Copyright Warning & Restrictions

The copyright law of the United States (Title 17, United States Code) governs the making of photocopies or other reproductions of copyrighted material.

Under certain conditions specified in the law, libraries and archives are authorized to furnish a photocopy or other reproduction. One of these specified conditions is that the photocopy or reproduction is not to be "used for any purpose other than private study, scholarship, or research." If a, user makes a request for, or later uses, a photocopy or reproduction for purposes in excess of "fair use" that user may be liable for copyright infringement,

This institution reserves the right to refuse to accept a copying order if, in its judgment, fulfillment of the order would involve violation of copyright law.

Please Note: The author retains the copyright while the New Jersey Institute of Technology reserves the right to distribute this thesis or dissertation

Printing note: If you do not wish to print this page, then select "Pages from: first page # to: last page #" on the print dialog screen

THE REACTION OF O-PROPYLPHENYL AZIDE WITH DI-N-PROPYLAMINE

BY

SEYED ZIAEDDIN RAZAVI

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCHIENCE IN CHEMISTRY

AT

NEWARK COLLEGE OF ENGINEERING

Newark, New Jersey
1971

APPROVAL OF THESIS

THE REACTION OF O-PROPYLPHENYL AZID WITH DI-N-PROPYLAMINE

BY

SEYED ZIAEDDIN RAZAVI

FOR

DEPARTMENT OF CHEMISTRY

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

_____

_____

NEWARK, NEW JERSEY

MAY, 1971

ABSTRACT

Nitration of n-propylbenzene resulted in o-nitro-n-propylbenzene. Reduction of this compound gave o-n-propylaniline. o-n-Propylphenyl azide was prepared by diazotization of o-n-propylaniline followed by treatment with sodium azide.

Photolysis of o-n-propylphenyl azide in di-n-propylamine yielded two new azepines, 2-di-n-propylamino-3n-propyl-3H azepine and 2-di-n-propylamino-7-n-propyl-7H-azepine. Their structures were assigned on the basis of their physical properties (i.e. I.R., U.V., N.M.R., N.S. and elemental analysis).

Photolysis of the azide at room temperature gave 26.9% o-n-propylaniline and 4.3% 2-di-n-propylamino-3-n-propyl-3H azepine, but when the photolysis was carried out in the presence of the triplet photosensitizer (xanthen-9-one) the yield of o-n-propylaniline was increased to 34.6% and the yield of 2-di-n-propylamino-3n-propyl-3H-azepine was decreased to 1.4%. Photolysis at the reflux temperature of di-n-propylamine (110c°) resulted in the formation of 42% o-n-propylaniline, 19.9% 2-di-n-propylamino-3n-propyl-3H azepine, 3.7% 2-di-n-propylamino 7n-propyl-7H azepine and 4.5% 2-methylindoline.

Based on these results, arguments are presented which suggest that singlet n-propylphenyl nitrene, which is in equilibrium with azabicyclic intermediates, is responsible for the formation of these two new asepines, 2-di-n-propylamino 3n-propyl-3H azepines and 2-di-n-propylamino-7n-propyl-7H azepine. Also, a mechanistic scheme is proposed to explain the formation of all products obtained from the photoysis of o-n-propylphenyl azide.

ACKNOWLEDGEMENT

The author wished to express his sincere appreciation to Dr. Richard B. Trattner who made many helpful suggestions and offered much useful advise during his valuable supervision on this work.

TABLE OF CONTENTS

LIST OF TABLES

INTRODUCTION

Aryl azides can decompose thermally or photochemically by the loss of molecular nitrogen to form a nitrene intermediate which has a monovalent nitrogen.

$$R\text{-}N_3 \xrightarrow{\Delta \text{ or } h\nu} R\text{-}\ddot{N}| + N_2$$

Nitrenes can exist in either the singlet state in which electrons are paired, $Ar\text{-}\ddot{N}$, or in the triplet state in which two electrons are unpaired, $Ar\text{-}\dot{\ddot{N}}\cdot$.

Reports in the literature suggest that the intermediate nitrene is in equilibrium with an azabicycloheptyl compound. In the presence of a secondary amine solvent, this azabicyclo-compound is trapped in the form of an azepine. This work is concerned with the mechanism of azepine formation and is aimed toward providing additional knowledge in the general area of the photochemistry of aryl azides.

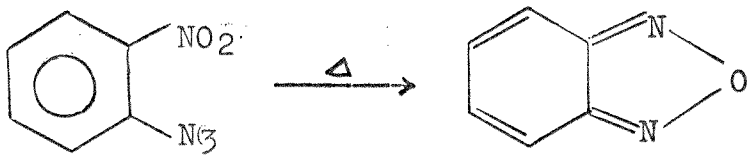
THEORY AND BACKGROUND

I. Nitrenes (a) Characterization and Nomenclature:

Nitrenes are intermediate monovalent nitrogen-containing species usually formed when organic azides are made to undergo loss of nitrogen.

$$RN_3 \longrightarrow R\text{-}\bar{N}| + N_2$$

Nitrenes possess an electron deficient nitrogen atom that has only a sextet of electrons in its outer shell (22, 24, 25, 13, 2, 1). They resemble a carbonium ion or a carbene in their reactions. The carbene like character of nitrenes is shown by the formation of benzfuroxan which results from the thermolysis of o-nitrophenyl azide.[1,2]

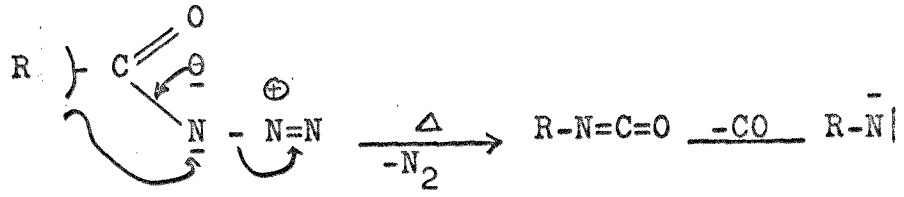


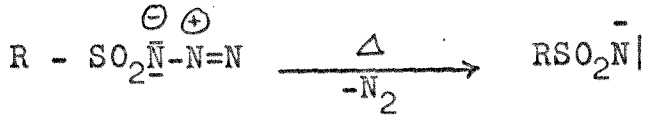
There are difference names, other than nitrene, for this type of nitrogen intermediate such as azene, azylene, imine radicals[9] and azacarbenes.[12]

The important characteristics of nitrenes are listed briefly as follows:

1. Nitrenes usually possess a ground state triplet electronic configuration. This has been determined by examination of the electron spin resonance at very low temperatures.(13,2)
2. At ambient or higher temperatures, nitrenes can exist in the triplet or singlet configuration depending on the nature of the nitrene and the reaction conditions.(13,2)
3. Nitrenes are not stable and possess a very short lifetime. Nitrenes undergo the following reactions; (a) isomerization to imines, (b) dimerization to azo compounds, (c) hydrogen abstraction from the solvent, (d) insertion into carbon-hydrogen bonds which can sometimes result in ring closure.(13,2)

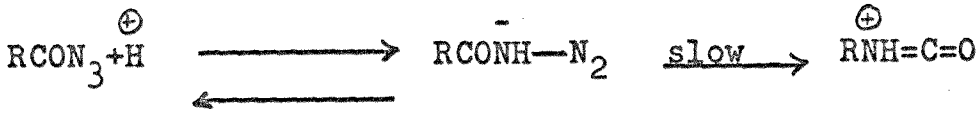
(b) Formation of Nitrenes; most alkyl azides, arylazides, sulfonyl azides and azido formates decompose on heating to yield nitrene intermediates.(13,2)



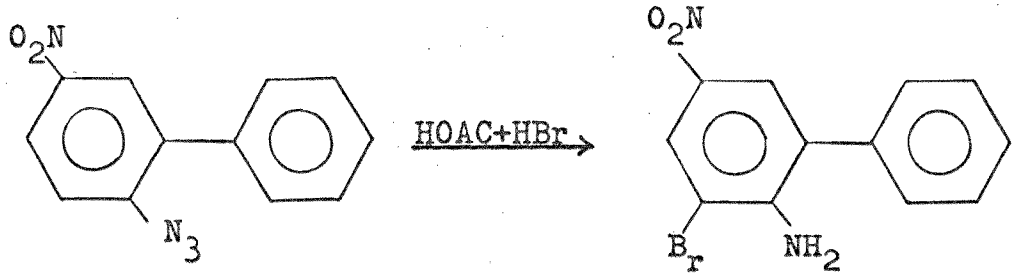


Decomposition temperatures decrease in order of alkyl and aryl azides > azidoformates and sulfonyl azides > acyl azides.(13,2)

Acyl azides will also undergo acid catalyzed decomposition.

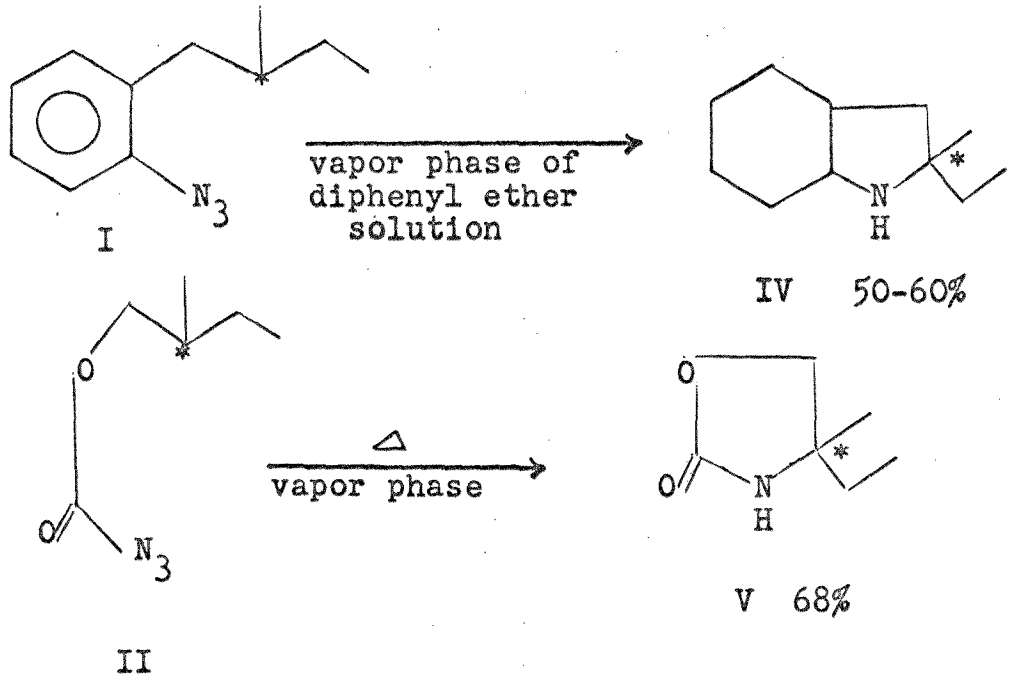


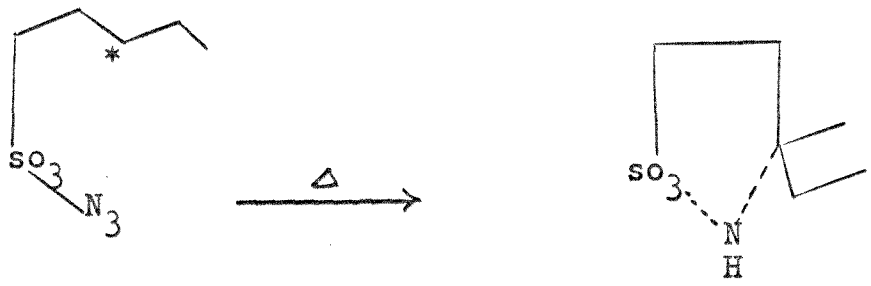
In solutions of hydrogen bromide in acetic acid, many o-azidobiphenyls decompose at 50-60°C as follows.(13,2)



Non-catalytic decomposition yields carbazoles:[13,2]

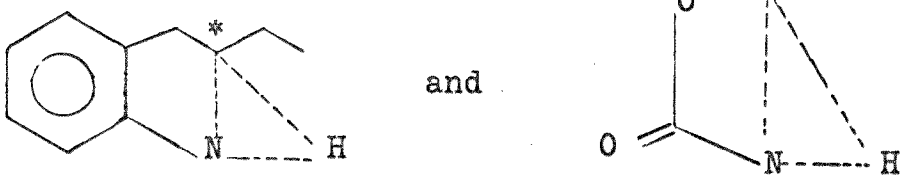
The thermal decomposition of optically active azides, 1-azido 2-(2-metyl butyl) (I), 2-methyl butyl azido formate (II) and 3-metyl pentane - 1-sulfonyl azide (III), gives optically active products shown below.[26]





III VI

A greater degree of optical activity is obtained in the vapor phase than in solution. To account for these results a concerted C-H insertion involving a singlet nitrene is suggested.(26) i.e.:



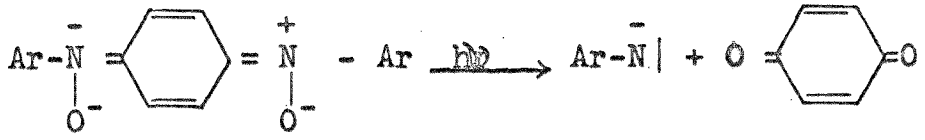
(c) Formation of Arylnitrenes Arylnitrenes can be obtained by the removal of a doubly bonded group from trivalent nitrogen (egs. 1,2), by elmination of two single bonded groups (egs. e,4), by the photolysis of some nitrenes to remove the singly and doubly bonded groups (eg. 5) or by fragmentation of a heterocyclic ring(14) (egs. 6,7).

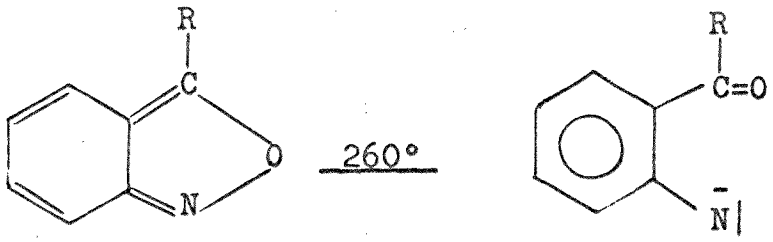
1) $Ar\text{-}N{=}N_2 \xrightarrow{\Delta \text{ or } h\nu} Ar\text{-}\bar{N}| + N_2$

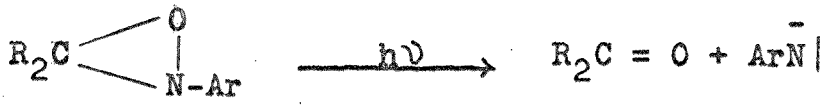
2) $Ar\text{-}N{=}O \xrightarrow{\text{o-acceptor}} Ar\text{-}\bar{N}| + (O)$

3) $Ar\text{-}NX_2 \xrightarrow{\Delta} Ar\text{-}\bar{N}| + X_2$

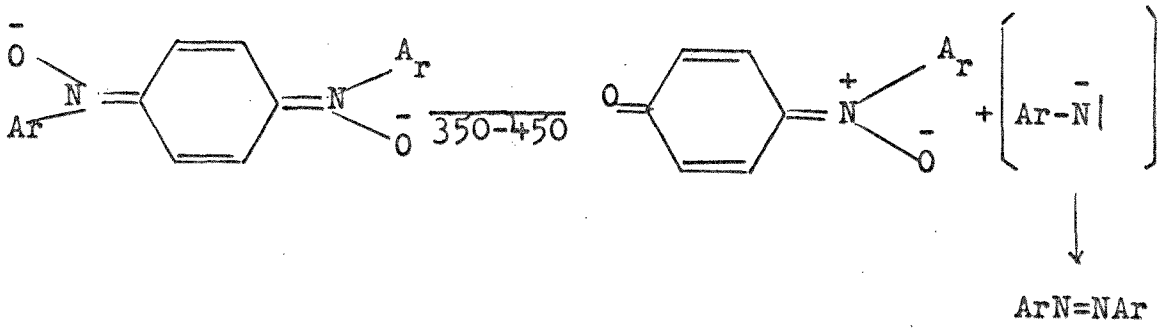
4) $Ar\text{-}NH_2 \xrightarrow{(O)} Ar\text{-}\bar{N}|$

5) 

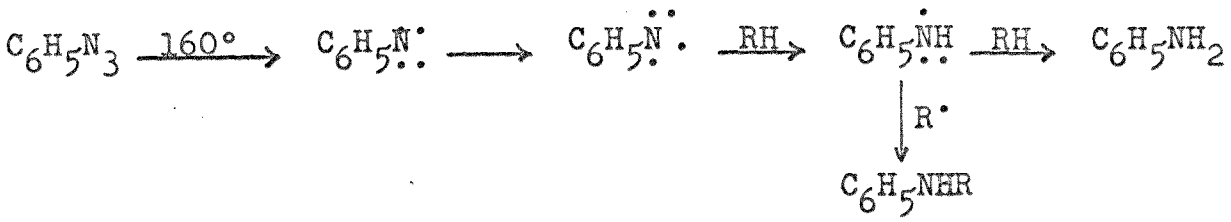
6) 

7) 

Arylnitrenes can also be formed from nitrenes via the following sequence of reactions.(14)



Thermal decomposition of phenyl azide in aliphatic hydrocarbons leads to the formation of aniline, alkylaniline, azobenzene and polymer. The aniline is believed to arise via hydrogen abstraction from the solvent by the triplet nitrene. The N-alkylaniline is obtained from triple nitrene by C-H insertion into the hydrocarbon C-H bond.(8)

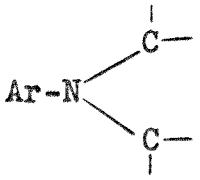


Most arylazides decompose in solution or in the vapor phase at 140°-200°C and are usually thermolyzed in dilute solution because the reaction is moderated.(12)

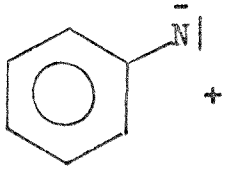
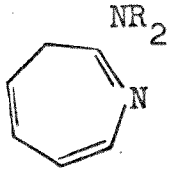
Nitrenes are known to undergo the following kinds of intramolecular reactions:(14)

Abstraction of hydrogen (eg. 1), addition to a multiple bond (eg. 2) insertion into a single bond (eg. C-H, eg. 3) ring expansion (eg. 4) bond formation (eg. 5) and dimerization (eg. 6).

1) $Ar\text{-}\bar{N}| + R\text{-}H \longrightarrow R + Ar\text{-}NH. \xrightarrow{RH} ArNH_2$

2) $Ar\text{-}\bar{N}| +$  $\longrightarrow$ 

3) $Ar\text{-}\bar{N}| + RH \longrightarrow Ar\text{-}NH\text{-}R$

4)  $+ R_2NH \longrightarrow$ 

5) $2Ar\text{-}\bar{N}| \longrightarrow Ar\text{-}N{=}N\text{-}Ar$

6) $Ar\text{-}\bar{N}_1 + (Eto)_3P \longrightarrow \left[Ar\text{-}\bar{N}|\right] \xrightarrow{(Eto)_3P} Ar\text{-}N\text{-}NP(oEt)_3$

The formation of azobenzene from arylazides can be shown as follows:

$ArN_3 \longrightarrow Ar\bar{N} + N_2$

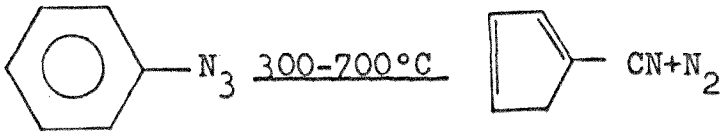
$2ArN \longrightarrow ArN{=}NAr$

It is also possible that undecomposed azide reacts with arylnitrene to yield azobenzenes:[14]

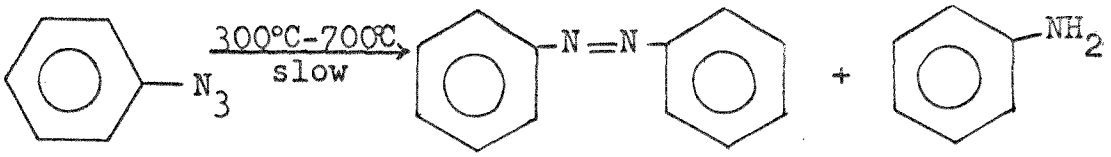
$$ArN: + ArN_3 \longrightarrow Ar\text{-}N{=}N\text{-}N{=}N\text{-}Ar$$

$$Ar\text{-}N{=}\overset{\overset{+}{|}}{\underset{Ar}{N}} - \overset{-}{N{=}N} \longrightarrow N_2 + ArN{=}NAr$$

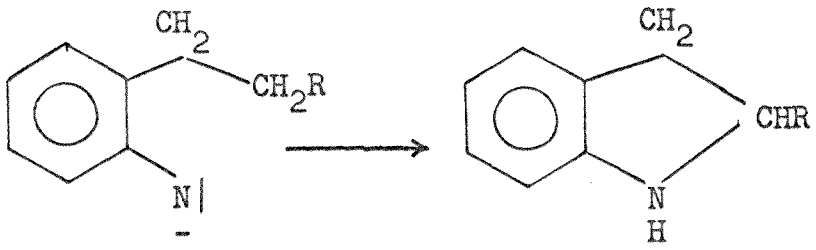
Contraction of the benzene ring occurs at high temperature in the vapor phase photolysis of phenyl azide. Cyclopentadiene carbonitrile is formed when the introduction of phenyl azide into the hot zone is rapid. Otherwise the products that result are azobenzene and aniline.[14]



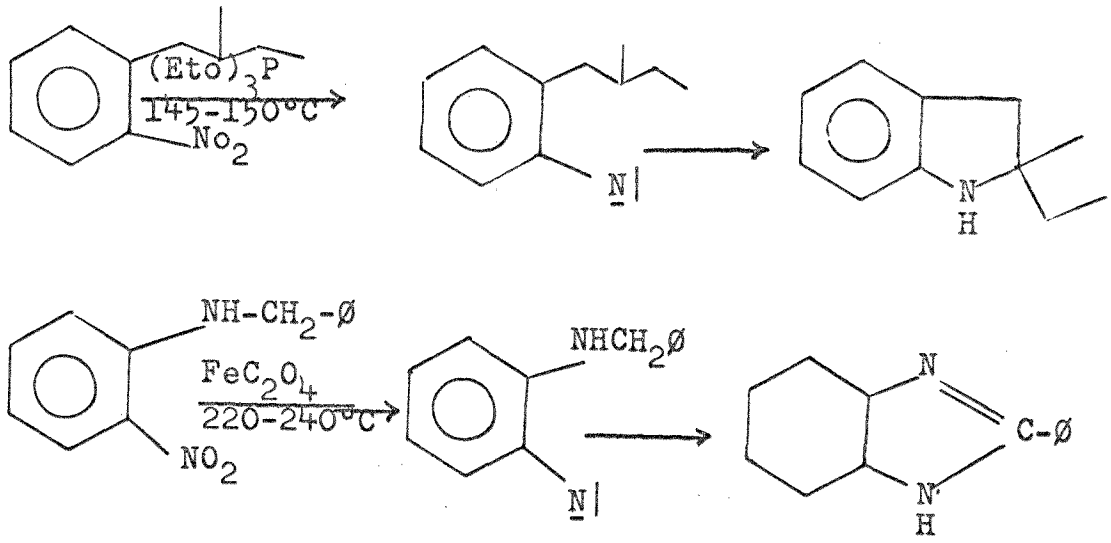
It was suggested that when phenyl nitrene passes through the hot zone, the excited singlet nitrene may be formed which then reacts to give ring contraction.[14] If passage through the hot zone is not fast enough, the single nitrene undergoes intersystem crossing to yield triplet nitrene, which can then undergo dimerization and hydrogen abstraction.[12]



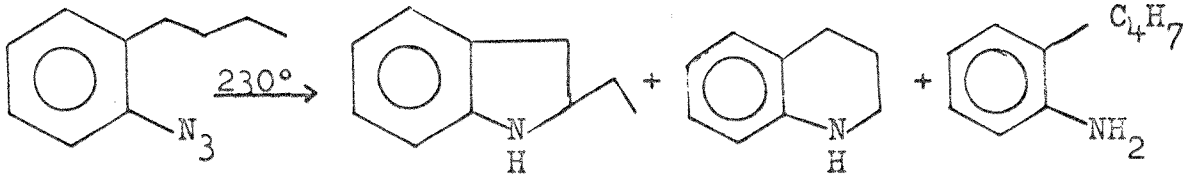
Intromolecular insertion of a nitrene into a saturated C-H bond results in ring formation, usually a five membered ring.(14)



Other examples of 5-membered ring formation resulting from the intramolecular C-H insertion of a nitrene are shown below:(14)

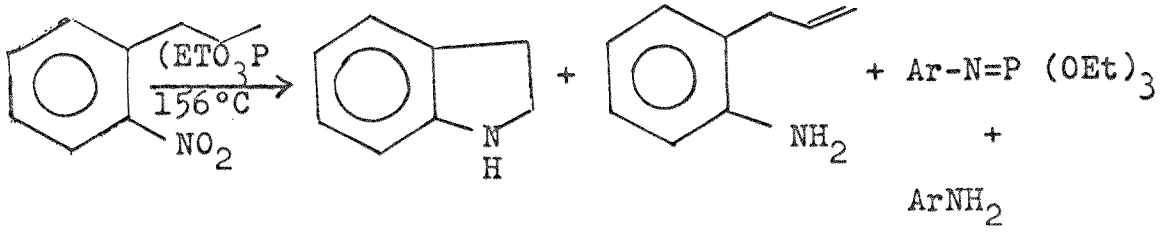


Formation of a 5-member ring also can occur via the vapor phase thermolysis of o- butylphenyl azide.(14)

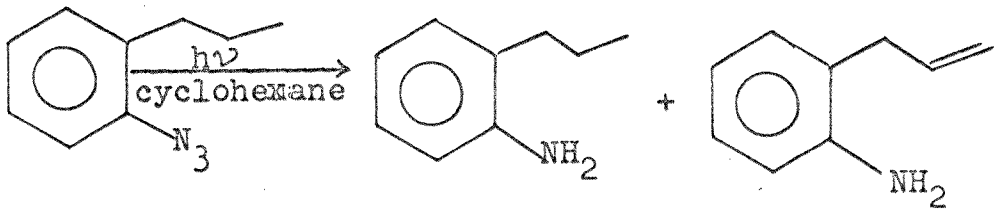


Heating of o-butyl nitrobenzene or o-butyl nitrobenzene with triethylphosphate results in the same product distribution, presumably via the nitrene.(14)

Under similar conditions o-propylphenyl azide yields -methylindoline and other products.(14)



The photolysis of o-propylphenyl azide in hydrocarbon solvents has also been investigated.(19) At ambient temperatures, the photolysis of o-propylphenly azide (in cyclohexane) gives o-propylaniline (19%) as a major product and o-allylaniline (2%) as a minor product with no trace of 2-methylindoline.



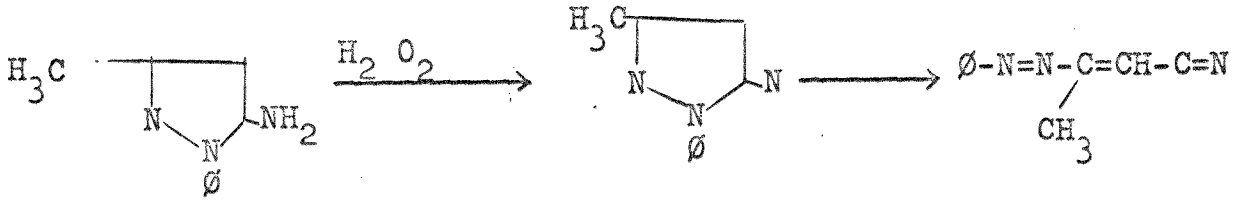
In the presence of triplet photosensetizer (xanthen-9-one), 45% o-propylaniline is observed with no trace of o-allylaniline or 2-methylindoline.

In boiling isooctane (99°C), 2-methylindoline (47% yield) is obtained as a major product along with o-allylaniline (18% yield) and o-propylaniline (5% yield). In boiling isooctane (99°C) and in the presence of triplet photosensetizer (xanthen-9-one), 37% o-propylaniline, 6% o-allylaniline and 3% 2-methylindoline is obtained.

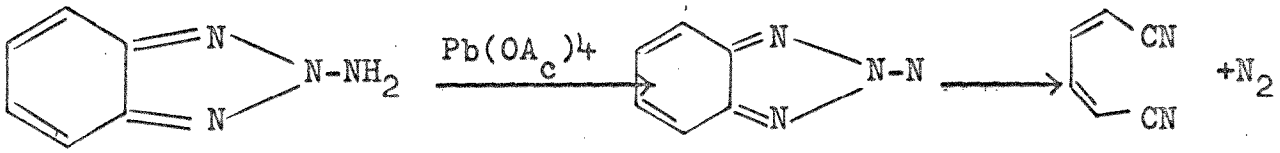
This increase in the yield of o-propylaniline in the presence of the xanthen-9-one at both ambient and elevated temperatures, is indicative of triplet sensitization of azides.[16] Likewise, the decrease in the amount of 2-methylindoline is cites as presumptive evidence that this compound is formed via a singlet nitrene.

Heterocyclic Nitrenes Very little work has been carried out on heterocyclic nitrenes, but there are some examples.

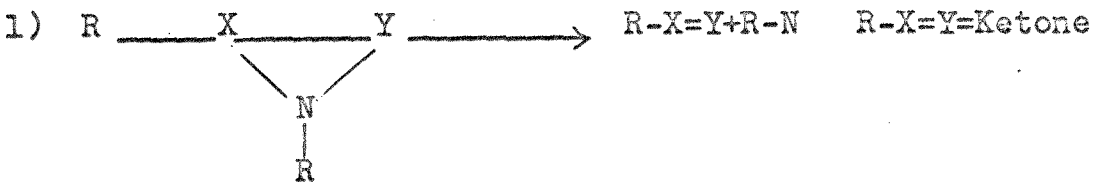
1. Phenyl-3-methyl-5-amino pyrazole was oxidized with hydrogen peroxide to yield a nitrene intermediate.(14)

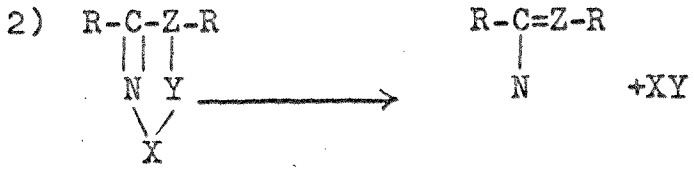


2. Aminobenzotriazole gives dicyanobutadiene when it is treated with lead tetraacetate. This reaction is also presumed to proceed via a nitrene.(14)

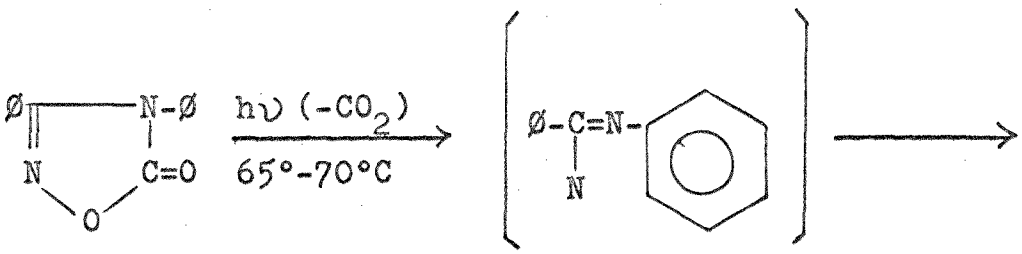


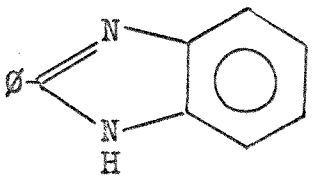
Nitrenes from Opening of Heterocyclic Rings: There are two types of ring opening that give nitrenes. The first type involves breaking the ring in only one place and yields a singlet nitrene initially which reacts further to give an azepine. This will be discussed in a later section on azepine formation. If the ring is broken in more than one place, this results in multiple fragments, e.g.

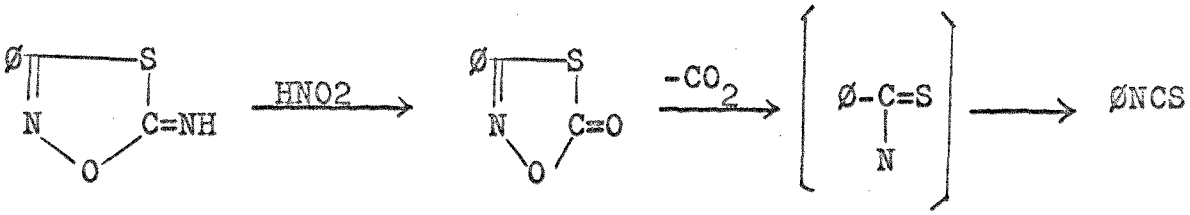
1) 

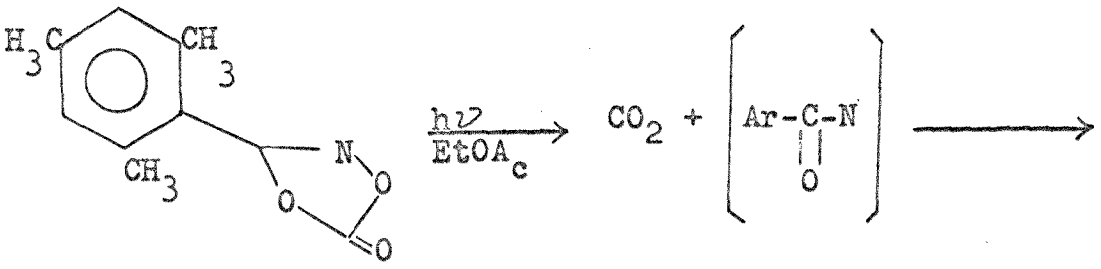
2) 

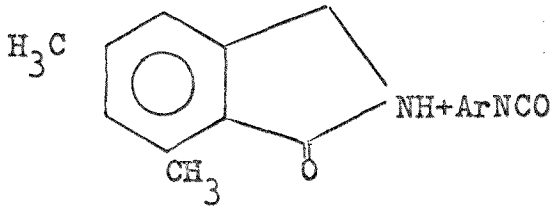
Equation (2) is represented by loss of carbon dioxide from 1,2, 4-oxadiazolone, thioxazolones and dioxazolones as follows.[14]



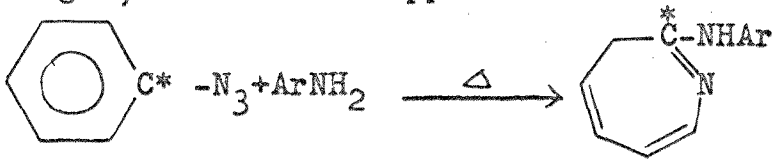






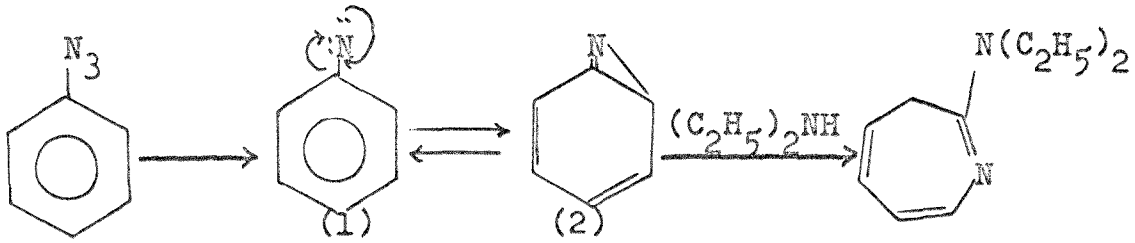


Formation of Azepines: The azepine was observed in 1912 by Wolff who named the product arising from the reaction of phenyl azide and aniline, "dibenzamil". The correct structure was not determined until 46 years later by Huisgen, Vossius and Appl.[2,10]

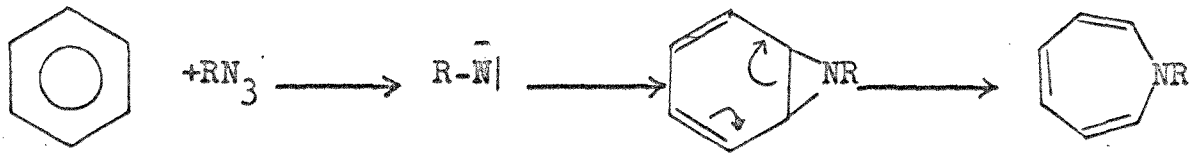


As was mentioned previously, the first type of ring opening in heterocyclic rings yields azepines. The possibility that an azirine (2) might be in equilibrum with a nitrene structure (1) has been postulated to explain the formation of azepines when arylnitrenes are generated in the presence of nucleophilic solvents.[14,6] To explain the formation of 2-diethylamino-3H-azepine, which was obtained from photolysis of phenyl azide in the

presence of diethylamine, the following mechanism was suggested:(6,7,28)

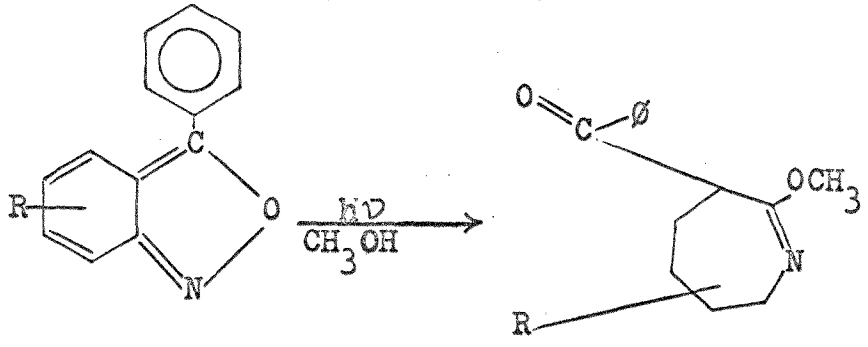


The photochemical decomposition of ethylazidoformate, cyanogen azide or $CO(N_3)_2$ in benzene solutions yields azepines, via nitrene intermediates.(4)

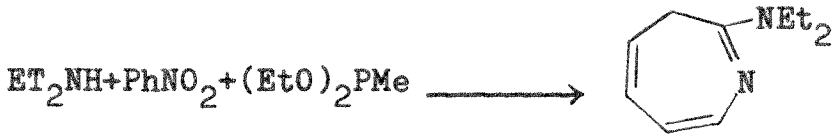


R=COOEt, CN, CON_3

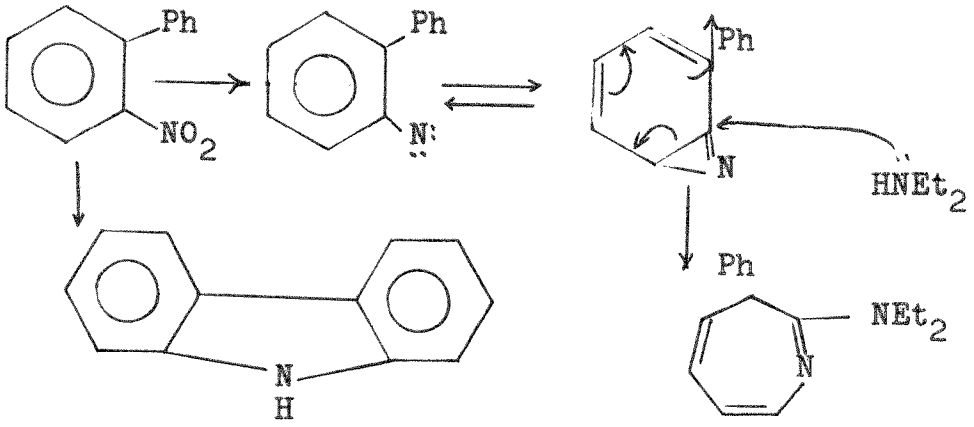
3-Arylanthranils isomerize with heating to acridones.(14) which when photolyzed in metyl alcohol form methoxyazepines.(14)



Azepines are formed by photolysis of azides in amines, but they also may be obtained from the deoygenation of nitro or nitroso-compounds, i.e. nitrosobenzene reacts with diethylmethyl phosphonite (as reducing reagent) in a large excess of diethylamine to give 2-diethylamino-3H-azepine (83%).[28,17]



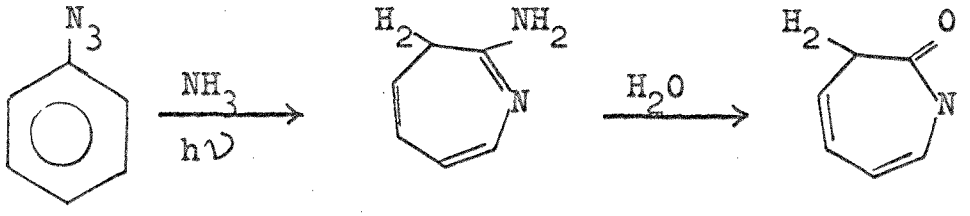
The corresponding reduction of 2-nitrobiphenyl also gives a 2-diethylamino-3H phenylazepine (13%) in addition to carbazole. Both products may arise from the same nitrene intermediate which may be in equilibrum with azabicyclo heptatriene.[28,17]

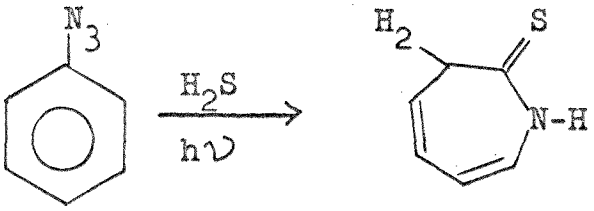


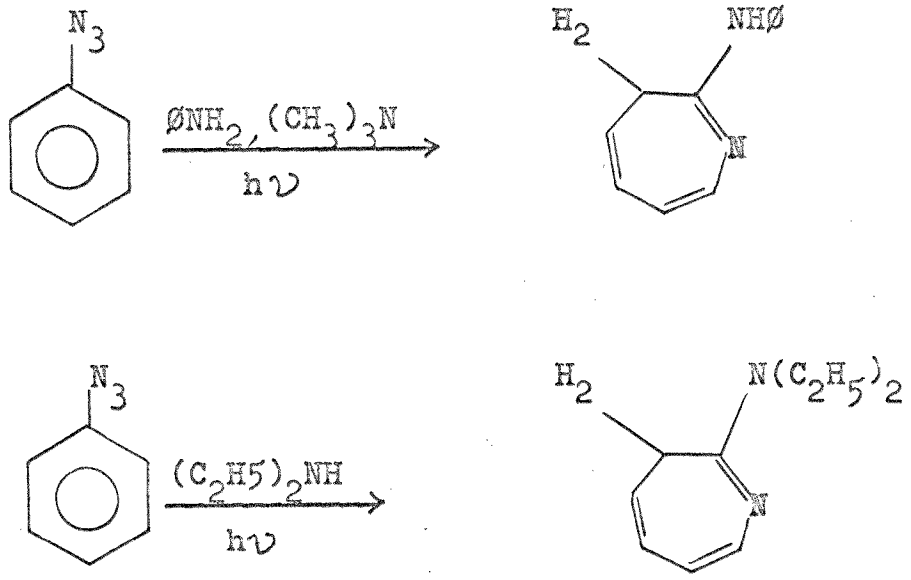
Abramovitch and Davis suggest that carbazole arises from the nitrene and azepine is formed from the azabicycloheptatriene o-nitrotoluene reacts with diethylmethyl phosphite in the presence of diethylamine to yield 2-diethylamino-3H-methyl azepine.(17)

Photolysis of p-methoyphenyl azide and p-chlorophenyl azide in diethylamine yields 2-dimethylamino-5-methoy azepine and 5-chloro-2-dimethylamino-3H-azepine together with a small amount of aniline.(16)

Azepines have also been obtained from the photolysis of phenyl azide in liquid ammonia, diethyl ether saturated with hydrogen sulfide and trimethylamine containing aniline and in diethylamine.(7)



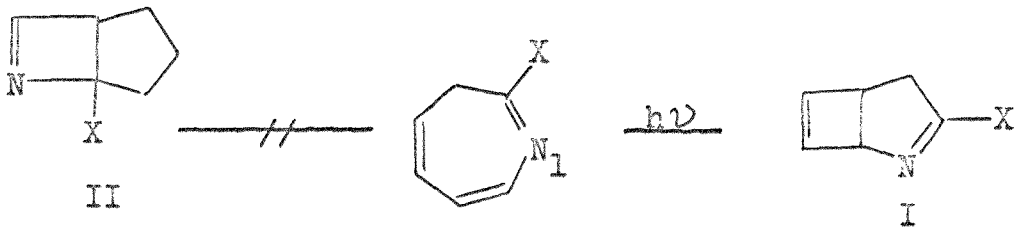




Splitter and Calvin have photoyzed phenyl azide in diethylamine containing equimolar amounts of p-dimethylaminohenzaldehyde, a triplet photosensitizer. Compared to the non-photosensitized reaction, the yield of 2-diethylamino-3H-azepine was reduced and the amount of aniline was increased.(27) This is additional supporting evidence that the aniline is formed via a triplet species while the azepine arises via a singlet nitrene.(27)

Reaction of Azepines: Odum and Schmall have shown that some 2-substituted 3H-azepines can be made to undergo electrocyclic addition reactions in the presence of ultraviolet light.(18) There are two possible modes of closure. However, only the 2-azabicyclo (3,2,0) hepta-2, 6-diene is obtained. None of the Product (II),

which would result from closure across the 2, 6-positions, was detected.[18]



II I

(a) $X=NMe_2$

(b) $X=NH_2$

(c) $X=OEt_2$

EXPERIMENTAL

Instrumentation: All photolysis were carried out in a Rayonet Srinivasan-Griffin Photochemical Reactor, Model No. 1363. The infrared spectra were obtained using Perkin-Elmer infrared spectrophotometers, Models No. 457 and No. 137. The nuclear magnetic resonance spectra were obtained on a Varian HA-100 spectrometer and are recorded in tau values from an internal $SiMe_4$ standard. Vpc analysis were obtained using an F&M (Model 810) dual column chromotograph, equipped with a flame ionization detector. The column used was a s.s. 8'x1/8" packed with 5% carbowax 20M on 80/100 Chrom W-H.P. The flow rate of helium carrier gas was approximately 25 c.c./min. The approximate temperature settings were: injection port, 230°C, detector, 330°C, oven 120°C. For preparative vpc, the Aerograph autoprep Model A-700 equipped with a thermal conductivity detector was used. The preparative column employed was a s.s. 10'x1/4" packed with 20% carbowax 20M on 60/80 Chrom P. The oven temperature was 180°C, the flow rate 100cc/min. Mass spectra were obtained using a Finnigan Model 1015 mass spectrometer equipped with solid inlet probe. U.V. spectra were obtained using a Beckman Model DBG spectrophotometer.

Chemicals: The di-n-propylamine used for photolysis was obtained from Virginia Chemicals and Pennsalt Chemical Corporation and was refluxed over potassium hydroxide overnight and then distilled (108°-110°C). The 1,2-bis (2-methoxyethoxy) ethane (1-6-1) which was used as the internal standard in the analytical vpc was purchased from Eastman Kodak and was purified by fractional distillation over sodium. The 2-methylindoline used was purchased from Pfaltz and Bauer Inc. and purified via its picrate derivative.

Analysis: The analysis was done by Schwarzkopf Micro-analytical Laboratory, Woodside, N.Y.

A sample calculation illustrating the method whereby yields of reactions were obtained is shown as follows:

$$\frac{\text{Standard}}{\frac{\text{moles of component A}}{\text{internal standard (g)}}} = \frac{\text{Experimental}}{\frac{\text{X moles of component A}}{\text{internal standard (g)}}}$$

$$\frac{\text{paper weight of A}}{\text{paper weight of 1-6-1}} \qquad \frac{\text{paper weight of component A}}{\text{paper weight of 1-6-1}}$$

Calculations based on Experiment No. V.

$$\frac{\frac{0.000070}{0.0094}}{} = \frac{\text{X moles of o-propylaniline}}{0.1485}$$

X=0.000161 moles of o-propylaniline

$$\frac{0.000161}{0.000622} \times 100 = 25.8\% \text{ o-propylaniline}$$

I. Nitration of Propylbenzene(11)

A nitration solution was prepared by mixing 104 ml. of fumic nitric acid (Fisher), 95 ml, of glacial acetic acid (Baker), and 83 ml. of acetic anhydride (Fisher). Before mixing, every component was cooled in an ice bath.

The cold solution was added dropwise, during ca. 4 hourse, to a stirred solution of 198.5g. propylbenzene in 742 ml. acetic anhydride in a 3 liter 3-neck flask. The temperature was kept at -5°C to 0°C with the use of an ice-salt bath.

When the addition was complete, the solution was poured onto ca. 2 liters of ice and permitted to stir up to room temperature. After saturating with salt, the organic layer was separated. The water layer was extracted successively with three 150 ml. portions of ether. The combined ether extracts were added to the first organic layer. The solution was neutralized with 10% KOH solution, washed well with distilled water and dried over anhydrous $MgSO_4$.

After separation of magnesium sulfate by filtration, the ether was removed by means of a rotatory evaporator under reduced pressure.

The residual liquid was fractionally distilled using a Todd column (90 cm. length by 12 mm. internal diameter). The distrillation was conducted at 15 mm. pressure and fractions were taken as follows:

No. of Fraction	B.P.°C	Amount (g.)	Characterization
I	50-60	20	Unreacted starting material
II	114-120	6	A mixture of o-m and p-nitro
III	121-122	74.8	o-nitro
IV	123-133	35	A mixture of o,m and p-nitro

The identity of various fractions were characterized by vpc and infrared spectroscopy.

The yield of o-nitro propylbenzene was 38%. The infrared (neat) showed 2 sharp peaks at 6.7μ (1530cm^{-1}) and 7.4μ (1350cm^{-1}) which are characteristic of the C-NO_2 bond.[4]

II. Reduction of o-Nitro propylbenzene[29]

74.8g. (0.44 mole) o-Nitro-propylbenzene and 20g. tin (mossy reagent, Matheson) were placed in a one liter flask. To this solution was slowly added 258 ml. concentrated hydrochloric acid (Baker), cooling when necessary by means of ice bath. The flask was then heated on a boiling water bath for 3 hours. At the end of this time, after cooling to room temperature, the reaction mixture

was carefully added to it and the mixture steam distilled. The distillate was saturated with salt and then extracted with ether. The ether solution was extracted twice with 200 ml. portions of 2N hydrochloric acid.

The acid extracts were combined, washed with ether and neutralized with sodium hydroxide (10%). The resulting suspension was extracted into ether. The ether extract was washed thoroughly with water and dried over anhydrous magnesium sulfate.

After the removal of the drying agent by filtration, the ether was distilled off under reduced pressure using a rotatory evaporator. Further distillation under reduced pressure (20mm.) gave 35.5g. (47% yield) of a clear liquid at 105°C. Gas chromotography showed it to be greater than 99% pure. The infrared spectrum (neat) showed two peaks at 3500 cm^{-1} and 3400 cm^{-1}, characteristic of the N-H stretching vibrations for primary amines.[4]

III. Preparation of o-Propylphenyl Azide[22]

32g. (0.23 mole) o-Propylaniline was dissolved in 96 ml. water and 54 ml. concentrated hydrochloric acid (Baker). Additional water was added to dissolve the hydrochloric salt.

Reaction was carried out in a 4-liter breaker with some ice in it to keep the temperature at 0_-5°C. A solution of 17g. (0.25 mole) sodium nitrite (Fisher) in 62 ml. water was dropped into the breaker while stirring at 0°-5°C. Stirring was continued for one more hour at this temperature. Then a solution of 15 g. (0.23 mole) of sodium azide (Matheson) in 64 ml. water was added slowly while occasionally adding ice to maintain the temperature at 0°-5°C. After the addition was complete, the reaction mixture was permitted to stir up to room temperature.

The reaction mixture was then extracted with ether (300 ml.), washed with 10% sodium carbonate several times, washed with water until neutral and dried over anhydrous magnesium sulfate. The drying agent was filtered off and the solution was concentrated on a rotatory evaporator to a volume of about 35 ml.

Chromotography of this solution of alumina (180g., 200 mesh, activity 1, Mallinckrodt) using pentane as the eluent afforded a yellow oil which was shown to be 90% pure and vpc. This oil was molecularly distilled at 0.1 mm. and 60°C to give 15 g. of azide (46% yield).

The infrared spectrum (neat) showed two sharp peaks; one at 4.86 μ (2060 cm^{-1}) and the other at 8 μ (1500 cm^{-1}) which are characteristic of the $C-N_3$ stretching vibrations of azide.[4]

IV. Preparative Photolysis of o-Propylphenyl Azide in di-n-Propylamine

o-Propylphenyl azide, 3.0082g., was diluted to 300 ml. with di-n-propylamine. The solution was transferred to a quartz reaction vessel and alternately evacuated (using a water aspirator) and flushed (with E.D. grade nitrogen Matheson) several times to remove any dissolved oxygen. The reactor vessel was then placed in the photoreactor and photolyzed at 2537A° while stirring and maintaining a blanket of nitrogen. Samples were removed from the reactor at periodic intervals and analyzed by vpc. During this time, the internal temperature of the reactor varied between 26°-44°C.

After 4 hours, vpc analysis indicated that almost all of the starting azide had reacted. Two major peaks appeared at longer retention times than any of the known products (i.e. o-propylaniline, o-allylaniline, and 2-methylindoline), 20 and 24 minutes respectively.

The solvent was removed under reduced pressure by means of a rotatory evaporator. The remaining residue was dissolved in 100 ml ether. The ether solution was

washed with water to remove traces of the di-n-propylamine. The ether layer was then extracted with 2N hydrochloric acid (3x50ml). The combined acid extracts were washed with ether, neutralized with 2N sodium hydroxide, and extracted with ether 3x100 ml.). The ether extract was washed thoroughly with water and dried over anhydrous magnesium sulfate.

After removal of drying agent by filtration, the solvent was removed by means of a rotatory evaporator to yield an oily mixture of 2.6756g. vpc analysis showed 4 peaks, including those peaks which exhibited retention times of 20 and 24 minutes.

This oil was molecularly distilled using a Kugelrohr apparatus over a temperature range of 70°-150°C (0.1 mm.). Three different fractions were obtained. Vpc analysis of these fractions indicate that each one contained the same four components (retention times of 12, 16, 20, 24 minutes). The combined fractions weighed 1.4751g. This oily material (light brown in color), was dissolved in a small amount of chloroform and chromotographed on 150g. of silica gell (200-325 mesh, Mallinckrodt, 35.5"x4.5" column). The column was eluted (in fractions of 15 ml.) using the following solvents: chloroform (400 ml.), 10% acetone -90% chloroform (200 ml.)

and 25% acetone - 75% chloroform (200ml.). The material which showed a retention time of 20 minutes by vpc (compound 3) was eluted using the 10% acetone - 90% chloroform solvent. The material which showed a retention time of 24.0 minutes (compound 4) was eluted by the 25% acetone - 75% chloroform solvent. The other two compounds originally present in the distilled material was eluted as a mixture by the chloroform eluent. The fractions contained compounds 3 and 4 were combined and concentrated. The resulting residual oils were molecularly distilled (60°-120°C, 0.05 mm.). The amounts of purified compounds 3 and 4 were 0.2319g. and o.1146g. respectively. Physical properties of compounds 2 and 4 (i.e. ultraviolet, infrared, nuclear magnetic resonance and mass spectra) were determined and are given as follows:

Ultraviolet Data (in Methanol)

Compounds 3 - λ_{max} 214 mμ (ε =18,000), λ_{max} 296mμ (ε =10,000)

Compounds 4 - λ_{max} 216 mμ (ε =8,400), λ_{max} 310mμ (ε =7,200)

Infrared (neat)

Compound 3 - 3010 (w), 2960 (s), 2930 (w), 2870 (m), 1565 (s), 1520 (s), 1451 (m), 1422 (w), 1394 (m), 1360 (s), 1215 (m), 1185 (m), 1160 (m), 1131 (m), 1098 (sh), 1000 (w), 875 (w), 780 (w), 710 (m), 660 (w) cm^{-1}

Compound 4 - 3008 (w), 2960 (s), 2930 (m), 2870 (m), 1640 (w), 1610 (w), 1555 (s), 1510 (s), 1452 (m), 1420 (sh), 1368 (m), 1280 (w), 1230 (w), 1148 (w), 1100 (w), 938 (w), 865 (w), 780 (m), 718 (m) cm^{-1}

N.M.R. Data

Compound 3 - 3.05 (1H, doublet), 3.82, (1H, quartet), 4.43 (1H, quartet), 5.06 (1H, quartet), 6.70 (4H, triplet), 7.48 (1H, doublet), 7.74 (2H, triplet), 8.44 (6H, multiplet) 9.16 (9H quartet)

Compound 4 - 3.10 (1H, doublet), 3.86 (1H, quartet), 4.54 (1H, triplet), 5.01 (1H, triplet), 6.02 (1H, triplet) 6.76 (4H multiplet), 8.49 (4H, multiplet), 8.90 (3H, multiplet), 9.15 (9H, multiplet)

Mass Spectral Data:

Compounds 2 and 4 both gave apparent peak of 234m/e.

Elemental Analysis

Compound 3 - Found; 76.87%C, 11.14%H and 12.20%N.
Calculated 76.92%C, 11.11%H and 11.96%N.

Compound 4 - Found; 76.71%C, 11.27%H and 11.97%N.
Calculated 76.92%C, 11.11%H and 11.96%N.

V. Photolysis of o-Propylphenyl azide

A mixture of o-prophylphenyl azide, 0.09890g. (0.000613 moles) and 0.1530g. of 1-6-1 was diluted to 100 ml. with di-n-propylamine. The solution was transferred to a pyrex reaction vessel. The system was deoygenated as was done in the previous photolysis (e.g. experiment IV).

Photolysis was conducted under nitrogen using 3500A° U.V. lamps while the solution was stirred. Samples were taken and analyzed by vpc. The photolysis was stopped after 4 hours. During this time the internal temperature of the reactor varied between 26°-44°C Calculation showed 2.66% of unreacted azide remained and that o-propylaniline and compound 3 were formed to the extent of 28% and 4.13% respectively.

The photolysis was repeated using the same conditions and procedure. The following results were obtained:

o-Propylaniline (25.8%), compound 3 (4.5%)
(97.5% of the azide was consumed).

VI Photolysis of o-Propylphenyl azide at Elevated Temperature

A mixture of o-propylphenyl azide 0.997g. (0.000619 mole) and 0.1496g. (1-6-1) was diluted to 100 ml. with di-n-propylamine and transferred to a pyrex reaction vessel. The system was deoygenated as done before.

The solution was brought to boil by means of a heating mantle and irradiated with 3500A° lamps (samples were tkane at periodic intervals and analyzed by vps.)

Vpc analysis showed the formation of four products. These products were identified by means of comparing their retention times with known materials. Calculation gave the following yield data: o-propylaniline 45.1%, compound 3 19.1%, 2-methylindoline 3.8% and compound 4 3.66%.

The photolysis was repeated under the same conditions and procedure. The following results were obtained: o-propylaniline 42%, compound 3 20.6%, 2-methylindoline 4.5% and compound 4 3.6%. 6.1% of azide remained unreacted.

VII Photolysis of o-Propylphenyl Azide in the Presence of Triplet Photosensitizer, Xanthen-9-One

A mixture of o-propylphenyl azide 0.1029g. (0.000639 mole) 0.1499g. 1-6-1 and 0.1378g. (0.000703 mole) xanthen-9-one was diluted to 100 ml. with di-n-propylamine. The solution was tranferred to a pyrex reaction vessel. The system was deoygenated as was done in the previous photolysis.

Photolysis was conducted under nitrogen using 3500°A lamps while the solution was stirred. Samples were taken and analyzed by vpc. The photolysis was stopped

after 1-3/4 hours. Calculation showed 8.7% unreacted azide remained and that o-propylaniline and compound 3 were formed to the extend of 34.6% and 1.73% respectively.

The photolysis was repeated using the same conditions and procedure. The following results were obtained: o-propylaniline 34.5%, compound 3 1.07%, unreacted azide 10.2%.

VIII Photolysis of o-Propylphenyl Azide at Elevated Temperature in the Presence of the Triplet Photosensitizer

A mixture of o-propylphenyl azide 0.0994g. (0.00617 mole), o.1469g. 1-6-1 and 0.1342g. (0.000684 mole) xanthen-9-one was diluted to 100 ml. with di-n-propylamine and the solution was transferred to a pyrex reaction vessel. The system was deoygenated as was done in previous photolysis (eg. Experiement IV). The solution was brought to a boil by means of a heating mantle and irradiated with 3500A° U.V. lamps. The photolysis was carried out under a blanket of nitrogen. Samples were taken every 15 minutes and analyzed by vpc. Photolysis was stopped after 45 minutes, 15.9% of the starting material remianing unreacted.

Vpc analysis showed formation of 3 peaks with the same retention times as 2-methylindoline, o-prophylaniline and compound 3.

Calculation gave the following yield data: 40% o-propylaniline, 20.1% compound 3, 3% 2-methylindoline.

The photolysis was repeated using the same conditions and procedure. The following results were obtained: 37.7% o-propylaniline, 19.4% compound 3, 2.5% 2-methylindoline and 13.4% unreacted azide.

IX Photolysis of o-Propylphenyl Azide at Elevated Temperature in the Presence of the Triplet Photosensitizer

A mixture of o-propylphenyl azide 0.1038g. (0.000645 mole), 0.1560g. 1-6-1 and 1.262g. xanthen-9-one was diluted to 100 ml. with di-n-propylamine and the solution was transferred to a pyrex reaction vessel. The system was deoygenated as was done in previous photolysis. The solution was brought to a boil by means of a heating mantle and irradiated with 3500A° U.V. lamps. The photolysis was carried out under a blanket of nitrogen. Samples were taken every 15 minutes and analyzed by vpc. Photolysis stopped after 45 minutes, 27.6% of the starting material remaining unreacted.

Vpc analysis showed formation of 3 peaks with the same retention times as 2-methylindoline, o-propylaniline and compound 3.

X. Refluxing of o-Propylphenly Azide, A Control Reaction

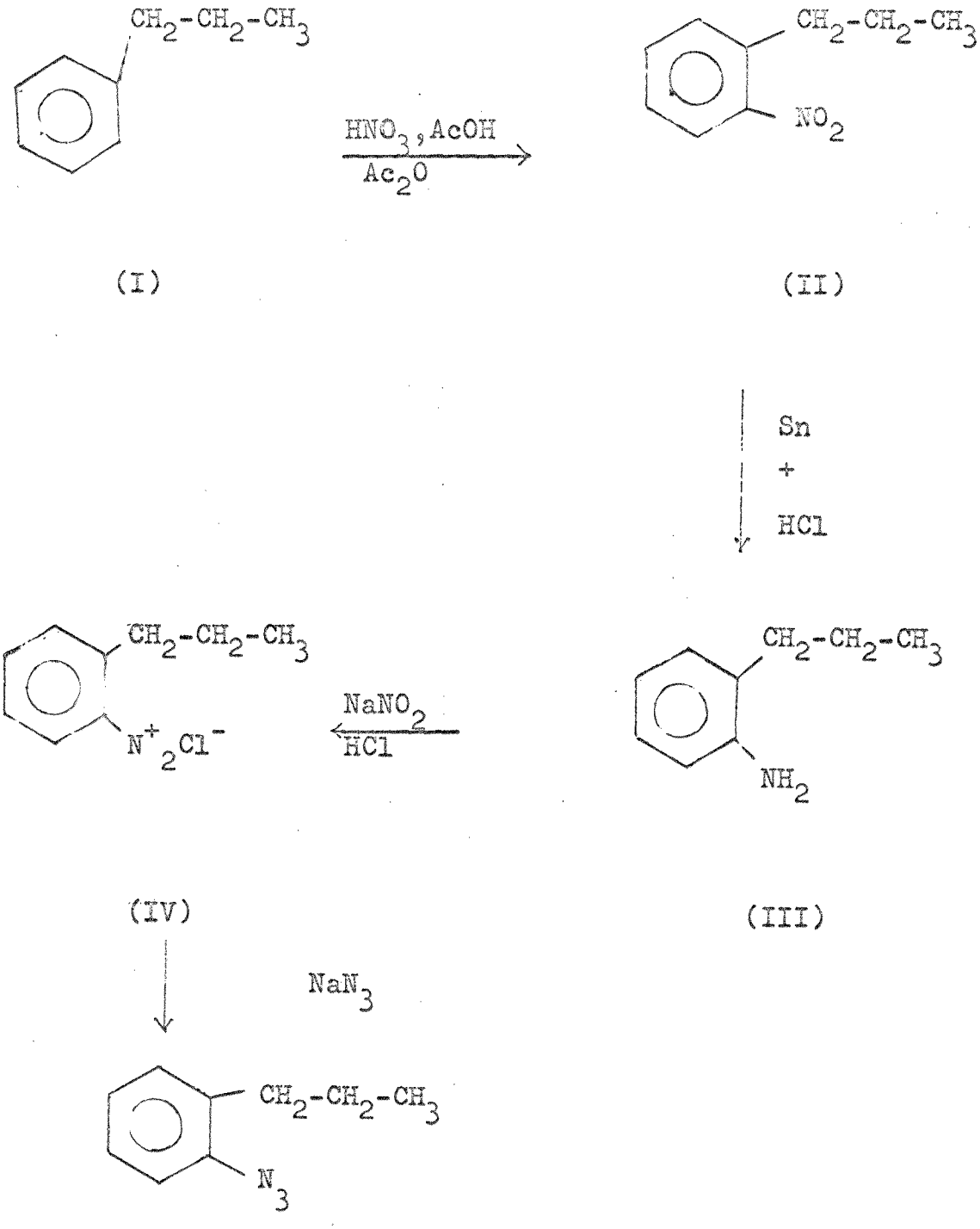
A mixture of o-propylphenly azide 0.1047g. (0.000637 mole) and 0.1497g. 1-6-1 was diluted to 100 ml. with di-n-propylamine and solution was transferred to a pyrex reaction vessel. The system was deonygenated as was done in previous photolysis (e.g. Experiment IV). The solution was brought to a boil by means of a heating mantle. The reflux was carried out under a blanket of nitrogen gas. The samples were taken every 15 minutes and the refluxing was stopped after 2 hours.

The vpc showed the ratio of azide 1-6-1 to be constant over the entire reaction period and no other peaks were observed.

RESULTS & DISCUSSION

I. The Synthesis of Ortho-Propylphenyl Azide

The synthetic scheme employed in the synthesis of o-propylphenyl azide is shown below:



Nitration of propylbenzene (I) in acetic anhydride using a mixture of fumic nitric acid, glacial acetic acid and acetic anhydride gave a mixture of ortho-, meta-, and para isomers. Fractional distillation under reduced pressure (15 mm.) using a Todd column gave o-nitropropylbenzene (II) in 38% yield. The purity of the product was shown to be greater than 99% by vpc.

o-Propylaniline (III) was prepared in 47% yield by reduction of o-nitroproplybenzene (II) using hydrochloric acid and tin as a reducing agent. Steam distillation, followed by distillation under reduced pressure (20 mm) was used for the isolation and purification of the product. Gas chromotography showed the product to be 99% pure.

o-Propylphenyl azide (V) was prepared in 46% yield from o-propylamiline (III) and sodium nitrate in hydrochloric acid (formation of the diazonium choride (IV) was intermediate), followed by addition of sodium azide. Column chromotography (alumina and pentane used as an absorbent and eluent, respectively) followed by molecular distillation (pressure 0.1 mm.) was used for purification of the azide. Gas chromotography showed the product to be more than 99% pure.

II. Preparation and Structure Proof of Compounds 3 and 4

Compounds 3 and 4 were prepared by photolysis of o-propylphenyl azide in a dilute solution of di-n-propylamine and were purified by absorption chromotography and molecular distillation.

Assignment of Structure to Compounds 3 and 4:

I. Physical Properties: Physical properties of compounds 3 and 4 were measured and are given as follows:

(A) Compound 3

(1) Mass spectrum - a parent peak of 234 m/e was obtained.

(2) Ultraviolet spectrum - λ_{max}^{meoH} 214 (ε =18,000 and λ_{max}^{meoH} 296 (ε =10,000)

(3) Infrared spectrum - Prominent bands were exhibited by the neat liquids at 3010 (w), 2960 (s), 2930 (m), 2870 (m), 1565 (s), 1360 (sh), 1451 (m), 1215 (m), 1160 (m) cm^{-1}

(4) Nuclear magnetic resonance spectrum - 3.05 (doublet, 1H), 3.82 (quartet, 1H), 4.43 (quartet, 1H), 5.06 (quartet, 1H), 6.70 (triplet, 4H), 7.48 (doublet, 1H), 7.74 (triplet, 2H), 8.44 (multiplet, 6H) 9.16 (quartet, 9H)

(5) Elemental Analysis - Compound 3 analyzed for $C_{15}H_{26}N_2$.

(B) Compound 4

(1) Mass Epectrum - a parent peak of 234 m/e was obtained.

(2) Ultraviolet Spectrum - λ^{meoH} 216 (ε=8,400) and λ^{meoH}_{max} 302 (ε=7,200)

(3) Inrared Spectrum - Prominent bonds were exhibited by the neat liquid at 3008 (w), 2960 (s), 2930 (m), 2870 (m), 1555 (s), 1510 (s), 1452 (m), 1368 (m), 1240 (w), 1148 (w), 1100 (w).

(4) Nuclear Magnetic Resonance Spectrum - 3.10 (doublet, 1H), 3.86 (quartet, 1H), 4.54 (triplet, 1H), 5.0k (triplet, 1H), 6.02 (multiplet, 1H), 6.76 (multiplet, 4H), 8.49 (multiplet, 6H), 8.90 (multiplet, 2H), 9.15 (multiplet, 9H).

(5) Elemental Analysis - Compound 4 analyzed for $C_{15}H_{26}N_2$.

II. Interpretation of Physical Properties Data

(A) Compound 3

Analysis of the data given above leads to the following structural assignment:

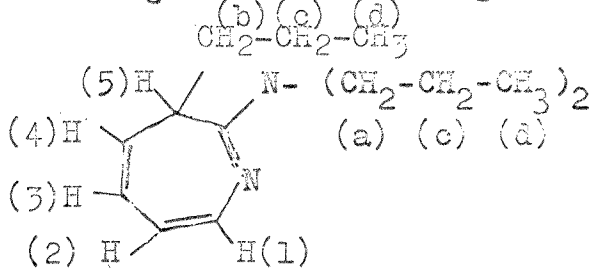


Figure (1)

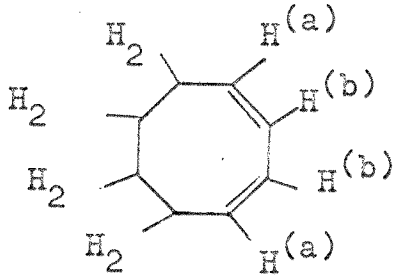
TABLE 1

N.M.R. Data for Compound 3

	$H_{(1)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	a-CH_2	b-CH_2	c-CH_2	d-CH_3
τ Values	3.05	4.43	3.82	5.06	7.48	6.70	7.74	8.44	9.16
Splitting Pattern	doublet	quartet	quartet	quartet	doublet	triplet	triplet	multiplet	multiplet
J Values	7.5	5.75 7.5	5.5 8.5	8	8				
Integration (in H)	1	1	1	1	1	4	4	6	9

Infrared spectrum indicates three major bands: 2960 cm^{-1} (C-H stretching alkanes), 1565 cm^{-1} (C=C) and 1510 cm^{-1} (C=N). In studies of mono and di-substituted amidines, Prevorsek[20] observed two bands in 1500-1600 cm^{-1} region. Odum and Deoring have also observed two peaks in the 1500-1600 cm^{-1} for 2-diethylamino-3H-azepine.[7] The other bands in the infrared can be assigned as follows: 3010 cm^{-1} (Vinyl H), 2930 cm^{-1}, 2870 cm^{-1} (C-H stretching of alkanes), 1451 cm^{-1} ($-CH_2$), 1360 cm^{-1} ($C-CH_3$), 1160 cm^{-1} (C-N).[20]

Nuclear Magnetic Resonance Spectra: The N.M.R. shows four different protons in the vinyl region. The quartet 5.06τ is assigned to the $H_{(4)}$ proton. The splitting pattern arises from a coupling of its spin with that of the $H_{(3)}$ and $H_{(5)}$ protons. Examination of the coupling constants supports this assignment. This proton should appear at higher field strength than any of the other vinyl protons since it is adjacent to a methinyl proton as well as a vinyl proton for example.[3]



a=4.37τ
b=4.32τ

The proton $H_{(2)}$ and $H_{(3)}$ are assigned to the peak occuring at 4.43τ and 3.82τ respectively on the basis of the splitting patterns and coupling constants which are shown in Table (I). Both protons should show a quartet due to coupling by adjacent non-equivalent vinyl protons. Analysis of J values supports this hypothesis. The $H_{(1)}$ proton appears as a doublet at 3.05τ since it is only split by the $H_{(2)}$ proton. It should be furthermost downfield of the four vinyl protons because it is adjacent to the ring nitrogen. The doublet centered at 7.48τ is assigned to the $H_{(5)}$ proton. It is apparently split only by the $H_{(4)}$ proton and not at all by the b-CH_2 protons of the ring n-propyl group. Absence of coupling may be explained by the dihedral angle of the H-C-C-H group concerned.[21] Support for this explanation is furnished by the appearance of the b-CH_2 protons at 7.72τ as only a triplet. This indicates that these protons are only being split by the adjacent methylene protons and not by the $H_{(5)}$ proton. This apparent distortion in the dihedral angle can be explained by involving a steric argument. The presence of an adjacent bulky di-n-propyl amine group may force the n-propyl group at the 3-position into a conformation in which the dihedral angle is essentially zero degrees.

The triplet at 6.70 integrates for four protons and is assigned to the methylene grou; which is bonded to the nitrogen (i.e. a-CH_2). The multiplet which is centered at 8.44τ integrates for 6 protons or 3 methylene groups, is presumed to arise from the resonance of the c-CH_2 groups shown in Figure (I). The quartet centered at 9.16 τ (9H) which appears at highest fields is undoubtedly due to the resonance of the three methylene groups. This latter splitting pattern can be explained by assuming that the expected pair of triplets are overlapping to a large extent.

The N.M.R. data assignments are in good agreement with the N.M.R. data of 2-diethylamino 3H azepine which was reported by Odum and Dearing[7] and 2-diethylamino 3H-methyl azepine which was reported by Cadogan.[5]

Ultraviolet Spectrum: Two peaks are observed in the U.V. spectrum of compound 3: λ_{max}^{meoH} 214mμ (ε=10,000) and λ_{max}^{meoH} 296mμ (ε=18,000). This in good agreement with the λ_{max} of 297m which was reported for 2-diethylamino 3H-azepine.[7]

Mass Spectrum: Mass spectrum shows 234m/e as a parent peak which is in agreement to the molecular weight of the proposed structure.

Analysis: Analysis shows $C_{15}H_{26}N_2$ for Compound 3 which again supports the proposed structure.

(B) Compound 4

Analysis of the data given above leads to the following structural assignment.

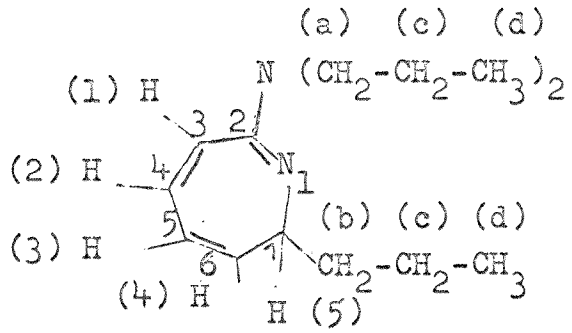


Figure 2

TABLE II

N.M.R. Data for Compound 4

	$H_{(1)}$	$H_{(2)}$	$H_{(3)}$	$H_{(4)}$	$H_{(5)}$	a-CH_2	b-CH_2	c-CH_2	d-CH_2
τ Values	3.10	4.54	3.86	5.01	6.02	6.76	8.49	8.90	9.15
Splitting Pattern	doublet	quartet	quartet	triplet	multiplet	triplet	multiplet	multiplet	quartet
J Values			6.5	9	9				
	7	7	9						
Integration (in H)	1	1	1	1	1	4	6	2	9

Infrared spectrum indicates three major bonds, 2960 cm^{-1}, (C-H stretching of alkanes), 1555 cm^{-1} (C=C) and 1520 cm^{-1} (C=N). The latter two bands are assigned to the amidine groups as was discussed for Compound 3. 3008 cm^{-1} (Vinyl H) 2930 cm^{-1}, 2870 cm^{-1} (C-H stretching of alkanes), 1452 cm^{-1} ($-CH_2-$), 1368 cm^{-1} ($C-CH_3$), 1230 cm^{-1}, 1148 cm^{-1} (C-N).[20]

Nuclear Magnetic Resonance Spectra: The N.M.R. shows four different protons in the vinyl region. The quartet at 5.01τ is assigned to the $H_{(4)}$ proton. The splitting pattern arises from a coupling of its spin with that of $H_{(3)}$ and $H_{(5)}$ protons. Examination of the coupling constants supports this assignment. This proton should appear at higher field strength than any of the other vinyl protons as was explained in Compound 3. The proton $H_{(2)}$ and $H_{(3)}$ are assigned on the basis of the splitting patterns and coupling constants which are shown in Table II. Both protons should show a quartet due to coupling by adjacent non-equivalent vinyl protons. Analysis of J values supports this hypothesis. The $H_{(1)}$ proton appears as a doublet at 3.10τ since it is only split by $H_{(2)}$ proton. It should be further most downfield of the four vinyl protons because it is adjacent to the ring nitrogen. The multiplet centered at 6.02τ is assigned to the $H_{(5)}$ proton, which is split by $H_{(4)}$ and the $c-CH_2$

protons of the ring n-propyl group. Support for this hypothesis is furnished by the appearance of the b-CH_2 protons at 8.90 τ as a multiplet. This indicates that these protons are being split by adjacent methylene protons and $H_{(5)}$ proton. The removal of the bulky di-n-propylamino group from the vicinity of the n-propyl groups has apparently restored the normal dihedral angle. As a result, a multiplet is now obtained for the b-CH_2 in Compound 4 (Figure 2) and for the $H_{(5)}$ proton.

A triplet at 6.76 τ integrates for four protons and is assigned to the methylene bound to the nitrogen substituent (i.e. a-CH_2). The multiplet which is centered at 8.49 τ integrates for 6 protons or 3-methylene groups is presumed to arise from the resonance of the (c-CH_2) groups shown in Figure 2. The quartet centered at 9.15 τ (9H), which appears at highest fields, is assigned to the overlapping resonance of the three methyl groups. This apparent splitting pattern can be explained by assuming that the expected pair of triplets are overlapping to a large extent.

Ultraviolet Spectrum: Two peaks are observed in the U.V. spectrum of Compound 4: λ_{max}^{meoH} 216mμ (ε =8,400) and λ_{max}^{meoH} 302mμ (ε =7,200). This is in good agreement with the λ_{max} 297mμ which was reported for 2-diethylamino

3H-azepine.[7]

Mass Spectrum: Mass spectrum shows 234 m/e as a parent peak which is in good agreement with the molecular weight of the proposed structure.

Analysis: Analysis shows a molecular formula of $C_{15}H_{26}N_2$ for Compound 4 which again supports the proposed structure.

III. Photolysis of o-Propylphenyl azide

All the experiments were carried out using di-n-propylamine as the solvent and in a quartz (used in the preparative reaction) or pyrex (used in the analytical reactions) reaction vessel under a blanket of nitrogen using 2537°A and 3500°A U.V. lamps respectively. The products were identified by the comparison of their vpc retention times with those of known compounds. The results of the photolysis are given in the following Table III.

TABLE III

Photolysis of o-n-Propylphenyl Azide

Experiment		Temperature °C	Azide Mole/Liter	Xanthen-9-One Mole/Liter	2-Methyl-indoline % Yield	o-n-Propyl-aniline % Yield	A* % Yield	B* % Yield
V	1	26-44	0.00613	-	-	28.0	4.1	-
	2	26-44	0.00646	-	-	25.8	4.5	-
VI	1	26-44	0.00639	0.00721	-	34.6	1.7	-
	2	26-44	0.00642	0.00715	-	34.5	1.1	-
VII	1	Reflux	0.00619	-	3.8	45.1	19.1	3.7
	2	"	0.00639	-	4.5	42.0	20.6	3.6
VIII	1	Reflux	0.00617	0.00684	3.0	40.0	20.1	-
	2	"	0.00593	0.00675	2.5	37.7	19.4	-
IX	1	Reflux	0.00645	0.0660	2.7	39.0	20.8	-

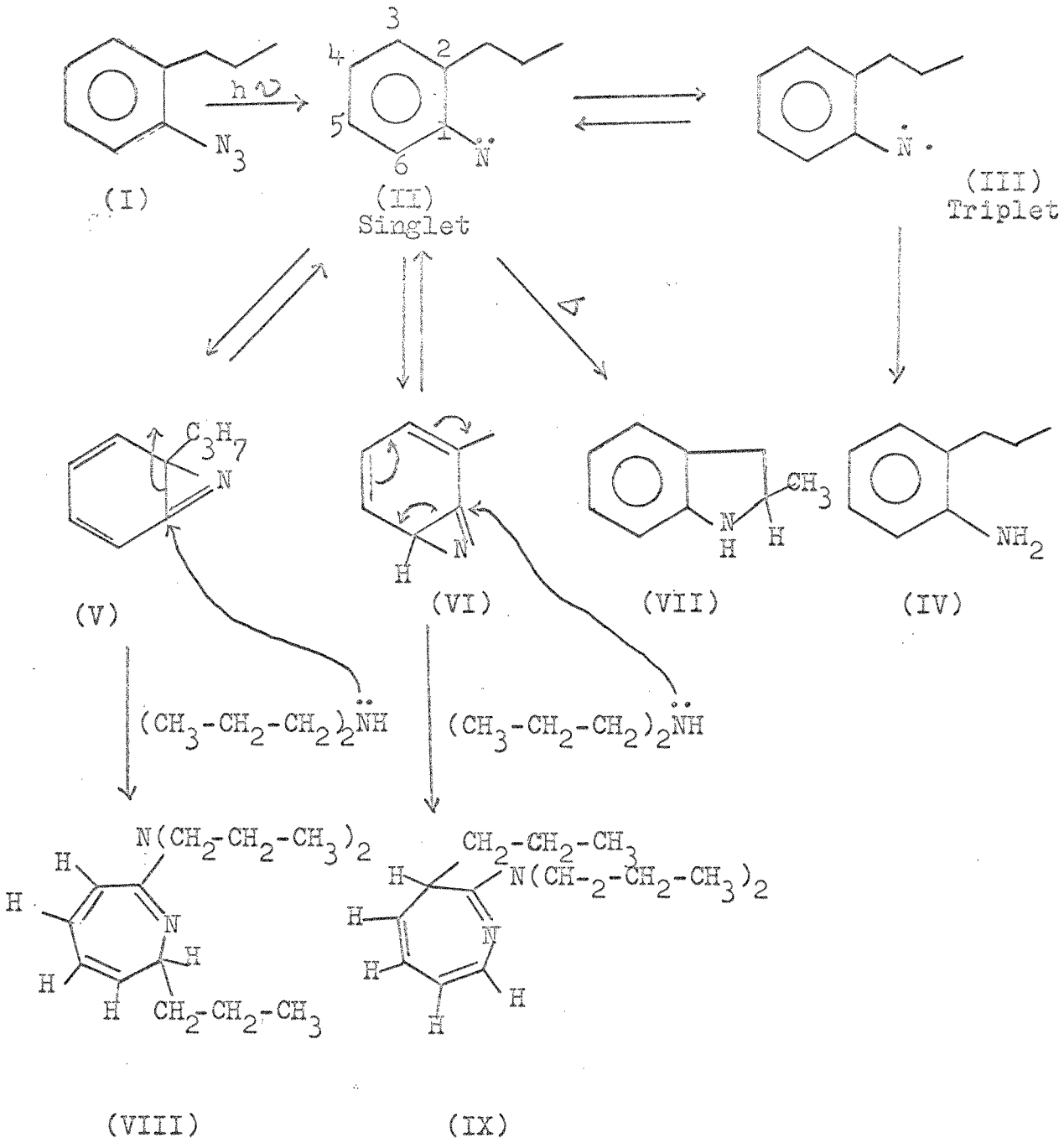
A* = 2-di-n-propylamino-3n-propyl-3H azepine

B* = 2-di-n-propylamino-7n-propyl-7H azepine

Discussion of the Results of Photolysis:

Photolysis at room temperature (Experiment 5) gave 26.9% (average yield) of o-n-propylaniline as a major product and 4.3% of 2-di-n-propylamino 3n-propyl-3H azepine. No di-n-propylamino-7n-propyl-7H azepine was observed. On the other hand, when the photolysis was carried out in the presence of the triplet photosensitizer, xanthen-9-one, the yield of o-n-propylaniline was increased to 34.6% (average yield) while the amount of 2-di-n-propylamino-3n-propyl-3H azepine decreased to 1.4% (average yield). The increase in the yield of o-n-propylaniline in the presence of the triplet photosensitizer (xanthen-9-one) is indicative of triple sensitization of azide.(16,-7) This is also in good agreement with the results obtained in the photolysis of o-n-propylphenyl azide in isooctane and cyclohexane in which the yield of o-n-propylaniline was increased in the presence of xanthen-9-one.(19) The concomitant decrease in the amount of 2-di-n-propylamino 3n-propyl-3H azepine formed in the presence of the triplet photosensitizer indicates that the azepine formation is occuring through the intermediacy of some singlet species, presumably singlet o-n-propylphenyl nitrene. Similar results had been observed in the formation of 2-diethylamino-3H-azepine(27) and 2-diethylamino-3H-phenyl azepine.(28,17)

Photolysis at the boilding point of di-n-propylamine (i.e. 110C°) gave 43.5% (average yield) of o-n-propylaniline, 19.9% yield (average) of 2-di-n-propylamino-3H-propyl-3H azepine and 3.7% yield (average) of 2-di-n-propylamino-7n propyl-7H azepine. Only a 4.7% yield 2-methylindoline was detected. These results are in marked contract to those obtained by Odum and Trattner who also reported no 2-methylindoline at ambient temperatures (for the photolysis of the same azide in isooctane) and observed a 47% yield of this C-H insertion product at 99°C.[19] They also presented evidence for the intermediacy of a singlet nitrene in the formation of 2-methylindoline. To account for these results the following mechanistic scheme is proposed.

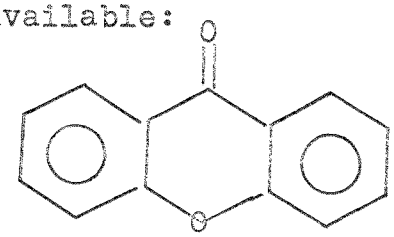

hν
Δ
(I)
(II)
Singlet
(III)
Triplet
(V)
(VI)
(VII)
(IV)
(CH3-CH2-CH2)2NH
(CH3-CH2-CH2)2NH
(VIII)
(IX)

At ambient temperatures, in the absence of photosensitizer, the azide (I) undergoes loss of nitrogen to give the singlet nitrene (II) as the first excited state. This intermediate can undergo intersystem crossing to the triplet nitrene (III) which will then abstract hydrogen from the solvent to yield an aniline (IV). This intersystem crossing can be enhanced by use of a triplet photosensitizer like xanthen-9-one. The singlet nitrene (II) is also in equilibrium with two azabicyclic compounds, V and VI, which result from internal attack on the benzene ring at either ortho positions (i.e. 2 or 6). The formation of the azabicyclic compound (V) which results from attack at 2-position should be less favored on steric grounds. These azabicyclic compounds can then undergo reaction with the secondary amine solvent to give the azepines VIII and IX. The formation of IX should also be disfavored relative to that of VIII because of steric factors. In the presence of a triplet photosensitizer the yield of the aniline IV is increased while the yield of azepine (V) is decreased.

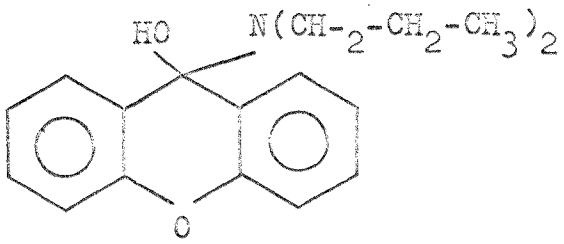
At elevated temperature (i.e. 100C°), the yield of azepines is increased markedly from 4.3% (ambient temperature) to 23.5% (total azepines). This is not an unexpected result since it is known that at elevated temperatures o-n-propylphenyl azide reacts primarily via

a singlet nitrene intermediate. However in a secondary amine solvent the azabicyclic compounds, which are in equilibrium with the singlet nitrene, react with the solvent to form the respective azepines. Only a small amount of 2-methylindoline (i.e. 4.2%) is obtained. The increase in temperature has apparently shifted the equilibrium between the singlet nitrene and azabicyclic in the direction of the azabicyclic which are then "trapped" by attack of the amine solvent. The relative amounts of the two azepines can again be explained in a steric basis, i.e. both formation of the azabicyclic (VI) and attack on it by the amine solvent is much more sterically hindered that the corresponding reactions leading to formation of azepine (VIII).

The addition of an ca. equimolar amount of photosensitizer to the elevated temperature reaction has very little effect (Experiment VIII). Even a ten fold excess of xanthen-9-one does not affect the product yield appreciably. It may be that at 110°C, the following reactions between the xanthen-9-one and the di-n-propylamine is favored[15] so that there is virtually no photosensitizer available:



$+HN(CH_2\text{-}CH_2\text{-}CH_3)_2 \longrightarrow$


HO
N(CH-2-CH2-CH3)2
O

CONCLUSION

The photolysis of o-propylphenyl azide in di-n-propylamine was studied and two different new azepines were obtained;2-di-n-propylamino-3n-propyl-3H azepine and 2-di-n-propylamino 7n-propyl-7H azepine. Their structures were assigned on the basis of their physical properties (i.e., I.R., N.M.R., U.V., M.S. and elemental analysis).

The mechanistic pathway leading to the formation of these azepines were also studied and a mechanistic "scheme" is proposed to account for their formation.

Support for this "scheme" is furnished by the use of temperature and photosensitizer effects.

REFERENCES

1. Abramovitch, R.A., Ahmad, Y. and Newman, D. Tetrahedron Letters, 752, (1961)

2. Abramovitch, R.A., and Davis, B.A., Chem. Rev. 64 148, (1964)

3. Bahacca, N.S., Johnson, L.F., Resolution N.M.R. Spectra Catalog, V.I. Paloalto, California, Varian Analytical Instrument Division, 1962, No. 209

4. Bellamy, L.J., The Infrared Spectra of Complex Molecules, New York; John Willey and Sons, Inc., 1969, pp. 5-9

5. Cadogan, J.I.G. and Mackie, R.K.J., Chem. Soc. (C) 81, (1969(

6. Cadogan, J.I.G. and Todd, M.J.J., Chem. Soc. Part 3, 2810 (1969)

7. Doering, W.Von, E. and Odum, R.A., Tetrahedron, 22, 81-93 (1966)

8. Hall, J. H. Hill, J. W. and Fargher, J.M., J. Amer. Chem. Soc. 90, 5313, (1968)

9. Heacock, J.F. and Edmison, M.T., J. Amer. Chem. Soc., 82, 3460 (1960)

10. Huisgen, R. and Appl. M. Chem. Ber., 91, 12, (1958)

11. Hurd. C.D. and Jenkis, W.W., J. Org. Chem., 22, 1418, (1957)

12. Knunyants, I.L. and Bykhouskaya, E.G., Proc, Acad. Soc. U.S.S.R. 131, 411 (1960)

13. Lalilie, G. Chem. Rev., 69, 345, (1969)

14. Lwowski, W., Nitrenes, New York, Willey, J. and Sons Inc. 99-106, (1970)

15. March, J., Advanced Organic Chemistry, New York, McGraw-Hill, pp. 667. (1968)

16. Odum, R.A. and Aaronson, A.M., J. Amer, Chem Soc. 91, 5680, (1969)

17. Odum, R.A. and Brenner, M., J. Amer. Chem. Soc. 88, 2974, (1966)

18. Odum, R.A. and Schmall, B., Chemical Communications, 66, 769, (1962)

19. Odum, R.A. and Trattner, R. B. (Unpublished work).

20. Prevarsek, D.C., J of Physical Chemistry, 66 769, (1962)

21. Silverstein and Bassler, Spectrometric Identification of Organic Compounds, N.Y. John Wiley & Sons, Inc. p. 31, 1967

22. Smith, P.A.S. and Brown, B.B., J. Amer. Chem. Soc., 73, 2435, (1951)

23. Smith, P.A., Krbecheck, L.O. and Resemann, W. Paper Presented at 44th National Meeting of Amer. Chem. Soc., April, 1963.

24. Smolinsky, G., J.,Amer. Chem. Soc., 82, 4717 (1960)

25. Smolinsky, G., J. Amer. Chem. Soc., 83, 2489, (1961)

26. Smolinsky, G. and Feuer, I.B., J. Amer. Chem. Soc., 86, 3085, (1964)

27. Splitter, J.S. Calvin, M., Tetrahedron Letters, 12, 1448 (1968)

28. Sunbery, R.J., Brenner, M. and Sutter, R., Tetrahedron Letters, 31, 2715, (1970)

29. Vogel, A.I., Practical Organic Chemistry, N.Y. John, Wiley & Sons, Inc., p. 563 (1966)

30. Wolff, L. Ann., 59, 394 (1912)