

Direct Observation of a Carbene–Pyridine Ylide by Matrix IR Spectroscopy. Rearrangements of 2-Pyridylacetylcarbenes

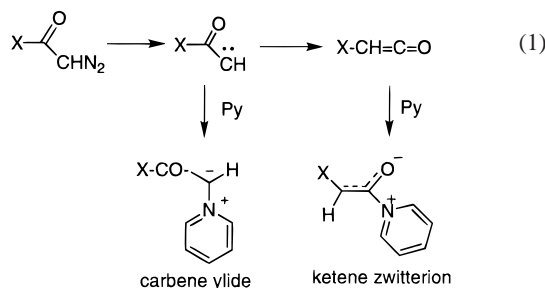
Arvid Kuhn, Carsten Plüg, and Curt Wentrup*

Contribution from the Department of Chemistry, The University of Queensland, Brisbane, Queensland 4072, Australia

Received October 29, 1999

Abstract: FVT of 2-(2-diazoacetyl)pyridine (**1**) yields 2-pyridylketene (**3**) (largely in the *s*-*Z* form **3Z**), which dimerizes to quinazolinone **5**. Matrix photolysis of **1** (largely in the *EZ* form **1EZ**) yields the carbene–pyridine ylide **6**, which on further photolysis at $\lambda > 320$ nm is converted to (mainly) the *s*-*E* ketene **3E**. Continued photolysis of **3E** at 320 nm converts it to **3Z**, and this process is reversed on photolysis at 254 nm.

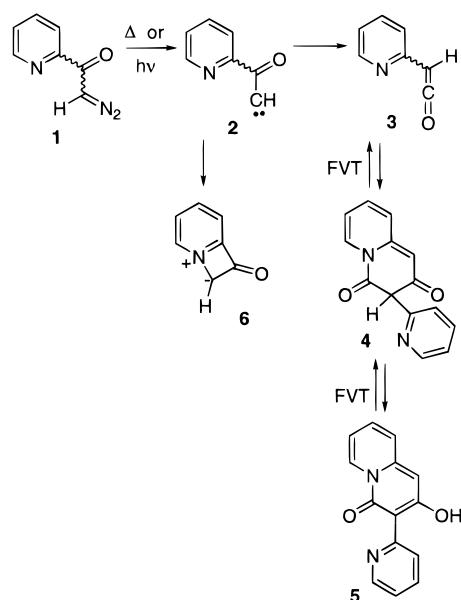
The mechanism of the Wolff rearrangement of diazocarbonyl compounds to ketenes and the question of acylcarbene and/or oxirene intermediates in this process are continuing problems of fundamental importance. The pyridine ylide method, viz. the trapping of short-lived carbenes with pyridine to form longer lived and hence observable ylides, has been used extensively in recent investigations of carbene chemistry.¹ A complication arises due to the fact that ketenes also react with pyridine to form zwitterions, sometimes at very low temperatures (e.g. 40 K), eq 1.^{1e,2,3}



The carbene ylides and the ketene zwitterions often absorb in the same range of the UV spectrum, thus making assignments difficult. It was shown recently that the transients trapped with pyridine on laser flash photolysis of benzoyl- and 1-naphthoyl-diazomethane were ketenes, not carbenes, and that if they were formed at all, the carbenes would have lifetimes of less than 20 ns.⁴

Ketene–pyridine zwitterions have been observed by low-temperature IR spectroscopy,³ but this has not been the case for the carbene–pyridine ylides. On photolysis of diazo compounds in low-temperature pyridine matrixes we found that the

Scheme 1



ketenes, not the carbenes, were trapped; yet, the putative carbenes were trappable with CO to give acylketenes.^{3c} We now report the direct monitoring of the formation of a carbene–pyridine ylide by matrix IR spectroscopy, made possible by the intramolecular nature of the reaction. We also report a new and reversible type of dimerization of ketenes,⁵ namely that of 2-pyridylketenes to produce novel quinolizinedione derivatives (Scheme 1).

Results

Flash vacuum thermolysis (FVT) of (2-diazoacetyl)pyridine (**1**) at 600 °C afforded a bright yellow material whose NMR data are consistent with the dimer structure **5**. This material would be formed in a formal [2 + 4] cycloaddition of the ketene **3**, which would probably take place in a pseudopericyclic manner, initiated by the attack of a pyridine lone pair on the carbonyl carbon of a second molecule of ketene. The initial dimer thus formed (**4**) would tautomerize to the observed product **5**. On Ar matrix isolation of the thermolysate from **1**,

(5) Cf.: Tidwell, T. T. *Ketenes*; Wiley: New York, 1995. Wentrup, C.; Heilmayer, W.; Kollenz, G. *Synthesis* **1994**, 1218.

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(3) (a) Kappe, C. O.; Färber, G.; Wentrup, C.; Kollenz, G. *J. Org. Chem.* **1992**, *57*, 7078. (b) Qiao, G. G.; Andraos, J.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 5634. (c) Visser, P.; Zuhse, R.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1996**, *118*, 12598.

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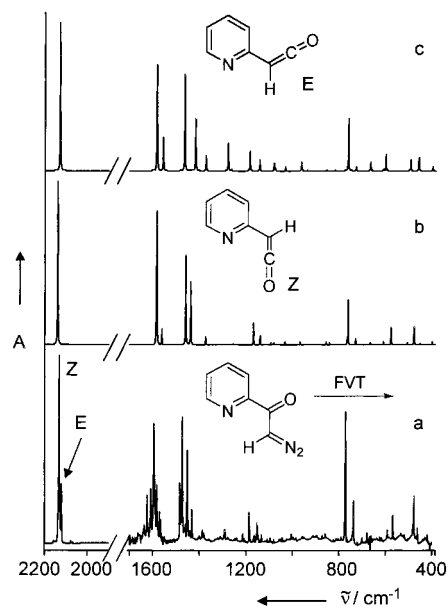
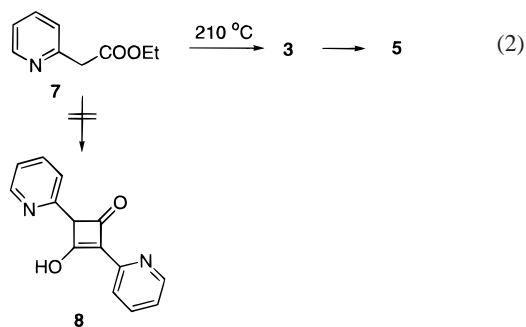


Figure 1. IR spectra of pyridylketene **3**: (a) FVT experiment (Ar matrix); (b) calculated spectrum of **3Z**; (c) calculated spectrum of **3E** (B3LYP/6-31G*, scaled by 0.9613). The intensities of the ketene bands in the 2100 cm^{-1} region are reduced by a factor of 4.

the ketene **3** was the only reaction product detectable by FTIR spectroscopy. The experimental IR spectrum is in very good agreement with the B3LYP/6-31G* calculated one, which strongly suggests that the ketene exists largely in the *s*-Z conformation **3Z** (Figure 1). Generally, we also find that other, substituted, 2-pyridylketenes are formed largely in the Z conformation under FVT conditions, and the *E* and Z conformers can be distinguished by comparison of the IR spectra with DFT calculations. The B3LYP calculations also indicate that the Z conformers are lower in energy (1.3 kcal/mol below the *E* conformer in the case of **3**). Ketenes are conformationally stable under matrix isolation conditions.⁶ The experimental wavenumbers for the ketene stretching vibrations of **3Z** and **3E** are 2132 and 2123 cm^{-1} , respectively (see below). The same IR spectrum of **3Z** was also obtained by FVT of the dimer **5** at 830 °C with Ar matrix isolation of the product, thereby demonstrating the reversibility of the dimerization.

A dimer of ketene **3** has been claimed before, namely the cyclobutenone **8**, formed on thermolysis of ester **7** at 210 °C.⁷ We repeated this reaction and found that the product formed in low yield was in fact identical with dimer **5** (eq 2).



In contrast to the clean thermolysis of diazo compound **1** to ketene **3**, photolysis of the Ar matrix isolated diazo compound gave rise to an IR spectrum consistent with a minor amount of the ketene **3** (but mostly the *E*-ketene in this case) together with a major amount of a new carbonyl compound absorbing strongly

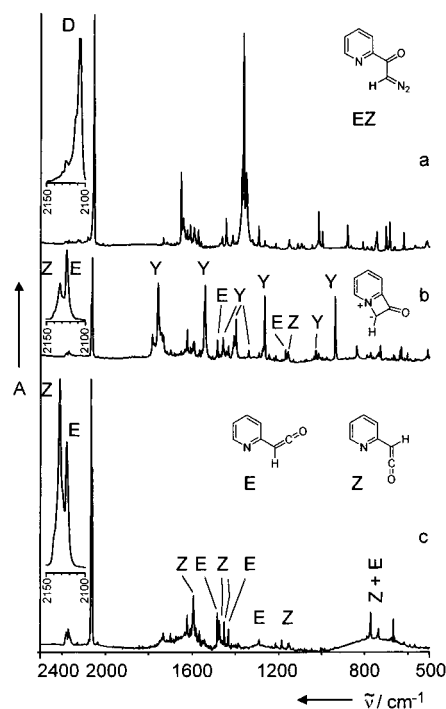


Figure 2. IR spectra (Ar, 10 K) of the photolysis of (2-diazoacetyl)pyridine (**1**) with light of the wavelength $\lambda = 313$ nm. (a) unphotolyzed **1**; (b) after 30 min of irradiation, mainly ylide **6**, with the small amount of ketenes comprising mainly the *E*-isomer; (c) after 12 h of irradiation, with predominance of **3Z**. Letters denote **1** (D), 2-pyridylketenes **3Z** and **3E** (Z, E), and ylide **6** (Y). Bands at 2340 and 668 cm^{-1} are due CO_2 ; the band at 1623 cm^{-1} is due to traces of water.

at ca. 1760 cm^{-1} (Figure 2). The excellent agreement between this spectrum and the B3LYP calculated one (Figure 3) strongly supports the conclusion that the new species is the ylide **6**.⁸ Other prominent bands due to this compound are at 1546, 1540, 1398, 1266, and 939 cm^{-1} .⁹ Even better agreement between experimental and calculated wavenumbers for the C=O stretching vibration was achieved by carrying out the calculation for a dipolar medium with a dielectric constant $\epsilon = 40$ using the SCRf dipolar solvation model incorporated in Gaussian 98. These spectra are shown in Figure S5 in the Supporting Information. We have found that calculations incorporating a polar solvent field often improve the agreement with IR spectra of mesoionic and zwitterionic compounds very considerably, particularly by giving rise to higher values for the C=O stretching frequency.^{3b,c,10}

(6) Calculated *s*-*E*/*s*-*Z* rotational barriers in ketenes are the following. Vinylketenes: ca. 5 kcal/mol: Bibas, H.; Wong, M. W.; Wentrup, C. *Chem. Eur. J.* **1997**, *3*, 237. Acylketenes, ca. 10 kcal/mol: Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1994**, *59*, 5279. Kappe, C. O.; Wong, M. W.; Wentrup, C. *J. Org. Chem.* **1995**, *60*, 1686. Finnerty, J.; Andraos, J.; Yamamoto, Y.; Wong, M. W.; Wentrup, C. *J. Am. Chem. Soc.* **1998**, *120*, 1701. Imidoylketenes, ca. 6 kcal/mol: Finnerty, J.; Wentrup, C. Unpublished results.

(7) Jaworski, T.; Kwiatkowski, S. *Rocz. Chem.* **1970**, *44*, 691; *Chem. Abstr.* **1970**, *73*, 130746r.

(8) An isomeric ketene-pyridine zwitterion could conceivably have been formed by cyclization of ketene **3Z**; this is unlikely because no trace of the 1760 cm^{-1} species was observed in the matrixes of the thermally generated ketene, nor did it ever appear on photolysis of the ketenes. Moreover, a B3LYP/6-31G* calculation indicated that the cyclic zwitterion from **3** is not an energy minimum in the gas phase, ring opening instead to the ketene.

(9) A small band at 1784 cm^{-1} may be due to a site of **6** or to another compound, e.g. cyclobuta[b]pyridin-6-one. On irradiation, this band disappears at the same time as those ascribed to **6**.

(10) Ye, X.; Andraos, J.; Bibas, H.; Wong, M. W.; Wentrup, C. *J. Chem. Soc., Perkin Trans. 1* **2000**, 401.

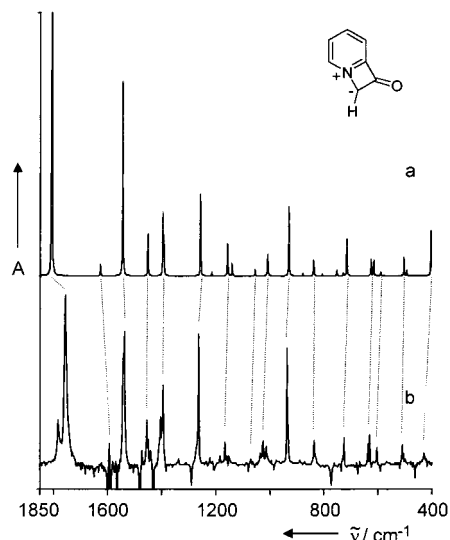


Figure 3. (a) Calculated IR spectrum of ylide **6** (B3LYP/6-31G(d) scaled by 0.9613). (b) Part of a difference spectrum (Ar, 10 K) from the photolysis ($\lambda = 313$ nm) of **1**, showing bands assigned to ylide **6**.

The rate of photolysis of **1** and the intensity ratios of bands ascribed to **3E**, **3Z**, and **6** differ under different irradiating conditions. The spectrum of **1** disappeared completely in just 90 s when using the unfiltered light of the 1000 W Hg–Xe lamp. Best results were obtained using the 313 nm line selected with a monochromator (bandwidth 15 nm). IR spectroscopic monitoring demonstrated gradual decrease of the diazo ketone bands due to **1** and, at the same time, appearance of the ketone and ketenes. After 30 min, the ketone and ketene bands had roughly the same intensities; both **3E** and **3Z** were present, but the intensity of **3E** was higher (Figure 2b). At this stage, the matrix was deep blue. The UV–vis spectrum showed a structured maximum around 390 nm and a weaker, very broad band from ca. 440 to 720 nm with a maximum at 580 nm. The UV spectrum had a minimum at 313 nm, and the ylide product **6** was photostable at this wavelength according to both UV and IR spectroscopy.

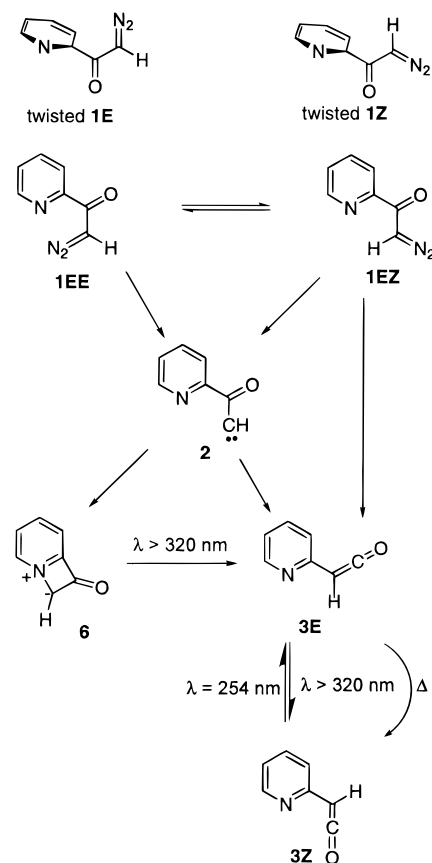
On further photolysis using either broad band irradiation or light of wavelength $\lambda > 320$ nm, the ketone band in the IR (1759 cm^{-1}) and the UV–vis bands disappeared completely, the matrix became colorless, and the ketene bands due to **3E** and **3Z** increased strongly in intensity. **3Z** now dominated the mixture (Figure 2c). The isomerization of **3E** to **3Z** continued after all the ylide had been converted to ketenes. The ketene interconversion can be reversed using light of 254 nm (low-pressure Hg lamp), whereby the signals due to **3E** become stronger again.

Moreover, the ketene produced by FVT of **1** as above and existing largely as **3Z** with a small amount of **3E** (cf. Figure 1) was photolyzed at 254 nm to yield an increase in the *E* and a decrease in the *Z* isomer (no diazo compound **1** was present in the matrix). Subsequent irradiation with $\lambda > 320$ nm reversed this change.

Discussion

Calculations at the B3LYP/6-31G(d) level indicate four possible conformers of diazo compound **1**, the *EZ*, the *EE*, and the twisted *Z* and the twisted *E* conformers, whereby the pyridine rings in the latter two are twisted ca. 40° out of the plane of the diazo ketone (see Scheme 2). The calculated energies of these species are 0, 2.4, 8.3, and 9.8 kcal/mol, respectively. Their calculated IR spectra are shown in the Supporting Information and clearly reveal that the global minimum, **1EZ**, corresponds

Scheme 2

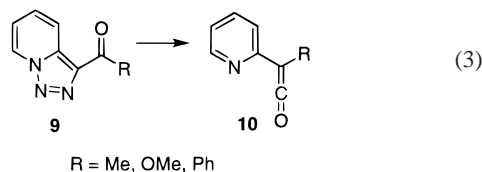


closely to the experimental spectrum in Figure 2a. It is possible that smaller amounts of other stable conformers are also present, in particular the twisted *Z* conformer, but since this is calculated to lie some 8 kcal/mol above **1EZ** and to have a small barrier for interconversion, it is most likely that the observed spectrum is in fact due to **1EZ**. The calculated structures of the diazo conformers and the energy surface for their interconversions as well as the structures and energies of the triplet and singlet carbenes are also given in the Supporting Information. [The only stable singlet carbene with a suitable conformation for formation of the ylide located at this computational level is a twisted C_1 carbene, in which the carbene C–H bond is almost perpendicular to the acylpyridine plane ($\theta_{\text{OCC}} = 81^\circ$). This structure lies ca. 71 kcal/mol above **3Z**. This carbene was also optimized at the B3LYP/6-311++G** level, where it still had the same structure.]

If it is accepted that cisoid diazoketones can undergo concerted Wolff rearrangement,¹¹ then the lowest energy diazoketone **1EZ** may be expected to give ketene **3E** in the matrix. This is the major ketene observed under matrix photolysis conditions. The transoid diazoketone **1EE** cannot undergo concerted Wolff rearrangement, but both **1EE** and **1EZ** may undergo nonconcerted reaction with formation of carbene **2**. This carbene possesses a vacant p orbital capable of overlap with the pyridine lone pair, leading to ylide **6**. Photolysis of **6** leads to ring opening and formation of more of ketene **3E**. The ketenes can be interconverted photochemically. The (thermodynamically controlled) FVT reaction produces predominantly **3Z** because this is the most stable ketene. Since ylide **6** has a calculated energy ca. 43 kcal/mol above the ketenes, there is no possibility of isolating and observing ylide **6** in the thermal gas-phase reaction.

(11) Kaplan, P.; Meloy, G. K. *J. Am. Chem. Soc.* **1966**, *88*, 950. Kaplan, F.; Mitchell, M. L. *Tetrahedron Lett.* **1979**, 759.

The work described here opens the prospect of trapping a wide variety of carbenes as intramolecular ylides for IR spectroscopic observation. Moreover, we have observed the phenomenon of formation of carbonyl compounds absorbing in the 1760 cm^{-1} range also when generating ketenes and/or carbenes by photolysis of acyltriazolopyridines **9** ($R = \text{Me}$ and MeO , weak carbonyl absorptions; $R = \text{Ph}$, strong carbonyl absorption). These carbonyl compounds could be due to pyridine ylides of type **6**, formed via carbene–oxirene–carbene rearrangement. FVT gives only ketenes. As always, the *s-Z* ketenes **10** are preferred according to the good agreement between experimental and DFT-calculated IR spectra (eq 3). These ketenes dimerize to novel quinolizinediones.¹² These reactions are the subject of further investigation.



Experimental Section

General Methods. Preparative FVT experiments were performed in electrically heated quartz tubes (length 40 cm, diameter 2 cm). Solid samples were sublimed into the pyrolysis tube using a Büchi sublimation oven, and liquids were evaporated using an oil bath. The system was evacuated to ca. 10^{-4} mbar and continuously pumped during the pyrolysis using a Leybold-Heraeus turbomolecular pump, PT150. The products were isolated on a coldfinger at liquid N_2 temperature. Matrix isolation experiments used Air Products CSW-2002-6.5 or Leybold-Heraeus ROK 10-300 closed-cycle liquid. He cryostats with BaF_2 or KBr windows, the former cryostat equipped with a Lakeshore model 330 temperature controller. For photolysis experiments, solids were sublimed onto the cold window at 7–30 K, and simultaneously a large excess of Ar (99.999%) was deposited. In FVT experiments, a mixture of Ar and sample was led through a quartz tube (10 cm length, 0.8 cm i.d., equipped with a heating wire and a thermocouple) and subsequently isolated on the cold window at ca. 30 K. Spectra were recorded at 7–30 K using Perkin-Elmer 1700X or System 2000 FTIR or Varian Cary 1 UV spectrometers. All calculations were performed using the Gaussian 98 suite of programs.¹³

Materials. (2-Diazoacetyl)pyridine (**1**) was obtained by the method of Ribereau and Queguiner¹⁴ to yield 75% of a yellow liquid which darkens on standing.

(12) Plüg, C.; Wentrup, C. Unpublished work.

(13) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; J. A. Pople, J. A. *Gaussian 98*; Gaussian, Inc.: Pittsburgh, PA, 1998.

Photolysis of (2-Diazoacetyl)pyridine (1). A sample was codeposited with Ar at 10 K (sample at room temperature; duration 1 h). Peak listings for **1** as well as **6**, **3E**, and **3Z** formed on photolysis are given in the Supporting Information.

FVT of (2-Diazoacetyl)pyridine (1). FVT at 750 °C with Ar matrix isolation of the thermolysate resulted in 2-pyridylketene (**3**) as the only IR-identifiable product (Figure 1 and Table S1 in the Supporting Information). In a similar experiment without Ar, subsequent warm-up to -40 °C caused the ketene bands to disappear, and new bands developed at 1723 (m), 1640 (m), 1573 (m), 1545 (m), and 1358 (m) cm^{-1} . After warm-up to room temperature, the product was isolated and identified as quinolizine **5** by comparison of TLC, melting point, and IR data with the material described below.

2-Hydroxy-3-(2-pyridyl)quinolizin-4(4H)-one (5). A sample of (diazoacetyl)pyridine (**1**, 2.50 g, 17 mmol) was subjected to preparative FVT at 600 °C (3 h, 10^{-4} mbar). The product was condensed on a coldfinger at -192 °C and, after warm-up to room temperature, taken up in dichloromethane, filtered over charcoal, and evaporated. The crude product was sublimed and recrystallized from ethyl acetate to yield 1.52 g (75%) of bright yellow crystals of mp 153–155 °C: IR (KBr) 1660 (s), 1630 (s) 1576 (s) and 798 (s) cm^{-1} ; UV (MeCN) λ_{max} 394 nm ($\log \epsilon$ 4.211), 293 (4.218), 240 (4.442) and 208 (4.406); ^1H NMR (200 MHz; CDCl_3 ; the assignments are based on specific decoupling experiments; coupling constants in Hz) δ 9.39 (1 H, ddd, $^3J = 8.6$, $^4J = 1.0$, $^5J = 1.0$, H6), 9.02 (1 H, dddd, $^3J = 7.6$, $^4J_1 = 1.0$, $^4J_2 = 1.0$, $^5J = 1.0$, H9), 8.39 (1 H, ddd, $^3J = 5.5$, $^4J = 2.0$, $^5J = 1.0$, H6'), 7.92 (1 H, ddd, $^3J_1 = 8.8$, $^3J_2 = 7.6$, $^4J = 2.0$, H5'), 7.28–7.19 (3 H, m), 6.76 (1 H, ddd, $^3J_1 = 7.6$, $^3J_2 = 4.4$, $^4J = 3.4$, H3'), 6.32 (1 H, d, $^4J = 1.0$, H1); ^{13}C NMR (50 MHz; CDCl_3 ; multiplicity assignments are supported by a DEPT spectrum) δ 170.65 (s), 158.30 (s), 157.08 (s), 143.24 (s), 142.43 (d), 138.57 (d), 130.73 (d), 127.58 (d), 123.81 (d), 123.70 (d), 120.42 (d), 112.34 (d), 98.03 (d), 95.58 (d). HRMS calcd for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$ m/z 238.0742, found 238.0743 (M^+ , 100%).

FVT of 2-Hydroxy-3-(2-pyridyl)quinolizin-4(4H)-one (5). FVT of **5** at 750 °C and IR investigation of the Ar matrix isolated product demonstrated the formation of 2-pyridylketene (**3Z**) as the major product: IR (Ar, 12 K) 2133 (vs), 2123 (m), 1595 (m), 1584 (m), 1474 (m), 1453 (m), and 774 (m) cm^{-1} . In addition, an unidentified band at 2260 cm^{-1} (m) was observed.

Acknowledgment. This work was supported by the Australian Research Council.

Supporting Information Available: IR difference spectra showing photochemical isomerization of **3Z** to **3E**, listings of experimental and calculated IR bands for **1**, **6**, **3E**, and **3Z**, relative energies of different conformers of **1**, **3Z**, **3E**, and **6** and different conformers of carbene **2**, calculated IR spectra of four conformers of **1** and the experimental spectrum, calculated energy profile for interconversion of the conformers of **1** (RHF/6-31G*) and experimental and calculated IR spectrum of **6** (B3LYP/6-31G* with $\epsilon = 40$), Cartesian coordinates of all calculated structures at the B3LYP/6-31G(d) level and of the twisted C_1 carbene **2** also at the B3LYP/6-311++G** level (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(14) Ribereau, P.; Queguiner, G. *Can. J. Chem.* **1983**, *61*, 334.