THE NORTROPINE IMINOXY RADICAL IN SOLUTION

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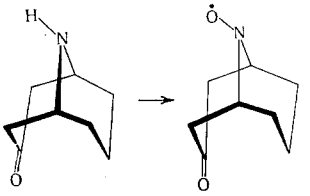
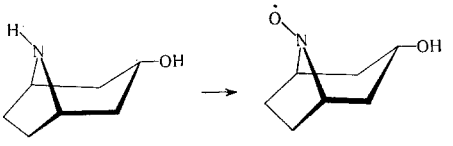
It is known that the stability of iminoxy radicals depends on steric [1-3] and energetic factors [4-6]. As a rule the possibility of valence tautomerism in the iminoxy radical with transfer of the free-radical center leads to a marked increase in its chemical activity. Usually in these cases if the paramagnetic solution of the radical is concentrated there is a disproportionation into diamagnetic products [6]. If this process is forbidden, for example by Bredt's rule, the radical can sometimes be isolated from the solution as a pure substance. Thus, in the oxidation of norpseudopelletierine one can obtain the corresponding iminoxy radical [7] in pure form, as seen by the hyperfine structure in its EPR spectrum, a classical triplet



Unlike norpseudopelletierine, the catalytic oxidation of nortropine by aqueous hydrogen peroxide goes through an unstable radical



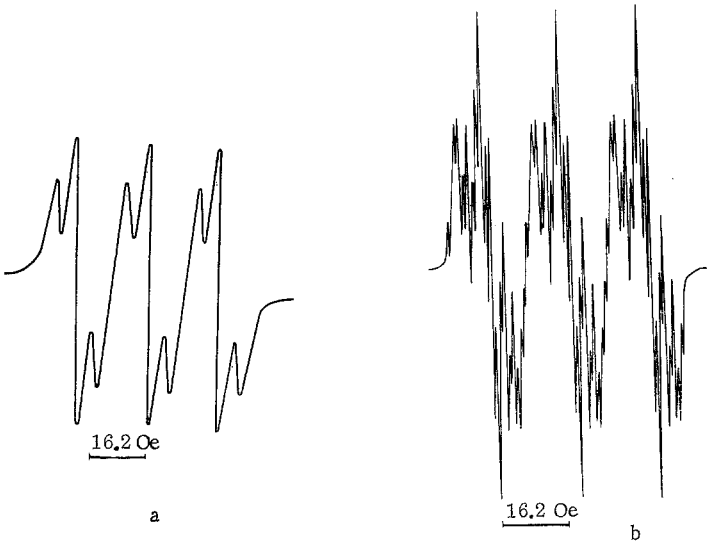


Fig. 1. EPR spectrum of a dilute solution of the nortropinoxy radical in benzene (a) and chloroform (b).

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A very dilute solution of the nortropinoxy radical gives an EPR spectrum which is unusual for iminoxy radicals [8], showing three groups of lines due to interaction of the unpaired electron with the magnetic moments of both N^{14} and the protons of the heterocyclic ring. In this respect it resembles the EPR spectra of nitroxides in which the unpaired electron is delocalized into an aromatic system [9]. Each component of the nitrogen triplet in the spectrum of the nortropinoxy radical is split into at least 17 lines in its hyperfine structure (Fig. 1). The additional splitting of the energy levels of the unpaired electron by the protons of the heterocyclic ring is apparently characteristic for all iminoxy radicals in the tropane series. The size of the isotropic hyperfine splitting constants for N^{14} seems unusual for iminoxy radicals, that is, 19.6 Oe instead of the 15.6 Oe typical for the majority of iminoxides. Such a complex hyperfine structure in the EPR spectrum, and the unusually large isotropic hyperfine splitting constant, suggests a specific electronic structure for the condensed pyrrolidine – piperidine system of alkaloids in the tropane series.

In this work we used nortropine prepared by oxidation of an aqueous, basic solution of synthetic tropine by potassium ferricyanide.

EXPERIMENTAL

Nortropine. To a solution of 3 g of synthetic tropine in 40 ml H_2O and 7.5 g NaOH was added (over 1.5 h at 15°) a solution of 42 g of potassium ferricyanide in 75 ml of H_2O. After 6 days of standing at room temperature, the reaction mixture was decanted away from the precipitated salts and extracted with ether. The dry extract was concentrated and cooled to yield crystals which were then recrystallized from toluene. The yield of tropine (mp 160°) was 1.5 g (54.4%); according to [10], mp 159-161°.

Oxidation of Nortropine to the Radical. To a solution of 0.5 g of nortropine in 25 ml H_2O was added 0.1 g of Trilon B, 0.1 g of sodium tungstate, and 2 ml of 30% H_2O_2. The reaction mixture darkened and got warm at first. After 10 h, a $CHCl_3$ or benzene extract of the mixture showed an intense EPR signal.

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CONCLUSIONS

1. The iminoxy radical of nortropine was prepared and studied by EPR.

2. The hyperfine structure in the EPR spectrum of the nortropinoxy radical differs markedly from that of iminoxy radicals previously reported.

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