

nmr triplet (1 H) τ 4.6 (vinylic H), multiplet (4 H) 6.05 ($-\text{OCH}_2\text{CH}_2\text{O}$), singlet (9 H) 6.67 (3-OCH) was obtained. This material remained oily but it was obtained completely pure by preparative tlc since its R_f value was quite different from the R_f 's of **6** and the isomer. Reduction of compound **8** by LiAlH_4 in dioxane and careful purification of the product by preparative tlc yielded the racemic compound **9**, which was indistinguishable from the corresponding optically active derivative by tlc in several systems and ir (CCl_4 and KBr), mass, and nmr spectroscopy.

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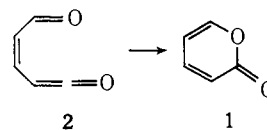
Laser Ultraviolet Irradiation of α -Pyrone. An Extremely Rapid Isomerization of a Transient Ketene

Sir:

Kinetic data of thermal, intramolecular cyclizations of hexatrienes and their heteroanalogs have been reported in a few, diverse systems.¹⁻⁵ One point that has been established is the effect of replacing a terminal olefinic double bond with a carbonyl, which leads to a dramatic increase in the rate of cyclization.³⁻⁷ Chapman's brilliant investigations on the role of ketenes in organic photochemistry have provided data from which the reactivity of a ketene moiety can be gauged.^{8,9} A kinetic study of a diene-ketene cyclization has been reported by Hobson.¹¹

The communication deals with the kinetics of ring closure of the transient species from the irradiation

of α -pyrone (**1**), which possesses both ketene and aldehydic functionality (**2**). Krantz,¹² Chapman,¹³ and



Shirk¹⁴ have previously reported the formation of a mixture of conformers of **2** as a primary photochemical reaction of matrix-isolated **1**. Although thermal reversion of the aldehyde-ketene (**2**) to starting material is not detected at cryogenic temperatures,¹²⁻¹⁵ the reaction is too fast to be measured when **2** is generated using a conventional flash photolysis system at normal temperatures.¹³ However, in nanosecond laser experiments using the fourth harmonic (265 nm) of the output of a Q-switched Nd glass laser (duration at half-maximum 30 nsec) as the excitation source,^{16,17} we have been able to study the transient absorption of **2** and the kinetics of the cyclization of **2** to **1**.

Irradiation of solutions of α -pyrone in cyclohexane (OD = 1.0-2.0 at 265 nm) gave good first-order curves (independent of the laser energy) for reversion of the transient spectrum to the initial absorption condition.¹⁸ These rates also were independent of concentration. The same results were obtained using either thoroughly degassed or air-saturated solutions.

Measurements at several temperatures between 26 and 48° gave $E_a = 9.4$ kcal/mol and $\log A = 12.4$ sec⁻¹ for the isomerization. The lifetimes ($\tau = 1/k$) at 26.5, 37, and 45.7° were 2.4, 1.37, and 0.92 μsec , respectively. The frequency factor of this internal isomerization indicates a cyclic transition state configuration which agrees with the most widely accepted mechanism for this reaction.^{10,11} The low value of the activation energy qualifies this ring closure as one of the fastest reactions of its type.

Table I includes relevant data for cyclizations to six-member rings. We emphasize the enormous rate enhancement due to the presence of a terminal carbonyl and/or ketene moiety in the acyclic form. Marvell^{3a} has discussed the rate enhancement due to a carbonyl but this effect has not been the subject of a theoretical analysis.

Our studies of the irradiation of cyclohexane solutions of **1** with added methanol indicate reaction rates very close to a diffusion controlled rate and the lifetime of excited α -pyrone.¹⁹ These results are consistent with the notion that an excited state of α -pyrone is

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(9) The enhanced reactivity of ketene in cycloaddition reactions has been recognized and explored experimentally^{10a} and in theoretical studies.^{10b}

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(18) Kinetics were monitored at 320 nm, since a preliminary investigation of the transient spectrum indicated that **1** showed its strongest absorption in the region 315-320 nm. Our matrix work with α -pyrone¹² has also shown new absorption above 300 nm upon irradiation of **1** in argon or nitrogen.

(19) It is possible to observe quenching of what probably is an excited state of **1**, under conditions in which the lifetime of transient aldoketene is essentially unaffected. This result is complicated by the production of a residual absorption in the methanol-doped solutions.

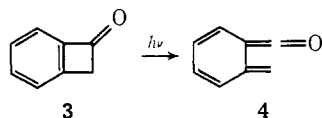
Table I. Activation Energy for Cyclization of Some *cis*-Hexatrienes and Their Analogs to Six-Member Rings

System	E_a , kcal/mol
	29.9 ^a
	9.4 ^b
	20
	~14.2 ^{c,d}

^a Reference 1a. ^b This work. ^c Reference 3. ^d See Schiess, *et al.*, in ref 4 for similar systems. ^e Estimated from data in ref 8 assuming $\log A = 12$. ^f See also Hobson in ref 11.

trapped by methanol, as hypothesized by Chapman based on product analyses in pyrone systems.²⁰

By contrast with the extraordinarily rapid rate of closure of **2**, we note here that the ketene **4** (λ_{\max} 397



nm, $\nu_{C=O}^{Ar} = 2120 \text{ cm}^{-1}$),²¹ derived from irradiation of benzocyclobutenone, does not show any decay to starting material during the time scale of our flash experiment.²³ Kinetic spectroscopic studies of these and other ketenes are continuing, which we view as a natural complement to our matrix studies of transients in organic photochemistry.

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(21) The ultraviolet spectrum of **4** was first obtained by irradiating solutions of **3** (0.01 M) in a 1:1 ether-methylcyclohexane glass at 77°K.²² A preliminary investigation of the spectrum of the primary product of irradiation (laser excitation wavelength at 265 or 353 nm) of **3** in cyclohexane yielded a similar spectrum which we attribute to **4**.

(22) J. Frank, A. Krantz, and S. L. Murov, unpublished results.

(23) The lifetime of **4** must therefore be greater than 500 μsec at 26°.

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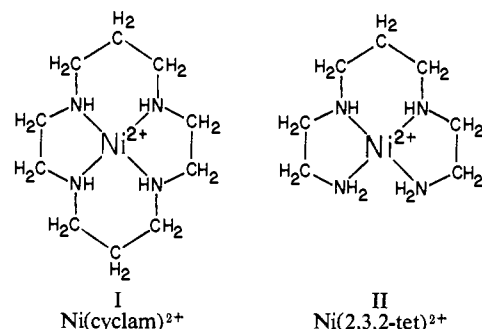
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Effect of Ligand Solvation on the Stability of Metal Complexes in Solution. An Explanation of the Macrocylic Effect

Sir:

Some macrocyclic ligands in aqueous solution form more stable complexes with metal ions than open-chain ligands with the same donor groups. This has been

termed the *macrocylic effect*¹ or *multiple juxtapositional fixedness*² in order to distinguish it from the well-known chelate effect because there is an additional enhancement in stability beyond that expected from the gain in translational entropy when chelates replace coordinated solvent from metal ions. Thus, there is more than a 10⁶-fold increase in the stability constant of Ni^{II}(cyclam), I, compared to Ni^{II}(2,3,2-tet), II.



It is not reasonable to assign this large increase in stability to stronger Ni-N bonds in the cyclam complex. Although cyclam has more secondary amine donors than 2,3,2-tet, secondary amines, in general, form less stable Ni²⁺ complexes than primary amines. Furthermore, the difference in the ΔH° values for the formation of Ni(2,3,2-tet)²⁺ and Ni(en)₂²⁺ is small.³ Obviously the macrocyclic ring cannot force a better coordination geometry than that which the open-chain ligand is free to adopt. Neither ligand can be regarded as very restrictive as there is no evidence of unfavorable ring conformations or of an unusual nickel-nitrogen geometry in the crystal structure of Ni(cyclam)Cl₂.⁴

Some correlations have been made between bond strength and electronic absorption bands⁵ but both I and II have a λ_{\max} at 450 nm. Neither Ni(cyclam)²⁺ nor Ni(2,3,2-tet)²⁺ has appreciable steric hindrance that would prevent the coordination of axial water molecules. The Ni(cyclam)²⁺ complex exists primarily as the yellow square-planar complex in aqueous solution while Ni(2,3,2-tet)²⁺ exists as a mixture of the blue octahedral complex and the yellow square-planar complex.^{6,7} If a correction is made so that the stability constants are compared for only the square-planar complexes in each case then Ni(cyclam)²⁺ has a larger stability constant than [Ni(2,3,2-tet)(square planar)]²⁺ by a factor of 10⁶.⁸

On the other hand it might seem quite reasonable to assign the macrocylic effect to differences in configurational entropy because a greater loss in entropy would be expected in the reaction of the open-chain ligand to form its complex than in the reaction of the macrocyclic ligand to form its complex. If these were gas phase reactions there certainly would be less of a loss in entropy in the latter case.

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