

## **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 Van Houten library has removed some of the personal information and all signatures from the approval page and biographical sketches of theses and dissertations in order to protect the identity of NJIT graduates and faculty.

THE CHEMISTRY OF AZIDES

BY

EDWARD D. NELSON

A Thesis  
Presented in Partial Fulfillment of  
The Requirements for the Degree  
of  
Master of Science in Engineering Science  
at  
Newark College of Engineering

This Thesis is to be used only with due regard to the rights of the author(s). Bibliographical references may be noted, but passages must not be copied without permission of the college and without credit being given in subsequent written or published work.

Newark, New Jersey, 1973

APPROVAL OF THESIS

The Chemistry of Azides  
by  
Edward D. Nelson  
for  
Department of Chemistry  
Newark College of Engineering  
by  
Faculty ~~Committee~~

Approved:

Newark, New Jersey  
February, 1973

## TABLE OF CONTENTS

- iv. List of Figures
- v. List of Tables
- vi. Abstract
- 1. Introduction
- 2. Background
- 3. Reactions of Azides
  - a. Specific
  - b. General
- 4. Thermolysis of Alkyl Azides
  - a. Thermal Rearrangements
  - b. Evidence of Alkyl Nitrene
- 5. Thermolysis of Aryl Azides
  - a. Rearrangements
  - b. Azepines
- 6. Photolysis
  - a. Mechanism
  - b. Azepine Formation
- 7. Conclusions
- 8. Bibliography

LIST OF FIGURES

FIGURE

- 1 Configurations of Organic Azides
- 2 Linear Structure of Azide Group

## LIST OF TABLES

### TABLE

- I. Decomposition of Ethyl Azidoformate in Cyclohexane
- II. Effect of Additive Concentration on the Decomposition of Ethyl Azidoformate in Cyclohexane
- III. Relative Reactivities of C-H Bonds with Phenyl Nitrene
- IV. Pyrolysis Products of Alkyl Azides

## ABSTRACT

A review of the decomposition of alkyl and aryl azides by thermolysis and photolysis has been accomplished. Organic azides are a very distinct species that undergo its own unique reactions. Azides decompose to form an electron deficient nitrogen having a sextet of electrons. This is called a Nitrene. Nitrenes can exist in the singlet or triplet state. The triplet behaves like a diradical. General and specific reactions of nitrenes have been shown with detailed mechanisms accounting for the products. The main modes of nitrene stabilization are rearrangement, hydrogen abstraction and insertion. Insertion is characteristic of singlet species and abstraction characteristic of the triplet. Some reaction mechanisms during decomposition are concerted while others occur via a stepwise process. Bond reorganization is another method of stabilization (although less common) and is usually limited to aryl compounds. Often, azepines ( a ring enlarged nitrogen compound) is the result of this reorganization. Such reactions occur in the thermolysis or photolysis of phenyl azides in amines.

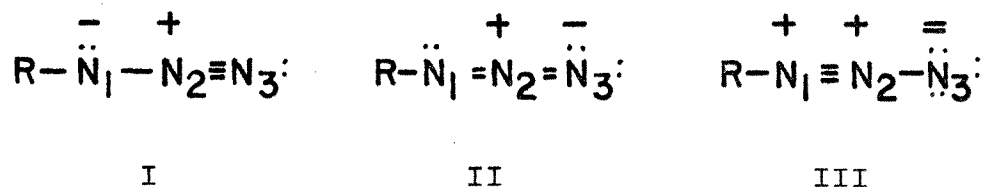


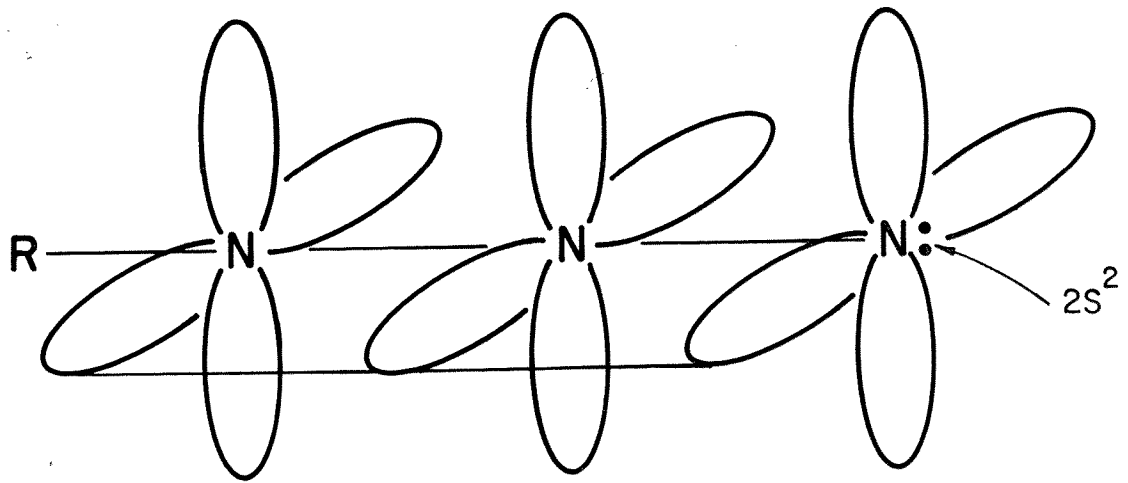
## INTRODUCTION

This review is concerned with the chemistry of species containing a monovalent nitrogen atom, i.e., an electron deficient nitrogen having a sextet of electrons in its outer shell. This species is postulated to be formed as intermediates in a large number of reactions, usually from decomposition of the azide linkage ( $N_3$ ). The two specific reaction types of concern here are thermolysis and photolysis. The decomposition of azides usually leads to the loss of the azide nitrogen and the formation of products derived from rearrangement, cyclization or hydrogen abstraction. These results have been interpreted as coming about by a concerted reaction path, by initial formation of an adduct, or by formation of a nitrene ( $R-N$ ). Many attempts have been made to interpret these intermediates but have led to many ambiguous results. This paper presents the major reactions of organic azides leading to formation of nitrene intermediates showing mechanistic pathways involved.

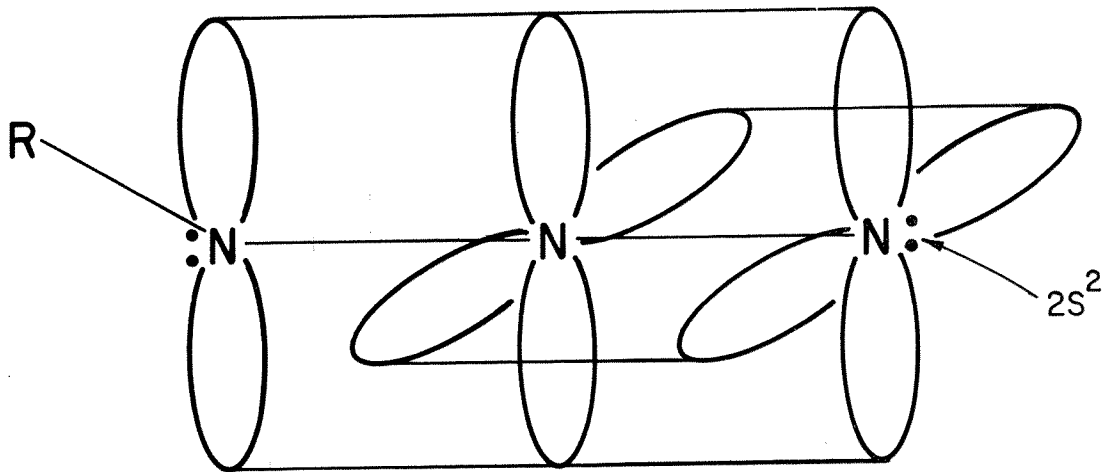
## BACKGROUND

The first review of the chemistry of alkyl and aryl azides was by Boyer and Canter in 1954.<sup>1</sup> The basic structure of covalent azides is pictured as resonance hybrids between structures I, II and III.<sup>2</sup>

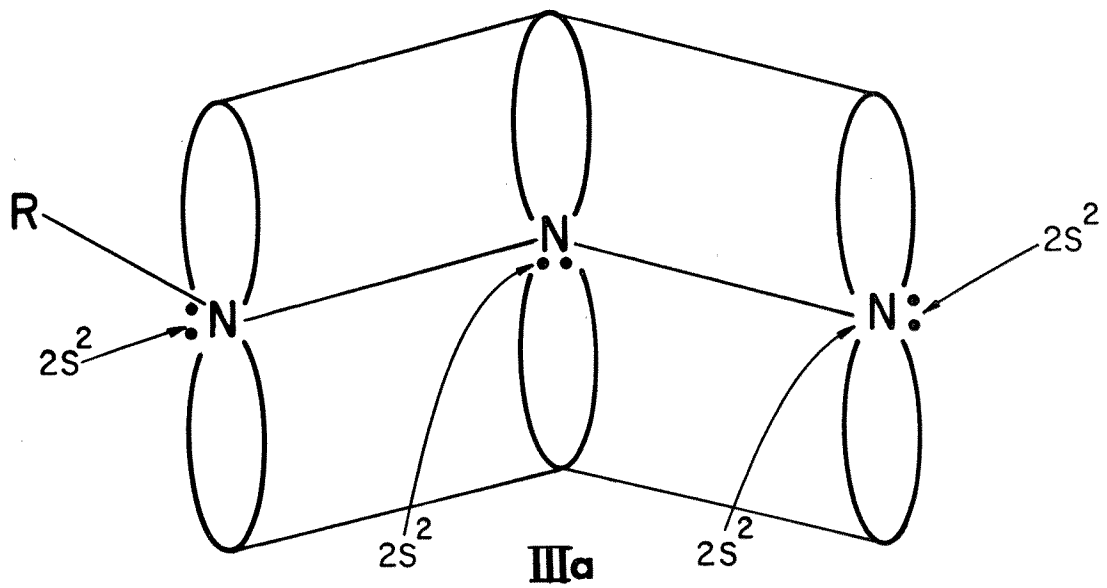




Ia

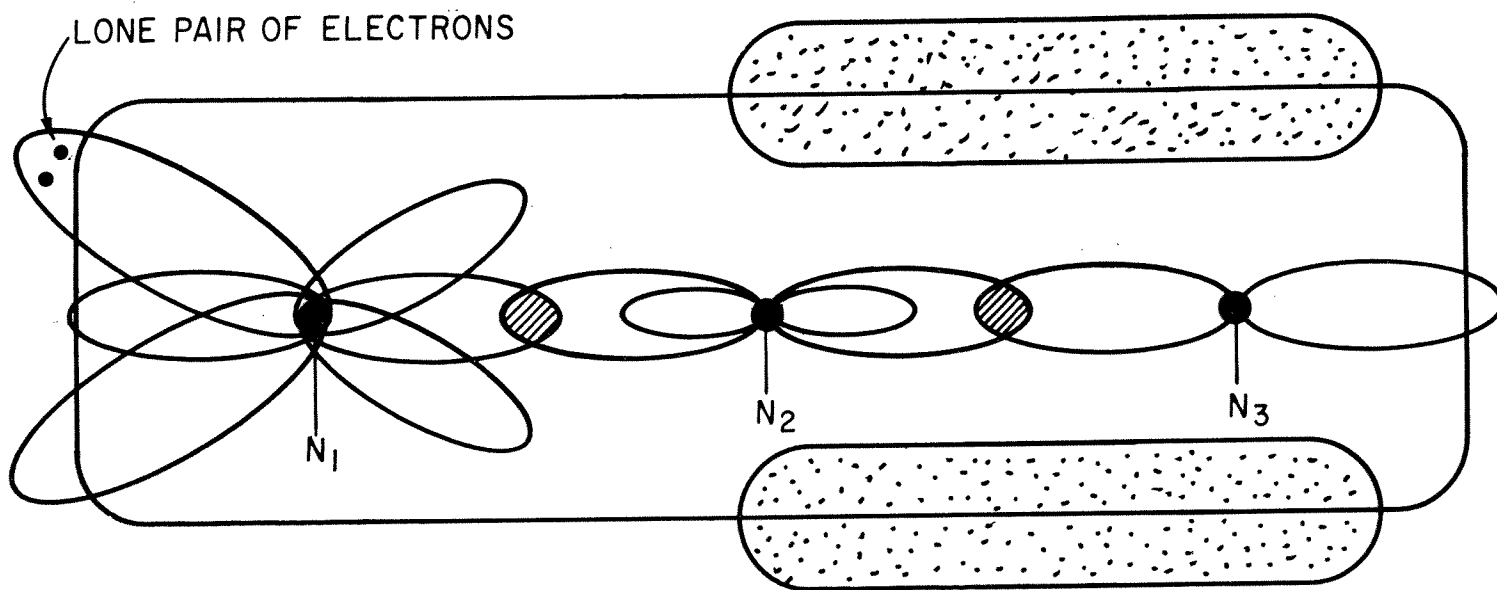


IIa



IIIa

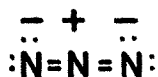
FIGURE I



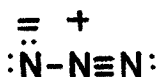
**Linear Structure of Azide Group**

**FIGURE 2**

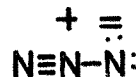
Structure III is generally not considered a major contributor to the hybrid. Pauling<sup>3</sup> has shown a correlation of resonance energies with azides stability. The azide ion can be represented as a hybrid of three major contributors IV, V, and VI.



IV



V



VI

The N - N distances in ionic azides are identical while the N - N distances in covalent azides would have different N<sub>1</sub> - N<sub>2</sub> and N<sub>2</sub> - N<sub>3</sub> distances.

Roberts<sup>4</sup> has studied the structure of organic azides through molecular orbital calculations. Organic azides could have configurations Ia, IIa, and IIIa shown in Figure 1. The structure of the azide group is linear and is due to the SP hybridization of the central nitrogen atom. This is illustrated in Figure 2. The Pi cloud in the figure represents the bonding Pi orbitals delocalization of electrons. Pi bonds above and below the plane of the molecule also exist but are not shown in this figure. Of these, structure V represents the best picture of an organic azide and satisfies structural observations. The Pi bond delocalization energies of forms IV, V and VI have been calculated by Roberts.<sup>4</sup> This data in conjunction with the known greater stability of structure V led to the important inference that

the bending of the nitrogen chain of an organic azide does not require much energy. This bent state of the azide has been used in discussing transition state configurations<sup>5</sup> and explaining certain cycloadditions of azide ion.<sup>6</sup>

### Specific Reactions of Azides

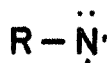
Azides undergo two distinct types of reactions, i.e., thermolysis and photolysis. It is felt that the most important step in the decomposition is the formation of a nitrene and nitrogen. A nitrene is a univalent nitrogen derivative of the general formula:



It can be generated in the singlet (VII) or triplet (VIII) state. The triplet behaves much like a diradical.



VII

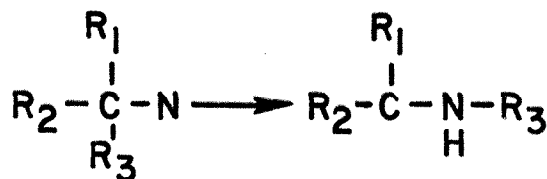


VIII

General reactions of nitrenes (usually through photolysis or pyrolysis)

The general reactions of nitrenes fall into these categories.

1. Rearrangement, ex.



2. Recombination

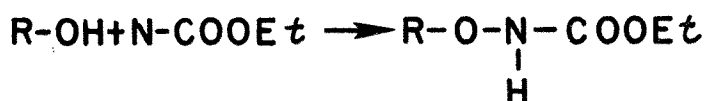
The recombination of two nitrenes to form an azo compound is spin permitted for both the singlet and the triplet species.



3. Electrophilic attack on bonding pairs via

a) Insertion into C-H bonds. This is exclusively a reaction of singlet nitrene. Aromatic nitrenes are very selective in their insertion reactions. For instance phenyl nitrene has insertion yields for primary, secondary and tertiary C-H bonds in the ratio of 1:10:100.<sup>7</sup>

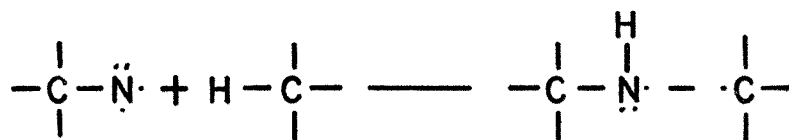
b) Insertion into O-H bonds.



c) Insertion into NH bonds.



d) Hydrogen abstraction. This is the most general reaction of triplet nitrenes.

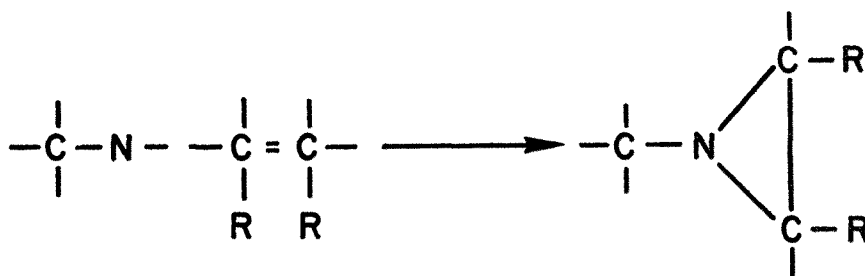


A carbon radical is produced by the abstraction of one hydrogen atom also forming an amino radical. The two radicals at this point have unpaired spins and cannot combine.

Eventually spin reversal occurs and a second hydrogen abstraction takes place forming an amine.

#### 4. Addition to Multiple Bonds

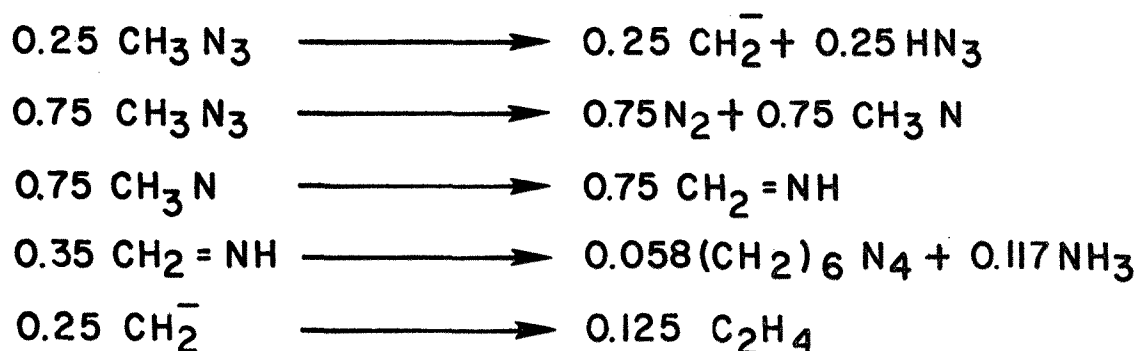
a) The addition to double bonds is a reaction of both singlet and triplet nitrenes and proceeds as such:



#### Thermolysis of Alkyl Azides

An introduction to the thermolysis of azides should include the simplest azide (methyl azide). Ramsperger<sup>8</sup> was the first to study the effect of the gas phase thermolysis of this compound and found it to be a homogenous first-order reaction.

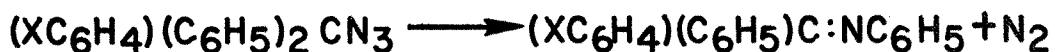
Leorsmakers<sup>9</sup> proposed a mechanism for the decomposition of methyl azide. He suggested two modes occurred with reactive intermediates of 75 percent methyl nitrene and nitrogen and 25 percent methylene and hydrazoic acid. Stoichiometric equations are given as follows:







In the rearrangement of the intermediate univalent nitrogen derivatives, in some of molecules, the phenyl radical would presumably migrate from the carbon to the nitrogen. In the other molecules, the derived radical ( $\text{XC}_6\text{H}_4$ ) or ( $\text{C}_6\text{H}_4$ ) would be the migrating group. Monosubstitution product should give simultaneous rearrangement:



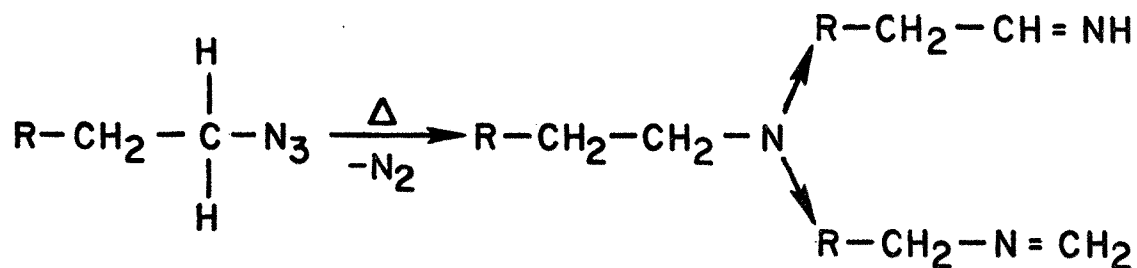
and



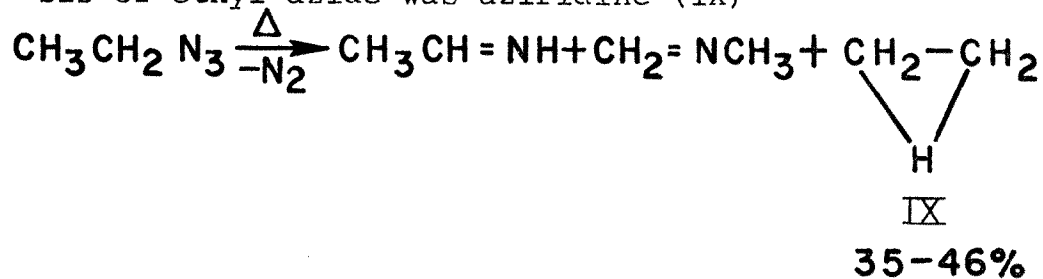
A determination of the ratio in which the groups migrate in a given case was determined. The entire series should give, according to Stieglitz<sup>10</sup> the same intermediate product  $(\text{XC}_6\text{H}_4)(\text{C}_6\text{H}_5)_2 \text{C} - \text{N}$ . Senior examined the rearrangement of *p*-chlorophenyl diphenyl methylazide.<sup>10</sup> He found that in 68.1% of the rearranging molecules, the phenyl radical migrates to the nitrogen. In 31.9 percent, the chlorophenyl group is the migrating one. For a corresponding *p*-chlorophenyldiphenylmethylhydroxyl amine the ratio was 70.8/29.2.<sup>12</sup> The ultimate conclusion was that triarylmethylazides behave qualitatively and quantitatively like the corresponding triarylmethylhydroxylamines which is in favor of the Stieglitz theory<sup>12</sup> of these molecular rearrangements and

against the Beckman theory<sup>12</sup> which is a direct exchange of the migrating group.

The most important step in the decomposition of alkyl azides was thought to be the formation of the nitrene and nitrogen. Pritzkow and Timm<sup>13</sup> studied the gas phase pyrolysis of eight alkyl azides.



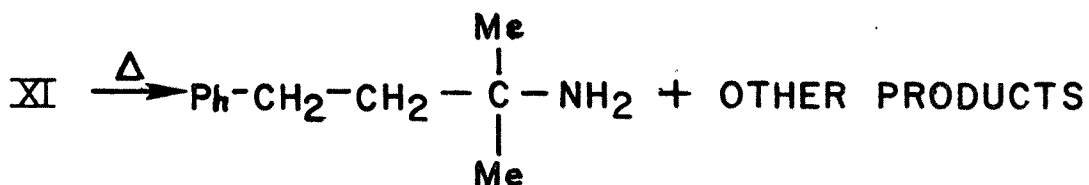
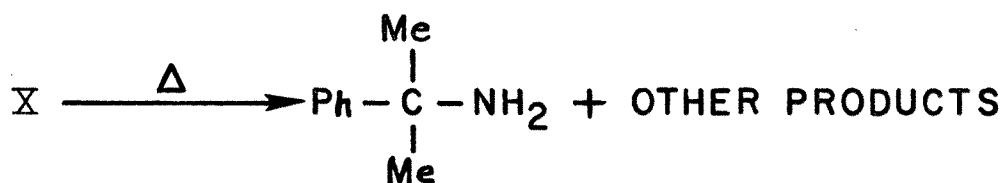
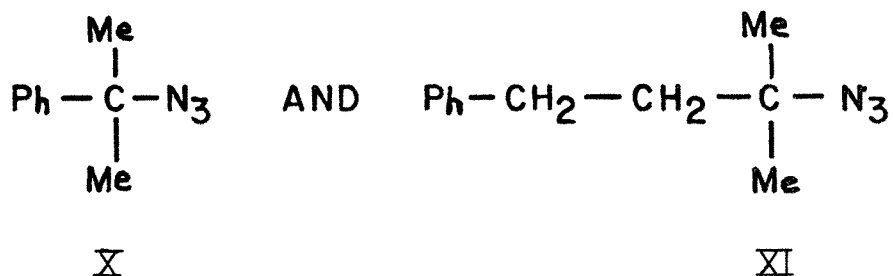
The major products obtained were a result of rearrangement in every case except one. Hydrogen migration predominated. Ethyl azide produced the non-rearrangement product. The product formed in abundance (35-46 percent) from the thermolysis of ethyl azide was aziridine (IX)



There exists little evidence for the production of nitrene intermediates in alkyl azide thermolysis. It is possible that the nitrene intermediate is formed in a stepwise process and then converts to the final product with

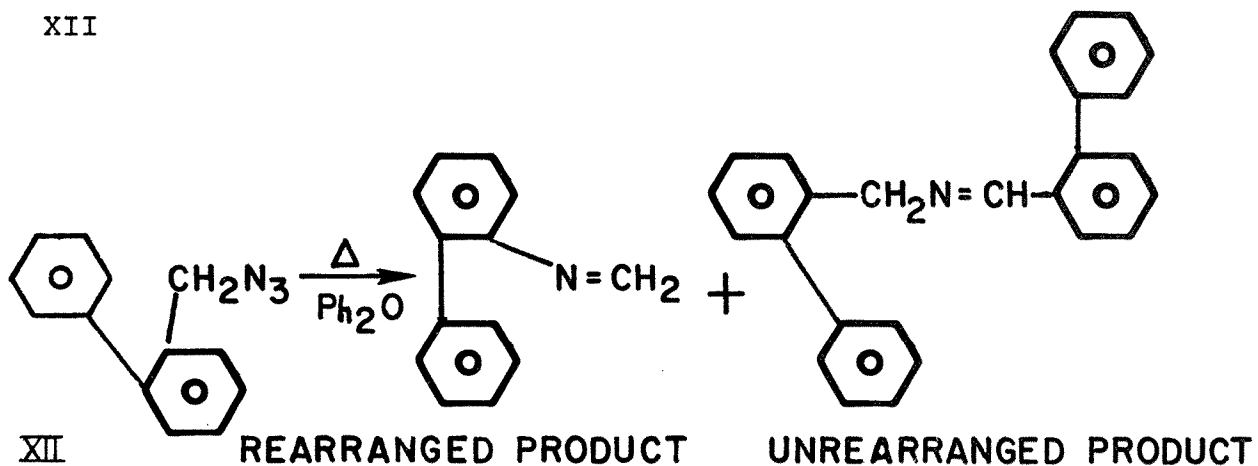
the formation of the nitrene being rate determining but, to date evidence shows the mechanism to be concerted with elimination of nitrogen. Under certain conditions, the nitrene intermediate is formed and the reaction can be controlled.

Evidence for the formation of an alkyl nitrene is obtained from the thermolysis of X and XI.

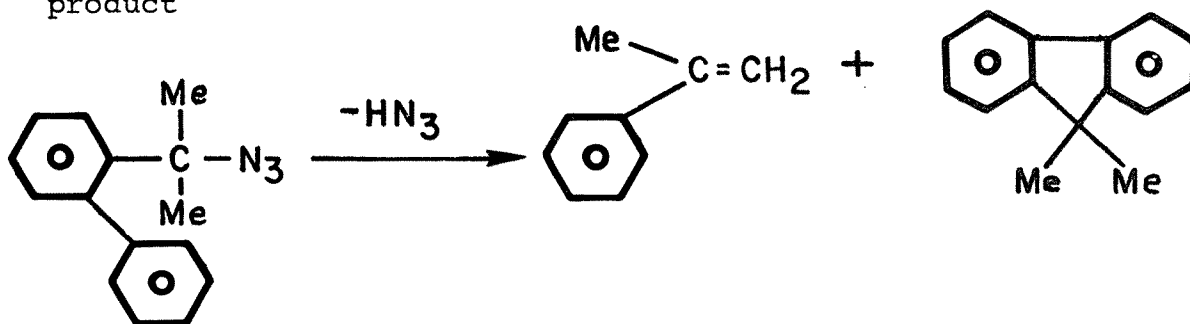


the formation of amine is support that a free alkyl nitrene is formed.<sup>14</sup> When the nitrene is formed, it abstracts hydrogen from the surroundings to produce the amine.

The absence of hydrogen atoms at the  $\alpha$  carbon atoms in azides increases the lifetime of the nitrene thus making it possible for the reaction to proceed without rearrangement.<sup>15</sup> This is evidenced by the thermolysis of XII

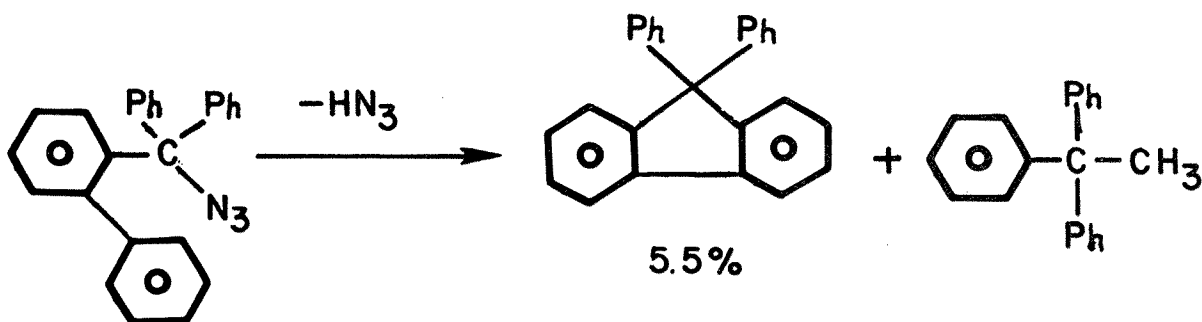


Decomposition of XIII also produces chiefly unrearranged product

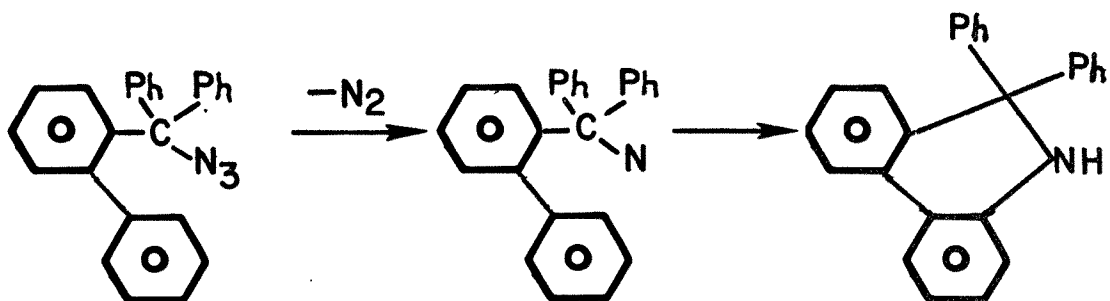


XIII

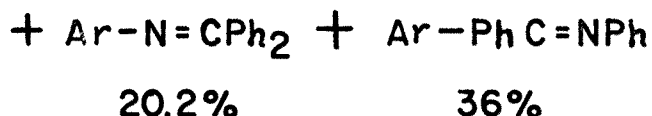
Decomposition of XIV produces both rearranged and unrearranged products depending on the mechanism.



XIV

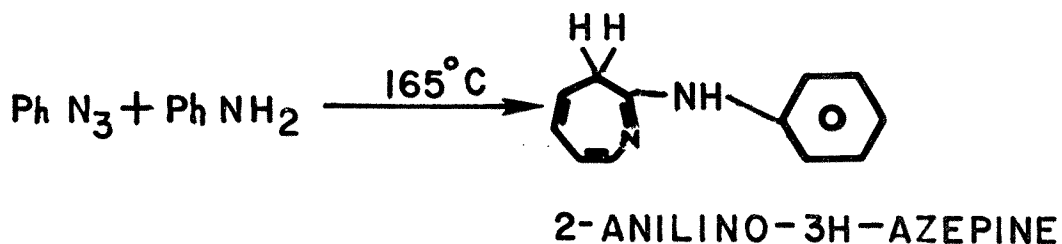


XIV



### Thermolysis of Aryl Azides

The thermal decomposition of aryl azides can lead to a much wider variety of products than alkyl azides. Addition of phenyl azide to an approximately equivalent amount of aniline at 150°C gave a ring expansion compound  $\text{C}_{12}\text{H}_{12}\text{N}_2$  (6-10 percent) that Wolff named dibenzamil.<sup>16</sup> The structure was not identified until Huisgen and coworkers<sup>17</sup> obtained improved yields by adding phenyl azide to excess aniline at 165°C. The compound which they obtained was identified as 2-anilino-3H-azepine

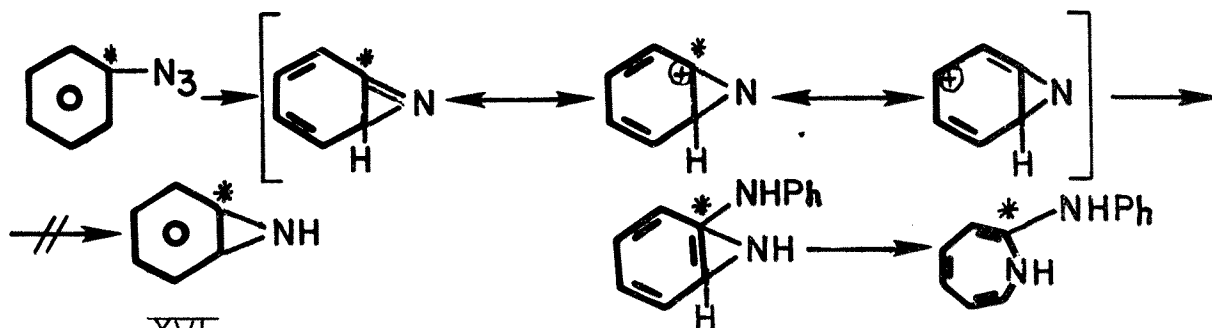


The intermediacy of the 1H-azirene derivative XV was eliminated by  $C^{14}$  labeling.



XV

The reaction intermediates were such that if XV were an intermediate the labeled carbon would be found in both the 2 and 7 positions of the 2-anilino-3H-azepine. One hundred percent of the label was found at C-2, with none at C-7 thus eliminating XVI as an intermediate.



XVI

The decomposition of *o*-azidodiphenyl methane in 1, 2, 4 - trichlorobenzene appears to proceed by the elimination of nitrogen and the attack of the nitrene on the neighboring phenyl group.<sup>18</sup>

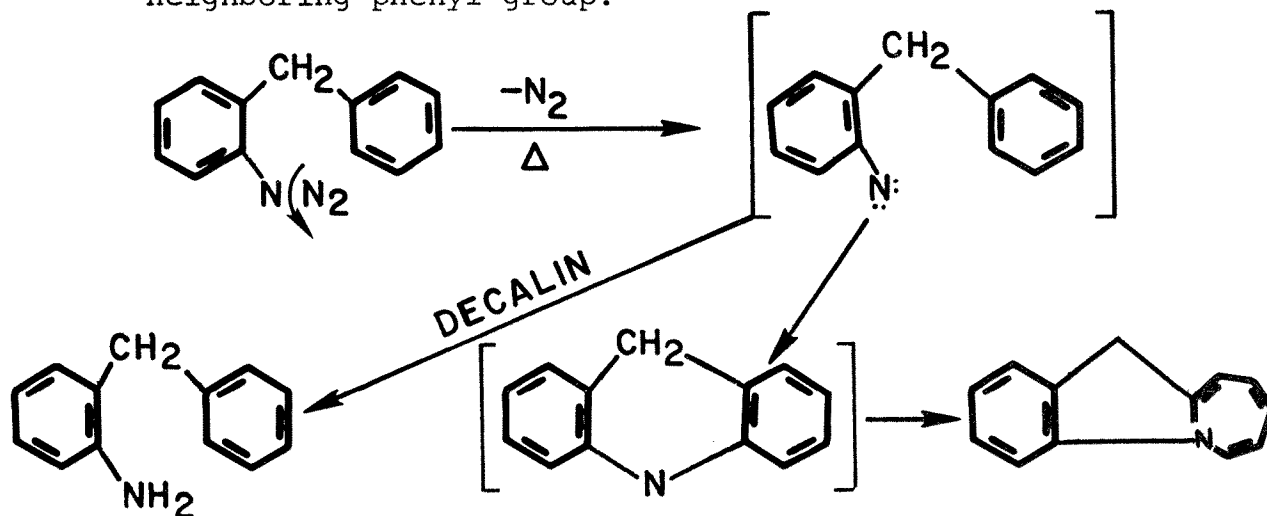


TABLE IDecomposition of Ethyl Azidoformate in Cyclohexane

<u>Additive</u>	<u>Conc, Mole % of Azidoformate</u>	<u>Yield, %</u>		<u>Total</u>
		<u>Insertion</u>	<u>Abstraction</u>	
None	-	52	25	77
m-dinitro- benzene	19	74	17	91
Nitrobenzene	14	70	17	87
2-Nitropropane	87	59	19	78
Sulfur	34	76	14	90
2,6-Di-t-butyl- P-Cresol	7	59	16	75
Hydroquinone	8	65	17	82
p-Quinone	7	65	17	82

TABLE IIEffect of Additive Concentration on the  
Decomposition of Ethyl Azidoformate in Cyclohexane

<u>Additive</u>	<u>Concentration</u>		<u>Yield, %</u>	
	<u>g/100 ML Sol</u>	<u>Mole % Azidoformate</u>	<u>Insertion</u>	<u>Abstraction</u>
None	-	-	52	25
Nitro- benzene	0.15	14	70	17
	0.46	43	70	15
	1.24	116	69	15
	2.37	221	65	13
	6.17	577	61	14
M-Dinitro- benzene	0.05	3.70	61	21
	0.13	8.73	70	17
	0.27	18.7	74	17
	1.09	75.0	71	14
	2.43	166	67	12
Sulfur	0.06	20.8	72	18
	0.10	34.2	76	14
	0.53	192	65	15
	0.99	354	61	13
	2.35	845	56	14



The elimination of nitrogen and the attack may occur either via a concerted or a stepwise reaction. The stepwise reaction is favored since o-amino-diphenyl-methane was obtained in decalin by the hydrogen abstraction from the solvent by the nitrene. The decalin, being a better donor of hydrogen than trichlorobenzene, traps the nitrene and prevents the azepine formation.

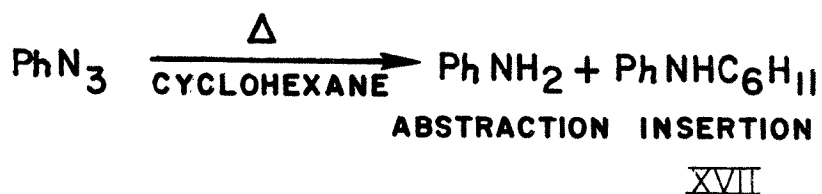
When thermolysis of aryl azides leads to an aryl nitrene, it is generated on the singlet or triplet state. It is generally agreed that hydrogen abstraction in aliphatic solvents is characteristic of the triplet diradical and insertion reactions characteristic of the singlet species.<sup>19,20,21,22</sup> It was concluded<sup>22</sup> that singlet stability falls in the order, sulfonyl>formyl>aryl and that insertion into the C-H bond of a saturated hydrocarbon and addition to an aromatic ring are singlet reactions.

Table I shows the effect of additives on the decompositions of ethyl azidoformate in cyclohexane.<sup>22</sup> The additives function as radical traps. In most cases, the insertion yield increases at the expense of both the abstraction product and an undetermined side reaction.

Table II shows the effect of additive concentration for three of the additives.<sup>22</sup> In each case, there is an optimum concentration of additive needed before a maximum yield of insertion product is obtained. The yield of abstraction product decreases with increasing additive

concentration but seems to level off at about 12-14 percent. Breslow and Edwards explanation for the increased amount of insertion product derived from singlet nitrene is that an unknown radical produced in the reaction can catalyze singlet-triplet intersystem crossing.<sup>22</sup> Reaction with the additive would decrease the radical concentration, resulting in a slower singlet to triplet conversion and therefore a higher yield of the product derived from the singlet. The decrease in insertion yield with increasing additive concentration is undoubtedly due to some reaction of the singlet with the additive. In other words, stereospecific C-H bond insertion reactions are due to the singlet nitrene.

One of the most common products of aryl azide thermolysis is aniline. This of course is a result of hydrogen abstraction from the surrounding species by the triplet nitrene. The yield of aniline for these reactions is generally high. Insertions in aliphatic C-H bonds on the other hand are normally low yield processes. An example of this is when phenyl azide was pyrolyzed in cyclohexane,<sup>23</sup> aniline was obtained and a mixture of solvent insertion products (XVII) of N-alkylanilines (8% yield) was formed.



Smólinisky and coworkers<sup>24</sup> have reported examples of the insertion of thermally generated aryl nitrenes into C-H bonds in some intramolecular reactions but the work by Hall, et al.<sup>23</sup> constitute the first example of an intermolecular insertion reaction by a thermally generated aryl nitrene. Aside from the N-alkyl anilines formed in the thermal decomposition of phenyl azide in hydrocarbon solvent, azobenzene and polymeric material are also formed.<sup>23</sup>

The relative reactivities of primary, secondary and tertiary C-H bonds was compared by Hall, et al.<sup>23</sup> Phenyl azide was thermally decomposed in n-pentane. The amines produced in the reaction were subjected to vapor phase chromatography. Three fractions were collected and identified by infrared spectroscopy as aniline (30 percent yield) and a mixture of N-pentyl anilines (10 percent yield) respectively. Synthesis of the three possible N-pentyl-anilines and subsequent examination of their retention times revealed that the experimental N-pentyl aniline mixture did not contain a detectable amount of N-(1 - pentyl) - aniline (retention time 13.5 min.). N-(2 - pentyl) - aniline and N-(3 - pentyl-aniline) exhibited the same retention times (10 minutes) and infrared spectra as the N-pentyl aniline mixture. The fact that the 2 - and/or 3-isomer but not the 1-isomer was detected strongly indicates that, under their conditions insertion into the secondary C-H bonds is preferred over the primary C-H bonds by a factor of at least 100.

TABLE III

Relative Reactivities of C-H Bonds With  
Phenyl Nitrene

<u>Insertion Ratio</u>	<u>N-Pentane</u>	<u>Isopentane</u>
2°/1°	>100	>7
3°/2°	-	20-40

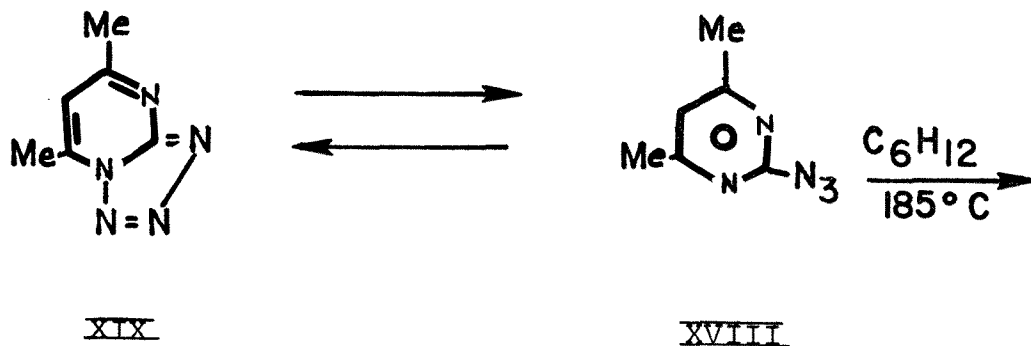
An identical study on decomposing phenyl azide in isopentane (Table III) shows insertion into the tertiary C-H bond is preferred over the secondary by a factor of 20-40. Insertion into the secondary C-H bonds to insertion into the primary C-H bonds is preferred by at least a factor of 7.

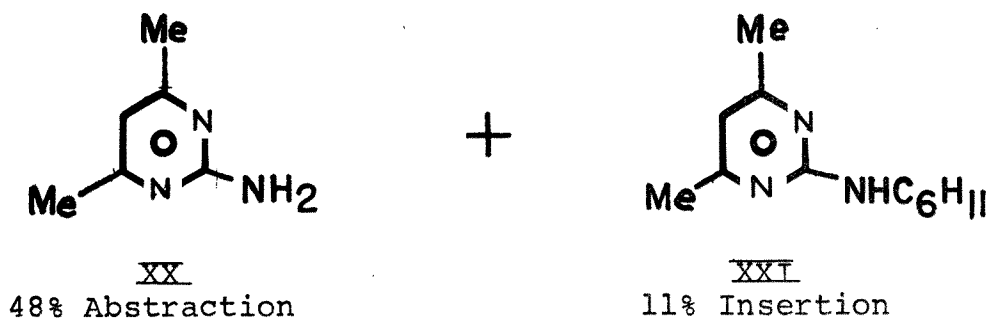
The selectivity of the phenyl nitrene is explained by its stability. Phenyl nitrene may undergo reaction in the singlet or triplet state. Both states should be stabilized by resonance with the aromatic ring as:



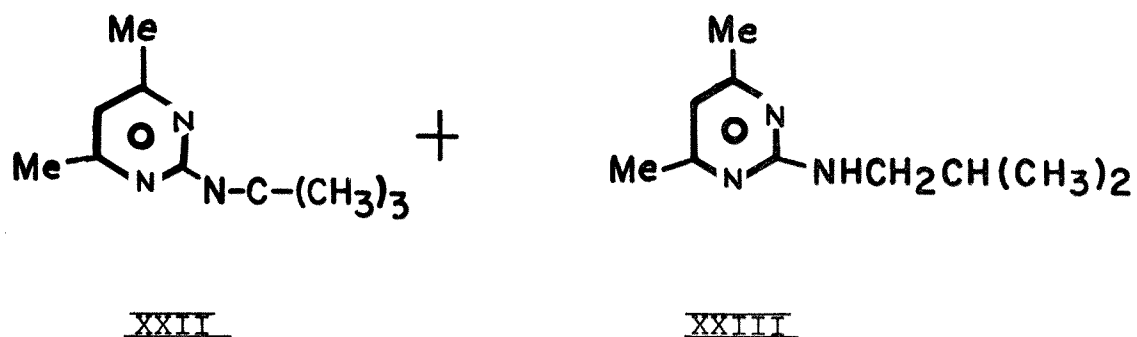
A stabilized nitrene should lead to a higher energy of activation for the insertion reaction, thus increasing the selectivity of the nitrene.

Another example of insertion and abstraction reactions of nitrenes is the thermolysis of dimethyl pyrimidine (XVIII) which is in equilibrium with the tetrazole (XIX) in cyclohexane.<sup>23</sup> This gave a yield of 48 percent hydrogen abstraction product (XX) and 11 percent insertion product (XXI).





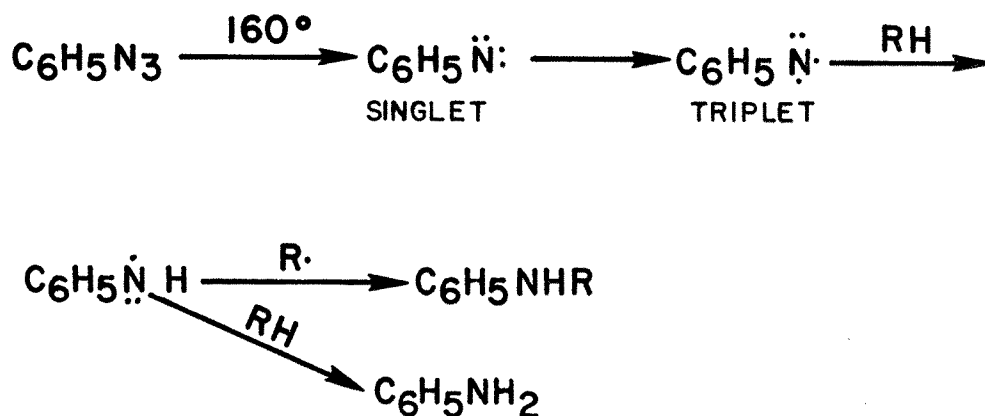
Thermolysis of XIX  $\downarrow$  XVIII in isobutane at 175°C gave XX in 48 percent yield and insertion products XXII and XXIII in 5.4 percent and 1.6 percent yield respectively.



These products show that the predominant intermediate in abstraction reactions is the triplet nitrene.

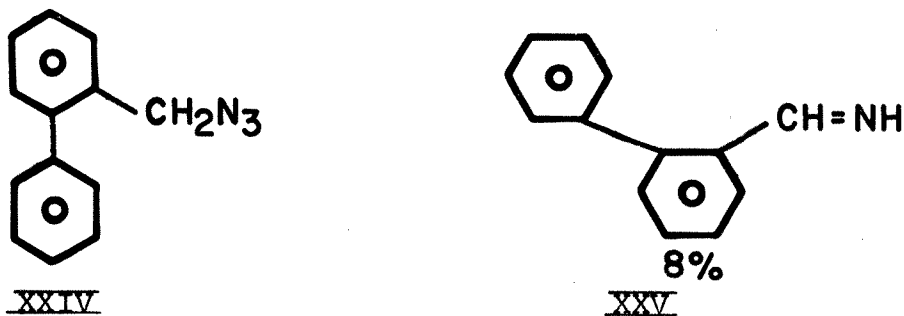
Recently, some evidence has been presented in favor of a triplet phenyl nitrene from the pyrolysis of phenyl azide in mixtures of cyclohexane - neopentane, giving rise to both hydrogen abstraction and insertion product.<sup>7</sup> Thermal decomposition of phenyl azide in aliphatic hydrocarbons leads to the formation of aniline, alkyl aniline, azobenzene and polymer.<sup>7,21,23</sup> In an attempt to account for these products, Hall, Hill and Fargher<sup>7</sup> adopted the hypothesis

that the N-alkyl aniline was formed by insertion of singlet nitrene into the hydrocarbon C-H bonds whereas the aniline was formed from triplet nitrene by abstraction of hydrogen from solvent. Phenyl azide was decomposed in mixtures of cyclohexane and neopentane at 160°C. Since insertion into the secondary C-H bonds of cyclohexane is much faster than insertion into the primary C-H bonds of neopentane, the neopentane acts as an inert solvent. The yields of the products varied erratically as the solvent composition was varied from pure cyclohexane to 25 percent cyclohexane - 75 percent neopentane. However, the ratio of aniline to N-cyclohexyl aniline remained constant at 4.0. This suggested that their original hypothesis was erroneous, because if insertion product was formed by the singlet nitrene, then addition of an inert solvent should convert some singlet to triplet and the amount of aniline formed should increase and the amount of N-cyclohexyl aniline should decrease. The conclusion was drawn that since the aniline/N-alkyl aniline ratio was constant, both products resulted from the same intermediate, most likely the anilino radical. The reaction scheme is this:

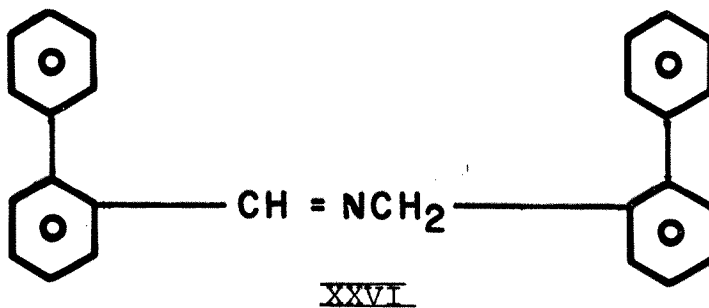


Rearrangements

Photolysis of 2 azido methyl biphenyl (XXIV) is believed to function as a biradical. Photolysis produced the azene  $AR-CH_2N$  (-2 YL) with characteristic intramolecular hydrogen abstraction to form the imine XXV



However, under the more energetic conditions of pyrolysis in boiling biphenyl ether, 2-azido methyl biphenyl evolved hydrazoic acid and gave two products. One of these was anil (XXVI) and the other 2 - amino biphenyl.



The anil formation was explained by the coupling of the appropriate azene with a radical produced by elimination of hydrozoic acid from 2 - azido methyl biphenyl thus:

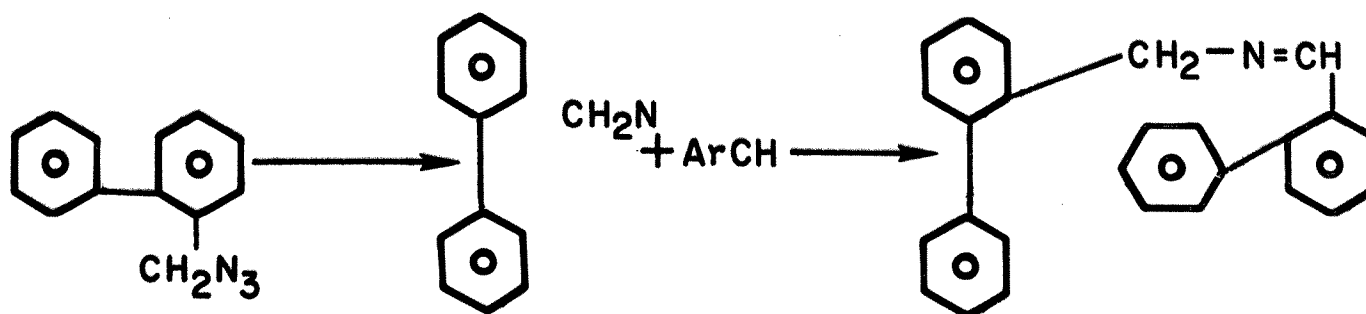


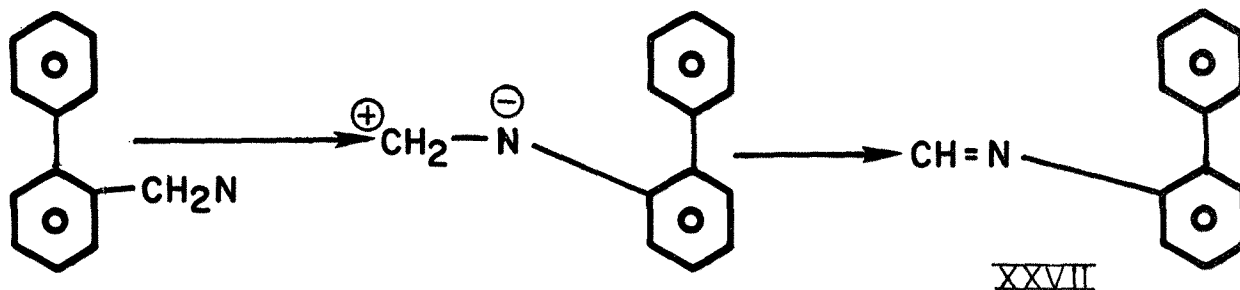


TABLE IV

Pyrolysis Products of Alkyl Azide's

<u>Azide</u>	<u>1,2-hydrogen Migration (%)</u>	<u>1,2-alkyl Migration (%)</u>	<u>Amine (%)</u>	<u>Aziridine (%)</u>
Ethyl	55	4	-	35
n-butyl	82	7	1	-
n-octyl	75	15	1	-
Isobutyl	85	5	3	0.02
4-Methyl pentyl	80	10	1	-
3,3 Dimethyl- butyl	80	16	-	-
t-butyl	-	60	-	11

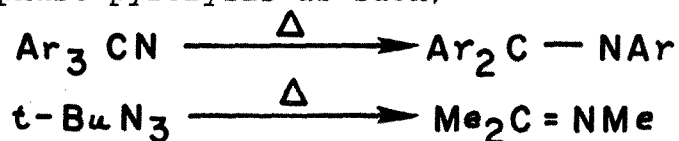
the azene from 2 - azido methyl biphenyl on rearrangement gives the formaldehyde anil (XXVII).



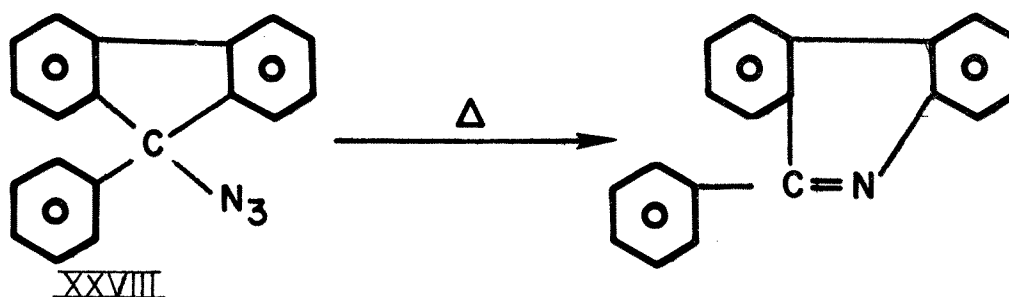
This mechanism would account for the products. Thermolysis of compounds XIII and XIV will give non-rearrangement products occurring by a similar mechanism.

Probably the most important mode of nitrene stabilization is 1, 2-hydrogen migration and 1, 2-alkyl migration. Other less important pathways are aziridine formation, hydrogen abstraction from solvent and insertion in solvent. Table IV lists the pyrolysis products of alkyl azides in the gas phase.<sup>13</sup> For the variety of azides pyrolyzed, 1, 2-migration accounts for most of the product formation, with amine and aziridine formation forming the minor products. This is an indication of the short lifetime of the alkyl nitrenes by the small amount of amine formed by intermolecular hydrogen abstraction which is a very easy reaction.

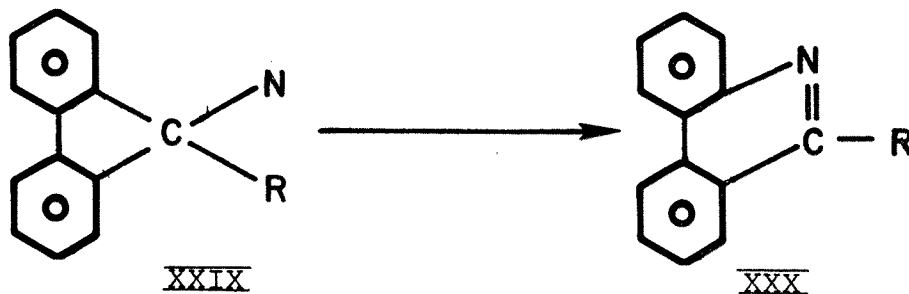
One of the main methods of stabilizing azides is from that of rearrangement. It has been observed that trimethylarylazides<sup>26</sup> and a few alkyl azides rearrange on gas phase pyrolysis as such;



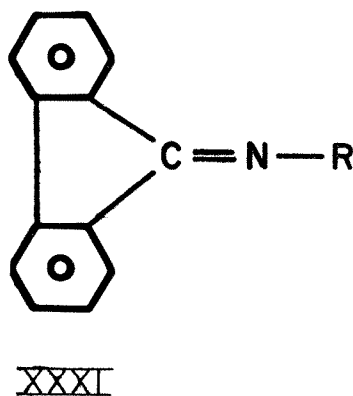
Pyrolysis of XXVIII is an example of thermally induced ring expansion and the ease of this reaction as compared to the reactions of the triarylmethylazide is probably due to relief of strain in the cyclopentyl ring and added resonance due to an extended conjugated system.<sup>27</sup>



Theoretically, the intermediate nitrene formed in XXIX can be stabilized by undergoing two possible types of rearrangement:

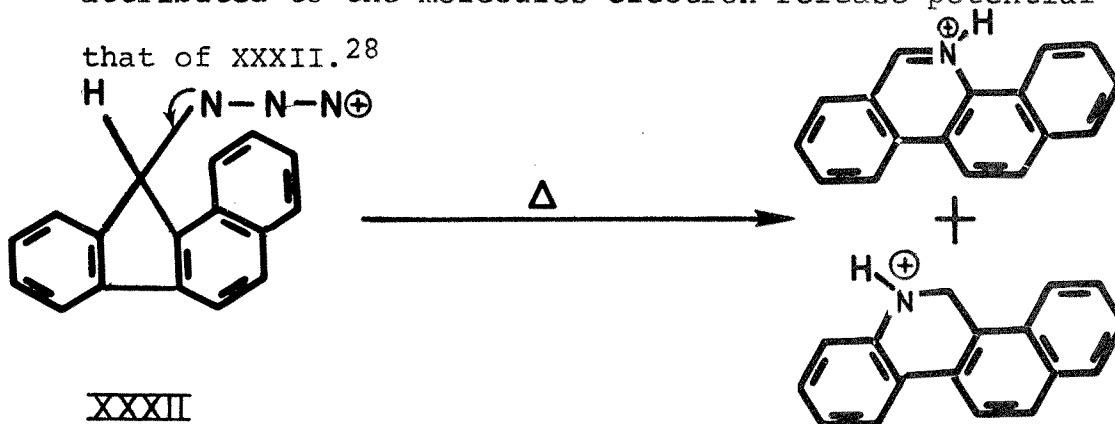


These are, opening of the ring with subsequent reformation to give XXX or migration of R to form the imide XXXI.

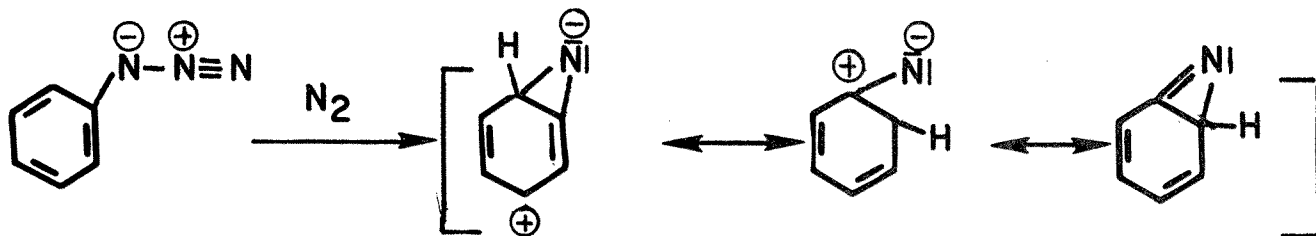


Even when R is more electronegative than the phenylene radical, the rearrangement involves primarily the formation of XXX. Thus, it follows that the strained condition of the five-membered ring is an important factor, if not the most important one, in directing the course of the rearrangement.

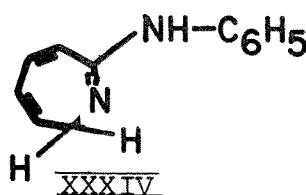
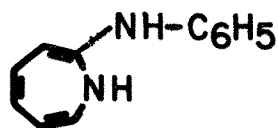
Another example of ring expansion which has been attributed to the molecule's electron release potential was that of XXXII.<sup>28</sup>



An interesting reaction which does not involve rearrangement is the production of an azepine derivative when phenyl azide is heated in an excess of aniline.<sup>29</sup> The nitrene is stabilized by three resonant structures:

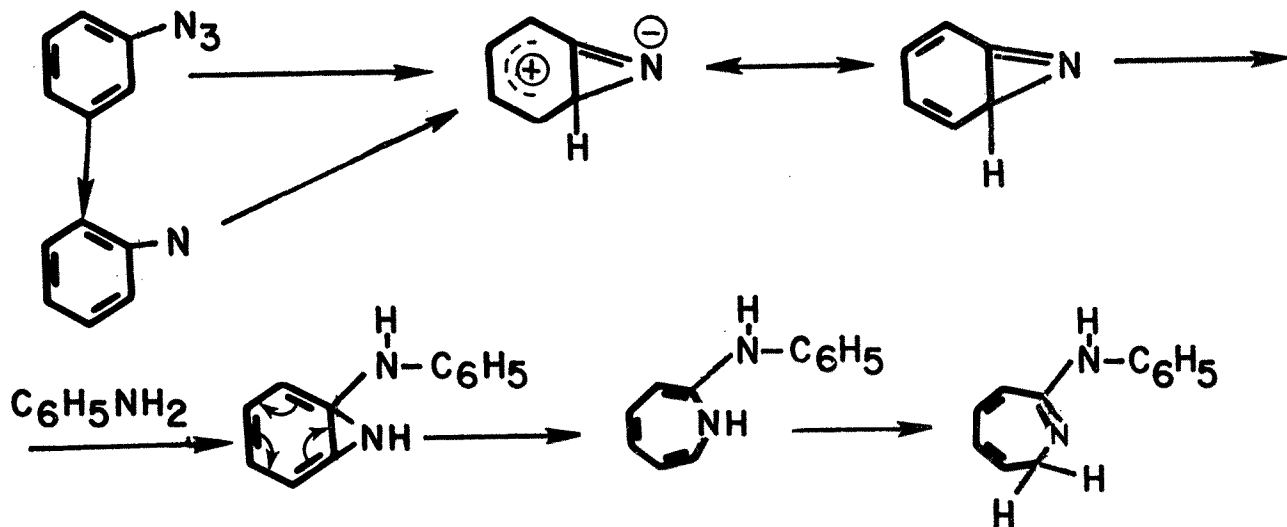


The azide converts to a ring expanded compound XXXIII and XXXIV.



Effects of substituents on the rate was consistent with the formation of a nitrene in the rate determining step.<sup>30</sup>

The mechanism proposed was such:



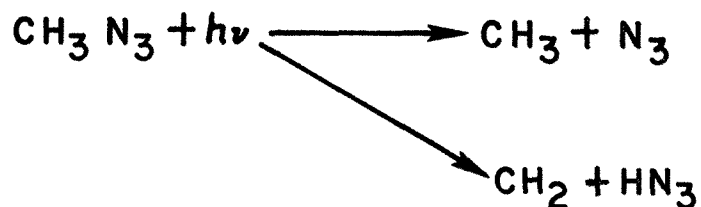
Heating phenyl or other aryl azides in an inert solvent usually results in an amorphous mass, apparently polymeric, together with amines, formed by hydrogen abstraction.<sup>31</sup> A kinetic examination of the thermal decomposition of phenyl, p-methoxyphenyl, and cyclohexyl azides in different media has been accomplished by Walker and Waters.<sup>32</sup> It was shown that free nitrene intermediates were formed. They also show that phenyl azide decomposes on pyrolysis in inert solvents to give azobenzene (small yield), hydrazobenzene and aniline together with small amounts of benzidine. Photolysis of phenyl azide gave no azobenzene but was slowly converted into benzotriazole. The reaction  $2 \ddot{R}N: \rightarrow R - N = N - R$  appears so obvious a route for stabilization of  $RN:$  intermediates that the small yield of azobenzene isolated from both

phenyl and P-methoxy phenyl azide (from pyrolysis) in comparison with the much higher yields of amines ( $\text{RNH}_2$ ) in the inert solvent decalin and ethyl benzoate is significant. Their nitrene intermediates, instead of combining directly with each other, nearly all abstract hydrogen from a solvent molecule or from each other. The hydrazobenzene isolated from the decomposition of phenyl azide is a precursor of azobenzene and colored products produced were allied with complex substances which have been isolated by many workers on homolytic oxidation of aromatic amines.<sup>32</sup>

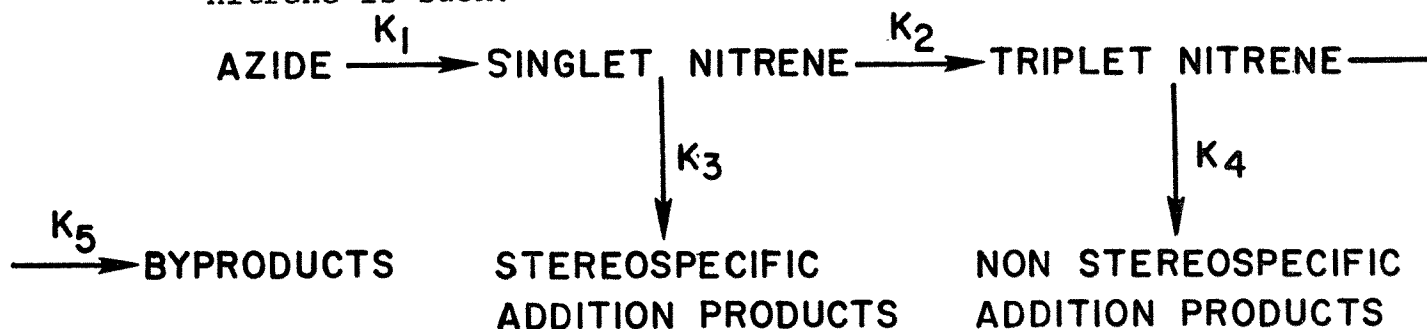
#### Photolysis of Azide Linkage

Photolysis, like thermolysis of azide linkages also eliminates nitrogen to generate a nitrene. Decomposition of alkyl azides is believed to go through a singlet nitrene.

The gas phase photolysis of methyl azide produces methyl nitrene ( $\text{CH}_3\text{N}$ ) +  $\text{N}_2$ .<sup>33</sup> The fact that  $\text{N}_2$  was found to be by far the most prevalent of the gaseous products suggested that the only important primary act was  $\text{CH}_3\text{N}_3 + h\nu \rightarrow \text{CH}_3\text{N} + \text{N}_2$ , so the very small yields of  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{HN}_3$  suggested that neither of these processes is important.



The reaction sequence following production of a singlet nitrene is such:



With aromatic azides, the mechanism of the primary step is slightly different from that of the isolated azide group. Bond dissociation occurs via a hot ground state, by vibrational excitation of a critical stretching made in the azide group.

The efficiency of bond fissure in response to irradiation is determined by the strength of the dissociating bond, by the excess vibrational energy available and by the efficiency of transmission of skeletal vibrations to the side chain. This last factor is thought to be sensitive to the geometry of the molecule and to the symmetry of the electronic transition involved. Upon irradiation, energy is absorbed in the aromatic system as a whole. Decomposition is preceded by a transfer of excitation from the hydrocarbon to the azide group. Excess vibrational energy is transmitted through the molecule until the singlet state is reached. Decomposition may then occur or it may pass over to the triplet state where

decomposition may then occur. All this depends on the mechanistic pathway involved in the reaction.

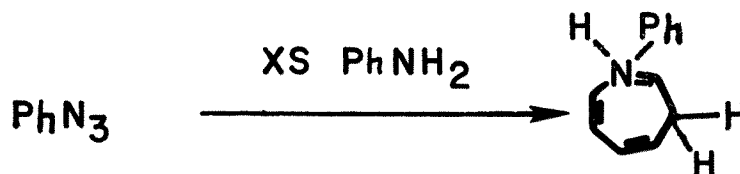
Electron spin resonance experiments upon irradiation at 77°K have shown that the ground state of alkyl, aryl and sulphonyl nitrenes is the triplet.<sup>34</sup> The nature of the products obtained from decomposition of an azide can be used to predict the electronic state of the intermediate nitrene. This was concluded from the investigation of eight azides. These were a) phenyl, b) benzenesulfonyl, c) p-toluenesulfonyl, d) o-trifluoromethylphenyl, e) cyclohexyl, f) styryl, g) ethyl azidoformate and, h) phenyl azidoformate. No resonance was observed for compounds (e) through (h). This was rationalized by noting that any nitrenes formed during irradiation could undergo further reactions less likely to occur for compounds (a) through (d). With compounds (a) through (d), electron paramagnetic resonance was detected and the intensity of the signal from (a) was stable at 77°K for at least 18 hours after irradiation was discontinued. On warming, the signals disappeared. These findings are indicative of a ground state triplet. Wasserman, et al.<sup>35</sup> obtained the first direct physical evidence for primary, secondary and tertiary alkyl nitrenes, R-N: through electron spin resonance. Such species have been postulated as intermediates in the decomposition of alkyl azides.



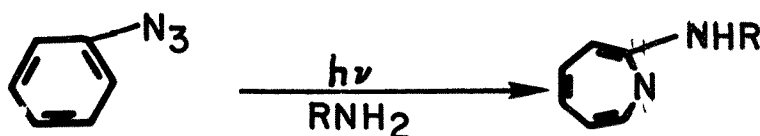
The electron spin resonance of several aromatic nitrenes have been reported<sup>19</sup> and were shown to be ground state triplets with significant delocalization occurring into an adjacent aromatic system. Other evidence for ground state triplet was shown by Moriarity et al.<sup>20</sup> They report the observation of triplet nitrenes by means of E.S.R. in single crystals.

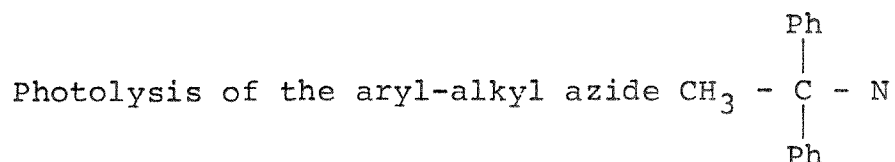
Irradiation of azide group results in the formation of monovalent nitrogen and  $N_2$ . The monovalent nitrogen as in thermolysis is a nitrene. This being extremely reactive has been generally conceded to be in the triplet state in photolysis.

Decomposition of phenyl azides had found that irradiation like pyrolysis in an excess of aniline produces a compound called 2-anilino-3H-azepine.<sup>36</sup>



This does not involve rearrangement but insertion of the nitrene. This is probably the same product that Wolff isolated in 1910 by pyrolysis. The same reaction holds true for irradiation of phenyl azide in alkylamines, giving quite efficient yield of up to 70%.<sup>37,38</sup>

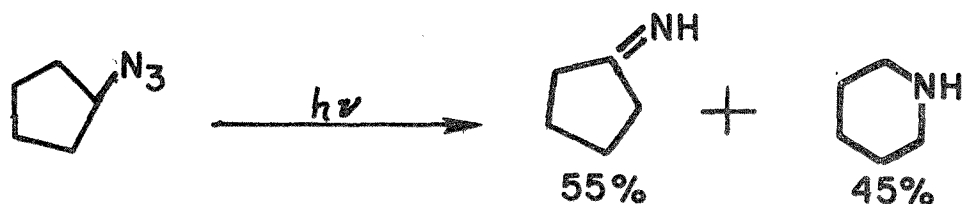




and  $\text{Ar}_3\text{C} - \text{N}_3$  showed that the migratory aptitude of the methyl and phenyl group were almost identical.<sup>39</sup> This lack of selectivity shown in migration aptitudes in triphenyl methylazide photolysis, and formation of triphenylmethylamine in photolysis of triphenylmethyl azide (in the presence of efficient hydrogen donors) support the existence of a discrete nitrene intermediate. The occurrence of a triplet sensitized decomposition showed that a triplet azide, and presumably a triplet nitrene can be involved. Efforts to detect the triplet azide failed. This failure and a high quantum yield indicated that part or all of the direct photolysis may occur via a singlet azide and a singlet nitrene.<sup>36</sup>

Irradiation of phenyl azide can yield a benzotriazole along with other not too well defined reaction products.<sup>40</sup> More generally a self insertion or attack on a solvent leads to azepines and related compounds.

Photolytic rearrangement of an alkyl azide is shown in this reaction:



This nitrene cyclization is probably best regarded as a bond insertion. Bond insertion implies retention of



Irradiation of XXXVIII prepared separately gave only product XLII but no XLI.

### Conclusions

The basic thermal and photolytic reactions of alkyl and aryl azides have been mentioned. It is seen that organic azides are a very distinct species that undergo its own unique reactions. Evidence has been presented suggesting various modes of nitrene stabilization with rearrangements, hydrogen abstraction and insertion as the most important. However, aryl azides were shown to undergo a fourth important method, that of bond reorganization (for example, azepine formation). It is believed that this particular mechanism is significant in the study of azide decomposition and will be the source of further investigations in the future.

BIBLIOGRAPHY

1. Boyer, J. H. and Canter, "Alkyl and Aryl Azides", Chem. Rev., 1954, 54, 1.
2. Lieber and Curtice, J. S., Structure and Reactivity of Organic Azides, Chemistry and Industry, April 2, 1965, 586-591.
3. Pauling, L., "The Nature of the Chemical Bond," Third Edition, Cornell University Press, Ithica, New York, 1960.
4. Roberts, J. D., "Understanding the Structure of Azides and Diazoazides from a Study of Molecular Orbital Theory," Chem. Ber., 1961, 94, 273.
5. Huisgen, R., "1, 3-Dipolar Cycloadditions", Proc. Chem. Soc., 1961, 357.
6. Lieber, E. and Dodd, J. G., "The Nature of the Bent State of the Azide Group," Proc. 10th Brg. Contractors Conference, 24-26, October, 1961, Basic Research Group, Fort Belvoir.
7. Hall, J. H., Hill, J. W., Fargher, J. M., "Evidence for the Involvement of Triplet Phenyl Nitrene in Inter-molecular C-H Insertion." J. Am. Chem. Soc. 90, 5313 (1968).
8. Ramsperger, H. C., "The Thermal Decomposition of Hydrazoic Acid and Methyl Azide", J. Am. Chem. Soc. 51, 2134 (1929).
9. Leersmakers, J. A., "The Thermal Decomposition of Methylazides, A Homogeneous Unimolecular Reaction," J. Am. Chem. Soc. 55, 3098 (1933).
10. Senior, J. K., "Molecular Rearrangement of Triarylmethyl Azides", J. Am. Chem. Soc. 38, 2718 (1916).
11. Curtius, et al., "Benzylamines," J. Prakt. Chem., 63, 428 (1901) or Ber., 35, 3229 (1902).
12. Stieglitz, J. and Leech, P., "The Molecular Rearrangement of Triarylmethylhydroxyamines and the Beckman Rearrangement of Keto Ximes", J. Amer. Chem. Soc., 36 272 (1914).

13. Pritzkow, W. and Timm, "Gas Phase Pyrolysis of Alkyl Azides", J. Prakt. Chem: 32, 178 (1966).
14. Patai, S., Chemistry of Azide Group, New York, 251-252.
15. Coffin, B. and Robbins, R. F., "The Decomposition of Some Ortho-substituted Azido - or Azido Methyl-biphenyls. J. Chem., Soc. 1252 (1965).
16. Wolff, L., Ann. Chem., 394, 59 (1912).
17. Huisgen, R., Vossius, D., and Appl, M., "The Thermolysis of Phenyl Azide in Primary Amines", Chem. Ber. 91, 1 (1958).
18. Krbechek, L. and Takimoto, H., "The Thermal Decomposition of O-Azidodiphenylmethane Leading to Azepino [2, 1-a]-11H-Indole" J. Org. Chem. 33, 4286 (1968).
19. Smolingsky, G., Yager, W. A., "EPR of Diphenylmethylene, a Ground State Triplet", J. Am. Chem. Soc. 84, 3213 (1962).
20. Moriarity, R. M., Rohman, M., and King, R. J., "Organic Nitrenes in Single Crystals. Observation of Hyperfine Structure in the E.S.R." 88, 842 (1966).
21. Breslow, D. S., Sloan, M. F., Newburg, N. R., and Renfrow, W. B., "Thermal Reactions of Sulfonyl Azides", J. Am. Chem. Soc. 91, 2273, (1969).
22. Breslow, D. S., and Edwards, E. I., "The Effect of Additives on the Reactions of Ethyl Azidoformate with Cyclohexane", Tetrahedron Letters, 2123, 1967.
23. Hall, J. H., Hill, J. W., Tsai, H., "Insertion Reactions of Aryl Nitrenes", Tetrahedron Letters, 2211, 1965.
24. Smolinsky, G. and Feuer, B. I., "Nitrene Insertion into a C-H Bond at an Asymmetric Carbon Atom with Retention of Optical Activity: Thermal Generated Nitrenes", J. Am. Chem. Soc., 86, 3085, (1964).
25. Lwowski, W., "Nitrenes and the Decomposition of Carbonylazides", Angew Chem. Ed., Engl. 6, 897, (1967).
26. Hantzsch, A. and Vogt, A., Ann. Chem., 314, 261, (1901).

27. Pink, L. A., and Hilbert, H. E., "Method for the Synthesis of Phenanthridine Derivatives by Stieglitz Rearrangement", J. Am. Chem. Soc., 59, 8 (1937).
28. Arcus, C. L., Marks, R. E., and Coombs, M. M., "Reactions of Organic Azides. Ring Expansion via Azides", J. Chem. Soc. 4064 (1957).
29. Huisgen, R., Vossius, D. and Appl, M., "Chemistry of Ring Closure of Phenyl Azides in Aniline", Chem. Ber., 91, 12 (1958).
30. Appl, M. and Huisgen, R., "Thermolysis of Arylazides in Amines", Chem. Ber. 92, 2961, 1959.
31. Patai, Saul, Chemistry of Azide Group, New York 425.
32. Walker, P. and Waters, W. A., "Pyrolysis of Organic Azides, A Mechanistic Study", J. Chem. Soc. 1632 (1962).
33. Currie, C. L. and B. Deb. Darwent, "The Photochemical Decomposition of Methyl Azide", Can. J. Chem., 40, 896 (1962).
34. Smolinsky, G., Wasserman, E., Yager, W. A., "The E.P.R. of Ground State Triplet Nitrenes," J. Am. Chem. Soc., 84, 3220, 1962.
35. Wasserman, E. Smolinsky, G. and Yager, W. A., "Electron Spin Resonance of Alkyl Nitrenes", J. Am. Chem. Soc. 86, 3166 (1964).
36. Patai, S., "Chemistry of Azide Group", New York, pg. 495.
37. Sundberg, R., et al., "Photolysis of Ortho-Substituted Aryl Azides in Diethyl Amine", J. Am. Chem. Soc., 94, 513, (1972).
38. Sundberg, R., et al., "Reaction of Aryl Nitrene Bond Reorganization in O-Biphenylnitrene and Phenyl Nitrene", Tetrahedron Letters, 2715 (1970).
39. Lewis, F. O. and Saunders, W. H., "The Intermediates in Direct Photolysis of Alkyl Azides", J. Am. Chem. Soc. 90, 7031 (1968).
40. Horner, L., Christman, A. and Gross, A., "Formation and Chemical Properties of Photolytically Produced Arylnitrenes," Chem. Ber. 96, 399 (1963).

41. Barton, D. R. and Morgan, L. R., "Photochemical Transformations. The Photolysis of Azides," J. Chem. Soc., 622 (1962).
42. Moriarity, R. M., Kliegmann, J. M., and Shovlin, C., "The Photochemical Decomposition of Geminal Diazides", "The Solution Photolysis of Benzophenone Diazide", J. Am. Chem. Soc. 89, 5958 (1967).