

Indoline Nitroxides

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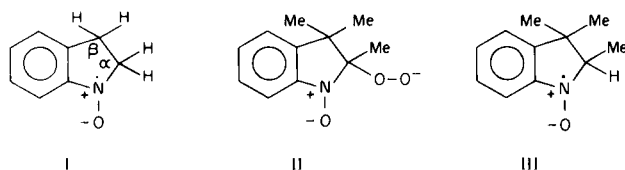
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Sir:

The use was recently proposed (1) of hydrogen peroxide in neutral or alkaline aqueous ethanol 50:50 solution as an agent for the oxidation of the dialkylamines to the corresponding nitroxides in order to lengthen the life of the radicals and to obtain better resolved esr signals when compared with the same nitroxides obtained by peracid oxidation of the amines. In that way dimethyl, diethyl, di-*n*-propyl and diisopropyl nitroxides were obtained. When such a method is used in the oxidation of simple indoline (2), a well-resolved esr signal corresponding to nitroxide I appears within three hours. This signal is stable for a few days and shows the interaction of the



unpaired electron with the nitrogen nucleus and with the eight protons (spectrum A in Figure). Good agreement between the experimental and the theoretical spectrum (spectrum B in the figure) was obtained using the hyperfine splitting constant reported in Table I.

Rosantev (3) reports the hyperfine splitting constant of the nitroxide corresponding to 2,2-dimethylindoline for which an $a_{\text{H}}^{\text{o,p}} = a_{\text{H}}^{\beta} = 3.18$ gauss and an $a_{\text{N}} = 11.26$ gauss were found. Rassat found an $a_{\text{N}} = 14.9$ gauss and an $a_{\text{H}} = 19.6$ gauss for the four α -protons in the

nitroxide derived from tetrahydropyrrole (4). In order to obtain an unambiguous assignment of the various hyperfine splitting constants, an attempt was made to oxidize 2,3,3-trimethylindoline. The oxidation of this compound succeeded only when a few drops of aqueous, potassium hydroxide were added to the oxidizing mixture, but the signal (see spectrum C in Figure) revealed no α -hydrogen. Perhaps a peroxidation on a carbanium intermediate, followed by *N*-oxidation into nitroxide II may occur here.

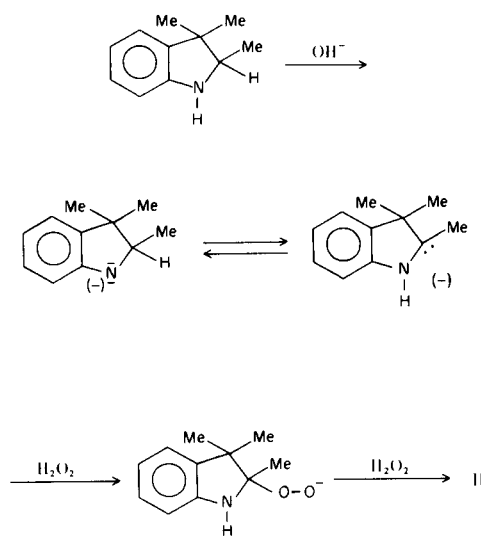


TABLE I

Hyperfine Splitting Constant (in Gauss)

Compound	a_{N}	a_{H}^{α}	a_{H}^{β}	$a_{\text{H}}^{\text{o,p}}$	a_{H}^{m}	oxidant/solvent
I	11.75	18.60	3.74	3.74	1.00	$\text{H}_2\text{O}_2/\text{H}_2\text{O-EtOH}$
II	11.80	-----	-----	3.60	1.00	$\text{H}_2\text{O}_2\text{-KOH}/\text{H}_2\text{O-EtOH}$
III	10.80	18.00	-----	3.25	-----	$\text{O}_2\text{N-C}_6\text{H}_4\text{-COOOH}/\text{CH}_2\text{Cl}_2$

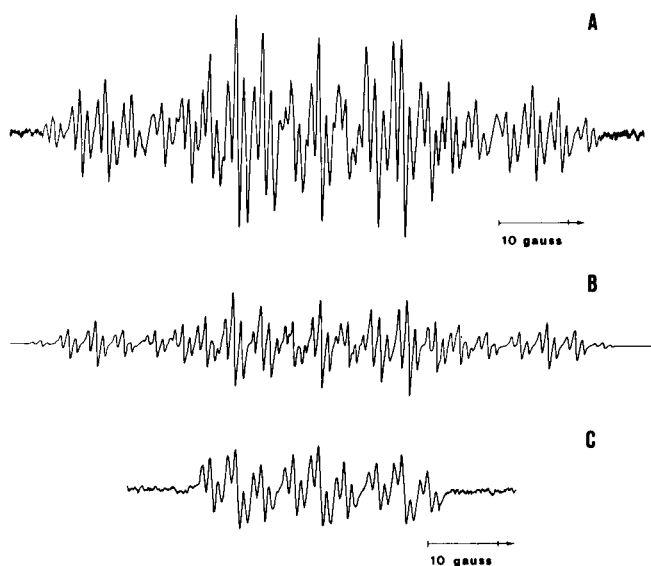


Figure - Top: Experimental esr spectrum attributed to radical I. Center: Calculated spectrum with Lorentzian linewidth of 0.7 gauss and hyperfine splitting constant given in the text. Bottom: Experimental esr spectrum of radical with assumed structure II.

We obtained the desired nitroxide III through the oxidation of the 2,3,3-trimethylindolenine with *p*-nitroperbenzoic acid in dichloromethane solution: although not well resolved, the spectrum clearly shows an 18 gauss splitting that must be attributed to the α -hydrogen.

The assignment of the hyperfine splitting constant for the *o*, *p* and *m*-hydrogens on the benzo-ring was not a particular problem, since we found values that are usual for such positions (5). The large $a_{\text{H}}^{\alpha} = 18.60$ and 18.00

gauss can be theoretically supported by using the formula

$$a_{\text{H}}^{\alpha} = Q(\theta) \rho_{\text{N}}^{\pi} = B \cos^2 \theta \rho_{\text{N}}^{\pi}$$

(6) which gives an $a_{\text{H}}^{\alpha} = 14.30 \pm 2.10$ gauss, if $B = 41 \pm 6$ gauss and $\rho_{\text{N}} = a_{\text{N}}/Q_{\text{N}}$ with $Q_{\text{N}} = 25.3$ are used as is usual. It must be noticed that no coupling with β -hydrogens was evidenced in *N*-oxotetrahydropyrrole (4). In fact, β -methylene hydrogens in I behave as *ortho*-benzylic

hydrogens with respect to the $>\text{N}^+ - \bar{\text{O}}$ group, going through the benzo-ring and a conjugative coupling may occur: for a good comparison of the relative values it is known that $a_{\text{H}}^{\text{O}} = a_{\text{H}}^{\text{p-CH}_3} = 1.86$ gauss in the *p*-tolyl-*t*-butyl nitroxide (7).

REFERENCES

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