This is to certify that the

thesis entitled

PART I: PHOTOENOLIZATION IN ALPHA-DIKETONES

PART II: DISPROPORTIONATION VERSUS COUPLING IN PHOTOCHEMICALLY GENERATED RADICALS

presented by

John Thomas Kondilas

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemistry

Major professor

Date March 12, 1979

PART I

PHOTOENOLIZATION IN ALPHA-DIKETONES

PART II

DISPROPORTIONATION VERSUS COUPLING IN PHOTOCHEMICALLY GENERATED RADICALS

By

John Thomas Kondilas

A DISSERTATION

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1979

ABSTRACT

PART I

PHOTOENOLIZATION IN ALPHA-DIKETONES

PART II

DISPROPORTIONATION VERSUS COUPLING IN PHOTOCHEMICALLY GENERATED RADICALS

By

John Thomas Kondilas

The photochemistry of several 1,3-diphenyl-1,2-propanediones was examined in an effort to elucidate the mechanism of photoenolization.

Unlike phenyl alkyl diketones, which undergo photoenolization competitively with photocyclization, the phenyl benzyl diketone systems fail to enolize upon photochemical excitation. This apparent lack of photochemistry was rationalized by charge-transfer complexation of the beta-phenyl ring with the excited carbonyl moiety.

Although the system provided no mechanistic information, it served as a precursor in the synthesis of 1,3-diphenyl-3-hydroxybutan-2-one. The photochemistry of the hydroxy ketone was studied in order to probe the reported inefficiency of the photoreduction of acetophenone by toluene.

John Thomas Kondilas

Upon absorption of light, the hydroxy ketone undergoes alpha-cleavage to produce an acetophenone ketyl radical and a phenylacetyl radical. Subsequent decarbonylation of the phenylacetyl radical, resulting in a benzyl radical, was found to be inefficient. This contrasts the high efficiency of decarbonylation in dibenzyl ketone and complicates the use of the hydroxy ketone for studying the inefficiency of the photoreduction. Indications for better studying the problem are offered in the conclusion.

This work is dedicated to the three most important people in my life, my parents and my wife Valorie.

ACKNOWLEDGMENTS

The author wishes to sincerely thank Professor Peter J. Wagner for his guidance, time and patience throughout the course of this work. His sense of humor and personableness have made the requirements and responsibilities at Michigan State a much easier task.

I would also like to extend my deepest gratitude to my fellow members of the Wagner group. Their technical assistance and friendship will always be remembered.

Finally, I would like to thank my wife Valorie, whose typing and retyping of the thesis, structural assistance and encouragement proved invaluable.

TABLE OF CONTENTS

Page

LIST OF TABLES

Table | Page

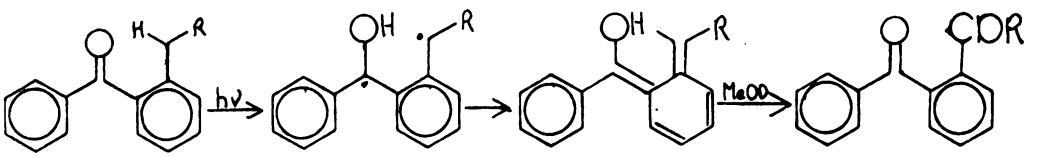
LIST OF FIGURES

PART I

PHOTOENOLIZATION IN ALPHA-DIKETONES

INTRODUCTION

Photoenolization of ketones was first detected by Yang and Rivas in 1961.[1] They studied the photoreduction of benzophenone in the presence of hydrogen atom donors. They noted the formation of benzpinacol via a ketyl radical. However, if benzophenone was substituted in the ortho position with an alkyl group bearing alpha-hydrogens, benzpinacol formation was suppressed completely. Intramolecular hydrogen abstraction predominates in the latter.



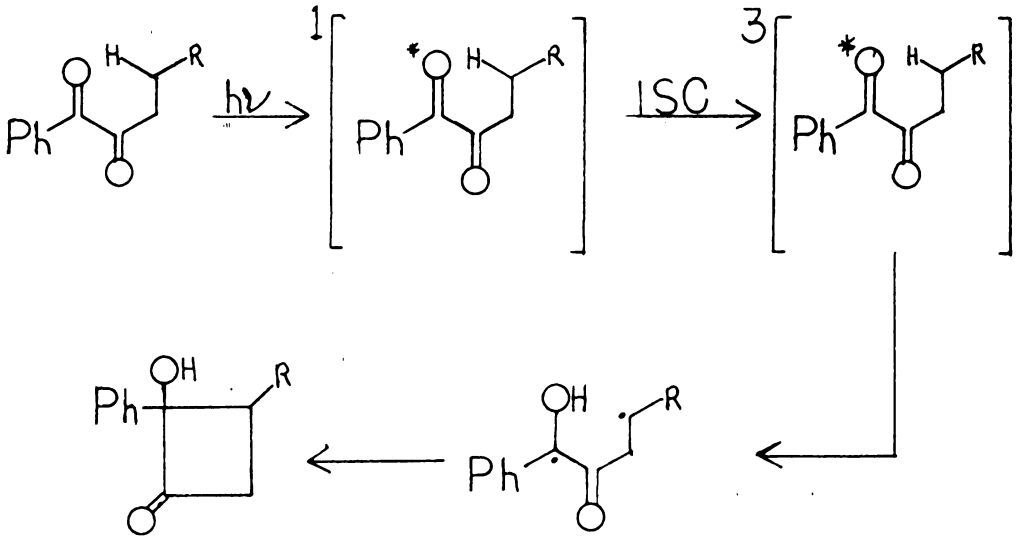
(1)

Deuterium incorporation in the photoproduct led to the identification of the enol intermediate.

The chemistry of alpha-diketones parallels that of monoketones. Type I cleavage is an important reaction in the vapor phase of many alpha-diketones. In solution, the major reactions of alpha-diketones are cyclization[2] and enolization.[3]

Cyclization occurs in alpha-diketones which have

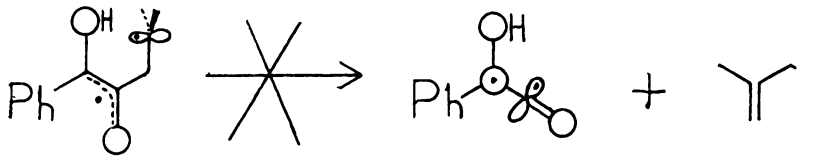
hydrogens gamma to the number-one carbonyl group. The reaction proceeds by the following mechanistic scheme:



(2)

Initial absorption of light produces an excited singlet which then intersystem crosses to the excited triplet. It is from the excited triplet state that hydrogen atom abstraction occurs to produce a 1,4-biradical. The hydrogen atom abstraction step is revertible. Therefore, the 1,4-biradical may cyclize to the hydroxycyclobutanone or may yield ground state diketone.[4]

Type II cleavage does not occur in alpha-diketones. This failure arises from the perpendicular orientation of the C-1 p orbital relative to the C-2, C-3 sigma bond in the biradical. For cleavage to occur, the two p orbitals should be parallel to the carbon-carbon sigma bond being broken. Such is not the case in alpha-diketones, as shown in equation 3.[5]



(3)

General Mechanistic Process

Before any further discussion on photoenolization of alpha-diketones is presented, a brief description of the fate of the electronic excitation is necessary to attain a better understanding of the mechanism.

A modified Jablonski diagram,[6] Figure 1, illustrates the fate of a molecule absorbing light. Initial excitation occurs vertically, according to the Frank-Condon principle, populating one of the upper singlet states, S_3. It then rapidly decays ($\sim 10^{12} sec^{-1}$) to the first excited singlet state by internal conversion. The lowest singlet state may decay to ground state by either fluorescence, k_f, or radiationless decay, k_i. It may also intersystem cross to the lowest excited triplet state, k_{isc}. For phenyl ketones, intersystem crossing is generally much faster than fluorescence or radiationless decay and usually occurs with unit efficiency.[7] The excited triplet state may then proceed to ground state by either radiationless decay, k_d, phosphorescence, k_p, or energy transfer to a quencher molecule, k_q. The triplet may also react to form a biradical intermediate, followed by product formation.

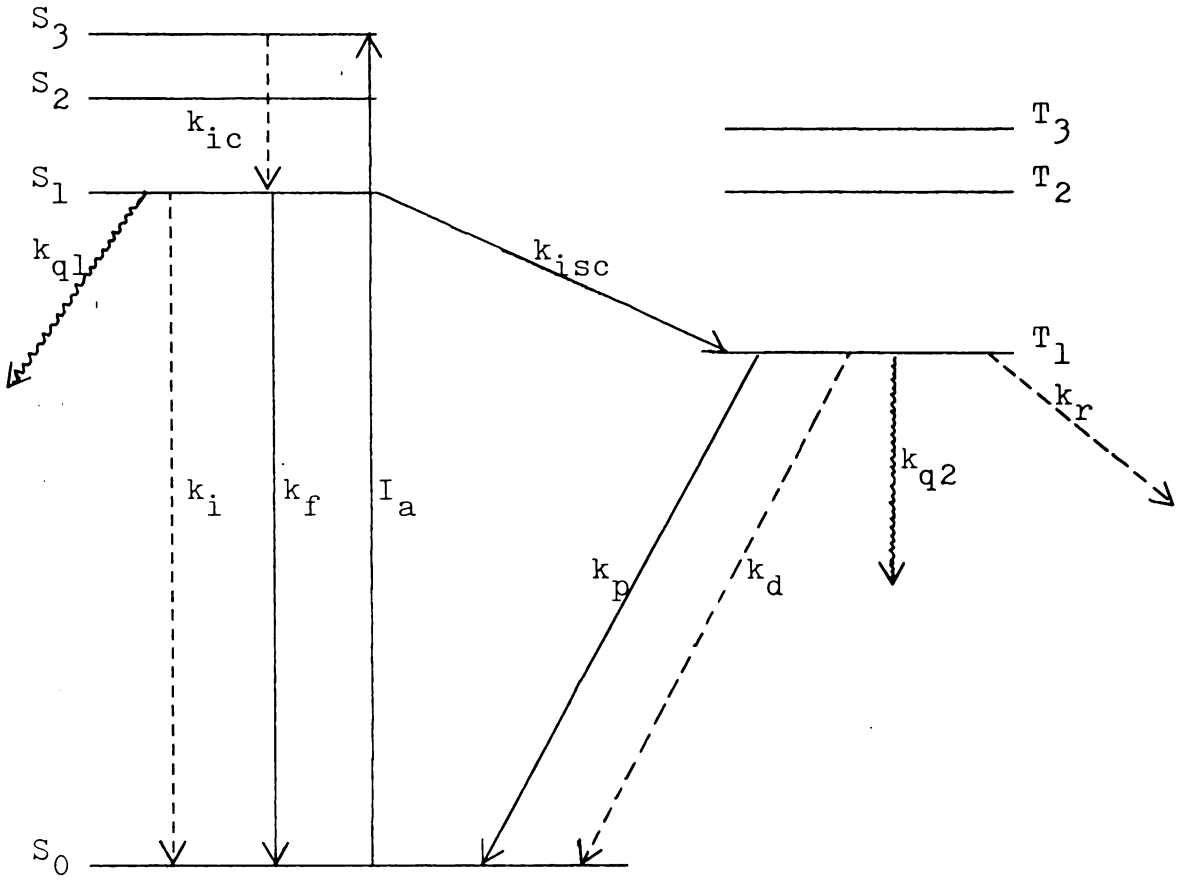


Figure 1. Modified Jablonski diagram. Solid arrows represent radiative processes, corresponding to absorption or emission of light. Dashed and wavy lines represent non-radiative unimolecular and bimolecular processes respectively.

Kinetic Expressions

In order to obtain information about the paths by which an electronically excited molecule disposes of its energy, the term quantum yield must be defined. The quantum yield, Φ, is simply:[8]

$$\Phi = \frac{\text{number of molecules undergoing a photoreaction}}{\text{number of quanta absorbed by the system}} \quad (4)$$

and is the only kinetic parameter associated with a photoreaction that is directly measurable under steady state conditions. For a particular photoreaction, the quantum yield is defined by the following equation:

$$\phi_i = \phi_{ES}\phi_R P_i \tag{5}$$

where ϕ_{ES} represents the probability that absorbed light will produce the requisite excited state; ϕ_R is the probability that the excited state will undergo the primary photoreaction necessary for process i; P_i is the probability that any metastable ground state intermediate will proceed to stable product.[9]

In terms of rates, the quantum yield (ϕ^o) for product formation in the absence of quencher is expressed as:

$$\phi^o = \frac{k_r}{k_r + k_d} \tag{6}$$

where k_r is the rate constant for the particular reaction and k_d is the summation of first order rate constants for deactivation of the excited state undergoing reaction. In the presence of added quencher, the expression for the quantum yield becomes:

$$\phi = \frac{k_r}{k_r + k_d + k_q[Q]} \tag{7}$$

where k_q is the rate constant for the bimolecular quenching process by quencher, Q, and is generally diffusion

controlled. Dividing equation (6) by (7) we obtain:

$$\Phi^{o}/\Phi = \frac{k_r + k_d + k_q[Q]}{k_r + k_d} \qquad (8)$$

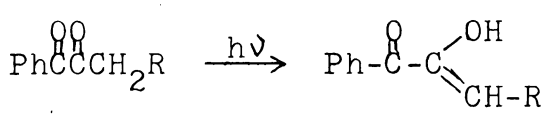
By slight manipulation of equation (8), we arrive at the familiar Stern-Volmer expression:

$$\Phi^{o}/\Phi = 1 + k_q \tau_o [Q] \qquad (9)$$

where τ_o is the reciprocal of the sum of the rates of all reactions undergone by the excited state and therefore represents the lifetime of the excited state in the absence of quencher.[10]

Previous Study of Diketone Photoenolization

Recent work in the area of photoenolization of alpha-diketones was reported by Wagner and Turro.[11] They studied the photoreactions of phenyl alkyl diketones and discovered that enolization (Equation 10) competes with cyclization.



(10)

In diketones bearing no gamma hydrogens, photoenolization proceeds very efficiently. No product formation arises from hydrogen abstraction gamma to the number-two carbonyl, in that no benzoylcyclobutanol formation was detected. Some of the results of this work are provided in Table 1.

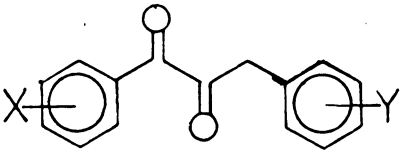
Table 1. Kinetic Parameters for Photoreactions of Phenyl Alkyl Diketones PhCOCOR[a]

Diketone	R	Φ_{CB}[b]	Φ_{-DK}[b]	$10^{-3}k_q\tau$;M^{-1}[b]	k_γ,$10^5 s^{-1}$	(k_d+k_e),$10^5 s^{-1}$
1	CH_3	-	0.01	190	-	0.25(0.05)
1-D	CD_3	-	-	-	-	(0.045)
2	CH_2CH_3	0.04(0.043)	0.50(0.23)	30	0.10	1.6(2.5)
2-D	CD_2CH_3	(0.052)	(0.12)	(38)	-	(1.2)
3	$CH_2CH_2CH_3$	0.52(0.40)	0.73(0.45)	9.1(7.6)	3.9	1.6(2.7)
3-D	$CD_2CH_2CH_3$	(0.37)	(0.38)	(9.0)	-	(1.9)
4	$CH_2CH(CH_3)_2$	0.81(0.60)	0.88(0.65)	3.4(1.7)	13.0	1.8
5	$CH_2CHMeEt$	0.80	0.89(0.63)	(1.7)	-	-
6	$CH_2C(CH_3)_3$	-	0.62	22	-	2.3
7	$CH(CH_2CH_3)_2$	0.015	0.53	0.19	5.0	260.0
8	$C(CH_3)_3$	0.28	-	1.04	36.0	-
o-Cl-3	$CH_2CH_2CH_3$	0.29	0.67	6.5	3.5	3.2
p-MeO-3	$CH_2CH_2CH_3$	0.56	0.81	12.0	3.3	0.9

[a]Irradiation of 0.05 M diketone at 365 nm in sealed, degassed tubes.
[b]Values in parentheses are for 0.2 M diketone for 3 and 4, 0.06 M for 2.

Objectives

This research effort was directed at elucidating the mechanism of photoenolization. A system was chosen in which enolization was reported to be the priniciple photoreaction[12] in order to eliminate the effects of structure-reactivity upon competing photoprocesses. The system chosen was:



(11)

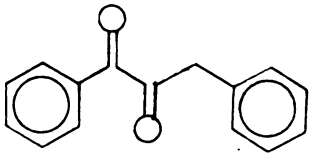
By altering the substituents on the phenyl rings, it was hoped that information on the mechanism would be obtained.

The method chosen for monitoring the photoprocess was ultraviolet-visible spectroscopy. The diketones are yellow in color, whereas the enols are colorless. Therefore, monitoring the disappearance of the n-π* absorption of the diketone in the visible region would provide the kinetic data for enol formation, providing that enolization is the only photoprocess occuring.

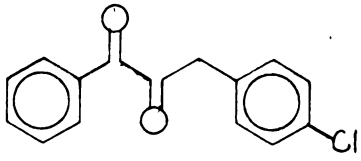
RESULTS

In order to obtain mechanistic information pertaining to photoenolization, both electron-donating and electron-withdrawing substituents on the phenyl rings were examined. The following diketones were synthesized:

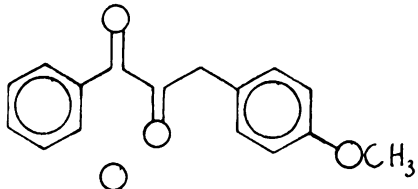
(A)



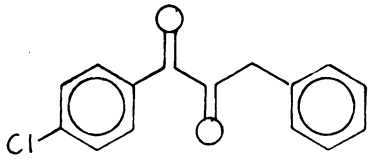
(B)



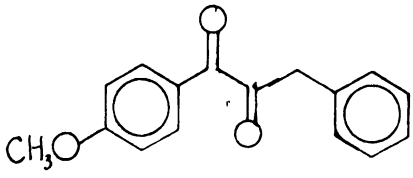
(C)



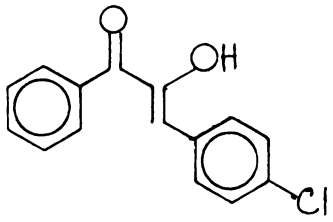
(D)



(E)



Also, in the course of recrystallizing the p-Cl-diketone (B) from 90% ethanol, tautomerization occurred, generating the enol (F):

(F) 

The enol was a quite stable solid and provided useful spectroscopic information.

Benzene solutions, from 0.02 M to 0.05 M in diketone (A) were degassed and irradiated in parallel at 366 nm, relative to a benzophenone sensitized cis-piperylene actinometer. Analysis of the extent of photoreaction was conducted after 4, 12, 36, and 62 hours of irradiation. In all cases, the yellow color remained intense and the visible spectrum indicated no disappearance of diketone.

It was then decided to conduct the photolysis at 313 nm, since the intensity of light was greater at this wavelength. Appropriately concentrated solutions of diketone (A) were prepared, degassed and irradiated versus a valerophenone actinometer. Again no disappearance of diketone occurred.

Photolysis of diketone (A) was also conducted at 435 nm, to check the possibility of a wavelength dependent photoreaction. No photoreaction at this wavelength was detected, however. Diketone (B) gave the same results. Photolysis of diketone (B) in the presence of its enol (F) gave no change in concentration of (F). Different solvents also had no effect upon the results, or

lack of, as the case may be.

Preliminary photolysis of diketone (A) in benzene indicated an apparent photoreaction. After several days irradiation at 313 nm, the yellow color faded. UV analysis of the product showed disappearance of the shoulder of the long wavelength n-π* band. This was believed to be the result of photoenolization and no further attempt was made to analyze the photoproduct. After photolysis, polymeric material was found coated to the inner walls of the tube. However, this was attributed to the polymerization of benzene. If enolization had indeed occurred, the inefficiency of the reaction would preclude the use of this system in a mechanistic study.

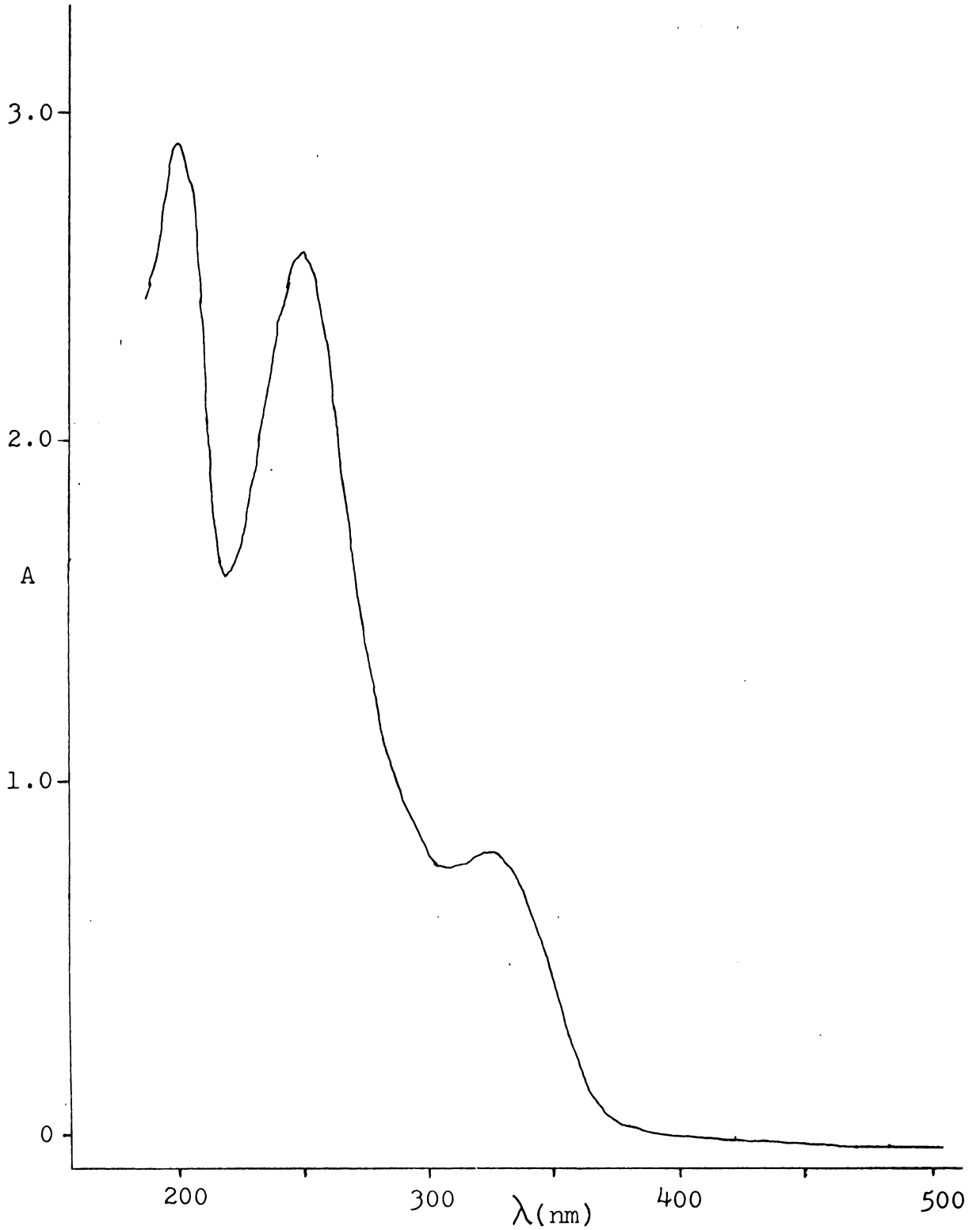


Figure 2. UV spectrum of 3.3×10^{-4} M diketone (A) in n-heptane.

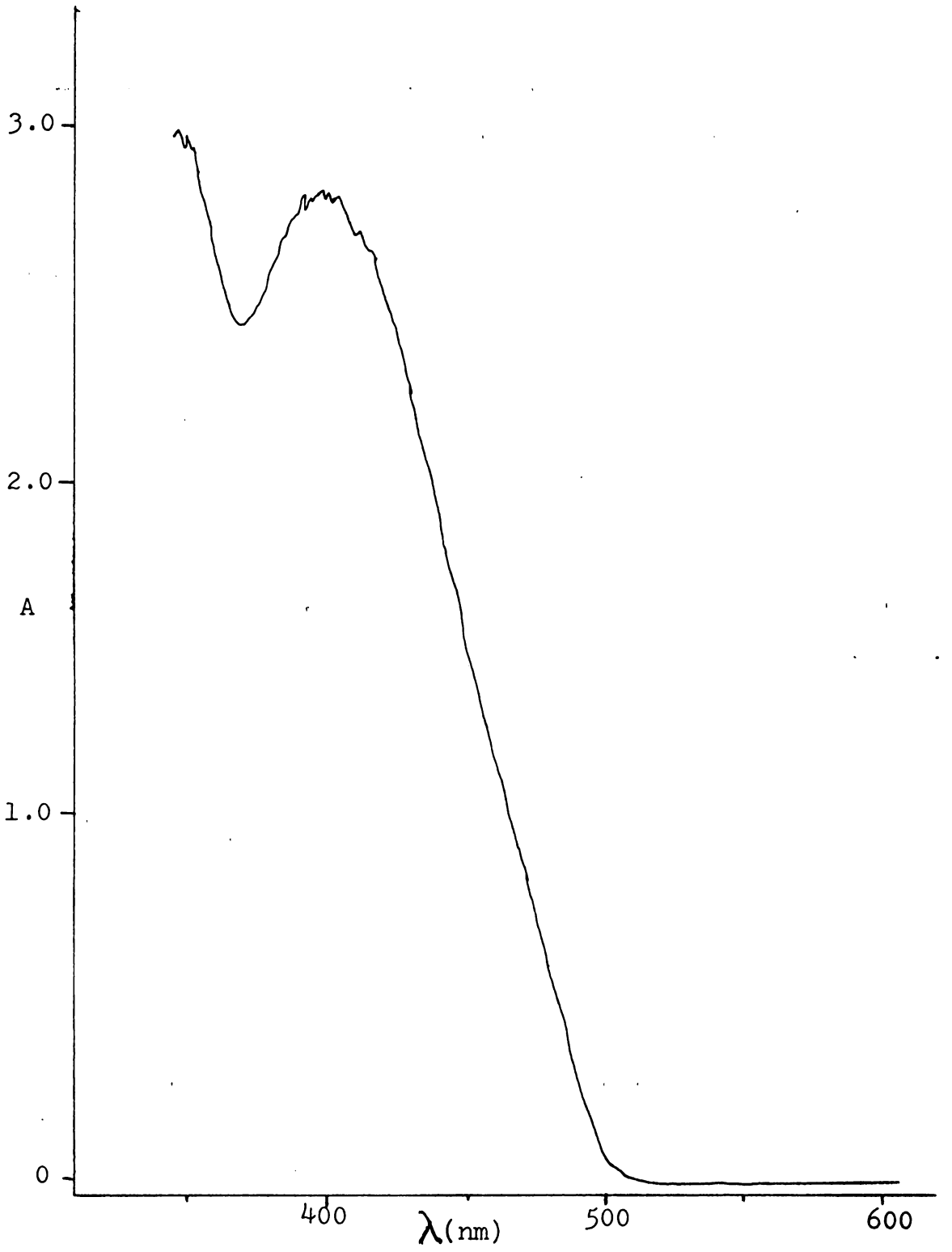


Figure 3. UV spectrum of 0.06 M diketone (A) in n-heptane.

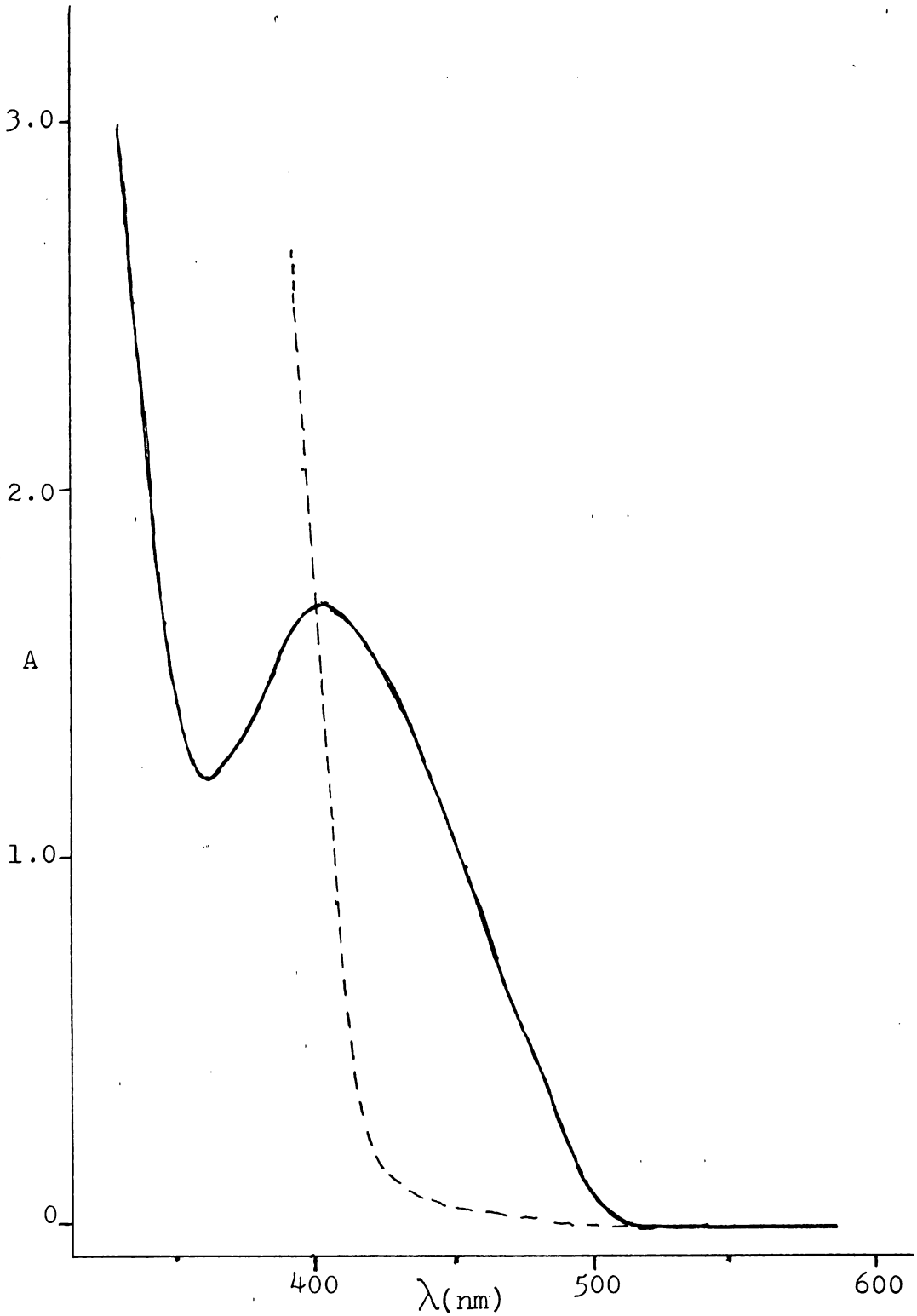


Figure 4. Solid line represents UV spectrum of 0.037 M diketone (B) in benzene and dashed line represents UV spectrum of 0.035 M enol (F) in benzene.

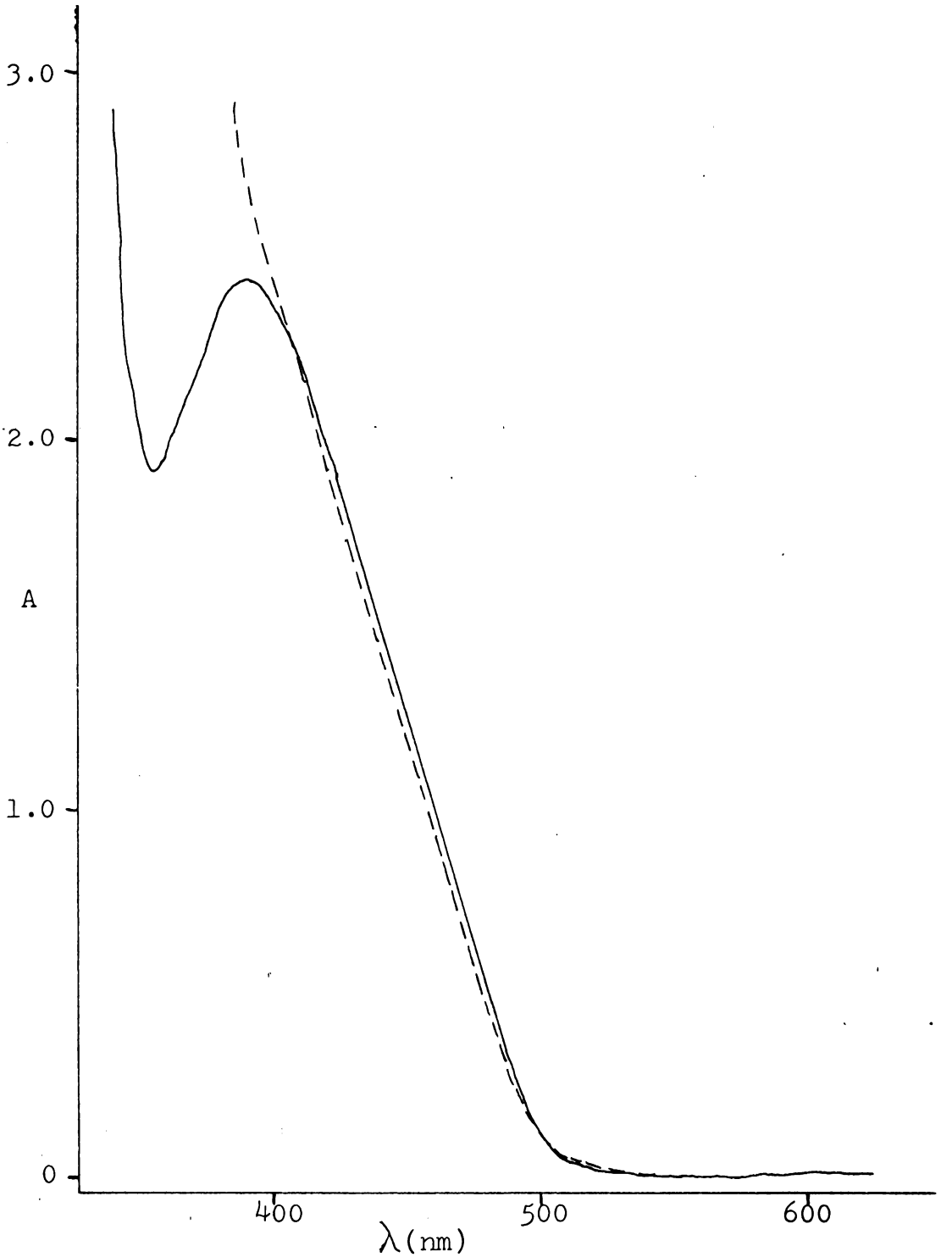
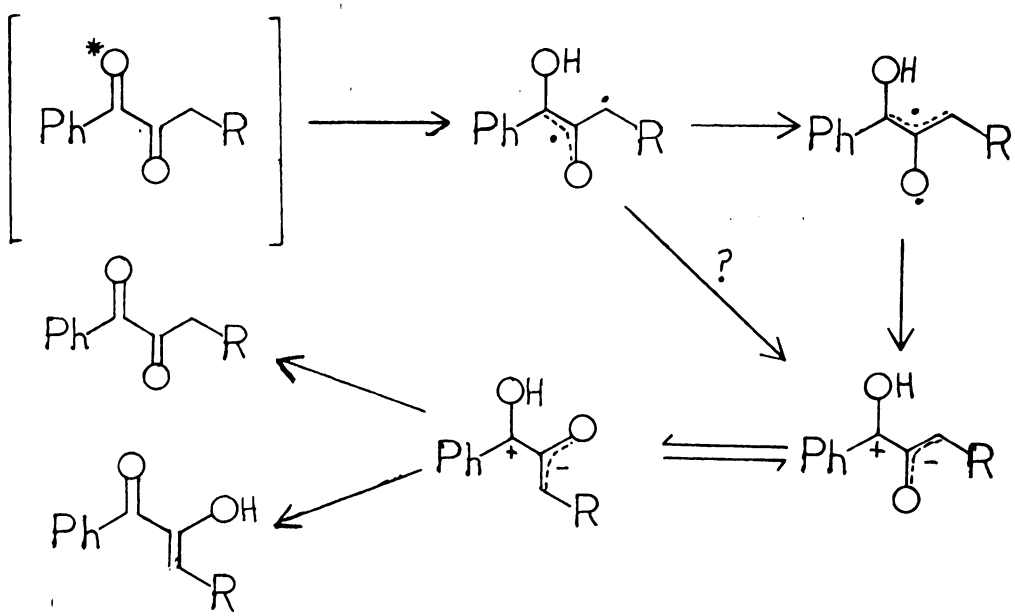


Figure 5. Solid line represents UV spectrum of 0.05 M diketone (A) in benzene prior to photolysis; dashed line shows UV spectrum of the result of 16 hours photolysis at 313 nm.

Discussion

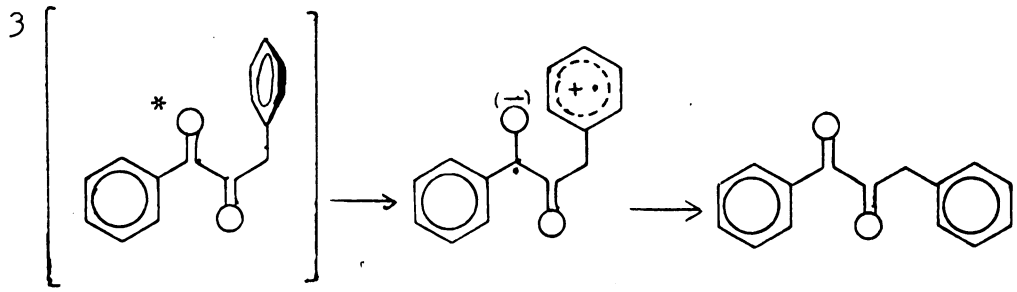
A postulated mechanism for photoenolization involves a 1,4-hydrogen transfer by the excited triplet to yield a relatively stable oxyallyl system. Intersystem crossing of the triplet to the ground state surface, followed by a proton shift to either end of its enolate moiety would yield product enol and ground state diketone. This mechanism is illustrated below:[13]



(12)

Substitution of the R group by a phenyl group might have a dramatic effect on the rate of deactivation of the triplet ketone. Studies of beta-phenyl substituted dialkyl ketones reveal low photoreactivities for these systems.[14] Beta-phenyl substitution in butyrophenone decreases its triplet lifetime in benzene by two orders of magnitude. An explanation for the apparent lack of photoreactivity may be a rapid irreversible, intramolecular

quenching process by the beta-phenyl ring competing with enolization. A charge transfer interaction would occur resulting in exciplex formation. The metastable product would have to revert to ground state diketone with near 100% efficiency.[15]



(13)

Enlightement[16]

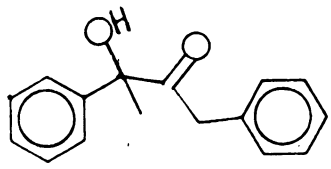
Although the results of this profect were not revelatory with respect to the mechanism of photoenolization, the alpha-diketone (A) provided a route for the preparation of a related compound, whose photochemistry was also of interest. Addition of methyl Grignard to the diketone gives an alpha-hydroxy ketone, whose Type I photochemistry could reveal information on the extent of disproportionation versus coupling in photochemically generated radicals.

PART II

DISPROPORTIONATION VERSUS COUPLING IN PHOTOCHEMICALLY GENERATED RADICALS

INTRODUCTION

The purpose of this research was to study the extent of two competing processes of photogenerated radicals, disproportionation and coupling. The reported inefficiency of acetophenone photoreduction by toluene[17] stimulated an effort to determine the amount of in-cage disproportionation between acetophenone ketyl radicals and benzyl radicals. A system was chosen, which upon photochemical excitation, could produce both radicals. The molecule studied was 1,3-diphenyl-3-hydroxybutan-2-one:



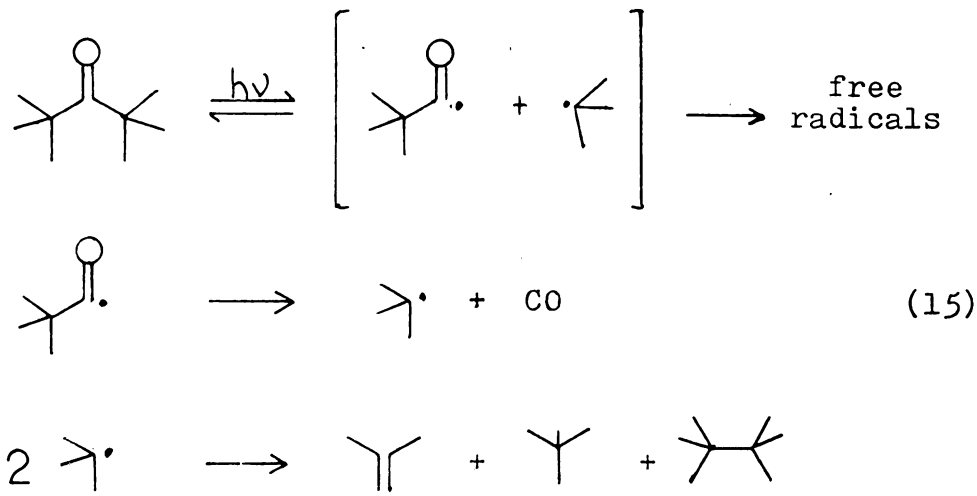
(14)

The molecule is a slight modification of dibenzyl ketone, whose photoreactions have been thoroughly investigated and to which parallel may be drawn.[18]

Norrish Type I Cleavage

The formation of radicals from the photolysis of ketones is called Norrish type I cleavage. Homolysis of the 1,2 bond results in the formation of an acyl and alkyl radical pair in acyclic aliphatic ketones. Type I

or alpha cleavage also occurs in other classes of compounds, such as acyl halides, acids, and aldehydes, to name a few. Secondary reactions depend upon structural features of the radicals. Decarbonylation, disproportionation, coupling and radical substitution are available paths, as shown in the scheme below:[19]



(15)

Alpha cleavage processes in solution are of minor importance if the excited state can undergo other processes, such as Norrish type 2 reactions. Decarbonylation often occurs during alpha cleavage reactions in the gas phase, but only when the alkyl radical is very stable does it occur in solution.[20]

Background

Decarbonylation is found to be very efficient when a t-butyl or benzyl radical is produced. Upon irradiation of dibenzylketone, a statistical ratio of coupling products is found in agreement with the intermediacy of completely

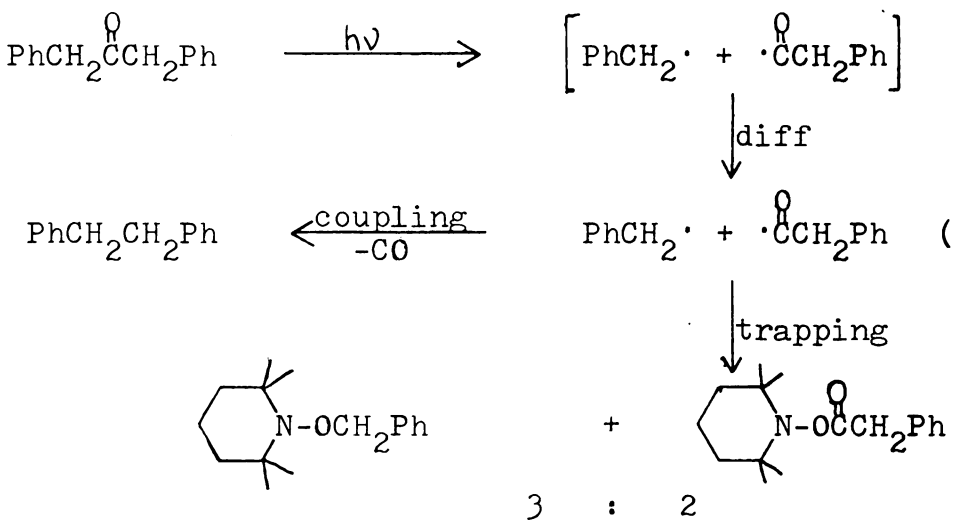
free radicals.[21]

$$\begin{array}{ccccc} PhCH_2\text{-}CO\text{-}CH_2Ph & & PhCH_2CH_2Ph & & \\ + & \xrightarrow{h\nu} & PhCH_2CHPh_2 & 93\%,\ 1:2:1 & (16) \\ Ph_2CH\text{-}CO\text{-}CH_2Ph & & Ph_2CHCHPh_2 & & \end{array}$$

Engel studied the photochemistry of dibenzyl ketone, in an effort to determine the nature of the excited state.[22] The decarbonylation proceeds in 100% yield with a quantum efficiency of 0.7 at 313 nm. Quenching studies were performed with two dienes. He found that 1,3-cyclohexadiene decreases the efficiency of CO formation more than it inhibits ketone disappearance. This effect was attributed to capture of the short-lived phenacetyl radicals by diene. The fluorescence quantum yield was determined to be 0.04, with a singlet lifetime of 3.6 nsec. Since 1,3-pentadiene inhibited dibenzyl ketone disappearance much more than it quenched its fluorescence, decarbonylation was thought to proceed via the excited triplet state, whose lifetime is 10^{-10} sec. Robbins and Eastman studied photoreactions of substituted dibenzyl ketones and found that the p-dicyano ketone fails to decarbonylate.[23] This failure arises from internal triplet quenching of the carbonyl by the lower triplet energy cyanobenzene moiety. That decarbonylation occurs from the triplet state has also been verified by CIDNP studies.[24]

The decarbonylation reaction was shown to occur in a

stepwise fashion, proceeding through a short-lived phenacetyl radical. Tri-n-butyltinhydride was ineffective in reducing the radical. Therefore, 2,2,6,6-tetramethylpiperidine-1-oxyl radical was employed. Both benzyl and phenacetyl radicals were trapped giving a 3:2 ratio of benzyl ether to phenyl acetate.



The formation of phenylacetate indicates that photodecarbonylation proceeds via a two-step mechanism involving the formation of the phenacetyl radical outside of a solvent cage. The rate of decarbonylation was determined to be of the order of 10^{-8} sec.[25]

Turro has recently reported the effect of irradiation of dibenzyl ketone in detergent solution.[26] Above the critical micelle concentration, detergent molecules aggregate to form globular micelles, having a hydrocarbon interior and a hydrophilic exterior. Control of the ketone/detergent ratio allows the photolysis of a single

molecule within a micelle. Photolysis of an unsymmetrical dibenzyl ketone, ACOB, resulted in formation of in cage coupling products, A-B, exclusive of out of cage coupling products, AA and BB.

$$PhCH_2\overset{O}{\overset{\|}{C}}CH_2Ar \xrightarrow{h\nu} PhCH_2CH_2Ph + PhCH_2CH_2Ar + ArCH_2CH_2Ar \qquad (18)$$

ACOB	AA	AB	BB
Homogeneous	25%	50%	25%
Detergent Solution	0%	100%	0%

Photoreduction of Acetophenone

The photoreduction of acetophenone in solution proceeds by intermolecular hydrogen abstraction from a donor molecule by the excited acetophenone triplet. This results in the formation of hydrogen donor radicals and ketyl radicals of acetophenone. These radicals may then undergo characteristic reactions depending on the conditions employed, as shown below:

$$PhC(=O)CH_3 + DH \underset{}{\overset{h\nu}{\rightleftharpoons}} PhC(OH)(\cdot)CH_3 + D\cdot$$

$$2PhC(OH)(\cdot)CH_3 \longrightarrow Ph\text{-}C(OH)(CH_3)\text{-}C(OH)(CH_3)\text{-}Ph \qquad (19)$$

$$2D\cdot \longrightarrow D\text{-}D$$

$$PhC(OH)(\cdot)CH_3 + D\cdot \longrightarrow Ph\text{-}C(OH)(CH_3)\text{-}D$$

A study of the photoreduction of acetophenone in toluene was reported by Wagner and Leavitt.[27] The efficiency of the reaction is governed by the formation of products from radical coupling. The kinetics of the reaction follow the equation below:

$$\Phi_{BB}^{-1} = Y_{BB}^{-1} P^{-1} \left[1 + \frac{k_d}{k_r [Tol]} \right] \qquad (20)$$

Y_{BB} represents the actual yield of bibenzyl: P is the probability that intermediates other than the excited state proceed on to products rather than revert to ground state; $[Tol]$ is the molar concentration of toluene; k_d is the rate of radiationless decay of the triplet; k_r is the bimolecular rate constant for interaction of the ketone triplet with substrate.

Rate constants were determined from Stern-Volmer quenching plots, assuming that the rate of radiationless decay was constant. Analysis of the double reciprocal plot gave a probability factor of 0.33 for acetophenone and benzyl radicals proceeding to products. This low probability for product formation might arise from disproportionation of the acetophenone and benzyl radicals within a solvent cage resulting in ground state reactants. This consideration is the focus of this research.

RESULTS

Quantum Yield Determination

Quantum yields for product formation were determined by irradiation at 313 nm in a merry-go-round apparatus at 25° C. Solutions of 0.05 M hydroxy ketone in various solvents containing internal standards were irradiated in parallel with degassed benzene solutions of 0.1 M valerophenone, which served as an actinometer.[28] Irradiations were kept below 10% conversion of ketone. Product analysis was determined by comparison to an internal standard as measured by vpc. The quantum yield for disappearance of ketone was determined at 20% conversion in benzene and found to be approximately 0.40.

Absorption and Emission Spectra

The UV spectrum of the hydroxy ketone was taken in spectro-grade n-heptane and is provided in Figure 6. The spectrum shows the n-π^* shoulder in the 313 nm region where the sample is irradiated.

The fluorescence spectrum was measured at room temperature in n-heptane (Figure 7). The quantum yield of fluorescence was determined by comparison of the

fluorescence spectrum of acetone, whose quantum yield is known.[29] The absorbances of the two solutions were matched at 313 nm, which was the excitation wavelength employed. Correction was made for the trivial absorbance by solvent. The value obtained for the fluorescence quantum yield of the hydroxy ketone is 0.03.

Chemically Induced Dynamic Nuclear Polarization[30]

CIDNP experiments were run on 0.2 M solutions of hydroxy ketone in C_6D_6 and CD_3CN. A weak enhanced absorption was detected in the proton nmr spectrum at 9.6 ppm, for the aldehydic proton of phenylacetaldehyde. The multiplicity of the radical pair is determined by the following equation.[31]

$$\Gamma = \epsilon \cdot \Delta g \cdot a \cdot \mu = (+) \qquad (21)$$

where Γ represents either enhanced absorption (+) or emission (-); ϵ is (+) for recombination or disproportionation products and (-) for products from out of cage; Δg is a constant for a particular system, in this case (+); a is (+) for a beta hydrogen; μ is (+) when the radical pair is formed from a triplet precursor and (-) when formed from a singlet precursor. In that there is enhanced absorption from the in-cage radical pair, the excited state is the triplet.

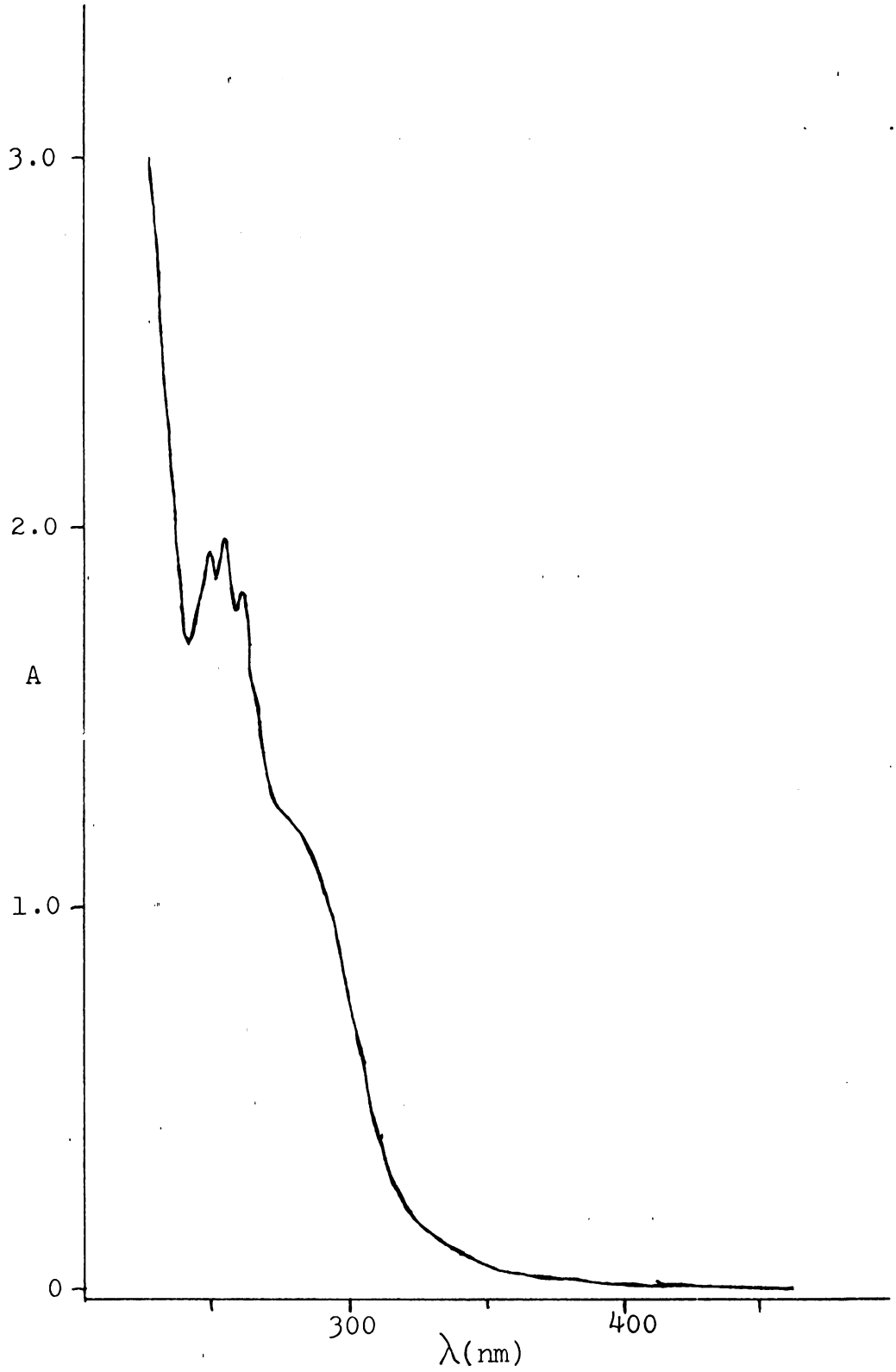


Figure 6. UV spectrum of 0.0012 M hydroxy ketone in n-heptane.

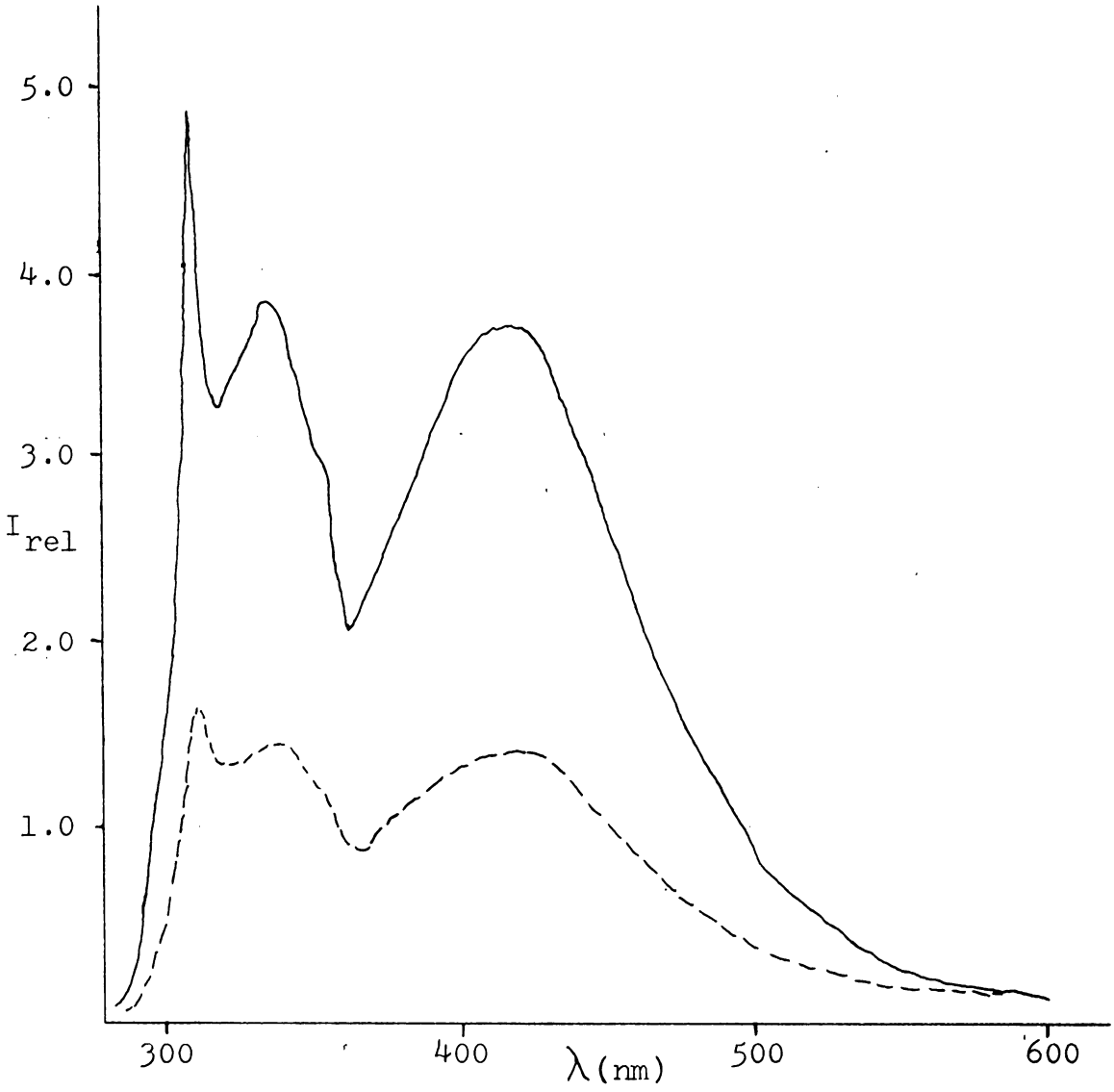


Figure 7. Fluorescence spectra. Solid line represents 0.006 M HK and dashed line represents 0.20 M acetone in n-heptane at 25° C.

Table 2. Photolysis of 0.022 M HK in Benzene, ~40% Conversion.

Photoproduct	Quantum Yield
Tol	0.013
PAA	0.060
AP	0.19
BB	0.056
Alc	0.045
Pin	0

Table 3. Photolysis of 0.05 M HK in Benzene, ~5% Conversion.

Photoproduct	Quantum Yield
Tol	0
PAA	0.044
AP	0.28
BB	0.052
Alc	0.030
Pin	0

Table 4. Photolysis of 0.043 M HK in Hexane, ~7% Conversion.

Photoproduct	Quantum Yield
Tol	0.012
PAA	0.047
AP	0.34
BB	0.079
Alc	0.01
Pin	0

Table 5. Photolysis of 0.05 M HK in t-Butyl Alcohol, ~2% Conversion.

Photoproduct	Quantum Yield
Tol	0
PAA	0.025
AP	0.10
BB	0.009
Alc	0.009
Pin	0

Table 6. Photolysis of 0.05 M HK in Benzene with Benzene Thiol Present, ~2% Conversion.

Photoproduct	Quantum Yield
Tol	0.13
PAA	0.10
AP	0.30
BB	0
Alc	0.018
Pin	0

[a]Values obtained from 2 different concentrations of benzene thiol, 0.026 M and 0.0321 M.

Table 7. Photolysis of 0.01 M HK in a Micellar Solution, Micelle = Hexadecyltrimethylammonium Chloride ~1% Conversion.

Photoproduct	Quantum Yield [HDTCl] = 0.5 M[a]	0.3 M[b]
Tol	0	.022
PAA	.02	.11
AP	.056	.21
BB	0	0
Alc	0	0
Pin	0	0

[a]Organic material extracted with ether after photolysis.
[b]Direct on-column injection of aqueous photolysis mixture.

Table 8. Photolysis of 0.05 M HK in Benzene with Acetophenone Pinacol[a] Present, ~7% Conversion.

Photoproduct	Quantum Yield
Tol	0
PAA	0.043
AP	0.28
BB	0.041
Alc	0.019
Pin	No Disappearance

[a]Pin = 0.0045 M, before and after photolysis.

Table 9. Response Factor Analysis.

Photoproduct	Abbreviation	Response Factor
Toluene	Tol	Tol/C_7[a] = 1.12
		Tol/C.O.[b] = 1.22
Phenylacetaldehyde	PAA	PAA/C_{19} = 3.0
Acetophenone	AP	AP/C_{19} = 3.0
Bibenzyl	BB	BB/C_{19} = 1.56
1,2-Diphenyl-2-propanol	Alc	Alc/C_{19} = 1.80
Acetophenone pinacol	Pin	Pin/C_{19} = 1.62
Hydroxy ketone	HK	HK/C_{19} = 1.5
		AP[c]/C_{13} 1.1

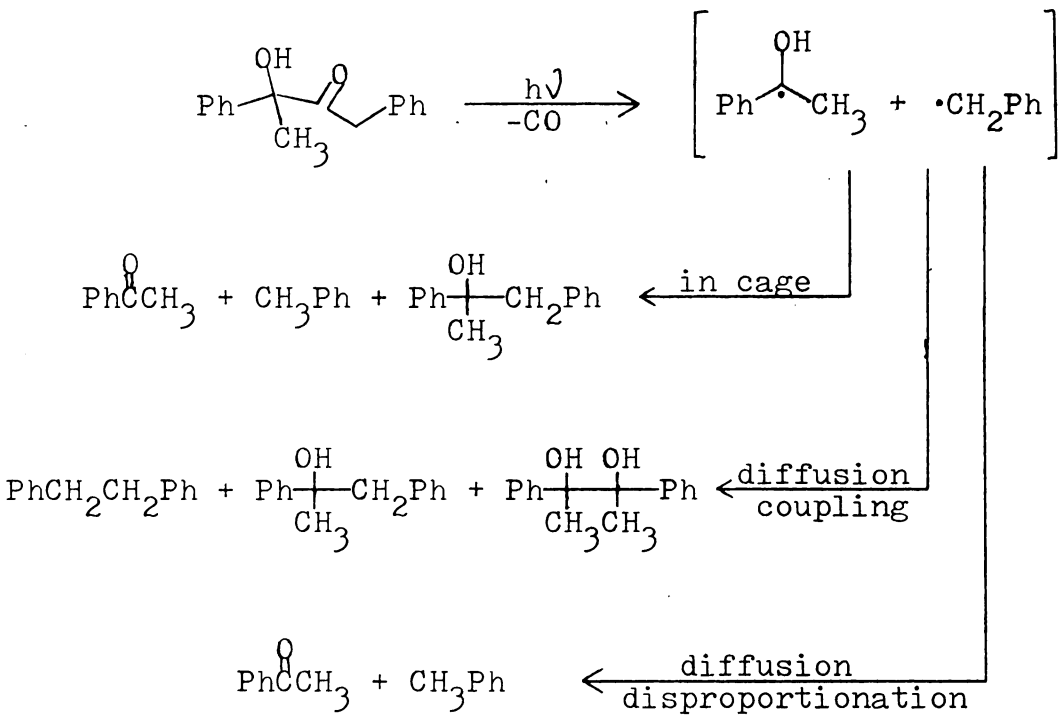
[a]Cycloheptane.

[b]Cyclooctane.

[c]Acetophenone produced from valerophenone.

Discussion

The expected results of the photolysis of the hydroxy ketone would have yielded a somewhat statistical ratio of coupling products. If decarbonylation were extremely efficient, the following scheme would represent the course of the reaction:



(22)

Out of cage coupling could have been eliminated with benzene thiol present to scavenge the free radicals. Elimination of out of cage disproportionations could have been affected by photolysis within a micelle. This would have left only in cage reactions and the extent of the two in cage processes would have been determined from product analysis.

From the tables of quantum yield results, it is seen that decarbonylation is not as efficient as in dibenzyl ketone. The multiplicity of the excited state is the same, an n-π* triplet, in both cases, as determined by the CIDNP study. Their quantum yields of fluorescence are also very close. However, the amount of phenylacetaldehyde product formed complicates the original goal of this project.

Upon examining the ratio of products arising from the acetophenone side of the molecule versus the phenacetyl side of the molecule, it is seen that the products do not add up correctly. The products from the former outweigh the production of products from the latter. This problem is extremely difficult to confront.

Another complication arises upon examining the ratio of out of cage coupling products. Acetophenone pinacol formation is completely suppressed. It was thought that perhaps the pinacol formed was dissociating into some acetophenone. However, upon photolysis of the hydroxy ketone with pinacol present, all is accounted for after photolysis. The crossed alcohol product would have been thought to occur in higher yields also, being both an in and out of cage reaction product. From the radical scavenging experiments it appears that the crossed alcohol product is solely an in cage reaction product, or that very little arises from out of cage combinations. This lack of out of cage coupling would explain the absence of

pinacol.

The micelle experiments show that disproportionation of acetophenone with phenacetyl radicals occurs to a large extent. The experiment is not as quantitative since the micelle environment inhibits quantum yields. Also, analysis is very difficult in that injection of the aqueous mixture onto the gc causes horendous peaks throughout the trace and only the ratios are significant. Attempting to extract the organic photoproducts is also difficult in view of the concentrations employed.

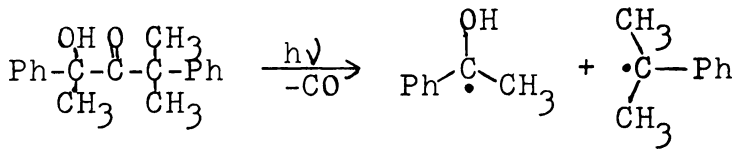
Conclusions

The results of the various photolyses show that the efficiency of hydroxy ketone photolysis is much lower than that of dibenzyl ketone. Fast recombination of the initially formed radicals would account for the low efficiency. Phenacetyl radicals which do not recombine are rapidly reduced by the acetophenone ketyl radicals before they can escape the solvent cage and undergo subsequent decarbonylation. This hinders the use of this system for studying acetophenone-benzyl radical cage reactions.

The larger amount of product formation from the acetophenone portion of the molecule remains a puzzle. Acetophenone oxidation is extremely efficient and could occur from slight traces of impurity, for example, metal. However, the unaccountability of the benzyl radicals complicates the analysis. Phenylacetaldehyde production is

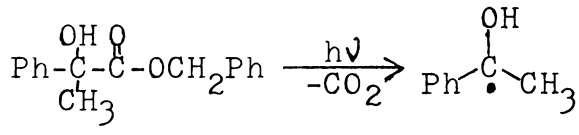
consistent throughout except in the case of added benzene thiol, where increased production occurs. The benzene thiol might be interfering with the in-cage reaction.

Selection of an alternate compound is necessary to determine the fate of acetophenone ketyl and benzyl radicals. A molecule which undergoes decarbonylation very efficiently might be the 1,1-dimethyl hydroxy ketone. Photolysis of this molecule would result in formation of acetophenone ketyl and cumyl radicals.



(23)

Decarbonylation to give the tertiary radical in this compound should be highly efficient. Another possible system is benzyl-2-hydroxy-2-phenylpropanoate.



(24)

Here loss of CO_2 would leave the radicals of interest.

EXPERIMENTAL

Preparation and Purification

Solvents and Additives

Benzene: (Mallinckrodt) was purified by stirring over concentrated sulfuric acid for several days. The benzene was washed with additional sulfuric acid until it remained clear, followed by neutralization with saturated aqueous sodium bicarbonate and finally with saturated aqueous sodium chloride. The benzene was dried over anhydrous magnesium sulfate and distilled from phosphorous pentoxide, collecting the middle 60%.

Acetonitrile: (Fisher Scientific) was distilled from potassium permanganate and sodium carbonate. The final cut was retained.

Carbon Tetrachloride: (Mallinckrodt) was purified by stirring over hot, concentrated alcoholic potassium hydroxide. This was followed by washing several times with water, drying over calcium chloride and distilling from phosphorous pentoxide. The middle 60% was retained.

Methanol: (Fisher Scientific or Mallinckrodt) was distilled from magnesium turnings. The middle fraction was collected.

Hexane: (Mallinckrodt) was purified in the same manner as benzene.

t-Butyl Alcohol: (Fisher Scientific) was purified by distillation from magnesium turnings, collecting the middle 60%.

Water: distilled water was passed through three Sargent-Welch mixed-bed ion-exchange columns and then distilled again prior to use as a photolysis solvent.

Thiophenol: (Aldrich) was used as received.

Hexadecyltrimethylammonium Chloride: (Eastman) was used as received.

Internal Standards

Cycloheptane: (Aldrich) was purified in a manner analogous to that of benzene.

Cyclooctane: (Aldrich) was purified in a manner analogous to that of benzene.

Tridecane: (Aldrich) was purified by distillation, collecting the middle fraction.

Nonadecane: (Chemical Samples) was purified by recrystallization from petroleum-ether.

Diketones

Two methods were used to prepare the diketones.

Method A:[32] (General Procedure) Benzaldehyde, or the para-substituted benzaldehyde, was dripped into 10% aqueous NaOH and ethanol. Acetophenone, or the para-substituted compound, was then dripped into the solution

maintained at 25° C. After several hours of stirring, the thick mixture was placed in a freezer over night. The product was then collected and rinsed with ice water until a neutral pH was obtained, and finally with ice-cold ethanol. The benzalacetophenone obtained was dissolved in ethanol, and to it was added a 30% hydrogen peroxide solution. Into this solution was dripped 5% aqueous NaOH. The mixture was cooled to 0° C to precipitate the epoxide, which was then collected and rinsed with ice-cold ethanol. The epoxyketone was then placed in an equal volume of glacial acetic acid while passing dry HCl gas through the stirring mixture. The solution was saturated with HCl at 0° C and then placed in a freezer overnight. Distillation under aspirator pressure removed the acetic acid and distillation under high vacuum afforded the diketone in good yields (~60%). Final purification was achieved by recrystallization from petroleum ether.

Method B:[33] (General Procedure) Phenethyl bromide in ether was dripped into magnesium turnings also in ether in order to prepare the Grignard reagent. Benzonitrile was then added to the Grignard, followed by acid hydrolysis and ether extraction. Rotory evaporation afforded the 1,3-diphenyl-1-propanone. The ketone was then dissolved in glacial acetic acid and liquid bromine was dripped into the solution, which was heated to 50° C to decolorize the bromine. This solution was poured into ice-cold saturated

aqueous NaCl and extracted with ether. Removal of the solvent left sufficiently pure alpha-bromoketone. This was then dissolved in acetonitrile to which was added $AgNo_3$ in acetonitrile and allowed to stir in the dark for 2 days. The AgBr was then filtered and rinsed with ether. The ether washings and acetonitrile were combined and evaporated under reduced pressure. The crude product was redissolved in ether, washed with water and dried over $MgSO_4$. The ether was evaporated and the nitratoketone was dissolved in DMSO. To the mixture was added a suspension of sodium acetate in DMSO. This was stirred at 25° C for ninety minutes and then poured into ice-cold saturated NaCl. Ether extraction, $NaHCO_3$ washing, and evaporation of the solvent yielded the crude diketone. Distillation under high vacuum, followed by recrystallization from petroleum ether, afforded the pure alpha-diketones.

Characterization

1,3-Diphenyl-1,2-propanedione: mp 35° C; IR(CCl_4) 3000, 1710, 1675 cm^{-1}; NMR($CDCl_3$) 4.09(s,2H), 7.07(s,5H), 7.6-8.0(dd,2H), 7.3(m,3H); m/e 224(M^+).

1-Phenyl-3-(p-chlorophenyl)-1,2-propanedione: mp 68° C; IR(CCl_4) 3000, 1710, 1675 cm^{-1}; NMR($CDCl_3$) 4.09(s,2H), 7.07(s,4H), 7.6-8.0(dd,2H), 7.3(m,3H); m/e 258(M^+).

1-Phenyl-3-(p-methoxyphenyl)-1,2-propanedione: mp 72° C; IR(CCl_4) 3000, 1710, 1675, 1250 cm^{-1};NMR($CDCl_3$)

3.67(s,3H), 4.09(s,2H), 6.7-7.5(m,7H), 7.6-8.0(dd,2H); m/e 254(M^+).

1-(p-Chlorophenyl)-3-phenyl-1,2-propanedione: bp 185° C (~2mm); IR(neat) 3000, 1710, 1675 cm^{-1}; NMR($CDCl_3$) 4.09(s,2H), 7.07(s,4H), 7.6-8.0(dd,2H), 7.3(m,3H); m/e 258(M^+).

1-(p-Methoxyphenyl)-3-phenyl-1,2-propanedione: bp 235° C (~2mm); IR(neat) 3000, 1710, 1675, 1250 cm^{-1}; NMR($CDCl_3$) 3.67(s,3H), 4.09(s,2H), 7.2(s,5H), 6.7-6.9 (dd,2H), 7.8-8.0(dd,2H); m/e 254(M^+).

1-Phenyl-3-(p-chlorophenyl)-2-hydroxy-1-propen-3-one: mp 95° C; IR(CCl_4) 1700, 1630, 1250 cm^{-1}; NMR($CDCl_3$) 6.24(s,1H), 7.1-7.8(m,9H); m/e 258(M^+).

Hydroxy Ketone

1,3-Diphenyl-1,2-propanedione is added to methyl magnesium iodide in a 1:2 mole ratio.[34] This mixture is allowed to stir for several hours after which it is poured into concentrated H_2SO_4 in ice to hydrolyse the magnesium salt. The solution was extracted with ether, washed with saturated aqueous $NaHCO_3$, saturated aqueous NaCl and dried over anhydrous $MgSO_4$. Removal of the solvent affords the crude hydroxy ketone. The crude product was then distilled under high vacuum to give the hydroxy ketone devoid of all starting material. The compound was then chromatographed through alumina which enabled crystallization. The hydroxy ketone was further purified by

several recrystallizations from ether-petroleum ether, achieving ~99% purity: mp 54-56° C; NMR($CDCl_3$) 1.9(s,3H), 3.6(s,2H), 6.9-7.4(m,10H); IR(CCl_4) 3460 cm^{-1} 2900-3050 cm^{-1}, 1725 cm^{-1}; m/e 222(M^{+}-18).

General Techniques

Preparation of Samples

All photochemical glassware, including class "A" pipets and class "A" volumetrics, was heated for two days in Alconox, followed by heating for several days in distilled water. After this time, the glassware was dried in a 150° oven for one day. Photolysis tubes (13 x 100 mm pyrex culture tubes) were cleaned analogously, and the necks were elongated by heating over a gas-oxygen flame. Samples weighed directly into the volumetric flask were diluted to the line with the appropriate solvent. A 5 cc syringe fitted with a 6" needle was used to transfer 3.0 ml of the solution into the test tube with the constricted neck.

Degassing Procedure

After the tubes were filled with the appropriate solutions, they were attached to a vacuum line with one-hole rubber stoppers (size 00). The tubes were then submerged in a liquid nitrogen bath and allowed to freeze slowly. After the tubes were frozen, the stopcocks were opened and the tubes were pumped on for fifteen minutes at 10^{-3} Torr. The stopcocks were then closed allowing

the tubes to thaw completely, thus completing a cycle. this freeze-pump-thaw cycle was performed three times. After completion of the third cycle, the tubes were again frozen, opened to the vacuum line and pumped on for a few minutes. A gas-oxygen torch was then used to remove the tubes from the line, by easily melting and sealing the constricted portion of the tube.

Irradiation Procedure

The degassed tubes were allowed to thaw and then placed in a rotating merry-go-round apparatus which was immersed in a water bath maintained at 25°. The tubes were irradiated in parallel to ensure that samples received the same amount of light. The light source was a 450 watt (Hanovia) medium-pressure mercury lamp, cooled by a quartz or pyrex immersion well. A filter solution, 0.0002 M potassium chromate in a 1% aqueous potassium carbonate solution, was used to isolate the 313 nm band of light. The 366 nm region was isolated by using a set of Corning No. 7-83 filters.

Sample Analysis

Analyses of photoproducts were conducted on a Varian Aerograph 1400 gas chromatograph equipped with a flame ionization detector. Relative peak areas were determined using a Leeds and Northrup Speedomax-H recorder attached to an Infotronics Automatic Digital Integrator. Sample injections were made with a Hamilton 1.0 microliter syringe onto one of two columns.

-Column #1: 8' x 1/8" aluminum column containing 3% QF-1 on 60/80 mesh chromosorb G.

-Column #2: 6' x 1/8" aluminum column containing 5% SE-30 on 60/80 mesh chromosorb W.

Response Factors

Concentrations of photoproducts were determined by comparison to internal standards, whose concentrations were known. Standards were chosen so as not to overlap with product peaks and also to come off in the immediate vicinity of product peaks. Correction factors were determined to correlate the molar response of the detector to the different products. The response factor was used to determine the molar concentration of product by the following equation:

$$\left[\text{Prod.}\right] = \text{RF} \cdot \left[\text{Int. Std.}\right] \cdot \frac{\text{Prod. Area}}{\text{Int. Std. Area}} \qquad (25)$$

The various response factors are listed in Table 9.

Actinometry and Quantum Yields

In order to calculate the quantum yield of the reaction, the amount of light that was absorbed by the system had to be determined. Actinometer tubes, containing 0.10 M valerophenone and a known concentration of tridecane, were irradiated in parallel with the sample tubes. The known quantum yield for acetophenone formation from valerophenone is 0.33.[35] Analysis for acetophenone was performed on column #1. The quantum yield for product formation was,

therefore, determined by the following expression:

$$\Phi_{prod} = \frac{[Prod]}{[Acet]^{val}} \times 0.33 \qquad (26)$$

where $[Acet]^{val}$ refers to the molar concentration of acetophenone produced from valerophenone.

Spectra

Proton magnetic resonance (nmr) spectra were recorded on a Varian T-60 spectrometer in $CDCl_3$ or CD_3CN solutions relative to TMS as an internal standard. Infrared spectra were taken on a Perkin-Elmer 237b grating spectrometer as thin films or in CCl_4 solutions using polystyrene (1601 cm^{-1}) calibration. The mass spectra were run on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Ultraviolet spectra were measured on a Carey 17 spectrophotometer. A Beckman DUR spectrophotometer equipped with a Gilford model 220 linear absorbance converter was used for routine UV work. Fluorescence spectra were measured on an Aminco-Bowman model #4-8202 spectrophotofluorometer equipped with a Perkin-Elmer recorder. Chemically Induced Dynamic Nuclear Polarization (CIDNP) spectra were measured by degassing benzene-d_6 and acetonitrile-d_3 solutions of ketone and transferring them to nmr tubes in a glove-bag under argon atmosphere. A quartz light-pipe was inserted and sealed to the tube. Samples were irradiated in a Varian model A56/60D nmr spectrophotometer by focusing pyrex and water filtered light from a 1000-W Hanovia high pressure Xenon-Mercury lamp onto the light-pipe. Proton nmr spectra were recorded

before, during, and after irradiation.

LIST OF REFERENCES

LIST OF REFERENCES

1. N. C. Yang and C. Rivas, J. Am. Chem. Soc., 83, 2213 (1961).

2. (a) W. H. Urry and D. J. Trecker, ibid., 84, 713 (1962).

   (b) W. H. Urry, D. J. Trecker, and D. A. Winey, Tetrahedron Letters, 609 (1962).

3. P. J. Wagner, R. G. Zepp, K. C. Liu, M. Thomas, T. J. Lee, and N. J. Turro, J. Am. Chem. Soc., 98, 8125 (1976).

4. P. J. Wagner, P. A. Kelso, and R. G. Zepp, ibid., 94, 7483 (1972).

5. P. J. Wagner, P. A. Kelso, A. E. Kemppainen, J. M. McGrath, H. N. Schott, and R. G. Zepp, ibid., 94, 7506 (1972).

6. J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," John Wiley and Sons, Inc., New York, 1966, p. 285.

7. A. A. Lamola and G. S. Hammond, J. Chem. Phys., 43, 2129 (1965).

8. N. J. Turro, "Molecular Photochemistry," W. A. Benjamin, Inc., Massachusetts, 1974, p. 6.

9. P. J. Wagner, "Creation and Detection of the Excited State," Vol. I, Marcel Dekker, New York, 1971, p. 175.

10. J. A. Barltrop and J. D. Coyle, "Excited States in Organic Chemistry," John Wiley and Sons, London, 1975, p. 521.

11. P. J. Wagner, R. G. Zepp, K. C. Liu, M. Thomas, T. J. Lee, and N. J. Turro, J. Am. Chem. Soc., 98, 8125 (1976).

12. P. J. Wagner, R. G. Zepp, K. C. Liu, M. Thomas, T. J. Lee, and N. J. Turro, ibid., 98, 8125 (1976).

13. P. J. Wagner, R. G. Zepp, K. C. Liu, M. Thomas, T. J. Lee, and N. J. Turro, ibid., 98, 8125 (1976).

14. (a) F. R. Stermitz, D. E. Nicodem, J. P. Muralidharan, and C. M. O'Donnell, Mol. Photochem., 2, 87 (1970).

(b) D. G. Whitten and W. E. Punch, ibid., 2, 77 (1970).

15. P. J. Wagner, P. A. Kelso, and A. E. Kemppainen, ibid., 2, 81 (1970).

16. Special thanks goes to Allen Puchalski for the enlightening discussion regarding the title of this section.

17. P. J. Wagner and R. A. Leavitt, J. Am. Chem. Soc., 92, 5806 (1970).

18. P. S. Engel, ibid., 92, 6074 (1970).

19. P. J. Wagner, Topics in Current Chemistry, 66, 1 (1976).

20. J. A. Barltrop and J. D. Coyle, "Excited States in Organic Chemistry," John Wiley and Sons, London, 1975, p. 180.

21. G. Quinkert, K. Opitz, W. W. Wiersdorff, and J. Weinlich, Tetrahedron Letters, 1863 (1963).

22. P. S. Engel, J. Am. Chem. Soc., 92, 6074 (1970).

23. W. K. Robbins and R. H. Eastman, ibid., 92, 6076 (1970).

24. M. Lehnig, Chemical Physics, 8, 419 (1975).

25. W. K. Robbins and R. H. Eastman, J. Am. Chem. Soc., 92, 6077 (1970).

26. N. J. Turro and W. R. Cherry, ibid., 100, 7431 (1978).

27. P. J. Wagner and R. A. Leavitt, ibid., 92, 5806 (1970).

28. P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, ibid., 94, 7489 (1972).

29. R. F. Borkman and D. R. Kearns, J. Chem. Phys., 44, 945 (1966).

30. (a) M. Tomkiewicz and M. P. Klein, Rev. Scientific Instr., 43, 1206 (1972).

(b) The author thanks Dr. Cynthia Chiu for conducting all CIDNP experiments.

31. R. Kaptein, Chem. Comm., 732 (1971).

32. E. P. Kohler and R. P. Barnes, J. Am. Chem. Soc., 56, 211 (1934).

33. N. Kornblum and H. W. Frazier, ibid., 88, 865 (1966).

34. E. P. Kohler and N. Weiner, ibid., 56, 434 (1934).

35. P. J. Wagner, I. E. Kochevar, and A. E. Kemppainen, ibid., 94, 7489 (1972).

APPENDIX

This section contains the raw experimental data, such as internal standard concentrations, product to standard ratios and analytical conditions employed in the analyses.

The arrangement of the tables is as follows: the particular photolysis is described in the title, which includes the percent conversion and irradiation time. Below the title appear the concentrations of the particular standards employed; column 1 lists the photoproducts; column 2 lists the gc columns used for the analyses; column 3 shows the temperatures at which the analyses were made; column 4 lists the concentrations of photoproducts; in column 5 is tabulated the ratios of photoproduct to standard. All photolyses were conducted at 313 nm.

Toluene was analysed with respect to either cycloheptane or cyclooctane. The actinometer in all cases was valerophenone. Acetophenone from valerophenone was analysed with respect to tridecane in all cases. The remaining photoproducts were analysed with respect to nonadecane.

Abbreviations used in this section are: C_7 =

cycloheptane; C.O. = cyclooctane; C_{19} = nonadecane; C_{13} = tridecane; Tol = toluene; PAA = phenylacetaldehyde; AP = acetophenone; BB = bibenzyl; Alc = 1,2-diphenyl-2-propanol; Act = actinometer, and represents acetophenone produced from valerophenone.

Table 10. Data for Photolysis of 0.022 M HK in Benzene at ~40% Conversion ($3\frac{1}{2}$ hours).

0.00468 M C_7, 0.00425 M C_{19}, 0.0271 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	1	35	3.09	0.59
PAA	2	150	1.38	0.11
AP	2	150	5.79	0.46
BB	2	150	1.33	0.20
Alc	2	150	1.07	0.14
Act	2	140	7.83	0.27

Table 11. Data for Photolysis of 0.05 M HK in Benzene at ~5% Conversion ($1\frac{1}{2}$ hours).

0.00392 M C.O., 0.00242 M C_{19}, 0.0282 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	2	35	0	0
PAA	2	150	0.294	0.041
AP	2	150	1.65	0.23
BB	2	150	0.313	0.083
Alc	2	150	0.205	0.047
Act	2	140	2.11	0.070

Table 12. Data for Photolysis of 0.043 M HK in Hexane at ~7% Conversion ($1\frac{1}{2}$ hours).

0.0104 M C_7, 0.00685 M C_{19}, 0.0197 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	1	35	0.0733	0.0063
PAA	2	150	0.288	0.014
AP	2	150	2.26	0.11
BB	2	150	0.470	0.044
Alc	2	150	0.059	0.0048
Act	2	140	1.96	0.093

Table 13. Data for Photolysis of 0.05 M HK in t-Butyl Alcohol at ~2% Conversion ($1\frac{1}{2}$ hours).

0.00339 M C.O., 0.00242 M C_{19}, 0.0262 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	2	35	0	0
PAA	2	150	0.160	0.022
AP	2	150	1.16	0.16
BB	2	150	0.208	0.055
Alc	2	150	0.030	0.0069
Act	2	140	1.25	0.044

Table 14. Data for Photolysis of 0.05 M HK in Benzene with 0.03 M Benzene Thiol Present at ~2% Conversion (2 hours).

0.00339 M C.O., 0.00190 M C_{19}, 0.0209 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	2	35	1.08	0.26
PAA	2	150	1.03	0.18
AP	2	150	3.42	0.60
BB	2	150	0	0
Alc	2	150	0.109	0.032
Act	2	140	3.45	0.15

Table 15. Data for Photolysis of 0.01 M HK in Micellar Solution at ~1% Conversion (1½ hours).

0.00339 M C.O., 0.00238 M C_{19}, 0.0234 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	2	35	0.014	0.0034
PAA	2	150	0.0435	0.0061
AP	2	150	0.0928	0.013
BB	2	150	0	0
Alc	2	150	0	0
Act	2	140	1.38	0.055

Table 16. Data for Photolysis of 0.05 M HK in Benzene with 0.0045 M Acetophenone Pinacol at ~7% Conversion ($1\frac{1}{2}$ hours).

0.00650 M C.O., 0.00272 M C_{19}, 0.0212 M C_{13}

Photoproduct	Column #	Temp. °C	[Prod], x10^3 M	Prod/Std
Tol	2	35	0	0
PAA	2	150	0.277	0.034
AP	2	150	1.88	0.23
BB	2	150	0.259	0.061
Alc	2	150	0.117	0.024
Act	2	140	2.09	0.092