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SYNTHESIS AND PHOTOLYSIS OF MODEL COMPOUNDS FOR MECHANISTIC STU--ETC(U)
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NO. 96

"SYNTHESIS AND PHOTOLYSIS OF MODEL COMPOUNDS FOR MECHANISTIC STUDIES OF 1,3,5-TRINITRO-1,3,5-TRIAZACYCLOHEXANE (RDX) DECOMPOSITION"

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Synthesis and Photolysis of Model Compounds for Mechanistic Studies of 1,3,5-Trinitro-1,3,5-triazacyclohexane (RDX) Decomposition.

A Trident Scholar Project Report
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ABSTRACT

This work has studied the photochemistry of nitramines. Initially, the synthesis of three nitramines which have similar properties to 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) was performed. The three compounds were: N-nitropiperidine, N,N-dinitro-piperazine, and 1,3-dinitro-1,3-diazacyclohexane. They were characterized by their infrared and NMR spectra, and by comparison of their physical properties with literature values.

The photochemistry of N-nitropiperidine and N-N-dinitropiperazine was conducted in a quartz cell using a Hanovia medium pressure, mercury-arc, immersion lamp (200w). The functionality of the decomposition products led to the proposal of a mechanism which describes the photochemical decomposition of cyclic nitramines.

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I. INTRODUCTION

The Environmental Protection Agency has in recent years placed stringent controls on what methods may be employed to dispose of military ordnance. In response to these controls, the Department of Defense conducted a symposium[1] on demilitarization of conventional munitions in April 1976. Hoffsommer and Kubose[2] have investigated the use of ultraviolet light to purify aqueous solutions of nitramine explosives since it has been proven that ultraviolet light decomposes these types of explosives[3]. The mechanism of the photochemical decomposition of cyclic nitramines is then important in order to investigate further the results of using ultraviolet light to demilitarize nitramine explosives.

II. HISTORICAL

Nitramines have been used as explosives for many years. 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) was first prepared in 1899[4]. Herz in 1920 proposed the correct structure for RDX and recognized its explosive properties. N,N-Dinitropiperazine[5], N-Nitropiperidine[6], and 1,3-Dinitro-1,3 diazacyclohexane[7] have been prepared and their physical properties determined.

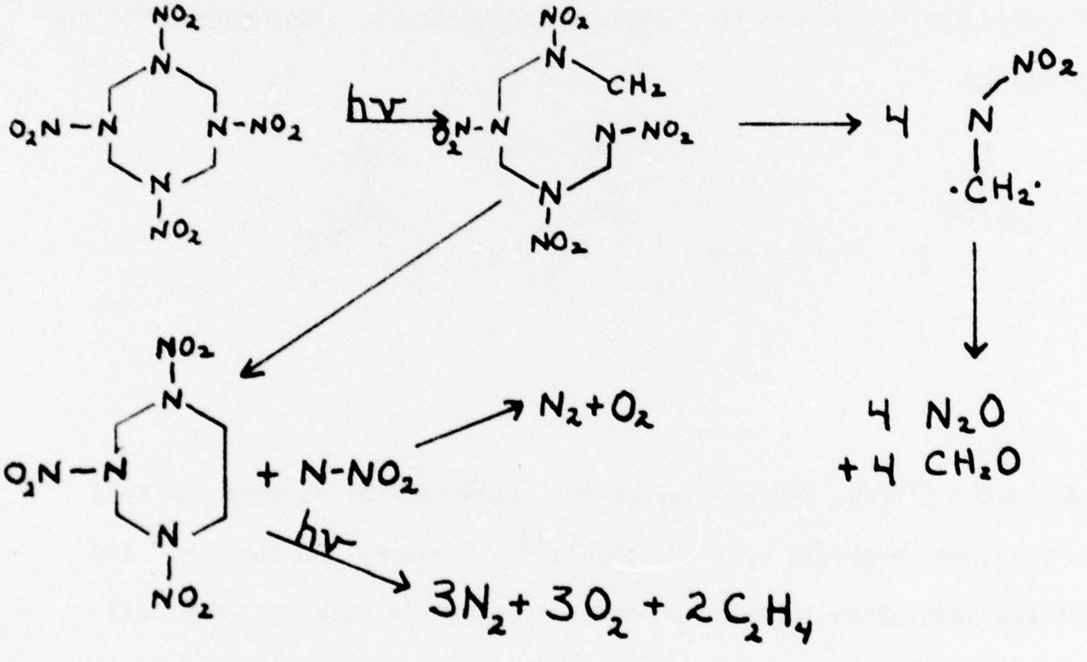
Several different groups have done studies on the thermal degradation of nitramines. The products of the decomposition are listed in table one as measured in percentages by mass spectrometry.

Table One

Investigator	Suryanarayana[8]	Masinov[9]	Robertson[10]	
Nitramine	HMX	HMX	RDX	HMX
Decomp. Prod.				
NO	40.0		14.0	38.5
N_2	9.9			
HCN	9.6	major (a)	17.2	16.6
CH_2O	4.5		34.4	18.5
CO_2	8.5			
CO	8.5	major (a)	present	
H_2			22.4	9.4
H_2O			11.8	16.4

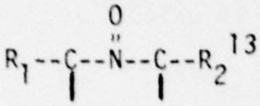
In the studies on the thermal decomposition products of dimethylnitramine, Flournoy[11] found that the overall reaction was first order and unaffected by the addition of NO.

The photolysis of nitramines has been done by several different workers. Torbit (3) found that by varying the medium in which the photolysis was done the decomposition products were different. For example, in acetone solution the products were N_2, C_2H_2, O_2, CO_2, and N_2O; for the solid in vacuo, N_2, C_2H_2, C_2H_4, CH_2O and N_2O. He proposed the following mechanism:

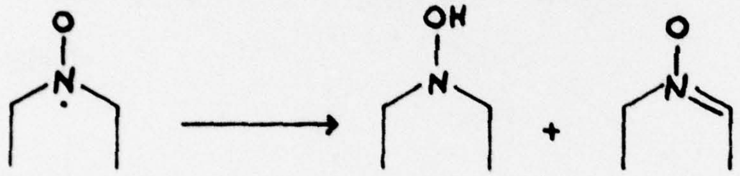


A study of the photolysis of RDX by both ultraviolet and gamma rays has been done by Darney[12]. For either energy source the results were the same. He reported that at $20^{\circ}C$ a NO_2+ radical was seen in the ESR spectrum. However, once irradiation was stopped the radical disappeared within a half hour. When the temperature was increased to 40°C the radical existed indefinitely. Explanation of these observations were not offered at that time nor subsequently.

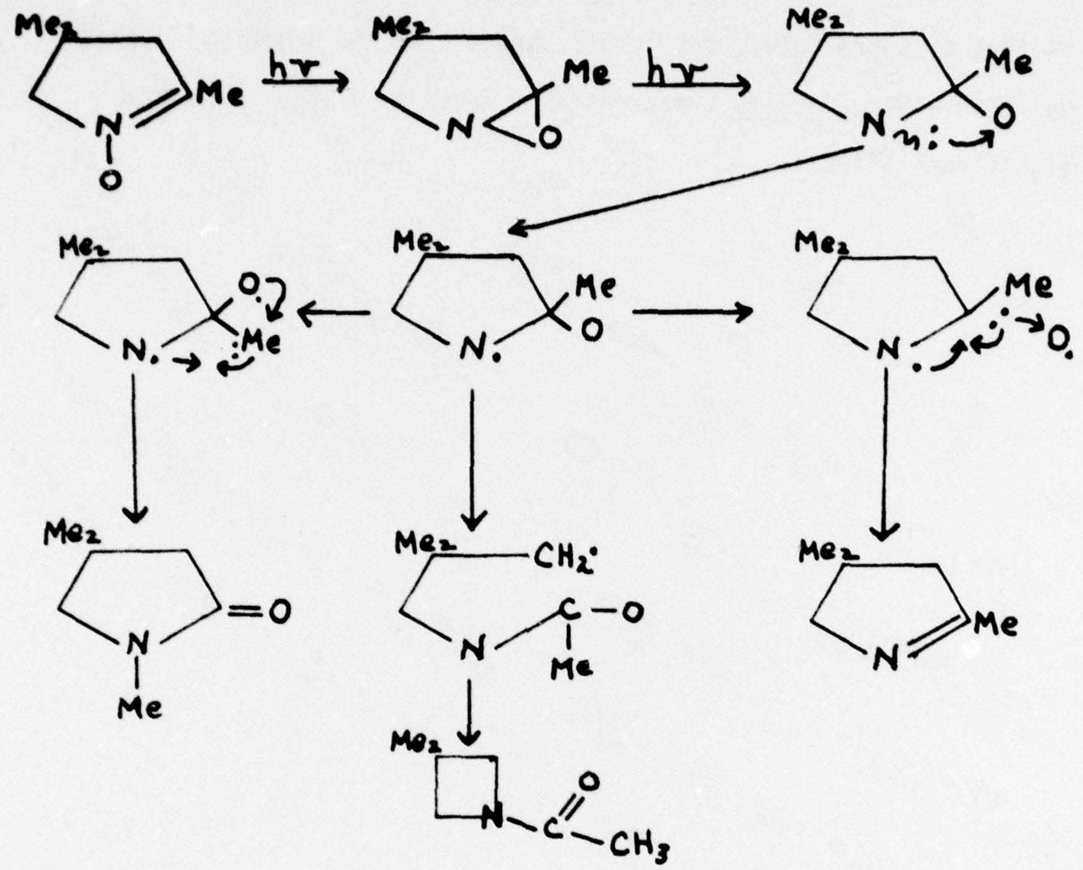
The irradiation of cyclic nitramines has produced cyclic nitroxides



$R_1\text{--}\underset{|}{C}\text{--}\overset{\overset{O}{''}}{N}\text{--}\underset{|}{C}\text{--}R_2$[13]. In the cases where R was hydrogen the radicals were very short-lived intermediates and only detectable by ESR techniques. If the R groups were alkyl the stability increased greatly. The mechanism for the decay of nitroxides having a beta hydrogen has been proposed[14]. Dupeyre and Russat proposed that the mechanism is bimolecular with the products



being the nitrone and hydroxylamine. Experimental support for this process was provided by K. U. Ingold[15]. Kaminsky and Lamchen[16] and others have shown that the photolysis of cyclic nitrones gives oxiziridines. They proposed the following mechanism for 2,4,4-trimethyl-1-pyrroline as follows:



The importance of the possibility of using ultraviolet light to demilitarize ordinance containing nitramines must not be overlooked. Hoffsommer observed that the use of water to remove the nitramine explosives from military hardware left non-biodegradable effluents[2]. Irradiation of aqueous solutions of RDX can be broken down to more ecologically compatable substances. Moreover; he observed that the product distribution is dependent on the radiation source as the decomposition mechanism seems to have two wavelength-dependent possibilities.

Since Darney observed gamma-rays caused damage of a similar sort as that of ultraviolet, and Torbit showed that the solid was dudded by irradiation, in situ treatment with gamma or X-rays might have significant effects.

III. EXPERIMENTAL

A. Synthesis of Model Compounds

In all these preparations the infrared and NMR spectra of both the final products and their respective intermediates were used to confirm physical characteristics. A Varian A-60 nuclear magnetic resonance spectrometer was used to record NMR data while a Perkin-Elmer grating infrared spectrophotometer model 467 was used for recording infrared data.

1. Preparation of N-Nitropiperidine[6]

Into a 100 ml. round bottom flask was placed 12 ml. of piperidine and 5.8 ml of 97% formic acid. The solution was refluxed for 50 min. The fraction boiling at 98-104°C was distilled off. Three solutions were cooled in ice: (a) 28 ml (0.67 mole) of red fuming HNO_3, (b) 20 ml. of F_3CCOOH and 48 ml. of acetic anhydride, and (c) the solution remaining from the above distillation. Solution (a) was added slowly to (b) and cooled to 0°C. (c) was added while stirring and maintaining the temperature below 10°C. The solution was gradually brought to room temperature and stirred for 35 min, then quenched on 50 gms of ice. Two 50 ml aliquots of chloroform were used to extract the product. This solution was then washed with 110 ml of 10% $NaHCO_3$ solution until neutral to litmus. It was then dried over Na_2SO_4(s) and the solvent was stripped off with a rotary evaporator. The resulting solution was distilled at 0.6 mm Hg, b.p. of 75°C, n_D^{20} = 1.470. Literature values for N-nitropiperidine are[17] b.p. of 62-64°C at 0.2 mm Hg and n_D^{20} = 1.468. The actual yield was 0.0852 moles resulting in a 55% yield.

2. Preparation of N-N Dinitropiperazine[5]

a. Piperazine dihydrochloride.

110 gms. of piperazine was placed in a 250 ml. round bottom flask fitted with a reflux column. 50 ml. of water was added (with stirring). Then, 50 ml. of conc. HCl were slowly added. This was done in an ice bath. The reaction mixture was warmed to room temperature and most of the solvent was stripped off with a rotary evaporator. The product was dissolved in 34.0 ml. of boiling water and recrystallized with 100% ethanol. After cooling, filtering, and drying a m.p. of 318°C was obtained as per literature. The actual yield was 0.1139 moles with a percent yield of 80.

b. N-N Dinitropiperazine.

A nitrating solution made up of the following compounds was made up and cooled to 0°C: 11.65 ml. of acetic acid, 22.7 ml. of acetic anhydride, and 18.0 ml. of red fuming HNO_3. 6.0 gms of above salt were added maintaining the temperature below 5°C. The mixture was stirred for 0.5 hours and warmed slowly to room temperature. It was left to stir for 70 hours under nitrogen. Then 200 ml. of water were added. $NaHCO_3(s)$ was added until the reaction ceased. Then a 10% $NaHCO_3$ solution was used to wash the solid until neutral to litmus.

The solid was filtered off and recrystallized from a minimum of boiling water. A m.p. of 212-213°C was found with a literature value of 214.8-216°C. The actual yield was 0.0217 moles and a percent yield of 57.

3. Preparation of 1,3,-Dinitro-1,3,-diazacyclohexane[7].

a. 1,3,Diaminopropane dihydrochloride.

44 ml. of conc. HCl was placed into a three necked round-bottom flask fitted with a reflux column. 23 ml. (0.270 moles) of 1,3,diaminopropane were added dropwise while stirring with a magnetic stirrer. After addition of the 1,3,diaminopropane the solid was filtered off. In order to obtain the rest of the salt, the solution was stripped off using a rotary evaporator. The m.p. was 243°C. The lit. value is 243°C[18]. 32.2 gms of 1,3,Diaminopropane dihydrochloride were obtained for a 87.4% yield.

b. Biscarbomethoxy 1,3,diaminopropane

34.00 gms of the above product was placed in a three necked round-bottom flask fitted with a reflux column. The apparatus was placed in an ice bath and 88.8 ml of 6M NaOH was added dropwise. Simultaneously, 88 ml. of 6M NaOH and 55 ml. of methyl chloroformate were added dropwise. The resulting solution was stirred for 3 hours. Then three 60 ml aliquots of chloroform were used to extract the product. After stripping off the chloroform and titration with hot hexane, 39.27 gms of the title compound were obtained, m.p. 64°C, lit. 74-76°C, for a 86.3% yield.

c. N,N'-Dicarbomethoxy-N,N'-dinitroaminopropane

43 ml. of acetic anhydride and 20 ml. of trifluoracetic anhydride were mixed together and cooled on an ice bath to -5°C. 90 ml. of red fuming HNO_3 were added dropwise. For 2 hours 34.0 gms of the above product were added maintaining the temperature below 10°C. The solution was slowly brought to room temperature and stirred for two hours. After pouring over 100 gms of ice, filtering, washing with 10% $NaHCO_3$, and drying, 42.54 gms of N,N'-Dicarbomethoxy-N,N'-dinitrodiaminopropane were obtained. The m.p. was 85°C, lit. m.p. 88-90°C[18], for a 84.8 yield.

d. N,N'-Dinitro-1,3-diaminopropane

42.5 gms of the above product was slowly added to 80.0 ml of conc. NH_4OH in a round bottom flask fitted with a reflux condenser. The solution was stirred at room temperature for 18 hours. It was then refluxed for 0.5 hours. 50 ml of water was added followed by enough 6N HCl to make the solution neutral to litmus paper (approx. 50 ml). Three 75 ml aliquots of ethyl acetate were used to extract the product. After stripping off the ethyl acetate, translucent, white crystals remained. The m.p. of these crystals was 52°C. The literature value for the m.p. of N,N'-diamino-1,3-diaminopropane is 69°C. All efforts failed to isolate the title compound as seen by the persistence of amide bands in the ir spectra of the isolated material.

B. Photolysis Reactions

The photolyses were carried out in a two liter, water-jacketed vessel equipped with a reflux condenser, a nitrogen sparger, and a water-jacketed quartz immersion well. The ultraviolet source was a Hanovia

200 watt, medium pressure, mercury arc. All runs were conducted under nitrogen gas unless indicated otherwise. It was found that hexane, which is an excellent choice for a solvent that does not quench the singlet, could not be used as it would not dissolve enough of the model compounds. Tetrahydrofuran and 1,4-dioxane were used as "singlet solvents." Acetone is a triplet sensitizer solvent but undergoes photodecomposition of its own thereby complicating the system. To sensitize the system to the triplet, 10% benzophenone, by weight, was added to the respective solvent. The 1,4-dioxane used was purified by adding five grams of $CuCl_2(s)$ per liter of dioxane, refluxing for one hour and then distilling of the pure 1,4-dioxane.

In order to determine whether the solvents chosen underwent photochemistry by themselves, a 500 ml. sample of each solvent was irradiated for two hours. By comparing infrared spectra of both the pure solvents and the photolyzed portions, it was found that no photolysis had occurred. The following photolysis experiments were conducted.

1. 0.87 grams of N,N-dinitropiperazine was added to 550 ml of 1,4 dioxane and the solution was photolyzed for two hours. The relatively poor solubility of N,N-dinitropiperazine in 1,4-dioxane prevented full solution and therefore photoreaction. After separating the solid and stripping off the solvent a reddish residue remained. The solvent was checked by gas chromatography using a six-foot stainless steel column packed with chromosorb W, carrying 0.65 percent EGA, at 150°C, to see if any products had distilled off with the solvent. None were detected. The residue was taken up in methanol. Thin Layer Chromatography using

Eastman Chromatoplates of silica gel and acetone, carbontetrachloride, chloroform, and methanol as solvents, was conducted with no noteworthy results. The residue in a minimum amount of methanol was added to a neutral alumina column charged with acetone. The following solutions were run through the column and samples collected: 20 ml of acetone, 20 ml of 5% methanol in acetone, 20 ml of 50% methanol in acetone, and two 20 ml aliquots of pure methanol. The infrared spectrum of the photolysis product and the infrared spectra of the five samples obtained from the column chromatography were recorded.

BANDS COMMON TO ALL SPECTRA (in cm^{-1})

3500-3000 broad	(S)	
2950-2850	(S)	
1660	(S)	
1520	(S)	except in last sample.
1440	(S)	
1250	(S)	
960	(M)	
870	(M)	

From the first sample of chromatographed material and from the solid residue, a strong band at 1740 cm^{-1} is present. This band does not appear in succeeding spectra. Also, the first three samples contained a band at 830 cm^{-1} which then disappears.

2. 0.50 grams of N,N-dinitropiperazine was added to 500 ml of tetrahydrofuran and photolyzed for two hours. Complete solution was assured before photolysis was begun. After stripping off the solvent a "gummy" residue remained. This residue was partially soluble in methanol.

The solid was washed with water and by its melting point and infrared spectrum was determined to be the starting material, N-N-dinitropiperazine. The methanol was stripped off the solution and the resulting residue was taken up in carbontetrachloride. At this point there was still an oily residue left in the flask. This was again taken up in methanol. Infrared spectra were obtained

MeOH soluble		CCl_4 soluble MeOH soluble	
3500-3100 (cm^{-1})	broad (S)	3650	(W)
2940	(S)	2960	(S)
1760	(M)	1780	(S)
1710	(M)	1730	(S)
1660	(S)	1365	(M)
1450-1380	(S)	1160	(S)
1250	(S)	1040	(W)
1170	(M)	930	(VW)
1030	(S)	860	(VW)
960	(M)		
930	(VW)		
830	(W)		
760	(M)		

3. 1.0 grams of N-nitropiperidine was added to 550 ml. of 1,4 dioxane and irradiated for two hours. After stripping off the solvent 0.84 grams of a reddish-brown liquid remained. This residue was taken up in carbontetrachloride. The molecular weight of the residue was determined by Vapor Pressure Osmometer to be 255 grams per mole. Some black residue remained insoluble. The infrared spectrum of the carbontetrachloride solution was obtained as follows after subtracting out those peaks present due to the carbontetrachloride.

2950 (cm^{-1})	(S)
2860	(M)
1720	(VS)
1680	(M)
1530	(S)
1450	(S)
1390	(W)
1370	(W)
1315	(M)
1275	(M)
1175	(S)
1100	(S)
1070	(S)
1030	(M)
1015	(S)
1000	(W)
870	(W)
850	(W)

4. 2.0 grams of N-nitropiperidine, 0.15 grams of benzophenone, and 500 ml. of 1,4 dioxane were mixed together and photolyzed for two hours. After stripping off the dioxane a reddish liquid remained. Column chromatography was employed to try to separate the benzophenone from the photolysis product(s). Neutral alumina was used as the column and was charged with hexane. After the red liquid was poured onto the column, the following solutions were run through the column: 10 ml of 10% methanol in hexane, 10 ml of 60% methanol in hexane, and two 20 ml aliquots of pure methanol. Two samples were obtained and their infrared spectra recorded. By subtracting out the benzophenone bands and those of carbontetrachloride where it was used as a solvent the following data was obtained.

Starting Material (not chromatographed)

3600-3000 (cm^{-1})	broad
2950,2850	(S)
1760,1730	(S)

Balance unresolved or due to benzophenone.

Starting Material (in CCl_4)

2950,2860 (cm^{-1})	(S)
1730	(W)
1670	(W)
1390	(M)
1060	(M)
960	(M)

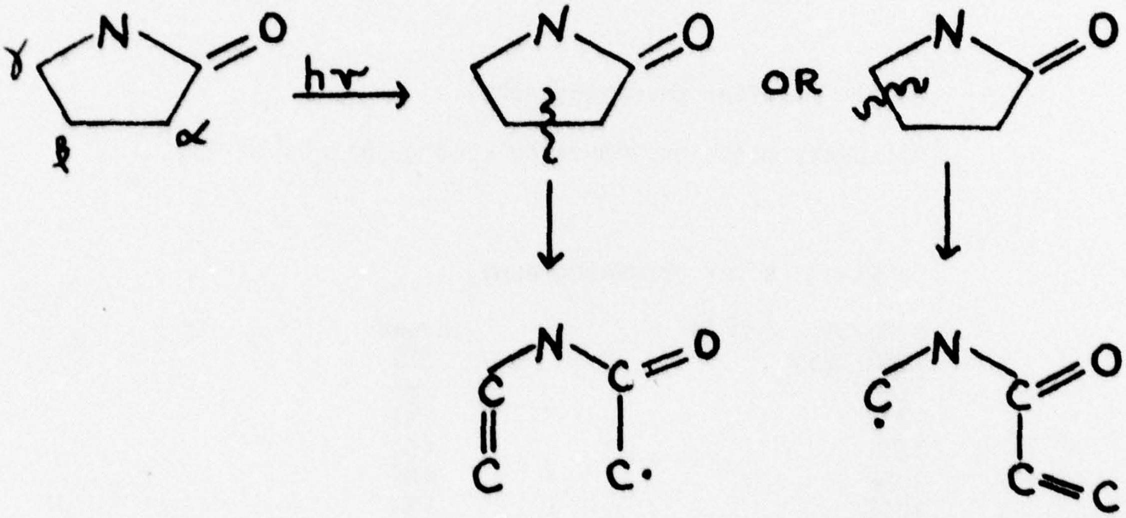
Sample 1 (after chromatography)

All peaks match benzophenone except one at 1300 cm^{-1}.

Sample 2 (after chromatography)

3700-3100 (cm^{-1})	broad
2950-2860	(S)
1760	(W)
1730	(W)
1510	(S)
1390	(M)
1245	(S)
1150	(M)
1120	(M)
1065	(S)
1010	(M)
860	(M)

5. 0.52 grams of 2-pyrrolidone was added to 500 ml. of 1,4-dioxane and irradiated for two hours. After stripping off the solvent a reddish liquid remains whereas 2-pyrrolidinone is a clear liquid. The infrared spectrum of the photolyzed 2-pynolidinone has three peaks in the fingerprint region at 1255 cm^{-1}, 1120 cm^{-1} and 870 cm^{-1} which do not occur in pure 2-pyrrolidinone. When comparing the nuclear magnetic resonance (NMR) spectrum of samples of the unphotolyzed and photolyzed 2-pyrrolidinone, the only difference is a broad unresolved peak at $\delta = 5.0$ in the spectrum of the photolyzed sample. This can be explained by Norrish type cleavage which can be one of two types.[19]



Cleavage which occurs between the alpha and beta carbons is Type I, and cleavage which occurs between the beta and gamma carbons is Type II. Cleavage of this type can explain the H-C=C in the NMR spectrum of the photolyzed sample. Integration of that spectrum shows that the contribution of the peak at $\delta = 5.0$ to the overall structure is very small. Therefore, the majority product upon photolysis is still the γ-lactam

(2-pyrrolidone). The molecular weight of 2-pyrrolidone is 85.0 gms. The molecular weight as determined by a Hewlett-Packard Vapor Pressure Osmometer is 97.3 grams.

6. 0.59 grams of 2-pyrrolidone was added to 500 ml. of 1,4-dioxane and photolyzed for two hours under NO. After stripping off the solvent a yellowish liquid remained. The infrared spectrum was recorded with new bands appearing at 1770 cm^{-1}, 1340 cm^{-1}, 1140 cm^{-1}, 1020 cm^{-1} and 870 cm^{-1}. This spectrum is also missing bands at 1070 cm^{-1} and 1000 cm^{-1} which are present in 2-pyrrolidone. The NMR spectrum shows that the peak at $\delta = 8.00$ is much smaller. Several new peaks appear that are not present in the spectrum of 2-pyrrolidone. There is a possible triplet centered at $\delta = 3.5$, a singlet at $\delta = 3.45$ (attributed to 1,4-dione, a doublet at $\delta = 2, 8$, and singlets at $\delta = 2.65$, $\delta = 2.5$, and $\delta = 2.1$.

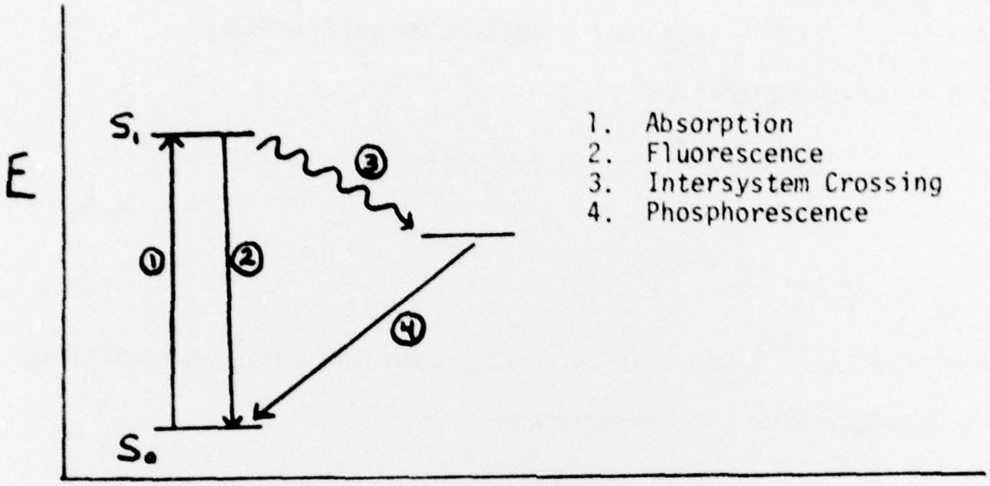
7. 500 ml. of 1,4-dioxane was irradiated for two hours under nitric oxide. The infrared spectrum of the photolyzed 1,4-dioxane was compared to a spectrum of an unphotolyzed sample. No shifts were noted. Likewise, the NMR spectra were compound. They too are identical with a singlet at $\delta = 3.50$.

C. Fluorescence Studies

Using a Baird-Atomic Fluorescence Spectrophotometer model SF-1, the fluorescence spectra of the following solutions were obtained. First, a 0.0173 M solution of N-nitropiperidine in 100% ethanol was prepared. The excitation wavelength (λ max.) was 380 nm and the fluorescence wavelength was 435 nm. Then a solution of 0.0100 M benzophenone in 100% ethanol was prepared. The exciting wavelength was 378 nm and it fluoresced at 418 nm. Finally an ethanol solution 0.0100 M with respect to benzophenone and 0.0135 M with respect to N-nitropiperidine was prepared. The exciting wavelength was 380 nm and the solution fluoresced at 422 nm.

III. DISCUSSION

It is known that photochemical reactions occur from both the singlet and the triplet states.



1. Absorption
2. Fluorescence
3. Intersystem Crossing
4. Phosphorescence

It is desirable to know if the model compounds when irradiated with ultraviolet light undergo reaction from the first excited singlet state or from the lowest triplet state. The following table represents the fluorescence data obtained from three ethanol solutions.

Compound	λ irradiation	λ emission
N-nitropiperidine 0.0173	380 nm	435 nm
Benzophenone 0.0100 M	378 nm	418 nm
N-nitropiperidine 0.0135 M Benzophenone 0.0100 M	380 nm	422 nm

The molar absorptivity of benzophenone is 1.0[19] at 378 nm. The molar absorptivity of N-nitropiperidine was computed as follows:

$$A = EbC$$

A = Absorbance
E = molar absorptivity (molar extinction coefficient)
b = cell path (1.0 cm)
C = molar concentration

$$\log \frac{1}{.975} = E\ (0.01732)(1.0$$

$$.0635 = E$$

The absorbance ($\frac{I_o}{I}$) can then be computed for the solution containing both N-nitropiperidine and benzophenone.

$$\frac{I_o}{I} = (0.635)(0.01365)(1.0) = 8.67 \times 10^{-3}$$

$$\frac{I_o}{I} = (1.0)(0.0100)(1.0) = 1 \times 10^{-2}$$

The benzophenone then absorbs 54% of the available energy and the N-nitropiperidine the remaining 46%. This indicates that the ΔE between the first singlet excited state of benzophenone and that of N-nitropiperidine is very small.

Since the fluorescence spectrum of this solution has only one peak (at 422 nm), assuming that the symmetry of the two separate fluorescence spectra were the same, the resulting spectrum can be considered as a linear combination of the two.

$$422 = (X)(418) + Y(435)$$

$$\text{where } y = \frac{4}{17} \quad y = \frac{4}{17} \quad \%\, y = \frac{4}{17}(100) = 23.5$$

Therefore the benzophenone is emitted 76.5 percent of the energy and the N-nitropiperidine only 23.5 percent. The N-nitropiperidine is transferring energy to the benzophenone. The benzophenone is acting as a quencher but does not quench the system completely. The full importance of this fact will come to light in the analysis of the actual interaction between benzophenone and N-nitropiperidine when photolyzed.

N-nitropiperidine and N,N-dinitropiperazine were prepared and their physical characteristics substantiated by refractive index, boiling or melting point, infrared and NMR spectra where applicable. The third compound under consideration was not prepared as N,N^1-dinitro-1,3-diaminopropane could not be isolated by any of the means attempted.

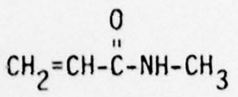
When N,N'-dinitropiperazine was photolyzed in 1,4 dioxane under nitrogen the resulting residue from the photolysis was chromatographed on Eastman Chromatoplates of silica gel. The fact that no separation was detected does not preclude the possibility of the residue containing more than one component. The band at 1740 cm^{-1} in the infrared spectrum of the methanol insoluble portion of the photolysis residue indicates the possible presence of a γ-lactams.

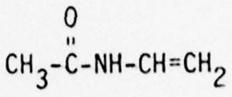
N-nitropiperidine was photolyzed in 1,4 dioxane under nitrogen. The residue remaining after stripping of the solvent was almost entirely soluble in carbontetrachloride. The infrared spectrum of the small amount of insoluble residue indicates some sort of epoxide or polymer. Interpretation of the infrared spectrum of this solution indicates the presence of the γ-lactam (very strong band at 1720 cm^{-1}) and possibly small quantities of other amides. The NMR spectrum of this solution shows poor resolution. However a peak at $\delta = 5.0$ indicates a vinylic hydrogen (H-C=C). As explained in the experimental (see page 16) this could be due to Norrish type cleavage.

Benzophenone was added to a solution of N-nitropiperidine in 1,4-dioxane and photolyzed for two hours. The resulting photolysis product showed γ-lactam bands (1730 cm^{-1}) even before it was chromatographed. After being chromatographed and the infrared spectra of the two samples were recorded, it was still possible to discern these bands indicative of both γ-lactams and amides *in general* (1730 cm^{-1}, 1670 cm^{-1}). The peaks due to benzophenone were subtracted out by comparison.

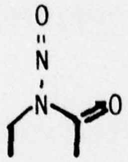
In order to determine if the γ-lactam is a stable product under the experimental conditions it was subjected to, several photolyses were conducted using 2-pyrrolidone whose structure is .

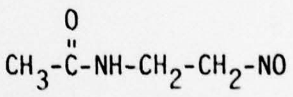
First a sample of 2-pyrrolidone in 1,4-dioxane was irradiated under nitrogen. Most of the product from the reaction was, in fact, still 2-pyrrolidone. New bands in the infrared spectrum of the photolysis product and the presence of a peak at $\gamma = 5.0$ in the NMR spectrum indicate that Norris type cleavage has occurred to a limited extent. This can be represented by either or both of the following two structures.

I. 
$CH_2{=}CH{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_3$

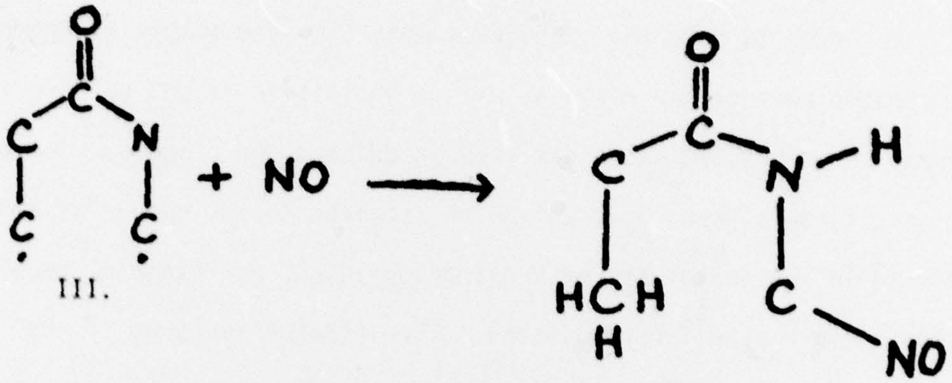
II. 
$CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH{=}CH_2$

In order to make the photolysis more like the actual experiments, the nitrogen sparger was replaced with a NO (nitric oxide) sparger. The 2-pyrrolidone in 1,4-dioxane was then irradiated for 2 hours. The conditions of a very large concentration of NO as compared to the amount of NO actually liberated in the photolysis of N-nitropiperidine, for example, provides the most severe conditions possible. The infrared spectrum of the photolysis product shows a significant change when compared to a spectrum of 2-pyrrolidone. The NMR spectrum of the photolysis product in conjunction with the infrared spectrum makes the following structures possibly new products.

I. 

II. 
$CH_3{-}\overset{O}{\overset{\|}{C}}{-}NH{-}CH_2{-}CH_2{-}NO$

Structure I. is N-nitroso-2-pyrrolidinone. This structure is substantiated by the N-N=O bands in the infrared spectrum. Structure II. is similar to those predicted by Norris type cleavage. However, the peak at $\delta = 5.0$ is missing in the NMR spectrum indicating that this structure must be saturated. This is substantiated by the fact that NO can act as a scavenger as indicated in the following reaction.

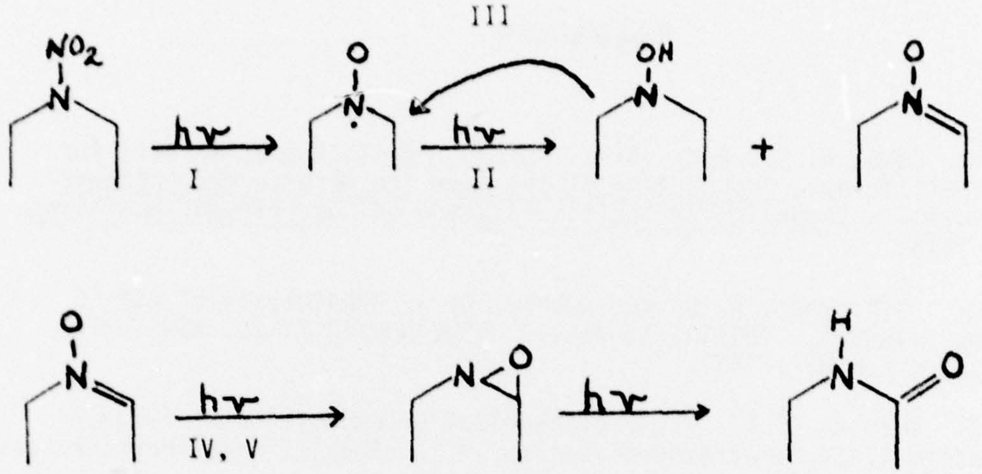


III.

It can be seen that structure III is simply the first step in Norris type I cleavage. The NO "traps" the radical on the carbon adjacent to the nitrogen then the other radical abstracts a hydrogen atom from the solvent.[19]

By subjecting 1,4-dioxane by itself to irradiation under NO, it was seen by comparison of infrared and NMR spectra of photolyzed and unphotolyzed dioxane that there is no decomposition of the 1,4-dioxane by itself. This does not preclude the possibility that when the model compound is present abstraction of a hydrogen atom and other processes can occur. The formation of small amounts of open-chain amides, i.e. Norrish cleavage, does support the assumption that indeed, hydrogens are abstracted from the 1,4-dioxane.

The following is proposed as a possible mechanism for the photochemical decomposition of cyclic nitramines.



I. (20)
II. (21)
III. (15)
IV. (22)
V. (23)

It was found that the majority of the end product of the decomposition reaction was a cyclic amide with traces of open-chained amides present as explained by Norrish cleavage. The evidence in the infrared spectrum of photolysis products (see Experimental page 13) of small quantities of high molecular weight polymers being present is supported by Bonnett[24] who said that nitrones tend to polymerize if not hindered. Since the absorption wavelengths are almost equal for all of the reaction intermediates it is not surprising that only small amounts of the nitrone would have time to polymerize. Attempts to isolate the reaction intermediate by several workers (Moon, Swanson, and others) were not successful due, at least in part, to their facile photochemical conversion.

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detailed examination and procedures enclosed.

The functionality of the decomposition products led to the proposal of a mechanism which describes the photochemical decomposition of cyclic nitramines.-

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