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ESR Studies of Nitrogen-centered Free Radicals, *N*-Aryl-*N*-phenylthioaminyls[1)]

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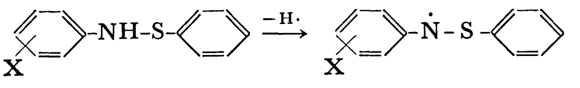
A variety of substituted *N*-phenyl-*N*-phenylthioaminyls (**2**), Ar–$\dot{\mathrm{N}}$–S–Ar′, were generated by the photolysis of benzenesulfenanilides (**1**) in benzene in the presence of di-*t*-butyl peroxide or by the oxidation of **1** in benzene with lead dioxide. The ESR spectra of the radicals were completely analyzed by labeling some radicals with deuterium and with the aid of a computer simulation technique. The unpaired electron is distributed mainly on the nitrogen atom and the *N*-phenyl ring. The values of a_N were plotted against the σ or σ^- in the Hammett equation, and it was found that **2**, in terms of Walter's criteria, belong to class S.

A number of nitrogen-centered free radicals have been prepared, and extensive ESR spectroscopic studies have been undertaken.[2)] In the course of our studies of nitrogen-centered free radicals bearing sulfur atoms adjacent to the radical centers, *N*-aryl-*N*-phenylthioaminyls (**2**) have been found to be easily generated by hydrogen-abstraction from benzenesulfenanilides (**1**). The radicals possess a divalent sulfur atom adjacent to the radical center and have never been reported to be detected unambiguously.[3)] A few radicals relating to **2** have thus far been reported, but no systematic ESR spectroscopic investigation of the radicals has yet been undertaken.[4–7)] More recently, however, Ingold *et al.* have reported a detailed ESR spectroscopic investigation of radicals which are generated by radical additions to di-*t*-butyl sulfur diimide.[8)]



1 **2**

The present authors have now generated a variety of substituted *N*-aryl-*N*-phenylthioaminyls (**2**) and investigated them in detail by means of ESR spectroscopy. In the present report, the results will be described and discussed.

Results and Discussion

The generation of **2** was performed by two procedures: a) the photolysis of **1** in degassed benzene in the presence of di-*t*-butyl peroxide, and b) the oxidation of **1** in degassed benzene with lead dioxide and potassium carbonate. In the present studies, procedure a has been mainly employed, because that the procedure is more convenient and, although a low-power mercury lamp (100 W) was used as the source, the procedure generated **2** at a sufficient concentration for us to record well-resolved ESR spectra (10^{-5} mol/l except for **2a** and **2c**, the concentrations of which were lower). The radicals **2a** and **2c**, after irradiation for 10 min, immediately decayed on the turning out of the lamp. On the other hand, the radicals **2f** and **2m** could be detected over a period of more than 1 h, and the radicals **2d** and **2g** over a period of at least 2 h.

The radical **2a** presented a very complex ESR spectrum (Fig. 1). In order to facilitate the analysis of the spectrum and to avoid erroneous assignments, the

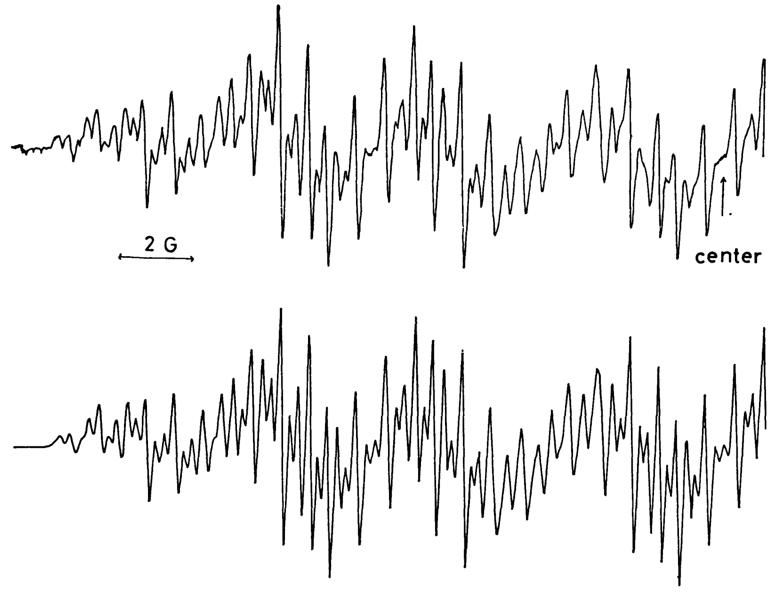


Fig. 1. Experimental ESR spectrum (low-field half) of *N*-phenyl-*N*-phenylthioaminyl (**2a**) in benzene (upper), and computer simulated, using Lorentzian line shapes and a line width of 0.20 G (lower).

radical was labeled with deuterium. The labeled radical, **2b**, gave a simple 1 : 1 : 1 triplet spectrum, which was obviously split by the interaction with the nitrogen nucleus. On the other hand, the spectrum of the other labeled radical, **2c**, was split into a 1 : 1 : 1 triplet due to the nitrogen nucleus, and each component of the triplet was split into 1 : 2 : 1 triplets of a 1 : 3 : 3 : 1 quartet due to the three equivalent *ortho*- and *para*-protons and the two *meta*-protons respectively. On the basis of these results, the spectrum of **2a** was analyzed.

Next, substituted *N*-phenyl-*N*-phenylthioaminyls were generated and the spectra were analyzed. The radicals **2f**—**h** each gave a relatively simple ESR spectrum (Fig. 2). On the other hand, the spectra of the other radicals were very complex (Figs. 3 and 4). Thus, some radicals were also labeled with deuterium, and the complex spectra were analyzed on the basis of the data from the labeled radicals. The ESR parameters for **2** are summarized in Table.

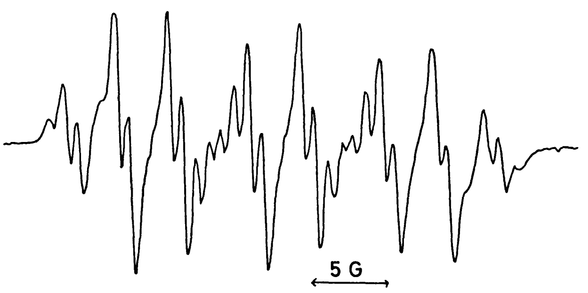


Fig. 2. Experimental ESR spectrum of *N*-3,5-dichlorophenyl-*N*-phenylthioaminyl (**2g**) in benzene.

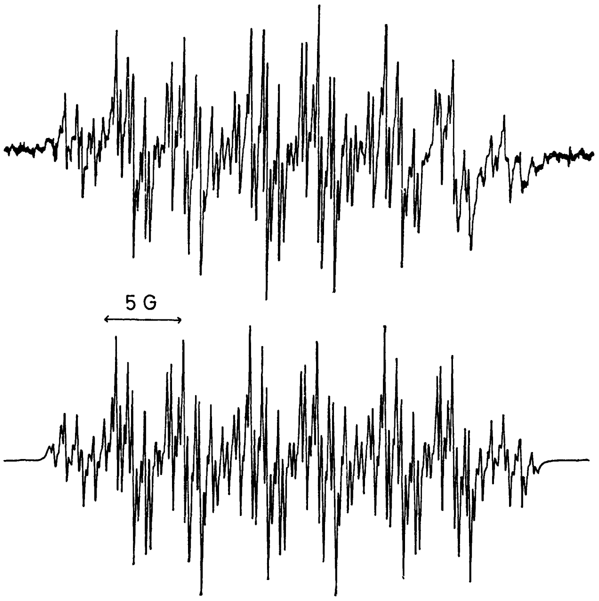


Fig. 3. Experimental ESR spectrum of *N*-3-acetylphenyl-*N*-phenylthioaminyl (**2k**) in benzene (upper), and compuer simulated, using Lorentzian line shapes and a line width of 0.19 G (lower).

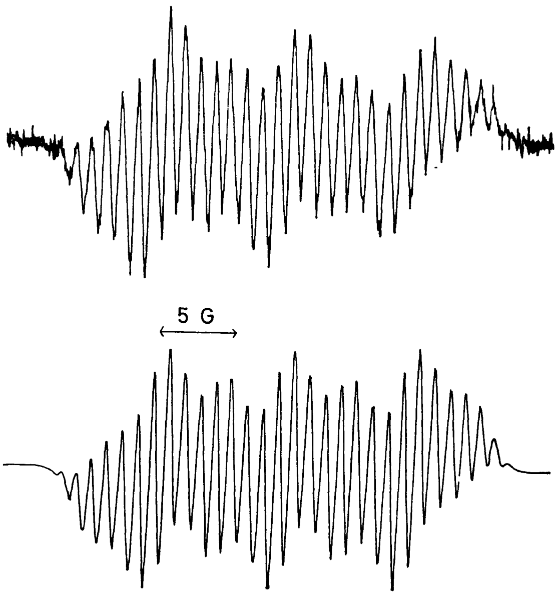


Fig. 4. Experimental ESR spectrum of *N*-4-nitrophenyl-*N*-phenylthioaminyl (**2m**) in benzene (upper), and computer simulated, using Lorentzian line shapes and a line width of 0.46 G (lower).

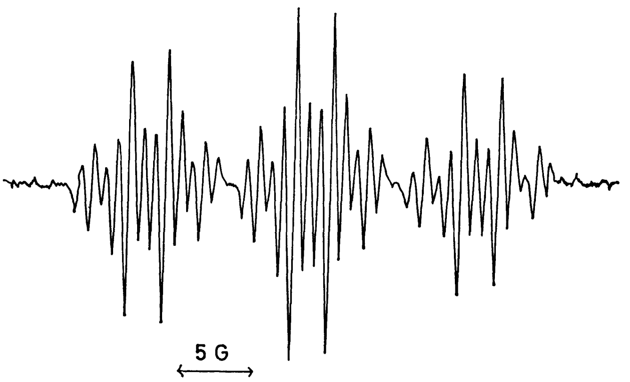
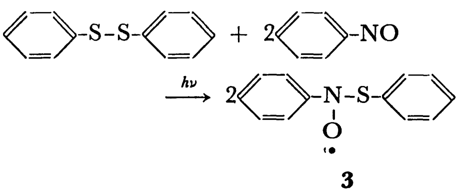


Fig. 5. Experimental ESR spectrum of the nitroxide radical **3** generated by photolysis of diphenyl disulfide in benzene in the presence of nitrosobenzene.

In general, it is well known that nitrogen-centered free radicals tend to convert into the corresonding nitroxide radicals by reactions with oxidizing agents (*e. g.* atmospheric oxygen, *etc.*). In order to exclude this possibility, the corresponding nitroxide radical, **3**, was generated by the photolysis of diphenyl disulfide in benzene in the presence of nitrosobenzene (Fig. 5). The ESR parameters for **3** are 11.52 (a_N), 2.56 ($a_{o\text{-H}}$ and $a_{p\text{-H}}$), and 0.86 G ($a_{m\text{-H}}$).[9] From the results, it is clear that the radicals **2** are not nitroxide radicals.



$$C_6H_5\text{-S-S-}C_6H_5 + 2\,C_6H_5\text{-NO} \xrightarrow{h\nu} 2\,C_6H_5\text{-}\underset{\substack{|\\ O^{\bullet}}}{N}\text{-S-}C_6H_5$$

3

The radicals **2** can also be generated by the treatment of **1** with lead dioxide and potassium carbonate. For example, the sulfenamide **1d** in benzene, on contact

TABLE 1. THE ESR PARAMETERS FOR *N*-ARYL-*N*-PNENYLTHIOAMINYLS (**2**)[a)]

Radical	$Ar_1-\dot{N}-S-Ar_2$		Coupling constant (G)								*g*-Value
				N-Phenyl			*S*-Phenyl				
	Ar_1	Ar_2	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$	a_{other}	
2a[b)]	C_6H_5	C_6H_5	9.59	3.70	1.26	4.18	0.78	0.27	0.84		2.0059
2b	C_6D_5	C_6H_5	9.56								2.0059
2c	C_6H_5	C_6D_5	9.59	3.78	1.23	3.78					2.0059
2d[b)]	4-$CH_3C_6H_4$	C_6H_5	9.55	3.79	1.17	—	0.79	0.27	0.82	4.83(CH_3)	2.0059
2e[b)]	4-$CH_3OC_6H_4$	C_6H_5	9.56	3.87	1.10	—	0.78		0.83	0.58(CH_3O)	2.0059
2f	4-ClC_6H_4	C_6H_5	9.48	3.79		—					2.0061
2g	3,5-$Cl_2C_6H_3$	C_6H_5	9.26	3.68	—	3.68	0.90		0.90		2.0061
2h	4-BrC_6H_4	C_6H_5	9.43	3.73		—					
2i[b)]	4-$CH_3COC_6H_4$	C_6H_5	8.97	3.46	1.24	—	0.90		0.94		
2j	4-$CH_3COC_6H_4$	C_6D_5	8.97	3.43	1.24	—					2.0063
2k[b)]	3-$CH_3COC_6H_4$	C_6H_5	9.45	3.59	1.22	3.92	0.83	0.25	0.87		
2l[b)]	4-$NO_2C_6H_4$	C_6H_5	8.77	3.35	1.23	—	0.95		0.95	0.89(NO_2)	2.0065
2m[b)]	4-$NO_2C_6H_4$	C_6D_5	8.75	3.37	1.22	—				0.88(NO_2)	2.0065
2n[b)]	3-$NO_2C_6H_4$	C_6H_5	9.25	3.45	1.25	3.74	0.89	0.26	0.92	0.26(NO_2)	

a) In benzene at room temperature. b) The coupling constants were determined by means of the computer simulation technique.

with the oxidizing agents under degassed conditions, instantly turned dark blue. The color remained for *ca.* 10 s, after which, it slowly turned brown. The blue color seems to be responsible for **2d**,[10)] while the brown color is probably attributable to decomposition products of **2d**. Similar blue solutions were also obtained in the cases of **1e**, **1f**, and **1m**. On the other hand, in **1j**, a greenish blue solution, and in **1g** and **1m**, green solutions were obtained. These colors immediately turned brown (except for **1g**, and in this case, the green color remained for *ca.* 20 min). From the brown solutions, however, only **2** was detected as a paramagnetic species by ESR spectroscopic measurements.

From the values of the coupling constants shown in the table, it may be concluded that, in **2**, the unpaired electron is distributed mainly on the nitrogen ($2p_z$ orbital) and the *N*-phenyl ring. On the other hand, it is of interest that couplings due to the *S*-phenyl ring protons are observed, indicating that the unpaired electron is also delocalized onto the *S*-phenyl ring across the divalent sulfur atom, though the degree of delocalization is small.

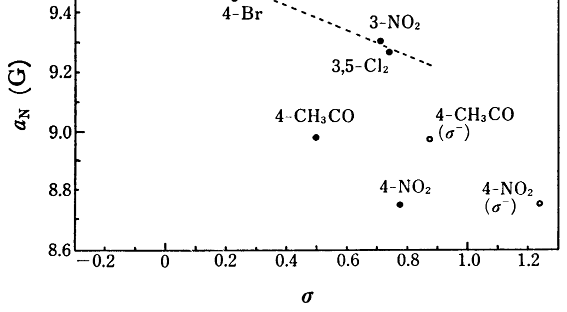
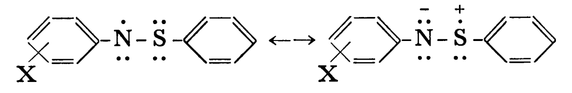


Fig. 6. Plot of nitrogen coupling constants (a_N) of *N*-aryl-*N*-phenylthioaminyls (**2**) *vs.* σ (and σ⁻).

The values of a_N were plotted against the Hammett σ and σ⁻ parameters (Fig. 6).[11)] In terms of Walter's criteria,[12)] substituted aryl nitroxide radicals and nitrobenzene anion radicals[11)] belong to class O, while *N*-alkyl-*N*-arylamino radicals have been reported to belong to class S.[13)] As may be found in the figure, the values of a_N are correlated by neither σ nor σ⁻,[14,15)] indicating that **2** belong to class S. In the present radicals, the values of a_N seem to be decreased by two effects:[16)] the delocalization of spin onto the substituents and the polar effect to be described below (Form B), as has been pointed out by Danen *at al.* in the case of *N*-alkoxy-*N*-arylamino radicals.[13)]



Form A Form B

About the polar effect, as more powerful electron-withdrawing substituents are introduced into the *N*-phenyl ring, the polar form B becomes more important. Therefore, the effect results in a decrease in the spin density on the nitrogen atom, while, on the contrary, that on the sulfur atom is increased. The degree of the effect may reflect the magnitude of coupling due to the *S*-phenyl ring protons. As can be seen in the table, the introduction of electron-withdrawing groups brings about an increase in the magnitude of the proton coupling constants. Although the difference in the magnitude of the coupling constants of the *para* protons in the *S*-phenyl ring is small, we attempted to plot the values against σ (and σ⁻), the values being correlated by σ (and σ⁻).

In the cases of non- and *meta*-substituted radicals (**2a**, **2g**, **2k**, and **2n**), only the polar effect is important because, as the spin density at the *meta* position is considerably smaller than those at the *ortho* and *para* positions, the delocalization of the spin onto the substituents is negligibly small. About the four free radicals, the values of a_N are well correlated by σ, as may be found in the figure. In the cases of the other free radicals, on the other hand, the two effects are operative and the values of a_N are significantly decreased. Therefore, the values of a_N are correlated by neither σ nor σ^-.

Experimental

All the melting points are uncorrected. The IR spectra were run on a Jasco Model IR-G Spectrometer. The NMR spectra were recorded on a Hitachi-Perkin Elmer R-20 Spectrometer, using TMS as the internal standard. The elemental analyses were carried out with a Yanaco MT-2 CHN Corder.

Meterials. The benzene used for the ESR measurement was purified by the usual method.[1] Commercially available di-*t*-butyl peroxide was used without further purification, while nitrosobenzene was recrystallized once from ethanol just before use.

Benzenethiol-2,3,4,5,6-d_5. Aniline-2,3,4,5,6-d_5 (*D*-content; 99%, E. Merck, Darmstadt, Germany) was diazotized and treated with potassium xanthate.[17] The resulting xanthate ester was hydrolyzed with potassium hydroxide in ethanol, and then neutralized with sulfuric acid and water-distilled. The resulting oily product was extracted with ether and dried over anhydrous sodium sulfate. After filtration, ether was evaporated and the product was distilled (82—83 °C/55 Torr) to give the desired benzenethiol in a 53% yield. The *D*-content was determined to be 98% from the proton ratio in the NMR spectrum.

General Procedure for the Preparation of Benzenesulfenanilides (1). Benzenethiol was allowed to react with chlorine gas in dry chloroform at −5—0 °C. After the subsequent removal of chloroform, the resulting oily residue was distilled (56—57 °C/3 Torr) to give pure benzenesulfenyl chloride.[1] However, benzenesulfenyl chloride-d_5 was used for the following step without distillation.

Benzenesulfenyl chloride (0.025 mol) in dry ether (25 ml) was added, drop by drop, to aniline (0.055 mol) in dry ether (100—1000 ml) at −20—−30 °C under stirring. After the completion of the addition, the reaction mixture was stirred for an additional 30 min and the reaction temperature was raised to room temperature. After the formed aniline hydrochloride had been filtered off, ether was evaporated to give crude **1**, which was treated with decoloring carbon and repeatedly recrystallized from the appropriate solvents.

Benzenesulfenanilide (**1a**): 54—56 °C (petroleum ether, lit,[18] 53—55 °C). 4′-Methylbenzenesulfenanilide (**1d**): 51—52 °C (petroleum ether, lit,[19] 52 °C). 4′-Methoxybenzenesulfenanilide (**1e**): 69—70 °C (hexane, lit,[19] 67 °C). 4′-Nitrobenzenesulfenanilide (**1l**): 109—110 °C (methanol-water, lit,[18] 108 °C).

Benzenesulfenanilide-2′,3′,4′,5′,6′-d_5 *(1b).* Mp 59—60 °C (petroleum ether). Yield 44%. IR (KBr): 3320 cm^{-1} (NH). NMR (CCl_4): δ 4.78 (s, NH) and 7.06 (s, C_6H_5). Found: C, 69.83; H, 5.53; N, 6.75%. Calcd for $C_{12}H_6D_5NS$: C, 69.85; H, 5.38; N, 6.79%.

Benzenesulfen-2,3,4,5,6-d_5*-anilide (1c).* Mp 57—58 °C (petroleum ether). Yield 69%. IR (KBr): 3350 cm^{-1} (NH). NMR (CCl_4): δ 5.10 (s, NH) and 6.70—7.25 (m, C_6H_5). Found: C, 69.57; H, 5.44; N, 6.69%. Calcd for $C_{12}H_6D_5NS$: C, 69.85, H, 5.38; N, 6.79%.

4′-Chlorobenzenesulfenanilide (1f). Mp 82—83 °C (hexane). Yield 75%. IR (KBr): 3340 cm^{-1} (NH). NMR ($CDCl_3$): δ 5.12 (s, NH) and 6.81—7.40 (m, C_6H_5 and C_6H_4). Found: C, 61.33; H, 4.35; N, 5.73%. Calcd for $C_{12}H_{10}ClNS$: C, 61.14; H, 4.28; N, 5.94%.

4′-Bromobenzenesulfenanilide (1h). Mp 94—95 °C (hexane). Yield 68%. IR (KBr); 3340 cm^{-1} (NH). NMR ($CDCl_3$): δ 5.10 (s, NH), and 6.74—7.43 (m, C_6H_5 and C_6H_4). Found: C, 51.45; H, 3.80; N, 4.93%. Calcd for $C_{12}H_{10}BrNS$: C, 51.43; H, 3.60; N, 5.00%.

3′,5′-Dichlorobenzenesulfenanilide (1g). Mp 95—96 °C (hexane). Yield 75%. IR (KBr): 3340 cm^{-1} (NH). NMR ($CDCl_3$): δ 5.17 (NH), 6.82—6.93 (m, C_6H_3), and 7.24 (s, C_6H_5). Found: C, 53.37; H, 3.26; N, 5.10%. Calcd for $C_{12}H_9Cl_2NS$: C, 53.34; H, 3.36; N, 5.19%.

4′-Acetylbenzenesulfenanilide (1i). Mp 98—99 °C (methanol-water and then benzene-hexane). Yield 52%. IR (KBr): 3230 and 3270 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.46 (s, CH_3), 5.82 (s, NH), 7.16 (s, C_6H_5), and 7.02 and 7.83 (d, J=9 Hz, C_6H_4). Found: C, 69.08; H, 5.28; N, 5.77%. Calcd for $C_{14}H_{13}NOS$: C, 69.10; H, 5.38; N, 5.76%.

4′-Acetylbenzenesulfen-2,3,4,5,6-d_5*-anilide (1j).* Mp 103—104 °C (methanol-water and then benzene-hexane). Yield 40%. IR (KBr): 3250 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.49 (s, CH_3), 5.80 (s, NH), and 7.02 and 7.83 (d, J=9 Hz, C_6H_4). Found: C, 67.49; H, 5.13; N, 5.59%. Calcd for $C_{14}H_8D_5NOS$: C, 67.70; H, 5.27; N, 5.64%.

3′-Acetylbenzenesulfenanilide (1k). Mp 84—85 °C (methanol-water and then benzene-hexane). Yield 61%. IR (KBr): 3290 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.50 (s, CH_3), 5.57 (s, NH), and 7.05—7.65 (m, C_6H_5 and C_6H_4). Found: C, 69.22; H, 5.27; N, 5.73%. Calcd for $C_{14}H_{13}NOS$: C, 69.10; H, 5.38; N, 5.76%.

4′-Nitrobenzenesulfen-2,3,4,5,6-d_5*-anilide (1m).* Mp 105—106 °C (methanol-water). Yield 33%. IR (KBr): 3300 and 3330 cm^{-1} (NH). NMR ($CDCl_3$): δ 5.86 (s, NH) and 7.08 and 8.12 (d, J=9 Hz, C_6H_4). Found: C, 56.98; H, 3.92; N, 11.41%. Calcd for $C_{12}H_5D_5N_2O_2S$: C, 57.35; H, 4.01; N, 11.15%.

3′-Nitrobenzenesulfenanilide (1n). Mp 110—111 °C methanol-water). IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 5.50 (s, NH) and 7.15—7.90 (m, C_6H_5 and C_6H_4). Found: C, 58.22; H, 4.13; N, 11.52%. Calcd for $C_{12}H_{10}N_2O_2S$: C, 58.51; H, 4.09; N, 11.38%.

Generation of N*-Aryl-*N*-phenylthioaminyls (2).* a) Benzenesulfenanilide (**1**, 5 mg), di-*t*-butyl peroxide (0.02 ml), and benzene (0.2 ml) were placed in an ESR tube. After the solution had been degassed by three freeze-and-thaw cycles, the tube was sealed off. An ESR spectrum of the solution was recorded while the solution was being UV-irradiated from a distance of 40 cm using a high-pressure mercury lamp (JES-UV-1, 100 W) at room temperature; b) in one arm of a two-armed glass tube which was attached to an ESR tube, **1** (0.1 g) and benzene (2 ml) were placed, while lead dioxide (0.5 g) and potassium carbonate (0.5 g) were placed in the second arm. After the contents had been degassed as has been described above and the tube had been sealed off, the benzene solution of **1** was poured into the second arm containing the oxidizing agents and the resulting mixture was shaken well. A part of the supernatant of the mixture was poured into the ESR tube, and the tube was sealed off.

Generation of the Nitroxide Radical 3. Nitrosobenzene (4 mg), diphenyl disulfide (5 mg), and benzene (0.2 ml) were placed in an ESR tube and the solution was degassed as has been described above, the tube was then sealed off. An ESR spectrum of the solution was recorded under UV-irradiation as has been described above.

The ESR spectra were recorded on a JES-ME 3X Spectrometer equipped with 100 kHz field modulation. Computer simulations of the ESR spectra were carried out using a FACOM 270-30 Computer with a FACOM 6201B Plotter; they were fitted by means of a trial-and-error method.

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