384 (1.8), 341 (1.3), 256 (49), 214 (56), 170 (21), 145 (26), 69 (23), 43 (100).

3b: mp 194–195 °C; UV (302 (3.33); IR 1779, 1724, 1639, 1565, 1407, 1365, 1179, 1014; ^{1}H NMR (400 MHz, $CDCl_3$) 7.31–7.18 (2 AA′BB′C, 10 H_{ar}), 5.92 + 5.85 (AB, $^4J_{1^3,1^5}$ = 2.0, 1^5- and 1^3-H, respectively), 4.48–4.43 + 4.32–4.28 (AA′BB′, 4 $H_{cyclobutane}$), 2.20 (s, 1^4- and 3^4-$OCOCH_3$); MS (evaporation at 185 °C) (pos CI) 530 (10, $M^+ + NH_4$), 462 (1.4), 420 (2.5), 274 (100, $M^+/2 + NH_4$), 137 (21), 120 (25).

Solid-state irradiation of the oxazinone **4** in aqueous suspension as described above did not lead to any photoreaction (analysis by IR and powder diagrams).

X-ray Data Collection, Data Processing, and Structure Refinements. Data for compounds **1b** and **4** were collected on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator. The experimental procedures were similar for both compounds. Pertinent experimental details are given in Table II. Suitable crystals of both compounds were sealed under argon in glass capillaries and kept at 100.0 (5) K during data collection. Cell constants were obtained from 75 (50) automatically centered reflections with 17.68 < 2θ < 41.04° (**1b**) and 24.0 < 2θ < 40.70° (**4**). Three standard reflections were used to monitor intensity fluctuations during measurement. The orientation matrices were established by least-squares refinement using 25 reflections in each case. Three of these reflections were used to record changes in the orientation of the crystals. Deviations in θ larger than 0.12° were followed by calculation of new orientation matrices. All data below θ = 20° were measured at 7 different Ψ angles in order to detect and minimize the effects of double reflections.[9] For all other reflections, two different Ψ settings (0°, 15°) were used. In addition, for both compounds half-spheres of reciprocal space were recorded. Strong reflections were remeasured at reduced tube power and scaled accordingly during data reduction using three standard reflections. Erroneous measurements were detected with an initial screening process (program PSICOM).[14]

The initial structure models were taken from room-temperature structural investigations. The structures were solved using direct methods (SHELXS-86).[15] Subsequent calculations were performed as described using the low-temperature data sets. Full-matrix least-squares refinements were carried out using a local (GFMLX) modification of ORFLS.[16] All hydrogen atom positions were determined from difference Fourier syntheses. Full data refinement (($\sin \theta)/\lambda$ < 0.85 Å^{-1}) included one scale factor, positional parameters for each atom, and ADP (atomic displacement parameters) for all non-hydrogen atoms. In order to obtain positional parameters and ADP unaffected by the valence electron densities, non-hydrogen atom parameters and the scale factors were refined on the basis of high-order data (see Table II). All refinements were based on F, and the weighting scheme applied was $\sigma^{-2}(F)$. Final high-order parameters are listed in Tables III–VI.

Standard atomic parameters of the heavier atoms were kept fixed during the subsequent multipole refinement. Hydrogen atom positions were refined to correct for the aspherical shift. The multipole structure model was designed for refinement with the program MOLLY.[10] Atomic scattering factors were taken from the literature.[17]

The multipole expansion was terminated at the octopole level for all non-hydrogen atoms. For each hydrogen atom, one dipole oriented in the direction of the C–H bonds was included. Its population was set to 0.2 electron and kept fixed during refinement. Constraints due to chemical equivalence and local site symmetry were used to maintain a reasonable ratio of observed reflections to refined parameters.[18] Radial shielding parameters κ were included in the refinement procedures. For the hydrogen atoms of **1b** this value was set to 1.144, and it was not refined subsequently.[19] The refinements of the multipole models were based on F, and the weighting scheme applied was $\sigma^{-1}(F)$; for further details, see Table II.

Acknowledgment. Part of this work was supported by the Fonds der Chemischen Industrie. I.O. thanks the Volkswagen-Stiftung for a doctoral fellowship.

Registry No. 1b, 138744-79-3; **2b**, 138744-80-6; **3b**, 138744-81-7; **4b**, 138744-82-8.

Supplementary Material Available: Tables of detailed information on the crystal structure determinations, final atomic position parameters, final thermal parameters, and interatomic distances and angles for **1b** and **4** (22 pages); listing of observed and calculated structure factors (36 pages). Ordering information is given on any current masthead page.

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(18) The corresponding multipole functions at the phenyl carbon atoms were constrained during the refinement procedures. In addition, model a assumed local mm2 symmetry within the phenyl substituent and local 3m symmetry at the methyl carbon atom. The corresponding multipole parameters were constrained for all hydrogen atoms.

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Chemistry and Kinetics of Singlet (Pentafluorophenyl)nitrene

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Abstract: The chemistry and kinetics of singlet (pentafluorophenyl)nitrene were studied by chemical trapping and laser flash photolysis techniques. Photolysis of pentafluorophenyl azide in cyclohexane, benzene, diethylamine, pyridine, tetramethylethylene, tetrahydrofuran, dimethyl sulfoxide, and dimethyl sulfide forms adducts in fair to good yields. At ambient temperature singlet (pentafluorophenyl)nitrene is intercepted, and intersystem crossing to the lower energy triplet state is unimportant. Triplet nitrene chemistry can be achieved by benzoylbiphenyl photosensitization, the presence of methanol or ethyl iodide, or by lowering the reaction temperature below 0 °C. The singlet nitrene adduct formed in pyridine is an ylide whose structure has been determined by X-ray crystallography. The ylide has an intense absorption maximum at 390 nm which varies only slightly with solvent. The pyridine ylide is a useful probe for monitoring the absolute kinetics of singlet (pentafluorophenyl)nitrene by laser flash photolysis techniques.

I. Introduction

Light and heat induced decomposition of phenyl azide **1** leads to the formation of polymeric tar along with small amounts of azobenzene and aniline.[1] The yields of the latter two volatile products can be improved by high dilution of phenyl azide.[2] Adducts derived from capture of phenylnitrene **2** are not produced

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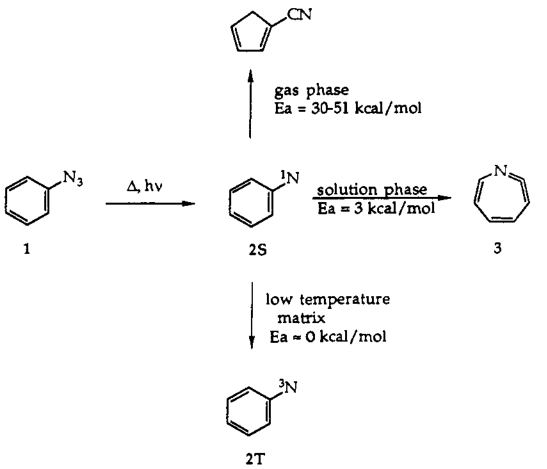
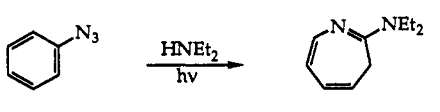
Scheme I



in any solvent trap in better than trivial yields at ambient temperature.[1] However, upon decomposition of phenyl azide in amine solvents, ring expanded adducts are formed which are derived from capture of ketenimine 3 (Scheme I).[3] This trend remains dis-



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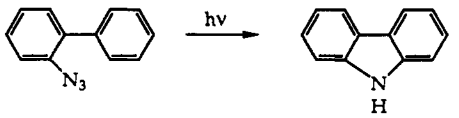
appointingly true for most derivatives of phenyl azide, although exceptions are known.[1] Decomposition of ortho substituted aryl azides leads to the intramolecular capture of the nitrene intermediate.[4]



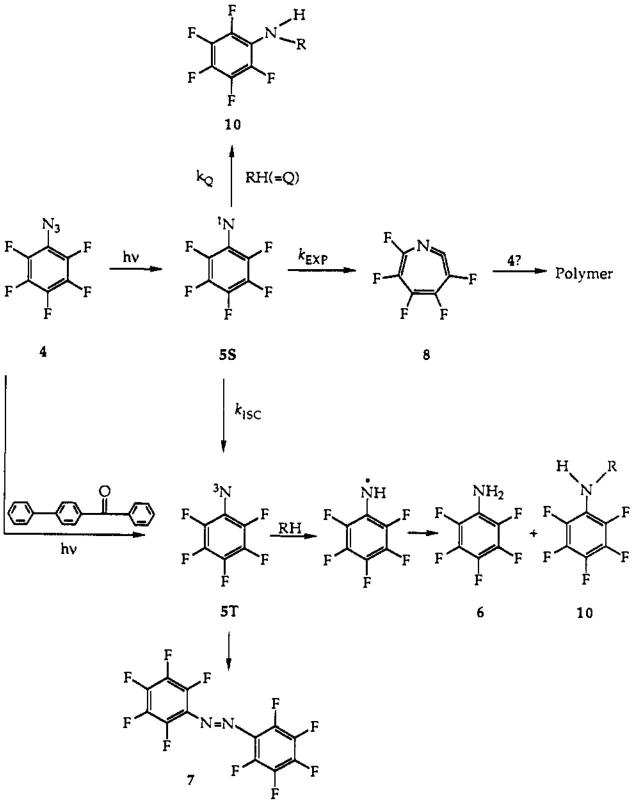
In 1972 Banks and Sparkes reported that pyrolysis of polyfluorinated aryl azides in alkane, alkene, and aromatic solvents produces adducts derived from intermolecular reactions of polyfluorinated arylnitrenes.[5] More recently this laboratory[6] and Keana's[7] group communicated that these reactions could be initiated photochemically. In this paper we are pleased to report our photochemical studies of pentafluorophenyl azide (**4**) using the tools of both chemical analysis and laser flash photolysis. Our results yield the absolute rates of reaction of singlet (pentafluorophenyl)nitrene **5**. The data reveal the origin of the fluorine effect on the photochemistry of pentafluorophenyl azide.

Table I. Yield of Singlet Nitrene Adducts Formed on Photolysis of **4** in Various Solvents[a]

solvent trap	yield adduct (%)	**6** (%)	**7** (%)
cyclohexane	22	2	0
cyclopentane	28	0	0
cyclopentane (triplet sensitized)	4.4	12	5
tetramethylethylene	49	*b*	*b*
benzene	39	5	0
benzene (triplet sensitized)	0	6.2	32
toluene	51	12	0
toluene (triplet sensitized)	10	26	6
tetrahydrofuran	41	3	0
dimethyl sulfide	12	*b*	*b*
dimethyl sulfoxide	41	*b*	*b*
diethylamine	58	22	0

[a] All yields are ±2%. [b] The yield was not quantified, but the product is formed in only minor amounts.

Scheme II



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It is now clear that the photochemistry of both phenyl azide **1** and pentafluorophenyl azide **4** conform to the same mechanistic scheme. Photolysis of phenyl azide **1** liberates singlet phenylnitrene **2S** whose ultimate fate depends on the temperature and phase in which it is generated (Scheme I). In the gas phase singlet phenylnitrene **2S** is formed with excess vibrational energy which allows it to overcome a relatively large barrier to form cyanocyclopentadiene, the global C_5H_5N minimum.[8] In solution phase singlet phenylnitrene **2S** is collisionally deactivated and only has energy sufficient to overcome a small barrier and expand to azacycloheptatetraene **3**.[9] At cryogenic temperatures singlet phenylnitrene **2S** does not ring expand but instead undergoes intersystem crossing to the lower energy triplet state, a process which probably does not traverse an enthalpic barrier.[9] The barrier to ring contraction of singlet phenylnitrene is 30–51 kcal/mol,[8a] the barrier to ring expansion is only 3 ± 1 kcal/mol. It will be demonstrated that the major difference between phenylnitrene and pentafluorophenylnitrene is that fluorine raises the barrier to ring expansion and retards the rate of rearrangement (k_{EXP}) of the singlet nitrene. This leads to an increased efficiency of the trapping of the nitrene with external reagents.

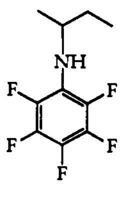
In the absence of amine trapping agents azacycloheptatetraene **3** undergoes polymerization. The polymer has been characterized by Meijer who found that it contains a repeating seven-membered ring unit.[10] Polymer formation is not associated with triplet phenylnitrene **2T**, and tars are not formed upon triplet sensitized photolysis of phenyl azide.[10]

II. Product Studies

Photolysis of pentafluorophenyl azide **4** in alkane, alkene, aromatic, ethereal, amine, sulfide, sulfoxide, and pyridine solvents yields adducts as shown in Figure 1 with yields listed in Table I. The yields of pentafluoroaniline **6** and pentafluoroazobenzene **7** are generally quite low or zero in all cases, which indicates that the adducts are primarily derived from capture of singlet nitrene **5S** (Scheme II).

The data are reminiscent of studies with phenylcarbene (PC).[11] Although PC and (pentafluorophenyl)nitrene both have triplet ground states,[12] the majority of products formed in each case derive from capture of a low lying highly reactive singlet state. No adducts are formed on the photolysis of pentafluorophenyl azide in methylene chloride (Scheme II). The only volatile product formed in this solvent is a small amount of decafluoroazobenzene **7**; the major product is polymeric tar. Tar formation is thought to be due to oligomerization of the ketenimine intermediate **8** by analogy to the well studied phenyl azide system. Thus, the data suggest that singlet pentafluorophenylnitrene does not react with CH_2Cl_2.

Alkane Solvents. We have recently reported our analysis of the photochemistry of pentafluorophenyl azide in alkanes,[13] which will be briefly reviewed. Adducts **11** and **12** were formed upon photolysis of **4** in butane and 2,3-dimethylbutane, respectively.[13] No evidence for the involvement of triplet pentafluorophenylnitrene was found at 25 °C.[13] We reported that upon photolysis of **4** at low temperatures the yield of products derived from triplet (pentafluorophenyl)nitrene is greatly enhanced.[6,13] This demonstrated that there must be enthalpic barriers to both ring expansion of **5S** and for its insertion into CH bonds, both of which are processes that compete with singlet to triplet nitrene ISC. It was concluded that intersystem crossing must be the process with the lowest enthalpic barrier but must have the poorest frequency factor.[13] The product analysis data which follows in various solvents were obtained in this study.



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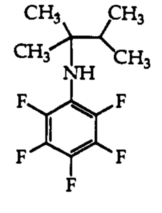

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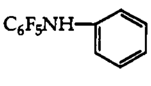
Aromatic Solvents. Singlet nitrene **5S** reacts with benzene to form **13**, toluene to produce **14–18**, and naphthalene to give adducts **19** and **20**.



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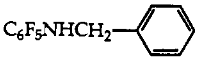

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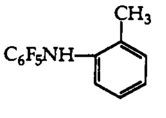

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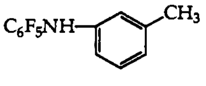

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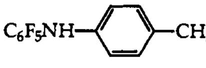

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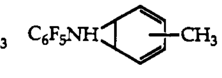

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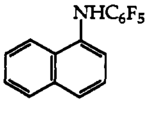

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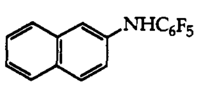

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A single adduct of pentafluorophenylnitrene is formed in benzene in 39% yield along with a small amount (5%) of (pentafluorophenyl)aniline **6**. The adduct is not formed upon triplet sensitized photolysis of **1**; under these conditions a 6% yield of aniline **6** and a 32% yield of decafluoroazobenzene **7** is realized. This demonstrates that the benzene adduct is a product of capture of singlet nitrene **5S**. The yield of adduct is also a function of the concentration of azide. With 4.78×10^{-2} M of azide **4**, a 39% yield of adduct is realized, when the concentration of **4** is reduced to 1.02×10^{-2} M the adduct yield jumps to 53%. This illustrates that reaction of **5S** or **8** with azide precursor is a major competitive pathway to adduct formation. The initially formed adduct is not the isolated diarylamine **13** but is an isomer of this material. The initially formed species rearranges to **13** in a dark reaction. Abramovitch[14] found that deoxygenation of pentafluoronitrosobenzene produced a yellow oil which underwent a Diels–Alder reaction with tetracyanoethylene. The product of this reaction was completely characterized by Abramovitch,[14] which led, in turn, to the identification of the structure of compound **21**. We suspect

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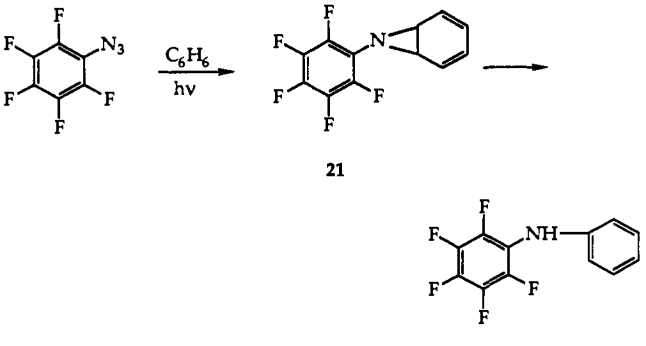
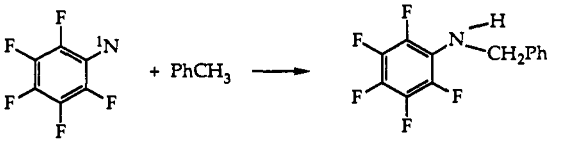


21

13

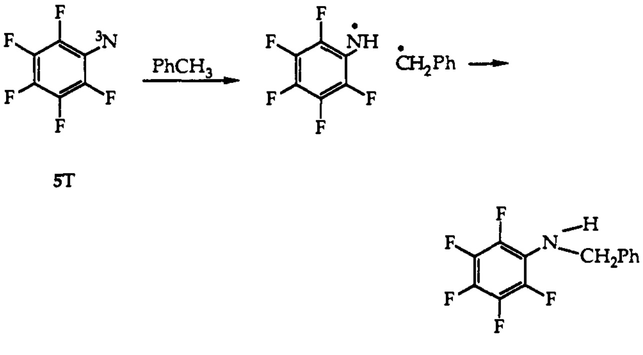
that the initially formed, transient benzene–nitrene adduct produced photochemically in our laboratory is actually compound **21**, but we have made no attempt to characterize it further.

The toluene studies are particularly revealing mechanistically (Table III).[15] Upon photolysis of **4** in neat toluene at ambient temperature neither 1,2-diphenylethane nor azo compound **7** is formed. Pentafluoroaniline **6** is formed in only small amounts. These observations indicate that there is little triplet nitrene chemistry under these conditions. Because of their ease of reduction, azide **5** may be converted in part to aniline **6** by non-nitrene pathways such as the photoreduction of an azide excited state or by reaction of the azide with a reactive intermediate generated in the course of photolysis. Thus small amounts of aniline **6** formed in the reaction do not necessarily signal the presence of triplet nitrene **5T**. We therefore conclude that in this solvent, photolysis of azide **4** produces minimal triplet nitrene **5T**. It is possible to achieve triplet nitrene chemistry upon sensitization with benzoylbiphenyl (Table III). This is clearly demonstrated by a sharp increase in the yield of both pentafluoroaniline **6** and decafluoroazobenzene **7** upon triplet photosensitization. The change in the ratio of toluene adducts **14**/(**15** + **17**) observed upon photosensitization is particularly revealing. As with benzene, aromatic substitution adducts **15** and **17** are formed only by interception of the singlet nitrene. However, benzylic insertion adduct **14** has a dual origin. It can be formed by a CH insertion reaction of **5S**



5S **14**

or by hydrogen atom abstraction–radical recombination reactions of **5T** with toluene.



5T

14

The ratio (**14**/**15** + **17**) is infinite upon triplet sensitization but is ≈0.1–0.2 upon direct photolysis at 25 °C. This is further evidence that triplet nitrene **5T** is not formed in significant amounts upon direct photolysis of **5** and that ISC of **5S** to **5T** is very slow at ambient temperature relative to other processes which consume singlet (pentafluorophenyl)nitrene. However, once formed the ground state **5T** does not regenerate the low lying singlet state.

Table II. Products Formed upon Photolysis (λ ≈ 350 nm) of **4** at 25 °C at Various Concentrations of Toluene in CH_2Cl_2

	absolute % yields						
[$PhCH_3$]	**6**	**14**	**15**	**17**	**18**	**7**	**14**/(**15** + **17**)
9.4 $M^{a,b}$	9.2	3.9	13	10			0.16
7.1 $M^{a,b}$	10	2.6	12	6.1			0.15
4.7 $M^{a,b}$	8.2	2.0	10	7.2			0.12
3.3 $M^{a,b}$	10	2.0	9.6	6.0			0.12
2.4 $M^{a,b}$	10	1.8	9.5	5.2			0.12
9.4 $M^{c,d,g}$	12	8.5	20	22			0.20
9.4 $M^{c,e,g}$	26	9.7				6	∞
9.4 $M^{a,b,f}$	8.8	2.6	0.59	1.0	6.9	3.9	0.24
7.1 $M^{a,b,f}$	9.0	2.8	0.85	2.2	8.5	3.4	0.21
4.7 $M^{a,b,f}$	7.9	2.1	0.52	2.9	8.9		0.17
3.3 $M^{a,b,f}$	8.2	1.3	0.77	2.7	8.7		0.11
2.4 $M^{a,b,f}$	8.3	1.7	3.2	11	9.5	5.1	0.072

[a] 30 minutes photolysis. [b] 0.03 M azide **4**. [c] 4 hours photolysis. [d] 0.0403 M azide **4**. [e] 0.0125 M azide **4** and .01 M 4-benzoylbiphenyl present as triplet sensitizer. [f] at −78 °C. [g] 2 hours photolysis.

Table III. Distribution of (Pentafluorophenyl)nitrene–Toluene Adducts Formed in the Presence and Absence of Oxygen as a Function of Temperature[a]

T (°C)	additive	**14**/(**15** + **17** + **18**[b])	**6**	**7**
25	N_2	0.07	11	0
25	O_2	0.20	10	0
−78	N_2	0.20	6.6	12
−78	O_2	0.50	8.0	0

[a] 0.0323 M azide, 4 hours photolysis. [b] This product is observed only upon photolysis at −78 °C.

Table IV. Effect of Alkylhalides and Methanol on the Products Formed on Photolysis of **4** in the Presence of Toluene

[toluene]	cosolvent/additive	**6**	**7**	**14**	**15**	**17**
6.3	CH_3CH_2I (0.5 M IP[a])	64.5				
6.3	CH_3CH_2I (0.13 M IP[a])	57				
4.7	CH_3CH_2I	44	10			
6.6	$CH_3CH_2CH_2CH_2Br$	36			28	6
7.5	CH_3OH	19		6	6	
5.6	CH_3OH	23				
3.8	CH_3OH	37				
0	CH_3OH	56				

[a] Isoprene.

At −78 °C some triplet nitrene **5T** is formed upon direct photolysis of **4** as demonstrated by the formation of decafluoroazobenzene **7**. Significantly, oxygen completely suppresses the formation of azo dimer **7** at −78 °C but has no effect on the yield of aniline **6** at this temperature, demonstrating the different origins (nitrene and non-nitrene) of these two products.

These results are very different from those realized with PC[10] or (pentafluorophenyl)carbene.[17] The singlet and triplet states of the carbenes equilibrate more rapidly than they react with hydrocarbon trapping agents, and they do not suffer ring expansion[18] in solution at 25 °C.

Catalyzed Intersystem Crossing. Triplet nitrene **5T** can be generated by sensitized photolysis of **4** or upon photolysis at low temperature but not upon direct photolysis and dilution with an inert solvent. In an attempt to catalyze intersystem crossing of

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(15) Poe, R.; Grayzar, J.; Young, M. J. T.; Leyva, E.; Schnapp, K. A.; Platz, M. S. *J. Am. Chem. Soc.* **1991**, *113*, 3209.

(16) (a) Abramovitch, R. A.; Challand, S. R. *J. Chem. Soc., Chem. Commun.* **1972**, 964. (c) Waddell, W. H.; Go, L. *J. Am. Chem. Soc.* **1982**, *104*, 5804.

(17) Admasu, A.; Platz, M. S.; unpublished research at The Ohio State University.

(18) (a) Jones, R. C.; Turner, A. B.; Jones, W. M. *J. Am. Chem. Soc.* **1969**, *91*, 7754. (b) Jones, W. M. *Accts. Chem. Res.* **1977**, *10*, 353. (c) Gaspar, P. P.; Hsu, J.-P.; Chari, S.; Jones, Jr., M. *Tetrahedron* **1985**, *41*, 1479. (d) Vander Stouw, G. G.; Kraska, A. R.; Shechter, H. *J. Am. Chem. Soc.* **1972**, *94*, 1655.

Scheme III

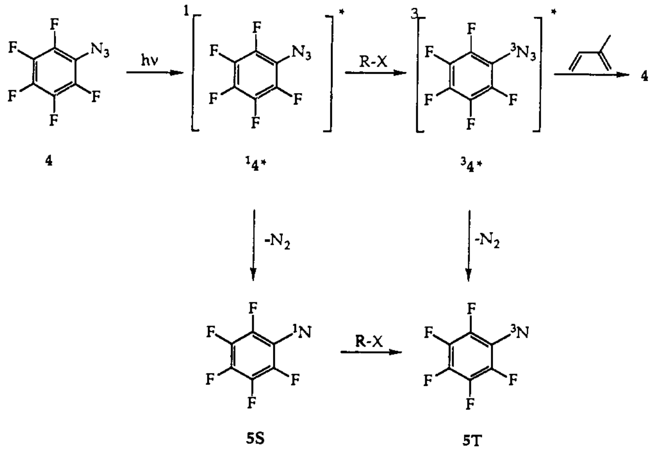


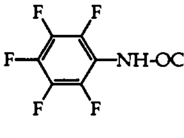
Table V. Distribution of Products Formed on Photolysis of Pentafluorophenylazide in Toluene Containing Naphthalene[a]

temp (°C)	absolute % yield						k_{Np}/k_{Tol}[b]
	6	**14**	**15**	**17**	**18**	**19**	
25	22	5.0	13	8.0	0	1.8	16
0	26	3.9	7.6	5.4	0	4.0	57
−25	23	3.4	6.0	8.4	0	4.5	59
−50	15	3.3	5.4	4.0	6.3	8.1	93
−78	11	4.5	0	0	18	12	128

[a] [Toluene]/[naphthalene] = 185/1. [b] Obtained from the relation **19**/(**14** + **15** + **17** + **18**) = k_{Np}[Np]/k_{Tol}[Tol].

5S → **5T**, ethyl iodide and *n*-butyl bromide were added to the photolysis mixture. These additives have a very dramatic effect on the product distribution in toluene (Table IV).[15] The yields of pentafluoroaniline **6** and decafluoroazobenzene **7** are dramatically enhanced in the presence of heavy atoms suggesting that triplet nitrene **5T** has been formed in solution. The presence of ethyl iodide results in a larger yield of triplet nitrene derived products than does *n*-butyl bromide as expected for the heavy atom effect. To test whether ISC has been catalyzed in the singlet excited state of azide **4** (Scheme III), or in the singlet nitrene, isoprene was added to the photolysis mixture. The fact that isoprene has no effect on the heavy atom catalyzed ISC indicates that ISC occurs from the singlet to the triplet state of the nitrene or that triplet azide ³**4*** is "unquenchable". The latter scenario requires that the lifetime of ³**4*** is exceedingly short or that its triplet energy falls below that of isoprene. As there is no evidence to substantiate these assumptions, the simplest explanation is that ISC occurs in the singlet state of the nitrene and this is the preferred interpretation at the present time. Alternatively it is conceivable that the alkyl halides have increased the efficiency of reduction of azide **4** by non-nitrene pathways, perhaps by the formation of radical chains (vide infra).

The insertion of a singlet carbene into the OH bond of an alcohol is a characteristic carbene reaction.[11] Thus we expected that photolysis of **4** in methanol might lead to the formation of a methoxylamine or of products derived from this compound.



However, upon photolysis of **4** in methanol, a large yield of pentafluoroaniline **6** was observed (Table V).[15] Methanol is apparently very effective at promoting ISC. This interpretation is supported by laser flash photolysis studies (vide infra).[15]

Toluene–Naphthalene Competition Study. Singlet nitrene **5S** reacts with naphthalene 16 times more rapidly than with toluene at 25 °C. The selectivity is even more pronounced at low temperature (a factor of 128 at −78 °C, Table V). A differential Arrhenius plot of the data (Figure 2) is approximately linear and

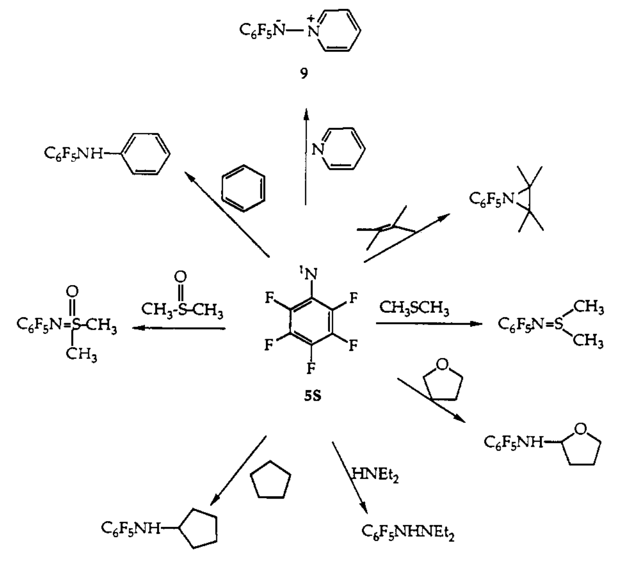


Figure 1. The products formed on photolysis of pentafluorophenylazide **4** in various solvents at ambient temperature.

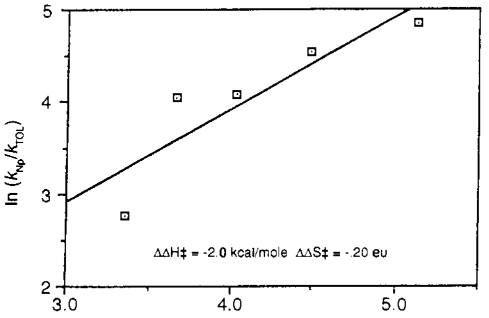


Figure 2. A logarithmic plot of the reactivity ratio of toluene/naphthalene towards **5S**, versus temperature^{-1}.

yields the following parameters for cycloaddition: $\Delta\Delta H^{\ddagger}$ = 2.0 kcal/mol and $\Delta\Delta S^{\ddagger}$ = −0.20 eu.

The $\Delta\Delta H^{\ddagger}$ data is significant because it requires that $\Delta H^{\ddagger} \neq 0$ for toluene trapping and that the selectivity of **5S** for naphthalene is in part enthalpically controlled. This is in contrast to the well studied singlet phenylchlorocarbene system in which $\Delta H^{\ddagger}$'s and $\Delta\Delta H^{\ddagger}$'s are close to zero for cycloaddition reactions with alkenes.[19]

The presence of an enthalpic barrier to the addition of **5S** to toluene is also evident upon photolysis of **4** at −78 °C. At this temperature the yield of adducts are dramatically reduced, more tar is formed, and there is an increase in the yield of decafluoroazo compound **7**, a product of dimerization of the triplet nitrene. This again demonstrates that the enthalpic barrier of both toluene trapping and ring expansion of **5S** is larger than that of intersystem crossing. Lowering the temperature favors triplet nitrene formation.

Diethylamine. Photolysis of **4** in neat diethylamine produces hydrazine **22** in 46% yield along with pentafluoroaniline **6** in 22% yield. The hydrazine product **22** is formed by insertion of the singlet nitrene into the NH bond of diethylamine.[1] Two additional products **23** and **24** were formed in low yield during the photolysis of **4** in neat diethylamine. Products similar to **23** and **24** were first observed by Polanc et al. in the decomposition of heterocyclic azides in diethylamine.[20] These workers postulated that some ethylvinylamine is formed in the course of the reaction, which in turn undergoes a 1,3-dipolar cycloaddition reaction with the azide precursor. The unstable triazoline so formed decomposes to form

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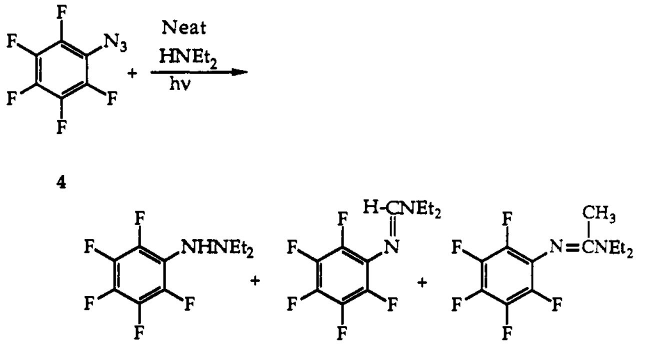
(19) Moss, R. A.; Turro, N. J. In *Kinetics and Spectroscopy of Carbenes and Biradicales*; Platz, M. S., Ed.; Plenum: New York, NY, 1990; p 213.
(20) (a) Polanc, S.; Stanovnik, B.; Tisler, M. *J. Org. Chem.* **1976**, *41*, 3152.

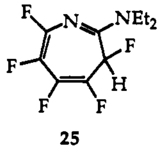


4

22 23 24

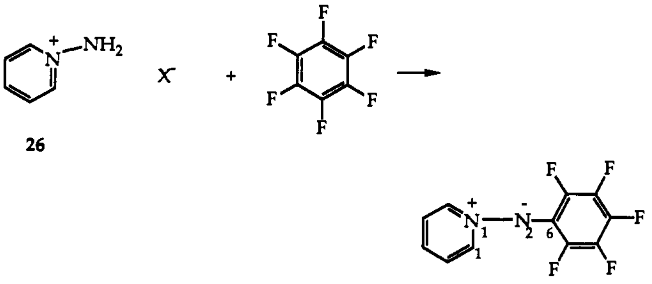
46% 5% 6.5%

the observed products. The yield of hydrazine **22** is dramatically reduced and there is an increase in the yields of products **23** and **24** upon photolysis of **4** in dilute diethylamine in methylene chloride (Table VI). We could not isolate adducts of perfluoroketenimine **8** with diethylamine, such as **25**, by photolysis of **4** in the presence of dilute diethylamine. Our previous studies[21] demonstrated that these types of adducts are unstable to further addition of 1 or more equiv of diethylamine which results in intractable mixtures.



25

Pyridine. Photolysis of **4** in pyridine produces pyridinium ylide **9**. The ylide can be independently prepared by reaction of *n*-aminopyridinium **26** with hexafluorobenzene. The structure of **9** was confirmed by X-ray crystallography (Figure 3). The N_1–N_2 bond distance is 1.378 Å, the N_2, N_1, C_1 bond angle is 125.6 °C, the N_1, N_2, C_6 bond angle is 115° and the angle between the planes of the two aromatic rings is 122.56°.



26

9

Ylide **9** is a yellow compound with λ_{max} = 394 nm in CH_2Cl_2. The absorption maximum varies only slightly with solvent polarity (Table IX) in contrast to the related compounds of Dimroth.[22]

Relative Rate Studies. Azide **4** was photolyzed in the presence of excess quantities of two traps to determine their relative ability to trap singlet nitrene **5S**. The product mixtures were analyzed either by capillary gas chromatography or by ^1H NMR spectroscopy. The results are given in Table VII. The data demonstrate that **5S** is a highly selective intermediate at ambient temperature. Amines, sulfides, and sulfoxides are particularly effective at intercepting singlet (pentafluorophenyl)nitrene. In fact the data of Table VII is not terribly precise because of the large selectivity differences. The data indicates that **5S** reacts more than 10^3 times more rapidly with DMSO than with cyclopentane. As the DMSO trapping rate constant (k_Q) must be less than k_{diff} ($\approx 10^{10}$ M^{-1} s^{-1}), the magnitude of k_Q of cyclopentane must be less than 10^7 M^{-1} s^{-1}. As intersystem crossing of **5S** is unimportant in neat cyclopentane, then $k_{isc} << k_Q[Q]$ where Q = cyclopentane = 10.6 M and $k_{isc} \leq 10^7$ s^{-1}. The intersystem crossing rate constant of singlet (pentafluorophenyl)nitrene **5S** must be at least a thousand times smaller than the ISC rate constants of diarylcarbenes.[23]

Table VI. Distribution of Products Formed on Photolysis of **4** in Diethylamine

	absolute % yields			
[diethylamine] (M)	**6**	**22**	**23**	**24**
9.7	22	46	5.0	6.5
7.7	28	5.6	17	34
5.8	20	11	12	18
3.9	19	23	9.9	15
1.9	20	31	5.3	8.7

Table VII. Relative Reactivity of Singlet (Pentafluorophenyl)nitrene to External Trapping Agents at 20 °C

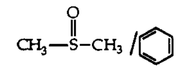
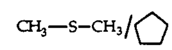
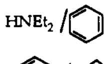
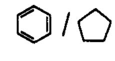
nitrene traps	relative reactivity
	809
	535
	75.9
	6.6

Table VIII. Absorption Maxima of Pyridine Ylide **9** as Function of Solvent

solvent	λ_{max} (nm)	solvent	λ_{max} (nm)
pyridine	398	methylene chloride	394
methanol	382	cyclohexane	394

Table IX. Values of $[PYR]^{1/2}$ as a Function of Solvent at 25 °C

solvent	$[PYR]^{1/2}$	k_{EXP} + $k_Q[Q]$ (s^{-1})	$k_Q{}^b[Q]^b$ (s^{-1})
dichloromethane	0.058	5.8 × 10^7	0
cyclohexane	0.063	6.3 × 10^7	0.5 × 10^7
benzene	0.19	1.9 × 10^8	1.3 × 10^8
tetrahydrofuran	0.34	3.4 × 10^8	2.8 × 10^8
tetrahydrofuran-d_8	0.32	3.2 × 10^8	2.6 × 10^6

[a] Assuming k_{PYR} = 10^9 M^{-1} s^{-1}. [b] Assuming k_{EXP} and k_{PYR} are independent of solvent (Q).

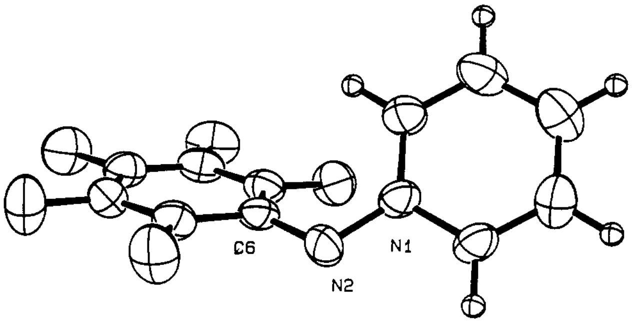


Figure 3. The crystal structure of ylide **9**.

III. Laser Flash Photolysis Studies

Laser flash photolysis (LFP, XeCl excimer laser, 308 nm, 17 ns, 150 mJ) of azide **4** in the inert solvent CH_2Cl_2 produces the

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(21) Soundararajan, N.; Platz, M. S. *J. Org. Chem.* **1990**, *55*, 2034.

(22) (a) Kosower, E. M. *J. Am. Chem. Soc.* **1958**, *80*, 3253. (b) Dimroth, K.; Reichardt, C.; Siepman, T.; Bohlmann, F. *Ann. Chem.* **1963**, *661*, 1. (c) Reichardt, C. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 29.

(23) (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Sitzman, E. V.; Eisenthal, K. B. *Applications of Picosecond Spectroscopy to Chemistry*; Reidel, O., Ed.; 1984; p 41. (c) Grasse, P. B.; Brauer, B.-E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833.

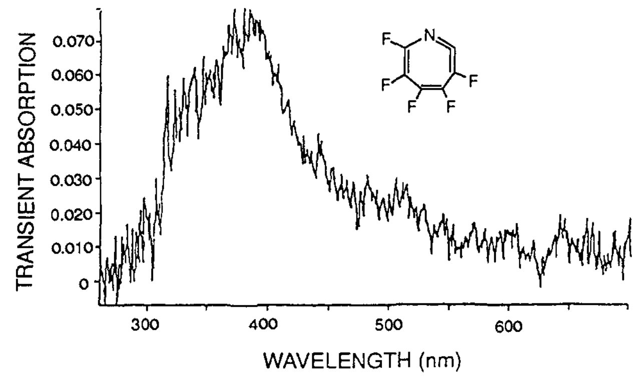


Figure 4. The transient spectrum of perfluoroketenimine **8** produced by LFP of **4** in CH_2Cl_2 at ambient temperature.

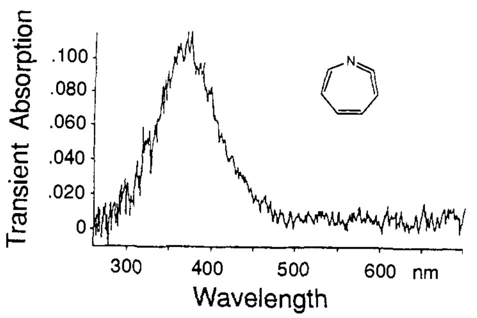


Figure 5. The transient spectrum of ketenimine **3** produced by LFP of phenyl azide **1** in CH_2Cl_2 at ambient temperature.

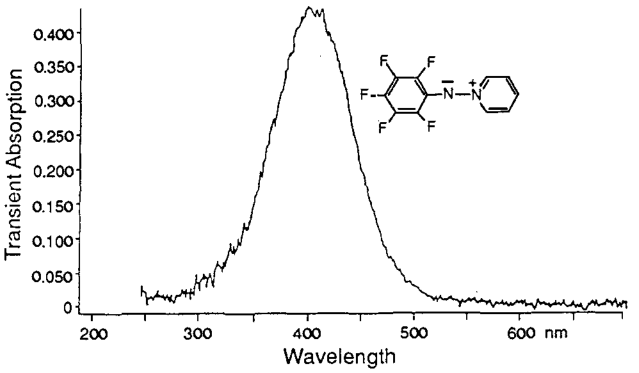


Figure 6. The spectrum of ylide **9** produced by LFP of **4** in CH_2Cl_2 containing 0.25 M pyridine at ambient temperature.

transient spectrum of Figure 4. This transient (Figure 4) is assigned to ketenimine **8** because it is similar to the transient produced by flash photolysis of phenyl azide which has been previously identified as that of azacycloheptatetraene **3** (Figure 5).[2,9]

LFP of azide **4** in neat pyridine produces an intense new transient absorption (Figure 6) which does not decay appreciably on the time scale of the LFP experiment ($\tau >> 1$ μs). The new absorption spectrum is clearly that of ylide **9** since it is identical to that of the authentic, isolated material.

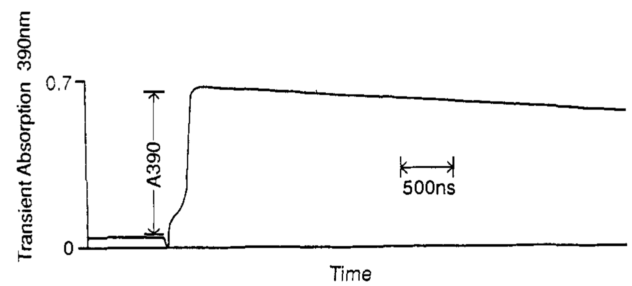
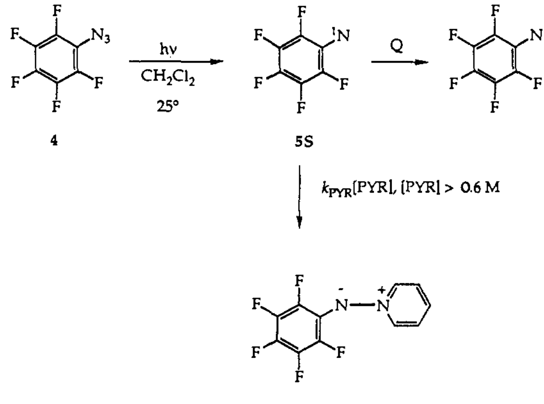


Figure 7. The increase in absorption at 390 nm following LFP of **4** in CH_2Cl_2/pyridine at ambient temperature.

Scheme IV



It was not possible to resolve the growth of **9** by nanosecond spectroscopy, even in dilute pyridine; however, it was possible to measure the optical yield of ylide (A_{390}) produced in a laser flash (Figure 7) as a function of [pyridine]. Of course $A_{390} \approx 0$[24] when [pyridine] = 0 and increases as [pyridine] increases (Figure 8). However in CH_2Cl_2 solvent the yield of ylide is saturated (A^{∞}_{390}) when [pyridine] = 0.6 M. Above [pyridine] = 0.6 M every singlet nitrene **5S** produced by the laser pulse is captured by pyridine to form ylide **9**. When $A_{390} = (1/2)A^{\infty}_{390}$ the rate of formation of ylide **9** equals the total rate of all non-pyridine dependent processes which consume **5S** in CH_2Cl_2. According to Scheme II, eq 1 is then valid[25]

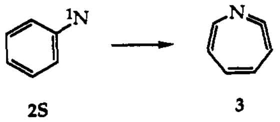
$$k_{PYR}[PYR]^{1/2} = k_{EXP} + k_Q[Q] \qquad (1)$$

where $[PYR]^{1/2}$ is the pyridine concentration at which $A_{390} = (^1/_2)A^{\infty}_{390}$. The size of k_{PYR} must be less than $k_{diff} \approx 10^{10}$ M^{-1} s^{-1}, the rate constant for a diffusion controlled process. The size of k_{PYR} must also exceed 10^8 M^{-1} s^{-1} as we cannot resolve the rate of formation of ylide **9** at [PYR] = 0.1 M. A reasonable guess for the magnitude of this rate constant is $k_{PYR} = 10^9$ M^{-1} s^{-1}, a value which is very similar to that observed in the reaction of many singlet carbenes with pyridine.[26]

Product studies indicate that **5S** does not react at a measurable rate with CH_2Cl_2, and, at the concentrations of **4** used in the LFP experiment (2.4×10^{-3} M) it is unlikely that **5S** is reacting with the azide precursor. Thus eq 2 is valid

$$k_{PYR}[PYR]^{1/2} = k_{EXP} \qquad (2)$$

and $k_{EXP} = 5.8 \times 10^7$ s^{-1} in CH_2Cl_2 at ambient temperature. The size of k_{EXP} for singlet phenylnitrene **2S** is 10^{10-11} s^{-1}.[9] Thus fluorine has retarded the rate of ring expansion of **5S** by a factor of approximately 170–1700 relative to **2S**. The much longer lifetime of **5S** relative to **2S** allows its capture by external trapping agents (Q). If we assume that the Arrhenius *A* factor for ring expansion (**5S** → **8**) is 10^{13} s^{-1},[9] we deduce that the activation energy barrier, E_a is 7.2 kcal/mol for this process in the fluorinated singlet nitrene. This is considerably larger than the barrier (3 kcal/mol) to ring expansion in singlet phenyl nitrene.[9]



2S **3**

Values of $[PYR]^{1/2}$ for several solvents are given in Table IX. If we assume that k_{PYR}[26] and k_{EXP} are independent of solvent then

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[24] A_{390} is not equal to zero in the absence of pyridine because ketenimine **8** absorbs weakly at this wavelength. This absorption is very small compared to that of ylide **9** at 390 nm.

[25] The authors are indebted to Professor J. C. Scaiano for teaching us this principle.

[26] Jones, M. B.; Platz, M. S. *J. Org. Chem.* **1991**, *56*, 1694.

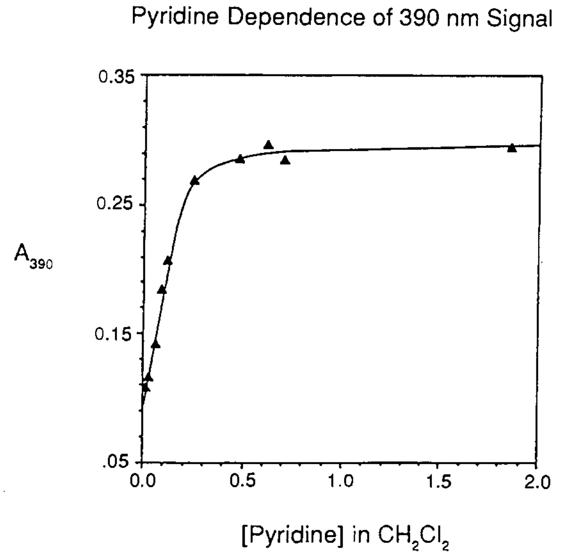


Figure 8. The optical yield of ylide 9 measured at 390 nm, following LFP of 4 in CH_2Cl_2 as a function of [pyridine].

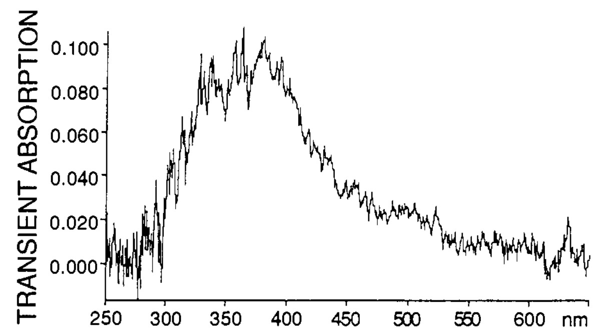
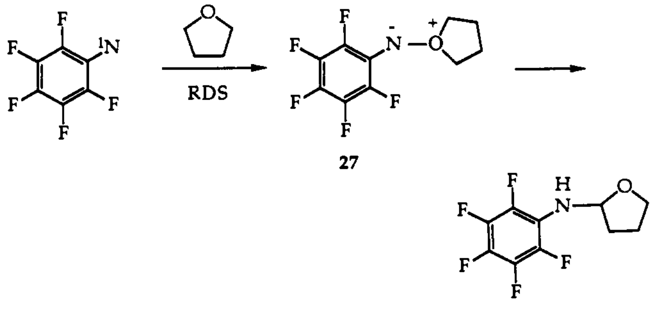


Figure 9. The transient spectrum of ylide 27 produced by LFP of 4 in tetrahydrofuran at ambient temperature.

the increase in $[PYR]^{1/2}$ can be related to $k_Q[Q]$, the rate of reaction of 5S with the solvent trap. The data (Table IX), reveal that 5S reacts to a limited extent with cyclohexane and much more rapidly with benzene and tetrahydrofuran (THF). The data demonstrate that 5S reacts with benzene 26 times faster than with cyclohexane. This is in only fair agreement with the chemical competition study discussed earlier.

We note that $[PYR]^{1/2}$ is the same in both THF and THF-d_8. We have previously[13] reported that $k_H/k_D = 3$ for insertion of 5S into a C–H bond of cyclohexane. Thus we conclude that the nitrene reacts irreversibly with THF to form an ylide 27, which undergoes subsequent rearrangement and CH insertion in a relatively slow step. LFP of 4 in neat THF produces a new transient (Figure 9) which we tentatively attribute to ylide 27. Presumably ylide 27 isomerizes to the isolated THF derivative; however, the details of this process are not established.



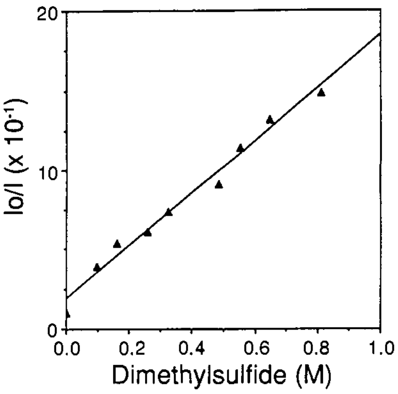


Figure 10. Stern–Volmer treatment of the quenching of ylide 9 by dimethyl sulfide.

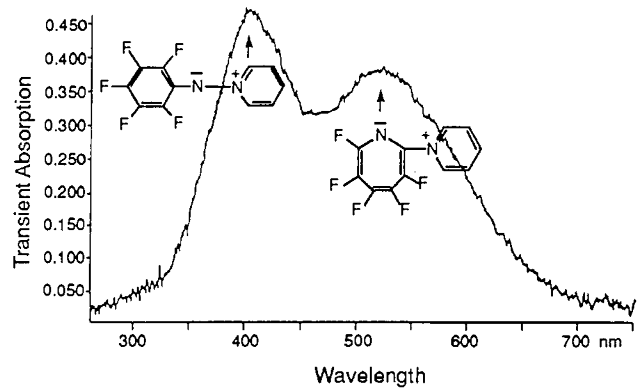


Figure 11. Transient spectra of ylides 9 and 30 following LFP of 4 in CH_2Cl_2 containing 0.046 M pyridine at ambient temperature.

Table X. Summary of Stern–Volmer Quenching of Ylide 9 by Quenchers of Singlet Nitrene 5S

quencher	k_Q/k_{PYR}	quencher	k_Q/k_{PYR}
CH_3OH	0.22	$HNEt_2$	4.81
CH_3OH	0.26	$(CH_3)_2SO$	3.23
CF_3CH_2OH	1.91	$(CH_3)_2S$	7.83
tetramethylethylene	2.32		

Stern–Volmer Quenching Studies. Our attention next turned to the effect of nitrene quenchers on the yield of ylide in the saturation region (A_{390}^{∞}) of Figure 8. In CH_2Cl_2 when [PYR] > 0.6 M and with no nitrene quencher present ([Q] = 0), all singlet nitrene 5S produced in a laser flash is captured by pyridine $(A_{390}^{\infty})^{\circ}$. LFP of azide 4 in the presence of pyridine and a competitive nitrene quencher reduces the yield of pyridine ylide (A_{390}^{∞}) according to Scheme IV, and eq 3 is now valid.[27] A plot of

$$\frac{(A_{390}^{\infty})^{\circ}}{(A_{390}^{\infty})} = 1 + \frac{k_Q[Q]}{k_{PYR}[PYR]} \tag{3}$$

$(A_{390}^{\infty})^{\circ}/(A_{390}^{\infty})$ versus [Q] is shown in Figure 10 for dimethyl sulfide as the nitrene quencher. Values of k_Q/k_{PYR} are listed in Table X. Absolute values of k_Q can be calculated by assuming, as before, that $k_{PYR} = 10^9\ M^{-1}\ s^{-1}$. Relative trapping rates of singlet nitrene 5S obtained chemically and by LFP methods are in only fair agreement. The LFP data is, we believe, more precise due to the large error associated with the relative reactivities determined chemically.

Ketenimine Pyridine Ylides. LFP of 4 in CH_2Cl_2 in the presence of dilute pyridine produces a new, intensely absorbing transient at 520 nm (Figure 11). As mentioned previously photolysis of phenyl azide 1 produces singlet phenylnitrene 2S which ring expands to ketenimine 3 more rapidly than it can be intercepted by an external trapping agent. LFP of 1 in *neat* pyridine also produces a long wavelength absorbing transient (Figure 12) which is very similar to that observed upon LFP of 4 in the presence of dilute pyridine. The rate of formation of this transient is readily

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(27) Wagner, P. J. *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1990; Vol. 1, p 251.

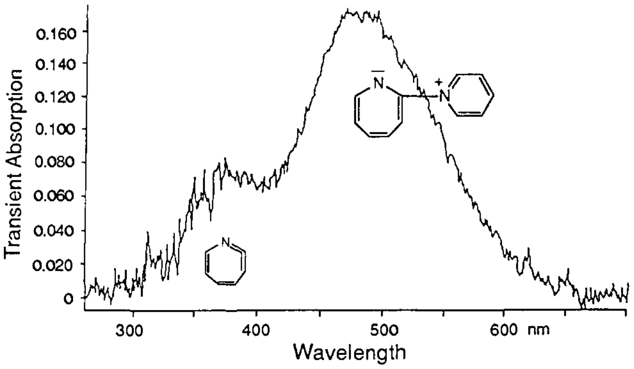


Figure 12. Transient spectrum of ylide **28** produced by LFP of phenyl azide in neat pyridine at ambient temperature.

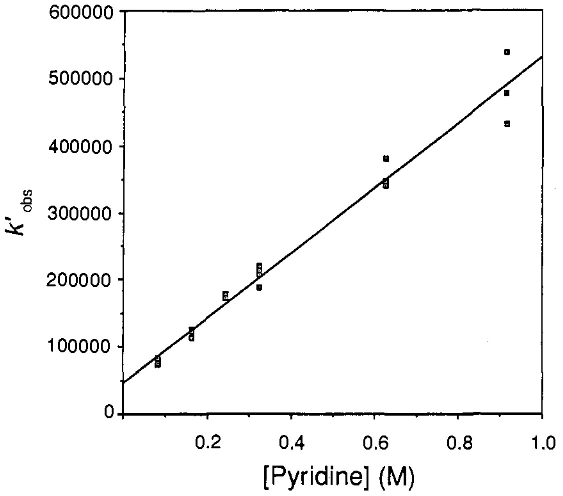


Figure 13. A plot of k'_{obs} versus [pyridine] obtained by LFP of phenyl azide **1** in CH_2Cl_2 at ambient temperature.

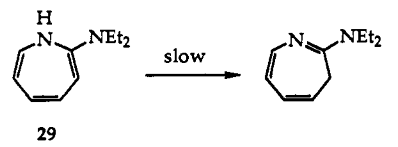
resolved and can be fit to an exponential function to yield an observed rate constant of formation, k'_{obs}, of the long wavelength absorbing transient where

$$k'_{obs} = 1/\tau + k'_{PYR}[PYR] \tag{4}$$

A plot of k'_{obs} versus [pyridine] for phenyl azide is linear (Figure 13) with a slope of $k'_{PYR} = 4.8 \times 10^5$ M^{-1} s^{-1} (Scheme IV). The transient of Figure 12 is attributed to ketenimine ylide **28** because the lifetime (τ) of the transient precursor of the pyridine ylide is 25 μs, in accord with the lifetime of **3** as determined by previous LFP studies.[28] Furthermore, the addition of a quencher of **3** (e.g., diethylamine) reduces the yield of ylide **28** upon LFP of phenyl azide in the presence of pyridine. Under these conditions eq 5 is valid. A plot of k'_{obs} versus [$HNEt_2$] at constant [PYR] was

$$k'_{obs} = 1/\tau + k'_{PYR}[PYR] + k'_{HNEt_2}[HNEt_2] \tag{5}$$

found to be linear. The slope of this plot is $k'_{HNEt_2} = 1.5 \times 10^6$ M^{-1} s^{-1} in CH_2Cl_2. The result compares reasonably well with the value of this rate constant obtained by monitoring the decay of **3** or the growth of 1*H*-azepine **29** in cyclohexane by flash photolysis.[2,28]



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The rate of formation of the transient produced from pentafluorophenyl azide **4** in dilute pyridine (Figure 11) can also be resolved. A plot of k'_{obs} versus [PYR] is linear (Figure 14) with a slope of $k'_{PYR} = 3.2 \times 10^9$ M^{-1} s^{-1}. The lifetime τ of the precursor of the ylide is 3.2 μs. This is much too long for nitrene **5S** to be the precursor of the 520 nm absorbing transient. The 520 nm absorbing transient is therefore associated with ketenimine ylide **30** (Scheme VI) as per the parent system, phenyl azide (Scheme V). Fluorine is found to dramatically accelerate the reactivity of the ketenimine toward pyridine. This is in agreement with the work of Schuster[28] et al. who found that electron withdrawing groups increase the reactivity of ketenimines toward nucleophiles. Unfortunately, attempts to isolate ylides **28** and **30** were unsuccessful.

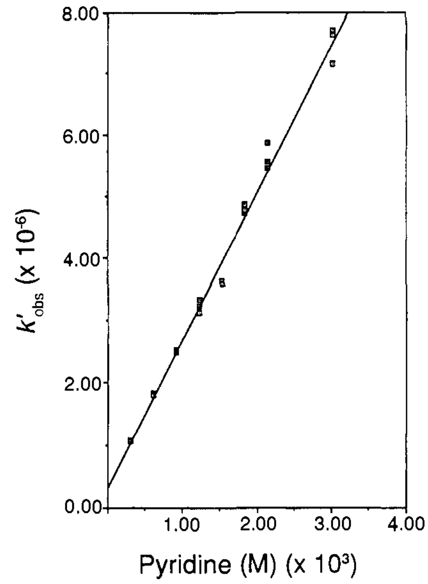
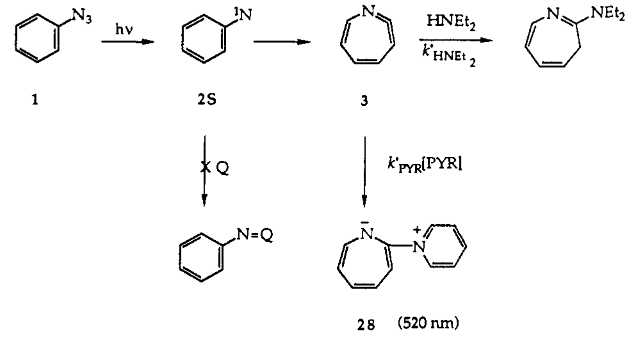
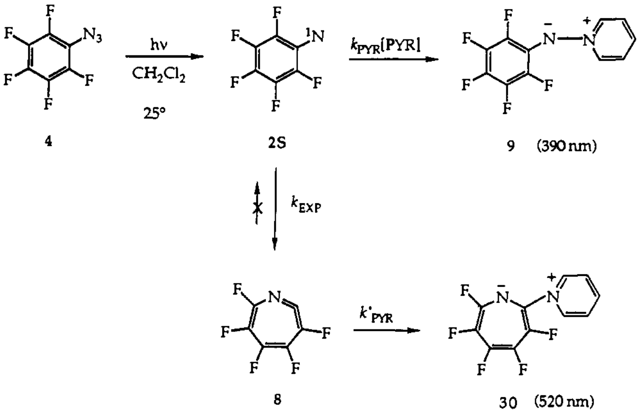


Figure 14. A plot of k'_{obs} versus [pyridine] obtained by LFP of **4** in CH_2Cl_2 at ambient temperature.

Scheme V



Scheme VI



To test these transient assignments the ratio of the absorbance of ylides **9** and **30** (A_{390}/A_{520}) was measured as a function of

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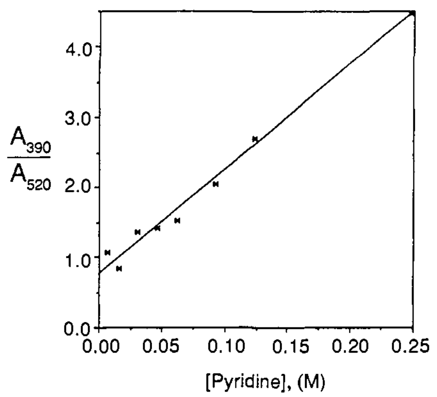
(28) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakof, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092.



* Data generated from O. M. A. Studies

Figure 15. The ratio of the absorbances of ylides **9** and **30** (A_{390}/A_{520}) versus [pyridine].

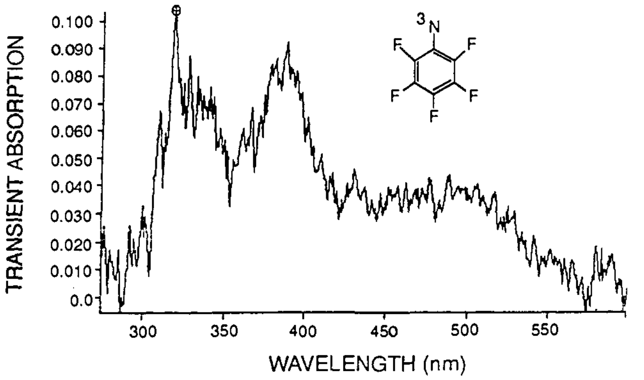


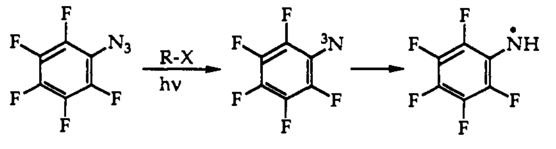
Figure 16. The transient spectrum of triplet nitrene **5T** produced by LFP of **4** in methanol at ambient temperature.

[pyridine]. As predicted by Scheme VI a plot of A_{390}/A_{520} is linear (Figure 15).

The effect of known quenchers of nitrene **5S** on the yield and rate of formation of ketenimine ylide **30** was also studied. **Dimethyl sulfide (DMS) reduces the yield of ketenimine ylide (A_{520}) but does not effect the rate of formation (k'_{obs}) of ylide 30.** This requires that DMS intercept a precursor of fluorinated ketenimine **8**, but does not itself react directly with **8**. Thus under the conditions of our experiment, nitrene **5S** and ketenimine **8** are kinetically independent species. They are not in equilibrium, and ring expansion of **5S** can be considered to be irreversible on these time scales.

Catalyzed ISC. LFP of **4** in methanol produces the transient of Figure 16. The transient absorption spectrum is clearly different from that of ketenimine **8** and is very similar to the low temperature (77 K) absorption spectrum of **5T**. Thus the LFP studies and product analyses agree that methanol has catalyzed ISC of the singlet to the ground triplet state of the nitrene.[15]

LFP of **4** in *n*-butyl bromide produces the transient spectra of Figure 17. The transient spectrum most closely resembles that of the anilino radical[29] and is attributed to **31**. It is not clear why triplet nitrene **5T** is converted into the anilino radical more rapidly in alkyl halide solvents than in methanol, unless perhaps the anilino radical and the aniline product **6** is formed in a radical chain process in the alkyl halide solvent and not formed from triplet nitrene **5T**.



31

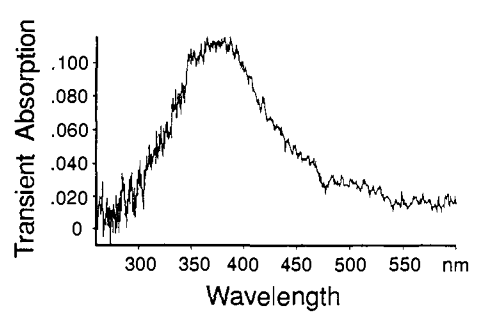
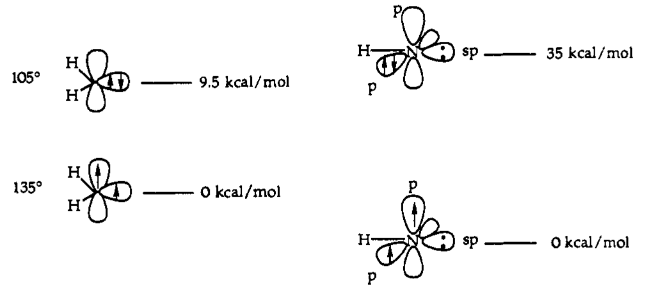
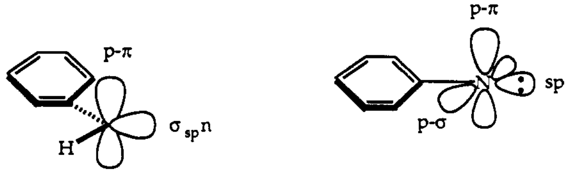


Figure 17. The transient spectrum of the pentafluoroanilino radical **31** produced by LFP of **4** in *n*-butyl bromide.

IV. Discussion

Many of the differences between phenylcarbene, phenylnitrene, and (pentafluorophenyl)nitrene can be understood on the basis of simple molecular orbital theory. Singlet and triplet methylene are both bent, the bond angles are 105° and 135°, respectively, and the energy gap is 9.5 kcal/mol.[30] The triplet states of NH and CH_2 are the ground states because electron–electron repulsion between the nonbonding electrons is minimized in this state. In CH_2 the benefit of placing the two electrons in different orbitals outweighs the benefit of placing both electrons in the lower energy, in plane, sp^n hybridized orbital.[31] The energy gap in NH is much larger than that of CH_2 because in NH the two orbitals in question are both pure p and the Coulombic benefit of separating the two electrons is not offset by a different hybridization of the two orbitals.[32] The energy gap and geometries of singlet and triplet phenylcarbene are not known, but calculations[33] indicate that both states are bent. Thus there will be a pure p and an sp^n hybridized nonbonding orbital in phenylcarbene. The hybridization of the nonbonding MOs of phenylnitrene are likely to resemble those of NH.[34] The energy gap of phenylnitrene is reported to be 4.3 kcal/mol,[35] a value which seems remarkably small considering the very large singlet triplet gap in NH. Nevertheless one can make a clear prediction that the singlet–triplet energy gap in phenylcarbene should be much smaller (≈0) than that of phenylnitrene.





ISC is a radiationless transition between electronic states of different multiplicity. It is well understood that ISC is fastest between states that are energetically degenerate.[36] Thus phe-

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[29] Leyva, E.; Platz, M. S.; Niu, B.; Wirz, J. *J. Phys. Chem.* **1987**, *91*, 2293.

[30] Leopold, D. G.; Murray, K. K.; Lineberger, W. C. *J. Chem. Phys.* **1984**, *81*, 1048.

[31] Gaspar, D. P.; Hammond, G. *Carbenes Vol. II*; Moss, R. A., Jones, M. B., Jr.; Eds.; Wiley: New York, NY, 1975.

[32] Engelking, P. C.; Lineberger, W. C. *J. Chem. Phys.* **1976**, *65*, 4323.

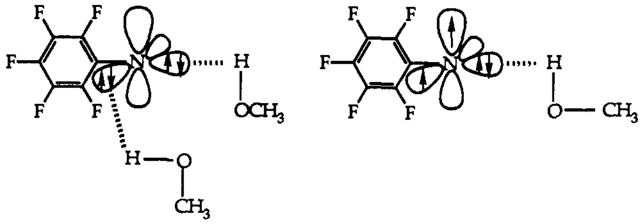
[33] Dannenberg, J. J.; Vinson, L. K.; Moreno, M.; Bertran, J. *J. Org. Chem.* **1989**, *54*, 5487.

[34] Private communication from Professor W. T. Borden.

[35] Drzaic, P. S.; Brauman, J. J. *J. Am. Chem. Soc.* **1984**, *106*, 3443.

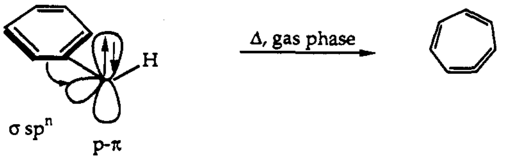
nylnitrene and presumably (pentafluorophenyl)nitrene with their large singlet–triplet gaps will undergo intersystem crossing more slowly than phenylcarbene. The fact that carbenes are divalent and nitrenes are monovalent may also be significant. The extra vibrational and binding modes of the carbene may assist the radiationless transition.

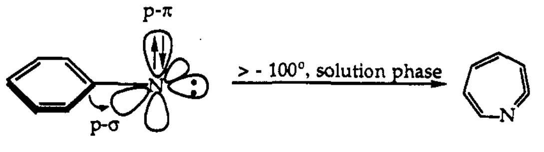
The putative catalysis of ISC by ethyl iodide and 1-bromobutane was anticipated,[37] the methanol effect was not. We speculate that methanol can form two hydrogen bonds to singlet pentafluorophenylnitrene but only one with the triplet nitrene.[38] The singlet nitrene is differentially stabilized by hydrogen bonding, the singlet–triplet gap is narrowed, and therefore the rate of ISC increases.



The major difference between phenylcarbene and phenylnitrene is the rate of ring expansion. In singlet phenylnitrene (**2S**) expansion is so rapid that bimolecular trapping of **2S** is impossible.[9] Ring expansion of phenylcarbene is known in the gas phase at high temperature but not in solution.[18]

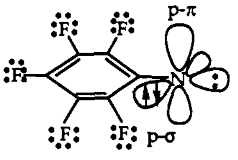
We visualize ring expansion as proceeding through p-π^2 configurations of the reactive intermediate, in which the electrons of a C–C bond slide into an adjacent, parallel and empty orbital.





Neither of these configurations is likely to be the most favorable singlet state configuration. However, the p-π^2 configuration of phenylnitrene is surely more accessible than that of phenylcarbene. The in- and out-of-plane orbitals of the nitrene nitrogen are both pure p and of comparable energy, whereas the in-plane, σ type orbital of phenylcarbene is an sp^n hybrid orbital that is much lower in energy than that of the p-π orbital. The p-π^2 configuration of the carbene is very much less accessible, and the rate of ring expansion of phenylcarbene is therefore much slower than that of phenylnitrene.

Perfluorination of the aryl ring will surely have an effect on the relative energies of the p-σ^2 and p-π^2 orbitals of nitrene **5S**.

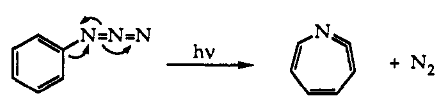


5S

We anticipate two effects of fluorine both of which will raise the energy of the p-π^2 configuration relative to the p-σ^2 configuration and retard ring expansion. First, π back bonding of the nonbonding electrons of fluorine will stabilize the p-σ^2 configuration by electron donation into the empty p-π orbital. Secondly, the filled, in-plane, p-σ^2 orbital can undergo hyperconjugative interactions with flanking C–F bonds. This puts electron density onto electronegative fluorine atoms. This further stabilizes the p-σ^2 configuration.[39] The p-π^2 configuration becomes less accessible, the barrier to ring expansion is raised, and the rate retarded. Thus perfluorinated singlet nitrene **5S** now has a lifetime sufficiently long to permit intermolecular trapping.

Two alternative explanations of the data are also consistent with the observed effect of polyfluorination. It is possible that fluorine greatly destabilizes ketenimine 8 and that the singlet nitrene/ketenimine interconversion is less exothermic in the pentafluoro system than in the singlet phenyl nitrene. This would reduce the rate of interconversion of **5S** to **8**, relative to the rate of interconversion of **2S** to **3**. There is however no data available at present to support this speculation. This underscores the need for high quality molecular orbital calculations of **2S**, **3**, **5S**, and **8**.

Alternatively it is conceivable that light induced ring expansion is concerted with nitrogen extrusion in phenyl azide, bypassing singlet nitrene **2S**. If this is the case then perhaps the effect of fluorine is to suppress the concerted decomposition of the azide and that only the fluorinated azide forms singlet nitrenes as shown in Scheme II. Experiments are in progress to distinguish these alternatives.



1 **3**

V. Conclusion

The properties of singlet (pentafluorophenyl)nitrene have been revealed by chemical analysis and by laser flash photolysis techniques. This nitrene can be efficiently intercepted with external traps because fluorine dramatically retards the rate of ring expansion. Ring expansion of the singlet nitrene to the ketenimine is irreversible in the presence of ketenimine traps. ISC from the singlet to triplet nitrene is found to be remarkably slow and can be catalyzed by alcohol.

VI. Experimental Section

General Procedures. Melting points were recorded on an Electrothermal capillary melting point apparatus and are uncorrected. ^{1}H NMR spectra were recorded either on a Varian EM-390L (90 MHz) or Bruker AM-250 (250 MHz) instrument. ^{19}F NMR spectra were recorded on a Bruker NR-80 (75 MHz) instrument. High field ^{1}H NMR and ^{19}F NMR spectra were obtained by Mr. Carl Engelman. ^{1}H NMR chemical shifts are reported in units of ppm relative to tetramethylsilane (0 ppm) and ^{19}F NMR chemical shifts are reported in units of ppm relative to $CFCl_3$ (0 ppm). Infrared spectra were recorded on a Perkin Elmer Model 457 infrared spectrophotometer or a Perkin Elmer 1710 Infrared Fourier Transform Spectrometer. Mass spectra and exact masses were obtained on a VG 70-250S or a Kratos MS-30 mass spectrometer by Dr. Dick Weisenberger of the OSU Campus Chemical Instrumentation Center.

Tetrahydrofuran was dried by distillation over sodium benzophenone ketyl; 2-methyltetrahydrofuran was distilled over CaH_2 and diethylamine over BaO before use. Toluene, benzene, dimethyl sulfide, dimethyl sulfoxide, pyridine, diethylamine, *n*-butylamine, cyclohexane, and dichloromethane were purified by distillation over either barium oxide or molecular sieves. Pyridine was stored over KOH.

Laser Flash Photolysis. General Procedures. All laser flash photolysis experiments utilized one or more 308-nm laser pulses generated by a

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(36) For a discussion of radiationless transitions, see: Michl, J.; Bonacic-Koutecky, V. *Electronic Aspects of Organic Photochemistry*; Wiley: New York, 1990.

(37) (a) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905. (b) McGlynn, S. R.; Azumi, T. J.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall Inc.: Englewood Cliffs, NY, 1969; pp 183–289.

(38) The authors are indebted to Professor Marshall Wilson for elucidating this point.

(39) (a) Bastide, J.; Hall, D.; Heilbronner, E.; Maier, J. P.; Plevey, R. G. *J. Electron Spectrosc. Photoelectron Relat. Phenom.* **1979**, *16*, 205. (b) Heilbronner, E. *Molecular Spectroscopy*; Institute of Petroleum: London, 1976; p 422. (c) Robin, M. B. *Higher Excited States of Polyatomic Molecules*; Academic Press: New York, 1974. (d) Eland, J. H. D. *Photoelectron Spectroscopy*; Butterworths: London, 1976.

Lumonics TE-860-4 or Lambda Physik excimer laser (maximum pulse energy 110 mJ, pulse duration 8–10 ns) which contained a fill mixture comprised of HCl, helium, and xenon. Details of the LFP system have been reported previously.[40] All transient absorbance spectra were obtained using the previously described excimer laser in conjunction with an EG & G Princeton Applied Research Model 1460 optical multichannel analyzer. All samples were capped with a septum and degassed with dry nitrogen or argon for 3–4 min prior to photolysis. All laser flash photolysis experiments utilized quartz cells and were performed at ambient temperature.

Stern–Volmer Quenching. In a typical Stern–Volmer quenching experiment a stock solution of the azide in dichloromethane was prepared, having an optical density at 308 nm of ca. 0.5. An exact volume of the stock solution was then syringed into several cells followed by an exact volume of neat pyridine or pyridine diluted with dichloromethane. To all but one cell, quencher was added in exact and increasing volume. The single cell without quencher therefore represented a standard ylid signal. All cells were then degassed and subjected to several laser pulses, and the resulting signals were recorded.

Gas Chromatography. Gas chromatographic analyses were performed either on a Hewlett Packard 5830A gas chromatograph equipped with a flame ionization detector and a 6 ft × $^1/_8$ in. column (5% SE-30, Chromosorb W-HP 80/100 or 5% OV-17, Chromosorb W-HP 80/100) or a Perkin Elmer 8500 gas chromatograph equipped with a split/splitless injector, a flame ionization detector, and a 30 m × 0.254 mm J & W Scientific fused silica capillary column (5% DB-1701, 0.25 μm). GC/MS spectra were obtained on a Finnegan 4021 gas chromatograph/mass spectrometer by Mr. David Chang and Ms. Kathy Ault of the OSU Campus Chemical Instrumentation Center.

Samples for most product studies were prepared by putting 0.5 mL of solution in 6-mm Pyrex tubes which were prewashed with ammonium hydroxide and oven dried. The solutions were then degassed using two to three freeze–pump–thaw cycles and then were placed in tubes sealed under vacuum. Samples were kept at specific temperatures by either one of the following methods: (a) keeping the samples in baths in Pyrex or quartz dewars or (b) keeping the samples in an evacuated quartz dewar through which warm or cold gas flows. The temperature of the sample is regulated by controlling the flow rate of nitrogen or air through a coil which is immersed in a bath and then connected to the dewar. Photolyses were done at 350 nm using Southern New England RPR 3500 Å bulbs.

The identities of the products formed after photolyses of samples were determined by GC/MS and by coinjection of authentic samples. The yields of the products were determined by using an internal standard. Response factors of the components of the photolysis mixtures were calculated from analyses of standard solutions.

Preparative Photolysis of Pentafluorophenyl Azide in Different Solvents. Tetramethylethylene. To a 16-mm Pyrex test tube was added azide **4** (221 mg, 1.06 mmol) in tetramethylethylene. The test tube was fitted with a rubber septum in which a nitrogen gas outlet was placed, and the solution was photolyzed for 23 h. The solution was concentrated to give a yellow oil which was passed through a column of silica gel and eluted with a solution of 1:4 benzene/petroleum ether. The eluent collected was concentrated to give a white crystalline solid (250 mg, 48.6%): mp 65–68 ^{1}H NMR ($CDCl_3$) 1.28 (s, 12 H); ^{19}F NMR ($CDCl_3$) −154 (m, 3 F), −165 (m, 2 F), −169 (m, 1 F); IR ($CHCl_3$) NaCl 29.76, 2894, 1526, 1451, 1382 cm^{-1}; MS calculated exact mass 265.08897; mol ion 265.0902.

Dimethyl Sulfoxide. To a 16-mm Pyrex test tube was added azide **4** (198.8 mg, 9.51×10^{-2} M) in freshly distilled dimethyl sulfoxide (10 mL). The tube was fitted with a rubber septum in which a gas outlet needle was inserted and photolyzed for 18 h. The solution was concentrated by vacuum distillation (37 °C, 0.75 mmHg) to give a red-brown oil which was passed through a column of silica gel and eluted with 4:1, 3:2, 1:1, 1:2 hexanes/ethyl acetate, respectively. The eluent collected while eluting with 1:2 hexanes/ethyl acetate was combined and concentrated to give cream colored leaf-like crystals (100 mg, 40.6%): mp 120–121 °C; ^{1}H NMR ($CDCl_3$) 3.23 (s, 6 H); ^{19}F NMR ($CDCl_3$)−165.1 (m, 3 F), −150.7 (m, 2 F); MS calculated exact mass 259.01349; exact mass 259.0101.

Dimethyl Sulfide. To a 16-mm Pyrex test tube was added azide **4** (225.9 mg, 18 mmol) in dimethyl sulfide (10 mL). The tube was sealed with a rubber septum in which a gas outlet needle was placed and photolyzed for 19 h. The solution was concentrated to give a brown solid which was recrystallized from a solution of hexane and dichloromethane, filtered, dried by suction filtration, and washed with cold hexane to give gray crystals (152 mg, 54%). The crystals were dissolved in dichloromethane and passed through a pasteur pipet column of alumina and eluted with dichloromethane. The eluent was concentrated to give gray crystals (26 mg, 11.5%): mp 101.5–102 °C; ^{1}H NMR ($CDCl_3$) 2.73 (s, 6 H); ^{19}F NMR ($CDCl_3$) −185.61 (m, 2 F), −167.292 (m, 2 F), −173.85 (m, 1 F); MS calculated mass 243.01409; exact mass 243.0168.

Benzene. A sample of azide **4** (1.95×10^{-2} M) in benzene was photolyzed at 350 nm for 2 h at 25 °C. To the sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solution was analyzed by GC. The nitrene–benzene adduct formed was quantified with the assumption that its response factor was identical to that of *N*-phenylpentafluoroaniline **13**. In addition to the adduct (26%), aniline **6** (5.1%) and tar were also formed.

Diethylamine. A sample of azide **4** (3.01×10^{-2} M) in diethylamine (DEA) was photolyzed at 350 nm for 4 h at 25 °C and then kept in the dark overnight. To the sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solution was analyzed by GC. The products were aniline **6** (22%), 1,1-diethyl-2-pentafluorophenylhydrazine **22** (46%), *N*,*N*-diethyl-*N'*-pentafluorophenylformamidine **23** (5.0%), and *N*,*N*-diethyl-*N'*-pentafluorophenylacetamidine **24** (6.5%).

Hydrazine **22** and the amidines **23** and **24** were isolated on a preparative scale experiment. Azide **4** (509 mg, 2.44 mmol) in 20 mL of DEA was photolyzed at 350 nm at room temperature for 24 h. The solution was concentrated, and the brown oil obtained was passed through a 20 cm × 1 cm column of neutral alumina and eluted first with 200 mL of cyclohexane to give 75 mg (12% yield) of **22** as a yellow oil: IR (neat, cm^{-1}) 3307 (–NH–), 2980, 2943, 2879, 2818, 2702, 2442 (aliphatic C–H); ^{1}H NMR ($CDCl_3$, δ) 1.110 (t, J = 7.1 Hz, 6 H), 2.739 (q, J = 7.1 Hz, 4 H), 4.183 (br, 1 H); ^{19}F NMR ($CDCl_3$, δ) −160.162 to −160.498 (m, 2 F), −168.408 to −169.097 (m, 2 F), −173.232 (t, t, J = 21.7 Hz, J = 4.6 Hz, 1 F); *m/e* calculated for $C_{10}H_{11}F_5N_2$ (M^+) 254.0842, found 254.0867.

The amidines **23** and **24** eluted together as a brown oil when 200 mL of cyclohexane/ethyl acetate (98:2, v/v) was used. The two compounds were separated by preparative TLC on silica gel (Merck, 20 cm × 10 cm, 0.5 mm thickness) by developing the plate in cyclohexane/ethyl acetate (98:2, v/v) four consecutive times. Compound **24**, the less polar of the two amidines, was obtained as a yellow oil (10 mg, 1.5% yield): ^{1}H NMR ($CDCl_3$, δ) 1.2160 (t, J = 7.1 Hz, 6 H), 1.8673 (s, 3 H), 3.4612 (br, 4 H); ^{19}F NMR ($CDCl_3$, δ) −158.4298 to −158.7187 (m, 2 F), −169.5551 to −170.3253 (m, 2 F), −172.1568 to −172.8487 (m, 1 F); *m/e* calcd for $C_{12}H_{13}F_5N_2$ (M^+) 280.0999, found 280.0996. Compound **23** was obtained as a pale yellow oil (12 mg, 1.8% yield): ^{1}H NMR ($CDCl_3$, δ) 1.2395 (t, J = 7.2 Hz, 6 H), 3.3025 (q, J = 7.1 Hz, 2 H), 3.5543 (q, J = 7.1 Hz, 2 H), 7.6289 (s, 1 H); ^{19}F NMR ($CDCl_3$, δ) −160.4885 to −161.0119 (m, 2 F), −169.3797 to −170.1360 (m, 2 F), −171.5339 to −172.2236 (m, 1 F); *m/e* calcd for $C_{11}H_{11}F_5N_2$ (M^+) 266.0842, found 266.0857.

Dichloromethane. A sample of azide **4** (4.4×10^{-2} M) in CH_2Cl_2 was photolyzed at 350 nm for 4 h at 25 °C and kept in the dark overnight at room temperature. The red-orange solution was analyzed by GC/MS and was found to contain some unreacted **4**, small amounts of aniline **6** and azo compound **7** and another peak corresponding to a compound with a molecular weight of 362, the same as that of azo compound **7** but having a different MS fragmentation pattern.

An attempt was made to isolate the second nitrene dimer by a large scale photolysis. In a Pyrex tube, azide **4** (503 mg) in 20 mL of CH_2Cl_2 was photolyzed at 350 nm for 23 h at 25 °C. The solution was concentrated, and the orange oil was passed through a 20 cm × 2 cm column of neutral alumina and eluted first with 200 mL of cyclohexane, 200 mL of cyclohexane/ethyl acetate (98:2, v/v), 200 mL of cyclohexane/ethyl acetate (95:5, v/v), and finally with 400 mL of CH_2Cl_2. A yellow band eluted with the second solvent and another with the last solvent. The first band collected was identified as the azo compound **7** (~2 mg) from its GC retention time, while the second band was identified as a mixture of azide **4** and aniline **6** by GC. No new compound was isolated. The second nitrene dimer may be the cis decafluoroazobenzene isomer.

Tetrahydrofuran. The azide **4** (0.2000 g, 0.957 mmol) was dissolved in 80 mL of THF and placed in a 100-mL photochemical reaction vessel. The reaction mixture was freeze–thaw degassed three times, with Ar purges. The reaction mixture was then irradiated in a Rayonet Photochemical Reactor at 350 nm for 18 h under argon. During the course of the photolysis, the reaction mixture darkened from pale yellow to yellow-orange in color. The reaction mixture was subsequently chromatographed through an 8-in. column of 230–400 mesh silica gel (40% CH_2Cl_2/hexanes to 60% CH_2Cl_2/hexanes). The fractions isolated in order of increasing polarity were recovered starting material **4**, aniline **6** (0.0052 g, 0.028 mmol, 3%), and the nitrene–THF adduct (0.0993 g,

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0.392 mmol, 41%) as colorless needles: mp 54–55 °C; ^{1}H NMR (250 MHz, CDCl$_3$) δ 1.85 (cm, 3 H), 2.3 (m, 1 H), 3.8 (cm, 3 H), 5.4 (cm, 1 H); ^{13}C NMR δ 86.95, 86.90, 66.78, 32.86, 29.70, 24.64, 4.00; ^{19}F NMR δ −158.105 (cm, 3 F), −165.111 (cm, 2 F), −196.812 (cm, 1 F); HRMS, *m/e* (M$^+$) calcd for C$_{10}$H$_8$F$_5$NO 253.0571, found 253.0564.

Pyridine. A mixture of 2 mL of dry pyridine and 0.39 mL of neat azide **4** was degassed by bubbling with argon for 3 min. The solution was then photolyzed for 30 min with three Rayonet RPR 350 bulbs. The solution evolved nitrogen and turned from light yellow to a deep amber color. TLC analysis (alumina, ethyl acetate) revealed azide **4** ($R_F = 1$) and ylide ($R_F = 0.4$) and some material with R_F = O. The photolysis mixture was concentrated by removal of pyridine in vacuo and chromatographed using Brockman basic alumina activity 1 using ethyl acetate as eluant. The yellow ylide fraction was collected and concentrated to yield 73 mg of **9** which is identical to independently prepared material: ^{1}H NMR (CD$_3$COCD$_3$, σ) 8.3, (m, 2 H), 7.4–7.6 (m, 3 H); ^{19}F NMR −152.39 to −152.54 (m, 2 F); −167.87 to −168.10 (m, 2 F), −176.45 to −176.81 (m, 1 F); ^{13}C NMR 135.24 (s), 127.20 (s), 143.32 (m), 141.44 (m), 139.54 (m), 137.51 (m), 137.30 (m), 136.25 (m).

Toluene. Samples of **4** (4.03×10^{-2} M) and naphthalene (6.9×10^{-3} M, internal standard) in toluene were photolyzed at 350 nm for 4 h at 25, −78, −150, and −196 °C. After photolysis, the first sample was kept in the dark at 25 °C overnight, the next two samples at −78 °C overnight, and the last sample at −196 °C for 46 h before they were brought to room temperature and analyzed by GC. The yields of *N*-(2-methylphenyl)pentafluoroaniline **35** and *N*-(4-methylphenyl)pentafluoroaniline **36** were calculated with the assumption that their response factors are both identical to that of *N*-benzylpentafluoroaniline **29**.

GC Analysis of Photolysate Mixtures. Triplet-Sensitized Photolysis of Pentafluorophenyl Azide (4) in Toluene. A N$_2$-purged solution (2.0 mL) of azide **4** (1.25×10^{-2} M) and 4-benzoylbiphenyl (0.01 M, sensitizer) was photolyzed at wavelengths >350 nm using the filtered output of a 1000-W Hg-Xe arc lamp for 2 h at room temperature. After photolysis, the solution was kept in the dark overnight. To the solution was added 50 μL of a 2.02×10^{-1} M solution of naphthalene (internal standard) in acetone. GC analysis showed that the volatile products formed were **14** (9.7%), pentafluoroaniline **6** (26%), and decafluoroazobenzene **7** (5.7%).

Photolysis of Pentafluorophenyl Azide (4) in Various Concentrations of Toluene. Solutions of azide **4** (3×10^{-2} M) were prepared by diluting various amounts of toluene with dichloromethane to make 2.0-mL solutions. A sample of each solution was photolyzed at 350 nm at 25 °C for 0.5 h and then kept in the dark at room temperature overnight. Another set of samples was photolyzed at −78 °C. To each sample was added 10 μL of a 0.25 M solution of PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC.

Photolysis of Pentafluorophenyl Azide (4) at 25 °C in Toluene for Various Lengths of Time. Samples of **4** (2.35×10^{-2} M) in toluene were photolyzed at 350 nm at 25 °C for 0.25, 0.5, 1.0, and 4.0 h and then kept in the dark at room temperature overnight. To each sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone solution, and the resulting solutions were analyzed by GC.

Photolysis of Pentafluorophenyl Azide 4 in Toluene with and without Oxygen. Two samples of **4** (3.23×10^{-2} M) in toluene were prepared as before, while two samples were bubbled with oxygen for about 10 min and then sealed with rubber septa. A set of samples with and without oxygen was photolyzed at 25 °C at 350 nm for 4 h while another set was photolyzed at −78 °C. After photolysis, the samples were kept at 25 and −78 °C, respectively, in the dark overnight. To each solution was added 20 μL of a 0.22 M solution of PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC/MS.

Toluene/Ethyl Iodide. A solution of **4** in toluene (1.64×10^{-2}) was prepared and 0.5 mL of this solution was added to each of three 6-mm Pyrex test tubes followed by 0.25 mL of freshly distilled ethyl iodide. The solutions were degassed using three freeze–pump–thaw cycles, sealed under vacuum, and photolyzed for 4 h at 20 °C. To each solution was added 15 μL of 0.25 M iodobenzene (4.9×10^{-3} M), and each solution was analyzed by GC with a 5% DB-1 capillary column.

Toluene/Dichloromethane. A stock solution of **4** (1.64×10^{-2} M) in toluene was prepared, and 0.5 mL of the solution was added to each of three 6-mm Pyrex test tubes. To each tube was added 0.25 mL of dichloromethane. The solutions were degassed using three freeze–pump–thaw cycles, sealed under vacuum, and photolyzed for 4 h at 20 °C. To each solution was added 15 μL of 0.25 M iodobenzene (4.9×10^{-3} M), and each sample was analyzed by GC with a 5% DB-1 capillary column. The integration was not initiated until 5.70 min post injection. The experiment was repeated with various rates of dichloromethane/toluene.

Toluene/Ethyl Iodide/Isoprene. To each of three 6-mm Pyrex test tubes were added 0.5 mL of a stock solution of azide **4** (1.54×10^{-2} M) in toluene, 0.25 mL of ethyl iodide, and isoprene (varied concentrations). The solutions were degassed using three freeze–pump–thaw cycles, sealed under vacuum, and photolyzed for 4 h (350 nm), and 15 μL of 0.25 M iodobenzene (4.9×10^{-3} M) was added to each solution. The solutions were analyzed by GC using as 5% DB-1 capillary column.

Toluene/*n*-Butyl Bromide. To each of three 6-mm Pyrex test tubes were added 0.50 mL of a stock solution of azide **4** (1.54×10^{-2} M) in toluene and 0.25 mL of *n*-butyl bromide. The solutions were degassed using three freeze–pump–thaw cycles, sealed under vacuum, and photolyzed for 4 h. To each solution was added 0.25 M iodobenzene (15 μL, 4.9×10^{-3} M). The solutions were analyzed by GC with a 5% DB-1 capillary column.

Photolysis of Pentafluorophenyl Azide (4) in Toluene Containing Naphthalene. Samples of **4** (2.56×10^{-2} M) and naphthalene (5.1×10^{-2} M) in toluene were photolyzed at 350 nm for 3 h at various temperatures. After photolysis, the solutions were kept in the dark at 0 °C overnight. To each sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC. In some samples **14** and **17** were formed, along with their isomeric azepines or aziridines. Their yields were quantified by assuming that their response factors were all identical to those of **14** and **17**. The relative rates of insertion of singlet nitrene **27S** into the aromatic C–H bonds of naphthalene and toluene, $k_{\mathrm{Np}}/k_{\mathrm{Tol}}$, were calculated from the integrated yields of the insertion products.

Photolysis of Pentafluorophenyl Azide (4) at 25 °C in Various Concentrations of Diethylamine. Solutions of azide **4** ($2\text{–}3 \times 10^{-2}$ M) were prepared by diluting various amounts of diethylamine with dichloromethane to make 2.0-mL solutions. A sample of each solution was photolyzed at 350 nm at 25 °C for 4 h and then kept in the dark at room temperature overnight. To each sample was added 10 μL of a solution of 0.25 M PhI (internal standard) in acetone, and the resulting solutions were analyzed by GC.

Photolysis of Pentafluorophenylazide (4) in Binary Solvent Mixtures Benzene/Cyclopentane. A solution of azide **4** (9.96×10^{-3} M) in 2:1 cyclopentane/benzene (by volume) was prepared, and 0.5 mL was added to 6-mm Pyrex test tubes. The solutions were degassed using three freeze–pump–thaw cycles and sealed under vacuum. A set of three solutions were photolyzed at 0, 10, 20, 30, and 40 °C, while maintaining the temperature at ±3 °C. To each solution was added 10 μL of 0.25 M iodobenzene (4.9×10^{-3}), and the solutions were analyzed by GC with a 5% DB-1 capillary column.

Benzene/Diethylamine. A solution of **4** (19.9 mg, 9.52×10^{-3}) and 19:1 benzene/diethylamine (10 mL) was prepared, and 0.5 mL was added to 6-mm Pyrex test tubes. The solutions were degassed using three freeze–pump–thaw cycles and sealed under vacuum. A set of three solutions was photolyzed at 0, 10, 20, 30, and 40 °C for 4 h while maintaining the temperature at ±2 °C. To each solution was added 10 μL of a 0.25 M iodobenzene solution and each tube was analyzed by GC with a 5% DB-1 capillary column to determine the relative rate of reaction of diethylamine/benzene.

Benzene/Dimethyl Sulfoxide. To three 6-mm Pyrex test tubes were added azide **4** [(2.0 mg, 9, 6×10^{-3} M), (2.8 mg, 1.3×10^{-2} M), (2.7 mg, 1.3×10^{-2} M)] and 1.0 mL of a 200:1 benzene/dimethyl sulfoxide mixture. The solutions were degassed using three freeze–pump–thaw cycles, sealed under vacuum, and photolyzed for 4 h at 20 °C. To each solution was added 10 μL of 0.25 M iodobenzene (4.9×10^{-3} M) which were analyzed by GC with a 5% DB-1 capillary column.

Cyclopentane/Dimethyl Sulfide. A solution of cyclopentane (10 mL) and dimethyl sulfide (1 μL) was prepared, 5 mL of the solution was added to azide **4** (20.3 mg, 9.7×10^{-3} M), and the solution was placed into a Pyrex test tube. The tube was sealed with a rubber septum in which a gas outlet needle was placed and then photolyzed for 4 h. The solution was concentrated and analyzed by ^{1}H NMR.

Synthesis. Pentafluorophenyl Azide (4).[5] A suspension of pentafluorophenylhydrazine (2.0 g, 10 mmol) in 50 mL of 5 N HCl solution was cooled to 0 °C with stirring for 15 min before 15 mL of ether was added. To this mixture was added dropwise a solution of NaNO$_2$ (0.90 g, 13 mmol) in 6 mL of H$_2$O, and the mixture was stirred at 0 °C for 1 h during which time the ether layer changed in color from colorless to yellow to orange and finally to red. The mixture was then allowed to warm up to room temperature and stirred for an additional hour. The ether layer was separated, and the aqueous layer was extracted with three 25-mL portions of ether. The combined extracts were washed with three 50-mL portions of H$_2$O to remove excess acid, dried over MgSO$_4$, and concentrated. The red oil obtained was passed through a 15 cm × 2 cm column of neutral alumina and eluted with CH$_2$Cl$_2$ to remove the side product pentafluoroaniline **6**. The eluent collected was concentrated, and 702 mg (33% yield) of **4** as a yellow liquid was collected in an ice bath by Kugel-Rohr distillation at 25 °C/0.01 mmHg: IR (neat, cm^{-1}) 2190, 2120 (−N$_3$), 1520 (aromatic ring vibration); ^{19}F NMR (CH$_2$Cl$_2$, δ)

−155.216 to −156.167 (m, 2 F), −163.870 to −164.430 (m 1 F), −165.301 to −166.297 (m, 2 F); *m/e* calculated for $C_6F_5N_4$ (M^+) 209.0012, found 208.9998.

***N*-Benzylpentafluoroaniline (14).** *N*-Benzylpentafluoroaniline (**14**) was prepared using the procedure developed by Ballas, Price, and Suschitzky[41] in their syntheses of various polyfluorophenyl-substituted amines. A mixture of benzylamine (5.35 g, 50 mmol) and hexafluorobenzene (11.0 g, 59 mmol) was stirred at 75 °C for 17 h in a round-bottom flask equipped with a reflux condenser. The reaction mixture was then poured into 100 mL of a 10% Na_2CO_3 solution, and the resulting mixture was extracted with three 50-mL portions of ether. The combined extracts were dried over $MgSO_4$ and concentrated to give a light yellow oil. Unreacted benzylamine (1.95 g, 18 mmol) was distilled at 36–45 °C/1 mmHg, and the residue was further purified by passing it through a 15 cm × 2 cm column of neutral alumina and eluting with hexane. Removal of the solvent from the eluent afforded 3.37 g (39% yield based on consumed benzylamine) of **14** as a light yellow oil: IR (neat, cm^{-1}) 3420 (–NH–), 3090, 3070, 3030 (aromatic C–H), 2940, 2880 ($-CH_2$), 1520, 1360 (–NH–), 1205, 1170 (C–F), 750, 700 (monosubstituted benzene); ^1H NMR ($CDCl_3$, δ) 2.8862 (br, 1 H), 4.4704 (d, *J* = 6.7 Hz, 2 H), 7.2583–7.3883 (m, 5 H); ^{19}F NMR ($CDCl_3$, δ) −162.8991 to −163.3321 (m, 2 F), −168.2563 to −168.9728 (m, 2 F), −175.3397 (t, t, *J* = 15.8 Hz, *J* = 6.1 Hz, 1 F); *m/e* calculated for $C_{13}H_8F_5N$ (M^+) 273.0577, found 273.0588.

Decafluoroazobenzene (7).[42] A suspension of pentafluoroaniline **6** (2.5 g, 14 mmol) in 90 mL of a 10.25% NaOCl solution was stirred vigorously at room temperature overnight (15 h). The mixture was extracted with three 35-mL portions of ether, and the combined extracts were washed with five 25-mL portions of demineralized water to remove chloride ions. The extracts were then dried over $MgSO_4$ and concentrated to give a red orange solid. Recrystallization from 95% ethanol gave 526 mg (21% yield) of **7** as red orange crystals: mp 140–141 °C (lit. mp[42] 142–143 °C); IR (CCl_4, cm^{-1}) 1258, 1150, 1039, 1006, 982 (C–F); ^{19}F NMR ($CDCl_3$, δ) −151.6852 to −152.5076 (m, 3 F), −164.5177 to −165.3232 (m, 2 F); *m/e* calculated for $C_{12}H_{10}N_2$ (M^+) 361.9901, found 361.9884.

***N*-Phenylpentafluoroaniline (13).**[43] Dry NH_3 (~100 mL) was condensed into a three-necked, round-bottom flask equipped with a dry ice–acetone condenser and nitrogen inlet at −78 °C. Li wire (0.8 g, 110 mmol) previously weighed out in hexane and cut into small pieces was added to liquid NH_3 to produce a blue solution. Unreacted pieces of Li were still present even after 10 min of stirring so a few crystals of $Fe(NO_3)_3{\cdot}9H_2O$ were added, and the blue color of the solution was discharged and a gray suspension was obtained. The excess NH_3 was allowed to evaporate by blowing N_2 through the flask, while the suspension was being warmed up to room temperature. To the pale white solid ($LiNH_2$) obtained was added 25 mL of anhydrous THF, and the suspension was cooled to 0 °C.

A solution of aniline (9.3 g, 100 mmol) in 20 mL of anhydrous THF was added dropwise to the cold suspension of $LiNH_2$ with stirring, and the mixture was stirred at 0 °C for an additional 35 min. To this cold solution of lithium anilide was slowly added hexafluorobenzene (9.3 g, 50 mmol), and the resulting solution was stirred at 0 °C for an additional 2 H. The reddish-brown solution was then allowed to warm up to room temperature and stirred at this temperature overnight (15 h).

The solution was cooled to 0 °C and hydrolyzed with 100 mL of 5% HCl solution, and the mixture was extracted with three 50-mL portions of ether. The combined extracts were then dried over $MgSO_4$ and concentrated to give a purple oil. This was passed through a 20 cm × 2 cm column of neutral alumina and eluted with ether. Removal of the solvent from the eluent gave a purple solid. During an attempt to recrystallize the solid from petroleum ether (bp 35–60 °C), a white insoluble solid impurity separated. Complete removal of the solvent gave 7.83 g (60% yield) of **13** as a beige solid with a slight purple tint: mp 64.0–65.5 °C (lit. mp[43] 69.5–71.5 °C); IR ($CHCl_3$, cm^{-1}) 3420 (–NH–), 1600 (C=O), 1080, 990 (C–F); ^1H NMR ($CDCl_3$, δ) 5.3981 (br, 1 H), 6.7999–6.8342 (m, 2 H), 6.8729–7.1134 (m, 1 H), 7.2305–7.3355 (m, 2 H); ^{19}F NMR ($CDCl_3$, δ) −153.5865 to −154.6220 (m, 2 F), −166.7794 to −168.3418 (m, 3 F); *m/e* calculated for $C_{12}H_6F_5N$ (M^+) 259.0420, found 259.0417.

***N*-(2-Methylphenyl)pentafluoroaniline (15).** This material was prepared in a similar manner ($NaNH_2$ instead of $LiNH_2$ was used as base) as **13** from *o*-toluidine in 19% yield as purple crystals (pentane): mp 49.5–50.5 °C; IR (CCl_4, cm^{-1}) 3420 (–NH–), 3030 (aromatic C–H), 2980, 2930, 2860 ($-CH_3$), 1250 (–NH–), 1110 (C–F); ^1H NMR ($CDCl_3$, δ) 2.3304 (s, 3 H), 5.0880 (br, 1 H), 6.6496–6.6813 (m, 1 H), 6.9195–6.9785 (m, 1 H), 7.0877–7.1986 (m, 1 H); ^{19}F NMR ($CDCl_3$, δ) −154.7352 to −155.1760 (m, 2 F), −166.9716 to −167.6633 (m, 2 F), −168.5027 to −169.1566 (m, 1 F); *m/e* calculated for $C_{13}H_8F_5N$ (M^+) 273.0577, found 273.0584.

***N*-(4-Methylphenyl)pentafluoroaniline 17.** This material was prepared in the same manner as **13** from *p*-toluidine in 9.1% yield as light purple crystals (pentane): mp 90–91 °C; IR (CCl_4, cm^{-1}) 3420 (–NH–), 3090, 3030 (aromatic C–H), 2960, 2920, 2860 ($-CH_3$), 1235 (–NH–), 1170, 1120, 1080 (C–F); ^1H NMR ($CDCl_3$, δ) 2.2976 (s, 3 H), 53365 (br, 1 H), 6.7300–6.7633 (m, 2 H), 7.0592–7.1029 (m, 2 H); ^{19}F NMR ($CDCl_3$, δ) −154.5701 to −154.9208 (m, 2 F), −167.0471 to −167.7616 (m, 2 F), −168.8512 to −169.5087 (m, 1 F); *m/e* calculated for $C_{13}H_8F_5N$ (M^+) 273.0577, found 273.0591.

***N*-(1-Naphthyl)pentafluoroaniline 19.** This material was prepared in the same manner as **13** from 1-aminonaphthalene in 16% yield as a light brown solid: mp 95.0–97.5 °C; IR (CCl_4, cm^{-1}) 3410 (–NH–), 3060, 3010 (aromatic C–H), 1270 (–NH–), 1090, 1050 (C–F); ^1H NMR ($CDCl_3$, δ) 5.7324 (br, 1 H), 6.8123–6.8421 (m, 1 H), 7.3232–7.3861 (m, 1 H), 7.4957–7.5951 (m, 3 H), 7.8486–7.9002 (m, 1 H); ^{19}F NMR ($CDCl_3$, δ) −154.8668 to −155.3074 (m, 2 F), −166.8120 to −167.5306 (m, 2 F), −168.7797 to −169.4376 (m, 1 F); *m/e* calculated for $C_{16}H_8F_5N$ (M^+) 309.0577, found 309.0581.

***N*-(2-Naphthyl)pentafluoroaniline 20.** This material was prepared in the same manner as **13** from 2-aminonaphthalene in 7.2% yield as dark orange crystals (petroleum ether, bp 35–60 °C): mp 110.5–112.0 °C; IR (CCl_4, cm^{-1}) 3419 (–NH–), 3058 (aromatic C–H), 1278 (–NH–), 1219, 1188, 1007 (C–F), 813, 744 (β-substituted naphthalene); ^1H NMR ($CDCl_3$, δ) 5.5242 (br, 1 H), 7.0424–7.0973 (m, 2 H), 7.2982–7.4537 (m, 2 H), 7.6306–7.7722 (m, 3 H); ^{19}F NMR ($CDCl_3$, δ) −153.1379 to −153.4665 (m, 2 F), −166.4760 to −167.7456 (m, 3 F); *m/e* calculated for $C_{16}H_8F_5N$ (M^+) 309.0577, found 309.0567.

1-Aminopyridinium Iodide. Hydroxylamine-*o*-sulfonic acid (11.363 g, 0.100 mol) in distilled water (65 mL) was cooled to 0 °C. To this solution was added freshly distilled pyridine (25 mL, 0.309 mol), and the reaction mixture was heated at 90 °C for 20 min with stirring. Upon cooling to room temperature, solid K_2CO_3 (13.8 g, 0.10 mol) was added. The water and excess pyridine were removed under reduced pressure with heating to 40 °C to render an off-white precipitate, to which absolute ethanol (120 mL) was added, and the remaining insoluble precipitate removed by gravity filtration. To the filtrate was added HI (20 mL, 47%), and the reaction mixture was cooled to −20 °C in a dry ice–methanol bath. Collection of the resulting precipitate by vacuum filtration produced lavender crystals of crude product. Upon recrystallization in absolute ethanol, pale pink crystals of pure material were isolated (35% mp 160–61 °C): ^1H NMR (DMSO-d_6, ppm) 8.040 (t, 1 H), 8.241 (t, 1 H), 8.440 (s, NH_2), 8.770 (d, 1 H).

Pyridinyl-*N*-perfluorophenylimine (9). 1-Aminopyridinium iodide (0.926 g, 0.004 mol) and sodium methoxide (0.420 g, 0.008 mol) were dissolved in absolute ethanol (50 mL) with stirring. To this mixture, hexafluorobenzene (3.8 mL, 6.125 g, 0.033 mol) was added, and the reaction mixture was refluxed for 3 h. Cooling to room temperature and removal of the solvent under reduced pressure rendered a brown-green solid. To this residue, hot ethanol (30 mL) was added, and, upon cooling, the precipitate was removed by gravity filtration to render grey crystals (mp > 300 °C, presumably NaF). The filtrate, upon removal of the ethanol under reduced pressure, yielded crude **9** as brown crystals (0.84 g, 78%, dec 143 °C). Crude **9** was further purified by passage through a basic alumina column with ethyl acetate as an eluent, to yield pure **9** (mp 139–40 °C, canary-yellow crystals): ^1H NMR ($CDCl_3$, ppm) 7.25 (m, 2 H), 8.10 (d, 1 H); ^{19}F NMR ($CDCl_3$, ppm) −150.564 to −150.706 (d, 2 F), −165.518 to −165.733 (t, 2 F), −171.197 to −171.421 (t, 1 F).

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