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ESR Studies of *N*-(Arylthio)-*t*-butylaminyls[1]

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It was found that *N*-(arylthio)-*t*-butylaminyls (**2**) are easily generated by the photolysis of *N*-*t*-butylbenzenesulfenamides (**1**). The ESR spectra of **2** were split into a 1 : 1 : 1 triplet by the interaction with the nitrogen nucleus (11.70—11.89 G), and each of the triplet was further split by the ring protons ($a_{o\text{-H}}$: 0.89—1.07 G). The *g*-values of **2** lie in the range from 2.0068—2.0073. The radicals persist in benzene and it appears that they are not sensitive to the atmospheric oxygen.

A number of nitrogen-centered free radicals have so far been prepared and extensive ESR spectroscopic studies of these radicals have been undertaken.[2] In the course of ESR studies on nitrogen-centered free radicals containing sulfur atoms adjacent to the radical center, it was found that *N*-(arylthio)-*t*-butylaminyls (**2**) can easily be generated by the photolysis of *N*-*t*-butylbenzenesulfenamides (**1**). Up to the present time, some structually related radicals have been detected, *e.g.* $2\text{-NO}_2C_6H_4S\dot{N}H$,[3] $Me_3C\dot{N}SN(CMe_3)MR_n$,[4] $Ar\dot{N}S\text{-}Ar'$,[1,5,6] and $4\text{-ClC}_6H_4S\dot{N}R$.[7] The last-mentioned radical, which was detected as an intermediate radical upon the thermal decomposition of *N*-alkenyl-*N*-(2,3-dihydro-2-oxobenzoxazol-3-yl)-*p*-chlorobenzenesulfenamides, is closely related to that examined in the present experiment. However, a detailed ESR spectroscopic investigation of $R\dot{N}SAr$ has not been undertaken. In this report, an ESR spectroscopic investigation of **2** will be described.

$$\underset{\mathbf{1}}{t\text{-Bu-NH-S-Ar}} \xrightarrow{-\text{H}\cdot} \underset{\mathbf{2}}{t\text{-Bu-}\dot{\text{N}}\text{-S-Ar}}$$

Ar: **a**$=C_6H_5$, **b**$=4\text{-FC}_6H_4$, **c**$=4\text{-ClC}_6H_4$, **d**$=4\text{-BrC}_6H_4$, **e**$=4\text{-NO}_2C_6H_4$

Results and Discussion

Generation of the Radicals. One of the most conventional methods for generating the desired free radicals is hydrogen-abstruction from an appropriate precursor by a *t*-butoxyl radical. This method was first employed for the generation of **2**. In a typical procedure, after a benzene solution of **1c** and di-*t*-butyl peroxide had been degassed, it was irradiated with a high-pressure mercury lamp. From the solution, two paramagnetic species were detected. The ratio drived from the intensities of the respective ESR signals was *ca.* 1 : 2. The stronger signal was present in the form of a 1 : 1 : 1 triplet (11.75 G) with each the triplet further split into a poorly-resolved 1 : 2 : 1 triplet (0.93 G). The *g*-value of the radical was found to be 2.0071. From these results, the radical was assigned to the desired radical, *N*-(4-chlorophenylthio)-*t*-butylaminyl (**2c**). The ESR parameters are close to those reported for $4\text{-ClC}_6H_4S\dot{N}R$ (a_N: 11 G, *g*-value: 2.0073).[7] The other radical resulted in a simple 1 : 1 : 1 triplet (a_N: 14.11 G) and its *g*-value was found to be 2.0051. These ESR parameters are close to those reported for *N*-alkoxyalkylaminyls.[8] Thus, it appears likely that it is an *N*-alkoxyalkylaminyl, *N*-(*t*-butoxy)-*t*-butylaminyl.[9] In the ESR spectrum obtained by this procedure, the two signals partially overlapped. Thus, it was difficult to accurately determine the ESR parameters of **2**. For this reason, another procedure for the generation of **2** was examined. It was found that after a degassed benzene solution containing **1** alone had been irradiated with a high-pressure mercury lamp, only **2** was detected in the solution. In this case, the mechanism for the generation of **2** may be illustrated as follows:

$$\mathbf{1} \xrightarrow{h\nu} t\text{-Bu-}\dot{\text{N}}\text{H} + \text{ArS}\cdot$$

$$\downarrow \mathbf{1}$$

$$t\text{-Bu-NH}_2 + \mathbf{2}$$

A typical ESR spectrum of **2** is illustrated in Fig. 1, and the ESR parameters for **2** are listed in Table.

Although the coupling due to the *ortho* and *para* protons could be observed for all the radicals, the values of coupling constant for the ring protons of **2a** could not be accurately determined because of poor resolution. In **2b**, further coupling due to the fluorine nucleus was observed in addition to that due to the ring protons (Fig. 2).

Radical **2** was also generated by oxidation with lead dioxide and potassium carbonate. A benzene solution of **1** was stirred for 5 min in the presence of the oxidizing agents under ambient conditions and, after the oxidizing agents were removed, only **2** was detected in the solution.

On the other hand, the ESR parameters for *t*-butyl arylthio nitroxide radicals (in benzene) are 15.90—

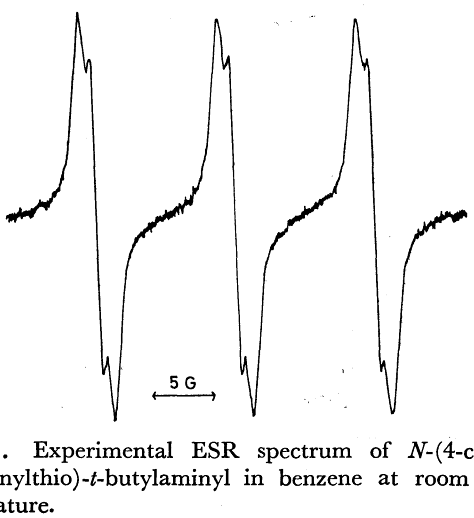


Fig. 1. Experimental ESR spectrum of *N*-(4-chlorophenylthio)-*t*-butylaminyl in benzene at room temperature.

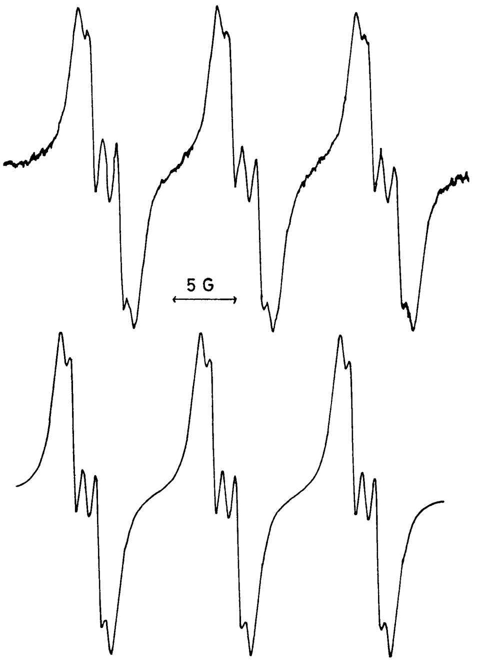
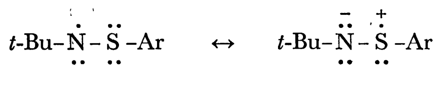


Fig. 2. Experimental ESR spectrum of *N*-(4-fluorophenylthio)-*t*-butylaminyl (**2b**) in benzene at room temperature (upper), and computer simulated, using Lorentzian line shapes and a line width of 0.96 G.

18.03 G (a_N) and 2.0066—2.0067 (g-value).[10,11] On the basis of these results, it is obvious that radical **2** is not the corresponding nitroxide radical.

From the ESR parameters shown in the table, it can be safely said that in **2** the unpaired electron is mainly located on the nitrogen ($2p_z$ orbital) because of the large a_N values. Considering the g-values, they are rather large for a nitrogen-centered free radical. This indicates that extent of delocalization of the spin onto the adjacent sulfur is not small.[12] In comparing the ESR parameters for **2** with those of the other related radicals described above, the values of a_N for **2** are somewhat smaller than those for $Me_3C\dot{N}S(Me_3)MR_n$-[$a_N(\alpha)$: 12.0—12.6 G],[5] and are considerably larger than those for $Ar\dot{N}SAr'$ (8.74—9.59 G).[6] This can be explained in terms of the larger ability of the phenyl rings to delocalize an unpaired electron in comparison with the $-SN(CMe_3)MR_n$ or the *t*-butyl group.

Decay Kinetics of the Radicals. Decay kinetic investigations were performed, and the results are illustrated in Fig. 3. As can be seen from the figure, the radicals are fairly long-lived.[7] This may be explained by a) the protection by the *t*-butyl group of the radical center and b) the absence of hydrogen atoms at the β position. In addition to this explanation, it appears likely that Form II makes an important contribution to the persistence.[6]



$$t\text{-Bu}-\ddot{\dot{N}}-\ddot{\underset{\cdot\cdot}{S}}-\text{Ar} \leftrightarrow t\text{-Bu}-\overset{-}{\ddot{N}}-\overset{+}{\dot{\underset{\cdot\cdot}{S}}}-\text{Ar}$$

Form I. Form II.

Moreover, decay kinetics were carried out both in the presence and absence of the atmosphere in order to examine whether or not radical **2** reacts with oxygen.

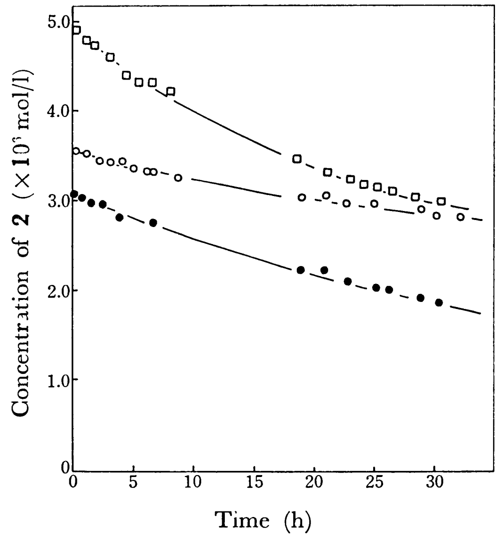


Fig. 3. Decay plots of *N*-(arylthio)-*t*-butylaminyls (**2**) in benzene at 15 °C; (□): **2a** in the absence of oxygen, (○): **2c** in the absence of oxygen, (●): **2c** in the presence of oxygen.

Table. ESR parameters for *N*-(arylthio)-*t*-butylaminyls[a)]

t-Bu-$\dot{N}$-S-Ar		Coupling constant			g-Value
	Ar	a_N	$a_{o\text{-H}}$	a_{other}	
2a	C_6H_5	11.70			2.0069
2b[b)]	4-FC_6H_4	11.83	0.89	2.22 (a_F)	2.0070
2c	4-ClC_6H_5	11.75	0.93		2.0071
2d	4-BrC_6H_4	11.76	1.00		2.0072
2e	4-$NO_2C_6H_4$	11.89	1.07		2.0068

a) In benzene at room temperature (15 °C). b) The coupling constants were determined by computer simulation.

In both cases, radical **2c** decayed at about the same rate. On the other hand, the *t*-butyl arylthio nitroxide radicals,[11] which were generated by the photolysis of diaryl disulfide in the presence of 2-methyl-2-nitrosopropane, decayed comletely within 20 s after turning off of the mercury lamp used to produce the arylthiyl radicals from the diaryl disulfides. This indicates that the *t*-butyl arylthio nitroxide radicals are extremely short-lived. From these results, it appears that **2** is not sensitive to the atmospheric oxygen.

Experimental

All melting points are uncorrected. The IR spectra were obtained on a Jasco model IR-G Spectrometer. The NMR spectra were recorded on a Hitachi-Perkin-Elmer R-20 Spectrometer using TMS as an internal standard.

Materials. The benzene used for the ESR measurements was purified by the usual method.[13] Benzenethiol, 4-chlorobenzenethiol, and *t*-butylamine were obtained commercially and used without further purification. 4-Fluoro-,[14] 4-bromo-,[15] and 4-nitrobenzenethiol[16] were prepared by the reported methods.

General Procedure for Preparation of N-t-*Butylbenzenesulfen-*

*amides (**1**).* Benzenethiol was treated with chlorine gas in dry chloroform at −5 to 0 °C. After removal of chloroform, the residual oil was distilled (56—57 °C/3 Torr for benzenesulfenyl chloride, and other sulfenyl chlorides were used in the following step without distillation).

A solution of *t*-butylamine (0.050 mol) and triethylamine (0.050 mol) in dry diethyl ether (ether, 200 ml) was cooled to 0 °C. To the solution was added dropwise benzenesulfenyl chloride (0.045 mol) in dry ether (30 ml) with stirring. After the addition of the sulfenyl chloride, the reaction mixture was further stirred at 0 °C for 30 min. After the triethylamine hydrochloride had been filtered off, ether was evaporated to give crude **1**. The purification of **1** is described below for each case. The purities of the **1** prepared were examined by TLC [alumina (E. Merck GF_{254})–hexane for **1a—d** and benzene–hexane (1 : 1 in vol) for **1e**].

N-t-*Butylbenzenesulfenamide (**1a**).* After the residue had been distilled (60—62 °C/0.07 Torr), a small amount of hexane (*ca.* 1 ml) was added to the distillate and the solution was cooled to −20 °C, giving colorless prisms. The parent solution was decanted, the residual crystals were then dissolved in hexane and the resulting solution was again cooled to −20 °C. This cycle was repeated several times, and finally, the crystals were dried in a vacuum at 0 °C. Yield 45% (before recrystallization). n_D^{25}: 1.5429 (lit,[17] n_D^{25}: 1.5435)). NMR (CCl_4): δ 1.17 (s, *t*-Bu), 2.65 (bs, NH), and 6.86—7.32 (m, C_6H_5).

N-t-*Butyl-4-fluorobenzenesulfenamide (**1b**).* After the residue had been distilled (69—71 °C/0.07 Torr), the distillate was treated similarly to the case of **1a**. Yield 63% (based on the amount of 4-fluorobenzenethiol and before recrystallization). n_D^{20}: 1.5227. IR (liquid): 3320 cm^{-1}(NH). NMR (CCl_4): δ 1.15 (s, *t*-Bu), 2.75 (bs, NH), and 6.76—7.73 (m, C_6H_4). Found: C, 60.01; H, 6.91; N, 6.99%. Calcd for $C_{10}H_{14}FNS$: C, 60.27; H, 7.08; N, 7.03%.

N-t-*Butyl-4-chlorobenzenesulfenamide (**1c**).* After the residue had been distilled (94—95 °C/0.07 Torr), the distillate was recrystallized from hexane (cooled to −20 °C), giving colorless prisms with mp 44—45 °C in a 34% yield (based on the amount of 4-chlorobenzenethiol). IR (KBr): 3320 cm^{-1}(NH). NMR (CCl_4): δ 1.14 (s, *t*-Bu), 2.68 (bs, NH), and 7.02 (s, C_6H_4). Found: C, 55.37; H, 6.31; N, 6.52%. Calcd for $C_{10}H_{14}ClNS$: C, 55.66; H, 6.55; N, 6.49%.

N-t-*Butyl-4-bromobenzenesulfenamide (**1d**).* After the residue had been distilled (111—113 °C/0.07 Torr), the distillate was recrystallized from hexane (cooled to −20 °C), giving colorless prisms with mp 37—38 °C in a 33% yield (based on the amount of 4-bromobenzenethiol). IR (KBr): 3320 cm^{-1}(NH). NMR (CCl_4): δ 1.14 (s, *t*-Bu), 2.63 (bs, NH), and 7.05 and 7.27 (d, *J*=8 Hz, C_6H_4). Found: C, 46.27; H, 5.18; N, 5.43%. Calcd for $C_{10}H_{14}BrNS$: C, 46.16; H, 5.42; N, 5.38%.

N-t-*Butyl-4-nitrobenzenesulfenamide (**1e**).*[18] The residue obtained was recrystallized from hexane, giving yellow needles with mp 78—79 °C in an 18% yield (based on the amount of 4-nitrobenzenethiol). IR (KBr): 3300 cm^{-1}(NH). NMR (CCl_4): δ 1.12 (s, *t*-Bu), 2.34 (bs, NH), and 7.18 and 8.02 (d, *J*=8 Hz, C_6H_4). Found: C, 53.07; H, 5.95; N, 12.26%. Calcd for $C_{10}H_{14}N_2O_2S$: C, 53.05; H, 6.23; N, 12.38%.

Generation of N-*(Arylthio)*-t-*butylaminyls (**2**).* *a)* The compound **1** (20 mg) and benzene (0.20 ml) were placed in an ESR tube. The solution was degassed by three freeze-thaw cycles and the tube was then sealed. After the solution had been irradiated for 5 min from a distance of 10 cm with a 100 W high-pressure mercury lamp (JES-UV-1), the tube was set in the ESR cavity; *b)* **1** (0.10 g) in benzene (2 ml) was stirred for 5 min in the presence of lead dioxide (0.50 g) and potassium carbonate (0.50 g). After the oxidizing agents had been filtered off, 0.2 ml of the filtrate was placed in an ESR tube and the soluion was degassed as described above, and the tube was then sealed.

Decay Kinetics. When the kinetics was carried out in degassed benzene, the sample was prepared according to procedure *a*. On the other hand, when the kinetics was carried out in a system containing air, the sample was prepared as follows: after photolysis of a degassed benzene solution of **1**, the solution was exposed to the atmosphere and shaken well, and then the tube was set in the ESR cavity. The decay rates of **2** were measured at 15 °C in the dark by monitoring the intensities of ESR signal. Integration of the ESR signals was achieved using a Model JES-ID-2 Integrator, with a benzene solution of 3,4-dihydro-2,4,6-triphenyl-2*H*-1,2,4,5-tetrazin-1-yl (1,3,5-triphenylverdazyl)[19] as a standard.

The ESR spectra were recorded at 15 °C on a JES-ME-3X Spectrometer equipped with 100 kHz field modulation. Computer simulation of the spectrum was carried out using a FACOM 270-30 Computer equipped with a FACOM 6201B Plotter. The simulation was fitted by trial and error.

References

1) Part V of this series, Y. Miura, Y. Katsura, and M. Kinoshita, *Chem. Lett.*, **1977**, 409.

2) For recent reviews see (a) A. R. Forrester, J. M. Hay, and R. H. Thomson, "Organic Chemistry of Stable Free Radicals," Academic Press, New York, N. Y. (1968); (b) S. F. Nelsen, "Free Radicals," Vol. II ed by J. K. Kochi, John Wiley, New York, N. Y. (1973), p. 527; (c) W. C. Danen and F. A. Neugebauer, *Angew. Chem.*, **87**, 823 (1975).

3) U. Schmidt, K. H. Kabitzke, and K. Markau, *Angew. Chem.*, **76**, 376 (1964).

4) G. Brunton, J. F. Taylor, and K. U. Ingold, *J. Am. Chem. Soc.*, **98**, 4879 (1976).

5) J. Flood and K. E. Russell, *Can. J. Chem.*, **53**, 1123 (1975).

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

7) R. S. Atkinson, S. B. Awad, E. A. Smith, and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, **1976**, 22.

8) (a) W. C. Danen, C. T. West, and T. T. Kensler, *J. Am. Chem. Soc.*, **95**, 5716 (1973); (b) R. A. Kaba and K. U. Ingold, *ibid.*, **98**, 7375 (1976).

9) This is an unidentified radical.

10) I. H. Leaver and G. C. Ramsay, *Tetrahedron*, **25**, 5669 (1969).

11) Unpublished results.

12) The spin-orbit coupling parameter of sulfur is 382 cm^{-1}; D. S. McClure, *J. Chem. Phys.*, **20** 682 (1952).

13) Y. Miura, N. Makita, and M. Kinoshita, *Bull. Chem. Soc. Jpn.*, **50**, 482 (1977).

14) H. Zahn and H. Zuber, *Chem. Ber.*, **86** 172 (1953).

15) H. F. Wilson and D. S. Tarbell, *J. Am. Chem. Soc.*, **72** 5200 (1950).

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

17) D. A. Armitage, M. J. Clark, and A. C. Kinsey, *J. Chem. Soc., C*, **1971**, 3867.

18) Brit. Amended 1123506; *Chem. Abstr.*, **76**, 26223u (1972).

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