ON THE RADICALS PRODUCED BY THE PHOTOLYSIS

OF AZOBENZENE IN CUMENE[1]

V. Malatesta[2] and K.U. Ingold*

Division of Chemistry,

National Research Council of Canada,

Ottawa, Canada

In a recent attempt to distinguish between diazenyl radicals, $R-N=N\cdot$, and hydrazyl radicals, $RR'N\dot{N}R''$, Marnett et al[3] relied heavily on the epr spectrum of an "authentic" hydrazyl, 1, prepared by Wan[4] by the photolysis of azobenzene in cumene.
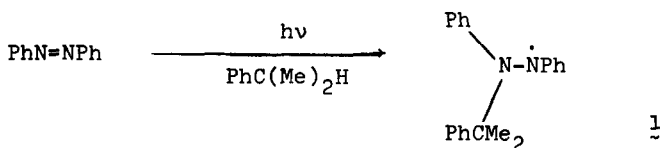
To avoid further confusion, we wish to point out that this "authentic" hydrazyl is, in fact, phenyl cumyl nitroxide, 2.
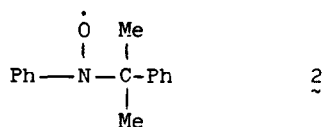

The epr parameters reported by Wan[4] were: $a_{N(1)} = 11.8$ G; $a_{N(2)} = 0.88$ G; a_H(2 ortho + 1 para) = 2.59 G; g = 2.0032±0.0002. For the analagous radical derived by photolysis of 4,4'-dimethoxy-azobenzene-cumene solutions the

interaction with the second nitrogen(!) was not resolved and the spectral parameters were[4]: a_N = 11.8 G; a_H(2 $\underline{o}$) = 2.2 G; a_H (2 $\underline{meta}$) = 1.1 G; g = 2.0032±0.0002.

The parameters for both these radicals are quite inconsistent with the spectra of all truly authentic hydrazyl radicals (including triaryl[5], diarylalkyl[5], diarylacyl[5], trialkyl[6], and 1,1 dialkyl[7,8]) which invariably show strong coupling of the unpaired electron with the second nitrogen. In general, the splittings by the two nitrogens are of comparable magnitude and are generally in the range 6-12G. Except for the $\underline{g}$ value (which is within the range found for hydrazyls) the epr parameters reported by Wan seemed to us representative of a phenyl $\underline{tert}$-alkyl nitroxide[9] and the following experiments prove that Wan's radical is indeed phenyl cumyl nitroxide.

No epr signal is generated upon photolysis of azobenzene in $\underline{pure}$ (peroxide free) cumene. However, upon the addition of a trace of cumene hydroperoxide a spectrum having very nearly the epr parameters reported by Wan appears. The same spectrum can be obtained by photolysis of azoxybenzene in pure cumene, and of azoxybenzene plus azocumene in benzene though photolysis of azoxybenzene in benzene and of azobenzene plus azocumene in benzene give no signals. The spectra obtained in our experiments are very much stronger and better resolved than Wan's (see Fig. 1) and there can be no doubt that the smallest triplet splitting is due to 2 equivalent hydrogens (intensity ratio 1:2:1) and not to a nitrogen atom (ratio 1:1:1). The radical had a lifetime of weeks at room temperature (when generated in the absence of cumene hydroperoxide) as would be expected of a phenyl $\underline{tert}$-alkyl nitroxide[10]. The epr parameters are: a_N = 11.21, a_H(2 $\underline{o}$ + 1 $\underline{p}$) = 2.46, a_H(2 $\underline{m}$) = 0.88 G, g = 2.0056.

The g value is in the range expected of a nitroxide[9,12,13]. It is almost inconceivable that a second nitrogen would not have been detected if present. We therefore assign structure 2 to this radical and confirmed this assignment by generating an $\underline{identical}$ spectrum by mixing azocumene and nitrosobenzene in benzene (reaction may have been initiated by room light).

$$PhCMe_2 + PhN=O \longrightarrow \underset{\sim}{2}$$
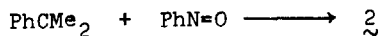
Further confirmation was obtained by repeating the appropriate experiments listed above in ethylbenzene. In all cases where cumene gave $\underset{\sim}{2}$, ethylbenzene gave an epr spectrum (Fig. 2) that we attribute to phenyl 1-phenylethyl nitroxide, $\underset{\sim}{3}$.

$$\begin{array}{c} \overset{\bullet}{O} \ H \\ | \ \ | \\ Ph-N-C-Ph \\ | \\ CH_3 \end{array} \underset{\sim}{3}$$
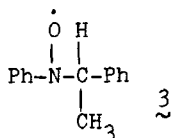
$a_N = 10.65$, a_H(methine H) = 5.13, $a_H(2 \underline{o} + 1 \underline{p})$ = 2.76, $a_H(2\underline{m})$ = 1.30, $a_H(CH_3)$ = 0.44 G, g = 2.0055.

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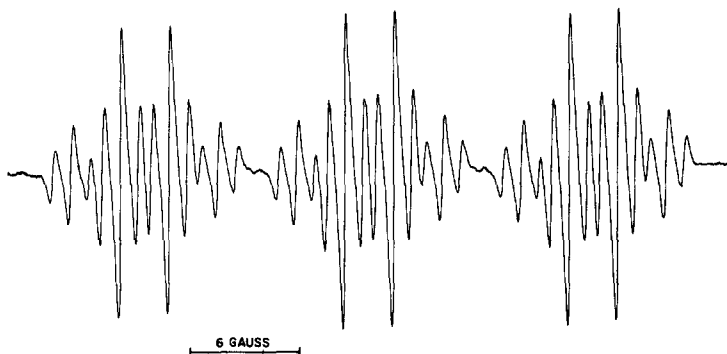
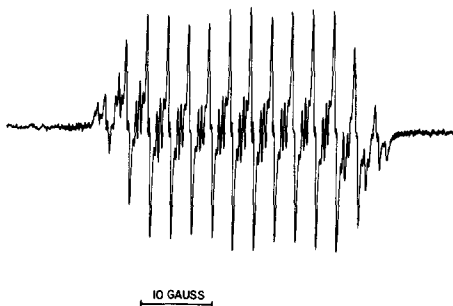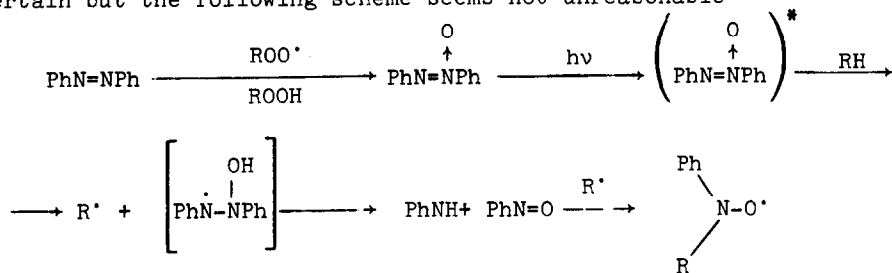Fig. 1. Epr spectrum of phenyl cumyl nitroxide, $\underset{\sim}{2}$

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Fig. 2. Epr spectrum of phenyl 1-phenylethyl nitroxide, $\underset{\sim}{3}$

The detailed mechanism of formation of phenyl alkyl nitroxides is uncertain but the following scheme seems not unreasonable

$$PhN=NPh \xrightarrow[\text{ROOH}]{\text{ROO}^\cdot} PhN\overset{O}{\underset{\uparrow}{=}}NPh \xrightarrow{h\nu} \left(PhN\overset{O}{\underset{\uparrow}{=}}NPh\right)^* \xrightarrow{RH}$$

$$\longrightarrow R^\cdot + \left[PhN\overset{OH}{\underset{\cdot}{-}}NPh\right] \dashrightarrow PhNH + PhN=O \xrightarrow{R^\cdot} \overset{Ph}{\underset{R}{\diagdown}}N-O^\cdot$$

The photolysis of azoxybenzene in solvents containing readily abstractable hydrogen atoms may have utility as a simple route to phenyl nitroxides.

References and Notes

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(2) NRCC Postdoctoral Fellow 1972-73.

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(9) E.g., $PhN(\dot{O})Bu^t$ in ethylene glycol[10], $a_N = 13.4$, $a_H(2\ \underline{o} + 1\ \underline{p}) = 1.9$, $a_H(2\ \underline{m}) = 0.8$ G; $4\text{-MeOC}_6H_4N(\dot{O})Bu^t$ in the same solvent[10], $a_N = 13.9$, $a_H(2\ \underline{o}) = 1.86$, $a_H(2\ \underline{m}) = 0.93$ G; and $PhN(\dot{O})CMe_2Ph$ in cumene[11], $a_N = 11.8$, $a_H(2\ \underline{o} + 1\ \underline{p}) = 2.5$, $a_H(2\ \underline{m}) = 0.91$ G).

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