

ALKYL ARYL NITROXIDES FROM IMINES AND NITROSOBENZENES

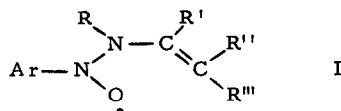
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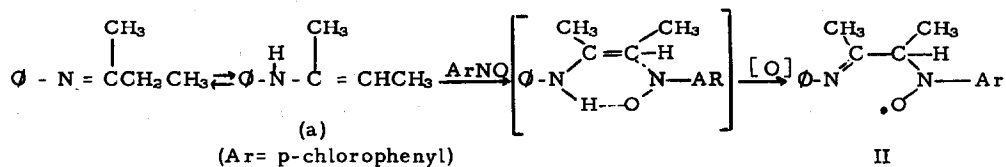
The reaction between an olefin, containing an alpha hydrogen, and a nitrosobenzene gives a stable nitroxide free radical¹. I have found that imines, which contain alpha hydrogens, also react with nitrosobenzenes to give nitroxide radicals readily detected by ESR spectroscopy. Their structure and hyperfine splitting constants have been established by matching a computer synthesized spectrum with the observed spectrum. The radicals are prepared by mixing degassed benzene solutions of the reagents. Excess imine is used with the concentration of nitrosobenzene adjusted to give the best spectral resolution using a Varian E-3 spectrometer. These radicals are not as stable as those obtained from olefins and nitrosobenzenes. And a slow spectral intensity decrease is noted with time. Neither type of radical can be isolated.

One would expect nitrosobenzenes to react with imines in the same way as they do with olefins, presumably by a six centered mechanism¹. Radical I could result from the oxidation of the intermediate hydroxylamine.



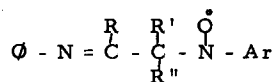
However, the ESR spectra of these radicals do not have the fivefold symmetry expected for radicals containing two conjugated nitrogen atoms. The spectra of these radicals have threefold symmetry which indicates that only one nitrogen atom is involved in the delocalization of the electron². Thus Structure I does not satisfactorily explain the ESR spectra of the radicals. Figure 1 gives the ESR spectrum of the radical from N-sec-butylideneaniline and p-chloronitrosobenzene. A satisfactory interpretation of this spectrum is obtained if one views the reaction

as proceeding via the enamine tautomer (a) to give radical II



Reactions of enamine tautomers of imines are well documented³. The structural assignment of II is supported by the similarity between its hyperfine splitting constants (in gauss) (a_{N} 10.3; $a_{\text{H}(\alpha)}$ 5.5; $a_{\text{H}(\text{o})}$ 2.75; $a_{\text{H}(\text{m})}$ 0.8) and those of an analogous radical; phenyl ethylnitroxide (a_{N} 11.1; $a_{\text{H}(\alpha)}$ 8.3; $a_{\text{H}(\text{o}, \text{p})}$ 2.9; $a_{\text{H}(\text{m})}$ 1.0)². The lower α -hydrogen splitting constant of radical II compared to phenyl ethylnitroxide is due to the electron interactions with an increased number of β -hydrogens. And it agrees with the α -hydrogen splitting constants of di-n-butylnitroxide ($a_{\text{H}(\alpha)}$ 10.5) and di-sec-butylnitroxide ($a_{\text{H}(\alpha)}$ 4.1)⁴.

A number of N-alkylideneanilines gave nitroxides with nitrosobenzenes which are interpretable on the basis of structure II and can be more generally written:



III

A computer program, which allows corrections to be made for line widths, was used to obtain the hyperfine splitting constants for these radicals. The program gave synthetic plots which very closely matched the actual ESR spectra (Figure 1). This computer program was written by Dr. J. C. Westfahl of our laboratories.

N-sec-Butylideneaniline which can exist in two tautomeric forms (a) and (b) reacts with nitrosobenzenes



as the enamine (a). The spectrum of the radical from N-sec-butylideneaniline and p-chloro-nitrosobenzene (Figure 1) is interpreted as follows: a_{N} 10.30 (one nitrogen); $a_{\text{H}(\alpha)}$ 5.50 (one proton); $a_{\text{H}(\text{o})}$ 2.80 (two protons); $a_{\text{H}(\text{m})}$ 0.8 (two protons).

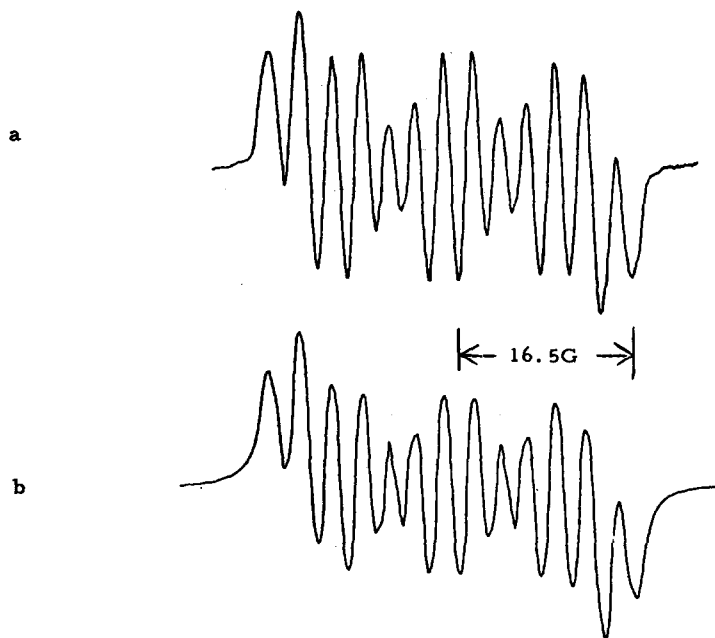


Figure 1: (a) Observed spectrum for radical from *N*-sec-butyldeneaniline and *p*-chloronitrosobenzene.
 (b) Computer synthesized spectrum for the radical (a); a_N 10.30; $a_{H(\alpha)}$ 5.50; $a_{H(o)}$ 2.75; $a_{H(m)}$ 0.80.

The spectrum of the radical from *N*-cyclohexylideneaniline and *p*-chloronitrosobenzene has the following hyperfine splitting constants: a_N 10.20 (one nitrogen); $a_{H(\alpha)}$ 6.90 (one proton); $a_{H(o)}$ 2.80 (two protons); $a_{H(m)}$ 0.90 (two protons).

The spectrum of the radical from *N*- β , β -diphenylethylideneaniline and nitrosobenzene gave the following values: a_N 11.25 (one nitrogen); $a_{H(o, p)}$ 2.33 (three protons); $a_{H(m)}$ 0.90 (two protons).

As further proof for the structure of the above radicals, catalytic hydrogenation of the reaction product of *N*-cyclohexylideneaniline and nitrosobenzene gave a 20% yield of *N*,*N*'-diphenyl-1,2-cyclohexanediamine, b. p. 184-90°C/0.5 mm, n_D^{23} 1.6152, nmr (CCl₄): τ 2.70-3.21 (multiplet, m-arom., 3.9H), 3.21-3.75 (multiplet, o, p-arom., 5.3H), 6.32-6.65 (singlet NH, 2.2H), 6.75-7.10 (multiplet, equatorial C-1-H, 1.1H), 7.5-9.25 (multiplet, axial C-2-H and CH₂, 9.5H). Anal. Calcd for CH₁₈H₂₂N₂: C 81.15; H 8.32; N 10.51. Found: C 80.03; H 8.15; N 10.50.

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