Electron Spin Resonance and Luminescence Studies of the Reaction of Photochemically Generated Nitrenes with Oxygen. Phosphorescence of Nitrobenzenes

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Abstract: Photolysis of *p*-diazidobenzene (I) in hydrocarbon solvents at 77°K results initially in the formation of the corresponding mononitrene II. This nitrene undergoes a slow chemical reaction (at 77°K in the dark) with molecular oxygen to form two different oxygen adducts. One of these adducts is a ground state triplet to which we have assigned the *p*-azidophenyliminodioxy diradical structure Va. The second species is diamagnetic and has been assigned the dipolar nitroso oxide structure Vb. On photolysis, Va and Vb yield *p*-nitrophenyl azide and continued photolysis leads to the formation of a phosphorescent diamagnetic material which is shown to be an *N*-alkyl-*p*-nitroaniline. A chemical reaction scheme is developed based on these observations. Photolysis of other azides and their subsequent reaction with oxygen is also discussed.

In a previous communication[1] we reported that the low-temperature photolysis of *p*-diazidobenzene (I) results in the formation of three triplet ground state species, 1-azido-4-nitrenobenzene (II), *p*-dinitrenobenzene (III), and 4,4′-dinitrenoazobenzene (IV). An additional triplet ground state species is formed in variable amounts in these photolyses. This is characterized by its esr spectrum, with $D^* = 0.110$ cm^{-1}. It was further reported that the intensity of this esr signal was greatly increased when nondegassed but stoppered solutions containing II and IV were allowed to stand in the dark at 77°K for several hours.

In this paper we report on the nature of this species, the mechanism by which it may be formed, and an account of the optical, esr, and luminescence studies that have led to its characterization.

Experimental Section

Photolysis experiments were performed in 3-methylpentane, methylcyclohexane, and ethanol at 77°K and the resulting esr spectra were measured using a Varian 4502 spectrometer equipped with a 9-in. magnet and Fieldial. Optical absorption spectra were measured during the course of the photolysis using a Cary Model 14 spectrophotometer which was modified to accommodate the liquid N_2 dewar used in the esr experiments. Total luminescence spectra were measured on apparatus which has previously been described in the literature.[2]

p-Diazidobenzene, 4,4′-diazidoazobenzene, and *p*-nitrophenyl azide, *p*-anisyl azide, and *p*-*N*,*N*-dimethylphenyl azide were prepared by procedures[3] described in the literature and were characterized by their infrared, ultraviolet, and nmr spectra. Para-substituted nitrobenzenes (methyl, methoxyl, amino, dimethylamino, bromo, and nitro) were obtained commercially and were purified by recrystallization before use.

Results of Spectroscopic Measurements. The esr spectrum of a dilute solution of *p*-diazidobenzene (I) in 3-methylpentane at 77°K which has been irradiated with 365-nm light is represented by the upper curve in Figure 1. This spectrum shows the presence of *p*-dinitrenobenzene (III) ($D^* = 0.172$ cm^{-1}) and 1-azido-4-nitrenobenzene ($D^* = 0.932$ cm^{-1}) in addition to a small amount of radical centered at $g = 2.00$. When the sample is kept at 77°K overnight in the dark in a stoppered but nondegassed tube the spectrum shown in the lower curve in Figure 1 is obtained. In addition to the growth of the new spectrum, the intensity of the 1-azido-4-nitrenobenzene spectrum is markedly reduced. The species giving rise to this spectrum is characterized by $D^* = 0.110$ cm^{-1}.

Corresponding changes in the optical absorption spectrum were also observed. Figure 2 shows the long wavelength absorption spectra of II (curve A) and of the same frozen solution after standing in the dark for ~4 hr (B) and ~24 hr (C). Note the marked decrease in the intensity of the sharp absorption band at ~330 nm which belongs to II and the two new bands at ~365 and 350 nm. When the sample is irradiated with visible light (436 nm), the broad intense visible absorption band is destroyed (curve D) but the esr spectrum remains unchanged; the concentration of the $D^* = 0.110$ cm^{-1} species is unaffected. It thus appears that II undergoes a dark chemical reaction and forms both a diamagnetic yellow species as well as a paramagnetic species.

Three additional significant observations were noted when the above solutions were subjected to irradiation by 313-nm light. First, a marked decrease in the intensity of the esr signal from the $D^* = 0.110$ cm^{-1} species as a function of irradiation time was observed. Second, the esr spectrum corresponding to II (~6700 *g*) was intensified together with another line in this region, presumably from another mononitrene species. The third observation and perhaps the most significant in terms of structural clue, was a blue-green delayed emission which grew in as the sample was continuously being irradiated. This luminescence is from a photoproduct of the $D^* = 0.110$ cm^{-1} species. An excitation spectrum revealed that the maximum emission intensity would be obtained by excitation in the 360- to 375-nm region. The emission observed from this solution (in 3-methylpentane) shown in Figure 3 has a lifetime of 0.17 sec. The structural characteristics of the spectrum are so unique that we have used (*vide infra*) it as a fingerprint in the elucidation of the structure of the $D^* = 0.110$ cm^{-1} intermediate.

In order to determine the role of oxygen in the formation of the new species, the photolysis of *p*-diazidobenzene (I) was carried out in dry solvents (distilled over $LiAlH_4$ directly into the esr tube) in the presence and absence of oxygen under carefully controlled conditions. Aliquots were degassed on a vacuum line using the freeze-and-thaw technique; the samples were frozen to 77°K and then photolyzed in the esr cavity. The esr spectra (low field) from a nondegassed sample (in 3-methylpentane) which has been irradiated for a relatively long period (~30–60 sec) are shown (Figure 4) as a function of the standing time in the dark at 77°K. The lines indicated by the arrows belong to the species formed by the dark reaction. It should be noted that a small amount of this species is also formed during the initial photolysis as reported by Trozzolo, *et al.*[4] In degassed solutions, however, these lines are totally absent. Only the lines belonging to *p*-dinitrenobenzene ($D^* = 0.172$ cm^{-1}) and 4,4′-dinitrenoazobenzene ($D^* = 0.059$ cm^{-1}) are observed.

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[1] B. Singh and J. S. Brinen, *J. Amer. Chem. Soc.*, **93**, 540 (1971).

[2] J. B. Gallivan, *Mol. Photochem.*, **2**, 191 (1970).

[3] The azido compounds used in this work are known compounds, and they were prepared by the reaction of diazonium fluoroborates with aqueous sodium azide.

[4] (a) A. M. Trozzolo, R. W. Murray, G. Smolinsky, W. A. Yager, and E. Wasserman, *J. Amer. Chem. Soc.*, **85**, 2526 (1963); (b) the dinitrene III may also be reacting with oxygen; however, we did not observe any signals corresponding to the expected adduct. Since *p*-dinitrobenzene does not emit, its formation under these conditions would not have been detected under our analytical technique.

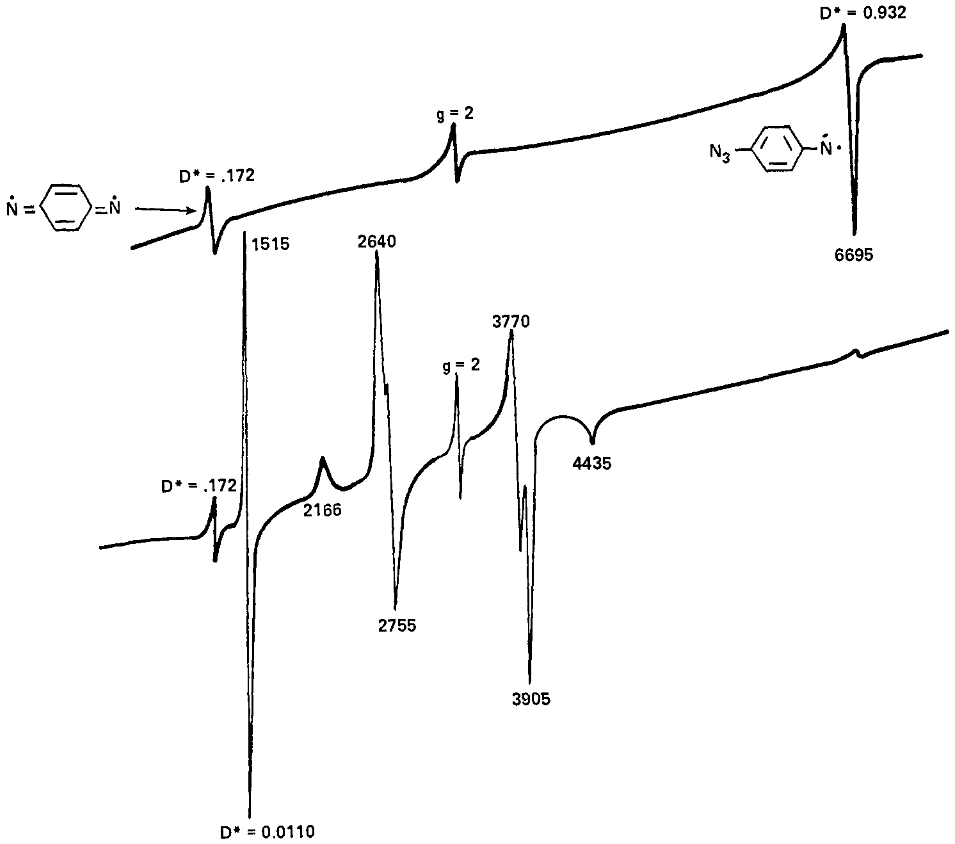


Figure 1. Top. The esr spectrum obtained from the photolysis of *p*-diazidobenzene in aerated 3MP at 77°K. The field positions given are in gauss, while the species are identified by the ZFS parameter D^* (in cm^{-1}). Bottom. The spectrum obtained when the above solution is left standing for 24 hr in the dark at 77°K.

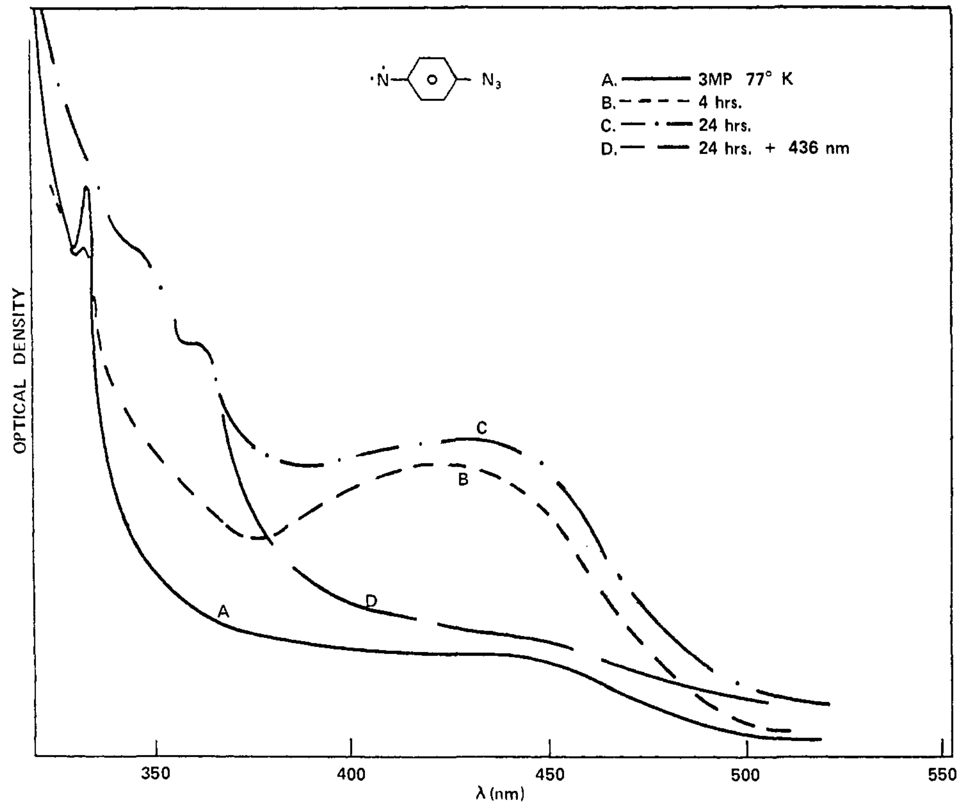


Figure 2. The low-temperature absorption spectrum of a photolyzed solution of *p*-diazidobenzene in aerated 3MP, at 77°K. Curve A is that of 1-nitreno-4-azidobenzene; curve B is the spectrum measured after 4 hr in the dark at 77°K; curve C is measured after 24 hr in the dark at 77°K; and curve D is that obtained from solution C after photolysis with 436-nm light.

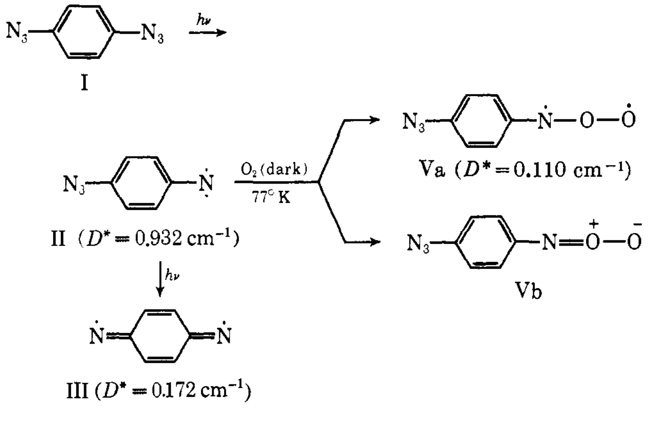
The same phenomenon is observed in methylcyclohexane showing that the transformation is independent of the hydrocarbon solvent used. Figure 5 shows the comparison of degassed and nondegassed solutions (methylcyclohexane) of I which have been irradiated under identical conditions and then allowed to stand at 77°K in the dark for 48 hr. Note again that the $D^* = 0.110\ \mathrm{cm}^{-1}$ species (arrow) is absent in the degassed sample. Also in the degassed solutions, the line due to the mononitrene (II) remains relatively unchanged on standing in the dark whereas for nondegassed solutions this line disappears with time with a corresponding increase in the intensity of the $D^* = 0.110\ \mathrm{cm}^{-1}$ species. Similar results were obtained in alcoholic solutions. It should be mentioned, however, that the extent of the dark reaction was much greater in 3-methylpentane than in methylcyclohexane glasses. This is presumably due to the different solubility and different rates of diffusion of oxygen in the two solvent matrices at 77°K.

On further irradiation (313 or 365 nm) the nondegassed solution containing the $D^* = 0.110\ \mathrm{cm}^{-1}$ species begins to luminesce. The luminescence intensity increases with time and is accompanied by a decrease in the intensity of the esr spectrum belonging to $D^* = 0.110\ \mathrm{cm}^{-1}$ species. The esr spectra measured after these luminescence spectra were obtained revealed two mononitrene signals in the nondegassed solution and only a single mononitrene (II) line somewhat intensified in the degassed sample.

The emission observed in alcoholic solutions was different from that observed in hydrocarbon solvents. The degassed solutions (which do not contain the $D^* = 0.110\ \mathrm{cm}^{-1}$ species), however, do not luminesce at all.

Discussion

Structures of the Nitrene II–Oxygen Adducts. The esr and optical absorption data presented above show that the dissolved molecular oxygen reacts with the nitrene II at 77°K in the dark to form a ground state triplet species, $D^* = 0.110\ \mathrm{cm}^{-1}$, and a yellow diamagnetic species. By analogy with the reaction of carbenes with oxygen,[5] these species may be represented by the *p*-azidophenyliminodioxy diradical[6] structure Va and the dipolar nitroso oxide structure Vb, respectively.[7,8] This assignment is supported by their facile phototransformation to *p*-nitrophenyl azide VI.[9] The latter presumably proceeds *via* the dioxazirane VIIa or the dimeric species VIIb.[10]



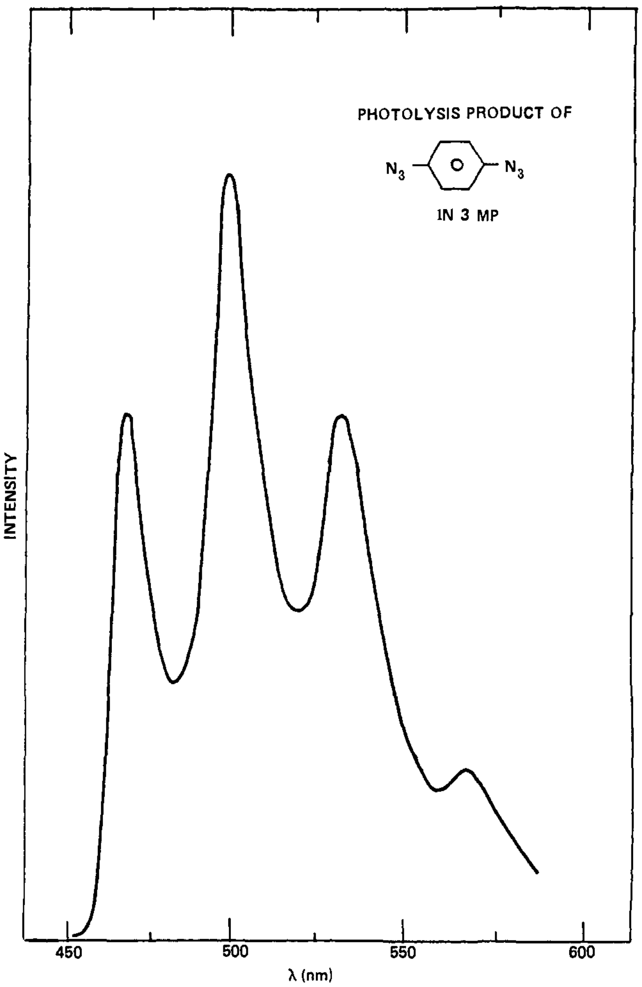


Figure 3. The phosphorescence spectrum which grows in when a photolyzed sample of *p*-diazidobenzene, left standing at 77°K in a nondegassed 3MP glass for ~24 hr, is irradiated with uv light.

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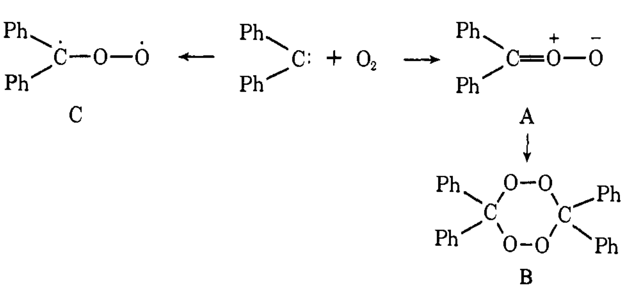
(5) (a) W. Kirmse, L. Horner, and H. Hoffmann, *Justus Liebigs Ann. Chem.*, **614**, 19 (1958); (b) P. D. Bartlett and T. G. Traylor, *J. Amer. Chem. Soc.*, **84**, 3408 (1962); (c) G. A. Hamilton and J. R. Giacin, *ibid.*, **88**, 1584 (1966); (d) R. W. Murray and A. M. Trozzolo, *J. Org. Chem.*, **26**, 3109 (1961).

(6) Name recommended by the Chemical Abstracts Service.

(7) The dipolar carbonyl oxide structure A has been suggested by Kirmse, *et al.*,[5a] as an intermediate in the oxidation of carbenes by molecular oxygen to give carbonyl compounds.[5] Bartlett and Traylor[5b] have presented evidence to support such a formulation. The actual isolation of the dimeric benzophenone peroxide B has been taken as additional evidence for the involvement of structure A rather than the diradical structure C in the oxidation reaction. Hamilton and Giacin,[5c] however, have obtained evidence which suggests that the carbene–oxygen adduct would be best represented as a diradical such as C.



(8) The reactions of ground state triplet nitrene with oxygen (a ground state triplet) to give both a triplet and a singlet adduct are quantum mechanically allowed. Vb is not intended to mean an excited state of Va.

(9) (a) Photolysis of ferrocerryl azide in solution at room temperature in the presence of oxygen has been reported to produce nitroferrocene [R. A. Abramovitch, C. I. Azogu, and R. G. S. Sutherland, Abstracts, 160th National Meeting of the American Chemical Society, Chicago, Ill., Sept 1970, Org 50. (b) Irradiation of phenyl azide in solution in the presence of oxygen has been found to produce nitrobenzene (R. A. Abramovitch, personal communication).

(10) An analogous dimeric compound (structure B, ref 7) has been isolated[5b] in the reaction of diphenylcarbene with oxygen.

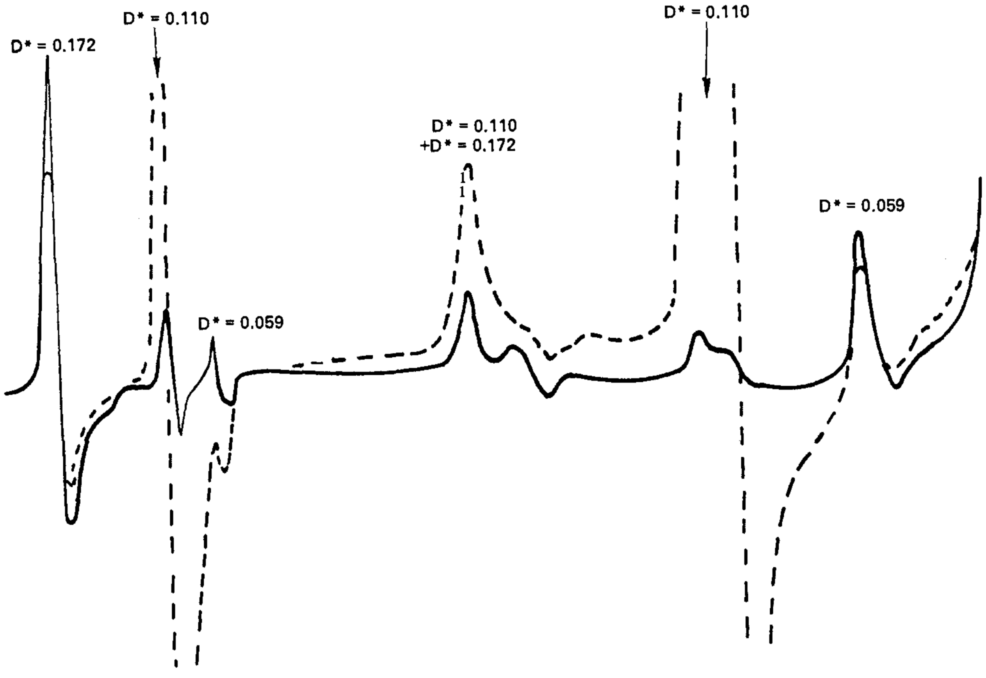


Figure 4. Low-field esr spectrum from a nondegassed solution of *p*-diazidobenzene in 3MP at 77°K which has been photolyzed for a long period of time by 313-nm light: (——) spectrum measured immediately after irradiation; (-----) spectrum after 24 hr in the dark at 77°K. The D^* values (in cm^{-1}) show the esr lines characteristic of the three different ground state triplet species present.

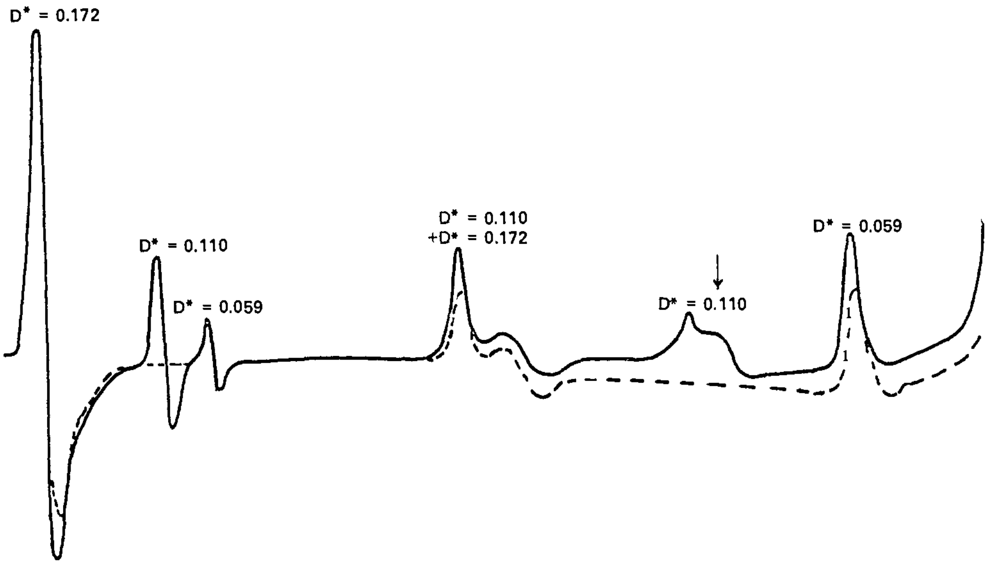
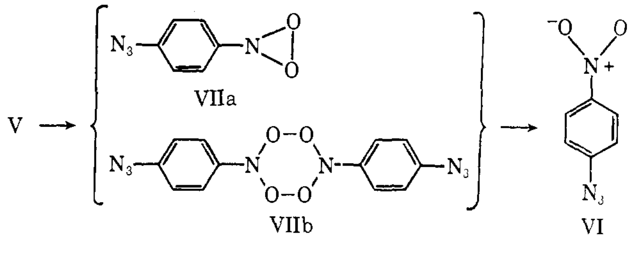


Figure 5. Low-field esr spectrum from photolyzed nondegassed (——) and degassed (- - -) solutions of *p*-diazidobenzene in MCH at 77°K. Both samples were left standing in the dark at 77°K for 48 hr. The D^* values (in cm^{-1}) show the esr lines characteristic of the three different ground state triplet species present.

The formation of *p*-nitrophenyl azide VI on irradiation of Va and Vb was confirmed by its subsequent photochemical transformation to the nitrene VIII which was identified by actual esr comparison with the nitrene VIII generated from an authentic sample of *p*-nitrophenyl azide at 77°K in 3-methylpentane. Furthermore, continued photolysis of the authentic nitro azide VI resulted in the same blue-green emission which was observed in the photolysis of Va and Vb.



Nature of the Blue-Green Emitting Compound. In contrast to the structured blue-green emission (Figure 3) observed from the photolysis of V or VI in 3-methylpentane, the photolysis in alcohol produced a yellow-green emission (Figure 6) together with the nitrene VIII. This emission was found to be very similar to, although not identical with, the one observed from authentic *p*-nitroaniline in ethanol (Figure 6) indicating

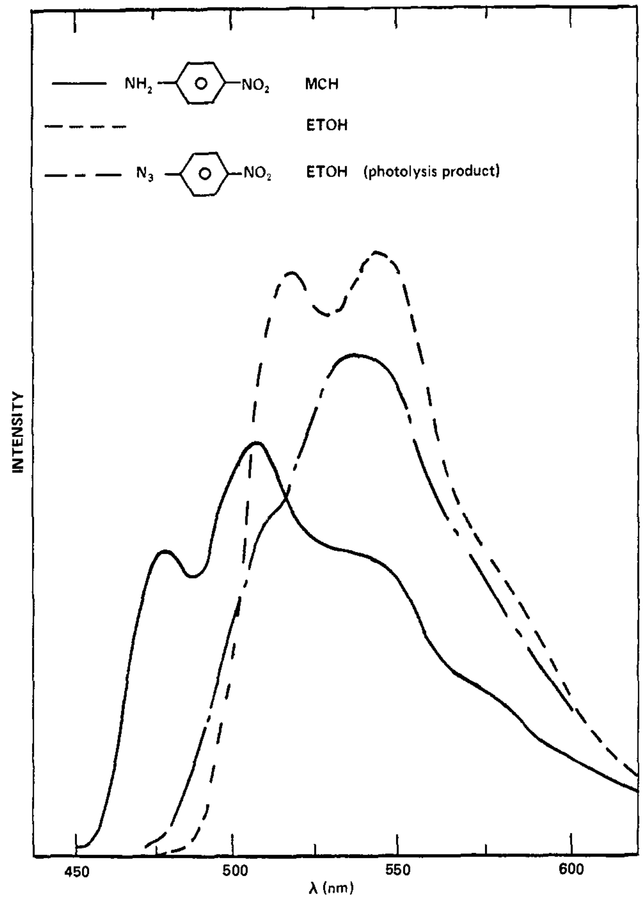


Figure 6. Phosphorescence spectra from (— - —) the photolysis of *p*-nitrophenyl azide in EtOH, (— - -) *p*-nitroaniline in EtOH, and (——) *p*-nitroaniline in MCH (all measured at 77°K.)

that *p*-nitroaniline may be formed in ethanol by hydrogen abstraction by the nitrene VIII. The small difference in the shape of the photoproduct emission is undoubtedly due to the distortion introduced by the nitrene VIII which has significant absorption on the short wavelength side of the emission spectrum. It was also found that the phosphorescence spectrum of *p*-nitroaniline in hydrocarbon solvents (*e.g.*, 3-methylpentane) is drastically shifted to higher energy with respect to the spectrum in ethanol and in addition possesses significant structure. This clearly suggests that in hydrocarbon solvents *p*-nitroaniline shows typical nitro-structured phosphorescence whereas in alcoholic solvents a charge-transfer emission is observed.[11]

The observation of *p*-nitroaniline-like emission from the photolyses of *p*-nitrophenyl azide VI or the nitrene II-oxygen adducts together with the marked solvent dependence of emission suggested that in ethanol the nitrene VIII may abstract two hydrogens to form *p*-nitroaniline whereas in hydrocarbon solvents the imino radical IX produced by abstraction of one hydrogen may recombine with the hydrocarbon radical in the solvent cage to form *N*-alkyl-*p*-nitroaniline (XI), the

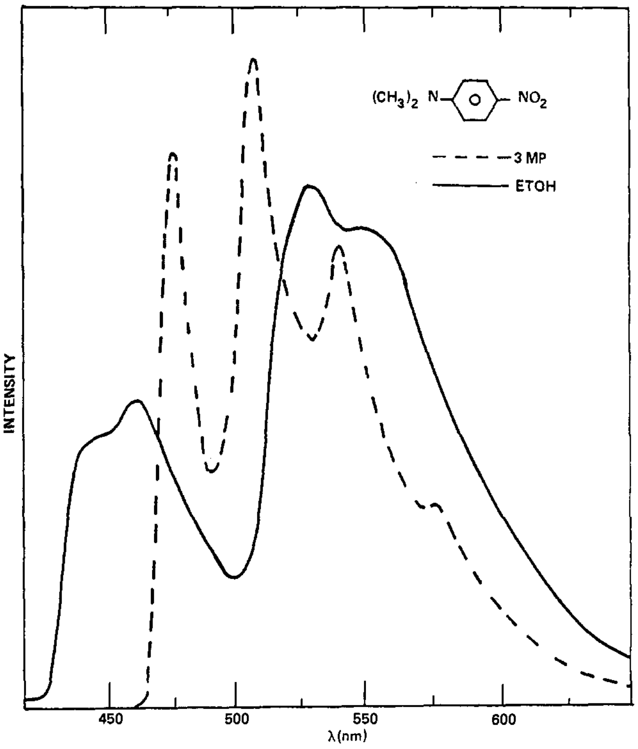


Figure 7. Total luminescence spectra of *p*-nitrodimethylaniline at 77°K in (- - -) 3MP and (——) EtOH.

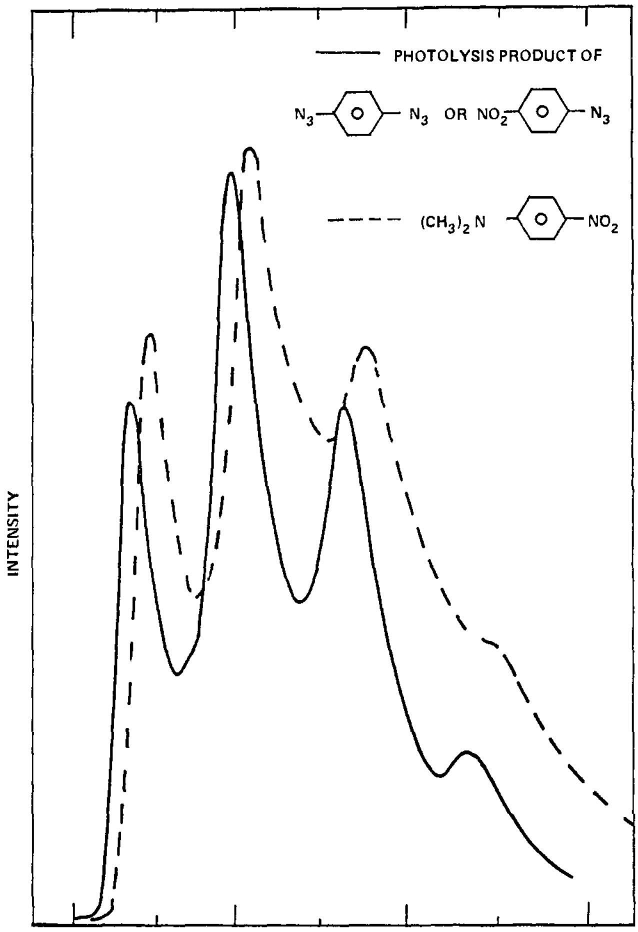


Figure 8. Comparison of the phosphorescence spectra in 3MP of (- - -) *p*-nitrodimethylaniline with that obtained from the photolysis product of *p*-nitrophenyl azide (or *p*-diazidobenzene).

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(11) Although the luminescence spectra of nitronaphthalenes and nitrobiphenyls have been reported [S. P. McGlynn, T. Azumi, and M. Kinoshita, "Molecular Spectroscopy of Triplet State," Prentice Hall, Englewood Cliffs, N. J., 1969, p 251], little or no reliable information on the luminescence of nitrobenzenes, with the exception of some nitroanilines in alcoholic solvents, has been reported. We have examined the emission of several nitro compounds in both types of solvents, and a summary is presented in Appendix I (Table I).

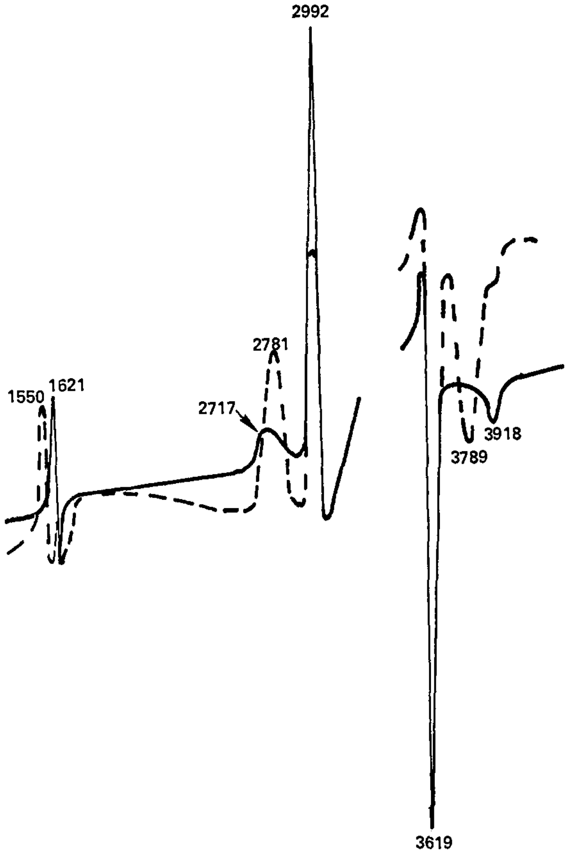
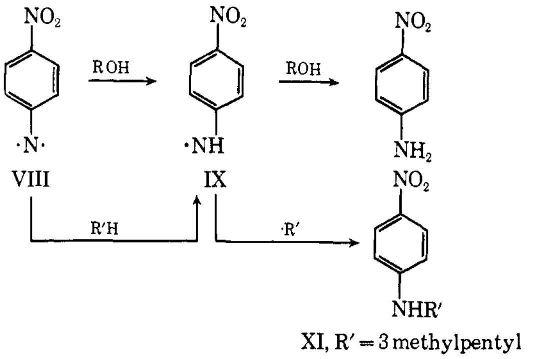


Figure 9. ESR spectrum in nondegassed MCH from the photolysis of 4,4'-diazidiazobenzene at 77 °K (——) immediately after photolysis and (- - -) after 48 hr. The field positions are given in gauss.

latter showing the structured blue-green emission in hydrocarbon solvents. This proposal was readily verified by examining the emission from *N*,*N*-dimethyl-*p*-nitroaniline. The total emission spectrum of *N*,*N*-dimethyl-*p*-nitroaniline in alcoholic and hydrocarbon solvents is shown in Figure 7. In alcohol, both fluorescence and phosphorescence emission are observed, the phosphorescence being quite similar to that observed from *p*-nitroaniline. The spectrum in hydrocarbon solvents, however, is highly structured and consists only of phosphorescence. The latter was virtually identical with that observed from the photolysis of the oxygen adducts V or the nitrophenyl azide VII, except for a wavelength shift of *ca.* 6 nm which would be expected because of the small differences in the nature of the substituents on the amino nitrogen (Figure 8). These results clearly show that the blue-green emitting species formed on the photolysis of the oxygen adducts is



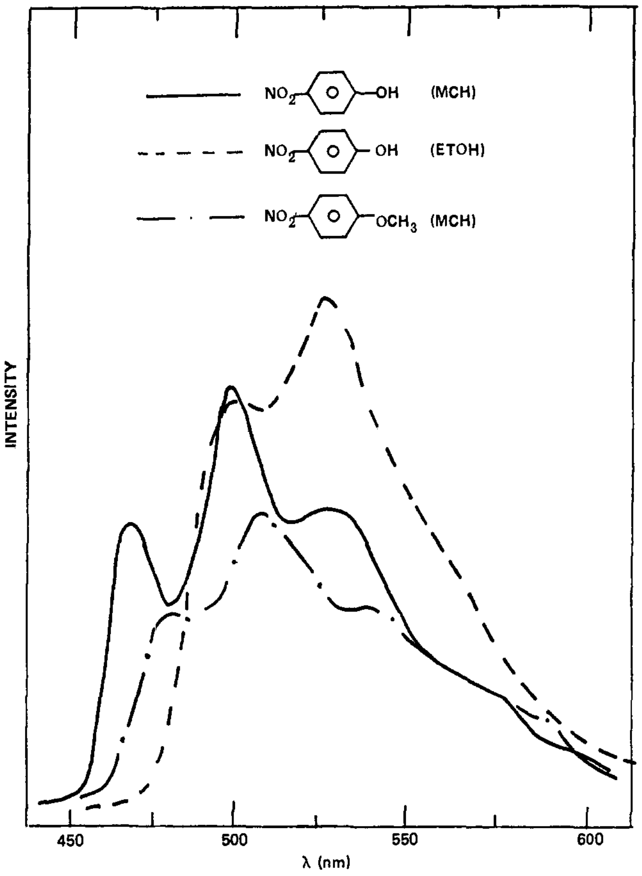
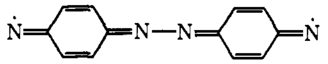


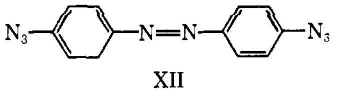
Figure 10. Phosphorescence spectra of (——) *p*-nitrophenol in MCH, (- - - -) *p*-nitrophenol in EtOH, and (— · —) *p*-nitroanisole in MCH at 77 °K.

N-alkyl-*p*-nitroaniline, where the alkyl group is derived from the hydrocarbon solvent.

Generality of the Reactions of Nitrenes with Oxygen. Irradiation of phenyl, *p*-anisyl, and *p*-*N*,*N*-dimethylaminophenyl azides in nondegassed hydrocarbon or alcoholic solvents at 77 °K produced the corresponding nitrenes. Upon standing overnight at 77 °K in the dark, the esr signals of these nitrenes decreased in intensity and simultaneously strong bands developed in the visible. Surprisingly, we were unable to detect the ground state triplet species analogous to Va in any of these azido compounds. It appears certain, however, that the nitrenes form diamagnetic adducts analogous to Vb, because photolyses of these adducts with uv or visible light produced the corresponding nitro compounds. This was shown by comparison of their emission spectra with those of authentic samples, except in the case of nitrobenzene which shows no emission.[9b] The only other example where we were able to see the ground state triplet species (analogous to Va) was in the case of the dinitrene IV derived from 4,4'-diazidoazobenzene (XII). The dinitrene signal ($D^* = 0.059$ cm^{-1}) was found to decrease slowly and a new



IV



XII

Table I. Luminescence Data for *p*-Nitrobenzenes at 77°K

Molecule	Solvent	Fluorescence, nm	Phosphorescence, nm	τ_p, sec
Nitrobenzene	3MP, EtOH, MCH	None	None	
p-Dinitrobenzene	3MP, EtOH, MCH	None	None	
p-Nitrotoluene	3MP, EtOH, MCH	None	None	
p-Bromonitrobenzene	3MP, EtOH, MCH	None	None	
p-Nitrophenol	MCH	None	468, 500, ~530	0.15
	EtOH	None	500, 527, ~570	0.26
p-Nitroanisole	MCH, 3MP	None	481, 508, ~540	0.11
	EtOH	None	None	
p-Nitroaniline	MCH, 3MP	None	478, 507, ~540	
	EtOH	None	518, 542, ~580	0.40
p-Nitro-*N*,*N*-dimethylaniline	3MP, MCH	None	473, 505, 540, ~580	0.21
	EtOH	~460	530, 552, ~590	0.42

triplet species ($D^* = 0.094$ cm^{-1}) (Figure 9) appeared. The structure of this species is not known at present. No emission was observed on further photolysis.

Conclusion

Triplet nitrenes formed in the photolyses of *p*-diazidobenzene, phenyl azide, and 4,4′-diazidoazobenzene react at low temperature (77°K) in rigid glasses with dissolved oxygen to form diamagnetic and or paramagnetic species. These intermediates appear to rearrange to nitro compounds upon photolysis with uv or visible light. In the case of *p*-diazidobenzene for instance, this product, when photolyzed, leads to the formation of *p*-nitroazidobenzene. Further photolysis of this solution (or a fresh solution of *p*-nitroazidobenzene synthesized independently) leads eventually to the production of *p*-nitroaniline (in EtOH) or *N*-alkyl-*p*-nitroaniline (or in 3MP). The last two species are identified from their phosphorescence behavior. The luminescence behaviors of related nitrobenzenes studied during the course of this investigation are briefly discussed in Appendix I.

Appendix I

During the course of the preceding study we had occasion to investigate the luminescence of several simple substituted nitrobenzenes. Since there is relatively little data on these systems in the literature we thought it suitable to include these data in the present article. Figure 10 shows the luminescence obtained for *p*-nitroanisole and *p*-nitrophenol in alcohol or hydrocarbon solvents. The anisole did not appear to luminesce in alcohol. The results on all the materials studied are given in Table I.

Studies on the Synthesis of Corrins and Related Ligands. I. General Approach and Model Studies[1]

R. V. Stevens,*[2] C. G. Christensen,[3] William L. Edmonson,[3] Morris Kaplan, Edward B. Reid, and Mark P. Wentland[4]

Contribution from the Department of Chemistry, Rice University, Houston, Texas 77001. Received February 24, 1971

Abstract: A fundamentally different approach to the synthesis of corrinoid substances is presented. The method involves the employment of isoxazole nuclei as a means of elaborating the crucial ring-bridging vinylogous amidine chromophores. Simple model systems were designed to test the feasibility of this approach. A simple synthesis of γ-substituted butyrolactams involving an unusually facile hydrolysis of β-cyano ketones and their conversion into semicorrinoid-like substances is outlined.

The detailed structure of vitamin B_{12} (**1**) was first revealed to the chemical world through the brilliant X-ray crystallographic studies of Crowfoot-Hodgkin.[5] In many respects this outstanding achievement may be regarded as a turning point in the history and development of the chemistry of natural products, since prior to this event, the discovery of the specific chemistry of new substances was secured most often as a by-product of extensive degradative studies. However, now, with an ever-increasing number of powerful physical tools at our disposal, we find ourselves in the rather enviable position of being able to ascertain even the most intimate structural details of a molecule often without ever having performed a single chemical transformation!

[1] For a preliminary account of a portion of this work, see R. V. Stevens and M. Kaplan, *Chem. Commun.*, 822 (1970).

[2] A. P. Sloan Fellow, 1969–1971.

[3] NSF Predoctoral Trainee.

[4] U. S. Public Health Service Predoctoral Fellow, 1967–1970.

[5] D. Crowfoot-Hodgkin, A. W. Johnson, and A. R. Todd, *Chem. Soc. Spec. Publ.*, **No. 3**, 109 (1955); D. Crowfoot-Hodgkin, J. Kamper, J. Lindsey, M. McKay, J. Pickworth, J. H. Robertson, C. B. Shoemaker, J. G. White, R. J. Prosen, and K. N. Trueblood, *Proc. Roy. Soc., Ser. A*, **242**, 288 (1957); for a review, see R. Bonnett, *Chem. Rev.*, **63**, 573 (1963).

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