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The Reaction of Benzenesulfenanilides with Lewis Acids: Involvement of Radical Cation Intermediates.

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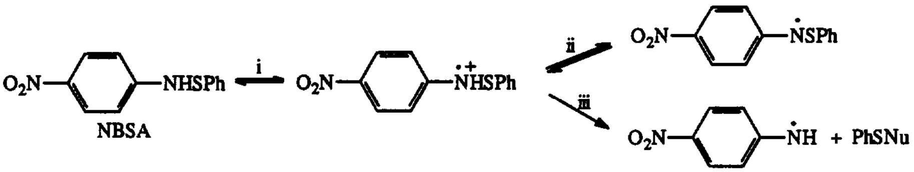
Abstract. The 4'-substituted N-methylbenzenesulfenanilides **1a-c** react with Lewis acids, including BF_3, $AlCl_3$ and $GaCl_3$, to afford the radical cation intermediates **9a-c**, some of which could be detected by e.p.r. spectroscopy. Thus, the 4'-methoxy substituted compound **1a** gave the fairly persistent radical cation **9a**. In contrast, the radical cation **9b**, derived from the 4'-nitro substituted compound **4b**, was not detected apparently because it decayed too rapidly forming the very stable radical cation **11b**, intermediate in the formation of the rearranged sulfide **10b**. The radical intermediates **9a-c** react with cyclohexene to give the 1,2-adducts **4a-c**, **5** and **6** which are believed to be formed from either the thiiranium ion **7b** or the sulfurane **8a,c**.

In recent years the reactions of benzenesulfenanilides (BSA) promoted by protic acids and Lewis acids have been the object of considerable interest[1]. In particular, it has been reported that boron trifluoride transforms 4'-nitrobenzenesulfenanilide (NBSA) into a highly reactive 'sulfenyl transfer' agent which can undergo electrophilic displacement at sulfur by several nucleophiles[2]. Thus, NBSA can be considered to be a phenylthio cation synthon and has been widely employed for this purpose in the 1,2-functionalization of alkenes and alkynes[3].

We recently reported[4] that the reaction of NBSA with Lewis acids, such as BF_3 and $AlCl_3$, leads to the formation of the thioaminyl radicals, ArNSPh (Ar = $4\text{-}NO_2C_6H_4$), and several lines of evidence suggested that these radicals were in rapid equilibrium with the 'sulfenyl transfer' species. In fact, when the Lewis acid promoted reaction of NBSA was examined, the persistent e.p.r. signal was found to be immediately quenched by the addition of nucleophiles, such as alkenes, alkynes or anisole and, if the thioaminyls radicals were scavenged with Bu_3SnH, the electrophilic addition of NBSA to carbon-carbon double or triple bonds was inhibited.

We suggested that a radical cation formed by a electron transfer between NBSA and the Lewis acid was the 'sulfenyl transfer' agent. However, no direct evidence was obtained for this radical cation which, if formed, would be expected to loose the amino proton or the phenylthio group by reaction with a base or a nucleophile, respectively, rather rapidly. (Scheme1).

In order to obtain direct evidence for the radical cation nature of the 'sulfenyl transfer' intermediates involved in reactions between BSAs and Lewis acids, we have now undertaken a chemical and spectroscopic study on the reactivity of 4'-substituted N-methylbenzenesulfenanilides **1a-c**. In these cases, the potential radical cations are expected either to undergo a rapid sulfenyl transfer or, if sufficiently persistent, to be directly detectable by e.p.r. spectroscopy.



Scheme 1. *Reagents :* i, $BF_3{\cdot}Et_2O$; ii, - H^+; iii, + Nu^-.

RESULTS AND DISCUSSION

The 4'-methoxy-N-methylbenzenesulfenanilide **1a** was reacted at room temperature in benzene solution with 1.5 molar equiv. of boron trifluoride-diethyl ether complex for 10 min.; the reaction mixture was neutralized with aqueous sodium carbonate and then chromatographed; diphenyl disulfide **2** was obtained in roughly quantitative yield, together with N-methyl-p-anisidine **3a** (ca. 40%) and unidentifiable coloured, tarry products. Similar results were obtained when the reaction was carried out in acetonitrile under the same conditions. The formation of the disulfide **2** and aniline **3a** was in agreement with the general behaviour exhibited by the BF_3-promoted reactions of BSAs when carried out in the absence of nucleophilic reagents[1]. The mechanism of this reaction is still unknown.

When the BF_3-promoted reaction of **1a** was carried out in the presence of cyclohexene, work-up and subsequent column chromatography led to the isolation of the addition products **4a**, **5**, and **6** together with major amounts of **2** and **3a**. According to previous work[1,3], the formation of these adducts can be inferred to an initial BF_3-promoted sulfenyl transfer from **1a** to the alkene double bond and subsequent capture of the resulting electrophilic intermediate, **7a** or **8a**. Thus, nucleophilic attack by the aniline **3a** and by the disulfide **2** would eventually lead to the amino sulfide **4a** and the bis-sulfide **5**, respectively. The cyclohexanol **6** was probably formed under the hydrolytic conditions employed during work-up (see Scheme 2). However, the observed yield of adducts **4a** and **5** had a ratio of 20:80, which does not parallel the relative nucleophilicities of the aniline **3a** and the disulfide **2**. The overall yield of the 1,2-adducts **4a**, **5**, and **6** (ca. 30%) is quite low when compared with related reactions involving other BSAs, which can afford up to 100% of addition products[1,3]. This suggested that the 'sulfenyl transfer' agent formed from **1a** has little tendency to undergo nucleophilic displacement at sulfur, which is consistent with the expected stabilizing effect of the two electron-releasing substituents, i.e. the 4'-methoxy and N-methyl groups.

When the reaction of **1a** with BF_3 was carried out in acetonitrile directly in the cavity of the e.p.r. spectrometer, a strong signal of a persistent radical was detected. (Fig.1a) Analysis of the spectrum, characterized by several sets of coupling constants, and its computer simulation (Fig. 1b) served to identify it as arising from the radical cation **9a** (see Table 1).

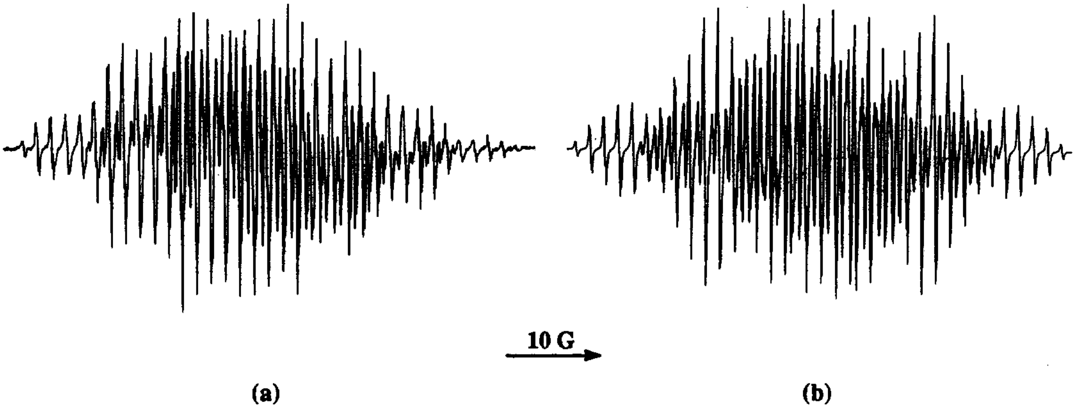
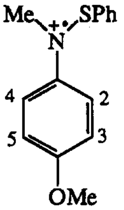


Fig. 1 **(a)** EPR spectrum of **9a** in acetonitrile, recorded at room temperature. **(b)** Computer simulation.

The spectrum exhibited an alternating line width effect at room temperature, most likely due to two concomitant restricted rotations about the C(1)-N and C(4)-O bonds. The energy barriers, previously reported for related radical species[5], lie in the range of 8-12 Kcal/mol.. To verify the assignment of the h.f.c. to radical **9a**, we synthetized the benzenesulfenanilide **1a**-d_5 with the deuterated phenylthio group. The BF_3-promoted reaction of **1a**-d_5 gave a radical species which shown an e.p.r. spectrum with a h.f.c. pattern identical to that of the non-deuterated **9a**, which proved that there was no unpaired electron density on the phenylthio group.

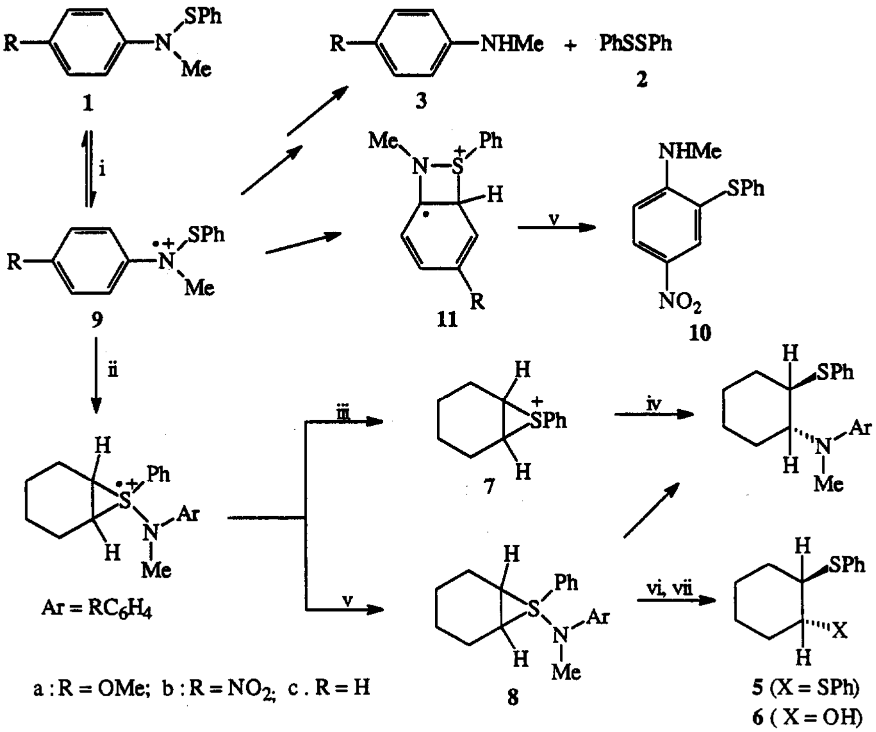
Table 1. Hyperfine coupling constants of radical cation **9a** (Gauss)



a (N)	a (H_{NMe})	$\bar{a}$ ($H^{2,6}$)[a]	a ($H^{3,5}$)	a (H_{OMe})	g-value
9.60	10.30	6.40	0.25	2.10	2.0034

[a] $a(H^{2,6})$ = [a (H^2) + a (H^6)]/2 ; because of the alternating line width effect the exact coupling constants cannot be assigned.

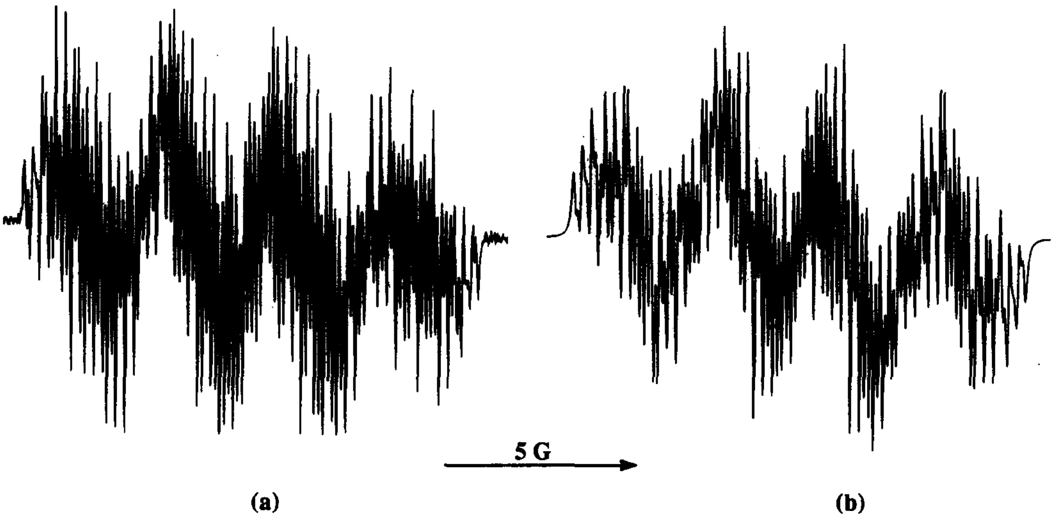
The boron trifluoride-promoted reaction of 4'-nitro-N-methylbenzenesulfenanilide **1b** gave results somewhat different from those obtained from **1a**. The reactions carried out in benzene or acetonitrile gave, besides the disulfide **2** and the aniline **3b**, the rearranged sulfide **10b**, with higher yield in benzene than in acetonitrile. Moreover, in the former solvent the rate of disappearance of the anilide **1b** was slower and noticeable amount (ca. 30%) of starting material was recovered after the usual work-up and column chromatography. This solvent effect can be explained by reasonable assumption that in the more polar solvent acetonitrile an ionic 'sulfenyl transfer intermediate is effectively stabilize, thus favouring its formation but disfavouring the electrophilic intramolecular *ortho*-sulfenylation leading to the rearranged sulfide **10b**.



Scheme 2. *Reagents and Conditions:* i, + BF_3, - $BF_3^{\cdot -}$, room temperature; ii, cyclohexene; iii, - $Ar\dot{N}Me$; iv, + **3**, - H^+; v, + e^-; vi, + **2**, - **1**; vii, + H_2O, - **3**.

When the BF_3-promoted reaction of **1b** was carried out in benzene in the presence of cyclohexene, we observed the rapid disappearance of starting anilide and the concomitant exclusive formation of the adduct **4b** in quantitative yield, at the expense of the disulfide **2**. Both findings were showing that reaction of the anilide **1b** with boron trifluoride is reversable and that the 'sulfenyl transfer' agent is a highly reactive species, as would be expected in view of the electron-withdrawing 4'-nitro-substituent. In agreement with this observed high reactivity, experiments performed directly in the e.p.r. spectrometer cavity did not show any trace of the radical **9b**. Instead, we detected a very stable radical cation, **11b**, (Fig. 2a and 3a) which reasonably arose from the initially formed **9b** by intramolecular attack of the electrophilic sulfur at a *ortho*-position of the anilino ring. Actually, the radical cation **11b** can be considered the precursor of the sulfide **10b**, obtained by 1,3-proton transfer and concomitant N-S bond fission. (see Scheme 2).

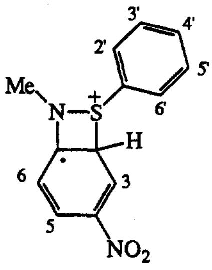
In repeated experiments, reactions of the anilides **1a,b** were also carried out with both $AlCl_3$ and $GaCl_3$, yielding just the same radical species that were obtained in the BF_3-promoted reactions.



(a) (b)

Fig. 2 (a) EPR spectrum recorded in acetonitrile at room temperature of the radical cation **11b**. (b) Computer simulation.

Table 2. Hyperfine coupling constants of radical cation **11a** (Gauss)[a]



a (N)	a (H^2)	a (H^3)[b]	a (N$_{NO_2}$)	a(H^5)[b]
5.75 (5.95)	6.80 (6.70)	0.82 (0.82)	0.59 (0.58)	0.48 (0.48)
a (H^6)[b]	a (H$^{2'}$)[c]	a (H$^{6'}$)[c]	a (H$^{4'}$)	g-value
0.21 (0.21)	1.12 (< lw.)	1.70 (< lw.)	2.15 (< lw.)	2.0056

[a] In brackets thecoupling constants of the corresponding radical with the deuterated phenylthio group are reported. [b]These coupling constants can not unambigously assigned to these positions. [c]a(H$^{2'}$) and a(H$^{6'}$) can be exchanged.

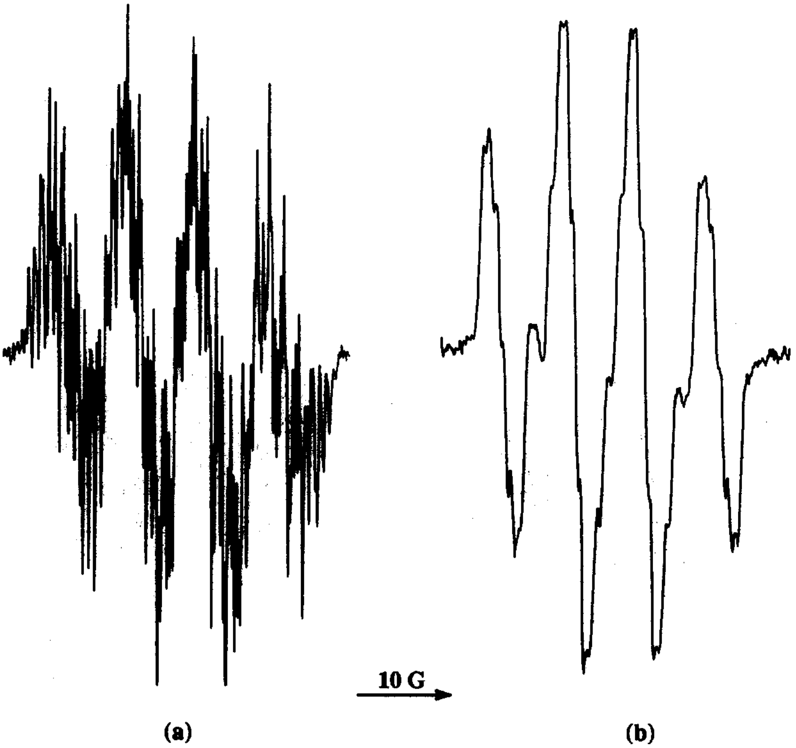


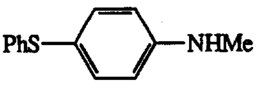
Fig. 3 EPR spectra recorded in acetonitrile at room temperature of (a) radical cation **11b** and (b) radical cation **11b**-d_5.

The identification of **11b** is supported by its e.p.r. spectroscopic parameters (Table 2) and the relative computer simulation. (Fig. 2b) In addition, the corresponding benzenesulfenanilide **1b**-d_5 with the deuterated phenylthio group was synthetized, and on reaction with BF_3 gave a radical cation having a spectrum with a different hyperfine pattern, as would be expected (Fig 3b). The deuterium coupling constants were not measurable as they were smaller than spectral line width.

The chemical reactivity of the parent N-methylbenzenesulfenanilide **1c** was intermediate, between that of **1a** and **1b**, as expected. In particular, the BF_3-promoted reaction in acetonitrile led to the formation of the disulfide **2** and the aniline **3c**, whereas the same reaction carried out in benzene afforded the rearranged sulfide **12** together with **2** and **3,c**. Furthermore, when the reaction was performed in the presence of cyclohexene, the 1,2-adducts **4c**, **5**, **6**, and **13** were isolated in good overall yield (>80%), which indicates a fairly high reactivity for this 'sulfenyl transfer' agent. The adducts **4c** and **13** are easily explained as arising from attack of the anilines **3c** and **12**, respectively, on the electrophilic intermediate obtained by sulfenyl group transfer to the carbon-carbon double bond. The pattern of the 1,2-adducts obtained from the anilide **1c** resembles the pattern obtained with **1a**, but is quite different from that exhibited by **1b**. This behaviour would suggest the involvement of different reaction intermediates. Thus, we claim that the BF_3-promoted reaction of the anilide

1b with cyclohexene might actually lead to the thiiranium ion intermediate **7b** which rapidly undergoes nucleophilic attack at carbon atom to give the adduct **4b**. By contrast, the anilides **4a** and **4c** might afford mainly the sulfurane intemediates **8a** and **8c** which can undergo both nucleophilic attack by the disulfide **2** or, after surviving the reaction environment, are hydrolized during work-up to form the cyclohexanol **6**. The involvement of sulfurane intermediates is generally accepted in addition of sulfenyl halides to alkenes.[6]

In agreement with the rather high reactivity exhibited by the 'sulfenyl transfer' agent formed from **1c**, the e.p.r experiments showed the initial formation of a non-persistent radical-cation, possibly **9c**, which rapidly decayed. Other persistent radical species were also detected, which appeared to have been formed from byproducts.



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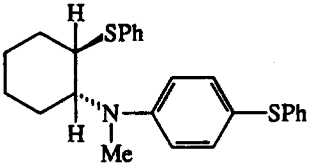

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In summary, we have shown that the N-methylbenzenesulphenanilides **1a-c** react with Lewis acids to give radical cation intermediates **9a-c** which, depending on the effect of the 4'-substituent, may survive long enough to be directly detected by e.s.r. spectroscopy.

The overall findings obtained in this and in our earlier work[4] indicate that BSAs reacts with Lewis acids through an initial mono-electron transfer process, leading to conclude that these reactions can not be strictly considered as acid-base Lewis type reactions. However, we wish to point out that a SET process can also account for an acid-base type reaction, if pairing of radical ions occurs before their escape from the solvent cage, leading to the acid-base zwitterionic complex.

EXPERIMENTAL SECTION

The N- methylbenzenesulfenanilides **1a**, **1b**[7], and **1c** were prepared by reaction of benzenesulfenyl chloride with the appropriate anilines **3a**, **3b**, and **3c**, respectively, in 70-90% yield. *N-Methyl-4'-methoxybenzenesulfenanilide* **1a** had m.p. 66-68 °C; δ_H 3.43 (3H, s), 3.77 (3H, s), and 6.7-7.3 (9H, m) (Found: M^+, 245.0880. $C_{14}H_{15}NOS$ requires M, 245.0874); m/z 245 (25), 137 (10), 136 (100), and 121 (11). *N-Methylbenzenesulfenanilide* **1c** had m.p. 57-58 °C; δ_H 3.40 (3H, s) and 6.9-7.4 (10H, m) (Found: M^+, 215.0762. $C_{13}H_{13}NOS$ requires M, 215.0769); m/z 215 (100), 109 (10), 106 (90), 105 (23), 104 (13), 79 (15), and 77 (43). The deuterated sulfenanilides **1a**-d_5 [δ_H 3.43 (3H, s), 3.77 (3H,s), 6.8 (2H, A part of a A_2B_2 system, J 9 Hz) and 7.2 (2H, B part of a A_2B_2 system, J 9 Hz); m/z 250 (M^+, 26) and 136 (100)] and **1b**-d5 [δ_H 3.8 (3H, s), 7.2 (2H, A part of a A_2B_2 system, J 9 Hz), and 8.2 (2H, B part of a A_2B_2 system, J 9 Hz); m/z 265 (M^+, 100), 115 (24), 114 (35), and 105 (40) were similarly prepared from deuterated sulfenyl chloride[8].

Reaction products such as the disulfide **2**, the anilines **3a-c**, the bis-sulfide **5**[9], the cyclohexanol **6**[9], and the aminosulfide **10b**[7] were each identified by spectral comparison with authentic specimens. The homogeneity of the hitherto unknown adducts **4b-c** and **13** and aminosulfide **12** was confirmed by TLC analysis.

EPR spectra were recorded on Varian E-104 X-band spectrometer, with 100 KHz modulation. ^{1}H NMR spectra were measured on Varian 200 (200 MHz) spectrometer, and are for $CDCl_3$ solutions with $SiMe_4$ as internal standard. Mass spectra were determined by the electron impsct method on VG 7070 instrument. 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.

BF_3-Promoted Reaction of N-Methylbenzenesulfenanilides 1a-c. General Procedure. To a solution of the benzenesulfenanilide **1a-c** (2 mmol.) in the appropriate solvent (20 cm^3) was added boron trifluoride-diethyl ether complex, ca. 47% BF_3 (0.38 cm^3, 3 mmol.) under vigorous stirring at room temperature. After being stirred for 10 min., the reaction mixture was treated with 10% aqueous sodium carbonate and extracted with diethyl ether. The organic layer was then separated, the excess solvent removed and the residue chromatographed.

Reaction of the Anilides 1a-c in acetonitrile. (a) N-Methyl-4'-methoxybenzenesulfenanilide 1a gave (i) diphenyl disulfide **2** (0.97 mmol., 97%); (ii) N-methyl-p-anisidine **3a** (0.8 mmol., 40%); and (iii) tarry material.

(b) N-Methyl-4'-nitrobenzenesulfenanilide 1b gave (i) diphenyl disulfide **2** (0.84 mmol., 84%); (ii) N-methyl-2-(phenylthio)-4-nitroaniline **10b** (0.4 mmol., 7%); and (iii) N-methyl-4-nitroaniline **3b** (1.30 mmol., 65%).

(c) N-Methylbenzenesulfenanilide 1c gave (i) diphenyl disulfide **2** (0.98 mmol., 98%); (ii) N-methylaniline **3c** (1.0 mmol., 50%); and (iii) tarry meterial.

Reaction of the Anilides 1a-c in benzene. (a) N-Methyl-4'-methoxybenzenesulfenanilide 1a gave (i) diphenyl disulfide **2** (1.0 mmol., 100%); (ii) N-methyl-p-anisidine **3a** (1.0 mmol., 50%); and (iii) tarry material.

(b) N-Methyl-4'-nitrobenzenesulfenanilide 1b gave (i) diphenyl disulfide **2** (0.44 mmol., 63%); (ii) unreacted anilide **1b** (0.6 mmol., 30%); (iii) N-methyl-2-(phenylthio)-4-nitroaniline **10a** (0.18 mmol., 26%); and (iv) N-methyl-4-nitroaniline **3b** (0.25 mmol., 36%).

(c) N-Methylbenzenesulfenanilide 1c gave (i) diphenyl disulfide **2** (0.7 mmol., 70%); (ii) *N-methyl-4-(phenylthio)aniline* **12** (0.60 mmol., 30%), thick oil; δ_H 2.83 (3H, s), 3.7 (1H, br s), 6.60 (2H, A part of a A_2B_2 system, J 9 Hz), 7.2 (5H, m), and 7.40 (2H, B part of a A_2B_2 system, J 9 Hz) (Found: M^+, 215.0775. $C_{13}H_{13}NS$ requires M, 215.0769); m/z 215 (100), 214 (12), 200 (11), 183 (12) and 138 (16); (iii) N-methylaniline **3c** (0.90 mmol., 45 %); and (iv) tarry material.

Reaction of the anilides 1a-c in benzene/cyclohexene 9:1. (a) N-Methyl-4'-methoxybenzenesulfenanilide 1a gave (i) diphenyl disulfide **2** (0.67 mmol., 67%); (ii) 1,2-bis-(phenylthio) cyclohexane **5** (0.20 mmol.), 20%); (iii) 2-(phenylthio)cyclohexanol **6** (0.12 mmol., 12%); (iv) *trans-1-[N-methyl-N-(4-methoxyphenyl)]amino-2-(phenylthio)- cyclohexane* **4a** (0.06 mmol., 6%), solid product which was not recrystalized; δ_H 1.2-2.2 (8H, m), 2.70 (3H, s), 3.28 (1H, dt, J_t 11.2, J_d 3.7 Hz), 3.47 (1H, dt, J_t 11.2, J_d 3.1 Hz), 6.85 (4H, m), 7.2-7.5 (5H, m) (Found: M^+, 327.1660. $C_{20}H_{25}NOS$ requires M, 327.1657); m/z 327 (90), 218 (30), 191 (10), 177 (13), 176 (100), 150 (20), and 81 (18); (v) N-methyl-p-anisidine **3a** (0.90 mmol., 45%); and (vi) tarry material.

(b) N-Methyl-4'-nitrobenzenesulfenanilide 1b gave *trans-1-[N-methyl-N-(4-nitrophenyl)] amino-2-(phenylthio)cyclohexane* **4b** (1.90 mmol., 95%), m. p. 144-145 °C; δ_H 1.2-2.2 (8H, m), 2.76 (3H, s), 3.3 (1H, m), 3.7 (1H, m), 6.7 (2H, d, J 9 Hz), 7.3 (5H, m), and 8.2 (2H, d, J 9Hz) (Found: M$^+$, 342.1408. $C_{19}H_{22}N_2O_2S$ requires M, 342.1402); m/z 342 (55), 325 (13), 233 (36), 191 (100), and 165 (10).

(c) N-Methylbenzenesulfenanilide 1c gave (i) 1,2-bis(phenylthio)cyclohexane **5** (0.03 mmol., 3%); (ii) *trans-1-(N-methyl-N-phenyl)amino-2-(phenylthio)cyclohexane* **4c** (0.58 mmol., 29%); m. p. 68-70 °C; δ_H 1.2-2.2 (8H, m), 2.70 (3H, s), 3.25 (1H, dt, J_t 11, J_d 3 Hz), 3.60 (1H, dt, J_t 11, J_d 3 Hz), 6.65-6.85 (2H, m), and 7.15-7.35 (8H,m) (Found: M^{+}, 297.1545. $C_{19}H_3NS$ requires M, 297.1551); m/z 297 (50), 188 (34), 146 (100), 120 (15), 77 (14); (iii) *trans-1-[N-methyl-N-(4-phenylthio)phenyl]amino-2-(phenylthio)cyclohexane* **13** (0.20 mmol., 20%); thick oil; δ_H 1.2-2.2 (8H, m), 2.70 (3H, s), 3.20 (1H, dt, J_t 11, J_d 4 Hz), 3.60 (1H, dt, J_t 11, J_d 4 Hz), 6.65 (2H, d, J 9Hz), 7.0-7.3 (10H, m), and 7.40 (2H, d, J 9 Hz) (Found: M$^+$, 405.1590. $C_{25}H_{27}NS_2$ requires M, 405.1585); m/z 405 (100), 296 (17), 254 (56), 228 (13) 191 (13) and 144 (25); (iv) N-methyl-4-(phenylthio)aniline **12** (0.06 mmol., 3%); (v) 2-(phenylthio)cyclohexanol **6** (0.60 mmol., 30%); and (vi) N-methylaniline **3c** (0.62 mmol., 62%).

EPR Experiments. The experiments were run matching the conditions in the current preparative reaction. A 'U' sample tube, to keep separate the two reactants, was used and the acetonitrile solution of $BF_3 \cdot Et_2O$ was deoxygenated with the freeze-thaw technique in a vacuum line. The reagents were mixed directly in the EPR sample tube, at room temperature, and then introduced in the spectrometer cavity. The g-values for the radical species were determined by comparison with the g-value (2.0037) of DPPH.

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