CONFORMATIONAL EFFECTS ON THE PHOTOCHEMISTRY OF SOME 2-PHENYLCYCLOHEXANONES

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ABSTRACT

CONFORMATIONAL EFFECTS ON THE PHOTOCHEMISTRY OF SOME 2-PHENYLCYCLOHEXANONES

by

Thomas C. Stratton

A careful study of the photochemistry of 2-phenylcyclohexanone revealed an interesting phenomenon. The major photoproducts, *cis* and *trans*-6-phenyl-5-hexenal were quenched by dienes at different rates, $k_q\tau$ values 1.7 and .41 M^{-1}, respectively. By measuring the singlet lifetime (4.4×10^{-9} sec), intersystem crossing quantum yield (.88) and fluorescence intensity ($\simeq .01$) it was determined that the singlet state of 2-phenylcyclohexanone was not one of the quenchable states. *Trans*-4-t-butyl-2-phenylcyclohexanone was found to be photoinert while *cis*-4-t-butyl-2-phenylcyclohexanone formed the expected alkenals *cis* and *trans*-4-t-butyl-6-phenyl-5-hexenal, $k_q\tau$ values 18.0 and 2.85 M^{-1}, respectively. It was postulated that formation of the *cis* alkenals could only occur from a twist-boat conformer of the cyclohexanone ring and that the twist-boat and chair conformers formed distinct triplet states of different lifetimes.

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To

Dr. David A. Bak

for his help, encouragement and understanding

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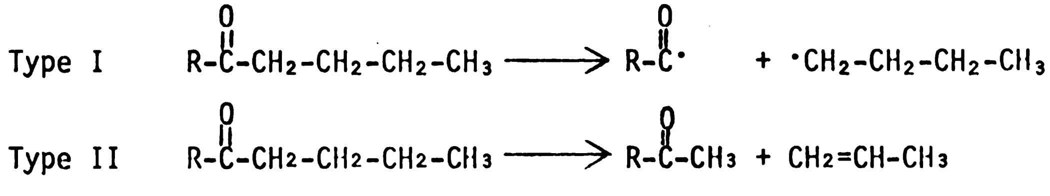
INTRODUCTION

A. Introductory remarks.

During the last decade perhaps no area of chemistry has generated as much interest as photochemistry. From the opening verses of Genesis to viable solutions for the energy crisis of the 1970's, light and its interaction with matter have been of prime interest and importance to man. Like other reagents, light can create a bewildering array of products from rather simple starting materials. One of the first steps in understanding the whys and wherefores of photochemical reactions is the classification of the various reaction types.

During the 1930's R. G. W. Norrish, while studying gas phase photodecarbonylation of aldehydes and ketones, characterized two new photochemical reactions of particular interest to us.[1] These reactions are now referred to as the Norrish type I and type II cleavages. The type I cleavage results in breaking the bond between the alpha carbon and the carbonyl, while the type II cleavage results in breaking the alpha-beta carbon carbon bond.



$$\text{Type I} \quad R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\cdot \quad + \cdot CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3$$

$$\text{Type II} \quad R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 \longrightarrow R\text{-}\overset{\overset{\displaystyle O}{\|}}{C}\text{-}CH_3 + CH_2\text{=}CH\text{-}CH_3$$

Figure 1. Norrish type I and type II photocleavages.

Mechanistic studies have been undertaken on both the type I and II cleavages.[2] Rather complete understanding of the mechanistic details of the type II cleavage has been gained through the exhaustive studies with phenyl alkyl ketones by Wagner.[3] The type I cleavage has been studied most conveniently with five and six membered cycloalkanones.[4] This thesis deals with some of the mechanistic aspects of the Norrish type I cleavage in 2-phenylcyclohexanones. Pertinent to our understanding of the mechanistic data relating to these photochemical reactions are brief descriptions of the following subjects: electronic transitions, Stern-Volmer kinetics, and some factors which affect the rates of α-cleavage in cyclohexanones.

B. Electronic Transitions

The absorption of light by an aliphatic ketone results in the promotion of an electron from the ground state to an excited state. Most stable ground state molecules have their electrons paired. The net electron spin is zero and therefore the multiplicity is one, $(2S + 1)$. Selection rules require that the transition between energy levels occur without a change in multiplicity.[5] Although forbidden by quantum mechanics, the electron can change its spin with the help of spin orbital coupling, producing an excited state molecule with a net electron spin of one and a multiplicity of three. The molecule is thus referred to as being in a triplet state. The triplet state is lower in energy than the singlet state according to Hund's rule.[6] Due to very rapid internal conversion (10^{-12} sec) from higher to lower vibrational levels, both the singlet and triplet states rapidly reach their lowest vibrational state.[7] The radiationless process involving electron spin changes is called intersystem crossing. Triplets are generally longer lived than singlets, since triplets require another forbidden spin flip before they can return to the ground state.

An excited state may be characterized by the origin of the electron which was promoted as well as by the molecular multiplicity. Aliphatic ketones have only one readily available source of electrons for excitation, the n (nonbonding) electrons on the oxygen of the carbonyl. Excitation of these electrons to the π^* antibonding orbital is design as n,π^* excitation.[8] Aromatic ketones, ketones which have their carbonyl conjugated with an aromatic system, show another type of transition due to the availability of π electrons, which is designated π,π^*.[8] The n,π^* transition is forbidden by symmetry and therefore occurs with less intensity than the allowed π,π^*.

The nature of an n,π^* triplet state ketone has been compared to that of an alkoxy radical.[9] The typically nucleophilic character of oxygen, often seen in its ground state reaction, has been reversed in the n,π^* state. Excitation of the n electron on oxygen has decreased the electron density of the oxygen and thus oxygen behaves as an electrophile in the excited state. The similarities between alkoxy radicals and n,π^* triplet ketones towards hydrogen abstraction is a striking and well studied phenomenon.[10]

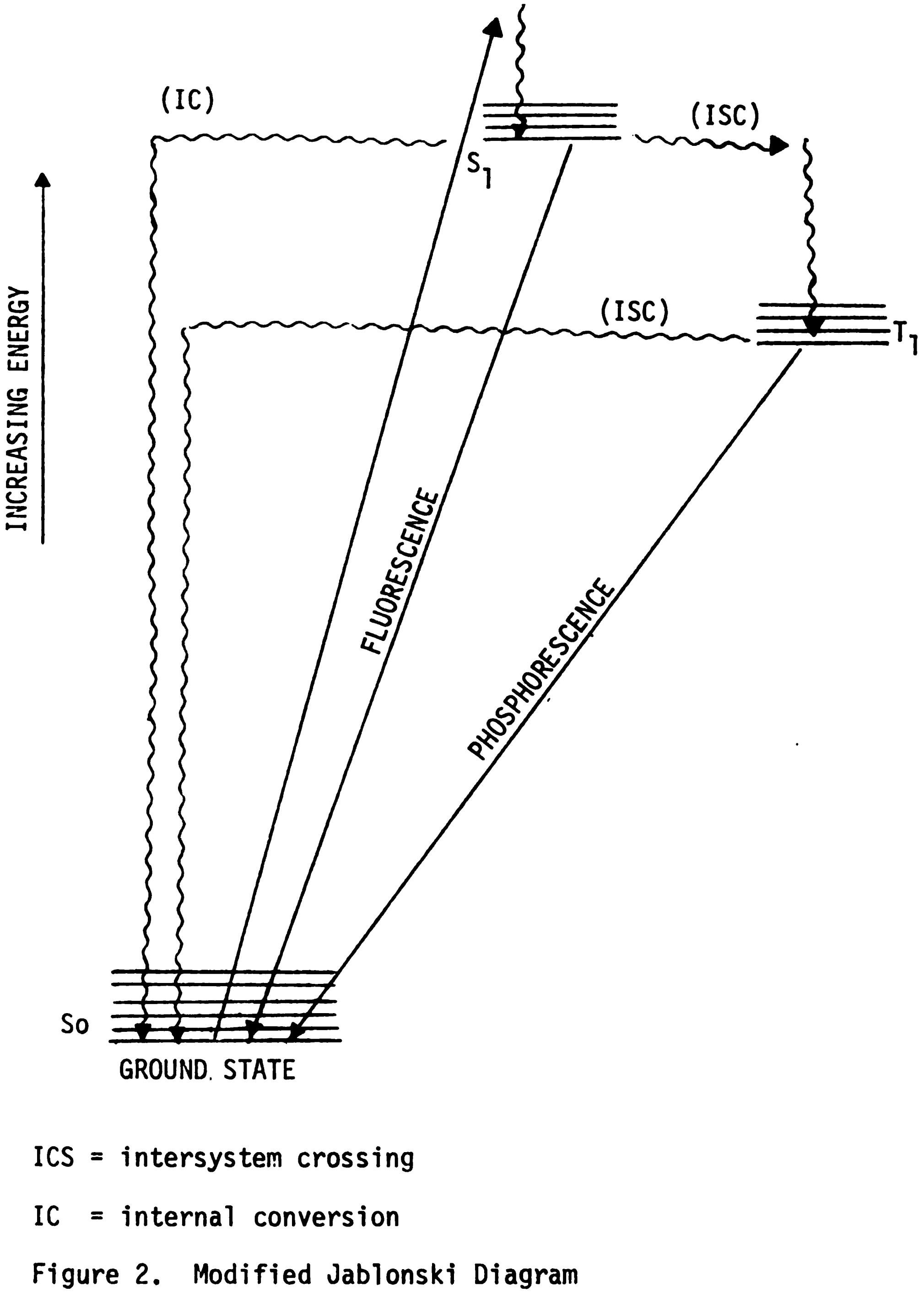
Rapidly, by a variety of pathways, molecules in the excited state return to the ground state. From the singlet state a molecule may intersystem cross, fluoresce, radiationless decay or undergo chemical reaction. From the triplet state a molecule may phosphoresce, radiationless decay or react. These processes are graphically represented by the Jablonski diagram,[11] Figure 2.

The quantum yields for intersystem crossing are high for many carbonyl compounds.[12] Photochemical reactions can occur from either the singlet or triplet state. The rate of reaction has to compete with the rates for all other processes occurring from the excited state. The quantum yield of singlet reaction, in carbonyl compounds, is many times limited by the rate of intersystem crossing. The rates of intersystem crossing in aliphatic ketones have been measured by Yang *et al.*[13] It was found that the rates of intersystem crossing for many aliphatic ketones were in the range of $1 - 5 \times 10^8$ sec.$^{-1}$.

C. Stern-Volmer kinetics.

Under steady state conditions one may measure directly only one quantity, the quantum yield.[14] The quantum yield may be defined as the number of molecules reacting in a given way divided by the number of photons that have been absorbed.

Excited state lifetimes may be measured indirectly by quenching experiments. Assuming a steady state concentration of excited state molecules, one may by quenching of the excited state determine the relative decrease of photoproduct as a function of quencher concentration. The Stern-Volmer equation $\phi_0/\phi = 1 + k_q\tau[Q]$ expresses this relationship.[15] ϕ_0 equals the quantum yield of photoreaction without quencher present, ϕ equals the quantum yield of photoreaction with quencher present, k_q is the rate constant for



ICS = intersystem crossing

IC = internal conversion

Figure 2. Modified Jablonski Diagram

quenching, which is usually assumed to be diffusion controlled and thus obeying a modified Debye equation, $k_q = 8RT/2000\eta$.[16] Tau, τ, the lifetime of the excited state is defined to be equal to $1/\ (k_1 + k_2 + \ldots k_n)$ where k represents rate constants for all other processes that occur from that excited state. Stern-Volmer plots of ϕ_0/ϕ versus quencher concentration should be linear with the slope equal to $k_q\tau$. By using a previously determined value for k_q one may calculate τ from the slope of such plots. The excited state lifetime may be equated to the reciprocal rate constant for reaction if the rate constant for reaction is large compared to all competing rate constants. Steady state kinetics for various excited state situations have been delineated by Wagner.[14]

D. Some factors controlling the rates of α-cleavage and the efficiency of product formation in cyclohexanones.

The major products formed from the photolysis of cyclohexanone in inert solvents, 5-hexenal and 1-hexenal, may be accounted for by a simple biradical mechanism arising from α-cleavage of the parent ketone. The 1,6-biradical formed by α-cleavage may disproportionate by intramolecular hydrogen abstraction. The suggestion that cyclohexanones reacted by a concerted mechanism appears to have been based upon inaccurate data.[17] The acyl radical can form 5-hexenal by abstracting a hydrogen alpha to the alkyl radical. Conversely, 1-hexenal can be formed when the alkyl radical abstracts a hydrogen alpha to the acyl radical, Figure 3. Ketenes, such as 1-hexenal, are usually trapped by alcohols as the corresponding esters or by amines as amides.

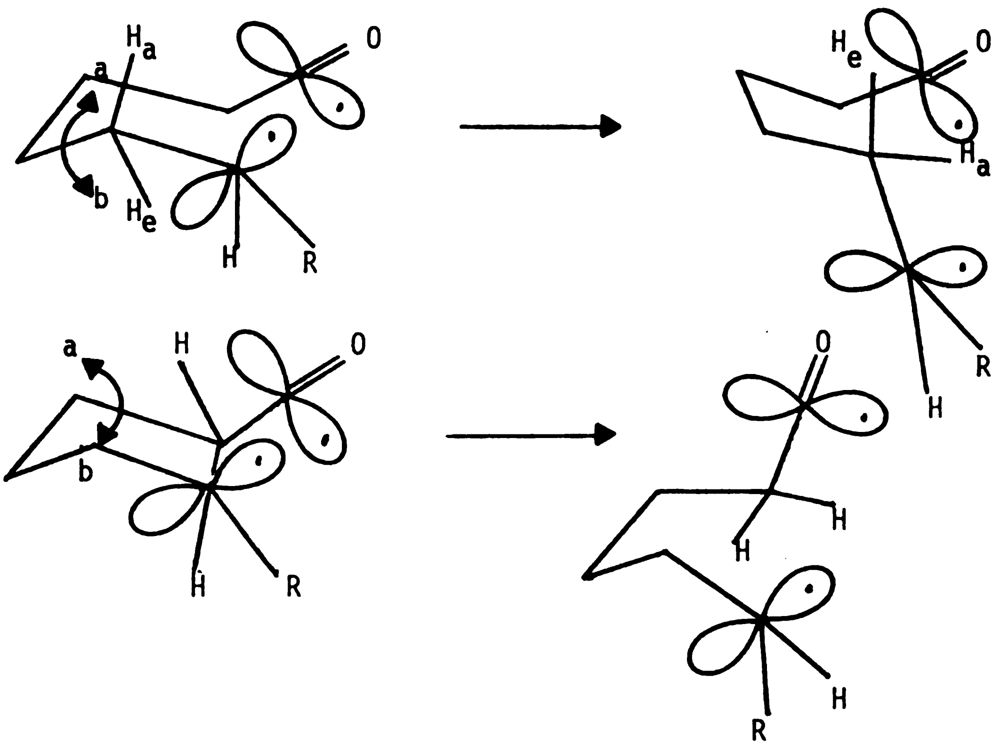


Figure 3. Bond rotations necessary for alkenal and ketene formation.

As the number and functionality of substituents on the cyclohexanone ring increase or as the reactivity of the solvents increases, the number and complexity of the photoproducts increase. Indeed, a bewildering array of products are possible. However, simply substituted cyclohexanones, photolyzed in inert solvents, provide a convenient vehicle for the study of the factors affecting the rates of α-cleavage and the efficiency of product formation from the biradical without untold complications.

Disappearance of cyclohexanone, upon photolysis in inert solvents such as benzene, has been accounted for by formation of alkenal and ketene products.[18] Any discrepancy between ketone disappearance and product appearance has been attributed to minor side products such as caused by photoreduction and/or decarbonylation. Surprisingly few quantum yields for ketene formation have been reported along with the rather more numerous quantum yields for alkenal formation.[4,19]

The alkenal/ketene ratio would be expected to be particularly sensitive to substitution in the 2 and 3 positions. The hydrogen abstracting ability of both the acyl and alkyl radicals are presumably related to their own stability and the strength of the carbon-hydrogen bond which is to be broken. The stability of the acyl radical should remain relatively unchanged by substitution on the cyclohexanone ring. While alkyl radical stability will increase with substitution in the 2-position. The strength of the carbon-hydrogen bond decreases as substitution changes the secondary 2 or 3 position carbon into a tertiary carbon.

The rates of α-cleavage in cyclohexanones may be interpreted as depending primarily upon two factors; 1. ring strain and 2. alkyl radical stability. The efficiency of product formation, as indicated by quantum yields, will reflect both the efficiency of α-cleavage and the ability of the 1,6-biradical formed from α-cleavage to disproportionate to products. The rates of α-cleavage and the efficiency of disproportionation are strongly affected by substituents on the cyclohexanone ring. It has been found that substituents as simple as methyl groups in the 2,3, or 4 positions can affect both the rate of α-cleavage and/or the efficiency of product formation.

The effect of ring strain on the rates of α-cleavage can be seen in the following series of ketones, cyclohexanone, cyclopentanone, 2-methylcyclopentanone and norcamphor, Table 1. Since norcamphor α-cleaves to a secondary alkyl radical the rate of α-cleavage should be compared to that of 2-methylcyclopentanone. Clearly as the degree of ring strain increases so do the rates of α-cleavage.

Alkyl radical stability is increased by substitution at the 2-position. The rates of α-cleavage increase with the increase in alkyl radical stability. The effect of alkyl radical stability is clearly and simply seen in the following series of 2-substituted cyclohexanones; cyclohexanone, 2-methylcyclohexanone, 2,2-dimethylcyclohexanone, Table 1.

The rates of α-cleavage in 3-methyl, 3,5-dimethyl, and 3,3,5-trimethyl cyclohexanone were found by Wagner and Spoerke[18] to be virtually identical to each other. The rate of α-cleavage from these three β-substituted cyclohexanones was found to be approximately twice as fast as the rate of α-cleavage from cyclohexanone. Approximately the same rate increase towards α-cleavage compared to cyclohexanone was found with 4-methylcyclohexanone . All α-cleavage rates, are assumed to be

Table 1. Effect of ring strain, radical stability and product stability on rates of α-cleavage in cycloalkanones.[4,18,20,21]

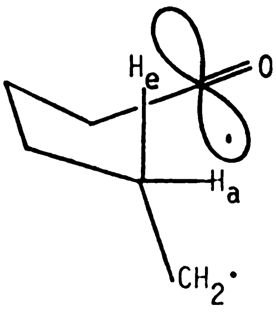
Ketone	Rate α-cleavage	$\phi_{alkenal}$	$\phi_{disappearance}$
Cyclohexanone	1.1×10^7	.08	.20
2-Methylcyclohexanone	2.5×10^8	.42	.50
2,2-Dimethylcyclohexanone	1.8×10^9	.41	.52
2,2,6,6-Tetramethylcyclohexanone	7.8×10^9	---	---
Cyclopentanone	1.1×10^8	.24	.28
2-Methylcyclopentanone	3.6×10^9	.26	---
2,2,5,5,-Tetramethylcyclopentanone	5.0×10^{10}	.61	---
Norcamphor	5.0×10^{10}	.28	---

equal to the reciprocal of the ketone lifetime, were measured by Stern-Volmer quenching of alkenal products. These rate increases in α-cleavage, caused by substitution in the 3 and 4 position are not reflected in larger quantum yields for product formation. In fact the quantum yields for alkenal formation from these ketones (.033, .005, .002, respectively) are smaller than for cyclohexanone and markedly smaller than for many 2-substituted cyclohexanones, Table 1.

The lack of correlation between rates of α-cleavage and efficiencies of alkenal formation suggest that there are significant substituent effects on the biradical behavior. Wagner and Spoerke from their study with β-substituted cyclohexanones found that the low quantum yields for alkenal formation were consistent with equally low quantum yields for ketone disappearance, .083, .003, .024 for 3-methyl, 3,5-dimethyl, 3,3,5-trimethyl cyclohexanone, respectively.

Regardless of the direction of α-cleavage, with these three β-substituted cyclohexanones, primary alkyl radicals are produced. It was conceivable that there might be a preference for α-cleavage towards the more substituted side. Alkenal stability is increased by substitution in the 3-position by increasing double bond stability and by decreasing β-carbon hydrogen bond strength by substitution in the 3-position. Both Wagner and Spoerke[18] and Agosta and Schreiber[23] report some preference for α-cleavage away from the substituted side, although the degree of preference is not at all clear. The surprising preference for α-cleavage away from the substituted side, along with the marked decrease in the efficiency of product formation suggest that the presence of even one β-methyl group seriously impaires the rotation of the biradical.

By deuterium labeling experiments with 3 and 4-methylcyclohexanone Agosta and Schreiber[23] determined the relative amounts of axial and equatorial hydrogen transfer from C_3 carbon to the acyl radical. It was found that two-thirds of the aldehydic hydrogens in the alkenal products were originally from the axial position and one-third from the equatorial position. In Figure 3 rotation (a) would be favored over rotation (b) by a 2:1 margin. Intermediate 1, Figure 4, where the $CH_2^{\bullet}$ group can maintain its equatorial position, would then be favored over intermediate 2, with substitution of a 3-methyl group then either rotation would require that the methyl group or the $CH_2^{\bullet}$ be in an axial position.



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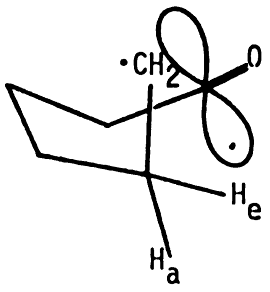

2

Figure 4. Intermediates in alkenal formation from cyclohexanone showing axial and equatorial positions of the $CH_2^{\bullet}$ group.

Wagner and Spoerke reported that for the series of ketones which they studied all alkenal formation occurred from the triplet state. Turro *et al.*[21] have shown that the rate of α-cleavage from the singlet is at least two orders of magnitude slower than for α-cleavage from the triplet state. As the number of α-alkyl substituents increase, the rate of α-cleavage increases. Singlet α-cleavage should start to compete with intersystem crossing when the rate of α-cleavage from the triplet approaches 10^{10} $\sec^{-1}$. Eastman and Beard[20] have suggested that the singlet state of 2,2,6,6-tetramethylcyclohexanone is sufficiently reactive to α-cleave in competition with intersystem crossing.

E. Research Objectives

1). The major product from the photolysis of 2-phenylcyclohexanone was unidentified by Wagner and Spoerke.[18] Baum[31] later reported that the product was *trans*-6-phenyl-5-hexenal. Since the VPC separation of the reportedly *cis* and *trans* isomers of 6-phenyl-5-hexenal was extraordinarily large, unlike that of other *cis-trans* isomers, Baum's report was somewhat puzzling.

2). The published rate of α-cleavage from 2-phenylcyclohexanone was inconsistent with the rates of α-cleavage from other 2-alkylcyclohexanones.

3). Wagner and Spoerke reported that the unidentified product was unquenchable, while a minor product was quenchable. This minor product was assumed by Wagner and Spoerke to be 6-phenyl-5-hexenal. Baum later confirmed that the product was the *cis* isomer. The possibility that the *cis*-alkenal was quenchable while the *trans*-alkenal was not suggested that perhaps competing photochemical mechanisms were operating in the photolysis of 2-phenylcyclohexanone.

4). If the *trans* isomer proved to be the major product, then this reaction would represent a very stereospecific photochemical reaction since the *trans* to *cis* alkenal ratio would be 45/1.

A careful study of 2-phenylcyclohexanone was undertaken to sort out the nature of these apparent anomalies.

RESULTS

The unraveling of the mechanistic details of 2-phenylcyclohexanone photochemistry began with the identification of the major photoproduct. Careful quenching experiments and quantum yield determinations on the two major photoproducts revealed surprising results. Further work determined the quantum yield for intersystem crossing and the singlet lifetime. A hypothesis to explain the surprising results of the quenching experiments was tested by studying the photochemistry of *cis* and *trans*-4-t-butyl-2-phenylcyclohexanone. Product identification, quantum yields and quenching studies were determined on these two ketones. The results from all of the ketones studied are presented in detail below.

A. Product Identification

The major photoproduct from 2-phenylcyclohexanone was found to be *trans*-6-phenyl-5-hexenal while *cis* and *trans*-6-phenyl-4-t-butyl-5-hexenal were identified as the major photoproducts from *cis*-4-t-butyl-2-phenylcyclohexanone. Photolysis of the parent ketones in benzene at 3130 Å followed by careful chromatographic separation of the resulting photolysis mixture yielded the photoproducts. IR and NMR analysis confirmed the identity of the products.

B. Quantum Yields

Quantum yields for alkenal formation and ketone disappearance were measured for both 2-phenylcyclohexanone and

Table 2. Lifetimes and Quantum Yields for 2-phenylcyclohexanones [a]

Piperylene quenching of 2-Phenylcyclohexanone

Product	$k_q\tau$	ϕ[b]	τ sec.
Cis-6-phenyl-5-hexenal	$1.69 \pm .15$	.01	3.4×10^{-10}
Trans-6-phenyl-5-hexenal	$0.41 \pm .04$	.45	$.8 \times 10^{-10}$
(Disappearance)		.65	
2,5-Dimethyl-2,4-hexadiene quenching of *cis*-4-t-butyl-2-phenylcyclohexanone			
Cis-6-phenyl-4-t-butyl-5-hexenal	18.0 ± 3.5	.03	3.6×10^{-9}
Trans-6-phenyl-4-t-butyl-5-hexenal	$2.85 \pm .73$	.30	$.57 \times 10^{-9}$
Disappearance		.59	
Biacetyl quenching of 2-phenylcyclohexanone			
Trans-6-phenyl-5-hexenal	$21.7 \pm .89$		4.3×10^{-9}
Intersystem Crossing Yield			
2-Phenylcyclohexanone	$.60 \pm .07$	$.88 \pm .06$	1.2×10^{-10}
Singlet Sensitization			
2-Phenylcyclohexanone		.14	

[a] Standard deviations indicated

[b] Quantum yields ± 10%

cis-4-t-butyl-2-phenylcyclohexanone, Table 2. Parent ketones, .2 M in benzene, were irradiated at 3130 Å to less than 5% conversion. Photoproduct/internal standard ratios were measured by VPC analysis. Conversion of these ratios to moles of product was accomplished by using previously determined conversion factors. Valerophenone actinometry, performed simultaneously with the photolysis of the ketone, was used.

Trans-4-t-butyl-2-phenylcyclohexanone, .02 M in benzene was irradiated at 3130 Å until .224 einsteins of light had been absorbed by the ketone. No photoproducts were seen by VPC analysis. Quantum yields for alkenal formation was less than .001 since VPC analysis would have easily detected concentrations as small as .001 M.

C. Stern-Volmer Quenching

Triplet lifetimes were measured from Stern-Volmer quenching plots. Plots of ϕ_0/ϕ versus quencher concentration are shown in Figures 5-8. Product to standard ratios for ketone solutions with varying concentrations of quencher were compared to product to standard ratios for ketone solutions with no quencher present to determine ϕ_0/ϕ. Absolute quantum yields were not measured, although for experimental simplicity actinometers were sometimes run during a quenching experiment so that quantum yield determination could be made from the ketone solutions with no quencher present. The slopes of these plots were set equal to $k_q\tau$, with k_q assumed to be 5 x 10^9 $\sec^{-1}$ M^{-1} in benzene.[24] Biacetyl was used to quench the singlet state of 2-phenylcyclohexanone.[13] Piperylene and 2,5-dimethyl-2,4-hexadiene were used to quench 2-phenylcyclohexanone and *cis*-4-t-butyl-2-phenylcyclohexanone. All $k_q\tau$ values were determined by least squares analysis of the data.

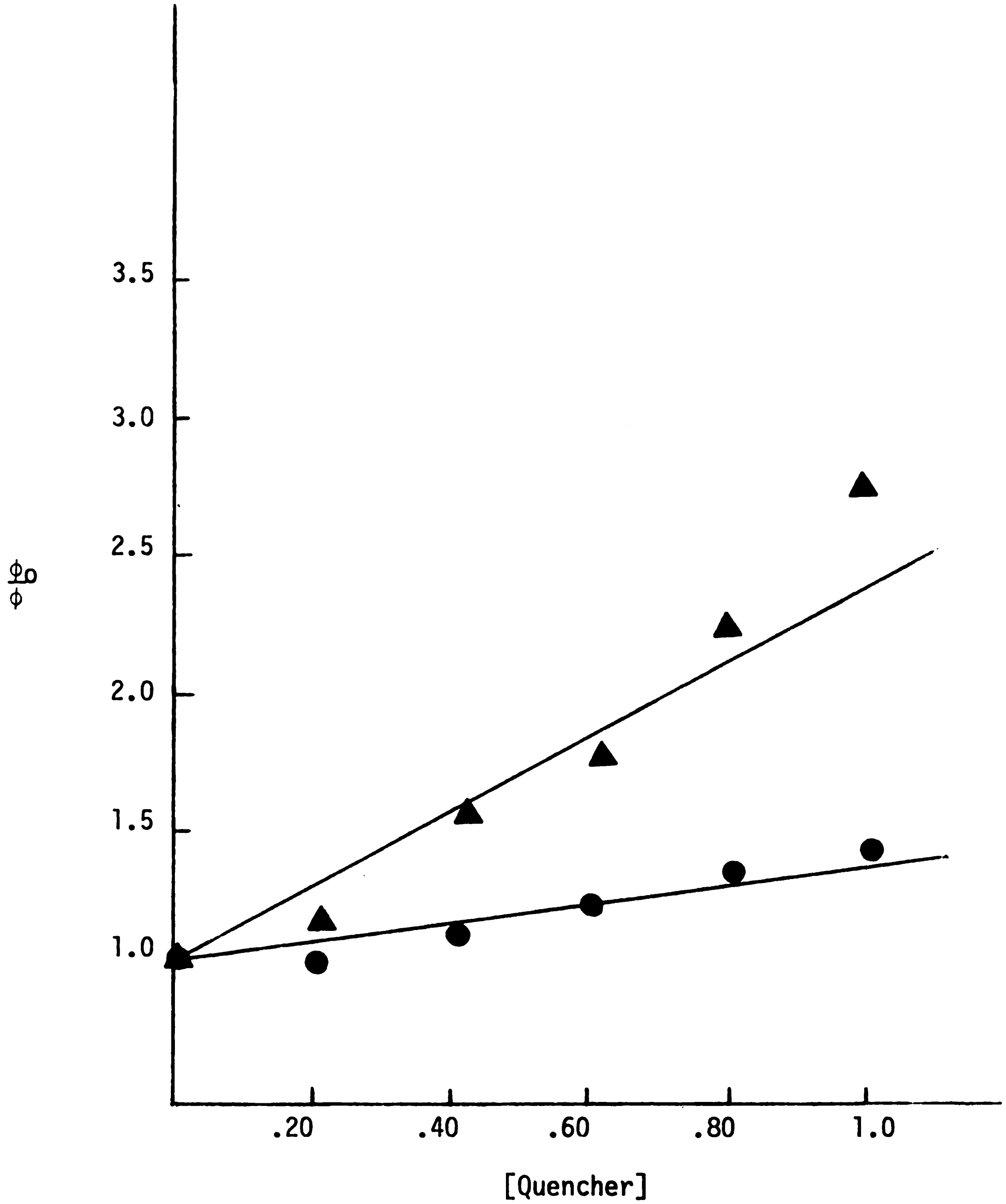

Figure 5. Stern-Volmer plot of piperylene quenching of *cis* (▲) and *trans* (●) 6-phenyl-5-hexenal products from 2-phenylcyclohexanone.

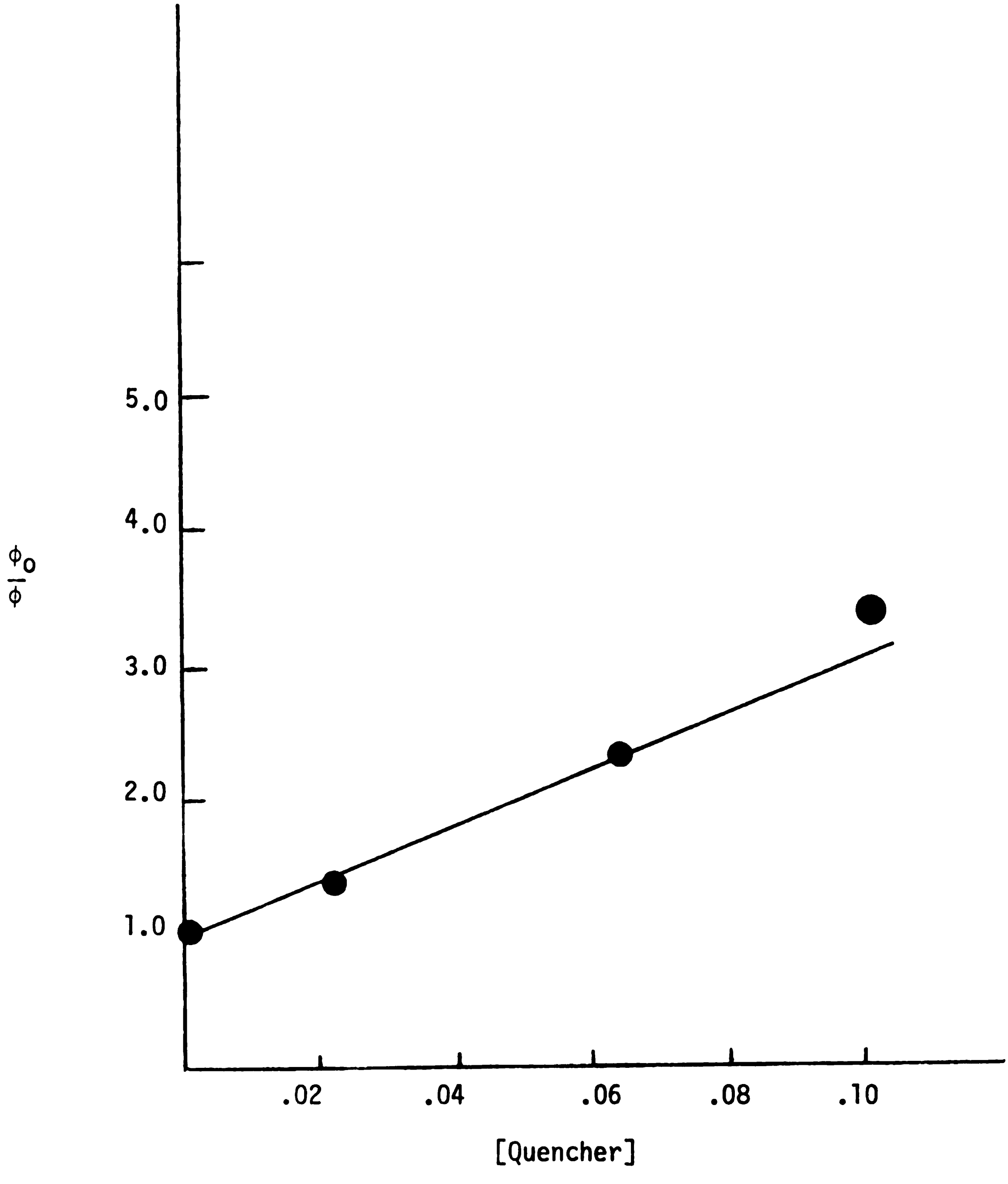

Figure 6. Stern-Volmer plot of biacetyl quenching of *trans*-6-phenyl-5-hexenal from 2-phenylcyclohexanone.

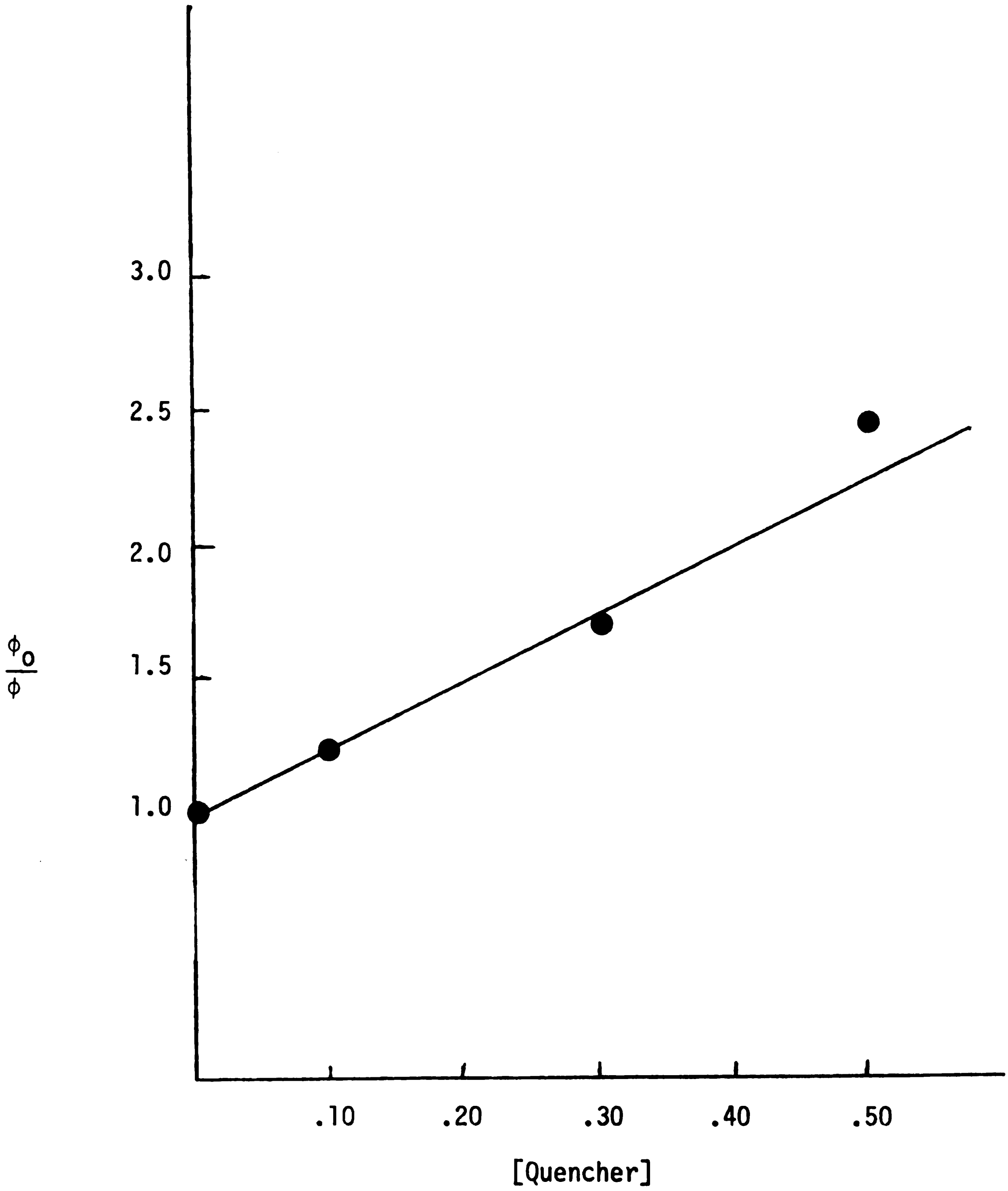

Figure 7. Stern-Volmer plot of 2,5-dimethyl-2,4-hexadiene quenching of *trans*-6-phenyl-4-t-butyl-5-hexenal from *cis*-4-t-butyl-2-phenylcyclohexanone.

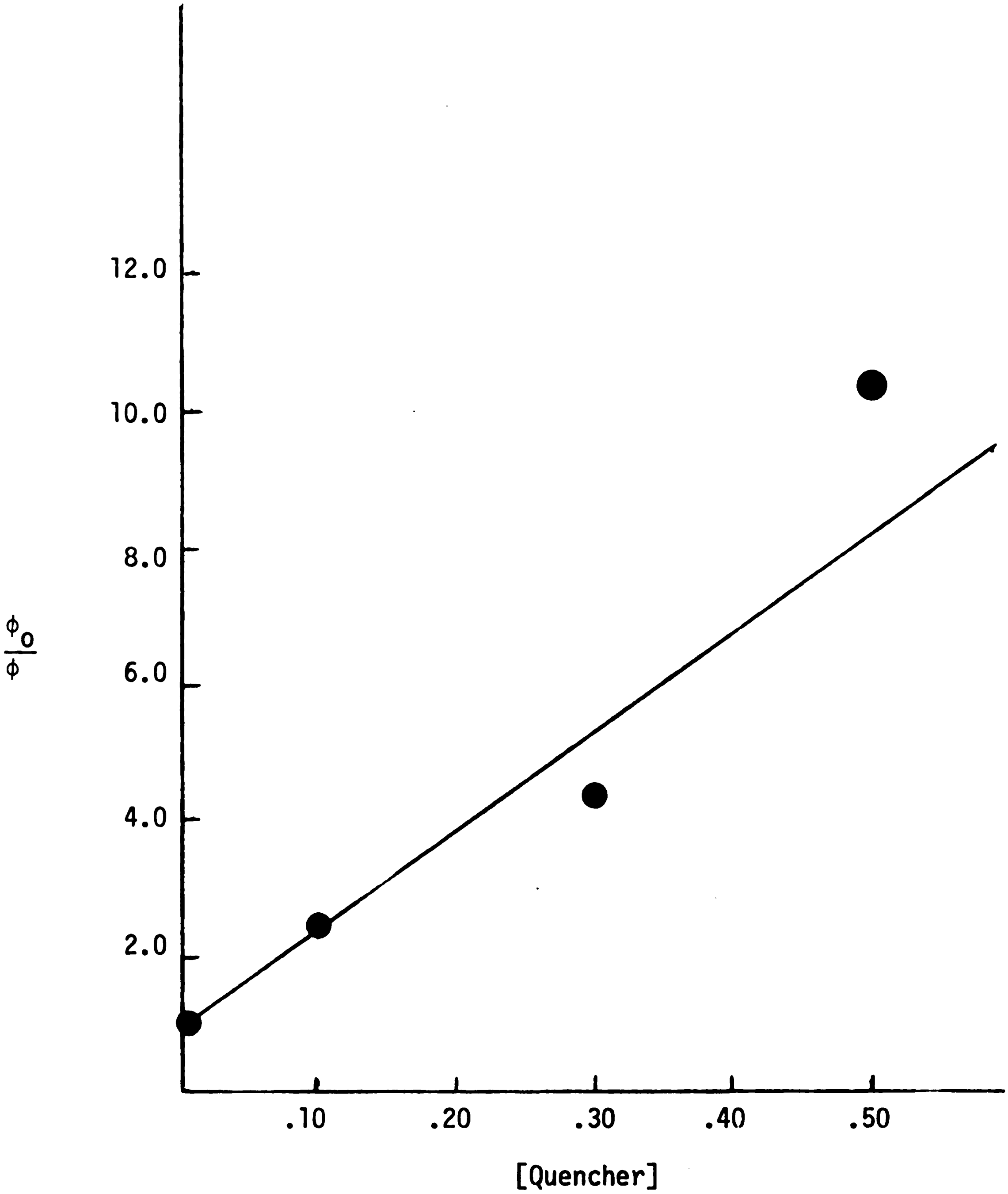

Figure 8. Stern-Volmer plot of 2,5-dimethyl-2,4-hexadiene quenching of *cis*-6-phenyl-4-t-butyl-5-hexenal from *cis*-4-t-butyl-2-phenylcyclohexanone.

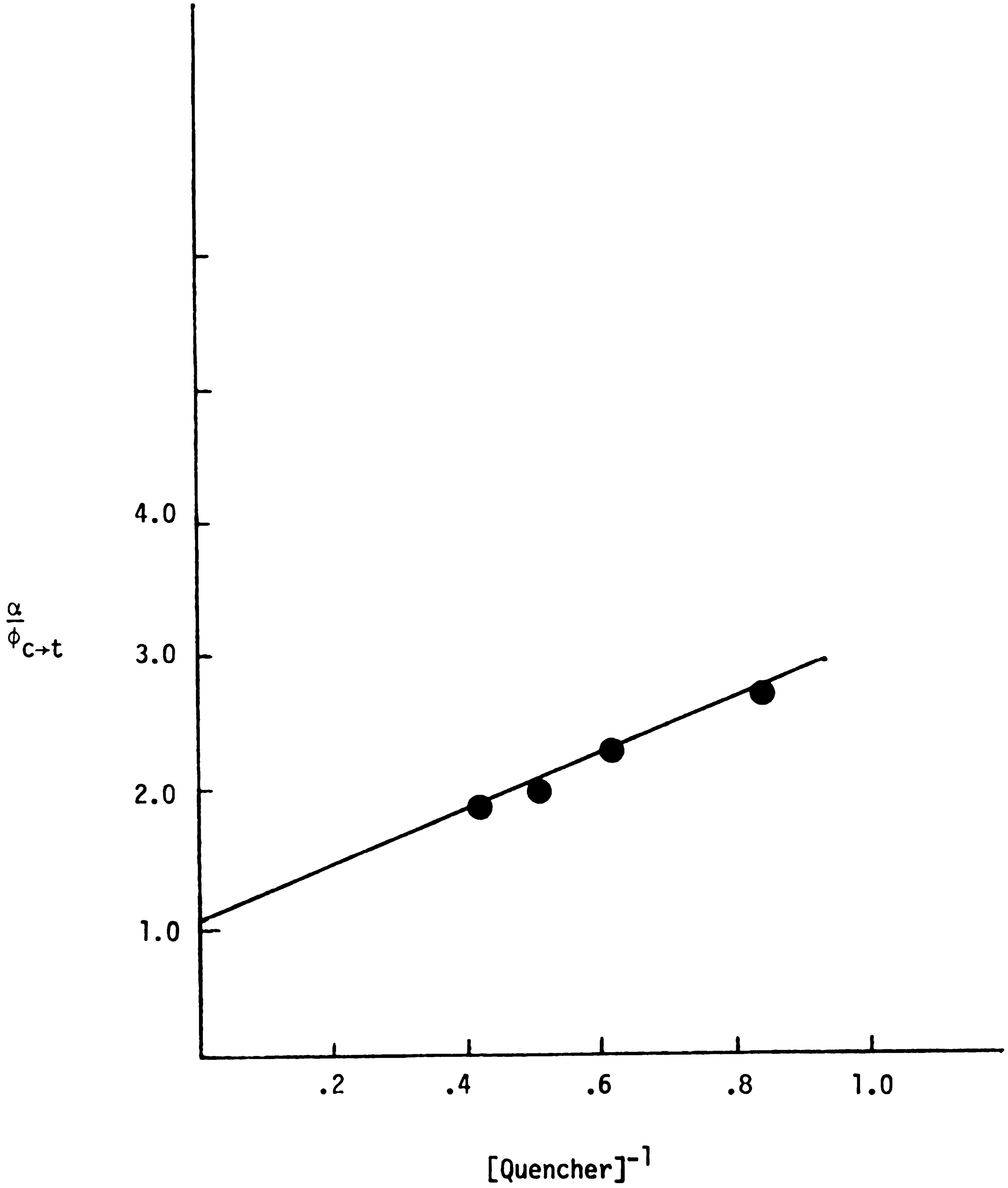

Figure 9. Intersystem crossing quantum yield determination of 2-phenylcyclohexanone.

D. Intersystem Crossing Quantum Yield

The intersystem crossing quantum yield was obtained by the sensitization of the *trans* isomerization of *cis*-piperylene, as described by Hammond and Lamola, Figure 9.[25] 2-Phenylcyclohexanone, .2 M in benzene, with varying concentrations of *cis*-piperylene was irradiated at 3130 Å. Benzene solutions, .68 M in acetone and .49 M in *cis*-piperylene, were irradiated concurrently with the 2-phenylcyclohexanone solutions. The quantum yields for 2-phenylcyclohexanone sensitized *cis* to *trans* isomerization of piperylene were measured. The acetone *cis*-piperylene solutions were used to determine light output.

The reciprocal quantum yield for sensitized *cis* to *trans* piperylene isomerization times the probability of triplet *cis*-piperylene decaying to *trans*-piperylene $\frac{\alpha}{\phi_{c \to t}}$ was plotted versus reciprocal *cis*-piperylene concentrations. The quantum yield for intersystem crossing was determined from the reciprocal intercept times .555. The quenching slope value, $k_q\tau$, was obtained from the reciprocal of the slope times the intercept. This $k_q\tau$ value agreed well with the $k_q\tau$ value from the quenching experiments. The intersystem crossing quantum yield for 2-phenylcyclohexanone was found to be 0.88. All data was analyzed by least squared treatment.

E. Singlet Sensitization

The sensitization of exclusively singlet reaction from 2-phenylcyclohexanone was attempted. The method follows the procedure outlined by Wagner.[26] Neat 1-methylnaphthalene (7.23 M) was used with varying concentrations, .05 - .25 M, of 2-phenylcyclohexanone. The

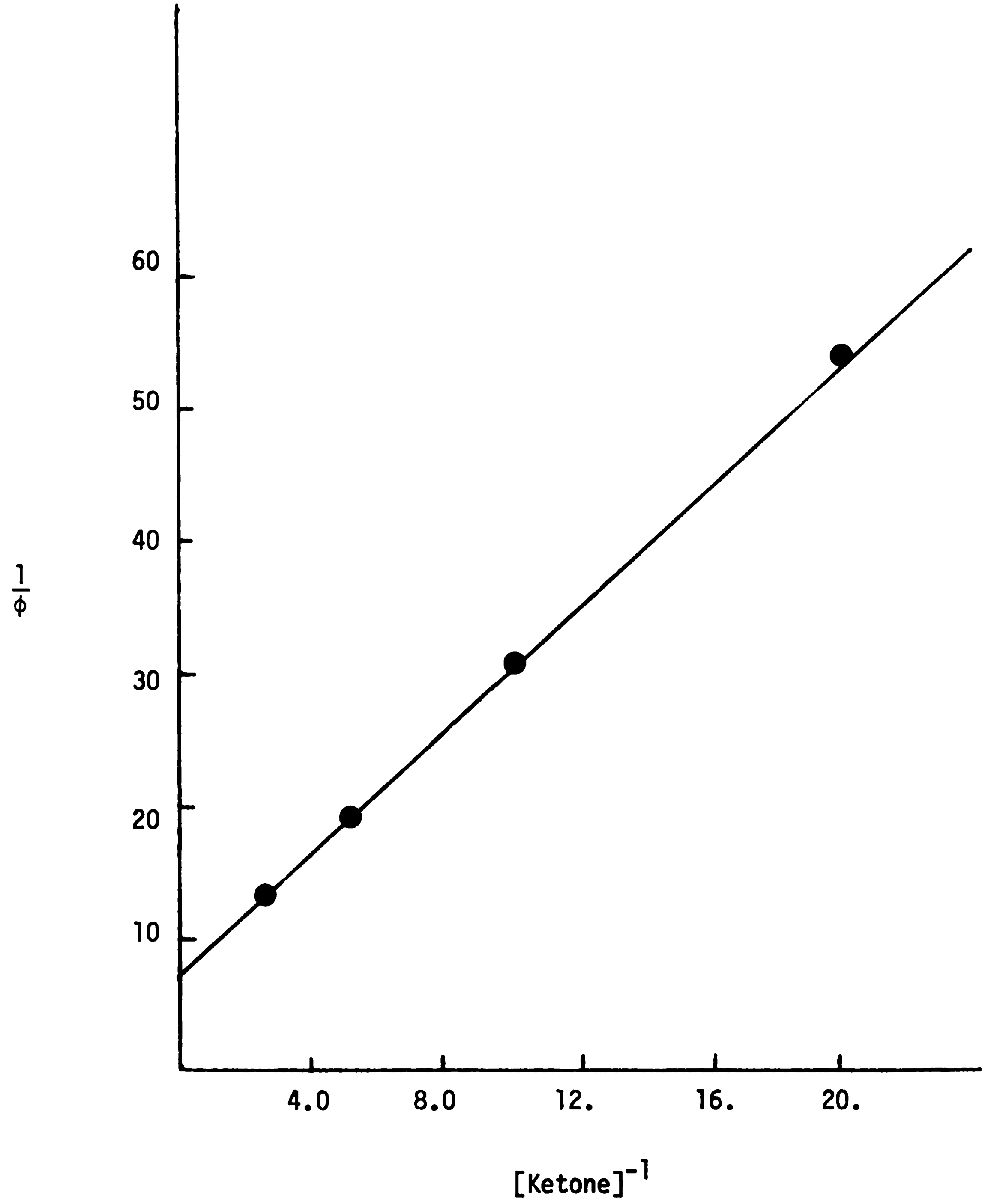

Figure 10. 1-Methylnaphthalene sensitization of *cis* and *trans*-6-phenyl-5-hexenal formation from 2-phenylcyclohexanone.

method works only for ketones with singlet and triplet energies that lie between the singlet (80 kcal/mole) and the triplet (60 kcal/mole) energies of the sensitizer 1-methylnaphthalene. The quantum yield of unquenchable, hopefully singlet, reaction is obtained from a plot of reciprocal quantum yield for alkenal formation versus reciprocal ketone concentration. The determination of the quantum yield of singlet reaction depends upon the complete quenching of the triplet. The quenching constant, k_q, for neat 1-methylnaphthalene is calculated to be 3.14×10^9 sec^{-1} M^{-1} (n = 3.1 cP[27]). Using a triplet lifetime of 1×10^{-10} sec and a quencher concentration of 7.23 M, it is calculated that only 69% of the triplet could be quenched. The quantum yield for unquenchable reaction was .14. Valerophenone actinometry was used.

F. Ultraviolet Spectra

Ultraviolet spectra of 2-phenylcyclohexanone and *cis* and *trans*-4-t-butyl-2-phenylcyclohexanone, .01 M in cyclohexane, were recorded. In accord with previously published spectra, 2-phenylcyclohexanone showed some enhancement of the n,π* absorption,[28] ε = 40 at 290 nm compared to a simple 2-alkyl substituted cyclohexanone, ε = 25 at 290 nm. *Trans*-4-t-butyl-2-phenylcyclohexanone showed a greater enhancement, ε = 82 at 290 nm, than did the *cis* isomer ε = 47 at 290 nm.

G. Emission Spectra

The fluorescence of 2-phenylcyclohexanone was recorded and appeared identical to that of 2-methylcyclohexanone in intensity and band shape both .01 M in cyclohexane with excitation at 3130 Å. 2-Phenylcyclohexanone did not show phosphorescence at 77°K; however, extremely weak phosphorescence with the vibrational structure

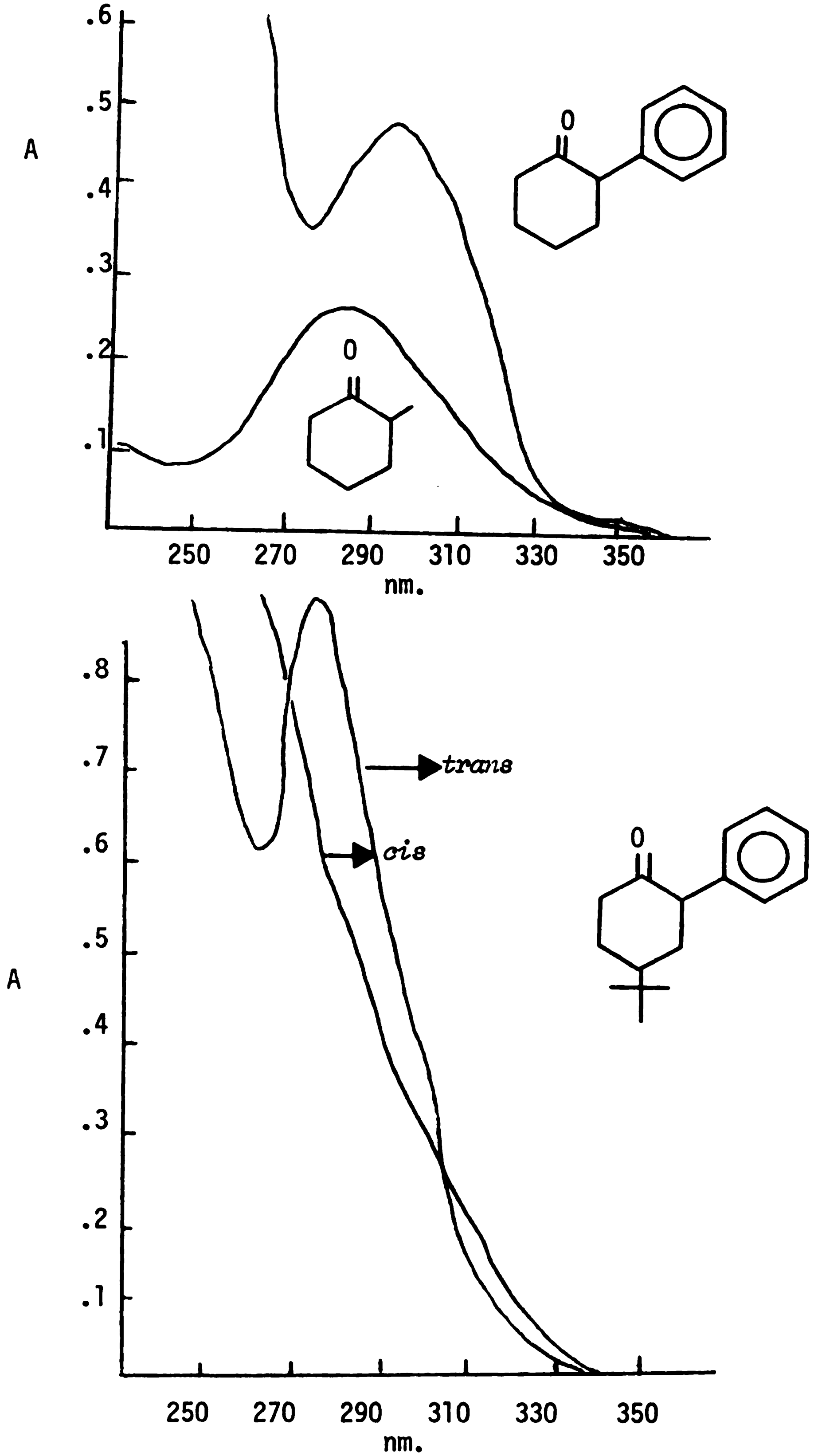

Figure 11. Ultraviolet absorption spectra of 2-phenylcyclohexanones (.01 M) in cyclohexane.

characteristic of a phenyl ketone was observed. Isolation of 3-t-butylcyclopentyl phenyl ketone from the reaction mixture of *cis* and *trans*-4-t-butyl-2-phenylcyclohexanone showed the phenyl ketone to be from a Favorskii rearrangement of the chloro-ketone used in the preparation of the 2-phenylcyclohexanones. All ketones made by the method of Newman and Farbman[29] probably are contaminated by varying quantities of such phenyl ketones.

H. Isomerization of β-methylstyrene

Dilute solutions of *cis* and *trans* β-methylstyrene in benzene containing a small amount of iodine were photolyzed.[30] After no further change was observed in the *cis* and *trans* ratios, the photolysis was stopped. The final *trans/cis* ratio was found to be 97/3 by VPC analysis of both the originally *cis* and originally *trans* solutions.

DISCUSSION

A. Products

Trans-6-phenyl-5-hexenal was identified as the major photoproduct from 2-phenylcyclohexanone confirming the earlier report by Baum.[31] *Cis*-6-phenyl-5-hexenal was also identified by Baum and agreed with Wagner and Spoerke's assumed identity. It appears that 2-phenylcyclohexanone photoreacts to give the expected alkenal products but that there is a large preference for the formation of the *trans*-6-phenyl-5-hexenal (ϕ_{trans} = .45) over the *cis* isomer (ϕ_{cis} = .01). The quantum yield for ketone disappearance (ϕ_{cis} = .65) is not accounted for by the quantum yields for alkenal formation, which accounted for 71% of the ketone disappearance. Baum has reported that no methyl esters were isolated from the photolysis of 2-phenylcyclohexanone in methanol. VPC traces from the photolysis of 2-phenylcyclohexanone show several small product peaks appearing after the solvent peak. These products were assumed to be from the decomposition of any ketene that might have been formed and from products formed by the photodecarbonylation of 2-phenylcyclohexanone. The difference between the quantum yield for ketone disappearance and the total quantum yield for alkenal formation was assumed to be a insignificant problem.

The quantum yield for disappearance of *cis*-4-t-butyl-2-phenylcyclohexanone (ϕ_{dis} = .59) like that for 2-phenylcyclohexanone was not equal to the sum of the quantum yields for alkenal formation,

($\phi_{alkenal}$ = .33), which only accounts for 56% of the ketone disappearance. VPC traces from the photolysis of *cis*-4-t-butyl-2-phenylcyclohexanone show several small peaks which can also be attributed to photodecarbonylation products or decomposition products from ketene.

Cis-4-t-butyl-2-phenylcyclohexanone was found to photoreact to form *trans*-6-phenyl-4-t-butyl-5-hexenal (ϕ_{trans} = .30) in a tenfold preference over the *cis* alkenal (ϕ_{cis} = .03). This preference was not as strong as that which was found for 2-phenylcyclohexanone.

The alkenal products from 2-phenylcyclohexanones are in effect β-substituted styrenes. To see whether or not the strong preference for formation of *trans* alkenal was unusual, the thermodynamic equilibrium ratio of *trans/cis* ratio of β-methylstyrene was measured. The equilibrium ratio of *trans/cis* β-methylstyrene was found to be 97/3, which was almost exactly the ratio of *trans/cis* 6-phenyl-5-hexenal found from the photolysis of 2-phenylcyclohexanone. If it were not for the differential quenching of the *cis* and *trans* products discussed below, it would appear that the rates of reaction from the excited state were reflecting the ground state preference for formation of the *trans* isomer over the *cis* isomer.

B. Differential quenching

As had been suspected 2-phenylcyclohexanone was found to react faster and thus to have a shorter lifetime than had been previously reported.[18] The quenching slope, $k_q\tau$, for *cis*-6-phenyl-5-hexenal formation was only 1.7 M^{-1} as compared to the published value of 15 M^{-1}. The smaller $k_q\tau$ value would be consistent with increasing rates of α-cleavage with increasing alkyl radical stability. Thus the rates of α-cleavage previously reported would now increase with the following relative rates: cyclohexanone (1), 2-methylcyclohexanone (14), 2,2-dimethylcyclohexanone (54), and 2-phenylcyclohexanone (100).

Stern-Volmer quenching slopes for *cis* and *trans*-6-phenyl-5-hexenal formed from the photolysis of 2-phenylcyclohexanone were not identical. Similarly, quenching slopes for formation of *cis* and *trans*-6-phenyl-4-t-butyl-5-hexenal from *cis*-4-t-butyl-2-phenylcyclohexanone were not identical. Stern-Volmer quenching slopes for products formed from the same excited state should have the same value.[14] The apparent presence of two distinct reactive states in these 2-phenylcyclohexanones was surprising. Photoproducts as similar as *cis* and *trans* isomers would not be expected to require different excited states for their formation.

At 3130 Å, saturated alicyclic ketones show only n,π* excitation. It has been shown that α-cleavage occurs only from the n,π* triplet in many substituted cyclohexanones. It was suggested because of the presence of two distinct reactive excited states in 2-phenylcyclohexanone that the n,π* singlet was also reacting. The stabilizing effect of the α-phenyl group may make the singlet state of these ketones sufficiently reactive towards α-cleavage to compete successfully with intersystem crossing. It appears that the photochemistry of these 2-phenylcyclohexanones is complicated by the presence of two different excited states.

C. Singlet Reaction

The singlet state of 2-phenylcyclohexanone was studied with the above mentioned possibility in mind. The intersystem crossing quantum yield of 2-phenylcyclohexanone was measured to be .88. If we assume that all the remaining 12% of excited singlet α-cleaves, then 18% of the total ketone disappearance and 26% of alkenal formation could be accounted for by singlet state reaction.

Biacetyl was used to quench the singlet state of 2-phenylcyclohexanone.[13] At 0.1 M biacetyl, 65% of the rearrangement is quenched, although this concentration can quench only 5% of the triplets. From the slope of the quenching plot in Figure 6, a singlet lifetime of 4.4×10^{-9} sec was calculated. *Cis*-6-phenyl-5-hexenal concentration doubled with small amounts of biacetyl quencher, .02 M, apparently by the *trans* to *cis* isomerization of alkenal product by the long lived biacetyl triplet (4.6×10^{-4} sec).[32] The singlet lifetime of 2-phenylcyclohexanone is similar to that of other cycloalkanones.[4]

The inability of 7 M quencher to quench all the triplet ketone molecules in the 1-methylnaphthalene sensitization experiment precludes any certain conclusion about the involvement of singlet state in the photoreactions of 2-phenylcyclohexanone. The quantum yield for unquenchable reaction was found to be .14 by this sensitization experiment, 30% of the normal unquenched value. It has already been pointed out that neat 1-methylnaphthalene should quench about 70% of the triplets, therefore it is possible that unquenched triplet reaction (30%) could account for all the unquenchable reaction (30%).

The room temperature fluorescence of 2-phenylcyclohexanone was identical to that of 2-methylcyclohexanone in intensity and band shape. The emission maximum was at 400 nm. Quantum yields for fluorescence from aliphatic ketones are typically .01 or less.[4] Apparently 2-phenylcyclohexanone is no different.

It is known that singlet states are poorly quenched by dienes, $k_q^S = 2 \times 10^7\ M^{-1}\ l^{-1}$.[33] It was found that the excited state leading to *cis*-6-phenyl-5-hexenal was 90% quenched by dienes. If the singlet state reacted to form the *cis*-6-phenyl-5-hexenal such complete quenching, by dienes, would not be expected. Indeed at 1.0 M diene only .5% of the singlet state would be quenched. Thus it appears that *cis*-6-phenyl-5-hexenal is formed from a triplet state and not a singlet state.

If the singlet state formed *trans*-6-phenyl-5-hexenal exclusively, then 26% of *trans* alkenal formation could be accounted for by singlet reaction. Triplet reaction would account for the remaining 74% of the *trans* product and also account for 100% of the *cis* product. At low diene concentrations, the *cis* and *trans* alkenal should have nearly identical quenching slopes since only triplet reaction is quenched and most of the *trans* (74%) and all of the *cis*-alkenal would be formed from this triplet. The slopes for the quenching of *cis* and *trans* alkenal were not identical at low diene concentration indicating that the *cis* and *trans* alkenals were not derived from the same triplet progenitor.

The following conclusions were drawn from the study of the singlet state of 2-phenylcyclohexanone. Although the intersystem crossing quantum yield (.88) did not rule out the possibility of some singlet reaction, the failure to quench all the triplet state precluded the singlets certain involvement. More importantly it was shown, by assuming the maximum amount of singlet reaction possible, that the extent of singlet reaction could not be large enough to explain the differential quenching observed with the *cis* and *trans*-6-phenyl-5-hexenal. An explanation of the two excited states observed in the photochemistry of 2-phenylcyclohexanone was now sought by considering configurationally and/or conformationally different triplet states.

D. Conformationally different molecules

The observation that 2-phenylcyclohexanone had a slightly enhanced n,π* absorption (ε = 40 at 290 nm) compared to 2-methylcyclohexanone (ε = 25 at 290 nm) suggested another possible explanation for the two reactive states of 2-phenylcyclohexanone. It has been shown that the degree of n,π* enhancement in α-phenyl ketones depends very strongly upon the orientation of the carbonyl and α-phenyl group.[34] It appears that the enhancement would be the largest when the phenyl group is free to swing 180°, around the bond between the carbonyl and α-carbon, maintaining the cisoid conformation of the carbonyl group and phenyl group around the bond joining them. α-Phenyl acetone is such a molecule and it shows considerable enhancement in the n,π* region (ε = 140 at 290 nm).[35] It was thought that the enhancement of the n,π* absorption in 2-phenylcyclohexanone was the sum of the enhancements caused by the phenyl group being either axial or equatorial. The greater interaction, as has been shown in other systems, occurs when the phenyl ring is in the less populated axial position, while a smaller contribution to the enhancement would come from the more populated equatorial conformation.

These two conformations could each have distinct excited states which could account for the differential quenching of the alkenals observed with 2-phenylcyclohexanone. Conformational effects on excited state reactivities have been reported.[36] It has been shown that in certain cases photoreactivity is completely dominated by conformational effects. Assuming different products are produced from the various conformers of a molecule, one can conceive of two simple distinct possibilities. 1). If photoreactivity is slower than conformational isomerization then product ratios will reflect only the relative rates of reaction from the same equilibrated excited state. 2). If conformational isomerization is slow compared to photoreactivity then excited populations will reflect the ground state population of conformers and thus be distinct excited states with individual characteristics. *Cis* and *trans*-4-t-butyl-2-phenylcyclohexanone were synthesized to test these ideas.

Photolysis of *cis*-4-t-butyl-2-phenylcyclohexanone yielded results similar to those for 2-phenylcyclohexanone, differential quenching of the *cis* and *trans* alkenal products, a large preference for formation of the *trans* isomer over the *cis* isomer, quantum yields for alkenal formation and ketone disappearance which were similar to those of 2-phenylcyclohexanone. The rate of α-cleavage from *cis*-4-t-butyl-2-phenylcyclohexanone, $\simeq 10^9$ sec.$^{-1}$, is seven times slower than from 2-phenylcyclohexanone, $\simeq 10^{10}$ sec.$^{-1}$, but considerably faster than the rate of α-cleavage from 4-t-butylcyclohexanone, $\simeq 5 \times 10^7$ sec.$^{-1}$.[22]

Surprisingly, *trans*-4-t-butyl-2-phenylcyclohexanone was found to be unreactive, the quantum yields for photoreactivity being <.001, under the analytical conditions used. Apparently the excited state does not α-cleave, for if some of the biradical formed it would have certainly recoupled forming the *cis* ketone. The *cis* ketone, with the phenyl group equatorial, is ≈ 3.1 kcal/mole[37] more stable than the *trans* ketone, with the phenyl group axial.

Any bond rotation in *trans*-4-t-butyl-2-phenylcyclohexanone which leads to the alkenal product is severely restricted by the carbonyl or 4-t-butyl group, see Figure 12.

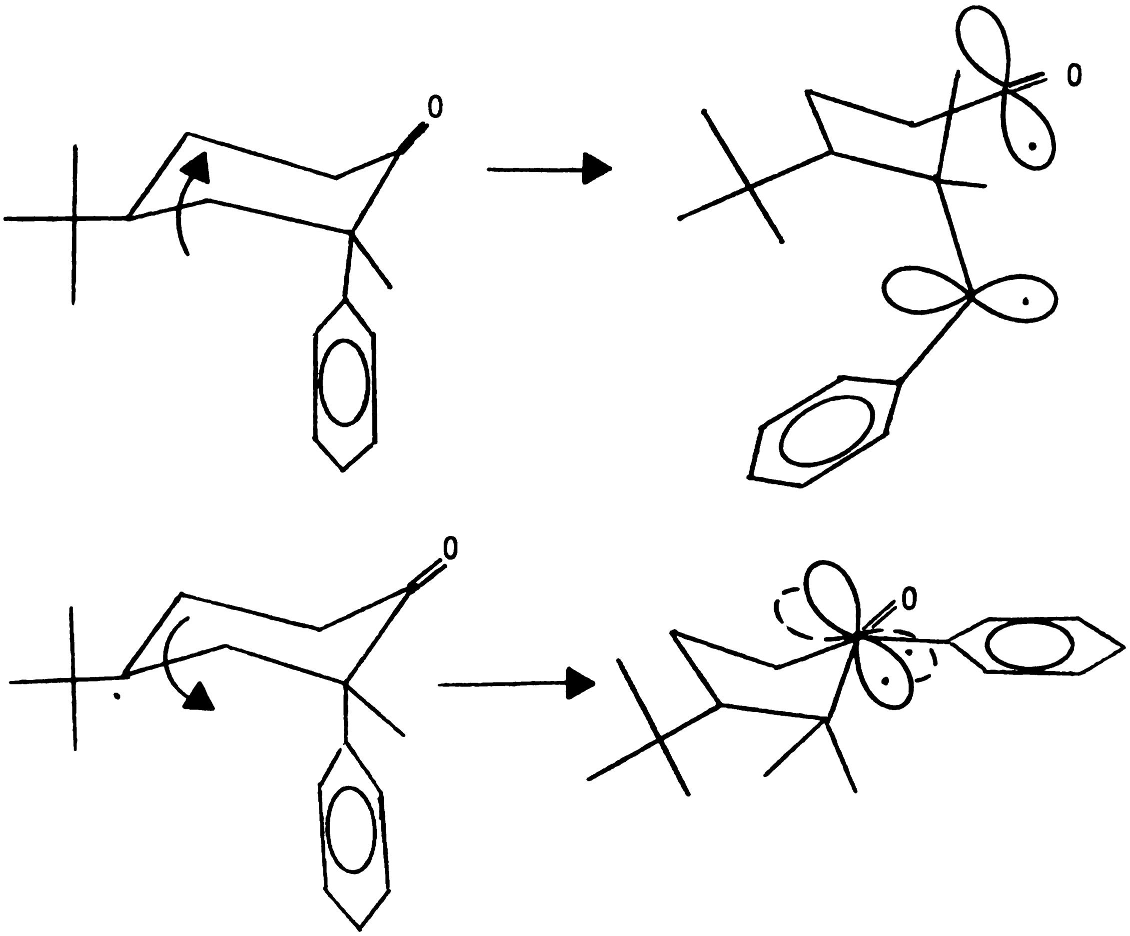

Figure 12. Alkenal formation from the chair formation of *trans*-4-t-butyl-2-phenylcyclohexanone showing t-butyl group (top) and carbonyl group (bottom) hindering required rotation of the phenyl group.

Stabilization of the radical formed by α-cleavage is difficult since the ortho hydrogens on the phenyl ring would be directly in line with the axial 4 position hydrogen. The inability of the phenyl group to stabilize the alkyl radical probably accounts for the failure of this molecule to α-cleave. It was therefore concluded that the two conformationally different 2-phenylcyclohexanones, one with the phenyl group axial and one with the phenyl group equatorial, were not responsible for the differential quenching observed with 2-phenylcyclohexanone.

It was noted with interest that unlike *trans* alkenal, formation of the *cis* alkenals from either 2-phenylcyclohexanone or *cis*-4-t-butyl-2-phenylcyclohexanone requires 180° rotation by the 1,6-biradical around the 2,3 bond. A study of *cis*-4-t-butyl-2-phenylcyclohexanone indicates that either the carbonyl group or the 4-t-butyl group, depending upon the direction of rotation, will interfere with this required rotation, see figure 13.

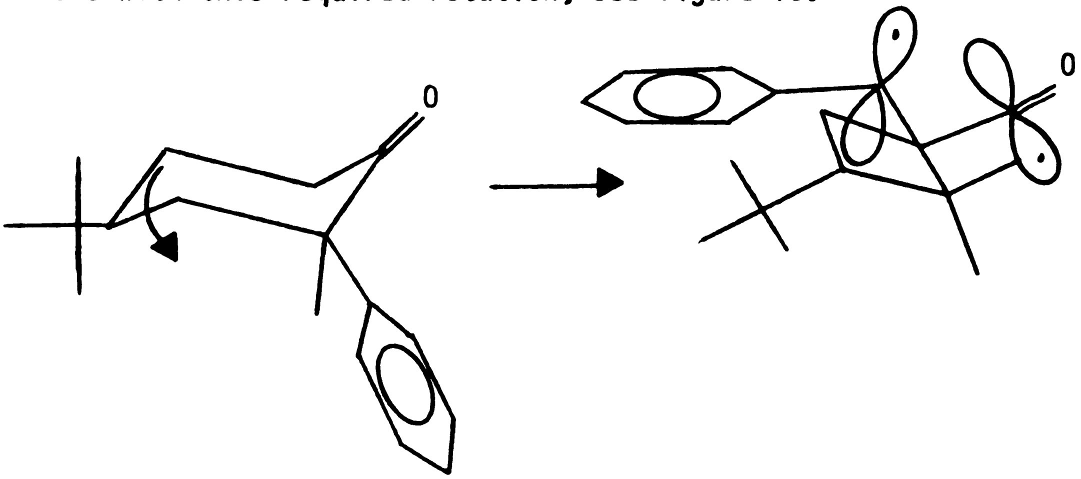

Figure 13. *Cis*-alkenal formation from the chair conformation of *cis*-4-t-butyl-2-phenylcyclohexanone.

Certainly formation of the *cis*-alkenal from the *cis* ketone could be prevented by these steric effects since photoreactivity is so strongly affected by smaller effects, such as those observed with 3-methylcyclohexanone, as discussed in the introduction. *Cis*-alkenal formation must be occurring from some conformation in which steric hinderance to the required bond rotation has been reduced.

The only conformation in which bond rotation for *cis*-alkenal formation is less hindered occurs when the cyclohexanone ring flips into a boat or twist-boat conformation. When *cis*-4-t-butyl-2-phenylcyclohexanone flips into a twist-boat conformation the phenyl ring is pushed towards a keel position,[38] here both the carbonyl and the 4-t-butyl group offer less hinderance to the required rotation, see Figure 14.

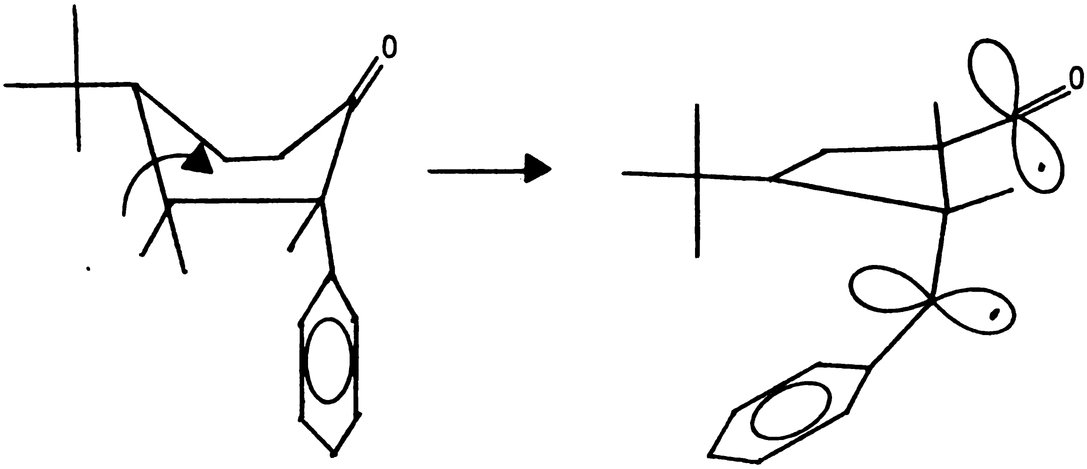

Figure 14. *Cis* alkenal formation from the twist-boat conformation of *cis*-4-t-butyl-2-cyclohexanone.

The energy difference between chair cyclohexane and its twist-boat form is 5.5 kcal/mole.[39] Since cyclohexanone has fewer

1,3-interactions than cyclohexane has, this is probably an upper limit to the energy difference. The twist-boat conformation with the phenyl ring in either a gunnel or keel position, offers little relief of eclipsing interaction since two 1,3-phenyl-hydrogen interaction have been replaced by one 1,2-eclipsing interaction, see Figures 14 and 15.

If *cis*-4-t-butyl-2-phenylcyclohexanone can flip into a twist-boat conformation to relieve some of the steric barriers for alkenal formation, what steric relief would be provided to the sterically troubled *trans*-4-t-butyl-2-phenylcyclohexanone by flipping into a twist-boat conformation? With *trans*-4-t-butyl-2-phenylcyclohexanone a flip into a twist conformation pushes the phenyl group to a gunnel position. This conformation does not relieve any of the hinderance for alkenal formation, however it does allow the phenyl group to obtain the necessary orientation to stabilize the alkyl radical,

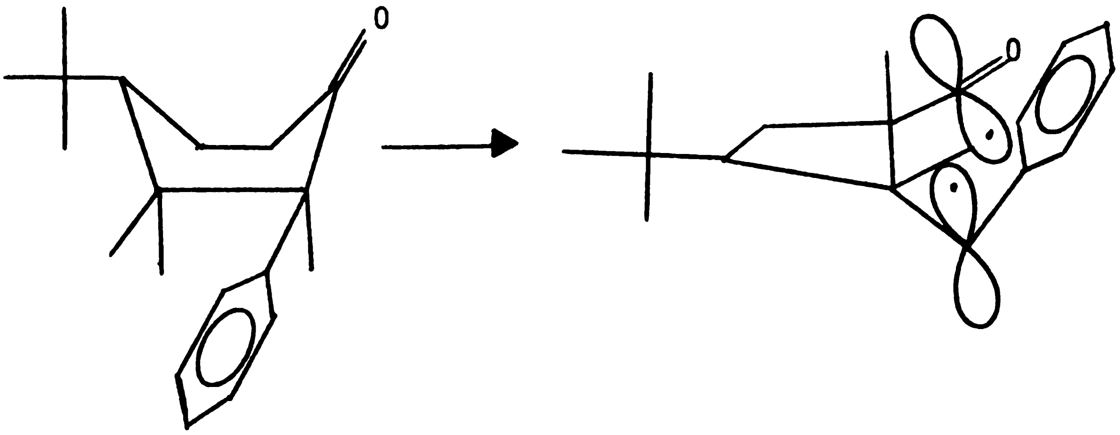

Figure 15. Alkenal formation from the twist-boat form of *trans*-4-t-butyl-2-phenylcyclohexanone.

which was not possible with the phenyl group in an axial position. Although alkenal formation is effectively blocked in this conformation, α-cleavage should occur and might be observed by the epimerization of the starting *trans* ketone to the *cis* ketone. The fact that epimerization was not observed is not understood.

It was concluded that the two excited states reacting in the two 2-phenylcyclohexanones studied could be arising from the chair and twist-boat conformers of the cyclohexanone ring. The much favored chair conformation would react to form only *trans* alkenal. The less favored twist-boat form would be reacting to product exclusively *cis* alkenal or both the *cis* and *trans* alkenal. Because of the small amounts of *trans* isomer formed from the twist-boat form its shorter lived excited state would not be detected in the quenching of the *cis* alkenal.

E. Summary

A careful study of the photochemistry of 2-phenylcyclohexanone revealed an interesting phenomenon. *Cis* and *trans*-6-phenyl-5-hexenal, the major photoproducts, were produced from two distinct quenchable excited states. The singlet state was not one of the reactive quenchable excited states. A chair conformation of the cyclohexanone ring, in which the phenyl group would be in an axial position was found to be unreactive. It was postulated that *cis*-6-phenyl-5-hexenal could be formed only when the cyclohexanone ring was in a twist-boat conformer, while *trans*-6-phenyl-5-hexenal could be formed from either the chair (phenyl ring equatorial) or the twist-boat conformer.

F. Future work

A number of interesting hypotheses could be tested in regards to the factors affecting α-cleavage in cycloalkanones.

1). Is differential quenching as observed with 2-phenylcyclohexanone occurring with other 2-substituted cyclohexanones?

2). How strongly is ketene formation in cycloalkanones affected by substituents?

3). How do α-alkyl substituents affect α-cleavage in seven and eight membered rings?

4). How important is conformation mobility in seven and eight membered rings with respect to α-cleavage?

5). Do β-phenyl groups reduce the efficiency of α-cleavage as has been observed with β-phenyl group in other photochemical reactions?[40]

EXPERIMENTAL

A. Chemicals

1. Ketones

a. 2-Phenylcyclohexanone (85%) was purchased from Aldrich Chemical Company. Numerous recrystallizations from 100% ethanol yielded ketone which showed no impurities by VPC analysis. 2-Phenylcyclohexanone was also prepared by the method of Newman and Farbman.[27] Three moles of cyclohexanone and 900 ml of water were vigorously stirred as three moles of chlorine (215 g) gas were rapidly bubbled into solution. The ice water bath was allowed to warm to room temperature with continued stirring. The dark lower layer was combined with three ether extracts of the water layer. After drying, the ether was removed and the residue distilled under vacuum, ≃ 20 mm, water aspirator. Redistillation of the reddish liquid yielded the clear 2-chlorocyclohexanone (125 g, .94 moles, 33%). To 1 mole of phenylmagnesium bromide in ether was added an ether solution of the 2-chlorocyclohexanone. Addition of the 2-chlorocyclohexanone was rapid enough to maintain reflux. Upon completion of addition the ether was distilled until a yellowish brown viscous slurry remained. Addition of benzene and overnight refluxing was followed by hydrolysis in ice water. Distillation, under vacuum .2 mm, of the residue from the ether extractions yielded the desired ketone, (25 g, 14%, m.p. 56-57°C). Numerous recrystallizations from 100% ethanol yielded pure ketone with no impurities by VPC analysis.

b. *Cis* and *trans*-4-t-butyl-2-phenylcyclohexanone were prepared by the method of Bordwell and Yee.[41] 4-t-Butylcyclohexanol (31.2 g, .2 moles) was oxidized by Jones reagent.[42] Direct chlorination of 4-t-butylcyclohexanone (22.8 g, .15 moles) in 90% acetic acid followed the procedure of Allinger *et al.*[43] Crude separation of the *cis* and *trans* isomers of 4-t-butyl-2-chlorocyclohexanone was obtained by careful vacuum distillation (3 mm). Addition of either the *cis* or *trans* isomer to phenylmagnesium bromide and work up as for 2-phenylcyclohexanone yielded predominately *cis*-4-t-butyl-2-phenylcyclohexanone. *Trans*-4-t-butyl-2-phenylcyclohexanone was prepared by careful column chromatographic separation of the reaction mixture, on silica gel with chloroform as eluent, after removal of the *cis* isomer by recrystallization and distillation. Recrystallization from 100% ethanol yielded pure *cis* ketone, m.p. 82-83, *trans* ketone m.p. 78-79°C.

c. Valerophenone was purchased from J. T. Baker Co. or prepared by addition of n-butylmagnesium bromide to benzonitrile following a procedure described by A. E. Kemppainen.[44] The ketone from either source was purified by passing the neat ketone through a small plug of alumina followed by vacuum distillation.

2. Internal standards

a. Tetradecane (Matheson, Coleman and Bell) was stirred over concentrated sulfuric acid until the acid no longer discolored. Base washing, drying over magnesium sulfate and distillation under reduced pressure followed.

b. Pentadecane (Chemical Samples Company) was used without further purification.

c. Heneicosane (Chemical Samples Company) was used without further purification.

d. *Cis* and *trans*-propenylbenzene (Chemical Samples Company) was used without further purification.

3. Quenchers

a. 1,3-Pentadiene (piperylene) (Chemical Samples Company) was used without further purification.

b. 2,5-Dimethyl-2,4-hexadiene (Chemical Samples Company) was used without further purification.

c. 2.3-Butanedione (biacetyl) (Aldrich Chemical Company) was distilled prior to use.

4. Sensitizers

a. 1-Methylnaphthalene (Aldrich Chemical Company) was used without further purification or was used after distillation from sodium. No difference was seen in results between either sample of 1-methylnaphthalene.

b. Acetophenone (Matheson, Coleman and Bell) was previously purified by Dr. R. A. Leavitt.

c. Acetone (Matheson, Coleman and Bell Spectroquality) was carefully distilled on a Perkin-Elmer NFT - 51 Annular Still. The center cut of approximately 50% was used.

5. Solvents

a. Benzene (Mallinckrodt nanograde) was stirred over concentrated sulfuric acid until no further discoloration occurred. The benzene was washed with water, saturated sodium bicarbonate and then dried over magnesium sulfate and distilled from phosphorous pentoxide through a 90 cm column packed with glass helicies. The first and last 15% were not used for solvent in photochemical studies.

b. Cyclohexane (Matheson, Colemen and Bell Spectroquality) was used without further purification.

B. Instrumentation

1. Vapor phase chromatography was the sole method of analysis for all photochemical quenching and quantum yield studies. Generally .3 microliter injections were used. Three injections per sample and three samples per data point were usually made.

a. Instruments. All analysis were carried out on either a Varian Hy-Fi Model 600D equipped with 550 oven and 328 programmer with a Leeds and Northrup Speedomax H recorder or a Varian Model 1200 gas chromatograph fitted with a flame ionization detector and Leeds and Northrup Speedomax W recorder.

b. Columns used were either 1/8" aluminum or stainless steel. The most commonly used column was 1/8" 6' to 12' aluminum column packed with 4% QF-1, 1.2% Carbowax 20 M on Chromosorb G 60/80. Other columns used were 6' x 1/8" stainless steel column packed with 5% SE-30 on DMCS treated Chromosorb W 60/80 and a 25' x 1/8" aluminum column packed with 25%, 1,2,3-tris (2-cyanoethoxy) propane on Chromosorb P 60/80 (β,β,β).

c. Standardization factors. Concentration of photoproducts can be calculated from VPC traces by comparing the area of the photoproduct to that of an inert internal standard. The relative response factor between the internal standard and the photoproduct has to be determined independently. It was assumed that the response ratio between the parent ketone and the isomeric alkenal photoproduct were identical. Parent ketone was used to determine all response ratios. (Photoproduct) = (Standardization Factor) x (Internal Standard).

d. Integration. Peak area obtained by VPC were measured by an Infotronics Model CRS - 208 automatic digital integrator. All analysis were done at the following integrator settings, tracking rate =300 micro volts, minimum peak width = 10 sec, maximum peak width = 100 sec, peak sensor gain = 4.

2. Infrared Spectra were obtained on a Perkin-Elmer Model 237-B Infrared Spectrometer. Samples were handled in one of three ways. Solids were either run as dilute solutions (10%) in CCl_4 with CCl_4 as reference. Liquids were run neat between KBr plates with air as reference.

3. Ultraviolet Spectra were obtained on a Cary Model 15 Visible Ultraviolet Spectrometer generously made available by Dr. W. A. Wood of the Michigan State University Biochemistry Department. Solvents were spectrograde cyclohexane (Matheson, Coleman and Bell).

4. Nuclear Magnetic Resonance Spectra were run on a Varian T-60 Spectrometer. Carbon tetrachloride was generally used as solvent but occasionally deuterated chloroform was used.

5. Fluorescence and Phosphorescence Spectra were obtained on an Aminco-Bowman Spectrophosfluorometer fitted with an off axis ellipsoidal mirror condensing system, a mercury xenon lamp and a side on potted IP-21 photomultiplier tube. Spectra were recorded on a Houston Instruments X-Y recorder.

C. Techniques

1. Irradiations were carried out in a merry-go-round device

described by Moses, Liu and Monroe.[45] A medium pressure mercury lamp (450 W Hanovia) was cooled by a pyrex water jacket. The jacketed lamp was surrounded by a 1 cm solution of basic .002 M $KCrO_4$. This isolated the 3130 Å region of the lamp.[46] Photolysis through pyrex reduced most of the irradiation below 3000 Å. Equivalent window size and rotation of the merry go round device around the lamp provided uniform light intensity in all sample tubes. The entire device is maintained at room temperature by a water bath of 15 gal. capacity.

Test tubes used for photolysis were either Corning Pyrex 13 x 100 mm or Kimble Kimax 13 x 100 mm culture tubes. Tubes of uniform 13 mm diameter were used for photolysis. Tubes were checked for uniformity of glass clarity, smoothness of lip for sealing on degassing apparatus. Tubes were washed in a dilute solution of warm Lakeseal Laboratory Glass Cleaner. (Peck's Product Co.) Repeated rinsing in distilled water was followed by oven drying. Tubes were drawn out to leave enough room on the closed end for 2.6 ml of solution and enough on the open end to give a good seal on the rubber stopper used for degassing. Tubes were filled with 2.6 ml of solution using a 5 ml syringe fitted with a 15 cm needle. Three freeze-thaw degassings at 77°K to a minimum pressure of 10^{-3} torr were used on most samples.

2. Actinometry was performed in either of two ways. The most commonly used and the simplest way consisted of measuring acetophenone formation (ϕ = .33)[40] from valerophenone (.1 - .3 M) in benzene. Tetradecane was used as an internal standard (.005 - .015 M). Actinometers were treated the same as all photolysis samples as described above. Conversion was generally kept to less than 5%. Three

actinometer tubes were generally used for determining light output.

3. Intersystem crossing quantum yields were determined following the method of Lamola and Hammond.[12] Light output was measured by acetone sensitized *cis*-to-*trans* isomerization of *cis*-piperylene. 2-Phenylcyclohexanone was used to sensitize the *cis* to *trans* isomerization of various concentrations of *cis*-piperylene. Quantum yields for *cis* to *trans* isomerization were calculated. The *cis* to *trans* conversion of *cis*-piperylene was kept to less than 5%. Any isomerization of the *trans*-piperylene to *cis*-piperylene is accounted for by the expression for the concentration of triplet state *cis*-piperylene formed. (*cis*-piperylene*) = (*cis*-piperylene)$_0$ x ln (.555/.555 - %*trans*), where % *trans* is the measured ratio. The reciprocal quantum yield for the sensitized *cis* to *trans*-piperylene isomerization times the probability of triplet *cis*-piperylene decaying to *trans*-piperylene was plotted versus reciprocal *cis*-piperylene concentration. Estimates of the quantum yields for *cis* to *trans* piperylene isomerization as a function of piperylene concentration were made from G. F. Vesley's data.[47] A generalized equation for the kinetics of a sensitized photochemical reaction has been derived by Wagner.[14]

4. Identification of *trans*-6-phenyl-5-hexenal was made after 2-phenylcyclohexanone, 1.0 M in benzene, was irradiated at 3130 Å until no decrease in parent ketone concentration was apparent by VPC analysis. Careful chromatography of the photolysis mixture on alumina with benzene as eluent yielded the desired unknown photoproduct. The yellow oil was identified by NMR and IR.[48] IR, CCl_4 solution, showed the following absorptions; 2710 cm^{-1} aldehydic hydrogen, 1725 cm^{-1}

aliphatic carbonyl, 970 cm^{-1} *trans* vinyl hydrogen. NMR, CCl_4, shows signals at δ 9.7, triplet 1 H aldehydic, δ 7.2 singlet 5 H aromatic, δ 6.3 multiplet 2 H vinylic δ 2.2 multiplet 6 H aliphatic. Positive identification of 6-phenyl-5-hexenal as the *trans* isomer was made by comparison of the vinylic region of a known sample of *trans* β-methylstyrene to that of the 6-phenyl-5-hexenal. The vinylic region of the *trans* β-methylstyrene was virtually identical to that of the photoproduct. The vinylic region of *cis*-β-methylstyrene did not match well with that of the photoproduct. Identification of the photoproducts from *cis*-4-t-butyl-2-phenylcyclohexanone was accomplished after irradiation, .2 M in benzene. Careful chromatography of the photolysis mixture on silica gel with chloroform as eluent yielded the photoproducts. IR showed, CCl_4 solution, 2710 cm^{-1} aldehydic hydrogen, 1725 cm^{-1} aliphatic carbonyl, 970 cm^{-1} *trans* vinyl hydrogen stretch. NMR, in CCl_4 solution, δ 9.6 and δ 9.4 triplets 1 H aldehydic, δ 7.2 singlet 5 H aromatic δ 6.2 multiplet 2 H vinylic, δ 2.0 multiplet 5 H aliphatic, δ .9 singlet 9 H t-butyl group.

The appearance of two aldehydic protons in the NMR spectrum of 6-phenyl-4-t-butyl-5-hexenal is in agreement with the report of Baum. Baum reported that the aldehydic protons in *cis* and *trans*-6-phenyl-5-hexenal had slightly different chemical shifts. Molecular models show that with the *cis* alkenal the carbonyl and phenyl groups can come close enough to each other to interact while with the *trans* alkenals very little if any interaction is possible. These different interactions probably explain the widely different retention characteristics of these isomers observed during the VPC analysis.

D. Photokinetic Data

Tables 3 - 8 contain the experimental data from which the results were obtained. Stern-Volmer quenching data and quantum yield data were obtained simultaneously. Quencher concentrations, product/ standard ratios and ϕ_0/ϕ values are listed along with the light output (I_a) and analytical conditions. For the intersystem crossing yield determination the following values are listed, *cis*-piperylene concentration, *trans/trans + cis,* the quantum yield for *cis-trans* isomerization, the probability of triplet *cis*-piperylene decaying to *trans* piperylene.

Table 3. Piperylene Quenching of 2-Phenylcyclohexanone

Quencher	Product (*trans*)/Standard	ϕ_0/ϕ
.0000	1.044	1.00
.2019	1.024	1.02
.4038	.939	1.11
.6057	.878	1.19
.8076	.790	1.32
1.010	.750	1.39

Quencher	Product (*cis*)/Standard	ϕ_0/ϕ
0000	.0308	1.00
.2019	.0276	1.12
.4038	.0200	1.54
.6057	.0176	1.75
.8076	.0140	2.20
1.010	.0114	2.70

I_a = .0213 einstein/liter 2 hrs. at 3130 Å.

Benzene solution .0992 M in 2-phenylcyclohexanone .0054 M in heneicosane, 2.6 ml per tube, 3 tubes per data point, Analysis 9' x 1/8" QF-1 (4%) Carbowax 20 M (1.2%) on Chromosorb G 60/80 175° Varian 1200.

Table 4. 2,5-Dimethyl-2,4-hexadiene quenching of 4-t-butyl-2-phenylcyclohexanone.

Quencher	Product (*trans*)/Standard	ϕ_o/ϕ
0000	1.611	1.00
.1000	1.308	1.23
.3000	.9440	1.71
.5000	.6590	2.44

Quencher	Product (*cis*)/Standard	ϕ_o/ϕ
0000	.1573	1.00
.1000	.0658	2.39
.3000	.0366	4.30
.5000	.0155	10.4

I_a = .0246 einstein/liter 4 hrs. at 3130 Å.

Benzene solution .1006 M in *cis*-4-t-butyl-2-phenylcyclohexanone, .0046 M in pentadecane, 2.6 ml per tube, two tubes per data point. Analysis 6' x 1.8" SE30 (5%) on Chromosorb W 60/80, 193°C. Varian Hy-Fi Model 600D equipped with oven 550 and 328 programmer.

Table 5. Biacetyl Quenching of 2-Phenylcyclohexanone

Quencher	Product (*trans*)/Standard	ϕ_0/ϕ
0000	.8242	1.00
.0211	.6046	1.36
.0634	.3641	2.26
.1056	.2512	3.28

Benzene solution .2004 M in 2-phenylcyclohexanone, .0104 M in heneicosane, 2.6 ml per tube, two tubes per data point, 3 hrs. at 3130 Å.

Analysis 9' x 1/8" QF-1 (4%) Carbowax 20 M (1.2%) on Chromosorb G 60/80, 175°C Varian 1200.

Table 6. 1-Methylnaphthalene sensitization of 2-phenylcyclohexanone

Ketone	Heneicosane	Product(*cis* and *trans*)/Standard	ϕ
.0502	.0025	.00106	.0189
.1008	.0025	.00188	.0335
.2016	.0025	.00302	.0535
.4065	.0025	.00434	.0774

I_a = .0561 einstein/liter 4 hrs. at 3130 Å.

1-Methylnaphthalene solvent, 2.6 ml per tube, two tubes per data point.

Analysis 9' x 1.8" QF-1 (4%) Carbowax 20 M (1.2%) on Chromosorb G 60/80, 175°C Varian 1200.

Table 7. Intersystem Crossing Quantum Yield for 2-Phenylcyclohexanone.

cis-piperylene	*trans/cis + cis*	ϕ_{c-t}	α
1.209	.0042	.205	.55
1.612	.0037	.241	.56
2.015	.0034	.277	.57
2.418	.0031	.301	.58

I_a = .0248 einstein/liter acetone .683 M *cis* piperylene .497 M benzene solvent 2-phenylcyclohexanone =.21 M

Analysis 25' x 1/8" 25% 1,2,3-tris (2-cyanoethoxy) propane on Chromosorb W 60/80 (β,β,β) Varian Hy-Fi Model 600D.

Table 8. Standardization Factors

$$\text{Standardization Factor} = \frac{\dfrac{\text{Ketone}}{\text{Standard}}\ \text{(actual)}}{\dfrac{\text{Ketone}}{\text{Standard}}\ \text{(measured)}}$$

Standardization Factor for Heneicosane and 2-Phenylcyclohexanone

Sample	Known ratio	Measured ratio	Standard Factor
0	18.34	11.72	1.56
3	18.34	10.20	1.80

Standardization Factor = 1.68

Standardization Factor for Pentadecane and 4-t-butyl ketone

Sample	Known ratio	Measured ratio	Standard Factor
1	.0873	.0862	1.01
2	.9827	.9833	.999
3	10.04	9.785	1.03

Standardization Factor = 1.01

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