

adducts correlates with carcinogenic activity of the hydrocarbons.

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### Electron Spin Resonance Study of Iminoxy Free Radicals

Sir:

The existence of nitroxides as a class of stable free radicals<sup>1-3</sup> suggests that a related class of radicals derived from oximes should also exist. This note reports the preparation of such species, iminoxy radicals (or alkylidene nitric oxides), as transient intermediates in the oxidation of oximes with ceric ammonium nitrate in methanol. The radicals were detected by e.s.r. using flow techniques suitable for observing transient species.<sup>4</sup> The procedures used have been previously described.<sup>5</sup>

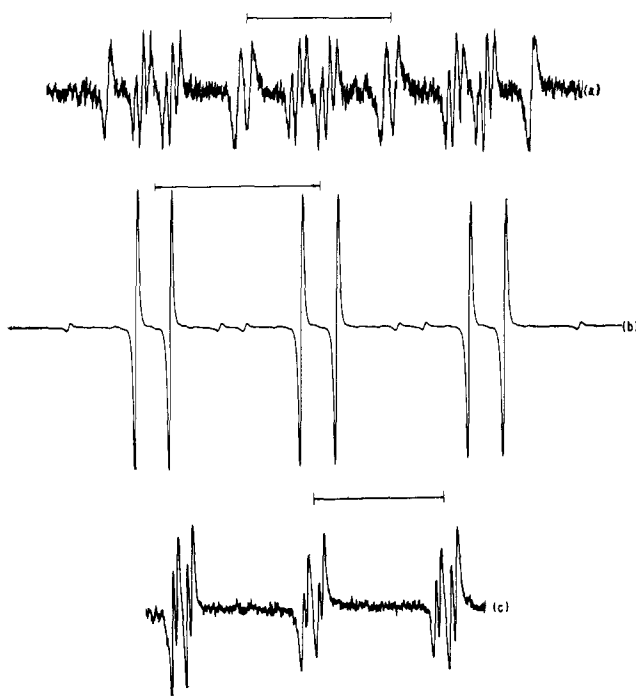


Fig. 1.—First derivative e.s.r. spectra of iminoxy radicals derived from (a) *syn*-benzaldoxime, (b) phenylglyoxaldoxime, and (c) *p*-nitrosophenol. The scale is 29.2 for a, 29.3 for b, and 33.0 gauss for c.

Iminoxy radicals exhibit two interesting features. First, their nitrogen coupling constants are large and characteristic. Values, ranging from 28–33 gauss, are listed in Table I for a variety of radicals and are considerably greater than the nitroxides (10–16),<sup>2</sup>  $\text{NH}_3^+$  (18.1),<sup>6</sup>  $\text{NH}_2$  (10.3),<sup>7</sup> and  $\text{N}_2\text{H}_4^+$  ( $2a_N = 23.0$  gauss).<sup>5</sup> Even though a significant portion of the electron density must reside upon the oxygen atom,

the measured coupling constants are comparable to those estimated for unit electron density on nitrogen in *para*<sup>8,9</sup> and *ortho*<sup>10</sup> azine anions. This suggests that the unpaired spin on nitrogen is not in a pure  $2p_z$  orbital, as it is presumed to be in the azine anions whose nitrogen splittings are explained in terms of  $\pi$ - $\sigma$  interactions,<sup>10</sup> but occupies a hybrid orbital containing some  $s$  character.

TABLE I  
HYPERFINE COUPLING CONSTANTS FOR IMINOXY FREE RADICALS

Radical	$a_N$	$a_H^*{}^a$	$a_{\text{ring H}}$
	33		
	32.5	5.2	
	29.2	26.9	
	31.6	6.2	1.4(2)
	33.0		1.2(1) 3.7(1)
	27.9		1.7(1)
	31.6		
	30.6		

<sup>a</sup> The asterisk denotes hydrogen attached to carbon of imino group.

The second interesting aspect of iminoxy radicals is the detection of *cis* and *trans* isomers. One clear example of this occurs with the iminoxy derived from benzaldoxime. Figure 1a shows the e.s.r. spectrum obtained from the oxidation of *syn*-benzaldoxime (hydrogen attached to imino carbon and oxime hydroxyl *cis*) which consists of the pattern 1,3-3,2,3-3,2,3-3,1 where the intensities of the paired triplet lines are in the ratio 1:2:1. The observed spectrum is interpreted as arising from approximately equal concentrations of *syn* and *anti* isomers. The 1,2,2,1

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grouping of lines is assigned to the *anti* isomer and the 3-3,3-3,3-3 grouping to the *syn* isomer. This assignment, and a rationalization of the hydrogen coupling constants, stems from the structure of the two isomers of *p*-chlorobenzaldoxime as determined by Jerslev.<sup>11</sup> The *syn* isomer is planar with normal conjugation between the oxime group and the phenyl ring. The three pairs of triplets assigned to the radical of this isomer result from hydrogen attached to imino carbon splitting with a 6.2 gauss coupling constant and two equivalent ring-protons with 1.4 gauss coupling. The *anti* isomer, however, is not planar. The oxime group is turned 19° out of the plane of the benzene ring, and little or no resonance between the two groups occurs as the imino carbon-benzene ring bond distance has the normal single bond value.<sup>11</sup> The larger hydrogen coupling constant (26.9 gauss) for the radical of this isomer is consistent with the difference in  $\beta$ -proton coupling constants of the 1-methylvinyl radical discussed by Fessenden and Schuler.<sup>12</sup> The e.s.r. spectrum observed with *anti*-benzaldoxime is identical with that obtained from the *syn* isomer indicating isomerization in the oxidation reaction.

A second example of *cis* and *trans* isomer detection is provided by the radicals from phenylglyoxaldoxime. The e.s.r. spectra of these radicals are given in Fig. 1b. For one isomer  $a_N = 29.3$ , and  $a_H^* = 6.2$  gauss. For the second isomer (present at about 2% the concentration of the first)  $a_N = 31.3$ , and  $a_H^* = 26.8$  gauss. These radicals are relatively long lived, having lifetimes of several minutes under the conditions of preparation.

Another iminoxide radical showing interesting features is that derived from quinone monoxime (*p*-nitrosophenol). The e.s.r. spectrum of this radical, shown in Fig. 1c, exhibits three well-separated groups of lines with each group consisting of a pair of doublets. The latter are assumed to arise from two ring hydrogens made nonequivalent by proximity of one to the iminoxy group. The radical from nitrosoresorcinol exhibits three widely spaced doublets indicating that the ring hydrogens *ortho* to the imino carbon are involved.

The iminoxy radical derived from acetoxime shows the expected three lines attributable to nitrogen, but meaningful examination for further splittings could not be made because of the low concentration of the radical. The iminoxy radical from acetaldoxime showed three resolvable doublets with a hydrogen splitting of 5.2 gauss. The hoped for detection of *syn* and *anti* isomers could not be accomplished again because of the low concentration of the radical. Strong signals were observed from radicals derived from formaldoxime prepared *in situ* in methanol, but the nature and complexity of the spectrum indicated that the predominant radical species was a nitroxide derived from the cyclic trimer of formaldoxime.

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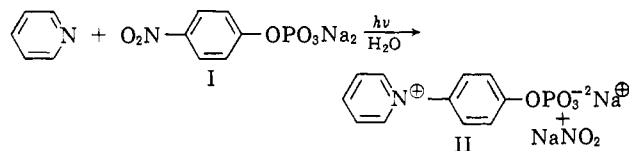
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## Photo-Induced Nucleophilic Aromatic Substitution<sup>1</sup>

Sir:

We have observed that pyridine reacts with *p*-nitrophenyl phosphate in the presence of light to give 1-phenylpyridinium 4'-phosphate. This photo-induced displacement which proceeds readily in dilute aqueous solution at 3° or in ice at about -70°, represents a new class of aromatic substitution reactions.



Havinga, deJongh, and Dorst<sup>2</sup> reported that the hydrolysis of both *p*-nitrophenyl phosphate and *m*-nitrophenyl phosphate was accelerated by light. On re-examining these reactions<sup>3</sup> we confirmed, by paper chromatography and electrophoresis, the formation of *m*-nitrophenol from the *meta* isomer but found that no more than trace quantities of *p*-nitrophenol were produced from the *para* isomer. *p*-Nitrophenyl phosphate did, however, decompose when irradiated in aqueous solution, the final products precipitating in part as tars from the solution.

It was then observed that a simple, clean reaction occurred when *p*-nitrophenyl phosphate was irradiated in a cold aqueous solution containing pyridine. The organic material remained in solution and appeared as a single spot on paper chromatography (brilliant white fluorescence in ultraviolet light,  $R_f$  0.04 in 7:1:2 isopropyl alcohol-ammonia-water; *p*-nitrophenyl phosphate,  $R_f$  0.3, and *p*-nitrophenol,  $R_f$  0.8, fluoresce blue in ultraviolet). In accord with the proposed equation, the irradiated solution gave a positive test for nitrite ion (darkening on addition of ferrous ion to the acidified solution) and the fluorescent product behaved as a singly charged negative ion on electrophoresis on paper at pH 9.2 (it moved at one-half the rate of *p*-nitrophenyl phosphate) and as an electrically neutral species at pH 3.8. Evaporation of the solution at room temperature and successive dissolution of the residual solid and reprecipitation by addition of alcohol afforded a pale tan powder (II), which corresponded in composition to  $C_{11}H_9NO_4PNa \cdot 6H_2O$ . *Anal.*<sup>4</sup> Calcd: C, 34.65; H, 5.55; N, 3.67; P, 8.12. Found: C, 34.82; H, 5.02; N, 4.03; P, 8.46.

As the hydrate, compound II was stable, but it partially decomposed, giving colored products, when heated or dried *in vacuo* at room temperature. It was also stable in hydrochloric acid and in dilute solutions of sodium hydroxide at room temperature; in 5 *M* sodium hydroxide it developed an intense yellow color ( $\lambda_{max}$  363  $m\mu$ ) over a 7-hr. period, following which the solution again became colorless (2 days). Absence of a nitro group in the photoproduct was indicated by infrared (absence of absorption in 7.0-7.8  $\mu$  region)

(1) This work was supported by the National Science Foundation.

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(3) Disodium *p*-nitrophenyl phosphate monohydrate was obtained from the Aldrich Chemical Company. Disodium *m*-nitrophenyl phosphate was prepared by J. McCain by the method of Havinga, *et al.*<sup>2</sup> A General Electric UA-11 1200-w. photochemical lamp was employed as a source and the light was filtered through 6 mm. of Vicor glass and 2 mm. of Pyrex glass.

(4) Analyses by the Micro-Tech Laboratories, Skokie, Ill.