An ESR Study of Polysubstituted *N*-Aryl-*N*-(arylthio)aminyls[1)]

Yozo Miura,* Yosuke Katsura, and Masayoshi Kinoshita

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558

(Received June 26, 1978)

An ESR spectroscopic investigation of *N*-(2,4,6-trimethyl-, trimethoxy-, triisopropyl-, and tri-*t*-butylphenyl)-*N*-(arylthio)aminyls (**2**), ArNSAr′, is described. The aminyls are generated from the corresponding *N*-arylarenesulfenamides, ArNHSAr′, by hydrogen-abstraction, the a_N values of which are 9.10—12.30 G and the *g*-values 2.0056—2.0067. On the basis of the ESR parameters the conformations for **2** have been discussed. Decay kinetic studies on **2** were conducted in benzene, and **2** were found to be persistent aminyls—particularly the *t*-butyl-substituted aminyl, *N*-(2,4,6-tri-*t*-butylphenyl)-*N*-(4-nitrophenylthio)aminyl.

A new family of nitrogen-centered free radicals has been investigated in which one or two divalent sulfur atoms are adjacent to the central nitrogens.[2)] In previous ESR studies on *N*-aryl-*N*-(arylthio)aminyls,[3,4)] ArNSAr′, it was established that, in the aminyls, the unpaired electron resides predominantly on the central nitrogen and the *N*-phenyl ring.

The present investigation was directed toward obtaining and isolating persistent *N*-aryl-*N*-(arylthio)-aminyls and for this purpose, several sterically protected thioaminyls have been prepared. In this report the ESR study on *N*-(2,4,6-trimethyl-, trimethoxy-, triisopropyl-, and tri-*t*-butylphenyl)-*N*-(arylthio)aminyls (**2**) is described.

Results and Discussion

Generation of Aminyls. The generation of **2** was achieved through hydrogen-abstraction from the appropriate *N*-arylarenesulfenamides (**1**, Eq. 2). Sulfenamides **1a**—**g** were obtained by the reaction of sulfenyl chlorides with two equivalents of anilines or one equivalent of anilines in the presence of triethylamine (Eq. 1). Sulfenamide **1h** was unobtainable by these procedures.

The hydrogen-abstraction of **1** was performed by two procedures: the photolysis of **1** in the presence of di-*t*-butyl peroxide,[5)] and the treatment of **1** with lead dioxide in the presence of potassium carbonate. The ESR parameters obtained for **2** are listed in Table 1, and a typical ESR spectrum is illustrated in Fig. 1.

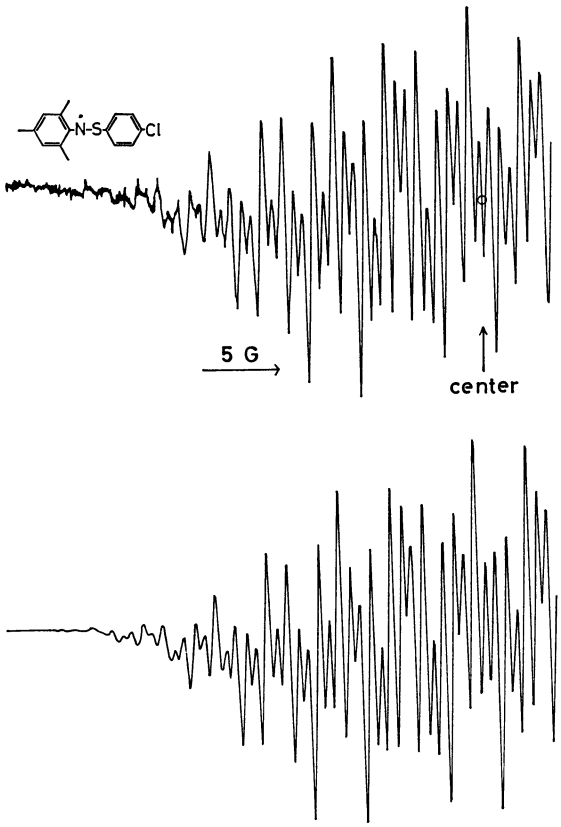
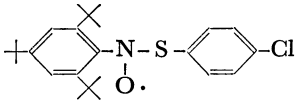


Fig. 1. Experimental ESR spectrum (low-field half) of **2a** in benzene (upper), and computer simulation, using Lorentzian line shapes and a line width of 0.52 G (lower).

Although **1h** could not be isolated as described above, the residue, resulting from filtration and subsequent concentration of the reaction mixture, gave rise to a strong 1:1:1 triplet ESR signal (12.27 G). The a_N value is in good agreement with that for the structurally similar aminyl, **2g** (12.30 G), and is quite different from that for the corresponding nitroxide, **3** (a_N: 16.40



3

Table 1. The ESR parameters for *N*-aryl-*N*-(arylthio)aminyls (**2**)[a]

	Coupling constant (G)									
		N-Phenyl ring			*S*-Phenyl ring				*g*-Value	λ_{max}[f] (nm)
	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]	9.32	—	1.29	—	0.79	g	—	3.56(*o*-CH_3), 4.92(*p*-CH_3)	2.0057	574
2b	9.10	—	g	—	g	g	—		2.0056	
2c[b]	9.50	—	1.22	—	—	—	—	3.61(*o*-CH_3),[c] 5.14(*p*-CH_3)[c]	2.0057	
2d	9.36	—	g	—	—	—	—		2.0057	
2e	9.84	4.15	1.30	4.36	—	—	—		2.0057	
2f	9.78	—	g	—	g	g	—		2.0056	
2g	12.30	—	g	—	g	g	—		2.0066	513, 545, 700
2h[d]	12.27	—	g	—	g	g	—		2.0067	
2i[e]	9.59	3.70	1.26	4.18	0.78	0.27	0.84		2.0059	

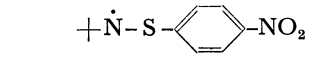
a) In benzene at room temperature (19 °C). b) The values of coupling constant were determined by computer simulation. c) In the *N*-phenyl ring. d) Ref. 7. e) Ref. 3. f) In benzene. g) Not resolved.

G, *g*-value: 2.0068 in benzene).[6] On the basis of these results, the species has been assigned as **2h**.

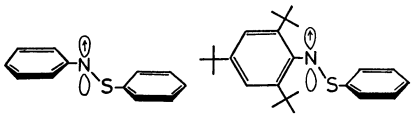
In the oxidation of the sulfenamides with lead dioxide, some of them gave purple or brown colored solutions.[7] For example, a benzene solution of **1a** immediately turned purple. Similarly, a solution of **1f** which was pale yellow turned reddish brown, and the pale yellow solution of **1g** turned dark brown. The colorled solutions gave rise to a strong ESR signal due to **2**. In the cases of **2a** and **2f**, the color faded in 10—20 min, and the resulting colorless (**2a**) or light orange solution (**2f**) no longer gave rise to a strong ESR signal. The brown color observed for **2g** persisted for several hours and, under deoxygenated conditions, persisted for several weeks without any apparent fading.

ESR Parameters. As may be seen from Table 1, the a_N values for **2a**—**f** are in the range 9.10—9.84 G, and the *g*-values in the range 2.0056—2.0057, being close to the value for the unsubstituted aminyl, **2i**. Thus, in these aminyls, the unpaired electron resides predominantly on the central nitrogen and the *N*-phenyl ring, as well as in **2i**. The a_N values for the *t*-butyl-substituted aminyls, **2g** and **2h**, are in the range 12.27—12.30 G, being 2.5—3.2 G larger than for the other aminyls, they are rather close to that (11.89 G) observed for *N*-(4-nitrophenylthio)-*t*-butylaminyl (**4**).[8] The relatively large a_N values observed for **2g** and **2h** may be explained as follows: in **2i**, the *N*-phenyl ring is probably perpendicular or nearly perpendicular with respect to the nitrogen $2p_z$ orbital containing the unpaired electron (conformation A). The aminyls **2g** and **2h** cannot adopt such a conformation because of the steric repulsion between the two *ortho*-*t*-butyl groups and the sulfur atom (and/or the ortho-protons in the *S*-pheny ring), as shown by a molecular model (Stuart model). Thus, the steric effect results in the *N*-phenyl ring twisting to be parallel or nearly parallel with respect to the nitrogen $2p_z$ orbital (conformation B). Therefore, in **2g** and **2h**, the unpaired electron is not effectively delocalized onto the *N*-phenyl ring, differing from the other aminyls, leading to an increase in the magnitude of the a_N values. The *g*-values (2.0066—2.0067) observed for **2g** and **2h** are larger than those for the other aminyls (2.0056—2.0059), indicating that the spin density on the sulfur atoms in **2g** and **2h** is greater compared with the other aminyls.[9] Thus, the steric situation assumed for **2g** and **2h** may be also supported by the relatively large *g*-values.

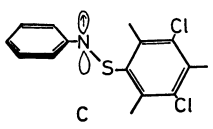
The a_N values for **2a** and **2b** are smaller by 0.3—0.5 G compared with that for **2i**, suggesting that the aminyls adopt conformation A, despite the introduction of methyl or methoxyl groups into the ortho-positions of the *N*-phenyl ring. In a previous report,[10] *N*-aryl-*N*-(phenylthio)aminyls, in terms of Walter's criteria, were classified as class *S*, *i.e.* the magnitude of the a_N values is determined predominantly by the degree of delocalization of the unpaired electron onto the substituents in the *N*-phenyl rings, and the polar effect is of secondary importance (Scheme 1). Therefore, the reduction in the magnitude of the a_N values observed for **2a** and **2b** is interpreted in terms of the delocalization of the unpaired electron onto the methyl and methoxyl groups.



4

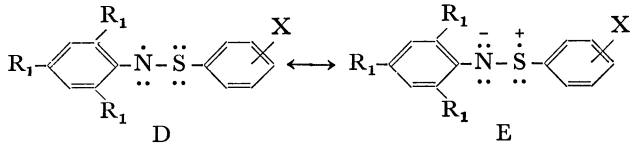


A B



C

Fig. 2.

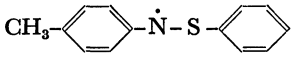


D E

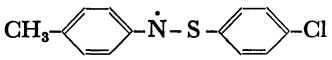
Scheme 1.

The a_N value for **2f** is slightly larger (0.2 G) compared with that for **2i**, suggesting that the *N*-phenyl ring in **2f** is twisted to some extent due to the steric repulsion from the relatively large isopropyl groups in the *N*-phenyl ring.

The a_N values for **2c**, **2d**, and **2e** are larger by 0.18—0.26 G compared with those for the aminyls, **2a**, **2b**, and **2i**. These increases are interpreted in two ways: a) increase in the relative importance of the resonance form D caused by the inductive effect of the substituents in the *S*-phenyl rings, and b) twisting of the *S*-phenyl rings caused by the steric repulsion from the *ortho*-methyl groups in the *S*-phenyl rings. With respect to the inductive effect, the total σ value for the substituents in the *S*-phenyl rings is calculated to be 0.23 ($3\sigma_{p\text{-CH}_3}+2\sigma_{Cl}$),[11] which is identical to the $\sigma_{p\text{-Cl}}$ value. From a comparison of the a_N value for **2k**[12] with that for **2j**,[3] it may be seen that the magnitude of the a_N value for **2k** is little affected by the chlorine atom in the *S*-phenyl ring. Thus, the increases observed for **2c**, **2d**, and **2e** are not due to the inductive effect, but should be interpreted in terms of the twisting of the *S*-phenyl rings (conformation C). Since the spin density on the *S*-phenyl rings of these aminyls is very small, as can be seen from the a_H values due to the *S*-phenyl aromatic protons (0.27—0.84 G), the increase in magnitude of the a_N values caused by the twisting of the *S*-phenyl rings, is not as large as in **2g** and **2h**.



2j: a_N=9.55 G



2k: a_N=9.52 G

Decay Kinetics of 2. Decay kinetic studies on **2a**, **2c**, and **2g** were conducted at 19 °C in the dark. A benzene solution containing **1** and di-*t*-butyl peroxide was irradiated with a high-pressure mercury lamp, and the decay rates were followed by measuring the ESR signal intensities. The results are illustrated in Fig. 3. The aminyl **2a** decayed initially at a relatively fast rate which was followed by a slower decay, and persisted for several weeks. Similarly, the aminyl **2c** decayed rapidly for *ca.* 500 min after which the decay slowed down, and persisted for several weeks. The aminyl **2g** decayed very little over several days, even at a relatively high radical concentration. The unsubstituted aminyl, **2i**, on the contrary, decayed immediately and completely upon interruption of the photolysis.[3] From the decay kinetic studies of the aminyls, it has been demonstrated that the polysubstituted aminyls are well protected by the methyl and *t*-butyl groups, **2g** is in particular very interesting.

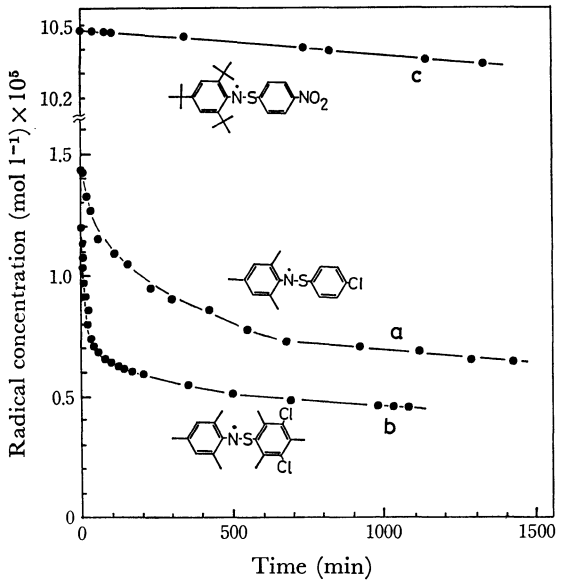


Fig. 3. Decay plots of **2a** (a), **2c** (b), and **2g** (c) in deoxygenated benzene at 19 °C.

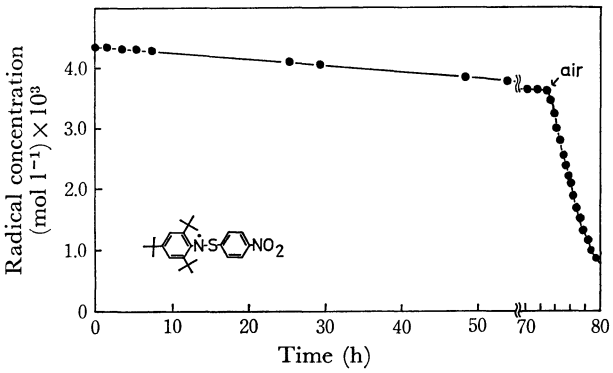


Fig. 4. Decay plots of **2g** in benzene at 19 °C in the absence and presence of oxygen.

Generation of 2g with Lead Dioxide. In order to isolate **2g**, it was generated by oxidation of **1g** with lead dioxide. The procedure was as follows: **1g** (0.10 mmol) was stirred in benzene for 5—15 min in the presence of lead dioxide and potassium carbonate, providing a dark brown solution containing **2g** in a concentration of 4.3 mmol l^{-1}. This value corresponds to 43% based on the **1g** used. On standing for 3 days in a deoxygenated ESR tube, the radical concentration in the solution remained at 3.6 mmol l^{-1} (Fig. 4), indicating little decomposition of **2g**. On the introduction of air, however, the aminyl began to decompose at a relatively fast rate, indicating that **2g** reacts with oxygen. In the range 0.13 to 3.60 mmol l^{-1} of **2g**, the reaction rate with oxygen was measured in benzene saturated with air,[13] and it was found that **2g** decayed with a pseudo first-order kinetics ($k=7.2\times10^{-5}$ s^{-1} at 19 °C).

For the other aminyls, the radical concentrations obtained by oxidation of **1** with lead dioxide were no more than 1% based on the **1** used.

In order to isolate **2g**, benzene was removed from the solution by freeze-drying, affording a dark brown crystalline powder in an almost quantitative yield. The powder gave a strong broad ESR signal (g=2.0068, ΔH=14.7 G) and contained **2g** in a concentration of 40 wt %. When the powder was dissolved in benzene, the resulting brown solution containing **2g** in a concent-

ration of 3.9 mmol l^{-1} (39%), indicating that **2g** was little decomposed during the operation of freeze-drying. The aminyl in the solid was also little decomposed under deoxygenated conditions for one week. On contact with air, however, the solid **2g** was decomposed gradually ($\tau_{1/2}$: half a day) and gave orange decomposition products. From these results, it has been established that **2g** is very stable, even in the solid. The aminyl however has not been isolated as a pure crystal.

Experimental

All melting points are uncorrected. IR spectra were conducted on a JASCO Model IR-G spectrometer. 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.

4-Nitro-[14] and 2,4,6-trimethylbenzenethiols,[15] 2,4,6-trimethoxy-,[16] 2,4,6-triisopropyl-,[17,18] 2,4,6-tri-*t*-butylanilines,[19] and 2,4,6-tri-*t*-butylnitrosobenzene[20] were prepared by reported methods. 2,4,6-Trimethylaniline, 4-chlorobenzenethiol, and di-*t*-butyl peroxide were obtained commercially and used without further purification.

*N-(2,4,6-Trimethylphenyl)-4-chlorobenzenesulfenamide (**1a**).* 4-Chlorobenzenethiol (6.36 g, 0.044 mol) was treated with chlorine gas in dry chloroform (100 ml) at 0 °C. After removal of the solvent, the resulting crude sulfenyl chloride was dissolved in dry ether (100 ml), and the solution was added dropwise to a stirred solution of 2,4,6-trimethylaniline (13.0 g, 0.096 mol) in dry ether (300 ml) at −30——40 °C. After stirring for 30 min, the reaction mixture was filtered and solvent was evaporated to give colorless needles. Recrystallization from hexane afforded colorless needles (11.1 g, 91%) mp 86—87 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.15 (s, *o*-CH_3, 6H), 2.22 (s, *p*-CH_3, 3H), 4.76 (br s, NH, 1H), 6.82 (s, C_6H_2, 2H), and 7.29 (s, C_6H_4, 4H). Found: C, 65.02; H, 5.80; N, 5.14%. Calcd for $C_{15}H_{16}NClS$: C, 64.84; H, 5.82; N, 5.04%.

*N-(2,4,6-Trimethoxyphenyl)-4-chlorobenzenesulfenamide (**1b**).* The 4-chlorobenzenesulfenyl chloride, prepared from 4-chlorobenzenethiol (4.60 g, 0.032 mol) as described above, was dissolved in dry ether (80 ml), and the solution was added dropwise to a stirred solution of 2,4,6-trimethoxyaniline (13.1 g, 0.072 mol) in dry ether (300 ml) at −30——40 °C. After stirring for 30 min, the reaction mixture was filtered, and solvent was evaporated to give a light brown crystalline residue. Recrystallization from hexane afforded light brown needles (6.30 g, 60%) with mp 77—78 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 3.70 (s, *o*-CH_3O, 6H), 3.75 (s, *p*-CH_3O, 3H), 5.14 (br s, NH, 1H), 6.19 (s, C_6H_2, 2H), and 7.28—7.32 (m, C_6H_4, 4H). Found: C, 55.20; H, 4.86; N, 4.36%. Calcd for $C_{15}H_{16}NO_3ClS$: C, 55.29; H, 4.95; N, 4.29%.

*N-(2,4,6-Trimethylphenyl)-3,5-dichloro-2,4,6-trimethylbenzenesulfenamide (**1c**).*[21] 2,4,6-Trimethylbenzenethiol (6.00 g, 0.039 mol) was treated with chlorine gas as described for **1a**. After removal of the solvent, the resulting sulfenyl chloride was dissolved in dry ether (100 ml), and the solution was added dropwise to a stirred solution of 2,4,6-trimethylaniline (11.6 g, 0.086 ml) at −30——40 °C. After stirring for 30 min, the reaction mixture was filtered, and solvent was evaporated to give a dark brown oily residue. Repeated recrystallization from hexane afforded colorless prisms (1.30 g, 9.4%) with mp 130—131 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.02 [s, *o*-CH_3(*N*-Ph), 6H], 2.19 [s, *p*-CH_3(*N*-Ph), 3H], 2.48 and 2.50 [s, *o*- and *p*-CH_3 (*S*-Ph), 9H], 4.38 (br s, NH, 1H), and 6.72 (s, C_6H_2, 2H). MS (50 eV), *m/e* 353 (M^+). Found: C, 60.90; H, 5.69; N, 3.74; Cl, 20.06; S, 9.26%. Calcd for $C_{18}H_{21}NCl_2S$: C, 61.01; H, 5.97; N, 3.95; Cl, 20.01; S, 9.05%.

*N-(2,4,6-Trimethoxyphenyl)-3,5-dichloro-2,4,6-trimethylbenzenesulfenamide (**1d**).*[21] The sulfenyl chloride, prepared from 2,4,6-trimethylbenzenethiol (5.00 g, 0.033 mol) as described for **1c**, was dissolved in dry ether (100 ml), and the solution was added dropwise to a stirred solution of 2,4,6-trimethoxyaniline (13.3 g, 0.073 mol) in dry ether (400 ml) at −30——40 °C. After stirring for 30 min, the reaction mixture was filtered, and solvent was evaporated to give a dark brown oily residue. Repeated recrystallization from hexane afforded light brown prisms (0.53 g, 4%) with mp 119—120 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.45 (s, *p*-CH_3, 3H), 2.54 (s, *o*-CH_3, 6H), 3.58 (s, *o*-OCH_3, 6H), 3.72 (s, *p*-OCH_3, 3H), 4.99 (br s, NH, 1H), and 5.98 (s, C_6H_2, 2H). Found: C, 54.22; H, 5.12; N, 3.55%. Calcd for $C_{18}H_{21}NO_3Cl_2S$: C, 53.73; H, 5.28; N, 3.48%.

*N-Phenyl-3,5-dichloro-2,4,6-trimethylbenzenesulfenamide (**1e**).*[21] The sulfenyl chloride, prepared from 2,4,6-trimethylbenzenethiol (2.00 g, 0.013 mol) as described for **1c**, was dissolved in dry ether (50 ml), and the solution was added dropwise to a stirred solution of aniline (2.50 g, 0.027 mol) in dry ether (200 ml) at −40——50 °C. After stirring for 30 min, the reaction mixture was filtered, and solvent was evaporated to give a dark brown oily residue. Repeated recrystallization from hexane afforded light brown plates (0.15 g, 4%) with mp 110—112 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 2.39 (s, *p*-CH_3, 3H), 2.75 (s, *o*-CH_3, 6H), 4.90 (br s, NH, 1H), and 6.85—7.30 (m, C_6H_5, 5H). Found: C, 58.10; H, 4.76; N, 4.64%. Calcd for $C_{15}H_{15}NCl_2S$: C, 57.69; H, 4.84; N, 4.49%.

*N-(2,4,6-Triisopropylphenyl)-4-nitrobenzenesulfenamide (**1f**).* The sulfenyl chloride, prepared from 4-nitrobenzenethiol (2.02 g, 0.013 mol) as described for **1a**, was dissolved in dry ether (50 ml), and the solution was added dropwise to a stirred solution of 2,4,6-triisopropylaniline (2.80 g, 0.013 mol) and triethylamine (1.94 g, 0.019 mol) in dry ether (250 ml) at −5—0 °C. After addition of the sulfenyl chloride, the reaction mixture was stirred for 5 h at room temperature. Filtration of the reaction mixture, and evaporation of solvent gave a yellow powdery residue, which was chromatographed on alumina [E. Merck, Art 1097, eluent: benzene/hexane (1/4), column size: 3×30 cm]. Recrystallization from hexane afforded light yellow prisms (2.5 g, 53%) with mp 132—133 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 1.18 [d, J=10 Hz, *p*-$CH(C\underline{H}_3)_2$, 6H], 1.25 [d, J=10 Hz, *o*-$CH(C\underline{H}_3)_2$, 12H], 2.75—3.42 [m, $C\underline{H}(CH_3)_2$, 3H], 4.88 (br s, NH, 1H), and 6.99—8.28 (m, C_6H_2 and C_6H_4, 6H). Found: C, 67.28; H, 7.57; N, 7.41%. Calcd for $C_{21}H_{28}N_2O_2S$: C, 67.71; H, 7.58; N, 7.52%.

*N-(2,4,6-Tri-t-butylphenyl)-4-nitrobenzenesulfenamide (**1g**).* The sulfenyl chloride, prepared from 4-nitrobenzenethiol (2.53 g, 0.016 mol) as described for **1a**, was dissolved in dry ether (50 ml), and the solution was added dropwise to a stirred solution of 2,4,6-tri-*t*-butylaniline (4.30 g, 0.016 mol) and triethylamine (2.50 g, 0.025 mol) in dry ether (300 ml) at −5—0 °C. After addition of the sulfenyl chloride, the reaction mixture was stirred for 5 h at room temperature. Filtration of the reaction mixture, and evaporation of solvent gave a yellow powdery residue, which was chromatographed on alumina as described for **1f**. Recrystallization from hexane and then methanol afforded yellow prisms (2.93 g, 46%) with mp 152—153 °C. IR (KBr): 3300 cm^{-1} (NH). NMR ($CDCl_3$): δ 1.30 (s, *p*-*t*-Bu, 9H), 1.50 (s, *o*-*t*-Bu, 18H),

5.20 (br s, NH, 1H), and 7.23—8.23 (m, C_6H_2 and C_6H_4, 6H). Found: C, 69.64; H, 8.27; N, 6.78%. Calcd for $C_{24}H_{34}N_2O_2S$: C, 69.53; H, 8.27; N, 6.76%.

Generation of Aminyls. a) Photolysis: sulfenamide (**1**, 5.0 mg) and a benzene solution (0.20 ml) of di-*t*-butyl peroxide (10% in vol) were placed in an ESR tube and the tube degassed by three freeze-pump-thaw cycles and then sealed. The ESR spectra were recorded during direct irradiation of the solution in the cavity of an ESR instrument with a high-pressure mercury lamp (JES-UV-1, 100W); b) oxidation with lead dioxide: **1** (6.0 mg) was stirred in benzene (3.0 ml) for 1—15 min in the presence of lead dioxide (0.2 g) and potassium carbonate (0.2 g). After filtration, 0.20 ml of the filtrate was placed in an ESR tube and degassed as described above and then sealed.

*Oxidation of **1g** with Lead Dioxide.* Sulfenamide **1g** (42.3 mg) in benzene (10 ml) was stirred for 5—15 min in the presence of lead dioxide (0.5 g) and potassium carbonate (0.5 g). After filtration, the benzene was removed from the filtrate by freeze-drying, giving a dark brown powder in an almost quantitative yield. For measurements of ESR spectra of the filtrate and the powder, 0.20 ml of the filtrate, and 4—5 mg of the powder were used, respectively.

*Generation of Nitroxide **3**.* Nitroxide **3** was generated by the procedure of Konaka *et al.*,[6] *i.e.* 2,4,6-tri-*t*-butylnitrosobenzene (3.0 mg), bis(4-chlorophenyl) disulfide (20.0 mg), and benzene (0.40 ml) were placed in an ESR tube, and degassed as described above, then sealed. ESR spectra were recorded during direct irradiation of the solution with the high-pressure mercury lamp.

*Decay Kinetics of **2**.* Decay kinetic studies on **2** were conducted at 19 °C in the dark. Sample preparation was as follows: **1** (5.0 mg) and a benzene solution (0.20 ml) of di-*t*-butyl peroxide (10% in vol) were placed in an ESR tube, and degassed as described above and then sealed. After the solution was irradiated for 10—20 min in the cavity of an ESR instrument with the high-pressure mercury lamp, the light source was turned off, and the decay rates were measured by monitoring the ESR signal intensities. Integration of the ESR signals was conducted with a Model JES-ID-2 integrator using a benzene solution of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (1,3,5-triphenylverdazyl)[22] as a standard.

ESR spectra were recorded at room tempcrature on a JES-ME-3X spectrometer with an X-band microwave unit and a 100 kHz field modulation. Coupling constatns and *g*-values were determined by comparison with the a_N value (13.09 G)[23] and the *g*-value (2.0057)[24] of Fremy's salt.

Computer simulation of spectra was performed using a FACOM 230-60 computer equipped with a FACOM F-6201D plotter.

References

1) Part X of this series, "ESR Studies of Nitrogen-centered Free Radicals." For Part IX, see Y. Miura, H. Asada, and M. Kinoshita, *Chem. Lett.*, **1978**, 1085.

2) For example, Y. Miura, Y. Katsura, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **51**, 3004 (1978).

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

4) H. Sayo and K. Mori, *Chem. Pharm. Bull.*, **25**, 1489 (1977).

5) The aminyls were also detected on the photolysis of the solutions containing arenesulfenamides **1** alone.

6) S. Terabe and R. Konaka, *J. Chem. Soc., Perkin Trans., 2*, **1973**, 369.

7) Y. Miura, Y. Katsura, and M. Kinoshita, *Chem. Lett.*, **1977**, 409.

8) Y. Miura, H. Asada, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 1857 (1977).

9) The spin orbit coupling parameter of the sulfur atom is 382 cm^{-1}; D. S. McClure, *J. Chem. Phys.*, **17**, 905 (1949).

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

11) For *a* values, see D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, **23**, 420 (1958).

12) The other values of coupling constant and the *g*-value for **2k** are $a_{o\text{-H}(N\text{-Ph})}$: 3.76, $a_{m\text{-H}(N\text{-Ph})}$: 1.16, $a_{o\text{-H}(S\text{-Ph})}$: 0.81, $a_{m\text{-H}(S\text{-Ph})}$: 0.26, and a_{CH_3}: 4.82 G, *g*-value: 2.0059.

13) The concentration of oxygen in benzene saturated with air is 2.0×10^{-3} mol l^{-1} (20 °C); J. Horiuti, *Scientific Papers*, **17**, 125 (1931).

14) C. C. Price and G. W. Stacy, *J. Am. Chem. Soc.*, **68**, 498 (1946).

15) C. H. Wang and S. G. Cohen, *J. Am. Chem. Soc.*, **79**, 1924 (1957).

16) Y. Fukui, Y. Kuwahara, and K. Saeki, and M. Mori, *Yakugaku Zasshi*, **80**, 1472 (1960).

17) A. Newton, *J. Am. Chem. Soc.*, **65**, 2434 (1943).

18) R. G. Wilson and D. H. Williams, *J. Chem. Soc., B*, **1968**, 1163.

19) J. Burgers, M. A. Hoefnagel, P. E. Verkade, H. Visser, and B. M. Wepster, *Recl. Trav. Chim., Pays-Bas*, **77**, 491 (1958).

20) R. Okazaki, T. Hosogai, E. Iwadare, M. Hashimoto, and N. Inamoto, *Bull. Chem. Soc. Jpn.*, **42**, 3611 (1969).

21) Sulfenamides isolated from the reaction mixture were **1c**, **1d**, and **1e**, unchlorinated and monochlorinated sulfenamides could not be isolated.

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

23) R. J. Faber and G. K. Fraenkel, *J. Chem. Phys.*, **47**, 2462 (1967).

24) J. E. Werz, D. C. Reitz, and F. Dravnieks, "Free Radicals in Biological Systems," Academic Press, New York, N. Y. (1961), p. 186.