In summary, (+)-3-methylpyrrolidin-2-one has been prepared. The compound shows a positive ellipticity band at 210–220 nm, which is red shifted upon going from water to solvents with lower polarity, which probably arises from an n → π* transition. The sign of this transition does not obey the simple quadrant rule postulated for amides by Litman and Schellman.[15] A second negative ellipticity band centered at 189–196 nm also red shifts with decreasing solvent polarity; it may be due to a π → π* transition despite its solvent dependence. The spectra of the compound cannot be resolved by only two Gaussian curves; however, the position of a third band at lower wavelength is not unique. Therefore, no conclusions can be drawn about the presence of transitions other than the n → π* and π → π*. The compound associates in *n*-hexane to produce an additional band at 202 nm which is lost upon dilution. The CD spectrum of (+)-3-methylpyrrolidin-2-one exhibits striking differences from that of 3-aminopyrrolidinone; however, it is difficult to determine if this is due solely to differences in charge and orientation of the amino group compared to the methyl group, or if the amino group has additional optical activity due to the presence of lone-pair electrons.

Acknowledgment. We thank Dr. Dragutin Fles for his interest in this project and his gracious gift of a sample of (+)-3-methylpyrrolidin-2-one and Professor Sherman Beychok for the use of his Du Pont curve resolver.

Photodimerization of Thymine and Uracil in Acetonitrile

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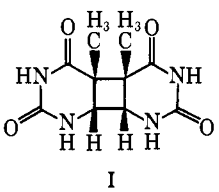
Abstract: Studies on the photodimerization of thymine and uracil in acetonitrile reveal the following facts. At low pyrimidine concentrations, the reaction occurs almost entirely from the triplet state. All four *cis*-fused cyclobutane dimers are formed. The very low quantum yields reflect primarily the existence of a metastable dimeric species, most of which dissociates into two ground-state pyrimidine molecules before proceeding on to stable dimer. Rates of radiationless decay of the triplet states are 2×10^5 sec^{-1}; rate constants for addition of triplet pyrimidine to ground-state pyrimidine are 6×10^8 M^{-1} sec^{-1} for thymine and 2×10^9 M^{-1} sec^{-1} for uracil; fractions of metastable dimers which yield stable dimers are 2% for thymine and 6% for uracil. This self-quenching of the triplet may be partially responsible for the low quantum yields of photodimerization in DNA.

Photodimerization of the pyrimidine bases thymine and uracil is of interest for two reasons: the reaction is responsible for the photodeactivation of the nucleic acids;[2,3] and cycloaddition of α,β-unsaturated carbonyl compounds is an important and confusing general class of photoreactions.

The nature of the excited states responsible for these photoreactions is of basic mechanistic interest. It is known that frozen aqueous solutions of thymine yield one major photodimer, the *cis–syn* head-to-head "ice-dimer" I.[4] The reaction proceeds in high quantum efficiency,[5] apparently from the singlet-excited state[6] *via* excimers.[7] The high stereoselectivity is due to precise stacking of the thymine molecules in frozen crystallites.[8] The thymine dimer obtained from irradiated DNA is I;[9] the uracil dimer from irradiated RNA also possesses a *cis–syn* head-to-head structure.[10] Here, too, the stereoselectivity must reflect the fixed relative configurations of the bases in the macromolecules. Since the thymine in DNA udergoes dimerization upon both direct and sensitized[11] irradiation, it is important to determine whether the product stereochemistry is affected by excited state multiplicity.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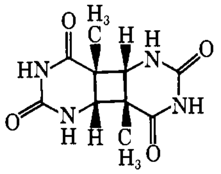
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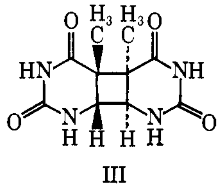
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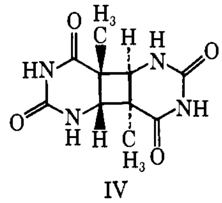
IV

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(1) (a) Alfred P. Sloan Fellow, 1968–1970; (b) National Institutes of Health Predoctoral Fellow, 1966–1969.

(2) R. Beukers and W. Berends, *Biochem. Biophys. Acta*, **41**, 550 (1960).

(3) R. B. Setlow and W. L. Carrier, *J. Mol. Biol.*, **17**, 237 (1966); R. B. Setlow, *Photochem. Photobiol.*, **7**, 643 (1968), and references cited in each.

(4) (a) D. L. Wulff and G. Fraenkel, *Biochem. Biophys. Acta*, **51**, 332 (1961); (b) T. Kunieda and B. Witkop, *J. Amer. Chem. Soc.*, **89**, 4232 (1967); (c) G. M. Blackburn and R. J. Davies, *ibid.*, **89**, 5941 (1967).

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(8) S. T. Wang, *Nature*, **190**, 690 (1961).

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(11) A. A. Lamola and T. Yamane, *Proc. Nat. Acad. Sci. U. S.*, **58**, 443 (1967).

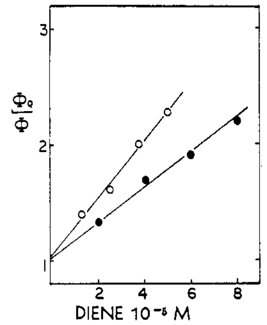

Figure 1. Representative Stern-Volmer plots for quenching of thymine photodimerization by 1,3-pentadiene: ○, $2.7 \times 10^{-4}\ M$; ●, $6.75 \times 10^{-4}\ M$.

Complete appreciation of the fascinating steric complexities of macromolecule chemistry requires an understanding of the behavior of isolated molecules. In solutions, the photodimerizations of thymine and uracil can be partially quenched by conjugated dienes.[12] This result implicates the intermediacy of triplet states. We have made a more thorough study of the solution photodimerization of the two bases. Our results, together with recent reports of other workers, demonstrate important kinetic differences between singlet- and triplet-state dimerizations.

Results

Triplet Lifetimes. Since the rate of addition of an excited molecule to a ground-state pyrimidine molecule must be first order in pyrimidine, the triplet lifetime should depend on pyrimidine concentration as described by eq 1, where k_i is the rate of unimolecular

$$1/\tau = k_i + k_a[\text{pyr}] \qquad (1)$$

radiationless decay of triplet pyrimidine and k_a is the rate constant for addition of triplet to ground-state pyrimidine. Triplet lifetimes were determined by Stern-Volmer quenching studies. Degassed acetonitrile solutions $2\text{-}10 \times 10^{-4}\ M$ in pyrimidine and containing various concentrations of *cis*-1,3-pentadiene were irradiated in parallel at 2750-2900 Å. Temperature was controlled at 25°. Relative quantum yields of pyrimidine disappearance were determined by uv analysis. Stern-Volmer plots (eq 2) were linear out to

$$\Phi_0/\Phi = 1 + k_q\tau[Q] \qquad (2)$$

large values of Φ_0/Φ. Therefore at these low concentrations the photodimerization of both bases occurs predominately from the triplet state. Very long irradiation of 0.007 M thymine solutions containing 0.01 M pentadiene revealed that 2.5% of the total (unquenched) dimerization is unquenchable and therefore presumably results from excited singlets. As much as 10% of comparable uracil dimerizations may arise from singlet states.[12]

Figure 1 displays representative Stern-Volmer plots. The slopes are tabulated in Table I and τ values are calculated on the assumption that k_q equals $1.1 \times 10^{10}\ M^{-1}\ \text{sec}^{-1}$ in acetonitrile.[13] The τ values are plotted according to eq 1 in Figure 2; the resulting values of k_i and k_a are contained in Table II.[13a]

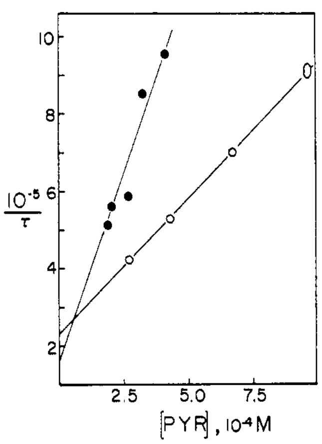

Figure 2. Plots of reciprocal triplet lifetimes *vs.* pyrimidine concentrations: ○, thymine; ●, uracil.

Quantum Yields. Since our experimental procedure provided polychromatic radiation, we employed the substrate pyrimidines themselves as actinometers. Degassed solutions $6.2 \times 10^{-4}\ M$ in thymine were irradiated in parallel with solutions containing $6.2 \times 10^{-4}\ M$ thymine and 0.10 M *cis*-1,3-pentadiene (enough to quench 99.99% of triplets). The same was done for $3.9 \times 10^{-4}\ M$ uracil solutions. Yields of pyrimidine disappearance were measured as usual by uv analysis.

Table I. Quenching of Thymine and Uracil Photodimerizations by 1,3-Pentadiene in Acetonitrile

[Pyrimidine], $10^{-4}\ M$[a]	$k_q\tau$, M^{-1} [b]	$10^5/\tau$, sec^{-1} [c]
	Thymine	
2.70	26,000	4.2
4.33	20,800	5.3
6.75	15,700	7.0
9.68	12,200	9.1
	Uracil	
1.89	21,300	5.2
1.96	19,600	5.6
2.70	18,600	5.9
3.19	12,900	8.5
4.08	11,500	9.6

[a] Average concentration during irradiation; total conversions 15-20%. [b] Slopes of Stern-Volmer plots reproducible to ±5%. [c] k_q assumed equal to $1.1 \times 10^{-10}\ M^{-1}\ \text{sec}^{-1}$, P. J. Wagner and I. Kochevar, *J. Amer. Chem. Soc.*, **90**, 2232 (1968).

Table II. Kinetic Data for Photodimerization of Thymine and Uracil

Quantity	Thymine	Uracil
k_i, 10^5 sec^{-1} [a]	2.2 ± 0.14	1.6 ± 0.50
k_a, 10^9 M^{-1} sec^{-1} [a]	0.70 ± 0.02	2.0 ± 0.17
Φ_{DIM}	0.0025[b]	0.019[c]
Φ_{iso}[d]	0.18	0.40
ϕ_{P}	0.02	0.06

[a] Least-squares analysis of plots in Figure 2, with standard deviations indicated. [b] $6.2 \times 10^{-4}\ M$. [c] $3.9 \times 10^{-4}\ M$. [d] From ref 12.

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(12) A. A. Lamola and J. P. Mittal, *Science*, **154**, 1560 (1966).

(13) See Table I, footnote *c*.

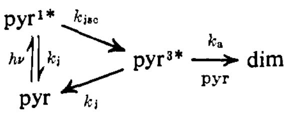
(13a) Note Added in Proof. E. Hayon, *J. Amer. Chem. Soc.*, **91**, 5397 (1969), has observed the decay of triplet uracil by flash spectroscopy and has reported a k_i value in acetonitrile only half as large as our value. Of course the exact value is probably determined largely by impurity quenching and may vary from lab to lab.

Yields of *cis* → *trans* isomerization of the diene were measured by glpc analysis. Consequently, quantum yields for dimerization could be compared directly to quantum yields for intersystem crossing.[14] The latter values have been measured at 2537 Å.[12] If the same values hold for 2750–2900 Å irradiation, the quantum yields listed in Table II for dimerization result. The value for thymine is identical with that already reported[12] for 2537 Å radiation and the uracil value is ~80% that reported for a 7×10^{-4} *M* solution.[12] Apart from the actual $\Phi_{\rm isc}$ values, our results demonstrate that, at the pyrimidine concentrations employed, only 1.4% of thymine triplets and 4.9% of uracil triplets actually yield stable dimers. In addition, these sensitization experiments show that the quenching of dimerization involves triplet energy transfer.

Product Stereochemistry. A degassed solution 0.0005 *M* in ^{14}C-labeled thymine was irradiated as usual to 15% conversion. The solvent was stripped off, and the solid residue was taken up in water, chromatographed on paper, and analyzed on a strip scanner. The resolution was only fair, but it was obvious that all four dimers were present, in agreement with other workers' recent results.[15–17] In particular, the "ice-dimer" I is the major product; the two *syn* dimers I and II account for 60–70% of the total, somewhat less than observed for dimethylthymine in acetonitrile[17] and about the same observed for thymine in water.[15] The acetone-sensitized dimerization of thymine proceeds five times faster and yields the same mixture of dimers, in agreement with the quenching conclusion that the direct reaction proceeds *via* triplet states. A product analysis of solution-phase uracil photodimers[18] had appeared before this work was performed and demonstrated that all four possible *cis*-fused dimers are formed.

Discussion

Revertibility. If dimerization were concerted or irreversible, the following commonly assumed mechanistic scheme[19] would adequately describe the whole pro-



cess. The dimerization quantum yield would then be described by eq 3 and 4.

$$\Phi_{\rm DIM} = {}^1/_2\,\Phi_{\rm -pyr} = \left(\frac{k_{\rm isc}}{k_{\rm j} + k_{\rm isc}}\right)\left(\frac{k_{\rm a}[{\rm pyr}]}{k_{\rm i} + k_{\rm a}[{\rm pyr}]}\right) \quad (3)$$

$$\Phi_{\rm DIM} = \Phi_{\rm isc}\,\Phi_{\rm A} \quad (4)$$

$$\Phi_{\rm A} = k_{\rm a}[{\rm pyr}]\tau \quad (5)$$

The triplet-state dimerization of uracil is roughly an order of magnitude more efficient than that of thymine. Our findings unravel some of the causes. In particular, the rates of the primary triplet-state photoprocesses have very little to do with quantum efficiencies. The effective rates of radiationless decay of both triplets are the same; more importantly, they are much smaller than the rate constants for reaction with ground states. The $k_{\rm a}$ value for uracil is three times that for thymine, the difference probably reflecting some steric hindrance imposed by the methyl group of thymine. However, at the pyrimidine concentrations at which we estimated quantum yields, $\Phi_{\rm A}$ of eq 5 equals 0.66 for thymine and 0.83 for uracil. Even with the twofold greater intersystem crossing yield for uracil, eq 4 would predict dimerization quantum yields of 0.12 and 0.33, respectively, for thymine and uracil. Not only are these values much higher than the observed values, they do not adequately reflect the real difference between the two bases. Obviously a further source of inefficiency is missing from the simple mechanistic scheme.

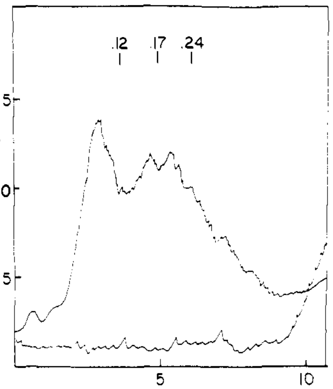
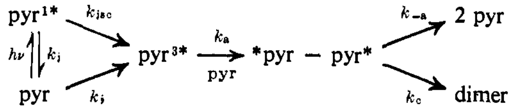


Figure 3. Radiochromatograph of thymine dimers. Solvent front moved 34 cm, thymine 16.5 cm. Notations at top indicate R_f values reported for dimers. Bottom trace is that of unirradiated blank and of irradiated sample containing 0.01 *M* pentadiene.

Including our preliminary communication of this work,[20] there are now several examples of triplet-state cycloaddition reactions in which a major source of inefficiency occurs after the excited state has reacted.[21] It would appear that in general the photodimerization mechanistic scheme must include a metastable dimeric species which partially collapses to stable ground-state dimer and also partially reverts to two ground-state pyrimidine molecules. The probability that the metastable intermediate will yield stable product is expressed by $\phi_{\rm P}$. Table II lists the $\phi_{\rm P}$ values for the two bases: that for uracil is three times higher than that for thymine.



$$\Phi_{\rm DIM} = \Phi_{\rm isc}\Phi_{\rm A}\phi_{\rm P} \quad (6)$$

$$\phi_{\rm P} = \frac{k_{\rm c}}{k_{\rm -a} + k_{\rm c}} \quad (7)$$

In summary, the greater photodimerization efficiency of uracil relative to thymine results primarily because singlet uracil undergoes intersystem crossing more effi-

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[14] A. A. Lamola and G. S. Hammond, *J. Chem. Phys.*, **43**, 2129 (1965).

[15] C. L. Greenstock and H. E. Johns, *Biochem. Biophys. Res. Commun.*, 30, 21 (1968).

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[18] C. H. Krauch, *Angew. Chem. Intern. Ed. Engl.*, **6**, 956 (1967).

[19] E. Sztumpf-Kulikowska, D. Shugar, and J. W. Boag, *Photochem. Photobiol.*, **6**, 41 (1967); C. L. Greenstock, I. H. Brown, J. W. Hunt, and H. E. Johns, *Biochem. Biophys. Res. Commun.*, **27**, 431 (1967).

[20] P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **90**, 6530 (1968).

[21] (a) S. Toki and H. Sakurai, *Bull. Chem. Soc. Jap.*, **40**, 2885 (1967); (b) P. de Mayo, A. A. Nicholson, and M. Tchir, *Can. J. Chem.*, **47**, 711 (1969); (c) P. J. Wagner and D. J. Bucheck, *ibid.*, **47**, 714 (1969).

ciently than singlet thymine and because a smaller fraction of the metastable uracil adducts fall apart. The quantum yields depend only slightly on the reaction rates of the excited triplets.

At high pyrimidine concentrations, some dimerization from excited singlet states apparently competes with intersystem crossing. Under these circumstances, a significant fraction of the initially formed excited singlet states encounter ground-state pyrimidine molecules before they can cross to triplets. This situation is analogous to that necessarily present in polynucleotides and in nucleic acids. Consequently, eq 8 is a more complete expression for the quantum yield of dimerization, where f is the probability that an encounter between pyr^{1*} and pyr_0 leads to stable dimer and F is the fraction of pyr^{1*} molecules which encounter pyr_0 molecules. Values of f are presumably close to unity.[5–7] The value of F may be linearly proportional to [pyr] if $k_{\mathrm{isc}} + k_{\mathrm{j}}$ are slower than diffusion, or it may represent the statistical chance that two pyr molecules are next to each other if $k_{\mathrm{isc}} + k_{\mathrm{j}}$ are faster than diffusion, or in macromolecules and other *rigid* systems.

$$\Phi_{\mathrm{DIM}} = fF + (1 - F)\Phi_{\mathrm{isc}}\Phi_{\mathrm{A}}\phi_{\mathrm{P}} \tag{8}$$

Product Stereochemistry. Since all four possible *cis*-fused cyclobutanes are formed in triplet dimerizations of the pyrimidines, there must be four separate k_{a} values and four separate ϕ_{P} values, one for each dimer I–IV. Unfortunately, the over-all values are the only ones we can measure, since there are three more unknowns than there are independent measurable quantities.

$$\mathrm{pyr}^{3*} + \mathrm{pyr}\left\{\begin{array}{l} \xrightarrow{k_{\mathrm{a1}}} (\mathrm{pyr{-}pyr})_{\mathrm{I}}^{*} \xrightarrow{\phi_{\mathrm{I}}} \mathrm{I} \\ \xrightarrow{k_{\mathrm{a2}}} (\mathrm{pyr{-}pyr})_{\mathrm{II}}^{*} \xrightarrow{\phi_{\mathrm{II}}} \mathrm{II} \\ \xrightarrow{k_{\mathrm{a3}}} (\mathrm{pyr{-}pyr})_{\mathrm{III}}^{*} \xrightarrow{\phi_{\mathrm{III}}} \mathrm{III} \\ \xrightarrow{k_{\mathrm{a4}}} (\mathrm{pyr{-}pyr})_{\mathrm{IV}}^{*} \xrightarrow{\phi_{\mathrm{IV}}} \mathrm{IV} \end{array}\right.$$

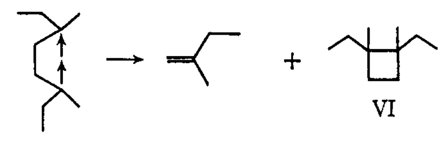
$$k_{\mathrm{a}} = k_{\mathrm{a1}} + k_{\mathrm{a2}} + k_{\mathrm{a3}} + k_{\mathrm{a3}} \tag{9}$$

$$k_{\mathrm{a}}\phi_{\mathrm{P}} = k_{\mathrm{a1}}\phi_{\mathrm{I}} + k_{\mathrm{a2}}\phi_{\mathrm{II}} + k_{\mathrm{a3}}\phi_{\mathrm{III}} + k_{\mathrm{a4}}\phi_{\mathrm{IV}} \tag{10}$$
$$\approx 1.5\,(k_{\mathrm{a1}}\phi_{\mathrm{I}} + k_{\mathrm{a2}}\phi_{\mathrm{II}})$$

$$\frac{\mathrm{I}}{\mathrm{I} + \mathrm{II} + \mathrm{III} + \mathrm{IV}} = \frac{k_{\mathrm{a1}}\,\phi_{\mathrm{I}}}{k_{\mathrm{a}}\phi_{\mathrm{P}}} \tag{11}$$

The predominance of dimers I and II may be due to k_{a1} and k_{a2} exceeding k_{a3} and k_{a4} or to ϕ_{I} and ϕ_{II} exceeding ϕ_{III} and ϕ_{IV}. The latter possibility does not seem probable, since steric effects would be expected to make ϕ_{I} and ϕ_{II} smaller than ϕ_{III} and ϕ_{IV}. In any event, since I is the major triplet dimer, the over-all ϕ_{P} must be reasonably close to ϕ_{I}. The value of ϕ_{I} is of major interest since I is the major dimer in DNA.

Structure of Metastable Adduct. There is considerable evidence that 1,4-biradicals intervene in triplet-state cycloaddition reactions.[22] We have already pointed out that cleavage of such species into two olefins is always a major reaction.[20–22] Bartlett and Porter[23] have shown that the bistertiary biradical V undergoes only 20% coupling and some 76% cleavage. One would expect a biradical such as VII to undergo even more cleavage in competition with coupling both because of the added steric strain in I relative to VI and because of the added conjugation in thymine relative to 2-methyl-1-butene. Consequently it is quite reasonable to ascribe most of the low value of ϕ_{P} to cleavage of intermediate biradicals. The probability of coupling in the bistertiary and secondary-tertiary biradicals from thymine would also be expected to be lower than in bis-secondary biradicals from uracil, since secondary radicals generally couple more efficiently than do tertiary radicals.[24]



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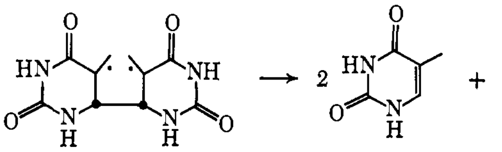

VII

It is also possible that an excimer prededes a biradical. The large values of k_{a}, which are 2–3 orders of magnitude greater than expected for a simple radical-like addition to an olefin, and the predominance of *syn* dimers are the best evidence that excimers intervene. Since triplet excimers probably are not very stable with respect to dissociation into two ground-state molecules,[25] such decay in competition with collapse to a biradical may also lower ϕ_{P}. If, in fact, both excimers and biradicals contribute to inefficient dimerization, each ϕ on the right side of eq 10 is the product of two separate probabilities; evaluation of individual kinetic parameters will then require unusual experimental elegance.

Photodimerization in Nucleic Acids. Our results indicate that even if thymine triplets were formed with 100% efficiency and even if every thymine had a thymine ground state within striking range, the maximum dimerzation quantum yield would be only 2%. In contrast, dimerization through singlet excimers is almost 100% efficient.[5,7] It is a remarkable coincidence that the dimerization quantum yields for $\mathrm{T_PT}$[26] and for adjacent thymines in DNA[27] are both reported to be 1–2% also. Tempting though it is to thus equate the low quantum efficiency in DNA with triplet intermediates, such an interpretation would require almost complete crossover of singlet excitation to triplet excitation in the macromolecules.

Photocycloaddition. Spectroscopic studies have shown that the lowest triplet levels of the pyrimidines are π,π^* in nature.[28] The much studied photocycloaddition reactions of α,β-unsaturated ketones are especially intriguing because of the near degeneracy of their n,π^* and π,π^* triplets. The photoreactions of the

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[22] See P. J. Wagner and D. J. Bucheck, *J. Amer. Chem. Soc.*, **91**, 5090 (1969), and references therein.

[23] P. D. Bartlett and N. A. Porter, *ibid.*, **90**, 5317 (1968).

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[25] A. K. Chandra and E. C. Lim, *J. Chem. Phys.*, **49**, 5066 (1968).

[26] H. E. Johns, M. L. Pearson, J. C. LeBlanc, and C. W. Helleiner, *J. Mol. Biol.*, **9**, 503 (1964).

[27] D. Wulff, *Biophys. J.*, **3**, 355 (1963).

[28] A. A. Lamola, *Photochem. Photobiol.*, **7**, 619 (1968).

pyrimidines thus are good models for what might be expected of π,π^* triplets. Since we have measured k_a values for photodimerizations of cycloalkenones very similar in value to those for the pyrimidines, we have concluded that the ketones also undergo cycloaddition at their C–C double bonds from their π,π^* triplet states.[22]

Experimental Section

Chemicals. Reagent grade acetonitrile was dried and purified[29] so that it was completely transparent above 2000 Å. Thymine and uracil were commercial materials that were sublimed after recrystallization from water. 1,3-Pentadiene was obtained from Chemical Samples Co. and was distilled before use. Methyl-^{14}C-labeled thymine (3 μCi/mmol) was obtained from New England Nuclear Corp.

Procedures. Ultraviolet analyses were performed on a Gilford Model 200 spectrophotometer with a linear absorbance converter. Glpc analysis of *cis*-to-*trans* pentadiene isomerization was performed on an Aerograph Model 600 Hy-Fi with a 25 ft × $^1/_8$ in. column packed with 25% 1,2,3-tris(β-cyanoethoxy)propane. A Packard Model 7201 strip scanner was used to analyze the radioactive thymine dimers.

After samples had been prepared, 3 ml of each was syringed into two separate 13 × 100-mm Pyrex tubes. The tubes were outgassed to 10^{-3} mm in three or four freeze–thaw cycles and then sealed *in vacuo*. All the tubes in a given run were irradiated in parallel for the same length of time on a rotating turntable apparatus held in a constant temperature bath such that the same intensity impinged on each sample. At the center of the turntable was a 450-W Hanovia medium-pressure mercury arc in a quartz immersion well. A Vycor sleeve and the 1-mm walls of the Pyrex tubes were the only filters. This set-up allowed the 2753-, 2804-, and 2894-Å lines of the mercury arc to be absorbed to varying degrees by the pyrimidines. Consequently, only the pyrimidines, and not the dimers, absorbed radiation. After several hours radiation, the concentration of thymine or uracil remaining was determined by uv analysis at 2700 Å, where neither the dimers nor pentadiene absorb significantly and where absorbance of both pyrimidines follows Beer law. It was assumed that, in the absence of water, only dimerization removed the pyrimidines. Percentage conversions in the samples with no quencher were 15–20%; those in samples with maximum quencher concentrations were 5–10%, since it is difficult to measure smaller differences accurately.

Since most of the filtering was provided by the sample tube walls, their uniformity was crucial. In fact, one batch of Corning tubes gave dreadful results. Most batches, however, gave excellent results: duplicate tubes gave precision of ±2%; Stern–Volmer slopes were reproducible to ±5%. Stern–Volmer slopes and the slopes and intercepts of Figure 2 were determined by least-squares analysis.

Quantum yield estimates were made by irradiating in parallel for the same length of time three tubes containing only pyrimidine and three tubes containing the same concentration of pyrimidine and 0.10 *M cis*-1,3-pentadiene. The amount of dimerization in the unquenched samples was measured as usual by uv; the sensitized formation of *trans* diene was measured by glpc analysis. Division of the per cent conversion of *cis*-to-*trans* (1–2%) by 0.56[14] yields a measure of how many pyrimidine triplets were formed, since 0.1 *M* diene is sufficient to quench all of them. Comparison of the amount of dimerization with the number of triplets thus gives a direct measure of the ratio of quantum yields for dimerization and for intersystem crossing.

A degassed 5 × 10^{-4} *M* solution of ^{14}C-labeled thymine in acetonitrile was irradiated to 15% conversion. A similar sample in acetone was irradiated in the same time to 76% conversion. The solvents were stripped off, and the solid residues were taken up in a few drops of water and chromatographed on Whatman No. 1 Paper with a 86:14 v/v mixture of 1-butanol and water. Analysis on a strip scanner gave almost identical traces for the direct and sensitized runs. The indicated R_f values are those reported by Weinblum and Johns: 0.12, I; 0.17, II; 0.24, III + IV; and 0.49, thymine.[30]

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