only cases in which homochiral segments can be assembled into achiral molecules and constitute a generalization of la coupe du roi, generally used for C_{nv} molecules only.

The first conclusion may have some relevance to the fact that living beings prefer homochirality, i.e., they use only the L series of amino acids in proteins and only the D family of nucleotides in nucleic acids, a fact closely related to the origin of life.[22,23] Since chain compounds can be regarded as cyclic systems with an infinite number of members,[24] our symmetry analysis above indicates that, in proteins or nucleic acids, an enantiomeric chain compound can only be obtained from homochiral building blocks.

Acknowledgment. The authors are indebted to P. Alemany, J. J. Novoa, and P. Braunstein for enlightening discussions, to R. Rycroft for carefully reading the manuscript, and to F. Vilardell for part of the drawings. Financial support from DGICYT (Grant No. PB89-0268) is gratefully acknowledged.

Supplementary Material Available: Drawings of 35 fragmentation patterns for 23 molecules (9 pages). Ordering information is given on any current masthead page.

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On the Photodecomposition Mechanism of *o*-Diazonaphthoquinones

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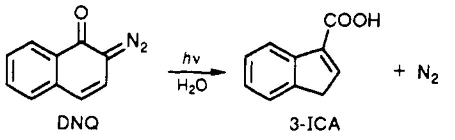
Abstract: The mechanism for the photodecomposition of several *o*-diazonaphthoquinones has been examined in acetonitrile solution using time-resolved laser flash photolysis techniques. It is concluded that the Wolff rearrangement, which involves the formation of a ketene intermediate, can be regarded as a concerted process in the nanosecond time scale. It is suggested that the reaction of the ketene with water, which is well known to yield 3-indenecarboxylic acids, involves the intermediacy of a ketene hydrate. Pyridine, a molecule frequently employed as a carbene trap/probe, efficiently traps the ketene in these systems; this scavenging reaction can be employed as a probe for the study of the dynamics of ketene reactions, but in some systems it may represent a problem in carbene studies if the possibility of ketene reactions is not considered.

Introduction

The phototransformation of 2-diazo-1,2-naphthoquinones (DNQs) into the corresponding 3-indenecarboxylic acids (3-ICAs) (eq 1) via the Wolff rearrangement has been widely studied and has numerous applications in photoresist technology.[4]

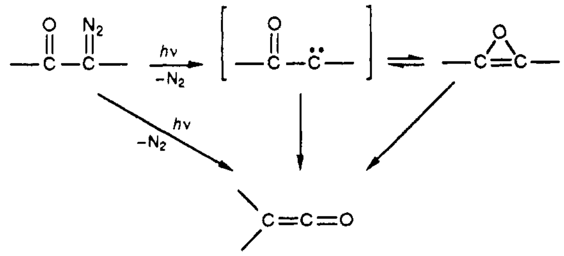


DNQ 3-ICA (1)

It is well known that the photodecomposition of DNQs produces an intermediate ketene, which upon reaction with water yields the corresponding 3-ICA. It has been suggested that in some cases a long-lived intermediate ketene (the transient decay time is of the order of seconds) can absorb another photon, leading to unwanted photochemistry, which in the photoresist field is usually referred to as a reciprocity failure.[5]

The conversion of *o*-diazo ketones into ketenes involves a 1,2 migration of a carbon atom, which is known as the Wolff rearrangement. Despite many investigations, the mechanism involved in this process is still being debated. The focus of the discussion is whether the loss of nitrogen and the 1,2 migration of the carbon atom occur in a concerted manner or the Wolff rearrangement is a two-step reaction which involves an α-keto carbene and/or an oxirene-like intermediate, as represented in Scheme I. On the basis of the studies already reported, one must point out that the mechanism will depend on the specific type of *o*-diazo ketone being studied.[6]

Scheme I



The mechanism for the photoconversion of DNQs into 3-ICAs in solution is a matter of some discussion and controversy. There have been different results on the number, sequence, and spectroscopic properties of the intermediates formed, such as the ketene.[7-12]

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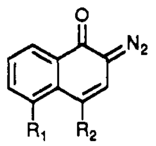
Chart I



R_1	R_2	abbrev
H	$SO_3C_6H_5$	DNQ-4Ph
$SO_3C_6H_5$	H	DNQ-5Ph
SO_3-*p*-$C_6H_4COCH_3$	H	DNQ-5Ac
SO_3-*p*-$C_6H_4COC_6H_5$	H	DNQ-5Bp

The present study was undertaken in an attempt to improve our understanding of the mechanism of the Wolff rearrangement. Thus, time-resolved laser flash photolysis techniques have been applied to the analysis of the photodecomposition mechanism of several *o*-diazonaphthoquinones in acetonitrile solutions. It is concluded that the Wolff rearrangement can be regarded as a concerted process in the nanosecond time scale. Our results, along with recent literature data,[13] provide strong evidence that a ketene hydrate, formed by hydrolysis of the ketene intermediate and yielding the final product, is involved.

As part of this work, we carried out experiments in the presence of pyridine in the hope that it would act as a carbene scavenger to yield an easily detectable ylide,[14,15] a technique developed by Platz, Liu, and co-workers, which has found many applications in carbene studies.[14,16-20] We find that in our system *the ketene, rather than the carbene, is trapped by pyridine.* This observation suggests the need for some control experiments when this valuable technique is used in carbene studies.

Experimental Section

Materials. Water was purified by passage through a Millipore Milli-Q system. Acetonitrile (Omnisolv), methanol (Omnisolv), and deuteriochloroform (MSD isotopes) were used as received. Pyridine (Anachemia) was dried with solid KOH followed by fractional distillation before use. 2-Adamantanethione was prepared as previously described.[21] The DNQ derivatives were synthesized according to standard procedures.[22,23] Triethylamine was added dropwise to a solution of the appropriate sulfonyl chloride and phenolic compound in THF. After the reaction was complete, the products were isolated by adding the reaction mixtures to water and filtering. Yields were in the 85–95% range. Structure and purity were confirmed by NMR and liquid chromatography.

Apparatus. UV-absorption spectra were obtained on an HP-8451A diode array spectrophotometer. GC/MS analyses were performed using a Hewlett-Packard Model 5995 system. ^1H and ^{13}C NMR spectra were recorded using a Varian 300-MHz and a Varian 200-MHz instrument, respectively.

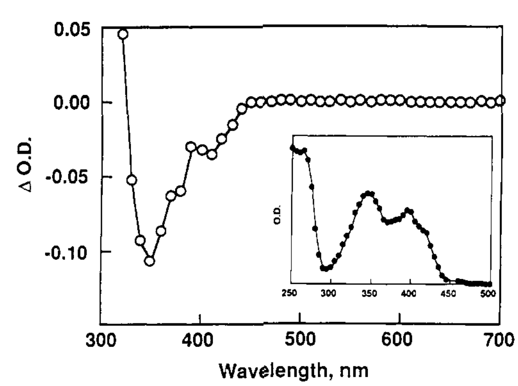


Figure 1. Transient absorption spectrum for DNQ-5Ph in ACN solution after 308-nm laser pulse. Inset: Absorption spectrum of the initial solution.

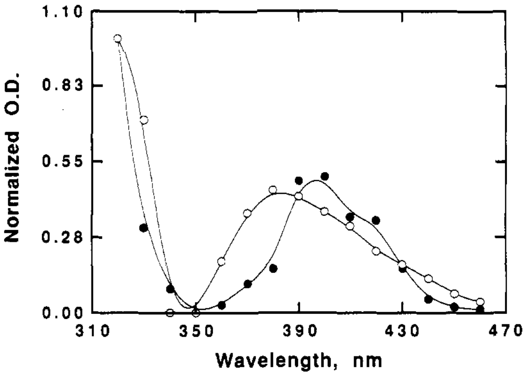


Figure 2. Calculated absorption spectra (normalized to zero at 350 nm) for the transients derived from DNQ-5Ph in ACN (●) and ACN/H_2O (1:1) (○) solutions.

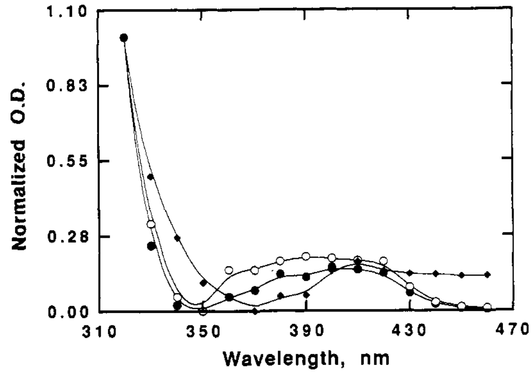


Figure 3. Calculated absorption spectra (normalized to zero at 350 nm) of transients in ACN solutions: DNQ-5Ac (●); DNQ-5Bp (○); DNQ-4Ph (◆).

Laser Flash Photolysis Studies. Since the samples readily deteriorate upon laser excitation, time-resolved measurements were performed using a flow system. The irradiation cell (built of 3 × 7 or 7 × 7 cm^2 Suprasil quartz) was connected with Teflon tubing to a reservoir where the solutions were deaerated by bubbling with oxygen-free nitrogen. The flow rate was adjusted to ensure the irradiation of a fresh portion of solution by each laser pulse. The laser flash photolysis system at NRC has been described earlier.[24,25] Excitation was achieved using either a Molectron UV-24 nitrogen laser (λ = 337 nm, ~10 ns, <10 mJ/pulse) or a Lumonics EX 510 excimer laser operated with Xe/HCl/He mixtures (λ = 308 nm, ~5 ns, <40 mJ/pulse). The solute concentrations were (0.8–2 × 10^{-4} M). All measurements were performed at room temperature.

Photodecomposition Product. Deaerated methanol/acetonitrile solutions ([MeOH] = 0.5–15 M) of DNQ-5Ph (2–6 mM) were irradiated in a "merry-go-round" apparatus with 9 RPR 3500-Å lamps or using a xenon lamp and a 395-nm cut-off filter. The solid photodecomposition product was obtained by solvent evaporation under reduced pressure at room temperature. This compound was characterized by GC/MS and ^1H and ^{13}C NMR spectroscopy. Mass spectrometry data: *m/z* (%) 330 (48, M^+), 237 (41), 173 (100), 143 (8), 114 (16). ^1H NMR ($CDCl_3$): δ 3.73 (d, 2 H, CH_2), 3.91 (s, 3 H, CH_3), 6.85–7.26 (m, 5 H, para-substituted ring), 7.49 (t, 1 H, H-5), 7.52 (t, 1 H, H-2), 7.68 (dd, 1 H, H-4), 8.36 (dd, 1 H, H-6). ^{13}C NMR ($CDCl_3$): 39.23 (C-1, methy-

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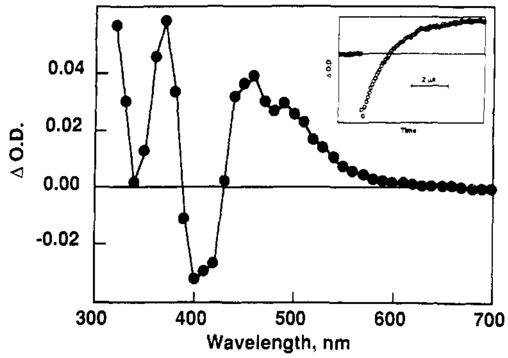

Figure 4. Transient absorption spectrum measured after 308-nm laser excitation of DNQ-5Ph in ACN containing 0.12 M pyridine. Inset: Growth of the transient absorption at 370 nm for a sample containing 0.65 mM pyridine.

lene-type carbon), 51.89 (CH_3), 163.76 (C=O).

Results

The *o*-diazonaphthoquinones used in this study are shown in Chart I. Our studies concentrate on DNQ-5Ph. We note that the rationale to prepare and examine some of the other substrates involved the introduction of groups that would facilitate singlet → triplet intersystem crossing, while retaining the basic features of typical photoacid generators employed in photoresist technology.

Figure 1 shows the transient absorption spectrum recorded within the first 500 ns after 308-nm laser excitation of DNQ-5Ph in acetonitrile solution. Besides bleaching between 330 and 450 nm, there is a long-lived absorption ($\tau \gg 100$ μs, longest time scale accessible) that shows no defined maximum in the wavelength range examined ($\lambda_{max} \leq 330$ nm). It should be noted that laser studies of this type lead to a difference (ΔOD) rather than an absolute spectrum. Thus, in order to estimate the net absorption spectrum of the transient, it was assumed that this species does not absorb at 350 nm (wavelength at which maximum bleaching is observed). A calculated spectrum due to a single bleaching reaction can then be obtained from the differential signals (ΔOD) observed and the known ground-state absorption spectrum of the original solution. The result of subtracting at each wavelength the ΔOD observed from the calculated value leads to an absorption spectrum having a band centered at ca. 400 nm and another more intense band below 320 nm (Figure 2). Similar behavior is observed with the other DNQs (Figure 3). We note that, while this approach is suitable to obtain approximate spectra for these transients, the technique is not suitable for kinetics studies.

Addition of water or methanol leads to the formation of new transient species. In the DNQ-5Ph/water system, the new species shows an absorption band centered at ca. 380 nm (Figure 2). We note that, while the spectra displayed are limited to wavelengths below 470 nm, no signals are detected between 470 and 700 nm.

Recent publications from this and other laboratories have shown that pyridine ylides can be employed as probes in carbene reactions.[14,21] Thus, given the possible existence of an α-carbene intermediate as a ketene precursor, pyridine was tested as a potential scavenger. The addition of pyridine to acetonitrile solutions of any of the DNQs studied here leads to a strong, readily detectable, and very long-lived absorption ($\tau \gg 100$ μs), which in the case of DNQ-5Ph shows λ_{max} at 370 nm and a shoulder at ca. 500 nm. The corresponding transient absorption spectrum and a trace showing its formation are shown in Figure 4. The inset shows that the bleaching of the precursor is followed by the formation of a pyridine ylide, which follows pseudo-first-order kinetics. The corresponding observed rate constants (k_{obsd}) are related to the rate constant for scavenging by pyridine (k_{Py}) according to eq 2, where τ_0 is the lifetime (in the absence of pyridine) of the intermediate being trapped.

$$k_{obsd} = \tau_0^{-1} + k_{Py}[\text{pyridine}] \qquad (2)$$

Figure 5 shows a plot according to eq 2 for DNQ-5Ph. From the slope of this plot, a k_{Py} value of 1.4×10^9 M^{-1} s^{-1} is obtained.

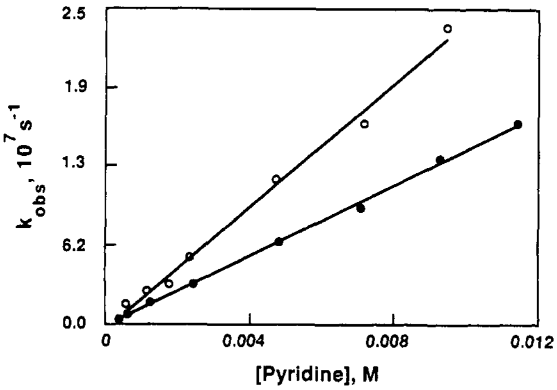

Figure 5. Observed rate constant for growth of the pyridine ylide derived from DNQ-4Ph (○) and DNQ-5Ph (●) in ACN as a function of pyridine concentration.

The intercept is very small and indicates that the intermediate being trapped is very long-lived. Following the reasoning of earlier carbene studies, we initially assumed that the species trapped was the carbene of Scheme I. In fact, when methanol was used as solvent, no pyridine ylide was observed. The lack of ylide formation was initially ascribed to an efficient scavenging of the carbene by methanol. However, further work (vide infra) demonstrated that this premature conclusion was incorrect.

2-Adamantanethione has also been shown to be a good carbene scavenger, yielding long-lived ylides with strong absorptions in the visible region.[21,26] However, no thiocarbonyl ylide could be detected with any of the DNQs. We had anticipated that if a long-lived carbene was involved, trapping by the thione would be straightforward.

Carbonyl oxides (Criegee intermediates) represent another group of easily detectable carbene-derived ylides.[27-30] However, attempts to detect carbonyl oxide formation by carbene trapping by oxygen also failed systematically. In fact, no oxygen effect could be observed on the reaction with pyridine. Thus, these results indicate that the pyridine-derived transient of Figure 4 is formed through a reaction with an intermediate which does not show typical carbene behavior. Despite this observation, it is still reasonable to assume that some kind of ylide is being formed (Figure 5). Using the strong signals due to the pyridine ylide as a probe, the reactions between the unidentified intermediate derived from DNQ-5Ph and water or methanol could be easily analyzed. In both cases, plots against the concentration of added substrate are nonlinear, but a quadratic plot leads to a straight line (Figure 6). Thus, the reaction follows second-order kinetics in water or methanol (eq 3, Figure 6), and the second-order rate constants (k_{ROH}) are 5.7×10^5 and 2.5×10^6 M^{-2} s^{-1} for water and methanol, respectively.

$$k_{obsd} = \tau_0^{-1} + k_{Py}[\text{pyridine}] + k_{ROH}[\text{ROH}]^2 \qquad R = H, CH_3 \qquad (3)$$

The corresponding rate constants for scavenging by pyridine and methanol of the intermediate derived from DNQ-4Ph in acetonitrile solutions are 2.44×10^9 M^{-1} s^{-1} and 7.1×10^6 M^{-2} s^{-1}, respectively, higher than those for DNQ-5Ph. We believe this reflects the fact that the electron-withdrawing sulfonic acid ester can decrease the electronic density at the carbonyl group more effectively in the case of DNQ substituted in the 4-position.

In order to obtain more information on the nature of the unidentified transient, product analyses were carried out for DNQ-5Ph in acetonitrile/methanol solutions after continuous irradiation

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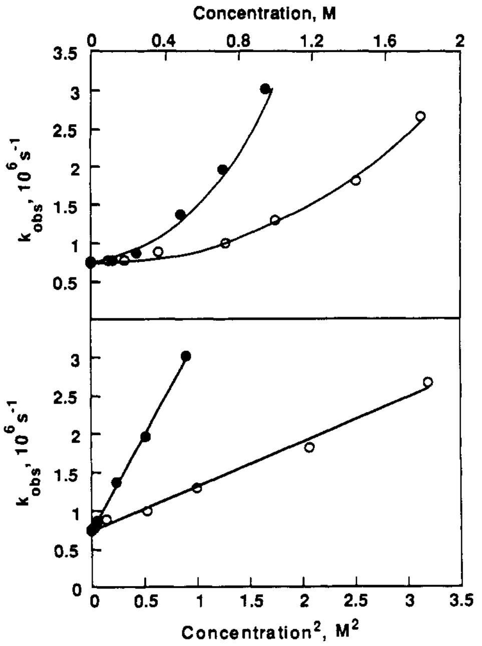
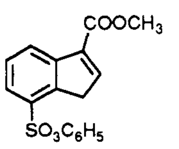


Figure 6. Observed rate constants for growth of the pyridine ylide derived from DNQ-5Ph in ACN as a function of both methanol (●) and water (○) concentration (top) and square concentration (bottom). [Pyridine] = 0.64 mM.

at 350 nm or λ > 395 nm. One product was almost exclusively formed, and it was identified as being the ester expected from the reaction between an intermediate ketene and methanol (**1**). The product of carbene trapping by methanol (**2**) could not be detected.



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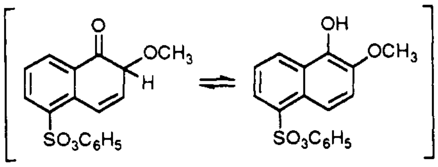


2

Discussion

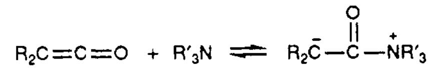
As already mentioned, the mechanism for the photoconversion of DNQs into the corresponding 3-ICAs in solution is a matter of some controversy.

Using nanosecond laser flash photolysis, Tanigaki and Ebbesen describe the involvement of two transients: the first is assigned to an oxirene-like intermediate and the second long-lived one to the ketene.[9,10] Their assignment of the chemical structures was based upon kinetic and thermodynamic results, and they did not discuss their results in the context of earlier work that ruled out the involvement of oxirene-like intermediates on the basis of labeling experiments.[31,32] On the basis of IR spectroscopy of novolak films at 77 K, Rosenfeld et al. have recently shown that the first transient is indeed the ketene.[33]

Delaire et al.[8] and Shibata et al.[11,12] also describe the involvement of two transients. These authors assign the first transient to the ketene (no evidence is found for a ketene precursor in any case), but the assignment of the long-lived second one, which yields the final product, is different. Delaire et al. find that the reaction between the ketene and water follows second-order kinetics in water (k_{H_2O} = 8.1 × 10^6 M^{-2} s^{-1}) in nonprotic solvents, and they assign the second transient to a cyclic hydrogen-bonded ketene–water complex formed of one molecule of ketene and two molecules of water. Shibata et al.[11,12] also find that the reaction between the ketene and water in dioxane is not first-order in water. However, no analysis of higher order kinetics was attempted, and the nonlinear dependence was attributed to a solvent effect. These authors assign the second transient to a ketene hydrate, which yields the corresponding 3-ICA through an acid-catalyzed process, and show that the formation of the proposed ketene hydrate occurs with a lifetime of 0.3 μs in water (which agrees with the lifetimes measured by Tanigaki and Ebbesen[9,10]). Therefore, the ketene–water complex suggested by Delaire et al.[8] is unlikely, since water solvation should occur in much shorter time scales. On the other hand, the ketene hydrate has been reported as a probable intermediate in the hydrolysis of ketenes.[34] In a very recent publication, Urwyler and Wirz[13] also propose the intermediacy of a ketene hydrate in the photolysis of 1,2-benzoquinone diazide; interestingly, the first pK_a of the hydrate is 1.31.

On the basis of the absence of HO-insertion products (a characteristic carbene reaction) and the failure to detect thiocarbonyl ylide and carbonyl oxide formation, we conclude that α-keto carbenes with lifetimes exceeding a few nanoseconds are not involved as ketene precursors. It follows that the Wolff rearrangement in the phototransformation of DNQs is likely to be a concerted process, an observation that agrees with a theoretical study based on semiempirical MINDO/3 molecular orbital calculations for 1,2-benzoquinone diazide, which shows that the Wolff rearrangement takes place simultaneously with the loss of nitrogen.[35]

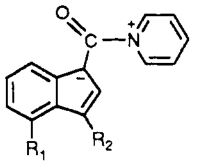
The long-lived transient monitored in acetonitrile solutions is therefore assigned to the ketene. This intermediate is able to react with pyridine, yielding a long-lived ylide. This proposal agrees



$$R_2C{=}C{=}O + R'_3N \rightleftharpoons R_2\overset{-}{C}-\overset{\overset{O}{\|}}{C}-\overset{+}{N}R'_3 \qquad (4)$$

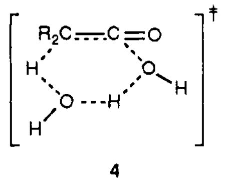
with the fact that tertiary amines have been found to catalyze the dimerization of ketenes, presumably through a pathway such as that shown in eq 4.[36]

In our case, the ylide (**3**) would be highly stabilized by resonance.



3

The ketene intermediate reacts with water or methanol in acetonitrile solutions with a second-order dependence in water or methanol to yield an intermediate addition compound. The reaction of ketenes with water or alcohols in nonprotic solvents usually involves the participation of water or alcohol polymers, most frequently dimers.[36] One of the proposed transition states for this reaction is a cyclic one, represented, in the case of reaction with water, by **4**.[37]



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However, **4** will lead directly to the indenecarboxylic acid and not to an intermediate species. Another proposed transition state is **5**, which in this case could lead to the ketene hydrate. Interestingly, a recent theoretical study[38] suggests that the reaction

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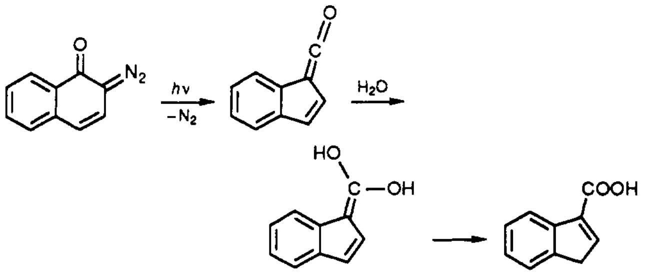
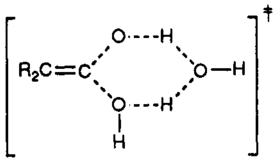
Scheme II



of the ketene with water may involve the dimer of water, a proposal that would be consistent with our experimental observations.



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Thus, the mechanism for the phototransformation of DNQs into 3-ICAs can be represented as shown in Scheme II.

Rosenfeld et al. have carried out, for the first time, time-resolved laser flash photolysis experiments (at room and low temperatures) using both commercial resists and model compounds under lithographic conditions.[33] The mechanism proposed agrees with Scheme II, except for the fact that for the systems based on DNQs substituted in the 5-position, at room temperature, a ketene precursor is observed. It was ascribed to an oxirene-like intermediate on the basis of thermodynamic considerations derived from *o*-diazo ketones. However, no explanation was offered to account for the labeling experiments using *o*-diazonaphthoquinones.[31,32] We note that Rosenfeld's results[33] agree entirely with our observations in solution; only in the case of films is a ketene precursor proposed.

Tanigaki and Ebbesen have measured negative entropies of activation for the conversion of the first transient into the second one,[10] a process which according to Scheme II would correspond to the conversion of the ketene into the ketene hydrate. This observation agrees with the negative entropies of activation found for the reaction between arylmethylketenes and α-arylethanol; the mechanism is postulated to involve an intermediate addition compound structurally equivalent to the ketene hydrate.[39]

The order of reactivity observed in acetonitrile solutions in the reaction between the ketene and water or methanol (MeOH > H_2O) parallels the relative nucleophilicities of these two reagents. It has been reported that only one transient is observed in methanol solutions,[10] and according to Scheme II this species would be the intermediate addition compound. This observation agrees with our results that no pyridine ylide is formed when methanol is used as solvent.

In conclusion, the transient ascribed to the ketene hydrate has been shown to have a decay time of the order of milliseconds in solution[8-12] and of seconds in films.[33] It follows that this would be the absorbing species responsible for the reciprocity failure.[5] No evidence for a carbene intermediate could be obtained either by direct spectroscopy or by use of a variety of efficient probes (e.g., oxygen and thioketones); thus, if a carbene is involved, it must have subnanosecond lifetimes or, more likely, the Wolff rearrangement is a concerted process. Pyridine, which has been widely employed as a carbene probe, should be used with some caution, since under some experimental conditions ketene-trapping can also lead to ylides with similar spectral characteristics.

Acknowledgment. Thanks are due to Mr. S. E. Sugamori and G. Charette for technical assistance and to Dr. R. Redmond for valuable discussions.

Registry No. **3** (isomer 1), 138924-04-6; **3** (isomer 2), 138924-05-7; DNQ-4Ph, 110673-14-8; DNQ-5Ph, 23295-00-3; DNQ-5Ac, 138924-03-5; DNQ-5Bp, 63669-79-4; pyridine, 110-86-1.

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(39) Jahme, J.; Ruchardt, C. *Tetrahedron Lett.* **1982**, *23*, 4011–4014.