

Photolysis of Azacyclohexadienyl Radical and Pyridinyl Radical in an Acidic Glassy Matrix

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Summary Azacyclohexadienyl radicals (I) trapped in an acidic glassy matrix may be photolysed by u.v. light, giving rise to the allyl radical (III); it is shown that pyridinyl radicals (II) formed in an intermediate step are photoisomerised into radical (III).

γ -IRRADIATION of 0.1 M pyridine solutions in a HCl-H₂O glassy matrix at 77 K¹ gives rise to the azacyclohexadienyl radical (I) and Cl₂⁻. After warming the sample to ca. 140 K to remove Cl₂⁻, the azacyclohexadienyl radicals were photolysed (250–350 nm) with a 500 W high pressure mercury arc at 77 K to give, within a few minutes, radical (III) (Figure 1).

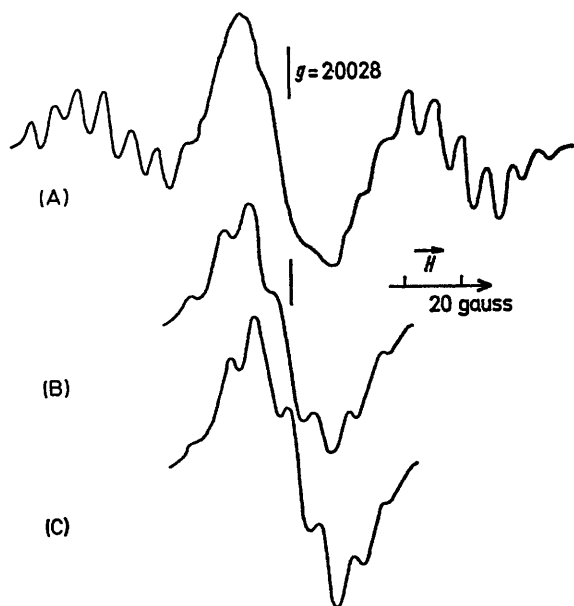


FIGURE 1. E.s.r. spectra of (A) radical (I), (B) radical (III) after photolysis of (I), and (C) radical (III) (simulated).

During this reaction the e.s.r. signal of Cl₂⁻ reappears, suggesting the release of electrons from azacyclohexadienyl radicals, the overall concentration of detected paramagnetic species remaining unchanged.

The structure of radical (III) (Figure 2) was deduced by comparison of the e.s.r. spectra from selectively deuteriated pyridines irradiated in HCl and DCl matrices. The assumed hyperfine coupling constants were checked by INDO calculations and computer simulation of the spectra.²

The configuration of radical (III) given in Figure 2 corresponds to the minimum energy given by INDO calculations and provides the best agreement with the experimental spectrum after a slight readjustment of the

hyperfine coupling constants, taking account of the anisotropy of the coupling of allyl protons.

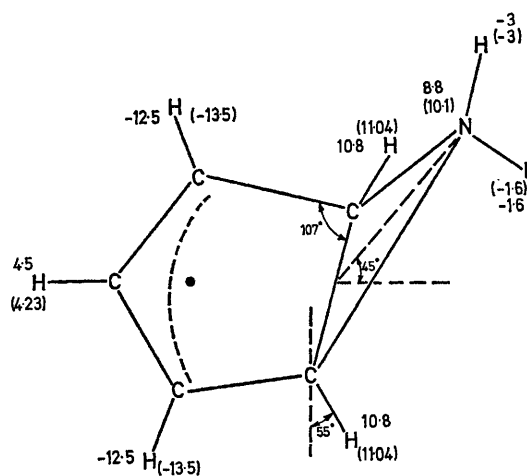


FIGURE 2. Molecular structure of radical (III). In parentheses: coupling constants given by INDO. The other values were used for calculation of the spectrum.

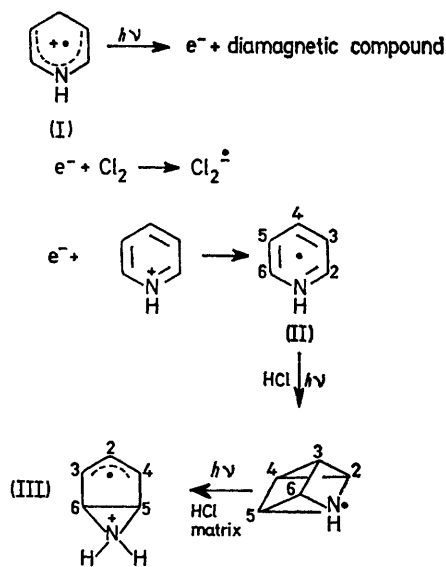
The experimental nitrogen coupling constant was estimated from the second moment of the poorly resolved spectrum given by perdeuteriated pyridine in a DCl-D₂O matrix.

When a 4 M solution of pyridine in a HCl-H₂O matrix was irradiated at 77 K, the pyridinyl radical (II) was selectively formed in addition to Cl₂⁻ radicals. The photolysis of this radical under similar conditions as those for azacyclohexadienyl radicals leads to the same radical (III). It may be therefore assumed that (II) is an intermediate in the formation of (III) by photoionization of (I) according to the Scheme.

It may be pointed out that an important rearrangement of the carbon backbone occurs in the photoisomerisation of radical (II). Such a reaction suggests the intermediate formation of an azaprismane type radical. Azaprismane derivatives were actually found in the photolysis products of some substituted pyridines.³

Figure 3 shows that the spectrum of some deuteriated pyridines calculated assuming this rearrangement fits with the experimental spectrum.

The mechanism assumed in the Scheme is therefore quite different from the electrocyclic reaction proposed by Monge and Schott in the case of the photolysis of a cyclohexadienyl type radical.⁴



SCHEME. Mechanism of photolysis of the azacyclohexadienyl radical (I).

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- ² R. Lefebvre and J. Maruani, *J. Chem. Phys.*, 1965, **49**, 1480.
- ³ K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1965, **87**, 4004; D. M. Lemal and J. P. Lokensgard, *ibid.*, 1966, **88**, 5935; D. M. Lemal and J. V. Staros, *ibid.*, 1969, **91**, 3373; M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *Chem. Comm.*, 1969, 202.
- ⁴ J. L. Monge and M. Schott, *J. Chim. Phys.*, 1973, **70**, 1555.
- ⁵ J. C. Ronfard-Haret, A. Lablache-Combiere, and C. Chachaty, *J. Phys. Chem.*, 1974, **78**, 899.

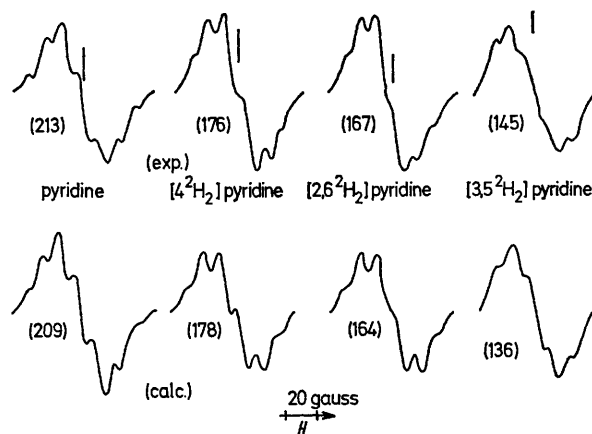


FIGURE 3. Experimental and calculated spectra of some deuteriated pyridines. In parentheses: second moment of the experimental and calculated spectra (G^2).

Similar photorearrangements were also observed when azacyclohexadienyl radicals derived from 2- or 4-polyvinylpyridines⁵ or picolines are photolysed in an HCl matrix. These results will be reported in a full paper.

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