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LIGHT ATTENUATION BY PHOTOCHEMICAL MEANS:
PHOTOCHROMISM

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INTRODUCTION

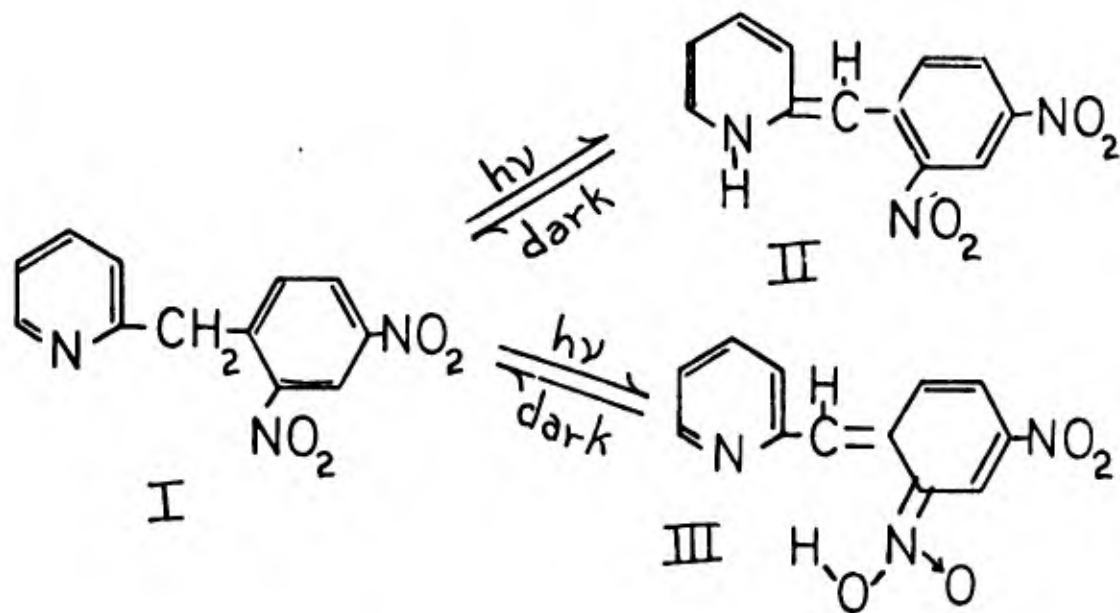
Photochromism, a fascinating phenomenon in itself, is also of great industrial and military interest. Photochromic materials change color when exposed to visible and/or ultraviolet light and revert to their original color when the irradiating source is removed. They can adjust their color automatically and rapidly according to the wavelength and intensity of the irradiating light. This capability suggests their potential use in protective eye lenses for the prevention of flashblindness, such as occurs when the intense light of a nuclear explosion strikes the retina.

Our work in this area involved a fundamental study of the phenomenon of photochromism, and began with the investigation of a system about which little was known.

The photochromic change from a pale yellow to a deep blue color observed when crystals of 2-(2,4-dinitrobenzyl)pyridine (I) are exposed to light was first reported in 1925 by Tschitschibabin and co-workers (1). They also observed that the crystals fade slowly to yellow when stored in the dark. At room temperature the half-life for this fading process was found to be approximately 6 hours (2). Several groups of workers (2), (3), (4) measured the activation energy for the fading reaction in the solid state and reported values ranging from 15 to 24 kcal./mole. The fading process is much faster for solutions of I, and it was not until 1960 that Hardwick, Mosher and Passailaigue (3) observed the photochromism of cooled solutions of the compound in a variety of solvents.

The mechanism of the color change was ascribed by early workers (1), (2), (3) to the tautomeric shift $I \rightleftharpoons II$. However, they also considered the structural change $I \rightleftharpoons III$ to be an alternative possibility.

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Our study was undertaken in order to help elucidate the mechanism of the color change by investigating the relationship of structure to photochromism and to the kinetic and thermodynamic properties of the dark reaction. This work established the essential structural features required for photochromism (5) and, together with the observations of others (6), (7), (8), supports the proposal that the formation of the aci-nitro compound (III) is responsible for the color change produced on irradiation. In addition, this work led to the discovery of a new class of photochromic nitro compounds.

RESULTS AND DISCUSSION

ortho-Nitrobenzyl Compounds. — The spectra in ethanol at -70.0° of the colored isomers of 2-(2,4-dinitrobenzyl)pyridine and 2-(2-nitro-4-cyanobenzyl)pyridine produced by ultraviolet irradiation are shown in Fig. 1. The rate of disappearance of color was followed at λ_{\max} of each absorption band. Measurements were made at low temperatures in the range -111 to -42.0° utilizing a specially designed cryostat, and at room temperature by flash photolysis techniques. First-order kinetics was observed for the fading reaction of both compounds in all the solvents employed. Illustrative plots are given in Fig. 2. For the cyano compound values of the first-order specific rate constant, k , measured at λ_{\max} of each band were found to be the same. The four observed absorption bands are, therefore, due to the same phenomenon.

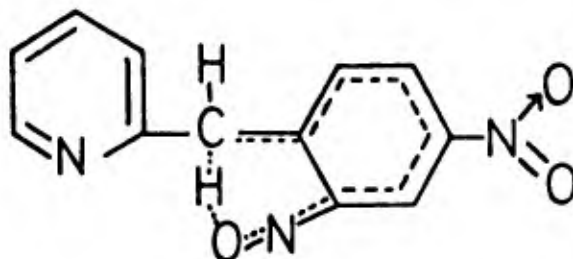
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In Table I the Arrhenius activation energies and the calculated entropies of activation are given for the fading reaction. A large decrease in entropy was observed for the formation of the

TABLE I
Values of E_{exp} and ΔS^* for the Fading Reaction

4 Substituent	Solvent	E_{exp} (kcal/mole)	ΔS^* (e. u.)
NO_2	Ethanol	5.8 ± 0.1	-44
NO_2	Ether	$4.8 \pm .1$	-47
$\text{C}\equiv\text{N}$	Ethanol	$4.7 \pm .1$	-46

activated complex. The structure in the activated state is, therefore, probably more rigid than in the ground state. The following structure may approximate that of the activated complex. It is of



interest that the values of E_{exp} fall in the range normally observed for the energy of hydrogen bonds (9).

The effect of solvent on the rate of the fading reaction was investigated for the dinitro compound by flash photolysis measurements at room temperature. The data is summarized in Table II.

TABLE II

Values of k for the Fading Reaction of 2-(2,4-Dinitrobenzyl)pyridine in Various Solvents at Room Temperature.

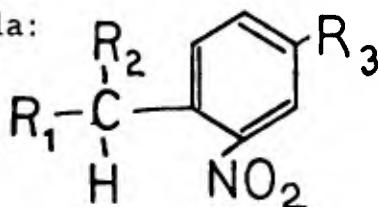
Solvent	$k_{\text{sec.}}^{-1}$
Ethyl alcohol	0.122
Isobutyl alcohol	.277
sec-Butyl alcohol	1.42
t-Butyl alcohol	0.153
Ether	.197
Benzene	15.2
Isooctane	1.02×10^3

While the rate of reaction does not differ greatly in the alcohols and in ether, it is seen to increase considerably in benzene and is 10^4 times greater in isooctane than in ethanol. This marked rate change may be explained on the basis of differences in solvation in the ground state (5).

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In addition to this solvent effect, the rate of fading is greatly affected by the acidity of the medium. For the dinitro compound in water, a 10^5 fold variation in rate constant was observed over the pH range 2 to 12 (10).

The relationship between structure and photochromism was investigated. Structural considerations are tabulated below for the following general formula:



Case	R_1	R_2	R_3
1	pyridine	H	$C\equiv N$
2	pyridine	H	NH_2
3	pyridine	H	H
4	OH	H	NO_2
5	$O-C-CH_3$	H	NO_2
6	pyridine	OH	NO_2
7	oxidation to ketone		

Replacing the p- NO_2 group with other substituents (R_3) as in cases 1, 2, and 3, or the pyridine ring by other groups (R_1) in situations 4 and 5, or one of the methylene hydrogen atoms (R_2) as in case 6 does not destroy photochromic properties. However, removal of both hydrogens by oxidation (case 7) to 2-(2,4-dinitrobenzoyl)pyridine does. Moreover, when the o- NO_2 group is absent, as in 2-p-nitrobenzylpyridine, photochromic properties are lost. It may be concluded that for compounds of the type under consideration, the essential structural feature for the isomerization is the presence of a nitro and a $\geq C-H$ group ortho to each other. This conclusion was further substantiated when o-nitrotoluene was found to be photochromic (11).

In our early work it was found that the fading reaction in ethanol was faster for the p-cyano compound than for the dinitro compound (5). This observation prompted us to prepare a series of compounds with various substituents in the para-position of the benzene ring and study the effect of these para-substituents on the rate of the dark reaction (12), (13).

Rate measurements were carried out in ethanol at room temperature by flash photolysis techniques. In every case studied, the fading process was found to follow first-order kinetics. The values of the rate constant, k , for the fading reaction are listed in Table III and are seen to be markedly sensitive to the electronegativity of the para-substituent. For example, in going from NO_2 to

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NH₂ the value of k is enhanced by a factor of 10⁴. Also, the rate constant is almost 500 times greater when H rather than NO₂ is the para-substituent.

The greater the electron-repelling power of the substituent, the faster the reaction proceeds. In Fig. 3, log k values are shown to be linearly proportional to Hammett σ_p values (14). The value of the reaction constant (ρ) for the least square line is -2.85, and the correlation coefficient for the line is 0.986.

TABLE III

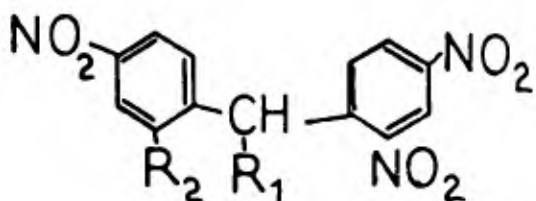
Values of k and $t_{\frac{1}{2}}$ for the Fading Reactions of 2-(2-Nitro-4-substituted benzyl)pyridine in Ethanol at 25^o.

4-Substituent	k sec ⁻¹	$t_{\frac{1}{2}}$ millisec.	σ_p (a)
NH ₂	370 NO	0.187	-0.660
OH	329	2.11	-.357
H	56.3	12.3	0
Cl	27.4	25.3	0.227
CO ₂ ⁻	26.3	26.3	.132
CONH ₂	5.94	117	
CO ₂ ET	2.45	283	.522
CO ₂ Me	2.42	.286	.463
C≡N	1.17	592	.628
NO ₂	.122	568 x 10 ¹	.778

^aValues given by H. H. Jaffe, Chem. Revs., 53, 222 (1953) except the value for the CO₂Me Group, which was determined by H. Van Beckum, P. E. Verkade, and B. M. Wepster, Rec. trav. chim. 78, 815 (1959).

The observed substituent effect is probably due to differences in energy of activation, since it was found previously (Table I) for the dark reactions of the *p*-C≡N and *p*-NO₂ derivatives that the energy of activation differs while the value of the entropy of activation is the same (5).

We prepared another group of *o*-nitrobenzyl compounds of the following type and investigated photochromic properties (15).



Colorless ethanolic solutions of these compounds (listed in Table IV) change to an intense blue color when irradiated with ultraviolet light in the cold.

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Table IV gives the values of the first-order specific rate constant, k , for the fading reactions of IV-VII determined in ethanol at -50° , the Arrhenius activation energies, and the calculated entropies of activation. The thermodynamic properties of these reactions are very close in value and are similar to those observed for the benzylpyridines. The mechanism of fading is, therefore, probably the same for all these compounds.

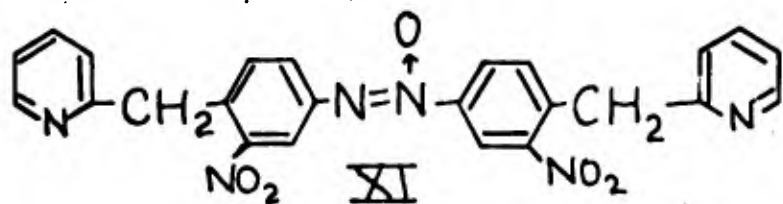
TABLE IV

Values of k , E_{exp} , and ΔS^* for the Fading Reaction in Ethanol

Compound		$k \times 10^3$ sec^{-1} (at -50°)	E_{exp} kcal./mole	ΔS^* e. u.
R_1	R_2			
IV C00Me	NO ₂	6.03	5.6 ± 0.1	-45
V C00Et	NO ₂	0.785	5.4 ± 0.1	-50
VI H	H	0.695	5.4 ± 0.1	-50
VII H	NO ₂	2.84	5.5 ± 0.1	-47
IX C00Me	H	(a)		
X C00Et	H	(a)		

^a The fading reaction was too rapid for acceptable measurements to be made over a wide temperature range.

In the course of our synthetic program, 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene (XI) was prepared (12). It was found that ultraviolet irradiation of this compound produces two reversible photoisomerizations (16).



The ultraviolet and visible spectra of an ethanol solution of XI before and after exposure to ultraviolet light are shown in Fig. 4. The absorption band in the visible region at $610 \text{ m}\mu$, observed after irradiation of the cooled solution, is similar in shape to the visible band observed for the photoisomer of 2-(2,4-dinitrobenzyl)pyridine (Fig. 1). This band decays rapidly by first-order kinetics when the exciting radiation is removed. Values of k were measured over a temperature range of 132° by cryoscopic and flash photolysis techniques. The values of the Arrhenius activation energy, entropy of activation and frequency factor were found to be $5.9 \pm 0.1 \text{ kcal./mole}$, -39 e.u. , and $4.2 \times 10^4 \text{ sec}^{-1}$, respectively. These values are consistent with those previously found for the thermal fading reaction

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of the photoisomers of 2-(2,4-dinitrobenzyl)pyridine (Table I) and other *o*-nitrobenzyl compounds (Table IV).

In the ultraviolet spectrum (Fig. 4) of the unirradiated sample, absorption bands are observed at 330 and 260 m μ . The effect of ultraviolet light on these bands can be observed at room temperature. The band at 330 m μ decreases markedly in intensity, while the absorbance at 260 m μ increases slightly. After irradiation the spectrum slowly reverts to that originally observed. The ultraviolet spectra before and after exposure closely resemble those reported (17) for the pure trans and cis isomers, respectively, of azoxybenzene and several of its derivatives. This geometrical isomerization also occurs at low temperatures. The thermal cis-trans isomerization, measured after irradiation by observing the increase in absorbance of the 330 m μ band with respect to time, was found to follow first-order kinetics in both ethanol and cyclohexane. Thermodynamic data for this reaction are presented in Table V.

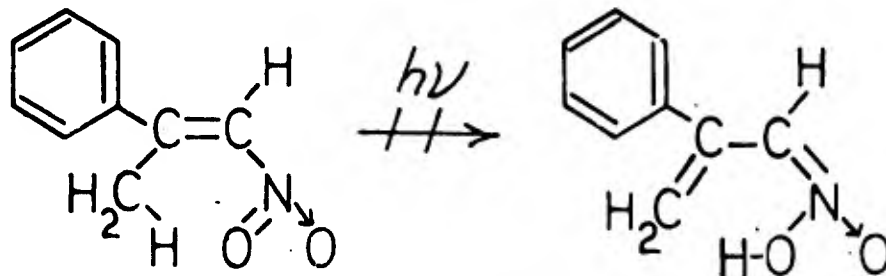
TABLE V

Thermodynamic Properties of the cis-trans Isomerization of
3,3'-Dinitro-4,4'-Di(2-Pyridylmethyl)Azoxybenzene

Solvent	E_{exp} , kcal/mole	ΔS^* , e. u.	A , sec. ⁻¹
Ethanol	23.1 \pm 0.1	0.79	2.6 $\times 10^{13}$
Cyclohexane	23.6 \pm 0.1	6.7	4.9 $\times 10^{14}$

The values of E_{exp} agree closely with those found by Luner and Winkler (18) for the isomerization of pure cis-azoxybenzene and cis-p,p'-azoxytoluene in the same solvents. For azoxybenzene in ethanol, we found the energy of activation to be 22.9 kcal/mole, the same value as that reported by the above workers.

1-Aryl-2-nitroalkenes. — We investigated the possibility of observing photochromism arising from a nitro \rightarrow aci-nitro tautomerization on an unsaturated side chain of an aromatic system, according to the following scheme.



While it was found that this transformation does not occur, the work led to the observation that many 1-aryl-2-nitroalkenes are photochromic when the aryl and nitro groups are cis with respect to each

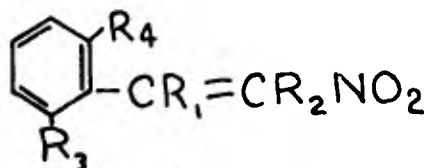
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other (19). The trans isomers, which are not photochromic, are converted to the cis isomers by a short irradiation period with ultraviolet light. Table VI lists the compounds studied.

Compounds XII-XVI are initially isolated from their chemical preparations in the trans form. Only after a short irradiation period do they become photochromic. Compound XVII, isolated as the cis isomer was found to be photochromic without preirradiation.

Compounds XVIII, XIX, and XXI can exist in only the configuration in which nitro and aryl groups are cis to each other. These three are photochromic without preirradiation.

TABLE VI



Compound	R_1	R_2	R_3	R_4
XII	H	H	H	H
XIII	Me	H	H	H
XIV	H	C ₆ H ₅	H	H
XV	H	H	OCH ₃	H
XVI	CH ₂ C ₆ H ₅	C ₆ H ₅	H	H
XVII	NO ₂	C ₆ H ₅	H	H
XVIII	C ₆ H ₅	H	H	H
XIX	C ₆ H ₅	C ₆ H ₅	H	H
XX	H	H	NO ₂	H
XXI	-CH ₂ CH ₂ CH ₂ -CH ₂ -		H	H

The fading reactions of some of the compounds were studied by flash photolysis and were found to follow first-order kinetics. Rate constants are listed in Table VII.

TABLE VII

Values of k for the Fading Reaction in Ethanol at Room Temperature

Compound	$k, \text{sec.}^{-1}$	$\lambda, \text{m}\mu$
XII	1490	415
XIII	7600	425
XIX	578	440
XXI	564	420

For the dark reaction of XXI in ethanol the activation energy was found to be 12.4 kcal./mole, and the entropy of activation was calculated to be -6.8 e. u.

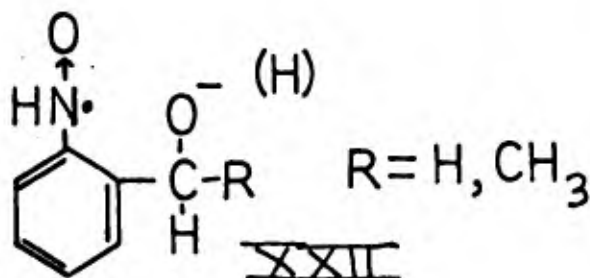
Details of the scope and mechanism of this new photochromic reaction are being investigated in these laboratories.

Photochemical Generation of Free Radicals. — An investigation was undertaken to determine whether free radicals are involved in the photochromic or photochemical reactions of aromatic nitro compounds.

Electron spin resonance measurements of 2-(2,4-dinitrobenzyl)pyridine irradiated in ethanol and of 2-o-nitrobenzylpyridine irradiated neat did not detect the formation of free radicals. However, free radicals were observed when o-nitrotoluene, o-nitroethylbenzene and o-nitrocumene were irradiated neat or in ethanol solution. Long-lived radicals were observed in either the presence or absence of oxygen. The concentration of radical formed from these compounds for a given period of exposure to ultraviolet light was in the order:

o-nitrocumene >> o-nitroethylbenzene > o-nitrotoluene

These free radicals appear to be too stable to be involved in the photochromic reactions of these compounds. They may, however, be of importance in the photoinduced decomposition processes. The radicals are identified as phenyl nitroxides (XXII) by comparison



with the hyperfine splitting constants observed previously for phenyl nitroxide in dimethyl sulfoxide-*t*-butyl alcohol (20) and for phenyl nitroxide-*o*-carboxylate in absolute alcohol (21). This interpretation also accounts for the 40 line spectrum observed for o-nitroethylbenzene and the 39 line spectrum observed for o-nitrocumene.

SUMMARY

1. It was shown that the photochromism of 2-(2,4-dinitrobenzyl)pyridine, first observed in 1925, is not limited to this compound, but is the common property of a class of aromatic nitro compounds which possesses certain structural characteristics:

2. The unique structural feature of these photochromic aromatic nitro compounds was shown to be the presence of a nitro and a >C-H group ortho to each other.

3. Utilizing cryoscopic and flash photolysis techniques, the dark fading reaction of all the o-nitrobenzyl compounds studied was found to follow first-order kinetics in a wide variety of solvents. Also, the thermodynamic properties of the fading process

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were evaluated.

4. Solvents were found to have a marked effect on the rate of the fading reactions. This effect is explained on the basis of solvation differences in the ground state.

5. Substituents in the para position of the aromatic ring of *o*-nitrobenzylpyridines were shown to exert a significant effect on the rate of the fading reactions. Log *k* values determined for ethanol solutions were shown to be linearly proportional to the Hammett σ constants of the substituents.

6. It was shown that on irradiation with ultraviolet light, 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene undergoes simultaneously aci-nitro-nitro tautomerization and geometrical isomerization.

7. A new class of photochromic nitro compounds was discovered. The essential structural requirement for photochromism in these 1-aryl-2-nitroalkenes is that the nitro and phenyl groups bear a cis relationship with respect to each other.

8. It was shown that some of the simpler *o*-nitrobenzyl compounds, such as *o*-nitrotoluene, are not only photochromic, but give relatively stable free radicals when irradiated with ultraviolet light. These radicals were identified as phenyl nitroxides.

EXPERIMENTAL

Materials. — The procedures used to prepare the compounds for this investigation were reported previously (5), (12), (13), (15), (16), (19).

Samples used for rate studies were recrystallized or redistilled at reduced pressure before use. "Spectro Grade" solvents dried further by conventional methods were used. Solutions approximately 10^{-3} M were used for the low temperature rate studies. For experiments at room temperature solutions were approximately 10^{-4} M.

Ac-Nitro-Nitro Tautomerism. — The rate studies at low temperatures in the range -110.0 to -40.0° were carried out in either a 1.0 or 2.5-cm. cell maintained at the required temperature in a specially constructed cryostat (28). Solutions cooled in the cryostat were exposed for 15-30 sec. to the unfiltered radiation from a General Electric H3FE 85-watt mercury lamp with a pyrex glass envelope. Uniform coloring of the solutions was observed. The cryostat was quickly transferred to the sample cell compartment of a Cary Model 14 spectrophotometer and the decrease in absorbance of the visible absorption band at λ_{\max} followed with respect to time. A matched cell containing pure solvent was in the reference beam. In all cases, the absorbance of the system ultimately fell to zero. At least

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three runs were made at each temperature.

Room temperature measurements were carried out by flash photolysis techniques (23). Solutions were contained in a 20-cm. cell surrounded by a cupric sulfate filter which absorbed all light less than 3200 Å in wave length. The optical transmission at λ_{\max} was recorded after flashing once with a flash energy of 2400 joules. In all cases, the transmission of visible light ultimately reached practically 100%. At least two experiments were made to determine the rate in each solvent.

Geometrical Isomerization. — Rate measurements in the temperature range 11 to 50° were carried out in a 2.5-cm. cell on solutions ($\sim 10^{-5}$ M) in ethanol and cyclohexane. Required temperatures were maintained by circulating water from a Haake temperature-regulating bath through a thermostatable cell jacket (24). Solutions were exposed for 30 sec. to the radiation from the lamp described above, and the cell was quickly transferred to the sample compartment of the spectrophotometer. For both compound XI and azoxybenzene, the increase in absorbance of the ultraviolet absorption band at 330 m μ was followed with respect to time. A matched cell containing pure solvent was in the reference beam. In all cases, the absorbance at 330 m μ ultimately returned to its value before irradiation.

Temperature Measurement. — Measurements of temperatures were made by a glass encased copper-constantan thermocouple which dipped into the solutions at the cell neck.

Calculations. — Values of the first-order specific rate constant, k , were calculated from the slope of the straight line obtained in plots of $\log D_t - D_\infty$ vs. time, where D_t is the optical density at a given time interval and D_∞ is the optical density after complete isomerization. In the case of the aci-nitro-nitro isomerization D_∞ was equal to zero. The reactions were followed for at least three half-lives. The Arrhenius activation energy, E_{exp} , the entropy of activation ΔS^* , were calculated by procedures given previously (5).

Ultraviolet and Visible Absorption Measurements. — A Cary Model 14 spectrophotometer was used. Solutions were measured in a 1.0- or 2.5-cm. cell against a reference of pure solvent in a matched cell.

Electron Spin Resonance Measurements. — Spectra were taken with a Varian V-4502 E.P.R. spectrometer equipped with a 9-inch magnet. Irradiations were performed with a Bausch and Lomb SP 200 mercury lamp using unfiltered light.

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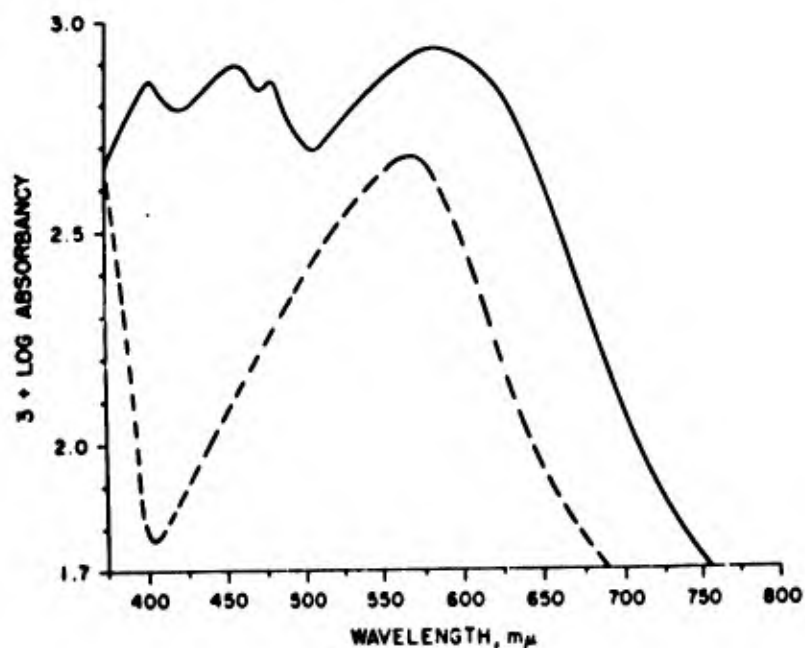


Fig. 1. — Visible absorption spectra of irradiated ethanol solutions of 2-(2,4-dinitrobenzyl)pyridine (-----), and 2-(2-nitro-4-cyanobenzyl)pyridine (—) measured at -70.0° . The ordinate is in arbitrary units.

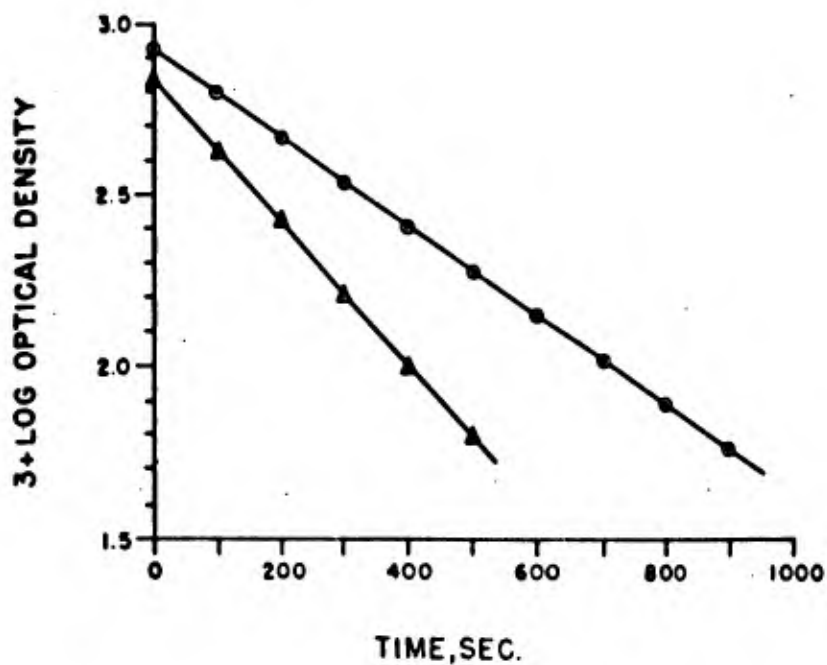


Fig. 2. — The fading reactions in absolute ethanol of irradiated 2-(2,4-dinitrobenzyl)pyridine at -50.9° , Δ ; and 2-(2-nitro-4-cyanobenzyl)pyridine at -87.8° ; O.

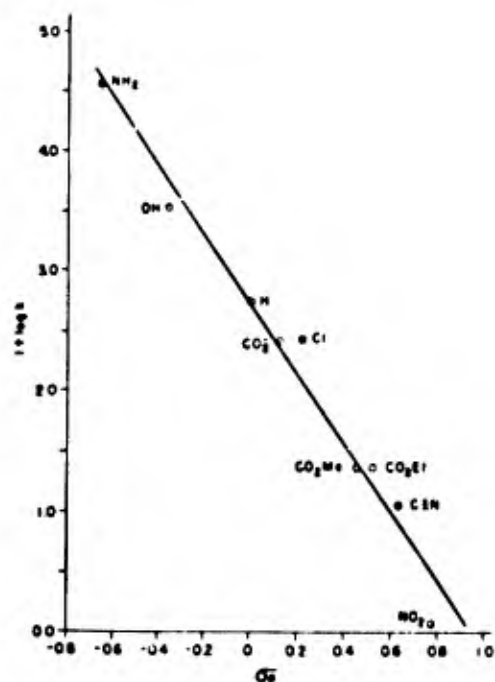


Fig. 3. — Plot of $\log k$ values versus Hammett σ_p -constants.

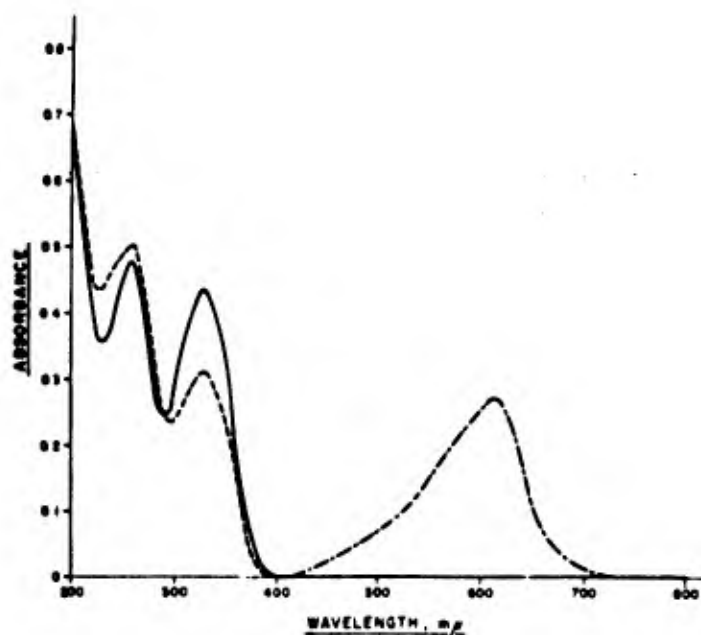


Fig. 4. — Absorption spectra of an ethanol solution of 3,3'-dinitro-4,4'-di(2-pyridylmethyl)azoxybenzene; —, ultraviolet and visible spectra before irradiation; ----, ultraviolet spectrum after irradiation for 3 min. at 25.0°; - · - · - ·, and visible spectrum after 1 min. at -90.0°.