

Aminoxyl Radicals Formed in the Reaction of *N*-Benzyl-*tert*-butylamine with Tetranitromethane and Pyridine. A New Route to Nitron Spin Adducts

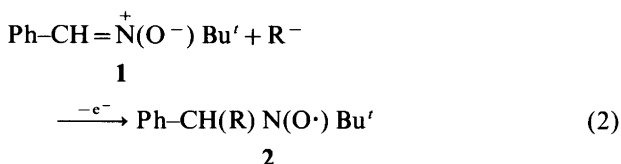
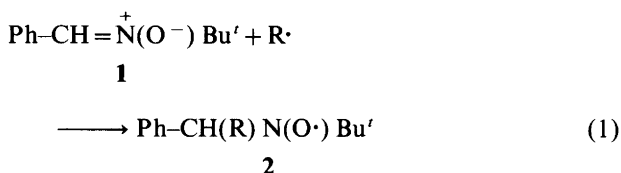
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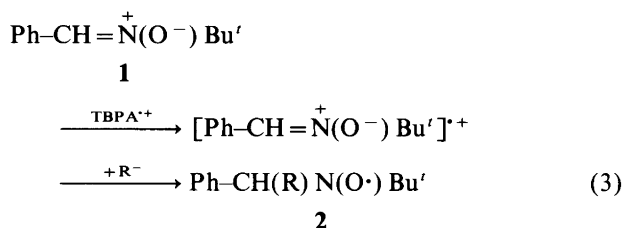
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The photochemical reaction between tetranitromethane (TNM) and *N*-benzyl-*tert*-butylamine dissolved in ethanol, acetone, dichloromethane, toluene or 2,6-dimethylpyridine gives rise to the aminoxyl radical Ph-CH[C(NO₂)₃]N(O·)Bu' by substitution of one of the methylene hydrogens of the parent substance with a C(NO₂)₃ group. When pyridine is also present in the reaction mixture, the radical Ph-CH(Py)N(O·)Bu' is produced. It is suggested that the reaction mechanism involves the formation of an unsaturated secondary amine, derived from *N*-benzyl-*tert*-butylamine, and an addition of trinitromethanide ion, or pyridine to the corresponding radical cation, followed by oxidation to the observed aminoxyl radical.

Spin adducts of the type Ph-CH(R)N(O·)Bu' (**2**) are formed either by addition to the spin trap α -phenyl-*N*-*tert*-butylnitron (PBN **1**) of a radical R·, or a nucleophile R⁻ followed by one-electron oxidation.^{1,2}



The reaction of eqn. (2) has recently been studied in more detail and extended in general terms by Ebersson.² In these experiments the spin trap PBN (**1**) was oxidized to the corresponding radical cation to which the nucleophile, neutral or ionic, was added in a subsequent reaction step.



TBPA^{·+} = tris (4-bromophenyl)aminium ion.

By use of this reaction—'inverted spin trapping'—spin adducts were formed from a number of nucleophiles that are difficult to oxidize such as F⁻, CN⁻, pyridine(s), succinimide(s), triethyl phosphite, or RCOO⁻.²

It has now been found that the technique of inverted spin trapping can be further extended for the formation of spin adducts by the use of *N*-benzyl-*tert*-butylamine, Ph-CH₂N(H)Bu' (**4**). This note describes the results obtained with tetranitromethane (TNM) and a number of pyridines.

Results and discussion

The following radical species were observed.

Type I. When the parent substance Ph-CH₂N(H)Bu' (**4**) was dissolved in ethanol, acetone, dichloromethane, toluene, or 2,6-dimethylpyridine together with TNM, a high yield of radicals was formed, subsequent to irradiation of the samples with UV light. The EPR spectra exhibited a 3 × 2 line system that indicated an interaction of the unpaired electron with one ¹⁴N nucleus and one hydrogen nucleus. Fig. 1 shows the spectrum obtained in 2,6-dimethylpyridine in the dark after UV irradiation for a few min: *a*_N = 1.40 mT, *a*_H = 0.44 mT, *g* = 2.0057.

Type II. With Ph-CH₂N(H)Bu' dissolved in a mixture of pyridine and dimethyl sulfoxide (1 : 1) together with TNM, a radical species was formed, subsequent to UV irradiation, that exhibited a 3 × 6 line system with all lines of equal intensity. The spectrum (Fig. 2) indicated an interaction with two ¹⁴N nuclei and one hydrogen nucleus: *a*_{N1} = 1.30 mT, *a*_{N2} = 0.312 mT and

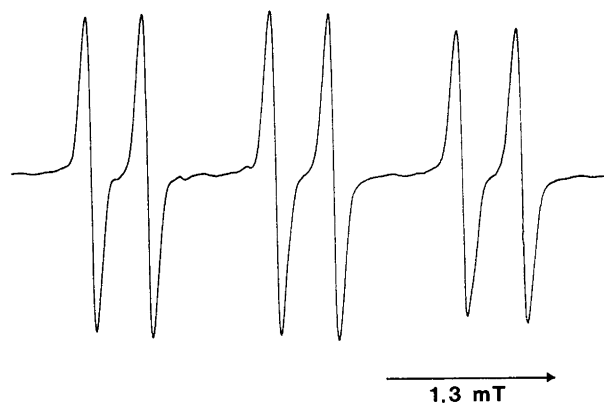


Fig. 1. EPR spectrum of the radicals present in the dark after a few min of UV irradiation of a mixture of *N*-benzyl-*tert*-butylamine (50 μ l), 2,6-dimethylpyridine (300 μ l) and tetranitromethane (50 μ l): $\text{Ph-CH}[\text{C}(\text{NO}_2)_3] \text{N}(\text{O}\cdot) \text{Bu}'$.

$a_{\text{H}} = 0.234$ mT, $g = 2.0057$. A similar spectrum was also obtained with 3,4-dimethylpyridine, or 3,5-dimethylpyridine.

The EPR spectra of the species of Type I (Fig. 1) and Type II (Fig. 2) indicated that the secondary amino group had been oxidized to an aminoxyl group, and that one of the methylene hydrogen atoms of $\text{Ph-CH}_2\text{N}(\text{H})\text{Bu}'$ had been replaced by a group X. Consequently, the doublet splitting ($a_{\text{H}} = 0.44$ mT in I, and $a_{\text{H}} = 0.234$ mT in II) originated from the remaining methylene hydrogen. Thus, the structure of the radicals was $\text{Ph-CH}(\text{X})\text{N}(\text{O}\cdot)\text{Bu}'$.

It should be pointed out that oxidation of the parent substance (4) with reagents such as H_2O_2 , 3-chloroperbenzoic acid or NO_2 together with UV irradiation gave rise to an aminoxyl radical of the structure $\text{Ph-CH}_2\text{N}(\text{O}\cdot)\text{Bu}'$: $a_{\text{N}} = 1.56$ mT, $a_{\text{H}} = 0.86$ mT (1:2:1) in dimethyl sulfoxide or H_2O .

It is suggested that the substituent group X in the radicals of Type I (Fig. 1) consists of a trinitromethyl group derived from TNM. Evidently, no splittings could

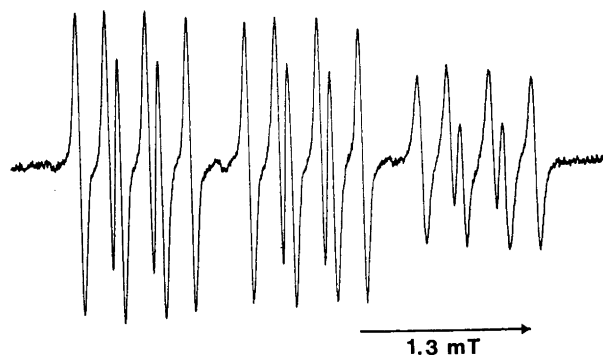


Fig. 2. Spectrum of the radical present in the dark after UV irradiation of a mixture of *N*-benzyl-*tert*-butylamine (50 μ l), ^{14}N pyridine (200 μ l), dimethyl sulfoxide (200 μ l) and tetranitromethane (50 μ l): $\text{Ph-CH}(\text{}^{14}\text{Py})\text{N}(\text{O}\cdot)\text{Bu}'$.

be resolved from the nitro groups. Thus, the structure of these radicals is $\text{Ph-CH-}[\text{C}(\text{NO}_2)_3] \text{N}(\text{O}\cdot) \text{Bu}'$. The same aminoxyl radical has been found in the photochemical reaction between TNM and the spin trap PBN, very probably formed by trapping of the trinitromethyl radical,³ or addition of the trinitromethanide ion in an inverted spin trapping reaction.²

The substituent group X of the radical species Type II (Fig. 2) contains a nitrogen atom that gives rise to the triplet splitting with $a_{\text{N}_2} = 0.312$ mT. The origin of this nitrogen atom, i.e., from TNM or pyridine, was settled by performing the reaction with ^{15}N pyridine. The EPR spectrum of the reaction mixture displayed a 3×4 line system with all lines of equal intensity. The nitrogen triplet of Fig. 2 was replaced by a doublet derived from the ^{15}N atom of pyridine: $a_{\text{N}_2}(^{15}) = 0.437$ mT. This value is consistent with the product of the ^{14}N splitting a_{N_2} and the ratio of the isotropic hyperfine coupling constants of ^{15}N and ^{14}N : $a_{\text{N}_2}(^{15}) = 0.312 \times 1.40 = 0.437$ mT. The coupling constants a_{N_1} and a_{H} were identical with those observed with ^{14}N pyridine. Thus, the structure of the radicals of Type II is $\text{Ph-CH}(\text{}^{15}\text{Py})\text{N}(\text{O}\cdot)\text{Bu}'$ where $\text{Py} = \text{pyridine}$. Fig. 3 shows the component $M_1 = 0$ of the main ^{14}N splittings corresponding to $a_{\text{N}_1} = 1.34$ mT of the EPR spectrum obtained with ^{15}N pyridine.

The very different results obtained with pyridine and the pyridine derivatives with methyl groups away from the nitrogen atom of the pyridine ring, i.e., in position 3, 4 or 5, on one hand (Fig. 2), and 2,6-dimethylpyridine on the other (Fig. 1), are very probably connected with steric hindrance to addition of the latter substances caused by the methyl groups. It is evident that the addition of pyridine leading to the formation of radicals of Type II (Figs. 2 and 3) predominates over the reaction that gives

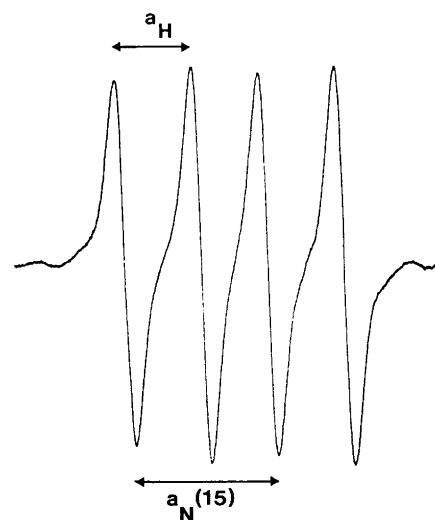
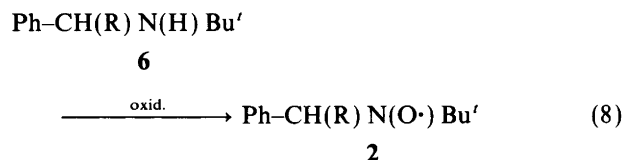
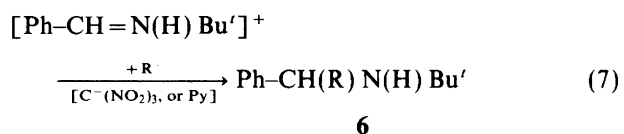
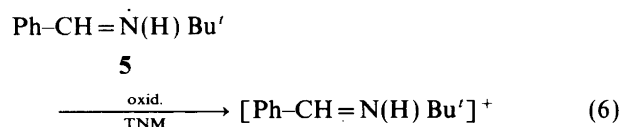
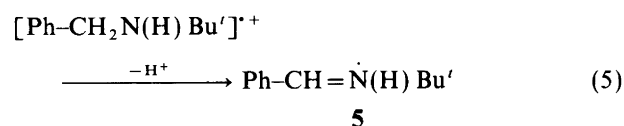
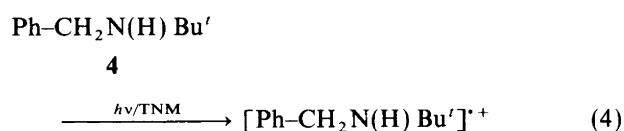


Fig. 3. The spectral component $M_1 = 0$ of the main ^{14}N splittings obtained after UV irradiation of a mixture of *N*-benzyl-*tert*-butylamine (50 μ l), ^{15}N pyridine (200 μ l), dimethyl sulfoxide (200 μ l) and tetranitromethane (50 μ l): $\text{Ph-CH}(\text{}^{15}\text{Py})\text{N}(\text{O}\cdot)\text{Bu}'$.

rise to the Type I radicals. The Py^+ adduct has also been obtained by inverted spin trapping.²

Prolonged UV irradiation of the reaction mixtures of both Type I and II gave rise to a radical species that exhibited a 3×1 line system: $a_N = 0.804$ mT, $g = 2.0065$. This species is very probably formed from the adducts, and is considered to have the structure $\text{Ph-C}(=\text{O})\text{N}(\text{O}\cdot)\text{Bu}'$. This radical species has also been observed in the reactions of inverted spin trapping with PBN.²

A tentative sequence of reactions leading to the observed radicals is given in eqns. (4)–(8).



The parent substance **4** is oxidized by $h\nu/\text{TNM}$ to the corresponding radical cation⁴ that is stabilized by loss of a proton [eqns. (4) and (5)] with the formation of the radical **5**. Subsequent oxidation of **5** produces a cation [eqn. (6)], to which the nucleophile R^- is added [eqn. (7)] to give the substituted secondary amine **6**. Finally, **6** is oxidized (NO_2 from TNM) to the observed aminoxyl radical **2** [eqn. (8)].

Experimental

The EPR spectra were recorded using a Varian E-9 spectrometer as described elsewhere.⁵ The samples were irradiated with UV light from a mercury lamp (Osram HBO-200) *in situ* in the EPR cavity when contained in a flat cell. The chemicals used were obtained from Aldrich or Fluka AG. [^{15}N]Pyridine was from ICON Services Inc., New Jersey.

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