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An ESR Study of *N*-(Alkylthio)arylaminyls. Substituent Effects on ESR Parameters[1]

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A series of *N*-(alkylthio)arylaminyls, $\mathrm{Ar\dot{N}SR}$, were generated by hydrogen-abstraction from *N*-(alkylthio)anilines or by the photolysis of *N*,*N*-bis(*t*-butylthio)anilines, and were studied by ESR spectroscopy. *N*-(*t*-Butylthio)aminyls were fairly long-lived, and their lifetimes were scarcely affected by oxygen. Substituent effects on the ESR parameters were also studied, and the results were compared with those for *N*-alkoxyarylaminyls.

A variety of *N*-alkoxyarylaminyls (**5**), $\mathrm{Ar\dot{N}OR}$, were produced by hydrogen-abstraction from *N*-alkoxyanilines,[2] by addition of alkyl or metal radicals,[3] and by the photolysis of peroxyoxalates,[4] and they were studied in detail by means of ESR spectroscopy. Since the aminyls prossess an aromatic ring and an oxygen atom adjacent to the central nitrogen, they are significantly stabilized by such contributing resonance forms as $-\dot{N}-\ddot{O}- \leftrightarrow -\ddot{\bar{N}}-\dot{O}^{+}-$.

N-(Alkylthio)arylaminyls (**3**) are structurally very close to **5**; therefore, the comparison of their ESR parameters and stabilities with those for **5** is interesting. However, the aminyls **3** have never been reported on. In this paper we wish to report on the generation of **3** and their ESR spectroscopic investigation. In addition, the results will be compared with those for **5**.

Results and Discussion

The aminyls **3** were generated by hydrogen-abstraction from *N*-(alkylthio)anilines (**1**) by the *t*-butoxyl radical, which were produced by the thermal decomposition of di-*t*-butyl diperoxyoxalate (Method A) or by the photolysis of *N*,*N*-bis(*t*-butylthio)anilines (**2**) (Method B).

$$\underset{\mathbf{1}}{\mathrm{ArNHSR}} \xrightarrow{-\mathrm{H}\cdot} \underset{\mathbf{3}}{\mathrm{Ar\dot{N}SR}} \quad \text{(Method A)}$$

a: Ar$=$4-$NO_2C_6H_4$, R$=$*t*-Bu
b: Ar$=$3-$NO_2C_6H_4$, R$=$*t*-Bu
f: Ar$=$3,5-*t*-$Bu_2C_6H_3$, R$=$*t*-Bu
n: Ar$=$3,5-*t*-$Bu_2C_6H_3$, R$=$*i*-Pr
o: Ar$=$3,5-*t*-$Bu_2C_6H_3$, R$=$*n*-Bu

$$\underset{\mathbf{2}}{\mathrm{ArN(SBu\text{-}}t)_2} \xrightarrow{h\nu} \underset{(\mathrm{R}=t\text{-Bu})}{\mathbf{3}} + t\text{-BuS}\cdot \quad \text{(Method B)}$$

c: Ar$=$$C_6H_5$
d: Ar$=$$C_6D_5$
e: Ar$=$4-$CH_3C_6H_4$
f: Ar$=$3,5-*t*-$Bu_2C_6H_3$
g: Ar$=$4-ClC_6H_4
h: Ar$=$3-ClC_6H_4
i: Ar$=$4-BrC_6H_4
j: Ar$=$4-$CH_3OC_6H_4$
k: Ar$=$3-$CH_3OC_6H_4$
l: Ar$=$4-$CH_3COC_6H_4$
m: Ar$=$3-$CH_3COC_6H_4$

The precursors, **1**, were prepared by the reaction of the appropriate anilines with sulfenyl chlorides in the presence of triethylamine; **1a** and **1b** were obtained as yellow crystals, while **1f**, **1n**, and **1o** were each obtained as a viscous oil.[5]

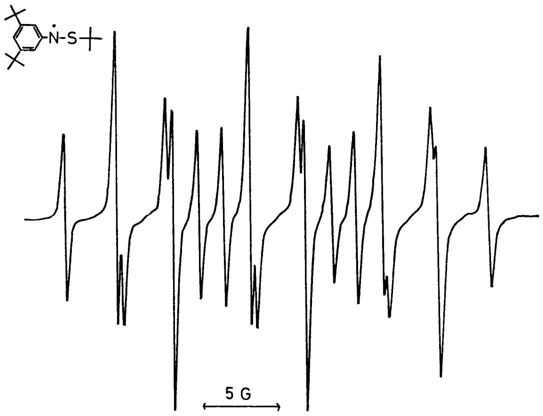


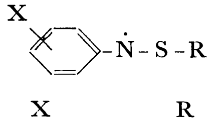
Fig. 1. ESR spectrum of **3f** recorded for the benzene solution containing **1f** and di-*t*-butyl diperoxyoxalate (17 °C).

Hydrogen-abstraction from **1** was performed by the reaction with di-*t*-butyl diperoxyoxalate at room temperature; relatively strong ESR signals were thus obtained. The assignment of the signals were performed on the basis of their splitting patterns and also on the basis of their relatively large *g*-values (2.0061—2.0071). For example, the ESR spectrum of **3f** (Fig. 1) is split into 1 : 2 : 1 triplets (3.68 G), 1 : 1 doublets (4.20 G), and a 1 : 1 : 1 triplet (9.93 G). The 1 : 1 : 1 triplet is obviously due to the central nitrogen nucleus, while the 1 : 1 doublets and the 1 : 2 : 1 triplets are due to the para- and ortho-protons respectively. In the cases of **3n** and **3o**, splittings due to the γ protons were observed in addition to the splittings due to the nitrogen nucleus and the ring protons.

The compounds **2** were prepared by the reaction of the appropriate anilines with more than two equivalents of sulfenyl chloride and were isolated as colorless crystals. The compounds **1** are relatively unstable because of the presence of the active hydrogen (NH). On the other hand, **2** are very stable and can be stored for a long time without any detectable decomposition.

The compounds **2** absorb light at 239—328 nm (ε: 2170—22500 in benzene) and, on irradiation with a high-pressure mercury lamp, undergo homolysis to give **3** in a moderate concentration. Therefore, this procedure (Method B) is excellent for the generation of **3**. However, when the irradiation was continued, secondary radicals often appeared and the analysis of the spectra was disturbed. For this reason, an appropriate period of irradiation, usually 0.5—3 min, is required in order to obtain clean ESR spectra of **3**. The aminyls, **3a**, **3b**, **3n**, and **3o**, were obtained by

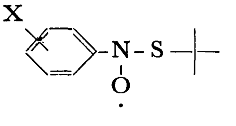
Table 1. ESR parameters for *N*-(alkylthio)arylaminyls (**3**)[a)]

			Coupling constant/G					g-Value
	X	R	a_N	$a_{o\text{-H}}$	$a_{m\text{-H}}$	$a_{p\text{-H}}$	a_{other}	
3a[b)]	4-NO_2	*t*-Bu	8.68	3.25	1.21	—	1.00 (NO_2)	2.0071
3b[b)]	3-NO_2	*t*-Bu	9.64	3.56[c)]	1.31	3.75		2.0068
3c[b)]	H	*t*-Bu	9.92	3.79	1.27	4.10		2.0065
3d	D_5	*t*-Bu	9.92	—	—	—		2.0065
3e[b)]	4-CH_3	*t*-Bu	9.83	3.83	1.27	—	4.71 (CH_3)	2.0062
3f[d)]	3,5-*t*-Bu_2	*t*-Bu	9.93	3.68	—	4.20		2.0065
3g[b)]	4-Cl	*t*-Bu	9.67	3.75	1.32	—		2.0068
3h[b)]	3-Cl	*t*-Bu	9.76	3.64 and 3.79	1.29	4.09		2.0065
3i[b)]	4-Br	*t*-Bu	9.58	3.79	1.29	—		2.0065
3j[b)]	4-CH_3O	*t*-Bu	9.45	3.75	1.09	—	0.54 (OCH_3)	2.0061
3k[b)]	3-CH_3O	*t*-Bu	9.88	3.54 and 4.08	1.29	4.29		2.0065
3l[b)]	4-CH_3CO	*t*-Bu	9.32	3.52	1.23	—		2.0069
3m[b)]	3-CH_3CO	*t*-Bu	9.78	3.70	1.22	3.97		2.0066
3n[b)]	3,5-*t*-Bu_2	*i*-Pr	9.86	3.79	—	4.21	2.64 (γ-1H)	2.0065
3o[b)]	3,5-*t*-Bu_2	*n*-Bu	9.75	3.73	—	4.21	2.59 (γ-2H)	2.0065

a) In benzene at 17 °C. b) The splitting constants were determined by computer simulation. c) The two ortho-protons seem to be magnetically unequivalent, but their a_H values were apparently equivalent because of the relatively broad hyperfine line. d) Absorbs at 556 nm (benzene).

Method A, while **3c**—**e** and **3g**—**m** were generated by method B and **3f** was obtained by both methods. The ESR parameters for the **3f** generated by Method A were identical with those for the **3f** obtained by Method B. The ESR parameters for **3** are summarized in Table 1.

In order to confirm that the present aminyls differ from the corresponding nitroxides **4**, **4a** was generated by the addition reaction of *t*-butylthiyl radical to nitrosobenzene and its ESR parameters were compared with those for **3c**. The ESR parameters for **4a** (in benzene) are 12.64 (a_N); 1.87 ($a_{o\text{-H}}$); 0.85 ($a_{m\text{-H}}$); 2.01 G ($a_{p\text{-H}}$); 2.0061 (g-value),[6)] quite different from those for **3c**. Thus, the possibility that the present aminyls may be **4** was completely excluded.



4 (**4a**: X=H)

The aminyl **3f** was also generated in some polar solvents (chloroform, THF, acetonitrile, and ethanol), and the ESR parameters were measured in order to examine the solvent effect on the splitting constants for **3**. The a_N values obtained for **3f** in these solvents are in the range of 9.89—9.93 G, indicating that the magnitudes of the a_N values are independent of the solvent polarity. From this result, it can be said that the spin distribution in **3** is scarcely influenced by the solvent polarity.

When R in **3** is *t*-butyl, the corresponding aminyls are fairly long-lived. The results of the decay kinetic studies are illustrated in Fig. 2. The aminyl, **3e**, decayed with clean second-order kinetics (k=1.7 l mol^{-1} s^{-1}), while **3c** and **3f** persisted for more than one day ($\tau_{1/2}$>half a day). The high persistence observed for these aminyls is comparable to those of the oxygen analogs, **5**.[2—4)]

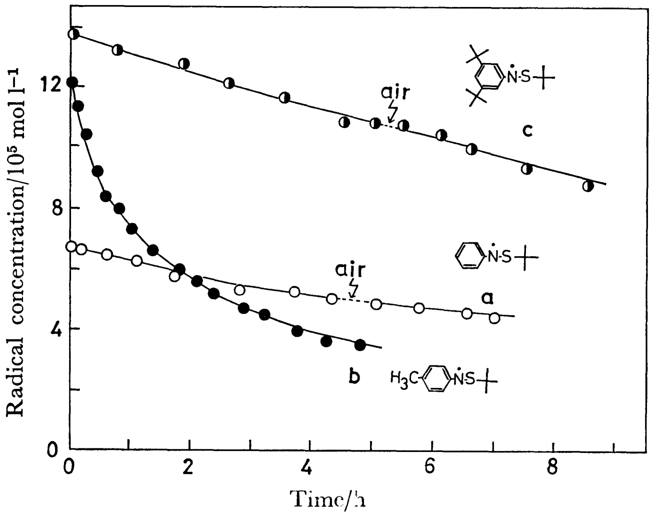


Fig. 2. Decay plots of **3c** (a), **3e** (b), and **3f** (c) in deoxygenated benzene and in benzene saturated with air (17 °C).

The ESR signal intensity of **3f** in toluen, when the temperature was lowered to *ca.* −75 °C, became weaker, while when the temperature was raised to room temperature (20 °C), it was again restored, and this cycle was reversible. From this observation, it seems that **3** exist in equilibrium with a dimer.[2d)]

In order to know whether **3** react with oxygen or not, the decay kinetics was also examined in the presence of oxygen. The results are shown in Fig. 2. After the measurement of the decay rate of **3** for 5 h under deoxygenated conditions, air was bubbled into the solution of **3** and the measurement was again carried out. As can be seen from the figure, the decay rates after

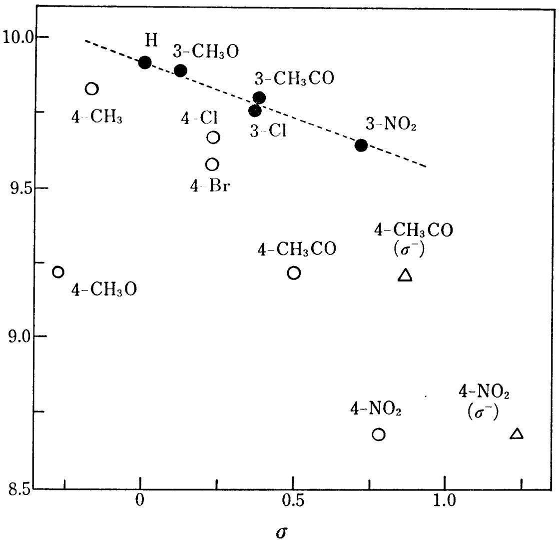


Fig. 3. Plots of a_N values *vs.* σ (○ and ●) and σ^- (△) for **3**.

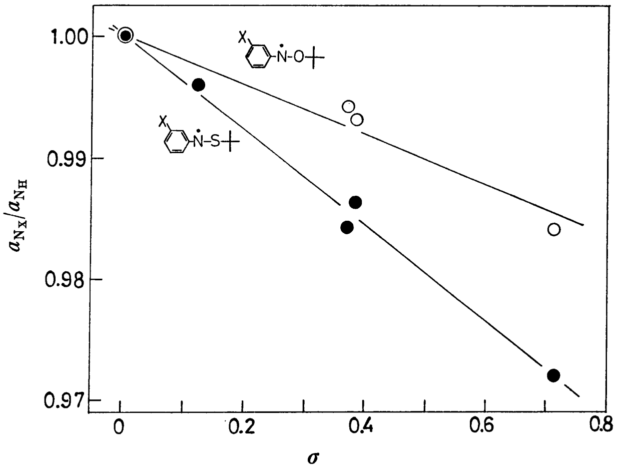


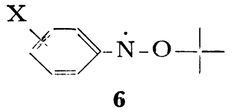
Fig. 4. Plots of a_{N_X}/a_{N_H} *vs.* σ for **3** (●) and **6** (○). a_{N_X}:a_N value for meta-substituted **3** and **6**; a_N:a_{N_H} value for unsubstituted **3** and **6**.

this point are almost identical with those observed under the deoxygenated conditions, suggesting that **3** do not react with oxygen much, if at all. Since **3** are typical nitrogen-centered free radicals, this result is of interest.

Substituent Effects. The a_N values for **3** lie in the range of 8.68—9.93 G, in the range of magnitude expected for nitrogen-centered free radicals in a π-electronic ground state.⁷⁾

When we consider the substituent effects on ESR parameters, two limiting cases may be envisioned; that is, in terms of Walter's criteria, Class O and Class S.⁸⁾ Numerous ESR spectroscopic investigations of substituent effects have been reported, and aryl nitroxide radicals and nitrobenzene anion radicals have been classified as Class O,⁹⁾ while *N*-*t*-butylarylaminyls,¹⁰⁾ *N*-*t*-butoxyarylaminyls (**6**),⁴⁾ *N*-aryl-*N*-(arylthio)-aminyls (**7**),¹¹⁾ *etc.* have been classified as Class S.

In Fig. 3, the a_N values for **3** are plotted against the Hammett σ and σ^- constants.¹²⁾ As can be seen from the figure, the a_N values do not correlate with these constants: both the electron-donating and electron-accepting substituents reduce the a_N values, and the unsubstituted aminyl, **3c**, exhibits the largest a_N value. Such a behavior of **3** in relation of the σ and σ^- constants indicates that **3** belong to Class S, where a_N values are determined predominantly by the extent of the delocalization of the unpaired electron onto the substituent. In the present aminyls, however, the substituents may also influence the relative importance of the resonance forms, A and B, just in the cases of **6**⁴⁾ and **7**.¹¹⁾ That is, substituents not only delocalize the unpaired electron, but also influence the relative importance of the resonance forms, A and B, as has been pointed out by Danen *et al.*⁴⁾ When more powerful electron-accepting substituents are introduced, the polar form B becomes more important, resulting in a reduction of the spin density on the central nitrogen with an increase in the spin density on the sulfur. In the case of the para-substituted **3**, the two effects compete with each other in the determination of the magnitude of the a_N value. That is, when σ and $\sigma^- > 0$, both the effects reduce the a_N value. On the other hand, when $\sigma < 0$, the former effect reduces the a_N value, while the latter effect (inductive effect) increases the a_N value. As can be seen from the figure, the a_N values are reduced in any case. From these results, it can be said that the magnitudes of the a_N values are determined predominantly by the extent of the delocalization of the unpaired electron onto the substituent, while the inductive effect is of secondary importance.



6

Form A Form B Form C Form D

On the other hand, in the case of the meta-substituted **3**, the extent of the delocalization of the unpaired electron onto the substituent is small. Therefore, the magnitudes of the a_N values are determined only by the inductive effect of the substituent; thus, the a_N values for the meta-substituted **3** are correlated with the σ constants (see Fig. 3). In conclusion, the magnitudes of the a_N values for **3** are determined predominantly by the extent of the delocalization of the unpaired electron onto the substituent; therefore, **3** belongs to Class S.

The aminyls **3** are structurally very close to **6**.²ᵈ,⁴⁾ The a_N values reported for **6** are in the range of 9.95—11.00 G, which are larger by *ca.* 1 G than those for **3**.¹³⁾ Similarly, the $a_{o\text{-H}}$ (4.34—4.80 G) and $a_{p\text{-H}}$ values (4.90—5.15 G) for **6** are also larger by *ca.* 1 G than those for **3**. This reduction in the magnitude of the splitting constants observed in going from **6** to **3** can be interpreted in terms of the greater ability of the sulfur to remove the spin from the central nitrogen compared with that of the oxygen.¹⁴⁾ In **3** and **6**, the spin is delocalized onto the sulfur or the oxygen by the contribution of the polar resonance form, B

TABLE 2. YIELDS, AND PHYSICAL AND ANALYTICAL DATA FOR *N*,*N*-BIS(*t*-BUTYLTHIO)ANILINES (**2**)

Compd	Yield[a)] / %	Mp / °C	λ_{max}[b)] / nm	ε[b)]	NMR[c)] δ/ppm	Formula	Found (%) (Calcd) C	H	N
2c	18	47— 48	252	11000	1.20 (s, *t*-Bu, 18H), 6.75—7.72 (m, aromatic, 5H)	$C_{14}H_{23}NS_2$	62.55 (62.40	8.62 8.60	5.03 5.20)
2d	20	48— 49	252	11300	1.18 (s, *t*-Bu, 18H)	$C_{14}H_{18}ND_5S_2$	61.41 (61.25	8.40 8.45	4.80 5.10)
2e	26	96— 97	254	12600	1.16 (s, *t*-Bu, 18H), 2.24 (s, CH_3, 3H), 6.88 and 7.45 (d, J=9 Hz, aromatic, 4H)	$C_{15}H_{25}NS_2$	63.23 (63.55	8.95 8.89	4.58 4.94)
2f	56	87— 88	253	10400	1.22 (s, *t*-Bu, 18H), 1.33 (s, *t*-Bu, 18H), 6.92—7.65 (m, aromatic, 3H)	$C_{22}H_{39}NS_2$	69.04 (69.23	10.22 10.30	3.46 3.67)
2g	15	127—128	258	15000	1.20 (s, *t*-Bu, 18H), 6.98 and 7.46 (d, J=9 Hz, aromatic, 4H)	$C_{14}H_{22}NClS_2$	55.51 (55.33	7.46 7.30	4.56 4.61)
2h	14	68— 60	255	11500	1.21 (s, *t*-Bu, 18H), 6.62—7.63 (m, aromatic, 4H)	$C_{14}H_{22}NClS_2$	55.40 (55.33	7.46 7.30	4.55 4.61)
2i	17	144—145	260	16400	1.19 (s, *t*-Bu, 18H), 7.16 and 7.50 (d, J=9 Hz, aromatic, 4H)	$C_{14}H_{22}NBrS_2$	48.38 (48.26	6.47 6.37	3.65 4.02)
2j	26	101—102	254 305	12200 2170	1.17 (s, *t*-Bu, 18H), 3.68 (s, CH_3, 3H), 6.59 and 7.40 (d, J=9 Hz, aromatic, 4H)	$C_{15}H_{25}NOS_2$	59.77 (60.15	8.62 8.41	4.43 4.68)
2k	18	66— 67	252 286 293	8870 3460 2990	1.20 (s, *t*-Bu, 18H), 3.71 (s, CH_3, 3H), 6.15—7.13 (m, aromatic, 4H)	$C_{15}H_{25}NOS_2$	60.00 (60.15	8.44 8.41	4.35 4.68)
2l[d)]	13	132—133	308	22500	1.20 (s, *t*-Bu, 18H), 2.42 (s, CH_3 3H), 7.65 (s, aromatic, 4H)	$C_{16}H_{25}NOS_2$	61.46 (61.69	7.96 8.09	4.38 4.50)
2m[e)]	16	100—101	239 328	24100 4330	1.20 (s, *t*-Bu, 18H), 2.46 s, CH_3, 3H), 7.15—8.19 (m, aromatic, 4H)	$C_{16}H_{25}NOS_2$	61.44 (61.69	8.04 8.09	4.40 4.50)

a) Yields are determined based on anilines. b) Solvent: hexane. c) Solvent: carbon tetrachloride. d) IR (KBr): 1670 cm^{-1} (CO). e) IR (KBr): 1680 cm^{-1} (CO).

or D.[15] When the relative importance of B in **3** is superior to that of D in **6**, the sulfur would remove the spin from the central nitrogen to a greater extent than the oxygen in **6**, and the central nitrogen in **3** would be charged more negatively than that in **6**. The greater ability of the sulfur to remove the spin compared with the oxygen can be explained from the results of the present study on the substituent effects. In Fig. 4, the ratio of a_{N_X}/a_{N_H} (a_{N_X} : a_N value for *meta*-substituted **3** and **6**; a_{N_H} : a_N value for unsubstituted **3** and **6**) are plotted against the σ constants. The slopes in the figure are determined by the amount of the negative charge on the central nitrogen in **3** or **6**. That is, the greater the negative charge on the central nitrogen, the larger becomes the slope. The slope obtained for **3** is −0.038, while it is −0.020 for **6**, indicating that the relative importance of B in **3** is superior to that of D in **6**. From this result, the greater ability of the sulfur to remove the spin from the central nitrogen can be explained by the greater contribution of B in **3** compared with that of D in **6**.

Experimental

All melting points are uncorrected. IR spectra were run on a JASCO Model IR-G spectrometer. UV and visible spectra were recorded with a Hitachi recording spectrometer, Model ESP-3T, and NMR spectra with a Hitachi Perkin Elmer R-20 spectrometer using TMS as an internal standard.

3,5-Di-*t*-butylaniline[16] and di-*t*-butyl diperoxyoxalate[17] were prepared by the reported methods. 2-Methyl-2-propanesulfenyl chloride was prepared as follows:[18] chlorine was bubbled into di-*t*-butyl disulfide (4.8 g, 0.027 mol) in hexane (50 ml) at 30±3 °C for 30—50 min, and then an excess of chloride dissolved in the reaction mixture was expelled by bubbling nitrogen. The hexane solution of the chloride thus obtained was used in the following reaction without any further purification. 1-Methylethanesulfenyl and butanesulfenyl chlorides were also prepared similarly. Other reagents were obtained commercially and were used without purification. Column chromatography was performed on alumina (E. Merck, Art 1097; column-size: 3×30 cm).

*N-(t-Buthylthio)-4-nitroaniline (**1a**).* A hexane solution of 2-methyl-2-propanesulfenyl chloride, prepared as has been described above, was added dropwise to a stirred solution of 4-nitroaniline (7.0 g, 0.051 mol) and triethylamine (6.0 g, 0.059 mol) in dry THF (400 ml) at 0—5 °C. After the addition, the reaction mixture was stirred for 2 h at the same temperature and then filtered. The filtrate was concentrated under reduced pressure, and the resulting residue was chromatographed [eluent: benzene–hexane (10:1)]. Recrystallization from hexane gave yellow needles; mp 124—125 °C: yield, 1.3 g (11%). IR (KBr): 3310 cm^{-1} (NH). NMR (CCl_4): δ 1.31 (s, *t*-Bu, 9H), 6.08 (br s, NH, 1H), and 7.25 and 8.23 (d, J=10 Hz, aromatic, 4H). Found: C, 52.90; H, 6.04; N, 12.52%. Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.07: H, 6.23; N, 12.38%.

N-*(*t*-Butylthio)-3-nitroaniline (**1b**).* The aniline was obtained analogously to **1a**. Yellow plates; mp 100—102 °C; yield, 2.4 g (21%). IR (KBr): 3350 cm^{-1} (NH). NMR (CCl_4): δ 1.30 (s, *t*-Bu, 9H), 5.38 (br s, NH, 1H), and 7.35—8.01 (m, aromatic, 4H). Found: C, 52.98; H, 5.93; N, 12.56%. Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.07; H, 6.23; N, 12.38%.

N-*(*t*-Butylthio)-3,5-di-*t*-butylaniline (**1f**).*5) A hexane solution of 2-methyl-2-propanesulfenyl chloride, prepared as has been described above, was added dropwise to a stirred solution of 3,5-di-*t*-butylaniline (10.4 g, 0.051 mol) and triethylamine (6.0 g, 0.059 mol) in dry ether (400 ml) at 0—5 °C. After the addition, the reaction mixture was stirred for 2 h at the same temperature and then filtered. The filtrate was concentrated under reduced pressure, and the resulting residue was chromatographed (eluent: hexane), giving a pale yellow oil of **1f** containing a slight amount of impurities. Yield, 2.4 g (15%). IR (neat): 3300 cm^{-1} (NH). NMR (CCl_4): δ 1.30 (s, *t*-Bu, 27H), 4.86 (br s, NH, 1H), and 6.92 (b, aromatic, 3H).

N-*(Isopropylthio)-3,5-di-*t*-buytlaniline (**1n**).*5) The aniline was prepared analogously to **1f** and was separated by column chromatography as a pale yellow oil containing a slight amount of impurities. Yield, 1.2 g (8%). IR (neat): 3320 cm^{-1} (NH). NMR (CCl_4): δ 1.20 (d, J=7 Hz, CH_3, 6H), 1.29 (s, *t*-Bu, 18H), 3.06 (sept. J=7 Hz, $C\underline{H}Me_2$, 1H), 4.70 (br s, NH, 1H), and 6.75 (s, aromatic, 3H).

N-*(Butylthio)-3,5-di-*t*-butylaniline (**1o**).*5) The aniline was prepared analogously to **1f** and was separated by column chromatography as a pale yellow oil containing a slight amount of impurities. Yield, 1.8 g (12%). IR (neat): 3350 cm^{-1} (NH). NMR (CCl_4): δ 0.90—1.46 (br m, $CH_3CH_2CH_2$, 7H), 1.28 (s, *t*-Bu, 18H), 2.57 (*t*, J=8 Hz, SCH_2, 2H), 6.70 (s, aromatic, 3H).

General Procedure for the Preparation of N,N-*Bis(*t*-butylthio)-aniline (**2**).* A hexane solution of 2-methyl-2-propanesulfenyl chloride, prepared as has been described above, was added dropwise to a stirred solution of aniline (0.015 mol) and triethylamine (0.069 mol) in dry ether (400 ml) at 0—5 °C. After the addition, the reaction mixture was stirred for 20 h at room temperature and then filtered. The filtrate was concentrated under reduced pressure, and the resulting oily residue was chromatographed on alumina [eluent: hexane for **2c**—**k** and benzene–hexane (1:2) for **2l** and **2m**]. Subsequent recrystallization from methanol afforded needles of **2**.19) The yield, and physical and analytical data are summarized in Table 2.

*Generation of **3** from **1**.* Aniline **1** (20 mg), di-*t*-butyl diperoxyoxalate (20 mg), and benzene (0.20 ml) were placed in an ESR cell, degassed by three freeze-and-thaw cycles, and then sealed. The ESR spectra were recorded at 17 °C.

*Generation of **3** by Photolysis of **2**.* An aniline, **2** and a solvent (0.20 ml) were placed in an ESR cell, degassed as has been described above, and then sealed. After photolysis for 0.5—3 min in the cavity of an ESR instrument with a high-pressure mercury lamp (JES-UV-1, 100 W), the ESR signal was recorded.

*Generation of Nitroxide **4a**.* Nitrosobenzene (10 mg), 2-methyl-2-propanethiol (10 mg), di-*t*-butyl diperoxyoxalate (10 mg), and benzene (0.20 ml) were placed in an ESR cell, degassed as has been described above, and then sealed. The ESR signal was recorded at 20 °C.

Decay Kinetics. A degassed benzene solution (0.20 ml) of **2** in an ESR cell was irradiated for 0.5—3 min as has been described above. The decay rates of **3** were measured at 17 °C in the dark by monitoring the ESR signal intensities. The concentrations of **3** were determined as follows: integrated signals were recorded on the ESR instrument eqipped with a JES-ID-2 integrator. The areas under integrated curves were determined by means of their weights. The calibration curves were obtained using benzene solutions of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl as a standard.20) Integrated signals of the samples and the references were recorded with the same instrument settings. The concentrations are believed to be accurated to ±10%.

The ESR spectra were recorded on a JES-ME-3X spectrometer with an X-band microwave unit and 100 kHz field modulation. The splitting constants and the *g*-values for **3** were determined by comparison with the a_N value (13.09 G) and the *g*-value (2.0057) of Fremy's salt. The computer simulations of the ESR spectra were performed using a FACOM 230-60 computer equipped with a FACOM F-6201D plotter.

References

1) Part XI of this series, "ESR Studies of Nitrogen-centered Free Radicals," For Part X, see Y. Miura, Y. Katsura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **52**, 1121 (1979).

2) a) A. T. Balaban, P. T. Frangopol, M. Frangopol, and N. Negoita, *Tetrahedron*, **23**, 4661 (1967); b) N. Negoita, R. Baican, and A. T. Balaban, *Tetrahedron Lett.*, **1973**, 1877; c) F. Maria, P. T. Frangopol, and N. Negoita, *Rev. Roum. Chim.*, **19**, 1773 (1974); d) R. A. Kaba and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 7375 (1976).

3) a) S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 369; b) W. Ahrens and A. Berndt, *Tetrahedron Lett.*, **1973**, 4281; c) K. Reuter and W. P. Neumann, *Tetrahedron Lett.*, **1978**, 5235.

4) W. C. Danen, C. T. West, and T. T. Kensler, *J. Am. Chem. Soc.*, **95**, 5716 (1973).

5) Since the oily products **1** were found from their NMR spectra to be slightly contaminated with impurities, the distillation of **1** was carried out in order to purify them. However, this operation resulted in the decomposition of **1**. For this reason, the crude **1** were used in the reaction with di-*t*-butyl diperoxyoxalate without any further purification.

6) The coupling constants were fitted by computer simulation.

7) W. C. Danen and F. A. Neugebauer, *Angew. Chem.*, **87**, 823 (1975).

8) R. I. Walter, *J. Am. Chem. Soc.*, **88**, 1923 (1966).

9) E. G. Janzen, *Acc. Chem. Res.*, **2**, 279 (1969).

10) S. F. Nelsen, R. T. Landis, L. H. Kiehle, and T. H. Leung, *J. Am. Chem. Soc.*, **94**, 1610 (1972).

11) Y. Miura and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 1142 (1977).

12) For σ constants, see D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958), and for σ^-, see A. I. Biggs and R. A. Robinson, *J. Chem. Soc.*, **1961**, 388.

13) For the equation $a_N = Q_N \rho_N$, the magnitude of Q_N for

3 seems to be similar to that for **6**. See Ref. 7 also.

14) a) A. Hudson and K. D. J. Root, *J. Chem. Soc., B*, **1970**, 656; b) A. Ohno, N, Kito, and Y. Ohnishi, *Bull. Chem. Soc. Jpn.*, **44**, 470 (1971); c) I. Biddles, A. Hudson, and J. T. Wiffen, *Tetrahedron*, **28**, 867 (1972); d) B. C. Gilbert, J. P. Larkin, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans. 2*, **1973**, 272; e) G. Brunton, J. F. Taylor, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 4879 (1976).

15) The participation of the d-orbital of the sulfur atom in **3** is not taken into consideration.

16) N. L. Allinger, H. M. Blatter, L. A. Freiberg, and F. M. Karkowski, *J. Am. Chem. Soc.*, **88**, 2999 (1966).

17) P. D. Bartlett, E. P. Benzing, and R. E. Pincock, *J. Am. Chem. Soc.*, **82**, 1762 (1960).

18) C. M. Himel, *Chem. Abstr.*, **52**, 14706a (1958). See also E. Kühle, *Synthetis*, **1970**, 561.

19) When **2** contained a significant amount of di-*t*-butyl disulfide, recrystallization was unsuccessful. In this case, the disulfide was removed by heating at 50 °C under a reduced pressure, and then the resulting residue was recrystallized.

20) R. Kuhn and H. Trischmann, *Monatsh. Chem.*, **95**, 457 (1964).