binding phosphine oxide 1^{8h} since picolinate, the product of hydrolysis, was observed to strongly chelate the metal. Experiments conducted with 4.82×10^{-4} M **5**:Co^{2+} or **6**:Co^{2+} as a function of increasing [pNPP] from 4.83×10^{-4} to 2.2×10^{-3} M at pH 6.85 showed no difference in the k_{obsd} values for hydrolysis. Thus it is clear that the complexes are indeed turnover catalysts and function as in Scheme II.

Conclusion

Tris(imidazole)-containing phosphines such as **3** or **4** when compared to Zn^{2+} provide modest catalysts for the hydrolysis of pNPP. They are from 2 to 10 times more active than either ligand alone or Zn^{2+} alone, and their catalytic activity increases as a function of pH. Because of the weak M^{2+} affinity neither ligand is completely complexed at the concentrations employed which complicates the kinetic analysis since free ligand and Zn^{2+} exist in the solution.

Ligands **5** and **6** bind M^{2+} more strongly and their complexes are nearly fully formed in 80% ethanol–H_2O at concentrations of $\sim 5 \times 10^{-4}$ M. While the Zn^{2+} complexes cannot be studied at pH's in excess of 7.2 due to precipitation, the Co^{2+} complexes remain in solution up to pH 8.6. Uncomplexed Co^{2+} precipitates

above pH 7.9. **5**:Co^{2+} and **6**:Co^{2+} show evidence of a titration phenomenon having a pK_a of ~ 7.6–7.8, the basic form of the complex being catalytically active. Since the Co^{2+} complexes have about the same $k_2^{cal.}$ values as uncomplexed Co^{2+} (at pHs below that where uncomplexed Co^{2+} precipitates from solution), the major virtue of the complexes is to hold the metal ion in solution at higher pH. Apparently the complexes act as bimolecular nucleophiles with the Co^{2+}–OH^- nucleophilically attacking pNPP, but the hydroxyethyl group in **6**:Co^{2+} is not of any catalytic benefit in the hydrolysis of this ester.

Photochemistry of Phenyl Azide: Chemical Properties of the Transient Intermediates

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Abstract: The photochemistry of phenyl azide was examined by laser–flash photolysis in inert and reactive (nucleophilic) solvents. Direct irradiation and triplet sensitization give triplet phenylnitrene ($Ph\ddot{N}^3$). The products of the reaction of $Ph\ddot{N}^3$ depend dramatically on the concentration of the azide and on the power of the light source. In the direct irradiation, a relatively long-lived precursor to $Ph\ddot{N}^3$ is formed. This singlet-state intermediate reacts with the nucleophilic solvents. The structure of this species and the rates of its reaction with secondary amines are discussed.

The photochemical and thermal reactions of aryl azides have been studied for over 60 years.[1] Despite this long history there are still many important details of these reactions that are incompletely understood. In this paper we report the results of our investigation of the photolysis of phenyl azide (PhN$_3$). The accompanying paper contains[2] a report on the investigation of some polynuclear aromatic azides.

The photochemistry of aromatic azides has gained considerable attention due to the utility of these compounds in photoimaging systems[3] and as photoaffinity labels.[4] Both applications take

Scheme I
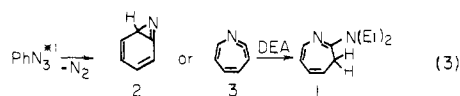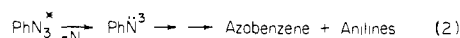
advantage of the unusually high reactivity of short-lived intermediates formed when these azides are irradiated with ultraviolet light. Our objective is to identify the structure of these intermediates and to characterize their chemical and physical properties.

Thermolysis or photolysis of phenyl azide in an inert solvent, such as benzene or acetonitrile, is reported by different investigators to give either intractable "tars" and a low yield (4%) of azobenzene[5] or, at sufficiently low conversion, exclusively azo-

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benzene by a chain reaction.[6] Thermolysis of PhN_3 in aliphatic hydrocarbons gives aniline and N-alkylanilines[7] which are presumed to result from recombination and disproportionation of anilino and alkyl radicals. When the thermolysis or direct irradiation of phenyl azide is carried out in a reactive, nucleophilic solvent, such as diethylamine (DEA), a very good yield of the 2-(diethylamino)-3H-azepine (1) is obtained.[5c,8] When this reaction is initiated by triplet sensitization the yield of azepine 1 is reduced, and aniline is a major product.[9] These findings have been used to support the conclusions that azobenzene and the anilines are products of triplet phenylnitrene ($Ph\ddot{N}^3$) and that azepine 1 and related nucleophile incorporation products results from the trapping of some other, presumably single state, intermediate.

The structure and properties of the singlet-state intermediate have been the object of intensive investigation. Huisgen and co-workers[10] first suggested that this intermediate is bicyclic azirine 2. Later, Sundberg and co-workers,[11] with close analogy in gas-phase reactions of aromatic nitrenes,[12] raised the possibility that this intermediate is the dehydroazepine 3. These suggestions are summarized in Scheme I.

Irradiation of PhN_3 at low temperature in a glass or matrix generates at least two metastable intermediates. Smolinksy and co-workers[16] were the first to observe the EPR spectrum of $Ph\ddot{N}^3$ following photolysis of PhN_3 in Fluorolube at 77 K. This observation ensures that some $Ph\ddot{N}^3$ is formed, but it does not reveal any information about the yield of this reaction. In a pioneering study, Chapman and LeRoux[17] obtained an IR spectrum of the intermediate formed from photolysis of PhN_3 isolated in argon at 8 K. They conclude that the major primary product is the dehydroazepine 3. On the basis of this observation they suggest that it is the reaction of 3 with DEA that is responsible for eventual formation of the 3H-azepine (1). In addition, Chapman and co-workers[17,18] report that the dehydroazopine is unstable toward further irradiation which converts it eventually to 2-pyridinylmethylene.

There have several reports in the literature of attempts to measure the UV–vis absorption spectrum of $Ph\ddot{N}^3$ at low temperature in frozen media.[19] These experiments reveal formation of an intermediate, claimed to be $Ph\ddot{N}^3$, that absorbs broadly between 300 and 420 nm. However, in light of the matrix IR experiments, and the susceptibility of 3 to further photochemical rearrangement, this assignment is, at best, uncertain.

There are several reports of attempts to employ flash photolysis in the investigation of PhN_3. In the most revealing of these, Sundberg and co-workers[5c] report observing two intermediates. The first is formed in inert solvents within the 80-μs rise time of their conventional flash apparatus, it absorbs at 366 nm, and it

Table I. Yield of Azobenzene from Photolysis of PhN_3 in Acetonitrile

[PhN_3], M	% conversion	energy source	azobenzene yield, %
1×10^{-4}	60	continuous	45
4.4×10^{-4}	70	continuous	44
1.5×10^{-3}	40	continuous	27
3.4×10^{-3}	8	continuous	15
4.4×10^{-3}	20	continuous	9
1×10^{-4}	20	laser	<5
4.4×10^{-3}	5	laser	3
$2 \times 10^{-4 a}$	60	continuous	16
$2 \times 10^{-4 a}$	30	laser	11

*a*The light is absorbed by benzophenone. *b*Based on the amount of PhN_3 consumed.

is not affected by oxygen. The second intermediate detected absorbs at 366 nm also, but it is formed in a second-order reaction that depends on the concentration of added secondary amine. Primarily on the basis of the subsequent acid–catalyzed conversion of this second intermediate to the 3H-azepine which is eventually isolated from the reaction, these authors chose to assign its structure to 1H-azepine 4, eq 4. However, in a reinvestigation

$$ \quad (4) $$
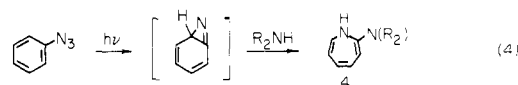
of the flash photolysis of PhN_3 and some substituted phenyl azides in the presence of secondary amines, Nielson and Buchardt[20] were unable to detect any intermediates absorbing at wavelengths longer than 300 nm, and the reactions they did observe do not show the expected first-order dependence on amine concentration. In a recent paper, Waddell and Feilchenfeld[21] report that irradiation of PhN_3 in acetonitrile gives an apparent transient that absorbs broadly from 310 to 550 nm which they identify, on the basis of comparison with the low-temperature optical spectrum, as $Ph\ddot{N}^3$.

The menagerie of structures that must be considered to interpret the photochemistry of PhN_3 includes three excited states and at least six short-lived ground-state intermediates. It is therefore not surprising the there is still some confusion about the role played by each of these compounds in forming the stable products eventually observed. We report herein a careful reexamination of the photochemistry of PhN_3 that combines product analysis with laser flash photolysis. Our findings permit some further clarification of this wonderfully complex system.

Results

A. **Products of Photolysis of PhN_3.** The chemical outcome of the photolysis of PhN_3 depends dramatically on the conditions of the reaction. We examined its irradiation in inert and reactive solvents using low-intensity continuous-light sources or high-power pulsed lasers.

Samples of PhN_3 were irradiated in deoxygenated solvents contained in quartz cells fitted with stopcocks and small magnetic stirring bars. The progress of the reaction was monitored by HPLC or gas chromatography as described in the Experimental Section. Azobenzene is a major product when a very dilute solution of PhN_3 (1×10^{-4} M) is irradiated in acetonitrile with a low-intensity source. However, when the concentration of PhN_3 is raised to only 4×10^{-3} M the yield of azobenzene plummets. Control experiments show that azobenzene is stable to the reaction conditions and that, contrary to the earlier report,[6b] its yield is not strongly dependent on the extent of convesion of PhN_3. We have not characterized the other products of this reaction beyond noting that they display the same solubility behavior previously assigned to the "intractable polymer".[5] These data are summarized in Table I.

Photolysis of "dilute" or "concentrated" solutions of PhN_3 with the frequency-quadrupled output of the Nd-YAG laser (266 nm)

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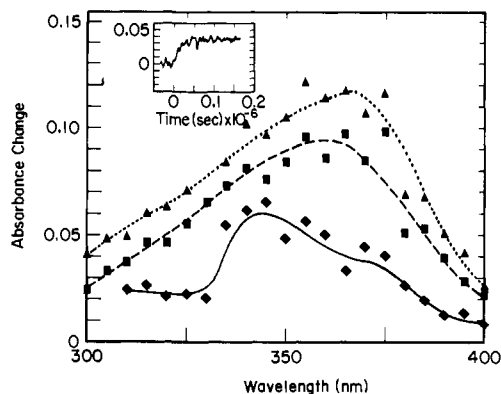
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Figure 1. Transient absorption spectra observed from pulsed irradiation of PhN_3 in hexane. The solid line (diamonds) was recorded 40 ns after the laser pulse and the dashed (squares) and dotted (triangles) lines at 30 and 80 μs, respectively. The inset shows the rise of the absorption at 340 nm.

Figure 2. Rate constants for quenching of benzophenone triplet (monitored at 525 nm) at increasing PhN_3 concentration.

instead of the continuous-light source leads to a remarkable decrease in the yield of azobenzene. Photolysis with the laser generates at least a 20 000 fold higher instantaneous concentration of transient products than does irradiation with the continuous source. Control experiments show that azobenzene is stable under the laser-photolysis conditions.

In some cases[2] we find that the yield of azoaromatics from photolysis of aromatic azides in inert solvents increases significantly as a consequence of a thermal reaction that occurs over a period of several hours after the irradiation has ceased. To examine the possibility that a metastable intermediate formed in the irradiation of PhN_3 can eventually give azobenzene, we analyzed the photolysis solution periodically for several days after the irradiation. There is no significant increase in the yield of azobenzene.

The formation of azobenzene is presumably a consequence of the reaction of $Ph\ddot{N}^3$. Indeed, it has been observed that triplet-sensitized reactions of PhN_3 do give azobenzene.[6a] We find that using either p-chlorotoluene as a triplet sensitizer in hexane, or benzophenone in acetonitrile leads to similar results. Azobenzene is formed in these reactions in significant amounts, and its yield is independent of whether the photolysis is carried out with the low-power continuous source or with the high-power laser.

Irradiation of PhN_3 in solutions containing secondary amines gives good yields of the substituted $3H$–azepine. We reexamined[9] the direct and triplet-sensitized photolysis of PhN_3 in the presence of DEA.

We confirm the earlier reports that the direct photolysis of PhN_3 in hexane containing 1 M DEA gives 2-(diethylamino)-$3H$–azepine in ca. 70% isolated yield.[5c,8] Under these conditions aniline is not a detectable product. When 2-acetonaphthone is included in the hexane solution of PhN_3 and DEA, and the mixture is irradiated at ca. 350 nm, aniline is formed in ca. 30% yield along with the $3H$-azepine 3. No aniline is formed when 7.2×10^{-2} M piperylene, a diffusion-controlled quencher of triplet 2-acetonaphthone, is included in the reaction solution. These findings show that triplet sensitization of PhN_3 with 2-acetonaphthone gives an intermediate, not formed by direct irradiation in the presence of DEA, which eventually can go on to become aniline. We presume, as have others,[9] that this intermediate is $Ph\ddot{N}^3$. This point of some importance in the identification of the transient intermediates observed by laser-flash photolysis.

B. Laser-Flash Photolysis: Detection of Transients. Deoxygenated solutions of PhN_3 (1.2×10^{-3} M) in both inert and and reactive solvents were irradiated at 266 nm with a 20-ns-wide ca. 5-mJ pulse from a Nd-YAG laser. Optical absorption spectra of the transient products formed were monitored at a right angle to the excitation pulse.

Displayed in Figure 1 is a trace showing the immediate (less than 20 ns) rise of a transient intermediate formed from the pulsed irradiation of PhN_3 in hexane. The intermediate absorbs broadly from ca. 320 to 380 nm with an apparent maximum at 340 nm (Figure 1). This spectrum changes over a period of 100 μs to
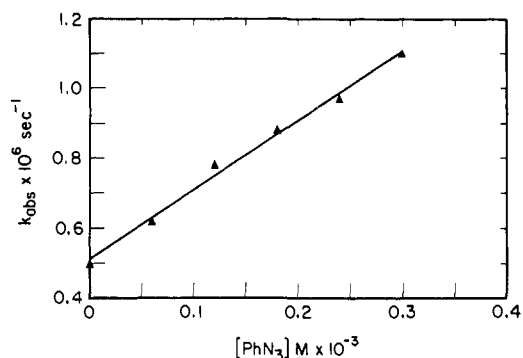
become identical with that of the stable products. Similar spectroscopic changes are observed when the irradiation is carried out in acetonitrile solution.

It should be noted that on the time scale of this experiment the first intermediate detected cannot result from the reaction of some transient product with PhN_3. The minimum rise time for such a process is more than 40 ns if it occurs at the diffusion-limited rate, and this is slower than the observed rise of the transient absorption (Figure 1).[22] Also, since the spectrum of the intermediate is essentially independent of the solvent (hexane or acetonitrile), we conclude that its formation is not a consequence of reaction of some transient with the solvent. With these restrictions in mind, it seems that the first-formed intermediate is generated unimolecularly from the singlet-excited azide (PhN_3^{*1}). There are six structures from the menagerie that satisfy this requirement, these are PhN_3^{*1}, PhN_3^{*3}, PhN^1, $Ph\ddot{N}^3$, azirine 2, or azepine 3. Several experiments were carried out in hopes of eliminating some of these possibilities.

There is no detectable fluorescence from PhN_3. If the observed transient product were PhN_3^{*1}, and its lifetime was hundreds of nanoseconds, then radiative relaxation should compete with the other reaction modes and fluorescence should be detectable. On this basis, and with the expectation that PhN_3^{*1} should be very short lived, we conclude that the observed transient is not the excited singlet azide.

Oxygen should be an efficient quencher of PhN_3^{*3}. However, the transient spectra obtained from flash photolysis of PhN_3 in air or O_2-saturated solvents are essentially identical with those obtained in deoxygenated solutions. Also, the transient absorption spectrum we measure resembles very closely the spectrum observed when PhN_3 is irradiated in frozen solution.[19] The spectrum is indefinitely stable at 77 K, and this behavior is not expected for PhN_3^{*3}.

The product study shows that triplet sensitizers effectively initiate reaction of PhN_3. These reactions most likely proceed through PhN_3^{*3}. Pulsed irradiation of benzophenone in acetonitrile solution gives the triplet ketone which is readily characterized by its absorption spectrum.[23] As expected, PhN_3 is a quencher of triplet benzophenone. Figure 2 shows a plot of the observed pseudo-first-order rate constant (k_{obsd}) for decay of triplet benzophenone at increasing concentrations of PhN_3. The slope of this plot gives a rate constant for quenching by PhN_3 of 2×10^9 M^{-1} s^{-1}. This value is over 1000 times greater than the estimate for this rate constant obtained by Lewis and Saunders[24] and later by Leyshon and Reiser.[25] These workers calculated the quenching rate constant indirectly from the measured quantum yield of N_2 loss from PhN_3. However, Waddell and Go[6b] have recently shown that the quantum yield for the reaction of PhN_3 is dependent on its concentration, and ranges up to 300 under the conditions

(22) This is estimated by assuming a limiting rate constant of 2×10^{10} M^{-1} s^{-1} in acetonitrile.

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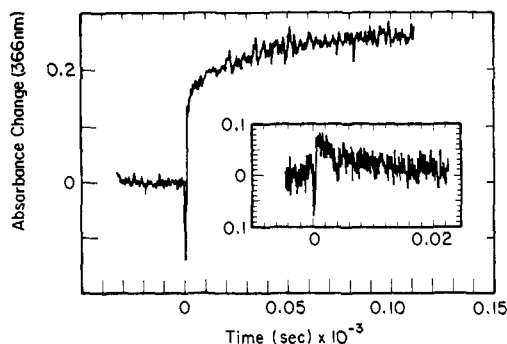
Photochemistry of Phenyl Azide

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Figure 3. Transient absorptions at 366 nm created by direct irradiation of PhN_3 and by triplet sensitization with benzophenone (inset) in acetonitrile solution.
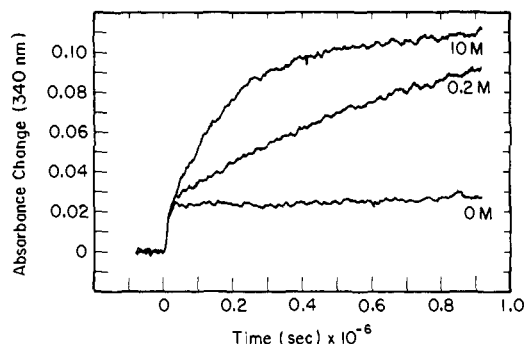

Figure 4. Absorbance change observed at 340 nm following pulsed irradiation of PhN_3 in hexane containing no, 0.2 M, and 10 M (neat) DEA.

Figure 5. Rate constants (k_A) for formation of 1*H*-azepines from irradiation of PhN_3 in hexane solutions containing DEA (triangles) or DBA (squares).

Table II. Reaction of PhN_3 with Amines

[DEA], M	$10^6 k_A$, s^{-1}	[DBA], M	$10^6 k_A$, s^{-1}	Az(DBA)/[Az(DBA) + Az(DEA)][a]
0.096	0.38	0.3	1.1	
0.19	1.2	0.6	2.3	
0.39	3.9	1.2	3.0	
0.77	4.8	1.5	3.5	
2.90	9.4	2.8	9.0	
4.65	8.1	3.8	9.0	
9.29	9.1	5.7	9.3	
0.12		0.12		0.40
1.0		1.0		0.40
3.8		3.8		0.42

[a] Relative yield of 3*H*-azepines formed from photolysis of PhN_3 in the presence of DBA (Az(DBA)) and DEA (Az(DEA)).

employed by Lewis and Saunders[24] and by Leyshon and Reiser.[25]

Pulsed irradiation of an acetonitrile solution containing benzophenone (2×10^{-4} M) and PhN_3 (2×10^{-4} M) at 266 nm under conditions where the light is absorbed primarily by the sensitizer shows the expected quenching of triplet benzophenone, but it does not give a detectable amount of the transient product absorbing at 340 nm obtained from the direct irradiation of PhN_3, Figure 3. This finding eliminates the possibility that the detected transient product in the direct irradiation of PhN_3 is PhN_3^{*3}. With certain restrictions, this result also excludes PhN̈[3] as the detected transient product.

The reaction between triplet benzophenone and PhN_3 presumably generates PhN_3^{*2} with high efficiency. However, we find that the quantum efficiency for consumption of PhN_3 by triplet sensitization with benzophenone irradiated at 254 nm is no more than ca. 20% of that obtained by the direct photolysis.[26] This result accounts for the residual 3*H*-azepine (**1**) formed during the triplet sensitization of PhN_3 in the presence of DEA and also for the low yields of azobenzene in the sensitization (vide supra). The small fraction of light absorbed directly by the PhN_3 is ca. five times more effective than is the light absorbed by the triplet sensitizer. This inefficiency in the triplet-sensitization reaction makes it difficult to eliminate PhN̈[3] as the detected transient product based solely on the pulsed sensitization experiment.

In principle it should be possible to decide if the detected transient is PhN̈[3] or the singlet-state intermediate by its behavior in the presence of DEA. If it is PhN̈[3], then it should not be formed when DEA is present in sufficient concentration because direct irradiation of PhN_3 gives no aniline (a triplet product). On the other hand, if it is the singlet-state intermediate, its formation should be unaffected by DEA, but it should react with the amine to give eventually 3*H*-azepine **1**.

Pulsed irradiation of PhN_3 in neat DEA at 266 nm generates a transient product that appears over a period of ca. 300 ns, Figure 4. The transient absorption spectrum is a composite of the one observed in inert solvent and that seen in neat amine when lower
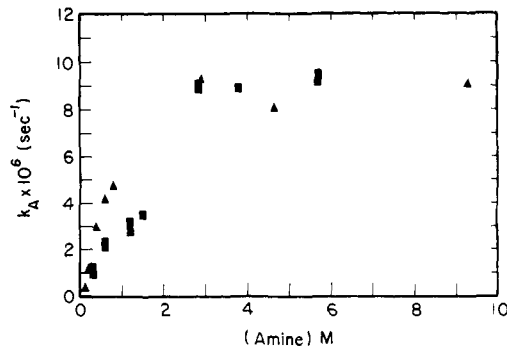
concentrations of DEA are used. That is, there is an immediate absorption change followed by a slower, amine-concentration-dependent growth in absorption, Figure 4. Plots of the observed pseudo-first-order rate constants for the growth at increasing amine concentrations (k_A) for DEA and for di-*n*-butylamine (DBA) are shown on Figure 5.

The dependence of k_A on the amine concentration is unusual. At high amine concentrations, above ca. 1 M for DEA, the value of k_A does not depend on the concentration or the structure of the amine. However, at lower concentrations the value of k_A depends on amine structure and its concentration in an approximately linear way. These observations indicate that the process being monitored has at least two steps and that the nature of the rate-limiting step in the sequence depends on the amine concentration. The second-order rate constants for the reaction at low amine concentration and the limiting first-order rate constants obtained at high amine concentrations are summarized in Table II.

To determine if the calculated second-order rate constants for the amine-dependent reaction correlate with eventual formation of the observed 3*H*-azepines, we carried out a classical competition experiment. A solution of PhN_3 in hexane containing both DEA and DBA over a range of total amine concentration was irradiated. The mixture of azepines obtained was analyzed by gas chromatography and shown to be within experimental error of that anticipated from consideration of the second-order rate constants derived from Figure 5, and also it is independent of the amine concentration. These data are summarized in Table II and show that the first step in the reaction of the singlet transient with the amines is irreversible.
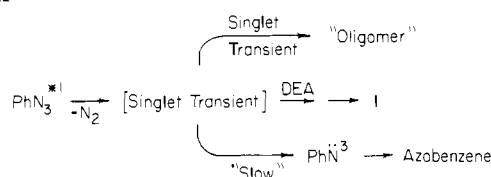
Discussion

The major objectives of this investigation were to identify the intermediates formed on photolysis of PhN_3 and to characterize their chemical and physical properties. These objectives have been achieved to a reasonable degree.

Photolysis of PhN_3 in a frozen glass or in solution at room temperature no doubt leads to some PhN̈[3].[16] However, our findings, and those of others,[17,18,28] indicate that under typical

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(26) The quantum yield for loss of N_2 on direct irradiation of PhN_3 is reported to be ca. 0.5.[6b,27]

Scheme II

$$PhN_3^{*1} \xrightarrow{-N_2} [\text{Singlet Transient}] \begin{cases} \text{Singlet Transient} \longrightarrow \text{"Oligomer"} \\ \xrightarrow{\text{DEA}} 1 \\ \xrightarrow{\text{"Slow"}} Ph\ddot{N}^3 \longrightarrow \text{Azobenzene} \end{cases}$$

conditions this is a quite minor path. By analogy with other aromatic azides,[1,13,14] and from the sensitization results, it is clear that azobenzene is formed from $Ph\ddot{N}^3$. When the concentration of PhN_3 in an inert solvent is greater than ca. 10^{-3} M, almost all of the PhN_3 is converted to intractable polymer, and the yield of azobenzene is very low. This result implies that there is a reaction, presumably of $Ph\ddot{N}^3$, or a precursor to $Ph\ddot{N}^3$, with PhN_3 that initiates polymerization. Some evidence for this has already been reported, in particular the quantum yield for disappearance of PhN_3 can be much greater than unity.[6b] This reaction is shown schematically in eq 5.
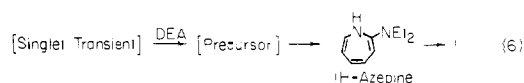
$$Ph\ddot{N}^3 + PhN_3 \xrightarrow{-N_2} [C_6H_5N]_2 \xrightarrow[-n\,N_2]{n\,PhN_3} [C_6H_5N]_{n+2} \quad (5)$$
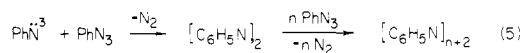
The observation that the yield of azobenzene decreases as the power of the photolysis source increases indicates that $Ph\ddot{N}^3$ is formed only slowly from a singlet-state reservoir. Irradiation with the laser generates a much higher instantaneous concentration of transient products than does conventional photolysis. If the transient product from photolysis of PhN_3 were primarily $Ph\ddot{N}^3$, then its rate of dimerization should increase under laser irradiation and give a concomitant increase in the yield of azobenzene. Just this behavior is observed for other aromatic azides,[2] but the opposite is seen for PhN_3. Thus, loss of N_2 from PhN_3^{*1} gives a transient product that can be trapped by amines, oligomerize to give intractable material, or, comparatively slowly, be converted to $Ph\ddot{N}^3$. This conclusion helps to exclude $Ph\ddot{N}^3$ as the transient product detected by laser spectroscopy in inert solvent and by optical absorption at low temperature.[19] These results are summarized in Scheme II.

In the scenario outlined in Scheme II the first intermediate detected in the direct laser photolysis of PhN_3 is associated with the singlet transient, not $Ph\ddot{N}^3$ as was previously suggested.[19c] Another observation that supports this assignment is that the transient product does not react rapidly with O_2. It is common for triplet intermediates to react with oxygen at the diffusion-limited rate. This reassignment is perfectly consistent with the results of Chapman and co-workers,[17,18] who identify the major low-temperature product unambiguously as dehydroazepine 3. Although the weight of the available evidence clearly supports the new assignment of the transient product, it is not unequivocal, nor is it ever likely to be so.

The structure of the singlet-state intermediate trapped by amines to give eventually the 3*H*-azepines has been a subject of considerately interest.[8,10,11,17,18] Our results provide some information on this question.
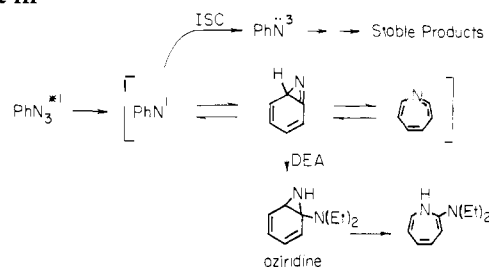
It is clear from the work of Sundberg[5c,11,15] that the reaction of DEA with the singlet-state intermediate does not give the 3*H*-azepine directly, but proceeds through the 1*H*-azepine. In the earlier work,[5c] the first transient observed from photolysis of PhN_3 in the amines is identified as the 1*H*-azepine. We concur with, or at least have no reason to doubt this assignment. However, the faster time resolution of our experiment reveals that there is a precursor to the 1*H*-azepine formed in the reaction of the singlet transient with the amine. Conversion of this precursor to the 1*H*-azepine does not depend on the amine concentration. These conclusions are summarized in eq 6.

$$[\text{Singlet Transient}] \xrightarrow{\text{DEA}} [\text{Precursor}] \longrightarrow \underset{1H\text{-Azepine}}{\text{(structure)}} \longrightarrow 1 \quad (6)$$

Scheme III

$$PhN_3^{*1} \longrightarrow \left[PhN^1 \rightleftharpoons \underset{\text{(azirine 2)}}{\text{(structure)}} \rightleftharpoons \underset{\text{(dehydroazepine 3)}}{\text{(structure)}} \right] \xrightarrow{\text{ISC}} Ph\ddot{N}^3 \longrightarrow \longrightarrow \text{Stable Products}$$

$$\downarrow \text{DEA}$$

$$\underset{\text{aziridine}}{\text{(structure)}} \longrightarrow \underset{}{\text{(structure)}}$$

There are three structures to be considered for the singlet transient; these are the singlet nitrene (PhN^1), azirine 2, and dehydroazepine 3. These intermediates are quite probably in equilibrium with each other since, eventually, $Ph\ddot{N}^3$ is formed on direct irradiation. Thus, the real questions are which isomer predominates at room temperature and which isomer reacts with the amines?

It is unlikely that PhN^1 will exist at a steady-state concentration high enough to undergo bimolecular reactions with reagents in solutions.[29] This is a consequence both of the anticipated rapid rate for irreversible intersystem crossing of PhN^1 to $Ph\ddot{N}^3$ and the expectation that the valence tautomeric azirine and dehydroazepine isomers are lower energy species than is PhN^1. For these reasons, and because it is unlikely that reaction of PhN^1 with amines will give the observed products, we conclude that PhN^1 is neither the predominant nor the reactive species in the singlet-transient equilibrium mixture.

The low-temperature IR spectroscopic studies leave little doubt that dehydroazepine 3 is the predominant species in the matrix at 8 K.[17,18] We have no reason to suspect that this is not true also at room temperature in solution, particularly if the dehydroazepine is the lowest energy isomer. On this basis we conclude that the first-formed transient product detected in the pulsed irradiation of PhN_3 is 3. Similarly, the optical spectrum previously[19] assigned to $Ph\ddot{N}^3$ formed by irradiation of PhN_3 at 77 K is also likely to be due, at least in part, to dehydroazepine 3.

Despite the conclusion that 3 is the predominant isomer in the equilibrium mixture comprising the singlet transient, it is not necessarily the isomer that is involved primarily in the reaction with amines. The experiments indicate that formation of the 1*H*-azepines is a two-step process from the singlet transient and that the second step is independent of amine concentration. These findings seem more consistent with the assignment of the reactive singlet transient to azirine rather than dehydroazepine. In this circumstance the first step in the sequence would generate an aziridine, and its subsequent valence tautomerization would give the 1*H*-azepine. In modest support of this assignment, it has been noted previously[31] that it is difficult to rationalize the isolation of only 3-amino-4-ethylthiotoluene when 4-azidotoluene is photolyzed in ethanethiol[30] if the dehydroazepine is the reactive isomer. Nonetheless, the assignment of the reactive singlet transient to the azirine, Scheme III, in this system still must be considered tentative.

Conclusions

Our findings reveal a reaonably complex series of reactions that connect PhN_3 to the ultimate products through a group of short-lived intermediates. Direct irradiation of PhN_3 generates its excited singlet state which rapidly loses N_2 to form a singlet transient. The singlet transient is probably the dehydroazepine, and it is in equilibrium with the singlet nitrene most likely forming the azirine first. Reaction of the azirine with amines initiates a series of reactions proceeding through the 1*H*-azepine and giving eventually the 3*H*-azepine.

(27) Reiser, A.; Marley, R. *Trans. Faraday Soc.* **1968**, *64*, 1806.
(28) Dunkin, I. R.; Thomson, P. C. P. *J. Chem. Soc., Chem. Commun.* **1982**, *1192*.

(29) Our results do not provide information on whether PhN_3^{*1} gives PhN^1 before becoming 2 or 3, but we feel that 2 or 3 must go through PhN^1 before becoming $Ph\ddot{N}^3$.
(30) Carroll, S. E.; Nay, E.; Scriven, E. F. V.; Suschitzky, H.; Thomas, D. R. *Tetrahedron Lett.* **1977**, 3175.
(31) This fact has been noted previously: Gallagher, P. T.; Idden, B.; Suschitzky, H. *J. Chem. Soc. Perkin Trans.* **1980**, 2362.

Formation of PhN_3 from the singlet transient is a slow process compared to the other reactions that it can undergo. We feel that this is a consequence of the relatively high energy of PhN^1 compared with the azirine and dehydroazepine. This point is presented more fully in the following paper.[2] The triplet nitrene can be formed by low-power direct irradiation of dilute solutions of PhN_3 in the absence of a nucleophilic trapping reagent or by triplet sensitization. This intermediate can be reduced to give ultimately aniline, it can dimerize to form azobenzene, or it can react with PhN_3.

It is evident from comparison of the naphthyl azides with phenyl azide that the balance between the stability of the azirine and dehydroazepine intermediates is quite close.[2,32,33] Also, substituents on phenyl azide clearly change the position and rate of attaining equilibrium of the singlet intermediates. This is seen for pentafluorophenyl azide which gives the triplet nitrene exclusively[28] and p-nitrophenyl azide which does not give nucleophile incorporation products.[34] These observations suggest that these electron-poor singlet nitrenes do not form the relatively long-lived azirine or dehydroazepine, and consequently, they intersystem cross rapidly and irreversibly to the triplet nitrenes. This conclusion has direct bearing on the use of these compounds is photoaffinity labeling and is discussed in detail elsewhere.[35]

Experimental Section

General. Proton magnetic resonance (^1H NMR) spectra were obtained on a Varian Associates HR220 Fourier transform spectrometer in deuteriochloroform with tetramethylsilane and as internal standard. Mass spectra were recorded on Varian MAT CH-5 and 731 mass spectrometers in the Mass Spectroscopy Laboratory, University of Illinois. Infrared absorption spectra were obtained on a Nicolet 7199 FT-IR instrument or a Perkin-Elmer model 1320 infrared spectrophotometer. Melting points were determined on a Nalge Company hot-stage apparatus or a Buchi melting point apparatus. Analytical gas chromatography was performed with use of a Varian Model 3700 or Model 2700 gas chromatograph equipped with flame ionization detectors and linear temperature programmer. Analyses were on 6-ft glass columns containing 5% Carbowax, or 5% OV-17 on DMCS treated acid washed Chromosorb W with use of helium as carrier gas at 30 mL/min. The column temperature was ramped linearly from 65 to 200 °C at 10 °C/min. High-performance liquid chromatography was performed on a Perkin-Elmer Series 2 liquid chromatograph equipped with a variable wavelength detector with a 10 μm silica column, 0.26 × 25 cm, with 1% 2-propanol in hexane as elutant. Reverse-phase HPLC was formed with a 0.46 × 28 cm C8/10 column eluting with an acetonitrile–water mixture.

Materials. Hexane (Mallinckrodt, spectrophotometric grade) and acetonitrile (Aldrich Gold Label) for laser spectroscopy were used without further purification. Diethylamine (Aldrich) and di-n-butylamine (Aldrich) were distilled under nitrogen. 2-Acetonaphthone (Baker) was recrystallized from ethanol, and p-chlorotoluene (Aldrich) was distilled under nitrogen. Acetonitrile (Burdick and Jackson distilled in glass, UV grade) for reverse-phase liquid chromatography was recycled by distillation recovering the acetonitrile–water azeotrope, taking no fractions boiling higher than 79 °C. Phenyl azide was vacuum distilled and the purity monitored by gas chromatography. 2-(Diethylamino)-3H-azepine was prepared by irradiation of PhN_3 in diethylamine and identified by comparison of its spectra with those reported previously.[8]

Pulsed Nanosecond Laser Photolysis Apparatus. The pulsed-laser apparatus is set up similarly to that previously described.[36] However, the excitation source is a Molectron Q switched Nd-YAG laser frequency quadrupled to 266 nm. The pulse width at half-height is typically 20 ns with base line to base line time duration of ca. 40 ns. Power measurements of the laser intensity indicate ca. 5 mJ per pulse.

The probe beam is generated for experiments at times shorter than 4 μs by a USSI 3CP-3 Xenon flash lamp. For experiments at times longer than 4 μs an Osram 450 W/2 Xenon arc lamp with power supply manufactured by SLM Instruments is employed as the probe beam source.

The probe beam intensities were monitored as previously described[36] or with data collection by a Biomation 8100 analog to digital converter interfaced with an LSI 11 computer. All of the laser flash photolysis experiments were performed with the probe perpendicular to the excitation beam.

2-(Di-n-butylamino)-3H-azepine. A solution of PhN_3 (1.0 g, 8.4 × 10^{-3} M) in 15 mL of hexane and 15 mL of freshly distilled di-n-butylamine was purged with nitrogen for 6 min and irradiated in a Rayonet photoreactor at 254 nm for 90 min. The dark solution was evaporated in vacuo, and the oily residue was chromatographed on silica gel eluting with 5% ether in benzene to yield 0.80 g (44%) of 2-(di-n-butylamino)-3H-azepine. NMR ($CDCl_3$) δ 7.10 (d, 1, J = 8 Hz), 6.31 (d of d, 1, J = 8 Hz and 5 Hz), 5.27 (d of d, 1, J = 8 Hz and 5 Hz), 5.08 (q, 1, J = 8 Hz), 3.27 (t, 4), 2.60 (b, 2), 1.51 (m, 4), 1.27 (m, 4), 0.92 (t, 6); IR (Nujol) 1600, 1505, 1310, 1275, 1210, 1135, 720, 670 cm^{-1}; MS (70 eV) m/e (rel intensity) 220 (100), 205 (11), 191 (19), 177 (11), 163 (55), 135 (32), 122 (32), 121 (46), 108 (45), 107 (85), 94 (41), 93 (87), 92 (91); molecular ion calcd for $C_{14}H_{24}N_2$, m/e 220.1935, found 220.1937.

Yield of 2-(Dialkylamino)-3H-azepines. A solution of PhN_3 (3.6 × 10^{-3} M), diethylamine (1 M) or di-n-butylamine (1 M), and pentadecane as internal standard in hexane was purged with nitrogen for 6 min. The samples were irradiated in a Rayonet photoreactor equipped with 350-lamps and then analyzed by gas chromatography on the Carbowax column. The yield of 2-(diethylamino)-3H-azepine is 71% and the yield of 2-(di-n-butylamino)-3H-azepine is 93%. Conversions of PhN_3 were kept below 50% to minimize photodecomposition of the products.

Direct Irradiation of Phenyl Azide. Solutions of PhN_3 (1 × 10^{-4} – 4.4 × 10^{-3} M) in acetonitrile were purged with nitrogen for 6 min. The samples were irradiated in a Rayonet photoreactor equpped with 254-nm lamps, with the frequency-quadrupled Nd-YAG laser at 2 Hz. or with an Ultraviolet Products Model SCT-1 Hg lamp. Internal standards added after irradiation were nitrobenzene (normal phase) or diethyl phthalate (reverse phase) and the yield of azobenzene was determined by HPLC analysis monitoring at 280 nm. Eluant for normal-phase analysis was 1% 2-propanol in hexane and for reverse-phase analysis was 50% water in acetonitrile. The results are reported in Table I.

The irradiated samples were stored in the dark at room temperature and monitored several times over a period of ca. 20 h. No change in the yield of azobenzene or the amount of PhN_3 was observed.

The azobenzene was shown to be stable to the photolysis conditions when the light is absorbed by PhN_3. A solution of 3.6 × 10^{-3} M PhN_3 and 1 × 10^{-3} M azobenzene was irradiated and analyzed as described above. No change in the concentration of azobenzene was found at ca. 50% conversion of PhN_3.

Triplet Sensitization of Phenyl Azide. A solution of PhN_3 (2 × 10^{-4} M) and benzophenone (2 × 10^{-4} M) in acetonitrile (or p-chlorotoluene (0.1 M) in hexane) was purged with nitrogen for 6 min. The samples were irradiated in the Rayonet at 254 nm, or with the frequency-quadruple Nd-YAG laser at 2 Hz. The yield of azobenzene was determined by reverse-phase HPLC with the sensitizers as internal standards. The results are reported in Table I.

Triplet Sensitization of Phenyl Azide in 1 M Diethylamine. A solution of PhN_3 (3.6 × 10^{-3} M), 2-acetonaphthone (1.5 × 10^{-2} M), DEA (1.0 M), and pentadecane as internal standard in hexane was purged with N_2 for 6 min in a Pyrex cell. A second sample was prepared that contained in addition to the above components 1.2 × 10^{-2} M piperylene. The samples were irradiated in the Rayonet photoreactor at 350 nm. Gas-chromatographic analysis on the Carbowax column shows aniline in 33% yield and 2-(diethylamino)-3H-azepine in 64% yield in the sample without piperylene. Only 2-(diethylamino)-3H-azepine in 67% yield is found in the sample containing piperylene.

Quantum Yield for Direct and Sensitized Phenyl Azide Photolyses. Separate samples of PhN_3 (2 × 10^{-4} M) in acetonitrile and PhN_3 (2 × 10^{-4} M) with benzophenone (1.2 × 10^{-3} M) in acetonitrile were purged with nitrogen for 6 min. The solutions were placed on a Merry-Go-Round and irradiated in a Rayonet photoreactor at 254 nm. The sample containing only PhN_3 was removed after 60 s of irradiation, and the sample with the sensitizer was photolyzed for 180 s. Nitrobenzene was added to each sample as an internal standard, and the consumption of PhN_3 was determined by gas chromatography on the OV-17 column. After correcting for the light absorbed directly by PhN_3 (ϕ_{-PhN_3} = 0.5)[6] in the sample containing benzophenone and the longer irradiation time for the sensitized sample, the quantum yield for loss of PhN_3 by triplet sensitization is estimated to be 20% of the direct-irradiation value.

Phenyl Azide Competition Reaction with Diethylamine (DEA) and Di-n-butylamine (DBA). Three solutions of (2 × 10^{-3} M) PhN_3 and pentadecane as internal standard in hexane containing equivalent amounts of both DEA and DBA each at 0.12, 1.0, and 3.7 M were prepared. Each solution was purged with nitrogen for 6 min and then

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irradiated in the Rayonet photoreactor at 254 nm. Gas-chromatographic analysis on the OV-17 column shows that the ratio of the yields of photoproducts 2-(diethylamino)-3*H*-azepine and 2-(di-*n*-butylamino)-3*H*-azepine is ca. 6:4 at each concentration of amines. The results are reported in Table II.

Kinetics of Benzophenone-Excited Triplet Quenching by Phenyl Azide. Solutions of benzophenone (2×10^{-4} M) and varying concentrations of PhN$_3$ in acetonitrile were prepared and purged with N$_2$. The samples were irradiated with the Nd-YAG laser at 266 nm, and the time dependence of the benzophenone triplet absorption was monitored at 525 nm. The first-order rate constants for the decay were obtained by least-squares fit and plotted against the PhN$_3$ concentrations, Figure 2.

Kinetics of Photoproduct Growth with Diethylamine and Di-*n*-butylamine. Solutions of PhN$_3$ (3.6×10^{-3} M) in hexane with diethylamine (9.6×10^{-2} to 9.30 M) or with di-*n*-butylamine (0.30–5.70 M) were prepared. Laser-flash photolysis with the Nd-YAG laser at 266 nm was

performed by monitoring the rate of growth of the photoproduct at 340 nm. The pseudo-first-order rate constants for the growth at 340 nm were obtained by a computer fit of the data by least squares. The observed rate constants were plotted against the concentration of amine to give Figure 5. The pseudo-first-order rate constants varied from 3.8×10^{5} to 9.5×10^{6} s^{-1}.

Photochemistry of Naphthyl and Pyrenyl Azides: Chemical Properties of the Transient Intermediates Probed by Laser Spectroscopy

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Abstract: The photochemistry of 1-naphthyl azide, 2-naphthyl azide, 1-pyrenyl azide, and 2-pyrenyl azide was examined in inert (benzene) and reactive (diethylamine) solvents. These studies employ a combination of product analysis, low-temperature spectroscopy, and laser-flash photolysis to reveal the chemical and physical properties of the highly reactive, short-lived intermediates formed in these reactions. In all cases two intermediates account for the observations. One of these is the triplet nitrene and the other is a ground-state singlet transient identified as an azirine. The relationship between these intermediates controls the chemical outcome of the reaction.

Thermolysis or photolysis of polynuclear aromatic azides in some cases leads to products clearly related to those obtained from phenyl azide,[1] and in other circumstances quite different results are observed. The eventual outcome of these reactions is a consequence of the chemical and physical properties of the short-lived intermediates formed when the azide is excited. We report herein results of an investigation of the photolysis of 1-naphthyl azide (1-NaN$_3$), 2-naphthyl azide (2-NaN$_3$), 1-pyrenyl azide (1-PyN$_3$), and 2-pyrenyl azide (2-PyN$_3$). These findings expose the properties of the intermediates generated in these reactions and permit some useful generalizations about the photochemistry of aromatic azides.


1-NaN$_3$ 2-NaN$_3$ 1-PyN$_3$ 2-PyN$_3$
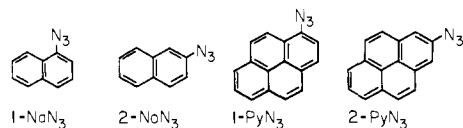
The photochemical and thermal reactions of the polynuclear aromatic azides have been studied for quite some time.[2] Of this

group 1-NaN$_3$ and 2-NaN$_3$ are the most thoroughly characterized. The chemistry of 1-PyN$_3$ has been examined and applied to photoaffinity labeling and to photoimaging systems.[3]

Irradiation of 1-NaN$_3$ in hydrocarbon solvents reveals two reactions. The first is coupling to form azonaphthalene, and the second is reduction to give 1-naphthylamine (1-NaNH$_2$).[4] The relative yields of the coupling and reduction products depend on the reaction conditions,[5] but both are presumed to be characteristic of triplet 1-naphthylnitrene (1-NaN^3).

Photolysis of 1-NaN$_3$ in diethylamine (DEA) is reported to give low yields of 1-NaNH$_2$ and azonaphthalene. However, quite in contrast, irradiation of 2-NaN$_3$ under the identical conditions gives a good yield of 2-(diethylamino)-1-naphthylamine, eq 1.[6] This product is believed to arise from the trapping of a short-lived, singlet-state intermediate by the nucleophilic DEA. This general
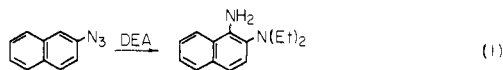
reaction, where substitution by a nucleophile causes regiospecific 1,2-migration of the azide nitrogen, was seen first in the photolysis of 5-benzo[*b*]thiophenyl azide.[7] It has since become generally observed from photolysis of 2-azido aromatics, but not from the corresponding 1-substituted isomers.[8-14]

(1) See previous paper in this issue.
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