ABSTRACT

EXCURSIONS INTO CHARGE AND ENERGY TRANSFER MECHANISMS: CONFORMATIONAL EFFECTS IN EXCITED STATES

By

Bernard Joseph Scheve

Part I Biphenyls

Electron spin resonance (ESR) spectra of chloro- and methyl-substituted biphenyls, coupled with the measured efficiencies with which these biphenyls quench the phosphorescence and photoreduction of benzophenone, indicate that two methyl groups located in the *ortho*, *ortho*'-positions of biphenyl are necessary to force triplet biphenyl from planarity.

The electron spin resonance data indicate that two triplet species are produced from both 3,3' and 2,2'-dimethylbiphenyl. These are interpreted as corresponding with the Z and E conformations. Only Z-2,2'-dimethylbiphenyl can be deduced to be non-planar as evidenced by its higher D value than those of the other biphenyls. Decay rates of the triplet produced from the chloroderivatives during the ESR studies indicate that chlorine is being expelled.

The data obtained from the Stern-Volmer analysis of the quenching of triplet benzophenone by the mono-substituted biphenyls suggest that *ortho*-substituents raise the triplet energy of biphenyl and that *para*-substituents lower the triplet energy of biphenyl. Methyl groups have less effect on the triplet energies than do chloro groups. These conclusions are reinforced by absorption and phosphorescence spectra.

Part II

Azidoalkyl Phenyl Ketones

The Type II photoelimination efficiencies were measured for γ-, δ-, and ε-, azidoalkyl phenyl ketones. Quenching of the excited state by an efficient triplet quencher allows kinetic analysis by the Stern-Volmer relationship. The rate data obtained for the δ- and ε- azidoketones were compared to a Hammett σ_ρ plot previously obtained with other substituents. The inductive substituent constant σ_I of the azido group is calculated to be 0.46. The rate data for the γ-azidoketones were quantitatively separated into inductive and radical stabilizing constituents, since ρ for the γ-carbon has been estimated to be -4.3. The Stern-Volmer treatment of the data also allows calculation of the rates of energy transfer from the carbonyl moiety to the azido moiety. The rate of this endothermic intramolecular energy transfer

was found to be lower than that of exothermic intermolecular energy transfer.

Part III

Piperidyl Ketones

A synthesis of N-substituted-4-methyl-4-benzoylpiperidine is described. Irradiation of this Demerol-type compound produces 2-methyl-5-methyl-6-phenyl-2-aza-bicyclo [3.1.1]hepta-6-ol (a member of the amphetamine family). The efficiencies with which the N-methyl derivative undergoes the Type I and Type II reactions were determined. Quenching studies indicate that the two reactions occur from two distinct triplets, presumably two different conformers. Their triplet lifetimes, determined by Stern-Volmer analysis, are compared to those of 1-methylcyclohexyl phenyl ketone and γ-dimethylaminobutyrophenone. The results indicate that there is no intramolecular charge-transfer quenching of the triplet carbonyl by the nitrogen lone pair in the piperidyl ketones. A Stern-Volmer quenching study of 1-methylcyclohexyl phenyl ketone by N-methylpiperidine indicates about a 50 fold decrease in the rate constant for intermolecular charge-transfer quenching relative to the quenching rate observed for diene quenching of the ketone. This suggests that there exists a large steric barrier to charge transfer quenching.

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Bernard Joseph Scheve

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To Anne, Tim, and Company

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INTRODUCTION

Introductory Remarks:

This thesis is composed of three overlapping but distinct problems. To avoid duplication of material, the Introduction is composed of one part, in which material relevant to each problem will be discussed as it applies under the specific heading. Thus each subject heading may deal with information relevant to one or more of the undertaken projects. The Experimental section is also composed of one part in which all the materials used in the various problems are presented. The Results section treats each project separately and the results of each project are followed immediately by the Discussion of those results.

Objectives:

The central objective of this thesis was to study sundry steric effects involved in energy and charge-transfer exchanges.

Steric effects were involved in all three separate projects: (1) Determination of the size of *ortho*-substituents necessary to force triplet biphenyl out of planarity and construction of a potential energy diagram for biphenyl. (2) The photochemistry of N-substituted-4-methyl-4-benzoyl piperidine. This kind of compound was interesting since the lone pair electrons located on nitrogen are held in a fairly rigid position relative to the carbonyl. Interaction of the lone pair electrons with the carbonyl moiety should be difficult in any conformation except the boat form. The rates for the various processes the ketone may undergo could be compared to those previously determined for the "model" compounds 1-methylcyclohexyl phenyl ketone and γ-dimethylaminobutyrophenone. (3) Determination of the rate of intramolecular endothermic energy transfer from a triplet carbonyl group to an azido-group as a function of the number of methylenes separating them. This last problem included as minor objectives determination of the unmeasured σ_I value for the azido group, and of the amount of stabilization an azido group imparts to an adjacent radical center.

In the course of this study all the major reactions of excited ketones were encountered. These include energy transfer, charge-transfer, hydrogen atom abstraction, and α-cleavage to radicals. Thus, the Introduction will continue with a brief survey of current knowledge about these reactions and will conclude with a brief description of each project. The presentation follows the following outline: (1) A Jablonski diagram showing the photophysical process undergone be excited state molecules, particularly phenyl ketones; (2) Energy transfer mechanisms involving aspects of intermolecular, intramolecular, and reversible exchanges; (3) Hydrogen abstraction processes relevant to the photoreduction of benzophenone and the Type II reactions; (4) Type I Photocleavage; (5) Inter-and intramolecular charge transfer mechanisms specifically related to amine quenching of carbonyls; (6) The triplet state of biphenyl; (7) Piperidyl phenyl ketones in relation to cyclohexyl phenyl ketones; (8) A discussion of the azide group during photoexcitation processes and a synopsis of triplet nitrene chemistry.

Jablonski Diagram:

The fate of electronic excitation in phenyl alkyl ketones is depicted in the modified Jablonski[1] diagram shown in Figure 1. The horizontal lines represent the lowest vibrational levels of different electronic states. The straight arrows represent radiative transitions and the wavy arrows non-radiative physical processes. The diagram depicts absorption of a photon to the excited singlet manifold with rapid internal conversion to the lowest vibration level of the first excited singlet.

In benzophenone and most alkyl phenyl ketones the probability for isoenergetic intersystem crossing to the triplet manifold from the singlet manifold is unity[2,3], thus radiationless decay from the singlet and fluorescence are negligible.

Once the triplet state is formed the molecule rapidly relaxes to the lowest triplet vibrational level (necessarily lower than the singlet because of Hund's rule). Solvent and

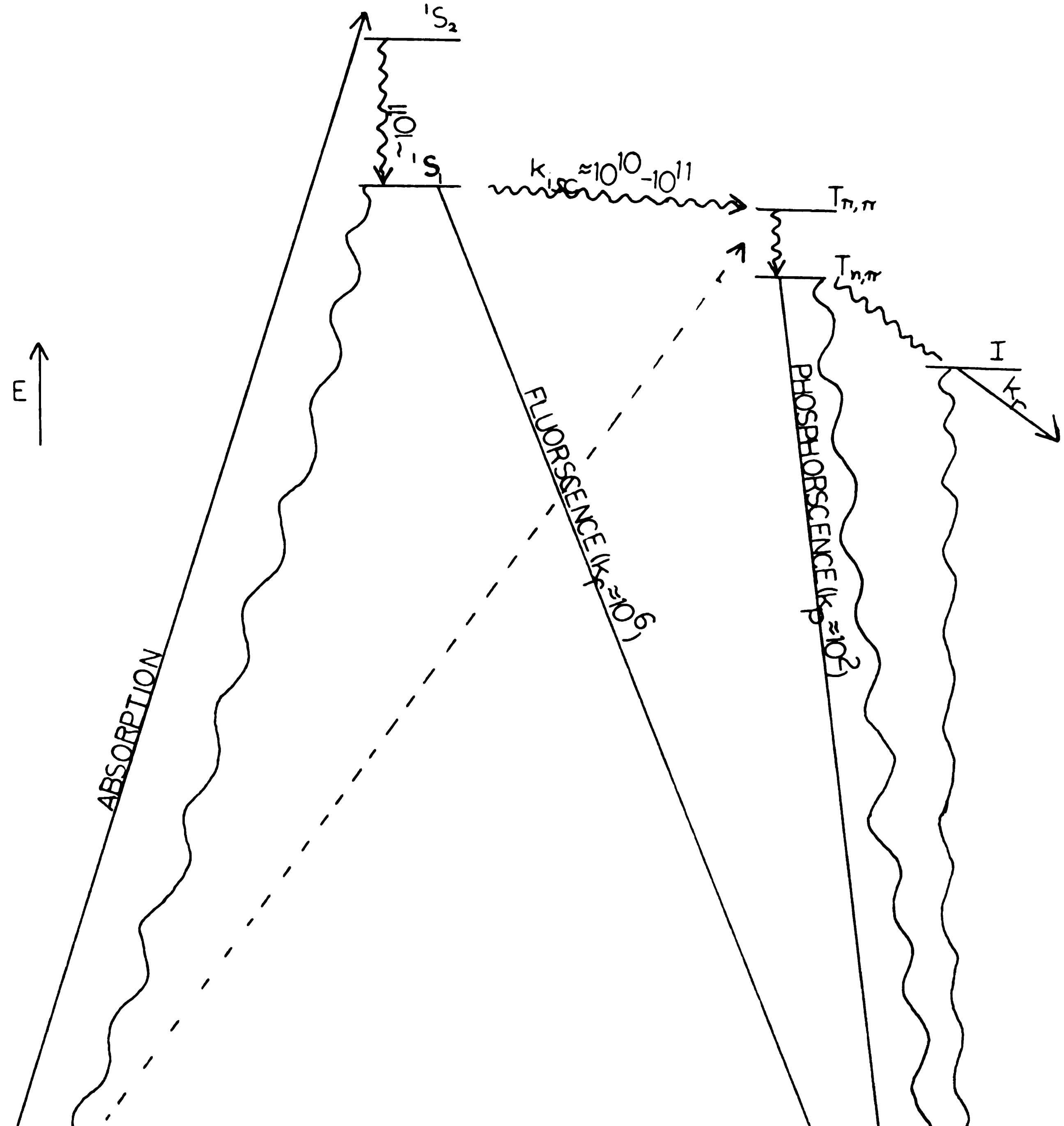
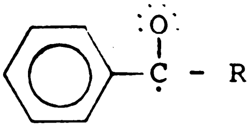


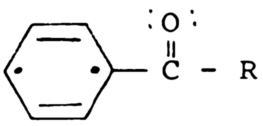
Figure 1

Modified Jablonski Diagram

substituents dictate the nature of the lowest triplet, since $^3n,\pi^*$ and $^3\pi,\pi^*$ states have similar energies in alkyl phenyl ketones. Polar solvents and electron donating ring substituents tend to lower the $^3\pi,\pi^*$ state relative to the $^3n,\pi^*$ state.[4]



$^3n,\pi^*$



$^3\pi,\pi^*$

Formally $^3n,\pi^*$ states arise via the promotion of a non-bonding electron on oxygen to an antibonding π^* orbital, while $^3\pi,\pi^*$ states involve the promotion of an electron from the π system to an anti-bonding π^* orbital. The nature of the lowest triplet naturally determines the rates of decay, phosphorescence, and reaction. Phosphorescence of $^3n,\pi^*$ triplets characteristically has a much shorter lifetime than that of their $^3\pi,\pi^*$ counterparts[4,5] and $^3\pi,\pi^*$ emission is much more solvent and substituent dependent.[6,7] Wagner and Kemppainen[8], by studying the rates of decay and γ-hydrogen abstraction of various alkyl phenyl ketones, have concluded that the two states are probably in thermal equilibrium and that the $^3n,\pi^*$ is responsible for all the reaction even when the $^3\pi,\pi^*$ is the lowest state.

In the case of the biphenyls the intersystem crossing yield is not unity, so fluorescence, radiationless decay, and reaction from the singlet can compete with intersystem crossing to the triplet.

The dotted line in Figure 1 indicates the strongly forbidden S→T* absorption process. When the ground and triplet states have the same geometry, S→T* absorption and T*→S phosphorescence spectra should be mirror images of each other and their 0-0 bands should overlap. Such is not the case either for phenyl ketones or for biphenyl,[9] as discussed later.

Energy Transfer:

Probably the most general reaction excited states undergo is the process of energy transfer. This is the process whereby a donor molecule transfers its electronic excitation to a ground state acceptor(quencher). The acceptor ends up in an electronically excited state and the donor in its ground state. Energy transfer can occur both inter-and intramolecularly by three distinct mechanisms: (1) reabsorption by a ground state molecule of light emitted by a fluorescent donor; (2) dipolar or quadrupolar interactions between excited donor and ground state acceptor molecules, which accounts for singlet-singlet energy transfer over relatively long distances; and (3) exchange interactions which are responsible for triplet-triplet energy transfer.[10] Several review chapters have been written on these processes. 11-13

The triplet-triplet energy transfer process is the most important with respect to phenyl ketones, since intersystem crossing yields are generally high. It involves a resonance exchange interaction which requires spatial overlap of the orbitals of donor and acceptor.[15-20] Uncertainty in just how close donor and acceptor must come to promote the exchange interaction required for the transfer has elicited a search for steric effects in triplet-triplet energy transfer processes[20-22]. Wagner and McGrath[23] have shown that donor and acceptor do not have to approach within bonding distance to achieve actual transfer.

Dexter[16] presented equation (1) to describe the dependence of rates of exchange-induced energy transfer on the distance R between donor and acceptor, where L is a fixed

$$k_{et}=Y \exp (-2R/L) \qquad (1)$$

distance related to the "average effective Bohr radius" (which has never been specified) and Y includes several parameters related to spin statistics and orbital overlap. Under conditions when exothermic energy transfer between triplet ketone and diene molecules in a solvent cage occurs, R is close to the sum of the van der Walls radii, 3.5-4 Å. The rate constant, k_{et}, for this process in benzene has been measured at 5×10^{9} M^{-1} sec^{-1}.[15,18,24-26] Cowan and Baum[27] have measured k_{et} values from 1×10^{11} to 3×10^{9} M^{-1} sec^{-1} for intramolecular energy transfer in styryl ketones where the separation between donor and acceptor varies from 2 to 4 methylene groups. In the ketones studied, the number of conformations in which the two ends of the molecule are in contact decreases rapidly with an increasing number of methylene groups. It has been estimated that every 1.2 Å increase in R results in an order of magnitude decrease in k_{et}.[23,28] It is quite possible that the observed rates measured by Cowan contain some measure of the rates of rotation of the olefin about the methylene chain or some measure of the ring strain formed in the energy transfer process.

The rate of exothermic triplet energy transfer in solution is influenced by the viscosity of the solvent[11,15,17,29,30]. In moderately viscous alcohols, glycols, or parafin oil-hexane mixtures, the quenching rate constant k_{et} is inversely proportional to viscosity, η, according to the modified Debye equation (2)[15,31].

$$k_{et}=k_{diff}=8RT/2000\eta \qquad (2)$$

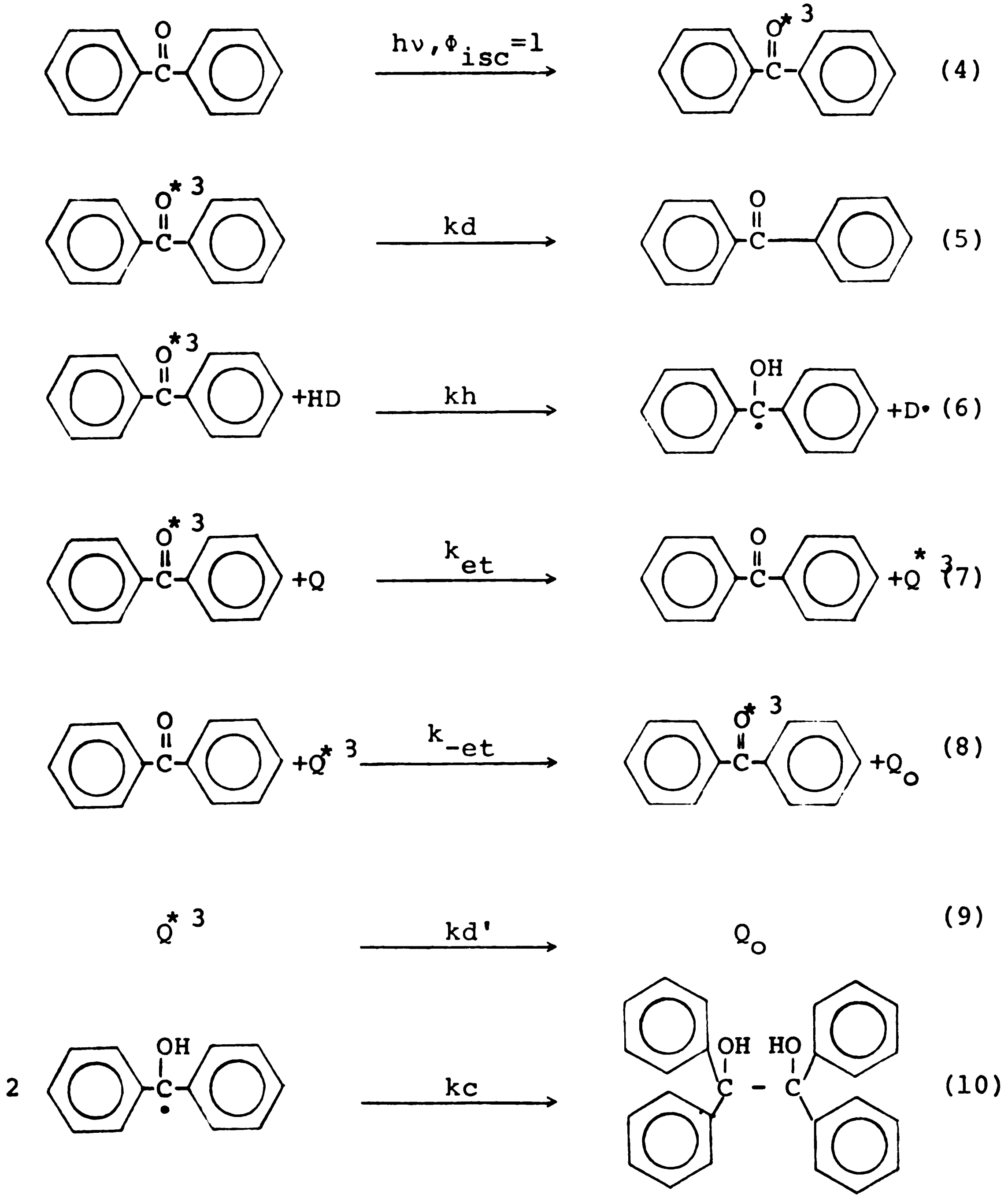
In less viscous solvents, the quenching rate constant still increases as the viscosity decreases but becomes lower than the calculated diffusion-controlled rate, indicating that there is inefficiency in the energy transfer process and that diffusion apart of the donor and acceptor can compete with energy transfer during the lifetime of a solution encounter.[15] The theoretical implication of k_{et} being less than k_{diff} 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, or simply that R does not get small enough.[23]

When the donor and acceptor have similar enough triplet energies such that energy transfer is reversible, the actually observed rate constant is given by equation (3) and depends on the donor concentration.[19]

$$k_{et}^{obs} = \frac{k_{et}}{1+k_{-et}[D]} \qquad (3)$$

In benzene at room temperature, the rate constant for quenching is 5 x 10^9 M^{-1} sec^{-1} when triplet energy transfer is exothermic and irreversible ($\Delta E \geq 3$-4 kcal/mole).[15,18,24,26] When reverse energy transfer[17,19] from the excited acceptor back to the original donor is possible, it appears that the rate of quenching is still 5 x 10^9 M^{-1} sec^{-1}, even where the energy transfer process is only 1 kcal/mole exothermic. The notion that vertical triplet energy transfer in solution proceeds at the same maximum rate as long as it is exothermic was originally proposed by Sandros[19], who first presented the kinetic treatment for reversible energy transfer. This treatment is similar to the ones used for the quenching of the photoreduction of benzophenone, where the triplet energies of the donor and acceptor are nearly identical.[9]

Knowledge of energy transfer rates is not only interesting in itself, but such concepts can be used for measuring excited state lifetimes. The most common technique for doing so involves Stern-Volmer quenching studies. This process is exemplified by the photoreduction of benzophenone presented in Scheme 1 where HD is a hydrogen donor and Q is a quencher molecule.



Scheme I

Mechanism for the Photoreduction of Benzophenone

Straightforward Stern-Volmer analysis (ignoring the reversible energy transfer equations 8 and 9) yields equation (11):

$$\frac{\Phi_o}{\Phi} = 1 + k_{et}\tau[Q] = 1 + \frac{k_{et}[Q]}{k_d + k_h[isp]} \qquad (11)$$

Equation (12) (which includes steps 8 and 9) substitutes equation (3) for k_{et}:

$$\frac{\Phi_o}{\Phi} = 1 + \frac{k_{et}\tau[Q]}{1 + \frac{k_{-et}[K]}{k_d'}} \qquad (12)$$

Equation (12) also describes the inverse relationship between the slopes of the Stern-Volmer plots and ketone concentration. Letting S equal the slope of a given Stern-Volmer, equation (13) results:

$$\frac{1}{S} = \frac{1}{k_{et}\tau}\left(1 + \frac{k_{-et}[K]}{k_{d'}}\right) \qquad (13)$$

The intercept of a plot of 1/S versus $[K]$ gives the true $k_{et}\tau$ value for the quencher in question and the slope divided by the intercept equals k_{-et}/k_d'.

Hydrogen-Atom Abstraction

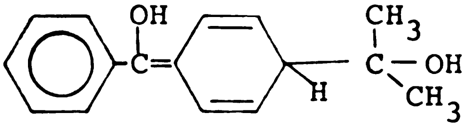
It has thus far been assumed that the species responsible for reactions involving carbonyl compounds is largely the triplet. Evidence for the triplet multiplicity of the excited state responsible for photoreduction and the Type II reaction comes from both chemical and spectroscopic evidence. Hammond measured the excited state lifetimes of benzophenone in several solvent systems,[32,33] finding them much too long to be singlets. Backstrom and Sandros[34] sensitized the phosphorescence emission of biacetyl with benzophenone, and Terenin and Ermolaev[14] observed that in EPA glass at 77° K benzophenone sensitizes the phosphorescence of naphthalene while simultaneously quenching its own phosphorescence. Both of these triplet quenchers (naphthalene & biacetyl) also quench ketone photoreduction. Walling and Gibian[35] and Padwa[36] have found that the behavior of the carbonyl triplet parallels very closely that of *tert*-butoxy radicals in hydrogen abstraction reactions.

(a) Photoreduction of Benzophenone:

Although photoreduction has always played an essential role in nature in the utilization of CO_2 by plants, products from even "simple" laboratory systems were not characterized until 1900, when Ciamician and Silber[37] first identified benzpinacol and acetone as the photoproducts from the action of sunlight on an isopropanol solution of benzophenone. Many other substrates have also been used as the hydrogen source, including alkanes,[36] amines,[38] alkyl benzenes[32] and tributylstannane.[39]

Since 1900 the photoreduction of benzophenone has been the subject of a plethora of studies, so that at the present time its mechanism is pretty well determined. In fact the photoreduction of benzophenone by benzhydrol has been used as an actinometer.[40] A recent review article concerning the mechanism of the photoreduction and rates of hydrogen abstraction from various substrates by a variety of carbonyl compounds has been published.[82] The mechanism for the photoreduction of benzophenone is shown in Scheme 1. Thus this system should serve as a good monitor for measuring rates of energy transfer to, and thus the triplet energies of, various substituted biphenyls.

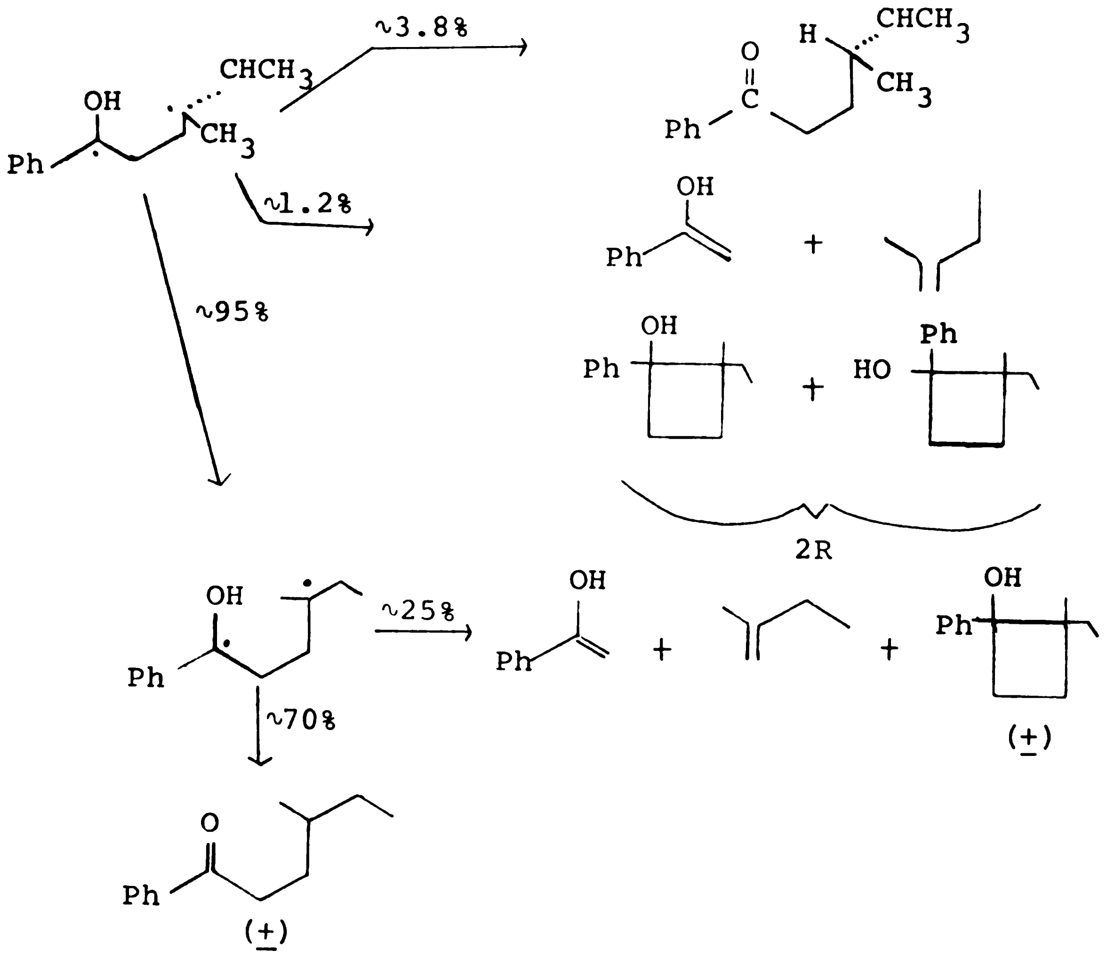
Although the photoreduction of benzophenone has been the subject of many studies, some minor points of its mechanism are still subject to controversy. The major controversy centers around the explanation of the yellow color which develops during the photoreduction.[41-43] The origin of this color has been found to be a long-lived intermediate whose nature has remained in doubt for nearly fifteen years. Recently, the enol coupling product (analogous to 1-diphenylmethylene-4-trityl-2,5-cyclohexadiene formed in the case of hexaphenylethane[44]) was proposed for this intermediate by several independent workers.[45-47]



Wagner[48] has estimated that for the photoreduction of benzophenone by benzhydrol, no more than 10% of the radicals produced form the coupled intermediates. Weiner[49] has questioned the intermediacy of such structures in the photoreduction. However, more recently, Lamb[50] presented product analysis studies on sterically hindered benzophenones which clearly indicate such coupled products are indeed formed.

(b) Type II Photoreaction:

Coincident with the developments in the photoreduction processes investigators were studying the Type II photoelimination process originally discovered by Norrish[51]. Noyes[52] first suggested that the Type II reaction proceeds by the intramolecular transfer of a γ-hydrogen yielding an olefin and an enol; the enol then rearranges to the carbonyl compound. The abstraction of the γ-hydrogen has been firmly established[53,54] and Yang[61] first observed that cyclobutanols are generally formed in conjunction with the elimination. The most compelling evidence for the presence of a 1,4-biradical via the 1,5-hydrogen shift has been presented by Wagner and Kelso. The photolysis of β,γ-diphenylbutyrophenone produced no triplet stilbene from triplet ketone even though energy and spin considerations showed that such a process could have proceeded concertedly. The combined quantum yield for α,β-cleavage, cyclization, and racemization of (4S)-(+)-methyl-1-phenyl-1-hexanone (MPH) was very near unity. Alcohol solvent caused the product quantum yield to be essentially unity while eliminating racemization of starting material. Thus, racemization and products arose from the same biradical intermediate. Furthermore, the biradical of valerophenone was actually trapped using alkyl thiols as trapping agents.[183] The mechanism for the Type II reaction can then be represented as in Scheme II:



Scheme II

Mechanism for Type II Reaction

The effect of substituents on the triplet state reactivity of phenyl alkyl ketones is continuing to be investigated. Electron withdrawing groups on the aromatic ring decrease the probability for product formation from the biradical by enhancing disproportionation to Type II products; electron donating groups have the opposite effect.[56,57] Strong electron withdrawing ring substituents double the triplet state reactivity, apparently by a simple inductive effect on the electrophilic $^3n,\pi^*$ carbonyl moiety.[56]

Phenyl ketones having γ- and δ-substituents show relative triplet state reactivities corresponding to the known reactivities of the various kinds of C-H bonds in the γ-position.[4,58] Ketones with γ- and δ-electron withdrawing groups have enhanced quantum yields in spite of their diminished rates of hydrogen abstraction. Apparently the reduced disproportionation of the biradical reflects the reduced nucleophilicity of the γ-radical site of the biradical. Quantum yields decrease with electron donating γ- and δ-substituents indicating enhanced disproportionation of the 1,4-biradical.

Wagner and Kemppainen[59] first indicated that Type II quantum yields do not directly relate to triplet state reactivity. Conversely they[60] have reported that rates of γ-hydrogen abstraction for various δ- and ε-substituted ketones do correlate with the σ_I values of the various substituents. By estimating the ρ value of the γ-substituted ketones as -4.3[60], the inductive and radical stabilizing effects of the γ-substituents can quantitatively be separated. Thus the ability of various substituents to stabilize a radical were calculated.

Lewis[62-66] has recently reported on the photochemistry of several conformationally interesting phenyl ketones, where the rates of γ-hydrogen abstraction are drastically affected by the geometry of the molecule. He[62] first noted that α-substitution increases the ratio of cyclobutanol formation to photoelimination products. Such substitution of α-methyl groups in alkyl phenyl ketones also leads to some competing α-cleavage.

Type I Photocleavage:

The Type I processes of ketones involve α-scission to give acyl and alkyl free radicals[67] which go on to form various stable products. In the case of ketones with differing degrees of alkyl substitution, Type I cleavage generally results in the formation of the more stable alkyl radical and the corresponding acyl radical.[68] In alkyl phenyl ketones containing α-substituents, the rate of the Type I process is fast enough to compete with the Type II process. Wagner and McGrath[69] have indicated that the rate of α-cleavage for α,α-dimethylvalerophenone is 1.4×10^7 sec^{-1}. This value is similar to the rates of α-cleavage obtained for exo-2-benzoyl-2-methylnorbornane (1.2×10^7 sec^{-1}) and 1-methylcyclopentyl phenyl ketone (1.3×10^7 sec^{-1}) reported by Lewis.[64] Johnson and Lewis[66] measured the rate of α-cleavage for 1-methylcyclohexylphenyl ketone as 2.5×10^7 sec^{-1}. However, this value is probably slightly high for reasons to be discussed below. Triplet phenyl t-butyl ketone cleaves with a rate of 2.3×10^7.[70]

Triplet aliphatic t-butylketones whether they contain either α-substituents or γ-hydrogens α-cleave about 4000 times faster than phenyl alkyl ketones containing α-substituents. The exact reason for this difference in rates between aliphatic ketones and phenyl alkyl ketones is not known, although it is probably due primarily to energetic differences or differences in geometry. It may be noted, however, that triplet phenyl ketones resemble triplet aliphatic ketones in rates of hydrogen abstraction[4] and singlet aliphatic ketones in rates of α-cleavage.[71,72]

Charge-Transfer:

A charge-transfer complex is defined as a combination of a donor and acceptor which exhibits a special light absorption called a charge-transfer transition. In its broadest terms it includes the newer concepts of excimers and exciplexes. The concept of charge-transfer was first formulated by Mulliken[73] to explain the fact that iodine dissolved in carbon tetrachloride is violet while in benzene solution it is brown. Charge transfer interactions are small in the ground state and often difficult to distinguish from other types of electrical interactions such as mutual polarization.[74] Interestingly, Leonhardt and Weller[75] demonstrated by flash-spectroscopic investigations of perylene solutions containing amine that electron transfer, not possible between the ground state donor and acceptor, could occur when the molecule was electronically excited. Mataga and Ezumi[76] observed long-wavelength fluorescence from some aromatic hydrocarbons in N,N-dimethyl aromatic amine solvents. This in conjunction with the electron affinities of the excited aromatic hydrocarbons and the ionization potentials of the amines led Mataga and Ezumi to conclude that the interaction between excited hydrocarbon and amine involved charge transfer from the amine to the excited hydrocarbon.

The ionization potentials of amines have been correlated with the rate of interaction between amine and electronically excited ketone. Davis[77] found that the efficiency of quenching of fluorenone fluorescence by various amines varied inversely with the ionization potential of the amine. Cohen and Stein[78] showed that amines with lower ionization potentials were more reactive in the photoreduction of 4-benzoylbenzoate anion than those amines with higher ionization potentials.

(A) Intermolecular:

Aromatic ketones can be photoreduced efficiently in the presence of molecules bearing the -CHN-group[79]. For example, triethyl amine[81] reduces triplet 2-acetonaphthone about one thousand times faster than does ethanol. Triplet fluorenone abstracts hydrogens from tributylstannane about one tenth as fast as it interacts with triethylamine[83]. Moreover, by quenching the photoreduction of benzophenone by 2-butylamine with naphthalene, the rate of reaction was determined to be about 5×10^7 M^{-1} sec^{-1} [84], which is more than an order of magnitude greater than that found when benzhydrol or 2-propanol are the hydrogen sources. Yet benzophenone interacts with triethylamine three orders of magnitude faster than with isopropyl alcohol.[80] Since the rate of quenching by amines of ketone phosphorescence and fluorescence is faster than the observed rate of photoreduction[83], the rate of interaction of the donor and acceptor is faster than the rate of hydrogen transfer. Thus the following mechanism has been proposed.[85]

$$R_2C{=}O^{*3}+RCH_2\ddot{N}R_2 \longrightarrow [\bar{R}_2\dot{C}{-}O^{-} \quad R_2\overset{\cdot+}{N}CH_2R] \longrightarrow R_2\dot{C}OH+R\dot{C}HNR_2$$

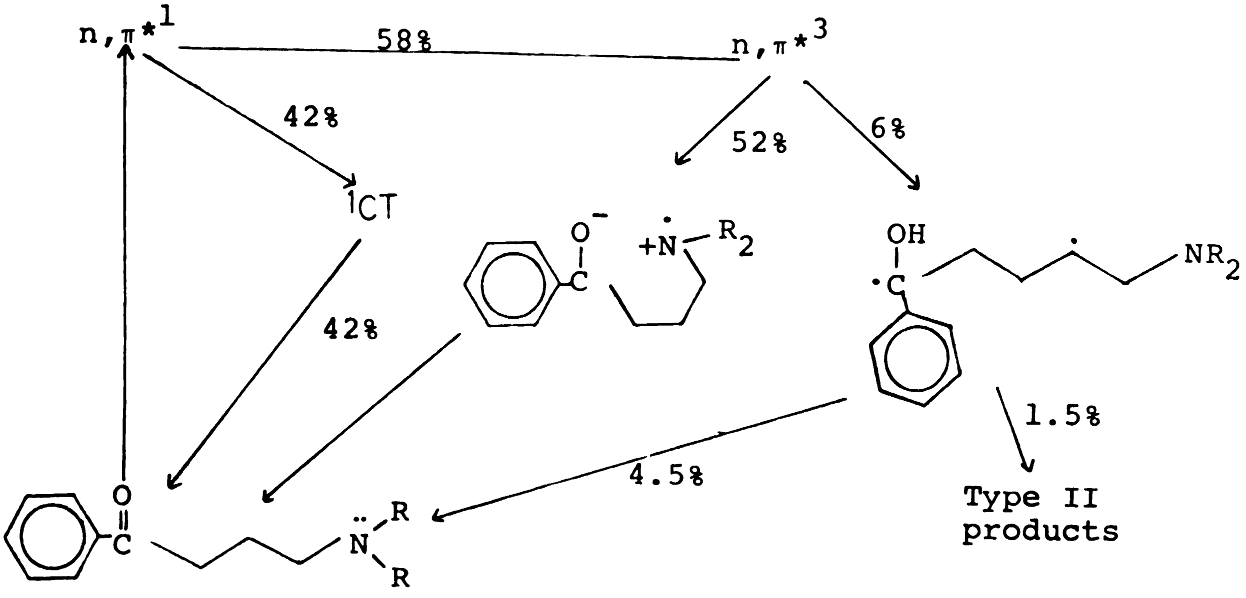
The intermediate can either form products or revert back to the ground state amine and ketone. Davidson[85] by the use of flash techniques has observed a transient with an absorption maxima at 670 nm which he attributes to the amine cation.

Further support for the above charge-transfer interaction between ketone triplet and the non-bonding electrons of nitrogen, followed by reverse-charge-transfer or proton transfer is given by: (1) the efficiency with which triethylenediamine photoreduces benzophenone[86]; (2) the inverse isotope effect observed for 2-butylamine-N,N-d_2 and cyclohexylamine-N,N-d_2[86]; (3) the fact that optically active 2-butylamine is not racemized during the reaction[84]; and (4) the lower quantum yields of benzophenone disappearance observed with amines as the hydrogen source relative to alcohols as the hydrogen source.[84]

Guttenplan and Cohen[83] have shown by plotting the rate constants for interaction of benzophenone triplets with a variety of donors versus the electron affinity of the donors that complete electron transfer does not take place. Further evidence that complete electron transfer does not take place in the charge-transfer interactions of ketones and amines is that only small solvent effects are observed[83] for the ketone systems relative to those systems where full electron transfer does occur.[75] Wagner and Kemppainen observed no increase in the quenching rate with which triethylamine and t-butylamine quench valerophenone in acetonitrile relative to that in benzene and the quenching rate decreased in methanol.

(B) Intramolecular:

The intramolecular Type II reaction shows close parallels with intermolecular photoreduction when amines are involved.[87-89] Wagner and Jellinek,[89] while studying alkylamino phenyl ketones of varying methylene chain length, observed that the intersystem crossing yield decreases and the rate of quenching by the amino group increases as the amino group moves closer to the carbonyl moiety. These results indicate that intramolecular charge-transfer quenching competes with intersystem crossing and the Type II reaction. Wagner and Kemppainen[88] also concluded that the geometry of the charge transfer state must be such that the γ-hydrogens are held away from the carbonyl oxygen, yet the nitrogen must be close enough to the oxygen to hold the complex in a cyclic configuration. The behavior of γ-dimethylaminobutyrophenone in benzene is reproduced in Scheme III.



Scheme III

Behavior of γ-Dimethylaminobutyrophenone in Benzene

<u>Biphenyl</u>:

For the past couple of decades photochemists have been intrigued by the triplet state geometries of excited states. That biphenyl should not escape this scrutiny is not surprising. Gardner[90] predicted the excited state geometry of biphenyl. Application of a semi-empirical exciton theory coupled with ESR data predicted a value of 26° between the two phenyl rings. A month earlier, however, Wagner[9] concluded that the triplet state of biphenyl prefers to be planar. This conclusion was based on two distinct pieces of evidence: First, the existence of a 10 kcal difference between the 0,0 band for phosphorescence and S→T absorption: Second, the fact that naphthalene and conjugated dienes are 2.5 times more effective than biphenyl at quenching triplet butyrophenone and at least 20 times more effective than biphenyl at quenching triplet benzophenone. It was also noted that the actual efficiency with which biphenyl quenches the photoreduction of benzophenone decreases with increasing benzophenone concentration because of reversible energy transfer. A brief study of <u>ortho</u>-substituted biphenyls showed them to be less efficient quenchers of the benzopheone photoreduction than biphenyl itself.

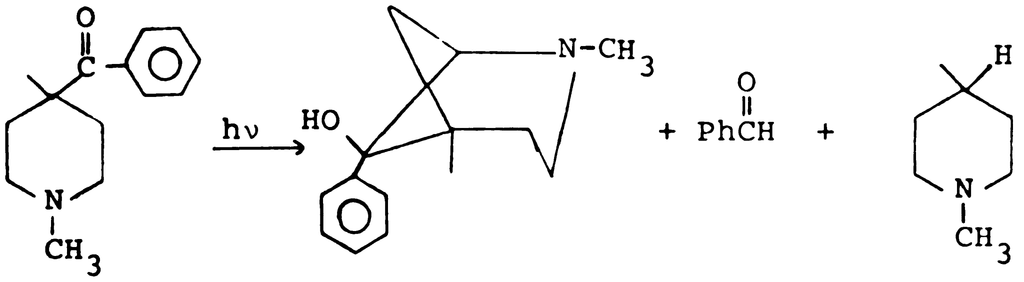
About the same time that Wagner reported his results, Brinen and Orloff[91] reported the D value of biphenyl. They first calculated the expected D value (0.116), then measured it (0.110). Good agreement between calculations and experimental results were not obtained until the calculations assumed considerable double bond character inherent in the 1-1' bond.

The conclusion that triplet biphenyl is planar has since been reinforced by several spectroscopic[92-94] and theoretical[95] investigations. Moreover, Mispelter[94], while studying 3,3'-difluorobiphenyl, hinted that there are two triplets observable in the ESR and that there is little or no spin localized at the three position. The spectrum was complicated by fluorine hyperfine splittings, but computer (CAT) analysis indicated two triplet species with different E values but identical D values.

The determination of the triplet state geometry of biphenyl and its analogues and the size of *ortho*-substituents necessary to force triplet biphenyl out of planarity has a practical significance. Certain commercially available pesticides (Arochlors) contain polychlorobiphenyls whose decomposition upon exposure to sunlight in the environment is of importance. At least one study has been undertaken on these polychlorobiphenyls[96]. The triplet state geometry is also important in studies of the photoracemization of optically active biphenyls.[97]

N-Substituted-4-Methyl-4-Benzoylpiperidine:

The study of N-methyl-4-methyl-4-benzoylpiperidine (NMMBP) is interesting on two accounts. First, very few photochemical studies on pharmacologically active substances have been performed.[98] This type of study would appear to be useful for determining shelf-life and/or the synthesis of novel compounds. NMMBP is potentially active as an analgesic, sedative (Demerol-Type).[99] Its Type II cyclization photoproduct is a potential stimulant (Amphetamine-Type).



Secondly, photochemically the compound is interesting because when the nitrogen containing the lone pair electrons is located in a ring, charge-transfer interactions between the carbonyl and nitrogen lone pair electrons should be less efficient than in a freely rotating compound. Stabilization by the lone pair electrons of the incipient radical in the Type II reaction should afford an extremely short-lived triplet. The photochemical behavior of these compounds should be comparable to the two compounds representing the extremes of behavior: 1-methylcyclohexyl phenyl ketone (MCPK) and γ-dimethylaminobutyrophenone. Substitution of different groups on the nitrogen atom of NMMBP might give some insight into the effects caused by such substitution on ground state conformations involving the lone pair electrons.

Lewis[66] reported that quenching of the competing Type I and Type II reactions of MCPK produced different $k_q\tau$ values while 1-methylcyclopentyl phenyl ketone gives the same $k_q\tau$ value for both Type I and Type II processes. These results indicate that MCPK undergoes the different reactions from two conformationally distinct triplets (Figure II).

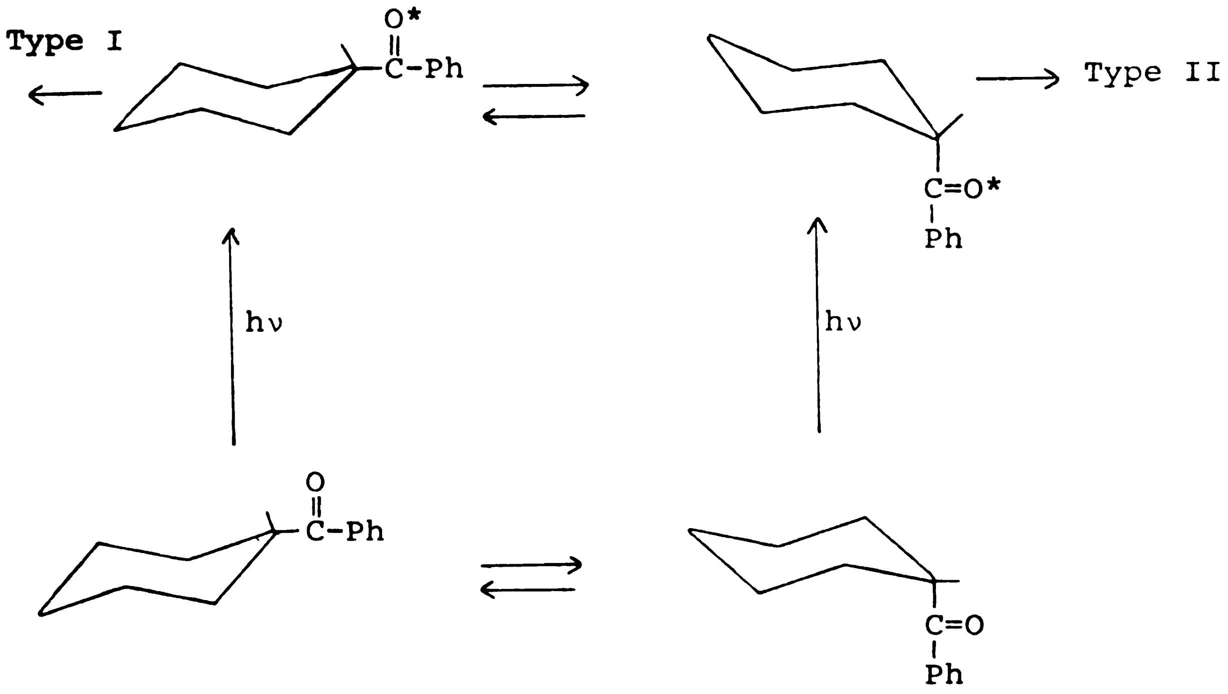


Figure II

Photochemical Scheme for 1-Methylcyclohexylphenyl Ketone

This conclusion demands that the energy barrier for excited state conformational isomerization is higher than the activation energy for formation of Type I or Type II products. It should be noted that in Lewis' original report the possibility that one isomer might sensitize the other was neglected. In any event the photochemistry of the aminoketone NMMBP should provide behavior quite similar to that observed for MCPK.

The quantum yield and quenching slope for the Type I reaction of NMMBP should be almost identical to that observed for MCPK, since the lone pair electrons on nitrogen should not be able to interact with the benzoyl group when it is in the equatorial position. The Type II reaction of NMMBP should be much faster than that observed for MCPK, because the lone pair electrons are in an orbital which is parallel to the incipient radical orbital. Thus the lifetime of the triplet formed from the Type II conformer of NMMBP should be shorter than that observed for MCPK. Since the boat conformation of NMMBP seems to be an unlikely species, charge-transfer quenching of the carbonyl by the amino group should be negligible.

Azidoalkyl Phenyl Ketones:

Since these compounds consist of two groups which can independently absorb incident light which impinges on the molecule, they can be called "bichromophoric". Relatively little is known about the excited state interactions of molecules containing two chromophores which do not interact in the ground state, although a few recent reports concerning such molecules are quite intriguing. Cowan and Baum[27] have measured the rate of energy transfer from a carbonyl to a styryl moiety separated by a varying number of methylene groups. Wagner and Nakahira[100] have irradiated several dibenzoyl ketones whose individual benzoyl groups were separated by a varying number of methylene groups. Hammond[101] has studied the rates of energy transfer between a benzophenone and the naphthalene moiety separated by a varying number of methylene groups. Several[102-104] other studies have been undertaken.

The study of the bichromophoric azidoketones has the added attraction that the rate of the Type II reaction should be competitive with the rate of energy transfer from the carbonyl to the azide group. As pointed out in the Type II section, from the rates of the Type II reaction it is possible to determine the previously unmeasured σ_I value of the azido group and the ability of the azido group to stabilize a radical. Also, since the azido group can undergo many interesting reactions, the confinement of the azido group to the same molecule with a carbonyl group might lead to new compounds or novel mechanisms.

The Azido Group:

The azide group is one of the most useful and versatile groups available to the Organic Chemist, yet its modes of photochemical reactions remain somewhat of a mystery. Its properties are classed with the group of inorganic radicals called the pseudohalides, and it possesses both a -I and a +R effect. In aromatic substitution reactions the group is pan-activating.[105] It can be used to synthesize a number of heterocyclic ring systems (tetrazoles,triazoles, oxazoles, carbozoles, etc.)[106]. It can be used to form imines, amines, amides (Schmidt reaction), azo compounds, and penicillins.[107]. Its inorganic salts can be explosive (copper azide). The group is both thermally and photochemically active. In fact, the photosensitized decomposition of the azide group has potential importance in photographic applications[108], and the groups pharmacological properties are just beginning to be investigated.[109] Since no quantitative photochemical studies have been performed on compounds containing the azido moiety, it seemed worthwhile to measure its σ_I value, its ability to stabilize a radical, and the rates of energy transfer to it from a nearby carbonyl group.

(a) The Azide Excited State:

Efforts[110-114] to relate the observed UV bands of alkyl azides (215 and 285 nm) with known types of spectroscopic transitions have been attempted. However, the exact nature of the transitions observed in the UV spectra of covalent alkyl azides is not known with any certainty. In fact it is not even certain whether these bands are due to π, π^* transitions or n, π^* transitions. It has been reported[110] that the 285 nm transition involves the P_y and P_x (presumed $\pi_y \rightarrow \pi_x^*$ transition) electrons. This transition is shown in Figure III.

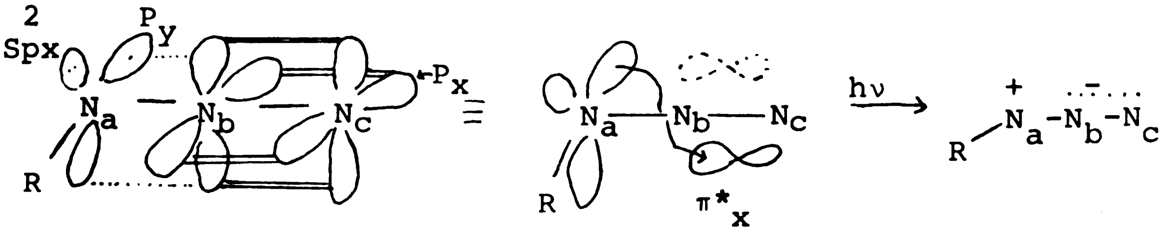


Figure III

$\pi_y \rightarrow \pi_x$ Transition in Alkyl Azides

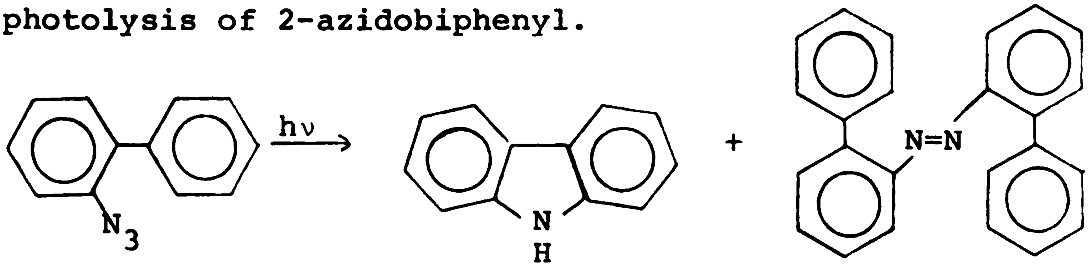
As seen in Figure III, the $\pi_y \rightarrow \pi_x^*$ transition leaves the P_y orbital on the N_a atom somewhat electron deficient.[114]

Lewis and Saunders[115] have attempted to measure the triplet energy of the azido group. Sensitized decomposition of the azides allowed calculation of rates of energy transfer. Even with the sensitizer of highest triplet energy (cyclopropyl phenyl ketone) an energy transfer rate equal to that of the rate of diffusion was not obtained. This result suggested an energy of 75-80 kcal/mole for the triplet. In this same study a Hückel calculation indicated that the first excited state of methyl azide is bent and shows two minima at about 140° and 220°. The transoid configuration was shown to be slightly more stable than the configuration with the methyl group out of the plane in which the three nitrogen atoms reside. Roberts[116] has shown that only 0.6 ev (less than 20 kcal) is required to bend a ground state azide from a linear arrangement to an angle of 120°. The ability of the azide group to bend from a linear arrangement is dramatized in the synthesis of triazoles and tetrazoles.

(b) Decomposition to Nitrenes:

Physical proof for the existence of organic nitrenes appeared only recently in the literature. Yager[117] reported the ESR signals of stable aromatic nitrenes at 77° K which are characteristic of two strongly interacting unpaired electrons on a single atom. Similar spectra were observed upon photolysis of alkyl azides at 4° K.[118] Reiser[119] has observed the nitrene from 1-azidoanthracene in flash photolysis experiments, and recently Lehman and Berry[120] have observed 2-nitrenobiphenyl under similar conditions. A large body of chemical evidence for the existence of discrete nitrenes exists in the literature.[119,122-125] However, Abramovitch[126] has recently reported that in certain alkyl migrations to the electron deficient N_a atom, a concerted mechanism is probably involved.

In the direct photolysis of azides four theoretically distinct species can form: singlet azide, triplet azide, singlet nitrene, and triplet nitrene (in triplet sensitized studies only triplet azide and triplet nitrene should form). The problem of determining which of the four species are formed and which give rise to specific products is not easy to discern. This problem is superbly illustrated by the photolysis of 2-azidobiphenyl.



Swenton[127] photolyzed 2-azidobiphenyl and found a 71% chemical yield of carbazole and 8% azocompound upon direct irradiation. In the presence of acetophenone (triplet sensitizer), a 43% chemical yield of the azo compound plus an 8% yield of the carbazol was found. Direct irradiation in the presence of piperylene (triplet quencher) produced a yield of 89% carbazole and 4% azo compound. Lehman and Berry[120] have recently measured the rate constant for the carbazole closure reaction at 10^3 sec^{-1} and in the process followed the reaction by flash studies. The results of Lehman and Berry indicate that the singlet azide decomposes to the singlet nitrene which either closes to the carbazole or undergoes fast intersystem crossing to the triplet nitrene to form the carbazole. Both the results of Swenton and of Lehman and Berry are consistent with the fact that singlet nitrene closure is competitive with nitrene intersystem crossing. The azo compound presumably comes from the triplet state of the azide rather than from the triplet nitrene. However, this mechanism is not proven unequivocally.

Since this thesis is concerned primarily with the triplet excited state, the following reactions of triplet nitrenes or of triplet azides are listed with brief comments:

1) Rearrangement: This reaction is probably the most general reaction of alkyl nitrenes. The imine is the favored product.[128]

$$R_2CH\text{——}\dot{N}\cdot \longrightarrow R_2\text{-}C{=}NH \tag{14}$$

2) Hydrogen Abstraction: Aromatic nitrenes[129] abstract hydrogens from ethanol with a rate constant about 2.4×10^2 $l\ mole^{-1}\ sec^{-1}$. In the reaction some amine is formed and a certain probability of radical recombination exists. Barton[130] originally reported that the photolysis of n-butylazide produced pyrrolidine by a 1,5 hydrogen shift and closure of the resulting diradical. The formation of pyrrolidine has since been shown by Barton[131] and others[132] not to occur.

3) Addition to Double Bonds: Triplet nitrenes add to double bonds in a two step non-stereospecific fashion to form aziridines[133,134]. The mechanism is probably similar to

that for the addition of nitrene to aromatic systems to produce azepines.[135,136]

4) Coupling to Form Azo Compounds:

$$2RN \rightarrow RN{=}NR \qquad (15)$$

Reiser[129] has shown that this process is diffusion controlled for aromatic nitrenes.

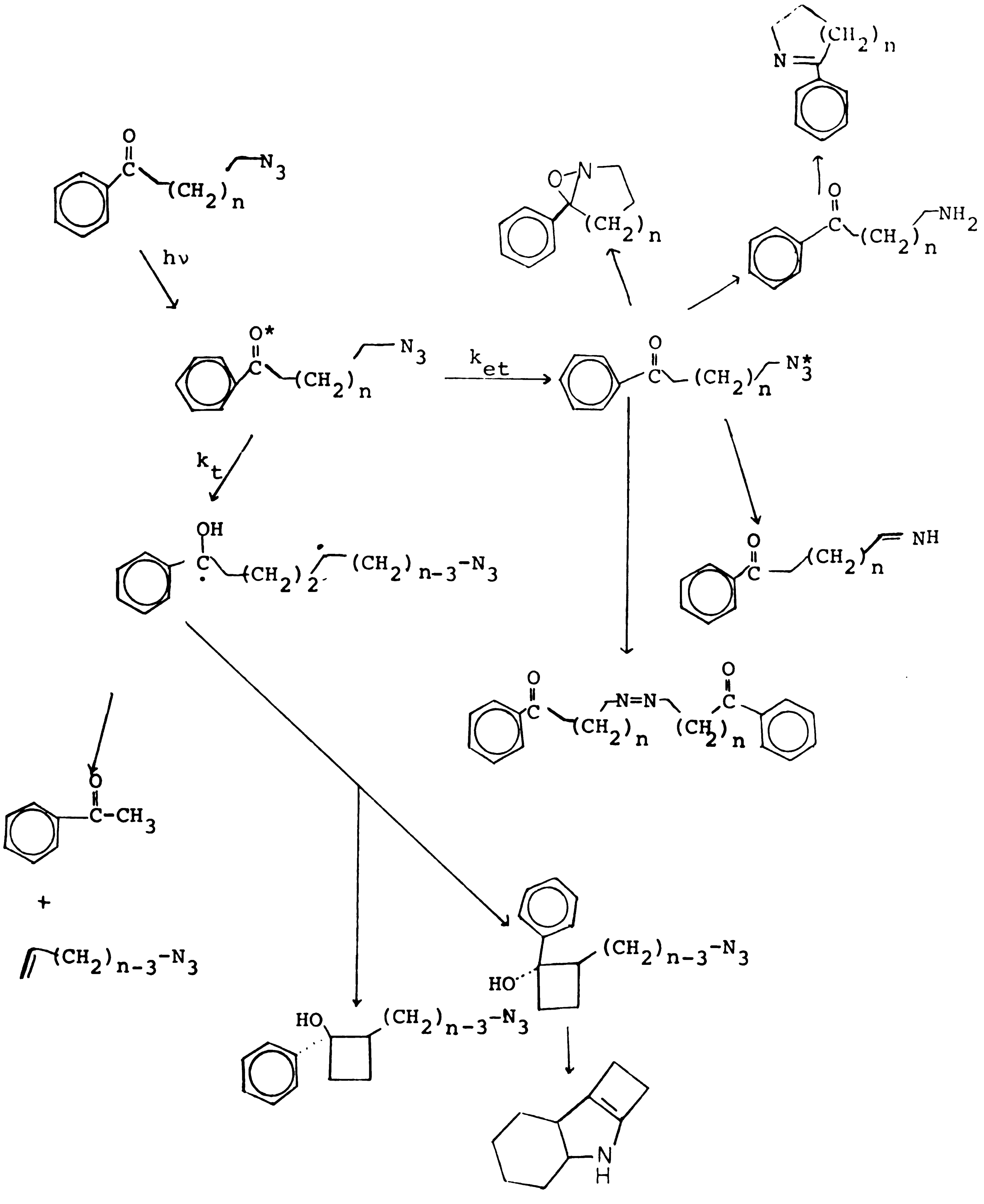
5) Reaction of the Nitrene with the Azide Group: This process accounts for a large proportion of decomposition of the azide and accounts for the high quantum yield of nitrogen evolution in the photolysis of azides in the gas phase.

$$R{-}\dot{N}\cdot + RN_3 \rightarrow R{-}N{=}NR + N_2 \qquad (16)$$

Reiser[129] has shown that this process is also diffusion controlled for aromatic nitrenes. Nitrenes also react with other atoms which possess electron pairs: such as amines,[134] the nitro group,[137] the carbonyl group,[138] and dimethyl sulfoxide.[139]

(c) Products from the Bichromophoric Azido Alkyl Phenyl Ketones:

Incorporation of the azido and carbonyl groups in the same molecule should, upon excitation, give energy transfer from one group to the other. If excitation is initially located in the carbonyl group, the reactions shown in Scheme IV can be envisioned. The references for these "a priori" reactions can be found in the former sections.



Scheme IV

Possible Products From Photolysis Of Azido Ketones

PART I

TRIPLET BIPHENYL

RESULTS

Quenching of triplet benzophenone by Biphenyls:

The efficiencies with which naphthalene, biphenyl, 2-, 3-, and 4-chlorobiphenyl, and 2-, and 4-methylbiphenyl quench the triplet state of benzophenone in benzene were determined by either one or both of two methods.

In method I degassed benzene solutions containing fixed concentrations of benzophenone, 0.5 M isoproprопyl alcohol, and varying concentrations of the quenchers listed above were irradiated in parallel at 25° C with the 365 nm region of a mercury arc. Disappearance of ketone was monitored by UV analysis. After irradiation each tube was opened and the contents poured into a vial which was kept in the dark for 15-24 hours. This pre-analysis procedure was employed since the UV absorbance of samples immediately after irradiation was high and decreased slowly to steady values. This phenomenon is probably related to the formation of thermally unstable radical-coupling products.[41-43]

In method II the phosphorescence of benzophenone in degassed benzene solutions was quenched. The phosphorescence was measured, oxygen was bubbled into the tube and the phosphorescence intensity remeasured. This background reading was subtracted from the initial sample reading. Stern-Volmer plots of Φ_o/Φ versus quencher concentrations were linear for the two methods employed and yielded the slopes ($k_t \tau$) listed in Table I.

Quenching rate constants increase with decreasing ketone concentration for biphenyl, 3- and 4-chlorobiphenyl, and 4-methylbiphenyl, but apparently not for 2-chloro- and 2-methylbiphenyl. Such dependence of $k_t \tau$ on ketone concentration indicates reversible energy transfer.[9] Figures IV-XII display the dependence of $k_t \tau$ for these quenchers on ketone concentration. Table II lists actual $k_t \tau$ values (1/intercept) obtained from equation (13) (Introduction) and Figures XI and XII. With k_t assumed equal to 5×10^9 $M^{-1}sec^{-1}$ for naphthalene[26] the τ value for triplet benzophenone in benzene and 0.5 M isopropanol can be calculated (Table II). With the aid of the known τ values, the k_t values for the biphenyls can be calculated (equation 13, Table II). The slopes divided by the intercepts of the plots in Figures XI and XII give the k_{-t}/k_d' values listed in Table II. Assuming the estimated k_d' value of 3×10^5 [48] can be applied to the present system, k_{-t} can be calculated for the biphenyls in isopropanol-benzene solvent. Since $k_{d'}$ can be expected to change in going from isopropanol-benzene solvent to pure benzene, the k_{-t} value obtained in the isopropanol-benzene for biphenyl was used to calculate a $k_{d'}$ value in benzene. That these estimated $k_{d'}$ values are in the correct ballpark is evidenced by the work of Ruzo and Zabik[55] who report that unhindered polychlorinated biphenyls have $k_{d'}$ values approximately 4×10^7 sec^{-1}. The change in solvent from benzene to isopropanol-benzene should have little effect on k_t,[15] moreover any effect the change in solvent does have on k_t would effect k_{-t} to the same degree.

Absorption Spectra of Biphenyls:

Absorption spectra of the biphenyls in heptane or ethanol solutions are quite similar. All the biphenyls, like biphenyl itself, display an intense, structureless band with λ_{max} near 250 nm corresponding to the $^1A \rightarrow {}^1L_a$ transition of benzene. Table III lists the λ_{max} values and molar extinction coefficients for the chloro- and methylbiphenyls. Meta-substitution whether chlorine or methyl produces only a slight change compared to biphenyl. A para-chlorine produces a red shift (740 cm^{-1}, 2.1 kcal/mole) and intensity enhancement as does para-methyl (845 cm^{-1}, 2.4 kcal/mole) and di-para-methyl (1,248 cm^{-1}, 3.7 kcal/mole) substitution; an ortho-chlorine cuts the intensity in half and produces a more sizable blue shift (1100 cm^{-1}, 3.1 kcal/mole) similar to the ortho-methyl (2,182 cm^{-1}, 6.2 kcal/mole) and di-ortho-methyl (3,681 cm^{-1}, 10.5 kcal/mole) substitution. These effects are well documented.[140]

Phosphorescence Spectra of Biphenyls

Phosphorescence spectra were recorded at 77° K in methylcyclohexane and cyclohexane for all the biphenyls. The spectra of the chlorobiphenyls were also obtained in heptane. All the biphenyls phosphoresce strongly with the

Table I

Quenching Data of Triplet Benzophenone by Biphenyls in Benzene

Quencher	Ketone Conc. (M)	S[a], M^{-1}	S[b], M^{-1}
Naphthalene	0.054	4335±105[c]	40,000
biphenyl	0.054	26.3±0.1: 24[d]	103
	0.035	------	152±15
	0.02	49±1.0	250
	0.0075	68	1286
4-chlorobiphenyl	0.054	164±3	----
	0.035	217±3	----
	0.02	346	----
	0.0075	500	----
3-Chlorobiphenyl	0.054	89	----
	0.025	144	----
	0.0083	219	----
2-Chlorobiphenyl	0.054	1.13	11.8
	0.035	----	13.9±0.2
	0.02	----	11.2
	0.0075	----	11.7
2-methylbiphenyl[e]	0.052	----	96
	0.0131	----	95
4-methylbiphenyl	0.035	----	520
	0.025	----	716
	0.017	----	833
	0.0088	----	2425±425

[a] Quenching of photoreduction in 0.5 M isopropanol (method 1); S with slope obtained from the Stern-Volmer plots of Figures IV, V, VIII and X.

[b] Quenching of phosphorescence in benzene (method 2); S is the slope obtained from the Stern-Volmer plots of Figures VI, VII, and IX.

[c] The error cited here is the actual range of values obtained for two or more runs. If no error is indicated the standard deviation of the run can be found in the experimental.

[d] Quenching of phosphorescence in 0.5 M isopropanol.

[e] Two points only for both determinations.

Table II

Kinetic Parameters for Biphenyl Quenching of Triplet Benzophenone[a]

Quencher	$k_t\tau$ isp	$k_t\tau$ phos	$k_{-t}/k_{d'}$ isp	$k_{-t}/k_{d'}$ phos	$k_t x10^8$ isp	$k_t x10^8$ phos	$k_{-t} x10^8$	$k_{d'}$[b]$x10^4$
Biphenyl	105	2500	58	435	1.21	3.12	1.73	4.0
2-Chlorobiphenyl	1.13	12.1	0	0	0.013	0.015	0	---
3-Chlorobiphenyl	286	---	46	---	3.28	---	1.36	---
4-Chlorobiphenyl	769	---	62	---	8.84	---	1.85	---
2-Methylbiphenyl	---	95.5	---	0	---	0.119	0	---
4-Methylbiphenyl	---	4000	---	189	---	5.0	0.756[c]	---
naphthalene	4335	40,000	---	---	50[c]	50[c]	---	---

[a] Variables are those defined in Introduction for equation (13); $k_t\tau$'s are the measured intercepts and $k_{-t}/k_{d'}$ values are the slopes divided by the intercept from Figures XI and XII.

[b] Calculated from $k_{-t}/k_{d'}$ using k_{-t} equal to 1.73×10^7.

[c] Calculated from $k_{d'}$ equal to 4×10^4.

[d] Reference 26.

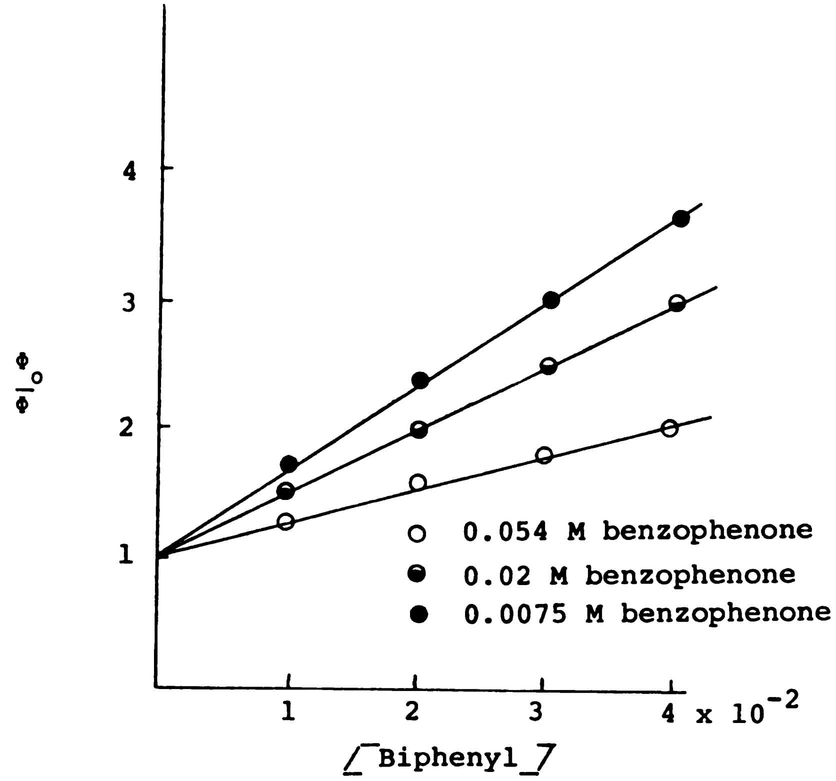


Figure IV: Stern-Volmer Plots for Quenching of Benzophenone Photoreduction by Biphenyl.

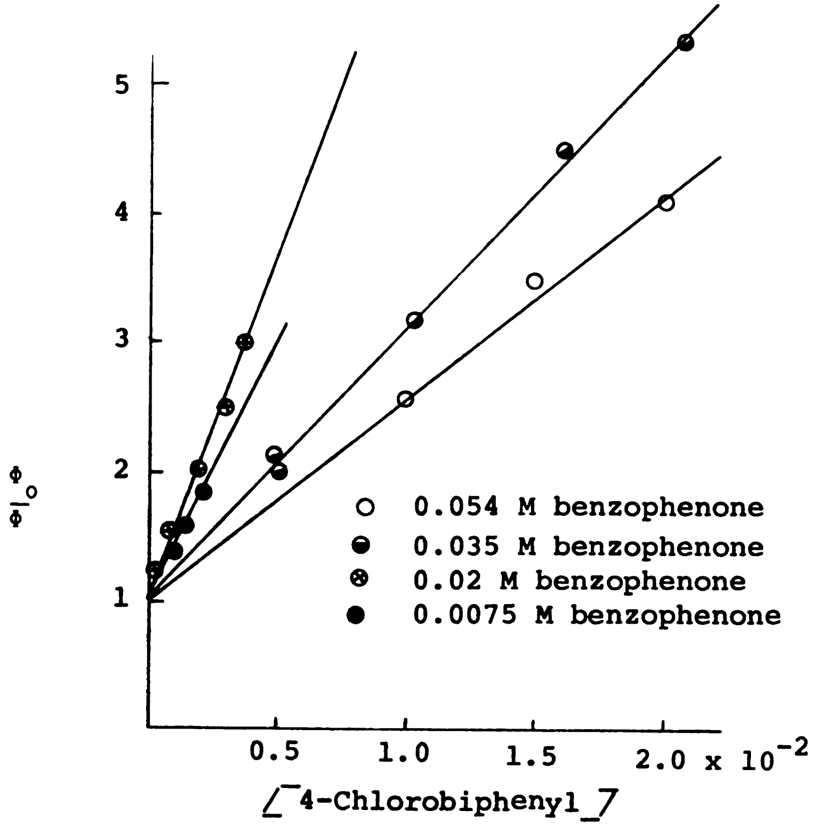


Figure V: Stern-Volmer Plots for Quenching of Benzophenone Photoreduction by 4-Chlorobiphenyl

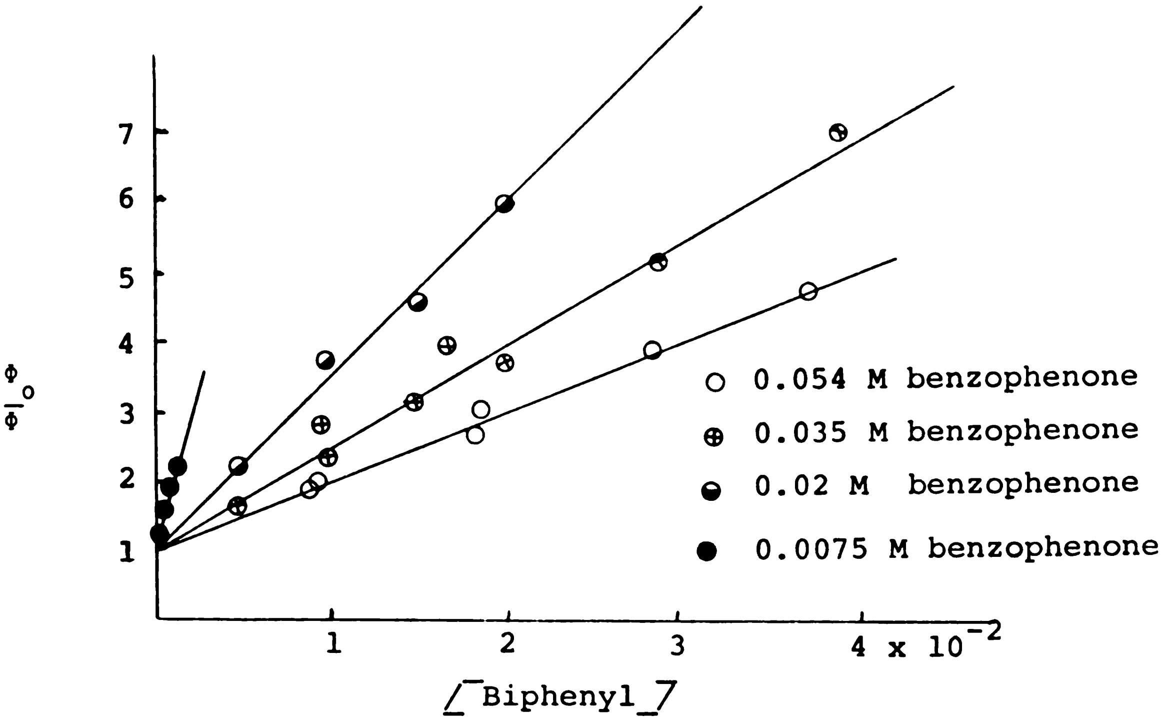


Figure VI: Stern-Volmer Plots for Quenching of Benzophenone Phosphorescence by Biphenyl.

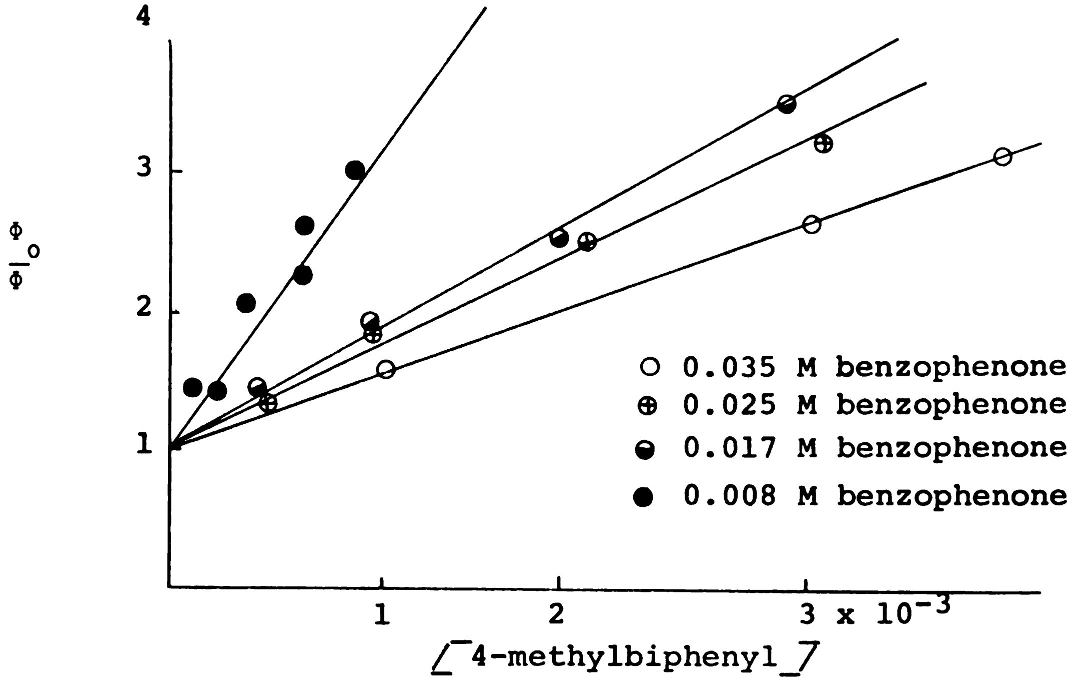


Figure VII: Stern-Volmer Quenching of Benzophenone Phosphorescence by 4-methylbiphenyl.

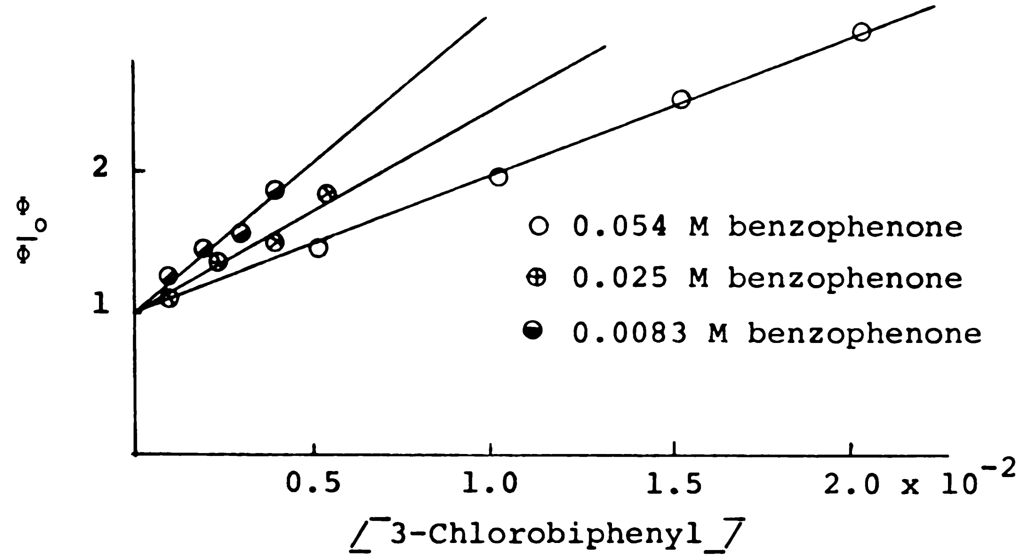


Figure VIII: Stern-Volmer Plots for Quenching of Benzophenone Photoreduction by 3-Chlorobiphenyl.

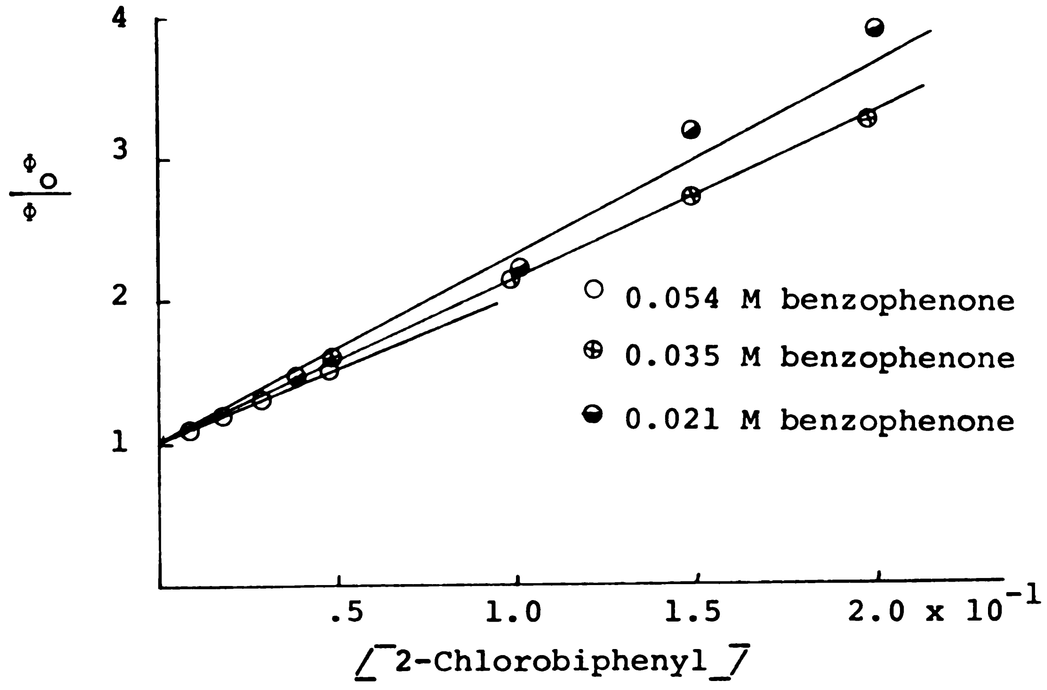


Figure IX: Stern-Volmer Plots for Quenching of Benzophenone Phosphorescence by 2-Chlorobiphenyl.

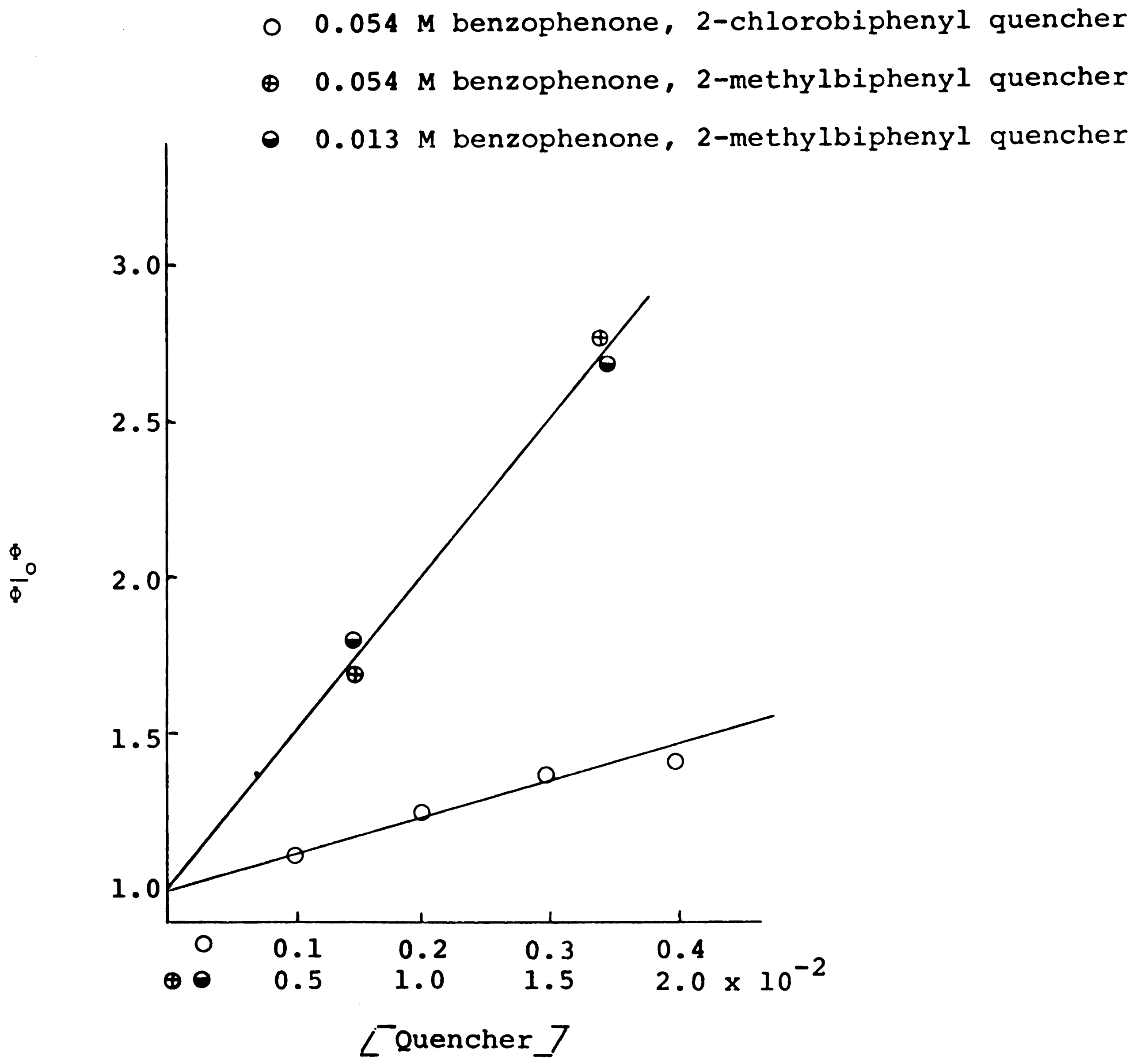


Figure X: Stern-Volmer Plots for Quenching of Benzophenone Photoreduction by 2-Chlorobiphenyl, and Benzophenone Phosphorescence by 2-Methylbiphenyl

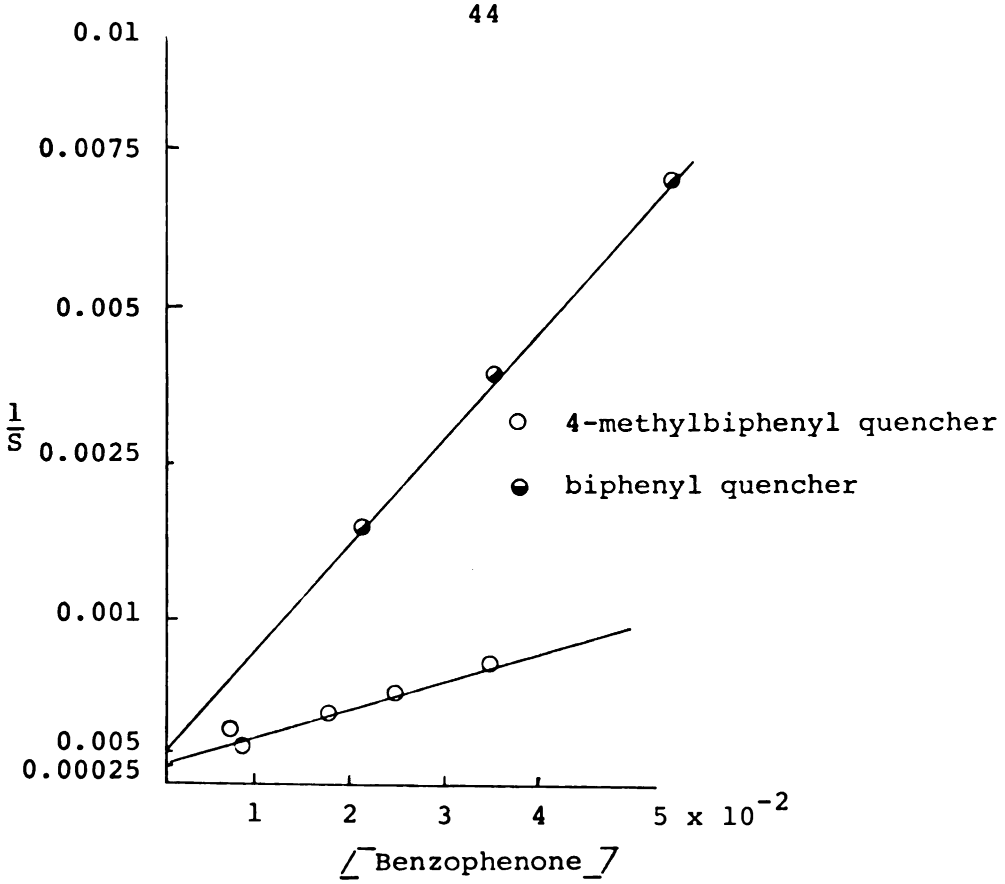


Figure XI: Plot of 1/S Versus Benzophenone Concentration (Phosphorescence)

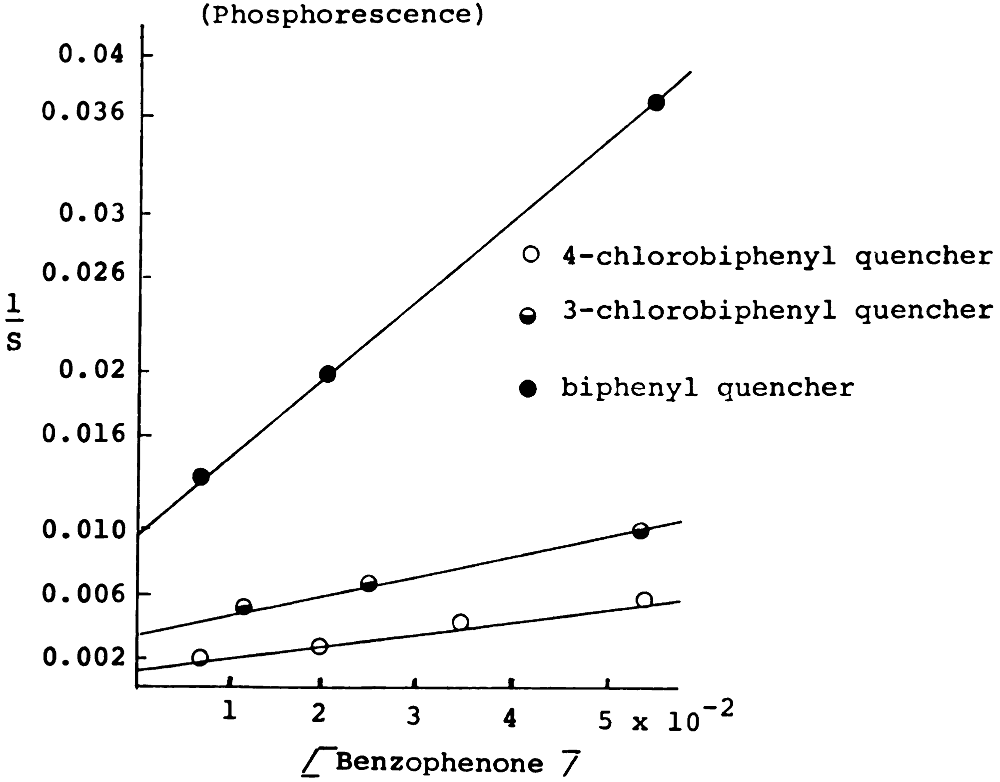


Figure XII: Plot of 1/S Versus Benzophenone Concentration (Photoreduction) *ortho*-substituted compounds phosphorescing most strongly. Figures XIII-XV and Table IV compare the phosphorescence spectra of biphenyl and the chloro-, methyl-, and dimethylbiphenyls. The presence of an *ortho*-group removes what little structure there is in the biphenyl spectrum and apparently shifts the whole spectrum to higher energy. The *ortho*-chloro- and methyl- groups shift the λ_{max} of phosphorescence emission by about 400 cm^{-1} and the onset by about 600 cm^{-1} while the *ortho*-dimethyl shifts the λ_{max} by about 600 cm^{-1} and the onset by 1400 cm^{-1}. This steric effect is consistent with those first reported by Lewis and Kasha. The *para*-substituents shift the emission to lower energy. *Para*-chloro- and methyl-groups produce a shift of about 600 cm^{-1} while the di-*para*-methyl compound produces a shift of about 1280 cm^{-1}. *Meta*-substitution produces little energy change. Meta chloro- and methylbiphenyl are identical to biphenyl, while di-*meta*-methylbiphenyl shifts the spectrum about 600 cm^{-1} to lower energy. Under the low resolution conditions used, biphenyl phosphorescence shows vibrational structure, including a prominent progression of about 1400 cm^{-1}, but with only shoulders corresponding to the lower-frequency vibrational modes reported by Lim.[51] The *meta*- and *para*-substituted compounds show this same progression.

Table III

Absorbance of Biphenyls

Compound	Absorbance	ε	Solvent
biphenyl	2477	16700	heptane
2-Chlorobiphenyl	2410	8450	heptane
3-Chlorobiphenyl	2480	16100	heptane
4-Chlorobiphenyl	2520	19200	heptane
2-Methylbiphenyl[a]	2350	10500	ethanol
3-Methylbiphenyl[a]	2490	16300	pentane
4-Methylbiphenyl[a]	2530	19000	ethanol
2,2'-dimethylbiphenyl[a]	2270	6800	ethanol
3,3'-dimethylbiphenyl[a]	2505	16100	pentane
4,4'-dimethylbiphenyl[a]	2556	20500	ethanol

[a] Value taken from reference 140 page 281.

Table IV

Phosphorescence of Biphenyls[a]

Biphenyl	Onset[b]			λ_{max} Methylcyclohexane			λ_{max} Heptane			λ_{max} Cyclohexane		
Biphenyl	375	428	425	437	468	486	438	462	495	440	468	490
2-Chloro	388	420	408	444	452	460	448	470		468		
3-Chloro	382	394	400	444	456	465	434	474		450	476	
4-Chloro	396	431	442	440	468		448	478	492	452	482	504
2,2'-Dichloro	380	---	388	441						452		
2-Methyl	400	---	398	464						452		
3-Methyl	418	---	425	444	470	502				440	480	
4-Methyl	416	---	416	444	468	500				436	468	494
2,2'-Dimethyl	367	---	400	450	464					460		
3,3'-Dimethyl	407	---	420	442	465	488				442	470	500
4,4'-Dimethyl	420	---	432	445	470	495				450	478	502

[a] Measured in nanometers

[b] Listed in order of solvent listed for λ_{max}: measured at about 80% scale deflection.

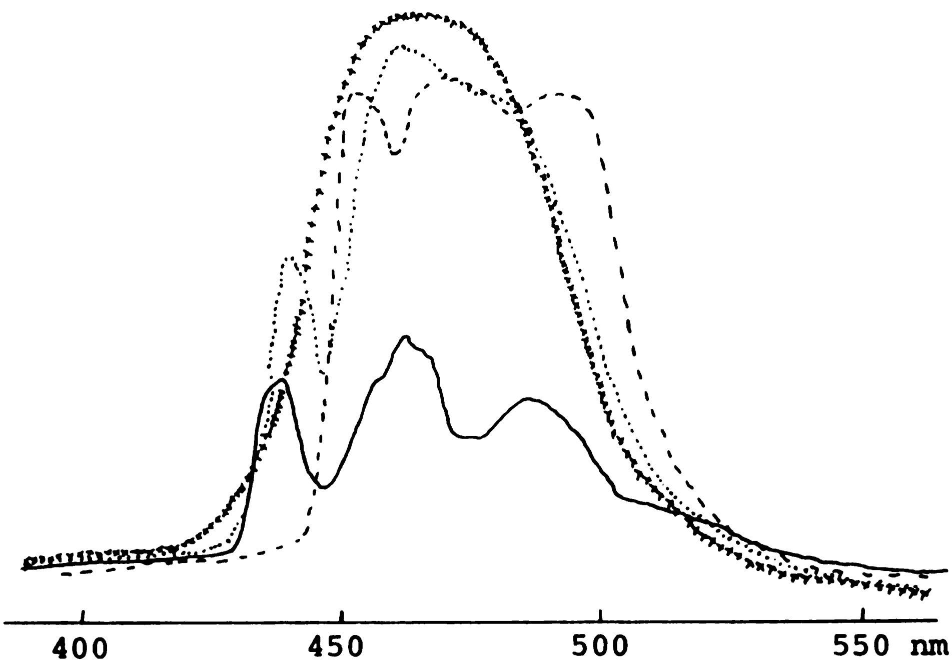
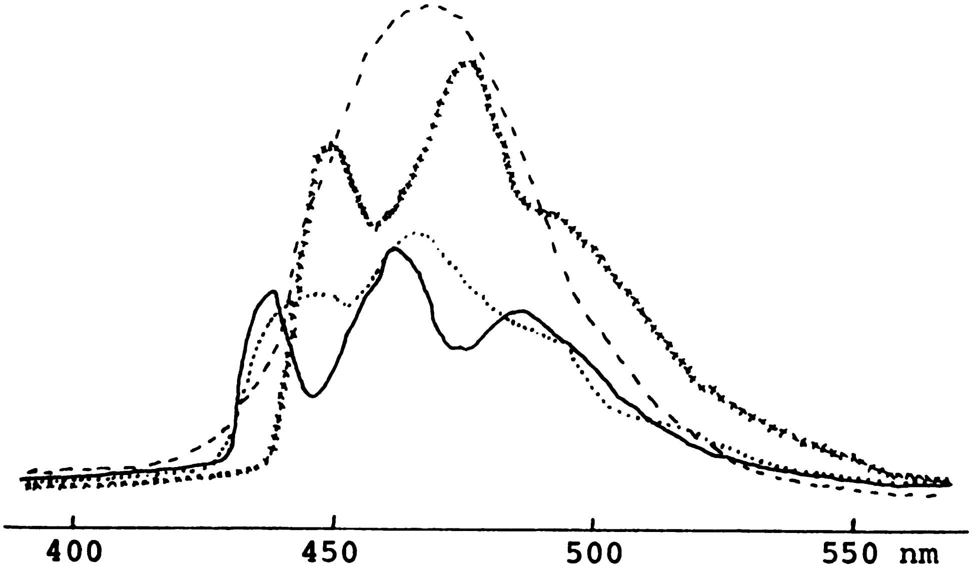


Figure XIII: Phosphorescence Spectra of Biphenyl and Methylbiphenyls. (——) Biphenyl, (---) 4-Methylbiphenyl, (xxx) 2-Methylbiphenyl, (···) 3-Methylbiphenyl.



Figures XIV: Phosphorescence Spectra of Biphenyl and Chlorobiphenyls. (——) Biphenyl, (---) 2-Chlorobiphenyl, (xxx) 4-Chlorobiphenyl, (···) 3-Chlorobiphenyl.

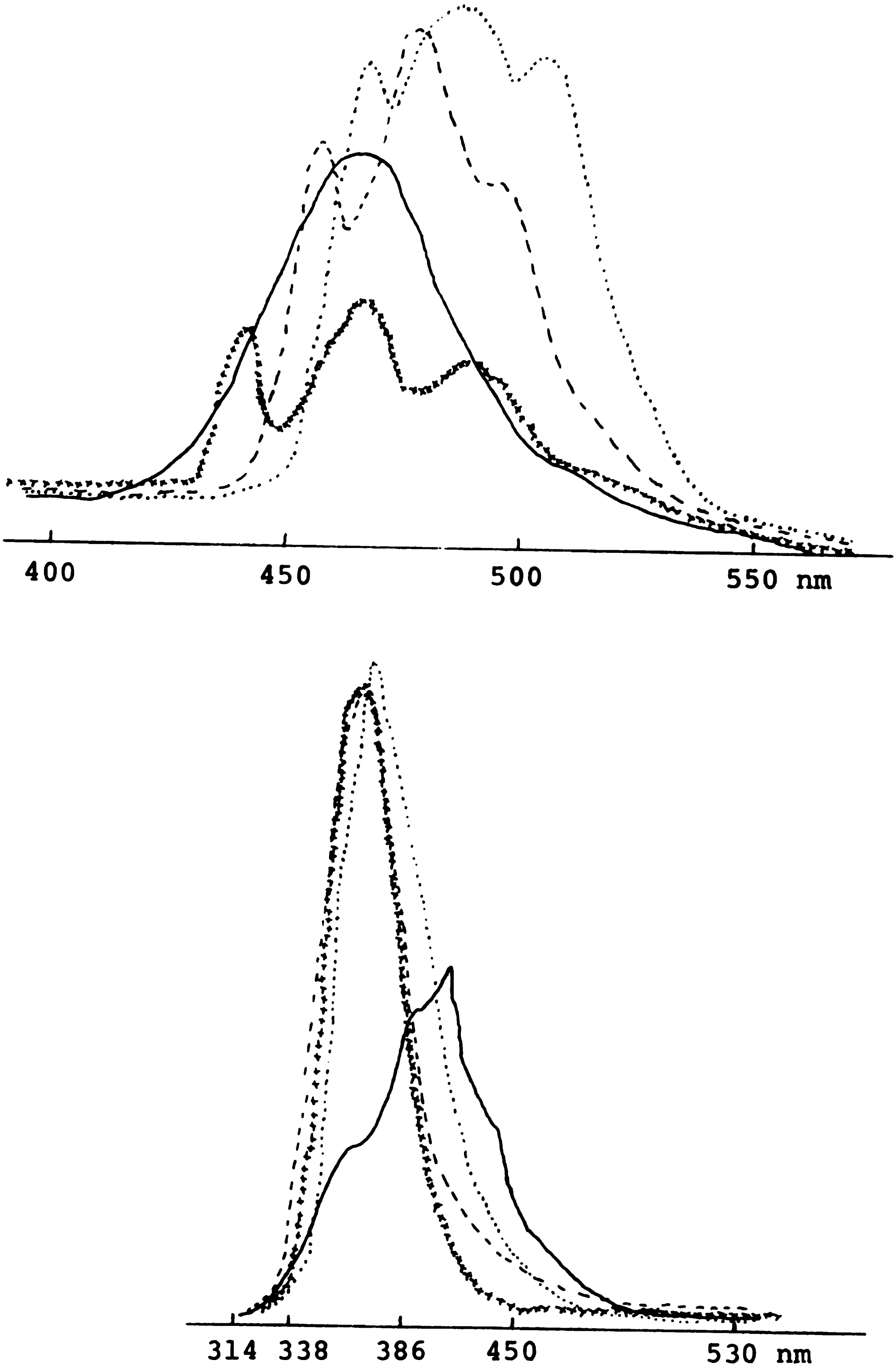


Figure XV: Phosphorescence (top) and Fluorescence (bottom) Spectra of Dimethylbiphenyls. (——) 2,2'-Dimethylbiphenyl, (---) 3,3'-Dimethylbiphenyl, (xxx) Biphenyl, (···) 4,4'-Dimethylbiphenyl.

Fluorescence Spectra of Biphenyls:

Fluorescence spectra were measured at 25° in cyclohexane and methylcyclohexane. Table V lists the λ_{max} of the biphenyls studied. Only slight changes are observable upon substitution, and all the spectra are essentially identical to that of biphenyl itself except for the two ortho-disubstituted compounds. (See Figure XV). The spectrum of 2,2-dimethylbiphenyl is lowered drastically compared to that of the other dimethylbiphenyls but shows the most structure. It is compared to the spectra of the other dimethyl compounds (which are characteristic of the other biphenyls) in Figure XV.

Triplet EPR Spectra of Biphenyls:

Triplet EPR spectra of biphenyl, the chlorobiphenyls and the six methylbiphenyls were measured at 9237 MHz in ethanol glass at 77°K. Both $\Delta m = 2$ and $\Delta m = 1$ transitions were readily measurable. Table VI lists the zero-field parameters. In the case of the three chlorobiphenyls there are no significant differences. These similarities lead in fact to the possibility that the loss of chlorine might be occurring with the formation of biphenyl. This process is known to be particularly efficient for ortho-chlorobiphenyl at room temperature.[142] Consequently the triplet lifetimes of the different chloro derivatives were measured[143] by monitoring both their phosphorescence and ESR decay. The reported τ_p for biphenyl itself is 4 sec.[52] The τ_p for ortho-chlorobiphenyl was found to be 0.12 sec. The decay of meta-chlorobiphenyl

Table V

Fluorescence Data for Biphenyls[a]

Biphenyl	Onset[b]		λ_{max} Methylcyclohexane			λ_{max} Cyclohexane		
Biphenyl	295	296	320	628		320	624	
2-Chloro	291	292	324	630		322	636	
3-Chloro	300	300	320	636		322	638	
4-Chloro	302	292	324	642		324	638	
2-Methyl	310	292	328	640		320	630	
3-Methyl	284	---	334	656				
4-Methyl	290	304	324	630		334	654	
2,2'-Dimethyl	306	290	328	350	356	320	351	359
3,3'-Dimethyl	292	300	318	638		326	632	
4,4'-Dimethyl	295	304	338	652		336	652	
2,2'-Dichloro	284	---	300					

---

[a] Measured in nanometers

[b] Listed in order of solvent listed for λ_{max}: measured at about 80% scale deflection.

consisted of two components with τ_p values of 0.18 and 0.45 sec. The latter accounts for only 25% of the total intensity. Clearly different triplets for the different chlorobiphenyls are being observed in the phosphorescence experiments. However, the ESR signals for all three chlorobiphenyls decayed with the same 2-4 sec lifetime, indicating that biphenyl itself is responsible for most of the ESR signal.

The zero-field parameters for the three methylbiphenyls and 4,4'-dimethylbiphenyl are essentially identical, although <u>ortho</u>-methylbiphenyl displays a higher than usual E value. Of all the biphenyls studied only 2,2'-dimethyl- and 3,3'-dimethylbiphenyl yield two triplet ESR spectra. In the 3,3'-compound two sets of $\Delta m = 1$ signals are apparent, independent of sample freezing rate. The 2,2'-compound also shows two quite distinct $\Delta m = 2$ signals as well as two $\Delta m = 1$ signals. These spectra are reproduced in Figures XVI-XVIII, while the ESR parameters for all the biphenyls are listed in Table VI. Under conditions in which the samples were frozen slowly the 2,2'-compound yielded largely one spectrum ($\Delta m = 2$ at 1511 G). The line widths of the $\Delta m = 1$ signals are broader for the 2- and 4-methyl substituted biphenyls than for the 3-methylbiphenyl, biphenyl or the chlorobiphenyls. The chlorobiphenyls and the 3-methylbiphenyl display linewidths identical to biphenyl itself. The linewidths of the Z-2,2'-dimethylbiphenyl (see Discussion section for structure) are twice as wide as those of the other biphenyls. The average E value (0.00456) for the two 3,3'-dimethylbiphenyl triplets is nearly that of the E value of 3-methylbiphenyl (0.00423). The fine structure constants were obtained by the use of the following equations:[144]

$$D^{*2} = (3/4)\left[\delta^2 - 4(g\beta)^2 H_{min}^{\ 2}\right] \qquad (17)$$

$$D^{*2} = (D^2 + 3E^2) \qquad (18)$$

$$D = -(3/2)Z \qquad (19)$$

$$E = 1/2(X-Y) \qquad (20)$$

$$X = (1/6)\delta(g\beta)^2\left[{}^{3}H_x^{\ 2} - {}^{2}H_x^{\ 2}\right] \qquad (21)$$

Y and Z are obtained from cyclic permutations of x,y, and z. In the above equations $\delta = h\nu$ which at $\nu = 9237.5$ MHz is 6.12104 x 10^{-17} erg.sec x MHz. $(g\beta)^2$ equals 1.3790 x 10^{-39} $Mcy^2 erg^2/gauss^4$. H is the observed field signal measured in gauss.

Table VI

Observed EPR Resonances and ZFS Parameters of Phosphorescent Biphenyls[a]

Biphenyl	D	E	D^*_{calc}	D^*_{obs}
Biphenyl	0.1089	0.00349	0.1090	0.1084
2-Methyl	0.1067	0.00698	0.1073	0.1054
3-Methyl	0.1077	0.00423	0.1079	0.1080
4-Methyl	0.1067	0.00365	0.1069	0.1051
4,4'-Dimethyl	0.1062	0.00369	0.1064	0.1046
E-3,3'-Dimethyl	0.1067	0.00335	0.1068	0.1069
Z-3,3'-Dimethyl	0.1067	0.00700	0.1073	0.1069
E-2,2'-Dimethyl	0.1068	0.00603	0.1051	0.1051
Z-2,2-Dimethyl	0.1211	0.00850	0.1237	0.1280
2-Chloro	0.1080	0.00348	0.1090	0.1083
3-Chloro	0.1092	0.00355	0.1094	0.1084
4-Chloro	0.1088	0.00357	0.1090	0.1076

---

[a] The spectra of the methylbiphenyls were recorded on a Varian E-4 spectrometer and the spectra of the chlorobiphenyls were recorded on a Varian X-band spectrometer.

Table VI (Con't)

Observed EPR Resonances and ZFS Parameters of Phosphorescent Biphenyls[a]

Biphenyl	H_{min}[b]	H_x[c]	H_y[c]	H_z[c]	X	Y	Z
Biphenyl	1506	2704 3779	2598 3897	2134 4463	0.0328	0.0398	0.0725
2-Methyl	1514	2797 3689	2584 3926	2164 4442	0.0273	0.0413	0.0715
3-Methyl	1507	2719 3758	2594 3905	2142 4448	0.0318	0.0403	0.0718
4-Methyl	1511	2719 3765	2610 3891	2166 4442	0.0320	0.0394	0.0723
4,4'-DImethyl	1516	2732 3758	2627 3889	2139 4423	0.0315	0.0389	0.0708
E-3,3'-Dimethyl	1510	2717 3770	2616 3885	2153 4437	0.0322	0.0382	0.0711
Z-3,3'-Dimethyl	1510	2756 3727	2583 3922	2153 4437	0.0298	0.0438	0.0711
E-2,2'-Dimethyl	1511	2729 3693	2582 3924	2163 4444	0.0292	0.0413	0.0712
Z-2,2-Dimethyl	1446	2793 3760	2496 4019	1982 4583	0.0299	0.0469	0.0807
2-Chloro	1502	2701 3776	2595 3895	2130 4461	0.0330	0.0399	0.0726
3-Chloro	1502	2701 3774	2592 3895	2125 4462	0.0329	0.0400	0.0728
4-Chloro	1504	2701 3769	2592 3891	2133 4459	0.0327	0.0498	0.0725

---

[b] Observed signal in gauss, measured half-way between top and bottom of curve.

[c] Observed signal in gauss, measured half-way between curve.

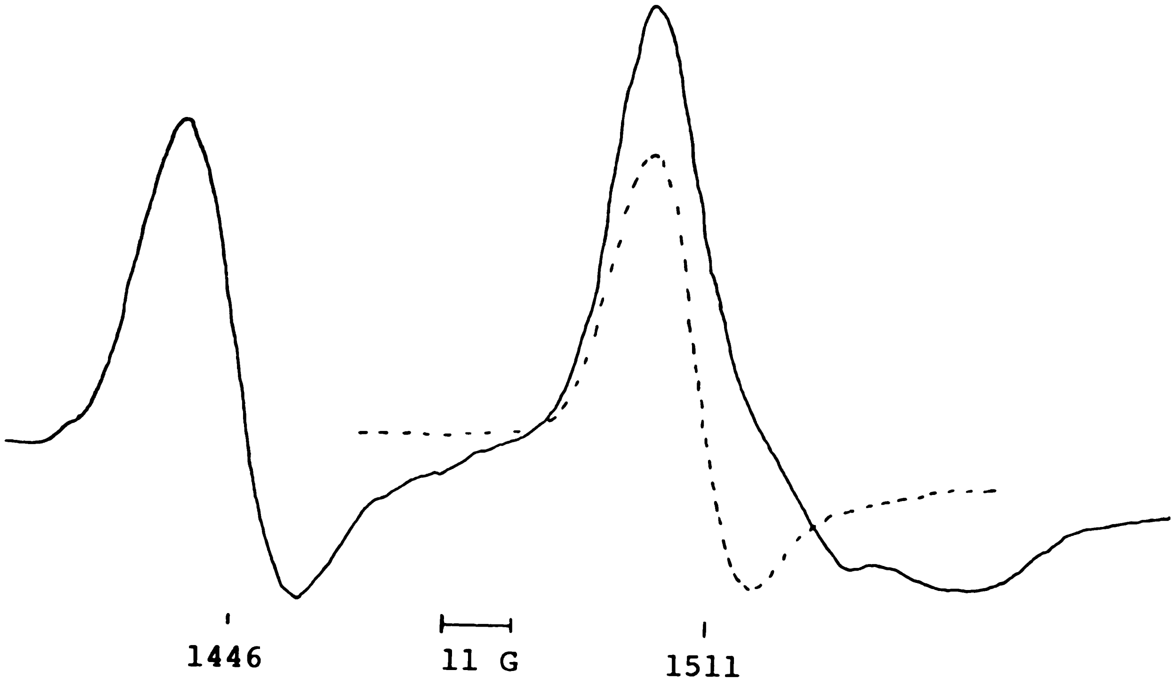


Figure XVI: Δm = 2 Signals for 2,2'-Dimethylbiphenyl (solid line) and 3,3'-dimethylbiphenyl (dotted line). Field measured in gauss.

Figure XVII: Z Signals for 2,2'-Dimethylbiphenyl (top) and 3,3'-Dimethylbiphenyl (bottom). Field measured in gauss.

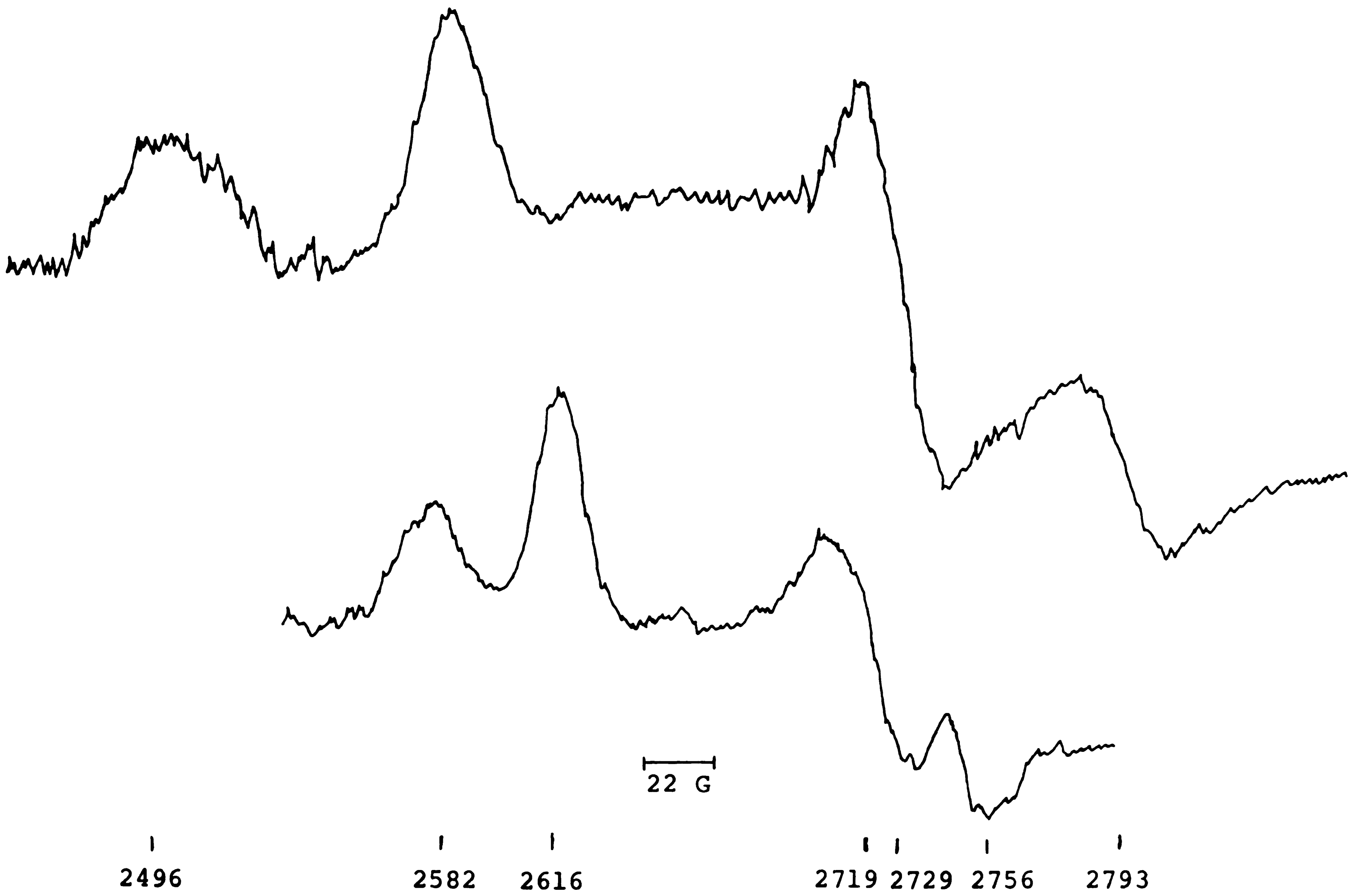


Figure XVIII: X and Y Signals for 2,2'-Dimethylbiphenyl (top) and 3,3'-dimethylbiphenyl (bottom). Field measured in gauss.

DISCUSSION

The goal of this work was to find the minimum sized *ortho*-substituents necessary to force triplet biphenyl out of planarity and to then construct a potential energy diagram which would describe: (1) the ESR spectra of the chloro and methylbiphenyls, (2) the opposite effects of *ortho*- and *para*-substituents on the energies of both $S_o \rightarrow S_1^*$ absorption and $T^* \rightarrow S_o$ emission, and (3) the opposite effects of *ortho*- and *para*-substituents on the rate constants for energy transfer from triplet benzophenone to biphenyl.

Planarity of the Biphenyl Triplet:

Zero-field spin-spin interactions should be strongly dependent on the degree of conjugation and thus coplanarity of the two rings in triplet biphenyl.[50] Yet, since the resonance energy varies with the $\cos^2$ of the angle of twist[145], slight changes from coplanarity might not show measurable effects. In fact a twist angle of 45° should destroy approximately 50% of the resonance energy of the molecule.[146] The very nearly identical D values for biphenyl, the monomethylbiphenyls, 4,4'-dimethylbiphenyl, and the two 3,3'-dimethylbiphenyls indicate that all seven triplets retain the same planar geometry.

Since both 2,2'- and 3,3'-dimethylbiphenyl can exist in two conformations, as illustrated below, the two triplet sp

th

co

wi

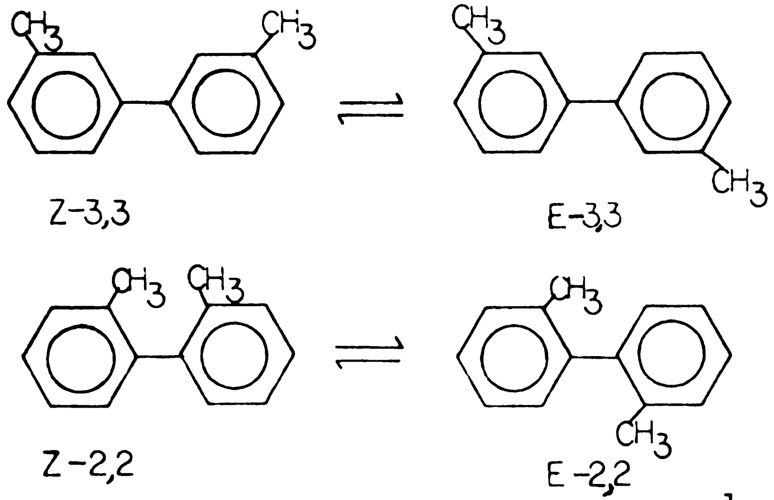
en

di

Th

s

species observed for each are most reasonably attributed to the separate conformers. It would be expected that the two conformers of 3,3'-dimethylbiphenyl would produce triplets with the same D value and with E values just different enough to yield distinguishable $\Delta m = 1$ signals, but not different enough to yield two different $\Delta m = 2$ signals. Two groups on the same side of the long molecular axis should produce a significant increase in anisotropy, so



Z-3,3 ⇌ E-3,3

Z-2,2 ⇌ E-2,2

Z-3,3 is assigned the larger (0.007 cm^{-1}) E value. It is interesting that an average of the two E values of the two triplets produced from 3,3'-dimethylbiphenyl (0.00480) is nearly that of 3-methylbiphenyl (0.00423).

Interestingly, the two conformers of 2,2'-dimethylbiphenyl produce triplets with distinctly different D and E values. The conformer with the lower D value has been assigned as E-2,2'-dimethylbiphenyl since the two o-methyl, o'-hydrogen interactions should be similar to the o-methyl, o'-hydrogen: o-hydrogen, o'-hydrogen interactions of

2-methylbiphenyl. The o-methyl, o'-methyl interaction should be the strongest interaction and thus the higher D value has been assigned as Z-2,2. Of all the biphenyls studied only Z-2,2 displays a large enough D value that it can be deduced to be non-planar.

It can be concluded then that the repulsive nonbonded interactions between an ortho-chlorine or ortho-methyl and an ortho'-hydrogen are not sufficient to cause triplet biphenyl to lose the conjugation stabilization afforded by planarity, at least not enough to produce measurable changes in the ESR. But these interactions are sufficient to produce measurable effects on the quenching rate constants, absorption, and emission of these compounds. The D value of benzene is 0.159[147] and allows a rough estimate of the angle of twist of triplet Z-2,2 of at least 20°.

Effects of Substituents on the Triplet:

The chlorobiphenyl ESR decay studies obtained by Mary May[143] clearly indicate that the signals are produced by biphenyl itself. Apparently chlorine is being ejected from the molecule during the irradiation to produce the triplet, although such is not observed during the phosphorescence studies. Since no useful ESR data could be obtained from the chlorobiphenyls, the methylbiphenyls were studied.

The moderately lower D values for the methyl substituted biphenyls coupled with the observed broadened linewidths of the $\Delta m = 1$ signals for the ortho- and para-methylsubstituted biphenyls indicate that hyperfine interactions between the electron spin and the nuclear spin of the benzylic hydrogens are occurring. It is interesting to note that the X and Y signals of the Z-2,2 triplet are twice as broad as those of the other biphenyls. This is probably due to the enhancement of spin density at the methyl-substituted *ortho* carbons of this nonplanar, less conjugated triplet.

The decrease in the energies of the ${}^1A \rightarrow {}^1L_a$ ($S_o \rightarrow S^*$) and ${}^3L_a \rightarrow {}^1A$ ($T^* \rightarrow S$) transitions caused by *para*-chlorosubstitution is a normal inductive substituent effect on the L_a states.[141] The decrease caused by the *para*-methyl group must be a combination of inductive and hyperconjugative effects. It is interesting that the 600 cm^{-1} shift in the phosphorescence spectrum shown by the *para*-chloro and methyl substituents and the 1280 cm^{-1} shift caused by di-*para*-methylbiphenyl are very close to the 700 cm^{-1} shift reported for the triplet energy of chlorobenzene, the 500 cm^{-1} shift for toluene, and the 1300 cm^{-1} shift for *para*-xylene[13] relative to benzene.

Effect of Meta-Substitution:

A *meta*-chlorine or methyl substituent produces no change in the energies of absorption or emission. The di-*meta*-methylbiphenyl shows a slight red-shift in absorption but no change in the extinction coefficient and a slight shift in emission. Moreover, the *meta*-chlorine does not shorten the phosphorescence lifetime of biphenyl nearly as much as does an *ortho*-chlorine, and the ESR line widths of the meta-substituted biphenyls are identical to those of biphenyl itself. These results are interesting in the light of Mispelter's[95] recent evidence that there is negligible free spin at the meta-position of triplet biphenyl. Meta-chlorobiphenyl is a better quencher of triplet benzophenone than biphenyl itself. Very small changes in triplet energy can have large effects on observed rates of reversible, approximately thermoneutral, energy transfer. Since commercially available 3-chlorobiphenyl is quite impure, it is possible that residual impurities enhanced the quenching efficiency. The second component observed in the lifetime studies may be due to this impurity.

Steric Effect of Ortho-Substituents:

It is relatively easy to rationalize the higher energy phosphorescence of the ortho-substituted biphenyls relative to biphenyl. Both chlorine and methyl groups are bulkier than hydrogen and therefore introduce a larger steric barrier to planarity than exists in biphenyl alone. This steric destabilization should be larger in the excited state than in the ground state since the shorter central bond in excited biphenyl brings the methyl or chlorine closer to an o'-hydrogen. The ortho-substituent increases the energy difference between the planar conformation of the ground and triplet states. Since phosphorescence involves just such a transition, its energy is increased.

It is interesting that of all the biphenyls studied only 2,2'-dimethylbiphenyl shows structure in the fluorescence spectrum. 2,2'-dichlorobiphenyl shows reduced fluorescence, as do all the ortho-substituted biphenyls, but no real structure. It is possible that this structure is due to the two conformers of the dimethylbiphenyl.

Effect of Substituents on Ground State Biphenyl:

Preconceived concepts about what ortho-groups should do to biphenyl's ground state can easily lead one into error. For example, one might expect that 2,2'-dibromo- and 2,2'-dichlorobiphenyl would prefer the trans-conformation. X-ray and other studies have indicated that these molecules prefer the cis-configuration, at least in the solid. London attractive forces have been involked to explain this preference. Unanue and Bothorel[148] have estimated the angle of twist and the Van der Waals distance beteen the ortho groups using a Rayleigh light scattering technique. These data are listed in Table VII.

Interestingly they predict from their observed data on 2,2'-dimethylbiphenyl and the results on 2-methylbiphenyl and 2,2',4,4',6,6'-hexamethylbiphenyl that the trans and cis conformers of 2,2'-dimethylbiphenyl are equally likely to exist. This same prediction is also true for 2,2'-dichlorobiphenyl albeit the angle of twist is greater. This result is in agreement with that of Suzuki's[140] who indicates that

Table VII

Observed Angles of Twist and Van der Waal's Radii for Biphenyls

Biphenyl	Observed (a) angle°	 radii Å	"Normal" (b) angle°	 radii Å
biphenyl[c]	31[d]	2.14	43°30'	2.40
4-methyl-[c]	34	2.18	43°30'	2.40
4-bromo-[c]	22°	1.97	---	---
2-methyl-[c]	46°30' (58)[e]	2.45	72°30'	3.20
2-chloro-[c]	48°30'	2.52	66°	3.15
2,2'-dimethyl-[c]				
cis-	49°(80°)[e]	2.50	84°	4.00
trans-	48°30'	2.52	72°30'	3.20
2,2',4,4',6,6'-[c] hexamethyl-	47°	2.45	---	---
2,2'-dichloro-				
cis-	64°(74°)[g]	3.07	98°30'	3.72
trans-	60°	2.90	66°	3.06
2,2'-dichloro-benzidine[f]	72°	---	---	---
2,2'-dimethyl-benzidine[g]	86°	---	---	---

---

[a] Angle of twist between rings

[b] Due to steric effect only

[c] Reference 148

[d] 0° (crystal), 45° (vapor), 20-30° (solution)

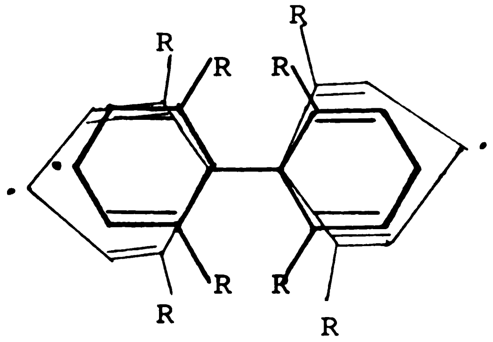
[e] Reference, 149

[f] Reference, 150

[g] References 151, 160

2,2'-dimethylbiphenyl is mostly in the trans conformer, but that some cis conformer is probably present. Suzuki's conclusion is based on the similarity of the UV spectra of 2,2'-dimethylbiphenyl and 2,6-dimethylbiphenyl viz. the inflection at 227 mu due to the vestigal A band. The ESR results reported here clearly indicate that both conformers are present.

It is interesting that the methyl groups have so much less net effect than the chloro groups. Quite obviously the angle of twist and compression of the C-H or C-R (ortho)bond, the bending of the ortho-hydrogens and halo and methyl groups away from one another, deformation (stretching) of the interannular bond, and the deformation of the benzene rings are in a delicate balance. In the excited state, this balance is even more delicate. The planar excited triplet then may be represented somewhat as indicated by Westheimer[152] for the transition state in the racemization of optically active biphenyls.



Distortion of the Triplet as Evidenced by the Quenching Rates:

The ESR data indicates that 2-chloro and 2-methylbiphenyl as well as 4-chloro- and 4-methylbiphenyl are planar in the triplet state. Yet the ortho-substituted compounds are poorer quenchers than biphenyl and the two para-substituted compounds do not approach a quenching constant near that of the diffusion controlled quenching rate. These results indicate that even for the 4-chlorobiphenyl good overlap between the π,π orbitals of the biphenyl and the n,π orbitals of the benzophenone can not be achieved. Implicit in this conclusion is that non-vertical energy-transfer must be occurring even in the para-substituted compounds and thus the 0-0 band for phosphorescence and that of the S→T* absorption should not coincide. Since greater geometric changes must occur in the ortho-substituted biphenyls during the energy-transfer process the observed quenching rates are lower. It is interesting that the smaller than predicted steric effect of the methyl groups in the ground state is carried over to the excited state. The ortho-methyl groups has no where near the effect of the ortho-chloro group on the quenching rate. The para-methyl group does not stabilize the triplet as well as the para- chloro group.

Triplet Energy of the Biphenyls:

The eight-fold increase in the forward rate constant for energy transfer from triplet benzophenone to biphenyl caused by para-chlorine substitution must reflect a decrease in the triplet energy of biphenyl. Since the triplet energy of biphenyl has been estimated as 68.5 kcal/mole,[9] the triplet energy of 4-chlorobiphenyl can be estimated as 67 kcal/mole. The *para*-chlorine presumably produces no change in the shape of either the ground or the excited state potential but lowers the excited state by 1.5-2 kilocalories relative to the ground state, independent of the angle of twist between the rings. The one and a half-fold increase in the forward rate constant observed for *para*-methylbiphenyl correlates with a triplet energy of 68.2 kcal/mole.

Attempts to estimate the triplet energy of the *ortho*-substituted biphenyls is not as fruitful. The *ortho*-group changes the ground state potential by producing a larger barrier to rotation and therefore a more twisted minimum. In the excited state this interaction broadens the potential well.

Construction of the Potential Energy Diagram:

The potential energy diagram is depicted in Figure XX. The points of highest energy in the ground state and excited state potential wells indicate the difference in energy between the ground and excited states in benzene (approximately 85 kcal/mole), toluene, or xylene. The excited state potential well is deeper than that of the ground state, since the 1-1' bond has more double bond character (higher bond order). The differences between the ground and excited state potential wells at 0° and at about 25° correspond to the values determined by the spectroscopic and nonspectroscopic T*→S transitions in biphenyl[9] (solid line). The dotted and dashed lines represent the estimated changes caused in the potential wells by the incorporation of *ortho*-substituents. The dotted line indicates the presumed distortion caused by a mono-*ortho*-substituent. The barrier to rotation is increased in the ground state and the potential well is broadened in the excited state. Placement of two groups in the *ortho*-position (dashed line) increases the barrier to rotation even more in the gound state and the excited state now shows that two conformationally distinct triplets are possible. The ESR data on the 2,2'-dimethylbiphenyl indicates that a slight activation energy barrier is established for the interconversion of the two conformers. Of the two possible conformations in the excited state of the di-*ortho*-substituted biphenyl, one probably has a lower energy well than the other. For a more complete description of changes in potential wells accompanied with steric effects the reader is referred to Jaffe and Orchin.[153]

Indications for Future Research:

The following studies would further elucidate the steric effects involved in excited state biphenyls:

(1) The ESR and low temperature NMR studies of 2,2'-di(trifluoromethyl)-6,6'-difluorobiphenyl would be quite intriguing. In the Z conformation the *ortho*-fluorine should split the *ortho*'-fluorine and in the E conformation it would be split by

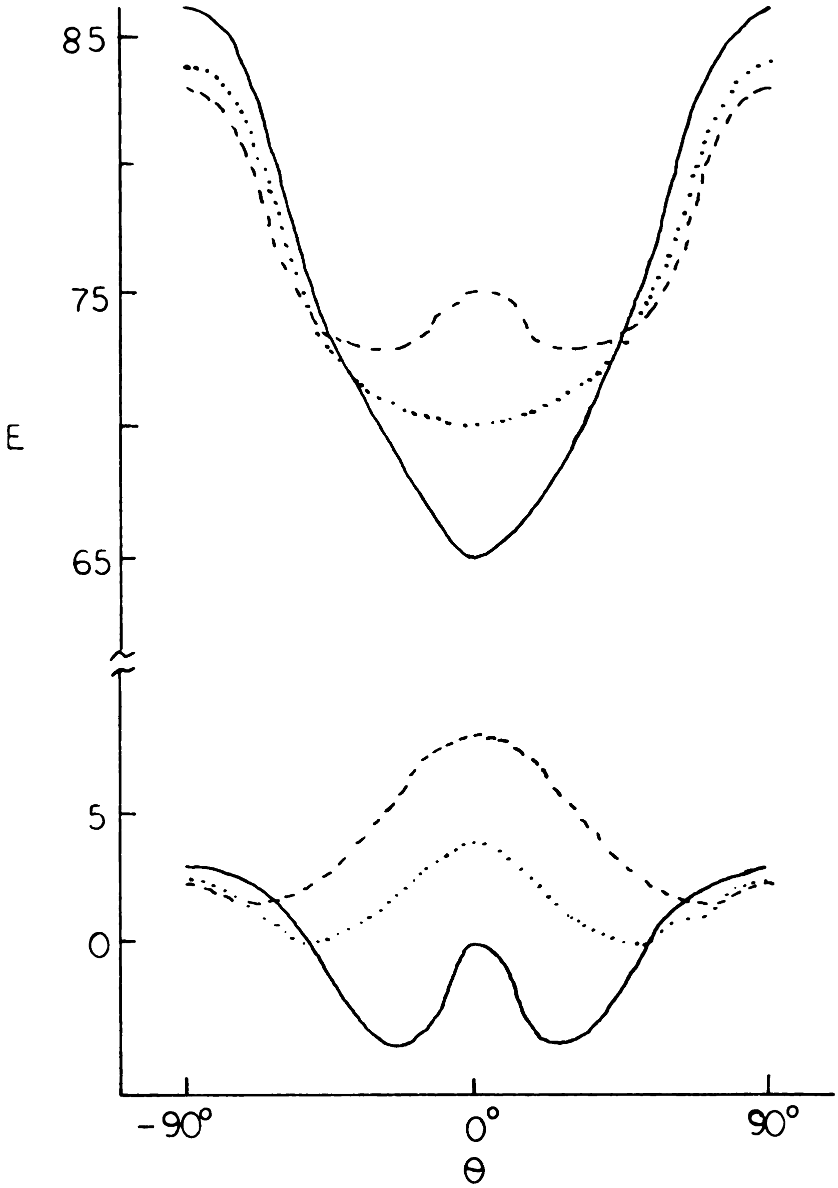


Figure XIX

Potential Energy Diagram for Biphenyls (——) Biphenyl, (···) monosubstituted *ortho*-biphenyls, (---) disubstituted *ortho*-biphenyls.

the trifluoromethyl fluorines. The ESR spectrum might be quite complex because of the hyperfine fluorine splittings.

(2) The quenching and ESR studies with one _ortho_-substituent and groups in the _meta_-position of biphenyl should give some idea as to how important "buttressing" effects are in the excited states. It would be interesting to see the effect of an _o_-_t_-butylgroup on the triplet state. The ESR of a series of _meta_-substituted biphenyls to determine if the E values of the two conformers from disubstituted biphenyls are really additive would be appropriate.

(3) The singlet and triplet lifetimes of the biphenyls would be interesting to determine. Hopefully the disubstituted materials would show two different decays indicative of the two possible conformers.

AZIDOALKYL PHENYL KETONES

RESULTS

Part II

Three azido phenyl ketones were prepared by an S_N2 reaction of sodium azide on the corresponding haloketone or ketal. The efficiencies with which γ,δ and ε-azidoalkyl phenyl ketones undergo the Type II photochemical reaction were measured in benzene. As indicated in Scheme II (Introduction) a large number of products might be formed upon irradiation of these ketones, yet the VPC traces of irradiated azido ketones are relatively simple. During irradiation benzene solutions of γ-azidobutyrophenone turn dark yellow or light orange. Solutions of δ-azidovalerophenone turn only a pale yellow and solutions of irradiated ε-azidophenone remain colorless. Type II quantum yields of γ-azidobutyrophenone exhibit a wavelength effect, concentration effect, and vary with irradiation time. Type II quantum yields of δ-azidovalerophenone exhibit a wavelength effect, and vary with irradiation time. Type II quantum yields of ε-azidohexanophenone behave normally.

Identification of Photoproducts of Azidoalkyl Phenyl Ketones:

(a) From γ-azidobutyrophenone:

The VPC trace of photolyzed γ-azidobutyrophenone is reproduced in Figure (XX). Peaks I and IV are the standards tetradecane and octadecane, respectively. Peak VII is the parent ketone and peaks II, III, V, and VI represent the photoproducts. Attempts to isolate all these products by preparative VPC proved futile. Passage of irradiated solution through a preparative VPC containing a thermal detector gave only 2-phenyl-Δ^1-pyrroline(PPRL) and acetophenone, while an unirradiated sample gave only PPRL. The PPRL was identified by comparing the VPC retention time of the material obtained from the preparative VPC with that of a pure sample (prepared by A. E. Kemppainen). The NMR and mass spectra of the pure PPRL and that of the isolated material were identical. Acetophenone was identified by its VPC retention time compared to that of a pure sample.

It was important to establish whether peaks V and VI were the cyclobutanols or nitrene-derived products. Since other methods of identification proved unsuccessful, the materials were analyzed by GC/mass spectrographic techniques. The data obtained are presented in Table VIa.

Table VI$_a$

GC/Mass Spectral Data for γ-Azidobutyrophenone

Compound	Peak, m/e
2-phenylpyrrole (Peak VI)	143
2-phenyl-Δ^1-pyrroline (Peak III)	145
γ-azidobutyrophenone (Peak VII)	161 (189-28)

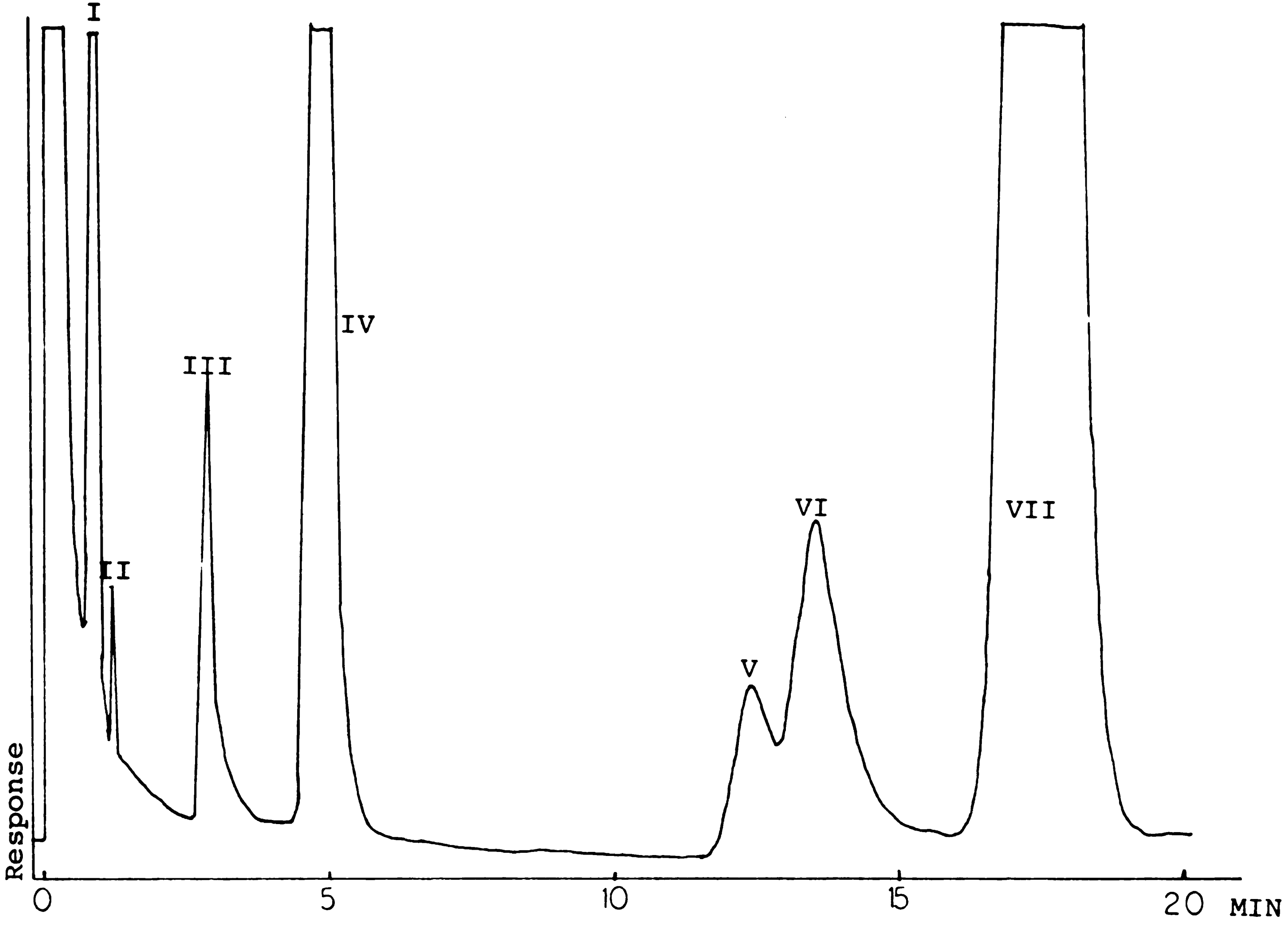


Figure XX: VPC Trace of Photolyzed γ-Azidobutyrophenone, Col-1 and Col-4

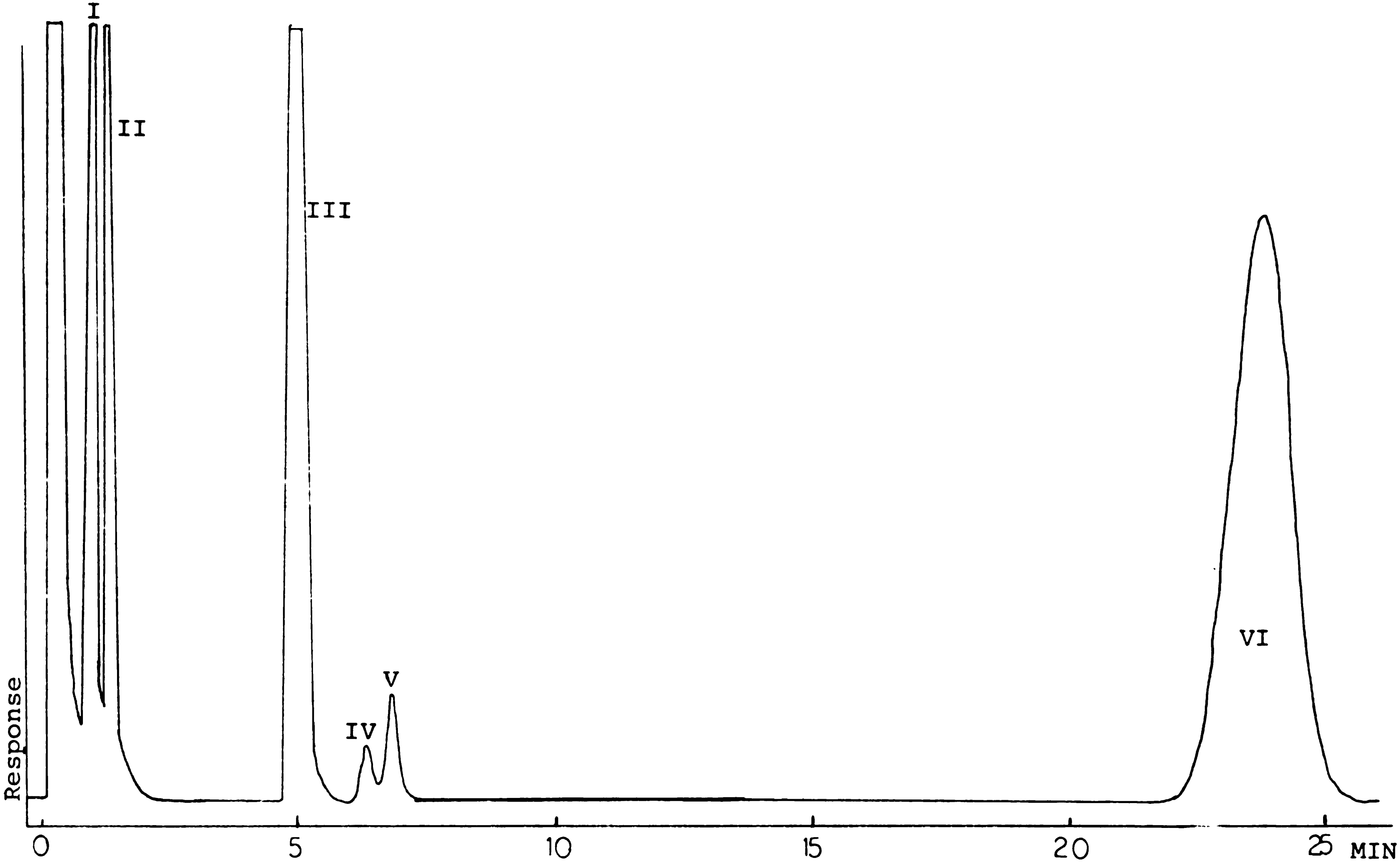


Figure XXI: VPC Trace of Photolyzed δ-azidovalerophenone Col-1

The GC/mass spectral data do not completely rule out the possibility that peaks V and VI are the cyclobutanols, since conceivably the cyclobutanol could loose nitrogen and water to give a parent peak of 143. An irradiated sample of γ-azidobutyrophenone (AZBP) was placed on an alumina column and eluted with 20% ethyl acetate benzene. Peak VI was eluted as a brown oil. This material was sublimed and resublimed. The physical properties and spectral data are consistent with this material being 2-phenylpyrrole. A 40% chemical yield of 2-phenylpyrrole was realized. Peak V was never eluted even after pure methanol was used as the elutant. It is possible that this material is the oxazirane (see Discussion) precursor to the 2-phenyl pyrrole. Peak V does not appear in the GC/mass spectral trace either. Peak V is also quite photoinert since prolonged irradiation caused peak VI to disappear while peak V neither decreased nor increased.

The GC/mass spectrum of peak VII is identical to the mass spectrum obtained for the unirradiated azidoketone. That peak VII is the parent ketone (AZBP) was further confirmed by isolation of the AZBP from an irradiated sample by column chromatography. Elution of the parent ketone from an alumina column was effected with hexane. The IR and NMR of this material were identical to that of the unirradiated material.

A brown oil eluted from the alumina column subsequent to the 2-phenylpyrrole shows azide, carbonyl, and either NH or OH absorbances in the IR. The NMR of the material is essentially that of the AZBP. It shows no VPC trace and is assumed to be polymers derived from AZBP, 2-phenylpyrrole, or γ-iminobutyrophenone. During the photolysis of AZBP in cyclohexane a yellow oil collects on the sides and bottom of the tube. This material turns brown when exposed to the air and IR and NMR data are identical to that of the brown oil collected from the chromatographic studies.

(b) From δ-azidovalerophenone:

The VPC trace of photolyzed δ-azidovalerophenone (AZVP) is reproduced in Figure (XXI). Peaks I and III are the standards tetradecane and heptadecane respectively. Peak II was identified as acetophenone by comparing its retention time to that of a pure sample. To identify the other peaks, an irradiated sample of AZVP was subjected to GC/mass spectral analysis. The results are indicated in Table VIIa.

Table VIIa

GC/Mass Spectral Data for δ-Azidovalerophenone

Compound	Parent Peak
2-phenyl-3,4,5,6-tetrahydropyridine (V)	159
δ-azidovalerophenone (VI)	175 (203-28)
VPC Peak IV	173

Peak IV appeared in the VPC trace before AZVP was irradiated and it neither increased nor decreased after irradiation. Its identity remains unknown. 2-Phenyl-3,4,5,6-tetrahydropyridine was identified by its GC/mass spectrum. The GC/mass spectrum of peak VI was identical to the mass spectrum of unirradiated

AZVP. It is assumed that peak VI is AZVP since AZBP was isolated by column chromatography.

(c) From ε-azidohexanophenone:

The VPC trace of irradiated ε-azidohexanophenone (AZHP) shows only acetophenone on Col-3. Parent ketone gives no signal. On Col-4 parent ketone and peaks presumed to be cyclobutanols can be detected. These cyclobutanols have one half the area of the acetophenone peak and produce a signal in the same general area that the cyclobutanols from valerophenone and N-methyl-4-methyl-4-benzoyl piperidine are observed.

Quantum Yields:

Quantum yields for acetophenone and other product formation were measured at 366 and 313 nm by concurrently irradiating degassed solutions of ketone in benzene containing various additives. Valerophenone actinometers of identical optical density as the studied ketone were present during the entire irradiation period. Per-cent conversions in the valerophenone samples were no more than 15%. Per-cent conversions in the azidoketone samples were usually kept at 5% or below except in the case of AZBP where per-cent conversions were usually about 10%. Product to standard ratios of photolyzed ketone and valerophenone were measured by VPC. The quantum yields for AZBP and AZVP were measured in cyclohexane following the procedure described for the studies in benzene.

Wavelength Effects:

At 313 nm the extinction coefficient of a 0.07 M solution of acetophenone is 42[30] while the extinction coefficient of a 0.07 M solution of butyl azide is 7[105]. At 366 nm the absorbance of the azide group is negligible while that of the phenyl ketone is about 10.

The photolysis of AZBP at 313 nm where the azide group is absorbing about 20% of the incident light gives interesting results. The quantum yield for disappearance of ketone is increased by a factor of two relative to 366 nm irradiation. This same increase in quantum yield is observed for 2-phenylpyrrole and peak V. The most intriguing result is observed for the acetophenone quantum yield. Its initial value at 313 nm is equal to that observed at 366 nm, but at 313 nm the quantum yield increases with irradiation time. These results are depicted in figures XXII and XXIII. In contrast to the behavior of the acetophenone quantum yield for AZBP, the acetophenone quantum yield for AZVP at 313 nm stays constant with irradiation time but is slightly lower than observed at 366 nm (0.167 versus 0.195, respectively). Since it appeared that strange occurrences might be happening when light is concurrently absorbed by the carbonyl and azide moieties, all further work was performed at 366 nm.

Variation of Quantum Yields with Per-cent Conversion:

If quencher molecules are formed as a result of irradiation, the Type II quantum yield can decrease.[60] Since the

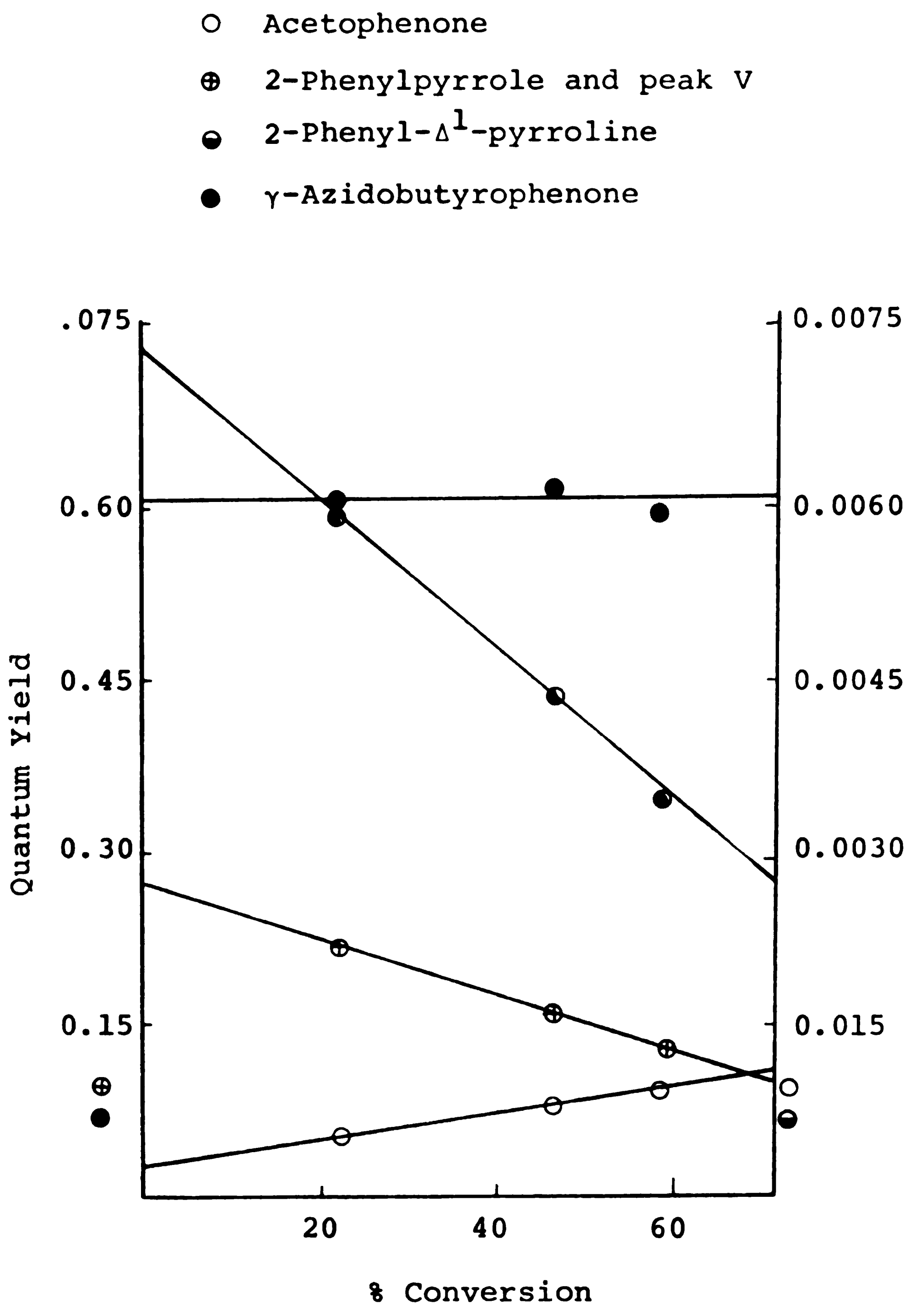


Figure XXII: Plot of quantum yields versus % conversion of γ-Azidobutyrophenone at 313 nm (scale on left is for disappearance of ketone and 2-Phenylpyrrole and peak V; scale on right is for acetophenone and 2-Phenyl-Δ^1-pyrroline.

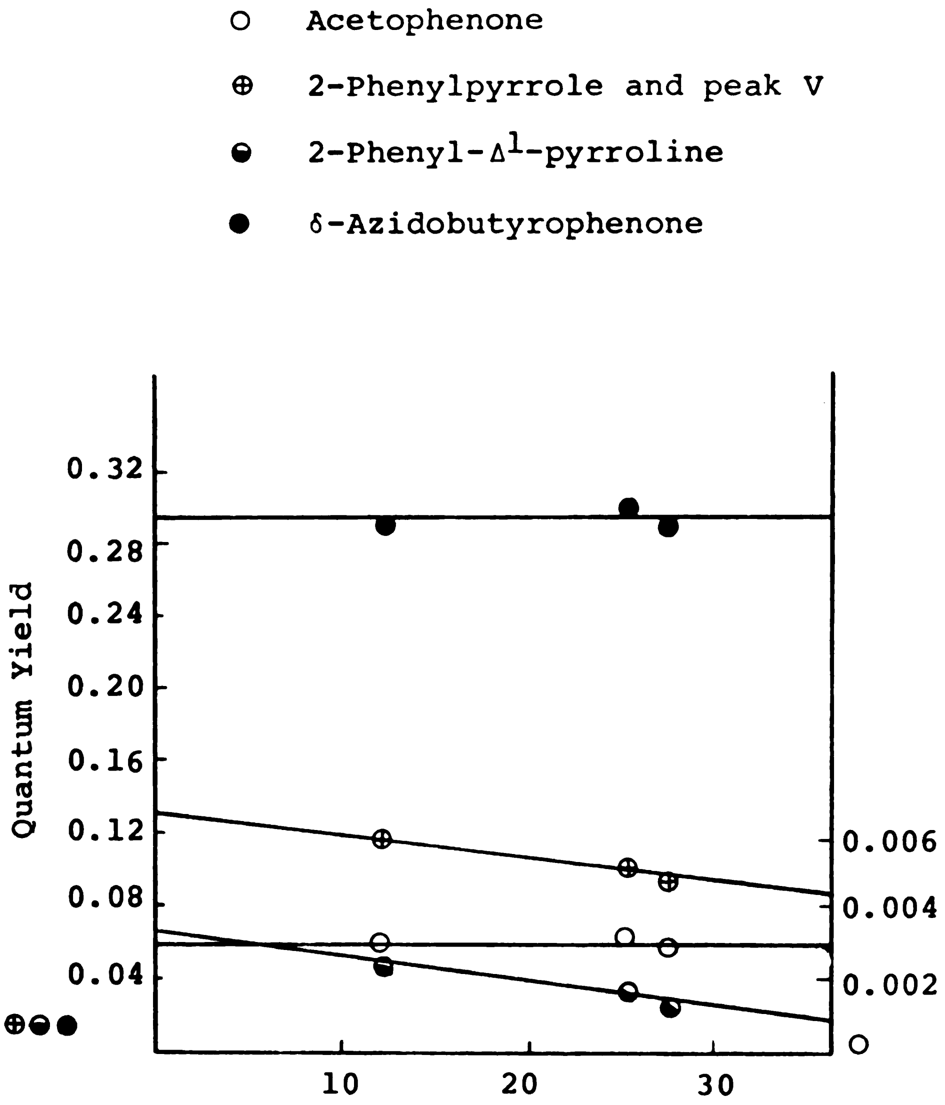


Figure XXIII: Plot of quantum yield versus % conversion at 366 nm (scale on left is for disappearance of ketone, 2-Phenylpyrrole and peak V, and 2-Phenyl-Δ^1-pyrroline; scale on right is for acetophenone.

azidoalkyl phenyl ketones do produce products which can act as quenchers, a check of Type II quantum yield with irradiation time in benzene was made. The actually observed decreases of Type II quantum yield for AZBP and AZVP with irradiation time are depicted in Figures XXIV, XXV. Certainly the 2-phenylpyrrole would be expected to act as a quencher because of the low triplet energies exhibited by heterocyclic aromatic molecules.[175] Since amines quench carbonyl triplets at about a diffusion-controlled rate[89], the cyclic imines formed in the photolyses of AZBP and AZVP might also be expected to act as quenchers. To check this notion 2-(4-*p*-fluorophenyl)-Δ^1-pyrroline was used to quench the Type II reaction from butyrophenone; a quenching constant (Stern-Volmer slope) of 264 M^{-1} was obtained. The olefinic azides produced from the Type II reaction of the azido ketones would also be expected to act as quenchers. The decrease in Type II quantum yield with increasing conversion can also occur if products are formed which can absorb incident light. The hypothetical iminoketones would absorb light and the observed decrease of Type II quantum yield may be enhanced slightly by the latter effect.

Concentration Effect:

Normally Type II quantum yields increase with an increase in ketone concentration.[4] However, since the azide moiety can act as a quencher[115] Type II quantum yields of the azido ketones might be expected to decrease with increasing ketone concentration. The variation of Type II quantum yield with ketone concentration for AZBP is indicated in Figure XXVI. The effect was almost negligible for AZVP and only somewhat larger for AZBP. The magnitude of this intermolecular quenching of triplet carbonyl by azide was measured by quenching the Type II reaction from butyrophenone. The measured $k_t\tau$ value was 10 M^{-1}. Since 0.07 M ketone seemed to minimize both the concentration effect and variation with per-cent conversion effect, all further work was performed at this ketone concentration.

Quenching Studies:

Stern-Volmer quenching slopes for the quenching of acetophenone formation were obtained by 366 nm photolysis of 0.07 M azidoketone solutions containing varying concentrations of 1-methylnaphthalene in benzene. Per-cent conversions were maintained as low as possible and the slopes were linear. A Stern-Volmer plot was also obtained for the quenching of 2-phenylpyrrole and peak V from AZBP. The slope of this plot was found to be similar to the slope of the plot obtained for acetophenone formation. The Stern-Volmer plots are depicted in Figures XXVII and XXVIII.

Intersystem Crossing Yields:

Intersystem crossing yields were determined by irradiating at 366 nm 0.07 M ketone solutions containing varying concentrations of cis-piperylene concurrently with a solution of 0.07 M acetophenone containing cis-piperylene. Plots of reciprocal quantum yield versus cis-piperylene concentration were linear.

There was some concern that in these studies the nitrene might add to the piperylene. However, photolyzed solutions of AZBP did not turn yellow in the presence of piperylene. No anomalous peaks were seen in the GC traces and the data was repeatable and internally consistent. Lewis[176] has indicated that triplet azide does not isomerize piperylene nor add to it. The plots obtained are shown in Figure XXIX. The ϕ_{isc} for γ-azidobutyrophenone is 0.80 while the ϕ_{isc} of δ-azidovalerophenone is 0.98.

Corrections Applied to Quantum Yields and Quenching Values:

In order to calculate the σ_I value for the azido group, the behavior of the azido ketones will be compared to valerophenone.[60] Thus it was necessary to correct the observed quantum yelds and $k_t\tau$ values for the conversion and concentration effects observed for AZBP and AZVP. No corrections were necessary for the observed AZHP values. The corrected and measured quantum yields and $k_t\tau$ values are listed in Table VIII.

The conversion effect was removed for AZBP and AZVP with the aid of the plots in Figures XXIV and XXV. The measured quantum yield of a 0.07 M AZVP benzene solution irradiated at 366 nm at three different per-cent conversions was extrapolated to zero per-cent conversion. It was assumed that during the pyridine and quenching studies, AZVP would behave proportionally the same as in benzene. Thus the measured Φ_{max} and $k_t\tau$ values at a particular per-cent conversion were extrapolated to 0% conversion using the quantum yield study in benzene as the reference ratio.[168] No per-cent conversion correction was

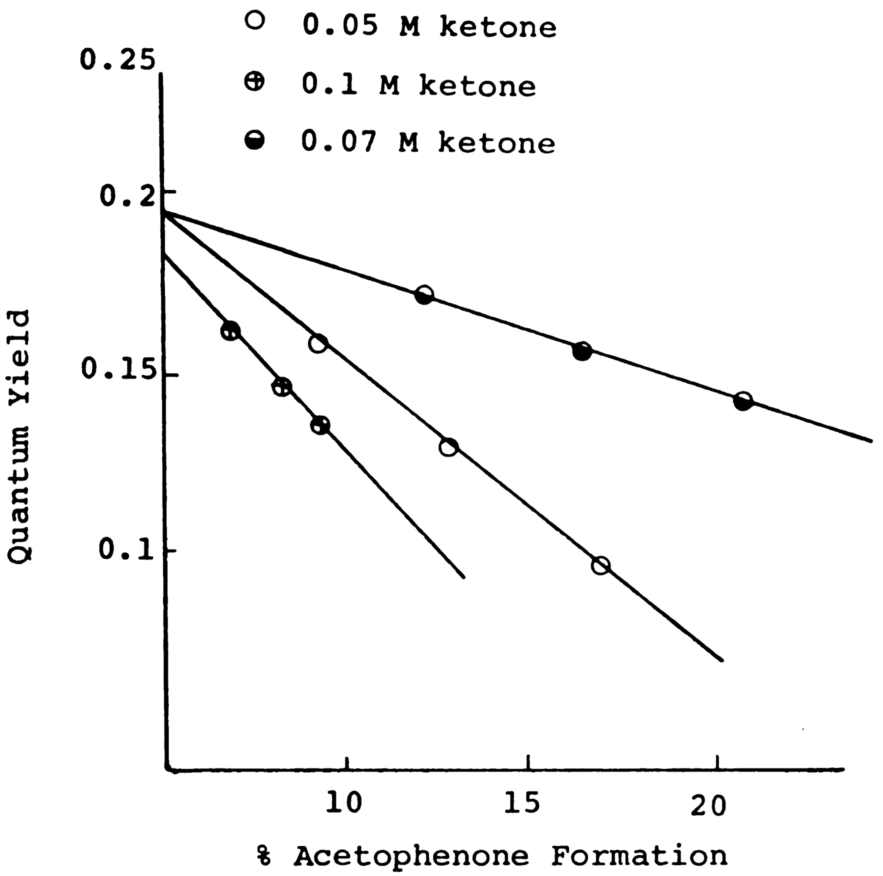


Figure XXIV: Plot of Type II quantum yield versus acetophenone formation at 366 nm of δ-azidovalerophenone.

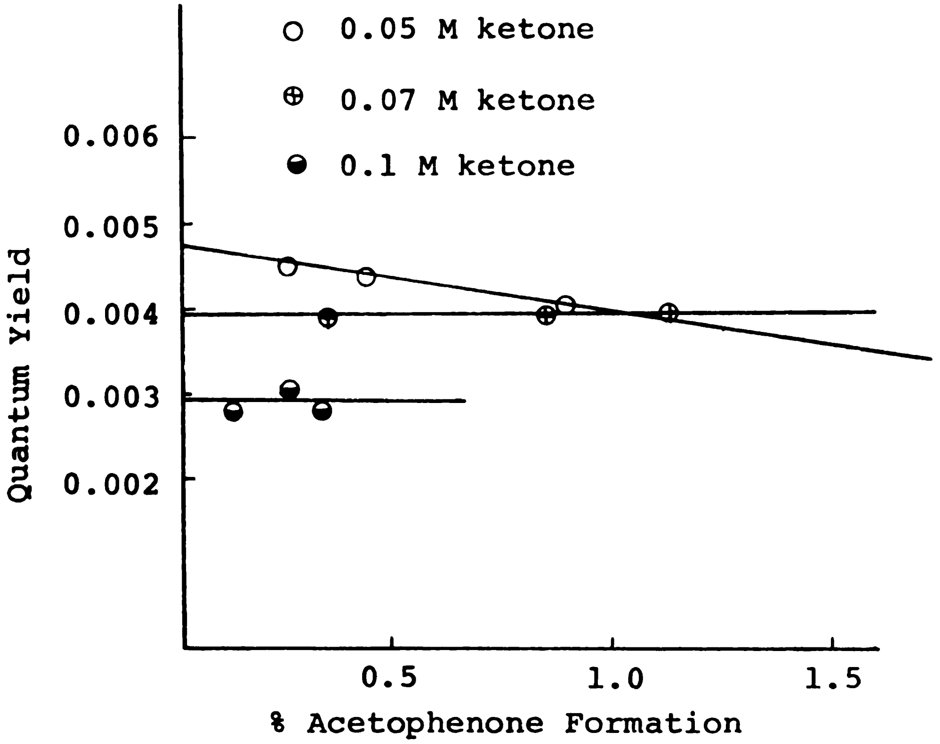


Figure XXV: Plot of Type II quantum yield versus % acetophenone formation at 366 nm for γ-azidobutyrophenone.

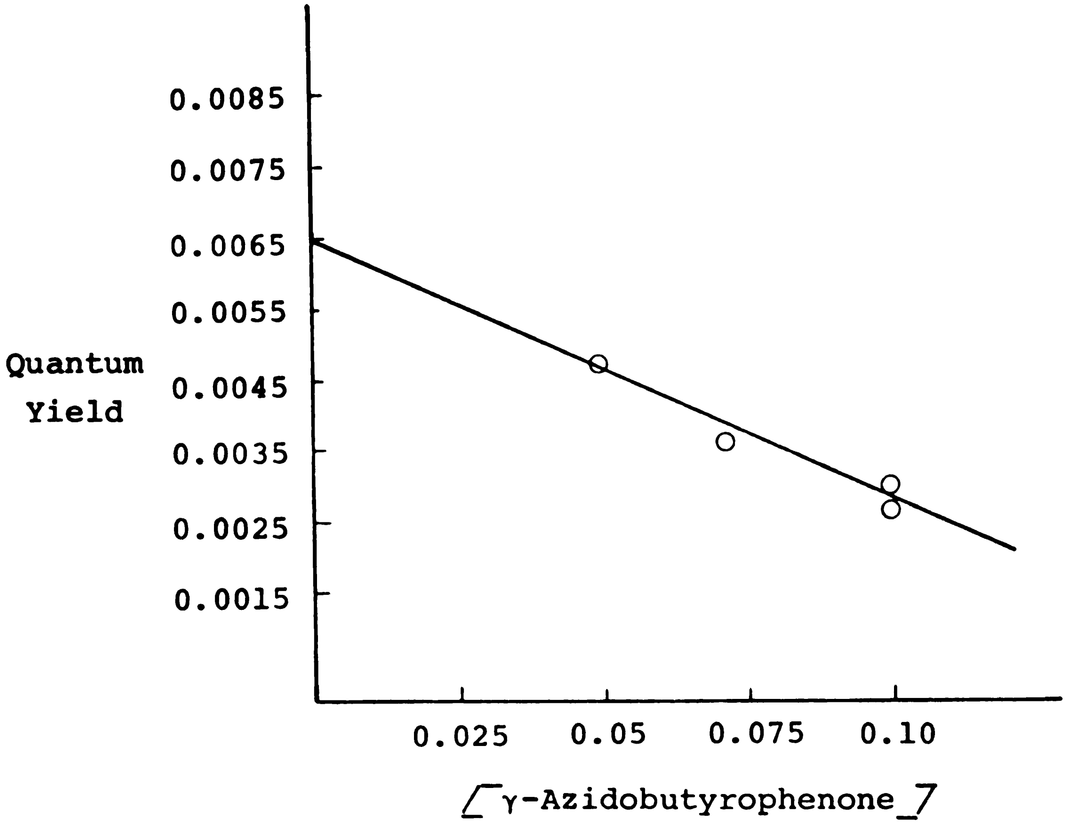


Figure XXVI: Plot of Type II Quantum Yield Versus [γ-azidobutyrophenone] Irradiated at 366 nm.

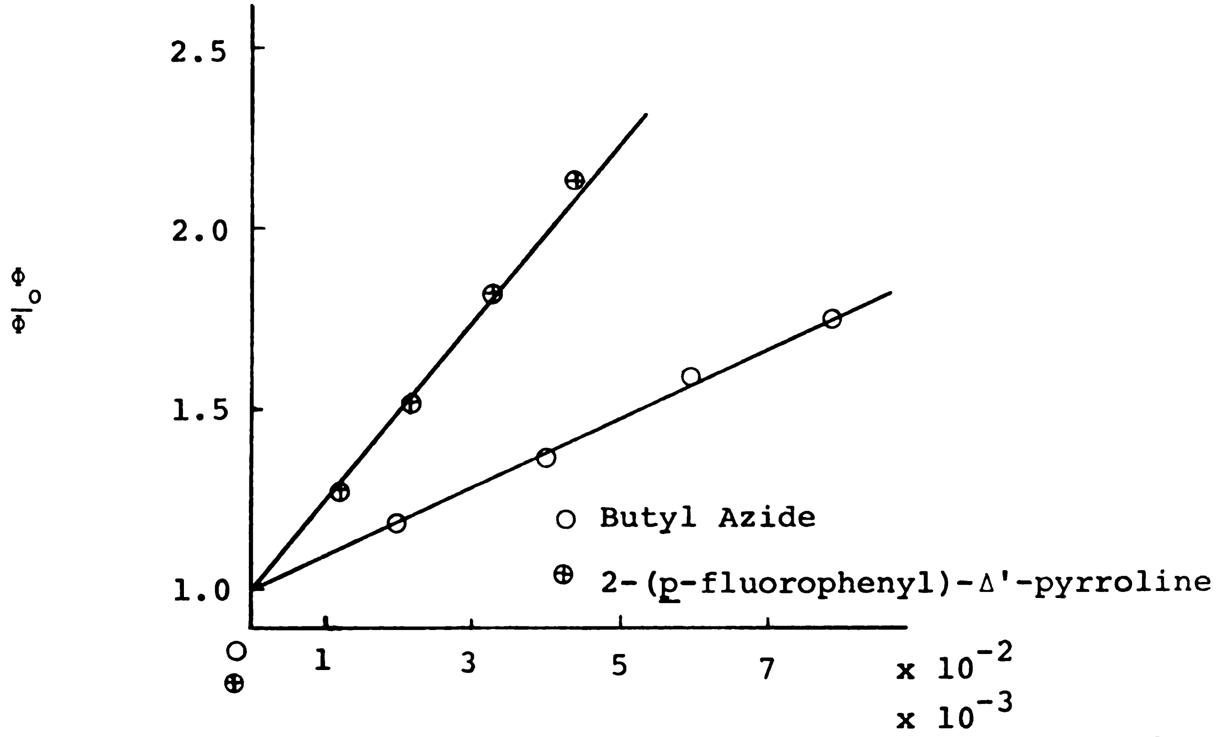


Figure XXVII: Stern-Volmer Quenching Plots of Butyrophenone by Butyl Azide and 2-(p-fluorophenyl)-Δ^1-pyrroline.

○ Acetophenone from γ-Azidobutyrophenone

⊕ Acetophenone from ε-Azidohexanophenone

◒ 2-Phenylpyrrole from γ-Azidobutyrophenone

● Acetophenone from δ-Azidovalerophenone

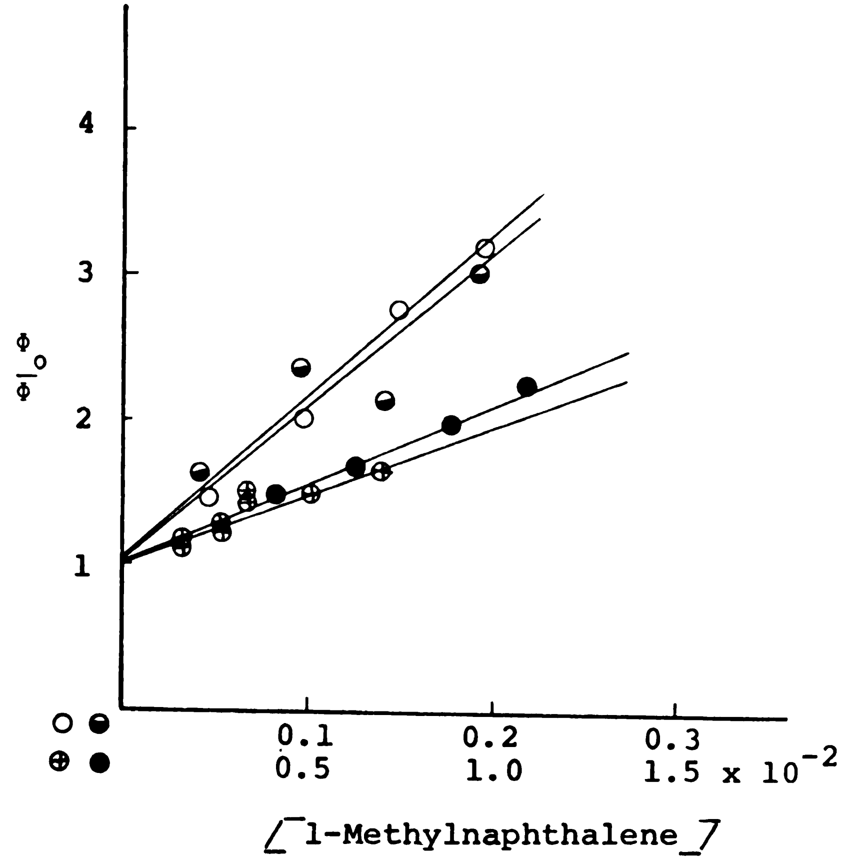


Figure XXVIII: Stern-Volmer Plots for the Azidoketones at 366nm.

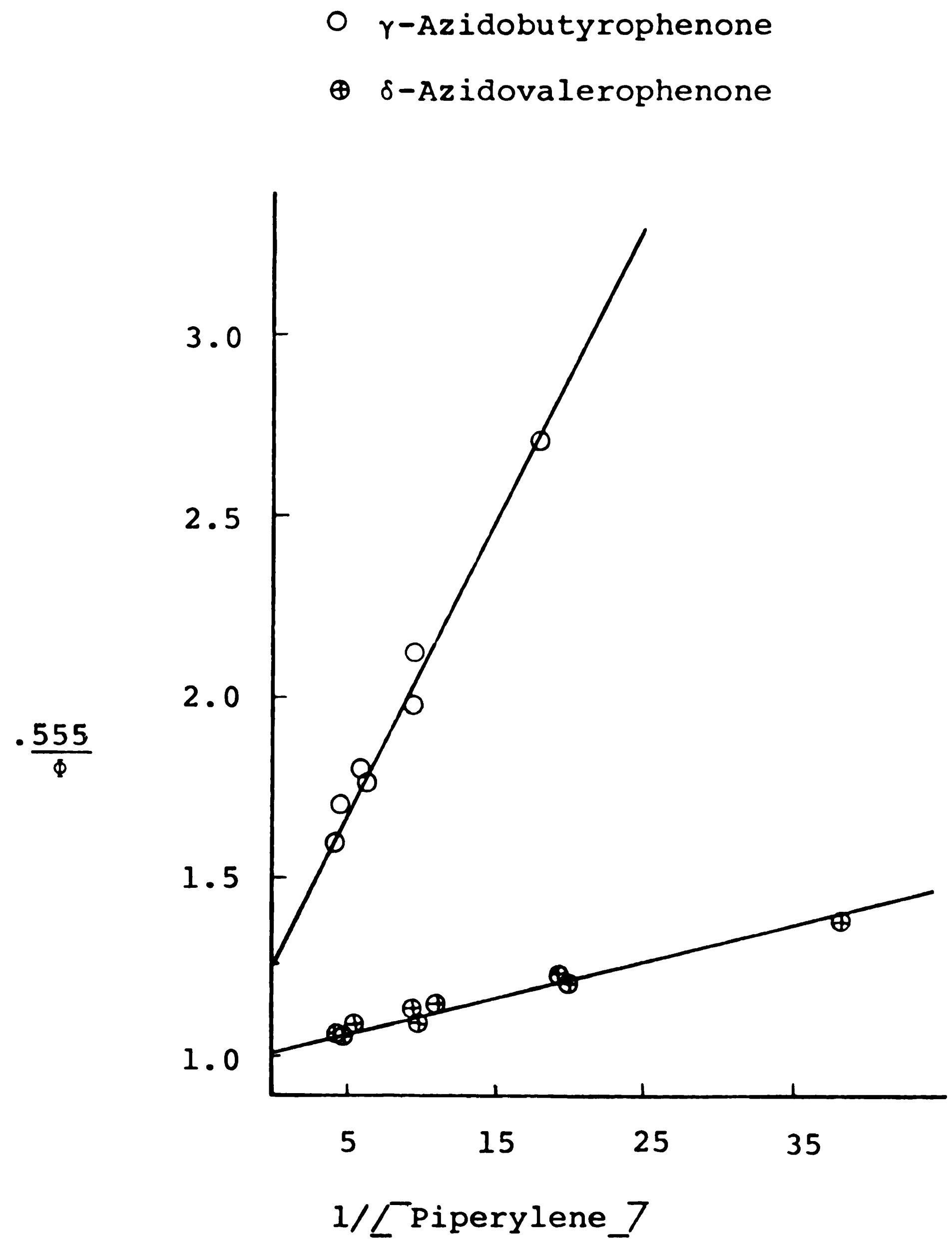


Figure XXIX: Sensitization Plots of γ-Azidobutyrophenone and δ-Azidovalerophenone.

applied to values measured for 0.07 M AZBP solutions since the quantum yield does not change with per-cent conversion.

Since the per-cent conversion slopes for the three different concentrations of AZVP studied all extroplate to about the same value at 0% conversion, no correction for a concentration effect was applied. The per-cent conversion plots for different concentrations of AZBP do not extrapolate to the same value at 0% conversion and thus a plot of ketone concentration versus quantum yield (Figure XXVI) was constructed. All the observed values (Φ, $k_t\tau$, Φ_{max}) for AZBP at 0.07 M ketone concentration were corrected by extrapolation to zero ketone concentration. In essence the $k_t\tau$, Φ, and Φ_{max} values were multiplied by a factor of 1.73 (Figure XXVII).

Since Wagner and Kemppainen[60] have indicated that phenyl ketones produce cyclobutanols with quantum yields that average 15% of the observed maximum Type II quantum yields, 15% of the maximum Type II quantum yield for AZVP and AZBP was assumed to be equal the cyclobutanol quantum yield for these ketones. It is assumed that the cyclobutanols formed are either decomposing under the VPC conditions or have the same retention time as the parent ketone.

Calculation of k_r Values:

The quantum yield for the Type II reaction can be written as a product of probabilities as shown in equation 21 or 22.

$$\Phi = \phi_{isc}\phi_{Br}\phi_{p} \qquad (21)$$

$$\Phi = k_r^{obs} t^{obs} \Phi_{isc} P_p \tag{22}$$

Rearrangement of this equation gives the following expression for k_r^{obs}:

$$k_r^{obs} = \frac{\Phi}{t^{obs} P_p \Phi_{isc}} \equiv k_r^{obs} = \frac{\Phi_{max}}{t^{obs} \Phi_{isc}} \tag{23}$$

The use of this equation requires that Φ_{max}, Φ, and $k_t\tau$ all be measured at the same per-cent conversion.[4] The observed lifetime, τ, was determined from the Stern-Volmer plot, where the slope is equal to $k_t\tau$. K_t for naphthalene and 1-methylnaphthalene was assumed to equal 5×10^9.[32] The value for the probability of the biradical to go on to product (P_p) was determined from the pyridine studies by dividing Φ_{max} into Φ.[4] The quantum yields and intersystem crossing yields (Φ_{isc}) were determined as previously described. The k_r, $1/\tau$, and P_p values obtained from equation 23 using the corrected quantum yields and $k_t\tau$ values are listed in Table IX.

Calculation of Rates of Energy Transfer:

Once k_r is known, the k_{et} values for energy transfer from triplet carbonyl to the azide group are easily calculable from equation 24 (see mechanism in DISCUSSION section).

$$1/\tau = k_d + k_r + k_{et} + k_q[Q_p] + k_t[RN_3] \tag{24}$$

K_d for similar type ketones is on the order of 10^5 sec^{-1} and can be ignored.[60] Even though k_t is about diffusion controlled, its effective quenching rate depends on the concentration of formed products. At low conversions (<10%), $k_q[Q_p]$ will be less than 10^7 sec^{-1} at 0.07 M ketone concentration. K_t for azide quenching has been measured in this work to be about 10^8 sec^{-1}. At 0.07 M ketone concentration, $k_t[RN_3]$ should have an effective quenching rate less than 10^7 sec^{-1}. Thus $k_q[Q_p]$ and $k_t[RN_3]$ should add only small contributions to the measured triplet decay rates. The calculated k_{et} values are listed in Table IX.

Table VIII

Data for Azido Ketones Measured at 0.07 M Ketone Concentration Irradiated at 366 nm[a]

Ketone	k_t	$\Phi_{II_{Acph}}$	Φ_{IImax} 0.5M pyr	Φ_{cybnol}	Φ_{isc}	Φ_{imine}	$\Phi_{pyrrole}$	Φ_{dis}
AZBP	18+3(13) 15±2)[b]	0.0065 0.0048[c]	0.013(0.0074)	0.002[g]	0.80	0.065	0.013	0.29 0.61[j]
AZVP	111 (97) (101)[b]	0.195 0.16[c]	0.32 (0.026)	0.048[g]	0.98 0.80[h]	0.02	---	---
AZHP	(93)	(0.34)[d] (0.40)[e] (0.34)[f]	(0.93)	(0.065)	(1.0)[i]	---	---	(0.36)[k]

[a] Values in ( ) are actual measured values. All other values for AZBP and AZVP are corrected as described in text. [b] From sensitization studies. [c] Measured in cyclohexane. [d] Measured at 0.05 M ketone concentration. [e] Measured at 0.07 M ketone concentration, highest value obtained. [f] Measured at 0.1 M ketone concentration. [g] Calculated from Φ_{IImax}. [h] Measured on yellow sample that had been sitting in refrigerator several months. [i] Assumed value since δ-azidoketone is almost 1.0[4]. [j] Measured at 3130. [k] Measured on 0.1 M ketone; Quantum yield for Acetophenone is 0.34, cyclobutanol quantum yield is 0.85.

Table IX

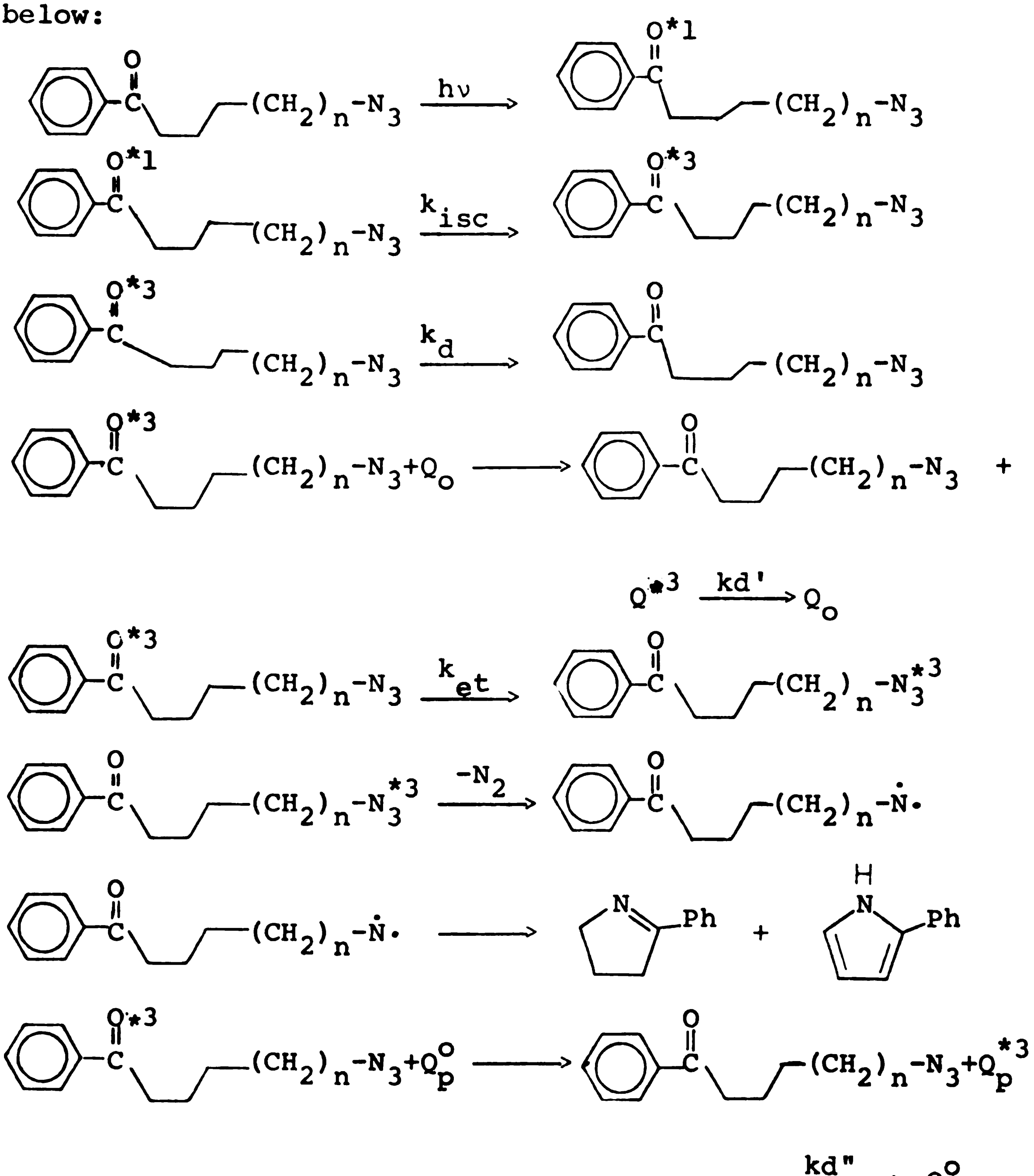
Rate Data for Alkyl Azido Ketones in Benzene

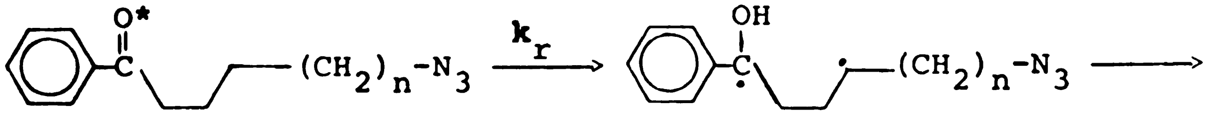
Ketone	$\tau \times 10^{-8}$	$1/\tau \times 10^{8}$ sec^{-1}	$k_r \times 10^{8}$ sec^{-1}	$k_{et} \times 10^{8}$ sec^{-1}	P_p
AZBP	0.36	2.7	0.05	2.7	0.57
AZVP	2.2	0.45	0.17	0.28	0.66
AZHP	1.86	0.54	0.54	<0.02	0.47

DISCUSSION

Mechanistic Scheme for Azido Alkyl Phenyl Ketones:

The products involved in the photochemistry of the azidoalkyl phenyl ketones indicate that the azido group does receive some of the triplet energy from the carbonyl group even at 366 nm where the absorbance of the azido group is approximately zero. An appropriate kinetic scheme is presented below:





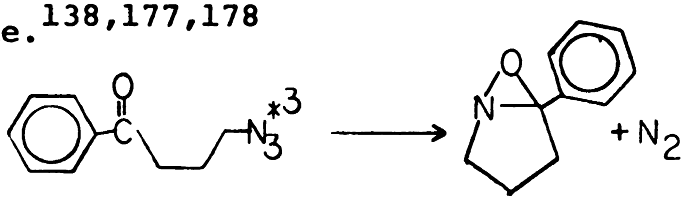
Type II

Straight forward Stern-Volmer kinetic analyses of this scheme lead to equation 24. (Results).

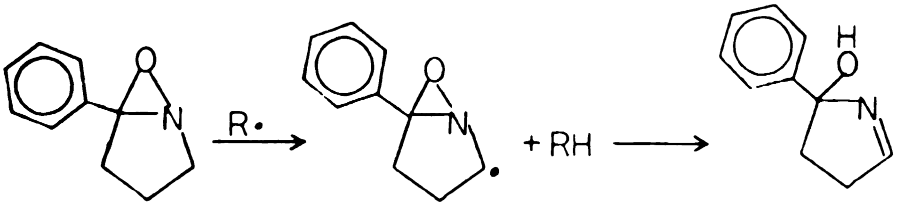
<u>Mechanism for Formation of Photoproducts from γ-Azidobutyrophenone</u>:

The 2-phenylpyrrole can be formed by two different pathways. Since its rate of formation at 366 nm is quenched at the same rate as acetophenone, its formation depends on the rate of formation of triplet carbonyl. Interception of the triplet carbonyl by a quencher molecule would in effect quench both inter- and intramolecular energy transfer to the azide group. 2-Phenylpyrrole must originate from the triplet azide.

A likely method for the formation of 2-phenylpyrrole is by nitrene insertion into the carbonyl group to give the oxazirane.[138,177,178]

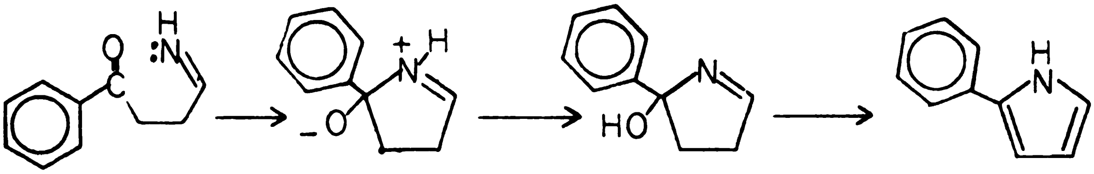


Emmons[179] has proposed that such a substance could lead to the imino alcohol by a radical chain-like mechanism.



Emmons found that a similar imino alcohol lost water to form the conjugated eneimine upon attempted isolation. In the present system the nitrene could be the radical source. In the process of abstracting the hydrogen from the oxazirane an amine radical would be formed which could abstract a second hydrogen and form the aminoketone which would close to PPRL. In the present system an extended radical chain mechanism is not likely, but with all the possible radicals around it is not surprising that polymeric material is formed. Intramolecular addition of the nitrene to the carbonyl is certainly possible but it should also be expected to occur intermolecularly as well. When butyrophenone was quenched with butyl azide, no such addition products were observed (although they were not specifically looked for) nor does the work of Lewis and Saunders[115,176] suggest such products.

Alternatively the 2-phenylpyrrole could arise from the hypothetical δ-iminoketone as shown below:

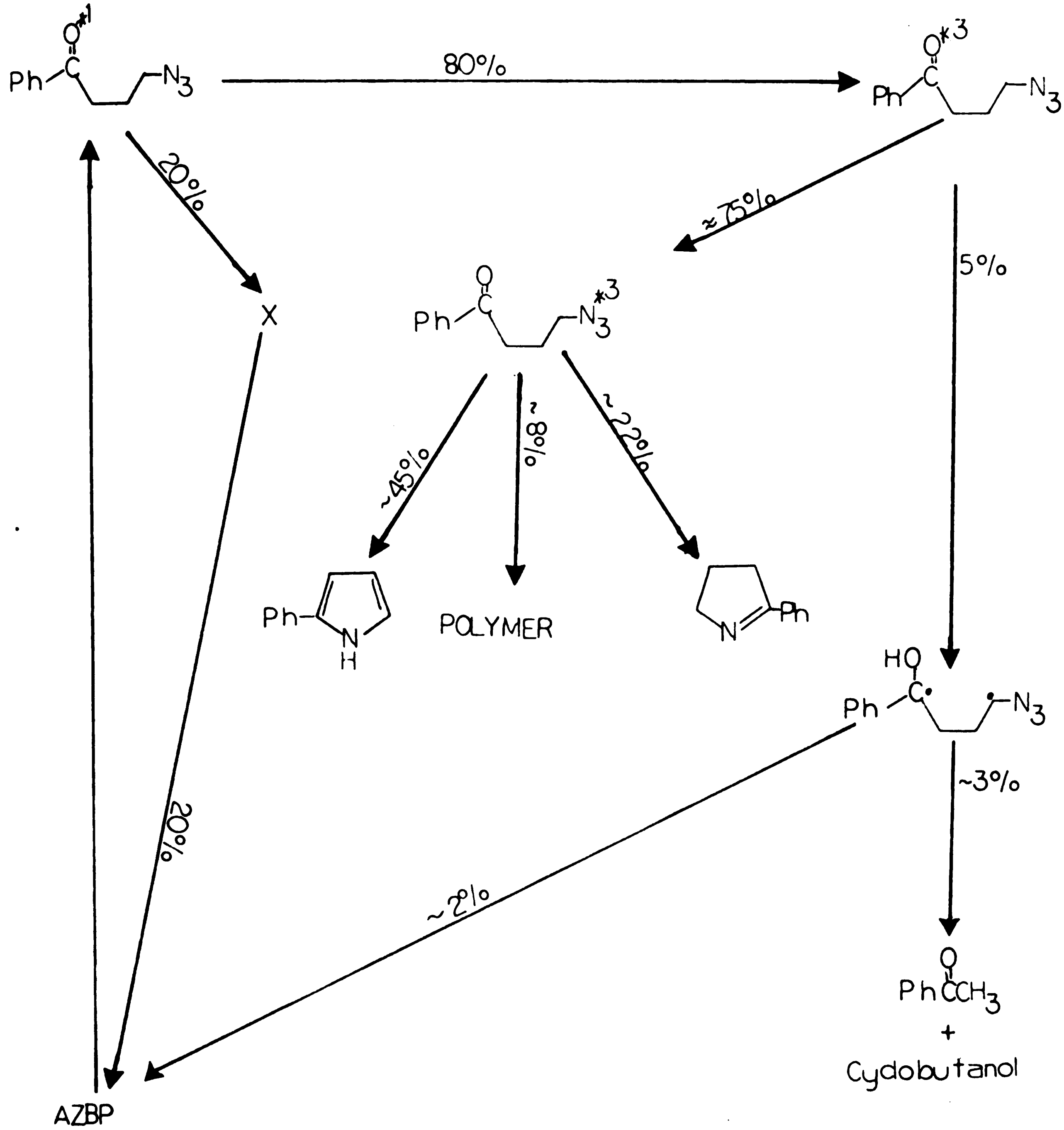


This mechanism is similar to that for the cyclization of aminoketone to PPRL. An exact analogy to this mechanism has been proposed by Mazzocchi and Thomas[196] for the cyclization of γ-iminoaldehydes to 2-substituted pyrroles. The γ-iminoaldehydes are proportedly formed during the photolysis of substituted pyrrolidones. Any iminoketone which did not form 2-phenylpyrrole would most likely polymerize,[166] or the 2-phenylpyrrole itself could polymerize. The behavior of AZBP in benzene is indicated in Scheme V.

Calculation of σ_I and Stabilization Factor for the Azide Group:

In hydrogen abstraction reactions the electrophilic triplet benzoyl group is quite selective in regard to both γ C-H bond strength and inductive effects of nearby substituents. Thus the Type II reaction would be expected to be a good monitor for the determination of the σ_I value of the azido group.

A Hammett plot of relative rates of triplet state γ-hydrogen abstraction has been reported by Wagner and Kemppainen.[60] This plot has been reproduced (Figure XXXI) by plotting several of the log k_r/k_r^o values versus the σ_I values reported in the above reference. The ρ value for the δ-substituents was found to be -1.85 and ρ for the ϵ-substituents was -0.76. Since k_r^o is known to be 12.5×10^7 sec^{-1} for valerophenone, the σ_I value for the azido group can be calculated by equations 25 and 26 with the aid of k_r values determined in this work for the azidoketones.



Scheme V

The Behavior of γ-Azidobutyrophenone in Benzene

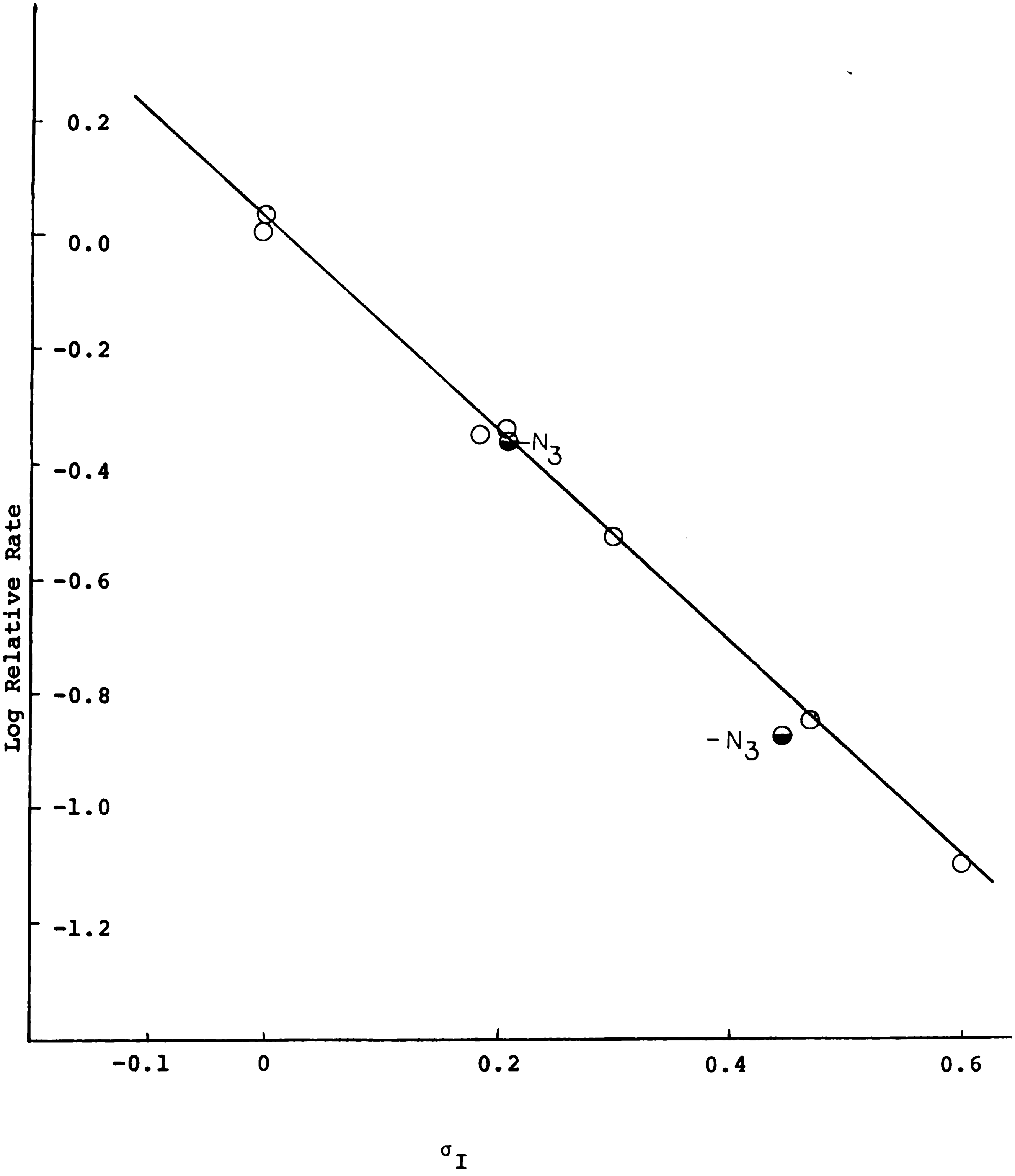


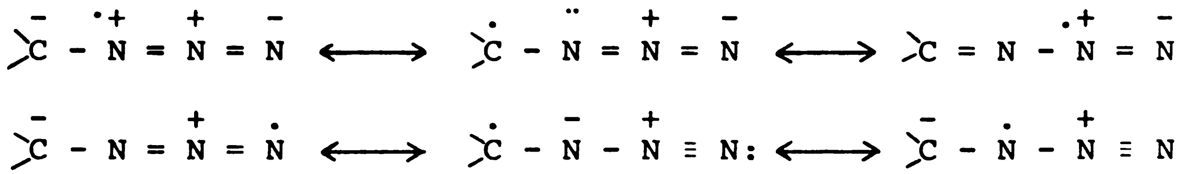
Figure XXX: Hammett Plot of Log of Relative Rates Versus σ_I

$$\log \frac{k_r}{k_r^o} = -1.85\ \sigma_I \tag{25}$$

$$\log \frac{k_r}{k_r^o} = -0.76\ \sigma_I \tag{26}$$

The σ_I value calculated from the measured k_r value of AZVP was found to be 0.47, while the σ_I value calculated from the k_r value of AZHP is 0.46. The log of the relative rates for the δ- and ε-ketones are plotted (half-filled circles) in Figure XXX. These points are in good agreement with the data determined by Wagner and Kemppainen. A value for σ_I of 0.44 for the azido group has been calculated from σ_p and σ_m.[180] The measured σ_I value is in good agreement with this calculated value. The measured σ_I value indicates that the azido group is as electron withdrawing as the chloro group. The good fit of both the δ- and ε-azidoketones with the same σ_I value, coupled with the previously found correlation for a large number of other substituents, suggest that the measured value is reasonably reliable.

All substituents should stabilize a radical at the γ-position,[60] and this stabilization should be reflected in the transition state for hydrogen abstraction. Since ρ_I for γ-substituted ketones has been estimated to be -4.3,[60] a $\sigma\rho$ value of -2.00 (using σ_I for the azido group as 0.465) and thus a relative reactivity of 0.0099 for AZBP relative was found to be 0.040. Thus the azido group has an apparent radical stabilization factor of 4.0 which can be attributed to conjugation of its Π-electrons with the incipient p-orbital. This group stabilizes the developing radical about as well as a phenyl, vinyl, or cyano substituent.[60] This is quite interesting since the chloro group (with a similar σ_I value) stabilizes a radical with a stabilization factor of 8-23.[60] This ability of the chloro group to stabilize a radical as well or better than groups containing Π systems has been attributed to the lone pair electrons on chlorine. Since the azide group possess both lone pair electrons and a Π system it might be expected to stabilize a radical center quite well. The measured stabilization factor suggests that the sp_x lone pair electrons are not available to stabilize the incipient radical. Two adjacent positive nitrogens would result if the lone pair electrons were delocalized onto the carbon. In the case where the radical is delocalized into the Π systems of the azide a separation of a + and - charge results, which separation is probably not a favorable process.



$$\overset{-}{>C} - \overset{\cdot +}{N} = \overset{+}{N} = \overset{-}{N} \longleftrightarrow \overset{\cdot}{>C} - \overset{\cdot\cdot}{N} = \overset{+}{N} = \overset{-}{N} \longleftrightarrow >C = N - \overset{\cdot +}{N} = \overset{-}{N}$$

$$\overset{-}{>C} - N = \overset{+}{N} = \overset{\cdot}{N} \longleftrightarrow \overset{\cdot}{>C} - \overset{-}{N} - \overset{+}{N} \equiv N: \longleftrightarrow >C - \overset{-\,\cdot}{N} - \overset{+}{N} \equiv N$$

Intramolecular Energy Transfer:

The only study reported of variation in rates of energy transfer with increasing methylene chain length between chromophores has been that reported by Cowan.[27] In the systems he studied, exothermic energy transfer from a carbonyl moiety to a styryl group occurs. If one accepts Lewis'[115] estimate of the triplet azide energy (75→80 kcal) to be close to the correct value, energy transfer to the azide group from the carbonyl is somewhat endothermic, in accord with the observed lower-than-diffusion-controlled intermolecular quenching rate constant.

Cowan has indicated that the rates for energy transfer in the γ- and δ-styryl ketones bracket the intermolecular rate constant of 5×10^9. He also observed that the rate of energy transfer from the β-styryl compound is seven times faster than that of the γ-ketone, which is only 3.3 times faster than that of the δ-ketone. These rates along with those measured for the azidoketones are listed in the Table X.

Table X

Rates for Intramolecular Energy Transfer in Phenyl Ketones

$\phi\ CO(CH_2)_nX$

X	n	k_{et}
-CH=CH-Ph	2	7.2×10^{10}
	3	1.0×10^{10}
	4	3.3×10^{9}
$-N_3$	3	2.6×10^{8}
	4	2.8×10^{7}
	5	$<2 \times 10^{6}$

The rate of energy transfer from the carbonyl group to the azide group drops off much faster than in the styryl ketone case. The rate of energy transfer to the azide group in the γ-ketone is about the same factor faster than the intermolecular rate constant as that observed by Cowan. However, the rate of decrease is about an order of magnitude for each of the azido ketones, while the styryl ketones show nowhere near that quick a drop in rate with increasing chain length.

The exact mechanism of energy transfer is not yet known, but the currently accepted theory is that the Π-orbitals of the carbonyl group must overlap with the Π-orbitals of the acceptor group. Just how stringent these requirements are is not known. In any study of intramolecular energy transfer versus chain length there are at least two factors which must be considered: (a) ring size of the transition state, and (b) rotations about the methylene chain. Molecular models indicate that on the average the distance between the two chromophores remains nearly constant, however, the number of conformations in which the two ends of the molecule are nearly in contact decreases rapidly with chain length. For energy transfer to occur from the carbonyl group to the azide the two groups must be parallel, whereas in the styryl group energy transfer could be to the olefinic Π-system (parallel conformation) or to the phenyl ring (somewhat perpendicular conformation). Thus in the azido group there may well be even a greater dependence on the number of conformations in which energy transfer can occur compared to the styryl system. This might explain the much faster decrease in rates of intramolecular energy transfer observed for the azido ketones.

As the number of methylenes is increased from 3 to 5, the ring size for the transition state involving energy transfer increases from 5 to 7 (conceivably 8 to 10) in the case of the azido ketones. Clearly some ring strain is involved in the formation of the transition state. The ring strain would presumably be larger in the case of the azido group than in the styryl case because of the azide's allene type structure. Energy transfer to the azide may also involve some geometric change which would affect the ring strain in the transition state for energy transfer.

It should be mentioned that in this Discussion two subtle factors have been ignored. It is not known whether the azido group undergoes any gross geometric changes in the energy transfer process. Also it is assumed that energy transfer from the azide to the ketone does not occur. Energy transfer from the azide to the carbonyl can explain why the acetophenone Type II quantum yield increases at 313 nm. If such transfer were reversible this would explain the lower than diffusion controlled rate constant observed for azide quenching. Such reversible energy transfer would increase the observed Type II $k_t\tau$ values.

Charge-Transfer Quenching by the Azido Group:

The intersystem crossing yield for AZBP is only 80% efficient. The 20% inefficiency may be due to singlet quenching of the carbonyl moiety by the azido group. This process would be endothermic in nature. Since the triplet quenching rate of the azide is only about 10^8 sec^{-1} it is unlikely that singlet quenching by the azide group would compete with the rapid (about 10^{11} sec^{-1}) intersystem crossing rate of phenyl ketones to the tune of 20%. Alternatively the azide could form a charge transfer complex with the excited carbonyl which would subsequently decay to the ground state ketone or possibly produce some uncharacterized product.

Indications for Further Research:

This work has been both intriguing and challenging to the author. As always new research requires a certain amount of "mopping up" and elicits a certain amount of further research:

(1) It would be interesting to further extend the meager solvent studies undertaken for these ketones.

(2) It would be interesting to study the benzene substituted compounds, i.e. p-azidovalerophenone etc. ESR studies of these compounds could be easily performed. In this work the ESR spectrum of p-azidoacetophenone was observed at 77°C. Whereas the only ESR spectra for the alkyl azides have been observed at 4°K.

(3) It would be interesting to study other pseudohalides, i.e. -SCN and -NCO both in the γ- and δ-positions and on the benzene ring. A study of δ-thiocyanatovalerophenone was initiated here, but its low quantum yield and the fact that butylthiocyanate has the same retention time as acetophenone caused this work to be put aside.

(4) It would be appropriate to find a molecule that would quench triplet azides to study the rate constants of ring closure and azo-formation in appropriate compounds such as 2-azidobiphenyl whose rates have been measured only by flash studies.

N-SUBSTITUTED-4-METHYL-4-BENZOYLPIPERIDINES

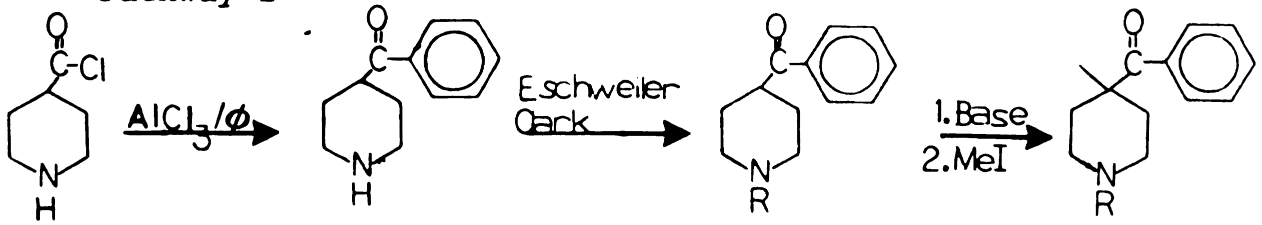
RESULTS

Part III

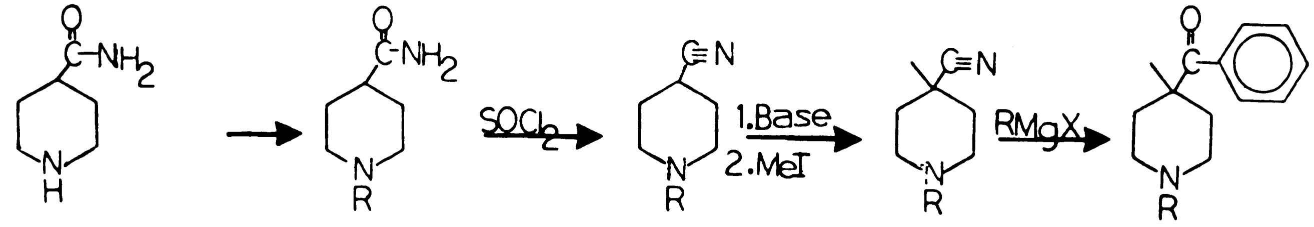
Synthesis:

Three separate syntheses of these compounds were considered (Scheme VI). Pathway III was ruled out since several steps would be required to obtain the starting chloroketone (6 steps overall). Since a small amount of the N-alkylated ketone necessary for the synthesis via pathway I was available, several attempts to prepare the desired compound using Rathke's base (lithium diisopropyl amine)[181] were undertaken. The ketonic material obtained appeared,by NMR analysis,to be about fifty percent alkylated. Since purification of the two similar ketones was seen as a problem, it was decided to use synthetic pathway II. Synthesis of the reported cyano compound[158] was achieved, albeit in low yield (38% overall). The next two steps were accomplished in an unexpected 60% overall yield. Several bases were used in the alkylation procedure with phenyl sodium giving the best overall yield. Rathke's base (lithium cyclohexylisopropyl amine) and trityllithium are sufficiently useful in the case of the N-benzyl compound, but in the case of the N-methyl compound the alkylated nitrile co-distills with the solvents used in the reaction.

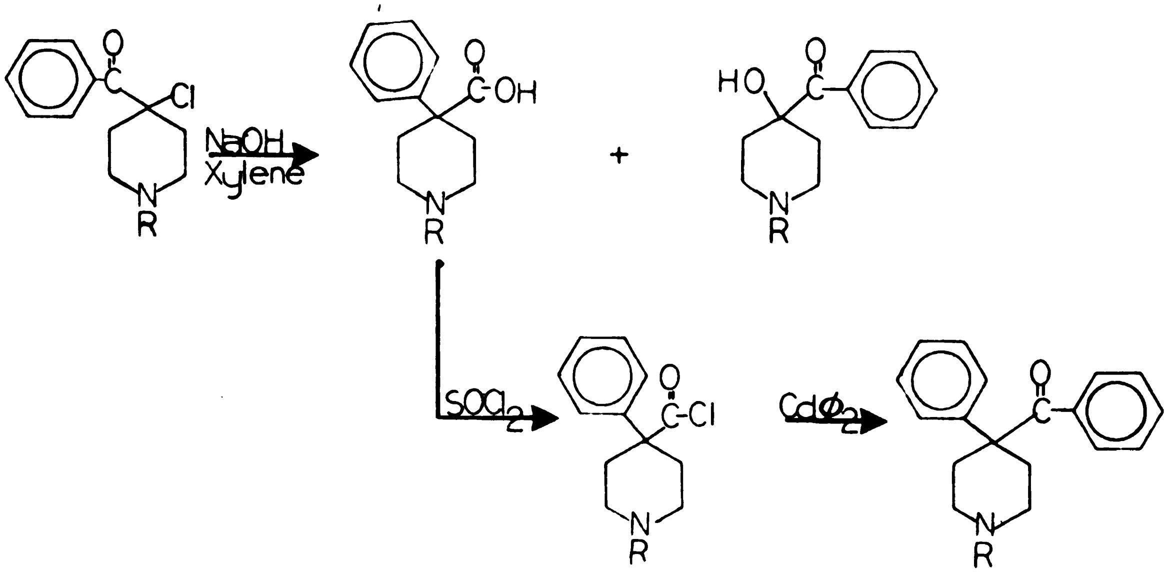
Pathway I



Pathway II



Pathway III



Scheme VI

Possible Synthetic Routes for the Preparation of

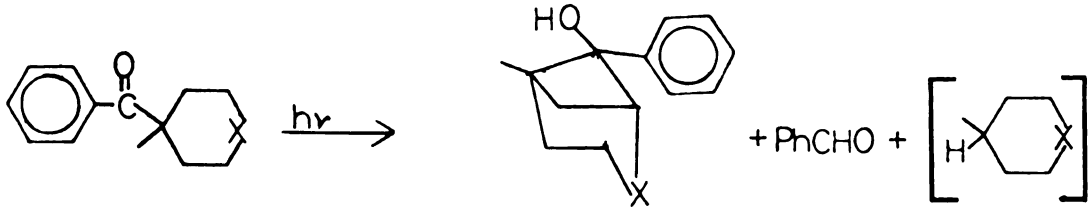
N-Methyl-4-Methyl-4-Benzoylpiperidine

1-methylcyclohexyl phenyl ketone was prepared from cyclohexane carboxamide by method II.

Identification of Photoproducts:

Irradiated solutions of these compounds yield relatively simple VPC traces. Benzaldehyde was identified as a product of all the ketones by comparison of its VPC retention time to that of the pure material. 4-methyl-N-methylpiperidine was assumed to be formed but would be lost in the benzene trace. Its olefinic counterpart formed in the Type I reaction is also assumed to be lost in the solvent peak.

An isomer of N-methyl-4-methyl-4-benzoylpiperidine(NMMBP) was isolated and identified as the Type II cyclobutanol. Three grams of NMMBP were irradiated in the presence of 0.1 M naphthalene through a vycor filter, and the resulting yellow oil was chromatographed on an alumina column. Two grams of 90-95% pure (NMR analysis) material were obtained. This compound had spectra consistent with the cyclobutanol:[182]



$X{=}CH_2$
$X{=}NCH_3$
$X{=}NCH_2Ph$

VPC analysis of irradiated 1-methylcyclohexylphenyl ketone (MCPK) solutions also showed only two high-boiling products, benzaldehyde and a peak presumed to be the cyclobutanol reported by Lewis.[66] N-benzyl-4- methyl-4-benzoylpiperidine (BMBP) showed benzaldehyde and a peak presumed to be the

N-benzylpiperidine. The Type II reaction was not studied for BMBP.

When photolyzed samples of NMMBP were injected on Col-4 at high temperatures and flow rates (170° at double the flow rate used to analyze the Type II product), materials which appear to be oligomers were observed.

Quantum Yields:

Quantum yields were determined by irradiating solutions of the ketone of interest concurrently with valerophenone actinometer. Since it was assumed that the amine portion of one NMMBP might quench the triplet of another and that energy transfer might occur between conformers, all work with these ketones was carried out at 0.04 M ketone concentration (the lowest concentration with an optical density greater than 2.00). In order to compare the behavior of these ketones to that of MCPK, it was necessary to measure its quantum yield at 0.04 M ketone concentration.

(a) Type I Cleavage:

Type I quantum yields of the amino ketones were determined with and without the presence of varying concentrations of dodecanethiol. Benzaldehyde formation was monitored with decyl alcohol as standard. Since little is known of the behavior of the Type I reaction in various solvents, the quantum yield was determined in pyridine and in 1-propanol. In general, the quantum yield is lowered in these polar solvents. The Type I quantum yield of a 0.04 M solution of MCPK was measured in the presence of 0.01 M dodecanethiol. The Type I quantum yield of MCPK at this concentration of ketone is significantly higher than that reported by Lewis[66]. These results are listed in Table XI.

(b) Type II Elimination:

Type II quantum yields for photocyclization of NMMBP were measured in benzene,pyridine,various concentrations of 1-propanol, and a 0.04 M dodecanethiol solution. The Type II quantum yield was depressed in the presence of pyridine and about equal to that in benzene in 1-propanol. An attempted measurement of the Type II quantum yield in 50:50 methanol:benzene gave a Type II quantum yield too small to measure. The Type II quantum yields for phtocyclization of a 0.04 M solution of MCPK were measured in neat 1-propanol, pyridine, and neat acetonitrile/1% water. The highest quantum yield obtained was that in 1-propanol. The observed Type II quantum yield of MCPK was only slightly lower than that observed by Lewis.[66] As in the case of NMMBP, pyridine depresses the Type II quantum yield from MCPK. These results are listed in Table XII.

(c) Disappearance:

The disappearance quantum yield of NMMBP was measured in benzene, pyridine, varying concentrations of 1-propanol, and 0.04 M dodecanethiol. In benzene and pyridine the disappearance quantum yield was five times that of the sum of the quantum yields for formation. In 1-propanol the disappearance quantum yield was only four times that of the sum of the quantum yields for formation. In the presence of

Table XI

Type I Quantum Yields for 0.04 M Ketones at 313 nm

Solvent	OBSERVED QUANTUM YIELD NMMBP	BMBP	MCPK
benzene	0.016±0.005	---	---
0.01 MSH/benzene	0.061	0.092	0.30
0.02 MSH/benzene	0.13	0.16	---
0.04 MSH/benzene	0.16	---	---
0.5M pyridine	0.00	---	---
10% PrOH/benzene	0.0056	---	---
20% PrOH/benzene	0.0030	---	---
30% PrOH/benzene	0.0024	---	---
40% PrOH/benzene	0.0022	---	---

1.0 M naphthalene the disappearance quantum yield also equals the sum of the quantum yields of formation of products. These data are listed in Table XII.

Behavior in the Presence of Quenchers:

(a) Type I:

Stern-Volmer slopes for quenching of the Type I reaction of 0.04 M benzene solutions of NMMBP and BMBP were obtained at 313 nm in the presence and absence of 0.02 M dodecanethiol using 1-methylnaphthalene or naphthalene as quencher. In the presence of mercaptan both BMBP and NMMBP give plots with identical slopes in the presence of low concentrations

Table XII

Type II Quantum Yields for 0.04 M Ketones at 313 nm

Solvent	OBSERVED TYPE IIΦ NMMBP	 MCPK	DISAPPEARANCEΦ NMMBP
benzene	0.017	---	0.139
benzene/ naphthalene	0.06	---	0.06
0.5 M pyridine	0.0098	0.032	0.048
PrOH	---	0.18	---
0.04M SH/benzene	0.053	---	0.22
acetonitrile	---	0.12	---
acetonitrile/ 1% H_2O	---	0.12	---
50% MeOH/benzene	0.00	---	---
10% PrOH/benzene	0.017	---	0.090
20% PrOH/benzene	0.014	---	0.068
30% PrOH/benzene	0.016	---	0.067
40% PrOH/benzene	0.015	---	0.069

Table XIII

Quenching Data for 0.04 M Ketones

Ketone	Solvent	$k_t\tau_I$[a]	$k_t\tau_{II}$[a]
NMMBP	benzene	250[b]	<0.2 (0.2)[c]
	0.02M SH/benzene	267	---
BNBP	0.02M SH/benzene	275	---
MCPK	benzene	3.3[d]	---
	acetonitrile/1%H_2O	---	0.25[d]

[a] naphthalene quencher unless noted

[b] initial slope

[c] from sensitization slope

[d] N-methylpiperidine quencher

of quencher. At higher concentrations of quencher the plot curves slightly upward for NMMBP. This same phenomenon is observed when the Type I reaction from the cyclohexyl ketone is quenched by N-methylpiperidine in the presence of mercaptan. In the absence of mercaptan the Type I Stern-Volmer plot for NMMBP curves downward. The observed $k_t\tau$ values observed for NMMBP and BMBP are similar to those values of other phenyl ketones possessing α-substituents. The obtained data are listed in Table XIII and the plots are reproduced in figures XXXI and XXXIII.

(b) Type II:

In the presence of 0.02 to 1 M naphthalene at 313 nm or 366 nm the Type II quantum yield in benzene of NMMBP increases. This behavior is also observed in the presence of tetramethylbutadiene at 366 nm. The maximum increase in quantum yield is reached in the presence of about 1 M quencher concentration, and is approximately four times that observed in benzene. Even in the presence of high concentrations of naphthalene (1-8M) the Type II quantum yield does not decrease. When tetramethylbutadiene was used as quencher at 366 nm the quantum yield did start to decrease at about 2 M quencher concentration. The highest slope indicated by this plot (obtained by subtracting 0.5 M quencher from each point and using the 0.5 M quencher tube as the 0 point reference tube) is 0.2. This value is at best an estimate, but does indicate that the Type II reaction comes from a fast triplet rather than from the singlet. The plot is reproduced in Figure XXXIV.

Since alcoholic solvents should hydrogen bond with the nitrogen lone pair electrons on NMMBP,[89] the ability of the lone pair electrons to stabilize the incipient radical should be reduced and the rate of hydrogen abstraction slowed down. Also it is postulated that alcoholic solvents slow down the rate of intramolecular charge transfer interactions.[89] However, the alcoholic solvents inhibit revertible hydrogen transfer of the biradical thus increasing Type II quantum yields.[4] Since a $k_t \tau$ value for the Type II reaction was not

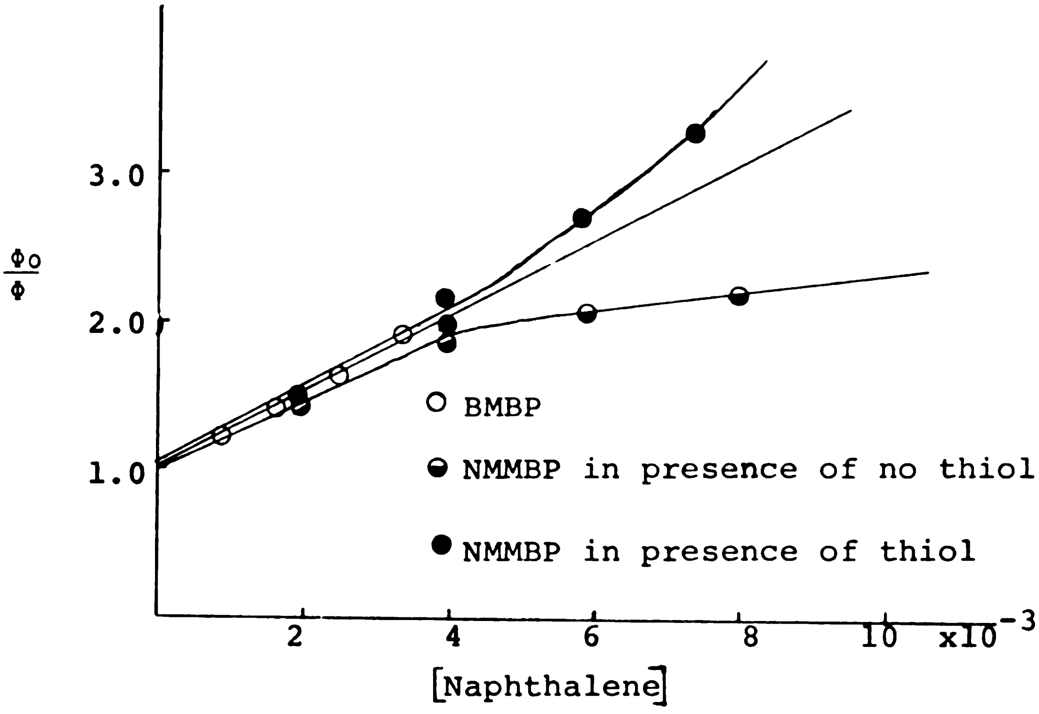


Figure XXXI: Stern-Volmer slopes for Type I reaction of N-methyl-and N-benzyl-4-methyl-4-benzoylpiperidine

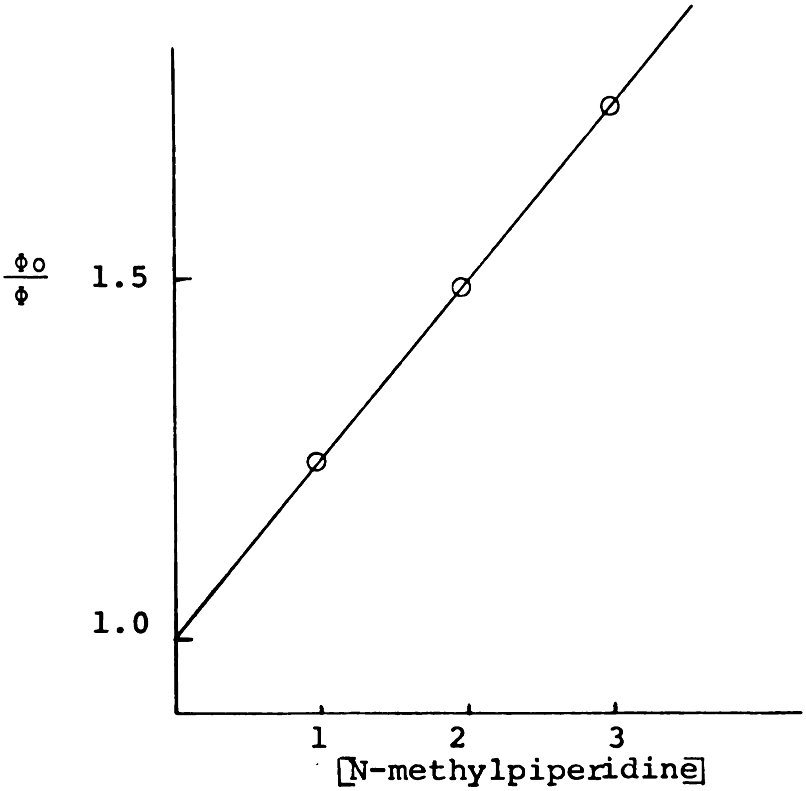


Figure XXXII: Stern-Volmer slope for Type II reaction from 1-methylcyclohexylphenyl ketone by N-methylpiperidine

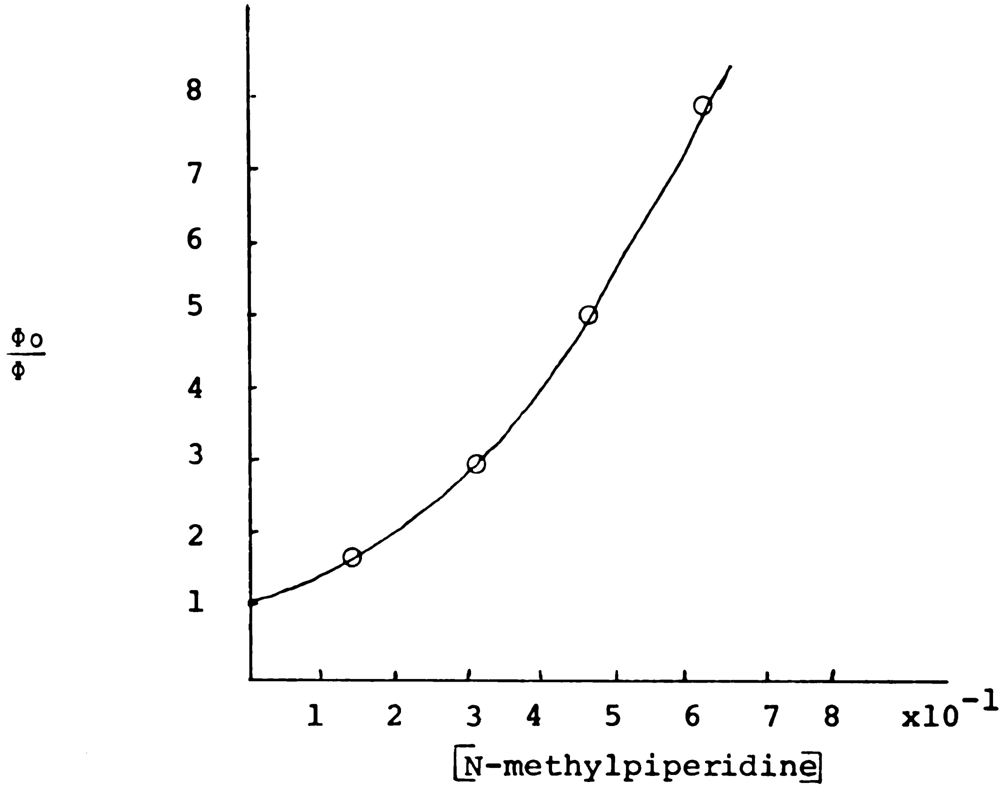


Figure XXXIII: Stern-Volmer plot for benzaldehyde formation of N-methyl-4-methyl-4-benzoylpiperidine

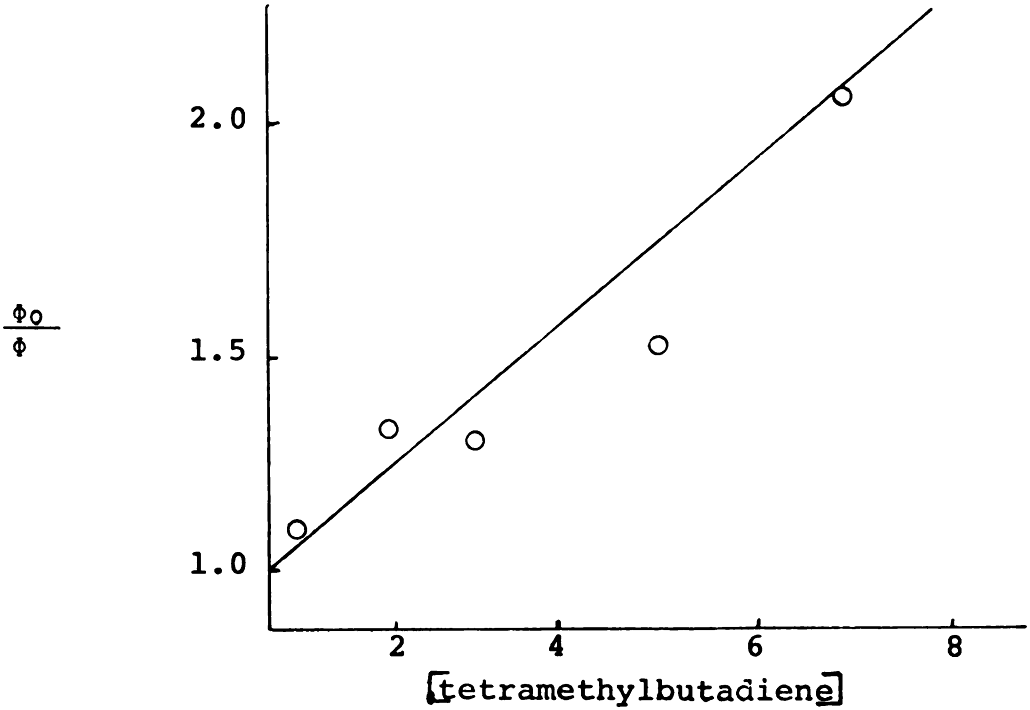


Figure XXXIV: Stern-Volmer plot for Type II formation of N-methyl-4-methyl-4-benzoylpiperidine at 366 nm obtainable in benzene solutions, attempts were made to quench the Type II reaction in alcoholic solvents. When the diene quencher (t-piperylene) was added to neat 1-propanol, t-butanol, or 1-pentanol the solutions turned cloudy, thus 50:50 1-propanol : benzene was chosen as the solvent system. Irradiation of 0.04 M ketone solutions containing 0-4M t-piperylene were irradiated at 313 nm. As in benzene, the quantum yield of the Type II product increases in the presence of quencher. The solution containing 0.5 M piperylene was thus used as the reference solution as described above. The solutions containing 1 and 2 M piperylene visibly quenched the Type II product with a slope of about 0.4 M^{-1}. However the tubes containing 3 and 4 M piperylene showed only little quenching (slope = 0.02 M^{-1}).

Since it is possible that the amine moiety of NMMBP can photoreduce the ketone portion of another NMMBP, the Type II reaction from MCPK was quenched by N-methylpiperidine The quenching slope was found to be about 100 times lower than that observed by Lewis[66] for diene quenching. The data are shown in Table XII and the plot reproduced in Figure XXXII.

Sensitization Studies:

Photolysis of 0.04 M NMMBP in the presence of low concentrations of cis-piperylene (0.05 M or below) at 313 nm yields a VPC trace indicating three peaks in the area of trans-piperylene. At higher piperylene concentrations (0.1M or above) the normal VPC trace for cis-and trans-piperylene is observed. A sensitization plot for NMMBP was obtained

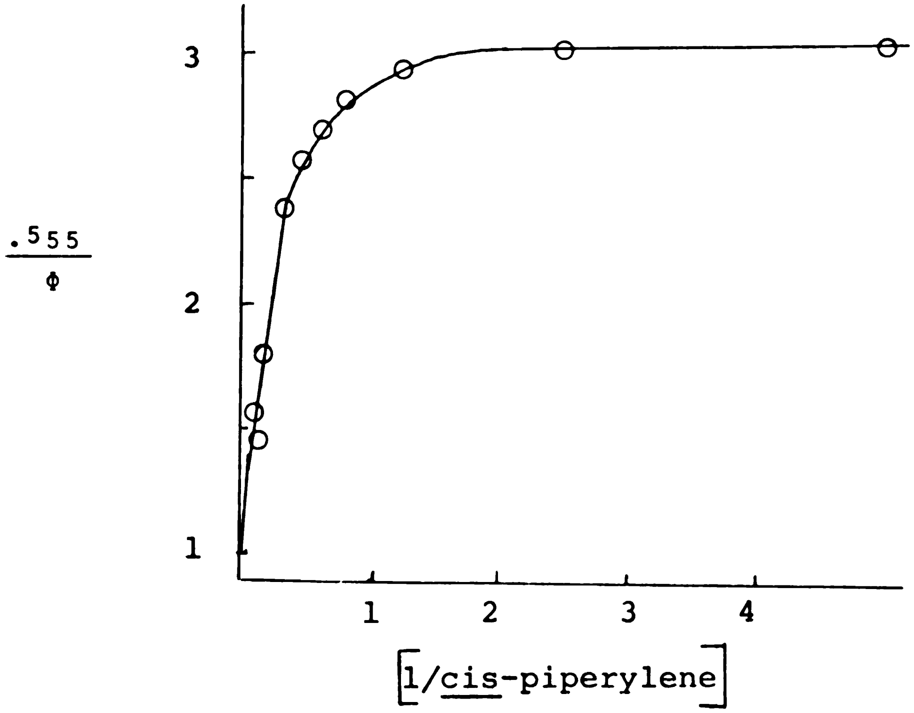


Figure XXXV: Sensitization Plot of N-methyl-4-methyl-4-benzoylpiperidine by irradiating 0.04 M solutions of the ketone in the presence of varying amounts of piperylene at 313 nm. This plot curved downward. Two different studies indicated that the intercept of the lower part of the curve is approximately unity. The average of two different studies indicate that the upper portion of the curve has an intercept of 3.05. The slope obtained from the lower portion of the curve is 0.2 M^{-1}. This curve is reproduced in Figure XXXV.

Disappearance of the Type II Photoproduct:

The increase in the Type II quantum yield in the presence of low concentrations of quenchers and the inability to quench the Type II product were preplexing problems. It was possible that the Type I products were scavenging the starting ketone and the Type II product. In the presence of quenchers the Type I reaction would be quenched and less NMMBP and Type II product would disappear. To test this hypothesis, a 0.04 M benzene solution of NMMBP containing 0.004 M Type II product was irradiated at 313 nm. When the irradiated sample was compared to the unirradiated sample, 15% of the Type II product had disappeared from the irradiated sample. Since an increase of about 33% in the Type II product should have been observed, about 50% of the product disappeared during the irradiation.

NMR Studies on Ground State NMMBP:

(a) Low temperature proton NMR:

The room temperature NMR spectrum of NMMBP in freon 11 with TMS standard obtained from the Varian HA-100 spectrometer was identical to that obtained on the Varian T-60 spectrometer. Broadening of the N-CH_3, -CH_3, and -CH_2 signals was observed but no splitting into two distinct signals was observed even at -90° C.

(b) ^{13}C Low Temperature NMR:

The room temperature proton decoupled ^{13}C spectrum of NMMBP in freon 21 with TMS standard is reproduced in figure XLV. The peaks were compared and assigned in accord with the shifts observed in piperidine[197], N-methylpiperidine[197], and MCPK[188]. The assignments were also assisted by the proton coupled room temperature spectrum [δ; 4-methyl-25.4 (quartet); C_3-35.9 (triplet); N-CH_3-46.2 (quartet); C_1-46.5 (singlet); C_2-53.0 (triplet); C=O-208.5; aromatics 128.1, 128.4, 131.1, 139.4] . The J value for the couplings in the proton coupled spectra were 5.61 ppm. The carbonyl signal remained a singlet down to -96°C. Apparently both the equatorial and axial carbonyl carbons have identical chemical shifts. At about -15° the α-methyl signal is broadened and below this temperature shows two peaks separated by 8.3 ppm (19.8, 28.1). At -50°C the ring carbons show two peaks separated by 2.2 ppm (C_3-34.0, 36.2). The difference between the shift of the methyl group at room temperature and each methyl signal at -70° indicates a 30%:70% axial: equatorial ratio, while the difference between the shift of the ring carbons at room temperature and both signals at -70°C indicates a ratio of 20%:80% axial:equatorial. Thus an average population of 25% axial conformer to 75% equatorial conformer is predicted for NMMBP. This data together with the photochemical data indicate that a large portion (≈40%) of the equatorial conformer of NMMBP is missing.

DISCUSSION

Ground State Conformations of NMMBP:

Figure XXXVI shows the possible ground state chair conformations and one high energy boat conformation of NMMBP.

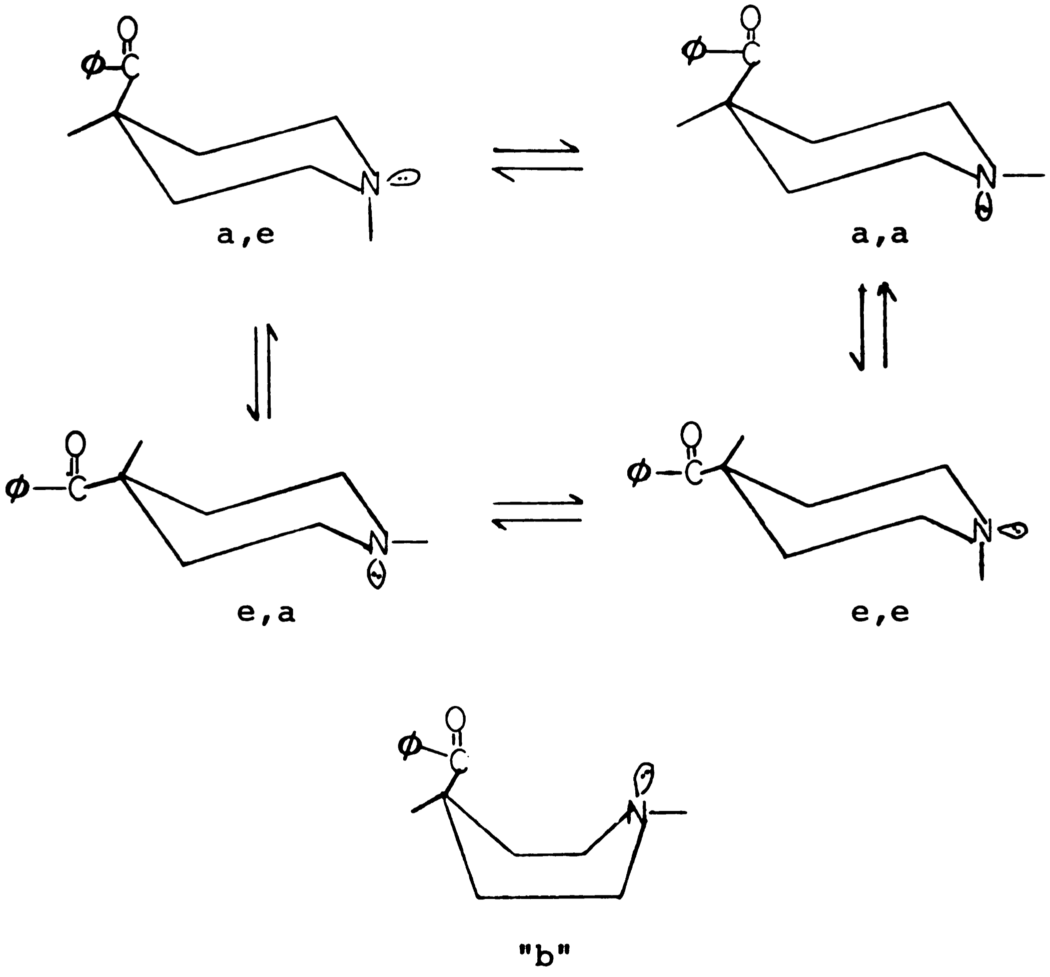


Figure XXXVI
Ground State Conformations of NMMBP

At present there is a controversy in the literature as to whether the methyl group or nitrogen lone pair is in the axial or equatorial position.[184-6] Booth and Little[184] indicate that N-methylpiperidine prefers a conformation in which the electron pair on nitrogen is axial, while Blackburne[185] indicates the preferred geometry is that with the electron pair equatorial. Lambert,[186] as well as Booth and Little and Blackburne, indicates that the preference of the nitrogen lone pair depends on substitution on the piperidine ring. In any event it is interesting to note that the equatorial position is particularly suitable for delocalization of the lone pair into various bonding situations of the saturated ring,[187] whereas such interactions are not possible for the axial lone pair electrons which are pointed away from the molecule.

According to Lewis[66] for the analogue MCPK, the ratio of conformers with the benzoyl moiety axial to that equatorial is 1.0:2.7 at 25° or about 25% of the molecules exist in the conformation with the benzoyl group axial. The ^{13}C NMR spectra for NMMBP indicates that NMMBP exists in about the same ratio of conformers.

Only in conformation "b" are the nitrogen lone pair electrons as close to the carbonyl as they can get in γ-dimethylaminobutyrophenone. Molecular models indicate that in conformation "a,e" the distance between the carbonyl group and the lone pair electrons is approximately six Å. However, the p orbitals of the two groups cannot attain a parallel orientation. Conformer "e,e" has the carbonyl group and the nitrogen lone pair electrons in the proper geometric alignment postulated for "synchronous fragmentation" reactions,[187] and thus may be set up for through bond charge-transfer interactions. In conformer "a,a" the nitrogen lone pair electrons are parallel with the hydrogen to be abstracted in the Type II reaction and such stabilization of the incipient radical should provide an extremely fast rate for hydrogen abstraction as well as revertible hydrogen transfer. Interaction of the carbonyl moiety with the back lobe of the sp^3 orbital in conformer "a,a" might also be possible. This type of interaction might also be able to occur in conformer "a,e".

Conformationally Interesting Compounds:

Lewis[62-66] has measured the rates of hydrogen abstraction for several conformationally interesting ketones. For convenience the data are reproduced in Table XIV along with the information obtained in this work. In the Table, Φ_{II} and Φ_{I} are the quantum yields for the Type II and Type I reactions respectively. Φ_{el} and Φ_{c} are the quantum yields for elimination and cyclization reactions. PrOH and *t*-BuOH are 1-propanol and *tert*-butyl alcohol respectively. SH is mercaptan and Bz is benzene.

Intermolecular Energy Transfer Between Conformers:

Until quite recently[188,189] energy transfer between identical molecules has either been ignored or found to be negligible in those systems where such transfer was reversible.[168] In the present systems (NMMBP and MCPK) energy transfer can be expected to be irreversible because of the low concentrations of ketone used and because of the relatively short lifetimes of the Type II conformers. Turro

Table XIV

Rate Data for Conformationally Interesting Ketones

Ketone	Solvent	Φel	ΦII Φc	 $1/\tau \times 10^8$	ΦI Φ	 $1/\tau \times 10^8$
Valerophenone	Bz	0.33	0.07	1.2	---	---
	t-BuOH	1.00	---	---	---	---
2-n-propyltetralone	Bz	0.09	0.03	5.9	---	---
	PrOH	0.36	0.03	---	---	---
α(1-adamantyl)-acetophenone	Bz	---	0.14	9.2	---	---
	PrOH	---	0.34	---	---	---
endo-2-benzoyl-norbornane	Bz	0.10	---	70	---	---
	t-BuOH	0.13	---	---	---	---
exo-2-benzoyl-norbornane	Bz	0.13	---	0.12	---	---
endo-2-benzoyl-2-methylnorbornane	Bz	---	0.49	0.86	---	---
	t-BuOH	---	0.63	---	---	---
exo-2-benzoyl-2-methylnorbornane	Bz	---	---	---	0.032	0.12
	Bz/SH	---	---	---	0.096	---
2-benzoylbicyclo-[2.2.2] octane	Bz	0.041	---	100	---	---
	t-BuOH	0.058	---	---	---	---
2-benzoyl-2-methyl-bicyclo [2.2.2] octane	Bz	---	0.13	3.0	---	---
	t-BuOH	---	0.26	---	---	---
cyclohexylphenyl ketone	Bz	---	0.008	17	---	---
	PrOH	---	0.13	---	---	---
4-(*t*-butylcyclo-hexylphenyl ketone	Bz	0.024	---	68	---	---
	PrOH	0.098	---	---	---	---
MCPK	Bz	---	0.045	1.7	---	---
	PrOH	---	0.21	---	---	---
	Bz/SH	---	---	---	0.20	0.25
Cyclopentylphenyl ketone	Bz	0.22	---	0.025	---	---
1-methylcyclopentyl-phenyl ketone	Bz	---	0.19	0.13	---	---
	Bz/SH	---	---	---	0.03	0.13
γ-Dimethylamino-butyrophenone	Bz	0.056	---	80	---	---
	MeOH	0.25	---	17	---	---
NMMBP	Bz	---	0.06	---	0.016	0.19
	Bz/SH	---	0.053	---	0.16	0.19

and Lechtken[189] have indicated that the rate of energy transfer between acetone and acetone-d_6 is about 3×10^6 M^{-1} sec^{-1}. Lewis[188] has measured the rate of energy transfer from the equatorial to the axial conformer in cyclohexylphenyl ketone (CHPK) as 4×10^8 M^{-1} sec^{-1}. In this study an attempt was not made to determine the rate of energy transfer between the conformers nor has Lewis performed a study on MCPK.

The 50% lower Type I quantum yield of NMMBP relative to MCPK yet the identical slopes of the two compounds is an intriguing problem. Either there is less Type I conformer in NMMBP relative to MCPK or the lowered quantum yield can be due to two factors: intermolecular quenching by the amine moiety of NMMBP (see next section) or intermolecular energy transfer from the equatorial conformer to the axial conformer. Assuming one half the difference is due to each process, 25% of the difference between the Type I quantum yield of NMMBP and MCPK is due to the energy transfer process. From the lifetime ($1/\tau = 1/k_{de} + 1/k_{et}[NMMBP]$) of the Type I conformer the rate of energy transfer from the equatorial conformer to the axial conformer at 0.04 M NMMBP can be estimated at about 4×10^6 sec^{-1}. Since the methyl group provides some steric hindrance to energy transfer, the rate of energy transfer for NMMBP might be expected to be somewhat slower than that observed for CHPK. In actuality the rate of energy transfer is only slightly less (about a factor of two) slower than that reported by Lewis for CHPK.

Steric Effect to Intermolecular Charge-Transfer Quenching:

Since intermolecular charge-transfer quenching and subsequent photoreduction of the triplet ketone by the amine moiety of NMMBP is conceivable, the Type I and Type II reactions from MCPK were quenched using N-methylpiperidine as quencher. The quenching plot of the Type II process in acetonitrile/1% H_2O was linear and indicated a quenching rate about 100 times less than that observed for dienes. The quenching plot of the Type I process curved upward but the highest slope indicated a quenching rate by the amine at least 20 times slower than diene. The lower portion of the curve indicated a rate 100 times slower than diene and this is probably the more reasonable number.

The diene quenching value was obtained by Lewis[65] for some unspecified ketone concentration and the amine quenching data was observed at 0.04 M ketone concentration. Since $k_t \tau$ is expected to decrease with ketone concentration, the 100 times difference in the quenching rate observed for amine relative to diene is probably on the order of only 50. Since the Type I conformer can sensitize the Type II conformer, the quantum yield and thus the $k_t \tau$ values will change with ketone concentration. The Type I process for MCPK at 0.04 M ketone concentration was measured as 0.3 versus 0.21 reported by Lewis. The Type II quantum yield was only slightly lower than that reported by Lewis (0.18 versus 0.21 respectively). Still the difference between amine and diene quenching is at least a factor of fifty, so that k_t for the quenching of NMMBP by N-methylpiperidine is about 1×10^8 M^{-1} sec^{-1}. The rate for intermolecular quenching by the amine moiety of 0.04 M NMMBP would be about 4×10^6 sec^{-1}. Thus both amine quenching and intermolecular energy transfer should compete about equally with the Type I process from NMMBP if they occur at all.

Sensitization Studies:

Attempts were made to determine the intersystem crossing yield of NMMBP by sensitizing the isomerization of piperylene. Two such plots were obtained in which the intercept for the lower part of the curve tended to one. Two different studies were also performed to determine the intercept of the upper portion of the curve. Values of 2.9 and 3.18 were obtained indicating an intercept of 3.05.

The plot is interesting in that it curves downward. Such behavior is expected for a system in which two reacting triplets can sensitize piperylene.[170]

Obtaining an intercept for the lower portion of the curve is not entirely accurate. However, it can be seen that the intercept of the lower portion of the curve is headed towards one and not two (Φ_{isc} γ-dimethylaminobutyrophenone (DMABP) = 0.58). Clearly there is less charge-transfer quenching of the carbonyl by the amine in NMMBP than in DMABP. And it appears that there are no charge-transfer interactions of the type that exist in DMABP in NMMBP at all.

The upper intercept indicates the population of each ketone present[190]. The intercept of 3.05 for the upper portion of the sensitization curve indicates about 1 Type I conformer for every 2 Type II conformers. This is not the ratio Lewis[65] obtained for MCPK from ^{13}C NMR studies, and the NMR studies in this report indicate that the population of the Type I conformer to the Type II conformer for NMMBP is about 3 to 1. Deactivation of conformer "e,e" by through bond charge-transfer interactions seems to be the best explanation for the observed discrepancy.

It is interesting that the $k_t\tau$ (0.2) of the lower portion of the curve is the same as that estimated for the Type II reaction (0.2). This observation does not rule out the possibility that there is some species other than conformers "e,a" or "a,a" and "a,e" sensitizing piperylene.

Disappearance of Type II Product:

Since the Type I product reacts with the Type II product and presumably with the parent ketone, the Φ values obtained in benzene for NMMBP cannot be taken as reliable. An indication of the true Φ values however is obtained from the studies in the presence of dodecanethiol and quenchers. Since the quantum yield for disappearance equals the quantum yield for formation of products in the presence of 0.04 M mercaptan, the mercaptan traps all the radicals thus preventing them from reacting with the Type II product. Thus the Φ_I in the presence of 0.04 M mercaptan is probably close to the correct value. Since 0.04 M mercaptan can intercept some of the Type II biradicals, the Type II quantum yield in the presence of high concentrations of quenchers (where the Type I reaction is almost completely quenched) is probably closer to the correct value.

Type I and Type II Quenching Slopes:

It is interesting that the Type I quenching plot of NMMBP curves downward at about 50% quencher concentration, since Lewis[65] indicates that the Type I quenching plot of MCPK is linear out to $>90\%$ quenching. This downward curvature indicates that some of the Type I product from NMMBP is either coming from the singlet or some other conformer. This other conformer is probably not the Type II conformer since neither MCPK nor t-butyl-1-methylcyclohexylphenyl ketone (BMCPK) give Type I products from the Type II conformation[65]. That the Type I reaction is coming from some other conformer is reinforced by the observation that even at high concentrations of quenchers (0.5 to 1M) where the Type I reaction should be completely quenched assuming a lifetime of 2×10^7 $\sec^{-1}$ the Type II quantum yield is still slightly increasing.

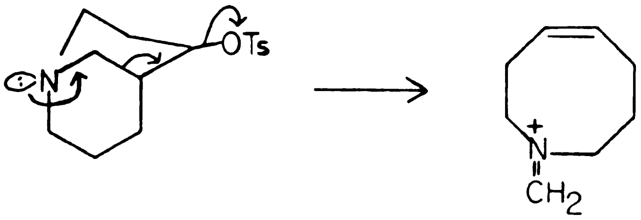
The inability to obtain a good Type II quenching slope can possibly be due to three factors: the Type II reaction occurs from 1) the singlet state, 2) an extremely fast triplet, or 3) an anomaly due to the Type I reaction. The occurrence of the Type II reaction from the singlet is unlikely although possible in the light of the work of Ersfeld.[191] It is entirely possible that the Type II reaction occurs from an extremely fast triplet, but in 1-propanol the Type II reaction should be slowed down to about the rate Lewis observed for MCPK. Thus it is likely that the inability to quench the Type II reaction is due to the fact that all the Type I product is not quenched even at high concentrations of quenchers. A small percentage of radicals reacting with the Type II product could cause just enough difference in the presence of differing amounts of quencher to observe no effective quenching.

Partitioning of Energy in Excited NMMBP:

The sensitization,quenching, and quantum yield studies coupled with the NMR studies on NMMBP indicate that at least three triplets are involved in the photochemistry of NMMBP. This third triplet appears to arise at the expense of the Type I conformer.

The observed results might also be explained by the Type II conformer photoeliminating to yield the corresponding eneaminoketone, which could subsequently polymerize with the Type I conformer, or sensitize piperylene. This explanation is not likely, however, since Lewis[188] does not see such eliminations from MCPK or BMCPK. Neither was there any evidence in the VPC traces of irradiated NMMBP of such an eneaminoketone being formed.

Alternatively conformer "e,e" could by through bond charge-transfer interactions (similar to the mechanism postulated for the participation of the nitrogen lone pair electrons in synchronous fragmentation reactions)[187] deactivate the Type I conformer. Such a species might be able to senistize high concentrations of piperylene and give Type I products at a different rate than observed for conformer "e,a". The behavior of NMMBP in benzene can be represented as shown in Scheme VII.



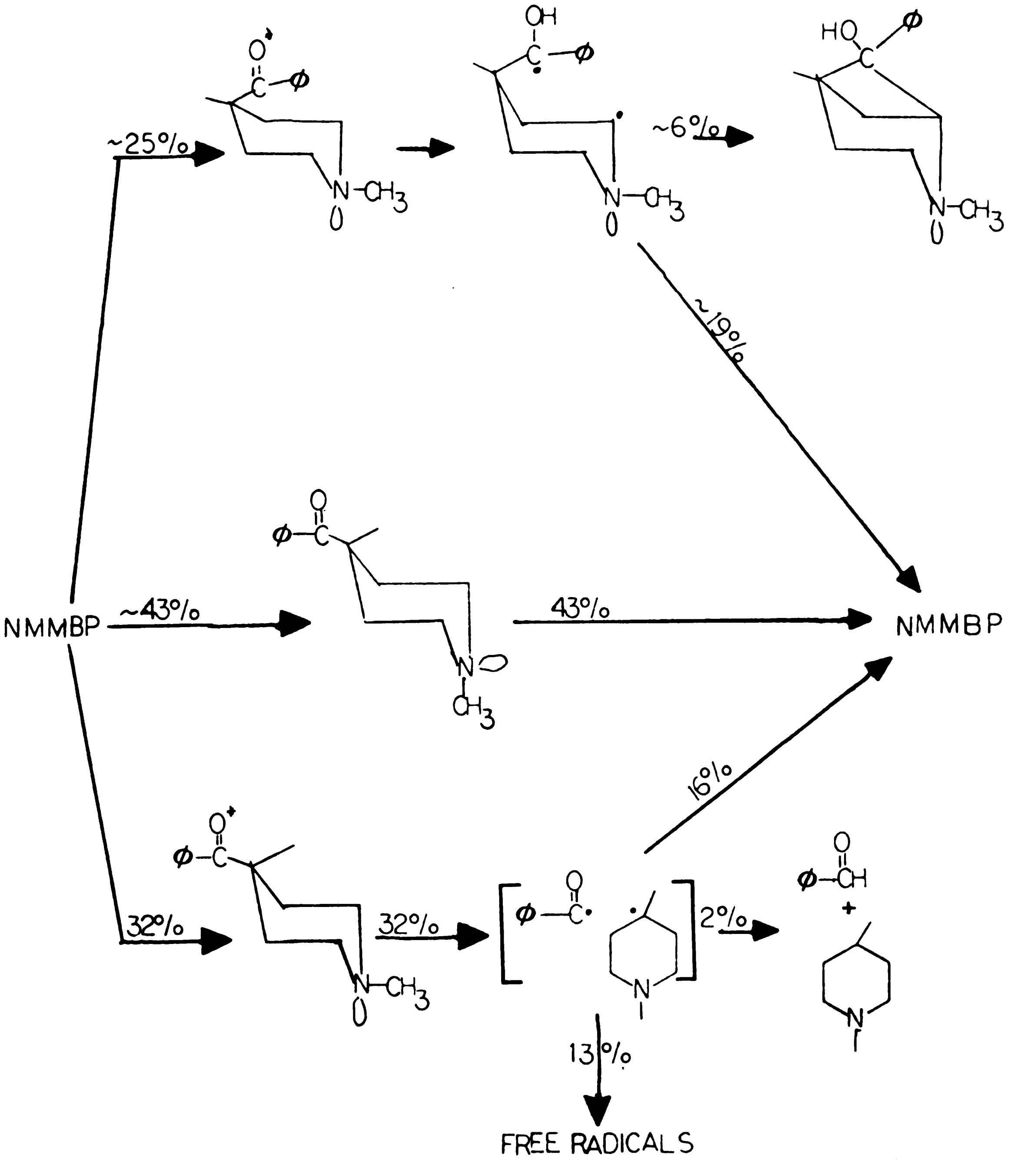
Behavior in Polar Solvents:

The behavior of NMMBP in polar solvents not containing a radical trap probably does not indicate much, since the results probably only reflect the behavior of the formed Type I free radicals in differing solvents. The results observed in this work do suggest that scavenging by the Type I radicals is probably occurring in other systems where competitive Type I and Type II reactions can occur i.e. MCPK, α,α-dimethylvalerophenone.

(a) Pyridine :

Normally pyridine increases the Type II quantum yield, maximizing it at about 0.5 M pyridine concentration. It is thus interesting that pyridine decreases the Type II quantum yield of NMMBP and MCPK by about a factor of 2.0. In NMMBP the disappearance quantum yield and Type I quantum yield are also lowered by about a factor of 2.0.

Lewis[192] has suggested that the order of magnitude decrease in the rate k_r for MCPK relative to CHPK is due to interaction between the ortho-hydrogens of the benzene ring and the α-methyl group which hinders rotation of the biradical. Certainly if the pyridine forms some complex



Scheme VII

Behavior of N-methyl-4-methyl-4-benzoylpiperidine in Benzene with the triplet carbonyl, the sheer bulkiness of the formed complex would slow the necessary rotation to produce cyclobutanol even more and might account for the observed decrease in the quantum yields.

The decrease in the Type I quantum yield in pyridine containing no mercaptan has no real precident in the literature. However, McGrath[193] has indicated that about a two-fold decrease in the Type I quantum yield for α,α- dimethylvalerophenone was observed in t-butanol and acetonitrile.

(b) Alcoholic Solvents:

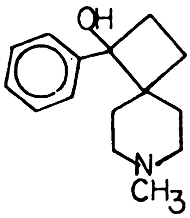
Alcoholic solvents normally increase Type II quantum yields, and this behavior was noted for MCPK. The expected increase for the Type II process of NMMBP was not observed in either methanol or 1-propanol. In fact 50% methanol drastically reduces the Type II quantum yield, while the quantum yield in varying concentrations of 1-propanol shows a slight decrease, then rise to the original value. (It is interesting that this same behavior in 1-propanol is observed for MCPK when varying concentrations of amine are added to the solutions.)

The alcoholic solvent should interact with the amine. The formed $-\overset{+}{N}(CH_3)_3-H-\overset{-}{O}R$ moiety would have a much more positive σ_I value than that of the $-N(CH_3)_3$ group thus giving rise to a reduction in quantum yield (i.e lone pair electrons less available to stabilize the forming radical). Coupled with the results of Wagner and Kemppainen[89] on DMABP where methanol increases the quantum yield but decreases k_r, these results suggest that there is little or no intramolecular charge-transfer quenching of the triplet carbonyl by the amine. The slight lowering then rise of the Type II quantum yield with varying concentrations of 1-propanol and the initial quenching then rise to the observed Φ in the quenching studies on NMMBP in 1-propanol indicate that the interactions of the alcohol with the amine, the inhibition of revertability, and the disappearance of the Type II product are in competition with one another. Which process will rule seems undeterminable at present.

Indications for Further Research:

The study of NMMBP has raised a number of questions, some of which would be answered by the following extensions of this work.

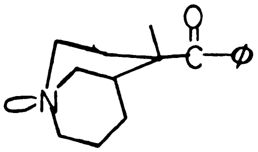
1) Substitution of different groups for the methyl group in the 4-position,i.e a trifluormethyl group would be interesting. This larger group should change the relative populations of each conformation thus giving rise to different amounts of Type II and Type I products. Substitution of an ethyl group for the methyl group might give rise to the following compound:

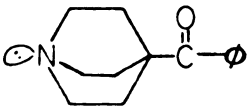


2) Substitution of a p-methoxy group on the benzene ring of the benzoyl group would be of interest since the Type II reaction should be slowed down. Hopefully this

compound would provide a handle for measuring the lifetime of the Type II conformer.

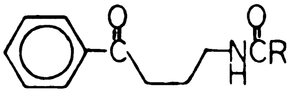
3) To test the hypothesis that through bond charge transfer might be the mode of deactivation of NMMBP, the synthesis and photochemical studies of the following compounds might be considered:





Also the study of compounds containing large groups(t-butyl) which would lock the molecule into conformations "a,a" and "e,a" would be appropriate.

4) Not totally relevent, but interesting, would be the study of:



The bond energy for the N-H bond is about 3-kcal less than that of the C-H bond and it would be interesting to see if this compound would Type II. The cyclization products from the Type II reaction would be β-lactams.

5) A study of the quenching of sterically hindered ketones by amines should be undertaken.

6) It would be interesting to further study the effects of polar solvents on the Type I reaction in the presence of a radical trap. In conjunction with this study it would be appropriate to study the effect of pyridine on the Type II reaction of other sterically hindered ketones.

EXPERIMENTAL

Part I

Preparation and Purification of Materials

Solvents:

a. Benzene: Benzene (Mallinckrodt) of nanograde quality was purified by stirring over concentrated sulfuric acid several times for several days. After the sulfuric acid was removed, the benzene was washed with a 10% aqueous solution of sodium bicarbonate followed by several washings with water and subsequently was dried over anhydrous calcium chloride (4 mesh). The benzene was finally distilled from P_2O_5 through a 45 cm column packed with glass helices. A reflux ratio of 10:1 or larger was maintained at the distilling head and the middle 80% was collected.

b. 2-Propanol: (Fisher Scientific) was distilled from sodium through a 20 cm glass helices packed column. The center cut was collected.

c. Cyclohexane: (Fisher Scientific) was stirred over sulfuric acid until the acid no longer turned yellow. It was then washed as described for benzene. It was finally distilled from P_2O_5, the middle fraction being retained and stored under nitrogen.

d. Pyridine (Mallinckrodt) was distilled from barium oxide and the middle fraction retained.

e. Methanol: (Fischer Scientific) was distilled from magnesium shavings. The middle cut of about 60% was retained.

f. Methylcyclohexane: (Eastman, spectral grade) was passed over alumina and used as received.

g. Heptane (J.T. Baker, spectral grade) was used as received.

h. Ethanol: was used as received.

i. Dodecanethiol: (Aldrich) was distilled at reduced pressure.

j. 1-Propanol: (Fischer Scientific) was distilled from sodium as in "b" above.

k. Acetonitrile: (Fischer Scientific) was distilled from potassium permanganate. Sulfuric acid was added to the distillate and the ammonium salts filtered. The material was redistilled and stored under argon.

Internal Standards:

The standards used in this thesis were purified as indicated below by Peter J. Wagner[4] unless otherwise noted.

a. Dodecane: (Aldrich Chemical Co.) was purified analogous to benzene with distillation under reduced pressure.

b. Tetradecane: (Columbia Organic) was purified as dodecane.

c. Hexadecane: (Aldrich Chemical Co.) was purified as dodecane.

d. Heptadecane: (Aldrich Chemical Co.) was purified as dodecane.

e. Octadecane: (Aldrich Chemical Co.) was treated as benzene with the final distillation being replaced with a recrystallization from ethanol:

f. Nonadecane: (Chemical Samples Co.) was purified as octadecane.

g. Decyl alcohol: (Eastman) was distilled at atmospheric pressure by Dr. Joseph McGrath.

Quenchers:

a. Naphthalene: (Matheson Coleman and Bell) was recrystallized three times from ethanol.

b. 1-Methylnaphthalene: (Aldrich Chemical Co.) was used as received.

c. Cis-piperylene: (Chemical Samples Co.) was used as received. It contained 0.3% of the trans isomer.

d. Biphenyl: (Matheson Coleman and Bell) was recrystallized three times from ethanol.

e. 2-Chlorobiphenyl: (K&K Laboratories) was recrystallized four times from ethanol.

f. 3-Chlorobiphenyl: (K&K Laboratories) was fractionally distilled under reduced pressure. The middle fraction boiling at 101-2° at 0.1 mm Hg was retained. The material was passed over alumina and frozen from ethanol several times.

g. 4-Chlorobiphenyl: (K&K Laboratories) was recrystallized three times from ethanol.

h. 2-Methylbiphenyl: (K&K Laboratories) originally about 80% pure was purified by preparative vapor phase chromatography. Two passes through a 6' x ¼" aluminum column packed with 15%

Carbowax 20M on Chromosorb W were necessary to obtain material 99.5% pure (analyzed by VPC on Col-3).

i. 3-Methylbiphenyl: (K&K Laboratories) was distilled, passed over alumina, and frozen from ethanol several times.

j. 4-Methylbiphenyl: (K&K Laboratores) was recrystallized from ethanol several times.

k. 2,2'-,3,3'-, and 4,4'-dimethylbiphenyl: were used as received from G.W. Griffin.[154]

l. Butyl azide: was prepared essentially by the method of Lieber, Chao, and Rao.[155] To a mixture of 27 grams of sodium azide in 450 ml of methyl carbitol and 75 ml of water was added 60 grams of butylbromide in one batch and heated to 95° for 24 hours. The butyl azide was collected by distillation from the reaction mixture.

m. 2-(4-p-fluorophenyl)-Δ^1-pyrroline: was synthesized by the method of Starr, Bulbrook, and Hixon[156]. p-Fluorophenyl magnesium bromide (prepared from magnesium and p-fluorobromobenzene) in ether was refluxed and γ-chlorobutylonitrile was added and refluxed four hours. The mixture was heated and xylene added dropwise while the ether distilled. When the temperature reached 100° the reaction was cooled, the magnesium complex was decomposed with 50% sodium hydroxide, and the salts were extracted with ether. The ether extract was extracted with 4N hydrochloric acid. The resulting aqueous layer was neutralized with ammonium hydroxide and then extracted with ether. The ether layer was dried and distilled.

n. 2,5-dimethyl-2,4-hexadiene: (Chemical Samples Co.) Crystals which had sublimed to the top of the bottle upon sitting in the refrigerator were scraped out and used without further purification.

o. N-methylpiperidine: (Aldrich) was distilled at atmospheric pressure and the center cut collected.

Ketones:

a. Benzophenone: (Eastman white label) was recrystallized from ligroin twice.

b. Acetophenone: (Matheson Coleman and Bell) was distilled under reduced pressure and the center cut retained.

c. Valerophenone: was prepared by the Friedel-Crafts acylation of benzene by valeryl chloride. The acid chloride was dissolved in a 15 fold excess of benzene and a 10% excess of anhydrous aluminum chloride added. The reaction was allowed to stir overnight. It was then poured into ice water, acidified to a clear solution, and extracted with ether which was dried and distilled. The ketone was passed through alumina and subsequently redistilled.

d. Butyrophenone: (Aldrich) was purified by Dr. Irene Kochevar in 1970.

e. *p*-Azidoacetophenone: was prepared by the method of Bader, Hansen, and McCarty.[157] 15 grams of *p*-fluoroacetophenone was added to 30 cc of dimethylsulfoxide and a 10% excess of sodium azide. The mixture was heated to 80-90° for 24 hours and then poured into chloroform and extracted three times with saturated sodium chloride. The chloroform layer was dried and evaporated. The crude ketone was dissolved in pentane and chromatographed on an alumina column. The material obtained crystallized upon standing and was recrystallized twice from ethanol, mp. 43° (lit. 44°). Six grams of material corresponding to a 30% yield were obtained.

f. γ-Azidobutyrophenone: To an equivalent amount of γ-chlorobutyrophenone was added ethylene glycol plus a catalytic amount of p-toluenesulfonic acid in four equivalents of benzene. The flask was fitted with a Dean-Stark trap and the solution refluxed several days and evaporated. The obtained oil was added to dimethylformamide and a 10% excess of sodium azide was added. This mixture was heated to 80° for 24 hours and worked up as described in "e". After evaporation of the chloroform the azidoketal was added to a 50:50 mixture of tetrahydrofuran and 0.2N hydrochloric acid. The mixture was stirred two days and then made neutral with ammonium hydroxide. The solvent was evaporated and the remaining water solution extracted with ether. This was dried, evaporated, and distilled. The ketone was redistilled and passed over alumina to remove any imino or aminoketone present. A 50% yield based on γ-chlorobutyrophenone was realized.

g. δ-Azidovalerophenone: To 25 grams of δ-chlorovalerylchloride in five times the equivalent amount of methylene chloride a 1.1 equivalent of aluminum chloride was added an equivalent of benzene. This mixture was reacted and worked up as in "c". To the formed δ-chlorovalerophenone (once distilled and recrystallized) dissolved in dimethylformamide was added a 10% excess of sodium azide. The reaction was completed and worked up as in "e". The material, after being passed over alumina, was dissolved in hexane twice and cooled. The hexane was poured off and the crystals collected while cold. The oil was dried under vacuum several days. Based on δ-chlorovalerophenone, a 50% yield of the azidoketone was realized.

h. ε-Azidohexanophenone: Phenylmagnesium bromide was prepared by the action of bromobenzene on magnesium turnings in ether. To this formed grignard reagent was added one equivalent of 6-chlorocapronitrile and the solution was refluxed for four hours. The reaction was poured onto ice cubes containing three equivalents of hydrochloric acid and the ether layer was quickly separated. The acid layer was heated on a steam bath for one hour and extracted with ether which was dried and distilled. The ε-chlorohexanophenone was recrystallized once from hexane and reacted with sodium azide as in "g". The azidoketone was recrystallized twice from hexane. Based on ε-chlorohexanophenone a 55% yield was realized.

i. δ-Thiocyanonatovalerophenone: δ-chlorovalerophenone was added to dimethylformamide. A 10% excess of potassium thiocyanonate was added and the mixture heated to 80° for 24 hours and worked up as in "e". The ketone was vacuum distilled and recrystallized twice from hexane. A 30% yield was realized.

j. N-methyl-4-methyl-4-benzoylpiperidine: N-methyl-4-cyanopiperidine was prepared essentially by the method of

Grob and Renk.[158] Forty grams of isonipecotamide (Aldrich) dissolved in 150 cc of methanol was added all at once to 25 cc of 40% formalin and stirred for four horus at room temperature. This mixture was then added to Raney Nickel (50% suspension in water; dry powder does not work) and hydrogenated on a Parr apparatus at 60 psi. After three hours at room temperature the hydrogen uptake stopped and the solution was filtered, evaporated, and titrated with acetone. The white amide was collected and dried (76% yield). Fifty grams of the amide was added to 300 cc of chloroform and 200 cc of thionyl chloride was slowly added. This solution was refluxed until all the material had dissolved and the solution was light brown in color. The excess thionyl chloride was evaporated and the brown oil neutralized with ammonium hydroxide. This solution was extracted with chloroform and the chloroform solution was dried and distilled. A 50% yield of the nitrile was obtained.

Sodium sand[159] was prepared by adding 29 grams of cleaned sodium to 400 cc of xylene and this mixture heated to reflux and stirred. The resulting sand was recovered by pouring off the xylene and washing the sand twice with dry benzene. To this sodium under nitrogen was added 150 cc of benzene and then 9 grams of chlorobenzene at 40°. When the exothermic reaction had subsided 50 grams of chlorobenzene was added dropwise at $30\text{-}40^{\circ}$ and stirred six more hours. This mixture of phenyl sodium was then cooled to 5° and 41 grams (2/3 theoretical) of the nitrile was added at $5\text{-}8^{\circ}$.

The mixture was stirred one hour longer and then 56 grams of methyl iodide (theoretical amount) was added at 8-10°, and the mixture was stirred one hour longer. Twelve cc of ethanol was added followed by 200 cc of water and the reaction mixture was subsequently filtered through Celite and the benzene layer collected. The water layer was extracted several times with ether and these washings were added to the benzene layer which was dried over anhydrous magnesium sulfate , filtered, and distilled. The residual oil was dissolved in ether and hydrogen chloride gas bubbled into the solution until precipitation no longer occurred. The hydrochloride of the alkylated nitrile was recrystallized twice from isopropanol. Based on the unalkylated nitrile a 75% yield was obtained.

Thirty grams of the alkylated nitrile was added to 0.660 moles (four times equivalent) of phenylmagnesium bromide (prepared as described in "h") whereupon a white precipitate formed. The reaction was refluxed eight hours after which 50% sodium hydroxide was added until reflux ceased. The layers were separated and the magnesium salts were extracted with chloroform and combined with the ether solution which was dried and distilled. This material proved to be the imine which was then added to 4 N hydrochloric acid and heated on a steam bath for one hour. The solution was neutralized with ammonium hydroxide and extracted with ether which was dried and evaporated. This aminoketone was added to ether and hydrogen chloride gas bubbled into the solution until precipitation ceased. The hydrochloride salt was collected and recrystallized twice from methanol-butanone (75% yield based on alkylated nitrile).

For use in photochemical studies the hydrochloride salt was added to a minimum amount of water, and 4N sodium hydroxide was added until the solution was alkaline. The solution was extracted with ether which was dried over anhydrous magnesium sulfate, filtered and evaporated. The ketone was dried under vacuum.

k. N-benzyl-4-methyl-4-benzoylpiperidine: N-benzyl-4-methyl-4-cyanopiperidine was prepared by the reported method of Kuhnis and Denss.[161] Fifty grams of isonipecotamide were added to 285 cc of 3-pentanone and heated to reflux. To the boiling solution was added 66 grams of sodium carbonate and a pinch of potassium iodide. Benzyl bromide (one equivalent: 67 grams) was added dropwise and this mixture was refluxed four hours. The solution was filtered while hot, and the filtrate was washed several times with hot acetone. This solution was allowed to cool and the benzylamide collected by evaporation of the ketone mixture. The solid was recrystallized twice from ethanol-ether (82% yield). The amide was reacted with thionyl chloride as in "j". After distillation the nitrile was added to ether and hydrogen chloride gas added until precipitation ceased. The solid was collected and recrystallized twice from methanol-butanone (80% yield based on amide).

An equivalent amount of bromobenzene was added to 12 times its amount of ether and an equivalent of lithium metal was added all at once. The solution was refluxed for 2½ hours and then an equivalent of triphenylmethane, dissolved in four times its amount of 1,2-dimethoxyethane, was added and stirred 20 minutes. The solution was then cooled in an ice-salt bath and the N-benzyl-4-cyanopiperidine added. The resulting solution was stirred ten minutes more, and an equivalent of methyl iodide was then added. The mixture was stirred 1½ hours longer and then five equivalents of water were added and the solution evaporated. The resulting water solution was extracted several times with ether which solution was extracted four times with 4N hydrochloric acid. The acid solution was neutralized with ammonium hydroxide and extracted with chloroform which was dried and distilled to yield a 37% yield of the alkylated nitrile. This material was dissolved in ether and hydrogen chloride gas added. The precipitate was collected and recrystallized two times from isopropanol. The alkylated ketone was made from this nitrile as indicated in "j" except that only 2.5 equivalents of the Grignard reagent were used and a white precipitate did not form. Again the imine was isolated. This time the hydrochloride salt had been made before this was realized and the imine was not isolated (methanol-butanone solution of iminohydrochloride turned red upon heating). This hydrochloride was neutralized with sodium hydroxide which solution was extracted with ether. The ether was evaporated and the material added to 4N hydrochloric acid and heated on a steam bath for an hour. This solution was extracted with ether which was dried and evaporated. The hydrochloride salt was remade and recrystallized two times from methanol-butanone (70% yield based on alkylated nitrile before spilling sample). The free base of the ketone was made as in "j".

1. Rathke's Base Method: (a) To 7.05 grams of isopropylcyclohexylamine in four times its volume of THF in a three-necked flask fitted with a nitrogen inlet valve and a septum cap was added 20 cc of 2.5M butyllithium. This was stirred under nitrogen for several minutes, then cooled to -70°C. Ten grams of the appropriate nitrile was added and this solution stirred 20-25 minutes. The solution was poured into a cooled addition funnel and added dropwise to 8.8 grams of methyl iodide in 30 cc of DMSO (dried over calcium hydride). This was stirred about an hour and evaporated. Water was added and the solution extracted with ether which was dried, evaporated, and distilled. A nitrile mixture of about 60:40 alkylated to non-alkylated (NMR analysis) material was obtained.

(b) To di-isopropylamine in four times its volume of THF was added an equivalent of n-butyllithium. This was cooled to -70°C. and the N-methyl-4-benzoylpiperidine dissolved in two times its amount of DMSO was added. This was stirred about an hour and then an equivalent of methyl iodide in THF was added. After stirring for about one-half hour the solution was evaporated and water added. The water solution was extracted with ether which was dried, filtered, and evaporated. A mixture of ketones containing about 30%

alkylated material (NMR analysis) was obtained.

m. Phenyl-(N-methyl-4-methyl-4-piperidinemethanol): To 0.5 grams of N-methyl-4-methyl-4-benzoylpiperidine in 20 cc of ethanol was added 1 gram of sodium borohydride. The solution was stirred four hours at room temperature and the ethanol evaporated. The white solid was stirred in water, which was made slightly acidic and extracted with ether. The ether solution was dried and evaporated. The alcohol obtained melted at 105-9°.

n. 1-Methylcyclohexylphenyl ketone: Cyclohexanecarboxamide was prepared essentially by the method of Baumgarten.[162] To 100 cc of chilled concentrated ammonium hydroxide was added 50 grams of cyclohexanecarbonyl chloride over a period of one hour. The formed cyclohexanecarboxamide was isolated by filtration. To a solution of 25 grams of the dried amide in 150 cc of chloroform was added 100 cc of thionyl chloride. The mixture was refluxed 16 hours, followed by distillation of the chloroform and thionyl chloride at atmospheric pressure. The formed cyclohexylnitrile distilled at 95-7° at water aspirator pressure.

To a solution of phenyl sodium (prepared from 8 g of sodium sand and 20 g of chlorobenzene as indicated in "j".) was added 13 grams of cyclohexylcarbonitrile at 5-8°. After stirring for one hour, 24 g of methyl iodide were added at 5-8°, and the mixture was stirred for ½ hour longer. Four cc of ethanol and 60 cc of water were then added. The mixture was filtered through celite, the benzene layer separated, and the water layer extracted with ether. The ether washings were combined with the benzene layer which was dried and distilled. The 1-methylcyclohexylcarbonitrile distilled at 96° at water aspirator pressure. A 50% yield based on the acid chloride was obtained.

To 0.15 mole of phenyl magnesium bromide in ether (prepared from 3.6 grams of magnesium and 24 grams of bromobenzene) was added 0.1 mole of the 1-methylcyclohexanecarbonitrile. The solution was refluxed seven hours and worked-up as in "h". The ketone distilled at 85° and a 50% yield based on starting nitrile was realized.

The crude ketone (10 g) was added to 3.5 grams of hydroxylamine hydrochloride dissolved in 67 cc of 95% ethanol and 137 cc of 7% aqueous sodium hydroxide. The solution was refluxed 5 hours and cooled. The white crystalline needles were collected and recrystallized from ethanol twice. The oxime melted at 145-7°. This material was added to 80 cc of 12% aqueous hydrochloric acid and refluxed two hours. After cooling the water solution was extracted with ether which was dried and evaporated. The 1-methylcyclohexylphenyl ketone distilled at 97-100° at 0.08 mm Hg.

Physical and Spectral Data for Synthesized Materials and Isolated Photoproducts:

The physical and spectral data for the synthesized materials and isolated photoproducts used in this thesis are listed in Table XV. The following is the key to the Table:

Physical Properties	Infrared:	NMR:	UV:
mp melting point	$-\overset{O}{\overset{\|}{C}}-$ carbonyl	s-singlet	wavelength in nm followed by extinction coefficient
bp boiling point at specified pressure	$-N_3$ azide	d-doublet	
	-CN cyano	t-triplet	
	-C=NH imino	m-multuplet	
	-SCN thiocyanate		
	$-\overset{O}{\overset{\|}{C}}N-$ amide		
	-NH amine or imine		
	-OH hydroxyl		

All NMR spectra were obtained in deuteriochloroform or carbon tetrachloride using TMS as standard. All shifts are in δ units and the number of protons producing the indicated signal are shown. The piperidine ring protons are not indicated. The IR spectra were obtained neat or in nujol. The mass spectral data are m/e ratios.

TABLE XV
SPECTRAL PROPERTIES OF SYNTHESIZED AND ISOLATED MATERIALS

Compound Formula/molecular Weight	Physical Properties	IR Spectrum	NMR Spectrum	Mass Spectrum	UV Spectrum
p-azidoacetophenone $C_8H_7ON_3$ 161	mp 43°	$-N_3$ 2100 2130 $-\overset{\overset{O}{\|}}{C}-$ 1680	s 2.55 3p	----	280 2120 217 2860
γ-azidobutyrophenone $C_{10}H_{11}ON_3$ 189	bp 140° (.05) 122° (.03)	$-N_3$ 2100 $-\overset{\overset{O}{\|}}{C}-$ 1680	m 1.94 2p t 3.00 2p t 3.40 2p m 7.70 2:3p	161	278 990 240 940 285 900
δ-azidovalerophenone $C_{11}H_{13}ON_3$ 203	bp 140° (0.08) mp 22-3°	$-N_3$ 2100 $-\overset{\overset{O}{\|}}{C}-$ 1690	m 1.80 4p t 2.92 2p t 3.30 2p m 7.70 2:3p	175	285 960 276 1120 238 1600
ε-azidohexanophenone $C_{12}H_{15}ON_3$ 217	bp 146° (.08) mp 27-8°	$-N_3$ 2100 $-\overset{\overset{O}{\|}}{C}-$ 1700	m 1.50 6p t 2.90 2p t 3.20 2p m 7.70 2:3p	189	286 850 276 893 238 1600
δ-thiocyanatovalerophenone $C_{12}H_{13}OSN$ 219	bp 170° (0.1) mp 48°	-SCN 2150 $-\overset{\overset{O}{\|}}{C}-$ 1685	m 1.94 4p m 3.10 4p m 7.80 2:3p	219	278 992 240 7250
N-methylisonipecotamide $C_7H_{14}ON_2$ 142	mp 193-6°	$-\overset{\overset{O}{\|}}{C}N-$ 1650 $-NH_2$ 3410 3515	s 2.30 3p s 6.30 2p	----	----

TABLE XV Continued

Compound Formula/molecular Weight	Physical Properties	IR Spectrum	NMR Spectrum	Mass Spectrum	UV Spectrum
N-formylisonipecotamide $C_7H_{12}O_2N_2$	mp 156°	$-\overset{\overset{O}{\|}}{C}N-$ 1650 $-NH_2$ 3400	----	----	----
N-benzylisonipecotamide $C_{13}H_{18}ON_2$ 218	mp 145-7°	$-\overset{\overset{O}{\|}}{C}N-$ 1650 $-NH_2$ 3410 3515	s 3.50 2p s 5.85 2p s 7.30 5p	----	----
N-benzyl-4-cyanopiperidine $C_{13}H_{16}N_2$ 200	bp 138°(.05)	-CN 2240	s 3.41 2p s 7.30 5p	----	----
N-benzyl-4-methyl-4-cyanopiperidine $C_{14}H_{18}N_2$ 214	mp·HCl 288°	-CN 2240	s 1.30 3p s 3.44 2p s 7.30 5p	----	----
N-methyl-4-cyanopiperidine $C_7H_{12}N_2$ 124	bp 100°(11.0)	-CN 2250	s 2.24 3p	124	----
N-methyl-4-methyl-4-cyanopiperidine $C_8H_{14}N_2$ 138	mp·HCl 223-6°	-CN 2240	s 1.20 3p s 2.30 3p	138	----
N-methyl-4-methyl-4-benziminopiperidine $C_{14}H_{20}N_2$ 216	bp 120-2°(.05)	$-\overset{\overset{NH}{\|}}{C}-$ 1680 -NH 3200	s 1.30 3p s 2.20 3p s 7.22 5p	----	----

TABLE XV Continued

Compound Formula/molecular Weight	Physical Properties	IR Spectrum	NMR Spectrum	Mass Spectrum	UV Spectrum
N-methyl-4-methyl-4-benzoylpiperidine $C_{14}H_{19}ON$ 217	mp·HCl 217-9°	$-\overset{O}{\overset{\|}{C}}-$ 1690	s 1.45 3p s 2.28 3p m 7.22 2:3p	217	275 660
N-benzyl-4-methyl-4-benzoylpiperidine $C_{20}H_{23}ON$ 293	bp 175°(.03) mp·HCl 185°	$-\overset{O}{\overset{\|}{C}}-$ 1680	s 1.32 3p s 3.30 2p s 7.18 5p m 7.42 2:3p	293	315 122 275 704 235 1450
2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-01 $C_{14}H_{19}ON$ 217	mp·HCl 180-4° mp 80-2°	-OH 3425	s 1.21 3p s 2.19 3p s 7.20 5p	217	----
Phenyl-(N-methyl-4-methyl-4-piperidine methanol $C_{14}H_{19}NO$ 219	mp 105-9°	-OH 3400	s 0.8 3p m 2.0 11p s 4.2 1p s 7.2 5p	219	----
cyclohexylcarbonitrile $C_7H_{11}N$ 109	bp 85°(20)	-CN 2250	m 2.60 1p m 1.50 10p	----	----
1-methylcyclohexyl carbonitrile $C_8H_{13}ON$ 123	bp 97°(20)	-CN 2250	s 1.30 11p s 1.70 2p	----	----
cyclohexylcarboxamide $C_7H_{13}ON$ 127	mp 184°	----	m 1.6 11p	----	----

TABLE XV Continued

Mass	UV

TABLE XV Continued

Compound Formula/molecular Weight	Physical Properties	IR Spectrum	NMR Spectrum	Mass Spectrum	UV Spectrum
1-methylcyclohexylphenyl ketone $C_{14}H_{18}O$ 202	bp 97^{O}(0.08)	$-\overset{\overset{O}{\|}}{C}-$ 1675	m 1.35 9p m 7.4 2:3p	202	----
1-methylcyclohexyl-phenyl oxime $C_{14}H_{19}NO$	mp 145-7^{O}	----	s 1.2 3p m 1.45 11p m 7.25 3:2p	219	----
γ-azidobutyrophenone ethylene ketal $C_{12}H_{15}O_2N_3$ 233	bp 120^{O}(0.1) 108^{O}(.07)	$-N_3$ 2100 no carbonyl	m 1.92 4p t 3.32 2p d 3.96 4p s 7.45 5p	----	----
Butyl Azide $C_4H_9N_3$ 99	bp 50^{O}(100)	$-N_3$ 2100	----	----	285 25
2-(4-p-fluorophenyl)-Δ'-pyrroline $C_{10}H_{10}NF$ 163	bp 77^{O}(.2)	C=N- 1650	m 2.00 2p t 3.00 2p t 4.00 2p m 7.60 2:2p	----	280 2700
2-phenyl-Δ^1-pyrroline $C_{10}H_{11}N$ 145	----	C=N- 1650	m 2.00 2p t 3.00 2p t 4.00 2p m 7.60 2:3p	145	----
2-phenylpyrrole $C_{10}H_9N$ 143	mp 105-118^{O}	-NH 3425	m 6.15 1p m 6.35 1p m 6.65 1p s 7.30 5p	143	----

Identification of Photoproducts:

(a) 2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-ol: Three grams of N-methyl-4-methyl-4-benzoylpiperidine were dissolved in benzene containing 0.1M naphthalene. The solution was added to a photolysis cell fitted with a nitrogen bubbler, magnetic stirrer, and a water cooled Hanovia medium pressure Hg lamp. The material was irradiated for twenty-four hours through a vycor filter. The benzene was evaporated and dissolved in 50% benzene-hexane and added to an alumina column. The material was eluted with 50% benzene-hexane and the fraction containing about 90-95% desired material (NMR and VPC analysis) was evaporated. About two grams of a yellow oil was obtained. A small portion of the isolated cyclobutanol was added to ether and hydrogen chloride gas bubbled into the ether until precipitation ceased. The hydrochloride was collected and recrystallized twice from butanone. The remaining portion of the originally isolated fraction was left to sit in hexane for several weeks. The formed crystals were isolated and recrystallized from hexane. Both the hydrochloride and free base have IR, NMR, and Mass Spectral data consistent with the above named structure and their data are listed in Table XVI. About one gram of pure material was obtained.

Under these high conversion conditions a peak which has a retention time between that of the cyclobutanol and ketone on Col-3 and Col-4 was observed. It was eluted with the naphthalene on the alumina column. It was not identified.

(b) Photoproducts from γ-azidobutyrophenone:

The 2-phenyl-Δ^1-pyrroline(PDP) was isolated by injecting γ-azidobutyrophenone on a prepmaster VPC containing a thermal detector. Passage of the ketone through a 6' x ¼' aluminum column packed with 15% carbowax on 60/80 chromosorb G afforded PDP which was identified by its characteristic spectra. It was also compared to a sample of (PDP) synthesized by AE Kemppainen. When irradiated samples of γ-azidobutyrophenone were injected only (PDP) and acetophenone were collected.

To isolate the materials producing the other peaks observed in the VPC traces, twelve tubes containing 0.07 M ketone were degassed and irradiated for two weeks at 366 nm. The tubes were broken open and the benzene evaporated. The 1.0 gram of brown oil obtained was placed on an alumina column containing about 100 g of alumina. Initially, elution was effected with benzene. Acetophenone, PDP, and γ-azidobutyrophenone were eluted together. The polarity of the elution solvent was subsequently increased by adding 10% increments of ethyl acetate to the benzene. When 20% ethyl acetate/benzene was used as the elutant 2-phenyl pyrrole was collected with some brown oil. The brown oil was the next fraction to be eluted with the 20% ethyl acetate/benzene. Even after the column was eluted with neat methanol no further materials were observed.

The 2-phenyl pyrrole was sublimed from the brown oil and subsequently resublimed. The spectra of the 2-phenyl pyrrole were obtained and compared to those in the literature.[163-5] The mass spectrum of the isolated 2-phenylpyrrole is identical to that obtained from the GC/mass spectral data. From the wide melting point range observed for the isolated material, it is suspected to contain a small amount of some other material.

The brown oil (common to most reactions involving azides[166]) showed carbonyl, azide, and either NH or OH absorbances in the IR. It does not produce a signal in the VPC, and its NMR spectrum is essentially that of the azidoketone. It is apparently some oligomer of the parent ketone but its structure is undetermined.

Part II

Techniques

Preparation of Samples:

a. Disappearance of Benzophenone:

Purified benzene solutions of varying concentrations of benzophenone and quencher were made up by adding two cc of a specific concentration of benzophenone, three cc of 3.33 M isopropanol, and one to four cc of quencher stock solution pipetted with class "A" pipets to a ten cc class "A" volumetric flask. Two solutions were made up in the same manner except that no quencher was added. One of these was used as standard and the other to measure the extent of photolysis in the presence of no quencher. After the solutions were diluted to volume, 2.8 cc of each, measured by a 5 cc syringe, were placed in 13 x 100 mm culture tubes with elongated necks. These tubes had previously been washed with a commercial glass cleaner followed by four rinsings with tap water and three rinsings with distilled water.

b. Phosphorescence of Benzophenone:

Solutions were prepared essentially as in the manner for the disappearance of benzophenone except that the standard solution was eliminated. Except in those cases where k_h was to be determined, no 3.33 M isopropanol or 5 M cyclohexane stock solution was added. In certain cases where the amount of quencher was limited (2-methylbiphenyl), only 1.5 cc of solution was added to the elongated tubes and solutions were made up in 5 cc class "A" volumetric flasks.

c. Azido and Amino Ketones:

For the Stern-Volmer quenching studies or quantum yield determinations, solutions were prepared by adding two cc of ketone stock solution, two cc of the appropriate internal standard (usually to be 0.004 M or 0.02 M) to a 10 cc class "A" volumetric flask. For quantum yield studies this was then diluted to the mark. If a Stern-Volmer study was being performed 1,2,3, and 4 cc of quencher stock solution was added using the appropriate class "A" pipet followed by dilution to the mark. Solutions for quantum yield studies in pyridine or methanol were prepared as previously described except that the appropriate amount of pyridine (0.5) was weighed into the ten cc flask or the appropriate amount of methanol was added by pipet followed by dilution to the mark. 2.0 cc of the final solution were added to elongated test tubes using a 5 cc syringe.

d. Sensitization Studies:

Solutions were mixed exactly as in the above section, except that cis-piperylene replaced the quencher. Also a solution containing the same concentration of acetophenone as ketone and a certain concentration of cis-piperylene was made up.

Degassing:

In order to remove dissolved gases from the solutions, sample tubes were attached to a vacuum line over 00 one-holed stoppers on individual stopcocks. The solutions were slowly frozen above liquid nitrogen and then immersed before opening to vacuum. After 20 minutes the stopcocks were closed and the tubes allowed to thaw (assisted with a water bath). For the benzophenone and aminoketone studies, the tubes were sealed off with a torch after the fifth or sixth cycle. In the azidoketone studies the tubes were sealed after the third cycle. In the cis-piperylene studies at high concentrations of piperylene only one cycle was used whereas at lower concentrations three cycles were performed.

Irradiation Procedure:

Sample tubes to be irradiated were placed in a rotating merry-go-round apparatus immersed in a water bath at room temperature and irradiated in parallel to insure that the same amount of light impinged upon each sample. A 450 watt Hanovia medium pressure mercury lamp housed in a water cooled quartz or pyrex immersion well was used. The 300-320 nm region was isolated with a one cm path of 0.0002 M potassium chromate in a 1% aqueous solution of potassium carbonate. The 366 nm region was isolated with a set of Corning no. 7-83 filter combinations which isolated about a 30 Å region of light about 3660 Å. The apparatus used is that described by Moses, Lui, and Monroe.[167]

Analysis of Samples:

a. Disappearance of Benzophenone:

After being irradiated the tubes were broken open and the contents poured into tightly capped one dram bottles and allowed to stand 24 hours. The disappearance of benzophenone was then measured on a Gilford Model 200 spectrophotometer. Samples with no quencher were carried to between 40 and 60% conversion. Analyses were made at 3440, 3500, 3600 and 3700 Å. Measured per-cent conversions varied by less than 1% or the data was discarded for that wavelength. For the 0.05 M benzophenone solutions 1 mm cells were used while 10 mm cells were used for the 0.0075 M ketone solutions. The 0.035 M and 0.02 M solutions were diluted 1:4 or 2:3 solution to benzene and analyzed in 10 mm cells.

b. Phosphorescence of Benzophenone:

After degassing, the tubes were placed in the adapted cell of an Aminco-Bowman spectrophotometer (the bottom taken out and a cork placed in the bottom) and the sample irradiated with 366 nm light. The phosphorescence of the desired benzophenone was monitored at 450 and 480 nm. Consistency was attempted by carefully taking readings on the same tube and slowly turning it until the highest reading was achieved. After all the readings were obtained the tubes were broken open and oxygen bubbled into the system and a "background" reading obtained. This value was subtracted from the initial reading.

c. Gas Chromatography Procedures:

Analysis for all photoproducts and standards were made on either an Areograph Hy-Fi model 600D gas chromatograph with 550 oven and 328 programmer connected to a Leeds and Northrup Speedomax H recorder or a Varian Aerograph 1200 gas chromatograph connected to a Leeds and Northrup Speedomax H recorder. Each of the instruments was prepared for on-column injection and used nitrogen as the carrier gas. Both instruments used flame ionization detectors and were connected to an Infrotronics Automatic Digital Integrator model CRS-208. The samples were injected with a Hamilton microliter syringe (#7101) using two or three 0.3 to 0.5 microliter shots per sample. Analysis were made on one of the columns below.

Col-1: 6' x 1/8" aluminum containing 4% QF-1, 0.5% Carbowax 20 M on 60/80 chromosorb G.

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

Col-3: 12' x 1/8" aluminum containing 4% QF-1, 1% Carbowax 20 M on 60/80 chromosorb G.

Col-4: 3' x 1/8" stainless steel containing 5% SE-30 on 30/40 high purity chromosorb W.

Col-5: 6' x 1/8" aluminum containing 3% SE-30 on 60/80 chromosorb G.

The concentration of a photoproduct can be easily determined by comparison of its VPC peak to that of an internal standard by the following equation:

$$[\text{Photoproduct}] = \text{Standardization factor} \times [\text{internal standard}] \times \frac{\text{counts photoproduct}}{\text{counts internal standard}}$$

The standardization factor which compensates for different molar responses for each compound is determined by weighing out known amounts of photoproduct and internal standard and measuring the relative VPC peak area ratio. The standard to product ratios and VPC conditions used in this work are listed in Tables XVI and XVIII.

Actinometry:

a. Valerophenone:

Samples containing the same concentration of valerophenone as unknown ketone and 0.004 M tetradecane as internal standard were irradiated concurrently with the ketone sample whose quantum yield was to be determined. At 366 nm it was important to use the same concentration of valerophenone as ketone since all the light that impinges on the sample tubes was not absorbed. Before each run was made a check was made to assure that the actinometer tubes and ketone tubes were absorbing the same amount of light. In cases where all the light was absorbed this precaution was not necessary. Analysis for acetophenone was subsequently made using Col-3. The quantum yield of valerophenone varies only slightly with ketone concentration. The quantum yield of a 0.1 M valerophenone solution is 0.33; a 0.07 M solution

Table XVI

Column Conditions Used to Determine Prod/Std. Ratios

Column Condition Set	Instrument	Column	Flow Rate	Oven Temperature
#1	Varian Aerograph 1200	Col-3	30ml/min	120-5°
#2	Aerograph HiFy 600-C	Col-2	20ml/min	50°
#3	Aerograph HiFy 600-C	Col-4	15ml/min	100-10°
#4	Varian Aerograph 1200	Col-1	20ml/min	100-10°
#5	Varian Aerograph 1200	Col-3	20ml/min	100-10°
#6	Aerograph HiFy 600-C	Col-4	15ml/min	110-128°
#7	Varian Aerograph 1200	Col-3	20ml/min	90-5°
#8	Varian Aerograph 1200	Col-3	20ml/min	150-5°

Table XVII

Standard/Product Ratios

Standard/Product	Area/mole(Std) Area/mole(Prod)	Column Cond. Set
tetradecane/acetophenone	2.00	1,5,7
dodecane/benzaldehyde	2.00	5
octadecane/γ-azidobutyrophenone	2.30	4
heptadecane/δ-azidovalerophenone	2.40	4
octadecane/ N-methyl-4-methyl-4-benzoylpiperidine	2.23	3
hexadecane/ N-methyl-4-methyl-4-benzoylpiperidine	2.53	1
decyl alcohol/benzaldehyde	1.53 1.75	5 7
octadecane/2-phenyl-Δ^1-pyrroline	3.01	4
hexadecane/ε-azidohexanophenone	3.24	6
octadecane/2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-ol	2.46	6
octadecane/1-methylcyclohexyl phenyl ketone	1.30	8
heptadecane/1-methylcyclohexyl phenyl ketone	1.24	8

0.32; and 0.05 M and 0.04 M solutions 0.31.[168] In cases of low quantum yield it was necessary to use several sets of actinometers assuring that an actinometer was present at all times during the photolysis. Per cent conversions were kept to about 10% and never allowed to go above 15%.

b. *Cis*-Piperylene-Acetophenone:

Cis-piperylene sensitization plots were made to determine the intersystem crossing yields for γ-azidobutyrophenone, δ-azidovalerophenone, and the amino ketone. Tubes containing the desired concentration of ketone with varying amounts of *cis*-piperylene were irradiated in parallel with tubes containing the same concentration of acetophenone as ketone and a specific concentration of *cis*-piperylene. The triplet state of acetophenone forms quantitatively ($\Phi_{isc}=1$). The triplet is quenched by *cis*-piperylene which then decays to both *cis*- and *trans*-piperylene in a 55:45 ratio.[169] The following relationship gives the amount of piperylene triplets formed:

$$\left[\underline{\text{Cis}}\text{-pip}_{o}\right] \times \ln \frac{0.555}{0.555\text{-ratio } \underline{\text{trans}}\text{-pip}} = \left[\text{Pip.}^{*3}\right]$$

The number of piperylene triplets formed is then divided into the concentration of *trans*-piperylene formed when the desired ketone is acting as sensitizer where *trans*-piperylene is given by:

$$\left[\underline{\text{trans}}\text{-pip}_{o}\right] = 0.555 \times \left[\underline{\text{Cis}}\text{-pip}\right] \times \ln \frac{0.555}{0.555\text{-ratio } \underline{\text{trans}}\text{ pip.}}$$

This value when divided into 0.555 gives the Φ at that particular concentration of piperylene. A plot of $0.555/\Phi$ versus 1/piperylene gives a curve with 1/intercept equal to the intersystem crossing quantum yield and whose intercept divided by the slope equals $k_t\tau$[170].

Spectra:

Infrared (IR) spectra were recorded on a Perkin-Elmer 237B grating spectrophotometer as neat solutions or as nujol films between NaCl plates. All IR spectra were calibrated at 1601.4 cm^{-1} with polystyrene film. Proton magnetic resonance (NMR) spectra were recorded on a Varian T-60spectrometer at ambient probe temperature as solutions in carbontetrachloride or deuteriochloroform using tetramethylsilane as an internal standard. The mass spectra were determined by Mrs. Lorraine Guile on a Hitachi-Perkin-Elmer RMU-6 mass spectrometer. Ultraviolet spectra and solutions used to check optical density were measured with a Gilford 200, Unicam SP-800, or Carey 14 spectrophotometer. The disappearance of benzophenone in samples was measured on the Gilford 200 instrument. Electron spin resonance spectra (ESR) were obtained on a Varian E-4 spectrophotometer fitted with a variable temperature unit cooled to the temperature of liquid nitrogen. The samples were irradiated with an Hanovia one-kilowatt high pressure mercury-xenon arc filtered only by five centimeters of water. The instrument was calibrated using DPPH (diphenylpicrylhydrazide: signal 3244 Gauss)[171] and $VOSO_4$ (splitting between fourth and fifth line equals 116.13 Gauss).[172]

Finally the spectrum of biphenyl was compared to that of biphenyl obtained on a Varian X-band EPR spectrometer Model 4502-15 with Mark II field regulator and 100 K Hz modulation unit. The latter machine was used by Dr. Alfred Haug to obtain the ESR spectra of the three chlorobiphenyls.

The GC/Mass spectral data were obtained by Jack E. Harten of the Biochemistry department on a system which consisted of an LKB 9000 gas chromatograph/mass spectral unit, a Digital Equipment Corporation PDP/I on line digital computer, an incremental plotter, and a KSR 35 teletypewriter.[173]

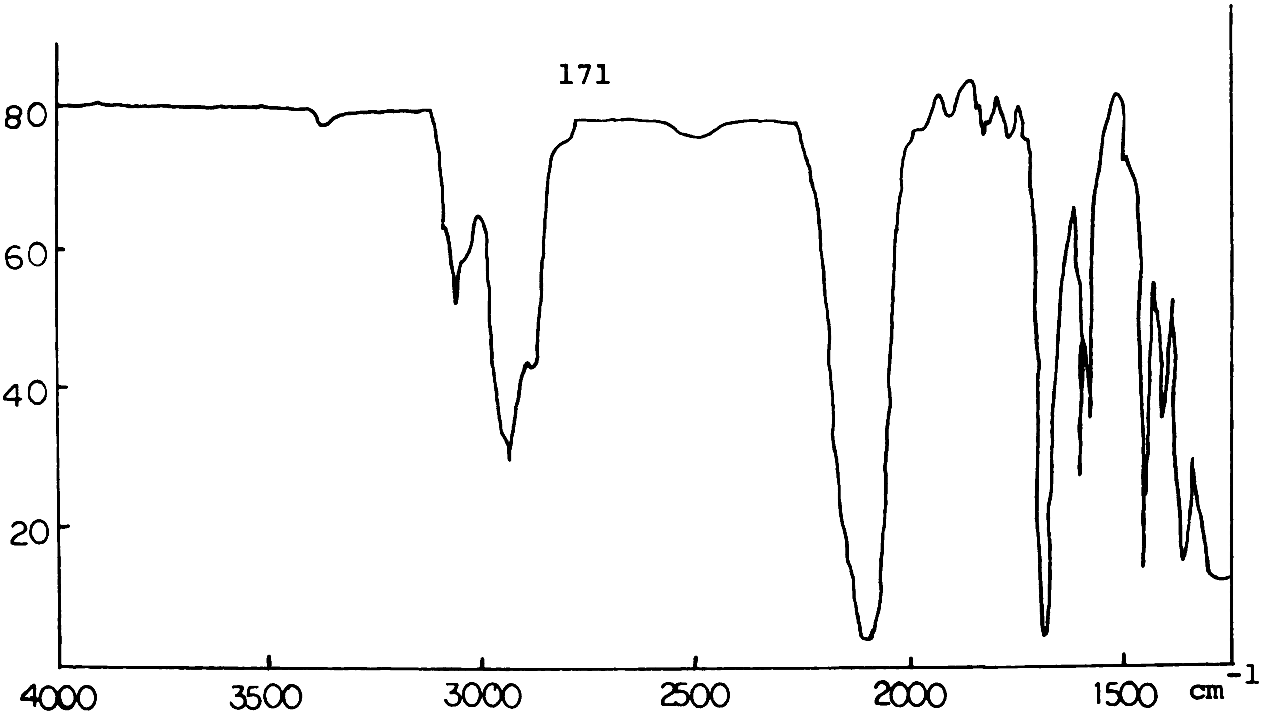
The triplet lifetimes of the chlorobiphenyls were determined by M. May.[143] Irradiation was effected with an Osram 6500 w Xenon arc filtered through a 5-cm quartz cell containing filter solution. The emission was fed to a Nuclear Data Model ND 2200 multichannel analyzer and the spectrum plotted on a Hewlet-Packard Model 7590 C x-y recorder.[174]

Phosphorescence and fluorescence spectra were obtained on an Aminco-Bowman spectrofluorometer fitted with an off-axis ellipsoidal mirror condensing system, a mercury-xenon lamp, and a side-on potted IP-21 photomultiplier tube. Spectra were recorded on a Houston Instruments X-Y recorder. For phosphorescence spectra of the biphenyls the sample was placed in a 3 mm quartz tube (same used for ESR studies) with a sealed bottom and placed in the small dewar supplied with the instrument. The Dewar which contained liquid nitrogen was placed in the cavity and the phosphorescope spun at the speed that gave the sharpest spectrum. The samples were

irradiated at 254 nm. The fluorescence spectra of the biphenyls were obtained at room temperature. The benzophenone phosphorescence samples were degassed and the tubes placed in the modified cavity of the instrument and irradiated at 366 nm.

Measurements of ^{13}C spectra were performed by Dr. R.C. Schoening on a Brucker HFX-10 nmr spectrometer at 22.6 MHz using the usual Fourier transform signal enhancement methods[194] in conjunction with broad band proton decoupling.[195] Solutions were 40% MMBP-60% Freon 2,1, the latter serving as a ^{19}F lock signal. Sample temperature was measured by directly inserting a thermometer into the 10-mm diameter sample tube spinning in a dewared insert. A thermocouple fixed near the bottom of the freely rotating sample tube serves to regulate a flow of cooled nitrogen gas. Control of temperature was accurate to $\pm 0.5\%^{o}$.

The low temperature proton NMR studies on MMBP were performed by Eric Roach on a Varian HA-100 nmr spectrometer. Temperature was monitored by measuring the shift between the methanol peaks and reading the temperature from the graph supplied by Varian.



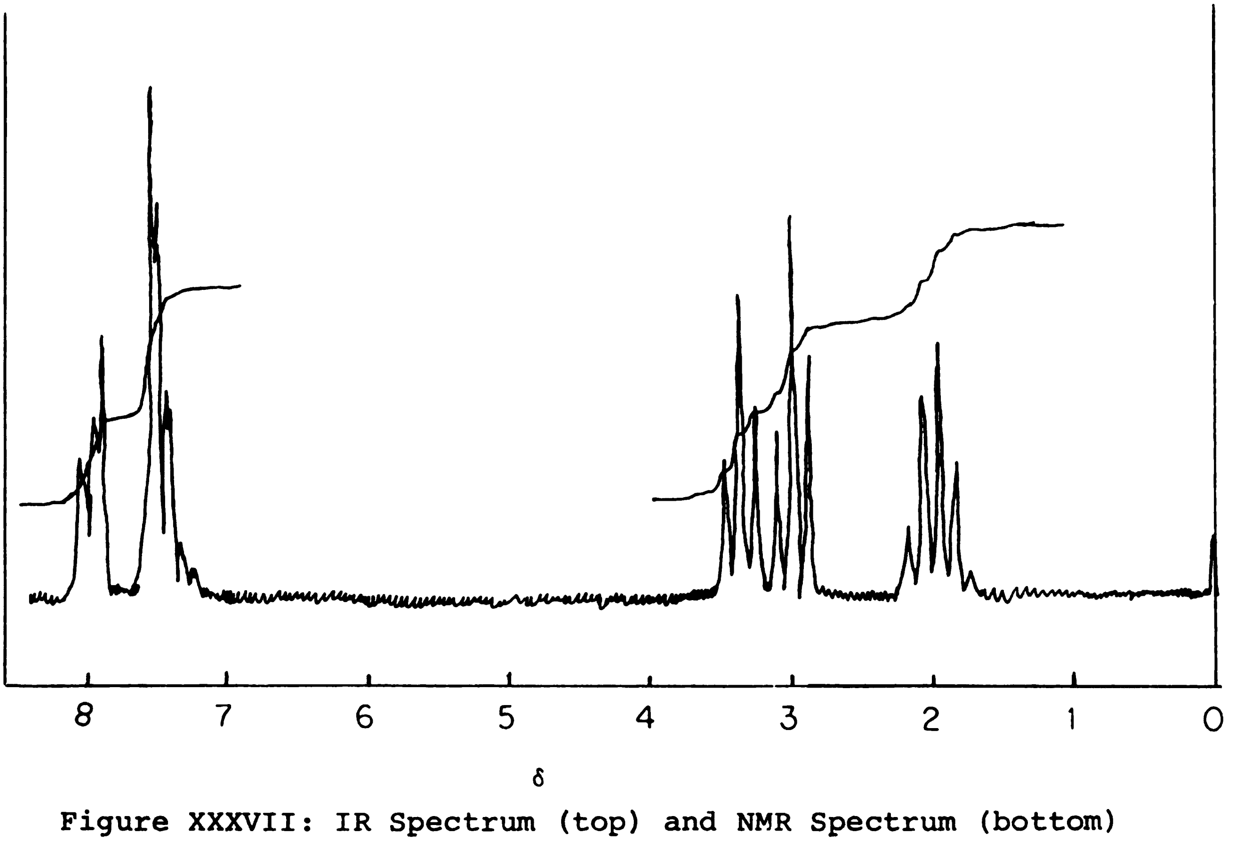
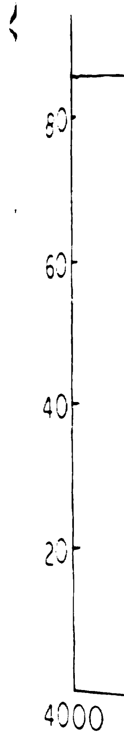
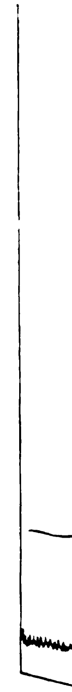


Figure XXXVII: IR Spectrum (top) and NMR Spectrum (bottom) of γ-azidobutyrophenone





F

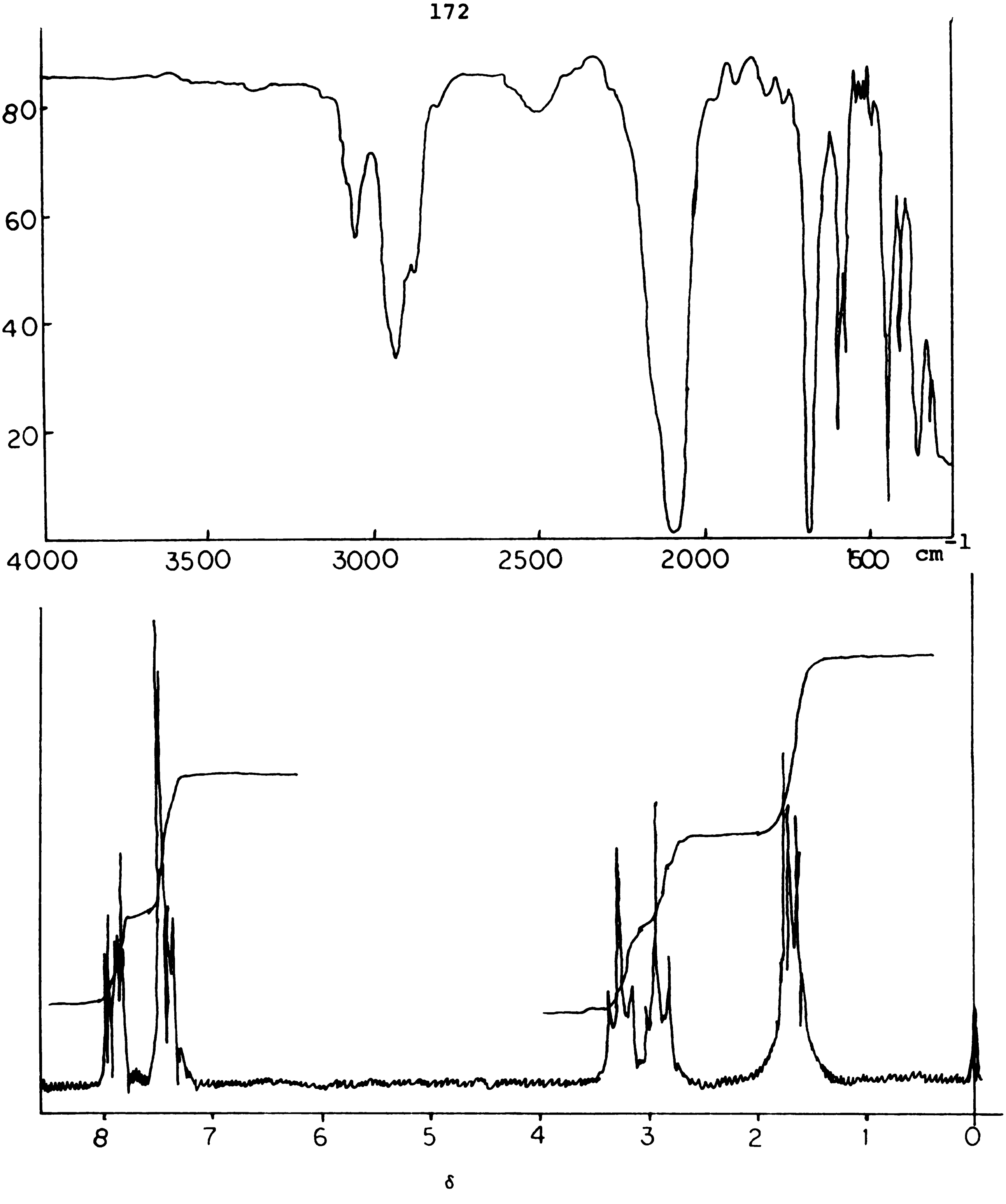


Figure XXXVIII: IR Spectrum (top) and NMR Spectrum (bottom) of δ-azidovalerophenone

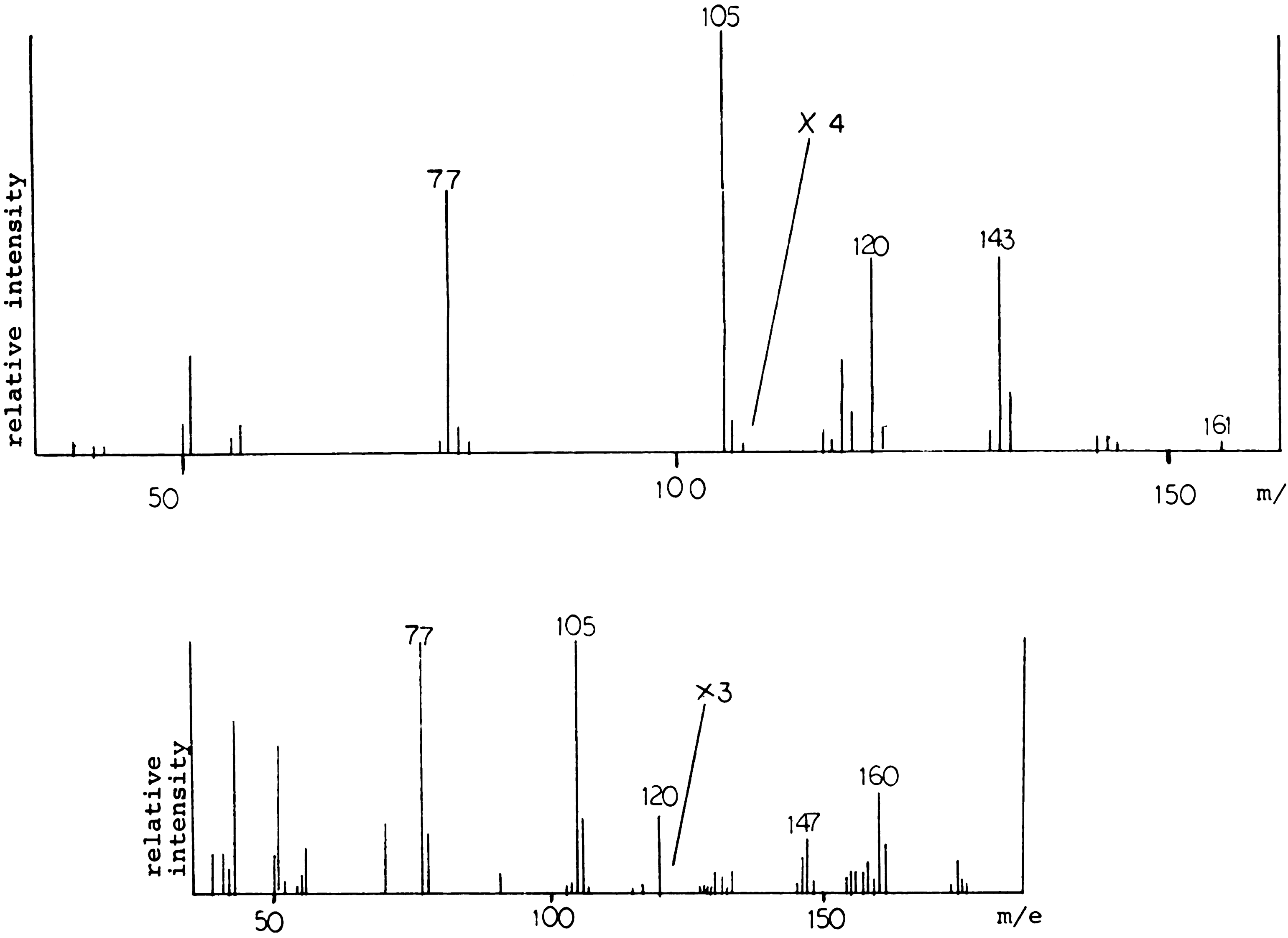


Figure XXXIX: Mass Spectra from GC/Mass Spectral Data of γ-azidobutyrophenone (top) and δ-azidovalerophenone (bottom)

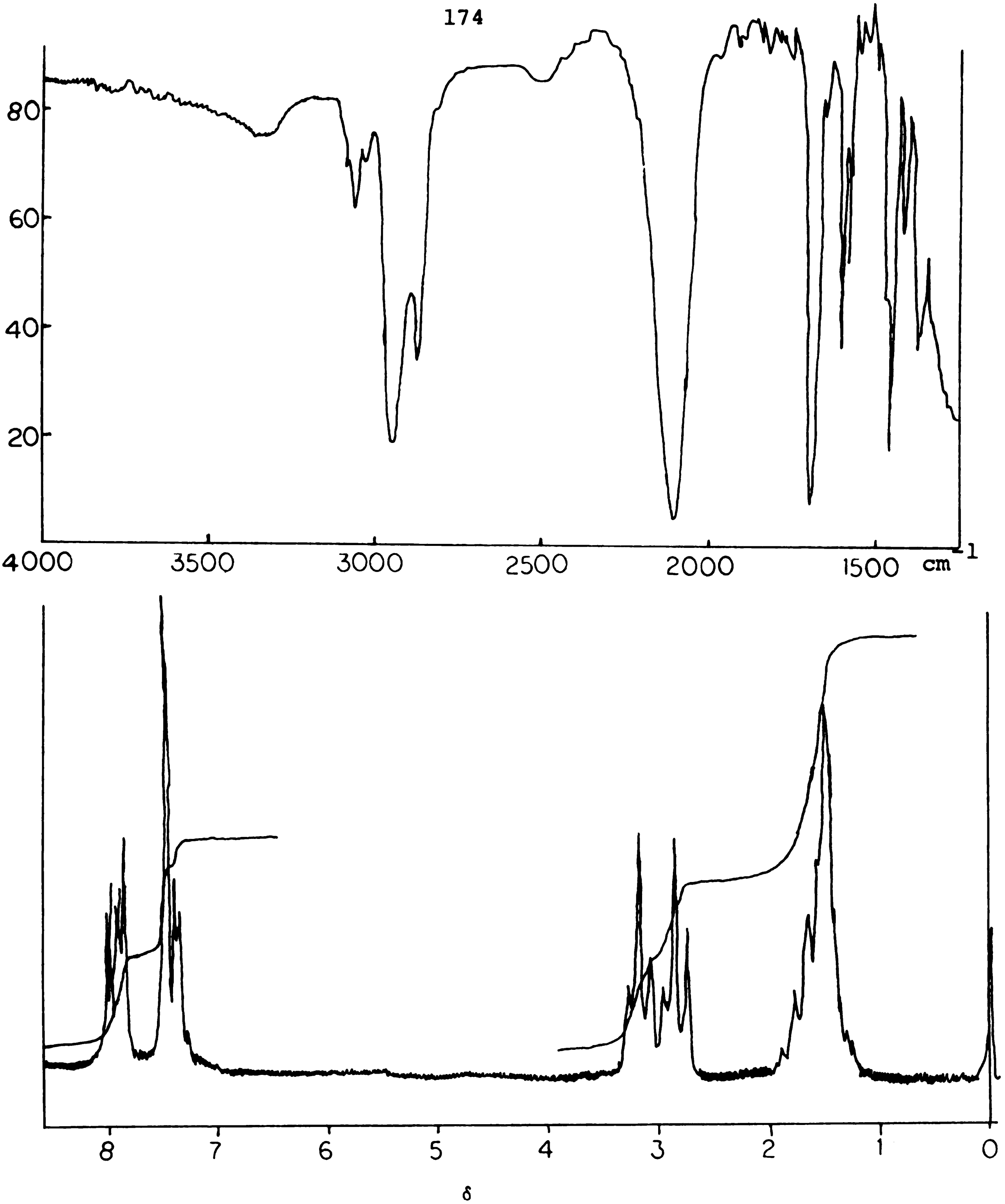


Figure XL: IR Spectrum (top) and NMR Spectrum (bottom) of ε-azidohexanophenone

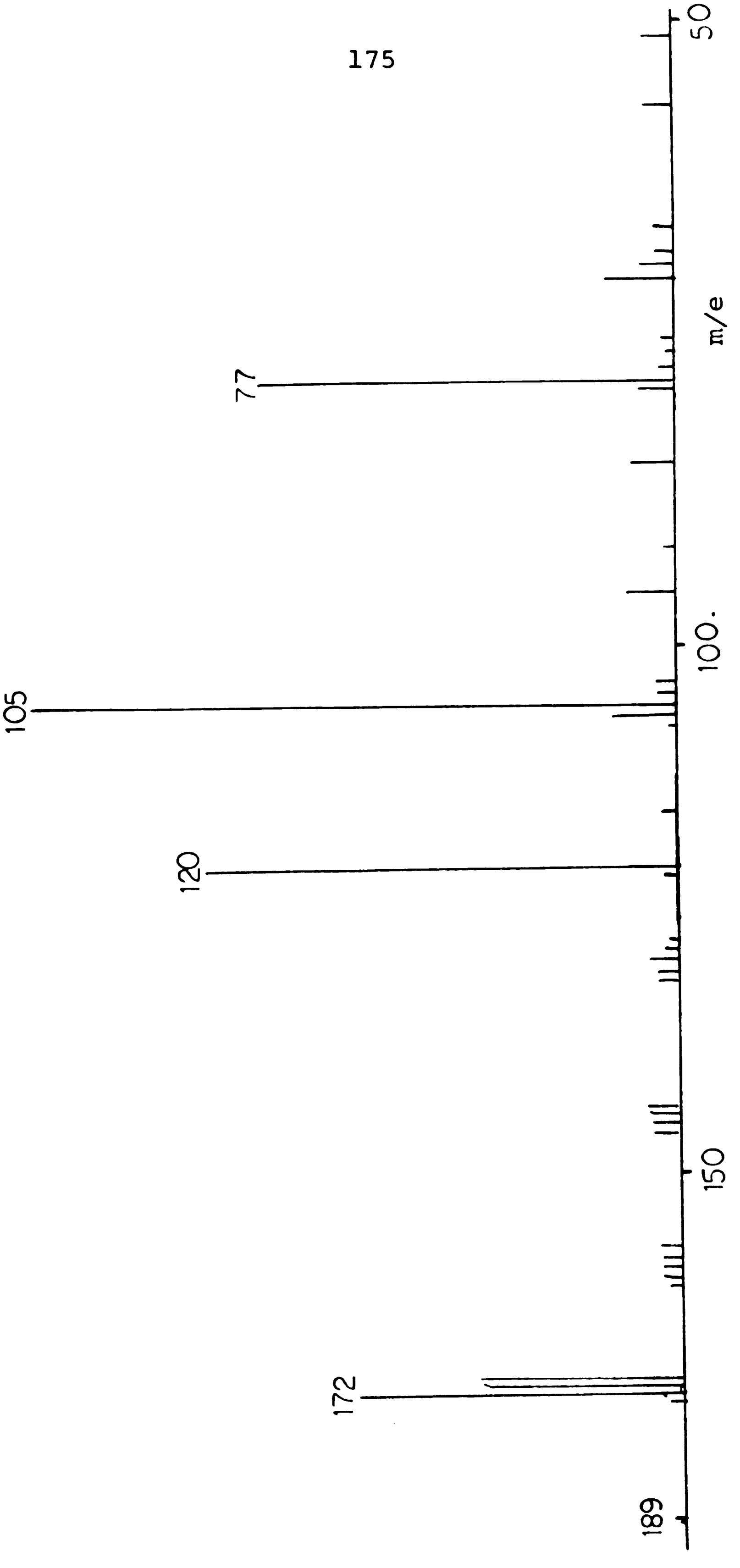


Figure XLI: Mass Spectrum of ε-azidohexanophenone

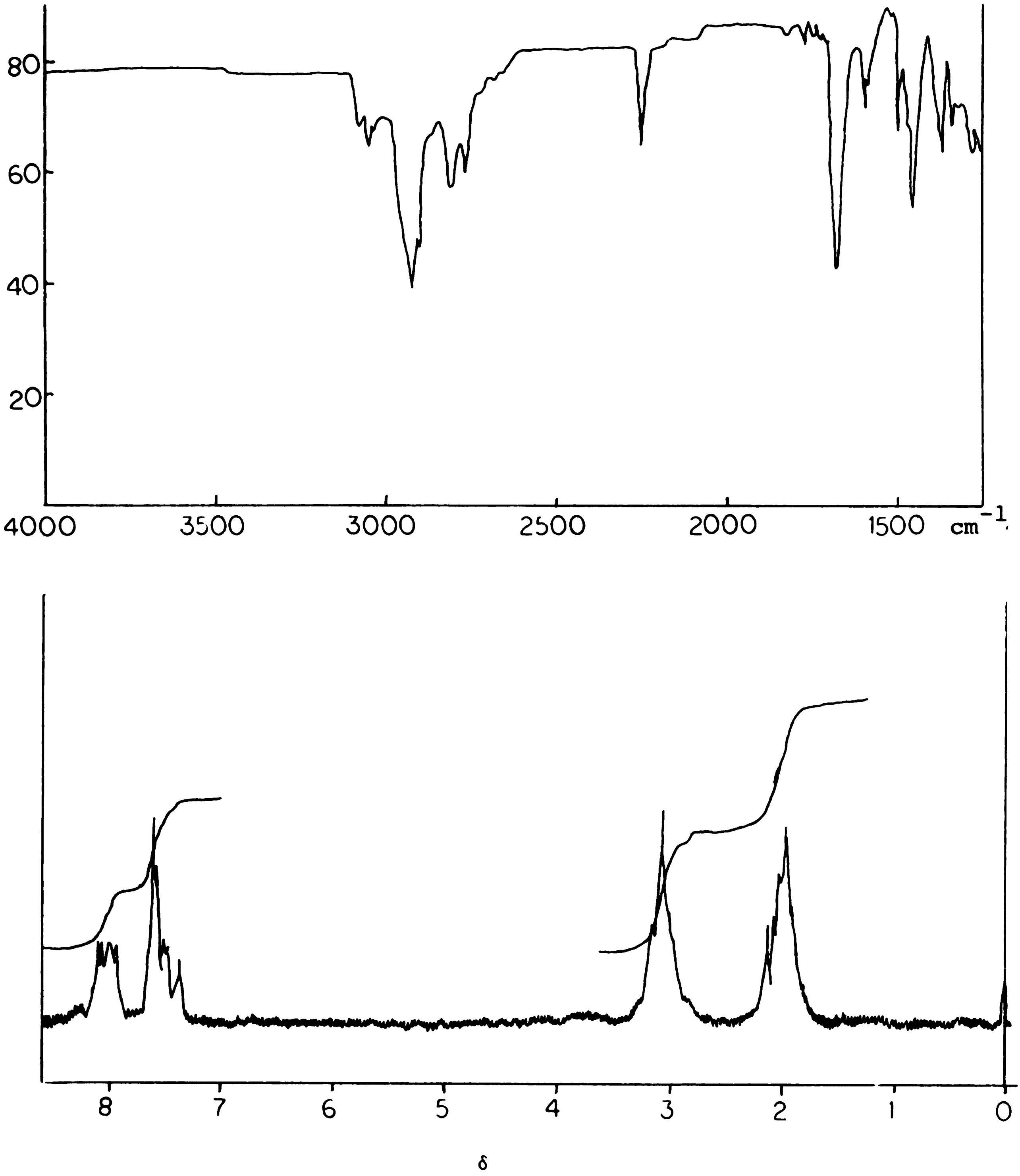


Figure XLII: IR Spectrum (top) and NMR Spectrum (bottom) of δ-thiocyanatovalerophenone

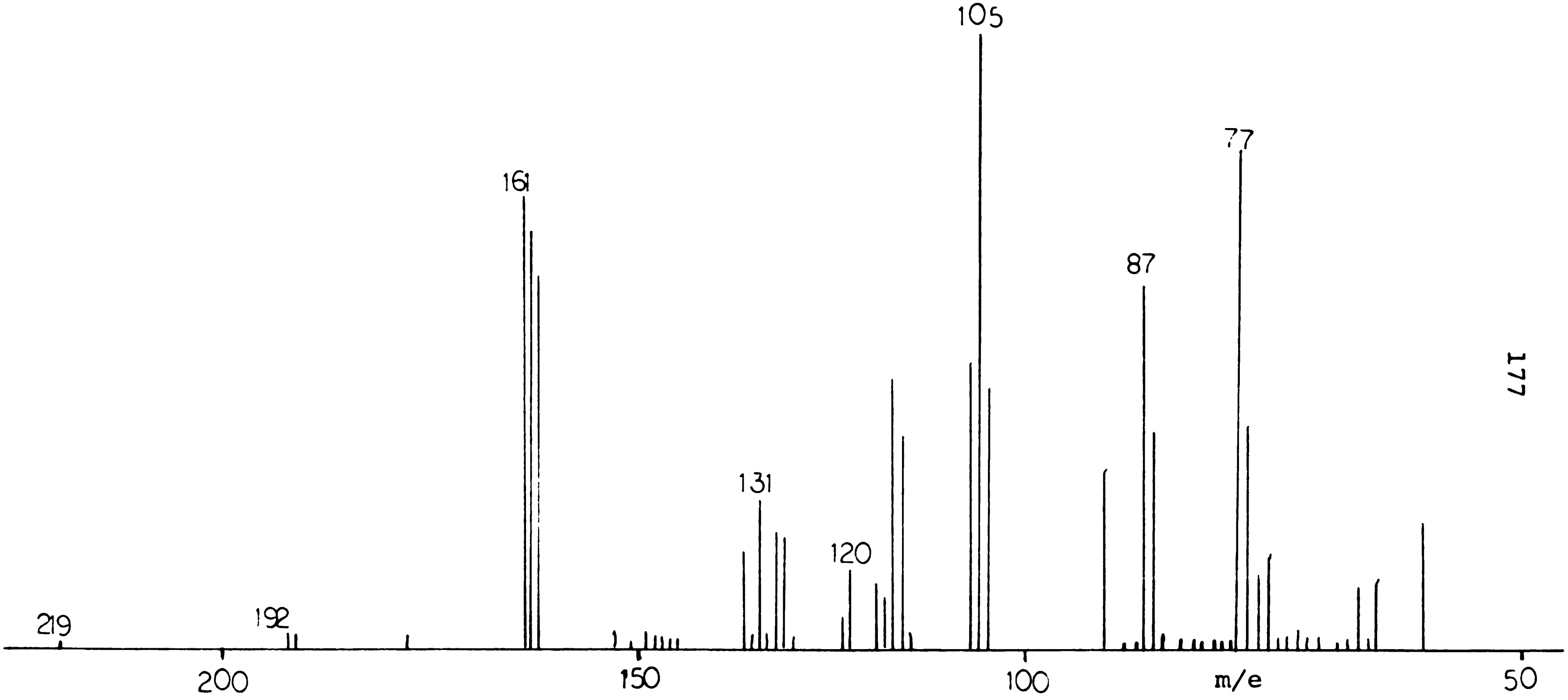


Figure XLIII: Mass Spectrum of δ-thiocyanatovalerophenone

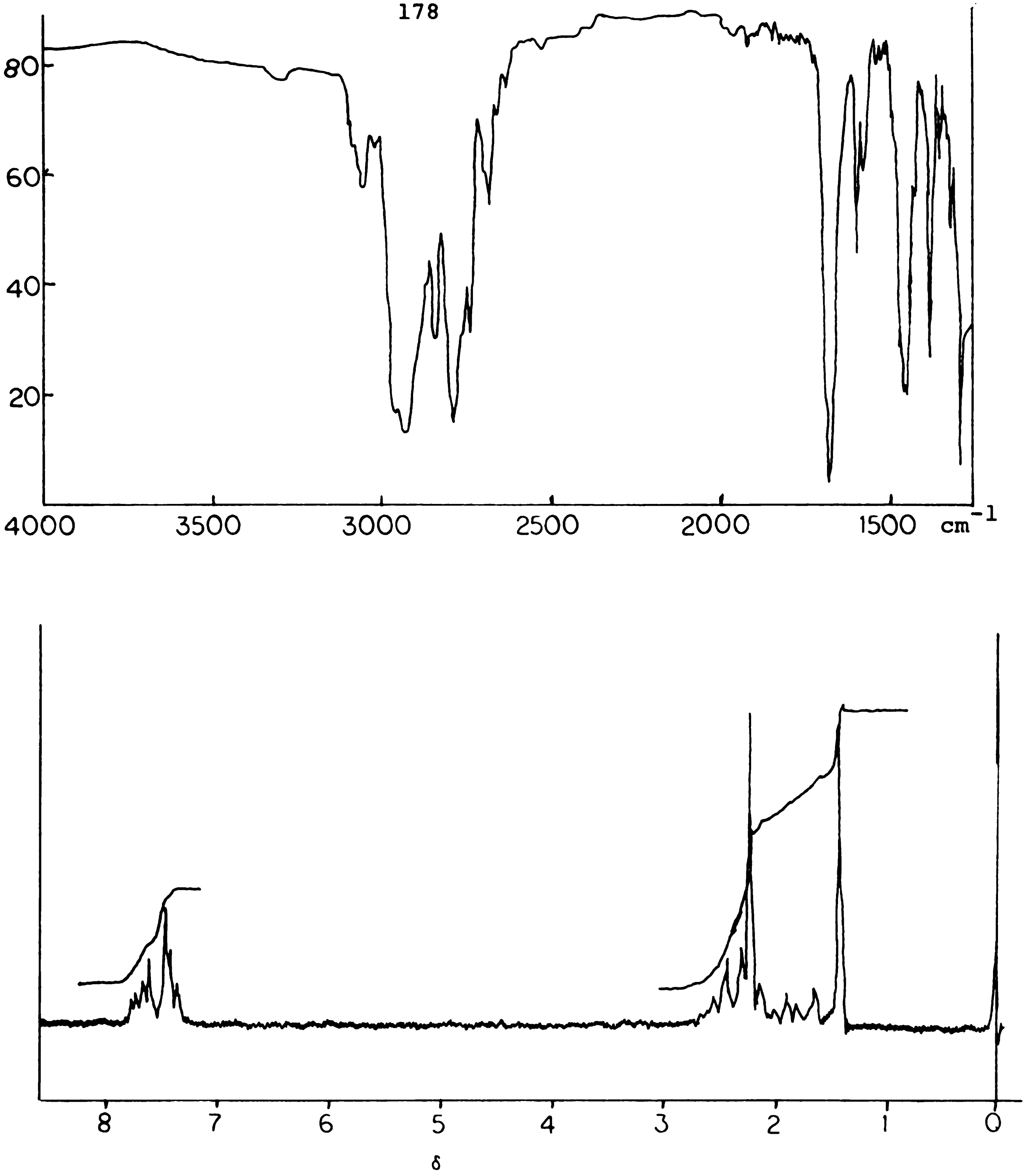


Figure XLIV: IR Spectrum (top) and NMR Spectrum (bottom) of N-methyl-4-methyl-4-benzoylpiperdine

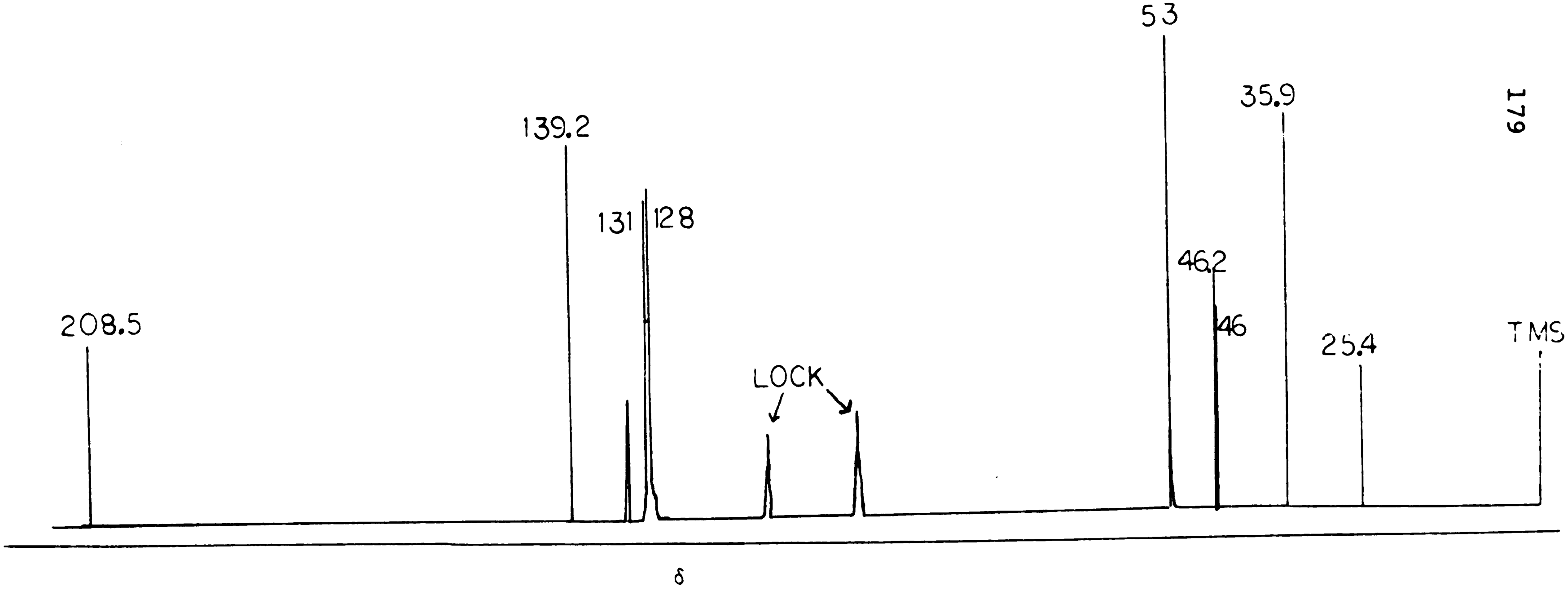


Figure XLV: Room Temperature proton decoupled ^{13}C NMR Spectrum of N-methyl-4-methyl-4-benzoylpiperidine with Freon 21 serving as ^{19}F lock

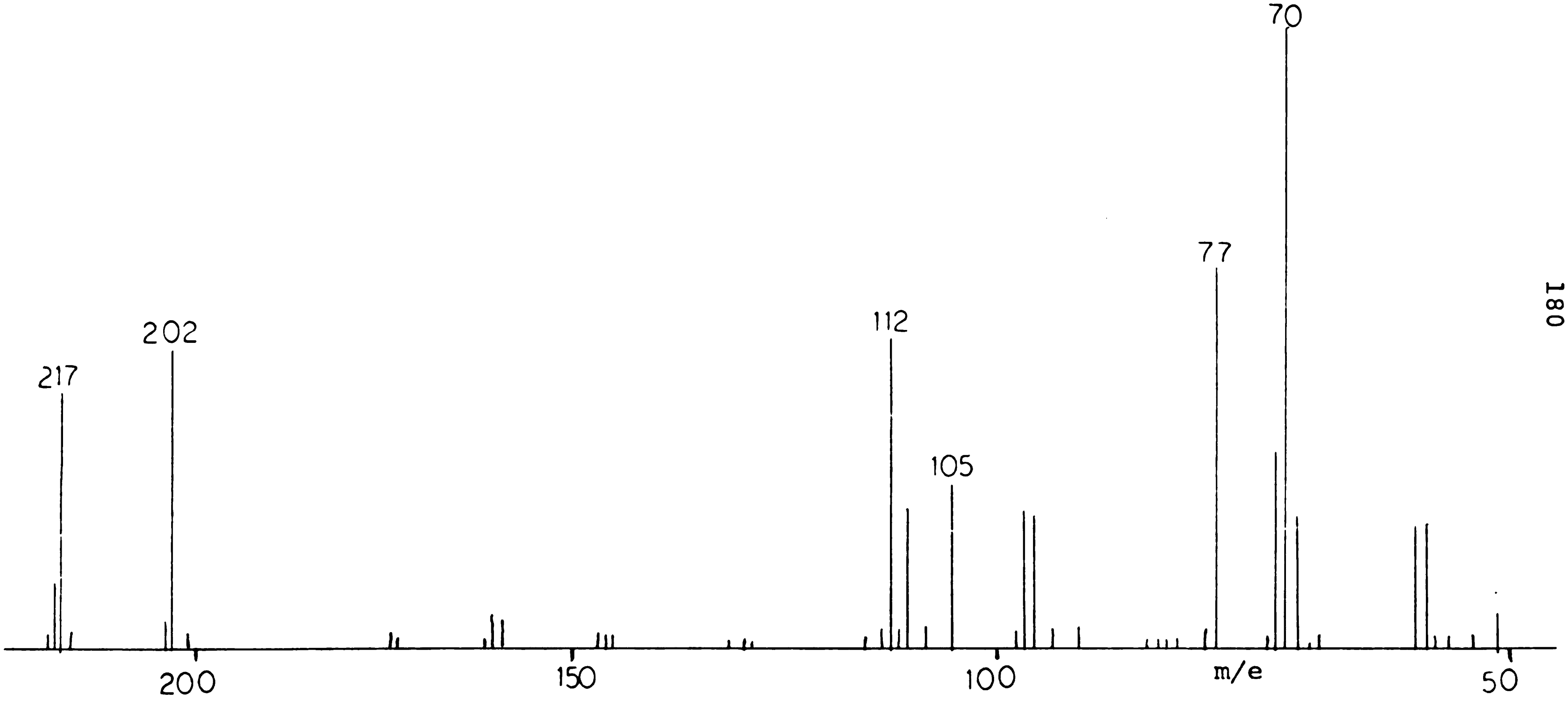
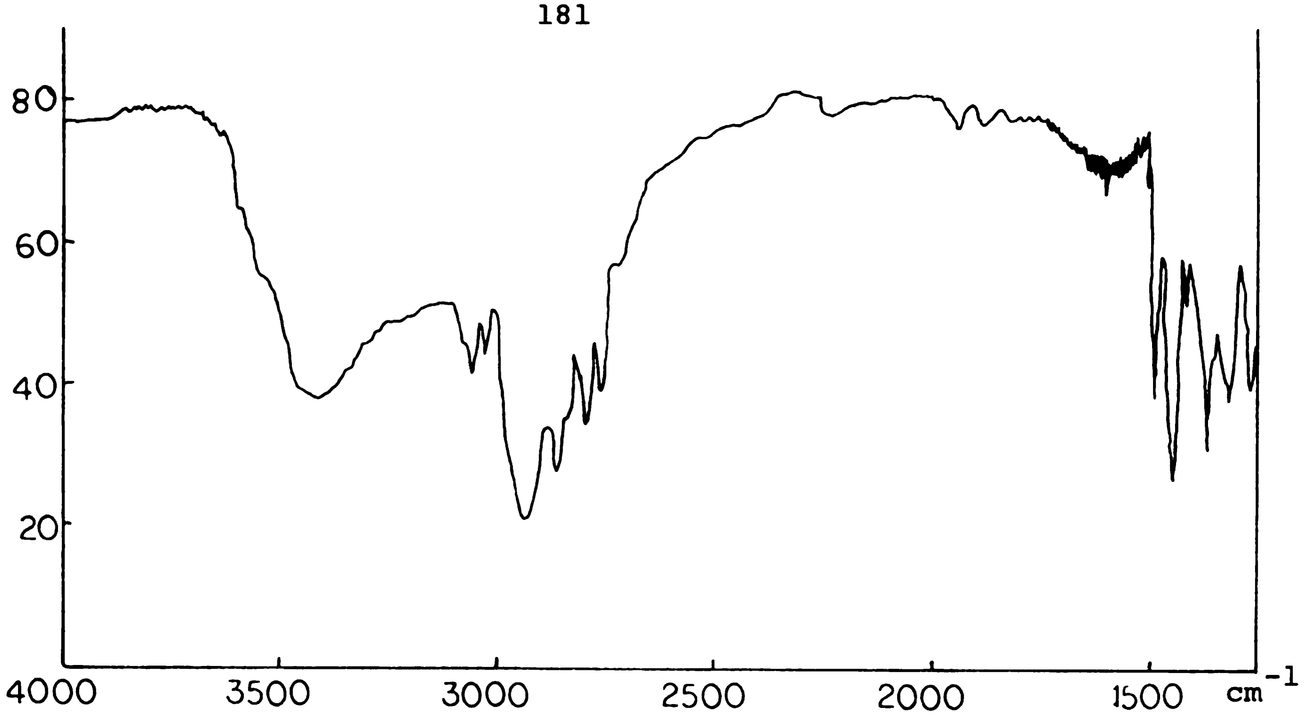


Figure XLVI: Mass Spectrum of N-methyl-4-methyl-4-benzoylpiperidine



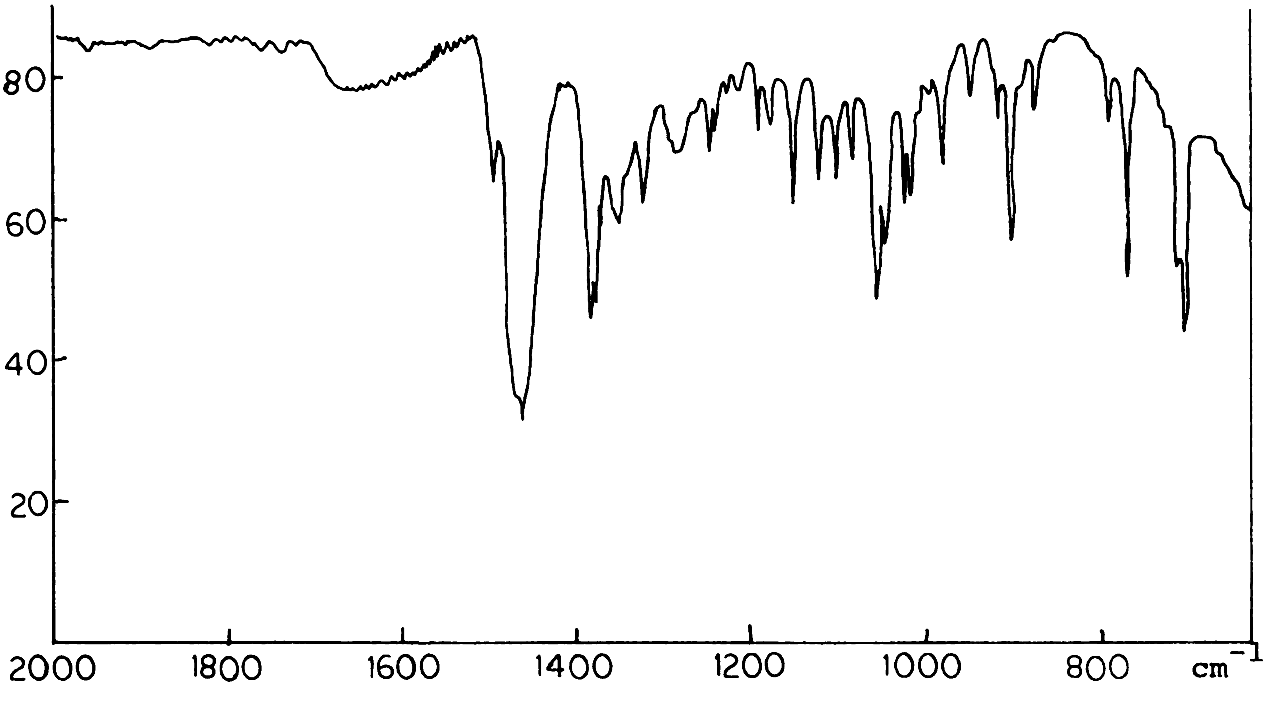


Figure XLVII: IR Spectrum of 2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-ol: Top (neat), Bottom (in nujol)

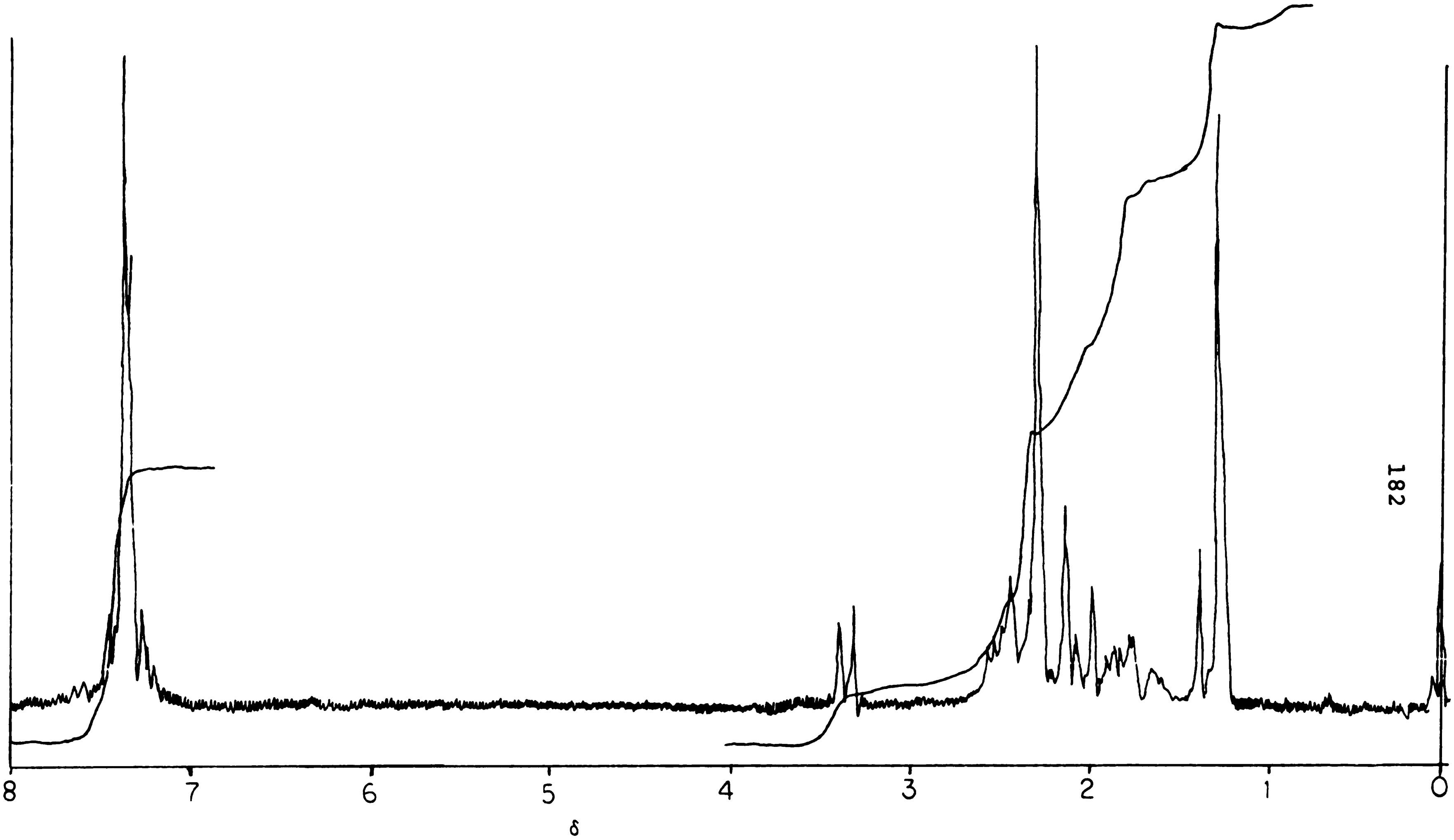


Figure XLVIII: NMR Spectrum of 2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-ol

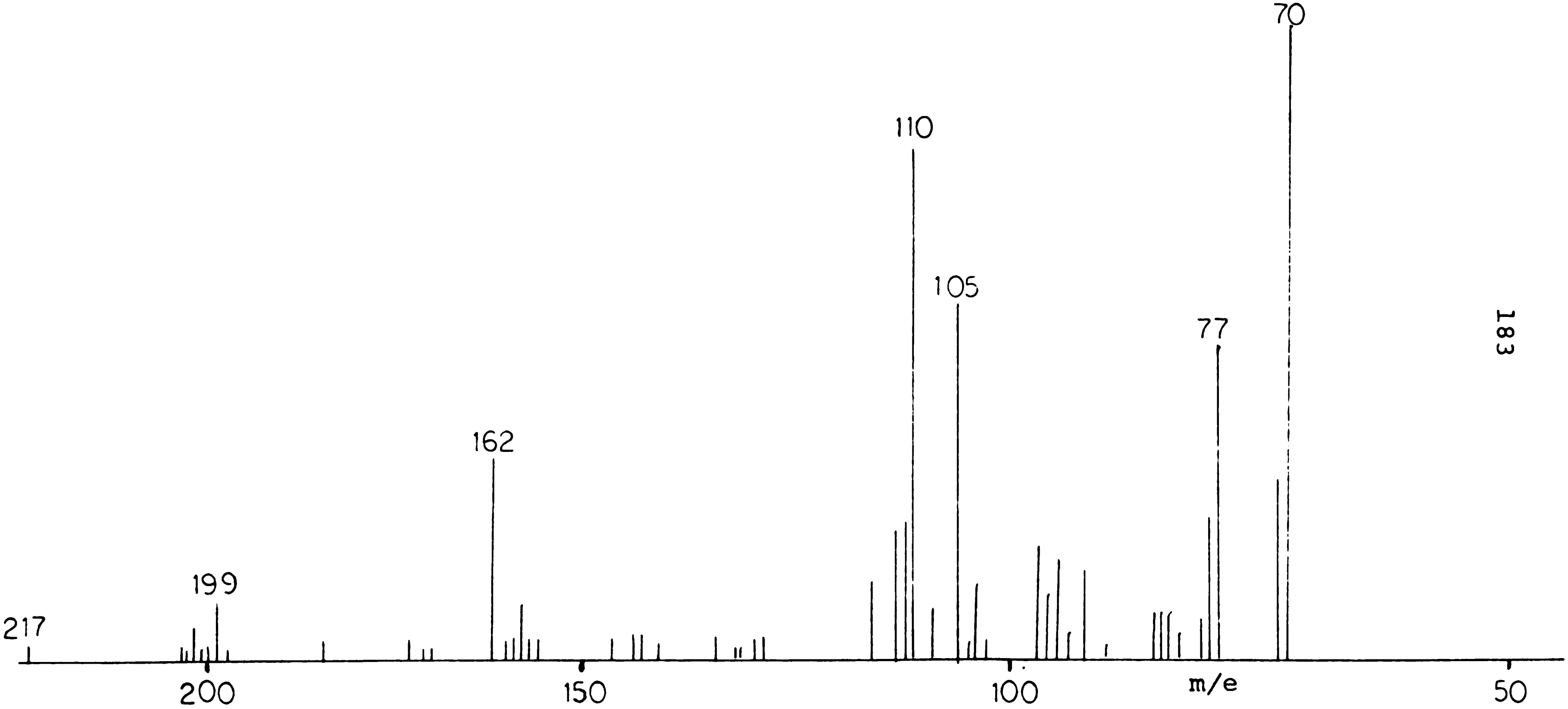
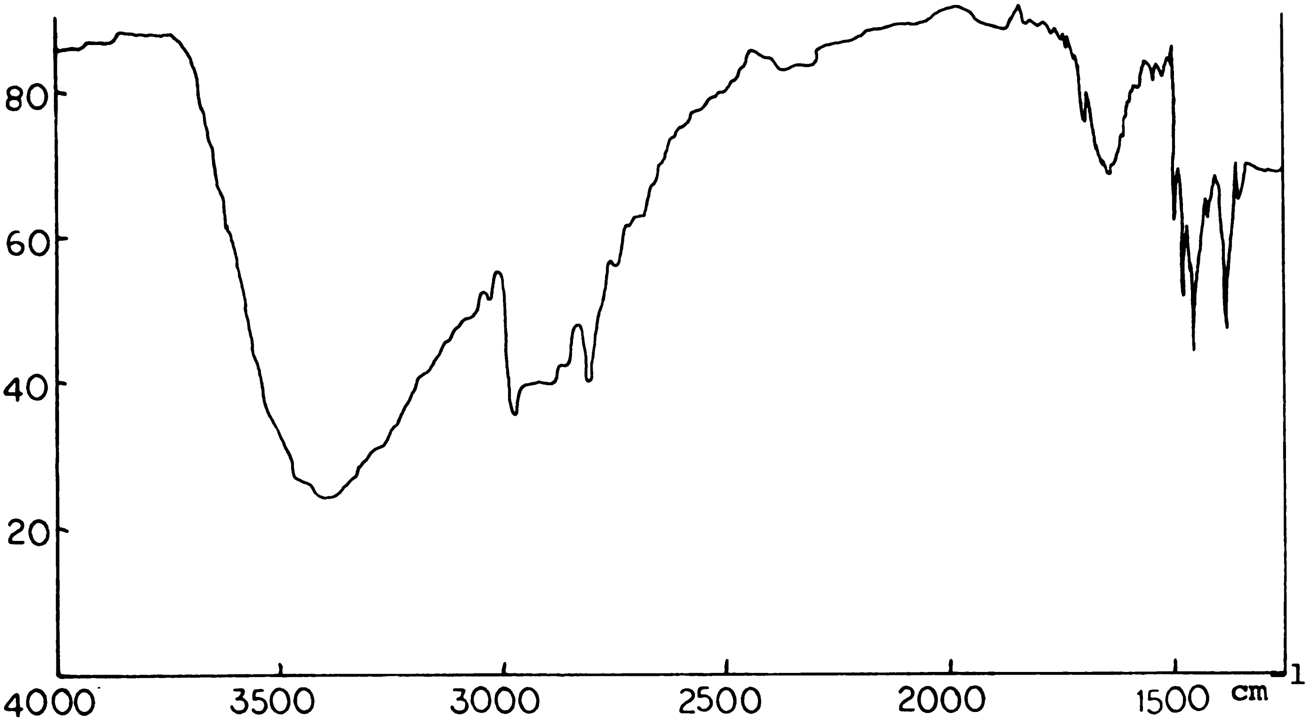


Figure XLIX: Mass Spectrum of 2-methyl-5-methyl-6-phenyl-2-azabicyclo [3.1.1] hepta-6-ol



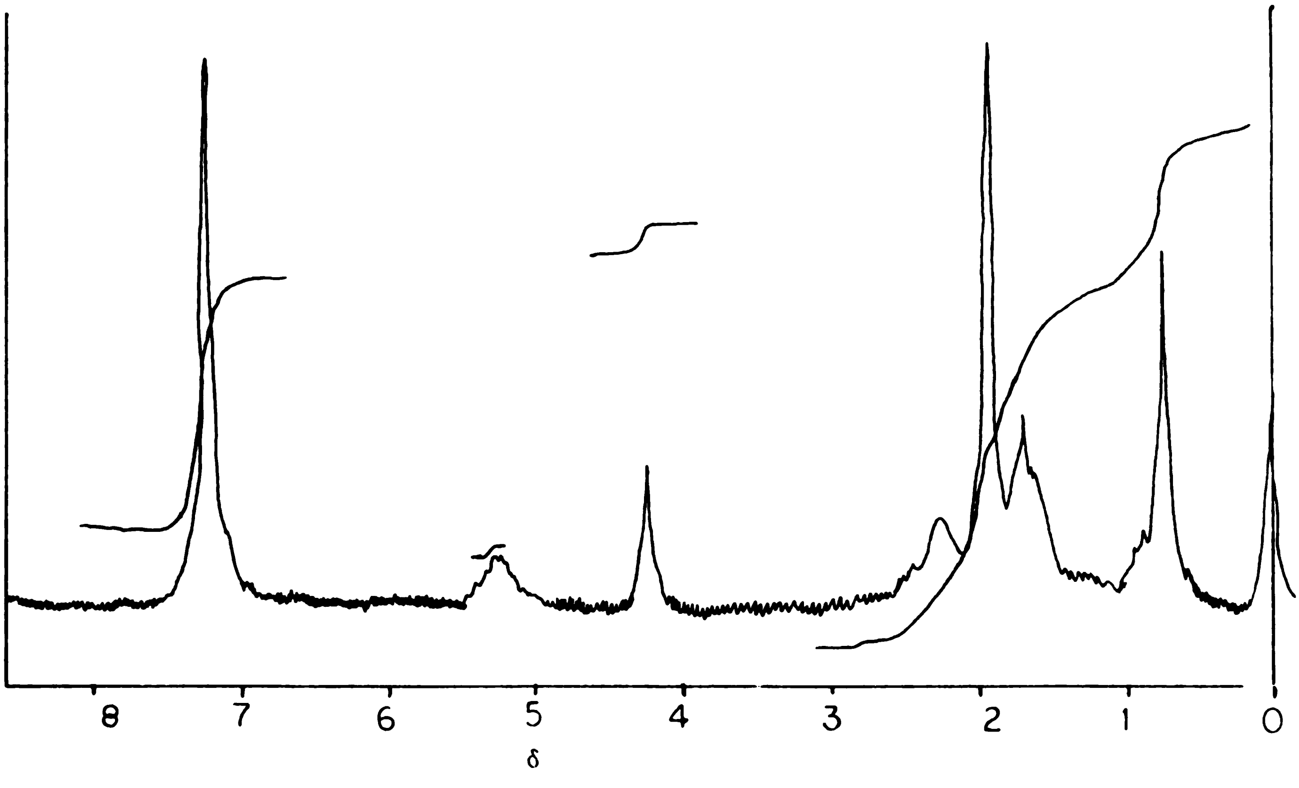


Figure L: IR Spectrum (top) and NMR Spectrum (bottom) of Phenyl-N-methyl-4-methylpiperidinemethanol

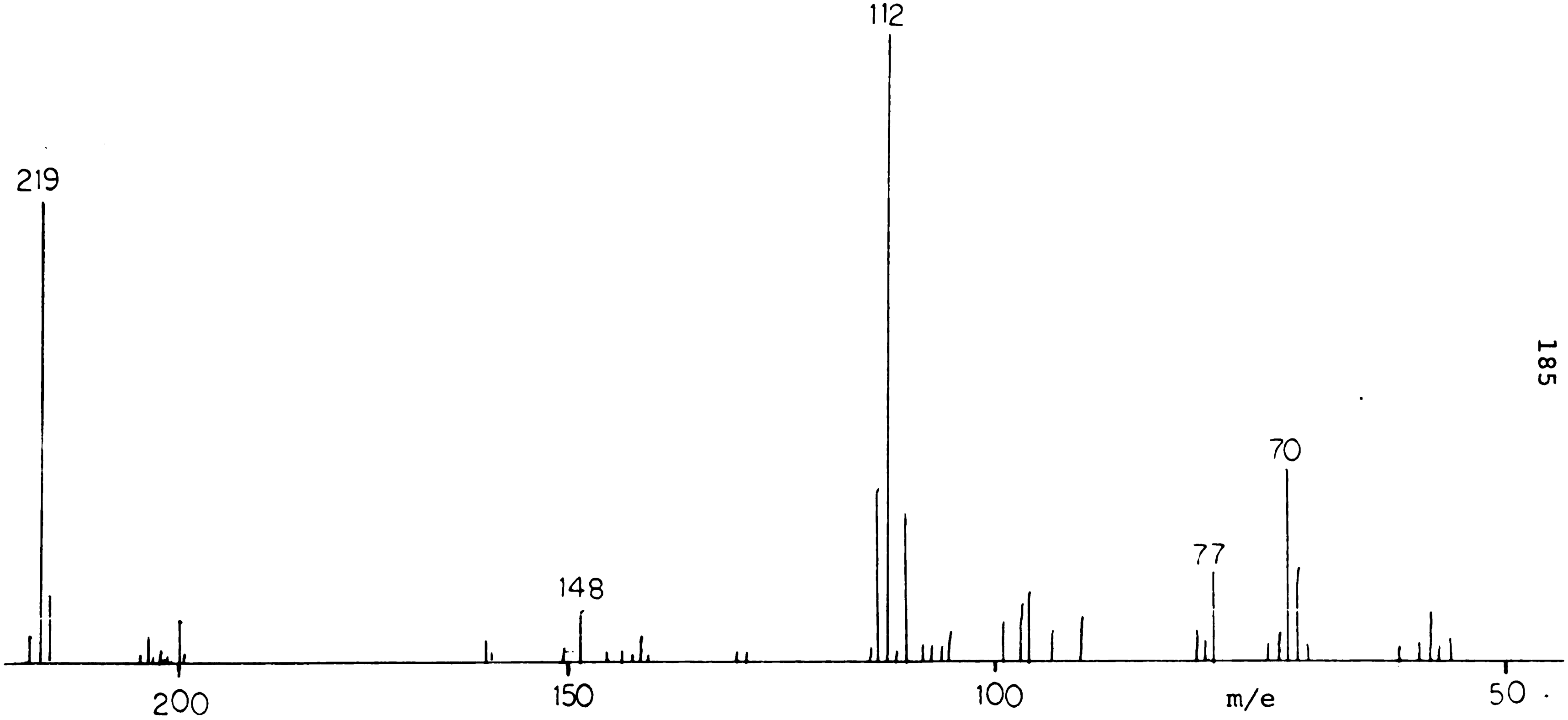


Figure LI: Mass Spectrum of Phenyl-N-methyl-4-methylpiperidinemethanol

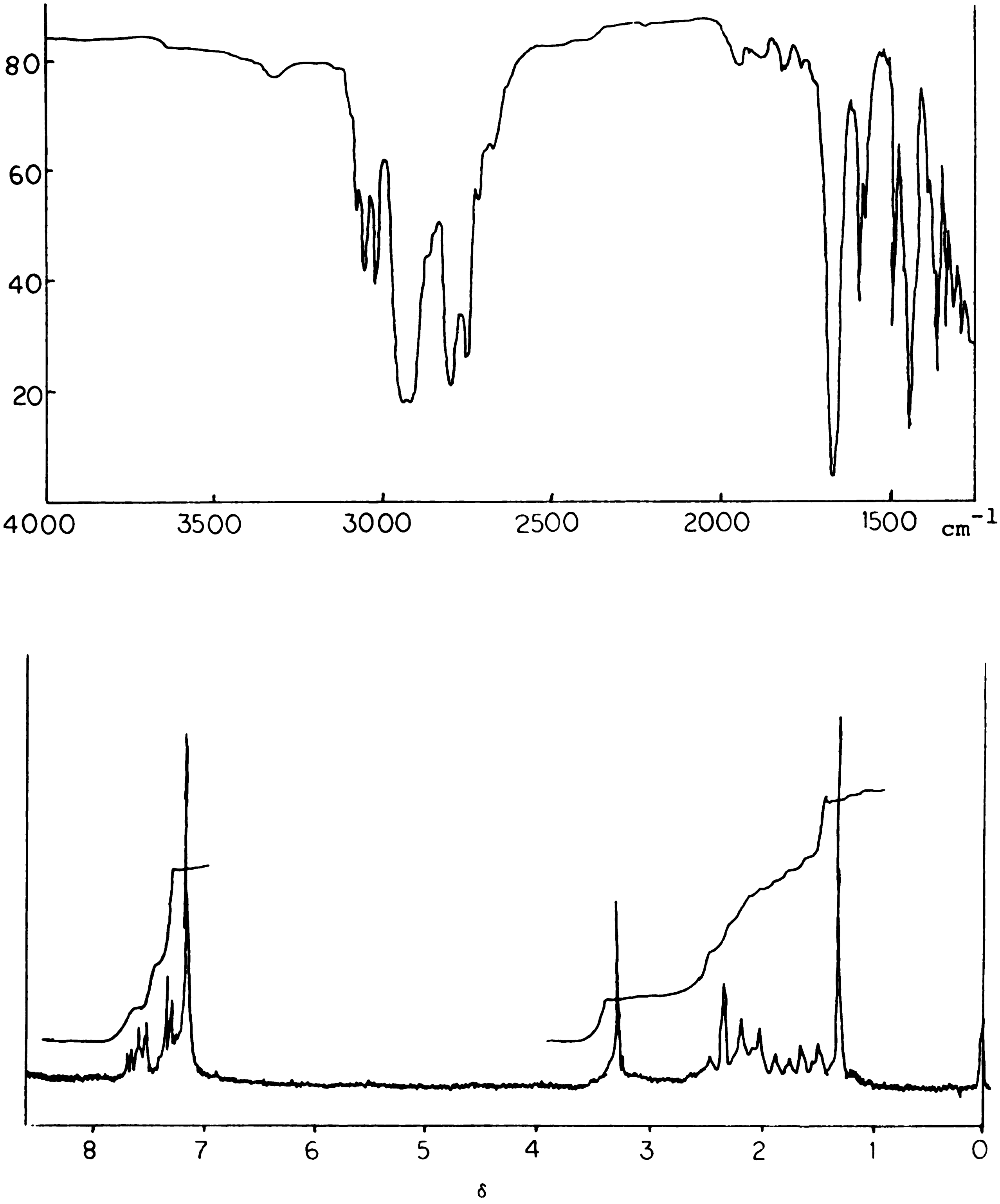


Figure LII: IR Spectrum (top) and NMR Spectrum (bottom) of N-benzyl-4-methyl-4-benzoylpiperidine

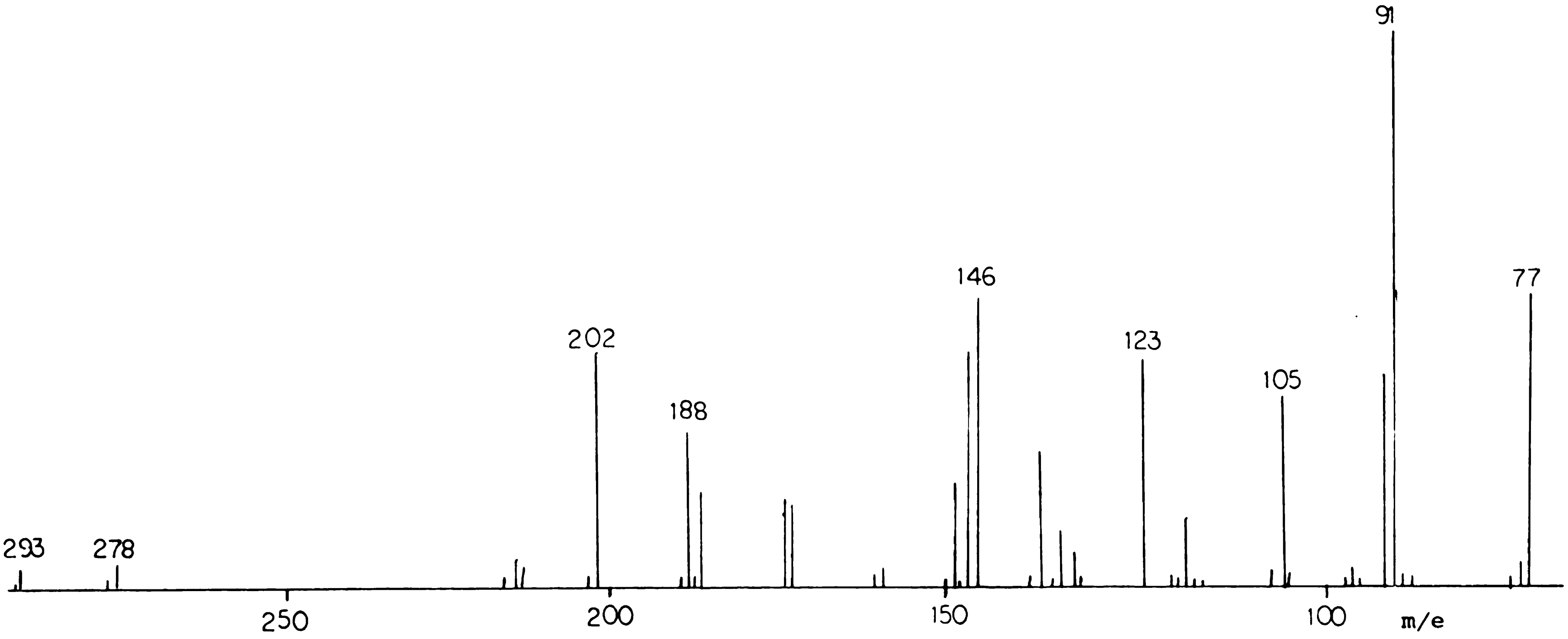


Figure LIII: Mass Spectrum of N-benzyl-4-methyl-4-benzoylpiperidine

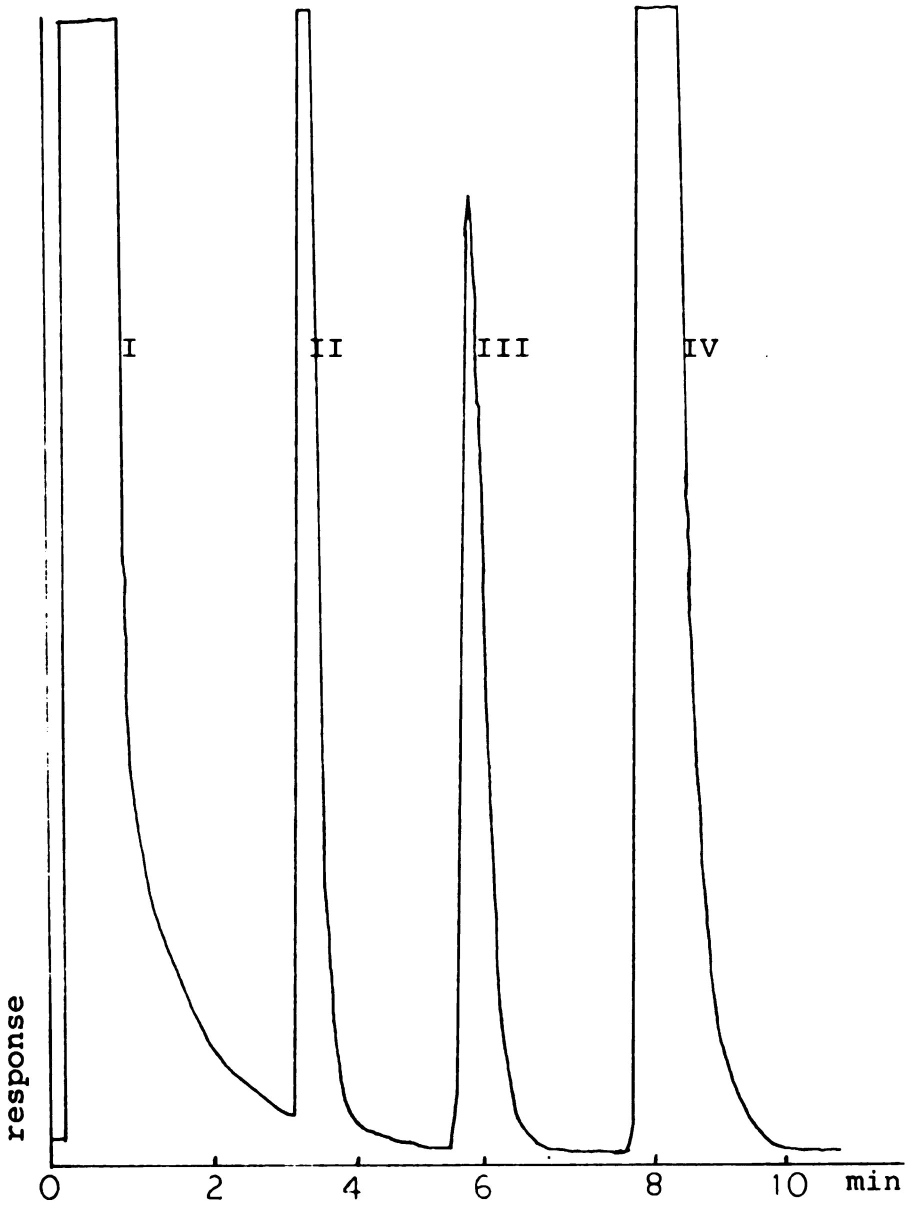


Figure LIV: VPC Trace for 1-methylcyclohexylphenyl Ketone (IV); Benzene (I), Octadecane (II), Type II Product (III)

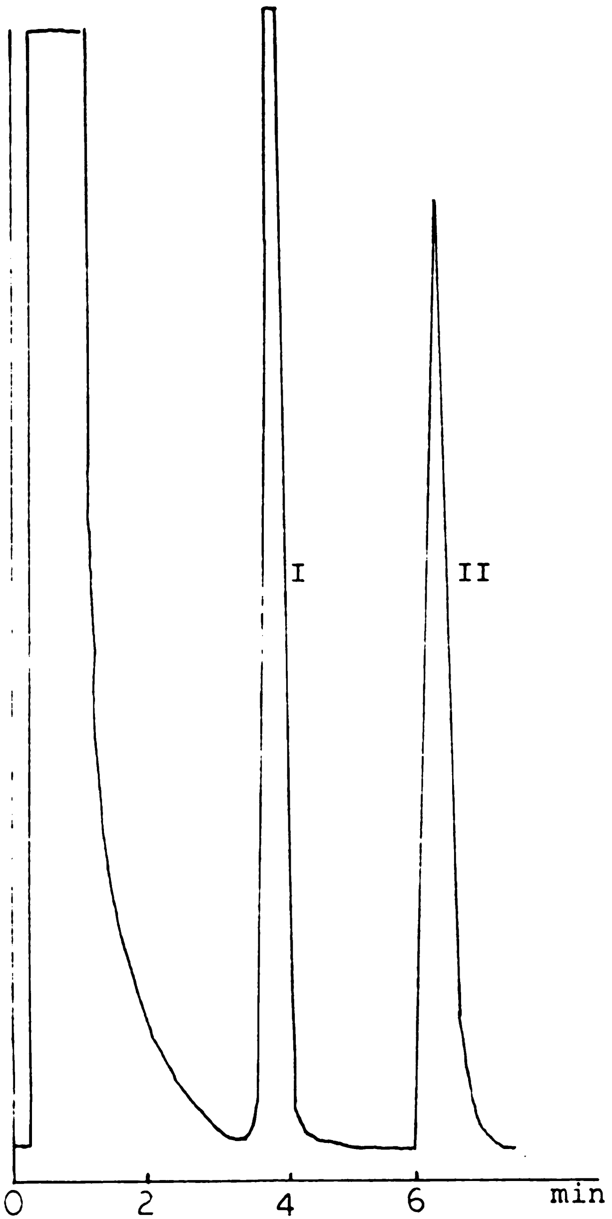


Figure LV: A Typical VPC Trace for Analysis of Acetophenone(II) Versus Tetradecane (I)

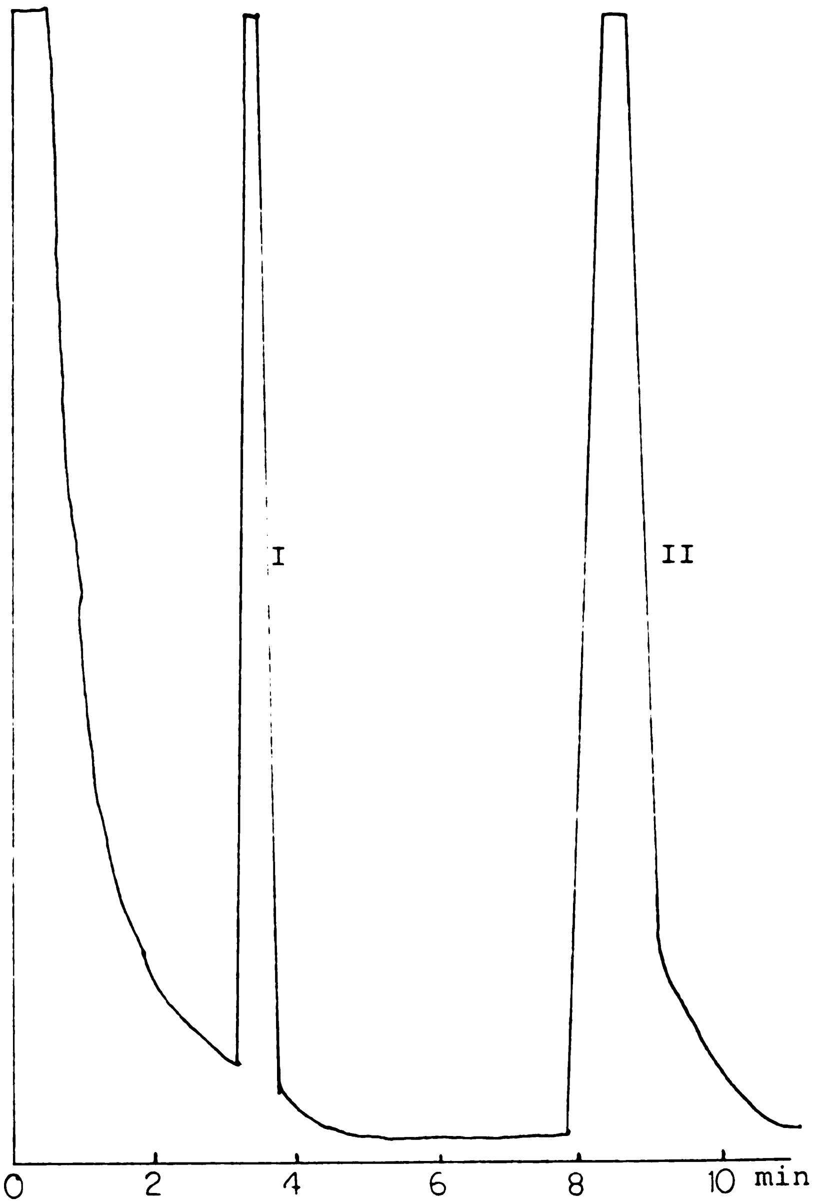


Figure LVI: A Typical VPC Trace for Analysis of Benzaldehyde (I) Versus Decylalcohol (II)

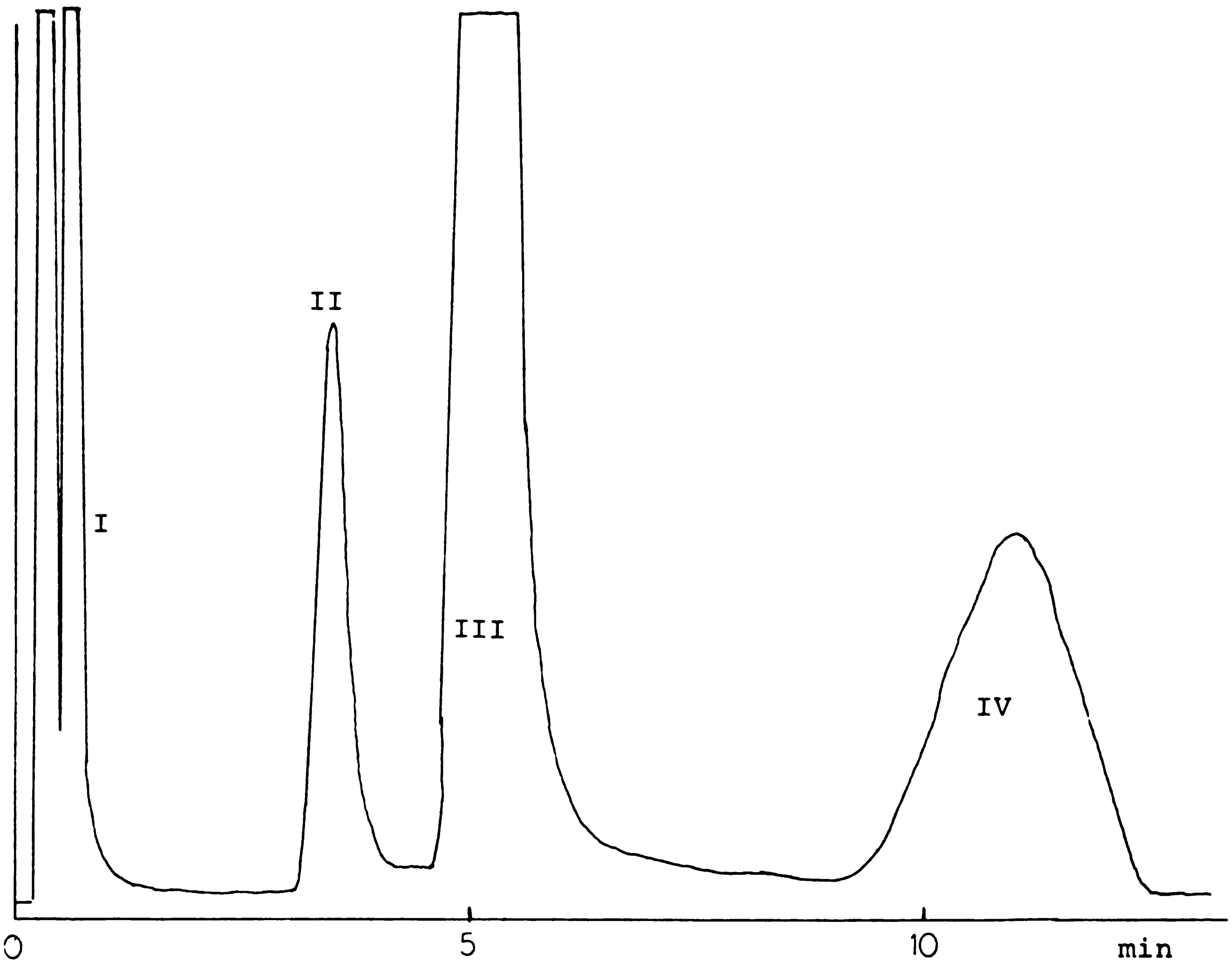


Figure LVII: VPC Trace of N-methyl-4-methyl-4-benzoylpiperidine(III); Naphthalene (I), Type II Product (II), Octadecane (IV)

Part III

Experimental Data

Photoreduction and Emission Studies:

The data of the following section are arranged according to quencher studied. The first number in the heading is the ketone concentration and all studies are in benzene unless otherwise noted. In the photoreduction studies the per-cent conversions are indicated and Abs_s-Abs is the absorbance of the standard solution(s) minus the absorbance of the specific solution. In the phosphorescence studies the conditions are given as follows: scale, high voltage setting, sensitivity setting. The wavelength of irradiation is the last number mentioned and the emission wavelengths were always at 450 and 480 nm.

The reproducibility of the photoreduction studies is about ±5%. Comparison of two or three solutions of the same composition were made and any solution which deviated by more than 4% from the others was discarded. Reproducibility in the phosphorescence is on the order of ±8%. Any deviation between two solutions greater than 5% caused those solutions to be repeated. Standard deviations for each quenching run are indicated after the calculated $k_t\tau$ value.

BENZOPHENONE, NAPHTHALENE QUENCHER

0.054 K in 0.5 M isopropanol

40% conversion

Quencher Conc (M)	Avg Abs	Abs_s -Abs	Φ_o/Φ
S	0.534	---	---
0.00	0.292	0.242	1.00
0.000109	0.364	0.170	1.42
0.000218	0.398	0.136	1.77
0.000328	0.434	0.100	2.42
0.000437	0.448	0.086	2.81

$k_t \tau$ =4300±296

0.054 K in 0.5 M isopropanol

59% conversion

Quencher Conc (M)	Avg Abs	Abs_s -Abs	Φ_o/Φ
S	0.581	---	---
0.00	0.264	0.317	1.00
0.000109	0.363	0.218	1.45
0.000218	0.417	0.164	1.93
0.000327	0.451	0.130	2.46
0.000436	0.474	0.107	2.95

$k_t \tau$ =4333±135

0.054 K in 0.5 M isopropanol

31% conversion

Quencher Conc (M)	Avg Abs	Abs_s -Abs	Φ_o/Φ
S	0.627	---	---
0.00	0.432	0.195	1.00
0.000118	0.499	0.127	1.53
0.000236	0.527	0.100	1.94
0.000355	0.544	0.082	2.37
0.000474	0.564	0.062	3.14

$k_t \tau$ =4212±291

0.054 K scale .1 HV 720 100

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	51	1.00
0.00000525	43	1.19
0.0000105	36.5	1.40
0.0000158	31	1.64
0.0000210	27	1.89
0.0000260	24	2.12

$k_t \tau$ =40,000±2326

0.02 K scale .3 HV 900 80

Phosphorescence Ex 366
in 1M C_6H_{12} Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	57	1.00
0.0000208	45.7	1.26
0.0000416	39.8	1.44
0.0000624	34	1.67
0.0000832	28	2.02

$k_t \tau$=11,518±861

BENZOPHENONE, BIPHENYL QUENCHER

0.054 K in 0.5 M isopropanol

31% conversion

Quencher Conc (M)	Avg Abs	Abs$_S$ -Abs	Φ_o/Φ
S	0.627	---	---
0.00	0.432	0.195	1.00
0.00925	0.473	0.154	1.26
0.0185	0.497	0.130	1.49
0.0278	0.519	0.108	1.81
0.0370	0.524	0.103	1.88

$k_t \tau=26.9\pm1.74$

0.054 K in 0.5 M isopropanol

27% conversion

Quencher Conc (M)	Avg Abs	Abs$_S$ -Abs	Φ_o/Φ
S	0.671	---	---
0.00	0.488	0.184	1.00
0.0101	0.533	0.138	1.33
0.0203	0.553	0.118	1.62
0.0304	0.568	0.103	1.78
0.0405	0.582	0.089	1.97

$k_t \tau =28.2\pm3.4$

0.02 K in 0.5 M isopropanol

59% conversion

Quencher Conc (M)	Avg Abs	Abs$_S$ -Abs	Φ_o/Φ
S	0.972	---	---
0.00	0.398	0.573	1.00
0.0101	0.598	0.373	1.54
0.0203	0.672	0.300	1.92
0.0304	0.718	0.254	2.44
0.0405	0.776	0.195	2.94

$k_t\tau =49\pm2.8$

0.02 K in 0.5 M isopropanol

42% conversion

Quencher Conc (M)	Avg Abs	Abs$_S$ -Abs	Φ_o/Φ
S	0.454	---	---
0.00	0.267	0.187	1.00
0.0101	0.327	0.127	1.51
0.0203	0.359	0.095	1.97
0.0303	0.378	0.076	2.46
0.0405	0.391	0.063	2.98

$k_t\tau =49\pm1.0$

0.0075 K in 0.5M isopropanol

30% conversion

Quencher Conc (M)	Avg Abs	Abs$_S$ -Abs	Φ_o/Φ
S	0.915	---	---
0.00	0.637	0.278	1.00
0.0101	0.749	0.166	1.68
0.0203	0.798	0.117	2.38
0.0304	0.821	0.094	2.94
0.0405	0.839	0.076	3.65

$k_t\tau =66.1\pm1.5$

0.054 K scale .1 HV 840 100

Phosphorescence Ex 375
in 0.5M isopropanol Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	61.2	1.00
0.0093	52	1.17
0.0185	45.2	1.40
0.0279	36	1.70
0.0372	31.2	1.98

$k_t\tau =22.8\pm2.8$

BENZOPHENONE, BIPHENYL QUENCHER (Continued)

0.054 K scale .3 HV 740 100

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	58.1	1.00
0.00926	28.8	2.06
0.0186	22.5	2.71
0.0278	16.7	3.86
0.0370	12.7	4.28

$k_t\tau$ =99.4±9.0

0.035 K scale .3 HV 720 85

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	67.3	1.00
0.00945	23.5	2.83
0.0184	17.3	3.86
0.0284	13	5.13
0.0378	9.4	7.12

$k_t\tau$=164±15

0.035 K scale .3 HV 720 85

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	65.9	1.00
0.005	39.5	1.67
0.010	29	2.27
0.015	20.5	3.20
0.020	18	3.66

$k_t\tau$ =135±5.9

0.021 K scale .3 HV 720 90

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	74.3	1.00
0.00103	64	1.16
0.00205	55.5	1.33
0.00308	47	1.58

$k_t\tau$ =168±13

0.025 K scale .3 HV 720 80

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	87	1.00
0.00503	36	2.42
0.0101	21	4.14
0.0151	17	5.12
0.0201	13	6.70

k_t τ=288±11.6

0.0075 K scale .3 HV 730 87

Phosphorescence Ex 375
EM 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	67.5	1.00
0.00016	54.8	1.22
0.00033	47.3	1.41
0.00050	39.6	1.69
0.00068	35.8	1.88

$k_t\tau$=1323±55

BENZOPHENONE, 4-CHLOROBIPHENYL QUENCHER

0.053 K in 0.5 M isopropanol

26% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.670	---	---
0.00	0.496	0.174	1.00
0.0101	0.607	0.063	2.77
0.0202	0.619	0.051	3.42
0.0303	0.640	0.030	5.82
0.0403	0.648	0.022	7.93

$k_t\tau$ =157 ±18

0.054 K in 0.5 M isopropanol

22% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.591	---	---
0.00	0.461	0.130	1.00
0.00504	0.528	0.0627	2.07
0.0101	0.542	0.0490	2.62
0.0152	0.557	0.0337	3.84
0.0202	0.561	0.0297	4.13

$k_t\tau$ =175±17

0.035 K in 0.5 M isopropanol

21% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.866	---	---
0.00	0.682	0.184	1.00
0.005	0.779	0.087	2.12
0.010	0.811	0.055	3.36
0.015	0.821	0.045	4.09
0.020	0.831	0.035	5.24

$k_t\tau$ =220±10

0.035 K in 0.5 M isopropanol

30% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.614	---	---
0.00	0.431	0.183	1.00
0.000512	0.444	0.170	1.08
0.00102	0.467	0.147	1.25
0.00154	0.483	0.131	1.40
0.00205	0.492	0.122	1.50

$k_t\tau$ =226±35

0.054 K in 0.5 M isopropanol

30% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.638	---	---
0.00	0.456	0.182	1.00
0.00504	0.544	0.094	1.94
0.0101	0.566	0.072	2.54
0.0152	0.581	0.057	3.22

$k_t\tau$ =165±22

0.054 K in 0.5 M isopropanol

29% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-\mathrm{Abs}_S$	Φ_o/Φ
S	0.491	---	---
0.00	0.350	0.141	1.00
0.0101	0.443	0.048	2.98
0.0202	0.453	0.038	3.78
0.0303	0.467	0.024	6.04
0.0403	0.474	0.017	8.60

$k_t\tau$ =172±20

BENZOPHENONE, 4-CHLOROBIPHENYL QUENCHER (Continued)

0.035 K in 0.5 M isopropanol

41% conversion

Quencher Conc (M)	Avg Abs	Abs_S -Abs§	Φ_o/Φ
S	0.454	---	---
0.00	0.251	0.203	1.00
0.0101	0.385	0.069	2.96
0.0202	0.421	0.033	6.66
0.0303	0.429	0.025	6.66
0.0404	0.435	0.019	11.83

$k_t\tau$ =240±39

0.02 K in 0.5 M isopropanol

40% conversion

Quencher Conc (M)	Avg Abs	Abs_S -Abs§	Φ_o/Φ
S	0.425	---	---
0.00	0.240	0.185	1.00
0.000512	0.272	0.153	1.21
0.00102	0.285	0.140	1.33
0.00154	0.302	0.123	1.51
0.00205	0.316	0.109	1.69

$k_t\tau$ =350±30

0.0075 K in 0.5 M isopropanol

29% conversion (20% conversion)

Quencher Conc (M)	Avg Abs	Abs_S -Abs§	Φ_o/Φ
S	0.977	---	---
0.00	0.722	0.255	1.00
S	1.00	---	---
0.00	0.830	0.197	1.00
0.000992	0.806	0.171	1.49
0.00198	0.845	0.132	1.94
0.00291	0.923	0.0767	2.59
0.00388	0.933	0.0670	2.94

$k_t\tau$ =504±21

BENZOPHENONE, 3-CHLOROBIPHENYL QUENCHER

0.054 K in 0.5 M isopropanol

37% conversion

Quencher Conc (M)	Avg Abs	Abs_S -Abs	Φ_o/Φ
S	0.599	---	---
0.00	0.378	0.221	1.00
0.00538	0.448	0.151	1.46
0.0107	0.485	0.114	1.94
0.0161	0.506	0.0928	2.38
0.0215	0.525	0.074	2.99

$k_t\tau$ =87±1.3

0.025 K in 0.5 M isopropanol

60% conversion

Quencher Conc (M)	Avg Abs	Abs_S -Abs	Φ_o/Φ
S	1.30	---	---
0.00	0.911	0.387	1.00
0.00112	0.971	0.327	1.17
0.00224	1.01	0.288	1.33
0.00336	1.04	0.253	1.50

$k_t\tau$=149±2

0.0083 K in 0.5 M isopropanol

30% conversion

Quencher Conc (M)	Avg Abs	Abs_S -Abs	Φ_o/Φ
S	0.786	---	---
0.00	0.552	0.234	1.00
0.0010	0.604	0.182	1.28
0.0020	0.625	0.161	1.46
0.0030	0.640	0.146	1.60
0.0040	0.656	0.130	1.80

$k_t\tau$ =228±28

BENZOPHENONE, 2-CHLOROBIPHENYL QUENCHER

0.054 K in 0.5 M isopropanol

24% conversion

Quencher Conc (M)	Avg Abs	Abs_S $-Abs$	Φ_o/Φ
S	0.601	---	---
0.00	0.457	0.144	1.00
0.10	0.471	0.130	1.11
0.20	0.485	0.116	1.25
0.30	0.506	0.095	1.36
0.40	0.515	0.086	1.42

$k_t\tau$ =1.15±0.08

0.054 K scale .3 HV 740 80

Phosphorescence' Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	63.4	1.00
0.05	39.5	1.63
0.10	29	2.18
0.15	23.3	2.71
0.20	17	3.71

$k_t\tau$ =12.3±0.7

0.035 K scale .3 HV 720 80

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	63.8	1.00
0.05	43.6	1.46
0.10	29.5	2.20
0.15	19.2	3.30
0.20	16.3	3.90

$k_t\tau$ =12.8±2.2

0.035 K scale .3 HV 720 90

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	75.5	1.00
0.05	48.5	1.56
0.10	31	2.50
0.15	23.5	3.20
0.20	18	4.19

$k_t\tau$ =14.2±1.5

0.021 K scale .3 HV 720 80

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	65.1	1.00
0.01	55.7	1.12
0.02	53.8	1.21
0.03	48.7	1.33
0.04	43.0	1.50

$k_t\tau$ =11.5±0.8

0.0075K scale.3 HV 710 72

Phosphorescence Ex 375
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	68.1	1.00
0.01	62	1.11
0.02	55.3	1.23
0.03	50.3	1.35
0.04	46.5	1.46

$k_t\tau$=11.4±0.2

BENZOPHENONE, 4-METHYLBIPHENYL QUENCHER

0.035 K scale .3 HV 800 85

Phosphorescence Ex 366
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	64.2	1.00
0.00109	38.2	1.70
0.00218	29	2.22
0.00326	24.6	2.59
0.00435	19	3.39

$k_t\tau$ =560±36

0.025 K scale .1 HV 740 80

Phosphorescence Ex 366
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	59.9	1.00
0.00052	44	1.35
0.00104	32.8	1.83
0.00208	20.7	2.50
0.00311	18.9	3.17

$k_t\tau$ =722±38

0.0017 K scale .1 HV 720 70

Phosphorescence Ex 366
Em 450, 480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	62.7	1.00
0.00046	42.8	1.46
0.00093	34.2	1.83
0.0018	26	2.42
0.0028	18.1	3.46

$k_t\tau$ =890±56

0.0087 K scale .3 HV 790 80

Phosphorescence Ex 366
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	79.8	1.00
0.000143	49.5	1.41
0.000286	43	1.85
0.000427	34	2.06
0.000572	26	2.70

$k_t\tau$ =2823±171

0.0086 K scale .1 HV 740 70

Phosphorescence Ex 366
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	65.8	1.00
0.00028	48.5	1.35
0.00057	29.2	2.76
0.00086	21.7	3.04

$k_t\tau$=2237±657

BENZOPHENONE, 2-METHYLBIPHENYL QUENCHER

0.052 K scale .3 HV 800 85

Phosphorescence Ex 366
Em 450,480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	50	1.00
0.00887	27.6	1.82
0.0177	18.7	2.64

$k_t\tau = 92.5 \pm 0.2$

0.0131 K scale .3 HV 780 80

Phosphorescence Ex 366
Em 450, 480

Quencher Conc (M)	Cor. Reading	Φ_o/Φ
0.00	66.1	1.00
0.00887	39	1.69
0.0177	24.3	2.74

$k_t\tau = 88 \pm 10$

Gas Chromatographic Studies:

The data are arranged according to the ketone studied. The first number given in the heading is the ketone concentration which is followed by the concentration of the standard used. Any number in parentheses indicates the concentration of the standard used for that particular solution (if different from the concentration of standard used for the rest of the run). The following abbreviations are used: Act for actinometer; C_6H_{12} for cyclohexane; pyr for pyridine; pipyl for piperylene; acph for acetophenone; Prod/Std for product to standard ratios; conc for concentration. All actinometers were valerophenone using the same concentration of valerophenone as ketone. Acetophenone-cis-piperylene was used as actinometer in the sensitization studies. Column conditions are listed in XVII.

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 actinometry. Errors in actinometry, either in the precision or accuracy, do not affect $k_t\tau$ since they cancel out in the ratio Φ_0/Φ. The $k_t\tau$ values obtained by quenching acetophenone or benzaldehyde are reproducible to within 5%.

δ-AZIDOVALEROPHENONE

0.1 K tetradecane 0.00405M 366

Column Conditions #1

Solvent System	Prod/Std Ratio	Φ_o/Φ
benzene	0.432	---
50% t-butanol	0.444	---
0.5 $\bar{M}$ pyr.	0.802	---
0.001 M Naph	0.457	---
0.01M Naph	0.346	1.63
Act	0.482	---
[Acph]	0.0035	

0.1 K tetradecane 0.00421 313

Column Conditions #1

Solvent System	Prod/Std Ratio	Φ_o/Φ
benzene	0.416	---
0.001 diene	0.416	---
0.002 diene	0.436	---
0.003 diene	0.368	1.16
Act	1.42	---
[Acph]	0.0035	

0.07 K tetradecane 0.0068M 366

Column Conditions #1

Solvent System	Prod/Std Ratio
benzene	0.401
C_6H_{12}	0.321
Act(0.00394)	0.695
[Acph]	0.0054

Column Conditions #1	Prod/Std ratios for irradiated times			
	8 hr	16 hr	24 hr	37.5 hr
0.1 K tetradecane 0.00457	0.211	0.352	0.479	---
366 Act	0.430	0.789	1.16	---
[Acph]	0.0019	0.0032	0.0044	---
0.07 K tetradecane 0.00197	1.22	1.90	2.69	---
366 Act	2.70	4.18	6.06	---
0.5M pyridine	1.88	---	---	---
[Acph]	0.0048	0.0075	0.0106	---
0.05 K tetradecane 0.00442	---	0.447	---	0.973
366 Act	---	1.08	---	2.16
[Acph]		0.00395		0.0086

Column Conditions #1	Prod/Std ratios for irradiated times		
	45 min	90 min	135 min
0.1 K tetradecane 0.00457	0.106	0.142	0.223
313 Act	0.120	0.280	0.442
[Acph]	0.0010	0.0013	0.0023
0.05 K tetradecane 0.00442	---	---	0.489
313 Act	---	---	1.09
[Acph]	---	---	0.0043

δ-AZIDOVALEROPHENONE (Continued)

0.07 K Piperylene sensitizee

Column Conditions #2

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
36.9	0.202	1.38
18.5	0.125	1.21
12.3	0.0930	1.15
9.55	0.0684	1.11
36.9 (Acph)	0.0814	---
19.1	0.149	1.25
9.23	0.0898	1.11
19.1 (Acph)	0.0538	---
19.1	0.0931	1.21
9.0	0.0548	1.09
19.1 (Acph)	0.0311	

$k_t\tau$= 101±5 intercept 1.01

0.07 K piperylene sensitizee

Column Conditions #2

Pipyl Conc.	Ratio trans	Φ_{isc}
0.101	0.072	0.98
Acph	0.073	

0.07 K 1-methylnaphthalene quencher
tetradecane 0.00405 366

Column Conditions #1

Quencher Conc.(M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.488	1.00
0.0043	0.348	1.40
0.0065	0.307	1.59
0.0089	0.255	1.91
0.011	0.225	2.19
Act	1.10	
[Acph]	0.004	

$k_t\tau$= 98.5±7.7

δ-THIOCYANATOVALEROPHENONE

0.07 K tetradecane 0.00197

Column Conditions #1 313

Solvent System	Prod/Std Ratio
benzene	0.209
Act	33.5
[Acph]	0.00082

BUTYROPHENONE

0.1 K tetradecane 0.00405

Butyl Azide Quencher 366

Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.821	1.00
0.0394	0.586	1.38
0.0591	0.518	1.59
0.0788	0.469	1.79
0.0985	0.428	1.92
[Acph]	0.007	

$k_t\tau=9.8\pm0.3$

0.07 K tetradecane 0.00429

2-(p-fluorophenyl)-Δ^1- pyrroline quencher

Column Conditions #1 313

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	1.59	1.00
0.00107	1.27	1.25
0.00214	1.03	1.54
0.00321	0.835	1.90
0.00428	0.694	2.25
[Acph]	0.014	

$k_t\tau=264\pm21.5$

ε-AZIDOHEXANOPHENONE

Column Conditions #1	Prod/Std Ratios for Irradiated Times		
	5 hr	10 hr	15 hr
0.1 K tetradecane 0.00410	0.409	0.745	1.05
366 Act	0.377	0.730	1.03
[Acph]	0.0034	0.0061	0.0086
0.07 K tetradecane 0.00375	0.384	0.787	1.10
366 Act(0.00505)	0.731	1.46	2.17
0.5 M pyr(0.00375)	0.780	---	---
0.01 M 1-methylnaphthalene(0.00418)	---	---	0.370
[Acph]	0.0029	0.0059	0.0082
0.05 K tetradecane 0.0041	0.260	0.518	0.696
366 Act	0.237	0.465	0.656
[Acph]	0.0021	0.0042	0.0057

0.07 K tetradecane 0.0041

1-methylnaphthalene quencher

Column Conditions #1 366

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.739	1.00
0.00174	0.639	1.16
0.00348	0.535	1.38
0.00522	0.510	1.45
0.00696	0.463	1.60
[Acph]	0.006	

$k_t\tau=93\pm7.9$

0.07 K hexadecane 0.0227

Column Conditions #3 366

Ketone/Std Ratio Before-After(hυ)		Cyclobutanol Prod/Std
2.62	2.30	0.62

Act = 1.03 (0.00410)

[K] reacted =0.021

γ-AZIDOBUTYROPHENONE

Column Conditions #1	Prod/Std Ratios for Irradiated Times			
	24 hr	56 hr	64 hr	72 hr
0.1 K tetradecane 0.00449	0.0113	0.0278	---	0.0345
366 Act(0.00457)	1.55	3.04	---	4.20
[Acph]	0.0001	0.00025	---	0.00031
0.07 K tetradecane 0.00197	0.0647	0.147	---	0.190
366 Act	6.07	29.82	31.87	33.50
0.5 M pyridine	---	---	0.358	---
[Acph]	0.00025	0.00058		0.00075
0.05 K tetradecane 0.00422	---	0.0255	---	0.0539
366 Act	---	1.81	---	4.09
[Acph]	---	0.00022		0.00046
0.03 K tetradecane 0.00396	---	0.0177	---	0.0237
366 Act	---	1.07	---	1.55
[Acph]		0.00014		0.00019

	4 hr	8 hr	16 hr
0.1 K tetradecane 0.00449	0.025	0.0696	0.116
313 Act(0.00457)	1.40	2.50	3.79
[Acph]	0.0002	0.00063	0.0010

0.1 K tetradecane 0.00422
313 Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio
0.00	0.095
Act	2.94
[Acph]	0.0008

0.1 K tetradecane 0.00422
366 Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio
0.00	0.0144
Act	1.64
0.5 M pyr	0.426
[Acph]	0.00012

0.07 K tetradecane 0.00422

313 Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio
0.00	0.0861
Act	2.88
[Acph]	0.00073

0.07 K tetradecane 0.00422

366 Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio
0.00	0.0121
Act	0.960
[Acph]	0.00010
0.00(0.00359)	0.036
C_6H_{12}(0.00505)	0.0195
Act (0.00375)	3.06
[Acph]	0.00026

γ-AZIDOBUTYROPHENONE (Continued)

0.07 K tetradecane 0.000506
1-methylnaphthalene quencher
acetophenone 366
Column Conditions #1

Quencher Conc(M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.405	1.00
0.0493	0.279	1.45
0.0986	0.210	1.93
0.148	0.138	2.93
0.197	0.117	3.46
[Acph]	0.00041	

$k_t\tau=11.0\pm1.7$

0.07 K Piperylene Sensitizee
Column Conditions #2 366

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
4.93	0.0354	1.60
6.58	0.0583	1.96
19.72	0.0826	2.72
4.93(Acph)	0.0559	---

$k_t\tau=17\pm1$ intercept=1.26

0.033 K tetradecane 0.00422
366 Column Conditions #1

Quencher Conc (M)	Prod/Std Ratio
0.00	0.0121
Act	0.960
[Acph]	0.0001

0.07 K octadecane 0.00555
1-methylnaphthalene quencher
2-phenylpyrrole 366
Column Conditions #4

Quencher Conc (M)	Prod/Std Ratio	$\Phi o/\Phi$
0.00	0.0846	1.00
0.0493	0.0553	1.52
0.0986	0.0347	2.43
0.148	0.0427	1.98
0.197	0.029	2.91
[Pyrrole]	0.0014	

$k_t\tau=10\pm2.3$

0.07 K Piperylene Sensitizee
Column Conditions #2 366

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
4.92	0.0567	1.73
6.56	0.0711	1.89
9.84	0.109	2.13
4.92 (Acph)	0.0951	---

$k_t\tau=13\pm1$ intercept=1.25

0.07 K piperylene Sensitizee
366 Column Conditions #2

Pipyl Conc (M)	Ratio Trans	Φ_{isc}
0.201	0.0291	0.72
Acph	0.0395	

γ-AZIDOBUTYROPHENONE (Continued)

0.1 K Octadecane 0.0079, Tetradecane 0.00449

Column Conditions #4 313

Compound	Prod/Std Ratios for Irradiated Times			
	0.00 hr	4 hr	8 hr	16 hr
cyclic imine	0.00	0.0992	0.142	0.162
Pyrrole	0.00	0.475	0.698	0.798(3:1)
Parent ketone	5.80	4.16	3.35	2.26
Act	0.00	1.414	2.78	4.09
[K] reacted	0.00	0.022	0.032	0.047

0.1 K Octadecane 0.0079, Tetradecane 0.00449

Column Conditions #4 366

Compound	Prod/Std Ratios for Irradiated Times			
	0.00 hr	30 hr	60 hr	90 hr
cyclic imine	0.00	0.0886	0.115	0.121
Pyrrole	0.00	0.276	0.326	0.568 (2.5:1)
Parent ketone	5.80	4.77	4.11	3.97
Act	0.00	1.58	3.09	4.28
[K] reacted	0.00	0.019	0.031	0.034

N-METHYL-4-METHYL-4-BENZOYLPIPERIDINE

0.04 K tetradecane 0.00507

313 dodecane 0.00876

Column Conditions #5

Mercaptan Conc (M)	Prod/Std Ratio
0.00	0.133
0.0154	1.26
Act	3.07
[Benzaldehyde]	0.002

0.04 K tetradecane 0.00507

313 nonadecane 0.00459

Column Conditions #6

Solvent System	Prod/Std Ratio
benzene	0.0966
0.5 M pyr	0.0285
Act	3.07
[Cyclobutanol]	0.00074

N-METHYL-4-METHYL-4-BENZOYLPIPERIDINE (Continued)

0.04 K tetradecane 0.00464

313 dodecane 0.00547

Column Conditions #5

Mercaptan Conc (M)	Prod/Std Ratio
0.0104	0.106
Act	0.428

[Benzaldehyde] 0.0012

0.04 K decyl alcohol 0.00423

1-methylnaphthalene quencher

Column Conditions #5 313

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.154	1.00
0.00199	0.105	1.47
0.00399	0.0830	1.86
0.00597	0.0745	2.07
0.00796	0.0698	2.26

[Benzaldehyde] 0.001

$k_t\tau$=250 initially; curves downward

0.04 K Piperylene Sensitizee

Column Conditions #2 313

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
5.03	0.0508	5.28
2.51	0.0315	4.74
1.25	0.0198	3.63
0.84	0.0138	2.72
0.63	0.0114	2.56
0.50	0.0094	2.21
5.03(Acph)	0.101	

Intercept tending to 1.00
Plot curves downward

0.04 K Octadecane 0.00449

Naphthalene quencher 313

Column Conditions #6

Quencher Conc (M)	Prod/Std Ratio Cyc.	Ketone
0.0008	0.261	2.34
0.008	0.481	2.98
0.08	0.703	3.57

[Cyclobutanol] 0.0029

0.04 K tetradecane 0.00331
313 decyl alcohol 0.00423
Column Conditions #5
Dodecyl mercaptan 0.0199
1-methylnaphthalene quencher

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.503	1.00
0.00199	0.343	1.47
0.00399	0.268	1.88
0.00597	0.192	2.62
0.00796	0.156	3.22
Act	1.125	---

[Benzaldehyde] 0.003

$k_t\tau$=251±24

0.04 K Piperylene Sensitizee

Column Conditions #2 313

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
5.03	0.214	2.97
2.40	0.120	2.95
2.00	0.0653	2.86
1.60	0.0477	2.67
1.20	0.0385	2.50
0.80	0.0325	2.38
0.40	0.0289	2.24
1.20(Acph)	0.127	
0.20	0.0192	1.79
0.158	0.0180	1.46
0.20(Acph)	0.317	

intercept tending to 1.00
$k_t\tau$=0.2

N-METHYL-4-METHYL-4-BENZOYLPIPERIDINE (Continued)

0.04 K Octadecane 0.00409

Tetramethylbutadiene quencher

Column Conditions #3 366

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.500	0.75	1.00
1.00	0.665	1.13
2.00	0.598	1.25
3.00	0.510	1.47
5.00	0.492	1.52
6.00	0.453	1.66
7.00	0.319	2.35

[Cyclobutanol] 0.0077

0.04 K octadecane 0.00402

Tetramethylbutadiene quencher

Column Conditions #3 366

Quencher Conc (M)	Prod/Std Ratio
0.00	0.196
0.0403	0.510
0.0806	0.582
0.161	0.630
0.242	0.634
0.322	0.649
0.403	0.653
0.405	0.646
0.810	0.662
1.22	0.634
1.62	0.629

[Cyclobutanol] 0.002

0.04 K Octadecane 0.00436

Naphthalene Quencher

Column Conditions #3 313

Quencher Conc (M)	Prod/Std Ratio
0.0312	0.0804
0.0624	0.112
0.0936	0.174
0.125	0.205
0.156	0.236

[Cyclobutanol] 0.0009

0.04 K Tetradecane 0.00477
313 Decyl alcohol 0.00430
Column Conditions #5
Dodecyl mercaptan 0.04 M

Quencher Conc (M)	Prod/Std Ratio
0.00	0.278
Act	0.437

[Benzaldehyde] 0.00209

0.04 K Tetradecane 0.00477
313 Octadecane 0.00397
Column Conditions #6
Dodecyl Mercaptan 0.04

Product	Prod/Std before hυ	Ratio after hυ
Cyclobunol	0.00	0.189
Ketone	6.78	5.56
Act		1.12

[K] reacted 0.00720

0.04 K Octadecane 0.00397

313 Type II product 0.00493

Column Conditions #6

Prod/Std before hυ	Ratio after hυ
0.339	0.288

8% conversion

N-METHYL-4-METHYL-4-BENZOYLPIPERIDINE (Continued)

0.04 K tetradecane 0.00464

313 Octadecane 0.00408

Column Conditions # 8

Solvent System	Prod/Std Ratio (cyc)	Prod/Std Ratio (DIS)
benzene	0.212	3.86
0.5 M pyridine	0.122	5.64
10% 1-PrOH	0.217	4.92
20% 1-PrOH	0.174	5.38
30% 1-PrOH	0.196	5.41
40% 1-PrOH	0.193	5.36
unirradiated	---	6.86
Act	4.19	---
[K] reacted	0.0206	

0.04 K tetradecane 0.00464

313 decyl alcohol 0.00414

Column Conditions # 7

Solvent System	Prod/Std Ratio
benzene	0.182
0.5 M pyridine	0.00
10% 1-PrOH	0.0933
20% 1-PrOH	0.0520
30% 1-PrOH	0.0411
40% 1-PrOH	0.0368
Act	4.19
[Benzaldehyde]	0.001

0.04 K Octadecane 0.00397
Piperylene quencher 313
(50:50 benzene:1-propanol)
Column Conditions # 3

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.516	0.500	1.00
1.04	0.409	1.22
2.08	0.328	1.52
3.13	0.458	1.09
4.01	0.428	1.17

$k_t\tau$ for first two points = 0.38

0.04 K piperylene sensitizee

Column Conditions # 2 313

$\frac{1}{\text{Pipyl}}$	Ratio trans	$\frac{.555}{\Phi}$
7.87	0.0714	3.80
3.92	0.0390	3.58
1.96	0.0217	3.26
1.96 (Acph)	0.0679	---

Intercept 3.18

N-BENZYL-4-METHYL-4-BENZOYLPIPERIDINE

0.04 K tetradecane 0.00331
313 decyl alcohol 0.00395
Column Conditions # 5
Dodecyl mercaptan 0.0199
1-methylnaphthalene quencher

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.686	1.00
0.000822	0.563	1.22
0.00164	0.475	1.44
0.00247	0.408	1.68
0.00329	0.362	1.90
Act	1.125	

[Benzaldehyde] 0.0034

$k_t\tau=271\pm5$

1-METHYLCYCLOHEXYLPHENYL KETONE

0.04 K Octadecane 0.0193
313 Column Conditions # 8

Solvent System	Prod/Std Ratio (cyc)	Prod/Std Ratio (K)
70% 1-PrOH	0.112	2.65
70% 1-PrOH 0.13 M NMP	0.128	2.65
0.5 M pyr	0.023	2.92
0.4 M pyr 0.1 M NMP	0.042	2.88
0.45 M pyr 0.05 M NMP	0.036	2.88

0.04 K tetradecane 0.00301
octadecane 0.00399
column conditions #8
neat isopropanol
N-methylpiperidine
quencher 313

Quencher Conc (M)	Prod/Std Ratio
0.00	0.740
0.094	0.643
1.87	0.676
2.80	0.698
Act	0.983

[Cyclobutanol] 0.0037

0.04 K tetradecane 0.00301
313 octadecane 0.00398
column conditions # 8

Solvent System	Prod/Std Ratio
0.5 M pyr	0.126
Act	0.983

1-METHYLCYCLOHEXYLPHENYL KETONE (Continued)

0.04 K tetradecane 0.00301
313 decyl alcohol 0.00402
column conditions #7
Dodecanethiol 0.0104
N-methylpiperidine quencher

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.927	1.00
0.156	0.553	1.68
0.312	0.308	3.01
0.468	0.184	5.04
0.625	0.118	7.86
Act	0.983	---

[Benzaldehyde] 0.0056

0.04 K tetradecane 0.00302
313 heptadecane 0.00434
column conditions # 8
Acetonitrile/1% H_2O
N-methylpiperidine quencher
diluted 2:5 for analysis

Quencher Conc (M)	Prod/Std Ratio	Φ_o/Φ
0.00	0.174	1.00
1.00	0.139	1.25
2.00	0.113	1.53
3.00	0.098	1.74
Act	0.987	---
0.00(noH_2o)	0.181	---
Act	1.09	---

[Cyclobutanol] 0.00083

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