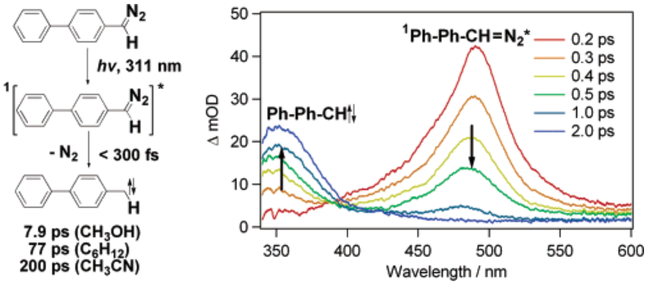
Ultrafast Study of *p*-Biphenylyldiazomethane and *p*-Biphenylylcarbene

Jin Wang, Gotard Burdzinski, Terry L. Gustafson, and Matthew S. Platz*

Department of Chemistry, The Ohio State University, 100 West 18th Avenue, Columbus, Ohio 43210, and Quantum Electronics Laboratory, Faculty of Physics, Adam Mickiewicz University, 85 Umultowska, Poznan 61-614, Poland

Platz.1@osu.edu

Received May 21, 2006



p-Biphenylyldiazomethane was excited by femtosecond pulses of UV light in acetonitrile, in cyclohexane, and in methanol. Ultrafast photolysis produces a singlet excited state of *p*-biphenylyldiazomethane with $\lambda_{\max} = 490$ nm, and lifetimes of less than 300 fs in acetonitrile, in cyclohexane, and in methanol. The decay of the excited state is accompanied by the growth of transient absorption with $\lambda_{\max} = 360$ nm. The carrier of this transient absorption is attributed to singlet *p*-biphenylylcarbene, a result that is consistent with the predictions of TD-DFT calculations. The singlet carbene lifetimes are 200 and 77 ps in acetonitrile and cyclohexane, respectively, and are controlled by intersystem crossing to the lower energy triplet state. The transient absorption does not decay to baseline in acetonitrile, because of the formation of nitrile ylide. The equilibrium mixture of singlet and triplet *p*-biphenylylcarbene reacts with acetonitrile to form a nitrile ylide ($\lambda_{\max} = 370$ nm), and with cyclohexane by C−H insertion 1−20 ns after the laser pulse. The singlet carbene lifetime is only 7.9 ps in methanol, owing to a rapid reaction with the solvent. Reaction with the solvent gives rise, in part, to a *p*-biphenylylbenzyl cation ($\lambda_{\max} = 450$ nm, $\tau = 6.3$ ps) in methanol.

I. Introduction

Mechanistic study of the photochemistry of aryl diazomethanes has a long and venerable history[1]. Much insight has been obtained by studying the stable products formed when aryl carbenes are generated in solution[2]. This has been augmented by matrix spectroscopy[3] of the ground triplet states of aryl carbenes and by nanosecond spectroscopy[4] of the same species in solution. Nanosecond (ns) time-resolved spectroscopy cannot directly observe singlet aryl carbenes because these intermediates intersystem cross (ISC) to the lower energy triplet states in less than 1 ns.[5,6] This frustrates our ability to understand how the rate of spin equilibration (k_{ST}, k_{TS}, Scheme 1) compares in both an absolute and relative sense to the rates of chemical reaction (k_S, k_T) and product (P) formation from the singlet (P_S) and triplet states (P_T) of the carbene.

Only a few ultrafast studies of diaryl carbenes have been reported and they deal exclusively with diphenylcarbene,[7,8] fluorenylidene,[5] and naphthylcarbomethoxycarbene.[9] These car-

---

[†] The Ohio State University.

[‡] Adam Mickiewicz University.

(1) Kirmse, W. *Carbene Chemistry*; Academic Press: New York,

(2) Moss, R. A., Jones, M., Jr., Eds. *Carbenes;* Academic Press: New York, Vol. 1.

(3) (a) Closs, G. L. *Carbenes*; Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. 2, p 159. (b) Trozzolo, A. M.; Wasserman, E. *Carbenes;* Moss, R. A., Jones, M., Jr., Eds.; Wiley: New York, 1973; Vol. 2, p 185.

(4) (a) Platz, M. S.; Maloney, V. M. *Kinetics & Spectroscopy of Carbenes & Biradicals*, Platz, M. S., Ed.; Plenum: New York, 1990; p 239. (b) Bucher, G.; Scaiano, J. C.; Platz, M. S.; *Landolt-Bornstein, Group II;* Springer: Berlin, Germany, 1998; Vol. 18, p 141;

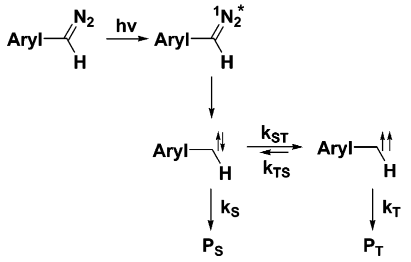
(5) Grasse, P. B.; Brauer, B. E.; Zupancic, J. J.; Kaufmann, K. J.; Schuster, G. B. *J. Am. Chem. Soc.* **1983**, *105*, 6833−6845.

(6) Dupuy, C.; Korenowski, G. M.; McAuliffe, M.; Hetherington, W. M., III.; Eisenthal, K. B. *Chem. Phys. Lett.* **1981**, *77*, 272−274.

(7) Peon, J.; Polshakov, D.; Kohler, B. *J. Am. Chem. Soc.* **2002**, *124*, 6428−6438.

10.1021/jo061029+ CCC: $33.50

SCHEME 1



benes were subject to initial study because of their historical importance to the development of mechanistic theory,[1-3] the ease of synthesis and handling of their precursor diazo compounds, and their favorable spectroscopic properties. Herein we report the first ultrafast time-resolved study of a monoaryl diazomethane and a monosubstituted carbene. The *p*-biphenyl system was chosen for initial study, rather than parent phenyl, because of its anticipated longer wavelength absorption spectra and because DFT calculations indicate that the *p*-phenyl substituent does not influence the singlet−triplet energy separation[10] (Supporting Information, SI, Table S1).

II. Ultrafast Spectroscopic Results

II.1. Acetonitrile. Ultrafast photolysis of *p*-biphenylyldiazomethane (BDM) in argon-purged acetonitrile (ACN) solution with a 300 fs pulse of 311 nm light results in the spectral changes shown in Figure 1. An intense transient absorption centered at 490 nm is produced at the earliest times that can be monitored after the laser pulse. The transient decay is accompanied by the growth of transient absorption centered at 360 nm, and an isosbestic point is observed at 395 nm. Within experimental error the time constant of the decay recorded at 490 nm is the same as that of the growth of transient absorption monitored at 360 nm. Within 1 ns of the laser pulse the 360 nm band decays monoexponentially and eventually the absorption maximum red-shifts to 370 nm.

The initially formed transient with $\lambda_{max} = 490$ nm is attributed to an excited singlet state of the precursor (^{1}BDM*) which decomposes to form the lowest singlet state of *p*-biphenylylcarbene (^{1}BPC) with $\lambda_{max} = 360$ nm and $\tau = 200$ ps in ACN at ambient temperature. TD-DFT calculations[11] predict that ^{1}BPC has a vertical transition at 335 nm ($f = 0.5254$) in fair agreement with our results (SI, Table S2).

The carrier of long-lived absorption at 370 nm can be confidently assigned as carbene−nitrile ylide Y (Scheme 2). It is observed by ns spectroscopy (Supporting Information (SI), Figure S1) and has a lifetime of 38 μs (SI, insert Figure S1). The spectra and lifetime of ylide Y are very similar to those of the phenyl and naphthylcarbene−acetonitrile ylides.[12] TD-DFT calculations predict the ylide Y has a vertical transition at 359 nm ($f = 0.8525$) (SI, Table S3).

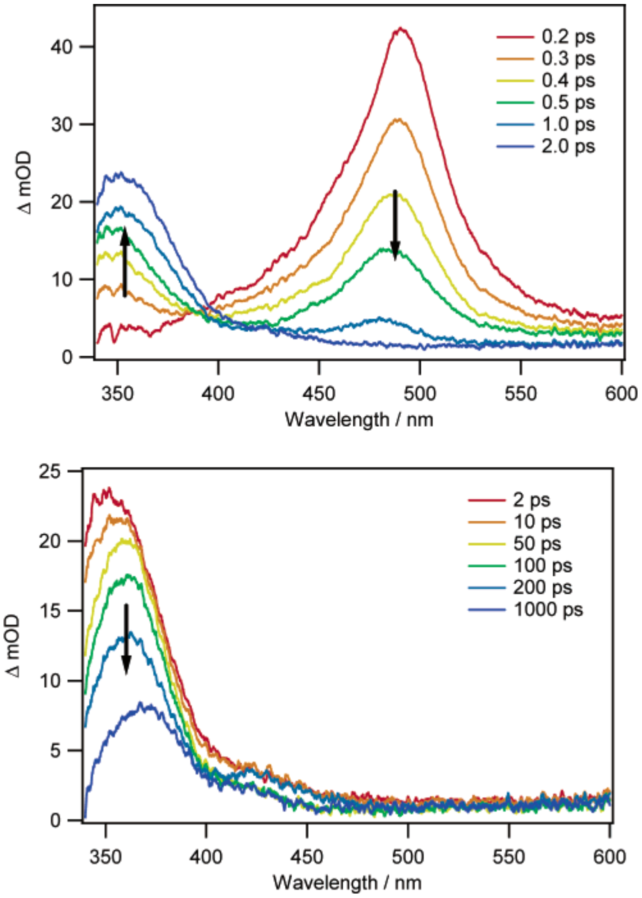
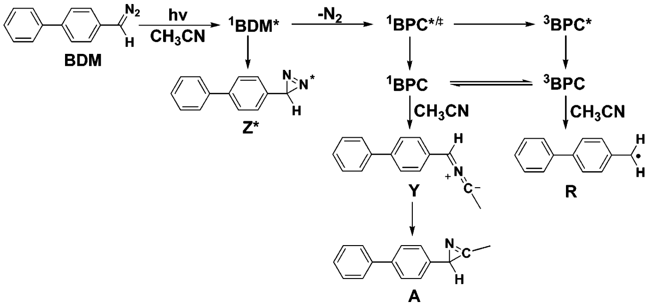


FIGURE 1. The transient spectra were generated by ultrafast LFP (311 nm) of *p*-biphenylyldiazomethane in acetonitrile within time windows 0.2−2.0 ps (top) and 2−1000 ps (bottom).

SCHEME 2



To better understand the spectra and kinetics obtained by ultrafast spectroscopy, we analyzed by proton NMR spectroscopy the stable products formed upon 308 nm photolysis of deoxygenated BDM (1 mg/mL) in ACN (SI, Table S4). The material balance can only be described as poor (∼25%). The yield of azirine A (Scheme 2) formed by cyclization of ylide Y is 10%, and the yield of carbene insertion into a CH bond of acetonitrile was 2%. *p*-Phenylbenzaldehyde was formed in 7% yield, azine in 2% yield, and a stilbene analogue in 3% yield. The material balance does not improve upon dilution of BDM to an absorbance of 1.0 at 308 nm (SI, Table S5) or upon

---

(8) Portella-Oberli, M. T.; Jeannin, C.; Soep, B.; Zerza, G.; Chergui, M. *Chem. Phys. Lett.* **1998**, *296*, 323−328.

(9) Hess, G. C.; Kohler, B.; Likhotvorik, I.; Peon, J.; Platz, M. S. *J. Am. Chem. Soc.* **2000**, *122*, 8087−8088.

(10) Geise, C. M.; Hadad, C. M. *J. Org. Chem.* **2000**, *65*, 8348−8356.

(11) (a) Stratmann, R. E.; Scuseria, G. E.; Frisch, M. J. *J. Chem. Phys.* **1998**, *109*, 8218−8224. (b) Casida, M. E.; Jamorski, C.; Casida, K. C.; Salahub, D. R. *J. Chem. Phys.* **1998**, *108*, 4439−4449.

(12) (a) Griller, D.; Montgomery, C. R.; Scaiano, J. C.; Platz, M. S.; Hadel, L. *J. Am. Chem. Soc.* **1982**, *104*, 6813−6814. (b) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *Chem. Phys. Lett.* **1983**, *97*, 446−449. (c) Admasu, A.; Gudmundsdottir, A. D.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 3832−3840. (d) Admasu, A.; Platz, M. S.; Marcinek, A.; Michalak, J.; Gudmundsdottir, A. D.; Gebicki, J. *J. Phys. Org. Chem.* **1997**, *10*, 207−220.

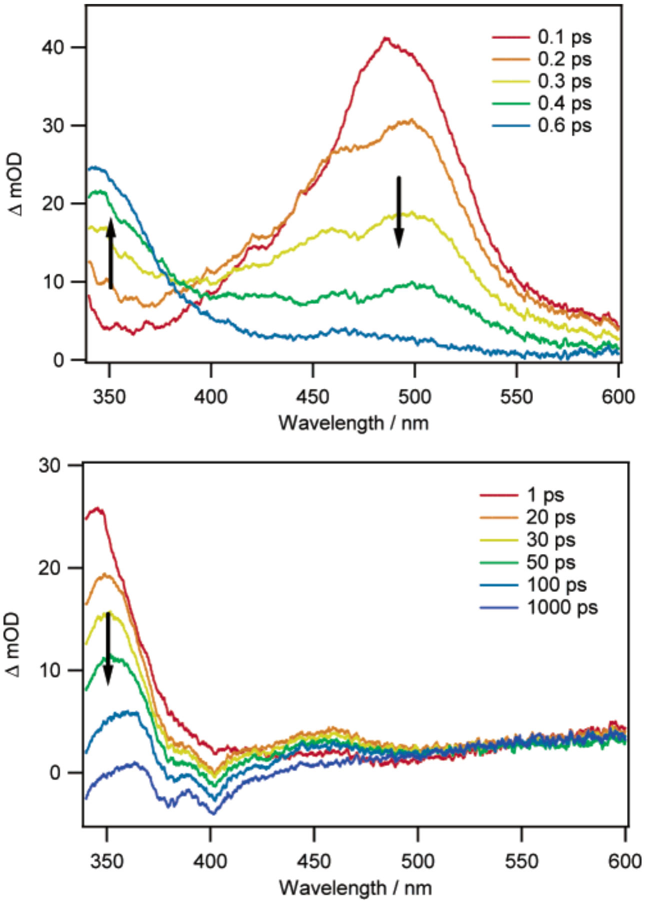


FIGURE 2. The transient spectra were generated by ultrafast LFP (311 nm) of *p*-biphenylyldiazomethane in cyclohexane within time windows 0.1−0.6 ps (top) and 1−1000 ps (bottom).

photolysis with 532 nm light (SI, Table S6). The material balance of carbene reactions in methanol and cyclohexane will later be found to be quite reasonable; thus, we suspect that the low material balance observed in ACN is due to a slow reaction of ylide Y with BDM to form intractable product(s) even though the lifetime of the ylide does not change as the concentration of *dilute* BDM varies over a factor of 4 ($A = 0.5{-}2.0$ at 308 nm). Thus, the product study provides evidence in the form of azirine A (Scheme 2) for the formation of at least some ylide Y upon photolysis of BDM in ACN.

II.2. Cyclohexane. The data obtained in cyclohexane are very similar to that observed in acetonitrile. Ultrafast photolysis of BDM again produces the intense absorption of ^{1}BDM* ($\lambda_{\max} = 480$ nm, Figure 2). In this solvent the excited-state lifetime is also within the instrument response function (300 fs). ^{1}BPC ($\lambda_{\max} = 360$ nm) is also formed during the decay of ^{1}BDM*. The lifetime of ^{1}BPC in cyclohexane is only 77 ps or less than half of that recorded in acetonitrile.

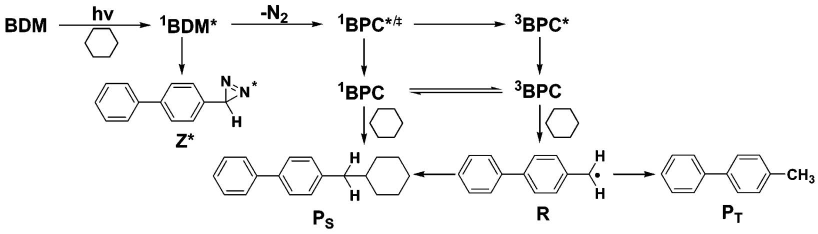
Phenylcarbene has a triplet ground state,[13] but most of the solution phase chemistry of this carbene proceeds via the low lying singlet state because this state of the carbene is very much more reactive than the ground triplet state with most trapping reagents (Scheme 3).[1−4] Our DFT calculations indicate that the singlet−triplet splitting of *p*-biphenylylcarbene is similar to that of phenylcarbene[13] and that the triplet is still the ground electronic state (SI, Table S1).

As before, deoxygenated solutions of BDM ($A_{308} = 1.0$, SI Table S7) were photolyzed with 308 nm light from an excimer laser and analyzed by proton NMR spectroscopy. In this solvent, 81% of the stable products formed were identified. The product of C−H insertion of the carbene with cyclohexane was formed in 70% yield. Another product, 1,2 di-*p*-biphenylylethane was formed in 6% yield, and *p*-methylbiphenyl was formed in 2% yield. The latter two products are generally associated with reactions of a triplet carbene. A classical interpretation of this product mixture, following earlier studies of aryl and diarylcarbenes,[1−4,14] is consistent with singlet−triplet carbene equilibration that is more rapid than reaction of either spin state with cyclohexane and that the equilibrium mixture of singlet and triplet carbene reacts with this solvent primarily but not exclusively through the low lying singlet state of *p*-biphenylylcarbene.

The singlet carbene transient absorption at 360 nm decays to baseline within 1 ns of the laser pulse. With our spectral probe range 350−620 nm, the formation of triplet *p*-biphenylylcarbene, ^{3}BPC, is not observed. TD-DFT calculations (SI, Table S9), predict that ^{3}BPC has a vertical transition at 321 nm ($f = 0.5434$). It has been previously noted that triplet aryl carbenes and their related benzylic radicals have identical π systems and consequently similar electronic spectra.[15] Yamaji has reported that the transient spectrum of *p*-phenylbenzyl radical R has a peak centered at 320 nm.[16] Because of their similar electronic configurations we therefore expect triplet carbene ^{3}BPC and its corresponding radical to have little absorption at 360 nm.

Nanosecond time-resolved laser flash photolysis (LFP) (308 nm) of BDM in $CF_2ClCFCl_2$ (Freon-113) was performed to observe ^{3}BPC. Unfortunately, we could not obtain a clear transient spectrum of ^{3}BPC with 308 nm light as the absorption of ^{3}BPC falls underneath the absorption of the BDM precursor. In the region we expect the triplet absorption (300−330 nm) to be present, only bleaching of BDM precursor is observed. However, bleaching at 305 nm is biphasic. The fast bleach cannot be resolved but the “slow” bleach proceeds with a rate constant of 2.6×10^6 s^{-1}. This is the pseudo-first-order rate constant of spin equilibrated carbene disappearance in Freon-113 in the absence of methanol. The slow bleach accelerates in the presence of methanol. The observed decay rate constant k_{obs} can be expressed as $k_0 + Kk_{\text{MeOH}}[\text{MeOH}]$, where k_0 is the pseudo-first-order rate constant of spin equilibrated carbene disappearance in Freon-113 in the absence of methanol, K is the singlet−triplet carbene equilibrium constant and k_{MeOH} is the absolute second-order rate constant of singlet carbene with

SCHEME 3



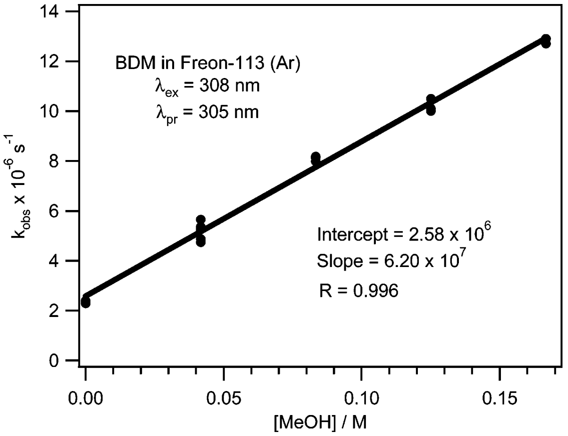


FIGURE 3. A plot of the pseudo-first-order rate constant of decay of ^{3}BPC (produced by 308 nm ns LFP of BDM in $CF_2ClCFCl_2$ (Freon-113)) versus the concentration of methanol. The decay was measured at 305 nm.

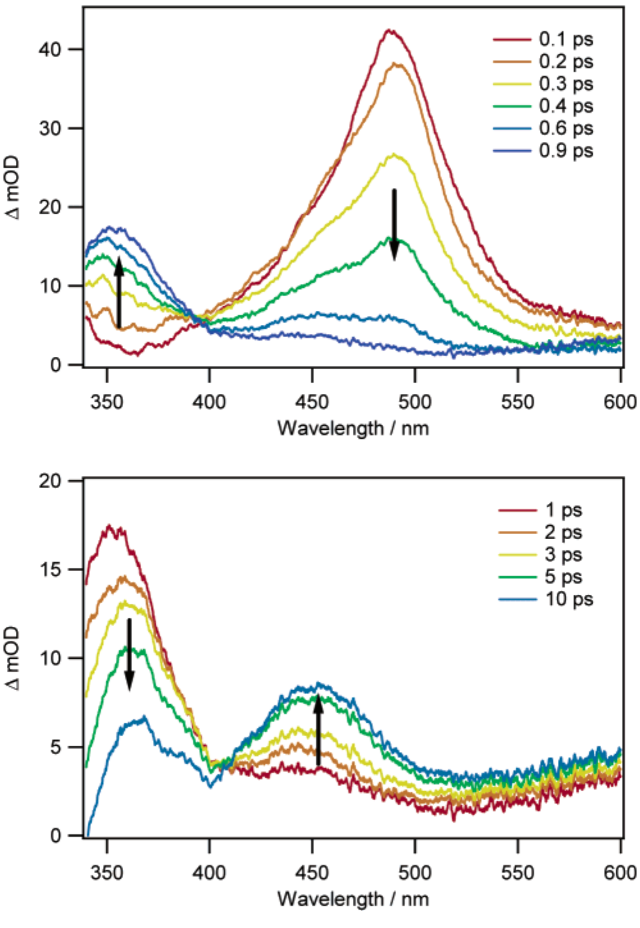
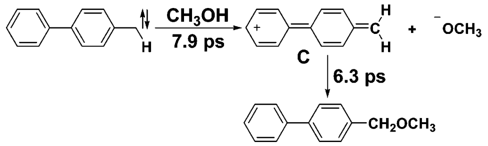


FIGURE 4. The transient spectra were generated by ultrafast LFP (311 nm) of *p*-biphenylyldiazomethane in methanol within time windows 0.1−0.9 ps (top) and 1−10 ps (bottom).

methanol. The plot of k_{obs} versus the concentration of methanol is linear (Figure 3) with a slope of 6.2×10^7 M^{-1} s^{-1}. So under these conditions Kk_{MeOH} equals to 6.2×10^7 M^{-1} s^{-1}.

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 unchanged, 140 fs, but the singlet carbene (λ_{max} = 360 nm) lifetime is reduced to only 7.9 ps in the reactive solvent. As the ^{1}BPC signal decays, a broad new band, centered at 450 nm, grows (7.9 ps) and decays (6.3 ps). An isosbestic point is also observed at 400 nm.

SCHEME 4



The carrier of the 450 nm band is assigned to *p*-phenylbenzyl cation C (Scheme 4) on the basis of the precedents established Kirmse and Steenken,[1717] Dix and Goodman,[18] and Kohler and co-workers.[7] 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. Kirmse observed the absorption of the *p*-biphenylylphenylcarbenium ion at 515 nm,[19] which shows a bathochromic shift relative to the absorption of diphenylcarbenium ion at 430 nm. Benzyl cation absorbs at 363 nm;[20] thus, absorption of quinoidal cation C at 450 nm does not seem unreasonable. Furthermore, TD-DFT calculations of the cation predict a vertical transition at 420 nm (f = 0.6904) in good agreement with experiment. Thus, the assignment of this transient absorption to cation C seems secure (SI, Table S10).

This interpretation is supported by chemical analysis of the stable products formed upon 308 nm photolysis of BDM in methanol (SI, Table S11). In methanol the expected methoxy ether is formed in 89% yield, along with a 2% yield of *p*-methylbiphenyl and a 6% yield of azine.

The ultrafast results obtained in methanol are very similar to those of diphenylcarbene in the same solvent.[7] The data in methanol-OD do not show a large isotope effect (Figure 5). Kohler et al. posited that the results indicated that the solvent reorganization is the rate determining step in the protonation process instead of the formation of C−H bond. Since the reaction is exothermic it will have an early, asymmetric transition state and consequently a small kinetic isotope effect. In addition, the lifetime of *p*-biphenylylcarbenium ion C (6.3 ps) is only about $^1/_5$ of that of diphenylcarbenium ion (30.5 ps),[7] which exemplifies diarylcarbenium ions are more stable than monoarylcarbenium ions.

Kohler and co-workers[7] concluded that proton transfer is a minor 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

---

(13) (a) Trozzolo, A. M.; Murray, R. W.; Wasserman, E. *J. Am. Chem. Soc.* **1962**, *84*, 4990−4991. (b) Matzinger, S.; Bally, T.; Patterson, E. V.; McMahon, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 1535−1542.

(14) Barcus, R. L.; Hadel, L. M.; Johnston, L. J.; Platz, M. S.; Savino, T. G.; Scaiano, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 3928−3937.

(15) Hadel, L. M.; Platz, M. S.; Scaiano, J. C. *J. Am. Chem. Soc.* **1984**, *106* (6), 283−287.

(16) (a) Tokumura, K.; Ozaki, T.; Nosaka, H.; Saigusa, Y.; Itoh, M. *J. Am. Chem. Soc.* **1991**, *113*, 4974−4980. (b) Yamaji, M.; Kobayashi, J.-i.; Tobita, S. *Photochemical & Photobiological Sciences* **2005**, *4*, 294−297.

(17) Kirmse, W.; Kilian, J.; Steenken, S. *J. Am. Chem. Soc.* **1990**, *112*, 6399−6400.

(18) (a) Chateauneuf, J. E. *Res. Chem, Intermed.* **1994**, *20*, 249−263. (b) Dix, E. J.; Goodman, J. L. *J. Phys. Chem.* **1994**, *98*, 12609−12612. (c) Steenken, S. *Pure Appl. Chem.* **1998**, *70*, 2031−2038.

(19) (a) Kirmse, W.; Krzossa, B.; Steenken, S. *J. Am. Chem. Soc.* **1996**, *118*, 7473−7477. (b) Dorra, M.; Gomann, K.; Guth, M.; Kirmse, W. *J. Phys. Org. Chem.* **1996**, *9*, 598−610.

(20) Jones, R. L.; Dorfman, L. M. *J. Am. Chem. Soc.* **1974**, *96*, 5715−5722.

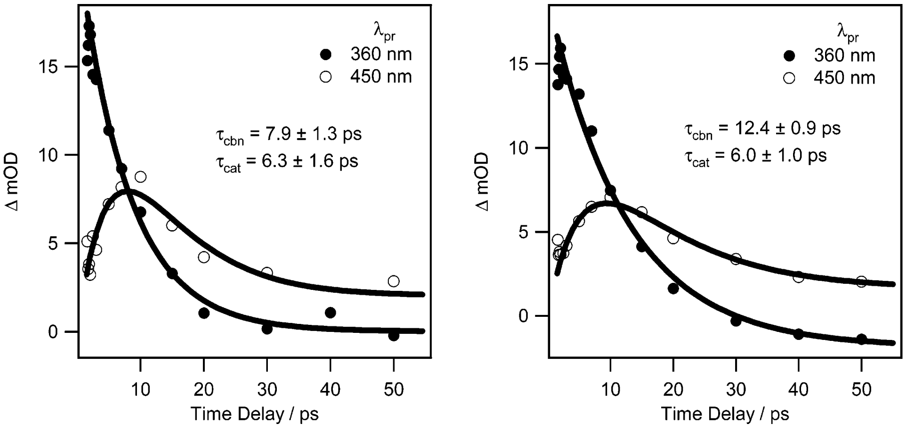


FIGURE 5. The decay of singlet carbene absorption at 360 nm (solid circles) and the growth and decay of transient absorption of *p*-phenylbenzyl cation at 450 nm (open circles) were probed in methanol (left) and in methanol-OD (right). The time constants τ_{cbn} (the lifetime of singlet *p*-biphenylylcarbene)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

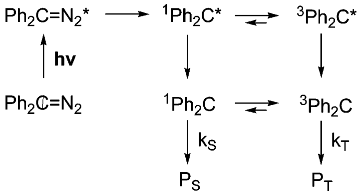
a UV−vis active reaction product as does proton transfer. Because the extinction coefficient of benzhydryl cation (which is persistent under certain conditions) was known, it was possible for the Kohler group to quantitate the yield of this ion from singlet diphenylcarbene. *p*-Phenylbenzyl cation is not a persistent species, and as a result its extinction coefficient at the absorption maximum is not known, and we cannot deduce its yield from *p*-biphenylylcarbene in methanol.

As mentioned previously the singlet−triplet equilibrium mixture of *p*-biphenylylcarbene reacts with methanol in CF_2-$ClCFCl_2$ (Freon-113) with absolute rate constant of 6.2×10^7 M^{-1} s^{-1}. The concentration of neat methanol is 24.7 M. The ultrafast study of BDM in methanol determined that the lifetime of the singlet carbene is 7.9 ps; thus, the bimolecular rate constant $k_{MeOH} = 5.12 \times 10^9$ M^{-1} s^{-1}. If one assumes that k_{MeOH} is the same in neat methanol and in Freon-113 one can conclude that $K_{ST} = 1.2 \times 10^{-2}$ and that $\Delta G_{ST} = 2.6$ kcal/mol. Further assuming that the intersystem crossing rate in Freon is the same as that in cyclohexane, then $k_{ST} = 1.3 \times 10^{10}$ s^{-1} and $k_{TS} = 1.6 \times 10^8$ s^{-1} in nonpolar solvents.

III. Discussion

The UV−vis spectrum of *p*-biphenylyldiazomethane is unremarkable (SI, Figure S2). TD-DFT calculations (SI, Table S12) are consistent with prior analyses[21] that concluded that the transition in the visible region is n−π* and the more intense UV band is a π−π* transition. We attempted to perform ultrafast photolysis at 500 nm on BDM without success. The extinction coefficients of BDM in the visible region are low, which necessitates using a rather high concentration of diazo compound. Photolysis of the concentrated solution leads to a precipitate (probably the azine formed by reaction of carbene with diazo precursor), which makes the solution opaque. Thus, we can assign the carrier of the 490 nm transient to a singlet excited state of the precursor BDM, but we have no evidence with which to assign it to either the S_1 or S_2 state of the excited state of the diazo compound.

SCHEME 5. Deactivation Pathways for Diphenyldiazomethane



It is well-known that photolysis and pyrolysis of nitrogenous precursors of carbenes give different mixtures of products.[22−24] It has been argued that photolysis can produce some vibrationally[22] or electronically[23] excited carbene that forms stable products in a different ratio than the relaxed carbene. Different carbene precursors give different product mixtures upon photolysis.[25] Thus, one must also consider the possibility that rearrangements and product formation can proceed in the excited states of the diazo or diazirine precursors of the carbene or in a vibrationally or electronically excited state of the carbene.[22−25]

Eisenthal et al.[6,26] demonstrated that 266 nm photolysis (S_0−S_2 excitation) of diphenyldiazomethane produces a low yield of electronically excited triplet diphenylcarbene (^{3}DPC*). This group concluded that 266 nm photolysis of diphenyldiazomethane produced the carbene in an electronically excited singlet state (^{1}DPC*) in a monophotonic process as anticipated by Chang and Shechter.[23] It was proposed that the excited singlet state, ^{1}DPC*, partitioned between relaxation to the lowest electronic singlet state (^{1}DPC, major) and an electronically excited triplet state, ^{3}DPC* (Scheme 5). This bifurcation took place in less than 15 ps, the time resolution of the experiment. ^{3}DPC* has a fluorescence lifetime in solution at ambient temperature of 4 ns.[26] The carbene fluorescence had been previously observed in glassy matrixes where ground-state triplet

---

(21) Bigot, B.; Ponec, R.; Sevin, A.; Devaquet, A. *J. Am. Chem. Soc.* **1978**, *100*, 6575−6580.

(22) (a) Friedman, L.; Shechter, H. *J. Am. Chem. Soc.* **1959**, *81*, 5512−5513. (b) Frey, H. M.; Stevens, I. D. R. *J. Am. Chem. Soc.* **1965**, 3101−3108. (c) Frey, H. M. *Adv. Photochem.* **1966**, *4*, 225−256.

(23) Chang, K. T.; Shechter, H. *J. Am. Chem. Soc.* **1979**, *101*, 5082−5084.

(24) Platz, M. S. *Adv. Carbene Chem.* **1998**, *2*, 133−174.

(25) (a) Huang, H.; Platz, M. S. *J. Am. Chem. Soc.* **1998**, *120*, 5990−5999. (b) Nigam, M.; Platz, M. S.; Showalter, B. M.; Toscano, J. P.; Johnson, R.; Abbot, S. C.; Kirchhoff, M. M. *J. Am. Chem. Soc.* **1998**, *120*, 8055−8059.

(26) (a) Wang, Y.; Sitzmann, E. V.; Novak, F.; Dupuy, C.; Eisenthal, K. B. *J. Am. Chem. Soc.* **1982**, *104*, 3238−3239. (b) Langan, J. G.; Sitzmann, E. V.; Eisenthal, K. B. *Chem. Phys. Lett.* **1986**, *124*, 59−62.

DPC is persistent.[27] Neither ^{1}DPC* nor ^{3}DPC* was detected by ps time-resolved absorption spectroscopy in this work.

Horn and Allison[28] measured the absorption spectrum of ^{3}DPC* using ns spectroscopy. In their experiment a single, intense pulse of 308 nm laser radiation decomposed diphenyldiazomethane and re-excited the triplet diphenylcarbene formed within the laser pulse. They observed a sharp absorbance at 360 nm and a broad, lower intensity absorption tail from 370 to 470 nm, with a lifetime of 9 ns. Moreover, a 510 nm fluorescence emission was also detected. Scaiano et al.[29] performed a related experiment with ditolylcarbene and observed the absorption and emission spectrum of the excited state of this diaryl triplet carbene.

The photophysics and photochemistry of diazomethane have been studied at high levels of theory.[30] It is interesting to note that theory predicts that the S_2 state of diazomethane can form an electronically excited singlet state of methylene by passage through a conical intersection. This is predicted to be a minor process; however, only a modest yield of electronically excited carbene is necessary to explain the unique mixture of products formed upon photolysis of nitrogenous precursors of alkyl carbenes. The predictions of modern theory support the conclusions of Chang and Shechter[23] and the Eisenthal group[6,26] that UV photolysis of a diazo compound can produce a carbene in an electronically excited state.

Gas-phase photolysis of parent diazirine excited at the origin (322.96 nm) of the S_0-S_1 transition has been shown to produce excited singlet methylene which fluoresces at $\lambda > 575$ nm with a lifetime of $\sim 16\ \mu$s.[31] This experiment demonstrates once again that UV photolysis of a carbene precursor can generate a carbene in an electronically excited state. To the best of our knowledge, the corresponding experiment has not been reported with diazomethane.

The major deactivation process of the S_2 state of diazomethane is predicted by theory to be relaxation to the S_1 state of diazomethane. The S_1 state of diazomethane is predicted to form methylene in its lowest excited state within $\sim$100 fs of photolysis. In addition the calculations predict that the S_1 state of diazomethane will not produce a singlet excited state of methylene.[30]

Ultrafast UV photolysis of *p*-biphenylyldiazomethane produces a transient with a broad absorption maximum at 490 nm and a lifetime of less than 300 fs. Transients with subpicosecond lifetimes have been observed previously upon photolysis of diphenyldiazomethane[7,8] and 2-naphthylcarbomethoxydiazomethane.[9] One can consider assigning this transient absorption to either a singlet or triplet excited state of the carbene. However, the lifetime of excited triplet diphenylcarbene in solution is on the order of a few ns.[28,29] Given the fs lifetime of the 490 nm transient absorption, it seems unreasonable to assign the carrier of this band to an excited triplet state of *p*-biphenylylcarbene.

The work of the Eisenthal group suggests that the lifetime of excited singlet diphenylcarbene is less than 15 ps;[6,26] thus, we cannot exclude the possibility that the carrier of the 490 nm band is excited singlet *p*-biphenylylcarbene. Following the Kohler group,[7] and consistent with the predictions of modern theory,[30] we prefer to assign the carrier of the 490 nm transient absorption to the singlet excited state of the diazo precursor.

As the singlet excited state of the diazo compound decays a new absorption band grows at the same rate at 360 nm. We are confident that the carrier of this transient absorption is the lowest singlet state of *p*-biphenylylcarbene, ^{1}BPC, because its spectrum is in agreement with the predictions of TD-DFT calculations, and it reacts, as expected, with acetonitrile to form a nitrile−ylide and reacts even faster with methanol to form *p*-phenylbenzyl cation.

The lifetime of ^{1}BPC is 200 ps in acetonitrile and is 77 ps in cyclohexane. These lifetimes are controlled by the rate of intersystem crossing of the singlet to the triplet ground state (^{3}BPC). Our results compare well with the scant data available in the literature. Eisenthal and co-workers reported that the lifetimes of singlet diphenylcarbene (^{1}DPC) in acetonitrile and 3-methylpentane are 310 and 95 ps, respectively.[6,26] It was argued that the polar solvent selectively stabilizes the singlet relative to triplet DPC. As a consequence singlet to triplet spin relaxation is more exothermic in cyclohexane and proceeds more rapidly. This interpretation is buttressed by the work of Toscano and Hadad[32] who have shown that polar solvents do preferentially stabilize singlet relative to triplet carbenes. Kohler et al.,[7] using ultrafast time-resolved absorption spectroscopy, reported the singlet diphenylcarbene has a lifetime of 340 ps in acetonitrile, in good agreement with the Eisenthal group.[6] Schuster and co-workers[5] deduced that the lifetime of singlet fluorenylidene is 280 ps in acetonitrile on the basis of measuring the growth of the absorption of the triplet state of this carbene. Thus, the absolute rates of ISC of ^{1}BPC and the solvent effect on the ISC rates support the assignment of the 360 nm absorbing transient to ^{1}BPC.

Upon UV ultrafast photolysis of diphenyldiazomethane, Kohler and co-workers observed the formation of vibrationally excited singlet diphenylcarbene.[7] Vibrationally hot molecules usually have absorption spectra that are similar to but broader than their relaxed counterparts. Vibrational cooling is usually accompanied by spectral reshaping on a 5−25 ps time scale with a decrease in absorption of the red edge of the absorption band and an increase in absorption at the blue edge of the band.[33] The vibrational cooling of ^{1}DPC has time constants of 9 ps in cyclohexane and 21 ps in acetonitrile.[7] In our work, vibrational cooling is not observed when BDM is excited at 311 nm. However, if the excitation wavelength is moved to a shorter wavelength (271 nm), the decay of the 360 nm band clearly shows a biphasic characteristic ($\tau = 22$ and 223 ps) in acetonitrile (Figure 6). The longer lifetime is the same as the lifetime with 311 nm excitation (200 ps) within experimental error. The 22 ps component is associated with vibrational

---

(27) (a) Trozzolo, A. M.; Gibbons, W. A. *J. Am. Chem. Soc.* **1967**, *89*, 239−243. (b) Ono, Y.; Ware, W. R. *J. Phys. Chem.* **1983**, *87*, 4426−4433.

(28) Horn, K. A.; Allison, B. D. *Chem. Phys. Lett.* **1985**, *116*, 114−118.

(29) Johnston, L. J.; Scaiano, J. C. *Chem. Phys. Lett.* **1985**, *116*, 109−113.

(30) (a) Yamamoto, N.; Bernardi, F.; Bottoni, A.; Olivucci, M.; Robb, M. A.; Wilsey, S. *J. Am. Chem. Soc.* **1994**, *116*, 2064−2074. (b) Bernardi, F.; Olivucci, M.; Robb, M. A.; Vreven, T.; Soto, J. *J. Org. Chem.* **2000**, *65*, 7847−7857. (c) Arenas, J. F.; Lopez-Tocon, I.; Otero, J. C.; Soto, J. *J. Am. Chem. Soc.* **2002**, *124*, 1728−1735.

(31) Lim, S.-M.; Kim, T.-S.; Lim, G.-I.; Kim, S. K.; Choi, Y. S. *Chem. Phys. Lett.* **1998**, *288*, 828−832.

(32) Geise, C. M.; Wang, Y.; Mykhaylova, O.; Frink, B. T.; Toscano, J. P.; Hadad, C. M. *J. Org. Chem.* **2002**, *67*, 3079−3088.

(33) (a) Laermer, F.; Elsaesser, T.; Kaiser, W. *Chem. Phys. Lett.* **1989**, *156*, 381−386. (b) Elsaesser, T.; Kaiser, W. *Annu. Rev. Phys. Chem.* **1991**, *42*, 83−107. (c) Miyasaka, H.; Hagihara, M.; Okada, T.; Mataga, N. *Chem. Phys. Lett.* **1992**, *188*, 259−264. (d) Schwarzer, D.; Troe, J.; Votsmeier, M.; Zerezke, M. *J. Chem. Phys.* **1996**, *105*, 3121−3131. (e) Burdzinski, G. T.; Gustafson, T. L.; Hackett, J. C.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 13764−13765.

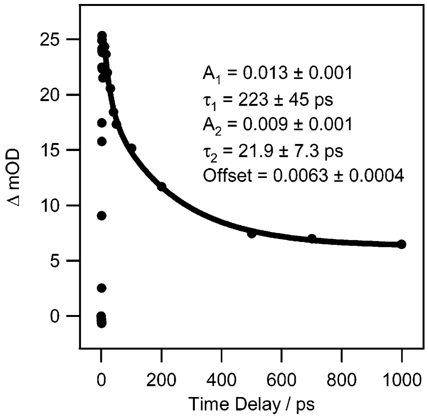


FIGURE 6. The kinetic trace was probed at 360 nm for ultrafast LFP (271 nm) of BDM in acetonitrile and fitted into a biexponential equation $\Delta OD = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) +$ offset.

cooling of ^{1}BPC. Monoaryl and diaryl carbenes thermalize at about the same rate in acetonitrile.

IV. Conclusions

Ultrafast photolysis of *p*-biphenylyldiazomethane produces the excited states of the diazo compound in acetonitrile, cyclohexane, and methanol with $\lambda_{max} = 490$ nm and lifetimes within 300 fs. As the diazo excited states decay, the growth of singlet carbene absorption at 360 nm is observed. In methanol the singlet carbene reacts within a few ps to form the *p*-phenylbenzyl cation with $\lambda_{max} = 450$ nm and $\tau = 6.3$ ps. In cyclohexane *p*-biphenylylcarbene decays by intersystem crossing to the triplet ground state with a time constant of 77 ps. In acetonitrile *p*-biphenylylcarbene decays to the lower energy triplet carbene in 200 ps. The singlet−triplet equilibrium mixture of carbenes reacts with the solvent to form a nitrile ylide.

V. Experimental Section

Calculations. DFT and TD-DFT calculations were performed using the Gaussian 03 suite of programs at The Ohio Supercomputer Center. Geometries were optimized at the B3LYP/6-31G* level of theory with single point energies obtained at the B3LYP/6-31+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 Function Theory of Gaussian 03 at the B3LYP/6-31+G** level and 20 allowed electronic transitions were calculated.

Nanosecond Time-Resolved Spectroscopy. Nanosecond time-resolved measurements were performed using the instrument described previously.[34] A commercially supplied laser (308 nm, ~17 ns) with a power of ~0.5 J/pulse was used. Samples were prepared in 1 cm quartz cuvettes with unit absorption and purged with argon for 5 min before experiments.

Ultrafast Spectroscopy. Ultrafast UV−vis broadband absorption measurements were performed using the home-built spectrometer described previously.[35] 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.

In addition to the two major transient absorption peaks mentioned earlier, a weak band at 425 nm can be clearly observed in acetonitrile 2 ps after the laser pulse. This band is not observed in either cyclohexane or methanol. The rate of formation of this absorption cannot be resolved because of overlapping absorption with the diazo excited state. This transient absorption shows no decay over a 1 ns time window (Figure 1, bottom). This band is not observed by ns LFP (308 nm) of BDM in acetonitrile. Thus, we conclude that the lifetime of the carrier of this transient absorption must be less than 10 ns.

Ultrafast spectra are obtained using a 1000 Hz ultrafast laser on a flowed sample. Considering the 1 ms time interval between two adjacent excitation pulses in this experiment, it is possible to excite photoproducts produced in the first few pulses before the sample fully flows out of the excitation region; thus, transients may be due to ultrafast photolysis of photoproducts. The intensity of the 425 nm band is more prominent when BDM is pumped at 271 nm than 311 nm suggesting that it is due to re-excitation of a photoproduct formed only in acetonitrile. The major transient absorption bands (490 nm, 360 nm) were shown not to be due to re-excitation of a photoproduct by the following control experiment. A sample of BDM was bleached by repeated pulses of 308 nm light from an excimer laser. Ultrafast photolysis (311 nm) of the bleached solution did not produce the short-lived transient absorption band at 490 nm assigned to the diazo excited state or the longer lived band at 360 nm assigned to *p*-biphenylylcarbene.

Additional control experiments ruled out other assignments of the 490 and 360 nm transient absorption bands. Ultrafast photolysis (311 nm) of the *p*-phenylbenzaldehyde does not produce transient absorption at 490 and 360 nm (SI, Figure S3). Furthermore, the intensities of the 490 and 360 nm bands produced from BDM are the same in both aerated and argon purged solution. Thus, we conclude that *p*-phenylbenzaldehyde is not the carrier of either the 490 or 360 nm bands produced upon ultrafast photolysis of BDM.

Diazo compounds photoisomerize to diazirines which have significant absorbance above 300 nm. Biphenylylmethyl diazirine was deemed easier to synthesize than *p*-biphenylyldiazirine, and we assumed that the extra methyl group would not significantly alter the spectra or lifetime of the excited diazirine. Ultrafast photolysis (380 nm) of biphenylylmethyl diazirine does not produce transient absorption at 490 nm (Figure S4), and thus the S_1 excited state of the diazirine cannot be the carrier of the 490 nm transient absorption band.

Materials. *p*-Biphenylcarboxaldehyde was purchased from a commercial supplier. The solvents for ultrafast studies were spectrophotometric grade and used as received.

p-Biphenylyldiazomethane (BDM) was synthesized as follows. Under argon, 0.17 g of sodium was dissolved in 10 mL of ethylene glycol by heating to 70 °C, and 1.75 g of *p*-biphenylcarboxaldehyde tosylhydrazone (5.0 mmol, which is made by refluxing *p*-biphenylcarboxaldehyde (1.82 g, 10 mmol) with *p*-toluenesulfonylhydrazide (1.86 g, 10 mmol) in 50 mL of ethanol) was added. After it was heated with vigorous stirring for 10 min at 70−80 °C, the mixture was cooled to about 35 °C, and 15 mL of pentane was added with continued stirring. The organic extract was removed by pipet, and the procedure was repeated a total of five times. The combined organic extracts were washed with 30 mL of 5% sodium hydroxide solution, washed with a saturated sodium chloride solution, and dried over sodium sulfate. After filtration, the solvent was removed on a rotary evaporator to give *p*-biphenylyldiazomethane as a reddish solid. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.57 (d, $J = 7.5$ Hz, 2 H), 7.54 (d, $J = 8.5$ Hz, 2 H), 7.43 (t, $J = 7.5$ Hz, 2 H), 7.32 (t, $J = 7.5$ Hz, 1 H), 6.99 (d, $J = 8.5$ Hz, 2 H), 4.99 (s, 1 H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.7, 136.8, 128.8, 127.8, 127.0, 126.6, 121.7, 47.3. FT-IR (neat): 2055 cm^{-1}. UV λ_{max} (acetonitrile): 227, 312, 490 nm.

^{1}H NMR Analysis of Photolysis Mixtures. Photolysis of *p*-biphenylyldiazomethane (BDM) was performed in acetonitrile, cyclohexane, and methanol using a 10 Hz laser (XeCl, 308 nm, 17

---

[34] Gritsan, N. P.; Zhai, H. B.; Yuzawa, T.; Karweik, D.; Brooke, J.; Platz, M. S. *J. Phys. Chem. A* **1997**, *101*, 2833−2840.

[35] Burdzinski, G. T.; Hackett, J. C.; Wang, J.; Gustafson, T. L.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.*, submitted for publication, 2006.

ns, ~0.5 J/pulse) for 30 min. In a quartz flask, a known quantity of BDM was dissolved in 50 mL of solvent to achieve unit absorption at 308 nm. The sample solution was purged with argon for 5 min before experiments. During photolysis, the sample solution was stirred magnetically, and argon kept bubbling through the solution. The completion of the photolysis was monitored by UV−vis spectra. After photolysis, the solvent was removed under vacuum, and the product mixture was dissolved in $CDCl_3$ and analyzed by ^{1}H NMR (500 MHz). To obtain a better integration, a 3 s relaxation time was used. We assumed that the products derived from BDM 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 comparing either with authentic samples, or the literature NMR data of the same compound, or their monophenyl counterparts in the literatures. 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.

Acknowledgment. Support of this work by the National Science Foundation, the Ohio State University Center for Chemical and Biophysical Dynamics, and the Ohio Supercomputer Center is gratefully acknowledged.

Supporting Information Available: Gas-phase DFT calculations of the singlet−triplet gap of *p*-biphenylylcarbene and phenylcarbene; gas-phase TD-DFT calculations of singlet *p*-biphenylylcarbene, acetonitrile ylide, triplet *p*-biphenylylcarbene, *p*-biphenylbenzyl radical, *p*-biphenylbenzyl carbocation, and *p*-biphenylyldiazomethane; product studies of BDM in acetonitrile, cyclohexane, and methanol; ns-LFP (308 nm) studies of BDM in acetonitrile; ultrafast LFP studies of *p*-phenylbenzaldehyde and *p*-biphenylmethyl diazirine; and ^{1}H and ^{13}C NMR of *p*-biphenylyldiazomethane. This material is available free of charge via the Internet at http://pubs.acs.org.

JO061029+