An ESR Study of *N*-Benzoyl- and *N*-Pivaloyl-*N*-(arylthio)aminyls[1)]

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N-Benzoyl-*N*-(arylthio)aminyls, ArCONSAr', and *N*-pivaloyl-*N*-(arylthio)aminyls, *t*-BuCONSAr, were generated in benzene by hydrogen-abstraction from *N*-benzoyl- and *N*-pivaloylbenzenesulfenamides. The hyperfine coupling constants (*hfcc*) for the radicals are in the range of 6.80—7.57 G for the nitrogen nucleus and 1.68—1.97 G for the *S*-phenyl ring protons. However, *hfcc* due to the benzoyl and pivaloyl protons were not detected. The *g*-values lie in the range of 2.0081—2.0084. On the basis of these ESR parameters, it is suggested that the acylaminyls exist in a π-electronic ground state and that the unpaired electron is located predominantly on the nitrogen atom ($2p_z$ orbital) and the phenylthio group. From the decay kinetic study of the radicals, it was found that *N*-benzoyl-*N*-(4-chlorophenylthio)aminyl persisted for more than 3 h in benzene at 24 °C, and *N*-pivaloyl-*N*-(4-chlorophenylthio)aminyl decayed only a little, even after 20 h.

Acylaminyls are of interest as an important intermediate in such photochemical reactions as Hoffmann-Löffler type intramolecular rearrangements.[2)] Some ESR spectroscopic investigations of acylaminyls have been undertaken for the purpose of determining whether they can best be classified as π or σ radicals.[3–6)] Acylaminyls are generally known as transient radicals and are easily converted into the corresponding nitroxides in the presence of oxygen. Thus, the unequivocal identification of the radicals by ESR spectroscopy is difficult, and other radicals have often been misassigned as acylaminyls. Recent ESR spectroscopic investigations of acylaminyls have shown that they exist in a π-electronic ground state.[3)]

In the past years we have studied some nitrogen-centered free radicals in which one or two divalent sulfur atoms are adjacent to the radical center.[7)] In this report we will describe an ESR study of a new class of acylaminyls, *N*-acyl-*N*-(arylthio)aminyls (**2**).

Results and Discussion

Preparation of N-*Acylbenzenesulfenamides (1).* The sulfenamides were prepared by the reactions of benzamides or pivalamide with benzenesulfenyl chlorides in THF or ether in the presence of triethylamine. In the reactions of pivalamides, sulfenamides were afforded in relatively good yields (*ca.* 50%), but with benzamides the yields were low (8—28%). The structures of **1** were identified by means of elemental and instrumental analyses.

$$RCNH_2 + ArSCl \xrightarrow[\text{in THF (ether)}]{Et_3N} RCNHSAr + Et_3N\cdot HCl$$

1

Generation of Radicals. Acylaminyls, **2**, were generated by two procedures: a) the photolysis of a benzene solution of **1** using a high-pressure mercury lamp and b) the thermolysis of a benzene solution containing **1** and di-*t*-butyl diperoxyoxalate. In the former procedure, the radicals **2** seem to be generated by hydrogen-abstraction from **1** by the amidyl radicals which are formed by the photoinduced S–N bond fission of **1** (Scheme 1).[8,9)]

$$\mathbf{1} \xrightarrow{h\nu} RCNH\cdot + ArS\cdot$$

$$RCNH\cdot + \mathbf{1} \rightarrow RCNH_2 + RCNSAr$$

2

Scheme 1.

The ESR spectra of **2** generated by Procedures a and b were in complete agreement with each other.

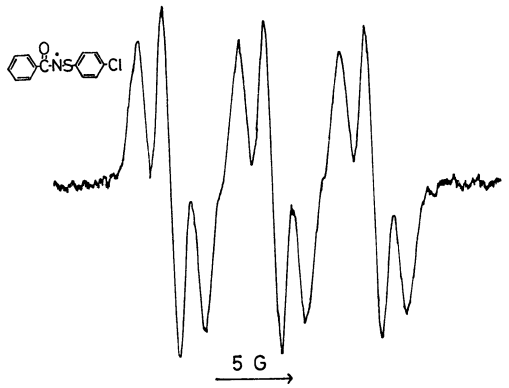


Fig. 1. An ESR spectrum of **2b** generated by photolysis of a benzene solution of **1b** at 24 °C.

The ESR spectrum (Fig. 1) of *N*-benzoyl-*N*-(4-chlorophenylthio)aminyl (**2b**) was split into a 1:1:1 triplet (7.16 G) by the interaction with one nitrogen nucleus, and each of the triplet was further split into a 1:2:1 triplet (1.72 G) by the interaction with two magnetically equivalent protons. The latter triplet is obviously due to the two ortho-protons in the *S*-phenyl ring, and no quartet splitting which could be expected on the basis of the benzoyl protons' participation could be detected. In order to confirm this assignment, an ESR spectrum of a *d*-labeled acylaminyl, **2g**, was measured. This ESR spectrum consisted of a simple 1:1:1 triplet (7.08 G), and no splitting due to the benzoyl protons was detected. The radicals **2c**, **2d**, and **2f** also showed spectra similar to that of **2b**. On the other hand, the spectra of *N*-benzoyl-*N*-(phenylthio)-aminyl (**2a**) and *N*-pivaloyl-*N*-(phenylthio)aminyl (**2e**) were constituted of 1:3:3:1 quartets (1.68—1.69 G)

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

	R–C(=O)–N(·)–S–R′		*S*-Phenyl ring			*g*-Value
	R	R′	a_N[b]	$a_{o\text{-}H}$[b]	$a_{p\text{-}H}$[b]	
2a	C_6H_5	C_6H_5	7.09	1.68	1.68	2.0081
2b	C_6H_5	4-ClC_6H_4	7.16	1.72	—	2.0083
2c	4-$CH_3OC_6H_4$	4-ClC_6H_4	7.38	1.73	—	2.0082
2d	4-$NO_2C_6H_4$	4-ClC_6H_4	6.80	1.97	—	2.0084
2e	*t*-C_4H_9	C_6H_5	7.49	1.69	1.69	2.0082
2f	*t*-C_4H_9	4-ClC_6H_4	7.57	1.69	—	2.0083
2g	C_6H_5	C_6D_5	7.08			2.0082

a) In benzene at 24 °C. b) In G.

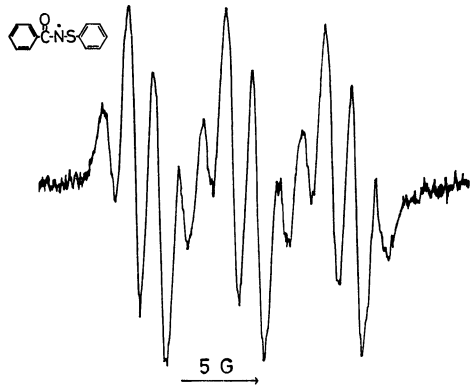


Fig. 2. An ESR spectrum of **2a** generated by photolysis of a benzene solution of **1a** at 24 °C.

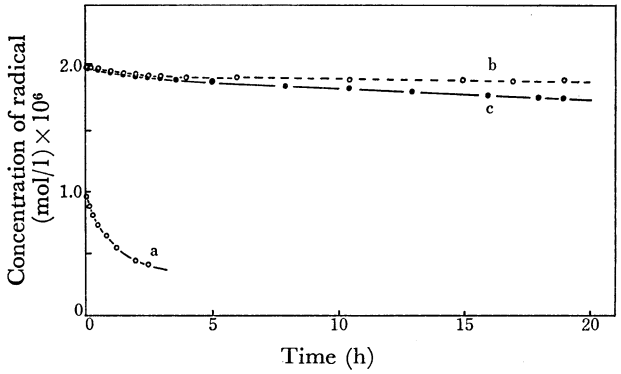
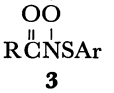


Fig. 3. Decay plots of *N*-acyl-*N*-(arylthio)aminyls (**2**) in benzene at 24 °C. a: **2b** in degassed benzene; b: **2f** in degassed benzene; c: **2f** in benzene saturated with air.

of a 1:1:1 triplet (7.09—7.49 G, see Fig. 2). The quartets were obviously due to the interaction with the magnetically equivalent two ortho- and one para-protons in the *S*-phenyl ring. The values of the coupling constants are listed in Table 1, together with the *g*-values.

It is well known that nitrogen-centered free radicals are easily converted into the corresponding nitroxides, even in the presence of such weak oxidants as atmospheric oxygen. In the present experiment, however, the possibility that **2** are identical with the corresponding nitroxides, **3**, may be excluded on the basis of the following points: 1) the *g*-values of **2** (2.0081—2.0084) are too high compared with those for nitroxides so far reported (*ca.* 2.006)[10] and 2) although, in *t*-BuNSAr, couplings due to the ring protons have never been detected,[11] in **2** relatively large couplings (a_H: 1.68—1.97 G) are observed.



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Decay Kinetics. The decay kinetic study of **2** was carried out in benzene at 24 °C in the dark. The results are illustrated in Fig. 3. As can be seen from the figure, the radical **2b** persisted in degassed benzene for more than 3 h, and **2f** decayed only a little, even after one day. Moreover, the decay rate of **2f** was measured in benzene saturated with air in order to examine the influence of oxygen on the stability. As may be found from the figure, the decay rate is almost the same as that obtained under the degassed conditions, indicating that the life-time of the radical is little affected by oxygen. Since other acylaminyls are very short-lived and are significantly sensitive to oxygen,[3,12] these results are of interest.

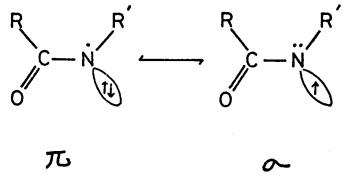


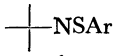
Fig. 4.

Consideration of ESR Parameters. Since, in acylaminyls, there is a carbonyl group which can potentially interact with the nitrogen lone-pair electrons, there has been considerable interest in determining whether they are π or σ radicals (Fig. 4). If in a σ-electronic ground state, they are expected to exhibit a large a_N value because the unpaired electron would reside in an orbital of an appreciable s character. Recent investigations of acylaminyls indicate that simple or *N*-alkoxyacylaminyls are π radicals, judging from the ESR parameters.[13]

With respect to the present radicals, the a_N values lie in the range of 6.80—7.57 G: they are considerably smaller than those observed for simple or *N*-alkoxyacylaminyls,[13] suggesting that **2** exist in a π-electronic ground state.

In **2a**—**d** and **2e**, no couplings due to the benzoyl protons were observed. Also, the replacement of the benzoyl groups in **2a** and **2b** by a pivaloyl group (**2a** or **2f**) increased the a_N values by only 0.4 G. Thus, in **2** there is a negligibly small delocalization of the unpaired electron onto the benzoyl aromatic ring.

When the a_H (1.68—1.97 G) and the *g*-values (2.0081—2.0084) for **2** are compared with those for *N*-(arylthio)-*t*-butylaminyls (**4**, a_H: 0.89—1.07 G, *g*-value: 2.0068—2.0072),[7] it is obvious that the extent of the delocalization of the unpaired electron onto the arylthio group in **2** is larger than in **4**. Since **4** is radical which the benzoyl or pivaloyl group in **2** is replaced by a *t*-butyl group with no ability to de-



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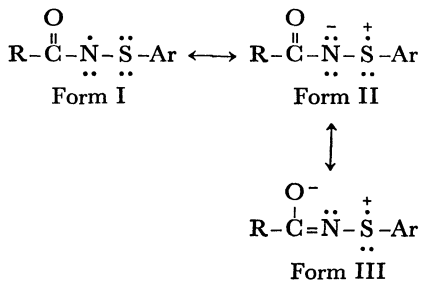
localize an unpaired electron, it is reasonable to think that, in **2**, the unpaired electron is little delocalized onto the carbonyl group.

The small a_N values observed for **2**, compared with those of other acylaminyls,[13] can be well explained in terms of the contribution of the resonance forms II and III, which reduce the spin density on the nitrogen. The contribution of II and III leads to an increase in



Form I Form II

Form III

the spin density on the sulfur atom possessing a large spin orbit coupling parameter,[15] resulting in the large *g*-values for **2**.

The contribution of II and III may become more important by the introduction of electron-withdrawing substituents into the benzoyl group, resulting in a reduction in the magnitude of the a_N value. In the *p*-nitro-substituted acylaminyl, **2d**, the a_N value is reduced by 0.36 G compared with that for **2b**. On the contrary, the introduction of electron-donating substituents may lead to an increase in the magnitude of the a_N value. In the *p*-methoxy-substituted acylaminyl, **2c**, the a_N value is increased by 0.22 G compared with that for **2b**.

From the results and discussion, it may be concluded that the acylaminyls **2** exist in a π-electronic ground state, and the unpaired electron is located predominantly on the nitrogen atom ($2p_z$ orbital) and the arylthio group.

Experimental

All the melting points are uncorrected. The IR spectra were run on a JASCO Model IR-G spectrometer, and the NMR spectra were recorded with a Hitachi-Perkin Elmer R-20 spectrometer, using TMS as an internal standard. Benzene-d_5-thiol[16] and di-*t*-butyl diperoxyoxalate[17] were prepared by the reported methods. The benzene used as a solvent in the ESR measurements was purified by the usual method.[18]

General Procedure for Preparation of N-*Acylbenzenesulfenamides (1).* Benzenesulfenyl chloride (0.024 mol) in dry THF [50 ml, or dry ether (50 ml) in the cases of **1e** and **1f**] was added dropwise to a stirred solution of amide (0.020 mol) and triethylamine (0.030 mol) in dry THF [250 ml, or dry ether (500 ml) in the cases of **1e** and **1f**] at 0 °C. After addition of the sulfenyl chloride, the reaction mixture was stirred for 3 h at 0 °C, and then for 10 h at room temperature. After the triethylamine hydrochloride thus formed was filtered off, the filtrate was concentrated under reduced pressure to give a powdery residue, which was subjected to column chromatography [alumina (E. Merck, Darmstate, Art 1097), column size 20×3 cm, eluent: benzene/ethanol: 100/1]. The **1** thus separated was recrystallized from the appropriate solvents.

N-*Benzoylbenzenesulfenamide (1a).* Colorless plates with mp 122—124 °C (from benzene/hexane: 2/1). Yield: 14%. IR(KBr): 3250 (NH) and 1635 cm^{-1} (CO). NMR (DMSO-d_6): δ 7.15—8.11 (m, aromatic, 10H) and 10.25 (br s, NH, 1H). Found: C, 67.77; H, 4.64; N, 5.88%. Calcd for $C_{13}H_{11}NOS$: C, 68.09; H, 4.84; N, 6.11%.

N-*Benzoyl-4-chlorobenzenesulfenamide (1b).* Colorless plates with mp 138—139 °C (from benzene/hexane: 2/1). Yield: 15%. IR (KBr): 3250 (NH), 1640 cm^{-1} (CO). NMR (DMSO-d_6): δ 7.19—8.10 (m, C_6H_4 and C_6H_5, 9H) and 10.33 (br s, NH, 1H). Found: C, 59.10; H, 3.70; N, 5.18%. Calcd for $C_{13}H_{10}NOClS$: C, 59.20; H, 3.82; N, 5.31%.

N-*(4-Methoxybenzol)-4-chlorobenesulfenemide (1c).* Colorless needles with mp 178—179 °C (from benzene). Yield: 13%. IR (KBr): 3200 (NH), 1650 cm^{-1} (CO). NMR (DMSO-d_6): δ 3.87 (s, CH_3, 3H), 7.12 and 8.04 (d, J=8 Hz, CO-C_6H_4, 4H), 7.25 and 7.49 (d, J=8 Hz, *S*-C_6H_4, 4H), and 10.12 (br s, NH, 1H). Found: C, 57.35; H, 4.25; N, 4.77%. Calcd for $C_{14}H_{12}NO_2ClS$: C, 57.24; H, 4.12; N, 4.77%.

N-*(4-Nitrobenzoyl)-4-chlorobenzenesulfenamide (1d).* Light yellow needles with mp 169—170 °C (from benzene). Yield: 8%. IR (KBr): 3250 (NH), 1660 cm^{-1} (CO). NMR (DMSO-d_6): δ 7.34 and 7.39 (s, *N*-C_6H_4, 4H), 8.16 and 8.41 (d, J=8 Hz, CO-C_6H_4, 4H), and 10.61 (br s, NH, 1H). Found: C, 50.57; H, 2.89; N, 9.09%. Calcd for $C_{13}H_9N_2O_3ClS$: C, 50.57; H, 2.94; N, 9.07%.

N-*Pivaloylbenzenesulfenamide (1e).* Colorless needles with mp 102—103 °C (from hexane). Yield 58%. IR (KBr): 3200 (NH), 1650 cm^{-1} (CO). NMR (CCl_4): δ 1.16 (s, *t*-Bu, 9H), 7.12 (s, C_6H_5, 5H), and 7.79 (br s, NH, 1H). Found: C, 62.95; H, 7.38; N, 6.65%. Calcd for $C_{11}H_{15}NOS$: C, 63.12; H, 7.22; N, 6.69%.

N-*Pivaloyl-4-chlorobenzenesulfenamide (1f).* Colorless plates with mp 119—120 °C (from hexane). Yield: 43%. IR (KBr): 3200 (NH) and 1650 cm^{-1} (CO). NMR (CCl_4): δ 1.20 (s, *t*-Bu, 9H), 7.00 and 7.13 (d, J=8 Hz, C_6H_4, 4H), and 7.66 (br s, NH, 1H). Found: C, 53.81; H, 6.08; N, 5.64%. Calcd for $C_{11}H_{14}NOClS$: C, 54.20; H, 5.79; N, 5.75%.

N-*Benzoylbenzenesulfenamide-2,3,4,5,6-*d_5 *(1g).* Colorless plates with mp 126—128 °C (from benzene/hexane: 2/1). Yield 28%. IR (KBr): 3250 (NH) and 1660 cm^{-1} (CO). NMR (DMSO-d_6): δ 7.25—8.22 (m, C_6H_5, 5H) and 10.44 (br s, NH, 1H). Found: C, 66.25; H, 4.50; N, 6.18%. Calcd for $C_{13}H_6NOD_5S$: C, 66.63; H, 4.74; N, 5.98%.

Generation of Radicals. a) Sulfenamide **1** (5.0 mg) and benzene (0.20 ml) were placed in an ESR tube. The solution

was degassed by three freeze-and-thaw cycles, and then sealed. The solution was directly irradiated in the cavity of an ESR instrument with an 100W high-pressure mercury lamp (JES-UV-1); b) **1** (5.0 mg), di-*t*-butyl diperoxyoxalate (10.0 mg), and benzene (0.20 ml) were placed in an ESR tube. The solution was degassed by the procedure described above, and then sealed. The ESR spectra from the solution were recorded at 24° C.

Decay Kinetics. The decay kinetic study of **2** was carried out in benzene at 24 °C in the dark. The sample was prepared as follows: **1** (5.0 mg) and benzene (0.20 ml) were placed in an ESR tube, degassed by the procedure described above, and then sealed. The solution was directly irradiated for *ca.* 20 min in the cavity of an ESR instrument with the mercury lamp, and then the light was turned off. The decay rates were followed by monitoring the ESR signal intensities, and the integration of the signals was carried out with a 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)[19] as a standard.

The ESR spectra were recorded on a JES-ME-3X spectrometer, with an X-band microwave unit and 100 kHz field modulation. The hyperfine coupling constants *(hfcc)* and *g*-values for **2** were determined by comparing them with the *hfcc* (a_N: 13.09 G)[20] and *g*-value (2.0057)[21] of Fremy's salt.

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