α-SUBSTITUENT EFFECTS ON ENERGY TRANSFER AND PHOTOREACTIVITY OF KETONES

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presented by

Joseph Michael McGrath

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry

Peter Wagner
Major professor

Date September 13, 1972

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ABSTRACT

α-SUBSTITUENT EFFECTS ON ENERGY TRANSFER AND PHOTOREACTIVITY OF KETONES

By

Joseph Michael McGrath

Photochemical studies of two α-substituted phenyl alkyl ketones, α,α-dimethylvalerophenone (DMVP) and α-chloro-α-methylvalerophenone (CMVP) were conducted primarily to determine whether exothermic triplet energy transfer in solution is subject to steric effects. The other major objective was to investigate the photochemistry of α-substituted ketones, including inductive effects on triplet excited state reactivity, steric effects on γ-hydrogen abstraction, behavior of the 1,4-biradical intermediate, and photoreactions of α-substituted ketones which are competitive with the type II processes.

The steric effect of the α-methyl groups on exothermic energy transfer is very small, since quenching of DMVP is "diffusion-controlled." With DMVP, the type I and type II photoprocesses compete and values for their rate constants from the excited triplet state are $k_\alpha = 1.4 \times 10^7$ sec^{-1} and $k_\gamma = 8.6 \times 10^7$ sec^{-1}. The rate constant for the α-cleavage

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reaction of phenyl *t*-alkyl ketones is much smaller than for aliphatic *t*-alkyl ketones, probably because of the differences in the enthalpies for α-cleavage reactions from those two types of ketones. With CMVP, the n,π* singlet state apparently loses chloride ion rapidly enough to compete with intersystem crossing. The triplet excited state of CMVP apparently undergoes two competitive reactions, homolytic loss of chlorine forming a radical ($k_{\alpha hom} = 3 \times 10^{9}$ sec^{-1}) and γ-hydrogen abstraction yielding a 1,4-biradical ($k_{\gamma} = 1 \times 10^{9}$ sec^{-1}). Those intermediates give rise to several photoproducts.

The small decrease in reactivity of excited DMVP in γ-hydrogen abstraction relative to valerophenone is likely due to the α-methyls making the triplet n,π* benzoyl slightly less electrophilic by induction and therefore slightly less reactive toward γ-hydrogen abstraction. The electron-withdrawing α-chlorine of CMVP makes the triplet benzoyl more electrophilic and correspondingly more reactive toward γ-hydrogen abstraction.

The geometry of the transition state for γ-hydrogen abstraction is probably staggered to minimize eclipsing interactions since the α-methyls of DMVP have only a small effect on the rate constant for this process. The 1,4-biradical intermediate resulting from γ-hydrogen abstraction, is however, subject to significant steric effects, since the cyclization/cleavage ratio in DMVP is increased to 1.8 from the 0.22 value of valerophenone.

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α-SUBSTITUENT EFFECTS ON ENERGY TRANSFER AND PHOTOREACTIVITY OF KETONES

By

Joseph Michael McGrath

A THESIS

Submitted to
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in partial fulfillment of the requirements
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DOCTOR OF PHILOSOPHY

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1972

To my famil

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inspiration.

To my family and friends, especially my parents, for their encouragement, patient understanding, and inspiration.

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ACKNOWLEDGMENTS

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Thanks is due the rest of the Chemistry Department's excellent faculty who have also helped to shape my development as a scientist and a human being.

The fellowship of the many truly fine people with whom I have studied, worked, relaxed, and philosophized during my stay at Michigan State University is deeply appreciated.

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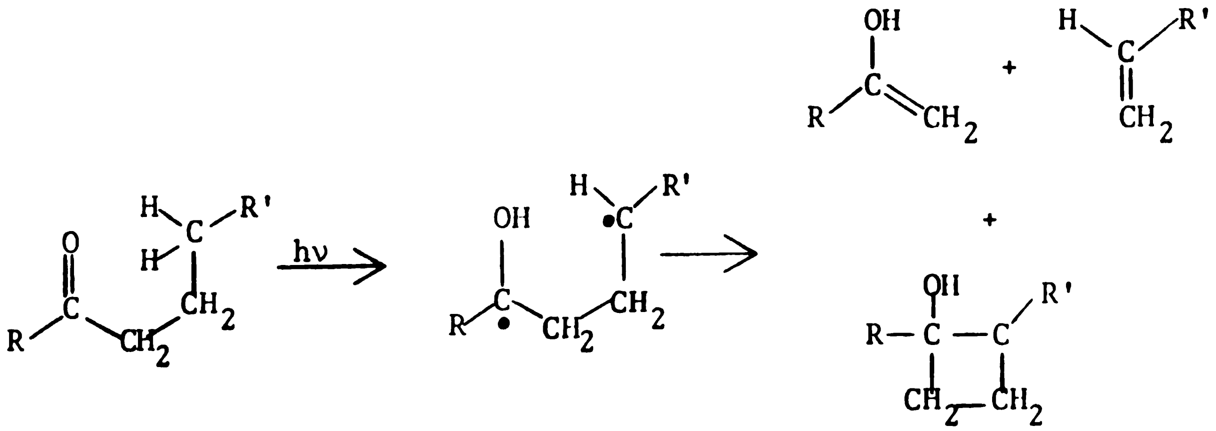
INTRODUCTION

1. Ketone Photochemistry

Extensive research has recently been conducted in the area of ketone photochemistry.[1-6] As a result, the chemical and physical properties of ketones in their electronically excited states are becoming quite well understood so that ketone photoreactions are the models for many other systems. Especially significant in mechanistic studies are the type II photoprocesses of ketones.[1] Upon electronic excitation, a carbonyl compound having a γ carbon-hydrogen bond undergoes a characteristic 1,5-hydrogen shift to yield cleavage and cyclization products.[1] Type I photocleavage, the homolytic



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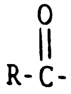

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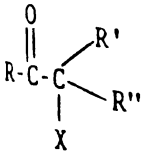

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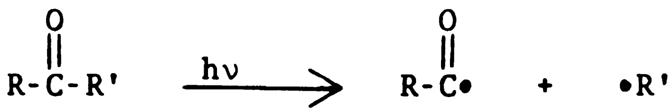

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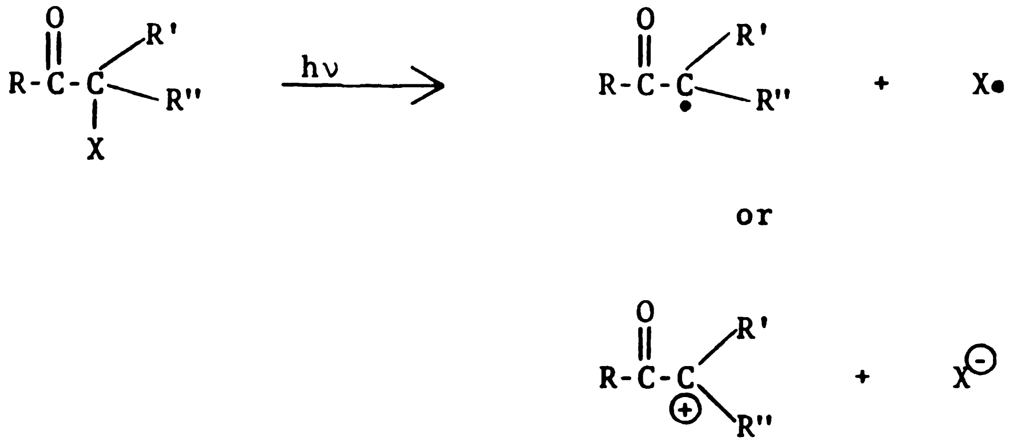
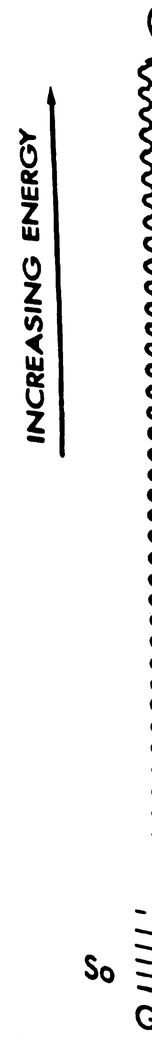
ketones. α-Haloketones are known to undergo photoinduced loss of the halogen.[6-11] There have been very few careful



studies of compounds in which these major reactions are competitive.[12]

2. Photophysical Processes

A brief description of the photophysical processes of a typical organic molecule is essential to an understanding of the chemistry of electronically excited ketones. Figure 1 is a modified Jablonski diagram[13] where various lower



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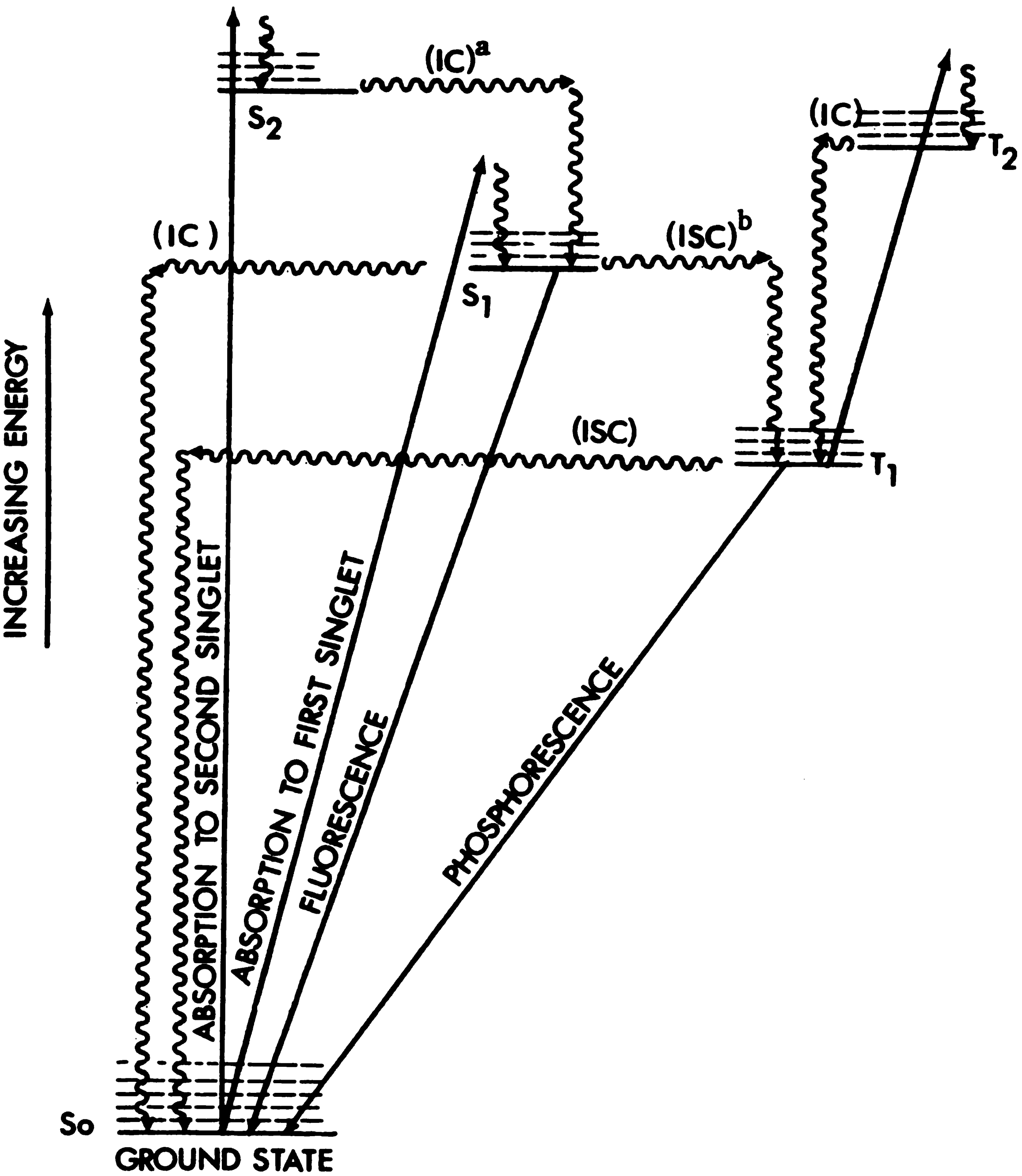

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Figure 1. Photophysical transitions between electronic states in a typical organic molecule.

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electronic states and their associated vibrational and rotational levels are schematically depicted.[14] The straight arrows represent possible physical radiative transitions and the wavy arrows non-radiative transitions. Selection rules require that spin angular momentum of the ground state be conserved in the light absorption process,[15] so that triplet states are generally populated by intersystem crossing from the directly excited singlet. Because of rapid vibrational relaxation in solution, only the lowest singlet and triplet excited states generally participate in chemical reactions. Theory predicts that the rate of radiationless crossing between states will generally decrease as the energy difference between the states increases; thus the more closely spaced upper excited states decay to the S_1 and T_1 states much more rapidly than the S_1 and T_1 states themselves cross to vibrationally excited ground state.[15]

3. Type II Photoprocesses

a. Preliminary investigations

In 1934, while examining photodecarbonylation of carbonyl compounds in the gas phase, Norrish was surprised to discover that 2-hexanone is converted to acetone and propylene.[16] Further investigation with other carbonyl compounds indicated that this reaction involves cleavage in the hydrocarbon chain between the carbon atoms lying in positions α and β to the carbonyl group to give an olefin and a simpler carbonyl compound.[17] Norrish designated this

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β-cleavage reaction of carbonyl compounds as the type II reaction to distinguish it from the previously known α-cleavage reaction which received the designation type I. The type I reaction yields carbon monoxide and free radical products in the gas phase;[17] in solution, aldehyde products and products due to hydrogen abstraction from the solvent are produced in addition to the gas phase reaction products.[18]

Noyes suggested that type II photocleavage proceeds by intramolecular transfer of a γ-hydrogen yielding an olefin and an enol; the enol then rearranges to the carbonyl compound.[19] The involvement of a γ-hydrogen has been firmly established.[20,21] Yang found that cyclobutanols are generally formed together with the type II cleavage products.[22]

b. Multiplicity of reactive excited states

Conjugated dienes and certain small polynuclear aromatic compounds are very efficient quenchers of triplet excited states but inefficient singlet quenchers.[1] Only part of the type II elimination reaction can be quenched in the case of aliphatic ketones.[23,24] Cyclobutanol formation from aliphatic ketones occurs mostly from the triplet state; increasing the concentrations of triplet quencher decreases the ratio of cyclization to elimination.[21,25,26] Comparing the unquenchable portion of the type II photoprocesses to the quenchable portion with a variety of aliphatic ketones shows that the reactions are due to two different excited states, presumably the lowest excited singlet and triplet

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n,π* states.[1,25-28] The type II cyclization and elimination reactions of aromatic ketones apparently occur only from triplet states since intersystem crossing quantum yields, which are determined from energy transfer experiments, are generally unity.[24]

c. The 1,4-biradical mechanism

The triplet n,π* state of a carbonyl compound resembles an alkoxy radical.[1,29] Yang has suggested that an intramolecular hydrogen abstraction by an n,π* ketone produces a 1,4-biradical intermediate for the formation of both type II elimination and cyclization products.[22] Support for the 1,4-biradical mechanism for ketone triplets has been provided by analyses of solvent effects,[1,27,30,31] substituent effects on reactivity,[1,32-35] isotopic labeling experiments,[36,37] and optically active systems.[1,36]

Phenyl alkyl ketones usually undergo intersystem crossing from the singlet to triplet manifold with an efficiency of unity,[1] and so are convenient for studying triplet state reactions. Figure 2 indicates the photochemistry of valerophenone, V, in the absence of quenchers or reactive solvents.[30]

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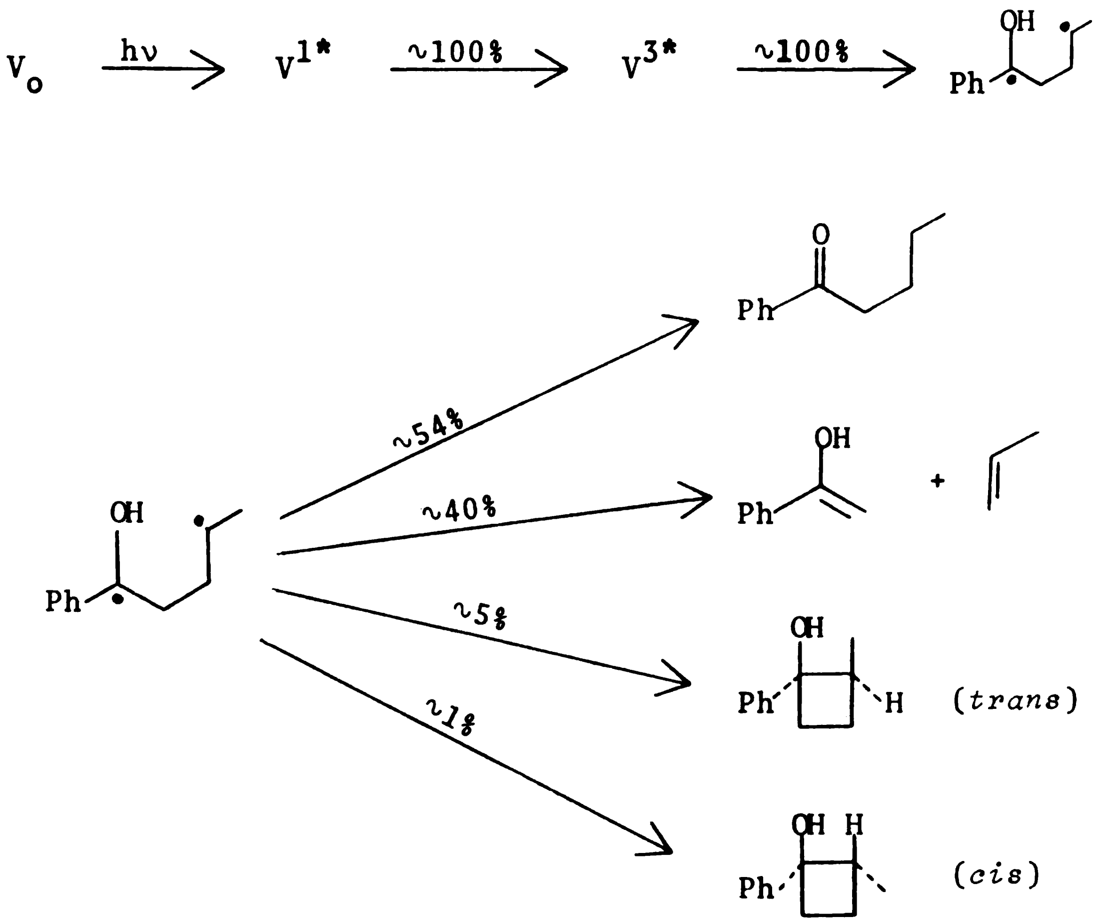
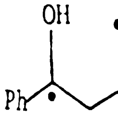


Figure 2. Photolysis of valerophenone in hexane.

In the presence of a polar solvent, the biradical behaves quite differently as seen in Figure 3.[30]



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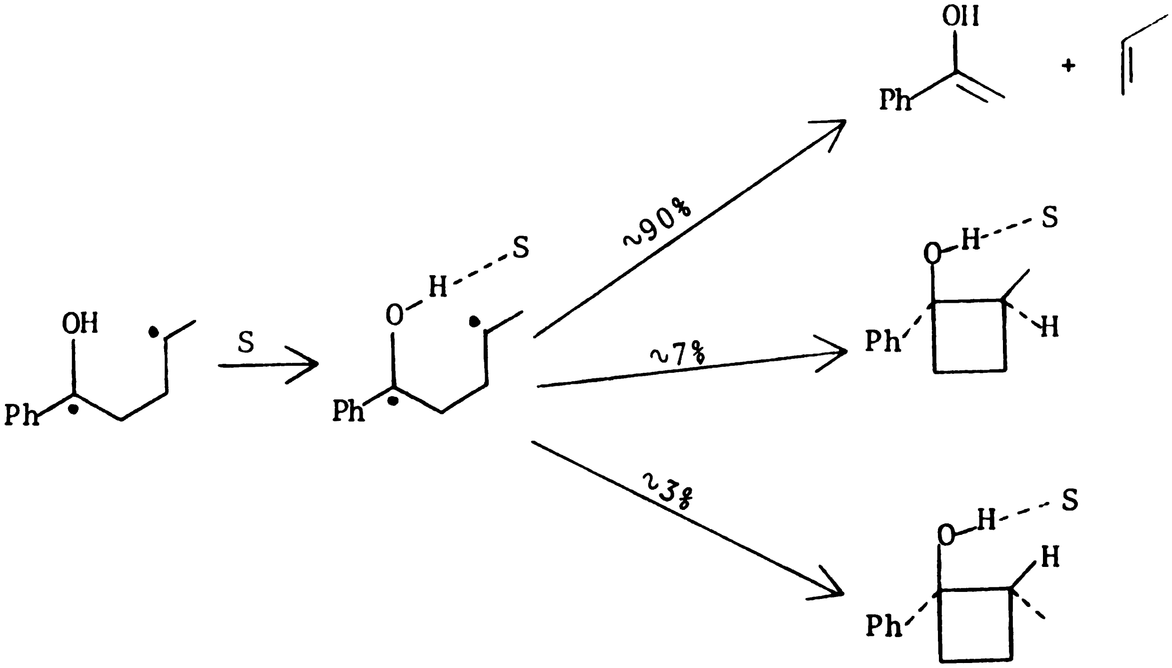

Figure 3. Effect of *t*-butanol on valerophenone photolysis.

Quantum yields for total photoreaction of valerophenone rise from 0.40 in hydrocarbons to 1.00 in alcohols.[27,30,31] The enhanced quantum yields with polar solvents can be explained by hydrogen bonding of the hydroxy biradical suppressing disproportionation back to the starting ketone.[30] This disproportionation of the biradical is responsible for the low quantum yields characteristic of type II reactions.[24,27,38]

d. Effects of substituents on type II processes

The effects of assorted substituents on triplet state reactivity and on quantum yields continue to be investigated,

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notably with phenyl ketones. Electron-withdrawing groups on the aromatic ring decrease the probability for product formation from the biradical by enhancing disproportionation; electron-donating groups have the opposite effect.[33,34] Strong electron-withdrawing ring substituents double the triple state reactivity, apparently by a simple inductive effect on the electrophilic $^3n,\pi^*$ carbonyl moiety.[33]

In all cases so far examined, phenyl alkyl ketones, PhCOR, where R is any alkyl group, have n,π^* lowest triplets. Electron-donating ring substituents or solvents of high polarity can invert the order of triplet state energies, causing the $^3\pi,\pi^*$ state to be more stable than the $^3n,\pi^*$ state.[1,39] All of the phenyl ketones with lowest π,π^* triplets show substantially reduced reactivity in intermolecular[40] and intramolecular[32] hydrogen abstraction reactions. Direct decay of the π,π^* triplet can compete with γ-hydrogen abstraction.[1,32] It should not be surprising that an electron-rich $^3\pi,\pi^*$ carbonyl does not behave like an alkoxy radical. Wagner has considered thermal equilibrium between close lying $^3n,\pi^*$ and $^3\pi,\pi^*$ states as a reasonable explanation for the observed spectroscopy and photochemistry of certain phenyl ketones having lower $^3\pi,\pi^*$ states.[35,39]

Phenyl ketones having γ- and δ-substituents show relative triplet state reactivities corresponding to the known reactivities of the various kinds of γ carbon-hydrogen bonds.[1,41] Ketones with γ and δ electron-withdrawing groups have enhanced quantum yields in spite of their diminished reactivity. Apparently the reduced disproportionation of the biradical reflects the reduced nucleophilicity of the γ-radical site of the biradical intermediate. Quantum yield decreases with electron-donating γ- and δ-substituents indicate enhanced disproportionation of the 1,4-biradical. The length of the alkyl chain produces no great alteration in the reactivity of ketone triplets[42] but about 5% δ-hydrogen abstraction may be occurring in hexanophenone and longer ketones.[1,36]

4. Type I Photocleavage

The type I processes of ketones involve α-scission to give acyl and alkyl free radicals[18] which go on to form various stable products. It is known that *t*-butyl phenyl ketone (pivalophenone) undergoes α-cleavage in solution by way of its triplet excited state.[43] Many investigations of type I reactions have been conducted using cycloalkanones.[5] The solution phase photochemical ring-opening, hydrogen-transfer, and epimerization reactions of various cyclic ketones proceed by way of the acyl-alkyl biradical obtained from α-cleavage.[44,45]

In the case of ketones with differing degrees of α-alkyl substitution, type I cleavage generally results in the formation of the more stable alkyl radical and the corresponding acyl radical.[5] The introduction of either α-methyl substituents,[45] or ring strain[45-47] in cyclic alkanones increases the rate constant for α-cleavage from the triplet

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state; it is likely that this also increases the rate constant for α-cleavage from the singlet excited state.[48] Di-*t*-butyl ketone undergoes the type I process with a rate constant of 6×10^7 sec^{-1} from the singlet excited state and with a rate constant of $7\text{-}9 \times 10^9$ sec^{-1} from the triplet state.[40] An analogous difference of at least two orders of magnitude is also observed in the reactivities of the singlet and triplet excited states of cyclic alkanones toward α-cleavage.[48]

Irradiation of *t*-butyl alkyl ketones produces type I cleavage and, if γ-hydrogens are present, type II processes also.[12] Type I cleavage occurs mainly from the triplet states of *t*-butyl alkyl ketones, while the type II processes occur almost entirely from the singlet excited state.[12] In straight chain ketones such as 2-hexanone, large fractions of the type II processes occur from the triplet state.[21,23,49] Straight chain aliphatic ketones with γ-hydrogens undergo the type II processes predominantly, if not exclusively; *t*-butyl alkyl ketones with γ-hydrogens, however, undergo mainly type I processes when photolyzed in solution.[12]

5. Photochemistry of α-Substituted Ketones

The preceeding discussion of the type I photocleavage reaction included the effect of α-methyl substitution on that photoprocess. An additional observation regarding α-alkyl substituents is that fluorescence quantum yields of aliphatic ketones increase with α-alkyl substitution, perhaps by slowing internal conversion to the ground state or intersystem

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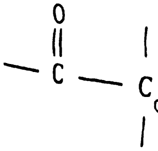

Figure 4. H
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crossing to the triplet state.[50] It is not known how α-substituents affect either the rate or quantum yields of the type II processes. Electronegative groups at the α-carbon seem to enhance the photoreactivity of carbonyl triplets.[1,51,52]

Photolysis of α-aryloxy ketones having no γ-hydrogens results in cleavage of the bond between the α-carbon and the aryloxy group.[53,54] This is an example of photocleavage of a bond between the α-carbon of a ketone and a substituent in a process other than type II cleavage. Consistent with the diradical and zwitterionic resonance model of the n,π* excited carbonyl,[55] there is the *a priori* possibility of ejecting such α-substituents as either free radicals or anions.[6,56] Figure 4 represents the homolytic and heterolytic modes of cleavage which may be operative for certain α-substituted ketones.[56,57]

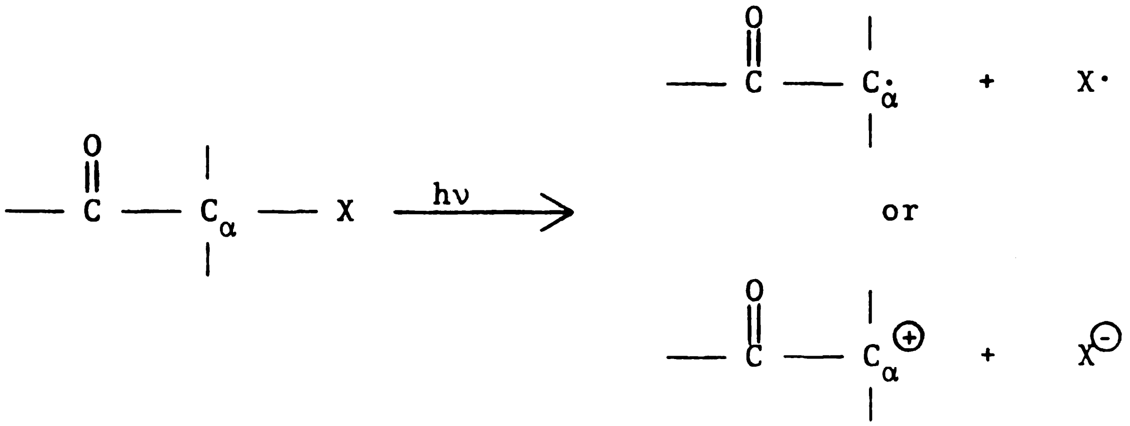

Figure 4. Homolytic and heterolytic cleavage pathways for loss of α-substituent.

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With certain β-ketosulfides the C_α--SR bond cleaves photolytically, but the mechanism is not known.[58] With some other β-ketosulfides, type I photocleavage has been observed.[59] Photolysis of dimethylphenacylsulphonium bromide is thought to proceed by way of homolysis of the C_α--$\overset{+}{S}Me_2$ bond.[60] The free radical mechanism is also invoked for the photocleavage of the C_α--SO_2R bond of β-ketosulphones.[61] The photorearrangement of α,β-epoxyketones to β-dicarbonyl products provides another example of this type of cleavage reaction; it apparently proceeds by homolytic C_α--O bond cleavage[6,56,62-66] to give a biradical intermediate which can undergo further rearrangement.[67] With α-sulfonyloxyketones, there is some evidence suggesting that heterolytic cleavage of the C_α--OSO_2R bond may be occurring together with homolysis.[57,67]

Various α-chloro and α-bromo[6,8] ketones, including an α-dichloroketone,[11] undergo photocleavage of the C_α--Cl or C_α--Br bond. Photolysis of chloroacetone in the vapor phase yields no type I cleavage products as acetone does.[7] Instead, homolysis of the C_α--Cl bond occurs and the resulting radicals react to give a variety of products.[7,8] When photolyzed in ethyl ether with triethyl phosphite, chloroacetone appears to lose its α-chloro substituent by both ionic and free radical pathways as determined from the nature of the products.[9] The ionic product may however result from a concerted reaction of triethyl phosphite and the electronically excited chloroacetone.[9] The photolysis of ring-substituted α-chloroacetophenones

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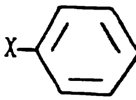

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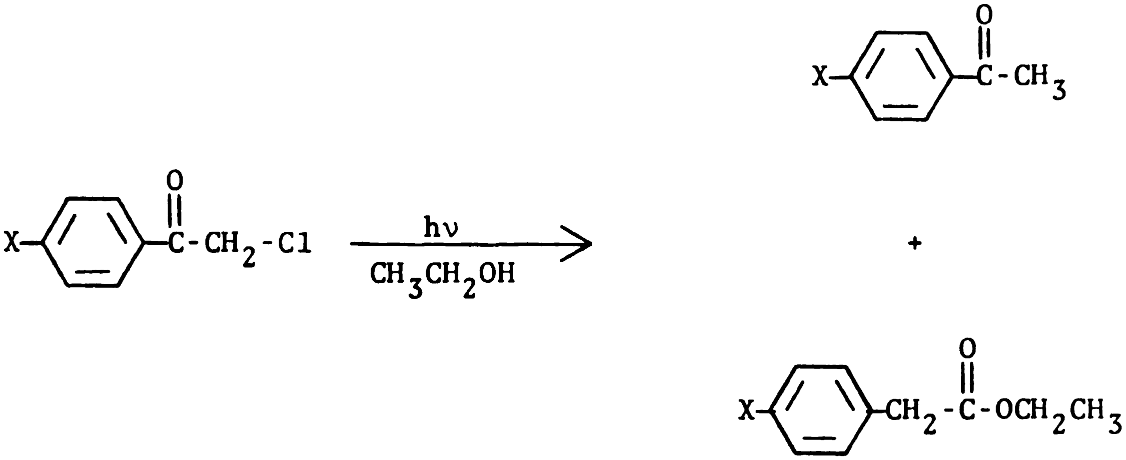
phenones in ethanol gives products which have lost the chloro group, including an ester where the aryl group has migrated to the α-carbon.[68]



The mechanism for this migration is a matter for speculation, but it is known that electron-donating groups in *ortho* or *para* positions are required to obtain the rearranged ester as a product.[68]

The photolytic cleavage of bonds attached to the α-carbon of ketones has been observed with electronegative and cyclopropyl α-substituents.[67] The reaction has been attributed to a π* assisted process of the n,π* excited carbonyl group,[55,69] perhaps with the antibonding orbital extending in some cases to the bond attaching the leaving substituent.[6,67] Photolytic cleavage of the C_{α}--NMe_2 bond in a cyclohexanone system occurs in the isomer with an axial α-dimethylamino group but not in the isomer with the equatorial α-substituent.[70]

A related phenomenon occurs with α-halogenated cyclohexanones, where the axial but not the equatorial halogen causes increases in the wavelength and intensity of the n,π* transition.[6]

6. Energy Transfer

One very important reaction of excited states is energy transfer, whereby a donor molecule in an electronically excited state transfers its excitation to a ground state acceptor (quencher).

$$D^* + Q_o \xrightarrow{k_q} D_o + Q^*$$

The acceptor ends up in an electronically excited state, the donor in its ground state. Energy transfer processes include: 1) the so-called "trivial" process of reabsorption by a ground-state molecule of light emitted by a fluorescent donor;[15] 2) the dipolar or quadrupolar interactions between excited donor and ground-state acceptor molecules known to account for singlet-singlet energy transfer over relatively long distances;[15] and 3) exchange interactions which are responsible for triplet-triplet energy transfer.[15,71]

The mechanism of this third process, collisional energy transfer, is thought to involve a resonance exchange interaction which requires spatial overlap of the orbitals of donor and acceptor.[15,71-77] Since energy transfer studies

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are widely used to determine reaction mechanisms and kinetics, knowledge of factors which influence the rate of energy transfer is essential.

The rate of exothermic triplet energy transfer in solution is influenced by the viscosity of the solvent.[71,74,78-80] It has often been assumed that exothermic triplet energy transfer is so efficient that every encounter in solution between excited donor and acceptor molecules results in energy transfer, so that the rate of energy transfer is limited by and equal to the rate of diffusion together of donor and acceptor. In moderately viscous alcohols, glycols, or paraffin oil - hexane mixtures, the quenching rate constant constant, k_q, is inversely proportional to viscosity, η, according to equation 1, a slightly modified Debye equation.[71,81]

$$k_q = k_{dif} = 8RT/2000\ \eta \qquad \text{(eq. 1)}$$

In less viscous solvents, the quenching rate constant still increases as the viscosity decreases but becomes lower than k_{dif}, the rate constant for diffusion, indicating that there is enough inefficiency in the energy transfer process that diffusion apart of donor and acceptor can compete with energy transfer during the lifetime of a solution encounter.[71] The theoretical implication of k_q being less than k_{dif} for exothermic triplet energy transfer in solvents of low viscosity may be that there is a preferred relative configuration of the donor and acceptor molecules.[71,82]

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In benzene at room temperature, the rate constant for quenching is (5 ± 1) x 10^9 M^{-1} sec^{-1} when the triplet excitation energy of the donor is ≥3-4 kcal/mol higher than that of the acceptor.[71,75,83,84,85] When reverse energy transfer from the excited acceptor back to the original donor is taken into account, it appears that this same rate of quenching holds even where the energy transfer process is only 1 kcal/mol exothermic.[71,76] This one rate constant which holds for exothermic energy transfer between dozens of donors and acceptors of different structures suggests that a common process is rate determining, that process being the rate which excited donor and acceptor molecules diffuse together.[71] The work of Wagner and Kochevar shows, however, that in the low viscosity solvents, the rate of energy transfer of the donor-acceptor pair competes with diffusion apart; further work is needed to determine why exothermic triplet energy transfer between so many different donors and acceptors occurs at such similar rates in benzene.[71]

7. Stern-Volmer Kinetics

The phenomenon of electronic energy transfer has been exploited in quenching and sensitization studies to determine which excited states of a given molecule are intermediates in photochemical reactions, to measure lifetimes of excited states, and to obtain rate constants for excited state reactions.[86] Quenching studies provide estimates of excited state lifetimes which together with quantum yields allow

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calculation of excited state rate constants.[86] The quantum yield is the only kinetic parameter associated with a photoreaction which is directly measureable under steady state conditions. It may be defined as follows.[86]

$$\Phi = \phi_{ES}\phi_{R}P \qquad \text{(eq. 2)}$$

Φ represents the quantum yield for a particular photoprocess, such as formation of a certain product or emission of light. ϕ_{ES} is the probability that absorption of light will produce the requisite excited state, ϕ_{R} is the probability that that excited state will undergo the necessary primary photoreaction, and P is the probability that any metastable intermediate will complete the desired process. If the photoprocess in question can arise from more than one excited state, the right hand side of equation 2 becomes a summation over all reactive states. The Stern-Volmer expression, equation 3, has been derived elsewhere.[86]

$$\Phi_o/\Phi = 1 + k_q\tau[Q] \qquad \text{(eq. 3)}$$

Φ_o is the quantum yield for a particular process in the absence of quencher, Φ is the quantum yield for the same process in the presence of some quencher, and [Q] is the concentration of the quencher. There is a linear relation between Φ_o/Φ and the quencher concentration, with slope $k_q\tau$, k_q being the bimolecular rate constant for quenching and

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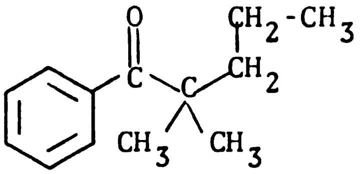
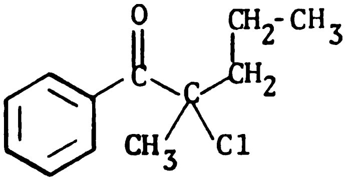
τ being the lifetime, in the absence of quencher, of the quenchable state. Stern-Volmer plots for each of several competing reactions have the same slope provided that all the products come from the same excited state and that the quencher does not react with any of the products or intermediates.[86]

8. Objectives

Studies of α,α-dimethylvalerophenone (DMVP) and α-chloro-α-methylvalerophenone (CMVP) were undertaken for several widely different reasons.



DMVP



CMVP

The primary reason for studying DMVP was to determine whether energy transfer in solution is subject to steric effects. Efficient triplet energy transfer requires close contact between donor and acceptor,[77] so it is reasonable to expect that bulky substituents appropriately located on the donor or acceptor should sterically hinder triplet energy transfer. Hammond and his co-workers have investigated many systems to demonstrate such steric hindrance. Acetoacetonate chelates are five-fold better as triplet quenchers than dipivaloylmethide chelates.[87,88] Quenching of *ortho*-substituted benzophenones probably reflects steric hindrance but is complicated by photoenolization.[77] Asymmetric induction is observed in the sensitized isomerization of 1,2-diphenylcyclopropane by an optically active substituted naphthalene compound[89] but apparently involves a chemical complex between singlet sensitizer and the 1,2-diphenylcyclopropane.[90] Several workers have performed Stern-Volmer quenching studies to determine the excited state lifetimes of *t*-alkyl ketones[12,40,43,91] in which they have assumed "diffusion-controlled" rate constants for energy transfer. This assumption of negligible steric effects on energy transfer warrants investigation in view of the steric effects which have been found for certain other excited state processes.[77,87,89,91]

In order to use DMVP as a monitor for energy transfer studies, its photochemistry had to be first understood. The observed photochemistry of DMVP suggested study of CMVP, with the inductive effect of the α-chlorine on the triplet state reactivity being of particular interest. Introduction of an α-chloro substituent also allows investigation of reactions involving cleavage of the carbon-chlorine bond. The effect of α-substituents on excited state carbonyl reactivity is relatively unknown.

Included in this study is an investigation of the steric and inductive effects of α-substituents on the rate of γ-hydrogen abstraction. Also studied is the competition between type I cleavage and the type II processes of DMVP and with CMVP, the competitive reactions, photocleavage of the carbon-chlorine bond and type II photocyclization.

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RESULTS

1. α,α-Dimethylvalerophenone

a. Quantum yields of photoproducts

Photolysis of α,α-dimethylvalerophenone, DMVP, in solution with either 313 nm or 366 nm light results in the production of type I cleavage products, 2-methylpentane (IH), 2-methyl-1-pentene (MP-1), 2-methyl-2-pentene (MP-2), and benzaldehyde (BA); type II cleavage products, propene and isobutyrophenone (IBP); and type II cyclization products, *trans*-1-phenyl-2,2,4-trimethylcyclobutanol (t-CB) and *cis*-1-phenyl-2,2,4-trimethylcyclobutanol (c-CB), the stereochemistry of the latter two photoproducts being established by Lewis and Hilliard,[92,93] in their independent investigation of DMVP. There are also a few unidentified photoproducts which vary with solvent and additives and are usually formed in low yield; these products presumably are an assortment of radical addition and coupling products. Table 1 lists the quantum yields for the various photoproducts of DMVP as obtained with a variety of solvents and additives. It was noticed during the vpc analyses that the areas of the IBP and, to a lesser extent, the BA photoproduct peaks diminish slowly by some thermal processes, likely condensation reactions. Where there is a

Table 1.

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Benzene, 1*M* t-C_4H
Benzene, 3*M* t-C_4H
Benzene, 5*M* t-C_4H
n-Hexane
Cyclooct
Cyclooct 0.1*M* RSH
Cyclooct 0.5*M* RSH
t-Butyl
1-Propan
1-Pentan
1-Heptan
Acetonitr 1% H_2O
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[a] MP-1 and

[b] 0.250*M* DM
0.100*M* DM

[c] Too low b

[d] 1-Dodecane

[e] 0.0500*M* DM

Table 1. Quantum Yields for DMVP Photoproducts

Solvent, Additive	Propene	IH	MP[a]	BA	IBP	t-CB	c-CB
Benzene				0.028[b]	0.028[b,c]	0.053[b]	0.040[b]
Benzene	0.032	0.020	0.026	0.029	0.050	0.051	0.037
Benzene, 0.1*M* RSH[d]	0.000	0.053	0.000	0.053	0.020[c]	0.053	
Benzene, 0.5*M* RSH	0.000	0.054	0.000	0.069	0.036[c]	0.111	
Benzene, 1*M* *t*-C_4H_9OH					0.066	0.063	
Benzene, 3*M* *t*-C_4H_9OH					0.049	0.068	
Benzene, 5*M* *t*-C_4H_9OH					0.064	0.093	
n-Hexane				0.025	0.040	0.047	0.035
Cyclooctane	0.042	0.034	0.021	0.029	0.059	0.056	0.033
Cyclooctane, 0.1*M* RSH	0.000	0.044	0.000				
Cyclooctane, 0.5*M* RSH	0.000	0.045	0.000				
t-Butyl Alcohol				0.015	0.138	0.115	
1-Propanol					0.177	0.123	0.144
1-Pentanol					0.131[e]	0.104	0.118
1-Heptanol						0.122	
Acetonitrile, 1% H_2O				0.012	0.135	0.155	
Acetonitrile, 2% H_2O				0.017	0.169	0.163	
Acetonitrile, 2% H_2O				0.013	0.174	0.161	
Acetonitrile, 5% H_2O				0.014	0.098	0.149	

[a] MP-1 and MP-2

[b] 0.250*M* DMVP. Other photolyses in this table done with 0.100*M* DMVP except as noted

[c] Too low because of thermal reaction prior to analysis

[d] 1-Dodecanethiol

[e] 0.0500*M* DMVP

choice of data from more than one photokinetic run, the higher values for the BA and IBP quantum yields are considered the more reliable and so are reported in Table 1; for the other photoproducts, averages are reported.

The disappearance quantum yield for photolysis of 0.100*M* DMVP in benzene is 0.225. This is somewhat larger than the 0.17 value obtained by adding the quantum yields for BA, IBP, t-CB, and c-CB, indicating that the unidentified products are formed with about 5% total quantum efficiency in benzene. Added *t*-butyl alcohol enhances the quantum yields for the type II cleavage and cyclization products; however, the effect is gradual and the expected leveling off of quantum yields with increasing amounts of alcohol[30,34] is not observed even with neat *t*-butyl alcohol. Other alcohols also enhance the type II quantum yields and, as seen for the photocyclization products, 1-dodecanethiol has the same effect. Wet acetonitrile increases the quantum yields for the type II processes with the optimum amount of water being 2-3% by weight. The total quantum yields for the identified products are 0.46 in 1-propanol and ∿0.52 in acetonitrile with 2% H_2O.

The absence of quenching impurities is shown by the expected[94] slight increase in quantum yields when DMVP concentration is raised from 0.100*M* to 0.250*M*; this increase is due to the increased polarity of the solution with increased ketone concentration.[94] The *cis*/*trans* ratio of the cyclobutanol products varies from 0.7 in hydrocarbon solvents to 1.2 in alcohols. In either polar or non-polar solvents, the cyclizat

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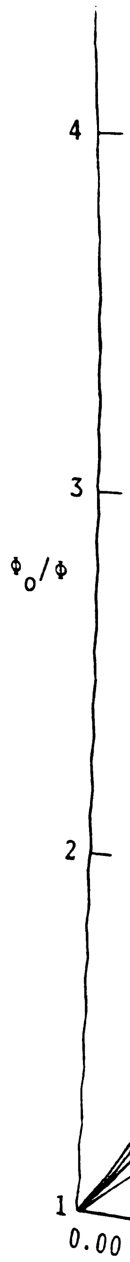
cyclization to elimination ratio is nearly 2 to 1. The ratio of MP-1 to MP-2 is about 5 as estimated from the vpc traces of the overlapping peaks.

b. Radical trapping experiments

1-Dodecanethiol was employed at concentrations which would not directly quench the triplet[95] to trap the free radicals produced from type I cleavage. The virtually identical quantum yields of 2-methylpentane with both 0.100*M* and 0.500*M* thiol together with complete quenching of the 2-methylpentenes indicates trapping of all radicals escaping the initial solvent cage. Propene formation is also totally quenched with these concentrations of thiol, however, so thiol radicals probably add quite efficiently to these olefins.

c. Quenching of DMVP photoreactions

Quenching of the triplet excited state of DMVP (E_T = 72 kcal mol^{-1})[39] was conducted with several different conjugated dienes (E_T = 58-60 kcal mol^{-1})[96] and 2-chloronaphthalene (E_T = 60 kcal mol^{-1}).[97] All of the products are quenchable; however, because of the gradual diminishing of the BA and IBP peak areas, Stern-Volmer plots of Φ_0/Φ *versus* quencher concentrations were made using the data from the cyclobutanol products, except as otherwise noted. Figure 5 contains Stern-Volmer plots for quenching production of cyclobutanols from excited DMVP in benzene.



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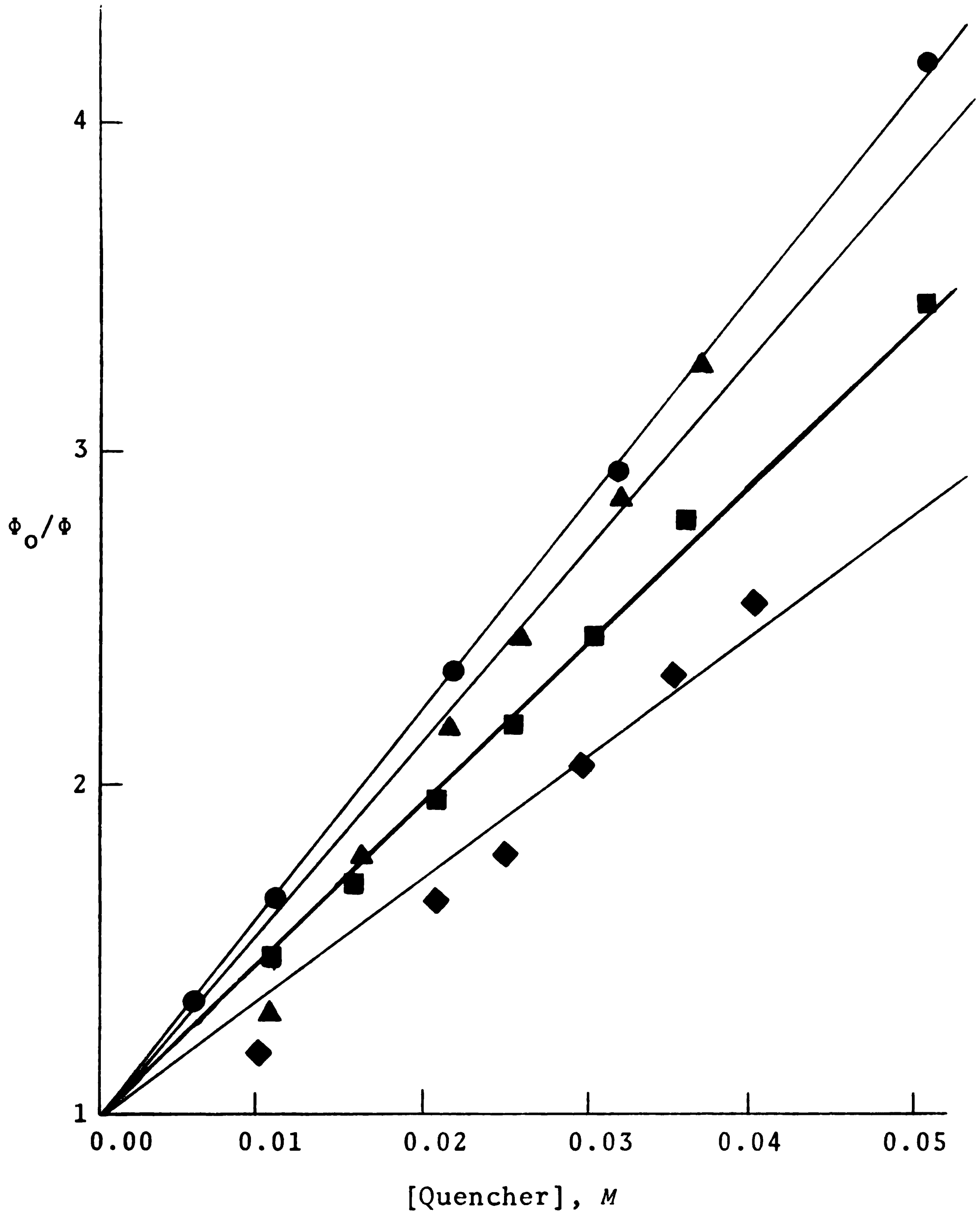

Figure 5. Quenching of excited DMVP in benzene by 2-chloronaphthalene (●), *cis*-piperylene (▲), 2,5-dimethyl-2,4-hexadiene (■), and 2,3-dimethyl-1,3-butadiene (◆).

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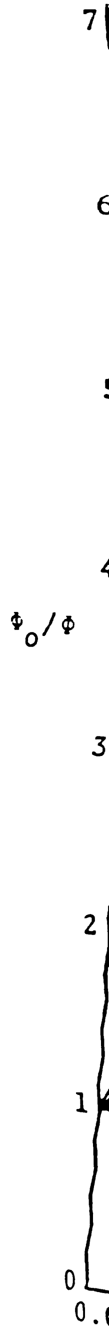
For 2,3-dimethyl-1,3-butadiene and *cis*-piperylene (*cis*-1,3-pentadiene) low Φ_o/Φ values are observed with low quencher concentrations, presumably because there is significant destruction of quencher by its reaction with radicals when type I cleavage is only slightly quenched. 2,5-Dimethyl-2,4-hexadiene and 2-chloronaphthalene do not exhibit similar behavior; they are known to be poor radical traps.[98]

Figure 6 graphically illustrates quenching studies which used hydrocarbon solvents other than benzene. For undetermined reasons, there is considerable scatter in the data for quenching by 2-chloronaphthalene in *n*-hexane. Figure 7 exhibits the effect of primary alcohol solvents on the quenching of excited DMVP by 2,5-dimethyl-2,4-hexadiene.

As discussed in the introduction, the slope of a Stern-Volmer plot, the quenching constant, is $k_q\tau$. Table 2 contains the values of $k_q\tau$ obtained graphically from the preceding quenching plots for DMVP with a variety of quenchers, solvents, and additives.

d. Effect of solvent viscosity on quenching constants

It is of interest to compare $k_q\tau$ values measured in similar solvents of differing viscosities since τ, which is determined solely by rates of intramolecular reactions, should be independent of solvent viscosity and k_q would decrease with increasing solvent viscosity if energy transfer is "diffusion-controlled".[71] Table 3 compares $k_q\tau$'s obtained using 2,5-dimethyl-2,4-hexadiene and 2-chloronaphthalene to quench



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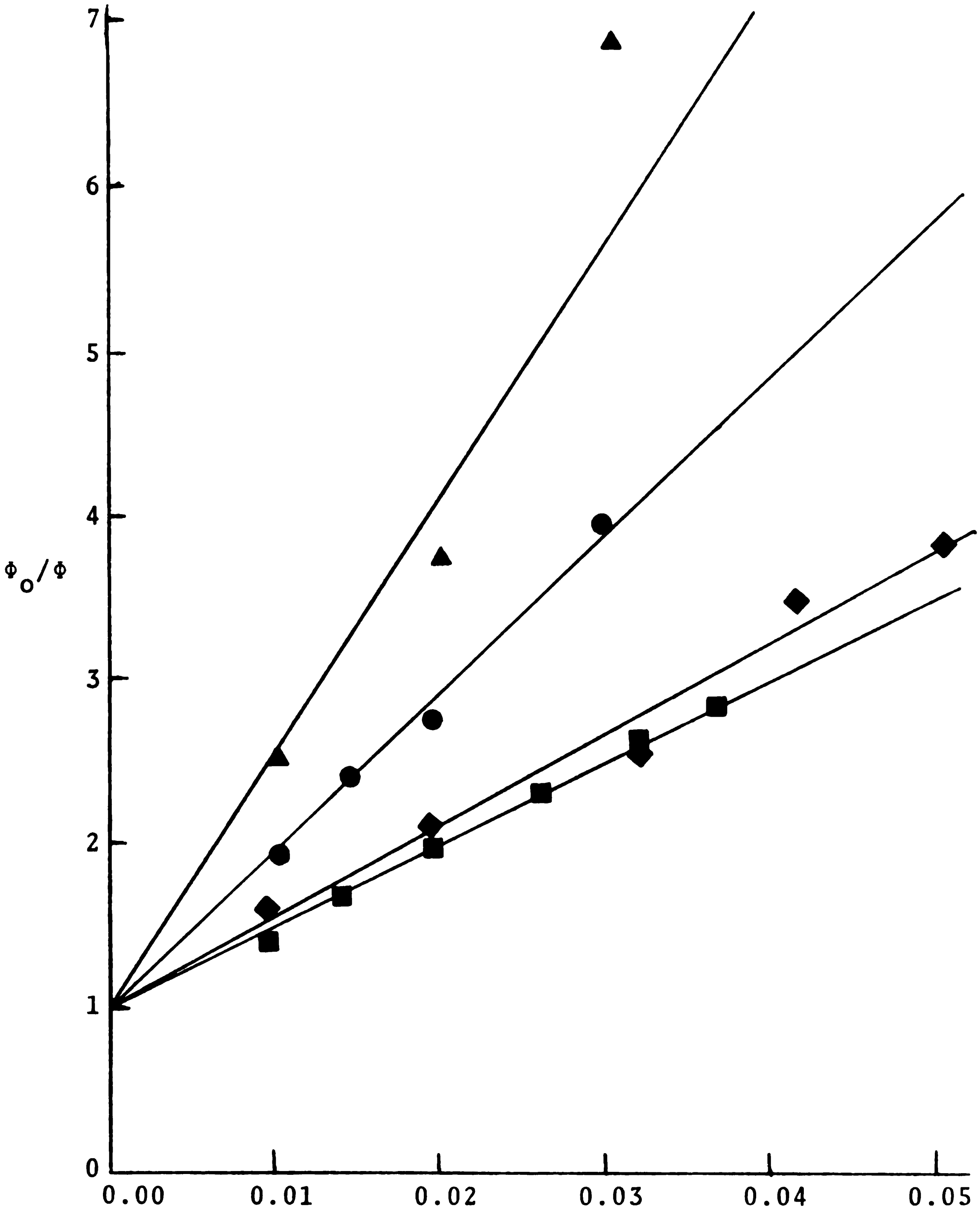

Figure 6. Quenching of excited DMVP by 2,5-dimethyl-2,4-hexadiene in *n*-hexane (●), 2-chloronaphthalene in *n*-hexane (▲), 2,5-dimethyl-2,4-hexadiene in cyclooctane (■),[a] and 2-chloronaphthalene in cyclooctane (◆).

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[a] Average of values for both IBP and t-CB used.

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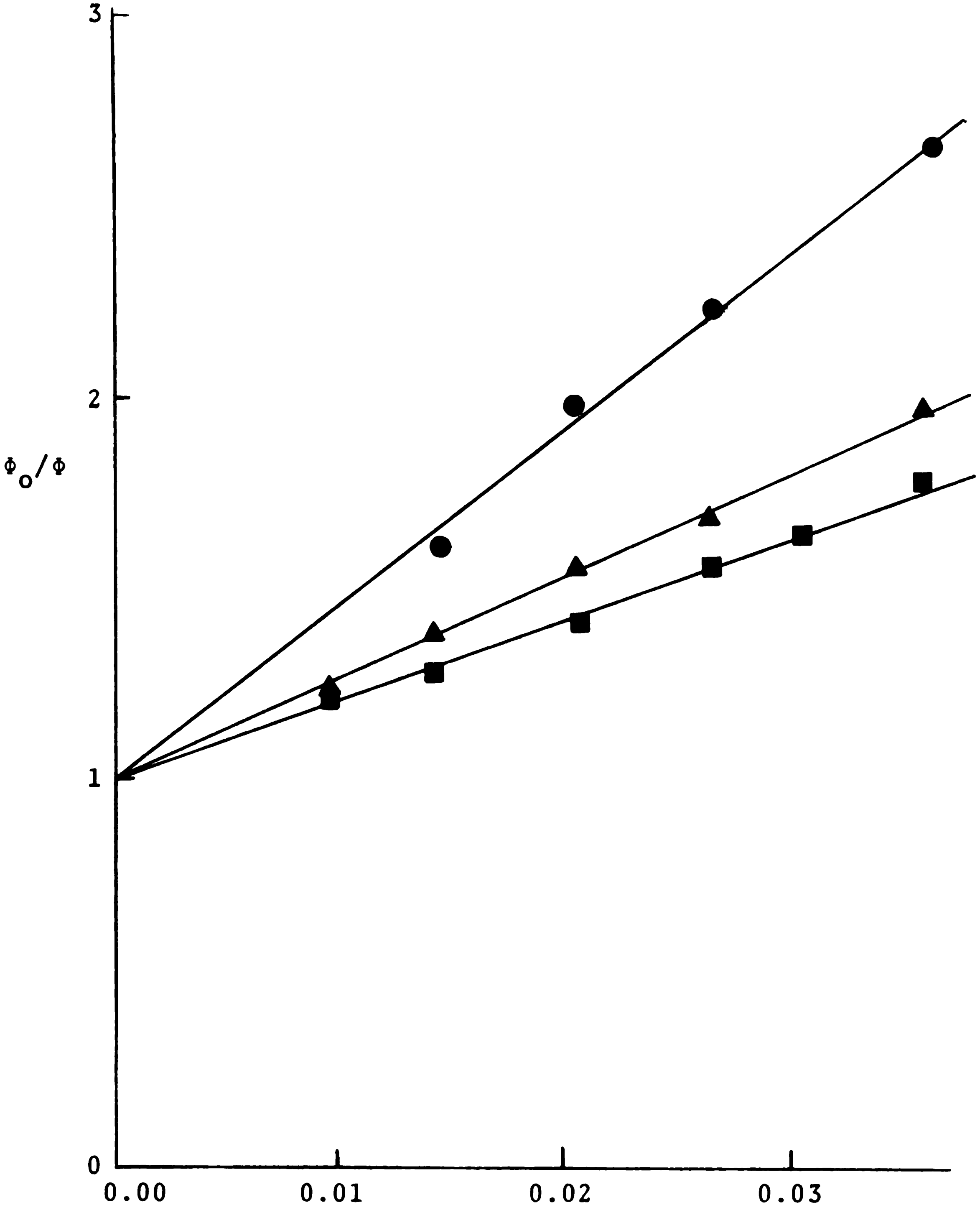

Figure 7. Quenching of excited DMVP by 2,5-dimethyl-2,4-hexadiene in 1-propanol (●), 1-pentanol (▲), and 1-heptanol (■).

Tab

Sol

Ben

Ben

Ben

Ben

n-He

n-He

Cycl

Cycl

1-Pr

1-Pe

1-He

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[a] Sta

Table 2. Quenching Constants Obtained from Quenching Photocyclization of DMVP in Various Solvents

Solvent	Quencher	$k_q\tau$, M^{-1} [a]
Benzene	*cis*-Piperylene	59 ± 2
Benzene	2,5-Dimethyl-2,4-hexadiene	49 ± 1
Benzene	2,3-Dimethyl-1,3-butadiene	38 ± 1
Benzene	2-Chloronaphthalene	64 ± 1
n-Hexane	2,5-Dimethyl-2,4-hexadiene	97 ± 1
n-Hexane	2-Chloronaphthalene	150 ± 9
Cyclooctane	2,5-Dimethyl-2,4-hexadiene	51 ± 1
Cyclooctane	2-Chloronaphthalene	56 ± 2
1-Propanol	2,5-Dimethyl-2,4-hexadiene	46 ± 1
1-Pentanol	2,5-Dimethyl-2,4-hexadiene	28 ± 1
1-Heptanol	2,5-Dimethyl-2,4-hexadiene	22 ± 1

---

[a] Standard deviations indicated.

Table 3.

Solvent (
n-Hexane
Benzene
Cycloocta
1-Propano
1-Pentano
1-Heptano

---

[a] Ref. 71

[b] 0.100*M* DM

[c] 0.100*M* DM

[d] 0.100*M* Va
Quencher,

Table 3. Quenching Constants for DMVP and Valerophenone in Similar Solvents of Varying Viscosity

Solvent (η, cP)[a]	DMVP-ArCl[b]	DMVP-diene[c]	VP-diene[d]
n-Hexane (0.33)	150 ± 9	97 ± 1	79
Benzene (0.63)	64 ± 1	49 ± 1	36
Cyclooctane (2.2)	56 ± 2	51 ± 1	31
1-Propanol (1.9)		46 ± 1	52
1-Pentanol (3.1)		28 ± 1	36
1-Heptanol (5.5)		22 ± 1	23

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[a] Ref. 71

[b] 0.100*M* DMVP with 2-Chloronaphthalene Quencher

[c] 0.100*M* DMVP with 2,5-Dimethyl-2,4-hexadiene Quencher

[d] 0.100*M* Valerophenone with 2,5-Dimethyl-2,4-hexadiene Quencher, Ref. 71

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excited DMVP in hydrocarbons and primary alcohols with $k_q\tau$'s obtained using 2,5-dimethyl-2,4-hexadiene to quench excited valerophenone in the same solvents. As solvent viscosity increases, $k_q\tau$ values do in fact decrease. Figure 8 compares the $k_q\tau$'s obtained from quenching excited DMVP against those obtained from quenching valerophenone with each point corresponding to measurements in a particular solvent. For a given quencher of DMVP and in similar solvents, the respective $k_q\tau$'s for DMVP and valerophenone-diene are close to being directly proportional. The consequences of "hindered" DMVP being quenched in parallel fashion to "unhindered" valerophenone in solvents of differing viscosities will be discussed later.

2. α-Chloro-α-methylvalerophenone

a. Photo and thermal products

Photolyses of α-chloro-α-methylvalerophenone, CMVP, are complicated by a large number of products, many of which are produced thermally. Some of the photo and thermal products are solvent dependent, some occur only in the presence of a certain quencher, and some are observed only when quencher is absent. In benzene with no quencher, at least 16 photo and thermal products are present with retention times shorter than that of CMVP and 5 products are observed with longer retention times. In acetonitrile, fewer products result. The large extent of thermal reactions in the photolysis solutions was unexpected since <0.2% of the neat CMVP thermally

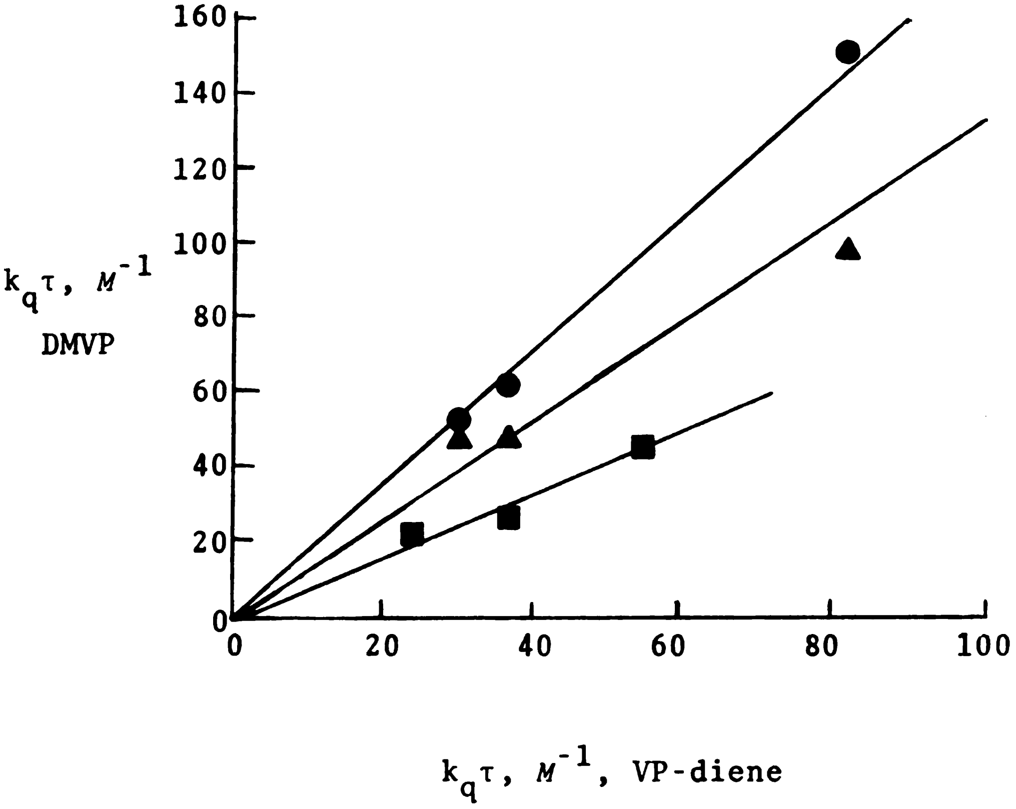

Figure 8. Quenching constants for DMVP *versus* quenching constants for VP-diene system in same solvent: DMVP-ArCl, hydrocarbon solvents (●); DMVP-diene, hydrocarbon solvents (▲); DMVP-diene, alcohol solvents (■).

decomposed during a 6 month period at ∿0°. The thermal reactions occurred appreciably even in the refrigerated photolysis sample solutions, so it was necessary to run blanks and substract the thermal product relative vpc peak areas from the relative vpc peak areas of the photoproducts with similar, though often not identical retention times.

The major and some minor photo and thermal products present at high conversion in both benzene and acetonitrile have been determined by mass spectral analyses and, where preparative scale vpc separations were successful, verified by nmr analyses. In order of increasing vpc retention times on analytical vpc columns using QF-1 and Carbowax 20M liquid phases, these products are: propiophenone, PP; 1-phenyl-2-propylprop-2-en-1-one, PPP; 1-phenyl-2-methylpent-3-en-1-one, β,γ-U; α-methylvalerophenone, MVP; 1-phenyl-2-methylpent-2-en-1-one, α,β-U; α-hydroxy-α-methylvalerophenone, HMVP; 1-phenyl-1,2-dihydroxy-2-methylpentane or an isomer of it, PDHMP; and 2 rearranged ketones which are isomers of CMVP. These rearranged ketones probably are γ-chloro-α-methylvalerophenone, γ-CMVP, and β-chloro-α-methylvalerophenone, β-CMVP. At high conversion in both benzene and acetonitrile solvents, β,γ-U is the major product. β,γ-U is especially dominant in benzene, suggesting a possible synthetic route to certain β,γ-unsaturated ketones from α-chloroketones. Smaller but significant amounts of PP, α,β-U, and β-CMVP are also observed, with the remaining products accounting for only a small portion of the product mixture at high conversion.

Most of the many photo and thermal products seen at low conversion disappear into the vpc baseline at high conversion. Unfortunately it was not possible to obtain spectral data on a certain product having a retention time just slightly less than that of CMVP since it is present to only a small extent at low conversion and it gets completely quenched at high conversion. This product is assumed to be a stereoisomer of 2-chloro-1-phenyl-2,4-dimethylcyclobutanol, CCB, based not only upon its vpc retention time, but also that it is formed in the three solvent systems studied and that it is produced only from a quenchable excited state. The correction for thermal reaction applied to the CCB vpc peak area is due to a thermal product having a slightly shorter retention time.

Table 4 lists the quantum yields for the CMVP photoproducts. At very low conversion, the rearranged ketones, γ-CMVP and β-CMVP, are not formed to any appreciable extent in benzene or acetonitrile; these products probably result from addition of HCl to the unsaturated ketones, β,γ-U and α,β-U, and therefore would show up more at the higher conversions where the HCl concentrations and concentrations of unsaturated ketones would be greater. Pyridine apparently enhances the yields of these rearranged chloroketones at the expense of β,γ-U and α,β-U. The HMVP product is formed thermally to a great extent, and photochemically to a small extent. In samples containing *cis*-piperylene, HMVP is still formed thermally, but its photochemical formation is almost completely quenched.

Table 4. Quantum Yields for CMVP Photoproducts[a]

Solvent, Additive	PPP	β,γ-U	α,β-U	CCB	HMVP	β-CMVP
Benzene	0.000	0.133	0.141	0.018	0.046	∿0.00
Benzene, 0.50*M* Pyridine		0.100	0.083	0.034	0.011	0.032
Acetonitrile[b]	0.029	0.040	0.342	0.014	0.006	∿0.00
Acetonitrile[b], 0.2*M* *t*-BuSH	0.011	0.071	0.253	0.013	0.007	∿0.00
Acetonitrile[b], 0.5*M* *t*-BuSH		0.113	0.168	0.012	0.013	∿0.00
MEK -- 0.0100*M* CMVP[c]	0.012	0.030	0.064	0.012	0.015	0.008 0.008[d]
MEK -- 0.0200*M* CMVP[c]	0.013	0.050	0.095	0.014	0.032	0.016

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[a] CMVP concentration is 0.100*M* in all solvents except methyl ethyl ketone, which was used to study photosensitization of CMVP.

[b] The acetonitrile contains ∿1% water (weight basis).

[c] Methyl ethyl ketone is used as both solvent and sensitizer with the specified concentrations of CMVP.

[d] γ-CMVP

b. Products from type II photoprocesses

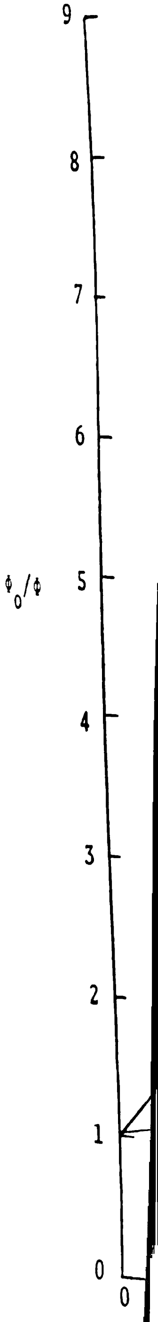
Among other reasons, CMVP was studied to investigate the competition between the type II processes and the relatively poorly understood reactions involving loss of an electronegative α-substituent. No propene, which would be a type II elimination product, was observed; this could be the result of HCl addition to the olefin, however. The other type II elimination product, α-chloropropiophenone, was also not observed; though, since its retention time would put it under the unsaturated ketone peaks in the vpc traces, the inability to find it does not rule out the possibility of it being a minor product. The unexpected presence of propiophenone as a product apparently would require the intermediacy of either α-chloropropiophenone or MVP (α-methylvalerophenone). The presence of a small amount of MVP was verified by mass spectral analysis of a high conversion sample; unfortunately this product occurs under the β,γ-U peak when using the analytical vpc columns, but it does appear to be a minor product. It seems that the type II photoprocesses of CMVP just barely compete with those photoreactions primarily involving loss of HCl since not very much more than the CCB product is likely to be a result of type II elimination or cyclization reactions.

c. Radical trapping experiments

The effects of *t*-butylmercaptan on CMVP photolyses in acetonitrile are reported in Table 4. The PPP and α,β-U photoproducts are diminished by increasing amounts of the thiol while the size of the β,γ-U peak increases, possibly because of some MVP beneath it. The CCB quantum yields remain essentially constant though those of HMVP appear to increase with added thiol. Only 10-20% of the HMVP is photochemically produced in acetonitrile with or without the thiol. It is possible that the fraction of HMVP, in any of the solvents, which appears to be photolytic in origin is actually due to the thermal reaction being accelerated by a photoproduct.

d. Quenching of CMVP photoreactions

Figures 9, 10, and 11 contain Stern-Volmer plots for quenching various photoproducts of CMVP in 3 different solvent systems. Figure 12 is a plot of Φ^{-1} *versus* quencher concentration for quenching formation of CCB in benzene; this kind of plot is used here because Φ_o is so high that a Stern-Volmer plot would not intercept at 1. Dividing the slope of such a plot by the intercept gives $k_q\tau$. Table 5 lists the $k_q\tau$ values obtained from the plots in Figures 9-12. In benzene and benzene with 0.50*M* pyridine β,γ-U is quenched >5 times faster than α,β-U; but in acetonitrile, β,γ-U formation is actually enhanced by the diene quencher while α,β-U is quenched 20-30% faster than in the benzene systems. Formation of CCB is quenched at approximately the same efficiency in the three solvent systems. Attempts to measure ϕ_{isc} by sensitizing the photoisomerization of *cis*-piperylene were unsuccessful since the low $k_q\tau$ for quenching excited CMVP requires such large quantities of quencher for any significant quenching that the amount of *trans*-piperylene formed by the sensitized isomerization is only slightly larger than the 0.19% initially present as an impurity.



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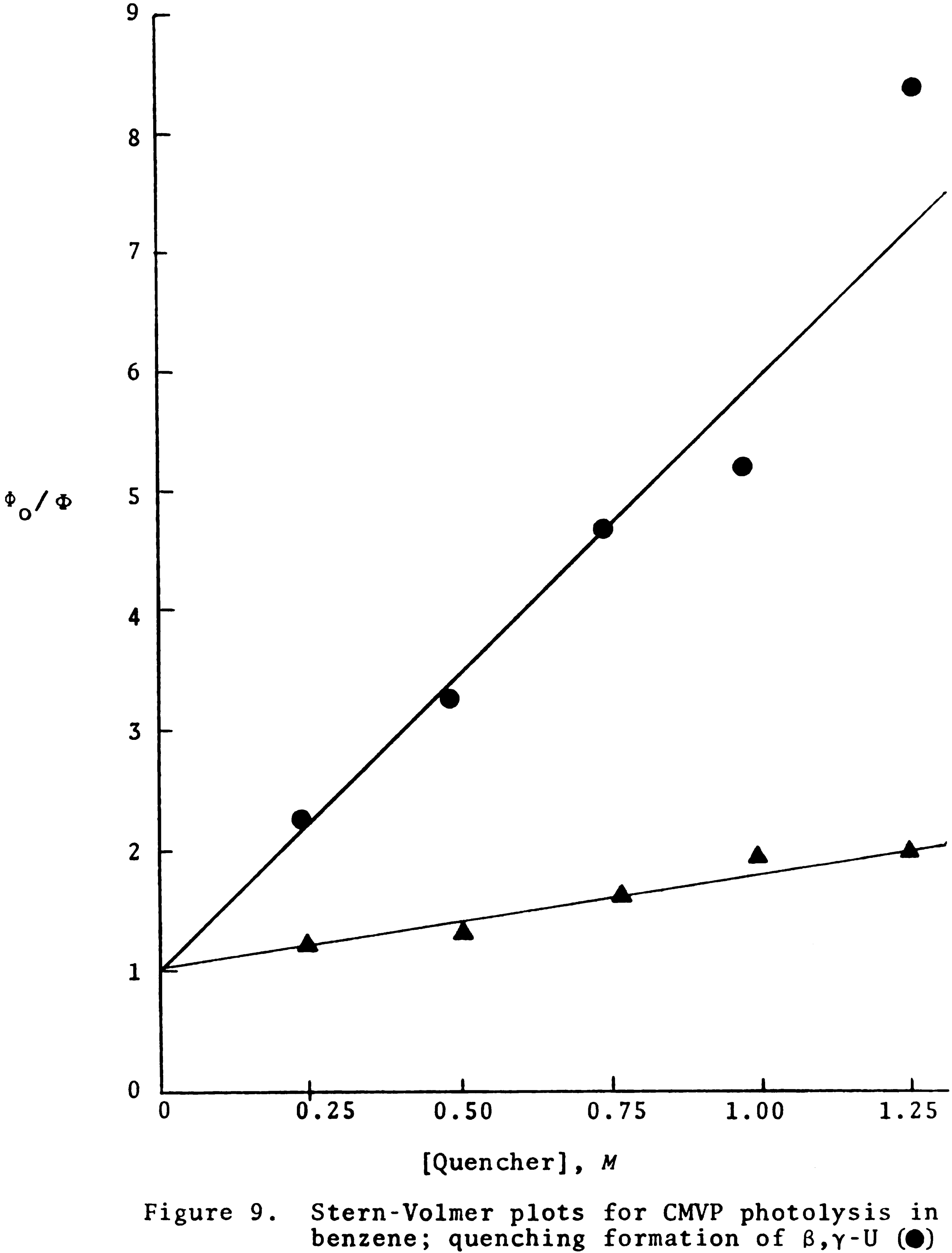

Figure 9. Stern-Volmer plots for CMVP photolysis in benzene; quenching formation of β,γ-U (●) and α,β-U (▲) with *cis*-piperylene.

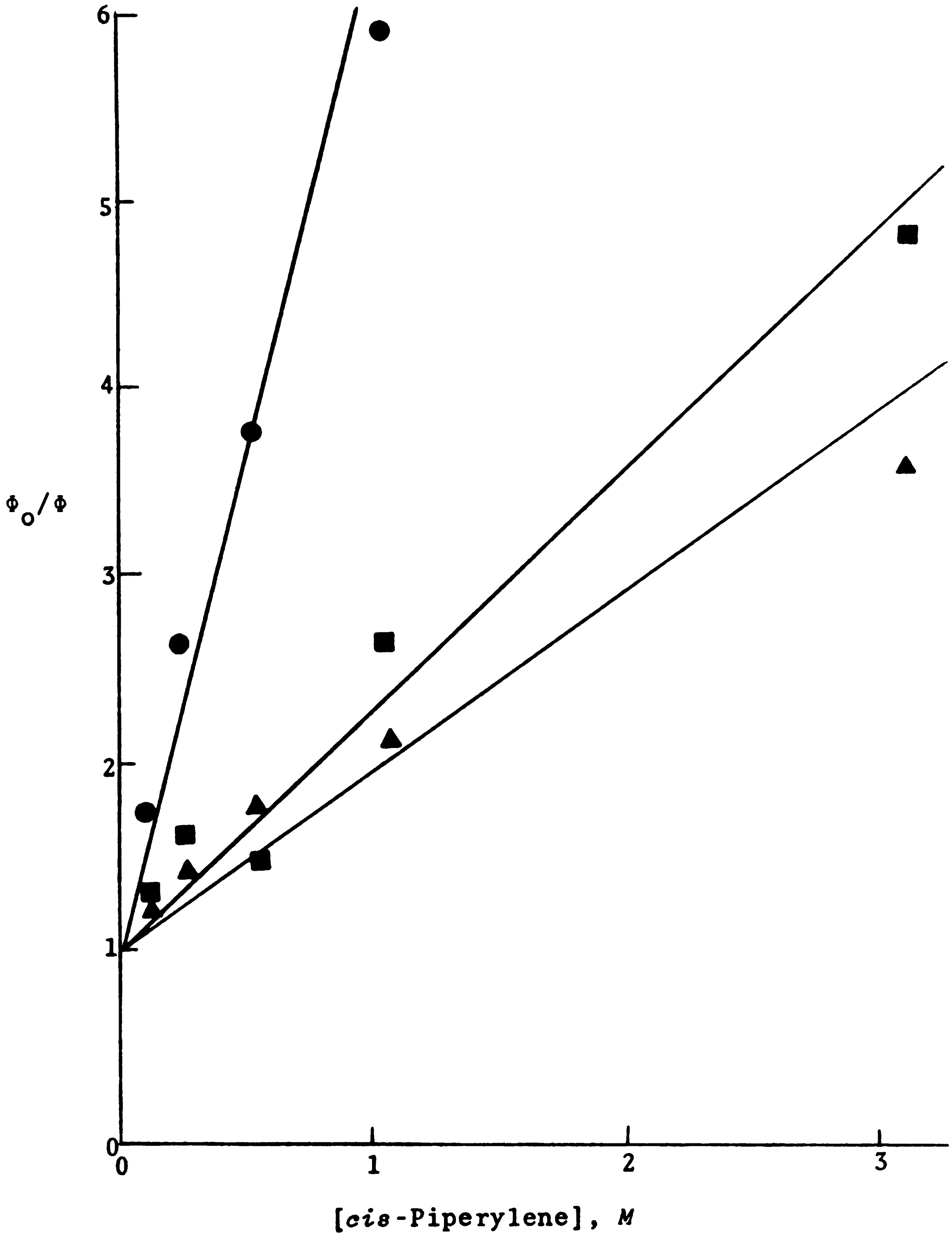

Figure 10. Stern-Volmer plots for CMVP photolysis in benzene with 0.50*M* pyridine; quenching formation of β,γ-U (●), α,β-U (▲), and CCB (■).

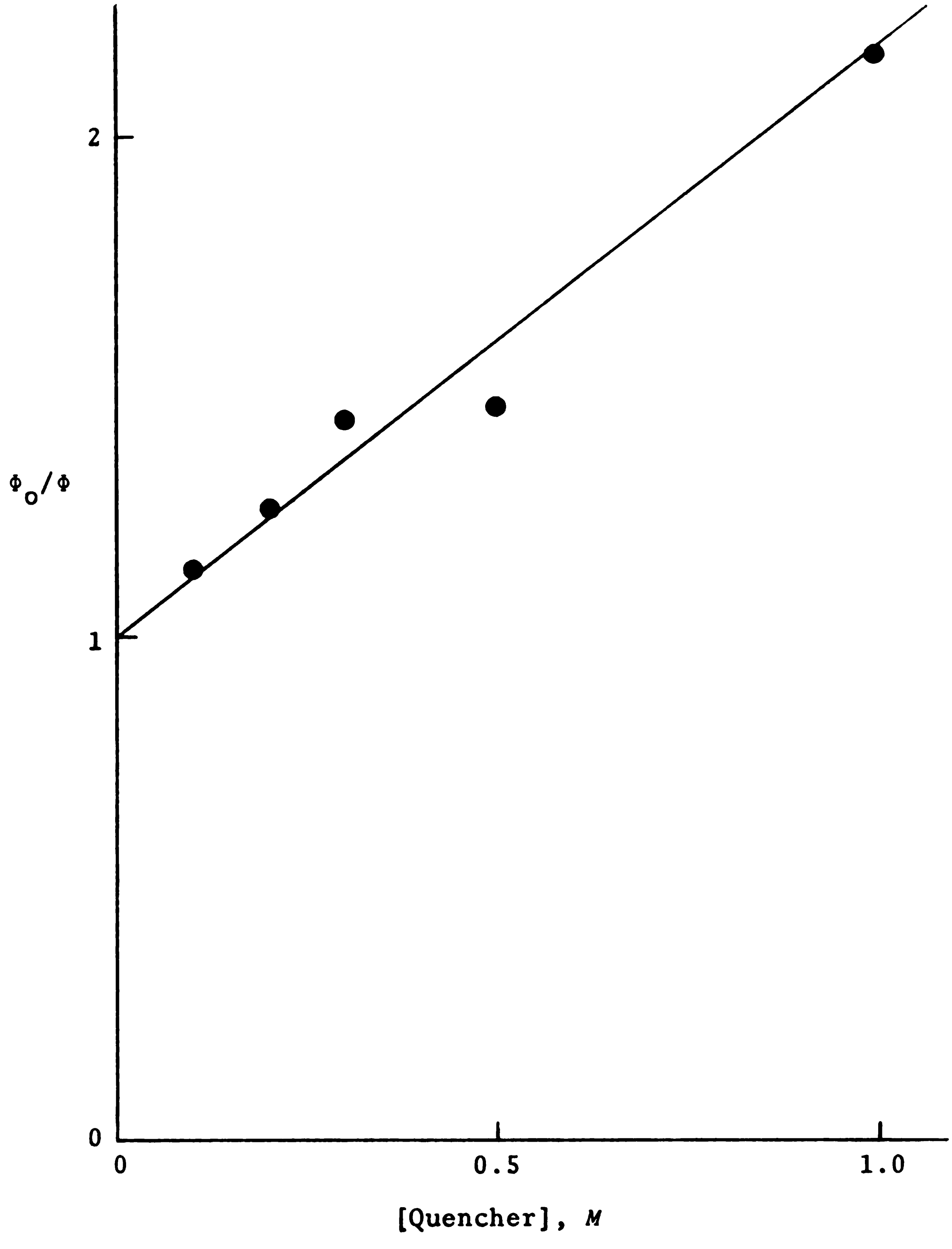

Figure 11. Quenching formation of α,β-U from CMVP by 2,5-dimethyl-2,4-hexadiene in acetonitrile.

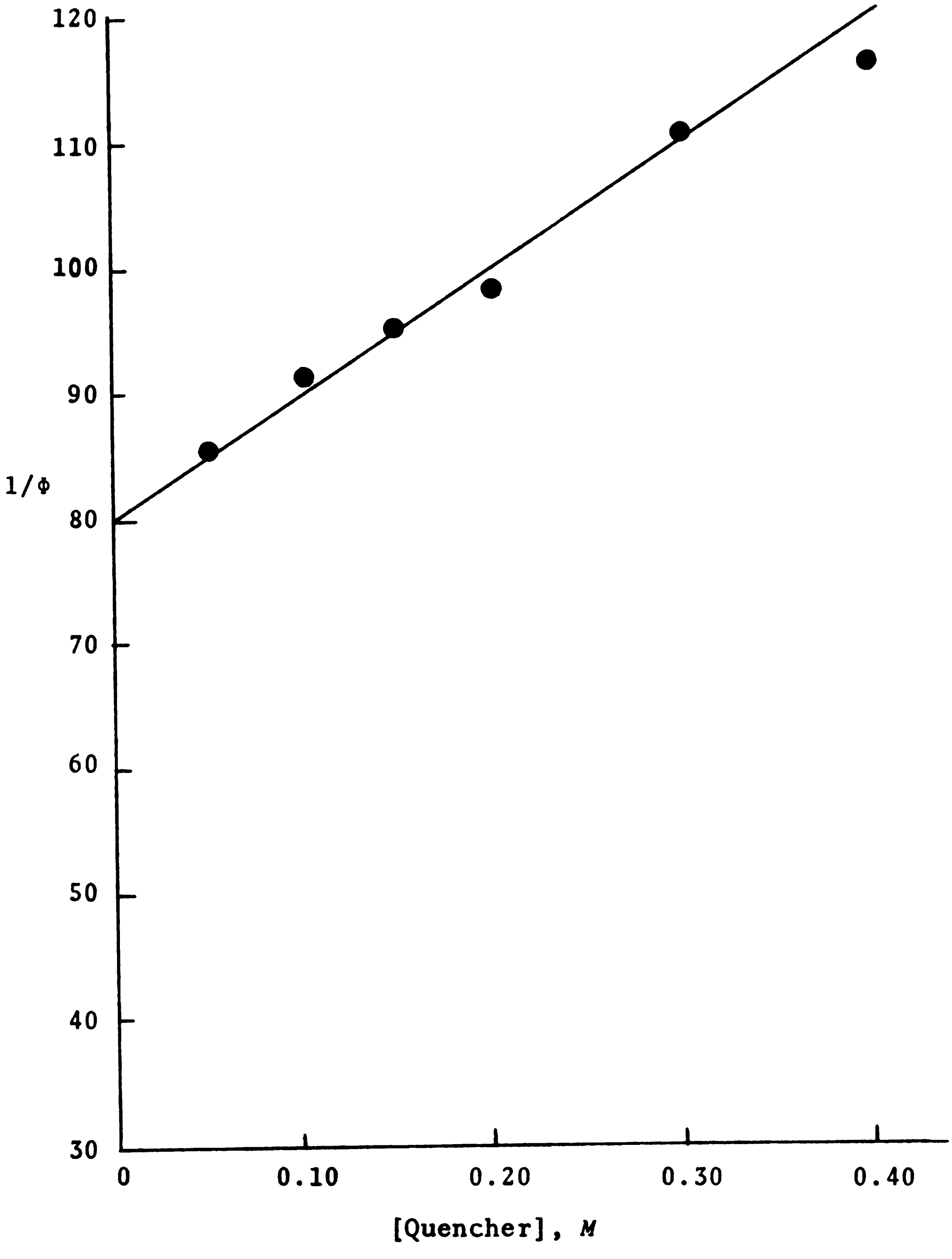

Figure 12. Plot of reciprocal quantum yield *versus* [Quencher] for quenching of formation of CCB in benzene by 2,5-dimethyl-2,4-hexadiene.

Table 5. Stern-Volmer Quenching Constants from Photolyses of 0.100*M* CMVP, M^{-1}

Solvent	Product Quenched: β,γ-U	α,β-U	CCB
Benzene	5.1[a]	0.9[a]	1.3[b,c]
Benzene, 0.50*M* Pyridine	5.4[a]	1.0[a]	1.3[a]
Acetonitrile, ∿1% H_2O	d	1.2[b]	∿1.2[b,e]

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[a] *cis*-Piperylene quencher

[b] 2,5-Dimethyl-2,4-hexadiene quencher

[c] Photolysis carried out to relatively high conversion

[d] Not quenched

[e] Vpc peaks are too small to accurately integrate, however; CCB is quenched to approximately the same extent as α,β-U in acetonitrile.

DISCUSSION

1. Photoreactivity of α,α-Dimethylvalerophenone

a. Competitive type I and type II processes

As determined by the thiol trapping experiments, free radical products from type I photocleavage of DMVP account for 5-7% of the triplet excited state reactivity. Since a significant portion of the radicals produced would recombine in the solvent cage,[99] ∿10-15% of triplet DMVP undergoes α-cleavage. The quantum yields for the type II processes are ∿45% in 1-propanol and ∿52% in wet acetonitrile; the usual leveling off of quantum yields at a near maximum value in polar solvents[41] was not observed for DMVP, perhaps indicating a steric effect on solvation of the biradical.

The ratio of excited state rate constants for α-cleavage and γ-hydrogen abstraction can be calculated using the data for DMVP and that found by Lewis and Hilliard for α,α-dimethylbutyrophenone, DMBP.[92,93] The α-dimethyl substituion of either valerophenone or butyrophenone can be viewed as introducing two unknowns into the triplet state lifetime: an inductive and/or steric effect on the rate constant for γ-hydrogen abstraction, k_γ; and competitive α-cleavage with rate constant k_α.[100]

$$\frac{1}{\tau} = k_\alpha + k_\gamma = k_\alpha \quad fk_\gamma^0 \qquad \text{(eq. 4)}$$

In equation 4 k_γ^0 is the known triplet state rate constant for γ-hydrogen abstraction by the corresponding unsubstituted ketones, valerophenone ($k_\gamma^0 = 1.4 \times 10^8$ sec^{-1})[41] and butyrophenone ($k_\gamma^0 = 7.5 \times 10^6$ sec^{-1}),[41] as determined by diene quenching experiments in benzene. The unknown rate factor on γ-hydrogen abstraction introduced by the α-methyls is f. Stern-Volmer studies in benzene yield $k_q\tau$ values of $49M^{-1}$ for DMVP and $260M^{-1}$ for DMBP[92] indicating $\frac{1}{\tau}$ values of 1.0×10^8 sec^{-1} and 1.9×10^7 sec^{-1} respectively for these two ketone triplets, assuming $k_q = 5 \times 10^9\ M^{-1}$ sec^{-1} in benzene.[71] Entering these values into equation 4 and solving the pair of simultaneous equations gives f = 0.61 and $k_\alpha = 1.4 \times 10^7$ sec^{-1}.

The fraction of type I cleavage, $k_\alpha/(k_\alpha + k_\gamma)$, is 0.14 for DMVP and 0.74 for DMBP. This agrees well with Lewis' estimate of five times the type I product yields from DMBP as from DMVP.[101] The low type II quantum yields for DMVP are only partially due to competing triplet state α-cleavage; dimethyl substitution of the α-position has lowered k_γ only slightly.

The percentage of α-cleavage of triplet DMVP suggests ∿50% cage recombination of the radicals formed. The competition between the type I and type II photoprocesses of DMVP is presented in Figure 13.

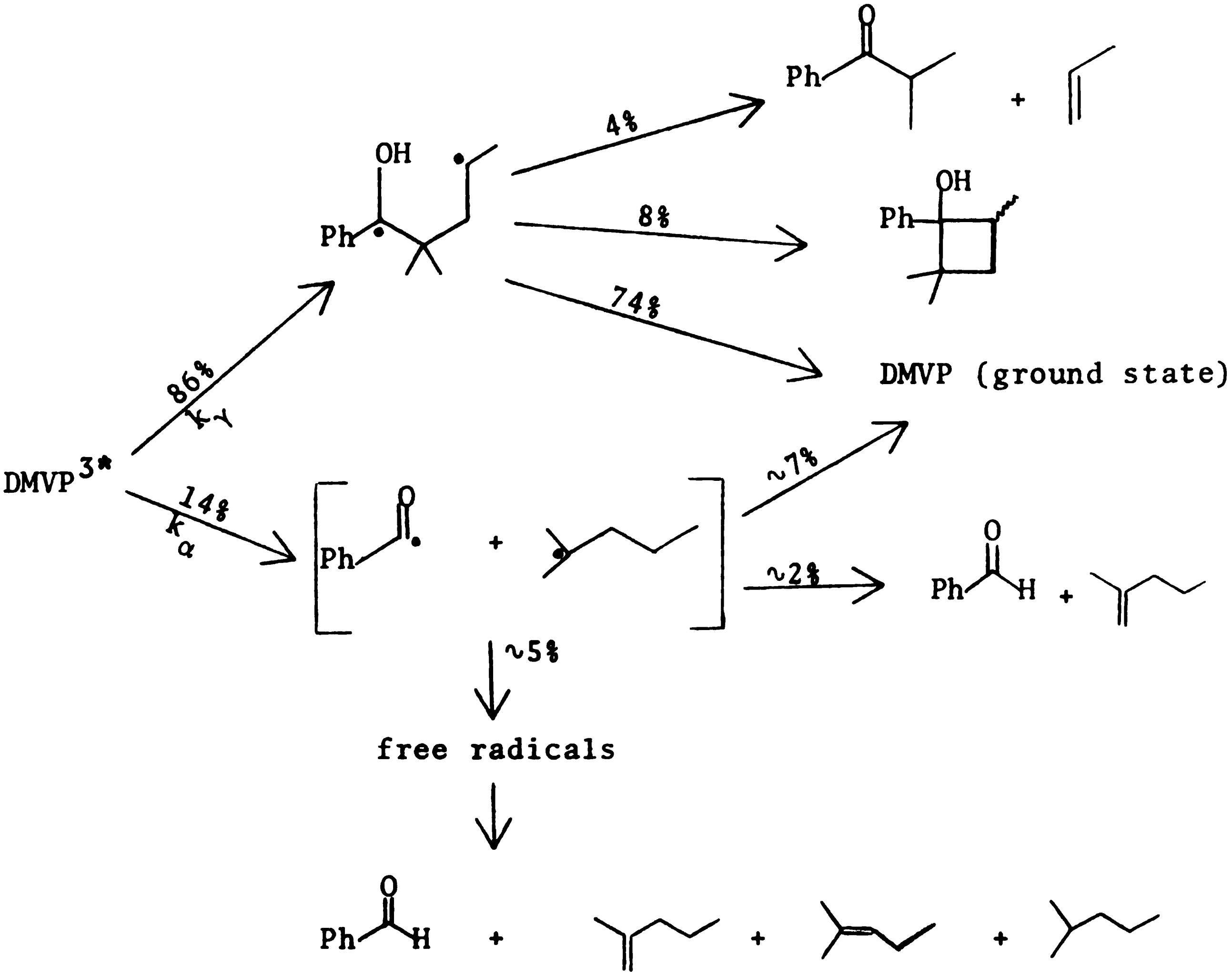


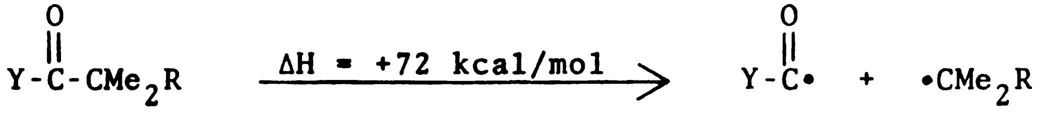
Figure 13. Photoreactions of DMVP in hydrocarbon solvents.

Polar solvents produce slight changes in the partitioning of the biradical. In the initial solvent cage, some disproportionation of radicals is assumed since it is the most likely route to benzaldehyde in unreactive solvents. The absence of the olefinic product in the thiol trapping experiments does not rule this out because thiol also completely quenches propene formation under conditions where its co-product, isobutyrophenone, is not quenched.

The value of k_α, 1.4 x 10^7 sec^{-1}, is even lower than the reported values of 2.3 x 10^7 sec^{-1}[91] and 3.0 x 10^7 sec^{-1}[43] for phenyl *t*-butyl ketone. The rate constant for α-cleavage of phenyl *t*-alkyl ketones, ∿2 x 10^7 sec^{-1}, is only 0.004 as large as that for aliphatic *t*-butyl ketones;[12,40] this fact has apparently escaped previous attention.[100] Triplet phenyl ketones resemble triplet aliphatic ketones in rates of hydrogen abstraction[1] and singlet aliphatic ketones in rates of α-cleavage.[12,102]

The reduced reactivity for α-cleavage of phenyl ketone triplets is not due to any increased π,π^* character in the lowest triplet state since α-dimethyl substitution stabilizes the n,π^* triplet of phenyl alkyl ketones.[39] Furthermore, it would be hard to rationalize why the rate of γ-hydrogen abstraction would not also be similarly affected. The relative rates of cleavage and intramolecular hydrogen abstraction in alkoxy radicals[103,104] are very similar to those for triplet aliphatic ketones; the cleavage reaction in excited ketones is likely also to be triggered by the free electron on oxygen. The fact that the excited electron is in a primarily benzene-like π^* orbital in a phenyl ketone triplet probably does not reduce the reactivity of that state.

The lower reactivity of phenyl ketones to α-cleavage is probably due primarily to energetic differences and possibly also to differences in geometry. Recent epr[105] and kinetic[106] studies indicate that the free electron of the benzoyl radical is not conjugated with the benzene ring. Thermochemical data[107,108] indicate that α-cleavage of *t*-alkyl ketones is 72 kcal/mol endothermic whether Y is alkyl or phenyl.



$$Y\text{-}\overset{O}{\overset{\|}{C}}\text{-}CMe_2R \xrightarrow{\Delta H = +72\ \text{kcal/mol}} Y\text{-}\overset{O}{\overset{\|}{C}}\bullet \; + \; \bullet CMe_2R$$

Conjugation of ketone triplets with the phenyl ring does provide extra stabilization to ketone triplets, the excitation energy of acetophenone being 72.5-75.6 kcal/mol compared with 78-80 kcal/mol for acetone.[109] α-Dimethyl substitution stabilizes the n,π* triplet of phenyl ketones[39] and the n,π* singlet of aliphatic ketones,[110] but apparently does not stabilize the n,π* triplet of aliphatic ketones.[110] Therefore, as Figure 14 shows, α-cleavage of DMVP is nearly thermoneutral while α-cleavage of pinacolone is ∿5 kcal/mol exothermic.[100]

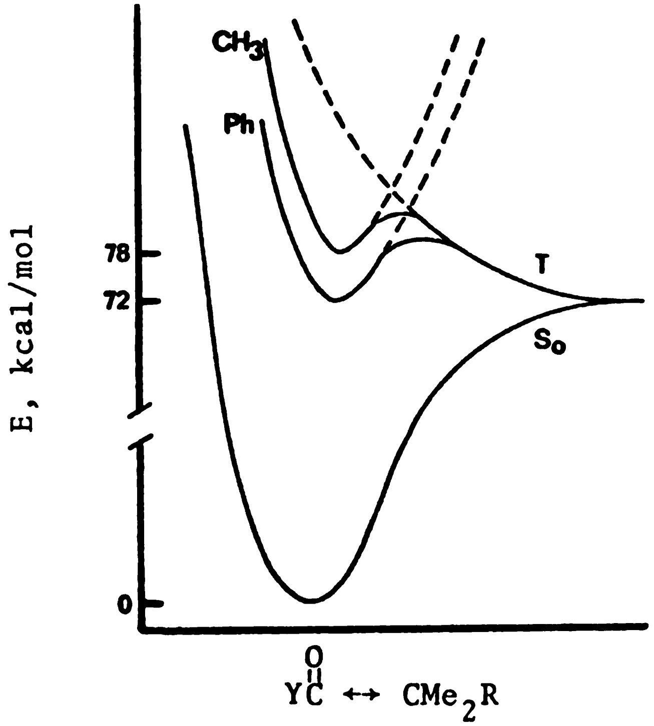


Figure 14. Potential energy diagram for α-cleavage of the n,π* triplets of methyl and phenyl *t*-alkyl ketones.

Both reactions proceed with loss of free energy because of the large positive change in entropy, but the difference in enthalpy is a reasonable explanation of the large difference in rates of α-cleavage for the two kinds of ketone triplets.

A geometric factor may be partially responsible for the rate difference between phenyl and aliphatic ketone triplets. Conjugation with a phenyl ring likely keeps the triplet carbonyl planar.[111] If aliphatic ketones imitate formaldehyde, their excited singlets are nearly planar and their triplets nearly tetrahedral. α-Cleavage from n,π* states of formaldehyde has been proposed to be a direct result of state mixing caused by nonplanarity of the excited state,[112] but further theoretical justification for this idea has not been presented.

b. γ-Hydrogen abstraction by triplet DMVP

The previously discussed quenching studies with DMVP and DMBP indicate that DMVP has a $\frac{1}{\tau}$ value of 10×10^7 sec^{-1} with $k_\alpha = 1.4 \times 10^7$ sec^{-1} and $k_\gamma = 8.6 \times 10^7$ sec^{-1}. Valerophenone's k_γ is 14×10^7 sec^{-1} indicating a small decrease in reactivity toward γ-hydrogen abstraction results with α-dimethyl substitution. The reactivity of triplet acetophenone in intermolecular hydrogen abstraction also slightly decreases with α-methyl substitution.[91] These decreases are likely due to a weak inductive effect on the triplet n,π* benzoyl rather than to any steric effect. Strong electron-withdrawing groups on the α-carbon greatly enhance the reactivity of phenyl ketone triplets,[52],[113] so methyl-substitution should produce a weak effect in the opposite direction.

Steric hindrance in an intramolecular reaction reflects extra torsional strain or nonbonded interactions which develop during rotation of the molecule into its transition state conformation. In an acyclic system, a transition state geometry which requires even partial eclipsing of one carbon-carbon bond would make the reaction subject to significant steric effects. Since α-, β-,[114] and δ-substituents[114] produce essentially no steric hindrance to type II γ-hydrogen abstraction, Wagner has proposed that the conformation of α,β and β,γ C-C bonds must be totally staggered in the transition state for γ-hydrogen transfer.[115]

c. Behavior of the 1,4-biradical from DMVP

The biradicals produced by γ-hydrogen abstraction by excited triplet carbonyls of phenyl alkyl ketones undergo competing type II cleavage, cyclization, and reverse hydrogen atom transfer; α-methyl groups cause significant changes in these competitive processes for the DMVP biradical. The large cyclization to cleavage ratio for DMVP and the low quantum yields for the type II cleavage and cyclization products are of considerable mechanistic interest. As with other phenyl alkyl ketones, the *trans*-cyclobutanol is the major isomer in hydrocarbon solvents and in polar solvents the *trans*/*cis* ratio is reduced;[116] however, DMVP shows much less stereoselectivity for cyclization than is typical.

Substituents, especially in the α- and β- positions, apparently affect the ease with which the biradicals reach the necessary conformations for cyclization and cleavage.[1,41,92,93] With α-dimethyl substitution, the conformation of the biradical which leads to cyclization is favored relative to that for cleavage; β-dimethyl substitution has the opposite effect. Lewis and Hilliard have observed this effect for α,α-dimethylbutyrophenone, DMBP, also.[92,93] Table 6 compares some kinetic data relevent to elimination and cyclization for valerophenone (VP), DMVP, butyrophenone (BP), DMBP, and β,β-dimethylbutyrophenone (β-DMBP).

Table 6. Type II Cyclization and Elimination Quantum Yields and Ratios in Benzene

Ketone	Φ_{cy}	Φ_{elim}	k_{cy}/k_{elim}
VP[114]	0.075	0.33	0.23
DMVP	0.088	0.05	1.8
BP[114]	0.033	0.35	0.094
DMBP[93]	0.032	0.004	8.0
β-DMBP	0.005[93]	0.19[114]	0.026[114]

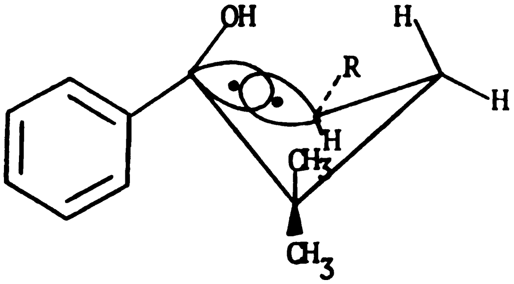
Table 6 shows that α-dimethyl substitution of valerophenone increases the cyclization to elimination ratio, k_{cy}/k_{elim}, by a factor of 8. The large decrease in the quantum yield for elimination accounts for most of this change. α-Dimethylation of butyrophenone diminishes the quantum yield for type II cleavage by a factor of over 80 while leaving the quantum yield for cyclization unchanged. These results indicate that changes in the cyclization to elimination ratio caused by α-dimethyl substitution are primarily due to diminished efficiency of elimination from the biradical.

Wagner has suggested that elimination requires continuous overlap of the σ bond being cleaved with both of the radical p orbitals.[1,41] Support for this hypothesis comes from several cyclic ketones in which the 1,4-biradicals cannot assume such a conformation.[117-121] Hoffman's calculations[122] indicate for tetramethylene that conformations having all four carbon atoms planar promotes cleavage by optimizing the mixing of π and σ molecular orbitals, a hypothesis similar to that of Stephenson.[123-125]

The reduced efficiency of type II cleavage with α-dimethyl substitution is very likely due to the steric repulsion of *ortho*-hydrogens of the phenyl group and the hydrogens of the α-methyl groups, impeding attainment of the optimum geometry for cleavage. Molecular models show this interaction to be quite severe if we make the reasonable assumption of the benzylic p-orbital being conjugated with the phenyl π-system.

Additional steric interaction between the hydroxyl and α-methyl groups would also contribute to the impairment of the cleavage process.

For cyclization, stereoelectronic requirements are looser than for cleavage since only the radical centers need overlap in the transition state. The four-membered cyclic transition state is most likely puckered to minimize 1,2-eclipsing interactions.[93,126]



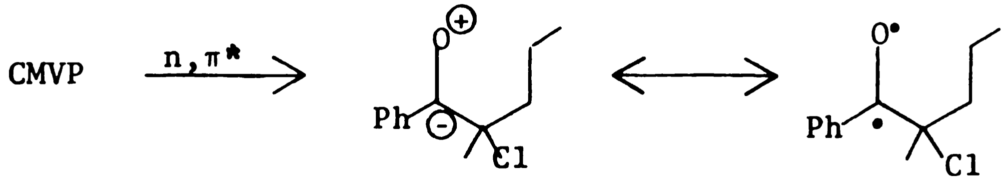
The above structure corresponds to the cyclization transition state for biradicals from either DMVP or DMBP. The α-methyls are so orientated that virtually the only extra steric interactions, compared to the unsubstituted cases, are the small 1,3-pseudodiaxial interactions between an α-methyl and a γ-H or γ-CH_3. This accounts for the negligible change in cyclization yields with α-dimethyl substitution. This mechanism for photocyclization not only accounts for the observed α- and β- substituent effects, but in phenyl alkyl ketones in general, where R ≠ H, the *trans*-cyclobutanol predominates in nonpolar solvents, as would be predicted by the model.

2. Photoreactivity of α-Chloro-α-methylvalerophenone

a. Competitive photocleavage and cyclization reactions

Quenching studies and radical trapping experiments show that the photoreactions of CMVP proceed largely from a triplet excited state *via* radical intermediates. In a polar solvent, wet acetonitrile, a portion of the photoreaction is unquenchable requiring the involvement of some short lived upper excited state whose photoreactivity is low in nonpolar media. Heterolytic cleavage, giving ionic intermediates, is suggested for this unquenchable upper excited state since such a process would be suppressed or rapidly reversed in nonpolar solvents. Attempts to measure the intersystem crossing quantum yield were unsuccessful in this preliminary investigation of CMVP photochemistry because of experimental complications.

Phosphorescence of trifluoroacetophenone, a ketone with α-halogen substituents, indicates that the π,π* triplet state lies very close to, and slightly lower in energy than, the ^{3}n,π* state.[113] It is likely, then, that the π,π* triplet of CMVP lies only slightly above the n,π* triplet state; perhaps the two states are in thermal equilibrium.[1] The ^{3}π,π* state, with increased electron density on the oxygen and diminished electron density on the carbonyl carbon, does not seem a good candidate for facile loss of chloride ion, however. The singlet n,π* state is a much better candidate because of the shift in electron density away from the oxygen as indicated in the zwitterionic resonance representation below.[6,55,56,127]



Ejection of chloride ion from an excited singlet state gives product ions which would be in their ground electronic states; however, with an excited triplet state one ion would have to be in a triplet excited state when formed. For these reasons, the unquenchable excited state is assumed to be the n,π* singlet of CMVP.

In Figure 15, the photoreactions of CMVP in a polar medium are presented with approximate quantum efficiencies indicated as percentages. The photoreactions of CMVP in a nonpolar medium are indicated in Figure 16, again with approximate quantum efficiencies for low conversion photolysis indicated as percentages.

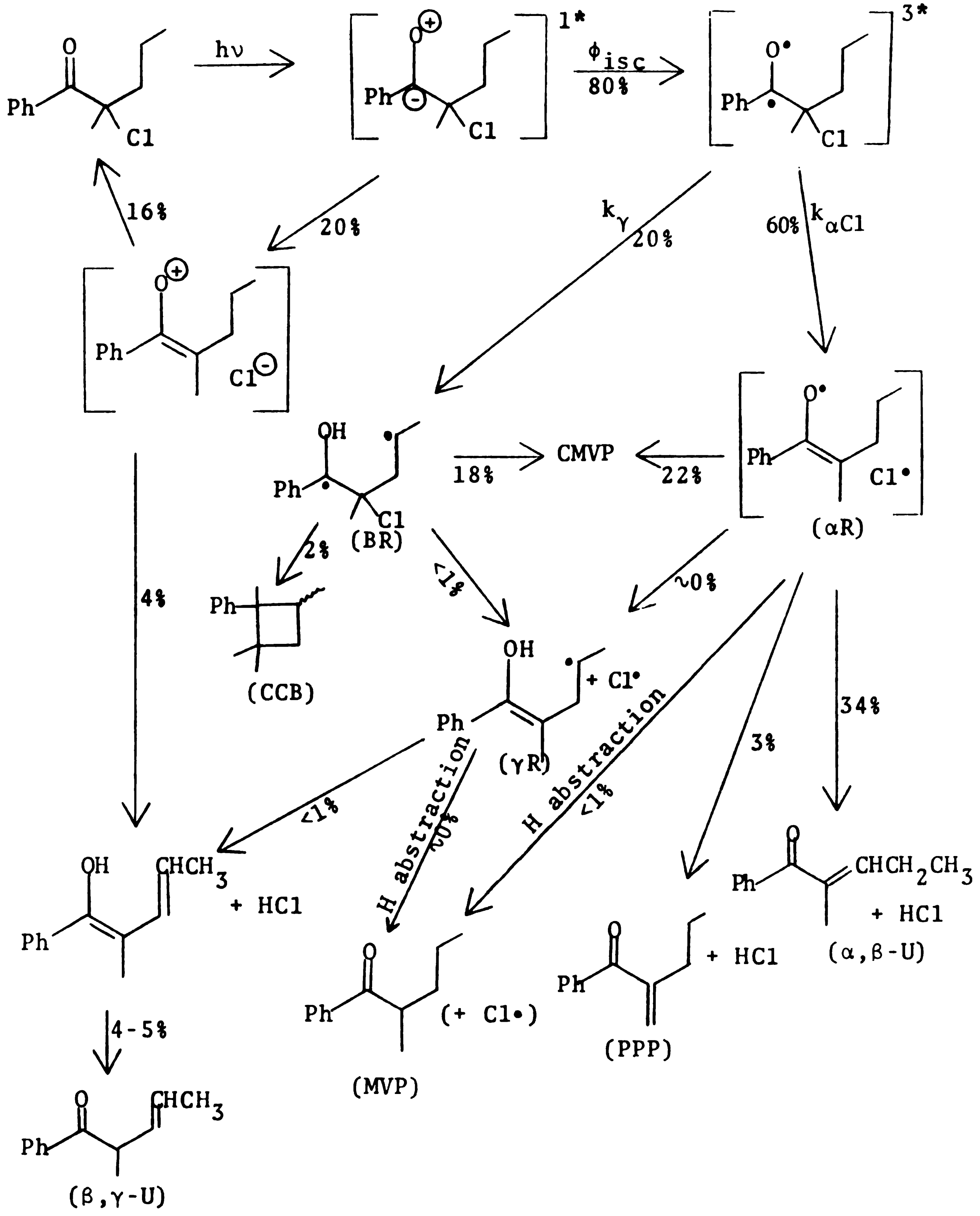


Figure 15. Photoreactions of CMVP in wet acetonitrile.

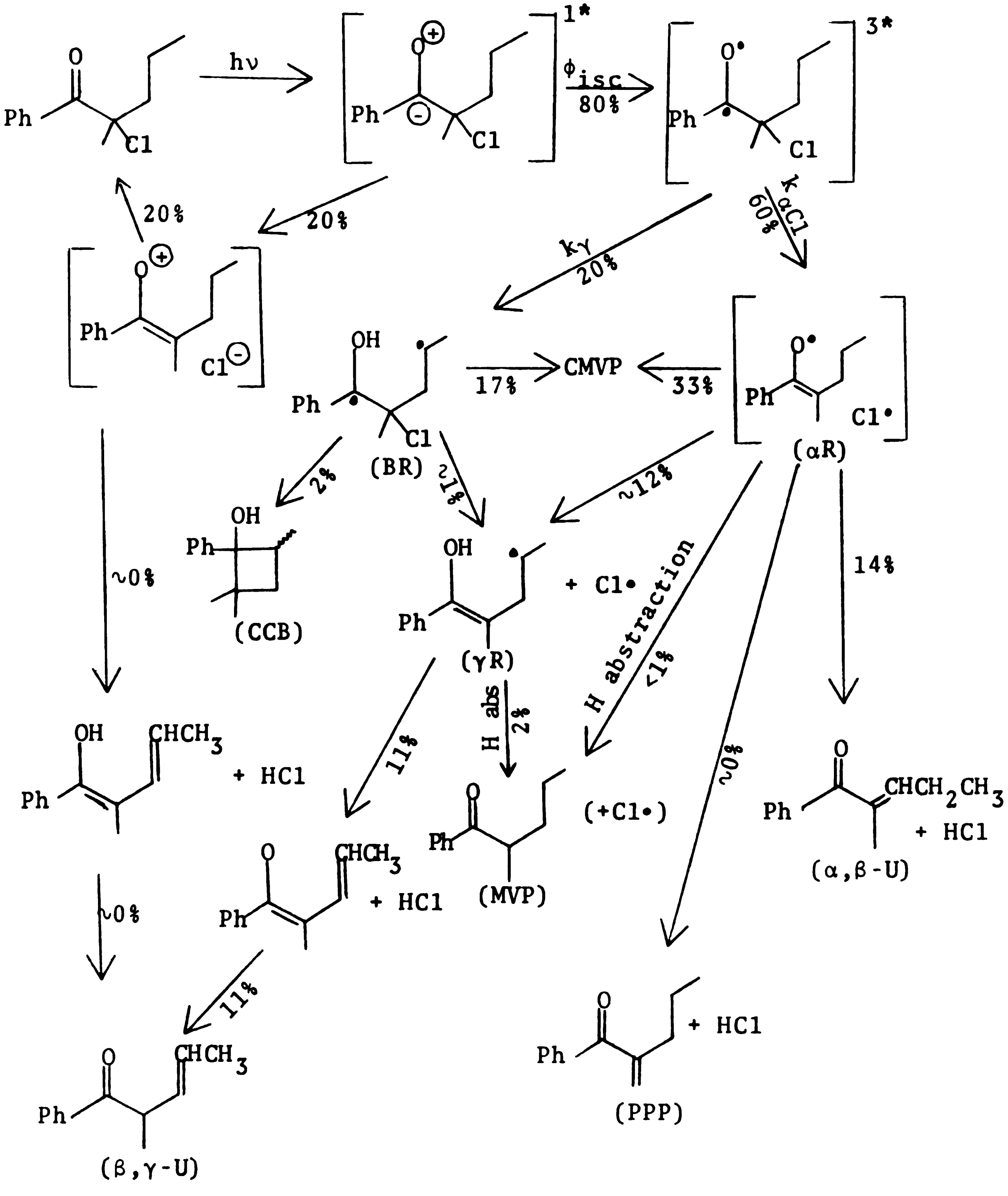
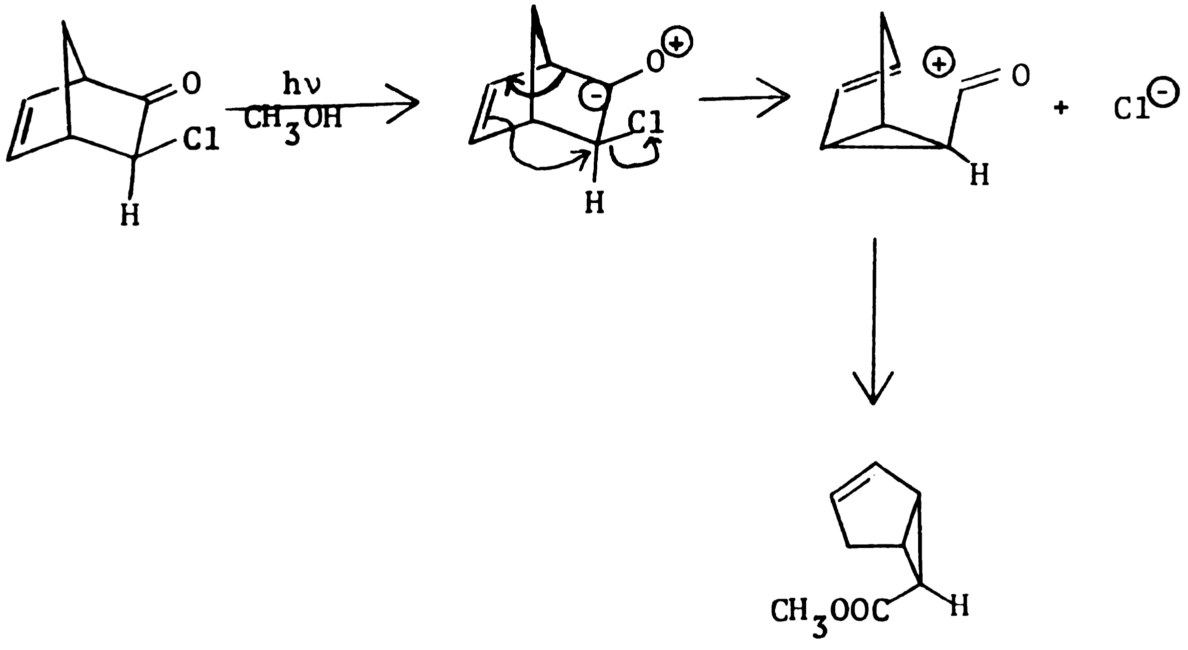


Figure 16. Photoreactions of CMVP in benzene.

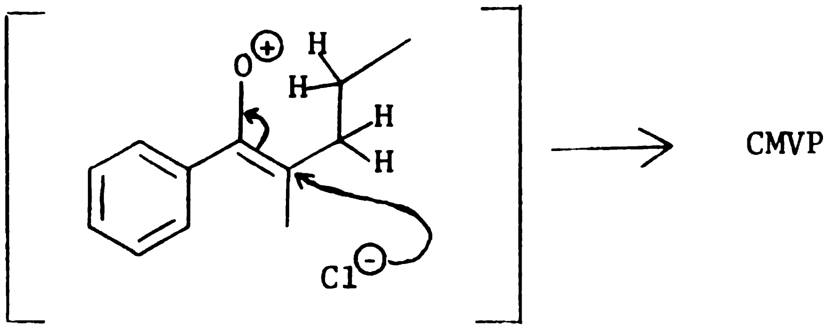
As the percent conversion of CMVP increases, either in acetonitrile or benzene, formation of photoproducts from the triplet excited state is strongly quenched and the unquenchable formation of β,γ-U becomes the major photoreaction with its quantum yield remaining low. In nonpolar solvents, the polarity of the medium increases with increasing percent conversion and so the heterolytic cleavage pathway becomes operative. The "photochemically" produced hydrolysis product, HMVP, is most likely a thermal product catalyzed by the photogenerated hydrochloric acid since pyridine and dienes quench the "photoproduction" of HMVP, probably by trapping the HCl. Formation of γ- and β-CMVP is insignificant at very low conversion, but at high conversion are a modest portion of the reaction mixture. Most likely these products are due to thermal addition of HCl to the corresponding unsaturated ketone products. Propiophenone, a very minor product at ∿5% conversion, is apparently present as the type II elimination product of MVP.

b. Photoreactivity from the unquenchable excited state

It is of interest that the unquenchable reactive state of CMVP yields essentially only ground state CMVP and the geometric isomers of β,γ-U within the limits of the measurements. High stereospecificity in a loss of chloride ion from an unquenchable photoexcited α-chloroketone has been reported for the following reaction,[10] admittedly a special case.

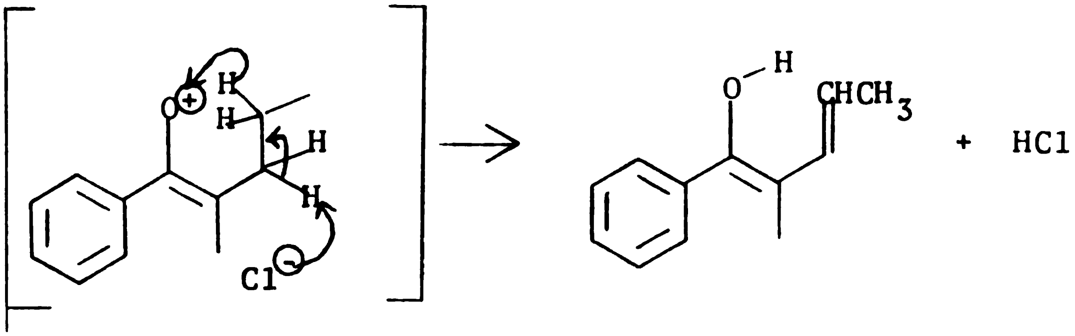


With CMVP, the specificity may be due to reactions following the heterolytic cleavage of the carbon-chlorine bond so rapidly that the two ions do not leave the solvent cage. The following representation is of this close ion pair immediately after heterolysis with the arrows indicating the major reaction,



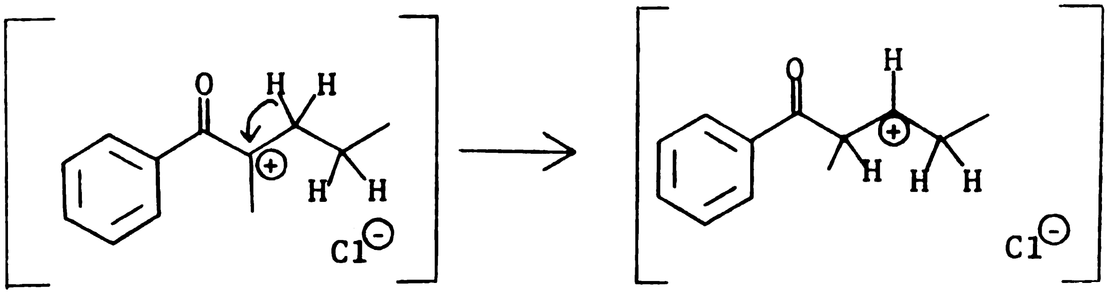
production of ground state CMVP. This ionic coupling reaction of the ion pair is virtually the exclusive reaction from the excited singlet state in nonpolar solvents, providing this mechanism is correct.

In the more polar solvents, the production of ground state CMVP from the excited singlet state occurs along with a competitive process, formation of HCl and the enol of β,γ-U. The solvent effect may be due to stabilization of the ion pair by partial solvation in the solvent cage. Transfer of a γ-hydride to the oxygen portion of the cation, either followed by or concerted with β-proton transfer to the chloride anion in the solvent cage accounts for the observed specificity of the unquenchable excited state. Production of HCl and the enol of β,γ-U is shown below in a concerted manner.



The failure to observe any other unquenchable photoproducts is taken as evidence that the enol of β,γ-U is formed in the solvent cage from a close ion pair, since if the ions diffuse apart, the other unsaturated ketones, PPP and α,β-U, would also be produced in significant amounts.

Another mechanism for the loss of hydrochloric acid from the unquenchable excited state of CMVP involves a 1,2-hydride shift immediately following heterolysis of the carbon-chlorine bond.



Loss of a γ-proton gives β,γ-U. Facile loss of the α-proton to produce α,β-U would also be expected from this intermediate; however, none of the α,β-U produced can be attributed to the unquenchable excited state and therefore this latter mechanism is less likely than the former.

c. Photoreactivity of the n,π* triplet state

The major portion of CMVP photoproducts at low conversion is produced from a quenchable excited state by pathways involving radical intermediates. This state apparently is the n,π* triplet which competitively forms two discrete intermediates, the radical resulting from homolytic cleavage of the carbon-chlorine bond and the biradical produced by γ-hydrogen abstraction. The biradical from triplet CMVP, BR, apparently yields only a small amount of type II cyclization products and an unmeasurably small amount of the type II cleavage product. There may be a fair amount of the radical intermediate, γR, formed by loss of the chlorine atom from BR; however, in the mechanistic schemes this pathway is arbitrarily assumed to be relatively unimportant. The estimate of 20% for the quantum efficiency of biradical formation is a rough but reasonable one considering its various possible reactions, especially reverse hydrogen transfer.

The major intermediate in the photochemistry of CMVP, having a quantum efficiency of about 60%, is the radical resulting from homolysis of the carbon-chlorine bond, αR. This radical can revert to CMVP, lose a hydrogen atom to a suitable acceptor thereby forming PPP and α,β-U, abstract a hydrogen atom to form MVP, and rearrange by γ hydrogen transfer followed by intermolecular hydrogen atom transfer to form β,γ-U. All of these processes are solvent and additive dependent. Consistent with this mechanism, the large number of very minor products indicate that a vast assortment of other radical addition, coupling, and disproportionation processes are occurring.

The radical intermediate γR leads to β,γ-U from the triplet excited state of CMVP. The high value for $k_q\tau$ obtained from monitoring the production of β,γ-U with added piperylene quencher likely is an artifact which reflects piperylene trapping of the unhindered, secondary free radical, γR. The other radical, αR, may be too hindered or too short lived to be trapped by piperylene. If αR prefers to transfer a hydrogen to piperylene rather than add to it, the slightly lower $k_q\tau$ obtained for quenching α,β-U with piperylene relative to 2,5-dimethyl-2,4-hexadiene as quencher is explained. The most reliable values of $k_q\tau$ are $1.2M^{-1}$ for 2,5-dimethyl-2,4-hexadiene quenching of triplet CMVP in acetonitrile and $1.3M^{-1}$ for *cis*-piperylene quenching of triplet CMVP in benzene.

The quenching data yield a $\frac{1}{\tau}$ value for triplet CMVP of 3.8×10^9 sec^{-1} (assuming the usual value for k_q, 5×10^9 M^{-1} sec^{-1}, in benzene).[71] This can be broken into $k_\gamma = 1 \times 10^9$ sec^{-1} and $k_{\alpha hom} = 3 \times 10^9$ sec^{-1} using the approximate quantum efficiences for these processes as previously indicated. Rate constants are not available for the reactions from the excited singlet state since its lifetime is unknown.

3. Inductive Effects on Triplet State Reactivity of Ketones

a. Effect of α-dimethyl substitution

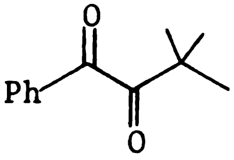
The rate constant for γ-hydrogen abstraction from the triplet n,π* state of valerophenone is 1.4×10^8 sec^{-1},[41] determined in benzene with diene quencher. The corresponding k_γ for DMVP is 0.86×10^8 sec^{-1}, indicating a reduction of ∿40% in the rate constant with α-dimethyl substitution. The reactivity of triplet acetophenone toward intramolecular hydrogen abstraction is also slightly lowered with α-methyl substitution.[91] Investigations by Wagner and coworkers have shown that electron donating groups on the β, γ, δ, and ε positions modestly enhance the reactivity of the γ-hydrogen abstraction reaction of triplet phenyl alkyl ketones,[1,114] presumably because the electron donation by induction to the γ C-H bond makes it more attractive to the very electrophilic triplet benzoyl group.[1] The inductive effect of methyl groups on the α-position, however, would tend to make the triplet benzoyl group slightly less electrophilic and therefore slightly less reactive to γ-hydrogen abstraction.

b. Effect of α-chloro substitution

The effect of an electron withdrawing α-substituent is a large enhancement in the reactivity of triplet benzoyl groups, as observed for α-alkoxyacetophenones[52] and α-trifluoroacetophenone.[113] Consistent with these reports, CMVP probably undergoes γ-hydrogen abstraction from its triplet state with $k_\gamma = \sim 1 \times 10^9$ sec; this is a 7 fold rate enhancement relative to valerophenone and over 11 times the k_γ for DMVP. Electron withdrawing groups on the α position would be expected to make the triplet benzoyl group more electrophilic and therefore more reactive in hydrogen abstraction reactions.

4. Sterically Indifferent Triplet Energy Transfer

This investigation of DMVP was undertaken primarily to determine the extent of steric hindrance to triplet energy transfer caused by the partial blocking of the excited carbonyl by α-dimethyl substitution. Since *t*-alkyl ketones are known to be resistant to nucleophilic attack on their carbonyl groups, and in view of the steric effects on energy transfer reported by Hammond,[77,87-89] it is reasonable to expect some steric hindrance to energy transfer from excited *t*-alkyl ketones. However, as described in Table 3 and Figure 8, exothermic energy transfer from triplet DMVP is just as "diffusion-controlled" as for the unhindered valerophenone. This same result has been also observed for a hindered diketone, β,β-dimethyl-α-ketobutyrophenone, DMKBP.[37,128]



DMKBP

As reported by Wagner and Kochevar, so-called "diffusion-controlled" energy transfer is not completely diffusion-controlled in low viscosity hydrocarbon solvents but approaches being so in viscous alcohols.[71] Energy transfer within an encounter pair competes with diffusion apart, with α in equation 5 decreasing with decreasing viscosity of the solution.

$$k_q = \alpha\, k_{dif} \qquad \text{(eq. 5)}$$

The proportionality constant, α, is defined in equation 6.[71]

$$\alpha = \frac{k_{et}}{k_{et} + 1/\tau_o + k_{-dif}} \approx \frac{k_{et}}{k_{et} + k_{-dif}} \qquad \text{(eq. 6)}$$

In the light hydrocarbon solvents, even unhindered triplet energy transfer is only partly diffusion controlled showing that k_{et} and k_{-dif} are similar in size; this fact is of crucial importance in demonstrating the paucity of steric hindrance in exothermic energy transfer involving triplet

DMVP. If k_{et} were much larger than k_{-dif}, a sterically induced decrease in k_{et} could be unnoticed since α would be near unity as long as k_{et} remained much larger than k_{-dif}. If k_{et} were much smaller than k_{-dif}, $k_q\tau$ values would be essentially independent of solvent viscosity. Since $k_q\tau$ values show a parallel dependence on solvent viscosity for the hindered ketones, DMVP and DMKBP, compared with valerophenone, an unhindered ketone, the rate constant for energy transfer between adjacent donor and acceptor molecules, k_{et}, cannot be subject to significant steric hindrance.[128] Apparently a small amount of steric hindrance is involved in quenching triplet DMVP, since different dienes have slightly different quenching efficiencies; no such difference has been reported in the quenching of unhindered phenyl ketone triplets.[128]

The lack of substantial steric effects in the quenching of triplet DMVP is not likely a result of the π^* orbital including the benzene ring, with which quenchers could overlap and avoid the hindered carbonyl. In DMKBP the triplet n,π^* excitation is mostly located on the α-dicarbonyl chromophore, yet it is also quenched without large steric effects.[128] Intramolecular γ-hydrogen abstraction by triplet *t*-butyl *n*-butyl ketone is calculated as 1×10^8 sec^{-1}[12] where "diffusion-controlled" quenching is assumed; the same value is measured for γ-hydrogen abstraction in 2-hexanone,[1] the corresponding unhindered ketone. Therefore partial delocalization of electronic excitation into the benzene ring, which cannot be possible in these other systems, is probably not responsible for the prevention of steric hindrance in quenching triplet DMVP either.

In ground state reactions, a *t*-alkyl group impedes the approach of moderate-sized reagents to the carbonyl. Furthermore, the triplet excited state of phenyl *t*-butyl ketone abstracts hydrogen from 2-propanol at 1/30 the rate of triplet acetophenone.[91,129] Since the bulky *t*-alkyl group does not interfere significantly with energy transfer from triplet carbonyl compounds, donor and acceptor must not need to approach bonding distance to attain the necessary orbital overlap for energy transfer. In equation 7, the theoretical dependence of rates of exchange-induced energy transfer on the distance R between donor and acceptor is presented.[72]

$$k_{et} = Y \exp(-2R/L) \qquad \text{(eq 7)}$$

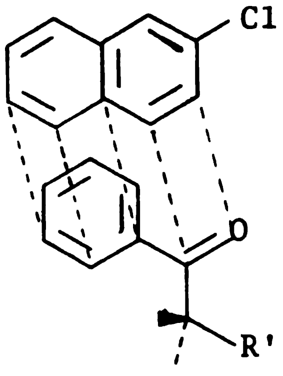
L is an unspecified fixed distance which may be thought of as an "average effective Bohr radius." Y includes a number of parameters such as spin statistics and orbital overlap.

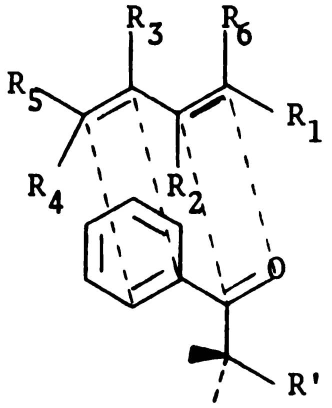
Energy transfer between triplet ketone and a diene acceptor in a solvent cage has been estimated as 8×10^{10} sec^{-1}.[71] In this instance, R should be close to 3.5-4Å, the sum of the van der Waals radii of the molecules. Energy transfer between ketones and acceptors where R varies from 3-5Å has been measured with $k_{et} = 3 \times 10^{9} - 1 \times 10^{11}$ sec^{-1}.[130]

In an intramolecular energy transfer process from a benzophenone to a naphthalene held 14-15Å apart in a substituted steroid, $k_{et} = 25\ sec^{-1}$.[131] Static energy transfer between the same two chromophores located 13Å apart in a rigid matrix occurs with $k_{et} = 200\ sec^{-1}$.[73] If we assume that in these four cases the Y values are similar since each donor and acceptor can freely rotate relative to each other, equation 7 can be solved for L. A value of 1.0Å is obtained which holds for triplet energy transfer at both close and medium range.

In the gas phase, 50-100 collisions are required for triplet energy transfer from ketones to dienes.[132-134] The fact that every collision between donor and acceptor does not produce energy transfer, even when energy transfer is highly exothermic, suggests an orientational requirement for orbital overlap. Ullman has proposed orbital symmetry requirements for triplet energy transfer.[15,135-137] Dexter's formulation of equation 7 for exchange-induced energy transfer contains a factor accounting for orbital symmetry or an orientational requirement.[72]

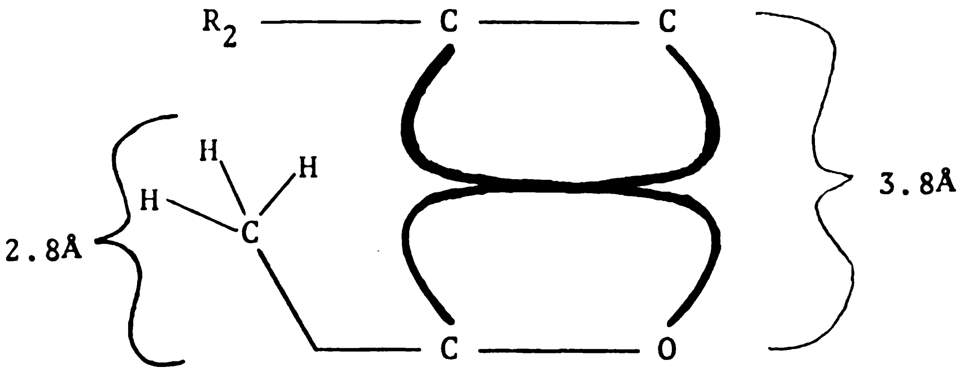
It is possible to construct a geometric model for triplet energy transfer which assumes maximum π-overlap, preferred orientation, and R being close to the sum of the van der Waals radii of π-systems of donor and acceptor; this model accounts for the observed steric effects in triplet energy transfer.[128] Representations for quenching triplet DMVP with 2-chloronaphthalene and with diene quenchers are shown below.





In the case of 2-chloronaphthalene or *cis*-1,3-pentadiene ($R_{1-5} = H$, $R_6 = CH_3$), only hydrogens need lie above the *t*-alkyl group and for these quenchers the highest values of $k_q\tau$ are measured. With 2,5-dimethyl-2,4-hexadiene ($R_{2,3} = H$, $R_{1,4-6} = CH_3$), a methyl group (R_1) must lie over part of the *t*-alkyl group and a lower $k_q\tau$ is observed. Using 2,3-dimethyl-1,3-butadiene ($R_{1,4-6} = H$, $R_{2,3} = CH_3$), a still lower $k_q\tau$ value results and a methyl group (R_2) must lie squarely over the *t*-alkyl group in the optimum geometry predicted by the model.

An edge-on view provides a better perspective of the distances involved in this model. Considering bond lengths, bond angles, and atomic van der Waals radii, the α-methyls of DMVP extend 2.8Å above the carbonyl plane. When $R_2 = H$, excited triplet DMVP and the quencher can approach to within 3.8-4.0Å, which is close to the van der Waals diameter of a π-system. If $R_2 = CH_3$ which has a 2Å van der Waals radius,



either the distance between donor and acceptor must increase or, more likely, the molecules tilt somewhat from their preferred orientation which decreases k_{et} by a $\cos^2\phi$ factor. This model presumably presents the optimum orientation of donor and acceptor for energy transfer. At longer distances and less favorable ϕ's, steric effects would be even less significant.

The one published example of significant steric hindrance in triplet energy transfer is neatly explained by the Wagner model. The efficiency of stilbene quenching of the triplet of a substituted 2,6-diisopropylbenzophenone relative to its 2,6-dimethyl analog is lowered by a factor of 15.[77] In this system, the large isopropyl *ortho*-substituents force the phenyl ring out of planarity with the carbonyl and thereby would prevent a quencher from approaching anywhere near the preferred distance of approximately the van der Waals diameter of the carbonyl π system.

5. Summary

The studies conducted with the α-substituted phenyl alkyl ketones, DMVP and CMVP, have significant implications for several photoprocesses. With DMVP, the type I and type II processes compete, $k_\alpha = 1.4 \times 10^7$ sec^{-1} and $k_\gamma = 8.6 \times 10^7$ sec^{-1}. The rate constant for the α-cleavage reaction of phenyl *t*-alkyl ketones is only about 0.004 of that for aliphatic *t*-butyl ketones, a difference which is largely explained by the differences in enthalpy for α-cleavage processes of the two types of ketones. With CMVP, the n,π* singlet state apparently loses chloride ion rapidly enough to compete with intersystem crossing. A further competition is present with the triplet n,π* state which can lose its chlorine to form a radical or abstract a γ-hydrogen to yield a biradical intermediate.

The small decrease in reactivity of excited DMVP toward γ-hydrogen abstraction is likely due to the α-methyls inductively making the triplet n,π* benzoyl slightly less electrophilic and therefore slightly less reactive toward γ-hydrogen abstraction. The electron-withdrawing α-chlorine of CMVP makes the triplet benzoyl more electrophilic and correspondingly more reactive toward γ-hydrogen abstraction.

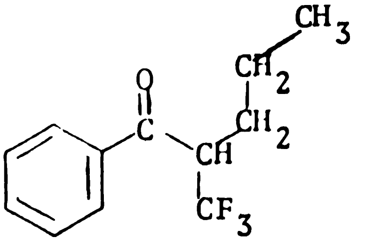
The geometry of the transition state for γ-hydrogen abstraction is probably staggered to minimize eclipsing interactions since the α-methyls of DMVP have only a small effect on the rate constant for this process. The resulting 1,4-biradical intermediate from DMVP is subject to significant steric effects in the conformation of the transition state required for cleavage, which has the radical p-orbitals overlap with the α,β bond, but not in the puckered ring configuration required for cyclization.

The steric effect of the α-methyl groups on exothermic triplet energy transfer is very small as indicated by quenching being "diffusion-controlled." Those small differences found between different diene quenchers can be explained by a geometric model which, for the optimum orientation favoring energy transfer, incorporates maximum π system overlap, preferred orientation, and the distance between donor and acceptor being close to the sum of the van der Waals radii of the two π systems, this distance being about 4Å. This geometric model for exothermic triplet energy transfer represents the fulfillment of the original purpose of this study, the investigation of steric effects on such energy transfer.

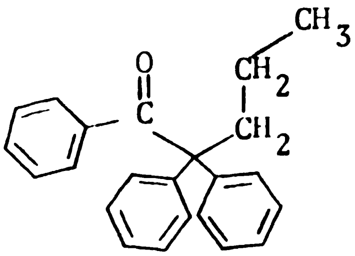
6. Suggestions for Further Research

a. Effects of α-substituents on energy transfer, triplet state reactivity, and reactivity of the 1,4 biradical intermediate

Investigation of the photochemistry of compounds such as α-(trifluoromethyl)valerophenone (TFMVP) and α,α-diphenylvalerophenone (DPVP) should yield further information on inductive effects and the various steric effects on energy transfer and biradical reactivity.



TFMVP



DPVP

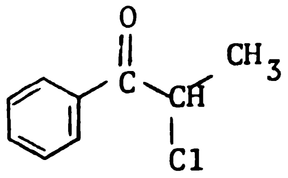
TFMVP would probably undergo the type II photoprocesses without other competing reactions and thereby simplify study of the inductive effect of the trifluoromethyl group. DPVP would be interesting because its triplet benzoyl group should be less electrophilic than that of valerophenone and therefore less reactive toward γ-hydrogen abstraction. The large steric bulk of the α-phenyl groups would enable testing the geometric model for exothermic triplet energy transfer, especially with appropriately substituted quenchers. Incidently, further study of DMVP with such sterically hindered quenchers should also be enlightening.

DPVP should exhibit a strong tendency to α-cleave based upon the stability of the resulting radicals. The biradical resulting from γ-hydrogen abstraction of DPVP should show an extremely large preference for cyclization relative to cleavage, thereby providing a test of the hypotheses regarding the configurations of the transition states for these processes.

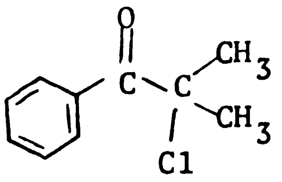
b. Investigations using CMVP and other α-haloketones

The study of CMVP was of a preliminary nature and there remain some details which deserve further work. These include the intersystem crossing quantum yield, a number which appears to be experimentally difficult to determine, the definite identification of type II photoproducts, and a careful investigation of the unquenchable photoreaction, thought to be heterolysis of the carbon-chlorine bond from the n,π* singlet state.

The photoreactivity of α-haloketones has not been studied much and further work employing simpler α-chloroketones than CMVP ought to be quite productive. The dechlorination reactions of α-chloropropiophenone (CPP) or α-chloro-α-methylpropiophenone (CMPP) would lead to only one unsaturated ketone product without the complication of competing γ-hydrogen abstraction, however; with CMPP, type I photocleavage may possibly occur.



CCP



CMPP

The photoreactivity of similar α-bromoketones should also be interesting.

c. Effect of *ortho*-substituents on exothermic triplet energy transfer

Blocking the excited carbonyl group to close approach of a suitable quencher molecule through the use of bulky *ortho*-substituents was attempted but subsequently discarded because of the synthetic difficulties encountered in each of many attempts involving *ortho*-*t*-butyl groups. If a suitable di-*ortho*-substituted phenyl alkyl ketone could be prepared, it would provide a further way of testing the geometric model proposed for exothermic triplet energy transfer. Again, quenching studies of such a hindered ketone with appropriately substituted quencher molecules should be informative.

EXPERIMENTAL

A. CHEMICALS

1. Ketones

a. α,α-Dimethylvalerophenone

α,α-Dimethylvalerophenone (DMVP) was prepared by several methods: from phenyl Grignard reagent and α,α-dimethylvaleryl chloride,[138] from the Grignard reagent of 2-bromo-2-methylpentane and benzoyl chloride,[138] from phenyl lithium and α,α-dimethylvaleric acid,[117] from *n*-propyl tosylate and the magnesium salt of the *t*-butylimine of isobutyrophenone,[139] and by the dialkylation of valerophenone with sodium hydride and methyl iodide.[92,140] Dimethylation of valerophenone gave the best yield of DMVP.

An ether slurry of 1.8 mol of sodium hydride was added, with stirring, under a nitrogen atmosphere, over a 1 hr period, to 300 ml of dry ether containing 0.6 mol valerophenone and 1.5 mol methyl iodide. Prior to use, the mineral oil dispersion of sodium hydride was washed with 3 successive portions of dry ether. The reactants were refluxed for 40 hr and then cooled to 0°; 150 ml of water was then slowly added to destroy excess sodium hydride. The ethereal layer was washed twice with aqueous sodium chloride and dried. Vacuum distillation gave a 91% yield of DMVP which was still contaminated by a small amount of some unidentified impurity. DMVP was purified *via* its oxime since distillation was ineffective in removing the impurity which was present regardless of the synthetic route employed. The oxime of DMVP was prepared by refluxing 0.17 mol of the impure ketone and 0.93 mol of hydroxylamine hydrochloride in 200 ml of ethanol and 400 ml of 7% aqueous sodium hydroxide solution for 5 hr. Upon cooling a nearly quantitative yield of the oxime was obtained as a white solid. Recrystallization from ethanol gave white needles (mp 131-133°, uncor.). Hydrolysis of 50 g of the oxime by refluxing with 600 ml of 12% aqueous hydrochloric acid for 2 hr was followed by steam distillation. The DMVP was extracted into ether, dried, and vacuum distilled (bp 70° at ∿0.3 torr.). Analysis by glpc indicated >99.9% purity. The success of this novel purification procedure depended upon the absence of enolizable hydrogens since otherwise aldol condensation would occur.[141]

The mass spectrum (70eV) of DMVP includes peaks with m/e 190 (parent), 105 (benzoyl), and 77 (phenyl). Proton nmr chemical shifts measured in CCl_4 are: δ 7.55 (m, 2, *o*-H), 7.20 (m, 3, *m*-H, *p*-H), 1.52 (m, 2, methylene β-H), 1.22 (s, 6, α-CH_3) and 0.78 (m, 5, γ-H, γ-CH_3). The carbonyl band is at 1670 cm^{-1} in the ir spectrum. The instruments used for these analyses are indicated in part C of the experimental section. Using a Cary 14 Spectrometer, the ultraviolet λ_{max} in cyclohexane are found at 235.5 nm (ε = 8,000), 273.5 nm (ε = 492), and 323.0 nm ($\varepsilon = 100$). The earliest reference to DMVP which could be found in the literature is in a communication on the phosphorescence of several phenyl alkyl ketones.[39] This paper includes measurements on a sample of DMVP which was prepared by this author.

b. α-Methylvalerophenone

Friedel-Crafts acylation of benzene, carried out by slowly adding 0.3 mol of α-methylvaleryl chloride in the presence of 0.75 mol anhydrous aluminum chloride to 2 mol of benzene, yielded α-methylvalerophenone. The reactants were refluxed 2 hr, then poured into a stirred mixture of 200 g of ice and 200 ml of concentrated hydrochloric acid. The ether extract was washed 3 times with aqueous sodium chloride, dried, and vacuum distilled (bp 69° at ∿0.3 torr), giving an 82% yield. Further distillation using a Nester Faust stainless steel spinning band column yielded >99% pure α-methylvalerophenone as determined by glpc.

Chemical shifts from the nmr spectrum of α-methylvalerophenone in CCl_4 are: δ 7.92 (m, 2, *o*-H), 7.36 (m, 3, *m*-H, *p*-H), 3.43 (m, 1, α-H), and 2.1-0.6 (m, 10). This 10 proton multiplet includes δ 1.15 (d J = 6.6 Hz, 3, α-CH_3), 0.86 (distorted triplet J = 5.4 Hz, 3, γ-CH_3), and the 4 methylene protons.

c. α-Chloro-α-methylvalerophenone

The chlorination of α-methylvalerophenone by sulfuryl chloride[142] gave α-chloro-α-methylvalerophenone (CMVP). Sulfuryl chloride (0.34 mol) was added to 0.17 mol of α-methylvalerophenone in 200 ml of carbon tetrachloride and stirred for 2 days in a flask equipped with a calcium chloride drying tube. The more volatile components of the reaction mixture were distilled away at water aspirator pressure. Since glpc analysis showed incomplete reaction, 0.17 mol of sulfuryl chloride was added and stirring was resumed for 3 days, this time without solvent. Again the relatively volatile compounds were removed at water aspirator pressure. Vacuum distillation (bp 75° at ∿0.1 torr) followed by washing the petroleum ether solution with aqueous sodium bicarbonate twice, washing with water once, drying, and redistilling gave >99.5% pure CMVP as determined by glpc.

Mass spectrometry (70eV): m/e 212 (Cl^{37} parent), 210 (Cl^{35} parent), 105 (benzoyl), and 77 (phenyl). Proton nmr in CCl_4: δ 8.10 (m, 2, *o*-H), 7.35 (m, 3, *m*-H, *p*-H), 2.16 (m, 2, methylene β-H), 1.76 (s, 3, α-CH_3), 1.30 (m, 2, γ-H), and 0.78 (distorted triplet J = 6.2 Hz, 3, γ-CH_3). The ir carbonyl band occurs at 1680 cm^{-1}. The uv λ_{max} in cyclohexane are: 248.5 nm (ε = 11,000), 277.0 nm (ε = 945), and 326.5 nm (ε = 113). A literature search reveals no references to the prior preparation or use of CMVP.

d. Valerophenone

Valerophenone (Aldrich Chemical Co.) was vacuum distilled, passed through activity I neutral alumina, and redistilled. A relatively large amount of the valerophenone used was prepared by acylating 3.4 mol of benzene by slow addition of 1.7 mol of valeryl chloride with 2.0 mol of anhydrous aluminum chloride as the catalyst. After refluxing for 2 hr, aqueous hydrochloric acid was added at 0° followed by ether extraction, washing, drying, and distillation. The valerophenone so obtained was then treated in the same manner as the commercial material.

e. Isobutyrophenone

Commercial isobutyrophenone (Alrich Chemical Co.) was used as received to calculate the standardization factors for the type II cleavage product of DMVP relative to the glpc internal standards used in this study.

f. α-Chloropropiophenone

The anticipated type II cleavage product from CMVP, α-chloropropiophenone, was prepared by monochlorinating 0.74 mol of Matheson Coleman and Bell propiophenone using 0.49 mol of sulfuryl chloride in 200 ml of carbon tetrachloride.[142] The reactants were stirred overnight in a flask equipped with a calcium chloride drying tube. The more volatile materials were removed by distillation at aspirator pressure yielding an oil which was approximately a 1:1 mixture of α-chloropropiophenone and propiophenone. Distillation at reduced pressure gave α-chloropropiophenone (bp 70° at ∿0.1 torr) which glpc analysis indicated as >95% pure.

Nmr chemical shifts in CCl_4 are: δ 7.97 (m, 2, *o*-H), 7.42 (m, 3, *m*-H, *p*-H), 5.31 (AB quartet $J_{AB} = 6.4$ Hz, 1, α-H), and 1.68 (d $J = 7.0$ Hz, 3, α-CH_3).

g. Methyl ethyl ketone

Methyl ethyl ketone (J. T. Baker Co.) was distilled through a 1.5 cm x 40 cm glass-helix packed column at atmospheric pressure (bp 78.9°, uncor.). The middle cut was passed through activity I neutral alumina and analyzed by glpc as >99.9% pure.

h. Acetophenone

Acetophenone supplied by Matheson Coleman and Bell was distilled under reduced pressure (bp 55° at 3 torr).

2. Solvents

a. Acetonitrile

Fisher Scientific Co. acetonitrile was purified by distillation from potassium permanganate at atmospheric pressure.

b. Benzene

Fisher Scientific Co. 99 mole %, thiophene free benzene was purified by stirring gallon quantities with ∿300 ml portions of concentrated sulfuric acid several times. The sulfuric acid was discarded and a new portion added on a daily basis until the sulfuric acid layer remained colorless after being stirred for a day in contact with the benzene. The benzene was washed with water, 10% aqueous sodium hydroxide, and aqueous sodium chloride. After drying, the benzene was distilled at atmospheric pressure from ∿100g of phosphorus pentoxide through a 45 cm glass-helix packed column with the still head adjusted to give a high reflux ratio. The first and last 10% of the distillate was discarded.

c. *n*-Hexane

n-Hexane (J. T. Baker Co.) was purified in the same manner as benzene, except on a smaller scale.

d. Cyclooctane

Previously distilled Aldrich Chemical Co. cyclooctane was stirred overnight twice with fresh portions of concentrated sulfuric acid, washed with aqueous sodium chloride solution, dried, and distilled from phosphorus pentoxide, the middle 80% of the distillate being retained.

e. 1-Propanol

Fisher Scientific Co. 1-propanol was distilled from calcium hydride at atmospheric pressure.

f. *t*-Butyl alcohol

The *t*-butyl alcohol (J. T. Baker Co.) used in this study was distilled from freshly cut sodium at atmospheric pressure by A. E. Kemppainen.

g. 1-Pentanol

1-Pentanol (Fisher Scientific Co. *n*-amyl alcohol) was purified by distillation from calcium hydride at atmospheric pressure.

h. 1-Heptanol

Matheson Coleman and Bell 1-heptanol was purified by atmospheric pressure distillation from calcium hydride, discarding a larger than usual forecut which contained several impurities.

3. Quenchers

a. *cis*-Piperylene

High purity *cis*-piperylene (Chemical Samples Co. *cis*-1,3-pentadiene) was used as received. Glpc analysis indicates 99.8% *cis*.

b. 2,3-Dimethyl-1,3-butadiene

2,3-Dimethyl-1,3-butadiene from Aldrich Chemical Co. was purified by distillation at atmospheric pressure.

c. 2,5-Dimethyl-2,4-hexadiene

Sublimed crystals of Chemical Samples Co. 2,5-dimethyl-2,4-hexadiene were used. This sublimation at ∿0° and atmospheric pressure conveniently occurred in the refrigerated bottle.

d. Naphthalene

Matheson Coleman and Bell naphthalene was recrystallized from absolute ethanol prior to use.

e. 1-Chloronaphthalene

Fisher Chemical Co. "Reagent Grade" 1-chloronaphthalene was used as received.

f. 2-Chloronaphthalene

2-Chloronaphthalene (Eastman Organic Chemicals) was recrystallized first from absolute ethanol and then from pentane prior to use.

4. Internal Standards

a. 1-Decanol

1-Decanol from Eastman Organic Chemicals was distilled at atmospheric pressure prior to use.

b. Cyclohexane

"Spectroquality" cyclohexane, supplied by Matheson Coleman and Bell was used as received.

c. Tetradecane

Tetradecane (Columbia Organic Chemicals) was purified by stirring over concentrated sulfuric acid, the acid being replaced daily until it no longer became discolored. The tetradecane was then rinsed with aqueous potassium hydroxide solution, dried, and distilled at reduced pressure.

d. Pentadecane

The pentadecane (Columbia Organic Chemicals) was purified the same way as the tetradecane.

e. Heptadecane

Aldrich Chemical Co. heptadecane was treated in the same way as tetradecane and pentadecane. These alkane internal standards were purified by Professor P. J. Wagner.

f. Nonadecane

Nonadecane supplied by Chemical Samples Co. was purified by recrystallization from petroleum ether at -78°.

g. Eicosane

Matheson Coleman and Bell eicosane was purified by recrystallization from absolute ethanol.

5. Other Chemicals

a. Pyridine

Baker Chemical Co. "Analyzed Reagent Grade" pyridine was used as received.

b. *t*-Butylmercaptan

The *t*-butylmercaptan (Aldrich Chemical Co. 2-methyl-2-propanethiol) was used as received.

c. 1-Dodecanethiol

Aldrich Chemical Co. 1-dodecanethiol was used as received.

d. Benzaldehyde

For photoproduct identification, Matheson Coleman and Bell benzaldehyde was used as received.

e. 2-Methyl-1-pentene, 2-methyl-2-pentene, and 2-methylpentane

Samples of these compounds from Aldrich Chemical Co. were used as received for photoproduct identification.

B. TECHNIQUES

1. Preparation of Samples for Photolysis

Using Pyrex and Kimax Class A volumetric glassware and a Sartorius analytical balance sensitive to tenths of milligrams, solutions containing the requisite amounts of ketones, internal standards, quenchers, solvents, and other additives were prepared at room temperature (about 25°). Generally, duplicate 2.8 ml samples of each solution were syringed into Pyrex photolysis tubes. These photolysis tubes were prepared from carefully sorted and cleaned 100 x 13 mm Pyrex culture tubes by heating them ∿3 cm from the neck and drawing out the softened tubes to a length of approximately

18 cm. The samples were attached to the stopcocks of a vacuum line using 1 hole rubber stoppers and degassed by freezing them in liquid nitrogen followed by evacuating them to 1 x 10^{-3} torr for 5 to 10 min; the samples were then isolated from the vacuum pump by closing the stopcocks and allowed to thaw. This freeze-pump-thaw sequence was carried out an additional 2 times, the tubes being sealed with a torch before the final thawing. Each tube was inverted several times after being degassed to ensure adequate mixing.

2. Irradiation

The sample tubes constituting a run were irradiated in a "merry-go-round" turntable apparatus so constructed as to give each sample a virtually identical amount of light.[143] The "merry-go-round" apparatus was immersed in a 25° water bath. A Hanovia 450 watt medium-pressure mercury lamp contained in a water-cooled quartz immersion well was the light source. A cylindrical Pyrex jar containing 0.002*M* potassium chromate in 1% aqueous potassium carbonate solution provided a 1 cm path of filter solution which transmitted the 313 nm radiation. Light of wavelength 366 nm was obtained by using Corning N-7-83 glass filters around the light source. The samples were generally irradiated until ~5% of the starting ketone was converted to products.

3. Analyses of Photolysates

a. Gas liquid partition chromatography

All of the analyses of the photolysates for product formation or ketone disappearance were carried out by gas liquid partition chromatography (glpc), also known as vapor phase chromatography (vpc) or more simply as gas chromatography (gc). Two different Varian Aerograph Model 1200 Hy-Fi III gas chromatographs equipped with several different 1/8" diameter columns and an Aerograph Hy-Fi Model 600D gas chromatograph fitted with a 1/8" x 25' 25% 1,2,3-tris(2-cyanoethoxy)propane (on 60/80 mesh acid washed Chromosorb P) column were used. The following analytical vpc columns were used with the Varian Model 1200 gas chromatographs:

5' 5% SE-30 on dimethyldichlorosilane (DMCS) treated acid washed Chromosorb W,

9' 4% QF-1, 1% Carbowax 20M on 60/80 mesh acid washed Chromosorb P,

6' 4% QF-1, 1.2% Carbowax 20M on DMCS treated 60/80 mesh acid washed Chromosorb G,

9' 5% QF-1, 1.2% Carbowax 20M on DMCS treated 60/80 mesh acid washed Chromosorb G, and

12' 5% QF-1, 1.2% Carbowax 20M on DMCS treated 60/80 mesh acid washed Chromosorb G.

The 3 analytical gas chromatographs used in this study all had flame ionization detectors, on-column injection, and nitrogen as the carrier gas. Hydrogen and nitrogen gas flow rates were adjusted to optimize separations; they were generally in the 20-30 ml/min range.

The vpc traces were obtained using Leeds and Northrup Speedomax recorders equipped with DISC integrators. Some of the vpc peak areas were integrated with an Infotronics Model CRS-208 Automatic Digital Integrator. Further information regarding the glpc conditions employed to analyze a particular run may be found in the tables of photokinetic data.

b. Standardization factors for internal standards

In order to obtain the concentrations of the various photoproducts by glpc, known concentrations of internal standards were used in the photolysis solutions. These internal standards were so selected as to not overlap any other peaks in the vpc traces and were used at concentrations which would make the internal standard peak similar in height to the larger product peaks after photolysis. The response of the vpc detector to a given compound relative to some internal standard is expressed by means of the relevant vpc standardization factor (SF). The SF's for the various photo and thermal products relative to the internal standards used in this study were calculated by equation 8 from solutions prepared with known concentrations of products and internal standards (IS).

$$\mathrm{SF} = \frac{[\text{Product}]}{[\text{IS}]} \times \frac{\text{Area of IS Peak}}{\text{Area of Product Peak}} \qquad \text{(eq. 8)}$$

Knowing the SF, the concentration of a given photoproduct was calculated according to equation 9, which is simply a rearranged form of equation 8.

$$[\text{Product}] = \text{SF} \times [\text{IS}] \times \frac{\text{Area of Product Peak}}{\text{Area of IS Peak}} \quad (\text{eq. } 9)$$

The standardization factors for cyclobutanol photoproducts and rearranged ketones were approximated by those for the isomeric ketones. The SF's for the unsaturated ketone products were approximated by those for the corresponding saturated ketones and the SF's of CMVP were used for α-hydroxy-α-methylvalerophenone. Table 7 contains the SF's which were determined for this study.

c. Actinometry and Quantum Yields

To determine a quantum yield the amount of the photoproduct formed and the amount of light absorbed by the parent ketone are needed. All of the samples for which quantum yields were determined absorbed >99% of the incident 313 nm light. Parallel irradiation of duplicate 0.100*M* samples of valerophenone in benzene, generally with 0.00250*M* tetradecane as the internal standard, provided the actinometry. For long irradiation times, several sets of these actinometer tubes were employed. Under these conditions, acetophenone formation is known to proceed with $\Phi = 0.33$[32] so vpc analysis to obtain the concentration of acetophenone produced in a given amount of time provided a simple way to measure the

Table 7. Standardization Factors

Internal Standard	SF	Product
Cyclohexane	2.0	Propene
	1.0	2-Methylpentane, 2-Methyl-1-pentene, 2-Methyl-2-pentene
n-$C_{10}H_{21}OH$	1.53	Benzaldehyde
	0.984	Isobutyrophenone
	0.844	α-Methylvalerophenone
	0.786	DMVP
	0.811	CMVP
n-$C_{14}H_{30}$	2.00	Acetophenone
n-$C_{15}H_{32}$	2.40	Benzaldehyde
	1.54	Isobutyrophenone
	1.23	DMVP
n-$C_{17}H_{36}$	1.51	α-Methylvalerophenone
	1.40	DMVP
	1.46	CMVP
n-$C_{19}H_{40}$	1.67	DMVP
n-$C_{20}H_{42}$	1.84	α-Methylvalerophenone
	1.79	CMVP

concentration of photons in einsteins l^{-1} (equivalent to mol l^{-1}) absorbed by each sample in that amount of time. The quantum yield for each photoproduct of the ketone was found by dividing the concentration of that product by the concentration of photons which were absorbed by the photolyzed ketone.

d. Measurement of $k_q\tau$

A Stern-Volmer plot of Φ_o/Φ *versus* the quencher concentration gives a line having slope $k_q\tau$ as previously discussed. In one instance, the value of Φ_o was too high as indicated by the intercept of a Stern-Volmer plot being substantially greater than 1. In this case, a plot of $1/\Phi$ *versus* quencher concentration was made. As seen from equation 10, a rearranged Stern-Volmer equation, $k_q\tau$ is the slope of such a plot divided by the intercept.

$$\frac{1}{\Phi} = \frac{1}{\Phi_o} + \frac{k_q\tau\ [Q]}{\Phi_o} \qquad \text{(eq. 10)}$$

C. PHOTOPRODUCTS

1. α,α-Dimethylvalerophenone

Identification of the various photoproducts of DMVP relied heavily on comparisons of retention times of the photoproducts with those of known compounds on the 1,2,3-tris(2-cyanoethoxy)propane analytical vpc column, for the more volatile products, and on several QF-1, Carbowax 20M analytical vpc columns for the other photoproducts.

a. Propene

Propene was identified as a DMVP photoproduct by its identical vpc retention time to the propene obtained from the photolysis of valerophenone.

b. 2-Methylpentane, 2-methyl-1-pentene, 2-methyl-2-pentene, benzaldehyde, and isobutyrophenone

Commercial samples of these compounds were used to verify the identities of these photoproducts by comparing vpc retention times.

c. *trans*- and *cis*-1-Phenyl-2,2,4-trimethylcyclobutanol

These two photocyclization products were expected from previous studies of the type II photoprocesses.[1] The cyclobutanol photoproducts from DMVP were isolated and their stereochemistry determined with the aid of a nmr shift reagent by Lewis and Hilliard.[93]

2. α-Chloro-α-methylvalerophenone

The photo and thermal products of CMVP were determined from the spectral data of the products present after irradiation to high conversion in degassed and sealed photolysis tubes. The brown colored solutions obtained using both acetonitrile and benzene as solvents were separated into fractions corresponding to product peaks on either a 1/4" x 5' 15% Carbowax 20M column or a 1/4" x 5' 20% SE-30 column, both columns being installed in an Aerograph Model A-350-B Gas Chromatograph. Those fractions which were sufficiently large were analyzed on a Hitachi Perkin-Elmer RMU-6 Mass

Spectrometer operated by Mrs. Lorraine A. Guile, Chemical Spectroscopist, a Varian A-60, A-56/60, T-60, or HA-100 Nuclear Magnetic Resonance (nmr) Spectrometer, and a Perkin-Elmer Model 237-B Infrared (ir) Spectrometer. The 100 MHz nmr spectra were run by Mr. Eric T. Roach, Chemical Spectroscopist. In addition to these analyses, the solvent and very high retention time components of CMVP photolysis mixtures in both benzene and acetonitrile were removed and the resulting cleaned-up reaction mixtures analyzed using a vpc/mass spectrometer/computer system[144] which enabled identification of several minor products. This system consisted of a LKB 9000 Gas Chromatograph-Mass Spectrometer, a Digital Equipment Corporation PDP8/I On-Line Digital Computer, an incremental plotter, and a KSR35 Teletypewriter and was operated by Mr. Jack E. Harten, Biochemistry Department Mass Spectrometer Technician. A 1/8" x 4' 3% SE-30 vpc column was used for these analyses. The CMVP photo and thermal products follow in order of increasing vpc retention times.

a. Propiophenone (PP)

Mass spectrometry (70eV for all analyses): m/e 134 (parent), 105 (benzoyl), and 77 (phenyl). The vpc retention time of this product matches that of commercial propiophenone.

b. 1-Phenyl-2-propylprop-2-en-1-one (PPP)

This is a minor product, the mass spectrum of which shows peaks at m/e 174 (parent), 105, and 77. This identification is assigned as that most likely based upon the molecular formula consistent with the mass spectrum and ruling out the β,γ-U and α,β-U isomers since they are known to correspond to other CMVP products. Another possibility not involving rearrangement of the side chain is 1-phenyl-2-methylpent-4-en-1-one, but formation of this product is not as likely as PPP.

c. 1-Phenyl-2-methylpent-3-en-1-one (β,γ-U)

The mass spectrum indicates ions with m/e 174 (parent), 105, and 77. Nmr chemical shifts in CCl_4 are: δ 7.93 (m, 2, *o*-H), 7.45 (m, 3, *m*-H, *p*-H), 5.75 (m, 1, vinyl H), 5.53 (m, 1, vinyl H), 3.42 (m, 1, α-H), 1.15 (d J = 6.6 Hz, 3, α-CH_3), and 0.94 (m, 3, γ-CH_3). The stereochemistry of the double bond is not definitely known but analysis of the nmr multiplets indicates that both the *cis*- and *trans*- pairs of enantiomers are probably present. The carbonyl-stretch occurs at 1680 cm^{-1}.

d. α-Methylvalerophenone (MVP)

Using a sample, collected by preparative vpc from a Carbowax 20M column, of the β,γ-U product from a high conversion photolysis of CMVP in benzene, an extra peak occurred in the mass spectrum with m/e 176. This peak was not present in the mass spectra obtained for β,γ-U when SE-30 columns were used, suggesting that a small amount of MVP is present as a product of CMVP, which on SE-30 columns goes unnoticed, probably hidden in the baseline. The retention times of authentic MVP are close to those of β,γ-U on several QF-1, Carbowax 20M analytical vpc columns.

e. 1-Phenyl-2-methylpent-2-en-1-one (α,β-U)

Peaks with m/e 174 (parent), 105, and 77 are observed in the mass spectrum of this product. Nmr chemical shifts in CCl_4 are: δ 7.65 (m, 2, *o*-H), 7.48 (m, 3, *m*-H, *p*-H), 6.23 (2 overlapping triplets, 1, vinyl H), 2.31 (m, 2 overlapping quartets, 2, γ-H), 1.93 (s, 3, α-CH_3), and 1.07 (t J = 8.0 Hz, 3, γ-CH_3). Apparently both pairs of diastereomerically related enantiomers are produced.

f. α-Hydroxy-α-methylvalerophenone (HMVP)

Significant peaks at m/e 192 (parent), 174 (P-H_2O), 105, and 77 are found in the mass spectrum. Nmr chemical shifts in CCl_4 are: δ 8.00 (m, 2, *o*-H), 7.45 (m, 3, *m*-H, *p*-H), 4.37 (s-broad, 1, α-O-H), 1.86 (m, 2, methylene β-H), 1.56 (s, 3, α-CH_3), 1.28 (m, 2, γ-H), and 0.93 (m, 3, γ-CH_3). Infrared spectroscopy discloses the carbonyl band at 1670 cm^{-1} and the hydroxyl band at 3460 cm^{-1}.

g. 1-Phenyl-1,2-dihydroxy-2-methylpentane (PDHMP)

The evidence of PDHMP or an isomer of it as a product from CMVP is the presence of a peak with m/e 194 in the mass spectrum of the HMVP vpc peak when benzene is the photolysis solvent. When acetonitrile is the photolysis solvent, the HMVP vpc peak does not have the m/e 194 peak in its mass spectrum.

h. γ- and β-Chloro-α-methylvalerophenone (γ- and β-CMVP)

There are two products at high conversion whose mass spectral peaks at m/e 212 (Cl^{37} parent), 210 (Cl^{35} parent), 105, and 77 indicate they are phenyl ketones isomeric with CMVP. The nmr chemical shifts in CCl_4, for the product having the longer retention time, are: δ 8.00 (m, 2, *o*-H), 7.50 (m, 3, *m*-H, *p*-H), 3.74 (m, 2, α-H, H α to C-Cl), and 2.5-0.6 (m, 8). This 8 proton multiplet can probably be broken into the following: δ 1.60 (m, 2, methylene H), 1.20 (2 overlapping doublets, 3, α-CH_3), and 0.93 (d or t J = 6.0 Hz, 3, γ-CH_3). If this compound has a chlorine γ to the carbonyl, the terminal methyl group protons should have a chemical shift of about 1.53 ppm[145] instead of 0.93 ppm. The product with the longer retention time is most likely a mixture of stereoisomers of β-CMVP and the other rearranged CMVP is probably γ-CMVP.

D. PHOTOKINETIC DATA

1. α,α-Dimethylvalerophenone

Tabulations for each kinetic run of the DMVP photoproduct vpc peak areas relative to an internal standard, the corresponding concentrations, and the resulting quantum yields, when actinometers were employed, follow. The concentrations of DMVP, internal standards, quenchers, and any other additives, along with a description of the analytical vpc column and the column temperature used are included in each table. Actinometry was not conducted during those irradiations using 366 nm light because the DMVP is then not absorbing all of the light incident to each sample tube; the amount of light absorbed by each photolysis sample is indicated for the 313 nm irradiations.

The reproducibility of the relative vpc peak areas and consequently of the concentrations of the major photoproducts is on the order of ±5%. The quantum yields incorporate an additional ±3% uncertainty in reproducibility because of the precision of the actinometry. Errors in actinometry, either in the precision or the accuracy, do not affect $k_q\tau$ since they cancel out in the ratio Φ_o/Φ. The $k_q\tau$ values obtained by quenching production of DMVP photoproducts are reproducible to within ±5%.

Table 8. Photolysis of 0.250*M* DMVP in Benzene

	BA[a]	IBP[b]	t-CB[c]	c-CB[d]
Relative vpc Areas:	0.323	0.505	1.22	0.900
Concentrations x 10^3, *M*:	1.55	1.56	2.99	2.21
Φ:	0.028	0.028	0.053	0.040

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0561 ξ/l

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 115°

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[a] Benzaldehyde

[b] *iso*-Butyrophenone

[c] *trans*-1-phenyl-2,2,4-trimethylcyclobutanol

[d] *cis*-1-phenyl-2,2,4-trimethylcyclobutanol

Table 9. Photolysis of 0.100*M* DMVP in Benzene

	BA	IBP	t-CB	c-CB
Relative vpc Areas:	0.344	0.407	1.23	0.875
Concentrations x 10^3, *M*:	1.65	1.25	3.02	2.15
Φ:	0.029	0.022	0.054	0.038

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0561 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 115°

Table 10. Photolysis of 0.100*M* DMVP in Benzene

	BA	IBP	t-CB	c-CB
Relative vpc Areas:	0.631	1.22	2.34	1.62
Concentrations x 10^3, *M*:	3.03	3.75	5.77	4.00
Φ (Photon output estimated):	0.028	0.034	0.052	0.036

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

366 nm Radiation: 0.11 ξ/1 (Estimate from preceding 313 nm photolysis)

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 150°

Table 11. Disappearance Quantum Yield Determination from Photolysis of 0.100*M* DMVP in Benzene

	Before Photolysis	After Photolysis
Relative vpc Areas:	0.928	0.827

Concentratnon of DMVP Which Reacted:
(0.100)(0.928-0.827)/(0.928) = 0.0109*M*

Disappearance Φ: 0.225

Internal Standard: 0.060*M* n-$C_{19}H_{40}$

313 nm Radiation: 0.0484 ξ/l

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 160°

Table 12. Photolysis of 0.100*M* DMVP in Benzene, *n*-Hexane, and Cyclooctane

	Solvent	BA	IBP	t-CB	c-CB
Relative vpc Areas:	Benzene	0.236	0.281	0.857	0.64
	n-Hexane	0.228	0.313	0.870	0.699
	Cyclooctane	0.217		0.880	0.59
Concentrations x 10^4, *M*:	Benzene	10.8	8.30	20.2	15.1
	n-Hexane	10.5	9.24	20.5	16.5
	Cyclooctane	10.0		20.8	13.9
Φ:	Benzene	0.026	0.020	0.048	0.036
	n-Hexane	0.025	0.022	0.049	0.039
	Cyclooctane	0.024		0.050	0.033

Internal Standard: 0.00300*M* $n\text{-}C_{10}H_{21}OH$

313 nm Radiation: 0.0420 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 133°

Table 13. Photolysis of 0.100*M* DMVP in Benzene, *t*-Butyl Alcohol, and Wet Acetonitrile

	Relative vpc Areas		Conc. x 10^4, *M*		Φ	
	IBP	t-CB	IBP	t-CB	IBP	t-CB
Benzene	0.185	0.281	5.46	6.63	0.040	0.048
1.0*M* *t*-C_4H_9OH in Benzene	0.304	0.364	8.97	8.58	0.066	0.063
3.0*M* *t*-C_4H_9OH in Benzene	0.226	0.395	6.67	9.31	0.049	0.068
5.0*M* *t*-C_4H_9OH in Benzene	0.298	0.544	8.80	12.8	0.064	0.093
t-C_4H_9OH (10.6*M*)	0.640	0.672	18.9	15.8	0.138	0.115
1% H_2O in CH_3CN	0.625	0.899	18.5	21.2	0.135	0.155
2% H_2O in CH_3CN	0.786	0.946	23.2	22.3	0.169	0.163
3% H_2O in CH_3CN	0.810	0.939	23.9	22.1	0.174	0.161
5% H_2O in CH_3CN	0.454	0.864	13.4	20.4	0.098	0.149

Internal Standard: 0.00300*M* *n*-$C_{10}H_{21}OH$

313 nm Radiation: 0.0137 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 145°

Table 14. Photolysis of 0.0500*M* DMVP in 1-Pentanol

	IBP
Relative vpc Area:	0.639
Concentration x 10^4, *M*:	9.84
Φ:	0.131

Internal Standard: 0.00100*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.00749 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 130°

Table 15. Photolysis of 0.0500*M* DMVP in 1-Heptanol

	t-CB
Relative vpc Area:	0.636
Concentration x 10^4, *M*:	8.90
Φ:	0.119

Internal Standard: 0.00100*M* n-$C_{17}H_{36}$

313 nm Radiation: 0.00749 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 130°

Table 16. Photolysis of 0.100*M* DMVP in Benzene: Effect of 1-Dodecanethiol

[*n*-$C_{12}H_{25}SH$]	Propene	IH[a]	MP[b]	BA	IBP	t-CB	c-CB
Relative vpc Areas:							
none	0.965	1.57	2.00	0.465	1.00	1.79	1.25
0.100*M*	0.000	4.56	0.00	0.939	0.549	1.85	
0.500*M*	0.000	4.57	0.00	1.23	0.990	3.84	
Concentrations x 10^3, *M*:							
none	1.93	1.57	2.00	2.23	3.09	4.39	3.07
0.100*M*	0.00	4.56	0.00	4.51	1.69	4.55	
0.500*M*	0.00	4.57	0.00	5.90	3.05	9.44	
Φ:							
none	0.023	0.018	0.024	0.026	0.036	0.051	0.036
0.100*M*	0.000	0.053	0.000	0.053	0.020	0.053	
0.500*M*	0.000	0.054	0.000	0.069	0.036	0.111	

Internal Standards: 0.00100*M* Cyclohexane for Propene, IH, and MP

0.00200*M* *n*-$C_{15}H_{32}$ for BA, IBP, t-CB, and c-CB

313 nm Radiation: 0.0854 ξ/l

vpc Columns: 25' 25% 1,2,3-tris(2-Cyanoethoxy)propane at 60°

6' 4% QF-1, 1.2% Carbowax 20M at 140°

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[a] *iso*-Hexane (2-Methylpentane)

[b] 2-Methyl-1-pentene and 2-Methyl-2-pentene

Table 17. Photolysis of 0.100*M* DMVP in Cyclooctane: Effect of 1-Dodecanethiol

[*n*-$C_{12}H_{25}SH$]	Propene	IH	MP
Relative vpc Areas:			
none	1.51	2.59	1.19
0.100*M*	0.00	3.80	0.00
0.500*M*	0.00	3.86	0.00
Concentrations x 10^3, *M*:			
none	3.02	2.59	1.19
0.100*M*	0.00	3.80	0.00
0.500*M*	0.00	3.86	0.00
Φ:			
none	0.035	0.030	0.014
0.100*M*	0.000	0.044	0.000
0.500*M*	0.000	0.045	0.000

Internal Standard: 0.00100*M* Cyclohexane

313 nm Radiation: 0.0854 ξ/1

vpc Column: 25' 25% 1,2,3-tris(2-Cyanoethoxy)-propane at 60°

Table 18. Photolysis of 0.100*M* DMVP in Benzene: *cis*-Piperylene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0250	0.0300
Relative vpc Areas:						
IBP	1.67	1.42	1.10	0.914	0.787	0.683
t-CB	2.09	1.60	1.22	1.02	0.868	0.762
c-CB	1.56	1.19	0.873	0.708	0.614	0.531
Concentrations x 10^3, *M*:						
IBP	5.13	4.36	3.38	2.82	2.42	2.10
t-CB	5.14	3.95	3.00	2.50	2.14	1.87
c-CB	3.83	2.93	2.15	1.74	1.51	1.31
Φ:						
IBP	0.050	0.042	0.033	0.027	0.024	0.020
t-CB	0.050	0.038	0.029	0.024	0.021	0.018
c-CB	0.037	0.028	0.021	0.017	0.015	0.013

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.103 ξ/l

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 125°

Table 19. Photolysis of 0.100*M* DMVP in Benzene: 2,3-Dimethyl-1,3-butadiene Quencher

[Quencher], *M*:	none	0.0100	0.0200	0.0250	0.0300	0.0350	0.0400
Relative vpc Areas:							
IBP	1.58	1.48	1.06	0.971	0.874	0.710	0.671
t-CB	2.03	1.81	1.27	1.14	0.978	0.864	0.794
c-CB	1.51	1.30	0.906	0.809	0.700	0.616	0.568
Concentrations x 10^3, *M*:							
IBP	4.88	4.54	3.26	2.99	2.69	2.19	2.07
t-CB	4.99	4.46	3.13	2.80	2.41	2.13	1.95
c-CB	3.72	3.21	2.23	1.99	1.72	1.52	1.40
Φ:							
IBP	0.050	0.046	0.033	0.030	0.027	0.022	0.021
t-CB	0.051	0.046	0.032	0.029	0.025	0.022	0.020
c-CB	0.038	0.033	0.023	0.020	0.018	0.016	0.014

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0980 ξ/1

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 125°

Table 20. Photolysis of 0.100*M* DMVP in Benzene: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
Relative vpc Areas:							
Propene	2.03						
IH	2.05						
MP	2.64						
BA	0.586						
IBP	1.22	0.948	0.854	0.769	0.705	0.630	0.592
t-CB	2.15	1.47	1.27	1.10	1.00	0.877	0.802
c-CB	1.48	1.03	0.888	0.745	0.675	0.586	0.537
Concentrations x 10^3, *M*:							
Propene	4.06						
IH	2.05						
MP	2.64						
BA	2.81						
IBP	3.75	2.92	2.63	2.37	2.17	1.94	1.82
t-CB	5.29	3.62	3.13	2.72	2.64	2.16	1.97
c-CB	3.64	2.53	2.18	1.83	1.66	1.44	1.32
Φ:							
Propene	0.041						
IH	0.021						
MP	0.027						
BA	0.029						
IBP	0.038	0.030	0.027	0.024	0.022	0.020	0.018
t-CB	0.054	0.037	0.032	0.028	0.027	0.022	0.020
c-CB	0.037	0.026	0.022	0.019	0.017	0.015	0.013

Internal Standards: 0.00100*M* Cyclohexane for Propene, IH, and MP

0.00200*M* *n*-$C_{15}H_{32}$ for BA, IBP, t-CB, and c-CB

313 nm Radiation: 0.0983 ξ/1

vpc Columns: 25' 25% 1,2,3-tris(2-Cyanoethoxy)propane at 60°

6' 4% QF-1, 1.2% Carbowax 20M at 135°

Table 21. Photolysis of 0.100*M* DMVP in Benzene: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0040	0.0100	0.0300	0.0500
Relative vpc Areas:					
BA	0.415	0.327	0.231	0.099	
IBP	0.550	0.527	0.457	0.299	0.223
t-CB	1.44	1.24	1.02	0.637	0.448
Concentrations x 10^4, *M*:					
BA	19.9	15.7	11.1	4.8	
IBP	16.9	16.2	14.1	9.21	6.87
t-CB	35.4	30.5	25.1	15.7	11.0
Φ:					
BA	0.027	0.021	0.015	0.0065	
IBP	0.023	0.022	0.019	0.012	0.0093
t-CB	0.048	0.041	0.034	0.021	0.015

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0742 ξ/l

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 140°

Table 22. Photolysis of 0.100*M* DMVP in Benzene:
2-Chloronaphthalene Quencher

[Quencher], *M*:	none	0.0050	0.0100	0.0200	0.0300	0.0500
Relative vpc Areas:						
BA	0.649	0.453	0.368	0.214	0.161	0.083
IBP	1.26	0.937	0.770	0.552	0.435	0.297
t-CB	2.43	1.92	1.62	1.13	0.887	0.65
c-CB	1.70					
Concentrations x 10^4, *M*:						
BA	29.8	20.8	16.9	9.8	7.4	3.8
IBP	37.2	27.7	22.7	16.3	12.8	8.8
t-CB	57.3	45.3	38.2	26.6	20.9	15.
c-CB	40.1					

Internal Standard: 0.00300*M* n-$C_{10}H_{21}OH$

366 nm Radiation

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 133°

Table 23. Photolysis of 0.100*M* DMVP in *n*-Hexane: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0300
Relative vpc Areas:					
BA	0.387				
IBP	1.26	0.723	0.568	0.489	0.338
t-CB	1.84	0.950	0.748	0.640	0.471
c-CB	1.25	0.652	0.502	0.444	0.310
Concentrations x 10^4, *M*:					
BA	18.6				
IBP	39.0	22.3	17.5	15.1	10.4
t-CB	45.2	23.4	18.4	15.7	11.6
c-CB	30.7	16.0	12.3	10.9	7.63
Φ:					
BA	0.019				
IBP	0.040	0.023	0.018	0.015	0.011
t-CB	0.046	0.024	0.019	0.016	0.012
c-CB	0.031	0.016	0.012	0.011	0.008

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0983 ξ/1

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 135°

Table 24. Photolysis of 0.100*M* DMVP in *n*-Hexane: 2-Chloronaphthalene Quencher

[Quencher], *M*:	none	0.0100	0.0200	0.0300
Relative vpc Areas:				
BA	0.536			
IBP	1.21			
t-CB	2.03	0.797	0.549	0.293
c-CB	1.40			
Concentrations x 10^4, *M*:				
BA	24.6			
IBP	35.7			
t-CB	47.9	18.8	12.9	6.91
c-CB	33.0			

Internal Standard: 0.00300*M* n-$C_{10}H_{21}OH$

366 nm Radiation

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 133°

Table 25. Photolysis of 0.100*M* DMVP in Cyclooctane: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
Relative vpc Areas:							
Propene	2.45						
IH	3.78						
MP	2.75						
BA	0.588						
IBP	1.88	1.29	1.04	0.912	0.820	0.746	0.687
t-CB	2.51	1.75	1.47	1.25	1.14	0.990	0.876
Concentrations x 10^3, *M*:							
Propene	4.90						
IH	3.78						
MP	2.75						
BA	2.82						
IBP	5.80	3.97	3.20	2.81	2.53	2.30	2.12
t-CB	6.17	4.30	3.61	3.07	2.82	2.44	2.15
Φ:							
Propene	0.050						
IH	0.038						
MP	0.028						
BA	0.029						
IBP	0.059	0.040	0.033	0.029	0.026	0.023	0.022
t-CB	0.063	0.044	0.037	0.031	0.029	0.025	0.022

Internal Standards: 0.00100*M* Cyclohexane for Propene, IH, and MP

0.00200*M* n-$C_{15}H_{32}$ for BA, IBP, and t-CB

313 nm Radiation: 0.0983 ξ/1

vpc Columns: 25' 25% 1,2,3-tris(2-Cyanoethoxy)propane at 60°

9' 4% QF-1, 1% Carbowax 20M at 160°

Table 26 Photolysis of 0.100*M* DMVP in Cyclooctane: 2-Chloronaphthalene Quencher

[Quencher], *M*:	none	0.0100	0.0200	0.0300	0.0400	0.0500
Relative vpc Areas:						
BA	0.368	0.194	0.148	0.105	0.082	0.066
IBP	1.19	0.799	0.605	0.493	0.366	0.278
t-CB	1.85	1.15	0.871	0.748	0.539	0.489
c-CB	1.27					
Concentrations x 10^4, *M*:						
BA	16.9	8.9	6.8	4.8	3.8	3.0
IBP	35.2	23.6	17.9	14.6	10.8	8.2
t-CB	48.0	29.8	22.6	19.4	14.0	12.7
c-CB	33.0					

Internal Standard: 0.00300*M* n-$C_{10}H_{21}OH$

366 nm Radiation

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 133°

Table 27. Photolysis of 0.100*M* DMVP in 1-Propanol: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0150	0.0200	0.0250	0.0350
Relative vpc Areas:					
IBP	1.72	1.09	0.999	0.852	0.718
t-CB	1.51	0.940	0.817	0.702	0.585
c-CB	1.76	1.05	0.919	0.786	0.657
Concentrations x 10^3, *M*:					
IBP	5.30	3.34	3.08	2.62	2.21
t-CB	3.70	2.31	2.01	1.73	1.44
c-CB	4.33	2.57	2.26	1.93	1.62
Φ:					
IBP	0.177	0.111	0.103	0.087	0.074
t-CB	0.123	0.077	0.067	0.058	0.048
c-CB	0.144	0.086	0.075	0.064	0.054

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0300 ξ/l

vpc Column: 9' 4% QF-1, 1% Carbowax 20M at 110°

Table 28. Photolysis of 0.100*M* DMVP in 1-Pentanol: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0250	0.0350
Relative vpc Areas:						
t-CB	1.27	1.02	0.902	0.820	0.781	0.649
c-CB	1.44	1.15	1.01	0.910	0.868	0.707
Concentrations x 10^3, *M*:						
t-CB	3.13	2.50	2.22	2.02	1.92	1.60
c-CB	3.53	2.83	2.49	2.24	2.14	1.74
Φ:						
t-CB	0.104	0.083	0.074	0.067	0.064	0.053
c-CB	0.118	0.094	0.083	0.075	0.071	0.058

Internal Standard: 0.00200*M* n-$C_{15}H_{32}$

313 nm Radiation: 0.0300 ξ/l

vpc Column: 9' 4% QF-1, 1% Carbowax 20M at 110°

Table 29. Photolysis of 0.0500*M* DMVP in 1-Heptanol: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
Relative vpc Areas:							
t-CB	2.60	2.10	2.00	1.86	1.67	1.57	1.44
Concentrations x 10^3, *M*:							
t-CB	3.64	2.94	2.80	2.61	2.34	2.20	2.02
Φ:							
t-CB	0.122	0.098	0.094	0.087	0.078	0.074	0.067

Internal Standard: 0.00100*M* n-$C_{17}H_{36}$

313 nm Radiation: 0.0300 ξ/1

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 120°

2. α-Chloro-α-methylvalerophenone

The tabulation of data for each photokinetic run using CMVP includes relative vpc peak area data for the photo and thermal products and, where measured, the relative vpc peak area data for the thermal products only. This thermal product data was determined by use of blanks, samples treated identically to the photolyzed tubes except for the irradiation step, when the blanks where kept in the dark at room temperature. The tables contain the concentrations of CMVP, internal standards, quenchers, other additives, if any, and products, together with the vpc analysis conditions, irradiation wavelengths, actinometer results, and quantum yields.

For the major CMVP photoproducts, the reproducibility of the relative vpc peak areas and concentrations is approximately ±15%, this large range being a result of the many minor products which complicate the analyses and of the need to adjust for the thermal products. As with the DMVP photokinetic runs, the precision of the actinometry introduces an additional ±3% uncertainty in the reproducibility of the quantum yields. The $k_q\tau$ values obtained from the CMVP data are reproducible to within ±15%.

Table 30. Photolysis of 0.100*M* CMVP in Benzene: *cis*-Piperylene Quencher

[Quencher], *M*:	none	0.250	0.500	0.750	1.000	1.250
Relative vpc Areas, Photo and Thermal Products:						
PPP[a]	0.016	0.074	0.182	0.232	0.285	0.368
β,γ-U[b]	1.03	0.503	0.394	0.279	0.212	0.188
α,β-U[c]	0.874	0.692	0.662	0.542	0.430	0.430
CCB[d]	0.130	0.113	0.087	0.064	0.040	0.039
HMVP[e]	0.438	0.178	0.167	0.156	0.152	0.168
Relative vpc Areas, Thermal Products Occurring under Designated Peaks:						
PPP	0.016	0.051	0.150	0.268	0.282	0.396
β,γ-U	0.267	0.174	0.173	0.120	0.073	0.096
α,β-U	0.065	0.047	0.069		0.038	0.044
CCB	0.023	0.023	0.024	0.025	0.019	0.023
HMVP	0.169	0.172	0.149	0.172	0.162	0.178
Relative vpc Areas, Photoproducts Only:						
β,γ-U	0.764	0.329	0.221	0.159	0.139	0.092
α,β-U	0.809	0.645	0.593	∿0.489	0.392	0.386
CCB	0.107	0.090	0.063	0.038	0.022	0.017
HMVP	0.269	0.00	0.00	0.00	0.00	0.00
Concentrations of Photoproducts x 10^5, *M*:						
β,γ-U	84.3	36.3	24.4	17.6	15.3	10.2
α,β-U	89.3	71.2	65.5	∿54.0	43.3	42.6
CCB	11.5	9.7	6.8	4.1	2.3	1.8
HMVP	28.9					
Φ:						
β,γ-U	0.133	0.057	0.038	0.028	0.024	0.016
α,β-U	0.141	0.112	0.103	∿0.085	0.068	0.067
CCB	0.0182	0.0153	0.0107	0.0065	0.0037	0.0028
HMVP	0.046					

Internal Standard: 0.000600*M* n-$C_{20}H_{42}$
313 nm Radiation: 0.00633 ξ/l
vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 145°

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[a] 1-Phenyl-2-propylprop-2-en-1-one. Product involving piperylene has same retention time.

[b] 1-Phenyl-2-methylpent-3-en-1-one

[c] 1-Phenyl-2-methylpent-2-en-1-one

[d] 2-Chloro-1-phenyl-2,4-dimethylcyclobutanol

[e] α-Hydroxy-α-methylvalerophenone

Table 31. Photolysis of 0.100*M* CMVP in Benzene with 0.50*M* Pyridine: *cis*-Piperylene Quencher

[Quencher], *M*:	none	0.100	0.200	0.500	1.00	3.00	6.99
Relative vpc Areas, Photo and Thermal Products:							
β,γ-U	0.519	0.344	0.257	0.199	0.153		
α,β-U	0.535	0.479	0.447	0.384	0.347	0.281	0.256
CCB	0.163	0.131	0.109	0.114	0.069	0.041	0.001
HMVP	0.224	0.180	0.189	0.175	0.174	0.172	0.146
RCMVP[a]	0.246	0.136	0.139	0.122	0.140	0.142	0.178
Relative vpc Areas, Thermal Products Occurring under Designated Peaks:							
β,γ-U	0.078						
α,β-U	0.166						
CCB	0.006						
HMVP	0.174						
RCMVP	0.102						
Relative vpc Areas, Photoproducts Only:							
β,γ-U	0.441	0.266	0.179	0.121	0.075		
α,β-U	0.369	0.313	0.281	0.218	0.181	0.115	0.090
CCB	0.157	0.125	0.103	0.108	0.063	0.035	0.000
HMVP	0.050	0.01	0.02	0.00	0.00	0.00	0.00
RCMVP	0.144	0.03	0.04	0.02	0.04	0.04	0.08
Concentrations of Photoproducts x 10^5, *M*:							
β,γ-U	81.1	48.9	32.9	22.3	13.8		
α,β-U	67.9	57.6	51.7	40.1	33.3	21.2	16.6
CCB	28.1	22.4	18.4	19.3	11.3	6.3	0.0
HMVP	9.0						
RCMVP	25.8						
Φ:							
β,γ-U	0.100	0.060	0.040	0.027	0.017		
α,β-U	0.083	0.071	0.063	0.049	0.041	0.026	0.020
CCB	0.034	0.028	0.023	0.024	0.014	0.008	0.000
HMVP	0.011						
RCMVP	0.032						

Internal Standard: 0.00100*M* n-$C_{20}H_{42}$
313 nm Radiation: 0.00815 ξ/l
vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 140°

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[a] γ- or β-CMVP

Table 32. Photolysis of 0.100*M* CMVP in Benzene to $\sim$15% Conversion: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.0500	0.100	0.150	0.200	0.300	0.400
Relative vpc Areas, Photo and Thermal Products:							
β,γ-U	1.25	1.36	1.29	1.23	1.17	1.11	1.07
α,β-U	0.440	0.668	0.634	0.616	0.592	0.564	0.543
CCB	0.098	0.076	0.070	0.066	0.065	0.058	0.054
RCMVP	0.564	0.420	0.416	0.394	0.398	0.373	0.364
Concentrations x 10^4, *M*, Photo and Thermal Products:							
β,γ-U	75.3	82.3	77.7	74.4	70.8	67.0	64.6
α,β-U	26.6	40.3	38.3	37.2	35.8	34.1	32.8
CCB	5.7	4.4	4.1	3.9	3.8	3.4	3.2
RCMVP	32.9	24.5	24.3	23.0	23.2	21.8	21.3
Concentrations of Photoproducts x 10^4, *M*, Estimated from Low Conversion Data:							
β,γ-U	49.4						
α,β-U	52.3						
CCB	6.8						
Φ:							
CCB	0.015	0.012	0.011	0.0105	0.010	0.0091	0.0086

Internal Standard: 0.00400*M* $n\text{-C}_{17}\text{H}_{36}$

313 nm Radiation: 0.0372 ξ/1

vpc Column: 6' 4% QF-1, 1.2% Carbowax 20M at 130°

Table 33. Photolysis of 0.100*M* CMVP in Acetonitrile: Effect of *t*-Butylmercaptan

[t-C_4H_9SH]	PPP	β,γ-U	α,β-U	CCB	HMVP	RCMVP
Relative vpc Areas, Photo and Thermal Products:						
none	0.105	0.251	1.32	0.052	0.219	
0.200*M*	0.041	0.339	0.988	0.050	0.224	
0.500*M*		0.487	0.665	0.046	0.238	
Relative vpc Areas, Thermal Products Occurring under Designated Peaks:						
none	0.000	0.105	0.086	0.000	0.195	0.157
0.200*M*	0.000	0.084	0.076	0.000	0.197	0.158
0.500*M*	0.000	0.082	0.060	0.000	0.189	0.153
Relative vpc Areas, Photoproducts Only:						
none	0.105	0.146	1.23	0.052	0.024	
0.200*M*	0.041	0.255	0.912	0.050	0.027	
0.500*M*		0.405	0.605	0.046	0.049	
Concentrations of Photoproducts x 10^5, *M*:						
none	17.7	24.6	208.	8.5	3.9	
0.200*M*	6.9	43.0	154.	8.1	4.4	
0.500*M*		68.4	102.	7.5	7.9	
Φ:						
none	0.029	0.040	0.342	0.014	0.006	
0.200*M*	0.011	0.071	0.253	0.013	0.007	
0.500*M*		0.113	0.168	0.012	0.013	

Internal Standard: 0.00200*M* n-$C_{10}H_{21}OH$

313 nm Radiation: 0.00608 ξ/l

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 130°

Table 34. Photolysis of 0.100*M* CMVP in Acetonitrile: 2,5-Dimethyl-2,4-hexadiene Quencher

[Quencher], *M*:	none	0.100	0.200	0.300	0.500	1.00
Relative vpc Areas, Photo and Thermal Products:						
β,γ-U	0.188	0.185	0.208	0.205	0.294	0.255
α,β-U	0.706	0.623	0.562	0.492	0.484	0.327
CCB	0.034					
HMVP	0.282	0.324	0.295	0.254	0.333	0.232
RCMVP	0.198					
Concentrations x 10^5, *M*, Photo and Thermal Products:						
β,γ-U	31.7	31.2	35.1	34.6	49.6	43.0
α,β-U	119.	105.	94.9	83.0	81.7	55.2
CCB	5.5					
HMVP	45.7	52.6	47.8	41.2	54.0	37.6
RCMVP	32.1					
Concentrations of Photoproducts x 10^5, *M*, Estimated from Preceding Table:						
β,γ-U	16.6					
α,β-U	140.					
CCB	5.7					
HMVP	2.6					
Concentrations of Photoproducts x 10^5, *M*, Based upon Above Estimates:						
β,γ-U	16.6	16.1	20.0	19.5	34.5	27.9
α,β-U	119.	105.	94.9	83.0	81.7	55.2
CCB	5.5					
Φ:						
β,γ-U	0.040	0.039	0.049	0.048	0.084	0.068
α,β-U	0.290	0.256	0.231	0.202	0.199	0.135
CCB	0.013					

Internal Standard: 0.00200*M* n-$C_{10}H_{21}OH$

313 nm Radiation: 0.00411 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 120°

Table 35. Photosensitization of CMVP by and in Methyl Ethyl Ketone[a]

[CMVP]	PPP	β,γ-U	α,β-U	CCB	HMVP	RCMVP	RCMVP[b]
Relative vpc Areas, Photo and Thermal Products:							
0.0100*M*	0.109	0.289	0.603	0.111	0.154	0.078	0.078
0.0200*M*	0.113	0.523	0.904	0.125	0.348	0.144	
Relative vpc Areas, Thermal Products Occurring under Designated Peaks:							
0.0100*M*	0.000	0.023	0.030	0.000	0.013	0.000	0.000
0.0200*M*	0.000	0.077	0.057	0.000	0.054	0.000	0.000
Relative vpc Areas, Photoproducts Only:							
0.0100*M*	0.109	0.266	0.573	0.111	0.141	0.078	0.078
0.0200*M*	0.113	0.446	0.847	0.125	0.294	0.144	
Concentrations of Photoproducts x 10^5, *M*:							
0.0100*M*	5.01	12.2	26.4	4.97	6.31	3.5	3.5
0.0200*M*	5.20	20.5	39.0	5.59	13.2	6.44	
Φ:							
0.0100*M*	0.012	0.030	0.064	0.012	0.015	0.008	0.008
0.0200*M*	0.013	0.050	0.095	0.014	0.032	0.016	

Internal Standard: 0.000250*M* $n\text{-}C_{20}H_{42}$

313 nm Radiation: 0.00411 ξ/1

vpc Column: 9' 5% QF-1, 1.2% Carbowax 20M at 140°

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[a] 11.1*M*

[b] Both isomers analyzed

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