

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.¹¹ 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.¹¹ The larger hydrogen coupling constant (26.9 gauss) for the radical of this isomer is consistent with the difference in β -proton coupling constants of the 1-methylvinyl radical discussed by Fessenden and Schuler.¹² 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 iminoxide 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.

Acknowledgment.—The author is indebted to Dr. D. J. Anderson, who proposed the nomenclature adopted here, and Dr. J. Q. Adams for helpful discussion.

(11) B. Jerslev, *Nature*, **180**, 1410 (1958).

(12) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **39**, 2147 (1963).

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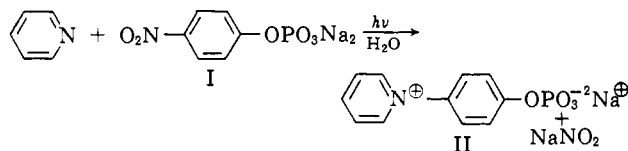
J. R. THOMAS

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Photo-Induced Nucleophilic Aromatic Substitution¹

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 Dorst² reported that the hydrolysis of both *p*-nitrophenyl phosphate and *m*-nitrophenyl phosphate was accelerated by light. On re-examining these reactions³ 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.*⁴ 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 (λ_{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 μ region)

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

(2) E. Havinga, R. O. deJongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(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.*² 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.

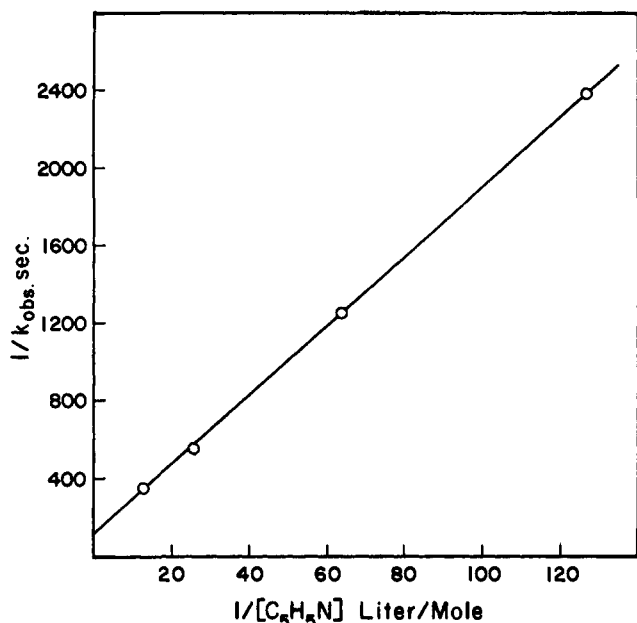
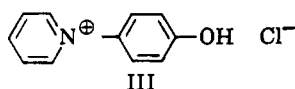


Fig. 1.—Photo-induced reaction of *p*-nitrophenyl phosphate with pyridine in aqueous solution.

and ultraviolet (λ_{\max} of II, 297 and 267 $m\mu$; λ_{\max} of I, 310 $m\mu$) spectral data. The structure of II was confirmed by hydrolysis in concentrated hydrochloric acid at 100° to phosphoric acid and 1-(*p*-hydroxyphenyl)pyridinium chloride (III). The latter, isolated in 50% yield, was identical in melting point, infrared and ultraviolet spectra, chromatographic behavior, and properties of the picrate derivative with an authentic sample of N-(*p*-hydroxyphenyl)pyridinium chloride prepared from *p*-aminophenol.⁵



In contrast to the results of the photochemical reaction, *p*-nitrophenyl phosphate was converted to *p*-nitrophenol when heated with an aqueous pyridine solution.

Rate data for the photo-induced reactions of *p*- and *m*-nitrophenyl phosphate are presented in Table I.

TABLE I

PHOTO-INDUCED REACTIONS OF *p*- AND *m*-NITROPHENYL PHOSPHATE IN AQUEOUS PYRIDINE SOLUTIONS^a

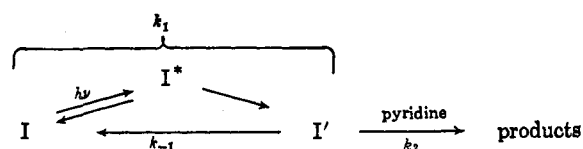
Isomer	10 ² × [pyridine], moles/l.	10 ² × $k_{\text{obs.}}$, ^b sec. ⁻¹	
		Ester disappearance	Nitrophenol appearance
<i>para</i>	0	(0.017)	(0.005)
	0.79	0.420	0
	1.58	0.802	
	3.95	1.82	
	7.90	2.89	
<i>meta</i>	0	0.648	0.588
	0.79	0.693	0.573
	7.90		0.635

^a Temperature +3°. *p*-nitrophenyl phosphate concentration 1.00×10^{-4} M, *m*-nitrophenyl phosphate concentration 1.33×10^{-4} M, pH 9.8 (0.004 M borate buffer). ^b In determining $k_{\text{obs.}}$ experimental infinity values were used except for reaction of the *para* isomer in absence of pyridine, in which case it was assumed that the absorbance of the product was the same as that for nitrophenol.

(5) Prepared by the method of N. E. Grigor'eva and M. D. Yavlinskii, *Ukr. Khim. Zh.*, **18**, 82 (1952); *Chem. Abstr.*, **48**, 11411a (1954).

Ester disappearance was followed by the absorbance decrease at 310 $m\mu$ for the *para* isomer and at 275 $m\mu$ for the *meta* isomer; nitrophenol appearance was followed by the absorbance increase at 400 $m\mu$. First-order kinetics were obtained for each individual run. It may be noted that (a) the observed first-order rate constants for disappearance of *p*-nitrophenyl phosphate depended upon the pyridine concentration, being approximately proportional to the pyridine concentration for the more dilute solutions, (b) *p*-nitrophenol was not formed in these reactions, and (c) the over-all rate of reaction of *m*-nitrophenyl phosphate was little affected by pyridine, whether observed at 275 or 400 $m\mu$.

These data are consistent with the view that photo-excited *p*-nitrophenyl phosphate (I*) yields an intermediate (I') which may either return to *p*-nitrophenyl phosphate in the ground state or undergo displacement by pyridine in a second-order process. On the basis

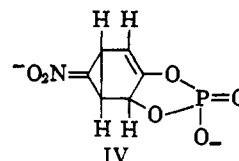


of this mechanism and the steady-state approximation, the following relation holds

$$\frac{1}{k_{\text{obsd}}} = \frac{k_{-1}}{k_1 k_2 [\text{pyridine}]} + \frac{1}{k_1}$$

As shown in Fig. 1, the rate data fit this equation well. From the intercept and slope of the line it is found that $k_{-1}/k_2 = 0.14$ mole/l.

Possibilities for I' include a triplet state or a cyclic phosphate (IV).⁶ The nature of the intermediate and the generality of photo-induced aromatic substitution reactions are under investigation.



(6) For a discussion of the photo-excited state, I*, of *p*-nitrophenyl phosphate see H. E. Zimmerman and S. Somasekhara [*J. Am. Chem. Soc.*, **85**, 922 (1963)].

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An Environmentally-Sensitive Reagent with Selectivity for the Tryptophan Residue in Proteins¹

Sir:

In order to explore the properties of enzymes during their catalytic action, we have been interested in compounds which would be sensitive to changes in environment and which could be introduced at specific positions in the protein molecule. The first such com-

(1) Research carried out at Brookhaven National Laboratory under the auspices of the U. S. Atomic Energy Commission.