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PART I: INTRAMOLECULAR CHARGE-TRANSFER QUENCHING OF EXCITED STATES BY SULFUR

PART II: RADICAL β-CLEAVAGE VIA EXCITED STATES AND PHOTOGENERATED DIRADICALS

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Michael Jeffrey Lindstrom

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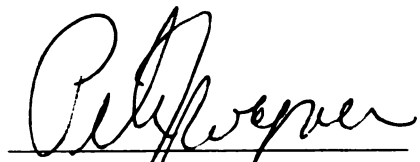

Major professor

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PART I

INTRAMOLECULAR CHARGE-TRANSFER QUENCHING OF EXCITED STATES BY SULFUR

PART II

RADICAL β-CLEAVAGE VIA EXCITED STATES AND PHOTOGENERATED DIRADICALS

By

Michael Jeffrey Lindstrom

A DISSERTATION

Submitted to
Michigan State University
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1978

ABSTRACT

PART I

INTRAMOLECULAR CHARGE-TRANSFER QUENCHING OF EXCITED STATES BY SULFUR

PART II

RADICAL β-CLEAVAGE VIA EXCITED STATES AND PHOTOGENERATED DIRADICALS

By

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PART I

The photochemistry of various benzoylsulfides, sulfoxides, and sulfones was studied to determine the effect of chain length upon the rate of interaction of the excited benzoyl with the sulfur moiety.

In general, the rate of charge-transfer quenching increases as the number of carbons between the donor and acceptor decreases, with the exception of the α-thioalkoxyacetophenones, which quench more slowly than the β- and γ-thioalkoxyketones. The observed trend is rationalized in terms of the ease of formation of various sized rings, which, in turn, corresponds to approach of donor and acceptor. Increasing the oxidation state of the sulfur group also dramatically decreases the rate of charge-transfer quenching.

In addition to Type II fragmentation, the α-thioalkoxyacetophenones undergo competitive β-cleavage in

varying degrees. The extent of β-cleavage is found to depend upon the nature of the leaving group. For instance, 2-methylsulfinylacetophenone reacts exclusively via β-cleavage, whereas for 2-thiomethylacetophenone such cleavage is a minor pathway. The competition between γ-hydrogen abstraction and β-cleavage was separated and its effect upon k_{ct} determined.

The rate data obtained through the standard Stern-Volmer analysis were separated into inductive and resonance constituents. The following order, listed in decreasing ability to stabilize an adjacent radical center, was determined: OMe > SPh ~ SBu ~ OPh > OH > SOBu > Ph > Me > SO_2Me.

PART II

Phenacylsulfides

A number of substituted phenacylsulfides were synthesized and studied to further investigate the nature of β-cleavage.

All compounds studied underwent photoinduced β-cleavage in benzene with the concomitant production of the appropriate acetophenones and radical coupling products. The addition of 0.05M benzenethiol was observed to maximize the quantum yields and eliminate the formation of out-of-cage coupling products.

The rate constants of β-cleavage were determined by standard Stern-Volmer analysis. Electron donating substituents on the benzene ring decrease the rate of β-cleavage

significantly. The rate of β-cleavage is also dependent on the nature of the leaving group. Relative rates of β-cleavage for various groups were determined as follows: SPh > SOMe > StBu > SO_2Me.

δ-Substituted Phenyl Ketones

A variety of δ-substituted phenyl ketones were synthesized and studied. All compounds formed varying amounts of 4-benzoyl-1-butene in addition to acetophenone upon uv irradiation. The effect of solvent upon the ratio of Type II products to 4-benzoyl-1-butene is negligible, indicating that elimination of HX was occurring by a free radical pathway rather than ionically. The mechanism was determined to proceed by initial 1,4 diradical formation followed by β-cleavage and rapid in-cage disproportionation to yield 4-benzoyl-1-butene and HX. Comparison of Type II products to 4-benzoyl-1-butene ratios allowed calculation of relative rates of β-cleavage for a variety of groups.

A novel cyclic phenyl ketone system in which the δ-substituents and benzoyl groups are inaccessible to each other was synthesized. Smooth photolytic elimination of HX in these cases was observed. A fairly large rate enhancement for γ-hydrogen abstraction was observed for trans-4-bromo-1,4-dimethyl-1-benzoylcyclohexane and is attributed to anchimeric assistance by bromine.

Competitive α-cleavage in these compounds revealed information concerning ground state equilibria.

To Joan

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INTRODUCTION

Objectives and Organization

The original objective of this thesis was, in a broad sense, to investigate structure-reactivity relationships in organic photochemistry. In particular, the effect of chain length upon the rate of intramolecular charge-transfer quenching of the excited benzoyl group by various sulfur moieties was to be investigated. However, as work progressed, unexpected results provided the stimuli to stray away from the original objective and pursue other paths. Thus, this thesis is composed of two separate but related parts. In an attempt to avoid duplication, the introduction is composed of one part in which topics relevant to the problems investigated will be discussed. The results for each part are treated separately and the corresponding discussion follows each section. The experimental section presents the procedures and materials for both parts.

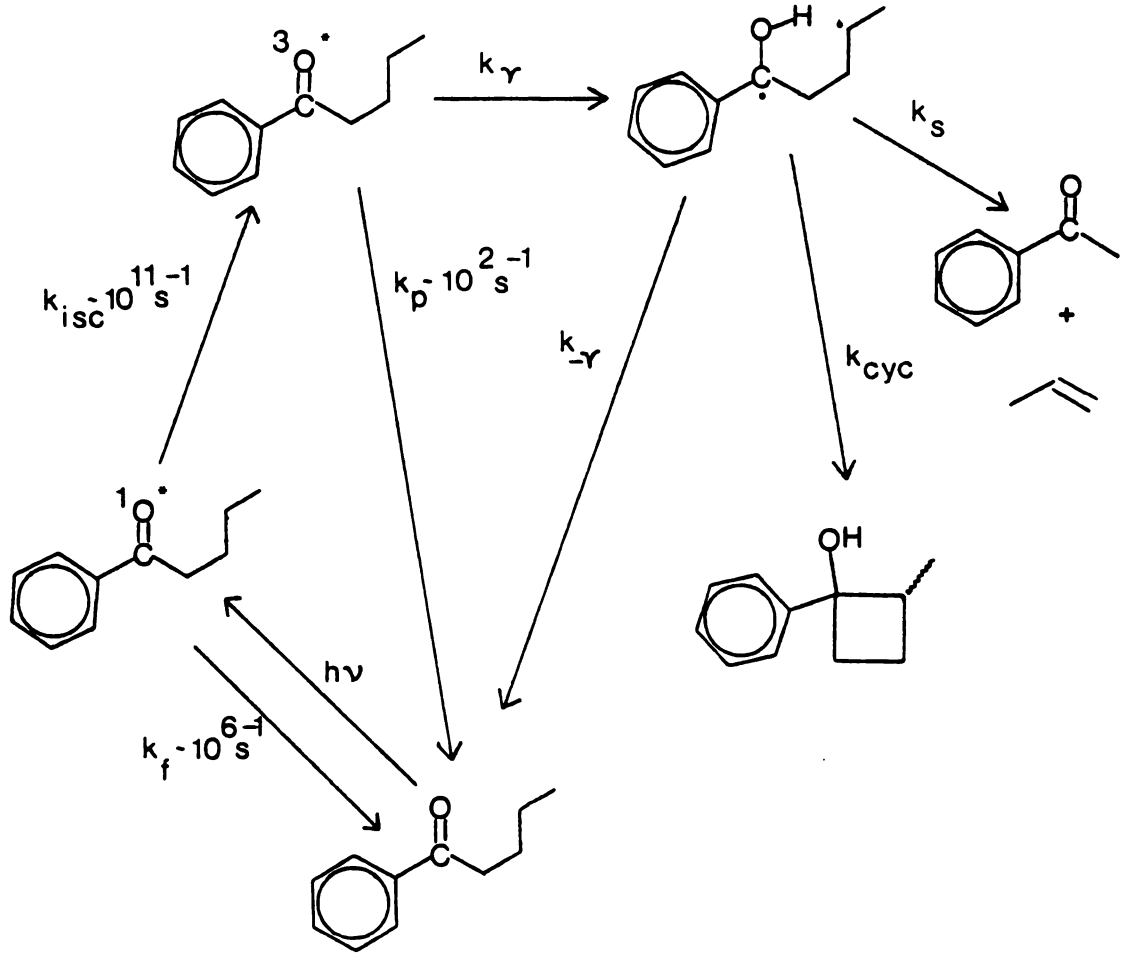
Part I deals solely with the effect of chain length upon the rate of quenching of the benzoyl group by various sulfur moieties. In particular, ketosulfides, sulfoxides, and sulfones were investigated.

Part II deals with radical β-cleavage of halo and thiyl radicals both from excited states and photogenerated biradicals. This includes the photochemistry of phenacyl sulfides, δ-halo and δ-thiyl substituted valerophenones, and a novel cyclic system.

The Norrish Type II Reaction

Ketones possessing γ-hydrogens undergo a characteristic 1,5-hydrogen transfer, followed by cleavage or cyclization, upon uv irradiation. Norrish and Appleyard[1] first observed this reaction in 1934 while investigating the photodecomposition of methyl butyl ketone in the gas phase. Yang,[2] who first noted the formation of cyclobutanols as products, hypothesized the intermediacy of a 1,4 biradical. Compelling evidence for the intermediacy of a 1,4 biradical has been presented by Wagner[3] and others.[4] In fact, the biradical from γ-methoxybutyrophenone has actually been trapped by thiols.[5] The formation of cleavage products and of cyclobutanols is collectively called the Norrish Type II Reaction. Scheme 1 presents the accepted mechanism.

For phenyl alkyl ketones the rate constant of intersystem crossing, k_{isc}, is $\sim 10^{11} sec^{-1}$; so fluorescence, k_f, which occurs on the order of $10^6 sec^{-1}$, and radiationless decay, k_d, are negligible. As a result, the intersystem crossing yield is equal to unity in most cases.[6] Thus, the triplet manifold is responsible for the majority of the photoreactivity observed in phenyl ketones. Population of



Scheme 1. The Mechanism of the Norrish Type II Reaction.

the triplet manifold results in γ-hydrogen abstraction followed by either reverse hydrogen transfer, $k_{-\gamma}$, or product formation, k_{cyc} and k_s. Reverse hydrogen transfer was first postulated by Hammond and Wagner[7] to account for low quantum yields in systems where the excited state reactivity was thought to be fairly high. Wagner[8] later showed that reverse hydrogen transfer could be eliminated by the use of polar solvents or various additives that are good Lewis bases.

Phosphorescence, k_p, from the triplet is slow relative to γ-hydrogen abstraction and is usually insignificant.

The reactivity of the triplet benzoyl group has been likened by Walling and Gibian[9] to that of the t-butoxy radical. Numerous studies investigating structure-reactivity relationships have been presented by Wagner[10] and others,[11] but in general the variation in reactivity in phenyl ketones can be ascribed to either inductive or resonance effects on the γ-radical center or the nature of the excited triplet.

Electron releasing substituents on the benzene ring generally lead to decreased or negligible reactivity of the triplet benzoyl due to the interposition of a $^3\pi,\pi^*$ state, which is unreactive toward γ-hydrogen abstraction.[12] Interestingly, Wagner[13] has shown that thermal equilibration of the $^3\pi,\pi^*$ state with the higher $^3n,\pi^*$ state in p-methoxy-valerophenone is taking place. In this case, the low equilibrium concentration of the upper $^3n,\pi^*$ state produces a low observed rate constant for γ-hydrogen abstraction.

Little work concerning the effect of structure on cleavage:cyclobutanol ratios has been done, but Lewis[14] has shown that α-substitution on phenyl alkyl ketones markedly increases the amount of cyclization. Wagner[15] has noted an analogous effect for α-fluoroketones.

Charge-Transfer

The phenomenon of charge-transfer was first invoked by Mulliken[16] to explain why iodine is violet in CCl_4 but

brown in benzene. Formally, one can envision charge-transfer as simply partial electron transfer from a donor to an acceptor.

$$D^{\cdot\cdot} + A^{\cdot} \longrightarrow D^{\cdot+}A^{-} \text{(C-T complex)}$$

Photochemical precedent was established by Leonhardt and Weller[17] who demonstrated by flash spectroscopy that solutions of perylene and an amine undergo electron transfer, a process not possible in the ground state. Cohen[18] later observed that benzophenone is photoreduced by Et_3N 1000 times faster than by isopropanol. This led to the suggestion that rapid electron transfer from the nitrogen to the triplet carbonyl followed by proton transfer was responsible for the observation. Davidson and Lambert[19] later suggested the following mechanism for the photoreduction of benzophenone by amines.

$$R_2C{=}O^{*3} + RCH_2\ddot{N}R_2 \longrightarrow (R_2\dot{C}\text{-}O^{-} \quad R_2\dot{\overset{+}{N}}CH_2R) \longrightarrow R_2\dot{C}OH + R\dot{C}HNR_2$$

Later experiments by Cohen and Chao[20] definitively ruled out direct hydrogen abstraction from the amine.

The ionization potentials of amines have been correlated with their ability to interact with triplet ketones. Cohen and Guttenplan[21] noticed an inverse relationship between the ionization potential of the amines and their ability to photoreduce a ketone. However, they noticed the results were inconsistent with full electron transfer and could best be described as partial electron transfer. The fact that small

solvent effects were noted, relative to those for ground state electron transfer reactions, further supported their contention. Wagner and Kemppainen[22] also noted no increase in the rate of quenching of valophenone by triethylamine or t-butylamine in CH_3CN relative to that in benzene.

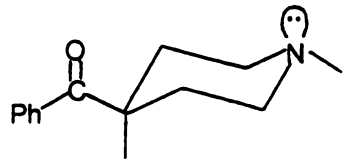
Other types of heteroatoms have demonstrated the ability to form C-T complexes with excited carbonyls. Thioethers have been shown to quench the phosphorescence of benzophenone and also its photoreduction by isoborneol.[23] Interestingly, little photoreduction by sulfides possessing α-hydrogens was found to occur, indicating that proton transfer analogous to that observed for amines[24] is not an important pathway for sulfides. The 4-carboxybenzophenone sensitized photooxidation of methionine was found to occur by initial charge-transfer complexation between triplet benzophenone and sulfur followed by internal electron transfer to nitrogen.[25]

Phosphorous, antimony, and arsenic have also been postulated to quench the Type II Reaction of butyrophenone via a charge-transfer interaction.[26]

Intramolecular charge-transfer quenching has not been extensively investigated. However, Wagner[27] has found that intersystem crossing yields decrease and rates of quenching increase as an amino group is moved closer to the carbonyl. These facts indicate a competition between intersystem crossing, charge-transfer quenching, and γ-hydrogen abstraction. Type II products have also been shown to arise from

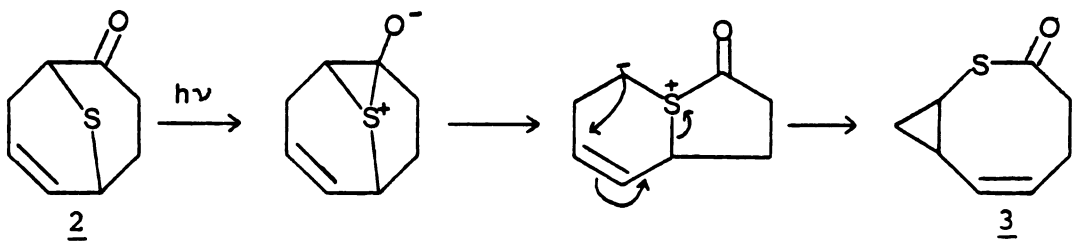
the C-T state of γ-dimethylaminobutyro-2-napthone by protonation of the ketyl radical anion.[28]

Strict conformational requirements for C-T quenching were demonstrated by Wagner and Scheve.[29] The lack of C-T quenching in 1-e demonstrates that such quenching requires through-space orbital overlap.



1-e

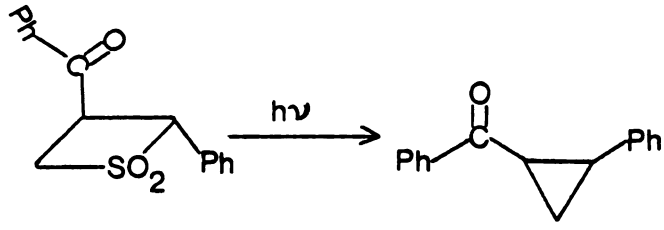
Intramolecular charge-transfer quenching of excited ketones with sulfur has not been previously measured. However, a "C-T type" intermediate has been proposed for the photorearrangement of 2 to 3.[30]



2 3

A variety of optically active sulfoxides have been shown to undergo photochemically induced stereomutation, resulting in racemization.[31] The charge-transfer nature of these transformations is indicated by the fact that energy transfer would be at least 10-15 kcal endothermic.[32]

Sulfones have not been previously shown to interact with excited carbonyls, but the conversion of 4 to 5 hints at some sort of direct interaction.[33]



4 5

Energy Transfer

Other mechanisms besides C-T interactions are possible for the quenching of triplets. When an acceptor has a lower triplet energy than the donor, triplet-triplet energy transfer occurs. Other types of energy transfer are possible, but in the case of phenyl ketones, intersystem crossing yields are usually high so triplet-triplet energy transfer predominates. Usually, the effectiveness of a quencher is determined by the position of its lowest triplet level and not by its molecular structure.[34] On the other hand, the rate of exothermic triplet energy transfer in solution is dependent on the viscosity of the solvent, which for moderately viscous solvents is described by the modified Debye Equation.[35]

$$k_{et} = k_{diff} = 8RT/2000\eta$$

However, in less viscous solvents the quenching rate constant is still lower than the calculated diffusion rate. The

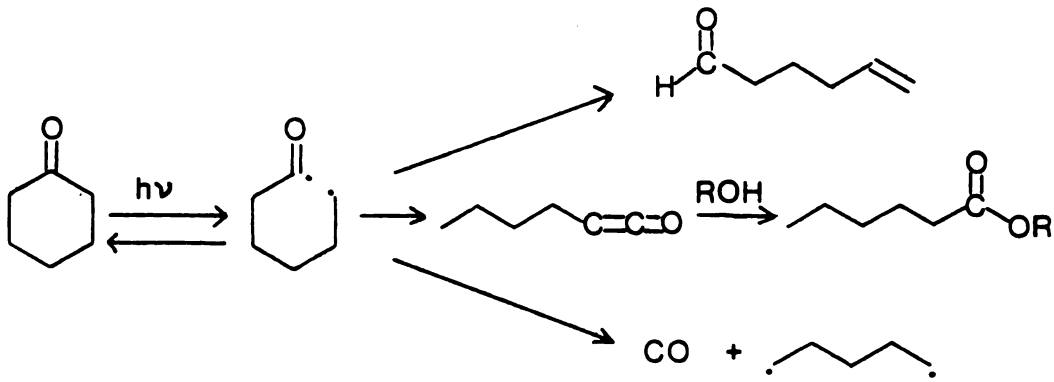
implication of this is that there is inefficiency in the energy transfer which may be indicative of a preferred configuration of the donor and acceptor molecules.

Interestingly, not much is known about the steric requirement to promote the exchange interaction needed for transfer; however, Wagner and McGrath[36] have shown that transfer is rapid at van der Waals separation of donor and acceptor. Cowan and Baum[37] have measured k_{et} in styryl-ketones where the separation between donor and acceptor varies from 2 to 4 methylene groups. Predictably, when $n = 2$, $k_{et} = \sim 10^{11}\ M^{-1}sec^{-1}$. As n is increased to 4, $k_{et} = \sim 10^{9}\ M^{-1}sec^{-1}$. Thus, the number of conformations in which the two ends of the molecule interact decreases rapidly as the number of methylene groups is increased. It has been estimated that for every 1.2Å increase in the distance between the donor and acceptor, an order of magnitude decrease in k_{et} results.[38]

The Norrish Type I Reaction, α-Cleavage

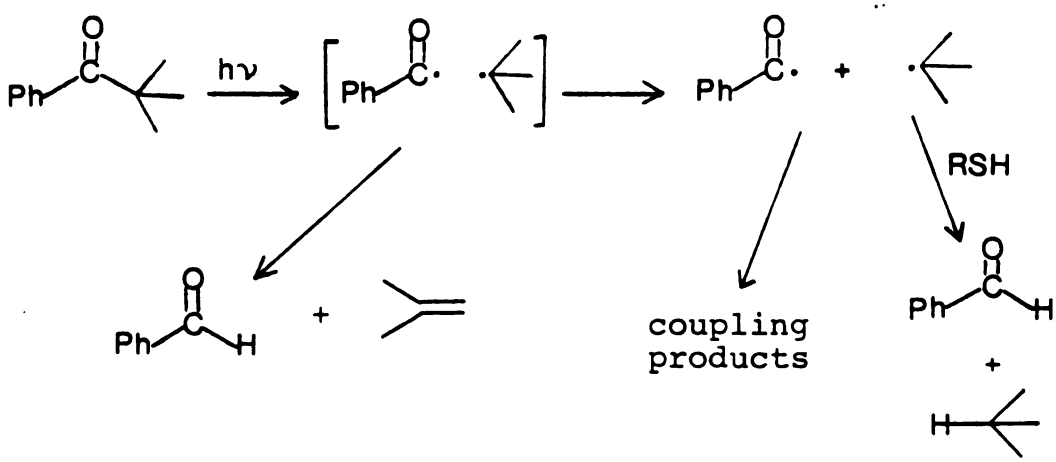
The Norrish Type I Reaction involves homolytic cleavage of the 1,2 bond in cyclic and acyclic ketones, resulting in the formation of an acyl and alkyl radical pair. Many other classes of compounds, such as the carboxylic acid derivatives,[39] which possess a heteroatom as the α-substituent, also undergo this reaction. Thus, the reaction will be referred to, in a broader sense, as α-cleavage. The fate of the radical pair varies depending largely on structural

features,[40] but the three possible routes as pictured in Scheme 2 are recoupling, two modes of disproportionation, and decarbonylation.



Scheme 2. Available Pathways for the Biradical Formed from α-Cleavage

In phenyl ketones, α-cleavage leads to a slightly different picture than that presented in Scheme 2. As shown below in Scheme 3, the photolysis of pivalophenone[41] results in the formation of a benzoyl radical and a t-butyl radical. In-cage radical-radical recombination competes effectively with

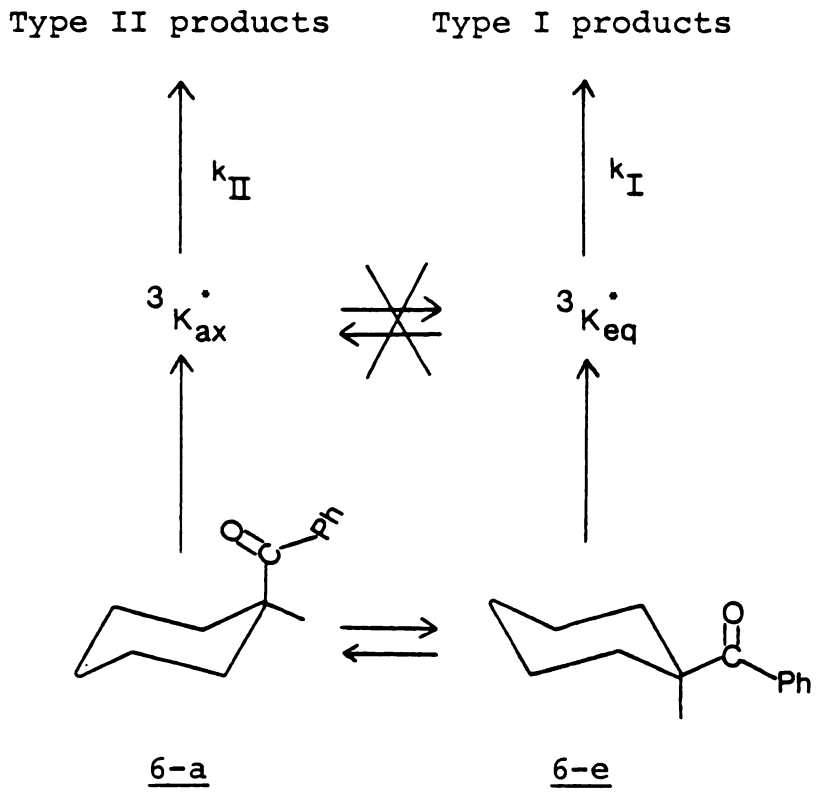


Scheme 3. Photolytic Cleavage of Pivalophenone.

diffusion out of the cage. Disproportionation to form benzaldehyde and isobutylene can occur in-cage or out-of-cage. However, in the presence of thiols, which are efficient radical scavengers,[42] the intermediate radicals are trapped, thus minimizing or eliminating out-of-cage disproportionation and coupling.

While α-cleavage is the major mode of decomposition for certain aliphatic ketones,[43] it is usually not observed for normal phenyl alkyl ketones. Even in α,α-dimethylvalerophenone, γ-hydrogen abstraction is sufficiently fast that α-cleavage comprises only about 5% of the reactivity.[44] In fact, triplet aliphatic t-butyl ketones α-cleave about 4000 times faster than triplet pivalophenone.[45] The nature of the excited state has also been found to greatly influence the rate of α-cleavage. Lewis[46] has shown that pivalophenone, which has a lowest $^3n,\pi^*$ state, cleaves with a rate constant of around 10^7 sec^{-1}; but p-phenylpivalophenone, which has a $^3\pi,\pi^*$ lowest triplet, is essentially stable to photolysis.

Lewis[47] has noted a competition between α-cleavage and γ-hydrogen abstraction in some very elegant work with several cycloalkyl phenyl ketones. Scheme 4 presents the conformational possibilities for 1-methyl-1-benzoylcyclohexane (6) Interestingly, 6-a only undergoes γ-hydrogen abstraction, whereas 6-e exhibits only α-cleavage. In this case, k_{II} and k_I were faster than interconversion of the excited conformers, so product ratios reflected the ground state population of the respective conformers. Thus, Lewis determined that the ground state equilibrium was about 65:35 in favor of 6-e.



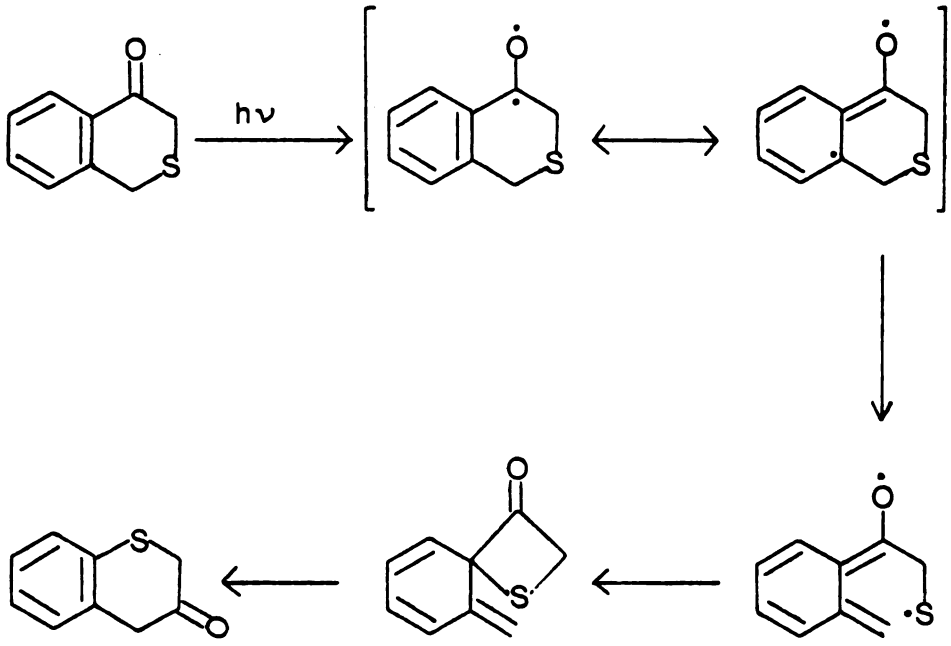
6-a 6-e

Scheme 4. Photochemical Fate of 1-Methyl-1-Benzoylcyclohexane.

β-Cleavage

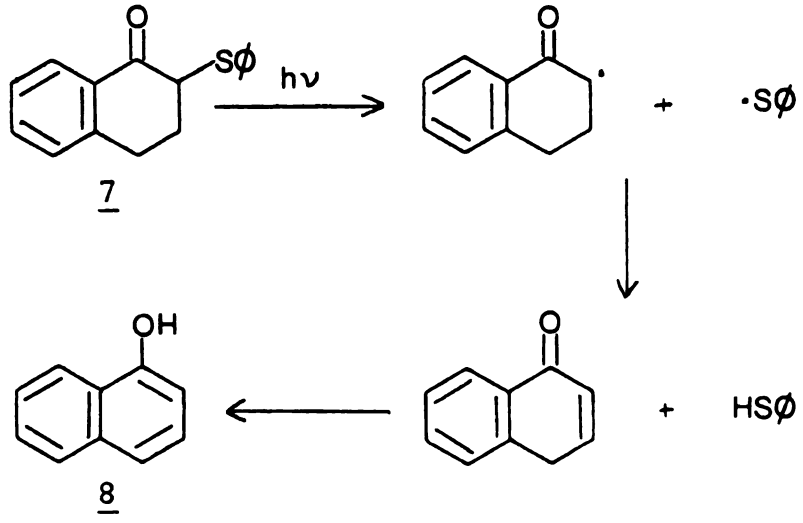
There is a wide variety of photochemical reactions of carbonyl moieties in which electronic excitation results in initial cleavage of one of the bonds β to the carbonyl group.[48] Also typical are β-eliminations in free-radical reactions.[49] In fact, α-haloacetophenones and, to a lesser extent, phenacylsulfides have been used to photoinitiate polymerization reactions.[50] To date no kinetic studies on β-cleavage reactions of ketones have been done.

There are, however, several interesting photoreactions involving β-elimination. The photoisomerization of isothiochroman-4-one is a classic example.[51]

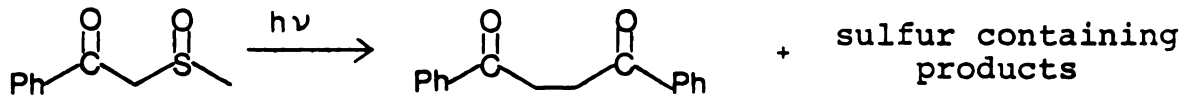


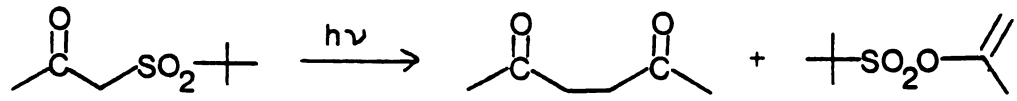
Surprisingly, when the benzene ring is replaced with a napthalene, the reaction does not go.

The photolysis of 7 yields 8 by β-cleavage of ·SPh followed by disproportionation and aromatization.[52]

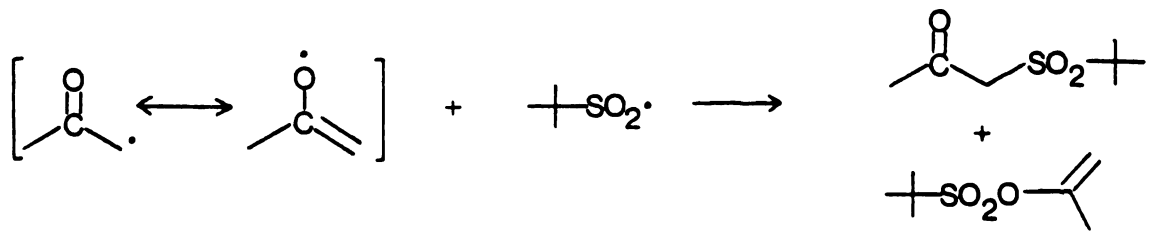


In other systems,[53,54] where disproportionation is not possible, coupling products are observed as shown below.





The formation of the vinylsulfonate in the second example arises from radical recombination on oxygen rather than carbon as shown below.



Stern-Volmer Kinetics

The quantum yield for any photochemical process can be expressed as a product of probabilities. Thus, for the Type II Reaction:

$$\phi_{II} = \phi_{isc} k_\gamma \tau P \qquad (1)$$

$$\frac{1}{\tau} = k_\gamma + k_d \qquad (2)$$

where ϕ_{isc} equals the intersystem crossing yield, k_γ equals the rate constant of hydrogen abstraction, k_d equals the rate constant of triplet decay, τ equals the triplet lifetime, and P equals the probability that the diradical will go on to product. In the presence of an external quencher, (2) becomes:

$$\frac{1}{\tau} = k_\gamma + k_d + k_q[Q] \qquad (3)$$

where k_q equals the bimolecular rate constant. Utilizing these facts, the Stern-Volmer Equation (4)[55] can be derived.

$$\frac{\phi^o}{\phi} = 1 + k_q \tau [Q] \qquad (4)$$

In the presence of polar solvents or Lewis bases, which minimize reverse hydrogen transfer, the maximum quantum yield can be expressed:

$$\phi_{max} = \phi_{isc} k_\gamma \tau_\tau \qquad (5)$$

Thus,

$$k_\gamma = \frac{\phi_{max}}{\tau} \qquad (6)$$

The sensitization equation (7)[56] allows measurement of ϕ_{isc}.

$$\phi_{sens.}^{-1} = \phi_{isc}^{-1} \alpha^{-1}(1 + \frac{1}{k_t \tau [Q]}) \qquad (7)$$

Thus, in the case of 1,3-pentadiene, α equals 0.55 and a plot of $0.55/\phi_{c \rightarrow t}$ versus [cis-1,3-pentadiene]$^{-1}$ yields a straight line in which the reciprocal of the intercept equals ϕ_{isc} and intercept divided by the slope equals $k_t \tau_\tau$.

PART I

INTRAMOLECULAR CHARGE-TRANSFER QUENCHING OF EXCITED STATES BY SULFUR

Results

Preparation and Product Identification

A variety of ketosulfides of varying chain length were prepared by S_n2 displacement on an appropriate haloketone by the corresponding sodium thiolate. The ketosulfoxides and sulfones were prepared by hydrogen peroxide oxidation of the corresponding ketosulfides. The corresponding compounds and their abbreviations are listed in Tables 1, 2, and 3. For example, α-thiomethylacetephenone is denoted as 2-SMe and α-methylsulfinylacetophenone as 2-SOMe.

All compounds except 3-SBu, 3-SOBu, and $3\text{-}SO_2Bu$ produced acetophenone upon uv irradiation. These compounds were stable to irradiation at 3130Å and underwent no disappearance of ketone. Acetophenone was actually isolated by preparative vpc for 4-SBu but was subsequently identified either by the appearance of a singlet at 2.3δ in the nmr or by comparison of its vpc retention time with that of an authentic sample. The olefinic moiety which results from cleavage was not observed since it probably came out under the solvent peak on the vpc. Small peaks which were assumed to be the

cyclobutanols were sometimes observed and usually corresponded to about 10-15% of the total product. No evidence of the corresponding thietanols was observed for 2-SMe and 2-SBu.

The δ-substituted valerophenones were found to produce varying amounts of 4-benzoyl-1-butene (4-BB) in addition to acetophenone. The mechanism for the formation of 4-BB will be discussed in Part II.

Quantum Yields

Quantum yields for acetophenone formation and other products were determined by irradiation at 3130Å in a merry-go-round apparatus at 25°C. Solutions containing 0.05M ketone in benzene, which sometimes contained various additives, were irradiated in parallel with degassed benzene solutions of 0.1M valerophenone, which served as an actinometer.[57] All samples were degassed by two or three freeze-thaw cycles prior to irradiation. Percent conversion of the ketone and/or actinometer was kept below 10% whenever possible. Disappearance quantum yields were measured at typically 20-30% conversion. Product to standard ratios were measured by vpc. The associated error was estimated by duplicate runs and was generally found to be about ±5% for acetophenone formation and about ±10-15% for disappearance quantum yields.

Polar solvents or Lewis base additives had little or no effect upon the quantum yields. The maximum quantum

yields, ϕ_{max}, were usually obtained in benzene containing 1.0M dioxane. The quantum yields are listed in Tables 1, 2, and 3.

Quenching Studies

Stern-Volmer quenching slopes were performed at 3130Å or 3660Å by photolysis of 0.05M ketone solutions containing varying amounts of either 1,3-pentadiene or 1-methylnapthalene. Conversions were usually kept below 10% for the tube with no quencher, and the slopes were linear out to a ϕ^{o}/ϕ value of about 7 or 8. The associated error was estimated by duplicate runs to be about ±10%. Values obtained from these studies are listed on Tables 1, 2, and 3. A representative Stern-Volmer plot is presented in Figure 1.

The bimolecular rate constants for quenching by n-butylsulfide, n-butylsulfoxide, and n-butylsulfone were determined by an analogous procedure through the utilization of butyrophenone and p-methoxybutyrophenone as substrates. No quenching of acetophenone formation was detected when n-butylsulfone was used as a quencher. The bimolecular rate constants are listed in Table 4, and the quenching plots are presented in Figure 2.

Intersystem Crossing Yields

Intersystem crossing yields were determined by parallel irradiation at 3130Å of 0.05M ketone solutions containing varying amounts of cis-1,3-pentadiene and a 0.10M

acetophenone solution containing 1.0M cis-1,3-pentadiene, the latter serving as an actinometer.[58] Plots of reciprocal quencher concentrations were linear. In all cases where measurement was possible, ϕ_{isc} was equal to 1. Irreproducible results were obtained for the α-thioalkylacetophenone and the δ-substituted valerophenones due probably to the production of low concentrations of radicals. The intersystem crossing yields are presented in Tables 1, 2, and 3, and a representative sensitization plot is presented in Figure 3.

Table 1. Photokinetic Data for Various Ketosulfides.

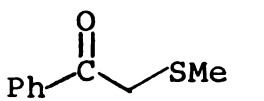
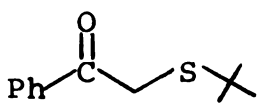
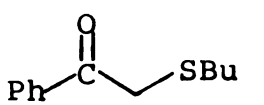
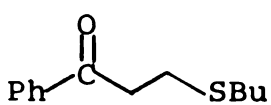
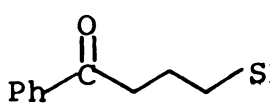
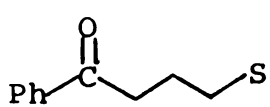
Compound	ϕ_{-K}	ϕ^{a}	ϕ_{max}^{b}	ϕ_{isc}	$k_q\tau$
 (2-SMe)	0.41	---	0.28 0.35 ± 0.02[c]	---	2.06 ± 0.2
 (2-StBu)	---	<0.001	0.04 ± 0.005[c]	---	3.9 ± 0.4
 (2-SBu)	0.48 ± 0.07	0.43	0.43 ± 0.03 0.53 ± 0.03[c]	---	1.6 ± 0.1
 (3-SBu)	---	---	---	1.0	1.10 ± 0.20[g]
 (4-SBu)	0.21	0.13	0.18 ± 0.01 0.10[d,e]	1.0	1.70 ± 0.20 2.0[g]
 (4-StBu)	---	---	0.27	1.0	1.73 2.2[g]

Table 1. (cont'd.)

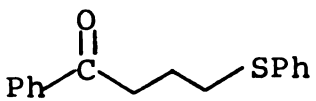
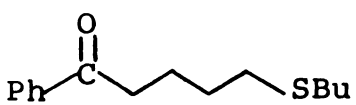
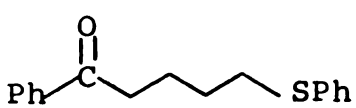
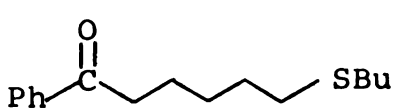
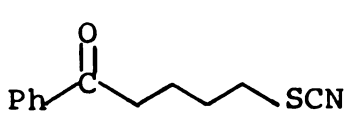
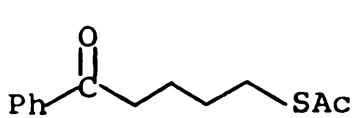
Compound	ϕ_{-K}	ϕ[a]	ϕ_{max}[b]	ϕ_{isc}	$k_q\tau$
 (4-SPh)	---	0.32 ± 0.02	0.36 ± 0.02	1.0	4.76 ± 0.40
 (5-SBu)	0.25	0.18	0.21 ± 0.01 0.006 ± 0.001[h]	---	27.8
 (5-SPh)	---	0.018 0.25[h]	0.018 0.28[h]	---	38.5
 (6-SBu)	0.37	0.22 ± 0.01	0.25 ± 0.01	1.0	36.6 40.0[g]
 (5-SCN)	---	0.22[h]	0.003 0.25[h]	---	106
 (5-SAc)	---	0.58 0.016[h]	0.78[e]	---	44 ± 5

Table 1. (cont'd.)

---

[a]Quantum yields for the formation of acetophenone in benzene at 3130Å.

[b]1.0M dioxane in benzene.

[c]0.05M ϕSH in benzene.

[d]Methanol solvent.

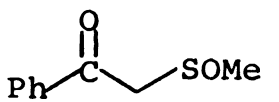
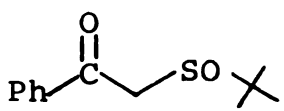
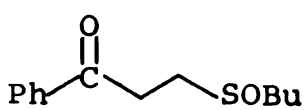
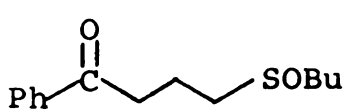
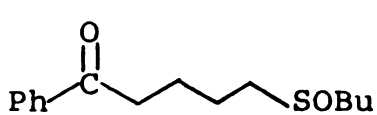
[e]1.0M pyridine in benzene.

[f]No disappearance of starting ketone observed.

[g]Value obtained from double reciprocal plot.

[h]4-benzoyl-1-butene.

Table 2. Photokinetic Data for Various Ketosulfoxides.

Compound	ϕ_{-K}	$\phi^{a,b}$	ϕ_{max}	ϕ_{isc}	$k_q\tau$
 (2-SOMe)	---	0.11	0.44 ± 0.02[c]	---	0.98 ± 0.05
 (2-SOtBu)	---	0.15	0.58 ± 0.04[c]	---	---
 (3-SOBu)	---	---	---	1.0	1.70 ± 0.20
 (4-SOBu)	---	0.03	0.03[b] 0.035[d]	1.0	15.6 ± 0.30
 (5-SOBu)	0.36	0.03	0.03[b] 0.39 ± 0.03[b,e] 0.35[e]	---	21.2 ± 0.2

[a]Irradiated in benzene at 3130Å.

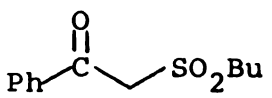
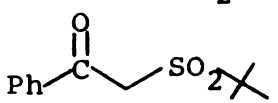
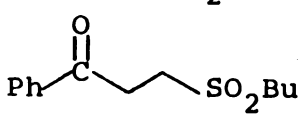
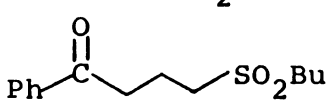
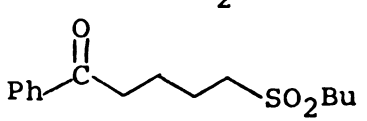
[b]1.0M dioxane.

[c]0.05M ϕSH.

[d]0.50M pyridine.

[e]4-benzoyl-1-butene.

Table 3. Photokinetic Data for Various Ketosulfones.

Compound	ϕ_{-K}	ϕ[a]	ϕ_{max}	ϕ_{isc}	$k_q\tau$
 (2-SO_2Bu)	---	0.20	0.24[b]	---	214 ± 10
 (2-SO_2tBu)	---	0.08	0.17[b]	---	---
 (3-SO_2Bu)	---	---	---	1.0	176
 (4-SO_2Bu)	---	---	0.20[c]	1.0	3750 ± 450
 (5-SO_2Bu)	0.45	---	0.40 ± 0.03[c] 0.03 ± 0.002[c,d]	---	205 ± 15

[a] Irradiated in benzene at 3130Å.

[b] 0.05M ϕSH in benzene.

[c] 1.0M dioxane.

[d] 4-benzoyl-1-butene.

Table 4. Bimolecular Rate Constants for Quenching by Sulfur.

Quencher	$k_q, 10^8 M^{-1} sec^{-1}$
n-butylsulfide	3.25[a]
n-butylsulfoxide	0.014[a] 0.012[b]
n-butylsulfone	---[c]

[a]Measured by quenching the formation of acetophenone from butyrophenone.

[b]Measured by quenching the formation of acetophenone from p-methoxyvalerophenone.

[c]No quenching of acetophenone formation from butyrophenone or p-methoxyvalerophenone observed.

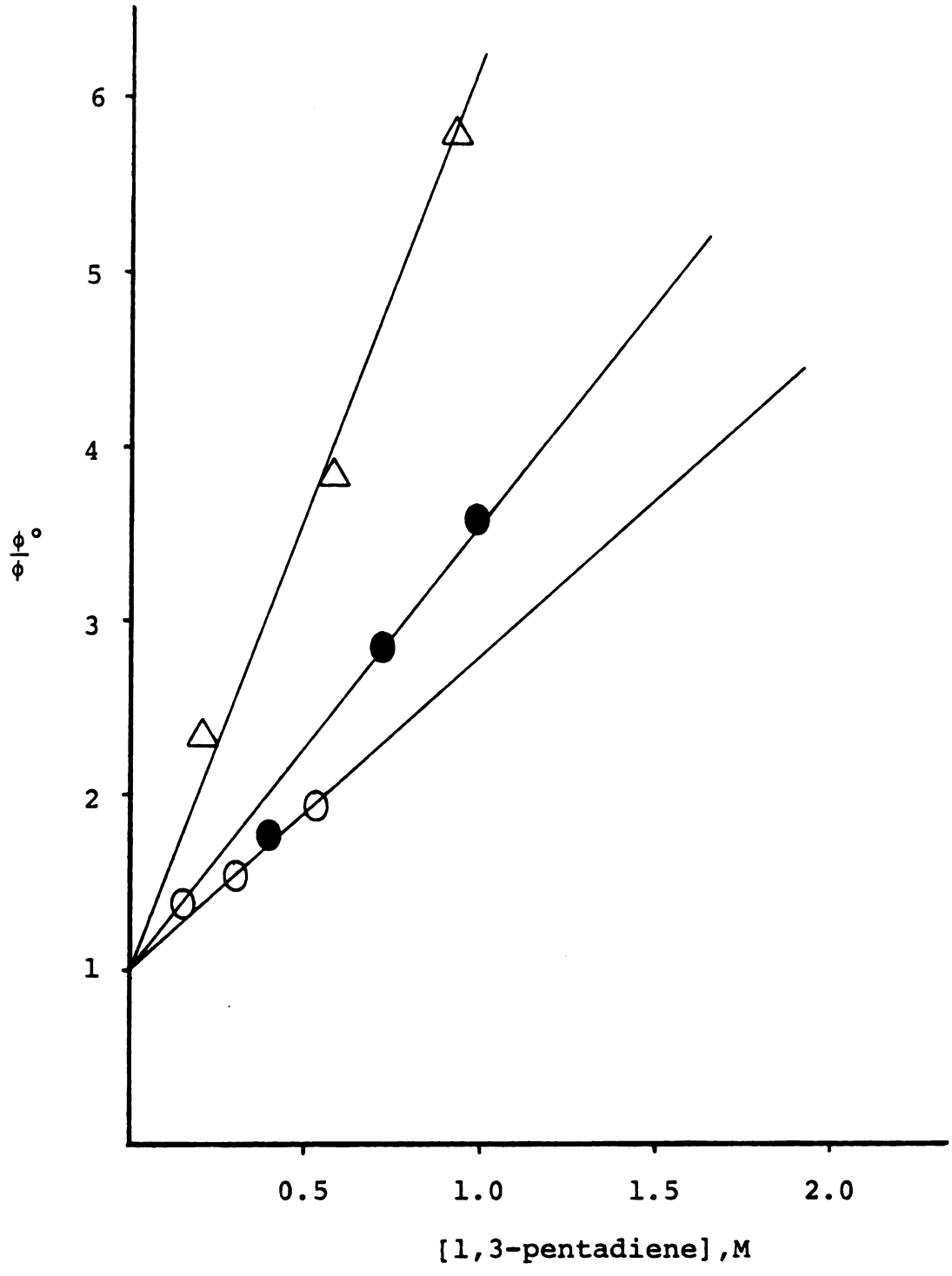


Figure 1. Stern-Volmer Quenching Plot for Acetophenone Formation from 4-SBu (○), 4-StBu (●), and 4-SPh(△) in Benzene with 1,3-pentadiene.

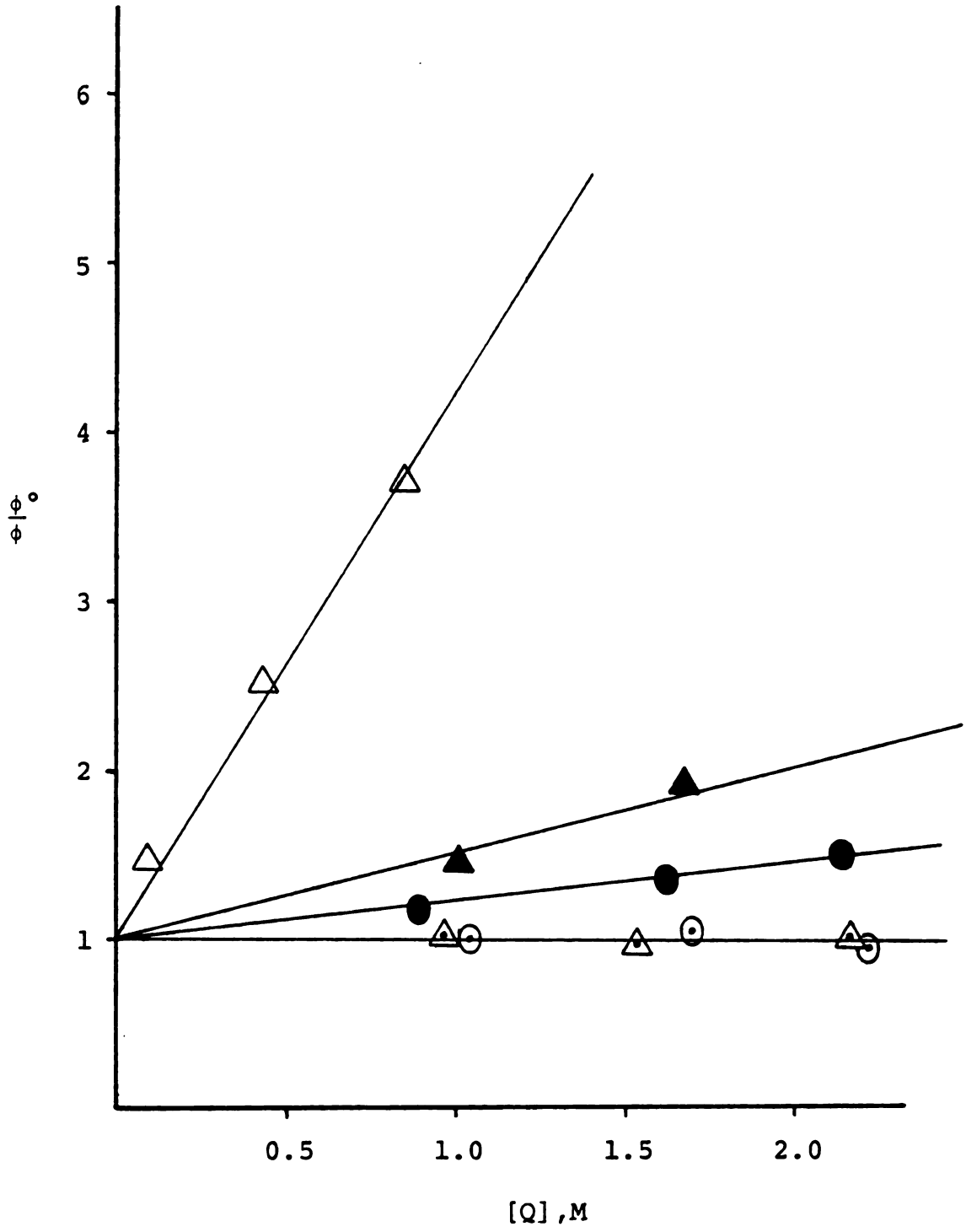


Figure 2. Quenching of Acetophenone Formation from Butyrophenone with BuSBu (△), BuSOBu (●), and $BuSO_2Bu$ (⊙); and Quenching of p-MeO Valerophenone with BuSOBu (▲) and $BuSO_2Bu$ (⊙).

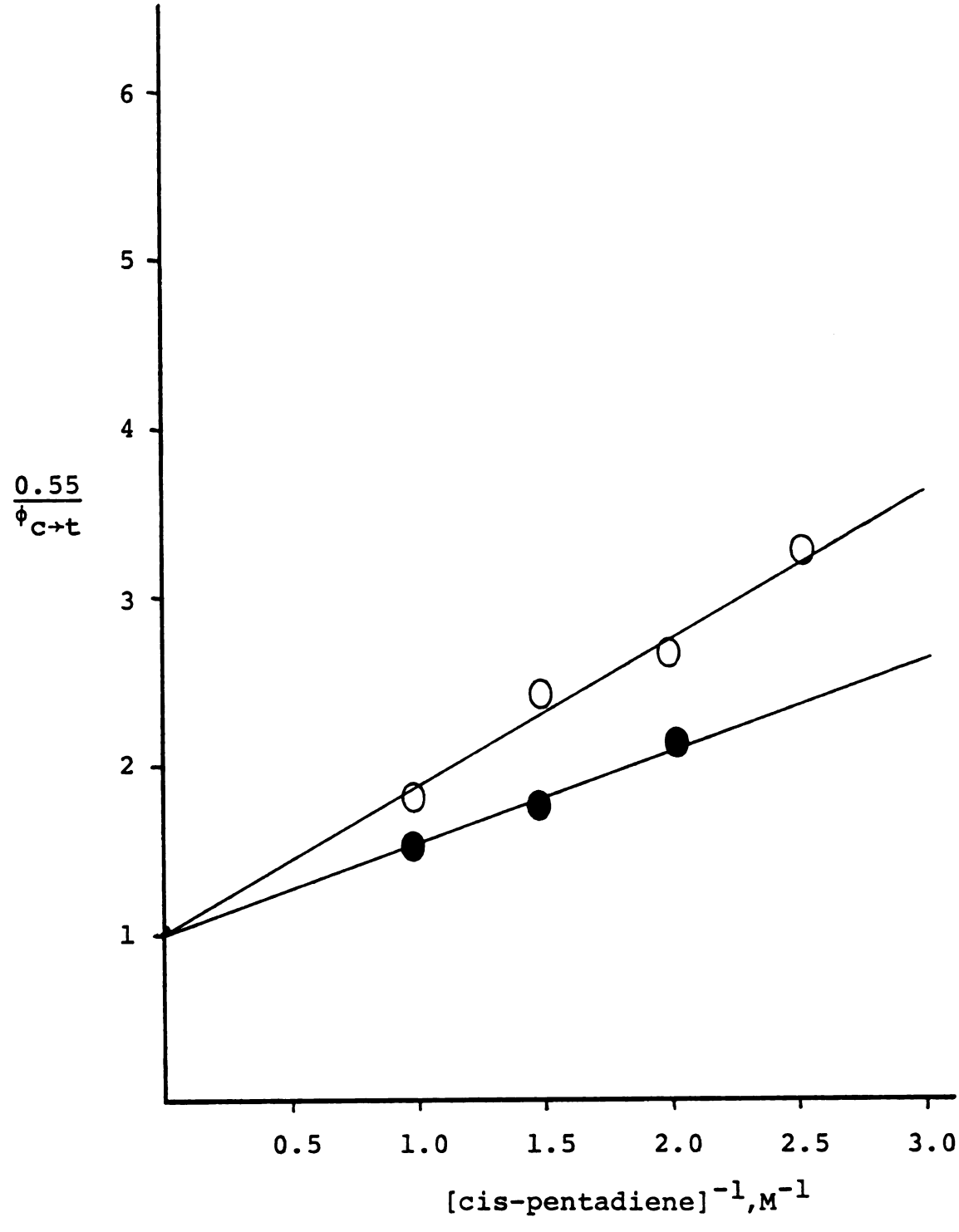
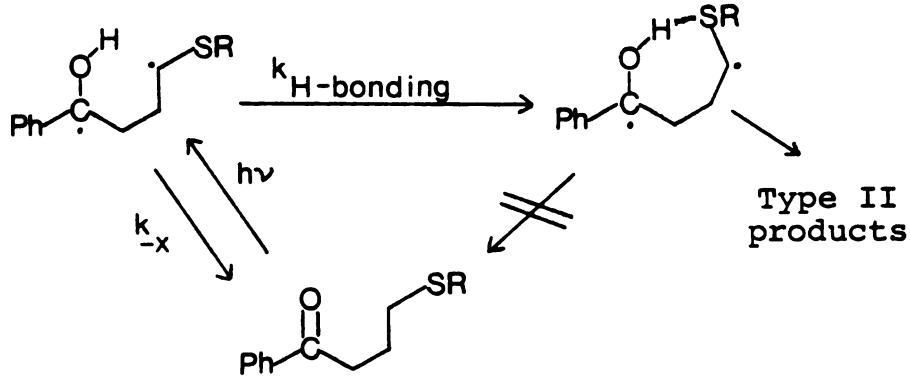


Figure 3. Dependence of Quantum Yield for 3-SBu (○) and 4-SBu (●) Sensitized Isomerization of cis-1,3-pentadiene on Diene Concentration in Benzene.

Discussion

General Observations

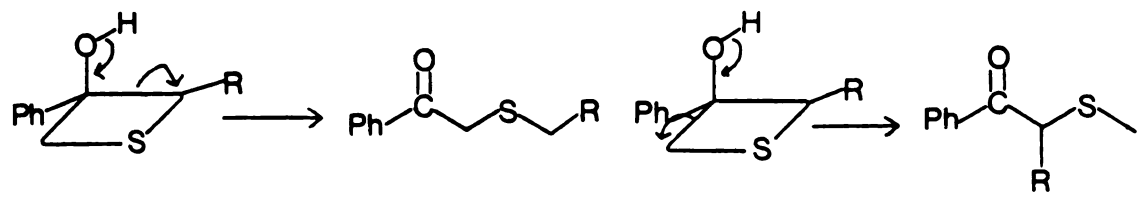
As indicated in Tables 1, 2, and 3, the quantum efficiencies for acetophenone formation are fairly low, typically around 20-30%. Normally, in the absence of alternative decay routes the inefficiency in the Type II Reaction is due to revertibility (reverse 1,5-hydrogen transfer).[59] In the present system, however, only a modest increase in quantum yield is observed in the presence of additives (e.g., pyridine or dioxane) which normally maximize the Type II yield. For example, 4-SBu goes from a quantum yield of 0.13 in benzene to only 0.18 in benzene containing 1.0M dioxane. Generally, enhancements by a factor of 2-3 are observed. Thus, intramolecular hydrogen bonding between the ketyl and sulfur moieties must be faster than reverse hydrogen transfer (i.e., $k_{H\text{-bonding}} >> k_{-x}$).



Such intramolecular hydrogen bonding has been postulated previously to explain the elimination of ROH in β-alkoxyketones.[60]

Difficulty in maximizing the quantum yield has been noted previously for δ-methoxyvalerophenone and was ascribed in part to δ-hydrogen abstraction.[61] The propensity of sulfides, sulfoxides, and sulfones toward hydrogen bonding is well documented;[62] and as such, intramolecular hydrogen bonding must be minimizing revertibility in the same manner as external Lewis bases.[63]

Polar solvents seem to depress cyclization slightly since solvation of the hydroxyl moiety presents some steric inhibition to coupling.[64] In contrast, analogous steric problems are absent for intramolecular solvation; and, in fact, an increase in cyclization might be expected since the conformation necessary for intramolecular hydrogen bonding favors that necessary for coupling. However, material balances indicate that the normal amount of cyclization is taking place, i.e., 10-20%. The anomalous lack of any thietanol formation for 2-SMe and 2-SBu has been noted previously[65] and seems surprising since the analogous compounds containing oxygen or nitrogen cyclize with ease.[66] Ground state reversion of the initially formed thietanol to starting material can be accommodated by two pathways; and as such, isomerization of the starting materials would be expected as shown below.



Since isomerization of starting material was not observed,[67] this process can be eliminated. Therefore, it seems likely the differing behavior of this system with respect to the analogous oxygen and nitrogen systems may be related to the relative weakness of the C-S bond (65 kcal) as compared to the C-O (85 kcal) and C-N (73 kcal) bonds. Also, the interposition of the fairly large sulfur atom may introduce subtle conformational effects, which inhibit cyclization.

Rate of Hydrogen Abstraction Versus Inductive and Resonance Effects

Calculation of the various rate constants deserves comment. The value of k_γ, the rate constant for γ-hydrogen abstraction, can be calculated from the measured lifetime and the maximum quantum yield of Type II products according to equation 6.

$$k_\gamma = \frac{\phi_{max}}{\tau} \qquad (6)$$

The calculated rate data is listed in Table 5. Now, in the case of the α-thioalkoxyacetophenones, β-cleavage is found to compete with γ-hydrogen abstraction, so in these cases the observed k_γ actually equals $k_\gamma + k_\beta$. The extent to which β-cleavage competes in the thioalkoxyketones and the corresponding corrections will be discussed in the following section. The rate constant of C-T quenching will be discussed in the appropriate section.

Table 5. Calculated Rate Data for Sulfur Containing Ketones.

Compound	$\frac{1}{\tau}, 10^8 sec^{-1}$	$k_\gamma, 10^7 sec^{-1}$	$k_{ct}, 10^7 sec^{-1}$
2-SMe	24.3	---[a]	149
2-SBu	31.3	---[a]	135
2-StBu	12.8	---[a]	118
2-SOMe	51.0	---[a]	61.0
2-SO_2Me	0.23	---[a]	1.4
3-SBu	45.4	---	455
3-SOBu	29.4	---	294
3-SO_2Bu	0.28	---	2.84
4-SBu	29.4	52.9	241
4-SOBu	3.21	0.96	31.0
4-SO_2Bu	0.013	0.03	0.10
4-StBu	28.9	78.0	211
4-SPh	10.5	37.8	67.2
5-SBu	1.80	3.96	14.0
5-SOBu	2.36	9.91	13.7
5-SO_2Bu	0.24	1.01	1.42
5-SPh	1.30	3.89	9.09
6-SBu	1.37	3.42	10.2
5-SCN	0.47	1.2	3.5
5-SAc	1.14	9.15	2.28

[a]See Table 7 for the separation of $k_\gamma + k_\beta$.

All substituents stabilize a radical center relative to the unsubstituted case. The fact that the various k_γ values vary greatly with substitution indicates that inductive deactivation of the γ-hydrogen center must be strong. In the case of γ-substitution, separation of the competing inductive and resonance effects is at best tricky; but Wagner[68] has separated the two by assuming a ρ value of -4.3 for γ-substituents. Table 6 lists various relative stabilization factors which were calculated using the data in Table 5.

Table 6. Relative Resonance Stabilization Factors for Various Groups.

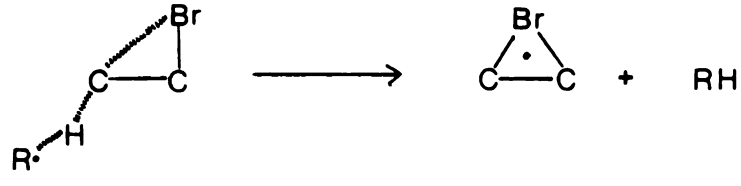
Substituent	σ_I	$10^{-4.3\sigma_I}$	k/k_o	Stabilization Factor
SPh	0.30	0.051	3.0	58.8
SBu	0.25	0.084	4.5	53.6
SOBu	0.52	0.0058	0.077	13.3
SO_2Bu	0.60	0.0026	0.022	0.78
OMe	0.30	0.051	5.0	98.0
Me	---	---	1.0	1.0
OH	0.25	0.085	3.1	37.0
ϕ	0.10	0.37	3.1	8.4
Oϕ	0.39	0.021	1.15	54.7

Table 6 reveals the following sequence listed in decreasing ability to stablize an adjacent radical center:

$$OMe > SPh \sim SBu \sim O\phi > OH > SOBu > \phi > Me > SO_2Me$$

As with alkoxy radicals,[69] the stabilizing effect of γ-substitution reflects the availability of the lone pair of electrons. Ethers are about 2-5 times better than the corresponding alcohols at stabilizing an adjacent radical center. Qualitatively, it is known that sulfur can stabilize a free radical since the α-hydrogens of sulfides are susceptible to hydrogen abstraction.[70] The present study indicates a factor of about 2 less than the corresponding ether. Interestingly, SBu and SPh stabilize an adjacent radical to about the same extent, indicating a lack of participation by the benzene ring. Although phenyl systems are known to participate in free radical stabilization,[71] ESR studies have indicated no participation by the phenyl ring when attached to a heteroatom.[72] The stabilizing effect of a methyl group is fairly small relative to heteroatoms as one might expect. The difference in k_γ for a primary carbon versus a secondary carbon, as in butyrophenone versus valerophenone, is about 16. However, a difference of about 2.0 between primary and secondary is apparent for 2-SMe and 2-SBu. In the case of γ-methoxybutyrophenone versus γ-methoxyvalerophenone, the former is slightly more reactive.[73] Here the greater reactivity of a 3° relative to 2° carbon is not great enough to offset the larger number of hydrogens in the latter. The same effect has been noted for the α-alkoxyacetophenones,[74] where the k_γ's for α-methoxy- and α-ethoxyacetophones are $3.2 \cdot 10^9 sec^{-1}$ and $8.4 \cdot 10^9 sec^{-1}$, respectively--a factor of 2.6.

Introduction of an insulating methyl group as in the δ-substituted valerophenones corresponds to a decrease in the inductive effect by a factor of 0.43[75] and at the same time eliminates any resonance stabilization of the γ-radical center. Figure 4 presents a Hammett plot for δ-substituents in which a plot of $\log(k/k_o)$, where k_o equals the rate constant of γ-hydrogen abstraction for valerophenone, versus σ_I yields a ρ-value of -1.85. Wagner[76] has calculated an identical ρ-value for various δ-substituents, and agreement here indicates the correctness of the present values and further illustrates the predictive value of such a plot. However, an anomalous result arises in that 5-SOBu falls way off the line and appears that γ-hydrogen abstraction is about ten times faster than that expected on purely inductive grounds. An analogous activation has been noted for δ-Br and δ-I valerophenone and was attributed to anchimeric assistance in the hydrogen abstraction step.[77] Comparable rate enhancements have been observed previously for sulfides,[78] and Shevlin[79] has recently observed a weak anchimeric effect by a sulfinyl group. Whereas assistance by bromine or iodine and formation of a bridge species can be pictured below,



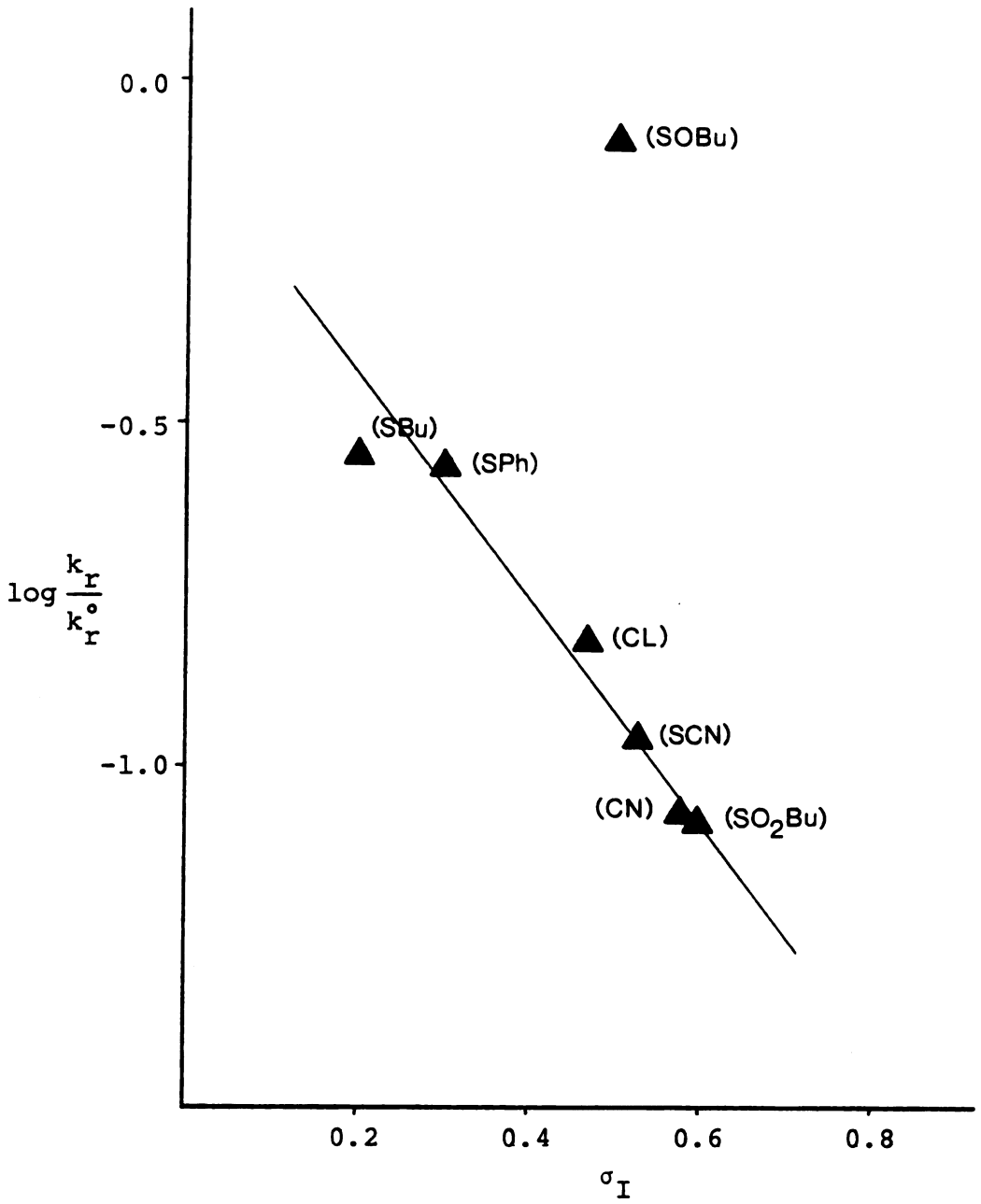


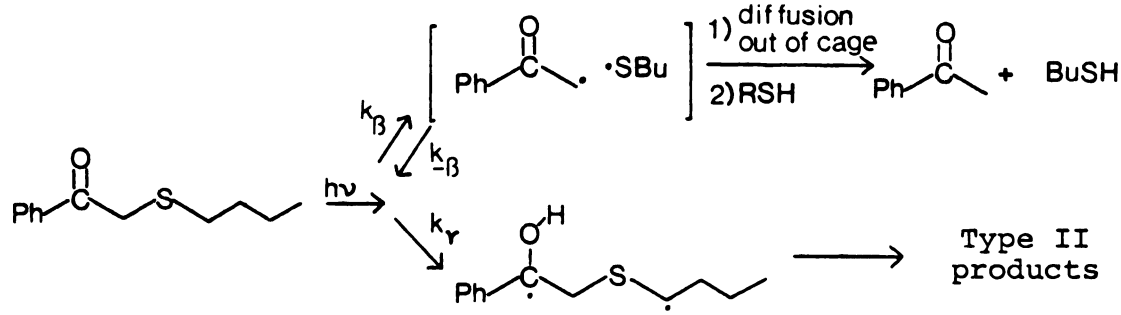
Figure 4. Hammet Plot of Relative Rates of Triplet State γ-Hydrogen Abstraction for δ-Substituted Valerophenones. (Points Cl and CN are included for comparison and can be found in reference 76.)

assistance by a sulfinyl group can be represented in two ways:

Unfortunately, only speculation concerning the nature of anchimeric assistance by sulfinyl groups is possible with the available data. The topic of anchimeric assistance will be discussed in depth in Part II.

Competitive β-Cleavage and γ-Hydrogen Abstraction

For the β-ketosulfides, sulfoxides, and sulfones, β-cleavage is found to compete with γ-hydrogen abstraction. This reaction is well documented[80] but has escaped a thorough kinetic examination. Thus, 2-SBu has two available routes for acetophenone formation as shown below.



Lewis[81] and Wagner[82] have separately estimated that about 50% of the initially formed radicals in Type I cleavage recombine in-cage to form starting material as indicated. Thus,

compounds which form acetophenone primarily via β-cleavage experience at least a 50% inefficiency. The addition of thiols has been shown to increase the quantum yield of product formation by trapping the radicals that diffuse out of the cage.[83] Enhancements on the order of two to five are typical in the present system as well as previous systems.[84]

Examination of Tables 1, 2, and 3 allows estimation of the amount of β-cleavage relative to γ-hydrogen abstraction in the thioalkoxyacetophenones. For instance, 2-StBu, which possesses no γ-hydrogens, forms acetophenone in the presence of 0.05M HSPh with a quantum yield of 0.04. Thus, at least 4% of acetophenone formation arises from β-cleavage in 2-SMe and 2-SBu. However, if one assumes about 50% in-cage recombination, 8% of the light is attributable to β-cleavage. If the total quantum yield of acetophenone is divided into that found via β-cleavage, the competition between β-cleavage and γ-hydrogen abstraction can then be separated. The results are presented in Tables 7 and 8. Interestingly, 2-SOMe and 2-SO_2Me appear to react mainly via β-cleavage, which is in agreement with that observed by Majeti[85] and deMayo.[86] A more detailed discussion of β-cleavage appears in Part II.

Table 7. Approximate Amounts of β-Cleavage Versus γ-Hydrogen Abstraction in α-Thioalkoxyacetophenones.

Compound	% β-Cleavage	% γ-Hydrogen Abstraction
2-SMe	21	79
2-SBu	14	86
2-SOMe	100	0
2-SO_2Me	83	17

Table 8. Calculated Rate Data for α-Thioalkoxyacetophenones.

Compound	ϕ_{corr} [a]	$k_\gamma, 10^8 s^{-1}$	$k_\beta, 10^8 s^{-1}$	$k_{ct}, 10^8 s^{-1}$
2-SMe	0.39	7.5	1.9	14.9
2-SBu	0.57	15.3	2.49	13.5
2-StBu	0.08	---	1.02	11.8
2-SOMe	0.88	---	44.9	6.1
2-SO_2Me	0.41	0.016	0.078	0.14

[a]Quantum yield of acetophenone corrected for 50% recombination of the initially formed radicals.

Charge-Transfer Quenching

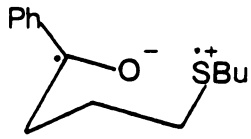
Previous work on aminoketones has indicated a competition between intersystem crossing, charge-transfer quenching, and γ-hydrogen abstraction. Since $k_{isc} \sim 10^{11} sec^{-1}$ for phenyl ketones,[87] interaction of the amine with the excited carbonyl must be comparably rapid to be able to quench the singlet. However, intersystem crossing yields for the ketosulfides are found to be one, indicating a much slower rate of interaction. Despite this, the general trends should be the same--that is, as the sulfur moiety is moved closer to the carbonyl, the amount of charge-transfer quenching should increase. The amount of charge-transfer quenching in the present case is assumed to be the only significant decay process of the triplet, as expressed by the following equation:

$$\frac{1}{\tau} = k_{\gamma} + k_{ct} \qquad (8)$$

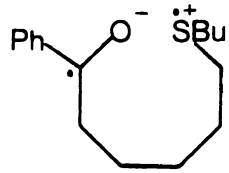
Thus, knowledge of τ and the quantum yield allows calculation of k_{ct}. The effect of competing β-cleavage on k_{ct} has already been discussed in the previous section. Examination of Table 5 reveals fairly high k_{ct} values for 5-SBu and 6-SBu at $14.2 \cdot 10^{7} sec^{-1}$ and $10.2 \cdot 10^{7} sec^{-1}$, respectively. As previously found in azidoketones,[88] k_{ct} is found to decrease by a factor of ten when the chain length is increased by one. For instance, k_{ct} goes from $0.28 \cdot 10^{8} sec^{-1}$ in δ-azidovalerophenone to $<0.02 \cdot 10^{8} sec^{-1}$ in ε-azidohexanophenone. The fact that k_{ct} for 5-SBu and 6-SBu are nearly identical is

disturbing. However, the $k_q\tau$ of 6-SBu--i.e., 36.6--is nearly identical to that for nonanophenone,[89] which is nearly equivalent to 6-SBu in size. Therefore, the sulfur does not seem to be influencing the lifetime, yet the quantum yields cannot be maximized. It then seems likely that most of the inefficiency in 6-SBu is due not to C-T quenching by sulfur but to some other effect which prevents solvation of the biradical. This effect has been observed previously for very long chain ketones[90] and in this laboratory for long chain ketones that contain a heteroatom.[91] The k_γ that one would expect on inductive grounds for 6-SBu is $\sim 10^8 sec^{-1}$, which is roughly a factor of ten less than 5-SBu.

Conformational Effects. The fact that overlap of donor and acceptor orbitals is necessary for efficient quenching was demonstrated by Wagner and Scheve[92] with the 1-methyl-1-benzoylpiperidine system. Thus, one would expect that intramolecular quenching in an acyclic system would depend upon the mobility of donor and acceptor relative to each other. The approach of the sulfur and carbonyl moieties corresponds to the formation of different sized rings and should compare qualitatively with the known propensities of molecules to form various sized rings in the ground state. For example, the k_{ct}'s for 5-SBu and 6-SBu are considerably less than those of 4-SBu and 3-SBu. The former case corresponds to 7- and 8-membered rings, whereas the latter, 6- and 5-membered rings, respectively.

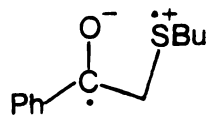


(4-SBu)
6-membered ring
stable



(6-SBu)
8-membered ring
unstable

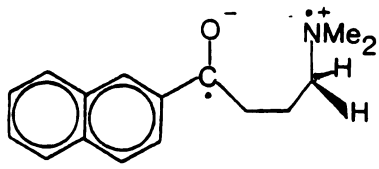
The formation of 5- and 6-membered rings--i.e., β- and γ-substituted phenylketones--represents the maximum amount of quenching. A dramatic reversal of trend is noted in going from 3-SBu to 2-SBu in that k_{ct} decreases markedly. This must reflect the conformational instability of small rings as well as large rings since approach of donor and acceptor in 2-SBu would represent a 4-membered ring.



(2-SBu)
4-membered ring
unstable

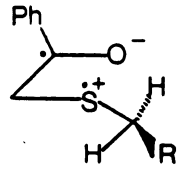
In the case of the α-thioalkoxyacetophenones, β-cleavage followed by rapid in-cage recombination leads to inefficiency not ascribable to C-T quenching. Table 8 lists the corrected k_{ct}'s for the α-substituted acetophenones.

Although full electron transfer is not taking place,[93] the C-T complex is conformationally constrained, resembling more a tight ion-pair. Wagner and Ersfeld[94] have shown that in benzene no proton transfer is taking place in 9 since the acidic hydrogens α to the positive nitrogen are inaccessible to the oxygen anion.

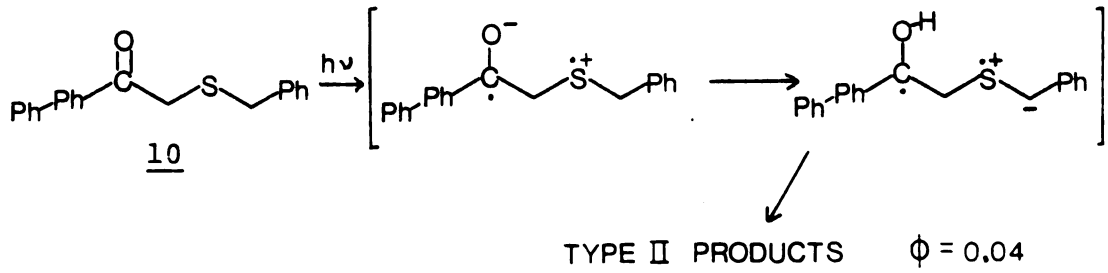


9

However, in the case of the α-thioalkoxyacetophenones, the charge-transfer complex presents a more favorable situation for proton transfer although formation of the complex itself may be slow.



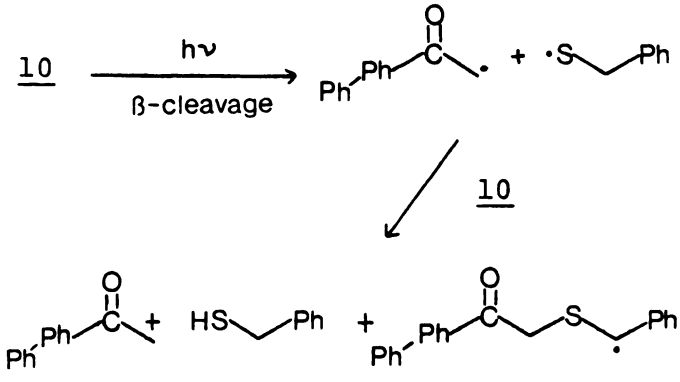
Padwa[95] has shown that products do indeed arise from the C-T state in 10 since 10 possesses a lowest $^3\pi,\pi^*$ triplet which is



10

TYPE II PRODUCTS $\Phi = 0.04$

inert to hydrogen abstraction. Perhaps coincidentally, the quantum yield Padwa observed was identical to the value measured for 2-StBu in the presence of 0.05M thiol. Therefore, it is possible that products arise in Padwa's system via ß-cleavage followed by hydrogen abstraction from starting material which possesses highly abstractable hydrogen atoms as shown below.



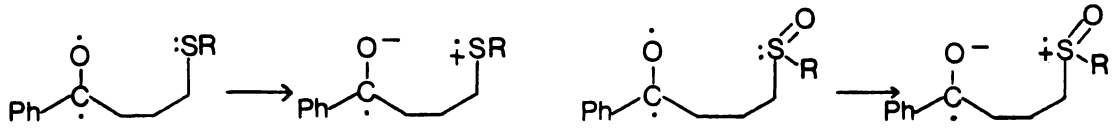
Unfortunately, the available data do not allow further speculation.

Product formation from the charge-transfer state in the present system has not been rigorously investigated.

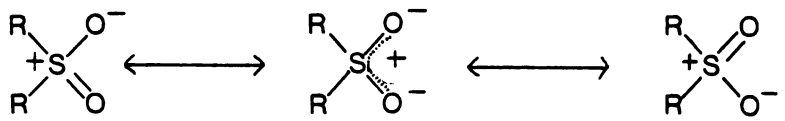
Effect of Donor on k_{ct}. In the case of phenylamines, the nitrogen leads to increased electron density in the ring which, in turn, leads to a more favorable interaction between excited species and the conjugated system, resulting in more efficient quenching relative to aliphatic amines.[96] However, phenylsulfides are less efficient quenchers than aliphatic sulfides,[97] which indicates that quenching arises primarily

by interaction of the non-bonding electrons of sulfur. Electron withdrawing groups on the sulfur, like phenyl, decrease its effectiveness. Thus, 3-SPh quenches about four times slower than 3-SBu. Cohen[98] noted a difference of about nine between n-butylsulfide and phenylsulfide in the bimolecular quenching of the photoreduction of benzophenone by isoborneol with sulfides. That 5-SAc and 5-SCN quench about seven times slower than 5-SBu is also indicative of the effect electron withdrawing groups have on the availability of the non-bonding pairs on sulfur.

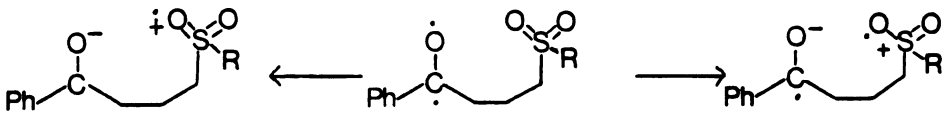
Expectedly, increasing the oxidation state of the sulfur moiety leads to a decrease in the rate of charge-transfer quenching. For instance, 4-SOBu quenches about eight times more slowly than 4-SBu, and 4-SO_2Bu about 2500 times more slowly than 4-SBu. The reduced rates of quenching for sulfoxides relative to sulfides is attributable to the decreased availablity of the electrons on sulfoxides. This, in turn, is manifested in a higher ionization potential than sulfides.[99] The nature of the C-T complex in sulfides and sulfoxides is pictured below and can be represented as interaction of the non-bonding electrons on sulfur with the triplet.



Sulfones, on the other hand, are completely oxidized and possess no non-bonding electrons except for those on oxygen; and, as such, the previous representation seems inappropriate. Sulfones can best be represented by a resonating decet structure.[100]



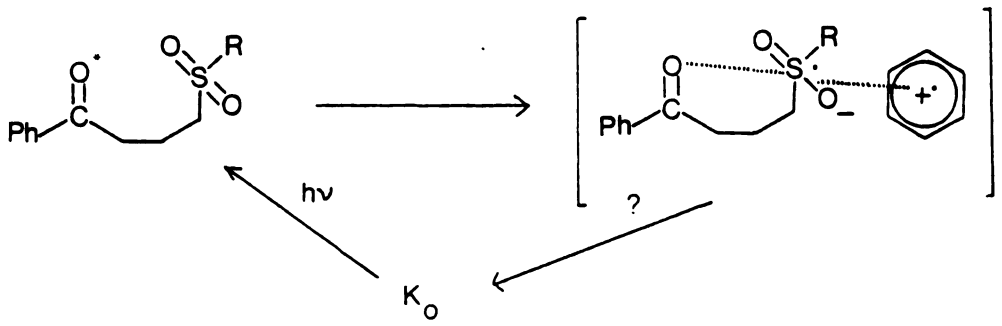
Formally, C-T quenching can arise by interaction with either the lone pair of electrons on oxygen (11a) or with a π-bond between the sulfur and oxygen (11b).



11a 11b

While these structures are aesthetically pleasing, they seem intuitively wrong in light of the high ionization potentials of sulfones.[101] Other mechanisms leading to inefficiency are possible. The polar nature of the sulfonyl group may lead to some ground state complexation which could, in turn, behave differently than uncomplexed ketone, leading to decay. Internal solvation of the benzoyl group by the sulfonyl group may actually be switching the triplet levels from lowest $^3n,\pi^*$ to a lowest $^3\pi,\pi^*$, which might lead to enhanced decay. One final intriguing mechanistic possibility to explain why

sulfones quench is by invoking "sandwich" type exciplex formation where the triplet carbonyl lowers the reduction potential of the sulfone enough to allow C-T complexation with the solvent, in this case benzene.



Such a mechanism may explain why sulfones quench intramolecularly but not intermolecularly, since such a mechanism would necessarily require strict conformational alignment, which would not be fast enough on a bimolecular level.

Direct energy transfer to sulfones is unlikely, however, due to its highly endothermic nature.[102]

Bimolecular Quenching. Cohen[103] has previously measured the bimolecular rate constant for quenching of benzophenone photoreduction with isoborneol by sulfides and found it to be $6.6 \cdot 10^8 M^{-1} sec^{-1}$. Cohen[104] later quenched the phosphorescence of benzophenone with various alkyl and aryl sulfides. The k_q for butylsulfide in benzene was measured at $8.3 \cdot 10^8 M^{-1} sec^{-1}$. This is in fairly good agreement with the present value of $3.25 \cdot 10^8 M^{-1} sec^{-1}$. Comparing this with the intramolecular k_{ct} for 5-SBu ($1.42 \cdot 10^8 sec^{-1}$), one finds that having the sulfur at the δ-position corresponds roughly to that found in the intermolecular case.

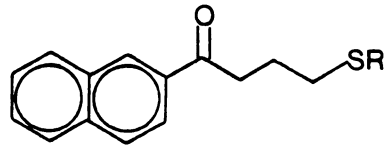
The apparent lack of correlation between the intra- and intermolecular rate constant for quenching by butylsulfoxide and butylsulfone is disturbing. That is, butylsulfoxide quenches 100 times more slowly intermolecularly than intramolecularly, while butylsulfone does not quench at all bimolecularly but quenches intramolecularly with a rate constant of about $10^7 sec^{-1}$. The explanation may lie in the fact that the orientation needed for approach of the sulfoxide or sulfone to the carbonyl is not known exactly. Therefore, the proper orientation for quenching may only be obtained fast enough intramolecularly. There are numerous examples[105] where intramolecular processes are immensely favored in rate over intermolecular processes, and the difference does indeed seem linked to the fact that effective concentrations of intramolecular processes are far greater than those normally achievable.

Indications for Further Research

Synthetic Utility. One of the questions most often asked of chemists is whether their research is good for anything. In this case the answer is a definitive yes. The synthetic utility of the Type II Reaction has been explored only sparingly. It offers an excellent way to prepare unusual olefins as well as substituted cyclobutanols. For instance, the Type II Reaction has been used to synthesize adamantene,[106] a molecule which has eluded synthesis by

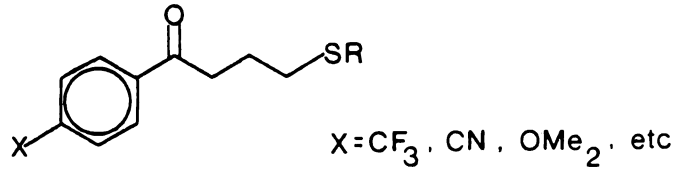
conventional methods. Lewis's[107] and others'[108] observations that α-substitution increases cyclization products relative to cleavage products have been ignored synthetically.

Products from C-T State. It is not clear in the present study whether products can arise from the C-T state. The compound below might give a definitive answer.



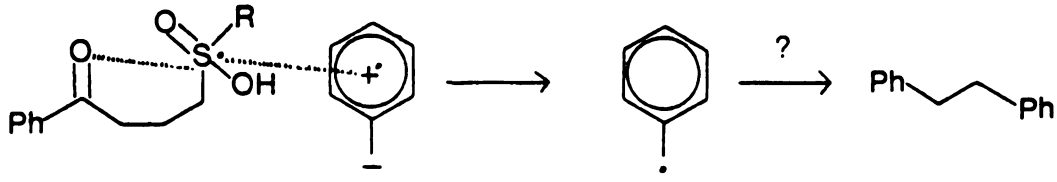
Since napthyl ketones have lowest π,π^* triplets,[109] formation of products here would be indicative of a C-T, proton transfer mechanism like that proposed by Wagner.[110]

Effect of Ring Substituents. The amount of charge-transfer is dependent upon the ionization potential of the donor. It should, therefore, also be dependent on the reduction potential of the acceptor, in this case the benzoyl moiety. Thus, electron donors or acceptors should raise or lower the reduction potential, respectively, resulting in decreased or increased rates of C-T quenching. The following system would be representative.

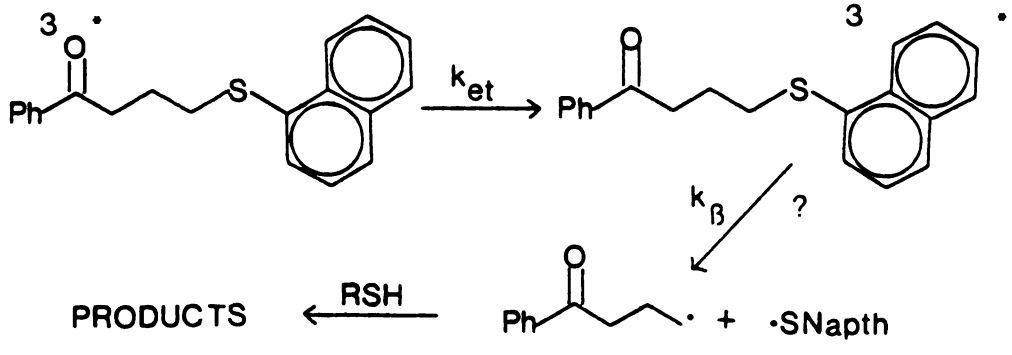


Nature of Quenching by the Sulfonyl Group. The idea of a "sandwich" type exciplex is intriguing and could probably

best be tested by varying the ionization potential of the benzene by using substituted benzenes. For instance, anisole should cause a slight increase in the rate of quenching since it donates an electron more easily. Perhaps coupling products resulting from proton transfer to the sulfonyl group from alkyl benzenes could be observed as shown below.



Energy Transfer Resulting in Homolytic Cleavage. Intramolecular energy transfer could be studied by the following system:



where energy transfer to the napthyl group could possibly promote β-cleavage resulting in radicals which could be trapped with thiols and measured. The effect of chain-length could then be investigated.

PART II

RADICAL β-CLEAVAGE VIA EXCITED STATES AND PHOTOGENERATED DIRADICALS

Phenacylsulfides

Results

Synthesis and Identification of Photoproducts

Various substituted phenacylsulfides were prepared by reaction of the phenacylhalide with sodium thiophenoxide in ethanol. The compounds and their respective abbreviations are listed in Tables 9 and 10. For example, α-thiophenoxyacetophenone is referred to as 2-SPh and p-chloro-α-thiophenoxyacetophenone as Cl-2SPh. In all cases the corresponding acetophenones were observed upon irradiation in benzene. In the case of 2-SPh, acetophenone was actually isolated by preparative vpc. For t-2SPh, isobutyrophenone was identified by nmr. The other acetophenones were identified by comparison of vpc retention times with authentic samples. Thiophenol and diphenyldisulphide were observed in most cases but not measured. In the cases of s-2SPh and t-2SPh the corresponding disproportionation products--i.e., acrylophenone and α-methylacrylophenone--were not separable from propiophenone and isobutyrophenone. However, α-methylacrylophenone was identified by observation of a singlet at about 1.6δ in the nmr.

The other radical coupling products--i.e., the 1,2-dibenzoylethanes--were not observed under the analysis conditions but have been identified and measured previously.[111] Surprisingly, no benzaldehyde formation was detected in PDS.

Quantum Yields

The quantum yields for the appropriate acetophenone formation were measured in benzene at 3130Å in the same manner as that described in Part I. The addition of benzenethiol was found to maximize the quantum yield as shown in Figure 5. Enhancements of quantum yields were typically on the order of two to five. Nearly 100% material balances were observed in the cases measured. The quantum yields are presented in Tables 9 and 10.

Quenching Studies

Stern-Volmer plots for the quenching of acetophenone were performed at 3660Å as previously described with either napthalene or 1-methylnapthalene as quenchers. The use of 1,3-pentadiene gave irreproducible results probably because of radical scavenging. The photoreactivity of certain compounds was found to be unquenchable even with 2.0M napthalene; thus, no information regarding the triplet was available. The corresponding kinetic parameters are listed in Tables 9 and 10, and a representative Stern-Volmer plot is shown in Figure 6.

Intersystem Crossing Yields

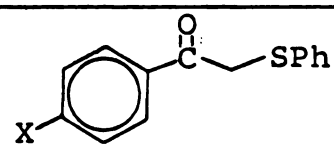
The intersystem crossing yields were not measurable for the phenacylsulfides. Attempted sensitization of cis-1,3-pentadiene resulted in meaningless numbers, probably because of the production of radicals which isomerized the olefin. Use of trans-stilbene as the sensitizee with OMe-2SPh resulted in an intersystem crossing yield in excess of 3. The intersystem crossing yield must be at least 50% for the quenchable compounds since the reactions were totally quenchable.

Spectroscopic Studies

The uv spectra of selected substituted phenacylsulfides were measured in heptane, and the λ_{max} for n,π^* and π,π^* transitions and ε's are listed in Table 11. Interestingly, vibrational fine structure on the n,π^* shoulder was observed in all cases. Substitution of ethanol as solvent eliminated the fine structure. Representative spectra indicating the solvent effect are presented in Figure 7.

Corrected phosphorescence spectra (see Experimental Section) were obtained at 77K at approximately 10^{-4}M ketone in methyltetrahydrofuran (MTHF) glasses. The triplet energies are presented in Table 12 and the actual spectra in Figures 8 through 12.

Table 9. Quantum Yields and Rate Data for p-Substituted Phenacylsulfides.

Compound		ϕ[a]	ϕ_{max}[b,c]	$k_q\tau$
				
X				
H	(2-SPh)	0.08	0.24 ± 0.02 0.26 ± 0.03[d]	---[c]
F	(F-2SPh)	0.05	0.24	---[c]
Cl	(Cl-2SPh)	0.05	0.24	0.80
Br	(Br-2SPh)	0.02	0.20	2.00 ± 0.10
Me	(Me-2SPh)	0.05	0.30	---[c]
OMe	(OMe-2SPh)	0.09	0.41 ± 0.03	2.20
SMe	(SMe-2SPh)	0.04	0.19	30.0 ± 2.0
NMe_2	(NMe_2-2SPh)	0.07	0.19	13.8 ± 0.8
ϕ	(ϕ-2SPh)	0.05	0.27	40.0
CN	(CN-2SPh)	0.04	0.16 ± 0.01	1.08 ± 0.2

[a]All ϕ's were obtained in benzene at 3130Å.

[b]Maximum yields were performed in the presence of 0.05M ϕSH.

[c]Unquenchable with 2.0M napthalene or 1-methylnapthalene.

[d]ϕ^{-1} vs. K

[e]These are the observed quantum yields. Table 14 lists the quantum yields corrected for about 50% in-cage recombination.

Table 10. Quantum Yields and Rate Data for Structurally Variant β-Benzoylsulfides.

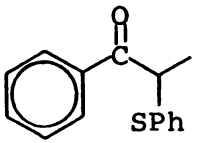
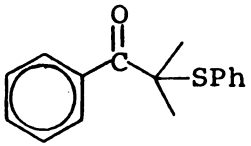
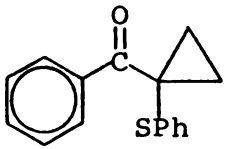
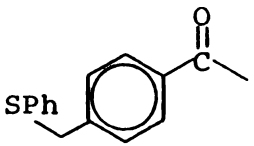
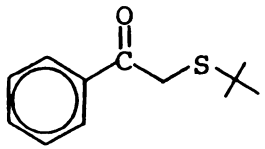
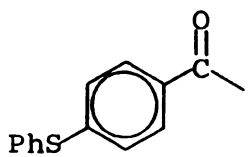
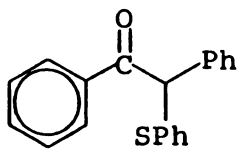
Compound		ϕ[a]	ϕ_{max}[b]	$k_q\tau$
	(s-2SPh)	0.20	0.32 ± 0.01 0.31[d]	---[c]
	(t-2SPh)	0.33	0.34 ± 0.02 0.35[d]	---[c]
	(cy-2SPh)	0.14	0.42	1.38 ± 0.06
	(4'-MSPh)	0.11	0.40	---[c]
	(2-StBu)	---	0.04 ± 0.008	3.90 ± 0.10

Table 10. (cont'd.)

Compound		ϕ [a]	ϕ_{max} [b]	$k_q\tau$
	(4'-SPh)	---	0.001	---[f]
	(PDS)	0.006	0.014	---[f]

[a] In benzene at 3130Å.

[b] 0.05M ϕSH.

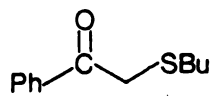
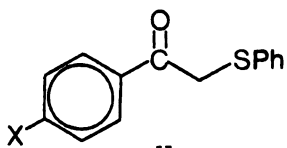
[c] Unquenchable.

[d] ϕ_{-K}.

[e] Corrected quantum yields are listed in Table 14.

[f] Not measured.

Table 11. Substituent Effects on n,π^* and π,π^* Transitions in Phenacylsulfides.[a]

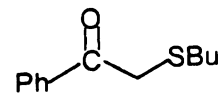
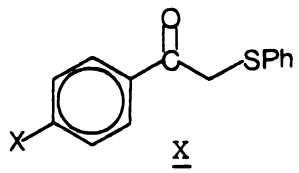
Compound	λ_{max}(n,π^*), nm	λ_{max}(π,π^*),nm
	340 (372) 336 (634)[b]	240 (8,157) 242 (10,382)[b]
 X		
H	341 (448)	246 (19,462)
CN	355 (809)	248 (31,181)
OMe	336 (649)	257 (19,603)
SMe	340[c]	307 (20,183)
NMe_2	330[c]	325 (27,067)

[a] In heptane; molar extinction coefficients in parentheses.

[b] In ethanol; fine structure on n,π^* band has disappeared.

[c] n,π^* buried under π,π^*; estimated by comparison of fine structure with other compounds.

Table 12. Triplet Energies of Ring-Substituted Phenacylsulfides.[a]

Compound	E_t(kcal)	
	70.9	(74)
		
X		
H	73.5	(74)
CN	68.4	(69.2)[b]
OMe	70.4	(71)
NMe_2	62.6	

[a]Numbers in parentheses refer to the corresponding ring-substituted valerophenone in 2-methylpentane. (See ref.112)

[b]E. J. Siebert, unpublished.

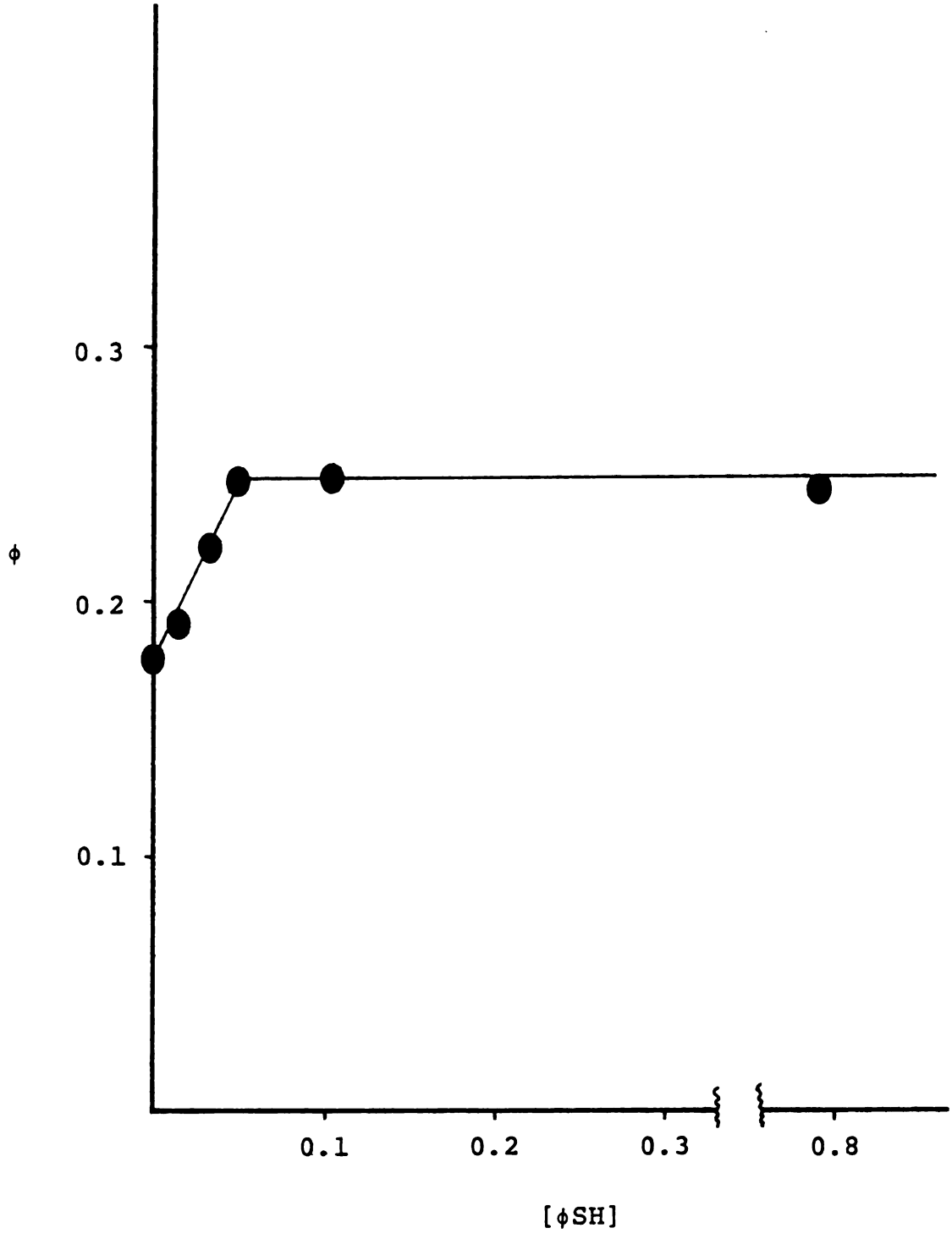


Figure 5. Quantum Yield of Acetophenone Formation in 2-SPh Versus [ϕSH].

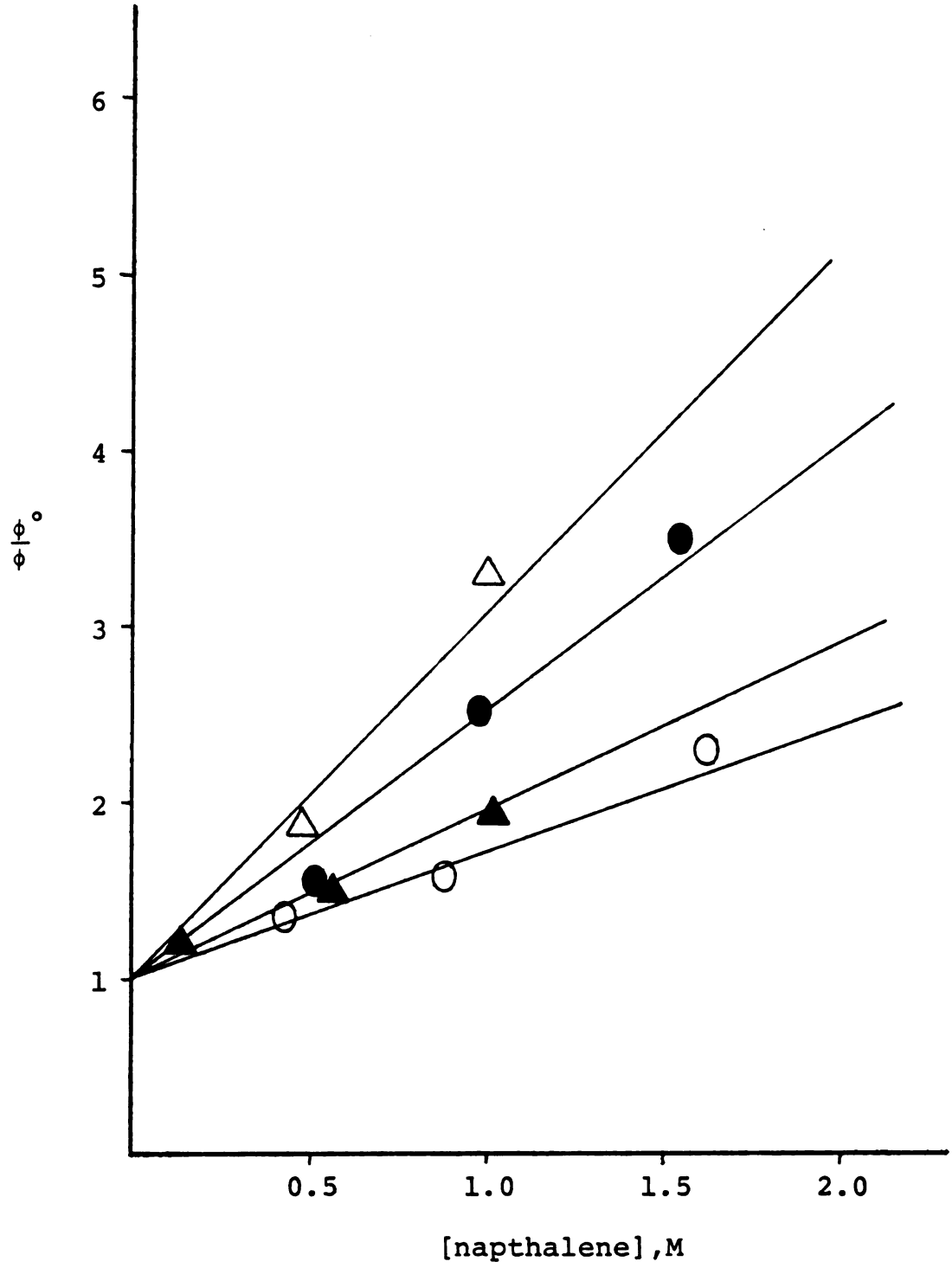


Figure 6. Stern-Volmer Quenching Plot for the Quenching of the p-Substituted Acetophenone Formation from Cl-2SPh (○), Br-2SPh (●), Me-2SPh (△), and CN-2SPh (▲) with Napthalene in Benzene.

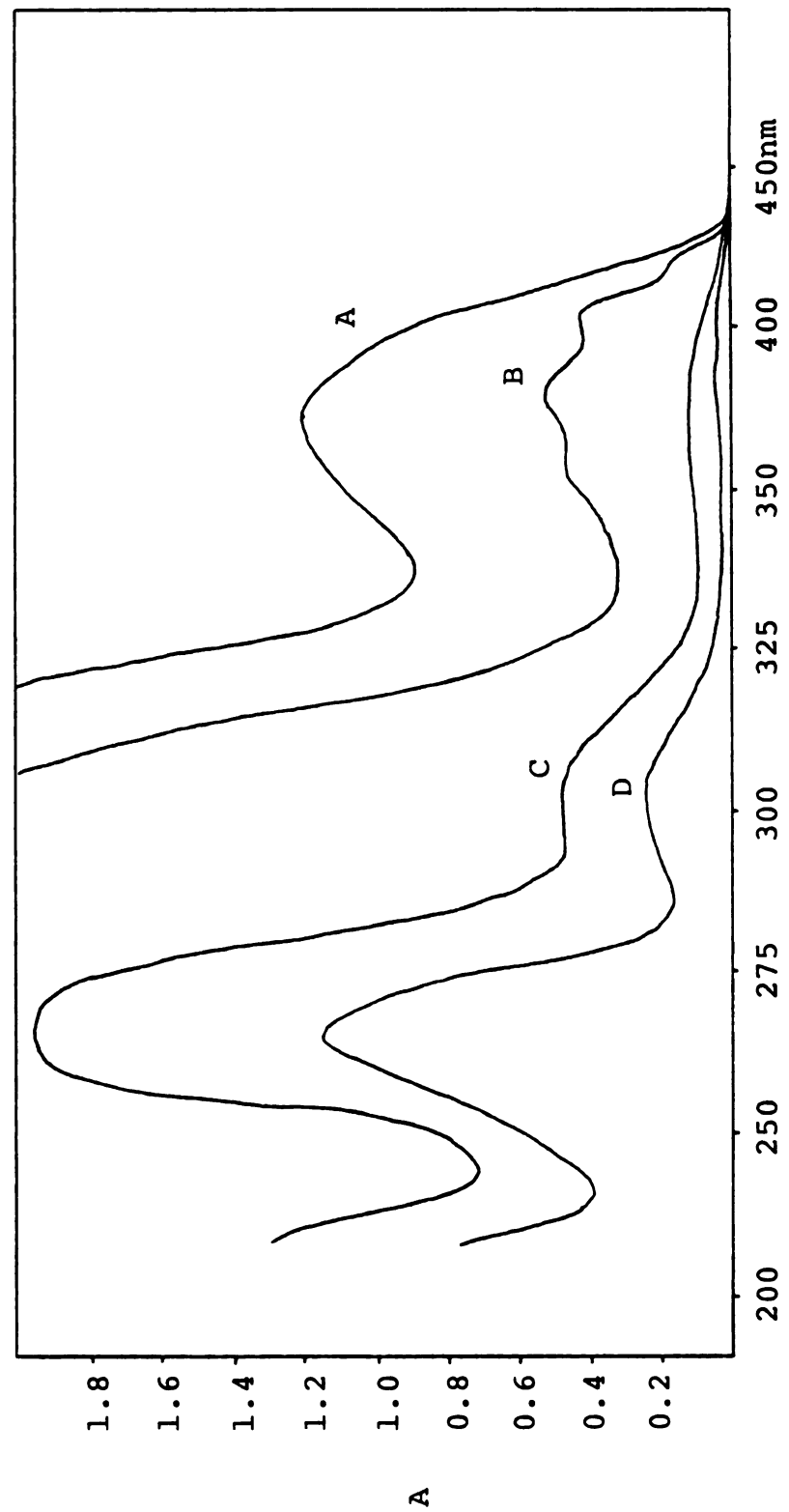


Figure 7. Ultraviolet Spectra of 2-SBu. [A = 0.00183M(EtOH), B = 0.0014M(heptane), C = 0.000183M(EtOH), D = 0.00014M(heptane)]

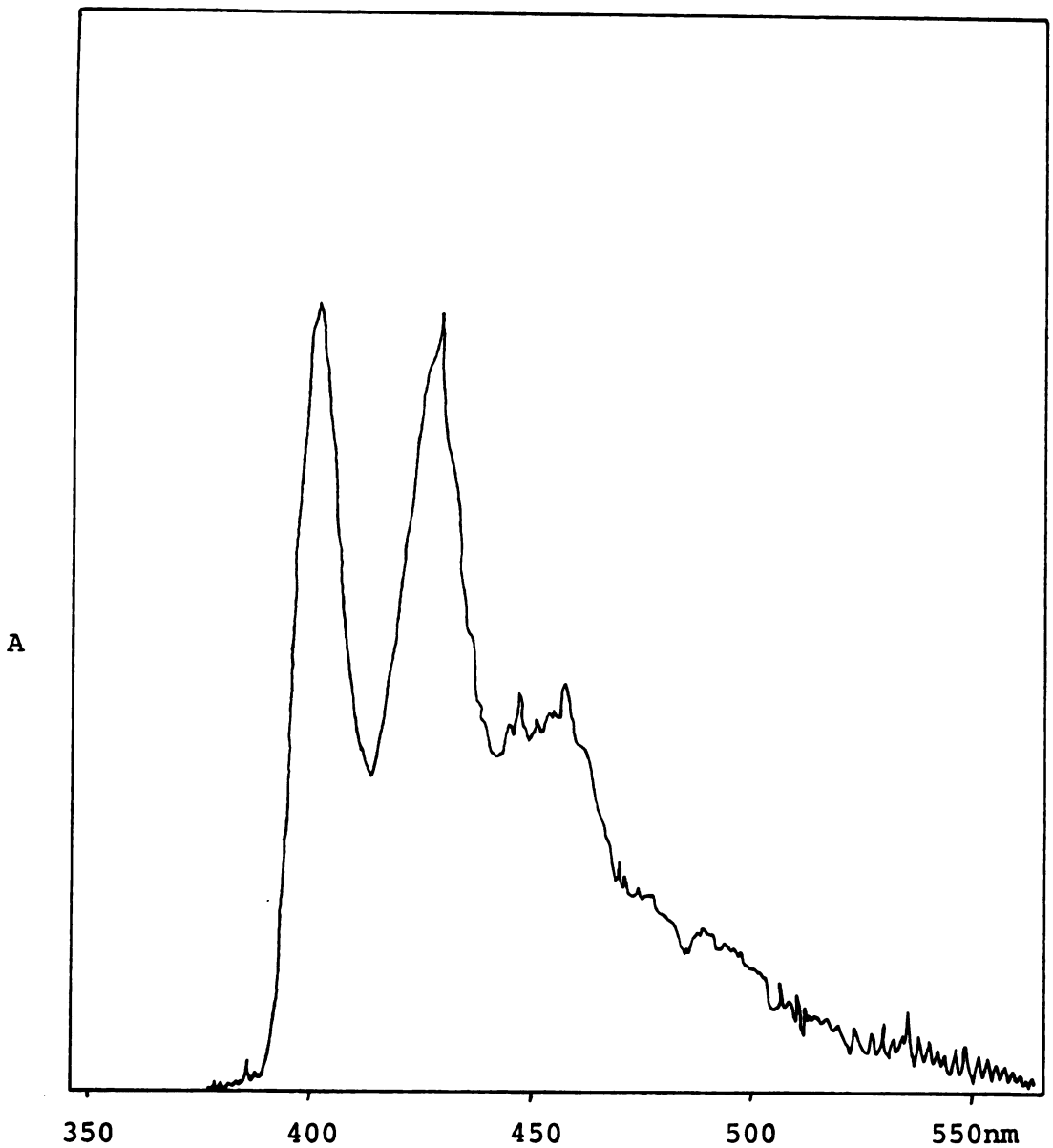


Figure 8. Phosphorescence Spectrum of 2-SBu in MTHF at 77K.

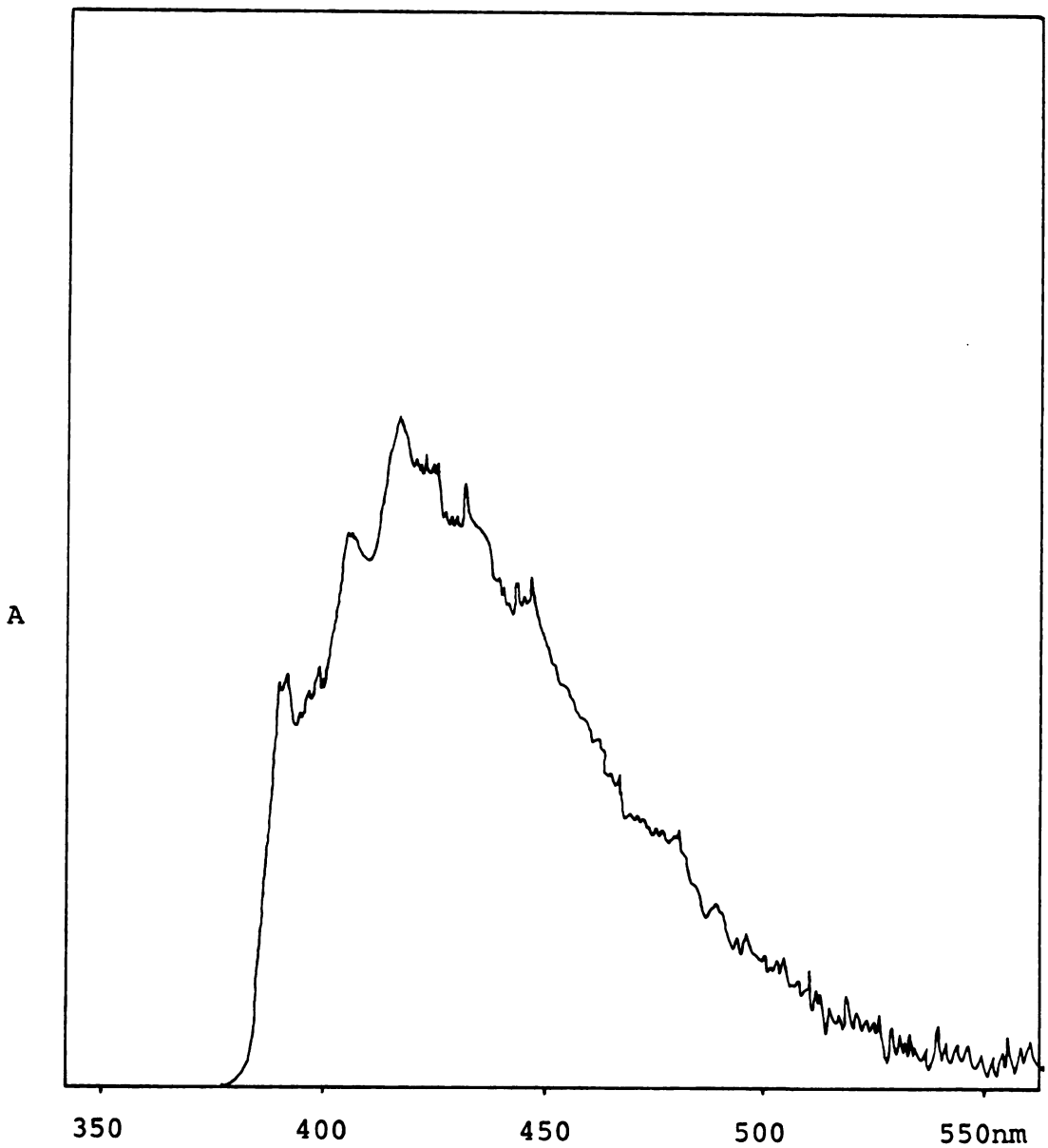


Figure 9. Phosphorescence Spectrum of 2-SPh in MTHF at 77K.

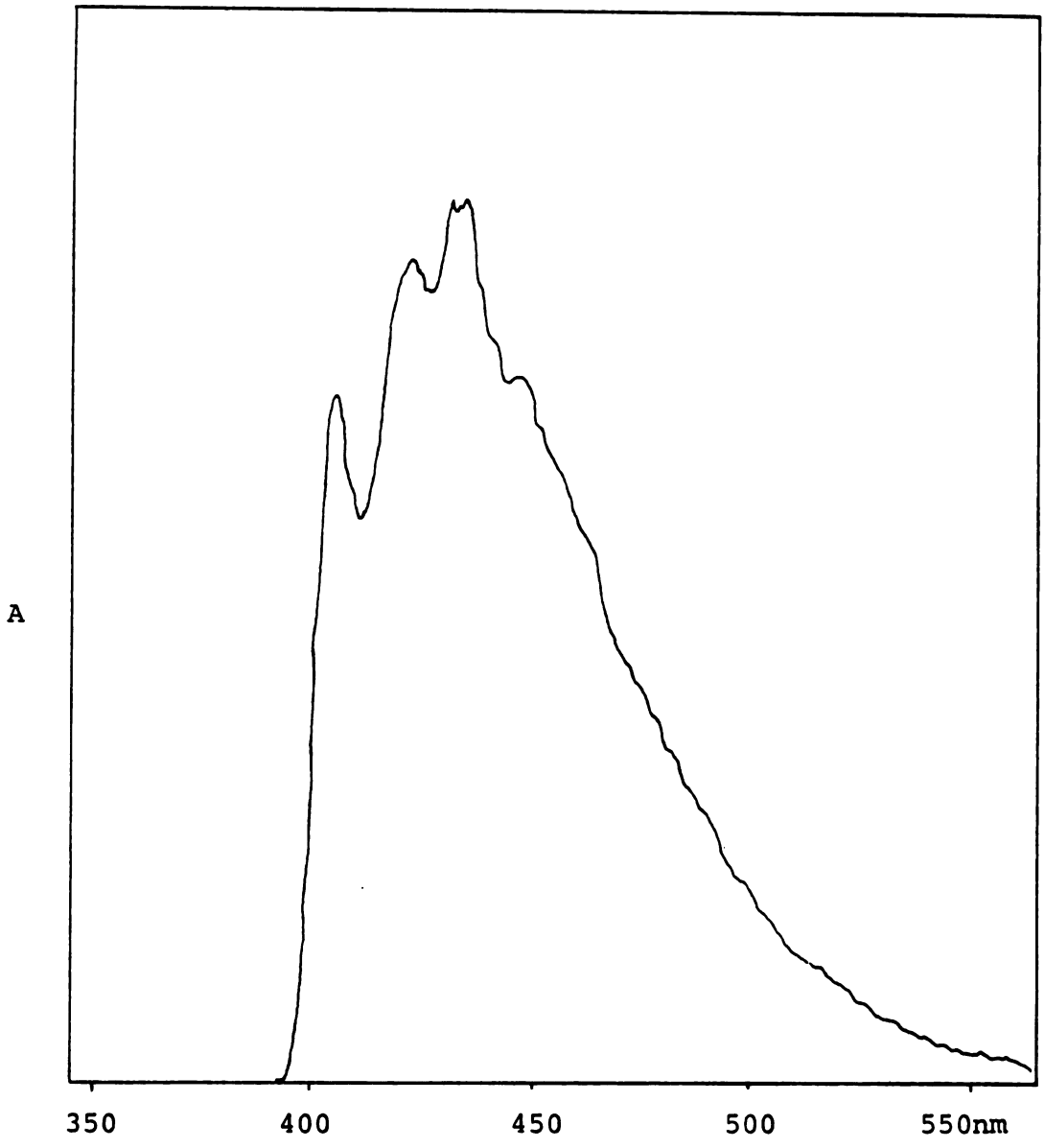


Figure 10. Phosphorescence Spectrum of OMe-2SPh in MTHF at 77K.

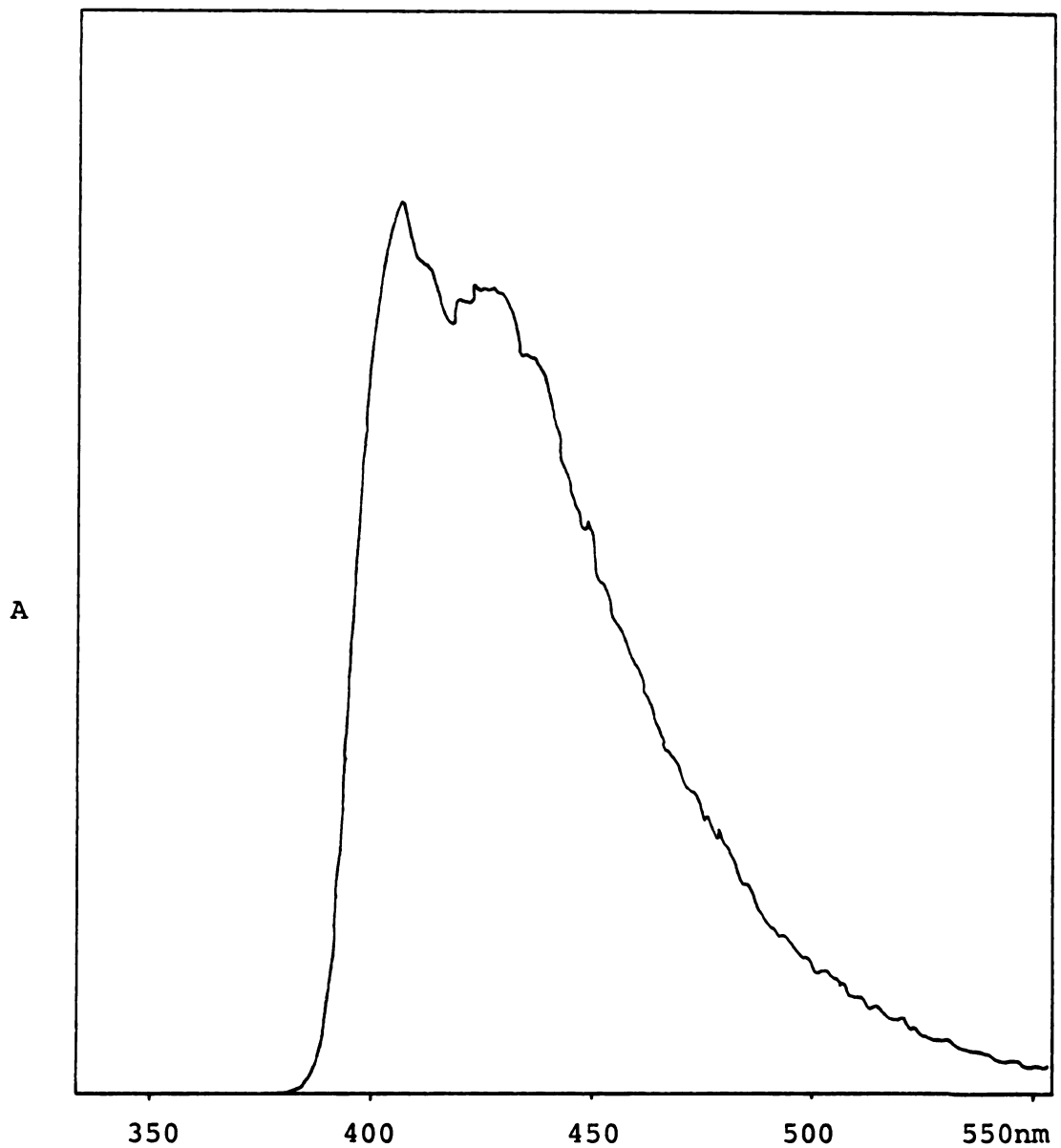


Figure 11. Phosphorescence Spectrum of NMe_2-2SPh in MTHF at 77K.

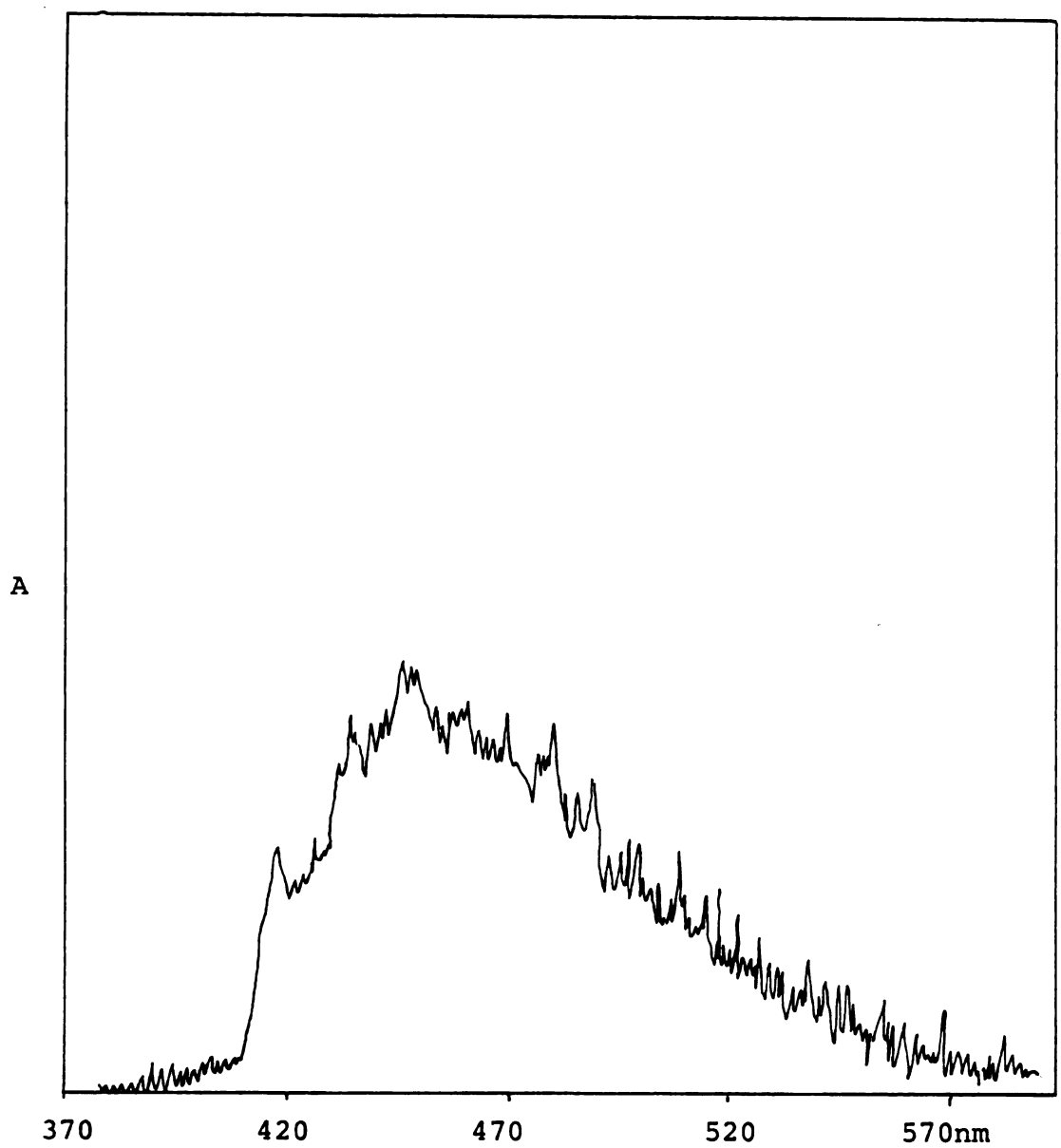
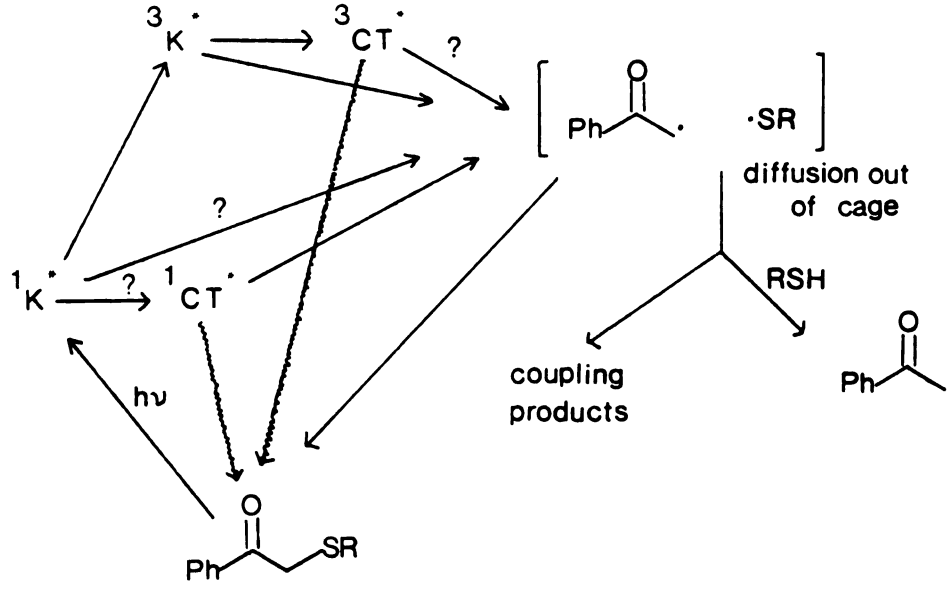


Figure 12. Phosphorescence Spectrum of CN-2SPh in MTHF at 77K.

Discussion

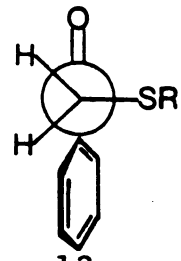
Mechanism

The free radical nature of photoinduced β-cleavage of β-ketosulfides has been firmly established by careful examination of product distributions.[113] On the other hand, certain substituents display a propensity toward heterolytic cleavage as in the case of α-tosylketones, which result in rearranged products typical of carbonium ion chemistry.[114] In the present system, the detection of coupling products--namely, diphenyldisulfide--and the fact that thiols, which are known radical scavengers, greatly enhanced the quantum yields, eliminated heterolytic cleavage as a mechanistic possibility. The mechanism of photoinduced β-cleavage of β-ketosulfides is presented in Scheme 5.

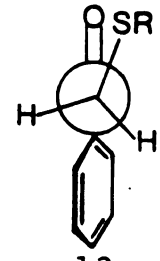


Scheme 5. Mechanism of β-Cleavage of β-Ketosulfides.

As in free radical systems,[115] fairly strict stereochemical alignments between the radical center and the bond that is breaking would be expected. Thus, two important conformations need to be considered: conformation 12, in which the bond that is breaking is parallel to the benzoyl π-system, and conformation 13, in which the breaking bond is parallel to the C-O bond and the sulfur and oxygen are eclipsed. Previous studies on carbonyl compounds[116] containing α-heteroatoms have indicated that conformations 12 and 13 are present in about equal amounts in solution. In fact, α-haloaldehydes and ketones exist primarily in conformation 13 where the carbonyl and halogen atom are nearly eclipsed. However, in the case of α-thioalkoxyaldehydes[117] conformation 12 is clearly dominant. The analogous thioalkoxyketones have not been studied. On the other hand, IR



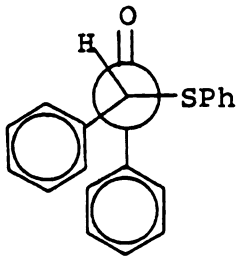
12



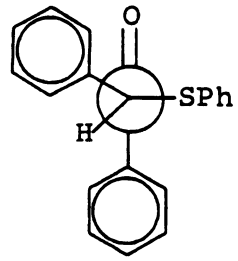
13

studies have shown α-bromocyclohexanone exists primarily in the conformation where the bromine is axial, while the α-chlorocyclohexanone exists in the conformation where it is equatorial. The situation is obviously fairly complicated; however, other factors aside, conformation 12 clearly represents the sterically favored orientation. In fact, such a conformation seems rigidly required by analogy with

the α-tosyloxy-[119] and α-aminocyclohexanones[120] which cleave only when axial. Further support for conformational control of β-cleavage can be gleaned from the fact that phenyldesyl-sulfide (PDS) reacts with a quantum efficiency far below the other phenacylsulfides. Examination of the three important conformational possibilities reveals a possible reason for this.



14



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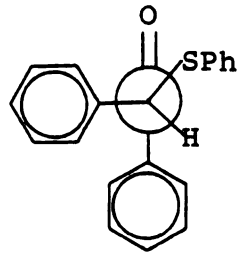
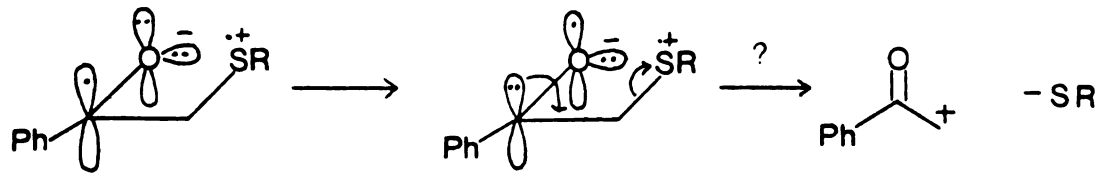


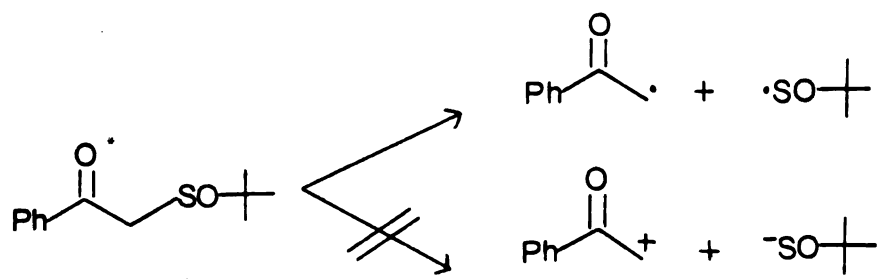
16

In this case, alignment of the proper orbitals as in 14 and 15 causes serious eclipsing interaction between the two phenyl rings or the carbonyl and phenyl ring. Therefore, the amount of conformation 16 present at any time will be higher than normal; and as such, the amount of C-T quenching will be increased.

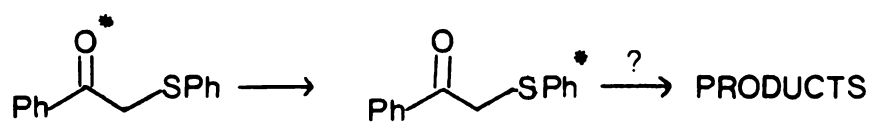
Consideration of conformation 13 does not suggest straightforward type of elimination. However, the geometry enables maximum overlap of the n-orbital on oxygen and one of the lone pairs on sulfur. This conformation allows C-T complexation as discussed in Part I and product formation from such a complex must be considered. One possible mode of cleavage can be envisioned as follows:



However, this seems unlikely in light of the fact that an analogous mechanism is also possible for equatorial α-tosyloxy- and α-aminocyclohexanones, which do not react. Also, 2-SOtBu cleaves smoothly in spite of the fact that SOtBu would be a poor anionic leaving group.[121]



Another mechanistic possibility exists. Direct energy transfer from the carbonyl to the sulfur moiety could result in homolytic cleavage as shown below.



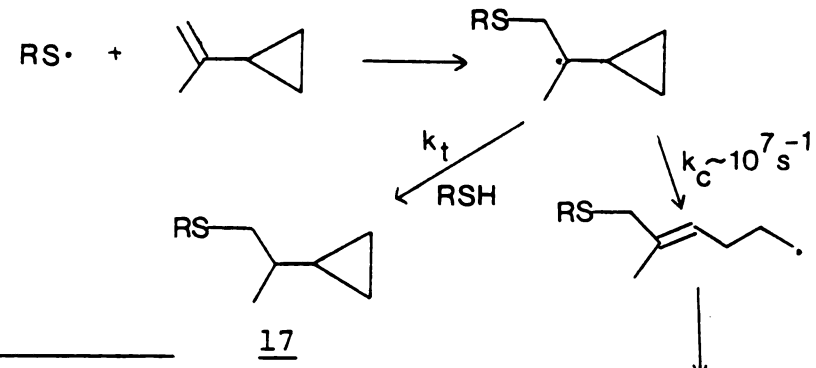
The preferred orientation necessary for energy transfer in this case is unclear. Charge-transfer complexation, on the other hand, between the n-orbital and the lone electron pair

on sulfur can occur only from conformation 13. Triplet-triplet energy transfer for 2-SPh would be slightly endothermic since the triplet energy of thioanisole is ~76 kcal.[122] As substitution on the benzoyl moiety lowers the triplet energy, the exchange would become even more endothermic. In any event, products from homolytic cleavage in 3-SPh and 4-SPh were not observed; so it seems that product formation via energy transfer is unlikely.

Therefore, conformation 13 results mainly in C-T quenching of the excited carbonyl. The amount of this quenching will be discussed later.

Quantum Yields

Tables 9 and 10 present the quantum yields for a variety of structurally variant phenacylsulfides. The addition of benzenethiol leads to fairly large quantum yield enhancements. Out-of-cage coupling is a fairly efficient process, usually leading to respectable yields of dibenzoylethane.[123] Near quantitative material balances in the presence of thiols indicate that all the radicals are scavenged before they get a chance to couple. The rate constant for trapping by alkylthiols (k_t) is on the order of $10^7 M^{-1} sec^{-1}$.[124] The rate constant for trapping by PhSH can be estimated from the addition of thiols to vinylcyclopropane[125] as shown in Scheme 6. When benzenethiol is used, 100% of product 17 is formed, which indicates that $k_t > k_c$. If $k_c \sim 10^7 sec^{-1}$,[126] k_t for PhSH must be $\sim 10^8 M^{-1} sec^{-1}$.

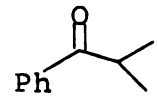
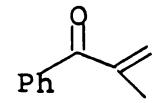


RSH	%17	%18
CH_3SH	12	88
ϕSH	100	0

Scheme 6. Addition of Thiols to Vinylcyclopropane.

Examination of Table 10 reveals some interesting information regarding s-2SPh and t-2SPh. Although the disproportionation products--i.e., vinylacetophenone and α-methylacrylophenone--could not be separated from their saturated analogues under the analytical conditions, nmr experiments on t-2SPh allowed approximate measurement of the amount of α-methylacrylophenone (MAP). Curiously, no enhancement of quantum yield was observed for either compound upon the addition of PhSH. Table 13 lists the approximate amounts of reduction and disproportionation products from t-SPh as estimated by nmr experiments. In the presence of thiol, it is assumed that most of the radicals that diffuse out of the cage are trapped. Thus, most of the disproportionation product (MAP) in the presence of thiol is probably coming from in-cage disproportionation. The slight

Table 13. Approximate Percentage of IBP and MAP Found in the Photolysis of t-2SPh.

Solvent	 (IBP)	 (MAP)	$\phi_{IPB + MAP}$
Benzene	45	55	0.33
Benzene 0.05M ϕSH	83	17	0.34

predominance of MAP in the absence of thiol is also indicative of in-cage disproportionation. The amounts of IBP and MAP are comparable in the absence of benzenethiol, indicating that out-of-cage disproportionation greatly predominates over coupling as is the case for t-butyl radicals.[127] Data are not available for s-2SPh, but one would expect a lesser predominance of disproportionation over recombination due to the diminished amount of β-hydrogens.[128]

Spectroscopy

Any discussion of substituent effects upon the rate of a photoreaction must include an examination of the nature of the excited state or states responsible. Since the $^3n,\pi^*$ and $^3\pi,\pi^*$ states are in energetic proximity for phenyl alkyl ketones[129] and the benzene π,π^* excitation energy is strongly influenced by substituents, the effects of substituents upon the energy levels of the n,π^* and π,π^* triplets must be noted.

Both electron donors and acceptors stabilize π,π^* transitions,[130] with the exception of the strongly withdrawing CF_3 group, which tends to increase the $S_o \rightarrow {}^1L_A$ transition energy since it cannot extend conjugation.[131] Thus, the conjugative effects generally outweigh any inductive effects. While electron donors stabilize the $S_o \rightarrow {}^1L_A$ transition of acylbenzenes, they tend to destabilize n,π^* transitions, eventually resulting in inversion of the triplet levels for strong donors.[132] The effect of substituents upon the ordering of n,π^* and π,π^* states is presented below.

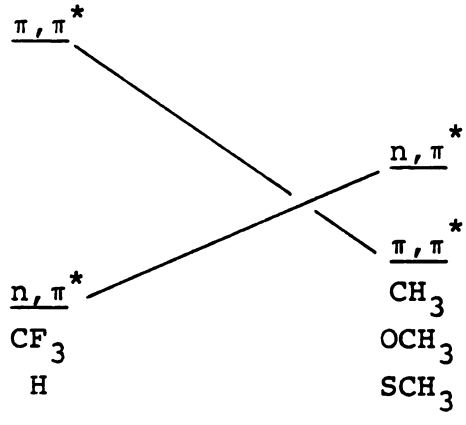


Table 12 presents the triplet energies of some ring-substituted phenacylsulfides. The phosphorescence spectrum of 2-SBu is presented in Figure 8 and strongly resembles valerophenone in which the vibrational structure corresponds to the ground state carbonyl stretch.[133] The triplet energy is about 3 kcal lower than valerophenone due to the inductive effect of the α-thioalkoxy group, which stablizes the n,π^* state slightly. The spectra of the α-thiophenylacetophenones (Figures 9 through 12), on the other hand, show a marked lack of structure, resembling more π,π^* states.

Disturbingly, the E_t for the α-thiophenylacetophenones are almost identical to the corresponding ring-substituted valerophenones. The discrepancy here is why does SBu lower the E_t energy relative to the corresponding valerophenone but SPh seems to have no effect. Several possibilities seem to exist. One possibility is that emission is being observed from two different n,π^* triplets, analogous to that observed in the dual phosphorescence of phenylalkylketones.[134] Thus, two excited state conformations, the higher in energy of which resembles the ground state conformation, would yield different E_t's. Extrapolation to the phenacylsulfide case presents the possibility that 70.9 kcal represents the conformationally relaxed emission of 2-SBu, whereas the values for the α-thiophenylacetophenones represent emission from a higher, unrelaxed state. Therefore, the increase in energy would offset the decrease expected on inductive grounds. The difference between SBu and SPh apart from extended conjugation in SPh are primarily steric in nature. Since dual phosphorescence is highly dependent upon the nature of the solvent,[135] which in turn determines the orientation of the carbonyl and sulfur groups in the glassy matrix, subtle changes in conformational orientation could result.

A more obvious possibility is that 2-SPh is actually a lowest π,π^* state (p-OMe and p-NMe_2 are most certainly so), whereas 2-SBu is n,π^* in nature. The inductive effect of the α-substituent would not be expected to affect a π,π^* state as much as an n,π^* state.

Lastly, a disturbing possibility is that β-cleavage to yield a radical pair is competitive with emission in the glassy matrix. If that is the case, the emission would actually be from the acetophenone moiety, and the lack of structure in the phosphorescence spectra could be explained by its free radical nature.

The effect of α-substituents on the uv spectra is also interesting. The intensification of the n,π^* transition and its subsequent red shift relative to the unsubstituted ketone has been noted previously for α-heteroketone spectra.[136] In fact, the original observation by Jones[137] has since been extensively used in conformational analysis. Again, two conformations need to be considered: one, where the C-X bond is parallel to the π-system which corresponds to an axial substituent for a cyclohexanone as in conformation 12, and two, where the C-X bond is parallel to the C-O bond corresponding roughly to the analogous equatorial cyclohexanone substitutent as in conformation 13.

The intensification of the n,π^* absorption and its shift to longer wavelength is observed only for axial substituents. Equatorial substituents on α-substituted cyclohexanones produce either no effect or cause a slight blue shift. Allinger[138] has ascribed this effect to hyperconjugation between the C-X bond and the carbonyl π-system. Interaction between the carbonyl π^* level and a low lying C-Xσ^* orbital when X is axial gives rise to a red shift. Hoffmann[139] has recently treated the α-aminoketones

theoretically and found Allinger's arguments essentially correct in that the hyperconjugation effect is extremely dependent upon C-N/π-system alignment. Little beyond this is known about the α-heteroatom effect, but the nature of the effect can perhaps be likened to the Murrel[140] or Labhart-Wagnier[141] models for β-γ unsaturated carbonyls. In any event, it seems that enhanced absorptions are observed whenever a carbonyl and group of low ionization potential are present with proper mutual geometric disposition.

Table 11 presents the uv data for selected substituted phenacylsulfides, and Figure 7 shows the actual spectra of 2-SBu in heptane and in ethanol. As mentioned previously, fine structure is observed in the n,π^* shoulder for all compounds in heptane but disappear when ethanol is used as solvent. This observation is a rare occurrence but has been observed previously in cyclobutanone[142] and exo-dicyclopentadienone.[143] Interestingly, the spacing of the structure corresponds to the stretching frequency of the excited carbonyl singlet (about 1200 cm^{-1}).[144]

Differing behavior between α-SBu and α-SPh substituents are also noted in the uv. SBu stabilizes the n,π^* transition relative to acetophenone (λ_{max} n,π^* = 316nm) but does nothing to the π,π^* transition. However, SPh stabilizes both n,π^* and π,π^* transitions. There is obviously some interaction between the phenyl ring and the benzoyl π-system but the exact nature of this observation is unknown. As noted previously,[145] electron donating groups tend to stabilize the π,π^* transition while raising the n,π^*

transition energy. Conversely, CN-2SPh stabilizes the n,π^* transition but also lowers the π,π^* band because of its ability to extend the conjugation.

Rates of β-Cleavage and Charge-Transfer

The rate constant of β-cleavage, k_β, is calculated from equation 9.

$$k_\beta = \frac{\phi_{corr}}{\tau} \qquad (9)$$

where ϕ_{corr} equals the observed quantum yield multiplied by two to correct for about 50% in-cage recombination. The remaining inefficiency is assumed to be due to C-T quenching and is calculated as mentioned previously from equation 8. The rate data are listed in Table 14.

The rate of β-cleavage can be influenced by three factors: the nature of the excited state, the stability of the incipient radicals, and the overall thermodynamics of the system.

A consideration of the effect of excited state upon reactivity centers upon the dichotomy between the n,π^* and π,π^* states. As can be seen from the phosphorescence studies, all substituents tend to lower the triplet energy. However, the lowering of the triplet energy is accompanied by an opposing effect. That is, electron donors are indeed lowering the E_t, but they are also inverting the ordering of the n,π^* and π,π^* states. Incomplete knowledge

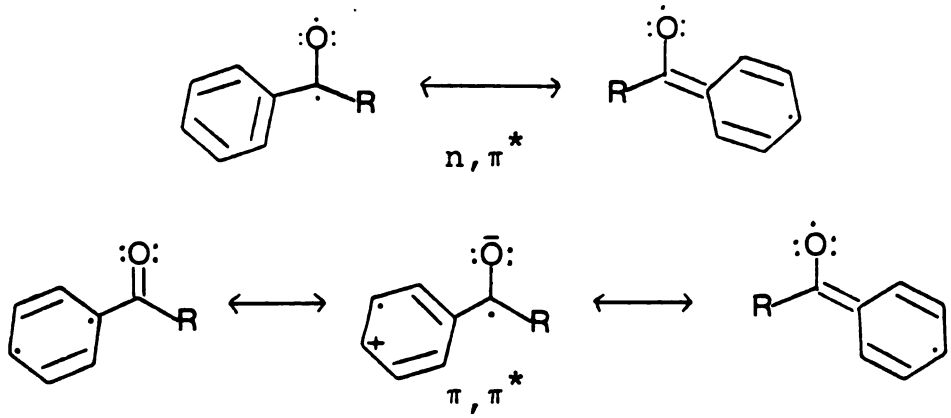
Table 14. Calculated Rate Data for Various Phenacylsulfides.

Compound	ϕ_{max}^{corr}[a]	$\frac{1}{\tau}, 10^8 s^{-1}$	$k_\beta, 10^8 s^{-1}$	$k_{ct}, 10^8 s^{-1}$
2-SPh	0.48	---	>100	---
F-2SPh	0.48	---	>100	---
Cl-2SPh	0.48	62.4	30.0	32.5
Br-2SPh	0.40	25.0	10.0	15.0
Me-2SPh	0.60	---	>100	---
OMe-2SPh	0.82	22.7	18.4	4.30
SMe-2SPh	0.38	1.67	0.63	1.04
NMe_2-2SPh	0.38	3.62	1.38	2.24
ϕ-2SPh	0.54	1.25	0.68	0.58
CN-2SPh	0.32	46.3	14.8	31.5
s-2SPh	0.64	---	>100	---
t-2SPh	0.68	---	>100	---
cy-2SPh	0.84	36.2	30.4	5.80
4'-MSPh	0.80	---	>100	---
2-StBu	0.08	12.8	1.02	11.8
4'-SPh	<0.002	---	---	---
PDS	0.02	---	---	---

[a]Calculated by doubling the observed quantum yield.

of the multiplicity of the reaction prevents a good correlation between the phosphorescence and uv data and the observed reactivity. However, all reactivity comes from the triplet state in the compounds which are quenchable--it is the efficienty of triplet formation which is unknown. One general observation is applicable--i.e., electron donors tend to slow down the reaction. However, this immedicately implies that π,π^* states are less reactive than n,π^* states. The reduced hydrogen abstraction ability of the carbonyl in the $^3\pi,\pi^*$ state is understandable in terms of its greatly reduced electrophilicity,[146] but the mechanism of β-cleavage requires only that there be free spin on the carbonyl carbon.

The valence bond representation of the respective states are shown below.



The main difference between the two is that in the n,π^* state, an electron from the n-orbital on oxygen is promoted to a π^*-orbital, whereas the π,π^* state results from promotion of an electron from the π-system to a π^*-orbital. Both representations, however, indicate significant amounts of spin on the carbonyl carbon, but in actuality it is known that most of the excitation in π,π^* states is localized in

the benzene ring.[147] Thus, it would appear that the observed decrease in rate with electron donating substituents is due to a decreased amount of spin density at the carbonyl carbon. In simpler terms, the n,π^* state resembles a 1,2-biradical, whereas a π,π^* does not.

Table 14 reveals a difference in the observed rate of C-T quenching, k_{ct}, between the electron donating and releasing substituents. Charge-transfer occurs primarily between the lone electron in the n-orbital and the lone pair on sulfur in the n,π^* state. Not much C-T formation between the π-system in the π,π^* state and sulfur is expected since the oxygen is already "electron rich." Thus, as the lowest triplet becomes π,π^*, a decrease in k_{ct} is observed. Any C-T involving the π-system would in any event be decreased by electron donating groups. The effect of a p-CN-substituent is curious. It has the effect of decreasing the rate of cleavage much like electron donors; and, in fact, its phosphorescence spectrum resembles a π,π^* state. However, its strong electron withdrawing effect increases the amount of k_{ct} by lowering the reduction potential of the carbonyl. As mentioned in the Introduction, the interposition of a π,π^* state for a n,π^* state has been shown to eliminate (or greatly slow down) β-cleavage.[148]

As is the case in free radical chemistry, the stability of the incipient radicals in part determines their rates of formation.[149] The k_β for cy-2SPh is less than t-2SPh. The difference here presumably lies in the difference in

a tertiary radical and a 3° cyclopropyl radical. The instability of the cyclopropyl radical probably reflects its inability to attain a planar sp^2 configuration.[150] The cyclopropyl radical is surpassed only by the phenyl radical in difficulty of formation.[151]

The nature of the leaving group--i.e., the sulfur moiety--probably has the greatest effect on the rate of β-cleavage. Table 15 lists some relative rates of β-cleavage for various phenacylsulfur moieties.

Table 15. Relative Rates of β-Cleavage in Phenacylsulfides.

Compound	$k_\beta, 10^8 sec^{-1}$	k_{rel}
2-StBu	1.02	1
2-SOMe	44.9[a]	44
2-SO_2Me	0.078	0.078
2-SPh	>100	>196

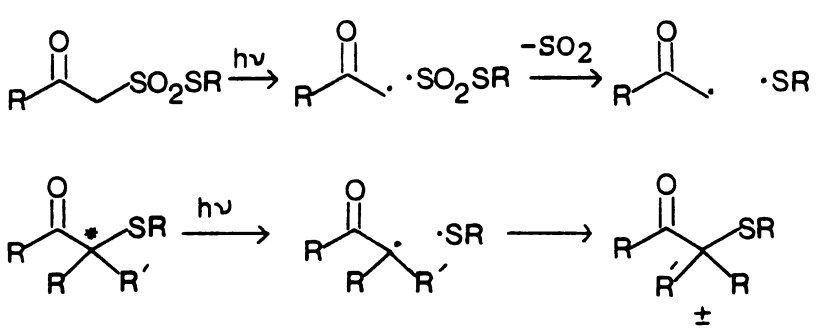
[a]Data from Table 8.

That ·SPh is more stable than SR has been demonstrated repeatedly.[152] The order of stabilities--i.e., SPh > SOR > SR > SO_2R--confirms Rice's[153] original suggestion that SOR has the greatest kinetic stability compared to SR or SO_2R. A more detailed discussion of leaving groups will be forthcoming in the section on δ-substituted valerophenones.

The strength of the C-S bond in the phenacylsulfides is intrinsically related to the stability of the incipient radicals. The bond dissociation energy for $CH_3SPh \rightarrow \cdot CH_3 + \cdot SPh$ equals about 60 kcal/mole[154] and would probably be lower for 2-SPh since an α-keto radical is being formed rather than a methyl radical. Thus, even in the case of NMe_2-2SPh, where the triplet energy is about 62 kcal/mole, the energy requirements are sufficiently met. However, as the triplet energies are lowered, the gap between the bond dissociation energy and the triplet energy becomes smaller, or less exothermic, and may explain the observed decrease in rate of β-cleavage. The bond dissociation energy for $CH_3SCH_3 \rightarrow \cdot CH_3 + \cdot SCH_3$, which would correspond roughly to β-cleavage in 2-SMe, is about 73 kcal/mole.

Indications for Further Research

Estimation of In-Cage Coupling. A more accurate estimates for the amount of in-cage radical recombination could be gained by studying the following compounds:

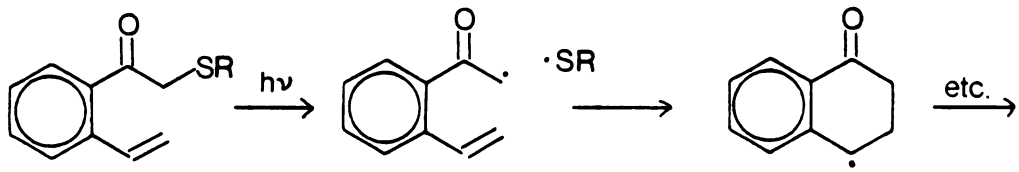


Generation of the two radicals might be possible by extrusion of SO_2 from the thiosulfonate, thus yielding the desired

radical pair. There is, however, the question as to whether this would be an in-cage process.

A measurement of the extent of racemization of an optically active phenacylsulfide might give some indication of the amount of in-cage recombination.

Generation of Free Radicals. This system offers an excellent way to generate free radicals. Processes such as intramolecular or intermolecular additions could be studied.



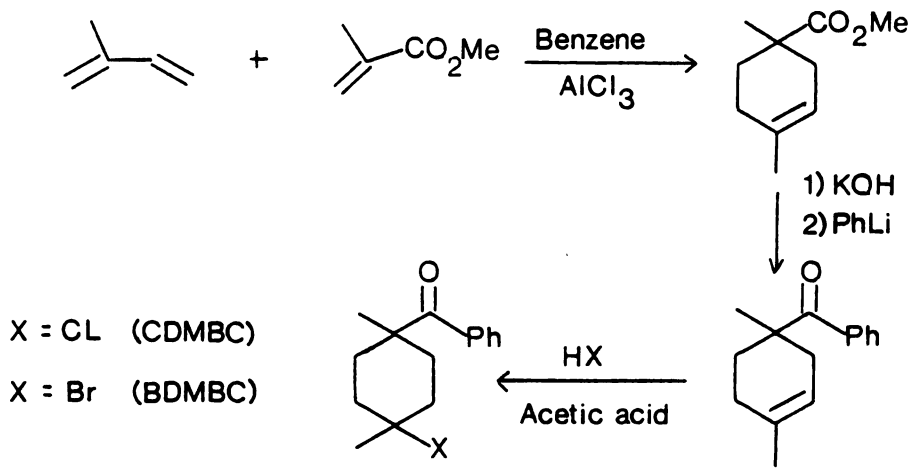
This system also offers an excellent opportunity to study solvent effects upon radical reactions since little is known in this respect.

δ-Substituted Phenyl Ketones

Results

Synthesis

The δ-substituted valerophenones listed in Table 16 were prepared by S_n2 displacement of δ-chlorovalerophenone with the sodium salt of the appropriate nucleophile. To eliminate direct interaction between the benzoyl group and δ-substituent as the cause of elimination of HX, compounds in which the benzoyl group and X were inaccessible to each other were synthesized as outlined in Scheme 7.



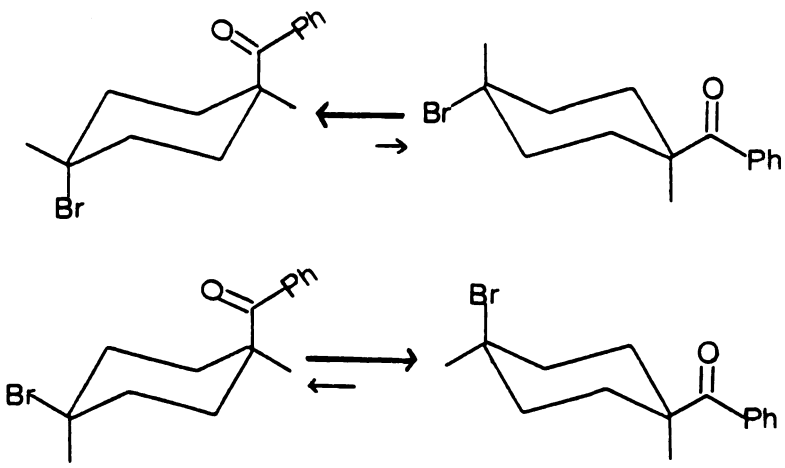
Scheme 7. Synthesis of 4-Halo-1,4-Dimethyl-1-Benzoylcyclohexanes.

The Diels-Alder Reaction between isoprene and α-methylmethacrylate proceeded smoothly in benzene in the presence of a catalytic amount of aluminum chloride. Interestingly, a high degree of regioselectivity is observed in that only the 4-methyl isomer is isolated. The directing effect of $AlCl_3$ and other Lewis acids is fortunate because the thermal reaction yields significant amounts of the 3-methyl isomer. Unfortunately, the analogous cycloaddition utilizing α-methylacrylophenone and isoprene did not go. It was feared that thermolysis would lead to a inseparable mixture, so this path was not pursued further. Subsequent hydrolysis of the ester to yield the acid and reaction with two equivalents of PhLi to form the phenyl ketone proceeded in 95% and 60% yields, respectively. Addition of HX was found to be

exceedingly sluggish in ether or hydrocarbon solvent but was found to proceed smoothly in glacial acetic acid. In the case of the bromo-derivative, the two diastereomers were separable by fractional crystallization, but such was not the case for the Cl isomer for which only one diastereomer was obtained.

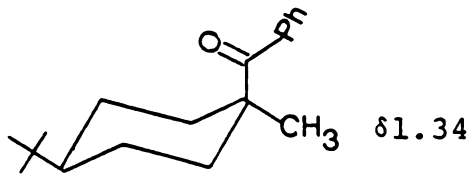
Identification of Diastereomers

Spectral comparison of the two bromide diastereomers revealed significant differences in the chemical shift in the ^{1}H and ^{13}C for the 1-methyl group. Based on experimental free energy differences between axial and equatorial substituents,[155] the following assumptions about the conformational equilibria were made:

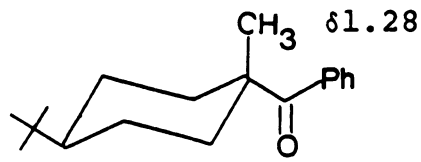


Differentiation between the 1- and 4-methyl groups is straightforward. The effective shielding constant[156] of Br is larger than COPh, so one would expect the 4-methyl group to appear farther downfield. A difference between axial and equatorial absorption in the nmr and ^{13}C have been

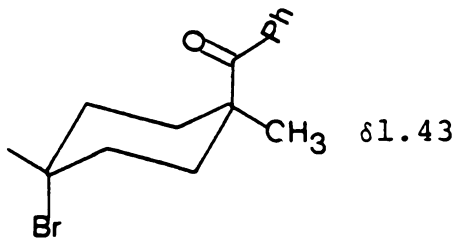
noted previously, where axial protons and methyl groups usually resonate at higher field strengths.[157] The conformational assumptions reveal that the 1-methyl group is equatorial most of the time in trans-BDMBC, whereas it is mostly axial for cis-BDMBC. Comparison with similar measurements on 18 and 19 by Lewis[158] is revealing.



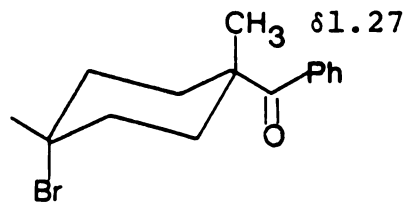
δ1.34



δ1.28



δ1.43



δ1.27

An analogous effect is noted in the ^{13}C where the 1-methyl group in cis-BDMBC resonates at much higher field strength than trans-BDMBC.

In the case of the chloride, the assignment was not so straightforward since only one diastereomer was obtained. However, by analogy with the bromo-derivatives, its physical properties suggested it was the trans-isomer. An X-ray structure (see Figure 13) confirmed the original suspicion.

Europium shift studies on the known trans-chloro isomer and the suspected trans-bromo isomer related the structures and

confirmed the original assignments (see Figures 14, 15, and 16). The photoreactivity of each diastereomer also supported the assignments.

Identification of Photoproducts

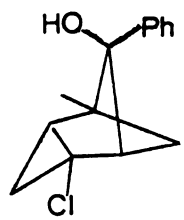
All the δ-substituted valerophenones produced acetophenone and 4-benzoyl-1-butene (4-BB) in varying amounts. In the case of 5-SPh, acetophenone and 4-BB were isolated by preparative vpc and compared to authentic samples. Subsequent identification of acetophenone and 4-BB was made by comparison of vpc retention times with authentic samples. The radical coupling product from 5-SPh--i.e., diphenyldisulfide--was identified by comparative vpc retention times. A small peak which was assumed to be the cyclobutanol was observed in the vpc for 5-SPh and certain other compounds. The coupling product from 5-SOBu--i.e., $BuSO_2SBu$--was identified by comparative vpc retention times. The olefinic fragments resulting from Type II cleavage were not identified or measured.

Elimination of p-methoxyphenol from 5-OPh was not observed. Only acetophenone formation was observed. Cleavage of a C-O bond in 4-OBzhydl, resulting in the formation of benzhydrol and β-benzoylpropionaldehyde was anticipated but not observed. Again, only Type II cleavage was observed.

Unfortunately, BDMBC and CDMBC were found to be extremely unstable to vpc analysis, yielding 1,4-dimethyl-1-benxoylcyclohex-3-ene (DMBC) as a broad, tailing peak upon

injection on QF-1, SE-30 or Carbowax columns at various column and injector temperatures. Analogous elimination of HX was observed upon column chromatography on either neutral alumina or silica gel. This decomposition greatly complicated the identification of DMBC as a photoproduct.

However, prolonged photolysis of CDMBC resulted in complete consumption of starting material and resulted in two peaks in the vpc trace. The shorter retention time peak was shown to be DMBC by comparison with an authentic sample, whereas the longer retention time peak was assumed to be the cyclization product resulting from γ-hydrogen abstraction. Attempts to isolate this compound proved futile.



However, an IR of the crude photolysate revealed a fairly intense OH absorption at about 3500 cm^{-1}. Addition of Br_2 to the crude photolysate resulted in the precipitation of an orange solid, which was found to be identical to the bromine addition product of DMBC. Furthermore, zinc dust debromination of the orange product yielded DMBC by vpc.

Lastly, the photolysis of trans-BDMBC in benzene-d_6 containing 0.05M pyridine resulted in the appearance of vinylic proton absorptions in the nmr. Since Type II cleavage products are not found to any significant extent in these

systems,[159] the vinylic absorptions can be ascribed with a fair degree of confidence to DMBC.

Quantum Yields

The quantum yields of acetophenone and 4-BB formation from the δ-substituted valerophenones were measured as previously described at 3130Å and are presented in Table 16. The solvent effects on II:4-BB ratios are presented in Table 17.

Since cis- and trans-BDMBC and trans-CDMBC decomposed upon analysis, yielding DMBC, the product could not be measured directly. Fortunately, trans-CDMBC was found to decompose in consistent amounts to the extent of around 25%. Enhancements beyond this value were taken to be equal to the amount formed upon photolysis. However, cis- and trans-BCMBC decomposed quantitatively, so quantum yields were determined by measuring the disappearance of pyridine, which complexed HBr to form insoluble pyridinium hydrobromide. Benzaldehyde quantum yields from cis- and trans-BDMBC and trans-CDMBC were measured in the usual manner. The quantum yields for formation of DMBC and benzaldehyde from cis- and trans-BDMBC and trans-CDMBC are listed in Table 18.

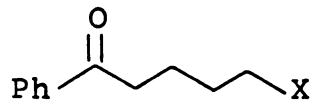
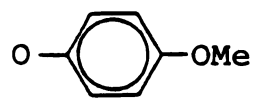
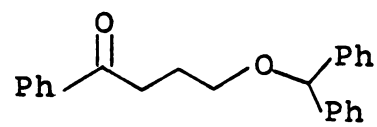
Quenching Studies

The Stern-Volmer quenching plots for the δ-substituted valerophenones were measured as previously described at 3130Å with 1,3-pentadiene as quencher and have been listed in Part I. The quenching plot for BDMBC and CDMBC were measured at 3660Å by quenching the disappearance of pyridine

with napthalene. The formation of benzaldehyde was quenched by napthalene. These values are listed in Tables 18.

The effect of temperature upon $k_q\tau$ for valerophenone and δ-iodovalerophenone in benzene was determined. The plot is presented in Figure 17.

Table 16. Quantum Yields of Acetophenone and 4-Benzoyl-1-Butene Formation from Various δ-Substituted Valerophenones.

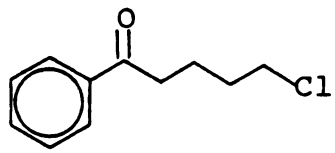
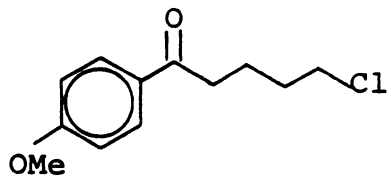
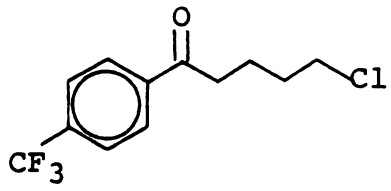
Compound	ϕ_{II}	$\phi_{4\text{-BB}}$
 (5-X)		
X		
Cl	0.58[a]	0.10[a]
Br	0.05[a]	0.55[a]
I	<0.002[a]	0.43[a]
SCN	0.003	0.25
SAc	0.78	0.02
SBu	0.21	0.006
SOBu	0.03	0.39
SO_2Bu	0.39	0.03
StBu	0.16	0.01
SOPh	0.003	0.32
SO_2Ph	0.19	0.22
SPh	0.015	0.28
	---[b]	0.00[b]
 (5-OBzhydl)	---[c]	---[c]

[a]Measured by J. H. Sedon in the presence of 0.1M pyridine (see reference 160).

[b]No 4-BB detected. Acetophenone present but not measured.

[c]No detectable β-benzoylpropionaldehyde. Acetophenone present but not measured.

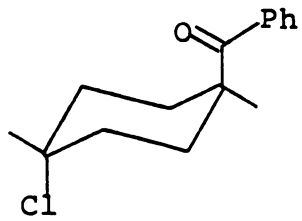
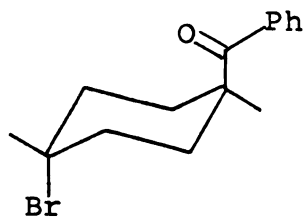
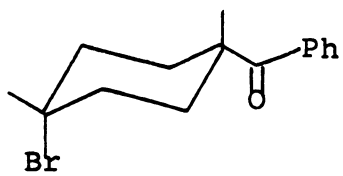
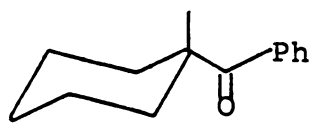
Table 17. Solvent Effects on β-Cleavage for Various δ-Chlorovalerophenones.[a]

Compound	Solvent	ϕ_{II}	$\phi_{4\text{-BB}}$	$II/_{4\text{-BB}}$
	Benzene	0.58	0.10	5.8
	Dioxane	0.36	0.06	6.0
	CH_3CN	0.54	0.08	6.8
	MeOH	0.36	0.06	6.0
	Benzene	0.045	0.008	5.6
	CH_3CN	---[b]	---[b]	(18)
	MeOH	---[b]	---[b]	(22)
	Benzene	0.63	0.07	9.0
	Dioxane	0.20	0.028	7.1
	CH_3CN	0.63	0.04	16
	MeOH	0.43	0.03	14

[a]All measurements made in benzene containing 0.10M pyridine.

[b]Too low to measure.

Table 18. Quantum Yields and Rate Data for 4-Halo-1,4-Dimethyl-1-Benzoylcyclohexanes.

Compound	ϕ_{CHO}[a]	$k_q\tau_{CHO}$	ϕ_{DMBC}	$k_q\tau_{DMBC}$
	0.008	233	0.21 0.01[b]	100
	0.019 0.017	208	0.45(0.05M)[d] 0.40(0.10M)[d]	10.7
	0.11	210	0.12(0.05M)[d]	65
	0.20[c]	200	0.045	29

[a] 0.02M ϕSH.

[b] Presumed to be bicyclic alcohol.

[c] See reference 161.

[d] Number in parenthesis refers to the concentration of added pyridine.

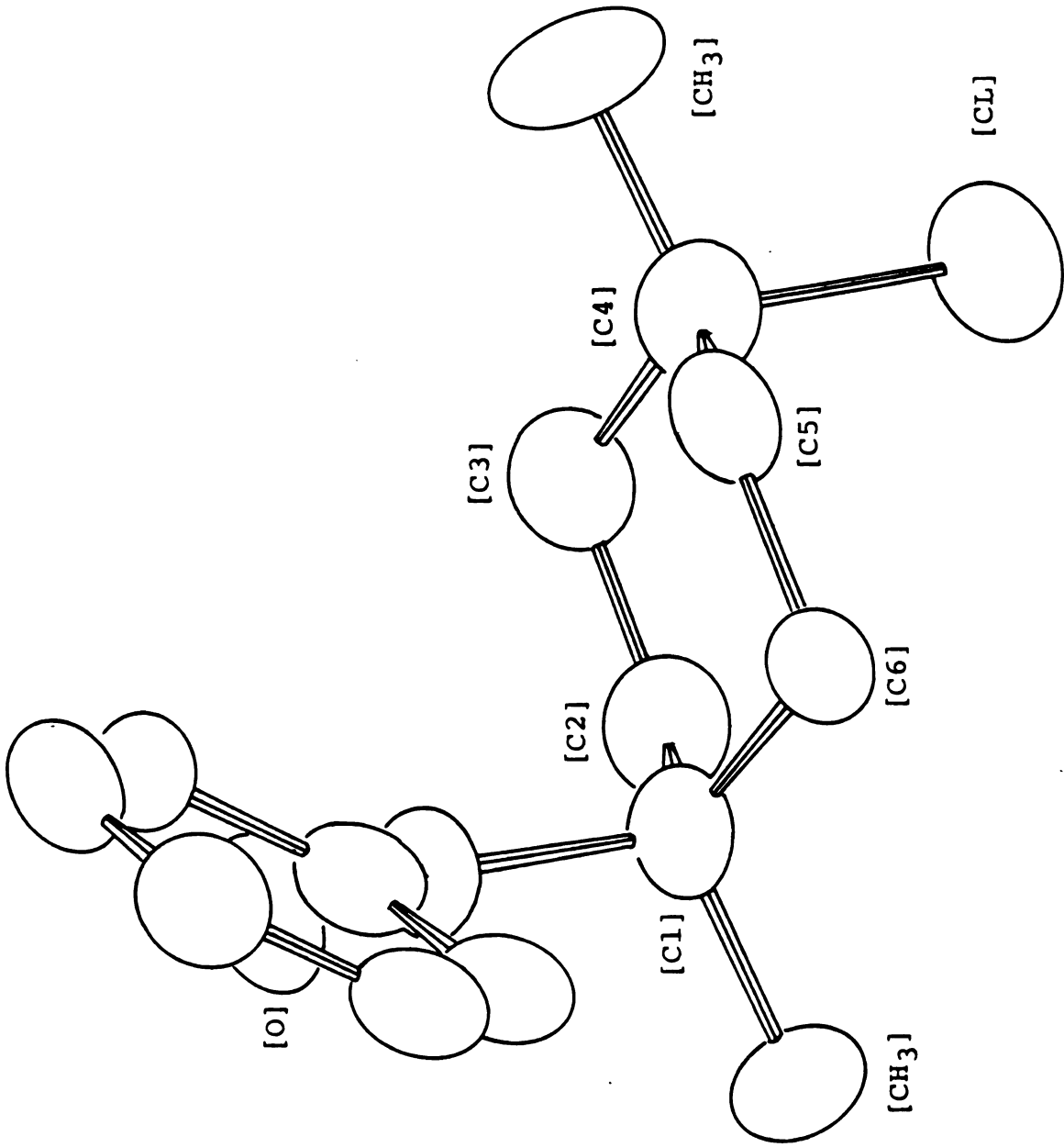


Figure 13. X-Ray Crystal Structure of trans-CDMBC.

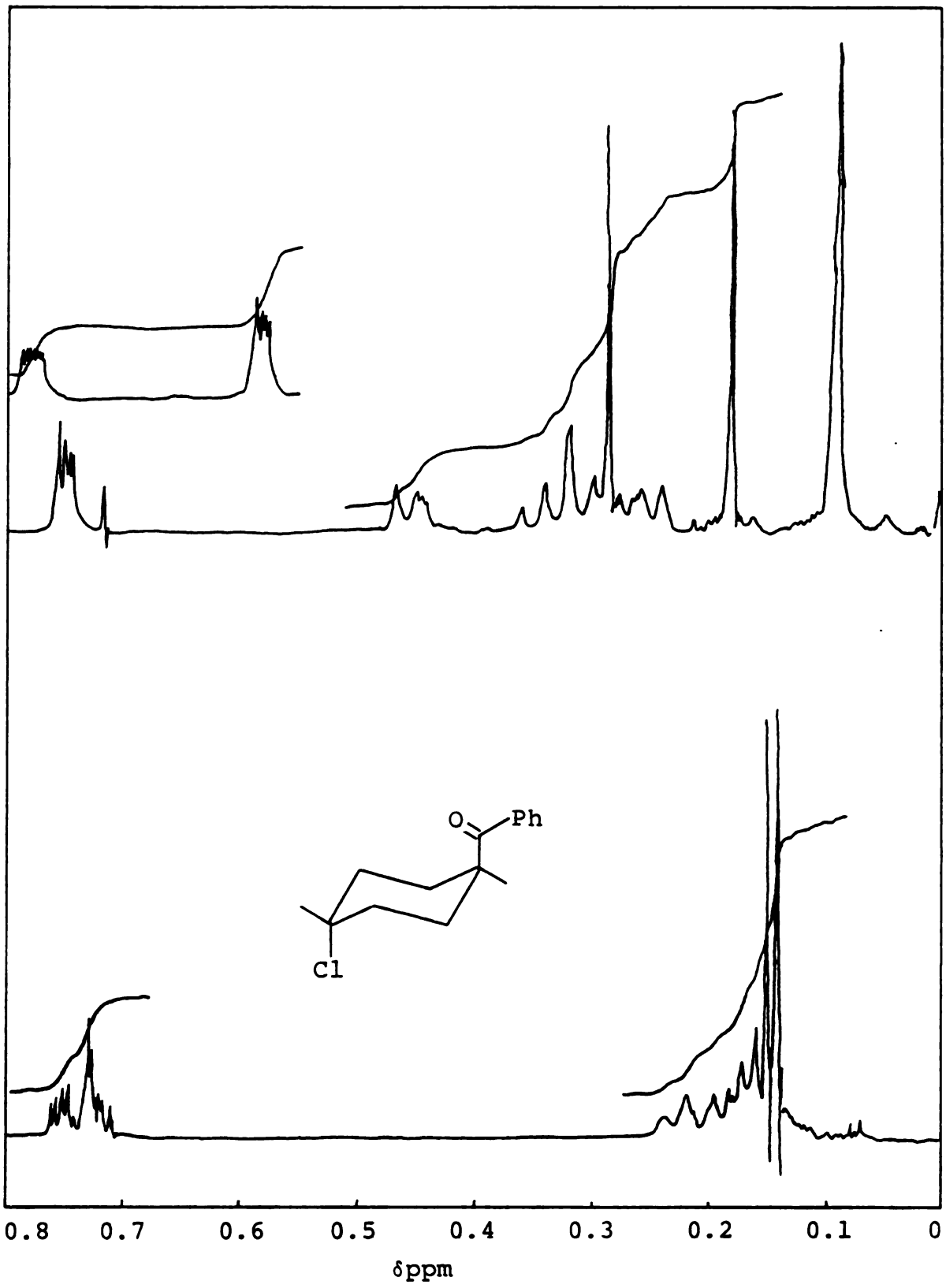


Figure 14. NMR Spectra of trans-CDMBC in $CDCl_3$ (Bottom); in $CDCl_3$ Containing 0.0259g/0.5ml $Eu(fod)_3$ (Top).

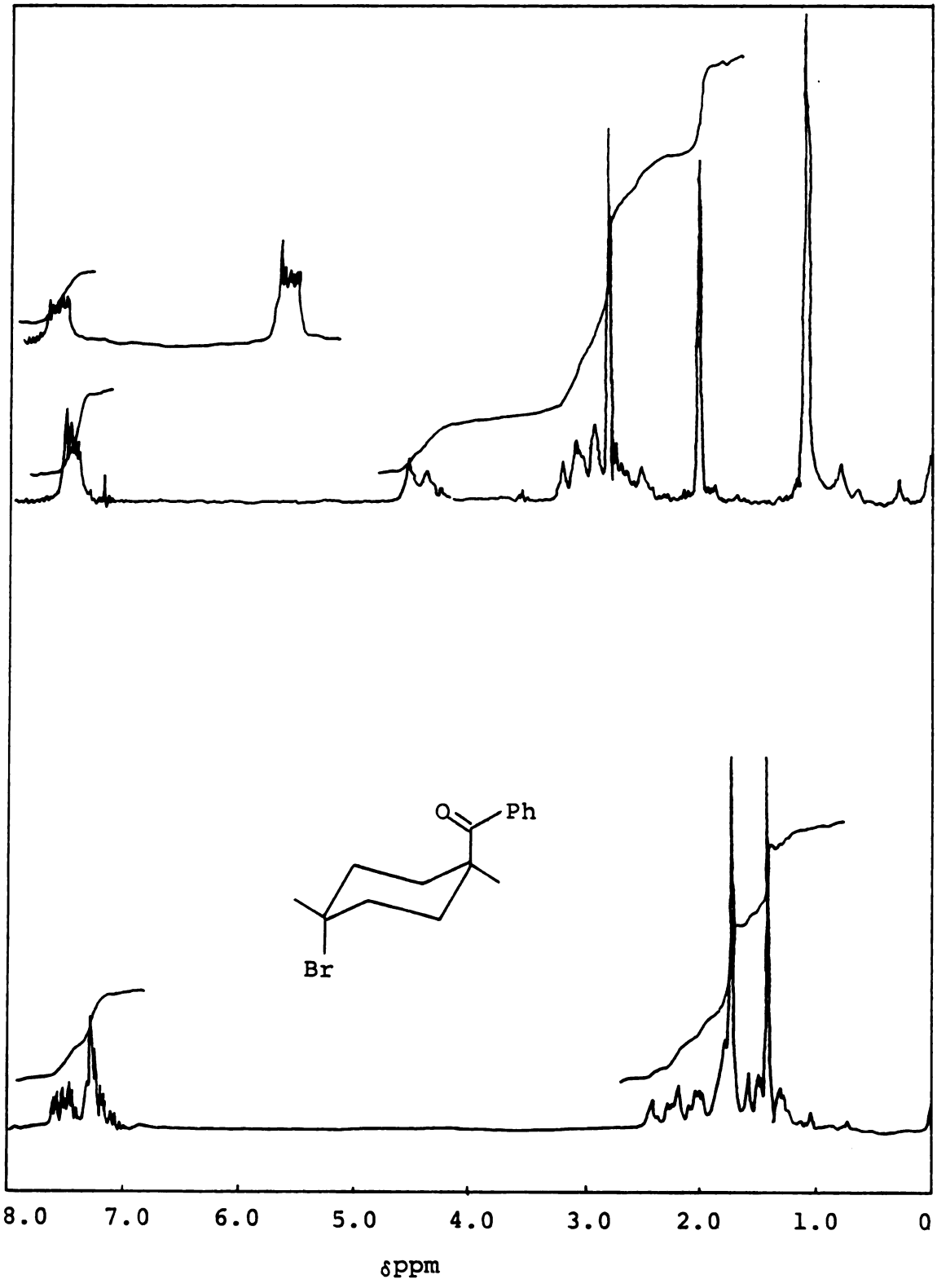


Figure 15. NMR Spectra of trans-BDMBC in $CHCl_3$ (Bottom); in $CDCl_3$ Containing 0.0259g/0.5ml $Eu(fod)_3$ (Top).

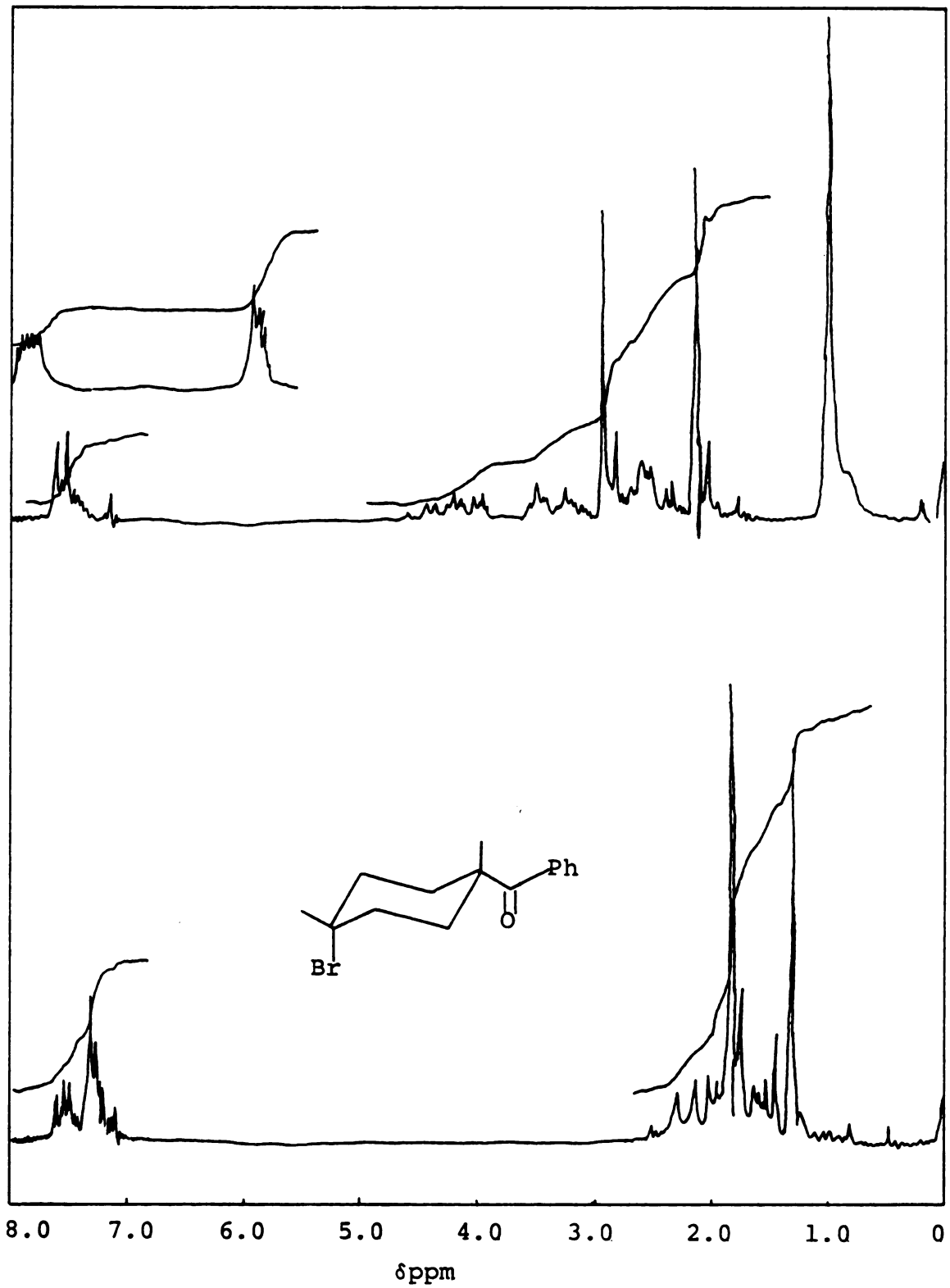


Figure 16. NMR Spectra of cis-BDMBC in $CDCl_3$ (Bottom); in $CDCl_3$ Containing 0.0259g/0.5ml $Eu(fod)_3$ (Top).

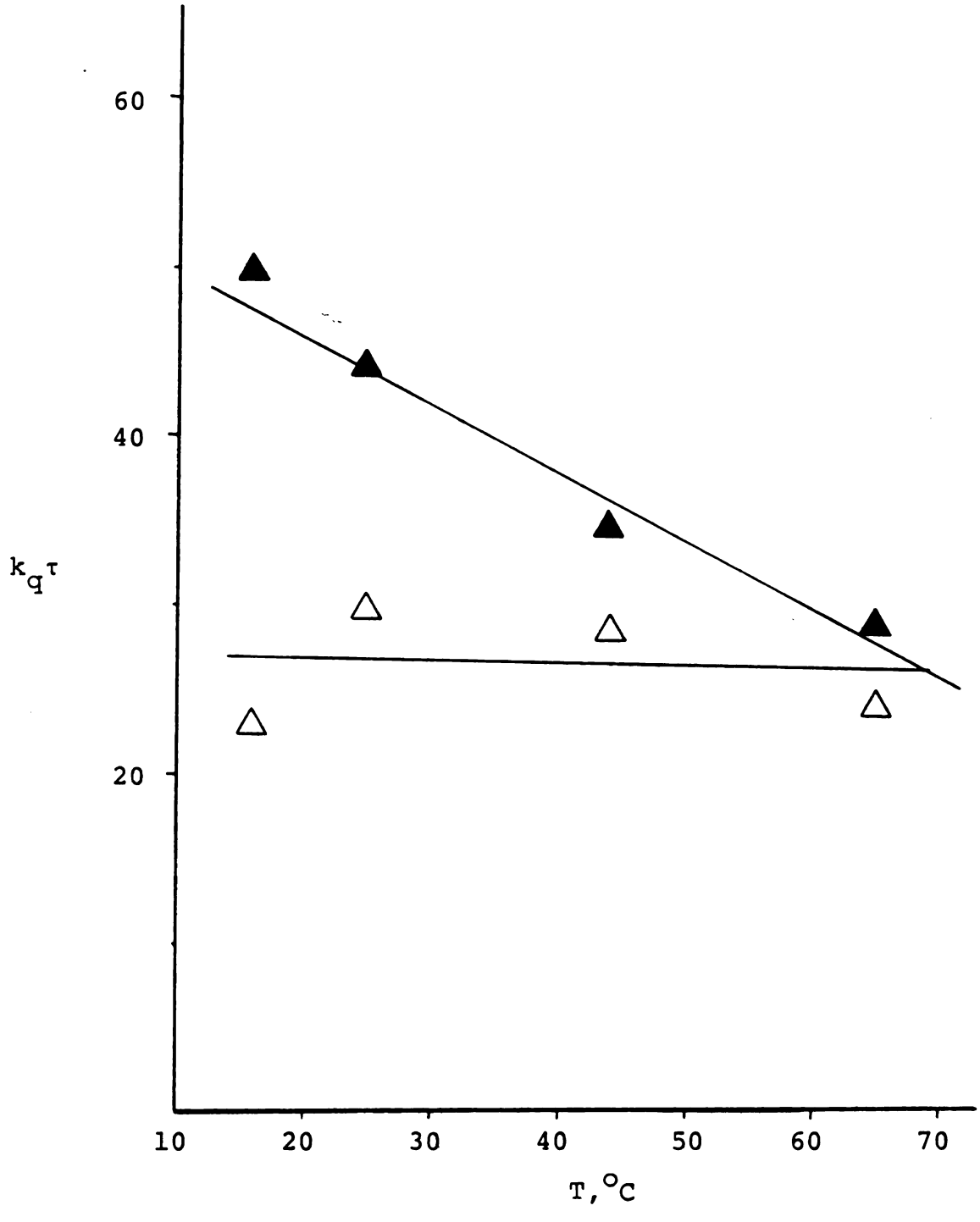
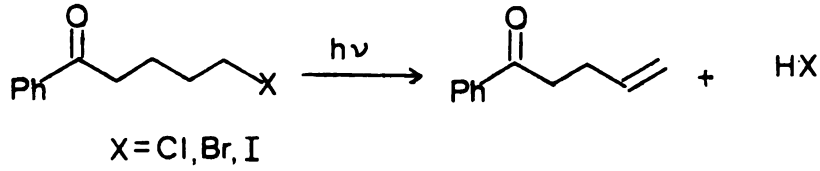


Figure 17. Temperature Dependence of $k_q\tau$ for Valerophenone (▲) and δ-Iodovalerophenone (△) in Benzene.

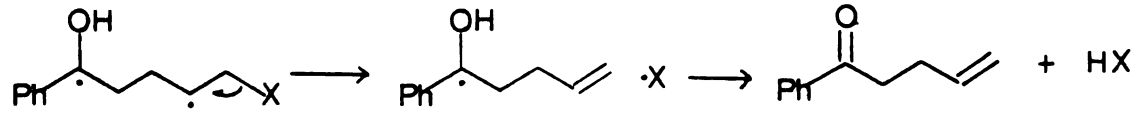
Discussion

Mechanism of Radical β-Cleavage via Photogenerated Diradicals

The following transformation was first observed by Wagner and Sedon.[162] In light of the known propensities for photoinduced biradicals to undergo rearrangements typical of monoradicals, the mechanism seemed straightforward,



proceeding by radical β-cleavage of the initially formed 1,4-biradical followed by disproportionation as shown below.



However, the rate of elimination of Cl deduced from such a mechanism is much faster than that usually assumed.[163] Inasmuch as all biradicals possess some zwitterionic character, anionic elimination as presented below seemed to be a viable mechanistic possibility.

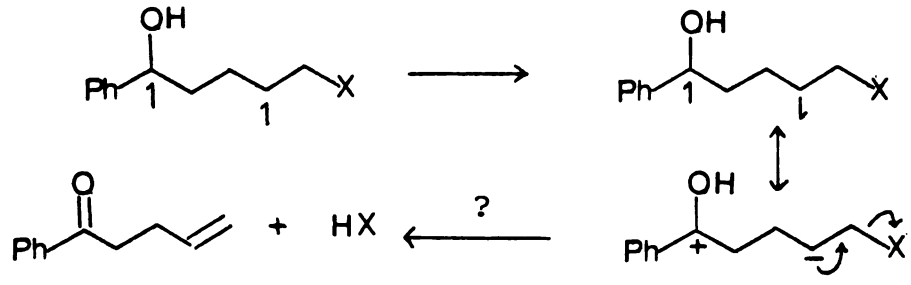
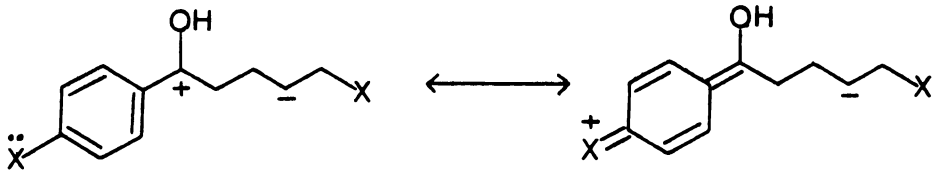


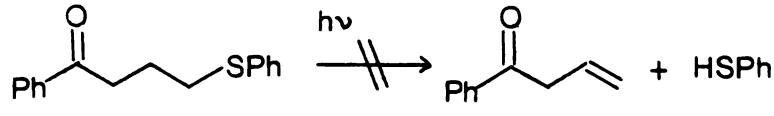
Table 17 presents the quantum yields of ϕ_{II} and $\phi_{4\text{-BB}}$ for various δ-chlorovalerophenones in different solvents. Little variation in II:4-BB ratios are observed with solvent, except in the case of p-methoxy-δ-chlorovalerophenone in CH_3CN and MeOH. The ability of polar solvents to stabilize carbonium ions is well known,[164] and as such any zwitterionic character of the 1,4-biradical should be stabilized in a polar solvent. Therefore, if X is being eliminated ionically, stabilization of the zwitterion form of the biradical should result in greater amounts of β-elimination relative to Type II cleavage. Stabilization or destabilization of the zwitterionic form can also be brought about by ring substitution.



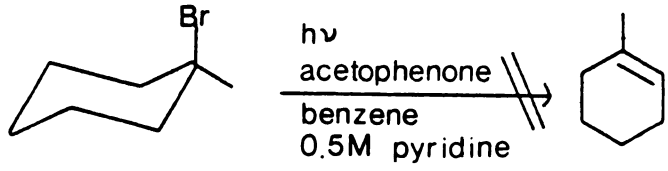
Whereas, p-MeO should stabilize the carbonium ion, p-CF_3 should destabilize it. In view of the 100 or 1000 fold effect p-substitutents have upon ground state carbonium ion formation,[165] the fact that II:4-BB varies little with p-OMe or CF_3 in benzene is enlightening. On the other hand, p-CF_3 substitution favors Type II elimination slightly in methanol and CH_3CN to the extent of a factor of about two. The results for p-OMe-5-Cl in CH_3CN and MeOH are confusing in that just the opposite effect is observed. Here, in a situation where β-cleavage should be favored, Type II cleavage predominates. However, the ability of polar solvents to

invert triplet levels is notorious,[166] and the effect in the p-OMe-5-Cl case is to lower the quantum yields to such an extent that accurate measurements are impossible. Thus, the discrepancy could be due to analytical difficulties. The extent to which p-substitution influences k_s, the rate constant of Type II cleavage, which is normally about $10^7 sec^{-1}$,[167] is unknown; however, it is safe to say that solvent or substituent effects are at best extremely small, and the ionic mode of elimination is probably only a small contributor for only the worst radical leaving groups.

Formation of 4-BB or DMBC from their respective precursors via either intramolecular or intermolecular interaction of the halide or thiyl groups with the excited benzoyl group can be definitely ruled out. Irradiation of 4-SPh resulted in no allylacetophenone formation.

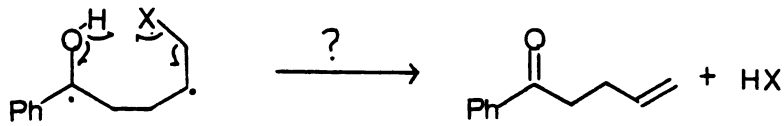


Interaction between the sulfur and the benzoyl groups in this case was shown in Part I to be faster than 5-SPh and should be even more favorable for photolytic elimination by the above mechanism. Intermolecular interaction in the case of BDMBC was ruled out by the following control experiment.

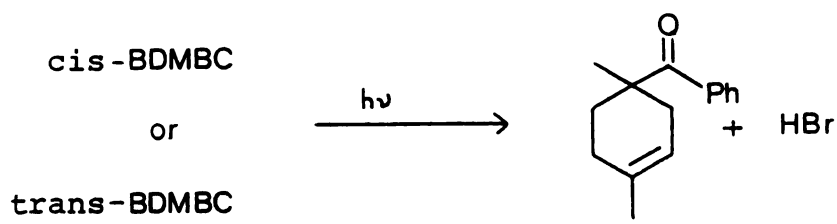


This coupled with the fact that alkyl halides do not quench triplets[168] eliminates any intermolecularly sensitized elimination mechanism.

Another interesting mechanistic alternative, analogous to that already suggested for β-alkoxyketones, is a cyclic concerted elimination as shown below.



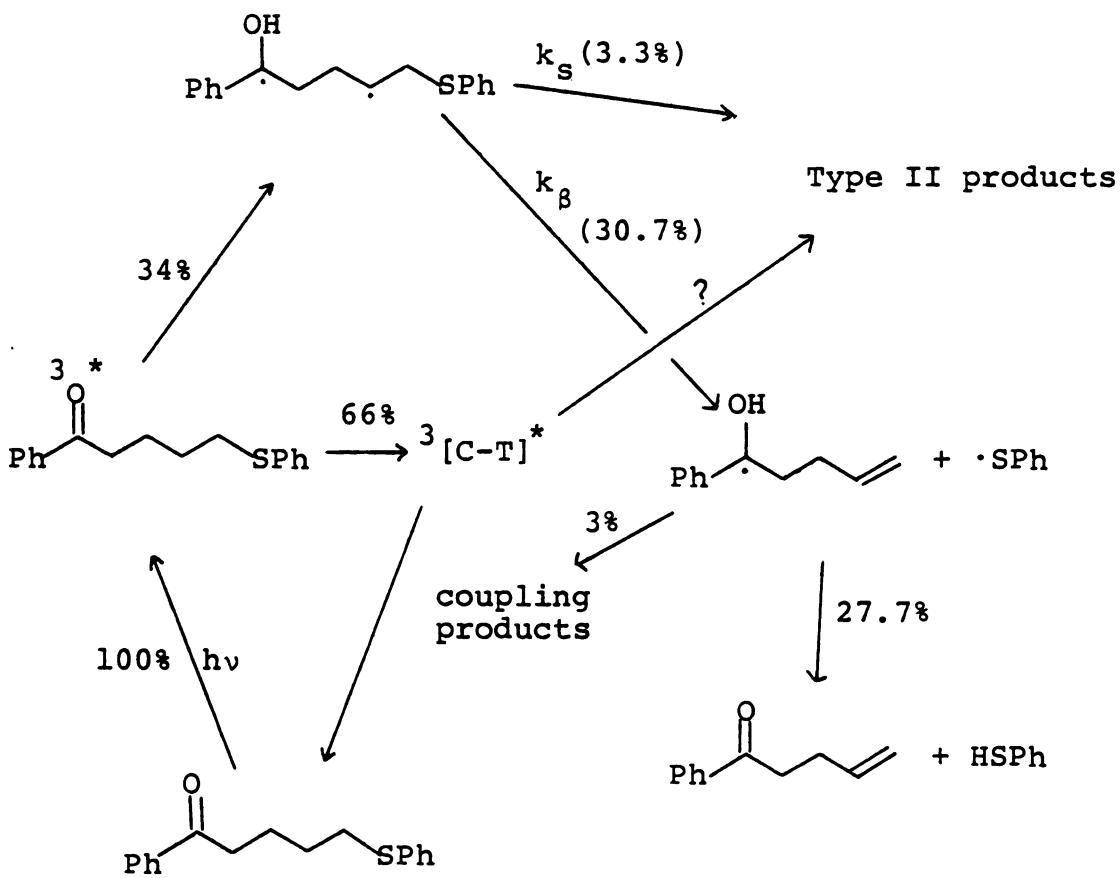
Here, "concerted" elimination of HX circumvents the disproportionation step but requires that the leaving group and the ketyl moieties come into close proximity. The cyclic haloketones--i.e., BDMBC and CDMBC--were prepared to test this hypothesis. As listed in Table 18 and illustrated below, both diastereomers undergo elimination of HX to some extent.



In the trans-diastereomer, X is totally inaccessible to the benzoyl group; and even in the cis-diastereomer, it is doubtful whether the required cyclic orientation would be possible. Therefore, such a cyclic orientation is not

necessary for photoinduced β-cleavage; however, these experiments do not preclude product formation from such an orientation in the acyclic analogues.

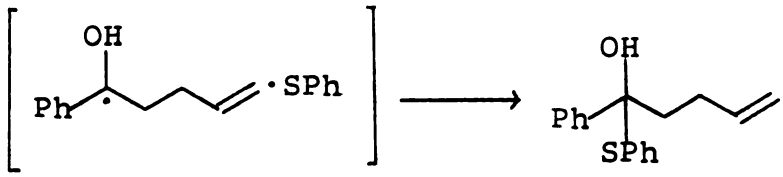
Therefore, it seems likely that initial 1,4-biradical formation followed by rapid β-elimination and in-cage disproportionation is the correct mechanism. The fate of δ-thiophenoxyvalerophenone is shown in Scheme 8 and is presented to be illustrative of the mechanism.



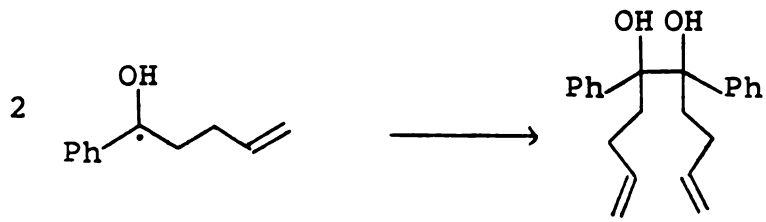
Scheme 8. Photolysis of δ-Thiophenoxyvalerophenone in Benzene.

Quantum Yields and Other Observations

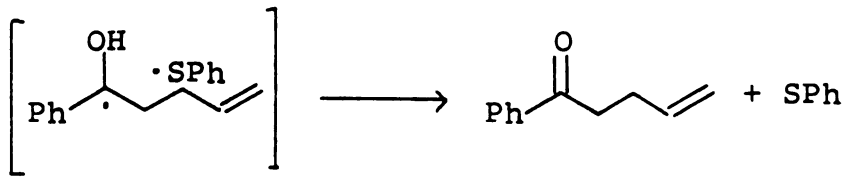
Examination of Table 16 and Scheme 8 reveals that in the case of 5-SPh, C-T quenching by sulfur is the major reaction followed by β-elimination to form 4-BB. Interestingly, very small yields of PhSSPh were measured, which at best comprised only about 3% of the total products. In-cage coupling of the radicals would result in the situation shown below, which would probably revert to starting material.



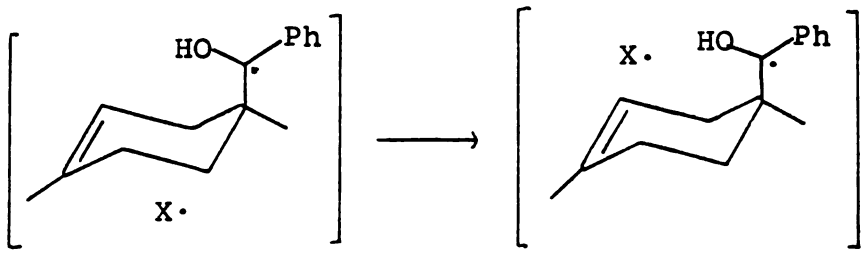
However, out-of-cage coupling would be statistical and result in the formation of disulfide and the corresponding pinacol.



The small quantum yield of disulfide coupled with the near 100% material balance allows one to ignore these small side reactions. However, the fact that they are small means that very rapid in-cage disproportionation must be taking place.



In the acyclic cases, the leaving group is already set up for disproportionation as shown in the previous diagram; but in the cyclic case, and especially for the trans-compounds, the leaving group is on the opposite side of the ring with respect to the ketyl.



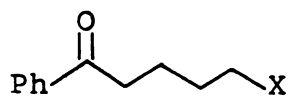
Therefore, it must migrate around inside the cage before disproportionation can occur. In-cage molecular reorganization must indeed be very rapid.

Rates of β-Elimination

Given the plausible assumption that δ-substitution effects little change in k_s,[169] comparison of II:4-BB ratios allows extraction of relative rates of β-elimination. Table 19 contains the relative rates of β-cleavage for a variety of groups. Comparison of Cl, Bu, and I reveals the expected order of ease of elimination--i.e., I > Br > Cl--which parallels that observed for ionic eliminations.[170]

The difference between SR and SPh is roughly a factor of 1000 in favor of SPh and can be rationalized in terms of resonance stabilization by the benzene ring, analogous to

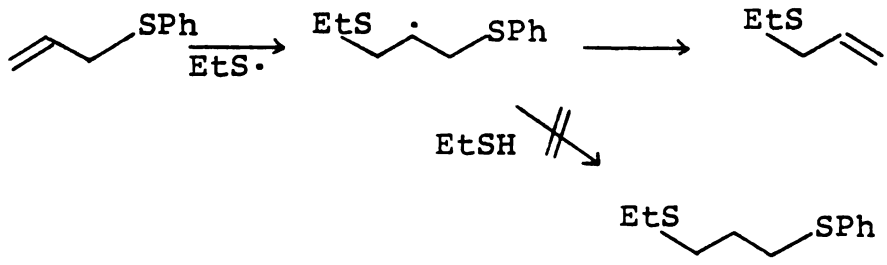
Table 19. Rate Constants of β-Elimination of Various Substituents in δ-Substituted Valerophenones.

Compound	$k_\beta, 10^8 sec^{-1}$ [a]	k_β^{rel}
		
X		
Cl	0.17	1
Br	1.1	65
I	21.5	1260
SCN	83.0	490
SAc	0.0026	0.15
SBu	0.0029	0.16
SOBu	1.3	76.0
SO_2Bu	0.0077	0.46
StBu	0.0064	0.41
SOPh	10.6	630
SO_2Ph	0.12	6.8
SPh	1.4	110

[a] Calculated assuming k_s equals $10^7 sec^{-1}$.

that in a benzylic radical, that is,

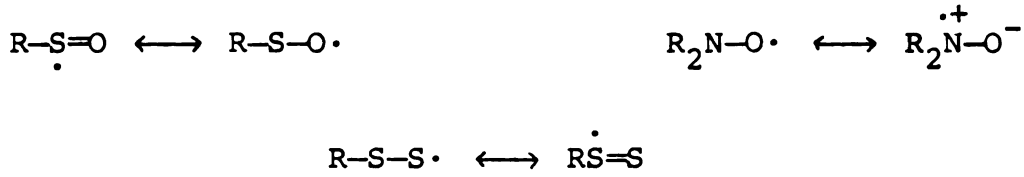
The enhanced rate of elimination of SPh relative to RS has been demonstrated previously[171] by the addition of ethanethiol to allylphenylsulfide as shown below.



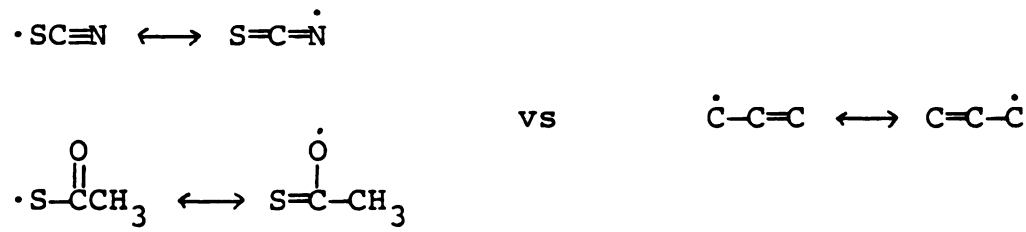
Here elimination of SPh is faster than chain-transfer with ethanethiol.

The three-fold difference in rates between SBu and S-tBu can be explained by increased hyperconjugation in the latter, analogous to that observed for alkyl radicals[172] and the fact that the steric bulk of the t-butyl group lowers the bond dissociation energy.

Surprisingly, oxidation of the sulfur to a sulfinyl moiety enhances its rate of elimination relative to the sulfide. Thus, the order PhSO > SOBu >> SO_2Bu and SBu confirms Kice's[173] suggestion that sulfinyl radicals have the greatest kinetic stability of the three. Sulfinyl radicals have been thought to be rather stable by analogy with the isoelectronic nitroxide and dithiyl radicals.[174]



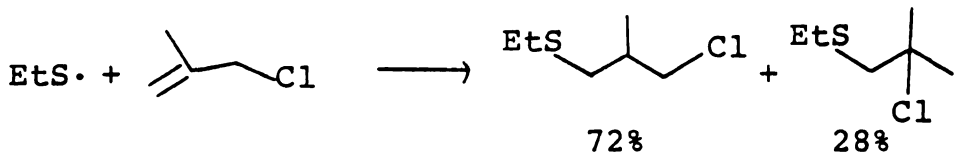
Interestingly, 5-SCN β-cleaves almost exclusively, whereas in 5-SAc β-cleavage is a minor product. One might expect these radicals to be fairly stable by analogy to allyl radicals.



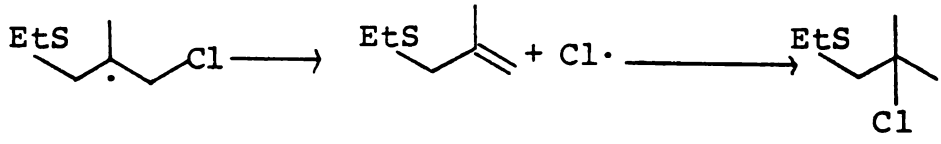
The known lack of conjugative stabilization in α-keto radicals[175] explains the order SCN >> SAc and further indicates the X leaves as a radical since ionic cleavage of $^{-}$SAc should be favorable.

The most surprising result of all is that Cl is eliminated faster than SR. Kineticists have assumed a much smaller value of k_{β} for Cl, and as such one would expect the observed order to be reversed.[176] However, it is possible that previous studies on monoradicals have indicated too low a value of k_{β} due to reverse additions. In the present system rapid in-cage disproportionation tends to minimize the effects of reversible addition.

Competitive elimination studies by Hall[177] are consistent with the present observations. That is, in the addition of ethanethiol to the allylchloride shown below, an unexpected product was observed.

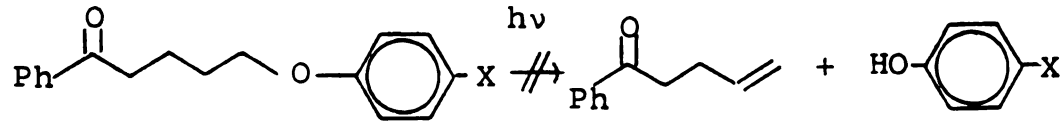


The lesser product can be explained by elimination of ·Cl followed by ionic addition of HCl to form the observed product.

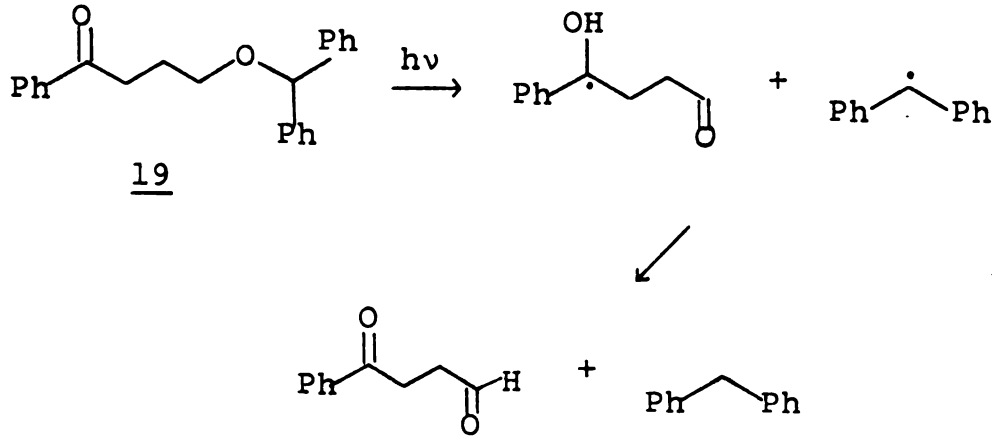


Relative rate constants for β-cleavage have not been previously reported. In fact, the actual rate constants can be estimated by assuming k_s equals $10^7 sec^{-1}$.[178] This would yield k_β's of $10^5 sec^{-1}$ and $10^8 sec^{-1}$ for SBu and Br, respectively.

The corresponding δ-phenoxyethers are observed not to undergo β-cleavage, indicating that $k_s >> k_\beta$ in these



cases. Cleavage of the comparatively strong C-O bond is apparently unfavorable. In fact, cleavage in 19, which would result in the formation of a C-O double bond and a relatively stable benzhydryl radical, is not observed, reflecting total kinetic control of the reaction.



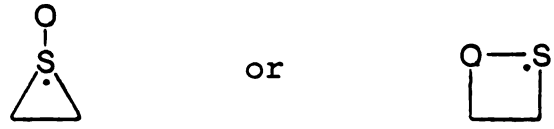
19

γ-Hydrogen Abstraction and Anchimeric Assistance

The rate constants of γ-hydrogen abstraction for 5-Br and 5-I have been found to be enhanced by 230% and 530%, respectively, relative to that expected if only inductive effects were operative.[179] The observed enhancements were attributed to anchimeric assistance by the β-haloatom.[180] Numerous examples of β-halo and β-thiyl assistance are known.[181] Recently, Shevlin[182] presented evidence that suggested a small amount of anchimeric assistance by a phenylsulfinyl group in the tin hydride induced elimination of the β-bromophenylsulfinyl group. Since the triplet benzoyl group mimics the behavior of alkoxy radicals,[183] only a minor effect is noted in the case of 5-Br and 5-I. The highly exothermic nature of abstraction of bromine atoms by

tin radicals is probably responsible for the small effect noted in the latter case.

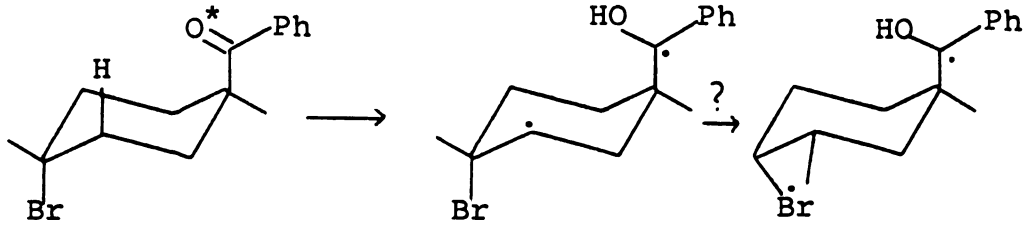
A fairly substantial enhancement in k_γ was noted in Part I for 5-SOBu--roughly a factor of ten. Assistance by the sulphinyl group can be envisioned to occur in two different ways in which three- or four-centered intermediates can be constructed. On the other hand, 5-SBu or 5-SPh show no such enhancements.



The concept of anchimeric assistance requires two clarifying observations: one, the lowering of the transitive state enthalpy by bridging and greater conformational restrictions on the structure of the transition state (i.e., a more negative $\Delta S^\dagger$) require that the temperature dependence of γ-hydrogen abstraction be different than that of a compound in which no bridging is occuring; and, two, stereoelectronic requirements lead one to expect significant stereochemical effects on the magnitude of anchimeric assistance, analogous to those observed by Skell[184] for axial and equatorial bromines in a rigid cyclohexyl system.

Figure 17 presents the temperature dependence of the $k_q\tau$ for δ-iodovalerophenone relative to valerophenone. The fact that the two slopes are different is consistent with the suggestion that anchimeric assistance is operative.

The effect of orientation upon the magnitude of anchimeric assistance is striking. Table 20 presents the k_γ and k_α of the various diastereomers of BDMBC and CDMBC. The k_γ for t-CDMBC is $1.1 \cdot 10^7 sec^{-1}$, which is comparable to the k_γ in δ-chlorovalerophenone. It is faster by a factor of two in the cyclic case due to the fact that the hydrogens are perfectly set up for abstraction. However, k_γ for trans-BDMBC is $1.9 \cdot 10^8 sec^{-1}$, a facter of about 200 times faster. The inductive effect of Br and Cl are comparable[185] so the enhanced rate must be due to assistance by Br.

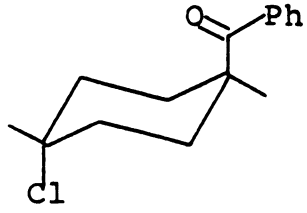
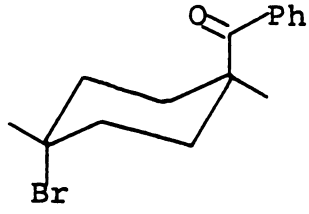
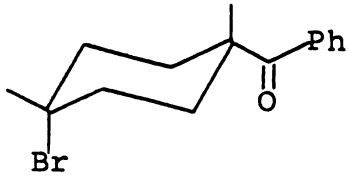
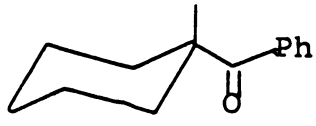


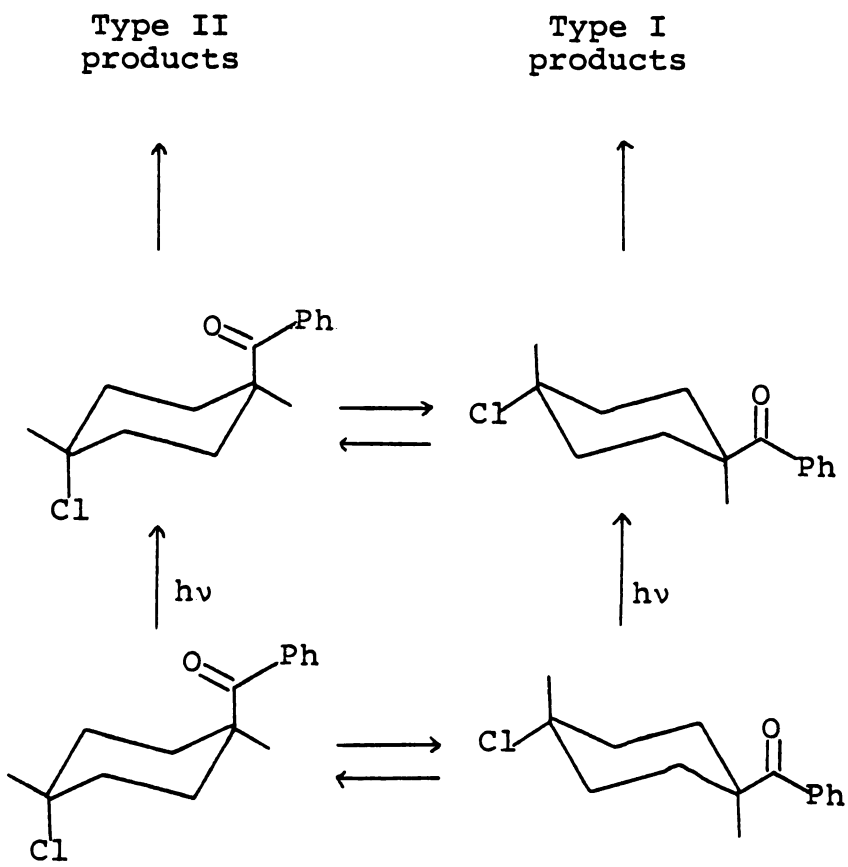
Formation of a bridged species as suggested by Skell[186] is possible, but the data do not permit any comment in this respect. The trans-isomer is, of course, perfectly set up for assistance since the C-H and C-Br bonds are trans-periplanar.[187]

Conformational Effects

Scheme 9 depicts the conformational effects in the photochemistry of trans-CDMBC. Lewis[188] has previously shown that when the benzoyl group is axial, only γ-abstraction occurs. Conversely, when it is held equatorially, only Type I cleavage occurs. Thus, analogous arguments can be made for the present system. If the respective rates of

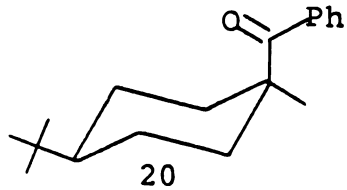
Table 20. Rate Constants of γ-Hydrogen Abstraction and α-Cleavage for the 4-Halo-1,4-Dimethyl-1-Benzoylcyclohexanes.

Compound	$\frac{1}{\tau}, 10^7 s^{-1}$	$k_\gamma, 10^7 s^{-1}$	$k_\alpha, 10^7 s^{-1}$
	(α) 2.14 (γ) 5.07	1.11	0.017
	(α) 2.40 (γ) 46.7	21.0	0.046
	(α) 2.38 (γ) 7.69	0.92	0.26
	(α) 2.50 (γ) 17.2	0.77	0.50



Scheme 9. Conformational Effects in the Photochemistry of trans-CDMBC.

reaction--i.e., k_γ and k_α--are faster than equilibration of the excited state conformers, two distinct triplet lifetimes will be observed (k_γ and k_α can, of course, be coincidentally equal, in which case a single lifetime will be observed). Thus, product distribution reflects the ground state equilibrium. Lewis[189] has found the Type I quantum yield for 20 in the presence of 0.01M dodecanethiol to be 0.31.



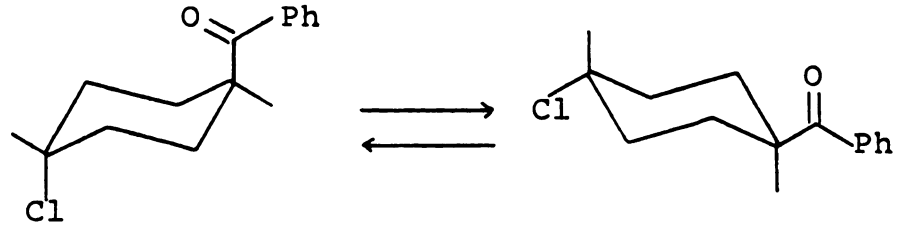
20

Assuming that remote substituents have little effect on ϕ_α, comparison of the quantum yields of benzaldehyde formation for the present system should yield the respective ground state population. Thus, utilizing the quantum yields in Table 18, the following ground state conformational equilibria can be calculated and are presented in Table 21.

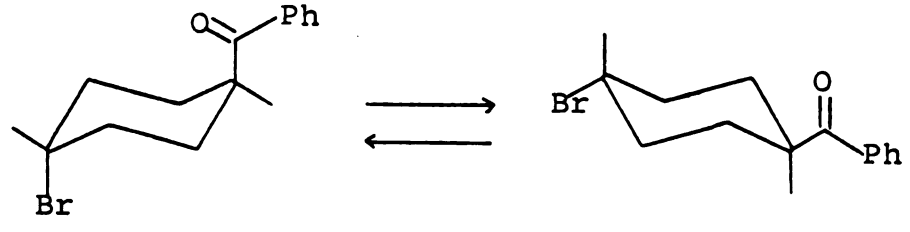
Obvisouly, the photochemical results and the corresponding determination of ground state equilibria agree nicely with the initial predictions and further illustrate how light can be used as a probe.

On the other hand, prior equilibration of the two excited conformers would lead to a single lifetime, in which case the product distribution would depend only upon the relative rates of γ-hydrogen abstraction and α-cleavage. This, in turn, would reveal little or no information about ground state equilibria. Complications arising from

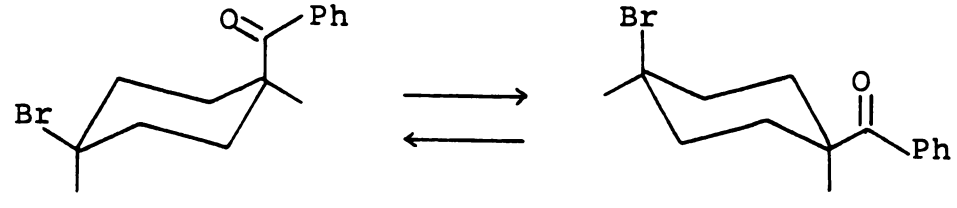
Table 21. Ground State Equilibria of 4-Halo-1,4-Dimethyl-1-Benzoylcyclohexanes.



99% 1%



94% 6%



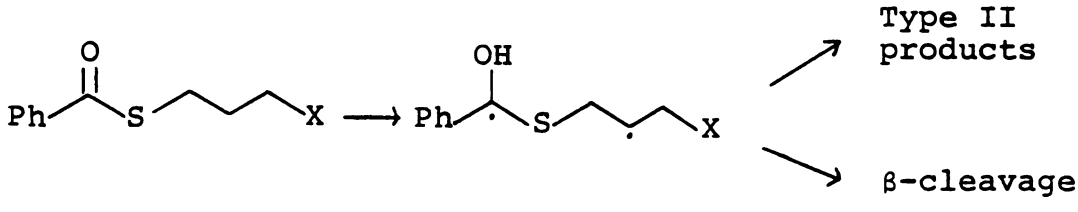
61% 39%

intermolecular energy transfer from one excited conformer to the other are not likely here in light of the low concentration used and the short triplet lifetimes.

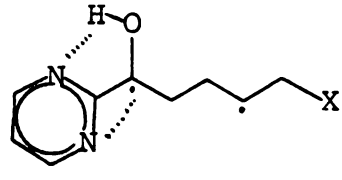
Indications for Further Research

Synthetic Utility. The synthetic utility of this reaction as a means of introducing double bonds in a highly regiospecific manner needs to be investigated.

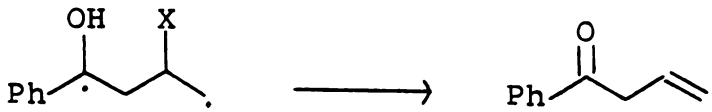
Relative Rates of β-Cleavage. This reaction provides an excellent handle for measuring relative rates of k_β for various groups. However, it presents a serious limitation in that k_s is too fast to allow elimination of other less stable radicals--i.e., ·OPh and $\cdot CH_2Ph$. Perhaps, if k_s could be slowed down, the utility of the reaction could be enhanced. Utilization of the thioester derivatives might accomplish this since formation of a C-S double bond is fairly unfavorable. However, α-cleavage would probably be a



competing reaction. Stabilization of the ketyl radical moiety as shown below might also serve to decrease k_s.

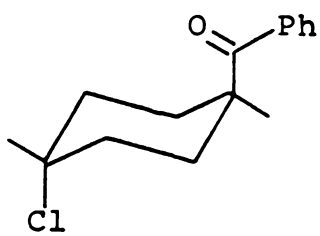


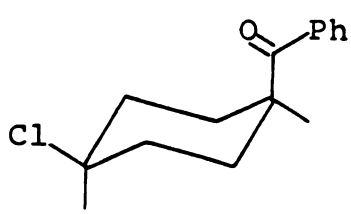
β-Substituted Butyrophenones. Analogous β-cleavage should also be observable for β-substituted butyrophenones as shown below.



These systems have not been previously investigated. A cyclic concerted mechanism as mentioned before should be more favorable for this system relative to the δ-substituted valerophenones.

Inductive Effects. An investigation into the effects of stereochemistry upon inductive effects would be interesting. For instance, comparison of the following two isomers would allow detection of any difference in the inductive effect upon γ-hydrogen abstraction between the axial and equatorial chlorines.





EXPERIMENTAL

Preparation and Purification of Materials

Solvents and Additives

Benzene: (Mallinckrodt) was purified by stirring over concentrated sulfuric acid for several days. The benzene was then washed with additional amounts of sulfuric acid until it remained clear, followed by several washings with water and one final washing with saturated sodium bicarbonate. The benzene was dried over magnesium sulfate or sodium sulfate and distilled from P_2O_5 through a column packed with glass helices. Only the middle 50% was collected.

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

Dioxane: (Mallinckrodt) was used as received or distilled through a short Vigreux column.

Pyridine: (Mallinckrodt) was distilled from barium oxide and the middle fraction collected.

Acetonitrile: (Fisher) was distilled rapidly from potassium permanganate. Sulfuric acid was added to the distillate and the distillate was decanted from the ammonium salts. It was then distilled through a short Vigreux column.

Ethanol: was used as received.

Hexane: (Mallinckrodt) was used as received.

Pentane: (Mallinckrodt or Drake Brothers) was used as received.

Benzenethiol: (Aldrich) was used as received.

Internal Standards

The standards used in this work were purified by Dr. P. J. Wagner as indicated below.

Dodecane: (Aldrich) was purified in the same manner as benzene with distillation under reduced pressure.

Tetradecane: (Columbia Organics) was purified in the same manner as dodecane.

Hexadecane: (Aldrich) was purified in the same manner as dodecane.

Heptadecane: (Aldrich) was purified in the same manner as dodecane.

Octadecane: (Aldrich) was purified by recrystallization from ethanol.

Nonadecane: (Chemical Samples) was purified in the same manner as octadecane.

Quenchers

Napthalene: (Matheson Coleman and Bell) was recrystallized several times from ethanol.

1-Methylnapthalene: (Aldrich) was used as received.

Cis- and Trans-1,3-Pentadiene: (Chemical Samples) was used as received.

Cis-1,3-Pentadiene: (Chemical Samples) was used as received and found to be 99.8% pure by vpc.

n-Butylsulfide: (Aldrich) was used as received.

n-Butylsulfoxide: was prepared by 30% hydrogen peroxide oxidation of n-butylsulfide in acetone. It was purified by recrystallization from hexane.

n-Butylsulfone: was prepared by 30% hydrogen peroxide oxidation of n-butylsulfide in glacial acetic acid. It was purified by recrystallization from hexane.

Ketones

Acetophenone: (Matheson Coleman and Bell) was distilled under reduced pressure by A. E. Puchalski.

Valerophenone: was prepared by the Friedel-Crafts acylation of benzene by valeryl chloride. The acid chloride was dripped alowly into a mixture of a ten-fold excess of benzene containing a 5% excess of aluminum chloride at 0-5^{o}C and stirred for 3-10 hours. The mixture was then poured onto cracked ice and concentrated HCl and the layers separated. The benzene layer was washed several times with dilute HCl, dried over sodium sulfate and evaporated under aspirator pressure. The crude produce was distilled under reduced pressure and the middle fraction collected.

Butyrophenone: (Aldrich) was purified by Dr. M. J. Thomas.

Phenacylchloride: (Aldrich) was used as received.

Phenacylbromide: (Aldrich) was used as received.

ß-Bromopropiophenone: was prepared by the Friedel-Crafts acylation of benzene with ß-bromopropionyl chloride in carbon disulfide at -5-0°C in an analogous manner as valerophenone: NMR($CDCl_3$) 3.2(m,4H), 7.2(m,3H), 7.8(m,2H).

γ-Chlorobutyrophenone: was prepared by the Friedel-Crafts acylation of benzene by γ-chlorobutyryl chloride (Aldrich) in the same manner as valerophenone: NMR($CDCl_3$) 2.0(m,2H), 3.0(t,2H), 3.5(t,2H), 7.2(m,3H), 7.8(m,2H).

δ-Chlorovalerophenone: was prepared by J. H. Sedon.

ε-Chlorohexanophenone: was prepared by W. B. Mueller.

Phenacylsulfides: (General Procedure) were prepared by treatment of the appropriate phenacyl chloride or bromide with the sodium salt of the corresponding thiol. The appropriate alkylthiol or arylthiol was added to an ethanolic NaOH solution and stirred for one hour. The phenacyl halide (one equivalent) was added in one portion, and a mild exothermic reaction ensued. The mixture was stirred overnight at room temperature and poured into water. It was then extracted with several portions of ether. The combined ether extracts were washed several times with water, dried over sodium sulfate and evaporated. The crude products were either distilled at reduced pressure or recrystallized from ethanol. The following compounds were prepared in this manner.

2-Thiomethylacetophenone (2-SMe): bp 80°C(0.05mm); IR(neat) 2900, 1655, 1360cm^{-1}; NMR($CDCl_3$) δ2.05(s,3H), 6.05(s,2H), 7.3(m,3H), 7.8(m,2H); m/e 166(M^+).

2-Thiobutylacetophenone (2-SBu): bp 120°C(0.50mm); IR(neat) 2950, 1690, 1275cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.4(m,4H), 2.5(t,2H), 3.7(s,2H) 7.3(m,3H) 7.8(m,2H); m/e 208(M^+).

2-Thio-t-butylacetophenone (2-StBu): bp 100°C(0.05mm); IR(neat) 2950, 1695, 1280cm^{-1}; NMR($CDCl_3$) δ1.3(s,9H), 3.8(s,2H), 7.3(m,3H), 7.8(m,2H); m/e 208(M^+).

2-Thiophenylpropiophenone (s-2SPh): bp 135°C(0.05mm); IR(neat) 3025, 1695, 1230cm^{-1}; NMR($CDCl_3$) δ1.5(d,3H), 4.5(m,1H), 7.2(m,8H), 7.8(m,2H); m/e 242(M^+).

2-Thiophenylisobutyrophenone (t-2SPh): bp 130°C (0.07mm); IR(neat) 3025, 1695, 1230cm^{-1}; NMR($CDCl_3$) δ1.5(s,6H), 7.3(m,8H), 8.2(m,2H); m/e 256(M^+).

Phenyldesylsulfide (PDS): mp 77°C; NMR($CDCl_3$) δ5.7(s,1H), 7.2(m,13H), 7.8(m,2H); m/e 304(M^+).

2-Thiophenylacetophenone (2-SPh): mp 49°C; IR($CHCl_3$) 3000, 1685, 1605, 1205cm^{-1}; NMR($CDCl_3$) δ4.2(s,2H), 7.2(m,8H), 7.8(m,2H); m/e 228(M^+).

2-Thiophenyl-4'-fluoroacetophenone (F-2SPh): bp 150-55°C(0.25mm); IR(neat) 3000, 1685, 1605, 1205cm^{-1}; NMR($CDCl_3$) δ4.05(s,2H), 7.08(m,8H), 7.8(m,2H); m/e 246(M^+).

2-Thiophenyl-4'-cloroacetophenone (Cl-2SPh): mp 65°C; IR($CHCl_3$) 3000, 1680, 1600, 1275cm^{-1}; NMR($CDCl_3$) δ4.1(s,2H), 7.1(m,8H), 7.7(d,2H); m/e 262(M^+).

2-Thiophenyl-4'-bromoacetophenone (Br-2SPh): mp 60°C; IR($CHCl_3$) 3000, 1680, 1595, 1280cm^{-1}; NMR($CDCl_3$) δ4.1(s,2H), 7.1(m,5H), 7.5(m,4H); m/e 307(M^+).

2-Thiophenyl-4'-methylacetophenone (Me-2SPh): mp 61°C; IR($CHCl_3$) 3000, 1660, 1605, 1275cm^{-1}; NMR($CDCl_3$) δ2.3(s,3H), 4.1(s,2H), 7.1(m,8H), 7.6(d,2H); m/e 242(M^+).

2-Thiophenyl-4'-methoxyacetophenone (OMe-2SPh): mp 86°C; IR($CHCl_3$) 3000, 1670, 1600, 1265cm^{-1}; NMR($CDCl_3$) δ3.7(s,3H), 4.1(s,2H), 6.8(d,2H), 7.1(m,5H), 7.8(d,2H); m/e 258(M^+).

2-Thiophenyl-4'-thiomethylacetophenone (SMe-2SPh): mp 48°C; IR($CHCl_3$) 3000, 1670, 1590, 1095cm^{-1}; NMR($CDCl_3$) δ2.4(s,3H), 4.2(s,2H), 7.1(m,8H), 7.6(d,2H); m/e 274(M^+).

2-Thiophenyl-4'-cyanoacetophenone (CN-2SPh): mp 65°C; IR($CHCl_3$) 3000, 2225, 1700, 1275cm^{-1}; NMR($CDCl_3$) δ4.2(s,2H), 7.2(s,5H), 7.7(m,4H); m/e 253(M^+).

2-Thiophenyl-4'-phenylacetophenone (φ-2SPh): mp 92°C; IR($CHCl_3$) 3000, 1700, 1275cm^{-1}; NMR($CDCl_3$) δ4.2(s,2H), 7.0-7.5(m,12H), 7.8(d,2H); m/e 304(M^+).

2-Thiophenyl-4'-dimethylaminoacetophenone (NMe_2-2SPh): was prepared by the reaction of dimethylamine and 2-thiophenyl-4'-fluoroacetophenone. 10g of 2-thiophenyl-4'-fluoroacetophenone was dissolved in 50ml of xylene and placed in a pressure bomb. The bomb was cooled in an ice-salt bath, and 25ml of anhydrous dimethylamine (Aldrich) was added. The bomb was sealed and heated at 80°C for 24 hours with vigorous stirring. The bomb was cooled before opening, and the

mixture was worked up as in the general procedure for the phenacylsulfides. The crude product was crystallized from ethanol and obtained pure in 85% yield: mp 78°C; IR($CHCl_3$) 3000, 1660, 1600, 1375cm^{-1}; NMR($CDCl_3$) δ2.9(s,6H), 4.1(s,2H), 6.5(d,2H), 7.1(m,5H), 7.7(d,2H); m/e 271(M^+).

1-Benzoyl-1-thiophenylcyclopropane (cy-2SPh): was prepared by the reaction of sodium thiophenoxide with 2-bromo-4-chlorobutyrophenone and subsequent base cyclization. 28g of 2-bromo-4-chlorobutyrophenone obtained by the bromination of 4-chlorobutyrophenone was dissolved in 100ml of ethanol. To this was added one equivalent of sodium thiophenoxide, and this was allowed to stir for four hours. A slight excess of sodium methoxide was added in one portion to effect cyclization, and the product worked up as in the phenacyl-sulfides. Recrystallization from ethanol gave a 91% yield of pure product: mp 62°C; NMR($CDCl_3$) δ1.3(m,2H), 1.7(m,2H), 7.2(m,8H), 7.8(m,2H); m/e 254(M^+).

4'-thiophenylmethylacetophenone (4'-MSPh): was prepared from sodium thiophenoxide and 4'-bromomethylacetophenone. 4'-bromomethylacetophenone was obtained by irradiation of a mixture of 40g 4'-methylacetophenone and 53g n-bromosuccinimide in 500ml carbon tetrachloride. Pure bromide was obtained by fractionation at reduced pressure in about 30% yield. The reaction of sodium thiophenoxide and 4'-bromoacetophenone was carried out in the same manner as the phenacylsulfides. Pure product was obtained from ethanol in a 95% yield: mp 91°C; IR($CHCl_3$) 3000, 1685, 1265cm^{-1};

NMR($CDCl_3$) δ2.5(s,3H), 4.1(s,2H), 7.2(m,8H), 7.7(d,2H); m/e 242(M^+).

Benzoylsulfides: (General Procedure) were prepared essentially the same as the phenacylsulfides except that the reaction mixtures were refluxed for a period of 5-12 hours. In the case of δ-benzoylsulfides, the carbonyl group of 4-chlorobutyrophenone was protected by forming the ethylene glycol ketal prior to reaction with sodium thiolates; otherwise, good yields of phenylcyclopropylketone were obtained. Intramolecular cyclization of the haloketones was only found in the case of 4-chlorobutyrophenone. The ketal was then hydrolyzed by vigorous stirring in 15% HCl overnight. The products were either distilled under reduced pressure or recrystallized from ethanol. The following compounds were prepared in this manner.

3-Thiobutylpropiophenone (3-SBu): bp 130-150°C (aspirator); IR(neat) 2950, 1680, 1450, 1350cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.4(m,4H), 2.4-3.4(m,6H), 7.3(m,3H), 7.8(m,2H); m/e 222(M^+).

4-Thiobutylbutyrophenone (4-SBu): bp 145°C(0.3mm); IR(neat) 2950, 1695, 1450, 1230cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.4(m,4H), 1.9(m,2H), 2.5(m,4H), 3.1(t,2H), 7.3(m,3H), 7.8(m,2H); m/e 236(M^+).

4-Thio-t-butylbutyrophenone (4-StBu): bp 125°C (0.15mm); IR(neat) 2950, 1695, 1225cm^{-1}; NMR($CDCl_3$) δ1.25(s,9H), 2.0(m,2H), 2.6(t,2H), 3.1(t,2H), 7.3(m,3H), 7.8(m,2H); m/e 236(M^+).

4-Thiophenylbutyrophenone (4-SPh): mp 35°C; IR($CHCl_3$) 2990, 1675, 1225cm^{-1}; NMR($CDCl_3$) δ2.0(m,2H), 3.0(M,4H), 7.2(m,8H), 7.8(m,2H); m/e 254(M^+).

5-Thiobutylvalerophenone (5-SBu): bp 155°C(0.3mm); IR(neat) 2930, 1685, 1450, 1220cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.6(m,8H), 2.4-3.0(m,6H), 7.3(m,3H), 7.8(m,2H); m/e 250(M^+).

5-Thio-t-butylvalerophenone (5-StBu): bp 140°C (0.06mm); IR(neat) 2950, 1695, 1220cm^{-1}; NMR($CDCl_3$) δ1.2(s,9H), 1.7(m,4H), 2.5(t-2H), 2.9(t-2H), 7.3(m-3H), 7.8(m-2H); m/e 250(M^+).

5-Thiophenylvalerophenone (5-SPh): mp 87°C; IR($CHCl_3$) 2995, 1675, 1200cm^{-1}; NMR($CDCl_3$) δ1.9(m,4H), 2.9(t,4H), 7.3(m,8H), 7.8(m,2H); m/e 270(M^+).

6-Thiobutylhexanophenone (6-SBu): bp 145-160°C (0.4-0.5mm); IR(neat) 2930, 1695, 1450, 1220cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.2-1.9(m,10H), 2.5(t-4H), 2.9(t-2H), 7.3(m,3H), 7.8(m,2H); m/e 264(M^+).

Benzoylsulfoxides: (General Procedure) were prepared by hydrogen peroxide oxidation of the corresponding benzoylsulfide. The benzoylsulfide was dissolved in acetone, and one equivalent of 30% H_2O_2 was added carefully behind safety shield. The solution was allowed to stir in dim light overnight. The solvent was evaporated at reduced pressure, and the crude crystalline product was recrystallized from ether: chloroform. The following compounds were prepared in this manner.

3-Butylsulfinylpropiophenone (3-SOBu): mp 78°C; IR($CHCl_3$) 2950, 1695, 1225, 1025cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.2-1.9(m,4H), 2.5-3.5(m,6H), 7.3(m,3H), 7.8(m,2H); m/e 238(M^+).

4-Butylsulfinylbutyrophenone (4-SOBu): mp 47°C; IR($CHCl_3$) 2950, 1698, 1225, 1030cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.2-2.0(m,4H), 2.2(m,2H), 2.7(m,4H), 3.2(t-2H), 7.3(m,3H), 7.8(m.2H); m/e 252(M^+).

5-Butylsulfinylvalerophenone (5-SOBu): mp 79°C; IR($CHCl_3$) 2950, 1695, 1010cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.2-2.0(m,8H), 2.6(t,4H), 3.8(t,2H), 7.3(m,3H), 7.8(M,2H); m/e 266(M^+).

5-Phenylsulfinylvalerophenone (5-SOPh): mp 60°C; IR($CHCl_3$) 3000, 1698, 1050cm^{-1}; NMR($CDCl_3$) δ1.8(m,4H), 2.9(m,4H), 7.3(m,8H), 7.8(m,2H); m/e 286(M^+).

Benzoylsulfones: (General Procedure) were prepared by the oxidation of the corresponding sulfoxide or alternatively the corresponding sulfide. A large excess of 30% H_2O_2 was added behind a safety shield to either the benzoylsulfide or benzoylsulfoxide in glacial acetic acid. The mixtures were allowed to stir for one or two days and then poured into H_2O. The aqueous mixture was extracted several times with chloroform. The chloroform layer was washed several times with H_2O and finally once with saturated sodium bicarbonate to remove the last traces of acetic acid. The $CHCl_3$ layer was then dried over sodium sulfate and evaporated. The crystalline products were purified in the same manner as the benzoylsulfoxides. This procedure was used for the following compounds.

3-Butylsulfonylpropiophenone (3-SO_2Bu): mp 116°C; IR($CHCl_3$) 2950, 1695, 1315, 1225, 1125cm^{-1}; NMR($CDCl_3$)

δ0.9(m,3H), 1.2-2.0(m,4H), 3.0(t,2H), 3.4(m,4H), 7.3(m,3H), 7.8(m,2H); m/e 254(M^+).

4-Butylsulfonylbutyrophenone (4-SO_2Bu): mp 65°C; IR($CHCl_3$) 2950, 1695, 1300, 1125cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.2-2.5(m,6H), 2.8(m,6H), 7.3(m,3H), 7.8(m,2); m/e 268(M^+).

5-Butylsulfonylvalerophenone (5-SO_2Bu): mp 66°C; IR($CHCl_3$) 2950, 1700, 1300, 1125cm^{-1}; NMR($CDCl_3$) δ0.9(m,3H), 1.5-2.1(m,8H), 3.0(m,6H), 7.4(m,3H), 7.8(m,2H); m/e 282(M^+).

5-Phenylsulfonylvalerophenone (5-SO_2Ph): mp 90°C; IR($CHCl_3$) 2950, 1695, 1305, 1150cm^{-1}; NMR($CDCl_3$) δ1.9(m,4H), 3.0(m,4H), 7.3(m,8H), 7.8(m,2H); m/e 302(M^+).

2-Methylsulfinylacetophenone (2-SOMe): was prepared by a slight modification of the method of Corey and Chaykovsky.[190] To a slurry of 37g potassium t-butoxide in 200ml DMSO was added 50g ethylbenzoate dropwise. The reaction micture was maintained at about 70°C for one hour with vigorous stirring. The mixture was then poured into ice-water and acidified with concentrated HCl. The entire mixture was extracted with $CHCl_3$ and worked as in the benzoylsulfoxides. The product was obtained in 70% yield as needles from ether-$CHCl_3$: mp 84°C; IR($CHCl_3$) 3000, 1680, 1275, 1050cm^{-1}; NMR($CDCl_3$) δ2.7(s,3H), 4.3(s,2H), 7.3(m,3H), 7.8(2,H).

2-Methylsulfonylacetophenone (2-SO_2Me): was prepared in the same manner as 2-SOMe except that the slurry also contained a 10% excess of dimethylsulfone (Aldrich) relative to ethylbenzoate. Recrystallization from ether-$CHCl_3$

afforded a 75% yield: mp 105°C; IR($CHCl_3$) 3000, 1695, 1325cm^{-1}; NMR($CDCl_3$) δ3.1(s,3H), 4.5(s,2H), 7.3(m,3H), 7.8(m,2H); m/e 198(M^+).

5-Thioacetoxyvalerophenone (5-SAc): was prepared by the free radical addition of thioacetic acid to 4-benzoylbutene. A two-fold excess of thiolacetic acid was added to 4-benzoylbutene (prepared by Dr. M. J. Thomas) and was refluxed overnight in benzene with a "pinch" of benzoyl peroxide. The mixture was washed with aqueous sodium bisulfite and worked up in the same manner as the benzoylsulfoxides. It was recrystallized from ethanol: mp 63°C; IR($CHCl_3$) 3000, 1690, 1220cm^{-1}; NMR($CDCl_3$) δ1.7(m,4H), 2.9(m,4H), 2.2(s,3H), 7.3(m,3H), 7.8(m,2H); m/e 236(M^+).

5-Thiocyanatovalerophenone (5-SCN): was prepared as described by Dr. B. J. Scheve.[191]

t-4-Chloro-1,4-dimethyl-1-Benzoylcyclohexane (t-CDMBC): was prepared by the addition of HCl to 1,4-dimethyl-1-benzoylcyclohex-3-ene (DMBC). 40g methyl methacrylate was dripped into 250ml benzene containing 5g of $AlCl_3$. 28g of isoprene was added slowly, and the mildly exothermic reaction was cooled in a water bath. It was allowed to stir overnight and worked up in the same manner as valerophenone. This procedure yielded a 80% crude yield of the olefin which was used without further purification. This was then hydrolyzed to the acid by refluxing in a 50:50 ethanol/water solution containing an excess of KOH. The solution was cooled and acidified with concentrate HCl. The precipitated acid was collected by suction filtration and washed with

copious amounts of water. The crude crystals were then recrystallized from hexane and obtained in 90% yield. The product was identified by its melting point, which was found to be identical to the literature value--i.e., 69°C.

The phenylketone was prepared by addition of two equivalents PhLi (Aldrich) to an ethereal solution of the acid followed by refluxing for three hours. The homogeneous solution was poured into water, and the layers separated. The ether layer was washed with water, dried over sodium sulfate, and evaporated. Attempts at vacuum distillation resulted in decomposition and polymerization, so the product was used without further purification.

DMBC was then dissolved in glacial acetic acid and dry HCl was bubbled through until the olefinic protons disappeared in the nmr. The product mixture was then poured into water and extracted with chloroform. The chloroform layer was washed with water and followed by one washing with saturated sodium bicarbonate. It was then dried over sodium sulfate and evaporated. Addition of pentane to the crude oil followed by cooling and scratching with a glass rod resulted in crystallization. The product was identified as t-CDMBC by a X-ray crystal structure. The nmr spectrum appears in Figure 14: mp 65°C; IR($CHCl_3$) 2920, 1670, 1500, 1275cm^{-1}; m/e 250(M^+); the ^{13}C spectrum appears in Figure 18.

cis- and trans-4-Bromo-1,4-dimethyl-1-benzoylcyclohexane (cis- and trans-BCMBC): was prepared in the same manner as trans-CBMBC except that HBr was used instead of HCl. It was then found that after the initial crop of crystals was collected,

concentration of the mother liquor and subsequent cooling resulted in the formation of another crop of crystals. These two crops were later found to be the cis and trans isomers, respectively. The assignment of these structures was discussed in the results section of δ-substituted valerophenone in Part II. The nmr spectra are presented in Figures 15 and 16, and the ^{13}C spectra are presented in Figures 19 and 20: trans-BDMBC--mp 82°C; IR($CHCl_3$) 2950, 1660, 1210cm^{-1}; m/e 295(M^+)--c-BDMBC--mp 32°C; IR($CHCl_3$) 2930, 1675, 1205cm^{-1}; m/e 295(M^+).

4'-Methoxy-5-chlorovalerophenone (OMe-5-Cl): was prepared by Dr. P. J. Wagner.

4'-Trifluoromethyl-5-chlorovalerophenone (CF_3-5-Cl): was prepared by the addition of 5-chlorovaleronitrile (Aldrich) to 4-trifluoromethylphenylmagnesiumbromide: bp 105°C(0.05mm); IR(neat) 2950, 1701, 1340, 1145cm^{-1}; NMR($CDCl_3$) δ1.9(m,4H), 3.0(m,2H), 3.5(m,2H), 7.5(d,2H), 7.8(d,2H); m/e 264(M^+).

5-Iodovalerophenone (5-I): was prepared by J. H. Sedon.

5-(4'-Methoxy)-phenoxyvalerophenone (5-OPh): was prepared by the reaction of 5-I with the sodium salt of p-methoxyphenol. To a DMSO solution containing freshly cut sodium was added one equivalent of p-methoxyphenol. It was allowed to stir until consumption of the sodium was complete. One equivalent of 5-I was added, and the mixture heated at 100°C for four hours. The mixture was then poured into H_2O and extracted with ether. The combined ether extracts were washed several times with H_2O, dried over sodium sulfate,

and evaporated. The crude product was recrystallized in hexane in low yield: mp 47°C; NMR($CDCl_3$) δ1.9(m,4H), 3.0(m,2H), 3.7(s,3H), 3.9(m,2H), 6.6(d,4H), 7.3(m,3H), 7.8(m,2).

4-Benzhydryloxybutyrophenone (4-OBzhydl): was prepared by the addition of phenylmagnesiumbromide to the appropriate nitrile. The nitrile was prepared by refluxing 42g trimethylenechlorohydrin in 35ml benzene containing 5ml concentrated H_2SO_4 and 55g benzhydrol for eight hours. The mixture was washed with H_2O, dried over sodium sulfate, and evaporated to give a near quantitative yield of benzhydryloxypropylchloride. This was converted to the nitrile directly by heating at 100°C in DMSO with a 20% excess of NaCN. Aqueous workup, followed by drying over sodium sulfate, yielded 4-benzhydryloxybutyronitrile, which was used without further purification. The Grignard Reaction with phenylmagnesiumbormide proceeded smoothly. Recrystallization from heptane resulted in a low yield: mp 74°C; NMR($CDCl_3$) δ2.0(m,2H), 3.0(t,2H), 3.5(t,2H), 5.2(2,1H), 7.2(m,13H), 7.8(m,2H); m/e 330(M^+).

Techniques

Preparation of Samples

Photochemical Glassware. All photochemical glassware, including class "A" pipets and class "A" volumetrics, were heated for a day or two in aqueous ammonium hydroxide, followed by rinsing and heating in distilled water, followed

finally by prolonged drying in a 160°C oven. Photolysis tubes (13 x 100mm culture tubes) were washed in a analogous manner, and the necks elongated by rotation in a flame and pulled until the desired length was attained.

Stock Solutions and Photolysis Solutions. All solutions were prepared either by weighing the desired amount of substrate directly into the volumetric flash and diluting to the line with the appropriate solvent, or by pipetting an aliquot of a stock solution into the volumetric and diluting to the appropriate volume.

Quantum Yields, Quenching, and Sensitization Studies. All solutions were prepared as described above. A 5cc syringe fitted with a 6" needle was used to transfer 3.8ml of the solution to the test tube with the constricted neck.

Degassing. After the tubes were filled with the appropriate solutions, they were attached via one-holed rubber stoppers (size 00) directly to a vacuum line. The solutions were then frozen by slow immersion in liquid nitrogen. When the tubes were completely immersed and frozen, the stopcocks were opened, and the tubes were pumped on for about five to ten minutes. The stopcocks were then closed, the liquid nitrogen was removed, and the tubes were allowed to thaw either by standing in the air or by immersion in cool water. This process, known as a "freeze-thaw cycle," was typically repeated a total of three times. On the final cycle, the tubes were sealed by a torch while they were frozen and open to the vacuum line.

Irradiation Procedures

Kinetic Runs. The degassed tubes were thawed and mixed thoroughly and wiped clean. Samples to be irradiated were then placed in a rotating merry-go-round apparatus which was immersed in a water bath held at 25°C. All tubes were irradiated in parallel to insure that each sample obtained an equal amount of light. The light source was a 450-watt (Hanovia) medium-pressure lamp, cooled by a quartz or pyrex immersion well. The 313nm region was isolated by employing a filter solution composed of 0.0002M potassium chromate in 1% potassium carbonate. The 366nm region was isolated by employing a set of Corning #7-83 filters.

Preparative Runs. Preparative photolysis runs were carried out in quartz or vycor immersion wells utilizing a pyrex filter around a 450-watt (Hanovia) medium-pressure lamp. Nitrogen was bubbled in vigorously through a subsurface inlet prior to irradiation, and a positive pressure was maintained above the solution during photolysis. Typically 160ml of 0.05-0.2M solutions were irradiated. The solutions were irradiated varying lengths of time, depending upon the quantum yields and desired conversions, and were followed by vpc when possible.

Analysis of Samples

Identification of Photoproducts. Photoproducts were identified by isolation via preparative vpc, comparison of vpc retention times with authentic samples, or nmr.

Acetophenones were identified by comparison of their retention times with those of authentic samples under identical conditions. In the cases of 4-SBu, 2-SPh, and 5-SPh, acetophenone was isolated by preparative vpc.

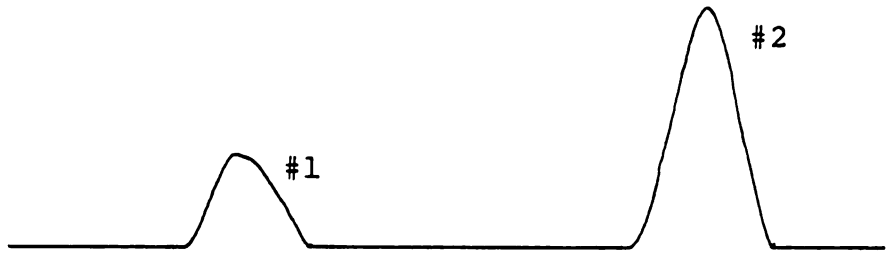
4-Benzoyl-1-butene (4-BB) was identified by photolysis of a 0.05M solution of ketone in benzene as previously described for 24 hours. Evaporation of the benzene under reduced pressure yielded a brown oil. Vpc analysis showed essentially one peak, which had an identical retention time to an authentic sample of 4-BB. Isolation of that peak was effected by preparative vpc, utilizing a 10% SE-30 column at 160^{o}C. The isolated compound was shown to be 4-BB by comparison of spectral data.

Butylbutanethiolsulfonate was identified by vpc retention time comparison with an authentic sample prepared by the method of Majeti.[192]

Diphenyldisulfide was identified by vpc retention time comparison with an authentic sample prepared by the addition of I_2 to a methanolic solution of benzenethiol.

1,4-Dimethyl-1-benzoylcyclohex-3-ene (DMBC) was identified by three methods. Since the 4-halo-1,4-dimethyl-1-benzoylcyclohexanes are unstable to vpc analysis and chromatography on silica or alumina, direct isolation of the olefin was impossible. However, three indirect methods provided substantial evidence for the production of DMBC in the photolysis of trans-CDMBC and cis- and trans-BDMBC. The first (Method I) involved photolysis of trans-CDMBC until it was

completely consumed. Injection of trans-CDMBC onto a 3% QF-1 column at 150°C resulted in two peaks as pictured below.



Peak #1 was identical with DMBC; peak #2 was assumed to be the chloride. After about 12 hours of photolysis, peak #2 had disappeared and a new peak (#3) had appeared as shown below.

Peak #3 was assumed to be the bicyclic alcohol resulting from γ-hydrogen abstraction. A fairly intense absorption in the IR at 3500cm^{-1} was observed for the crude photolysate. Derivatization of the photolysate formed the basis for identification by Method II. The benzene was removed by rotary evaporation and the crude oil dissolved in CCl_4. Addition of bromine resulted in the precipitation of an orange solid, which melted at 79°C. An authentic sample of the dibromide was prepared in an analogous fashion from authentic DMBC. This compound melted at 83°C and was judged to be identical to the photolysate addition product. The photolysate Br_2 addition product was found to yield DMBC upon zinc dust

debromination (vpc), whereas injection of the dibromide on the vpc resulted in no DMBC formation. Lastly, Method III involved identification of DMBC by nmr. A dilute solution of t-BDMBC in benzene-d_6 containing 0.05M pyridine was placed in an nmr tube and degassed by one freeze-thaw cycle. After several hours of irradiation at 313nm, a white precipitate, which was assumed to be pyridinium hydrobromide, had formed; and the nmr possessed some vinylic absorptions, which were assumed to arise from DMBC.

Benzaldehyde was identified by comparison of its vpc retention time with that of an authentic sample.

Gas Chromatography Procedures. Analyses for all photoproducts were made on either an Aerograph Hy-Fi model 600D gas chromatograph or a Varian Aerograph 1200 gas chromatograph. Recorders were used interchangeably but were either a Leeds and Northrup Speedomax-H recorder or a Sargent Model SR recorder. Each of the instruments were prepared for on-column injection and utilized nitrogen as the carrier gas. Both used flame ionization detectors and were connected to a Infrotronics Automatic Digital Integrator Model CRS 309. Sample injections were made via a Hamilton syringe using varying amounts from 0.02-0.2 microliters per injection. All analyses were made on one of the following columns:

-- Column #1: 6' x 1/8" aluminum containing 3% QF-1 on 60/80 chromosorb G.

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

-- Column #3: 10' x 1/8" aluminum containing 25% Carbowax 20m on 60/80 chromosorb G.

-- Column #4: 25' x 1/8" aluminum containing 25% 1,2,3-Tris(2-cyanoethoxy)propane on 60/80 chromosorb W.

Actinometry and Quantum Yields. Photoproduct concentrations were easily determined using vpc product:internal standard ratios. A correction factor (CF) to correct for the difference in molar responses for the different compounds was determined by measuring the relative vpc peak areas of products and standards of known concentrations. Thus, the concentration of the appropriate photoproduct can be determined from the following equation:

$$[\text{prod.}] = CF \cdot [\text{int. stand.}] \cdot \frac{\text{area product}}{\text{area int. stand.}}$$

The CF's will be listed in the Appendix.

Valerophenone actinometry was used exclusively for all quantum yields and ketone disappearance yields. A 0.1M solution of valerophenone in benzene containing a known amount of hexadecane was irradiated in parallel with the desired compound. Analysis for acetophenone was made using column #1. The known quantum yield of a 0.1M valerophenone solution is 0.33.[193] The quantum yield for product formation was determined via the following euqation:

$$\phi_{\text{prod.}} = \frac{[\text{prod.}]}{[\text{acet.}]^{\text{val}}} \cdot 0.33$$

where $[acet.]^{val}$ refers to the concentration of acetophenone formed in the valerophenone actinometer.

Disappearance yields were determined by comparing ketone:standard ratios before and after irradiation. This fraction multiplied by the initial concentration of ketone yields Δ[ketone] which, when plugged into the following equation, yields ϕ_{-K}.

$$\left(\frac{\text{ketone}}{\text{stand.}}\right)^{after} / \left(\frac{\text{ketone}}{\text{stand.}}\right)^{before} = R$$

$$R \cdot [ketone]^{initial} - [ketone]^{initial} = \Delta[ketone]$$

$$\phi_{-K} = \frac{\Delta[ketone]}{[acet.]^{val}} \cdot 0.33$$

Cis-1,3-pentadiene sensitization plots were constructed to determine the intersystem crossing yields and in cases where no product was formed, the triplet lifetime. Tubes containing 0.05M ketone with varying amounts of c-1,3-pentadiene were irradiated in parallel with a tube containing 0.1M acetophenone and 1M c-1,3-pentadiene. Actual quantum yields of c→t were calculated in the following manner:

$$[trans] = \beta'[cis]$$

$$\text{where } \beta' = 0.55 \ln \frac{0.55}{0.55 - \beta}$$

$$\text{and } \beta = \frac{R}{R + 1} \text{ where } R = \frac{\text{area t}}{\text{area c}}$$

$$\text{Thus, } I = \frac{[\text{trans}]^{\text{actinometer}}}{0.55}$$

$$\text{Then, } \phi_{c\rightarrow t} = \frac{[\text{trans}]^{\text{ketone}}}{I}$$

A plot of $0.55/\phi_{c\rightarrow t}$ versus $1/[\text{c-1,3-pentadiene}]$ yields a line in which the reciprocal of the intercept equals ϕ_{isc} and the intercept divided by the slope equals $k_q\tau$.

Spectra

Proton magnetic resonance (nmr) spectra were recorded on a Varian T-60 spectrometer as CCl_4 or $CDCl_3$ solutions utilizing TMS as an internal standard. ^{13}C spectra were recorded on a Varian CFT-20 spectrometer utilizing the usual Fourier transform signal enhancement with broad band proton decoupling. Spectra were run in $CHCl_3$, which also served as a lock. Infrared spectra were recorded on a Perkin-Elmer 237B grating spectrometer as thin films or $CHCl_3$ solutions using polystyrene (1601cm^{-1}) calibration. The mass spectra were run on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Ultraviolet spectra were measured on either a Unicam SP-800 or a Carey 14 spectrophotometer. The crystal structure on trans-CDMBC was performed by Dr. D. Ward on a Picker FACS-I automatic X-ray diffractometer. Phosphorescence spectra were obtained on a Perkin-Elmer MPF-44A Fluorescence spectrometer connected to a Perkin-Elmer Differential Corrected Spectra Unit.

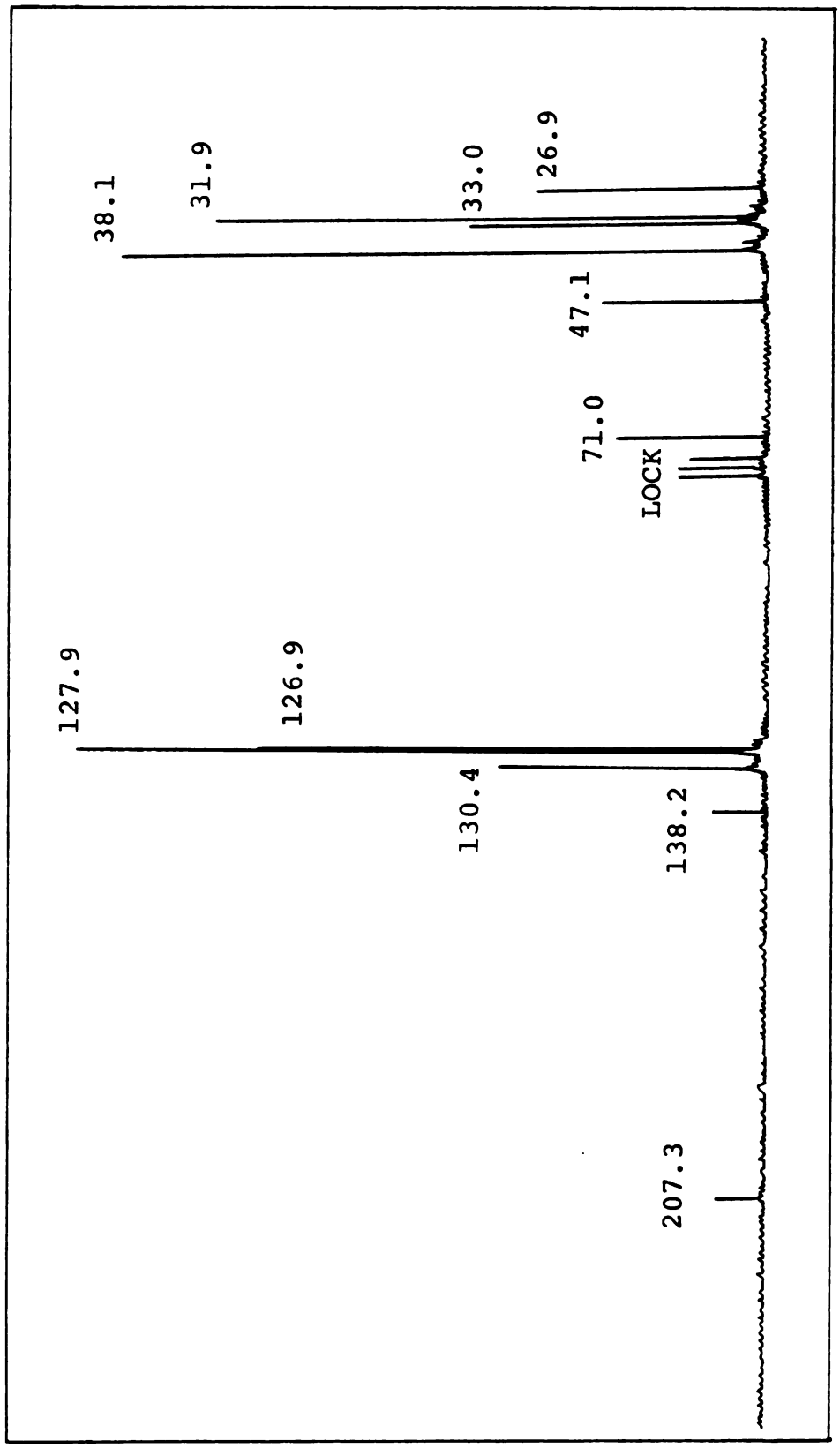


Figure 18. ^{13}C Spectrum of trans-CDMBC in $CHCl_3$.

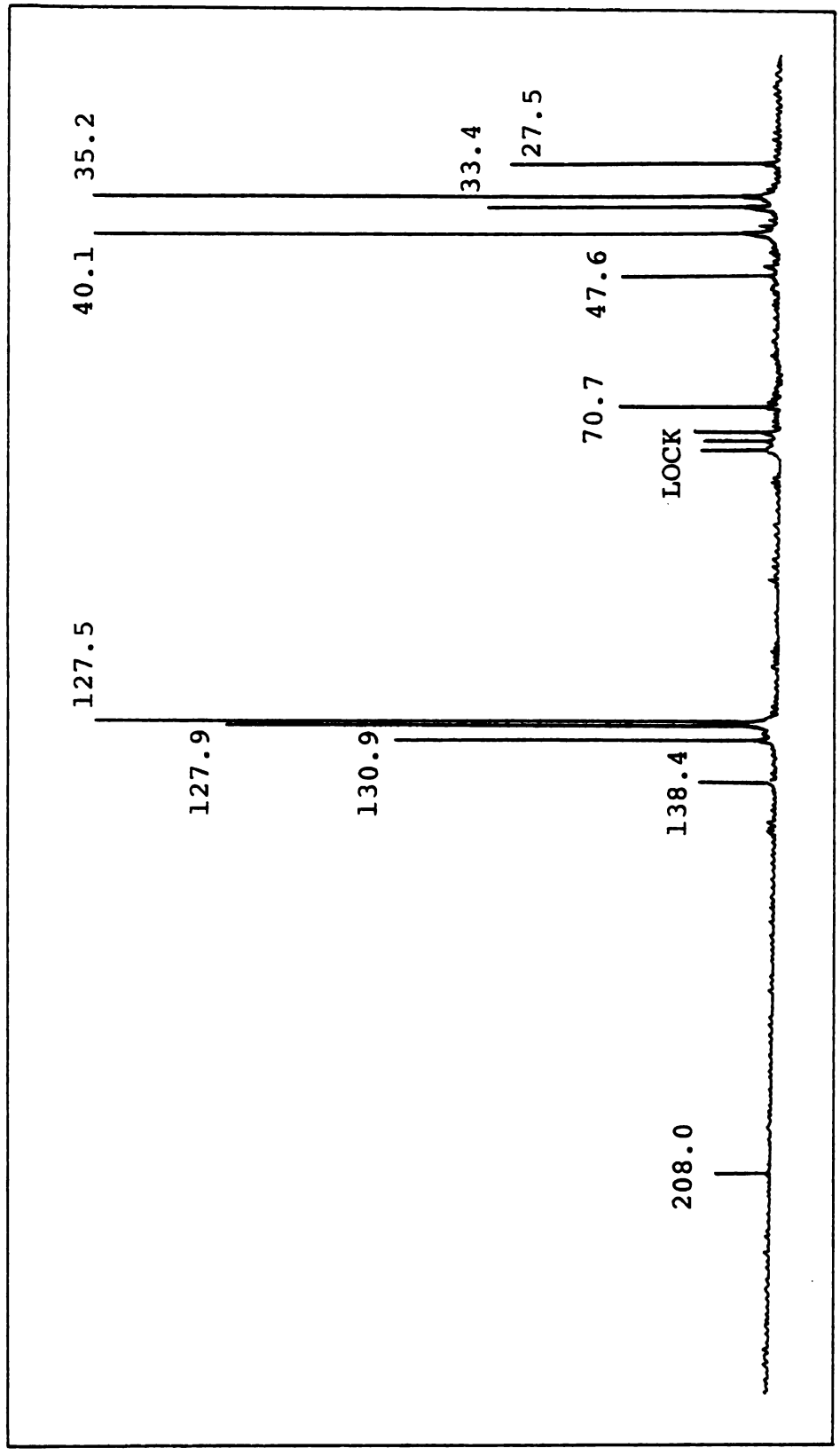


Figure 19. ^{13}C Spectrum of trans-BDMBC in $CHCl_3$.

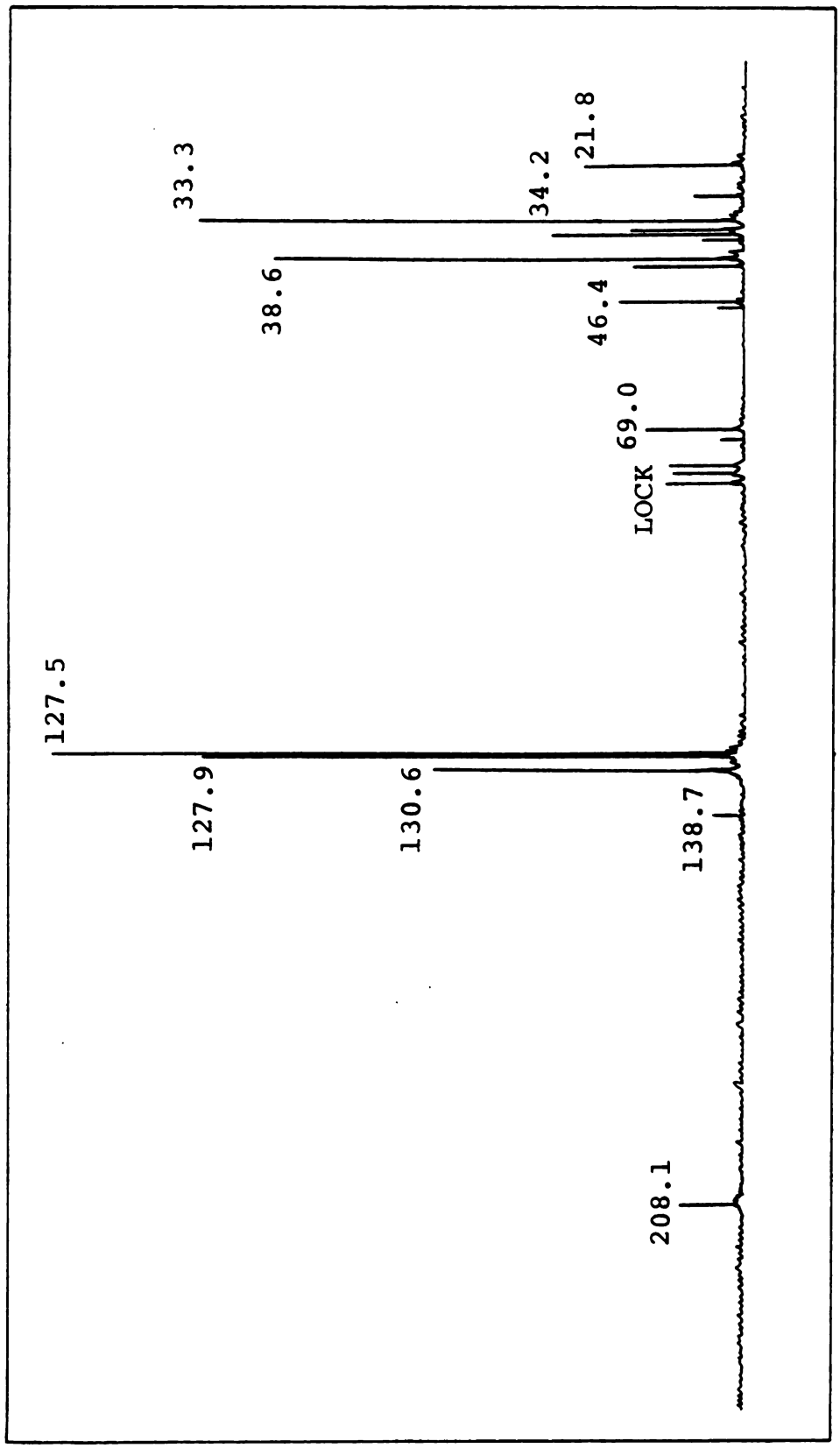


Figure 20. ^{13}C Spectrum of cis-BDMBC in $CHCl_3$.

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APPENDIX

APPENDIX

This section contains the raw experimental data, such as product to standard ratios, internal standard concentrations, etc., used to calculate the various photokinetic parameters.

The data is arranged in tabular form as follows: the concentration of internal standard for the actinometry is listed first. C16 was used exclusively for all valerophenone actinometry. The correction factor for acetophenone versus C16 is 2.3. Other correction factors are listed (in parentheses) after the concentration of standard to which it refers. The quencher that was used for the Stern-Volmer plot is listed next, followed by the column and column conditions. The description of the various columns are listed in the Experimental section.

Quenching data, including quencher concentrations, product to standard ratios, and $\phi°/\phi$ values, are listed next. The concentrations of internal standards for the quenching runs were not measured but were in the range 10^{-3} to 10^{-2}M.

The values immediately below the quenching data are the prod/std ratios used for calculating the respective quantum yields. In most cases the concentration of standard in all tubes is the same as the actinometer. In some cases

different concentrations of standard were used for each tube. In these cases the prod/std ratios are listed in the same order as previously listed concentrations.

Abbreviations used in this section are: Pip = piperylene; 1-NM = 1-methylnapthalene; Napth = napthalene; act = actinometer (valerophenone in all cases); acet = acetophenone; Bzald = benzaldehyde; DMBC = 1,4-dimethyl-1-benzoylcyclohexane; 4-BB = 4-benzoyl-1-butene; and pyr = pyridine. All quantum yields were performed at 3130Å. Quenching runs utilizing piperylene were performed at 3130Å. Quenching runs utilizing napthalene or 1-methyl-napthalene were performed at 3660Å. Photolysis times were usually between one and three hours. The intensity of the lamp varied between 0.005 and 0.01 Einsteins M^{-1}.

Table 22. Data for 2-Thiomethylacetophenone.

0.0140M C16, 0.0154M C16, 0.0139M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	2.38	--
0.24	1.40	1.70
0.55	0.96	2.30
1.26	0.66	3.60
1.53	0.59	4.10
act	0.158	
acet	0.122	
acet(0.05M PhSH)	0.169	

Table 23. Data for Thio-t-butylacetophenone.

0.0139M C16
1-MN quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.88	--
0.08	0.68	1.29
0.16	0.53	1.66
0.50	0.29	3.00
act	0.140	
acet(0.05M PhSH)	0.017	

Table 24. Data for 2-Thiobutylacetophenone.

0.025M C16
1-MN quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.0	0.49	--
0.3	0.29	1.67
0.7	0.24	2.00
1.0	0.19	2.50
act	1.82	
acet	2.37	
acet(0.05M PhSH)	2.84	

Table 25. Data for 4-Thiobutylbutyrophenone.

0.011M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.0	0.20	--
0.3	0.13	1.5
0.6	0.10	1.9
1.0	0.08	2.6
act	0.27	
acet	0.08	
acet(1.0M dioxane)	0.15	

Table 26. Data for 4-Thio-t-butylbutyrophenone.

0.014M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.29	--
0.4	0.16	1.8
0.8	0.09	2.9
1.2	0.07	3.6
act	0.49	
acet	0.39	

Table 27. Data for 4-Thiophenylbutyrophenone.

0.005M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.37	--
0.3	0.16	2.4
0.6	0.09	3.9
1.0	0.06	5.9
act	0.52	
acet	0.50	
acet(1.0M dioxane)	0.57	

Table 28. Data for 5-Thiobutylvalerophenone.

0.006M C12 (1.63)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.72	--
0.02	0.44	1.6
0.06	0.22	3.3
0.10	0.16	4.5
act	0.330	
acet(1.0M dioxane)	0.210	
4-BB(1.0M dioxane)	0.003	

Table 29. Data for 5-Thiophenylvalerophenone.

0.011M C16 (1.67)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.72	--
0.02	0.44	1.6
0.06	0.22	3.3
0.10	0.16	4.5
act	0.615	
acet(1.0M dioxane)	0.029	
4-BB(1.0M dioxane)	0.840	

Table 30. Data for 6-Thiobutylhexanophenone.

0.026M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.32	--
0.02	0.20	1.6
0.06	0.09	3.3
0.10	0.06	5.2
act	0.16	
acet	0.10	
acet(1.0M dioxane)	0.12	

Table 31. Data for 5-Thiocyanatovalerophenone.

0.041M C16 (1.67)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	2.0	--
0.2	0.64	3.10
0.4	0.39	5.10
0.6	0.17	11.0
act	1.38	
acet(1.0M dioxane)	0.02	
4-BB(1.0M dioxane)	1.27	

Table 32. Data for 5-Thioacetoxyvalerophenone.

0.0548M C16 (1.67)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	1.61	--
0.06	0.42	3.8
0.12	0.26	6.0
act	0.370	
acet	0.023	
acet(1.0M pyridene)	0.870	
4-BB	0.648	

Table 33. Data for 2-Methylsulfinylacetophenone.

0.025M C16
1-MN quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	1.58	--
0.5	1.06	1.48
1.0	0.80	1.97
act	1.13	
acet	0.37	
acet(0.05M PhSH)	1.49	

Table 34. Data for 4-Butylsulfinylbutyrophenone.

0.011M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.00	0.52	--
0.02	0.41	1.28
0.04	0.29	1.78
0.06	0.27	1.89
0.08	0.23	2.27
act	0.516	
acet	0.048	
acet(1.0M dioxane)	0.052	

Table 35. Data for 5-Butylsulfinylvalerophenone.

0.0088M C16 (1.67)
Pip quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.00	0.78	--
0.02	0.52	1.5
0.04	0.41	1.9
0.06	0.35	2.3
0.08	0.29	2.7
act	0.56	
acet(1.0M dioxane)	0.05	
4-BB(1.0M dioxane)	0.92	

Table 36. Data for 2-Butylsulfonylacetophenone.

0.021M C16
1-MN quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.000	0.63	--
0.012	0.19	3.2
0.016	0.14	4.6
0.020	0.11	5.7
act	1.78	
acet	1.05	
acet(0.05M PhSH)	0.28	

Table 37. Data for 5-Butylsulfonylbutyrophenone.

0.0075M C16
Pip quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.0000	1.75	--
0.0004	0.746	2.3
0.0008	0.481	3.6
0.0010	0.300	5.8
act	0.932	
acet	0.566	
acet(1.0M dioxane)	0.263	

Table 38. Data for 5-Butylsulfonylvalerophenone.

0.0085M C16 (1.67)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.000	1.36	--
0.002	1.10	1.24
0.004	0.75	1.81
0.006	0.61	2.23
act	0.66	
acet(1.0M dioxane)	0.78	
4-BB(1.0M dioxane)	0.07	

Table 39. Data for 2-Thiophenylacetophenone.

0.016M C16
1-MN quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.53	--
2.0	0.51	1.0
act	0.220	
acet	0.051	
acet(0.05M PhSH)	0.162	

Table 40. Data for 2-Thiophenyl-4'-Fluoroacetophenone.

0.012M C16(2.3)
1-MN quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.0	0.6	--
2.0	0.6	1.0
act	0.45	
acet	0.063	
acet(0.05M PhSH)	0.312	

Table 41. Data for Thiophenyl-4'-chloroacetophenone.

0.012M C14, 01014M C14 (2.0)
Napth quencher
Col #1 145°C

[Q]	prod/std	ϕ°/ϕ
0.00	0.52	--
0.44	0.38	1.36
0.86	0.32	1.61
1.76	0.21	2.41
act	0.450	
acet	0.075	
acet(0.05M PhSH)	0.344	

Table 42. Data for 2-Thiophenyl-4'-bromoacetophenone.

0.012M C16, 0.0136M C16 (2.0)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	1.01	--
0.56	0.51	1.78
0.96	0.39	2.61
1.45	0.27	3.70
act	0.450	
acet	0.085	
acet(0.05M PhSH)	0.265	

Table 43. Data for 2-Thiophenyl-4'-methylacetophenone.

0.012M C16, 0.013M C14 (1.8)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.32	--
2.0	0.31	1.0
act	0.45	
acet	0.078	
acet(0.05M PhSH)	0.462	

Table 44. Data for 2-Thiophenyl-4'-methoxyacetophenone.

0.0026M C16 (2.04)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.39	--
0.48	0.20	1.97
0.98	0.12	3.36
act	0.263	
acet	0.078	
acet(0.05M PhSH)	0.367	

Table 45. Data for 2-Thiophenyl-4'-thiomethoxyacetophenone.

0.011M C16, 0.007M C19 (2.09)
Napth quencher
Col #1 170°C

[Q]	prod/std	$\phi°/\phi$
0.000	0.57	--
0.007	0.38	1.48
0.040	0.24	2.32
0.090	0.15	3.68
act	0.39	
acet	0.09	
acet(0.05M PhSH)	0.42	

Table 46. Data for 2-Thiophenyl-4'-dimethylaminoacetophenone.

0.011M C16, 0.002M C20 (2.37)
Napth quencher
Col #1 190°C

[Q]	prod/std	$\phi°/\phi$
0.00	1.68	--
0.04	1.21	1.34
0.06	0.900	1.87
0.10	0.600	2.80
act	0.210	
acet	0.267	
acet(0.05M PhSH)	0.443	

Table 47. Data for 2-Thiophenyl-4'-phenylacetophenone.

0.016M C16, 0.005M C20 (2.3)
Napth quencher
Col #1 190°C

[Q]	prod/std	$\phi°/\phi$
0.000	4.43	--
0.008	2.99	1.48
0.015	2.57	1.72
0.026	2.17	2.00
act	0.630	
acet	0.270	
acet(0.05M PhSH)	1.670	

Table 48. Data for 2-Thiophenyl-4'-cyanoacetophenone.

0.0126M C16, 0.0020M C19 (1.72)
Napth quencher
Col #1 190°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.44	--
0.16	0.34	1.29
0.56	0.29	1.52
0.96	0.22	2.00
act	0.31	
acet	0.25	
acet(0.05M PhSH)	1.14	

Table 49. Data for 2-Thiophenylpropriophenone.

0.027M C16 (2.04)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.61	--
2.0	0.60	1.0
act	0.580	
acet	0.256	
acet(0.05M PhSH)	0.637	

Table 50. Data for 2-Thiophenylisobutyrophenone.

0.0026M C16 (1.84)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.24	--
2.0	0.25	1.0
act	0.49	
acet	0.67	
acet(0.05M PhSH)	0.69	

Table 51. Data for 1-Thiophenyl-1-benzoylcyclopropane.

0.013M C16, 0.015M C15 (1.89), 0.014M C15 (1.89)
Pip quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00	0.77	--
1.12	0.33	2.33
1.65	0.20	3.61
act	0.274	
acet	0.119	
acet(0.05M PhSH)	0.382	

Table 52. Data for 4'-Thiophenylmethylacetophenone.

0.0136M C16, 0.0070M C18 (2.3), 0.0063M C18 (2.3)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	0.19	--
2.0	0.17	1.0
act	0.29	
acet	0.19	
acet(0.05M PhSH)	0.77	

Table 53. Data for 4'-Thiophenylacetophenone.

0.0125M C16, 0.0137M C16
Col #1 145°C

	prod/std
act	0.64
acet(0.05M PhSH)	0.001

Table 54. Data for Phenyldesylsulfide.

0.0126M C16, 0.0090M C20 (1.5), 0.0100M C20 (1.5)
Col #1 190°C

	prod/std
act	0.14
acet	0.0018
acet(0.05M PhSH)	0.0144

Table 55. Data for 5-Phenylsulfinylvalerophenone.

0.0028M C16 (1.67)
Col #1 145°C

	prod/std
act	1.66
acet	0.009
acet(1.0M dioxane)	0.010
4-BB	1.770
4-BB(1.0M dioxane)	1.730

Table 56. Data for 5-Phenylsulfonylvalerophenone.

0.0026M C16 (1.67)
Col #1 145°C

	prod/std
act	1.27
acet	0.71
acet(1.0M dioxane)	0.59
4-BB	1.16
4-BB(1.0M dioxane)	1.16

Table 57. Solvent Effects on Quantum Yield for 5-Chlorovalerophenone.

0.00264M C16 (1.67)
0.10M pyr
Col #1 145°C

	prod/std (acet)	prod/std (4-BB)
act	1.60	--
benzene	2.68	0.59
dioxane	1.76	0.39
acetonitrile	2.60	0.55
methanol	1.75	0.39

Table 58. Solvent Effects on Quantum Yield for 5-Chloro-4'-methoxyvalerophenone.

0.025M C16 (1.67)
0.10M pyr
Col #1 145°C

	acet/4-BB
acetonitrile	18
methanol	22

Table 59. Solvent Effects on Quantum Yield for 5-Chloro-4'-trifluoromethylvalerophenone.

0.00242M C16 (2.04)
0.10M pyr
Col #1 145°C

	prod/std (acet)	prod/std (4-BB)
act	1.41	--
benzene	3.04	0.47
dioxane	0.99	0.18
acetonitrile	3.05	0.24
methanol	2.10	0.15

Table 60. Data for trans-4-Chloro-1,4-dimethyl-1-benzoyl-cyclohexane.

0.0119M C16, 0.0024M C19 (1.56), 0.0028M C14 (2.3)
Napth quencher, 0.05M pyr
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.0	1.62[a] (0.16)[b]	---
0.002	1.28 (0.11)	1.27[a] (1.41)[b]
0.004	1.20 (0.08)	1.35 (2.06)
0.008	0.95 (0.06)	1.70 (2.78)
act	1.22	
DMNC	3.97	
Bzald	0.13	
alc[c]	0.18	

[a]Refers to DMBC.

[b]Refers to benzaldehyde.

[c]Refers to the assumed bicyclic alcohol.

Table 61. Data for trans-4-Bromo-1,4-dimethyl-1-benzoyl-cyclohexane.

0.0129M C16, 0.0134M C14 (2.3)
Napth quencher
Col #1 145°C

[Q]	prod/std	$\phi°/\phi$
0.00[a](0.00)[b]	0.265(0.52)	---
0.004(0.02)	0.145(0.60)	1.83(1.17)
0.008(0.04)	0.100(0.78)	2.65(1.53)
-- (0.08)	-- (0.92)	-- (1.80)
act	0.442	
Bzald(0.05M pyr)	0.025	
Bzald(0.10M pyr)	0.026	
DMBC(0.05M pyr)[c]	Δ[pyr] = 0.016	
DMBC(0.10M pyr)[c]	Δ[pyr] = 0.018	

[a]Refers to benzaldehyde.

[b]Refers to DMBC.

[c]ϕ_{DMBC} determined by measuring the disappearance of pyridine.

Table 62. Data for cis-4-Bromo-1,4-dimethyl-1-benzoylcyclohexane.

0.0143M C16, 0.015M C14 (2.3)
Napth quencher
Col #4 145°C

[Q]	prod/std	$\phi°/\phi$
0.000	0.050 (0.040)	---
0.010	0.030 (0.014)	1.70 (2.85)
0.017	0.023 (0.001)	2.17 (4.80)
act	0.304	
Bzald(0.05M pyr)	0.092	
DMBC (0.05M pyr)	0.110	

Table 63. The 3-Thiobutylpropiophenone Sensitized Isomerization of cis-1,3-pentadiene.

Col #4 58°C

	[t-P],M	$0.55/\phi_{c\rightarrow t}$
1.0(act)	0.0522	---
1.0	0.0278	1.98
1.5	0.0221	2.42
2.0	0.0203	2.64
2.5	0.0167	3.22

Table 64. The 4-Thiobutylbutyrophenone Sensitized Isomerization of cis-1,3-pentadiene.

Col #4 58°C

$[c\text{-}P]^{-1}, M^{-1}$	[t-P],M	$0.55/\phi_{c\rightarrow t}$
1.0(act)	0.0673	---
1.0	0.0429	1.57
1.5	0.0392	1.71
2.0	0.0329	2.04

Table 65. The 3-Butylsulfinylpropiophenone Sensitized Isomerization of cis-1,3-pentadiene.

Col #4 58°C

$[c\text{-}P]^{-1}, M^{-1}$	[t-P],M	$0.55/\phi_{c\rightarrow t}$
1.0(act)	0.0652	---
1.8	0.0296	2.20
5.0	0.0163	3.98

Table 66. The 3-Butylsulfonylpropiophenone Sensitized Isomerization of cis-1,3-pentadiene.

Col #4 58°C

$[c\text{-}P]^{-1}, M^{-1}$	[t-P],M	$0.55/\phi_{c\rightarrow t}$
2.0(act)	0.0068	---
125.0	0.0040	1.71
83.0	0.0016	1.45