KINETICS OF PHOTODIMERIZATION OF CERTAIN CYCLIC ENONES

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This is to certify that the

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KINETICS OF PHOTODIMERIZATION
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David Joseph Bucheck

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ABSTRACT

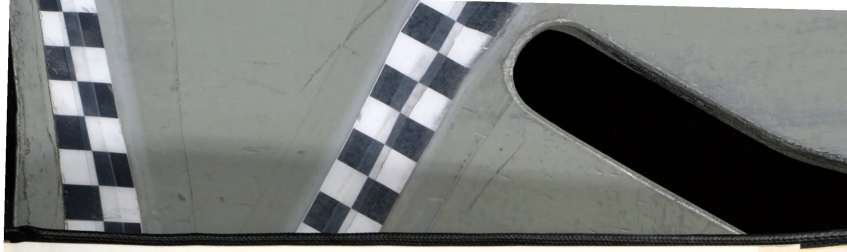
KINETICS OF PHOTODIMERIZATION
OF CERTAIN CYCLIC ENONES

By

David Joseph Bucheck

The kinetics of ultraviolet light induced dimerization of four alicyclic α,β-unsaturated ketones were studied in this work. The enones thymine, uracil, cyclopent-2-enone, and cyclohex-2-enone undergo a cycloaddition reaction to form known cyclobutane adducts in each case. The dimerization of the pyrimidines, thymine and uracil, is known to be the primary cause of ultraviolet radiation damage to DNA and RNA in cells (1). In dilute acetonitrile solution the reaction of the pyrimidines is solely from the excited triplet state. The kinetics were studied by Stern-Volmer quenching analysis and triplet counting. From these data quantum yields and rate constants of the primary processes were derived.

The simple enones, cyclopent-2-enone and cyclohex-2-enone, react in a similar manner, but from the second excited triplet (T_2). Their kinetics were studied by Stern-Volmer quenching analysis and determination of quantum yields of dimerization and intersystem crossing. Again the rate constants were derived.



David Joseph Bucheck

The rates of addition, k_a, of the excited enone to the ground-state enone were in all four cases about $10^8 M^{-1}$ sec. The unimolecular decay rate, k_d, of the triplet was low for the pyrimidines at 10^5 sec, but three orders of magnitude higher for the simple enones. The implications of the values themselves are discussed fully.

Use of the derived rate constants and quantum yields and the rate law for the generally postulated mechanism (2) indicates that there is a further source of inefficiency that is not accounted for in the mechanism. The inefficiency is caused by reversible formation of an intermediate photoadduct that can react further to form stable dimer or decay back to two ground-state molecules. The intermediate may be a complex or a triplet excimer that goes on to dimer itself or collapses to a 1,4-biradical. This adduct may be formed with nearly identical rates from either π, π^* or n, π^* configuration of the excited enone.

The results indicate that only 2% of the original metastable thymine dimers formed eventually yield stable ground state dimers. The corresponding values are 6% for uracil, 36% for cyclopent-2-enone, and 74% for cyclohex-2-enone.

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2. P. deMayo, J-P. Pete, and M. Tchir, Can. J. Chem., 46, 2535 (1968).

KINETICS OF PHOTODIMERIZATION OF CERTAIN CYCLIC ENONES

By

David J Rogers Bacheck

A THESIS

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This thesis is dedicated to my parents who helped and encouraged me to continue my studies, and to my wife, Ann, who helped me to conclude them.

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It is hard for me to express fully my deep appreciation to Professor Peter J. Wagner. He rescued me in troubled times, encouraged me to the completion of this work and most of all taught me some of his knowledge.

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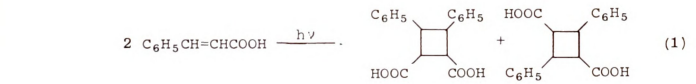
I. INTRODUCTION

The light induced dimerization of α,β-unsaturated carbonyl compounds to form cyclobutane rings is a very old reaction in organic chemistry. It was first reported over a half century ago in the photoreaction of cinnamic acid to form truxinic and truxillic acids (1) (Equation 1).

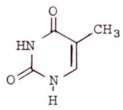


(1)

From this time until the middle fifties, many other examples of this reaction have been investigated (2). This earlier era of photochemistry was accomplished mainly by an Edisonian approach using sunlight as the energy source and yielded few if any mechanistic implications (although very elegant structural determinations of the "photoproducts" were done in this period). In the last decade, however, methods have become available which, while not giving complete knowledge, enable us to derive insights into the mechanisms and pathways of excited state chemistry.

In this thesis, a study of the kinetics of dimerization of certain alicyclic, α,β-unsaturated ketones will enable us to propose a mechanism for this reaction. The kinetic measurements made (such as intersystem-crossing efficiencies

and triplet lifetimes for these compounds) add to the previously published work and allow comparisons between structures and photochemical behavior to be drawn. Four compounds have been studied in this work: thymine (1), uracil (2), cyclopent-2-enone (3), and cyclohex-2-enone (4).



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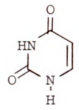


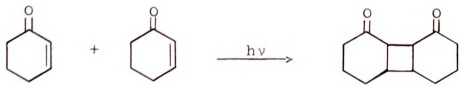
2

3

4

Because of both their impact on different areas of chemistry and the different methods used to study them, the pyrimidines (1 and 2) and the simple enones (3 and 4) will be treated separately.

When the enone chromophore is excited by incident ultraviolet light, three reactions may result. The dimerization reaction (Equation 2) occurs when the excited enone adds to a ground state enone and is the one studied in this work. The cycloaddition reaction (Equation 3) is the addition of the excited enone to a simple olefin; it may be considered the general reaction of which dimerization is only the special case.



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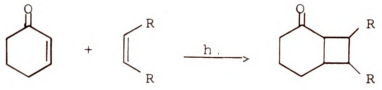

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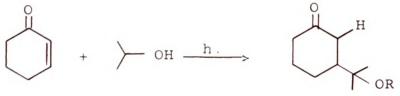
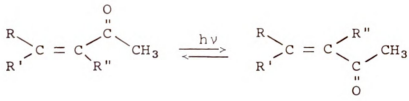


(4)

The cycloaddition reaction is very useful for mechanistic studies (3) and has also been the basis for the synthesis of many natural products containing new ring systems such as caryophyllene (4), bourbonene (5), atisine (6), stipitotanoic acid (7), ;-himachalene (8), and others. The reduction reaction (Equation 4) can occur under certain circumstances with the addition of alcohol or water to the unsaturated portion of the enone (9). These side reactions are all unimportant when studying dimerization since the adding molecule must be present in solution. The reverse is not true, of course, for when studying olefin or alcohol addition, the concentration of enone must be kept low in order to minimize dimerization.

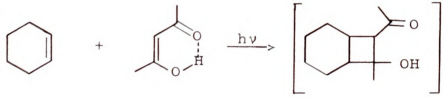
It should be noted that a five or six-membered cyclic enone is necessary for the dimerization to take place.

Acyclic enones undergo a photoinduced cis-trans isomerization (Equation 5). Apparently intermolecular cycloaddition cannot compete with this reversible intramolecular process (10a).

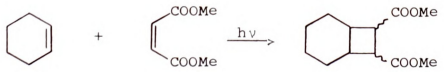


(5)

The only known cases of intermolecular cycloaddition from acyclic enones are with acetoacetone (11), dimethylmaleate (12), and chalcone (12a). The former is held in a rigid ring by H-bonding (Equation 6) and the second compound has a transition state that is for some reason stabilized by the carbonyls on each end (Equation 7). The third compound, chalcone, isomerizes at high wavelengths (320 nm) but dimerizes at low wavelengths (Equation 7a).



(6)



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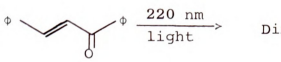
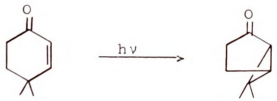


(7a)

The size of the ring is also an important consideration because it has been shown that in cyclohept-2-enone (13) and cyclooct-2-enone (14) the cis-trans isomerization occurs exclusively and the cycloaddition reactions noticed proceed entirely from trans-enones and take place readily in the dark.

The last limiting factor in cycloaddition reactions is the substitution of the C-4 position of 6-membered cyclic enones. Irradiation of a 4,4-dialkyl compound will give the lumirearrangement (15) to form a bicyclo[3.1.0]hexan-2-one system (16) (Equation 8). Various substitutions at other positions do not change the cycloaddition reaction.

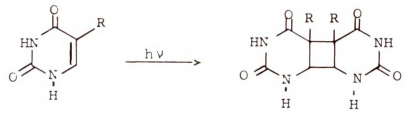


(8)

So, in summary, properly substituted five- and six-membered alicyclic α,β-unsaturated ketones can be made to dimerize under a variety of conditions by the action of ultraviolet light.

In 1928 Gates (17) pointed out the probable relationship between the bactericidal effectiveness of the various wavelengths of uv light and the absorption of uv light by DNA (18). Generally in these cases the death of bacteria and other living organisms is caused by lesions which block DNA or RNA synthesis. Investigation of these lesions

continued until 1958 when Beukers and Berends found an irreversible reaction of the pyrimidine bases, thymine and uracil, resulting from uv irradiation (19). Two years later, they postulated that this reaction formed a dimer of uracil or thymine (Equation 9) and that this dimeric structure was responsible for uv damage to cells (20).



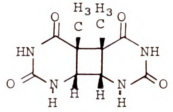
(9)

R = H (uracil) or CH_3 (thymine)

In the following decade this theory was shown to be true by a large number of researchers (21). In fact Setlow has estimated that cyclobutane dimers occur in irradiated bacteria about a thousand times more often than the other types of photodamage such as interstrand cross-links, chain breaks or DNA-protein links (22).

There are two main approaches to determining the process which leads to the formation of dimers: first, looking at the isolated thymine and uracil moieties and applying these results to biological systems; and second to investigate the photoinduced imerizations in DNA and RNA, both *in vitro* and *in vivo*. The former method was much easier to undertake, and the results quickly reported by many workers. Irradiation of frozen aqueous solutions of

thymine gave a single dimeric compound (23). Since four configurations about the cyclobutane ring are possible, the isolation of a single product earned it the name "ice-dimer". The structure of the "ice-dimer" was shown to be syn-head-to-head (5) (24).



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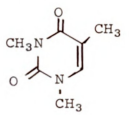
The remarkable stereochemistry was explained by Wang who showed that the pyrmidines freeze in crystallites where regular arrays of molecules are stacked in a precise geometry which enables formation of 5 by irradiation (25). The ice reaction is very efficient (high quantum yield (26)) and was also shown to be a singlet reaction (27). It is known that there is no fluorescence from frozen thymine solutions and because of this, the reaction of dimer formation must be fast enough to quench fluorescence, a known fast process. This fluorescence quenching and high dimer quantum yield suggest excimer formation (28). This is quite reasonable since there must be aggregation of some sort to account for the stereospecific production of the ice dimer.

In solution at room temperature, the pyrimidines can react through both singlet and triplet manifolds. Thymine

and uracil dimerization in dilute solutions ($\sim 1 \times 10^{-3}$M) is quenched by dienes and this indicates a triplet mechanism (29). On the other hand an analogous compound, dimethyl thymine (6) is much more soluble and therefore concentrated solutions can be prepared (0.1M). These react



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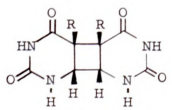
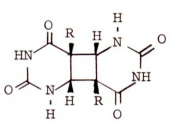
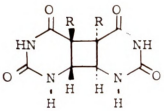
through both the triplet and singlet states (30). This behavior can be explained by a moderate rate of intersystem crossing which promotes population of the triplet state in dilute solutions, but allows singlet reaction to compete with intersystem crossing at high concentrations. Although irradiation of pyrimidines in ice gives only one product, solution photolysis gives all possible products with cis ring junctions (30,31):



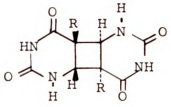
syn-head-to-head



syn-head-to-tail



anti-head-to-head



anti-head-to-tail

In the simple enones (vide infra) there is a polarity effect in the dimerization reaction. The use of different solvents changes the relative yields of isomeric products (10a). This effect would be expected in the pyrimidines but has not been demonstrated as yet. Their limited solubility even in very polar solvents will probably preclude solvent studies

Since the solution dimerization has been shown to proceed by a triplet, it would be expected that the reaction would take place if the triplet state was populated by energy transfer from a suitable sensitizer. Krauch has dimerized both uracil (32) and thymine (33) in water with the use of acetone as a sensitizer. This work was repeated by Johns (31) using other sensitizers. As would be expected, all possible dimers are formed, in nearly the same ratio as the direct photolysis.

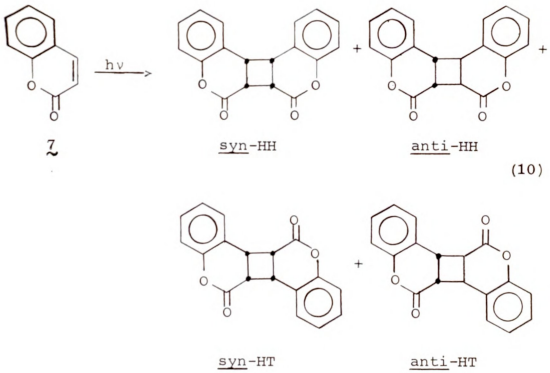
The alternate approach to the determination of the cause of biological damage by uv light was an investigation of the dimerization of the pyrimidines in DNA and RNA themselves. Early in 1960 Wacker (34) recovered a dimer of thymine identical in structure to Frankel's "ice-dimer" (23), by hydrolysis of the DNA of irradiated bacteria. Similarly, the syn-head-to-head dimer of uracil was found in the

photolysis of RNA (35). It would be expected that a single thymine-dimer would be formed in native DNA because of the rigidly ordered stereochemistry of the nucleic acids. That the dimer found is the syn-HH dimer lends much support to the fact that thymines attached to adjacent ribose moieties are coupled (intrastrand dimerization (36)). It is postulated that the interstrand dimerization (23) would give anti-HH or anti-HT and that reaction of the bases in complimentary strands would require gross distortion of the helical structure and therefore be unlikely.

It should be mentioned that cytosine dimers and mixed cytosine-thymine dimers are formed in the irradiated DNA, but these mixed bases have not been studied in much detail.

Very recently Lamola has reported the formation of dimers in bacterial DNA by sensitized irradiation (37). This indicates that reaction of DNA can be through the triplet state. But whether the direct irradiation of DNA proceeds in this manner or through a singlet state mechanism has not yet been determined.

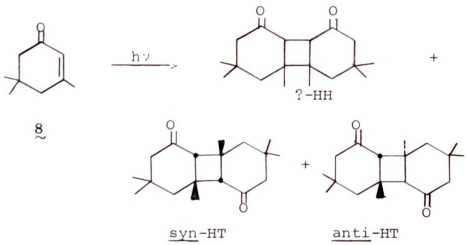
Turning to simple unsaturated ketones, the literature indicates that only four dimerizations have been studied in detail coumarin (7), isophorone (8), cyclopent-2-enone (3), and cyclohex-2-enone (4). Although much work has been done on the coumarin dimerization (Equation 10) it is hard to draw any definite conclusions.



Direct irradiation of concentrated solutions (> 0.5M) gives mostly the syn products with some anti-HH dimer. Dilute solutions produce only anti products upon direct photolysis (38) and sensitized irradiation using benzophenone also yields the anti-products. From these and many other experimental results, Schenck (39) and Morrison (40) both postulate a singlet excimer intermediate which goes on to form only the syn products. The anti products arise from the small amount of triplet formed by intersystem crossing in direct irradiation and the complete triplet state population in sensitized experiments. The variance of product yields in different solvents reflect the polarity changes

of the solvents evidently allowing changing population of singlet and triplet states. In addition different solvation of the intermediates lead to changeable amounts of HH or HT products. The complexity of the reaction indicates the problem of deriving a mechanism to explain all the results and therefore the need of more work in this area.

All of the work on the dimerization of isophorone (Equation 11) has been done by Chapman (41). The reaction proceeds completely from the triplet state and gives varying amounts of dimers, depending on the solvent used.



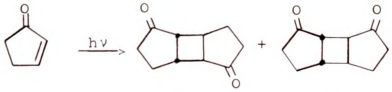
8 (11)

syn-HT anti-HT

Based on sensitized and direct irradiation experiments, Chapman postulates two distinct triplet states, each giving rise to one of the dimers, HH or HT. This observation is interesting, but at this time insufficient information is available to warrant further discussion.

The dimerization of cyclopent-2-enone (Equation 12) was first reported by Eaton (42) in 1962. The reaction has been well studied since then and several important

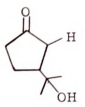
results are evident. After some opinions to the contrary (notably from Leermakers (43)) Eaton showed that the reaction proceeds from the triplet state exclusively and the variance of HH/HT products could be easily explained by a solvent effect (44). But the most significant result was



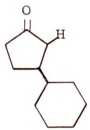
(12)

anti-HT anti-HH

that of deMayo (3a) who demonstrated that sensitizers with triplet energy below that of benzophenone (E_T = 69.2 kcal/mole) would not sensitize the cycloaddition reaction. Instead these compounds sensitized the formation of a reduction product. This indicates the existence of two triplet states: a higher state ($E_T \approx 74$ kcal/mole) which leads to cycloaddition, and a lower state ($E_T \approx 61$ kcal/mole) which can give only reduction product. The reduction product in isopropyl alcohol solution (3c) is 9, and in cyclohexane (45) is 10.

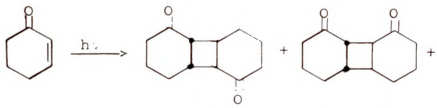


9



10

Hammond in a single publication (46) has reported the only study of the dimerization of cyclohex-2-enone (Equation 13).



(13)

anti-HT anti-HH

The reaction can be quenched by dienes and can be sensitized. This behavior indicates a triplet excited state intermediate. The HH/HT dimer yields vary as before with concentration and solvent polarity. Since naphthalene sensitized the reaction, Hammond suggested that it proceeded by the lowest triplet, but the possibility of singlet sensitization makes this conclusion questionable (3c).

In the following sections of the thesis, the determination of the primary rate constants for the dimerization of four enones (thymine, uracil, cyclopent-2-enone, and cyclohex-2-enone) is reported. The values obtained enable us to postulate the intermediacy of a metastable dimeric species which can go on to dimer, or revert to two ground state molecules in varying amounts depending on the structure of the enone.

II. RESULTS AND DISCUSSION

A. Thymine and Uracil

One of the general methods for the determination of the mechanism of a reaction is to postulate a reasonable mechanism, derive kinetic functions which describe that mechanism, and do experiments to see whether the results correspond with it. A good correlation will lend support to the postulated mechanism and a poor correlation will indicate an erroneous mechanism. This approach was used to study the dimerization reaction of unsaturated ketones. The generally postulated mechanism for this reaction (3c,46) is shown in Scheme I. Light is absorbed by the enone which is excited vertically to the first singlet state ($^1E^*$). The singlet can decay with a rate k_i to the ground state or intersystem cross with a rate k_{isc} to the excited triplet state ($^3E^*$). The triplet can decay (k_d), transfer energy with a rate k_q to a quencher (Q) or add to a ground state enone molecule with a rate k_a to give a dimer (EE).

Scheme I

$$E + h\nu \xrightarrow{I_a} {}^1E^*$$

$$^1E^* \xrightarrow{k_i} E$$

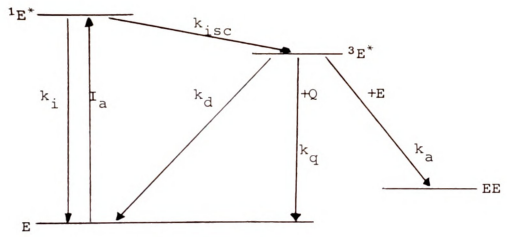
$$^1E^* \xrightarrow{k_{isc}} {}^3E^*$$

$$^3E^* \xrightarrow{k_d} E$$

$$^3E^* + Q \xrightarrow{k_q} E + {}^3Q^*$$

$$^3E^* + E \xrightarrow{k_a} EE$$

These processes can also be represented by a rough energy level diagram which is shown below:



In photochemical reactions, the quantum yield is a very important and fundamental quantity. The primary quantum yield of a process (48) is defined as:

$$\Phi = \frac{d[X]\ dt}{I_a} = \frac{\text{No. of molecules of X formed/cm}^3\ \text{sec}}{\text{No. quanta absorbed by reactant/cm}^3\ \text{sec}} \quad (14)$$

The quantity X can be a molecule, radical or ion. It is also useful to consider quantum yields as probabilities. The absorptions of light by a molecule is a one-quantum process and the sum of the primary process quantum yields Φ must be unity. Quantitatively, $\Sigma\ \Phi_i = 1.00$, where Φ_i is the quantum yield of the i^{th} primary process.

Referring to the energy level diagram, the total quantum yield for dimerization can be written as a product of all the process quantum yields:

$$\Phi_{dim} = \Phi_{isc} \cdot \Phi_a \quad . \quad (15)$$

Each process quantum yield can be written as the rate for that process divided by the sum of all possible processes proceeding from that intermediate (49).

$$\Phi_{dim} = \frac{k_{isc}}{k_{isc} + k_i} \cdot \frac{k_a[E]}{k_d + k_q[Q] + k_a[E]} \qquad (16)$$

When no quencher is present, [Q] = 0 and

$$\Phi^0_{dim} = \frac{k_{isc}}{k_{isc} + k_i} \cdot \frac{k_a[E]}{k_d + k_a[E]} \qquad (17)$$

Taking a ratio of these two relations and defining τ as the lifetime of the triplet state in the absence of quenchers (Equation 19) the following equations are derived:

$$\frac{\Phi^0}{\Phi} = \frac{k_d + k_a[E] + k_q[Q]}{k_d + k_a[E]} = 1 + \frac{k_q[Q]}{k_d + k_a[E]} \qquad (18)$$

$$\tau = \frac{1}{k_d + k_a[E]} \qquad (19)$$

$$\frac{\Phi^0}{\Phi} = 1 + k_q \tau [Q] \qquad (20)$$

Equation 20 is the Stern-Volmer expression from which $k_q\tau$ can be determined by varying the quencher concentration and measuring the unquenched to quenched ratio of quantum yields.

The reciprocal quantum yield expression (Equation 22) follows from the reciprocal of Equation 17.

$$\frac{1}{\Phi_{dim}} = \frac{1}{\Phi_{isc}} \cdot \frac{k_d + k_a[E]}{k_a[E]} \qquad (21)$$

$$\frac{1}{\Phi_{dim}} = \frac{1}{\Phi_{isc}} \left(1 + \frac{k_d}{k_a[E]} \right) \qquad (22)$$

Using this relation, the change in Φ_{dim} with varying enone concentration can be measured and the ratio of rate constants k_d/k_a can be determined (if Φ_{isc} is known).

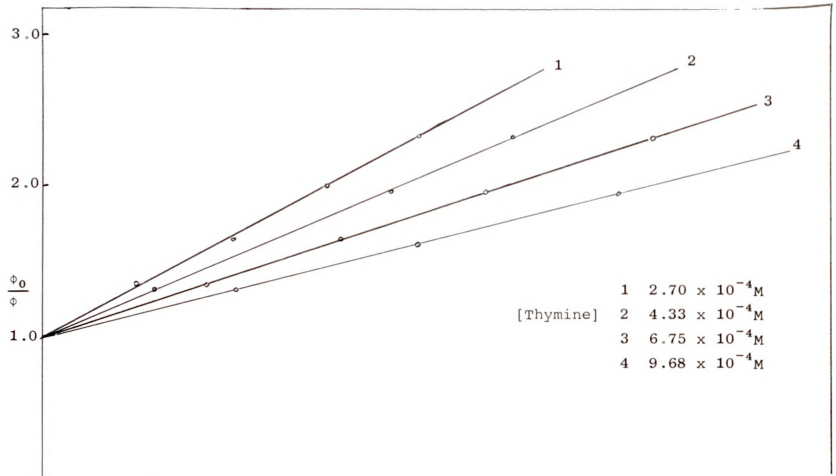
Both of these expressions (Equations 20 and 22) can also be derived by writing the rate laws and applying the steady state approximation to the intermediates $^1E^*$ and $^3E^*$.

The kinetics of dimerization of the pyrimidine bases, thymine and uracil, were determined by quenching studies and triplet counting. Their low solubility precluded product analysis in a quantitative manner and therefore disappearance of pyrimidine was followed by uv spectroscopy. In the large amount of literature on this reaction (vide supra) no report has mentioned any loss of pyrimidines in non-protic medium except by dimerization. The solutions were irradiated with the 2753-, 2804-, and 2894 Å lines of a medium pressure mercury arc. The pyrimidines absorbed varying amounts of this light through the 1 mm Pyrex wall of the sample tubes. This method was not optimal, but the necessity of using a large number of samples for the kinetics and the impossibility of obtaining Corex tubes left no alternative. Because of these conditions, absolute quantum yields could not be determined directly. However, another

method was used by which the quantum yield at certain concentrations could be estimated (vide infra).

The products of the dimerization of thymine in acetonitrile were analyzed by the use of ^{14}C-labeled pyrimidine. Irradiated samples were chromatographed on paper and analyzed by a strip-scanner. The resulting trace is indicated in Figure IX. Unfortunately, the resolution of the dimers is only fair, but the following observations can be made: first, all four dimers are present; second, the syn dimers (HH and HT) account for about 55-60% of the mixture, slightly less than Morrison has noted for dimethyl thymine where he could measure the syn products accurately at 85% in acetonitrile (30); third, there is much less formation of syn dimers in solution than in the frozen state where they approach 100%; and fourth, the result is in close agreement with John's who finds 65% syn dimers in the direct photolysis in water (31). These results are in agreement with the fact that the reaction proceeds by the singlet excited state in frozen medium, partially singlet in Morrison's work (high concentration), and triplet in dilute solution at room temperature. It is assumed that uracil behaves in a similar manner.

Degassed acetonitrile solutions 2-10 x 10^{-4}M in pyrimidine and containing various concentrations of piperylene were irradiated and analyzed. The Stern-Volmer plots were linear out to large percentages of quenching (Figure I), indicating that at these concentrations the photodimerization


3.0
2.0
1.0
$\frac{\Phi_0}{\Phi}$
1
2
3
4
[Thymine]
1 2.70 x 10^{-4}M
2 4.33 x 10^{-4}M
3 6.75 x 10^{-4}M
4 9.68 x 10^{-4}M

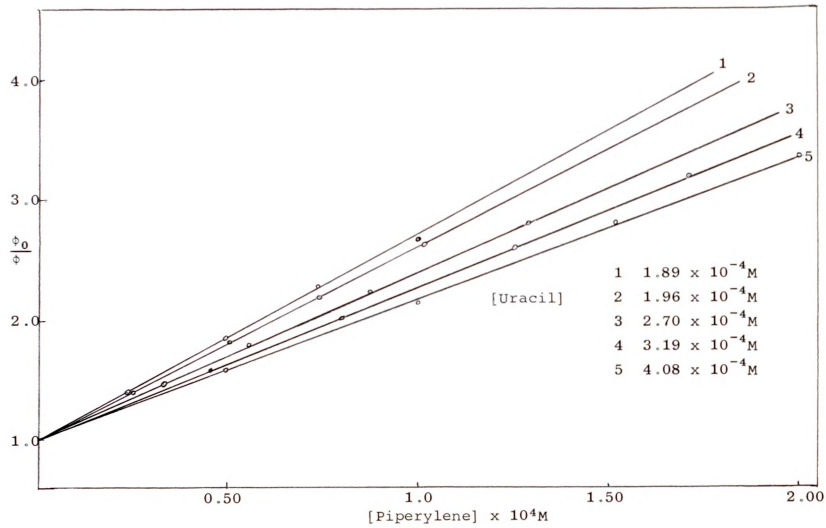


Figure Ia. Stern-Volmer plots for varying concentrations of uracil in acetonitrile.

is predominantly a triplet-state reaction. The reactions, in fact, could be quenched over 99% by the addition of 0.01M piperylene. Table I contains values of the slopes obtained at various base concentrations.

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]	τ, 10^{-6} sec
	Thymine	
2.70	26,000	2.36
4.33	20,800	1.89
6.75	15,700	1.43
9.68	12,200	1.12
	Uracil	
1.89	21,300	1.94
1.96	19,600	1.78
2.70	18,600	1.69
3.19	12,900	1.17
4.08	11,500	1.04

[a]Average concentration. [b]Slopes of Stern-Volmer plots reproducible to ±5%.

The rate constant for energy transfer, k_q, is dependent on the viscosity of the solvent and has a value in acetonitrile of $1.1 \times 10^{10} M^{-1}$ sec^{-1} (50). This value was used to determine the τ values in Table I. The quantum yields for the two pyrimidines were found by comparing the amount of dimerization of a given concentration of base to the amount of isomerization of 0.1M cis-1,3-pentadiene sensitized by the same concentration of base. The pentadiene

isomerized gives a count of the total number of triplets formed (51) and the dimer produced (assumed to be one-half of the pyrimidine that disappeared) gives the number of triplets that actually went on to form dimer. A ratio of these values for 6.2×10^{-4}M thymine indicates that only 1.4% of the thymine triplets actually dimerize. In a 3.9×10^{-4}M uracil solution, only 4.9% of the triplets dimerize. Using Lamola's (29) values for Φ_{isc} (0.18 for thymine and 0.40 for uracil) the quantum yields of dimerization at these concentrations can be calculated as 0.0025 for thymine and 0.019 for uracil.

The triplet state lifetime, τ, is a function of the concentration of enone as in Equation 19. The various τ-values have been determined from the Stern-Volmer quenching plots and when these are plotted (Figure II) according to Equation 23 (which is the reciprocal of Equation 19) the slope is the bimolecular rate constant of addition, k_a, and the intercept is the triplet decay rate constant, k_d.

$$\frac{1}{\tau} = k_d + k_a[E] \quad . \tag{23}$$

The values of the rate constants and quantum yields are indicated in Table II. The quantum yield of addition, Φ_a, can be calculated from the rate constants and the concentrations indicated, by using Equation 24.

$$\Phi_a = \frac{k_a[E]}{k_d + k_a[E]} \tag{24}$$

The quantum yields for dimerization predicted by Equations 14

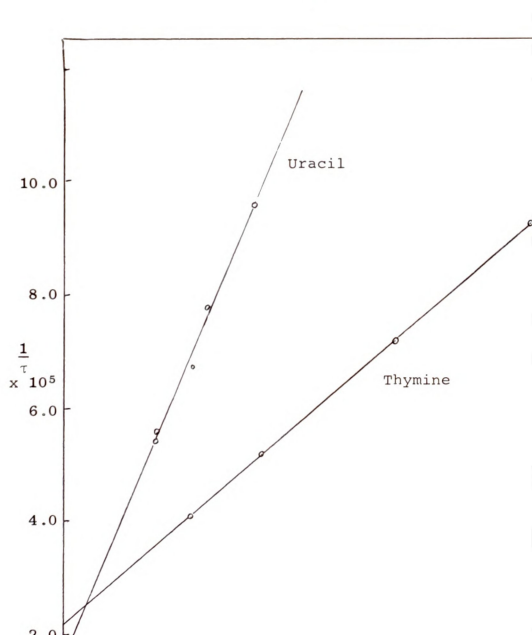


Figure II. Dependence of triplet-state lifetimes o thymine and uracil on ground-state con- centrations.

and 16 and rate constants are much greater than the observed values. That there is a further source of inefficiency in the reaction is quite evident and this will be discussed at length below.

Table II. Kinetic data for photodimerization of thymine and uracil

Quantity	Thymine	Uracil
k_d, sec[a]	2.2 ± .14 x 10^5	1.6 ± .5 x 10^5
k_a, $M^{-1}sec$[a]	0.70 ± .02 x 10^9	2.0 ± .17 x 10^9
Φ_a	0.65[b]	0.78[c]
Φ_{isc}[d]	0.18	0.40
Φ_{dim}	0.0025[b]	0.019[c]

[a]Slopes and intercepts analyzed by Least Squares. Standard Deviation indicated.

[b]6.2 x 10^{-4}M thymine. [c]3.9 x 10^{-4}M Uracil. [d]Values from reference 29.

B. Kinetics of Cyclopent-2-enone and Cyclohex-2-enone

The kinetics of the dimerization of the simple enones, cyclopent-2-enone and cyclohex-2-enone were determined by measurement of quantum yields and Stern-Volmer quenching slopes. Previous studies were complicated by the fact that product ratios of head-to-head and head-to-tail products were dependent on enone concentration. This behavior apparently reflects a polar solvent effect which enhances the formation of head-to-head dimer (10a). The use of

acetonitrile as solvent alleviates this problem. Only two dimeric product peaks appear in the vpc traces of irradiated cyclopent-2-enone. The HH/HT ratio remains constant at 4:5 from 0.1M to 3.0M concentrations. With cyclohex-2-enone, the HH/HT ratio is 2:1 and also independent of concentration. A third product peak, amounting to 4% of the total, appears just before the two major dimers on the vpc traces and is probably a dimer with a trans-6/4 ring junction (3b). Thus, the kinetics of dimerization were conveniently studied by measuring product appearance by vpc relative to an internal standard.

The quantum yield of intersystem crossing was found by measuring the amount of isomerization of different concentrations of cis-pentadiene sensitized by a constant concentration of each enone (the method is described in detail in the Experimental section). Extrapolation to infinite diene concentration indicates that both enones have unit efficiency of intersystem crossing.

Equation 22 describes the dependence of quantum yield on enone concentration. By measuring the amount of enone found from parallel irradiation of various concentrations of enone and the light flux by acetophenone-cis-piperylene actinometry, the absolute quantum yields were determined. These values are in Table III. Plotting these according to Equation 22 with the value of Φ_{isc} equal to unity gives good straight lines (Figure III). The quantum yields at infinite concentration (intercept) are only .36 and .75 for

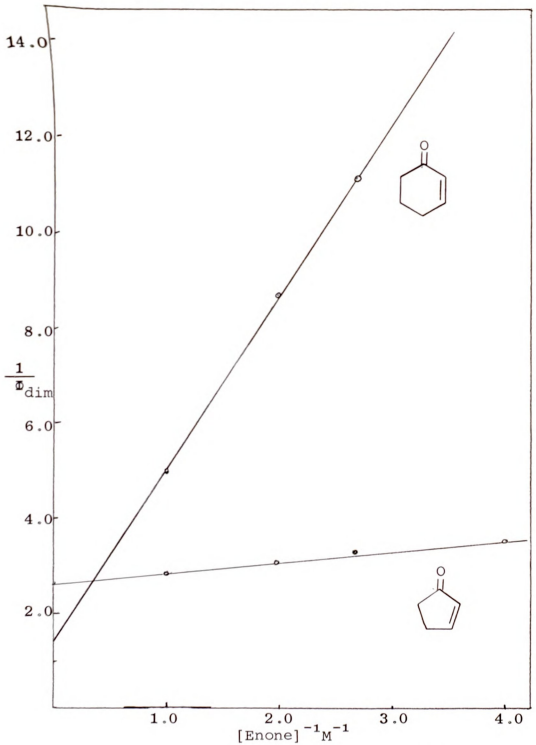


Figure III. Dependence of quantum yields on concentration of cyclopent-2-enone and cyclohex-2-enone.

cyclopent-2-enone and cyclohex-2-enone, respectively. This will be discussed at length below. The ratio of rate constants k_d/k_a is 0.06 and 2.7 for the two enones.

Table III. Quantum yields for various concentrations of cyclopent-2-enone and cyclohex-2-enone

[Enone], M	Φ_{dim} Cyclopent-2-enone[a]	Φ_{dim} Cyclohex-2-enone[a]
1.00	0.342	0.204
0.50	0.324	0.115
0.375	0.308	0.091
0.25	0.292	0.064

[a]Average of two runs; each value reproducible to ±1%.

Stern-Volmer analysis of the relative quantum yields as a function of quencher concentration was done for each enone. Both 1,3-cyclohexadiene and 1,3-pentadiene have been shown to be equally effective at quenching the photodimerization of cyclopent-2-enone (52). However, 1,3-pentadiene is only 60% as efficient as 1,3-cyclohexadiene at quenching the cyclohex-2-enone reaction. The reason for this is not known, but the same phenomenon has been observed with other 6-membered, cyclic enones (52,53). Table IV contains the $k_q\tau$ values for Stern-Volmer analysis (Figure IV) of both enones using pentadiene and that of the 6-membered enone using 1,3-cyclohexadiene. The τ-values are calculated using $1.0 \times 10^{10} M^{-1} sec^{-1}$ for k_q because the high concentration

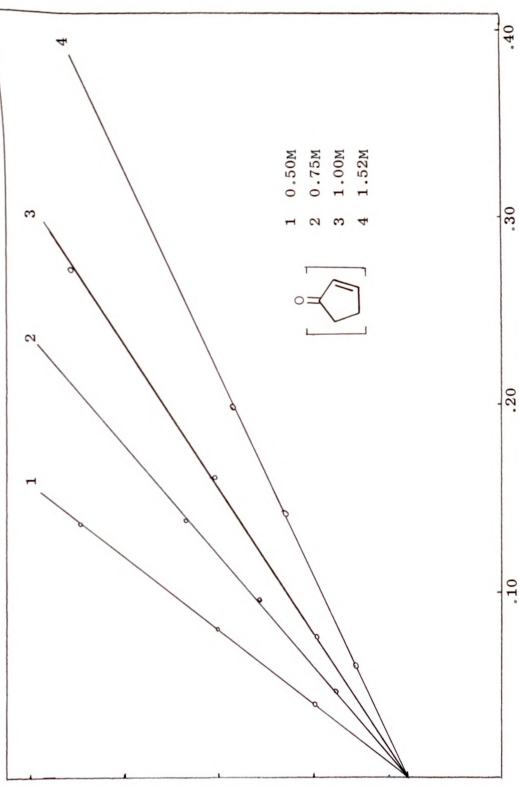


Figure IV. Stern-Volmer plots for varying concentrations of cyclopent-2-enone.

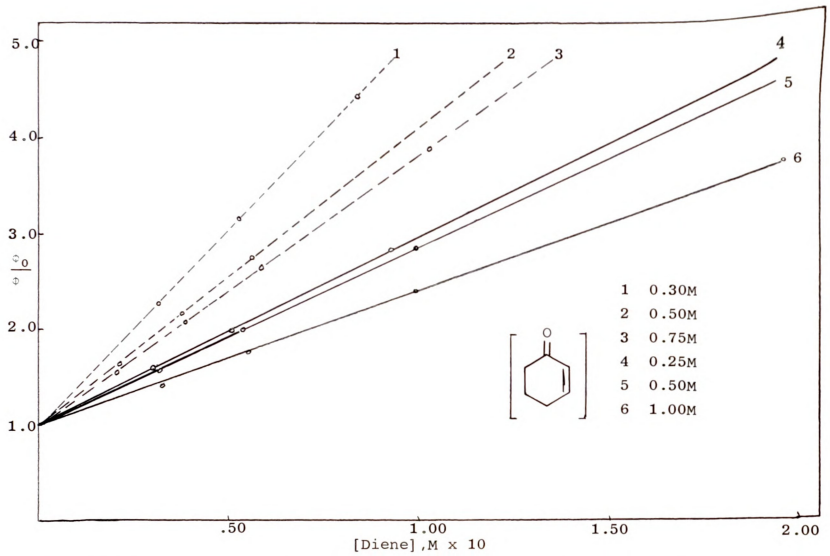


Figure IVa. Stern-Volmer plots for varying concentrations of cyclohex-2-enone: _____, represents 1,3-pentadiene runs; – – – –, represents 1,3-cyclohexadiene runs.

Table IV. Quenching of cyclopent-2-enone and cyclohex-2-enone photodimerizations by dienes in acetonitrile.

Enone	Diene	[Enone], M	$k_q\tau$, M^{-1}	$1/\tau$, 10^8 sec^{-1}
Cyclopent-2-enone	1,3-pentadiene	1.52	9.1[a]	10.5
		1.00	12.5	7.7
		0.75	16.5	5.9
		0.50	26.5	3.7
Cyclohex-2-enone	1,3-pentadiene	1.00	13.7	7.3
		0.50	17.5	5.8
		0.48	17.5	5.8
		0.25	18.5	5.5
	1,3-cyclohexadiene	0.75	27.0	3.6
		0.50	28.1	3.5
		0.30	38.7	2.7

[a]The error for $k_q\tau$ values is $\pm 0.2 M^{-1}$.

Table V. Kinetic data for photodimerization of cyclopent-2-enone and cyclohex-2-enone.

Quantity	Cyclopent-2-enone	Cyclohex-2-enone
k_d, sec	$0.40 \pm .1 \times 10^8$[a]	$3.0 \pm .4 \times 10^8$[a]
k_a, $M^{-1}sec$	$6.6 \pm .4 \times 10^8$	$1.1 \pm .2 \times 10^8$
Φ_{isc}	1.0	1.0

[a]Slopes and intercepts analyzed by Least Squares. Standard Deviation indicated.

of enone changes the viscosity slightly. Evidently the value of k_q for the pentadiene quench of cyclohex-2-enone must be less than this because it is not diffusion controlled. The $1/\tau$ values are plotted for all three cases according to Equation 23 in Figure V. All further kinetic treatment of cyclohex-2-enone was based on the 1,3-cyclohexadiene quenching results because these are more nearly diffusion controlled.

The rate constant for addition, k_a, is the slope of the $1/\tau$ vs. [E] graph and although k_d, the triplet decay rate, is the intercept, its value was determined instead from the rate ratio k_d/k_a as found from the reciprocal quantum yield plots. This was done because there is much less error in the value of a slope than in that of an intercept.

The rate constants and other data for the two enones are listed in Table V.

C. Mechanistic Interpretations

The values of the rate constants themselves are interesting. The decay rate, k_d, for the pyrimidines is very low at 10^5 sec. This value is comparable to the rate for simple carbonyl triplets in solution. The simple enones are about three orders of magnitude faster in their decay. This great difference may partially reflect the greater flexibility of the simple enones as compared to the rigidity

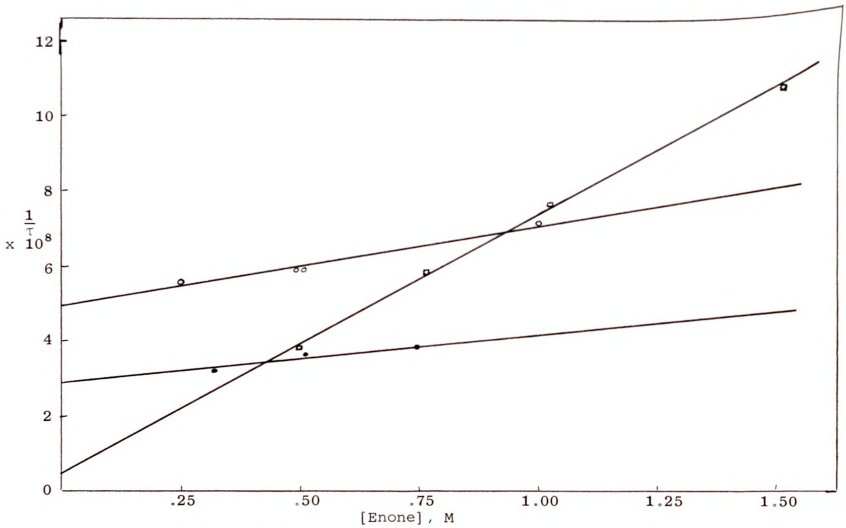
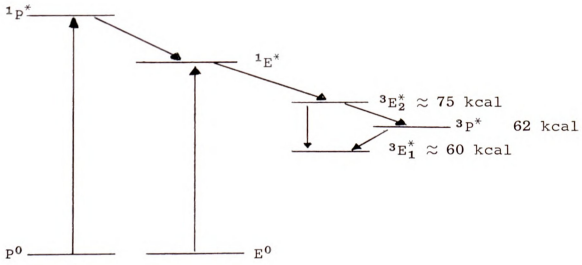


Figure V. Dependence of triplet lifetime on the concentrations of cyclopent-2-enone (□) and cyclohex-2-enone (○): ○ or □, represent 1,3-pentadiene runs; and ●, represents 1,3-hexadiene runs.

of the pyrimidine rings, for it is generally postulated that the primary mode of radiationless decay is through vibration of the molecule.

However, an even more important factor contributing to the decay of enones is the fact that they dimerize from a second triplet state (T_2). The work of deMayo (3c) has shown this to be true for cyclopentenone. Although Hammond initially postulated cyclohex-2-enone dimerization occurring from the lowest triplet on the basis of a naphthalene sensitizing experiment, our own work has shown that this too is a T_2 reaction. Irradiating solutions of cyclohex-2-enone containing increasing amounts of the sensitizer phenanthrene, which in all cases absorbed most of the light, caused the quantum yields of dimerization to decrease. Inspection of the energy level diagram shows that both singlet (3c) and triplet energy transfers are likely from phenanthrene to cyclohex-2-enone.



The only explanation for the decrease in sensitized quantum yield is that triplet energy transfer from the intermediate which leads to dimer ($^3E_2^*$) to the phenanthrene occurs to form $^3P^*$. Transfer from $^3E_1^*$ to phenanthrene is endothermic by at least 1 kcal and therefore unlikely.

Because of these considerations, it is possible that quenching of both enones done in the Stern-Volmer experiments is quenching of the $T_2 \rightarrow T_1$ conversion. If this is the case, it is likely that the k_d values are low. Liu has estimated $T_2 \rightarrow T_1$ internal conversion at $5 \times 10^{10} sec^{-1}$ for anthracene (58). It was previously mentioned above that the higher homologues, cycloheptenone and cyclooctenone, do not dimerize upon photolysis. Rather, they undergo a cis $\rightarrow$ trans isomerization (10a). Zimmerman has postulated that the difference between the two triplet states may be geometric, the higher triplet T_2 being more planar and lower triplet being twisted at the β-carbon (53). The facile twisting in the higher homologues may preclude dimerization, whereas constraint in the smaller 6-membered enone and the even smaller 5-membered ring compound may lower this rate of internal conversion to about $10^8 sec^{-1}$ and allow dimerization to occur at high enough enone concentration. If this is true the rates, k_d, are the first measurement of internal conversion in ketones.

The rates of addition, k_a, are all quite large at about $10^8 M^{-1}$ sec. Lamola (37b) has postulated that the pyrimidines dimerize from a $\pi \rightarrow \pi^*$ triplet state on the basis of the very long-lived phosphorescence emission. The work of deMayo (3c has shown that the simple enones react from the (second) triplet state which is presumed to have $n \rightarrow \pi^*$ configuration. It has been argued for some time that rates of reaction could be used to predict the electronic state, the $\pi \rightarrow \pi^*$ configuration reacting much slower. This work shows at least one case of similar rates arising from different electronic states. It is interesting to note that triplet thymine adds to ground-state thymine only one-third as fast as triplet uracil adds to ground-state uracil. In a qualitative manner this effect is probably due to some steric hindrance by the methyl group of thymine. But, it is still hard to draw any good conclusions about the effect of structure on the rate of addition. The fact is that this is a dimerization reaction and the excited moiety is adding to itself. The ground-state enones must act as olefins for this cycloaddition and therefore overall effects are very complicated. The only way to resolve this difficulty is to add a series of enones to a single olefin under the same conditions and from this get a good idea of the reactivities.

Using the measured data for all four enones and the derived equation for the dimerization reaction (Equation 14), Φ_{dim} can be calculated for each enone at any given

concentration. It is obvious that these calculated values of Φ_{dim} are too large and that there must be a further major source of inefficiency in the reaction. The data require that some of the original photoadduct must be able to decay back to two ground state molecules. The original mechanistic scheme must be altered to include the formation of some sort of intermediate $(EE)^*$ that can either decay or go on to dimer. The modified scheme and rough energy level diagram are shown below.

$$E + h\nu \xrightarrow{\overline{I_a}} {}^1E^*$$

$${}^1E^* \xrightarrow{k_i} E$$

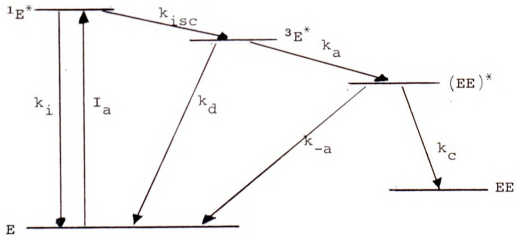
$${}^1E^* \xrightarrow{k_{isc}} {}^3E^*$$

$${}^3E^* \xrightarrow{k_d} E$$

$${}^3E^* + E \xrightarrow{k_a} (EE)^*$$

$$(EE)^* \xrightarrow{k_{-a}} 2E$$

$$(EE)^* \xrightarrow{k_c} EE$$



This new mechanism yields Equation 25 in place of Equation 14 to describe the total quantum yield of dimerization.

$$\Phi_{dim} = \Phi_{isc} \Phi_{ad} \Phi_{p} \quad (25)$$

$$\Phi_{p} = \frac{k_c}{k_{-a} + k_c} \quad (26)$$

The quantity Φ_p can be defined in terms of rate constants (Equation 26) of coupling (k_c) and uncoupling (k_{-a}) and is the probability that the intermediate will proceed on to stable dimer. The quantity Φ_{ad} is now the probability that triplet enone will react with ground-state enone. Using Equation 25 and the measured data, the Φ_p values for each enone can be calculated and are listed in Table VI. The results indicate that only 2% of the original metastable thymine dimers formed eventually yield stable ground state dimers. The corresponding percentages are 6% for uracil, 36% for cyclopent-2-enone, and 74% for cyclohex-2-enone.

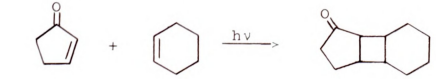
Table VI. Kinetic data for photodimerization of enones in acetonitrile

Quantity	Thymine	Uracil	Cyclopent-2-enone	Cyclohex-2-enone
[Enone], M	6.2×10^{-4}	3.9×10^{-4}	1.00	1.00
Φ_{isc}	0.18	0.40	1.0	1.0
Φ_{a}	0.65	0.78	0.94	0.27
Φ_{dim}	0.0025	0.019	0.34	0.20
Φ_{p} [a]	0.021	0.061	0.36	0.74

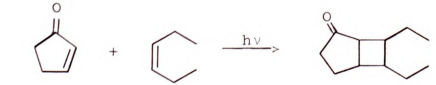
[a] Calculated from Equation 25.

In the plethora of literature on the reaction of pyrimidines there have been no mechanisms advanced for the triplet reaction in solution except the vague statement by Johns (54) that "it is conceivable that the reaction [uracil dimerization] might lead to an unstable product which would not be detected." The only mechanism proposed for simple enones that is largely different is that of Chapman who postulates two triplets, each leading to different dimers of isophorone. As of this writing his hypothesis has not been further verified.

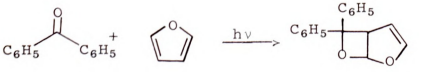
Several groups have found results similar to ours in related reactions, in that maximum quantum yields are significantly lower than unity. DeMayo's cycloadditions to cyclopent-2-enone triplets proceed only 48% with cyclohexene (Equation 27) and 21% with 3-hexene (Equation 28). Tropone dimerizes with 39% efficiency from the triplet state (55). The cycloaddition of benzophenone and furan (Equation 29) proceeds only 3% as reported by Sokurai (56).



(27)

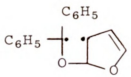


(28)



(29)

DeMayo suggests some sort of "complex" which can fall apart to two ground-state molecules or couple to produce product. Sokurai postulates a 1,4-biradical (11) that behaves in an identical manner.



11

So there are two possibilities for the reversible intermediate in enone dimerizations: (1) a triplet excimer; or (2) a σ-bonded biradical. A singlet excimer is responsible for singlet-state dimerizations of the pyrimidines in frozen solutions (28), but it proceeds on to dimer with 100% efficiency ($\Phi_p = 1.00$). The high rate of addition, $10^8 M^{-1}$sec, argues for the initial formation of some sort of complex or excimer. This could either go directly to dimer or collapse to a biradical. The intermediacy of biradicals somewhere in the reaction scheme is supported by much evidence. Corey showed (3b) that identical product mixtures were found upon the photolysis of cyclohex-2-enone with either cis-2-butene or trans-2-butene. This requires a two-step mechanism with an intermediate long lived enough to allow isomerization of the double bond. Also 1,4-biradicals are implicated in the photolysis of phenylalkyl ketones (57). The major result of this reaction is cleavage, but

combination to cyclobutanols is also important. So it is not possible to completely define the intermediate of the photodimerization reaction at this time.

Since the pyrimidines give four dimers and the simple enones two each, the rates (k_a) and the probabilities (Φ_p) measured for each system are undoubtedly composites of sets of sets of such values. For thymine and uracil, for example,

$$k_a\Phi_p = k_1\Phi_1 + k_2\Phi_2 + k_3\Phi_3 + k_4\Phi_4 \tag{30}$$

and

$$k_a = k_1 + k_2 + k_3 + k_4 \tag{31}$$

The quantity k_1 is the rate of addition in a head-to-head mode and Φ_1 is the probability of the formed intermediate closing to give cis-head-to-head product. The other quantities describe the formation of the other three dimers. Until the actual amounts of the dimers in acetonitrile are found further calculation is not possible. Even then the series of four sets of unknowns make the problem immensely complex. In the simple enone cases only two dimers are formed and the complete expression would be:

$$k_a\Phi_p = k_H\Phi_H + k_T\Phi_T \tag{32}$$

and

$$k_a = k_H + k_T \tag{33}$$

For cyclopent-2-enone the ratio of these dimer products is known in acetonitrile and it can be calculated from Equations 32 and 34 that $k_H\Phi_H = 1.1 \times 10^8 M^{-1}$ sec

$$\frac{k_H\Phi_H}{k_T\Phi_T} = \frac{45}{55} \qquad (34)$$

and $k_T\Phi_T = 1.4 \times 10^8 M^{-1}$sec, where the H refers to head-to-head product and the T to head-to-tail.

For cyclohex-2-enone, the ratio of dimer products is HT/HH = 36/64. Using Equations 32 and 35 it can be calculated that $k_H\Phi_H = 5.2 \times 10^7 M^{-1}$sec and $k_T\Phi_T = 2.9 \times 10^7 M^{-1}$sec.

$$\frac{k_H\Phi_H}{k_T\Phi_T} = \frac{64}{36} \qquad (35)$$

The absolute values for k's or Φ's cannot be found until some other relationship is derived.

In conclusion, we have determined the primary rate constants and quantum yields for the dimerization reaction of a series of four alicyclic α,β-unsaturated ketones. Requirements for the transition state of the reaction have been determined. These include: (1) its formation is reversible and the primary cause of low quantum efficienty; (2) it may be a complex or triplet excimer that goes to dimer or collapses to a 1,4-biradical; and (3) it may be formed with nearly identical rates from either the π,π^* or n,π^* configuration of the excited enone.

III. EXPERIMENTAL

A. General Procedures

1. Ultraviolet Spectra. Ultraviolet spectra were taken on a Unicam SP 800 recording spectrophotometer. Matched quartz cells with 10.00 mm path length were used. Beer's Law plots of thymine and uracil were obtained by use of a Beckman DB spectrophotometer with a Gilford model 220 linear absorbance converter. Kinetic analyses of the two pyrimidines were done using the latter instrument to read absorbances which were changed to concentrations by use of the linear Beer's Law plots.

2. Vapor Phase Chromatography. Two instruments were used for all vapor phase chromatographic analyses: a) Varian Aerograph HiFi III Series 1200, with a 6' x 1/8" column containing 5% QF-1 and 1% Carbowax 20M on Chromosorb G; and b) Aerograph HiFi Model 600-D, with a 25' x 1/8" column containing 25% 1,2,3-tris(2-cyanoethoxy)propane 60/80 on Chromosorb P. Both instruments are equipped with flame ionization detectors. An internal standard was used for all quantitative work. Each standard was evaluated by use of the following formula:

$$K \cdot [\text{standard}] \cdot \frac{\text{counts unknown}}{\text{counts standard}} = [\text{unknown}]$$

The counts correspond to relative peak area as measured by the disk integrators and K is a sensitivity factor relating the standard to a specific unknown.

3. Irradiation Procedure. In a given run, all tubes were irradiated in parallel for the same length of time on a "merry-go-round" apparatus. This assured that each sample absorbed the same intensity of light. For the pyrimidines, a simple Vycor filter sleeve was used to screen the light from a 450-w Hanovia medium-pressure mercury arc. This filter allows only wavelengths longer than 2350 Å to pass. Cyclopent-2-enone and cyclohex-2-enone were irradiated with the light from an identical arc, but the 3130 Å line was isolated with a 1 cm path of 0.002 M potassium chromate in 1% aqueous solution of potassium carbonate.

B. Compound Preparation and Solvent Purification

1. Acetonitrile. Acetonitrile was used as solvent for all runs and was purified by the method of O'Donnell (60). This procedure lowered the ultraviolet cutoff to about 200 nm and the liquid was completely transparent above that value.

2. Thymine. Thymine (5-methyluracil) was purchased from the Nutritional Biochemicals Corporation, Cleveland, Ohio. It was recrystallized twice from water and sublimed under vacuum.

3. Uracil. Uracil was purchased from Eastman Organic, Rochester, New York. It was purified by recrystallization from hot water and sublimation, 175°C at 0.50 mm Hg.

4. Cyclopent-2-enone. Cyclopent-2-enone was prepared by the method of Garbisch (61 . Cyclopentanone was subjected to bromo-ketalization, dehydrohalogenation and hydrolysis, yielding 32% of colorless liquid, bp 51-53° at 18 mm; >99% pure by vpc (column a Since photolyses were only carried out to about 4%, it was found that much of the cyclopentenone could be recovered by simple extraction from salt water with ether. Distillation gave ~99% pure material again; ir (CCl_4) 1720 cm^{-1}; uv reproduced in Figure VII.

5. Cyclopent-2-enone Dimers. A sample of the pure dimers was needed in order to calibrate mole ratio:peak area on the vpc. A 1.2 ml aliquot of cyclopentenone was placed in a Pyrex tube, sealed at atmospheric pressure, and irradiated for 16 hours strapped to the side of a quartz immersion well. The light was from a 450-w Hanovia medium pressure arc, filtered with a Pyrex sleeve. Addition of ether to the crude product caused the dimers to precipitate. Three crops were obtained in this manner. The off-white solid was sublimed (90° at 0.1 mm) to give white crystals, mp 115-118°, lit (42) 125-126 5°. Vpc analysis indicated 95% head-to-tail and 5% head-to-head dimer. Each pure dimer was not needed because it is assumed that their vpc response would be

identical on the flame detector. Ir ($CHCl_3$) 1730 cm^{-1}; uv (CH_3CN) 208 nm (ϵ = 350), 298 nm (ϵ = 59).

6. Cyclohex-2-enone. Cyclohex-2-enone was prepared from cyclohexanone using the Garbisch (61) procedure in 66% overall yield. The product distilled cleanly at 70-71° at 30 mm Hg to give a colorless liquid which was >99% pure by vpc (column a): ir (CCl_4) 1685 cm^{-1}; uv max (CH_3CN) 222 nm (ϵ = 11,500), 327 nm (ϵ = 30). Uv reproduced in Figure VII.

7. Cyclohex-2-enone Dimers. Again a sample of pure dimers was needed for vpc calibration. A 4.3 g sample of pure cyclohex-2-enone was sealed in a Pyrex tube at atmospheric pressure, strapped to the side of the immersion well and irradiated through a Pyrex sleeve for 24 hours. The orange oil which resulted was distilled on a short path apparatus at 128-132° at 0.4 mm Hg. The product was 3.8 g of yellow oil. The entire sample was chromatographed on a silica gel column and the fractions eluted with methylene chloride were combined and caused to crystallize from pentane (which contained a small amount of ethyl acetate) at dry ice-isopropanol temperature. Recrystallization from hexane and sublimation at 50-60° at 0.4 mm Hg gave a white solid whose composition was 85% HT and 15% HH by vpc (column a) mp 40-45°, lit. (62) 53-55° (for pure HT). Ir ($CHCl_3$) 1700 cm^{-1}; uv (CH_3CN) 212 nm (ϵ = 344), 287 nm (ϵ = 52).

8. Isophthalonitrile. Isophthalonitrile (Eastman Organic Chemicals, Rochester, New York) was used without further purification as an internal standard for the cyclopentenone-dimer analysis. Acetonitrile solutions are uv transparent above 2950 Å.

9. Ethyl Stearate. Ethyl stearate (Eastman Organic Chemicals, Rochester, New York) was recrystallized twice from carbon tetrachloride before use in vpc analysis of cyclohexenone-dimers. The resulting compound was 98% pure by vpc (column a at 180°) and showed only a small absorbance above 2500 Å in the uv (relative max at 2950 Å, ϵ = 10).

10. Piperylene. Piperylene (1,3-pentadiene) as a mixture of isomers was used for quenching studies (Aldrich Chemical Company, Milwaukee, Wisconsin). It is reasonably stable if kept at refrigerator temperature, but was redistilled every two months to remove dimers. Pure cis-piperylene (>99%) was obtained from the Chemical Samples Co., Columbus, Ohio and was used without further purification.

11. 1,3-Cyclohexadiene. 1,3-Cyclohexadiene (Chemical Samples Co., Columbus, Ohio) was used after one distillation at 80.0°.

C. Kinetic Measurements

1. Thymine. Thymine dissolves poorly in Acetonitrile. Typically the weighed amount of thymine was placed in a

100 ml volumetric flask with ~80 ml acetonitrile and a small stirring bar was used to stir the mixture overnight. The stirrer was removed by use of a large magnet on the outside of the flask. After washing the stir-bar with fresh acetonitrile, the flask was brought up to the mark with solvent.

a. Stern-Volmer Quenching Studies. The thymine stock solution was prepared by weighing 18.5 mg of thymine into a 100 ml volumetric flask with the addition of purified acetonitrile as described above. After the solid dissolved the flask was filled to the mark which resulted in a 1.465×10^{-3}M solution. To prepare piperylene 86.0 mg were weighed into a 25 ml volumetric flask and solvent added to the mark, which resulted in a 5.05×10^{-2}M solution. One ml of this solution was diluted to 10 ml to give a 5.05×10^{-3}M solution which was further diluted 1 to 25 to leave a stock solution 2.02×10^{-4}M in piperylene. The solutions for the run were prepared as in Table VII.

Table VII. Preparation of samples for Stern-Volmer quenching study of 7.32×10^{-4}M thymine.

Sample[a]	How Made	[Piperylene] 10^{-5}M
1,1a	5ml Thy stock + 1ml pip stock/to 10ml	2.0
2,2a	5ml Thy stock + 2ml pip stock/to 10ml	4.0
3,3a	5ml Thy stock + 3ml pip stock/to 10ml	6.1
4,4a	5ml Thy stock + 4ml pip stock/to 10ml	8.1
5,6,7	5ml Thy stock + 00 pip stock/to 10ml	0.0
8	5ml Thy stock + 00 pip stock/to 10ml	0.0

[a]All samples contained 7.32×10^{-4}M thymine.

Two 3.0 ml aliquots of each solution were added by syringe to separate 13 x 100 mm Pyrex tubes, constricted about 10 mm from the open end. After all the samples were prepared in this manner, they were degassed three times by freeze-thaw at less than 0.05 torr using liquid nitrogen. The sample tubes were sealed under vacuum and irradiated for 6.6 hours in the previously mentioned apparatus. Sample 8 was analyzed after 4 hours to check progress of the reaction. The tubes were opened and each sample diluted 2/10 for uv analysis. The absorbances were converted to concentrations (by use of the Beer's Law plot) and these were corrected to values before dilution by multiplying by five. Each concentration was subtracted from the starting material concentration in order to determine amount of dimer formed. Ratios were then taken between the unquenched sample [5,6] and each quenched sample [1,2,3,4] to give the Φ_0/Φ values. The values for this run are in Table VIII.

Table VIII. Results of Stern-Volmer quenching study of 7.32×10^{-4} thymine.

Sample	A_{270nm}	[Thy] 10^{-5}M	x 5	$[Thy]_0-[Thy]_x$	Φ_0/Φ
1	.864	1.36			
1a	.862	1.36	6.80×10^{-5}	.050	2.20
2	.856	1.345			
2a	.854	1.345	6.725	.0575	1.91
3	.844	1.33			
3a	.844	1.33	6.65	.065	1.70
4	.828	1.30			
4a	.821	1.29	6.475	.0825	1.33
5	.789	1.24			
6	.792	1.24	6.20	.110	Φ_0
$[Thy]_0$	.924	1.45			
$[Thy]_0$	.928	1.46	7.30	---	---

The ratio Φ_0/Φ was plotted versus the corresponding piperylene concentration and the resulting straight line graph intercepted at unity and had a slope (equal to $k_q\tau$) of 1.57×10^4 (Figure I). This procedure was repeated for several runs at different thymine concentrations (Tables XX to XXIV). The piperylene concentration was set to keep Φ_0/Φ ratios less than 3.0 (at this value over 66% of the reaction is quenched and very low conversions result in larger error in single points). The $k_q\tau$ values at each concentration are recorded in Table I.

b. Determination of Φ_{dim}. Thymine stock solution was prepared as before to make 1.54×10^{-3}M solution. To prepare pure cis-piperylene solution 283.0 mg were dissolved in 5 ml of acetonitrile to give a 0.830M solution. Samples were made up as:

Quenched Samples

3 ml piperylene stock plus 10 ml thymine stock diluted to 25 ml.

Unquenched Samples

10 ml thymine stock diluted to 25 ml.

The quenched samples contained 0.10M cis-piperylene and 6.15×10^{-4}M thymine. The unquenched samples contained only 6.15×10^{-4}M thymine. A total of three quenched and three unquenched tubes were made using exactly 3.0 ml of sample solution and were degassed, sealed, and irradiated for nine hours. The tubes were opened and analyzed. The unquenched tubes (diluted 1/5 for uv measurement) indicated a final

thymine concentration of 5.50×10^{-4}M, showing that 0.65×10^{-4}M thymine disappeared. Half of this value is the amount of excited thymine that went on to dimer: 0.325×10^{-4}M. The quenched samples were analyzed by vpc (column b) for the amount of trans-piperylene formed: $1.27 \pm 0.10\%$. Since the excited piperylene decays to both cis- and trans- forms in a known ratio (63) calculations for the total amount of piperylene excited (and thereby the total amount of thymine excited) can be made:

$$\frac{[\text{trans piperylene}]}{[\text{cis-piperylene}]} = 1.22 \quad \text{at the steady state}$$

[cis-piperylene] x % trans = moles trans $(.101)(.0127) = .00128$

moles trans $\div$ 1.22 = moles cis $(.00128)/(1.22) = .00105$

moles trans + moles cis = moles excited .00233

The above calculation neglects back conversion for moles of cis formed and re-excited, but for extremely low conversion this is not necessary. Finally, taking the ratio of moles of excited thymine which dimerized to the total moles of thymine that reached triplet gives:

$$\frac{3.25 \times 10^{-5}}{2.33 \times 10^{-3}} = 1.40\%$$

Therefore 1.40% of excited triplet thymine molecules eventually dimerize. Since Φ_{isc} is equal to 0.18 (29), Φ_{dim} under these conditions is only 0.0025.

$$(\Phi_{isc})(\text{excited thymines that dimerize}) = \Phi_{dim}$$

$$(0.18)\ (0.0140) = 0.0025 .$$

c. Completely Quenched Reaction. A thymine stock solution (9.85×10^{-4}M) and a piperylene stock solution (5.00×10^{-2}M) were prepared and diluted to make quenched and unquenched samples of thymine. The 0.01M quencher concentration was sufficient to stop over 99.5% of the triplet reaction. The starting concentrations and results are in Table IX.

Table IX. Results of completely quenched thymine irradiation.

Sample[a]	$[Thy]_0$ 10^{-4}M	[Pip] M	Irrad. Time	$[Thy]_{fin}$	% Rx.[b]
3 U	2.95	-0-	2.0 hr	2.62	11%
3 Q	2.95	0.010	20.1	3.07	0% (0%)
5 U	4.92	-0-	4.0	4.05	18%
5 Q	4.92	0.010	39.7	4.85	1% (.1%)
7 U	6.89	-0-	6.0	5.95	14%
7 Q	6.89	0 010	60.0	6.60	4% (.4%)

[a] U, represents unquenched; Q, represents quenched. [b] The % Rx. of quenched samples is divided by 10 to account for that much longer irradiation time.

2 Uracil Uracil dissolved even less readily than did thymine in acetonitrile. Consequently the same technique of stock solution preparation was followed for uracil.

a. Stern-Volmer Quenching Studies. The method of determination of $k_q\tau$ values for uracil at different concentrations was exactly analogous to that for thymine. The initial uracil concentrations were somewhat lower

(0.40 to 0.20×10^{-3}M) and this enabled uv analysis of undiluted samples to be measured at 270 nm, thus simplifying the procedure. The Stern-Volmer data for each concentration of uracil are found in Tables XXV to XXIX and the corresponding plots in Figure I. The resulting slopes ($k_q\tau$) are listed in Table I.

b. Determination of Φ_{dim}. The determination of Φ_{dim} for uracil was again completely analogous to that for thymine. It was found that 0.042×10^{-3}M uracil dimerized and that 0.484% trans-piperylene was formed, which indicated 0.880×10^{-3}M uracil molecules were excited. A ratio of these values indicated 4.84% of excited uracil molecules actually dimerized. Lamola's value (29) of 0.40 for Φ_{isc} yields 0.019 for Φ_{dim}.

$$(\Phi_{isc}) \cdot (\text{excited uracils that dimerized}) = \Phi_{dim}$$

$$(0.40) \cdot (0.0484) = 0.019.$$

3. Cyclopent-2-enone

a. Stern-Volmer Quenching Studies. To prepare a stock solution of cyclopentenone 6.233 g were weighed into a 10 ml volumetric flask; this was diluted to the mark with acetonitrile, which resulted in a 7.59M solution. Isophthalonitrile (IPN) was used as the internal standard. Solution A of IPN (0.0556M) was prepared as follows: 71.6 mg were weighed into a 10 ml volumetric flask, then diluted to the mark. This solution was diluted 5/10 to give stock

solution B (0.0278M). Piperylene was similarly made in two stock solutions. Dilution of 687.2 mg to 10 ml gave solution A (1.01M) and 3 ml of A was further diluted to 10 ml to yield solution B (0.30M). The solutions for the run were prepared as in Table X.

Table X. Preparation of samples for Stern-Volmer quenching study of 1.52M cyclopent-2-enone.

Sample	Enone Stock		IPN Stock		Pip Stock	Diluted to
1	1 ml	+	1 ml	+	2 ml A	5 ml
2	1 ml	+	1 ml	+	1 ml A	5 ml
3	1 ml	+	1 ml	+	2 ml B	5 ml
4	1 ml	+	1 ml	+	1 ml B	5 ml
5,6	2 ml	+	2 ml	+	-0-	10 ml

The concentrations for this run are found in Table XI.

Table XI. Concentrations of samples in Stern-Volmer quenching study of 1.52M cyclopent-2-enone

Sample	[Enone], M	[IPN], M	[Piperylene], M
1	1.52	0.00556	0.40
2	1.52	0.00556	0.20
3	1.52	0.00556	0.12
4	1.52	0.00556	0.06
5,6	1.52	0.00556	0.00

Exactly 3.0 ml of each sample was placed in the constricted Pyrex tubes, degassed, sealed and irradiated for

5.3 hours. The samples were opened and analyzed by vpc using column a. The IPN had a retention time of 2.3 min.; the head-to-tail dimer, 5.5 min.; and the head-to-head dimer, 7.5 min., at 170°. Table XXXIII contains the dimer to standard ratios and Φ_0/Φ calculations. The vpc trace is reproduced in Figure X.

Plotting of these results according to the Stern-Volmer expression gives an excellent straight-line graph (Figure IV), with a slope ($k_q\tau$) of 9.1. The ratio of HT:HH dimer of 55:45 in this run is typical to that found for all cyclopentenone kinetic experiments. Several other (Tables XXX to XXXII) quenching runs were done (at enone concentrations down to 0.50M) and the slopes ($k_q\tau$) are found in Table IV.

b. Determination of Φ_{isc}. To prepare a stock solution of cyclopentenone (2.48M) 2.030 g were diluted to 10 ml. The quantity 0.681 g of cis-piperylene weighed into a 25 ml volumetric flask followed by addition of solvent to the mark gives a 0.400M stock solution. Acetone (purified by distillation from potassium permanganate) was used to make the actinometer solution. The sample solutions were prepared as in Table XII and the concentrations which resulted are listed in Table XIII. The samples were placed in tubes as before and irradiated for two hours. The tubes were opened and analysed by vpc. Column b was used to determine the percent trans-piperylene formed. By use of the relationship:

Table XII. Preparation of samples for determination of Φ_{isc} of cyclopent-2-enone.

Sample	Enone Stock		cis-Pip Stock	Diluted to
1	2 ml	+	4 ml	10 ml
2	2 ml	+	3 ml	10 ml
3	2 ml	+	2 ml	10 ml
4	2 ml	+	1 ml	10 ml
Actinometer	2 ml[a]	+	6 ml	25 ml

[a]Pure acetone.

Table XIII. Composition of samples for determination of Φ_{isc} of cyclopent-2-enone.

Sample	[Enone] M	[cis-Piperylene] M	[Acetone]
1	0.495	0.160	--
2	0.495	0.120	--
3	0.495	0.080	--
4	0.495	0.040	--
Actinometer	--	0.096	1.06M

Table XIV Results of determination of Φ_{isc} of cyclo-2-enone

Sample	% trans	ln Z[a]	^{3}[Pip]*	$\Phi_{c\rightarrow t}$	$\Phi_{c\rightarrow t}^{-1}$
Actinometer	11.2	0.224	0.0388	--	--
1	6.01	0.114	0.0328	0.846	1.18
2	7.68	0.148	0.0319	0.823	1.21
3	9.63	0.182	0.0252	0.675	1.48
4	13.36	0.274	0.0198	0.510	1.96
4a	13.15	0.277	0.0203	0.503	2.01

[a]Z represents $(0.555)/(0.555 - \%\ trans)$.

$$[\underline{\text{cis}}\text{-piperylene}]_0 \ln \frac{.555}{.555 - \% \underline{\text{trans}}} = [\text{excited triplet piperylene}]$$

The amount of triplet piperylene formed in each sample can be calculated. This value divided by the amount of triplet piperylene formed in the actinometer samples determined the $\ddagger_{c \rightarrow t}$. These results are listed in Table XIV. The $1/\ddagger_{c \rightarrow t}$ plotted versus the reciprocal cis-piperylene concentration gives a straight line whose intercept is $1/\Phi_{isc}$ (Figure VIII). The value for the intercept is 0.95. This makes $\ddagger_{isc} = 1.05$ which is within experimental error of unity.

c Reciprocal Quantum Yield. Cyclopentenone (2.5549 g) was diluted to 25 ml to give a 1.250M stock solution. Isophthalonitrile (IPN) was again used as the internal standard. Exactly 40.3 mg was dissolved in acetonitrile in a 10 ml volumetric flask, which gave a 0.0314M stock solution. The actinometer was acetophenone sensitized isomerization of cis-piperylene. To prepare this solution both the acetophenone (0.310 g) and the cis-piperylene (0.2564 g) were weighed into a 25 ml volumetric flask and diluted with solvent. This resulted in a 0.1508M cis-piperylene solution which was used directly to make the samples. The samples which contained varying enone concentrations were prepared as in Table XV.

Table XV. Preparation of samples for dependence of quantum yield on concentration of cyclopent-2-enone.

Sample	Enone Stock		IPN Stock	Diluted to	[Enone] M	[IPN] 10^{-3}M
2	2 ml	+	1 ml	10 ml	0.25	3.14
3	3 ml	+	1 ml	10 ml	0.375	3.14
4	4 ml	+	1 ml	10 ml	0.50	3.14
8	8 ml	+	1 ml	10 ml	1.00	3.14

The samples were placed in tubes and prepared as before. They were irradiated for one hour, opened and analyzed. The amount of trans-piperylene (actinometer) was measured on vpc column b and the ratio of counts of standard versus dimers were determined on column a at 170°. The total number of piperylene triplets was determined as before by use of the equation:

$$[\text{cis-piperylene}]_0 \ln \frac{.555}{.555 - \% \text{ trans}} =$$

$$0.1508 \ln \frac{.555}{.555 - .055} = 0.0157\text{M}$$

Finally, to calculate the actual quantum yields the total amount of dimers formed is found and divided by the total amount of photons absorbed (0.0157M). These values are found in Table XVI. A plot of reciprocal quantum yield versus reciprocal enone concentration (Figure III) gives a straight line which intercepts at $1/\Phi_\infty$ and has a slope of $(1/\Phi_\infty)(k_d/k_a)$. The quantum yield at infinite enone concentration is 0.36 and the ratio of rate constants is 0.06.

Table XVI. Results of dependence of quantum yield on concentration of cyclopent-2-enone.

Sample	Dim/IPN		S. F.[a]		[IPN]		Moles Dimer	Φ	Φ^{-1}
2	2.01	x	0.853	x	.00314	=	.00538	.342	2.93
3	1.90	x	0.853	x	.00314	=	.00510	.324	3.09
4	1.81	x	0.853	x	.00314	=	.00485	.308	3.25
8	1.72	x	0.853	x	.00314	=	.00460	.292	3.42

[a] S. F. represents the vpc standardization factor.

4. Cyclohex-2-enone

a. Stern-Volmer Quenching Studies. The quenching studies for cyclohexenone were done in an analogous manner to those described in detail for cyclopentenone. Ethyl stearate was used as the internal standard and had a retention time (vpc column a at 190°) of 3.0 min. The head-to-tail dimer (rt = 4.8 min) and the head-to-head dimer (rt = 6.2 min) were found in a ratio of 36/64 in all the kinetic experiments. A typical vpc trace is reproduced in Figure X. Both 1,3-pentadiene and 1,3-cyclohexadiene were used as quenchers. The results for the quenching runs at various enone concentrations are indicated in Tables XXXIV to XXXVIII, the $k_q\tau$ values in Table IV, and the plots given by the Stern-Volmer expression are in Figure IV.

b. Determination of Φ_{isc}. The determination of Φ_{isc} was done in the same manner as for cyclopentenone. The

cyclohexenone concentration was held constant (0.500M) and the cis-piperylene was varied from 0.04 to 0.16M. Acetophenone was the sensitizer for the actinometer. A plot of the results is in Figure VIII and the straight line graph gives a quantum yield for intersystem crossing of 1.05, which can be taken as unity.

c. Reciprocal Quantum Yield. Again the reciprocal quantum yield determination was done the same way as that of cyclopentenone, except for the use of ethyl stearate as the internal standard. The quantum yield at infinite enone concentration was 0.75 (average of two runs) and the ratio of rate constants (k_d/k_a) was 2.67. The results are listed in Table XL and plotted in Figure III.

d. Sensitized Formation of Dimers. Stock solutions of cyclohex-2-enone (1.25M) and phenanthrene (0.276M) were prepared in acetonitrile. These were diluted to make three samples which had the compositions as indicated in Table XVII. These concentrations were expressly chosen to vary the light absorption of the enone (also noted in Table XVII). The samples were placed in tubes, degassed and sealed as usual. After irradiation for five hours, the tubes were opened. The amount of dimer formation relative to added ethyl stearate standard was measured on vpc column a at 190°. The results are in Table XVIII.

Table XVII. Preparation of samples for phenanthrene sensitized photodimerization of cyclohex-2-enone.

Sample	[Enone] M	[Phenanthrene] M	% light absorbed by enone
0P	0.125	-0-	100
1P	0.125	0.027	32
8P	0.125	0.220	5

Table XVIII. Dependence of quantum yield of sensitized dimerization of cyclohex-2-enone on concentration of phenanthrene.

Sample	Moles Dimer	Φ_{dim} [a]
0P	0.00228	0.033
1P	0.00131	0.019
8P	0.00049	0.007

[a] Quantum yield of dimerization without added sensitizer is calculated from Figure III.

IV. LITERATURE CITED

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18. Abbreviations used throughout the paper: DNA, deoxyribonucleic acid; RNA, ribonucleic acid; T or Thy, thymine; U or Ura, uracil.

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V. APPENDIX

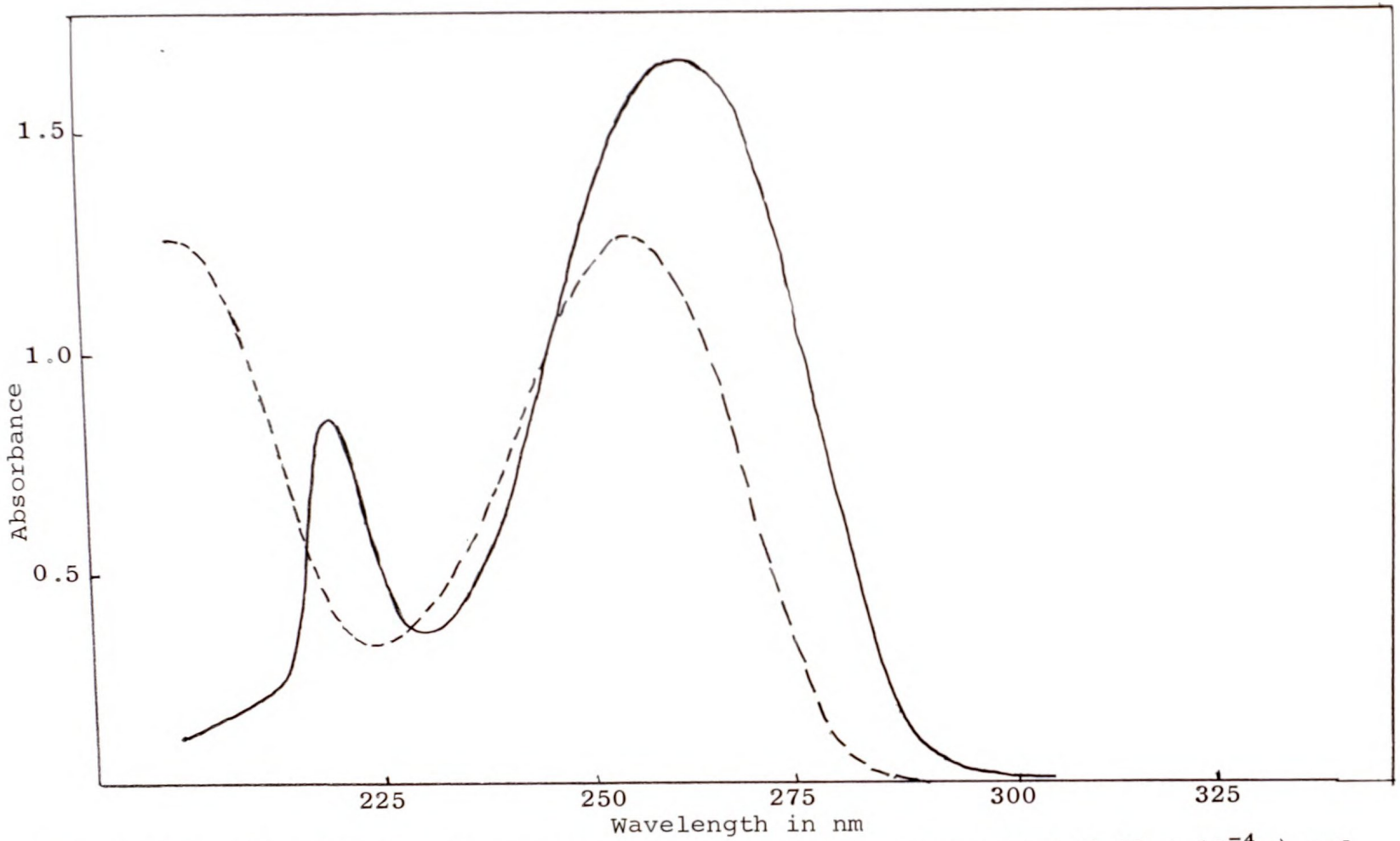

Figure VI. The ultraviolet spectra of thymine (———, represents 1.68×10^{-4}M) and uracil (— — — —, represents 1.65×10^{-4}M) in acetonitrile.

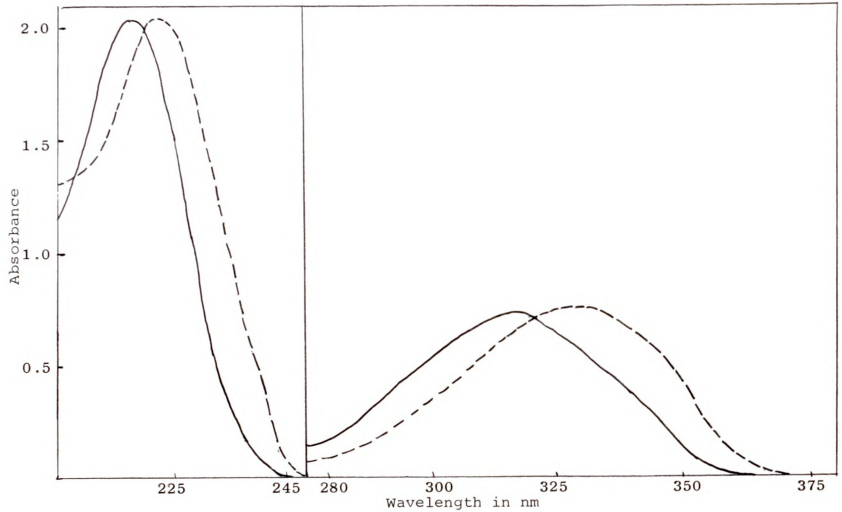

Figure VII. The ultraviolet spectra of cyclopent-2-enone (———, represents 1.48×10^{-4}M at low wavelengths and 0.0198M at high wavelengths) and cyclohex-2-enone (— — —, represents 2.00×10^{-4}M at low wavelengths and 0.0200M at high wavelengths) in acetonitrile.

Table XIX. Results for determination of Φ_{isc} for cyclohex-2-enone.

Sample[a]	[cis-Piperylene]	% Trans	$\Phi_{c\rightarrow t}$	$\Phi_{c\rightarrow t}^{-1}$
Actinometer[b]	0.096M	9.71		
Actinometer	0.096	9.61		
Actinometer	0.096	9.61		
1	0.040	10.58	0.467	2.14
2	0.080	7.15	0.610	1.695
3	0.120	5.61	0.701	1.43
4	0.160	4.53	0.753	1.33

[a]Numbered samples contained 0.500M cyclohex-2-enone.

[b]Actinometer contained 0.98M acetophenone.

Table XX. Results of Stern-Volmer quenching study of 2.99×10^{-4}M thymine[a].

Sample	[Piperylene], 10^{-5}M	$[Thy]_{disap}$, 10^{-4}	Φ_0/Φ
1	1.25	0.43	1.43
2	2.50	0.39	1.57
3	3.75	0.31	1.99
4	5.00	0.27	2.28
Φ_0	-0-	0.61	1.00

[a]Plotted in Figure I. Irradiated 2.2 hrs. A_{270nm} of 1/5 diluted Thy_0 = 0.760.

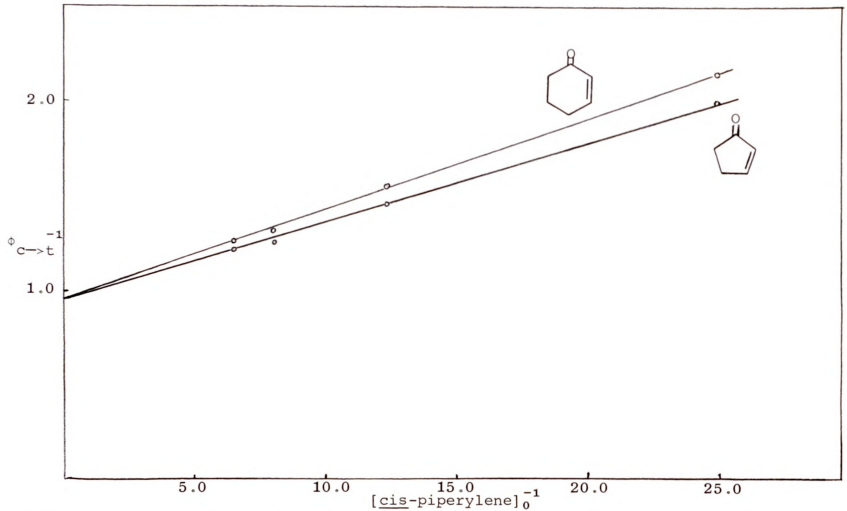

Figure VIII. Dependence of cyclopent-2-enone and cyclohex-2-enone sensitized isomerization of cis-piperylene on the concentration of diene.

Table XXI. Results of Stern-Volmer quenching study of 4.67×10^{-4}M thymine[a].

Sample	[Piperylene], 10^{-5}M	$[Thy]_{disap}$, 10^{-4}M	Φ_0/Φ
1	1.55	0.345	1.39
2	3.10	0.29	1.65
3	4.65	0.245	1.96
4	6.20	0.21	2.29
Φ_0	-0-	0.48	1.00

[a]Plotted in Figure I. Irradiated 6.0 hrs. A_{270nm} of 1/5 diluted Thy_0 = 0.835.

Table XXII. Results of Stern-Volmer quenching study of 7.30×10^{-4}M Thymine[a].

Sample	[Piperylene], 10^{-5}M	$[Thy]_{disap}$, 10^{-4}M	Φ_0/Φ
1	2.02	0.825	1.33
2	4.04	0.65	1.70
3	6.06	0.575	1.91
4	8.08	0.50	2.20
Φ_0	-0-	1.10	1.00

[a]Plotted in Figure I. Irradiated 6.6 hrs. A_{270nm} of 1/5 diluted Thy_0 = 0.926.

Table XXIII. Results of Stern-Volmer quenching study of 1.00×10^{-3}M thymine[a].

Sample	[Piperylene], 10^{-4}M	$[Thy]_{disap}$, 10^{-4}M	Φ_0/Φ
1	0.256	0.47	1.48
2	0.512	0.42	1.68
3	0.768	0.34	2.06
4	1.02	0.315	2.22
Φ_0	-0-	0.70	1.00

[a]Plotted in Figure I. Irradiated 7.2 hrs. A_{270nm} of 1/5 diluted Thy_0 = 1.283.

Table XXIV. Results of Stern-Volmer quenching study of 1.05×10^{-3}M thymine[a].

Sample	[Piperylene], 10^{-4}M	$[Thy]_{disap}$, 10^{-4}M	Φ_0/Φ
1	0.254	1.33	1.35
2	0.508	1.14	1.58
3	0.762	1.01	1.79
4	1.016	0.88	2.04
Φ_0	-0-	1.80	1.00

[a]Plotted in Figure I. Irradiated 5.0 hrs. A_{270nm} of 1/5 diluted Thy_0 = 1.351.

Table XXV. Results of Stern-Volmer quenching study of 2.12×10^{-4}M uracil[a].

Sample	[Piperylene], 10^{-5}	$[Ura]_{disap}$, 10^{-4}	Φ_0/Φ
1	2.5	0.24	1.79
2	5.1	0.19	2.25
3	7.6	0.18	2.35
4	10.1	0.165	2.64
Φ_0	-0-	0.43	1.00

[a]Plotted in Figure I. Irradiated 0.5 hr. A_{270nm} for Ura_0 = 0.756.

Table XXVI. Results of Stern-Volmer quenching study of 2.22×10^{-4}M uracil[a].

Sample	[Piperylene], 10^{-5}M	$[Ura]_{disap}$, 10^{-4}M	Φ_0/Φ
1	2.5	0.275	1.50
2	5.0	0.195	2.10
3	7.5	0.16	2.54
4	10.0	0.15	2.69
Φ_0	-0-	0.41	1.00

[a]Plotted in Figure I. Irradiates 0.5 hr. A_{270nm} for Ura_0 = 0.788.

Table XXVII. Results of Stern-Volmer quenching study of 2.89×10^{-4}M uracil[a].

Sample	[Piperylene], 10^{-5}M	$[Ura]_{disap}$, 10^{-4}M	Φ_0/Φ
1	3.1	0.24	1.50
2	6.2	0.22	1.64
3	9.3	0.125	2.88
4	12.4	0.11	3.32
Φ_0	-0-	0.36	1.00

[a]Plotted in Figure I. Irradiated 4.0 hrs. A_{270nm} for Ura_0 = 1.017.

Table XXVIII. Results of Stern-Volmer quenching study of 3.44×10^{-4}M uracil[a].

Sample	[Piperylene], 10^{-4}M	$[Ura]_{disap}$, 10^{-4}M	Φ_0/Φ
1	0.40	0.28	1.72
2	0.80	0.24	2.00
3	1.20	0.18	2.65
4	1.60	0.17	2.78
Φ_0	-0-	0.48	1.00

[a]Plotted in Figure I. Irradiated 0.5 hr. A_{270nm} for Ura_0 = 1.208.

Table XXIX. Results of Stern-Volmer quenching study of 4.37×10^{-4}M uracil[a].

Sample	[Piperylene], 10^{-4}M	$[Ura]_{disap}$, 10^{-4}M	Φ_0/Φ
1	0.51	0.34	1.64
2	1.03	0.265	2.11
3	1.55	0.19	2.94
4	2.06	0.175	3.24
Φ_0	-0-	0.56	1.00

[a]Plotted in Figure I. Irradiated 0.5 hr. A_{270nm} for Ura_0 = 1.513.

Table XXX. Results of Stern-Volmer quenching study of 0.500M cyclopent-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.040	0.921	2.02
2	0.080	0.628	2.96
3	0.133	0.421	4.41
4	0.266	0.227	8.20
Φ_0	-0-	1.86	1.00

[a]Plotted in Figure IV. Irradiated 2.0 hrs. [b]IPN, internal standard, at 5.9 x 10^{-3}M analyzed on vpc column a at 170°.

Table XXXI. Results of Stern-Volmer quenching study of 0.750M cyclopent-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.046	1.46	1.73
2	0.092	1.06	2.46
3	0.135	0.767	3.30
4	0.270	0.407	6.22
Φ_0	-0-	2.53	1.00

[a]Plotted in Figure IV. Irradiated 4.3 hrs. [b]IPN, internal standard, at 6.4 x 10^{-3}M, analyzed on vpc column a at 170°.

Table XXXII. Results of Stern-Volmer quenching study of 1.00M cyclopent-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.082	3.86	2.00
2	0.164	2.55	3.01
3	0.270	1.69	4.53
4	0.544	--	--
Φ_0	-0-	7.71	1.00

[a]Plotted in Figure IV. Irradiated 2.3 hrs. [b]IPN, internal standard, at 1.88 x 10^{-3}M, analyzed on vpc column a at 170°.

Table XXXIII. Results of Stern-Volmer[a] quenching study of 1.52M cyclopent-2-enone.

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.06	3.37	1.55
2	0.12	2.42	2.16
3	0.20	1.83	2.86
4	0.40	1.12	4.67
Φ_0	-0-	5.24	1.00

[a]Plotted in Figure IV. Irradiated 5.3 hrs. [b]IPN, internal standard, at 5.56×10^{-3}M; analyzed on vpc column a at 170°.

Table XXXIV. Results of piperylene Stern-Volmer quenching study of 0.25M cyclohex-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.0274	0.3815	1.47
2	0.0548	0.295	1.90
3	0.0915	0.208	2.69
4	0.183	0.121	4.61
Φ_0	-0-	0.5595	

[a]Plotted in Figure IV. Irradiated 4.3 hrs. [b]Ethyl stearate, internal standard, at 4.4×10^{-3}M; analyzed on vpc column a at 190°.

Table XXXV. Results of piperylene Stern-Volmer quenching study of 0.50M cyclohex-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.0294	0.540	1.48
2	0.0586	--	--
3	0.0980	0.286	2.80
4	0.196	0.173	4.62
Φ_0	-0-	0.799	1.00

[a]Plotted in Figure IV. Irradiated 3.2 hrs. [b]Ethyl stearate, internal standard, at 4.16×10^{-3}M; analyzed on vpc column a at 190°.

Table XXXVI. Results of piperylene Stern-Volmer quenching study of 0.48M cyclohex-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.015	0.967	1.25
2	0.030	0.794	1.52
3	0.049	0.639	1.89
4	0.098	0.435	2.76
Φ_0	-0-	1.205	1.00

[a]Plotted in Figure IV. Irradiated 4.5 hrs. [b]Ethyl stearate, internal standard, at 4.42×10^{-3}M; analyzed on vpc column a at 190°.

Table XXXVII. Results of piperylene Stern-Volmer quenching study of 1.00M cyclohex-2-enone[a].

Sample	[Piperylene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.029	0.719	1.43
2	0.058	0.582	1.76
3	0.097	0.446	2.30
4	0.194	0.279	3.68
Φ_0	-0-	1.026	1.00

[a]Plotted in Figure IV. Irradiated 2.7 hrs. [b]Ethyl stearate, internal standard, at 4.98×10^{-3}M; analyzed on vpc column a at 190°.

Table XXXVIII. Results of 1,3-cyclohexadiene Stern-Volmer quenching study of 0.30M cyclohex-2-enone[a].

Sample	[1,3-Cyclohexadiene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.0238	0.395	1.74
2	0.0476	0.248	2.77
3	0.0796	0.159	4.32
4	0.159	0.0824	8.34
Φ_0	-0-	0.687	1.00

[a]Plotted in Figure IV. Irradiated 3.5 hrs. [b]Ethyl stearate, internal standard, at 4.12×10^{-3}M; analyzed on vpc column a at 190°.

Table XXXIX. Results of 1,3-cyclohexadiene Stern-Volmer quenching study of 0.50M cyclohex-2-enone[a].

Sample	[1,3-Cyclohexadiene], M	Dim/Stnd[b]	Φ_0/Φ
1	0.0088	0.944	1.20
2	0.0176	0.796	1.43
3	0.0293	0.660	1.72
4	0.0585	0.420	2.70
Φ_0	-0-	1.135	1.00

[a]Plotted in Figure IV. Irradiated 3.5 hrs. [b]Ethyl stearate, internal standard, at 4.16×10^{-3}M; analyzed on vpc column a at 190°.

Table XL. Results for reciprocal quantum yield determination of cyclohex-2-enone[a].

Sample	$[Enone]_0$, M	Dim/Stnd[b]	[Dim], M	Φ[c]	Φ^{-1}
2	0.25	0.383	0.00149	0.0646	15.48
3	0.375	0.541	0.00210	0.0913	10.92
4	0.50	0.681	0.00264	0.115	8.72
8	1.00	1.18	0.00458	0.200	5.00

[a]Plotted in Figure III. [b]Based on actinometer (0.10M acetophenone and 0.104M cis-piperylene) isomerization to 11.36% trans. [c]Ethyl stearate, internal standard, at 2.11×10^{-3}M.

Sample	$[Enone]_0$, M	Dim/Stnd[a]	[Dim], M	Φ[b]	Φ^{-1}
2	0.25	0.443	0.00162	0.063	15.80
3	0.375	0.638	0.00238	0.091	10.95
4	0.50	0.801	0.00298	0.114	8.74
8	1.00	1.445	0.00537	0.207	4.84

[a]Ethyl stearate, internal standard, at 2.02×10^{-3}M. [b]Based on actinometer (0.10M acetophenone and 0.112M cis-piperylene) isomerization to 11.48% trans.

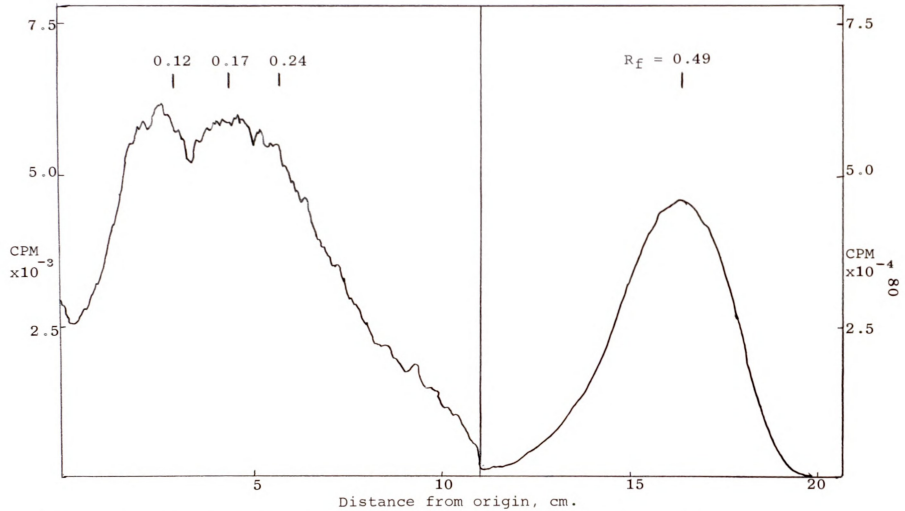

Figure IX. Strip-scan of paper chromatogram ^{14}C-labeled thymine and dimers. R_f values indicated refer to work of Johns (58).

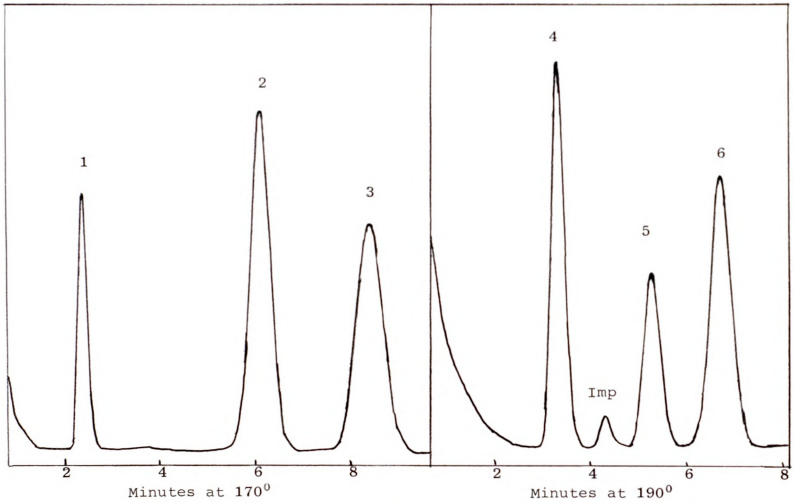

Figure X. Vapor phase chromatography traces of cyclopent-2-enone dimers (1, IPN; 2, HT-dimer; 3, HH-dimer) and cyclohex-2-enone dimers (4, ethyl stearate; 5, HT dimer; 6, HH-dimer) on column a.