anthrylene (**9d**) (81 mg, 82%) as a white solid, mp 205–206 °C (benzene): NMR δ 8.92 (d, 1, H_{12}, $J_{11,12}$ = 8.2 Hz), 8.22 (d, 1, H_7, $J_{7,8}$ = 9.3 Hz), 8.05 (d, 1, H_5, $J_{4,5}$ = 9.1 Hz), 7.90 (d, 1, H_9, $J_{9,10}$ = 7.6 Hz), 7.67–7.85 (m, 8, Ar), 4.79 (s, 2, CH_2), 3.04 (s, 3, CH_3); UV λ_{max} (EtOH) 393 (ϵ 8830), 292 (12 530), 303 (99 450), 287 (89 525), 257 (62 055), 233 (49 635), 221 (61 030), 206 (62 000). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.29. Found: C, 94.65; H, 5.32.

Reduction of **10c** (245 mg, 0.77 mmol) by the same procedure (reaction time 18 h) afforded 6-methyl-4*H*-benzo[*b*]cyclopenta[*mno*]chrysene (**10d**) (204 mg, 87%) as pale yellow crystals, mp 202–204 °C (benzene): NMR δ 9.09 (s, 1, H_{11}), 8.66 (d, 1, H_{12}, $J_{12,13}$ = 8.8 Hz), 8.35–8.38 (overlapping d + s, 2, $H_{5,7}$), 8.15 (dd, 1, H_{10}, $J_{9,10}$ = 8.6 Hz, $J_{8,10}$ = 2.0 Hz), 8.02 (d, 1, H_{13}, $J_{12,13}$ = 8.8 Hz), 7.88 (dd, 1, H_1, $J_{1,2}$ = 8.3 Hz, $J_{1,3}$ = 1.6 Hz), 7.55–7.67 (m, 3, Ar), 4.54 (s, 2, CH_2), 3.19 (s, 3, CH_3); UV λ_{max} (EtOH) 396 (ϵ 9130), 373 (10 285), 355 (6515), 335 (6090), 308 (33 175), 288 (12 650), 245 (35 700), 214 (19 055), 201 (21 670). Anal. Calcd for $C_{24}H_{16}$: C, 94.70; H, 5.29. Found: C, 94.74; H, 5.52.

Acknowledgment. This research was supported by a grant from the National Institute of Environmental Health Sciences (ES 04266).

Registry No. 2, 202-94-8; 3, 202-98-2; 4, 141046-06-2; 5, 141046-07-3; **6a**, 141046-08-4; **6c**, 141046-09-5; **6d**, 63041-88-3; **7a**, 141046-10-8; **7c**, 141046-11-9; **7d**, 141046-12-0; **8a**, 141046-13-1; **9a**, 141046-14-2; **9c**, 141046-15-3; **9d**, 141046-16-4; **10a**, 141046-17-5; **10c**, 141046-18-6; **10d**, 141046-19-7.

Photochemistry of *N*-(Benzoylimino)-1,2,4-triazolium and *N*-(Benzoylimino)pyridinium Ylides: A Source of Benzoylnitrene Useful in Photolabeling and Photo-Cross-Linking Experiments

Charles R. Arnold, Tracy Melvin, William M. Nelson, and Gary B. Schuster*

Department of Chemistry, Roger Adams Laboratory, University of Illinois, Urbana, Illinois 61801

Received January 17, 1992

The photochemistry of substituted 1-(benzoylimino)pyridinium and 4-(*N*-benzoylimino)-1,2,4-triazolium ylides was investigated to judge their capacity to give aroylnitrenes and their suitability for use in photolabeling experiments. Evidence presented indicates that the triplet states of the ylides cleave to generate aroylnitrenes. In an attempt to enhance triplet formation, nitro- and acetyl-substituted pyridinium ylides were examined. Their irradiation does not give nitrenes in meaningful yield. However, irradiation of the triazolium ylides gives nitrenes in excellent yield. The mechanism of these reactions was probed, and additional evidence is obtained that supports the proposal that benzoylnitrene is a singlet in its ground state. The triazolium ylides may be suitable reagents for photolabeling applications.

Introduction

Photochemical generation of an intermediate with high reactivity toward intermolecular covalent bond formation is the basis for many chemical and biochemical marking methods.[1] In the most often used procedures, photolysis of a diazo compound, a diazirine, or an azide gives a carbene or nitrene which may subsequently be incorporated into the targeted substrate.[2] The azides most commonly used in this application are substituted aryl azides. However, in recent years it has been clearly shown that photolysis of such azides usually leads to formation of dehydroazepines—not nitrenes.[3] When a nucleophilic group is present at the targeted site, the dehydroazepines may be sufficiently reactive to meet the objectives of the procedure, but often this is not the case. In general, the photolysis of an aryl azide will not give an intermediate of sufficient reactivity to ensure its reaction at the site of creation irrespective of the chemical composition of the site. With this restriction in mind, we undertook research aimed at the development of new reagents and intermediates that could achieve the objective of global reactivity. In this connection, global reactivity of an intermediate is defined as rapid, irreversible reaction with unactivated, carbon-bound hydrogen to form a covalent bond at the targeted site.

Earlier work on this project revealed that aroylnitrenes exhibit the desired chemical reactivity toward carbon–hydrogen bonds.[4] These intermediates display chemical and physical properties that led us to conclude that they have singlet spin multiplicity in the ground state. As singlets, the aroylnitrenes are strongly electrophilic and insert concertedly into carbon–hydrogen bonds. Unfortunately, photolysis of aroyl azides, the most commonly used reaction for generation of an aroylnitrene, leads to approximately equal amounts of the nitrene formed by nitrogen elimination and the isocyanate formed from the photo-Curtius rearrangement of a singlet excited state of the azide.[5] The isocyanate is a comparatively weak electrophile that can migrate from the site of its creation before it is trapped by a nucleophilic group.

Triplet sensitization of the aroyl azide stops formation of the isocyanate and gives singlet nitrene-trapping products in essentially quantitative yield.[4] Two intersystem crossing reactions facilitate this process: the sensitizer excited singlet state is converted to its triplet before energy transfer to the aroyl azide, and the triplet nitrene formed by nitrogen loss from the azide intersystem crosses to its singlet ground state before the intermolecular reaction occurs. It is possible to carry out the triplet "sensitization" intramolecularly. Light absorbed by the ketone chromophore of 4-acetylbenzoyl azide, for example, leads to reaction of the azide group and formation of singlet nitr-

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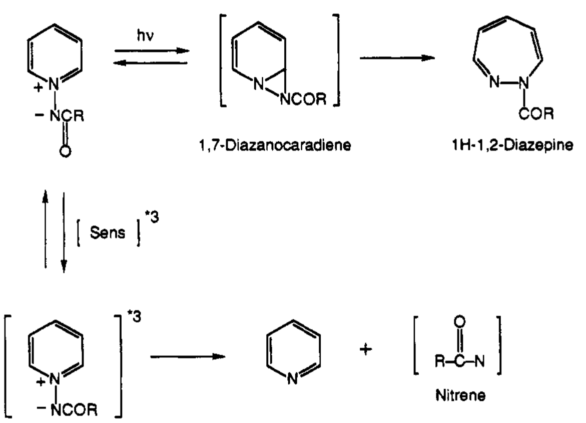
Scheme I



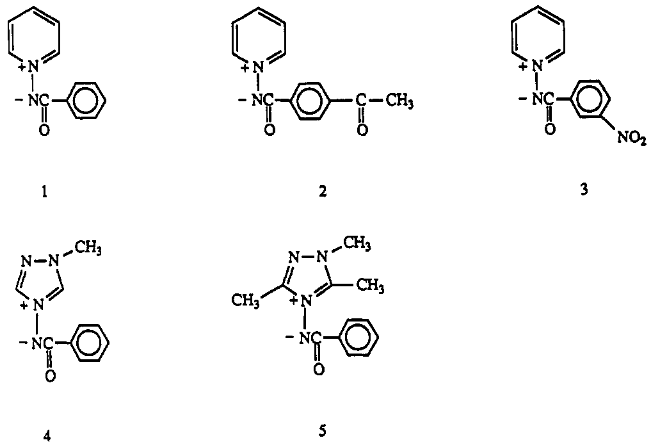
ene-derived products. Unfortunately, substitution of an electron-withdrawing group, such as a ketone, on the aroyl azide increases its ground-state reactivity with nucleophiles.[6] Consequently, these substituted aroyl azides are not useful in the development of photochemical marking methods that must be carried out in aqueous solutions containing nucleophilic reagents. In order to take full advantage of the global reactivity of aroylnitrenes their photochemical generation must proceed from a reagent that is stable under the conditions of the experiment.

In 1968 Streith and Cassal reported an investigation of the photochemistry of *N*-carbethoxy-substituted iminopyridinium ylides.[7] Their work and the subsequent investigations of Snieckus[8] and of Sasaki[9] on related compounds revealed that the excited singlet state of these pyridinium ylides undergoes valence tautomerization that leads eventually to 1*H*-1,2-diazepines. Significantly, in 1971 Streith and co-workers reported that triplet sensitization of these iminopyridinium ylides leads to nitrogen–nitrogen bond cleavage with formation of a nitrene.[7] These findings and more recent results were reviewed by Streith in 1991;[10] the key reactions are summarized by Scheme I.

Tsuchiya and Sento,[11] and more recently Halpern and co-workers,[12] applied computational methods to study the photochemistry of iminopyridinium ylides. The potential energy surfaces for the ground state, the first singlet state, and the first triplet state were computed. These calculations are in accord with the experimental observations: the singlet excited state is expected to rearrange and the triplet is expected to cleave the nitrogen–nitrogen bond and form a nitrene.

In 1970, Becker and co-workers reported that irradiation of 4-(acylimino)-1,2,4-triazolium ylides gives a mixture of products some of which indicate formation of the intermediate acylnitrene.[13] This work stimulated research by Bird and co-workers who discovered that irradiation of (nitrophenyl)imino-substituted triazolium ylides similarly give (nitrophenyl)nitrene.[14]

Chart I



The experimental and theoretical findings described above, our expectation that the ground-state ylides will be stable in aqueous solutions, and our quest for an efficient photochemical source of aroyl nitrenes led us to study the photochemistry of the aroyl substituted iminopyridinium and iminotriazolium ylides shown in Chart I. While this work was underway, Abraham and co-workers reported results from a study of similarly substituted imino-1,2,4-triazolium ylides.[15] There are some meaningful differences between their results and the findings reported in this paper.

Results and Discussion

(1) Preparation and Characterization of Ylides 1–5. The procedure for preparation of the iminopyridinium ylides follows that reported by Streith[16]—details are presented in the Experimental Section. The iminotriazolium ylides were prepared by reaction of 4-aminotriazolium tosylate salts with benzoyl chloride in acetonitrile solution. The resulting salts were deprotonated with Na_2CO_3, and the ylides were isolated as white solids.

The UV absorption spectra of the iminopyridinium ylides have previously been characterized.[17] The lowest energy transition is a solvent dependent charge-transfer absorption that shifts toward higher energy as the solvent polarity is increased. Iminopyridinium ylide 1 in methanol solution has a maximum absorption at 310 nm. For the 4-acetyl- and 3-nitro-substituted ylides 2 and 3, this band is found at 313 and 315 nm (ethanol solution), respectively. The iminotriazolium ylides 4 and 5 also show strong absorption bands. In methanol solution they exhibit absorption maxima at 262 and 230 nm, respectively. In both cases these absorptions have tails that extend beyond 300 nm. The 30-nm blue shift of the maximum for ylide 5 compared with 4 probably is due to decreased π-overlap of the ylide nitrogen atoms due to steric interactions with the methyl groups of 5.

The iminopyridinium ylides fluoresce very weakly (if at all) at room temperature. However at 77 K in frozen ethanol–methanol (4:1) solution, ylide 1 shows a strong emission with a maximum at 425 nm. The intensity of this emission decreases after the sample has been irradiated

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at 350 nm. We conclude, therefore, that this emission is due to the ylide itself and not a consequence of the buildup of a photochemically generated product. Assignment of this emission to phosphorescence from the ylide allows estimation of its triplet energy to be 66 kcal/mol.

At room temperature, aqueous solutions of the iminopyridinium and iminotriazolium ylides are indefinitely stable. For example, there is no measurable consumption of 1 when a 5×10^{-4} M solution in Tris buffer (pH = 7.4) is stored in the dark for 48 h. Similarly, aqueous 10^{-3} M solutions of 5 show no reaction after 3 days in the dark at pH 4, 6, or 12.

(2) Photochemistry of Iminopyridinium Ylide 1. The photochemistry of iminopyridinium ylide 1 and variously substituted analogs has been carefully studied.[18] Generally these compounds give 1,2-diazepines in high chemical yield but with low quantum efficiency. The inefficiency is generally thought to be due to intermediate formation of 1,7-diazanorcaradienes (see Scheme I) which more often revert to the starting ylides than go on to products. A small fraction of the net reaction of the ylides is thought to proceed through the triplet state formed by intersystem crossing of the first-formed excited singlet state. We attempted to verify this mechanism by application of time-resolved spectroscopic methods.

Laser irradiation of ylide 1 (308 nm, 20 ns, 20 mJ) in methanol solution produces a broadly featured absorption extending from 350 to beyond 550 nm. The laser-induced absorption does not disappear completely, and its decay rate appears to vary somewhat with the monitoring wavelength. When the reaction is monitored at 380 nm the laser-induced absorption decays with an apparent lifetime of ca. 4 μs, at 520 nm the lifetime appears to be ca. 2 μs. The rate of decay at ca. 500 nm increases in the presence of oxygen thus indicating that it is probably due in part to a triplet species.

The complex spectral and kinetic behavior is a result of these being several species formed from irradiation of ylide 1 that have overlapping spectra. For example, the expected 1,2-diazepine is known to absorb in the visible spectral region up to ca. 460 nm, and CNDO calculations indicate that the 1,7-diazanorcaradiene will also absorb in this region.[10] The observed oxygen dependence suggests that the triplet ylide absorption spectrum is also to be found in this spectral region. The time-resolved experiments seem to support the generally accepted mechanism for the photochemistry of these ylides, but the complication caused by spectral overlap prevents its quantitative confirmation.

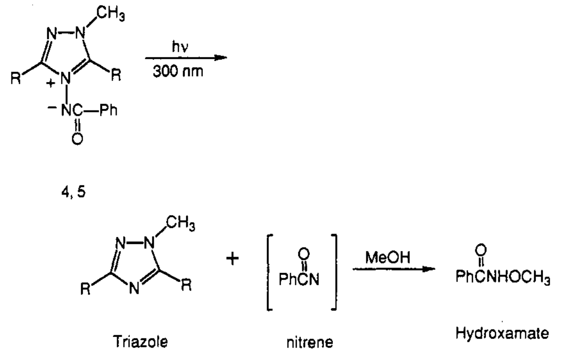
(3) Attempt To Enhance Intersystem Crossing of Iminopyridinium Ylides. Since a prime objective of this research is the discovery of new photochemical sources of aroylnitrenes, and the experimental evidence seems to support the hypothesis that nitrenes are formed only from triplet states of the ylides, we examined approaches that might lead to enhanced intersystem crossing of the ylide singlet state. In previous examinations of aryl and aroyl azides we showed that acetyl and nitro substituents increase the intersystem crossing rate by providing low-energy $n\pi^*$ excited states.[3,4] We examined the photochemistry of iminopyridinium ylides 2 and 3 to assess this effect in these compounds.

Irradiation of iminopyridinium ylide 2 or 3 in *tert*-butyl alcohol solution results in their slow conversion to the corresponding 1*H*-1,2-diazepines with no evidence for enhanced formation of the aroylnitrenes. However, when these ylides are irradiated in ethyl alcohol solution, a complex product mixture is obtained that is characteristic of reactions initiated by hydrogen abstraction from a triplet state. These findings indicate that nitrene formation is not enhanced by placing low energy $n\pi^*$ states in the system. Instead, substitution with the acetyl or nitro group appears not to affect the chemistry of the singlet state of the ylide but to open an undesirable hydrogen atom abstraction route for reaction of the triplet state. Consequently, we sought a different means to enhance nitrene formation from photolysis of this class of ylides.

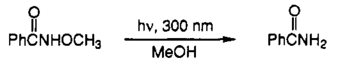
(4) Photochemistry of *N*-(Benzoylimino)-1,2,4-triazolium Ylides 4 and 5. In contrast to the iminopyridinium ylides, irradiation of the iminotriazolium ylides does not lead to valence tautomerization and ring expansion.[13] This might result from inhibiting formation of the assumed bicyclic intermediate due to an increase in its ring strain or might be a consequence of this intermediate rearranging exclusively to the starting ylide. Some evidence in favor of the former explanation comes from examination of the fluorescence of ylide 4.

In methanol solution 4 exhibits moderately intense fluorescence with a maximum at 330 nm. The quantum yield for this emission is 0.08 ± 0.02. The marked increase in fluorescence efficiency of the triazolium compared with the pyridinium ylide suggests that valence tautomerization in the excited singlet state is slower in the former than in the latter. Whatever the cause of the decreased reactivity of the singlet, this finding suggests that iminotriazolium ylides such as 4 or 5 might be suitable photochemical sources of aroylnitrenes.

Photolysis of either ylide 4 or 5 gives essentially identical results. Irradiation of methanol solutions of these compounds (10^{-2}–10^{-3} M) at room temperature in a Rayonet reactor equipped with 300-nm lamps causes their steady conversion to products. In the early stages of the reactions, consumption of the ylides leads to exclusive formation of the expected triazole and to the methyl hydroxamate. Formation of the hydroxamate is acknowledged to be characteristic of the intermediacy of singlet benzoylnitrene.[4,5] These reactions are shown in eq 1. As the conversion of the ylide to products proceeds, the hydroxamate concentration in solution increases and benzamide is detected in the reaction mixture. It was shown independently that irradiation of the methyl hydroxamate under these conditions results in its conversion to benzamide as is shown in eq 2.



(1)



$$\mathrm{PhC(=O)NHOCH_3} \xrightarrow[\text{MeOH}]{h\nu,\ 300\ \text{nm}} \mathrm{PhC(=O)NH_2} \quad (2)$$

We carefully examined the time-dependence of the product mixture composition formed from photolysis of ylides 4 and 5 since other investigators[15] have suggested that the formation of benzamide from related ylides establishes the intermediacy of triplet benzoylnitrene. The

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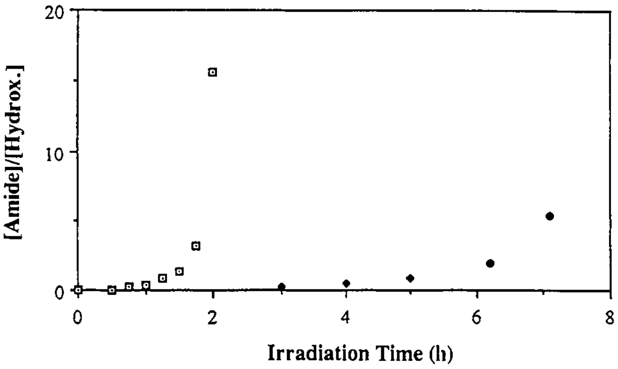

Figure 1. Plot of the ratio of the concentration of benzamide to the concentration of the methyl hydroxamate as a function of irradiation time for ylide 4 (starting concn 2 × 10^{-3} M, ▣) and for ylide 5 (starting concn 1 × 10^{-3} M, ◆) in N_2-purged methanol solution at room temperature.

results are shown graphically in Figure 1. At low conversion of ylides 4 or 5 the only detectable nitrene-derived product is the methyl hydroxamate. At higher conversion of the ylide, when the hydroxamate absorbs a significant fraction of the incident light, benzamide formation is detectable. At longer irradiation times when the hydroxamate absorbance is greater than that of the ylide, benzamide becomes the major product. This behavior is clearly characteristic of a sequential reaction mechanism: photolysis of the ylides gives the hydroxamate and irradiation of the hydroxamate leads to benzamide formation.

A sensitization experiment provides evidence that benzoylnitrene is formed from reaction of the triplet state of the triazolium ylide. Irradiation of a methanol solution containing ylide 4 and 2-isopropylthioxanthone sensitizer at 350 nm (only the sensitizer absorbs light) leads to formation of the methyl hydroxamate. Since only triplet–triplet energy transfer is possible energetically in this experiment, the benzoylnitrene intermediate must have a triplet precursor. Formation of the hydroxamate in this reaction, a singlet-derived product, supports our previous conclusion[4b,c] that aroylnitrenes have singlet ground states.

Conclusions

The primary aim of this research was to discover a photochemical source of singlet aroyl nitrenes that is stable in aqueous solution and whose irradiation does not simultaneously generate a comparatively weak electrophile. That aim has been achieved. Our attempts to enhance intersystem crossing in the iminopyridinium ylides were not successful. However, we found that ylides 4 and 5 are stable indefinitely in aqueous solutions and that their irradiation with UV light leads to formation of benzoylnitrene. We interpret the exclusive generation of the methyl hydroxamate at low conversion of ylides 4 and 5 to indicate reaction of only a singlet nitrene intermediate. This finding is consistent with our earlier conclusion[4b,c,6] that the singlet is the ground state of benzoylnitrene. Efforts to apply these findings to the development of useful chemical and biochemical marking methods are underway in our laboratory.

Experimental Section

General. Melting points were determined in open capillaries and are uncorrected. NMR spectra were determined on either Varian XL-200 or General Electric QE-300 spectrometers. Chemical shifts are reported as ppm downfield from TMS. UV spectra were obtained on a Perkin-Elmer 552 spectrophotometer. All photochemical experiments were carried out in N_2-purged solutions. Irradiations were performed in an air-cooled Rayonet reactor equipped with 300- or 350-nm lamps. All solvents were distilled before use. Elemental analyses were performed by the microanalysis lab at the University of Illinois.

1-[(4′-Acetylbenzoyl)imino]pyridinium Ylide 2. The procedure of Streith[7] was used starting with 4-acetylbenzoyl chloride. Ylide 2 was purified by recrystallization from ether–pentane: ^1H NMR ($CDCl_3$) δ 8.84 (d, 2 H), 8.24 (d, 2 H), 8.00 (m, 4 H), 7.73 (m, 2 H), 2.64 (s, 3 H). Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.04; N, 11.66. Found: C, 69.73; H, 5.10; N, 11.62.

1-[(3′-Nitrobenzoyl)imino]pyridinium Ylide 3. The procedure of Streith[7] was used starting with 3-nitrobenzoyl chloride. Ylide 3 was purified by recrystallization from ether–pentane: ^1H NMR ($CDCl_3$) δ 9.02 (t, 1 H), 8.86 (dd, 2 H), 8.50 (dt, 1 H), 8.28 (m, 1 H), 8.00 (m, 1 H), 7.73 (t, 2 H), 7.50 (m, 1 H). Anal. Calcd for $C_{12}H_9N_3O_3$: C, 59.26; H, 3.73. Found: C, 58.96; H, 3.65.

4-Amino-3,5-dimethyl-1,2,4-triazole. The procedure of Herbst and Garrison[19] was followed: ^1H NMR ($CDCl_3$) δ 4.45 (s, 2 H), 2.45 (s, 6 H); mp 196–197 °C (lit.[19] mp 197.5 °C).

4-Amino-1,3,5-trimethyl-1,2,4-triazolium tosylate salt:[20] ^1H NMR (CD_3CN) δ 2.31 (s, 3 H), 2.42 (s, 3 H), 2.55 (s, 3 H), 3.80 (s, 3 H), 5.64 (s, 2 H), 7.13 (d, 2 H), 7.55 (d, 2 H); mp 178–179 °C. Anal. Calcd for $C_{12}H_{18}N_4SO_3$: C, 48.31; H, 6.08; N, 18.78. Found: C, 48.26; H, 6.10; N, 18.76.

4-(*N*-Benzoylimino)-1-methyl-1,2,4-triazolium Ylide 4. The tosylate salt formed from reaction of methyl tosylate with *N*-amino-1-methyl-1,2,4-triazole (Aldrich Chemical Co.) and benzoyl chloride (1 equiv) was heated at reflux in acetonitrile solution for 3 h. Removal of the solvent left a brown oil which was dissolved in aqueous Na_2CO_3. The aqueous solution was extracted with ethyl acetate, and the organic layer was isolated. Removal of the solvent yielded a white crystalline solid: ^1H NMR ($CDCl_3$) δ 3.95 (s, 3 H), 7.40 (m, 3 H), 8.05 (m, 2 H), 8.54 (s, 1 H), 10.93 (s, 1 H); mp 185 °C. Anal. Calcd for $C_{10}H_{10}N_4O$: C, 59.40; H, 4.98; N, 27.71. Found: C, 59.26; H, 5.00; N, 27.75.

4-(*N*-Benzoylimino)-1,3,5-trimethyl-1,2,4-triazolium Ylide 5. 4-Amino-1,3,5-trimethyl-1,2,4-triazolium tosylate salt was combined with 2 equiv of benzoyl chloride and 3.5 equiv of Na_2CO_3 in acetonitrile solution. The mixture was stirred and heated at reflux for 7 h. The solid obtained from removal of the solvent was added to CH_2Cl_2, and the mixture was filtered. The filtrate was washed with 5% aqueous $NaHCO_3$ solution and then extracted with CH_2Cl_2. The CH_2Cl_2 solution was dried, and evaporation of the solvent yielded a colorless crystalline solid: ^1H NMR ($CDCl_3$) δ 2.42 (s, 3 H), 2.56 (s, 3 H), 3.95 (s, 3 H), 7.41 (m, 3 H), 8.15 (d, 2 H). Anal. Calcd for $C_{12}H_{14}N_4O$: C, 62.59; H, 6.13; N, 24.33. Found: C, 61.91; H, 6.33; N, 23.87.

Photolysis of 4-(*N*-Benzoylimino)-1,3,5-trimethyl-1,2,4-triazolium Ylide. A 9.58 × 10^{-3} M solution of the ylide in methanol was prepared and purged with N_2 (UV ϵ_{300} = 290 M^{-1} cm^{-1}). The solution was irradiated in a Rayonet photolysis apparatus fitted with 300-nm lamps. Aliquots of the reaction mixture were removed at regular intervals and analyzed by ^1H NMR spectroscopy (in CD_3OD solution) by integration of the peaks corresponding to the ylide (δ 8.00), methyl hydroxamate (δ 7.75), and amide (δ 7.87). These resonances were identified by comparison with authentic samples independently prepared.

Photolysis of 4-(*N*-Benzoylimino)-1-methyl-1,2,4-triazolium Ylide. A 1.82 × 10^{-3} M methanol solution of this ylide has the same absorbance at 300 nm as the solution of ylide 5 (ϵ_{300} = 1500 M^{-1} cm^{-1}). The solution was irradiated in the Rayonet apparatus, and aliquots were withdrawn at regular intervals. The course of the reaction was monitored by spectroscopy as described above: ylide 4 in CD_3OD solution shows a characteristic absorption at δ 7.97.

Acknowledgment. This work was supported by a grant from the National Institutes for Health (GM28190) for which we are grateful.

Registry No. 1, 23031-08-5; 2, 140929-06-2; 3, 49684-70-0; 4, 61820-48-2; 5, 140929-07-3.

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