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Solution Phase Isomerization of Vibrationally Excited Singlet Nitrenes to Vibrationally Excited 1,2-Didehydroazepine

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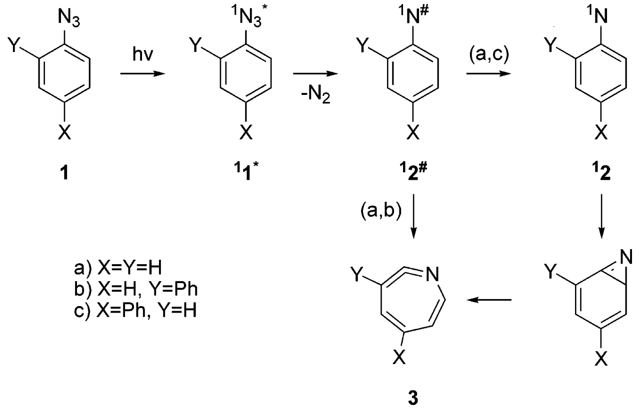
The earliest transformations associated with the formation of nitrenes and carbenes following photoexcitation of azides and diazo/diazirine compounds, respectively, remain unresolved.[1−7] In recent studies, we have used ultrafast UV−vis transient absorption spectroscopy to probe the electronic spectra and dynamics of the intermediates formed following photoexcitation of aryl azides and aryl diazo compounds in solution.[8−10] There are, however, many important reactive intermediates (RIs) whose electronic spectra are at too short a wavelength range to be accessible with current technology. In addition, there are often subtle structural differences and conformational changes that are not readily observed with time-resolved electronic spectroscopy. Ultrafast time-resolved vibrational spectroscopy has the potential for observing structural dynamics for intermediates, regardless of whether their electronic spectra are readily observable. In this work we present the femtosecond time-resolved infrared (IR) spectra of RIs derived from phenyl (**1a**) and *o*-biphenylyl (**1b**) azide. We observe a prompt bleach in the vibrational bands of the parent azide compounds and a rise of the characteristic vibrational band for the corresponding 1,2-4,6-azacycloheptatetraene (1,2-didehydroazepine, **3a** and **3b**).

Scheme 1



As the simplest of the aryl azides, the photochemistry of phenyl azide has been studied extensively.[1−6] Photolysis of biphenylyl azides (**1b** and **1c**) releases singlet nitrene (**2b** and **2c)** within 1 ps.[10] It is reasonable then to expect that singlet phenylnitrene (**2a**) will also be formed rapidly upon photolysis of phenyl azide (**1a**). Thermalized singlet phenylnitrene isomerizes to benzazirine (E_a = 5.6 kcal/mol),[2] which rapidly opens to form 1,2-didehydroazepine (**3a**) (Scheme 1).[3] This occurs in ~1 ns in organic solvents at ambient temperature. Cyclic ketemimine (**3a)** has been detected by matrix IR spectroscopy[4] and in solution by nanosecond/microsecond time-resolved UV−vis[2a,5] and IR spectroscopy.[6]

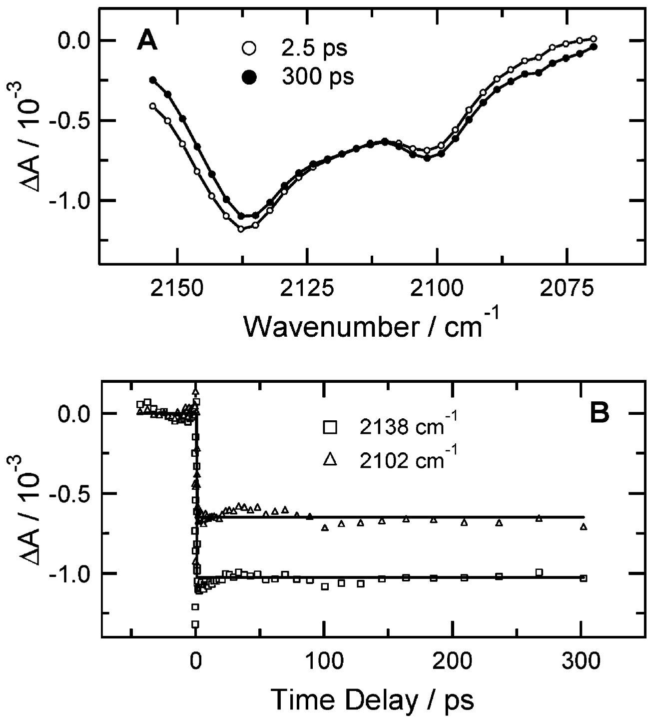


Figure 1. Time-resolved IR spectra produced upon ultrafast photolysis of *o*-biphenylyl azide in acetonitrile (270 nm excitation).

In the femtosecond time-resolved infrared experiment, we excite the sample in the ultraviolet (270 nm; 300 fs) and probe the photoexcited volume with a broadband (ca. 250 cm^{-1}) infrared probe pulse (300 fs). Pump and probe polarizations are set at the magic angle to eliminate rotational reorientation effects. For all samples we observe a prompt bleach of the vibrational bands associated with the ground state azide that persists for >300 ps. Representative difference (transient) spectra at 2.5 and 300 ps for *o*-biphenylyl azide in acetonitrile are shown in Figure 1A, along with the dynamics at 2102 and 2138 cm^{-1} in Figure 1B.

In addition to bleaching bands we also observe new positive features in the vibrational spectra, corresponding to the formation of 1,2-didehydroazepine on a picosecond time scale. In Figure 2 we present the time-resolved IR spectra of phenyl azide (A) and *o*-biphenylyl azide (B) in the region of 1880 cm^{-1}, where the 1,2-didehydroazepine is known to absorb.[4,6,7] The initially observed vibration for both compounds is broad, but the band sharpens and blue shifts in 10−50 ps. We conclude that singlet

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10.1021/ja065783o CCC: $33.50 © 2006 American Chemical Society

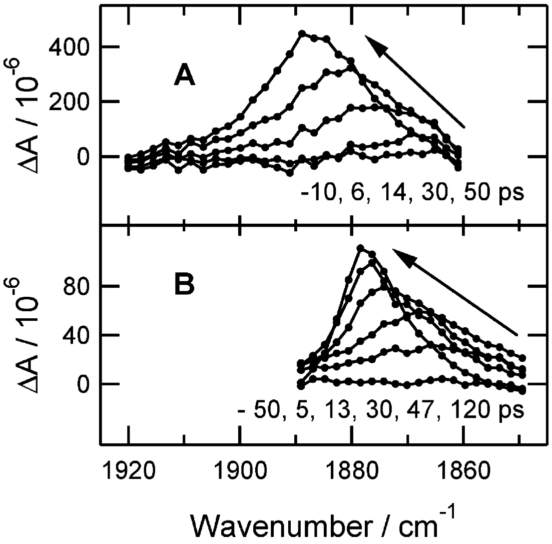

Figure 2. Time-resolved IR spectra produced upon ultrafast photolysis of phenyl azide in chloroform (A) and *o*-biphenylyl azide in acetonitrile (B) (270 nm excitation).

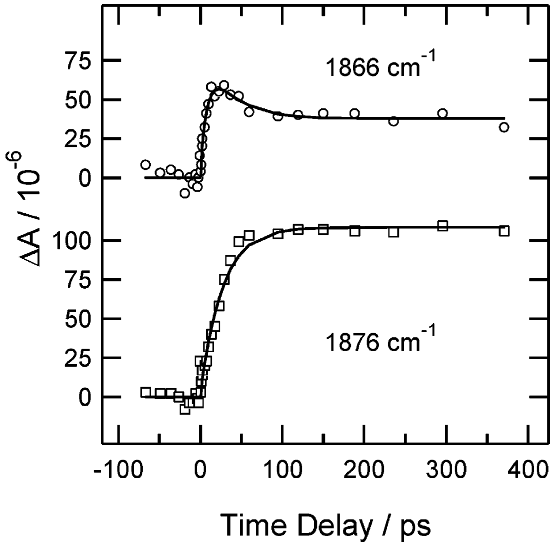

Figure 3. Selected kinetic traces recorded at 1866 and 1876 cm^{-1} for *o*-biphenylyl azide in acetonitrile (270 nm excitation). Solid lines are fits to data with either one or two exponential functions, respectively, as well as an offset.

nitrenes (**2a** and **2b**) isomerize to thermally excited 1,2-didehydroazepine (**3a** and **3b**) which relax in 10−50 ps. Ultrafast UV−vis studies of *p*-biphenylylnitrene demonstrate that it is formed thermally excited and undergoes vibrational cooling in 13 ps.[8,10] It is reasonable then to expect that singlet phenylnitrene will also be born with excess vibrational energy and that, for nascent singlet phenylnitrene, isomerization must compete with vibrational cooling to thermalized **2a** which is detected in nanosecond time-resolved experiments.[2] The femtosecond UV−vis data[8,10] indicate that singlet nitrenes, in general, are formed with excess vibrational energy. We also note that, within the signal-to-noise of the femtosecond IR experiment, we could not observe the formation of the corresponding 1,2-didehydroazepine (**3c**) following ultrafast photolysis of *p*-biphenylyl azide (**1c**). We attribute this to the relatively large barrier (6.8 kcal/mol for **3c** vs 5.6 kcal/mol for **3a**) to rearrangement of *p*-biphenylylnitrene, which effectively prohibits isomerization of the corresponding hot nitrene (**2c**).

The kinetics of the formation of the 1,2-didehydroazepine intermediates are complicated by the changes in the band shape and peak position associated with vibrational cooling.[11] In Figure 3 we present the dynamics at 1866 and 1876 cm^{-1} from the time-resolved IR spectra of *o*-biphenylyl azide (**1b**) in acetonitrile. Using ultrafast transient UV−vis spectroscopy, we have previously reported that ultrafast photolysis of *o*-biphenylyl azide (**1b**) produces singlet nitrene (**2b**) which has a lifetime of 16 ± 3 ps in acetonitrile.[8,10] 1,2-Didehydroazepine (**3b**) is formed with a time consistent with the decay of the singlet nitrene (Figures 2 and 3). Fits to the kinetic traces in Figure 3 indicate that the 1,2-didehydroazepine is formed with a time constant of ∼10 ps and undergoes vibrational cooling with a time constant of ∼29 ps. The picture that emerges is that nitrenes (**2a** and **2b**) are born with excess vibrational energy and isomerize to vibrationally excited 1,2-didehydroazepine (**3a** and **3b**).

We have observed the direct formation of 1,2-didehydroazepine from hot phenylnitrene and *o*-biphenylylnitrene. In future studies we will determine the percentage of 1,2-didehydroazepine formed in the picosecond and nanosecond pathways as a function of pump wavelength, solvent, and nitrene structure.

Acknowledgment. This work was performed at The Ohio State University Center for Chemical and Biophysical Dynamics. Support of this work by the National Science Foundation is gratefully acknowledged. The authors are indebted to Professor Michael W. George for sharing with us his unpublished results and for useful conversations.

References

(1) (a) Gritsan, N. P.; Platz, M. S. *Adv. Phys. Org. Chem.* **2001**, 36, 255−304. (b) Gritsan, N. P.; Platz, M. S.; Borden, W. T. *Mol. Supramol. Photochem.* **2005**, *13*, 235.

(2) (a) Gritsan, N. P.; Yuzawa, T.; Platz, M S. *J. Am. Chem. Soc.* **1997**, *119*, 5059−5060. (b) Born, R.; Burda, C.; Senn, P.; Wirz, J. *J. Am. Chem. Soc.* **1997**, *119*, 5061−5062. (c) Gritsan, N. P.; Zhu, Z.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **1999**, *121*, 1202−1207. (d) Borden, W. T.; Gritsan, N. P.; Hadad, C. M.; Karney, W. L.; Kemnitz, C. R.; Platz, M. S. *Acc. Chem. Res.* **2000**, *33*, 765−771. (e) Platz, M. S. In *Reactive Intermediates Chemistry*; Moss, R. A., Platz, M. S., Jones M., Jr., Eds.; Wiley: New York, 2004; p 501.

(3) Karney, W. L.; Borden, W. T. *J. Am. Chem. Soc.* **1997**, *119*, 1378−1387.

(4) Chapman, O. L.; Le Roux, J.-P. *J. Am. Chem. Soc.* **1978**, *100*, 282−285.

(5) (a) Schrock, A. K; Schuster, G. B. *J. Am. Chem. Soc.* **1984**, *106*, 5228−5234. (b) Leyva, E.; Platz, M. S.; Persy, G.; Wirz, J. *J. Am. Chem. Soc.* **1986**, *108*, 3783−3790.

(6) (a) Shields, C. J.; Chrisope, D. R.; Schuster, G. B.; Dixon, A. J.; Poliakoff, M.; Turner, J. J. *J. Am. Chem. Soc.* **1987**, *109*, 4723−4726. (b) Li, Y.-Z.; Kirby, J. P.; George, M. W.; Poliakoff, M.; Schuster, G. B. *J. Am. Chem. Soc.* **1988**, *110*, 8092−8098.

(7) Tsao, M.-L.; Gritsan, N.; James, T. R.; Platz, M. S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **2003**, *125*, 9343−9358.

(8) Burdzinski, G. T.; Gustafson, T. L.; Hackett, J. C.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2005**, *127*, 13764−13765.

(9) Wang, J.; Burdzinski, G. T.; Gustafson, T. L.; Platz, M. S. *J. Org. Chem.* **2006**, *71*, 6221−6228.

(10) Burdzinski, G. T.; Gustafson, T. L.; Wang, J.; Hackett, J. C.; Hadad, C. M.; Platz, M. S. *J. Am. Chem. Soc.* **2006**, *128*, 13402−13411.

(11) (a) Hamm, P.; Ohline, S. M.; Zinth, W. *J. Chem. Phys.* **1997**, *106*, 519−529. (b) Schrader, T.; Sieg, A.; Koller, F.; Schreier, W.; An, Q.; Zinth, W.; Gilch, P. *Chem. Phys. Lett.* **2004**, *392*, 358−364.

JA065783O