

use of an air-sensitive reagent at low concentration, are considerable. We cannot be confident of its reliability; we can, however, confidently state that persulfate reacts *much* more rapidly with  $\text{Cu}^+_{\text{aq}}$  than  $\text{H}_2\text{O}_2$  and *t*-BuOOH do.

The latter result is somewhat surprising. Thus, for example, the specific rates of reaction of  $\text{Cr}^{2+}_{\text{aq}}$  with  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{H}_2\text{O}_2$ , and *t*-BuOOH are  $2.5 \times 10^4$ ,<sup>53</sup>  $7 \times 10^4$ ,<sup>54</sup> and  $1.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$ .<sup>55</sup> An inner-sphere mechanism was proposed for all three reactions. It is possible that  $\text{Cu}^+_{\text{aq}}$  reacts with  $\text{S}_2\text{O}_8^{2-}$  by an outer-sphere mechanism.

### Experimental Section

Peroxides were determined iodometrically; anaerobic conditions were required for precise results. Solutions of  $\text{Cu}^+_{\text{aq}}$  were prepared by reaction of  $\text{Cr}^{2+}_{\text{aq}}$  (from  $\text{Cr}^{3+}_{\text{aq}}$  on zinc amalgam and from Cr metal with acid) with excess  $\text{Cu}^{2+}_{\text{aq}}$ .<sup>56</sup> The concentrations of  $\text{Cr}^{2+}_{\text{aq}}$  were determined from the absorbance at 713 nm taking  $\epsilon = 5 \text{ M}^{-1} \text{ cm}^{-1}$ . The reaction medium contained only perchlorate ions, supplied by perchloric acid and lithium perchlorate. Ionic strength was not always maintained constant.

Kinetic data were determined at 25 °C by the stopped-flow technique with use of a Durrum-Gibson stopped-flow spectrophotometer interfaced

with an OLIS 3820 data acquisition and analysis system. The data from every experiment followed pseudo-first-order kinetics and the rate constants were evaluated by standard methods. The values given are the average of six replicate determinations with any given set of solutions.

Hydrocarbon products were determined with Varian 3700 and Hewlett Packard 5790 chromatographs, calibrated with all the necessary standards. Prior to the analysis of olefins formed in solutions containing  $\text{Cu}^+_{\text{aq}}$ , an excess of  $\text{Fe}_2(\text{SO}_4)_3$  was added. This is required in order to decrease the solubility of the olefins which form stable complexes with  $\text{Cu}^+_{\text{aq}}$ . All experiments were carried out anaerobically with  $\text{Cr}^{2+}$  or  $\text{V}^{2+}$ -scrubbed argon or nitrogen.

Irradiations were performed with a  $^{60}\text{Co}$   $\gamma$ -source with a dose rate of ca.  $2.5 \times 10^3$  Gray/h or by a series of pulses from the linear electron accelerator of the Hebrew University of Jerusalem.

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**Registry No.**  $\text{H}_2\text{O}_2$ , 7722-84-1;  $\text{Cu}^+$ , 17493-86-6;  $\text{Cr}^{2+}$ , 22541-79-3;  $\text{CH}_3\text{CH}_2\text{OH}$ , 64-17-5;  $(\text{CH}_3)_2\text{CHOH}$ , 67-63-0;  $\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{OH}$ , 78-92-2; *t*-BuOOH, 110-05-4;  $\text{S}_2\text{O}_8^{2-}$ , 15092-81-6.

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## Aroylnitrenes with Singlet Ground States: Photochemistry of Acetyl-Substituted Aroyl and Aryloxycarbonyl Azides

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**Abstract:** The photochemistry of 4-acetylbenzoyl azide (ABA), 4-acetyl-4'-biphenoyl azide (ADA), and 4-acetylphenoxy carbonyl azide (APA) shows unusual wavelength and structural effects. Irradiation of ABA or ADA into their  $\pi-\pi^*$  bands with deep-UV light leads to formation of 4-acetylbenzoylnitrene (ABN) and 4-acetyl-4'-biphenoylnitrene (ADN), respectively, in competition with photo-Curtius rearrangement to form isocyanates. Irradiation of these azides into their  $n-\pi^*$  bands with near-UV light gives only the aroylnitrenes. The triplet excited states of the azides were detected chemically and by transient spectroscopic techniques. Nitrogen loss following near-UV irradiation occurs exclusively from the excited triplet azides. However, the chemical properties of ABN and ADN are consistent only with reactions originating from their singlet states. An ESR spectrum is observed at 8 K for ((4-acetylphenoxy)carbonyl)nitrene (APN) but not for 4-acetylbenzoylnitrene (ABN) or 4-acetyl-4'-biphenylcarbonylnitrene (ADN). The chemical properties of APN in *tert*-butyl alcohol show that its triplet is no more than 5 kcal/mol below its lowest singlet state. In contrast, the chemical properties of ABN and ADN indicate that these nitrenes have singlet ground states.

Photochemical reactions of organic azides are specially important because of their use in lithography and in affinity labeling of biological macromolecules.<sup>1,2</sup> It is often assumed in these applications that irradiation of an aryl azide ( $\text{ArN}_3$ ) generates an intermediate nitrene ( $\text{ArN}$ ) which then plays the key role by determining the outcome of the reaction. For example, photolyses of the aryl diazides used in lithography is believed to give triplet nitrenes which crosslink a Novolac resin to modify its solubility properties.<sup>3</sup> Similarly, irradiation of nitro-substituted aryl azides, commonly used photolabeling agents, causes loss of nitrogen and, in favorable cases, formation of a covalent bond between the label

and the targeted macromolecule.<sup>4</sup> The critical requirement for the intermediate in these applications is high chemical reactivity with a wide range of substrates. This is particularly true in a photolabeling experiment where the chemical composition of the target site is unknown.

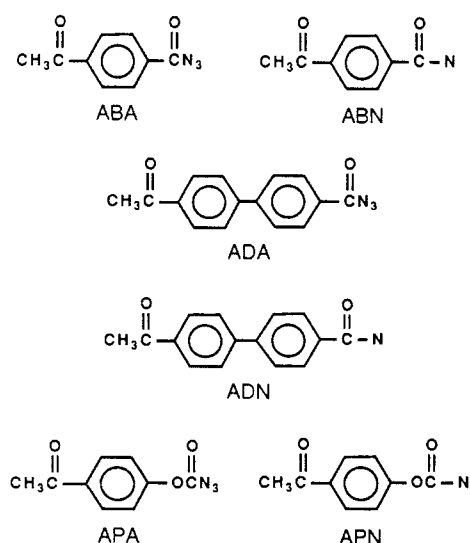
All of the aroylnitrenes that have been investigated to date have triplet ground states.<sup>5</sup> This is unfortunate with respect to applications since singlet nitrenes are generally much more reactive than are triplets. Indeed, we recently concluded that the triplet nitrenes formed from irradiation of nitro-substituted aryl azides may be of only modest utility in photolabeling experiments.<sup>6</sup>

Irradiation of aroyl azides ( $\text{ArCON}_3$ ) or aryloxycarbonyl azides ( $\text{ArOCON}_3$ ) leads to loss of nitrogen with formation of the corresponding nitrene ( $\text{ArCON}$  or  $\text{ArOCON}$ , respectively) and,

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Chart I

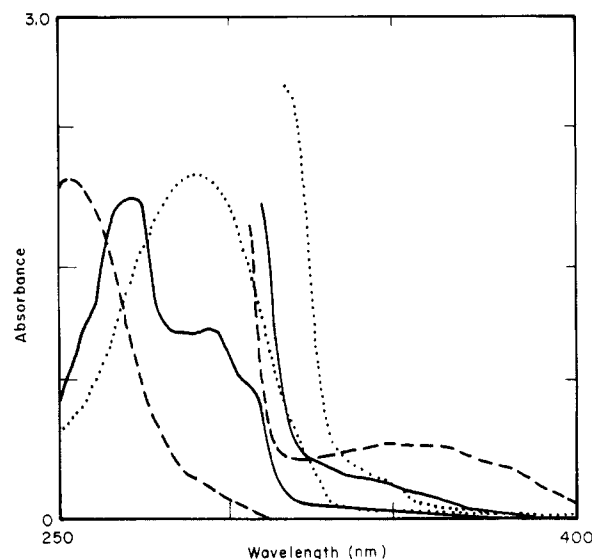


in the case of aroyl azides, an approximately equal amount of the isocyanate ( $\text{ArNCO}$ ) from Curtius rearrangement of the excited azide.<sup>7</sup> Until recently, all computational<sup>8</sup> and experimental<sup>9</sup> investigations of aroyl- and aryloxycarbonylnitrenes were judged to be consistent with triplet ground states for these intermediates. However, we concluded from an investigation of the photochemistry of  $\beta$ -naphthoyl azide that aroylnitrenes may have singlet ground states.<sup>10</sup> This is an important finding with significant theoretical implications and practical consequences. In particular, the extraordinarily high reactivity of ground-state singlet nitrenes may eliminate many of the complications encountered when triplet aroylnitrenes are the reactive intermediates. Unfortunately, the concomitant formation of isocyanates from the photo-Curtius rearrangement of the aroyl azides restricts potential uses of these reagents. Formation of the isocyanates, comparatively weak electrophiles, consumes about half of the starting reagent and may give rise to unacceptable amounts of nonspecific bond formation in photolabeling experiments.

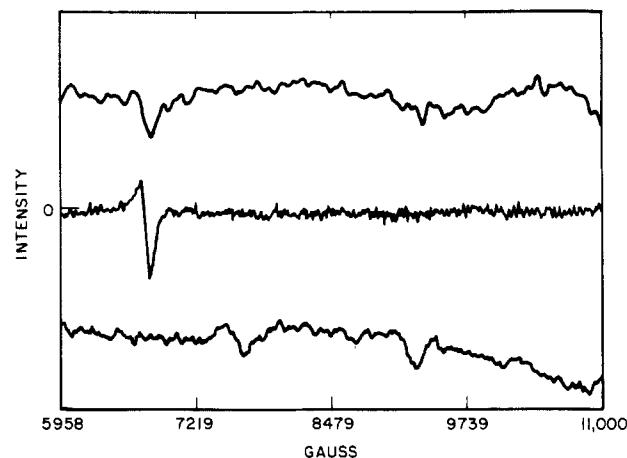
We report herein an investigation of the photochemistry of 4-acetylbenzoyl azide (ABA), 4-acetyl-4'-biphenylcarbonyl azide (ADA), and (4-acetylphenoxy)carbonyl azide (APA), generically AXA, Chart I. We reasoned that the acetyl substituents would shift the electronic absorption of the azides into the convenient near-UV spectral region, that rapid intersystem crossing, typical of aryl ketones, might overwhelm the photo-Curtius rearrangement, and that unimolecular formation of the triplet azides could provide data for assignment of the nitrene spin states. The results demonstrate prevention of isocyanate formation, support singlet multiplicities for the ground states of 4-acetylbenzoylnitrene and 4-acetyl-4'-biphenylcarbonylnitrene (ABN and ADN, respectively), identify a triplet ground state for ((4-acetylphenoxy)carbonyl)nitrene (APN), and provide an estimate for the energy gap ( $\Delta G_{\text{ST}}$ ) separating the singlet and triplet states of APN.

## Results

**(1) Optical Spectroscopy of AXA.** The optical absorption spectra of the three azides in cyclohexane solution are shown in Figure 1. Each compound shows two features in the UV spectral region: low-energy bands ( $\lambda_{\text{max}}$  ca. 350 nm,  $\epsilon_{\text{max}}$  ca.  $50 \text{ M}^{-1} \text{ cm}^{-1}$ ) assigned to  $n-\pi^*$  absorptions of the acetylbenzene chromophore



**Figure 1.** Electronic absorption spectra: ABA (solid line) in cyclohexane solution,  $6.8 \times 10^{-4} \text{ M}$ ; expansion,  $2.9 \times 10^{-3} \text{ M}$ ; ADA (dotted line) in cyclohexane solution,  $5.1 \times 10^{-5} \text{ M}$ ; expansion  $5.1 \times 10^{-4} \text{ M}$ ; APA (dashed line) in cyclohexane solution,  $1.9 \times 10^{-4} \text{ M}$ , expansion,  $9.4 \times 10^{-3} \text{ M}$ .



**Figure 2.** ESR spectra recorded at 8 K after irradiation of suspensions of azides in Fluorolube at 254 nm: top, ABA, the observed resonance is identical with that of (4-acetylphenyl)nitrene; middle, ADA; bottom, APN.

by reference to the spectrum of acetophenone<sup>11</sup> and higher energy bands ( $\lambda_{\text{max}}$  ca. 250–280 nm,  $\epsilon_{\text{max}}$  ca.  $10^4 \text{ M}^{-1} \text{ cm}^{-1}$ ) assigned with similar criteria to  $\pi-\pi^*$  absorptions of this chromophore.

Emission spectra of ABA, ADA, and APA at 77 K were recorded in frozen 2-methyltetrahydrofuran (MTHF) solution. Under these conditions ADA shows two sets of features. The first is a relatively intense fluorescence band with maximum intensity at ca. 410 nm. The second is a weaker phosphorescence emission having apparent maxima at 495 and 525 nm and a lifetime of 0.26 s. Both features decrease in intensity as the ADA is consumed by irradiation showing that they originate with ADA and not with one of its photoproducts. The lowest triplet state of ADA is revealed by these experiments to have an energy of ca. 60 kcal/mol and to be predominantly  $\pi-\pi^*$  in character. The emission spectrum of ABA under these conditions resembles that of acetophenone.<sup>11</sup> It shows a structured phosphorescence band with maximum intensity at 445 nm. As the ABA is consumed by irradiation, this emission is replaced by a strong emission from a product having a maximum at 430 nm. These spectral data show that ABA has a triplet energy of ca. 70 kcal/mol.

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Table I. Chemical and Physical Properties of AXA and AXN

experiment	ABA	ADA	APA
ESR <sup>a</sup>	ArN <sup>3</sup>	ArN <sup>3</sup>	ArOCON <sup>3</sup>
azide phosphorescence <sup>b</sup>	yes	yes	?
(emission max, nm)	(445)	(495, 525)	
triplet-triplet absorptn of azide absorptn max, nm ( $\tau$ )	380 (0.46 $\mu$ s) <sup>c</sup>	410 (8.4 $\mu$ s) <sup>c</sup>	440 (40 ns) <sup>d</sup>
reaction with <i>tert</i> -butyl alcohol <sup>e</sup>	hydroxamate <b>1</b>	hydroxamate <b>5</b>	hydroxamate <b>11</b> benzoxazoline <b>10</b>
reaction with <i>cis</i> -pentene <sup>f</sup>	aziridine <b>3</b> <sup>h</sup>	aziridine <b>6</b> <sup>h</sup>	aziridines <b>8</b> and <b>9</b> <sup>i</sup>
relative reactivity <i>tert</i> -butyl alcohol/ <i>cis</i> -2-pentene	3:1		1:1200
reaction with BHT ( $k_{\text{BHT}}$ , M <sup>-1</sup> s <sup>-1</sup> ) <sup>c</sup>	$2.9 \times 10^9$	$5.6 \times 10^7$	
triplet azide with TMDD ( $k_{\text{TMDD}}$ M <sup>-1</sup> s <sup>-1</sup> )	$7.0 \times 10^9$	$6.7 \times 10^9$	<i>g</i>

<sup>a</sup>Species detected after irradiation in Fluorolube at 8 K. <sup>b</sup>Frozen in an MTHF glass at 77 K. <sup>c</sup>In benzene solution at room temperature. <sup>d</sup>In hexafluorobenzene solution at room temperature. <sup>e</sup>Only the major products are reported here. See the text and Experimental Section for details. <sup>f</sup>In *tert*-butyl alcohol solution containing 0.3 M *cis*-4-methyl-2-pentene. <sup>g</sup>Triplet APA is quenched by TMDD, but the low solubility of the quencher prohibits quantitative analysis. <sup>h</sup>Stereospecific. <sup>i</sup>Nonstereospecific.

The emission observed from irradiation of APA under the low-temperature conditions cannot be confidently assigned. The strong phosphorescence of a photoproduct grows into the spectrum when the APA sample is irradiated. The product emission obscures the spectral region that might contain the phosphorescence of APA.

(2) **Electron Spin Resonance Spectroscopy.** Nitrenes with triplet ground states give distinctive ESR spectra.<sup>5</sup> Irradiation (254 nm) of a Fluorolube suspension of APA at 8 K in the cavity of an X-band ESR spectrometer gives the readily detectable spectrum characteristic of triplet APN shown in Figure 2 ( $|D| = 1.65 \text{ cm}^{-1}$ ,  $|E| = 0.024 \text{ cm}^{-1}$ ). Identical irradiations of Fluorolube suspensions of ABN or ADA do not give spectra that can be assigned to the triplet of ABN or ADN. However, prolonged photolysis of these samples does generate ESR spectra characteristic of 4-acetylphenylnitrene and of 4-acetyl-4'-biphenylnitrene, respectively. The aryl nitrenes observed in these experiments arise from secondary photodecarbonylation<sup>5,12</sup> of the isocyanates formed in the initial photo-Curtius rearrangement of the azides (see below). These and other experiments are summarized in Table I.

The observation of an ESR spectrum at low temperature for the case of APN all but confirms a triplet ground state for this intermediate. The absence of observable ESR spectra for ABN and ADN suggests that the ground states of these nitrenes have singlet spin multiplicity. This finding is supported strongly by analysis of the chemical properties of these nitrenes.

(3A) **Transient Absorption Spectroscopy at Room Temperature:** ABA. Irradiation of a N<sub>2</sub>-purged solution of ABA in benzene with the output of a pulsed nitrogen laser (337 nm, 13 ns, 7 mJ) gives a transient absorption spectrum with a strong band near 380 nm and a second, weaker, broad band with maximum at ca. 480 nm (Figure 3A), a profile quite similar to the absorption spectrum of triplet acetophenone.<sup>13</sup> This transient species is formed within the rise time of the laser pulse and then decays following a first-order rate law with a lifetime of 0.46  $\mu$ s.

The lifetime of the transient species formed by irradiation of ABA in benzene is reduced when naphthalene (which does not absorb light at 337 nm) is included in the reaction mixture. The transient is quenched by naphthalene with a rate constant of  $6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the diffusion limited value, and results in readily detected (by its characteristic absorption spectrum) formation of triplet naphthalene,<sup>13</sup> Figure 3B. Significantly, naphthalene is also a quencher of the photochemical reactions of ABA (see below). Identical results are obtained (except that the triplet-triplet absorption spectrum cannot be detected) when tetramethyldiazetidine dioxido TMDD<sup>14</sup> or oxygen is the quencher of the transient species. In contrast, *tert*-butyl alcohol, which reacts efficiently with ABN, has no effect on the lifetime of the detected intermediate. These experiments and the similarity of its absorption profile to that of triplet acetophenone allow confident assignment of the transient intermediate detected from photolysis

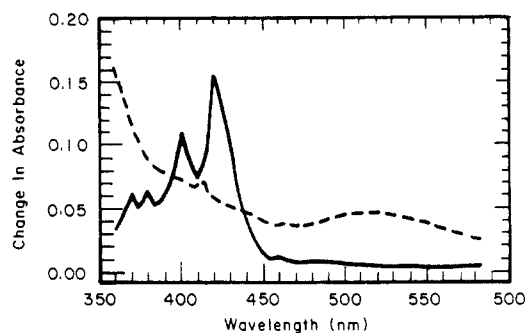
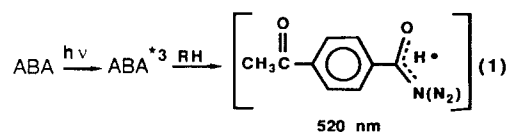


Figure 3. A (dashed): transient spectrum recorded 100 ns after irradiation of a benzene solution of ABA with the output of a nitrogen laser. B (solid): transient spectrum recorded 1.5  $\mu$ s after irradiation of a benzene solution of ABA containing naphthalene (0.01 M) with the output of a nitrogen laser.

of ABA in benzene as the triplet azide (ABA<sup>\*3</sup>).

Pulsed irradiation of ABA in cyclohexane solution gives a significantly different result. In addition to the absorptions assigned to ABA<sup>\*3</sup>, a second feature is detected that has an absorption maximum at ca. 520 nm. This second species grows into the spectrum over an ca. 2  $\mu$ s time scale as the triplet azide absorption decays and is consumed in subsequent reactions over a period of several hundred microseconds. The lifetime of the 520 nm absorbing species is unaffected by naphthalene, but the amount of this species formed decreases as the naphthalene concentration in the sample is raised. When the cyclohexane in this experiment is replaced by cyclohexane-*d*<sub>12</sub>, the amount of the 520 nm absorbing transient formed is reduced by about a factor of two, and, importantly, its rate of formation is similarly slowed. Finally, tri-*n*-butylstannane and 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT) are observed to quench ABA<sup>\*3</sup> in benzene with bimolecular rate constants of  $8 \times 10^8$  and  $2.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , respectively. Reaction of ABA<sup>\*3</sup> with these reagents results in formation of the product absorbing at 520 nm and isolation of the corresponding primary amide (see below).

The experiments in cyclohexane solution and the similarity of the spectrum of the 520 nm absorbing transient to the ketyl radical of acetophenone<sup>15</sup> clearly show that ABA<sup>\*3</sup> abstracts a hydrogen atom from cyclohexane to form a radical, eq 1. The precise



structure of this radical is not revealed by these experiments. The product studies show that the hydrogen atom is transferred to the carbonyl azide group not to the acetyl group. However, it is not possible to say from these results whether or not the detected radical still contains the nitrogen molecule it must eventually lose.

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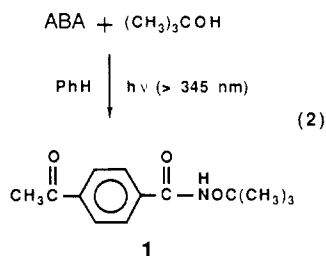
(14) Ullman, E. F.; Singh, P. *J. Am. Chem. Soc.* **1972**, *94*, 5077.

(15) Reference 11, page 385.

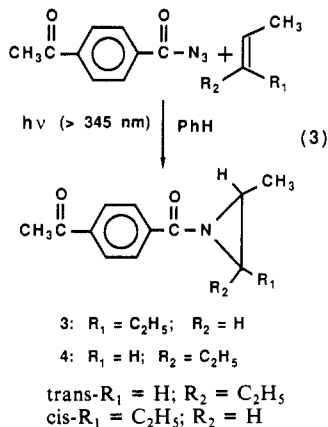
**(3B) Transient Absorption Spectroscopy at Room Temperature: ADA.** Pulsed irradiation of ADA in a  $N_2$ -purged benzene solution generates a strongly absorbing ( $\lambda_{\max} = 410$  nm) transient intermediate with a lifetime of 8.4  $\mu$ s. The intermediate is quenched rapidly by oxygen or TMDD ( $k_{\text{TMDD}} = 6.7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ) to reform the azide (see below). In contrast to the behavior of ABA, the intermediate formed from ADA does not react with cyclohexane; the spectrum and the lifetime of the transient are the same in cyclohexane as they are in benzene solution. The intermediate does react with BHT ( $k_{\text{BHT}} = 5.6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ ) to give eventually 4-acetyl-4'-diphenylcarboxamide. The transient species detected in the pulsed irradiation of ADA is assigned to the triplet azide (ADA\*)<sup>3</sup> based upon the close similarity of its spectrum to that of triplet 4-acetyl-4'-biphenyl<sup>13</sup> and on its chemical and physical properties.

**(3C) Transient Absorption Spectroscopy at Room Temperature: APA.** Pulsed irradiation of APA in hexafluorobenzene solution reveals an intermediate, formed immediately on this time scale, with a broad absorbance maximum at ca. 440 nm. The absorption decays with a lifetime of 40 ns (100 ns when *tert*-butyl alcohol is the solvent), is quenched by TMDD, and transfers energy to form triplet naphthalene. The structure of this species is assigned to triplet azide (APA\*)<sup>3</sup>. When this experiment is repeated in benzene solution, a second species with a weak, broad, long-lived absorption from 400–600 nm is present in the spectrum. The structure of the compound responsible for this absorption feature cannot be assigned with confidence, but we suspect it to be a product from reaction with benzene since this absorption is absent when hexafluorobenzene<sup>16</sup> is the solvent.

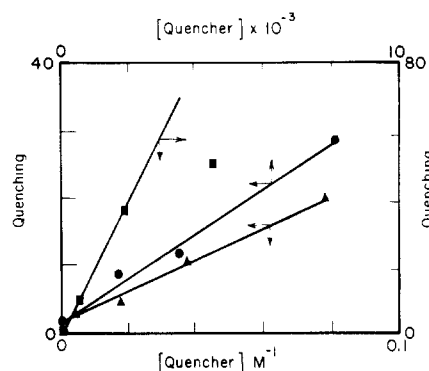
**(4A) Photochemistry of ABA: Alcohol and Olefins.** Irradiation of ABA in an  $N_2$ -purged benzene solution containing 2.1 M *tert*-butyl alcohol into its  $n \rightarrow \pi^*$  absorption band ( $\lambda > 345$  nm) gives hydroxamate **1** in essentially quantitative yield, eq 2: no



isocyanate (**2**) from Curtius rearrangement of the azide can be detected in this reaction. Similar photolyses of ABA in benzene solutions containing either *cis*- or *trans*-4-methyl-2-pentene (0.05 M) gives only aziridines (**3** and **4**, respectively) with total retention of the olefin's stereochemistry in both cases, eq 3. Both hy-



droxamate formation<sup>17</sup> and stereospecific aziridination<sup>18</sup> are



**Figure 4.** Stern-Volmer quenching plots: A (squares), inhibition of the stereospecific aziridination of *cis*-4-methyl-2-pentene by ABN with naphthalene in benzene solution; B (triangles), inhibition of the stereospecific aziridination of *cis*-4-methyl-2-pentene by ADN with TMDD in benzene solution; C (circles), quenching of the nonstereospecific aziridination of *cis*-4-methyl-2-pentene by APN with naphthalene in benzene solution.

processes traditionally considered to signal the reaction of a singlet nitrene. Irradiation of ABA in *tert*-butyl alcohol containing the *cis*-pentene (0.3 M) gives both hydroxamate **1** and *cis*-aziridine **3** in a ratio of 100:1. This competition experiment shows that ABN combines with the alcohol three times faster than it reacts with the olefin.

The photoreactions of ABA are quenched when naphthalene is included in the reaction mixture. For example, increasing the concentration of naphthalene in benzene solutions of ABA containing the *cis*-pentene slows the photoreaction without changing the identity of the product. At high naphthalene concentration (0.03 M), the inhibition of this reaction is greater than 97%. Quantitative analysis of the quenching data by the Stern-Volmer approach is shown on Figure 4A. Significantly, the Stern-Volmer slopes for quenching of the photoreactions of ABA are consistent with the value obtained spectroscopically for the quenching of ABA\*<sup>3</sup> by naphthalene. These experiments show clearly that under these conditions the products characteristic of the reaction of the nitrene singlet (ABN<sup>1</sup>) are formed by a route that passes through the excited triplet azide (ABA\*<sup>3</sup>).

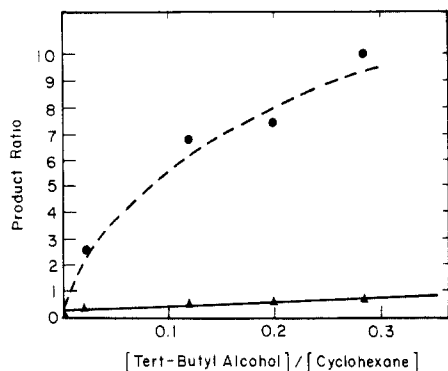
**(4B) Photochemistry of ADA: Alcohol and Olefins.** Photolysis of ADA in benzene solutions gives results that are precisely analogous to those obtained for irradiations of ABA. Hydroxamate (**5**) is formed exclusively when *tert*-butyl alcohol is present in the solution, aziridines **6** and **7** are formed with complete retention of stereochemistry when the *cis*- or *trans*-2-pentenes are the nitrene trapping agents, and no isocyanate from the Curtius rearrangement can be detected. Consumption of the azide, formation of the hydroxamate, and formation of the aziridines are quenched by TMDD. The Stern-Volmer slope ( $k_q\tau = 6.0 \times 10^4 \text{ M}^{-1}$ , Figure 4B) for quenching of aziridine formation from the *cis*-pentene agrees well with the kinetic data for quenching of ADA\*<sup>3</sup> by TMDD obtained spectroscopically (see above). These results show that the nitrene singlet (ADN<sup>1</sup>) is formed by a path that passes through the excited triplet azide (ADA\*<sup>3</sup>).

**(4C) Photochemistry of APA: Alcohol and Olefins.** Irradiation of APA in benzene solution gives results that are significantly different from those obtained by photolyses of ABA or ADA: both *cis*- and *trans*-pentenes (0.05–3 M) give mixtures of aziridine isomers in high overall yields (**8** and **9**; *cis*:*trans* = 1:2 from the *cis*-pentene and 1:3 when the *trans*-olefin is the nitrene trap). Control experiments show that the olefins are not isomerized prior to aziridine formation and that the aziridines themselves are not isomerized under these reaction conditions after they are formed. As expected from the spectroscopic results described above, naphthalene stops the reactions of APA by quenching ( $k_q\tau = 230$

(16) Hexafluorobenzene is expected to be particularly inert to reaction with the nitrene: Gale, D. M. *J. Org. Chem.* **1968**, *33*, 2536.

(17) Eibler, E.; Sauer, J. *Tetrahedron Lett.* **1974**, 2569. Shingaki, T.; Inagaki, M.; Takebayashi, M.; Lwowski, W. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 3567.

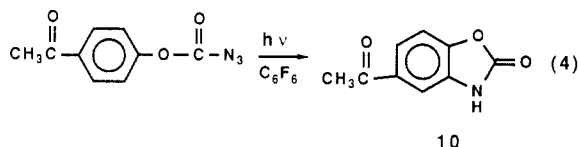
(18) Woodworth, R. C.; Skell, P. S. *J. Am. Chem. Soc.* **1959**, *81*, 3383. Atkinson, R. S.; Awad, S. B., *J. Chem. Soc., Perkin Trans. 1* **1977**, 346. Atkinson, R. S.; Malpass, J. R. *J. Chem. Soc., Perkin Trans. 1* **1977**, 2242. Lwowski, W. *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 897.



**Figure 5.** Circles: yield of hydroxamate **1** divided by that of insertion product **14** for irradiation of ABA in cyclohexane solution as the concentration of *tert*-butyl alcohol is increased. Triangles: yield of hydroxamate **1** divided by that of amide **13** for irradiation of ABA in cyclohexane as the concentration of *tert*-butyl alcohol is increased.

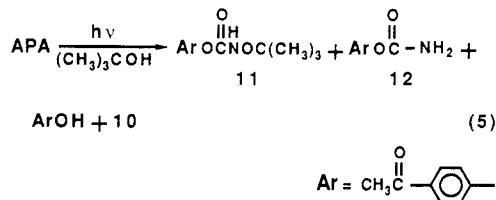
$M^{-1}$ , Figure 4C) the azide triplet ( $APA^{*3}$ ). The stereochemistry of the aziridination reaction, however, is unaffected by the presence of the quencher. Interestingly, thermolysis of APA in benzene solutions containing either the *cis*- or *trans*-pentene (6.0 M) gives aziridines with high retention of olefin configuration (ca. 95:5 in both cases). The nonstereospecific aziridination observed photochemically is characteristic of a triplet nitrene. These experiments and the ESR spectroscopic studies described above show convincingly that the ground state of APN is a triplet ( $APN^3$ ) and that it is formed in these photolyses exclusively by a route that passes through the triplet azide.

Irradiation ( $>345$  nm) of a hexafluorobenzene solution of APA gives 4-acetylbenzoxazolinone (**10**), eq 4. This reaction, too, is



quenched by naphthalene. Related intramolecular addition reactions of aryloxy carbonyl nitrenes to arene substituents have been observed previously in the gas phase.<sup>19</sup> Evidently hexafluorobenzene is sufficiently inert that APN attacks itself rather than react with this solvent.

Photolysis of APA in *tert*-butyl alcohol solution gives two major and two minor products: **10** (40%) from the intramolecular addition of the nitrene, hydroxamate **11** (44%) from capture of the nitrene by the solvent, 4-hydroxyacetophenone (7%), and 4-acetylphenyl carbamate **12** (5%), eq 5. Significantly, the

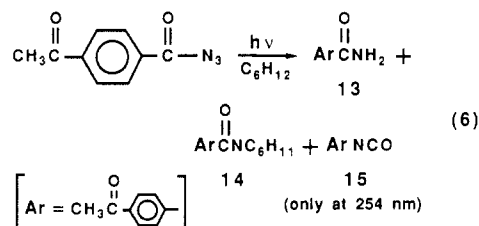


formation of hydroxamate **11** in this experiment is quenched by naphthalene ( $k_q\tau = 400 M^{-1}$ ). Irradiation of APA in *tert*-butyl alcohol containing a small amount of the *cis*-pentene (0.3 M) gives *cis*- and *trans*-aziridines **8** and **9** (1:2.5) and hydroxamate **11** in a ratio of 40:1. Thus, in striking contrast to the behavior of ABN, this competition experiment shows that APN combines with the alcohol ca. 1200 times slower than it reacts with the olefin.

Formation of hydroxamate **11** from APN seems to contradict the ESR spectroscopy results and the implication from the olefin trapping results that this nitrene is a triplet in its ground state. The dilemma is resolved by consideration of the results of the

competition experiment. APN behaves like a normal triplet nitrene in its reaction with the *cis*-pentene, but its reaction with *tert*-butyl alcohol is much slower than the comparable reaction of ABN. Indeed, APN is so unreactive toward *tert*-butyl alcohol that even the intramolecular arene addition to form **10** competes successfully with hydroxamate formation. This rate retardation must signal operation of a special path for the reaction of APN with the alcohol to form hydroxamate. Further consideration of this path is reserved for the Discussion section.

**(5A) Photochemistry of ABA in Cyclohexane Solution.** Irradiation of ABA in a  $N_2$ -purged cyclohexane solution into its  $n-\pi^*$  absorption band ( $\lambda > 345$  nm) gives two products. The first is 4-acetylbenzamide (**13**) and the second is 4-acetyl-*N*-cyclohexylbenzamide (**14**) formed by insertion into a carbon-hydrogen bond of the solvent; a reaction characteristic of singlet nitrenes, eq 6.<sup>20</sup> Under these photolysis conditions no ( $<2\%$ ) 4-acetylphenyl



isocyanate (**15**) could be detected in the reaction mixture. In contrast, irradiation of an identical solution of ABA at 254 nm, into the  $\pi-\pi^*$  band of the azide, gives amides **13** (27%) and **14** (41%) and 23% yield of isocyanate **15** from the photo-Curtius rearrangement.

It is a matter of some importance to identify the mechanism for formation of amide **13** in the irradiation of ABA in cyclohexane. Observation of related products from other azides has been used as evidence in support of postulation of triplet multiplicity for the ground states of aroylnitrenes.<sup>9</sup> We considered two intermediates that might be responsible for initiating the reactions that lead to formation of amide **13**: the triplet nitrene and the electronically excited triplet azide. A series of experiments was carried out in an attempt to distinguish between these choices.

Irradiation of ABA in cyclohexane solution containing *tert*-butyl alcohol gives amide **13**, insertion product **14**, and hydroxamate **1**. The yields of these products change in a meaningful way as the concentration of the alcohol in the solution is varied. Figure 5 shows plots of the ratios for the yields of hydroxamate **1** to amide **13** and for **1** to insertion product **14** versus the concentration of *tert*-butyl alcohol divided by the concentration of cyclohexane in the reaction mixture. It is evident from inspection of these plots that formation of the hydroxamate and the insertion product compete directly for the same intermediate, both of these products are characteristic of reactions from the singlet nitrene, but that the path leading to amide **13** does not involve competition between the alcohol and cyclohexane (the slight change in the hydroxamate to amide ratio is due to dilution of the cyclohexane as the alcohol concentration increases). The curvature in the plot for hydroxamate to insertion product yield is a consequence of association of the alcohol in nonpolar solvents and has been seen previously for reactions of carbenes.<sup>21</sup> These experiments show that two distinct, nonequilibrating reactive intermediates were formed from photolysis of ABA; one gives amide **13**, the other gives both the hydroxamate and the insertion product.

Early studies of the photochemistry of benzoylazide in alcohol solution revealed operation of a chain reaction that gives benzamide in high yield.<sup>22</sup> The possibility that a related process operates in cyclohexane solution to form amide **13** in the irradiation of ABA was probed with a crossover experiment. If some intermediate free radical transfers a hydrogen atom to ABA in

(20) Simson, J. M.; Lwowski, W. *J. Am. Chem. Soc.* **1969**, *91*, 5107.

(21) Griller, D.; Liu, M. T. H.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5549.

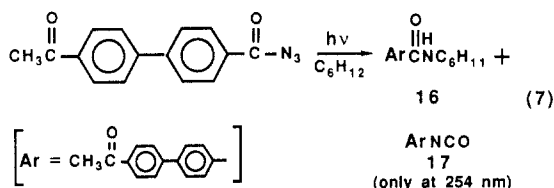
(22) Sukigara, M.; Sato, Y.; Honda, K.; Kikuchi, S. *Nippon Shashin Gakkaishi* **1971**, *35*, 94.

(19) Meth-Cohn, O. *Heterocycles* **1980**, *14*, 1497. Meth-Cohn, O.; Rhouati, S. *J. Chem. Soc., Chem. Commun.* **1981**, 241. Meth-Cohn, O. *Acc. Chem. Res.* **1987**, *20*, 18.

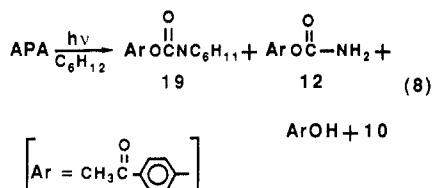
the chain propagation step leading to **13**, then the same radical should also transfer a hydrogen atom to benzoyl azide and give benzamide as a product. Irradiation of a cyclohexane solution containing both ABA (0.005 M) and benzoyl azide (0.027 M) at 350 nm (only ABA absorbs light) gives amide **13** and insertion product **14**; no benzamide could be detected in the product mixture. In contrast, when this experiment was repeated with ethanol as the solvent, the products formed are amide **13** and benzamide from crossover. Evidently, the free-radical chain reaction that converts aroyl azides to amides requires ethanol as a reagent and does not occur in cyclohexane solutions.

Further evidence for the identity of the intermediate leading to amide **13** comes from analysis of the quantum yields for the reactions of ABA. The laser spectroscopic results show that the triplet azide reacts slowly with cyclohexane and more rapidly with BHT by a hydrogen abstraction path. If this process leads to amide **13**, then addition of BHT to solutions of ABA should increase the quantum yield for azide consumption. The quantum yields for reaction of ABA were determined in hexafluorobenzene solution (formation of a trace amount of an absorbing product complicates the analysis when benzene is the solvent) by comparison with an Aberchrome actinometer.<sup>23</sup> The quantum yield for consumption of the azide in the absence of BHT is  $0.4 \pm 0.1$  at 10% conversion. When this experiment is repeated with BHT added to the solution, the quantum yield for azide disappearance increases to  $1.3 \pm 0.3$ . This result shows that amide **13** is formed, at least in part, by a reaction of the triplet azide.

**(5B) Photochemistry of ADA in Cyclohexane Solution.** Comparison of the photochemistry of ABA with that of ADA in cyclohexane solution provides insight into a key factor that controls hydrogen atom abstraction by aroyl azides. Irradiation of ADA into its  $n-\pi^*$  chromophore leads exclusively to formation of insertion product **16**. Its irradiation at 254 nm gives **16** (60%) and isocyanate **17** (40%). We are unable to detect a significant yield of 4-acetyl-4'-biphenylcarboxamide (**18**) from photolysis of ADA under these conditions, eq 7. The contrasting behavior of ABA and ADA may be traced to the change in the electronic configurations of their triplet states.



**(5C) Photochemistry of APA in Cyclohexane Solution.** Irradiation of APA in cyclohexane solution of 350 nm gives two major products, carbamate **12** in 60% yield and 4-acetyl-*N*-cyclohexyl phenylcarbamate (**19**) in 30% yield, and small amounts (ca. 5%) of 4-hydroxyacetophenone and 5-acetylbenzoxazolinone (**10**), eq 8. In contrast to photolyses of ABA or ADA in cyclohexane



solutions, the yields of the amides from APA are essentially unchanged when 3.0 M *tert*-butyl alcohol is included in the reaction mixture. The yield of hydroxamate **11** in this experiment is only 3%, thus even the reaction of the APN with cyclohexane is much faster than its reaction with *tert*-butyl alcohol.

## Discussion

The results reported above provide clear pictures of the photochemistry of acetyl-substituted aroyl and aryloxy-carbonyl azides

and of the chemical and physical properties of their derived nitrenes. Three critical parameters are revealed to control the behavior of these materials: the electronic configuration of the excited singlet azide reached by absorption of light; the electronic configuration of the lowest energy triplet state of the azide; and the spin multiplicity of the ground-state nitrene. Here we discuss the properties of each azide and nitrene in an attempt to relate their structures systematically to their reactivity.

**(1) Wavelength Dependent Photochemistry.** Irradiation of ABA or ADA at 254 nm (deep-UV) causes both photo-Curtius rearrangement to form isocyanates and loss of nitrogen to generate nitrenes, Scheme I (Ar represents phenyl or diphenyl). In contrast, irradiation of these azides at wavelengths greater than 345 nm (near-UV) gives only the products derived from nitrenes; no isocyanates are detected. The quenching and spectroscopic results show that the nitrenes formed by near-UV photolyses arise entirely from loss of nitrogen by the triplet excited states for both of these azides. The triplet states of aroyl azides are known not to undergo the Curtius rearrangement,<sup>10</sup> thus the difference between deep- and near-UV photolysis of these azides must depend on the nature of the excited state reached by absorption of light.

Deep-UV irradiation creates an upper excited singlet state of the azide ( $^{11}$ ) with a predominantly  $\pi-\pi^*$  electronic configuration. Curtius rearrangement from this state competes successfully with its other relaxation or reaction paths. Near-UV photolysis forms the lower energy  $n-\pi^*$  singlet states ( $^1$ ) of the azides. Intersystem crossing, a process typically very rapid for aryl ketones have nearly degenerate  $n-\pi^*$  and  $\pi-\pi^*$  states,<sup>11</sup> evidently depopulates the singlet azide before it can rearrange to isocyanate. The results in hand do not identify the source of the nitrenes in the deep-UV irradiations; nitrogen loss could occur directly from the upper singlet state, or this state might relax or intersystem cross prior to nitrene generation. However, it is clear that the aroyl nitrenes themselves do not rearrange to form isocyanates. Related wavelength dependent reactions have recently been reported for some diazo compounds.<sup>24</sup>

**(2) Electronic Configuration Dependent Chemistry of Triplet Aroyl Azides.** Irradiation of ABA in cyclohexane solution gives a significant yield of amide **13**. In contrast, irradiation of ADA under these conditions does not give a detectable amount of the analogous primary amide **18**. The chemical and spectroscopic findings indicate that the source of amide **13** in the photolysis of ABA is the triplet azide. Thus the contrasting chemical behavior of ABA and ADA must be traced to a difference between their triplet states.

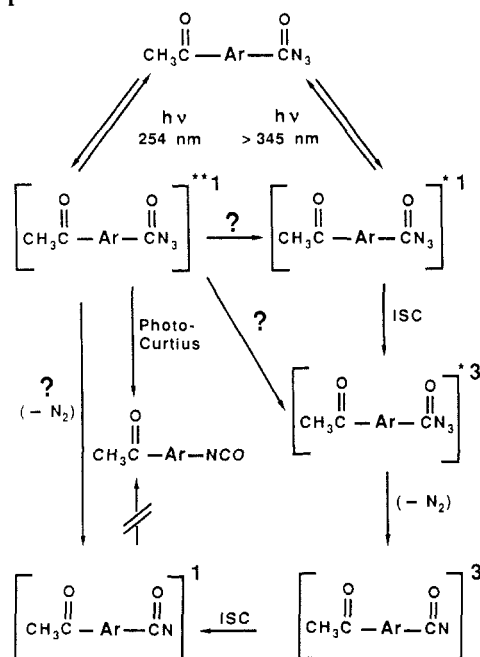
Analogy with the photochemistry of acetophenone and 4-acetylphenyl<sup>11</sup> and the ca. 100-fold greater rate constant for reaction of ABA<sup>3</sup> than ADA<sup>3</sup> with BHT suggests a straightforward explanation for the different chemical behavior of these azides. The electronic configuration of the lowest energy triplet state of ABA has more  $n-\pi^*$  character than the triplet state of ADA. In general,  $n-\pi^*$  states are effective hydrogen atom abstractors and  $\pi-\pi^*$  states are not. This pattern evidently holds for the reactions of the acetyl-substituted aroyl azides. Triplets ABA and APA, but not triplet ADA, abstract hydrogen atoms from cyclohexane in competition with their loss of nitrogen to form nitrenes.

**(3) Ground-State Spin Multiplicity of Aroyl- and Aryloxy-carbonylnitrenes.** One of the prime objectives in undertaking this work was to determine the multiplicity of ground-state aroyl-nitrenes. This task is difficult when such a highly reactive intermediate is a singlet. In these cases ESR spectroscopic experiments can only give "negative" results, and the chemical evidence that can be brought to bear is always subject to interpretation. For example, it is often possible to classify an observed reaction as one from a singlet nitrene, but it is difficult to determine if the characterizing reaction is merely faster than intersystem crossing to the triplet or a process originating from a ground-state singlet. The results reported above, in particular the comparison of APN with ABN and ADN, resolve this particular dilemma

(23) Heller, H. G.; Langan, J. R. *J. Chem. Soc., Perkin Trans. 2* **1981**, 341.

(24) Li, Y.-Z.; Schuster, G. B. *J. Org. Chem.* **1987**, 52, 4460.

Scheme I



and leave little doubt that aroyl nitrenes generally have singlet ground states.<sup>10</sup>

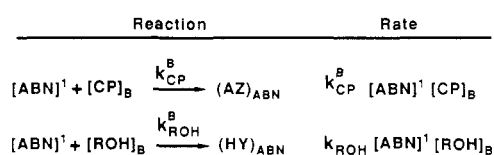
The ESR spectra of many nitrenes generated by photolysis of azides at low temperature have been observed.<sup>5,25</sup> However, despite efforts by us and others<sup>10</sup> irradiation of an aroyl azide has never been reported to give an ESR spectrum characteristic of an aroyl nitrene. Two important control experiments substantiate this negative finding in the present work. First, irradiation of APA, certainly a very close model for ABA and ADA, does give the ESR spectrum of APN. Second, deep-UV irradiation of ABA or ADA solutions for extended times generate ESR spectra characteristic of aryl nitrenes formed by photodecarbonylation of the first-formed isocyanates. The first observation validates the experimental design, and the second verifies azide photochemistry at low temperature and the stability of triplet nitrenes under these conditions.

The chemical properties of these nitrenes are consistent with the ESR spectroscopic results. APN usually behaves as a classical triplet in its reactions: it abstracts hydrogen atoms from hydrocarbons, and its reactions with olefins forms aziridines with scrambled stereochemistry. On the other hand, both ABN and ADN behave exclusively as singlet nitrenes: stereochemical orientation is maintained in their aziridination reactions, they form hydroxamates rapidly in nearly quantitative yields, and they insert efficiently into unactivated carbon-hydrogen bonds. The contrasting chemical properties of the nitrenes are easily understood to be a consequence of a change in multiplicity of the reacting state.

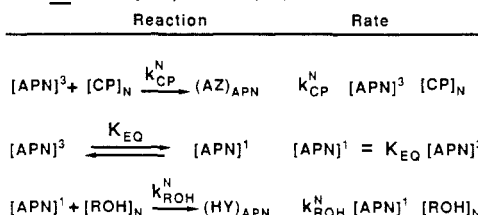
The path for formation of these nitrenes insures in each case that their first-formed state is a triplet. The photoreactions of the azides are stopped by triplet quenchers with rate constants that correspond to those obtained spectroscopically by direct observation of the triplet azides. These experiments support the reaction sequence outlined in Scheme I. Near-UV irradiation generates an  $n-\pi^*$  singlet state of the azide, but intersystem crossing to its triplet occurs before any significant (<3% in the case of ABA) chemical reaction. Spin conservation during nitrogen loss from the triplet azide requires that the first nitrene state be a triplet. The triplet is usually the reactive state for APN, but for ABN and ADN the reactive states are always singlets. The only way that these singlets can be formed is by intersystem crossing of the triplet nitrenes. This requires that the energy of

Scheme II

A) Reactions of ABN with *tert*-Butyl Alcohol (ROH) and *cis*-4-methyl-2-pentene (CP).



B) Reactions of APN with *tert*-Butyl Alcohol (ROH) and *cis*-4-methyl-2-pentene (CP).



Where: (AZ)<sub>AXN</sub> stands for the aziridines from CP and APN or ABN respectively and (HY)<sub>AXN</sub> similarly represents the hydroxamates.

these singlet nitrenes be below or only very slightly above the triplets.

APN provides an example of a nitrene where the singlet is only slightly above the triplet ground state. The reaction of APN with *tert*-butyl alcohol is especially significant since in this instance a triplet nitrene appears to give a product usually taken as characteristic of the reaction of the singlet. This reaction occurs with a rate much smaller than that of the corresponding reactions of ABN and ADN with the alcohol, and inclusion of even a small amount of olefin in the alcohol solution causes nearly exclusive formation of aziridine from triplet APN.

The most economical interpretation of the experiments conducted in *tert*-butyl alcohol suggests that triplet APN is in equilibrium with its upper singlet state. This hypothesis leads to the network of equations for the competition reactions of ABN and APN with the *cis*-pentene and *tert*-butyl alcohol shown in Scheme II. Analysis of this scheme gives eq 9 which relates the

$$\frac{[AZ/HY]_{ABN}}{[AZ/HY]_{APN}} = \frac{[CP]_B [ROH]_N}{[CP]_N [ROH]_B} \left[ \frac{k_{ROH}^N}{k_{ROH}^B} \right] \left[ \frac{k_{CP}^B}{k_{CP}^N} \right] K_{EQ} \quad (9)$$

yields of aziridines and hydroxamates to the concentrations of the alcohol and olefin and the rate and equilibrium constants defined in the scheme. The data in hand do not permit direct solution of eq 9. However, with two reasonable approximations, an upper limit for the magnitude of  $K_{EQ}$  can be obtained. First, we assume that singlet APN and singlet ABN are equally reactive toward *tert*-butyl alcohol ( $k_{ROH}^N/k_{ROH}^B = 1$ ). It is known from studies of carbenes that their analogous reaction to form ethers with alcohols occurs at approximately the diffusion-limited rate.<sup>26</sup> Second, we assume that singlet ABN reacts with the *cis*-pentene faster than triplet APN reacts with this olefin ( $k_{CP}^B/k_{CP}^N > 1$ ). This view is supported by extended basis set ab initio calculations which show that singlet HN (imidogen) adds concertedly to ethylene with no activation barrier, but addition of triplet HN to ethylene has a barrier height of ca. 24 kcal/mol.<sup>27</sup> With these approximations, the upper limit for  $K_{EQ}$  is calculated from eq 9 to be 5000; this corresponds to  $\Delta G_{ST} < 5$  kcal/mol for APN in *tert*-butyl alcohol.

Only two other experimental measurements of a singlet-triplet gap for nitrenes have been reported. Gas-phase spectroscopy of

(25) Platz, M. S. In *Azides and Nitrenes*; Scriven, E. F. V., Ed.; Academic Press: 1984; Chapter 7.

(26) Schuster, G. B. *Adv. Phys. Org. Chem.* **1986**, 22, 311.

(27) Fueno, T.; Bonacic-Koutecky, V.; Koutecky, J. *J. Am. Chem. Soc.* **1983**, 105, 5547.



HN gives a value of 36 kcal/mol,<sup>28</sup> and electron photodetachment experiments yield a value of ca. 4 kcal/mol for phenylnitrene.<sup>29</sup> Our estimate for APN relies on several assumptions; however, the qualitative conclusion that the singlet of this nitrene is only slightly above its triplet ground state seems sound regardless of the quantitative validity of the approximations.

We have previously suggested that the interaction of the nitrene–nitrogen orbitals with those of the adjacent carbonyl group on aroylnitrenes breaks symmetry and causes inversion of the normal ordering of nitrene states.<sup>10</sup> Some documentation for this view is revealed by consideration of the zero-field parameters for APN. The ESR spectra of aryl- and alkyl nitrenes show that these triplets have *E* values indistinguishable from zero.<sup>5,30</sup> In contrast, the *E* value for APN (and for ethoxycarbonylnitrene)<sup>5</sup> is significantly different from zero. This shows that the *x* and *y* axes for APN are not interchangeable—precisely the broken symmetry required for reducing the singlet–triplet gap. This gap is reduced in APN by more than 30 kcal/mol compared with its value in symmetrical HN. For ABN and ADN the energy of their singlets is lowered to the extent that they become the ground states ( $\Delta G_{ST} < 0$ ).

## Conclusion

All experimental evidence shows that aroylnitrenes have singlet ground states. Aryloxycarbonylnitrenes are triplets but have nearby singlet states. These findings have significant theoretical and practical implications.

## Experimental Section

**4-Acetylbenzoyl Azide (ABA).** 4-Acetylbenzoic acid<sup>32,33</sup> (2 g, 12.1 mmol) was dissolved in 30 mL of DMF, and the solution was cooled to 0 °C under a nitrogen atmosphere. Triethylamine (1 equiv) was added to the stirred solution, and then ethyl chloroformate (1 equiv) was slowly added. The reaction mixture was stirred at 0 °C for 30 min and then warmed to room temperature. Sodium azide (1 equiv) in 7 mL of H<sub>2</sub>O was added dropwise to the reaction mixture. Stirring was continued for an additional 30 min at room temperature, and then the mixture was poured into ice water. ABA was collected by filtration. The crude azide was purified by radial chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>: mp 64–65 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.11 (d, 2 H, *J* = 8.4 Hz), 8.00 (d, 2 H, *J* = 8.4 Hz), 2.63 (s, 3 H); IR (CHCl<sub>3</sub>) 2182, 2137, 1688, 1250 cm<sup>-1</sup>. Anal. Calcd for C<sub>9</sub>H<sub>7</sub>O<sub>2</sub>N<sub>3</sub>: C, 57.14; H, 3.73; N, 22.21. Found: C, 57.28; H, 3.85; N, 22.08.

**4-Acetyl-4'-biphenylcarboxylic Acid.** A sample of 4-acetyl-4'-bromobiphenyl (12 g, 43.6 mmol) was converted to its ethylene ketal by reaction in benzene with ethylene glycol (2.64 mL) and a catalytic amount of *p*-toluenesulfonic acid, and the H<sub>2</sub>O was removed as it was formed with a Dean–Stark trap. The ketal was recrystallized from benzene–pentane [<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.2 (d, 2 H, *J* = 8.4 Hz) d 7.6–7.3 (m, 6 H), 4.05 (m, 2 H), 3.80 (m, 2 H), 1.68 (s, 3 H)]. The ketal (1 g, 3.1 mmol) and Mg (76 mg) were heated at reflux in 25 mL of dry THF for 12 h, the resulting dark brown solution was cooled to room temperature, and dry CO<sub>2</sub> was bubbled into the reaction mixture. The mixture was poured into 10% aqueous HCl and extracted with a 1:1 (v/v) mixture of ethyl acetate and ether. The organic layer was extracted with concentrated NaOH and discarded. The hydroxide extract was acidified with HCl and extracted with ethyl acetate. Removal of the ethyl acetate gave the acid as an off-white solid (0.4 g, 53% yield): <sup>1</sup>H NMR (200 MHz, DMF-*d*<sub>7</sub>)  $\delta$  8.15 (m, 4 H), 7.50 (d, 4 H, *J* = 8.3 Hz), 3.50 (s, 3 H).

**4-Acetyl-4'-biphenylcarbonyl Azide (ADA).** A solution of 4-acetyl-4'-biphenylcarboxylic acid (0.4 g, 1.7 mmol) and triethylamine (0.21 mL) was prepared in 15 mL of DMF. Ethyl chloroformate (1 equiv, 0.15 mL) was added to the solution with stirring over 30 min followed by the addition of NaN<sub>3</sub> (0.13 g, 2 mmol) dissolved in a 1:1 (v/v) mixture of H<sub>2</sub>O and acetone. The reaction mixture was stirred for 20 min and poured into ice-water, and the off-white precipitate was removed by filtration. The azide was purified by radial chromatography with CH<sub>2</sub>Cl<sub>2</sub>: mp 105–107 °C (with dec); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$

8.13 (d, 2 H, *J* = 7.4 Hz), 8.04 (d, 2 H, *J* = 7.4 Hz), 7.69 (d, 4H, *J* = 7.4 Hz), 2.64 (s, 3 H); IR (CHCl<sub>3</sub>) 2180, 2137, 1684, 1605 cm<sup>-1</sup>. Anal. Calcd for C<sub>15</sub>H<sub>11</sub>O<sub>2</sub>N<sub>3</sub>: C, 67.92; H, 4.18; N, 15.84. Found: C, 67.99; H, 4.22; N, 15.62.

**Preparation of (4-Acetylphenoxy)carbonyl Azide (APA).** NaH (2.2 g, 92 mmol from an oil dispersion) was added in small portions with stirring to a solution of 4-hydroxyacetophenone (12 g, 88 mmol) in 150 mL of THF. Stirring was continued until hydrogen evolution ceased, and then the resulting slurry was added dropwise over 30 min to a cold (ice bath), stirred solution of phosgene (100 g, 1 mol) dissolved in 50 mL of THF. The reaction mixture was stirred for 12 h at room temperature, and then the unreacted phosgene was removed under reduced pressure (aspirator). The resulting residue was dissolved in 150 mL of THF, and then NaN<sub>3</sub> (6 g, 92 mmol) was added in 1 portion. The reaction mixture was stirred for 12 h at room temperature, the salts were removed by filtration, and then the solvent was removed in vacuo leaving crude (4-acetylphenoxy)carbonyl azide as a yellow solid. The azide was purified by chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub> followed by recrystallization from pentane/CH<sub>2</sub>Cl<sub>2</sub> (20:1, v/v) to yield APA: 1.8 g (8.8 mmol, 10% overall yield); mp 58–59 °C; IR (CH<sub>2</sub>Cl<sub>2</sub>) 2163, 1742, 1686, 1601 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  2.605 (s, 3 H), 7.29 (d, 2 H), 8.01 (d, 2 H). Anal. Calcd for C<sub>9</sub>H<sub>8</sub>N<sub>3</sub>O<sub>3</sub>: C, 52.68; H, 3.44; N, 20.48. Found: C, 53.00; H, 3.47; N, 20.59.

**ESR Spectroscopy: Irradiation of AXA at 8 K.** A suspension of APA (5 mg in 2 g of Fluorolube) in a quartz ESR tube was frozen at 8 K in the spectrometer and irradiated in the cavity through a grating with a pen lamp (low-pressure Hg, 254 nm) for 45 min. The spectrum of APN recorded from 6000 to 11,000 g is shown in Figure 2. Similar experiments were performed for ABA and ADA, but spectra of ABN and ADN could not be detected. After 45 min of irradiation, the ESR spectra of (4-acetylphenyl)nitrene and 4'-acetyl-4-biphenylnitrene were observed.

**4-Acetylbenzamide.** 4-Acetylbenzoic acid (0.25 g, 1.5 mmol) was converted to the amide by the procedure described for preparation of ABA except that the mixed anhydride was quenched with concentrated NH<sub>4</sub>OH. The amide was isolated as a white solid and purified by recrystallization from ethanol: mp 191–194 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.02 (d, 2 H, *J* = 8.2 Hz), 7.88 (d, 2 H, *J* = 8.2 Hz), 6.1–5.7 (br, 2 H), 2.63 (s, 3 H); IR (CHCl<sub>3</sub>) 3387, 1669 cm<sup>-1</sup>; high resolution mass spectrum calcd for C<sub>9</sub>H<sub>9</sub>O<sub>2</sub>N 163.0633, found 163.0634.

**N-Cyclohexyl-4-acetylbenzamide.** A solution of 4-acetylbenzoyl chloride (0.20 g, 1.1 mmol) in 10 mL of ether was added dropwise over 10 min to cyclohexyl amine (0.15 g, 1.5 mmol) in 10 mL of 10% NaOH. The product formed immediately and was collected by filtration and recrystallized from ethanol: mp 209–210 °C; <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  7.97 (d, 2 H, *J* = 8.6 Hz),  $\delta$  7.81 (d, 2 H, *J* = 8.6 Hz), 6.0 (br, 1 H), 4.0 (m, 1 H), 2.61 (s, 3 H), 2.1–0.8 (m, 10 H); IR (CHCl<sub>3</sub>) 3929, 1664 cm<sup>-1</sup>; high resolution mass spectrum calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>N 245.1416, found 242.1414.

**Aziridines from ABA and 4-Methyl-2-penten-3-one (3 and 4).** In each case a 5 × 10<sup>-3</sup> M benzene solution of ABA containing 0.05 M olefin was irradiated with a 400-W Hg lamp filtered through a 345-nm cutoff filter to ca. 20% completion. The solvent and excess olefin were removed, and the crude reaction mixture, analyzed by <sup>1</sup>H NMR spectroscopy, showed only unreacted azide and aziridine (97% mass balance from the *cis*-pentene). The aziridines were isolated from photolyses by radial chromatography on silica gel. *cis*-Aziridine 3 was isolated as an oil: <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.06 (d, 2 H, *J* = 8.5 Hz), 8.02 (d, 2 H, *J* = 8.5 Hz), 2.87 (s, 3 H), 2.5 (m, 1 H), d 2.41 (m, 1 H), 1.6 (m, 1 H), 1.45 (d, 3 H, *J* = 6 Hz), 1.18 (d, 3 H, *J* = 6.5 Hz), 1.04 (d, 3 H, *J* = 6 Hz); mass spectrum (10 eV) *m/e* 245 (M<sup>+</sup>), 202, 147, 98, 55; high resolution mass spectrum calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>N 245.1416, found 245.1409. *trans*-Aziridine 4 was isolated as an oil: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.08 (d, 2 H, *J* = 8.0 Hz), 8.00 (d, 2 H, *J* = 8.0 Hz), 2.72 (m, 1 H), 2.63 (s, 3 H), 2.24 (m, 1 H), 1.6 (m, 1 H), 1.05 (d, 6 H, *J* = 6 Hz), 1.01 (d, 3 H, *J* = 6.7 Hz); mass spectrum (10 eV) *m/e* 245 (M<sup>+</sup>), 202, 147, 98, 55; high resolution mass spectrum calcd for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>N 245.1416, found 245.1411.

***tert*-Butyl 4-Acetylbenzohydroxamate (1).** A sample of ABA (5 × 10<sup>-3</sup> M) in benzene-containing *tert*-butyl alcohol (2.12 M) was photolyzed with a 400-W Hg lamp through a 345-nm cutoff filter to approximately 20% completion. Hydroxamate 1 was isolated as an oil by radial chromatography on silica gel with CH<sub>2</sub>Cl<sub>2</sub>–10% methanol: <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>)  $\delta$  8.26 (br, 1 H), 7.98 (d, 2 H, *J* = 8.8 Hz), 7.82 (d, 2 H, *J* = 8.8 Hz), 2.63 (s, 3 H), 1.35 (s, 9 H); mass spectrum (70 eV) *m/e* 235.1 (M<sup>+</sup>), 179, 164, 148, 147, 57; IR (CHCl<sub>3</sub>) 3021, 1686, 1217 cm<sup>-1</sup>; high resolution mass spectrum calcd for C<sub>15</sub>H<sub>17</sub>O<sub>3</sub>N 235.1208, found 235.1209.

**N-(4-Acetylphenyl)urethane from Isocyanate 15.** A sample of ABA (0.20 g, 1.1 mmol) was dissolved in 20 mL of ethanol and heated at reflux

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for 20 min. The urethane was isolated by radial chromatography with cyclohexane–5% ether: mp 155–158 °C;  $^1\text{H}$  NMR (200 MHz, acetone- $d_6$ )  $\delta$  8.02 (d, 2 H,  $J$  = 9 Hz), 7.74 (d, 2 H,  $J$  = 9 Hz), 4.23 (q, 2 H,  $J$  = 6.8 Hz), 2.58 (s, 3 H), 1.32 (t, 3 H,  $J$  = 6.8 Hz). Anal. Calcd for  $\text{C}_{11}\text{H}_{13}\text{O}_3\text{N}$ : C, 63.77; H, 6.28; N, 6.76. Found: C, 63.18; H, 6.23; N, 6.76.

***N*-(Cyclohexyl)-4-acetyl-4'-biphenylcarboxylic Acid Amide.** The procedure described above for preparation of ADA was followed except that cyclohexylamine (0.4 mL, 3.5 mmol) was added to the mixed anhydride instead of  $\text{NaN}_3$ . The organic phase was separated and washed with saturated  $\text{NaHCO}_3$  and then water and dried with  $\text{MgSO}_4$ . The solvent was removed, and amide was purified by radial chromatography with  $\text{CH}_2\text{Cl}_2$ : mp 246–248 °C;  $^1\text{H}$  NMR (200 MHz, DMF- $d_7$ )  $\delta$  8.14 (m, 4 H), 7.90 (m, 4 H), 3.9 (m, 1 H), 2.66 (s, 3 H), 2.1–1.0 (m, 11 H); mass spectrum (10 eV)  $m/e$  321, 240, 239, 223, 224. Anal. Calcd for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}$ : C, 78.47; H, 7.21; N, 4.36. Found: C, 78.12; H, 7.40; N, 4.25.

**4-Acetyl-4'-biphenylcarboxylic Acid Amide.** The procedure described above for preparation of ADA was followed except that  $\text{NH}_3$  was added to the mixed anhydride instead of  $\text{NaN}_3$ . The organic phase was separated and washed with saturated  $\text{NaHCO}_3$  and then water and dried with  $\text{MgSO}_4$ . The solvent was removed, and the amide was purified by radial chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ : mp 268–270 °C;  $^1\text{H}$  NMR (200 MHz, DMF- $d_7$ )  $\delta$  8.4 (m, 2 H), 7.92 (m, 4 H), 7.44 (br, 2 H), 2.68 (s, 3 H); mass spectrum (10 eV)  $m/e$  239, 224, 153; high resolution mass spectrum calcd for  $\text{C}_{15}\text{H}_{13}\text{O}_2\text{N}$  239.0946, found 239.0949.

***N*-(4-Acetyl-4'-biphenyl)urethane.** A sample of ADA (6.3 mg,  $2.4 \times 10^{-5}$  mol) was dissolved in 30 mL of ethanol and heated at reflux for 48 h. The solvent was removed, and the product was purified by radial chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ : mp 186–188 °C;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  8.0 (d, 2 H,  $J$  = 8.0 Hz), 7.7–7.4 (m, 6 H), 6.7 (br, 1 H), 4.22 (q, 2 H,  $J$  = 6.4 Hz), 2.64 (s, 3 H), 1.32 (t, 3 H,  $J$  = 6.4 Hz); IR (CHCl<sub>3</sub>) 1732, 1679, 1605  $\text{cm}^{-1}$ ; mass spectrum (10 eV)  $m/e$  283, 268, 240, 237, 224, 222, 210; high resolution mass spectrum calcd for  $\text{C}_{17}\text{H}_{17}\text{O}_3\text{N}$  283.1208, found 283.1207.

***N*-(*tert*-Butoxy)-4-acetyl-4'-biphenylcarboxylic Acid Amide.** A solution of ADA ( $5 \times 10^{-3}$  M) in benzene containing 2.12 M *tert*-butyl alcohol was irradiated ( $>345$  nm) to ca. 10% conversion. Hydroxamate **5**, the only product, was isolated from the mixture as an oil by radial chromatography on silica with  $\text{CH}_2\text{Cl}_2$ :  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d, 2 H,  $J$  = 7.2 Hz), 8.05 (d, 2 H,  $J$  = 7.6 Hz), 7.71 (d, 4 H,  $J$  = 7.6 Hz), 2.65 (s, 3 H), 1.56 (s, 9 H); mass spectrum (10 eV)  $m/e$  265, 237, 220, 194, 166.

**Aziridines 6 and 7.** ADA dissolved in benzene ( $5 \times 10^{-3}$  M) containing *cis*- or *trans*-4-methyl-2-pentene (0.05 M) was irradiated ( $>345$  nm). The aziridines, the only product in each case, were isolated by radial chromatography on silica gel with  $\text{CH}_2\text{Cl}_2$ . The *trans*-aziridine was contaminated with a small amount of unreacted ADA. ***cis*-Aziridine 6:**  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  8.09 (d, 2 H,  $J$  = 8.0 Hz), 8.05 (d, 2 H,  $J$  = 8.0 Hz), 7.72 (d, 2 H,  $J$  = 8.0 Hz), 7.70 (d, 2 H,  $J$  = 8.0 Hz), 2.65 (s, 3 H), 2.48 (m, 2 H), 1.6 (m, 1 H), 1.47 (d, 3 H,  $J$  = 6.0 Hz), 1.18 (d, 3 H,  $J$  = 6.0 Hz), 1.03 (d, 3 H,  $J$  = 6.4 Hz); mass spectrum (10 eV)  $m/e$  321, 265, 237, 223, 222, 98; high resolution mass spectrum calcd for  $\text{C}_{21}\text{H}_{23}\text{O}_2\text{N}$  321.1729, found 321.1728. ***trans*-Aziridine 7:**  $^1\text{H}$  NMR (500 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  8.22 (d, 2 H), 7.80 (d, 2 H), 7.39 (d, 2 H), 7.30 (d, 2 H), 2.15 (s, 3 H), 1.08 (d, 3 H), 0.89 (d, 3 H), 0.84 (d, 3 H).

**Thermolysis of APA in the Presence of *trans*- and *cis*-4-Methyl-2-pentene.** A solution of APA (50 mg, 244  $\mu\text{mol}$ ) in benzene (5 mL total volume) containing the *trans*-pentene (6 M) was prepared in a thick-walled Pyrex tube and sealed under vacuum. The solution was heated at 100 °C in a sand bath for 12 h. The solvent and unreacted olefin were removed, and the residue was purified by radial chromatography on silica

gel with  $\text{CH}_2\text{Cl}_2$ . The first fraction contained *trans*-*N*-((4-acetylphenoxy)carbonyl)-2-isopropyl-3-methylaziridine, **9**, isolated as a viscous oil (14 mg, 22% yield) containing a small amount (ca. 5%) of the isomeric *cis*-aziridine **8**: IR ( $\text{CDCl}_3$ ) 1730, 1682, 1601  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.03 (d, 2 H), 1.11 (d, 2 H), 1.43 (d, 2 H), 1.55 (m, 1 H), 2.17 (d of d, 1 H), 2.55 (m, 1 H), 2.60 (s, 3 H), 7.26 (d, 2 H), 7.90 (d, 2 H); high resolution mass spectrum calcd for  $\text{C}_{15}\text{H}_{19}\text{O}_3$  261.1365, found 261.1366.

***cis*-*N*-((4-Acetylphenoxy)carbonyl)-2-isopropyl-3-methylaziridine, **8**,** was prepared by the procedure described above from the *cis*-pentene (16 mg, 32% yield, contaminated with 5% of the isomeric *trans*-aziridine): IR ( $\text{CDCl}_3$ ) 1736, 1684, 1601  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.00 (d, 2 H), 1.21 (d, 2 H), 1.34 (d, 2 H), 1.54 (m, 1 H), 2.33 (d of d, 1 H), 2.60 (s, 3 H), 2.79 (m, 1 H), 7.23 (d, 2 H), 7.98 (d, 2 H); high resolution mass spectrum calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_3$  261.1365, found 261.1362.

**Thermolysis of APA in *tert*-Butyl Alcohol Solution.** A solution of APA (50 mg) in benzene containing *tert*-butyl alcohol (9 M) in a sealed tube was heated at 100 °C for 20 h. 4-Acetylphenoxy *tert*-butylhydroxamate, **11**, was isolated from this reaction mixture by chromatography on silica gel (10 mg, 20% yield): IR (CHCl<sub>3</sub>) 3340, 1776, 1682, 1601  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.327 (s, 9 H), 2.598 (s, 3 H), 7.26 (d, 2 H,  $J$  = 1.2 Hz), 7.75 (d of d, 2 H,  $J$  = 1.4 Hz and  $J$  = 10.2 Hz), 8.22 (s, br, 1 H); high resolution mass spectrum calcd for  $\text{C}_{12}\text{H}_{17}\text{NO}_3$  251.1157, found 251.1157.

**Irradiation of APA in Hexafluorobenzene.** A solution of APA (40 mg) in 20 mL of hexafluorobenzene was purged with nitrogen for 20 min and then irradiated (350 nm) for 90 min. The white solid that formed during irradiation was isolated by filtration: 5-acetylbenzoxazolinone (**10**): mp 231 °C (lit. mp 232 °C);<sup>34</sup> IR ( $\text{CD}_3\text{CN}$ ) 1811, 1788, 1685  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.62 (s, 3 H), 7.27 (d, 2 H,  $J$  = 10.5 Hz), 7.71 (d, 2 H,  $J$  = 1.2 Hz), 7.75 (d of d, 2 H,  $J$  = 1.4 Hz and  $J$  = 10.2 Hz), 8.22 (s, br, 1 H); high resolution mass spectrum calcd for  $\text{C}_{12}\text{H}_7\text{NO}_3$  177.0426, found 177.0422.

**Irradiation of APA in Cyclohexane and *tert*-Butyl Alcohol Solution.** Two solutions were prepared in cyclohexane containing 0.5 M benzene (to increase the solubility of the azide), each contained APA ( $5.0 \times 10^{-3}$  M), one contained *tert*-butyl alcohol (3 M). Both solutions were purged with nitrogen and irradiated (350 nm, Rayonet) for 20 min. The solvent was evaporated, and the residues were analyzed by  $^1\text{H}$  NMR spectroscopy. In the first sample, the yield of amide **19** was 51% amide **12**, 22%, 4-acetylphenol, 5%, and the benzoxazolinone **10**, 5%. Hydroxamate **11** was formed in only 3% yield. In the second sample, the yield of amide **19** was 60%, amide **12** was formed in 20% yield, 4-acetylphenol in 6% yield, and the benzoxazolinone **10** in 3% yield. Irradiation on a preparative scale (13 mmol) in cyclohexane gave 4-acetylphenyl carbamate **12**: (15 mg, 25%), mp 140 °C, (lit. mp<sup>35</sup> 151 °C); IR ( $\text{CDCl}_3$ ) 3431, 1673, 1605  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  2.596 (s, 3 H), 5.09 (s, br, 1 H), 7.24 (d, 2 H), 7.99 (d, 2 H); high resolution mass spectrum calcd for  $\text{C}_9\text{H}_9\text{NO}_3$  179.0582, found 179.0577. 4-Acetylphenyl *N*-cyclohexylcarbamate **19** (5 mg, 6%): mp 124 °C, IR ( $\text{CDCl}_3$ ) 3411, 1742, 1682, 1603  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  1.1–2.05 (m, 11 H), 2.590 (s, 3 H), 3.59 (s, br, 1 H), 4.94 (s, br, 1 H), 7.23 (d, 2 H), 7.96 (d, 2 H); high resolution mass spectrum calcd for  $\text{C}_{15}\text{H}_{19}\text{NO}_3$  261.1365, found 261.1366.

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