

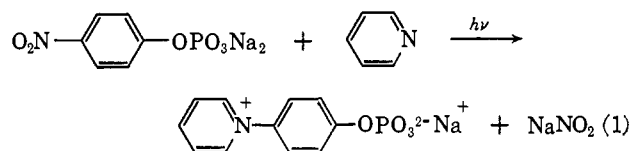
Photoinduced Substitution. II. Substituent Effects in Nucleophilic Displacement on Substituted Nitrobenzenes^{1,2}

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On irradiation with light of wave length >289 $m\mu$ *p*-nitrophenyl phosphate and *p*-nitroanisole react with pyridine in dilute aqueous solution to give 1-arylpyridinium nitrites. This aromatic substitution proceeds readily at 3°. Under similar conditions *m*-nitroanisole, nitrobenzene, and *p*-dinitrobenzene fail to react. We infer that *p*-phosphoryl and -methoxyl may function as "activating" substituents in nucleophilic displacement of a nitro group from an aromatic compound in the excited state, in marked contrast to chemistry for ground-state molecules. The kinetics of the photoinduced reactions of *p*-nitroanisole with pyridine, 4-methylpyridine, and hydroxide ion are consistent with a mechanism in which quenching processes, both dependent on and independent of the added nucleophile, are competitive with substitution. An increase in temperature favors the deactivation process relative to substitution. In displacement activity toward excited *p*-nitroanisole at 3°, pyridine is about one-fifth as active as 4-methylpyridine and hydroxide ion, and triethylenediamine is inactive. Photoexcited *p*-nitrophenol does not undergo substitution by pyridine under the conditions studied.

Nucleophilic aromatic substitution reactions involving displacement of nitrite or halide ions by an amine are generally extremely slow at room temperature unless the nitro group or the halogen atom is "activated" by a strong electron-withdrawing group in an *ortho* or *para* position.⁴ Thus, whereas 2,4-dinitrochlorobenzene reacts readily with alcoholic ammonium hydroxide at 25° and *p*-nitrochlorobenzene reacts satisfactorily with ammonium hydroxide at 200°, the reaction of chlorobenzene with ammonium hydroxide is slow even at 300°. Electron-donating substituents *ortho* or *para* to the departing group exert a retarding effect relative to hydrogen. We were therefore surprised to find that on irradiation with light *p*-nitrophenyl phosphate reacted rapidly with pyridine in aqueous solution to give a 1-phenylpyridinium 4'-phosphate salt¹ (eq. 1). Not only did the reaction proceed at a relative low temperature (3°), the departing group was also *para* to an electron-donating substituent. This unusual result prompted a survey of other aromatic compounds and nucleophilic agents. The present paper records the results of experiments on *p*-



and *m*-nitroanisole, nitrobenzene, *p*-dinitrobenzene, and *p*-nitrophenol, as well as on *p*- and *m*-nitrophenyl phosphate.

A few other cases of photoinduced nucleophilic aromatic substitution have recently been described. Havinga and de Jongh⁵ reported that *m*-nitro-*N*-methylaniline is formed in a photochemical reaction of methylamine with either *m*-nitroanisole or *m*-nitrophenyl phosphate, and Gold and Rochester⁶ observed that, under the influence of light, hydroxide ion displaces nitrite from trinitrobenzene and from several picric acid derivatives. In these examples the departing group is *meta* to a nitro group. It is reasonable to assume, as for a number of photoinduced hydrolytic reactions,^{7,8} that a nitro group in an aromatic compound in an excited state withdraws electrons effectively from a *meta* position, facilitating nucleophilic attack at the *meta* carbon atom or solvolysis of a substituent joined to it. Finally, Johnson and Rees⁹ found that light accelerates the formation of 4-piperidinopyridine 1-oxide from 4-nitropyridine 1-oxide and piperidine. Both the photochemical and the dark reaction afford the same product, the *N*-oxide function presumably assisting the displacement of nitrite in each case by reducing electron density at the carbon at which substitution occurs.

Nitrophenyl Phosphates. Our initial experiments were stimulated by the report of Havinga, *et al.*, that conversion of *p*- and *m*-nitrophenyl phosphate to the corresponding nitrophenols and *o*-phosphate in water is markedly accelerated by ultraviolet light.⁷ In surveying potential phosphorylating agents we reinvestigated this reaction, using a 1200-w. G.E. photochemical lamp as the source. Radiation below 280 $m\mu$ was excluded by a Pyrex filter. It was confirmed that *m*-nitrophenol is formed from *m*-nitrophenyl phosphate and that the rate of the photoinduced reaction of *m*-nitrophenyl phosphate is greater than that of the photoinduced reaction of *p*-nitrophenyl phosphate.¹⁰

(1) For a preliminary communication (part I) see: R. L. Letsinger and O. B. Ramsay, *J. Am. Chem. Soc.*, **86**, 1447 (1964). A portion of the material was also presented at the 148th National Meeting of the American Chemical Society, Chicago, Ill., Sept. 1964.

(2) This research has been supported by the National Science Foundation (Grant NSF-G25069) and by a Public Health Service fellowship (1-F1-GM-25, 182-01).

(3) National Institutes of Health Predoctoral Fellow, 1964.

(4) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); J. F. Bunnett, *Quart. Rev.* (London), **12**, 1 (1958); J. Sauer and R. Huisgen, *Angew. Chem.*, **72**, 294 (1960); S. D. Ross in "Progress in Physical Organic Chemistry," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1963, p. 31.

(5) E. Havinga and R. O. de Jongh, *Bull. soc. chim. Belges*, **71**, 803 (1962).

(6) V. Gold and C. H. Rochester, *J. Chem. Soc.*, 1687 (1964); *Proc. Chem. Soc.*, 403 (1960).

(7) E. Havinga, R. O. de Jongh, and W. Dorst, *Rec. trav. chim.*, **75**, 378 (1956).

(8) H. E. Zimmerman and S. Somasekhara, *J. Am. Chem. Soc.*, **85**, 922 (1963).

(9) R. M. Johnson and C. W. Rees, *Proc. Chem. Soc.*, 213 (1964). For a photoinduced substitution involving a polyhedral borane, see S. Trofimenko and H. N. Cripps, *J. Am. Chem. Soc.*, **87**, 653 (1965).

(10) The relative reactivity of the two isomers in the photochemical reaction is the reverse of that for hydrolysis in absence of light. For a

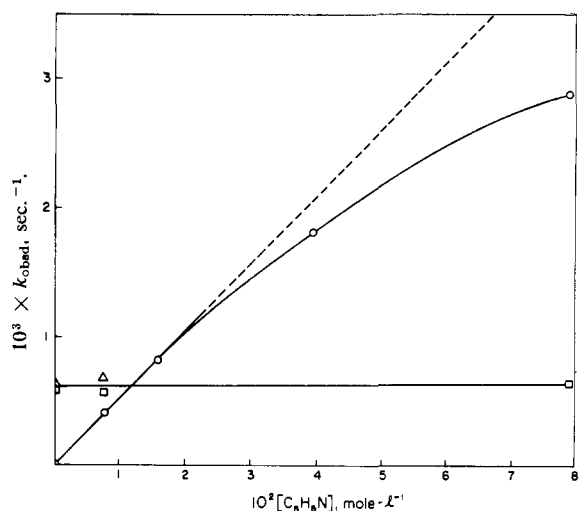


Figure 1. Reactions of *p*- and *m*-nitrophenyl phosphate in aqueous pyridine solutions at 3°; pH 10.1 (0.004 *M* borate buffer): O, *para* isomer (measured at 310 $m\mu$); □, *meta* isomer (measured at 400 $m\mu$); Δ, *meta* isomer (measured at 275 $m\mu$).

Under our conditions, however, very little *p*-nitrophenol was formed from *p*-nitrophenyl phosphate. Most of the organic material was converted to a tarry product which did not move from the origin on electrophoresis in alkaline solution.

It was then observed that the photoinduced reaction of *p*-nitrophenyl phosphate in water is altered in a remarkable way when pyridine is added to the solution. In place of the tarry material, a single organic substance was obtained. On paper it appeared as a brilliant white fluorescent spot under ultraviolet light and it migrated electrophoretically as an ion with a net charge of -1 . This substance was identified as a 1-phenylpyridinium 4'-phosphate (eq. 1) by isolation and analysis of the sodium salt and by acid hydrolysis to the 1-(4-hydroxyphenyl)pyridinium ion, which was obtained as a picrate and shown to be identical with 1-(4-hydroxyphenyl)pyridinium picrate prepared independently from *p*-aminophenol and 1-(2,4-dinitrophenyl)pyridinium chloride.¹¹ Particularly striking was the fact that the photochemical reaction also occurred when a dilute aqueous solution of *p*-nitrophenyl phosphate and pyridine was frozen and irradiated while cooled by Dry Ice. Since diffusion of the reactants in the frozen matrix would be extremely slow, it must be assumed that the reaction involved organic components which had been concentrated into pockets in the ice structure.¹²

In contrast, pyridine had very little effect upon the reaction of *m*-nitrophenyl phosphate. *m*-Nitrophenol was the major product even when the pyridine concentration was 0.08 *M*. Only a trace of a white fluorescent spot, indicative of formation of a 1-arylpyridinium salt, was observed on paper chromatograms of the product.

theoretical rationalization of this phenomenon and a discussion of the electronic distribution in the excited states and ground states of the nitrophenyl phosphates see Zimmerman and Somasekhara, ref. 8.

(11) N. E. Grigor'eva and M. D. Yavlinskii, *Ukr. Khim. Zh.*, **18**, 82 (1952); *Chem. Abstr.*, **48**, 11411a (1954).

(12) Compare R. Beukers, J. Yistra, and W. Berends, *Rec. trav. chim.*, **77**, 729 (1958); R. Beukers and W. Berends, *Biochim. Biophys. Acta*, **38**, 573 (1960); D. Shugar in "The Nucleic Acids," Vol. III, E. Chargaff and J. N. Davidson, Ed., Academic Press Inc., New York, N. Y., p. 40.

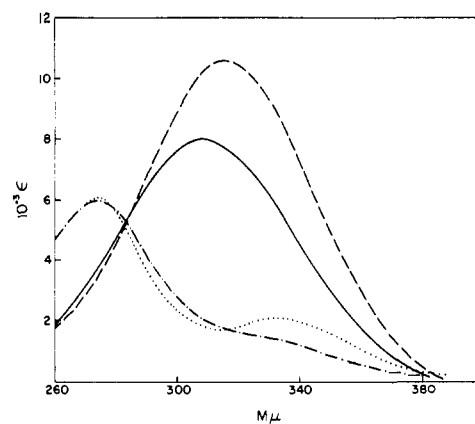
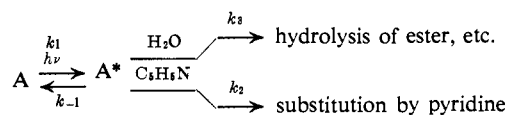


Figure 2. Ultraviolet spectra: —, *p*-nitrophenyl phosphate in water; - - -, *m*-nitrophenyl phosphate in water; - · - ·, *p*-nitroanisole in 22% aqueous *t*-butyl alcohol; · · · ·, *m*-nitroanisole in 22% aqueous *t*-butyl alcohol.

Rate data for reactions of *p*- and *m*-nitrophenyl phosphate in the presence of excess pyridine are presented in Figure 1. For individual runs the disappearance of the nitro substrate or appearance of nitrophenol fitted a first-order rate equation. As shown, the pseudo-first-order rate constants for *p*-nitrophenyl phosphate increase linearly with the pyridine concentration at low concentrations but deviate from the linear relation at high pyridine concentrations. On the other hand, the rate of formation of *m*-nitrophenol from *m*-nitrophenyl phosphate is independent of the pyridine concentration.

Ultraviolet spectra of *p*- and *m*-nitrophenyl phosphate are included in Figure 2. Both compounds absorb above 289 $m\mu$, whereas pyridine, even at a concentration of 0.1 *M*, does not absorb in this region. It is therefore apparent that (1) the nitrophenyl phosphates are the species activated in the initial photochemical step and (2) the curvature in the k_{obsd} vs. [pyridine] plot for *p*-nitrophenyl phosphate cannot be ascribed to internal filtering by pyridine.¹³ A plausible reaction pathway consistent with the rate data is



where A and A* represent the aromatic nitro compound in the ground state and an excited state, respectively. According to this scheme deactivation of A*, either spontaneously or by solvent quenching, competes with substitution. For *m*-nitrophenyl phosphate $k_2 \cdot [\text{pyridine}]$ is small relative to k_3 (or $k_3'[\text{H}_2\text{O}]$)¹⁴ and the reaction is primarily one of hydrolysis of the phosphate; for *p*-nitrophenyl phosphate k_3 is relatively unimportant and displacement of nitrite by pyridine is the preferred pathway.

(13) A very small fraction of the incident light was in the 280–290- $m\mu$ region (See Experimental section). As a check on the possibility that this light might play a role in the reaction several experiments were made with a filter, containing more pyridine than present in solution with *p*-nitrophenyl phosphate, inserted between the light source and the reaction vessel. The filter did not retard the photochemical reaction.

(14) It is not known whether the hydrolysis involves unimolecular dissociation of excited *m*-nitrophenyl phosphate or a bimolecular reaction with water.⁷

With this model and the steady-state approximation eq. 2 may be derived. This equation predicts a linear

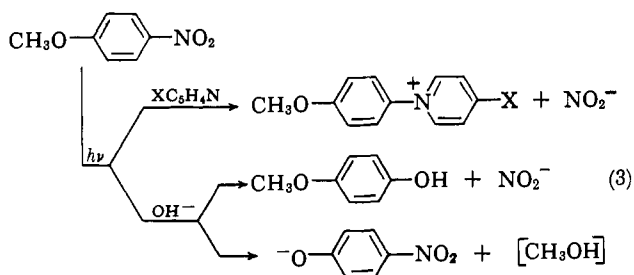
$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} + \frac{k - 1}{k_1 k_2 [\text{C}_5\text{H}_5\text{N}]} \quad (2)$$

relation between $1/k_{\text{obsd}}$ for the reactions of *p*-nitrophenyl phosphate and the reciprocal of the pyridine concentration. As shown in Figure 3, plots of $1/k_{\text{obsd}}$ vs. $1/[\text{pyridine}]$ indeed yield straight lines for reactions conducted in both water and in 24% aqueous ethanol. It may be noted that the displacement reactions in water are faster than those in the mixed solvent.

p-Nitroanisole. While it is clear that pyridine attacks *p*-nitrophenyl phosphate more readily than *m*-nitrophenyl phosphate under the photolytic conditions, interpretation of the result is somewhat clouded by the rapid photoinduced hydrolysis exhibited by the *meta* isomer. For the study of substituent effects in photoinduced displacement it appeared desirable to utilize substituents which would have an electronic effect similar to the phosphate group yet would be more resistant to hydrolysis. The methoxyl group was selected as a good candidate. The reactions of *p*-nitroanisole are treated in this section; *m*-nitroanisole is considered in the following section.

It was found that *p*-nitroanisole does react readily with pyridine in aqueous solution on irradiation, 1 equiv. of nitrite ion being liberated per mole of *p*-nitroanisole consumed.¹⁵ No reaction occurs in the absence of light. Concentration and electrophoresis of a solution which had been irradiated for >10 half-lives revealed a single fluorescent product, which migrated as a +1 ion. This substance was identified as a 1-(*p*-methoxyphenyl)pyridinium salt by isolation as a picrate derivative. Neither sweeping oxygen from the system with nitrogen nor addition of ferric nitrate ($1 \times 10^{-4} M$) influenced the rate of the photochemical reaction.¹⁶

4-Methylpyridine reacted with photoexcited *p*-nitroanisole analogously to pyridine, forming 1-(*p*-methoxyphenyl)-4-methylpyridinium ion by displacing the nitro group. Hydroxide also reacted with *p*-nitroanisole in the presence of light. In this case the nucleophile attacked the ether function as well as $\geq\text{CNO}_2$ to yield *p*-nitrophenol (~20%) in addition to *p*-methoxyphenol (~80%). Whether nitrophenol arises by attack at the methyl carbon or at an aromatic carbon has not been determined. It is noteworthy that triethylenediamine, an aliphatic tertiary amine, failed to displace the nitro group from photoexcited



(15) Nitrite was determined quantitatively by the method of B. F. Rider and M. G. Mellon, *Anal. Chem.*, **18**, 96 (1946).

(16) Both oxygen and ferric ion are efficient quenchers for molecules in the triplet state. To date all experiments designed as a test for a triplet-state intermediate in these reactions have been negative. These include attempts to obtain photosensitized reactions.

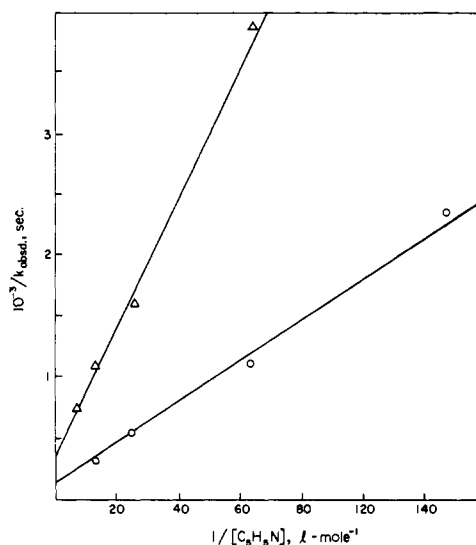


Figure 3. Reaction of *p*-nitrophenyl phosphate with pyridine at 3°: O, in water; Δ, in 24% aqueous ethanol.

p-nitroanisole. Triethylamine formed a complex with *p*-nitroanisole on irradiation but failed to displace nitrite.

The hydroxide ion reactions differed from those involving the pyridine bases in that they were sensitive to oxygen. Reactions carried out in the presence of air at 26° proceeded 1.1–1.35 times faster than comparable reactions conducted in solutions that had been flushed with nitrogen. In addition, the product distribution was altered by oxygen. When a nitrogen atmosphere was used, the spectrum of the final solution could be satisfactorily duplicated by superposition of appropriately weighted spectra of *p*-methoxyphenol, *p*-nitrophenol, and nitrite. When the experiment was conducted in air additional absorption ($\lambda_{\text{max}} \sim 335 m\mu$) was exhibited in the spectrum of the products. Consistent with these observations are the results of paper chromatography, which showed two products, *p*-methoxyphenol and *p*-nitrophenol, for the reaction conducted in nitrogen and three products, *p*-methoxyphenol, *p*-nitrophenol, and a material which did not move from the origin, for the reaction conducted in air. The higher rate of the reaction in air suggests that a photoinduced oxidation may have occurred; however, the identity of the new product was not established. It is interesting that oxygen did not significantly affect the rate of the reaction of *p*-nitroanisole with hydroxide at 3°, although it did cause formation of some of the material absorbing at 335 $m\mu$.

With kinetic and spectral data, Gold and Rochester⁶ demonstrated that the photoinduced formation of nitrite from methyl picrate, picric acid, and picamide in methanol solutions of sodium methoxide and from trinitrobenzene in aqueous solutions of sodium hydroxide involves formation of a 1:1 complex (e.g., $\text{NaOCH}_3 \cdot \text{C}_6\text{H}_2(\text{NO}_2)_3\text{OCH}_3$), which on absorption of light reacts with a second equivalent of base to give the observed products. We looked carefully, without success, for spectral evidence that a complex might also form between *p*-nitroanisole and the pyridine bases or hydroxide. Addition of these nucleophiles to aqueous alcoholic solutions of *p*-nitroanisole did not alter in any way the ultraviolet spectrum of the *p*-nitroanisole.

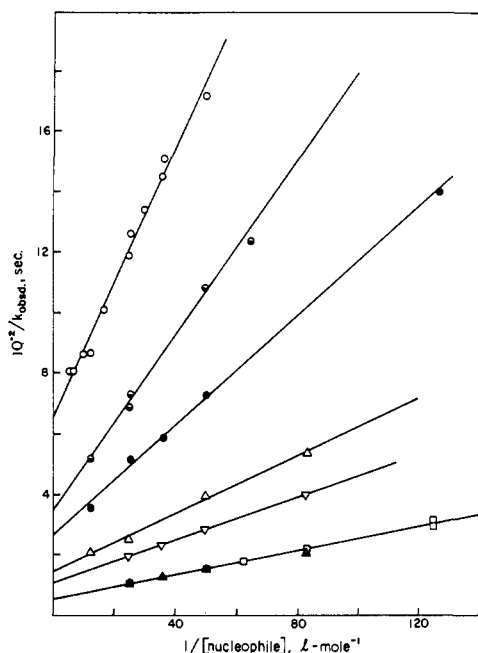


Figure 4. Reactions of *p*-nitroanisole with nucleophiles. (a) Pyridine: O, in 22% aqueous *t*-butyl alcohol at 26°; ●, in 22% aqueous *t*-butyl alcohol at 3°; ●, in water at 3°. (b) 4-Methylpyridine: Δ, in 22% aqueous *t*-butyl alcohol at 26°; ▽, in 22% aqueous *t*-butyl alcohol at 3°; ▲, in water at 3°. (c) Hydroxide: □, in water at 3°.

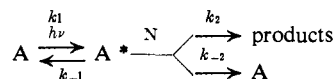
In view of this result and the kinetic data described in the following section we conclude that *p*-nitroanisole is converted to the excited state prior to any reaction with the nucleophile.

Rate data for photoinduced reactions of *p*-nitroanisole with pyridine, 4-methylpyridine, and hydroxide ion are recorded in Figure 4 as plots of $1/k_{\text{obsd}}$ vs. $1/[N]$, where $[N]$ is the nucleophile concentration.¹⁷ As shown, pyridine is a somewhat less effective displacing agent than 4-methylpyridine or hydroxide, though the difference is not great. Increasing the temperature from 3 to 26° or decreasing the polarity of the solvent, by changing from water to 22% aqueous *t*-butyl alcohol, retards the rate of displacement of nitrite by the pyridine bases. Of particular interest is the fact that the plots in Figure 4, though linear, do not have a common intercept. Since the intercept for eq. 2 is $1/k_1$, and k_1 should be independent of the nucleophile in these reactions, the intercepts should be constant for experiments with *p*-nitroanisole conducted in a given solvent at a given temperature (e.g., at 3° in water), if eq. 2 adequately describes the system. Furthermore, since the absorption of light by *p*-nitroanisole is altered very little by the changes in temperature and solvent involved here, the intercepts for the other experiments should be very close to this value.

The observed variation in the intercepts may be rationalized by assuming that the nucleophiles can quench excited *p*-nitroanisole (convert it to the ground state) as well as displace nitrite.¹⁸ With this feature the over-all process becomes

(17) In the remaining discussion "nucleophile" refers to pyridine, 4-methylpyridine, or hydroxide ion.

(18) Quenching of excited aromatic molecules by aliphatic amines is a well recognized reaction. See A. Weller, "Progress in Reaction Kinetics," Vol. I, Pergamon Press, London, 1961, p. 189.



and the equation relating k_{obsd} to the kinetic constants becomes

$$\frac{1}{k_{\text{obsd}}} = \frac{1}{k_1} \left(1 + \frac{k_{-2}}{k_2} \right) + \frac{k_{-1}}{k_1 k_2 [N]} \quad (4)$$

This model satisfactorily accounts for all of the results. Accepting it as a reasonable hypothesis, we may extract several ratios of interest from the rate data, namely, the relative displacement activity of different nucleophiles toward *p*-nitroanisole in the excited state, the fraction of photoexcited molecules of *p*-nitroanisole which interact with a given nucleophile, and, for pyridine, a lower limit for the ratio of quenching to displacing activity of the nucleophile.

Numerical values for the intercepts, $(1/k_1)(1 + k_{-2}/k_2)$, and the slopes, $k_{-1}/k_1 k_2$, for the lines in Figure 4 are collected in Table I. Ratios of k_2 values, which

Table I. Photoinduced Reactions of *p*-Nitroanisole

Expt.	Nucleophile	Temp., °C.	Solvent	Intercept, sec.	Slope, sec. moles/l.	Intercept/slope, l./mole
1	Pyridine	3	H ₂ O	264	9.0	29
2	Pyridine	3	22% aq. <i>t</i> -BuOH	342	14.5	24
3	Pyridine	26	22% aq. <i>t</i> -BuOH	656	22.1	30
4	4-Methylpyridine	3	H ₂ O	57	1.9	30
5	4-Methylpyridine	3	22% aq. <i>t</i> -BuOH	105	3.5	30
6	4-Methylpyridine	26	22% aq. <i>t</i> -BuOH	145	4.8	30
7	Hydroxide	3	H ₂ O	50.5 ± 0.4 ^a	2.0 ± 0.05 ^a	25
8	Hydroxide	3	22% aq. <i>t</i> -BuOH	51.4 ± 3.4 ^a	1.6 ± 0.3 ^a	32

^a These experiments were followed at both 400 (nitrophenol increase) and at 317 mμ (nitroanisole decrease). The number given is the average of the two sets of measurements.

represent the relative displacement activity of the nucleophiles,¹⁹ may be obtained from ratios of slopes for experiments conducted in the same solvent at the same temperature. Thus, from experiments 1, 4, and 7 (Table I), for which k_{-1}/k_1 should be constant, the relative activity of pyridine, 4-methylpyridine, and hydroxide in water at 3° is 1:4.7:4.5.

Dividing the intercept by the slope for a given line yields $(k_2 + k_{-2})/k_{-1}$. It is interesting that this quotient is almost constant for the experiments reported in Table I, the average being near 30 l./mole. The product of this number and the nucleophile concentration should give the rate of reaction of excited *p*-nitroanisole with the nucleophile relative to the rate of deactivation of excited *p*-nitroanisole in nucleophile-independent processes. On this basis approximately three-fourths of the total number of excited molecules of *p*-nitroanisole interact directly with the added nucleophile, either with substitution or with

(19) It must be borne in mind, however, that the hydroxide reaction involves attack at the ether function as well as displacement of nitrite.

quenching, when the nucleophile concentration is 0.1 *M*.²⁰

A lower limit for k_{-2}/k_2 for the reaction of pyridine with *p*-nitroanisole in water at 3° may be obtained from the intercepts for experiments 1 and 4 by setting k_{-2} for the reaction of 4-methylpyridine equal to zero and solving for a lower limit for k_1 . The values thus obtained are 0.0175 sec.⁻¹ for k_1 and 3.6 for k_{-2}/k_2 . Accordingly, at least 3.6 molecules of excited *p*-nitroanisole are quenched by pyridine for each molecule that undergoes substitution.

m-Nitroanisole. An aqueous solution of *m*-nitroanisole (5.2×10^{-4} *M*) and pyridine²¹ at pH 6.2 and 26° was irradiated for 8500 sec. No reaction occurred, as indicated by two criteria: (1) there was no significant change in the ultraviolet spectrum of the solution (300–400 m μ), and (2) no fluorescent ionic products could be detected when the solution was concentrated and submitted to paper electrophoresis. For comparison, the half-life of *p*-nitroanisole (9.2×10^{-5} *M*) under the same conditions is 430 sec.

That *m*-nitroanisole undergoes photochemical activation may be inferred from the absorption spectra in Figure 2. Indeed, at the concentrations of the nitroanisoles used in these experiments *m*-nitroanisole absorbs 0.8 times as much light as *p*-nitroanisole at 312 m μ and more than 0.8 times as much in the other regions of the incident light. It is therefore clear that the position of the methoxyl group in the aromatic ring has a profound effect upon the reactivity of the excited state of the nitroanisole, at least with respect to nucleophilic displacement of nitrite by pyridine.

The analysis of substituent effects is more complicated than for reactions of substances in the ground state since a substituent may alter the lifetime as well as the electronic distribution of the excited state. If, for example, an *m*-methoxyl group greatly shortens the lifetime of the pertinent excited state of the nitrobenzene, a bimolecular photoinduced reaction could fail to proceed even though the energetics were otherwise satisfactory.

For the case at hand experimental evidence is available which indicates that the excited state of *m*-nitroanisole does survive long enough to encounter pyridine. First, in agreement with Havinga and de Jongh,⁵ we observed that *m*-nitroanisole is converted to *m*-nitrophenoxide when irradiated in alkaline solution. For a reaction conducted under the same conditions used in studying the reactivity of *m*-nitroanisole toward pyridine, with the exception that the solution contained sodium hydroxide (0.02 *M*) in place of the pyridine buffer, k_{obsd} for formation of *m*-nitrophenol was found to be 8.7×10^{-3} sec.⁻¹. Second, it was found that *m*-nitroanisole exhibited the same ultraviolet spectrum in both neutral and in alkaline solution, indicating the absence of any complex involving hydroxide and *m*-nitroanisole in the ground state.²²

(20) The close grouping of the values of $(k_2 + k_{-2})/k_{-1}$, as well as the similarity of the k_2 values, suggests that attack of pyridine, 4-methylpyridine, and hydroxide on photoexcited *p*-nitroanisole might be largely diffusion controlled. Other explanations for this pattern, however, are possible.

(21) The concentration of pyridine, including the pyridinium ion, was 0.12 *M*. The concentration of the free base was approximately 0.11 *M*.

(22) It is conceivable that a hydrogen-bonded complex of hydroxide

Since photoexcited *m*-nitroanisole survived long enough to react with 0.02 *M* hydroxide, it must have survived long enough also to encounter pyridine at the concentrations employed (~ 0.11 *M*). These results suggest that the failure of *m*-nitroanisole to react with pyridine stems from the low reactivity of the excited state toward pyridine.²³

Nitrobenzene and p-Dinitrobenzene. In order that a comparison of the substituent effects of *p*-OCH₃, *p*-H, and *p*-NO₂ in photoinduced substitution reactions might be made, we investigated the behavior of nitrobenzene and *p*-dinitrobenzene with both pyridine and hydroxide. Concentrations of the nitro compounds were selected such that the initial absorbance of the solutions would be close to that for the solutions of *p*-nitroanisole.

The experiments showed that the rate of reaction of excited nitrobenzene and *p*-dinitrobenzene with pyridine is at least several orders of magnitude less than the rate of excited *p*-nitroanisole with pyridine; indeed, it is doubtful that any substitution occurred within the time span investigated (> 5000 sec.). *p*-Dinitrobenzene did react with hydroxide ion on irradiation; however, the rate was very low. The initial rate of formation of *p*-nitrophenol was about 1/100th the rate at which *p*-nitroanisole reacted. Photoinduced substitution involving nitrobenzene and hydroxide was even slower, if indeed any at all took place. We conclude that a nitro group situated *para* to a methoxyl group is much more susceptible to displacement in photoinduced reactions of the type under discussion than nitro *para* to hydrogen or to another nitro group.

p-Nitrophenol. *p*-Nitrophenol was interesting since, although possessing an oxygen function *para* to the nitro group, it failed to react significantly with pyridine under conditions for a photoinduced displacement. Experiments were carried out both at pH 10.1, where the nitrophenol is extensively ionized, and at 6.2, where it is present largely (89%) as the phenol. Failure to react in the former case is perhaps not surprising since displacement of nitrite from the negatively charged nitrophenoxide ion might well be difficult. In view of the structural similarity of *p*-nitroanisole and *p*-nitrophenol and the similarity of the absorption spectra of these substances (see Figure 5 for the spectrum of a solution of *p*-nitrophenol at pH 6.2), the lack of reactivity of *p*-nitrophenol at pH 6.2 is more unexpected. It seems likely that *p*-nitrophenol in the excited state is extensively ionized at pH 6.2, in which case pyridine would have to attack a nitrophenoxide ion, just as in the reaction conducted at pH 10.1. Direct experimental information on the acidity of *p*-nitrophenol in the excited state is not available; however, it has been established that another phenolic compound, β -naphthol, is approximately a million times more acidic in the singlet state than in the ground state.²⁴ If this explanation is valid, the failure of *p*-nitrophenol to react with pyridine photochemically would add

and *m*-nitroanisole could exhibit the same spectrum as *m*-nitroanisole and be formed in sufficient concentration to affect the photochemical reaction; however, this event seems improbable.

(23) The low reactivity could reflect either a low tendency for displacement (low k_2) or a high tendency for quenching (high k_{-2}) by pyridine.

(24) (a) T. Förster, *Z. Elektrochem.*, **54**, 531 (1950); (b) A. Weller, *ibid.*, **56**, 662 (1952); (c) G. Jackson and G. Porter, *Proc. Roy. Soc. (London)*, **A260**, 13 (1961).

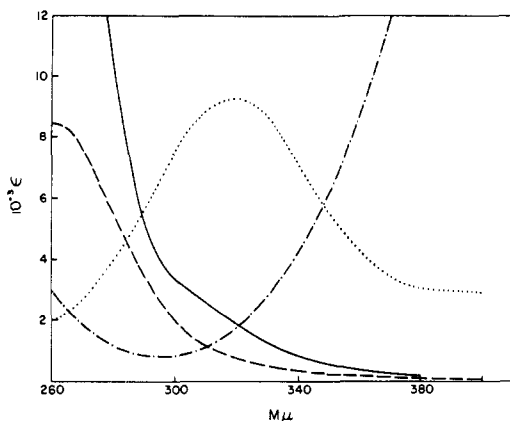


Figure 5. Ultraviolet spectra: —, *p*-dinitrobenzene in 22% aqueous *t*-butyl alcohol; ---, nitrobenzene in 22% aqueous *t*-butyl alcohol; ·····, *p*-nitrophenol in 22% aqueous *t*-butyl alcohol at pH 6.2; -·-·-, *p*-nitrophenol in 0.012 *M* sodium hydroxide in water.

weight to evidence that the excited state involved in the substitution reaction is a singlet state, since triplet-state species generally have about the same pK_a as the ground-state molecules.^{24c}

Summary and Discussion

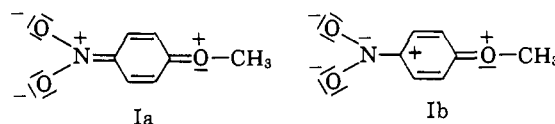
Spectral and kinetic evidence indicate that the initial step in these photoinduced substitution reactions is absorption of light by the nitro substrate. The excited molecules may return to the ground state spontaneously or by deactivation with solvent molecules or they may react with nucleophilic agents in the solution. The nucleophiles may either displace a group from the excited molecule or induce a transition to the ground state of the aromatic substrate. Pyridine bases²⁵ are particularly effective in displacing nitro groups from suitably substituted aromatic compounds. Hydroxide ion also displaces the nitro group but it is much less selective. Thus, it attacks the ether function in *p*-nitroanisole as well as $\geq\text{CNO}_2$ and it converts *m*-nitroanisole to *m*-nitrophenol. For the reaction of pyridine with excited *p*-nitroanisole, kinetic data suggest that more than three excited molecules are deactivated by pyridine for each that undergoes substitution.

An interesting feature to emerge from this study is that *p*-methoxyl and *p*-phosphoryl may function as "activating" groups relative to *p*-hydrogen, *p*-nitro, *p*-hydroxyl, and *m*-methoxyl in the displacement of a nitro group from a photoexcited aromatic molecule. Substitution reactions of this type complement the photoinduced reactions in which a nitro group facilitates cleavage of a substituent group at a *meta* position.

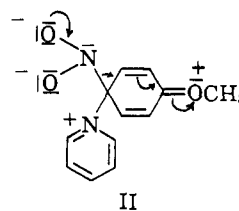
In view of uncertainties regarding the effects of substituent groups upon the lifetimes of the excited states, rationalizations of substituent effects in terms of electronic structures are open to some question. With this reservation in mind, it may be noted that the present results are explicable in terms of an excited state with high electron density on the nitro group and low electron density on the adjacent carbon. Important contributors to the resonance hybrid for the

(25) Charge-transfer complexes between the excited aromatic molecule and the pyridine base may be involved. Evidence for the formation of excited complexes of pyrene and related compounds has been cited by Weller.¹⁸

ground state and excited state of *p*-nitroanisole may be represented by Ia and Ib, respectively. These formulations are compatible with molecular orbital calcula-

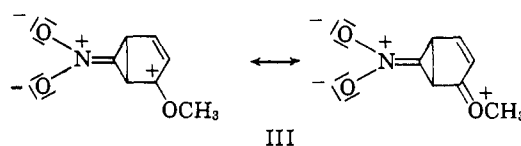


tions which indicate (1) that an electron acceptor group *para* to an electron donor group on a benzene ring acquires negative charge, primarily at the expense of the aromatic ring, when the molecule passes from the ground state to the first excited state,²⁶ and (2) that the *para* position in anisole in the first excited state is electron deficient relative to both the *para* and *meta* positions in the ground state and also to the *meta* position in the first excited state.²⁷ Photoinduced substitution would involve attack of pyridine at the electron-deficient carbon in Ib and subsequent expulsion of nitrite. In comparison to *p*-hydrogen or *p*-nitro, a *p*-methoxyl group or a similar electron-donating substituent should assist development of the



requisite charge distribution by donating electrons to the ring.²⁸ This mechanism differs from that conventionally used for nucleophilic displacement on ground-state aromatic molecules in that the pair of electrons joining the nitro group to the aromatic ring returns to the ring rather than departs with the leaving group. It predicts that the departing groups X, which are labilized by *p*-methoxyl groups in photoinduced substitution reactions, will be substituents capable of accepting electrons from the aromatic ring prior to fission of the C-X bond.

The role of a *nitro* group in labilizing a substituent at a *meta* position seems well pictured by the formulas (e.g., III), previously proposed^{5,8} for this type of reaction. In principle, the nucleophile could attack either the



aromatic carbon or the substituent group, displacing a negative ion *with* the bonding electrons.

(26) R. Grinter and E. Heilbronner, *Helv. Chem. Acta*, **45**, 2496 (1962).

(27) H. E. Zimmerman and V. R. Sandel, *J. Am. Chem. Soc.*, **85**, 915 (1963).

(28) The lack of reactivity of *p*-nitrophenol is ascribed to conversion of the phenol to the *p*-nitrophenoxide ion in the excited state (see previous discussion), and the lack of reactivity of the *p*-nitrophenoxide ion is attributed to the net negative charge on the ion, which greatly reduces the electrophilic character of the aromatic ring. It is interesting that 4-nitropyridine N-oxide, which is isoelectronic with *p*-nitrophenoxide yet has a net charge of zero, has been reported to react photochemically with piperidine.⁹

Experimental

Ultraviolet spectra were determined with a Cary Model 11 or a Beckman DU spectrophotometer. A Baird Model AB2 spectrometer was used for the infrared spectra; samples were pressed in potassium bromide disks. Melting points were determined with a Fisher-Johns apparatus. Elemental analyses were performed by the Micro-Tech Laboratories, Skokie, Ill.

Chromatography. Descending paper chromatography was carried out on Whatman 3MM paper with solvent A (isopropyl alcohol, concentrated ammonium hydroxide, and water in proportions 7:1:2 by volume). Aromatic compounds were observed by their fluorescence in ultraviolet light ($\sim 2537 \text{ \AA}$). Inorganic phosphate was detected as a reduced phosphomolybdate complex.²⁹ Characteristic R_f values for the reagents and products of the photochemical reactions are summarized in Table II.

Table II. R_f Values for Reagents and Photoproducts

Compd.	R_f^a
<i>o</i> -Phosphate	0.03
<i>p</i> -Nitrophenyl phosphate	0.30
<i>m</i> -Nitrophenyl phosphate	0.33
<i>p</i> -Nitrophenol	0.81
<i>m</i> -Nitrophenol	0.84
<i>p</i> -Nitroanisole	0.95
<i>p</i> -Dinitrobenzene	0.93
1-Phenylpyridinium ion	0.59
1-(<i>p</i> -Hydroxyphenyl)pyridinium ion	0.31 ^b
1-(<i>p</i> -Methoxyphenyl)pyridinium ion	0.61 ^c
1-Phenylpyridinium 4'-phosphate ion	0.04 ^c
1-(<i>p</i> -Methoxyphenyl)-4-methylpyridinium ion	0.64 ^c

^a The fluorescence was blue unless otherwise noted. ^b Yellow fluorescence. ^c White fluorescence.

Electrophoresis. The separations were carried out on Whatman 3MM paper with a Savant Flat Plate electrophoresis apparatus operated at 2000 v. The buffer solutions were 0.05 *M* in ammonium bicarbonate (pH 7.5), ammonium acetate (pH 4.2), sodium borate (pH 9.2), or sodium carbonate (pH 10.8). Typical results are indicated below, where the numbers refer to the distance moved by the compound in centimeters/hour at pH 4.2 and 9.2, respectively: *p*-nitrophenyl phosphate (−9, −19), 1-phenylpyridinium 4'-phosphate (−0.9, −9), 1-(*p*-hydroxyphenyl)pyridinium ion (+9, 0 at pH 10.8).

Reagents. Disodium *p*-nitrophenyl phosphate monohydrate was obtained from the Aldrich Chemical Co. It was homogeneous by the criteria of paper chromatography, thin layer chromatography on DEAE cellulose with 0.01 *M* hydrochloric acid, and high-voltage electrophoresis at three different pH values. Disodium *m*-nitrophenyl phosphate was prepared by hydrolysis of *m*-nitrophenylphosphorodichloridate³⁰ and neutralization of the product. It was homogeneous by paper chromatography and electrophoresis, and the ultraviolet spectrum agreed with that reported by Havinga, de Jongh, and Dorst.⁷ Other substrates were obtained from commercial sources and were recrystal-

(29) C. S. Hanes and F. A. Isherwood, *Nature*, **164**, 1107 (1949).

(30) M. Y. Kraft and V. V. Katyshkina, *Dokl. Akad. Nauk. SSSR*, **86**, 725 (1952); *Chem. Abstr.*, **47**, 8032 (1953).

lized from ethanol–water or ether–hexane prior to use; nitrobenzene was redistilled.

Apparatus and Kinetic Procedure. The reactions were carried out in a Pyrex jacketed vessel with an inside diameter of 5.7 cm. Temperature control was achieved by circulating water or ethylene glycol at constant temperature (Forma bath) through the jacket. Due to the heating effect of the photochemical lamp the temperature control during a run was of the order of $\pm 0.5^\circ$. The vessel was fitted through a 60/50 standard taper joint to a Pyrex cap equipped with entrance and exit ports for nitrogen, the exit port being angled so that aliquots could be removed without removing the cap. For a photochemical reaction this vessel with contents was placed in a light box 17 cm. below a 1200-w. G.E. photochemical lamp, which was cooled by a Vicor water condenser. The spectrum of the ultraviolet light emitted by this lamp and transmitted through the Vicor condenser and the Pyrex filter was measured with a Jarrell–Ash spectrometer. Since the bands were very sharp the data are summarized (in Table III) by indicating the number of bands in a given spectral region and the sum of the relative intensities.

Table III. Light Incident on the Reaction Mixture

λ , $m\mu$	No. of bands	Sum of relative band intensities
<280	0	0
280	1	0.02
289–303	6	0.87
312–313	2	2.5
334	1	1.0
364.9–366	3	14.5
404–408	2	7.5
434–436	3	7.7

Each kinetic run was made with 25 ml. of solution approximately 10^{-4} or 10^{-3} *M* in the nitro compound and 10^{-1} to 10^{-2} *M* in nucleophile. The solvent was generally either water or 22% aqueous *t*-butyl alcohol. The latter solutions, approximately 17.4% *t*-butyl alcohol by weight, were prepared by mixing 0.5 ml. of a solution of the nitro compound in *t*-butyl alcohol with 5 ml. of *t*-butyl alcohol, adding this to a solution of the nucleophile in water or suitable buffer, and diluting the mixture to 25 ml. with water. For reactions run in a nitrogen atmosphere the solvent was saturated with nitrogen by bubbling a stream of nitrogen through it, and, after addition of the substrate, the mixture was again swept with nitrogen. Thereafter a positive nitrogen pressure was maintained in the reaction vessel during irradiation. Rates of the photoinduced reactions were obtained by periodically withdrawing the vessel from the light zone, removing an aliquot of solution, and measuring the optical density at the absorption maximum for the substrate or at 400 $m\mu$ (when nitrophenol was a product) in a Beckman DU spectrophotometer. While the solution was out of the light zone no reaction occurred and the timer was stopped. Typically, the optical density changes were of the order of 0.5 absorbance unit. Pseudo-first-order rate constants, k_{obsd} , were obtained from plots of $\log(A - A_\infty)/(A_0 - A_\infty)$ vs. time, where A_0 , A_∞ , and A are the optical densities for the solution

at zero time, at completion of the reaction, and at intermediate times when the measurements were made. The data generally gave good first-order plots. In the case of the reactions of hydroxide ion with *p*-nitroanisole in a nitrogen atmosphere the reaction rates decreased somewhat faster than predicted at high conversions; in these cases the rate constants apply to the first 50% of reaction. The slopes and intercepts recorded in Table I were computed from k_{obsd} values by the least-squares method.

Product Isolation. The products of reactions carried out on a kinetic scale were characterized and separated by paper chromatography and electrophoresis. As further proof of their structure, several larger scale experiments were carried out in order that the reaction products could be isolated. The properties of compounds thus isolated corresponded in chromatographic and electrophoretic properties with those of the substances produced in the kinetic scale experiments. The larger scale experiments are described in this section.

A. Product from *p*-Nitrophenyl Phosphate and Pyridine. A solution containing 0.344 g. (1.15 mmoles) of disodium *p*-nitrophenyl phosphate monohydrate, 3 ml. of pyridine, and 22 ml. of water was irradiated for 7 hr. at 4°. Acidification of a small portion with sulfuric acid and addition of ferrous sulfate afforded a brown color, indicative of nitrite ion. The major portion of the solution was evaporated to dryness and the yellow-brown residue was taken up in 3 ml. of water. On addition of about 15 ml. of ethanol a salt precipitated. Dissolution in water and reprecipitation of the salt was repeated several times, and the final pale tan powder was collected and dried in air; weight, 0.11 g. (23%), λ_{max} 270 μ (ϵ 5.8×10^3) and 294 μ (ϵ 5.8×10^3). Significant features in the infrared spectrum include a strong band at 7.88 μ , which may be attributed to the P-O bond, and the absence of absorption between 7.1 and 7.6 μ , which indicates the absence of a nitro group. Disodium *p*-nitrophenyl phosphate monohydrate exhibits strong bands at both 7.88 and 7.37 μ . When the product was heated or an attempt was made to dehydrate it under vacuum over phosphorus pentoxide, it partially decomposed, yielding a reddish solid. The analysis of the air-dried sample corresponded to a hexahydrate of sodium 1-phenylpyridinium 4'-phosphate.

Anal. Calcd. for $\text{C}_{11}\text{H}_9\text{NNaO}_4 \cdot 6\text{H}_2\text{O}$: C, 34.86; H, 5.57; N, 3.68; P, 8.14. Found: C, 34.83; H, 5.02; N, 4.03; P, 8.46.

For further identification, a mixture of 0.1 g. of the photoproduct and 3 ml. of concentrated hydrochloric acid was heated in a sealed tube at 100° for 18 hr.; then the mixture was evaporated to dryness. Ethanol was added to the residue and the mixture was filtered to remove the insoluble inorganic salt. On addition of a saturated solution of picric acid in ethanol, 1-(*p*-hydroxyphenyl)pyridinium picrate precipitated, m.p. 199–200°. For comparison, the same compound was prepared from 1-(*p*-hydroxyphenyl)pyridinium chloride ($\lambda_{\text{max}}^{0.02 M \text{HCl}}$ 263 μ (ϵ 4.3×10^3) and 305 μ (ϵ 5.4×10^3) that had been synthesized from *p*-hydroxyphenol and 1-(2,4-dinitrophenyl)pyridinium chloride by the method of Grigor'eva and Yavlinskii.¹¹ The latter

sample melted at 199–200° and the mixture melting point was 199–200°.

B. Product from *p*-Nitroanisole and Pyridine. A solution containing 0.2 g. (1.3 mmoles) of *p*-nitroanisole, 20 ml. of pyridine, 100 ml. of *t*-butyl alcohol, and 400 ml. of water was irradiated for 3 hr. at 25°. The solution was taken to dryness and the residual solid was dissolved in a small quantity of ethanol. Picric acid in ethanol was then added until no further precipitation occurred. The solid derivative thus obtained weighed 0.2 g. (38%) and melted at 142–146°. After recrystallization from 95% ethanol it melted at 155.5–157.5° (lit.¹¹ m.p. for 1-(*p*-methoxyphenyl)pyridinium picrate 158°). On electrophoresis, spots for the picrate ion (–) and for an ion which moved as a +1 fragment were observed.

C. Product from *p*-Nitroanisole and 4-Methylpyridine. A solution containing 0.10 g. of *p*-nitroanisole and 2 ml. of 4-methylpyridine in 12 ml. of water and 36 ml. of *t*-butyl alcohol was irradiated for 2 hr. at 27°; then it was evaporated to dryness and the residue was taken up in ethanol. On addition of picric acid in ethanol, 1-(*p*-methoxyphenyl)-4-methylpyridinium picrate separated as yellow crystals, m.p. 158–160°, yield 0.154 g. (55%). For analysis the product was recrystallized three times from alcohol, m.p. 160–161°; the major bands in the infrared spectrum were found at 6.10, 6.43, 6.66, 7.31, and 7.60 μ .

Anal. Calcd. for $\text{C}_{15}\text{H}_{16}\text{N}_4\text{O}_8$: C, 53.27; H, 3.97; N, 13.34. Found: C, 53.27; H, 3.73; N, 13.14.

Reaction of *p*-Nitroanisole with Hydroxide. Two identical aqueous solutions $1.08 \times 10^{-4} M$ in *p*-nitroanisole and $0.012 M$ in sodium hydroxide were irradiated at 3° for 1200 sec. (10 half-lives). A nitrogen atmosphere was used for one and an air atmosphere for the other. The solutions were then evaporated almost to dryness on a flash evaporator and samples were spotted on Whatman 3MM paper. Descending chromatography with acetone–water–diethylamine (921:77:2) afforded two spots, R_f 0.88 (observed by yellow color) and 0.97 (observed as a brown color after spraying with an aqueous solution of *p*-nitrobenzenediazonium fluoroborate), for the reaction conducted under nitrogen. These spots correspond in appearance, chemical behavior, and R_f values to those for samples of *p*-nitrophenol and *p*-methoxyphenol. For the reaction conducted in air the same two spots were observed and, in addition, a small amount of a yellow material appeared at the origin in the chromatogram (R_f 0).

In another experiment, identical solutions of *p*-nitroanisole ($1.08 \times 10^{-4} M$) and sodium hydroxide ($0.012 M$) were irradiated for 1100 sec. at 26°; again nitrogen was the atmosphere for one and air the atmosphere for the other. The spectra for the final solutions are shown in Figure 6. It may be noted that the spectrum of the mixture from the reaction in nitrogen corresponds well with a spectrum calculated from the extinction coefficients for *p*-nitrophenol, *p*-methoxyphenol, and nitrite ion on the assumption that 82% of the reaction occurs with displacement of the nitro group (formation of *p*-methoxyphenol) and 18% by cleavage of the ether (formation of *p*-nitroanisole). (*p*-Methoxyphenol reacts slowly photochemically whereas *p*-nitrophenol is stable under these conditions;

the calculations were based on the absorbance of a solution of *p*-methoxyphenol in 0.012 *M* sodium hydroxide which had been irradiated for 800 sec. The correction is small.) The product of the oxygen reaction is seen to absorb most strongly in the 320–360- $m\mu$ region.

The effect of oxygen on the reaction rate is indicated in Table IV. Each value listed is an average of the rate constants for disappearance of nitroanisole (fol-

Table IV. Effect of Oxygen on Rate of Reaction of *p*-Nitroanisole with Hydroxide in Water

Temp., °C.	[OH ⁻], moles/l.	$10^3 \times k_{\text{obsd}}, \text{sec.}^{-1}$	
		Air	Nitrogen
3	0.008	3.52	3.60
3	0.012	4.63	4.84
3	0.020	6.70	6.51
26	0.012	4.55 ^a	3.67

^a Deviation $\pm 0.33 \times 10^{-3} \text{ sec.}^{-1}$; the rate measured at 400 was somewhat faster than that measured at 317 $m\mu$.

lowed at 317 $m\mu$) and appearance of nitrophenol (400 $m\mu$), the average deviation being $0.06 \times 10^{-3} \text{ sec.}^{-1}$.

Dinitrobenzene. A solution of dinitrobenzene ($4.29 \times 10^{-4} M$) and sodium hydroxide (0.02 *M*) in 22% aqueous *t*-butyl alcohol was irradiated at 3° for 6500 sec. in a nitrogen atmosphere. The absorbance change was relatively small; O.D.₃₁₀ decreased from 0.997 to 0.925 and O.D.₄₀₀ increased from 0.025 to 0.790. The increase at 400 $m\mu$ corresponds to formation of $0.43 \times 10^{-4} M$ nitrophenol, *i.e.*, 10% conversion of the dinitrobenzene. On this basis the initial rate of formation of *p*-nitrophenol was approximately $6.6 \times 10^{-9} \text{ mole/l./sec.}$ For comparison, the initial rate of reaction of *p*-nitroanisole, under the same conditions and for a concentration of nitroanisole ($1 \times 10^{-4} M$) for which the initial absorbance at 317 $m\mu$ equaled 1.0, was $6.9 \times 10^{-7} \text{ mole/l./sec.}$

The absorbance at 310 and 400 $m\mu$ did not change within the accuracy of the measurements when a solution of dinitrobenzene ($4.29 \times 10^{-4} M$) in 22% aqueous *t*-butyl alcohol buffered with pyridine–pyridine hydrochloride (0.118 *M* total pyridine) at pH 6.2 was irradiated for 5550 sec. A test for nitrite ion¹⁵ indicated that the extent of reaction was less than 2.2%.

Nitrobenzene. When a solution of nitrobenzene ($1.38 \times 10^{-3} M$) and sodium hydroxide (0.04 *M*) in 22%

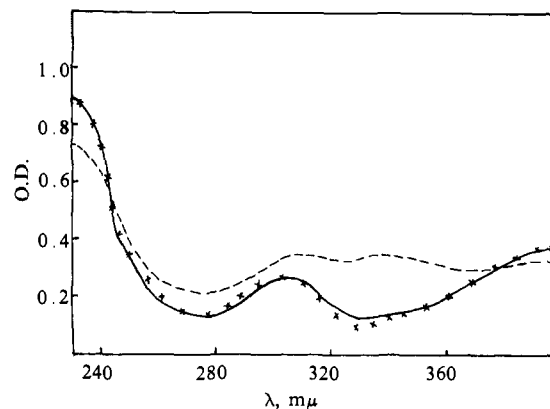


Figure 6. Spectrum of products of reaction of *p*-nitroanisole and hydroxide: —, nitrogen atmosphere; ---, air atmosphere; ×, calculated curve if products are *p*-nitroanisole (18%) and *p*-methoxyphenol (82%).

aqueous *t*-butyl alcohol was irradiated at 26° for 9500 sec., only small changes in the absorbance took place; O.D. at 310, 260, and 235 $m\mu$, respectively, decreased from 1.62, 0.77, and 0.335 to 1.56, 0.65, and 0.28. Since at 235 $m\mu$ ϵ for nitrobenzene is 3.5×10^3 whereas ϵ for the phenoxide ion is 1.06×10^4 , the absorbance at 235 should have increased if hydroxide had displaced the nitro group. The small spectral changes that occurred may indicate some type of photoinduced reaction; however, the rate is extremely slow compared to the photoinduced reactions of *p*-nitroanisole.

For the test with pyridine a solution of nitrobenzene ($3.07 \times 10^{-3} M$) and pyridine (0.2 *M*) in 22% aqueous *t*-butyl alcohol was irradiated for 18,000 sec. at 26°. On evaporation no charged products could be detected by electrophoresis. 1-Phenylpyridinium chloride³¹ was prepared independently as a control. The cation migrated normally on electrophoresis and was easily detected by its fluorescence.

***p*-Nitrophenol.** A solution of *p*-nitrophenol ($1.33 \times 10^{-4} M$) and pyridine (0.11 *M*) in 22% aqueous *t*-butyl alcohol at pH 6.2 was irradiated for 7500 sec. No change in the spectrum was noted after 2000 sec. After 7500 sec. of irradiation a slight decrease was noted in the optical density at both 321 (1.207 to 1.174) and at 400 $m\mu$ (0.315 to 0.304); however, concentration of the solution and electrophoresis revealed no materials other than *p*-nitrophenol.

(31) T. Zincke, *Ann.*, 333, 329 (1904).