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First isolation of *N*-alkoxyaminyl radicals

Yozo Miura* and Tatsuya Tomimura

Department of Applied Chemistry, Faculty of Engineering, Osaka City University, Sumiyoshi-ku, Osaka 558-8585, Japan. E-mail: miura@a-chem.erg.osaka-cu.ac.jp

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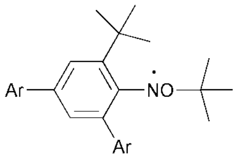
N-(*tert*-Butoxy)-*N*-(2,4-diaryl-6-*tert*-butylphenyl)aminyls have been isolated; this is the first isolation of *N*-alkoxyaminyl radicals.

Although a variety of *N*-alkoxyalkylaminyl ($R\dot{N}OR$),[1–3] *N*-alkoxyvinylaminy[4] and *N*-alkoxyarylaminyl radicals ($Ar\dot{N}OR$)[1,2,5–10] have been investigated for a long period and persistent *N*-alkoxyaminyls have been found, there are no reports of isolation of *N*-alkoxyaminyls. This is in contrast to the chemistry of thioaminyl radicals ($R\dot{N}SR$). In the case of thioaminyls a variety of radicals have been isolated and their X-ray crystallographic and magnetic studies have been carried out.[11,12] Isolable stable free radicals have attracted much attention as spin sources or building blocks of organic magnetic materials.[13,14] In this communication we report on the first isolation of *N*-alkoxyarylaminyl radicals and their characterization.

N-(*tert*-Butoxy)-*N*-(2,4-diphenyl-6-*tert*-butylphenyl)aminyl (**1a**) was prepared by treating the lithium salt of 2,4-diphenyl-6-*tert*-butylaniline with two equiv. of *tert*-butyl peroxybenzoate at −78 °C in THF.[15] The reaction mixture showed a deep red colour, and TLC analysis indicated formation of a red coloured product, along with the presence of the unreacted starting aniline and some minor products. Separation of the red zone by column chromatography (silica gel, 3:1 hexane–benzene) gave **1a** in 24% yield. In the same manner, **1b** and **1c** were isolated in 17 and 20% yields, respectively. Recrystallization of the isolated radical solid from MeOH afforded red plates (**1a**, **c**) or red needles (**1c**). The structures of radicals were confirmed by the IR spectra and elemental analyses. In the IR spectra no NH absorption was observed and the elemental analyses were in satisfactory agreement with the calculations in all cases. For **1a** single crystal X-ray crystallographic analysis was performed.



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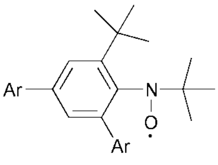

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a Ar = Ph
b Ar = 4-FC_6H_4
c Ar = 4-ClC_6H_4
a-d_{10} Ar = C_6D_5

N-Alkoxyarylaminyls **1** were stable in solution, even in the presence of atmospheric oxygen and, although **1a** was heated at 80 °C in degassed benzene for 10 d, 80% of the radical survived and no rearrangement to the corresponding aminoxyl **2** was observed.[8,16] These observations indicate that **1** is an oxygen insensitive and thermally stable radical.

Since **1a** gave a single crystal suitable for the X-ray crystallographic analysis on recrystallization from MeOH, we performed an X-ray crystallographic study on **1a**.† The ORTEP drawing of the molecular structure is shown in Fig. 1. The X-ray crystallographic data shows the following structural characteristics. The N and O atoms are coplanar with the benzene ring A within 0.05 Å. While benzene ring C makes a dihedral angle of 41.5° with benzene ring A, benzene ring B makes a dihedral angle of 86.0° with benzene ring A, indicating that there is a large steric congestion around the radical center. Accordingly, it is likely that delocalization of the unpaired electron spin onto benzene ring B is very or negligibly small, and this means that the benzene ring B plays an important role in steric protection, but does not contribute to electronic stabilization of the radical. Since the N–O bond has the character of a two center–three electron bond where the unpaired electron is accommodated in the anti-bonding orbital,[17] its bond length in **1** [1.358(2) Å] is somewhat shorter than typical N(sp^2)–O bonds (1.397 Å).[18]

The EPR parameters are summarized in Table 1. All the EPR spectra of **1** were a simple 1:1:1 triplet signal (a_N = 0.997–1.01 mT, g = 2.0041–2.0042) with a large peak-to-peak linewidth (ΔH_{pp}) of 0.31–0.33 mT, and no hyperfine couplings due to protons were observed. The large ΔH_{pp} is attributed to the presence of many unresolved protons with very small

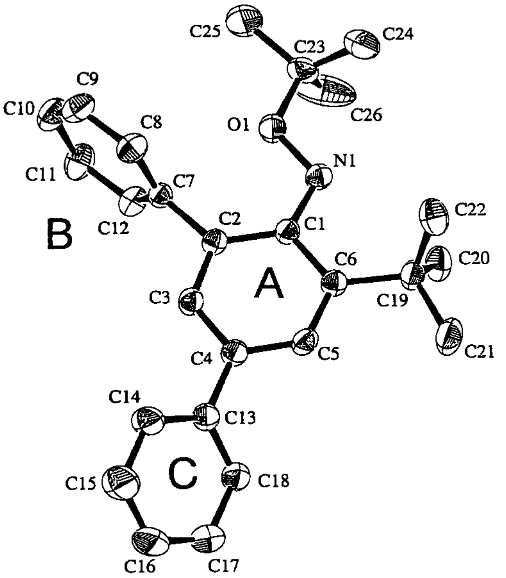

Fig. 1 ORTEP drawing of **1a**. Selected bond lengths and angles and torsion angles are as follows: C1–N1 1.368(3) and N1–O1 1.358(2) Å; C1–N1–O1 111.1(2) and N1–O1–C(23) 113.1(2)°; C2–C1–N1–O1 6.8(3), C6–C1–N1–O1 −175.4(2) and C1–N1–O1–C23 −173.9(2)°.

Table 1 EPR and UV-Vis spectroscopic data for **1**, **3** and **4** in benzene at 20 °C

Radical	a_N/mT	g	λmax/nm (ε/l mol^{-1}cm^{-1})
1a	1.01	2 .0042	545 (1230), 334 (28 600)
1b	0.997	2.0041	545 (1270), 334 (27 200)
1c	0.999	2.0042	553 (1120), 342 (29 900)
1a-d_{10}[ab]	1.00	2.0042	—
3	1.27	2.0062	—
4	0.987	2.0038	—

[a] The hyperfine coupling constants are determined by computer simulation. [b] a_H for the anilino *meta* protons (2H) is 0.170 mT.

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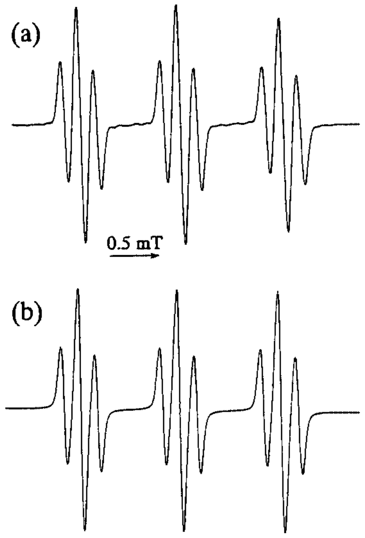
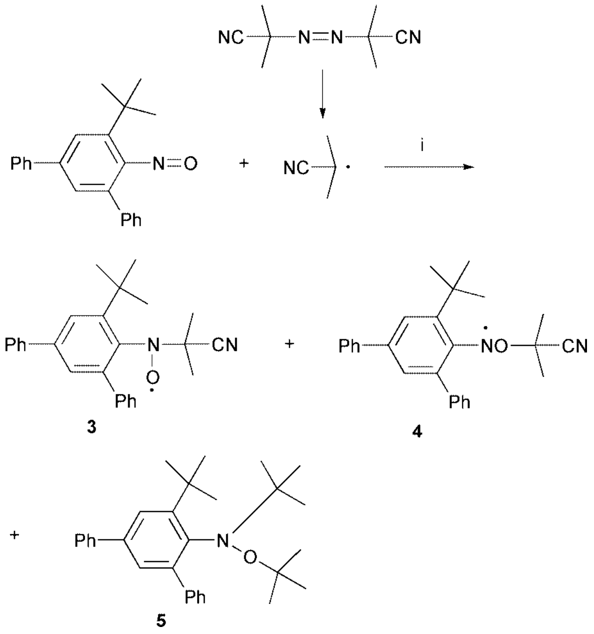


Fig. 2 EPR spectrum of **1a**-d_{10} in benzene at 20 °C. (a) Observed spectrum; (b) computer simulated spectrum.



Scheme 1

hyperfine coupling constants. To reduce the ΔH_{pp} values, the two benzene rings of **1a** were deuterated. The deuterated radical **1a**-d_{10} was prepared from (2,4-diphenyl-d_5)-6-*tert*-butylaniline and *tert*-butyl peroxybenzoate in the same manner as for that of **1a**. As shown in Fig. 2, the EPR spectrum of **1a**-d_{10} is split into 1:2:1 triplets of a 1:1:1 triplet, and computer simulation gave a_N = 1.00 mT and a_H (2H) = 0.170 mT. The protons giving a_H of 0.170 mT are assigned to the anilino *meta* protons.

To compare the a_N and g values of **1** with those for the corresponding aminoxyls **3** was generated by addition of the 2-cyanoprop-2-yl radical to 2,4-diphenyl-6-*tert*-butylnitrosobenzene (Scheme 1). After a mixture of 2,4-diphenyl-6-*tert*-butylnitrosobenzene and 1,1′-azobis(propane-2-carbonitrile) in benzene was heated at 80 °C for 1 h, EPR spectra of the solution were measured at 20 °C. The spectra showed the presence of **3** and **4** in a ratio of *ca.* 3 : 1. While the a_N and g values for **3** are 1.27 mT and 2.0062, those for **4** are 0.989 mT and 2.0038, indicating that a_N of **3** are much larger than those for **1** or **4**, as well as the g value. Although **4** could be isolated as a red oil with a spin concentration of 89% in 3.9% yield by column chromatography, **3** could not be isolated in pure form. Since **5** is the main product and its mobility (R_f) in column chromatography was almost the same as that of **3**, **3** was separated as a mixture with **5**.

The UV-Vis spectra were measured using benzene as the solvent. The data are listed in Table 1. A λmax at 545–553 nm with ε of 1120–1270 l mol^{-1}cm^{-1} is observed, which is attributable to the characteristic red colours of **1**.

Notes and references

† Crystal data for **1a**: $C_{26}H_{30}ON$, M = 372.53, orthorhombic, a = 36.9243(9), b = 11.2495(3), c = 10.9599(3) Å, V = 4552.5(5) Å^3, T = 296 K, space group *Pbca* (# 61), Z = 8, μ(Mo-Kα) = 0.65 cm^{-1}, 13507 reflections measured, 5112 unique (R_{int} = 0.017) which were used in all calculations. R = 0.078, R_w = 0.116, GOF = 1.57. CCDC 159014. See http://www.rsc.org/suppdata/cc/b1/b100698n/ for crystallographic files in .cif format.

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