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NOVEL PHOTOCYCLIZATION REACTIONS OF 1-VINYL-2-PYRIDONES LEADING TO OXAZOLO[3,2-a]PYRIDINIUM SALTS.[1]

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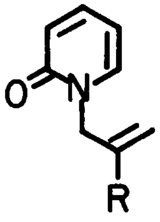
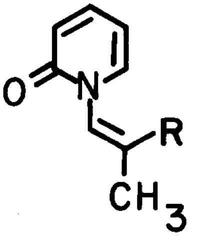
Previous investigations of the solution phase photochemistry of 1-alkyl-2-pyridones have demonstrated that the predominant excited state reaction pathways followed by these systems involve 4+4-dimerization[2] and electrocyclization leading to Dewar-pyridones.[3] During the course of recent synthetic investigations we have explored the photochemistry of related 1-vinyl-2-pyridones with the thought that the vinyl group on nitrogen could introduce the possibility for alternate reaction pathways involving the enamide[4] or di-π-amine[5] chromophores. Indeed, these studies have shown that 1-vinyl-2-pyridones display novel excited state behavior.

1-(2-Methyl-2-propenyl)-2-pyridone (1) and 1-(*trans*-1-propenyl)-2-pyridone (2) were prepared by reaction of 2-hydroxypyridine with allyl and methallyl chloride followed by potassium t-butoxide isomerization of the intermediate allylpyridones 3 and 4.[6] Irradiation of acetonitrile or benzene solutions of either 1 or 2 leads to formation of products resulting from the familiar electrocyclization[3] and dimerization reactions.[1,7] Dramatically different results are noted when water is employed as solvent. Irradiation of a dilute (3.73×10^{-3} M, pyrex filter) aqueous solution of the isobutenylpyridone 3 leads to efficient production of the pyridonylbutanol 11 (87.9%).[6] The propanol derivative 12[6] is obtained (81%) from photolysis of the propenylpyridone 4 using the same conditions.[7] Structural assignments to photoproducts from these reactions were made on the basis of spectral data and their independent synthesis from 1-acetonyl-2-pyridone (5). Uv spectroscopic monitoring of the photoreaction of 3 showed that the λ_{max} of the photolysis solution varies from 309 nm initially, to 288 nm after irradiation, and then to 305 nm after concentration of the photolysate. Similar changes from 302 nm to 287 nm then to 303 nmr are noted during reaction of 4.[8] In addition, these photohydration reactions were shown to occur from the singlet excited states of the vinylpyridones by the failure to detect alcohol products when xanthone was used as triplet sensitizer.[9]

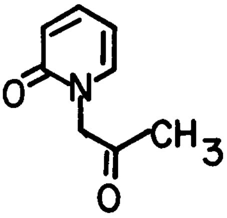
Irradiation of 3 and 4 (3.73 mM, pyrex) in aqueous solutions containing perchloric acid (12 mM) leads to formation of the crystalline oxazolo[3,2-a]pyridinium perchlorates 9 ($X{=}ClO_4^-$) (mp 156-8°, 45%) and 10 ($X{=}ClO_4^-$) (mp 124-6°, 50%), respectively.[6,10] The spectroscopic properties of these salts are consistent with the assigned structures.[11] Also, 9 and 10 ($X{=}ClO_4^-$) are transformed to 3 and 4 by treatment with K-t-butoxide and to the alcohols 11 and 12 by treatment with KOH in methanol.



1 R=CH_3
2 R=H



3 R=CH_3
4 R=H



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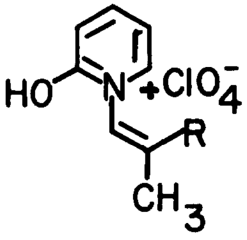
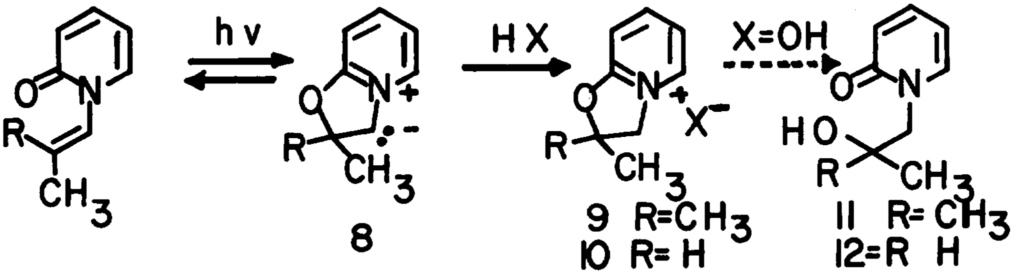


6 R=CH_3
7 R=H



8

9 R=CH_3
10 R=H

11 R=CH_3
12=R H

On the basis of observations noted thus far, two mechanisms appear likely for formation of the oxazolopyridinium salts. One involves intramolecular addition from excited states of the reversibly formed hydroxypyridinium salts 6 and 7 in a manner similar to conversions of ortho-allylphenols to benzodihydrofurans and chromans.[12] However, concentrations of protonated pyridones at the neutral or slightly lower pH used are diminishingly small.[13] Also, irradiation of either the methallyl 1 or ally pyridone 2 leads only to production of small quantities of polymeric materials and mainly (70–80%) recovered pyridones. It would appear reasonable that if the internal addition mechanism were operating both 1 and 2 would have reacted in an analogous fashion to produce oxazolopyridinium salts. Lastly irradiation of the hydroxypyridinium salts 6 and 7, prepared from the parent pyridones, does not lead to production of either the pyridonyl alcohols or cyclized pyridinium salts.

In light of this, operation of an alternate mechanism involving reversible electrocyclic closure from the singlet excited 1-vinyl-2-pyridones to generate the highly stabilized azomethine ylids 8 appear likely. Capture of 8 by added perchloric acid would lead to the observed oxazolopyridinium perchlorates. Moreover, this mechanism accounts for alcohol formation from photolyses conducted in the absence of added acid. Under these conditions, the initially formed pyridinium hydroxides 9 and 10 ($X=OH^-$) should undergo nucleophilic aromatic substitution by hydroxide ion at C-2 of the pyridine ring when the concentration of the nucleophile is increased. Evidence to support the existance of the pyridinium hydroxides in the photolysate and their conversion to the pyridonyl alcohols has been presented above. Experimental observations, summarized in Figures 1 and 2, indicate that the photohydration reaction efficiency ($3\rightarrow 11$) varies directly with water concentration (in THF-water mixtures) and the efficiency of perchlorate salt formation ($3\rightarrow 9$)

increases as $[H_3O^+]$ increases. This behavior is consistent with a mechanism involving the intermediacy of the short-lived ylid, since as concentrations of the Bronsted acids H_2O and H_3O^+ increase, trapping of the ylid becomes more competitive with reversion to starting pyridone.

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References

(1) A preliminary report of this work has been presented at the 173rd National ACS Meeting, ORGN 107, New Orleans, 1977.

(2) E. C. Taylor and R. O. Kahn, *J. Amer. Chem. Soc.*, **85**, 776 (1963); L. A. Paquette and G. Slomp, *ibid.*, **85**, 765 (1963).

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

(5) C. Kashima, M. Yamamoto, Y. Sato and N. Sugiyama, *Bull. Chem. Soc., Jap.*, **42**, 3596 (1969); N. Ishibe and J. Masui, *J. Amer. Chem. Soc.*, **96**, 1152 (1974).

(6) All new compounds gave satisfactory spectroscopic data and elemental compositions. Complete synthetic details will be given in our full paper on the subject.

(7) In the case of irradiations of the propenylpyridone **2** cis-trans isomerization is also observed.

(8) Uv maximum for **5** and **6** in aqueous solution occur at 305 nm and 303 nm, respectively.

(9) (a) Energy transfer from the triplet excited state of xanthone to the pyridones **1** and **2** was documented by the observation that **1** quenches the familiar[9b] xanthone triplet photoreduction; (b) A. Schonberg and A. Mustafa, *J. Chem. Soc.*, 67, (1944).

(10) Dark controls performed using a variety of conditions failed to produce detectable quantities of the pyridonyl alcohols or oxazolopyridinium salts.

(11) *Eg*, for **8** ir absence of carbonyl; H-nmr, characteristic pyridinium salt aromatic resonances at δ 8.1(m, 2H, H-3 and H-5), 9.10 (t, 1H, H-4), 9.50 (d, 1H, H-6) and equivalent methyls at δ 2.50; uv (H_2O) 288 nm.

(12) W. M. Horspool and P. L. Pauson, *Chem. Commun.*, 195 (1967); G. Frater and H. Schmid, *Helv. Chem. Acta.*, **50**, 255 (1967).

(13) The pKa of 1-methyl-2-hydroxypyridinium salts are *ca*. 0.3 in water (A. Albert, *Heterocyclic Chemistry*, Athlon Press, London, 1968, p. 80). This is confirmed by uv.

(14) (a) This reaction mode is analogous to those followed by excited sates of isoelectronic divinylamines;[14b] (b) O. L. Chapman, G. L. Eian, A. Bloom and J. Clardy, *J. Amer. Chem. Soc.*, **93**, 2918 (1971).

(15) (a) A process like this might be responsible for the observed[15b] conversion of α-acylamino-β-thioalkylacrylamides to amidoyloxazoles which could proceed through the oxazolo ylids; (b) C. J. Veal and D. W. Young, *Tetrahedron Lett.*, 2985 (1976).

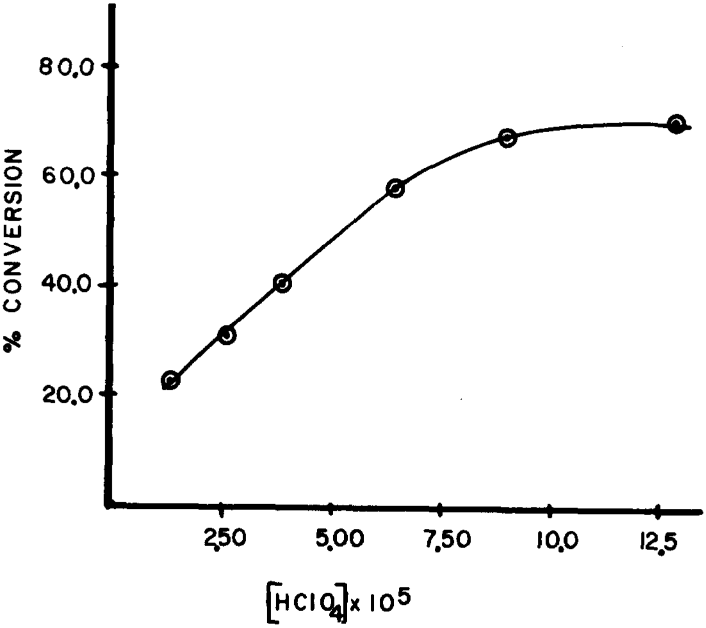

Figure 1. The effect of $HClO_4$ concentration on the efficiency of the photocyclization reaction of vinylpyridone **3** leading to oxazolopyridinium salt **9**. Simultaneous irradiations were conducted on aqueous solutions of **3** using pyrex filtered light. Analyses of crude photolysates were by glc in which the perchlorate salt is assayed in terms of methallylpyridone **1**.

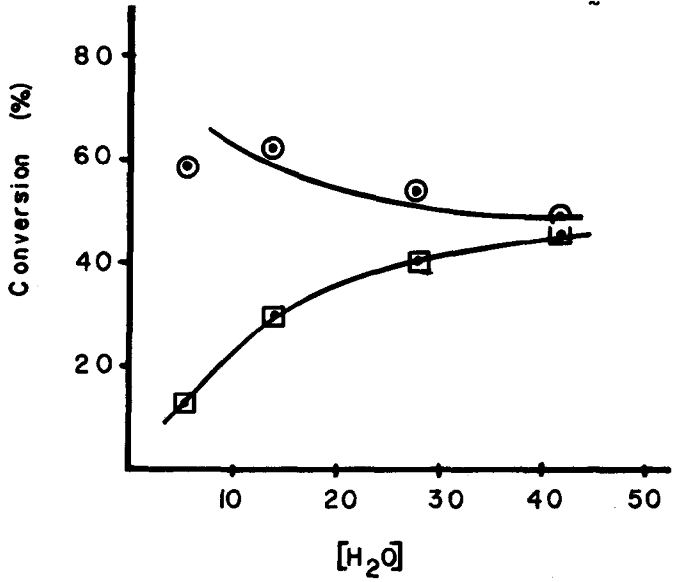

Figure 2. The effect of H_2O concentration on the efficiency of the photohydration reaction of vinylpyridone **3** leading to the pyridonylethanol **11**. Simultaneous irradiations were conducted on aqueous THF solutions of **3** using pyrex filtered light. Analyses of the crude photolysates for pyridonylethanol **11** (⊡) and unreacted vinylpyridone **3** (⊙), were by glc. Plotted are percent conversion to **11** and percent disappearance of **3** vs. [H_2O].