2	Cyclohexene (2)	Me	C	87 (**7A**)	12 (**5Aa**)	
3	Cyclohexene (2)	Ph	C	86 (**7A**)	12 (**5Aa**)	
4	Hex-1-ene (2)	Me	C	77 (**7B**)	20 (**5Ba**)	
5	2-Methylpropene (*a*)	Me	A			88 (**8C**)
6	2-Methylpropene (*a*)	Me	C	60 (**7C**)	14 (**5Ca**)	
7	Styrene (1)	Me	C	74 (**7D**)	13 (**5Da**)	

[a] Saturated acetonitrile solution. [b] See Experimental section. [c] Isolated yields based on (**1a**) (%). 4-Nitroaniline (**10a**) was also generally isolated.

of the amidino sulphide (**5Da**) as major product accompanied by minor amounts of the amido sulphide (**7D**) and other unidentified products (Table 1, entry 12). Under these conditions, the first-formed arylamino sulphide (**4Da**) can give back the episulphonium ion (**3D**), which then reacts with acetonitrile to lead ultimately to the terminal sulphides (**5Da**) and (**7D**).

In all cases we have examined the addition of the anilides (**1**) to terminal alkenes proceed with high regioselectivity to give exclusive formation of the terminal sulphides. The high regioselectivity observed with these addition reactions is fully consistent with previous related studies.[2–4]

In the light of the above results we reasoned that the amido sulphides (**7**; R = Me, Ph) might be conveniently prepared by treating 4′-nitrobenzenesulphenanilide (**1a**) with alkenes in acetonitrile or benzonitrile in the presence of water. In fact, when the anilide (**1a**) was allowed to react with cyclohexene at room temperature in acetonitrile containing 1% water the acetamido sulphide (**7A**; R = Me) was produced in fair yield, but it was accompanied by noticeable amounts of the hydroxy sulphide (**8A**) (Table 2, entry 1). Similar results were observed with hex-1-ene, as evidenced by a qualitative experiment (t.l.c.), whereas with 2-methylpropene the hydroxy sulphide (**8C**) was the exclusive adduct (Table 2, entry 5). However, satisfactory yields of the acetamido sulphides (**7A**—**C**; R = Me) [and suppression of the hydroxy sulphides (**8A**—**C**)] could be achieved when the same reactions were carried out at 100 °C for a suitable time (60—90 min) (Table 2, entries 2, 4, 6). Under analogous conditions the acetamido sulphide (**7D**; R = Me) and the benzamido sulphide (**7A**; R = Ph) could also be obtained in good yield (Table 2, entries 3, 7).

Thus, the added water can efficiently trap the episulphonium ion (**3**), but this can suitably be re-formed from the ensuing hydroxy sulphide (**8**).

We believe that this one-pot procedure for amidosulphenylation of alkenes can offer an attractive alternative to previously reported methods, involving the use of rather unstable sulphenyl halides and silver salts or electrochemical oxidation of disulphides.[2,3] In fact, our procedure is simple, rapid, and requires 4′-nitrobenzenesulphenanilide (**1a**) which is readily available and is a quite stable, crystalline solid.

Experimental

The benzenesulphenanilides (**1a**—**d**) were prepared as previously reported.[1c] Reaction products, such as the arylamino sulphides (**4Aa**—**d**)[1e] and (**4Da**),[1e] *trans*-1-acetamido-2-(phenylthio)cyclohexane (**7A**; R = Me),[3a] 1-acetamido-1-phenyl-2-(phenylthio)ethane (**7D**; R = Me),[3b] *trans*-2-(phenylthio)cyclohexanol (**8A**),[6] 2-methyl-1-(phenylthio)propan-2-ol (**8C**),[7] and diphenyl disulphide (**9**) were each identified by spectral comparison with authentic specimens. Column chromatography was carried out on neutral aluminium oxide (Brockmann III, 0.063—0.200 mm particle size) 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 for solutions in $CDCl_3$ with Me_4Si as internal standard.

I.r. spectra were recorded on a Perkin-Elmer 257 spectrometer for solutions in $CHCl_3$. Yields of reaction products from the BF_3-promoted reaction of the benzenesulphenanilides (**1a**—**d**) with alkenes in acetonitrile or benzonitrile are given in Table 1. Product yields from the BF_3-promoted reaction of 4′-nitrobenzenesulphenanilide (**1a**) with alkenes in acetonitrile or benzonitrile containing 1% water are reported in Table 2.

BF_3-Promoted Reaction of Benzenesulphenanilides (**1**) *with Alkenes in Acetonitrile and Benzonitrile. Procedure A.*—Boron trifluoride–diethyl ether (*ca.* 47% BF_3) (7.5 mmol, 0.95 ml) was added with vigorous stirring to a solution of the appropriate benzenesulphenanilide (**1**) (5 mmol) and alkene in acetonitrile or water–acetonitrile (1%) (50 ml) at room temperature. After being stirred for *ca.* 10 min the reaction mixture was treated with 10% aqueous potassium carbonate; the organic layer was then separated, the excess of solvent distilled off, and the residue chromatographed.

Procedure B. Boron trifluoride–diethyl ether (10—12 or 20 mmol respectively) was added to to a solution of the appropriate benzenesulphenanilide (**1**) (5 mmol) and alkene in acetonitrile or benzonitrile (50 ml) at room temperature. The resulting reaction mixture was stirred for *ca.* 15 min (acetonitrile) or 30 min (benzonitrile), treated with 10 mmol of the appropriate arylamine (**10**) for a few minutes, and then worked-up as described above for procedure A.

Procedure C. Boron trifluoride–diethyl ether (10 mmol) was added to a solution of 4′-nitrobenzenesulphenanilide (**1a**) (5 mmol) and the appropriate alkene in 50 ml of acetonitrile or water–acetonitrile or water–benzonitrile (1%) at room temperature. After being stirred for *ca.* 10 min, the reaction mixture was heated at 100 °C in a sealed tube for 60—90 min and then worked-up as described for procedure A.

The following new products were obtained: N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-(4-*nitrophenyl*)*acetamidine* (**5Aa**; R = Me) a thick yellow oil, $\nu_{max.}$ 3 460, 1 650, 1 600, 1 340, and 1 120 cm^{-1}; *m/z* 369 (M^+), 191, 190, 180, 163, and 118; δ 1.0—2.5 (8 H, m), 1.9 (3 H, s), 3.1 (1 H, dt, J_t 10 and J_d 4 Hz), 3.6—4.23 (1 H, m), 4.97 (1 H, br d, *J* 7 Hz), 6.9 (2 H, d, *J* 9 Hz), 7.2—7.7 (5 H, m) and 8.23 (2 H, d, *J* 9 Hz) (Found: C, 64.5; H, 6.25; N, 11.3; S, 8.75. $C_{20}H_{23}N_3O_2S$ requires C, 65.0; H, 6.25; N, 11.4; S, 8.7%); N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-*phenylacetamidine* (**5Ab**; R = Me), a thick oil, $\nu_{max.}$ 3 465, 3 390br, 1 650, and 1 610 cm^{-1}; *m/z* 324 (M^+), 242, 215, 190, 135, and 118; δ 1.0—2.5 (8 H, m), 1.8 (3 H, s), 3.05 (1 H, dt, J_t 10 and J_d 4 Hz), 3.6—4.43 (1 H, m), 5.0 (1 H, br s) and 6.72—7.73 (10 H, m)

(Found: C, 74.15; H, 7.5; N, 8.7; S, 10.05. $C_{20}H_{24}N_2S$ requires C, 74.05; H, 7.45; N, 8.65; S, 10.0%); N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-(4-*methylphenyl*)*acetamidine* (**5Ac**; R = Me), a thick oil, $\nu_{max.}$ 3 480, 3 400br, 1 650, and 1 620 cm^{-1}; *m/z* 338 (M^+), 190, 150, 147, 132, 110, 107, and 106; δ 0.93—2.57 (8 H, m), 1.77 (3 H, s), 2.3 (3 H, s), 3.0 (1 H, dt, J_t 10 and J_d 4 Hz), 3.63—4.13 (1 H, m), 4.63 (1 H, br s), 6.77 (2 H, d, *J* 9 Hz), 7.15 (2 H, d, *J* 9 Hz), and 7.0—7.77 (5 H, m) (Found: C, 73.0; H, 7.8; N, 7.65; S, 8.25. $C_{21}H_{26}N_2S$ requires C, 74.5; H, 7.75; N, 8.3; S, 9.45%); N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-(4-*methoxyphenyl*)*acetamidine* (**5Ad**; R = Me), a thick oil, $\nu_{max.}$ 3 470, 3 400br, 1 640, and 1 600 cm^{-1}; *m/z* 354 (M^+), 244, 218, 190, 164, 148, 123, 109, and 108; δ 1.0—2.6 (8 H, m), 1.82 (3 H, s), 3.10 (1 H, dt, J_t 10 and J_d 4 Hz), 3.8 (3 H, s), 3.63—4.13 (1 H, m), 5.52 (1 H, br s), and 6.77—7.83 (9 H, m) (Found: C, 71.25; H, 7.35; N, 7.8; S, 9.0. $C_{21}H_{26}N_2OS$ requires C, 71.15; H, 7.4; N, 7.9; S, 9.05%); N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-(4-*nitrophenyl*)*benzamidine* (**5Aa**; R = Ph), a yellow thick oil, $\nu_{max.}$ 3 440, 1 630, 1 585, and 1 330 cm^{-1}, *m/z* 431 (M^+), 322, 242, 225, 190, and 179; δ 1.07—2.67 (8 H, m), 3.2 (1 H, dt, J_t 10 and J_d 4 Hz), 3.77—4.4 (1 H, m), 5.3 (1 H, br s), 6.7 (2 H, d, *J* 9 Hz), 7.10—7.73 (10 H, m), and 7.97 (2 H, d, *J* 9 Hz) (Found: C, 69.5; H, 5.8; N, 9.8; S, 7.35. $C_{25}H_{25}N_3O_2S$ requires C, 69.6; H, 5.85; N, 9.75; S, 7.45%); N-[trans-2-(*phenylthio*)*cyclohexyl*]-N′-*phenylbenzamidine* (**5Ab**; R = Ph), a thick oil, $\nu_{max.}$ 3 440, 1 630, 1 590, and 1 480 cm^{-1}; *m/z* 386 (M^+), 294, 260, 197, 190, and 180; δ 0.97—2.73 (8 H, m), 3.1 (1 H, dt, J_t 10 and J_d 4 Hz), 3.77—4.35 (1 H, m), 4.67 (1 H, br s), and 6.58—7.77 (15 H, m) (Found: C, 77.6; H, 6.85; N, 7.35; S, 8.25. $C_{25}H_{26}N_2S$ requires C, 77.7; H, 6.8; N, 7.25; S, 8.3%); N-[1-(*phenylthio*)*hexan*-2-*yl*]-N′-(4-*nitrophenyl*)-*acetamidine* (**5Ba**; R = Me), a thick yellow oil, $\nu_{max.}$ 3 460, 1 640, 1 590, and 1 340 cm^{-1}; *m/z* 371 (M^+), 207, 192, 163, 117, and 110; δ 0.77—1.67 (9 H, m), 1.77 (3 H, s), 3.27 (2 H, d, *J* 6 Hz), 4.05—4.5 (1 H, m), 4.6—5.0 (1 H, br d), 6.77 (2 H, d, *J* 9 Hz), 7.13—7.63 (5 H, m), and 8.18 (2 H, d, *J* 9 Hz) (Found: C, 64.55; H, 6.75; N, 11.25; S, 8.7. $C_{20}H_{25}N_3O_2S$ requires C, 64.65; H, 6.8; N, 11.3; S, 8.65%); N-[2-(*phenylthio*)-1,1-*dimethylethyl*]-N′-*phenylacetamidine* (**5Cb**; R = Me), a thick pale yellow oil, $\nu_{max.}$ 3 460, 1 650, and 1 600 cm^{-1}; *m/z* 298 (M^+), 189, 164, 135, 134, 133, and 118; δ 1.53 (6 H, s), 1.63 (3 H, s), 3.7 (2 H, s), 4.13 (1 H, br s), and 6.6—7.67 (10 H, m) (Found: C, 72.55; H, 7.4; N, 9.35; S, 10.85. $C_{18}H_{22}N_2S$ requires C, 72.45; H, 7.45; N, 9.4; S, 10.75%); N-[2-(*phenylthio*)-1,1-*dimethylethyl*]-N′-(4-*methylphenyl*)-*acetamidine* (**5Cc**; R = Me), a thick oil, $\nu_{max.}$ 3 460, 1 650, 1 620, and 1 590 cm^{-1}; *m/z* 312 (M^+), 164, 149, 148, 147, and 132; δ 1.52 (6 H, s), 1.6 (3 H, s), 2.3 (3 H, s), 3.68 (2 H, s), 4.12 (1 H, br s), and 6.5—7.67 (9 H, m) (Found: C, 72.95; H, 7.8; N, 8.9; S, 10.15. $C_{19}H_{24}N_2S$ requires C, 73.05; H, 7.75; N, 8.95; S, 10.25%); N-[2-(*phenylthio*)-1,1-*dimethylethyl*]-N′-(4-*nitrophenyl*)*acetamidine* (**5Ca**; R = Me), m.p. 120—121 °C, $\nu_{max.}$ 3 470, 1 650, 1 595, 1 340, and 1 140 cm^{-1}; *m/z* 343 (M^+), 164 and 163; δ 1.5 (6 H, s), 1.67 (3 H, s), 3.63 (2 H, s), 4.53 (1 H, br s), 6.63 (2 H, d, *J* 9 Hz), 7.17—7.63 (5 H, m), and 8.17 (2 H, d, *J* 9 Hz) (Found: C, 63.05; H, 6.1; N, 12.15; S, 9.4. $C_{18}H_{21}N_3O_2S$ requires C, 62.95; H, 6.15; N, 12.25; S, 9.35%); N-[2-(*phenylthio*)-1-*phenylethyl*]-N′-(4-*nitrophenyl*)*acetamidine* (**5Da**; R = Me), a thick oil, $\nu_{max.}$ 3 450, 1 650, 1 590, 1 340, and 1 110 cm^{-1}; *m/z* 391 (M^+), 283, 282, 227, 212, 163, 120, 117, and 105; δ 1.85 (3 H, s), 3.48 (2 H, d, *J* 6 Hz), 5.0—5.6 (2 H, m, collapsing to 1 H, t, *J* 6 Hz, upon D_2O shake), 6.82 (2 H, d, *J* 9, Hz), 7.23—7.67 (5 H, m), and 8.23 (2 H, d, *J* 9 Hz) (Found: C, 67.6; H, 5.4; N, 10.7; S, 8.25. $C_{22}H_{21}N_3O_2S$ requires C, 67.5; H, 5.4; N, 10.75; S, 8.2%); trans-1-*benzamido*-2-(*phenylthio*)*cyclohexane* (**7A**; R = Ph), m.p. 138—139 °C, $\nu_{max.}$ 3 460 and 1 670 cm^{-1}; *m/z* 311 (M^+), 190 and 105; δ 1.07—2.4 (8 H, m), 3.13 (1 H, dt, J_t 10 and J_d 4 Hz), 3.63—4.13 (1 H, m), 6.62 (1 H, br d, *J* 7.5 Hz), and 7.13—7.8 (10 H, m) (Found: C, 73.15; H, 6.75; N, 4.55; S, 10.25. $C_{19}H_{21}NOS$ requires C, 73.25; H, 6.8; N, 4.5; S, 10.3%); 2-*acetamido*-1-(*phenylthio*)*hexane* (**7B**; R = Me), m.p. 65—67 °C, $\nu_{max.}$ 3 440 and 1 670 cm^{-1}; *m/z* 251 (M^+), 192, 151, 150, and 123; δ 0.77—1.67 (9 H, m), 1.9 (3 H, s), 3.07 (2 H, d, *J* 6 Hz), 3.9—4.35 (1 H, m), 6.32 (1 H, br d, *J* 7.5 Hz), and 7.1—7.6 (5 H, m) (Found: C, 66.8; H, 8.35; N, 5.6; S, 12.65. $C_{14}H_{21}NOS$ requires C, 66.9; H, 8.4; N, 5.55; S, 12.75%); 2-*acetamido*-2-*methyl*-1-(*phenylthio*)-*propane* (**7C**; R = Me), m.p. 75—77 °C, $\nu_{max.}$ 3 450 and 1 670 cm^{-1}; *m/z* 223 (M^+), 164 and 124; δ 1.47 (6 H, s), 1.8 (3 H, s), 3.12 (2 H, s), 5.67 (1 H, br s), and 7.27—7.67 (5 H, m) (Found: C, 64.45; H, 7.6; N, 6.3; S, 14.45. $C_{12}H_{17}NOS$ requires C, 64.55; H, 7.65; N, 6.25; S, 14.35%); 2-*anilino*-2-*methyl*-1-(*phenylthio*)-*propane* (**4Cb**), a thick oil, $\nu_{max.}$ 3 430 cm^{-1}; *m/z* 257 (M^+), 218, 134, 109, and 91; δ 1.45 (6 H, s), 3.23 (2 H, s), 4.7 (1 H, br s), and 6.8—7.67 (10 H, m) (Found: C, 74.75; H, 7.4; N, 5.5; S, 12.5. $C_{16}H_{19}NS$ requires C, 74.65; H, 7.45; N, 5.45; S, 12.45%).

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References

1 (*a*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1577; (*b*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *Tetrahedron Lett.*, 1984, **25**, 2039; (*c*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1985, 2261; (*d*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *Tetrahedron Lett.*, 1986, **27**, 1739; (*e*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *Tetrahedron*, 1986, **42**, 1145; (*f*) L. Benati, P. C. Montevecchi, and P. Spagnolo, *J. Chem. Soc., Perkin Trans. 1*, 1987, 99.

2 W. A. Smit, M. Z. Krimer, and E. A. Vorobeva, *Tetrahedron Lett.*, 1975, **16**, 2451; W. A. Smit, N. S. Zefirov, I. V. Bodrikov, and M. Z. Krimer, *Acc. Chem. Res.*, 1979, **12**, 282; L. Rasteikiene, D. Greicinte, M. G. Linkova, and I. L. Knunyants, *Russ. Chem. Rev. (Engl. Transl.)*, 1977, **46**, 548; G. H. Schmid and D. G. Garratt, *Tetrahedron Lett.*, 1983, **24**, 5299.

3 (*a*) A. Bewick, D. E. Coe, J. M. Mellor, and W. M. Owton, *J. Chem. Soc., Perkin Trans. 1*, 1985, 1033; (*b*) A. Bewick, J. M. Mellor, and W. M. Owton, *ibid.*, p. 1039.

4 P. Brownbridge, *Tetrahedron Lett.*, 1984, **25**, 3759.

5 E. Raczynska and J. Oszczapowicz, *Tetrahedron*, 1985, **41**, 5175 and references therein.

6 R. S. Torr and S. Warren, *J. Chem. Soc., Perkin Trans. 1*, 1983, 1169.

7 E. J. Corey and D. Seebach, *J. Org. Chem.*, 1966, **31**, 4097.

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