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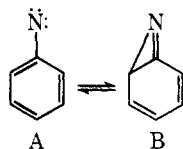
Phenyl Nitrene. A Flash Photolytic Investigation of the Reaction with Secondary Amines^{1a}

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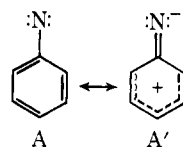
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Abstract: The flash photolysis of aryl azides in the presence of secondary amines, which serve as nucleophilic trapping agents, has been studied. As in steady illumination photolyses under similar conditions the major reaction products are 2-dialkylamino-3*H*-azepines. The kinetics of the reactions of dibutylamine (DBA) with the intermediate generated by photolysis of phenyl azide and its *o*-methyl, *o*-ethyl, and *o*-trifluoromethyl analogs have been measured. The rates are sensitive both to solvent and the aryl substituent and fall in the range 10^4 – 10^9 l. mol⁻¹ sec⁻¹. The intermediate which reacts with DBA is not believed to be the nitrene but a species derived therefrom, most likely a strained closed-shell azirine. This intermediate does not absorb strongly above 300 nm and has a lifetime of ~5 msec in the unsubstituted system in the absence of an amine. Formation of the final 3*H*-azepine proceeds through the 1*H* tautomer and rates for uncatalyzed and dibutylammonium ion catalyzed tautomerism are reported for the unsubstituted *o*-methyl and *o*-trifluoromethyl compounds. Activation data are recorded for several of the reactions. An apparent negative E_a is observed for the reaction of the intermediate from phenyl nitrene and DBA.

Phenyl nitrene exhibits little of the reactivity commonly associated with nitrene or carbene intermediates. It gives neither efficient intermolecular insertion reactions with saturated hydrocarbons² nor addition to olefins or benzene.³ Such processes do occur in intramolecular thermal reactions.⁴ Two factors have been suggested to be responsible for the apparent lack of reactivity. The nitrene may be in equilibrium with a closed shell azirine B.⁵ Loss of nitrene

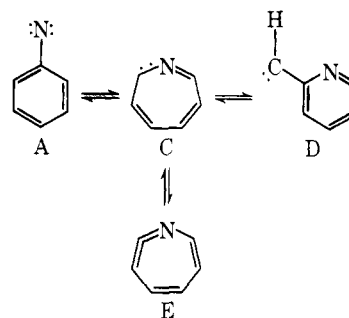


reactivity might also be the result of a large contribution to the structure by the dipolar resonance form A' which would diminish the electron deficiency at nitrogen.¹⁰ Support for



this proposal can be drawn from the tendency for nitrene reactivity to be accentuated in systems with electron attracting aryl substituents.¹¹ The two factors are not mutually exclusive.

Interest in phenyl nitrene is further enhanced by studies of gas phase pyrolyses which suggest rearrangements to azacycloheptatrienylidene (C) and pyridyl carbene (D).¹²



Related studies of structural isomerizations of aryl carbenes in the gas phase and in solution also suggest the possibility of a strained ketenimine structure.¹³ Recent efforts aimed at using photolysis of azido groups to mark biological active sites¹⁴ provided an additional impetus for developing a firm mechanistic understanding of aryl nitrene intermediates.

Previous studies of phenyl nitrene have been directed at the triplet species, and the esr¹⁵ and ultraviolet spectrum¹⁶ have been reported. As our work neared completion a study of phenyl nitrene by flash photolysis in the gas phase was reported.¹⁷ The only process which was firmly identified was reaction of triplet nitrene with phenyl azide to give azobenzene. This reaction accounts for only a fraction of the phenyl azide, however, since the yield of azobenzene is only 6%. These studies provide little basis for understanding the solution chemistry of phenyl nitrene since the species primarily involved in solution reactions is the singlet.^{18,19}

The present study concentrates on the photolysis of aryl azides in the presence of secondary amines using the techniques of flash photolysis and fast kinetic spectroscopy. The

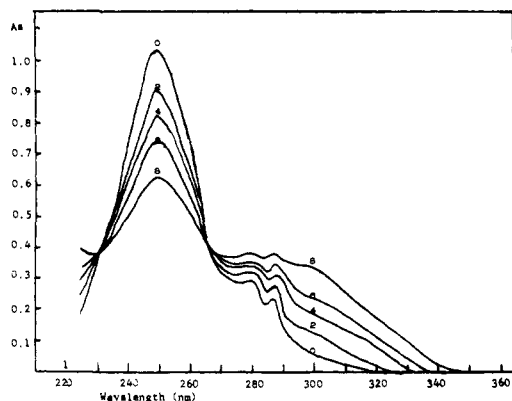


Figure 1. Successive changes in the spectrum of a $9.0 \times 10^{-5} M$ solution of phenyl azide containing $2.0 \times 10^{-3} M$ DEA in hexane. The numbers above the spectra indicate the number of repetitive 100-J flashes prior to recording each spectrum. Flash number 8 was a 340-J flash.

most detailed attention has been devoted to phenyl azide and *o*-methylphenyl azide, but some data for *o*-ethylphenyl azide and *o*-trifluoromethylphenyl azide are included.

Results

Flash photolysis of $10^{-4} M$ phenyl azide in hexane in the absence of any amine was followed by an absorbance increase monitored at 366 nm. The reaction rate was unaffected by careful deoxygenation, oxygen saturation, or the extent of solvent purification. It was decreased by nearly half in the presence of 0.01 *M* piperylene. The rate constants are given in Table I.

Table I. Rates of Absorbance Change in the Absence of Secondary Amines

—Photolysis of Phenyl Azide in Hexane—	
Solvent conditions	k , sec^{-1} ^a
Not dried	145
Dried over Na-Pb	144
Oxygen free	132
Oxygen saturated	147
0.01 <i>M</i> Piperylene	85

^a The reproducibility and estimated accuracy of the rate constants are $\pm 10\%$. Temperature was $21.7 \pm 0.3^\circ$.

The product(s) of this reaction was not identified but is assumed to be primarily the intractable polymeric material formed under steady photolysis conditions in the absence of amines.^{3,11e,19,20} The final absorption spectrum excludes the formation of large amounts of aniline, nitrobenzene or azobenzene, although any of these might be minor products.

Steady illumination of solutions of phenyl azide ($\sim 0.04 M$) containing $>0.2 M$ diethylamine (DEA) gives 2-diethylamino-3*H*-azepine in about 70% yield.²¹ This compound is also the dominant product from flash photolysis of more dilute solutions of phenyl azide in the presence of DEA. The development of the azepine absorption band at about 305 nm on successive flashes is shown in Figure 1. The isobestic points indicate that photodecomposition of the azepine is minimal. From Figure 1 and extinction coefficient data, the calculated azepine yield is $\sim 85\%$. A small mass deficit is expected due to the formation of aniline,^{19,21} and possibly azobenzene,¹⁹ both of which are minor products in steady illumination photolyses.

The quantum yield of azepine formation for 253.7-nm light under steady illumination was determined using a cali-

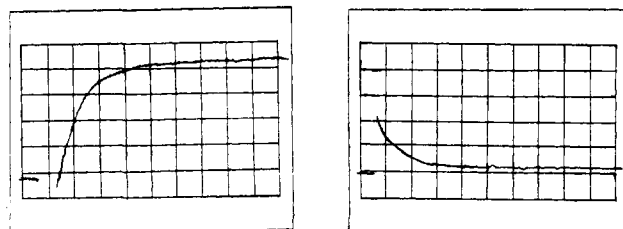


Figure 2. Oscilloscope traces: left, appearance of 1*H*-azepine monitored by absorbance increase at 366 nm, time scale 100 $\mu\text{sec}/\text{division}$; right, disappearance of 1*H*-azepine monitored by absorbance decrease at 366 nm, time scale 200 $\text{msec}/\text{division}$.

brated low pressure mercury lamp. At reactant concentrations similar to those used in the flash experiments, the quantum yield was 0.42 ± 0.05 as determined from the slope of absorbance vs. time plots. Reported values for the photodecomposition of phenyl azide are near 0.52 ± 0.05 ^{13,22} and are not strongly dependent on experimental conditions. The two values are compatible with the conclusion that $\sim 85\%$ of the azide is converted to azepine under both steady and flash photolysis in the presence of amine.

Kinetic studies were carried out using di-*n*-butylamine (DBA) to avoid experimental difficulties resulting from the volatility of DEA. Decomposition of phenyl azide by a broad spectrum light pulse of $\sim 50 \mu\text{sec}$ (to 1% intensity) in the presence of DBA (phenyl azide $\sim 1 \times 10^{-4} M$, DBA $\sim 1-5 \times 10^{-3} M$) in hexane was followed by two successive reactions which were monitored by the absorbance changes between 320 and 370 nm. The absorbance at 366 nm initially increased after the flash and this was followed by a slower decrease in absorbance. A typical set of oscilloscope traces is shown in Figure 2. The pseudo-first-order plot for the faster initial reaction is shown in Figure 3. The initial reaction exhibited a first-order dependence on DBA concentration as shown in Figure 4. The reaction rate was unaffected by the presence of piperylene (0.01 *M*) in agreement with previous conclusions that the reaction with secondary amines involves a singlet species.¹⁸ The slower absorbance decrease was a first-order reaction independent of amine concentration. A similar sequence of reactions was observed in acetonitrile, although, as shown by the data in Table II, the second-order rate constant for reaction with DBA is more than an order of magnitude greater than in hexane.

Table II. Rate Constants for Observed Reactions^a

Substituent	Trapping k , $\text{l. mol}^{-1} \text{sec}^{-1}$	Rearrangement k , sec^{-1}	Bu_2NH_2^- - catalyzed rearrangement k , $\text{l. mol}^{-1} \text{sec}^{-1}$
H	3.5×10^7 (9.7×10^6) ^b	11 (0.11) ^c	3.1×10^6
CH_3	7.5×10^4	$\sim 10^{-4}$ ^d	72
C_2H_5	2.9×10^4	$\sim 10^{-4}$ ^d	
CF_3	7.8×10^6	$\sim 2 \times 10^{-3}$	250

^a All reactions were in acetonitrile except as noted. The temperature was $21.7 \pm 0.3^\circ$. Reproducibility is $\pm 10\%$. ^b In hexane; the rate with 0.01 *M* piperylene is 8.8×10^6 . ^c In hexane. ^d In dioxane.

The first-order dependence of the absorbance increase on the DBA concentration and the identification of the final product as a 3*H*-azepine suggest that the two successive reactions being observed are the trapping of phenyl nitrene or, much more likely, a derived intermediate with DBA to give a 1*H*-azepine followed by unimolecular rearrangement to the stable 3*H*-azepine tautomer. The involvement of a

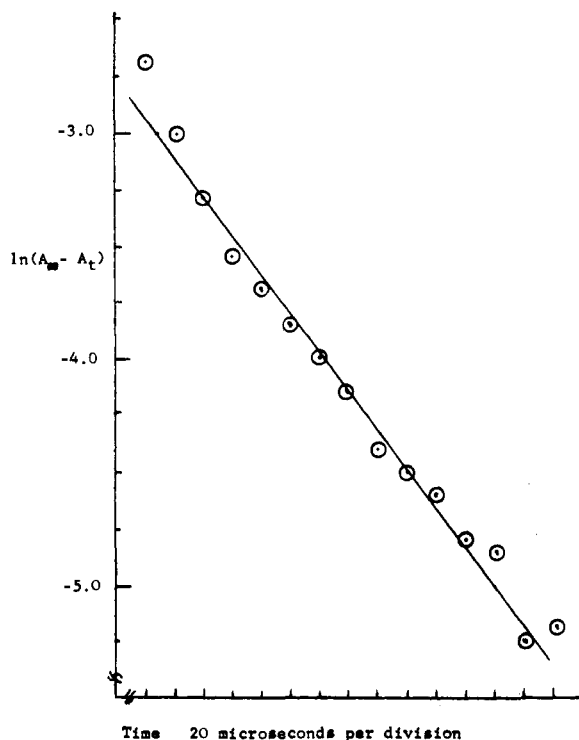
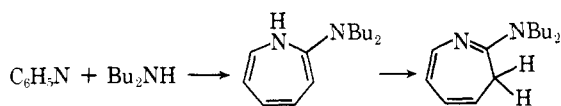


Figure 3. Typical first-order plot of absorbance data for appearance of 1*H*-azepine. Line is derived by least-squares calculation.

1*H*-azepine has previously been suggested.^{8,23} The identity of the specific C_6H_5N species involved in the reaction is considered in the discussion section.



The rate of the second reaction was strongly accelerated by the presence of dibutylammonium ion, as would be expected for a prototropic tautomerism. Second-order rate constants are included in Table II.

Analogous experiments in acetonitrile were carried out using *o*-methylphenyl azide, *o*-ethylphenyl azide, and *o*-trifluoromethylphenyl azide. The rate data are included in Table II. In each instance a reaction first order in DBA was observed following the flash. The reactions were slower for the *o*-methyl and *o*-ethyl compounds by factors of about 500 and 1000, respectively, than for phenyl azide. The trifluoromethyl azide was faster than the unsubstituted compound by a factor of 20.

In each of the ortho-substituted compounds, the unimolecular reaction was much slower than in the phenyl case, and rates were not accurately measurable because of decomposition (probably oxidative) of the intermediate. The low rate for rearrangement of 1*H*-azepines derived from ortho-substituted azides was expected on the basis of previous steady illumination studies which provided spectroscopic and chemical evidence for long-lived 1*H*-azepines.⁸ The spectra of these intermediates could be readily measured and comparison of these spectra with the kinetic spectra for the intermediate in the phenyl azide reaction supports the identification of the transient species in that reaction as the 1*H*-azepine.

The rearrangement of the ortho-substituted analogs was also strongly catalyzed by dibutylammonium ion, although the rates remained four-five orders of magnitude below that of the unsubstituted system.

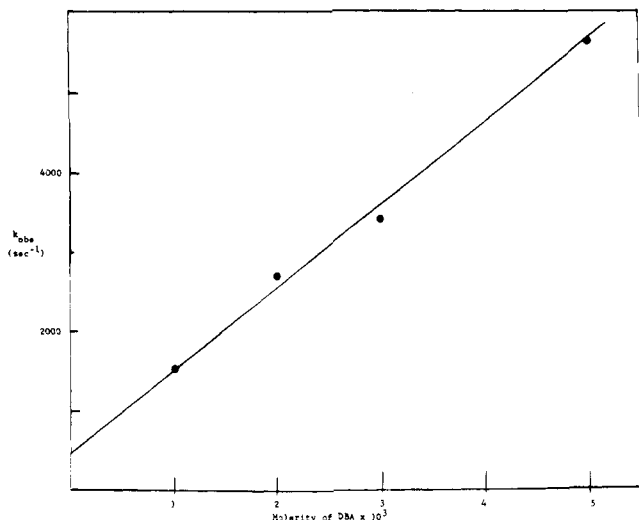


Figure 4. Dependence of observed pseudo-first-order rate constants on DBA concentration.

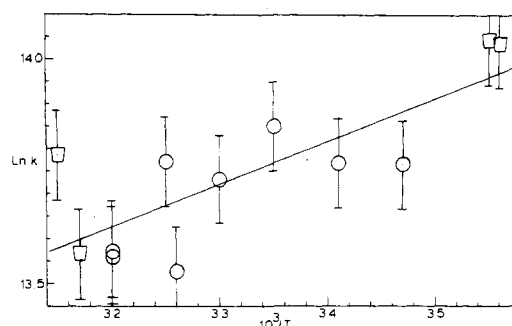
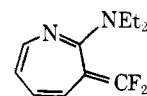


Figure 5. Temperature dependence of rate of trapping of C_6H_5N by DBA in hexane. Circled points and squared points represent separate series of runs several months apart with some equipment modifications. The least-squares line for all points gives a value of $E_a = -1.85$ kcal/mol. The separate series give $E_a = -1.68$ kcal/mol (circles) and $E_a = -1.73$ kcal/mol (squares).

The apparent activation energies and preexponential terms for selected reactions were determined in the conventional manner using a jacketed photolysis cell. Though temperature control was not a problem (*i.e.*, $\pm 0.05^\circ$), the available temperature range was limited. As a consequence, the suggested error limits on E_a (apparent) are about twice the least-squares σ value. The Arrhenius plot for the reaction with DBA in hexane is shown in Figure 5. The results of the temperature studies are collected in Table III.

Previous preparative studies have established that 3-alkyl-2-diethylamino-3*H*-azepines are the major products from steady-state photolysis of *o*-alkylphenyl azides.⁸ Product identification studies carried out under identical conditions for the *o*-trifluoromethyl system resulted in the isolation of 3-difluoromethylene-2-diethylamino-3*H*-azepine. This product is derived from the expected azepine by elimination of HF. The first-order dependence of the trapping



reaction on DBA concentration and the strong $Bu_2NH_2^+$ catalysis of the rearrangement reaction convince us that the two observed reactions are analogous to those in the other systems. Elimination of HF presumably takes place during

Table III. Activation Energies and Preexponential Factors for Selected Reactions^a

Reactants		Solvent	Reaction	E_a (obsd), kcal mol ⁻¹	A
Phenyl azide	DBA	Hexane	Trapping	-1.8 ± 0.2	$(4.2 \pm 1.4) \times 10^4 M^{-1} \text{sec}^{-1}$
<i>o</i> -Tolyl azide	DBA	CH ₃ CN	Trapping	1.1 ± 0.2	$(5.9 \pm 1.3) \times 10^6 M^{-1} \text{sec}^{-1}$
Phenyl azide	DBA	Hexane	Rearrangement	1.1 ± 0.4	$0.7 \pm 0.3 \text{sec}^{-1}$
Phenyl azide	DBA	CH ₃ CN	Rearrangement	2.0 ± 0.2	$(4.2 \pm 1.0) \times 10^2 \text{sec}^{-1}$
Phenyl azide	Bu ₂ NH ₂ Cl, DBA	CH ₃ CN	Rearrangement	2.6 ± 0.2	$(3.8 \pm 0.7) \times 10^8 M^{-1} \text{sec}^{-1}$
<i>o</i> -Tolyl azide	Bu ₂ NH ₂ PF ₆ , DBA	CH ₃ CN	Rearrangement	9.9 ± 0.5	$(5.9 \pm 0.8) \times 10^9 M^{-1} \text{sec}^{-1}$

^a The rate data and Arrhenius plots from which the activation data are taken will appear following these pages in the microfilm edition of this volume of the journal. See paragraph at end of paper regarding supplementary material.

the preparative work-up. The facile elimination of HF from somewhat related molecules has been reported.²⁴

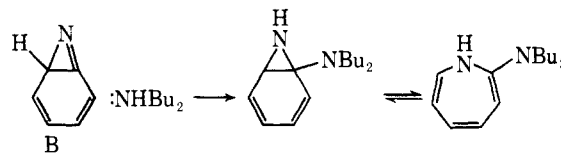
Discussion

In the presence of DBA, the first absorbance change observable after the flash is that of a reaction which is first order in amine and leads to a 1*H*-azepine. It will be referred to as the trapping reaction. This has usually been formulated as the reaction of the amine with the highly strained azirine B.⁶⁻⁸ Phenyl nitrene is unlikely to be involved directly in the trapping reaction for several reasons. It is difficult to envisage a satisfactory mechanism for the formation of an azepine from the unrearranged nitrene. More definitively, the intermediate which reacts with DBA shows no prominent absorption beyond 300 nm. It is expected that, if it had a sufficient lifetime, singlet phenyl nitrene would be observed spectroscopically, although only a crude model for the spectrum is available. Simple derivatives of the isoelectronic benzyl carbonium ion absorb with strong maxima near 300–320 nm and weaker bands near 400 nm.²⁵ Triplet phenyl nitrene absorbs at 241, 303, 314, 368, and 402 nm.¹⁶ This is similar to the spectrum of the benzyl radical²⁶ in which the π -electron system is identical. Shillady and Trindle²⁷ have used semiempirical MO methods to calculate the absorbance spectrum of phenyl nitrene. They predict a band near 360 nm of medium intensity. Finally, the trapping reaction occurs over a period of around 300 μsec . This implies a lifetime in the millisecond range for the intermediate. Indeed, if the rate constants measured in the absence of amine are taken as a measure of the lifetime, then it has a half-life of about 5 msec. Although direct measurements of singlet carbene and nitrene lifetimes have not been accomplished, there is general agreement that such intermediates are characterized by very short lifetimes.²⁸ Since formation of the C₆H₅N species which reacts with DBA is complete within $\sim 80 \mu\text{sec}$ of the flash, an upper limit of $\sim 30 \mu\text{sec}$ can be placed on the lifetime of phenyl nitrene. The fact that the intermediate does not absorb above 300 nm and has a lifetime in the millisecond range is compatible with structure B.

The mechanism shown in Scheme I, which excludes separate steps for fast proton transfers between nitrogen atoms, indicates that a 7-azabicyclo[4.1.0]diene is a required intermediate. No absorbance changes attributable to the valence tautomerism were detected. Kinetic studies on the related oxepin-arene oxide valence tautomerism have shown that this reaction occurs at rates around 10^6 – 10^7sec^{-1} at room temperature.²⁹ With DBA concentrations about $10^{-3} M$ resulting in pseudo-first-order rate constants in the range 10^4sec^{-1} and less, the unimolecular valence tautomerism would be faster than trapping and, therefore, not observable.

An alternative formulation of the reaction in which C is the reactive species is not incompatible with our kinetic results. Only a crude experimental model for the spectrum of C is available. The isoelectronic cycloheptatrienyl ion has an absorption maximum at 275 nm which trails into the visible.³⁰ Shillady and Trindle²⁷ predict that C would ab-

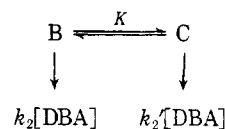
Scheme I



sorb significantly above 300 nm. This would tend to argue against structure C but is not conclusive. The 1*H*-azepine could also be formed from azacycloheptatetraene, E. Both C and E are calculated²⁷ to be higher in energy than B and we therefore favor B as the species trapped by amine.

Activation data were obtained for the trapping reaction for the intermediate from phenyl azide in hexane and for the *o*-methyl system in acetonitrile. The former system exhibits a small negative E_a (Figure 5) and the latter a small positive E_a . The data for the unsubstituted system were obtained from two separate series of runs with some instrumental modifications. The two independent series are in good agreement, and the observed negative E_a is unlikely to be an experimental artifact.

A possible, though not unique, explanation for the negative E_a can be formulated in terms of two C₆H₅N intermediates in rapid equilibrium. A negative E_a would be observed if the two species were in rapid equilibrium with the enthalpically favored intermediate being more reactive toward DBA. Specifically, the negative E_a could arise if $K \geq 0.1$ and $k'_2 \leq 0.5k_2$ and with ΔH° for the equilibrium

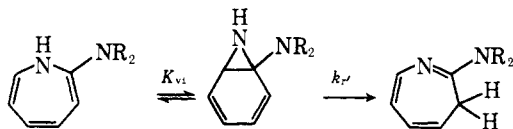


positive. These conditions are not unduly restrictive.³¹ The equilibrium might involve any of the possible C₆H₅N isomers, but we formulate it in terms of C. The requirement that C be less reactive than B is not unreasonable in view of the demonstration that cycloheptatrienylidene reacts preferentially with electron deficient molecules and exhibits a positive ρ value in reactions with styrenes.³³ The electron deficiency at the carbene center can apparently be effectively delocalized over the π -system.

The substituent effects in the trapping reactions are probably a combination of steric and electronic effects. These would work together in the *o*-methyl and *o*-ethyl systems to retard reaction both by inductive electron release and steric hindrance. The increased reactivity of the trifluoromethyl compound can be attributed to inductive electron withdrawal outweighing steric retardation. Interpretation of these substituent effects is clouded by the fact that they might also operate by affecting any B \rightleftharpoons C equilibrium.

The uncatalyzed rearrangement of the unsubstituted 1*H*-azepine in hexane is characterized by a low E_a and very low A factor. The cause of these anomalous activation parameters may lie in geometric restrictions on a unimolecular reaction of the 1*H*-azepine. We considered the possi-

bility that the reaction could effectively proceed only through a 7-azabicyclo[4.1.0]hepta-2,4-diene valence tautomer. If this were the case the measured activation parameters would reflect the prior equilibrium.

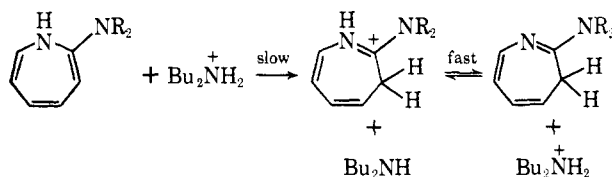


If this mechanism were to obtain the observed rate (k_r) of decay of the 1H-azepine would be given by

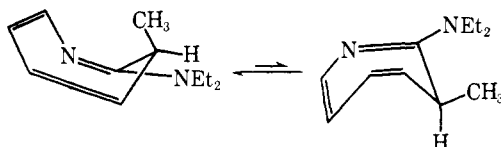
$$k_r = \frac{k_r' K_{vt}}{1 + K_{vt}}$$

The details of valence tautomerism in the azepine-7-azabicyclo[4.1.0]hepta-2,4-diene system³⁴ are not so well known as in the oxepin-arene oxide^{29,35} or norcaradiene-cycloheptatriene systems³⁶ but the available data for these systems provide some basis for estimating its thermodynamic characteristics. If the valence tautomerism is considered to be limited by $K_{vt} = 10^{-1}$ - 10^{-2} and by values of ΔS° between -5 and -10 eu, then ΔH° is between -1.6 and $+1.2$ kcal/mol. The effect of the equilibrium on the observed A value can then be calculated. With these limits the A value for the process designated by rate constant k_r' remains very low (10 - 10^2). Thus it appears that the hydrogen shift is "forbidden" by steric or stereoelectronic factors whether it occurs directly from the 1H-azepine or *via* a prior valence tautomerism. The A value increases somewhat on changing to acetonitrile as the solvent but remains low.

The presence of the proton donor dibutylammonium ion greatly increases the rate of rearrangement and leads to a reaction which is first order in both intermediate and amine salt. The rate-limiting step under these conditions is presumably C-protonation of the 1H-azepine. The activation energy for the acid-catalyzed rearrangement is low in the unsubstituted case but is about 9 kcal/mol for the *o*-methyl



system. The increase in E_a is primarily responsible for the 43,000-fold difference in the two rates. An explanation previously advanced,⁸ suggests the basis for this substituent effect. The preferred conformation for the methyl group in the 3H-azepine is in the "axial" position. This conformation minimizes eclipsing between the dialkylamino and alkyl substituents. The stereoelectronic preference for axial approach of the proton on the π -system leads to the unfavorable conformation.



The increased E_a in the substituted system is attributed to the eclipsing which develops.

Summary

This study provides the first kinetic data on the reaction of phenyl nitrene with secondary amines. The existence of at least two steps resulting in formation of 1H-azepine and 3H-azepine derivatives, respectively, has been established. The fact that the intermediate which is trapped does not ab-

sorb strongly beyond 300 nm is consistent with prior mechanistic postulates which have assigned structure **B** to the C₆H₅N species that reacts with nucleophiles. A short lifetime for phenyl nitrene itself is implied. Substituent effects, solvent effects, and, especially, activation energies and A values are suggestive of possible additional complications to the basic mechanism of Scheme I, but none of these effects are subject to unique interpretations on the basis of current data.

Experimental Section

The flash photolysis system was of generally conventional design.³⁷ Up to four 5- μ F, low-inductance capacitors were discharged through two 25-cm flash tubes filled with xenon-nitrogen mixture. Cylindrical cells of 5-, 10-, and 20-cm path length were mounted coaxially to the lamps in an aluminum chamber which served as a reflector. Three different analysis lamps were used: an Osram 100-W Hg lamp for observations at 366 nm of less than 10-msec duration, an Osram 75-W Xe lamp for observations at other wavelengths of less than 10-msec duration, and a Phillips 50-W tungsten-iodine lamp for observations of longer duration. A Jarrell-Ash Model 82-410 monochromator served to isolate the desired wavelength. A 1P28 photomultiplier was used as the detector. The output of the photomultiplier was power amplified by an Analog Devices 144 A operational amplifier in the voltage follower configuration. The output was displayed on an oscilloscope with the initial and final transmittances read from a 10-mV recorder.

Rate constants were derived from Polaroid pictures of the oscilloscope traces. Points on the voltage-time curve were read with calipers and converted to absorbances with the aid of a Hewlett-Packard 9100B programmable calculator. The usual least-squares plots were then constructed to obtain the rate constant.

The hexane was solvent grade material, distilled from and stored over Dri-Na prior to use. The acetonitrile was obtained from Matheson Coleman and Bell and was distilled from CaH₂ and stored over molecular sieves prior to use. The azides had been previously prepared in this laboratory by method A of Smith and Brown.³⁸ They were distilled at reduced pressure before use, except for *o*-trifluoromethylphenyl azide which was recrystallized. Di-*n*-butylamine was obtained from Aldrich. It was distilled at reduced pressure from KOH before use. Di-*n*-butylammonium hydrochloride was prepared by the treatment of the free amine in ether solution with HCl gas. It was recrystallized from benzene before use.

Di-*n*-butylammonium Hexafluorophosphate. Di-*n*-butylammonium hydrochloride (0.032-mol, 5.34 g), and 5.25 g of ammonium hexafluorophosphate (0.032 mol) obtained from Alfa were stirred together for 16 hr in 25.0 ml of dry tetrahydrofuran. The ammonium chloride was filtered off and the THF removed on a rotary evaporator. The crude product was recrystallized from methylene chloride before use.

Anal. Calcd: C, 34.91; H, 7.33; N, 5.09. Found: C, 35.01; H, 7.42; N, 5.08.

3-Difluoromethylene-2-diethylamino-3H-azepine. A solution of *o*-trifluoromethylphenyl azide (302 mg) in 60 ml of 5% by volume DEA in THF was purged with N₂. The solution was irradiated for 17 min using a 450 W Hanovia lamp maintaining a continuous nitrogen flow. At this point tlc indicated complete disappearance of the starting material. The solution was transferred by syringe to a solution of deoxygenated methanol and refluxed under an N₂ atmosphere for 4 hr. The solvent was partially evaporated and the residue analyzed by glpc on a 6 ft FS-1265 on Anakrom 50/60 ABS column temperature programmed from 80 to 150° at 10°/min. The yield was 71% based on an internal standard. An analytical sample was prepared by preparative glpc on a similar column: UV λ_{max} 318 (95% EtOH, log ϵ 3.78), $\nu_{C=CF_2}$ 1730 cm⁻¹; nmr peaks (CDCl₃) at δ 6.95 (d, J = 8 Hz, 1 H) 6.30 (m, 1 H), 5.40 (t superimposed on m, J = 8 Hz, 2 H), 3.46 (q, 4 H), 1.12 (5, 6 H); mass spectrum, 212, 197, 183.

Anal. Calcd for C₁₁H₁₄N₂F₂: C, 62.33; H, 6.65; N, 13.20. Found: C, 62.05; H, 6.82; N, 13.14.

Supplementary Material Available. The rate data and Arrhenius plots from which the activation data are taken will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this

paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-7491.

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