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DETERMINATION OF THE ELECTRONIC STATE OF ARYL NITRENES IN AN INTRAMOLECULAR C-H INSERTION REACTION

BY

ALI MOHAMMAD KHONSARI

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

MASTER OF SCIENCE IN CHEMISTRY

AT

NEWARK COLLEGE OF ENGINEERING

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Newark, New Jersey

1970

ABSTRACT

β,γ-Dideuteriopropylbenzene was obtained in 84% yield from deuteration of allylbenzene. Nitration of this compound resulted in o-nitro (β,γ-dideuteriopropyl)-benzene. Reduction of this compound gave o-(β,γ-dideuterio-propyl)aniline. o-(β,γ-Dideuteriopropyl)phenyl azide was prepared by dizotization of the aniline compound, followed by treatment with sodium azide.

Decomposition of the azide in isooctane solution by photolysis at room temperature gave no trace of deuterio-2-methylindoline (intramolecular C-H insertion product).

Photolysis of the azide at the reflux temperature of the solvent (99°C) resulted in the formation of deuterated-2-methylindoline as the major product (40%) yield. The reaction is presumed to proceed through an aryl nitrene intermediate. Analysis of the nuclear magnetic resonance spectrum of this compound indicates that the nitrene shows no preference for insertion into the C-H bond versus the C-D bond (i.e. no kinetic isotope effect) ($k_H/k_D = 1$).

When the elevated temperature photolysis is carried out in the presence of a triplet photosensitizer (xanthen-9-one) the yield of 2-methylindoline is dramatically decreased.

Based on these results, arguments are presented which suggest that intramolecular C-H insertion reactions of an aryl nitrene proceeds via the intermediacy of a singlet rather than a triplet aryl nitrene.

APPROVAL OF THESIS

DETERMINATION OF THE ELECTRONIC STATE OF ARYL NITRENES IN AN INTRAMOLECULAR C-H INSERTION REACTION

BY

ALI MOHAMMAD KHONSARI

FOR

DEPARTMENT OF CHEMISTRY

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: _____

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NEWARK, NEW JERSEY

MAY, 1970

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The author would like to express his sincere gratitude and appreciation to Dr. Richard B. Trattner, Thesis Advisor, for his inspiration and guidance throughout all phases of this research project.

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INTRODUCTION

Aryl azides in general decompose thermally or photochemically by the loss of molecular nitrogen to form an intermediate containing a monovalant nitrogen with a sextet of electrons.

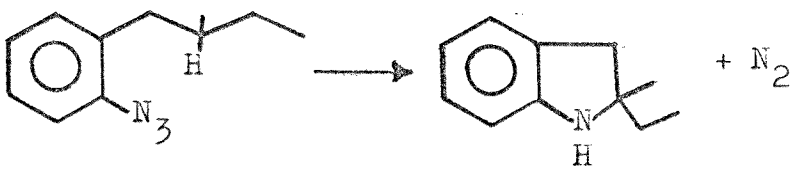
$$Ar\text{-}N_3 \xrightarrow{\Delta} Ar\text{-}\ddot{\underline{N}} + N_2$$

These intermediates are known as nitrenes. They can exist in either the singlet state in which all the electrons are spin paired, Ar-$\ddot{\underline{N}}$, or in the triplet state in which two electrons are unpaired, Ar-$\dot{N}\!:$.

An important reaction of aryl nitrene is the insertion into the C-H bond. If the decomposition is carried out in a hydrocarbon solvent, intermolecular C-H insertion products are obtained:

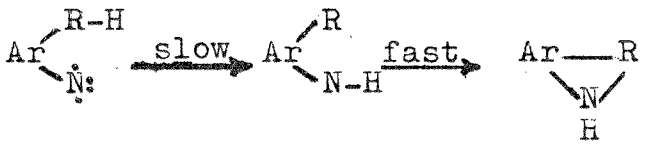
$$Ar\text{-}N_3 \xrightarrow[R\text{-}H]{} Ar\text{-}\overset{H}{\underset{\cdot\cdot}{N}}\text{-}R + N_2$$

If the aromatic azide has an ortho-alkyl group present, intramolecular C-H insertion products can be found.

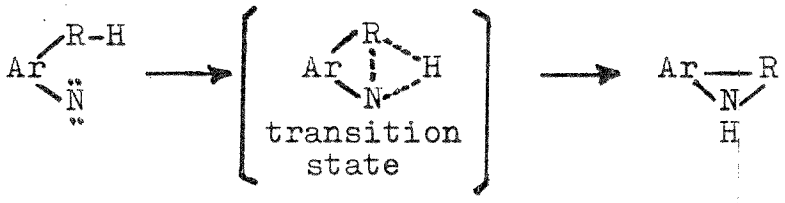


This work is concerned primarily with the intramolecular insertion of aryl nitrene into the C-H bond in the photolysis of an ortho-alkylphenyl azide.

There are two reasonable mechanisms for the intramolecular insertion of nitrene into the C-H bond. If the nitrene is in the triplet state, an insertion reaction would be expected to proceed via a free radical mechanism:



If the nitrene is in the singlet state, it could insert into the C-H bond via a concerted reaction involving a three-centered mechanism.



The general goal of this investigation was the determination of the electronic state of aryl nitrene which is responsible for the intramolecular C-H insertion product by the use of kinetic isotope effect. It

was thought that if triplet aryl nitrene was responsible for the intramolecular insertion product, a relatively large deuterium isotope effect would be observed when insertion into a C-H bond was compared with insertion into a C-D bond. On the other hand, a small kinetic isotope effect (or none at all) would be expected if the aryl nitrene is in the singlet state when it inserts intramolecularly into the C-H bond.

THEORY AND BACKGROUND

I. Nitrenes:

Species containing a monovalant nitrogen atom, i.e., an electron deficient nitrogen atom having a sextet of electrons in its outer shell, have been formed as intermediates in a large number of reactions. Such intermediates have the general formula R-N, where R may be a hydrogen, a halogen, an alkyl, an aryl, an acyl, a sulfonyl, etc., and are isoelectronic with carbenes. These species may theoretically either exist in the triplet diradical state R-$\dot{N}$: with unpaired electrons having the same spin direction or in the singlet state, R-$\ddot{N}$ wherein the electrons are paired.

A variety of names are recommended by various authors in the literature: nitrenes[1,25], azenes[24,26], imine radicals[10,21], azacarbene[14] and others. The term "imidogen", or imidointermediates has been used in past years for N-H by chemical abstacts. Currently, the term "nitrene" is used to describe R-N.

The formation of a nitrene intermediate was first postulated by Stieglitz and Brown in 1921 to account for the mechanism of the Hofmann, Curtius, Lossen and Beckman rearrangements.[32] The intermediacy of NH in the

Raschig hydrazine synthesis from chloramine and ammonia was suggested by Raschig in 1924.[20] It was proposed that $[NHCl]^-$ was formed initially which could either give NH or attack ammonia directly.[3]

$$OH^- + NH_2Cl \longrightarrow [NHCl]^-$$

$$[NHCl]^- \longrightarrow NH + Cl^-$$

$$NH + NH_3 \longrightarrow N_2H_4$$

$$\text{or } [NHCl]^- + NH_3 \longrightarrow N_2H_4 + Cl^-$$

Decomposition of hydrazoic acid, which is analogous to the production of carbene from diazomethane, was used to generate nitrene in 1928.[5]

$$HN_3 \xrightarrow[\text{or } h\nu]{\Delta} N_2 + (NH) \xrightarrow{H_2O} NH_2OH$$

The generation of free NH by a high temperature (2000°C) pyrolysis or flash photolysis of ammonia was shown spectroscopically.[8]

$$NH_3 \xrightarrow[\text{or } h\nu]{2000^\circ C} NH + H_2 \text{ (or } NH + 2H \text{)}$$

The fluoro, chloro, and bromo nitrenes have been prepared by the photolysis of corresponding azide in solid argon or nitrogen at 4.2°K and their appearance observed spectoscopically.[17]

$$X\text{-}N_3 \xrightarrow[4.2^{\circ}K,\ Ar]{} X\text{-}N + N_2 \quad (X = F, Cl, Br)$$

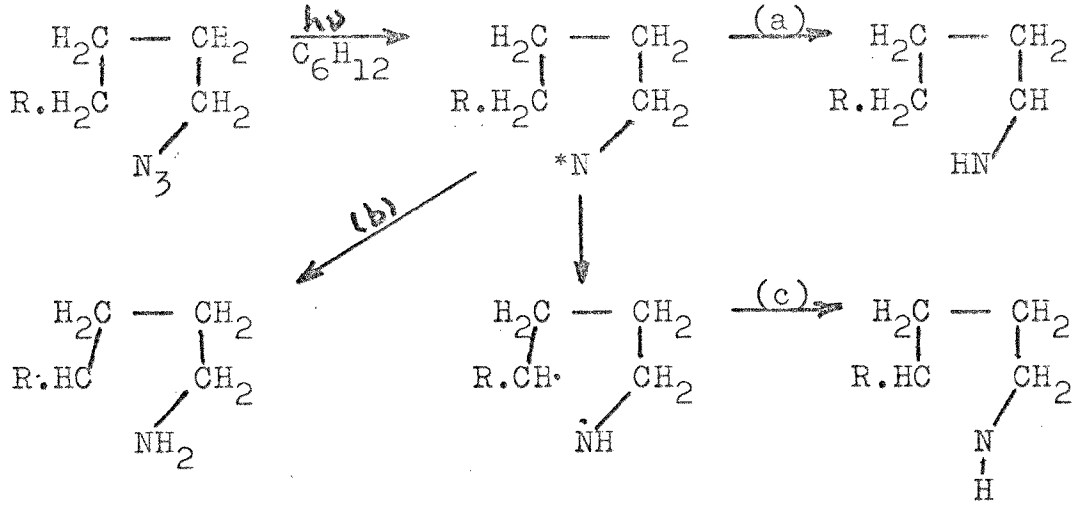
Prolonged photolysis of more complex azides containing a hydrogen at the 5-position in different solvents led to the conclusion that " activated " nitrenes are formed which can stabilize themselves in three ways:[4]

a) isomerization to imine

b) hydrogen abstraction to give amine

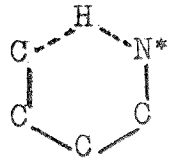
c) 1,5- hydrogen abstraction followed by cyclization to pyrolidines

Also, insertion into the C-H bonds and additions to the double bonds were observed.[4]

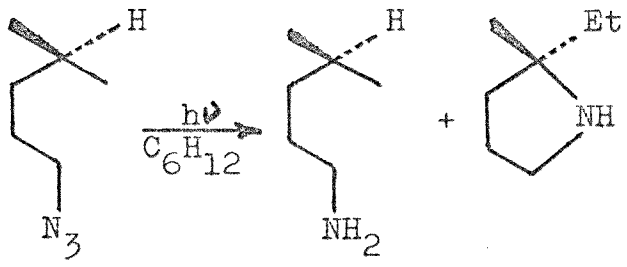


It was suggested that an important conformational requirement has to be met if cyclization of the activated

nitrene is to proceed smoothly either by the preferred conformation of the starting material or by a conformation which is populated as a result of thermal equilibrium, that is, a " six-membered " transition state:

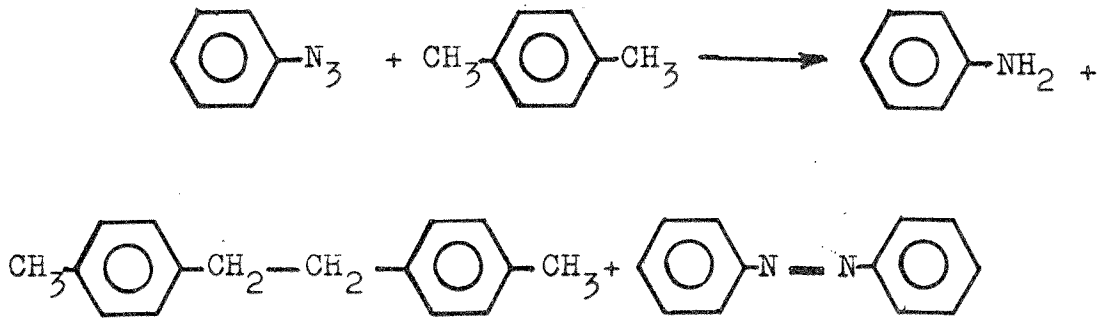


To study whether cyclization involved a bond-insertion mechanism or a hydrogen-abstraction pathway (c), photolysis was carried out on (+) -4-methylhexyl azide (I) in cyclohexane. (+) -4-Methylcyclohexylamine(II) (35%), and racemic 2-ethyl-2-methylpyrolidine (III) (16%) were said to have been obtained, presumably excluding a bond insertion mechanism in which retention of configuration was expected.[4]



However, a number of attempts to repeat this work have failed.

The thermal decomposition of an aromatic azide, phenyl azide, in benzene was first studied by Bertho who ran the reaction at 150°-160°C for 7-8 hours under pressure and found azobenzene as the main product together with a small amount of aniline (azobenzene + amiline = 30%). With p-xylene as the solvent, a much larger amount of aniline was obtained (43%), due to hydrogen abstraction from the side chain as well as 1,2 -di-p-tolylethane(I)(5%) and a small amount of azobenzene.[7]

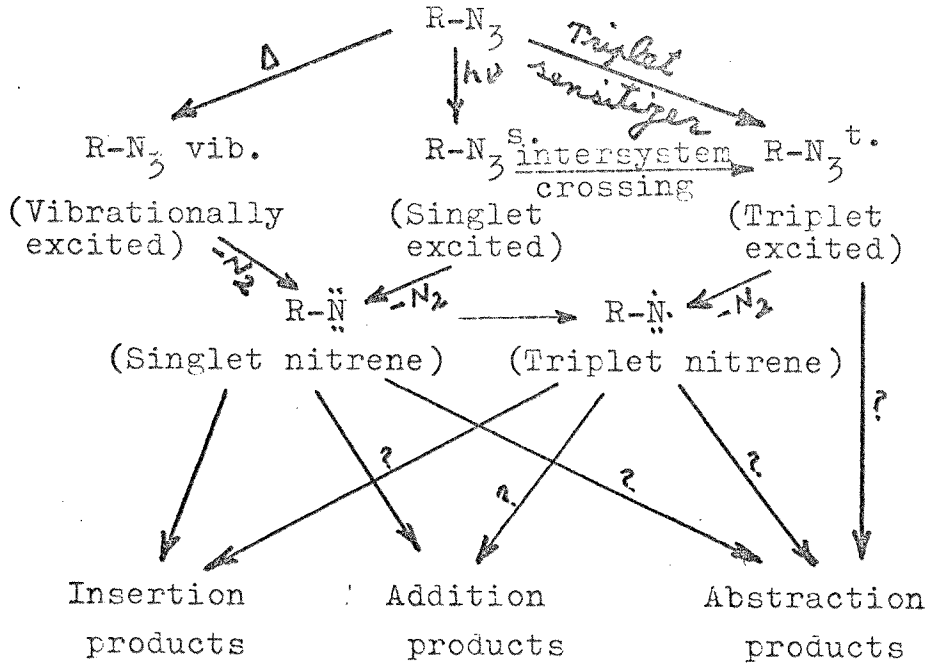


(I)

The electron spin resonance spectra of aromatic nitrene intermediates generated at 77°K in a fluoroluble matrix by U.V. irradiation of the corresponding azide were detected and assigned the triplet ground state for the $C_6H_5-\dot{N}:$, $o-CF_3C_6H_4-\dot{N}:$, $C_6H_5SO_2-\dot{N}:$, and $p-CH_3C_6H_4SO_2\dot{N}:$.

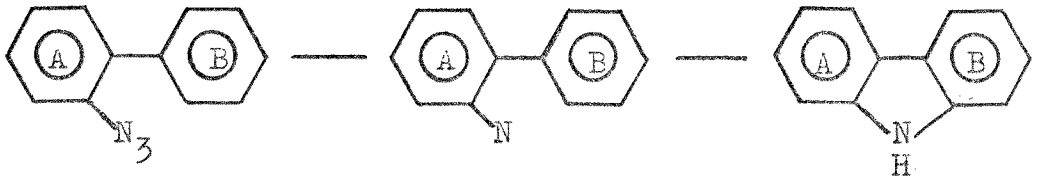
No resonance was observed for $C_6H_{11}N$, $C_6H_5CH{=}CHN$, C_2H_5OCON, and C_6H_5OCON, probably because they react further too quickly to permit a sufficient concentration to be detected. The signal for C_6H_5-N was stable at 77°K for 18 hours after irradiation was discontinued, but disappeared on warming.

The evidence presented thus far indicates that aromatic nitrene can exhibit the properties of either singlet or triplet. The ground state for nitrene is expected to be the triplet.[2] Also, if a singlet nitrene is formed in the primary step, but finds no suitable substrate to react with, it might decay to the triplet state.



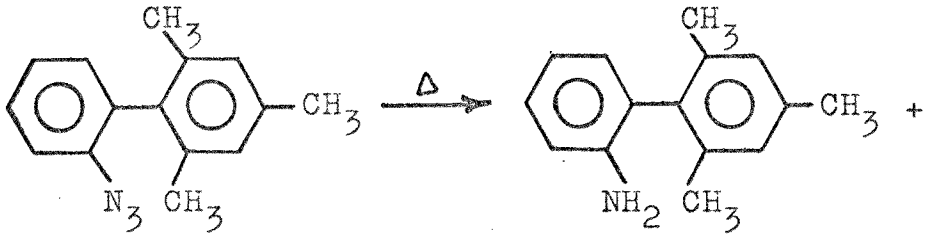
II. Insertion on Reaction of Nitrenes:

The intermediacy of a nitrene in the decomposition of o-azidobiaryls to give carbazole was suggested in 1957 by Smith and co-workers.[23]

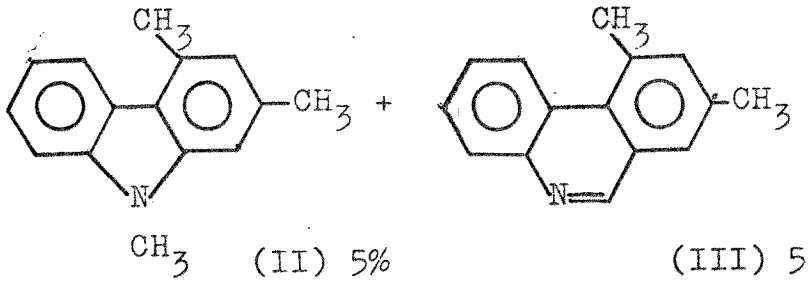


They found no significant difference in the rate of decomposition of these azides when different substituents like hydroxyl or methoxyl groups were placed in the (B) ring, indicating that decomposition was probably not a concerted reaction.

Thermal decomposition of 2, 4, 6 - trimethyl 2-azidobiphenyl at 230°C in hexadecane by Smolinsky gave three products, identical to primary amine (I) carbazole (II) and phenanthridine (III).[25]



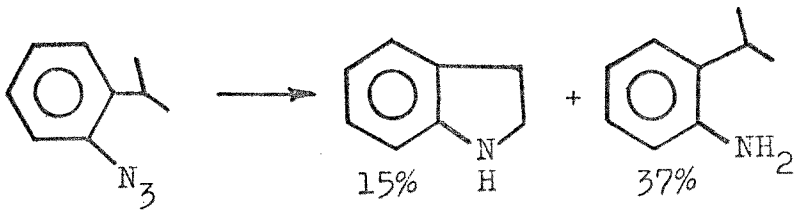
(I) 30%



(II) 5% (III) 50%

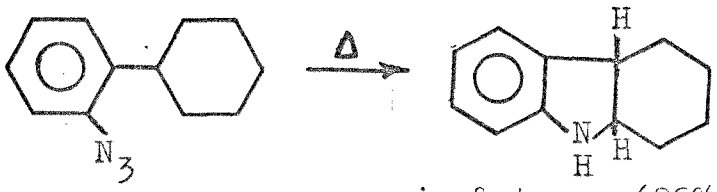
The results were raticnalized by a mechanism involving the loss of nitrogen to give a nitrene, which could abstract hydrogen to form primary amine, insert in a C-C bond to form carbazole and insert intramolecularly into a C-H bond to form a dihydrophenantridine.

Smolinsky investigated other intramolecular C-H insertion reactions in the thermal decomposition of ortho-alkylazidobenzene in solution.[26] Decomposition of o-azidocumene in diphenylether formed 3-methylindoline and o-aminocumene.



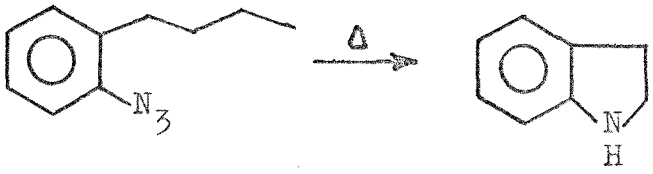
15% 37%

Also, o-azidophenylcyclohexane gave equal amounts of cis-and trans- hexahydrocarbazole as the only isolable compounds.

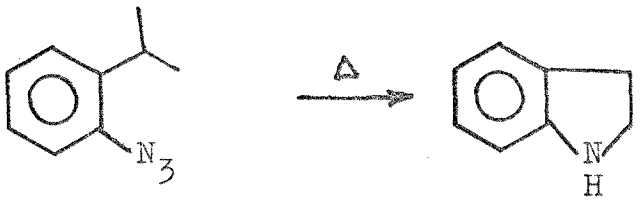


cis & trans (86%)

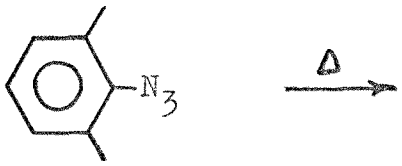
To reduce the opportunity of reaction of nitrene with solvents, ortho-substituted phenylazides were thermolyzed in the vapor phase.[27] It was found that only alkyl groups with β-hydrogens tended to form indolines.



43% yield



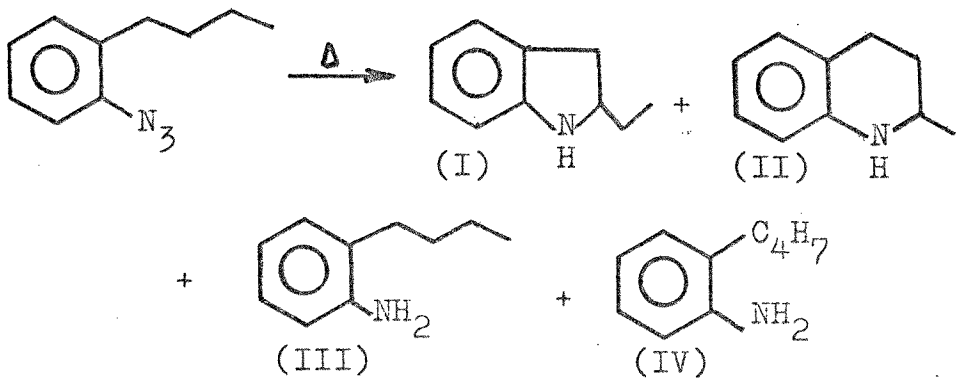
55% yield



Polymer

72% yield

Smolinsky found different results in the pyrolysis of o-butylphenylbutyl azide in the solution and vapor phase.[27,29]

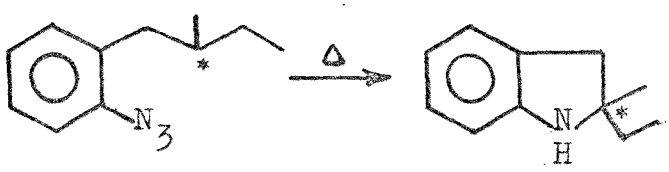


	I	II	III	IV
vapor phase%	43	11	1	46
liquid phase%	37	10	29	25

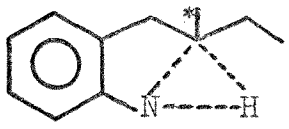
In both cases, yields of indoline and tetrahydroquinoline (results of insertion reactions) are almost the same. In the vapor phase, because of absence of any solvents, yield of o-butylaniline is very low. Intramolecular abstraction of hydrogen results in the formation of the o-butenylaniline. In the liquid phase, the hydrogen abstraction is both inter- and intramolecular.

In an effort to identify the electronic state of the nitrene intermediate in intramolecular insertion reactions, Smolinsky and Feuer studied the decomposition of optically active o-alkylphenyl azides.[28]

Optically active 1-azido-2-(2-methylbutyl)benzene gave optically active 2-ethyl, 2-methylindoline upon pyrolysis in the gas phase or in diphenyl ether as solvent.



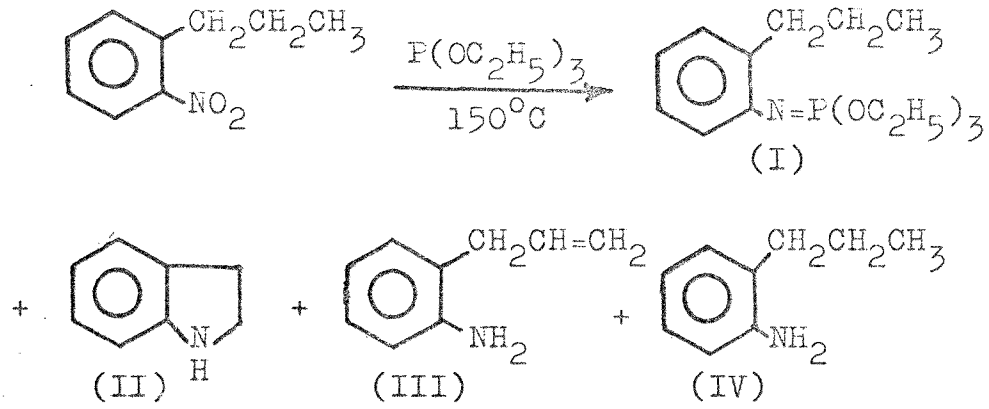
It was assumed that there was 100% retention in the gas phase because the rotation of the product was close to rotation of pure optically active 2-ethyl, 2-methylindoline. The solution pyrolysis resulted in a product with 65% retention of configuration. These studies provided the first examples of retention of optical activity in the insertions of the nitrene into a C-H bond at an asymmetric carbon atom. Based on this result, they proposed that a singlet nitrene is responsible for the intramolecular C-H insertion reaction via a three-centered transition state.



A biradical mechanism invelving the intermediacy of triplet nitrene in which radical recombination occur

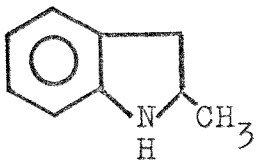
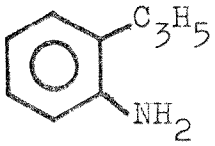
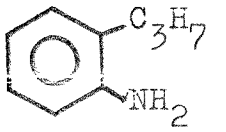
faster than rotation about C-C bond was considered by them to be less likely.

Intermediacy of aryl nitrenes have been postulated in the deoxygenation of aromatic nitro-and nitroso compounds by the trivalent derivatives of phosphorous.[2] Deoxygenation of nitropropylbenzene in refluxing (150°C) triethylphosphite by Sundberg resulted in triethyl N-arylphosphorimidate (I) as major product, 2-methylindoline (II), insertion product, (6-7%), o-allylaniline (III), (6-6.5%) and o-propylaniline (IV), (2-4%).[33]

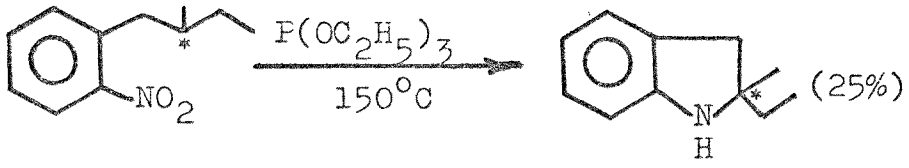


In the following table the composition of the amine mixtures formed by deoxygenation of o-nitropropylbenzene is compared with the composition of the amine fraction obtained by vapor phase and solution (tri-

ethylphosphite) pyrolysis of o-azidopropylbenzene:

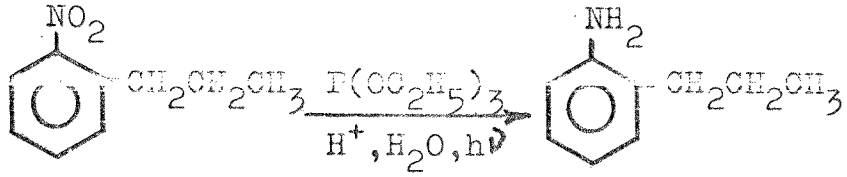
Compound	Deoxygenation	Azide Pyrolysis	
		Solution	Vapor
	43	38	51
	39	34	49
	18	28	trace

Smolinsky and Feuer deoxygenated in refluxing triethyl phosphite (150°C) optically active 2-nitro-1-(2-methylbutyl)benzene and got 2- ethyl-2-methyl-indoline in 25% yield with 50% retention of configuration.[30]



Since the same products in about the same proportions can be produced in two different reactions, they concluded that both, deoxygenation of aromatic nitro compounds and pyrolysis of aromatic azides must proceed through a common nitrene intermediate.

Deoxygenation of o-nitropropylbenzene by photolysis was carried out by Sundberg and co-workers at 30°C and resulted in o-propylaniline (14%) and a lesser amount of a rearrangement product.[34]



No traces of the C-H insertion product (2-methylindoline) or the intramolecular hydrogen abstraction product (o-allylaniline) were found under reaction conditions. Since no significant amounts of insertion products are formed in the deoxygenation at low temperatures, they suggested that the activation energies for C-H insertion and other irreversible transformations of o-propylphenyl nitrene are such that the C-H insertion reaction is competitive at 150°C but not at 30°C and below.

Hall, Hill and Fargher studied the thermal decomposition of phenyl azide in aliphatic hydrocarbons and obtained varying yields of aniline (I), alkylaniline (II), azobenzene (III) and polymer.[9,11]

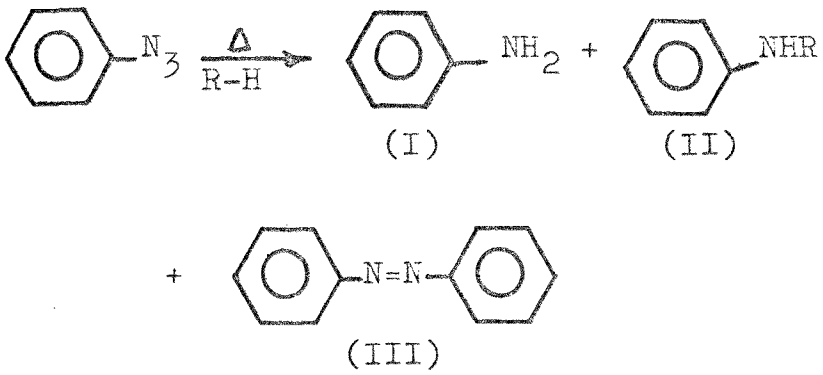


Table (I)

Insertion Preferences of Phenyl Nitrene

Solvent	Type of C-H Bond			
	3°	2°	1°	3°/2°
Pentane	-	26	1	-
Isopentane	97	21	1	4.6
Butane	-	13	1	-
Isobutane	58	-	1	-
Propane	-	25	1	-

First they adopted Smolinsky and Feuer's hypothesis that the N-alkylaniline was formed by the intermolecu-

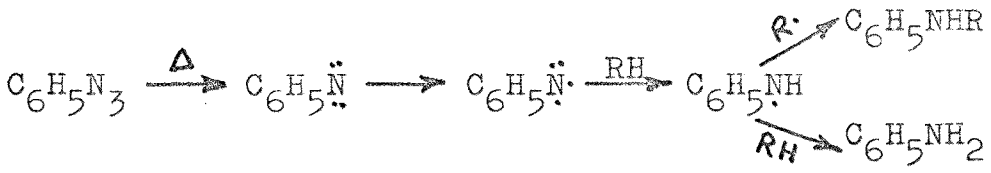
lar insertion of the singlet nitrene into the hydrocarbon C-H bonds. To test this hypothesis they decomposed substitued phenyl azides in mixtures of cyclohexane and neopentane at 160°C. As the solvent composition changed from pure cyclohexane to 25% cyclohexane- 75% neopentane, the yields of the products changed sharply but the ratio of the aniline to N-alkylaniline remained constant at 4. From this result together with the fact that insertion into secondary C-H bonds of cyclohexane is much faster that the primary C-H bonds of neopentane, they decided that their hypothesis was incorrect for, if insertion product was formed by the singlet nitrene, addition of an inert solvent, neopentane, should convert some of the singlet to triplet and the amount of aniline should have increased.[11] They also found that when various meta- and para-substituted phenyl azides were decomposed in n-butane and iso-butane, the ratio of aniline: N-alkylaniline was a constant dependent only on the substituent and not on the hydrocarbon used. (Table II)

Table (II)

Yields of Compounds From Substituted Phenyl Azide Decomposition.[11]

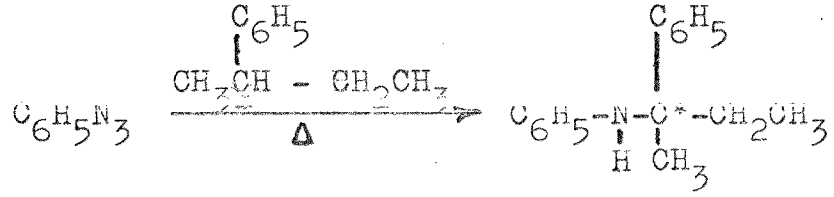
Substituted Phenyl Azide	Solvent	Amine%	N-Alkyl amine%	Aniline / N-Alkyl-aniline
H	Butane	36	5.6	6.4
	Isobutane	17	2.6	6.4
p-methyl	Butane	16	1.4	10
	Isobutane	21	2.1	9.9
p-chloro	Butane	12	0.2	77
	Isobutane	5.9	0.1	77
m-methyl	Butane	25	1.8	14
	Isobutane	31	2.3	14

The constancy of aniline: N-alkylaniline ratio led to the conclusion that both of these products were being formed from the same intermediate, the anilino radical.



With the stepwise process indicated, a large hydrogen isotope effect should be observable. To verify this,

phenyl azide was decomposed in 2-methylpropane and in 2-methyl 2-deuteriopropane. The ratio of insertion into primary versus tertiary C-H bond was found to be 1:88 for 2-methylpropane and 1:21 for 2-methyl-2-deuteriopropane. This result shows an isotope effect k_H/k_D of 4.1 which indicates a removal of a hydrogen prior to the product forming step. The value is too large to be accounted for by a concerted insertion of singlet phenylnitrene into the C-H bond. Also, phenyl azide was decomposed in optically active 2-phenylbutane.



Comparison of the 2-anilino-2-phenylbutane formed with the optically pure material showed that the insertion had proceeded with a maximum of 40% net retention of configuration, i.e., 30% of the radicals had inverted. If the mechanism involved a direct insertion of a singlet nitrene into the C-H bond, the conformation about an asymmetric carbon would be expected to remain uneffected. Based on the aforementioned evidence therefore, Hall and co-workers concluded that intermolecular C-H insertion proceeds via a triplet aromatic nitrene.

Contrasted with this finding, is Smolinsky and Feuers' conclusion that intramolecular C-H insertion occurs through a singlet aromatic nitrene (vide infra).

III. Kinetic Isotope Effect:[15,16]

The vibrational and rotational energy levels of a system depend upon the atomic masses. Atoms in a molecule are in motion and the molecule is under normal vibrations even when it is in lowest energy state. This vibrational energy, which always exists is called the zero point energy. Because the atoms within a molecule are vibrating, replacing one atom by its' isotope changes the vibrational energy levels of the molecule. Since they affect the energy of the systems, changes in the vibrational energy affect the rates of reaction. As the mass of the isotope increases, the vibrational frequency and consequently, the vibrational energy of the system decreases. Therefore, D-C, D-O, D-N bonds, etc., have lower zero point energies that the corresponding H-C, H-O, H-N bonds, etc., in the same vibrational level. As a result, complete dissociation of a deuterium bond requires more energy than that for a corresponding hydrogen bond in the same environment.

Isotope effect provides a very valuable tool

for determination of mechanisms of reactions. For example, in the bromination of acetone:

$$CH_3COCH_3 + Br_2 \longrightarrow CH_3COCH_2Br + HBr$$

The fact that the rate is independent of bromine concentration led to the postulate that the rate determining step was tautomerization of acetone.

$$CH_3COCH_3 \underset{\text{slow}}{\rightleftharpoons} CH_3\text{-}\underset{\underset{OH}{|}}{C}\text{=}CH_2$$

The rate determining tautomerization step involves cleavage of a C-H bond. Thus, there should be a substantial isotope effect if deuterated acetone is used. In fact, the deuterium isotope effect was found to be about 7. (i.e. the $^{k}H/k_D = 7$).

If a reaction is a several step process, the magnitude of the observed kinetic isotope effect will naturally depend upon the importance of the step involving bond breakage to hydrogen or deuterium. When this bond breakage is not the rate determining step, smaller values for the kinetic isotope effect, or no kinetic isotope effect will be observed.

Deterium isctope effects range from 1 (no isotope effect at all) to 9. Tritium isotope effect

is numerically larger. Isotope effects have also been observed with other elements but, they are much smaller, about 1.02 - 1.10.

The effects associated with reactions in which hydrogen or deuterium bonds are broken, are called primary isotope effects. The replacement of hydrogen by deuterium also affects the rate of reactions where these bonds are not being broken. These smaller effects are called secondary isotope effects.

Isotope effects have also been used in the determination of the electronic state of aryl nitrene in its insertion into the C-H bond of hydrocarbon solvent (vide infra). [9,11]

IV. Sensitization: The Transfer of Excitation Energy [13,19]

The absorption of light by molecules or atoms, which normally exist in a state of minimum electronic energy or ground state, raises them to a less stable state of higher electronic energy or excited state. Excited species can lose their excess energy by emission of radiation and/or the loss to surroundings through collision. The excitation energy can also be utilized to excite another species electronically in-

volving decay of the first excited-species to the ground state. This phenomena is called energy transfer or sensitization. For such a transfer to occur, the excitation energy of the acceptor should not exceed that of the donor molecule.

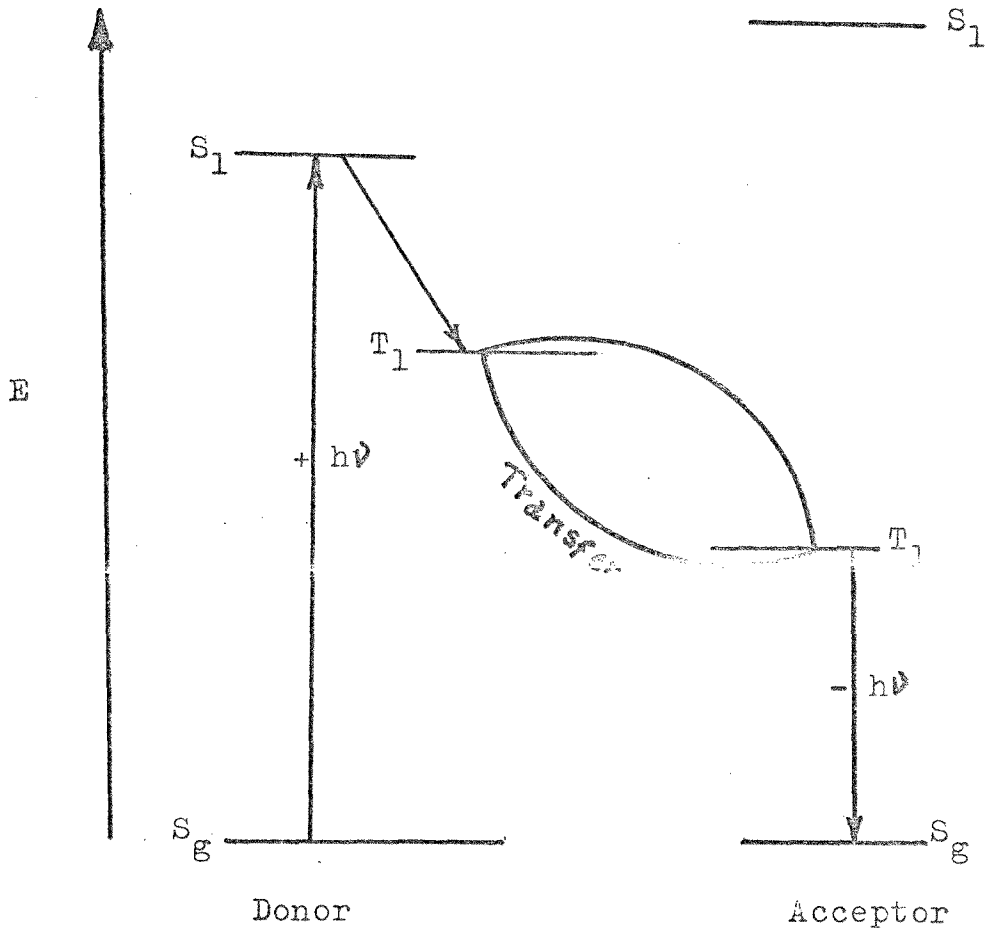
Triplet energy transfer can be represented as follows:

$$D \longrightarrow D^*(\text{Singlet}) \longrightarrow D^* \text{ (Triplet)}$$

$$D^* \text{ (Triplet)} + A \longrightarrow D + A^* \text{ (Triplet)}$$

In the above equations, D is the donor molecule, A is the acceptor and the asterisk designates an excited electronic state. The most effective sensitizers are those that absorb at longer wave lengths than the acceptor and are photochemically unreactive. In this study, xanthen-9-one with a triplet energy of 74 K cal/mole, was used as a triplet photosensitizer.

The following diagram shows the triplet energy transfer in sensitization:



In the above diagram, S_g, S_1, and T_1 represent the singlet ground state, the excited singlet state and the triplet state respectively.

EXPERIMENTAL

In all the experiments, products were identified by the comparison of their vpc retention times and intrared specta with the retention times and spectra of known compounds.

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 Associates A-60 spectrometer and are recorded in tau values from an internal SiMe4 standard.

The photolysis were carried out in a Rayonet Srinivasan-Griffin Photochemical Reactor, Model No. 1363.

Vpc analysis were obtained using an F & M, Model 810, dual column chromatograph, equiped with a flame ionization detector. The column used was a S.S., 7' x 1/8", packed with 5% carbowax 20 M on 80-100 mesh chromosorb W(H.P.). The flow rate of helium carrier gas was approximately 25c.c./min. The approximate temperature settings were: injection port 180°,

detector 220°, oven 110°C. Injection of 1-10 l were used for analytical determination.

Preparative vpc was carried out on an Aerograph Autoprep Model A-700 equipped with a thermoconductivity detector. The preparative columns used were a S.S. 10' x 1/4" packed with 20% carbowax - 3% potassium hydroxide on 20 mesh fluoro-pack (for isolation and collection of deuterio-2-methylindoline) and a S.S. 6' x 1/4" packed with 20% carbowax - 5% potassium hydroxide on 60-80 mesh chrom P (for isolation and collection of propyl- and allylanilines). The flow rate of helium carrier gas in both cases were 50cc/min. The approximate temperature settings were: injection port 225°, detector 240°, oven 155°, and collector 230°C.

The isooctane used as solvent for photolysis was Phillips 99 + mole%. The bis(2-methoxyethyl) ether of ethylene glycol (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.

A sample of calculations (experiment No.VIII) which were used to obtain product yields is shown below:

$$\frac{\text{Standard Solution}}{\dfrac{\dfrac{\text{azide (g.)}}{\text{1-6-1 (g.)}}}{\dfrac{\text{peak area of azide}}{\text{peak area of internal standard}}}} = \frac{\text{Experimental Solution}}{\dfrac{\dfrac{\text{unreacted azide (g.)}}{\text{1-6-1 (g.)}}}{\dfrac{\text{peak area of azide}}{\text{peak area of internal standard}}}}$$

$$\frac{\dfrac{0.3208}{0.3829}}{\dfrac{235}{130}} = \frac{\dfrac{\text{unreacted azide}}{0.3829}}{\dfrac{29}{345}}$$

unreacted azide = 0.0149g.

$$\frac{0.0149}{0.3208} \times 100 = 4.6\% \text{ unreacted azide}$$

I. Deuteration of Allylbenzene

50g. (0.424 mole) Allylbenzene (Aldrich) was dissolved in 150 ml methanol and the mixture poured into a 500 ml centrifuge bottle containing 0.1g. of 10% palladium on charcoal (Matheson) as catalyst. The bottle was then placed on a 3910 shaker type hydrogenetion apparatus, Parr Instrument Company, and deuteration commenced. During the deuteration time

(ca. 1½ hour), the shaker was stopped several times for a period of a few minutes to permit the solution to cool down to room temperature.

The same procedure was repeated for 62.5g(0.530 mole) and 61.5g (0.521 mole) quantities of allylbenzene. 118 p.s.i. of deuterium was used for 174 g allylbenzene which was almost theoretical (i.e. 1.475 moles of deuterium).

After removal of the catalyst by filtration, the solution was distilled from a water bath using a 12 inch vigreoux column. When all of the methanol had come off, an oil bath was used to distill the β,γ-dideuterio-propylbenzene. A colorless liquid was obtained at 155°C (150g., 85% yield)*. The purity of material was shown to be greater than 99% by vpc.

The infrared spectrum (neat) of the material was virtually identical with that exhibited by n-propyl-benzene except for the C-D bond stretching at 4.5μ (2200 cm^{-1})[6].

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* b.p. of n-propylbenzene is 159°C.

II. Nitration of β,β-Dideuteriopropylbenzene[12]

A nitrating solution was prepared by mixing 78 ml of fuming nitric acid (Fisher), 71 ml of glacial acetic acid (Baker), and 62 ml of acetic anhydride (Fisher). Before mixing, every component was cooled in an ice bath.

The cold solution was added dropwise, during ca.4 hours, to a stirred solution of 150g. β,β-dideuteriopropylbenzene in 556 ml acetic anhydride in a 2 liter 2-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 sucessively with three 200 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 $MgSO_4$.

After separation of magnesium sulfate by filtration, 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 distillation was conducted at 12 mm pressure and fractions were taken as follows:

No. of fraction	B.P. °C	Amount(g.)	Characterization
I	50-55	10.25	unreacting starting material
II	115-120	1.35	a mixture of o-nitro & starting material
III	123	44.80	o-nitro
IV	124-126	17.50	o-nitro
V	126-130	6.60	a mixture of o-, m-, p-nitro

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

The yield of o-nitro (β,β-dideuteriopropyl)-benzene (based on the fractions III & IV) was 31.2%. The infrared (neat) showed 2 sharp peaks at 6.7 μ (1530cm^{-1}) and 7.4 μ (1350cm^{-1}) which are characteristic of the C-NO_2 bond.[6]

III. Reduction of o-Nitro (β,γ-Dideuteriopropyl)-benzene.

62 g. (0.38 mole) o-Nitro(β,γ-dideuteriopropyl)-benzene + 110 g. tin (Mossy reagent, Matheson) were placed in a one liter flask and 220 ml concentrated hydrochloric acid (Baker) was added slowly, cooling when necessary by means of an 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 transferred to a 2 liter three-neck flask. A solution of 160 g. sodium hydroxide in 400 ml water 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 150 ml portions of 2 N 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 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 (15mm) gave 19.8 g. (39% yield) of a clear liquid at 107-109°C. Gas chromatography 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.[6]

IV. Preparation of o-(β,β-Dideuteriopropyl)phenyl Azide

19 g. (0.14 mole) o-(β,β-Dideuteriopropyl)aniline was dissolved in 56 ml water and 32 ml concentrated hydrochloric acid (Baker). Additional water was added to dissolve the hydrochloride salt.

Reaction was carried out in a 2 liter beaker with some ice in it to keep the temperature at 0°- 5°C. A solution of 10.5 g. (0.15 mole) sodium nitrite (Fisher) in 36 ml water was dropped into the beaker while stirring at 0°- 5°C. Stirring was continued for one more hour at this temperature. Then a solution of 9 g. (0.14 mole) of sodium azide (Matheson) in 33 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 petroleum ether (3 x 150 ml), washed with 10% sodium carbonate several times, washed with water until neutral and dried over magnesium sulfate. The drying agent was filtered off and the solution was concentrated on a rotatory evaporator to a volume of about 25 ml.

Chromatography of this solution on alumina (120 g., 200 mesh, activity 1, Mallinckrodt) using pentane as the eluent afforded a yellow oil which was shown to be 90% pure by vpc. This oil was molecularly distilled at 0.03 mm and 60°C to give 9.75 g. of azide (42% yield).

The infrared spectrum (neat) showed two sharp peaks, one at 4.86 μ (2060 cm^{-1}) and the other at 8 μ (1500cm^{-1}) which are characteristic of the C-N_3 stretching vibrations of azide.[6]

V. Photolysis of o-(β,β-Dideuteriopropyl)phenyl Azide at Room Temperature.

o-(β,β-Dideuteriopropyl)phenyl azide 0.0523 g. (0.00032 mole) and 0.0732 g. 1-6-1 as an internal standard were diluted to 100 ml with isooctane. 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 dissolve oxygen. The reactor vessel was then placed in a photoreactor and photolyzed at 3500 A while stirring and maintaining a blanket of nitrogen. Samples were removed from the reactor at periodic intervals and analyzed by vpc (vide supra). The photolysis was stopped after vpc had indicated that more than 94% of the starting azide had disappeared (ca.5 hours). During this time the internal temperature of the reactor varied between 26° & 40°C. Calculation showed (vide supra) that 6% unreacted azide remained after 5 hours of photolysis and that o-nitropropylbenzene* and o-propylaniline were formed to the extent of 5% and 1% respectively. Identity of the materials was established by comparison with the retention times of authentic samples. The photolysis was repeated using the same conditions and procedures. The following results were obtained: azide consumed 95%, yield of o-nitropropylbenzene and o-propylaniline were 6.0 & 1.8%, respectively. In both photolysis, an orange-brown precipitate was deposited on the walls of the reactor vessel. It is assumed that most of the

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* The oxygen responsible for the formation of the o-nitropropylbenzene is suspected to come from the nitrogen which was used in the experiment (E.D. grade nitrogen was 99.7% pure). By using a trap for oxygen, the nitro compound was eliminated.

azide reacted to give this material (possibly an azo-compound, Ar-N=N-Ar).

VI. Photolysis of o-(β,γ-Dideuteriopropyl)phenyl Azide at Room Temperature in The Presence of a Triplet Photosensitizer.

A mixture of o-(β,γ-dideuteriopropyl)phenyl azide 0.0508 g. (0.00031 mole) and 0.0838 g. 1-6-1 as internal standard + 0.0687 g. (0.00035 mole) xanthen-9-one was diluted to 100 ml with isooctane. The solution was transferred to a quartz reaction vessel and alternately evacuated (by means of a water aspirator) and flushed (U.D. grade nitrogen, Matheson) several times to remove any oxygen.

The photolysis was carried out under a blanket of nitrogen using 3500 Å U.V. lamps while stirring the solution. Samples were taken at every 20 minutes and analyzed by vpc. The photolysis was stopped after 2 hours. At the end of this time only 4% of azide remained. By the comparison of the retention times of products on vpc and the retention times of known compounds, it was determined that the products were o-nitro(β,γ-dideuteriopropyl)benzene (29.0%) and o(β,γ-dideuteriopropyl)aniline (2.0%).

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

o-Nitropropylbenzene 26.5%, o-propylaniline 1.5%, (95% of the azide was consumed). In both photolysis, an orange-brown precipitate was deposited on the walls of the reactor vessel. It is assumed that more than 1/2 of the azide reacted to give this material (possibly an azo-compound Ar-N=N-Ar).

VII. Preparative Photolysis of o-(β,β-Dideuteriopropyl)-phenyl Azide in The Presence of The Triplet Photosensitizer, Xanthen-9-one.

A mixture of o-(β,β-dideuteriopropyl)phenyl azide, 0.3208 g. (0.001818 mole), 0.3829 g. 1-6-1 + 0.3515 g. (0.00179 mole) xanthen-9-one was diluted to 600 ml with isooctane. The solution was transferred into a quartz reaction vessel. The system was deoxygenated as was done in the previous photolysis (e.g. experiment V).

Photolysis was conducted under nitrogen using 3500 Å lamps while the solution was stirred. Samples were taken and analyzed by vpc. The photolysis was stopped after 2 hours. Calculation showed 4.6% of unreacted azide remained and that o-nitropropylbenzene

and o-propylaniline were formed to the extent of 14.6% and 11.8%, respectively. The retention times of these materials were identical with those shown by autehntic samples.

The solution was cooled in an ice bath and then filtered to remove some insoluble material. The filtrate was concentrated to a volume of about 25 ml by means of a rotating evaporator. This concentrated solution was then diluted with 150 ml of ether and extracted with 2 N hydrochloric acid (2 x 100 ml). The combined acid extracts were washed with ether. The ether wash was added to the original organic layer, washed well with water and dried over magnesium sulfate. This ether extract contained any non-basic compound and as such is designated as the "neutral fraction". The original acid extract was neutralized with 10% sodium hydroxide, extracted with ether (3 x 100 ml). The ether extract was washed with H_2O and dried over magnesium sulfate. This acid extract is designated the "basic fraction".

After removal of drying agent by filtration, vpc of the "basic fraction" showed only one peak with the same retention time as o-propylaniline. The solvent was removed on a rotatory evaporator and an infrared spectrum (in CCl_4) was obtained on the residual liquid.

The infrared spectrum was virtually identical with that exhibited by the authentic o-(β,γ-dideuteriopropyl)-aniline.

The "neutral fraction" was filtered to remove the drying agent and the filtrate concentrated on a rotatory evaporator. Vpc anaylsis showed a major peak with the same retention time as authentic o-nitro-(β,γ-dideuteriopropyl)benzene. Several minor peaks were also present. After removal of impurities by column chromatography (alumina as adsorbent and 25% benzene: 75% pentane as eluent) the infrared spectrum (in CCl_4) of this major component was identical with the spectrum of known nitro-compound.

VIII. Photolysis of o-(β,γ-Dideuteriopropyl)phenyl Azide at Elevated Temperature.

A mixture of o-(β,γ-dideuteriopropyl)phenyl azide 0.0605 g. (0.000371 mole) and 0.0930 g. 1-6-1 was diluted to 100 ml with isooctane and transferred to a quartz reaction vessel. The system was deoxygenated as was done in previous photolysis (e.g. experiment V). The solution was then brought to a boil by means of a heating mantle and irradiated with 3500 Å U.V. lamps as before. The

photolysis was carried out under a blanket of nitrogen. Samples were taken every 15 minutes and photolysis was stopped after 1½ hours.* At the end of this period, only ca. 2% of the starting material remained.

Vpc analysis showed the formation of three products (3peaks) having the same retention times as 2-methylindoline, o-propylaniline and o-allylaniline.

Calculation (vide supra) gave the following yield data: 35.6% methylindoline, 11.4% propylaniline and 19.4% o-allylaniline.**

The photolysis was repeated using the same conditions and procedure. The following results were obtained: 2-methylindoline 35%, o-(α,β-dideuteriopropyl)-aniline 12.9% and o-allylaniline 19.2%.

IX. Photolysis of o-(α,β-Dideuteriopropyl)phenyl Azide at Elevated Temperature in The Presence of The Triplet Sensitizer, Xanthen-9-One.

A mixture of o-(α,β-dideuteriopropyl)phenyl azide 0.0525 g. (0.00322 mole), 0.0670 g. 1-6-1 and 0.0716 g. (0.000366 mole) xanthen-9-one was diluted to 100 ml

*Control experiments, conducted by Dr. Richard Trattner, have demonstrated the stability of o-propylphenyl azide under the reaction conditions used for this experiment.
**Estimation based on the corrected detector response of o-propylaniline.

with isooctane and solution was transferred to a quartz reaction vessel. The system was deoxygenated as was done in previous photolysis (e.g Experiment V). The solution brought to a boil by means of a heating mantle and irradiated with 3500 Å U.V. lamps. The photolysis was carried out under a blanket of nitrogen. Samples were taken every 15 minutes and photolysis was stopped after 1 hour, after which time, 2% of the starting material remained.

Vpc analysis showed formation of six products (6 peaks) four of them with the same retention time of 2-methylindoline, o-nitropropylbenzene, o-propylaniline and o-allylaniline. The other two peaks were not identified.

Calculation gave the following yield data: 5% deuterio-2-methylindoline, 3% o-nitro(β,γ-dideuteriopropyl)benzene, 40.2% o-(β,γ-dideuteriopropyl)aniline, and 8% o-allylaniline. The yields of the two unknown compounds were estimated to be 8.2% and 13.5%.

The photolysis was repeated using the same conditions and procedure. The following results were obtained: Deuterio-2-methylindoline, 4.0%; o-nitro-(β,γ-dideuteriopropyl)benzene, 3.4%; o-(β,γ-dideuterio-

propyl)aniline, 36.0%; o-allylaniline, 6.7%; 8.2% and 11.3% for the fifth and sixth peaks.

X. Preparative Photolysis of o-(β,β-Dideuteriopropyl)phenyl Azide at Elevated Temperature

A mixture of o-(β,β-dideuteropropyl)phenyl azide 0.3109 g. (0.001908 mole) and 0.4923 g. 1-6-1 was diluted to 300 ml with isooctane and transferred to a quartz reaction vessel. The system was deoxygenated as done before. The solution brought to boil by means of a heating mantle and irradiated with 3500 Å U.V. lamps as before. The photolysis was carried out under nitrogen and stopped after 2 hours. At the end of this period, only about 5% of the starting material remained.

Vpc analysis showed the formation of three products, two of them with the same retention times of 2-methylindoline and propylaniline. The third peak was presumed to be o-allylaniline.

Calculation gave the follcwing yield data: deuterio-2-methylindoline 37.4%, o-(β,β-dideuteriopropyl)aniline 12.6% and o-allylaniline 16.7%.

The photolysis was repeated on two more batches

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

Azide used	Unreacted azide%	Methyl-indoline%	Propyl-aniline%	Allyl-aniline%
0.304 g. (0.00187 mole)	4.2	41.0	13.5	16.7
0.320 g. (0.00197 mole)	4.8	36.2	13.7	15.7

The three reaction results were combined and the solution was concentrated to a volume of about 20 ml by means of a rotatory evaporator. This concentrated solution was then diluted with 150 ml of ether and extracted with 2 N hydrochloric acid (2 x 100 ml). The aqueous phase was separated and washed with ether. The ether wash was combined with the original organic layer (neutral fraction). The original aqueous phase was neutralized with 10% sodium hydroxide, extracted with ether (3 x 100 ml) washed with water and dried over magnesium sulfate. This acid extract was designated as the "basic fraction". After removal of drying agent by filtration, the solution was concentrated to a volume of about 2 ml.

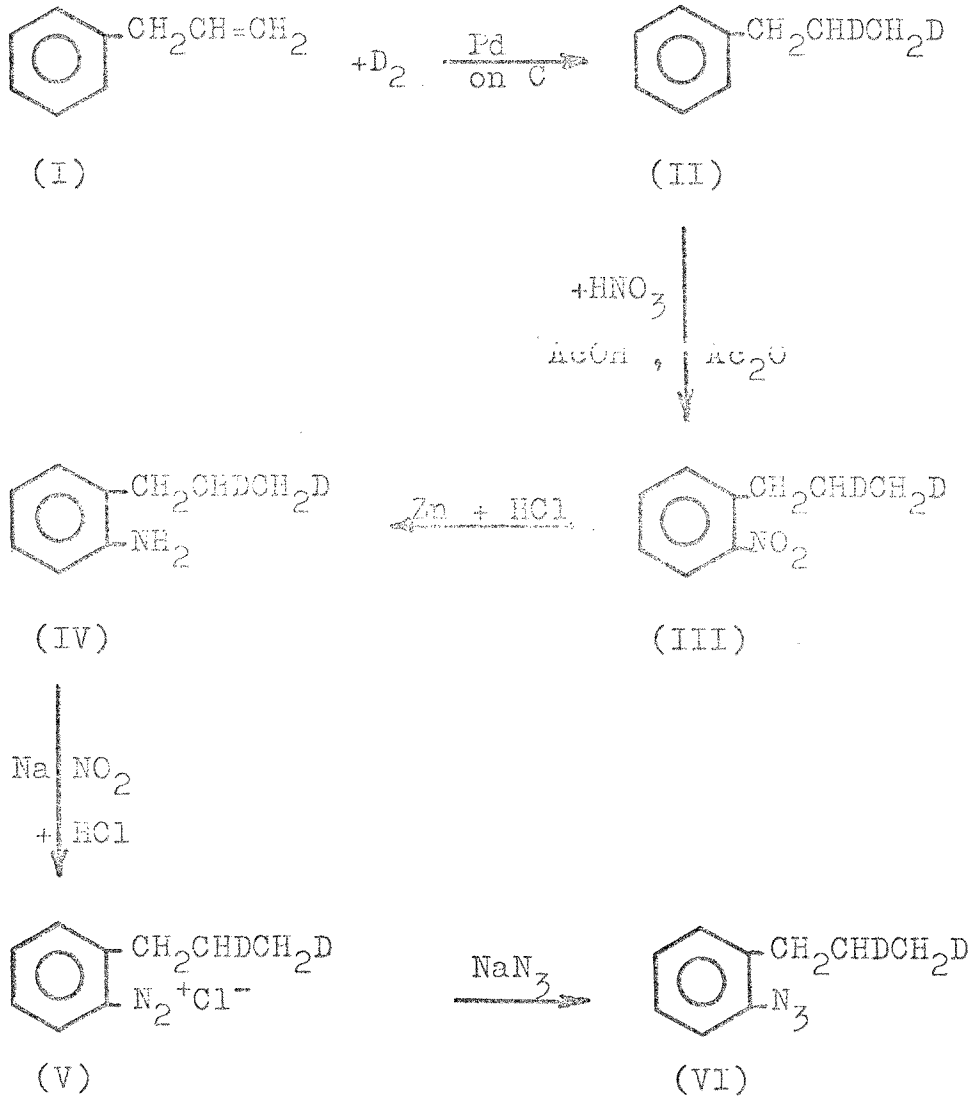
Preparative vpc was used for isolation and puri-

fication of three basic products. 75mg Deuterio-2-methylindoline was obtained. The infrared spectrum (in CCl_4) of this material was identical with the spectrum of a known 2-methylindoline. The other two products (o-propylaniline and o-allylaniline) were also characterized by their infrared spectra.

RESULTS & DISCUSSION

I. The Synthesis of Ortho-(β,β-Dideuteriopropyl)-phenyl Azide.

The synthetic scheme employed in the synthesis of o-(β,β-dideuteriopropyl)phenyl azide is shown below:



β,γ-Dideuteriopropylbenzene (II) was prepared in 84% yield by deuteration of allylbenzene (I). The product purity was greater than 99% as determined by gas chromatography. The infrared spectrum of the product was identical with that exhitited by n-propylbenzene except for a peak at 4.5μ (2200cm^{-1}) for C-D stretching vibration.[6] No peak for C=C stretching was observed.

Nitration of β,γ-dideuteriopropylbenzene (II) in acetic anhydride using a mixture of fuming nitric acid, glacial acetic acid and acetic anhydride gave a mixture of ortho-, meta-, and para- isomers. Fractional distillation under reduced pressure (15 m m.) using a Todd column gave o-nitro(β,γ-dideuteriopropyl)benzene (III) in 38% yield. The purity of the product was shown to be greater than 99% by vpc. The infrared spectrum of the material showed two sharp peaks at 6.7μ(1500cm^{-1}) and 7.4μ(1350cm^{-1}) indicating the presence of C-NO_2 bond.[6]

o-(β,γ-Dideuteriopropyl)aniline (IV) was prepared in 38% yield by reduction of o-nitro-(β,γ-dideuteriopropyl)benzene (III) using hydrochloric acid and tin as a reducing agent. Steam distillation followed by distillation under reduced pressure (15 mm.) was used for

the isolation and purification of the product. Gas chromatography showed the product to be 99% pure. The infrared spectrum showed two peaks at 2.85 μ ($3500cm^{-1}$) and 2.94 μ ($3400cm^{-1}$) for primary N-H streching vibration.[6]

o-(β,δ-Dideuterioproyl)phenyl azide (VI) was prepared in 44% yield by reactions of o-(β,δ-dideuteriopropyl)aniline (IV) and sodium nitrite in hydrochloric acid (formation of the diazonium chloride (V) as intermediate.) followed by addition of sodium azide. Column chromatography (alumina and pentane used as adsorbent and eluent, respectively) and then molecular distillation (pressure 0.03 m m.) were used for purification of the azide. Gas chromatography showed the product to be more than 95% pure. The infrared spectrum showed two peaks at 4.86 μ ($2060cm^{-1}$) and 8 μ ($1250cm^{-1}$) for $C-N_3$ stretching vibrations.[6]

II. Photolysis of o-(β,δ-Dideuteriopropyl)phenyl Azide

All the experiments were carried out using isooctane as the solvent in a quartz reaction vessel under a blanket of nitrogen using 3500 $\mathring{A}$ U.V. lamps and the products were identified by the comparison of their vpc retention times and the infrared spectra with the retention times and spectra of the known compounds. The results of photolysis are given in the following table (III):

Table (III)

Photolysis of o-(α,α-Dideuteriopropyl)phenyl Azide

Experiment		Temp.	Azide moles/ liter	Xanthen -9-one moles/ liter	2-Methyl indoline % yield	o-Propyl aniline % yield	o-Allyl aniline % yield	o-Nitro propyl benzene % yield
V	1	26-40	0.00303	-	-	1.0	-	4.8
	2	26-40	0.00320	-	-	1.8	-	6.0
VI	1	27-40	0.00311	0.00350	-	2.0	-	29.2
	2	27-40	0.00316	0.00353	-	1.2	-	26.5
VII prep.		26-39	0.00303	0.00299	-	14.6	-	11.3
VIII	1	reflux	0.00371	-	35.6	11.4	19.4	-
	2	"	0.00322	-	35.0	12.9	19.2	-
* IX	1	reflux	0.00322	0.00366	5.0	40.2	8.0	2.9
	2	"	0.00306	0.00338	4.0	36.0	6.7	3.4
X prep.	1	reflux	0.00636	-	37.4	12.6	16.7	-
	2	"	0.00622	-	41.0	13.5	16.7	-
	3	"	0.00655	-	36.2	13.7	15.7	-

* Two unknown materials were obtained in this experiment

1. x=9.2, y=13.5 ; 2. x=8.2, y=11.3

III. Discussion of the Results of Photolysis

Photolysis at room temperature (Experiment No.V) showed no detectable amount of 2-methylindoline, C-H insertion product (i.e. less than 1%). On the other hand, photolysis at the boiling point of isooctane (99°C) (Experiments No. VIII & X) gave 2-methylindoline as the major product (ca. 40% yield)*.

These results are in good agreement with the results of photolysis of o-nitropropylbenzene by Sundberg and co-workers who obtained no insertion product (2-methylindoline) at 30°C but found it to be the major product at 150°C 6.7%.[33,34] To explain this result, they proposed that the energy for C-H insertion of o-propylphenylnitrene is such that the C-H insertion reaction is competitive at 150°C but, not at room temperature. In other words, the intramolecular C-H insertion process has a high energy of activation.

The electronic state of the aryl nitrene intermediate in intramolecular insertion reactions was proposed by Smolinsky and Feuer to be a singlet which reacts via a three centered transition state.[28] Contrasted with this

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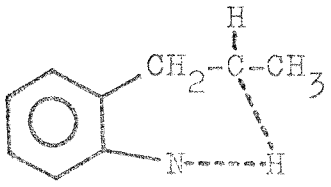
* It has been shown that o-propylphenyl azide is thermally stable under the reaction conditions used for this experiment(cf. experimental section)

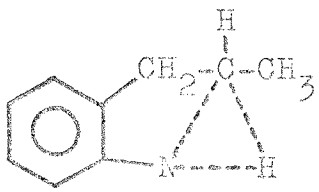
is H-11 and co-workers' conclusion that the intermolecular C-H insertion reactions proceed via triplet aryl nitrene.[9,11]

To resolve this apparent contradiction, we desired to obtain evidence which would permit us to know if a singlet or a triplet aryl nitrene is responsible for the intramolecular C-H insertion product in the photolysis of o-propylphenyl azide. Ortho(α,α-dideuteriopropyl)-phenyl azide was prepared (vide supra) and photolyzed.

It was believed that if a triplet aryl nitrene was responsible for the formation of the insertion product (2-methylindoline), a relatively large deuterium isotope effect k_H/k_D= 3-7, would be observed. This follows from a consideration of the transition states of the intramolecular reactions of triplet (I) and singlet (II) nitrene:



(I)

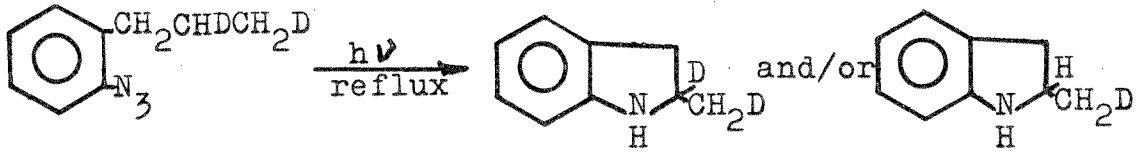


(II)

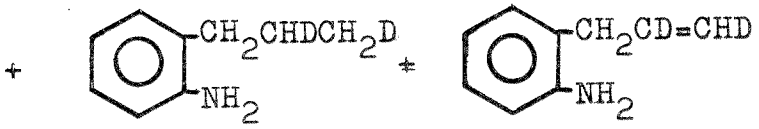
Since triplet nitrene is of lower energy than singlet, the amount of zero point energy lost in the C-H bond in transition state (I) should be greater than that

lost in transition state (II). Hence reaction (I) should have a larger $^{k}H/k_{D}$ than (II).

Preparative photolysis of o-(β,γ-dideuteriopropyl)-phenyl azide at reflux temperature resulted in the formation of three products: 2-methylindoline (I) (insertion product), o-dideuteriopropylaniline (II) (intermolecular abstraction product) and o-allylaniline (III) (intramolecular abstraction product) (Experiment No. X Table 3).



(I)



(II) (III)

The intrared spectrum (in CCl_4) of (I) was identical with that exhibited by 2-methylindoline except for the C-D stretching vibration. Nuclear magnetic resonance spectra of (I) was almost identical with the spectra of unlabeled 2-methylindoline. Integration of the methyne proton area (6.15τ) showed a decrease

of 50% relative to the area obtained from an authentic sample of 2-methylindoline which was not deuterated in the α-position. This is taken to mean that only one-half of the intramolecular C-H insertion product contains deuterium in the α-position. This shows that insertion of nitrene into the C-H and C-D bond occurs equally or that there is no preference for insertion the C-H bond compared with the C-D bond. Therefore, there is no kinetic isotope effect. (i.e. $k_H/k_D=1$).

This result indicates (when considered in conjunction with the arguments presented above) that the singlet nitrene is responsible for the formation of 2-methylindoline (intramolecular insertion product) in the photolysis of the o-propylphenyl azide. This is in agreement with Smolinsky and Feuers' finding in the pyrolysis of o-alkylphenyl azide.[28]

Additional supporting evidence was obtained when photolysis was conducted in the presence of the triplet photosensitizer xanthen-9-one, (Experiment No. IX). The yield of intramolecular insertion product decreased markedly. This shows that the triplet aryl nitrene is not responsible for the intramolecular C-H insertion under the condition utilized in these experiments and therefore implies the intermediacy of singlet aryl nitrene.

CONCLUSION

Photolysis of ortho-(β,γ-dideuteriopropyl)-phenyl azide in isooctane at room temperature gave 5% o-nitro(β,γ-dideuteriopropyl)benzene and 2% o-(β,γ-dideuteriopropyl)aniline. No trace of 2-methylindoline (intramolecular insertion product of nitrene into C-H bond) was obtained.

Photolysis at the reflux temperature of isooctane resulted in a 40% yield of 2-methylindoline, together with a 13% yield of o-propylaniline and 16% of o-allylaniline. The nuclear magnetic resonance spectrum of the 2-methylindoline showed that the area of the C-H bond in the 2 position had decreased by 50%, indicating the presence of 50% C-D bond. The resultant k_{H}/k_{D} is therefore equal to one. This absence of kinetic isotope effect (absence of preference of insertion into C-H to the C-D bond) indicates that the insertion reaction of an aryl nitrene, generated under our experimental conditions, proceeds via a singlet state by means of a concerted reaction involving a 3-centered mechanism and not through the intermediacy of the triplet state since the latter would be expected to give a large kinetic isotope effect.

Photolysis at the reflux temperature of isooctane in the presence of a triplet photosensitizer (xanthen-9-one) resulted in only 5% 2-methylindoline, together with 40% of o-propylaniline, 8% of o-allylaniline, 3% of o-nitropropylbenzene and two other products. This result suggests that triplet nitrene is not responsible for the formation of the insertion products because if it were not, more 2-methylindoline would have been formed in the presence of the triplet sensitizer.

RECOMMENDATION

Although my thesis research was concerned primarily with the mechanism of intramolecular C-H insertion by an aryl nitrene, several interesting reactions presented themselves which might benefit from further studies, namely:

1) To study the formation of o-nitropropylbenzene resulting from the room temperature photolysis of o-propylphenylazide in the presence and absence of the triplet photosensitizer.
2) To study the formation of two unidentified materials which resulted from the elevated temperature reaction in the triplet photosensitizer.
3) To isolate and identify the orange precipitate to which the starting azide is apparently quantitatively converted in the room temperature photolysis in the absence of photosensitizer.

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