

Figure 1. INDO p orbital spin densities calculated in (A) the triplet diradical, (B) the ketone radical anion, and (C) the pent-4-en-1-yl radical. Note that in 1A and 1B the nonbonding p orbital on oxygen is perpendicular to the O-C bond and is not exactly parallel with the p orbitals of the olefin system.

with those predicted by the simple arguments above and are also in accord with those calculated for the pent-4-en-1-yl radical (Figure 1C). This latter radical serves as our model for estimating the effect of an unpaired p electron on the spin distribution in the  $\sigma$  framework. In order to isolate the effect of a single carbonyl  $\pi^*$  electron on the spin distribution in the  $\sigma$  system, in the presence of a  $p_y$  electron pair on oxygen, calculations were also performed for the ketone radical anion. It is noted that in this case, the magnitude of spin density induced in the  $\sigma$  system is much reduced and the signs are in complete disagreement with the other systems.

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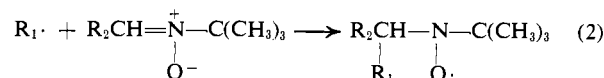
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### Spin Trapping of Short-Lived Free Radicals by Use of 2,4,6-Tri-*tert*-butylnitrosobenzene

Sir:

The detection and identification of short-lived free radicals by electron spin resonance trapping techniques ("spin trapping") has recently received wide attention.

Stable nitroxide radicals ("spin adducts") can be formed by radical addition to C-nitroso compounds (eq 1)<sup>1</sup> and nitrones (eq 2)<sup>2</sup> ("spin traps"). Previously, we utilized reaction 1 to detect and identify free radicals as reaction



intermediates in nickel peroxide oxidations.<sup>4</sup> Janzen<sup>3</sup> made a comparison of the effectiveness of different spin traps and pointed out that of the spin traps used (nitroso compounds and nitrones) certain advantages and certain disadvantages exist for each. Of interest is a recent report<sup>5</sup> that  $\alpha$ -(3,5-di-*tert*-butyl-4-hydroxyphenyl)-*N-tert*-butylnitronone is useful as a novel "bifunctional" trap.

We wish to report some of our observations on spin trapping using 2,4,6-tri-*tert*-butylnitrosobenzene (1), which was prepared by the oxidation of 2,4,6-tri-*tert*-butylaniline with *m*-chloroperbenzoic acid.<sup>6</sup> The purpose of this choice of spin trap was to get a simple spectrum for elucidation and to examine the steric effects in this reaction. The generation of radicals was achieved either by the abstraction of hydrogen from substrates by *tert*-butoxy radicals (formed by photolysis of di-*tert*-butyl peroxide or by thermolysis of di-*tert*-butyl peroxyoxalate) or by the abstraction of halogens from alkyl halides by the tri-*n*-butyltin radical.

The spin adducts produced with primary alkyl radicals were the same as those produced by the normal type of addition to ordinary nitroso spin traps. The values of the hyperfine splitting constants for nitroxides are shown in Table I (note that another spin adduct of isopropyl radical will be described later). Since the  $\beta$ -methylene hydrogen couplings vary with the kind of the group in the  $\gamma$  position, the structure of the attacking radical can be distinguished. Of interest is the finding that the order of the  $\beta$ -hydrogen couplings of the nitroxides is secondary > primary > methyl, in contrast to that found in the usual nitroxides,<sup>7</sup> presumably because of steric repulsion between the groups at the  $\gamma$  position and the *tert*-butyl groups of the benzene ring.

Upon heating azobisisobutyronitrile (AIBN) in benzene in the presence of 1, the esr spectrum of a 1:1:1 triplet of 1:2:1 triplets was observed. This spectrum is different from those of the nitroxides because of the small *g* value, the small nitrogen coupling, and the large meta hydrogen coupling (see Table II). To help in the structural assignment of this spectrum, 2,4,6-tri-*tert*-butylaniline in benzene was oxidized with nickel per-

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
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**Table I.** Hyperfine Splitting Constants (Gauss) for Nitroxide in Benzene Solution<sup>a,b</sup>

Spin adduct	$a^N$	$a_{\beta}^H$	$a_m^H$
RN(O·)CH <sub>3</sub> <sup>c,d</sup>	13.03	12.33 (3 H)	0.81
RN(O·)CH <sub>2</sub> CH <sub>3</sub> <sup>d</sup>	13.46	17.99 (2 H)	0.83
RN(O·)CH(CH <sub>3</sub> ) <sub>2</sub> <sup>d,h</sup>	13.29	22.19 (1 H)	0.76
RN(O·)CH <sub>2</sub> CH=CH <sub>2</sub> <sup>d</sup>	13.40	16.42 (2 H)	0.84
RN(O·)CH <sub>2</sub> - 	13.62	14.75 (2 H)	0.83
RN(O·)CH <sub>2</sub> OH <sup>e-v</sup>	13.73	13.73 (2 H)	0.95

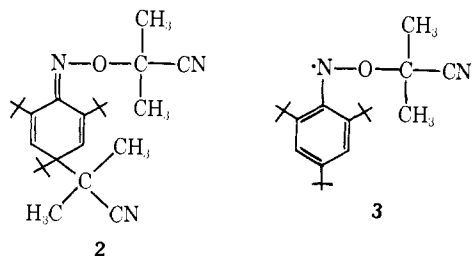
<sup>a</sup> A Varian V4502-15 epr spectrometer was used with 100-kHz field modulation. <sup>b</sup>  $g$  value: 2.0060. <sup>c</sup> *tert*-BuO· → CH<sub>3</sub>· + CH<sub>3</sub>COCH<sub>3</sub>. <sup>d</sup> Abstraction of Br or I by (*n*-Bu)<sub>3</sub>Sn·. <sup>e</sup> Hydrogen abstraction by *tert*-BuO· generated by photolysis or thermolysis. <sup>f</sup> Hydrogen abstraction by photoexcited benzophenone. <sup>g</sup> In solution of a substrate. <sup>h</sup>  $a_{\text{CH}_3}^H = 0.38$  G (6 H).

**Table II.** Hyperfine Splitting Constants (Gauss) for Anilino Radical in Benzene Solution<sup>a</sup>

Spin adduct	$a^N$	$a^H$
RNOC(CN)(CH <sub>3</sub> ) <sub>2</sub> <sup>b</sup>	10.01	1.98 (2 H)
RNOCH(CH <sub>3</sub> ) <sub>2</sub> <sup>c</sup>	11.01	1.82 (3 H)
RNOC(=O)C <sub>6</sub> H <sub>5</sub> <sup>d</sup>	10.53	2.07 (2 H)
RNO- <i>c</i> -C <sub>6</sub> H <sub>11</sub> <sup>d-f</sup>	10.95	1.79 (3 H)

<sup>a</sup>  $g$  value: 2.0036–2.0040. <sup>b</sup> Thermolysis or photolysis of AIBN. <sup>c</sup> Bromine abstraction by (*n*-Bu)<sub>3</sub>Sn·. <sup>d</sup> Hydrogen abstraction by *tert*-BuO· generated by photolysis. <sup>e</sup> In solution of a substrate. <sup>f</sup> Only anilino radical.

oxide<sup>8</sup> to produce the stable anilino radical, the esr spectrum of which showed the following  $g$  value and coupling constants:  $g = 2.00324$ ,  $a^N = 6.80$  G (1 N),  $a_{\text{NH}}^H = 11.97$  G (1 H),  $a_m^H = 1.90$  G (2 H),  $a_{i\text{-Bu}}^H = 0.28$  G (27 H). From these results, together with the general esr character of anilino radicals,<sup>9</sup> and the additional fact that Hosogai, Inamoto, and Okazaki<sup>10</sup> isolated the dienone oxime ether **2** on heating a mixture of AIBN and **1**, we conclude that the radical described above is the *N*-(1-cyano-1-methylethoxy)-2,4,6-*tert*-butylanilino radical (**3**). The *tert*-butyl radical also



attacks the oxygen of **1** to produce an anilino radical rather than a nitroxide.

Secondary alkyl radicals attack both the oxygen and nitrogen atoms of **1**, and spectra of a mixture of a ni-

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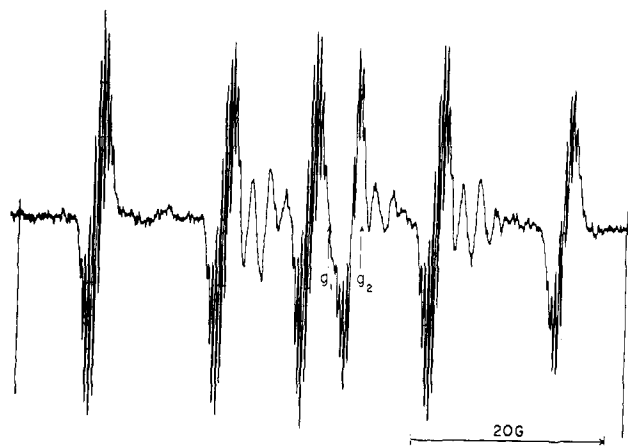
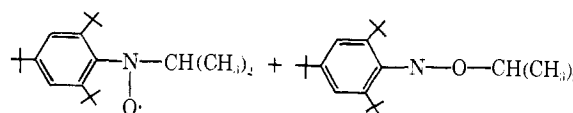
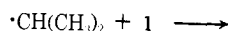


Figure 1. Esr spectrum of a mixture of 2,4,6-*tert*-butylphenyl isopropyl nitroxide and *N*-isopropoxy-2,4,6-*tert*-butylanilino radical in benzene solution at 2.5 hr after spin trapping. Arrows in spectrum indicate center of each:  $g_1 = 2.00602$ ,  $g_2 = 2.00402$ .

troxide and an anilino radical are observed. The spectrum of the spin adducts of the isopropyl radical is shown in Figure 1. The tendency to produce either a nitroxide or an anilino radical may depend on the steric hindrance of **1** for the attacking radicals. It is possible



to distinguish between attacking secondary and tertiary alkyl radicals from the spectra of the anilino radicals produced by spin trapping as shown in Table II.

The main advantages of using **1**, which is a novel "bi-functional" trap, are that information concerning the structure of the radical trapped is more easily obtained from the spectrum of the spin adduct. Moreover, being stable to light both in solution and in the solid state, **1** is useful for application to photoradical reactions. Another merit of **1** is that it is essentially a monomer and does not dimerize.<sup>6</sup>

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### Solvated Proton Mass Spectra of a Tripeptide Derivative

Sir:

Mass spectrometry has had significant but limited success for determination of peptide amino acid sequences.<sup>1-3</sup> It is a rapid sensitive technique but it

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