methyl-*S*-phenylsulfoximine was obtained as an oil. Butyl phenyl sulfide, bp 125–130 °C (3 mm), was oxidized to the sulfoxide with hydrogen peroxide. The sulfoxide was converted to the oily sulfoximine by hydrazoic acid. The sulfoximine was methylated using formaldehyde and formic acid using the procedure described above.

***S*-Cyclohexyl-*N*-methyl-*S*-phenylsulfoximine** (**8**).[20] Cyclohexyl phenyl sulfide, bp 117–120 °C (1.5 mm), was prepared in 50% yield by the reaction of sodium thiophenoxide with bromocyclohexane. Periodate oxidation of the sulfide gave cyclohexyl phenyl sulfoxide, mp 63–65 °C, in 89% yield. Reaction of the sulfoxide with mesitylsulfonyloxyamine gave *S*-cyclohexyl-*S*-phenylsulfoximine, mp 74–75 °C, in 65% yield. The sulfoximine was methylated with trimethyloxonium fluoroborate in the presence of sodium carbonate to give **8** in 80% yield as a viscous oil.

Acknowledgments. This work was supported by a grant from the National Science Foundation. We thank Dr. James Shanklin for suggestions and assistance with the early stages of this work.

Supplementary Material Available: Analytical and spectral data (8 pages). Ordering information is given on any current masthead page.

References and Notes

(1) A. Maercker, *Org. React.*, **14**, 270 (1965).
(2) B. M. Trost and L. S. Melvin, Jr., "Sulfur Ylides", Academic Press, New York, 1975; E. Block, "Reactions of Organosulfur Compounds", Academic Press, New York, 1978.
(3) E. J. Corey and T. Durst, *J. Am. Chem. Soc.*, **88**, 5656 (1966).
(4) F. Jung, N. K. Sharma, and T. Durst, *J. Am. Chem. Soc.*, **95**, 3420 (1973).
(5) R. M. Coates and R. L. Sowerby, *J. Am. Chem. Soc.*, **94**, 4758 (1972).
(6) T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, 2807 (1978).
(7) T. Mukaiyama and M. Hayashi, *Chem. Lett.*, 15 (1974).
(8) M. Julia and J. M. Paris, *Tetrahedron Lett.*, 4833 (1973).
(9) M. Julia, personal communication.
(10) B. Lythgoe and I. Waterhouse, *Tetrahedron Lett.*, 4223 (1977).
(11) A. G. M. Barrett, D. H. R. Barton, R. Bielski, and S. W. McCombie, *J. Chem. Soc., Chem. Commun.*, 866 (1977).
(12) (a) C. R. Johnson, *Acc. Chem. Res.*, **6**, 341 (1973); (b) C. R. Johnson, J. R. Shanklin, and R. A. Kirchhoff, *J. Am. Chem. Soc.*, **95**, 6462 (1973).
(13) (a) C. W. Schroeck and C. R. Johnson, *J. Am. Chem. Soc.*, **93**, 5305 (1971); (b) C. R. Johnson, C. W. Schroeck, and J. R. Shanklin, *ibid.*, **95**, 7424 (1973).
(14) H. Hoffmann, *Arch. Pharm. (Weinheim, Ger.)*, **306**, 567 (1973).
(15) A. Schriesheim, R. J. Muller, and C. A. Rowe, Jr., *J. Am. Chem. Soc.*, **84**, 3164 (1962).
(16) T. F. Corbin, R. C. Hahn, and H. Shechter, *Org. Synth.*, **44**, 30 (1964).
(17) T. Shono, Y. Matsumura, S. Kashimura, and H. Kyutoku, *Tetrahedron Lett.*, 1205 (1978).
(18) H. O. House and R. S. Ro, *J. Am. Chem. Soc.*, **80**, 182 (1958); J. K. Kochi and D. M. Singleton, *ibid.*, **90**, 1582 (1968).
(19) J. K. Kochi and D. M. Singleton, *J. Am. Chem. Soc.*, **90**, 1582 (1968).
(20) C. R. Johnson and H. G. Corkins, *J. Org. Chem.*, **43**, 4136 (1978).

Excited-State Chemistry of 1-Alkenyl-2-pyridones. Exploratory and Mechanistic Investigations and Kinetic Analysis of Photocyclization Reactions Involving Conversion of the *N*-Vinylamide to Oxazolium Ylide Function[1]

Patrick S. Mariano*[2] and Andrea A. Leone

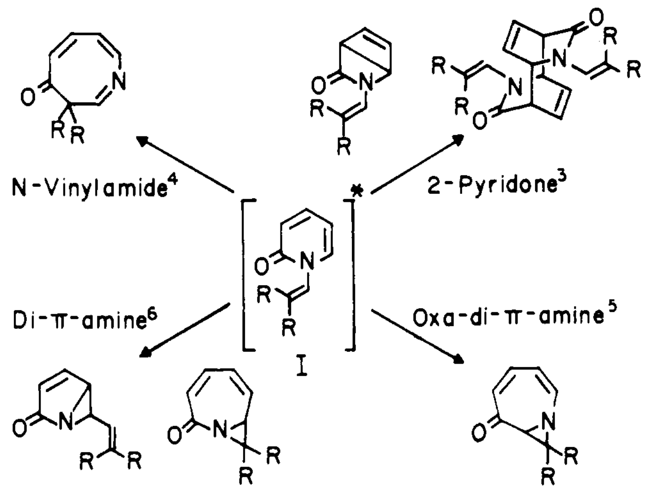
Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843. *Received August 13, 1978*

Abstract: The excited-state chemistry of 1-alkenyl-2-pyridones has been subjected to detailed study. The isobutenyl- (**1**) and propenyl- (**2**) 2-pyridones undergo the familiar Dewar-pyridone forming electrocyclization and $_\pi4 + _\pi4$ dimerization when irradiated in solvents of low polarity. The nature of pathways followed by these systems changes when reactions are conducted in polar solvents such as methanol and water. Under these conditions electrocyclization of the *N*-vinylamide occurs to generate eventually the pyridonylethanol derivatives **7** and **8** from singlet excited alkenylpyridones. Irradiations of aqueous solutions of **1** and **2** containing perchloric acid lead to production of the oxazolo[3,2-*a*]pyridinium perchlorates (**9** and **10**). Information has been accumulated to support mechanisms for these processes involving initial generation of azomethine ylides **28**, which are trapped by water or hydronium ion to give oxazolopyridinium salts. The hydroxide salts produced by proton transfer from water are then transformed under mild workup conditions to the corresponding pyridonylethanols. Detailed kinetic analysis of the singlet reaction and decay pathways for the isobutenyl-2-pyridone has been performed using a variety of photochemical and photophysical techniques. This has yielded individual rate constants for singlet-pyridone conversion to Dewar pyridone and pyridinium ylide, singlet decay and emission, and ylide trapping by water and return to ground-state pyridone. The interesting solvent polarity dependence of the nature of photochemical reaction pathways followed by the 1-alkenyl-2-pyridones has been explored using measured singlet lifetimes, fluorescence efficiencies, and reaction quantum yields and interpreted in terms of a dramatic effect of solvent polarity on rate constants for conversion of singlet 1-alkenyl-2-pyridones to the dipolar, azomethine ylides. Solvent polarity effects on singlet lifetimes of a number of systems containing *N*-vinylamide and related divinylamine chromophores have been noted. Lastly, the effect of alkyl substitution on 1-alkenyl-2-pyridone cyclization efficiency is discussed in terms of ground and singlet excited state conformational control.

Photochemical investigations of systems containing more than one potentially reactive chromophore have uncovered a wealth of information about the physical and chemical characteristics of excited states of organic substances. As a result, organic materials containing numbers of different photochemically reactive groupings continue to serve as appealing targets for ongoing explorations. An analysis of one such system, the 1-alkenyl-2-pyridones (**1**), reveals the potential for diverse types of photochemical behavior due to the presence of the pyridone,[3] 1-vinylamide,[4] oxadi-π-amine,[5] and di-π-amine[6,7] chromophores. Indeed, the excited-state chemistry of systems containing each of these moieties either has been

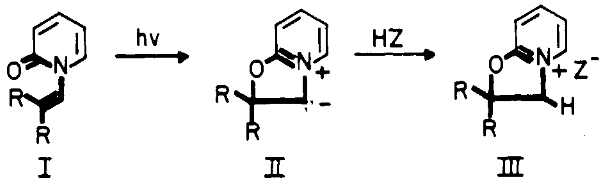
0002-7863/79/1501-3607$01.00/0

Chart I



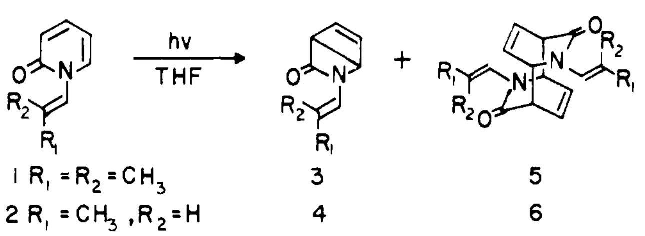
well explored or can be speculated about on the basis of analogy. Thus, one might conceive of the pathways outlined in Chart I as being potentially available to excited states of 1-alkenyl-2-pyridones. As a result of this interesting feature and the potential synthetic importance of these possible reactions, an exploration of the excited-state chemistry of 1-alkenyl-2-pyridones was initiated.

Our investigations of 1-alkenyl-2-pyridones have led quite unexpectedly to the unveiling of a new photochemical reaction involving the *N*-vinylamide grouping. This report describes the complete details of our studies in this area which have shown that (1) 1-alkenyl-2-pyridones (I) undergo a novel photocyclization reaction to produce oxazolopyridinium ylides (II), (2) the rate constant for photocyclization of I is strongly dependent on solvent polarity, and (3) trapping of ylides II by acid or water leads to production of cyclization products (III).

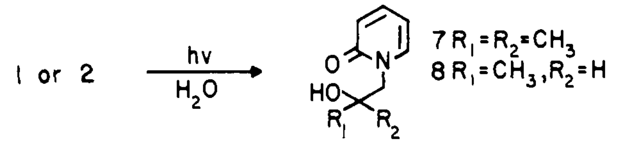


Results

Preparative Photochemistry. Irradiations of solutions of 1-(2-methyl-1-propenyl)-2-pyridone (**1**)[8] and 1-(1-*trans*-propenyl)-2-pyridone (**2**)[8] in a variety of nonpolar organic solvents including tetrahydrofuran and benzene led to clean production of the isobutenyl and *trans*-propenyl Dewar pyridones (**3** and **4**) and crystalline [4 + 4] dimers (**5** and **6**). The Dewar pyridone to [4 + 4] dimer product ratio, as expected, was found to be dependent upon the concentration of starting alkenylpyridone; maximal yields of ca. 60–80% for **3** and **4** were obtained using concentrations of **1** and **2** of ca. 4 mM while those for the [4 + 4] dimers were ca. 30% starting with alkenylpyridone concentrations of ca. 30–50 mM. Comparisons of the spectroscopic properties of the alkenyl Dewar pyridones and [4 + 4] dimers with those recorded for the analogous substances derived from irradiations of 1-methylpyridone[9] made structural assignments simple. Lastly, low-conversion irradiation of the *trans*-propenylpyridone **2** in these solvents results in cis–trans isomerization.[8] However, none of the corresponding Dewar pyridone or [4 + 4] dimer products from **2** have the cis configuration about the exocyclic propenyl π bond.

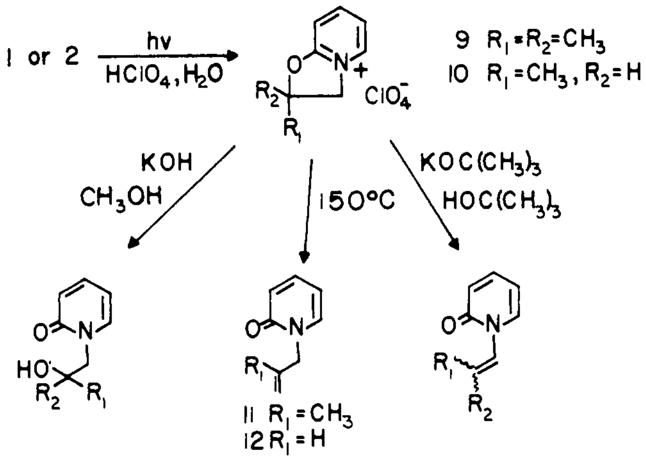


The photochemistry of **1** and **2** is markedly altered when irradiations are conducted using water or wet methanol as solvent. Accordingly, both **1** and **2** are transformed in a reasonably efficient (ca. 40–80%) manner to their corresponding 1-(2-pyridonyl)ethanol derivatives **7** and **8** when irradiated in water using Pyrex-filtered light. Characterization of the alcohol photoproducts was made by comparison of accumulated physical and spectroscopic data with those for authentic samples previously prepared[8] by sodium borohydride reduction of or methyllithium addition to 1-acetonyl-2-pyridone.



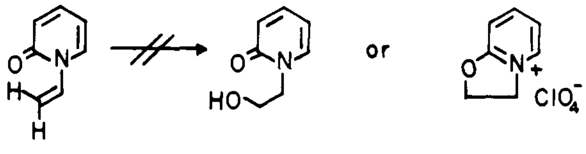
Interesting changes are noted when the courses of the aqueous solution photoreactions of **1** and **2** are monitored using UV spectrophotometric methods. Shifts in the UV maxima of the respective photolysates derived from **1** and **2** were as follows: 309 and 302 nm before irradiation, 288 and 287 nm immediately after irradiation, and 305 and 303 nm after concentration in vacuo. In addition, the long-wavelength shifts in absorption maxima detected when the crude photolysates were concentrated could be induced by the addition of excess potassium hydroxide. These observations suggest that the initial photochemical step of each reaction leads to generation of a short wavelength absorbing intermediate which is converted to alcohol in a secondary dark reaction occurring during the room temperature concentration process and, possibly, involving hydroxide ion. An understanding of these observations was gained when irradiations of **1** and **2** were performed on aqueous solutions containing sixfold molar excesses of perchloric acid. Under these conditions, 45–50% yields of two crystalline salts were obtained by chloroform trituration of the concentrated photolysates. These substances were shown to have physical and chemical properties consistent with their assignment as 5,5-dimethyl- and 5-methyloxazolo[3,2-*a*]-pyridinium perchlorates, **9** (UV max 285 nm) and **10** (UV max 284 nm), respectively. Identical materials could be generated by irradiation of **1** and **2** in aqueous formic acid followed by perchlorate ion exchange using Dowex 1-X8.

Further supportive evidence for the structural assignments of the salts **9** and **10** was gained using chemical methods. Reaction of **9** and **10** in methanolic potassium hydroxide at room temperature led to smooth production of the pyridonylethanol derivatives **7** and **8**. Thermolyses of the pyridinium perchlorate



salts at >150 °C led to rapid generation of the known[8] methallyl- and allylpyridones **11** and **12**. Lastly, both **9** and **10** were efficiently converted to the 1-alkenyl-2-pyridones, **1** and **2** (mixture of cis and trans isomers), when stirred with potassium *tert*-butoxide in *tert*-butyl alcohol.

Dark control reactions of the alkenylpyridones **1** and **2** were attempted using conditions which mimic those present during the photochemical reactions in water or aqueous acid. In no cases were the pyridonylethanol derivatives or pyridinium perchlorates detected and unreacted starting materials were recovered quantitatively. In addition, irradiations of 1-vinyl-2-pyridone (**13**),[10] using conditions found to be ideal for photoconversion of **1** and **2**, did not produce isolable quantities of 1-(2-pyridonyl)ethanol (**14**) or the oxazolo[3,2-*a*]pyridinium salt **15**.

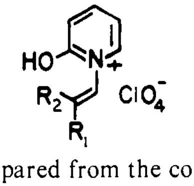


13 14 15

Mechanistic Aspects. Triplet photosensitized reactions of isobutenylpyridone **1** were attempted using xanthone (E_T = 74.2 kcal/mol)[11a] and Michler's ketone (E_T = 60 kcal/mol)[11a] as sensitizers in wet methanol as solvent and employing conditions which guaranteed light absorption by the sensitizer and high triplet energy transfer efficiencies. In each case, unreacted starting material was quantitatively recovered. It is certain that energy transfer from triplet xanthone to **1** was occurring, since results from parallel irradiations of methanolic solutions of xanthone and **1**, and xanthone alone, indicated the ability of **1** to quench the familiar xanthone triplet photoreduction reaction.[11b]

Additional information necessary to assign the singlet as the reactive 1-alkenyl-2-pyridone excited state undergoing photocyclization and alcohol production was gained from quenching studies using 2,5-dimethyl-2,4-hexadiene, a known singlet quencher.[12a] Photoreactions of **1** in methanolic acetonitrile solutions containing this diene in concentrations ranging from 0 to 0.5 M were conducted under simultaneous irradiation conditions. A plot of the ratio of unquenched to quenched relative quantum yields for alcohol **3** production (ϕ_{r_0}/ϕ_{r_q}) vs. diene concentration gave a straight line with slope (1.9 M^{-1} with σ = 0.89) approximately equal to those obtained from plots of corresponding unquenched to quenched fluorescence quantum yield (2.1 M^{-1} with σ = 0.95) and singlet lifetime ratios (2.1 M^{-1} with σ = 0.99) (see Figure 1).[12b]

In an attempt to further explore the mechanistic details of the novel photochemical reactions observed, the 1-alkenyl-2-hydroxypyridinium perchlorates, **16** and **17**, were independently prepared from the corresponding pyridones by treatment with perchloric acid. Irradiation of aqueous methanolic solutions of **16** and **17**, containing 0.54 M perchloric acid to ensure >99% of the pyridinium salt form, led to complete consumption of these substances. However, none of the corresponding oxazolo[3,2-*a*]pyridinium salts was formed in either case. Likewise, the methallyl- and allylpyridones, **11** and **12**, remained unreacted when irradiated in water for time periods which would have led to complete reaction of **1** and **2**.



16 $R_1 = R_2 = CH_3$
17 $R_1 = CH_3, R_2 = H$

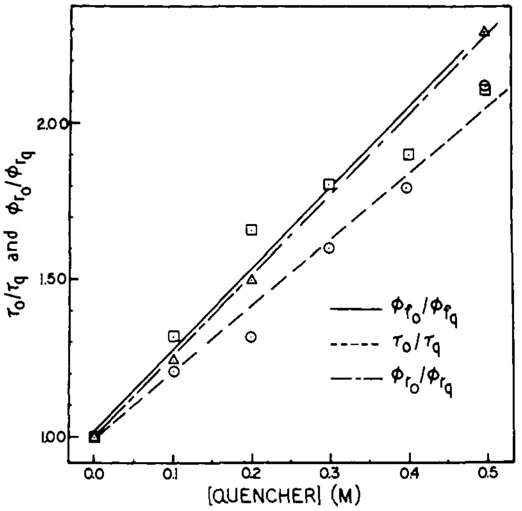


Figure 1. Quenching of the fluorescence lifetime and photohydration reaction of 1-(2-methyl-1-propenyl)-2-pyridone by 2,5-dimethyl-2,4-hexadiene. Plotted are the ratios of unquenched to quenched singlet lifetimes (○), fluorescence quantum yields (□), and reaction quantum yields (△) vs. quencher concentration.

On the basis of the results presented thus far, it is possible to conclude that the singlet transformations to pyridonyl alcohols and oxazolopyridinium salts require that the starting pyridone contain an *N*-vinylamide grouping. An important exception to this is the parent 1-vinylpyridone which is lacking alkyl substitution at the terminal carbon of the exocyclic vinyl grouping. In order to clarify the apparent critical role played by alkyl substituents, information about the relative efficiencies for reaction of the *cis*- and *trans*-propenylpyridones was sought. This turned out to be quite difficult owing to the competitive cis-trans isomerization process which efficiently interconverts both isomers. However, qualitative evidence obtained from varying conversion and competitive irradiation experiments seems to indicate that transformation of the cis isomer to alcohol **8** is slightly more efficient than that of the trans isomer.

Lastly, the divergent photochemical behavior of the 1-alkenyl-2-pyridones in nonpolar organic solvents as compared to methanol and water required closer inspection. Dewar pyridone **3** and alcohol **7** production from fixed-time irradiations of **1** were monitored as a function of the amounts of water in the tetrahydrofuran solutions used. The data obtained from these experiments, plotted in Figure 2, clearly shows that the efficiency of alcohol production increases at the expense of Dewar pyridone as the percentage of water in the aqueous tetrahydrofuran solvent is increased. In addition, the quantum efficiency for production of Dewar pyridone **3** from isobutenylpyridone **1** was found to decrease dramatically as solvent polarity increases (Table I).

Quantitative Photochemical and Photophysical Data. Quantum efficiencies (ϕ_r) for alcohol **7** and pyridinium salt **9** production from isobutenylpyridone **1** were measured using a "linear optical bench" apparatus and potassium ferrioxalate actinometry.[13] Necessary precautions were taken to prevent singlet self-quenching and secondary reactions of the products (conversions of 8-18%), to ensure that all light is captured by actinometer or photoreaction substrate, and to guarantee that the filter solutions used to isolate desired wavelength regions remained transparent throughout irradiations. Product analyses for reactions conducted in aqueous acetonitrile solutions were performed on the crude photolysate after concentration in vacuo, while those performed in aqueous perchloric acid reactions required prior treatment of the crude photolysate with stoichiometric amounts of potassium hydroxide. This latter procedure was employed to convert quantitatively the

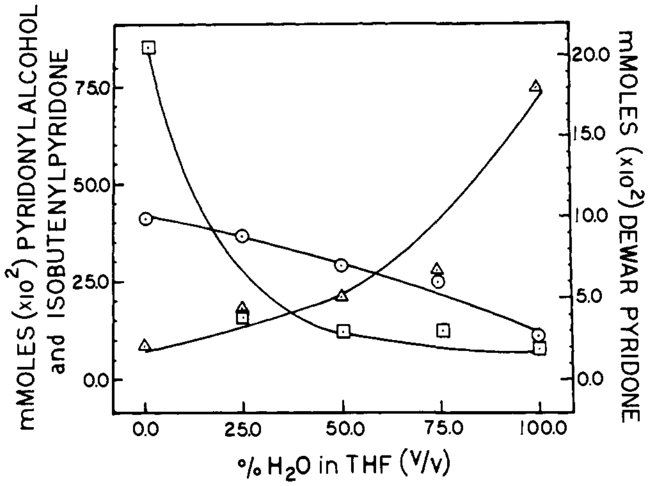


Figure 2. The relative efficiencies for formation of isobutenyl Dewar pyridone (■) and 1-pyridonyl-2-methyl-2-propanol (▲) and disappearance of isobutenyl-2-pyridone as a function of water concentration in aqueous tetrahydrofuran solutions.

Table I. Quantum Yields and Rate Constants (25 °C) for Dewar Pyridone Formation from 1-Isobutenyl-2-pyridone in Solvents of Varying Polarity

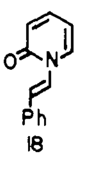
solvent[a]	solvent E_T value[b]	ϕ_{DP} $1 \rightarrow 3$	τ, ns[c]	k_{DP} (25 °C), s^{-1}
CH_3OH	37.4	0.061	7.3 ± 1.0	8.36×10^6
CH_3CN	46.0	0.143	16.6	8.61×10^6
THF	55.5	0.260	30.0	8.67×10^6

[a] Solvents were rendered anhydrous by rigorous drying and distillation prior to use. [b] E_T values are those given by K. Dimroth et al., *Justus Liebigs Ann. Chem.*, **661**, 1 (1962). [c] Degassed, nitrogen-purged solutions were used at 25 °C.

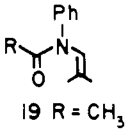
primary photoproduct, oxazolopyridinium perchlorate **9**, to the more easily analyzed alcohol **7**. The data obtained from irradiations of **1** in solvents containing varying water and perchloric acid concentrations (Table II) show that ϕ_r increases dramatically as either water or acid concentrations increase (see also Figure 3).

In order to examine the source of these changes, fluorescence quantum yields (ϕ_f) and singlet lifetimes (τ) for **1** were measured under conditions identical with those employed for the ϕ_r determinations. ϕ_f and τ were found to be dependent upon $[H_2O]$ but to be invariant with changes in $[H_3O^+]$ (Table II). In addition, through the use of this data it is possible to calculate the rate constant for fluorescence of **1** ($k_f = \phi_f/\tau$).

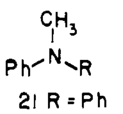
The changes noted in ϕ_f as a function of $[H_2O]$ appeared interesting and worthy of further exploration. Accordingly, the fluorescence efficiencies of **1**, in a variety of single-component solvents (Table III), and ethanol-water mixtures of differing polarity (Table IV), were recorded. This data reveals a clear inverse dependence of ϕ_f on solvent polarity. In order to test the generality of this phenomenon and to probe for its source, singlet lifetimes of a number of 1-alkenyl-2-pyridones (**2**-*cis*, **2**-*trans*, **13**, **18**[14]) and related methallylpyridone (**11**), along with a variety of substances containing the isoelectronic *N*-vinylamide (**19** and **20**)[15] and di-π-amine (**21** and **22**[16]) chromophores, were measured in water, 1:1 water-acetonitrile, and acetonitrile solutions (Table V).



18



19 R = CH_3
20 R = Ph



21 R = Ph
22 R = 1-cyclohexenyl

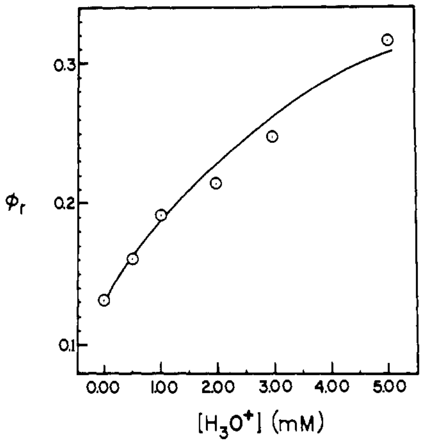
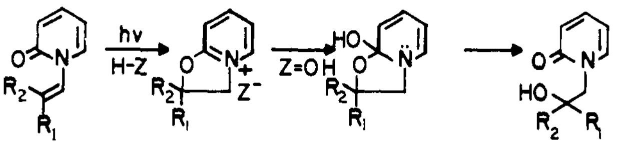


Figure 3. Quantum efficiency for production of 5,5-dimethyloxazolo[3,2-*a*]pyridinium perchlorate as a function of hydronium ion concentration from irradiation of 1-(2-methyl-1-propenyl)-2-pyridone in aqueous perchloric acid solutions.

Discussion

Mechanistic Features. Several possible mechanisms can be envisaged to rationalize the photochemical reactivity of 1-alkenyl-2-pyridones in polar protic solvents. It appears almost certain that the initial photoproducts from irradiations of **1** and **2** under these conditions are oxazolo[3,2-*a*]pyridinium salts. When produced in acid solution, these salts (**9** and **10**) possessing the nonnucleophilic perchlorate counterion are sufficiently stable to survive isolation and purification. The primary photoproducts produced from reactions of **1** and **2** in water have UV spectroscopic characteristics indicative of cyclized pyridinium salt structures **23** and most probably contain hydroxide as the counterion (Z = OH). The secondary dark reactions leading to the pyridonylethanol products, occurring upon concentration of or by addition of hydroxide to solution containing the pyridinium salts **23**, most probably involve nucleophilic attack at the pyridinium C-2 position followed by uncoupling of the hemiketal linkage in the transient dihydropyridine **24**.



23 24

The more important mechanistic question, however, concerns the nature of the pathway(s) used by singlet 1-alkenyl-2-pyridones for transformation to oxazolopyridinium salts. Simple photohydration[17] of the exocyclic vinyl groupings in **1** and **2** followed by dehydrative cyclization appears an unlikely possibility since the pyridonyl alcohols **7** and **8** show no tendency to cyclize to the pyridinium salts in aqueous or dilute acid solutions used for the photoreactions.

Another mechanism, worthy of more serious consideration, finds analogy in the results of studies by Schmid[18] and Horspool[19] of the photocyclization reactions of *o*-allylphenols to benzodihydrofurans. These transformations are most probably due to the enhanced facilities for intramolecular proton transfer in the excited-state manifold of the allylphenols. Accordingly, oxazolopyridinium salts may arise from analogous pathways involving intramolecular proton transfer in initially formed singlet excited hydroxypyridinium salts followed by

Table II. Experimental and Calculated Photophysical and Photochemical Properties of 1-Isobutenyl-2-pyridone

water concn,[a] M	$HClO_4$ concn, mM	singlet lifetimes, τ,[b] ns	fluorescence quantum yields,[c] ϕ_f	Reaction quantum yields,[d] ϕ_r	fluorescence rate constants k_f, s^{-1}
27.7	0	10.3 ± 1.0	0.007 ± 0.001	0.071	7×10^5
50.0	0	6.5 ± 1.0	0.004	0.110	6×10^5
55.6	0	5.1 ± 1.0	0.003	0.130	6×10^5
55.6	0.50			0.160	
55.6	1.00			0.190	
55.6	2.00			0.213	
55.6	3.00			0.248	
55.6	5.00	5.1 ± 1.0	0.003	0.315	6×10^5

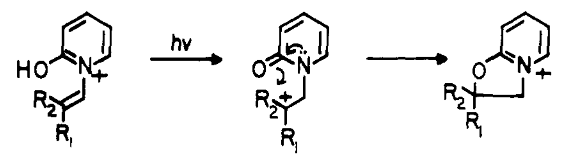
[a] Acetonitrile was used as cosolvent for solutions containing less than 55.6 M water. [b] Singlet lifetimes were measured using degassed, nitrogen-purged solutions at room temperature with a single photon counting nanosecond spectrofluorimeter based on ORTEC components. Values for τ were calculated by a digital RX-01 computer using the method of moments program. [c] Fluorescence quantum yields were measured using degassed, nitrogen-purged solutions at room temperature with a Spex-Fluorolog in the E/R mode. Benzene and naphthalene were used as fluorescence standards for ϕ_f determinations. [d] Reaction quantum yields were measured for product production using degassed, nitrogen-purged solutions and an optical bench apparatus. Light output was determined using potassium ferrioxalate actinometry. Alcohol product analysis was performed by GLC using internal standards. The pyridinium salts obtained from irradiation of acid solutions were first converted to alcohol by treatment with base before analysis. Conversions to product were in the range of 11-17%. Estimated error for ϕ_r measurements is 5%. Irradiations of aqueous solutions of the isobutenylpyridone in the absence of acid lead directly to the pyridonyl alcohol.

Table III. Fluorescence Quantum Yields for 1-Isobutenyl-2-pyridone in Single Component Solvents of Varying Polarity

fluorescence quantum yields, ϕ_f[a]	solvent	solvent Z value[b]
0.003	H_2O	94.6
0.017	EtOH	79.6
0.024	DMF	68.5
0.031	Me_2SO	71.1

[a] Solutions used for these measurements were degassed and nitrogen purged. Benzene and naphthalene were used as fluorescence standards. Estimated errors are ±0.001. [b] Z values for solvents are those reported by E. M. Kosower, *J. Am. Chem. Soc.*, **80,** 3253 (1958).

rapid cyclization of the intermediate pyridonylethyl cations **25.** Although this mechanism appears attractive since it nicely serves to rationalize the large differences in reactivity between the isobutenyl and vinylpyridone systems, several critical observations appear to limit its serious consideration. The concentrations of **16** and **17** in water or dilute acid solution should be exceptionally low owing to the expected large pK_b of N-substituted pyridones (pK_as of 1-methyl-2-hydroxypyridinium salts are 0.3).[20] Ultraviolet measurements on aqueous solutions of **1** and **2**, and **16** and **17**, strongly support this expectation and further demonstrate that the amount of light competitively absorbed by the shorter wavelength absorbing pyridinium salts under the reaction conditions would be exceedingly low. Likewise, proton transfer from water to singlet excited 1-alkenyl-2-pyridones as a mechanism for formation of **16** and **17** can be deemed improbable on the basis of the results of Bridges and co-workers,[21] which show that the singlet state pK_as of O-protonated 2-pyridones are in the range of −4, and our observations, which demonstrate that fluorescence of **1** is not quenched by acid. Lastly, the hydroxypyridinium perchlorates **16** and **17** did not serve as photochemical precursors of the oxazolopyridinium salts. Likewise, the methallyl- and allyl-2-pyridones, **11** and **12,** which are closer analogues of the allylphenol systems studied earlier,[18,19] are also unreactive when irradiated in water or aqueous acid solutions.



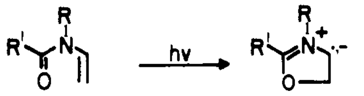
16 or 17 **25**

Table IV. Fluorescence Quantum Yields for 1-Isobutenyl-2-pyridone in Aqueous Ethanol Solutions

fluorescence quantum yields, ϕ_f[a]	ethanol content, % v/v	solvent Y value[b]
0.017	100	−2.033
0.016	90	−0.747
0.015	80	0.000
0.014	70	0.595
0.013	60	1.124
0.012	50	1.660
0.011	40	2.196
0.009	30	2.720
0.007	20	3.051
0.005	10	3.310
0.003	0	3.493

[a] Solutions used for these measurements were degassed and nitrogen purged. Benzene and naphthalene were used as fluorescence standards. Estimated errors are ±0.001. [b] Y values are those derived by Grunwald and Winstein[30] using measured rate constants for solvolysis on *tert*-butyl chloride in aqueous ethanol solutions.

In considering other likely candidates for the mechanism operating in converting singlet 1-alkenyl-2-pyridones to oxazolopyridinium salts, it is instructive to consider the structural and electronic makeup of the center in these substances at which reaction is occurring. The *N*-vinylamide moiety **26,** comprising the exocyclic alkenyl and endocyclic amide groupings, is isoelectronic with chromophores found in divinyl- and diarylamines, ethers, and sulfides all of which possess patterned excited-state reactivity.[7,22,23] Thus, the related *N*-vinylamide function, when present in appropriate environments established by structural features and solvent, could undergo electrocyclic closure to produce oxygen-substituted, cyclic azomethine ylides **27.**[24]



26 **27**

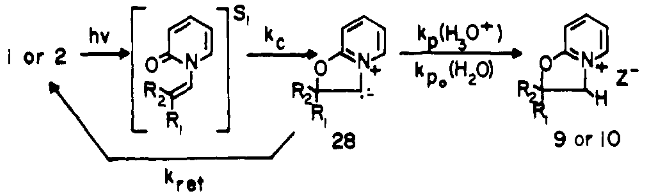
Based upon these thoughts, we suggest that the conversion of 1-alkenyl-2-pyridones to oxazolo[3,2-*a*]pyridinium salts can best be explained by a mechanism involving initial singlet excited state electrocyclization to generate the pyridinium ylides **28.** The ylide intermediates could then be rapidly trapped by

Table V. Fluorescent Quantum Yields and Lifetimes of a Series of 1-Vinyl-2-pyridones and Analogous Compounds Containing the Enamide and Related Chromophores in Solvent Systems of Differing Polarity

compd	emission monitored, nm (all solvents)	singlet lifetimes, ns[a] τ CH_3CN	τ 50% CH_3CN-H_2O	τ H_2O	fluorescence efficiencies[b] emission max nm, CH_3CN (H_2O)	ϕ_f (H_2O)
1	395	16.5	10.3	5.1	395 (387)	0.003
2-*cis*	395	14.1	5.7	2.5	400 (395)	0.057
2-*trans*	395	15.7	6.1	3.4	403 (395)	0.130
13	395	26.2	24.3	25.1	405 (395)	0.147
11	395	11.2	11.8	13.7	380 (370)	0.012
19	395	18.1	13.1	12.7	408 (390)	0.005
20	395	16.5	15.0	11.9	405 (395)	0.025
18	400	5.9		0.4		
21	300	20.1	15.1	13.5		
22	300	27.7	15.7	17.8		
N,*N*-dimethylaniline	300	28.8	29.9	26.3		

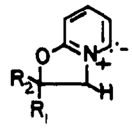
[a] Solutions used for these measurements were degassed and nitrogen purged. Estimated error is ±1.0 ns. [b] Solution used were degassed and nitrogen purged. Benzene and naphthalene were used as standards. Estimated error is ±0.001.

proton transfer from water or hydronium ion, or in competition could revert to starting pyridone by the retro process. Inclusion of the latter pathway for ylide disappearance is dictated by our observations on the reactions of **9** and **10** with potassium *tert*-butoxide, which most probably proceed via **28**. Additional

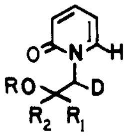


support for the ring-opening process comes from studies by Huisgen and his co-workers[24b] that demonstrate a similar fate for monocyclic ylides of general structure **27**. Although not explored experimentally, ylide formation and return to ground-state pyridone might well be the major if not exclusive pathway for singlet cis–trans isomerization of 1-alkenyl-2-pyridones, or, more generally, of *N*-vinylamides.[4]

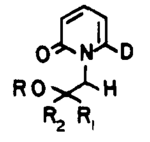
Another important feature of this process, especially in regard to the validity of methods chosen for kinetic analysis (vide infra), concerns the manner in which proton transfer occurs to the carbanionic center in **28**. Howe and Ratts[25] have suggested on the basis of deuterium exchange results that the pK_a of ring α protons of *N*-alkylpyridinium salts is lower than that of the *N*-alkyl α protons. If this is the case, and intramolecular proton transfer converts **28** to the related ylide **29** in competition with return to pyridone, the product-formation step from **28** would have a rate independent of the nature and concentration of the external proton source. However, irradiation of **1** conducted in D_2O results in the exclusive production of the oxazolo-ring monodeuterated alcohol **30a**, thus ruling out an internal proton switch mechanism for salt production. If the latter pathway were functioning, pyridone ring deuterated alcohol **30b** would have been generated.



29



30a



30b

Kinetic Analysis. As is suggested by the mechanism postulated above, the quantum efficiency for conversion of 1-alkenyl-2-pyridones to oxazolo[3,2-*a*]pyridinium salts should be dependent on the nature and concentration of proton donors in solution. Partitioning of the ylide to pyridinium salt rather than to ground-state pyridone should be enhanced by inclusion of higher concentrations of acid in the reaction medium since proton-transfer rate constants (k_p) from H_3O^+ to **28** are expected to be close to diffusion controlled ($k_{diff}(H_2O) = 1 \times 10^{10}\ M^{-1}\ s^{-1}$).[26] In contrast, the bimolecular rate constant for protonation of **28** by H_2O (k_{p_0}) should lie in the range of $1 \times 10^6\ M^{-1}\ s^{-1}$ at room temperature[26] due to an expected pK_a of **9** and **10** of ca. 10.[27] Indeed, as inspection of Figure 3 indicates, the quantum efficiency for production of **9** from **1** (ϕ_r) rapidly increases as perchloric acid concentration in the range of 0 to 5 mM is increased.

Chart II

$$1^{S_0} \xrightarrow{h\nu} 1^{S_1}$$

$$1^{S_1} \xrightarrow[k_d]{} 1^{S_0}$$

$$1^{S_1} \xrightarrow[k_f]{} 1^{S_0}$$

$$1^{S_1} \xrightarrow[k_{DP}]{} 3$$

$$1^{S_1} \xrightarrow[k_c]{} 28$$

$$28 \xrightarrow{k_{ret}} 1^{S_0}$$

$$28 + H_2O \xrightarrow{k_{p0}} 9$$

$$28 + H_3O^+ \xrightarrow{k_p} 9$$

The dependence of quantum efficiency on $[H_3O^+]$ is expressed mathematically in the relationship derived for ϕ_r (eq 1) using the kinetic sequence shown in Chart II, steady-state assumptions for 1^{S_1} and **28**, and the definition of $\tau = 1/(k_d + k_{DP} + k_f + k_c)$. It is instructive to point out here that both the singlet lifetime (τ) and fluorescence quantum yield (ϕ_f) of **1** are independent of $[H_3O^+]$, suggesting that alternate explanations for the dependence of ϕ_r on acid concentration involving protonation of 1^{S_1} cannot be invoked. This kinetic treatment provides us with a rare opportunity to dissect out

$$\frac{1}{\phi_r} = \frac{1}{\tau k_c} + \frac{k_{ret}}{\tau k_c}\left[\frac{1}{k_{p_0}[H_2O] + k_p[H_3O^+]}\right] \quad (1)$$

the individual rate constants for 1^{S_1} cyclization (k_c), ylide **28** return to **1** (k_{ret}), and protonation of **28** by H_2O (k_{p0}) and thus to obtain nearly all of the rate constants for processes involved

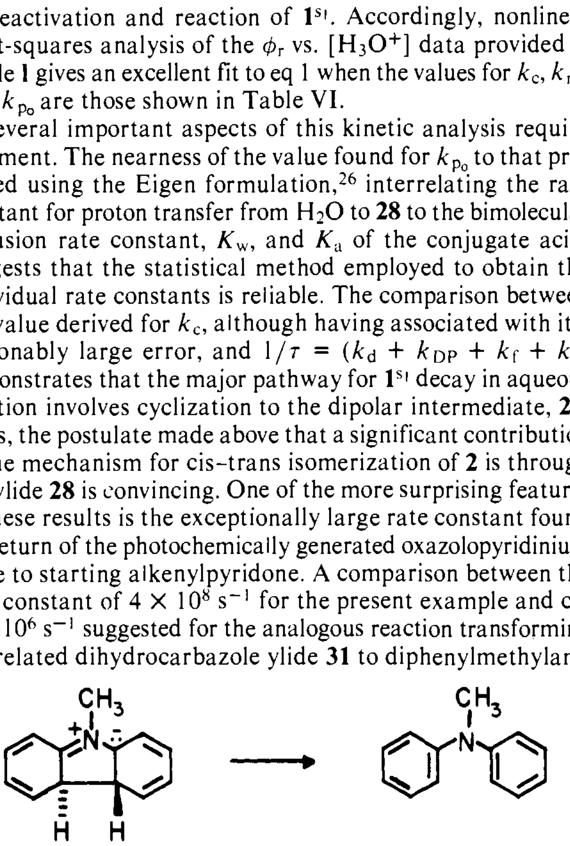
Table VI. Summary of the Rate Constants (25 °C, H_2O) of Processes Used in Deactivation and Reaction of Isobutenylpyridone (**1**)

$k_f = (6 \pm 1) \times 10^5\ s^{-1}$
$k_c = (3.5 \pm 2) \times 10^8\ s^{-1}$
$k_{DP} = 8.5 \times 10^6\ s^{-1}$
$k_d{}^a = 3.2 \times 10^7\ s^{-1}$
$k_{ret} = (3.9 \pm 3) \times 10^8\ s^{-1}$
$k_{p_0} = (6.3 \pm 3) \times 10^5\ M^{-1}\ s^{-1}$
$k_p{}^b = k_{diff} = 1 \times 10^{10}\ M^{-1}\ s^{-1}$

[a] Derived from $(k_d + k_{DP})$ value found using solvent-associated linear free energy treatment of ϕ_f data and value of k_{DP}. [b] Assumed for proton transfer from H_3O^+ to **28**.[26]

in deactivation and reaction of $\mathbf{1}^{S_1}$. Accordingly, nonlinear least-squares analysis of the ϕ_r vs. $[H_3O^+]$ data provided in Table I gives an excellent fit to eq 1 when the values for k_c, k_{ret}, and k_{p_0} are those shown in Table VI.

Several important aspects of this kinetic analysis require comment. The nearness of the value found for k_{p_0} to that predicted using the Eigen formulation,[26] interrelating the rate constant for proton transfer from H_2O to **28** to the bimolecular diffusion rate constant, K_w, and K_a of the conjugate acid, suggests that the statistical method employed to obtain the individual rate constants is reliable. The comparison between the value derived for k_c, although having associated with it a reasonably large error, and $1/\tau = (k_d + k_{DP} + k_f + k_c)$ demonstrates that the major pathway for $\mathbf{1}^{S_1}$ decay in aqueous solution involves cyclization to the dipolar intermediate, **28**. Thus, the postulate made above that a significant contribution to the mechanism for cis–trans isomerization of **2** is through the ylide **28** is convincing. One of the more surprising features of these results is the exceptionally large rate constant found for return of the photochemically generated oxazolopyridinium ylide to starting alkenylpyridone. A comparison between the rate constant of $4 \times 10^8\ s^{-1}$ for the present example and ca. 10^2–$10^6\ s^{-1}$ suggested for the analogous reaction transforming the related dihydrocarbazole ylide **31** to diphenylmethylamine[28] serves to further emphasize this intriguing aspect of 1-alkenyl-2-pyridone photocyclizations.



31

Solvent Polarity Effects. One of the more significant consequences of observations made during the course of our investigations relates to the dramatic role played by solvent in controlling the photochemical reaction pathways followed by 1-alkenyl-2-pyridones. We have shown that direct irradiation of **1** and **2** in solvent systems of low polarity, such an CH_3CN and C_6H_6, leads exclusively to formation of Dewar pyridone and [4 + 4]-dimeric products, in a concentration-dependent ratio, and that pyridonylethanol derivatives result from reactions conducted in wet methanol and water. Moreover, the efficiency of isobutenyl Dewar pyridone **3** production is reduced in a continuous fashion as $[H_2O]$ in H_2O–THF solutions is increased (Figure 2). Simultaneously, the efficiencies of disappearance of **1** and production of **7** are increased as $[H_2O]$ is increased. Moreover, the quantum yield for Dewar pyridone production from **1** decreases dramatically as solvent is varied from the less polar THF to the more polar CH_3CN and CH_3OH. It is quite likely that these observations are reflective of an interesting effect of solvent polarity on partitioning of $\mathbf{1}^{S_1}$ to ylide **28** and Dewar pyridone **3**, i.e., on the k_{DP}/k_c ratio. This effect is almost certainly due to changes in the rate constant (k_c) for formation of the dipolar ylide caused by variation in medium polarity. Hammond and Sharp[29] have shown that the quantum yield for Dewar pyridone production from 1-methyl-2-pyridone, and thus the rate constant, is solvent polarity independent. Likewise, we have shown that k_{DP} for the isobutenyl-2-pyridone **1** is solvent polarity independent and, thus, not responsible for the changes noted.

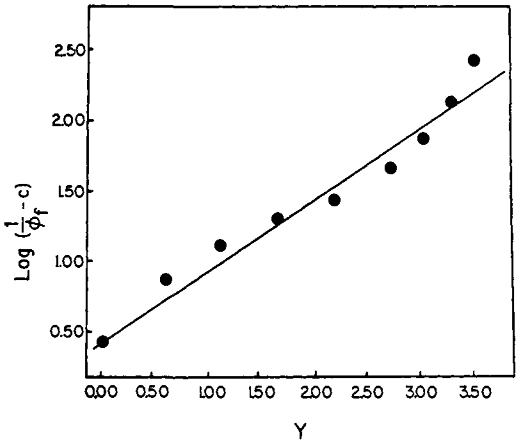


Figure 4. Fluorescence quantum efficiencies for IBP in ethanol-water solutions plotted in the logarithmic form of eq 3 as a function of the solvent Y values using $c = 63.9$.

The solvent-polarity dependence of k_c should be reflected in solvent effects on the singlet lifetimes ($\tau = 1/(k_d + k_{DP} + k_f + k_c)$) and fluorescence efficiencies ($\phi_f = k_f\tau$) of **1**, as shown in Tables II–V. A reasonably simple, quantitative treatment of the solvent polarity effects has turned out to be quite informative. The solvent associated linear free energy of activation relationship, suggested by Grunwald and Winstein,[30] applied to the ylide forming process is shown in eq 2,

$$\log k_c = mY + \log k_{c0} \qquad (2)$$

where k_c and k_{c0} are the cyclization rate constants in aqueous ethanol and 20% H_2O–EtOH (v/v), m is the reaction parameter reflecting the sensitivity of k_c to changes in solvent polarity or the degree of charge separation in the transition state for $\mathbf{1}^{S_1} \rightarrow \mathbf{28}$, and Y is the solvent polarity parameters. Substitution for k_c and k_{c0} by functions containing the easily measured ϕ_f gives eq 3 in which $c = 1 + ((k_d + k_{DP})/k_f)$. Analysis of the data for ϕ_f vs. Y shown in Table IV, using nonlinear least-squares methods, in which the best m and c values are found, gives an exceptionally close fit to eq 3 when

$$\log\left(\frac{1}{\phi_f} - c\right) = mY + \log\left(\frac{1}{\phi_{f_0}} - c\right) \qquad (3)$$

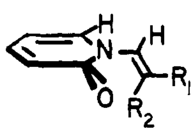
the reaction parameter m is 0.49 ± 0.07 and $(k_d + k_{DP})/k_f$ is 63 ± 1. The results of this analysis are displayed in Figure 4.

The large value of m obtained for cyclization of $\mathbf{1}^{S_1}$ when compared to those observed for ground-state solvolysis reactions (ca. 1) strongly suggests that a significant polarity change is occurring in proceeding from the singlet pyridone to the transition state for ylide formation. It seems reasonable to postulate that this is reflective of a late transition state for conversion of $\mathbf{1}^{S_1}$ to the ylide **28** in either its ground or singlet excited state.

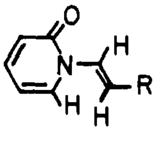
The possibility that the large m value stems not necessarily from a transition state with a large degree of charge separation but, rather, from a reversed polarity in $\mathbf{1}^{S_1}$ appears unlikely since the fluorescence maximum and band shape of **1** are unchanged over a large range of solvent polarities.

In summary, the solvent polarity treatment described above offers additional support for the proposed mechanism for conversion of 1-alkenyl-2-pyridones to oxazolopyridinium salts. It is clear from the fact that k_c varies ca. four orders of magnitude in changing solvent from THF[31] to H_2O and ca. two orders of magnitude from EtOH to H_2O that this process would be an insignificant competitor of Dewar pyridone formation in photoreactions of alkenylpyridones conducted in nonpolar organic solvents. Lastly, from the value of $(k_d + k_{DP})/k_f$ obtained from this treatment it is possible to calculate the rate constant for radiationless decay of 1^{S_1} (k_d) (see Table VI).

Structural Effects. Another interesting feature of the results presented above concerns the apparent substituent effects on the reactivity of singlet 1-alkenyl-2-pyridones. Our preliminary results indicate that the efficiency for oxazolopyridinium salt formation is critically dependent on both the number and geometrical location of substituents on the exocyclic vinyl moiety, i.e., a qualitatively judged order of reactivity of isobutenyl > *cis*-propenyl > *trans*-propenyl ≫ vinyl. Importantly, the source of the reactivity differences might lie in substituent effects on the rates of ylide formation from the singlet pyridones, as judged by the correlation between reactivity and solvent polarity effects on singlet lifetimes and fluorescence efficiencies of the 1-alkenyl-2-pyridones. Although a rationalization for the substituent effects on k_c is not readily apparent, information which might be suggestive of the source of the control is found in earlier studies[8] on the preferred C–N conformations of 1-alkenyl-2-pyridones. Spectroscopic data presented at that time showed that the presence of cis-alkyl substitution of the terminal vinyl carbon of 1-vinyl-2-pyridones causes bisected conformers, **32**, to be preferred. In conformations of this type, the terminal vinyl carbon is preparatorily oriented in the direction of motion required for cyclization. Moreover, the preferred C–N conformations in cases lacking large cis-alkyl substituents, such as the parent vinylpyridone **13**, are known[8] to be planar and to most probably have the vinyl moiety oriented anti with respect to the amide carbonyl. Conformations of this type, **33**, for singlet excited systems would of course be incapable of cyclization. Thus, the substituent effects may be stereoelectronic or conformational in nature and may be manifested in terms of least motion or orbital overlap control. Further studies should clarify these questions.



32



33

Lastly, if our interpretation of the solvent effects is correct, then changes in singlet lifetimes and fluorescence quantum yields of other substances containing the *N*-vinylamide or related diaryl- or divinylamine chromophores might serve as good indicators of when singlet states of these systems have available to them reaction pathways involving electrocyclization to form dipolar ylides. Processes of this type have been invoked to rationalize the triplet photochemistry of the enamine **22**[7] and diphenylmethylamine.[28] This feature has been preliminarily investigated using the acyclic enamides, **19** and **20**, and amines **21** and **22** (Table V). For all cases in which the *N*-vinylamide and diaryl- or arylvinylamine chromophores are present, small but definite decreases in the singlet lifetimes were noted when the solvent system was made more polar by changing from acetonitrile to water.[32]

Summary

The results of studies conducted thus far in the area of 1-alkenyl-2-pyridone photochemistry have led to the unmasking of a novel photocyclization reaction involving the *N*-vinylamide chromophore. Although only tentative, the results indicate that this excited-state process may well be quite general and operable in a number of systems containing this and related chromophores.[32-34] In addition the study has demonstrated the wealth of information that can be made available from detailed analyses of photophysical and photochemical data obtained by employing the modern tools of photochemistry. Moreover, the 1-alkenyl-2-pyridones should serve as useful models in future studies aimed at probing the detailed electronic and structural features of excited-state processes.

Experimental Section

Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. NMR spectra were recorded on Varian HA-100 or T-60 (proton) and JEOL PS-100 (carbon) spectrometers with tetramethylsilane as an internal standard. Infrared spectra were taken using Beckman IR-8 or Perkin-Elmer 237 spectrometers using polystyrene as reference. Ultraviolet absorption spectra were measured using a Beckman Acta-III spectrophotometer. Gas chromatographic analyses were performed with a Varian Model 940 chromatograph with flame ionization detection. Mass spectroscopic measurements were made at 70 eV on a CEC-21-110 double-focusing, high-resolution mass spectrometer. Melting points were obtained uncorrected using a Griffin Mel-Temp apparatus. Preparative irradiations were conducted in an apparatus consisting of a Hanovia 450-W medium-pressure lamp surrounded by the appropriate glass filter within a quartz, water-cooled immersion well surrounded by the solution being irradiated. Photolyses requiring simultaneous irradiation of multiple samples were performed using the lamp housing, described above, located at the center of a merry-go-round apparatus containing the tubes with samples. Preparative TLC was performed using 20 × 20 cm plates coated with silica gel (E. Merck, GF-254, type 60). Fluorescence measurements were made using a Spex-Fluorolog emission spectrometer.

Irradiation of 1-(2-Methyl-1-propenyl)-2-pyridone (1) in Nonaqueous Solvents. Preparation of the Isobutenyl Dewar Pyridone 3. A solution of 1-(2-methyl-1-propenyl)-2-pyridone[8] (250 mg, 1.68 mmol) in 450 mL of degassed tetrahydrofuran was irradiated in a preparative apparatus for 2.0 h using Pyrex glass filtered light. Nitrogen was bubbled through the solution during the irradiation. The crude photolysate was concentrated in vacuo, giving a golden oil which was subjected to preparative TLC (50% ethyl acetate–chloroform). This purification method gave 150 mg (60%) of pure 2-(2-methyl-1-propenyl)-2-azabicyclo[2.2.0]hex-5-en-3-one as a golden oil: ^1H NMR ($CDCl_3$) δ 6.64 (m, 2 H, H-5 and H-6), 6.02 (m, 1 H, isobutenyl), 4.72 (m, 1 H, H-1), 4.19 (m, 1 H, H-4), 1.85 (s, 3 H, CH_3), and 1.75 (s, 3 H, CH_3); ^{13}C NMR ($CDCl_3$) δ 167.0 (s, C-3), 141.8 and 140.7 (d, C-5 and C-6), 120.5 (s, isobutenyl quaternary), 117.9 (d, isobutenyl methine), 57.6 and 56.0 (d, C-1 and C-4), 23.0 and 17.4 (q, methyls); UV (95% EtOH) max 228 nm (ϵ 12 800); IR (liquid film) 3000, 1725, 1635, 1400, and 1370 cm^{-1}; mass spectrum *m/e* (rel intensity) 149 (P, 9), 134 (100), 120 (19), 107 (26), and 94 (17); high-resolution mass spectrum *m/e* 149.084 06 (calcd for $C_9H_{11}NO$, 149.084 75).

Preparation of the Bisisobutenyl [4 + 4] Dimer 5. A solution of 1.50 g (10.1 mmol) of 1-(2-methyl-1-propenyl)-2-pyridone[8] in 200 mL of degassed tetrahydrofuran was irradiated in a preparative apparatus using Pyrex glass filtered light for 2.0 h. Nitrogen was bubbled through the solution during irradiation. Concentration of the crude photolysate in vacuo to ca. 20 mL followed by the addition of ca. 20 mL of ether caused precipitation of the [4 + 4] dimer **5** as a white, crystalline solid (0.96 g, 64%): mp 227–228 °C; ^1H NMR ($CDCl_3$) δ 6.80 (m, 2 H, endocyclic vinyls), 6.30 (t, 2 H, endocyclic vinyls), 5.7 (d, 2 H, isobutenyl), 4.2 and 3.6 (m, 4 H, bridgehead), 1.8 and 1.6 (s, 12 H, methyl); mass spectrum *m/e* (rel intensity) 149 (P, 69), 148 (44), 134 (100); high-resolution mass spectrum base peak *m/e* 149.084 46 (calcd for $C_9H_{11}NO$, 149.084 06).

Irradiation of 1-(1-*trans*-Propenyl)-2-pyridone (2) in Nonaqueous Solvents. Preparation of the *trans*-Propenyl Dewar Pyridone (4). Irradiation through Pyrex glass of 1-(1-*trans*-propenyl)-2-pyridone[8] (500 mg, 3.70 mmol, in 850 mL of tetrahydrofuran), using the conditions, workup, and purification procedure described above for preparation of the Dewar pyridone **4**, gave 414 mg (83%) of pure 2-

(1-*trans*-propenyl)-2-azabicyclo[2.2.0]hex-5-en-3-one as a clear oil: ^{1}H NMR (CDCl$_3$) δ 6.70 (m, 2 H, H-5 and H-6), 6.25 (d, 1 H, propenyl H-1), 4.85 (m, 2 H, H-1 and propenyl H-2), 4.25 (m, 1 H, H-4), 1.9 (d, 3 H, CH$_3$); ^{13}C NMR (CDCl$_3$) δ 166.7 (s, C-3), 142.2 and 140.4 (d, C-5 and C-6), 122.0 (d, propenyl C-1), 107.1 (d, propenyl C-2), 58.3 and 56.2 (d, C-1 and C-4), 11.6 (q, CH$_3$); UV (95% EtOH) max 242 nm (ε 11 400); IR (liquid film) 2900, 1725, 1665, 1535, and 1360 cm^{-1}. Attempts at obtaining elemental analytical data for this material failed owing to exceptional difficulties with purification and the low intensity of the parent ion in the mass spectrum.

Preparation of the Bispropenyl [4 + 4] Dimer 6. Irradiation of a degassed, nitrogen-purged solution of 1-(1-*trans*-propenyl)-2-pyridone[8] (3.00 g, 0.022 mmol) in 800 mL of acetonitrile in the preparative apparatus for 0.5 h gave after concentration in vacuo and addition of ether 1.00 g (33%) of the [4 + 4] dimer **6** as a white, crystalline solid: mp 216–217 °C; ^{1}H NMR (CDCl$_3$) δ 6.90 (m, 2 H, propenyl H-1), 6.6 (m, 4 H, endocyclic vinyls), 5.3 (m, 2 H, propenyl H-2), 4.5 and 3.7 (m, 4 H, bridgehead), 1.7 (d, 6 H, CH$_3$); high-resolution mass spectrum base peak *m/e* 135.068 86 (calcd for C$_8$H$_9$NO, 135.068 41).

Irradiation of Aqueous Solutions of 1-(2-Methyl-1-propenyl)-2-pyridone. Preparation of 1-(2-Hydroxy-2-methylpropyl)-2-pyridone (7). A solution of 1-(2-methyl-1-propenyl)-2-pyridone[8] (1.00 g, 6.7 mmol) in 2.0 L of degassed, deionized water was irradiated in the preparative apparatus for 2.0 h using Pyrex glass filtered light. Nitrogen was bubbled through the solution during irradiation. Concentration of the photolysate in vacuo gave 0.98 g of a red oil (88%) characterized by spectroscopic methods as 1-(2-hydroxy-2-methylpropyl)-2-pyridone.[8] UV absorption spectrophotometric monitoring of the photolysis and workup showed the following changes: max 309 (before irradiation), 288 (crude photolysate before concentration), and 305 nm (after concentration). The colorless, crystalline pyridonyl alcohol **7** (0.615 g, 55% mp 119–119.5 °C), identical in all respects with material previously prepared,[8] can be derived by preparative TLC (30% ethyl acetate–chloroform) of the crude reaction mixture.

Irradiation of methanolic solutions of the isobutenyl-2-pyridone (no precautions were taken prior to irradiation to exclude water from the methanol) led to production of the pyridonylethanol derivative. Adventitious water presumably is partaking in this reaction.

Irradiation of Aqueous Solutions of 1-(1-*trans*-Propenyl)-2-pyridones. Preparation of 1-(2-Hydroxypropyl)-2-pyridone (8). A solution of 1-(1-*trans*-propenyl)-2-pyridone[8] (0.20 g, 1.5 mmol) in 250 mL of degassed, deionized water was irradiated in the preparative apparatus for 3.0 h using Pyrex glass filtered light. Nitrogen was bubbled through the solution during irradiation. Concentration of the photolysate in vacuo gave 0.19 g of a golden oil (81%) characterized by spectroscopic methods as pure 1-(2-hydroxypropyl)-2-pyridone.[8] UV absorption spectrophotometric monitoring of the photolysis and workup showed the following changes: maxima at 302 (before irradiation), 287 (crude photolysate before concentration), and 303 nm (after concentration). The colorless, crystalline pyridonyl alcohol **8** (0.079 g, 35%, mp 95–96.5 °C), identical in all respects with material previously prepared,[8] can be derived by preparative TLC (30% ethyl acetate–chloroform) of the crude reaction mixture.

Irradiation of 1-(2-Methyl-1-propenyl)-2-pyridone in Aqueous Perchloric Acid Solution. Preparation of 5,5-Dimethyloxazolo[3,2-*a*]pyridinium Perchlorate (9). A solution of 1-(2-methyl-1-propenyl)-2-pyridone[8] (0.250 g, 1.7 mmol) in 450 mL of degassed, deionized water containing 0.3 mL of 70% perchloric acid (12 mmol) was irradiated in the preparative apparatus under a nitrogen atmosphere using Pyrex glass filtered light for 1.5 h. The disappearance of the isobutenylpyridone and appearance of the pyridinium salt were monitored by UV spectroscopic changes in the 250–320-nm region. The photolysate was concentrated in vacuo, giving an oil which crystallized upon addition of 5 mL of chloroform yielding 188 mg (45%) of pure 5,5-dimethyloxazolo[3,2-*a*]pyridinium perchlorate: mp 156–158 °C; ^{1}H NMR (D$_2$O) δ 2.20 (s, 6 H, CH$_3$), 5.25 (s, 2 H, methylene), 7.85 (d, 1 H, *J* = 11.0 Hz, pyridinium H-2), 7.93 (1 H, t, *J* = 9.0 Hz, pyridinium H-5), 8.80 (m, 2 H, pyridinium H-4 and H-6); ^{13}C NMR (CDCl$_3$) δ 159.3 (s, pyridinium C-2), 147.9 (d, pyridinium C-6), 140.8, 140.2, and 139.5 (d, pyridinium C-3, C-4, and C-5), 92.0 (s, C-5), 61.2 (t, C-4), 26.6 (q, CH$_3$); UV (H$_2$O) max 285 nm (δ 5140); IR (Nujol) 1650, 1575, and 1085 cm^{-1}; mass spectrum *m/e* (rel intensity) (for parent minus HClO$_4$ fragment) 149 (37), 148 (42), 134 (100), 128 (68), and 127 (41); high-resolution mass spectrum *m/e* (for parent minus HClO$_4$ fragment) 149.084 60 (calcd for C$_9$H$_{11}$NO, 149.084 06).

Anal. Calcd for C$_9$H$_{12}$NClO$_6$: C, 43.30; H, 4.84; N, 5.61; Cl, 14.20. Found: C, 43.12; H, 5.09; N, 5.78; Cl, 14.05.

Irradiation of the isobutenyl-2-pyridone in aqueous solutions containing formic acid led to formation of the 5,5-dimethyloxazolo[3,2-*a*]pyridinium formate salt, which was not purified directly but rather converted to the perchlorate salt by perchlorate ion exchange using Dowex-1-X8.

Irradiation of 1-(1-*trans*-Propenyl)-2-pyridone in Aqueous Perchloric Acid Solution. Preparation of 5-Methyloxazolo[3,2-*a*]pyridinium Perchlorate (10). A solution of 1-(1-*trans*-propenyl)-2-pyridone[8] (0.250 g, 1.90 mmol) in 450 mL of degassed, deionized water containing 0.3 mL of 70% perchloric acid (12 mmol) was irradiated in the preparative apparatus under a nitrogen atmosphere using Pyrex glass filtered light for 3 h. Concentration in vacuo in the photolysate gave a gold oil which crystallized upon addition of 5 mL of chloroform to yield 217 mg (50%) of pure 5-methyloxazolo[3,2-*a*]pyridinium perchlorate: mp 124–126 °C; ^{1}H NMR (D$_2$O) δ 2.1 (d, 3 H, *J* = 7 Hz, CH$_3$), 5.50 (AB q, 2 H, *J* = 11 Hz, methylene), 6.00 (m, 1 H, methine H-5), 7.85 (d, 1 H, *J* = 11 Hz, pyridinium H-2), 7.93 (1 H, t, *J* = 9 Hz, pyridinium H-5), 8.80 (m, 2 H, pyridinium H-4 and H-6); ^{13}C NMR (D$_2$O) δ 160.2 (s, pyridinium C-2), 147.9 (d, pyridinium C-6), 140.0, 138.3, and 128.5 (d, pyridinium C-3, C-4, and C-5), 106.0 (d, C-5), 56.8 (t, C-4), 19.6 (q, CH$_3$); UV (H$_2$O) max 285 nm (ε 4740); IR (Nujol) 1635, 1575, 1080 cm^{-1}; mass spectrum *m/e* (rel intensity) (for parent minus HClO$_4$ fragment) 135 (50), 134 (57), 120 (100), 95 (40), 67 (53); high-resolution mass spectrum *m/e* (for parent minus HClO$_4$) 135.069 10 (calcd for C$_8$H$_9$NO, 135.068 40). Attempts to obtain elemental analyses for this salt were unsuccessful, presumably owing to its extreme hygroscopic nature.

Reactions of the Oxazolo[3,2-*a*]pyridinium Salts 9 and 10 with Potassium Hydroxide. Solutions of 5,5-dimethyl- and 5-methyloxazolo[3,2-*a*]pyridinium perchlorate (137 mg (0.9 mmol) and 120 mg (0.8 mmol), respectively) in 4 mL of methanol containing equimolar amounts of potassium hydroxide were independently stirred at room temperature for 12 h. The reaction mixtures were concentrated in vacuo, giving oils which were purified by preparative TLC (30% ethyl acetate–chloroform). This procedure yielded the dimethyl- and methylpyridonylethanols **7** and **8** in yields of 105 (77%) and 95 mg (79%), respectively. Spectroscopic data on these compounds matched that reported previously.[8]

Reactions of the Oxazolo[3,2-*a*]pyridinium Salts 9 and 10 with Potassium *tert*-Butoxide. Solutions of 5,5-dimethyl- and 5-methyloxazolo[3,2-*a*]pyridinium perchlorate (90 mg (0.4 mmol) and 100 mg (0.4 mmol), respectively) in *tert*-butyl alcohol (25 mL) and potassium *tert*-butoxide (from 1.0 g of potassium) were independently heated at 50 °C under argon for 4 h. These solutions, after addition of water, were concentrated in vacuo, giving oils which were subjected to preparative TLC (chloroform) giving 1-(2-methyl-1-propenyl)-2-pyridone (82 mg, 91%) and a mixture of *cis*- and *trans*-1-(1-propenyl)-2-pyridone (87 mg, 87%), respectively. Spectroscopic data for these compounds were identical with those previously reported.[8]

Pyrolyses of the Oxazolo[3,2-*a*]pyridinium Salts 9 and 10. Crystalline dimethyl- and methyloxazolopyridinium perchlorates (50 mg (0.20 mmol) and 60 mg (0.20 mmol), respectively) were heated independently at 150 °C under argon for 1 h. The oils obtained were purified by preparative TLC (chloroform), yielding 37 mg (74%) of 1-(2-methyl-2-propenyl)-2-pyridone and 51 mg (85%) of 1-(2-propenyl)-2-pyridone, respectively. These substances displayed spectroscopic properties equivalent to those obtained for independently prepared materials.[8]

This pyrolytic reaction can be conducted in the injector block (220 °C) during GLC analysis. Accordingly, GLC analyses of aqueous solutions of the oxazolopyridinium salts showed peaks with retention times identical with those of the corresponding allyl- and methallylpyridones.

Dark Control Experiments. A variety of dark control reactions were attempted using 1-(2-methyl-1-propenyl)-2-pyridone and related substances. (1) A solution of this pyridone (100 mg) and *p*-toluenesulfonic acid (115 mg) in 15 mL of water was heated at 75 °C under argon for 12 h. The crude reaction mixture was extracted with chloroform. The chloroform extracts were dried and concentrated in vacuo, giving quantitative recovery of the pure starting isobutenylpyridone. (2) The isobutenyl-2-pyridone was heated at 150 °C under argon for 1 h. Unreacted starting material was recovered quantitatively. (3) A solution of 1-(2-hydroxy-2-methylpropyl)-2-pyridone (100 mg) and 90% formic acid (0.1 mL) in 10 mL of methanol was heated at reflux for 12 h. Concentration in vacuo of the crude reaction mixture gave quantitative recovery of the starting pyridonylethanol derivative.

Irradiation of 1-(2-Methyl-2-propenyl)-2-pyridone (11). A solution of 1-(2-methyl-2-propenyl)-2-pyridone[8] (250 mg, 1.68 mmol) in 450 mL of degassed, deionized water, containing 0.3 mL of 70% perchloric acid, was irradiated in the preparative apparatus under nitrogen using Pyrex glass filtered light. Disappearance of the starting pyridone was monitored by UV spectroscopic methods and found to be nearly complete after 5.0 h. Concentration in vacuo of the crude photolysate gave a mixture which was shown not to contain any of the 5,5-dimethyloxazolo[3,2-*a*]pyridinium perchlorate salt or corresponding pyridonylethanol derivative **7**. Further characterization of the complex reaction mixture was not attempted.

Irradiation of 1-Vinyl-2-pyridone (13). A solution of 1-vinyl-2-pyridone[10] (250 mg, 2.07 mmol) in 450 mL of degassed, deionized water was irradiated under nitrogen in the preparative apparatus using Pyrex glass filtered light for 18.5 h. Concentration in vacuo of the crude photolysate gave a mixture which was shown by spectroscopic and chromatographic methods to contain a number of materials of high molecular weight none of which corresponded to the pyridonylethanol derivative.

Triplet-Sensitized Photochemical Studies of 1-(2-Methyl-1-propenyl)-2-pyridone (1). The following solutions were prepared: I, 1-(2-methyl-1-propenyl)-2-pyridone (50 mg, 3.36 mmol) and 90% formic acid (100 μL) in 100 mL of methanol containing 1.3×10^{-5} M xanthone; II, the isobutenylpyridone (50 mg) in 100 mL of methanol containing 1.3×10^{-5} M xanthone; III, the isobutenylpyridone (50 mg) and 100 μL of 90% formic acid in 100 mL of methanol containing 1.3×10^{-5} M Michler's ketone; IV, the isobutenylpyridone (50 mg) in 100 mL of methanol containing 1.3×10^{-5} M Michler's ketone; V, the isobutenylpyridone (50 mg) in 100 mL of methanol; VI, the isobutenylpyridone (50 mg) and 100 μL of 90% formic acid in 100 mL of methanol; VII, 100 mL of methanol containing 1.3×10^{-5} M xanthone; VIII 100 μL of 90% formic acid in 100 mL of methanol containing 1.3×10^{-5} M xanthone; IX, 100 mL of methanol containing 1.3×10^{-5} M Michler's ketone; X, 100 μL of 90% formic acid in 100 mL of methanol; VII, 100 mL of methanol containing 1.3×10^{-5} M xanthone; VIII, 100 μL of 90% formic acid in 100 mL of methanol containing 1.3×10^{-5} M Michler's ketone. These solutions were degassed and placed individually into sealed Pyrex glass tubes. Simultaneous irradiation of these tubes was performed using uranium glass filtered light for 3 h. Analyses of the crude photolysates were performed using UV spectroscopic methods and GLC (5 ft × $^1/_8$ in., 1.4% OV101 on Anasorb, 150 °C, 20 mL/min). Solutions I–IV containing the light-absorbing triplet sensitizers were shown to contain unreacted sensitizer and isobutenylpyridone. Solutions V and VI were shown to contain trace amounts of the pyridonylethanol derivative and oxazolopyridinium salt, respectively. Solutions VII and VIII were shown to contain the photoreduction products of xanthone.[11b]

Preparation of 1-(2-Methyl-1-propenyl)- and 1-(1-*trans*-Propenyl)-2-hydroxypyridinium Perchlorate (16 and 17). Solutions of 1-(2-methyl-1-propenyl)-2-pyridone[8] (100 mg, 0.67 mmol) and of 1-(1-*trans*-propenyl)-2-pyridone[8] (250 mg, 1.85 mmol) in 10 mL of 0.54 M perchloric acid in methanol were individually stirred under nitrogen at room temperature for 12 h. The reaction mixtures were concentrated in vacuo, giving products as waxy solids characterized as the desired hydroxypyridinium salts **16** (98 mg, 98%, mp 75–77 °C) and **17** (240 mg, 97%, mp 68–71 °C). Spectroscopic properties of these compounds are as follows. **16:** ^{1}H NMR (CDCl$_3$) δ 2.2 and 2.5 (d, 6 H, CH$_3$), 7.1 (br s, 1 H, vinyl), 7.7 (overlapping t and d, 2 H, pyridinium H-3 and H-5), 8.7 (overlapping t and d, 2 H pyridinium H-4 and H-6); UV (0.5 M HClO$_4$/CH$_3$OH) max 285 nm (ϵ 5220). **17:** ^{1}H NMR (CDCl$_3$) δ 2.5 (d, 3 H, CH$_3$), 6.8 (dq, 1 H, β-vinyl), 7.7 (m, 3 H, α-vinyl and pyridinium H-3 and H-5), 8.7 (overlapping d and t, 3 H, pyridinium H-44 and H-6); UV (0.5 M HClO$_4$/CH$_3$OH) max 281 nm (ϵ 7820).

Irradiation of 1-(2-Methyl-1-propenyl)- and 1-(1-*trans*-Propenyl)-2-hydroxypyridinium Perchlorate (16 and 17). Solutions of 1-(2-methyl-1-propenyl)- and 1-(1-*trans*-propenyl)-2-hydroxypyridinium perchlorate (50 mg) in 100 mL of 0.54 M, degassed, methanolic perchloric acid within Pyrex glass tubes were independently, simultaneously irradiated using unfiltered light. GLC analysis (5 ft × $^1/_8$ in., 1.4% OV101 on Anasorb, 150 °C, 20 mL/min) of the crude photolysates after 3 h showed nearly total decomposition of the starting perchlorate salts and no conversion to the corresponding oxazolo[3,2-*a*]pyridinium salts.

Irradiation of Tetrahydrofuran Solutions of 1-(2-Methyl-1-propenyl)-2-pyridone (1) of Varying Water Concentration. Solutions containing 50 mg (0.34 mmol) of 1-(2-methyl-1-propenyl)-2-pyridone in 100 mL of solvent consisting of the following composition of tetrahydrofuran and water (percent by volume), 100% THF, 75% THF-H$_2$O, 50% THF-H$_2$O, 25% THF-H$_2$O, and 100% H$_2$O, were degassed and irradiated simultaneously using Pyrex glass filtered light for 1 h. GLC analysis (5 ft × $^1/_8$ in., 1.5% OV101 on Anasorb, 150 °C, 20 mL/min) using 1-vinyl-2-pyridone as an internal standard gave the results recorded in Figure 2.

Quantum Yield Measurements. Quantum yields were measured using a "linear optical bench" system equipped with a high-pressure, 500-W mercury lamp (Osram HBO-500-W/2), the output of which was focused with a quartz collimator and passed through a quartz-faced, water-cooled, three 1-cm compartment filter solution cell containing, separately, 2 M NiSO$_4$·6H$_2$O in 5% H$_2$SO$_4$, saturated CoSO$_4$·7H$_2$O in 5% H$_2$SO$_4$, and 7.2×10^{-4} M K$_2$CrO$_4$ in 0.2% NaOAc. This solution filter combination gave relative transmission characteristics before and after irradiations as follows: 230 nm, 10%; 250 nm, 0%; 300 nm, 35%; 315 nm, 79%; 325 nm, 60%; 335 nm, 7%. The filtered light then passed through two quartz-faced, water-cooled cells aligned in series. During actinometry runs, both the front and back cells were filled with 0.006 M potassium ferrioxalate.[13] During photolysis runs, the front cell contained 1-(2-methyl-1-propenyl)-2-pyridone solutions and the back cell potassium ferrioxalate in order to monitor light not absorbed by the substrate. Light output was determined before and after each photolysis and was found to be exceptionally constant.

Product analyses for reactions conducted in aqueous acetonitrile solutions were performed by GLC (5 ft × $^1/_8$ in., 1.5% OV101 on Anasorb, 120 °C, 20 mL/min) using 1-vinyl-2-pyridone as an internal standard. Product analyses for reactions conducted in aqueous acid solution involved initial treatment of the crude photolysate with stoichiometric amounts of potassium hydroxide to convert the oxazolopyridinium salt to pyridonylethanol derivative followed by GLC. Conversions in quantum yield runs were maintained in the region of 8–18%. Quantum yields for product formation obtained under a variety of conditions are recorded in Table II.

The quantum yields for conversion of the isobutenylpyridone to the corresponding Dewar pyridone were measured using 5.4×10^{-3} M solutions of pyridone in freshly distilled tetrahydrofuran, acetonitrile, and methanol under N$_2$ at 25 °C. Product analyses were performed by GLC (5 ft × $^1/_8$ in., 1.5% OV101 on Anasorb, 120 °C, 20 mL/min) using benzophenone as an internal standard added after irradiation. The quantum yields were 0.261 at 5.9% conversion in tetrahydrofuran, 0.143 at 3.1% conversion in acetonitrile, and 0.061 at 1.4% conversion in methanol.

Fluorescence Quantum Yields. Fluorescence measurements were taken using a Spex Fluorolog. The observed emission was shown to correspond to fluorescence of the substrates by the identities of excitation and absorption curves and by the mirror image relationships between excitation and emission curves. The relative fluorescence quantum yields of the *N*-vinylpyridones and related substances were measured in degassed solutions at 25 °C according to the method of Parker and Rees[35] using benzene ($\phi_f = 0.07$ in cyclohexane[36]) and naphthalene ($\phi_f = 0.23$ in cyclohexane[36]) as standards.

Singlet Lifetime Measurements. Singlet lifetimes were measured using a single photon counting, nanosecond spectrofluorometer based upon ORTEC components. Solutions containing the *N*-vinylpyridones and related substances were degassed prior to and maintained at 25 °C during measurements. Values for τ were calculated by a Digital RX01 computer using the method of moments program. The instrument was calibrated using the quinine bisulfate standardization method.[37]

Irradiation of 1-(2-Methyl-1-propenyl)-2-pyridone (1) in Deuterium Oxide. A solution of 1-(2-methyl-1-propenyl)-2-pyridone (50 mg, 0.34 mmol) in 50 mL of degassed deuterium oxide was irradiated in a Pyrex tube for 6 h. Concentration of the photolysate in vacuo gave a gold oil which was purified by preparative TLC (chloroform) yielding 18 mg of 1-(2-methyl-2-hydroxypropyl)-2-pyridone. ^{1}H NMR analysis of this material (integration of proton resonances at δ 4.1 (α-CH$_2$) and 7.4 (ring α-CH) showed that one deuterium atom had been incorporated at the α-methylene position of the alcohol side chain. Mass spectrometric analysis confirmed that only one deuterium had been incorporated: parent, *m/e* 168.100 40 (calcd for C$_9$H$_{12}$DNO$_2$, 168.100 90) and P-1 (0%).

2,5-Dimethyl-2,4-hexadiene Quenching of 1-(2-Methyl-1-propenyl)-2-pyridone (1) Fluorescence and Reaction. Quantum Yields and Singlet Lifetimes. Singlet lifetimes and fluorescence quantum yields were measured, using the techniques described above, with degassed solutions at 25 °C containing 6.0×10^{-5} M 1-(2-methyl-1-propenyl)-2-pyridone in 50% MeOH-CH_3CN (v/v) and varying concentrations of 2,5-dimethyl-2,4-hexadiene. Using these conditions all light is absorbed by the isobutenyl-2-pyridone. The results of this experiment are given in Figure 1.

Relative quantum yields for production of 1-(2-methyl-2-hydroxypropyl)-2-pyridone were determined using simultaneous irradiations of degassed solutions (50% CH_3OH-CH_3CN (v/v), containing 1-(2-methyl-1-propenyl)-2-pyridone (25 mg, 0.17 mmol, in 25 mL of solvent) and varying concentrations of 2,5-dimethyl-2,4-hexadiene, with Pyrex glass filtered light (all light absorbed by the pyridone), for 1.5 h. The photolysates were analyzed by GLC (5 ft × in., ⅛ in., 1.5% OV101 on Anasorb, 120 °C, 22 mL/min) using 1-vinyl-2-pyridone as an internal standard. The results of this experiment are displayed in Figure 1.

Acknowledgments. Financial support of this research initially by the National Institutes of Health (CA-16695) and currently by the Robert A. Welch Foundation, the Department of Energy (EC-77G-055621), and the Texas A&M University Center for Energy and Mineral Resources is acknowledged. We would like to acknowledge the exceptionally competent and generous assistance given to us by Professor Janos Fendler and Michael Hall in developing methods for photophysical measurements and statistical analyses. In addition, Dr. Emil Krochmal is thanked for his technical assistance with initial photochemical studies.

References and Notes

(1) Preliminary reports of portions of these studies have appeared: P. S. Mariano, A. A. Leone, and E. Krochmal, *Tetrahedron Lett.*, 2227 (1977); P. S. Mariano and A. A. Leone, *J. Am. Chem. Soc.*, **100,** 3947 (1978).

(2) Camille and Henry Dreyfus Teacher-Scholar grantee, 1975–1980.

(3) (a) E. C. Taylor and P. O. Kahn, *J. Am. Chem. Soc.*, **85,** 776 (1963); (b) L. A. Paquette and G. Slomp, *ibid.*, **85,** 765 (1963); (c) E. J. Corey and J. Streith, *ibid.*, **86,** 459 (1964); (d) R. C. Deselms and W. R. Scheigh, *Tetrahedron Lett.*, 3563 (1972); (e) H. Furrer, *Chem. Ber.*, **105,** 2780 (1972).

(4) (a) N. C. Yang and G. R. Lenz, *Tetrahedron Lett.*, 4897 (1967); (b) R. W. Hoffman and K. R. Eicken, *ibid.*, 1759 (1968).

(5) (a) The analogous oxadi-π-methane rearrangement has been well explored[5b,5c] and one example of an oxadi-π-amine rearrangement has been presented;[5d] (b) H. E. Zimmerman, S. S. Hixson, and P. S. Mariano, *Chem. Rev.*, **73,** 531 (1973); (c) K. N. Houk, *ibid.*, **76,** 1 (1976); (d) A. Padwa and E. Vega, *J. Org. Chem.*, **40,** 175 (1975).

(6) No examples of the di-π-amine rearrangement to our knowledge have been found but the familiar di-π-methane rearrangement has been well explored.[5b]

(7) (a) Chapman-type photocyclizations[7b] are prevented in 1-alkenyl-2-pyridone systems by structural constraints; (b) O. L. Chapman, G. L. Elian, A. Bloom, and J. Clardy, *J. Am. Chem. Soc.*, **93,** 2918 (1971).

(8) P. S. Mariano, E. Krochmal, P. L. Huesmann, R. L. Beamer, and D. Dunaway-Mariano, *Tetrahedron*, in press.

(9) (a) The spectroscopic properties of *N*-methyl Dewar pyridone have been described by Corey[3c] and those of the *N*-deuterio material by Deselms.[3d] (b) Spectroscopic properties of the [4 + 4] dimer derived from *N*-methyl-2-pyridone have been detailed by Taylor[3a] and Paquette.[3b]

(10) H. Kaye and S. H. Chang, *Tetrahedron*, **26,** 1369 (1970).

(11) (a) S. L. Murov, "Handbook of Photochemistry," Marcel Dekker, New York, 1973. (b) Accurate methods for analysis of pinacol formation from photolysis of xanthone in methanol have been described.[11c] These were used in this work. (c) V. Zanker and E. Ehrhardt, *Bull. Chem. Soc. Jpn.*, **39,** 1694 (1966).

(12) (a) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Am. Chem. Soc.*, **88,** 3665 (1966); L. M. Stephenson and G. S. Hammond *Angew. Chem., Int. Ed. Engl.*, **8,** 261 (1969). (b) Indeed, quenching of $\mathbf{1}^{S_1}$ by tetramethylbutadiene would have led to the observation of reaction quenching even if the alcohol **3** arises via the triplet of **1.** However, we would have fully expected much more efficient quenching of $\mathbf{1}^{T_1}$ by this diene at the high concentrations used, since $\mathbf{1}^{T_1}$ should possess a greater lifetime than $\mathbf{1}^{S_1}$ and the triplet quenching rate constant should be k_{diff}. Also, if reactions were occurring from both singlet and triplet excited states, then a biphasic quenching curve would have been obtained.

(13) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235,** 518 (1956).

(14) P. S. Mariano, E. Krochmal, and A. Leone, *J. Org. Chem.*, **42,** 1122 (1977).

(15) The preparation and photochemistry of these *N*-vinylamides will be described at a future date.

(16) J. Hoch, *C. R. Acad. Sci.*, **200,** 938 (1935).

(17) P. J. Kropp, Z. L. F. Gaibel, E. J. Reardon, K. E. Willard, and J. H. Hattaway, *J. Am. Chem. Soc.*, **95,** 7058 (1973), and references cited therein.

(18) G. Frater and H. Schmid, *Helv. Chim. Acta*, **50,** 255 (1967).

(19) W. M. Horspool and P. L. Pauson, *Chem. Commun.*, 195 (1967).

(20) A. Albert, "Heterocyclic Chemistry," Athlone Press, London, 1968, p 80.

(21) J. W. Bridges, D. S. Davies, and R. T. Williams, *Biochem. J.*, **98,** 451 (1966).

(22) (a) A. G. Schultz and M. B. DeTar, *J. Am. Chem. Soc.*, **96,** 296 (1974); (b) S. H. Groen, R. M. Kellog, J. Butler, and H. Wynberg, *J. Org. Chem.*, **33,** 2218 (1968).

(23) (a) W. A. Henderson and A. Zweig, *Tetrahedron Lett.*, 625 (1969); (b) J. A. Elix, D. P. H. Murphy, and M. V. Sargent, *Synth. Commun.*, **2,** 427 (1972); A. G. Schultz and R. D. Lucci, *J. Org. Chem.*, **40,** 1371 (1975).

(24) (a) Ylides of this nature have been prepared previously by reactions of munchnones with reactive aldehydes and ketones.[24b] (b) E. Funke, R. Huisgen, and F. C. Schaefer, *Chem. Ber.*, **104,** 352 (1971); R. Huisgen, E. Funke, H. Gotthardt, and H. L. Panke, *ibid.*, **104,** 1532 (1971).

(25) R. K. Howe and K. W. Ratts, *Tetrahedron Lett.*, 4743 (1967).

(26) (a) Although the rate constants for protonation of delocalized carbon bases are often smaller than that for bimolecular diffusion,[26b] the assumption $k_p = 1 \times 10^{10}\ M^{-1}\ s^{-1}$ in this case appears valid since this value (9.95×10^9) gives the smallest errors for k_c, k_{p_0}, and k_{rel} by the nonlinear least-squares analytical methods used. In addition, the value for k_{p_0} obtained using this method and assumption appears reasonable.[26b] Perhaps the degree of charge delocalization to the ylide **28** is low, thus accounting for proton transfer rate constants characteristic of localized anionic bases. (b) M. Eigen, *Angew. Chem., Int. Ed. Engl.*, **3,** 1 (1964).

(27) I. Zugravescu and M. Petrovand, "Nitrogen Ylid Chemistry," McGraw-Hill, New York, 1976, p 204, and references cited therein.

(28) (a) H. Shizuka, T. Takayama, T. Morita, S. Matsumoto, and I. Tanaka, *J. Am. Chem. Soc.*, **93,** 5987 (1971); (b) E. W. Förster, K. H. Grellman, and H. Linschitz, *ibid.*, **95,** 3108 (1973).

(29) L. J. Sharp and G. S. Hammond, *Mol. Photochem.*, **2,** 225 (1970).

(30) E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, **78,** 2770 (1956); S. W. Winstein, E. Grunwald, and H. W. Jones, *ibid.*, **73,** 2700 (1951).

(31) Based upon a predicted *Y* value for THF in the range of ca. −6 using data recorded in C. Reichardt, *Angew. Chem., Int. Ed. Engl.*, **4,** 29 (1965).

(32) Preliminary studies have shown that water serves to effectively quench the familiar 1,3-acyl shift reactions[4a] of *N*-phenyl-*N*-isobutenylacetamide.

(33) This process might be responsible for the conversion of α-acylamino-β-thioalkylacrylamides to amidoyloxazoles: C. J. Veal and D. W. Young, *Tetrahedron Lett.*, 2985 (1976).

(34) A heteroatom analogue of this cyclization process appears to be operating in the cyclization reactions of 10-phenylisoalloxazines occurring upon irradiation in acid solution: W. R. Knappe, *Chem. Ber.*, **107,** 1614 (1974).

(35) C. A. Parker and W. T. Rees, *Analyst*, **85,** 587 (1969).

(36) I. B. Berlman, "Handbook of Fluorescence Data of Aromatic Molecules," 2nd ed., Academic Press, New York, 1971.

(37) W. H. Melhuish, *J. Phys. Chem.*, **65,** 229 (1961).