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Ultrafast Study of *p*-Biphenylyldiazoethane. The Chemistry of the Diazo Excited State and the Relaxed Carbene

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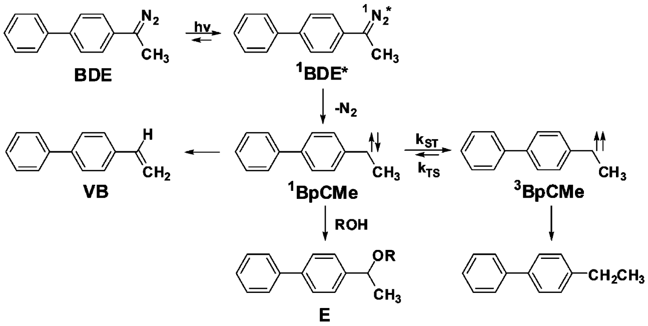
Abstract: Ultrafast photolysis of *p*-biphenylyldiazoethane (BDE) produces an excited state of the diazo compound in acetonitrile, cyclohexane, and methanol with $\lambda_{max} = 490$ nm and lifetimes of less than 300 fs. The decay of the diazo excited state correlates with the growth of singlet carbene absorption at 360 nm. The optical yields of diazo excited states produced by photolysis of *p*-biphenylyldiazomethane (BDM) and BDE are the same; however, the optical yield of singlet *p*-biphenylylmethylcarbene (^{1}BpCMe) is 30−40% less than that of *p*-biphenylylcarbene (^{1}BpCH) in all three solvents. The results are explained by rearrangement in the excited state (RIES) of BDE to form *p*-vinylbiphenyl (VB) in parallel with extrusion of nitrogen to form ^{1}BpCMe in reduced yield. This interpretation is consistent with product studies (ethanol-OD in cyclohexane) which indicate that there is an ∼25% yield of VB that is formed by a mechanism that bypasses the relaxed singlet carbene. The decay of ^{1}BpCMe is biexponential, and that of ^{1}BpCH is monoexponential. This is attributed either to efficient relaxation of vibrationally excited ^{1}BpCMe by 1,2 migration of hydrogen to form VB (minor) or to the increased number of low-frequency vibrational modes provided by the methyl group (major). A methyl group retards the rate of intersystem crossing (ISC), relative to a hydrogen atom, and ISC is more rapid in nonpolar solvents. Reaction of ^{1}BpCMe with methanol is much faster than spin equilibration. Both the lifetime of ^{1}BpCMe and ^{1}BpCH are the same in cyclohexane and in cyclohexane-d_{12}. This demonstrates that spin equilibration is faster than reaction of either carbene with the solvent. The lifetimes of ^{1}BpCMe and ^{1}BpCMe-d_3 are the same in cyclohexane. This indicates that 1,2 hydrogen migration of ^{1}BpCMe to form VB is slower than spin equilibration in cyclohexane. In acetonitrile, however, the lifetime of ^{1}BpCMe-d_3 is 1.5 times longer than that of ^{1}BpCMe in the same solvent. Thus, in acetonitrile, where ISC is slow, the rate of 1,2 hydrogen shift of ^{1}BpCMe is competitive with ISC. In cyclohexene, the lifetime of ^{1}BpCH is shortened relative to that in cyclohexane. The lifetime of ^{1}BpCMe is the same in cyclohexene and cyclohexane. The data indicate that spin relaxation is slow relative to reaction of ^{1}BpCH with neat alkene but that spin relaxation is fast for ^{1}BpCMe relative to reaction with neat cyclohexene.

I. Introduction

Fifty years of study of carbenes by chemical, physical, and computational methods have produced a sturdy structural and mechanistic framework to organize the data and understand this class of reactive intermediates.[1−3] As shown in Scheme 1, singlet carbenes can be generated by activation of a precursor (typically a diazirine or diazo compound). The nascent singlet carbene can either rearrange (as in a 1,2 hydrogen shift to form an alkene), react with an external trap (such as methanol to form an ether, E), or, in the case of aryl- and alkylarylcarbenes, relax to the lower energy triplet carbene, which undergoes distinctly different reactions than the singlet carbene.[1−3] This simple mechanistic scheme accommodates much of the known chemistry of carbenes, but exceptions are known. Alkylcarbenes undergo numerous rearrangements to form a spectrum of products.[3] Scheme 1 predicts that the same product distribution

Scheme 1



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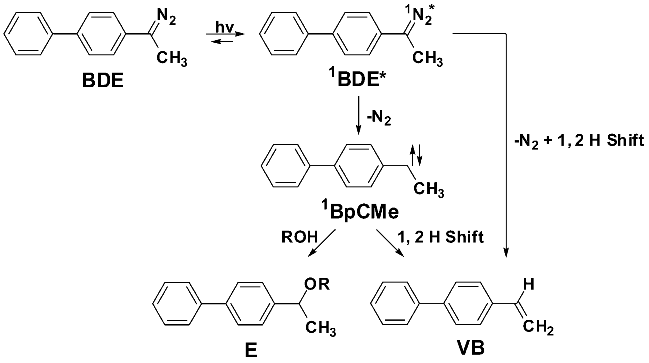
Scheme 2

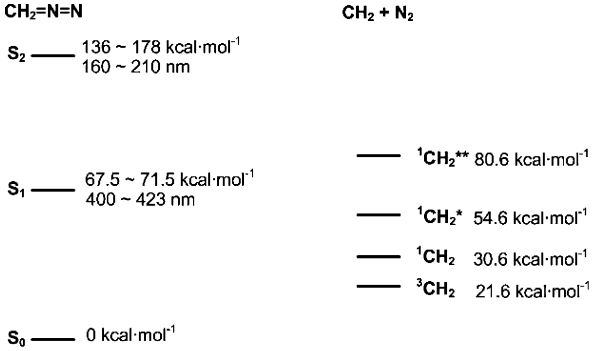


will be observed when the same precursor is activated in different ways (pyrolysis, photolysis, sensitized photolysis[4,5]) or when different precursors (diazirine, diazo compound, other non-nitrogenous precursors[6−8]) are activated in the same way. Often these predictions are not realized,[8] pointing to inadequacies in the simple mechanistic framework. Scheme 1 predicts that the ratio of intermolecular/intramolecular singlet carbene-derived products will be a linear function of the concentration of trapping agent. This test is also known to fail at times because, even in the presence of neat trapping agent, "too much" rearrangement product is produced.[6−8]

These observations can be explained by positing that there is a "non-trappable carbene" route to the formation of rearrangement products.[8] It has been proposed that rearrangements in the excited state (RIES) of the precursor can compete with carbene formation (Scheme 2).[7,9] In this mechanism, the excited state of the precursor partitions between the formation of trappable carbene *and* suffers a carbene-mimetic 1,2 hydrogen migration in concert with nitrogen extrusion. The latter process cannot be suppressed even by the presence of a neat trap, and too much intramolecular reaction product will form relative to intermolecular product (according to Scheme 1). Furthermore, the rearrangement in the excited state of the precursor will give a different mixture of rearrangement products than the relaxed singlet carbene and thereby explain the experimental results.

Modern theory has not provided support for the RIES mechanism to date and, in fact, argues against this mechanism for simple diazirines,[10−12] but it does predict that the S_1, electronically excited singlet state of diazomethane can fragment to form methylene in its lowest energy singlet state (major) and, in a minor process, decompose to form methylene in an electronically singlet excited state (carbene*, Schemes 3 and 4). One can explain the experimental observations by positing that electronically excited singlet carbenes are formed upon photolysis of precursor and can rearrange to form a different mixture of products than do relaxed singlet carbenes, and they may rearrange faster than they can be chemically intercepted.[4]

Scheme 3



The Eisenthal group[13] has demonstrated that photolysis of diphenyldiazomethane with 266 nm light does produce diphenylcarbene in an electronically excited triplet state, which was detected by fluorescence spectroscopy.[14] It was posited that the excited triplet carbene was formed by relaxation of singlet excited diphenylcarbene initially produced by mono-photonic excitation of the diazo precursor. The electronically excited singlet state of diphenylcarbene was not observed in this study.

The C═N double bond energy in diazomethane slightly exceeds 30.6 kcal/mol.[10] The S_1 state of diazomethane is 67.5−71.5 kcal/mol above the ground state.[12] Thus, when the S_1 state of diazomethane decomposes to form the lowest *electronic* carbene singlet state and molecular nitrogen, these fragments can be born with 37−41 kcal/mol of excess energy. Decomposition of the S_2 state of diazomethane produces singlet methylene with even more excess vibrational energy. Thus, one can explain the product study data by positing that vibrationally excited singlet carbenes (carbene$^{\#}$) are formed upon photolysis of precursor and rearrange to a unique mixture of products at a rate competitive with relaxation to the thermally equilibrated carbene (Scheme 5).[8]

Recently, we have reported the study of *p*-biphenylyldiazomethane (BDM) using ultrafast spectroscopic techniques.[15] Ultrafast spectroscopy provides a tool for the study of diazo excited states and of the formation and relaxation of electronically and vibrationally excited singlet carbenes. This technology seems well suited for the study of the "non-trappable carbene" route to reaction products, thereby motivating this study of the photochemistry of *p*-biphenylyldiazoethane (BDE) and the chemistry of *p*-biphenylylmethylcarbene (BpCMe). Evidence will be presented in favor of the RIES mechanism. The question of whether or not vibrationally excited carbene (BpCMe$^{\#}$) undergoes 1,2 hydrogen migration to form *p*-vinylbiphenyl (VB)

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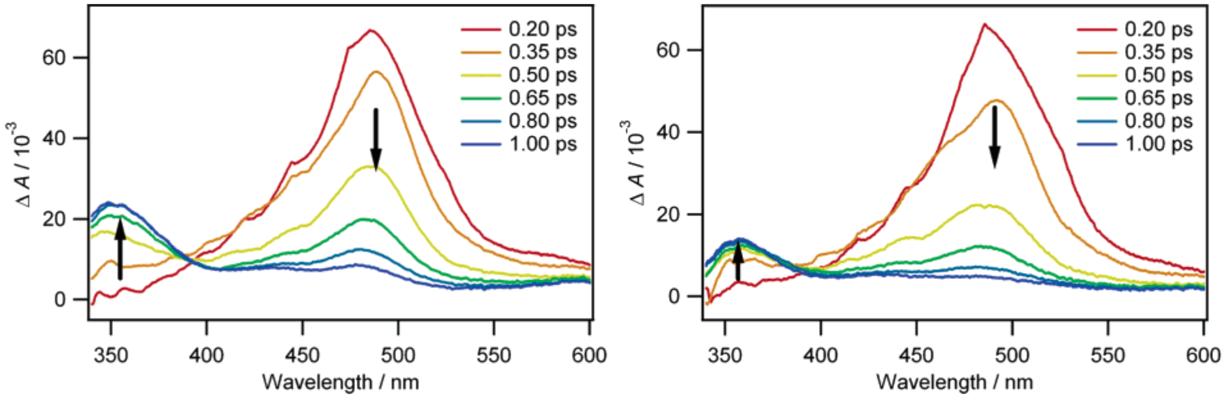
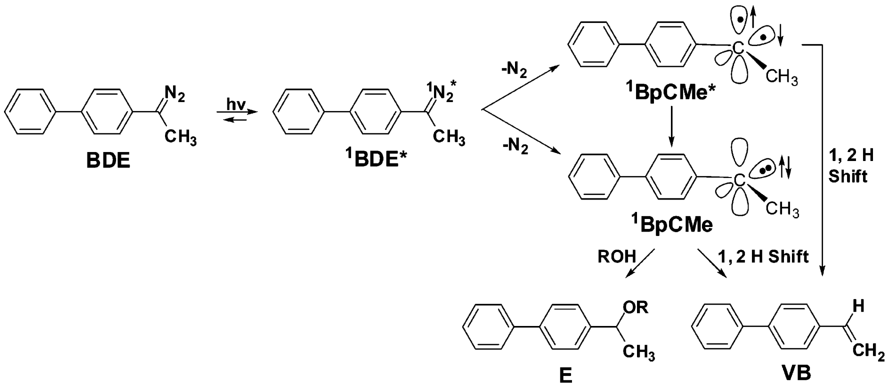
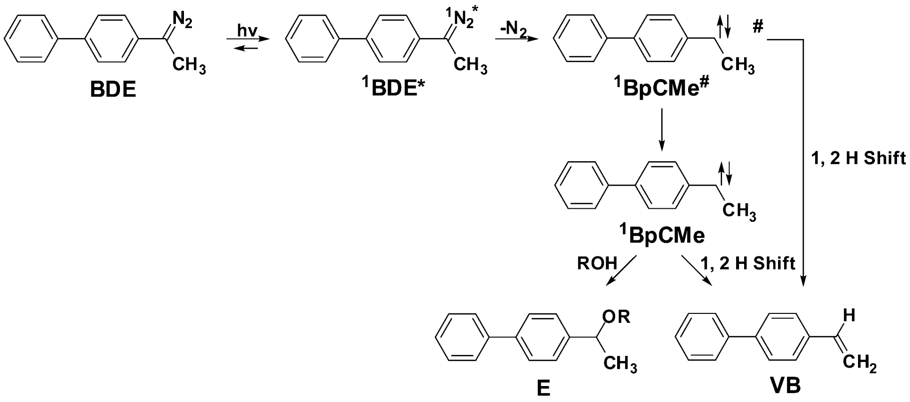


Figure 1. Transient spectra of *p*-biphenylyldiazomethane (left) and *p*-biphenylyldiazoethane (right) in acetonitrile. Spectra were generated by ultrafast LFP (311 nm) with a time window of 0.20−1.00 ps.

Scheme 4



Scheme 5



remains open. We have not detected an electronically excited singlet state of the carbene (^{1}BpCMe*) in this study.

II. Ultrafast Spectroscopic Results

Our prior ultrafast experiments with BDM[15] were conducted in acetonitrile, methanol, and cyclohexane. The same solvents will be used in the study of BDE in addition to cyclohexene to learn whether singlet carbenes react with alkene solvent at a rate faster or slower than intersystem crossing to their lower energy triplet spin isomer. Biphenyl compounds were used instead of phenyldiazomethanes because the extra phenyl group shifts the absorption spectrum of transient species to longer wavelengths and facilitates the detection of carbenes.[15]

II.1. Acetonitrile. Ultrafast photolysis (311 nm) of BDE in acetonitrile produces the transient spectra shown in Figure 1. As expected, the spectral data greatly resemble those obtained with BDM. The excited state of *p*-biphenylyldioazoethane (BDE*) has a broad transient spectrum centered at 480 nm, and it decays with a time constant of less than 300 fs. As the excited state of the diazo precursor decays, transient absorption grows at 360 nm, which can be attributed to the singlet carbene, ^{1}BpCMe. The absorption spectrum of ^{1}BpCMe is in excellent agreement with the predictions of time-dependent density functional theory (TD-DFT) calculations (Supporting Information (SI), Table S1)[16] and the experimental and predicted spectra of singlet *p*-biphenylylcarbene[15] (^{1}BpCH).

There are several important differences, however, in the BDM and BDE data. It is interesting to note that the optical yields of diazo excited states are about the same (BDM* versus BDE*)

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Table 1. Optical Yields of Singlet Carbenes ^{1}BpCH, ^{1}BpCMe, and ^{1}BpCMe-d_3 in Acetonitrile, Cyclohexane, and Methanol, Produced with Ultrafast LFP (311 nm)[a]

	solvent								
	acetonitrile			cyclohexane			methanol		
	BpCH	BpCMe	BpCMe-d_3	BpCH	BpCMe	BpCMe-d_3	BpCH	BpCMe	BpCMe-d_3
optical yield[b]	0.023	0.015	0.012	0.025	0.014	0.012	0.017	0.013	0.010

[a] All the samples were argon-degassed for 5 min prior to experiments. [b] Optical yields are the highest intensities of the singlet carbene bands, measured 1 ps after the laser pulse.

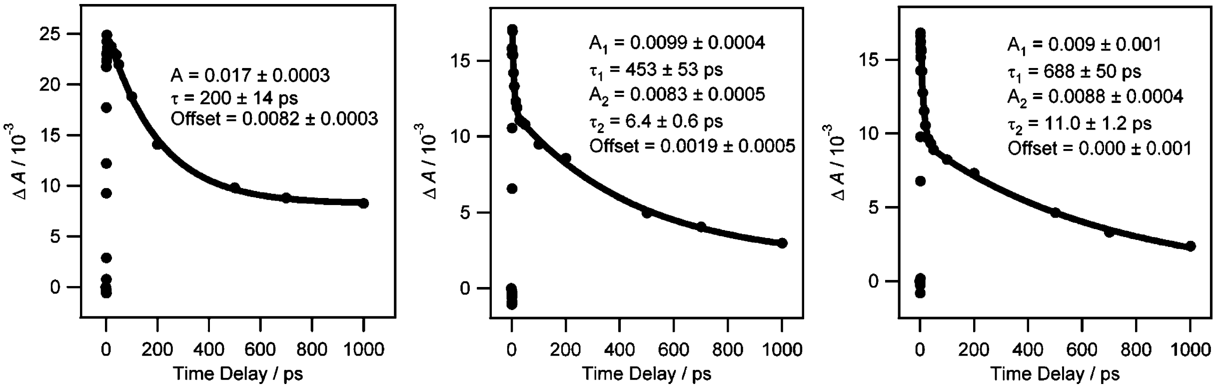

Figure 2. Ultrafast LFP (311 nm) of *p*-biphenylyldiazomethane (left), *p*-biphenylyldiazoethane (middle), and *p*-biphenylyldiazoethane-d_3 (right) in acetonitrile. The kinetic traces were probed at 360 nm and fitted to a mono- or biexponential function.

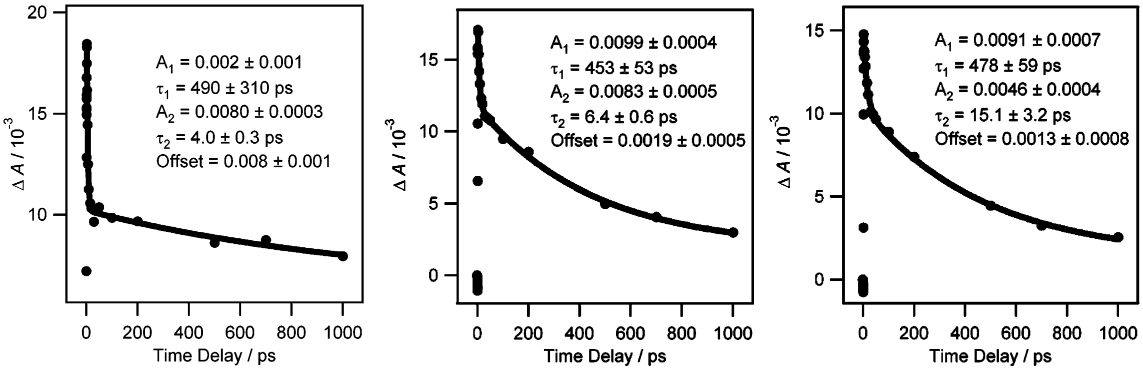

Figure 3. Ultrafast LFP of *p*-biphenylyldiazoethane in acetonitrile. The kinetic traces were excited at 271 (left), 311 (middle), and 328 nm (right), probed at 360 nm (all), and fitted to a biexponential function, $\Delta A = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + \text{Offset}$.

but that the yield of ^{1}BpCMe is ~40% less than that of ^{1}BpCH, as measured 1 ps after the laser pulse (Figure 1, Table 1). These experiments were performed on the same day, using the same optical alignment of the spectrometer, and using solutions of equal diazo absorbance at the wavelength of excitation (311 nm).

There is also a significant difference in the time dependence of the transient spectra of ^{1}BpCH and ^{1}BpCMe. As shown in Figure 2, ^{1}BpCH decays monoexponentially when excited at 311 nm, but ^{1}BpCMe and its deuterated isotopomer ^{1}BpCMe-d_3 both decay biexponentially when pumped at the same wavelength. Furthermore, the ratio of fast to slow decay of ^{1}BpCMe is wavelength dependent (Figure 3). The ratio of the fast to the slow component of alkylarylcarbene disappearance increases as the excitation wavelength decreases (0.5 at 328 nm, 0.8 at 311 nm, and 4.0 at 271 nm).[17]

The slow component of decay of ^{1}BpCMe has a longer lifetime in acetonitrile than (the single lifetime) of ^{1}BpCH in this solvent. But in the case of ^{1}BpCH, the transient spectrum of the carbene evolves into that of the carbene−nitrile ylide, whereas the corresponding ylide is formed in very low yield in the case of ^{1}BpCMe. There is a weak band observed at 420 nm in the case of BDM and BDE (not shown). As discussed previously, this band is attributed to secondary photolysis of a reaction product, which transpires during signal averaging.[15] The data obtained by ultrafast photolysis of BDE and BDE-d_3 differ somewhat. There is a kinetic isotope effect (KIE) of 1.5 on the slow component of the decay of ^{1}BpCMe-d_3 in acetonitrile (Figure 2 and Table 2).

II.2. Cyclohexane. Ultrafast photolysis (328 nm) of BDE in cyclohexane gives results reminiscent of the acetonitrile data. The diazo excited state is observed at 480 nm; it is formed instantaneously and decays with a time constant of less than 300 fs. The decay of the diazo excited state is accompanied by the growth of the singlet carbene absorption at 360 nm (SI, Figure S1). The optical yield of ^{1}BpCMe is 40% less than that of ^{1}BpCH. Although ^{1}BpCH decays in a monoexponential process in cyclohexane, the disappearance of ^{1}BpCMe is

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(17) The short component of ^{1}BpCMe or ^{1}BpCMe-d_3 is attributed to the vibrational cooling of the carbene. The long component is assigned to the intrinsic lifetime of ^{1}BpCMe or ^{1}BpCMe-d_3. If not specified, the lifetime of ^{1}BpCMe or ^{1}BpCMe-d_3 refers to the long component.

Table 2. Lifetimes and Normalized Amplitudes ($\lambda_{ex} = 311$ nm) of Singlet Carbenes ^{1}BpCH, ^{1}BpCMe, and ^{1}BpCMe-d_3 in Acetonitrile, Cyclohexane, and Methanol[a]

solvent	carbene	A_1	τ_1/ps	A_2	τ_2/ps	A_2/A_1
acetonitrile	^{1}BpCH	1.00	200 ± 14			
	^{1}BpCMe	0.54	453 ± 53	0.46	6.4 ± 0.6	0.8
	^{1}BpCMe-d_3	0.51	688 ± 50	0.49	11.0 ± 1.2	1.0
cyclohexane	^{1}BpCH	1.00	77 ± 5			
	^{1}BpCMe	0.31	189 ± 20	0.69	6.4 ± 1.3	2.2
	^{1}BpCMe-d_3	0.33	174 ± 29	0.67	5.7 ± 1.0	2.0
methanol	^{1}BpCH	1.00	7.9 ± 1.3			
	^{1}BpCMe	1.00	10.8 ± 1.1			
	^{1}BpCMe-d_3	1.00	13.8 ± 2.3			

[a] All the samples were argon-degassed for 5 min prior to experiments. All the kinetic traces were probed at 360 nm and fitted in either monoexponential (A_2 and τ_2 are not applicable) or biexponential equations.

biexponential (SI, Figure S2). The time constant of the fast component is 6.4 ps, and the time constant of the slow component, 189 ps, is longer than that of the decay of ^{1}BpCH (77 ps) in cyclohexane.

Isotopic substitution of the methyl group has no discernible influence on the data. ^{1}BpCMe-d_3 decays biexponentially with the same time constant of its slow component as ^{1}BpCMe. The amplitude ratio of fast to slow decay is the same for ^{1}BpCMe and ^{1}BpCMe-d_3 as well.

The fast and slow decay lifetimes of ^{1}BpCMe are the same in cyclohexane and in cyclohexane-d_{12} within experimental error (SI, Figure S3). Similarly, ^{1}BpCH decays with the same rate in both cyclohexane and cyclohexane-d_{12} (SI, Figure S4).

II.3. Methanol. The results obtained in methanol (Figure 4), an excellent trap of singlet carbenes, differ substantially from those obtained in cyclohexane and acetonitrile. The diazo excited-state lifetime is still less than 300 fs, but the singlet carbene ($\lambda_{max} = 360$ nm) lifetime is reduced to only 10.8 ps in the reactive solvent. As the ^{1}BpCMe signal decays, a broad new band, centered at 445 nm, grows (10.8 ps) and decays (7.4 ps) (Figure 5). An isosbestic point is also observed at 385 nm.

The carrier of the 445 nm band is assigned to *p*-biphenylylmethyl cation C (Scheme 6) on the basis of the precedents established by Kirmse and Steenken,[18] Chateauneuf,[19] Dix and Goodman,[20] and Peon and Kohler and co-workers.[21] The cation is formed by abstraction of a proton of methanol by the singlet carbene. To our knowledge, the transient spectrum of cation C has not been reported previously. However, benzyl cation absorbs at 363 nm;[22] thus, absorption of quinoidal cation C at 445 nm does not seem unreasonable. Furthermore, TD-DFT calculations[16] of the cation predict a vertical transition at 428 nm ($f = 0.7229$), in good agreement with experiment (SI, Table S2). Thus, the assignment of this transient absorption band to cation C seems secure. For the sake of comparison, a TD-DFT calculation of parent benzyl cation is also included in the Supporting Information (SI, Table S3, $\lambda_{max} = 264$ nm).

The ultrafast results obtained in methanol are very similar to those reported for diphenylcarbene in the same solvent.[21] The data in methanol-OD do not show a large isotope effect. Peon et al.[21] posited that the results indicated that the solvent reorganization is the rate-determining step in the protonation process rather than the formation of a C−H bond. Since the reaction is exothermic, it will have an early, asymmetric transition state and consequently a small kinetic isotope effect.

Kohler and co-workers[21] concluded that proton transfer is a minor (30%) component of the reaction of singlet diphenylcarbene with methanol. The predominant reaction pathway is actually direct insertion into the OH bond, but this pathway does not lead to a UV−vis-active reaction product as does proton transfer. Because the extinction coefficient of benzhydryl cation (which is persistent under certain conditions) was known, it was possible for the Kohler group to quantitate the yield of this ion from singlet diphenylcarbene. *p*-Biphenylylmethyl cation is not a persistent species; as a result, its extinction coefficient at the absorption maximum is not known, and we cannot deduce its yield from ^{1}BpCMe in methanol using absorption spectroscopy. Following the Kohler group,[21] we will assume that cation formation is a minor pathway of the reaction of ^{1}BpCMe with methanol.

II.4. Cyclohexene. Alkenes react rapidly with carbenes,[1] and study of the photochemistry of aryl diazo compounds in neat alkene solvents played a large role in the development of mechanistic carbene chemistry.[3] Hence, we have studied the photochemistry of BDM and BDE in neat cyclohexene. Ultrafast photolysis (315 nm) of BDM and BDE in neat cyclohexene produces the transient spectra of ^{1}BpCH and ^{1}BpCMe, respectively (SI, Figures S5 and S6). Similar to the data in acetonitrile, the carbene formation efficiency is higher for BDM than for BDE in cyclohexene. The lifetime of ^{1}BpCH is shortened to 25 ps in cyclohexene, as compared to 77 ps in cyclohexane (Figure 6a). However, the lifetime of ^{1}BpCMe is 170 ± 25 ps in cyclohexene, which is the same as that determined in cyclohexane 189 ± 20 ps (Figure 6b).

III. Discussion

The first striking observation to explain is the ∼40% lower optical yield of singlet carbene realized upon replacing a hydrogen atom (^{1}BpCH) with a methyl group (^{1}BpCMe), as measured 1 ps after the laser pulse. Part of the 40% difference is due to the fact that ^{1}BpCMe has a fast decay component ($\tau = 6$ ps) and ^{1}BpCH does not. The optical yield of ^{1}BpCMe is depressed relative to that of ^{1}BpCH for this reason. Using a standard kinetic analysis,[40] we estimate that the yield of ^{1}BpCMe is depressed by 10% for this reason.

One can posit that a methyl group will depress the extinction coefficient of the carbene. This hypothesis is not supported by TD-DFT calculations (SI, Tables S1 and S4). The calculations support the intuitive expectation that the two carbenes have similar molar absorptivities.

Alternatively, one can posit that the replacement of hydrogen by methyl increases the rate and quantum yield of a process which competes against the formation of singlet carbene. The competing process is not emission, as neither diazo compound fluoresces to a measurable extent. Enhanced internal conversion of the excited state to the diazo ground state by methyl substitution could account for the experimental observation. To test this possibility, solutions of BDM and BDE were prepared in methanol. The initial optical densities of the two solutions were the same. The solutions were then exposed to the same number of pulses from a XeCl excimer laser (308 nm). As

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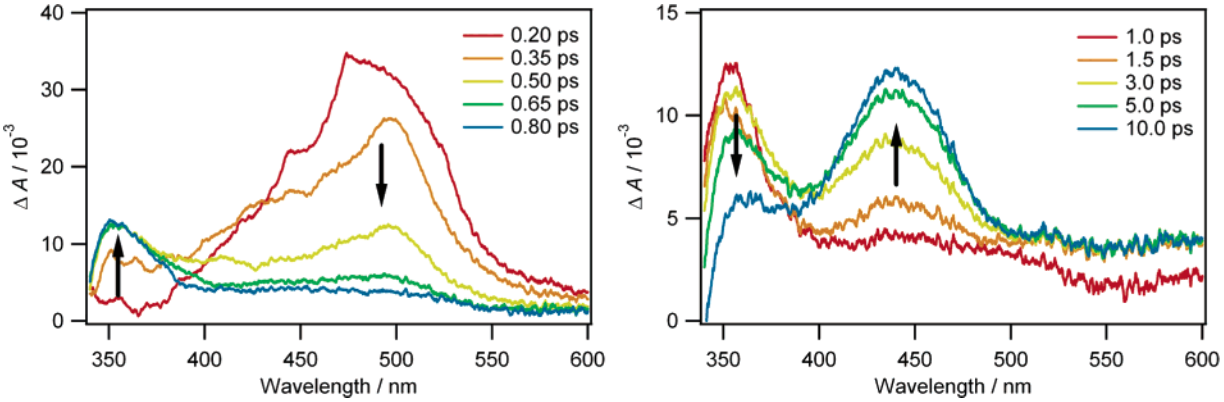
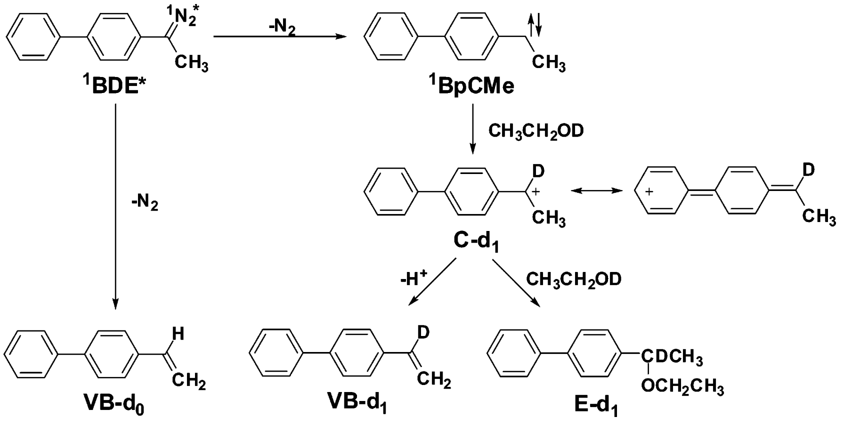


Figure 4. Transient spectra of *p*-biphenylyldiazoethane in methanol. Spectra were generated by ultrafast LFP (311 nm) with time windows of 0.20−0.80 (left) and 1−10 ps (right).

Scheme 6



shown in Figure 7, the two diazo compounds are consumed at the same rate upon exposure to 308 nm light. The quantum yields for decomposition of BDM and BDE are the same; thus, there is no evidence to suggest that internal conversion of the diazo excited state to the ground state is more efficient in BDE than in BDM.

We propose that the lower yield of carbene, per laser pulse, for ^{1}BpCMe relative to ^{1}BpCH is due to 1,2 migration of hydrogen in the excited state of BDE, as shown in Scheme 2.[7−9] This process is possible in excited BDE, but it is not available in excited BDM, hence the greater yield of carbene in the latter precursor.

To test this possibility, we measured the ratio of “untrappable carbene” product (*p*-vinylbiphenyl, VB) to relaxed carbene product (E) as a function of ethanol-OD concentration in cyclohexane. If Scheme 1 were operative, then a plot of E/VB versus [ethanol-OD] would be linear. As shown in Figure 8, however, the plot reaches a limiting value at ∼0.3 M ethanol-OD when BDE in cyclohexane/ethanol-OD is exposed to monochromatic 308 nm light. These data demonstrate that there is a non-trappable carbene route to form VB.

One can argue that photolysis of BDE in ethanol can lead to the formation of cation C, and this in turn could produce VB. In other words, the cation might be the source of the “untrappable” carbene product. As shown in Scheme 6, however, the reaction of carbene with ethanol-OD will produce cation C-d_1 and VB-d_1. Both ^{1}H NMR and GC-MS analysis of the VB produced by photolysis of the precursor reveal that the yield of VB-d_1, the product of the cationic route, depends on the concentration of ethanol-OD, increasing from 0% to 15% of the yield of all VB isotopomers with increasing ethanol-OD concentration under our experimental conditions. Even in neat ethanol-OD, the yield of VB-d_1 is only 15% of the yield of all VB isotopomers. Thus, the cation is only a minor source of all isotopomers of VB. Control experiments demonstrate that photolysis of VB in cylohexane with 0.5 M ethanol-OD does not lead to incorporation of deuterium and that both VB and ether E are stable to the photolysis conditions used in this experiment. Photolysis with times substantially longer than those used to generate Figure 8 results in the conversion of VB to ether E.

Figure 8 depicts a plot of the ratio of [ether E-d_1]/[VB-d_0] versus the concentration of ethanol-OD in cyclohexane, produced by 308 nm photolysis of BDE. This plot is corrected for the formation of alkene formed via cation C. The limiting value of this plot is 3.0. Thus, we conclude that, with 308 nm light, ∼25% of the photochemistry of BDE proceeds to form VB by rearrangement in the exited state of the diazo precursor, in excellent agreement with the spectroscopic data after correcting for the effect of the fast decay component of ^{1}BpCMe on the transient absorbance.

The second remarkable observation is that the decay of ^{1}BpCMe is biexponential, whereas the decay of ^{1}BpCH can be described by a single-exponential function. The fast component of the disappearance of ^{1}BpCMe is on a time scale typical of vibrational cooling. Vibrational cooling is obvious when a spectroscopic band of a species formed on the femtosecond time

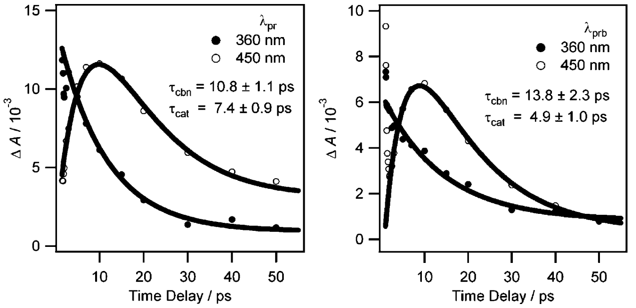


Figure 5. Decay of singlet carbenes ^{1}BpCMe (left) and ^{1}BpCMe-d_3 (right) at 360 nm (solid circles) and the growth and decay of transient absorption of *p*-phenylbenzyl methyl cation at 450 nm (open circles), probed in methanol. The time constants τ_{cbn} (lifetime of ^{1}BpCMe) and τ_{cat} (lifetime of *p*-phenylbenzyl methyl cation) were obtained by globally fitting the decay at 360 nm into the function $\Delta A = A_1 \exp(-t/\tau_{cbn}) + A_2$ and the growth and decay at 450 nm into the function $\Delta A = A_3\{\tau_{cat}/(\tau_{cat} - \tau_{cbn})\}\{\exp(-t/\tau_{cat}) - \exp(-t/\tau_{cbn})\} + A_4$.

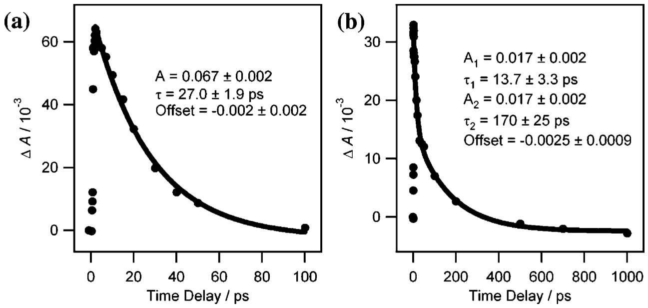


Figure 6. Ultrafast LFP (315 nm) of (a) *p*-biphenylyldiazomethane and (b) *p*-biphenylyldiazoethane in cyclohexene. The kinetic traces were probed at 350 nm and fitted to a mono- or biexponential function.

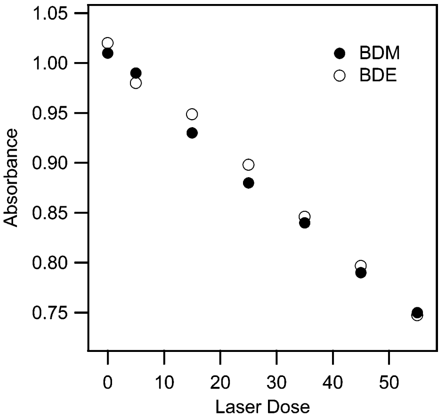


Figure 7. Decrease in absorbance of solutions of BDM and BDE in methanol as a function of exposure to 308 nm light from a XeCl excimer laser.

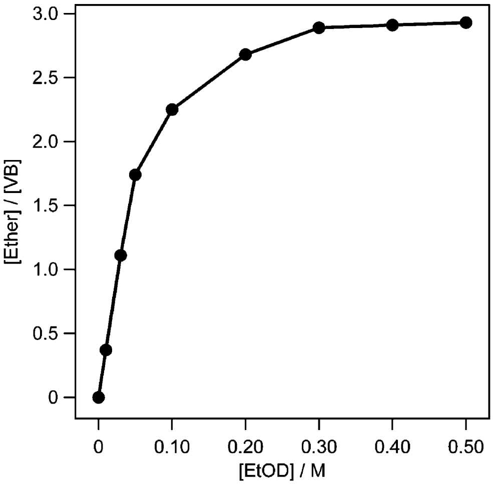


Figure 8. Plot of the ratio of the yield between ether E and *p*-vinylbiphenyl, formed by 1,2 H shift upon photolyzing BDE in cyclohexane, as a function of EtOD concentration. The contribution of *p*-vinylbiphenyl formed by the deprotonation mechanism has been eliminated.

scale undergoes reshaping in ∼10−20 ps.[23] The absence of spectral reshaping, however, does not indicate the absence of vibrational cooling. We posit that both ^{1}BpCH and ^{1}BpCMe are formed with excess vibrational energy (see Schemes 3 and 4) but that this does not lead to dramatic spectral reshaping. Replacement of the hydrogen atom of ^{1}BpCH with a methyl group clearly leads to vibrational cooling with increased efficiency.[24] The methyl group provides an increased density of low-frequency vibrational modes, relative to that found with a hydrogen atom.[25] Alternatively, the vibrationally excited methyl-substituted singlet carbene may be isomerizing to VB in 6 ps, as shown in Scheme 5. If this were the case, however, then the yield of relaxed ^{1}BpCMe (and ether E-d_1 in chemical trapping studies with 308 nm light) would be very small, ∼25% in cyclohexane.[26] This is not consistent with the data of Figure 8, indicating that there is a ∼75% yield of relaxed and trappable carbene. Thus, we conclude that, while there may be some isomerization of “hot” carbene to VB, this is not the major relaxation pathway of the “hot” carbene produced by 308 nm radiation.

It is also possible that ^{1}BpCMe$^{\#}$ undergoes intersystem crossing to ^{3}BpCMe$^{\#}$ much more rapidly than does ^{1}BpCMe. Sadly, we can provide no evidence for this hypothesis, because ^{3}BpCMe$^{\#}$ was not detected in this experiments. In a separate study,[27] we are able to detect the interconversion of singlet fluorenylidene to its triplet (λ_{max} = 470 nm). In this case, it is clear that there is no prompt formation of the triplet carbene, which casts doubt on this proposal.[27]

Moss and Sheridan and co-workers[28] studied a singlet carbene (by matrix IR spectroscopy) in which different products were formed by an RIES mechanism than from an excited carbene. In the present study, unfortunately, RIES mechanisms and mechanisms involving electronically or vibrationally excited carbenes all produce the same compound VB. Thus, the nature

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(24) An alternative explanation for the fast component of ^{1}BpCMe biexponential decay at 360 nm could be the vibrational cooling of the ground-state BDE. This requires that the excited state of BDE regenerates its ground state with excess vibrational energy via an ultrafast internal conversion. As shown in Figure S8, the red edge of the BDE ground state UV spectrum is 360 nm; however, in the case of BDM, the red edge of its UV spectrum is blue-shifted to 345 nm. This could account for the absence of biexponential decay feature in the decay of ^{1}BpCH at 360 nm. However, usually the quantum yield of diazo compounds is close to unity. We conclude that the explanation of hot ground-state BDE might account for the data to some extent, but it is not the main reason.

(25) (a) Ito, M. *J. Phys. Chem.* **1987**, *91*, 517. (b) Assmann, J.; von Benten, R.; Charvat, A.; Abel, B. *J. Phys. Chem. A* **2003**, *107*, 1904.

(26) This value is deduced assuming that the 50% of the transient absorption with a 6 ps decay component and the missing 20% of the ^{1}BpCMe signal (relative to ^{1}BpCH after correction) are both due to formation of VB.

(27) Wang, J.; Kubicki, J.; Platz, M. S., unpublished results.

(28) Moss, R. A.; Tian, J.; Sauers, R. R.; Sheridan, R. S.; Bhakta, A.; Zuev, P. S. *Org. Lett.* **2005**, *7*, 4645.

of the products cannot be used to determine the relative yields of these different pathways.

III.1. Solvent and Structural Effects on Intersystem Crossing Rates. Eisenthal and co-workers[13] have studied the rates of intersystem crossing (ISC) of diphenylcarbene (DPC) as a function of solvent. The lifetime of singlet DPC in acetonitrile is 310 ps, and this lifetime shortens to 95 ps in isooctane. A plot of the log of the first-order rate constant of ISC of ^{1}DPC versus the Dimroth $E_T(30)$ parameter[29] was linear. Normally, one expects that the rate of ISC will increase as the energy separation between the singlet and triplet states decreases.[30] Eisenthal et al. proposed that polar solvents preferentially stabilize singlet relative to triplet arylcarbenes, a postulate to later receive experimental[31] and computational support.[32] They then advanced density-of-states arguments to explain why ISC rates of ^{1}DPC are largest in nonpolar solvents, whereas the singlet−triplet energy separation is largest in solution.

Our results are consistent with the DPC data. Both ^{1}BpCH and ^{1}BpCMe have longer lifetimes in acetonitrile than in cyclohexane. We have also studied the influence of propionitrile in cyclohexane on the ISC rates of ^{1}BpCH (note that acetonitrile and cyclohexane are not miscible). The lifetimes of ^{1}BpCH in cyclohexane containing 0, 0.5, 1.0, and 2.0 M propionitrile are all the same (62−72 ps) within experimental error (SI, Figure S7). Thus, this is a bulk solvent effect on the ISC rate and not an effect due to complexation of a small amount of nitrile with ^{1}BpCH.

In both cyclohexane and acetonitrile, the lifetimes of ^{1}BpCMe are longer than those of ^{1}BpCH in the same solvent. Theory predicts that methylcarbene[33] has a triplet ground state but dimethylcarbene[34] has a singlet ground state. Methyl substitution for hydrogen stabilizes singlet carbenes relative to triplet carbenes. Thus, one can easily explain our ISC rate data, in a manner consistent with Eisenthal et al.,[13,14] by positing that the singlet−triplet energy gap of ^{1}BpCH is greater than that of ^{1}BpCMe.

III.2. Spin Relaxation versus Intermolecular Chemical Reactions of ^{1}BpCH and ^{1}BpCMe. Mechanistic carbene chemists[1−3] have long wondered about the timing of arylcarbene ISC relative to the rate of intermolecular reactions. It is clear from this study that ^{1}BpCH has the same lifetime in cyclohexane and in cyclohexane-d_{12}. This is true as well for ^{1}BpCMe. Singlet carbenes will react with cyclohexane by insertion into a C−H bond. A typical kinetic isotope effect (KIE) on this reaction is ∼2.[35,36] As no solvent KIE on the lifetimes of ^{1}BpCH and ^{1}BpCMe is observed in cyclohexane, we conclude that these singlet carbenes relax faster to their lower energy triplet states than by reaction with this solvent. We conclude, as before,[35,36] that it is the equilibrium mixture of singlet and triplet carbene which reacts with the cyclohexane solvent. The lifetimes of spin-equilibrated phenyl- and naphthylcarbenes[35] are tens of nanoseconds in cyclohexane, and the equilibrium mixture decays primarily by reactions of the singlet carbenes.

Cyclohexane and cyclohexene are both nonpolar, and for that reason the rates of ISC of singlet arylcarbenes should be the same in these two solvents. The lifetime of ^{1}BpCH in neat cyclohexene is 25 ps, as opposed to 77 ps in cyclohexane. This indicates that ^{1}BpCH reacts with solvent alkene to form products faster than it relaxes to form the lower energy triplet carbene. On the other hand, the lifetime of ^{1}BpCMe is the same in cyclohexane and in cyclohexene. This indicates that the alkylarylcarbene achieves spin equilibration in cyclohexene; ISC is fast relative to bimolecular reaction of the alkylarylcarbene with the alkene solvent. Unsurprisingly, ^{1}BpCMe is less reactive than ^{1}BpCH. This must be a consequence of both steric and electronic factors, as methyl differentially stabilizes singlet carbenes relative to triplet carbenes, as compared to hydrogen.[33,34]

Methanol is a polar solvent, and for that reason one predicts that ^{1}BpCMe and ^{1}BpCH in methanol will have ISC rates slower than those found in cyclohexane and comparable to those found in acetonitrile. The lifetimes of both ^{1}BpCMe and ^{1}BpCH are quite short in methanol (τ < 10 ps) and are much shorter than the lifetimes measured in cyclohexane or acetonitrile. Thus, it is clear that ^{1}BpCMe and ^{1}BpCH react with methanol before they relax to their lower energy triplet states.

^{1}BpCMe forms very little ylide in acetonitrile; thus, reaction of ^{1}BpCMe with this solvent is only a minor contributor to the consumption of this carbene in acetonitrile. In the next section, we will conclude that intramolecular 1,2 hydrogen shift is an important reaction pathway, consuming the alkylarylcarbene in acetonitrile. It is a spin-equilibrated alkylarylcarbene mixture which reacts with this solvent to form ylide in low yield.

The situation of ^{1}BpCH in acetonitrile is less clear. The lifetime of ^{1}BpCH in acetonitrile is 200 ps, and nitrile ylide is clearly present 1 ns after the laser pulse. It is difficult to resolve the growth of the ylide precisely because of significant spectral overlap with ^{1}BpCH. It is possible, perhaps even likely, that ^{1}BpCH decays in acetonitrile by both ylide formation and relaxation to the lower energy triplet state of the carbene. Thus, the nitrile ylide may well have a biphasic growth: a picosecond growth due to capture of nascent ^{1}BpCH and a nanosecond growth due to reaction of the equilibrium mixture of singlet and triplet carbene with acetonitrile.

III.3. Spin Relaxation versus Intramolecular Chemical Reactions of ^{1}BpCH and ^{1}BpCMe. It is interesting to note that the lifetime of ^{1}BpCMe-d_3 is the same as that of ^{1}BpCMe in cyclohexane, a solvent in which ISC is relatively rapid compared to that in acetonitrile. It is also longer than that of ^{1}BpCH in the same solvent. If there were very rapid 1,2 migration of hydrogen in ^{1}BpCMe, then ^{1}BpCMe would have a shorter lifetime than ^{1}BpCH, which cannot undergo this reaction. Since this is not the case and there is no KIE, we conclude that ISC of ^{1}BpCMe proceeds more rapidly in cyclohexane than isomerization to VB.

In acetonitrile, ISC is slower than in cyclohexane. This provides the opportunity for another reaction that consumes the

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singlet alkylarylcarbene, such as isomerization by 1,2 hydrogen migration, to become competitive with spin relaxation. The importance of this reaction is indicated by the KIE of 1.5 observed with ^{1}BpCMe-d_3 in cyclohexane. Sugiyama et al.[37] have reported that polar solvents increase the rate of isomerization of singlet methylphenylcarbene to styrene. Given that polar solvents both increase the rate of 1,2 hydrogen shift and decrease the rate of ISC, we propose that rearrangement of ^{1}BpCMe is at least competitive with ISC in acetonitrile and possibly even faster. Furthermore, this explains the low yield of nitrile ylide produced from ^{1}BpCMe, relative to that produced from ^{1}BpCH. In acetonitrile, ^{1}BpCH achieves spin equilibrium and reacts with solvent to form ylide. The singlet methylcarbene analogue isomerizes in competition with relaxation to the triplet, hence the low efficiency of its reaction with solvent and corresponding low yield of ylide.

IV. Experimental Section

IV.1. Calculations. DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs[38] at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G* level of theory, with single-point energies obtained at the B3LYP/6-311+G**//B3LYP/6-31G* level of theory. Vibrational frequency analyses at the B3LYP/6-31G* level were utilized to verify that stationary points obtained corresponded to energy minima. The electronic spectra were computed using time-dependent density functional theory in Gaussian 03 at the B3LYP/6-311+G** level, and 20 allowed electronic transitions were calculated.

IV.2. Ultrafast Spectroscopy. Ultrafast UV−vis broadband absorption measurements were performed using the home-built spectrometer described previously.[39] Samples were prepared in 50 mL of solvent with absorption 0.70−0.80 at the excitation wavelength with 1.0 mm optical length. All the sample solutions were purged with argon prior to the experiments for 5 min and during the experiments.

IV.3. Materials. All materials and solvents were purchased from Aldrich. The solvents for ultrafast studies were spectrophotometric grade from Aldrich and used as received.

***p*-Biphenylyldiazoethane (BDE).** In a 25 mL, single-necked, round-bottomed flask was placed 1.82 g of 4-acetylbiphenyl tosylhydrazone (5.0 mmol, which is prepared by refluxing 4-acetylbiphenyl (1.96 g, 10 mmol) with *p*-toluenesulfonylhydrazide (1.86 g, 10 mmol) in 50 mL of ethanol). A 1.0 M solution (10 mL) of sodium methoxide in methanol (10.0 mmol) was added via syringe, and the mixture was swirled until dissolution was complete. The methanol was then removed by a rotary evaporator. The solid tosylhydrazone salt was broken up with a spatula and transferred to a sublimator. The sublimator was immersed in an oil bath, and the temperature was raised to 140 °C. At this temperature, red *p*-biphenylyldiazoethane was collected on the coldfinger. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.60 (m, 4 H), 7.43 (t, $J = 6.3$ Hz, 2 H), 7.32 (t, $J = 7.4$ Hz, 1 H), 6.98 (m, 2 H), 2.20 (s, 3 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 136.1, 131.4, 128.8, 127.6, 127.2, 127.0, 126.7, 121.6, 10.3. FT-IR (neat): 2031 cm^{-1}. GC-MS: the molecular ion peak of the thermal rearrangement product VB was detected with $m/z = 180$.

***p*-Acetylbiphenyl-α,α,α-*d*$_3$.** 4-Acetylbiphenyl (1.96 g, 10.0 mmol) was dissolved in a mixture of 10 mL of anhydrous THF and 10 mL of D_2O. A catalytic amount of sodium methoxide was added, and the solution was stirred overnight. The solution was extracted by 10 mL of ether three times. The organic layer was dried by sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give 4-acetylbiphenyl-α,α,α-d_3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.04 (d, $J = 9.0$ Hz, 2 H), 7.69 (d, $J = 8.5$ Hz, 2 H), 7.63 (t, $J = 7.0$ Hz, 2 H), 7.48 (t, $J = 7.5$ Hz, 2 H), 7.41 (t, $J = 7.5$ Hz, 1 H), 2.61 (t, $J = 2.0$ Hz, 0.15 H, 95% D atom). GC-MS: the purity of the d_3 isotopomer is 97%, calculated from the relative intensities between m/z 198 and 199.

***p*-Toluenesulfonylhydrazide-*N,N,N*-*d*$_3$.** *p*-Toluenesulfonylhydrazide (1.86 g, 10.0 mmol) was dissolved in a mixture of 10 mL of anhydrous THF and 10 mL of D_2O. The solution was stirred overnight and then extracted by 10 mL of ether three times. The organic layer was dried by sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give *p*-toluenesulfonylhydrazide-*N*,*N*,*N*-d_3. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.80 (m, 2 H), 7.36 (m, 2 H), 5.52 (s, 0.30 H, 85% D atom), 3.74 (t, $J = 6.5$ Hz, 0.17 H, 83% D atom), 2.46 (s, 3 H).

***p*-Biphenylyldiazoethane-*d*$_3$ (BDE-*d*$_3$).** *p*-Acetylbiphenyl-α,α,α-d_3 tosylhydrazone (1.82 g, 5.0 mmol, which is made by refluxing *p*-acetylbiphenyl-α,α,α-d_3 (1.96 g, 10 mmol) with *p*-toluenesulfonylhydrazide-*N*,*N*,*N*-d_3 (1.86 g, 10 mmol)) was dissolved in 50 mL of anhydrous THF. Sodium (0.23 g, 10.0 mmol) was dissolved in 10 mL of methanol-*O*-*d*. This sodium methoxide solution was added via syringe, and the mixture solution was stirred for 5 h. The methanol and THF were then removed by a rotary evaporator. The solid tosylhydrazone salt was broken up with a spatula and transferred to a sublimator. The sublimator was immersed in an oil bath, and the temperature was raised to 140 °C. At this temperature, red *p*-biphenylyldiazoethane-d_3 was collected on the coldfinger. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57−7.60 (m, 4 H), 7.43 (t, $J = 6.3$ Hz, 2 H), 7.32 (t, $J = 7.4$ Hz, 1 H), 6.98 (m, 2 H), 2.17 (s, 0.3 H, 90% D atom). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.6, 136.1, 131.4, 128.8, 127.6, 127.2, 127.0, 126.7, 121.6, 9.7 (septet, $J = 10.0$ Hz). FT-IR (neat): 2026 cm^{-1}. GC-MS: the purity of the d_3 isotopomer is 90%; this purity is indirectly determined by the thermal rearrangement product VB-d_3 and calculated from the relative intensities between m/z 182 and 183.

IV.4. ^{1}H NMR Analysis of Photolysis Mixtures. Photolysis of *p*-biphenylyldiazoethane (BDE) was performed in cyclohexane containing various concentrations of ethanol-*O*-*d* using a 10 Hz excimer laser (XeCl, 308 nm, 17 ns, ∼0.5 J/pulse) for 5 min. *Note*: Photolysis for a substantially longer time reduces the yield of *p*-vinylbiphenyl. BDE stock solutions were prepared by dissolving a known quantity of BDE in 300 mL of cyclohexane to achieve $A = 0.7$ at 308 nm. In a quartz flask, 23.00 g of the stock solution was weighed, and a known amount of ethanol-*O*-*d* was added. The sample solution was degassed for 5 min by bubbling with argon before photolysis. During photolysis, the sample solution was stirred magnetically. The completion of the photolysis was monitored by UV−vis spectroscopy. After photolysis, the solvent was removed under vacuum at 35 °C, and the product mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR (500 MHz). To obtain the best possible integration, a 3 s relaxation time was used. We assumed that the products derived from BDE will have an intact biphenyl ring system. The aromatic hydrogens (δ 7.2−8.0) were integrated and defined as the total yield (100%). The peaks in the mixture NMR were identified by comparison with either spectra of authentic samples or the literature NMR data of the same compound or its monophenyl counterpart in the literature. Generally speaking, changing from phenyl to biphenyl should only change the chemical shifts of their nonconjugated substituents downfield within 0.1 ppm, such as toluene (CH_3, δ 2.34) and *p*-phenyltoluene (CH_3, δ 2.39), and acetophenone (CH_3, δ 2.59) and *p*-phenylacetophenone (CH_3, δ 2.61). On the basis of this rule and the NMR literature data of the phenyl counterparts, the chemical shifts of the biphenyl photoproducts can be reasonably estimated.

The NMR chemical shifts of the three vinyl hydrogens of *p*-vinylbiphenyl are δ 6.76 (α H, dd, $J = 17.5$ Hz, $J = 10.5$ Hz), 5.80 (trans H, dd, $J = 17.5$ Hz, $J = 0.5$ Hz), and 5.28 (cis H, dd, $J = 10.5$ Hz, $J = 0.5$ Hz). The α vinyl hydrogen of *p*-vinylbiphenyl-d_1 is

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deuterated and does not have any H NMR signals. Therefore, the hydrogen with chemical shift δ 6.76 has a contribution only from *p*-vinylbiphenyl-d_0, which is formed by the 1,2 H shift mechanism.

V. Conclusions

Ultrafast photolysis of BDE produces an excited state of the diazo compound in acetonitrile, cyclohexane, cylohexene, and methanol with $\lambda_{\max} = 480$ nm and a lifetime of 300 fs. As the diazo excited states decay, growth of singlet carbene absorption at 360 nm is observed. The optical yields of diazo excited state produced by photolysis of BDM and BDE are the same; however, the optical yield of ^{1}BpCMe is ~40% less than that of ^{1}BpCH in all four solvents. The results cannot be explained by differences in the molar absorptivities of the two carbenes, nor can they be explained by differences in the quantum yields of decomposition of the two diazo compounds. Instead, we propose that the methyl-substituted diazo excited state suffers 1,2 migration of hydrogen to form VB and extrusion of nitrogen to form carbene in reduced yield. The decay of ^{1}BpCMe is biexponential, and that of ^{1}BpCH is monoexponential. The ratio of fast (6 ps) to slow (450 ps) decay of ^{1}BpCMe in acetonitrile strongly depends on the wavelength of excitation of the diazo compound. The ratio of the fast to the slow component of alkylarylcarbene disappearance increases as the excitation wavelength decreases (0.5 at 328 nm, 0.8 at 311 nm, and 4.0 at 271 nm). This is attributed either to efficient relaxation of vibrationally hot carbene by 1,2 migration of hydrogen to form VB or to the increased number of low-frequency vibrational modes provided by the methyl group.

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Supporting Information Available: Tables S1–S4, TD DFT calculations; Figures S1–S12, ultrafast LFP spectra, kinetic traces, and NMR spectra; and complete ref 38. This material is available free of charge via the Internet at http://pubs.acs.org.

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