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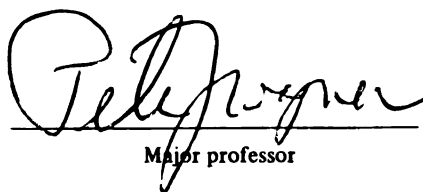
INTRAMOLECULAR INTERACTIONS
OF TRIPLET STATE
DI-[PHENYL ALKYL KETONES]

presented by

Harlan William Frerking, Jr.

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry


Major professor

Date Aug. 25, 1978

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INTRAMOLECULAR INTERACTIONS OF TRIPLET STATE
DI-[PHENYL ALKYL KETONES]

By

Harlan William Frerking, Jr.

A DISSERTATION

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

DOCTOR OF PHILOSOPHY

Department of Chemistry

1978

ABSTRACT

INTRAMOLECULAR INTERACTIONS OF TRIPLET STATE DI-[PHENYL ALKYL KETONES]

By

Harlan William Frerking, Jr.

The intramolecular interactions of the triplet excited state of one aroyl chromophore with the ground state of a second aroyl chromophore are reported for a number of symmetric and unsymmetric diketones. Two phenomena involving both chromophores were commonly observed: reversible energy transfer between the two chromophores, and self-quenching of the excited chromophore by the ground state chromophore.

It is shown how rates for both the endothermic and exothermic energy transfer steps may be obtained for unsymmetric diketones where the rate of decay of one of the isolated chromophores is fast enough to compete with the slower energy transfer process. If the rates of decay for the chromophores are slow compared to energy transfer then equilibrium between the triplet states of the two chromophores is observed and the minimum rates of energy transfer necessary to attain this equilibrium are determined. The rates observed range from greater than 1.0×10^8 and $4.6 \times 10^7 \text{ sec}^{-1}$ for

Harlan William Frerking, Jr.

1-phenyl-5-(4'-valerylphenyl)-pentan-1-one (the triplet states for this ketone equilibrate) to 1.0×10^8 and $1.0 \times 10^7 \text{ sec}^{-1}$ for 1-phenyl-5-(4'-valerylphenoxy)-pentan-1-one. The ratio of the rates of energy transfer is determined by Boltzmann's Law.

The symmetric diketones studied show self-quenching at rates of approximately 1.0×10^7 to $3.4 \times 10^6 \text{ sec}^{-1}$ for diketones where the carbonyl oxygens can approach each other without too much steric hindrance. The absence of measurable self-quenching for 1,5-diphenylpentan-1,5-dione allows one to establish some of the geometric constraints on the self-quenching phenomenon observed. Ab-initio calculations including a reasonably large CI study on systems containing two formaldehyde molecules indicate the presence of a weak singlet excimer for head-to-head in-plane orientations of the formaldehydes. This is in qualitative agreement with the observed kinetics for the symmetric diketones studied.

ACKNOWLEDGMENTS

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I also wish to thank the Department of Chemistry for its financial support through teaching and research assistantships and the National Science Foundation for its financial support through research assistantships paid out of Dr. Wagner's research grants.

A special thanks is due to my wife, Mary, who, in addition to typing and retyping this manuscript, has offered me considerable moral support during the many crises, both large and small, which mark my graduate career at Michigan State University.

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 δ ValPhOVP System (● Ac, δ ValPhOVP;
 ○ Pr, δ ValPhOVP;
 — $1.0 \times 10^8 \text{ sec}^{-1}$, $1.0 \times 10^7 \text{ sec}^{-1}$;
 ---- $9.1 \times 10^7 \text{ sec}^{-1}$, $1.1 \times 10^7 \text{ sec}^{-1}$;
 --- $1.1 \times 10^8 \text{ sec}^{-1}$, $8.9 \times 10^6 \text{ sec}^{-1}$;
 ---- $2.0 \times 10^8 \text{ sec}^{-1}$, $2.0 \times 10^7 \text{ sec}^{-1}$;
 $5.0 \times 10^8 \text{ sec}^{-1}$, $5.0 \times 10^6 \text{ sec}^{-1}$) . . . 84

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LIST OF ABBREVIATIONS

Pr	Propene
An	Anisoyl
Ac	Acetophenone
Tl	Toluoyl
VP	1-Phenylpentan-1-one (Valerophenone)
pMeOAc	4-Methoxyacetophenone
pMeOVP	1-(4'-Methoxyphenyl)-pentan-1-one (pMethoxyvalerophenone)
pEtAc	4-Ethylacetophenone
pEtVp	1-(4-Ethylphenyl)-pentan-1-one (p Ethylvalerophenone)
δPhVP	1,5-Diphenylpentan-1-one (δ Phenylvalerophenone)
δAcPhVP	5-(4'-Acetylphenyl)-1-phenylpentan-1-one
δValPhVP	5-(4'-Valerylphenyl)-1-phenylpentan-1-one
γPhOBP	4-Phenoxy-1-phenylbutan-1-one (γ Phenoxybutyrophenone)
γCNPhOBP	4-(4'-Cyanophenoxy)-1-phenylbutan-1-one
γAcPhOBP	4-(4'-Acetylphenoxy)-1-phenylbutan-1-one
γValPhOBP	4-(4'-Valerylphenoxy)-1-phenylbutan-1-one
δPhOVP	5-Phenoxy-1-phenylpentan-1-one (δ Phenoxyvalerophenone)
δCNPhOVP	5-(4'-Cyanophenoxy)-1-phenylpentan-1-one
δAcPhOVP	5-(4'-Acetylphenoxy)-1-phenylpentan-1-one
δValPhOVP	5-(4'-Valerylphenoxy)-1-phenylpentan-1-one

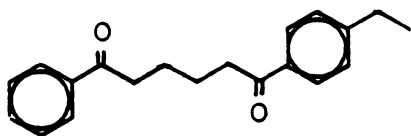
DiBzdiMeMt	2,2-Dimethyl-1,3-diphenylpropan-1,3-dione
DiBzEt	1,4-Diphenylbutan-1,4-dione (1,2-dibenzoylthane)
DiBzPr	1,5-Diphenylpentan-1,5-dione (1,3-dibenzoylpropane)
DiBzBt	1,6-Diphenylhexan-1,6-dione (1,4-dibenzoylbutane)
DiBzPt	1,7-Diphenylheptan-1,7-dione (1,5-dibenzoylpentane)
DipEtBzBt	1,6-Bis-(4'-ethylphenyl)-hexane-1,6-dione
DiAnBt	1,6-Bis-(4'-methoxyphenyl)-hexane-1,6-dione
lBz4EtBzBt	1-(4'-Ethylphenyl)-6-phenylhexane-1,6-dione
lBz4AnBt	1-(4'-Methoxyphenyl)-6-phenylhexane-1,6-dione
γ CarbOMEBP	Methyl 5-phenyl-4-oxocaproate
δ CarbOMEVP	Methyl 4-phenyl-3-oxovalerate
PhBten	1-phenylbut-3-en-1-one

INTRODUCTION

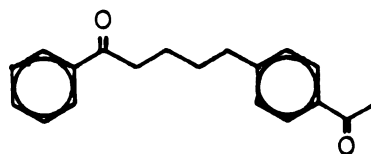
The main area of study covered in this dissertation is triplet energy transfer. Intramolecular systems, such as those shown in Figure 1, were used because they offered more control over the distances and orientations involved in energy transfer than intermolecular systems. During the course of these studies a second phenomenon was frequently observed which, at the beginning of this project, was not defined in the chemical literature. This process involves the interaction of the triplet state of one chromophore with the ground state of a second similar or identical chromophore resulting in thermal dissipation of energy to give two ground state chromophores. This process is called self-quenching.

I. Reasons for Studying Triplet Energy Transfer

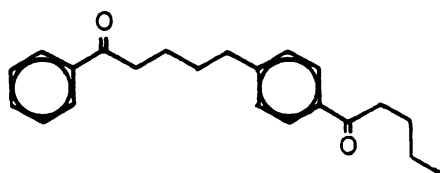
Triplet energy transfer is a common means of electronically exciting a molecule when direct irradiation is impossible, inconvenient, or does not give an excited state of the desired multiplicity.¹ My initial interest in triplet energy transfer arose from research I carried out on the sensitization of photopolymer etching resists. In such systems direct irradiation would require high



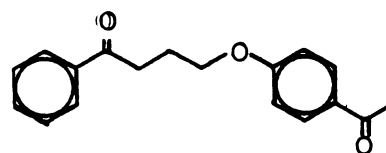
1-(4'-Ethylphenyl)-6-phenylhexan-1,6-dione
(1Bz4EtBzBt)



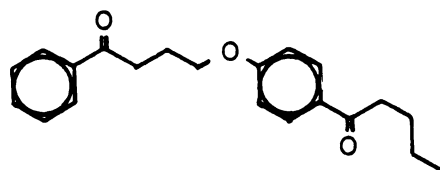
5-(4'-Acetylphenyl)-1-phenylpentan-1-one
(δAcPhVP)



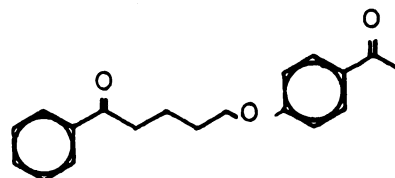
1-Phenyl-5-(4'-valeryl-phenyl)-pentan-1-one
(δValPhVP)



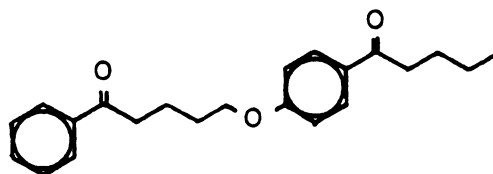
4-(4'-Acetylphenoxy)-1-phenylbutan-1-one
(γAcPhOBP)



1-Phenyl-4-(4'-valeryl-phenoxy)-butan-1-one
(γValPhOBP)



5-(4'-Acetylphenoxy)-1-phenylpentan-1-one
(δAcPhOVP)



1-Phenyl-5-(4'-valeryl-phenoxy)-pentan-1-one
(δValPhOVP)

Figure 1: Intramolecular Energy Transfer Systems

energy light sources and quartz optics. By the correct choice of sensitizer it is possible to use near ultraviolet light and pyrex optics, or, in some cases, even visible light and flint glass optics.²

Many compounds of interest to organic photochemists have low intersystem crossing yields or substantial reactivity from the singlet state. The use of a triplet sensitizer is often convenient and sometimes essential in the study of the photochemistry of the triplet states of such compounds.³ Triplet energy transfer from a molecule under study to a triplet quencher is often used to make a qualitative judgment about the multiplicity of the reactive state of the molecule.⁴ In a more quantitative sense quenching studies involving diffusion controlled triplet energy transfer have been one of the main tools of photokineticists for several decades.⁵

II. Previous Work Involving Intramolecular Triplet Energy Transfer

At the onset of my research very little was actually known about the mechanism of triplet energy transfer. It was generally understood that the difference in triplet energies between the donor and acceptor chromophores has to be at least 3 kcal/mole if energy transfer is to be efficient.⁶ This is simply recognition that the processes involved in energy transfer are reversible,⁷⁻¹¹ and that, if the rates of energy transfer are fast compared to the other decay paths of the chromophores, the populations

of the triplet states involved would follow a Boltzmann distribution.⁸⁻¹¹ At room temperature under these conditions a triplet energy separation of 3 kcal/mole between the chromophores would result in 99.3% of the excitation residing in the chromophore with the lowest triplet energy. It had also been observed that the collision radii needed for triplet energy transfer are generally small, usually on the order of only a few angstroms.¹²

The dipole-dipole mechanism for singlet energy transfer was correctly described by Forster¹³ and very convincingly proved by Latt, Cheung, and Blout¹⁴ with molecules where the two chromophores were separated by a rigid steroid bridge. Dexter¹⁵ has considered several possible mechanisms for triplet energy transfer including dipole-dipole, dipole-quadrupole, and exchange mechanisms. Only the exchange mechanism comes close to predicting the inter-chromophore distance relationships observed for triplet energy transfer and as a result it is favored by most researchers.

Several researchers have studied triplet energy transfer using intramolecular systems. These studies can be divided into three classes: those in which triplet energy transfer is totally efficient in one direction, those in which triplet energy transfer is not complete but no attempt was made to estimate the rate of energy transfer, and those for which estimates of the rates

of energy transfer were obtained. Among the earliest of the first type of these studies was a study of the phosphorescence of 4-(1-naphthyl-methyl)-benzophenone undertaken by Hammond.¹⁶ In this system singlet energy transfer from the naphthalene chromophore to the benzophenone chromophore occurs with about 90% efficiency and triplet energy transfer from the benzophenone chromophore to the naphthalene chromophore is 100% efficient.

Breen and Keller¹⁷ also studied several systems in the first class in which naphthalene and either phthalimide or carbazole chromophores were separated by one to three methylene groups. The phosphorescence spectra and lifetimes of these systems indicate that triplet energy transfer to the chromophore of lowest energy is complete in all systems. Since these studies were carried out in a rigid glass matrix it is safe to assume that triplet energy transfer between these chromophores is fast over the average separation of the systems ($\approx 5 \text{ \AA}$ for three methylene groups).

Both Dexter's¹⁵ and Forster's¹³ descriptions of energy transfer mechanisms contain orientation terms which would imply that chromophores held perpendicular to each other should not undergo energy transfer. A number of researchers have attempted to verify these predictions with rigid systems.¹⁸⁻²¹ No one has succeeded, primarily because it takes only a small amount

of distortion in the molecule to make energy transfer allowed; but the attempts have led to a number of well defined systems in which energy transfer does occur. Keller¹⁸ studied the emission spectra of spiro-[9,10-dihydro-9-oxoanthracene-10,2'-(3'H)-phenalene] and spiro-[9,10-dihydro-9-oxoanthracene-10,2'-5',6'-benzidan] and observed complete energy transfer to the chromophore with the lower energy in both the singlet and triplet manifolds. The structures of these molecules are shown in Figure 2. When Filipescu and DeMember¹⁹ studied the

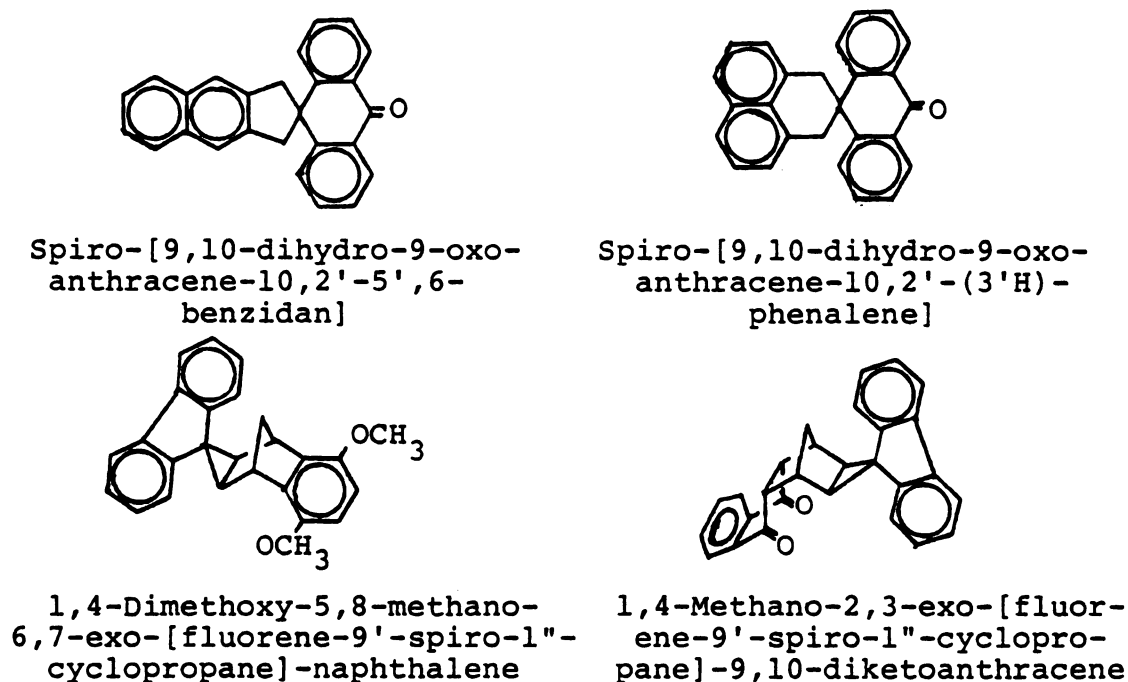


Figure 2: Rigid Energy Transfer Systems

spectroscopy of 1,4-dimethoxy-5,8-methano-6,7-exo-[fluorene-9'-spiro-1''-cyclopropane]-naphthalene (structure in Figure 2) they were unable to detect either singlet or triplet

energy transfer, but Lamola²⁰ was able to observe efficient singlet energy transfer in this system. Filipescu, De-Member, and Minn²¹ studied 1,4-methano-2,3-exo-[fluorene-9'-spiro-1"-cyclopropane]-9,10-diketoanthracene (structure in Figure 2) and observed efficient triplet energy transfer but were unable to detect any singlet energy transfer.

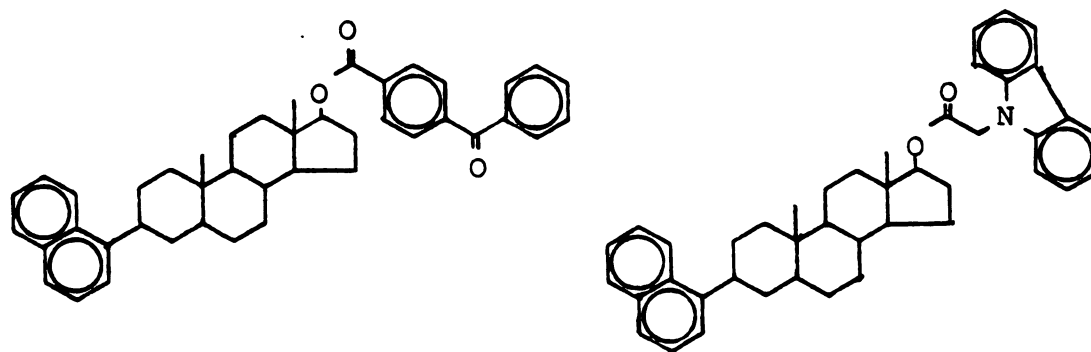
There are numerous examples in the literature where triplet energy transfer from a suitable sensitizer to an olefin has been used to study the triplet state photochemistry of the olefin.²² Several intramolecular systems have been studied. Morrison and Peiffer²³ and later Nakagawa and Sigel²⁴ studied 1-phenyl-2-butene and found triplet energy transfer from the phenyl chromophore to the olefin to be essentially complete and about 360 times as efficient as in the comparable intermolecular case. Cowan and Baum²⁵ studied a series of compounds in which styryl and benzoyl chromophores are separated by one to four methylene groups and observed that irradiation of the benzoyl chromophore results in efficient isomerization of the styryl chromophore.

One potential pitfall of studying energy transfer through photochemical products has been illustrated by Morrison's²⁶ observation that trans-4-hexen-2-one and trans-5-hepten-2-one are efficiently isomerized by light absorbed by the carbonyl group, presumably as a result of energy transfer. Later studies of the 1-phenylhexen-1-one and 1-phenyl-2-ethyl-4-penten-1-one systems by

Morrison, Tisdale, Wagner, and Liu²⁷ indicate that the observed isomerization occurs by a chemical (Schenk) mechanism involving the formation of a charge transfer complex and the products of its collapse.

Zimmerman and McKelvey²⁸ studied the emission spectroscopy of 1-benzoyl-4-(α -naphthyl)-bicyclo[2.2.2]-octane and observed that irradiation of the naphthalene chromophore results in approximately 99% efficient singlet energy transfer to the benzoyl chromophore while irradiation of the benzoyl group results in complete triplet energy transfer to the naphthalene. Since the bridge between the chromophores is rigid the interchromophore spacing is known to be about 3 Å with very little possible variation.

Keller and Dolby²⁹ investigated energy transfer using two systems in which the chromophores are held apart by rigid steroid bridges, 3-naphthyl-5 α -androstan-17 β -(p-benzoylbenzoate) and 3-naphthyl-5 α -androstan-17 β -(9-carbazoleacetate). The structures of these systems are shown in Figure 3. The interchromophore separations for these compounds, determined using Forster's equation,¹³ are 14 Å and 15 Å respectively. The phosphorescence emission intensity for the first system indicates that triplet energy transfer is 35-39% efficient while the phosphorescence lifetimes indicate a 12% efficiency with a rate of 25 sec⁻¹. The phosphorescence spectral intensity for the second system indicates 30% efficient triplet



3-Naphthyl-5 α -androstan-
17 β -(p-benzoylbenzoate)

3-Naphthyl-5 α -androstan-
17 β -(9-carbazoeacetate)

Figure 3: Keller and Dolby's Systems

energy transfer while the triplet lifetimes indicate 21% efficient triplet energy transfer with a rate of 0.04 sec^{-1} . Reverse energy transfer was not considered for either system but may be important in the second.

Lamola⁸ studied 2-hydroxymethyltriphenylene 4-benzoylbenzoate and found that at room temperature in a cured poly (methylemethacrylate) film the phosphorescence observed is the sum of the phosphorescence of the two chromophores in a 2:3 ratio. At liquid nitrogen temperature only phosphorescence from the benzophenone chromophore is observed. It appears that triplet excitation equilibrates between the two chromophores and that the position of the equilibrium can be predicted by a Boltzmann distribution.

By observing the Norrish type II reactions³⁰ of

6-(4'-methoxyphenyl)-1-phenylhexan-1,6-dione Wagner and Nakahira¹⁰ were able to determine that the triplet lifetimes of the two chromophores are almost identical. This indicates that the triplet states of the two chromophores must be almost equilibrated since the lifetimes of these chromophores when in separate molecules are quite different. The product ratios obtained are close to what one would predict from a Boltzmann distribution of triplet excitation. A scheme depicting this situation is shown in Figure 4.

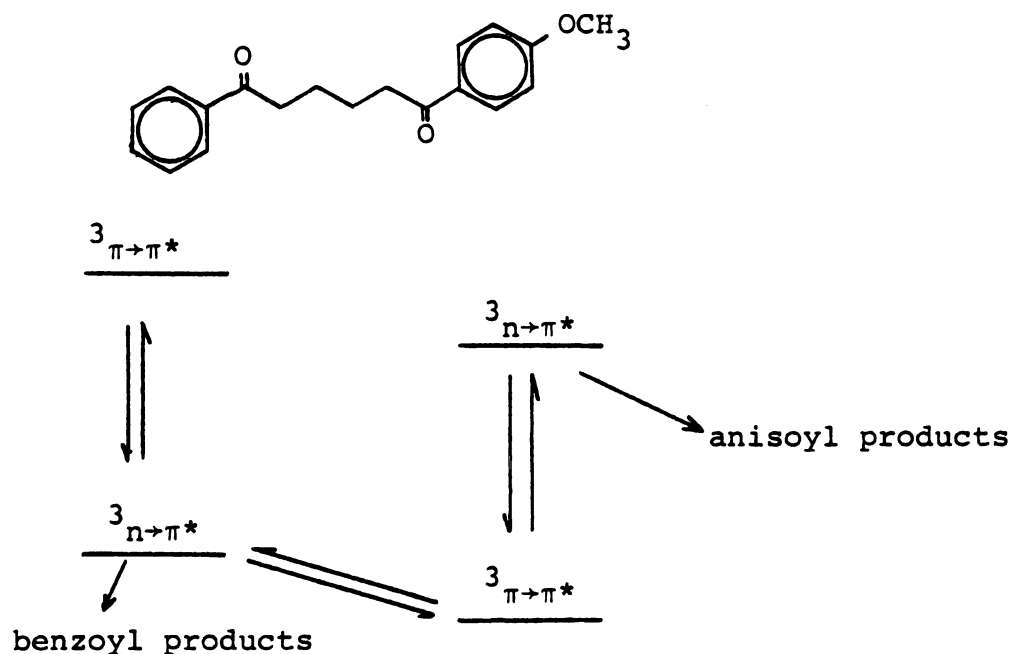


Figure 4: Equilibrating Chromophores in the 1-Benzoyl-4-p-anisoylbutane System

III. The Approach Used in this Dissertation

When one looked at the data available at the start of this research, it was obvious that most triplet energy transfer could be explained, at least qualitatively, by the exchange mechanism proposed by Dexter.¹⁵

There do seem to be two general factors that control the rate of triplet energy transfer. The first is the physical separation between the two chromophores. It is obvious that the rate of triplet energy transfer drops off very rapidly with increasing distance. Thus the rates of energy transfer observed by Keller and Dolby²⁹ at 15 Å are seven to eight orders of magnitude slower than those estimated by Wagner and Nakahira¹⁰ at an average distance of about 7 Å. The second is that the rate of triplet energy transfer is dependent upon the energy differences between the triplet states of the chromophores involved. In most of the studies done to date the triplet energy separation between the chromophores is greater than about 3 kcal/mole and only the exothermic process is observed. With the exception of Keller and Dolby's systems²⁹ energy transfer is always complete in the exothermic direction. There are three systems reported in the literature in which the triplet energy separation is less than 3 kcal/mole. In the earliest, Keller and Dolby's naphthalene-carbazole system,²⁹ it is not known whether triplet energy transfer takes place in the endothermic direction. In Lamola's⁸

and in Wagner and Nakahira's,¹⁰ it obviously does. In most of the systems which have been studied, no estimation of the rates of energy transfer is possible.

The data which would be most useful in establishing the mechanism(s) of triplet energy transfer are the rates of triplet energy transfer in systems where the distances between chromophores can be estimated and the energy separation between the triplet states is known. The first of these requires an intramolecular system while the second requires some knowledge of the energy levels in the individual chromophores, usually obtainable from their phosphorescence spectra. In order to obtain rate constants it is necessary to have some process of known rate that can compete successfully with triplet energy transfer. While most of the systems discussed meet the first two of these requirements, it is impossible to do more than put lower limits on the rate constants for triplet energy transfer since none of the decay processes of the donor chromophore can compete successfully with triplet energy transfer to the acceptor chromophore. In Keller and Dolby's systems²⁹ the large distance between the chromophores results in rates of triplet energy transfer that are slow enough to allow the natural decay processes of the donor chromophores to compete with energy transfer. In Wagner and Nakahira's¹⁰ system the same result was obtained by choosing a triplet energy separation such that endothermic energy transfer is slow

enough to allow the natural decay rates of the lower energy chromophore to perturb the equilibrium between the triplet states in the system. This allows one to estimate the rate constants for energy transfer in both directions, as will be shown later in this dissertation.

I chose to follow Wagner and Nakahira's approach for this research because I could use the Norrish type II reaction of phenyl alkyl ketones to monitor energy transfer. The mechanistic aspects of the Norrish type II reaction are well understood,³¹ and it is relatively fast which makes it an ideal monitor for triplet energy transfer. Intersystem crossing yields for most phenyl alkyl ketones are unity³⁵ so that complications arising from the singlet states are eliminated. Other reasons for using this approach include the relative ease of synthesis for compounds which are held apart by simple methylene chains and a greater interest in rate constants of energy transfer which are closer to those involved in intermolecular sensitization and quenching studies where diffusion is often the rate limiting factor.

In addition to Wagner and Nakahira's communication,¹⁰ three other research groups have published papers in which the photochemistry of molecules containing two or more phenyl ketone chromophores was reported. David, Demarteau, and Geuskens³² reported the quantum yields of Norrish type II cleavage for poly (phenyl vinyl ketone) and the

copolymer of styrene and acrylophenone. Guillet and his coworkers³³ studied the photochemistry of these polymers in considerable detail. The main interest of both of these research groups involved the facile photodegradation observed for these polymers. There is no way to observe energy transfer in these systems since the chromophores are identical.

Salvin and his coworkers³⁴ studied the photochemistry of the symmetric and unsymmetric dimers and trimers of acrylophenone. While it is theoretically possible to establish the position of equilibrium between the triplet states of the chromophores in the unsymmetric molecules the difference in triplet energies is so small that such an exercise is fruitless. Some very interesting stereochemical effects on the Norrish type II reactions of these systems were observed but these effects have no bearing on the work presented in this dissertation.

IV. Phenyl Alkyl Ketone Photochemistry

Since almost all of the results presented in this dissertation depend on the Norrish type II reaction of phenyl alkyl ketones some discussion of the mechanism of this reaction and the processes known to compete with it is in order. A comprehensive review of this reaction has been published by Wagner.³¹ Only the aspects of phenyl alkyl ketone photochemistry which are pertinent to the results presented in this dissertation will be

discussed here.

In simple phenyl alkyl ketones the intersystem crossing yields are almost always unity³⁵ indicating that intersystem crossing is faster than the normal decay processes of the singlet states of phenyl alkyl ketones. The rate of intersystem crossing has been estimated to be approximately 10^{11} sec^{-1} for phenyl alkyl ketones.^{36,37} Therefore almost all photochemistry observed from phenyl alkyl ketones arises from their triplet states.

In the triplet manifold of a phenyl alkyl ketone there are two triplet states which lie reasonably close to each other in energy, an $n \rightarrow \pi^*$ state and a $\pi \rightarrow \pi^*$ state.³⁸ In simple valence bond terms the $n \rightarrow \pi^*$ triplet closely resembles an alkoxy radical,³⁹ and its chemical behavior supports this resemblance.^{31,40} The $\pi \rightarrow \pi^*$ triplet has most of its excitation localized on the aromatic ring⁴¹ and spectroscopically resembles the lowest triplet state of benzene (^3L_a).³⁸ These two triplet states are generally close enough to each other in energy to equilibrate, their relative populations being determined by a Boltzmann distribution,⁴² with the position of the equilibrium determined by the substituents on the phenyl ring. There are several routes by which the triplet states can decay. They can phosphoresce, undergo intersystem crossing to an upper vibrational state of the ground state singlet which then undergoes internal conversion to the ground

state, transfer their excitation to some quencher, and react. Since they equilibrate it is usually convenient to treat them kinetically as a single state with some mixture of the characters of both states.

At room temperature phosphorescence can be observed from phenyl alkyl ketones only if they possess no γ hydrogens. At liquid nitrogen temperature most simple phenyl alkyl ketones phosphoresce because the small (3-4 kcal/mole) activation energy for hydrogen abstraction is insurmountable.⁴³

Random intermolecular quenching of the triplet is a decay process which can be eliminated by scrupulous purification of the solvents and ketones used. It can be intentionally introduced and its effects measured quantitatively to provide one of the most powerful tools available to the photochemist.⁵ Intramolecular quenching of the triplet falls into two classes, those processes which form another excited state at a different location within the molecule, and those processes which result in decay to a ground state without the formation of a second excited state. The first of these intramolecular quenching processes is triplet energy transfer and the main subject of this dissertation.

The second involves several possible chemical interactions. The best understood mechanism is the formation of an intramolecular charge transfer complex which can decay to the starting ketone.⁴⁴ Such processes have

been thoroughly studied with a variety of ketones.⁴⁵

In most of the non-conjugated diketones discussed in this dissertation which contain two phenyl ketone chromophores internal quenching occurs by yet another process, self-quenching, which involves quenching, without energy transfer, of an excited chromophore by an identical or almost identical ground state chromophore. When the research for this dissertation was initiated the literature contained several reports of intermolecular self-quenching by ketones containing other functionalities conducive to charge transfer quenching, such as 4,4'-bis-(dimethylamino)-benzophenone,⁴⁶⁻⁵¹ but only two brief communications existed concerning self-quenching of phenyl ketones without such substituents.^{52,53} During the course of my research, Singer and his coworkers⁵⁴ reported the bimolecular rate constants for self-quenching of various benzophenones substituted in both para positions. They found that the rate constant of self-quenching was enhanced by both electron withdrawing and electron donating substituents and proposed the formation of exciplexes having some charge transfer character in both cases. For benzophenones with electron-donating substituents they proposed an n-type exciplex in which the carbonyl triplet acts as an acceptor and the phenyl ring of another benzophenone as a donor. In the case of electron withdrawing substituents the π system of the triplet was proposed to act as a donor and

the phenyl ring of an adjacent benzophenone as an acceptor. They called this a π -type exciplex. The self-quenching processes observed during the course of this research allow important clarifications of this model.

In most phenyl alkyl ketones containing γ -hydrogens the main decay process of the triplet state is the Norrish type II reaction.³¹ The mechanism of this reaction is shown in Figure 5. The reaction proceeds by abstraction

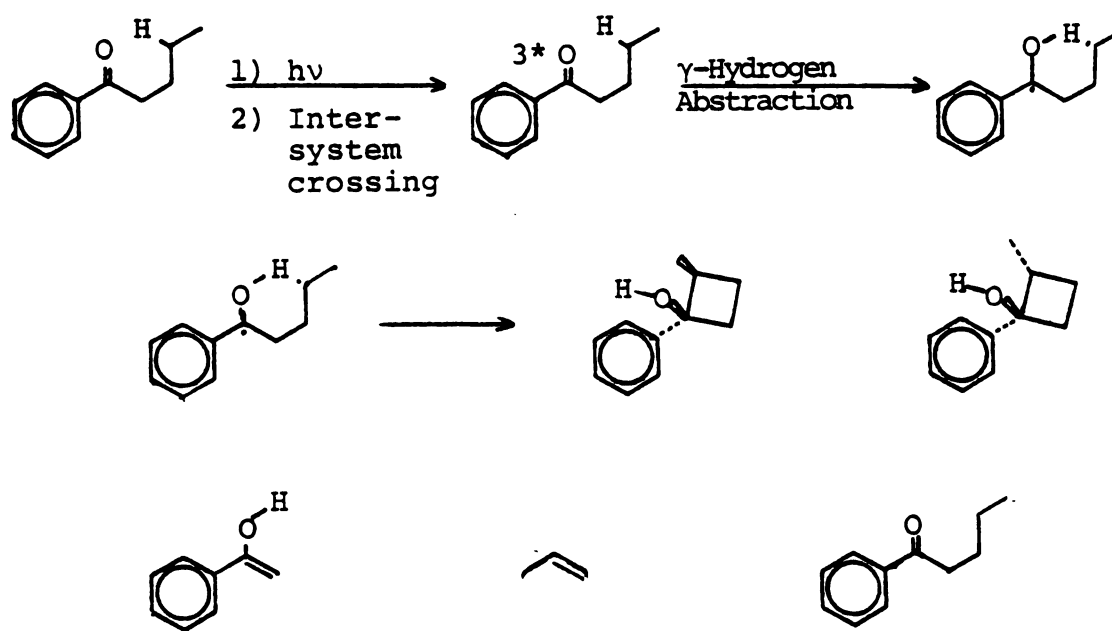


Figure 5: The Norrish Type II Reaction

of the γ -hydrogen by the triplet $n \rightarrow \pi^*$ state of the ketone to form a 1,4 biradical.^{55,56} The rate of γ -hydrogen abstraction is controlled by the ease with which the γ -hydrogen bond can be cleaved, which is determined by the inductive and resonance effects of the substituents

on or near the γ -carbon,⁵⁷ and by the reactivity of the triplet carbonyl towards hydrogen abstraction, determined by the substituents on the phenyl ring.⁵⁸

Once the 1,4-biradical has been formed it can react by three different pathways: β cleavage, cyclobutanol formation, and abstraction of the hydroxy hydrogen by the γ radical site. The various parameters affecting these processes have been considered in depth by Wagner and coworkers.⁵⁹ The most important parameter affecting the reactions of 1,4-biradicals is the effect of Lewis bases on the revertibility of the biradical to starting ketone. For simple phenyl alkyl ketones addition of enough Lewis base raises the sum of quantum yields of cleavage and cyclization to unity, at which point reversion back to the ground state of the starting ketone has been eliminated.⁶⁰ Presumably this suppression of reverse H-transfer occurs because the hydroxyl group of the 1,4-biradical forms a strong hydrogen bond with the Lewis base.

The second major observation concerning the behavior of 1,4-biradicals is that the yield of cyclobutanols is about 10 to 20% of the yields of cleavage products and that similar biradicals give similar ratios of cleavage to cyclization.⁵⁹ Addition of Lewis bases usually decreases the proportion of cyclization, generally reducing the yield of trans-cyclobutanol by about half while not affecting the cis-cyclobutanol yield.⁵⁹ This constancy

of behavior allows one to estimate the yield of cyclobutanols with a reasonable amount of certainty in situations where neither the disappearance of the ketone nor the formation of cyclobutanols can be readily measured.

In systems which have a δ -hydrogen the carbonyl can abstract this hydrogen in competition with the γ -hydrogen.⁶¹ This reaction is generally mostly reversible. The apparent rates of δ -hydrogen abstraction have been reported,⁶¹ and are generally about 5% of the rates of γ -hydrogen abstraction for similar hydrogens.

V. Photokinetics of Phenyl Alkyl Ketones

The photokinetics of simple phenyl alkyl ketones are relatively straightforward. The only things that can be measured directly are the formation of cleavage products, the formation of cyclization products, and the disappearance of the starting ketone. The mass balance is usually good. The effects of added quencher or Lewis base on the quantum yields of these products completes the picture of type II kinetics.

The quantum yield for the cleavage product from the Norrish type II reaction may be expressed as follows:

$$\Phi_{II} = \Phi_{isc} k_{\gamma} \tau^{\circ} P_{II} \quad (1)$$

where

Φ_{isc} = quantum yield of intersystem crossing

k_{γ} = the rate of hydrogen abstraction

τ° = the lifetime of the triplet state in the absence of quencher

P_{II} = the probability that the 1,4-biradical will cleave to enol plus olefin

By definition

$1/\tau$ = the sum of all decay processes of the triplet state

and

$P_{II} = \frac{\text{the rate of cleavage}}{\text{sum of the rates of all biradical decay processes}}$

If one adds a known amount of quencher the equation for the quantum yield becomes:

$$\phi_{II} = \frac{k_Y P_{II}}{1/\tau^\circ + k_q [Q]} \quad (2)$$

It is possible to extract the lifetime, τ° , from these equations using the Stern-Volmer relationship (equation 3)^{35,62} if one knows k_q for the solvent and quencher used.

$$\phi^\circ/\phi = 1 + k_q \tau^\circ [Q] \quad (3)$$

Measurement of P_{II} , the quantum yield and the lifetime allow determination of the rate of γ -hydrogen abstraction. Since, in a large number of cases, the sum of the quantum yields of the Norrish type II products is unity in the presence of a sufficient amount of Lewis base,⁶⁰ it is usually safe to assume that $P_{II} + P_{Cy} = 1$ at the maximum quantum yield rises no further upon addition of more Lewis base.

In phenyl ketone systems where no photochemical reaction occurs it is possible to measure the triplet

lifetime by allowing the ketone to sensitize the cis-trans isomerization of either piperylene or stilbene and measuring the quantum yield of this isomerization.⁶³

The equation describing this procedure kinetically is:

$$\alpha/\phi_{c \rightarrow t} = \phi_{isc}^{-1} (1 + 1/(k_q \tau^0 [Q])) \quad (4)$$

where α is the photostationary cis/trans ratio of the olefin quencher and $\phi_{c \rightarrow t}$ is the measured quantum yield for isomerization of the olefin.

When two chromophores are placed in the same molecule the situation becomes considerably more complicated. All of the processes mentioned above can occur at both chromophores giving two complete sets of products to analyze. In addition two new processes involving the interaction of the two chromophores can occur. These processes are the subject of this dissertation. The first is energy transfer from the triplet state of one chromophore to the other chromophore. The second process is self-quenching of the excited chromophore by the ground state chromophore which returns both chromophores to their ground states.

The kinetics of two chromophore systems have been derived by Wagner and Nakahira¹¹ and Shetlar⁶⁴ and are expressed by Equations 5 and 6. An equation equivalent to 5 describes the quantum yield for products from chromophore B.

$$\phi_A = \frac{k_q^A}{1/\tau_A + k_q[Q]} \left[\frac{\frac{\epsilon_A}{\epsilon_A + \epsilon_B} + \frac{\epsilon_B}{\epsilon_A + \epsilon_B} \frac{k_t}{1/\tau_B + k_q[Q]}}{1 - \frac{k_{-t}}{1/\tau_A + k_q[Q]} \frac{k_t}{1/\tau_B + k_q[Q]}} \right] P_A \quad (5)$$

$$\frac{\phi_A^0}{\phi_A} = \frac{(1+k_q\tau_A[Q])(1+k_q\tau_B[Q]) - k_{-t}\tau_A k_t\tau_B}{(1-k_{-t}k_t\tau_A\tau_B) \left[1 + \frac{k_q[Q]\tau_B}{1 + \frac{\epsilon_B}{\epsilon_A} k_t\tau_B} \right]} \quad (6)$$

where

ϕ_A = the quantum yield for product formation from chromophore A

$$1/\tau_A = 1/\tau_A^0 + k_{-t} + k_{sq} \quad (7)$$

ϵ_A = the extinction coefficient of chromophore A

k_{-t} = the rate of energy transfer from chromophore A to chromophore B

k_{sq} = the rate of self-quenching of chromophore A by chromophore B

All the terms of this equation except the rates of energy transfer can be determined from the appropriate model systems. While these equations are too complex to computer curve fit, it is possible to generate a family of curves and compare the experimental data to these curves to obtain the approximate rates of energy transfer. The exact forms of equations 5 and 6 used to do this will be discussed later.

One special case of the Stern-Volmer equation for bichromophoric systems deserves special consideration.

If the decay rates of the individual chromophores are slow compared to the rates of energy transfer away from that chromophore then the triplets will equilibrate and the position of this equilibrium will be determined by a Boltzmann distribution.¹⁰ Under these conditions the equations for the quantum yield and Stern-Volmer relationship simplify as follows:

$$\phi_{II} = \chi_A k_{\gamma}^A \tau P_A \quad (8)$$

$$1/\tau_A = \chi_A (k_{\gamma}^A + k_d^A + k_{sq}^A [B]) + \chi_B (k_{\gamma}^B + k_d^B + k_{sq}^B [A]) \quad (9)$$

$$\frac{(\phi_{II}^A)^{\circ}}{\phi_{II}^A} = 1 + (\chi_A + \chi_B) k_q \tau [Q] \quad (10)$$

assuming

$$(k_{\gamma}^B + k_d^B + k_{sq}^B [A]) \ll k_{-t} [B]$$

and

$$(k_{\gamma}^B + k_d^B + k_{sq}^B [A]) \ll k_t [A]$$

When these conditions are met the lifetimes of both chromophores are equal and determined by the equilibrium distribution of triplet excitation between the chromophores. The quantum yields of products from the individual chromophores are also determined by this distribution. Under these conditions all one can do is set lower limits on the rates of energy transfer. It is possible to calculate the position of equilibrium from either the equation for the lifetime and the fact that $\chi_A + \chi_B = 1$ or from the equation $\chi_A = (k_{\gamma}^A)^{obs} / k_{\gamma}^A$

since k_{γ}^A , k_d^A , and $k_{sq}^A[B]$ can be determined from model systems.

RESULTS

I. General Techniques

Several general techniques were used to obtain the kinetic parameters which form the basis for this dissertation. Most of these were discussed briefly in the introduction and the experimental details will be presented in the experimental section. This section discusses only those aspects of these techniques necessary to understand and critically evaluate the data presented.

A. Irradiations

Unless otherwise specified irradiations used to determine kinetic data were carried out at 0.01 M ketone concentration in degassed, highly purified benzene at wavelengths where the $n \rightarrow \pi^*$ singlets were populated almost exclusively. A merry-go-round immersed in a constant temperature bath was used to insure equal amounts of incident light for all samples in a given run and to maintain a constant temperature, usually 30.0°, throughout a series of experiments.

B. Product Quantum Yields

Quantum yields of product formation were determined relative to 1-phenylpentan-1-one (VP) secondary actinometers. Acetophenone (Ac), 4-ethylacetophenone (p-EtAc), and propene were the products most generally determined because the experimental conditions required for their determination were well developed. All results presented are corrected for differences in the amount of light absorbed by the sample and actinometer and for their different gas chromatograph detector responses.

C. Disappearance Quantum Yields

Quantum yields of disappearance were determined relative to the cleavage products of the same ketone. The errors in these determinations are fairly large, but they are accurate enough to determine if any significant photoreactions other than the Norrish type II reaction and the normal 10 to 20% cyclobutanol⁵⁹ formation occur.

D. Maximum Quantum Yields

Quantum yields of the cleavage products in the presence of various amounts of added Lewis bases were determined using the same techniques discussed above. For most of the ketones discussed in this dissertation it is not possible to obtain a quantum yield of unity for total product formation no matter how much or which Lewis base is used, but they do reach a point at which further increases in the concentration of Lewis base

leave ϕ_{II} unchanged or cause it to decrease. The results reported here are the maximum quantum yields observable.

E. Intersystem Crossing Yields

Intersystem crossing yields were determined by comparing the relative abilities of the ketone in question and of acetophenone at sensitizing the cis-trans isomerization of 1,3-pentadiene at concentrations of both ketone and acetophenone where essentially all the incident light was absorbed and at 1,3-pentadiene concentrations where the triplet states of both the ketone and acetophenone are essentially completely quenched. The quantum yield for acetophenone is known to be unity.⁶⁵ With the exception of 2,2-dimethyl-1,3-diphenylpropan-1,3-dione (diBzdiMeMt) all of the ketones whose intersystem crossing yields were measured have intersystem crossing yields of unity. Since this is what is generally observed for phenyl ketones³⁵ and since there are no structural differences which would be expected to affect the intersystem crossing yield in any of the ketones whose intersystem crossing yields were not measured, it can safely be assumed that their intersystem crossing yields are also unity.

F. Triplet Lifetimes

The triplet lifetimes of all ketones which undergo the Norrish type II reaction were determined by Stern-Volmer kinetics^{35,62} with 2,5-dimethylhexa-2,4-diene as a quencher. Equations 3, 6, and 10 in the introduction

describe this type of kinetics for the three types of systems discussed in this dissertation. In all cases a plot of Φ°/Φ versus quencher concentration gives a straight line at low quencher concentration with the slope equal to $k_q\tau^\circ$ where τ° is the triplet lifetime in the absence of quencher. The lifetimes can be determined from $k_q\tau^\circ$ since the value of k_q for 2,5-dimethylhexa-2,4-diene is known to be $5 \times 10^9 \text{ M}^{-1}\text{sec}^{-1}$ in benzene.⁶⁶

In cases where no photochemical reaction was observed, values for $k_q\tau^\circ$ were obtained from the efficiency with which the ketone sensitizes the cis-trans isomerization of either 1,3-pentadiene⁶⁷ or stilbene. Equation 4 in the introduction describes sensitization⁶³ kinetics. When $\alpha/\Phi_{\text{isomerization}}$ is plotted versus the inverse of the quencher concentration, where α is 0.55 for 1,3-pentadiene⁶⁸ and 0.59 for stilbene,⁶⁸ a straight line is obtained with intercept of $1/\Phi_{\text{isc}}$ and slope $k_q\tau^\circ/\Phi_{\text{isc}}$.

G. Spectroscopy

Ultraviolet spectra were taken in benzene in order to determine the extinction coefficient at the wavelength used to irradiate the ketone. These data are necessary in order to correct for differences in the amount of light absorbed by the actinometer and diketone solutions used. Spectra were also taken in alkane solvents in order to check for ground state interactions between

chromophores. Occasionally spectra were also taken in ethanol.

Phosphorescence spectra were taken in methyltetrahydrofuran glass at 77° K in order to determine the energy of the lowest triplet state in the system and also to check for interchromophore complexation. In almost all of the spectra dual phosphorescence is observed.⁶⁹ This phenomenon is believed to arise from several causes including slow relaxation of the Franck-Condon triplet to the conformationally relaxed triplet. Both values are reported for ketones where they were observable. Attempts to take spectra in hydrocarbon solvents resulted in broad, structureless, red shifted spectra for most of the diketones discussed in this dissertation. This is probably due to microcrystallization upon cooling caused by the low solubilities of the ketones in hydrocarbon solvents.

II. Energy Transfer Studies

The results obtained from several unsymmetric diketones and the ketones containing the appropriate model chromophores are presented in this section. It is possible to determine approximate rates for the energy transfer between the chromophores of these diketones using the methods presented in the discussion section of this dissertation. The diketones studied and their abbreviations are presented in Figure 1. The ketones used to provide models for the independent chromophores are as

follows: 1,5-diphenylpentan-1-one (δ PhVP), 1-(4'-ethylphenyl)-pentan-1-one (pEtVP), 4-ethylacetophenone (pEtAc), 1,6-bis-(4'-ethylphenyl)-hexan-1,6-dione (dipEtBzBt), 1,6-diphenylhexan-1,6-dione (diBzBt),⁷⁰ 4-(4'-cyano-phenoxy)-1-phenylbutan-1-one (γ CNPhOBP), 4-phenoxy-1-phenylbutan-1-one (γ PhOBP),⁵⁷ 1-(4'-methoxyphenyl)-pentan-1-one (pMeOVP),^{59,60} 4-methoxyacetophenone (4MeOAc), 5-(4'-cyanophenoxy)-1-phenylpentan-1-one (δ CNPhOVP), and 5-phenoxy-1-phenylpentan-1-one (δ PhOVP). The syntheses or sources of these ketones are presented in the experimental section of this dissertation.

A. Photokinetic Results

The basic types of studies used to determine the photokinetic results were presented in the introduction and section I of the results portion of this dissertation. The detailed descriptions of the techniques used and the experimental data are presented in the experimental section. The quantum yields and $k_q\tau$ values are presented in Table 1. The Stern-Volmer plots (slope = $k_q\tau$) are presented in Figures 6-9. In all cases the $k_q\tau$ values obtained for the chromophores of an unsymmetric diketone lie between those obtained for model ketones containing the individual chromophores.

In the δ ValPhVP system the data for the benzoyl chromophore (Bz) were obtained by measuring the amount of acetophenone produced under the appropriate conditions. The data for the toluoyl chromophore (Tl) was obtained

Table 1: Quantum Yields and $k_q \tau^\circ$ Values for Unsymmetric Diketones and Model Monoketones

Ketone ^a	Chromo- phore	ϕ_{II}	ϕ_{II}^{Max}	ϕ_{Dis}	ϕ_{Dis}^{Max}	ϕ_{isc}	$k_q \tau^\circ$
4'VP δ PhVP	Bz	.21 $\pm$.01(.22) ^b	.34 $\pm$.01 ^c		.55 ^c	1.04 ^b	99.5(107) ^b
	Tl	.12 $\pm$.01(.14) ^b	.23 $\pm$.03 ^c				92.1(99.0) ^b
4'Ac δ PhVP		.30 $\pm$.01(.33) ^b	.51 $\pm$.03 ^{c,d}	.39	.49 ^c	1.03 ^b	177(171) ^b
1Bz4pEtBzBt	Bz	.26 $\pm$.03	.36 $\pm$.03 ^{c,d}				149 $\pm$ 5
	pEtBz	.072 $\pm$.01	.11 $\pm$.01 ^{c,d}	.42			165 $\pm$ 2
4'VP γ PhOBP	Bz	.33 $\pm$.01	.49 ^d				349
	An	.039 $\pm$.004	.065 ^d				438
4'Ac γ PhOBP		.29 $\pm$.01	.53 ^d				552 $\pm$ 16
4'VP δ PhOVP	Bz	.21 $\pm$.01	.31 ^d				1134
	An	.075 $\pm$.005	.16 ^d				1579
4'Ac δ PhOVP		.34 $\pm$.01	.42 ^d				2012
δ PhVP		.30 $\pm$.01(.33) ^b	.64 $\pm$.02 ^c				42.3 $\pm$ 2.5 ^b
pEtVP		.27 $\pm$.01(.31) ^b	.54 $\pm$.01 ^c			1.02 ^b	253 $\pm$ 22 ^b

Table 1 (cont'd.)

Ketone ^a	Chromo- phore	ϕ_{II}	ϕ_{II}^{Max}	ϕ_{Dis}	ϕ_{Dis}^{Max}	ϕ_{isc}	$k_q \tau^\circ$
diBzBt		.42±.02	.54±.01 ^c	.45±.01	.59 ^c	1.02	80.1±2.4
diBzBt ^e		.33±.03	.43 ^f				55±3
dipEtBzBt		.27±.03	.28±.01 ^c	.30±.01		1.06	371±10
δCarboMeOVP ^g		.61		.79	1.0		131±3
4'CNγPhOBP		.40±.05	.56±.06 ^d				80.9±1.6
γPhOBP		.32 ^g	.66 ^d				23 ^g
pMeOVP		.14 ^h	.22 ^h				2200 ⁱ
4'CNδPhOVP		.38±.03	.53±.01 ^d				404±9
δPhOVP		.43±.04	.70 ^d				193±6

- a. 0.01 M in benzene unless otherwise stated
b. 0.05 M diketone
c. dioxane added
d. pyridine added
e. values from ref. 68 (0.1 M diketone)
f. t-BuOH added
g. values from ref. 56
h. values from ref. 58
i. values from ref. 59

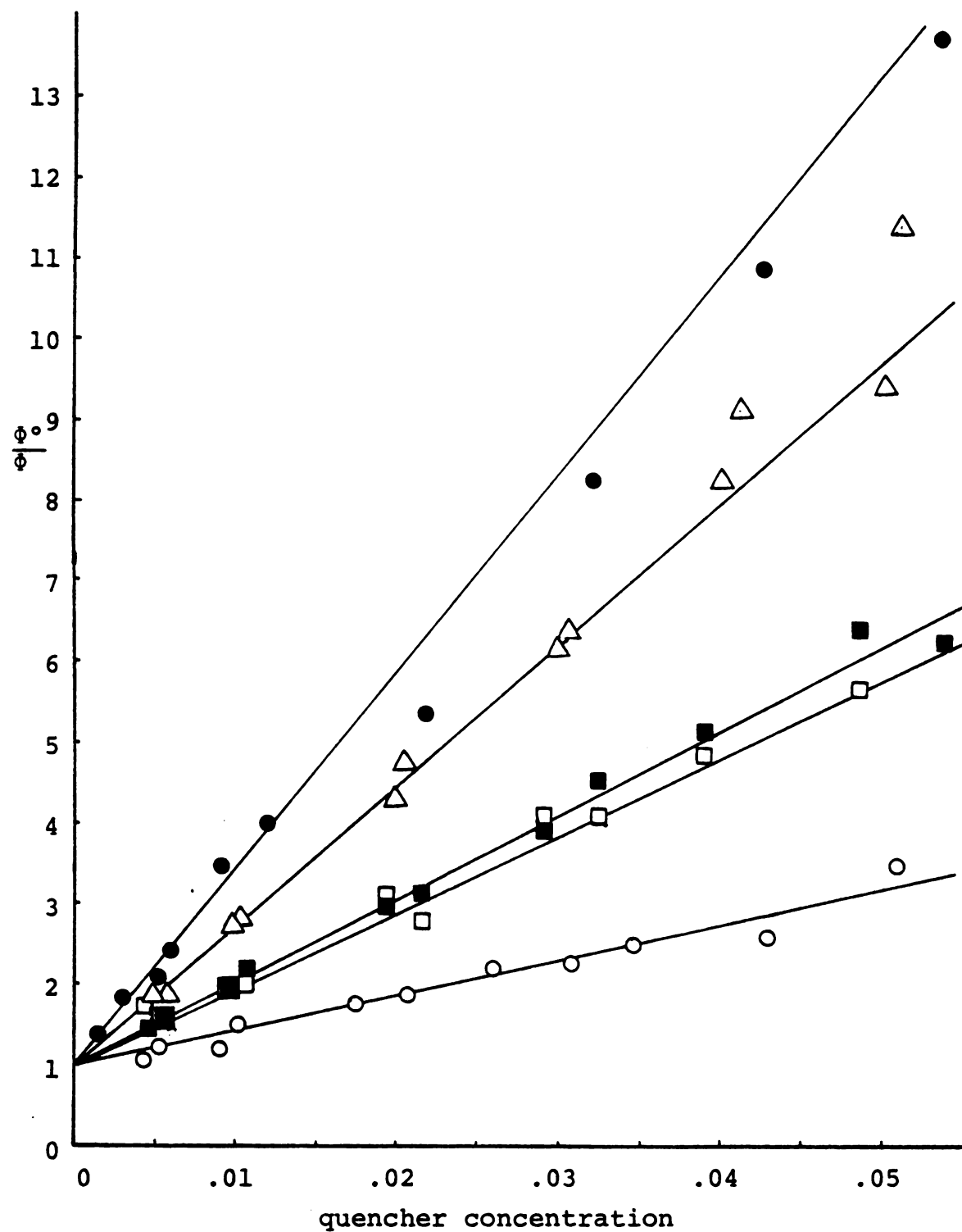


Figure 6: Stern-Volmer Kinetics for the δ ValPhVP System

($\circ$ δ PhVP; $\blacksquare$ Ac, δ ValPhVP; $\square$ Pr, δ ValPhVP; $\triangle$ δ AcPhVP;
 $\bullet$ pEtVP)

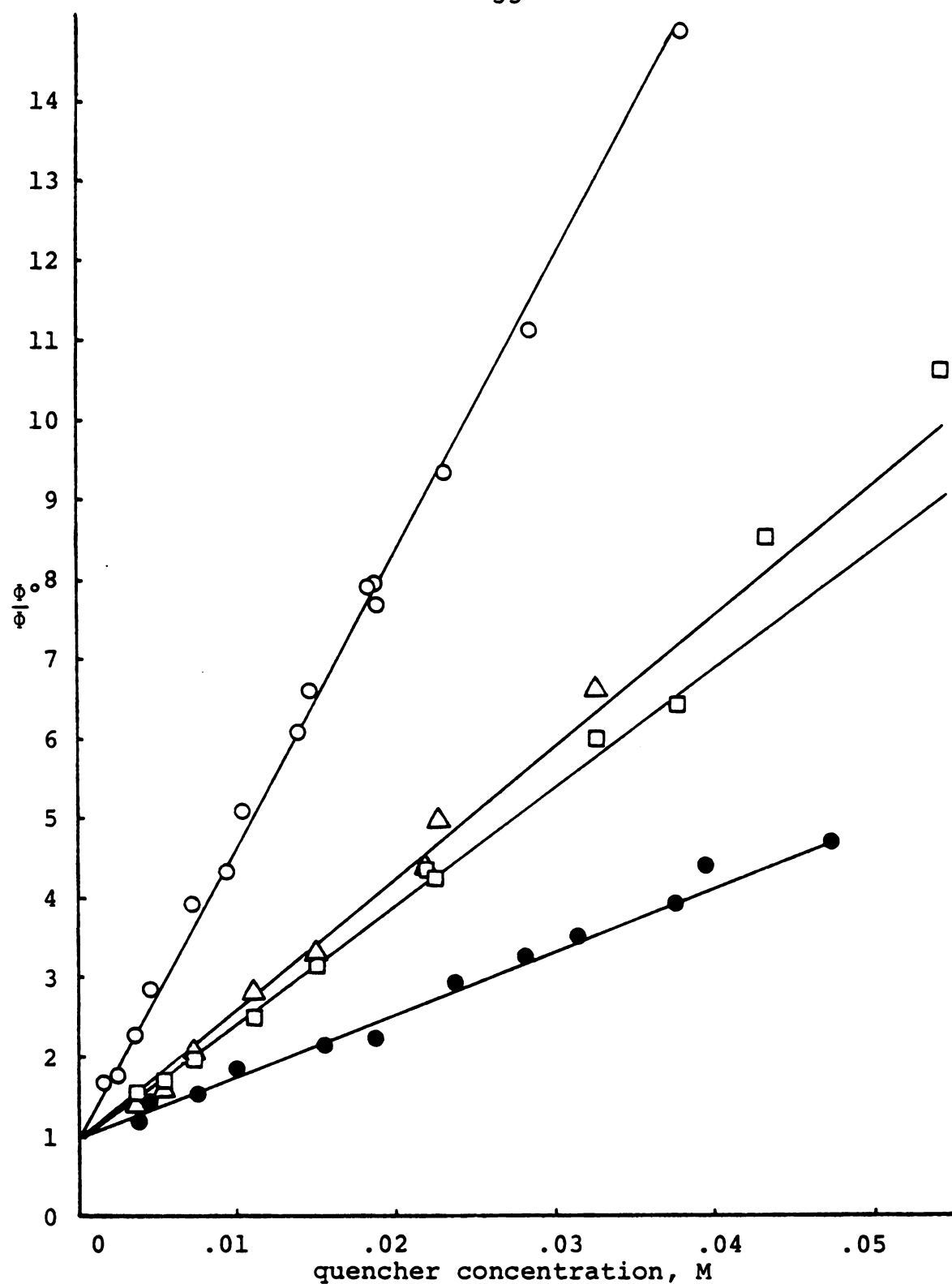
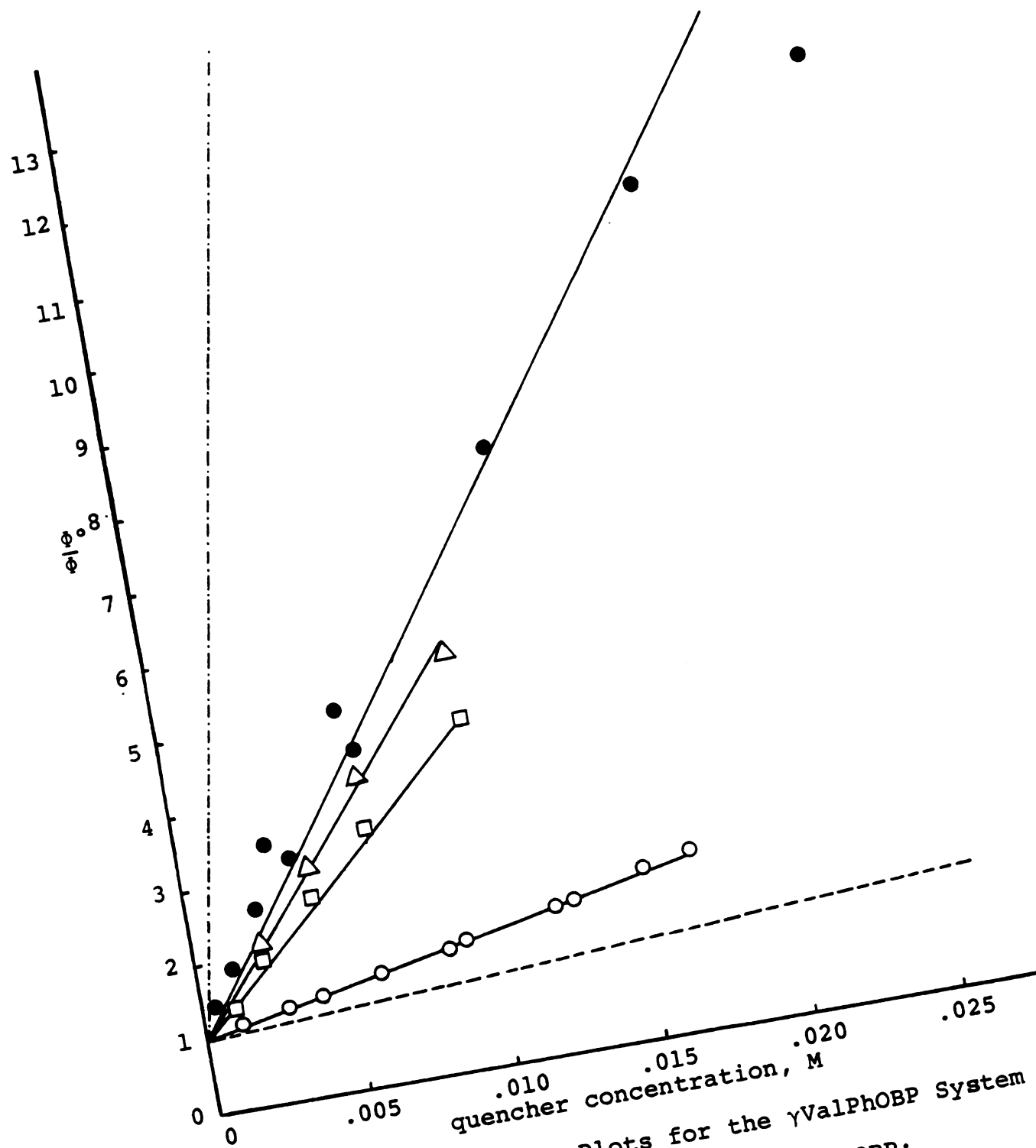


Figure 7: Stern-Volmer Plots for the 1Bz4pEtBzBt System
 (● diBzBt; ○ dipEtBzBt; □ 1Bz4pEtBzBt, Ac; △ 1Bz4pEtBzBt, pEtAc)



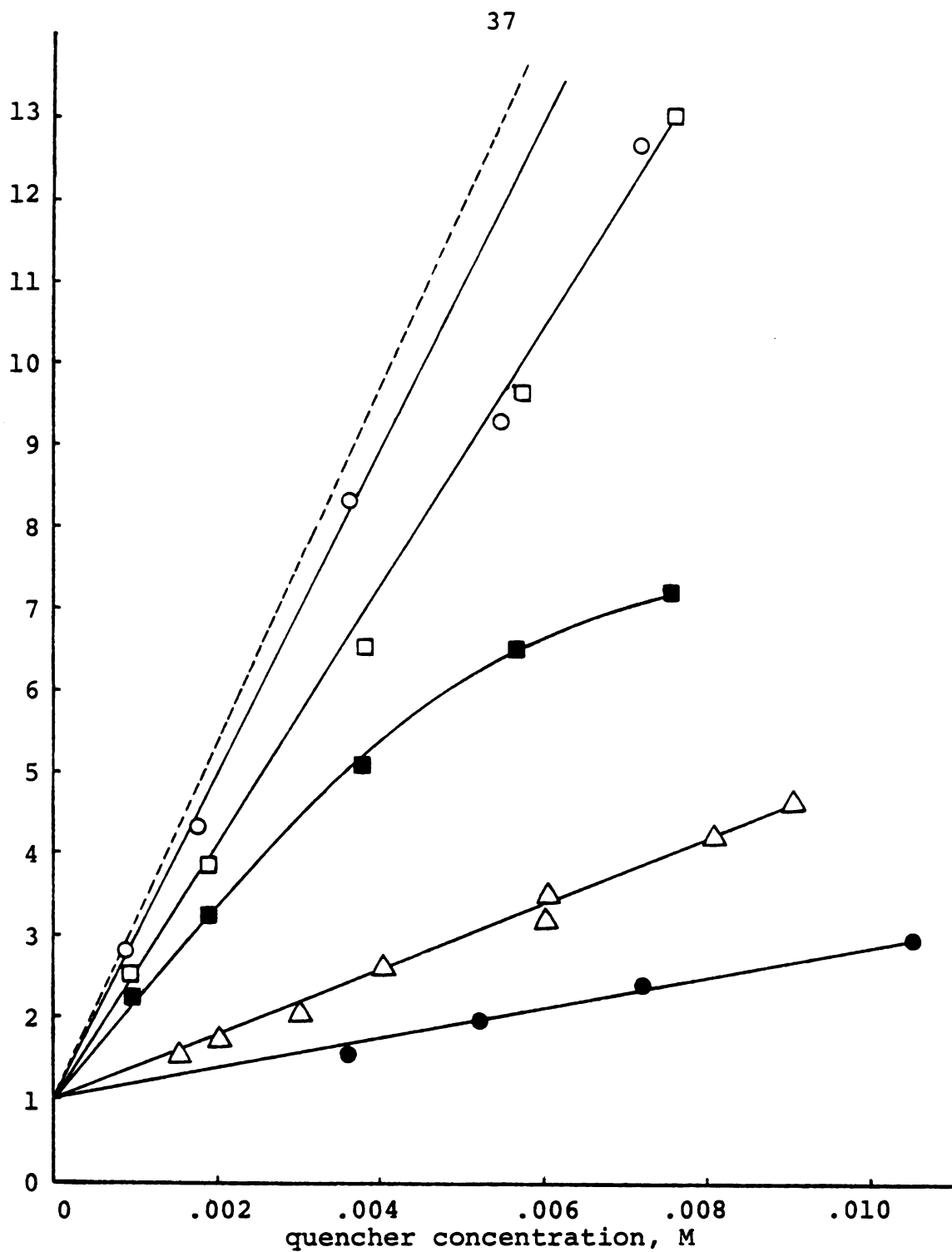


Figure 9: Stern-Volmer Plots for the $\delta\text{ValPhOVP}$ System
 (□ $\delta\text{ValPhOVP}$, Pr; ■ $\delta\text{ValPhOVP}$, Ac; ○ $\delta\text{AcPhOVP}$;
 △ $\delta\text{CNPhOVP}$; ● δPhOVP ; ----- pMeOVP)

from propene measurements. The results for the δ AcPhVP system and the model ketones used for these systems, δ PhVP and pEtVP, were obtained from the appropriate acetophenone determinations. The values obtained at 0.05 M and 0.01 M show only the slight enhancement in the Norrish type II quantum yields normally observed for phenyl alkyl ketones when the ketone concentration is increased.⁶⁰ Within experimental error the $k_q\tau$ values observed for the two chromophores in the δ ValPhVP system are the same. The ϕ_{Cy} for δ AcPhVP, determined from product ratios observed in preparative scale photolysis, is 0.060. The ϕ_{Cy} and ϕ_{Cy}^{Max} for pEtVP are 0.058 ± 0.001 and 0.085 ± 0.003 . The values obtained for ϕ_{Dis}^{Max} for δ ValPhVP and δ AcPhVP are slightly less than those observed for the sum of the product quantum yields under these conditions due to the large error involved in the determination of disappearance quantum yields.

The 1Bz4pEtBzBt system contains the same chromophores at approximately the same spacing as the δ ValPhVP system but the toluoyl chromophore is turned around. The Stern-Volmer data for the toluoyl chromophore in 1Bz4pEtBzBt was obtained from measurements of the amount of 1-phenylbut-3-en-1-one under the appropriate conditions while quantum yields for this chromophore were obtained from measurements of the amount of pEtAc produced. All the data for the toluoyl chromophore of 1Bz4pEtBzBt as well

as for the model ketones, diBzBt and dipEtBzBt, were obtained by measurement of the appropriate acetophenone. The quantum yields and $k_q\tau$ value Kemppainen⁷⁰ reported for diBzBt are lower than those I obtained for this ketone indicating that the ketone he used may have contained a quenching impurity. The maximum quantum yields observed for diBzBt, dipEtBzBt, and lBz4pEtBzBt are much lower than in model ketones, including methyl 5-phenyl-4-oxocaproate (δ -CarbOMeVP).⁵⁷ The ϕ_{Dis}^{Max} for diBzBt is in good agreement with the 10% cyclobutanol formation expected for this ketone.⁵⁹ As in the case of δ ValPhVP the $k_q\tau$ values for the two chromophores of lBz4pEtBzBt are the same within experimental error.

The γ ValPhOBP system contains the same chromophores as the 1-(4'-methoxyphenyl)-6-phenylhexan-1,6-dione (lBz4AnBt) system studied by Wagner and Nakahira,¹⁰ and if the ether oxygen is not considered part of the anisoyl chromophore, approximately the same interchromophore spacing. The data for the anisoyl chromophore was determined by measuring the propene produced under the appropriate conditions. For the benzoyl chromophore of γ ValPhOBP and γ AcPhOBP and their model ketones, γ CNPhOBP, γ PhOBP,⁵⁷ and pMeOVP,⁵⁹ the data was obtained from the appropriate acetophenone determination. In order to estimate the effects of the substituents on the phenoxy group on the rate of γ -hydrogen abstraction by the benzoyl group, it is

necessary to consider both $\gamma\text{CNPhOBP}$ and γPhOBP . As was observed for 1Bz4AnBt ¹⁰ the difference in the $k_q\tau$ values for the two chromophores of the $\gamma\text{ValPhOBP}$ system is just barely greater than the experimental error in their determination, with the lifetimes of the chromophores displaced from their average towards the lifetimes observed for these chromophores in the appropriate model ketones.

The $\delta\text{ValPhOVP}$ system also contains the same chromophores as the 1Bz4AnBt system studied by Wagner and Nakahira,¹⁰ but in this system the same interchromophore distance would be observed with the anisoyl chromophore turned around if the ether oxygen is considered part of the anisoyl chromophore. The data was obtained by measuring the same products as were measured for the $\gamma\text{ValPhOBP}$ and $\gamma\text{AcPhOBP}$ systems. The observed $k_q\tau$ values for both chromophores of $\delta\text{ValPhOVP}$, $\delta\text{AcPhOVP}$, and for $\delta\text{CNPhOVP}$ and δPhOVP are considerably higher than those observed for $\gamma\text{ValPhOBP}$ and its model systems. There is a much greater difference in the $k_q\tau$ values obtained for the $\delta\text{ValPhOVP}$ system than was observed with the $\gamma\text{ValPhOBP}$ system.

B. Spectroscopic Results

The spectroscopic results for the ketones used in these energy transfer studies are tabulated in Table 2. The ultraviolet spectra of the unsymmetric diketones are essentially the sum of the spectra observed for the individual chromophores from model systems. As can be

Table 2: Spectroscopic Data for Unsymmetric Diketones and Monoketone Models

Ketone	n $\rightarrow$ π^* λ_{Max} nm	absorption ^a		phosphorescence ^b	
		ϵ_{313} [M] ⁻¹ cm ⁻¹	relaxed nm(kcal/mole)	Franck-Condon nm(kcal/mole)	
δ ValPhVP	320	127.7	400 (71.5)	392 (72.9)	
δ AcPhVP	317	128.4	401 (71.3)	392 (72.9)	
lBz4pEtBzBt	317	144.6	401 (71.3)	392 (72.7)	
γ ValPhOBP	316	211.2	409 (69.9)	401 (71.3)	
γ AcPhOBP	316	226.7	411 (69.6)	401 (71.3)	
δ ValPhOVP	317	224.6	408 (70.1)	400 (71.5)	
δ AcPhOVP	317	190.7	411 (69.6)	402 (71.1)	
δ PhVP	319	49.0	390 (73.3)	384 (74.5)	
pEtVP	309	75.7	401 (71.3)	392 (72.9)	
pEtAc	309	77.7	401 (71.3)	392 (72.9)	
diBzBt	319	109.7	392 (72.9)	385 (74.3)	
dipEtBzBt	318	157.0	402 (71.1)	393 (72.7)	
γ CNPhOBP	316	59.8	392 (72.9)	384 (74.5)	
γ PhOBP	316	53.7	392 (72.9)	384 (74.5)	
pMeOVP	313	147.1		397 (72.0)	
pMeOAc		132.1	408 (70.1)	399 (71.7)	
δ CNPhOVP	318	57.3	391 (73.1)	384 (74.5)	
δ PhOVP	318	52.2	392 (72.9)	384 (74.5)	
VP	320	47.3	393 (72.7)	385 (74.3)	

a. in benzene

b. in 2-methyltetrahydrofuran at 77°

seen from the representative phosphorescence spectra shown in Figures 10-13, the phosphorescence spectra of the unsymmetric diketones are identical to those of the model ketones containing their lowest energy chromophores. The phosphorescence spectra for the γ AcPhOBP, δ ValPhOVP, and δ AcPhOVP systems are identical to those of the γ ValPhOBP system.

III. Self-Quenching Studies

The results obtained from several symmetric diketones in which self-quenching appears to occur are presented in this section. A detailed discussion of the self-quenching phenomena will be given in the discussion section of this dissertation. The ketones studied and their abbreviations are as follows: 2,2-dimethyl-1,3-diphenylpropan-1,3-dione (diBzdiMeMt), 1,4-diphenylbutan-1,4-dione (diBzEt), 1,5-diphenylpentan-1,5-dione (diBzPr),³⁴ 1,6-diphenylhexan-1,6-dione (diBzBt),⁷⁰ 1,7-diphenylheptan-1,7-dione (diBzPt), and 1,6-bis-(4'-ethylphenyl)-hexan-1,6-dione (dipEtBzBt). The synthesis and sources of these ketones may be found in the experimental section of this dissertation.

A. Photokinetic Results

The basic types of studies used to determine the photokinetic results were presented in the introduction and section I of the results portion of this dissertation. The detailed descriptions of the techniques used and the experimental data are presented in the experimental section.

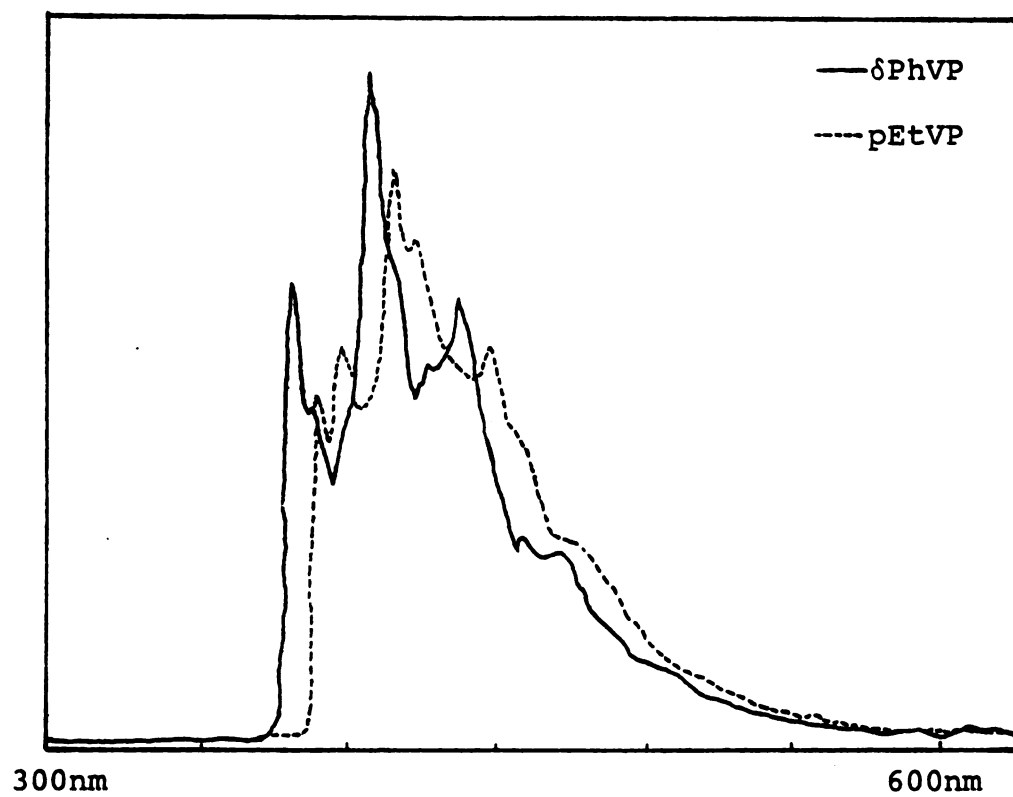
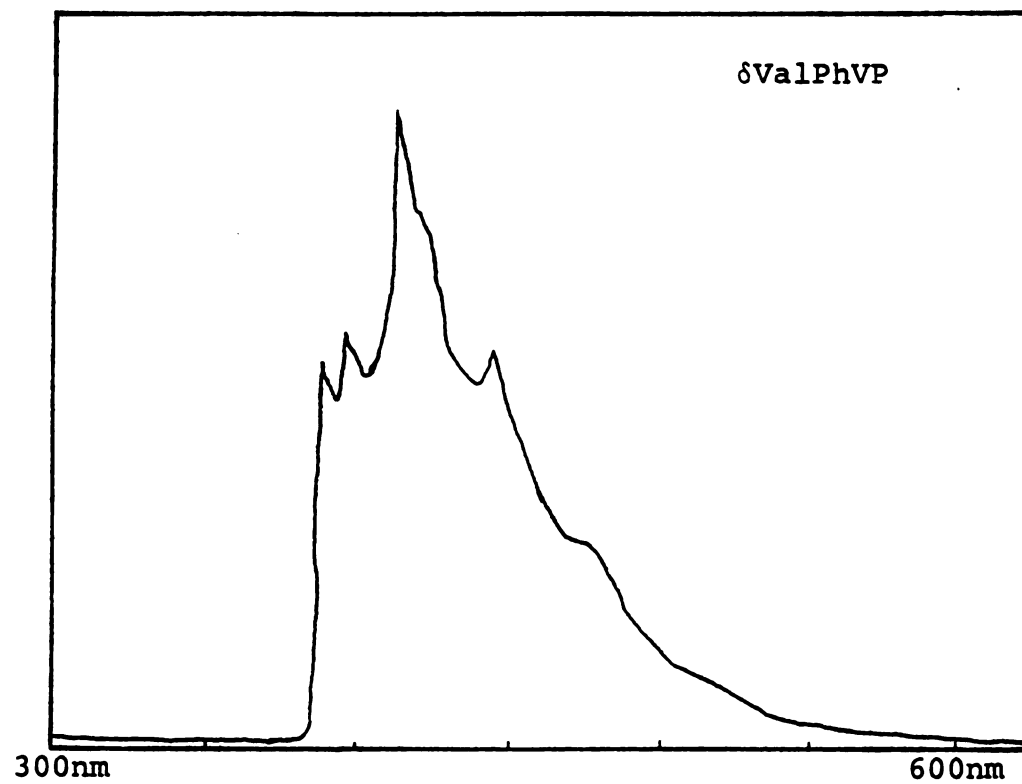


Figure 10: Phosphorescence Spectra for the $\delta\text{ValPhVP}$ System

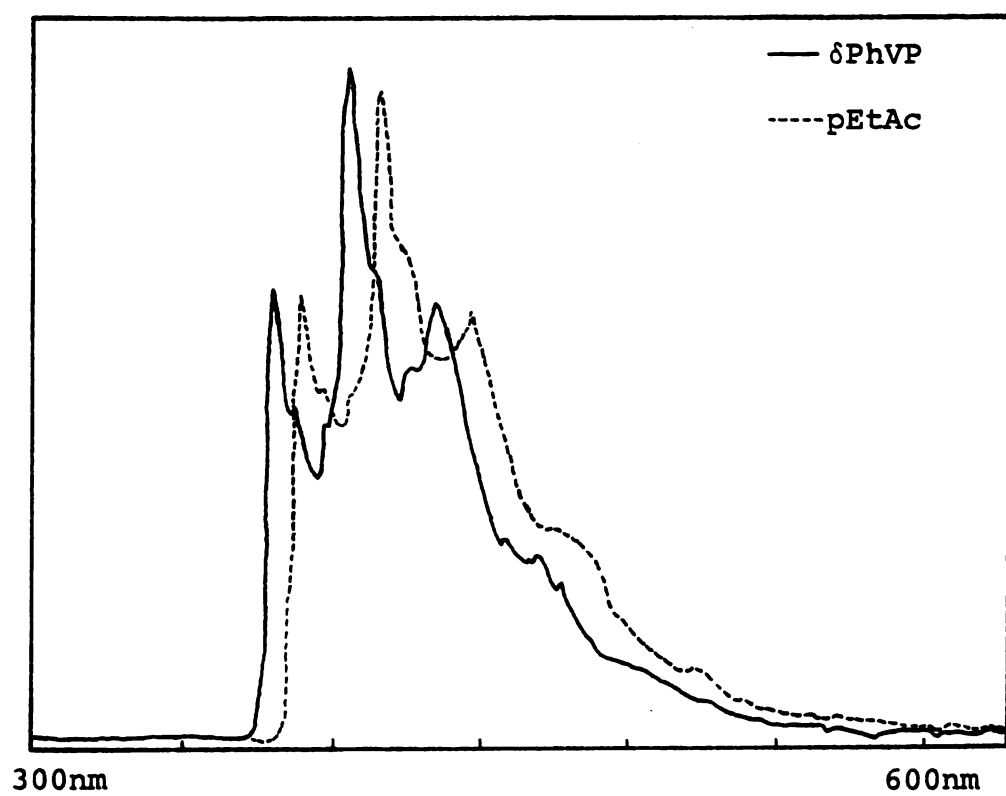
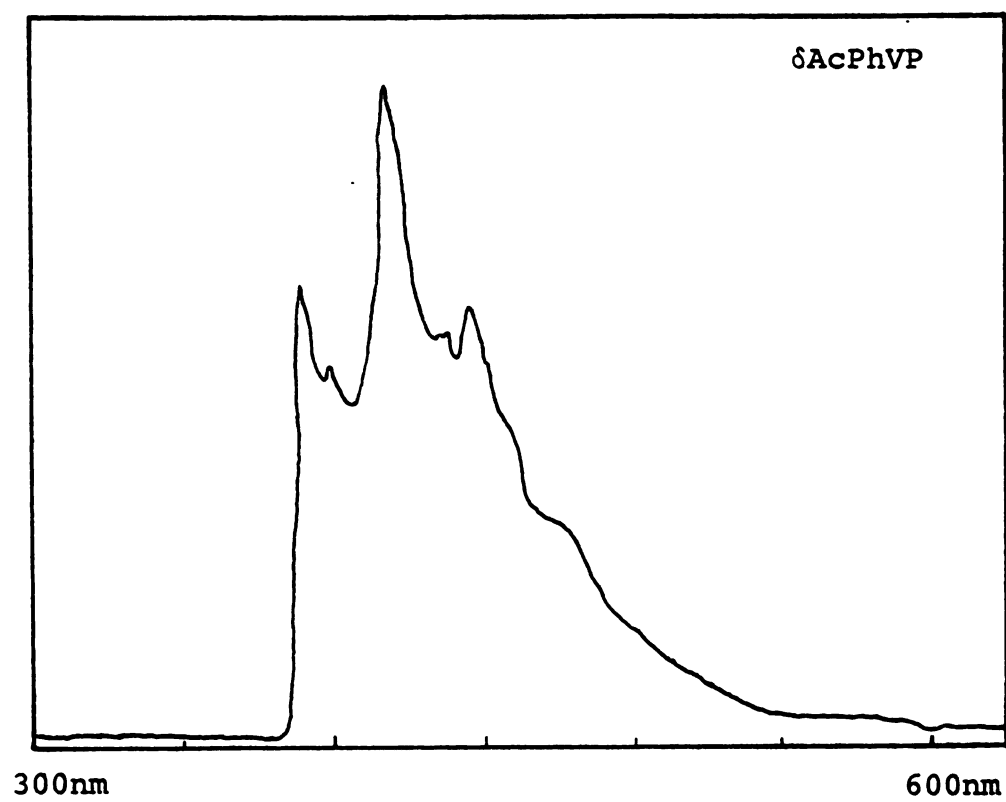


Figure 11: Phosphorescence Spectra for the δ AcPhVP System

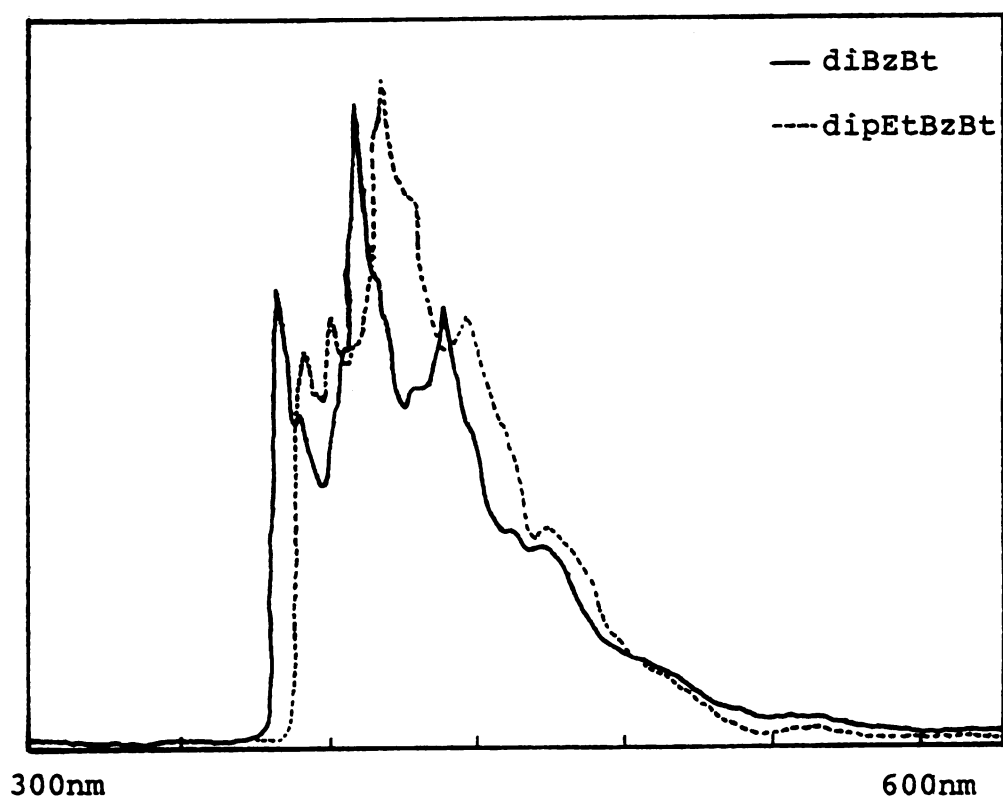
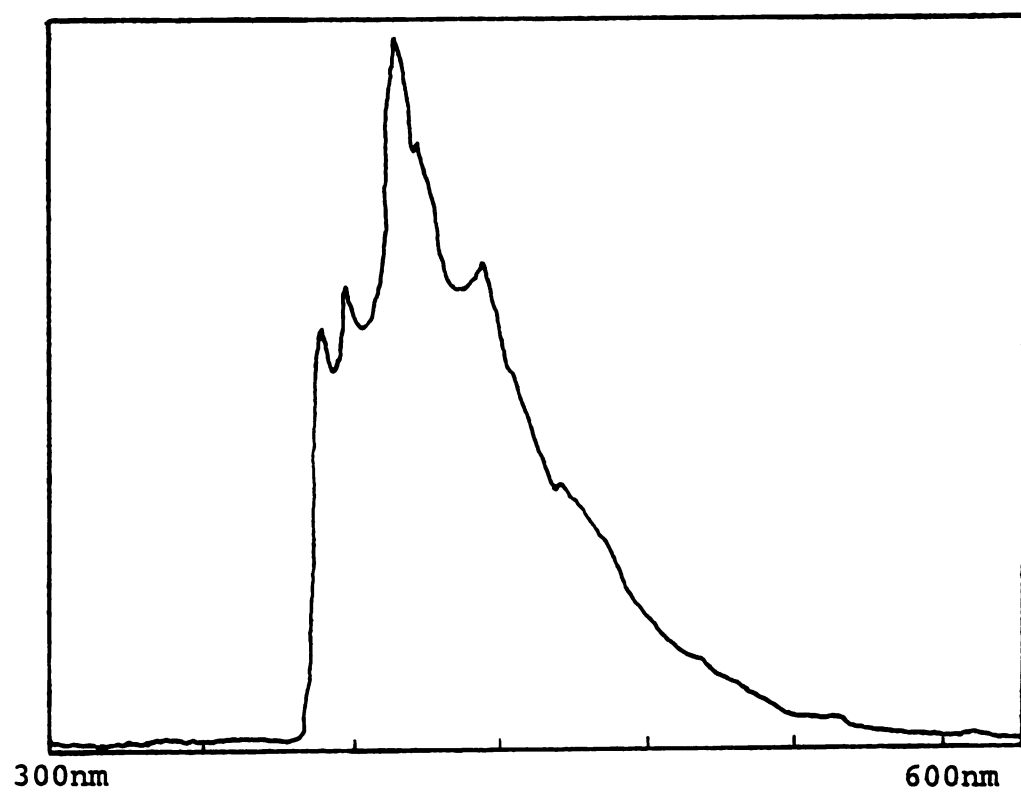


Figure 12: Phosphorescence Spectra for the 1Bz4pEtBzBt System

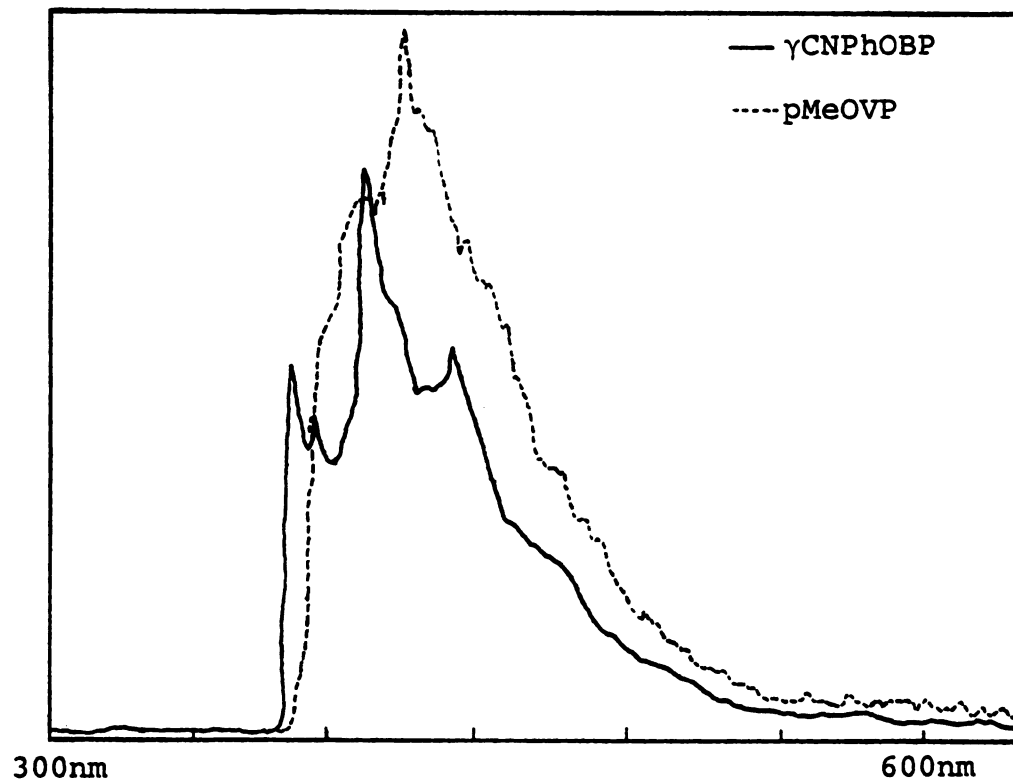
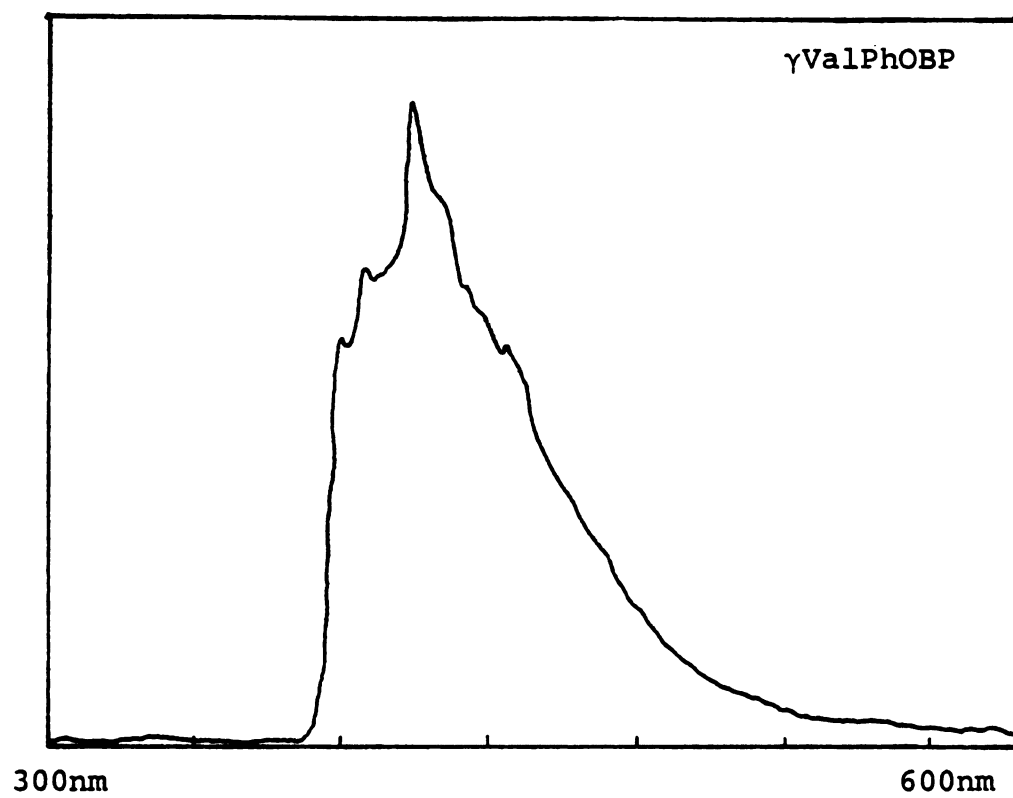


Figure 13: Phosphorescence Spectra for the γ ValPhOBP System

The quantum yields and $k_q\tau$ values are presented in Table 3. The quantum yields of intersystem crossing and $k_q\tau$ values of diBzdiMeMt and diBzEt were obtained from sensitization studies, and the resulting plots are presented in Figures 14 and 15. Extended irradiation of either diBzdiMeMt or diBzEt shows no disappearance of the diketone by either glc or pmr.

Because one of the Norrish type II cleavage products of diBzPr, 1-phenylprop-2-en-1-one, is a very good triplet quencher, it is necessary to extrapolate the quantum yields to zero ketone conversion and to correct the $k_q\tau$ values for added quenching by product. While Salvin³⁴ reports $k_q\tau$ and ϕ_{II} values for diBzPr, it is unclear whether any attempts were made to correct for this problem; and in general insufficient experimental data were presented to allow direct comparison of his numbers for this ketone to those I obtained. Values for 1,6-bis-(4'-methoxyphenyl)-hexan-1,6-dione (diAnBt),¹⁰ methyl 5-phenyl-4-oxocaproate (δ CarbOMeVP),⁵⁷ and methyl 4-phenyl-3-oxovalerate (γ CarbOMeBP) were obtained from the references cited. The variation of the quantum yield of acetophenone formation with conversion for diBzPr, both in the presence and absence of added Lewis base, is presented in Figure 16. The kinetics necessary to obtain the quantum yield at zero diketone conversion have been discussed by Wagner⁶³ and equation 11 correctly describes this phenomenon.

Table 3: Quantum Yields and $k_q\tau$ Values for Symmetric Diketones

Ketone	ϕ_{II}	ϕ_{II}^{Max}	ϕ_{Dis}	ϕ_{Dis}^{Max}	ϕ_{isc}	$k_q\tau, M^{-1}$
diBzdiMeMt			0		.70 ^a	488 ^a
diBzEt			0		1.0 ^a	300±3 ^a
diBzPr	.22 ^b	.77 ^{b,c}	.27±.01 ^b	1.0±.05 ^{b,c}	1.02	154±1 ^b
diBzPr ^d	.20					180
diBzBt	.42±.02	.54±.01 ^c	.45±.01	.59 ^c	1.02	80.1±2.4
diBzBt ^e	.33±.03	.43 ^f				55±3
diBzPt	.37±.03	.55±.03 ^{c,g}				45.1±1.4
dipEtBzBt	.27±.03	.28±.01 ^c	.30±.01		1.06	371±10
diAnBt ^h	.04	.06 ^g				1000
γ CarbOMeBP ⁱ	.50			1.0		490
δ CarbOMeVP ⁱ	.61		.79	1.0		131±3

a. from sensitization plots
 b. values extrapolated to 0% ketone conv.
 c. dioxane added
 d. values from ref. 34
 e. from ref. 68
 f. rBuOH added
 g. pyridine added
 h. values from ref. 10
 i. values from ref. 56

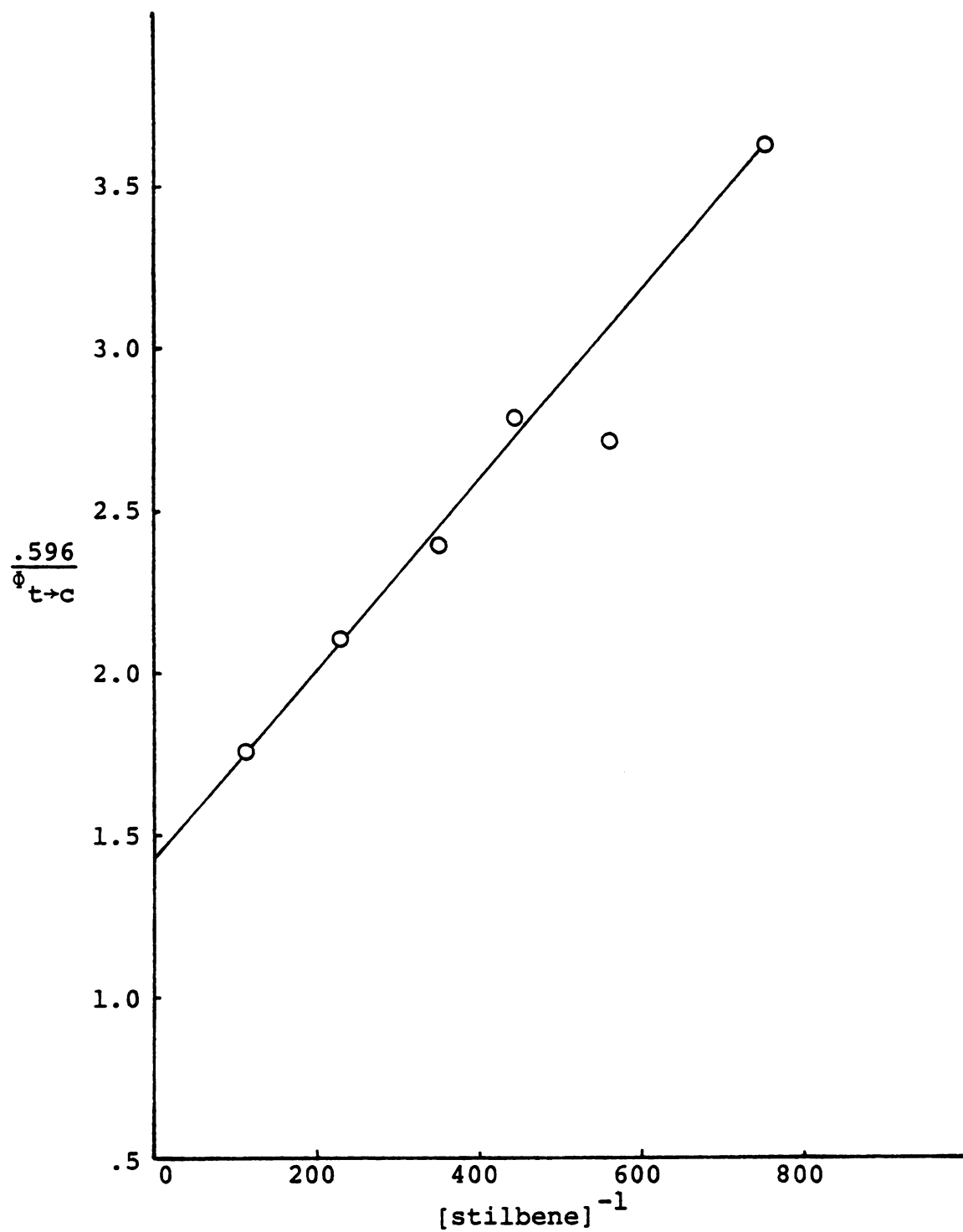


Figure 14: Sensitization Plot for diBzdiMeMt

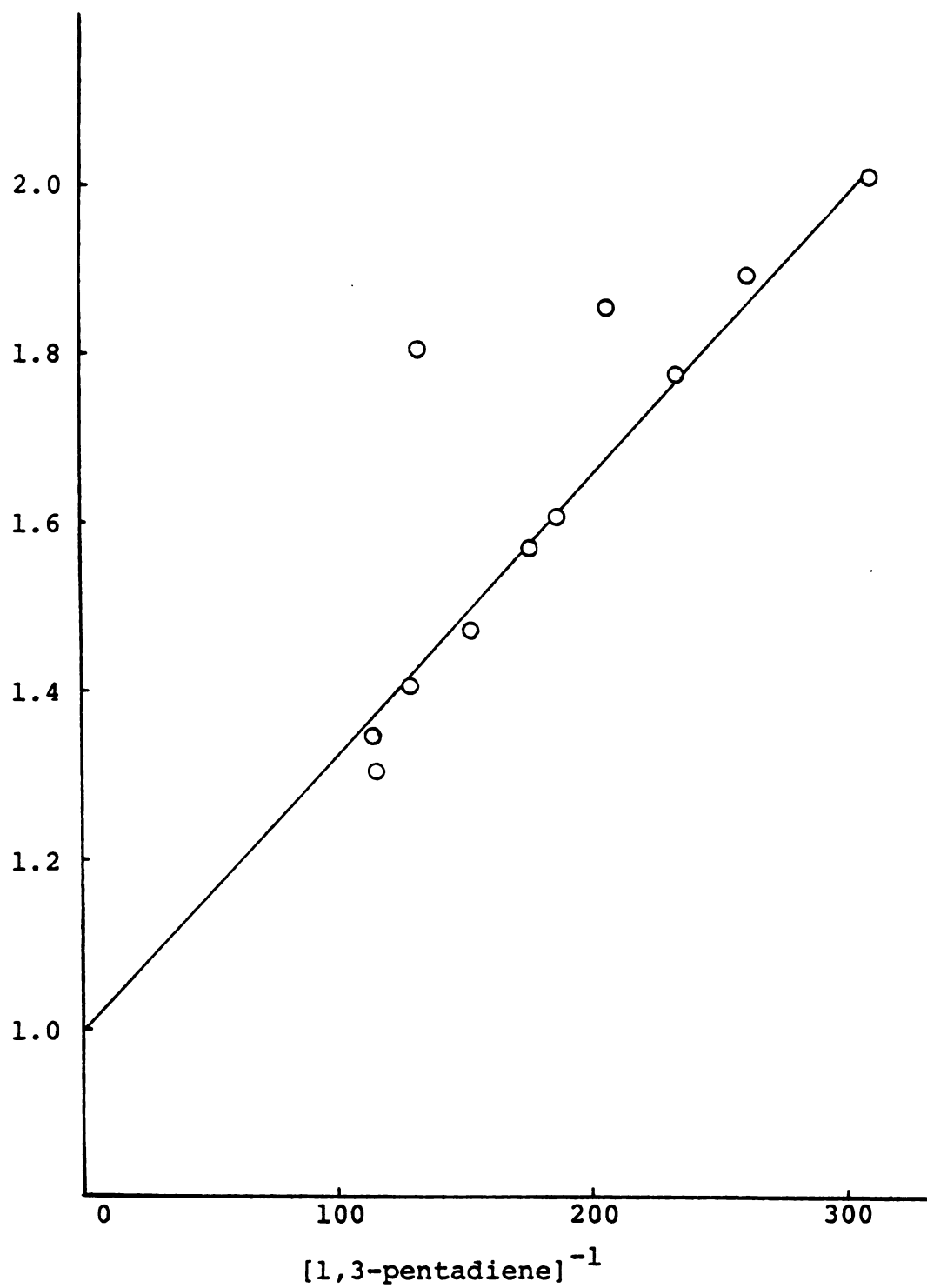
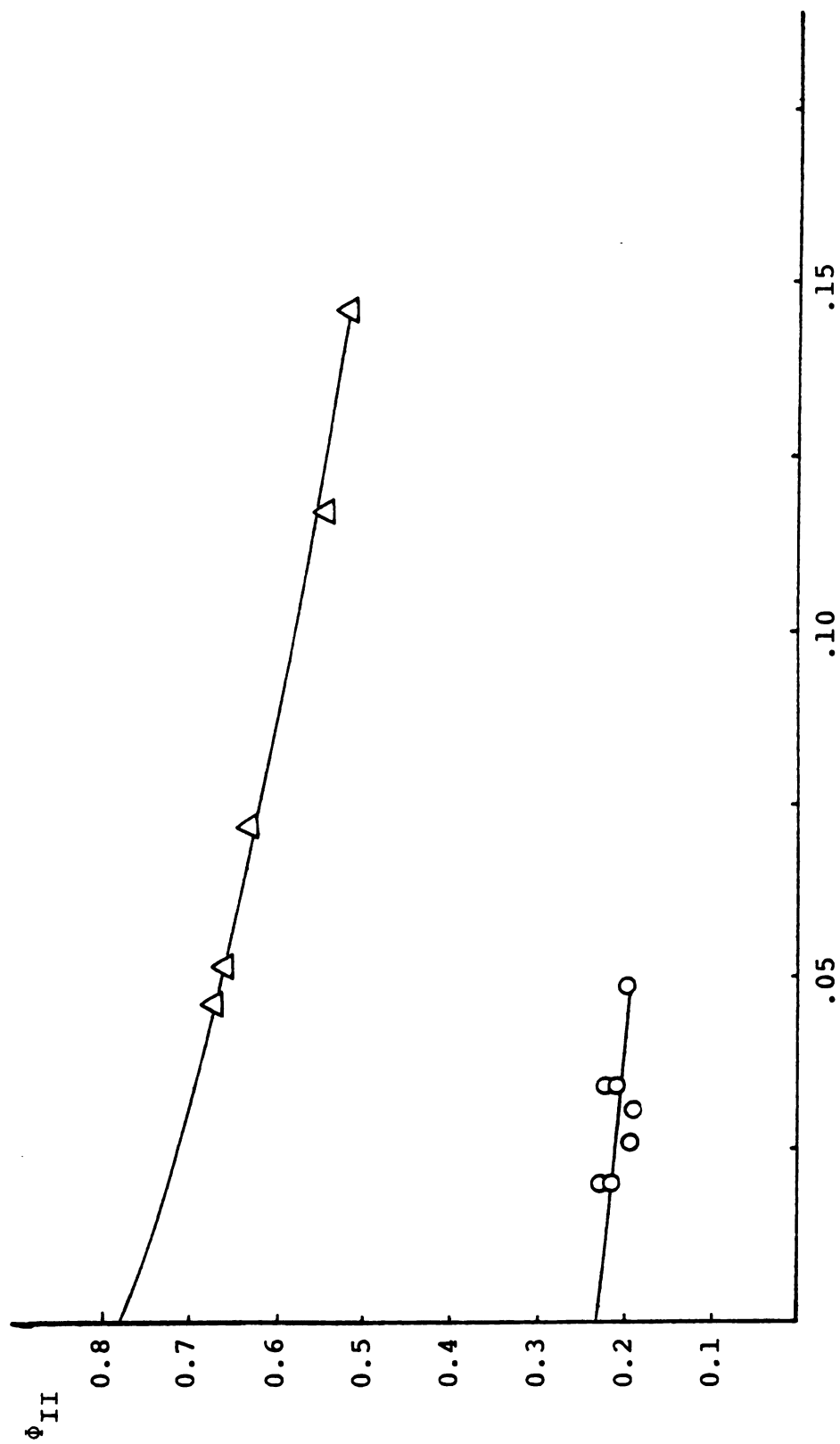


Figure 15: Sensitization Plot for diBzEt



Conversion x Diketone Concentration

Figure 16: Variation of ϕ_{II} with Conversion for diBzPr

(O no additive, Δ 4.5 M Dioxane)

$$\frac{1}{\phi_{II}} = \frac{1}{\phi_{II}^0} + \frac{k_q X C [K]}{\phi_{isc} P_{II} k_\gamma} \quad (11)$$

where X is the fraction of the final quenching product concentration which gives the effective quencher concentration over the full length of the experiment and C is the percent conversion of diketone.

The intercept of a plot of $1/\phi_{II}$ versus C[K] is $1/\phi_{II}^0$. These plots for diBzPr in the presence and absence of added Lewis base are shown in Figure 17. Stern-Volmer plots for diBzPr are presented in Figure 18. The $k_q \tau$ values obtained from these plots may be corrected for product quenching using equation 12.⁶⁰

$$(k_q \tau)^0 = \frac{\phi^0}{\phi_{obs}} (k_q \tau)_{obs} \quad (12)$$

The Stern-Volmer plot of diBzPt is also presented in Figure 18. The Stern-Volmer plots for diBzBt and dipEtBzBt were presented in Figure 6. The values of $k_q \tau$, ϕ_{II} , and ϕ_{II}^{Max} for diAnBt,¹⁰ γ CarbOMeBP⁵⁶ and δ CarbOMeVP,⁵⁶ obtained from the literature, are included in Table 3.

B. Spectroscopic Results

The spectroscopic results for symmetric diketones and the appropriate monoketone models are tabulated in Table 4. The extinction coefficients for diBzdiMeMt and diBzEt are considerably higher than those of the other dibenzoyl alkanes. The other dibenzoylalkanes

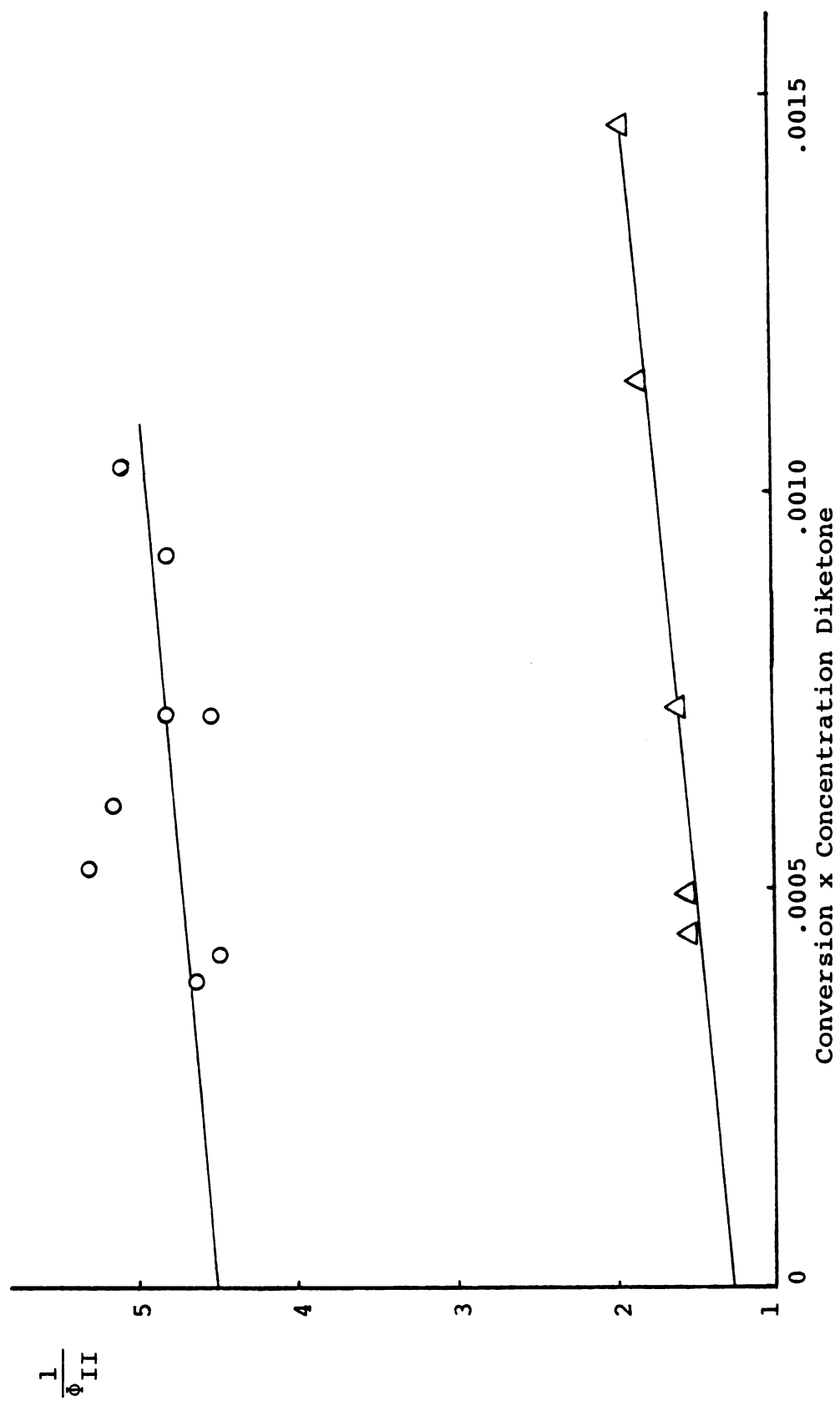


Figure 17: Determination of ϕ_{II}° for diBzPr (O no additive, Δ 4.5 M Dioxane)

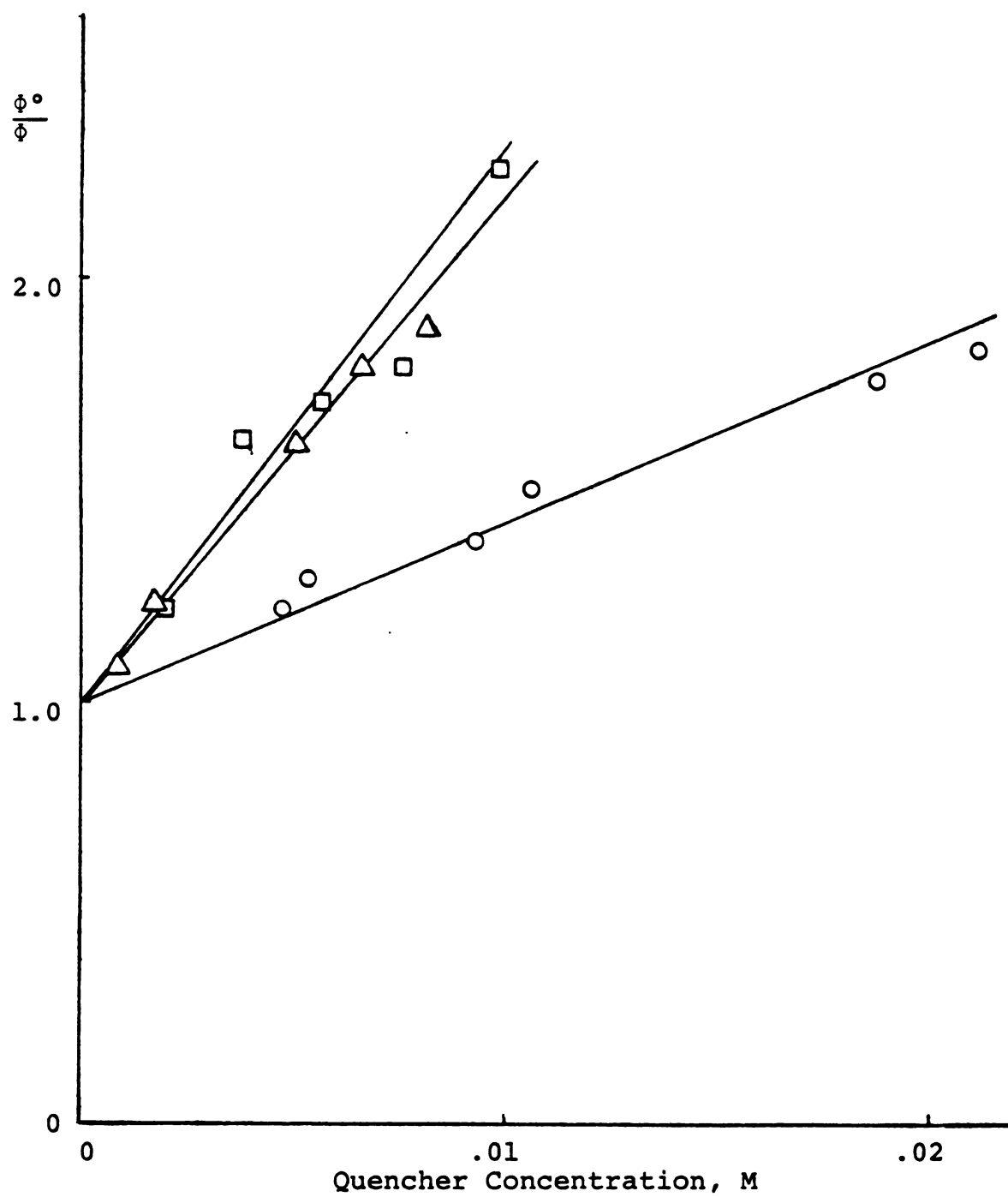


Figure 18: Stern-Volmer Plots for diBzPr and diBzPt
 ($\square$ diBzPr, 7.85% conv.; $\triangle$ diBzPr, 4.89% conv.; $\circ$ diBzPt)

Table 4: Spectroscopic Data for Symmetric Diketones

Ketone	n $\rightarrow$ π^* absorption ^a		phosphorescence ^b	
	λ_{Max} nm	ϵ_{313} [M] ⁻¹ cm ⁻¹	relaxed nm(kcal/mole)	Franck-Condon nm(kcal/mole)
diBzdiMeMt	320	214.8	394 (72.6)	^c
diBzEt	313	128.8	392 (72.9)	384 (74.5)
diBzPr	317	100.0	393 (72.7)	386 (74.1)
diBzBt	319	109.7	392 (72.9)	385 (74.3)
diBzPt	318	109.8	391 (73.1)	384 (74.5)
dipEtBzBt	318	157.0	402 (71.1)	393 (72.7)
VP	320	47.3	393 (72.7)	385 (74.3)
pEtVP	309	75.7	401 (71.3)	392 (72.9)

a. in benzene

b. at 77° in methyltetrahydrofuran glass

c. only one set of peaks observed for this ketone

appear to be only the sum of two valerophenone chromophores. The phosphorescence spectra of diBzdiMeMt and diBzEt are shown in Figure 19. The phosphorescence spectra of diBzBt and dipEtBzBt were presented in Figure 12. The phosphorescence spectra of diBzPr and diBzPt are identical with that of diBzBt. The spectrum of diBzdiMeMt is interesting in that it does not show the dual phosphorescence normally observed with phenyl alkyl ketones in 2-methyltetrahydrofuran.

IV. Quantum Mechanical Calculations

The self-quenching data presented in the previous section prompted a more theoretical study of possible carbonyl excimer formation. The ground state and lowest excited singlet and triplet states of a pair of formaldehyde molecules at various separations for two different relative orientations were studied by ab-initio SCF and CI theory. The first was a head-to-tail orientation in which the two molecules are placed in parallel planes of varying separations with the oxygen of one formaldehyde occupying the same coordinates in its plane as the carbon atom of the second molecule does in its plane. This orientation should leave both the π and n orbitals unavailable for possible interactions. The second orientation studied was one in which the two molecules are placed in the same plane with the oxygens aligned with the carbons. This orientation should give rise to almost the maximum amount of n orbital interaction.

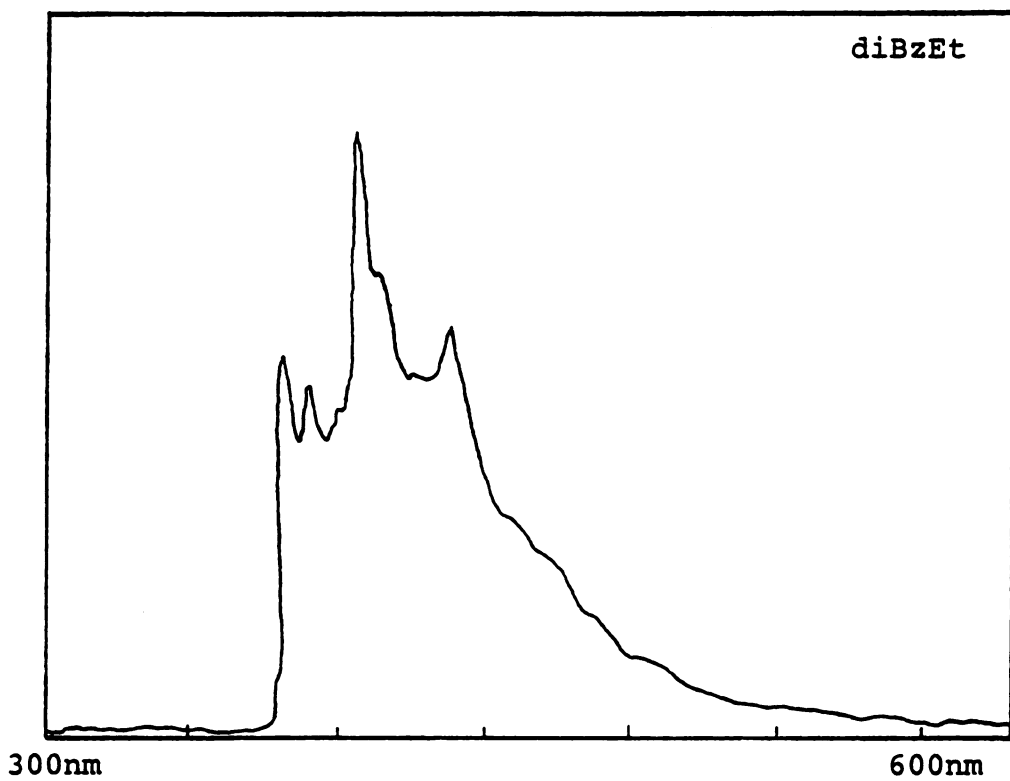
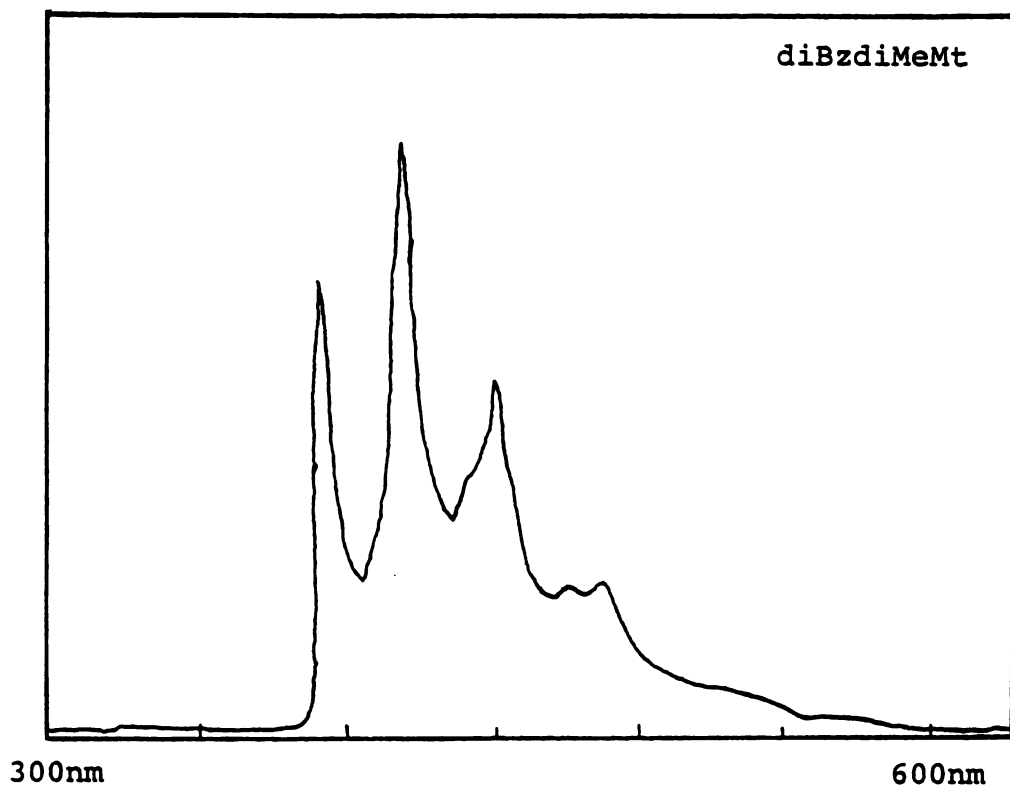


Figure 19: Phosphorescence Spectra of diBzdiMeMt and diBzEt

A third orientation in which the formaldehydes are placed head-to-head in parallel planes would also be of interest. This orientation, which should lead to maximum π orbital interaction, would amount to a broken dioxatane at small separations and possible exciplexes arising from it have been designated as "crypto" excimers by Turro.⁷¹ This orientation had already been studied by Dewar and Kirschner.⁷²

The calculations were carried out using standard integral and SCF programs, IBMOL and POLYATOM,⁷³ and a CI program, CIDAW, developed at Michigan State University by Dr. J. F. Harrison. The computer used was a Control Data Corporation model 6500. A STO-2G basis set was used for reasons of economy. The geometry of the formaldehyde molecules used was the standard one proposed by Gordon and Pople⁷⁴ and was held constant throughout the calculations. The results of these calculations are presented in Tables 5 and 6. To check the reliability of the STO-2G basis set the SCF calculations for the head-to-head approach were repeated using a STO-3G basis set and the results are presented in Table 7 and show the same relative changes with geometry.

The one electron-energies for the n and π orbitals in the head-to-head and head-to-tail orientations are given in Table 8. The head-to-head orientation produces the predicted n orbital interactions. The energy differences relative to the ground state for the two

Table 5: Di-Formaldehyde Energies^a vs Distance
Head-to-Tail Orientation

State	R=	5 Å	4 Å	3 Å	2 Å
¹ A _g (SCF)		-218.02076	-218.02074	-218.01976	-217.93266
¹ A _g (CI)		-218.05366	-218.05471	-218.05576	-217.96625
³ B _g		-217.90165	-217.90181	-217.90168	-217.86264
¹ B _g		-217.87087	-217.87113	-217.87143	-217.84812

a. Energies in Hartrees

Table 6: Di-Formaldehyde Energies^a vs Distance
Head-to-Head Orientation

State	R=	5 Å	4 Å	3 Å	2.5 Å
¹ A ₁ (SCF)		-218.02056	-218.01968	-217.99944	-217.92529
¹ A ₁ (CI)		-218.05340	-218.05348	-218.03301	-217.96016
³ A ₂		-217.90136	-217.90081	-217.89690	-217.83587
¹ B ₁		-217.87054	-217.87018	-217.87072	-217.81048

a. Energies in Hartrees

Table 7: SCF Energies^a for the Head-to-Head Orientation of the Di-Formaldehyde System

Carbonyl separation, Å	STO-3G	STO-2G	Difference
5	-224.41866	-218.02056	-6.39810
4	-224.41790	-218.01968	-6.39822
3	-224.40295	-217.99944	-6.40351
2.5	-224.33968	-217.92529	-6.41438

a. Energies in Hartrees

Table 8: Orbital Interactions for the Di-Formaldehyde System

Head-to-Head Orientation		
Orbital	one electron energy ^a	separation ^a
$ n_+>$	-0.3122290	0.0145182
$ n_->$	-0.2977718	
$ \pi_+>$	-0.4300376	0.0000967
$ \pi_->$	-0.4301343	
Head-to-Tail Orientation		
$ n_+>$	-0.3077229	.0002296
$ n_->$	-0.3079525	
$ \pi_+>$	-0.4327992	.0011729
$ \pi_->$	-0.4339721	

a. Energies in Hartrees

orientations studied are presented in Table 9.

Table 9: Energy^a Differences Relative to the Ground State for the Di-formaldehyde System

Symmetry	Separation ^b between Carbonyls, Å				
	2.0	2.5	3.0	4.0	5.0
¹ B ₁	---	0.14968	0.16229	0.18330	0.18294
³ B ₂	---	0.12429	0.13611	0.15267	0.15212
Head-to-Tail Orientation					
¹ B _g	0.11813	---	0.18433	0.18358	0.18279
³ A _g	0.07852	---	0.16637	0.16474	0.16353

a. Energies in Hartrees

b. Distance in Angstroms

DISCUSSION

I. Derivation of Rate Constants

Several rate constants can be obtained from the results presented in this dissertation. Most of these are derived in the same manner for all the ketones discussed. It is the derivations of these rate constants which are presented in this section.

A. Triplet Lifetimes

Triplet lifetimes, τ , for the various chromophores considered in this dissertation were obtained from the $k_q\tau$ values for the chromophores. The value of k_q has been determined to be $5 \times 10^9 \text{ sec}^{-1}\text{M}^{-1}$ in benzene for all the quenchers used in this dissertation.⁶⁶ Since all the conclusions of this dissertation are based on relative lifetimes, a systematic error in the value of k_q would not affect them. Because $1/\tau$ is equal to the sum of all the rates of decay of the state whose quenching is being observed, it is more useful to report $1/\tau$ values rather than τ values.

B. Maximum Quantum Yields of Disappearance and Cyclobutanol Formation

For some of the ketones discussed in this dissertation the maximum quantum yields of disappearance were measured

directly and a reasonable value for this quantity obtained. For most of the ketones discussed satisfactory conditions for the analysis of the ketones were not available or the conditions used were not sufficiently accurate to be useful except to eliminate substantial reaction pathways other than the Norrish type II reaction and concurrent cyclobutanol formation. In no instance was any other product expected or observed; so, in general, the assumption was made that $\phi_{\text{Dis}}^{\text{Max}}$ equaled the sum of $\phi_{\text{II}}^{\text{Max}}$ and $\phi_{\text{Cy}}^{\text{Max}}$. For most of the ketones involved the cyclobutanols were no easier to determine than the parent ketones; but, fortunately for this dissertation, the fate of the biradicals involved can be reasonably well predicted from the fate of similar biradicals where the starting ketone or cyclobutanols are more readily determined.⁵⁹ The validity of these predictions may be estimated by considering the observed predictability of the reaction patterns of a large number of biradicals formed as intermediates in the Norrish type II reactions of phenyl alkyl ketones.⁵⁹

C. The Rate of γ -Hydrogen Abstraction

The rate of γ -hydrogen abstraction, k_{γ} , was obtained by multiplying $\phi_{\text{Dis}}^{\text{Max}}$ by $1/\tau$.⁵⁷ The most important assumption involved in this calculation is that $\phi_{\text{Dis}}^{\text{Max}}$ represents the quantum yield of γ -hydrogen abstraction, or, in other words, that solvation by the Lewis base used in the determination of $\phi_{\text{Dis}}^{\text{Max}}$ completely eliminates all

revertibility of the biradical. This is what is observed for most phenyl alkyl ketones,⁶⁰ and there is no reason to believe it is not the case for the ketones discussed in this dissertation.

D. The Rate of Non-Productive Triplet Decay

The rate of non-productive triplet decay, k_d , is the sum of the rates of all processes occurring from the triplet state which do not produce measurable products. Since the Norrish type II reaction products and cyclobutanols are the only products observed from the ketones discussed in this dissertation and since these products come from a common biradical intermediate which is the result of γ -hydrogen abstraction by the triplet states of the chromophore,³¹ k_d is the difference between $1/\tau$ and k_γ . Traditionally k_d is divided into radiative processes. For the ketones discussed in this dissertation one would not expect to be able to observe phosphorescence at room temperature since the rates of phosphorescence from phenyl alkyl ketones which do phosphoresce at room temperature⁶⁸ are 10^5 times slower than the values of $1/\tau$ obtained for the chromophores discussed in this dissertation.

The non-radiative decay observed for the chromophores discussed in this dissertation can be expected to include at least three specific processes, δ -hydrogen abstraction,⁶¹ intramolecular charge transfer quenching,⁴⁵ and intramolecular self-quenching. In order to determine the

rates of energy transfer for the unsymmetric diketones included in this thesis it is only necessary to estimate the total k_d for each chromophore involved in the system. This is done by first determining the fraction of excitation residing at the chromophore in question and then multiplying this fraction by the k_d obtained from the best model system for this chromophore. There are several ways in which the fraction of excitation residing at one chromophore can be determined; these will be discussed in a later section. For the self-quenching studies it is necessary to separate the rate of self-quenching, k_{sq} , from the rest of k_d . The methods used to estimate k_{sq} are discussed below.

Methods of estimating the rate of δ -hydrogen abstraction were discussed briefly in the introduction and have been discussed in more detail by Wagner, Kelso, Kemppainen, and Zepp.⁶¹ Methods of estimating the rates of intramolecular charge transfer have been described by Weller.⁷⁵ Charge transfer quenching of phenyl alkyl ketones by amines,^{45,76} olefins,^{27,77} and aromatic compounds⁷⁸ has been observed. Since neither of these processes are being studied in this dissertation, no attempt was made to separate them from the other decay routes of an individual chromophore. In order to obtain the rate of self-quenching, k_{sq} , it is necessary to estimate what the rate of non-radiative decay for the chromophore would be in the absence of the second

chromophore involved in the self-quenching. This estimated k_d for the chromophore is obtained by multiplying k_d from an appropriate model system by the fraction of excitation residing at the chromophore in question.

For symmetric ketones and for ketones with equilibrating chromophores k_{sq} is estimated by subtracting the sum of the estimated k_d values for the two chromophores from $1/\tau$. For unsymmetric ketones it is necessary to determine the quantum yield expected for non-radiative decay from each chromophore in the system and then subtract all the quantum yields, known and estimated, for that chromophore from the fraction of excitation residing at the chromophore to obtain a quantum yield of self-quenching for the chromophore. The rate of self-quenching for the chromophore is then obtained by multiplying the quantum yield of self-quenching for the chromophore by the $1/\tau$ value for the chromophore.

E. Rates of Energy Transfer

In systems in which the chromophores do not equilibrate the rates of energy transfer, k_{et} , can be estimated by comparing the Stern-Volmer plots of the chromophores with those predicted for the system with various values of k_{et} using equation 13, which is a rearranged version of equation 6. When the rates of energy transfer become fast compared to $1/\tau$ for the chromophores the triplet states of the chromophores almost reach equilibrium before

$$\frac{\phi_A^0}{\phi_A} = \left[\frac{(1/\tau_A' + k_{AB} + k_q[Q])(1/\tau_B' + k_{BA} + k_q[Q]) - k_{AB}k_{BA}}{(1/\tau_A' + k_{AB})(k_{BA} + 1/\tau_B') - k_{AB}k_{BA}} \right] \times \left[1 + \frac{k_q[Q]}{1/\tau_B' + (1 + \epsilon_B/\epsilon_A)k_{BA}} \right]^{-1} \quad (13)$$

$$\text{where } 1/\tau_A' = k_Y^A + k_d^A \quad (14)$$

$$\text{and } 1/\tau_B' = k_Y^B + k_d^B \quad (15)$$

reaction or decay takes place. Under these conditions all that can be obtained is a lower limit on the rates of energy transfer. This is done by finding what rates of energy transfer are required to give a deviation from equilibrium equal to the experimental error in the Stern-Volmer plots for the chromophores involved.

It is also possible to determine the rates of energy transfer by solving the equations for quantum yields of product formation from the individual chromophores (equation 16, which is a rearranged version of equation 5) simultaneously for the rates of energy

$$\phi_A = k_Y^A \left[\frac{\frac{\epsilon_A}{\epsilon_B + \epsilon_A} (1/\tau_B' + k_{BA} + k_q[Q]) + k_{BA} \frac{\epsilon_B}{\epsilon_A + \epsilon_B}}{(1/\tau_A' + k_{AB} + k_q[Q])(1/\tau_B' + k_{BA} + k_q[Q]) - k_{AB}k_{BA}} \right] \quad (16)$$

transfer. The main problem with this approach is that it is based on ϕ_{Dis}^{Max} for the chromophore which includes a number of approximations. In Table 10 the rates of energy transfer obtained by both methods are reported under the donor chromophore.

Table 10: Derived Kinetic Parameters for Unsymmetric Diketones

Ketone	Chromo- phore	Max ϕ_{Dis}	$1/\tau^a$	$k_{\gamma}^{a,b}$	$k_d^{a,c}$	k_{sq}^a	$k_{\text{et}}^{a,d}$	$k_{\text{et}}^{a,e}$
$\delta\text{ValPhVP}$	Bz	.38 ^f	4.9	1.9	.7		>10.0	10.0
	Tl	.25 ^f	5.2	1.3	.7	0.4	> 4.6	3.0
δAcPhVP	Bz	.57	2.9	1.7	.7	0.3		
$1\text{Bz}4\text{pEtBzBt}$	Bz	.40 ^f	3.4	1.4	.95		8.0	10.0
	pEtBz	.12 ^f	3.0	0.36	.25	1.4	6.4	5.0
$\gamma\text{ValPhOBP}$	Bz	.61 ^g	1.4	0.85	.27		12.0	15.0
	An	.076	1.1	0.084	.24	0.0	3.0	1.3
$\gamma\text{AcPhOBP}$	Bz	.66 ^g	0.91	0.60	.19	0.0		
$\delta\text{ValPhOVP}$	Bz	.36	0.44	0.16	.077		10.0	≈ 15.0
	An	.19	0.32	0.061	.17	0.0	1.0	≈ 3.0
$\delta\text{AcPhOVP}$	Bz	.49	0.25	0.12	.12	0.02		
$1\text{Bz}4\text{AnBt}$	Bz	.20	2.1	0.42	.28		.9	≈ 10.0
	An	.011	1.4	0.015	.21	1.5	1.0	≈ 0.5

a. $\times 10^7 \text{ sec}^{-1}$ b. $k_{\gamma} = \chi_i k_{\gamma}^{\text{model}}$ c. $k_d = \chi_i k_d^{\text{model}}$
 d. values based on $1/\tau$ e. values based on $\phi_{\text{II}}^{\text{Max}}$ f. 10% cyclobutanols assumed
 g. 20% cyclobutanols assumed h. 15% cyclobutanols i. values based on ref. 10

F. The Fraction of Excitation at a Chromophore

There are three ways which may be used to determine the fraction of excitation at a given chromophore. Probably the most accurate method for systems in which the triplet states are equilibrated or almost equilibrated is based on the lifetime of the equilibrated system, $1/\tau$, and the lifetimes of the separated chromophores, $1/\tau'$ using equation 17 for chromophores A and B.

$$\chi_A = \frac{1/\tau - 1/\tau_B'}{1/\tau_A' - 1/\tau_B'} \quad (17)$$

If the triplet states do not equilibrate equation 17 can not be used. For such systems the fraction of excitation at chromophore A is determined by dividing k_γ^A by the k_γ obtained from the appropriate model system. This method contains the errors from both the lifetime determination and the ϕ_{Dis}^{Max} determination. This method was used to obtain the values for the more reactive chromophore of a system. The fraction of excitation for the less reactive chromophore was obtained by subtracting the fraction of excitation of the most reactive chromophore from one.

II. Energy Transfer Systems

The derived kinetic parameters for the energy transfer systems and their model compounds are presented in Table 10 and 11. The k_γ values reported in the table were obtained from ϕ_{Dis}^{Max} and $1/\tau$ and hence are equivalent to $\chi_i k_\gamma^i$ where k_γ^i is the k_γ which would be observed

Table 11: Kinetic Parameters for Model Ketones

Ketone	$\phi_{\text{Dis}}^{\text{Max}}$	$1/\tau$ $\times 10^{-7} \text{ sec}^{-1}$	k_{γ} $\times 10^{-7} \text{ sec}^{-1}$	k_d $\times 10^{-7} \text{ sec}^{-1}$
δPhVP	.71 ^a	11.8	8.4	3.4
$p\text{EtVP}$	.63	2.0	1.3	1.0
$di\text{BzBt}$	.59	6.2	3.7	2.5
$dip\text{EtBzBt}$	.31 ^a	1.3	0.40	0.90
$\gamma\text{CNPhOBP}$	.70 ^b	6.2	4.3	1.9
γPhOBP	.83 ^b	21.7	18.0	3.7
$p\text{MeOVP}$	.26 ^c	0.23 ^d	0.060	0.17
$\delta\text{CNPhOVP}$	.62 ^e	1.2	0.74	0.46
δPhOVP	.82 ^e	2.6	2.1	0.5
$di\text{AnBt}^f$	.066 ^a	0.50	0.033	.47

a. 10% cyclobutanols assumed

b. 20% cyclobutanols assumed

c. values based on reference 59

d. values based on reference 58

e. 15% cyclobutanols assumed

f. values based on reference 10

if χ_i was one.

A. The δ ValPhVP and δ AcPhVP Systems

The lack of significant concentration effects for these ketones indicates that the interactions observed are intramolecular in nature. If they were intermolecular one would expect to see 1) a decrease in the quantum yields with increasing diketone concentration due to an increase in the rates of decay, and 2) a significant shift in the ratio of the quantum yields of products due to increased rates of energy transfer. All that was observed was a slight increase in the quantum yields with no shift in their relative values. This increase is expected and probably caused by solvation of the biradical intermediates by ground state ketone.⁶⁰

The $1/\tau$ values obtained for the benzoyl and toluoyl chromophores of δ ValPhVP are within experimental error of being the same indicating that the triplet states of the system have essentially equilibrated. Since the decay rate of the toluoyl chromophore of δ AcPhVP is certainly smaller than the sum of the decay rate and rate of γ -hydrogen abstraction for the toluoyl chromophore in δ ValPhVP, the triplet states of δ AcPhVP should also be equilibrated.

The sum of the cyclobutanol yield obtained from the preparative scale photolysis of δ AcPhVP and the maximum quantum yield of acetophenone formation is in

good agreement with the $\phi_{\text{Dis}}^{\text{Max}}$ measured for δAcPhVP and hence no estimates are needed in order to obtain $\phi_{\text{Dis}}^{\text{Max}}$ for this ketone. The $\phi_{\text{Dis}}^{\text{Max}}$ obtained for $\delta\text{ValPhVP}$ is less than the sum of the $\phi_{\text{II}}^{\text{Max}}$ for the two chromophores of this ketone. For this reason it is necessary to make some sort of estimate of the quantum yields of cyclobutanol formation from these chromophores. The percentage of cyclobutanol formation out of the total quantum yield in the presence of Lewis base is about 10% for VP, pEtVP, δAcPhVP , and several other ketones which form similar biradicals⁵⁹ and for this reason it was assumed to be 10% for both chromophores of the $\delta\text{ValPhVP}$ system.

The ratio of the rates of energy transfer should be predictable by use of the Boltzmann equation, on the assumption that energy transfer is microscopically reversible. The main problems with the ratios thus obtained arise from the difficulties involved in obtaining accurate room temperature energies for the triplet states involved. For $\delta\text{ValPhVP}$ the observed difference in triplet energy at liquid nitrogen temperature is 1.6 kcal, which predicts a Boltzmann ratio of 0.07 for this system and χ values of 0.065 and 0.935. This is very different from what is observed. If one matches the Stern-Volmer plots obtained for this ketone to those predicted for this system (Figure 20) one determines that the ratio of rates of energy transfer must be 0.46 and the actual rates at least

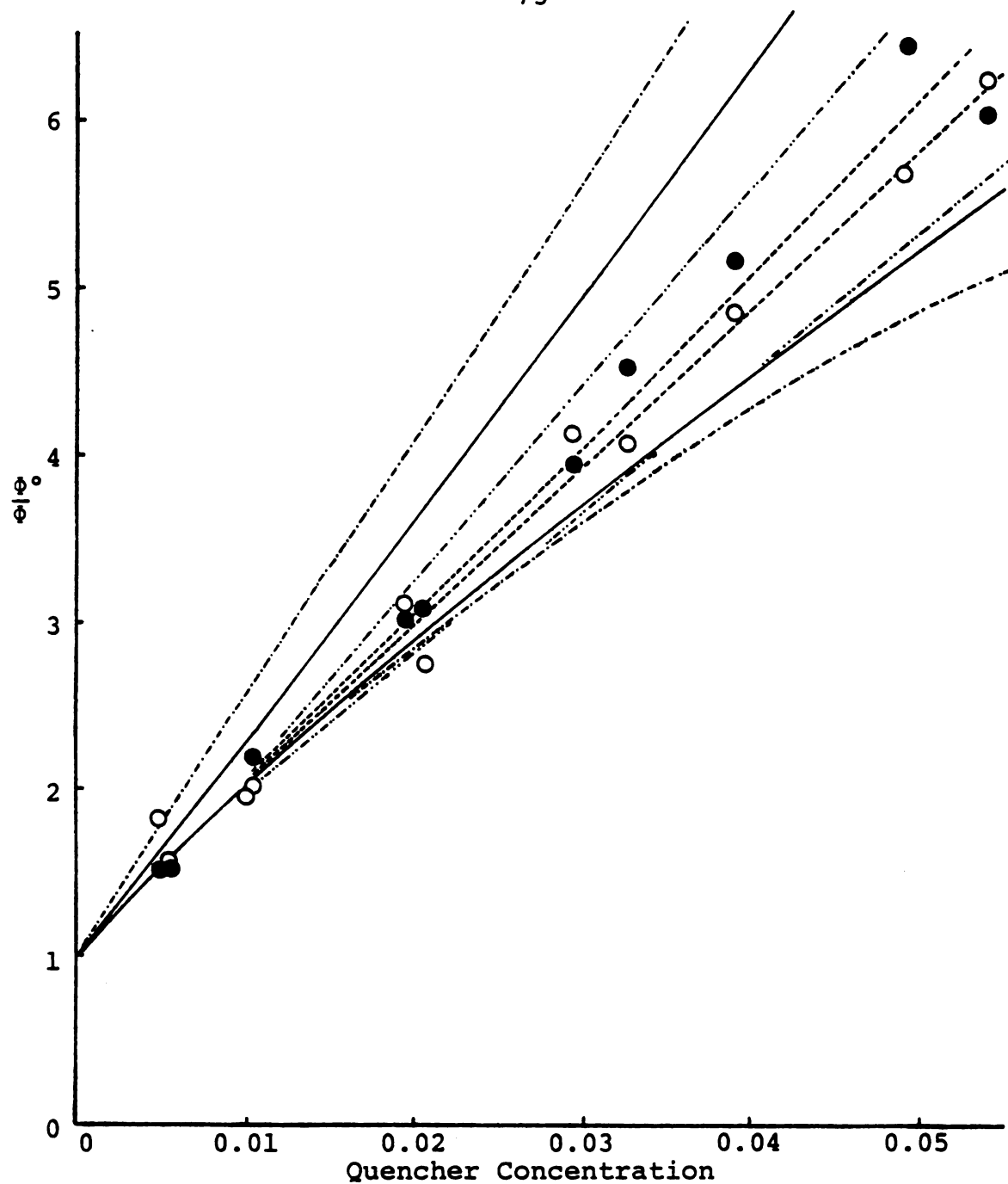


Figure 20: Predicted Stern-Volmer Plots for the δ ValPhVP System

(● Observed for acetophenone; ○ observed for propene;
 $-1.0 \times 10^8 \text{ sec}^{-1}$, $4.6 \times 10^7 \text{ sec}^{-1}$; ---- $1.0 \times 10^9 \text{ sec}^{-1}$,
 $4.6 \times 10^8 \text{ sec}^{-1}$; - - $1.2 \times 10^8 \text{ sec}^{-1}$, $3.7 \times 10^7 \text{ sec}^{-1}$;
 ---- $8.0 \times 10^7 \text{ sec}^{-1}$, $5.5 \times 10^7 \text{ sec}^{-1}$)

$1.0 \times 10^8 \text{ sec}^{-1}$ and $4.6 \times 10^7 \text{ sec}^{-1}$. Similarly the observed quantum yields require a ratio of .3 and rates of at least $1.0 \times 10^8 \text{ sec}^{-1}$ and $3.0 \times 10^7 \text{ sec}^{-1}$. These determinations require a large number of rate constants each of which contains some error but even so the energy difference in the two chromophores must be between 0.42 and 0.72 kcal to account for the observed data. One must conclude that the changes in energy levels on warming are not the same for each chromophore. Wagner, Thomas, and Harris⁷⁹ have made similar conclusions for various phenyl alkyl ketones.

Because no photochemistry occurs at the toluoyl chromophore of δAcPhVP no direct measurement of $1/\tau$ for this chromophore can be made. If it is assumed that the triplet states of the two chromophores of δAcPhVP equilibrate and that k_d for the toluoyl chromophore is the same as observed for pEtVP then the rates of energy transfer must be greater than $1.0 \times 10^9 \text{ sec}^{-1}$ and $2.4 \times 10^8 \text{ sec}^{-1}$ based on the observed $1/\tau$ value. This is in good agreement with the observed χ of 0.20 for the toluoyl chromophore of δAcPhVP . These rates predict an energy difference of 0.69 kcal which is quite different from the 1.6 kcal observed for the phosphorescence of these chromophores at liquid nitrogen temperatures.

Inspection of the observed rates of reaction and decay for the chromophores of $\delta\text{ValPhVP}$ and δAcPhVP

indicate that the maximum rates of self-quenching for these systems are $4 \times 10^6 \text{ sec}^{-1}$ and $3 \times 10^6 \text{ sec}^{-1}$, both of which are less than the experimental error in the $1/\tau$ values for these diketones.

B. The 1Bz4pEtBzBt System

The $1/\tau$ values obtained from the benzoyl and p-ethylbenzoyl chromophores of 1Bz4pEtBzBt are separated from each other by just about the experimental error in their determination. This means that the energy transfer processes are no slower than the minimum rates which would allow measurable perturbation by the rates of reaction and decay of the individual chromophores.

The only $\phi_{\text{Dis}}^{\text{Max}}$ determined for ketones related to this system was for diBzBt. It is in good agreement with the expected 10% cyclobutanol formation. It was assumed that the ratio of cyclobutanol formation to Norrish type II products for dipEtBzBt and the individual chromophores of 1Bz4pEtBzBt are the same, and this assumption was used to calculate the $\phi_{\text{Dis}}^{\text{Max}}$ values reported for these compounds in Table 10.

The k_d values reported for 1Bz4pEtBzBt and its model compounds, diBzBt and dipEtBzBt, are much larger than one would predict from VP or pEtVP. While some of this increase in k_d may be due to δ -hydrogen abstraction and charge transfer quenching, neither of these routes of decay can adequately explain the large k_d values observed, indicating rates of self-quenching

of $1.4 \times 10^7 \text{ sec}^{-1}$ for 1Bz4pEtBzBt, $2.5 \times 10^7 \text{ sec}^{-1}$ for DiBzBt and $4.5 \times 10^6 \text{ sec}^{-1}$ for dipEtBzBt. The explanation must therefore involve self-quenching. This phenomenon will be discussed in more detail later. From an energy transfer point of view all that is necessary is that the model systems used contain the same ratio of decay to reaction as the equivalent chromophore in the unsymmetric diketone and for this reason the symmetric diketones were chosen as models.

The phosphorescence spectra for these ketones indicate that the energy difference between the two chromophores of 1Bz4pEtBzBt should be about 1.6 kcal. If the triplet states involved equilibrate then the ratio of χ values should be .07. The observed ratio of χ values for 1Bz4pEtBzBt is 0.61. If the system were equilibrated the energy difference required to obtain this ratio would be .30 kcal. It is worth remembering that this system may not be equilibrated and lack of equilibrium would cause the χ values to shift towards the ratio of the chromophores' extinction coefficients.

The rates of energy transfer between the chromophores of 1Bz4pEtBzBt were estimated to be $8.0 \times 10^7 \text{ sec}^{-1}$ and $6.4 \times 10^7 \text{ sec}^{-1}$ from the $1/\tau$ values (Figure 21). The ratio of these rates of 0.8 and would require an energy difference of 0.13 kcal. When the rates of energy transfer are estimated using the product quantum yields,

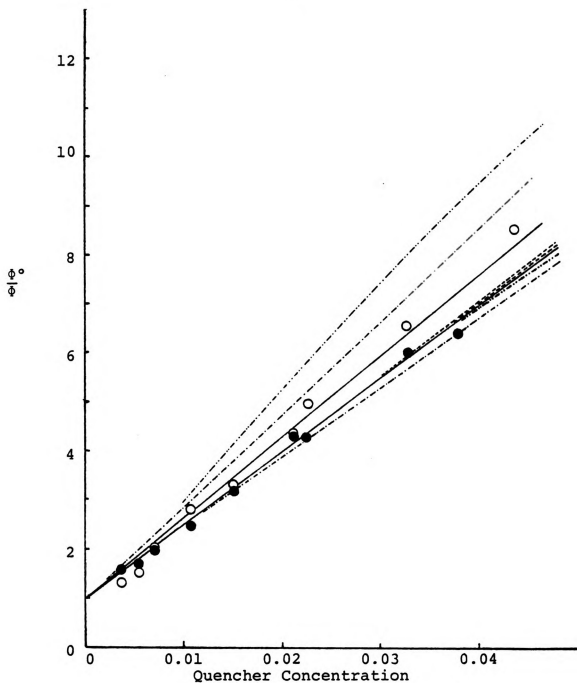


Figure 21: Predicted Stern-Volmer Plots for the 1Bz4pEtBzBt System

(● observed for acetophenone; ○ observed for pEtAc;
 — $8 \times 10^7 \text{ sec}^{-1}$, $6.4 \times 10^7 \text{ sec}^{-1}$; ---- $1.6 \times 10^8 \text{ sec}^{-1}$,
 $1.28 \times 10^8 \text{ sec}^{-1}$; - - $4 \times 10^7 \text{ sec}^{-1}$, $3.2 \times 10^7 \text{ sec}^{-1}$;
 $1.0 \times 10^8 \text{ sec}^{-1}$, $5.1 \times 10^7 \text{ sec}^{-1}$)

rates of 1.0×10^8 and 5×10^7 are obtained. The ratio of these rates is 0.50 requiring an energy difference between chromophores of 0.42 kcal. It is obvious that there is a large amount of error in these rates of energy transfer but the difference in energy between the states responsible for phosphorescence at liquid nitrogen temperatures and the difference in energy between the states involved in energy transfer at room temperature are quite different.

C. The γ ValPhOBP and γ AcPhOBP Systems

The difference in the values of $1/\tau$ for the two chromophores of γ ValPhOBP is greater than the experimental error in their determination. The lifetimes observed for the individual chromophores are displaced from their average towards the lifetimes of model systems containing only the single chromophore being considered. This indicates that the Norrish type II reactions and decay paths of the chromophores are causing considerable disruption of the equilibrium between the triplet states of the two chromophores.

γ CNPhOBP is a better model for the rate of γ -hydrogen abstraction by the benzoyl chromophore of these systems than γ PhOBP because the resonance and inductive effects of the cyano group should be similar to those of a ketone carbonyl group. If it is used as a model one would predict a k_d of $3.8 \times 10^6 \text{ sec}^{-1}$ for this chromophore. A more exact prediction can be made by using the k_γ values of

γ CNPhOBP and γ PhOBP to produce a Hammett plot. The σ_p value for a cyano group is .66.⁸⁰ This predicts a ρ value of -.95 for this system. Since an aliphatic acyl group has a σ_p value of .50⁸⁰ one would predict that k_γ for an ideal model system should be $6.1 \times 10^7 \text{ sec}^{-1}$ and that k_d should be $2.7 \times 10^6 \text{ sec}^{-1}$ for the benzoyl chromophore in γ ValPhOBP. The various rates applicable to the γ AcPhOBP system may be estimated in a similar manner.

The maximum disappearance quantum yield for the anisoyl chromophore was estimated using the percent cyclobutanol observed in the Norrish type II reaction of pMeOVP.⁵⁹ Similar data for γ PhOBP⁵⁷ was used to estimate the maximum disappearance quantum yields of the benzoyl chromophores.

The rates of self-quenching for γ ValPhOBP can be estimated by adding the expected quantum yields of decay for the benzoyl and toluoyl chromophores, 0.19 and 0.22 to the observed ϕ_{II}^{Max} values for these chromophores. Since 110 percent of the light is accounted for in this manner it is unlikely that any self-quenching occurs in this system. A similar analysis of the γ AcPhOBP system also accounts for all the light absorbed in the system.

The phosphorescence spectra of γ ValPhOBP and γ AcPhOBP and their model ketones indicate triplet energy differences between chromophores of 2.5 and 2.8 kcal respectively.

These systems are clearly not equilibrated. The energy differences do, however, predict ratios of energy transfer rate constants of 0.016 and 0.0096 for these systems. Since reversible energy transfer obviously occurs in both systems the spectroscopic energy differences obtained at liquid nitrogen temperature must be much larger than the energy differences between the states involved in energy transfer at room temperature.

When one uses the $1/\tau$ values to estimate the rates of energy transfer for the γ ValPhOBP system (Figure 22) rates of $1.2 \times 10^8 \text{ sec}^{-1}$ and $3.0 \times 10^7 \text{ sec}^{-1}$ are obtained. The ratio of these rate constants predicts an energy difference of 0.66 kcal for the two chromophores in this system. If one uses the quantum yields of product formation to estimate these rates values of $1.5 \times 10^8 \text{ sec}^{-1}$ and $1.3 \times 10^7 \text{ sec}^{-1}$ are obtained indicating an energy difference of 0.87 kcal between the two chromophores in this system.

If one assumes the k_{et} rate ratio of 0.10 predicted by Wagner and Nakahira¹⁰ for benzoyl and anisoyl chromophores and that $1/\tau'$ for the anisoyl chromophore of γ AcPhOBP is equal to k_d for pMeOVP then the rates of energy transfer calculated from the observed $1/\tau$ value for γ AcPhOBP are 2.0×10^8 and $2.0 \times 10^7 \text{ M}^{-1}\text{sec}^{-1}$. These predict an energy difference of 1.4 kcal.

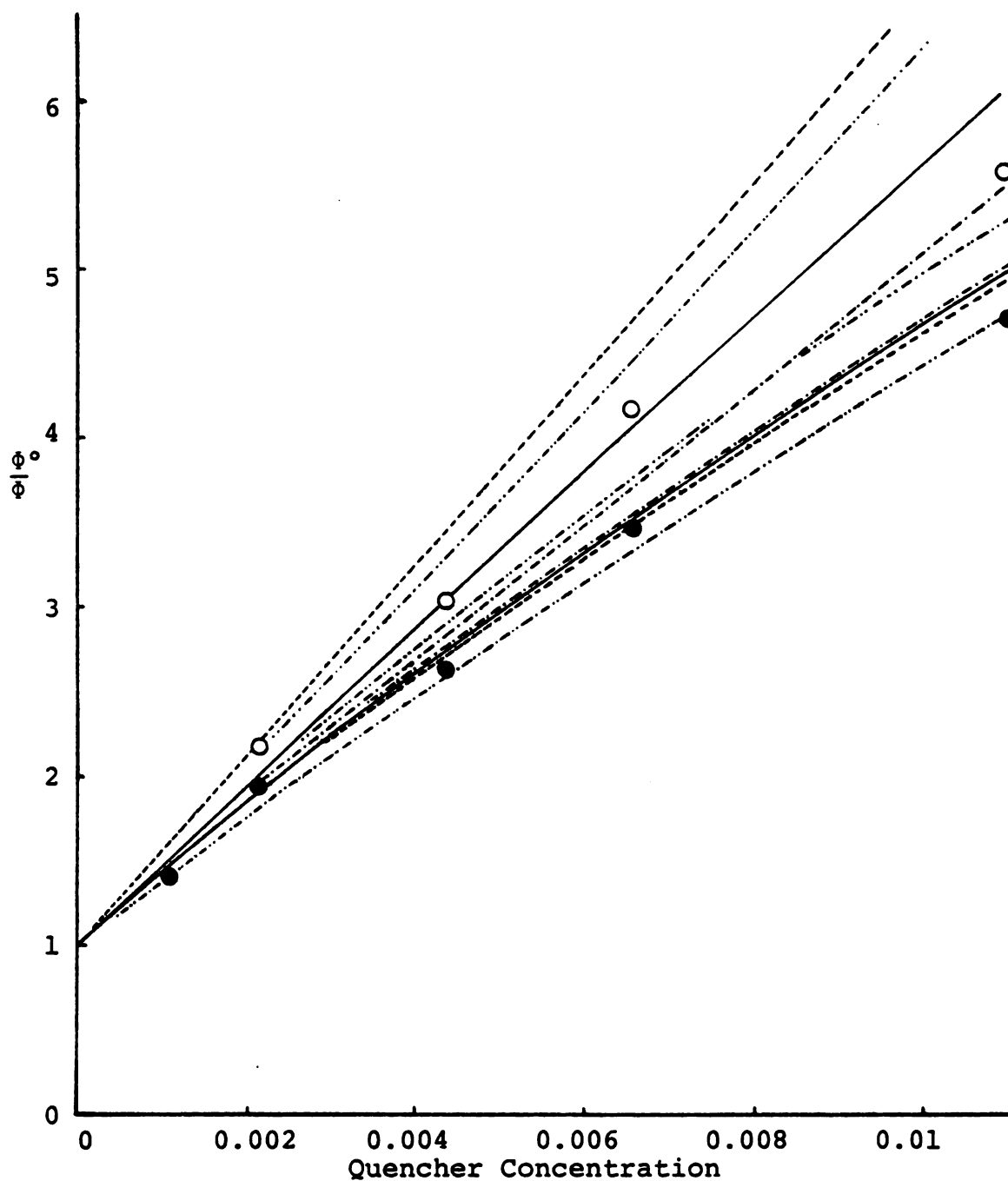


Figure 22: Predicted Stern-Volmer Plots for the γ ValPhOBP System

(● observed for Ac; ○ observed for propene; — $1.2 \times 10^8 \text{ sec}^{-1}$, $3.0 \times 10^7 \text{ sec}^{-1}$; ---- $6.0 \times 10^7 \text{ sec}^{-1}$, $1.5 \times 10^7 \text{ sec}^{-1}$; -.- $2.4 \times 10^8 \text{ sec}^{-1}$, $6.0 \times 10^7 \text{ sec}^{-1}$; --- $1.3 \times 10^8 \text{ sec}^{-1}$, $2.7 \times 10^7 \text{ sec}^{-1}$; ··· $1.1 \times 10^8 \text{ sec}^{-1}$, $3.3 \times 10^7 \text{ sec}^{-1}$)

D. The δ ValPhOVP and δ AcPhOVP Systems

The relative difference in the values of $1/\tau$ for the two chromophores of δ ValPhOVP is greater than it was for γ ValPhOBP. This indicates that there is an even greater disruption of the equilibrium between the triplet states of the two chromophores.

The maximum disappearance quantum yield for the anisoyl chromophore was again estimated from the reported behavior of pMeOVP.⁵⁹ Similar data for 5-methoxy-1-phenylpentan-1-one⁵⁷ was used to estimate the maximum disappearance quantum yields of the benzoyl chromophores in both δ ValPhOVP and δ AcPhOVP.

The same types of arguments that were used to predict the inductive and resonance effects of the carbonyl group on k_γ for the γ ValPhOBP system can be used for these systems. The Hammett equation gives a ρ of $-.69$ for this system which allows one to predict a model k_γ of $9.5 \times 10^6 \text{ sec}^{-1}$. The rates of self-quenching for δ ValPhOVP and δ AcPhOVP are predicted to be 0.0 and 2×10^{-5} by the same methods used for γ ValPhOBP. In both cases this is insignificant when compared to the $1/\tau$ values for these diketones.

The phosphorescence spectra of δ ValPhOVP and δ AcPhOVP and their appropriate model ketones indicate triplet energy differences between chromophores of 2.5 and 2.8 kcal respectively. These energy differences predict ratios of rates of energy transfer of $.016$ and $.0096$. As in

the γ ValPhOBP and γ AcPhOBP systems reversible energy transfer obviously occurs in both systems so the spectroscopic energy differences obtained at liquid nitrogen temperature must be much larger than the energy differences between the states involved in energy transfer at room temperature.

Since $1/\tau$ for pMeOAc is not known it is impossible to estimate energy transfer rate constants for δ AcPhOVP. If one assumes the k_{et} rate ratio is 0.10 for benzoyl and anisoyl chromophores as predicted by Wagner and Nakahira¹⁰ and that $1/\tau'$ for the anisoyl chromophore is equal to k_d for pMeOVP one finds that it is mathematically impossible to obtain rates for energy transfer equations 13 and 16. Either $1/\tau'$ for the anisoyl chromophore is smaller than k_d for pMeOVP or the ratio of rates of energy transfer is smaller. It is, however, possible to estimate rates of energy transfer for the δ ValPhOVP system. When one uses the $1/\tau$ values to estimate the rates of energy transfer for the δ ValPhOVP system (Figure 22) rates of 1.0×10^8 and 1.0×10^7 are obtained. The ratio of these rate constants predicts an energy difference of 1.4 kcal for the two chromophores in this system. If one uses the quantum yields of product formation to estimate these rates, values of $1.5 \times 10^8 \text{ sec}^{-1}$ and $3 \times 10^7 \text{ sec}^{-1}$ are obtained indicating an energy difference of 0.97 kcal between the two chromophores.

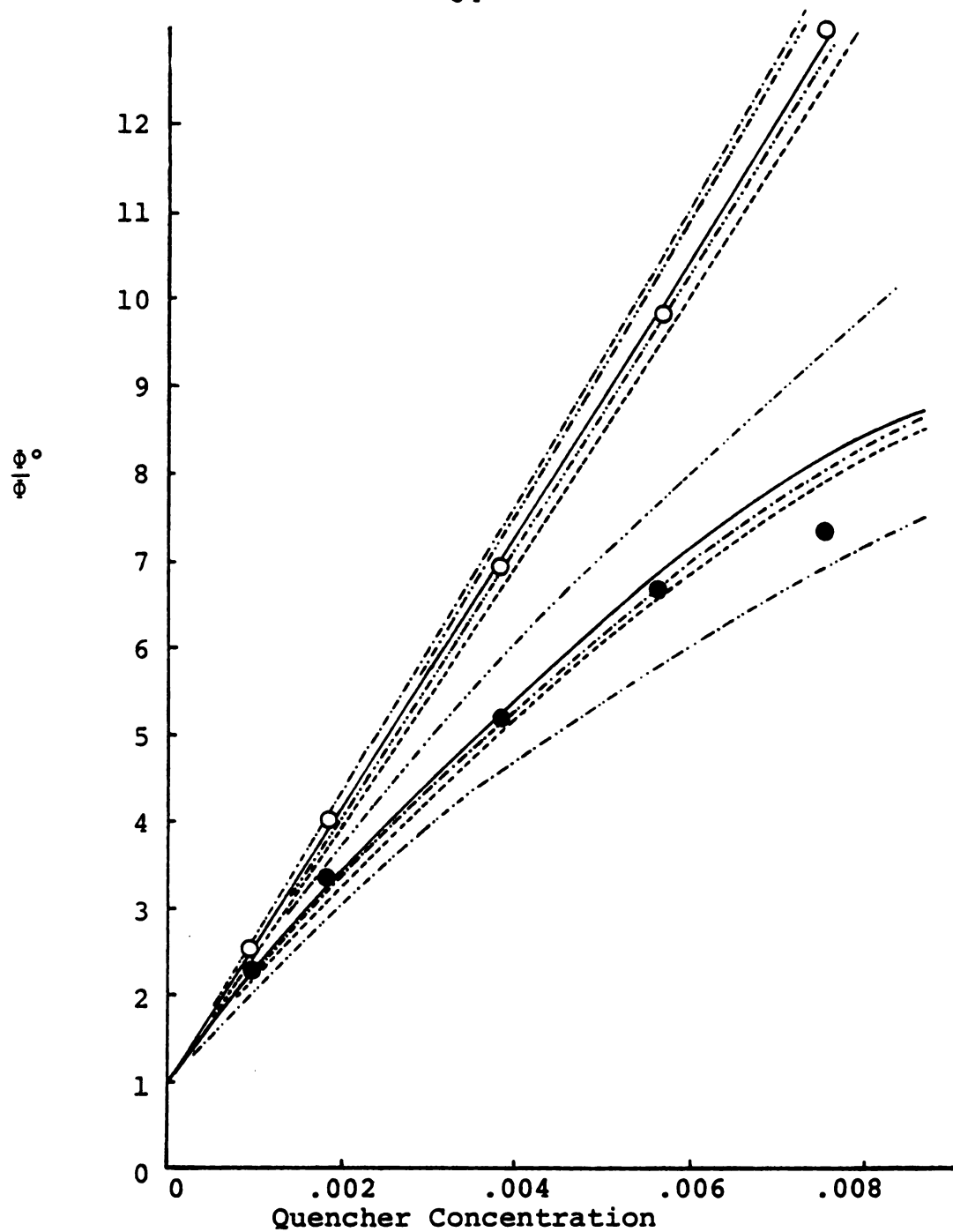


Figure 23: Predicted Stern-Volmer Plots for the $\delta\text{ValPhOVP}$ System

(● Ac, $\delta\text{ValPhOVP}$; O Pr, $\delta\text{ValPhOVP}$; — $1.0 \times 10^8 \text{ sec}^{-1}$, $1.0 \times 10^7 \text{ sec}^{-1}$; ---- $9.1 \times 10^7 \text{ sec}^{-1}$, $1.1 \times 10^7 \text{ sec}^{-1}$; -.- $1.1 \times 10^8 \text{ sec}^{-1}$, $8.9 \times 10^6 \text{ sec}^{-1}$; -.- $2.0 \times 10^8 \text{ sec}^{-1}$, $2.0 \times 10^7 \text{ sec}^{-1}$; -.- $5.0 \times 10^8 \text{ sec}^{-1}$, $5.0 \times 10^6 \text{ sec}^{-1}$)

E. The 1Bz4AnBt System

The basic results for this system were reported by Wagner and Nakahira.¹⁰ In this dissertation I have analyzed their results using the same approaches I have used with my compounds. When Wagner and Nakahira¹⁰ originally reported their results for this diketone they assumed that the $1/\tau$ values for the two chromophores in the system were the same within experimental error and that the triplet states of 1Bz4AnBt equilibrate. The $1/\tau$ values reported deviate from their average by 20% which is at least twice the normal error in a $1/\tau$ value determined by Stern-Volmer kinetics. For this reason I have decided to consider this system as a non-equilibrating system.

The phosphorescence spectra of the appropriate model systems for the 1Bz4AnBt system indicate that the energy difference between chromophores at liquid nitrogen temperature is 2.5 kcal. This energy difference would predict a ratio of rates of energy transfer of 0.016. Since reversible energy transfer obviously occurs in this system, the energy difference between chromophores at room temperature must be considerably less than that observed at liquid nitrogen temperature. If one uses the reported $1/\tau$ values to determine the rates of energy transfer for this system one obtains values of 0.9×10^7 and $1.0 \times 10^7 \text{ sec}^{-1}$ which would indicate practically no energy difference between the two chromophores. If one

uses the quantum yields of product formation to determine the rates of energy transfer for the 1Bz4AnBt system values of 1.0×10^8 and $5 \times 10^6 \text{ sec}^{-1}$ are obtained. These rates predict an energy difference of about 1.09 kcal for the two chromophores in this system. This second value is not very different from the 1.4 kcal value Wagner and Nakahira¹⁰ predict for this diketone.

F. Energy Transfer Conclusions

The most obvious observation which can be made from the mixed chromophore systems discussed above is that the energy difference observed for the chromophores at liquid nitrogen temperature is much greater than the energy differences implied by their room temperature photochemistry. This observation, in addition to the fact that decreasing the temperature decreases the Boltzman population of higher energy states for a given energy separation, explains why phosphorescence is only observed from the lowest energy chromophore for the mixed chromophore systems discussed in this dissertation.

Comparison of the relative rates of energy transfer between benzoyl and toluoyl chromophores and benzoyl and anisoyl chromophores show a definite increase in the rate of back energy transfer in the benzoyl/toluoyl systems over that observed in benzoyl/anisoyl systems. This is an indication that a decrease in the energy separation between chromophores increases the rate of

the endothermic energy transfer. If the rate of exothermic energy transfer decreases as the energies of the two chromophores approach each other, this decrease is not observed for the system discussed in this dissertation. The experimental errors in the rates of energy transfer may be too large to detect any subtle changes.

Comparison of the rates of energy transfer in the δ ValPhVP system to those obtained in the 1Bz4pEtBzBt system and the rates of energy transfer in the γ ValPhOBP or δ ValPhOVP systems to those obtained in the 1Bz4AnBt system indicate that the rate of endothermic energy transfer is slowed slightly when the anisoyl or toluoyl chromophore is positioned with its carbonyl closer to the benzoyl chromophore. This is probably a result of the anisoyl and toluoyl chromophores having $\pi \rightarrow \pi^*$ lowest triplets resulting in the center of excitation residing in the phenyl ring of these chromophores and hence being farther away from the benzoyl chromophore when the carbonyl group is turned in. Unfortunately the observed effect is not much greater than the experimental error in the determinations of the energy transfer rates.

The only clear cut systems in which the effects of increased separation between chromophores might be observed are the γ ValPhOBP and δ ValPhOVP systems. While it looks like the rates of energy transfer may decrease slightly when the additional methylene group is placed

between them, the observed change is less than the errors in the rates of energy transfer determined for these systems and is no more than that observed by simply turning one of the chromophores around. This is somewhat different than half an order of magnitude change in rate of energy transfer observed for the styryl/benzoyl system at somewhat smaller separations²⁵ but a combination of the relatively large experimental errors involved in both sets of energy transfer rates and the greater separation between the chromophores in my systems adequately explains these differences.

The results reported in this dissertation indicate that it is possible to obtain actual rates for energy transfer in intramolecular systems where reversible energy transfer occurs. Future work in the area should involve systems in which the separation between chromophores is greater and perhaps in which the energy separation between the chromophores is smaller. It would also be interesting to do temperature studies on some of the mixed chromophore systems reported in this dissertation in order to determine activation parameters for the various processes involved and to check the applicability of Boltzmann's Law to these systems.

III. Self-Quenching Studies

The derived kinetic parameters for the self-quenching systems discussed in this dissertation and their model systems are presented in Table 12. As can be seen from

Table 12: Derived Kinetic Parameters for Symmetric Diketones

Ketone	$\phi_{\text{Dis}}^{\text{Max}}$	$1/\tau$ $\times 10^{-7} \text{ sec}^{-1}$	k_{γ} $\times 10^{-7} \text{ sec}^{-1}$	est k_{γ} $\times 10^{-7} \text{ sec}^{-1}$	k_d $\times 10^{-7} \text{ sec}^{-1}$	est k_d $\times 10^{-7} \text{ sec}^{-1}$	k_{sq} $\times 10^{-7} \text{ sec}^{-1}$
diBzdiMeMt	0	1.0	0	0	1.0		1.0
diBzEt	0	1.7	0	0	1.7		1.7
diBzPr	1.0	3.2	3.2		0	0	0
diBzBt	0.59	6.2	3.7	3.8	2.5	0	2.5
diBzPt	0.65 ^a	11.0	7.2	7.6	3.8	0	3.8
dipEtBzBt	0.31 ^b	1.3	0.40	0.40	0.90	0.45	0.45
diAnBt ^c	0.66	0.50	0.033	0.018	0.47	0.13	0.34
γ CarbOMEbP ^d	1.0	1.0	1.0		0		0
δ CarbOMEVP ^d	1.0	3.8	3.8		0		0
VP ^e	1.0	12.5	12.5		0		0
pEtVP	0.63	2.0	1.3		0.7		0
pMeOVp ^e	0.26	0.23	0.06		0.17		0

a. assumes 15% cyclobutanols

b. assumes 10% cyclobutanols

c. values from reference 10

d. values from reference 56

e. values from reference 58

the k_{sq} values reported in Table 10 the only unsymmetric diketones in which significant self-quenching occurs are 1Bz4pEtBzBt and 1Bz4AnBt.

It is possible to estimate k_γ for these ketones from assorted model ketones and the closeness of these estimates to the observed k_γ values provides a check on the accuracy of the values of $1/\tau$ and ϕ_{Dis}^{Max} obtained. Since diBzdiMeMt and diBzEt do not contain γ -hydrogens, k_γ must be zero. The k_γ for diBzBt can be predicted using the Hammett plot for rates of γ -hydrogen abstraction by phenyl alkyl ketones substituted in the δ position developed by Wagner and Kemppainen.⁵⁷ This plot has a slope of -1.85 and the σ_I value for a carbonyl group is 0.28.⁸¹ These data predict a value of $3.8 \times 10^7 \text{ sec}^{-1}$ for k_γ which is easily within experimental error of the value actually observed. One obtains an estimate of k_γ for diBzPt of $7.6 \times 10^7 \text{ sec}^{-1}$ using a ρ value of -0.76 for the inductive effects of ϵ -substituents on γ -hydrogen abstraction. The rate of γ -hydrogen abstraction for diBzPr cannot be estimated in this manner because the rates of γ -hydrogen abstraction for compounds substituted in the γ -hydrogen position do not form a good Hammett plot. If one assumes that the reactivity of a triplet phenyl ketone should be affected the same way by ring substituents regardless of what substituents are attached to the δ carbon then one can estimate k_γ for dipEtBzBt and diAnBt using valerophenones

with similar ring substituents. The values obtained in this manner are $4 \times 10^6 \text{ sec}^{-1}$ and $1.8 \times 10^5 \text{ sec}^{-1}$ respectively.

The close match of the k_Y values to the k_Y^{est} values for these ketones is evidence that the low maximum quantum yields observed for these ketones are not the result of a failure to totally solvate the biradical intermediates, but indicate instead some type of quenching of the triplet state of the carbonyl. External quenching by impurities in the solvents and additives used can be ruled out since these same solvents and additives do not quench other systems with longer triplet lifetimes. It would take about 50% quenching impurity in diBzBt and about 80% quenching impurity in diBzPt to account for the quenching observed. For these reasons it must be assumed that the quenching observed is a true self-quenching phenomenon.

The ultraviolet spectra of diBzdiMeMt and diBzEt show considerably greater extinction coefficients at 313 nm than would be predicted for two benzoyl chromophores acting independently. Some of the enhancement observed in the case of diBzdiMeMt may be due to the α methyl groups but much of it is probably due to ground state interactions of the carbonyl groups in these diketones. It is also interesting that the phosphorescence spectrum of diBzdiMeMt shows only a single set of lines, presumably from the conformationally relaxed triplet

while the dual phosphorescence spectra of diBzEt shows much more emission from the relaxed triplet state than is observed for the other symmetric diketones studied. This probably arises from increased restrictions on bond rotations in the relatively hard 2-methyltetrahydrofuran glass as the chain length between chromophores increases.

Several more general statements may be made about the self-quenching observed for these diketones. Since no self-quenching is observed for γ CarbOMeBP and δ CarbOMeVP the self-quenching phenomenon must arise from some property of the second carbonyl group which is greatly diminished in esters. The absence of self-quenching in diBzPr indicates that the self-quenching requires a geometry which is not available to this ketone. It is possible that one such conformation is one in which both carbonyl groups are in the same plane with their oxygens approaching each other. Such a conformation requires that the α carbons attached to the carbonyl carbon also lie in the same plane resulting in considerable eclipsing of the various hydrogens in the system. The addition of methylene groups between the two chromophores which can account for the increase in the rate of self-quenching observed in diBzBt and diBzPt. In diBzEt this conformation is somewhat eclipsed but no more unstable than the conformation of a 1,5-hexadiene necessary for a Cope rearrangement. The increase

in extinction coefficient observed for this diketone is in fact an indication of a ground state interaction of the carbonyls. The resulting preassociation of the chromophores might aid in attaining the proposed conformation for self-quenching. DiBzdiMeMt is interesting because, in addition to a fairly rapid triplet decay rate, its intersystem crossing yield is less than one. Apparently a decay route is available to the singlet which is faster than the rate of intersystem crossing. The ab initio calculations which will be discussed in the next section predict a weak singlet excimer for conformations of formaldehyde pairs which are similar to the orientation of this molecule in which the carbonyls are adjacent. Such an excimer would be enhanced by the addition of phenyl groups to the carbonyls and may therefore account for the intersystem crossing yield observed in this ketone. The rapid decay of the triplet state of this ketone is probably self-quenching, the geometry proposed for self-quenching being readily obtainable. It should be noted however, that no adequate model system is available to estimate the natural decay of these chromophores. Such a system would have to account for the inductive and resonance effects of the benzoyl group on the excited carbonyl as well as the effects of α,α -dimethyl substitution.

The effects of ring substituents on the rates of self-quenching indicate that it is a phenomenon of $n \rightarrow \pi^*$ triplets and not of $\pi \rightarrow \pi^*$ triplets. This observation is exactly the opposite of the observation made by Singer and coworkers⁵³ for the intermolecular self-quenching of substituted benzophenones. They speculate that the self-quenching they observed was a charge transfer phenomenon involving the excited carbonyl and the ground state phenyl ring of an adjacent benzophenone. Such intramolecular charge transfer quenching was observed in the δ ValPhOBP and γ ValPhOBP systems and perhaps even in the δ ValPhVP system discussed in the energy transfer section of this discussion, but is clearly not a function of the second carbonyl group in these systems since it can be adequately predicted by model systems which do not contain a second carbonyl group. The larger rates of self-quenching observed for $n \rightarrow \pi^*$ triplets in my systems are probably due to the greater electrophilicity of an $n \rightarrow \pi^*$ triplet when compared to a $\pi \rightarrow \pi^*$ triplet. If this is the case self-quenching in my systems may simply be charge transfer quenching of the triplet state of the excited chromophore by the non-bonding electron pairs on the carbonyl oxygen of the second chromophore.

Future work in the area of self-quenching of phenyl ketones should include investigations of systems where the chromophores are separated by more methylenes, at

least to the point where the rate of self-quenching begins to drop off significantly, and also studies involving a larger number of ring substituents. It would also be interesting to study aliphatic diketones to see if a similar self-quenching phenomenon occurs.

IV. Quantum Mechanical Calculations

The self-quenching discussed above prompted a more theoretical study of possible carbonyl excimer formation. The results of this study were reported in the results section of this dissertation and are discussed in this section. They are not directly applicable to the photochemical results presented in this dissertation due to the necessity of using greatly simplified systems to carry out the type of calculations required. They do, however, offer some insight into the types of phenomena which may be occurring, particularly in the diBzdiMeMt and diBzEt systems.

Experimental results indicate that excimers formed by encounters between excited and ground state aliphatic ketones do not exist at detectable levels.⁷¹ Physically this corresponds to the absence of any substantial minimum in the potential surfaces described by the excited states of the encounter pairs (Figure 24). A minimum may exist in an excited state surface but must be too shallow with respect to the thermal energy in solution to allow the existence of a well defined, long lived excimer.

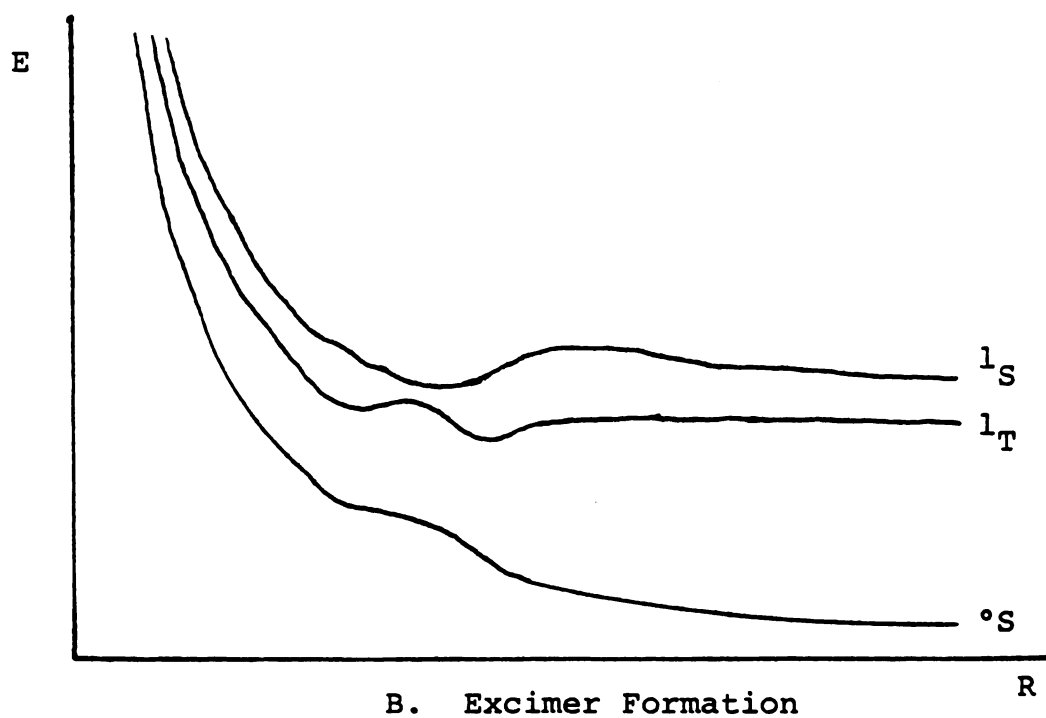
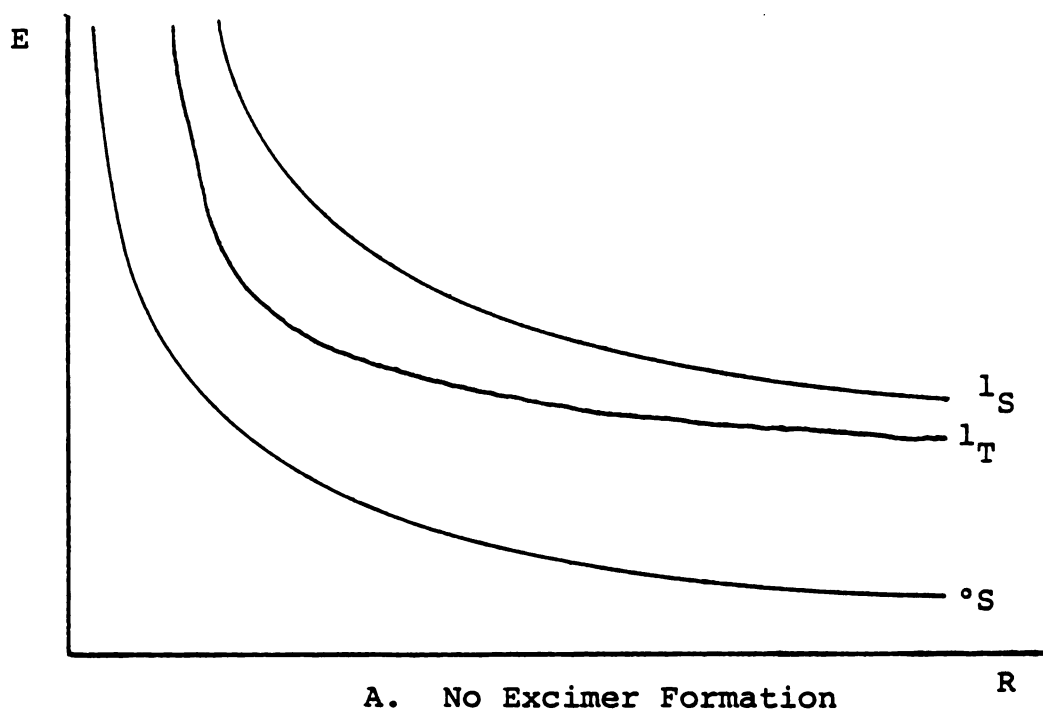
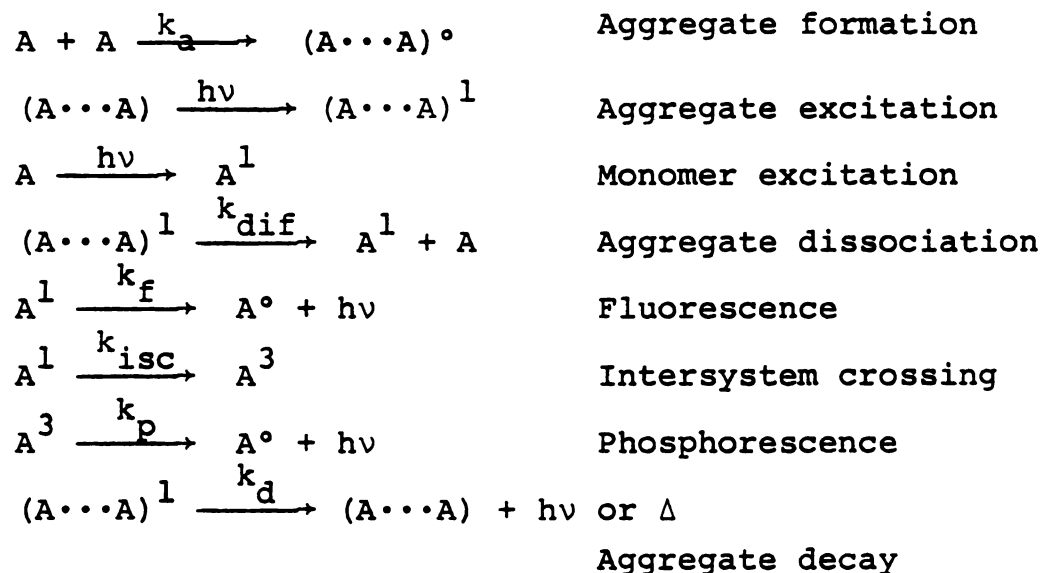


Figure 24: Excited State Interactions

The theoretical predictions for formaldehyde excimers appear to bear this out. In the case of the head-to-tail orientation a stabilization of .1004 kcal/mole is observed for the ^3B_g state at $4 \text{ \AA}$ and .3515 kcal/mole for the ^1B_g state at $3 \text{ \AA}$. In addition a stabilization of 1.32 kcal/mole is observed in the ground state complex. Ground state aggregates of acetone have been observed.⁸² The stabilization energies in the excited states represent reductions in the ground state stabilization energy and at room temperature do not have sufficient binding energy to exist for any length of time. The following scheme depicts the kinetics of such systems:

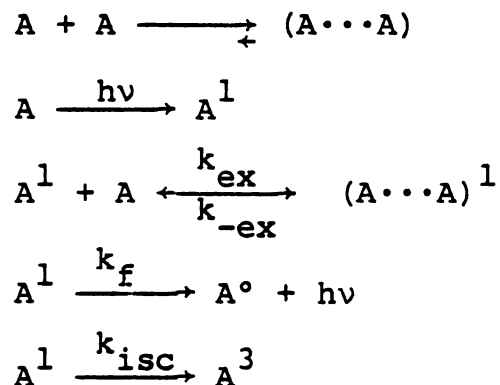


where

$$k_d (A \cdots A)^1 \ll k_{dif} (A \cdots A)^1$$

For the head-to-head orientation the $^3A_2$ state shows no stabilization while the singlet state has a shallow dip of .1129 kcal/mole at $3 \text{ \AA}$ and a ground state stabilization of .05021 kcal/mole at $4 \text{ \AA}$. Since the

ground state stabilization is small with respect to thermal energy at room temperature no ground state aggregate should exist. Under these circumstances, a true excimer can exist as depicted by the following scheme:



In the case of formaldehyde and, by intuitive extension, acetone, k_{-ex} would be expected to be approximately equal to k_{ex} so that the complex would be little more than an encounter complex and observable properties such as fluorescence would not be affected noticeably.⁸³

Addition of a phenyl group to the system would be expected to stabilize such an exciplex but the rate of intersystem crossing in phenyl ketones is relatively fast, probably fast enough so that exciplex formation could not successfully compete with it. It should be noted, however, that the separation between the excited states and ground state decreases with proximity in all cases (Table 9). While this means very little in bimolecular systems since the probability of two molecules approaching each other this closely is low due to obvious energetic disadvantages, in intramolecular systems the

energy in the ground state should show less of an increase as the carbonyls are brought together increasing the chance of excimer formation or at least an easy route back to the ground state for a reasonably long lived excited state.

EXPERIMENTAL

I. Chemicals

A. Ketones

1. General Comments

While the syntheses of the ketones were varied, all ketones were identified by their spectroscopic characteristics. The instruments used were as follows: infrared spectra, Perkin-Elmer 237B Grating Infrared Spectrometer; proton spectra, Varian T-60 NMR Spectrometer; carbon-13 spectra, Varian CFT-20 NMR Spectrometer; mass spectra, Hitachi RMU-6 Mass Spectrometer. All chemical shifts are reported in ppm downfield from tetramethylsilane.

The purity of solid ketones was estimated from their physical appearance and melting point range obtained on a Thomas-Hoover Unimelt Capillary Melting Point Apparatus. The reported melting points are uncorrected. Ketones which were sufficiently volatile were checked for purity by phase chromatography. Further proof of purity is available in the constancy of their photochemical properties.

2. 2,2-Dimethyl-1,3-diphenylpropan-1,3-dione
(DiBzdiMeMt)

This diketone was prepared by Smedley's procedure⁸⁴ in 25% yield from 25g of dimethyl malonic acid (Aldrich Chemical Company) by treatment with excess thionyl chloride followed by Friedel-Crafts acylation with excess benzene and aluminum chloride. It was then purified by several recrystallizations from ethanol to yield white crystals, mp 97.0 - 97.25°, dec. (lit. 99°⁸⁴); ir (CHCl₃) 1670cm⁻¹; pmr (CDCl₃) 1.6ppm (s, 6H, CH₃), 7.2 (m, 6H, Ph), 7.7 (m, 4H, Ph); cmr (CDCl₃) 25.14ppm, 59.32, 128.36, 128.95, 132.69, 135.50, 200.01; ms, m/e 252 (2.2%), 147 (.5%), 105 (100%), 77 (41.5%); UV, $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 320nm.

3. 1,4-Diphenylbutane-1,4-dione (DiBzEt)

This diketone was prepared by the photolysis of 450 ml of acetophenone catalyzed by phenol on silica gel in 5% yield by Becker's procedure⁸⁵ and purified by three recrystallizations from ethanol to yield white crystals, mp 144.9 - 145.1° (lit. 144 - 145°⁸⁵); ir (CHCl₃) 1690cm⁻¹; pmr (CDCl₃) 3.39ppm (s, 4H, CH₂), 7.35 (m, 6H, Ph), 7.90 (m, 4H, Ph); cmr (CDCl₃) 32.43ppm, 127.9, 128.38, 132.91, 136.66, 198.4; ms, m/e 239 (1.8%), 238 (8.7%), 221 (1.1%), 220 (6.0%), 134 (1.1%), 133 (10.1%), 115 (2.7%), 106 (8.1%), 105 (100%), 99 (2.1%), 91 (1.0%), 86 (1.8%), 78 (3.9%), 77 (40.6%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 313nm.

4. 1,5-Diphenylpentane-1,5-dione (DiBzPr)

This diketone was prepared by Donna Nezich by the Friedel-Crafts acylation of benzene⁸⁶ with 17.0g of glutaryl chloride (Aldrich Chemical Company) and 44g of aluminum chloride in 85% yield and purified by six recrystallizations from ethanol/water to yield white crystals, mp 64.0 - 64.25° (lit. 66 - 67°⁸⁷); ir (CHCl₃) 1690cm⁻¹; pmr (CDCl₃) 2.15ppm (t, 2H, j=3Hz, CH₂), 3.00 (t, 4H, j=3Hz, CH₂), 7.35 (m, 6H, Ph), 7.80 (m, 4H, Ph); cmr (CDCl₃) 18.45ppm, 37.24, 127.69, 128.23, 132.69, 136.61, 199.36; ms, m/e 253 (3%), 252 (14%), 147 (5%), 133 (11%), 120 (19%), 106 (100%), 77 (41%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 317nm.

5. 1,6-Diphenylhexane-1,6-dione (DiBzBt)

This diketone was prepared by the Friedel-Crafts acylation of benzene⁸⁸ with 18.3g of adipoyl chloride (Aldrich Chemical Company) and 40g of aluminum chloride in 95% yield and purified by four recrystallizations from ethanol/water to yield white crystals, mp 105.9 - 106.0°C (lit. 106 - 108°⁸⁹); ir (CHCl₃) 1.80ppm (m, 4H, CH₂), 2.95 (t, 4H, j=3H₂, CH₂), 7.35 (m, 6H, Ph), 7.80 (m, 4H, Ph); cmr (CDCl₃) 23.52ppm, 37.97, 127.63, 128.18, 132.54, 136.63, 199.45; ms, m/e 266 (2%), 248 (16.3%), 247 (19.7%), 147 (21%), 146 (74.8%), 120 (55.8%), 106 (16.3%), 105 (57.8%), 77 (100%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 319nm.

6. 1,7-Diphenylheptane-1,7-dione (DiBzPt)

This diketone was prepared by the Friedel-Crafts acylation of benzene⁸⁶ with 33h of pimeloyl chloride

(prepared by the treatment of pimelic acid (Aldrich Chemical Company) with a 2.2 molar excess of thionyl chloride) and 62.4g of aluminum chloride in 90% yield and purified by five recrystallizations from ethanol to yield white crystals, mp 65.5 - 66.0° (lit. 67 - 68°⁸⁹); ir (CHCl₃) 1690cm⁻¹; pmr (CDCl₃) 1.7ppm (m, 10H, CH₂), 2.95 (t, 4H, j=3Hz, CH₂), 7.35 (m, 6H, Ph), 7.80 (m, 4H, Ph); cmr 23.54ppm, 28.39, 37.71, 127.45, 128.00, 132.31, 136.38, 199.44; ms, m/e 280 (2.2%), 175 (6.8%), 162 (6.8%), 161 (56.9%), 160 (11.1%), 146 (10.3%), 144 (5.3%), 133 (14.4%), 130 (7.4%), 121 (10.2%), 120 (100%), 106 (27.9%), 105 (69.2%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 318nm.

7. 1,6-Bis-(4-ethylphenyl)-hexane-1,6-dione
(DipEtBzBt)

40.0g of aluminum chloride and 250ml of ethylbenzene were cooled to ice water temperature and 18.3g of adipoyl chloride (Aldrich Chemical Company) was added dropwise with stirring. The mixture was stirred for three hours and then poured onto about 500g of ice. The layers were separated and the water layer extracted with three 100ml portions of ether. The combined organic layers were washed with three 100ml portions of water, three 100ml portions of saturated NaHCO₃ solution, three 100ml portions of water, and one 100ml portion of saturated NaCl solution and then dried over magnesium sulfate. The solvents were removed to yield 52.3g of solid which was shown by pmr to be mostly ethylbenzene. One

recrystallization from ethanol/water yielded 8.0g of crude product, mp 92 - 93°, 25% yield. Two additional recrystallizations from ethanol/water yielded pure white, crystalline product, mp 96.0 - 96.25°; ir (CHCl₃) 1685cm⁻¹; pmr (CDCl₃) 1.22ppm (t, 6H, j=4Hz, CH₃), 1.80 (m, 4H, CH₂), 2.70 (q, 4H, j=4Hz, CH₂), 2.99 (t, 4H, j=3Hz, CH₂), 7.18 (d, 4H, j=4Hz, Ph), 7.82 (d, 4H, j=4Hz, Ph); cmr 14.71ppm, 23.70, 28.48, 37.87, 127.61, 127.85, 134.42, 149.29, 199.06; ms, m/e 322 (1.3%), 175 (7.5%), 174 (25.0%), 161 (5.2%), 149 (6.0%), 148 (48.3%), 145 (13.0%), 134 (11.8%), 133 (100.0%), 105 (18.8%), 79 (15.7%), 77 (13.0%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 318nm.

8. 1-(4'-Ethylphenyl)-6-phenylhexane-1,6-dione
(1Bz4pEtBzBt)

a. Methyl 5-Benzoylvalerate

This ester was prepared by Friedel-Crafts acylation of excess benzene with the 41.8g of acid chloride of adipic acid monomethyl ester (prepared by treating adipic acid monomethyl ester (Aldrich Chemical Company) with excess thionyl chloride at room temperature) and 86.0g of aluminum chloride at room temperature in 94% yield by Kemppainen's procedure.⁷⁰ The crude product was used for the next step of the synthesis. ir (neat 1750cm⁻¹, 1690cm⁻¹, 1600cm⁻¹, 1450cm⁻¹; pmr (CCl₄) 1.6ppm (m, 4H, CH₂), 2.2 (t, 2H, j=3Hz, CH₂), 2.75 (t, 2H, j=3Hz, CH₂), 3.40 (s, 3H, CO₂CH₃), 7.1 (m, 3H, Ph), 7.75 (m, 2H, Ph).

b. 5-Benzoylvaleric acid

The acid was prepared in 52% yield by refluxing Methyl 5-Benzoylvalerate with an excess of 6% aqueous sodium hydroxide for 2 hours and neutralizing the resulting salt with concentrated hydrochloric acid. Recrystallization from ethanol/water gave a solid of mp 70 - 73° (lit. 77 - 78°⁹⁰); ir (CHCl₃) 3100cm⁻¹ (broad), 1720cm⁻¹, 1690cm⁻¹; pmr (CDCl₃) 1.80ppm (m, 4H, CH₂), 2.2 (t, 2H, j=3Hz, CH₂), 2.95 (t, 2H, j=3Hz, CH₂), 7.4 (m, 3H, Ph), 7.9 (m, 3H, Ph), 7.9 (m, 2H, Ph), 11 (s, 1H, COOH).

c. 5-Benzoylvaleroyl chloride

9.2g of 5-benzoylvaleric acid and 5.85g of thionyl chloride were stirred together at room temperature for two hours and then the excess thionyl chloride was removed at aspirator pressure to give 9.0g (90%) of brown solid, ir (neat) 1810cm⁻¹, 1690cm⁻¹; pmr (CCl₄) 1.7ppm (m, 4H, CH₂), 2.95 (m, 4H, CH₂), 7.3 (m, 3H, Ph), 7.8 (m, 2H, Ph).

d. 1-(4'-Ethylphenyl)-6-phenylhexan-1,6-dione

(1Bz4pEtBzBt)

16.5g of aluminum chloride and 20ml of methylene chloride were placed in a flask and cooled with an ice water bath. 9.0g of 5-Benzoylvaleroyl chloride dissolved in 15ml of methylene chloride were added dropwise, then 5.0g of ethyl benzene dissolved in 15ml of methylene chloride was added dropwise. The mixture was stirred for 2.5 hours and then poured onto about 200g of ice.

The resulting mixture was extracted with three 100ml portions of benzene. The combined benzene extracts were washed with three 100ml portions of distilled water, three 100ml portions of saturated sodium bicarbonate solution, three 100ml portions of water and one 100ml portion of saturated sodium chloride solution and then dried over potassium carbonate. The solvent was removed on a rotary evaporator to give 8.8g (75%) of brown solid. Six recrystallizations from ethanol/water gave a white, crystalline solid, mp 77.5 - 78.0°; ir (CCl_4) 1690cm^{-1} , 1605cm^{-1} , 1450cm^{-1} , 1410cm^{-1} , 1360cm^{-1} , 1270cm^{-1} , 1220cm^{-1} , 1180cm^{-1} ; pmr (CCl_4) 1.2ppm (t, 3H, $j=4\text{Hz}$, CH_3), 1.75 (m, 4H, CH_2), 2.65 (q, 2H, $j=4\text{Hz}$, CH_2), 2.85 (m, 4H, CH_2), 6.9 - 7.9 (m, 9H, Ph); ms, m/e 294 (1.48%), 276 (2.96%), 174 (15.5%), 148 (44.4%), 146 (17.0%), 134 (11.8%), 133 (100%), 105 (55.6%), UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 317nm.

9. 1,5-Diphenylpentan-1-one (δPhVP)

a. Method A

1) Acetophenone cyclohexylimine

120g of acetophenone (Eastman Organic Chemicals), 100g of cyclohexylamine (Aldrich Chemical Company), 112ml of benzene and 0.5ml of concentrated H_2SO_4 were placed in a flask equipped with a Dean-Stark trap and refluxed until 21ml of H_2O had been collected (21 hours). The benzene was removed on a rotary evaporator and then the resulting oil was distilled under reduced pressure. After removal of the unreacted starting materials, 68.3g

(34%) of the desired product was collected at bp. 112 - 115° (0.25 torr); ir (neat) 3050cm^{-1} , 2925cm^{-1} , 2850cm^{-1} , 1640cm^{-1} , 1580cm^{-1} , 1450cm^{-1} , 1280cm^{-1} , 765cm^{-1} , 695cm^{-1} ; pmr (CCl_4) 1.6ppm (m, 11H, CH_2), 2.1 (s, 3H, CH_3), 7.1 (m, 3H, Ph), 7.6 (m, 2H, Ph).

2) 1,5-Diphenylpentan-1-one (δPhVP)

The procedure used is similar to one used by Stork and Dowd.⁹¹ 4.68g of magnesium and 50ml of tetrahydrofuran (THF) (freshly distilled from lithium aluminum hydride) were placed in a flame dried flask under nitrogen. A small portion of 21.96g of bromoethane was added and Grignard formation initiated. 300ml of THF (freshly distilled from lithium aluminum hydride) was added, then the rest of the bromoethane was added at a rate which maintained a gently reflux. The mixture was refluxed for one hour. 32.37g of acetophenone cyclohexylimine was then added dropwise and the mixture refluxed for two hours. 35.35g of 1-bromo-3-phenylpropane (Aldrich Chemical Company) was then added dropwise and refluxed for 24 hours. 200ml of 6M hydrochloric acid solution was then added dropwise and the mixture allowed to stir overnight. The resulting mixture was extracted with three 200ml portions of benzene and the combined benzene extracts were washed with three 200ml portions of 6 M hydrochloric acid, three 200ml portions of distilled water, three 200ml portions of saturated aqueous sodium bicarbonate solution, two 200ml portions

of distilled water, and one 200ml portion of saturated aqueous sodium chloride solution and were then dried over sodium sulfate. The benzene was removed with a rotary evaporator to give 44.5g of oil. This oil was fractionally distilled at reduced pressure, 10.3g (23%) of the product being collected at bp 133 - 142° (.025 torr).

b. Method B

One pint of freshly opened dimethylsulfoxide was placed in a flame dried flask under nitrogen. 13g of 50% NaH/mineral oil dispersion was washed with benzene to remove the mineral oil and placed in the flask. 30g of acetophenone was added dropwise over about an hour and the resulting solution was stirred for an additional two hours. 50g of 1-bromo-3-phenylpropane was then added dropwise over about an hour and the mixture was stirred for 24 hours. 200ml of water was added and the mixture stirred overnight. The mixture was extracted with three 300ml portions of ether. The combined ether extracts were washed with three 300ml portions of distilled water, three 300ml portions of 3 M hydrochloric acid solution, three 300ml portions of distilled water, three 300ml portions of saturated aqueous sodium bicarbonate, two 300ml portions of distilled water and one 300ml portion of saturated aqueous sodium chloride solution and then was dried over sodium sulfate. The ether was removed on a rotary evaporator to give 58.6g

of oil. This oil was fractionally distilled distilled at reduced pressure, 10.7g of product being collected at bp 130 - 150° (.01 torr).

c. Purification

Crude δ PhVP was recrystallized six times from ethanol/water to give white crystals, mp 44.25 - 44.50° (lit. 47°⁹²), ir (CCl₄) 1695cm⁻¹, 1450cm⁻¹; pmr (CDCl₃) 1.65ppm (m, 4H, CH₂), 2.60 (t, 2H, j=3Hz, CH₂), 3.05 (t, 2H, j=3Hz, CH₂), 7.1 (m, 5H, Ph), 7.3 (m, 3H, Ph), 7.8 (m, 2H, Ph); cmr (CDCl₃) 23.70ppm, 30.75, 35.51, 38.03, 125.42, 127.69, 128.23, 132.54, 136.82, 141.93, 199.74; ms, m/e 238 (12.6%), 148 (12.9%), 133 (58.2%), 120 (97.9%), 118 (16.5%), 117 (15.5%), 105 (100%), 91 (62.2%), 77 (75.5%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 319nm.

10. 1-Phenyl-5-(4'-acetylphenyl)-pentan-1-one (δ AcPhVP)

15.2g of aluminum chloride and 25ml of methylene chloride were placed in a flask and cooled in an ice water bath. 3.6g of acetyl chloride dissolved in 10ml of methylene was added dropwise and stirred for 30 minutes. 9.0g of 1,5-diphenylpentan-1-one dissolved in 10ml of methylene chloride was added dropwise and stirred for two hours at room temperature. The resulting mixture was poured onto about 150g of ice. Enough additional water was added to dissolve the inorganic salts. The mixture was extracted with three 100ml portions of ether. The combined ether extracts were washed with

three 100ml portions of distilled water, three 100ml portions of saturated aqueous sodium bicarbonate solution, two 100ml portions of distilled water, and one 100ml portion of saturated aqueous sodium chloride solution and then dried over sodium sulfate. The ether was removed on a rotary evaporator to give 10.0g (94%) of solid. Four recrystallizations from methanol/water gave white crystals, mp 64.25 - 64.50°; ir (CHCl_3) 1695cm^{-1} , 1610cm^{-1} , 1450cm^{-1} , 1420cm^{-1} , 1370cm^{-1} , 1275cm^{-1} ; pmr (CDCl_3) 1.75ppm (m, 4H, CH_2), 2.50 (s, 3H, CH_3), 2.65 (t, 2H, $j=3\text{Hz}$, CH_2), 2.95 (t, 2H, $j=3\text{Hz}$, CH_2), 7.25 (m, 5H, Ph), 7.80 (m, 4H, Ph); cmr (CDCl_3) 23.55ppm, 26.13, 30.28, 35.44, 37.87, 127.64, 128.23, 132.63, 134.79, 136.69, 147.73, 199.53; ms, m/e 281 (8.42%), 280 (41.3%), 162 (25.6%), 160 (100%), 133 (13.8%), 120 (20.4%), 105 (88%), 77 (52%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 317nm.

11. 1-Phenyl-5-(4'-valerylphenyl)-pentan-1-one
($\delta\text{ValPhVP}$)

This compound was prepared in the same manner as the δAcPhVP except valeryl chloride was used. 9.0g of 1,5-diphenylpentan-1-one gave 12.2g (100%) of crude product. Five recrystallizations from methanol gave white crystals, mp 60.0 - 60.25°; ir (CCl_4) 1695cm^{-1} , 1610cm^{-1} , 1450cm^{-1} ; pmr (CCl_4) 1.0ppm (t, 3H, $j=3\text{Hz}$, CH_3), 1.7 (m, 8H, CH_2), 2.9 (m, 4H, CH_2), 7.25 (m, 5H, Ph), 7.8 (m, 4H, Ph); cmr (CDCl_3) 13.68ppm, 22.23, 23.62, 26.36, 30.36, 35.52, 37.95, 127.76, 128.01, 128.31, 132.69,

134.81, 136.76, 147.49, 199.68, 199.84; ms, m/e 323 (8.12%), 322 (31.5%), 280 (3.94%), 266 (20.4%), 265 (100%), 203 (25.36%), 202 (93.88%), 167 (12.8%), 161 (15.3%), 160 (30.0%), 147 (10.1%), 133 (12.3%), 131 (11.1%), 120 (12.2%), 105 (71.1%), 91 (16.4%), 90 (13.9%), 77 (59.5%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 320nm.

12. 1-(4'Ethylphenyl)-pentan-1-one (pEtVP)

This ketone was prepared in 86% yield by the Friedel-Crafts acylation⁸⁶ of excess ethyl benzene with 14.5g of valeryl chloride and 26.6g of aluminum chloride, and then purified by repeated distillation at reduced pressure to give a colorless oil, bp 93.0 - 93.1° (.35 torr) (lit. bp 169 - 171° (32 torr)⁹³). The purity of this ketone was checked by vpc on an 8' x 1/8" 4% QF-1, 1% Carbowax 20 M on Chromosorb G column with a carrier gas flow rate of 30m/min at 115° C. The ketone contains 99.15% of the para isomer, 0.84% of the ortho isomer and 0.01% of an unknown contaminate. The spectral data for this ketone are as follows:

ir (neat) 1690cm⁻¹, 1605cm⁻¹; pmr (CCl₄) 1.2ppm (m, 10H, CH₂, CH₃), 2.65 (m, 4H, CH₂), 7.0 (d, 2H, Ph), 7.65 (d, 2H, Ph); cmr (CDCl₃) 13.60ppm, 14.85, 22.21, 26.35, 28.62, 37.88, 127.69, 238.00, 134.64, 149.36, 199.75; ms, m/e 190 (1.3%), 161 (13.8%), 148 (37.7%), 134 (10.4%), 133 (100%), 105 (15.1%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 309nm.

13. 4-Phenoxy-1-phenylbutan-1-one (γ PhOBP)

The synthesis of this ketone is similar to a number of syntheses carried out by Kalir and Balderman.⁹⁴ 125ml of dimethylsulfoxide and 3.16g of dry sodium hydride were placed in a flask under a nitrogen atmosphere. 15.2g of O-(tetrahydropyran-2-yl)-mandelonitrile (prepared by Michael J. Thomas by Kalir and Balderman's procedure⁹⁴) was added dropwise and the mixture stirred for 22 hours. 15.0g of 1-bromo-3-phenoxypropane (Aldrich Chemical Company) was added and the reaction stirred for 2 hours. The reaction mixture was then poured onto 250ml of 10% hydrochloric acid ice water and stirred for 5 hours. The resulting mixture was then extracted with three 100ml portions of ether and the combined ether extracts were washed with three 100ml portions of distilled water, three 100ml portions of saturated aqueous sodium bicarbonate solution, two 100ml portions of distilled water, and one 100ml portion of saturated aqueous sodium chloride solution. The ether was removed with a rotary evaporator and the resulting oil was refluxed for two hours in 15% aqueous hydrochloric acid. The mixture was cooled and extracted with three 100ml portions of ether. The combined ether extracts were washed with three 100ml portions of distilled water, three 100ml portions of saturated aqueous sodium bicarbonate, two 100ml portions of distilled water and one 100ml portion of saturated aqueous sodium chloride

solution and then was dried over Na_2SO_4 . The ether was removed with a rotary evaporator and the resulting oil was stirred overnight with 200ml water, 10g sodium bicarbonate, 5g potassium carbonate, and 0.5g sodium hydroxide. The resulting mixture was extracted with three 100ml portions ether and the combined ether extracts washed with three 100ml portions of distilled water and one 100ml portion of saturated aqueous sodium chloride, then dried over sodium sulfate. The ether was removed with a rotary evaporator to give 16.5g (97%) of pale yellow crystals. Three recrystallizations from ethanol gave white crystals, mp $61.75 - 62.0^\circ \text{C}$ (lit. $62.5 - 63.5^\circ$ ⁵⁷); ir (CHCl_3) 1695cm^{-1} , 1603cm^{-1} , 1500cm^{-1} , 1475cm^{-1} , 1450cm^{-1} ; pmr (CDCl_3) 2.25ppm (q, 2H, $j=3\text{Hz}$, CH_2), 3.15 (t, 2H, $j=3\text{Hz}$, CH_2), 4.05 (t, 2H, $j=3\text{Hz}$, CH_2), 7.0 (m, 8H, Ph), 7.85 (m, 2H, Ph); cmr (CDCl_3) 23.53ppm, 34.57, 66.50, 114.21, 120.36, 127.68, 128.23, 129.13, 132.66, 136.63, 158.59, 199.07; ms, m/e 240 (2.3%), 148 (9%), 147 (100%), 120 (10%), 106 (5.7%), 105 (58%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 316nm.

14. 4-(4-Acetylphenoxy)-1-phenylbutan-1-one
($\gamma\text{AcPhOBP}$)

This diketone was prepared in 76% yield by the same procedure as δAcPhVP using 8.0g of γPhOBP , 3.2g of acetyl chloride and 13.5g of aluminum chloride and then purified by three recrystallizations from ethanol to give white crystals, mp $91.75 - 92.0^\circ$; ir (CHCl_3) 1690cm^{-1} , 1605cm^{-1} ,

1510 cm^{-1} , 1365 cm^{-1} ; pmr (CDCl_3) 2.20ppm (t, 2H, $j=3\text{Hz}$, CH_2), 2.40 (s, 3H, CH_3), 3.1 (t, 2H, $j=3\text{Hz}$, CH_2), 4.0 (t, 2H, $j=3\text{Hz}$, CH_2), 6.75 (d, 2H, $j=4\text{Hz}$, Ph), 7.35 (m, 3H, Ph), 7.75 (m, 4H, Ph); cmr (CDCl_3) 23.47ppm, 26.12, 34.51, 67.06, 113.99, 127.83, 128.46, 130.21, 130.41, 132.96, 135.64, 162.71, 196.46, 199.04; ms, m/e 282 (2%), 163 (5%), 149 (2%), 148 (11%), 147 (100%), 121 (5%), 120 (5%), 106 (5%), 105 (66%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 316nm.

15. 4-(4'-Valerylphenoxy)-1-phenylbutan-1-one
($\gamma\text{ValPhOBP}$)

This diketone was prepared in 87% yield by the same procedure as δAcPhVP using 7.7g of γPhOBP , 4.7g of valeryl chloride and 13.0g of aluminum chloride and then purified by two recrystallizations from ethanol to yield white crystals, mp 115.75 - 116.0°; ir (CHCl_3) 1690 cm^{-1} , 1603 cm^{-1} , 1510 cm^{-1} , 1450 cm^{-1} ; pmr (CDCl_3) 1.0ppm (t, 3H, $j=3\text{Hz}$, CH_3), 1.6 (m, 4H, CH_2), 2.25 (q, 2H, $j=3\text{Hz}$, CH_2), 2.85 (t, 2H, $j=3\text{Hz}$, CH_2), 3.15 (t, 2H, $j=3\text{Hz}$, CH_2), 4.10 (t, 2H, $j=3\text{Hz}$, CH_2), 6.85 (d, 2H, $j=4\text{Hz}$, Ph), 7.35 (m, 3H, Ph), 7.85 (m, 4H, Ph); cmr (CDCl_3) 13.71ppm, 22.30, 23.42, 26.54, 34.49, 37.76, 67.01, 113.94, 127.80, 128.41, 130.09, 132.93, 136.66, 162.43, 198.91, 199.05; ms, m/e 324 (0.1%), 282 (0.23%), 268 (0.28%), 206 (0.51%), 205 (3.6%), 191 (0.20%), 186 (0.36%), 178 (0.23%), 177 (1.42%), 149 (10.3%), 148 (100%), 121 (5.6%), 120 (2.3%), 106 (3.6%), 105 (39%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 316nm.

16. 4-(4'-Cyanophenoxy)-1-phenylbutan-1-one
(γ CnPhOBP)

a. 4-Chloro-1-phenylbutan-1-one

This ketone was prepared in 95% yield by the Friedel-Crafts acylation⁸⁶ of excess benzene with 35.3g of 4-chloro-butyryl chloride (Aldrich Chemical Company) and 36.0g of aluminum chloride at ice water bath temperature. Distillation of the crude material gave a 70% yield of pure product, bp 100 - 103° (0.55 torr) (lit. 126 - 129° (5 torr)⁹⁶), ir (neat) 1690cm^{-1} , 1600cm^{-1} , 1450cm^{-1} , 1225cm^{-1} ; pmr (CCl_4) 2.15ppm (q, 2H, $j=3\text{Hz}$, CH_2), 3.0 (t, 2H, $j=3\text{Hz}$, CH_2), 3.55 (t, 2H, $j=3\text{Hz}$, CH_2), 7.35 (m, 3H, Ph), 7.80 (m, 2H, Ph).

b. 4-Iodo-1-phenylbutan-1-one

43.1g of 4-chloro-1-phenylbutan-1-one, 75g of sodium iodide and 500ml of butan-2-one were placed in a flask and refluxed for two hours. The butan-2-one was then removed on a rotary evaporator. The resulting sludge was dissolved in 500ml of ether and 500ml of distilled water. The layers were separated, and the ether layer was washed with three 300ml portions of distilled water and one 300ml portion of saturated aqueous sodium chloride solution and then dried over sodium sulfate. The ether was removed with a rotary evaporator to give 50.7g (78%) of oil, ir (neat) 1690cm^{-1} , 1450cm^{-1} , 1230cm^{-1} , 745cm^{-1} , 695cm^{-1} ; pmr (CDCl_3) 2.2ppm (m, 2H, CH_2), 3.0 (t, 2H, $j=3\text{Hz}$, CH_2), 3.3 (t, 2H, $j=3\text{Hz}$, CH_2), 7.35 (m, 3H, Ph), 7.85 (m, 2H, Ph).

c. Ethylene Glycol Ketal of 4-Iodo-1-phenylbutan-1-one

50.7g of 4-Iodo-1-phenylbutan-1-one, 50ml of ethylene glycol, 0.5g of toluenesulfonic acid and 500ml of benzene were placed in a flask equipped with a Dean-Stark trap and refluxed for 24 hours. The resulting mixture was washed with three 300ml portions of distilled water and one 300ml portion of saturated aqueous sodium chloride solution and then was dried over sodium sulfate. The benzene was removed with a rotary evaporator to give 54.5g (93%) of oil, pmr (CDCl_3) 1.9ppm (t, 2H, $j=2\text{Hz}$, CH_2), 3.0-4.0 (m, 8H, CH_2), 7.25 (m, 5H, Ph).

d. 4-(4'-Cyanophenoxy)-1-phenylbutan-1-one
($\gamma\text{CNPhOBP}$)

300ml of dimethylsulfoxide and 4.6g of sodium were placed in a flame dried flask under nitrogen. 23.8g of 4-cyanophenol (Aldrich Chemical Company) dissolved in 300ml of dimethylsulfoxide was added dropwise and then stirred until all the sodium had reacted. 54.4g of the ethylene glycol ketal of 4-iodo-1-phenylbutan-1-one dissolved in 300ml of dimethylsulfoxide was then added over about a 6 hour period and let stir for an additional 24 hours. the mixture was then heated to 60° for one hour. 500ml of distilled water was added and the resulting mixture was extracted with four 500ml portions of ether. The combined ether extracts were washed with three 500ml portions of distilled water,

three 500ml portions of 3 M aqueous hydrochloric acid, three 500ml portions of distilled water, three 500ml portions of 10% aqueous sodium hydroxide solution, two 500ml portions of distilled water, and one 500ml portion of saturated aqueous sodium chloride solution and then dried over sodium sulfate. The ether was removed on a rotary evaporator to give 33.3g (73%) of light brown solid. Two recrystallizations from ethanol gave a white crystalline solid, mp 117.0 - 117.25°; ir (CHCl₃) 2210cm⁻¹, 1690cm⁻¹, 1515cm⁻¹, 1260cm⁻¹, 1175cm⁻¹; pmr (CDCl₃) 2.2ppm (q, 2H, j=3Hz, CH₂), 3.15 (t, 2H, j=3Hz, CH₂), 4.05 (t, 2H, j=3Hz, CH₂), 6.75 (d, 2H, j=4Hz, Ph), 7.35 (m, 5H, Ph), 7.8 (m, 2H, Ph); cmr (CDCl₃) 23.16ppm, 34.25, 67.12, 103.57, 114.94, 118.91, 127.66, 128.33, 132.88, 133.63, 136.48, 161.88, 198.81; ms, m/e 265 (0.5%), 148 (10%), 147 (100%), 120 (12%), 106 (4%), 105 (44%), 77 (22%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 316nm.

17. 5-Phenoxy-1-phenylpentan-1-one (δPhOVP)

a. Method A

1) 1-Phenylcyclopentanol

This alcohol was prepared in 90% yield, by a method similar to Fieser's,⁹⁰ from 60.0g of cyclopentanone and phenyl Grignard prepared from 20.8g of magnesium and

135.0g of bromobenzene in ether. It was not purified before use in the next step of the reaction sequence; ir (neat) 3400cm^{-1} (broad), 1500cm^{-1} , 1450cm^{-1} ; pmr (CDCl_3) 1.95ppm (m, 10H, CH_2), 2.6 (m, 1H, CH), 3.0 (s, 1H, OH), 7.2 (m, 5H, Ph).

2) 5-Chloro-1-phenylpentan-1-one

This ketone was prepared by a method similar to that of Wilt and Hill.⁹⁶ 1150ml of commercial household bleach (5.25% sodium hypochlorite, 94.75% "inert ingredients"), 80ml of carbon tetrachloride and 92ml of glacial acetic acid were placed in a flask and cooled to 15° . 57.5g of 1-phenylcyclopentanol was added dropwise and stirred for three hours. The mixture was extracted with four 200ml portions of carbon tetrachloride and the combined carbon tetrachloride extracts washed with three 200ml portions of distilled water, three 200ml portions of saturated aqueous sodium bicarbonate solution, three 200ml portions of distilled water, and one 200ml portion of saturated sodium chloride solution and then dried over sodium sulfate. Nitrogen was bubbled through the resulting solution while it was irradiated for three hours with a 250 watt sunlamp. The carbon tetrachloride was then removed with a rotary evaporator to give 63.0g of brown solid which contained 65% of the desired product by pmr (59% yield). Repeated recrystallization from hexane gave 20.8g (30%) of light brown solid, mp $40 - 45^\circ$ (lit. $49 - 50^\circ$ ⁹⁷); ir (neat) 1690cm^{-1} , 1600cm^{-1} , 1450cm^{-1} ;

pmr (CDCl_3) 1.9ppm (m, 4H, CH_2), 3.0 (t, 2H, $j=3\text{Hz}$, CH_2), 3.55 (t, 2H, $j=3\text{Hz}$, CH_2), 7.45 (m, 3H, Ph), 7.85 (m, 2H, Ph).

3) 5-Iodo-1-phenylpentan-1-one

This ketone was prepared in 75% yield by the Finklestein Reaction from 50.0g of 5-chloro-1-phenylpentan-1-one and 285.6g of sodium iodide in acetone following the procedures described by J. H. Sedon.⁹⁸
 ir (CCl_4) 1700cm^{-1} , 1601cm^{-1} , 1451cm^{-1} , 1210cm^{-1} ;
 pmr (CDCl_3) 1.85ppm (m, 4H, CH_2), 3.0 (m, 4H, CH_2), 7.35 (m, 3H, Ph), 7.80 (m, 3H, Ph).

4) 5-Phenoxy-1-phenylpentan-1-one

500ml of dimethylsulfoxide and 8.2g of sodium were placed in a flame dried flask under nitrogen. 41.8g of phenol dissolved in 250ml of dimethylsulfoxide was added dropwise and the mixture stirred until all of the sodium had reacted. 64.0g of 5-Iodo-1-phenylpentan-1-one dissolved in 250ml of dimethylsulfoxide was added dropwise. The reaction mixture was heated to 60° and kept there one hour then allowed to cool to room temperature and stirred overnight. 175ml of 3 M aqueous hydrochloric acid was added followed by 300ml of distilled water. The resulting mixture was extracted with four 300ml portions of ether. The combined ether layers were washed with three 200ml portions of distilled water, three 200ml portions of 1 M aqueous sodium hydroxide solution, three 300ml portions of distilled water, and one 300ml portion of saturated aqueous sodium chloride solution and then

dried over sodium sulfate. The ether was removed on a rotary evaporator to give 45.8g of dark brown oil whose pmr showed it to be a complex mixture of products. The mixture was refluxed for two hours with 600ml of xylene and 71.0g of pyrrolidine. It was then washed with three 300ml portions of 6 M aqueous hydrochloric acid, three 300ml portions of distilled water, three 200ml portions of 1 M aqueous sodium hydroxide solution, two 300ml portions of distilled water, and one 300ml portion of saturated aqueous sodium chloride solution and then dried over sodium sulfate. The xylene was removed with a rotary evaporator to give 30.2g of brown oil. A pmr spectrum of this oil showed that the starting iodide had been removed but it was still a very complex mixture. It was chromatographed through 3 pounds of alumina using continuously varying solvent mixtures ranging from hexane to ethylacetate. 11.7g (21%) of the desired product was collected in the chloroform fraction; it solidified upon removal of the chloroform.

b. Method B

1) 5-Phenoxy-1-phenylpentan-1-one

The desired ketone was prepared in 39% yield from 24.7g of O-(tetrahydropyran-2-yl)-mandelonitrile and 25g of 1-bromo-4-phenoxy-butane following the procedure used for γ PhOBP.

c. Purification

Three recrystallizations from ethanol gave white crystals, mp 68.75 - 69.0° C; ir (CHCl₃) 1690cm⁻¹, 1603cm⁻¹, 1500cm⁻¹, 1475cm⁻¹, 1450cm⁻¹; pmr (CDCl₃) 1.95ppm (m, 4H, CH₂), 3.0 (t, 2H, j=3Hz, CH₂), 3.95 (t, 2H, j=3Hz, CH₂), 6.85 (d, 2H, j=4Hz, Ph), 7.20 (m, 5H, Ph), 7.85 (m, 2H, Ph); cmr (CDCl₃) 20.74ppm, 28.63, 37.87, 67.28, 114.31, 120.41, 127.84, 128.38, 129.18, 132.70, 136.84, 158.82, 199.59; ms, m/e 254 (2%), 162 (9.7%), 161 (74%), 131 (12.6%), 106 (8%), 105 (100%), 94 (12.6%), 91 (11.5%), 78 (6.9%), 77 (54%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 318nm.

18. 5-(4'-Acetylphenoxy)-1-phenylpentan-1-one
($\delta\text{AcPhOVP}$)

This diketone was prepared in 98% yield from 5.0g of δPhOVP , 1.5g of acetyl chloride and 8.0g of aluminum chloride by the same procedure used to prepare δAcPhVP . It was recrystallized seven times from ethanol to give white crystals, mp 125.25 - 125.50°; ir (CHCl₃) 1685cm⁻¹, 1603cm⁻¹, 1515cm⁻¹, 1365cm⁻¹, 1175cm⁻¹; pmr (CDCl₃) 1.9ppm (m, 4H, CH₂), 2.5 (s, 3H, CH₃), 3.0 (m, 2H, CH₂), 4.0 (t, 2H, j=3Hz, CH₂), 6.75 (d, 2H, j=5Hz, Ph), 7.35 (m, 3H, Ph), 7.8 (m, 4H, Ph); cmr (CDCl₃) 20.56ppm, 26.05, 28.40, 37.72, 67.68, 113.93, 127.79, 128.40, 130.05, 130.36, 132.81, 136.73, 162.71, 196.47, 199.54; ms, m/e 296 (3%), 162 (12%), 161 (100%), 149 (6%), 120 (10%), 106 (9%), 105 (99%), 77 (35%); UV $\lambda_{\text{Max}, \phi\text{H}}^{\text{n} \rightarrow \pi^*}$ 317nm.

19. 5-(4'-Valerylphenoxy)-1-phenylpentan-1-one
(δ ValPhOVP)

This dione was prepared in 82% yield from 5.0g of δ PhOVP, 4.0g valeryl chloride, and 8.0g of aluminum chloride by the same procedure used to prepare δ AcPhVP. Six recrystallizations from ethanol gave a white crystalline material, mp 111.75 - 112.0°; ir (CHCl_3) 1690cm^{-1} , 1600cm^{-1} , 1515cm^{-1} , 1175cm^{-1} ; pmr (CDCl_3) 1.0ppm (t, 3H, j=3Hz, CH_3), 1.2 - 2.0 (m, 8H, CH_2), 3.0 (m, 4H, CH_2), 4.1 (t, 2H, j=3Hz, CH_2), 6.85 (d, 2H, j=5Hz, Ph), 7.35 (m, 3H, Ph), 7.85 (m, 4H, Ph); cmr (CDCl_3) 13.77ppm, 20.61, 22.33, 26.59, 28.48, 37.80, 67.69, 113.84, 128.37, 129.94, 130.06, 132.79, 136.75, 162.53, 199.02, 199.63; ms, m/e 338 (3%), 296 (4%), 281 (3%), 177 (5%), 162 (13%), 161 (100%), 147 (6%), 121 (11%), 120 (4%), 106 (4%), 105 (43%), 77 (17%), UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 317nm.

20. 5-(4'-Cyanophenoxy)-1-phenylpentan-1-one
(δ CNPhOVP)

This ketone was prepared in 70% yield from 11.0g of 5-iodo-1-phenylpentan-1-one and 9.08g of 4-cyanophenol by the procedure described for the preparation of γ CNPhOBP. Six recrystallizations from ethanol gave a white crystalline material, mp 96.25 - 96.50°; ir (CHCl_3) 2215cm^{-1} , 1690cm^{-1} , 1605cm^{-1} , 1515cm^{-1} , 1175cm^{-1} ; pmr (CDCl_3) 1.9ppm (m, 4H, CH_2), 3.05 (t, 2H, j=3Hz, CH_2), 4.0 (t, 2H, j=3Hz, CH_2), 6.85 (d, 2H, j=5Hz, Ph), 7.40 (m, 5H, Ph), 7.85 (m, 2H, Ph); cmr (CDCl_3) 20.46ppm, 28.32, 37.67, 103.57,

114.99, 127.75, 128.06, 128.36, 132.81, 133.68, 136.72, 162.05, 199.41; ms m/e 279 (1.4%), 162 (39.6%), 161 (100%), 160 (4.8%), 143 (5.2%), 133 (12.3%), 132 (8.6%), 120 (7.9%), 119 (13.0%), 106 (38.2%), 105 (100%), 104 (7.4%), 103 (6.7%), 102 (20.1%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 318nm.

21. 4-Ethylacetophenone (pEtAc)

This ketone was prepared in 92% yield by the Friedel-Crafts acylation⁸⁶ of excess ethyl benzene with 9.4g of acetyl chloride and 26.6g of aluminum chloride. Repeated distillation gave a material of bp 50.5 - 51.0° (0.1 torr) (lit. 125° (20 torr)⁹⁹). Analysis by gas chromatography using the same column used to check the purity of pEtVP at 120° showed it to be 99.07% of para and .85% ortho. ir (neat) 1690cm⁻¹, 1605cm⁻¹, 1420cm⁻¹, 1360cm⁻¹, 1275cm⁻¹, 1180cm⁻¹, 955cm⁻¹, 830cm⁻¹; pmr (CCl₄) 1.25ppm (t, 3H, j=4Hz, CH₃), 2.45 (s, 3H, CH₃), 2.65 (q, 2H, j=4Hz, CH₂), 7.10 (d, 2H, j=4Hz, Ph), 7.70 (d, 2H, j=4Hz, Ph); ms, m/e 148 (24.5%), 134 (10.1%), 133 (100%), 105 (29.4%), 103 (10.3%), 90 (5.5%), 89 (5.7%), 79 (18.1%), 78 (5.7%), 77 (20.6%); UV $\lambda_{\text{Max}, \phi\text{H}}^{n \rightarrow \pi^*}$ 309nm.

22. Acetophenone (Ac)

This ketone was obtained from Eastman Chemical Company and purified by A. E. Puchalski by repeated distillation through a spinning band column.

23. 1-Phenylpentan-1-one (VP)

This ketone was prepared by either E. J. Siebert or M. J. Thomas by the Friedel-Crafts acylation of benzene

with valeryl chloride and purified by repeated distillation at reduced pressure.

24. Benzophenone

This ketone was obtained from Aldrich Chemical Company and purified by W. B. Mueller by repeated recrystallization from ethanol.

25. 4-Methoxyacetophenone (pMeOAc)

This ketone was obtained from Aldrich Chemical Company and had been purified by H. N. Schott by repeated recrystallization from petroleum ether.

26. 1-(4-Methoxyphenyl)-pentan-1-one (pMeOVP)

This ketone was prepared by Friedel-Crafts acylation of anisoyl with valeroylchloride and purified by repeated recrystallization from pentane/methanol by H. N. Schott.

B. Internal Standards

1. Tetradecane

Tetradecane was obtained from Columbia Organic Chemicals and purified by washing with sulfuric acid then distilling (bp 119 - 120° (10 torr)) by Dr. Peter J. Wagner.

2. Hexadecane

Hexadecane was obtained from Aldrich Chemical Company and purified by washing with sulfuric acid then distilling (bp 146/10 torr) by Dr. Peter J. Wagner.

3. Octadecane

Octadecane was obtained from Aldrich Chemical Company and purified by recrystallization from ethanol by Dr. Peter J. Wagner.

4. Di-n-ethyl Phthalate

This ester was used as received from Aldrich Chemical Company.

5. Di-n-propyl Phthalate

This ester was prepared by Fischer esterification of phthalic anhydride with 1-propanol and purified by distillation, bp 128°/1.2 torr.

6. Di-n-Butyl Phthalate

This ester was used as received from Aldrich Chemical Company.

C. Quenchers

1. 2,5-Dimethylhexa-2,4-diene

2,5-Dimethylhexa-2,4-diene was obtained from Chemical Samples Company and upon sitting in the refrigerator sublimed up around the sides of the bottle. This sublimed material was used.⁶⁸

2. cis-1,3-Pentadiene

This diene was used as received from Chemical Samples Company.

3. trans-Stilbene

This olefin was used as received from J. T. Baker Company.

D. Solvents

1. Benzene

The method used to purify benzene was similar to the method used by Kemppainen.⁶⁹ One gallon of A. C. S. reagent grade benzene obtained either from Fisher Scientific Company, Mallinckrodt Chemical Company, or Drake Brothers Chemical Company, was stirred over several changes of concentrated sulfuric acid (200ml/gal benzene; minimum stirring time per change, one day) until the sulfuric acid no longer discolored. It was then washed with three 300ml portions of distilled water, three 300ml portions of saturated aqueous sodium bicarbonate solution, two 300ml portions of distilled water, and one 300ml portion of saturated aqueous sodium chloride solution and then dried over magnesium sulfate. It was then refluxed over phosphorous pentoxide overnight and distilled through a one meter column packed with stainless steel helices at a rate of about two liters a day. The first and last 750ml portions were discarded. The center cut was distilled a second time through this same column with the first and last 450ml portions being discarded.

2. Pyridine

A. C. S. reagent grade pyridine obtained from Fisher Scientific Company, Mallinckrodt Chemical Company, or Drake Brothers Chemical was distilled from barium oxide through a half meter column packed with stainless steel

helices. All material boiling below 115° C was discarded along with about a 10% forerun.

3. Dioxane

Dioxane was purified by Riddick's technique.¹⁰⁰ 1500ml of Fischer Scientific Company Scintanalyzed grade dioxane was allowed to stand over ferrous sulfate for several weeks. It was then refluxed under nitrogen with 150ml of distilled water and 42ml of concentrated hydrochloric acid overnight. Potassium hydroxide pellets were added at a temperature just below boiling until the pellets maintained their integrity. This mixture was allowed to sit overnight under nitrogen. The dioxane was then decanted from the saturated potassium hydroxide solution and distilled from sodium using a three foot column packed with glass helices. A forerun of about 300ml was discarded and 300ml were left in the distillation pot. The dioxane was then recrystallized from itself three times, discarding about 20% each time. It was then stored frozen. Towards the end of the work presented in this thesis it was determined that distillation through a half meter column packed with stainless steel helices immediately before use was as effective as the above procedure.

4. Ethanol

Ethanol was purified by Riddich's Technique.¹⁰⁰ One gallon of U. S. P. grade 190 proof ethanol was distilled from 100ml of concentrated sulfuric acid

through a one meter column packed with glass helices at a rate of one liter every 24 hours. The first and last 500ml portions were discarded. The middle fraction was then distilled from 60g of potassium hydroxide and 30g of silver nitrate through the same column at the same rate discarding the first and last 10%. 200ml of distilled water was then added to the middle fraction and the mixture distilled through the same column at the same rate discarding the first and last 10%.

5. Methylcyclohexane

Methylcyclohexane was purified by Forster's technique.¹⁰¹ 500ml of Methylcyclohexane (Eastman Chemical Company) was stirred over concentrated sulfuric acid until the acid was no longer discolored. It was then washed with three 100ml portions of distilled water, three 100ml portions of saturated aqueous sodium bicarbonate, three 100ml portions of distilled water, and then dried over magnesium sulfate. It was distilled through a half meter column packed with stainless steel helices. The first and last 20% was discarded.

6. Cyclohexane

Cyclohexane (Matheson, Coleman, and Bell, spectrograde) was recrystallized from itself twice.

7. 2-Methyltetrahydrofuran

2-Methyltetrahydrofuran was purified by Gordon and Fords procedure.¹⁰² 750ml of 2-methyltetrahydrofuran

(Aldrich Chemical Company) was distilled from cuprous chloride through a 40cm Vigreux column, the first and last 20% being discarded, and then from lithium aluminum hydride, the first and last 10% being discarded.

8. 2-Methylbutane

Gold label grade 2-methylbutane was used as received from Aldrich Chemical Company.

II. Preparative Scale Photolysis of 5-(4-Acetylphenyl)-1-phenylpentan-1-one (δ AcPhVP)

2.0g of δ AcPhVP and 450ml of benzene were placed in a flask equipped with a quartz well holding a 450 watt medium pressure mercury lamp. Nitrogen was bubbled through the solution. After six hours of irradiation the diketone was no longer detectable by high pressure liquid chromatography. Removal of the benzene with the aid of a rotary evaporator left 2.0g of oil. This oil was dissolved in a small amount of hexane; the solution was placed on 5.0g of silica gel (Mallinckrodt Silicar CC-7) and the hexane then removed with the aid of a rotary evaporator. This coated silica gel was placed on top of a 2.0cm o.d. column packed with 60g of silica gel (about 50cm in height) and was eluted with the following solvent mixtures:

Fraction numbers	Solvent	total mls
1-20	hexane	200
21-31	10:90 Methylene chloride/hexane	100
32-41	20:80 Methylene chloride/hexane	100
42-51	30:70 Methylene chloride/hexane	100
52-61	40:60 Methylene chloride/hexane	100
62-72	50:50 Methylene chloride/hexane	100
73-82	60:40 Methylene chloride/hexane	100
83-92	70:30 Methylene chloride/hexane	100
93-101	80:20 Methylene chloride/hexane	100
102-112	90:10 Methylene chloride/hexane	100
113-121	Methylene chloride	100
122-131	10:90 Ethylacetate/methylene chloride	100
132-141	20:80 Ethylacetate/methylene chloride	100
142-151	30:70 Ethylacetate/methylene chloride	100
152-160	40:60 Ethylacetate/methylene chloride	100
161-169	50:50 Ethylacetate/methylene chloride	100
170-179	60:40 Ethylacetate/methylene chloride	100
180-189	70:30 Ethylacetate/methylene chloride	100
190-199	80:20 Ethylacetate/methylene chloride	100
200-208	90:10 Ethylacetate/methylene chloride	100
208-214	Ethylacetate	100

The average flow rate was 1.46ml/minute. Analysis by gas chromatography indicated that fractions 55-80 were a mixture of acetophenone and 4-allylacetophenone, and that 81-100 were 4-allylacetophenone. Fractions 55-80 were combined and analysis indicated that the combined

fractions were 39% acetophenone. The solvent was removed from these fractions. Evaporation of fractions 81-100 gave .1675g of white crystals. Before spectra could be taken of this material it became partially insoluble. Fractions 109-138 were analyzed by high pressure liquid chromatography and found to contain a mixture of the starting diketone and cis-1-phenyl-2,4'-acetylphenylmethylcyclobutanol. The combined fractions were evaporated to give 0.0489g which was found to be 57% cyclobutanol. Fractions 139-143 were found to contain essentially pure cis-1-phenyl-2,4'-acetylphenylmethylcyclobutanol. Evaporation of the solvents gave .2062g of oil, ir (CHCl_3) 3580cm^{-1} , 3475cm^{-1} , 1690cm^{-1} , 1605cm^{-1} , 1450cm^{-1} , 1420cm^{-1} , 1365cm^{-1} , 1275cm^{-1} , 1185cm^{-1} ; pmr (CDCl_3) 1.5ppm (m, 1H, CH_2), 2.0 (m, 2H, CH_2), 2.2 (d, 1H, $j=2\text{Hz}$, OH), 2.4 (s, 3H, CH_3), 2.95 (m, 4H, CH_2), 7.15 (m, 3H, Ph), 7.65 (m, 2H, Ph); ms, m/e 281 (.813%), 280 (3.66%), 252 (7.72%), 237 (3.66%), 162 (7.59%), 161 (53.7%), 145 (8.81%), 134 (16.5%), 122 (51.2%), 121 (100%), 120 (46.3%), 115 (6.91%), 107 (10.3%), 106 (12.7%), 105 (61.8%); UV $\lambda_{\text{Max}}^{\text{methylene chloride}}$ 254 (1.5×10^4). Fractions 144-149 were found to contain a 30:70 mixture of cis and trans-cyclobutanols. Evaporation of the solvent gave 0.2056g of oil. Fractions 150-154 were found to contain 0.0741g of oil that was 93% trans-cyclobutanol. ir (CHCl_3) 3580cm^{-1} , 3450cm^{-1} , 1690cm^{-1} , 1605cm^{-1} , 1365cm^{-1} , 1275cm^{-1} , 1185cm^{-1} ; pmr (CDCl_3) 1.2 - 3.0 (m, 11H),

6.8 - 7.75 (m, 9H); ms, m/e 821 (1.21%), 280 (5.1%), 252 (7.7%), 237 (4.2%), 162 (9.7%), 161 (76.1%), 145 (10.6%), 134 (11.0%), 122 (2.7%), 121 (16.4%), 120 (100%), 115 (10.4%), 107 (2.3%), 106 (7.7%), 105 (82.6%);
 UV λ_{Max} methylene chloride 254 (9.5×10^3).

III. Electronic Absorption Spectra

Ultraviolet spectra were taken using a Cary Model 17 Spectrophotometer and 1 cm quartz cells.

IV. Emission Spectra

Phosphorescence spectra were taken with either a Perkin-Elmer MPF-44A Fluorescence Spectrophotometer equipped with a Differential Corrected Spectra Unit and Hitachi Phosphorescence Accessory, or with an Aminco Bowman Spectrophotofluorometer. Spectra were taken at 77° K using a quartz dewar and 5mm quartz tubes. The choppers were used only to assure that the observed total emission was only phosphorescence.

V. Photokinetic Data

A. General Comments

1. Glassware

All glassware used was class A volumetric ware except for syringes used to fill irradiation tubes which were pyrex with chrome plated brass needles. All glassware was cleaned by rinsing with acetone and then distilled water followed by soaking in a 90° distilled water solution of laboratory glassware detergent for 24 hours, repeating the detergent soak, then soaking in distilled

water at 90° for four days changing the water daily.

2. Weights

All weighing was done on Sartorius Model 2403 analytical balance which was accurate to a tenth of a milligram.

3. Irradiation tubes

Irradiation tubes were prepared by carefully sizing pyrex culture tubes to an outside diameter of 13.5mm $\pm$ 0.1mm, cleaning these tubes by the procedure described for glassware and then drawing them out to a uniform length with a neck of 2 to 3 mm diameter.

4. Degassing procedure

Irradiation tubes were filled with 3.0ml of the solution to be irradiated with a 5 ml syringe. Great care was taken to make sure that all tubes for a given run contained exactly the same amount of solution. All samples were degassed by six freeze-pump-thaw cycles on a vacuum line at 5×10^{-4} torr and were then sealed in vacuo.

5. Irradiation lamps

Three different irradiation apparati were used during the course of this research. In all cases the light source was a Hanovia 450 watt medium pressure mercury lamp cooled by a quartz immersion well. To assure equal irradiation of the samples and minimize temperature changes during photolysis, these wells were placed inside a merry-go-round apparatus¹⁰⁰ with slit

widths of 7.0 mm, and the whole apparatus placed inside a large crock filled with distilled water. Two of these apparatus contained 1 cm filters consisting of a 0.002 M potassium chromate, 1% potassium carbonate aqueous filter solution to isolate the $3130 \text{ \AA}$ mercury line. One of the $3130 \text{ \AA}$ setups was equipped with a thermostat system capable of maintaining at a temperature of $30.0 \pm 0.1^\circ \text{ C}$. The other was operated at ambient temperature ($17 - 28^\circ \text{ C}$). The third apparatus was equipped with a set of Corning No. 7083 filter to isolate the $3660 \text{ \AA}$ mercury line. This apparatus was operated at ambient temperature.

6. Sample Analysis

Samples were generally analyzed for cleavage products or cis - trans isomerization of the quencher by vapor phase chromatography. Several different conditions and instruments were used during the course of this research. The most common conditions are listed in Table 13. All gas chromatographs used were equipped with flame ionization detectors. Internal standards were used for all analyses except cis - trans isomerizations. The response factors for the various internal standards with respect to the acetophenones analyzed are as follows:

tetradecane/acetophenone	2.000
hexadecane/acetophenone	2.324
hexadecane/4-ethylacetophenone	1.8514
octadecane/4-ethylacetophenone	1.9000

Table 13: Gas Chromatography Conditions

Condition Set	Column	temper- ature	flow rate	Instrument
1	4% QF-1, 1% Carbowax 20 M on Chromosorb G (acid washed, DMCS treated) 10' x 1/8".	105°	25ml/min	Varian Aerograph Series 1200
2	Same as in 1	120°	25ml/min	Varian Aerograph Series 1200
3	10% QF-1, 2% Carbowax 20 M on Chromosorb W 14' x 1/8".	85°	35ml/min	Varian Aerograph Series 1200
4	Same as in 3	140°	35ml/min	Varian Aerograph Series 1200
5	Same as in 3	110°	35ml/min	Varian Aerograph Series 1200
6	5% QF-1, 1.25% Carbowax 20 M on Chromosorb G (acid washed, DMCS treated) 14' x 1/8".	145°	60ml/min	Varian Aerograph Series 1400
7	Same as in 6	90°	60ml/min	Varian Aerograph Series 1400
8	25% 1,2,3-tris (β-cyanoethoxy) propane on Chromosorb P 25' x 1/8"	30°	25ml/min	Varian Aerograph Model 600D
9	5% SE-30 on Chromosorb P (acid washed, DMCS treated) 6' x 1/8".	150°	60ml/min	Varian Aerograph Series 1400

The response factor for cyclohexane/propene was never determined because cyclohexane is almost always a contaminant in purified benzene. Relative peak areas were determined using either an Infotronics CRS 208 Automatic Digital Integrator or an Infotronics CRS 309 Computing Integrator for Chromatography.

Analysis for the various diketones was carried out using a Waters Associates Analytical Liquid Chromatograph Model 202 with Differential U. V. Detector. The conditions used varied greatly and will be reported with the actual data. Di-n-ethyl, Di-n-propyl, and Di-n-Butyl phthalates were used as internal standards.

B. Stern-Volmer Plots

Solutions for irradiation were normally prepared by making stock ketone solution containing both ketone and internal standard in a 10 ml volumetric flask. 2.0 ml of this stock solution was then pipetted into a 10 ml volumetric flask and diluted to be used to make unquenched ketone samples. 1.0 ml of the ketone stock solution was pipetted into a number of 5 ml volumetric flasks and the desired amount of a stock 2,5-dimethyl-2,4-hexadiene solution added by use of a graduated pipette and the flasks brought to volume. Irradiation tubes were then filled, degassed, irradiated, and analyzed in the manner previously described. ϕ^0/ϕ was obtained for each quenched solution by dividing the average ratio of the area under the product peak to the area under the

internal standard peak for the unquenched tubes by the equivalent ratio for the quenched tubes. ϕ°/ϕ is plotted versus the concentration of 2,5-dimethyl-2,4-hexadiene. The error in the slope arises from a combination of the precision with which the unquenched tubes were filled and the accuracy of the dilution of the quencher.

Normally a valerophenone (VP) solution was prepared at the same time with the same concentration of internal standard so that the quantum yields for product formation could be determined from the unquenched ketone solution.

C. Lewis Base Studies, Maximum Quantum Yields

Samples were prepared in the same manner as for Stern-Volmer kinetics except a stock Lewis base solution was used instead of a stock quencher solution.

D. Product Quantum Yields, Actinometry

Quantum yields were calculated using the following formula:

$$\phi = \frac{(\text{Prod/Std})}{(\text{Prod/Std})_{\text{Act.}}} (\phi_{\text{Act.}}) \times (\text{absorb. corr.})$$

$$\times \frac{(\text{conc. Std.}) (\text{RF})}{(\text{conc. Std.})_{\text{Act.}} (\text{RF})_{\text{Act.}}}$$

where RF is the gc detector response factor.

The absorbance correction was calculated using the following equation based on Biers Law:

$$\text{Absorb. Corr.} = \frac{1 - T_{\text{act}}}{1 - T_{\text{ketone}}}$$

where $T = \text{antilog } (-\epsilon lc)$

It can be demonstrated by simple geometry that the average path length for the irradiation tubes used (1.10 cm inside diameter and slit width .70 cm) is 1.018 cm.

Valerophenone (VP) was used as an actinometer for the product quantum yields. Its ϕ of acetophenone or propene formation at 0.05 M is .315 and at 0.01 M is .300.⁶⁰

E. Sensitization Plots, Quantum Yields of Intersystem Crossing

For ketones with no photochemistry, lifetimes were obtained by observing their effectiveness as sensitizers for the cis - trans isomerization of either cis-1,3-pentadiene or trans-stilbene. Normally solutions for these studies were prepared by preparing a stock ketone solution 1.0 ml of which was pipetted into several 5 ml volumetric flasks. A quencher stock solution was prepared and the appropriate amount of this solution pipetted into the flasks containing the ketone solution. Actinometers were prepared by making a solution of the appropriate ketone (acetophenone for 3130 Å, benzophenone for 3660 Å) and adding enough quencher stock solution to quench more than 99% of the triplet state. Irradiation tubes were then filled with 3.0 ml of the appropriate solution and then degassed, irradiated, and analyzed by the procedures described above. Results were analyzed by plotting $\alpha/\phi_{\text{isomerization}}$ versus $1/[\text{quencher}]$.

$$\alpha/\phi_{\text{isomerization}} = \frac{(\beta'')_{\text{ketone}} [\text{quencher}]_{\text{ketone}}}{(\beta'')_{\text{act.}} [\text{quencher}]_{\text{act.}}}$$

where α is the photostationary state for the quencher isomerization ($\alpha = 0.555$ for cis-1,4-pentadiene, and 0.596 for trans-stilbene⁶⁸) and β'' is the percentage of the newly formed isomer corrected for backreaction as follows:¹⁰⁴

$$\beta'' = \beta' - \beta \quad \text{unirradiated quencher}$$

$$\beta' = \alpha \text{ in } (\alpha/(\alpha - \% \text{ new isomer}))$$

For ketones where products were formed by comparing the efficiency with which they sensitized the cis - trans isomerization of cis-1,3-pentadiene to the efficiency of acetophenone at causing the same isomerization. The solutions for these experiments were prepared by weighing ketone and acetophenone into two separate flasks and pipetting enough quencher stock solution into each to quench 99% of the ketone's reaction.

F. Disappearance Yields

Solutions for determining disappearance yields were prepared by weighing the amount of ketone required to make the desired concentration into three separate 5.0 ml volumetric flasks and adding 1.0 ml of a stock solution of the internal standard used to measure one of the cleavage products. Irradiation tubes were filled, degassed, and irradiated as previously described. The irradiated samples were then analyzed by gas chromatography for the cleavage product and the percent conversion to the

cleavage product determined as follows:

$$\% \text{ conv. Cl.} = \frac{(\text{area prod. peak}) [\text{std}] (\text{RF}) (100\%)}{(\text{area std. peak}) [\text{ketone}]}$$

the percent conversion of the ketone was then determined by pipetting 0.5 ml of irradiated ketone solution and 0.5 ml of a solution of the appropriate phthalate ester into a vial and analyzing by high pressure liquid chromatography. The same procedure was followed with the unirradiated ketone solution.

$$\% \text{ conv ketone} = 100\% \frac{\left[\frac{\text{ketone peak area}}{\text{std peak area}} \right]_{\text{irr. ketone}}}{\left[\frac{\text{ketone peak area}}{\text{std peak area}} \right]_{\text{unirr. ketone}}}$$

The disappearance quantum yield is then calculated as follows:

$$\phi_{\text{Dis}} = \frac{\% \text{ conv. ketone}}{\% \text{ conv. to product}} \times \phi_{\text{prod}}$$

G. Data

1. DiBzdiMeMt

Stilbene sensitization data for this diketone indicating a ϕ_{isc} of 0.70 and a $k_q\tau$ value of $488 \text{ M}^{-1}\text{sec}^{-1}$ are presented in Table 14. The disappearance yield for this ketone was determined to be 0.00 by irradiation of a 0.51 M solution of the diketone in benzene- d_6 in a pyrex nmr tube at 313 nm for 184 hours. No change was detectable by either pmr or gc.

Table 14: Stilbene Sensitization Data for DiBzdiMeMt

$$\phi_{isc} = 0.70, k_q\tau = 488 \text{ M}^{-1}\text{sec}^{-1}$$

[Stilbene] x10 ³ M	$\frac{\text{cis}}{\text{cis+trans}}$	.596/ $\phi_{t \rightarrow c}$
1.34	.336	3.61
1.79	.337	2.71
2.24	.284	2.77
3.58	.233	2.38
4.48	.210	2.08
8.96	.137	1.75

Benzophenone Actinometer (average of 3 tubes)

8.96 .217±.007

[diketone] = 0.0541 M, [benzophenone] = 0.0307 M,
benzene solvent, 366 nm, ambient temperature, g.c.
condition set 9.

2. DiBzEt

1,3-pentadiene sensitization data for this diketone indicating a ϕ_{isc} of 1.0 and a $k_q\tau$ value of $300 \pm 3 \text{ M}^{-1}\text{sec}^{-1}$ are presented in Table 15. The disappearance yield for this ketone was determined to be 0.00 by irradiation of a 0.5 M solution of the diketone in benzene- d_6 in a pyrex nmr tube at 313 nm for 72 hours. No change was detectable by either pmr or gc.

3. DiBzPr

All data presented here are not corrected for product quenching. The crude Stern-Volmer data are presented in Table 16. Data used to extrapolate ϕ_{II} to zero conversion are shown in Table 17. The data used to determine the crude ϕ_{II}^{Max} with dioxane as a Lewis base are shown in Table 18. The data used to extrapolate ϕ_{II}^{Max} to zero conversion are shown in Table 19. The data used to determine ϕ_{isc} are shown in Table 20. The data used to determine ϕ_{Dis} and ϕ_{Dis}^{Max} are presented in Tables 21 and 22.

4. DiBzBt

The Stern-Volmer data for this diketone are presented in Table 23. The observed $k_q\tau$ value is $80.1 \pm 2.4 \text{ M}^{-1}\text{sec}^{-1}$. The effects of various concentrations of dioxane on ϕ_{II} are presented in Table 24. ϕ_{II}^{Max} was observed to be $0.54 \pm .01$, and the average ϕ_{II} observed in the Stern-Volmer and ϕ_{II}^{Max} experiments was $0.42 \pm .02$. The data used to determine ϕ_{isc} are shown in Table 25. The data

Table 15: 1,3-Pentadiene Sensitization Data for DiBzEt

Run 1

$\phi_{isc}=1.0$, $k_q\tau=297M^{-1}sec^{-1}$, lamp intensity=0.00179E/hr

[1,3-Pentadiene] $\times 10^3 M$	$\frac{trans}{cis+trans}$	$.555/\phi_{c \rightarrow t}$
3.86	.345	1.89
4.83	.304	1.86
5.80	.302	1.57
6.76	.284	1.47
7.73	.266	1.41
8.69	.252	1.35

Acetophenone Actinometer (average of three tubes)
242 .0163 $\pm$.0002

[diketone] = .0249M, [acetophenone] = .0288M, Benzene
solvent, 313nm, 30.0°, g.c. condition set 8.

Run 2

$\phi_{isc}=1.0$, $k_q\tau=303M^{-1}sec^{-1}$, Lamp intensity=0.00185E/hr

[1,3-Pentadiene] $\times 10^3 M$	$\frac{trans}{cis+trans}$	$.555/\phi_{c \rightarrow t}$
3.24	.320	2.01
4.32	.288	1.78
5.40	.264	1.61
7.56	.186	1.81
8.64	.216	1.31

Acetophenone Actinometer (average of three tubes)
270 .0114 $\pm$.0007

[diketone]=.0249M, [acetophenone]=.0288M, benzene solvent,
313nm, 30.0°, g.c. condition set 8.

Table 16: Stern-Volmer Data for DiBzPr

Run 1

$\phi_{II}=0.176$, $k_q\tau=122M^{-1}sec^{-1}$, Lamp intensity=0.00651E/hr

$[Q]$ $\times 10^3 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	$.831 \pm .08^a$		7.81 (7.58% conv)
.935	.643	1.29	6.04
1.87	.681	1.22	6.40
3.74	.514	1.62	4.83
5.61	.492	1.69	4.62
7.48	.467	1.77	4.39
9.35	.370	2.25	3.48
VP Actinometer (average from three tubes)			
0.0	$1.121 \pm .03$		10.54

[diketone]=0.0103M(0.0894%T), [VP]=0.0115M(0.279%),
 $[C_{14}]=4.70 \times 10^{-4} M$, benzene solvent; 313nm, 30.0°, g.c.
 condition set 5.

Run 2

$\phi_{II}=.192$, $k_q\tau=131M^{-1}sec^{-1}$, Lamp intensity=0.00317E/hr

$[Q]$ $\times 10^3 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	$.590 \pm .020^a$		10.62 (4.89% conv)
0.818	.562	1.05	10.12
1.64	.473	1.24	8.51
3.27	.359	1.65	6.46
4.91	.369	1.60	6.64
6.55	.327	1.80	5.89
8.18	.318	1.85	5.72
VP Actinometer (average from three tubes)			
0.0	$.860 \pm .020$		15.48

[diketone]=0.0217M(0.00618%T), [VP]=0.0239M(0.071%T),
 $[C_{14}]=9.00 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°, g.c.
 condition set 5.

a. average from three tubes

Table 17: Conversion Dependence of ϕ_{II} for DiBzPr

Run 1

Diketone			VP Actinometer		ϕ_{II}
$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\frac{[Ac]}{x10^4 M}$	% conv	$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\frac{[Ac]}{x10^4 M}$	
.0634	1.72	.875	.119	3.24	.143
.142	3.86	1.96	.174	4.73	.219
.142	3.86	1.96	.174	4.73	.219
.192	5.22	2.65	.269	7.32	.191
.222	6.04	3.07	.309	8.40	.192
.280	7.62	3.87	.336	9.14	.224

[Diketone]=0.0197M(0.00988%T), [VP]=0.0195M(0.115%T),

[C₁₄]=0.00136M, benzene solvent, 313nm, 30.0°, g.c.

condition set 5.

Run 2

Diketone			VP Actinometer		ϕ_{II}
$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\frac{[Ac]}{x10^4 M}$	% conv	$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\frac{[Ac]}{x10^4 M}$	
.0958	2.30	1.09	.139	3.34	.191
.173	4.15	1.97	.214	5.14	.225
.299	7.18	3.40	.372	8.93	.223
.299	7.18	3.40	.397	9.53	.209
.385	9.24	4.38	.513	12.3	.208
.427	10.02	4.86	.609	14.6	.195

[Diketone]=0.0211M(0.00711%T), [VP]=0.0230M(0.0781%T),

[C₁₄]=0.00120M, benzene solvent, 313nm, 30.0°, g.c.

condition set 5.

Table 18: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for DiBzPr

Run 1

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	0.615 $\pm$.01	0.659	.179
0.500	0.927	0.994	.270
0.999	1.13	1.21	.330
2.00	1.26	1.35	.367
3.00	1.52	1.63	.442
4.00	1.58	1.69	.460
5.00	1.65	1.77	.477
VP Actinometer (average from three tubes)			
0.0	0.971 $\pm$.03	1.04	

[diketone]=0.00985M(0.0994%T), [VP]=0.0170M(0.152%T),

[C₁₄]=5.36 $\times 10^{-4}$ M, benzene solvent, 313nm, 30.0°,

g.c. condition set 5, lamp intensity=.00136E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	0.627 $\pm$.01 ^a	0.764	.187
1.50	1.16	1.41	.345
2.50	1.39	1.69	.413
3.50	1.58	1.92	.470
4.50	1.43	1.74	.425
6.00	1.45	1.77	.431
7.00	1.12	1.36	.333
VP Actinometer (average from three tubes)			
0.0	0.949 $\pm$.04	1.16	

[diketone]=0.00988M(0.0987%T), [VP]=0.0170M(0.152%T),

[C₁₄]=6.09 $\times 10^{-4}$ M, benzene solvent, 313nm, 30.0°,

g.c. condition set 5, lamp intensity = .00152E/hr

a. average from three tubes

Table 19: Conversion Dependence of ϕ_{II} in 4.5M Dioxane
for DiBzPr

Diketone			VP Actinometer(no Dioxane) ϕ_{II}		
$\frac{\text{area Ac}}{\text{area } C_{14}}$	$[Ac] \times 10^4 M$	% conv	$\frac{\text{area Ac}}{\text{area } C_{14}}$	$[Ac] \times 10^4 M$	
.361	4.40	4.53	.121	1.48	.667
.403	4.92	5.05	.138	1.68	.653
.595	7.26	7.46	.212	2.59	.627
.632	7.71	7.92	.287	3.50	.492
.923	11.26	11.6	.379	4.62	.544
1.16	14.15	14.5	.501	6.11	.517

$[\text{diketone}] = 0.00973M(0.102\%T)$, $[\text{VP}] = 0.00998M(0.331\%T)$,

$[C_{14}] = 6.10 \times 10^{-4}M$, 4.5M Dioxane in benzene solvent, 313nm,
30.0°, g.c. condition set 5.

Table 20: Intersystem Crossing Yield for DiBzPr

Ketone	$[1,3\text{-pentadiene}]$ M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.0506 M DiBzPr	0.535	.0261	1.02
0.0650 M Ac	0.535	.0266	1.00

Benzene solvent, 313nm, 30.0°, g.c. condition set 8.

Table 21: ϕ_{Dis} for DiBzPr

	run 1	run 2
[diketone]	0.00985M	0.00988M
[tetradecane]	0.000536M	0.000609M
[diethylphthalate]	0.0304M	0.0304M
avg. ratio, diketone/phthalate		
unirradiated	1.658	1.373
irradiated	1.522	1.246
% conv of ketone	8.20%	9.25%
area Ac/area C ₁₄	0.615	0.627
% conv to Ac	6.69%	7.73%
% conv ketone/% conv Ac	1.23	1.20

Benzene solvent; 313nm; 30.0°; g.c. condition set 5;

h.p.l.c. conditions neutral alumina; 2' x 1/8", 700psig,
methylene chloride.

Table 22: $\phi_{\text{Dis}}^{\text{Max}}$ for DiBzPr

[diketone]	0.0101M
[tetradecane]	0.00128M
[di-n-propyl phthalate]	0.0836
avg. ratio, diketone/phthalate	
unirradiated	1.02
irradiated	0.771
% conv of ketone	24.4
Area Ac/area C ₁₄	0.701
% conv to Ac	17.8
% conv ketone/% conv Ac	1.37

4.5M Dioxane in benzene solvent; 313nm; 30.0°; g.c.

condition set 5; h.p.l.c. conditions Porasil 1000pft,

2' x 1/8", 50% stroke, 60:40 hexane/methylene chloride

Table 23: Stern-Volmer Data for DiBzBt

Run 1

$\phi_{II}=0.434$, $k_q\tau=82.5\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity= 0.00503E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 \text{M}$
0.0	2.62 ± 0.04^a		10.1
0.393	2.17	1.22	8.38
0.787	1.66	1.58	6.41
1.57	1.23	2.13	4.75
2.36	0.896	2.92	3.46
3.15	0.748	3.50	2.89
3.93	0.604	4.34	2.33
VP Actinometer (average from three tubes)			
0.0	1.28 ± 0.04		4.94

$[\text{diketone}] = 0.0101\text{M}(0.0745\%T)$, $[\text{VP}] = 0.00957\text{M}(0.346\%T)$,

$[C_{14}] = 1.93 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0°,

g.c. condition set 5.

Run 2

$\phi_{II}=0.423$, $k_q\tau=77.6$, Lamp intensity= 0.00761 E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 \text{M}$
0.0	2.68 ± 0.05^a		14.9
0.468	1.80	1.49	10.0
0.936	1.47	1.82	8.17
1.87	1.18	2.27	6.56
2.81	0.819	3.28	4.55
3.74	0.678	3.96	3.77
4.68	0.570	4.71	3.17
VP Actinometer (average from three tubes)			
0.0	1.48 ± 0.10		8.23

$[\text{diketone}] = 0.0101\text{M}(0.0745\%T)$, $[\text{VP}] = 0.0115\text{M}(0.279\%T)$,

$[C_{14}] = 2.78 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0°,

g.c. condition set 5.

a. average from three tubes

Tabel 24: Effects of Varying Concentrations of Dioxane on ϕ_{II} for DiBzBt

Run 1			
[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	0.793 ± 0.01^a	0.917	0.427
0.500	0.771	0.891	0.415
1.00	0.917	1.06	0.493
2.00	0.874	1.01	0.470
3.00	0.881	1.02	0.474
4.00	0.968	1.11	0.521
5.00	1.00	1.16	0.538
VP Actinometer (average from three tubes)			
0.0	0.390 ± 0.03	0.451	

[diketone]=0.01023M(0.0720%T), [VP]=0.00944M(0.351%T),
 $[C_{14}] = 5.78 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity = 0.00154 E/hr

Run 2			
[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	1.25 ± 0.04^a	1.10	0.376
1.5	1.46	1.28	0.439
2.5	1.61	1.41	0.484
3.5	1.67	1.47	0.502
4.5	1.78	1.56	0.535
6.0	1.48	1.30	0.445
7.0	1.50	1.32	0.451
VP Actinometer (average from three tubes)			
0.0	0.927 ± 0.06	0.814	

[diketone]=0.0101M(0.0745%T), [VP]=0.0177M(0.141%T),
 $[C_{14}] = 4.39 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity = 0.00158 E/hr

a. average from three tubes

Table 25: Intersystem Crossing Yield for DiBzBt

Ketone	[1,3-pentadiene] M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.0496M DiBzBt	0.985	0.0272	1.02
0.0542M Ac	0.985	0.0267	1.00

Benzene solvent, 313nm, 30.0°, g.c.condition set 8

Table 26: ϕ_{Dis} for DiBzBt

	run 1	run 2
[diketone]	0.0102M	0.0101M
[tetradecane]	0.000578M	0.000439M
[diethylphthalate]	0.0679	0.0629
avg. ratio, diketone/phthalate		
unirradiated	1.30	1.51
irradiated	1.18	1.33
% conv of ketone	9.23	11.9
area Ac/area C ₁₄	0.793	1.25
% conv to Ac	8.99	10.9
% conv ketone/% conv Ac	1.03	1.09

Benzene solvent; 313nm; 30.0°; g.c. condition set 5;

h.p.l.c. conditions, 2' x 1/8" Corasil x 1000pft, 400psig,
methylene chloride

used to determine ϕ_{Dis} and $\phi_{\text{Dis}}^{\text{Max}}$ are presented in Tables 26 and 27.

5. DiBzPt

The Stern-Volmer data for this diketone are presented in Table 28. The observed $k_q\tau$ value is $45.1 \pm 1.4 \text{ M}^{-1} \text{ sec}^{-1}$. The effects of various concentrations of dioxane and pyridine on ϕ_{II} are presented in Tables 29 and 30. $\phi_{\text{II}}^{\text{Max}}$ was observed to be 0.55 ± 0.03 , and the average ϕ_{II} observed for all experiments was 0.37 ± 0.03 .

6. DipEtBt

The Stern-Volmer data for this diketone are presented in Table 31. The observed $k_q\tau$ value is $371 \pm 10 \text{ M}^{-1} \text{ sec}^{-1}$. The effects of various concentrations of dioxane on ϕ_{II} are presented in Table 32. $\phi_{\text{II}}^{\text{Max}}$ was observed to be 0.28 ± 0.01 and the average ϕ_{II} observed in the Stern-Volmer and $\phi_{\text{II}}^{\text{Max}}$ experiments was 0.27 ± 0.03 . The data used to determine ϕ_{isc} are shown in Table 33. The data used to determine ϕ_{Dis} are shown in Table 34.

7. 1Bz4pEtBzBt

The Stern-Volmer data for this diketone are presented in Table 35. The observed $k_q\tau$ values for acetophenone and 1-phenylbut-3-en-1-one are $149 \pm 5 \text{ M}^{-1} \text{ sec}^{-1}$ and $165 \pm 2 \text{ M}^{-1} \text{ sec}^{-1}$. The effects of various concentrations of dioxane and pyridine on the ϕ_{Ac} and ϕ_{pEtAc} are reported in Tables 36 and 37. $\phi_{\text{Ac}}^{\text{Max}}$ and $\phi_{\text{pEtAc}}^{\text{Max}}$ were observed to be 0.36 ± 0.03 and 0.11 ± 0.01 . The average ϕ_{Ac} and ϕ_{pEtAc} observed in the Stern-Volmer and ϕ^{Max} experiments were

Table 27: $\phi_{\text{Dis}}^{\text{Max}}$ for DiBzBt

[diketone]	0.0100 M
[tetradecane]	0.00128 M
[diethylphthalate]	0.103 M
avg. ratio, diketone/phthalate unirradiated	0.841
irradiated	0.655
% conv of ketone	22.1
area Ac/area C ₁₄	0.790
% conv to Ac	20.2
% conv ketone/% conv Ac	1.09
4.5 M Dioxane in benzene solvent; 313nm; 30.0°;	
g.c.condition set 5; h.p.l.c. conditions, 2' x 1/8"	
Porasil 1000pft, 50% stroke, 40:60 hexane/methylene chloride	

Table 28: Stern-Volmer Data for DiBzPt

Run 1

$\phi_{II}=0.367$, $k_q\tau=46.5M^{-1}sec^{-1}$, Lamp intensity=0.000719E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	$2.06 \pm .07^a$		7.29
0.467	1.72	1.20	6.09
0.933	1.53	1.35	4.78
1.87	1.17	1.76	4.14
2.80	0.872	2.37	3.09
3.73	0.742	2.78	2.63
4.67	0.659	3.13	2.33
VP Actinometer (average from three tubes)			
0.0	$1.37 \pm .09$		4.85

[diketone]=0.0103M(0.0706%T), [VP]=0.0125M(0.250%T),

$[C_{14}]=1.77 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6.

Run 2

$\phi_{II}=0.379$, $k_q\tau=43.7M^{-1}sec^{-1}$, Lamp intensity=0.000981E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	$1.62 \pm .05^a$		10.30
0.524	1.26	1.29	8.01
0.105	1.08	1.50	6.87
0.210	0.892	1.82	5.67
0.315	0.691	2.35	4.39
0.419	0.549	2.96	3.49
0.524	0.500	3.24	3.18
VP Actinometer (average from three tubes)			
0.0	$0.910 \pm .01$		5.79

[diketone]=0.0100M(0.0762%T), [VP]=0.00963M(0.344%T),

$[C_{14}]=3.18 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6.

a. average from three tubes

Table 29: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for DiBzPt

Run 1

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{II}
0.0	1.33 ± 0.07^a	6.04	0.374
1.00	1.70	7.72	0.478
2.00	1.74	7.90	0.489
3.00	1.88	8.54	0.528
4.00	1.95	8.85	0.548
5.00	2.09	9.49	0.587
6.00	2.04	9.26	0.573
VP Actinometer (average from three tubes)			
0.0	1.00 ± 0.07	4.54	

[diketone] = 0.0101M(0.0743%T), [VP] = 0.0182M(0.133%T),

$[C_{14}] = 2.27 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6, lamp intensity = 0.00116 E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{II}
0.0	1.11 ± 0.04^a	5.82	0.372
1.00	1.26	6.60	0.423
2.00	1.45	7.60	0.486
3.00	1.53	8.02	0.513
4.00	1.43	7.49	0.480
5.00	1.51	7.91	0.506
6.00	1.51	7.91	0.506
VP Actinometer (average from three tubes)			
0.0	0.63 ± 0.06	3.30	

[diketone] = 0.0100M(0.0762%T), [VP] = 0.00951M(0.348%T),

$[C_{14}] = 2.62 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6, lamp intensity = 0.00125E/hr

a. average from three tubes

Table 30: Effects of Varying Concentrations of Pyridine
on ϕ_{II} for DiBzPt

Run 1

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{II}
0.0	$0.401 \pm .004^a$	4.03	0.399
0.0255	0.447	4.49	0.445
0.0511	0.464	4.66	0.461
0.0766	0.491	4.93	0.488
0.102	0.481	4.83	0.478
0.128	0.520	5.22	0.517
0.153	0.560	5.62	0.557
VP Actinometer (average from three tubes)			
0.0	$0.295 \pm .01$	2.96	

[diketone]=0.0101M(0.0743%T), [VP]=0.0213M(0.0943%T),

$[C_{14}] = 5.02 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6.

Run 2

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{II}
0.0	$0.338 \pm .03$	3.95	0.334
0.253	0.421	4.93	0.416
0.507	0.544	6.36	0.538
0.760	0.527	6.17	0.521
1.27	0.527	6.17	0.521
VP Actinometer (average from three tubes)			
0.0	$0.306 \pm .04$	3.58	

[diketone]=0.00990M(0.0782%T), [VP]=0.0239M(0.0707%T),

$[C_{14}] = 5.85 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,

g.c. condition set 6, lamp intensity=0.000642E/hr

a. average from three tubes

Table 31: Stern-Volmer Data for DipEtBzBt

Run 1

$\phi_{II}=0.253$, $k_q\tau=364\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity=0.00935E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	ϕ°/ϕ	$[\text{pEtAc}]$ $\times 10^4 \text{M}$
0.0	1.89 ± 0.02^a		17.30
0.469	0.679	2.79	6.21
0.938	0.432	4.38	3.95
1.88	0.246	7.71	2.25
2.81	0.171	11.1	1.56
3.75	0.127	14.9	1.16
4.69	0.105	18.0	0.961

VP Actinometer (average of three tubes)

0.0 1.23 ± 0.09 (area Ac/area C_{14}) 14.1 [Ac]

[diketone]=0.0101M(0.0243%T), [VP]=0.0100M(0.330%T),

$[C_{18}]=5.72 \times 10^{-4} \text{M}$, $[C_{14}]=5.72 \times 10^{-4} \text{M}$, benzene solvent,

313nm, 30.0°, g.c. condition set 4, actinometer g.c.

condition set 5.

Run 2

$\phi_{II}=0.258$, $k_q\tau=383\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity=0.00928E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	ϕ°/ϕ	$[\text{pEtAc}]$ $\times 10^4 \text{M}$
0.0	3.82 ± 0.04^a		17.5
0.181	2.34	1.64	10.7
0.363	1.79	2.14	8.22
0.725	0.979	3.90	4.50
1.09	0.749	5.10	3.44
1.45	0.581	6.58	2.67
1.81	0.482	7.93	2.21

VP Actinometer (average of two tubes)

0.0 1.79 ± 0.03 (area Ac/area C_{14}) 19.2 [Ac]

[diketone]=0.0106M(0.0202%T), [VP]=0.0227M(0.0807%T),

$[C_{18}]=2.87 \times 10^{-4} \text{M}$, $[C_{14}]=5.35 \times 10^{-4} \text{M}$, benzene solvent,

313nm, 30.0°, g.c. condition set 4, actinometer g.c.

condition set 5.

Table 31: (cont'd.)

Run 3

 $\phi_{II}=0.313$, $k_q\tau=365M^{-1}sec^{-1}$, Lamp intensity=0.00732E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	ϕ°/ϕ	$[pEtAc]$ $\times 10^4 M$
0.0	1.46 ± 0.03^a		17.21
0.231	0.829	1.75	9.78
0.462	0.513	2.84	6.05
0.924	0.338	4.31	3.99
1.39	0.242	6.02	2.85
1.85	0.184	7.92	2.17
2.31	0.156	9.35	1.84

VP Actinometer (average of three tubes)

0.0 0.864 ± 0.025 (area Ac/area C_{14}) 14.8 [Ac]

[diketone]=0.0200M(0.000636%T), [VP]=0.0206M(0.102%T),

[C_{18}]= $7.37 \times 10^{-4} M$, [C_{14}]= $8.59 \times 10^{-4} M$, benzene solvent,

313nm, 30.0°, g.c. condition set 4, actinometer g.c.

condition set 5

a. average from three tubes

Table 32: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for DipEtBzBt

Run 1

[Dioxane] M	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	$\frac{[\text{pEtAc}]}{10^4 \text{ M}}$	ϕ_{II}
0.0	$1.33 \pm .09^a$	10.6	0.277
1.00	1.34	10.7	0.279
2.00	1.20	9.58	0.250
3.00	1.25	9.98	0.260
4.00	1.36	10.86	0.283
5.00	1.18	9.42	0.246
6.00	1.15	9.18	0.240
VP Actinometer (average from three tubes)			
0.0	$1.22 \pm .04$ (area Ac/area C_{14})	[Ac]=0.00102M	

[diketone]=0.0103M(0.0226%T), [VP]=0.0185M(0.129%T),
[C_{18}]= 4.99×10^{-4} M, [C_{14}]= 4.20×10^{-4} M, benzene solvent,
313nm, 30.0°, g.c. condition set 4, actinometer g.c.
condition set 5, lamp intensity = 0.00196E/hr

Run 2

[Dioxane] M	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	$\frac{[\text{pEtAc}]}{10^4 \text{ M}}$	ϕ_{II}
0.00	0.705 ± 0.006^a	6.20	0.245
1.00	0.726	6.39	0.253
2.00	0.605	5.32	0.210
4.00	0.709	6.24	0.247
5.00	0.769	6.77	0.277
6.01	0.764	6.72	0.266
VP Actinometer (average from three tubes)			
0.0	$0.524 \pm .04$ (area Ac/area C_{14})	[Ac]=0.000665M	

[diketone]=0.00998M(0.0254%T), [VP]=0.0174M(0.145%T),
[C_{18}]= 5.50×10^{-4} M, [C_{14}]= 6.35×10^{-4} M, benzene solvent,
313nm, 30.0°, g.c. condition set 4, actinometer g.c.
condition set 5, lamp intensity = 0.00117E/hr

a. average from three tubes

Table 33: Intersystem Crossing Yield for DipEtBzBt

Ketone	[1,3-pentadiene] M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.0551 M DipEtBzBt	0.526	.0332	1.06
0.0583 M Ac	0.526	.0313	1.00

cis/(cis+trans) unirradiated diene = 0.00200, benzene solvent, 313nm, 30.0°, g.c. condition set 8.

Table 34: ϕ_{Dis} for DipEtBzBt

	Run 1	Run 2
[diketone]	0.0103M	0.00998M
[octadecane]	0.000499M	0.000550M
[diethylphthalate]	0.188M	0.188M
avg. ratio, diketone/phthalate		
unirradiated	1.24	1.11
irradiated	1.10	1.03
% conv of ketone	11.7	6.85
area pEtAc/area C ₁₈	1.33	.705
% conv to pEtAc	10.3	6.22
% conv ketone/% conv pEtAc	1.14	1.10

Benzene solvent; 313nm; 30.0°; g.c. condition set 4;
h.p.l.c. conditions, 2' x 1/8" Corasil 1000pft,
400psig, methylene chloride

Table 35: Stern-Volmer Data for 1Bz4pEtBzBt

Run 1

$$\phi_{Ac}=0.241, \phi_{pEtAc}=0.0661, k_q\tau_{Ac}=153M^{-1}sec^{-1}, k_q\tau_{PhBten}=166M^{-1}sec^{-1}$$

$[Q]$ $\times 10^2 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\left(\frac{\phi^0}{\phi}\right)_{Ac}$	$\frac{\text{area PhBten}}{\text{area } C_{14}}$	$\left(\frac{\phi^0}{\phi}\right)_{PhBten}$	$[Ac]$ $\times 10^4 M$
0.0	4.95 ± 0.2^a		2.63 ± 0.1^a		19.1
0.540	2.95	1.68	1.61	1.63	11.4
1.08	1.97	2.51	0.928	2.83	7.60
2.16	1.14	4.34	0.600	4.38	4.40
3.24	0.825	6.00	0.401	6.56	3.18
4.32	0.579	8.54			2.23
5.40	0.462	10.7			1.78

VP Actinometer (area Ac/area C_{14} = 4.36 ± 0.08^a , $[Ac]$ = 0.00168M),
 PetAc (area PetAc/area C_{18} = 2.19 ± 0.1^a , $[pEtAc]$ = 0.000466M),
 $[diketone]$ = 0.0102 (0.0315%T), $[VP]$ = 0.0104 (0.316%T), $[C_{14}]$ =
 $1.93 \times 10^{-4} M$, $[C_{18}]$ = $1.33 \times 10^{-4} M$, benzene solvent, 313nm, ambient
 temperature, g.c. condition set 5, lamp intensity = 0.0108E/hr

Run 2

$$\phi_{Ac}=0.263, \phi_{pEtAc}=0.0718, k_q\tau_{Ac}=144M^{-1}sec^{-1}, k_q\tau_{PhBten}=163M^{-1}sec^{-1}$$

$[Q]$ $\times 10^2 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	$\left(\frac{\phi^0}{\phi}\right)_{Ac}$	$\frac{\text{area PhBten}}{\text{area } C_{14}}$	$\left(\frac{\phi^0}{\phi}\right)_{PhBten}$	$[Ac]$ $\times 10^3 M$
0.0	3.92 ± 0.09^a		2.25 ± 0.01^a		3.25
0.375	2.48	1.58	1.70	1.32	2.06
0.750	1.97	1.99	1.10	2.03	1.64
1.50	1.25	3.13	0.708	3.17	1.04
2.25	0.922	4.26	0.452	4.97	0.765
3.75	0.615	6.38			0.510

VP Actinometer (area Ac/area C_{14} = 4.14 ± 0.09^a , $[Ac]$ = 0.00344M),
 PEtAc (area PEtAc/area C_{18} = 1.73 ± 0.03^a , $[pEtAc]$ = 0.000972M),
 $[diketone]$ = 0.0207M (0.000897%T), $[VP]$ = 0.0232M (0.0764%T),
 $[C_{14}]$ = $4.15 \times 10^{-4} M$, $[C_{18}]$ = $3.51 \times 10^{-4} M$, benzene solvent, 313nm,
 ambinet temperature, g.c. condition set 5, lamp intensity =
 0.00993E/hr

a. average from three tubes

Table 36: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for 1Bz4pEtBzBt

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{Ac}	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	[pEtAc] $\times 10^4 M$	ϕ_{pEtAc}
0.0	$1.39 \pm .08^a$	6.06	0.289	$0.404 \pm .04^a$	1.76	0.0843
1.0	1.47	6.41	0.306	0.390	1.70	0.0814
2.0	1.37	5.97	0.285	0.384	1.68	0.0801
3.0	1.47	6.41	0.306	0.422	1.84	0.0880
4.0	1.51	6.58	0.314	0.482	2.11	0.101
5.0	1.48	6.45	0.308	0.450	1.97	0.0939
6.0	1.58	6.89	0.329	0.473	2.07	0.0987
VP Actinometer (average from three tubes)						
0.0	$1.01 \pm .02$	4.40				

[diketone]=0.0100M(0.0337%T), [VP]=0.0102M(0.323%T), $[C_{18}] = 2.73 \times 10^{-4} M$, $[C_{14}] = 2.18 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°, g.c. condition set 5, Lamp intensity=0.000496E/hr

a. average from three tubes

Table 37: Effects of Varying Concentrations of Pyridine
on ϕ_{II} for 1Bz4pEtBzBt

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 M$	ϕ_{Ac}	$\frac{\text{area pEtAc}}{\text{area } C_{18}}$	[pEtAc] $\times 10^4 M$	ϕ_{pEtAc}
0.0	$.654 \pm .01^a$	7.64	0.230	$0.261 \pm .03$	2.19	0.0659
0.249	0.923	10.78	0.323	0.413	3.46	0.104
0.499	1.07	12.50	0.376	0.418	3.50	0.106
0.748	1.01	11.80	0.355	0.409	3.43	0.103
0.998	1.04	12.15	0.366	0.429	3.60	0.108
1.25	0.996	11.63	0.350	0.403	3.38	0.101
1.50	1.08	12.61	0.380	0.422	3.54	0.106
VP Actinometer (average from three tubes)						
0.0	$0.625 \pm .01$	7.30				

[diketone]=0.00999M(0.0315%T), [VP]=0.0111M(0.292%T), $[C_{18}] = 5.24 \times 10^{-4} M$, $[C_{14}] = 5.84 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°, g.c. condition set 5, Lamp intensity=0.000610E/hr

a. average from three tubes

0.26±0.03 and 0.072±0.01. The data used to determine ϕ_{Dis} are shown in Table 38.

8. δPhVP

The Stern-Volmer data for this ketone are presented in Table 39. The observed $k_q\tau$ value is 42.3±2.5 M⁻¹sec⁻¹. The effects of various concentrations of dioxane on ϕ_{II} are presented in Table 40. $\phi_{\text{II}}^{\text{Max}}$ was observed to be 0.64±0.02 and the average ϕ_{II} observed in the Stern-Volmer and $\phi_{\text{II}}^{\text{Max}}$ experiments was 0.32±0.02.

9. pEtVP

The Stern-Volmer data for this ketone are presented in Table 41. The observed $k_q\tau$ value is 253±22 M⁻¹sec⁻¹. The data used to determine ϕ_{isc} are presented in Table 42. The effects of various concentrations of dioxane on ϕ_{II} and ϕ_{cy} are presented in Table 43. $\phi_{\text{II}}^{\text{Max}}$ and $\phi_{\text{cy}}^{\text{Max}}$ were observed to be 0.54±0.01 and 0.085±0.003. The average ϕ_{II} and ϕ_{cy} observed were 0.29±0.03 and 0.058±0.001.

10. δAcPhVP

The Stern-Volmer data for this ketone are presented in Table 44. The observed $k_q\tau$ value is 174±3 M⁻¹sec⁻¹. The effects of various concentrations of dioxane and pyridine on ϕ_{II} are presented in Tables 45 and 46. $\phi_{\text{II}}^{\text{Max}}$ was observed to be 0.51±0.03. The average ϕ_{II} observed was 0.30±0.01. The data used to determine ϕ_{isc} , ϕ_{Dis} , and $\phi_{\text{Dis}}^{\text{Max}}$ are presented in Tables 47, 48, and 49.

Table 38: ϕ_{Dis} for 1Bz4pEtBzBt

[diketone]	0.0109M
[tetradecane]	0.00154M
[diethylphthalate]	0.0934
avg. ratio, diketone/phthalate	
unirradiated	2.20
irradiated	1.81
% conv of ketone	17.7
area Ac/area C ₁₄	0.360
% conv to Ac	10.7
% conv ketone/% conv Ac	1.65
Benzene solvent; 313nm; 30.0°; g.c. condition set 5;	
h.p.l.c. conditions, 2' x 1/8" Corasil 1000pft, 1000psig,	
50:50 hexane /methylene chloride.	

Table 39: Stern-Volmer Data for δ PhVP

Run 1

$\phi_{II}=0.338$, $k_q\tau=39.8M^{-1}sec^{-1}$, Lamp intensity=0.00780E/hr

[Q] $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	ϕ°/ϕ	[Ac] $\times 10^3 M$
0.0	0.782 ± 0.05^a		7.78
0.430	0.761	1.03	7.57
0.859	0.662	1.18	6.58
1.72	0.451	1.73	4.49
2.58	0.358	2.18	3.56
3.44	0.319	2.45	3.17
4.30	0.305	2.56	3.03

VP Actinometer (average from two tubes)

0.0	0.764 ± 0.07	7.60
-----	------------------	------

[ketone]=0.0818M($8.31 \times 10^{-5}\%$ T), [VP]=0.0750M($2.4 \times 10^{-4}\%$ T),
 $[C_{16}]=0.00428M$, benzene solvent, 313nm, ambient
 temperature, g.c. condition set 1.

Run 2

$\phi_{II}=0.331$, $k_q\tau=44.8M^{-1}sec^{-1}$, Lamp intensity=0.00776E/hr

[Q] $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	ϕ°/ϕ	[Ac] $\times 10^3 M$
0.0	0.950 ± 0.02^a		4.72
0.509	0.793	1.20	3.94
1.02	0.662	1.44	3.29
2.04	0.508	1.87	2.53
3.06	0.434	2.19	2.16
5.09	0.280	3.40	1.39

VP Actinometer (average from two tubes)

0.0	0.905 ± 0.01	4.50
-----	------------------	------

[ketone]=0.0501M(0.00317% T), [VP]=0.0515M(0.00331% T),
 $[C_{16}]=0.00214M$, benzene solvent, 313nm, ambient
 temperature, g.c. condition set 1.

a. average from three tubes

Table 40: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for δPhVP

Run 1

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{II}
0.0	0.188 ± 0.012^a	4.51	0.292
1.00	0.317	7.61	0.492
2.00	0.367	8.81	0.570
3.00	0.392	9.41	0.608
4.00	0.367	8.81	0.570
5.00	0.419	10.1	0.650
6.00	0.415	9.96	0.644
VP Actinometer (average from three tubes)			
0.0	0.172 ± 0.013	4.13	

[ketone]=0.0108M(0.289%T), [VP]=0.00907M(0.366%T),
 $[C_{14}] = 0.00120\text{M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00109E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{II}
0.0	0.392 ± 0.03^a	4.89	0.304
1.00	0.623	7.78	0.485
2.00	0.687	8.57	0.535
3.00	0.759	9.47	0.591
4.00	0.754	9.41	0.587
5.00	0.796	9.93	0.620
6.00	0.797	9.95	0.620
VP Actinometer (average from three tubes)			
0.0	0.439 ± 0.004	5.48	

[ketone]=0.0103M(0.306%T), [VP]=0.0140M(0.212%T),
 $[C_{14}] = 6.24 \times 10^{-4} \text{M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00116E/hr

a. average from three tubes

Table 41: Stern-Volmer Data for pEtVP

Run 1

$\phi_{II}=0.275$, $k_q\tau=231\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity=0.00662E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area pEtAc}}{\text{area C}_{16}}$	ϕ°/ϕ	$[\text{pEtAc}]$ $\times 10^3 \text{M}$
0.0	1.14 ± 0.01^a		5.47
0.533	0.548	2.07	2.63
1.07	0.369	3.08	1.77
2.13	0.214	5.31	1.03
3.20	0.139	8.18	0.667
4.26	0.105	10.8	0.503
5.33	0.0828	13.7	0.397
VP Actinometer (average of three tubes)			
0.0	1.04 ± 0.07		6.26

$[\text{ketone}]=0.0502\text{M}(0.000135\%T)$, $[\text{VP}]=0.0581\text{M}(0.00159\%T)$,
 $[\text{C}_{16}]=0.00259\text{M}$, benzene solvent, 313nm, ambient temperature,
 g.c. condition set 4, actinometer g.c. condition set 5.

Run 2

$\phi_{II}=0.344$, $k_q\tau=318\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity=0.00596E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area pEtAc}}{\text{area C}_{16}}$	ϕ°/ϕ	$[\text{pEtAc}]$ $\times 10^3 \text{M}$
0.0	2.57 ± 0.2^a		5.90
0.299	1.54	1.67	3.54
0.598	1.02	2.51	2.34
1.20	0.652	3.94	1.50
1.79	0.345	7.44	0.792
VP Actinometer (average of three tubes)			
0.0	1.87 ± 0.02		5.39

$[\text{ketone}]=0.0512\text{M}(0.000113\%T)$, $[\text{VP}]=0.0516\text{M}(0.00328\%T)$,
 $[\text{C}_{16}]=0.00124\text{M}$, benzene solvent, 313nm, ambient temperature,
 g.c. condition set 4, actinometer g.c. condition set 5.

Table 41: (cont'd.)

Run 3

$\phi_{II}=0.318$, $\phi_{CB}=0.0589$, $k_q\tau=275M^{-1}sec^{-1}$, Lamp intensity=0.00705E/hr

$[Q]$ $\times 10^3 M$	$\frac{\text{area pEtAc}}{\text{area } C_{16}}$	ϕ°/ϕ	$[pEtAc]$ $\times 10^3 M$
0.0	2.47 ± 0.02^a		5.62
1.49	1.84	1.34	4.19
2.99	1.39	1.77	3.17
5.97	1.04	2.37	2.37
8.96	0.710	3.48	1.62
11.9	0.620	3.98	1.41
14.9	0.455	5.43	1.04
VP Actinometer (average of three tubes)			
0.0	1.94 ± 0.03		5.55

$\text{area CB}/\text{area } C_{16}=0.592 \pm 0.04^a$, $[\text{ketone}]=0.0522M(9.49 \times 10^{-5}\%T)$,
 $[VP]=0.0479M(0.00494\%T)$, $[C_{16}]=0.00123M$, Benzene solvent,
 313nm, ambient temperature, g.c. condition set 4,
 actinometer g.c. condition set 5.

a. average from three tubes

Table 42: Intersystem Crossing Yield for pEtVP

Ketone	$[1,3\text{-pentadiene}]$ M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.0558 M pEtVP	0.526	0.0319	1.02
0.0583 M Ac	0.526	0.0312	1.00

cis/(cis+trans) unirradiated diene = 0.00200, benzene
 solvent, 313nm, 30.0°, g.c. condition set 8

Table 43: Effects of Varying Concentrations of Dioxane on ϕ_{II} and ϕ_{CB} for pEtVP

Run 1

[Dioxane] M	$\frac{\text{area pEtAc}}{\text{area } C_{16}}$	[Ac] $\times 10^3 M$	ϕ_{II}	$\frac{\text{area CB}}{\text{area } C_{16}}$	[CB] $\times 10^4 M$	ϕ_{CB}
0.0	$0.637 \pm .01^a$	0.659	0.256	$0.212 \pm .01^a$	1.45	0.0566
0.999	1.07	1.11	0.430	0.278	1.91	0.0742
2.00	1.27	1.31	0.510	0.306	2.11	0.0817
3.00	1.20	1.24	0.482	0.292	2.01	0.0779
4.00	1.32	1.37	0.530	0.298	2.05	0.0795
5.00	1.33	1.38	0.534	0.305	2.10	0.0814
6.00	1.28	1.32	0.514	0.277	1.91	0.0739

VP Actinometer($\text{area Ac}/\text{area } C_{16}$)= $0.295 \pm .01^a$, [Ac]= $7.97 \times 10^{-4} M$,
[ketone]= $0.00996 M$ (0.171%T), [VP]= $0.0176 M$ (0.142%T), [C_{16}]=
 $5.59 \times 10^{-4} M$, [C_{14}]= $0.00135 M$, benzene solvent, 313nm, 30.0°,
g.c. condition set 5, actinometer g.c. condition set 5,
lamp intensity = 0.00155E/hr

Run 2

[Dioxane] M	$\frac{\text{area pEtAc}}{\text{area } C_{16}}$	[Ac] $\times 10^3 M$	ϕ_{II}	$\frac{\text{area CB}}{\text{area } C_{16}}$	[CB] $\times 10^4 M$	ϕ_{CB}
0.0	$0.660 \pm .02^a$	0.720	0.271	$0.214 \pm .001^a$	1.55	0.0584
1.00	1.07	1.17	0.440	0.249	1.81	0.0679
2.00	1.20	1.31	0.493	0.296	2.15	0.0808
3.00	1.32	1.44	0.542	0.320	2.32	0.0873
5.00	1.34	1.46	0.550	0.323	2.35	0.0881
6.00	1.38	1.51	0.567	0.340	2.47	0.0928

VP Actinometer($\text{area AC}/\text{area } C_{16}$)= $0.288 \pm .02^a$, [Ac]= $8.06 \times 10^{-4} M$,
[ketone]= $0.0107 M$ (0.150%T), [VP]= $0.0177 M$ (0.141%T), [C_{16}]=
 $5.90 \times 10^{-4} M$, [C_{14}]= $0.00140 M$, benzene solvent, 313nm, 30.0°,
g.c. condition set 4, actinometer g.c. condition set 5,
lamp intensity = 0.00141E/hr

a. average from three tubes

Table 44: Stern-Volmer Data for δ AcPhVP

Run 1

$\phi_{II}=0.331, k_q\tau=171\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity=0.00917E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area Ac}}{\text{area } C_{16}}$	ϕ°/ϕ	$[Ac]$ $\times 10^3 \text{M}$
0.0	0.876 ± 0.004^a		4.23
0.503	0.483	1.81	2.33
1.01	0.325	2.70	1.57
2.01	0.205	4.27	0.991
3.02	0.143	6.14	0.691
4.02	0.106	8.23	0.512
5.03	0.0932	9.40	0.451

VP Actinometer (average from two tubes)

0.0	0.831 ± 0.04	4.02
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$[\text{diketone}] = 0.0501\text{M}(2.83 \times 10^{-7}\%T)$, $[\text{VP}] = 0.0518\text{M}(0.00320\%T)$,
 $[C_{16}] = 0.00208\text{M}$, benzene solvent, 313nm, ambient
 temperature, g.c. condition set 1.

Run 2

$\phi_{II}=0.295, k_q\tau=177\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity = 0.00844E/hr

$[Q]$ $\times 10^2 \text{M}$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 \text{M}$
0.0	2.01 ± 0.03^a		17.7
0.510	1.06	1.89	9.35
1.02	0.729	2.76	6.43
2.04	0.430	4.68	3.79
3.06	0.316	6.36	2.79
4.08	0.221	9.11	1.95
5.10	0.176	11.4	1.55

VP Actinometer (average from two tubes)

0.0	1.45 ± 0.02	12.8
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$[\text{diketone}] = 0.0100\text{M}(0.0493\%T)$, $[\text{VP}] = 0.0101\text{M}(0.326\%T)$,
 $[C_{14}] = 4.41 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5

a. average from three tubes

Table 45: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for δ AcPhVP

Run 1

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	0.769 ± 0.02^a	0.872	0.312
0.499	0.923	1.05	0.374
0.999	1.01	1.15	0.409
2.00	1.04	1.18	0.421
3.00	1.12	1.27	0.454
4.00	1.19	1.35	0.482
5.00	1.19	1.35	0.482
VP Actinometer (average from two tubes)			
0.0	0.565 ± 0.02	0.641	

[diketone]=0.0104M(0.0437%T), [VP]=0.0118M(0.270%T),
 $[C_{14}] = 5.67 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00146E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	0.886 ± 0.08^a	0.886	0.301
1.50	1.23	1.23	0.418
2.50	1.36	1.36	0.463
3.50	1.41	1.41	0.480
4.51	1.53	1.53	0.520
6.01	1.36	1.36	0.463
7.01	1.31	1.31	0.446
VP Actinometer (average from three tubes)			
0.0	0.618 ± 0.06	0.618	

[diketone]=0.00996M(0.0499%T), [VP]=0.00988M(0.334%T),
 $[C_{14}] = 5.00 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00155E/hr

a. average from three tubes

Table 46: Effects of Varying Concentrations of Pyridine
on ϕ_{II} for δ AcPhVP

Run 1

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	1.28 ± 0.01^a	1.21	0.288
0.0635	1.69	1.60	0.380
0.127	1.82	1.73	0.409
0.254	1.93	1.83	0.434
0.508	1.98	1.88	0.445
1.02	2.06	1.95	0.463
1.52	2.19	2.08	0.492
VP Actinometer (average from three tubes)			
0.0	0.931 ± 0.04	0.883	

[diketone]=0.00999M(0.0495%T), [VP]=0.00982M(0.337%T),
 $[C_{14}]=4.74 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity = 0.00888E/hr

Run 2

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{II}
0.0	1.15 ± 0.02	1.23	0.297
0.0315	1.35	1.44	0.349
0.0630	1.54	1.65	0.398
0.126	1.95	2.09	0.504
0.252	1.96	2.10	0.506
0.504	1.93	2.07	0.499
1.01	2.04	2.18	0.527
2.02	2.03	2.17	0.524
VP Actinometer (average from three tubes)			
0.0	0.805 ± 0.03	0.861	

[diketone]=0.00995M(0.0501%T), [VP]=0.00969M(0.342%T),
 $[C_{14}]=5.35 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00872E/hr

a. average from three tubes

Table 47: Intersystem Crossing Yield for δ AcPhVP

Ketone	[1,3-pentadiene] M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.0495 M δ AcPhVP	0.526	0.0312	1.03
0.0583 M Ac	0.526	0.0321	1.00

cis/(cis+trans) unirradiated diene=0.00200, benzene solvent,
313nm, 30.0°, g.c. condition set 8.

Table 48: ϕ_{Dis} for δ AcPhVP

[diketone]	0.00996M
[tetradecane]	0.000500M
[diethylphthalate]	0.0990M
avg. ratio, diketone/phthalate	
unirradiated	1.82
irradiated	1.61
% conv. of ketone	11.5
area Ac/area C ₁₄	0.886
% conv to Ac	8.90
% conv ketone/% conv Ac	1.29

Benzene solvent; 313nm; 30.0°; g.c. condition set 5;
h.p.l.c. conditions, 2' x 1/8" Corasil 1000pft, 400psig,
methylene chloride.

Table 49: ϕ_{Dis} for δ AcPhVP in 4.5 M Dioxane

[diketone]	0.0100M
[tetradecane]	0.00128M
[diethylphthalate]	0.103M
avg. ratio, diketone/phthalate	
unirradiated	1.73
irradiated	1.42
% conv of ketone	18.2
area Ac/area C ₁₄	0.742
% conv to Ac	18.9
% conv ketone/% conv Ac	0.963

4.5M dioxane in benzene; 313nm; 30.0°; g.c. condition set 5;
h.p.l.c. conditions, 2' x 1/8" Porasil 1000pft, 800psig,
1:4 hexane/methylene chloride

11. δ ValPhVP

The Stern-Volmer data for this ketone are presented in Table 50. The observed $k_q \tau$ values for acetophenone and propene are $103 \pm 4 \text{ M}^{-1} \text{sec}^{-1}$ and $96 \pm 3 \text{ M}^{-1} \text{sec}^{-1}$. The effects of various concentrations of dioxane on ϕ_{II} from the two chromophores are reported in Table 51. The ϕ^{Max} for acetophenone formation was observed to be 0.34 ± 0.01 and the ϕ^{Max} for propene formation was observed to be 0.23 ± 0.03 . The average ϕ for acetophenone formation was observed to be 0.21 ± 0.01 and 0.13 ± 0.01 for propene formation. The data used to determine ϕ_{isc} and ϕ_{Dis}^{Max} for this ketone are presented in Tables 52 and 53.

12. γ PhOBP

The effects of various concentrations of pyridine on the ϕ_{II} of this ketone are reported in Table 54. ϕ_{II}^{Max} was observed to be 0.66.

13. γ CNPhOBP

The Stern-Volmer data for this ketone are presented in Table 55. The $k_q \tau$ value is $80.9 \pm 1.6 \text{ M}^{-1} \text{sec}^{-1}$. The effects of various concentrations of pyridine on ϕ_{II} are reported in Table 56. The ϕ_{II}^{Max} was observed to be 0.56 ± 0.06 and the average ϕ_{II} was observed to be 0.40 ± 0.05 .

14. γ AcPhOBP

The Stern-Volmer data for this ketone are presented in Table 57. The observed $k_q \tau$ value is $552 \pm 16 \text{ M}^{-1} \text{sec}^{-1}$.

Table 50: Stern-Volmer Data for δ ValPhVP

Run 1

$$\phi_{Ac}=0.217, \phi_{Pr}=0.143, k_q \tau_{Ac}=107M^{-1}sec^{-1}, k_q \tau_{Pr}=99.0M^{-1}sec^{-1}$$

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	$\left(\frac{\phi^\circ}{\phi}\right)_{Ac}$	$[Ac]$ $\times 10^3 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	$\left(\frac{\phi^\circ}{\phi}\right)_{Pr}$	$[Pr]$ $\times 10^4 M$
0.0	$0.480 \pm .03^a$		2.87	$0.412 \pm .03^a$		18.9
0.484	0.324	1.48	1.94	0.230	1.79	10.6
0.967	0.248	1.93	1.48	0.213	1.93	9.78
1.93	0.162	2.97	0.968	0.134	3.08	6.15
2.90	0.123	3.90	0.735	0.101	4.09	4.64
3.87	0.0940	5.11	0.561	0.0859	4.80	3.94
4.84	0.0751	6.39	0.449	0.0734	5.62	3.37

VP Actinometer (average from three tubes)

0.0	0.694 ± 0.02	4.15	0.903 ± 0.04	41.5
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$$[\text{diketone}] = 0.0501M(3.07 \times 10^{-7} \%T), [VP] = 0.0523M(0.00303 \%T),$$

 $[C_{16}] = 0.00257M$, benzene solvent, 313nm, ambient temperature,

g.c. condition set 1, lamp intensity=0.00663E/hr

Run 2

$$\phi_{Ac}=0.212, \phi_{Pr}=0.116, k_q \tau_{Ac}=99.5M^{-1}sec^{-1}, k_q \tau_{Pr}=92.1M^{-1}sec^{-1}$$

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	$\left(\frac{\phi^\circ}{\phi}\right)_{Ac}$	$[Ac]$ $\times 10^4 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	$\left(\frac{\phi^\circ}{\phi}\right)_{Pr}$	$[Pr]$ $\times 10^4 M$
0.0	$1.14 \pm .03^a$		11.2	$1.16 \pm .04^a$		6.14
0.537	0.748	1.53	7.35	0.776	1.50	4.11
1.07	0.531	2.15	5.22	0.587	1.97	3.11
2.15	0.378	3.02	3.72	0.424	2.71	2.24
3.22	0.254	4.49	2.50	0.286	4.04	1.51
5.37	0.184	6.21	1.81	0.193	6.00	1.02

VP Actinometer (average from three tubes)

0.0	1.12 ± 0.01	11.0	2.08 ± 0.10	11.0
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$$[\text{diketone}] = 0.00993M(0.0512 \%T), [VP] = 0.00969M(0.342 \%T),$$

 $[C_{16}] = 4.23 \times 10^{-4}M$, benzene solvent, 313nm, ambient temperature,

g.c. condition set 5, lamp intensity=0.0112E/hr

a. average from three tubes

Table 51: Effects of Varying Concentrations of Dioxane
on ϕ_{II} for $\delta\text{ValPhVP}$

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^3 \text{ M}$	ϕ_{Ac}	$\frac{\text{area Pr}}{\text{area } cC_6}$	[Pr] $\times 10^4 \text{ M}$	ϕ_{Pr}
0.0	$1.12 \pm .05^a$	0.889	0.207	$0.148 \pm .02^a$	5.49	0.128
1.00	1.56	1.24	0.288	0.227	8.42	0.196
2.00	1.73	1.37	0.319	0.256	9.50	0.221
4.00	1.58	1.25	0.291	0.257	9.54	0.221
5.00	1.83	1.45	0.337	0.231	8.57	0.199
6.00	1.73	1.37	0.319	0.228	8.46	0.196
VP Actinometer (average from three tubes)						
0.0	1.50 ± 0.10	1.19		$0.321 \pm .02$	11.9	

[diketone]=0.0103M(0.0458%T), [VP]=0.0191M(0.120%T),
 $[C_{14}] = 3.97 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00225E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}	$\frac{\text{area Pr}}{\text{area } cC_6}$	[Pr] $\times 10^4 \text{ M}$	ϕ_{Pr}
0.0	$0.588 \pm .04^a$	5.64	0.199	$0.100 \pm .02^a$	3.44	0.121
1.00	0.842	8.08	0.284	0.158	5.43	0.191
2.00	0.916	8.79	0.309	0.166	5.71	0.201
3.00	1.14	10.9	0.385	0.214	7.36	0.259
4.00	1.01	9.70	0.341	0.196	6.74	0.237
5.01	1.01	9.70	0.341	0.216	7.43	0.261
6.01	0.989	9.49	0.334	0.206	7.08	0.248
VP Actinometer (average from three tubes)						
0.0	$0.662 \pm .03$	6.36		$0.185 \pm .01$	6.36	

[diketone]=0.00999M(0.0502%T), [VP]=0.0111M(0.292%T),
 $[C_{14}] = 4.80 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5, lamp intensity=0.00150E/hr

a. average from three tubes

Table 52: Intersystem Crossing Yield for δ ValPhVP

Ketone	[1,3-pentadiene] M	$\frac{\text{cis}}{\text{cis+trans}}$	ϕ_{isc}
0.05304 M δ ValPhVP	0.5349	0.0270	1.04
0.06500 M Ac	0.5349	0.0261	1.00

cis/(cis+trans) unirradiated diene = 0.00361, benzene solvent, 313nm, 30.0°, g.c. condition set 8

Table 53: ϕ_{Dis} for δ ValPhVP in 4.5 M Dioxane

[diketone]	0.00996
[tetradecane]	0.000500
[di-n-propylphthalate]	0.0990
avg. ratio, diketone/phthalate	
unirradiated	1.82
irradiated	1.61
% conv of ketone	11.5
area Ac/area C ₁₄	0.886
% conv to Ac	8.90
% conv ketone/% conv Ac	1.29

4.5 M dioxane in benzene; 313nm; 30.0°; g.c. condition set 5; h.p.l.c. conditions, 2' x 1/8" Porasil 1000pft, 800psig, 1:1 hexane/methylene chloride

Table 54: Effects of Varying Concentrations of Pyridine
on ϕ_{II} for γ PhOBP

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	[Ac] $\times 10^4$ M	ϕ_{Ac}
0.0	0.424 ± 0.01^a	5.22	0.361
0.254	0.744	9.16	0.634
0.509	0.722	8.89	0.615
1.02	0.770	9.48	0.656

VP Actinometer (average from two tubes)

0.0	0.444 ± 0.001	5.47
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[ketone]=0.0104M(0.270%T), [VP]=0.0228M(0.0798%T),

$[C_{16}] = 5.30 \times 10^{-4}$ M, benzene solvent, 313nm, 30.0°,

g.c.condition set 6, lamp intensity = 0.000140E/hr

a. average from two tubes

Table 55: Stern-Volmer Data for γ CNPhOBP

Run 1

$\phi_{Ac}=0.459, k_q\tau=82.5M^{-1}sec^{-1}$, Lamp intensity=0.000309E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	0.587 ± 0.004^a		6.44
0.153	0.509	1.15	5.58
0.306	0.461	1.27	5.06
0.612	0.406	1.45	4.45
0.917	0.339	1.73	3.72
1.22	0.295	1.98	3.24
1.53	0.256	2.30	2.81
VP Actinometer (average from three tubes)			
0.0	0.464 ± 0.01		5.09

$[\text{ketone}]=0.0101M(0.243\%T)$, $[VP]=0.0223M(0.0844\%T)$,
 $[C_{16}]=4.72 \times 10^{-4}M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6

Run 2

$\phi_{Ac}=0.350, k_q\tau=79.3M^{-1}sec^{-1}$, Lamp intensity=0.000277E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	0.449 ± 0.01^a		5.85
0.428	0.332	1.35	4.33
0.857	0.273	1.64	3.56
1.29	0.223	2.01	2.91
1.71	0.189	2.37	2.46
VP Actinometer (average from two tubes)			
0.0	0.449 ± 0.01		5.85

$[\text{ketone}]=0.0100M(0.246\%T)$, $[VP]=0.0191M(0.120\%T)$,
 $[C_{16}]=5.61 \times 10^{-4}M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6

a. average from three tubes

Table 56: Effects of Varying Concentrations of Pyridine
on ϕ_{II} for $\gamma\text{CNPhOBP}$

Run 1

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.471 ± 0.02^a	5.80	0.391
0.254	0.713	8.78	0.593
0.509	0.743	9.15	0.617
1.02	0.723	8.91	0.601
VP Actinometer (average from two tubes)			
0.0	0.444 ± 0.001	5.47	

[ketone]=0.00986M(0.251%T), [VP]=0.0228M(0.0798%T),
 $[C_{16}] = 5.30 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity = 0.000140E/hr

Run 2

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.449 ± 0.01^a	5.85	0.351
0.248	0.629	8.20	0.492
0.496	0.623	8.12	0.487
0.992	0.651	8.49	0.509
VP Actinometer (average from two tubes)			
0.0	0.449 ± 0.01	5.85	

[ketone]=0.0100M(0.246%T), [VP]=0.0191M(0.120%T),
 $[C_{16}] = 5.61 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity=0.000277E/hr

a. average from two tubes

Table 57: Stern-Volmer Data for γ AcPhOBP

Run 1

$\phi_{Ac}=0.291, k_q\tau=568M^{-1}sec^{-1}$, Lamp intensity=0.00507E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	1.84 ± 0.03^a		11.0
0.314	0.537	3.42	3.21
0.628	0.367	5.00	2.19
1.26	0.226	8.13	1.35
1.88	0.164	11.2	0.981
2.51	0.146	12.5	0.873
3.14	0.0966	19.0	0.578
VP Actinometer (average from two tubes)			
0.0	1.32 ± 0.10		7.89

[diketone]=0.00998M(0.00498%T), [VP]=0.0106M(0.309%T),
 $[C_{14}]=2.99 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5

Run 2

$\phi_{Ac}=0.303, k_q\tau=646M^{-1}sec^{-1}$, Lamp intensity=0.000904E/hr

$[Q]$ $\times 10^3 M$	$\frac{\text{area Ac}}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	1.66 ± 0.07^a		3.41
0.788	0.975	1.71	2.01
1.58	0.751	2.20	1.56
3.15	0.490	3.39	1.01
4.73	0.437	3.80	0.900
6.30	0.337	4.94	0.694
7.88	0.269	6.18	0.554
VP Actinometer (average from three tubes)			
0.0	1.51 ± 0.03		3.11

[diketone]=0.0203M(2.07×10^{-5} %T), [VP]=0.0225M(0.0825%T),
 $[C_{14}]=1.03 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 5

Table 57: (cont'd.)

Run 3

 $\phi_{Ac} = 0.285, k_q \tau = 535 M^{-1} \text{sec}^{-1}$, Lamp intensity = 0.000369E/hr

$[Q]$ $\times 10^3 M$	$\frac{\text{area } Ac}{\text{area } C_{16}}$	ϕ° / ϕ	$[Ac]$ $\times 10^4 M$
0.0	0.505 ± 0.01^a		6.29
0.665	0.347	1.45	4.32
1.33	0.284	1.78	3.54
2.66	0.199	2.54	2.48
3.99	0.160	3.16	1.99
5.32	0.129	3.91	1.61
6.65	0.113	4.45	1.41
VP Actinometer (average from three tubes)			
0.0	0.470 ± 0.04		5.85

[diketone] = 0.00999M(0.00495%T), [VP] = 0.0192M(0.119%T),
 $[C_{16}] = 5.36 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6

a. average from three tubes

Table 58: Effects of Varying Concentrations of Pyridine on ϕ_{II} for γ AcPhOBP

[pyridine] M	$\frac{\text{area } Ac}{\text{area } C_{16}}$	$[Ac]$ $\times 10^3 M$	ϕ_{Ac}
0.0	1.64 ± 0.02^a	0.819	0.344
0.258	2.53	1.26	0.531
0.516	2.50	1.25	0.524
1.03	2.46	1.23	0.516
VP Actinometer (average from two tubes)			
0.0	1.32 ± 0.02	0.660	

[diketone] = 0.0104M(0.00398%T), [VP] = 0.0227M(0.0807%T),
 $[C_{16}] = 2.15 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity = 0.000403E/hr

a. average from two tubes

The effects of various concentrations of pyridine on ϕ_{II} are reported in Table 58. The ϕ_{II}^{Max} was observed to be 0.53 and the average ϕ_{II} was observed to be 0.29 ± 0.01 .

15. γ ValPhOBP

The Stern-Volmer data for this diketone are presented in Table 59. The observed $k_q\tau$ values for acetophenone and propene formation from this diketone are $349 \text{ M}^{-1}\text{sec}^{-1}$ and $438 \text{ M}^{-1}\text{sec}^{-1}$. The effects of various concentrations of pyridine on the ϕ_{II} values for the two chromophores are reported in Table 60. The ϕ^{Max} for acetophenone formation was observed to be 0.49 and the ϕ^{Max} for propene formation was observed to be 0.065. The average ϕ for acetophenone formation was observed to be 0.33 ± 0.01 and 0.39 ± 0.004 for propene formation.

16. δ PhOVP

The Stern-Volmer data for this ketone are presented in Table 61. The observed $k_q\tau$ value is $193 \pm 6 \text{ M}^{-1}\text{sec}^{-1}$. The effects of various concentrations of dioxane and pyridine on ϕ_{II} are presented in Tables 62 and 63. The ϕ_{II}^{Max} was observed to be 0.70 with pyridine. Dioxane did not produce ϕ_{II}^{Max} for this ketone. The average ϕ_{II} observed was 0.43 ± 0.04 .

17. δ CNPhOVP

The Stern-Volmer data for this ketone are presented in Table 64. The observed $k_q\tau$ value is $404 \pm 9 \text{ M}^{-1}\text{sec}^{-1}$. The effects of various concentrations of pyridine on

Table 59: Stern-Volmer Data for γ ValPhOBP

$$\phi_{Ac}=0.344, \phi_{Pr}=0.0348, k_q\tau_{Ac}=394M^{-1}sec^{-1}, k_q\tau_{Pr}=438M^{-1}sec^{-1}$$

$[Q]$ $\times 10^3 M$	$\frac{\text{area Ac}}{\text{area } C_{16}}$	$\left(\frac{\phi^o}{\phi}\right)_{Ac}$	$[Ac]$ $\times 10^4 M$	$\frac{\text{area Pr}}{\text{area } cC_6}$	$\left(\frac{\phi^o}{\phi}\right)_{Pr}$	$[Pr]$ $\times 10^4 M$
0.0	$2.53 \pm .02^a$		12.9	$0.027 \pm .001^a$		1.31
1.09	1.64	1.37	8.38	0.0126	2.15	0.611
2.17	1.31	1.92	6.70	0.0126	2.15	0.611
4.35	0.961	2.63	4.91	0.00895	3.02	0.434
6.52	0.738	3.42	3.77	0.00647	4.17	0.314
8.70	0.475	5.31	2.43	0.00415	6.51	0.201
10.9	0.542	4.66	2.77	0.00488	5.53	0.237
VP Actinometer (average from three tubes)						
0.0	2.04 ± 0.03		10.4	0.215 ± 0.03		10.4

[diketone]=0.0100M(0.00708%T), [VP]=0.0226M(0.0816%T),
 $[C_{16}]=2.20 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6 and 7, lamp intensity=0.000629E/hr

a. average from three tubes

Table 60: Effects of Varying Concentrations of Pyridine on ϕ_{II} for γ ValPhOBP

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	$[Ac]$ $\times 10^3 M$	ϕ_{Ac}	$\frac{\text{area Pr}}{\text{area } cC_6}$	$[Pr]$ $\times 10^4 M$	ϕ_{Pr}
0.0	$1.53 \pm .02^a$	0.764	0.322	$0.165 \pm .002^a$	1.03	0.0432
0.258	2.16	1.08	0.454	0.225	1.40	0.0589
0.516	2.30	1.11	0.483	0.234	1.46	0.0613
1.03	2.31	1.15	0.485	0.250	1.56	0.0654
VP Actinometer (average from two tubes)						
0.0	$1.32 \pm .02$	0.660		$1.06 \pm .02$	6.60	

[diketone]=0.0104M(0.00581%T), [VP]=0.0227M(0.0807%T),
 $[C_{16}]=2.15 \times 10^{-4} M$, benzene solvent, 313nm, 30.0°,
 g.c. condition sets 6 and 7, lamp intensity=0.000403E/hr

a. average from two tubes

Table 61: Stern-Volmer Data for δ PhOVP

Run 1

$\phi_{Ac}=0.389$, $k_q\tau=199M^{-1}sec^{-1}$, Lamp intensity=0.00190E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	1.69 ± 0.1^a		10.4
0.521	0.846	1.99	5.23
1.04	0.569	2.96	3.52
2.08	0.371	4.55	2.29
3.13	0.218	7.72	1.35
4.17	0.173	9.75	1.07
5.21	0.155	10.9	0.958
VP Actinometer (average from three tubes)			
0.0	1.58 ± 0.1		9.76

$[\text{ketone}]=0.0100M(0.294\%T)$, $[\text{VP}]=0.0174M(0.145\%T)$,
 $[C_{14}]=3.09 \times 10^{-4}M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6.

Run 2

$\phi_{Ac}=0.470$, $k_q\tau=187M^{-1}sec^{-1}$, Lamp intensity=0.00147E/hr

$[Q]$ $\times 10^2 M$	$\frac{\text{area } Ac}{\text{area } C_{14}}$	ϕ°/ϕ	$[Ac]$ $\times 10^4 M$
0.0	0.969 ± 0.03^a		9.79
0.360	0.608	1.59	6.14
0.719	0.392	2.47	3.96
1.44	0.258	3.76	2.61
2.16	0.200	4.84	2.02
2.88	0.152	6.37	1.54
3.60	0.124	7.82	1.25
VP Actinometer (average from three tubes)			
0.0	0.766 ± 0.03		7.74

$[\text{ketone}]=0.0101M(0.294\%T)$, $[\text{VP}]=0.0190M(0.122\%T)$,
 $[C_{14}]=5.05 \times 10^{-4}M$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6

a. average from three tubes

Table 62: Effects of Various Concentrations of Dioxane
on ϕ_{II} for δPhOVP

Run 1

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.845 ± 0.005^a	7.86	0.439
1.00	0.870	8.09	0.452
2.00	0.922	8.57	0.479
3.00	0.944	8.78	0.490
4.00	0.955	7.95	0.444
5.00	0.883	8.21	0.458
6.00	0.887	8.25	0.460
VP Actinometer (average from three tubes)			
0.0	0.701 ± 0.05	6.52	

[ketone]=0.0100M(0.294%T), [VP]=0.0175M(0.144%T),
 $[C_{14}]=4.65 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity = 0.00169E/hr

Run 2

[Dioxane] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.535 ± 0.02^a	4.24	0.424
1.00	0.547	4.33	0.434
2.00	0.530	4.20	0.420
3.00	0.560	4.44	0.444
5.01	0.535	4.24	0.424
VP Actinometer (average from two tubes)			
0.0	0.391 ± 0.03	3.10	

[ketone]=0.0100M(0.294%T), [VP]=0.0118M(0.270%T),
 $[C_{14}]=3.96 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity=0.000708E/hr

a. average from three tubes

Table 63: Effects of Various Concentrations of Pyridine
on ϕ_{II} for δPhOVP

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{14}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	1.01 ± 0.04^a	4.24	0.447
0.254	1.21	5.08	0.535
0.507	1.46	6.13	0.646
0.761	1.52	6.38	0.672
1.01	1.58	6.64	0.699
1.52	1.42	5.96	0.628
VP Actinometer (average from two tubes)			
0.0	0.644 ± 0.01	2.70	

[ketone]=0.00999M(0.295%T), [VP]=0.0100M(0.330%T),
 $[C_{14}]=2.10 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity=0.000537E/hr

a. average from three tubes

Table 64: Stern-Volmer Data for $\delta\text{CNPhOVP}$

Run 1

$\phi_{\text{Ac}}=0.371$, $k_{\text{q}\tau}=413\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity= 0.000116E/hr

$[\text{Q}]$ $\times 10^3 \text{M}$	$\frac{\text{area Ac}}{\text{area C}_{16}}$	ϕ°/ϕ	$[\text{Ac}]$ $\times 10^4 \text{M}$
0.0	$2.46 \pm 0.05^{\text{a}}$		12.5
2.00	1.38	1.79	6.99
3.99	0.937	2.63	4.74
5.99	0.695	3.54	3.52
7.99	0.578	4.26	2.93
9.98	0.588	4.18	2.98
VP Actinometer (average from two tubes)			
0.0	1.85 ± 0.02		9.37

$[\text{ketone}]=0.00982\text{M}(0.267\% \text{T})$, $[\text{VP}]=0.0101\text{M}(0.326\% \text{T})$,
 $[\text{C}_{16}]=2.18 \times 10^{-4} \text{M}$, benzene solvent, 313nm, 30.0° ,
 g.c. condition set 6

Run 2

$\phi_{\text{Ac}}=0.334$, $k_{\text{q}\tau}=395\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity= 0.000176E/hr

$[\text{Q}]$ $\times 10^2 \text{M}$	$\frac{\text{area Ac}}{\text{area C}_{16}}$	ϕ°/ϕ	$[\text{Ac}]$ $\times 10^5 \text{M}$
0.0	$0.352 \pm 0.04^{\text{a}}$		9.24
0.151	0.221	1.59	5.80
0.301	0.170	2.08	4.46
0.603	0.107	3.28	2.81
0.904	0.0756	4.66	1.99
1.21	0.0700	5.03	1.84
1.51	0.0619	5.69	1.63
VP Actinometer (average from two tubes)			
0.0	0.288 ± 0.03		7.56

$[\text{ketone}]=0.00977\text{M}(0.269\% \text{T})$, $[\text{VP}]=0.00988\text{M}(0.334\% \text{T})$,
 $[\text{C}_{16}]=1.13 \times 10^{-4} \text{M}$, benzene solvent, 313nm, 30.0° ,
 g.c. condition set 6

a. average from two tubes

ϕ_{II} are presented in Table 65. The ϕ_{II}^{Max} was observed to be 0.53 ± 0.01 . The average ϕ_{II} observed was 0.38 ± 0.03 .

18. δ AcPhOVP

The Stern-Volmer data for this diketone are presented in Table 66. The observed $k_q \tau$ value is $2012 \text{ M}^{-1} \text{sec}^{-1}$. The effects of various concentrations of pyridine on ϕ_{II} are presented in Table 67. The ϕ_{II}^{Max} was observed to be 0.42. The average ϕ_{II} was observed to be 0.34 ± 0.01 .

19. δ ValPhOVP

The Stern-Volmer data for this diketone are presented in Table 68. The observed $k_q \tau$ values for acetophenone and propene formation from this diketone are $1134 \text{ M}^{-1} \text{sec}^{-1}$ and $1579 \text{ M}^{-1} \text{sec}^{-1}$. The Stern-Volmer plot for acetophenone curves downward, particularly at high quencher concentrations. The effects of various concentrations of pyridine on the ϕ_{II} values for the two chromophores are reported in Table 69. The ϕ^{Max} for propene formation was observed to be 0.16. The average ϕ for acetophenone formation was observed to be 0.21 ± 0.01 and 0.075 ± 0.005 for propene formation.

Table 65: Effects of Various Concentrations of Pyridine
on ϕ_{II} for $\delta\text{CNPhOVP}$

Run 1

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.571 ± 0.03^a	6.83	0.402
0.728	0.762	9.12	0.536
0.971	0.703	8.41	0.495
1.21	0.583	6.98	0.410
1.46	0.534	6.39	0.376
VP Actinometer (average from three tubes)			
0.0	0.370 ± 0.02	4.43	

[ketone]=0.00994M(0.263%T), [VP]=0.00920M(0.361%T),
 $[C_{16}] = 5.15 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity=0.000498E/hr

Run 2

[Pyridine] M	$\frac{\text{area Ac}}{\text{area } C_{16}}$	[Ac] $\times 10^4 \text{ M}$	ϕ_{Ac}
0.0	0.708 ± 0.02^a	8.42	0.412
0.242	1.02	12.1	0.594
0.484	0.915	10.9	0.533
0.967	0.894	10.6	0.521
1.21	0.891	10.6	0.519
1.45	0.884	10.5	0.514
VP Actinometer (average from three tubes)			
0.0	0.608 ± 0.02	7.23	

[ketone]=0.00991M(0.264%T), [VP]=0.0183M(0.131%T),
 $[C_{16}] = 5.12 \times 10^{-4} \text{ M}$, benzene solvent, 313nm, 30.0°,
 g.c. condition set 6, lamp intensity=0.000555E/hr

a. average from three tubes

Table 66: Stern-Volmer Data for $\delta\text{AcPhOVP}$

$\phi_{\text{Ac}}=0.331$, $k_q\tau=2012\text{M}^{-1}\text{sec}^{-1}$, Lamp intensity= 0.000453E/hr

$[\text{Q}]$ $\times 10^3 \text{M}$	$\frac{\text{area Ac}}{\text{area C}_{16}}$	ϕ°/ϕ	$[\text{Ac}]$ $\times 10^4 \text{M}$
0.0	1.77 ± 0.02^a		8.89
0.896	0.629	2.82	3.16
1.79	0.408	4.38	2.05
3.59	0.213	8.32	1.07
5.38	0.190	9.30	0.954
7.17	0.140	12.6	0.703
VP Actinometer (average from three tubes)			
0.0	1.41 ± 0.06		7.08

$[\text{diketone}] = 0.0101\text{M}(0.0109\%T)$, $[\text{VP}] = 0.0183\text{M}(0.131\%T)$,
 $[\text{C}_{16}] = 2.16 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0° ,
 g.c. condition set 6.

a. average from three tubes

Table 67: Effects of Various Concentrations of Pyridine on ϕ_{II} for $\delta\text{AcPhOVP}$

$[\text{Pyridine}]$ M	$\frac{\text{area Ac}}{\text{area C}_{16}}$	$[\text{Ac}]$ $\times 10^4 \text{M}$	ϕ_{Ac}
0.0	0.705 ± 0.003^a	8.06	0.352
0.250	0.777	8.88	0.388
0.499	0.831	9.50	0.415
1.00	0.792	9.06	0.395
VP Actinometer (average from two tubes)			
0.0	0.526 ± 0.005	6.01	

$[\text{diketone}] = 0.0104\text{M}(0.00957\%T)$, $[\text{VP}] = 0.0182\text{M}(0.133\%T)$,
 $[\text{C}_{16}] = 4.92 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0° ,
 g.c. condition set 6, lamp intensity= 0.000385E/hr

a. average from two tubes

Table 68: Stern-Volmer Data for $\delta\text{ValPhOVP}$

$$\phi_{\text{Ac}}=0.214, \phi_{\text{Pr}}=0.0798, k_q\tau_{\text{Ac}}=1134\text{M}^{-1}\text{sec}^{-1}, k_q\tau_{\text{Pr}}=1579\text{M}^{-1}\text{sec}^{-1}$$

$[\text{Q}]$ $\times 10^3 \text{M}$	$\frac{\text{area Ac}}{\text{area C}_{16}}$	$\frac{\phi^\circ}{\phi}$	$[\text{Ac}]$ $\times 10^4 \text{M}$	$\frac{\text{area Pr}}{\text{area cC}_6}$	$\frac{\phi^\circ}{\phi}$	$[\text{Pr}]$ $\times 10^5 \text{M}$
0.0	0.459 ± 0.01^a		5.08	0.366 ± 0.02^a		19.0
0.936	0.198	2.31	2.19	0.141	2.59	7.31
1.87	0.139	3.30	1.54	0.0931	3.93	4.83
3.75	0.0896	5.12	0.991	0.0557	6.58	2.89
5.62	0.0703	6.53	0.778	0.0377	9.71	1.95
7.49	0.0634	7.24	0.701	0.0279	13.1	1.45
VP Actinometer (average from three tubes)						
0.0	0.539 ± 0.03		5.96	1.15 ± 0.1		59.6

$[\text{diketone}] = 0.0103\text{M}(0.00442\%T)$, $[\text{VP}] = 0.0161\text{M}(0.200\%T)$,
 $[\text{C}_{16}] = 4.76 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0°,
g.c. condition set 6 and 7, lamp intensity = 0.000414E/hr

a. average from three tubes

Table 69: Effects of Varying Concentrations of Pyridine on ϕ_{II} for $\delta\text{ValPhOVP}$

$[\text{Pyridine}]$ M	$\frac{\text{area Ac}}{\text{area C}_{16}}$	$[\text{Ac}]$ $\times 10^4 \text{M}$	ϕ_{Ac}	$\frac{\text{area Pr}}{\text{area cC}_6}$	$[\text{Pr}]$ $\times 10^4 \text{M}$	ϕ_{Pr}
0.0	0.403 ± 0.01^a	4.61	0.200	0.338 ± 0.02^a	1.63	0.0706
0.250	0.406	4.64	0.206	0.324	1.56	0.0677
0.499	0.596	6.81	0.296	0.694	3.34	0.145
1.00	0.619	7.08	0.307	0.776	3.73	0.162
VP Actinometer (average from two tubes)						
0.0	0.526 ± 0.005	6.01		1.25 ± 0.07	6.01	

$[\text{diketone}] = 0.0104\text{M}(0.00419\%T)$, $[\text{VP}] = 0.0182\text{M}(0.133\%T)$,
 $[\text{C}_{16}] = 4.92 \times 10^{-4}\text{M}$, benzene solvent, 313nm, 30.0°,
g.c. condition set 6 and 7, lamp intensity = 0.000385E/hr

a. average from two tubes

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