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REACTIVITY OF FLUORENYLIDENEKETENE TOWARDS AMINES. A LASER PHOTOLYSIS STUDY WITH ULTRAVIOLET AND INFRARED DETECTION.

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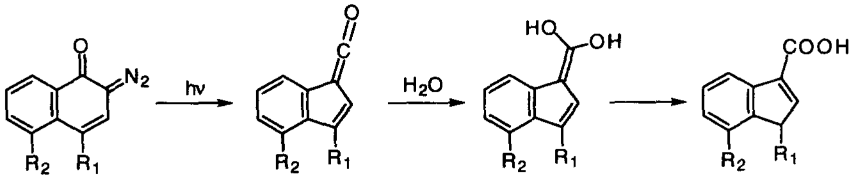
Abstract: The ketene derived from diazoquinone **5** can be readily detected by laser photolysis techniques with IR detection and its behavior agrees with that observed with more conventional UV-visible detection. The ketene reacts with amines (e.g. $k \sim 7 \times 10^{7}$ M^{-1} s^{-1} for diethylamine) to give ylides (yielding amides as final products) that absorb in the 300-340 nm and 1670-1680 cm^{-1} regions.

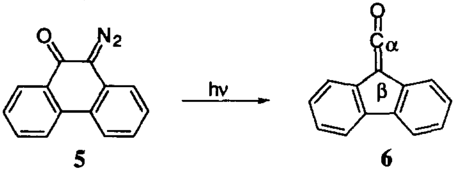
Introduction.

The Wolff rearrangement involves the conversion of α-diazoketones into carboxylic acids or their derivatives.[1,2] The reaction has received considerable attention due to the rich chemistry of the reactive intermediates that mediate the process[3-5], and due to its numerous applications in photoresist technology.[6] Recent work from our[7,8] and other laboratories[9] has shown that the ring contraction of diazonaphthoquinones to 3-indenecarboxylic acids involves the intermediacy of a ketene and that, at least in the nanosecond time scale, there is no need to invoke the participation of either a carbene or an oxirene-like intermediate in this reaction (equation 1). Recent studies suggest that the carbene is detectable in the picosecond time scale, although probably too short-lived to participate in intermolecular reactions.[10]



1 2 3 4 (1)

Studies of **1** in acetonitrile lead to a long-lived ketene that can be trapped by water, alcohols and pyridine. The long lived ketene-pyridine ylide formed with the latter can be detected with laser flash photolysis (LFP) techniques.[7] Product[11] and matrix isolation low temperature IR[12] studies suggest that the photochemistry of **5** follows a mechanism similar to that for **1**. In this work we have combined product studies and LFP measurements with IR and UV-visible detection to explore the photochemistry of **5** and kinetics and mechanisms for **6** in non-aqueous solvents (equation 2).



5 6 (2)

Results and Discussion

Laser flash photolysis with IR detection[13,14] of **5** in acetonitrile showed the instantaneous formation of a transient at 2121 cm^{-1} ($\nu_{C=C=O}$), Figure 1A, characteristic for a ketene.[12,15] This transient is stable over a time scale of 32 μs.[16] Photobleaching was also observed at 2103 cm^{-1} ($\nu_{C=N_2}$) and 1628 cm^{-1} ($\nu_{C=O}$) due to diazoketone depletion. Photolysis of **5** in the presence of amines led to a band at 2121 cm^{-1} corresponding to the $\nu_{C=C=O}$ of the ketene (see Figure 1B). The corresponding decay rate constants (k_{obs}) are linearly dependent on the amine concentration. A plot k_{obs} *versus* $[NR_1R_2R_3]$ leads to $k_{NR1R2R3}$, the second order rate constants ($k_{NR1R2R3}$) for scavenging of ketene **6** by amines. The plots were linear and led to the rate constants in Table 1.

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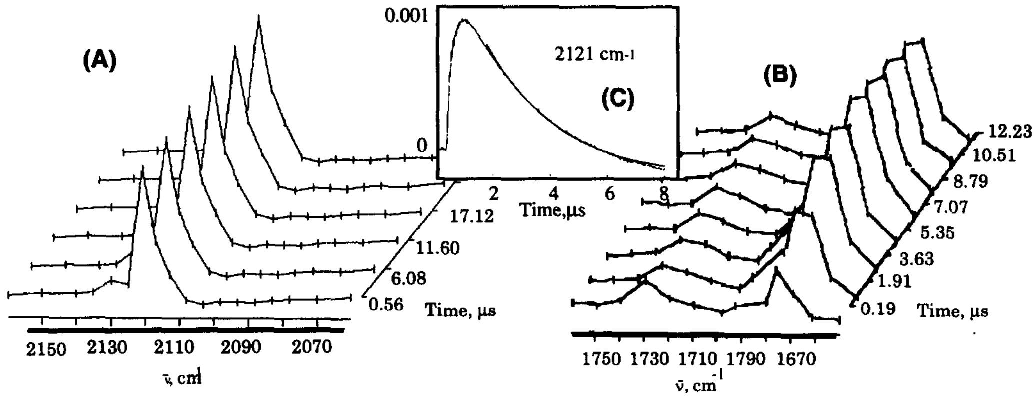


Figure 1: (A) Transient absorption spectrum after 308 nm excitation of **5** in acetonitrile; (B) Same as (A) in the presence of 3 mM diethylamine, and (C) time dependence of the absorbance at 2121 cm^{-1} for sample (B).

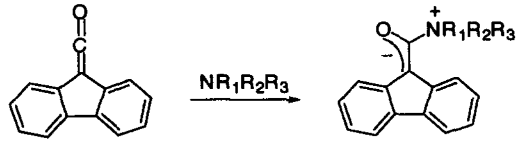
Table 1: Second order rate constants for the reaction of ketene **6** with various amines in acetonitrile solution.[a]

Amine	$k_{NR_1R_2R_3}$ ($M^{-1}s^{-1}$)	wavenumber, cm^{-1}	λ_{max}, nm
diethylamine	$(7.61 \pm 0.29) \times 10^7$		320
	$(6 \pm 1) \times 10^7$	2121	
	$(7 \pm 1) \times 10^7$	1676	
triethylamine	$(5.5 \pm 0.2) \times 10^5$		320
	$(2.4 \pm 0.3) \times 10^5$	2121	
piperidine	$(1.7 \pm 0.1) \times 10^8$		330
	$(8 \pm 2) \times 10^7$	2121	
morpholine	$(3.4 \pm 0.1) \times 10^7$		340
	$(2.9 \pm 0.4) \times 10^7$	2121	
pyridine	$(1.31 \pm 0.12) \times 10^7$		300
	$(1.7 \pm 0.4) \times 10^7$	2121	

[a] For comparison, the corresponding rate constants for diphenylketene are 2.4 x 10^7 $M^{-1}s^{-1}$ for diethylamine, < 10^5 $M^{-1}s^{-1}$ for triethylamine, 3.0 x 10^7 $M^{-1}s^{-1}$ for piperidine, and < 10^5 $M^{-1}s^{-1}$ for pyridine.[14]

The mechanism of the reaction of amine with ketenes is thought to proceed by nucleophillic in-plane attack of the amine on the Cα of the ketene.[17] Our data indicate that **6** is more reactive toward amines than diphenylketene, in spite of the former's aromatic stabilization.[18] The results suggest that the difference in the transition state energies may be more favorable for **6**. A more restrained geometry for **6** possibly reduces steric hindrance.

The growth of a transient with absorption at 1674 cm^{-1} was observed upon photolysis of **5** in the presence of amines (Figure 1C). This transient was assigned to a ketene-amine ylide (i.e., **I** in equation 3). The kinetic trace for the formation of this transient follows first order kinetics; from a plot of the k_{obs} obtained from the growth at 1674 cm^{-1} *vs.* $[NR_1R_2R_3]$ it was also possible to obtain rate constants for the reaction of ketene **6** with amines, Table 1.



6 **I** (3)

Similar results were obtained by using UV-visible detection.[19] Thus, 308 nm LFP of **5** in acetonitrile solution led to a weak and long lived absorption (τ > 100 μs), detected at ~310 nm. Bleaching at 370 nm was consistent with the depletion of the starting material. In agreement with earlier LFP experiments,[7,8,20-22] this transient was assigned to the ketene **6**, and it was formed within our time resolution (≤ 20 ns). LFP of diazoketone **5** in acetonitrile in the presence of amines showed the formation of a new transient with an absorption band centered between 300 - 340 nm, depending upon the amine, with no signal being detected between 450 - 700 nm. Figure 2 shows the transient absorption spectrum after 308 nm LFP of **5** in acetonitrile containing 0.143 M Et_3N. We assign this transient to **I** (equation 3). The inset of Figure 2 shows the formation of the **6**-Et_3N ylide, which follows first-order kinetics. Similar behavior was observed for the different amines listed in Table 1.

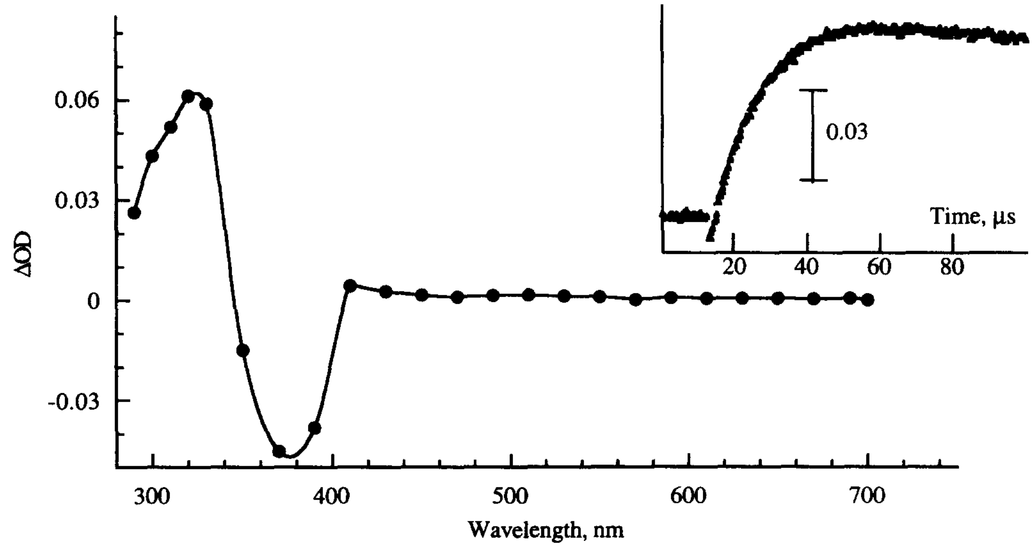
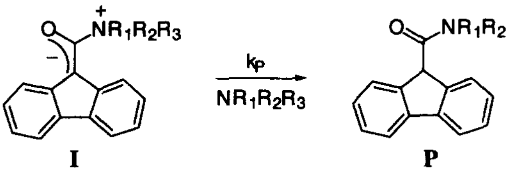


Figure 2: Transient absorption spectrum measured after 308 nm excitation of **5** in ACN containing 0.143 M Et_3N. Inset: Growth of the transient absorption at 320 nm.

The formation of a ketene-amine ylide (**I**) is followed by a decay on longer time-scales. For the amines under study, the decay of **I** follows first order kinetics, and is linearly dependent upon amine concentration and leads to product formation from the decomposition of the ylide (equation 4). A plot of k_{obs} *versus* $[NR_1R_2R_3]$ gives the rate constant k_P. Table 2 shows the second order rate constants k_P for the reaction of intermediate **I** with amines in acetonitrile. We note that for reaction with pyridine, this intermediate was stable over a time-scale of ≥ 200 μs, whereas for morpholine its decay followed complex kinetics.



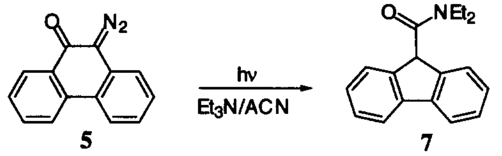
(4)

Table 2: Second order rate constants for the reaction of **I** with amines in acetonitrile solution.

Amine	k_p ($M^{-1}s^{-1}$)	LFP technique
diethylamine	$(6.5\pm0.4)\times10^6$	UV-Visible
	$(1.7\pm0.4)\times10^7$	IR at 1676 cm^{-1}
piperidine	$(1.9\pm0.1)\times10^7$	UV-Visible
triethylamine	$(7.3\pm0.5)\times10^4$	UV-Visible

In the case of diethylamine, LFP with IR detection led to a rate constant for ylide reaction with the amine of ~7 x 10^7 M^{-1} s^{-1} with good linear dependence of the rate constant for ylide decay with amine concentration. However, the growth of the amide (monitored at 1630 or 1640 cm^{-1}) agreed with ylide decay only for $[Et_2NH]$ ≤ 0.01 M. At higher concentrations, the growth remained at a lifetime of ~5 μs. It is unclear whether this is simply a reflection of extensive spectral overlap (bleaching occurs at 1628 cm^{-1}), or if reaction 4 involves an additional intermediate. We favor the former explanation. We note that in simpler cases (where spectral overlap is not as much of a problem), such as phenyl ketene, formation of the amide is concurrent with ylide decay.[14]

In order to obtain further support for the assignments proposed above, product studies were carried out for the reaction of **5** with triethylamine. GC/MS analysis confirms that the final product is the amide, **7** (equation 5).



(5)

In summary, our studies show that ketenes derived from cyclic diazoquinones can be readily detected by LFP techniques with IR detection and that their behavior fully agrees with that observed with the more conventional UV-visible detection. The ketenes react readily with amines (e.g. k ~7 x 10^7 M^{-1} s^{-1} for diethylamine) to give ylides that absorb in the 300-340 nm and 1670-1680 cm^{-1} regions. The ylides convert to the corresponding amides through a reaction mediated by the same amines involved in their formation.[23]

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