

## Nucleophilicity toward Ketenes: Rate Constants for Addition of Amines to Aryl Ketenes in Acetonitrile Solution

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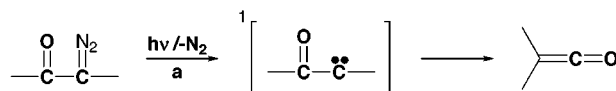
Second-order rate constants ( $k_{\text{Nu}}$ ) have been measured for the addition of amines to ketenes **4–6** in acetonitrile solution by the laser flash photolysis technique. These ketenes are formed from a photochemical Wolff rearrangement of diazoketones **1–3**, respectively. For all diazoketones studied, the presence of amines as nucleophiles in the reaction medium results in the formation of an intermediate that later converts to the amide. The rate of formation of these intermediates is linearly dependent on amine concentration. Various classes of amines, such as primary, secondary, and tertiary, aromatic, and aliphatic, have been used to investigate the ketene reactivity, and rate constants in the range  $10^4$ – $10^9$   $\text{M}^{-1} \text{s}^{-1}$  have been measured. Reaction rates are dependent upon steric effects in both the ketene and the nucleophile, which is consistent with a reaction mechanism involving nucleophilic attack at C $\alpha$  in the molecular plane of the ketene. On the basis of these data, a set of  $N_+$  parameters for the reaction of amines with ketenes was determined.

### Introduction

The reaction of ketenes with various nucleophiles has been known since the beginning of the century and has been reviewed.<sup>1</sup> Reaction with water generates carboxylic acids,<sup>2,3</sup> whereas addition of alcohols<sup>4,5</sup> or amines<sup>1,6,7</sup> yields esters and amides, respectively. Sulfur and phosphorus nucleophiles have also been shown to add to ketenes.<sup>8,9</sup> Most of the kinetic studies of ketene reactivity have focused on its hydration.<sup>1,10–17</sup>

Ketenes are commonly generated by a photo-Wolff rearrangement from the corresponding diazoketones, as

### Scheme 1



shown in Scheme 1. It has been recently shown by picosecond spectroscopy that in the cases of 2-diazonaphthalen-1(2*H*)-one and methyl 2-diazo-(2-naphthyl) acetate the precursor for the ketene is a short-lived singlet carbene.<sup>18</sup>

In this paper, we present results on the characterization of ketenes **4–6** (eqs 1–3), and their reactivity toward amines based on laser flash photolysis studies.

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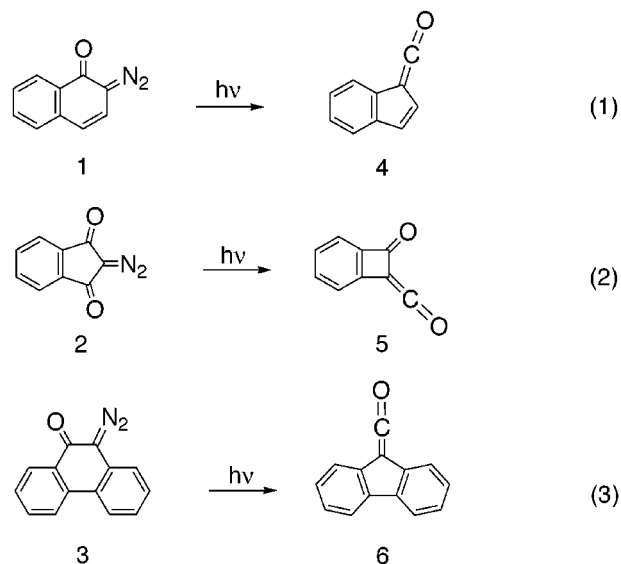
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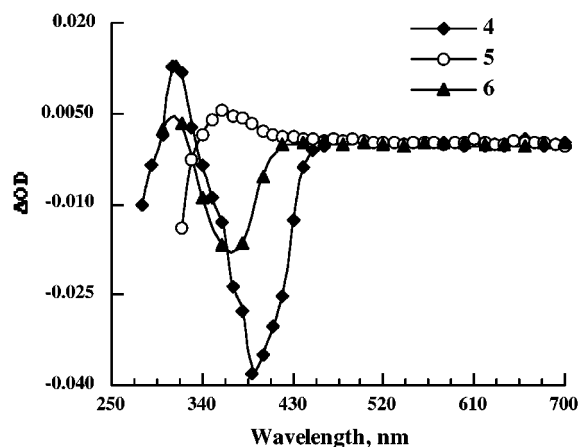
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**Figure 1.** Transient absorption spectra measured after 308 nm laser excitation of **1** (76  $\mu$ s after laser pulse), **2** (30  $\mu$ s after laser pulse), and **3** (0.4  $\mu$ s after laser pulse) in ACN solution.

## Results

### Generation of Ketenes in Acetonitrile Solution.

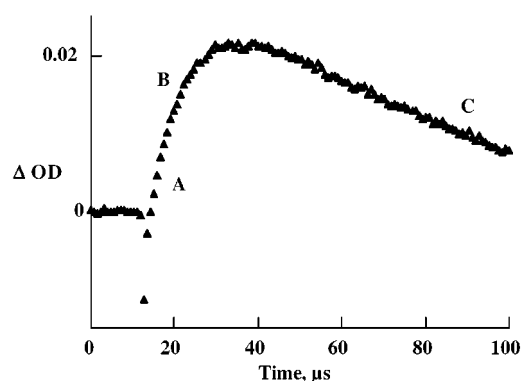
It has been previously shown that the photo-Wolff rearrangement of 2-diazo-1,2-naphthoquinone (**1**),<sup>17,19,20</sup> 2-diazo-1,3-indandione (**2**),<sup>3</sup> and 9-diazo-9,10-phenanthrenequinone (**3**)<sup>21</sup> generates benzofulvenketene (**4**),  $\alpha$ -ketenylbenzocyclobutenone (**5**), and dibenzofulvenketene (**6**), respectively (eqs 1–3).

Figure 1 shows the transient absorption spectra recorded after 308 nm laser excitation of the  $\alpha$ -diazoketones **1–3** in acetonitrile solution. Besides a considerable bleaching, resulting from the depletion of ground-state absorption by the starting material at 370, 310, and 370 nm for **1**, **2**, and **3**, respectively, we also observed a very weak long-lived absorption ( $\tau > 100 \mu$ s) in the three systems. The transient species generated from  $\alpha$ -diazoketones **1** and **3** have UV absorption maxima centered at 310 nm, while that of **2** is centered at 360 nm. It was not possible to time resolve the formation of this transient, as it is formed during the laser pulse ( $\leq 10$  ns). These transients were assigned to the ketenes **4**, **5**, and **6**, respectively, in agreement with earlier reports<sup>3,17,19–21</sup> as well as with previously published results using infrared detection laser flash photolysis.<sup>22</sup>

No evidence has been found for the presence of any other intermediate such as a triplet diazoketone or ketocarbene<sup>23</sup> (see Scheme 1). If such an intermediate had been formed it must have been converted to the ketene during the time scale of the laser pulse ( $\sim 10$  ns). This observation is in agreement with reported experiments on the hydration of **1** using picosecond laser flash photolysis.<sup>20</sup>

### Intermolecular Reaction of Ketenes with Amines.

The flash photolysis of  $\alpha$ -diazoketones **1–3** in the pres-



**Figure 2.** Kinetic trace at 320 nm obtained after excitation of **1** in  $9.6 \times 10^{-5}$  M diethylamine in ACN solution.

ence of amines in acetonitrile solution revealed starting material bleaching, followed by a recovery and a concomitant absorbance increase around 300 nm. During the first few microseconds after the laser pulse, the formation of a second, more strongly absorbing intermediate, was observed in the range of 300–340 nm. This absorption increased over a period of  $\sim 20 \mu$ s and finally decayed with considerably slower kinetics. These absorbance changes, i.e., step, growth, and decay, are similar to those observed in previous flash photolysis studies of diazonaphthoquinones in aqueous solution.<sup>17,19,20</sup> Figure 2 shows a kinetic trace at 320 nm obtained after excitation of **1** in  $9.6 \times 10^{-5}$  M diethylamine in acetonitrile solution. The trace clearly shows the growth (B) resulting from nucleophilic addition of amine, yielding the intermediate **I**, and the final decay (C), reflecting the tautomerization of **I** to the final product according eq 4, where the normal product is the amide. In the case of tertiary amines product formation involves alkene loss, for example, diethylamine and triethylamine give the same product, but in the latter case ethylene is lost.<sup>22</sup>

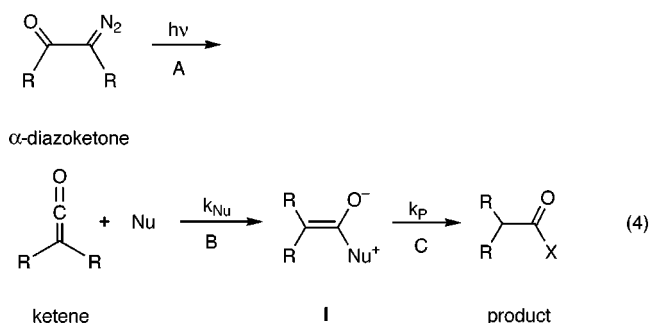


Figure 3 shows a representative example (photolysis of **2** in the presence of 0.014 M triethylamine, in acetonitrile solution) of the transient absorption spectra at four different time intervals after the laser pulse. These spectra clearly show that in the presence of amine the absorption due to the ketene intermediate (310 nm) is quenched while two new absorption bands (assigned to intermediate **I**), centered at 300 and 420 nm, grow in. In all cases, no signal was detected in the region between 500 and 700 nm.

Figure 4 shows the transient spectrum obtained after 355 nm excitation of **1** in acetonitrile solution containing  $1.9 \times 10^{-4}$  M pyrrolidine, and the inset shows a kinetic trace monitored at 330 nm.

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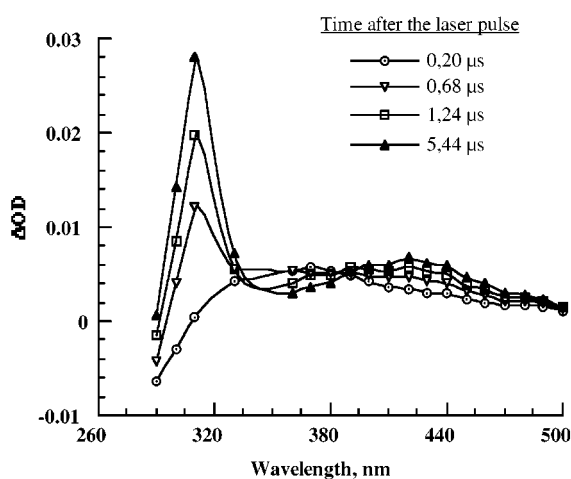
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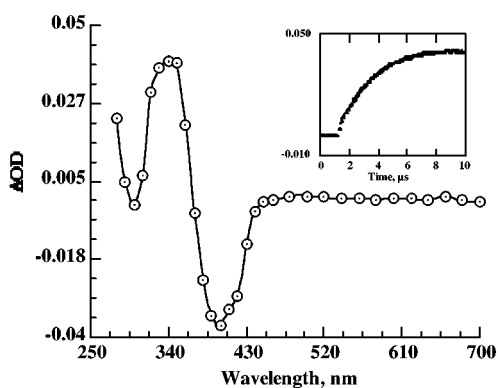
**Table 1.** Second-Order Rate Constants for the Intermolecular Quenching of the Ketenes 4–6 by Various Amines in Acetonitrile

| amines                                 | $k_{\text{Nu}} (\text{M}^{-1} \text{s}^{-1})^a$ |                               |                               |
|--|---|-------------------------------|-------------------------------|
|  | ketene 4  | ketene 5                      | ketene 6                      |
| (a) diethylamine                       | $(1.02 \pm 0.04) \times 10^9$                   | $(1.08 \pm 0.02) \times 10^9$ | $(7.61 \pm 0.29) \times 10^7$ |
| (b) triethylamine                      | $(7.64 \pm 0.18) \times 10^7$                   | $(7.99 \pm 0.50) \times 10^7$ | $(5.52 \pm 0.13) \times 10^5$ |
| (c) tri- <i>n</i> -butylamine          | $(2.96 \pm 0.20) \times 10^6$                   | $(2.70 \pm 0.04) \times 10^7$ | $(4.86 \pm 0.11) \times 10^5$ |
| (d) quinuclidine                       | $(1.41 \pm 0.02) \times 10^9$                   | $(9.88 \pm 0.17) \times 10^8$ | $(3.48 \pm 0.08) \times 10^6$ |
| (e) piperazine                         | $(2.75 \pm 0.03) \times 10^9$                   | $(6.92 \pm 0.18) \times 10^9$ | $(1.75 \pm 0.05) \times 10^8$ |
| (f) piperidine                         | $(1.92 \pm 0.04) \times 10^9$                   | $(3.47 \pm 0.10) \times 10^9$ | $(1.77 \pm 0.05) \times 10^8$ |
| (g) 2-methylpiperidine                 | $(3.42 \pm 0.09) \times 10^8$                   | $(9.07 \pm 0.59) \times 10^8$ | $(3.50 \pm 0.15) \times 10^7$ |
| (h) 3-methylpiperidine                 | $(1.92 \pm 0.04) \times 10^9$                   | $(2.26 \pm 0.04) \times 10^9$ | $(9.28 \pm 0.31) \times 10^7$ |
| (i) 4-methylpiperidine                 | $(1.84 \pm 0.04) \times 10^9$                   | $(2.70 \pm 0.07) \times 10^9$ | $(1.12 \pm 0.03) \times 10^8$ |
| (j) <i>cis</i> -2,6-dimethylpiperidine | $(1.87 \pm 0.04) \times 10^8$                   | $(3.56 \pm 0.17) \times 10^8$ | $(1.13 \pm 0.02) \times 10^7$ |
| (k) 2,2,6,6-tetramethylpiperidine      | $(1.23 \pm 0.02) \times 10^7$                   | $(1.34 \pm 0.03) \times 10^8$ | $(6.19 \pm 0.17) \times 10^4$ |
| (l) pyrrolidine                        | $(2.32 \pm 0.04) \times 10^9$                   | $(4.83 \pm 0.10) \times 10^9$ | $(2.46 \pm 0.04) \times 10^8$ |
| (m) morpholine                         | $(1.40 \pm 0.03) \times 10^9$                   | $(2.03 \pm 0.04) \times 10^9$ | $(3.40 \pm 0.11) \times 10^7$ |
| (n) thiomorpholine                     | $(1.38 \pm 0.03) \times 10^9$                   | $(1.95 \pm 0.04) \times 10^9$ | $(6.87 \pm 0.29) \times 10^7$ |
| (o) pyridine                           | $(2.72 \pm 0.26) \times 10^8$                   | $(6.77 \pm 0.17) \times 10^8$ | $(1.31 \pm 0.12) \times 10^7$ |
| (p) 2,6-lutidine                       | $(2.38 \pm 0.08) \times 10^8$                   | $(1.53 \pm 0.17) \times 10^7$ | $(7.73 \pm 0.05) \times 10^6$ |

<sup>a</sup> Error limits reported as one standard deviation.

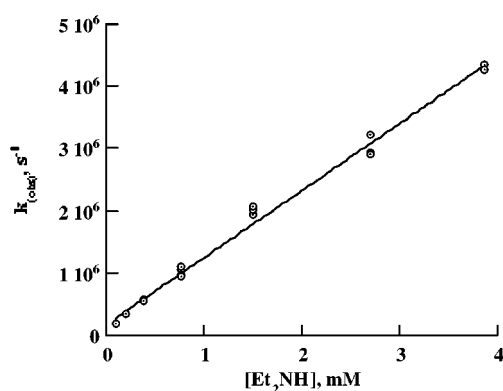


**Figure 3.** Transient spectra measured at various time intervals after 308 nm excitation of **2** in ACN containing 0.014 M of  $\text{Et}_3\text{N}$ .



**Figure 4.** Transient absorption spectrum for the transient obtained (8  $\mu\text{s}$  after the laser pulse) after excitation (355 nm) of **1** in  $1.9 \times 10^{-4}$  M pyrrolidine, in ACN. Upper right inset reveals the growth at 330 nm.

A rate constant,  $k_{\text{Nu}}$ , can be obtained as the slope of a plot of  $k_{\text{obs}}$  vs  $[\text{Nu}]$ , according to the simple relationship given in eq 5, where  $\tau_0$  is the ketene lifetime in the absence of amine and  $k_{\text{obs}}$  is the observed first-order growth rate constant for the intermediate **I** in the presence of a given concentration of amine. Thus, a



**Figure 5.** Observed first-order rate constant for the growth of the intermediate **I** formed upon photolysis of **2** in ACN as a function of the concentration of diethylamine.  $\lambda_{\text{exc}} = 308$  nm;  $\lambda_{\text{mon}} = 320$  nm.

number of rate constants for the reaction of ketenes **4–6** with amines were determined in quenching experiments and the results are presented in Table 1. Figure 5 shows a representative plot according to eq 5 for the diazoketone **2**/ $\text{Et}_2\text{NH}$  system, in acetonitrile.

$$k_{\text{obs}} = \tau_0^{-1} + k_{\text{Nu}}[\text{amine}] \quad (5)$$

By using ultraviolet detection with the laser flash photolysis system, intermediates of general structure **I** were directly observed as a grow-in trace with first order kinetics for all ketene and nucleophile structures. In some cases it was possible to observe the ketene decay, however the signal was usually weak, preventing a detailed kinetic analysis. For the diazoketone **3**/diethylamine system, using infrared detection in the laser flash photolysis experiments, it was possible to observe the growth of intermediate **I**, together with the decay of ketene **6** by monitoring their absorption frequencies at 1674 and 2121  $\text{cm}^{-1}$ , respectively.<sup>22</sup>

## Discussion

The relative reactivity of nucleophiles with electrophiles can be expressed in the form of a Brønsted plot ( $\log k_{\text{Nu}}$  vs  $\text{p}K_{\text{a}}$ ), eq 6. However, it is important to note that this reactivity is governed not only by the basic

strength of the nucleophile but also by the degree of steric hindrance associated with it, as well as to the polarizability of the electron density of the nucleophilic atom.

$$\log k_{\text{Nu}} = pK_a + \beta_{\text{Nu}} + \text{constant} \quad (6)$$

Another important factor is desolvation of the nucleophile (and of the electrophile) in protic solvents, which must occur as the initial step along the reaction coordinate. A direct demonstration of how solvation can influence nucleophilic reactions can be observed by an inverse relationship between nucleophilicity and basicity, i.e., negative values for  $\beta_{\text{Nu}}$ .<sup>24</sup> In our studies, acetonitrile has been used as the solvent in order to minimize desolvation effects and thus limit solvent/amine and solvent/ketene interactions to moderate dipole-dipole interactions.

Plots according to eq 6 for the reaction of ketenes **4–6** with a series of seven amines used in this work, and compared with  $pK_a$  values available in the literature,<sup>25</sup> show that there is no simple correlation between basicity and reactivity for the nucleophilic attack of these amines to ketenes. A similar observation has been made for the reactivity of  $\text{Ph}_2\text{C}=\text{C}=\text{O}$  with bases in aqueous solution.<sup>7</sup> The absence of such a correlation between basicity and reactivity is frequently encountered in nucleophilic reactions, and a classic example can be seen in the reaction of *p*-nitrophenylacetate with amines.<sup>26</sup>

Nucleophilicity is a fundamental concept in the description of a large class of chemical reactions occurring in solution. However, a broad applicability of quantitative measurements of nucleophilicity continues to be difficult, despite various concepts that can be utilized to relate nucleophilicity and basicity. Many parameters that describe nucleophilic character have been defined and evaluated for a series of nucleophiles reacting with carbon electrophiles. Ritchie defined and determined values for the parameter  $N_+$  for describing the reactivity of a series of nucleophiles with  $\text{sp}^2$  hybridized carbon electrophiles.<sup>27,28</sup> While this parameter was originally defined for the reaction of carbocations with nucleophiles,<sup>29</sup> it has also been applied to the analysis of nucleophilic attack on aromatic rings<sup>30</sup> or carbonyl compounds.<sup>27</sup> In contrast to other linear free energy relationships, the correlation of reactivity with nucleophilicity in terms of eq 7 yields slopes of one that indicate that the selectivity for various nucleophiles is independent of the reactivity of the electrophile that is being investigated. An interesting characteristic of the Ritchie equation is the absence of a reactivity parameter, which appears to violate the reactivity-selectivity principle.

$$\log k - \log k_0 = N_+ \quad (7)$$

For the Ritchie equation,  $k$  is the second-order rate constant for the reaction of a cation-nucleophile pair in

a specific solvent and  $k_0$  is the rate constant for the reference nucleophile, usually water.

It was later shown that eq 7 is not strictly valid, and that a better correlation is obtained when families of different electrophiles are treated separately.<sup>28</sup> A large number of publications show the limitations<sup>31–35</sup> of eq 7, in contrast with the large volume of data reported by Ritchie.<sup>27,29,36</sup>

Ritchie defined  $N_+$  values for 26 amines reacting with a series of carbocations, diazonium cations, and acyl derivatives in aqueous solution.<sup>27</sup> However, subsequent examination of these data for amine reactivity with diphenylmethyl cations<sup>28</sup> indicated variations in  $N_+$  for individual amines by more than one unit in several cases. Some of these differences could be explained by differences in steric effects at the electrophile center, which were not taken into account in Ritchie's model.

Heo and co-workers<sup>37</sup> suggested that a better system for the determination of  $N_+$  values should be a reaction involving a nucleophilic attack as the rate-determining step of the reaction with a carbon electrophile that presents the minimum of steric hindrance. To achieve these conditions, the Michael addition to 1-methyl-4-vinylpyridinium cation was used to determine  $N_+$  values for a series of amines in aqueous solution.

Since the data reported by Heo<sup>37</sup> were obtained for a system that more closely resembles ours than the addition to a cation reported by Ritchie (see above), values of  $N_+$  obtained by Heo were employed in the analysis of our results. Thus, correlations of rate constants for the ketenes **4–6** with these  $N_+$  parameters are summarized in eqs 8–10, respectively.

$$\log k_{\text{Nu}}(\mathbf{4}) = 7.28(\pm 0.21) + 0.25(\pm 0.03)N_+ \quad (r = 0.98) \quad (8)$$

$$\log k_{\text{Nu}}(\mathbf{5}) = 5.94(\pm 0.46) + 0.45(\pm 0.06)N_+ \quad (r = 0.97) \quad (9)$$

$$\log k_{\text{Nu}}(\mathbf{6}) = 3.97(\pm 1.5) + 0.54(\pm 0.06)N_+ \quad (r = 0.79) \quad (10)$$

Applying Ritchie's equation and  $N_+$  values obtained by Heo to our data, the values for the slopes obtained from eqs 8–10 are quite different from 1. These results can reflect differences in the solvation of the nucleophile, as we are comparing results obtained in different solvents and with different electrophiles. Therefore, the  $N_+$  values of Heo may not be applicable to our system due to the large structural differences between the electrophiles employed in the two cases.

To facilitate the comparison between structure and reactivity for ketenes **4–6**, we have used Ritchie's equation (eq 7) and calculated our own set of  $N_+$  parameters. In doing so, the reaction of ketene **5** with nucleophiles

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**Table 2.** Second-Order Rate Constants for the Intermolecular Quenching of the Ketenes 4–6 by Various Nucleophiles in Acetonitrile

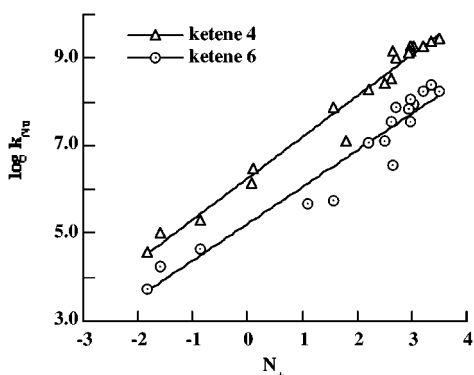
| nucleophiles                          | $k_{\text{Nu}} (\text{M}^{-1}\text{s}^{-1})^a$ |                               |                               |
|---------------------------------------|--|-------------------------------|-------------------------------|
|                                       | ketene 4                                       | ketene 5                      | ketene 6                      |
| (q) 2-propanol <sup>b</sup>           | $(1.36 \pm 0.07) \times 10^6$                  | $(7.02 \pm 0.25) \times 10^5$ | $(2.33 \pm 0.17) \times 10^5$ |
| (r) methanol <sup>b</sup>             | $(5.12 \pm 0.32) \times 10^6$                  | $(7.14 \pm 0.10) \times 10^6$ | $(1.07 \pm 0.06) \times 10^6$ |
| (s) P(EtO) <sub>3</sub>               | $(1.39 \pm 0.04) \times 10^6$                  | $(2.54 \pm 0.16) \times 10^6$ | $(6.60 \pm 0.08) \times 10^3$ |
| (t) DMSO                              | $(3.68 \pm 0.19) \times 10^4$                  | $(3.07 \pm 0.24) \times 10^4$ | $(5.56 \pm 0.60) \times 10^3$ |
| (u) (CH <sub>3</sub> ) <sub>2</sub> S |  | $(1.48 \pm 0.04) \times 10^4$ |                               |

<sup>a</sup> Error limits reported as one standard deviation. <sup>b</sup> Pseudo-first-order rate constant.

**Table 3.**  $N_+$  Parameters of Nucleophilicity<sup>a</sup>

| nucleophiles                           | $N_+(\mathbf{5})_{\text{ketene 5}}$ |
|--|-------------------------------------|
| (a) diethylamine                       | 2.70                                |
| (b) triethylamine                      | 1.57                                |
| (c) tri- <i>n</i> -butylamine          | 0.10                                |
| (d) quinuclidine                       | 2.67                                |
| (e) piperazine                         | 3.51                                |
| (f) piperidine                         | 3.21                                |
| (g) 2-methylpiperidine                 | 2.63                                |
| (h) 3-methylpiperidine                 | 3.02                                |
| (i) 4-methylpiperidine                 | 2.98                                |
| (j) <i>cis</i> -2,6-dimethylpiperidine | 2.22                                |
| (k) 2,2,6,6-tetramethylpiperidine      | 1.78                                |
| (l) pyrrolidine                        | 3.35                                |
| (m) morpholine                         | 2.98                                |
| (n) thiomorpholine                     | 2.96                                |
| (o) pyridine                           | 2.50                                |
| (p) 2,6-lutidine                       | 0.85                                |
| (q) 2-propanol <sup>b</sup>            | -1.60                               |
| (r) methanol <sup>b</sup>              | -0.87                               |
| (s) P(EtO) <sub>3</sub>                | 0.07                                |
| (t) DMSO                               | -1.84                               |
| (u) (CH <sub>3</sub> ) <sub>2</sub> S  | -2.17                               |

<sup>a</sup>  $\log k_0 = 6.08, 6.33,$  and  $5.02$  for the ketenes **4**, **5**, and **6**, respectively. <sup>b</sup> Value obtained from the pseudo-first-order rate constant divided by the molarity of the solvent (24.7 M for methanol and 13.06 M for 2-propanol).

**Figure 6.** Correlation between  $N_+$  parameters obtained from the reaction of ketene **5** with amines and the rate constant for the reaction of ketenes **4** and **6** with amines.

(including alcohols such as methanol and 2-propanol,<sup>38</sup> dimethyl sulfoxide–DMSO, trimethyl phosphite–TMP, and dimethyl sulfide–DMS; see Table 2) was chosen as a standard. We have used the pseudo-first-order rate constants for the hydration of the ketenes as our  $\log k_0$  (see eq 7), and the results are presented in Table 3.

Figure 6 shows a plot of the log of the second-order rate constant for reaction of the ketenes **4** and **6** with different nucleophiles versus  $N_+$  values determined from

the data for ketene **5** with the same nucleophiles. Equations 11 and 12 describe the correlation for ketenes **4** and **6**, respectively. Data for amines that have large steric effects such as 2,6-lutidine (for ketene **4** and **6**), tri-*n*-butylamine (ketene **4**), and 2,2,6,6-tetramethylpiperidine (ketene **6**) were excluded from the plot as substrates with large steric effects do not correlate well with the values of  $N_+$  used.

$$\log k_{\text{Nu}}(\mathbf{4}) = 6.26(\pm 0.09) + 0.94(\pm 0.04)N_+ \quad (r = 0.97) \quad (11)$$

$$\log k_{\text{Nu}}(\mathbf{6}) = 5.22(\pm 0.15) + 0.84(\pm 0.06)N_+ \quad (r = 0.96) \quad (12)$$

Figure 6 reveals that nucleophilic addition to ketenes **4–6** has comparable selectivity. A quantitative comparison of the selectivity relationships can be made from the values of the slopes obtained from these plots. The plot for ketene **4** gives a slope close to 1, which indicates that the selectivity for this ketene is similar to that for ketene **5**.<sup>3</sup> The large difference in selectivity between ketenes **4** and **5**, in comparison to **6**, can be attributed to the steric hindrance in the molecular plane of ketene **6**, which considerably influences its selectivity (vide supra).

In general, secondary amines are better nucleophiles than tertiary amines. This order of reactivity is in agreement with a mechanism in which the base acts as a nucleophile by attacking the ketene  $\alpha$ -carbon. In nucleophilic reactions, tertiary amines have a lower reactivity than secondary amines due to a steric hindrance in the plane of attack of the molecule. Substituents on the ketene are positioned in the molecular plane of attack, and when they are large they can hinder the approach of the nucleophile. For example, the low reactivity observed for the hydration of  $(t\text{-Bu})_2\text{C}=\text{C}=\text{O}$  has been attributed to this effect.<sup>11,39</sup> In our case, ketenes **4** and **5** present less steric hindrance in the plane of attack in comparison to ketene **6**. In the case of **6**, the presence of two hydrogen atoms in the vicinity of the reactive center (Scheme 2) results in a considerable steric effect for a nucleophilic attack on the ketene moiety, and consequently, **6** has a lower reactivity than ketenes **4** and **5**.

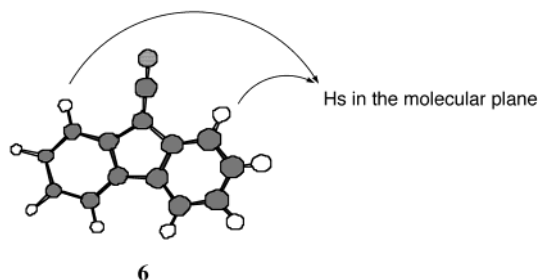
We note that despite the high reactivity of ketenes **4–6** a fairly good correlation between reactivity and nucleophile basicity is observed. For example, pyridine is a weaker base than piperidine and reacts 1 order of magnitude slower than piperidine with the three ketenes.

The importance of steric effects in the nucleophile can be confirmed by comparing the reactivity of amines with similar  $pK_a$ 's but different substitution patterns at the nitrogen. For example, diethylamine is approximately 2

(38) Rate constants for these two nucleophiles have been previously reported (cf. ref 3):  $k_{\text{methanol}} = 7.14 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ ;  $k_{2\text{-propanol}} = 7.02 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}$ .

(39) Kabir, S. H.; Seikaly, H. R.; Tidwell, T. T. *J. Am. Chem. Soc.* **1979**, *101*, 1059.

Scheme 2



orders of magnitude more reactive than triethylamine or tri-*n*-butylamine. Similar effects can also be observed when comparing the reactivities of the ketenes with a series of piperidines substituted in positions 2 and 6 (see Table 1). For the three systems, incorporation of methyl groups at positions 2 and 6 in piperidine reduces the reactivity by a factor of 5 for ketenes **4** and **5**. On the other hand, a factor of 200 is observed when one compares the reactivity of ketene **6** with 2,6-dimethylpiperidine or 2,2,6,6-tetramethylpiperidine. This large difference probably reflects steric effects originating in both the ketene **6** and the nucleophile.

Another interesting observation deals with the comparison of the reactivity of ketene **4** with tertiary amines such as tri-*n*-butylamine and quinuclidine. This ketene is 500 times more reactive toward quinuclidine than tri-*n*-butylamine, which appears to reflect the steric effect of the free aliphatic groups of tri-*n*-butylamine in comparison to the tied-back groups in quinuclidine.

The similarity in the reactivity of morpholine and thiomorpholine for the three ketenes **4–6** suggests that nitrogen is acting as the nucleophilic center in both cases.

## Experimental Section

**Materials.** Acetonitrile, spectroscopic grade, was used as received. The amines used (Aldrich) in quenching experiments were distilled before use when necessary (purity grade <99%). Dimethyl sulfoxide (spectroscopic grade), triethyl phosphite, and dimethyl sulfide (Aldrich) were used as received.

**Synthesis.** 2-Diazo-1,2-naphthoquinone (**1**) was synthesized according to a literature procedure.<sup>40</sup> Mp: 77–78 °C (lit.<sup>41</sup> mp 77 °C). Yield: 70%. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) 6.52 (1H, d, *J* = 9.34 Hz); 6.82 (1H, d, *J* = 9.38 Hz); 7.57–7.36 (3H, m); 8.27 (1H, dd). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 180.0 (C=O), 137.4; 132.6; 129.4; 128.1; 127.1; 125.2; 117.2; 116.2; 77.2 (C=N<sub>2</sub>). MS *m/z* (EI) 170 (M<sup>+</sup>, 35), 142 (45), 114 (100), 88 (21). IR: 2145, 2112, 1609, 1588 cm<sup>-1</sup>. UV λ<sub>max</sub>

(acetonitrile): 248 nm (ε = 1.40 × 10<sup>4</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>), 389 nm (ε = 7.20 × 10<sup>3</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>).

2-Diazo-1,3-indandione (**2**) was synthesized according to a literature procedure.<sup>42,43</sup> Mp: 146–148 °C (lit.<sup>44</sup> mp 149 °C). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) 7.23–7.83 (m, 4H). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 182.09 (C=O), 137.02; 134.74; 122.65; 70.11 (C=N<sub>2</sub>). MS *m/z* (EI): 172 (M<sup>+</sup>, 89.7), 144 (8), 88 (100), 62 (56.8). IR: 2120, 1682, 1591 cm<sup>-1</sup>. UV λ<sub>max</sub> (acetonitrile): 248 nm (ε = 5.52 × 10<sup>4</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>), 286 nm (ε = 7.80 × 10<sup>3</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>), 314 nm (ε = 5.14 × 10<sup>3</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>).

9-Diazo-9,10-phenanthrenequinone (**3**) was prepared according to a literature method.<sup>45</sup> Mp: 111–112 °C (lit.<sup>46</sup> mp 113–114 °C). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>): δ (ppm) 7.20–7.76, 8.24–8.43 (8H, m). <sup>13</sup>C NMR (300 MHz, CDCl<sub>3</sub>): δ (ppm) 179.5 (C=O), 134.8; 133.1; 129.6; 128.9; 127.9; 126.3; 125.1; 125.0; 124.2; 124.0; 123.0; 120.3; 75.0 (C=N<sub>2</sub>). MS *m/z* (EI): 220 (M<sup>+</sup>, 22.2); 192 (68.6); 164 (100). IR: 2087, 1598, 1567 cm<sup>-1</sup>. UV λ<sub>max</sub> (acetonitrile): 250 nm (ε = 4.20 × 10<sup>4</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>), 360 nm (ε = 9.12 × 10<sup>3</sup> L·mol<sup>-1</sup>·cm<sup>-1</sup>).

**Apparatus.** UV absorption spectra were obtained on an HP-8451A diode array spectrophotometer. Liquid chromatography was performed using a Varian model 9090 instrument with a diode-array detector. Gas chromatography analyses were performed using a Perkin-Elmer model 8320 system. GC–MS analyses were performed using a VG 7070 or a CONCEPT II. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded using a Varian Gemini XL 200 or XL 300.

**Laser Flash Photolysis Studies.** Since the samples readily deteriorated upon laser excitation, time-resolved measurements were performed using a flow system. The irradiation cell built from 7 × 7 cm<sup>2</sup> Suprasil quartz was connected with Teflon tubing to a reservoir where the solution was deaerated by bubbling with oxygen-free nitrogen. The laser flash photolysis system with UV–vis detection at the University of Ottawa is similar to that described earlier.<sup>46,47</sup> Excitation was achieved using a Lumonics EX-530 excimer laser operated with XeCl (λ = 308 nm, ~6 ns, <120 mJ/pulse); a Lumonics EX-510 excimer laser operated with KrF (λ = 248 nm, ~6 ns, ≤80 mJ/pulse), or a Nd:YAG Surelite laser, using the third harmonic (λ = 355 nm, <10 ns, 20 mJ/pulse). The solute concentrations were 0.1–0.01 mM. All measurements were performed at room temperature.

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