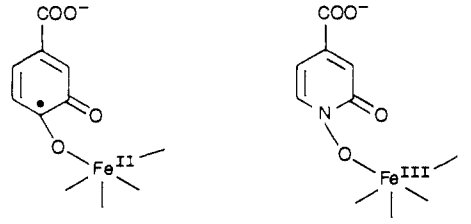
fashion to the ferric center via the *N*-oxide oxygen, leaving the other exogenous ligand coordination site accessible to a solvent molecule. Our current studies suggest that the monodentate coordination in the activated substrate may result from electron transfer from the catecholate to the ferric center yielding a ferrous–semiquinone complex (Scheme II); such a complex would allow the C–O and O–Fe bonds to form in rapid succession, yielding the intermediate peroxide complex. In this proposed mechanism, the ketonized isonicotinate *N*-oxide would be a close steric and electronic analogue to the putative monodentate semiquinone, i.e.



The synthetic complexes we have discussed serve as good functional mimics for the dioxygenase-catalyzed oxidative cleavage of catechols to the extent that an Fe^{III}–catecholate complex reacts with O_2 to yield specifically the intradiol cleavage product as dictated by the experimental observations on the enzymes. However, there is still a long way to go toward a full understanding of the enzyme–substrate complex and its reaction with O_2. First, it is of interest to note that, while the synthetic complex of the tripodal ligand with one phenolate is the slowest reacting of the complexes studied, the dioxygenases have active sites with *2* tyrosines coordinated to the iron center.[1,37] Second, though the synthetic complexes exhibit visible and Raman spectral features that grossly mimic those of the dioxygenase ES complexes, i.e., the presence of low-energy catecholate-to-Fe^{III} charge-transfer transitions, the model complexes do not simulate the spectral shape of the ES complexes well. Most importantly, the ES complexes react with O_2 six orders of magnitude faster[7] than [Fe(BPG)DBC]. Clearly, the dioxygenase active site possesses features yet to be duplicated in the models. What features are missing may become apparent with a careful scrutiny of the active site as crystallographic studies of protocatechuate 3,4-dioxygenase from *Pseudomonas aeruginosa* unfold.[37]

Acknowledgment. This work has been supported by the National Institutes of Health (GM-33162). We thank Professor Doyle Britton and Paul D. Boyle for their invaluable assistance in the crystallographic studies and Dr. A. S. Borovik for his efforts in the synthesis of the HDP ligand.

Supplementary Material Available: A listing of atomic positional parameters and thermal parameters (4 pages). Ordering information is given on any current masthead page.

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1,2-Didehydroazepines from the Photolysis of Substituted Aryl Azides: Analysis of Their Chemical and Physical Properties by Time-Resolved Spectroscopic Methods

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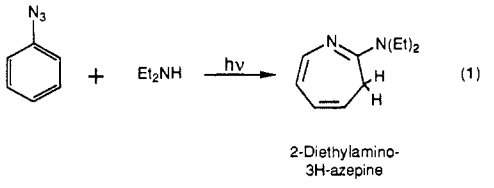
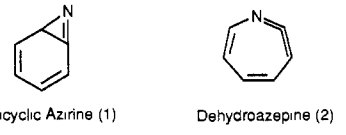
Abstract: A series of substituted 1,2-didehydroazepines was prepared by photolysis of their precursor aryl azides. The chemical and physical properties of the didehydroazepines were probed by means of conventional chemical trapping experiments and by time-resolved spectroscopy with IR and UV detection. The experimental results are compared with predictions from MNDO calculations. The didehydroazepines are formed from the azides with efficiencies that depend systematically on the nature of the substituent. In some cases, didehydroazepines are not formed at all. The didehydroazepines react relatively rapidly with starting aryl azide and with added amines. The rate of their reaction is largely controlled by the electronic properties of the substituent on the didehydroazepine. These results permit prediction of the reactivity of didehydroazepines from their structure.

It is well established that irradiation of phenyl azide at room temperature in a solution containing diethylamine gives 2-(diethylamino)-3*H*-azepine in good yield[3] (eq 1). It was recognized



a long time ago that this reaction must proceed through a metastable intermediate whose structure was formulated as either 7-azabicyclo[4.1.0]hepta-2,4,7-triene (bicyclic azirine **1**) or 1,2-didehydroazepine (**2**) (Chart I).[4] Subsequently, didehydroazepine from photolysis of phenyl azide was observed by means of infrared spectroscopy in rare-gas matrices at 8 K.[5] We recently confirmed

Chart I



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participation of a substituted didehydroazepine in the photochemistry of an aryl azide in solution at room temperature by means of time-resolved infrared spectroscopy.[6] Neither didehydroazepine nor any of its derivatives have ever been isolated.

Several important issues still limit the understanding of the photochemistry of aryl azides and the chemical and physical properties of didehydroazepines. Platz and co-workers have shown convincingly that irradiation of phenyl azide in a frozen glass at 77 K gives predominantly phenylnitrene—not didehydroazepine.[7] Waddell and co-workers allege that irradiation of phenyl azide solutions at room temperature initiates an explosive chain reaction of the triplet nitrene and phenyl azide without any participation by dehydroazepine.[8] Substituents affect the irradiation of aryl azides in mysterious ways. For example, neither *p*-nitro-[9] nor *p*-(dimethylamino)phenyl[10] azides give the expected 3*H*-azepine products when they are irradiated in the presence of diethylamine. Similarly, ring-expanded azepine products are not obtained from irradiation of either α- or β-naphthyl azide.[11] It is specially important to understand these substituent effects since many of the photolabeling and photolithographic applications require highly derivatized aryl azides.[12]

We report herein the results of the systematic investigation of an extensive series of aryl azides. Their chemical and physical properties were probed by conventional product studies in combination with time-resolved infrared and ultraviolet spectroscopy and semiempirical molecular orbital calculations. These procedures reveal a complex but systematic pattern that enables reliable prediction of the properties of the azide and its dehydroazepine from their structures.

Results

I. Chemical Properties. The photochemistry of phenyl azide has been studied in considerable detail.[7,13] Its irradiation in inert solvent (cyclohexane) leads to azobenzene by dimerization of triplet phenylnitrene and to a poorly characterized product commonly identified as "tar". The yield of azobenzene from this reaction decreases as the concentration of the azide in the reaction solution is increased. Irradiation of phenyl azide (5×10^{-3} M) in solutions containing diethylamine gives the 2-(diethylamino)-3*H*-azepine in good yield. Aryl azides having electron-donor substituents behave similarly. For example, the yield of 4,4′-diphenylazobenzene decreases from 55% to 13% as the initial concentration of *p*-phenylphenyl azide is increased from 1×10^{-4} to 0.1 M. The yields of the corresponding substituted azobenzenes are greater for the *p*-thiomethylphenyl, methoxyphenyl, and (dimethylamino)phenyl azides than they are for phenyl and *p*-phenylphenyl azides under comparable conditions; these and other findings are summarized in Table I.

Table I. Product Studies: Irradiation of Aryl Azides in Cyclohexane and in the Presence of Diethylamine

p-X-PhN$_3$, X	cyclohexane: azo compound, %[a]	cyclohexane + (Et)$_2$NH	
		3*H*-azepine, %[b]	aniline, %[c]
H	15	80	
Ph	55[d]	71	10
SMe	71	51	18
OMe	80	27	30
NMe_2	92	0	44[e]
CO_2H		70	15[g]
$CONMe_2$	70	74	trace
$COCH_3$	87	70	30
CN	74	68[f]	10
m-NO_2	50	10	30
p-NO_2	73	<3	80
Cl	80	100	
Br	80	71	trace
I	96	34	12

[a] Refers to the yield of the azobenzene derivative obtained by irradiation of a 5×10^{-3} M solution of the azide in cyclohexane. [b] Refers to the yield of the 5-substituted 2-(diethylamino)-3*H*-azepine obtained from photolysis of the azide in cyclohexane containing 2.0 M diethylamine. [c] Refers to the yield of the para-substituted aniline derivative obtained from photolysis of the azide in cyclohexane containing 2.0 M diethylamine. [d] The product mixture also contains *p*-aminobiphenyl (15%). [e] The product mixture also contains 4,4′-bis(dimethylamino)-azobenzene (55%). [f] This experiment was carried out in the presence of 1.0 M diethylamine. The yield of the 3*H*-azepine decreases at higher amine concentration. [g] This experiment was done in acetonitrile solution because the azide is not sufficiently soluble in cyclohexane.

Irradiation of *p*-phenylphenyl azide in cyclohexane containing diethylamine (2.0 M), as expected, gives 2-(diethylamino)-5-phenyl-3*H*-azepine and *p*-aminobiphenyl. A clear trend emerges from inspection of the data for the aryl azides in Table I. Under comparable reaction conditions, the yields of azepines decrease as the electron-donating power of the para substituent increases. When the powerful *p*-dimethylamino group is the donor, no azepine is formed at all. In principle, this result might be due to a substituent effect on the efficiency of forming the 1,2-didehydroazepine, to a decrease in the rate of reaction of the substituted didehydroazepine with diethylamine, or to some combination of these effects.

The results of irradiation of aryl azides substituted with electron-withdrawing groups are also summarized in Table I. In cyclohexane solution, the expected azobenzenes are formed in respectable yields. There is a trend in the response of the 3*H*-azepine yields to the nature of the substituent. The formation of this product for the ketone-, acid-, amide-, and nitrile-substituted[14] aryl azides is quite high, but it drops to only 10% for the *m*-nitro-substituted case and is immeasurably small (<3%) for *p*-nitrophenyl azide. The nitro substituents evidently exert a special influence that inhibits formation of the 3*H*-azepines.

The findings from the product studies for the *p*-halo-substituted aryl azides are also summarized in Table I. Their irradiation in cyclohexane solution gives 4,4′-dihaloazobenzenes in good yield when compared with the yield of azobenzene from phenyl azide itself. Irradiation of the halogen-substituted azides in cyclohexane solution containing diethylamine (2.0 M) gives 2-(diethylamino)-5-halo-3*H*-azepines. The yields of these 3*H*-azepines depend on the halogen. It is nearly quantitative in the case of *p*-chlorophenyl azide, but irradiation of *p*-iodophenyl azide under identical reaction conditions gives only a 34% yield of the 3*H*-azepine. This behavior could indicate operation of a heavy-atom effect[15] somewhere on the reaction path leading from the aryl azides to the 3*H*-azepines.

II. Time-Resolved Infrared Spectroscopy. The spectral feature most characteristic of the 1,2-didehydroazepines occurs in the infrared region. The IR spectra of these compounds have been recorded following photolyses of aryl azides isolated in inert-gas

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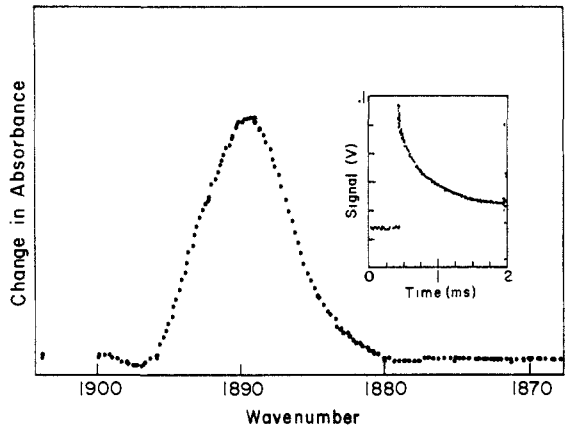

Figure 1. Transient IR absorption spectrum recorded 10 μs after irradiation of phenyl azide with 20-ns pulse at 308 nm. The inset shows the time dependence of the transient IR signal monitored at 1887 cm^{-1}.

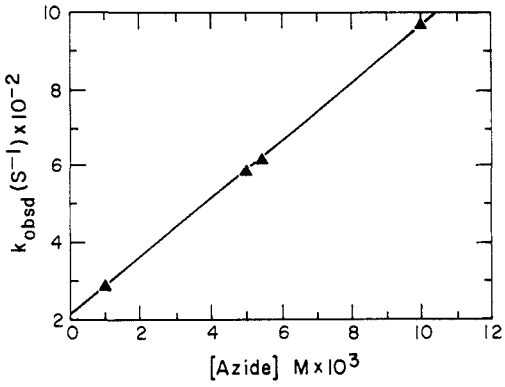

Figure 2. The observed pseudo-first-order rate constant for decay of didehydroazepine at increasing concentrations of phenyl azide.

matrices at low temperature.[5] In all cases examined, the didehydroazepines exhibit a strong absorption band for their cumulated double bonds at ca. 1890 cm^{-1}. This same spectral feature can be used to detect and characterize the reactions of didehydroazepines following laser flash photolysis of aryl azides in fluid solution at room temperature.

Irradiation of a degassed heptane solution (ca. 5×10^{-3} M) of phenyl azide with the output of an excimer laser (308 nm, 20 ns, 10 mJ) gives the IR spectrum (probed from 1700 to 2000 cm^{-1}, 1 μs after the laser pulse) shown in Figure 1. The strong absorption band at 1887 cm^{-1} is assigned to didehydroazepine. This assignment was confirmed by irradiation of phenyl azide partially enriched with ^{15}N (50% enrichment of ^{15}N at the N_1 position). The time-resolved IR spectrum of this enriched sample exhibits an absorption at 1877 cm^{-1}, consistent with a ^{15}N isotopomer of didehydroazepine. Irradiation of the ^{15}N-enriched phenyl azide in the presence of diethylamine gives the (diethylamino)-3*H*-azepine also with 50% ^{15}N enrichment. Thus, there is no scrambling or exchange of the azide nitrogen atoms in the photolysis.

The lifetimes of didehydroazepine can be determined by monitoring the time dependence of its infrared absorption spectrum. Under the laser irradiation conditions defined above, the didehydroazepine absorption decay follows a first-order rate law with a lifetime of 1.6 ms (Figure 1, inset). The observed lifetime of the didehydroazepine is independent of the power of the generating laser pulse (7–100 mJ). However, since the response time of the detection system for the IR spectrometer is ca. 1 μs, the earliest times, when the concentration of didehydroazepine is highest and a second-order kinetic component to its reactions would be most important, cannot be probed.

The observed rate for decay of didehydroazepine increases with the concentration of phenyl azide in the solution. Figure 2 shows a plot of the rate constant for decay of the didehydroazepine as the azide concentration is varied; the rate is directly related to

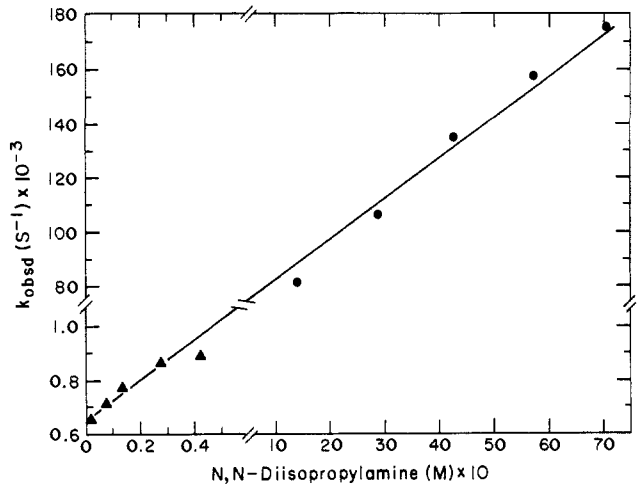

Figure 3. The observed rate constant for reaction of didehydroazepine with diisopropylamine; the triangles are for reaction rates monitored by time-resolved IR spectroscopy, the circles are for reaction rates monitored by time-resolved UV spectroscopy.

Table II. Kinetic and Spectroscopic Data for the Reaction of Didehydroazepines with Diethylamine and the Formation of Didehydroazepine

p-XPhN_3, X	k_{DEA}, M^{-1} s^{-1}	rel[a] ΔOD at 1887 cm^{-1}
H	6.5×10^6	0.83
Ph	3.6×10^5	
	1.4×10^{4b}	
SMe	1.6×10^5	
OMe	2.5×10^4	0.48
CO_2H	3.0×10^7	
CO_2NMe_2	4.4×10^7	
$COCH_3$	2.8×10^8	
m-NO_2		0.12
p-NO_2		<0.05
Cl	1.3×10^8	1.00
Br	1.7×10^8	1.14
I	2.7×10^8	0.22

[a] Normalized to 5-chloro-1,2-didehydroazepine = 1.0 and corrected for the fraction of the laser light absorbed by the azide. [b] The rate constant for reaction of didehydroazepine with *N,N*-diisopropylamine determined by means of time-resolved IR and UV spectroscopy.

the azide concentration. The slope of the line in this plot gives the bimolecular rate constant for the reaction of phenyl azide with didehydroazepine. In heptane solution at room temperature this rate constant is 7.5×10^4 M^{-1} s^{-1}. Extrapolation to zero phenyl azide concentration gives a lifetime for didehydroazepine of 4.8 ms. This value represents the rate of irreversible conversion of didehydroazepine to triplet phenylnitrene, a process required by the product studies.[16] The reaction of phenyl azide with didehydroazepine may account, at least in part, for formation of tar and for the quantum yields greater than unity for photolyses in concentrated solutions of the azide.

The reaction of didehydroazepine with amines can be monitored by time-resolved IR spectroscopy. The rate of this reaction with diethylamine could not be determined accurately for didehydroazepine itself. The rate constant for this process is so great that, at a sufficient diethylamine concentration to ensure pseudo-first-order conditions, the reaction rate is too fast to resolve with the spectrometer. To solve this problem for this case, the rate of reaction of didehydroazepine with *N,N*-diisopropylamine was measured. Figure 3 is a plot of the lifetime of didehydroazepine determined by measuring the rate of disappearance of the 1887-cm^{-1} absorption band as the concentration of the diisopropylamine was increased from 1×10^{-2} to 5×10^{-2} M. The slope of the line in this plot, which also contains data from

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time-resolved UV spectroscopy (see below), is 1.4×10^4 M^{-1} s^{-1}, the rate constant for reaction of diisopropylamine with didehydroazepine. Additional kinetic findings are summarized in Table II.

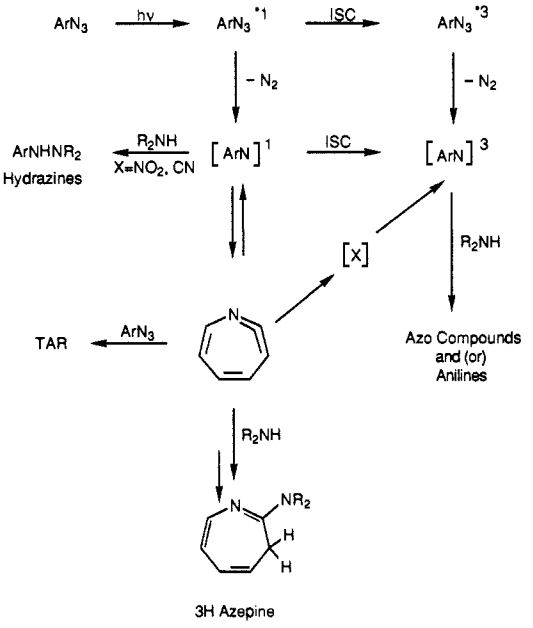
The results of examination of the other aryl azides of this study by time-resolved IR spectroscopy, with some notable exceptions, are quite similar to those of phenyl azide and are also summarized in Table II. Of particular note is the observation that irradiation of (*N,N*-dimethylamino)phenyl azide does not give a detectable absorption band for a didehydroazepine. This finding is consistent with the inability to isolate the 3*H*-azepine from photolysis of this azide in the presence of amines. A second interesting example is *p*-nitrophenyl azide. For this azide, too, none of the 3*H*-azepine can be isolated from photolysis in the presence of amines. However, in this case a didehydroazepine is easily detected by time-resolved IR spectroscopy. Moreover, 5-nitro-1,2-didehydroazepine is observed to react rapidly with diethylamine. One resolution of this dilemma is that this didehydroazepine is formed only by laser irradiation (i.e., high power) in a multiphoton process that cannot occur with a conventional light source (product conditions). This explanation was ruled out by showing that the initial absorbance for the nitro-substituted didehydroazepine does not show any unusual dependence on the laser power. Also, irradiation of a diethylamine-containing solution of *p*-nitrophenyl azide with high-power laser pulses at 308 nm does not result in a detectable yield of the 3*H*-azepine. The dilemma is resolved by examination of the normalized (for the fraction of the laser pulse absorbed) initial absorbances of the didehydroazepines (Table II). The absorbance at 1887 cm^{-1} from irradiation of *p*-nitrophenyl azide is only 5% of that seen from irradiation of *p*-chlorophenyl azide (where the yield of the 3*H*-azepine is nearly quantitative). The quantum yields for consumption of these azides are essentially the same, so, with the reasonable assumption that the extinction coefficients for the IR absorption of the didehydroazepines are insensitive to remote substituents, this finding indicates that only ca. 5% of the *p*-nitrophenyl azide that reacts forms 5-nitro-1,2-didehydroazepine.

The photolysis of *p*-iodophenyl azide is also quite revealing. The lifetime of 5-iodo-1,2-didehydroazepine, obtained by extrapolation of its decay rate to zero azide concentration, is 4.2 ms, the same within experimental error as for didehydroazepine itself. Evidently, there is no observable heavy-atom effect on the rate of conversion of 5-iodo-1,2-didehydroazepine to triplet (*p*-iodophenyl)nitrene. On the other hand, an effect of iodine substitution is revealed by comparison of the normalized initial absorbances at 1887 cm^{-1} for *p*-chloro- and *p*-iodophenyl azides; the latter is only ca. 20% of the former. This observation accounts for the difference in the yields of the 3*H*-azepines when these azides are irradiated in the presence of diethylamine.

Both spectral studies in low-temperature matrices[11,17] and product studies show that the photochemistry of the polynuclear aryl azides does not follow the same pattern as that found for the phenyl azides. In particular, the primary products from irradiation of polynuclear azides are azirines, not didehydroazepines. Laser flash photolysis of α-naphthyl or α-pyrenyl azide—under conditions that readily give the characteristic IR absorption of didehydroazepine from phenyl azide—gives no measurable absorption change in the region from 1700 to 2000 cm^{-1}. This finding confirms the different reactivity pattern. But, unfortunately, we are unable to observe the relatively weak IR absorption band at 1700 cm^{-1} believed to be characteristic of the azirines.[17]

III. Time-Resolved UV Spectroscopy. Laser flash photolysis of the aryl azides with UV detection compliments perfectly the time-resolved IR spectral studies. The IR analysis provides for the clear identification of intermediate didehydroazepines, but cannot be used to study processes that occur in less than 1 μs. On the other hand, analysis in the UV spectral region permits the study of processes that occur on a nanosecond time scale, but does not usually provide sufficient information to permit unambiguous identification of the signal carrier. In this work we have combined the two techniques to provide both clear structural and kinetic data for the didehydroazepines.

Scheme I



We previously reported the results of a detailed investigation of phenyl azide by time-resolved UV spectroscopy.[13a] In that work an intermediate species with an absorption maximum at 340 nm was observed following laser irradiation (266 nm, 20 ns, 5 mJ) of the azide in cyclohexane solution. The intermediate was found to react with amines and was identified tentatively as didehydroazepine. In order to confirm the assignment, we measured the rate of reaction of the 340-nm-absorbing species with *N,N*-diisopropylamine. The results are shown in Figure 3 where it is clear from inspection that didehydroazepine and the 340-nm-absorbing species react with the amine with the same rate constant. This finding leaves litle doubt that the intermediate detected by time-resolved UV absorption is didehydroazepine.

Laser flash photolysis of the substituted phenyl azides in the presence of low concentrations of diethylamine reveals an interesting pattern. For example, irradiation of *p*-chlorophenyl azide yields 5-chloro-1,2-didehydroazepine. Its rate constant for reaction with diethylamine was measured by monitoring the growth in absorption at 375 nm. Significantly, the chloro-substituted derivative reacts with diethylamine ca. 20 times faster than does didehydroazepine itself. Similarly, the rate of reaction of 5-methoxy-1,2-didehydroazepine with diethylamine was found to be ca. 300 times slower than for the unsubstituted compound. These and other findings are summarized in Table II. Evidently, through their electronic properties, substituents exert considerable influence on the rate of reaction of didehydroazepines with amines. This fact, in part, controls the outcome of aryl azide photolyses.

Discussion

I. Analysis of the Experimental Results. The findings presented above offer some guidance for analysis of the factors that control the chemical and physical properties of aryl azides and 1,2-didehydroazepines. With the exception of *p*-(dimethylamino)phenyl azide, all of the examined single-ring aryl azides give didehydroazepines when irradiated. However, the efficiency of didehydroazepine formation and the chemical properties of the didehydroazepines themselves are sensitive functions of the electronic nature of the substituent.

A mechanistic proposal for the photochemistry of the substituted phenyl azides and the reactions of their derived didehydroazepines in fluid solution at room temperature is shown in Scheme I. Irradiation of the azide generates its singlet excited state which may lose nitrogen to form the singlet nitrene or intersystem cross (ISC) to form the triplet azide. The triplet azides can lose nitrogen

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to form triplet nitrenes. Not shown on the scheme, but necessary to account for quantum yields less than one, are energy-wasting steps leading back to the ground-state azide from its singlet or triplet excited state. The singlet nitrenes may intersystem cross to form their ground triplet states, react with amines to form hydrazines,[9,14] or undergo ring expansion to didehydroazepines. The triplet nitrenes can dimerize to form azo compounds or react with amines to form anilines. The didehydroazepines formed in the ring expansion have several reaction paths available: in the presence of amines they may be trapped and eventually give 3*H*-azepines; they can react with ground-state azides and, perhaps, initiate a process that leads to tar; or they may be slowly converted to triplet nitrenes. The conversion of the didehydroazepines to triplet nitrenes may proceed via the singlet nitrene or through intermediate X. We will comment further on a possible identity for this intermediate later. The outcome of photolysis of an aryl azide depends on the relative rates of the reactions identified in Scheme I. The rates of these processes are sensitive to perturbation by substituents.

Consider first the possible effect of heavy atoms on the rate of conversion of singlet-state intermediates to their lower energy triplets. Three opportunities for ISC of this sort are identified in Scheme I: conversion of excited singlet azide to its triplet, relaxation of singlet nitrene to triplet nitrene, and ISC of didehydroazepine to intermediate X. The experimental results reveal no effect of heavy atoms on the lifetime of didehydroazepines. On this basis we conclude that ISC of didehydroazepine is not the rate-limiting step in any reaction that leads to its consumption. On the other hand, a heavy-atom effect may affect, in part, the formation of the didehydroazepines. The evidence in support of this hypothesis comes from the yields of the didehydroazepines produced from the halogen-substituted azides. There is a clear trend in the series chloro, bromo, and iodo that cannot be related to electronic perturbation since the σ values of these groups vary only slightly.[18] The two steps on the path to didehydroazepines that might be affected by a heavy atom are ISC of the excited singlet azide and ISC of the singlet nitrene. We tend to discount the latter possibility since ISC rates are generally not very sensitive to heavy-atom perturbation when nearby $n\pi$ and $\pi\pi$ electronic configurations can mix.[19]

Some support for the proposal that ISC of the excited azide is subject to a heavy-atom effect can be found by examination of the fluorescence efficiencies of the halo-substituted arenes. The fluorescence quantum yield for α-chloronaphthalene is 0.058, this value decreases to 0.0016 for the bromo-substituted compound, and no fluorescence at all can be detected for α-iodonaphthalene.[20] The decrease in fluorescence efficiencies for the haloarene series is generally traced to an increase in intersystem-crossing rates. This analysis implies that the loss of nitrogen from the excited singlet azides is competitive with its intersystem crossing. Regardless of which step on the path to the didehydroazepines is subject to perturbation, these findings are of significance since iodine-substituted aryl azides are often used as photolabeling agents. Covalent bond formation to a target molecule, required in this application, occurs efficiently only from the intermediate didehydroazepines. Thus a reduction in the didehydroazepine yield adversely affects photolabeling efficiency.

A related hypothesis may explain the behavior of the nitro-substituted aryl azides. In a recent report we considered as one of several possibilities that the low (or nonexistent) yield of 3*H*-azepines from photolyses of *m*- or *p*-nitrophenyl azide in the presence of amines was a consequence of shortened lifetimes for the corresponding nitro-substituted didehydroazepines.[9] This hypothesis can now be discarded on the basis of the time-resolved IR spectral results which reveal little change in the lifetime upon nitro-substitution of didehydroazepine. The new findings show that reduced yields of the 3*H*-azepines are a direct consequence

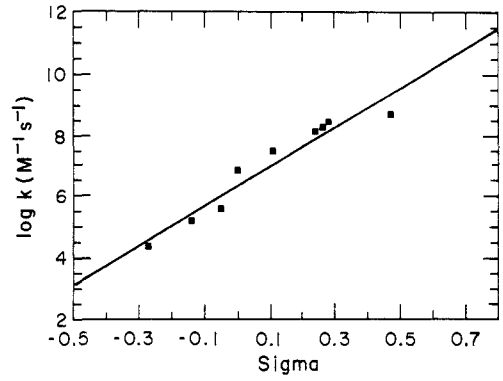

Figure 4. Dependence of the rate constant for reaction of 5-substituted didehydroazepines on the σ substituent constant.

of reduced yields of didehydroazepine formation. This might be caused either by a decrease in the rate of ring expansion of the singlet nitrene or by an increase in the rate of ISC for the nitrene or the excited azide. 5-Nitro-1,2-didehydroazepine is detected when *p*-nitrophenyl azide is irradiated at 8 K in a matrix,[21] perhaps showing that temperature has little effect on ring expansion. The proposal that increases in the ISC rates for the nitro-substituted singlet excited azides accounts for the diminished didehydroazepine yield is supported by analogy with nitrobenzene photophysics. The singlet excited state of nitrobenzene does not fluoresce, presumably because the rate of ISC to its triplet is enhanced by the mixing of states in the nitro group.

Only *p*-(dimethylamino)phenyl azide from among the substituted phenyl azides examined in this work fails to give a detectable yield of didehydroazepine by time-resolved IR spectroscopy. This result may be understood qualitatively to be a consequence of the reduced electrophilicity of the donor-substituted singlet nitrene. Support for this hypothesis comes from the observation that irradiation of this azide in the presence of diethylamine gives only triplet nitrene-derived products (Table I). If ring expansion to the didehydroazepine is slowed, the singlet nitrene will cross to the triplet with high efficiency.[10] This postulate can be put on a firmer basis by consideration of the semiempirical molecular orbital calculations discussed below.

Once formed from the singlet nitrene, control of the reaction outcome shifts to the properties of the 1,2-didehydroazepine. The rate of reaction of the 1,2-didehydroazepines with diethylamine varies over more than 2 orders of magnitude, depending on the nature of the substituent at the 5-position. In general, the rate constant for this reaction increases along with the electron-withdrawing power of the substituent. This observation can be put on a more quantitative basis by comparison of the measured rate constants with the Hammett σ substituent constants (Figure 4). It is apparent from inspection of this figure that the change in reaction rate is predictably dependent on the electronic nature of the substituent. This finding accounts for the increased yield of *p*-methoxyaniline when *p*-methoxyphenyl azide is irradiated in the presence of diethylamine, for example. The rate of reaction of the methoxy-substituted didehydroazepine with diethylamine is slowed and its conversion to the triplet nitrene, precursor of the aniline, occurs with greater efficiency than for didehydroazepine itself under comparable reaction conditions.

It is clear from the results that didehydroazepines react with aryl azides with significant rate constants. It is informative to consider the recent reports of an explosive chain reaction of triplet phenylnitrene in light of this finding.[8] The major evidence in support of this hypothesis is the observation that the quantum yield for consumption of phenyl azide increases to values above one at high initial phenyl azide concentrations. However, at the high concentrations employed to study this process, hardly any of the phenyl azide consumed forms phenylnitrene. For example, at 0.05 M phenyl azide, fewer than one phenyl azide out of 20 forms a

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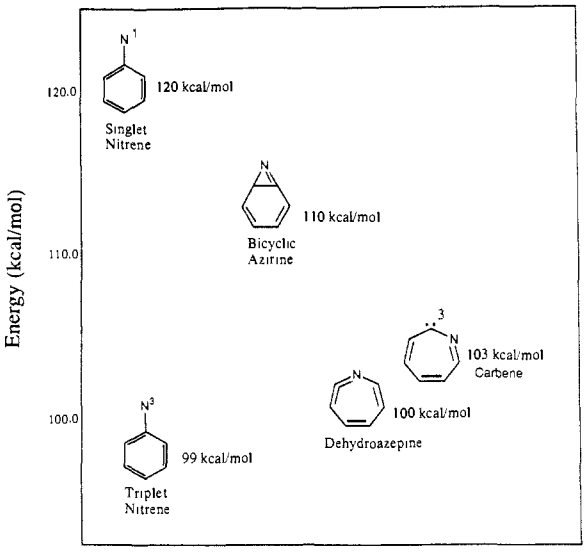

Figure 5. Results of the MNDO calculation for the C_6H_5N potential energy surface.

triplet nitrene. This conclusion is supported additionally by the finding that the yield of azobenzene is greatly reduced when the initial concentration of phenyl azide is high. These observations do not rule out conclusively the operation of the proposed chain reaction, but they certainly limit its possible significance.

II. Comparison of Experimental Results with Semiempirical Calculations. In 1976 Shillady and Trindle[22] reported results of a MINDO/2 calculation that seemed to support the experiments of Sundberg and co-workers,[23] which, at the time, were interpreted to show that a bicyclic azirine, not didehydroazepine, is the intermediate trapped by amines in the irradiation of phenyl azide. This conclusion clearly must be discarded in light of the experimental findings reported in this work. Additionally, we have reexamined the C_6H_5N potential surface by means of the MNDO semiempirical method;[24] the results of these calculations are summarized in Figure 5.[25]

The MNDO calculation for phenylnitrene agrees with the experimental finding that the triplet nitrene has a lower energy than its singlet state. Brauman and Drzaic estimated the singlet-triplet gap in this case to be ca. 4 kcal/mol by means of an electron photodetachment experiment;[28] the MNDO calculation predicts a gap of 21 kcal/mol. The magnitude of this disagreement is disappointing but not surprising. Recent results have shown that MNDO calculations give reliable predictions of relative, but not absolute, energy differences for a series of related singlet and triplet carbenes.[26]

Of most immediate significance to the present report is the prediction from the MNDO calculation that the bicyclic azirine has a greater heat of formation than does didehydroazepine. Additionally, examination of the reaction paths from singlet phenylnitrene to the bicyclic azirine or didehydroazepine reveals an activation barrier of 12.4 kcal/mol for the former and only 3.6 kcal/mol for the latter. Thus the computational findings indicate that didehydroazepine is the preferred intermediate by consideration of either thermodynamic or kinetic criteria—a result consistent with the experimental findings. Examination of the reaction coordinate for α-naphthylnitrene provides an additional check on the reliability of the computational method. The MNDO calculations indicate that the naphthylazirine is more stable than its isomeric dehydroazepine by 10 kcal/mol and that the activation barriers for their formation are 3.1 and 13 kcal/mol, respectively. Here, too, the computation is consistent with the experimental findings: irradiation of α-naphthyl azide gives an azirine, not a didehydroazepine. Finally, a MNDO calculation of the reaction coordinate for *p*-(dimethylamino)phenylnitrene gives activation barriers for formation of the didehydroazepine and, less stable, bicyclic azirine of 36 and 56 kcal/mol, respectively. The very high barriers are consistent with the experimental finding that this nitrene does not form a didehydroazepine. At least qualitatively, MNDO calculations seem to predict well the preferred path for reaction of singlet arylnitrenes.

Irradiation of cyclohexane solutions of aryl azides can lead to azobenzenes in good yield (Table I). Similarly, irradiation of an azide in the presence of an amine trapping reagent can give a 3*H*-azepine in good yield. Since the azo compounds are formed by dimerization of triplet nitrenes, it was recognized long ago that there must be a path linking the 3*H*-azepine precursors (didehydroazepines) to triplet nitrenes. Conventionally, it was proposed that didehydroazepine is converted to the triplet nitrene via the single nitrene.[16] The MNDO calculations reveal an alternative, perhaps more attractive, hypothesis. Triplet 2-azacycloheptatrienylidene (the intermediate X mentioned earlier) is calculated to have an energy that is only ca. 3 kcal/mol above that of didehydroazepine. Thus it seems reasonable to suggest that conversion to the triplet carbene, not formation of the singlet nitrene, whose energy is estimated to be 20 kcal/mol above that of didehydroazepine, is the path that leads to triplet phenylnitrene. An analogous process has been postulated for conversion of 1,2,4,6-cycloheptatetraene to cycloheptatrienylidene.[29]

Conclusions

The experiments described above show conclusively that irradiation of phenyl azide in solution at room temperature leads to ring expansion to 1,2-didehydroazepine. The yields of didehydroazepines are subject to perturbation by substituents on the aryl ring. Heavy atoms reduce their yields, as do nitro substituents and strong electron-donor groups. Naphthyl azides do not ring expand photochemically, but tautomerize to azirines.

The reaction of didehydroazepines with amines is subject to perturbation by substituents. In particular, electron-donor groups slow this reaction, and consequently, conversion of the didehydroazepine to the triplet nitrene occurs more effectively for donor-substituted cases.

Didehydroazepines react with aryl azides. This fact may account, at least in part, for tar formation in this reaction and obviates the need to postulate a molecular explosion for photolysis of concentrated phenyl azide solutions.

MNDO calculations appear to offer reliable guidance for prediction of the reaction path for singlet aryl nitrenes.

These results have bearing on the selection of substituted aryl azides for photolabeling and photolithographic applications. In particular, iodo or nitro substituents significantly reduce the yield of the didehydroazepines that are formed.

Experimental Section

Flash Photolysis with IR and UV Detection. (A) UV Detection. Cyclohexane solutions of each aryl azide were prepared so that the absorbance in a 1-cm cell was ca. 5 at 266 nm. A 5-mL portion of the solution was placed in a cuvette equipped with a stopcock and purged with N_2. In some cases an amine was added to the cuvette before purging. The pulsed laser apparatus was as previously[30] described except that the excitation wavelength (Molectron, Q-switched Nd-YAG) was 266 nm. The pulse width at half-height was typically 20 ns with an intensity of 5 mJ/pulse. The probe beam was generated with a USSI 3CP-3 xenon flash lamp and monitored at a right angle to the laser excitation beam with a Hamamatsu photomultiplier tube and the previously described Tektronix R7912 digitizer. The rate of growth of the

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Table III. Spectral Characterization of Products from Irradiation of the Aryl Azides

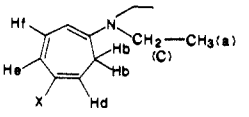
2-(Diethylamino)-5-X-3*H*-azepine[a]

X	^{1}H NMR spectrum, δ							mass spectrum, *m/e*		
	a	b	c	d	e	f	x	formula	calcd	found
H	1.04	2.59	3.30	5.05	5.67	7.08	6.18			
C_6H_5	1.15	2.60	3.35	5.35	5.98	7.2	7.9	$C_{16}H_{20}$	240.1632	240.1629
SMe	1.15	2.60	3.38	4.94	5.74	7.10	2.28	$C_{11}H_{18}NS$	210.0357	210.0365
Cl	1.25	2.64	3.35	5.10	5.70	7.05		$C_{10}H_{15}ClN$	198.0924	198.0924
Br	1.15	2.60	3.30	5.20	5.88	7.00		$C_{10}H_{15}BrN$	242.0418	242.0418
I	1.15	2.60	3.35	5.49	5.92	6.86		$C_{10}H_{15}IN$	290.0272	290.0276
$COCH_3$	1.20	2.60	3.40	6.00	6.20	6.60	7.45	$C_{12}H_{18}ON$	206.1417	206.1417
CO_2H	1.20	2.60	3.40	6.10	6.35	7.10		$C_{11}H_{16}O_2N$	208.1218	208.1215
CN	1.15	2.70	3.40	5.70	5.90	7.21		$C_{11}H_{15}N_2$	189.1264	189.1265

4,4′-Di-X-azobenzene[b]

X	^{1}H NMR spectrum, δ			mass spectrum, *m/e*		
	a	b	x	formula	calcd	found
C_6H_5	8.02	7.78	7.5 (m, 10 H)	$C_{24}H_{18}N_2$	334.1457	334.1463
SMe	7.82	7.32	2.56 (s, 6 H)	$C_{14}H_{14}N_2S_2$	274.0602	274.0600
OMe	7.90	7.05	3.90 (s, 6 H)	$C_{14}H_4N_2O_2$	242.1058	242.1057
$N(Me)_2$	7.80	6.72	3.05 (s, 6 H)	$C_{16}H_{20}N_4$		
Cl	7.78	7.44		$C_{12}H_8Cl_2N_2$	250.0063	250.0063
Br	7.80	7.64		$C_{12}H_8Br_2N_2$	339.9031	339.9079
I	7.85	7.62		$C_{12}H_8I_2N_2$	434.8740	434.8759
$COCH_3$	8.12	8.02	2.71 (s, 6 H)	$C_{16}H_{14}N_2O_2$	266.1056	266.1056
CN	8.05	7.85		$C_{14}H_8N_4$	232.0743	232.0746

[a] The assignments of the resonances in the NMR spectrum for the 3*H*-azepines are made according to the structure shown below:



The observed multiplicities (X ± H) and integrals are a (t, 6 H), b (br s, 2 H), c (q, 4 H), d (t, 1 H), e (d, 1 H), and f (d, 1 H). [b] The resonances labeled a and b appear as doublets in the spectrum. The proper assignments of these resonances is not always clear.

photoproducts were monitored at ca. 370 nm.

(B) **IR Detection.** Solutions of the aryl azides (5×10^{-3} M) prepared in the standard flow-cell were degassed by multiple evacuation and then irradiated at 308 nm with the output of a pulsed excimer laser. The time-resolved IR spectrometer has been previously described.[31]

Preparation of the Aryl Azides. The substituted aryl azides were prepared by following the procedures described by Smith.[32] Phenyl azide was prepared precisely as previously described.[33] For biphenyl, *p*-acetylphenyl, *p*-iodophenyl, and *p*-bromophenyl azides, the crude product was precipitated directly from the reaction solution and then purified by recrystallization from a water/methanol solution. For *p*-chlorophenyl, *p*-(dimethylamino)phenyl, and *p*-methoxyphenyl azides, the crude product was extracted from the reaction mixture with ether and then purified chromatographically on silica gel by eluting with petroleum ether.

Preparation of ^{15}N-Enriched Phenyl Azide. A mixture of [^{14}N]- and [^{15}N]-nitrobenzene (2.1 g of each) was reduced to aniline with Zn in methanol solution according to the standard procedure (ca. 80% yield).[34] The enriched aniline was converted to its diazonium salt and titrated with a solution of sodium azide.[33,35] The labeled phenyl azide thus obtained was purified by means of column chromatography. The infrared spectrum of the enriched azide showed no important differences from a spectrum of a natural abundance sample; i.e. there was no detectable splitting of the absorbances at 2100 cm^{-1} or 1350 cm^{-1}. The isotope incorporation was determined by mass spectroscopy to be 50%. The ^{15}N NMR spectrum showed that only the nitrogen connected to the phenyl ring was labeled (δ 284 referenced to nitromethane at 0.00).

Photolysis of the Aryl Azides in Cyclohexane Solution. A 5×10^{-3} M solution of the azide in cyclohexane was prepared. A 10-mL portion of the solution was removed and used as a "dark" control sample. A 20-mL, N_2-purged portion of the solution was irradiated at 254 nm (Rayonet Photoreactor) in a quartz tube for ca. 10 min. After removal of the solvent under vacuum and addition of hexamethyldisiloxane as an internal standard, the photolysis and control solutions were analyzed by means of ^{1}H NMR spectroscopy. The findings are reported in Table I.

The azo compounds formed by irradiation of the aryl azides in cyclohexane were isolated from the photolysis mixture by chromatography on silica gel. The characterization of these compounds is detailed in Table III. The anilines formed in some of these reactions were identified by comparison with authentic samples.

Photolysis of Aryl Azides in Cyclohexane Containing Diethylamine. A cyclohexane solution of the aryl azide (5×10^{-3} M) containing diethylamine (2.0 M) was purged with N_2 and irradiated as described above. The products were isolated by means of chromatography on silica gel; characteristic spectral features are reported in Table III. The yields of the products were determined by analysis of the ^{1}H NMR spectrum of the concentrated, crude reaction mixture; the findings are summarized in Table I. For the case of *p*-iodophenyl azide, the yield of the 3*H*-azepine is not dependent on the degree of conversion of the azide.

Acknowledgment. The work at the University of Illinois was supported by a grant from the National Institutes of Health. The work at Nottingham was supported by SERC, the Paul Instrument Fund of the Royal Society, and Perkin-Elmer Ltd. We thank Dr. M. A. Healy, P. M. Hodges, and Professor J. J. Turner for their advice, and J. M. Whalley for his technical assistance with the time-resolved IR experiments, and Dr. Charles Shields for his help with the preparation of the labeled phenyl azide.

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