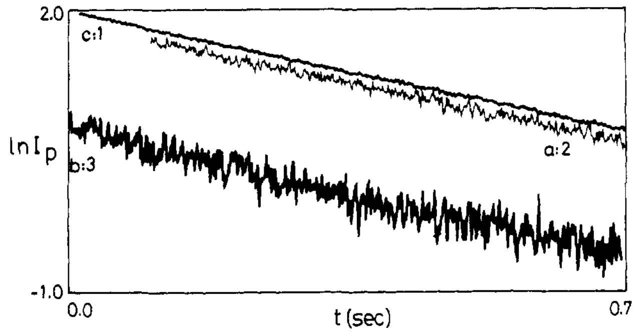

Figure 3. Phosphorescence decay: (a) compound **2**; (b) compound **3**; (c) Tinuvin P. The averaged lifetimes corresponding to five experiments are (a) 0.564 ± 0.007, (b) 0.613 ± 0.003, and (c) 0.611 ± 0.002 s.

by rotation of the aryl group as shown in Scheme I. The inverse order of rotation seems unlikely. It would not explain the role of the *tert*-butyl group since, in that event, the OH group would remain free to form an *inter*molecular hydrogen bond with the solvent.

Other possible explanations for the *tert*-butyl effect can be excluded, at least as the main cause. For instance, the loose bolt effect of the *tert*-butyl group[23] on the ISC $T_1 \rightsquigarrow S_0$[24,25] and the CI $S_1 \rightsquigarrow S_0$[26] cannot be invoked to explain the dramatic reduction in luminescence observed on going from the para isomer to the ortho isomer, because their phosphorescence decays (measurable for the ortho isomer in spite of its exceedingly weak phosphorescence) (see Figure 3) have lifetimes similar to that of Tinuvin P.

It seems likely that the "*tert*-butyl ortho effect" could be used with similar effectiveness in other families of photoprotecting agents (cf. ref 27), e.g., the 2-hydroxybenzophenones and the 2-(2′-hydroxyphenyl)-*s*-triazines.

Acknowledgment. We are greatly indebted to CICYT of Spain for financial support (Project No. PB87-0094-CO2-00). Tinuvin P was supplied by Ciba-Geigy.

Registry No. 2, 3147-76-0; **3**, 34074-96-9.

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A Significant Barrier to 1,2 Hydrogen Migration in Singlet 1-Phenylethylidene. A Laser Flash Photolysis Study

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Contribution from the Department of Chemistry, The Ohio State University, Columbus, Ohio 43210, and Department of Environmental Engineering, Dokuz Eylül Universitesi, Izmir, Turkey. *Received July 29, 1991. Revised Manuscript Received September 12, 1991*

Abstract: Laser flash photolysis of 1-phenyldiazoethane in heptane releases 1-phenylethylidene which can be intercepted with pyridine to form an ylide (λ_{max} = 475 nm). Oxygen trapping experiments indicate that relaxation of singlet 1-phenylethylidene to the ground triplet state is rapid relative to pyridine trapping. Analysis of the data reveals that the (singlet/triplet) carbene equilibrium constant $K = 2 \times 10^{-2}$ and $\Delta G_{ST}(298\ K) = 2.3$ kcal/mol at ambient temperature in *n*-heptane. Furthermore, the rate constant for 1,2 hydrogen migration in the singlet state ($k_{1,2}$) is less than $6 \times 10^6\ s^{-1}$, and the 1,2 hydrogen shift reaction in the singlet state must traverse an activation energy of at least 4.3 kcal/mol in alkane solvent. The 1,2 hydrogen shift reaction is accelerated by more than a factor of 30 in polar acetonitrile solvent and by substitution of an additional methyl group on the migrating CH group (1-phenylpropylidene).

1. Introduction

Over the past 10 years there has been tremendous activity in the study of the absolute kinetics of carbene processes utilizing laser flash photolysis (LFP) techniques.[1] For the most part, these studies were concerned with aromatic carbenes to take advantage of their benzylic chromophores.

These studies were designed to study carbenes which did not undergo intramolecular rearrangements and thereby facilitate the study of the kinetics of their intermolecular reactions. Recently attention has turned to the study of the intra- and intermolecular reaction rates of alkyl-substituted carbenes. To date, these studies have been confined to alkylhalocarbenes[2] and small-ring dialkylcarbenes,[3] both of which have *singlet* ground states. The absolute Arrhenius parameters associated with the *intramolecular* rearrangements of singlet carbenes which are now known are given in Figure 1. Surprising features of the data are the relatively low Arrhenius preexponential *A* factors and negative entropies of activation. In this paper we report the dynamics of an arylalkylcarbene, 1-phenylethylidene (**1a**), a species with a triplet ground state. The data are consistent with a small singlet–triplet energy separation (ΔG_{ST}) in this carbene and a significant barrier to 1,2 hydrogen migration in the singlet state. We have also found

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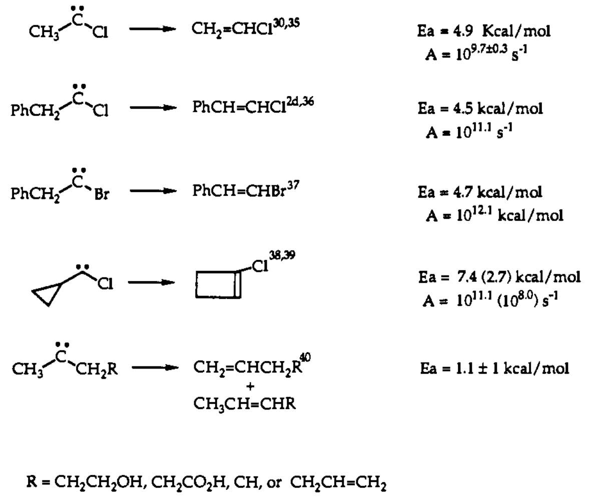


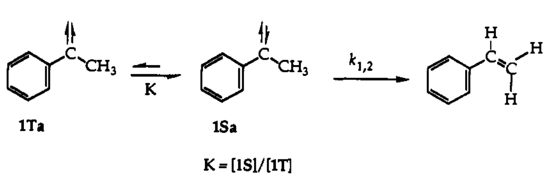
Figure 1. Previously reported activation parameters of carbene rearrangements.

that the 1,2 hydrogen shift reaction is dramatically accelerated by the polar solvent acetonitrile and by substitution of methyl at the migrating CH carbon (1-phenylpropylidene). The data suggest charge development in the transition state.

2. Previous Studies of 1-Phenylethylidene

A. Studies in Rigid Matrices. Photolysis of 1-phenyldiazoethane (**2a**; Scheme I) in organic glasses at 77 K or in rare-gas matrices at 10 K releases 1-phenylethylidene. This species is persistent when immobilized in a rigid medium which allows the carbene to be characterized by infrared,[4] ultraviolet–visible[4] (UV–vis), fluorescence,[5] and electron paramagnetic resonance spectroscopy.[6] The results clearly indicate that 1-phenylethylidene has a triplet ground state as per phenylcarbene[7] and methylene[8] itself.

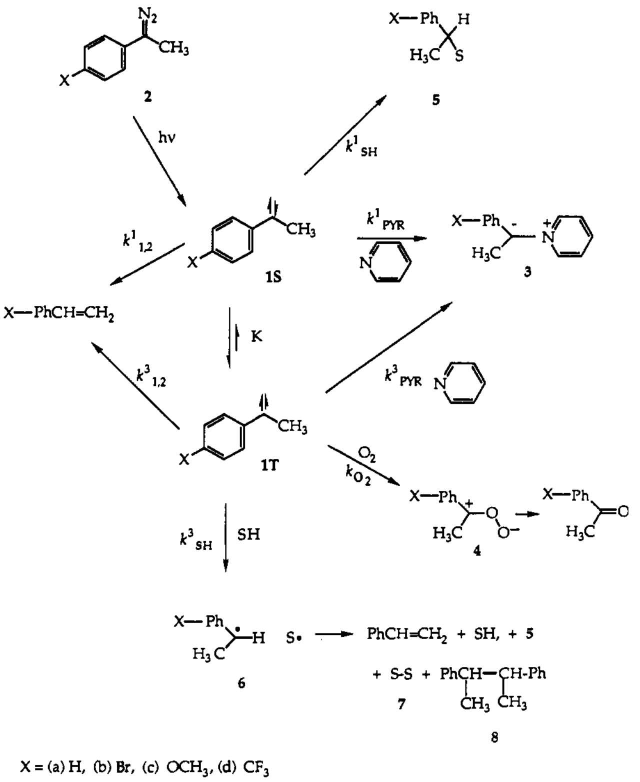
Chapman and McMahon have studied the 1,2 hydrogen shift isomerization of **1T** to styrene at cryogenic temperatures.[4] It was assumed that hydrogen migration proceeds through the low-lying singlet state of the carbene. The triplet carbene is stable for 14 h in argon at 12 K and even to warming to 36 K, but photolysis of **1T** in argon at 12 K effects its ready isomerization to styrene. Warming **1T** in argon to 39 K also led to the disappearance of the IR bands of the triplet carbene and to the appearance of the IR bands of styrene. The best kinetic results were obtained in soft xenon matrices between 55 and 75 K. At 65 K the rate constant for triplet carbene disappearance was $2.9 \times 10^{-4}\ s^{-1}$. It was reasoned then that triplet 1-phenylethylidene must surmount a free energy barrier of 4.7 kcal/mol to rearrange to styrene at this temperature. As entropic contributions to $\Delta G^{\ddagger}$ are minimal at cryogenic temperatures, it was concluded that $\Delta G^{\ddagger}(65\ K) \approx \Delta H^{\ddagger}(65\ K)$. Thus, the singlet–triplet enthalpy difference and the enthalpic barrier to 1,2 hydrogen shift in singlet **1Sa** must sum to 4.7 kcal/mol (eq 1).



$K = [1S]/[1T]$

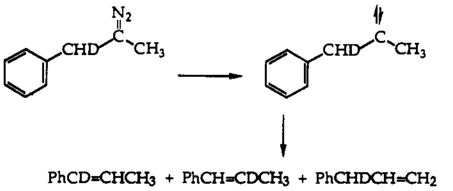
$$\Delta H_{ST} + \Delta H^{\ddagger}_{1,2} = 4.7\ \text{kcal/mol} \qquad (1)$$

Scheme I



X = (a) H, (b) Br, (c) OCH_3, (d) CF_3

B. Chemical Analyses and Isotope Effect Data. Chapman and McMahon's conclusion that there is a barrier to the 1,2 hydrogen shift process was anticipated by the studies of earlier workers using the tools of classical chemical analysis. The discovery of stereoselectivity in the 1,2 hydrogen shift reaction in biased dialkyl carbenic systems by Nickon,[9] Kyba,[10] Shechter,[11] and Freeman[12] requires that there are enthalpic and entropic preferences in the reaction. This in turn implies the existence of enthalpic or entropic barriers on the singlet surface. Thornton's[13] discovery of isotope effects (k_H/k_D = 1.34–1.47) in the closely related 1-phenyl-2-diazopropane series



implied the presence of a small, but nonzero barrier to carbene rearrangement. Thornton also determined that the Hammett ρ value for the rearrangement is ≈−1, which can be interpreted to mean that positive charge accumulates on the carbenic center in the transition state and supports the view that the hydrogen shift reaction resembles hydride transfer in carbocations.

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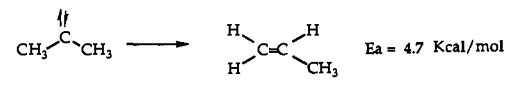
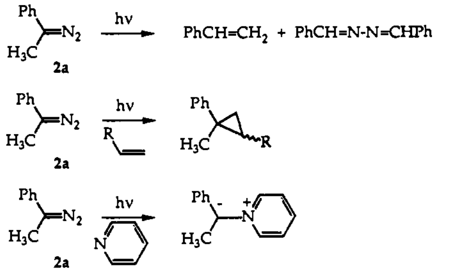
Theory has not explicitly studied the isomerization of **1S** to styrene. The most recent calculation of a simpler system by Houk and Evanseck does find an enthalpic barrier to rearrangement of the singlet state of dimethylcarbene.[14]



Previous workers have analyzed the products formed upon photochemical decomposition of 1-phenyldiazoethane (**2a**).[15]



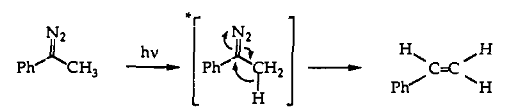
(2)

(3)

(4)

Photolysis of 1-phenyldiazoethane in alkane and ethereal solvents produces acetophenone azine and variable amounts of styrene. The reported yield of styrene ranges from between 0 and 30% (eq 2). It is clear that photolysis of **2a** in the presence of alkenes gives the anticipated cyclopropanes in good yields (eq 3). This gave us confidence that **1Sa** and **1Ta** are not so short-lived as to preclude their interception with pyridine (eq 4) to form the desired ylide of this work.

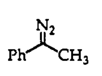
Carbene chemists have long appreciated the danger that stable photochemical reaction products may derive from the reactions of both the carbene of interest and the excited state of the precursor. In fact, Yamamoto et al. concluded that styrene is formed by a rearrangement of the excited state of 1-phenyldiazoethane.[16]

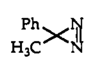


Thus, the pyridine ylide trapping method seems particularly advantageous in this system because although pyridine is a near-diffusion-controlled trap of singlet carbenes,[2,3,15] it apparently does not react with precursor excited states.[3] Thus, in principle, the pyridine ylide–LFP method would seem to provide a useful tool for separating carbene from excited-state precursor chemistry.

3. Results

Laser Flash Photolysis Studies. Laser flash photolysis (LFP, excimer laser, 308 nm, 15 ns) of dilute 1-phenyldiazoethane (**2a**) or 3-phenyl-3-methyldiazirine (**9**) in *n*-heptane fails to produce


2a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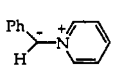
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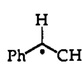
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an useable transient absorption spectrum of carbene **1Ta**. There was no evidence either for the formation of free radical **11** by transient spectroscopy. Thus, there would seem to be little triplet carbene chemistry in this solvent at this temperature. Pyridine is an excellent trap of singlet carbenes. The trapping reaction forms ylides, some of which are sufficiently stable to be isolated.[2a,17] Ylide formation proceeds with rate constants that approach a diffusion-limited rate.[2,3] We have demonstrated that these ylides are excellent probes of carbene dynamics because of their intense absorptions in the UV–vis region, their long lifetimes, and rapid rate of formation.[2,3]

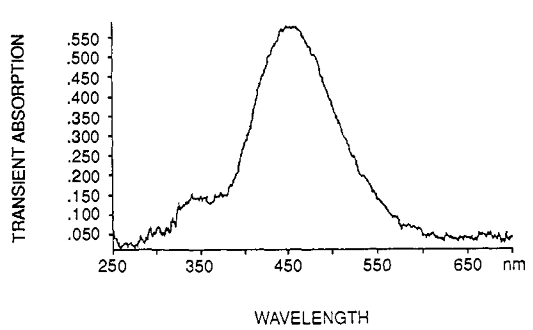


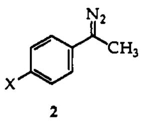
Figure 2. Transient absorption spectrum of **3a** produced by LFP of 1-phenyldiazoethane in heptane in the presence of pyridine.

Table I. Yields of Ylides **3a–d** in the Absence and Presence of Oxygen

ylide	para substituent	conditions	ΔA_{475}	λ_{max} (nm)
3a	H	N_2	0.120	450
3a	H	O_2	0.090	450
3b	Br	N_2	0.073	468
3b	Br	O_2	0.042	468
3c	OCH_3	N_2	0.079	427
3c	OCH_3	O_2	0.062	427
3d	CF_3	N_2	0.124	520
3d	CF_3	O_2	0.115	520

LFP of **2a** or **9** in *n*-heptane in the presence of pyridine produces an intense transient absorption of 475 nm which is attributed to ylide **3** (Figure 2). In support of this assignment, we note that the transient spectrum is very similar to that of ylide **10** which is formed from the reaction of phenylcarbene with pyridine.[18] Furthermore, the absolute rate of formation of the transient is first order in the concentration of pyridine (vide infra). The yield of the transient signal is reduced and the rate of formation of the transient is increased by oxygen, a scavenger which reacts with triplet carbenes with rates close to diffusion control (Table I).[19]

These experiments were repeated with the substituted carbenes **1b–d**. As before, LFP of **2b–d** in heptane fails to produce useable transient signals, but flash photolysis of **2b–d** in the presence of pyridine produces intensely absorbing transients. The rates of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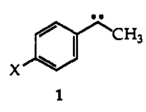
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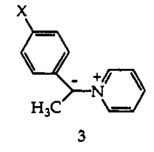
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X = (a) H (b) Br (C) OCH$_3$ (d) CF$_3$

formation of these transients are first order in pyridine concentration (vide infra), and the yields of ylides are reduced by the presence of oxygen, a triplet carbene trap. It is known that **1a** has a triplet ground state[6] and assumed that **1b–d** have triplet ground states as well because these substituents do not alter the ground-state multiplicities of phenylcarbene and diphenylcarbene.[20]

A working mechanistic hypothesis including ideas proposed by earlier workers[4] is given in Scheme I. Photolysis of **2a** leads to nitrogen extrusion and by spin conservation the formation of 1-phenylethylidene in a singlet electronic state **1Sa**. Singlet

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Table II. Absolute Kinetics Obtained from LFP of 1-Phenyldiazoethane and Its Derivatives in Dilute Pyridine at 298 K

diazo	substituent (p-X)	solvent	$k^1_{PYR}K$ or k^3_{PXR} (s^{-1})	k_T (s^{-1})	$1/k_T$(τ ns)	K	ΔG_{ST} (kcal/mol)
2a	H	heptane	$(2.00 + 0.007) \times 10^7$	1.20×10^6	833	2.0×10^{-2}	2.3
2a	H	α,α,α-trifluorotoluene	$(2.61 \pm 0.041) \times 10^7$	1.68×10^6	595	2.6×10^{-2}	2.2
2a	H	benzene	$(1.65 \pm 0.050) \times 10^7$	1.64×10^6	610	1.6×10^{-2}	2.5
2a-d_3	H	heptane	$(1.10 \pm 0.040) \times 10^7$	1.74×10^6	575	1.1×10^{-2}	2.7
2a-d_3	H	α,α,α-trifluorotoluene	$(2.21 \pm 0.069) \times 10^7$	1.87×10^6	535	2.2×10^{-2}	2.3
2a-d_3	H	benzene	$(1.09 \pm 0.017) \times 10^7$	1.13×10^6	885	1.1×10^{-2}	2.7
2a	H	CH_3CN	3.12×10^7	6.15×10^6	162	3.12×10^{-2}	2.0
2b	Br	heptane	$(6.61 \pm 0.45) \times 10^6$	2.11×10^6	474	6.6×10^{-3}	3.0
2c	OCH_3	heptane	$(1.01 \pm 0.013) \times 10^8$	3.23×10^6	309	1.0×10^{-1}	1.4
2d	CF_3	heptane	$(2.56 \pm 0.091) \times 10^6$	2.49×10^6	401	2.6×10^{-3}	3.5

carbene **1Sa** can rearrange to styrene (k^1_{12}), react with solvent (k^1_{SH}), diazo precursor to form an azine (k_{AZ}), or pyridine (k^1_{PYR}), or intersystem cross (ISC) to the ground triplet state **1Ta**. The triplet carbene can react with solvent k^3_{SH} or oxygen and ISC back to the low-lying singlet state. This type of preequilibrium mechanism was first proposed by Bethell.[21] In this view, the chemistry of singlet and triplet arylcarbenes is chemically but not kinetically distinct.

Griller, Nazran, and Scaiano[22] (GNS) have pointed out a second mechanistic possibility. They note that most of the available mechanistic data with arylcarbenes is consistent with the presence of a single reactive intermediate which can react to form products traditionally ascribed to either the singlet or triplet state of the carbene. GNS postulate that triplet- and singlet-state surfaces cross along the reaction coordinate, and not necessarily at the geometry corresponding to the minimum of the low-lying singlet state of the carbene as required in the traditional view. In a surface crossing pathway the triplet carbene can react directly to form styrene in its ground state ($k^3_{1,2}$) and react with pyridine to form an ylide (k^3_{PYR}) without accessing the singlet carbene in its potential minimum. The surface crossing mechanism resolves inconsistencies in the traditional interpretation of the kinetics of reaction of triplet diphenylcarbene and methanol. Unfortunately, the data of this study do not distinguish a preequilibrium from a surface crossing mechanism and will be interpreted within the context of each mechanism.

An immediate question that arises in the traditional Bethell[21] mechanism is whether the singlet carbene **1Sa** is captured by pyridine prior to relaxation to the triplet state or after spin equilibration has been achieved. The fact that oxygen, a selective triplet-state scavenger, quenches the yield of ylide demonstrates that the singlet carbene has not been intercepted prior to spin relaxation. Complete spin state equilibration is also indicated by the time scale of ylide formation. Ylide formation is complete within 2–3 μs at the typical concentrations of pyridine employed in this study. Singlet to triplet ISC is complete within 1 ns for diarylcarbenes (diphenylcarbene, fluorenylidene, dibenzocycloheptadienylidene).[23] Thus, we feel confident in assuming a rapid interconversion of **1S** and **1T** relative to chemical reactions of the carbenes and treating the equilibrium mixture of spin states as a singlet kinetic unit.

The lifetime data also rule out the excited state of the diazo precursor as the reagent which reacts with pyridine to form an ylide. It is extremely unlikely that the nonfluorescent excited states of **2a–d*** will have lifetimes as long as 2–3 μs. Thus, there is no question that pyridine is intercepting carbenes **1a–d** and not their nitrogenous excited-state precursors. Our results do not contradict Yamamoto's[16] conclusions that the excited state of **2a*** rearranges to styrene concurrent with the loss of nitrogen. However, this excited state cannot live long enough to react with pyridine nor can it *only* form styrene. It must have a significant quantum yield to carbene formation as well.

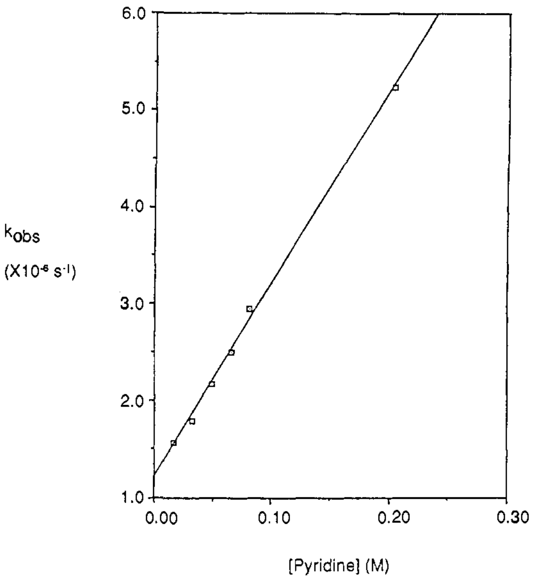

Figure 3. Observed pseudo-first-order rate constant k_{obs} to formation of ylide **3a** in pentane as a function of pyridine concentration.

The ylide is formed with a rate defined by a simple exponential function which can be analyzed to yield an observed rate constant of formation (k_{obs}). It can be shown[2,24] that k_{obs} can be related to the processes of Scheme I as given in eqs 5 and 6, where K is

$$k_{obs} = k^1_{PYR}K[\text{pyridine}] + k_{12}K + k_{AZ}K[\mathbf{2}] + k^1_{SH}K[\text{SH}] + k^3_{SH}[\text{SH}] \quad (5)$$

$$k_{obs} = k^1_{PYR}K[\text{pyridine}] + k_T \quad (6)$$

$$k_{obs} = k^3_{PYR}[\text{PYR}] + k_T \quad (7)$$

the equilibrium constant defined as $K = [\mathbf{1S}]/[\mathbf{1T}]$ and k_T is the total rate constant of all first-order and pseudo-first-order processes which consume the carbene in the absence of pyridine. If a GNS surface crossing mechanism is operative, then eq 7 is valid where k^3_{PYR} is the absolute rate constant of reaction of the triplet carbene with pyridine. Plots of k_{obs} versus [pyridine] are predicted[25] by both mechanisms and found to be linear (Figure 3) for ylides **3a–d** (and dilute pyridine) with slopes equal to $k^1_{PYR}K$ (or k^3_{PYR}) and with intercepts of k_T. Values of $k^1_{PYR}K$ are listed in Table II for carbenes **1a–d** in heptane along with values of K and ΔG_{298} derived by assuming the Bethell mechanism and (independent of substituent) that $k^1_{PYR} = 1 \times 10^9$ M^{-1} s^{-1}, as is common for singlet carbenes.[2,3,15] This analysis indicates that electron-donating groups lower the singlet–triplet gap, presumably by differential stabili-

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[21] Bethell, D.; Hayes, J.; Newall, A. R. *J. Chem. Soc., Perkin Trans. 2* **1974**, *2*, 1307.

[22] Griller, D.; Nazran, A. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 198.

[23] (a) Sitzmann, E. V.; Langan, J.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1984**, *106*, 1868. (b) Sitzmann, E. V.; Eisenthal, K. B. *Applications of Picosecond Spectroscopy to Chemistry*; Reidel: Dordrecht, 1985; 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.

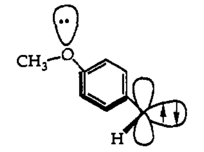
[24] The pyridine probe method is based upon models developed by Scaiano to probe free-radical reactions. For examples, see: (a) Small, R. D., Jr.; Scaiano, J. C. *Phys. Chem.* **1977**, *81*, 828. (b) Small, R. D., Jr.; Scaiano, J. C. *Chem. Phys. Lett.* **1977**, *50*, 431. (c) *Ibid.* **1978**, *59*, 246.

[25] The Bethel mechanism predicts curvature in these plots when k_{PYR}[PYR] becomes comparable to the rate of **1S** → **1T** intersystem crossing.

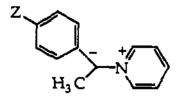
Table III. Substituent Effects on the Rates of Reaction of 1-Phenylethylidene in Heptane at 298 K and PCC in Toluene at 293 K with Pyridine

para substituent	1-phenylethylidene $k^1_{PYR}K$ or k^3_{PYR} (M^{-1} s^{-1}) (k_{REL})	chlorophenylcarbene[26] k^1_{PYR} (M^{-1} s^{-1}) (k_{REL})
MeO	$(1.01 \pm 0.013) \times 10^8$ (5.05)	$(2.92 \pm 0.36) \times 10^7$ (0.08)
H	$(2.00 \pm 0.007) \times 10^7$ (1.00)	$(3.74 \pm 0.38) \times 10^8$ (1.00)
CF_3	$(2.56 \pm 0.091) \times 10^6$ (0.13)	
NO_2		$(2.26 \pm 0.37) \times 10^9$ (6.04)

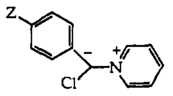
zation of the closed-shell singlet configuration shown below. The ΔG values of Table II are not meaningful if there is a triplet–singlet surface crossing in the reaction of the triplet carbene with pyridine but merely indicate the relative accessibility of the singlet surfaces as a function of substituent.



One could argue that the observed variation in $k^1_{PYR}K$ is due solely to variation in k^1_{PYR}. However, this would require that electron donors accelerate and electron-accepting groups retard the rate of ylide formation.



3a-d



11a-d

This reasoning is inconsistent though with the expected electronic structure of the ylide. Furthermore, Jones[26] has determined the absolute reactivities of para-substituted chlorophenylcarbenes (CPC's), all of which are ground-state singlets, with pyridine, and the results are opposite to the trend in $k^1_{PYR}K$ observed in this study (Table III). Jones[26] found that (*p*-nitrophenyl)chlorocarbene is more reactive toward pyridine than is PCC but that PCC is substantially more reactive toward pyridine than its *p*-methoxy derivative. Thus, if there is variation in k^1_{PYR} among the 1-phenylethylidenes, it is expected to be in the direction opposite to that observed and is clearly less important than the variation in K with substituent.

A spin inversion occurs at some point during the isomerization of triplet 1-phenylethylidene to styrene. It is interesting to note that *p*-bromo, a heavy-atom substituent, does not assist the rate of rearrangement.[27] Furthermore, there is no dramatic variation in k_T with the electrical properties of the *p*-phenyl substituent. Thus, there is no kinetic evidence for charge development at the carbene carbon in the 1,2 hydrogen shift transition state.

It is easily demonstrated that $k_{AZ}K$ is not an important contributor to k_T in *n*-heptane at ambient temperature. We measured k_T over a wide range of precursor concentrations at constant [pyridine] and found it to be invariant (Table IV). This is not surprising considering the large molar absorptivity of **2a** (ϵ_{308} = 3.6×10^3 M^{-1} cm^{-1}) at the excitation wavelength and the very low concentrations of precursor employed in the LFP studies.

The value of k_T was measured next in cyclohexane and cyclohexane-d_{12} to determine the importance of $k^1_{SH}K$ and k^3_{SH} to the carbene lifetime in the absence of pyridine. As shown in Figure 4 there is a significant solvent isotope effect to k_T

$$k_T^H/k_T^D = 1.6$$

which indicates that either $k^1_{SH}K$ or k^3_{SH}, or both terms, makes significant contributions to k_T in alkane solvents. It is interesting to note that the measured isotope effect on k_T is very similar to the reported isotope effect to the CH insertion reactions of singlet phenylcarbene[18,28] and singlet 1-naphthylcarbene[29] with cyclohexane ($k^1_H/k^1_D \approx 2.0$) and significantly smaller than the isotope effect to hydrogen atom abstraction reactions of triplet 1-naphthylcarbene[29] with the same solvent ($k^3_H/k^3_D = 3.5$). Thus, on the basis it appears that $k^1_{SH}K$ is a larger contributor to k_T than is k^3_{SH} for 1-phenylethylidene.

Table IV. Observed Rate Constants of Reaction (k_{obs}) upon the Photolysis of **2a** and 2,2,2-Trideuterio-1-phenyldiazoethane (**2**-d_3) in Dilute Pyridine with [PYR] = 0.10 M as a Function of Precursor Concentration

diazo absorbance (308 nm)	k_T (s^{-1}) **2a**	k_T (s^{-1}) **2a**-d_3
0.3	2.24×10^6	2.25×10^6
0.6	2.69×10^6	2.41×10^6
0.8	2.59×10^6	2.27×10^6
1.0	2.69×10^6	2.28×10^6

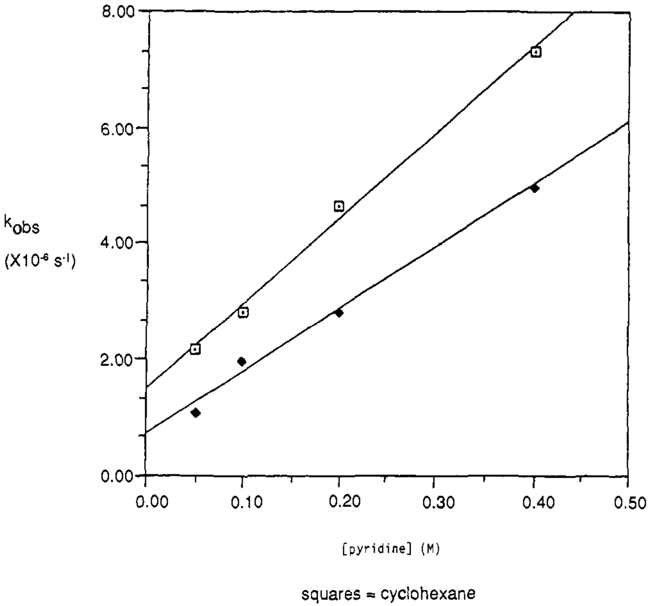
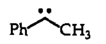


Figure 4. Observed pseudo-first-order rate constant k_{obs} to formation of ylide **3a** in cyclohexane and cyclohexane-d_{12} at equivalent concentrations of diazo precursor.

On the other hand, there is no kinetic evidence supporting a contribution of $k_{1,2}$ to k_T for carbene **1a**. Values of k_{obs} for **1**-d_0 and **1**-d_3 were measured at constant [pyridine] as a function of precursor concentration (Table IV).



1-d₀

1-d₃

Within experimental error, the lifetimes of **1**-d_0 and **1**-d_3 are identical at constant [pyridine]. This is not terribly surprising because Goodman[30] found that the isotope effect to 1,2 hydrogen shift in methylchlorocarbene is small. Thus, the LFP studies demonstrate that $k^1_{SH}K$ and k^3_{SH} contribute to k_T in alkanes but there is no kinetic isotope evidence for a contribution of $k^1_{1,2}K$ (or $k^3_{1,2}$) in this solvent. In an attempt to increase the importance of $k^1_{1,2}K$, other solvents were employed. However, LFP studies of diazo compound **2a** in benzene or α,α,α-trifluorotoluene, in which the importance of solvent CH insertion or hydrogen atom abstraction may be reduced, gave essentially the same values of $k_{PYR}K$ and k_T as were observed in *n*-heptane and no evidence for

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

(27) (a) McClure, D. S. *J. Chem. Phys.* **1949**, *17*, 905. (b) McGlynn, S. P.; Azumi, T.; Kinoshita, M. *Molecular Spectroscopy of the Triplet State*; Prentice Hall: Englewood Cliffs, NJ, 1969; p 183.

(28) (a) Baer, T. A.; Gutsche, C. D. *J. Am. Chem. Soc.* **1971**, *93*, 954. (b) Savino, T. G.; Kanakarajan, K.; Platz, M. S. *J. Org. Chem.* **1986**, *51*, 1305.

(29) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928.

(30) LaVilla, J. A.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 6877.

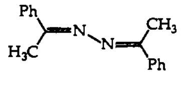
a contribution of $k^1_{1,2}$ to k_T (Table II).

A very large polar solvent effect was observed. The observed rate constant (k_{obs}) to ylide formation is much larger in acetonitrile than in *n*-pentane or *n*-heptane. It is possible to dissect k_{obs} into $k^1_{PYR}K$ (or k^3_{PYR}) and k_T as before (Table II), and it is clear that the polar solvent has little effect on the rate constant of reaction of the carbene with pyridine but it reduces the lifetime (τ) of the carbene in the *absence* of pyridine ($1/k_T = \tau$) by more than a factor of 5. The temperature dependences of $k^1_{PYR}K$ and k_T were also examined in acetonitrile. The activation energy for pyridine capture ($k_{PYR}K$ or k^3_{PYR})) is 0 kcal/mol within experimental error. The Arrhenius parameters associated with k_T in this solvent are $E_a = 2.06$ kcal/mol and $A = 10^{8.32}$ s^{-1}.

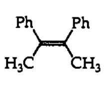
The zero activation energy to pyridine capture requires comment. If the Bethell[21] preexperimental mechanism is operative, it is possible that both ΔH_{ST}, the singlet–triplet enthalpy gap, and the activation energy ($E_a{}^1{}_{PYR}$) to pyridine capture of the singlet carbene are both very close to zero. A ΔH_{ST} of close to zero requires that the 2.3 kcal/mol free energy separation of **1S** and **1T** at 298 K is largely entropic ($\approx$8 eu). This is slightly larger than the contribution of ΔS_{ST} which can be attributed to spin statistics ($R \ln 3 = 2.18$ eu). We speculate that a closed-shell singlet carbene, with one filled and one empty orbital, is dipolar and requires greater solvation than the open-shell triplet state of the carbene. This leads to greater ordering of the solvent and a less favorable entropy of formation of the singlet carbene. It is also possible that ΔH_{ST} may be +(1 to 3) kcal/mol with the triplet the ground state, but this would require $E_a{}^1{}_{PYR}$ to be −1–3 kcal/mol. This is not impossible as negative activation energies for singlet carbene processes are well-known.[31] Alternatively, if the GNS surface crossing mechanism is operative, then the singlet–triplet surface crossing occurs at a point that is very close (in energy) to the triplet carbene minimum. This in turn implies that ΔH_{ST} is very close to zero.

Product Analysis. The conclusions of the laser flash photolysis studies were fully supported by gas chromatography–mass spectrometric analysis of the stable products formed on extended photolysis of highly dilute ($A_{308} = 1.0$) solutions of **2a**. Photolysis of **2a**-d_0 and **2a**-d_3 in *n*-pentane produced the products of formal carbene insertion into solvent, some solvent-derived radical dimers, and only a small yield of styrene. The concentration of the diazo compound used in the extended photolysis was the same as that used in the LFP studies. A conservative estimate is that styrene formation accounts for less than 10% of the volatile products formed on extended, conventional photolysis of **2a** or **2a**-d_0 in *n*-pentane.

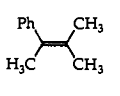
In more concentrated pentane solutions the major product is now acetophenone azine **12**, along with some solvent insertion products **5** and styrene. Different results were obtained upon photolysis of 1-phenyldiazoethane in acetonitrile. The yield of styrene produced on photolysis of 0.01 M **2a** in acetonitrile is 5 times greater than that observed in *n*-pentane at this concentration of precursor. There was no evidence for insertion into a CH bond of acetonitrile to form **14** and no evidence for the formation of azirine **15** which would have indicated the intermediacy of nitrile ylide **16**. In dilute acetonitrile solvent the photolysis of **2a** gives styrene as the only volatile product at ambient temperature. However, upon photolysis of **2a** in cold (−40 °C) acetonitrile a significant amount of acetophenone azine is produced.



12

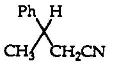


13Z

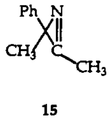


13T

+ 5 + 8



14



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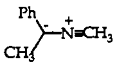

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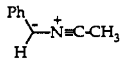


17

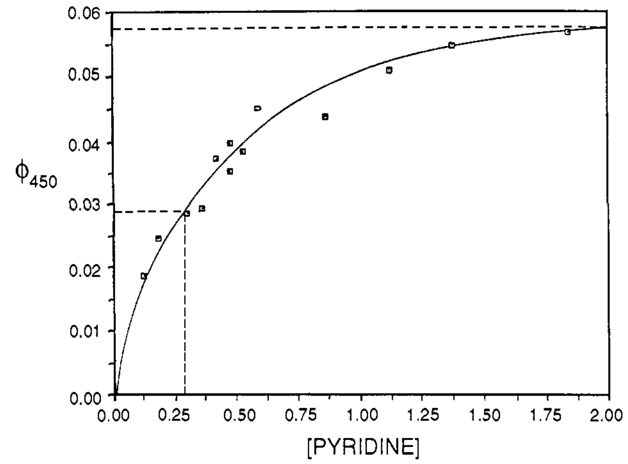
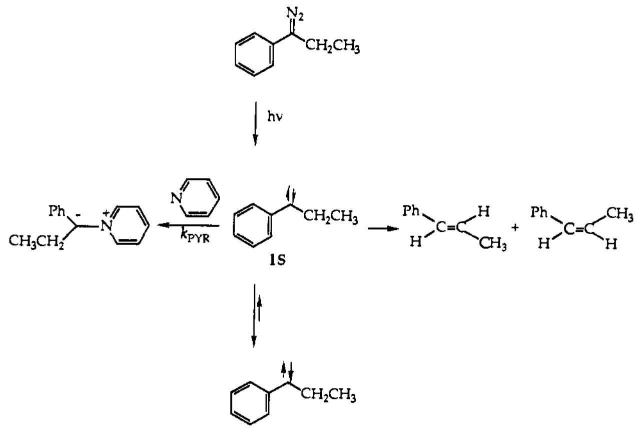


Figure 5. Maximum change in absorbance at 450 nm following LFP of 1-phenyldiazopropane in *n*-pentane as a function of pyridine concentration.

Scheme II



LFP of phenyldiazomethane in acetonitrile produces the intense transient spectrum of nitrile ylide **17** ($\lambda_{max} \approx$ 330–350 nm).[2,29] LFP of 1-phenyldiazoethane in acetonitrile does not produce a transient absorption. Thus, there is neither chemical nor spectroscopic evidence for the formation of **16** in acetonitrile. The increase in k_T in acetonitrile relative to *n*-alkane solvents at ambient temperature is most likely due to an increase in $k_{1,2}$ with solvent polarity and not due to reaction of the carbene with solvent. The rate constant of the 1,2 hydrogen shift reaction ($k_{1,2}$) is at least 50 times larger in acetonitrile than in *n*-pentane.

The distributions of products (styrene, acetophenone, solvent insertion adducts, azine, carbene dimer) formed on extended photolysis of 0.01 M solutions of **1a**, **2c**, and **2d** in *n*-pentane are virtually identical. Neither a *p*-trifluoromethyl nor a *p*-methoxyl group has significantly increased the yield of styrene relative to the yield of products derived from carbene reaction with solvent or diazo precursor or the yield of carbene dimer. Thus, there is no evidence for charge development at the carbene carbon during 1,2 hydrogen migration. The only significant substituent effect observed is that the yield of solvent insertion adducts has been significantly decreased by the presence of a *p*-methoxyl substituent relative to the yield of azine and stilbene.

We have also studied the photochemistry of 1-phenyldiazopropane (**18**) (Scheme II). LFP of **18** in pentane containing pyridine produces the transient spectrum of ylide **20**. The rate of formation of **20** in *n*-pentane is much faster than that of ylide **3a** in this solvent but could not be resolved at reasonable pyridine concentrations due to the fluorescence of the sample. However, it was possible to measure the yield of ylide (ϕ_{450}) following the laser flash as a function of [pyridine] (Figure 5). The yield of ylide produced in a single laser pulse reaches a maximum value and remains constant when [PYR] > 1.75 M. When [PYR] =

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(31) Çelebi, S.; Platz, M. S. *J. Am. Chem. Soc.*, submitted for publication.

0.28 M, the yield of ylide is exactly half that formed in the saturation limit. At this pyridine concentration (0.28 M) eq 8 is valid for 1-phenylpropylidene. If we assume that carbenes **1**

$$k_T \approx k^1_{PYR}[PYR]K \text{ or } k^3_{PYR} \qquad (8)$$

and **19** can capture pyridine with equal facility (identical $k^1_{PYR}K$ or k^3_{PYR} values), then k_T for 1-phenylpropylidene is found to be 7.28×10^6 s^{-1} and the carbene lifetime in the *absence* of pyridine is 137 ns in *n*-pentane. This is 10 times shorter than the lifetime of carbene **1** in the same solvent. However, this lifetime is still sufficiently long to allow us to assume complete singlet–triplet carbene spin equilibrium and to preclude the intervention of the diazo excited state in the formation of ylide **20**.

Product analysis indicates that $k_T \approx k^1_{1,2}K$ (or $k^3_{1,2}$) for 1-phenylpropylidene as extended photolysis of 0.01 M **18** in *n*-pentane cleanly produces a mixture of *Z* and *E* styrenes **21** and only a very small amount of propiophenone azine as the only volatile reaction products. No traces of solvent insertion products were detected by GC–MS analysis. If the traditional preequilibrium mechanism is operative, it seems reasonable to assume that 1-phenylethylidene and 1-phenylpropylidene have the same singlet–triplet energy gap ($K = 0.02$, 298 K). One can then deduce that $k_{1,2} = 3.64 \times 10^8$ s^{-1} for singlet 1-phenylpropylidene in *n*-pentane. This is more than 60 times larger than the value of $k^1_{1,2}$ of singlet 1-phenylethylidene in an *n*-alkane solvent. If one assumes that the Arrhenius *A* factor to 1,2 hydrogen shift is 10^{10} s^{-1} (as per methylchlorocarbene),[30] then the activation energy barrier is calculated to be 1.96 kcal/mol for this process in 1-phenylpropylidene.

It is interesting to note that LFP of 1-phenyldiazopropane gives a much lower optical yield of ylide **20** than LFP of 1-phenyldiazoethane under identical conditions. This implies that the yield of carbene is larger with 1-phenyldiazoethane and that a significant fraction of *E* and *Z* styrenes **21** are formed by hydrogen atom shift in the excited state of phenyldiazopropane.[16,32]

4. Discussion

Product analysis and kinetic isotope effect data both indicate that the value of $k^1_{1,2}K$ for 1-phenylethylidene **1Sa** in *n*-alkanes is less than 10% of k_T. Thus

$$k^1_{1,2}K \leq 0.10k_T = (0.10)(1.2 \times 10^6) = 1.2 \times 10^5 \text{ s}^{-1}$$

Recall that the value of *K* could be estimated from the assumption that $k^1_{PYR} \approx 1 \times 10^9$ M^{-1} s^{-1}, as is typical for most singlet carbenes within the context of the Bethell mechanism.[2] This analysis reveals that the rate constant of 1,2 hydrogen migration in *singlet* 1-phenylethylidene in alkane solvent is surprisingly small, $k^1_{1,2} \leq 6 \times 10^6$ s^{-1} at ambient temperature, and that the free energy barrier to the rearrangement of the singlet carbene is at least 8 kcal/mol at ambient temperature. If one assumes that the Arrhenius preexponential factor for the unimolecular rearrangement is 10^{10} s^{-1} (as per Goodman's study of methylchlorocarbene),[2] then one deduces that the activation energy to the singlet-state rearrangement of 1-phenylethylidene **1Sa** is at least 4.3 kcal/mol in an *n*-alkane solvent, a value which is in reasonable agreement with McMahon and Chapman's work in cryogenic matrices if $\Delta H_{ST} \leq 0.4$ kcal/mol.[4]

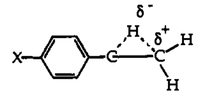
It is clear that the polar solvent acetonitrile has dramatically increased the value of $k_{1,2}K$. It is unlikely that the polar solvent has made *K* larger because $k^1_{PYR}K$ (or k^3_{PYR}) is essentially the same in *n*-pentane and acetonitrile and k_{PYR} is insensitive to changes in solvent polarity for chlorophenylcarbene.[26] Thus, it seems likely that acetonitrile solvent has only reduced the activation energy to 1,2 hydrogen shift in 1-phenylethylidene (**1**) regardless of mechanism, relative to *n*-pentane.

In acetonitrile, the rate of 1,2 hydrogen shift has increased and GC–MS analysis reveals that $k_T \approx k^1_{1,2}K = 6.15 \times 10^6$ s^{-1} or that $k^1_{1,2} = 2.0 \times 10^8$ s^{-1} (298 K) in this solvent. If the preexponential factor is once again assumed[30] to be 10^{10} s^{-1}, we can calculate an activation energy of 2.3 kcal/mol in acetonitrile. Thus, the polar solvent has lowered the activation energy to the 1,2 hydrogen shift by at least 2 kcal/mol.

Recall that styrene is formed cleanly upon photolysis of 1-phenyldiazoethane in acetonitrile at ambient temperature. Thus, it is tempting to associate the Arrhenius parameters determined for k_T with $k_{1,2}K$ in this solvent. The measured Arrhenius *A* factor and ΔS^* associated with k_T and $k^1_{PYR}K$ are then found to be quite low, as per the data of Figure 1. However, upon photolysis of 1-phenyldiazoethane in acetonitrile at −40 °C, acetophenone azine is formed in significant yield; thus, $k_T \neq k^1_{1,2}K$ at this temperature. Lowering the reaction temperature will always enhance the yield of the reaction process with the lowest activation energy when there is temperature-dependent partitioning of a reactive intermediate among various reaction pathways. Thus, the increased importance of azine formation at low temperature, relative to room temperature, produced experimental activation parameters *A* and E_a that were substantially lower than that of the true value of the hydrogen shift reaction.

It is also clear that $k^1_{1,2}K$ for 1-phenylpropylidene (**19**) is at least 60 times larger than that of 1-phenylethylidene (**1**) in *n*-pentane. Thus, the data indicate that $k_{1,2}$ is dramatically accelerated by the extra methyl group in 1-phenylpropylidene. Similar effects have been reported by Goodman[30] and by Bonneau and Liu with alkylchlorocarbenes.[33]

The solvent effect and β-methyl effect data indicate that there is charge development in the transition state of the 1,2 H shift reaction in phenylalkylcarbenes. The large acceleration provided by methyl substitution of the carbon adjacent to the carbene center suggests that positive charge develops at this position in the 1,2 hydrogen shift transition state.



There is no evidence for the development of negative charge at the carbene carbon in the transition state. The lifetime (τ) of 1-phenylethylidene in heptane shows little response to the electrical properties of the para substituent, nor does *p*-trifluoromethyl enhance the yield of styrene. Thus, we conclude that it is the migrating hydrogen that develops negative charge in the transition state of the reaction.

5. Conclusions

The solvent polarity and substituent effect data both indicate that there is charge development in the 1,2 hydrogen shift transition state and that the reaction must traverse a small but finite barrier. The singlet–triplet energy separation (ΔH_{ST}) in 1-phenylethylidene is very small, 0–2.1 kcal/mol. The Arrhenius activation barrier to 1,2 hydrogen shift in singlet 1-phenylethylidene is at least 4.3 kcal/mol in alkanes but is only 2.3 kcal/mol in acetonitrile. These conclusions are in agreement with those of earlier studies that were inferred from the traditional tools of physical organic chemistry. The present LFP study has provided more quantitative measurements of singlet carbene rate constants and energy barriers and has allowed us to disregard complications in the kinetics of the carbene due to chemistry of the precursor excited states.

6. Experimental Section

Melting Points. Melting points were measured on an electrothermal melting point apparatus.

Infrared Spectroscopy. Infrared spectra were measured on a Perkin-Elmer model 457 infrared spectrophotometer.

Nuclear Magnetic Resonance. ^{1}H NMR spectra were recorded by Mr. Carl Engleman on a Varian AM-25 instrument. Chemical shifts were referenced to tetramethylsilane (0.0 ppm).

Ultraviolet/Visible Spectrophotometry. UV/vis spectra and absorptions were measured using a Hewlett-Packard diode array instrument.

Elemental Analysis. Analyses were performed by M-H-W Laboratories (Phoenix, AZ).

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Mass Spectrometry. Mass spectra were recorded by Mr. Dick Weisenberger of the OSU Campus Chemical Instrumentation Center on a Kratos MS-30.

Gas Chromatography/Mass Spectrometry. GC–MS data were recorded by Mr. David Chang of the OSU Campus Chemical Instrumentation Center on a HP-MSD.

General Procedure for Tosylhydrazone Preparation. The ketone was added to a magnetically stirred slurry of 1.0 equiv of *p*-toluenesulfonhydrazide (Aldrich) in absolute ethanol. The mixture was allowed to stir overnight at room temperature or at reflux under nitrogen. The white solid was collected by suction filtration and recrystallized from absolute ethanol.

Acetophenone tosylhydrazone was prepared from acetophenone (Fisher) in 90% yield: mp 143–144 °C; ^{1}H NMR (CDCl$_3$/MeSO-d_6) δ 2.12 (s, 3 H), 2.34 (s, 3 H), 7.25 (s, 5 H), 7.51 (s, 2 H), 7.77 (d, 2 H), 10.2 (s, 1 H); mass spectrum (16 eV) *m*/*z* (relative intensity) 289 (M$^+$, 23), 133 (98), 132 (39), 104 (80), 92 (100), 91 (47), 77 (27), 65 (42). Anal. (theory/found): C (62.48/61.88), H (5.60/5.79), N, (9.79/9.69).

4-Bromoacetophenone tosylhydrazone was prepared from 4-bromoacetophenone (Aldrich) in 79% yield: mp 176–177 °C dec; ^{1}H NMR (CDCl$_3$/MeSO-d_6) δ 2.11 (s, 3 H), 2.34 (s, 3 H), 7.27 (s, 5 H), 7.46 (s, 2 H), 7.75 (d, 2 H), 10.37 (s, 1 H); mass spectrum (16 eV) *m*/*z* (relative intensity) 366 (M$^+$, 10), 219 (27), 213 (24), 211 (26), 184 (55), 182 (56), 132 (100), 131 (42), 103 (30), 91 (30), 77 (28). Anal. (theory/found): C (49.06/49.03), H (4.12/4.24), N (7.63/7.66), Br (21.79/21.66).

4-Methoxyacetophenone tosylhydrazone was prepared from 4-methoxyacetophenone (Aldrich) in 69% yield: mp 163–171 °C dec; ^{1}H NMR (CDCl$_3$/MeSO-d_6) δ 2.09 (s, 3 H), 2.35 (s, 3 H), 3.73 (s, 3 H), 6.80 (d, 2 H), 7.29 (d, 2 H), 7.50 (d, 2 H), 7.77 (d, 2 H), 10.15 (s, 1 H); mass spectrum (16 eV) *m*/*z* (relative intensity) 318 (M$^+$, 5), 164 (11), 163 (100), 148 (45), 134 (41), 122 (17), 119 (26), 91 (41), 65 (19). Anal. (theory/found): C (60.36/60.44), H (5.69/5.86), N (8.79/8.89). Both the mass spectra and elemental analysis were recorded from the first recrystallized product.

4-(Trifluoromethyl)acetophenone tosylhydrazone was prepared from 4-(trifluoromethyl)acetophenone (Aldrich) in 78% yield: mp 186–187 °C; ^{1}H NMR (CDCl$_3$/Me$_2$SO-d_6) δ 2.16 (s, 3 H), 2.35 (s, 3 H), 7.28 (d, 2 H), 7.56 (d, 1 H), 7.75 (m, 4 H), 10.53 (s, 1 H); mass spectrum (16 eV) *m*/*z* (relative intensity) 356 (M$^+$, 10), 201 (65), 200 (19), 172 (100), 160 (32), 103 (19), 91 (23). Anal. (theory/found): C (53.92/53.89), H (4.24/4.47), N (7.86/7.92). Both the mass spectrum and the elemental analysis were recorded from the first recrystallized product.

Acetophenone-*methyl-d*$_3$ tosylhydrazone was prepared from acetophenone-*methyl-d*$_3$ (Aldrich) in ethyl alcohol-*d* in 85% yield: mp 145–146 °C; ^{1}H NMR (CDCl$_3$/MeSO-d_6) δ 2.34 (s, 3 H), 7.26 (s, 5 H), 7.51 (s, 2 H), 7.78 (d, 2 H), 10.26 (s, 1 H); mass spectrum (16 eV) *m*/*z* (relative intensity) 291 (M, 7), 136 (100), 135 (41), 107 (75), 92 (77), 65 (37). Anal. (theory/found): C (61.82/61.88), H (9.61/9.65). Elemental analysis data were recorded from the first recrystallized product.

Propiophenone tosylhydrazone was prepared from propiophenone (Aldrich) in 51% yield as white crystals of a mixture of cis and trans isomers: mp 115–116 °C; ^{1}H NMR (CDCl$_3$) δ 1.05 (3 H, two t), 2.4 (3 H, two s), 2.5 (2 H, two d), 7.05 (1 H, m), 7.3 (5 H, m), 7.4 (1 H, m), 7.6 (2 H, m), 7.8 (1 H, d), 7.9 (2 H, d); ^{13}C NMR (CDCl$_3$) δ 10.236, 10.583, 19.988, 21.545, 31.446, 126.308, 126.700, 127.931, 128.021, 128.346, 128.504, 129.444, 129.492, 129.492, 129.532, 129.559, 129.694, 132.914, 135.466, 136.173, 143.868, 144.045, 156.944, 159.141; MS, *m*/*e* 302 (10), 147 (100), 132 (15), 119 (60), 91 (40), 77 (17), 65 (18), 51 (12), 39 (16). Anal. Calcd for $C_{16}H_{18}N_2O_2S$: C, 63.55; H, 5.99; N, 9.26; S, 10.60. Found: C, 63.55; H, 6.01; N, 9.28; S, 10.93.

General Procedure for Tosylhydrazone Sodium Salt Preparation. The tosylhydrazone (ca. 7.0 mmol) was dissolved in 80 mL of dry THF while being magnetically stirred and cooled to 0 °C with an ice–salt bath. A 1.0-equiv portion of NaH/oil was slowly added, and the mixture was allowed to stir overnight at room temperature under nitrogen. The colored solid was collected by suction filtration, washed with dry THF, and dried in vacuo.

General Procedure for Diazo Compound Preparation. The tosylhydrazone sodium salt (ca. 0.10 g) and a magnetic stir bar were placed in a 25-mL, round-bottom flask. A short condenser allowed the diazo compound to distill from the flask directly into a receiving flask. The apparatus was evacuated to 0.01 Torr. The receiver was cooled with a dry ice–acetone bath, and the magnetically stirred salt was heated to 90–100 or 125–130 °C over a 30–40-min time period. The apparatus was vented with dry nitrogen, and the diazo compound was stored in pentane at −15 °C.

1-Phenyldiazoethane (2a): IR (heptane) 2050 s cm^{-1}; UV (pentane) 230, 285 nm; ^{1}H NMR (CDCl$_3$) δ 2.16 (s, 3 H), 6.0 (dd, 2 H), 7.05 (t, 1 H), 7.35 (m, 2 H).

1-(4-Bromophenyl)diazoethane (2b): IR (heptane) 2050 s cm^{-1}; UV (pentane) 232, 252, 284 nm; ^{1}H NMR (CDCl$_3$) δ 2.14 (s, 3 H), 6.75 (d, 2 H), 7.42 (d, 2 H).

1-(4-Methoxyphenyl)diazoethane (2c): IR (heptane) 2050 s cm^{-1}; UV (pentane) 224, 282 nm; ^{1}H NMR (CDCl$_3$) δ 2.15 (s, 3 H), 3.30 (s, 3 H), 6.85 (dd, 4 H).

1-[4-(Trifluoromethyl)phenyl]diazoethane (2d): IR (heptane) 2050 s cm^{-1}; UV (pentane) 236, 286 nm; ^{1}H NMR (CDCl$_3$) δ 2.18 (s, 3 H), 6.95 (d, 2 H), 7.55 (d, 2 H).

2,2,2-Trideuterio-1-phenyldiazoethane (2a-*d*$_3$): IR (heptane) 2050 s cm^{-1}; UV (pentane) 230, 282 nm; ^{1}H NMR (CDCl$_3$) δ 6.90 (dd, 2 H), 7.05 (t, 1 H), 7.32 (m, 2 H).

1-Phenyldiazopropane was prepared by methods A and B: IR, 2025 cm^{-1}; UV 232, 286 nm; ^{1}H NMR (CDCl$_3$) δ 1.25 (3 H, t), 2.55 (2 H), 6.9 (2 H, d), 7.05 (1 H, m), 7.25 (2 H, m); ^{13}C NMR (CDCl$_3$) δ 11.211, 17.142, 121.368, 123.243, 127.975, 128.542, 128.959, 131.870, 131.854.

General Information. Heptane and α,α,α-trifluorotoluene were purified by distillation over 4-Å molecular sieves. Benzene and pyridine were purified by distillation from sodium/benzophenone and barium oxide, respectively.

Laser Flash Photolysis. The laser flash photolysis apparatus has been described previously[34] and employed a Lumonics TE -860-4 excimer laser filled with a XeCl gas mixture in order to emit one or more laser pulses of 308 nm. All absorbance values were measured at 308 nm unless otherwise noted. An EG&G Princeton Applied Research Model 1460 optical multichannel analyzer (OMA) recorded all transient absorption spectra. In all OMA and kinetic measurement studies, the samples were placed in quartz laser cells, degassed with nitrogen for approximately 2 min, and irradiated at ambient temperature.

Extended Photolysis. General Information. A standard Rayonet photoreaction apparatus equipped with 300-nm source bulbs was utilized for the extended photolysis experiments. The samples were degassed with nitrogen for approximately 4 min and photolyzed using quartz tubes at 21–28 °C for several hours. The technique used to purify benzene was as previously mentioned. Pentane was purified by distillation over 4-Å molecular sieves.

Extended Photolysis of Diazo Compounds. Solutions containing the colored diazo compound in pentane or acetonitrile with a UV absorption of 0.7 at 308 nm or at a 0.01 M concentration were prepared. Approximately 1–2 mL of the mixture was placed in a quartz tube and photolyzed for 2.5 h in a Rayonet reactor. The clear solution was analyzed by GC–MS without concentration. GC peaks were identified by their MS and by comparison with authentic samples.

Acknowledgment. Support of this work by the National Science Foundation is gratefully acknowledged (Grant CHE 8814950).

Registry No. 2a, 22293-10-3; **2a**-*d*$_3$, 105930-66-3; **2b**, 66751-80-2; **2c**, 52506-27-1; **2d**, 137871-13-7; **3a**, 137871-14-8; **3b**, 137871-15-9; **3c**, 137871-16-0; **3d**, 137871-17-1; O$_2$, 7782-44-7; acetophenone, 98-86-2; acetophenone-*methyl-d*$_3$, 17537-31-4; 4-bromoacetophenone, 99-90-1; 4-methoxyacetophenone, 100-06-1; 4-(trifluoromethyl)acetophenone, 709-63-7; propiophenone, 93-55-0; *p*-tosylhydrazine, 1576-35-8; acetophenone tosylhydrazone, 4545-21-5; acetophenone-*methyl-d*$_3$ tosylhydrazone, 105930-65-2; 4-bromoacetophenone tosylhydrazone, 75230-51-2; 4-methoxyacetophenone tosylhydrazone, 32117-52-5; 4-(trifluoromethyl)acetophenone tosylhydrazone, 123077-46-3; propiophenone tosylhydrazone, 17336-66-2; 1-phenyldiazopropane, 52686-70-1; pyridine, 110-86-1; 1-(*p*-nitrophenyl)ethylidene, 137871-18-2.

Supplementary Material Available: GC–MS analyses of the extended photolyses (6 pages). Ordering information is given on any current masthead page.

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