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BORON TRIFLUORIDE PROMOTED REACTION OF BENZENESULPHENANILIDES WITH ALKENES.

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Abstract. The boron trifluoride-promoted reaction of a series of 3'- and 4'-substituted benzenesulphenanilides (1) with various alkenes has been investigated as a potential synthetic route to arylaminosulphides. The benzenesulphenanilides (1) investigated generally afford arylaminosulphenylation adducts in fair to good yields except for the methoxy-substituted anilides (1e and f), which largely lead to decomposition products under comparable conditions. In all cases examined, the addition proceeds with trans-stereospecificity and, with terminal alkenes, leads regioselectively to the exclusive (or predominant) formation of the terminal sulphides. The findings are interpreted by assuming that boron trifluoride transforms the sluggish benzenesulphenanilides (1) into reactive electrophilic species, which can undergo nucleophilic attack at sulphur by an alkene, presumably affording episulphonium-borate ion-pair intermediates, in competition with attack by another sulphenanilide unit.

Sulphenamides are important intermediates in organic synthesis which have proven useful as sulphenyl-transfer reagents in the synthesis of sulphides,[1] disulphides,[2] trisulphides,[2b] sulphenate esters,[3] and sulphenamides.[4] Bond polarization effects resulting from the difference in electronegativity between sulphur and nitrogen in sulphenamides activate the S-N bond for attack by both nucleophilic and electrophilic species and appear to be essentially responsible for the chemistry of these compounds.[5-7]

Recently we have shown[8] that the 3'- and 4'-substituted benzenesulphenanilides (1a-g) suffer from smooth decomposition in benzene in the presence of trifluoroacetic acid or boron trifluoride etherate in a manner largely dependent on the nature of the N-aryl substituent (and its position). The anilides (1b-e) afford, in addition to diphenyl disulphide (3) and anilines (4b-e), phenazines (8) and/or p-quinone di-imines (9) as the ultimate products resulting from decomposition of initially formed N-aryl bis(benzenesulphen)imides [ArN(SPh)$_2$], arising from nucleophilic attack by the sulphenanilide nitrogen at the acid-activated S-N bond of another sulphenanilide unit. The 3'-methoxybenzenesulphenanilide (1f) leads mainly to products arising from sulphenylation of the N-aryl ring, whereas disulphide (3) and aniline (4a,g) are the main products from the 4'-nitro- and 3'- nitro-benzenesulphenanilides (1a and g). During the course of this study it occurred to us that compounds (1) are capable of adding to alkenes in the presence of boron trifluoride etherate to give β-arylaminosulphenylation adducts. These findings led us to undertake a study of the BF$_3$-

promoted reactions of the anilides (**1a–g**) with various alkenes in order to throw light on the mechanism involved and explore the potential utility of these reactions in the synthesis of β-arylaminosulphides. A preliminary account of this study has been previously reported.[9]

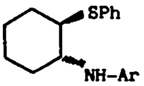
Regioselective 1,2-difunctionalization of alkenes with a nitrogen nucleophile and a sulphenyl group has received considerable attention recently,[10] but at the outset of this work additions of sulphenamides to alkenes were virtually unknown.[10d] However, shortly after the publication of our preliminary account, a number of N-alkyl- and N,N-dialkyl-benzenesulphenamides have been reported to react with alkenes in the presence of trifluoromethanesulphonic acid to give moderate yields of aminosulphides.[11]

RESULTS AND DISCUSSION

Treatment of the benzenesulphenanilides (**1a–f**) (0.05 M) in benzene, containing 2 equiv of cyclohexene, with 1.5 equiv of boron trifluoride etherate at room temperature brought about smooth reaction of the starting anilide (**1a–f**) within a few minutes. After hydrolysis of the reaction mixtures and column chromatography, the anilides (**1a–d**) gave the trans-arylaminosulphenylation adducts (**2a–d**) in fair to good yields (Table, entries 1–4) in addition to varying amounts of diphenyl disulphide (**3**)[8] and the corresponding aniline (**4a–d**).[8] The adducts (**5**) and (**6**) were also obtained in 17% overall yield from the anilide (**1c**), whereas the 2,7-dimethyl- and 2,7-dichlorophenazine (**8a**)[8] and (**8b**)[8] (9 and 4%) could also be isolated from (**1d**) and (**1b**), respectively.

ArNHSPh

(1)


(2)

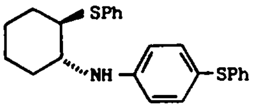
PhSSPh

(3)

$ArNH_2$

(4)

a: Ar=4-$NO_2C_6H_4$; b: Ar=4-ClC_6H_4; c: Ar=C_6H_5; d: Ar=4-$CH_3C_6H_4$
e: Ar=4-$CH_3OC_6H_4$; f: Ar=3-$CH_3OC_6H_4$; g: Ar=3-$NO_2C_6H_4$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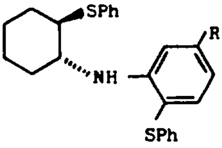
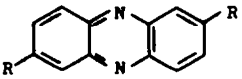
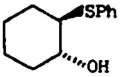
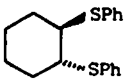

(6) R=H (7) R=OCH_3


(8)

a; R=Me b; R=Cl


(10)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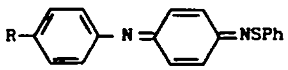
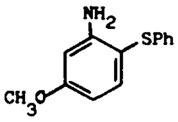
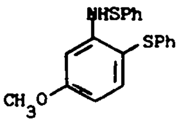

(9)


(12)


(15)

The reaction mixtures obtained from (1e and f) were rather complex. After chromatography, the anilide (1e) gave the disulphide (3) (58%), *trans*-2- (phenylthio)cyclohexanol (10) (2%), *trans*-1,2-bis(phenylthio)cyclohexane (11) (13%), the *p*-benzoquinone di-imine (9; R=OCH_3) (20%), *p*-anisidine (4e) (23%) together with the aminosulphide (2e) (4%), contaminated by unchanged anilide (1e). The sulphenanilide (1f) gave 2-phenylthio-5-methoxyaniline (12) (14%), the compound (7) (27%) and *m*-anisidine (4f) (34%) in addition to a mixture of an unknown and the aminosulphide (2f) (7%). The *trans*-geometry in the aminosulphide (2a) was shown by its proton n.m.r. spectrum at 300 MHz which clearly exhibited the *trans*-diaxial coupling of the SC*H*C*H*N system in the cyclohexane ring; moreover, the *trans*-geometry in the adducts (2a) and (2d) was established by spectral identity with samples of (2a and d) independently prepared by treatment of *trans*-1-chloro-2-(phenylthio)-cyclohexane with silver tetrafluoroborate followed by the appropriate aniline (4a,d).[12] For the remaining cases the *trans*-configuration in the adducts (2) was assumed.

Thus the yields of the resulting adducts (2a-f) strongly decrease with increasing the electron-donating character of the N-aryl substituent (Table , entries 1-6), with concomitant

Table. Arylaminosulphenylation products obtained from BF_3-promoted decomposition of benzenesulphenanilides (1) (0.05 M) in benzene in the presence of various alkenes and in cyclohexene.[a]

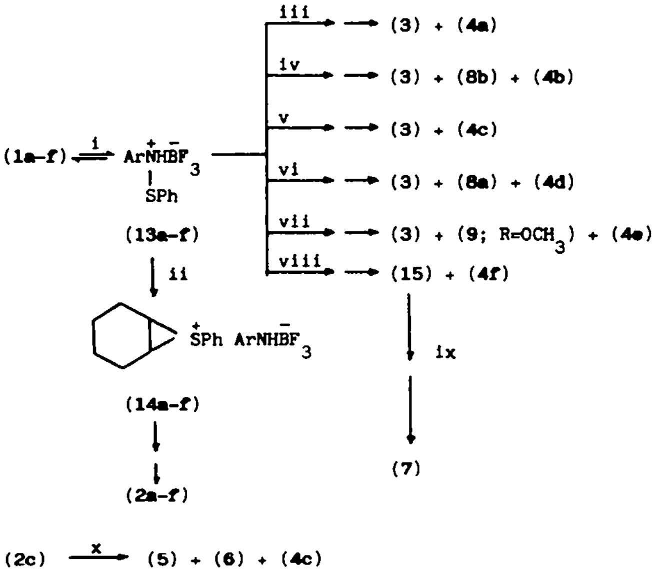
Entry	Benzene-sulphenanilide	Alkene ([Alkene])	Product	Yield,[b] (%)
1	(1a)	Cyclohexene (0.1 M)	(2a)	85
2	(1b)	Cyclohexene (0.1 M)	(2b)	82
3	(1c)	Cyclohexene (0.1 M)	(2c)	66
4	(1d)	Cyclohexene (0.1 M)	(2d)	58
5	(1e)	Cyclohexene (0.1 M)	(2e)	4
6	(1f)	Cyclohexene (0.1 M)	(2f)	7
7	(1a)	Cyclohexene (neat)	(2a)	94
8	(1b)	Cyclohexene (neat)	(2b)	81
9	(1d)	Cyclohexene (neat)	(2d)	80
10	(1e)	Cyclohexene (neat)	(2e)	27
11	(1e)	Cyclohexene (neat)[c]	(2e)	38
12	(1f)	Cyclohexene (neat)	(2f)	25
13	(1a)	*trans*-But-2-ene (d)	(17a)	88
14	(1b)	*trans*-But-2-ene (d)	(17b)	78
15	(1a)	*cis*-But-2-ene (d)	(16a)	88
16	(1b)	*cis*-But-2-ene (d)	(16b)	79
17	(1a)	2-Methylpropene (d)	(19a)	80
18	(1b)	2-Methylpropene (d)	(19b)	77
19	(1a)	Styrene (0.1 M)	(18a)	98
20	(1d)	Styrene (0.1 M)	(18d)	61
21	(1g)	Styrene (0.1 M)	(18g)	98
22	(1d)	Styrene (0.4 M)	(18d)	90
23	(1a)	1-Hexene (0.1 M)[e]	(20a)+(21a)	91 (77:23)
24	(1a)	1-Hexene (2.5 M)	(20a)[g]	50
25	(1d)	1-Hexene (2.5 M)	(20d)+(21d)	48 (73:27)[h]
26	(1d)	1-Hexene (2.5 M)[f]	(20d)+(21d)	56

[a] Reactions were run at room temperature for *ca* 15 min. in the presence of 1.5 equiv of $BF_3.Et_2O$, unless otherwise stated. [b] Isolated yields. [c] Reaction carried out for 18 h in the presence of 1.0 equiv of $BF_3.Et_2O$. [d] Saturated benzene solution. [e] Reaction carried out for 6 h. [f] Reaction carried out for 2 h in the presence of 1 equiv of $BF_3.Et_2O$. [g] The regioisomer (21a) was also formed, but the yield was not determined (see exp.). [h] Isomer ratio was determined by h.p.l.c..

increase in the formation of products primarily ascribable to decomposition of the anilides (1), irrespective of the alkene. In fact, the anilide (1e) gives mainly the disulphide (3), the di-imine (9; R=OCH$_3$), and p-anisidine (4e),^{8} whereas the isomeric anilide (1f) leads effectively to the sulphenylated anilide (15)^{8} as suggested by the occurrence of fairly large amounts of the aminosulphide (7) and the aniline (12). Under the reaction conditions, the initially formed benzenesulphenanilide (15) might reasonably add to cyclohexene to give the adduct (7) or undergo desulphenylation to give (12).

These findings indicate that boron trifluoride transforms the benzenesulphenanilides (1) into reactive electrophilic species, presumably PhSNHAr^{+}BF$_3^{-}$ (13), which can undergo nucleophilic attack at sulphur by the alkene, likely leading to episulphonium-borate ion-pair intermediates (14) and then to the aminosulphides (2) (through a mechanism related to that generally suggested for the sulphenyl chloride addition to alkenes),^{13} in competition with nucleophilic attack by unchanged sulphenanilide, ultimately affording the expected decomposition products (Scheme).^{8} Evidently the efficiency, by which cyclohexene can trap the BF$_3$-anilide complex (13) in comparison with the unchanged sulphenanilide (1), decreases with increasing the electron-donating character of the substituent, as a consequence of an enhancement of the nucleophilic power of the benzenesulphenanilide itself.

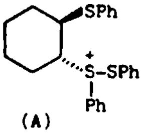
As for the occurrence of the aminosulphides (5) and (6) in the decomposition of the anilide (1c), their formation is ascribable to sulphenylation at the ortho and para positions of the anilino ring of the adduct (2c), occurring to some extent under the reaction conditions. A control experiment clearly showed that the aminosulphide (2c) can react with (1c) in the presence of boron trifluoride etherate to give (5) and (6) (and aniline 4c) (Scheme).



Scheme. Reagents and conditions: i, BF$_3$.Et$_2$O, benzene; ii, cyclohexene; iii, (13a),+(1a); iv, (13b),+(1b); v, (13c),+(1c); vi, (13d),+(1d); vii, (13e),+(1e); viii, (13f),+(1f); ix, +BF$_3$.Et$_2$O, +cyclohexene; x, +(13c), -BF$_3$.

The decomposition of the sulphenanilides (1a,b,d,e, and f) was also investigated in neat cyclohexene. For anilides (1a and b) this did not lead to substantial change (Table, entries 7-8); 4'-methylbenzenesulphenanide (1d) exhibited a considerable increase in the yield of the aminosulphide (2d), at the expense of the by-products disulphide (3), aniline (4d), and 2,7-dimethylphenazine (8a), (Table, entry 9). Under these conditions, also the 4'- methoxybenzenesulphenanilide (1e) led to a marked increase in the yield of the corresponding aminosulphide (2e), which could be isolated pure in 27% yield; moreover, substantial increase in the yield of trans-1,2-bis(phenylthio)cyclohexane (11) (33%) and, to a lesser extent, of the cyclohexanol (10) (11%) was concomitantly observed together with a strong reduction in the disulphide (3) (13%) and suppression of the quinone di-imine (9; R=OCH_3). On the basis of these results, it might be inferred that in neat cyclohexene the BF_3-anilide complex (13e) is trapped rather effectively by the alkene to give the episulphonium ion intermediate. This would be diverted to a considerable extent from its subsequent reaction leading to the aminosulphide (2e), by undergoing alternative reactions probably with the disulphide (3), eventually affording the bis-sulphide (11), and with water to give the cyclohexanol (10).

In fact, trapping of the episulphonium ion intermediate by the disulphide (3) might give the thiosulphonium ion (A), from which the compound (11) would be ultimately formed by subsequent nucleophilic attack at the activated S-S bond. A similar mechanism has been put forward for the stereospecific formation of the bis-sulphides resulting from addition of $[(ClC_6H_4S)_2SC_6H_4Cl]^+SbCl_6^-$ to Z- and E-1-phenylpropene.[14]

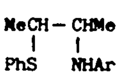


(A)

The suggested involvement of the disulphide (3) in the formation of (11) is supported by the results obtained from the decomposition of the anilide (1e) in cyclohexene in the presence of 3 and 1 equiv of boron trifluoride etherate. In the former case the reaction led to the formation of larger amounts of the bis-sulphide (11) (46%), at the expense of the adduct (2e) (15%) and the disulphide (3) (4%), whereas in the latter case a significant increase in the yield of the aminosulphide (2e) (38%) was observed, the amounts of the disulphide (3) and the bis-sulphide (11) remaining roughly constant. Apparently, an increase in the concentration of BF_3 favours attack by the disulphide (3) at the expense of the more basic arylamino nucleophile.

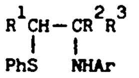
In neat cyclohexene, the 3'-methoxybenzenesulphenanilide (1f) in the presence of 1.5 equiv of boron trifluoride etherate led to the isolation of the aminosulphide (2f) in moderate yield (25%); the adduct (7) (9%), the benzenesulphenanilide (15) (10%), and 2-(phenylthio)cyclohexanol (10) (10%) were also obtained, in addition to small amounts of 2-phenylthio-5-methoxyaniline (12). These findings suggest that even under such conditions the reaction of the BF_3-anilide complex (13f) with unchanged anilide (1f) can still occur effectively. These findings prompted us to carry out the decomposition of the compound (1f) in cyclohexene in the presence of a larger excess of boron trifluoride etherate (3 equiv) in the expectation that an increase in the amount of the acid would promote the formation of the BF_3-anilide complex (13f), thus favouring its reaction with cyclohexene. However, this reaction did not lead to any appreciable change in the yield of the aminosulphide (2f); the only remarkable difference was the occurrence of larger amounts of the compound (7) (18%), apparently at the expense of the benzenesulphenanilide (15), and the cyclohexanol (10) (22%). In the light of these results, the same reaction was quenched with m-anisidine (2 equiv) and then hydrolysed as usual; in such case the yield of the aminosulphide (2f) (39%) was significantly enhanced at the expense of the alcohol (10).

In line with the postulated intermediacy of episulphonium ions in these addition reactions, the decomposition of the 4'-nitro- and 4'-chloro-benzenesulphenanilide (1a and b) in benzene saturated with cis- or trans-but-2-ene led stereospecifically to the formation of high yields of the corresponding threo- or erythro-aminosulphides, (16a,b) or (17a,b) (Table, entries 13-16).


$\underset{PhS}{MeCH}-\underset{NHAr}{CHMe}$

(16) threo

(17) erythro

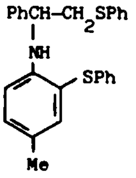

$\underset{PhS}{R^1CH}-\underset{NHAr}{CR^2R^3}$

(18) $R^1=R^2=H$, $R^3=Ph$

(19) $R^1=H$, $R^2=R^3=Me$

(20) $R^1=R^2=H$, $R^3=n\text{-}C_4H_9$

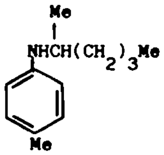
(21) $R^1=n\text{-}C_4H_9$, $R^2=R^3=H$


(22)

The reaction of the anilides (1a), (1d), and (1g) with styrene (2 equiv) in benzene exclusively afforded the corresponding adducts (18a,d,g) in a highly regioselective fashion (Table, entries 19-21). The yields of the aminosulphides (18a) and (18g) were quantitative. The aminosulphide (18d) was obtained in a fairly good yield and was accompanied by minor amounts of the adduct (22), likely resulting from sulphenylation of the compound (18d), as supported by a control experiment, which showed that (18d) reacted with the anilide (1d) under analogous conditions to give (22). In the presence of a larger excess of styrene (8 equiv), the yield of the aminosulphide (18d) could be significantly enhanced at the expense of the compound (22) (Table, entry 22).

The 4'-nitro- and 4'-chloro-benzenesulphenanilide (1a and b) in benzene saturated with 2-methylpropene led smoothly to the exclusive formation of corresponding adducts (19a and b); thus, the addition to 2-methylpropene is higly regioselective, analogously to that observed with styrene (Table, entries 17-18).

In a 1-hexene(2.5 M)-benzene mixture the anilide (1d) gave an inseparable mixture of the regioisomers (20d) and (21d) (48%) in the ratio of 73:27, as determined by h.p.l.c.; desulphurisation of this mixture with Raney nickel led to a mixture of the p-toluidines (23) and (24), which were shown by g.l.c. to be in ca 70:30 ratio. From this reaction, there was also separated the disulphide (3) (16%), 1,2-bis(phenylthio)hexane (25) (13%), the alcohol (26) (possibly contaminated by its regioisomer), and p-toluidine (4d) (26%). When the reaction was carried out in the presence of equivalent amounts of BF_3 a slight increase in the overall yield of the adducts (20d) and (21d) (56%) was obtained with concomitant reduction of the alcohol (26) and the bis(phenylthio)hexane (25).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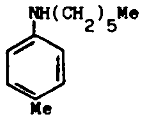
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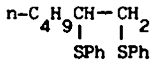
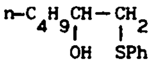

$n\text{-}C_4H_9\underset{SPh}{CH}-\underset{SPh}{CH_2}$

(25)


$n\text{-}C_4H_9\underset{OH}{CH}-\underset{SPh}{CH_2}$

(26)

The reaction of 4'-nitrobenzenesulphenanilide (1a) in 1- hexene (0.1M)-benzene smoothly gave the aminosulphide (20a) (70%) and its regioisomer (21a) (21%). In this case, the reaction time was prolonged for 6 h since t.l.c. showed significant presence of the alcohol (26) when hydrolysis of the reaction mixture was carried out after a shorter time.

In our preliminary report of this work we claimed that the decomposition of the anilide (1a), carried out in 1-hexene (2.5 M)-benzene for 15 min, led to the exclusive formation of the aminosulphide (20a) in 51% yield; no mention of formation of the regioisomer (21a) was given since this compound had not been identified at that time. Our subsequent reinvestigation of this reaction, led us to the separation of the alcohol (26) (24%), the aminosulphide (20a) (50%), the aniline (4a) (30%) in addition to a mixture of two inseparable products, made up of actually the compound (21a) and an unknown.

In all cases that we have examined, the addition of the benzenesulphenanilides (1) to terminal alkenes has been found to proceed regioselectively to give exclusive (or predominant) formation of terminal sulphides (Markownikoff-type adducts); thus, the regioselectivity exhibited by these addition reactions is consistent with the intermediacy of episulphonium ions,[13b] in line with the evidence provided by the trans-stereospecificity observed.

In the light of all our findings obtained from the present study, it may be inferred that the benzenesulphenanilides (1) can generally react with alkenes in the presence of 1.5 equiv of boron trifluoride etherate to give β-arylamminosulphides. However, the extent to which these reactions can lead to the desired adducts depends upon the nature of the N-aryl substituent. Benzenesulphenanilides carrying an electron-attracting group appear to give excellent to good yields of arylaminosulphides in the presence of even a slight excess of alkene. With anilides carrying an electron-releasing group there is a serious limitation represented by the fact that such anilides are effective nucleophilic species and thus can effectively compete with the alkene present for attack at the S-N bond of another sulphenanilide unit. A further limitation is that under the reaction conditions the resulting arylaminosulphides can undergo sulphenylation at the electron-rich arylamino ring. Thus, with anilides carrying an electron-donating substituent practicable yields of arylaminosulphenylation adducts can be achieved by using a suitably large excess of alkene and a proper amount of boron trifluoride etherate.

EXPERIMENTAL

The benzenesulphenanilides (1a-g) were prepared as previously reported.[8] Reaction products, such as the anilines (4a-g),[8] diphenyl disulphide (3), the phenazines (8a,b),[8] the p-benzoquinone di-imine (9; R=OCH$_3$),[8] 2-phenylthio-5-methoxyaniline (12),[15] 2'-phenylthio-5'-methoxybenzenesulphenanilide (15),[8] trans-2-(phenylthio)cyclohexanol (10),[16] and trans- 1,2-bis(phenylthio)cyclohexane (11)[17] were each identified by spectral comparison with authentic specimen independently prepared or commercially available. Column chromatography was carried out on Merck silica gel (0.040-0.063 particle size) by gradual elution with light petroleum (b.p. 40-70°C)-diethyl ether (20:80). ^{1}H-N.m.r. spectra were generally recorded at 60 MHz on a Varian T60 instrument for solutions in CDCl$_3$ with Me$_4$Si as internal standard. G.l.c. analyses were performed on a Varian 3700 instrument using a 5% SP 2250 Supelcoport column. IR spectra were recorded on a Perkin Elmer 257 spectrometer. The absorptions are given in cm^{-1}.

Reaction of Benzenesulphenanilides (1) in the presence of Alkenes. General Procedure.- To a solution of the appropriate benzenesulphenanilide (1a-g) (5mmol) in 100 ml of cyclohexene or a mixture of benzene and the appropriate alkene was added boron trifluoride etherate, ca 47% BF$_3$ (0.95 ml, 7.5 mmol), under vigorous stirring at room temperature. After being stirred for ca. 15 min the reaction mixture was treated with 10% aqueous potassium carbonate; the organic layer was then separated, the excess solvent removed and the residue chromatographed, unless stated otherwise.

Reaction of the Anilides (1a-f) in Cyclohexene (0.1M)-Benzene.- (a) 4'-Nitrobenzenesulphenanilide (1a) gave (i) trans-2-(phenylthio)cyclohexanol (10) (0.30 mmol, 6%); (ii) trans-1-(phenylthio)-2-(4-nitrophenylamino)cyclohexane (2a) (4.25 mmol, 85%), as a yellow thick oil, νmax (CCl$_4$) 3430 br, 1600, and 1330; m/z 328 (M$^+$), 218, and 176; δ(300 MHz, CDCl$_3$) 1.2-2.2 (8H,m), 3.0 (1H,dt,J$_d$ 4 and J$_t$ 9.3 Hz), 3.25 (1H,m), 4.0 (1H,br s), 6.4 (1H,d,J 9Hz), 7.2-7.4 (5H,m), and 8.04

(1H,d,J 9Hz). (Found: C, 66.1; H, 6.05; N, 8.45; S, 9.9. $C_{18}H_{20}N_2O_2S$ requires C, 65.8; H, 6.15; N, 8.55; S, 9.75%); this compound (2a) was identical in all respects to the one obtained in 45% yield by treatment of *trans*-1-chloro-2-(phenylthio)cyclohexane (2.1 mmol) in $MeNO_2$ (10 ml) with $AgBF_4$ (5 mmol) at 0°C followed by addition of 4-nitroaniline (4a) (2 mmol), by an adaptation of a known procedure;[12] and (iii) 4-nitroaniline (4a) (0.7 mmol, 14%).

(b) 4'-Chlorobenzenesulphenanilide (1b) gave (i) an unknown product (50 mg); (ii) *trans*-1-(phenylthio)-2-(4-chlorophenylamino)cyclohexane (2b) (4.10 mmol, 82%) as a thick oil; ν_{max} (CCl_4) 3420 br (NH), 1605 and 1500; m/z 317(M^+), 208 and 166; δ 1.2-2.4 (8H,m), 2.7-3.33 (2H,m), 3.9 (1H,br s), 6.4 (2H,d,J 9Hz), and 7.0-7.57 (7H,m). (Found: C, 68.3; H, 6.4; Cl, 11.0; N, 4.3; S, 10.0. $C_{18}H_{20}ClNS$ requires C, 68.0; H, 6.35; Cl, 11.15; N, 4.4; S, 10.1%); (iii) 2,7-dichlorophenazine (8b) (0.10 mmol, 4%); and (iv) 4-chloroaniline (4b) (0.20 mmol, 4%).

(c) Benzenesulphenanilide (1c) gave (i) diphenyl disulphide (3) (0.21 mmol, 9%); (ii) an unidentified product (30 mg); (iii) *trans*-1-(phenylthio)-2-[2-(phenylthio)phenylamino]cyclohexane (6) (0.20 mmol, 8%), as a thick oil; ν_{max} (CS_2) 3390 br (NH), 750, 740, and 695; m/z 391(M^+), 282, 240, 201, 191, 110, and 109; δ1.0-2.65 (8H,m), 2.83-3.6 (2H,m), 5.27 (1H,br d,J 7Hz), 6.37-6.86 (2H,m), 6.95-7.73 (12H,m). (Found: C, 74.0; H, 6.5; N, 3.5; S, 16.25. $C_{24}H_{25}NS_2$ requires C, 73.6; H, 6.45; N, 3.6; S, 16.4 %); (iv) *trans*-1-(phenylthio)-2-(phenylamino)cyclohexane (2c) (3.3 mmol, 66%) as a thick oil; ν_{max} (CCl_4) 3415 br (NH), 1605, 1505 and 1320; m/z 283 (M^+), 174, 132, and 109; δ1.02-2.65 (8H,m), 2.83-3.47 (2H,m), 3.95 (1H,br s), 6.4-6.9 (3H,m), and 7.0-7.65 (7H,m). (Found: C, 75.9; H, 7.35; N, 5.0; S, 11.5. $C_{18}H_{21}NS$ requires C, 76.3; H, 7.45; N, 4.95; S, 11.3%); (v) *trans*-1-(phenylthio)-2-[4-(phenylthio)phenylamino]cyclohexane (5) (0.22 mmol, 9%) as a thick oil; ν_{max} (CS_2) 3405 br (NH), 820, 740, and 695; m/z 391 (M^+), 283, 201, 200, 191, 174, and 132; δ1.0-2.7 (8H,m), 2.9-3.43 (2H,m), 4.13 (1H,br s), 6.43 (2H,d,J 9Hz), 6.94-7.6 (12 H,m). (Found: C, 74.1; H, 6.4, N, 3.55; S, 16.3%); and (vi) aniline (4c) (0.46 mmol, 9%).

(d) 4'-Methylbenzenesulphenanilide (1d) gave (i) diphenyl disulphide (3) (0.58 mmol, 23%); (ii) an unidentified product (80 mg); (iii) *trans*-1-(phenylthio)-2-(4-methylphenylamino)cyclohexane (2d) (2.9 mmol, 58%), as a thick oil; ν_{max} (CCl_4) 3400 br(NH); m/z 297 (M^+), 191, 188, 146, and 109; δ1.2-2.3 (8H,m), 2.2 (3H,s), 2.7-3.5 (2H,m), 3.8 (1H,br s), 6.33 (2H,d,J 9Hz), 6.93 (2H,d,J 9Hz) and 7.13-7.5 (5H,m). (Found: C, 77.1; H, 7.9; N, 4.6; 11.0. $C_{19}H_{23}NS$ requires C, 76.7; H, 7.8; N, 4.7; S, 10.8%). Compound (2d) was identical in all respects with that prepared in 48% yield from *trans*-1-chloro-2-(phenylthio)cyclohexane by a procedure analogous to that employed for the corresponding preparation of (2a); (iv) 2,7-dimethylphenazine (8a) (0.23 mmol, 9%); and (v) *p*-toluidine (4d) (0.93 mmol, 19%).

(e) 4'-Methoxybenzenesulphenanilide (1e) gave (i) diphenyl disulphide (3) (1.45 mmol, 58%); (ii) 1,2-bis(phenylthio)cyclohexane (11) (0.32 mmol, 13%); (iii) 100 mg of a mixture of products made up of unreacted anilide (1e) and *trans*-1-(phenylthio)-2-(4-methoxyphenylamino)cyclohexane (2e). G.l.c. analysis of this mixture carried out by using pure (2e) independently obtained (vide infra) as reference showed that the yield of (2e) was *ca.* 4%; (iv) *trans*-2-(phenylthio)cyclohexanol (10) (2%); (v) N-(4-methoxyphenyl)-N'-phenylthio-*p*-benzoquinone di-imine (9; R=OCH_3) (0.5 mmol, 20%); and (vi) *p*-anisidine (4e) (1.15 mmol, 23%).

(f) 3'-Methoxybenzenesulphenanilide (1f) gave (i) *trans*-1-(phenylthio)-2-[2-(phenylthio)-5-methoxyphenylamino]cyclohexane (7) (0.68 mmol, 27%), as a thick oil; ν_{max} (CS_2) 3380 br (NH), 2840, 755, 740, and 695; m/z 421 (M^+), 312, 270, 191, and 160; δ 1.03-2.5 (8H,m), 2.83-3.57 (2H,m), 3.77 (3H,s), 5.3 (1H,br s), 6.07-6.43 (2H,m), 7.1-7.6 (11H, m). (Found: C, 71.0; H, 6.35; N, 3.4; S, 15.0. $C_{25}H_{27}NOS_2$ requires C, 71.2; H, 6.45; N, 3.3; S, 15.2%); (ii) an inseparable mixture of *trans*-1-(phenylthio)-2-(3-methoxyphenylamino)cyclohexane (2f) and an unknown (350 mg); the yield of (2f) was found to be *ca.* 7% by quantitative g.l.c. analysis of this mixture carried out by using pure (2f) independently obtained (vide infra) as reference; (iii) 2-phenylthio-5-methoxyaniline (12) (0.68 mmol, 14%); (iv) an unknown product (40 mg); and (v) *m*-anisidine (4f) (1.67 mmol, 34%).

Reaction of the Anilides (1a,b,c,d,e and f) in Cyclohexene. (a) 4'-Nitrobenzenesulphenanilide (1a) gave (i) trace amounts of diphenyl disulphide (3) and (ii) the adduct (2a) (4.7 mmol, 94%).

(b) 4'-Chlorobenzenesulphenanilide (1b) gave (i) diphenyl disulphide (3) (0.25 mmol, 10%); (ii) the adduct (2b) (0.41 mmol, 81%); and (iii) *p*-chloroaniline (4b) (0.4 mmol, 8%).

(c) 4'-Methylbenzenesulphenanilide (1d) gave (i) diphenyl disulphide (3) (0.26 mmol, 10%); (ii) the adduct (2c) (4.0 mmol, 80%); and (iii) *p*-toluidine (4d) (0.45 mmol, 9%).

(d) 4'-Methoxybenzenesulphenanilide (1e) gave (i) disulphide (3); (ii) 1,2-bis(phenylthio)cyclohexane (11); (iii) *trans*-2-(phenylthio)cyclohexanol (10); (iv) *p*-anisidine (4e); and (v) *trans*-1-(phenylthio)-2-(4-methoxyphenylamino)cyclohexane (2e) (1.35 mmol, 27%), as a thick oil; ν_{max} (CCl_4) 3390 br (NH) and 2840; m/z 313 (M^+), 204, and 162; δ1.2-2.45 (8H,m), 3.0-3.3 (2H,m), 3.6 (1H,br s), 3.77 (3H,s), 6.57 (2H,d,J 9Hz), 6.87 (2H,d,J 9Hz), and 7.23-7.67 (5H,m).

(Found: C, 72.5; H, 7.25; N, 4.5; S, 10.45. $C_{19}H_{23}NOS$ requires: C, 72.8; H, 7.4; N, 4.45; S, 10.25%). Quantitative g.l.c. analysis of an aliquot of the reaction mixture gave (3) (13%), (2e) (27%), (10) (11%), and (11) (33%).

The reaction of the anilide (1e) in the presence of 1 equiv of $BF_3.Et_2O$ was carried out for 18 h. After hydrolysis, quantitative g.l.c. determination of the reaction products gave (3) (11%), (2e) (38%), (10) (5%), and (11) (38%).

The reaction of the anilide (1e) in the presence of 3 equiv of $BF_3.Et_2O$ gave (3) (4%), (2e) (15%), (10) (7%), and (11) (46%) as determined by quantitative g.l.c. analysis of the reaction mixture.

(e) 3'-Methoxybenzenesulphenanilide (1f) gave (i) 2'-phenylthio-5'-methoxybenzenesulphenanilide (15); (ii) the adduct (7), (iii) *trans*-1-(phenylthio)-2-(3-methoxyphenylamino)cyclohexane (2f) (1.25 mmol, 25%), as a thick oil; νmax (CCl_4) 3410 br (NH) and 2840; m/z 313 (M^+), 204, 162, and 109; δ 1.2-2.5 (8H,m), 2.93-3.23 (2H,m), 3.7 (3H,s), 4.0 (1H,br s), 6.0-6.37 (3H,m) and 6.87-7.6 (6H,m). (Found: C, 72.1; H, 7.3; N, 4.35; S, 10.4%); (iv) 2-phenylthio-5-methoxyaniline (12); and (v) *m*-anisidine (4f) (1.15 mmol, 23%).

Quantitative g.l.c. analysis of an aliquot of the reaction mixture gave (2f) (27%), (7) (9%), (15) (10%), (10) (10%), (11) (3%), and (12) (3%).

The reaction of (1f) in the presence of 3 equiv of $BF_3.Et_2O$ gave (2f) (28%), (7) (18%), (10) (22%), and (11) (3%) as determined by quantitative g.l.c. analysis. When the same reaction was quenched with *m*-anisidine (2 mmol) after *ca*. 10 min. and then hydrolysed, g.l.c. analysis gave (2f) (39%), (7) (13%), (15) (8%), (10) (3%), and (11) (4%).

Reaction of the Anilides (1a and b) in cis- and trans-But-2-ene-saturated Benzene. (a) With *cis*-but-2-ene the 4'-nitrobenzenesulphenanilide (1a) gave *threo*-2-(phenylthio)-3-(4-nitrophenylamino)butane (16a) (4.40 mmol, 88%), m.p. 94-96°C; νmax (CCl_4) 3440 and 3420 sh (NH), 1610 and 1335; m/z 302 (M^+), 165, 138, and 119; δ 1.3 (6H,d,J 6Hz), 3.2-3.9 (2H,m), 5.0 (1H,d,J 8Hz), 6.28 (2H,d,J 9Hz), 7.2-7.5 (5H,m), and 8.0 (2H,d,J 9Hz). (Found: C, 63.0; H, 6.1; N, 9.3; S, 10.45. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.0; N, 9.25; S, 10.6%).

(b) With *trans*-but-2-ene the anilide (1a) gave *erythro*-2-(phenylthio)-3-(4-nitrophenylamino)-butane (17a) (4.40 mmol, 88%), as a yellow thick oil; νmax (CCl_4) 3420 br (NH), 1600, and 1330; m/z 302 (M^+), 165, 138, 119 and 109; δ 1.31 (3H,d,J 6Hz), 1.42 (3H,d,J 6Hz), 3.2-4.0 (2H,m), 4.97 (1H,d,J 8Hz), 6.4 (2H,d,J 9Hz), 7.2-7.5 (5H,m), and 8.1 (2H,d,J 9Hz). (Found: C, 62.85; H, 5.95; N, 9.35; S, 10.7%).

(c) With *cis*-but-2-ene the 4'-chlorobenzenesulphenanilide (1b) gave (i) diphenyl disulphide (3) (0.25 mmol, 10%); (ii) *threo*-2-(phenylthio)-3-(4-chlorophenylamino)butane (16b) (3.95 mmol, 79%), m.p. 53-54°C; νmax (CCl_4) 3450 br (NH); m/z 291 (M^+), 154 and 138; δ1.2 (6H,d,J 7Hz), 3.3-3.8 (3H,m; 2H,m, after D_2O shake), 6.27 (2H,d,J 9Hz), 7.03 (2H,d,J 9Hz), and 7.1-7.55 (5H,m). (Found: C, 65.2; H, 6.25; Cl, 12.05; N, 4.9; S, 10.85. $C_{16}H_{18}ClNS$ requires C, 65.85; H, 6.2; Cl, 12.15; N, 4.8; S, 11.0%); and (iii) 4-chloroaniline (4b) (0.55 mmol, 11%).

(d) With *trans*-but-2-ene the anilide (1b) gave (i) diphenyl disulphide (3) (0.3 mmol, 12%); (ii) *erythro*-2-(phenylthio)-3-(4-chlorophenylamino)butane (17b) (3.9 mmol, 78%), as a thick oil; νmax (CCl_4) 3400 br (NH); m/z 291 (M^+), 154, and 138; δ1.22 (3H,d,J 7Hz), 1.34 (3H,d,J 7Hz) 3.2-4.0 (3H,m; 2H,m, after D_2O shake), 6.33 (2H,d,J 9Hz), 7.07 (2H,d,J 9Hz), and 7.17-7.33 (5H,m) (Found: C, 65.35; H, 6.15; Cl, 12.05; N, 4.85; S, 11.1 %); and (iii) 4-chloroaniline (4b) (0.6 mmol, 12%).

The *threo*- and *erythro*-compounds (16a,b) and (17a,b) were identical with those prepared in 35-45% yield from *threo*- and *erythro*-2-chloro-3-(phenylthio)butane, respectively, by the same method as described above for the preparation of (2a) from 1-chloro-2-(phenylthio)cyclohexane.

Reaction of the Anilides (1a and b) in 2-Methylpropene-saturated Benzene. (a) 4'-Nitrobenzenesulphenanilide (1a) gave (i) a mixture of disulphide (3) and an unknown (60 mg); (ii) 1-(phenylthio)-2-(4-nitrophenylamino)-2-methylpropane (19a) (4.00 mmol, 80%), as a yellow thick oil; νmax (CS_2) 3430 (NH), 1330, 835, 740, and 695; m/z 302 (M^+), 179, 133, 124, and 123; δ1.5 (6H,s), 3.33 (2H,s), 4.9 (1H,br s), 6.55 (2H,d,J 9Hz), 7.05-7.55 (5H,m), and 8.05 (2H,d,J 9Hz) (Found: C, 63.85; H, 6.05; N, 9.1; S, 10.65. $C_{16}H_{18}N_2O_2S$ requires C, 63.55; H, 6.0; N, 9.25; S, 10.6%); and (iii) 4-nitroaniline (4a) (0.45 mmol, 9%).

(b) 4'-Chlorobenzenesulphenanilide (1b) gave (i) a mixture of unidentified products (20 mg); (ii) 1-(phenylthio)-2-(4-chlorophenylamino)-2-methylpropane (19b) (3.85 mmol, 77%), as a thick oil; νmax (CS_2) 3430 (NH), 840, 740, and 695; m/z 291 (M^+), 168, 133, 132, and 123; δ1.4 (6H,s), 3.17 (2H,s), 3.70 (1H,br s), 5.27 (2H,d,J 9Hz), and 5.6-6.13 (7H,m) (Found: C, 65.4; H, 6.15; Cl, 12.1; N, 4.85; S, 11.1. $C_{16}H_{18}ClNS$ requires C, 65.85; H, 6.2; Cl, 12.15; N, 4.8; S, 11.0%); and (iii) a mixture of 4-chloroaniline (4b) and, probably, 1-(phenylthio)-2-methyl-2-propanol (110 mg); νmax(CS_2) 3550 (OH), and 3495 and 3400 (NH_2); m/z 182 ($C_{10}H_{14}OS^+$), 129 and 127 ($C_6H_6ClN^+$), 124, 123, and 59.

Reaction of the Anilides (1a,d, and g) in Styrene (0.1 M)-Benzene. (a) 4'-Nitrobenzenesulphenanilide (**1a**) gave 1-phenyl-1-(4-nitrophenylamino)-2-(phenylthio)ethane (**18a**) (4.9 mmol, 98%), m.p. 113-115°C; νmax ($CHCl_3$) 3420 br (NH), 1605, and 1320; m/z 350 (M^+), 227, 181, and 124; δ3.0–3.6 (2H,m), 4.5 (1H,m, collapsing to dd,J 4.8 and 8.8Hz, upon D_2O exchange), 5.6 (1H,d,J 5Hz, removed upon D_2O exchange), 6.42 (2H,d,J 9Hz), 7.3–7.5 (10H,m), and 8.03 (2H, d,J 9Hz). (Found: C, 68.1; H, 5.15; N, 8.05; S, 9.2. $C_{20}H_{18}N_2O_2S$ requires C, 68.55; H, 5.2; N, 8.0; S, 9.15%).

(b) 3'-Nitrobenzenesulphenanilide (**1g**) gave 1-phenyl-1-(3-nitrophenylamino)-2-(phenylthio)ethane (**18g**) (4.9 mmol, 98%), m.p. 94-96°C; νmax ($CHCl_3$) 3420 br (NH), 1625, and 1345; m/z 350 (M^+), 227, 181, and 124; δ 2.87-3.67 (2H,m), 4.47 (1H,dd,J 5 and 8.5 Hz), 4.6 (1H,s), 6.9–7.67 (14H,m). (Found: C, 68.3; H, 5.25; N, 7.95; S, 9.1 %).

(c) 4'-Methylbenzenesulphenanilide (**1d**) gave (i) diphenyl disulphide (**3**) (0.45 mmol, 18%); (ii) 1-phenyl-1-[2-(phenylthio)-4-methylphenylamino]-2-(phenylthio)ethane (**22**) (0.5 mmol, 20%), as a thick oil; νmax (CCl_4) 3400 br (NH); m/z 427 (M^+), 304, 218, 109, and 105; δ2.17 (3H,s), 2.9–3.3 (2H,m); 4.03–4.5 (1H,m), 5.6 (1H,d,J 5Hz), 6.13 (1H,d,J 9Hz), 6.95 (1H,dd,J 2.5 and 9 Hz), and 6.97–7.47 (16H,m). (Found: C, 75.3; H, 5.9; N, 3.25; S, 14.85. $C_{27}H_{25}NS_2$ requires C, 75.85; H, 5.9; N, 3.3; S, 15.0%); (iii) 1-phenyl- 1-(4-methylphenylamino)-2-(phenylthio)ethane (**18d**) (3.05 mmol, 61%), m.p. 73–74°C; νmax (CCl_4) 3420 and 3380; m/z 319 (M^+), 196, 195, and 194; δ(CCl_4) 2.1 (3H,s), 2.83–3.4 (2H,m), 4.1 (1H,s), 4.21 (1H,dd,J 4.6 and 8.8 Hz), 6.23 (2H,d,J 8.5Hz), 6.77 (2H,d,J 8.5Hz), and 7–7.4 (10H,m). (Found: C, 78.7; H, 6.6; N, 4.35; S, 10.1. $C_{21}H_{21}NS$ requires C, 78.95; H, 6.65; N, 4.4; S, 10.05%); (iv) *p*-toluidine (**4d**) (1.4 mmol, 28%).

Reaction of the Anilide (1d) in Styrene (0.4M)-Benzene. This reaction gave 1-phenyl-1-(4-methylphenylamino)-2-(phenylthio)ethane (**18d**) (4.5 mmol, 90%) in addition to small amounts of disulphide (**3**) and *p*-toluidine (**4d**) (2 and 4% respectively).

Reaction of the Anilides (1a and d) in 1-Hexene (2.5M)-Benzene. (a) 4'-Nitrobenzenesulphenanilide (**1a**) gave (i) 1-(phenylthio)-2-hexanol (**26**)[18] (1.2 mmol, 24%), as an oil; νmax (CS_2) 3550 br (OH), 740, and 695; m/z 210 (M^+), 124, 123, 110, and 109; δ0.7–1.87 (9H,m), 2.4–3.4 (3H,m), 3.67 (1H,br s), and 6.83–7.57 (5H, br s); (ii) an inseparable mixture of the compound (**21a**) (see later) and an unknown (330 mg); (iii) 1-(phenylthio)-2-(4-nitrophenylamino)hexane (**20a**) (2.5 mmol, 50%), as a yellow thick oil; νmax (CS_2) 3420 and 3400 sh (NH), 1330, 840, 745, and 695; m/z 330 (M^+), 207, 161, 151, 124, and 123; δ 0.9–1.7 (9H,m), 3.03 (2H,d), 3.4–3.8 (1H,m), 4.93 (1H,d,J 8Hz), 6.3 (2H,d,J 9Hz), 7.1–7.33 (5H,m), and 7.95 (2H,d,J 9Hz). (Found: C, 65.0; H, 6.75; N, 8.6; S, 9.75. $C_{18}H_{22}N_2O_2S$ requires C, 65.4; H, 6.7; N, 8.5; S, 9.7%); and (iv) 4-nitroaniline (**4a**) (1.5 mmol, 30%).

(b) 4'-Methylbenzenesulphenanilide (**1d**) gave (i) diphenyl disulphide (**3**) (0.4 mmol, 16%); (ii) 1,2-bis(phenylthio)hexane (**25**) (0.33 mmol, 13%), as an oil; νmax (CS_2) 750, 740, and 695; m/z 302 (M^+), 193, 179, 123, 110, and 109; δ 0.7–2.1 (9H,m), 2.73–3.43 (3H,m), and 7.1–7.43 (10H,m). (Found: C, 71.6; H, 7.3; S, 21.35. $C_{18}H_{22}S_2$ requires C, 71.5; H, 7.35; S, 21.2%); (iii) an unidentified oily product (140 mg, 0.34 mmol, 14%); νmax (CCl_4) 3400 br (NH); m/z 407 ($C_{25}H_{29}NS_2^+$) 298, 284, 215, 119 and 117; (iv) a mixture of 1-(phenylthio)-2-(4-methylphenylamino)hexane (**20d**) and 2-(phenylthio)-1-(4-methylphenylamino)hexane (**21d**) (2.4 mmol, 48%); νmax (CCl_4) 3420 and 3390 sh (NH); m/z 299 (M^+), 189, 176, 123, 120, and 110; δ 0.7–2.0 (9H,m), 2.23 (3H,s), 2.73–3.83 (4H,m), 6.33–7.67 (9H,m). (Found: C, 76.45; H, 8.35; N, 4.75; S, 10.8. $C_{19}H_{25}NS$ requires C, 76.2; H, 8.4; N, 4.7; S, 10.7%). H.p.l.c. analysis on a C18 Erbasil column using acetonitrile-water (70:30 v/v) as eluant showed the two components to be in 73:27 ratio.

Treatment of this mixture (450 mg) with Raney nickel[19] (3 g) in absolute ethanol (30 ml) at room temperature for 24 h gave a mixture of N-(2-hexyl)- and N-(1-hexyl)-*p*-toluidine (**23**) and (**24**) in 80% yield; νmax (CCl_4) 3440; m/z 191 (M^+). The two isomeric *p*-toluidines (**23**) and (**24**) were present in *ca.* 70:30 ratio, as indicated by g.l.c. analysis by comparison of their retention times with those of authentic compounds (**23**) and (**24**)[20] prepared in *ca.* 50–60% yield by refluxing 2-bromo- or 1-bromo-hexane (10 mmol) and *p*-toluidine (10 mmol) in 95% ethanol (30 ml) containing potassium hydroxide (10 mmol). The hitherto unknown *p*-toluidine (**23**) was an oil; νmax (CCl_4) 3440 (NH); m/z 191 (M^+), 176, 134, 119, 118, 117, 106, and 91; δ 0.73–1.8 (12H,m), 2.27 (3H,s), 3.13–3.7 (2H,m), 6.6 (2H,d,9Hz), and 7.1 (2H,d,9Hz). (v) 1-(phenylthio)-2-hexanol (**26**) (0.4 mmol, 8%); and (vi) *p*-toluidine (**4d**) (26%).

The same reaction, carried out for 2 h in the presence of 1 equiv of $BF_3.Et_2O$, gave (i) diphenyl disulphide (**3**) (0.35 mmol, 14%); (ii) 1,2-bis(phenylthio)hexane (**25**) (0.05 mmol, 2%); (iii) an unidentified oily product which was identical to product (iii) obtained from the corresponding reaction in the presence of 1.5 equiv of $BF_3.Et_2O$ (200 mg, 0.50 mmol, 20%); (iv) a mixture of the isomeric adducts (**20d**) and (**21d**) (2.8 mmol, 56%); (v) 1-(phenylthio)-2-hexanol (**26**) (0.2 mmol, 4%); and (vi) *p*-toluidine (**4d**).

Reaction of the Anilide (1a) in 1-Hexene (0.1 M)-Benzene. This reaction was carried out for *ca.* 6 h. After usual work-up, chromatography gave (i) diphenyl disulphide (**3**) (0.05 mmol, 2%); (ii)

2-(phenylthio)-1-(4-nitrophenylamino)hexane (**21a**) (1.05 mmol, 21%), as a yellow oil; νmax (CS_2) 3440 and 3400 sh (NH), 1340, 835, 750, and 695; m/z 330 (M^+), 220, 180, 179, 177, and 151; δ0.7-1.73 (9H,m), 3.13-3.37 (3H,m), 5.15 (1H,br t), 6.45 (2H,d,J 9Hz), 7.2-7.6 (5H,m), and 8.05 (2H,d,J 9Hz). (Found: C, 65.65; H, 6.65; N, 8.4; S, 9.65. $C_{18}H_{22}N_2O_2S$ requires C, 65.4; H, 6.7; N, 8.5; S, 9.7%); (iii) 1-(phenylthio)-2-(4-nitrophenylamino)hexane (**20a**) (3.5 mmol, 70%); and (iv) 4-nitroaniline (**4a**) (0.25 mmol, 5%).

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