(1) In the low-temperature phase A, the molecular arrangement is highly ordered. A crystal lattice with long-range order in terms of position, orientation, and conformation is observed. However, rather complex molecular motions occur. The coalescence of CP/MAS NMR resonances below 200 K indicates a interconversion process between identical conformations that, however, leads to an exchange of the carbons between the different sites in the ring structure. A pseudorotationlike motion, similar to that of cyclotetradecane molecules in solution is proposed. Additional jumplike reorientations of the molecules as a whole may superimpose the conformational interconversion to restore the crystalline order. At temperatures above the coalescence of the NMR spectrum, substantial line broadening of the NMR resonances occurs, which is due to motional modulation of the dipolar C-H decoupling. At that temperature the molecular motion has reached a correlation time comparable with the inverse of the decoupling field frequency, i.e., $10^{\frac{1}{5}}$ Hz. The T_2 minimum may be either due to the same conformational interconversion or to the onset of an additional motion like a whole-body rotation. All motions do not result in disorder that would affect the entropy.

(2) At the transition to the mesophase B, the symmetry of the lattice increases but still remains low (monoclinic). There is a considerable decrease in the density. The transition appears by thermal analysis as an order-disorder transition of high cooperativity. Sudden narrowing of the MAS NMR resonance indicates a sharp increase of the rate of the molecular motion observed at low temperature, or more likely, the onset of an additional type of molecular motion. The molecules remain, however, conformationally largely homogeneous. Also, recent ²H NMR experiments show two steps for the onset of motion.³³ The first is the conformational interconversion process below the solid-solid transition and the second most probably a whole-body rotation, starting at the solid-solid transition. Consistent with the known crystal lattice, a jumplike reorientation between different orientational positions acceptable by the crystal, caused by confor-mational mobility, is proposed. This could explain the rather drastic change in molecular packing and the high entropy of transition and at the same time is consistent with the observed high long-range positional, orientational, and conformational order. The low degree of molecular symmetry results thus in rather large

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transition entropies, even though the molecular motions are jumplike and lead to disordering between only few different sites with identical molecular conformation.

The third point follows from the first two and relates to the classification of mesophases discussed in the beginning.

(3) Although the thermotropic formation of mesomorphic states on heating results from onset of larger scale molecular motion, molecular dynamics alone may not always also produce disorder. Considerable and complex motions, such as the ring inversions, can occur in a fully ordered crystal, provided the crystalline order is not changed. Conformational interconversion in the A polymorph of cyclotetradecane does not result in conformational disorder. At the transition to the B polymorph conformational mobility causes dynamic orientational disordering, but again no substantial conformational disorder. The transition is linked to the changes in the crystal lattice that, in turn, increase the molecular mobility. The orientational disordering is not diffuse, but discrete and jumplike. In this way, the crystal-lattice symmetry remains low and the anisotropy high. Although conformational disorder is not the main characteristic feature of this mesophase, conformational mobility is certainly the driving force for its formation.

Because of the positional order, the mesophase of cyclotetradecane (polymorph B) does not fit into the concept of liquid crystals. It also does not fit fully into the definition of a plastic crystal due to its rather high orientational order. But since the molecules are also not significantly disordered conformationally, the condis concept may also not apply. Cyclotetradecane represents an intermediate case. It demonstrates the need to discuss not only positional, orientational, and conformational order, but also the positional, orientational, and conformational dynamics. Ordered crystals may be dynamically mobile in one or several of the types of motion. Cyclotetradecane is an example of a molecule that displays a mesophase with partial orientational disorder and high conformational mobility.

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Registry No. Cyclotetradecane, 295-17-0.

Photochemistry of 3- and 4-Nitrophenyl Azides: Detection and Characterization of Reactive Intermediates

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Abstract: Irradiation of nitro-substituted aromatic azides initiates a complex series of chemical reactions that lead to different products depending on the details of the experiment. There is evidence that four reactive intermediates participate in product-determining reactions. These are the singlet nitrene, the triplet nitrene, the triplet azide, and the ring-expanded dehydroazepine. The chemical and physical properties of each of these species is modified by the nitro substituent. The reactivity of the singlet nitrene with nucleophilic amines is increased, the lifetime of the dehydroazepine is shortened, and the triplet nitrene becomes a powerful single-electron acceptor. Nitro-substituted aromatic azides are widely used in photolabeling experiments. The findings of this study suggest that they may be inappropriate choices as photolabeling agents in many circumstances.

Systematic investigation of the photochemistry of aromatic azides began in 1951¹ and has endured to the present time.² The continuous high level of interest in these reactions for more than 35 years is a result of both their challenging, enigmatic nature and the importance of their practical applications.^{3,4} A major objective of this inquisition has been the identification and

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	product and yields, %							
	azo 1	aniline 2	nitroso 4	nitro 3	azoxy 5	hydrazine 8	mixed azoxy 11	
CH ₃ CN/LP ^a /N ₂ -purged	75					1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.1.		
$CH_3CH/HP^b/N_2$ -purged	>96							
$CH_3CN/LP/O_2$ -purged	20		11	12	28			
$CH_3CN/HP/O_2$ -purged	97		3					
DTA $(0.5 \text{ M})/\text{PhCl/LP/N}_2$ -purged	50	30						
DTA $(0.5 \text{ M})/\text{PhCl}/\text{HP}/\text{N}_2$ -purged	~ 100							
$DEA/LP/N_2$ -purged		80				9		
$DEA/HP/N_2$ -purged		80				9		
RNO ^c (0.15 M)/CH ₃ CN/LP/N ₂ -purged							75	
RNO (0.15 M)/CH ₃ CN/LP/O ₂ -purged			4				80	
RNO (0.15 M)/CH ₃ CN/HP/N ₂ -purged ($\lambda = 355$ nm)	55						31	
RNO (0.15 M)/CH ₃ CN/HP/O ₂ -purged (λ = 355 nm)			2				80	
RNO $(4.8 \times 10^{-3} \text{ M})/\text{CH}_3\text{CN}/\text{LP}/\text{O}_2$ -purged	9		19	9	20		17	

^aLP indicates irradiation under low-power conditions. ^bHP indicates irradiation under high-power conditions. ^cRNO is 3-methylnitrosopropane.

Chart I



characterization of the reactive intermediates formed when these azides are irradiated. The complexity of this task is revealed simply by considering the number of these species. Included in the count are at least three excited states and a minimum of six short-lived, ground-state intermediates. The role played by these species varies with the structure of the aromatic azide and with the conditions of its irradiation. This complexity is clearly documented for the case of phenyl azide, where the existing literature is both profuse in theories and contradictory in claims.⁵⁻¹⁶

The nitro-substituted aromatic azides occupy a special position because of their widespread use as photolabeling agents of biological macromolecules.¹⁷ The success of this application depends largely on the specific properties of the intermediates formed from their irradiation. The photochemistry of these azides has been the subject of several previous studies. Of great significance is the observation by Wasserman of ESR spectra characteristic of nitrenes when 3- or 4-nitrophenyl azide (3NPA and 4NPA, respectively; Chart I) was irradiated at low temperature in frozen media. These findings certify that the ground states of 3- and

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4-nitrophenyl nitrenes (3NPN and 4NPN, respectively) are triplets.¹⁸ Smirnov and co-workers also irradiated 4NPA in frozen media.¹⁹ They report an optical absorption band at ca. 377 nm that is assigned to triplet 4NPN.

Photolysis of 4NPA in benzene solution gives primarily 4,4'dinitroazobenzene (1); in methyl alcohol 4-nitroaniline (2, 4%)is formed along with azobenzene 1; and when O_2 is present, p-dinitrobenzene (3), 4-nitrosonitrobenzene (4), and 4,4'-dinitroazoxybenzene (5) are formed too. These are believed to be products characteristic of reaction of the triplet nitrene.^{20,21} Irradiation of phenyl azide in the presence of an amine (diethylamine, for example) gives good yields of 2-amino-3H-azepines. This reaction signals formation of an intermediate dehydroazepine from singlet phenyl nitrene (or the excited azide).^{11,22} Irradiation of 4NPA in dimethylamine is reported to give aniline 2 (90%) with no trace of the amino-3*H*-azepine.²³

The photochemistry of 3NPA is largely unstudied. A recent report by Platz and co-workers²⁴ describes its irradiation in toluene solution at temperatures ranging from +25 to -196 °C. In all cases, 3,3'-dinitroazobenzene (6) is formed, but 3-nitroaniline (7) is observed only in fluid solutions, while N-benzyl-3-nitroaniline is formed exclusively in frozen, solid samples. All of these products are attributed to reactions of triplet 3NPN.

We report herein the results of examination of the photochemistry of 3- and 4NPA with a range of trapping agents and under a variety of conditions.²⁵ The findings permit the characterization of reactive intermediates and allow some general comment on the applicability of these compounds to photolabeling experiments.

Results

4-Nitrophenyl Azide. Interpretation of the photochemistry of aromatic azides is often embrangled by unstoppable formation of uncharacterizable products euphemistically called "tar". This problem occurs under some conditions in the photolysis of 4NPA. Its irradiation in deoxygenated acetonitrile solution at ca. 313 nm (200-W Hg lamp filtered through aqueous potassium chromate; referred to below as "low-power" photolysis) gives as the only characterizable product azobenzene 1 in 75% yield; the remainder is tar. The azobenzene is stable under these photolysis conditions; its irradiation does not give tar. A similar result is obtained when

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Figure 1. Bottom: Transient absorption spectra recorded following flash photolysis of 4NPA in benzene. Key: solid line, recorded 20 ns after laser pulse, assigned to triplet 4NPN; dotted, dashed, and broken lines, recorded 5, 15, and 36 μ s after the laser pulse, assigned to 4,4'-dinitro-azobenzene. Top: Rate of change of the absorbance of 4,4'-dinitro-azobenzene fit to a second-order kinetic rate law.

4NPA is irradiated in deoxygenated benzene. However, when 4NPA in either acetonitrile or benzene is irradiated with a 1-MW pulsed N₂ laser at 337 nm ("high-power" photolysis), the exclusive product is azobenzene 1 in >96% yield. High-power photolysis creates a much greater initial concentration of excited states than does irradiation under low-power conditions. This difference will not affect the relative yields of reactions whose rates are first order in the excited state (or its successor intermediates) but will of course greatly increase the yields of all reactions whose rates are higher order in these species. The results of these experiments and of the others described below are summarized in Table I.

There are two routes possible for the formation of 1 from irradiation of 4NPA. Both require formation of triplet 4NPN. In the first, triplet 4NPN combines with ground-state azide and gives the azobenzene after loss of N₂. The second, more traditional route is dimerization of triplet 4NPN. The power dependence of the yield of 1 is consistent with the second possibility. Additional support for this path comes from a crossover experiment. Irradiation of an acetonitrile solution of 4NPA (2×10^{-3} M) also containing phenyl azide (6×10^{-3} M) under low-power conditions (4NPA absorbs the light) gives only azobenzene 1; (4-nitrophenyl)azobenzene, the crossover product, is not detected (eq 1).

$$NO_2 - O_2 - N_3 + O_2 - N_3 \frac{hv}{low-power}$$

 $NO_2 - O_2 - N = N - O_2 (1)$

The rate of dimerization of triplet 4NPN can be measured by laser transient absorption spectroscopy. Irradiation of a benzene or acetonitrile solution of 4NPA (5×10^{-4} M) with the output of a nitrogen laser (337 nm, 13 ns, 7 mJ) creates a transient species with an absorption maximum at 380 nm (Figure 1). The transient is formed within the rise time of the laser. This absorption is assigned to triplet 4NPN by comparison with its spectrum at low temperature¹⁹ and because of the nearly quantitative yield of azobenzene 1 formed from irradiation of the azide under these conditions. The absorption of azobenzene 1 grows into the spectrum over several microseconds following a second-order rate law (Figure 1). Least-squares analysis of these data gives the rate constant for dimerization of triplet 4NPN (k_{azo}) equal to 1.0 × 10⁹ M⁻¹ s⁻¹. We carefully measured the quantum yields for reaction of 4NPA in acetonitrile solution at several azide concentrations. Low-power photolyses of degassed solutions of the azide (an additional Corning UG-11 filter was used in these experiments to stop irradiation of the actinometer with visible light) were analyzed both by gas chromatography and by absorption spectroscopy. The relative quantum yield for reaction of 4NPA shows no sensitivity to its concentration (ca. 0.001-0.1 M), and the absolute quantum yield (0.7, calculated by comparison with a ferrioxalate actinometer) is not greater than one. These experiments are in conflict with the recent report²⁷ of a dramatic increase of this quantum yield to values above 400 for concentrated solutions of 4NPA.

Reaction of 4NPN with Amines. Irradiation of 4NPA in the presence of N,N-dimethyl-*tert*-butylamine (DTA) gives azobenzene 1 and 4-nitroaniline (2) from the azide and N-methyl-*tert*-butylamine (MTA) from oxidative demethylation²⁸ of the amine (eq 2). Under low-power conditions, the yield of 1 de-

$$NO_{2} - \bigvee N_{3} + (CH_{3})_{3} CN(CH_{3})_{2} \xrightarrow{h_{2}}_{low-power}$$

$$DTA$$

$$1 + NO_{2} - \bigvee NH_{2} + (CH_{3})_{3} CN(H_{3})_{2} \xrightarrow{H_{3}} (2)$$

$$MTA \xrightarrow{H_{3}} (2)$$

creases and that of 2 increases as the concentration of DTA is raised. For example, irradiation of solutions containing 0.5 M DTA gives 1 and 2 with yields of 50 and 30%, respectively, at 40% conversion of 4NPA (2 is consumed by secondary photolysis at higher conversion). Critically, irradiation of an identical solution under high-power conditions gives only the azobenzene in nearly quantitative yield. At high concentration of triplet 4NPN (high-power condition), where its dimerization to 1 is fast, the efficiency for formation of aniline 2 is greatly reduced. This shows that aniline formation competes directly with the dimerization of triplet 4NPN, and thus aniline must arise from reaction of the triplet nitrene with DTA.

Traditionally, the photoreduction of aromatics azides to anilines is postulated to proceed by hydrogen abstraction by the triplet nitrene to give a radical pair whose subsequent reactions generate the final products (eq 3).² A second possibility is that a sin-

$$\left[NO_{2} - (N)\right]^{3} + R_{2}N \cdot CH_{3} \longrightarrow NO_{2} - (N) + R_{2}N \cdot CH_{2}$$
(3)

$$\begin{bmatrix} NO_2 & & & \\ & & & & \\ & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & & & \\ & & &$$

gle-electron transfer forms radical ion intermediates (eq 4). This route may be specially favored in the present case, because the electron-withdrawing nitro group will facilitate the reduction of the nitrene and because DTA (a tertiary amine) has a low oxidation potential. Döpp and co-workers²⁹ developed an isotope test to distinguish between hydrogen abstraction and single-electron-transfer processes. We applied this test to the reaction of triplet 4NPN with DTA.

The product isotope effect for the reaction of triplet 4NPN with DTA was determined in an intramolecular competition with N-(trideuteriomethyl)-N-methyl-*tert*-butylamine (DTA- d_3) and then for an intermolecular competition with a 1/1 mixture of N,N-bis(trideuteriomethyl)-*tert*-butylamine (DTA- d_6) and DTA. The isotope effects were measured by analysis of the CI mass spectra of the MTA formed from reactions in chlorobenzene or benzonitrile solutions (these solvents were chosen to facilitate the mass spectroscopy). The data are summarized in Table II; they support operation of an electron-transfer mechanism.

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Table II. Isotope Effect for Photolysis of 4NPA with DTA

solvent	amine	isotope effect
PhCl	DTA-d ₃	3.2 ± 0.9
PhCl	$DTA-d_6 + DTA$	1.8 ± 0.1
PhCN	$DTA-d_3$	3.3 ± 0.2
PhCN	$DTA-d_6 + DTA$	1.5 ± 0.1

Irradiation of 4NPA under low-power conditions in neat diethylamine (DEA) gives two products (eq 5). The major component (80%) is aniline 2, the minor is N-(4-nitrophenyl)-N', N'-diethylhydrazine (8, 9%). These products are not formed from



the same reactive intermediate. When the concentration of DEA is lowered to 0.1 M, the ratio of aniline 2 and azobenzene 1 (the products from triplet 4NPN) to hydrazine 8 in the product mixture increases to ca. 40. Significantly, high-power irradiation of 4NPA in neat DEA gives 1 at the expense of 2 but does not change the yield of 8. Clearly, aniline 2 and azobenzene 1 are formed from reaction of triplet 4NPN, and hydrazine 8 is formed from a precursor to the triplet nitrene. There are two plausible precursors to triplet 4NPN, the triplet azide and the singlet nitrene. Only singlet 4NPN can reasonably form 8.

Analysis by infrared spectroscopy of the products from irradiation of 4NPA in an Ar matrix at 8 K clearly reveals 5-nitro-1,2-dehydroazepine (9) (eq 6).³⁰ It is significant that no 5nitro-2-(diethylamino)-3*H*-azepine (see below) can be detected from the irradiation of 4NPA at room temperature, even in neat DEA.

$$NO_2 \longrightarrow N_3 \xrightarrow{h_V} NO_2$$
 (6)

Reaction of 4NPN with O₂ or Nitroso Compounds. Low-power irradiation of 4NPA (to 40% conversion) in O₂-saturated solution gives azobenzene 1 (20%), dinitrobenzene 3 (12%), nitroso compound 4 (11%), and azoxybenzene 5 (28%) (eq 7). High-power

irradiation of an identical solution gives 1 almost exclusively (97%) and a low yield (ca. 3%) of nitrosobenzene 4. Significantly, dinitrobenzene 3 cannot be detected among the products from irradiation of 4NPA in O_2 -saturated solutions under high-power conditions. The product yields from irradiation under the lowpower conditions change with the extent of conversion of 4NPA. In particular, as the reaction proceeds, the yield of nitrosobenzene 4 decreases and the yield of azoxybenzene 5 increases. Control experiments show that this is not due to the secondary photolysis of 1 or of 4.

The route for formation of azoxybenzene 5 was investigated by examining the photolysis of 4NPA in deoxygenated solutions containing either nitrosobenzene or 2-methyl-2-nitrosopropane (0.15 M). Irradiation under low-power conditions gives the mixed azoxy compound 10 or 11 in 75% yield (for 11); only a trace of azobenzene 1 could be detected (eq 8). In contrast, high-power

$$NO_{2} - \bigvee_{N_{3}} NO_{3} + R - NO \xrightarrow{h_{v}}_{low power} NO_{2} - \bigvee_{N=}^{O} N = \overset{O}{\overset{+}{N-R}} R$$

$$R = Ph, (CH_{3})_{3}C \qquad 10; R = Ph \\ 11; R = (CH_{3})_{3}C \qquad 10; R = Ph \\ 11; R = (CH_{3})_{3}C \qquad R = ($$

photolysis of an identical solution gives azobenzene 1 (55%) and mixed azoxybenzene 11 in only 31% yield. In addition, low-power irradiation of an oxygen-saturated solution of 4NPA that also contains the nitrosopropane inhibits the formation of most of the oxygen-trapping products. Significantly, formation of nitrosobenzene 3 cannot be stopped completely by the nitrosopropane. Clearly, these experiments show that triplet 4NPN can be trapped by O_2 to give eventually dinitrobenzene 3 and nitrosobenzene 4. Similarly, the triplet nitrene can be captured by nitroso compounds to form azoxybenzene products. The data are summarized in Table I.

Limits to the rates for reaction of triplet 4NPN with O_2 and with the nitrosopropane can be obtained by laser spectroscopy. Unfortunately, the overlap of the absorption spectra of 4NPA and azobenzene 1 with those of azoxybenzene 11 and the nitrosopropane prohibits the direct measurement of these rates. However, the results of competition experiments establish relative rates of reactivity and define upper limits to the absolute rate constants.

The initial concentration of triplet 4NPN in the irradiated zone, $[4NPN]_0$, under high-power conditions is readily calculated from the final absorbance of azobenzene **1** formed from a single laser pulse to be 4×10^{-5} M. The rate of dimerization of triplet 4NPN has its maximum value at early times in the reaction, since this rate is directly proportional to the square of the triplet nitrene concentration. Combination of the triplet nitrene with the nitrosopropane (k_{RNO}) is a pseudo-first-order process whose rate is directly proportional to the first power of the triplet nitrene concentration. The kinetic network for competition between dimerization and capture of triplet 4NPN by the nitrosopropane can be easily solved to give an upper limit to k_{RNO} by assuming that the nitrene concentration (eq 9). In this experiment the yields

$$k_{\rm RNO} < \frac{k_{\rm azo} \left[4{\rm NPN}\right]_{\rm o}}{\left[{\rm RNO}\right]} \quad X \left[\begin{array}{c} {\rm Azoxybenzene \ 10} \\ {\rm Azobenzene \ 1} \end{array} \right] = 1 \times 10^5 \, {\rm M}^{-1} \, {\rm s}^{-1} \tag{9}$$

of azobenzene 1 and azoxybenzene 11 were determined by irradiation of 4NPA at 355 nm (where the nitrosopropane does not absorb) under high-power conditions. This analysis shows that the maximum value $k_{\rm RNO}$ can have is 1×10^5 M⁻¹ s⁻¹. Similarly, analysis of the product yields from a competition between reaction of triplet 4NPN with O₂ and the nitrosopropane gives an upper limit to the rate constant for reaction of the nitrene with oxygen ($k_{\rm O_2}$). Irradiation of 4NPA under low-power conditions, where the yield of azobenzene 1 is low (Table I), gives a value for $k_{\rm O_2}$, according to eq 10 (where ArN[O₂] is the sum of the yields of all products from trapping of the nitrene by oxygen), of less than 2×10^5 M⁻¹ s⁻¹.

$$k_{O_2} < \frac{k_{RNO} [RNO]}{[O_2]} \times \left[\frac{ArN[O_2]}{Azoxybenene \ 10}\right] = 2 \times 10^5 \ M^{\cdot 1} \ s^{\cdot 1}$$
 (10)

3-Nitrophenyl Azide. The photochemistry of 3NPA is similar to that of 4NPA with a few important exceptions. Irradiation of 3NPA (5×10^{-3} M) in deoxygenated acetonitrile or benzene solution under low-power conditions gives 3,3'-dinitroazobenzene (6) in only ca. 42% yield; the remainder of the azide is converted to tar. The yield of 6 is increased by high-power photolysis, but only to ca. 65%. Control experiments show that the azobenzene is stable to irradiation under these conditions. These experiments are summarized in Table III.

Reaction of 3NPA with DEA. The results of irradiation of 3NPA in solutions containing DEA depend dramatically on the concentration of the amine. This is illustrated graphically in Figure 2. At the lowest DEA concentrations the major products are azobenzene 6 and 3-nitroaniline (7) (Scheme I). As the concentration of DEA is raised, the yield of 7 increases, that for 6 decreases, and three additional products are formed. Two of these, 2-(diethylamino)-6-nitro-3H-azepine (12) and its 4-nitro isomer

⁽³⁰⁾ Professor I. Dunkin, University of Strathclyde, private communication.

Table III. Product Distribution from Photolysis of 3NPA $(5 \times 10^{-3} \text{ M})$

	product yield, %						
	azo 6	nitroso ^c	nitrod	azoxy ^e			
CH ₃ CN/LP ^a /N ₂ -purged	42						
$CH_3CN/HP^b/N_2$ -purged	65						
CH ₃ CN/LP/O ₂ -purged	5	7	10	13			
CH ₃ CN/HP/O ₂ -purged	60	3	2				

^aLP indicates low-power irradiation. ^bHP indicates high-power irradiation. ^c3-Nitrosobenzene. ^dm-Dinitrobenzene. ^c3,3'-Dinitroazoxybenzene.



Figure 2. Relative yields of products from irradiation of 3NPA at various concentrations of DEA in benzene. Key: (∇) 3,3'-dinitroazobenzene; (Δ) 3-nitroaniline; (O) ratio of hydrazine 14 to azepine 12; (\Box) ratio of hydrazine 14 to azepine 13.

Scheme I



(13), are formed at moderate DEA concentrations. At the highest amine concentrations, formation of N,N-diethyl-N'-(3-nitrophenyl)hydrazine (14) becomes a significant process. This concentration-dependent behavior signals the participation of at least three intermediates in the photoreaction of 3NPA. Aniline 7 and azobenzene 6 come from reaction of the triplet amine, adducts 12 and 13 arise from capture of dehydroazepines, and hydrazine 14 is formed by interception of the singlet nitrene. Laser absorption spectroscopy reveals a transient species with maximum at ca. 400 nm that is formed within the 13-ns rise time of the laser. It is not possible to assign this absorption uniquely to triplet 3NPN or to the dehydroazepines with the data in hand.

Irradiation of 3NPA in the Presence of O_2 . Photolysis of 3NPA in O_2 -saturated solutions gives *m*-dinitrobenzene, 3-nitrosonitrobenzene, 3,3'-dinitroazoxybenzene, and azobenzene 6. The effect of the power of the light sources and the presence of added nitroso compounds is the same in this case as it is for 4NPA (Table III). Thus, triplet 3NPN can be captured by O_2 or by a nitroso compound in competition with its dimerization to form the azobenzene.

Discussion

The results reported above provide a detailed description of the photochemistry of nitro-substituted aryl azides under a variety of conditions. It is clear that irradiation causes loss of nitrogen and formation of reactive intermediates. Three classes of intermediates are revealed by these experiments: the singlet nitrenes, dehydroazepines, and the triplet nitrenes. There is a commonality of structure and reactivity among the intermediates that is almost independent of the position of nitro substitution. Below we discuss the properties of each intermediate class in an attempt to relate structure to reactivity in a systematic way.

Irradiation of 4NPA leads to loss of N₂ and formation of the singlet 4NPN. In neat DEA, 9% of the singlet nitrene can be trapped as hydrazine 8. Similarly, hydrazine 14 is obtained from irradiation of 3NPA in neat amine. A related reaction has been observed from photolysis of 4-cyanophenyl azide,³¹ but no hydrazines are detected from irradiation of phenyl azide under these conditions.^{2,6,32} Apparently, singlet aryl nitrenes may be trapped by amines to form hydrazines only if they are substituted with powerful electron-withdrawing groups. This may be associated either with an increase in the electrophilicity of the singlet nitrene or with an increase in its lifetime. It is reasonable that the first effect is the dominant one. Electron withdrawal from the already electron-deficient nitrene nitrogen atom will increase the rate of its reaction with nucleophiles. On the other hand, the lifetime of the singlet nitrene will be determined primarily by intersystem crossing to the triplet. The rate of this process is unknown, but for related carbenes it is very fast and not particularly sensitive to structural change.33

One of the hallmarks of aryl azides is their ring expansion to dehydroazepines and subsequent reaction with amines to give 2-amino-3*H*-azepines.^{2,6,32} Irradiation of 4NPA in a low-temperature, rare gas matrix does form 5-nitro-1,2-dehydroazepine (9),³⁰ but this intermediate cannot be captured by DEA at room temperature. There are several possible explanations for this result. First, it could be that dehydroazepine 9 is not formed at room temperature. This could be the case if formation of the dehydroazepine at low temperature is a multi-photon process or if special matrix effects control the reaction pathway.³⁴ Second, it is possible that dehydroazepine 9 is formed, but that it is specially unreactive and thus not captured by DEA. This possibility seems unlikely; if it does anything, the electron-withdrawing nitro group should increase the rate of reaction of the dehydroazepine with amines. A third possibility is that the lifetime of dehydroazepine 9 is so short at room temperature that its reaction with DEA cannot compete with its departure. The dehydroazepine may exist in a shallow, but inescapable minimum at 8 K, which provides only an insignificant barrier to it departure at 298 K. The bimolecular rate constant for reaction of the related 5-(N,N-dimethylamido)-1,2-dehydroazepine with DEA is $4.4 \times 10^7 \text{ M}^{-1}$ $s^{-1,22}$ Even if the electron-withdrawing nitro group does not significantly increase the rate constant for the nucleophilic trapping reaction, the lifetime for dehydroazepine 9, if it is formed at all at room temperature, is calculated to be less than 1 ns from these results. This conclusion gains additional support from the transient absorption experiments that show formation of triplet 4NPN in less than 13 ns. In contrast, the 4- and 6-nitro-1,2-dehydroazepines formed from photolysis of 3NPA are captured by DEA, albeit never in high yield. This result implies a somewhat longer lifetime for the dehydroazepines from this azide.

Triplet nitrenes are formed from irradiation of 3NPA and 4NPA with high efficiency. The reactions of these triplets account for most of the products isolated from photolysis of these azides under all conditions examined. We explored four reactions that are characteristic of these intermediates: dimerization to azobenzenes, reduction to anilines, capture by oxygen, and reaction with nitroso compounds.

Formation of azobenzene from triplet 4NPN occurs by dimerization, not by combination of the nitrene with the ground-state azide. This conclusion is supported both by the kinetic results (second-order formation of azobenzene 1) and by the absence of crossover products with phenyl azide. The dimerization of triplet

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Scheme II



4NPN occurs at a rate very close to the diffusion-limited value. This is as expected for the combination of triplet species to form a singlet (and perhaps triplet, but certainly not quintet) product. Since we observe no increase in the quantum yield when the irradiation of 4NPA is performed at high concentration, there is no evidence to support postulation of a chain reaction involving 4NPN.²⁷ To the extent examined, formation of azobenzene **6** from triplet 3NPN parallels the reaction of 4NPN.

The formation of nitroaniline 2 from irradiation of 4NPA in the presence of amines is an intriguing process. The power-dependent yield of this reaction identifies it as a process that competes with formation of azobenzene 1, and thus one that originates with triplet 4NPN. The mechanism of this reaction is revealed by analysis of the product isotope effects when reaction with DTA plus DTA- d_6 is compared with that of DTA- d_3 . If hydrogen atom abstraction by the triplet nitrene is the product-determining step, then these two cases should give nearly identical primary isotope effects. On the other hand, if a process whose rate is independent of the hydrogen isotope (electron transfer, for example) determines the outcome of the reaction, then $DTA-d_3$ may exhibit an isotope effect, but in the first approximation, there should be no isotope effect for the mixture of DTA and DTA- d_6 . The results (Table II) support the second hypothesis more strongly. There is a clearly significant difference between the isotope effect for $DTA-d_3$ and for the 1:1 mixture of DTA- d_6 and DTA, but the isotope effect for DTA- d_3 is not unity. Similar results have been obtained in related experiments and interpreted to signal either a competition between electron-transfer and hydrogen abstraction pathways or hopping of the radical cation from one amine to another (selfexchange) in competition with loss of hydrogen.³⁵ Whichever explanation is correct, the results of this experiment eliminate hydrogen atom abstraction by the triplet nitrene as the exclusive mechanism for reduction to aniline and support product-determining electron transfer to form the nitrene radical anion and the amine radical cation. The MTA and 4-nitroaniline isolated from this reaction can be formed from a sequence that includes subsequent hydrogen atom transfer from the radical cation to the radical anion, protonation of the anion, and hydrolysis of the resulting iminium cation to give N-methyl-tert-butylamine (Scheme II). Unfortunately, we could not analyze the reaction of 3NPA with DTA. The absorption spectrum of photoreactive 3-nitroaniline overlaps too strongly with that of the azide.

The reaction of triplet intermediates with oxygen occupies a special position in chemistry. It is usually the case that triplets react with O_2 at a rate close to the encounter-limited value. This is true when the triplet is an excited state and energy transfer to form singlet oxygen occurs and when the triplet is a ground state and irreversible chemical reactions are dominant. A particularly relevant example is the combination of triplet carbenes with oxygen to form carbonyl oxides. This spin-allowed reaction occurs rapidly

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Scheme III



and irreversibly in all of the examined cases.36

Triplet 4NPN reacts with O_2 . This fact is revealed by the power dependence of the yields of nitrosobenzene 4 and dinitrobenzene 3 in oxygen-saturated solutions. At high power, when dimerization of the triplet nitrene is fast, 3 is not formed and the yield of 4 is reduced by a factor of ca. 4 when compared with low-power irradiations, (Scheme III). The low residual yield of the nitrosobenzene in the high-power experiment indicates that there is a second, minor, triplet nitrene concentration-independent path that also leads to formation of this product (see text below).

Our results indicate that the reaction of triplet 4NPN with O_2 gives first (4-nitrophenyl)nitroso oxide (16, Scheme III). This is the expected product by analogy with the reaction of triplet carbenes with oxygen.³⁶ Also, a recent study of the reaction of phenylnitrene with oxygen reveals that phenylnitroso oxide may be trapped by sulfoxides in competition with its conversion to nitrobenzene by competing bimolecular and unimolecular processes.³⁷ Nitroso oxides may exist either as zwitterions or biradicals. In either case, dimerization of 16 to the six-membered ring diperoxide (17) is expected to occur rapidly.³⁸ Two fragmentation paths from 17 are possible; the first gives nitrosobenzene 4 and O_2 , the second forms dinitrobenzene ³.

A new reaction channel becomes available as the photolysis of 4NPA proceeds in O_2 -containing solutions. At high conversion, when the concentration of nitrosobenzene 4 has built up, some triplet 4NPN is captured by the nitrosobenzene to form azoxybenzene 5. The operation of this path is documented by the crossover and power-dependence experiments run with nitrosobenzene and the nitrosopropane. Competition experiments reveal that triplet 4NPN reacts with both nitroso compounds and oxygen. The fact that all of the triplet nitrene is diverted to the mixed azoxy compound is indicated by the absence of dinitrobenzene 3 from the products at high nitrosopropane concentration. Nitrosobenzene 4 is still formed under these conditions, but in much reduced yield. This observation points again to operation of a second route for formation of 4 that does not pass through triplet 4NPN. One possibility for the non-nitrene route to 4, previously considered from a different point of view,²¹ is the reaction of the excited triplet azide with O_2 . This hypothesis, also shown in Scheme III, is consistent with the data, but there is no direct evidence to support it.

One surprising feature concerning the reaction of triplet 4NPN with O_2 is that it occurs at a relatively slow rate. We are unable to obtain a direct measure of the rate constant, but the estimate of its upper limit reveals a value ca. 5 orders of magnitude less than the diffusion-limited value found for the reaction of triplet

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carbenes with oxygen. A related observation was recently reported by Platz and co-workers from their study of triplet phenylnitrene.⁵ Their results in combination with our own now show clearly that this is a general phenomenon. Although it is not possible with the data in hand to explain the huge difference between the rates of reaction of oxygen with nitrenes and carbenes with certainty, we propose that the additional nonbonding electrons of the former play an important role. Comparison of the electronic interactions as O₂ approaches either a nitrene or a carbene reveals an unavoidable, repulsive, four-electron interaction in the former that is absent in the latter. This interaction will certainly increase the energy of the transition state for the combination of a triplet nitrene with oxygen and thereby slow the reaction in this case. We are planning additional experiments to test this hypothesis.

Conclusions

Irradiation of nitro-substituted aromatic azides initiates a complex series of chemical reactions that lead to different products depending on the details of the experiment. There is evidence for participation of four reactive intermediates: the singlet nitrene, the triplet nitrene, the triplet azide, and the ring-expanded dehydroazepine. The chemical properties of these intermediates are profoundly affected by the nitro substituent. This is revealed most clearly by comparison with the chemistry of phenyl azide. Singlet phenyl nitrene cannot be trapped by amines to give hydrazines, but the nitro-substituted nitrenes combine with diethylamine in this way. The nitro-substituted nitrenes ring expand to dehydroazepines at low temperature, as does phenyl nitrene, but the nitro-substituted compounds appear to be short-lived and, at best, are only inefficiently trapped by amines at room temperature. The triplet nitro-substituted nitrenes are formed efficiently, and their reactions account for most of the products obtained when the azides are irradiated. The reaction of triplet 4NPN with amines follows a novel electron-transfer route. Also, it is generally true that triplet aryl nitrenes react with oxygen only very slowly.

These findings have important implications for the use of nitro-substituted azides in photolabeling procedures. This application requires formation of a covalent bond between the photolabel and a targeted biological macromolecule. Nitro-substituted aromatic azides are often used in this way. However, our experiments reveal that these azides will only be effective when there is a nucleophilic functional group at the targeted site. And, even under these circumstances, covalent bond formation will occur only inefficiently because of the short lifetime of the singlet nitrene and dehydroazepine. Nitro-substituted aromatic azides may be inappropriate choices as photolabeling agents in many circumstances.

Experimental Section

Laser Spectroscopy. Unless otherwise noted, transient absorption spectra were recorded with the previously described nitrogen laser apparatus.³⁹ Sample solutions were prepared in quartz cells with Teflon stopcocks and purged with N_2 prior to each experiment. The samples were prepared so that the absorbance of the compound to be irradiated was ca. 3.0 in a 1-cm cell at the excitation wavelength. The concentrations of 4-nitrophenyl azide and 3-nitrophenyl azide were adjusted to be 4.8×10^{-4} and 2×10^{-3} M, respectively. To monitor the second-order kinetics, the probe beam was parallel to the laser beam and the concentrations of azides were adjusted to be 1.2×10^{-4} M so that the absorbance of azide at 337.1 nm was ca. 0.6.

Preparation of 4-Nitrophenyl Azide. 4-Nitrophenyl azide was prepared according to the literature procedure⁴⁰ and recrystallized from ethanol to give pale yellow needles: mp 70.1 °C; IR (CHCl₃, cm⁻¹) 2050, 1050, 1320, 1270; ¹H NMR (CDCl₃, δ) 8.25 (d, 2 H, J = 10 Hz), 7.15 (d, 2 H, J = 10 Hz); UV-vis (CH₃CN, nm) 310 ($\epsilon = 1.55 \times 10^4$ M⁻¹ cm⁻¹). Anal. Calcd for $C_6H_4N_4O_2$: C, 43.91; H, 2.45; N, 34.13. Found: C, 43.78; H, 2.21; N, 33.78.

Preparation of 3-Nitrophenyl Azide. 3-Nitrophenyl azide was prepared according to the literature procedure⁴⁰ and recrystallized from anhydrous ethanol to give pale yellow needles: mp 52.0-52.5 °C; IR (CHCl₃, cm⁻¹) 2123, 1533, 1354, 1300; ¹H NMR (CDCl₃, δ) 8.01 (d, m, 1 H, J = 8 Hz), 7.89 (t, 1 H, J = 2 Hz), 7.54 (t, 1 H, J = 8 Hz), 7.35 (d, m, 1 H, J = 8 Hz); UV-vis (CH₃CN, nm) 260 ($\epsilon = 1.08 \times 10^4$ $M^{-1} \text{ cm}^{-1}$), 325 ($\epsilon = 1600 \text{ M}^{-1} \text{ cm}^{-1}$). Anal. Calcd for $C_6H_4N_4O_2$: C, 43.91; H, 2.46; N, 34.14. Found: C, 43.53; H, 2.35; N, 33.68.

Quantum Yield for Photolysis of 4-Nitrophenyl Azide. A solution of 4-nitrophenyl azide (0.1 M) and tridecane (12.6 mg, as internal standard for GC) in acetonitrile was prepared. An aliquot of this solution (0.5 mL) was diluted to 5×10^{-3} M. The concentrated and diluted azide samples (2.0 mL) were placed in Pyrex cuvettes and degassed by three freeze-pump-thaw cycles. The degassed samples were irradiated at 310 nm with a mercury lamp through a glass filter (UG-11) and a filter solution of K_2CrO_4 in water. The dilute sample was removed after 16 min (18% conversion) of irradiation; the concentrated solution was irradiated for 140 min (7% conversion). The consumption of 4-nitrophenyl azide was determined by UV-vis absorption spectroscopy and by GC on a 5-m OV-1 megabore column. The quantum yield of disappearance of 4-nitrophenyl azide was determined by comparison with a ferrioxalate actinometer.⁴¹ Irradiation of the azide solutions under these conditions gives a quantum yield of 0.7 ± 0.2 independent of its starting concentration.

Preparation of DTA- d_6 . A 50-mL three-necked flask was equipped with a condenser, a N_2 inlet, and a magnetic stir bar. The flask was cooled in an ice-salt bath and 5.72 g (0.078 mol) of tert-butylamine (purified by distillation from sodium) and 15 mL of ether were added. To the stirred mixture was added 55.6 mL of *n*-butyllithium in hexane (1.55 M) by injection. Cooling was continued for 15 min after the final addition, and then the mixture was heated at 40–50 $^{\circ}\mathrm{C}$ for 2 h. The turbid solution was cooled in an ice bath, and then 12.5 g (0.086 mol) of iodomethane- d_3 in 5 mL of ether was added by injection. A white precipitate formed gradually, and then the mixture was heated at 40-50 °C for 2 h. The reaction mixture was cooled in an ice bath and treated a second time with *n*-butyllithium and iodomethane- d_3 with the same quantities and procedure as above. At the conclusion of the second reaction period, a 25% sodium hydroxide solution was added until the solution was strongly basic. Excess sodium chloride was added to saturate the solution. The organic layer was separated, and the aqueous layer was extracted with ether. The combined ether extracts were acidified with 8 N hydrochloric acid and washed with water. The aqueous wash was placed in an ice bath, and solid sodium hydroxide was added gradually to the cooled mixture until the solution became strongly basic and sodium chloride precipitated. The solution was extracted with ether, and the organic layer was dried over potassium hydroxide. The crude product was purified by fractional distillation from sodium: bp 83-86 °C; ¹H NMR (CDCl₃, δ) 1.05 (s), MS (CI) 99% d_6 .

Preparation of DTA-d₃. The trideuterio amine was prepared in two steps. First, methylation of tert-butylamine with benzaldehyde and dimethyl- d_6 sulfate according to the previously described procedure⁴² gives tert-butylmethylamine (MS (CI) 91.7% CD₃). Second, the tert-butyldimethylamine-d₃ was prepared by alkylation of the deuteriated tertbutylmethylamine with formaldehyde and formic acid:⁴³ bp 67 °C, ¹H NMR (CDCl₃, δ) 1.10 (s, 1 H), 1.05 (S, 9 H); MS (CI, 70 eV) m/e 90, 72; 86.4% d₃.

Photolysis of 4-Nitrophenyl Azide in Benzene or Acetonitrile. A solution of 4-nitrophenyl azide (5 × 10^{-3} M) in benzene or acetonitrile was prepared, placed in a quartz cell with a Teflon stopcock, and then purged with nitrogen. This solution was irradiated with a 200-W Hg lamp through a filter of aqueous potassium chromate ($\lambda = 295-315$ nm) for 6 min. Analysis by gas chromatography showed azobenzene 1 in 75% yield. When an identical solution was irradiated with a nitrogen laser at 337 nm, the yield of azobenzene 1 increased to 96%. The yield of azobenzene 1 is independent of the concentration of azide and the conversion of 4-nitrophenyl azide in the sample.

Photolysis of 4-Nitrophenyl Azide in 0.5 M tert-Butyldimethylamine. A solution of 4-nitrophenyl azide $(1 \times 10^{-2} \text{ M})$, tert-butyldimethylamine (0.5 M), and undecane (as an internal standard) in chlorobenzene was prepared, placed in a quartz cell, and then purged with N_2 for 6 min. This solution, stirred with a small magnetic bar, was irradiated at 310 nm with a 200-W Xe/Hg lamp through a filter of potassium chromate in water for 4 min. Gas chromatographic analyses on an OV-101 packed column showed 4-nitroaniline in 30% yield and azobenzene 1 in 50% yield. The product tert-butylmethylamine, formed by demethylation of DTA, was analyzed by GC on a 15-m SE-54 cross-linked capillary column at 35 °C. The yield of tert-butylmethylamine was 35%.

A solution of 4-nitrophenyl azide $(1 \times 10^{-3} \text{ M})$, tert-butyldimethylamine (0.5 M), and undecane in chlorobenzene or benzonitrile was prepared, placed in a quartz cell, and purged with N_2 for 10 min. This

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solution was irradiated with the pulsed nitrogen laser for 10 min at 4 pulses/s and then analyzed by GC. The yield of 4,4'-dinitroazobenzene was ca. 100%. Neither *tert*-butylmethylamine nor *p*-nitroaniline were detected by GC.

Photolysis of 4-Nitrophenyl Azide in the Presence of Diethylamine (DEA). A solution of 4-nitrophenyl azide (300 mg) and DEA (4.6 g) in 200 mL of hexane was prepared and placed in a 250-mL round-bottom flask fitted with a magnetic stirring bar. The azide solution was purged with N₂ for 10 min, then it was irradiated in a Rayonet photoreactor with 350-nm lamps for 6 h. The reaction mixture was purified by thick-layer chromatography on basic alumina, eluting with a mixture of ethyl acetate and hexane (1:8) to give azobenzene 1, 4-nitroaniline, and hydrazine 8: IR (CHCl₃, cm⁻¹) 1559, 1325, 1111, 887; MS (70 eV) m/e 209, 194, 180, 119; ¹H NMR (CDCl₃, δ) 8.08 (d, 2 H, J = 9 Hz), 6.82 (d, 2 H, J = 9 Hz), 4.89 (br, 1 H), 2.74 (br, 4 H), 1.07 (t, 6 H, J = 7 Hz); high-resolution mass spectrum, m/e 209.1165.

The yields of these products depend on the concentration of DEA. A solution of 4-nitrophenyl azide $(5 \times 10^{-3} \text{ M})$ in neat DEA was purged with N₂ and irradiated in a Rayonet photoreactor with 350-nm lamps for 4 min. Analysis by GC showed 4-nitroaniline in 80% yield and hydrazine 8 in 9% yield.

Deuterium Labeling Studies. A solution of 4-nitrophenyl azide $(1 \times 10^{-2} \text{ M})$ in chlorobenzene or benzonitrile in the presence of DTA- d_6 (0.5 M) or a 1:1 mixture of DTA and DTA- d_3 was prepared and purged with N₂ for 6 min. These solutions were irradiated at 310 nm with a 200-W Xe/Hg lamp through a filter of K₂CrO₄ aqueous solution for 4 min. *tert*-Butylmethylamine was analyzed by GC/MS on a 30-m SE-30 capillary column at room temperature. The deuterium content of the *tert*-butylmethylamine was analyzed by chemical ionization mass spectroscopy with ammonia as the reagent gas. The molecular ion was monitored. The results are shown in Table II.

Photolysis of 4-Nitrophenyl Azide in O_2 -Saturated Acetonitrile. A solution of 4-nitrophenyl azide $(6.0 \times 10^{-3} \text{ M})$ in acetonitrile was prepared and placed in a Pyrex cell. The azide solution was purged with O_2 for 10 min and then irradiated with a 200-W Xe/Hg lamp through a filter of K₂CrO₄ aqueous solution for 6 min. The solution was analyzed by GC/MS, which showed that the photoproducts were nitrobenzene 4, dinitrobenzene 3, azobenzene 1, and azoxybenzene 5; identified by comparison with authentic samples independently prepared. The yields of the photoproducts were determined by GC on a 10-m megabore OV-17 column. The yields of the nitrosobenzene and azoxybenzene 5, 28%; and azobenzene 1, 20%.

When an identical solution of 4NPA was irradiated at 337 nm with the nitrogen laser at 4 pulses/s, nitrosobenzene 4 was formed in 3% yield and azobenzene 1 was formed in 96% yield at 20% conversion of the azide. Nitrobenzene 3 and azoxybenzene 5 were not detected by GC analysis.

Photolysis of 4NPA with Nitroso Compounds. A solution of 4-nitrophenyl azide $(6.0 \times 10^{-3} \text{ M})$ and nitrosobenzene $(1.5 \times 10^{-2} \text{ M})$ was purged with N₂ for 6 min and then irradiated and analyzed as described above. Only the mixed azoxybenzene **10** was formed at 60% conversion of the azide. The product was characterized by mass spectroscopy and by comparison with previously reported data:⁴⁴ mp 153.8-154.5 °C;

UV-vis (CH₃CN, nm) 337 ($\epsilon = 1.84 \times 10^4$ M⁻¹ cm⁻¹), 380 ($\epsilon = 6100$ M⁻¹ cm⁻¹); MS (70 eV) m/e 243, 105, 77. A solution of 4-nitrophenyl azide (5×10^{-3} M) and 2-methyl-2-nitrosopropane (0.15 M) in 100 mL of acetonitrile that was purged with N₂ for 5 min and irradiated at 350 nm in a Rayonet photoreactor for 40 min gave azoxybenzene 11: mp 116-117 °C; UV-vis (CH₃CN, nm) 311 ($\epsilon = 1.5 \times 10^4$ M⁻¹ cm⁻¹); NMR (CDCl₃, δ) 8.25 (d, 2 H, J = 9 Hz), 7.85 (d, 2 H, J = 9 Hz), 1.70 (s, 9 H).

Photolysis of 3-Nitrophenyl Azide in Benzene. A solution of 3-nitrophenyl azide (80 mg, 1.6×10^{-2} M) in 30 mL of benzene was placed in a round-bottom flask and purged with N₂ for 10 min. This solution was irradiated in a Rayonet photoreactor with 350-nm lamps for 140 min. The solution was concentrated on a rotary evaporator and purified by preparative TLC on silica, eluting with a mixture of chloroform and benzene (1:2.5). The isolated product was recrystallized from ethanol, dried in vacuo, and identified as azobenzene 6: mp 154–155 °C;⁴⁵ UV-vis (CH₃CN, nm) 440 (ϵ = 435 M⁻¹ cm⁻¹), 310 (ϵ = 4700 M⁻¹ cm⁻¹), 270 (ϵ = 1.8 × 10⁴ M⁻¹ cm⁻¹); ¹H NMR (CDCl₃, δ) 8.80 (t, 2 H, J = 2 Hz), 8.40 (d, m, 2 H, J = 8 Hz), 8.32 (d, m, 2 H, J = 8 Hz).

Photolysis of 3-Nitrophenyl Azide with DEA. A solution of 3-nitrophenyl azide (50 mg, 6.1×10^{-3} M) in 25 mL of hexane and 25 mL of freshly distilled DEA was placed in a glass cylinder with quartz windows, purged with N₂ for 5 min, and irradiated with stirring through a filter of aqueous K₂CrO₄ for 1.5 h. The photolyzed solution was concentrated on a rotary evaporator and then chromatographed on basic alumina, eluting with benzene, to give 3-nitroaniline, azepine 12, azepine 13, and hydrazine 14. The yields of the photoproducts were determined by GC on a 6-ft 10% OV-101 packed column; they depend on the concentration of DEA as shown in Figure 2.

Azepine 12: IR (CHCl₃, cm⁻¹) 1530, 1320; ¹H NMR (CDCl₃, δ) 8.70 (d, 1 H, J = 2 Hz), 7.15 (d, d, 1 H, $J_1 = 9$ Hz, $J_2 = 2$ Hz), 5.20 (t, d, 1 H, $J_1 = 7$ Hz, $J_2 = 9$ Hz), 3.39 (q, 2 H, J = 7 Hz), 3.2 (q, 2 H, J = 7Hz), 2.80 (br, 2 H), 1.29 (t, 3 H, J = 7 Hz), 1.08 (t, 3 H, J = 7 Hz); high-resolution mass spectroscopy, m/e 209.1164 (M⁺, C₁₀H₁₅N₃O₂). Azepine 13: IR (CHCl₃, cm⁻¹) 1580, 1480, 1320; ¹H NMR (CDCl₃, δ) 7.82 (d, 1 H, J = 7 Hz), 7.54 (d, 1 H, J = 7 Hz), 5.71 (t, 1 H, J = 7Hz), 3.71 (q, 2 H, J = 7 Hz), 3.52 (q, 2 H, J = 7 Hz), 3.50 (br, 2 H), 1.31 (t, 3 H, J = 7 Hz), 1.05 (t, 3 H, J = 7 Hz); high-resolution mass spectroscopy, m/e 209.1165 (M⁺, C₁₀H₁₅N₃O₂). Hydrazine 14: IR (CHCl₃, cm⁻¹) 1530, 1320; ¹H NMR (CDCl₃, δ) 7.71 (t, 1 H, J = 2 Hz), 7.50 (d, d, 1 H, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 7.25 (t, 1 H, J = 8 Hz), 7.12 (d, d, 1 H, $J_1 = 8$ Hz, $J_2 = 2$ Hz), 4.51 (br, 1 H), 2.71 (q, 4 H, J = 7Hz), 1.07 (t, 6 H, J = 7 Hz); high-resolution mass spectroscopy, m/e209.1163 (M⁺, C₁₀H₁₅N₃O₂).

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