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THESIS

PHOTOCHEMISTRY OF NITRAMINES III
SOME POTENTIAL INTERMEDIATES

by

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June 1972

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Gas chromatographic analysis revealed evidence of the presence of 1-hydroxypyrrolidine in the photochemical decomposition products of 1-nitropyrrolidine.

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Photochemistry of Nitramines III

Some Potential Intermediates

by

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I. INTRODUCTION

The purpose of this investigation is to find evidence in support of the photochemical decomposition mechanism of 1-nitropyrrolidine postulated by Whittaker [40]. Evidence was obtained by synthesizing possible intermediates and finding evidence for their existence in the decomposition products of the nitramine. Also some steps of the mechanism were shown to function independently.

Finally the information obtained from this investigation was used to comment upon the major postulated mechanisms for the decomposition of the nitramine, HMX.

II. HISTORICAL

A. THE DECOMPOSITION OF HMX

Besides the standard considerations in explosive chemistry such as shelf-life and thermal stability, in recent years investigations into problems such as reclamation of old or damaged explosives and intentional deactivation have become very important. Critical to the understanding of all these questions is the knowledge of the mechanism of the explosive's chemical decomposition. There are a number of explosives which are nitramines, e.g. RDX, HMX, and Tetryl. Studies of the degradative chemistry of HMX have led to various postulated mechanisms.

The first mechanistic studies considered the thermal degradation of HMX (I), 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane. Surayanarayana [33] with the use of nitrogen-15 and mass spectrometry postulated a thermal mechanism which explained his major products of CH_2O and N_2O. The mechanism is shown in Figure 1.

Maycock [29] next irradiated HMX with light from a low pressure mercury lamp. Mass spectrometric analysis of the gaseous products showed major peaks at 14, 30, and 44 m/e. He reasoned therefore that the probable main species were CH_2O and N_2O. He postulated a possible photochemical mechanism as shown in Figure 2.

Torbit [36] photolyzed HMX in an acetone solution, in solid-state under a vacuum, and in solid state under Helium. The major products from these irradiations were N_2, C_2H_4, O_2, and N_2O. His proposed mechanism is seen in Figure 3.

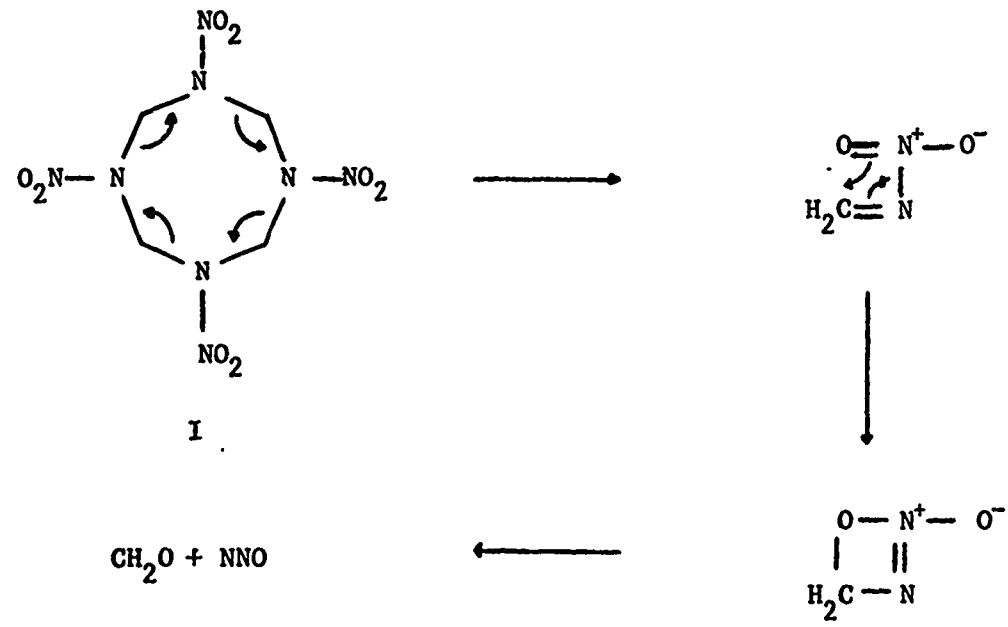

Figure 1. Surayanarayana's Proposed Thermal Decomposition Mechanism for HMX

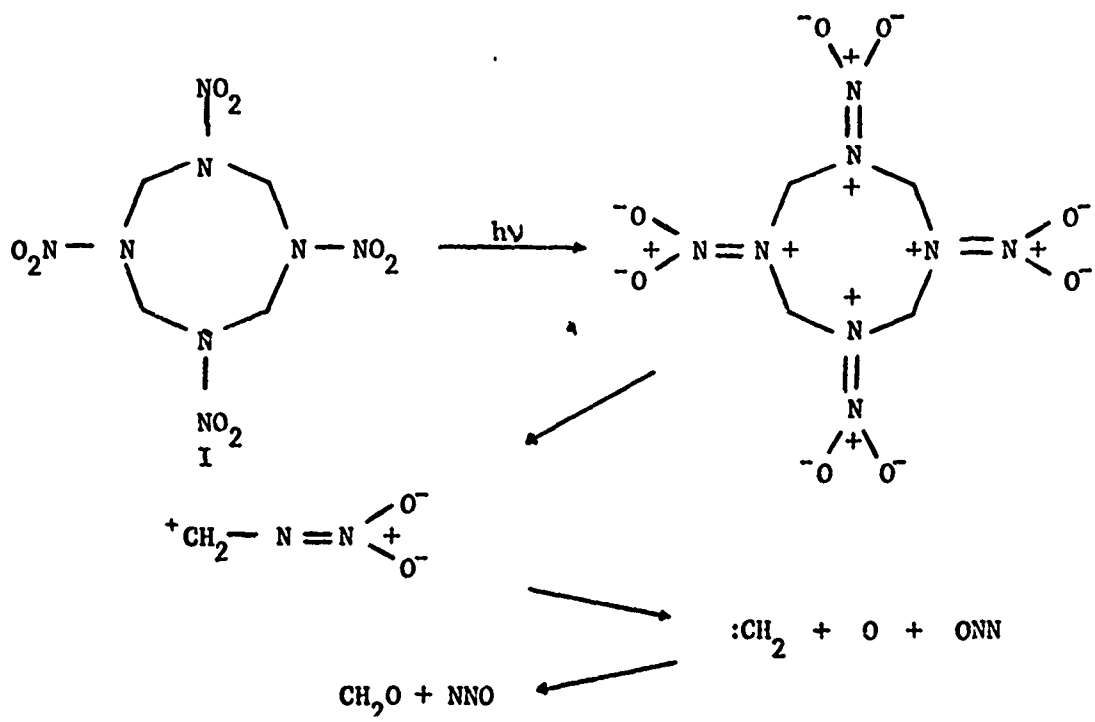

Figure 2. Maycock's Proposed Photochemical Mechanism for HMX

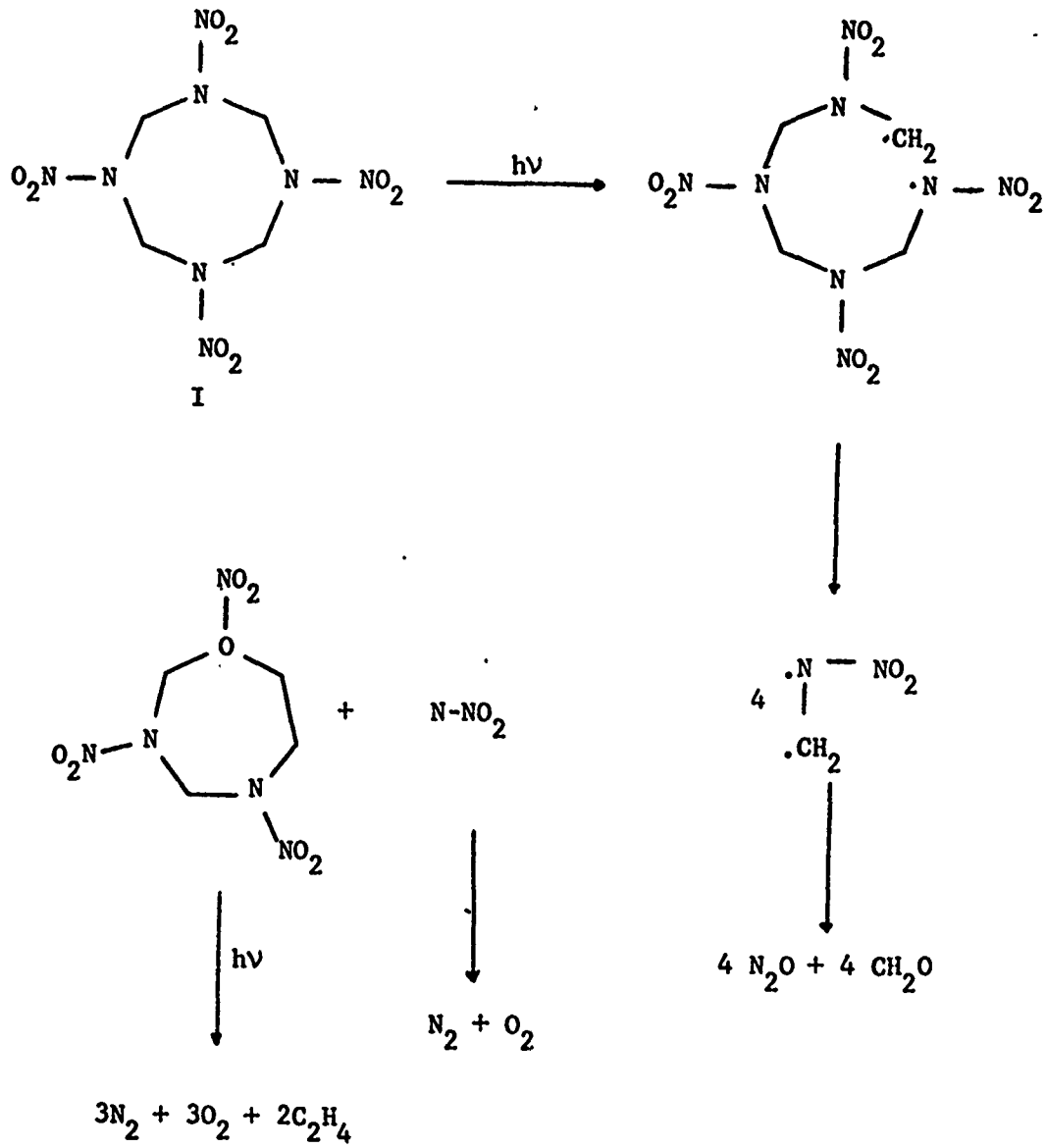

Figure 3. Torbit's Proposed Photochemical Mechanism for HMX

B. MODEL COMPOUND CHEMISTRY

Because the four nitramine groups in HMX add much complexity in the determination of the mechanism, another approach was sought. The starting material was simplified by elimination of all but one of the nitramine groups. The primary interest was centered upon the cyclic aliphatic nitramines, and, in particular, 1-nitropyrrolidine (II).

It was noticed by Bodnar [6 and 7] that when 1-nitropyrrolidine (II) was irradiated by ultraviolet light, an ESR spectrum could be detected. This spectrum was assigned to pyrrolidine-1-oxide (III). Therefore at least one of the reactions occurring is the formation of the nitroxide radical. This is shown as Step I in Figure 4.

Then major emphasis was put upon determining a possible mechanistic route starting from the nitroxide. There is evidence that dialkyl nitroxides in general [1, 2, 19 and 27] and this nitroxide (III), in particular [12], disproportionate by β-hydrogen abstraction to give the corresponding hydroxlamine and nitrone, Step II.

Again there is much evidence for hydroxylamines in general [1 and 2] and 1-hydroxypyrrolidine (IV) in particular [38 and 39] to regenerate the nitroxide photochemically, Step III. The hydroxylamine (IV) can also be oxidized to the nitroxide (III) by various chemical oxidizing agents [1 and 8].

Bonnett [9] and Lamchen [24] have both reported that numerous substituted nitrones of pyrrolidine have undergone photolysis to the corresponding oxaziridines, Step IV. From the work of Emmons [22], the predicted stability of the unsubstituted bicyclic oxaziranes should be on the order of two weeks. Therefore it can be expected

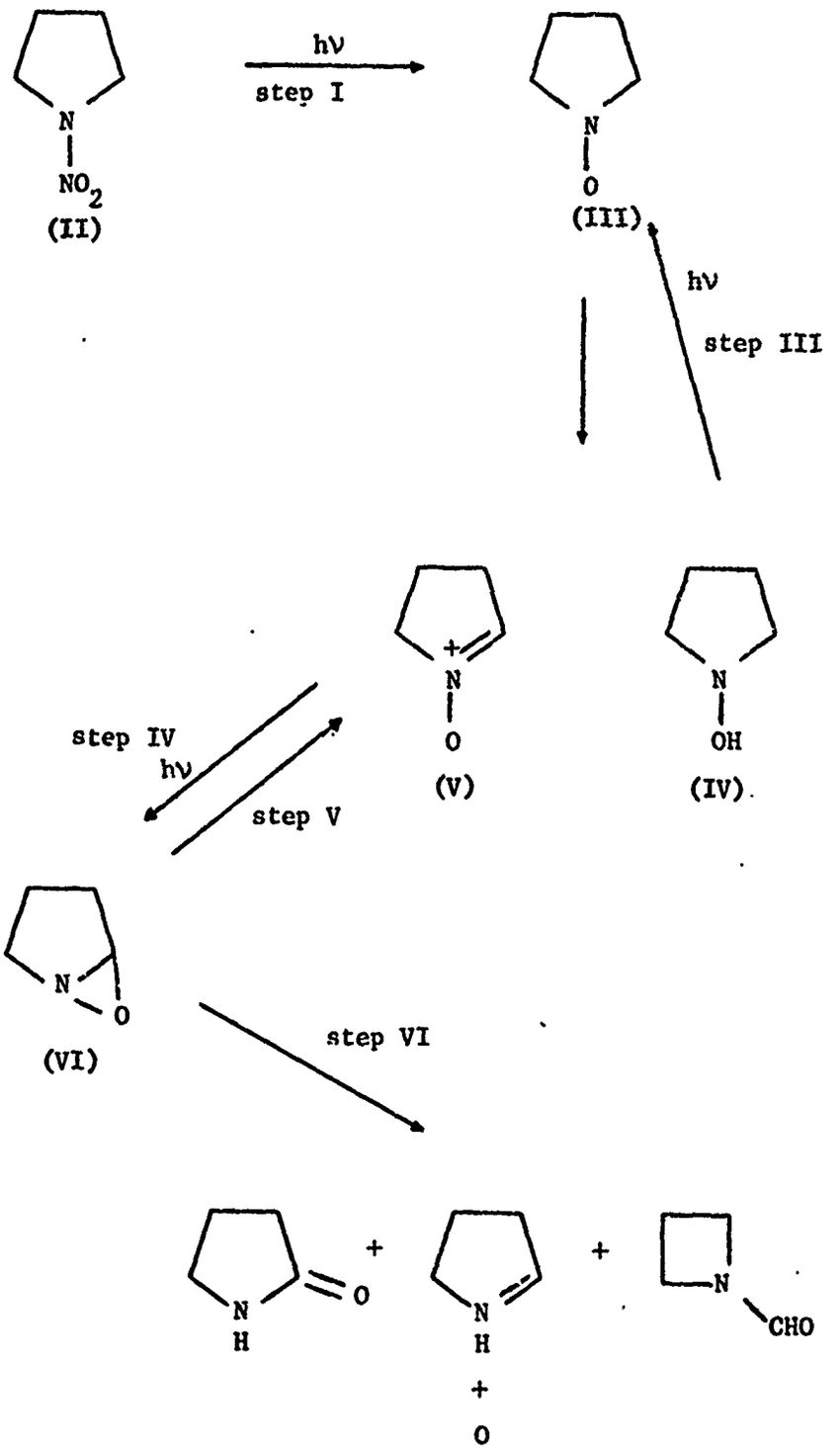

Figure 4. Proposed Mechanism for the Decomposition of 1-Nitropyrrolidine

that the nitrone (V) can be photolyzed to the oxaziridine (IV), Step IV.

The next step from the oxaziridine has many possibilities. Emmons [22] detected both the corresponding nitrone and the isomeric amide from the thermal degradation of oxaziranes. Bonnett [9] found only the isomeric amide from oxaziridines. Lamchen [24 and 25] has isolated three products from both the thermal and photochemical degradation of oxaziridines; these are the corresponding proline, pyrrolidone, and N-acetylazetidine. Therefore, for the oxaziridine (VI), all possible paths seem open as shown in Steps V and VI.

Work on the possible mechanism has been done by Whittaker [40]. He has obtained NMR and IR spectroscopic evidence of nitrone's existance when the nitramine (II) was photolyzed. Nitrones are known to undergo 1,3-cycloaddition with unsaturated compounds [13, 21, and 18]. Acrylonitrile will condense with nitrones spontaneously [13]. When Whittaker photolyzed the nitramine in acrylonitrile, he was not able to isolate the desired condensation adduct.

III. EXPERIMENTAL

A. INSTRUMENTATION AND SPOT TESTS

All melting points were taken on a Fisher-Johns melting point apparatus and are corrected.

The infrared absorption spectra were determined at room temperature with a Perkin-Elmer 337 Grating Infrared Spectrophotometer. The spectra were calibrated with the known peaks of polystyrene. The peaks are reported in wavenumbers and are followed by two sets of letters. The first set refers to the peak's relative intensity with the following meanings: s-strong, m-medium, and w-weak. The last set refers to the peak's general shape with the following meanings: s-sharp, b-broad, and sh-shoulder. A prefix of "v" means very. Liquids were examined as neat liquids between KBr plates. Solids were examined in KBr as a pressed disc.

The NMR absorption spectra were determined at 30°C with a Hitachi Perkin-Elmer R-20A High Resolution NMR Spectrometer. The applied frequency was 60 MHz, and the solvent used is given with the specific compound. The peaks location is given in ppm relative to TMS, following the ppm is the relative area in parantheses.

All ultraviolet spectra were determined with a Beckman DB Spectrophotometer. All spectra were run in cyclohexane.

The gas chromatograms were determined with a Bendix Chroma-lab Series 2200. The retention times are reported in minutes from the time of injection. The operating conditions were:

Column:	coating	SE-30
	concentration	20%
	support	Chromosorb W
	length	8 ft.
	diameter	1/8 in.
Temperature:	column	110°C
	injection point	200°C
	detector	150°C
Detector:	flame ionization	
Carrier gas:	helium	
Flow rates:	helium	50 ml/min
	hydrogen	40 ml/min
	air	1.8 cfm

The Snow test is a spot test for hydroxylamines taken from Snow [32] and Rogers [30]. A small amount of 2,3,5-triphenyl-2H-tetrazolium chloride (about 1 mg) was dissolved in an aqueous solution of the test compound on a spot plate. Then a drop of 2N sodium hydroxide was added. A positive test is the development of a red or purple-red color of the reduction product.

All other spot test and derivatives were done using standard procedures.

B. SYNTHETIC

1. 1-Formylpyrrolidine [15]

Into a 100 ml round-bottomed flask was placed 30 ml of freshly distilled pyrrolidine (0.36 moles). The flask was put into an ice bath and a condenser attached. To the well-stirred pyrrolidine, 16 ml of 97% formic acid (0.41 moles) was added slowly down the condenser. During this addition, the white misty plume was never allowed to reach more than halfway to the top of the condenser. The reaction mixture was then refluxed for two hours in an oil bath at 150°C. After

cooling, 100 ml of CH_2Cl_2 was added and the neutral aqueous layer was removed. The CH_2Cl_2 was washed with 25 ml of 2N NaOH. The CH_2Cl_2 was dried over Na_2SO_4 and removed with a rotary evaporator. The residual yellow oil was distilled at 108°C/25mm (lit. 98°C/14mm [3]), yielding 25.0 gm of a clear liquid. This was a 72% yield. The following physical constants were collected:

NMR (CCl_4)

singlet	8.05 (1)
multiplet	3.35 (4)
multiplet	1.80 (4)

(lit. 3.8 and 2.2 [11])

$n_D^{24} = 1.4766$ (lit. $n_D^{25} = 1.4770$ [3])

IR

3480 (s-vb)	1425 (s-s)	1188 (m-s)	910 (w-s)
2980 (s-b)	1390 (s-s)	1158 (m-s)	870 (w-b)
2890 (s-b)	1333 (m-s)	1115 (w-s)	813 (w-s)
1660 (s-b)	1245 (m-s)	1028 (w-s)	708 (m-s)
1480 (m-s)	1223 (m-s)	968 (w-s)	576 (w-b)
1460 (m-s)		938 (w-s)	509 (m-b)

2. <u>1-Nitropyrrolidine [15]</u>

Into a 250 ml three-necked flask, 50 ml of acetic anhydride and 50 ml of trifluoroacetic acid were combined. The flask was placed in a salted-ice bath at around -8°C. When the temperature of the reaction mixture reached -3°C, 35 ml of "red fuming" nitric acid was very slowly added to the well-stirred solution over the next hour. Temperature during addition was kept between -3°C and 0°C. Over the next 25 minutes,

15.7 g of 95% pure 1-formylpyrrolidine (0.15 moles) was added slowly; again the temperature was kept between -3°C and 0°C. The reaction mixture was stirred for one hour, and the temperature was not allowed to exceed 30°C. During this time NO_2 was continually being given off. The reaction mixture was poured over 100 g of ice; the resulting solution was blue. After an attempt to precipitate the product out by the addition of solid K_2CO_3 which only yielded salts as precipitates, the solution was extracted with 5 x 50 ml of CH_2Cl_2. The CH_2Cl_2 was then washed with 50 ml of water. The CH_2Cl_2 was removed first by a rotary evaporator and then by simple pumping on the residual oil. The remaining viscous red liquid was iced and a solid immediately formed. The solid was recrystallized from practical heptane, yielding 11.2 g of light tannish-red crystals melting 54-6°C. The crude product was treated with 200 ml of boiling heptane. The heptane was decanted away from the red liquid and then iced. After one-half hour, the crystalling material was collected by filtration and washed with heptane. This product was a white crystalline material, melting 56-7°C (lit. 58-9°C [15]), and amounted to 5.01 g. The residue was treated again with the mother liquor in the same manner. This yielded 3.97 g of product which melted 57-8°C. A total of 8.98 g of product (0.0774 moles) was obtained which was a 51% yield. The following physical data were collected:

NMR	(CCl_4)	
	deformed triplet	3.73 (1)
	deformed quintet	2.01 (1)

IR

3000 (m-s)	1370 (s-s)	1027 (m-s)	761 (s-s)
2975 (m-s)	1313 (s-s)	970 (m-b)	710 (w-b)
2940 (w-s)	1220 (m-s)	925 (w-b)	608 (m-s)
2900 (m-s)	1187 (w-s)	907 (m-s)	563 (m-s)
1490 (s-s)	1165 (w-s)	851 (m-s)	430 (m-s)
1450 (s-s)	1130 (w-s)		

UV

$\lambda max = 234$ nm (lit. 235 [15])

3. Attempted Oxidation of 1-Formylpyrrolidine [40]

Into a stoppered 250 ml flask was added 50 ml of $CHCl_3$, 1.31 g of 1-formylpyrrolidine, and 5.0 g of red HgO. The mixture was stirred vigorously for two hours. The solution was filtered and the $CHCl_3$ was removed with a rotary evaporator. A gas chromatogram showed a small solvent peak and starting material only. An IR showed only the peaks of 1-formylpyrrolidine.

4. Attempted Synthesis of 1-Hydroxypyrrolidine [31]

Into a 500 ml three-necked flask was placed 87 ml of pyrrolidine (1.04 moles), which was freshly distilled away from KOH. To the stirred chilled pyrrolidine was added slowly 71 ml of freshly distilled ethyl formate (0.875 moles). A dropping funnel, condenser, and thermometer were fitted to the flask and the temperature of the mixture raised to 45°C by the use of a Bunsen burner. Into the dropping funnel was placed 220 ml of 30% H_2O_2 (2.50 moles). The H_2O_2 was added slowly over the next two hours, amd the reaction mixture temperature was kept between 40°C and 50°C. The greenish-yellow mixture was extracted with

3 x 100 ml of ether. The ether was dried over Na_2SO_4 and removed with a rotary evaporator, yielding a viscous greenish-yellow oil. An attempt to distill under reduced pressure led to decomposition when air was vented into the system in order to change receivers.

When the reaction mixture was extracted continuously with ether for 24 hours, only a few more ml of the same material was obtained.

This material was obtained in other runs by extracting with 4 x 50 ml of CH_2Cl_2. The CH_2Cl_2 was dried over Na_2SO_4, and removed with a rotary evaporator. The yellow-green oil distilled at 108°C/~25mm. The yield was 17.7 g of material which had the same IR and NMR as 1-formylpyrrolidine.

5. <u>1-Hydroxypyrrolidine (method one) [41 and 39]</u>

Into a 250 ml three-necked flask was placed 100 ml of freshly distilled pyrrolidine (1.16 moles). A thermometer, condenser, and dropping funnel were attached. Into the dropping funnel was placed 100 ml of 30% H_2O_2 (1.16 moles). The temperature of the pyrrolidine was raised to 44°C by the use of a Bunsen burner. To the well-stirred pyrrolidine, the H_2O_2 was added over 50 minutes. During this time the temperature was maintained between 40°C and 50°C through the use of an ice bath and adjustment of the addition flow rate. After the addition, the reaction mixture was allowed the stir at room temperature for one and one-half hours. The reaction mixture was acidified with conc. HCl to pH 8, during which time the reaction mixture turned from an orange to a red-orange in color. The reaction mixture was then extracted with 5 x 50 ml of CH_2Cl_2. The CH_2Cl_2 was washed with 50 ml of water. The CH_3Cl_2 was dried over Na_2SO_4 and removed with a rotary evaporator.

Through distillation at 75°C/25mm, 1.96 g of material was obtained. By gas chromatographic analysis, the material had three major components.

In 20 ml of acetone was dissolved 2.2 g of oxalic acid dihydrate (0.017 moles). The light yellow distillate was added to this, resulting in a white precipitate which was collected by filtration. The precipitate was recrystallized from 20 ml of boiling methanol. The yield was 1.312 g of a white crystalline solid (0.0074 moles) which melted 122-3°C (lit. 123-4°C [35]). This was an overall yield of 0.64%. The following is the IR of the oxalate salt of 1-hydroxypyrrolidine:

3440 (m-vb)	1700 (s-s)	1219 (s-vb)	870 (w-s)
3060 (s-b)	1630 (s-b)	1119 (m-b)	849 (w-s)
2900 (s-vb)	1500 (m-s)	1009 (w-b)	825 (w-b)
2720 (s-b)	1445 (s-s)	982 (m-s)	731 (w-s)
2625 (s-b)	1400 (s-b)	940 (w-b)	715 (s-s)
2575 (s-b)	1340 (m-s)	903 (w-s)	619 (w-b)
1725 (s-b)	1282 (s-s)	891 (w-s)	495 (s-b)

This material was decomposed in liquid ammonia at dry ice-acetone temperature under a nitrogen atmosphere. The ammonia was allowed to evaporate off. The residual oil and solid were treated with CH_2Cl_2, which was then filtered to remove the solids. The CH_2Cl_2 was removed with a rotary evaporator. Since there was not enough to distill, only a gas chromatogram and infrared spectra were taken. The GC showed a solvent peak and another peak which had the same retention time as 1-hydroxypyrrolidine. The IR bore little resemblance to 1-hydroxypyrrolidine.

6. N-Hydroxysuccinimide [5]

Into a 500 ml flask, 50.0 g of succinic anhydride (0.50 moles) and 34.75 g of hydroxylamine hydrochloride were combined. The flask was placed on a rotary evaporator evacuated by a water aspirator. The flask was immersed in a silicone-oil bath at 125°C, where fusion soon occurred with the evolution of gases. Over the next hour, the temperature of the oil bath was raised to 150-60°C by which time the evolution of gases had stopped. The heating was stopped. When the oil bath temperature reached 125°C, the amber liquid was poured into 200 ml of ether. (It is seriously suggested that the entire ether part be done in a fumehood where the ether fumes can be quickly dispersed. Failure to do this can lead to fires.) The solution was vigorously stirred. The amber liquid first formed a gum and then solidified. The ether was decanted off. Then 200 ml of boiling 1-butanol was added to the solid, and then heated to boiling again. The hot liquid was filtered away from the insoluble solid, probably ammonium chloride. The liquid was iced for about one hour, after which time the crystalline material was collected by filtration and washed first by butanol and then by ether. The crude material had a tannish-white color, melted from 85-90°C, and amounted to 26.0 g. The crude product was treated with 170 ml of boiling ethyl acetate (6.5 ml/g crude product). The ethyl acetate layer was decanted away from the liquid layer of the crude product. After chilling the ethyl acetate layer for one hour, the crystalline material was collected by filtration and washed first by ethyl acetate and then by ether. This product was a white crystalline material melting 97-8.5°C, and amounted to 13.92 g.

The liquid residue which had now solidified was treated twice more with the same ethyl acetate, yielding respectively 4.57 g and 2.58 g with melting points 97-8.5°C and 96-7°C respectively. A total of 20.87 g of product was obtained which was a 36% yield. The following physical data were collected:

Acetate derivative 133-4°C (lit. 131-2°C [4])

NMR (acetone-d_6)

singlet 2.63

Snow test light purple

$FeCl_3$ red brown

IR

3450 (m-vb)	1705 (m-s)	1220 (s-b)	995 (m-s)
3020 (m-b)	1460 (m-s)	1150 (w-b)	815 (m-s)
2940 (m-b)	1420 (m-s)	1075 (s-s)	712 (s-s)
2830 (m-b)	1380 (w-s)	1045 (m-s)	645 (s-s)
1780 (m-s)	1303 (m-s)		

This matched authentic material from K&K Laboratory and Ref. [37].

The butanol was reduced to approximately half volume by the use of a rotary evaporator. The resulting liquid was heated to boiling to redissolve the solid which had precipitated out. The hot liquid was filtered away from the insoluble solid. After being iced for about one hour, a crystalline material was collected by filtration. The material was acidic in water and is believed to be succinic acid.

The ethyl acetate was treated in the same manner except that there was no insoluble solid. The only material recovered melted around 43°C. At times this material was a very significant impurity

in the product; also if the product was not kept in a dessiccator, the solid which melted around 43°C appeared as a significant impurity overnight. When a mixture of approximately two-thirds 43°C material and one-third 97°C material was dried over P_2O_5 in a vacuum at 80°C for 64 hours, a tannish-white solid was recovered which melted 91-3°C with no evidence of melting around 43°C.

7. 1-Hydroxypyrrolidine (method two) [42 and 35]

Into a 250 ml round-bottomed flask, was added 200 ml of ether and 9.21 g of N-hydroxysuccinimide (0.08 moles). Into an extraction thimble was placed 6.1 g of crushed $LiAlH_4$ (0.16 moles). The thimble was placed in a Soxhlet extractor and a condenser attached. The round-bottomed flask was immersed in an oil bath at 55°C. After one hour the Soxhlet extractor became plugged. Most of the remaining $LiAlH_4$ was transferred to the round-bottomed flask. A condenser was attached and the reflux continued. After 24 hours of refluxing, the $LiAlH_4$ was decomposed with 15 ml of 15% NaOH. The precipitate was filtered away from the ether. The gray precipitate was dissolved in a minimum of 50% NaOH. Enough water was added to the sirupy solution, which finally turned yellow, to allow the solution to be extracted with 5 x 50 ml of ether. This ether was combined with the reaction medium and dried over Na_2SO_4. The ether was removed with a rotary evaporator. The remaining yellow oil distilled at 81-2°C/29 mm to yield 235 mg of a clear liquid. This was 0.0026 moles of 1-hydroxypyrrolidine which was a 3.2% yield. The following physical constants were collected:

NMR (CCl_4)

singlet 8.20 (1)

triplet of triplets 2.88 (4)

J's = 3 Hz & 2 Hz

quintet 1.76 (4)

Picrate m.p. 149-50°C with decomposition

(lit. 146°C [35])

$n_D^{23.5}$ = 1.4599 (lit. n_D^{20} = 1.4606 [42])

$FeCl_3$ red-orange precipitate

Snow test very-deep red-purple, developed immediately

IR

3200 (s-vb)	1288 (m-s)	1005 (m-s)	805 (m-vb)
2980 (s-b)	1210 (m-b)	940 (w-b)	555 (m-s)
2870 (s-b)	1193 (m-s)	930 (m-b)	466 (m-s)
1445 (m-b)	1122 (m-s)	895 (m-s)	422 (m-s)
1328 (m-s)	1025 (m-b)	871 (m-s)	

The peak at 1445 was a broad peak which was topped by a sharp doublet.

8. <u>1-Pyrroline-1-Oxide [10]</u>

Into a 25 ml round-bottomed flask was added 185 mg of 1-hydroxypyrrolidine (2.1 moles), 912 mg of red HgO (4.2 moles), and 10 ml of $CHCl_3$. The mixture was vigorously stirred for two hours in the dark at which time beads of metallic mercury could be seen with the oxide. Then 231 mg HgO (1.05 moles) was added, and the stirring was continued for one and one-half hours. The solution was decanted away from the mercury and mecuric oxide. Most of the $CHCl_3$ was removed with a rotary evaporator. The round-bottomed flask was placed in warm water and was evacuated with a water aspirator for another half hour at which time bubbling had ceased. A gas chromatogram showed that 88% had been converted to

the nitrone. The following physical constants were collected:

Picrate mp 125-6° with decomposition

(lit. 125.5-6.5 [35])

$FeCl_3$ green turning to brown with time

Snow Test slow developing purple-red

NMR (CCl_4)

deformed triplet	6.66	(1)
triplet of triplets	3.8	(2)
J's = 2 Hz & 6 Hz		
multiplet	2.6	(2)
deformed quintet	2.2	(2)

UV λ_{max} = 240 nm (lit. 232 nm [35])

IR

3420 (s-vb)	1595 (s-s)	1075 (m-s)	745 (s-b)*
3080 (s-b)	1450 (s-s)	1040 (m-s)	681 (m-b)
2970 (s-b)	1340 (m-s)	972 (m-s)	661 (m-s)*
2815 (m-sh)	1255 (s-vb)*	919 (w-s)	612 (m-s)
2495 (m-b)*	1205 (s-b)	892 (m-b)	495 (m-s)
1870 (w-b)	1160 (m-b)	789 (m-sh)	451 (m-s)
1670 (m-b)			

Peaks followed by an asterisk are believed to belong to $CHCl_3$.

9. <u>3-Cyano-1-aza-2-oxa-[3.3.0]-bicyclooctane [18]</u>

In a 10 ml round-bottomed flask were combined 1 ml of distilled acrylonitrile and 231 mg of 1-pyrroline-1-oxide which by gas chromatography was 62% pure; the rest was 1-hydroxypyrrolidine. The stoppered flask was placed in a refrigerator. The next day the solvent was

removed with a rotary evaporator. The residual reddish oil was triturated with practical heptane, but the oil never crystallized. The heptane was removed first with a rotary evaporator, then by simple pumping on the residue. The following physical constants were collected on the reddish oil:

GC retention time 8.0

IR

3375 (s-vb)	2240 (w-s)	1400 (s-b)	1025 (w-vb)
2960 (s-b)	1675 (s-b)	1360 (m-b)	650 (w-b)
2880 (m-sh)	1400 (m-b)	1250 (w-vb)	615 (w-b)

10. Attempted Synthesis of 1-Ethylpyrrole

A 250 ml three-necked flask to which a condenser and dropping funnel were attached was filled approximately halfway with liquid ammonia. Through the condenser, 21.4 g of potassium (0.55 moles) was added to the liquid ammonia. Not all of the metal dissolved. Into the dropping funnel, 33.9 g of distilled pyrrole (0.55 moles) was placed and then slowly added. More liquid ammonia was added to replace that which had boiled off. Then 200 ml of ether was added in two parts. The ammonia was boiled off by placing the flask in a tray of cool water. Into 50 ml of ether was added 76.0 g of ethyl iodide (0.50 moles). Then the solution was placed into the dropping funnel and slowly added to the reaction mixture. The reaction mixture was refluxed for two hours. A gas chromatogram showed that only a very small fraction had been converted to a new component.

B. PHOTOLYTIC

The source of all photolyses was a Christie 200 W medium-pressure arc operated at 110 W. The samples were at a distance of three feet from the source. If there was a filter, it was placed halfway between the source and the sample.

1. 1-Hydroxypyrrolidine in Acrylonitrile

The photolysis cell for this experiment was a 50 ml round-bottomed flask inside a 1000 ml round-bottomed flask. The glass was Pyrex. The outer flask was filled with CCl_4 which gave around a 4 cm CCl_4 layer.

Into the inner flask of the photolysis cell was combined 0.2 ml of a mixture (GC retention time = 0.6, probably acetic acid, 35.0%; 0.80, 1-hydroxypyrrolidine, 21.3%; 1.6, unknown compound, 43.7%), and 10 ml of distilled acrylonitrile. The results of this photolysis are shown in Table I.

2. 1-Nitropyrrolidine in Acrylonitrile

A 10 cm quartz-windowed UV cell was filled with a 0.10 N solution of the nitramine in acrylonitrile. A chemical filter [14] for the isolation of the 2357 A region of a medium-pressure Hg arc spectrum was used.

After 25 hours of irradiation, no new peaks were observable on the gas chromatograms and the nitramine peak did not show any observable decrease. The filter was removed and the solution was irradiated for one hour more. The solution had yellowed and a precipitate formed. A peak at 6.00 was just bearly perceivable when the recorder attenuation was decreased by a factor of 50. The solution was filtered leaving a white solid which started to turn brown around 120°C and did not melt below 200°C.

TABLE I: RESULTS OF THE PHOTOLYSIS OF THE 1-HYDROXYPYRROLIDINE MIXTURE

The numbers refer to the percentage area of the peaks

time (hr)	GC retention time (min)		$\frac{height_{0.80}}{height_{8.60}}$
	0.80	8.60	
0	9.7	90.3	1.23
½	8.4	91.6	0.94
2	7.8	92.2	0.84
3	8.1	91.9	0.83

TABLE II: RESULTS OF THE PHOTOLYSIS OF 1-NITROPYRROLIDINE IN CH_2Cl_2

Retention times and areas of peaks of the red oil

Retention time (min)	Area (%)
0.60	(shoulder)
0.75	3.1
0.80	9.7
0.90	2.3
1.10	0.6
1.40	2.8
1.70	0.6
2.10	1.2
3.50	2.3
7.40	14.8
10.60	62.5

3. 1-Nitropyrrolidine in CH_2Cl_2

A 10 cm quartz-windowed UV cell was filled with a 0.010 N solution of the nitramine in CH_2Cl_2. After 18 hours of irradiation, the solution had deeply yellowed and a red precipitate had formed. Gas chromatograms taken at the start and the end of the photolysis showed that the nitramine peak had disappeared; the recorder attenuation was kept constant.

The solution was filtered. An IR of the red precipitate had only a few discernable peaks:

3440 (s-b) 1640 (s-b) 1395 (s-s) 1375 (s-s)

The solvent was removed from the filtrate first by a rotary evaporator, then by simple pumping on the residue. A gas chromatogram of the residual oil was taken. The results are given in Table II. The major material was starting material.

4. 1-Pyrroline-1-Oxide

About 50 mg of 88% nitrone was dissolved in a solution of 2 ml of cyclohexane and 2 ml of absolute ethanol. The solution was placed in a quartz-windowed cell with a 1.5 cm path length. The solution was irradiated without a filter.

After two hours of irradiation, the solution had lightly yellowed. After removal of the solvent first with a rotary evaporator then by simple pumping on the residue, an IR was recorded. The IR showed only the peaks of the starting material.

After another five hours irradiation under the same conditions, except this time it was under a nitrogen atmosphere, the solution was warm and very yellow. After removal of the solvent in the same manner

an IR in ethylene tetrachloride showed only four discernable peaks:

2960 (s-sh) 2940 (s-s) 2860 (m-s) 1700 (s-b).

IV. DISCUSSION

A. SYNTHETIC

1. N-Hydroxysuccinimide

There was only one problem with the procedure for the synthesis of N-hydroxysuccinimide where succinic anhydride and hydroxylamine hydrochloride were fused in a rotary evaporator. A white-subliming solid, possibly ammonium chloride, condensed on the stainless steel sleeve of the evaporator. This problem was eliminated by the use of a Teflon sleeve.

The product was found to exist in two forms, one of which was a hydrate melting around 43°C. The product can be recovered from this hydrate by drying over P_2O_5 in a vacuum at 80°C. The pure product melted at 96-7°C.

2. 1-Hydroxypyrrolidine

a. Ruppert's Procedure

While this method appeared to have great promise, other researchers besides the author have not met with great success using this procedure. Thesing [35] isolated the picrate of 1-hydroxypyrrolidine in 4% yield. Whittaker [40] claimed an 18% yield, but further examination of a sample of this material showed it to be 1-formylpyrrolidine. A gas chromatogram of the material had only one peak at 6.10, which is the retention time of 1-formylpyrrolidine. An IR of the material was an exact match for 1-formylpyrrolidine. Finally a UV spectrum from Whittaker's thesis showed 1-formylpyrrolidine's end absorption around 230 nm.

The mechanism for this procedure is believed to be: The

H_2O_2 first hydrolyses the ethyl formate to performic acid which in turn reacts with the pyrrolidine to yield the product. There seems to be two possible problems with this procedure. First, ethyl formate is a formylating agent itself with primary and secondary amines at elevated temperatures [23]. Second, if the ethyl formate is hydrolyzed to formic acid, formic acid is also a good formylating agent. This cannot be solved by combining the ethyl formate with the H_2O_2 and then adding the mixture to the pyrrolidine, because both Whittaker and this researcher tried this route, but only 1-formylpyrrolidine was isolated.

Therefore, because of the above synthetic problems, and because of the inability to find any trace of 1-hydroxypyrrolidine, this procedure was not considered a viable synthetic route.

b. Zinner and Moll's Procedure

This procedure also seemed promising. $LiAlH_4$ is known to reduce the carbonyl functionality of an amide to methylene; therefore, N-hydroxysuccinimide should be reduced to 1-hydroxypyrrolidine by $LiAlH_4$.

The first attempts were worked up exactly according to Zinner and Moll [42]. The $LiAlH_4$ was destroyed with water; then the ether was filtered away from the precipitate. After removal of the ether from the filtrate, distillation of the residual oil yielded around 4% of a two component system, which had GC retention time of 0.80 and 1.60 respectively.

Since the starting material was not very soluble in ether, at the start of the reactions most of the N-hydroxysuccinimide was on the bottom of the flask. At the end of the reaction there was either

very little or none of the starting material on the walls and bottom of the flask. Therefore, some reaction had occurred. It was reasoned that since there was not much product in the ether most of the product must have remained in the precipitate. Acid was first used to try to decompose the precipitate. Stoichiometric amounts of acid did not dissolve the precipitate even upon standing several days. When glacial acetic acid was used, again around a 4% yield of a two component mixture was isolated.

At this time, it was noticed that Thesing [35] reduced the nitrone to the hydroxylamine with $LiAlH_4$ and that he worked up the precipitate and not the ether. While this procedure did not improve the yield, it did improve the purity. Pure 1-hydroxlpyrrolidine was isolated.

c.. Woffenstein's Procedure [41]

This procedure had been used successfully though with poor yields [34 and 38]. Again the yields were poor, and the same two components were present with a third small impurity. Weil and Windle [38] also noticed that their product gave two spots on TLC. They mentioned a purification technique which was given in better detail in another paper [39]. While the isolation and purification of the oxalate salt was easily done, its decomposition in liquid ammonia did not work. The crude liquid recovered was nowhere near the amount expected.

It is believed that a possible alternative to the liquid ammonia is to use 50% NaOH to decompose the oxalate salt. Thesing [35] recovered the hydroxylamine from this solution, and the oxalic acid would stay in the aqueous phase. This modified procedure should

greatly simplify the procedure.

d. Thesing's procedure

Finally there remains another synthetic route to the desired hydroxylamine, that used by Thesing [35] as shown in Figure 5. This route requires the synthesis of the starting material, 1-ethylpyrrolidine. Thesing used a rather complex procedure from Organic Synthesis [46]. A more promising route should be from the catalytic reduction of 1-ethylpyrrole. But attempts at the synthesis of 1-ethylpyrrole from ethyl iodide and the potassium salt of pyrrole failed. Once this problem has been solved, this synthetic route should be very good.

3. <u>1-Pyrroline-1-Oxide</u>

This compound is most readily made by oxidation of the hydroxylamine. Thesing [35], Bonnett [10], and Lamchen [21] all used yellow mercuric oxide. After just ten minutes, the red mercuric oxide had started to discolor showing that the reaction was occurring. Since yellow mercuric oxide was never available, a comparison was not made. But based upon the above results, red mercuric oxide should suffice in the place of the yellow form.

Whittaker [40] also reported the synthesis of this nitrone by the oxidation of his 1-hydroxypyrrolidine with red mercuric oxide. His characterization data was quite plausible for the nitrone. Since his hydroxylamine was known to be 1-formylpyrrolidine, a repetition of his experiment was in order. The mercuric oxide never discolored and only starting material was recovered. Therefore his observation remains unexplained.

The one anomaly of this nitrone was that it gave a green to brown color with aqueous $FeCl_3$. Lamchen [20 and 21] reports that 2-unsubstituted nitrones rapidly reduce $FeCl_3$ to form an intense wine-red solution.

4. 3-Cyano-1-aza-2-oxa-[3.3.0]-bicyclooctane

Nitrones are known to condense with acrylonitrile [18, 28, and 13] without any thermal driving of the reaction as shown in Figure 6. Therefore when 1-pyrroline-1-oxide was mixed with acrylonitrile, the above adduct should have been formed. After the removal of the excess acrylonitrile the residual oil was triturated with practical heptane. Never did the oil solidify on any of the several attempts. A gas chromatogram showed only one peak besides the solvent at 8.0 min, Characteristic for this adduct should be a strong nitrile peak in the IR. Only a very weak absorption at 2240 was observed. No IR data on this or similar nitrone adducts were available. But there was IR data on the adducts of monocyclic α-dinitrones [28]. The nitrile bands for these compounds ranged from weak to just detectable. Therefore the weak nitrile peak for this adduct is not unreasonable in light of the above data.

Another way Lamchen [28] isolates these adducts was to add the α-dinitrones to a 50/50 solution of dioxane and acrylonitrile. The adducts precipitated out of this solution. Whittaker [40] photolyzed the nitramine in the same solution and got a precipitate but he was not able to isolate any adduct from this precipitate.

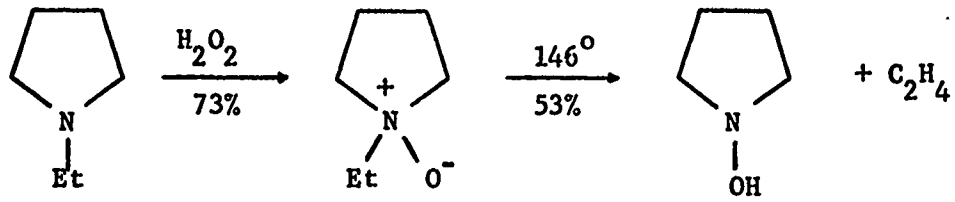

Figure 5. Thesing's Synthetic Route to 1-Hydroxypyrrolidine

TABLE III. GC RETENTION TIMES OF KNOWN COMPOUNDS

Compound	Retention Time (min)
pyrrolidine	0.75
1-pyrroline-1-oxide	0.60
pyrrole	0.70
1-hydroxypyrrolidine	0.80
2-pyrrolidone	6.40
adduct	8.0 - 8.6
1-nitropyrrolidine	10.0 - 11.0
1-formylpyrrolidine	6.10

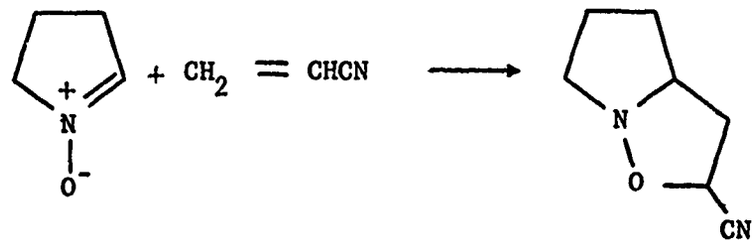

Figure 6. Mechanism of Adduct Formation

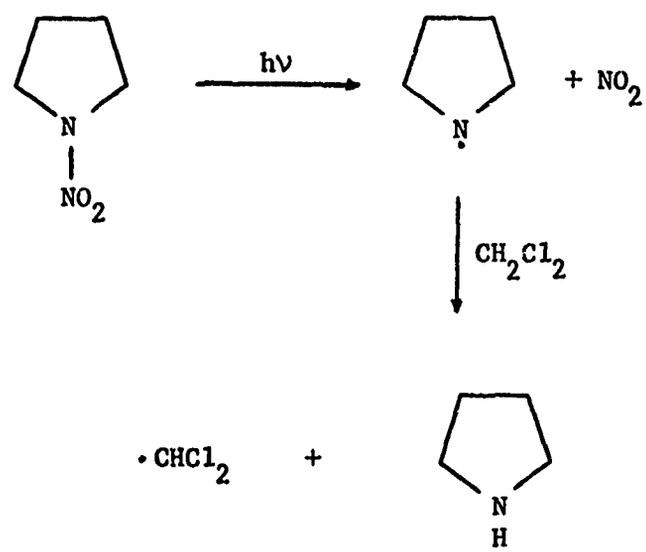

Figure 7. Mechanism of Pyrrolidine Formation in Nitramine Photolysis

B. PHOTOLYTIC

1. 1-Nitropyrrolidine

From the photolysis of the nitramine in CH_2Cl_2, there were two products, a red solid and a red oil. An assignment of the red solid could not be made from the IR. The IR does suggest a rather impure polyamide. The two peaks at 1395 and 1375 are very similar to the doublet at 1445 of 1-hydroxypyrrolidine. This doublet appears at 1460 for hydroxylamine hydrochloride. While there are peaks in this area, none show this doublet for N-hydroxysuccinimide. This data at least suggests that the red solid might have a N-hydroxy functionality. This IR was in no way similar to the IR of the unknown compound X of Whittaker's [40], whose IR characteristic region is very similar to that of the dimer of 1-piperidine-1-oxide [34].

But the red oil does give some good results. Some of the peaks in the gas chromatogram can be tentatively assigned. The peak at 0.80 contains 9.7% of the total area; the peak also has the retention time of 1-hydroxypyrrolidine. The peak at 0.75 probably corresponds to pyrrolidine which can arise as shown in Figure 7. The first step in the decomposition of the nitramine is homolytic cleavage of the N-N bond [6] yielding NO_2 and pyrrolidine radical. Instead of the pyrrolidine radical reacting with the oxides of nitrogen present to yield the nitroxide radical, the pyrrolidine radical could abstract a hydrogen atom from the solvent which would yield pyrrolidine. There is a shoulder at 0.60 on the solvent peak which suggested the presence of nitrone, but the shoulder could not be resolved into a peak at this temperature. There were no peaks corresponding to 2-pyrrolidone which

is another postulated intermediate.

Unfortunately, the photolysis of the nitramine in acrylonitrile did not yield any results. The explanation of this could lie with two possible problems. The UV absorption of the nitramine does overlap the transmittance of the chemical filter used. Therefore, possibly the intensity of the light through the filter was just too weak to affect a noticeable photochemical reaction during the time of irradiation. Or possibly, this part of the absorption curve is not photochemically active. So no matter what the intensity of light through the filter, no photochemical reaction could occur.

2. 1-Hydroxypyrrolidine

This experiment raises several questions while answering others. In this experiment a three component mixture containing 1-hydroxypyrrolidine was photolyzed in acrylonitrile. Samples were taken at intervals, and gas chromatograms taken. Since the hydroxylamine peak was superimposed upon the decaying solvent peak, good measurement of the peak was difficult. But clearly the trend was for the height of the peak at 8.60 to grow larger in comparison to the hydroxylamine peak. Since the adduct peak did move around slightly, the peak at 8.60 has been assigned to be that of the adduct. This peak appeared with the addition of acrylonitrile which implies that the nitrone had to be present at the start. The peak at 0.60 has the same retention time as the nitrone and as acetic acid. Since acetic acid was used in the work up, it is believed that this peak is due to acetic acid. Since this peak was obscured by the acrylonitrile peak, it was not known whether this peak disappeared or not. The disappearance of the peak at 1.60 implies

that it is a nitrone, but it did not have the correct retention time. It is known that 1-pyrroline-1-oxide does not form a dimer easily [17]. Therefore, this peak might be the dimer, but how it could arise is unknown. One way to test this hypothesis would be to reduce the two component mixture with either $LiAlH_4$ [35] or KBH_4 [8] which are known to reduce nitrones to hydroxylamines. The result should be a single peak at 0.60 remaining which corresponds to the hydroxylamine.

The design for the photolysis cell used in this experiment was taken from Lamchen [28], because it increases the yield of adduct while decreasing the photochemistry of the nitrone by absorbing light to which the nitrone is photochemically sensitive. But this also filters out the wavelength of light to which the hydroxylamine is sensitive. Weil and Windle [38] observed nitroxide radicals in pure hydroxylamines samples only with light no longer than 254 nm. Only with trace impurities did nitroxides appear with longer wavelength light. Adamic [1] got nitroxides using a filter with maximum transmittance of 365 nm in deoxygenated solvents. The only possible explanation for this result is that enough short wavelength light from the high pressure mercury arc passed through the filter to cause photochemistry to occur. Finally, the explanation for the results from the mixture photolysis is that the nitroxide formation probably did not occur directly but indirectly through oxygen or impurity sensitization.

3. <u>1-Pyrroline-1-Oxide</u>

This photolysis was attempted in order to show the viability of Step IV in Figure 4. Since the amount of the starting material was so small, the product was not much. The IR does show that it is not starting material and it does not really fit any of the postulated

products, either the oxaziridine of its decomposition products.

C. THE APPLICABILITY OF GAS CHROMATOGRAPHY

The general problem of previous methods, such as IR and NMR, of following reactions was their insensitivity to trace amounts. Another problem, which also affects UV, is the lack of knowledge of what and how much is in the reaction solutions. Gas chromatography using flame ionization detector helps diminish both of these problems by supplying this general information. The retention times can also help in identifying the components. Therefore gas chromatography most definitely should be used along with the other techniques in following reactions.

There is only one solvable problem encountered in using the gas chromatograph. The operating conditions were chosen early in the research and kept standard throughout so that comparisons could be made from experiment to experiment. Since the nitrone was not synthesized until late in the research, it was not discovered that its retention time was so short that solvent peaks would normally obscure it. There are two possible solutions. The first solution is to use a solvent with retention time that is beyond the area of interest, but solvents with these characteristics were non-existent. The second and more plausible solution is to temperature program the gas chromatograph. By operating the first part of the chromatogram at low temperature around 50°C, the solvent and products should be resoluable. When this was tried, the separation of multiple peaks was very promising. Although no actual samples were available at this time, the above results clearly indicate that temperature programming of the gas chromatograph should

be done.

D. MECHANISTIC

1. Decomposition of Nitramines

The proposed mechanism is shown in Figure 4. Step I has been shown to occur through the work of Bodnar [6 and7]. Since the nitroxide (III) might not always abstract a proton from another nitroxide, the hydroxylamine (IV) should be present in larger concentration than the nitrone (V). There is strong evidence that this is indeed true from the analysis of the decomposition products of 1-nitropyrrolidine in CH_2Cl_2. The photolysis of the hydroxylamine mixture in acrylonitrile indicate that Step III to Step II to adduct formation is viable. No conclusions can be drawn for Step IV since the photolysis to test this step has uninterpretable results.

One aspect of the proposed mechanism which has not been mentioned before is its photochemical homogeneity. The λ_{max} for nitramines is 234 nm. The hydroxylamines are photochemically active below 254 nm [38]. And finally, nitrones in general absorb from 220-50 nm depending upon the solvent [26]. Therefore, unless trapping agents are in the reaction solution, the proposed mechanism is photochemically active at least down to oxaziridine (VI) formation.

2. Decomposition of HMX

No conclusions should be drawn concerning Surayanarayana's mechanism because his is thermal while this investigation work was photochemical, but conclusions can be drawn concerning the postulated mechanisms of Maycock [29] and Torbit [36]. Bodnar [6 and 7] has assigned a nitroxide ESR spectrum to a very similar nitramine, RDX,

under photochemical conditions. This investigation has shown evidence that hydroxylamine is present under the same conditions. One of the major factors Maycock used in support of his mechanism is the appearance of N_2O as the product. This product is really not inconsistent with the present mechanism because in a system which contains the various oxides of nitrogen, hydroxylamines, and ammonia will yield as a product, N_2O. Therefore, from the results of this and previous works, the postulated mechanism by Maycock and Torbit seems to lead in the wrong direction and the present proposed mechanism is strengthened.

LIST OF REFERENCES

1. Adamic, K., Bowman, D.F., Gillam, T., and Ingold, K.U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. I. Self-Reactions of Diethyl Nitroxide Radicals," Journal of the American Chemical Society, v. 93, p. 902 - 8, 1971.

2. Adamic, K., Bowman, D.F., and Ingold, K.U., "Self-Reaction of Diethylnitroxide Radicals," Journal of the American Chemical Society, v. 92, p. 1093 - 4, 1970.

3. Adelman, R.L., "Studies on the Base Strength of N,N-Disubstituded Amides," Journal of Organic Chemistry, v. 29, p. 1837 - 44, 1964.

4. Ames, D.E., and Grey, T.F., "The Synthesis of Some N-Hydroxyimides," Journal of the Chemical Society, p. 631 - 6, 1955.

5. Anderson, G.W., Zimmerman, J.E., and Callahan, F.M., "The Use of Esters of N-Hydroxysuccinimide in Peptide Synthesis," Journal of the American Chemical Society, v. 86, p. 1839 - 42, 1964.

6. Bodnar, J.W., The Photochemistry of Nitramines I: Preparation of Nitroxides in Solution in situ in Single Crystal, thesis, Naval Postgraduate School, Monterey, California, 1971.

7. Bodnar, J.W., and Rowell, C.F., "ESR Studies of Unsubstituted Cyclic Nitroxides in Solids," Journal of Chemical Physics, v. 56, p. 707 - 9, 1971.

8. Bonnett, R., Brown, R.F.C., Clark, V.M., Sutherland, I.O., Sir Alexander Todd, "Experiments toward the Synthesis of Corrins. Part II. The Preparation and Reactions of Δ^1-Pyrroline-1-Oxides," Journal of the Chemical Society, p. 2094 - 102, 1959.

9. Bonnett, R., Clark, V.M., and Sir Alexander Todd, "Experiments towards the Synthesis of Corrins. Part III. Formation of a Bicyclic Oxazirans from a Δ^1-Pyrroline and from the Corresponding Nitrone," Journal of the Chemical Society, p. 2102 - 4, 1959.

10. Bonnett, R., Ho, S.C., and Raleigh, J.A., "Studies in the Pyrroline Series. V. 3,3-Diethyl-1-Pyrroline-1-Oxide," Canadian Journal of Chemistry, v. 43, p. 2717 - 23, 1965.

11. Bottini, A.T., and Roberts, J.D., "Nuclear Magnetic Resonance Spectra. Nitrogen Inversion Rates of N-Substituted Aziridines (Ethylenimines)," Journal of the American Chemical Society, v. 80, p. 5203 - 8, 1958.

12. Bowman, D.F., Gillan, T., and Ingold, K.U., "Kinetic Applications of Electron Paramagnetic Resonance Spectroscopy. III. Self-Reactions of Dialkyl Nitroxide Radicals," Journal of the American Chemical Society, v. 93, p. 6555 - 61, 1971.

13. Brown, C.W., Marsden, K., Rogers, M.A.T., Tylor, C.M.B., and Wright, R., "The Condensation of Nitrones and Olefins," Proceedings of the Chemical Society, p. 254 - 5, 1960.

14. Calvert, J.G., and Pitts, Jr., J.N., Photochemistry, p. 729 - 30, John Wiley & Sons, Inc., 1967.

15. Coburn, M.D., and Ungnade, H.E., "Synthesis and Structure of the N-Nitropyrrolidinones (1)," Journal of Heterocyclic Chemistry, v. 2, p 308 - 9, 1965.

16. Coleman, G.H., Nichols, G., and Martens, T.F., "1-n-Butylpyrrolidine," Organic Synthesis, v. 25, p. 14 - 9, 1945.

17. Delpierre, G.R., and Lamchen, M.,"Nitrones," Quarterly Reviews, p. 329 - 48, 1965.

18. Delpierre, G.R., and Lamchen, M., "Nitrones. Part I. Cycloaddition of Unsymmetrical Olefins to the 1-pyrroline-1-Oxides," Journal of the Chemical Society, p. 4693 - 701, 1963.

19. Dupeyre, R.M., and Rassat, A., "Nitroxides XIX. Norpsuedopelletierine-N-Oxyl, a New, Stable, Unhindered Free Radical," Journal of the American Chemical Society, v. 88, p. 3180 - 1, 1966.

20. Elsworth, J.F., and Lamchen, M., "Cyclic Nitrones. Part II. The Oxidation of Cyclic Nitrones by Iron (III) Chloride," Journal of the Chemical Society (C), p. 1477 - 81, 1966.

21. Elsworth, J.F., and Lamchen, M., "Nitrones. Part IX. The Synthesis and Reactions of 2,3-Dihydro-1,4-oxazine, a Heterocyclic Nitrone," Journal of the Chemical Society (C), p. 2423 - 7, 1968.

22. Emmons, W.D., "The Preparation and Properties of Oxazirines," Journal of the American Chemical Society, v. 79, p. 5739 - 54, 1957.

23. Fieser, L.F., and Fieser, M., Reagents for Organic Synthesis, p. 382, John Wiley and Son, Inc., 1968.

24. Kaminsky, L.S., and Lamchen, M., "Nitrones. Part III. Photolysis of Cyclic Nitrones," Journal of the Chemical Society (C), p. 2295 - 9, 1966.

25. Kaminsky, L.S., and Lamchen, M., "Nitrones. Part VI. The Pyrolysis of Oxaziridines Derived by Photolysis of Cyclic Nitrones," Journal of the Chemical Society (C), p. 2128 - 30, 1967.

26. Kaminsky, L.S., and Lamchen, M., "Nitrones. Part VIII. The Ultraviolet Absorption of 1-Pyrroline-1-Oxides," Journal of the Chemical Society (B), p. 1085 - 7, 1968.

27. Keana, J.F.W., Dinerstein, R.J., and Baitis, F., "Photolytic Studies on 4-Hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl, a Stable Nitroxide Free Radical," Journal of Organic Chemistry v. 36, p. 209 - 11, 1971.

28. Lamchen, M., and Mittag, T.W., "Nitrones. Part VII. The Photochemistry and Cycloaddition of a Monocyclic α-Dinitrone," Journal of the Chemical Society (C), p. 1917 - 21, 1968.

29. Maycock, J.N., Pai Vernaker, V.R., and Lochte, W.,"Physico-Chemical Properties of 1,3,5,7-Tetranitro-1,3,5,7-Tetraazacyclooctane (HMX) II. Spectra and Ultraviolet Radiation Damage Phenomena," Physica Status Solidi, v. 35, p. 849 - 60, 1969.

30. Rogers, M.A.T., "Aliphatic Hydroxlamines. Part I. Preparation," Journal of the Chemical Society, p. 769 - 72, 1955.

31. Ruppert, W., "Verfahren zur Herstellung von organischen Hydroxylaminverbindungen," German Patent 1004191, 14 March 1957.

32. Snow, G.A., "Mycobactin. A Growth Factor for Mycobacterium johnei. Part II. Degradation, and Identification of Fragments," Journal of the Chemical Society, p. 2588 - 96, 1954.

33. Surayanarayana, B., Graybush, R.J., and Autera, J.R., "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)," Chemistry and Industry, p. 2177 - 78, 1967.

34. Thesing, J., and Mayer, H., "Cyclishe Nitrone I: Dimeres 2.3.4.5-Tetrahydro-pyridin-N-oxyd," Chemische Berichte, v. 89, p. 2159 - 67, 1956.

35. Thesing, J., and Sirrenberg, W., "Cyclische Nitrone, IV. Darstellung und Eigenschaften des Δ^1-Pyrrolin-N-Oxyds," Chemische Berichte, v. 92, p. 1748 - 55, 1959.

36. Torbit, J.B., The Photochemical Decomposition of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane, thesis, Naval Postgraduate School, Monterey, California, 1970.

37. Wang, K., Brattesani, D.N., and Weinstein, B., "Heterocyclic Compounds. Vi. An Improved Preparation of N-Hydroxysuccinide," Journal of Heterocyclic Chemistry, v 3 p. 98, 1966.

38. Weil, J.T., and Windle, J.J., "Electron Spin Resonance Study of Nitroxide Radicals from Diethylhydroxlamine, Dioctylhydroxylamine, and N-Hydroxypyrrolidine," Nature, v. 217, p. 842 - 3, 1968.

39. Windle, J.J., Kunhle, J.A., and Beck, B.H., "ESR Study of Interconversion in Substituted Piperdine Iminoxyls," Journal of Chemical Physics, V. 50, p. 2630 - 56, 1969.

40. Whittaker, H., Photochemistry of Nitramines II: Stoichiometry, Intermediates, and Products, thesis, Naval Postgraduate School, Monterey, California, 1971.

41. Wolffenstein, R., "Oxydation des Piperinins mit Wasserstoffsuperoxyd," Chemische Berichte, v. 25, p. 2777 - 85, 1892

42. Zinner, G., and Moll, R., "Zur Kenntnis der 1-Alkoxy-2,4-dioxoazetidine," Chemische Berichte, v. 89, p. 1292 - 8, 1966.