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PHOTOREDUCTION OF PHENYL KETONES BY AROMATIC DONORS

By

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ABSTRACT

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Substituent effects on the photoreductions (k_r and ϕ_{Max}) of phenyl ketones by aromatic donors were examined for a series of benzophenones, acetophenones, and α,α,α-trifluoroacetophenones. Linear log k_r vs E^*_{red} plots were obtained for the photoreductions of substituted benzophenones (lowest n,π^* triplets; slope = -0.162/kcal) and substituted α,α,α-trifluoroacetophenones (lowest π,π^* triplets; slope = -0.209/kcal) using p-xylene in acetonitrile. A break in the plot for substituted acetophenones indicated that the acetophenone π,π^* triplets are less reactive.

The substituents p-Cl, p-CN, and p-Ac were found to decrease the k_r values of acetophenones but not of benzophenones. Apparently these substituents cause triplet state inversion so that the π,π^* state is lowest for the acetophenones.

A log k_r vs E^*_{red} plot for acetophenones with lowest

π,π^* triplets showed about a 10-fold decrease in reactivity compared to the extrapolated line which includes only acetophenones with lowest n,π^* triplets.

Replacing p-methyl by p-tert-butyl led to greater k_r values for valerophenone, benzophenone, acetophenone and α,α,α-trifluoroacetophenone, but the last two compounds showed reduced ϕ_{Max} values with bulky substitution.

Isotope effect studies involving toluene and toluene-d_8 were performed with several compounds: $k_r^H/k_r^D = 3.3$ for benzophenone (but the ϕ_{Max}^{BB} values were similar), and 2.4 for 4,4'-dimethylbenzophenone. In contrast, p-trifluoromethylbenzophenone showed an isotope effect of 3.4 on ϕ_{Max}^{BB} but the same k_r values, indicating that the photoreduction proceeds via an exciplex pathway, with a difficult proton-transfer step following the initial complexation. Finally, p-methoxy-α,α,α-trifluoroacetophenone showed almost no isotope effect on k_r and ϕ_{Max}^{BB}.

Primary/tertiary P/T product ratios from the photoreductions of phenyl ketones by p-cymene correlate with E_{red}^* and log k_r values. This indicates that the amount of CT varies in an exciplex according to the thermodynamic demand of the ketones. The correlations were much better for compounds possessing lowest π,π^* triplets.

Steric interactions were found to lower P/T ratios, especially for ketones with low E_{red}^* values.

To My Parents, Clifford and Cathy

and

My Wife, Debbie

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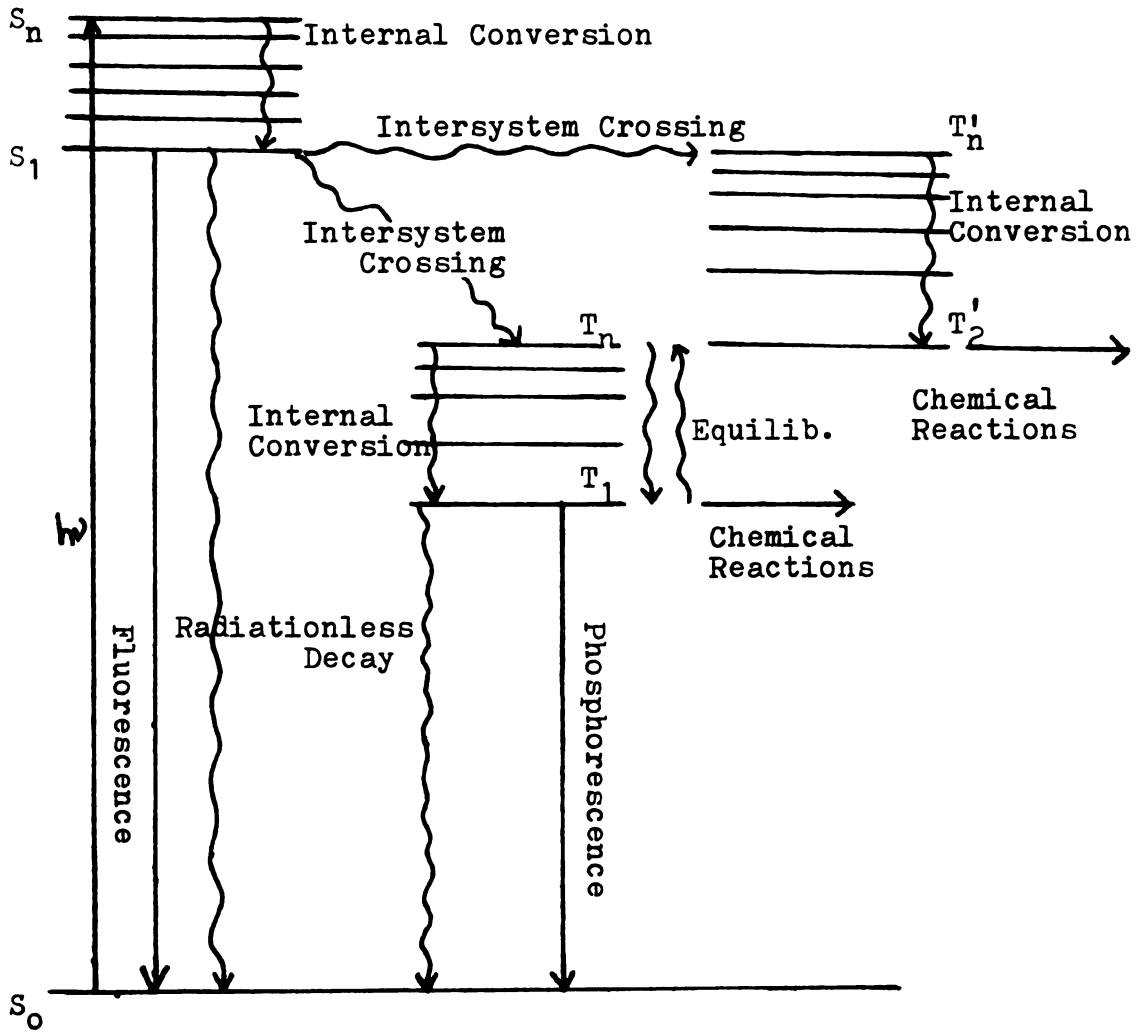
ACP	Acetophenone
BB	Bibenzyl
BP	Benzophenone
C_n	Normal hydrocarbon, n carbons
CP	Cyclopentane
DTE	1,2-di-p-Tolylethane
E_{red}	Reduction potential
E^*_{red}	Excited state reduction potential: $E^*_{red} = -E_T - E_{red}$.
E_T	Triplet energy at the 0,0 band, measured by phosphorescence emission
Hexadiene	2,5-diMethyl-2,4-hexadiene
k_{CT}	The rate constant for exciplex formation
k_H	The rate constant for direct hydrogen abstraction
k_r	The rate constant for quenching of an excited triplet ketone
I_a	Light absorbed by a ketone solution, in Eisteins/liter
KP	The ketyl-cyclopentyl cross-coupling product
Pentadiene	Trans-1,3-pentadiene

PhC_n, $PhCOOC_nH_{2n+1}$	Benzoate with a normal side chain of n carbon atoms
PP	1,2-bis-p-isoPropylphenylethane ("primary-primary")
P/T	Primary/tertiary product concentration
PT	1,1-diMethyl-1-p-methylphenyl-2-p-isopropylphenyl ethane ("primary-tertiary")
Q	Quencher
SF	Standardization Factor: corrects for g.c. response toward [product]/[standard]
TFA	α,α,α-Trifluoroacetophenone
TT	1,2-bis(p-Methylphenyl)-tetramethylethane
xyl,xylene	p-Xylene
VP	Valerophenone
ϕ_{Max}	Product quantum yield extrapolated to infinite donor concentration (inverse of the intercept from a double reciprocal plot)

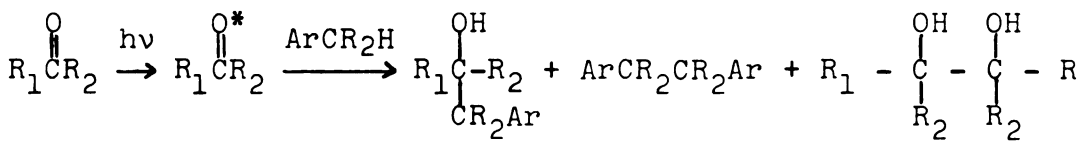
INTRODUCTION

Photochemistry, the study of chemical and physical properties of electronically excited compounds, is a relatively young science. Yet the application of this science allows Sir George Porter to forsee "a world where photosynthesis continues to supply mankind with energy needs, not only of food but also of fuel, where energy farming takes its place alongside food farming to provide, on a renewable basis, the essential requirements of modern life. The photosynthesis would include purely chemical non-living systems"[1].

The most active area of photochemical research has been the study of the carbonyl group. Upon absorption of light, this functional group can undergo a wide variety of photophysical and photochemical processes. A modified Jablonski diagram[2] shown in Scheme I gives a good intuitive understanding of the physical processes an electronically excited carbonyl can undergo. The research project described in this thesis deals with the chemical reactivity of the T_1 and T_2 excited states (Scheme I). The reaction of interest is the photoreduction of ketones by alkyl-aromatic substrates.



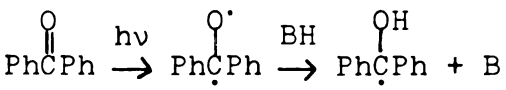
Scheme 1. Modified Jablonski Diagram Depicting the Physical Processes an Excited State Ketone can Undergo.



Historical Background

The first report on ketone photoreduction was in 1900 by Ciamician and Silber[3] who examined the sunlight-induced conversion of benzophenone in the presence of ethanol to benzpinacol.

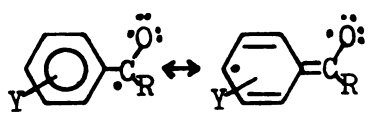
In the years since this early work, much progress has been made in the understanding of the various processes involved in carbonyl photochemistry. Bodenstein[4] suggested in 1931 that a carbonyl could absorb light, resulting in a biradical structure, allowing the oxygen to abstract a hydrogen atom from a suitable donor to give a pair of radicals. These radicals may couple, leading to stable products.



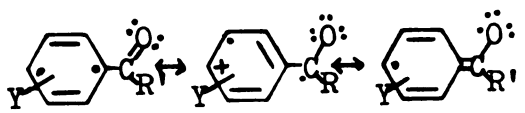
Another important step in the understanding of carbonyl photochemistry came when the excited states responsible for this hydrogen atom abstraction were characterized as singlets or triplets[5,6]. It was discovered that an excited singlet state could intersystem cross to a lower

triplet[2], or an excited state could be selectively populated by energy transfer from another compound already in a triplet excited state[6,7]. Phenyl-alkyl ketones intersystem cross to the triplet state with unit efficiency in almost all cases.[8]

Other investigators have shown the need to distinguish the excited triplet states into n,π* and π,π* states[9-15], depending on whether a non-bonding or a π electron is promoted to the π* level. The n,π* triplets have a carbonyl oxygen characterized as electron-deficient[16,17] and the locus of excitation[18,19]. The π,π* triplets have increased electron density about the oxygen, and the ring is viewed as 1,4-biradical-like[18]. Shown below are valence bond representations depicting the character of these two states[20].

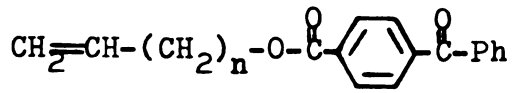


$^3n,\pi^*$



$^3\pi,\pi^*$

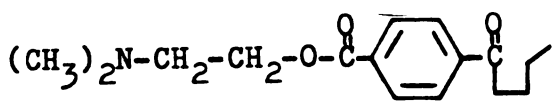
The locus of chemical reactivity for the two states depicted above has been determined by some recent studies. Winnick[19] examined a class of compounds of structure I, which have an n,π* lowest triplet state. Alkenes are known



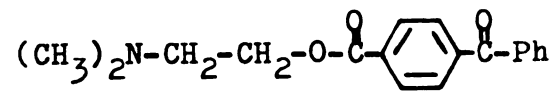
I

to quench excited state ketones[21-23], but Winnik showed that when n<8 no intramolecular quenching is observed, which indicates that the n,π* excitation is not found on the benzene ring.

In a more recent study[18], Wagner and Siebert followed up on this idea, using an amine function since it is a better quencher than the carbon-carbon double bond due to its lower oxidation potential. The study involved compounds II and III.



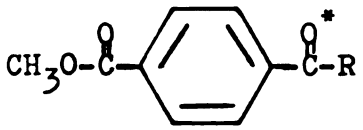
II $^3\pi,\pi^*$



III $^3n,\pi^*$

The amine nitrogen in compound II (lowest $^3\pi,\pi^*$) can reach the aromatic ring but not the ketone carbonyl: rapid quenching was observed. However, intramolecular quenching was very slow in the case of compound III (lowest $^3n,\pi^*$), for which the nitrogen also cannot reach the keto function. The authors point out that compounds IV and V are quenched by triethylamine with the same large rate constant

(k_q = 5 x 10^9 $M^{-1}s^{-1}$ in benzene), implying that both the triplet n,π* and π,π* states are equally quenchable if the lone pair is able to come into contact with the site of excitation.



IV: R=Ph (n,π* lowest triplet)

V: R = CH_2-CH_2-CH_2-CH_3 (π,π* lowest triplet)

The discussion so far has shown that there are definite differences between the triplet n,π* and π,π* states. Several factors can determine which of these triplet states is energetically lowest.

(a) The inductive effect of ring substituents affects the n,π* and π,π* states in a different manner[24-28]: electron-donating substituents selectively stabilize the π,π* state, whereas electron-withdrawing substituents stabilize the n,π* state.

(b) Conjugated ring-substituents stabilize the π,π* state[29]. For example, p-cyano, which inductively is electron-withdrawing, nevertheless stabilizes the π,π* triplet to a greater extent than the n,π* state[29].

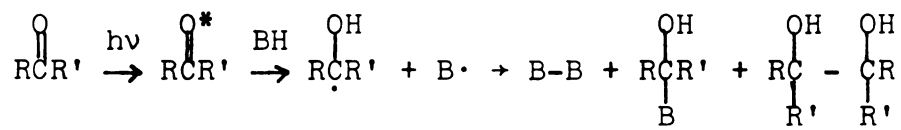
(c) Increasing the solvent polarity preferentially stabilizes the π,π* state[30,31] (especially hydrogen-bonding

solvents) due to its greater dipole moment.

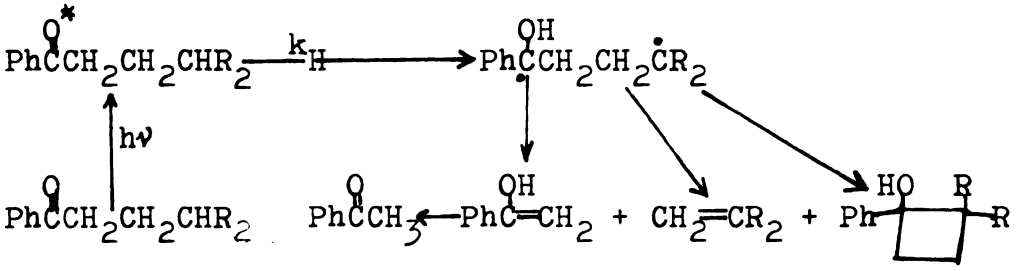
In many compounds, the $n,\pi^*-\pi,\pi^*$ energy spacing is so small that one has difficulty in describing the reactive state. Vibronic coupling can mix the character of the states[32], such that discrete entities may no longer exist.

Direct Hydrogen Atom Abstraction

As already mentioned[4], an excited state carbonyl can be photoreduced by a simple mechanism involving direct hydrogen abstraction from a substrate, leading to intermediate radicals which can then couple:



Excited-state ketones abstract a hydrogen atom from a wide variety of compounds: alcohols[33,34], hydrocarbons[33], amines[35-41], ethers[42-43], tributylstannane[44], sulfides[40, 45,46], mercaptans[47], and phenols[48]. In addition, intramolecular hydrogen atom abstraction has also been studied. In the Norrish Type II reaction[49,50], a hydrogen atom is abstracted from the γ position, leading to intermediate 1,4 biradicals which go on to products.



Direct Hydrogen Atom Abstraction by n,π* and π,π* Triplet States

The n,π* triplets of ketones undergo chemistry that resembles that of alkoxy radicals[10,51-54] and are known to be much more reactive in direct hydrogen atom abstractions than π,π* triplets[14,55-57,58].

The following table shows how various ring substituents determine which triplet state is lowest in benzene solvent and illustrates the lower reactivities of valerophenones possessing lowest π,π* triplet states.

The substituent inductive effect on k_H values is relatively small when the n,π* state remains lowest. However, electron-donating and para-conjugated substituents stabilize the π,π* triplets. The low reactivities of these compounds are believed to arise from thermally populated Boltzman concentrations of upper n,π* states[27,27,58], with little or no direct hydrogen abstraction from the π,π* triplets[58]: $k_H = x_n k_n$, where k_n is the actual rate constant for the reacting n,π* state, k_H is the observed rate

Substituted Valerophenone	$k_H(10^7)$, s^{-1}	Lowest Triplet
m-CF_3[a]	32	n,π*
p-CF_3[a]	28	n,π*
m-Cl[a]	16	n,π*
m-F[a]	18	n,π*
p-F[a]	15	n,π*
p-Cl[a]	3.0	π,π*
m-CN[b]	26	n,π*
p-CN[b]	6.8	π,π*
m-CO_2CH_3[b]	28	n,π*
p-CO_2CH_3[b]	12	π,π*
p-Ac[b]	1.4	π,π*
H[a]	12.5	n,π*
m-CH_3[a]	3.9	π,π*
p-CH_3[a]	1.8	π,π*
3,5-di-CH_3[c]	0.90	π,π*
3,4-di-CH_3[c]	0.34	π,π*
3,4,5-tri-CH_3[c]	0.034	π,π*
p-MeO[c]	0.05	π,π*
m-MeO[c]	0.02	π,π*

[a]Reference 27.

[b]Reference 29.

[c]Reference 28.

constant, and χ_n is the equilibrium fractional population of the n,π* state, which can be calculated from the expression below.[29]

$$\chi_n = (1 + e^{\Delta E/RT})^{-1} ,$$

where ΔE is the energy difference between the n,π* and π,π* triplets.

Alternatively, ΔE values can be calculated by rearranging the relationship shown below[28].

$$\frac{\chi_{n,\pi}}{\chi_{\pi,\pi}} = e^{-(\Delta E/RT)}$$

Several of the k_H values were measured in acetonitrile[29], and showed an average increase of about 50% over the values measured in benzene. This suggests that the more polar solvent cannot be stabilizing the less reactive π,π* state very much. On the other hand, k_H values are much lower in a hydrogen-bonding solvent than in benzene, as shown in the following table, indicating that the π,π* triplet is strongly stabilized in such solvents.

In addition to the direct hydrogen atom abstraction mechanism, the photoreduction of ketones may occur by another mechanism: an intermediate excited state complex, or "exciplex", may form between the ketone and a ground

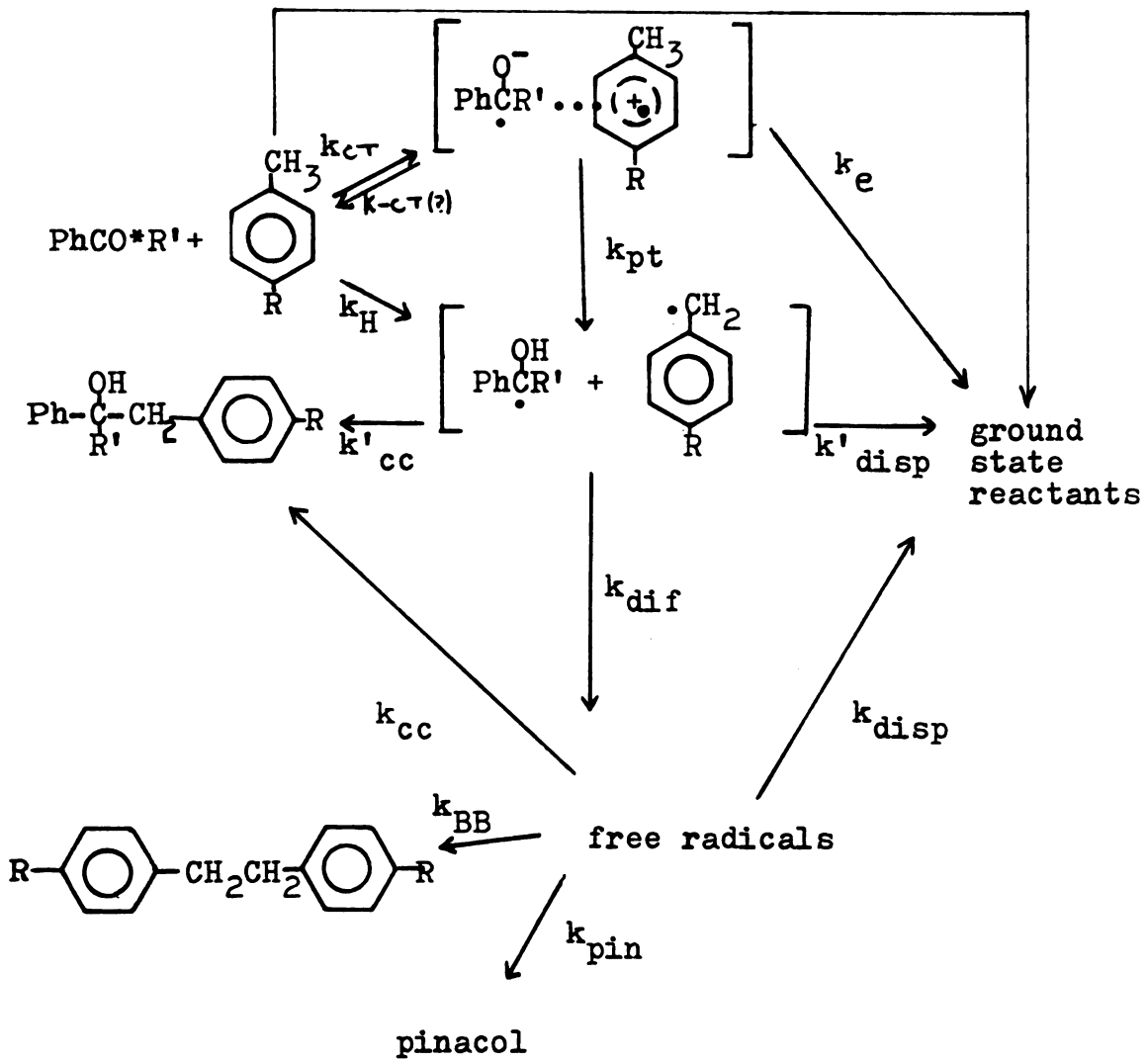
Substituted Valerophenone	Solvent	$k_H(10^6)$, s^{-1}[a]
H	benzene	125
H	methanol	75
p-CH_3	benzene	18
p-CH_3	methanol	3.7
p-OCH_3	benzene	0.56
p-OCH_3	methanol	0.06

[a]Reference 27.

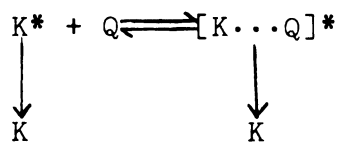
state molecule, followed by hydrogen transfer from within this complex[59-62]. The work reported in this thesis was directed at gaining a better understanding of this process.

Scheme 2 illustrates the two pathways by which a ketone can abstract hydrogen from a substrate. Since both mechanisms require that the same intermediate radicals form, then the same products must be formed and in the same relative concentrations[61,62].

There is direct evidence that exciplexes do form. The quenching of fluorescence and phosphorescence by other substrates is often accompanied by new, red-shifted emissions[63-69], indicating that a new excited state intermediate has formed.



Scheme 2. Photoreduction of Triplet Phenyl Ketone by an Alkyl Benzene.



Background Studies on Exciplexes

Weller[70-73] studied the quenching of singlet excited state aromatic hydrocarbons by amines.

$$^1A^* \; D \rightleftharpoons [A \cdots D]^* \longrightarrow A^- \cdots D^+$$

The excited state acceptor, A interacts with a ground state donor, D, which transfers an electron to the acceptor if the thermodynamic factors are favorable.

When the log k_r values (the rate constants for excited state quenching) were plotted against the calculated ΔG_{et} values (free energy of electron transfer), two limits were found: when $\Delta G_{et} < -5$ kcal/mole, $k_r = k_{diffusion}$; and when $\Delta G_{et} > 5$ kcal/mole, log k_r varied linearly with ΔG_{et}, with a slope equal to -1/RT which confirmed that an electron is completely transferred to the hydrocarbon. Weller's theoretical treatment of adiabatic electron transfer predicts that when the transfer is very endothermic ($\Delta G_{et} >$ 5 kcal/mole) then $\Delta G^{\neq}_{et}$ is proportional to ΔG_{et}. The following relationships hold:

$$\Delta G_{et} = E(D/D+)-E(A^-/A)-{}^1E_{0,0}(A^*)-e^2/\varepsilon a \qquad (1)$$

The minus sign before the reduction potential, $E(A^-/A)$, makes these values positive, since it is usual to report these values as negative with respect to the standard calomel electrode (SCE). $-E(A^-/A)$ values are positive, that is, an endothermic process.

$$\Delta G^{\neq}_{et} = \Delta G_{et} + C \qquad (2)$$

$$\log k_r = 2.303\Delta G_{et}/RT + C' \qquad (3)$$

where $E(D/D^+)$ represents the donor oxidation potential, $^1E_{0,0}(A^*)$ the excited singlet energy, and $e^2/\varepsilon a$ the Coulombic interaction between the ions formed.

Cohen[74,75] modified Equation (1) for excited state ketone quenching via a charge-transfer exciplex, using the more available ionization potentials instead of oxidation potentials, and using the lowest triplet energy of a ketone acceptor:

$$\Delta G_{CT} \doteq IP - E(A^-/A) - {}^3\Delta E_{0,0}(A^*) + C \qquad (4)$$

A $\log k_r$ against IP plot[74] for the quenching of benzophenone (BP) by a series of aliphatic quenchers gave a straight line with a slope = -0.067 mole/kcal. A second line correlated primarily aromatic quenchers, and a

slope = -0.105 mole/kcal was found. In this work, ΔG for exciplex formation was endothermic by >5 kcal/mole for almost all the compounds studied, yet the two slopes mentioned are far less than the value of -1/RT found by Weller for full electron-transfer reactions. Qualitatively, one can say confidently that some charge must be transferred in triplet ketone quenching[74] but it is not clear just what the slopes mean.

Wagner and Kechevar[76,77] used a wide variety of olefins to quench the type II photoelimination of butyrophenone. A log k_r vs. ionization potential plot gave a good correlation for those olefins expected to produce minimal steric hindrance to complexation. The authors concluded, in agreement with Caldwell[78], that alkene quenching of triplet ketones involves an intermediate charge-transfer complex.

In another study, Loutfy and Dogra[79] examined the luminescent decay of triplet butyrophenone, acetone, and benzophenone in the presence of electron-rich quenchers, and concluded that the amount of charge transferred in all the exciplexes represents about 10% of a full electron transfer. The authors argued that slopes from log k_r vs. IP or E^*_{red} ($-E_{0,0}-E_{red}$, the excited state reduction potential) are equal to b^2/RT, where b^2 is the fraction of an electron that is transferred. It was suggested that b^2 is constant for a single excited state being quenched by a series of

electron donors or electron acceptors. In the examples just discussed, the excited state ketone was the charge acceptor. Winnik examined the case in which the ketone is the donor. The triplet state of 4-carboxymethylbenzophenone was quenched by a series of electron-poor olefins in CCl_4. A linear dependence of log k_r on E^*_{red} values was found, where the acceptors are olefins. Deviation from linearity was observed when using fumaronitrile since the quenching interaction in this case is nearly diffusion-controlled.

In most of the studies reported, log k_r values were correlated with IP. Wagner and Lam[81] examined the photoreduction of ring-substituted α,α,α-trifluoroacetophenones by a single donor, toluene, and plotted log k_r against E^*_{red}. The low reduction potential of α,α,α-trifluoroacetophenone (TFA) facilitates exciplex formation. This was confirmed in an earlier study[61,62] in which TFA was photoreduced by toluene and toluene-d_3. The k_r values measured showed no deuterium isotope effect, indicating that this rate constant is not measuring C-H bond breaking. The authors also found that cumene was less reactive than toluene, which is inconsistent with a direct hydrogen atom abstraction mechanism.

The log k_r versus IP plot reported by Lam[81] would suggest that $\Delta G^{\neq}_{CT}$ equals 22% ΔG for full electron transfer, if the interpretation of the slope argued by Dogra[79] is accepted. The same authors[81] also reported that a log k_r

vs E^*_{red} plot for the photoreduction of substituted TFA by toluene gave a slope 42% that for full electron transfer. Arguing that thermodynamically it is impossible for the acceptor reduction potential to be twice as important as the donor oxidation potential, the discrepancy was suggested to involve differing reactivities of n,π* and π,π* triplets.

A priori, four classes of exciplexes can form (a) A molecule in an n,π* state may interact with a ground state n orbital[74,82-84], or (b) it may interact with a ground state π orbital[61,62,74,77,79,85,86]. (c) A molecule in a π,π* state may interact with a ground state n orbital[70-73,84,87], or (d) it may interact with a ground state orbital[61,88]. Thus, Lam[81] was suggesting differing reactivities for exciplexes involving equilibrating n,π* and π,π* triplets interacting with a π ground state orbital. A log k_r vs. E^*_{red} plot for these α,α,α-trifluoroacetophenones can be linear only if both triplets have the same intrinsic reactivities. The following equations[81] describe the observed rate constant for CT quenching of two proximate, equilibrating triplets, where χ_N is the equilibrium fractional population of the upper n,π* state and B is the ratio of the relative reactivities of the two states.

$$k_r = (1-\chi_N)k_\pi + k_N\chi_N \qquad (5)$$

$$k_r = k_\pi[1 + \chi_N(B-1)] \qquad (6)$$

$$B = k_N/k_\pi \qquad (7)$$

If $B > 1$, then from Equation (6) k_r increases with increasing χ_N at a fixed ΔG_{CT} value. However, B is not a constant value, as the upper n,π^* triplet is more energetic by ΔE and thermodynamically more reactive. An intrinsic reactivity difference between both triplets may exist under the same thermodynamic conditions. This thermodynamics-independent k_N/k_π ratio will be symbolized as R_N. Using the assumption that log k_r is proportional to the free energy of electron transfer[74] (Equation (8)), then B can be separated into two factors as shown in Equation (9). For lowest π,π^* triplets, $E \geq 0$.

$$\log k_r = \frac{\beta\Delta G}{RT} + C \qquad (8)$$

$$B = R_N e^{\beta\Delta E/RT} \qquad (9)$$

β represents the amount of charge-transfer involved in the intermediate exciplex, and has a maximum value of 1.0 (full electron-transfer).

$$\chi_N = \frac{e^{-\Delta E/RT}}{1 + e^{-\Delta E/RT}} \qquad (10)$$

Substituting Equation (9) and (10) into Equation (6) yields Equation (11)-(14), where the first two possess $\Delta E \geq 0$ (lowest π,π^* triplets).

$$k_r = k_\pi\left[\frac{1 + R_N e^{(\beta-1)\Delta E/RT}}{1 + e^{-\Delta E/RT}}\right] \qquad (11)$$

$$\log k_r = C + \frac{\beta}{RT}[E_{\pi,\pi} + E(A^-/A)] + \log\left[\frac{1+R_N e^{(\beta-1)\Delta E/RT}}{1+e^{-\Delta E/RT}}\right] \qquad (12)$$

$$k_r = k_\pi\left[\frac{R_N + e^{(1-\beta)\Delta E/RT}}{1 + e^{\Delta E/RT}}\right] \qquad (13)$$

$$\log k_r = C + \frac{\beta}{RT}[E_{n,\pi} + E(A^-/A) + \log\left[\frac{R_N + e^{(1-\beta)\Delta E/RT}}{1 + e^{\Delta E/RT}}\right] \qquad (14)$$

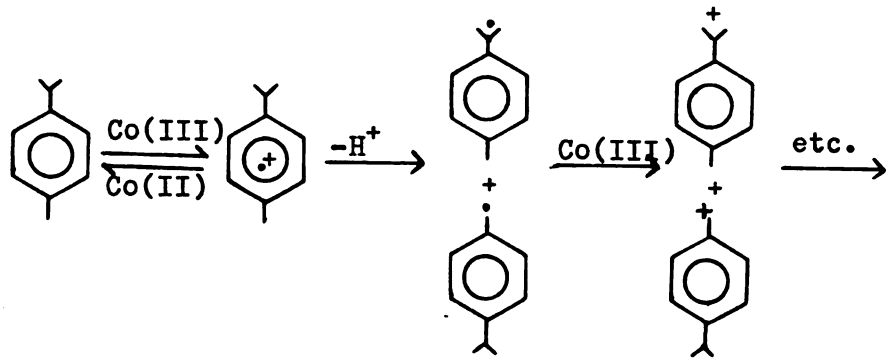
When ΔE is large and positive, the bracketed factors in Equation (11) and (13) approach 1 ($\beta < 1$); when ΔE is large and negative they approach R_N. If substituents can strongly affect the relative energy of both triplets, then from Equation (12) and (14) one predicts that a log k_r vs. E^*_{red} should contain 3 separate regions: ketones with

$|\Delta E| > 3$-4 kcal should determine two lines separated by an S-shaped curve. Lam's work[81] involved only compounds possessing lowest π,π^* triplets. It was not possible from these experiments to determine whether the predicted curvature was present or not. If $R_N = 10$ or less, the curvature would still be insignificant. This problem was reexamined in the current project, using substituted acetophenones which possess both n,π^* and π,π^* lowest triplets[11,56], as the question of differing inherent reactivities of n,π^* and π,π^* triplets is the central question examined in this effort.

In the experiments discussed[74,76,77,79,81] so far the authors have implied that for a single excited state log k_r vs. IP or E^*_{red} plots give slopes proportional to the amount of CT involved in forming the exciplexes. An alternative viewpoint has been developed: the amount of charge transferred will depend on the electronic demand.

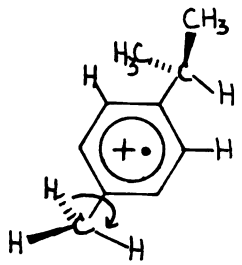
Evidence for Variable Amount of CT in an Exciplex

Schulz[89] has reported that the oxidation of p-cymene by cobalt(III) acetate led to products showing that the primary center was more reactive than the tertiary: the methyl hydrogens were selected 9:1 over the isopropyl one. The first step in this reaction is a full electron-transfer from p-cymene to Co(III), which is followed by proton transfer.



Similarly, a study involving the photoreduction of esters by p-cymene[90] also showed that the primary center was the most reactive. Such studies suggest that the tertiary center of p-cymene is more difficult to oxidize than its primary center. Schulz[91] has explained this as a stereoelectronic effect. In the radical cation, the preferred geometry of the isopropyl group has the tertiary hydrogen located in the nodal plane of the aromatic ring where its interaction with the π system is minimized. On the other hand, the methyl group rotates freely, allowing these protons to be preferentially abstracted.

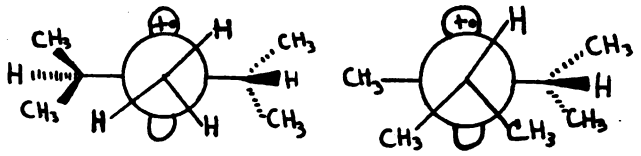
There are other examples of primary protons being selectively removed in preference to secondary or tertiary ones. Cohen[92] examined the photoreduction of benzophenone by tertiary amines and concluded by examining the oxidation products that primary and secondary proton transfer



was preferred over tertiary.

In similar work, Lewis[93,99] showed that the photooxidation of non-symmetrical tertiary amines, R_2NR', by the excited singlet state of trans-stilbene in acetonitrile can result in the formation of two stilbene-amine adducts via a sequential electron-transfer, proton-transfer mechanism leading to radical intermediates. Two different α-amino radicals may form, and the authors found that oxidation of the less substituted alkyl group was preferred. The effect was explained as a stereoelectronic effect on the deprotonation of an intermediate amine radical cation. Methyldiisopropyl amine showed a preference of primary hydrogen abstraction over tertiary greater than 2 0:1, corrected for the relative number of abstractable hydrogens. If deprotonation requires at least partial overlap of the half vacant nitrogen p orbital with the developing radical p orbital, the intermediate conformations

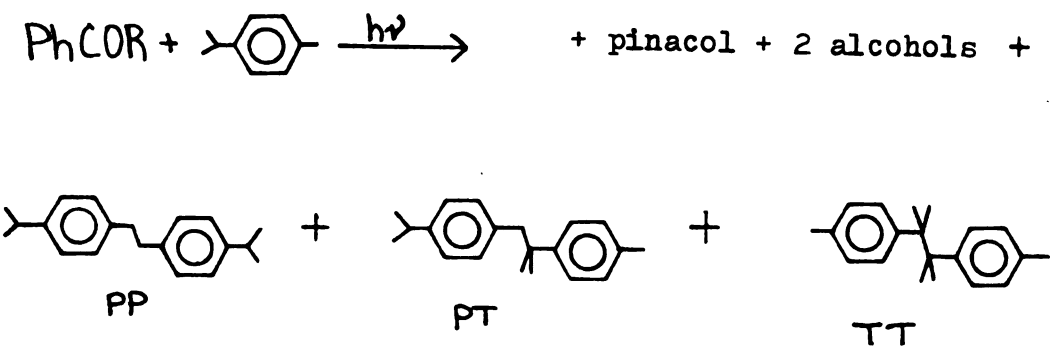
necessary for loss of primary and tertiary proton must be as shown below.



Loss of primary H^+ Loss of tertiary H^+

The steric interactions are clearly more severe for the conformation leading to loss of the tertiary proton.

Since the photoreduction of electron-deficient ketones by alkyl benzenes had already been shown to involve a CT exciplex intermediate[61,62,81], Wagner and Puchalski[95-97] decided to examine the photoreduction of such ketones by p-cymene to see if the selectivity varies. Several substituted acetophenones, α,α,α-trifluoroacetophenones and benzophenones were photoreduced in the presence of p-cymene and the relative amount of primary to tertiary benzylic radical formed was determined by examining the concentrations of the various photoproducts. They reported that electron-withdrawing substituents on the phenyl ring of the ketone increases the primary to tertiary (P/T) ratio obtained, whereas electron-releasing substituents decrease this ratio with respect to the unsubstituted ketone.

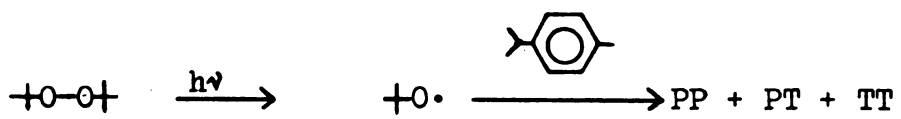


As was discussed earlier, abstraction of benzylic hydrogen can occur directly or following a prior complexation step (Scheme 2). The interpretation of P/T product ratios may be obscured if both pathways are occurring simultaneously for various ketones. If the E^*_{red} is favorable, then the CT exciplex mechanism should be dominant. Since TFA is photoreduced by toluene and by p-xylene almost entirely by this mechanism[61,81], the ring-substituted compounds probably also do not undergo very much direct hydrogen abstraction.

Puchalski[96] found that an electron-withdrawing substituent (p-CF_3) on TFA increases the P/T ratio, whereas electron-donating ring substituents such as p-CH_3 and p-OCH_3 decrease the ratio. The same trend was observed when examining acetophenones, though the magnitude of the P/T variation was not as great. The trend in P/T ratios parallel E^*_{red} values and was interpreted to mean that the amount of CT involved in the exciplexes varies, affecting the acidity of the primary proton. Since the P/T values

reported for TFA (3.5) and for m-CF_3-TFA (4.7) are both greater than 3, the value expected for statistically random hydrogen abstraction, then one cannot argue that increased ketone reactivity merely results in a lower selectivity.

The same authors[96] report that irradiation of di-tert-butyl peroxide in the presence of p-cymene in benzene produces bibenzyl products in concentrations that indicate a P/T ratio of 1:2.7, which may serve as a model for direct hydrogen abstraction behavior.



The effect of solvent polarity on P/T values was also reported[97].

Solvent	Φ^{PP}_{Max}	Φ^{PT}_{Max}	Φ^{TT}_{Max}	P/T
Benzene	0.031	0.015	0.0040	3.3
CH_3CN	0.045	0.015	0.0226	5.2

Apparently the more polar solvent facilitates CT, thus increasing the acidity of the primary proton.

The authors also found that the P/T values calculated by considering the concentration of all the photoproducts agree well with ratios calculated by using only the three

hydrocarbons, PP, PT, and TT.

To summarize, Puchalski's work provided strong evidence that the amount of CT involved in exciplexes between excited state ketones and alkylbenzenes varies according to the thermodynamic demand. To test the generality of this conclusion, many ketones were examined and photoreduced in the presence of p-cymene. The results of this study will be presented in this thesis. The wide variety of substituents allows one to examine the effect of several factors on P/T ratios: the electronic inductive effect; the effect of substituent size; and whether it matters which triplet state (n,π^* or π,π^*) reacts. In fact, the central goal of the current project was to compare and contrast the behavior of n,π^* and π,π^* triplet states. Of the four classes of exciplexes discussed previously, this thesis will be focusing on two: the interaction of n,π^* and π,π^* triplets with a π ground state orbital. It is already known that these triplets behave differently towards a ground state n orbital. Cohen and Guttenplan[84] examined the quenching of triplet fluorenone (lowest π,π^* triplet) by a series of amines and a sulfide. The authors reported that all the compounds examined could be correlated by a single linear plot of log k_r versus IP. The slope (-0.135 mole/kcal) is greater than was found for the quenching of triplet benzophenone[74] (lowest n,π^*), slope = -0.067 mole/kcal, and the authors suggested that the triplet fluorenone,

with a lowest π,π^* triplet, has a greater sensitivity toward the donor ionization potential than does benzophenone with a triplet n,π^* excited state. In another study[98] Cohen et al. reported rate constants for the photoreduction of triplet acylnaphthalenes (lowest π,π^* triplets) by triethylamine. Wagner and Lam[84] pointed out that the k_r values in benzene are about an order of magnitude lower than predicted by extrapolation of the rate constants for those ketones[84] having lowest n,π^* lowest triplets.

Research Goals

The primary goal was to discover if there is an inherent reactivity difference between n,π^* and π,π^* triplet states in charge-transfer quenching. The major objectives in answering this question were:

I. To measure rate constants, k_r, for triplet state quenching, using compounds with low-lying n,π^* or π,π^* states or proximate levels.

II. To examine Lam's[81] suggestion that a log k_r vs. E^*_{red} plot may show an S shaped curve.

III. To determine the relative contribution of direct hydrogen atom abstraction and of exciplex formation in the initial quenching interaction.

IV. To discover whether bulky ring substituents hinder exciplex formation or the subsequent

proton-transfer step for ketones with n,π* or π,π* lowest triplet states.

V. To examine the efficiency of the proton transfer step following exciplex formation.

VI. To re-examine Puchalski's work with p-cymene[95,96], to see if it is indeed possible to correlate P/T product ratios with excited-state reduction potentials (E^*_{red}), and whether the nature of the excited state (n,π* vs π,π*) affects this ratio.

To answer these questions, rate constants and ϕ_{Max} values were measured for the photoreduction of a series of phenyl ketones by some alkylbenzenes and hydrocarbons. A series of substituted benzophenones were prepared to examine the behavior of a pure n,π* state[56,99-103], α,α,α-trifluoroacetophenones for lowest π,π* triplets[84], and acetophenones which can possess either triplet as its lowest excited state[55,100]. Toluene and p-xylene were used as donors to measure rate constants for exciplex formation (k_{ex}), and cyclopentane was used in an attempt to measure rate constants for direct hydrogen atom abstraction (k_H). Isotope effects were studied using toluene and toluene-d_8 to gain some insight into the proton-transfer step (Scheme 2) following exciplex formation. P/T product ratios were measured using p-cymene, and the P/T ratios obtained were compared with primary/tertiary product ratios

measured using 2,3-dimethylbutane as a model for direct hydrogen atom abstraction behavior.

The k_r and ϕ_{Max} values were measured as outlined in the following section.

Kinetics

To obtain k_r values, the rate constants for triplet state quenching, quantum yields and lifetimes were measured as outlined below.

The quantum yield, ϕ[104], is defined as:

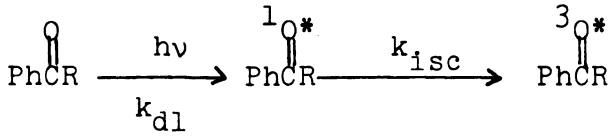
$$\phi = \frac{\text{number of molecules of product}}{\text{number of photons of light absorbed}} \qquad (15)$$

The numerator is determined by analyzing product concentration, using gas or liquid chromatography and a reference compound of known concentration. The denominator is obtained using an actinometer which yields product with a known quantum efficiency.

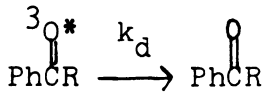
The mechanisms for triplet phenyl ketone photoreduction were shown in Scheme 2. The key concept shown in this scheme is that two competing pathways may exist: (a) direct hydrogen atom abstraction, (k_H), or (b) exciplex formation (k_{CT}) followed by "proton" transfer (k_{pt}), also leading to radicals. If the rate of both these last steps in the second mechanism are much faster than direct

hydrogen atom abstraction, then it must represent the dominant pathway. A priori, one cannot state whether the initial complexation step or the proton transfer step will be slower.

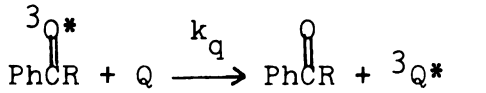
The steps in the photoreduction are as follows[97]:



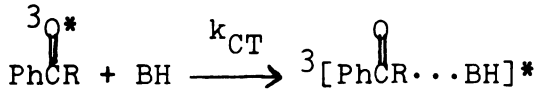
(16)



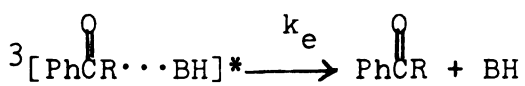
(17)



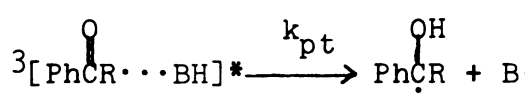
(18)



(19)



(20)



(21)

$$^3PhC(=O^*)R + BH \xrightarrow{k_H} PhC(OH)\dot{}R + B\cdot \qquad (22)$$

$$PhC(OH)\dot{}R + B\cdot \xrightarrow{\alpha'} \text{Products} \qquad (23)$$

$$PhC(OH)\dot{}R + B\cdot \xrightarrow{1-\alpha'} PhC(=O)R + BH \qquad (24)$$

In general, the triplet ketone interacts with donor to form either an exciplex intermediate or radicals directly.

$$^3PhC(=O)R + BH \xrightarrow{k_r} [\text{Intermediates}] \qquad (25)$$

$$k_r = k_H + k_{CT} \qquad (26)$$

$$[\text{Intermediates}] \xrightarrow{\alpha} \text{Products} \qquad (27)$$

$$\alpha = (\alpha') \left(\frac{k_{pt}}{k_{pt}+k_e}\right) \qquad (28)$$

$$[\text{Intermediates}] \xrightarrow{1-\alpha} K + BH \qquad (29)$$

The intermediates may be an exciplex or a pair of radicals from hydrogen abstraction.

The efficiency of product formation can be expressed as the mathematical product of the efficiency of each step:

(1) Efficiency of triplet state formation from an excited singlet state,

$$\phi_{isc} = \frac{k_{isc}}{k_{isc} + k_{dl}} \tag{30}$$

where k_{dl} includes all decay pathways from the ketone singlet excited state;

(2) Efficiency of intermediate formation from the triplet state (radicals in the case of direct abstraction, exciplex otherwise)

$$\phi_{int} = \frac{k_r[BH]}{k_r[BH] + k_q[Q] + k_d} \tag{31}$$

where BH represents the donor molecule, k_q quenching by added quencher Q, and k_d decay of the triplet state;

(3) Efficiency with which the intermediates give products = α. (32)

With an added quencher, the product of these three terms leads to:

$$\phi_{Product} = \frac{\phi_{isc} \cdot \alpha \cdot k_r[BH]}{(k_r[BH] + k_q[Q] + k_d)} \qquad (33)$$

In the absence of quencher, one obtains:

$$\phi^{\circ}_{Product} = \frac{\phi_{isc} \cdot \alpha \cdot k_r[BH]}{k_r[BH] + k_d} \qquad (34)$$

Dividing (34) by (33) gives the Stern-Volmer[105] equation:

$$\frac{\phi^{\circ}}{\phi} = \frac{k_r[BH] + k_d + k_q[Q]}{k_r[BH] + k_d} = 1 + k_q[q]\tau \ , \qquad (35)$$

where τ, the lifetime = $(k_r[BH] + k_d)^{-1}$.

From Equation (35), one sees that a plot of $\frac{\phi^{\circ}}{\phi}$ vs. [Q] gives a slope of $k_q\tau$. Values of k_q have been reported for a large number of triplet quenchers in various solvents[85,106,107]. With both k_q and $k_q\tau$ known, the triplet lifetime is easily calculated.

Inverting Equation (34) leads to,

$$\phi^{o-1} = (\phi_{isc}\alpha)^{-1} \left(1 + \frac{k_d}{k_r[BH]}\right) , \qquad (36)$$

From Equation (36), it is apparent that plotting ϕ^{o-1} against $[BH]^{-1}$ gives an intercept value of $(\phi_{isc}\alpha)^{-1} = \phi_{Max}^{-1}$ and that slope/intercept = k_d/k_r. Thus, a Stern-Volmer experiment and a double reciprocal plot allow one to calculate k_d and k_r values. In addition, since ϕ_{isc} for phenyl ketones = 1[8,61,62,81], then from the intercept of the double reciprocal plot one can measure α.

The k_r and k_d values can be obtained by monitoring the concentrations of only one photoproduct. As discussed earlier, photoreductions carried out in the presence of toluene or p-xylene lead to three major products: a bibenzyl, a cross-coupling product and diastereomeric pinacols[62]. The bibenzyl concentrations were monitored to obtain k_r and ϕ_{Max} values. The significance of ϕ_{Max} (=α) values will be discussed in the next section.

ϕ_{Max} Values

When studying the photoreduction of α,α,α-trifluoroacetophenones by toluene, Lam[81] found very small ϕ_{Max} values for bibenzyl (BB) formation. Statistical coupling of the intermediate radicals (Scheme 2) predicts a 1:2:1 ratio of BB:cross product:pinacol, such that half the benzyl radicals

formed lead to bibenzyl. Leavitt[62] has shown that bibenzyl/cross product concentration ratios near 0.5 form when ACP and TFA are photoreduced by toluene and p-xylene, which was re-examined and confirmed (this work). The ϕ_{Max}^{BB} values found by Lam[81] (ca. 0.05) are far less than the value of 0.25 predicted by statistical coupling (assuming $\phi_{isc} = 1$). The source of this inefficiency was investigated by Puchalski[97], who examined the amount of ketyl-benzylic radical disproportionation (Scheme 2). Though the inefficiency of the overall reaction due to this process was found to be sizeable, it was concluded to be insufficient to account for such low ϕ_{Max} values, and that an intermediate preceding the formation of ketyl and benzylic radicals must be responsible, as was shown in Equation (28):

$$\alpha = (\alpha') \left(\frac{k_{pt}}{k_{pt} + k_e}\right)$$

The proton transfer step, k_{pt}, must be slower than back CT in the exciplex (k_e). Wagner and Puchalski[97] have suggested that the low quantum yields observed in ketone-toluene photoreductions are due to decay from an exciplex, and may be used as evidence for the presence of such an intermediate complex.

In the studies performed and reported in this thesis, it must be remembered that the ϕ_{Max} values refer to only

the bibenzyl product, and the largest values possible are ca. 0.25.

Self-Quenching

In order to measure k_r and ϕ_{Max} values, Stern-Volmer and double reciprocal plots are needed, as discussed. The quantum yields needed for these experiments may vary as a function of the ketone concentration[108-112]. That is, a ground state ketone deactivates an excited state ketone. This process is usually referred to as self-quenching[108]. If k_{sq} is competitive with other processes of interest involving that excited state, then one should work with dilute ketone concentrations.

$$PhC(=O^{*})R + PhC(=O)R \longrightarrow 2\ PhC(=O)R$$

The rate constant for self-quenching of acetophenone (ACP) in CH_3CN has been reported[110]: $k_{sq} = 1.9 \times 10^7\ M^{-1}\ s^{-1}$. The table below shows the k_{sq} values for substituted benzophenones[108].

Quantum yields of product formation and lifetimes as a function of ketone concentration were measured and will be reported in this thesis. Dilute ketone solutions were used ($\sim$0.05 M) in the kinetic experiments, especially for the acetophenones (ca. 0.02 M).

Substituent	k_{sq} (10^5) $M^{-1}s^{-1}$[a]	k_{sq} (10^5) $M^{-1}s^{-1}$[b]
4,4'-di-NMe_2	2,800	---
4,4'-di-OMe	220	170
4,4'-di-Me	18	10
4,4'-di-F	3.9	---
4,4'-di-Cl	3.4	---
H	4.7	2.6
4,4'-di-CF_3	---	120
4,4'-di-CN	---	430

[a] In CCl_4. [b] In benzene.

Steric Hindrance in Forming Exciplexes

In the studies that will be presented in this thesis, steric interactions hindering exciplex formation were avoided as much as possible to facilitate the interpretation of the electronic factors of interest. This is an area still poorly understood at this time.

Wagner and Leavitt[62] reported that the quenching interaction (k_r) of toluene with triplet TFA is about twice as large as that found using cumene. In addition, triplet TFA is quenched much more rapidly by p-xylene than by p-ditert-butylbenzene. The bulky substituents are clearly

hindering exciplex formation.

As mentioned before, Wagner and Kochevar[76] found a linear correlation between log k_r and ionization potential for the quenching of triplet butyrophenone by a series of olefins. However, several points which lie significantly below the log k_r vs. IP line contain at least one large alkyl group. This effect was interpreted as steric hindrance to complexation with the ketone acceptor.

It is also possible that steric interaction may influence processes occurring after an exciplex forms. To illustrate, Hammond et al.[113] used the cis and trans isomers of 4,4-dimethyl-2-pentene; 3,3-dimethyl-3-hexene; and 3,4-dimethyl-2-pentene to quench triplet acetophenone (ACP), which has a lowest n,π* triplet.

$CH_3CH_2CH{=}CHC(CH_3)_3$ $(CH_3)_3CH{=}CHCH_3$

2,2-dimethyl-3-hexene (1) 4,4-dimethyl-2-pentene (2)

$(CH_3)_2CHC(CH_3){=}CHCH_3$

3,4-dimethyl-2-pentene (3)

The authors found that these sterically hindered quenchers gave very low oxetane[102] and isomerization quantum yields, but high quenching efficiency of triplet ACP. They suggested that a triplet exciplex forms between the ketone and olefin, leading mostly to energy wastage. The

trialkylethylenes (3) were found to be more reactive than dialkyl derivatives in quenching ACP triplets, which is consistent with the idea that CT interactions contribute to binding in the exciplexes leading to faster interaction rate constants. So one does not know whether the bulky tert-butyl groups of compounds (1) and (2) have hindered the rate of exciplex formation. What is significant is pointed out in the author's words: "Our data indicate that some kind of steric effects inhibit isomerization without interfering with quenching. Probably some relative orientations of substrate and sensitizer which permit efficient decay to ground states are not effective in energy transfer or addition".

To summarize, steric factors can play a role in determining quenching rate constants (k_r) and the efficiency of subsequent processes (ϕ_{Max}). To facilitate the interpretation of the electronic effects of interest in the current project, only <u>meta</u> and <u>para</u> ring-substituted ketones were studied.

RESULTS

A. Photoreduction of Substituted α,α,α-Trifluoroacetophenones by Toluene and p-Xylene

A series of meta and para-substituted α,α,α-trifluoroacetophenones were synthesized using a modification of the method of Dishart and Levine[114]. In general, the appropriate phenyl magnesium bromide was prepared and added to the lithium salt of trifluoroacetic acid. Hydrolysis and work-up followed by a single distillation afforded in general about a 50% yield, based on the amount of halide used. A spinning band distillation afforded samples usually in greater than 99.5% purity by vpc analysis.

Degassed acetonitrile solutions 0.05 M in ketone containing a given concentration of toluene and various concentrations of naphthalene were irradiated in parallel at 365 nm in a merry-go-round apparatus. Stern-Volmer plots (Equation 22) of relative bibenzyl concentrations are shown in Figures (1)-(4) and Table I summarizes the experimental results. Analogous work using p-xylene as the donor is reported in Table III and Figures (5)-(7).

Degassed acetonitrile solutions 0.05 M in ketone and containing various concentrations of toluene were irradiated

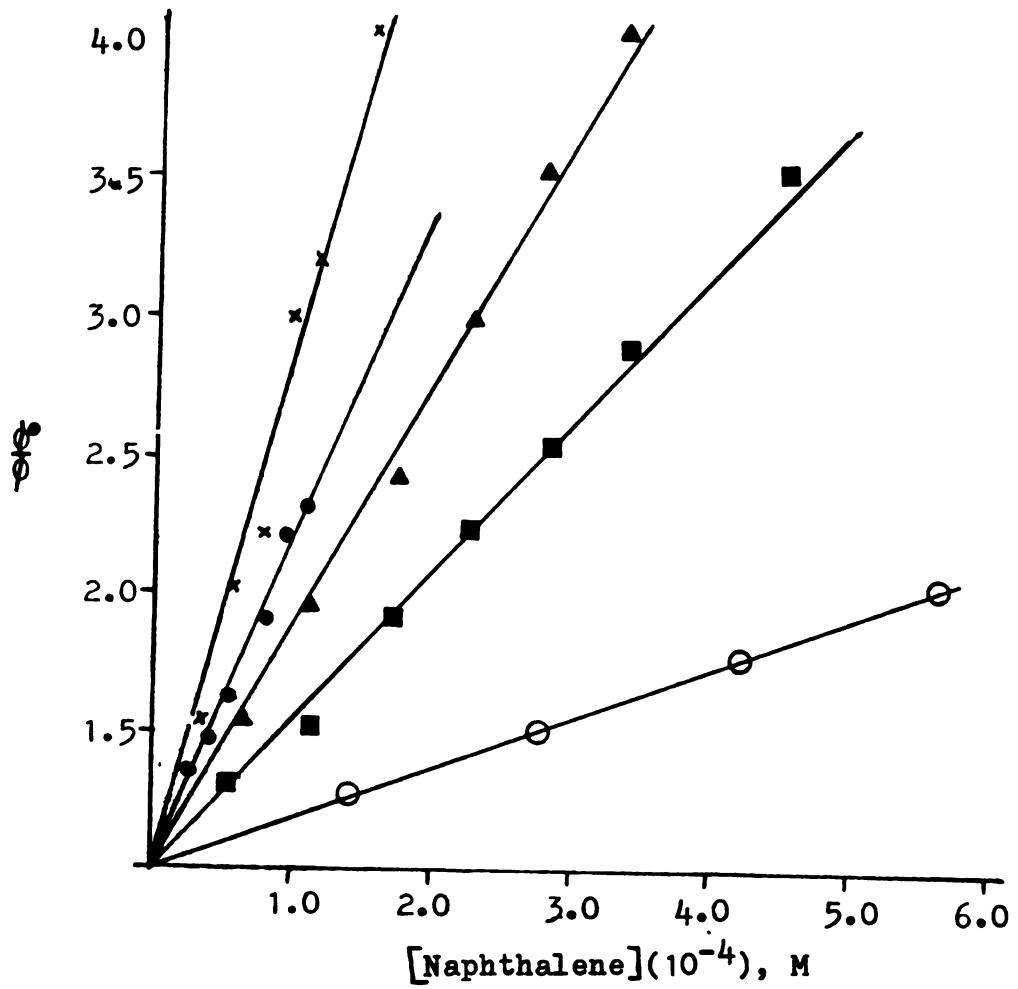


Figure 1. Stern-Volmer Plots: Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by 1 M Toluene: p-MeO (×), 3,4-di-Me (○), p-Me (▲), m-Me (■), p-t-Bu (●). 1.6 M Toluene for 3,4-di-Me-TFA.

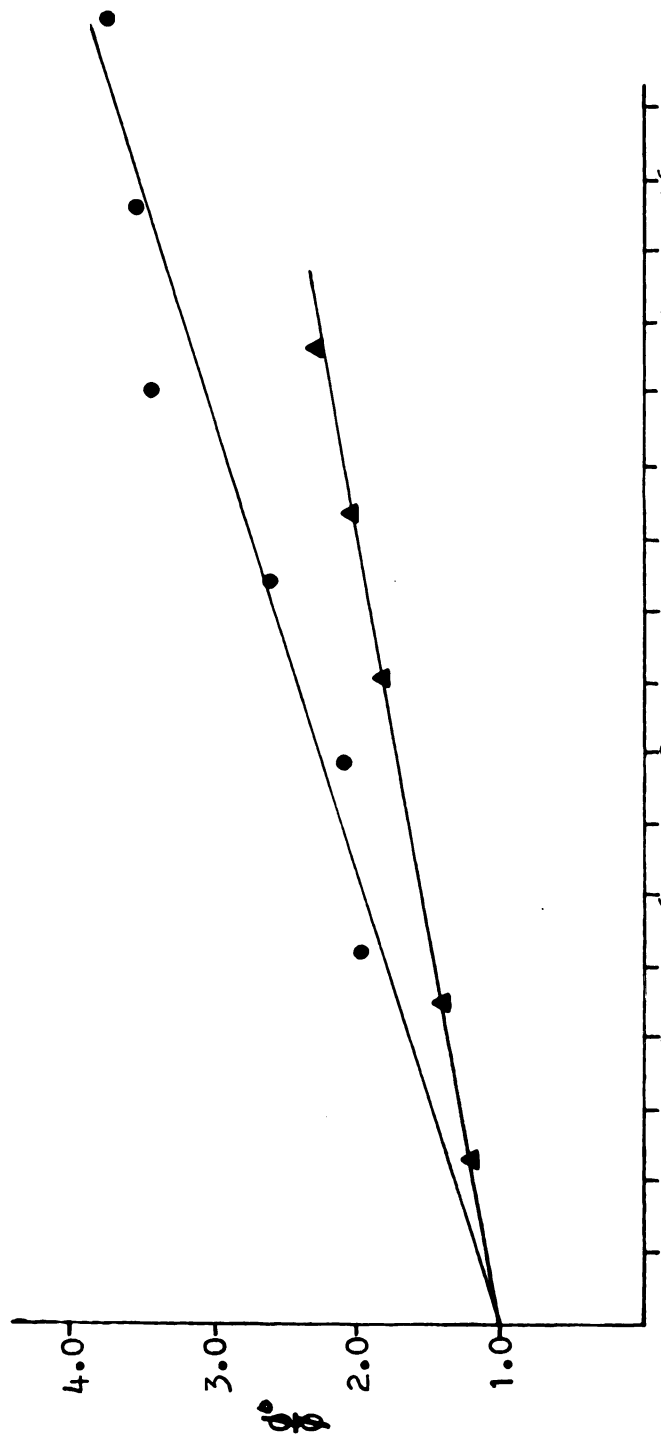


Figure 2. Stern-Volmer Plots: Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by 0.1 M Toluene: p-CF_3 (●) and m-CF_3 (▲).

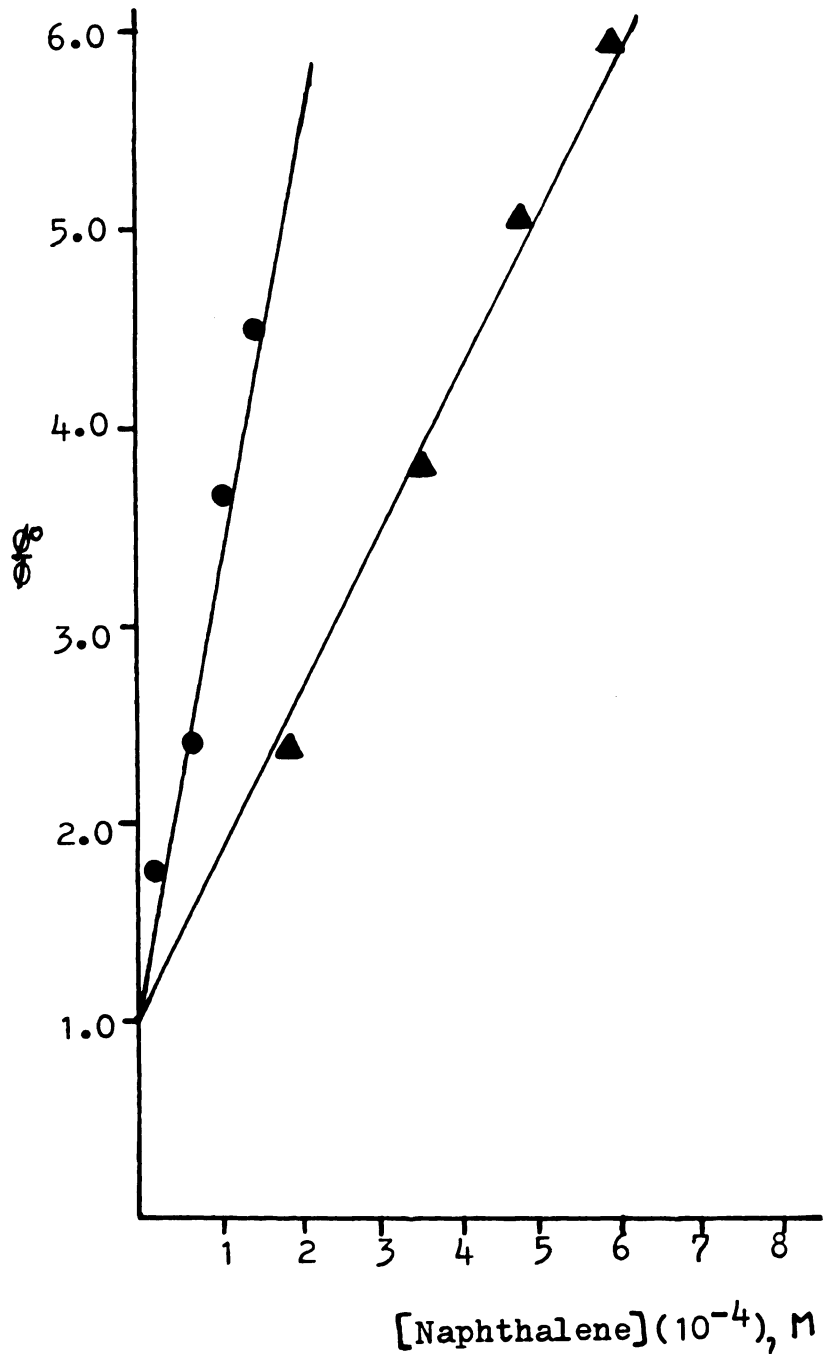


Figure 3. Stern-Volmer Plots: Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN: m-Cl (●), 1 M Toluene, and p-F (▲), 0.05 M Toluene.

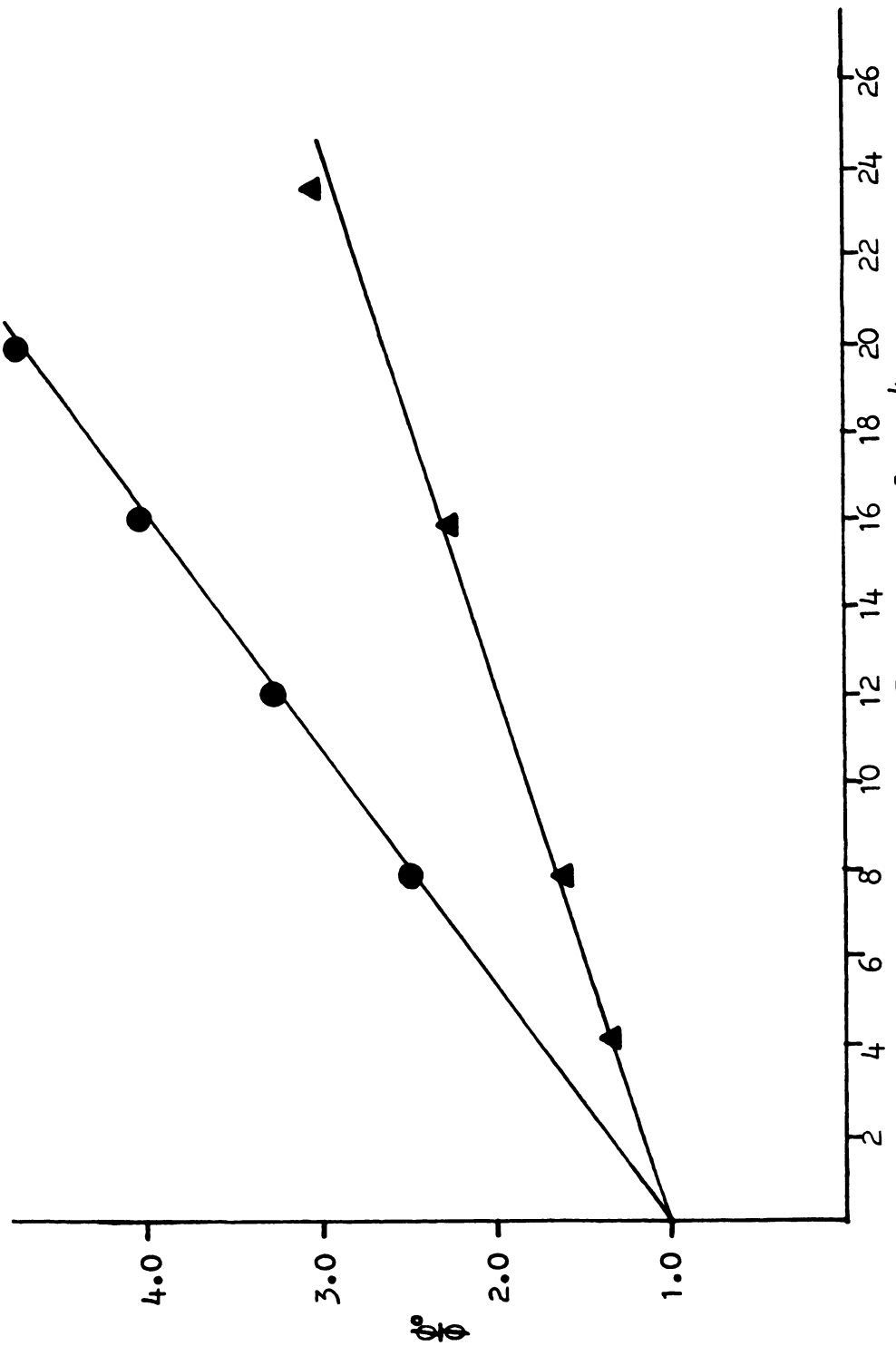


Figure 4. Stern-Volmer Plots: Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by 1 M Toluene: p-Cl (●) and H (▲).

Table I. Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by Toluene: Stern-Volmer Experiments.

Subst.	[Toluene] M[a]	Slope[a,b]	# Runs
p-CF_3	0.100	107±18	2
m-CF_3	0.103	135±18	3
m-Cl	1.11	190±42	3
p-$COCH_3$	1.03	246±26	2
p-F	0.046	9970±2040	2
H	1.01	810±27	4
p-Cl	1.11	1780±26	3
p-t-Bu	1.08	1850	1
p-CH_3	1.09	7500±1250	2
m-CH_3	1.08	5610±278	2
3,4-di-Me	1.60	15700±2300	4
p-MeO	1.07	21300±7130	3

[a]Average of all the runs. 0.05 M ketone in acetonitrile irradiated at 366 or 313 nm. Formation of bibenzyl monitored.

[b]Average deviation.

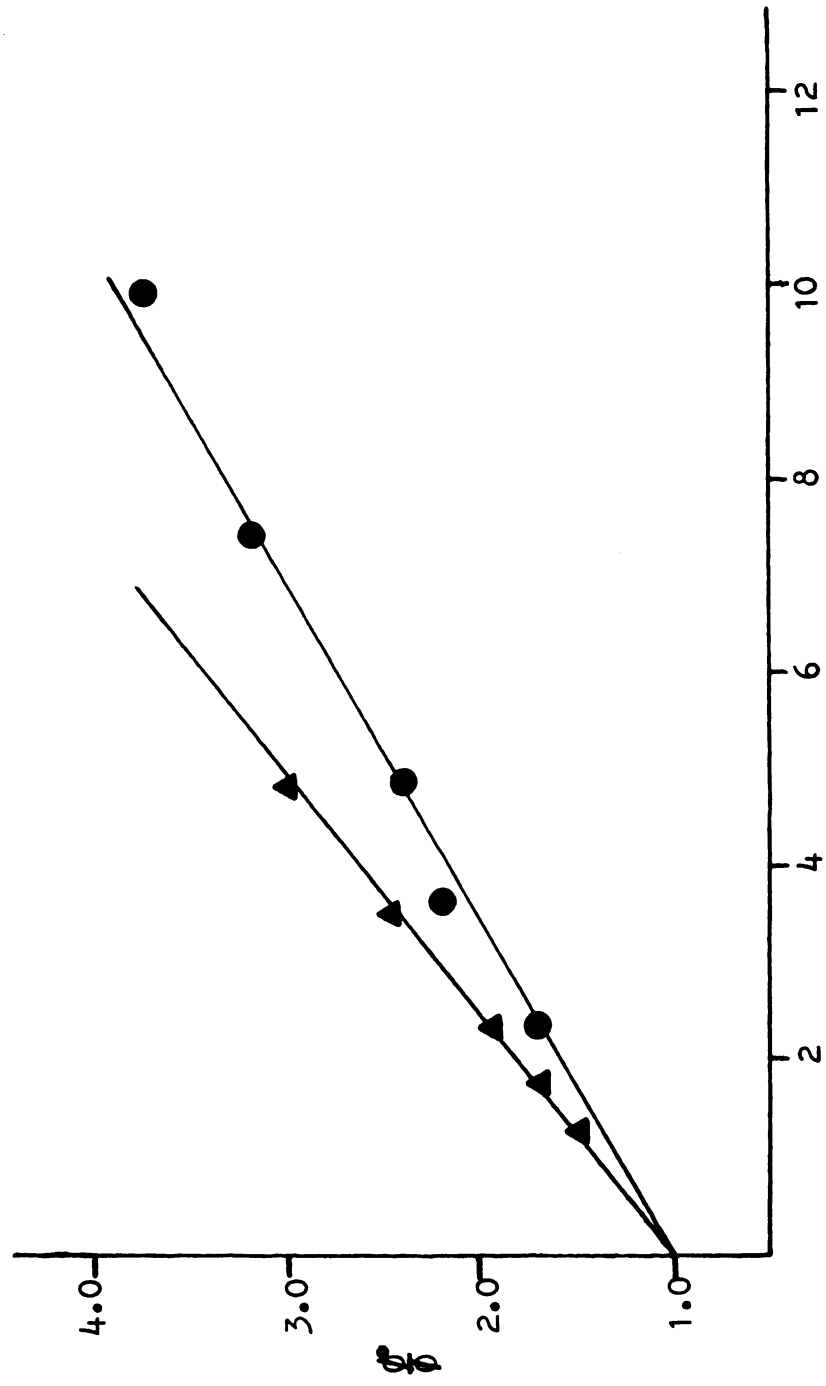


Figure 5. Stern-Volmer Plots: Photoreduction of TFA (▲) and m-Me-TFA (●) by 1.0 M p-Xylene in CH_3CN.

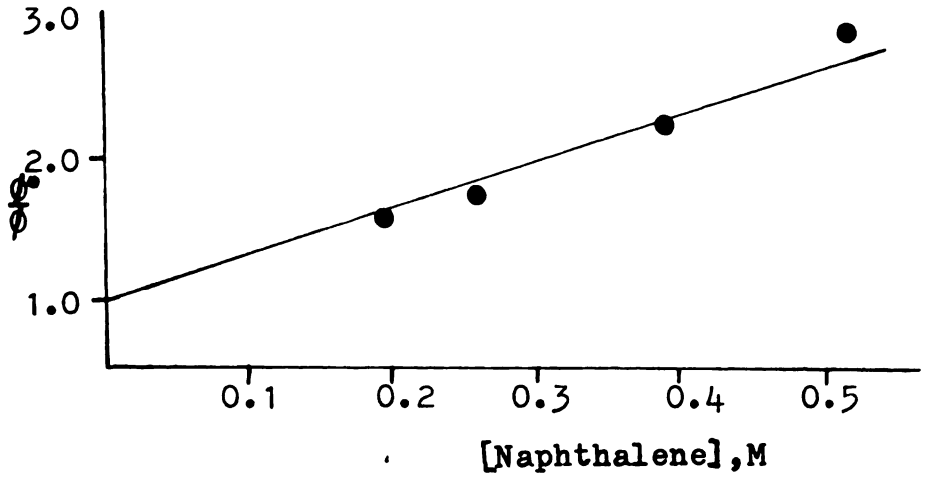


Figure 6. Stern-Volmer Plot: Photoreduction of TFA by 1.0 M p-Xylene in CH_3CN.

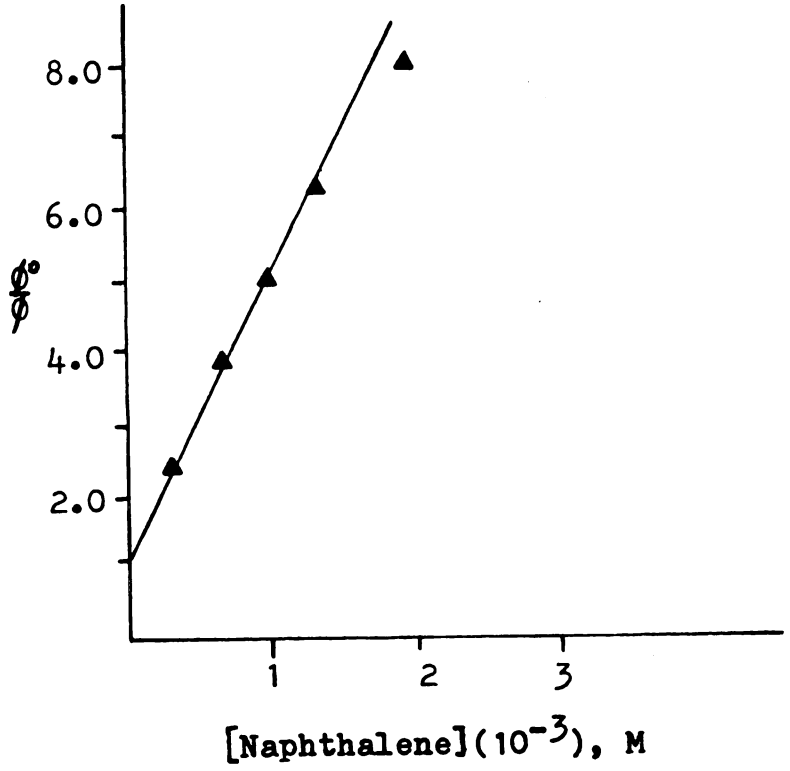


Figure 7. Stern-Volmer Plot: Photoreduction of m-Me-TFA by 1 M p-Xylene in CH_3CN.

Table II. Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by Toluene: Double Reciprocal Plots.

Subst.	Slope[a,c]	Interc.[a,c]	Slope/Interc.[a,c]	ϕ_{Max}[b,c]	# Runs
m-CF_3	1.27±0.12	63.2±1.4	0.0201±0.00015	0.016±0.0003	2
p-CF_3	1.03±0.16	15.8±0.8	0.0652±0.018	0.063±0.003	3
m-Cl	1.40±0.18	20.8±3.3	0.0673±0.0218	0.048±0.008	2
p-$COCH_3$	9.84±5.96	38.5±15.5	0.256±0.088	0.0260±0.0105	
p-F	0.35 ±0.085	16.7±4.7	0.0210±0.0042	0.060±0.017	3
H	6.44±1.05	20.9±4.0	0.308±0.039	0.048±0.009	4
p-Cl	4.51±1.48	18.5±2.1	0.244±0.093	0.054±0.006	4
p-t-Bu	26.3	33.3	0.790	0.030	1
p-CH_3	12.7±0.4	17.7±0.8	0.718±0.010	0.056±0.003	2
m-CH_3	39.0±4.9	25.4±0.5	1.54±0.15	0.039±0.0005	2
3,4-di-Me	36.4±17.0	21.2±2.0	1.72±1.36	0.047±0.004	5
p-MeO	75.3±7.3	15.6±1.6	4.83±1.07	0.064±0.007	2

[a]Average of all runs. 0.05 M ketone in acetonitrile, irradiated at 313 nm. Formation of bibenzyl monitored.

[b]Reciprocal of the intercept. Amount of light absorbed was determined by valerophenone actinometry.[25]

[c]Average deviation.

Table III. Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by p-Xylene: Stern-Volmer Experiments.[3]

Subst.	[p-Xylene][a], M	Slope[a]	# Runs
p-CF_3	1.01	3.15±0.2	2
H	1.08	41.7±1.7	2
m-CH_3	1.02	296±4.0	2
p-MeO	1.01	3780±373	2

[a]Average of all the experiments. 0.05 M ketone in acetonitrile, irradiated at 335 nm. Formation of 1,2-di-tolyl ethane monitored. Average deviation reported.

in parallel at 313 nm in a merry-go-round apparatus. Quantum yields of bibenzyl formation were determined by GC analysis. The light intensity was measured by valerophenone actinometry[25]. The double reciprocal plots are shown in Figures (8)-(12) and the results are summarized in Table II (page 48). Analogous work using p-xylene as the donor is reported in Table IV and Figure (13).

In the double reciprocal plots, the slope and intercept values are coupled, and the reproducibility of slopes and intercepts is often not very good. However, the parameter of interest is the ratio of slope over intercept and this value was usually found to be quite reproducible. The average deviation reported for slope/intercept values for a given ketone were calculated from the ratios obtained from different runs. The slopes and intercepts reported were calculated by a least squares program supplied by a desk calculator.

As shown in Scheme 3, three major photoproducts are formed in the photoreductions of the phenyl ketones. The slope and intercept values reported were determined by monitoring only the bibenzyl product.

A high material balance has been reported for the photoreduction of TFA by p-xylene[62]: the bibenzyl and cross-coupling products accounted for 90% of the TFA consumed, and 94% of ACP reacted in a second experiment. The authors were unable to detect any other products by

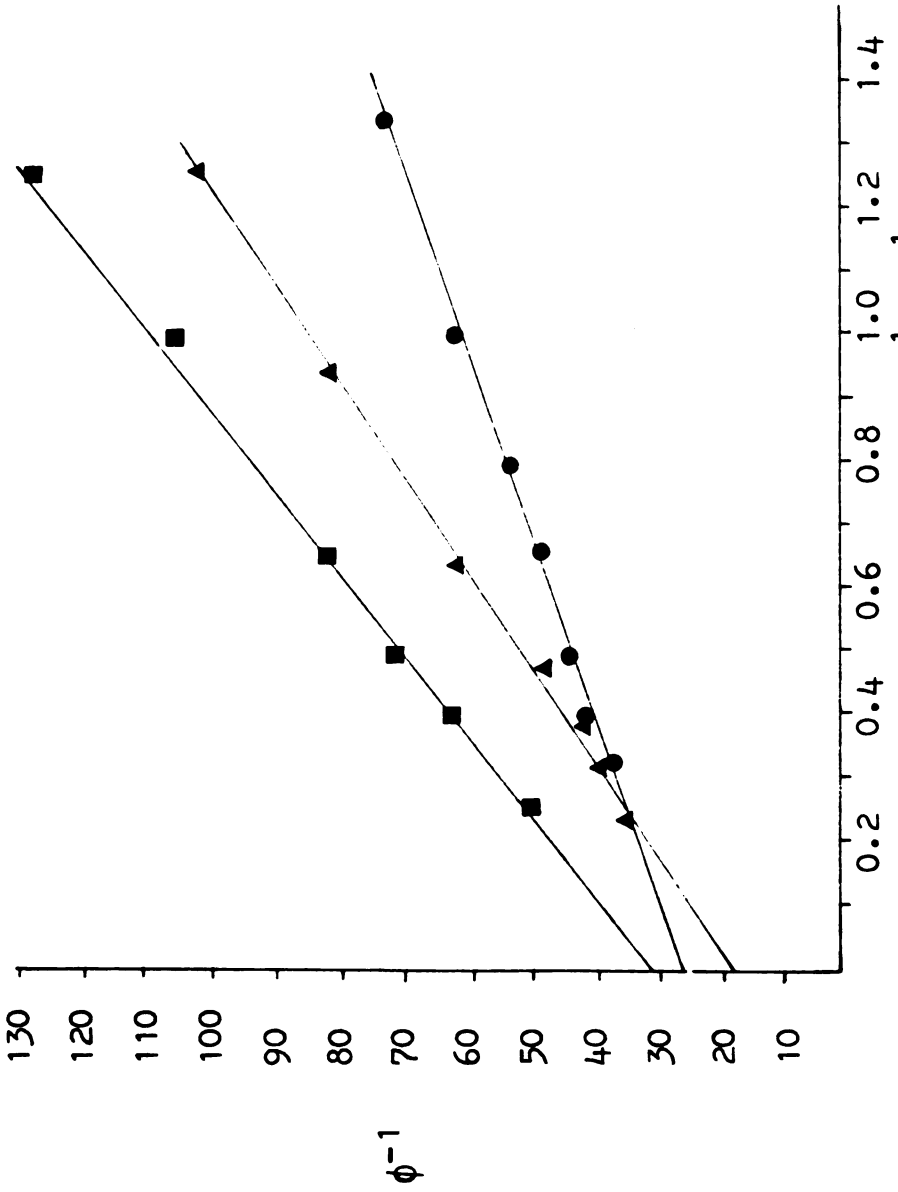


Figure 8. Double Reciprocal Plots: Photoreduction of 3,4-di-Me-TFA (■), p-MeO-TFA (▲), and m-Me-TFA (●) in CH_3CN by Toluene.

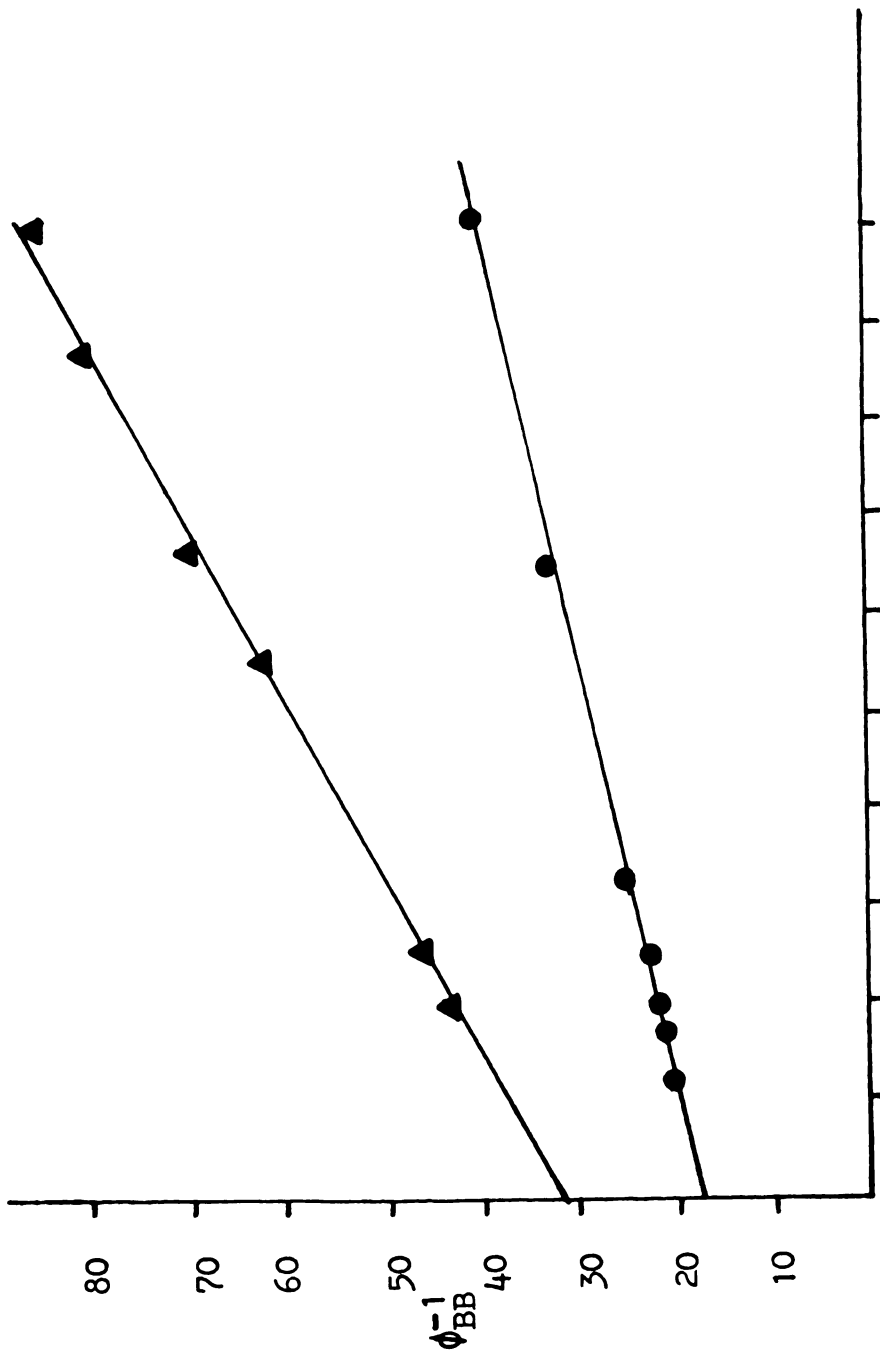


Figure 9. Double Reciprocal Plots: Photoreduction of p-t-Bu-TFA (▲) and p-Me-TFA (●) in CH_3CN by Toluene.

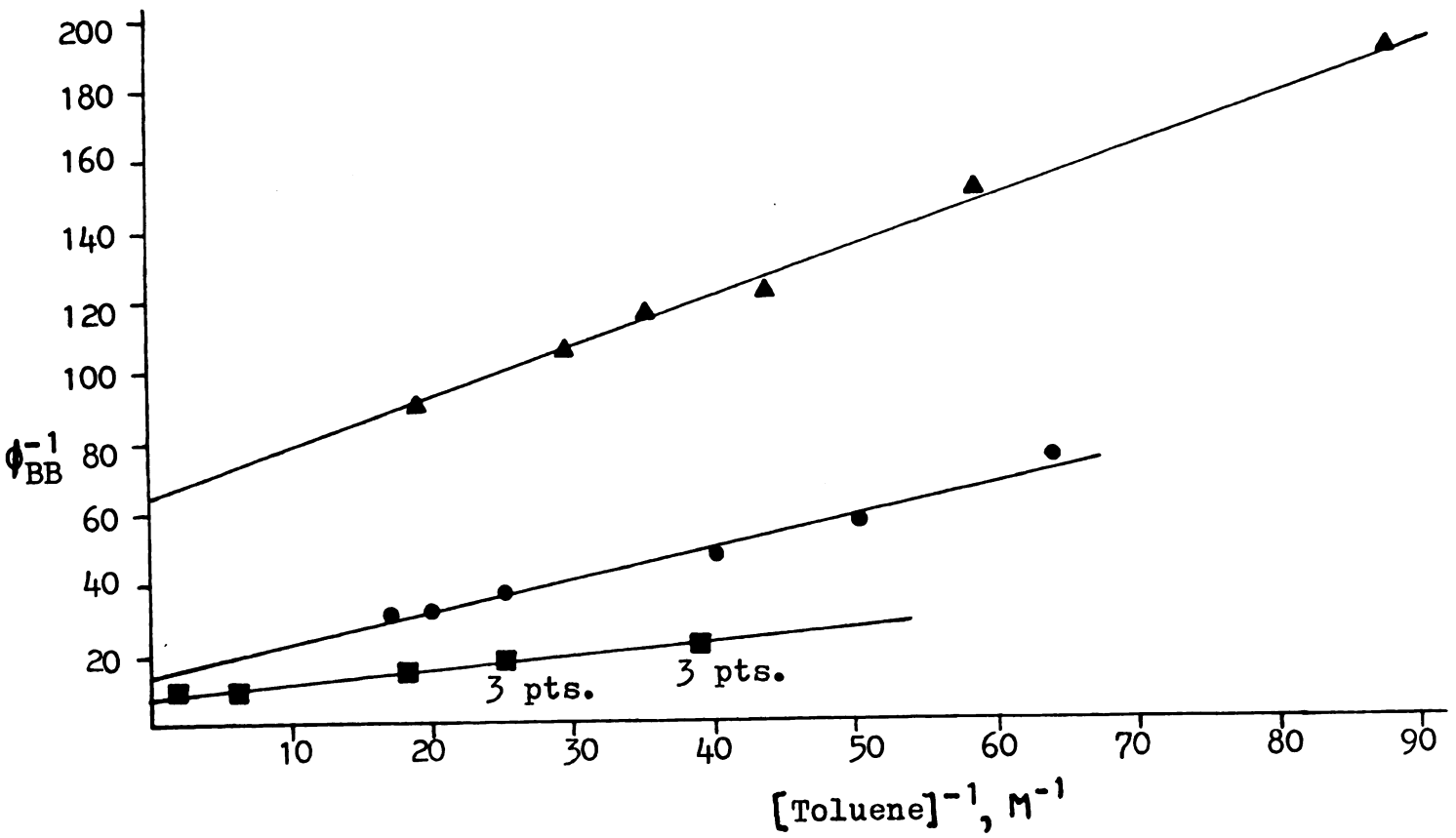


Figure 10. Double Reciprocal Plots: Photoreduction of m-CF_3-TFA (▲), p-CF_3-TFA (●), and p-F-TFA (■) in CH_3CN by Toluene.

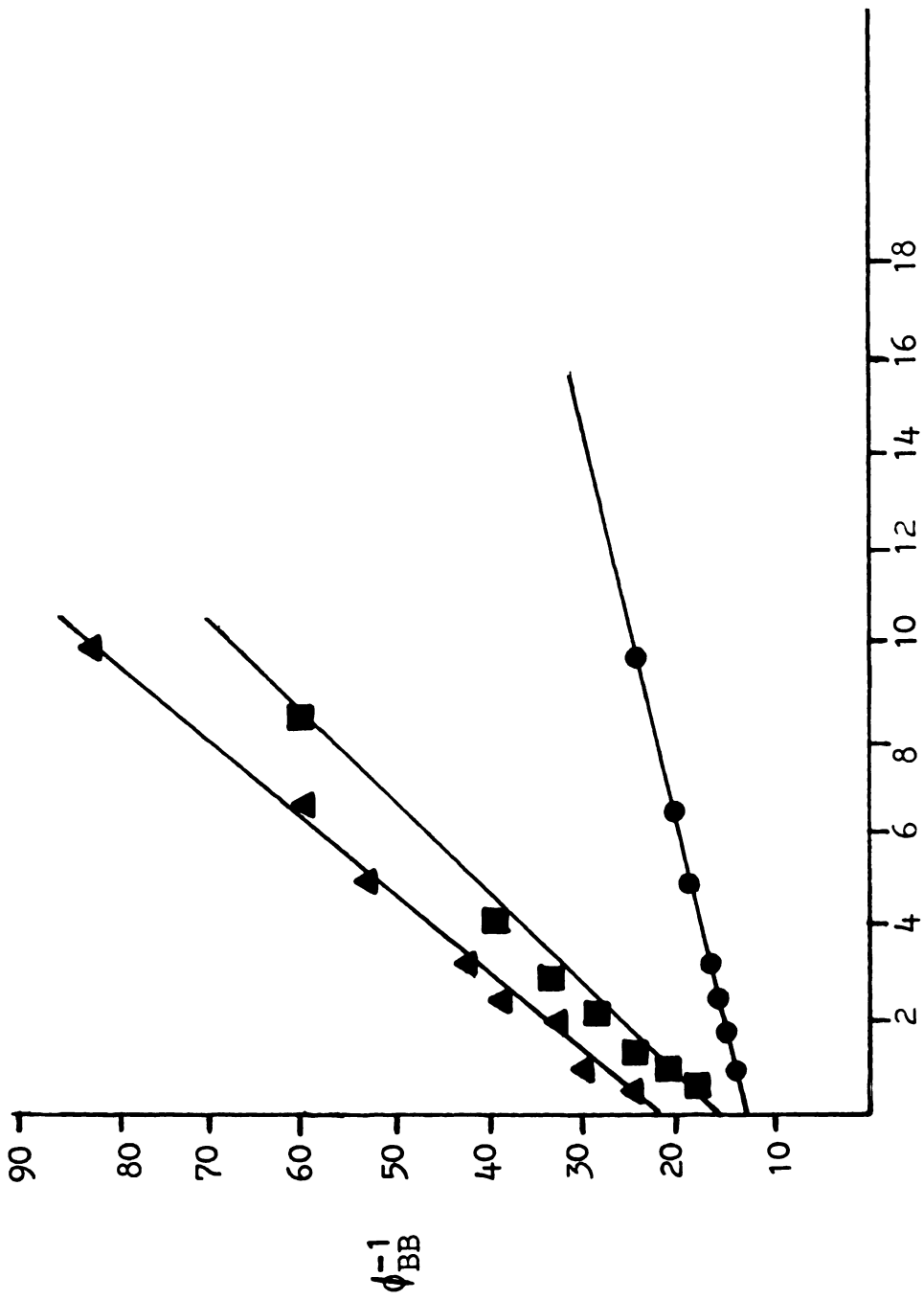


Figure 11. Double Reciprocal Plots: Photoreduction of p-Cl-TFA (▲), m-Cl-TFA (●), and TFA (■) in CH_3CN by Toluene.

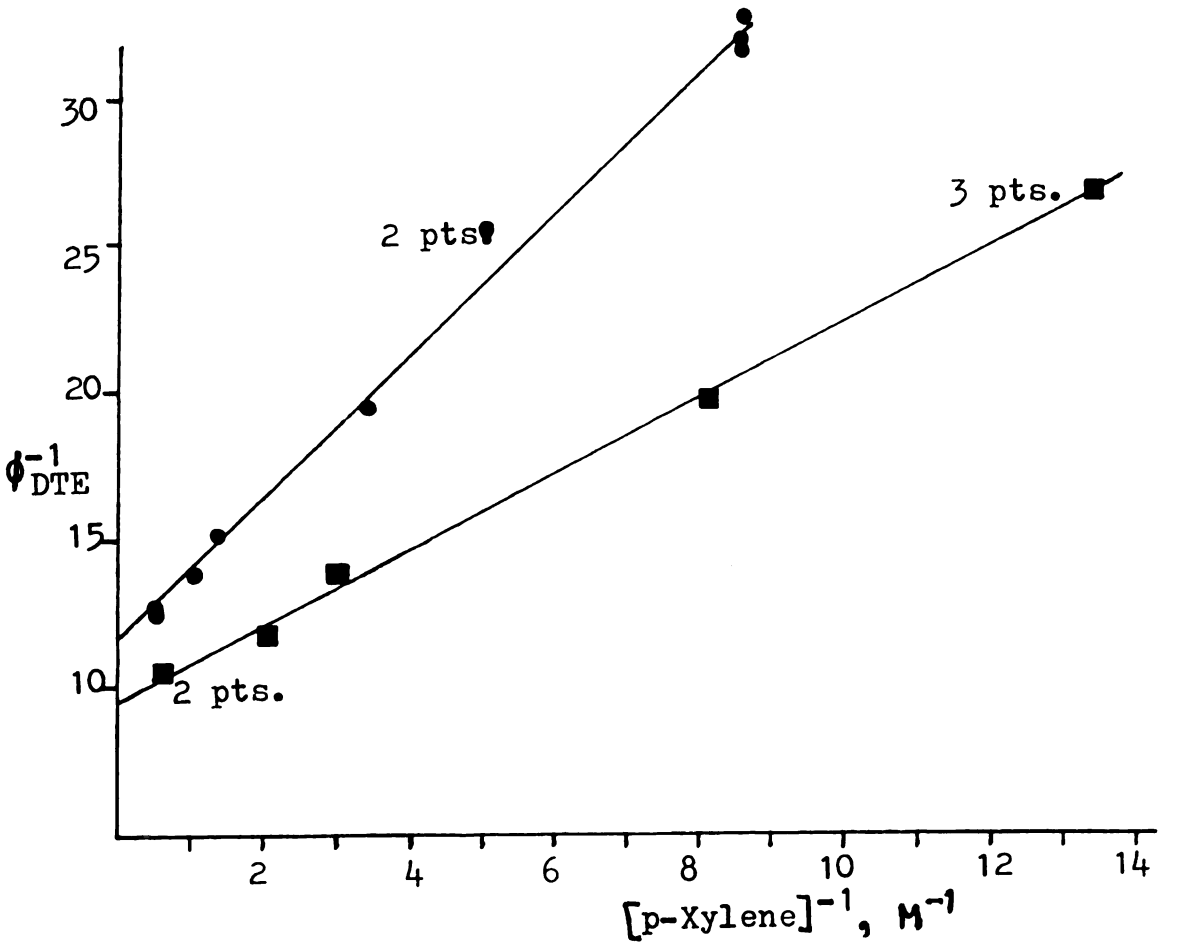


Figure 12. Double Reciprocal Plots: Photoreduction of p-MeO-TFA (●) and m-Me-TFA (■) in CH_3CN by p-Xylene.

Table IV. Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by p-Xylene: Double Reciprocal Plots.

Subst.	Slope[a]	Interc.[a]	Slope/Interc.	ϕ_{Max}[b]	# Run
p-CH_3CO	0.121	10.8	0.0112	0.093	1
H	0.301	8.82	0.0341	0.113	1
m-CH_3	1.27	9.44	0.135	0.106	1
p-MeO	2.38±0.28	10.9±0.3	0.218±0.018	0.092±0.003	2

[a]Average of all experiments. 0.05 M ketone in acetonitrile, irradiated at 335 nm.

[b]Reciprocal of the intercept. Formation of 1,2-di-para-tolyl-ethane monitored.

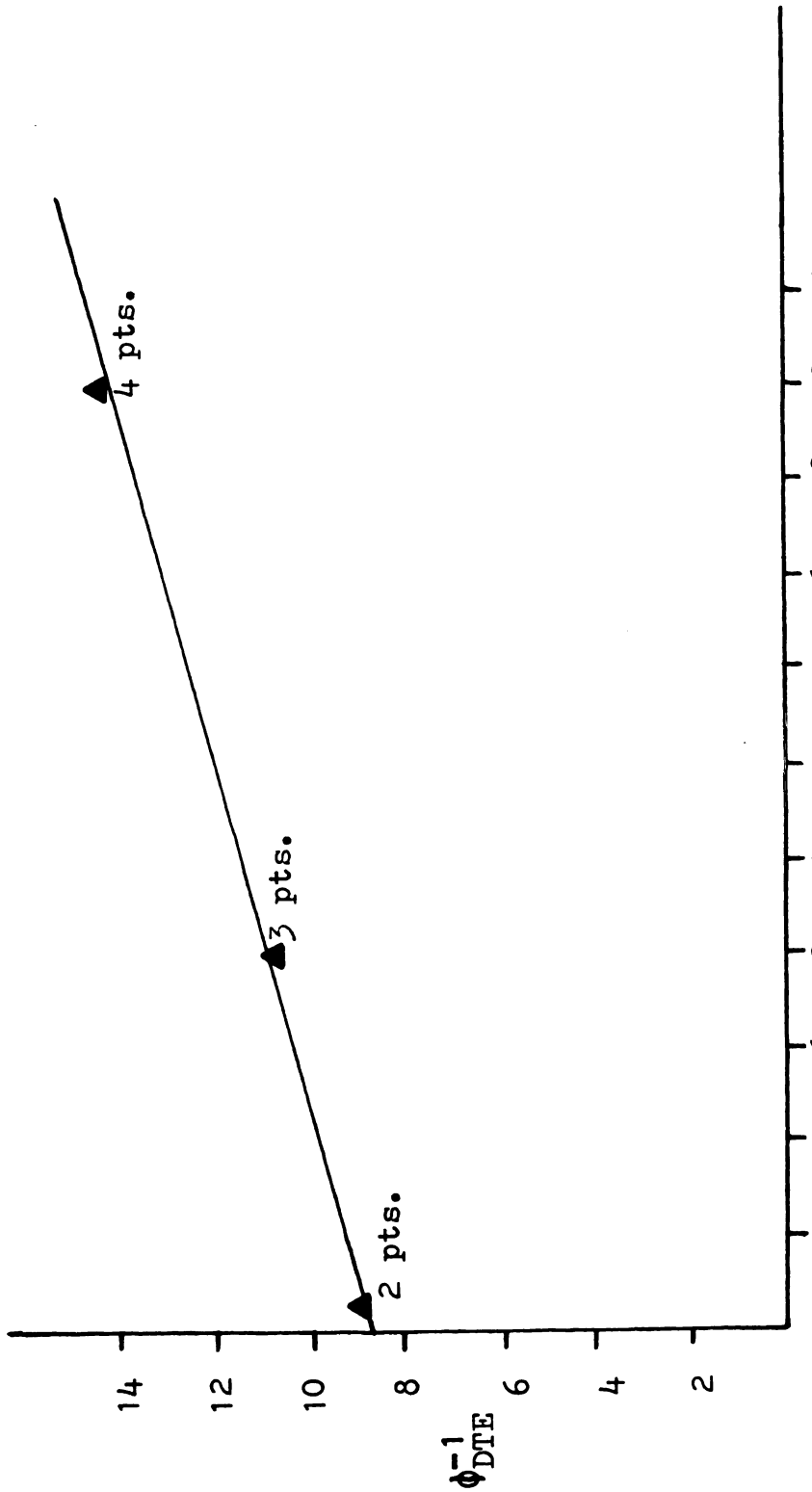
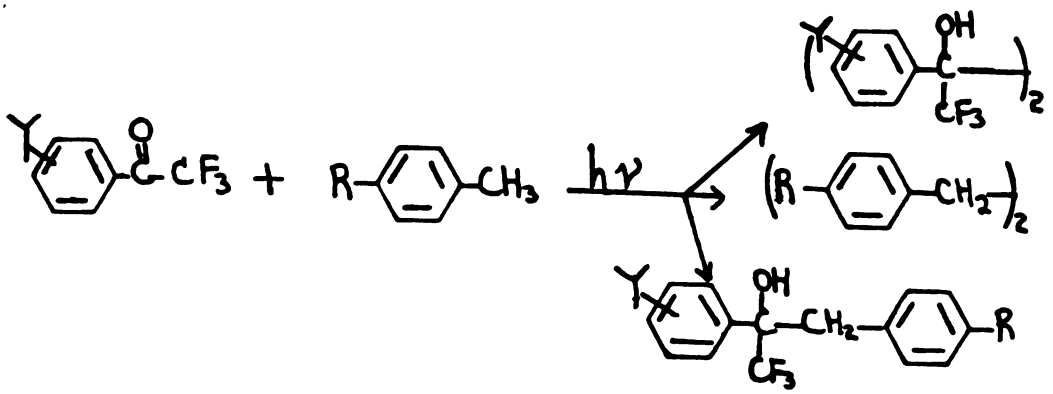


Figure 13. Double Reciprocal Plot: Photoreduction of TFA in CH_3CN by p-Xylene.



Scheme 3. Products from the Photoreduction of α,α,α-Trifluoroacetophenone by Toluene and p-Xylene.

vpc beside those shown in Scheme 3. A mass balance study for the photoreduction of ACP by p-xylene is summarized in Table V. Three experiments all showed that the pinacol and cross-coupling products account for over 80% of the ACP consumed.

Reduction potentials were measured by cyclic voltammetry in Aldrich gold label acetonitrile. The equipment is described in the Experimental section. In general, argon was bubbled for about 2 minutes through 10^{-4} M ketone solutions containing 0.1-1 M TEAP and the voltammagrams were recorded on a chart recorder at rapid scan rates, usually around 400 mV/sec. The values reported are the average of the forward and reverse wave and are summarized in Tables VI, XIII, and XVI.

Phosphorescence emission triplet energies were measured at 77°K in 2-methyltetrahydrofuran, which had been purified

Table V. Concentrations ($x10^{-2}$) of the Major Products from the Photoreduction of ACP by p-Xylene.

-[ACP], M[a]	[DTE], M	[KB],[b] M	[Pinacol], M	[Ketyl],[c] M	[Ketyl]/[ACP]
2.76	0.73	1.13	0.55	2.23	0.81
2.50	0.57	1.03	0.50	2.03	0.81
2.33	0.54	0.840	0.52	1.88	0.81

[a]Acetophenone consumed.

[b]The ketyl-benzyl cross coupling product.

[c]Calculated from 2x[Pinacol] + [KB].

Table VI. Spectroscopic Data for Ring Substituted α,α,α-Trifluoroacetophenones.

Subst.	λ(nm)	E_T [a]	E_{red} [b]	$-E^*_{red}$ kcal	E_T [c], kcal	$-E_{red}$ [c], eV	$-E^*_{red}$ [c], kcal
m-CF_3	405	70.6	1.28(27.4)	43.2	70.6	1.19	43.2
p-CF_3	405	70.6	1.27(29.2)	41.4	70.4	1.13	44.4
m-Cl	413	69.2	1.25(28.7)	40.5	69.9	1.25	41.1
p-CH_3CO	395	72.4	1.15(26.5)	45.9	----	----	----
p-F	408	70.1	1.47(33.9)	36.2	----	----	----
H	409	69.9	1.38(31.9)	38.0	71.0	1.43	38.1
p-Cl	423	67.6	1.37(31.6)	36.0	68.4	1.30	38.5
p-t-Bu	423	67.6	1.54(35.5	32.1	----	----	----
p-CH_3	425	67.3	1.57(36.2)	32.8	69.0	1.51	34.4
m-CH_3	428	66.8	1.42(32.9)	31.1	69.4	1.45	36.0
3,4-Di-Me	430	66.5	1.61(37.1)	29.4	----	----	----
p-MeO	434	65.9	1.63(37.5)	28.4	66.5	1.57	30.1

[a] Triplet energies determined from the 0,0 band (nm) of phosphorescence spectra at 77°K in 2-methyltetrahydrofuran. Values in kcal/mole. $E_T = 2.86 \times 10^4/\lambda(nm)$.

[b] By cyclic voltammetry in acetonitrile relative to SCE. Values in eV (kcal)/mole. 1 eV = 23.03 kcal.

[c] From Reference 81.

by Dr. Meador[115]. The equipment used is described in the Experimental section. The results are summarized in Tables VI, XIII, and XVI.

B. Photoreduction of Substituted Acetophenones by p-Xylene

A series of meta and para-substituted acetophenones were synthesized or bought and photoreduced by p-xylene.

In general, 0.01-0.03 M ketone solutions with an n-alkyl benzoate standard ($PhCOOC_nH_{2n+1}$, n=7-9) in CH_3CN containing a) varying amounts of naphthalene quencher at a fixed donor concentration, or b) varying amounts of donor, were irradiated at 313, >335 or 365 nm. The concentration of p-di-tolylethane (DTE) was measured by vpc.

Plots of ϕ°/ϕ versus quencher concentration gave straight lines, and the results are given in Table VII (Figures 14-17).

Plots of ϕ^{-1} versus $[\text{p-xylene}]^{-1}$ gave straight lines, and the relevant parameters are given in Table VIII (Figure 18).

The quantum yield of DTE or BB was measured as a function of ketone concentration as a test for self-quenching. The results are presented in Tables IX-XI.

Stern-Volmer quenching of triplet ACP as a function of ketone and of p-xylene concentration led to the results summarized in Table XII (Figures 19,20).

Table VII. Photoreduction of Substituted Acetophenones in CH_3CN by p-Xylene: Stern-Volmer Experiments.

Subst.	[Ketone], M[a]	[p-Xylene], M	Slope[a,b]	# Runs
m-CN	0.02	1.60	396±60	2
m-CF_3	0.02	1.60	924±52	2
p-CF_3	0.02	1.60	1270±307	3
m-Cl	0.02	1.60	1960±446	5
p-CN	0.02	1.60	3350±140	2
p-$COCH_3$	0.03	1.59	3090±364	2
H	0.01	1.61	2930±330	3
m-Me	0.01	1.60	9470±800	2
p-t-Bu	0.02	1.58	18300	1
p-Cl	0.02	1.60	25600±2500	3
p-Me	0.01	1.60	17200±2700	3
3,4-Di-Me	0.02	1.60	26000±3000	2
p-MeO	0.02	1.60	43500±3900	2

[a]Average of all the runs. Solutions were irradiated at >335 or 366 nm, and p-di-tolylethane (DTE) photoproduct examined by vpc.

[b]Average deviation.

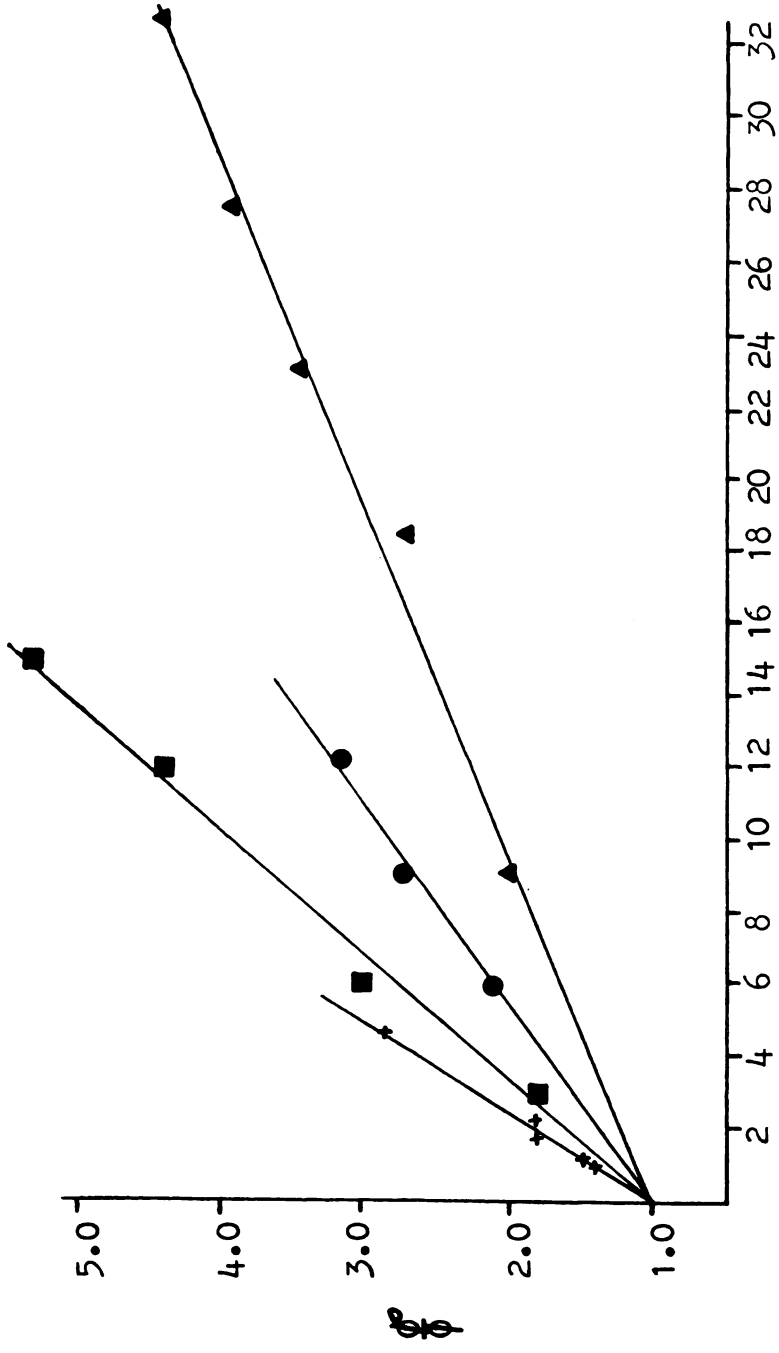


Figure 14. Stern-Volmer Plots: Photoreduction of Substituted Acetophenones in CH_3CN by 1.6 M p-Xylene: p-MeO (+); 3,4-di-Me (■); p-Me (●); and m-Me (▲).

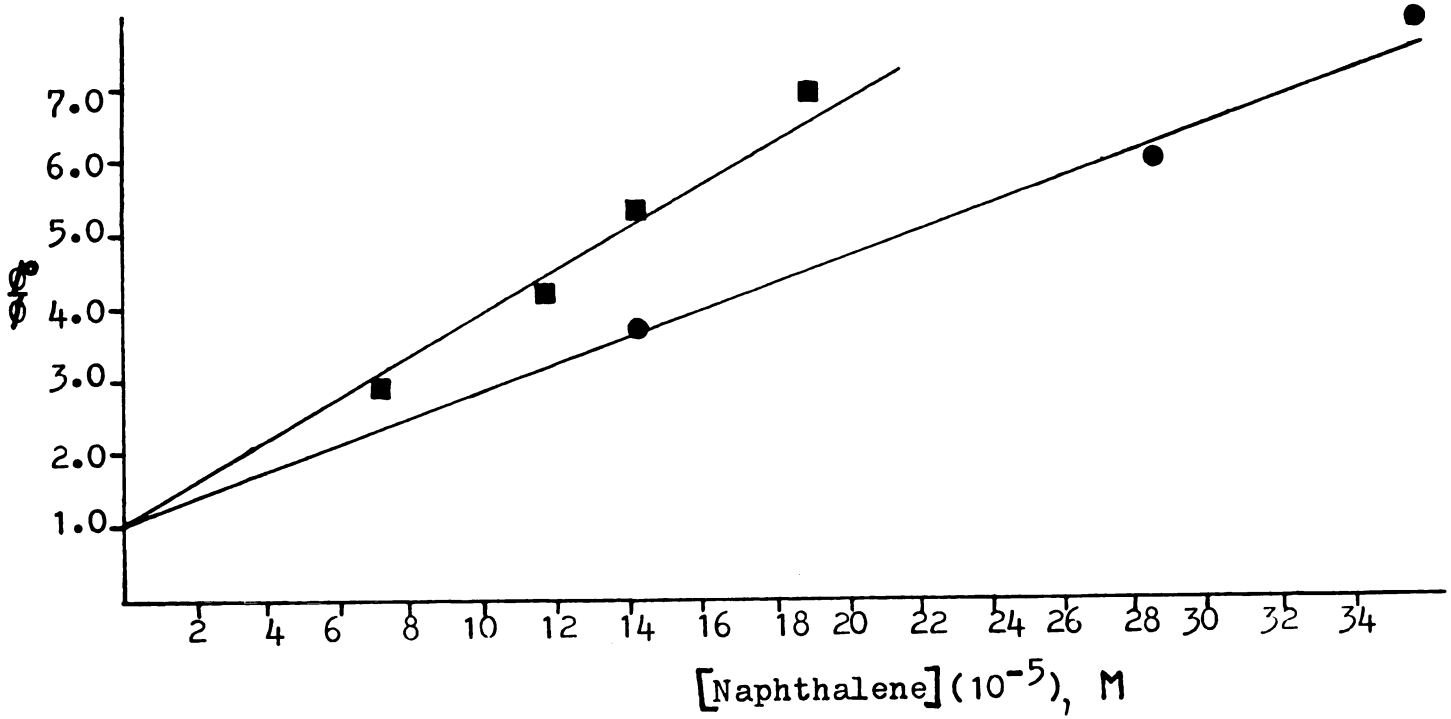


Figure 15. Stern-Volmer Plots: Photoreduction of Substituted Acetophenones in CH_3CN by 1.6 M p-Xylene: p-Cl (■); p-t-Bu (●).

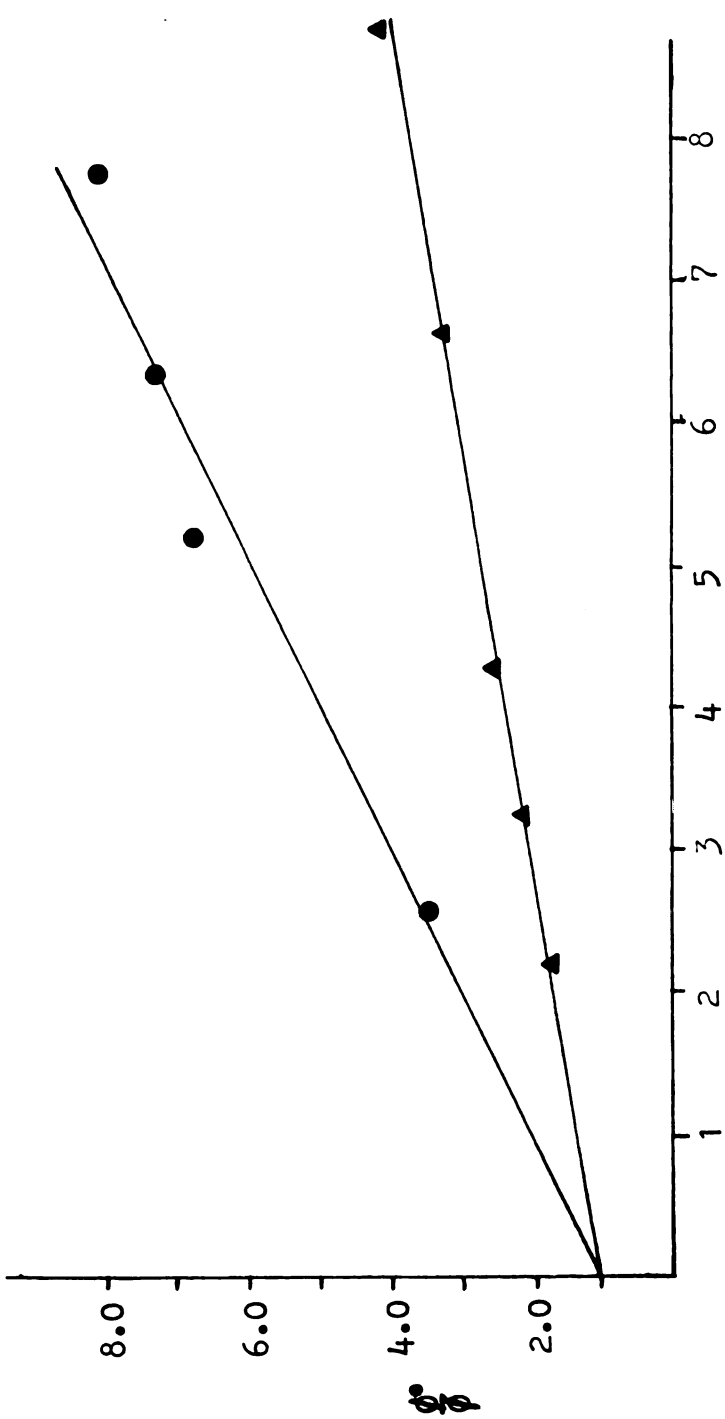


Figure 16. Stern-Volmer Plots: Photoreduction of Substituted Acetophenones in CH_3CN by 1.6 M p-Xylene: m-CF_3 (●), and m-CN (▲).

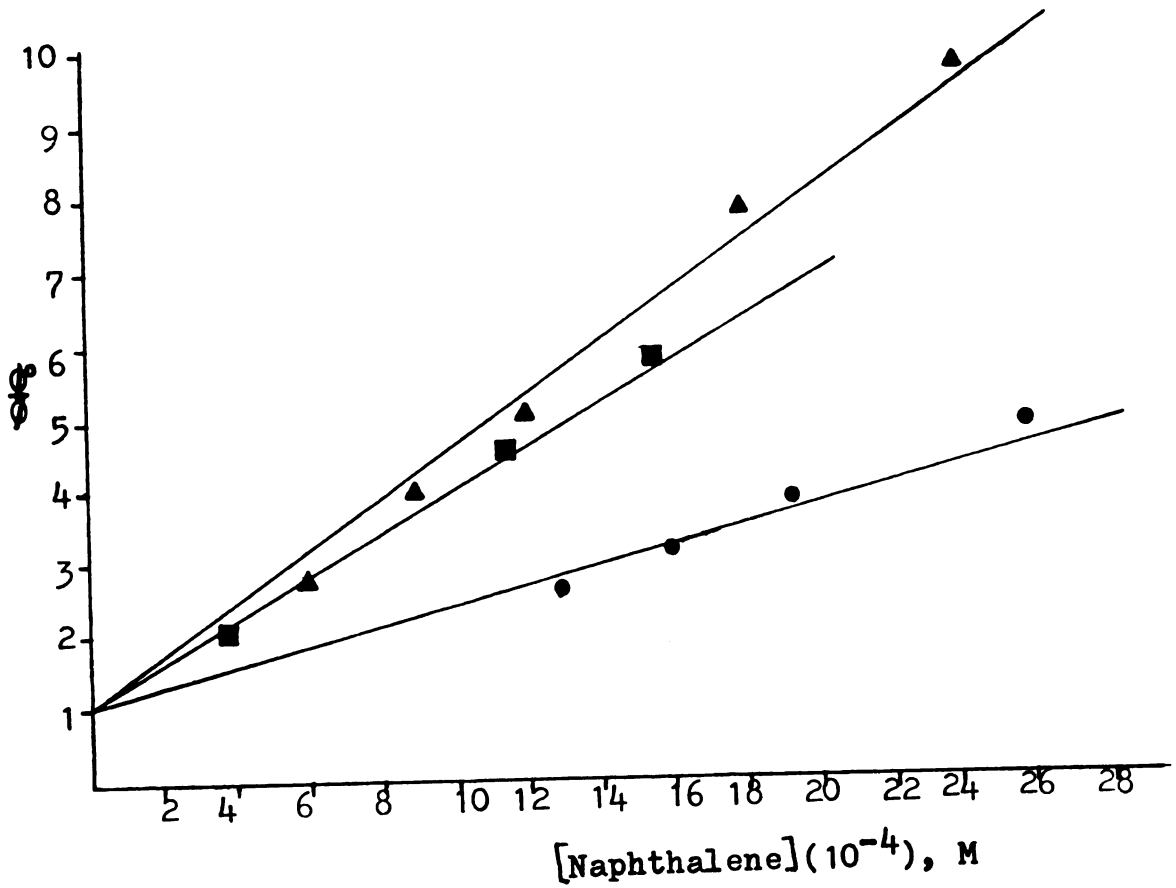


Figure 17. Stern-Volmer Plots: Photoreduction of Substituted Acetophenones in CH_3CN by 1.6 M p-Xylene: p-CN (▲), m-Cl (■), and p-CF_3 (●).

Table VIII. Photoreduction of Substituted Acetophenones in CH_3CN p-Xylene: Double Reciprocal Experiments.

Subst.	[Ketone]M	Slope[a,c]	Interc.[a,c]	Slope/Interc.[c]	ϕ_{Max}[b]	# Runs
m-CN	0.02	2.31±0.10	31.5±2.5	0.0676±0.0066	0.0317±0.003	2
m-CF_3	0.02	0.639±0.054	7.22±0.25	0.0885±0.0044	0.139±0.012	2
p-CF_3	0.02	0.308±0.053	4.86±0.78	0.0634±0.0037	0.206±0.035	3
m-Cl	0.02	1.70±0.02	9.51±1.06	0.179±0.020	0.105±0.001	2
p-CN	0.02	0.582±0.024	7.79±0.21	0.0747±0.0011	0.128±0.005	2
p-$COCH_3$	0.03	3.98	17.4	0.229	0.057	1
H	0.01	11.6±0.8	3.54±0.29	3.28±0.45	0.282±0.019	2
m-Me	0.02	14.5±5.4	6.31±0.95	2.30±1.04	0.158±0.059	2
p-t-Bu	0.02	22.2±6.3	19.2±5.4	1.16±0.09	0.052±0.015	3
p-Cl	0.02	2.39±0.58	6.56±2.43	0.364±0.193	0.132±0.037	3
p-Me	0.01	52.4±17.0	9.32±5.30	5.62±2.44	0.107±0.0035	6
3,4-di-Me	0.02	420±29	43.1±9.8	9.74±3.34	0.023±0.002	3
p-MeO	0.01	134±24	25.7±11.4	5.21±1.43	0.039±0.007	3

[a]Average of all the experiments. Solutions were irradiated at 313 nm, and p-di-tolylethane (DTE) examined by vpc.

[b]Inverse of the intercept.

[c]Average deviation.

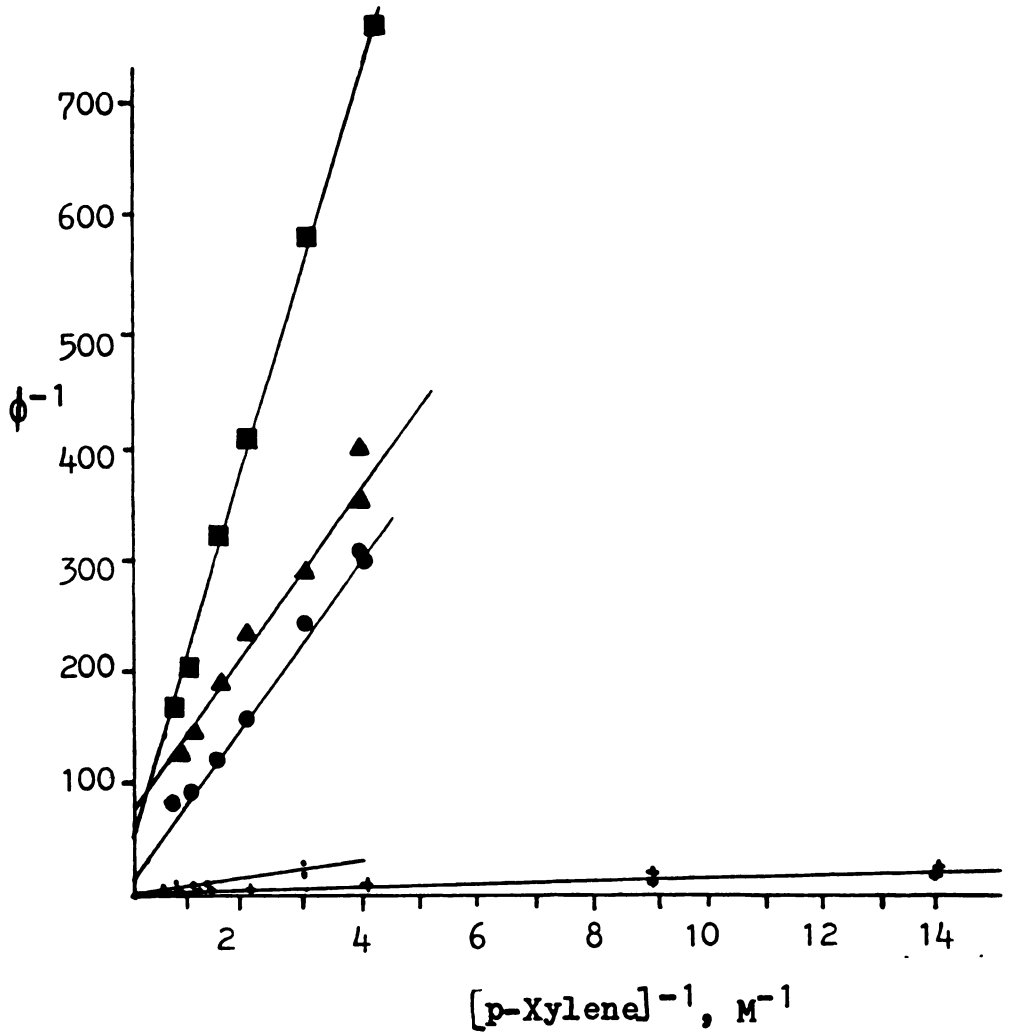


Figure 18. Double Reciprocal Plots: Photoreduction of Substituted Acetophenones in CH_3CN by p-Xylene: p-MeO (■), 3,4-di-Me (▲), p-Me (●), m-Me (•), and p-CN (+).

Table IX. Photoreduction of Substituted Acetophenones in CH_3CN by p-Xylene: Quantum Yield of 1,2-di-p-Tolylethane as a Function of Ketone Concentration.

[ACP], M[a]	ϕ_{DTE}
0.01	0.035±0.0006
0.05	0.026
0.10	0.022
0.15	0.018
0.22	0.014±0.005
[p-Me-ACP], M[a]	**ϕ_{DTE}**
0.018	0.0046±0.001
0.10	0.0033
0.20	0.0017±0.0002
[3,4-di-Me-ACP], M[b]	**ϕ_{DTE}**
0.00857	0.0125±0.0009
0.106	0.0050±0.0008
[m-Me-ACP], M[b]	**ϕ_{DTE}**
0.01	0.010
0.10	0.0051
[p-MeO-ACP], M[b]	**ϕ_{DTE}**
0.0106	0.0096±0.0014
0.104	0.0044±0.0006
[p-t-Bu-ACP], M[a]	**ϕ_{DTE}**
0.012	0.0080±0.0006
0.074	0.0071±0.0005
0.15	0.0040±0.0001

[a][p-xylene] = 0.15 M. [b][p-xylene] = 0.17 M.

Table X. Photoreduction of Benzophenones in CH_3CN by p-Xylene: Quantum Yield of 1,2-di-p-Tolylethane as a Function of Ketone Concentration.

[Benzophenone], M	ϕ_{DTE}[a]
0.01	0.053±0.002
0.05	0.048
0.10	0.047
0.15	0.047
0.20	0.048±0.001
[4,4'-di-MeO-BP], M	ϕ_{DTE}[b]
0.01	0.016
0.03	0.014±0.001
0.05	0.015±0.001

[a] [p-xylene] = 0.15 M.

[b] [p-xylene] = 0.16 M.

Table XI. Photoreduction of α,α,α-Trifluoroacetophenones in CH_3CN by Toluene: Quantum Yield of Bibenzyl as a Function of Ketone Concentration.

[TFA], M	ϕ_{BB}[a]
0.02	0.034±0.001
0.10	0.025
0.20	0.024±0.001

[p-CF_3-TFA], M	ϕ_{BB}[a]
0.02	0.062
0.10	0.067±0.003
0.20	0.066±0.003

[a][Toluene] = 0.15 M.

Table XII. Stern-Volmer Quenching of ACP by p-Xylene in Acetonitrile.

[ACP], M	[p-Xylene], M	$k_q\tau$[a]	$\tau^{-1}(10^6)M^{-1}s^{-1}$
0.01	1.44	2050	4.88
0.01	0.15	10700	0.937
0.20	1.44	1550	6.44
0.20	0.15	5500	1.82

[a]Naphthalene used as quencher. $k_q = 1 \times 10^{10}\ M^{-1}s^{-1}$. Triplet energies at 77°K and reduction potentials for acetophenones are presented in Table XIII.

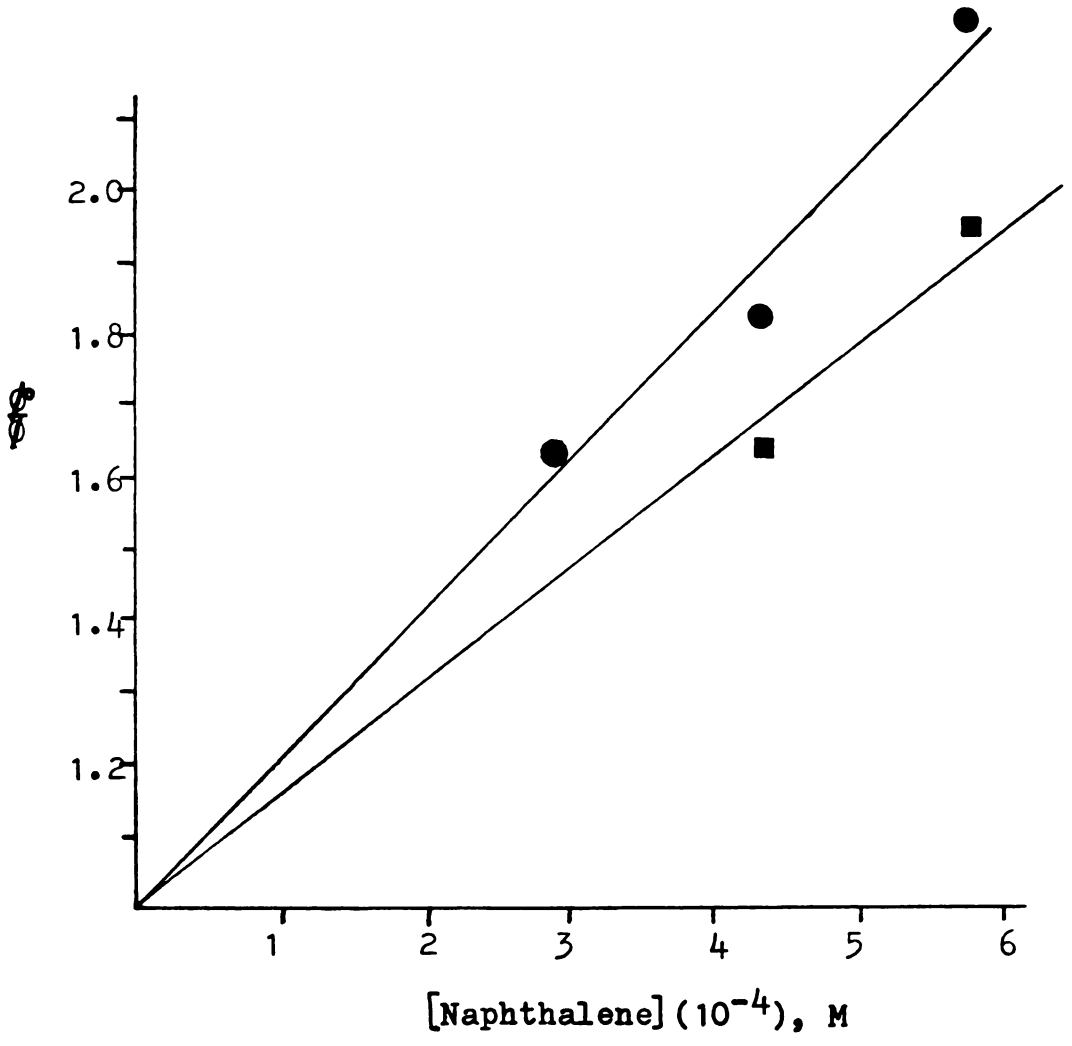


Figure 19. Stern-Volmer Plots: Photoreduction of ACP (0.01 M, ● and 0.2 M, ■) by 1.4 M p-Xylene in CH_3CN.

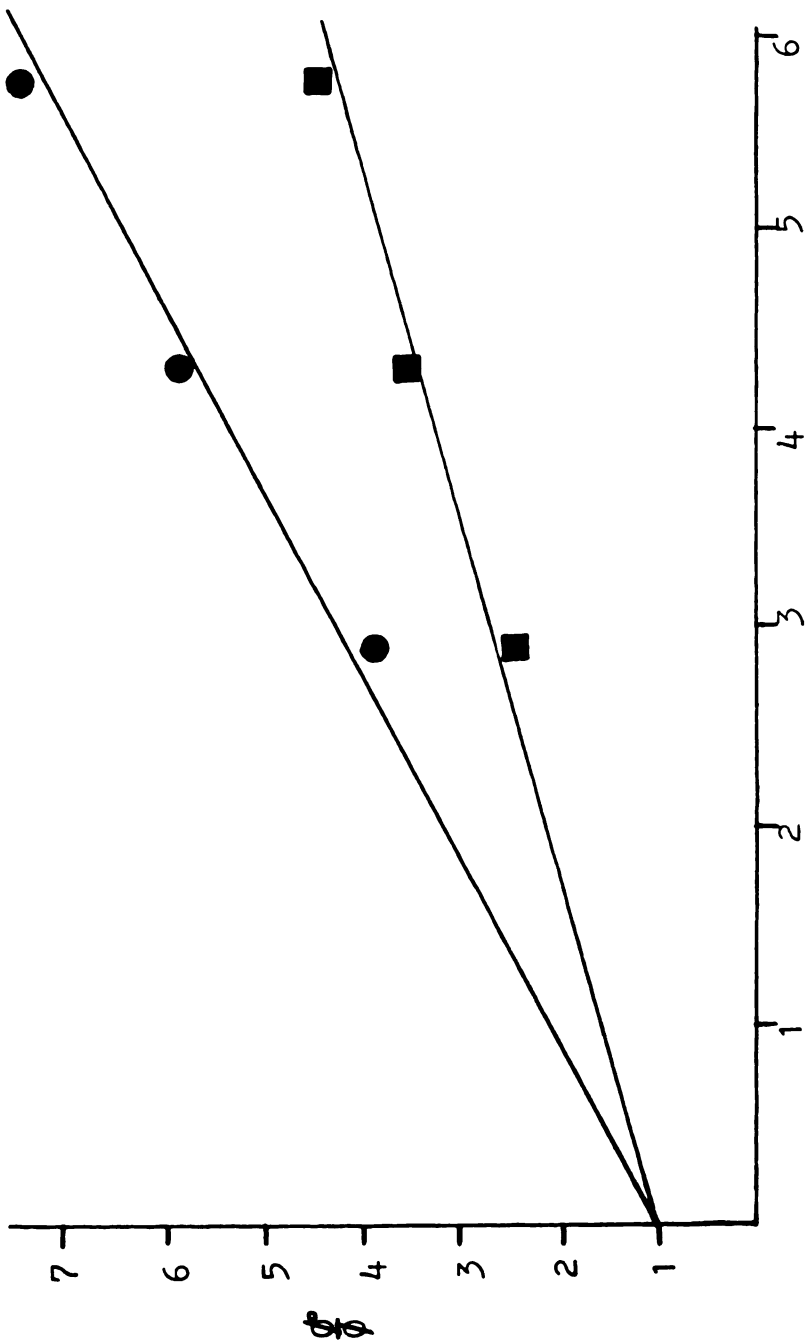


Figure 20. Stern-Volmer Plots: Photoreduction of ACP (0.01 M, ● and 0.2 M, ■) by 0.5 M p-Xylene in CH_3CN.

Table XIII. Spectroscopic Data for Substituted Acetophenones.

Subst.	λ(nm)	E_T[a]	E_T[b] (kcal)	E_T[f]	-Red Pot[c]	-Red Pot[b]	-Red Pot[e]	E^*_{red}[d]
m-CN	392	73.0	70.7 (iso-pent.)	73.8	1.75(40.3)	1.78(41.0)	----	-32.7
m-CF_3	392	73.0	71.5 (iso-pent.)	71.6	1.90(43.8)	1.86(42.8)	----	-29.2
p-CF_3	399	71.7	70.8 (iso-pent.)	70.9	1.81(41.7)	1.76(40.5)	1.80	-30.0
m-Cl	394	72.6	----------	----	1.94(44.7)	1.90(43.8)	----	-27.9
p-CN	413	69.2	69.5(EtOH)	69.6	1.58(36.4)	1.58(36.4)	1.62	-32.8
p-CH_3CO	426	67.1	67.7(EtOH)	67.7	1.56(35.9)	1.55(35.7)	----	-31.2
H	389	73.5	71.6(iso-pent.)	73.6	2.14(49.3	2.07(47.7)	2.09	-24.2
m-Me	401	71.3	71.4(EPA)	----	2.12(48.8)	2.08(47.9)	----	-22.5
p-t-Bu	394	72.6	----------	----	2.21(50.9)	----------	----	-21.7
p-Cl	399	71.7	70.6(iso-pent.)	72.1	1.87(43.1)	1.83(42.1)	1.93	-28.6
p-Me	396	72.2	71.5(EPA)	73.0	2.19(50.4)	2.15(49.5)	2.20	-21.8
3,4-di-Me	407	70.3	----------	----	2.20(50.7)	2.16(49.7)	----	-19.6
p-MeO	408	70.1	68.8(EPA)	----	2.23(51.4)	2.21(50.9)	2.28	-19.2

[a]Triplet energies determined from the 0,0 band (nm) of phosphorescence spectra at 77°K in 2-methyltetrahydrofuran, in kcal/mole. $E_T=2.86 \times 10^4/\lambda(nm)$.
[b]From Reference 116, substituted valerophenones: eV(kcal)/mole in CH_3CN.
[c]Reduction potential, by cyclic voltammetry vs SCE, in CH_3CN with TEAP, in eV(kcal)/mole 1 eV = 2303
[d]This work, in kcal/mole. [e]Ref. 118, in CH_3CN with TEAP:eV/mole. [f]Ref. 102, in hydrocarbon solvent: kcal/mole.

C. Photoreduction of Substituted Benzophenones by p-Xylene

A series of substituted benzophenones were synthesized or purchased and photoreduced in the presence of p-xylene.

Degassed 0.05 M ketone solutions with an alkyl benzoate standard ($PhCOOC_nH_{2n+1}$, n=7-9) in CH_3CN containing a) varying amounts of naphthalene quencher at a fixed donor concentration, or b) varying amounts of donor, were irradiated at 313, 335, or 365 nm. The concentrations of DTE were measured by vpc.

The results from Stern-Volmer quenching experiments are presented in Table XIV (Figures 21-24), and from the double reciprocal plots in Table XV (Figures 25-26).

Reduction potentials and triplet energies were measured, and the values are summarized in Table XVI.

D. Isotope Effect Studies

Degassed 0.05 M ketone solutions in acetonitrile containing $PhCOOC_7$ and varying amounts of toluene or toluene-d_8 were irradiated in a merry-go-round apparatus at 313 nm. The quantum yields of the bibenzyl product were used to plot ϕ^{-1} vs $[Donor]^{-1}$ (Figures 27-30). Table XVII summarizes the experimental results.

Table XIV. Photoreduction of Substituted Benzophenones in CH_3CN by p-Xylene: Stern-Volmer Experiments.

Subst.	[Ketone][a]	[p-Xylene][a]	Slope[a,b]	# Runs
m-CF_3	0.05	0.50	610±21	2
p-CN	0.02	0.50	659±50	2
m-Cl	0.05	0.51	660±60	2
p-CF_3	0.05	0.50	734±56	2
4,4'-Cl	0.02	0.51	2230	1
4,4'-F	0.02	0.50	2540±215	2
p-Cl	0.05	0.51	2490±15	2
H	0.05	0.50	2950±50	2
4,4'-t-Bu	0.02	0.50	4770	1
4,4'-Me	0.02	0.50	6130±572	2
4,4'-MeO	0.05	0.50	6370	1

[a]Average of all the experiments. Solutions were irradiated at >335 or 366 nm, and p-di-tolylethane photoproduct measured by vpc. Naphthalene used as quencher.

[b]Average deviation.

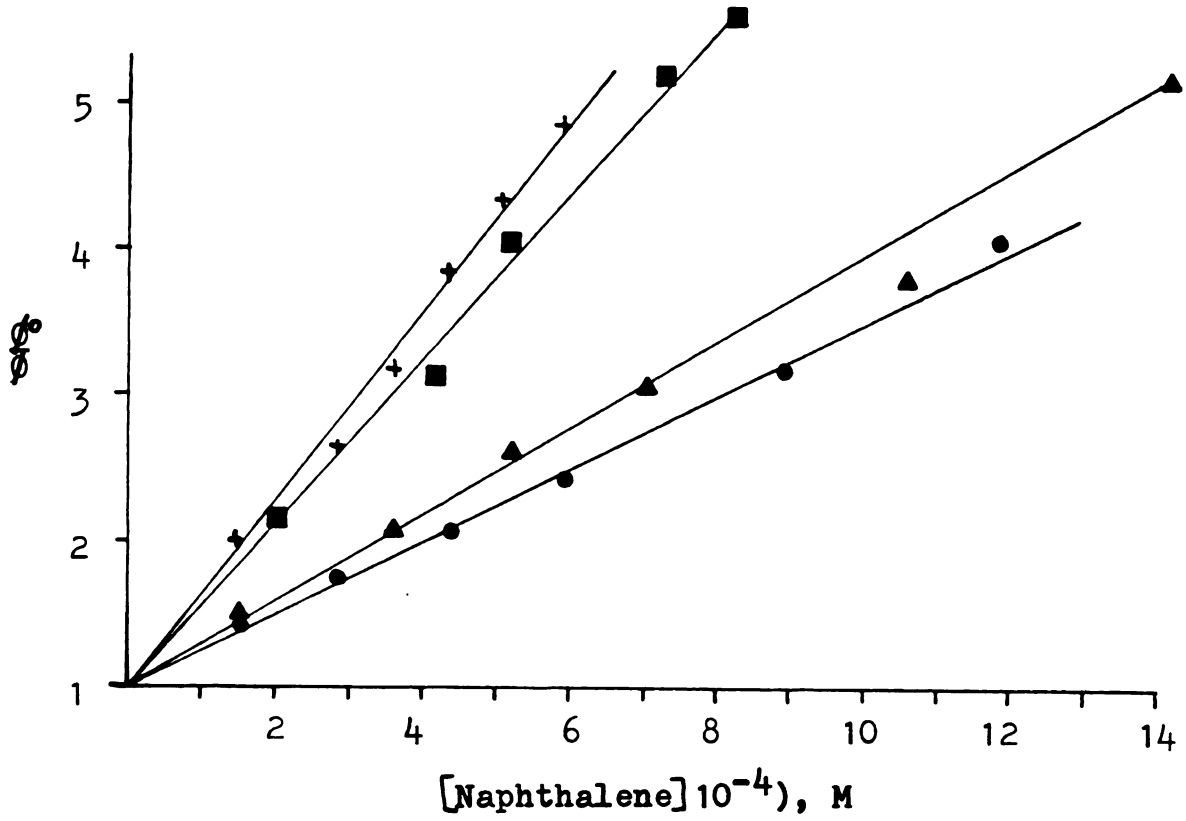


Figure 21. Stern-Volmer Plots: Photoreduction of Substituted Benzophenones in CH_3CN by 0.5 M p-Xylene: 4,4'MeO (+), 4,4'Me (■), p-Cl (●), and H (▲).

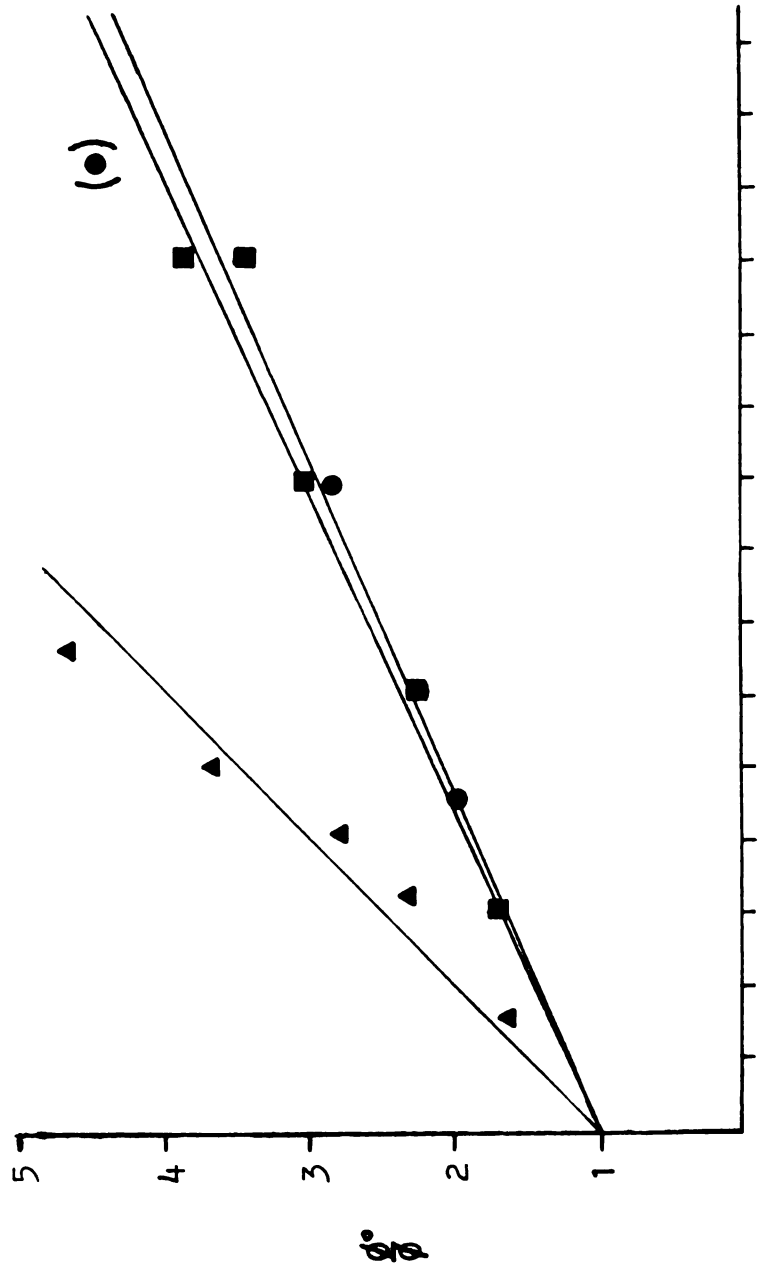


Figure 22. Stern-Volmer Plots: Photoreduction of Substituted Benzophenones in CH_3CN by 0.5 M p-Xylene: 4,4'-t-Bu (▲), 4,4'-F (■), and 4,4'-Cl (●).

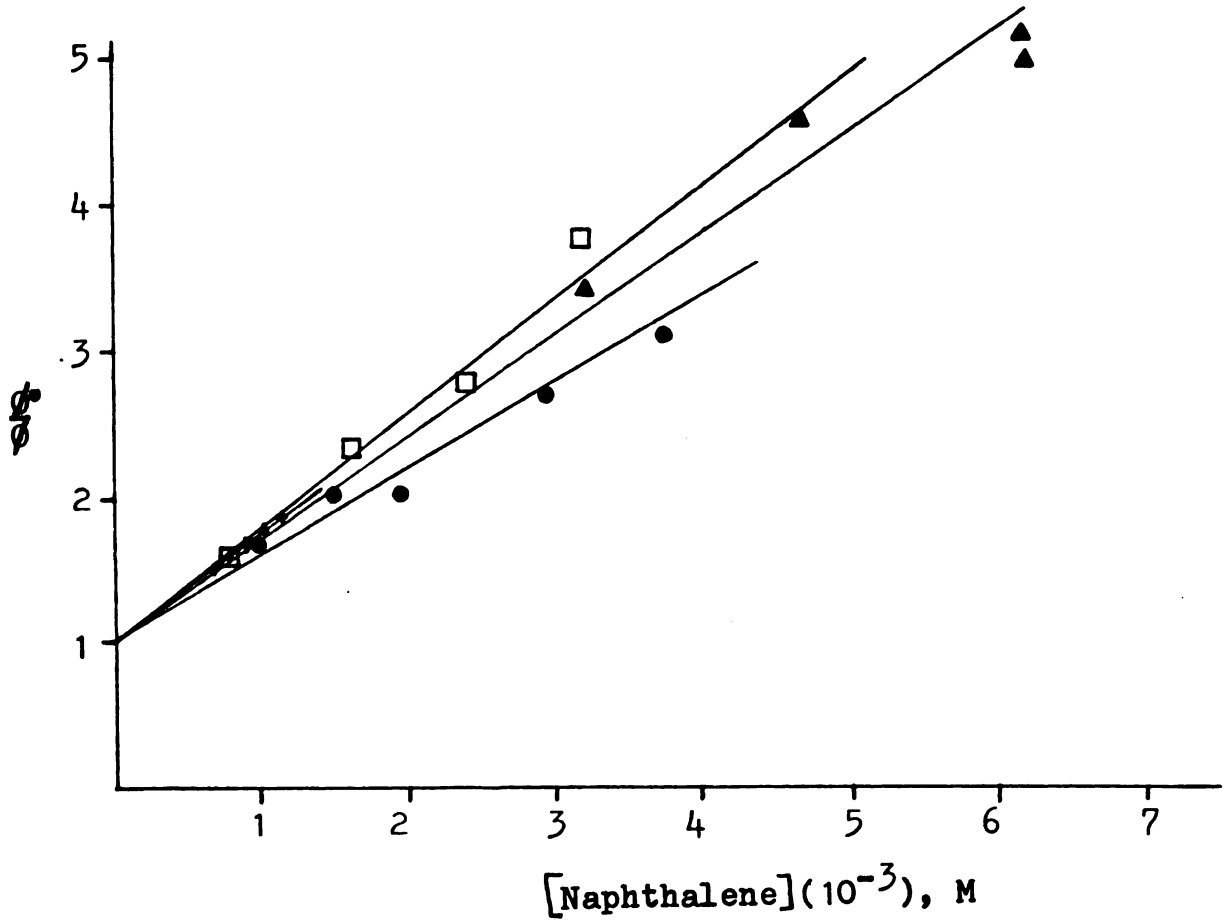


Figure 23. Stern-Volmer Plots: Photoreduction of Substituted Benzophenones in CH_3CN by 0.5 M p-Xylene: p-CF_3 (□), p-CN (▲), m-CF_3 (●), and m-Cl (+).

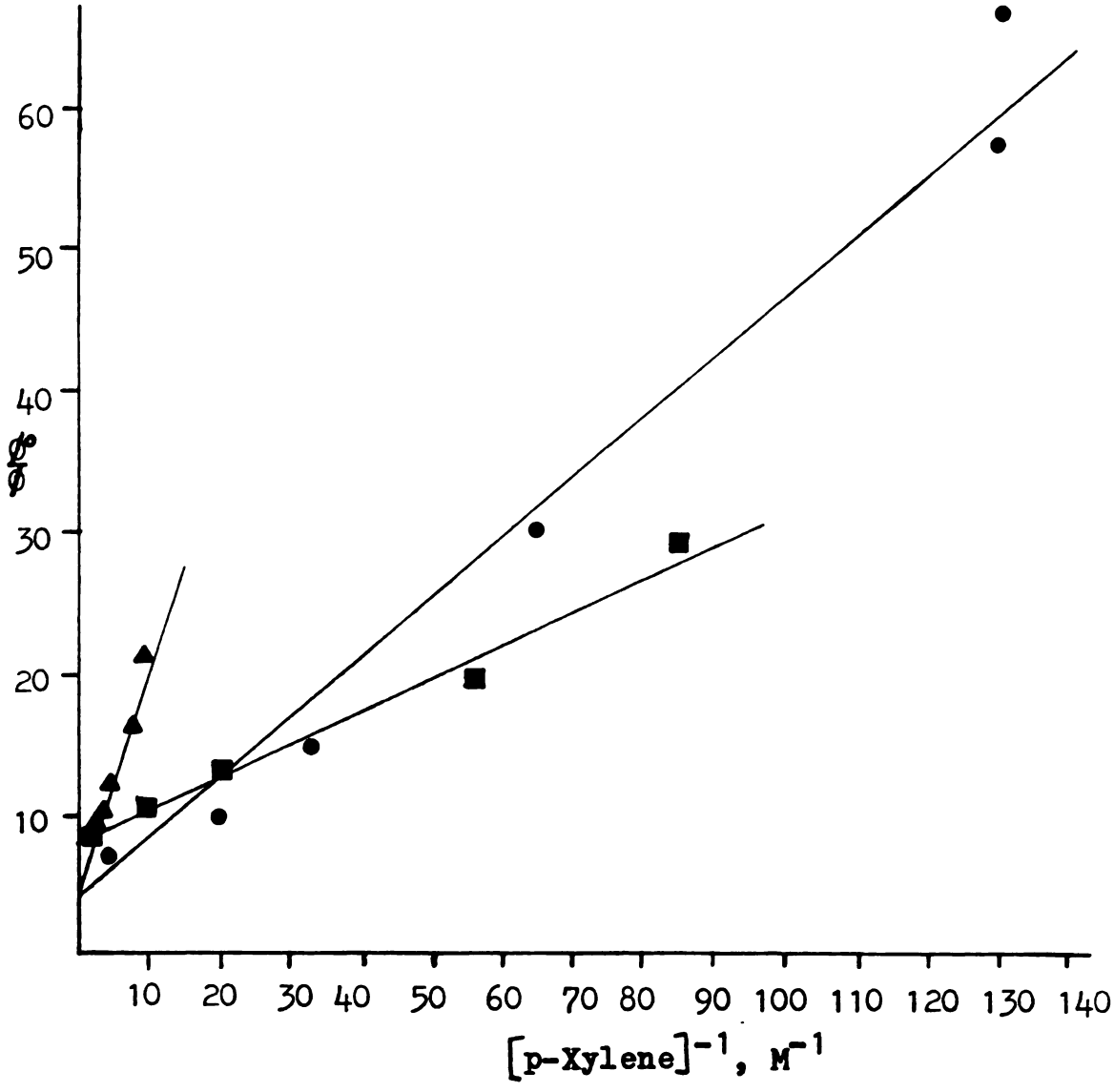


Figure 24. Double Reciprocal Plots: Photoreduction of Substituted Benzophenones in CH_3CN by p-Xylene: p-CF_3 (▲), p-CN (●), and m-CF_3 (■).

Table XV. Photoreduction of Substituted Benzophenones in CH_3CN by p-Xylene: Double Reciprocal Plots

Subst.	Slope[a,c]	Interc.[a,c]	Slope/Interc.[c]	ϕ_{Max}[b,c]	[Ketone] M	# Runs
m-CF_3	1.05±0.02	24.6±0.4	0.0427±0.0005	0.0407±0.0007	0.05	2
p-CN	0.112±0.008	8.95±0.44	0.0125±0.0015	0.118±0.008	0.02	2
m-Cl	0.60±0.10	19.0±1.0	0.0316±0.0066	0.0526±0.009	0.05	2
p-CF_3	0.33±0.00	17.9±0.1	0.0184±0.0002	0.0559±0.0001	0.05	2
4,4'-Cl	0.24	7.61	0.0315	0.131	0.05	1
4,4'-F	0.69±0.47	11.0±8.5	0.0627±0.0125	0.0909±0.062	0.05	3
p-Cl	0.56±0.05	10.9±0.2	0.0514±0.004	0.0917±0.0082	0.05	2
H	1.00±0.15	15.5±0.7	0.0645±0.0104	0.0645±0.0097	0.05	3
4,4'-t-Bu	1.62	4.20	0.386	0.238	0.02	1
4,4'-Me	2.06±0.10	4.68±0.69	0.440±0.074	0.214±0.0104	0.05	2
4,4'-MeO	7.01±1.92	5.12±0.92	1.37±0.24	0.195±0.053	0.02	3

[a]Average of all the experiments. Solutions were irradiated at 313 nm, and p-ditolylethane measured by vpc.

[b]Inverse of the intercept.

[c]Average deviation reported.

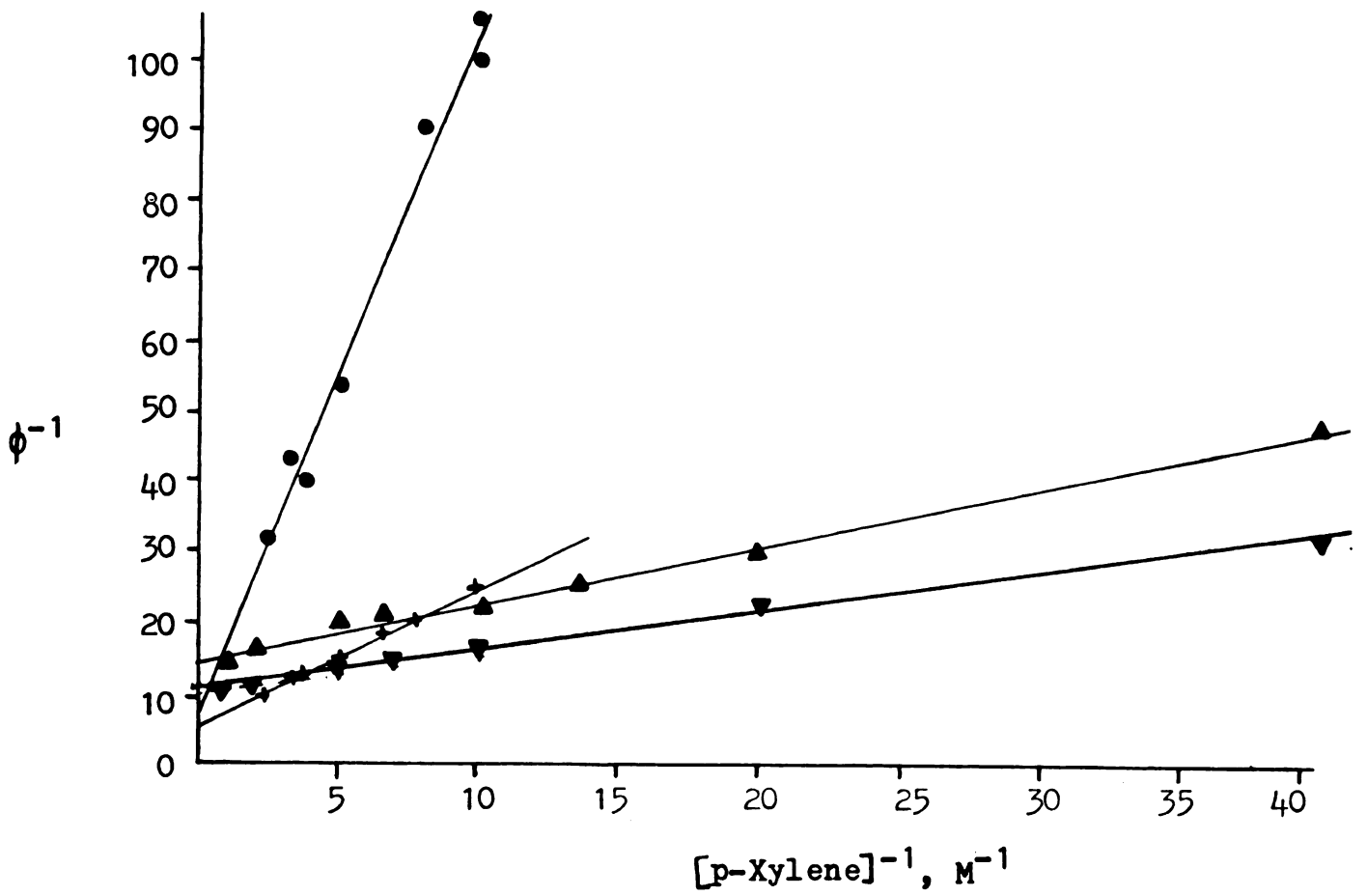


Figure 25. Double Reciprocal Plots: Photoreduction of Substituted Benzophenones in CH_3CN by p-Xylene: 4,4'-MeO (●), 4,4'-Me (+), p-Cl (▼), and H (▲).

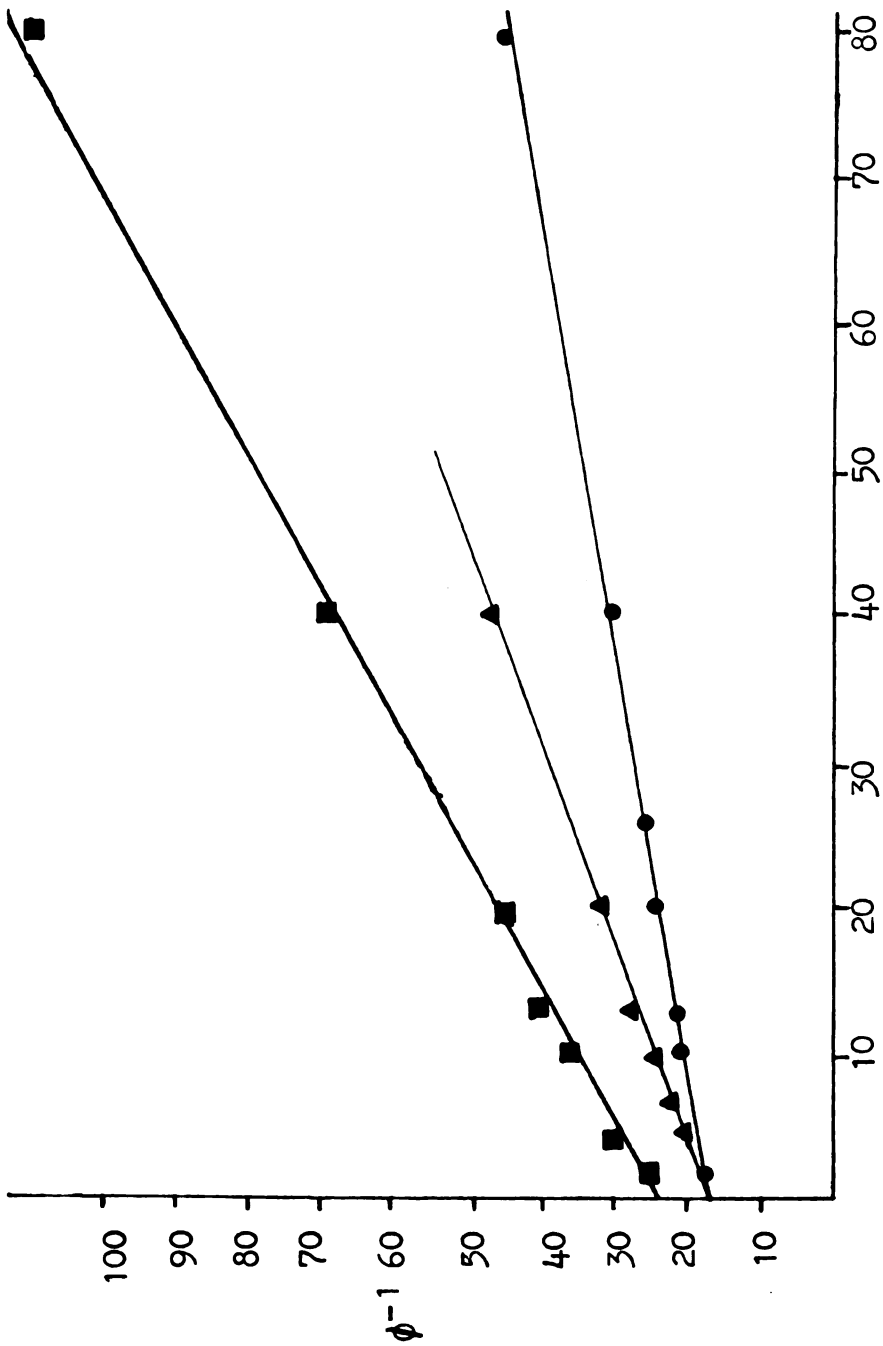


Figure 26. Double Reciprocal Plots: Photoreduction of Substituted Benzophenones in CH_3CN by p-Xylene: m-CF_3 (■), m-Cl (▲), and p-CF_3 (●).

Table XVI. Spectroscopic Data for Substituted Benzophenones.

Subst.	λ(nm)	E_T, kcal/mole[a]	E_T, kcal/mole[c]	$-E_{red}$[b]	$-E_{red}$[d]	E^*_{red}, kcal/mole[e]
m-CF_3	414	69.1	----	1.64(37.8)	----	-31.3
p-CN	428	66.8	66.4	1.42(32.7)	----	-34.1
m-Cl	416	68.8	68.4	1.67(38.4)	----	-30.3
p-CF_3	419	68.3	67.6	1.58(36.4)	1.61	-31.9
4,4'-di-Cl	417	68.6	----	1.67(38.5)	1.68	-30.1
4,4'-di-F	407	70.3	----	1.78(41.0)	----	-29.3
p-Cl	415	68.9	68.3	1.82(41.9)	----	-27.0
H	413	69.2	69.1	1.83(42.1)	1.84	-27.1
4,4'-di-t-Bu	413	69.2	----	1.87(43.1)	----	-26.1
4,4'-di-Me	414	69.1	68.9	1.90(43.8)	1.88	-25.3
4,4'-di-OMe	412	69.4	69.4	2.02(46.5)	2.01	-22.9

[a]Triplet energies determined from the 0,0 band (nm) of phosphorescence spectra at 77°K in 2-methyltetrahydrofuran. $E_T=2.86 \times 10^4/\lambda(nm)$.

[b]By cyclic voltammetry in acetonitrile relative to SCE. Values in eV(kcal)/mole. 1 eV = 23.03 kcal.

[c]From Reference 117.

[d]From Reference 119. Values in eV/mole.

[e]This work.

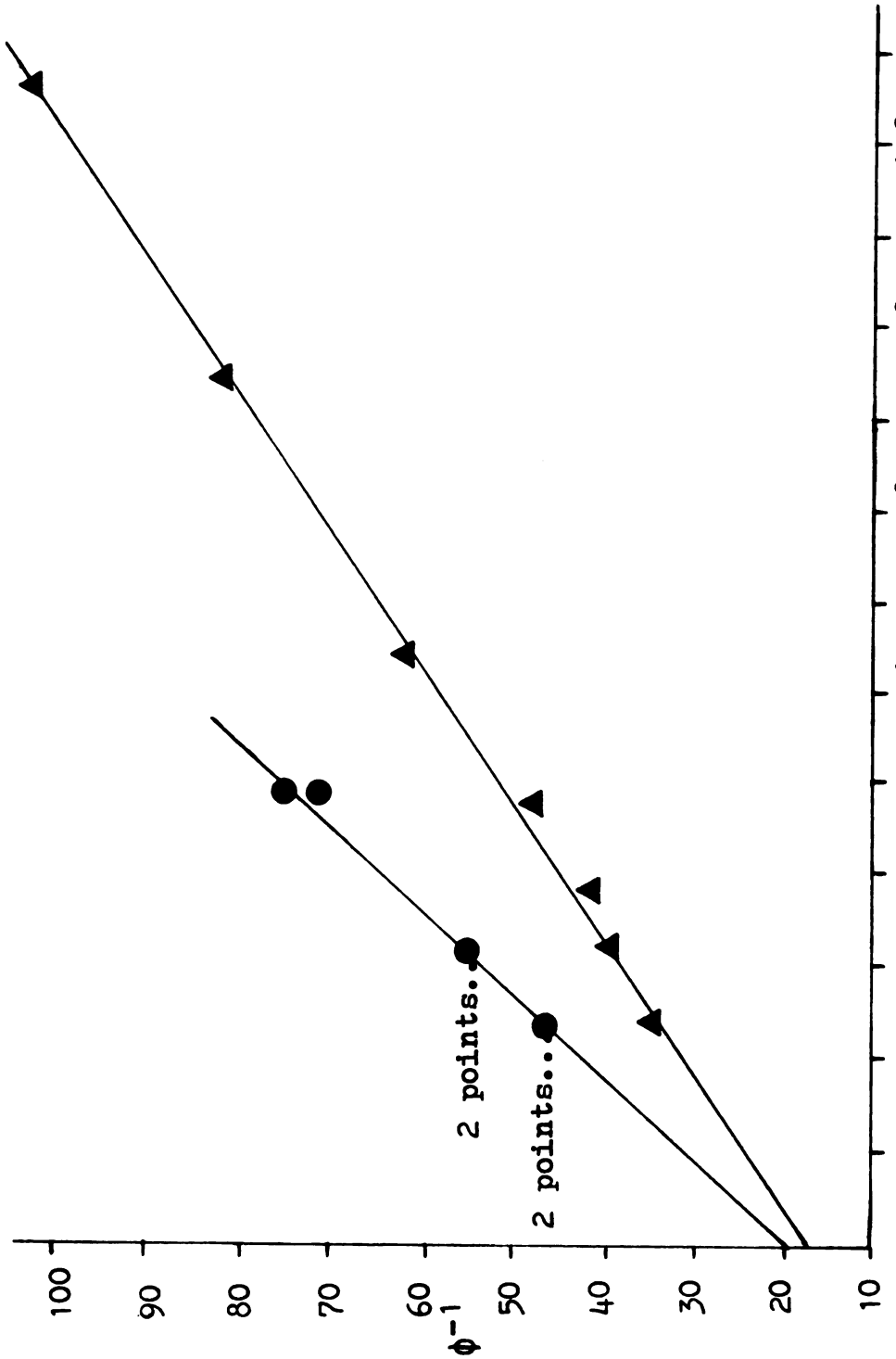


Figure 27. Photoreduction of p-MeO-TFA in CH_3CN: (●), Toluene-d_8; (▲), Toluene.

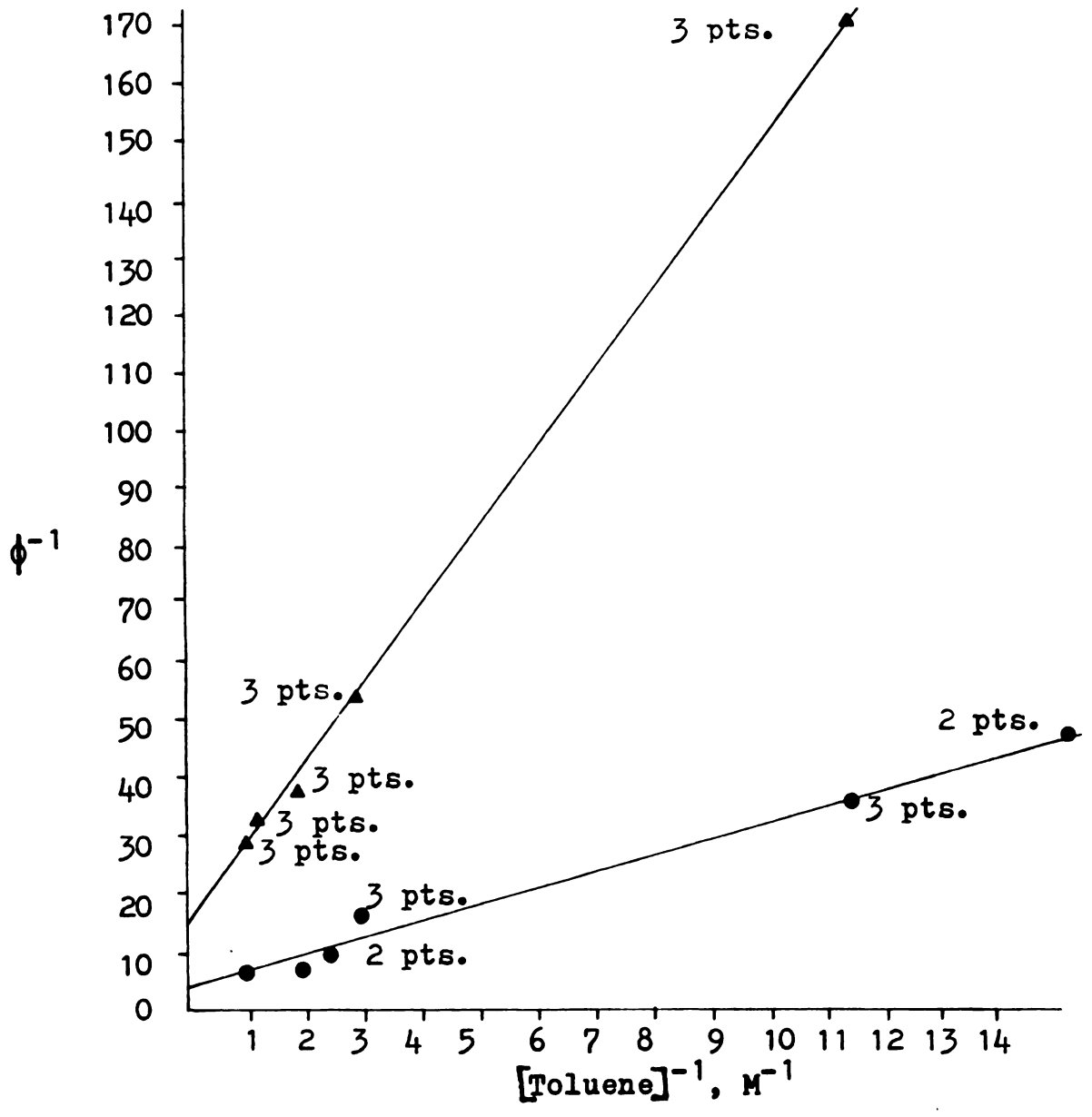


Figure 28. Double Reciprocal Plots: Photoreduction of p-CF_3-BP by Toluene$_{d_8}$ (top), and p-CF_3-BP by Toluene (bottom) in CH_3CN.

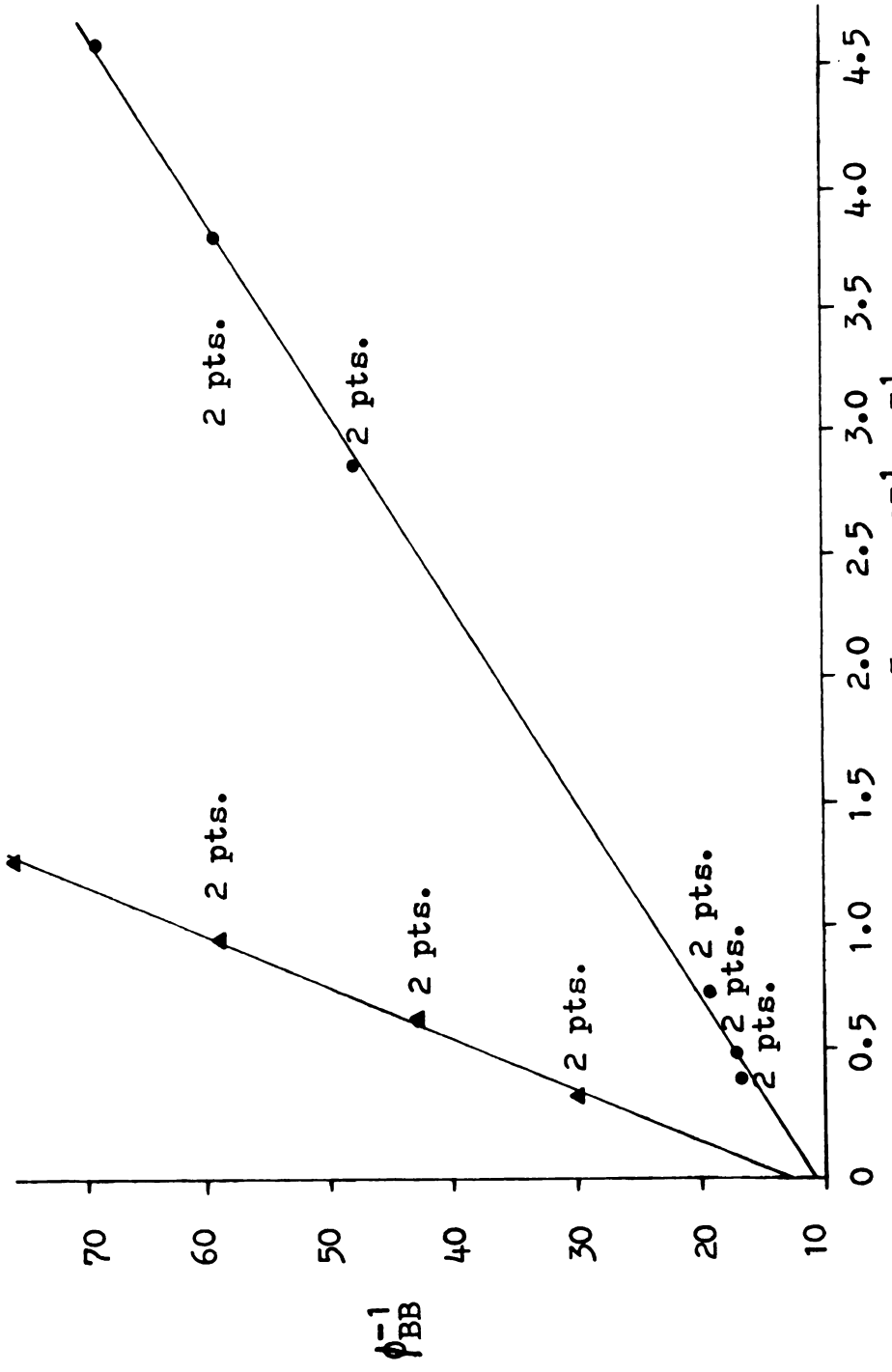


Figure 29. Double Reciprocal Plots: Photoreduction of BP by $Toluene_{d-8}$ (top), and Toluene (bottom) in CH_3CN.

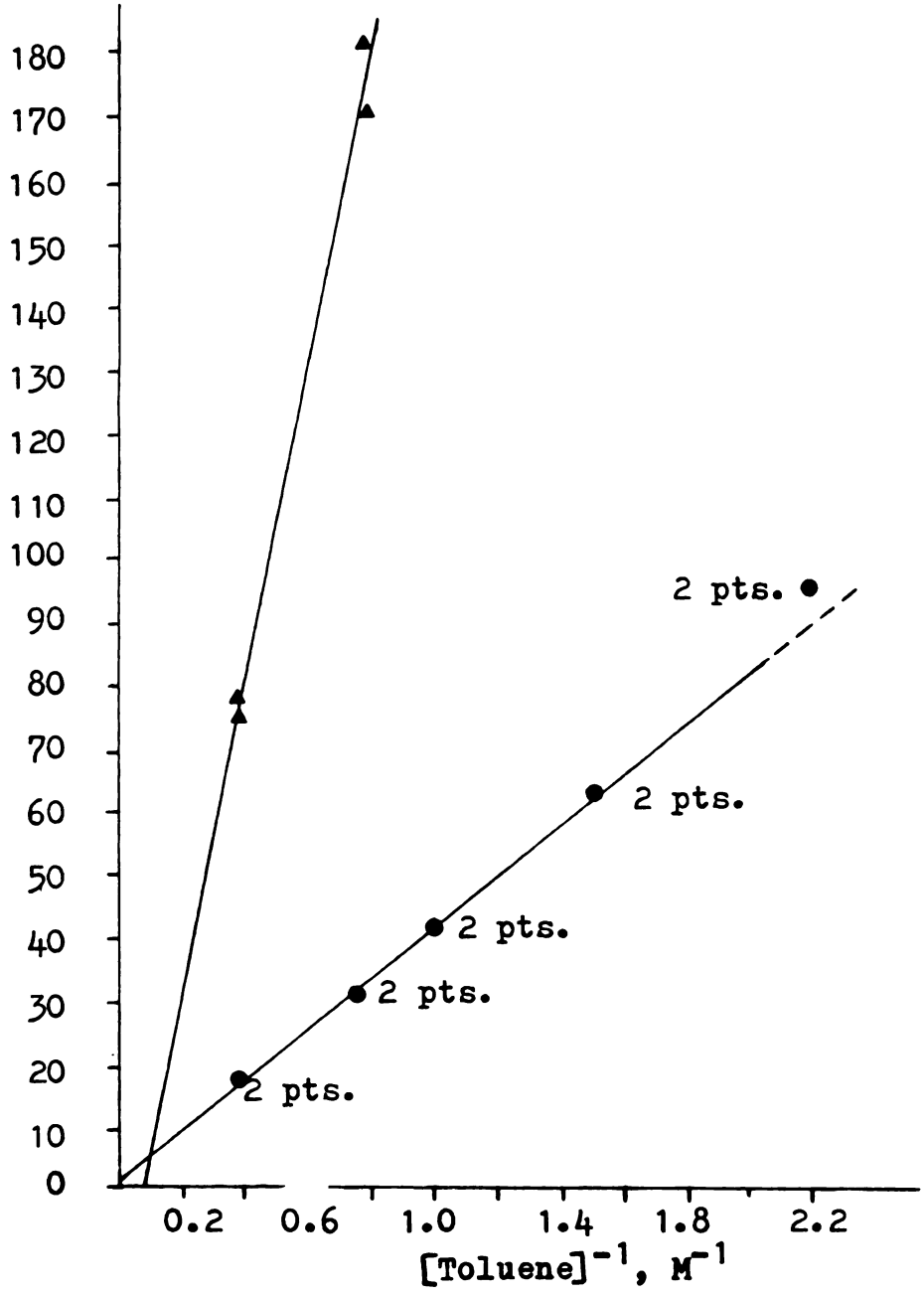


Figure 30. Double Reciprocal Plots: Photoreduction of 4,4'-di-Me-BP by Toluene$_{d_8}$ (top), and Toluene (bottom) in CH_3CN.

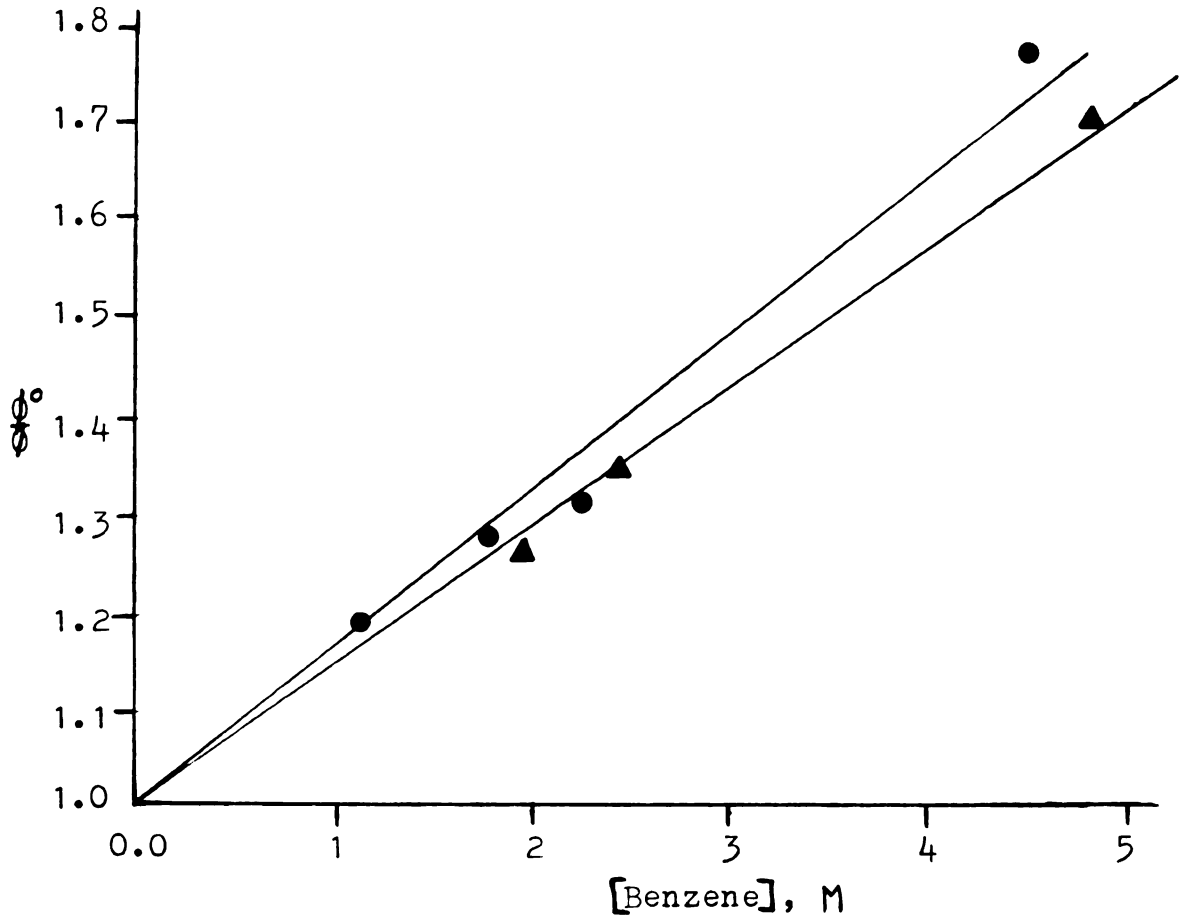


Figure 31. Stern-Volmer Quenching Plots: Photoreduction of p-CF_3-TFA by Toluene using Benzene (●) and $Benzene_{d-8}$ (▲) as Quencher.

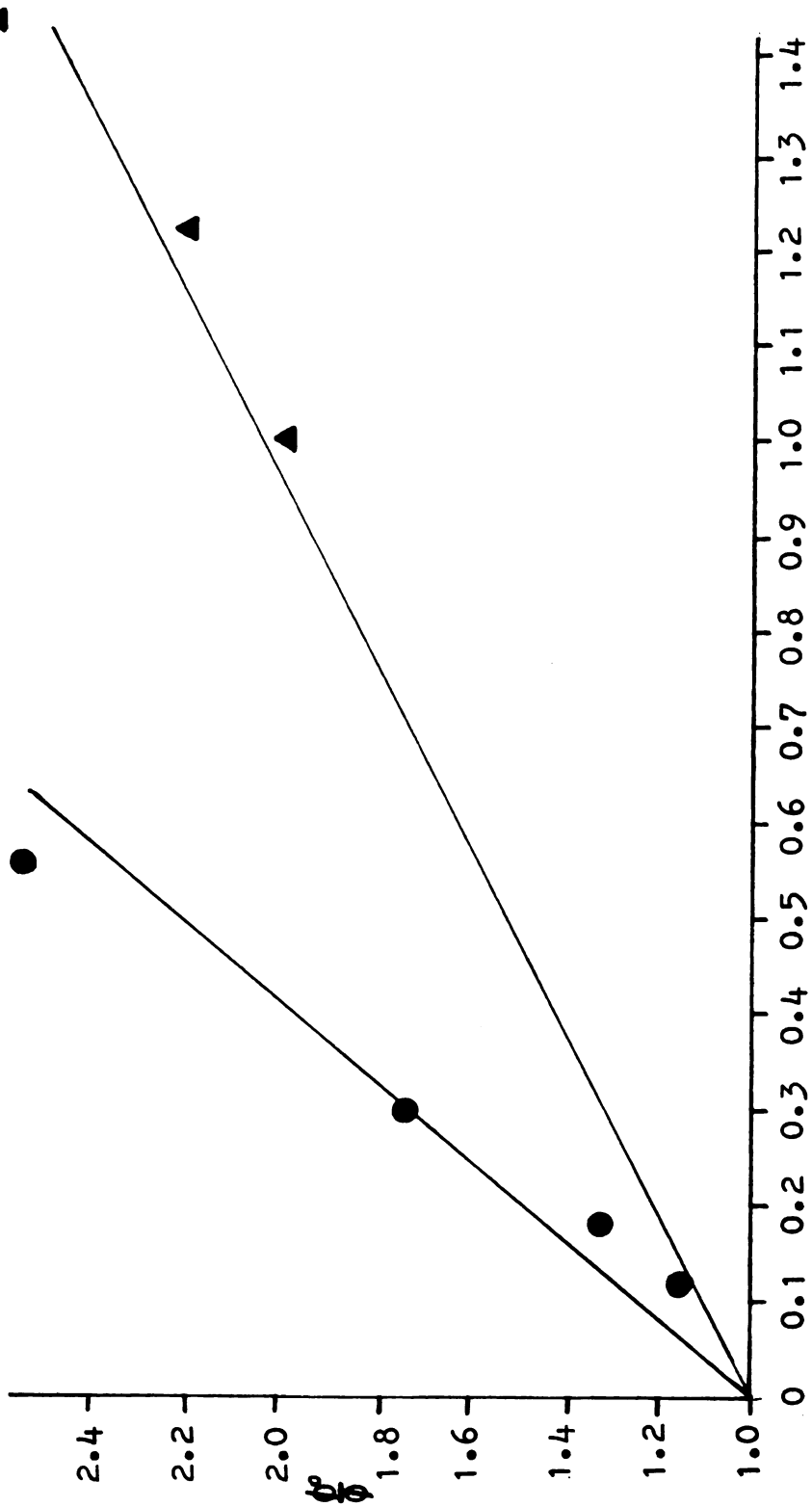


Figure 32. Phosphorescence Quenching Plots: $2.0X10^{-4}$ M 4,4'-di-Me-BP in Benzene, Quenched by Toluene (●), and $Toluene_{d-8}$ (▲).

Table XVII. Photoreduction by Toluene versus Toluene-d_8.

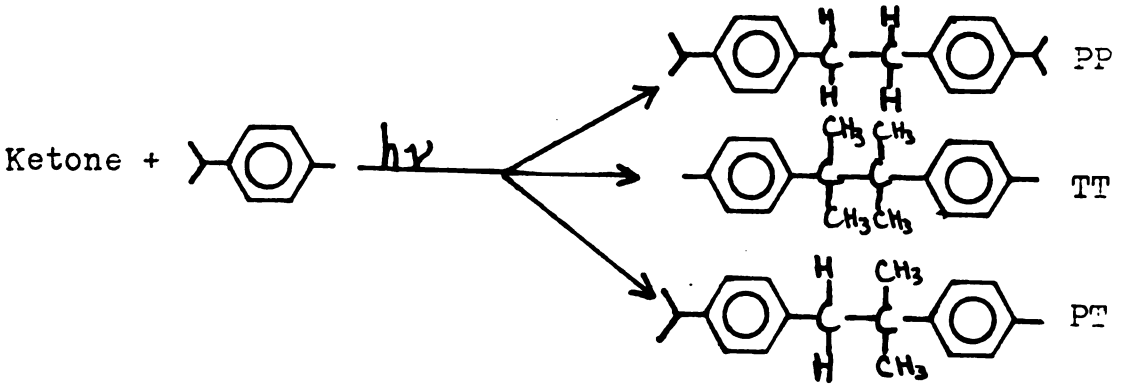
Ketone[a]	Donor	Slope	Inter.	Slope/Inter.	ϕ_{Max}[d]
p-MeO-TFA[b]	Toluene	75.3	15.6±1.6	4.83[e]±1.07	0.064±0.001
p-MeO-TFA	Toluene-d_8	109	20.4	5.34[e]	0.049
BP	Toluene	12.7	10.8	1.18[e]	0.093
BP	Toluene-d_8	48.9	12.9	3.79[e]	0.078
p-CF_3-BP	Toluene	2.78	4.54	0.612[e]	0.22
p-CF_3-BP	Toluene-d_8	13.4	15.4	0.870[e]	0.065
4,4'-Me-BP	Toluene	40.1	1.44	27.8[e]	
4,4'-Me-BP	Toluene-d_8	252	-19.2	175[c,e]	
4,4'-Me-BP	Toluene	2.4[f]			
4,4'-Me-BP	Toluene-d_8	1.0[f]			
p-CF_3-TFA	Toluene	0.16 (Quencher = benzene)[g]			
p-CF_3-TFA	Toluene	0.14 (Quencher = benzene-d_{10})[g]			

[a]Single run, in CH_3CN solvent. [b]Average of 2 runs. [c]Assuming an intercept of 1.44, as found when using toluene as the donor. [d]Inverse of the intercept. [e]Double reciprocal plot. [f]Phosphorescence quenching: slope = $k_r\tau$. Benzene solvent. [g]Stern-Volmer plot: slope = $k_q\tau$.

E. Photoreduction by p-Cymene

Substituted α,α,α-trifluoroacetophenones, acetophenones and benzophenones, 0.1 M in CH_3CN, were irradiated at 313 nm in the presence of 1 M p-cymene.

The three hydrocarbons formed, PP, PT, and TT shown in Scheme 4 were available from a previous study[120] and were used to identify the photoproducts observed.



Scheme 4. Hydrocarbon Photoproducts from the Reaction of Ketone and p-Cymene.

The percentage of each hydrocarbon relative to total hydrocarbon product was determined by vpc and the values are given in Tables XVIII-XX. It is assumed that relative standardization factors are identical.

Table XVIII. Photoreduction of Substituted α,α,α-Trifluoroacetophenones in CH_3CN by 1 M p-Cymene.

Subst.[a]	%PT	%TT	%PP	# Runs
m-CF_3	41	0	59	2
p-CF_3	52	0	48	1
m-Cl	37	8	56	2
p-F	35	5	60	2
H	29	13	58	1
p-Cl	43	11	47	2
p-t-Bu	44	21	35	1
p-CH_3[b]	42	16	43	1
3,4-di-Me	46	22	33	2
p-MeO	46	23	32	1
p-Ac	43	42	15	1

[a] 0.1 M ketone solutions. ±5% from the average.

[b] The photoreduction of m-Me-ACP gave alcohols which could not be separated from PP even though a wide variety of gc columns were used.

Table XIX. Photoreduction of Substituted Acetophenones in CH_3CN by 1 M p-Cymene.

Subst.[a]	%PT	%TT	TPP	# Runs
α,α-F_2	39	7	55	2
p-CN	52	25	24	1
p-Cl	44	29	27	2
3,4-di-Cl	48	29	24	1
m-CN	45	35	20	1
m-CF_3	45	36	19	1
m-Cl	44	37	19	1
p-CF_3	44	38	19	1
α-F	45	38	17	1
p-F	43	41	16	1
p-MeO	42	41	17	1
m-CH_3	41	45	15	2
p-CH_3	40	47	14	3
p-t-Bu	41	48	12	1
3,4-di-Me	40	48	13	2
H	41	47	11	3
p-CH_3CO	32	68	--[b]	1

[a] 0.1 M ketone solutions. ±5% from the average.

[b] ~20% of PT, estimated from vpc trace.

Table XX. Photoreduction of Substituted Benzophenones in CH_3CN by 1 M p-Cymene.

Subst.[a]	%PT	%TT	%PP	# RUNS
p-CN	42	40	19	2
m-CF_3	34	56	10	1
m-Cl	39	51	11	1
p-CF_3	42	43	15	1
4,4'-di-Cl	41	43	16	1
4,4'-di-F	41	46	13	2
p-Cl	42	48	10	1
H	44	49	8	3
4,4'-di-t-Bu	31	64	5	1
4,4'-di-Me	34	59	8	1
4,4'-di-MeO	33	59	8	1
3,4-di-Cl	32	61	7	1
3,3'-di-Me	41	42	17	1

[a] 0.1 M ketone solutions. ±5% from the average.

F. Photoreduction of Substituted Benzophenones by 2,3-Dimethylbutane in CCl_4

Degassed 0.1 M solutions of ketone with 1.4 M 2,3-dimethylbutane in CCl_4 were irradiated at 313 nm. Table XXI summarizes the relative ratios of 2-chloro-2,3-dimethylbutane (2-Cl-B) and 1-chloro-2,3-dimethylbutane (1-Cl-B) produced. From this table it is observed that hexachloroethane accounts for 2/3 of the tri-chloromethyl radical formed. Chloroform and cross coupling products involving the ketyl and dimethylbutyl radicals are assumed to account for the rest of the trichloromethyl radicals formed.

G. Photoreduction by Cyclopentane

Solutions of benzophenone (0.1 M) with cyclopentane (0.1 M) in CCl_4 were irradiated at 313 nm. Table XXII compares the amount of cyclopentane consumed with chlorocyclopentane produced.

In the following experiment, 0.1 M solutions of α,α,α-trifluoroacetophenone were irradiated in the presence of 1.0 M cyclopentane in CCl_4. Table XXIII shows the amount of ketone consumed, and chlorocyclopentane and cross product formed.

The relative reactivity of cyclopentane and cyclohexane were compared by co-irradiating both compounds together in CCl_4 in the presence of 0.1 M acetophenone. The

Table XXI. Photoreduction of Substituted Benzophenones by 1.4 M 2,3-Dimethylbutane in CCl_4.

Ketone[a]	2-Cl-B/1-Cl-B[b]	$[\cdot CCl_3]/[2\text{-Cl-B}]$
4,4'-di-MeO-BP	30.4	
4,4'-di-Me-BP	38.6	0.50
BP	74.5	0.68
4,4'-di-Cl-BP	108	
4,4'-di-F-BP	117	
4-CN-BP	228	0.68

[a] 0.1 M ketone solutions.

[b] 1-Cl-B=1-chloro-2,3-dimethylbutane; 2-Cl-B = 2-chloro-2,3-dimethylbutane. Ratio reported is that taken directly from vpc analysis.

[c] $[\cdot CCl_3]$ is twice that of hexachloroethane concentration produced.

Table XXII. Photoreduction of Benzophenone by Cyclopentane in CCl_4. Ratio of Chlorocyclopentane Produced to Cyclopentane Consumed.

	-[CP], $M_{(consumed)}$[a]	[Cl-CP], M[b]
Exp #1	0.0303	0.0306
Exp. #2	0.0439	0.0426

[a]Cyclopentane consumed. Original concentration=0.1 M.

[b]Cl-CP=chlorocyclopentane.

Table XXIII. Photoreduction of 0.10 M TFA in CCl_4 by 1 M Cyclopentane: Concentration of Major Photoproducts.

$-[TFA]_{(consumed)}$[a]	[Cl-CP][b]	[KP][c]	[KP]/[Cl-CP]
2.05	3.37	0.394	0.12
2.15	3.70	0.421	0.11
6.95	9.57	1.02	0.11
8.11	9.76	0.890	0.091

[a]$X10^{-2}$ M. Final concentration determined by vpc, which was subtracted from the initial concentration weighed out.

[b]$X10^{-2}$ M. Cl-CP=chlorocyclopentane.

[c]$X10^{-2}$ M. KP=ketyl-pentyl cross-coupling product.

concentrations of the major photoproducts, chlorocyclopentane and chlorocyclohexane, are reported in Table XXIV.

Table XXIV. Photoreduction of 0.1 M ACP by Cyclopentane and Cyclohexane in CCl_4: Concentration of Chlorohydrocarbons Formed.

[CP][a]	[CH][b]	[Cl-CP][c]	[Cl-CH][d]	[Cl-CP]/[Cl-CH]
1.0	1.0	0.00737	0.00830	0.89
1.0	1.0	0.0144	0.0140	1.03
1.0	1.0	1.91	1.94	0.98
1.0	2.0	2.74	5.15	0.53
1.0	2.0	5.61	10.6	0.53

[a]CP=cyclopentane. Concentration reported is that weighed out, in moles/liter. 0.1 M acetophenone.

[b]CH=cyclohexane. Concentration reported is that weighed out, in moles/liter.

[c]Cl-CP=chlorocyclopentane, in moles/liter.

[d]Cl-CH=chlorocyclohexane, in moles/liter.

Some representative substituted acetophenones, benzophenones, and α,α,α-trifluoroacetophenones were photolyzed in CCl_4 in the presence of cyclopentane. The experimental results from Stern-Volmer plots are shown in Table XXV,

Table XXV. Photoreduction of Several Phenyl Alkyl Ketones by Cyclopentane in CCl_4: Stern-Volmer Experiments.

Ketone[a]	[Ketone]	[Cyclopentane], M	Slope	# Runs
ACP	0.02	1.01	1500	1
p-CF_3-ACP	0.03	1.00	908	1
p-CH_3-ACP	0.03	1.03	840±40	2
BP	0.05	1.07	674±191	3
BP	0.05	1.09[b]	547	1
BP	0.05	1.06[c]	933	1
BP	0.05	10.4[c]	375	1
4,4'-Me-BP	0.05	1.05	597±126	2
4,4'-MeO-BP	0.025	1.03	249±49	2
TFA	0.05	1.01	603±35	3
m-Cl-TFA	0.05	1.05	965±194	2
p-MeO-TFA	0.05	1.02	95.7±69	3
p-MeO-TFA	0.05	1.03[b]	3500	1
p-Me-TFA	0.05	1.03[b]	4400	1
p-Me-TFA	0.05	1.06[d]	2400	1
3,4-di-Me-TFA	----	----[e]	----	1

[a] ACP=acetophenone; BP-benzophenone; TFA=α,α,α-Trifluoroacetophenone. Chlorocyclopentane product analyzed unless otherwise stated.

[b] The ketyl-benzyl cross product was analyzed.

[c] Bicyclopentyl product was analyzed.

[d] 4 experiments curved and levelled off at higher naphthalene concentration.

[e] The plot was insensitive to quencher concentration.

and from the double reciprocal plots in Table XXVI (Figures 33-55). Several of the Stern-Volmer plots curve.

The quantum yield of chlorocyclopentane from the photoreduction of BP in the presence of 1 M cyclopentane was measured by vpc as a function of conversion (Table XXVII). The total amount of light absorbed affected the product quantum yield very little.

The effect of light intensity on photoproduct quantum yields for the photoreduction of BP in CCl_4 by 1 M cyclopentane was examined by varying the pathlength of the filter solution (Table XXVIII). Varying the pathlength by a factor of 3 led to essentially the same product quantum yields.

Degassed 0.02 M BP solutions in CCl_4 containing 1 M cyclopentane were irradiated at 313 nm for various lengths of time. Irradiation for 3 hours gave a very pale yellow solution, but the UV spectrum (Figure 56) resembled closely that of the non-photolyzed solution. Irradiation for 5 hours produced a slightly darker yellow solution, but once again the UV spectrum resembled the non-photolyzed sample. Photolysis for 36 hours gave a darker yellow solution, a decrease in the n,π^* absorption of BP, and a new absorption appeared, beginning around 500 nm. A final sample was irradiated for 48 hours, giving a dark yellow solution which absorbed strongly beginning around 500 nm. The yellow color produced did not disappear when the solutions were left at room temperature for several days.

Table XXVI. Photoreduction of Several Phenyl Alkyl Ketones by Cyclopentane in CCl_4. Values from ϕ^{-1} Versus $[Donor]^{-1}$ Plots.

Ketone	Slope[b]	Intercept.[b]	Slope/ Intercept	ϕ_{Max}[c]	[Ketone] M	# Runs
ACP	2.06	2.23	0.924	0.45	0.02	1
p-CF_3-ACP	0.134	1.67	0.0802	0.60	0.03	1
p-CH_3-ACP	2.58	2.61	0.989	0.38	0.03	1
BP	0.497	3.79	0.131	0.26	0.05	1
4,4'-Me-BP	2.65	9.13	0.290	0.110	0.05	1
4,4'-MeO-BP	8.37±0.15	11.0±0.9	0.761±0.045	0.0909	0.025	2
TFA	1.19	3.97	0.300	0.252	0.05	1
m-Cl-TFA	1.75	3.54	0.494	0.282	0.05	1
p-MeO-TFA	11.1±2.6	18.7±2.2	0.594±0.083	0.0535	0.05	2
p-Me-TFA	3.34	2.98	1.12	0.336	0.05	1

[a]ACP = acetophenone; BP = benzophenone; TFA = α,α,α-trifluoroacetophenone.

[b]Chlorocyclopentane product examined. Average of all experiments for a given compound.

[c]Reciprocal of the intercept value.

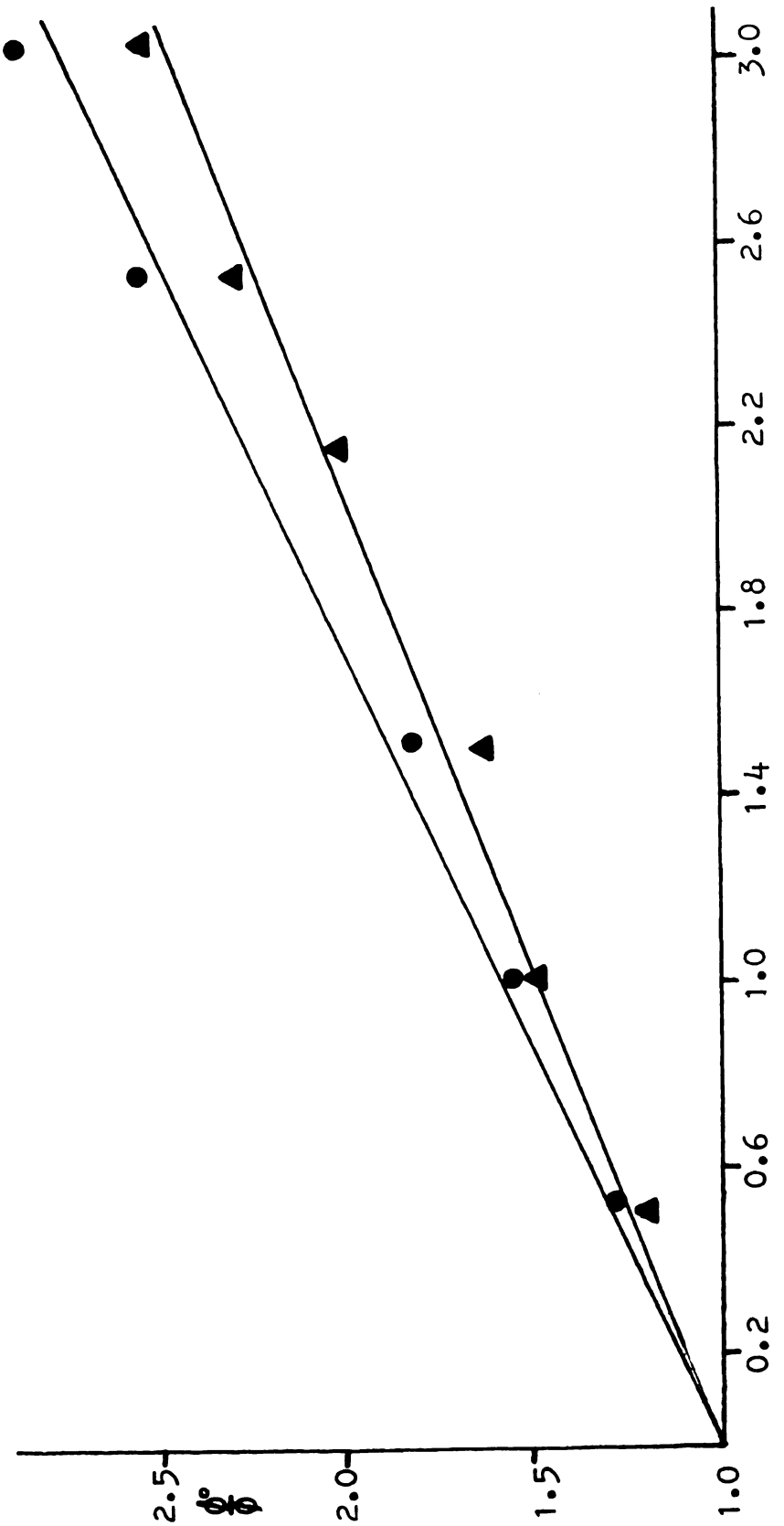


Figure 33. Stern-Volmer Plots: Photoreduction of BP by 1 M Cyclopentane in CCl_4. (●) Cross Product, (▲) Chlorocyclopentane Monitored.

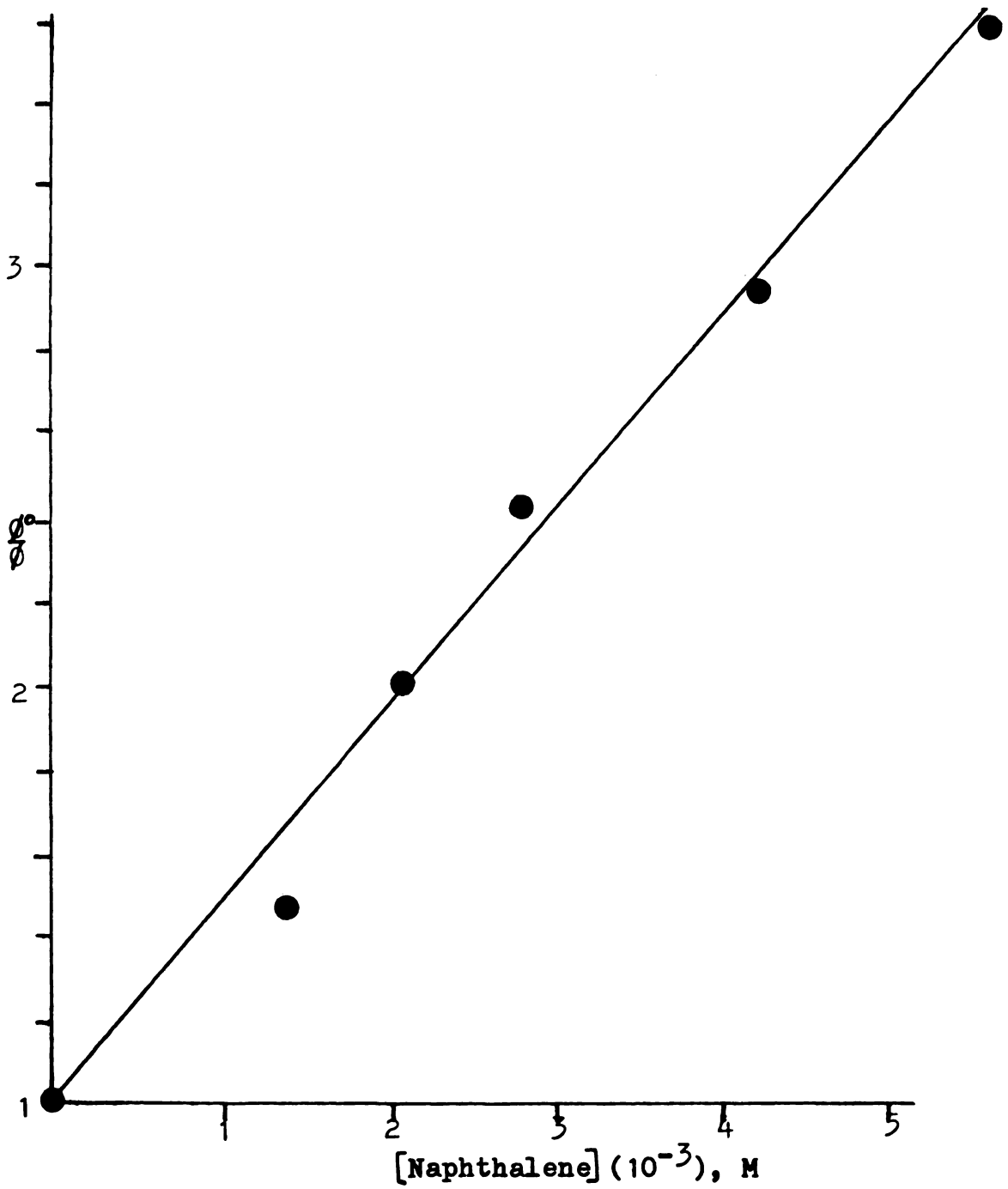


Figure 34. Stern-Volmer Plot: Photoreduction of 4,4'-Me-BP by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Product Monitored.

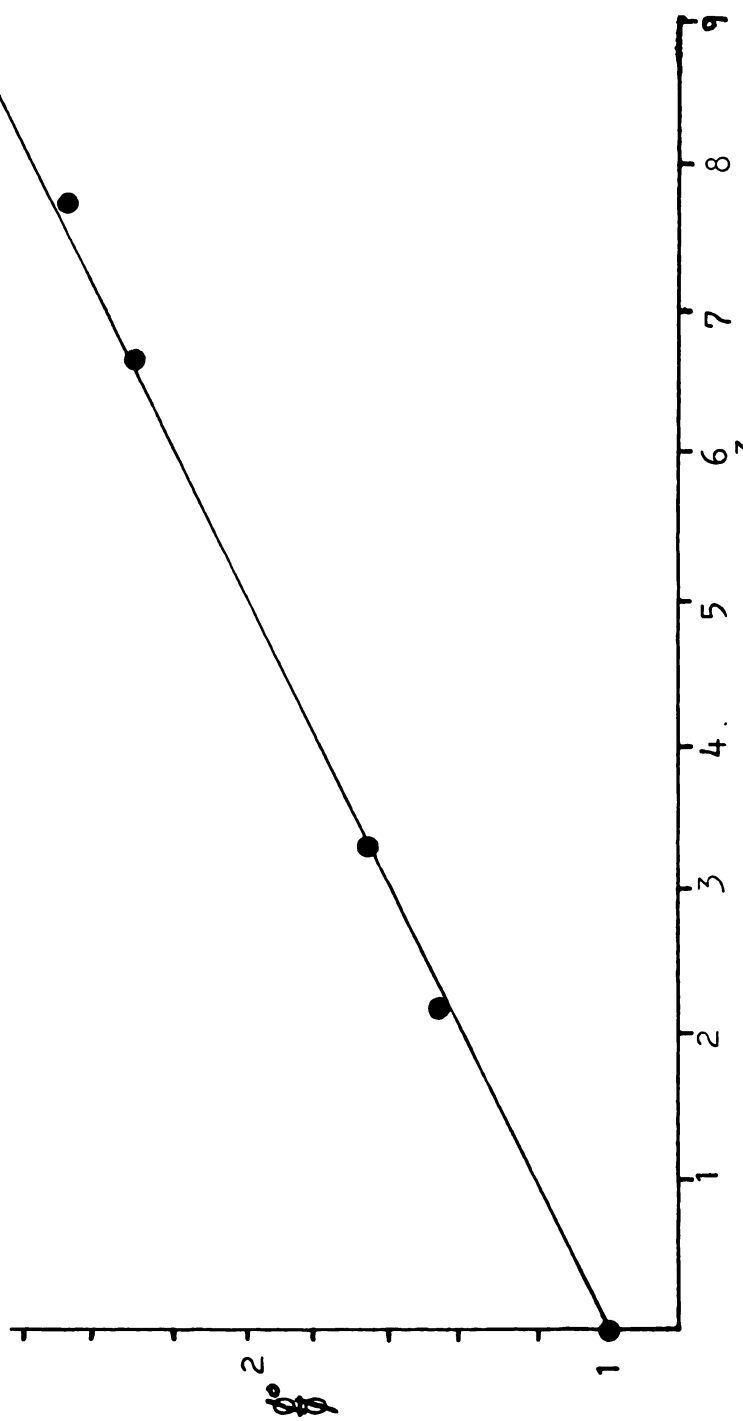


Figure 35. Stern-Volmer Plot: Photoreduction of 4,4'-MeO-BP by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

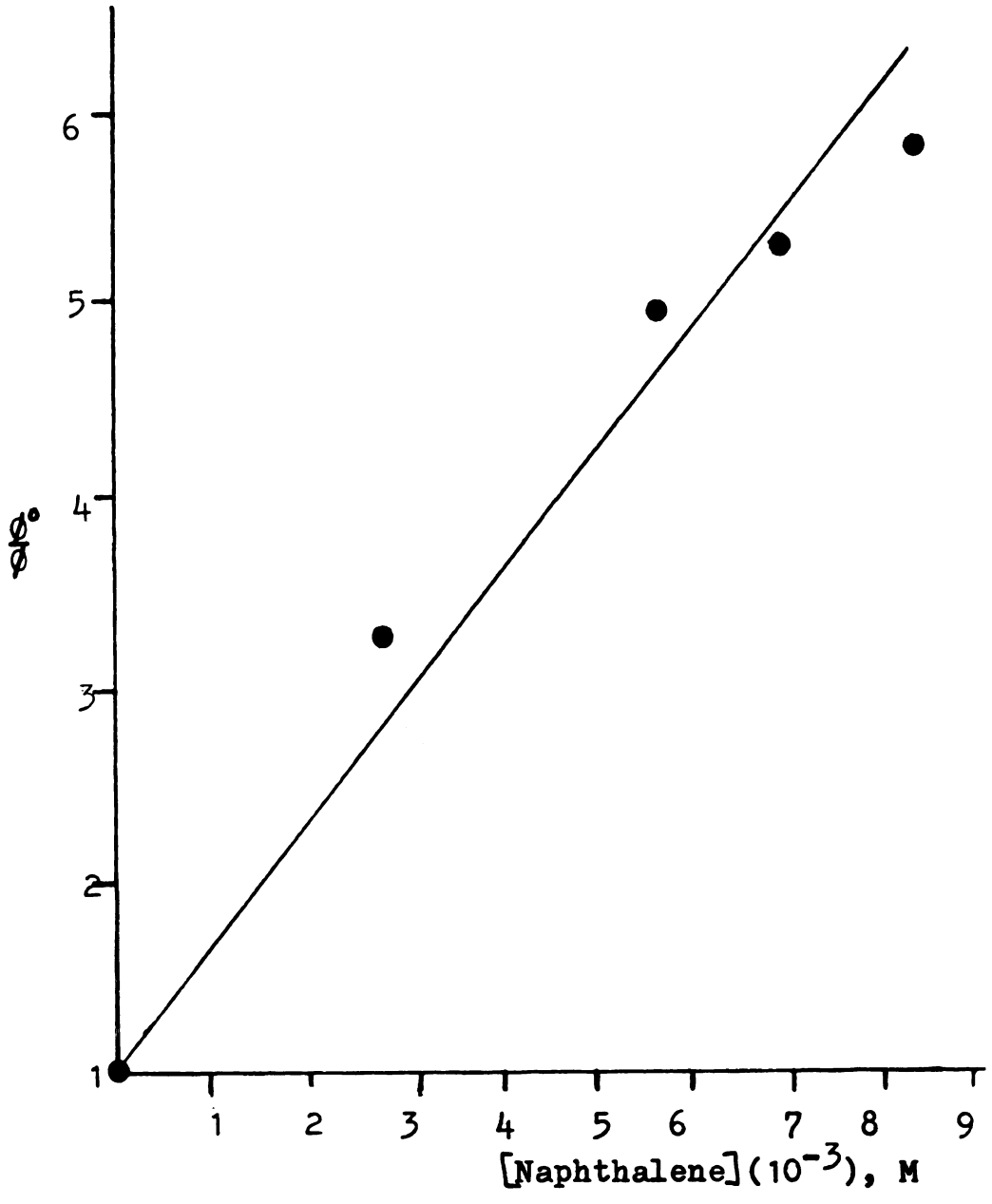


Figure 36. Stern-Volmer Plot: Photoreduction of TFA by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

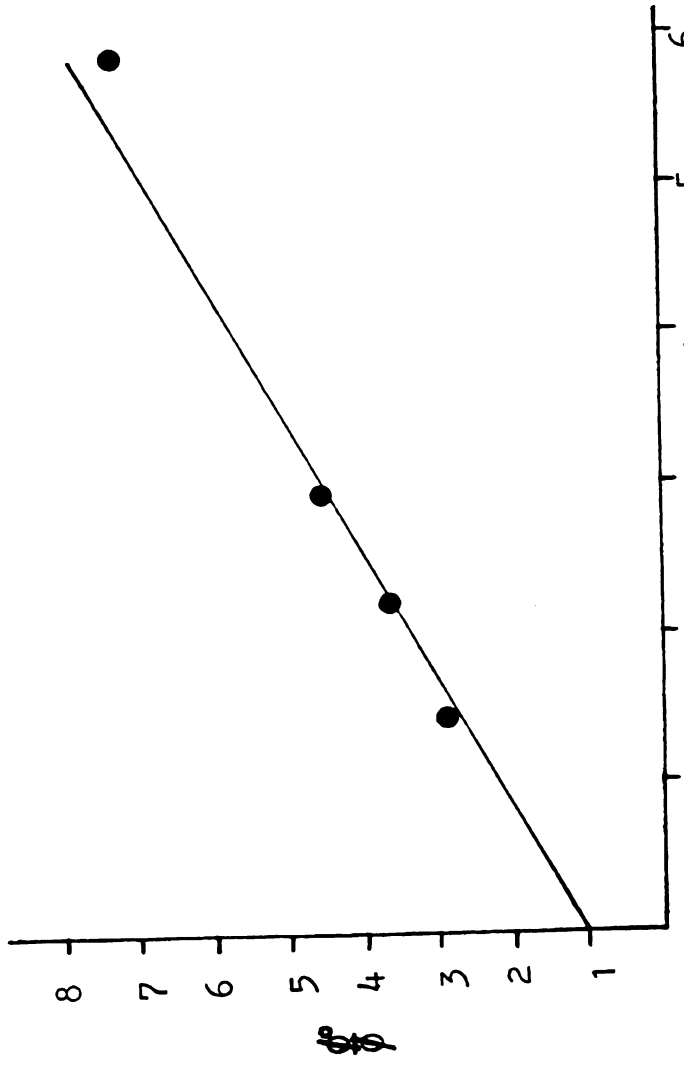


Figure 37. Stern-Volmer Plot: Photoreduction of m-Cl-TFA by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

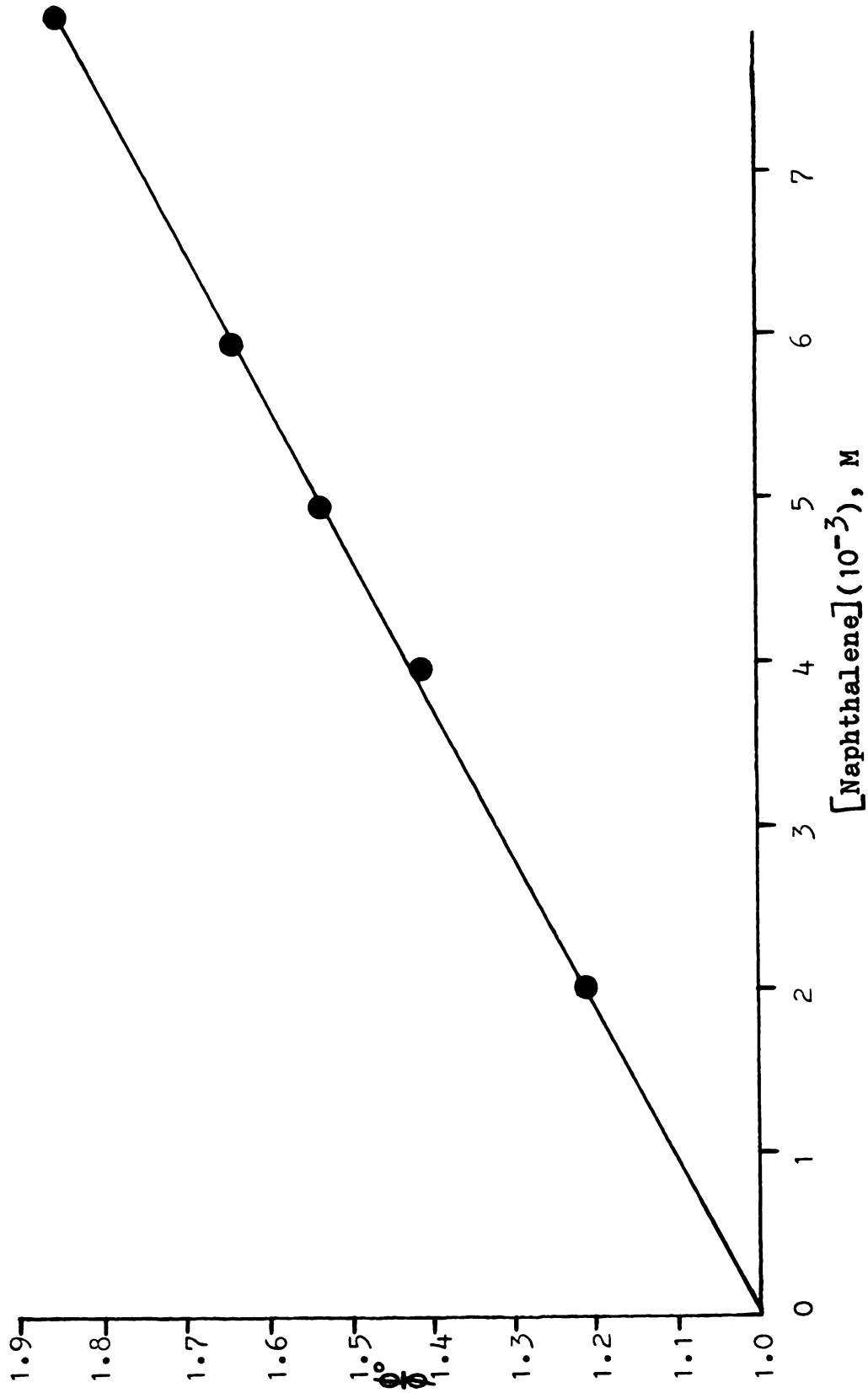


Figure 38. Stern-Volmer Plot: Photoreduction of p-MeO-TFA by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

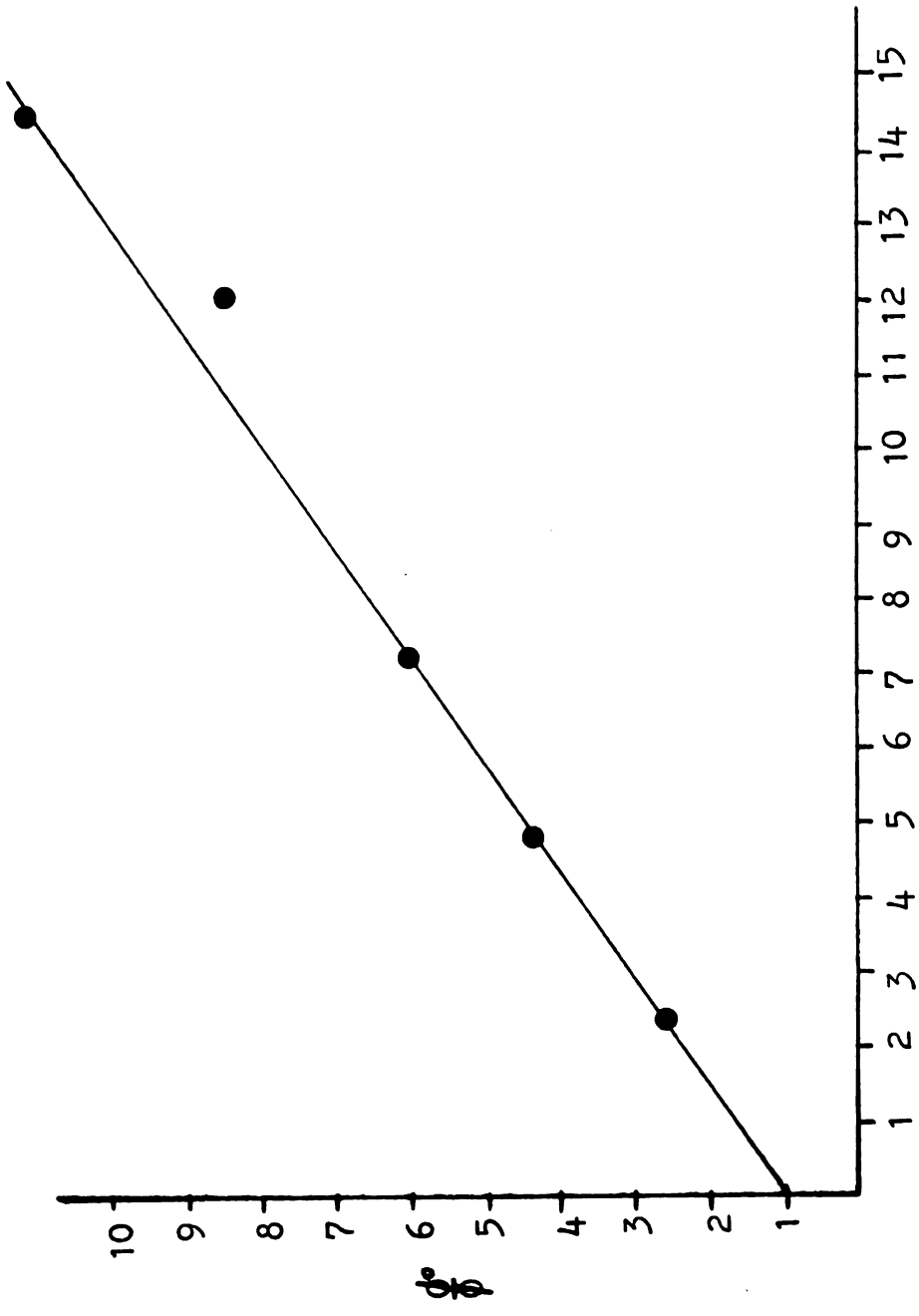


Figure 39. Stern-Volmer Plot: Photoreduction of p-MeO-TFA by 1 M Cyclopentane in CCl_4.

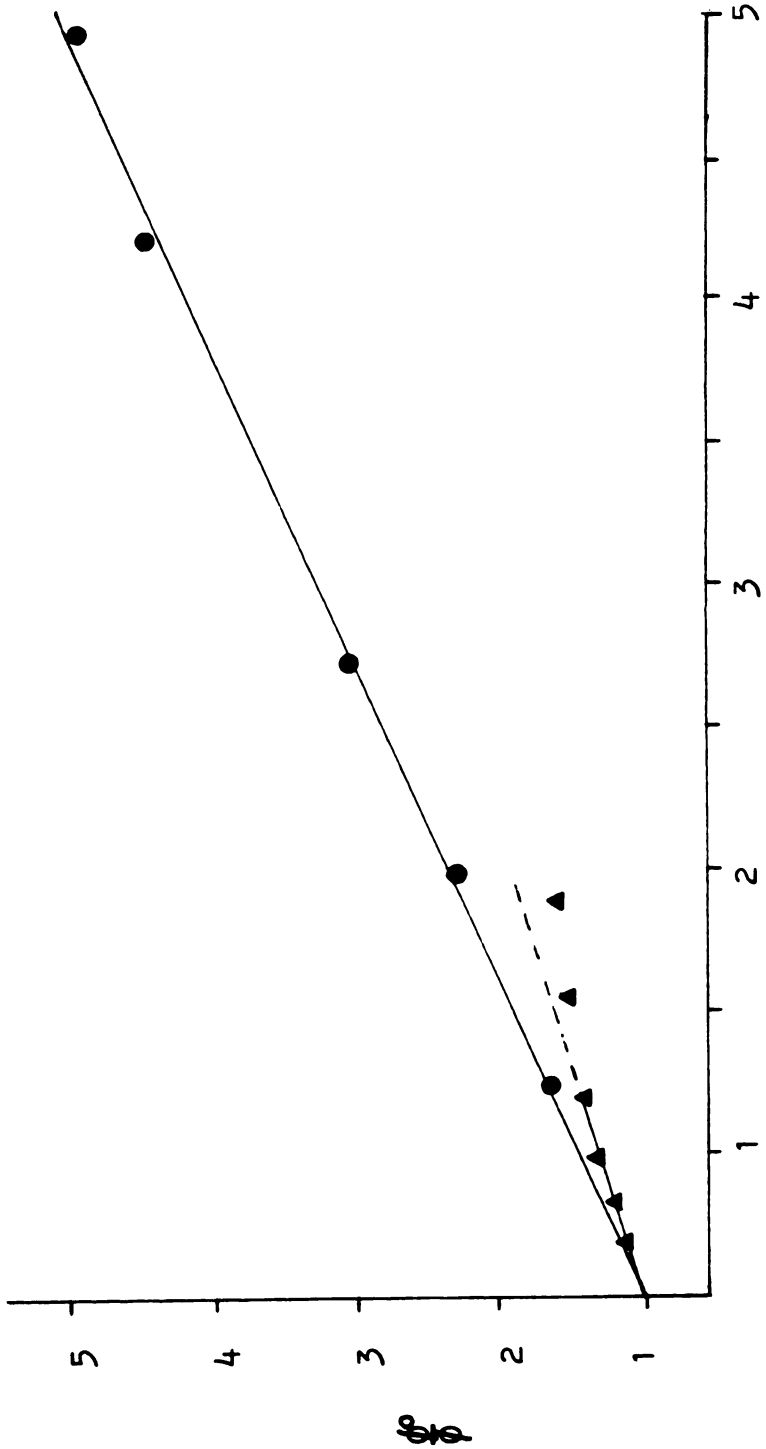


Figure 40. Stern-Volmer Plot: Photoreduction of p-Me-TFA by 1 M Cyclopentane in CCl_4. (●) Cross-coupling Product, (▲) Chlorocyclopentane Monitored.

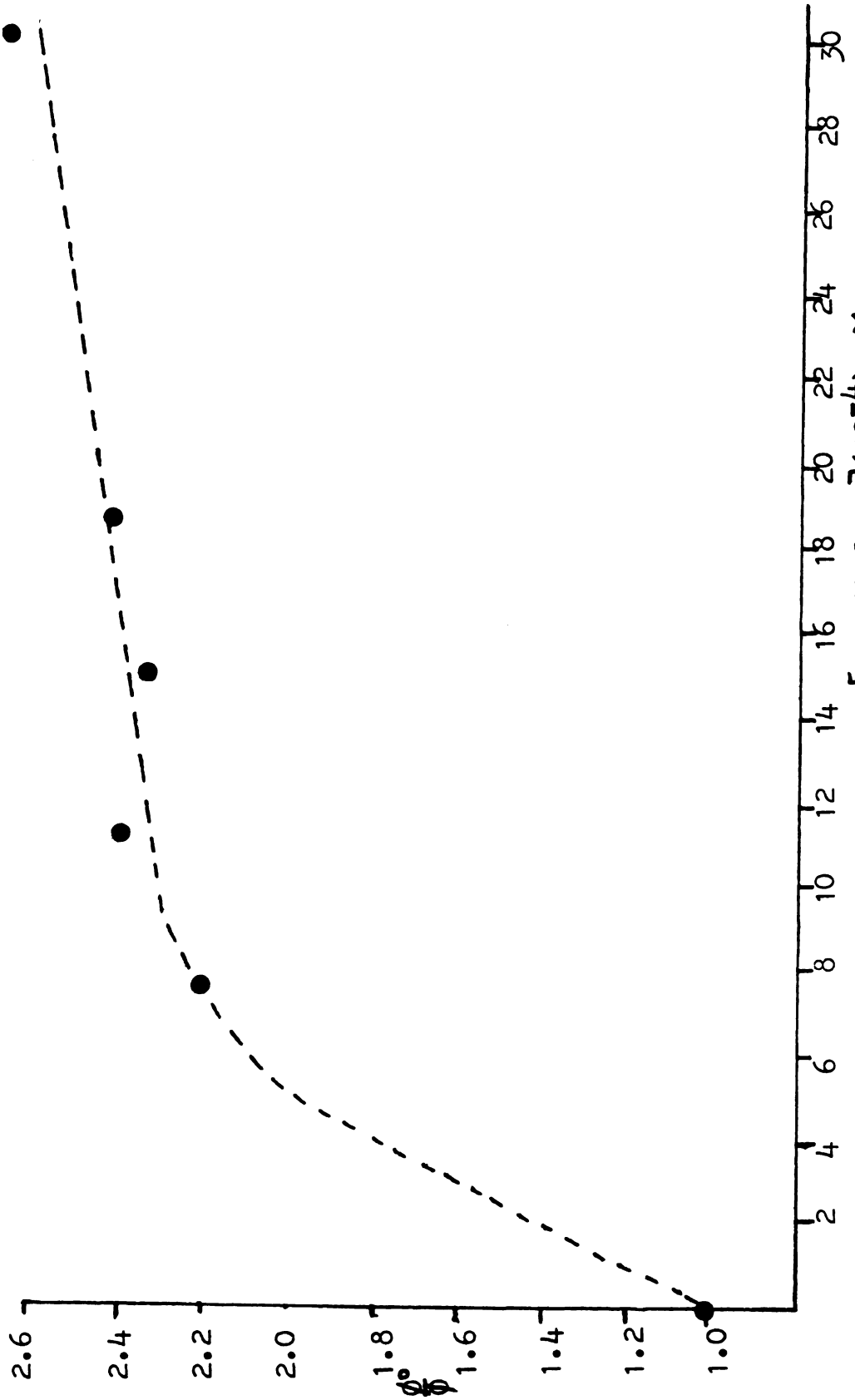


Figure 41. Stern-Volmer Plot: Photoreduction of 3,4-di-Me-TFA by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

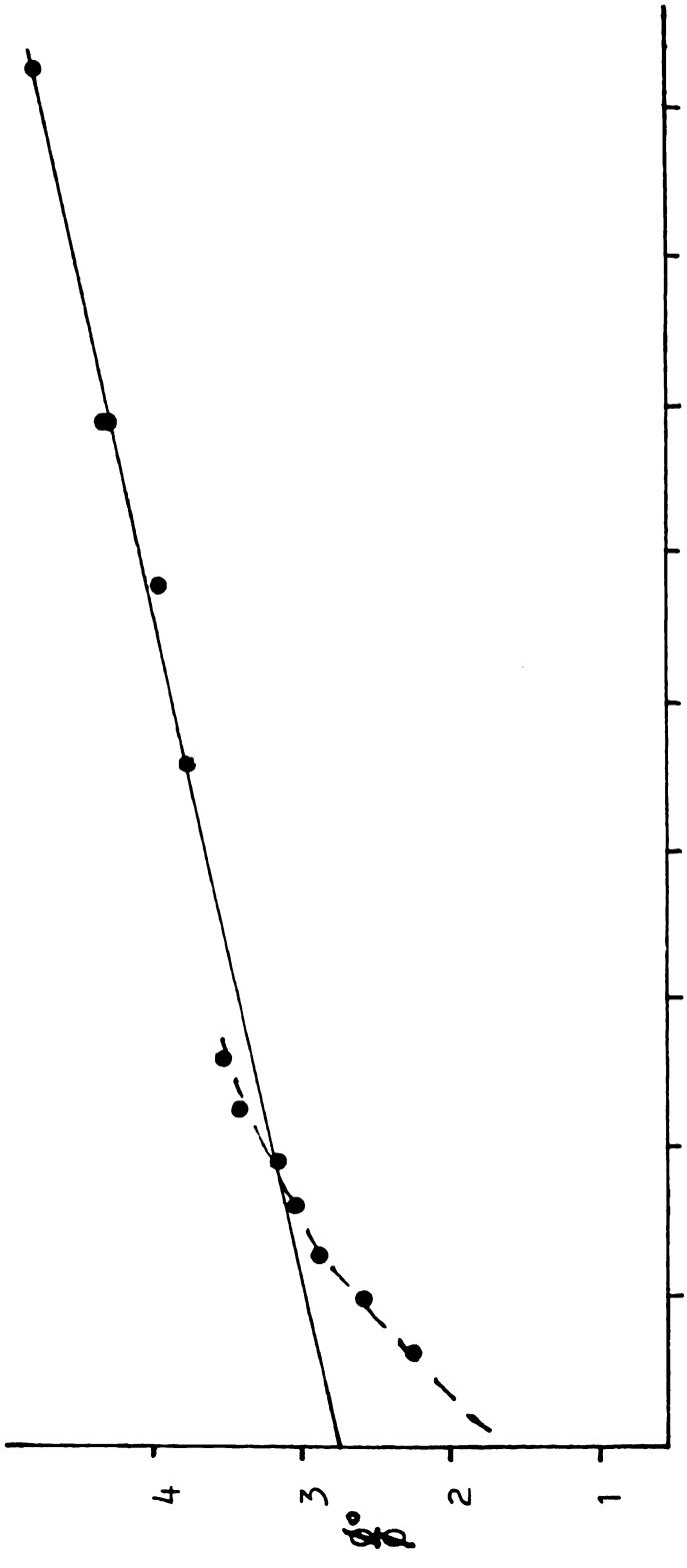


Figure 42. Stern-Volmer Plot: Photoreduction of p-Me-TFA by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

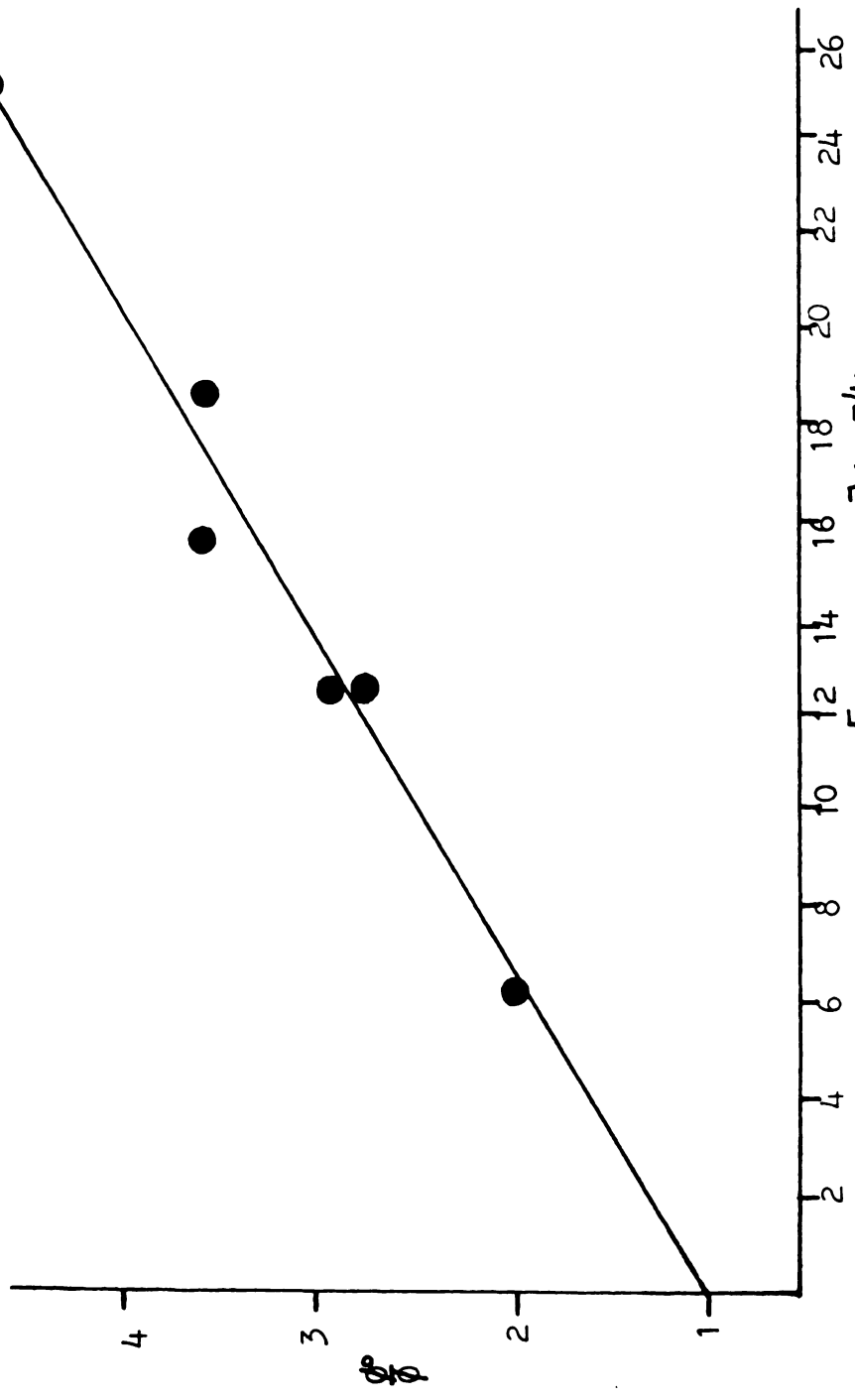


Figure 43. Stern-Volmer Plot: Photoreduction of ACP by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

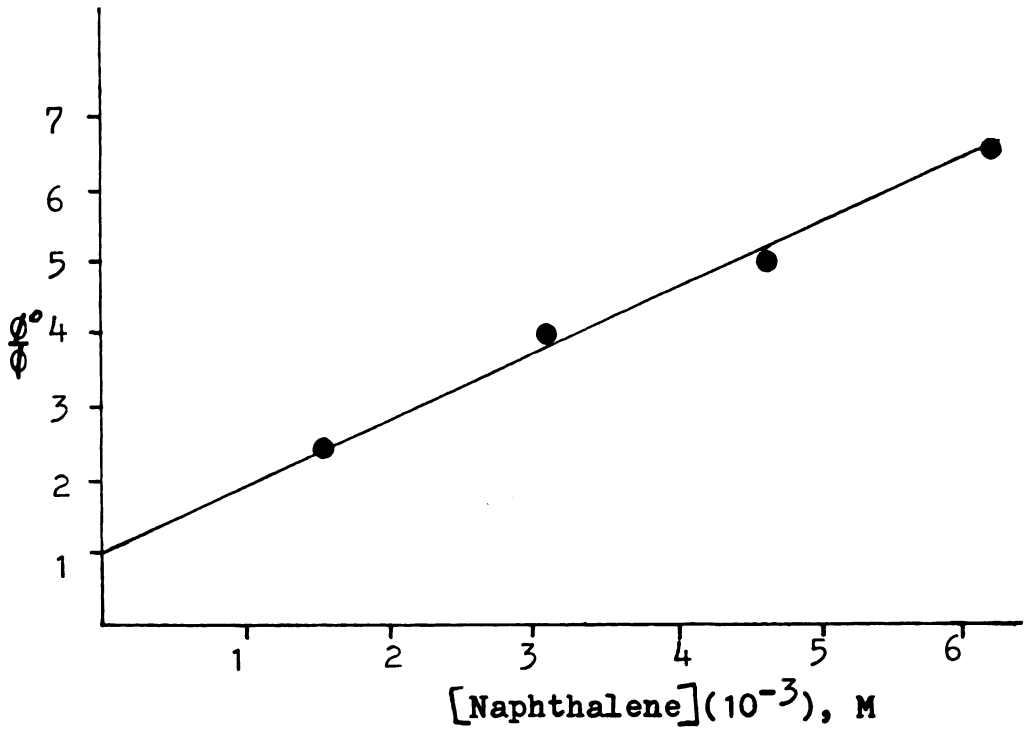


Figure 44. Stern-Volmer Plot: Photoreduction of p-CF_3-ACP by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

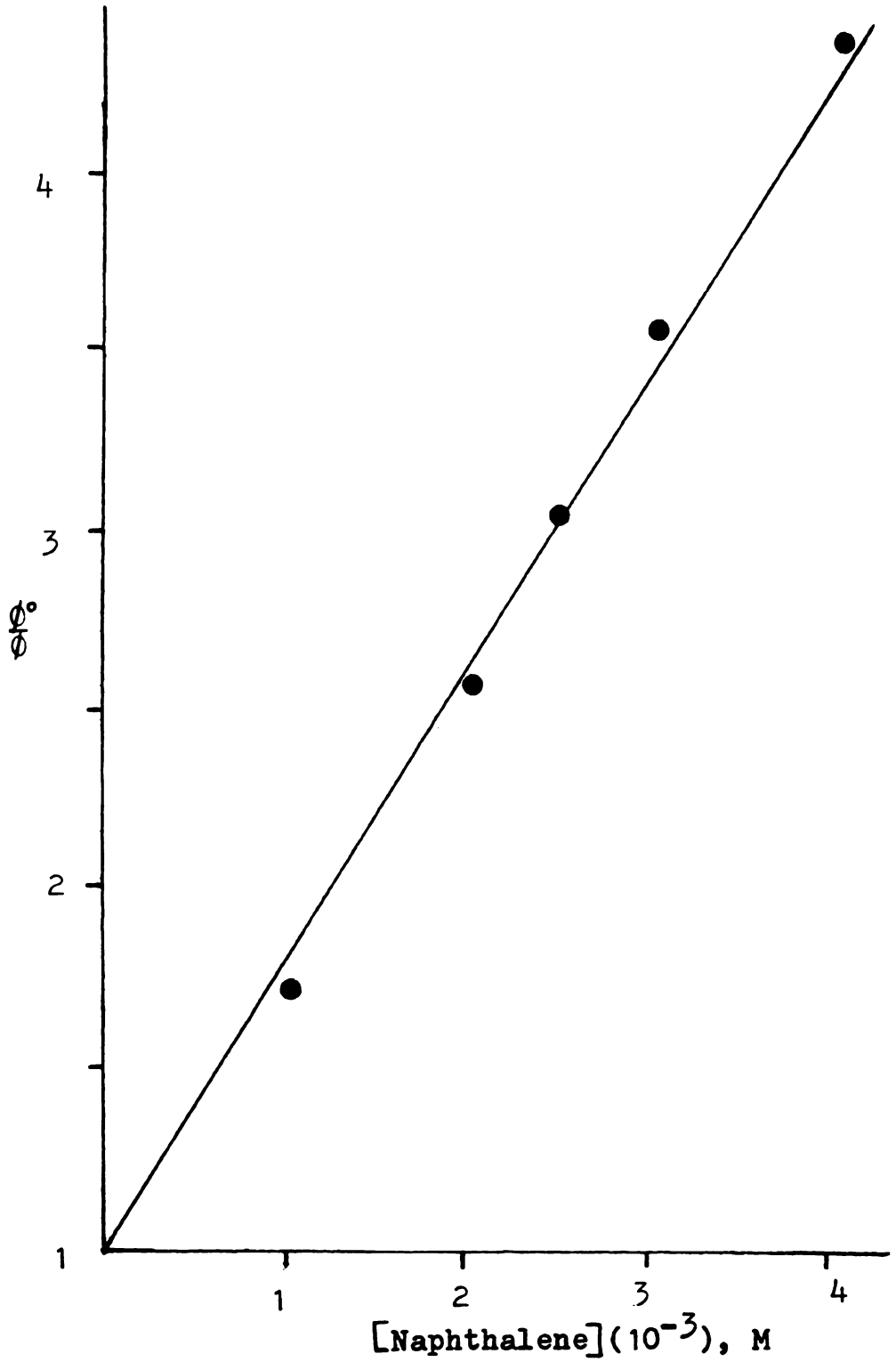


Figure 45. Stern-Volmer Plot: Photoreduction of p-Me-ACP by 1 M Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

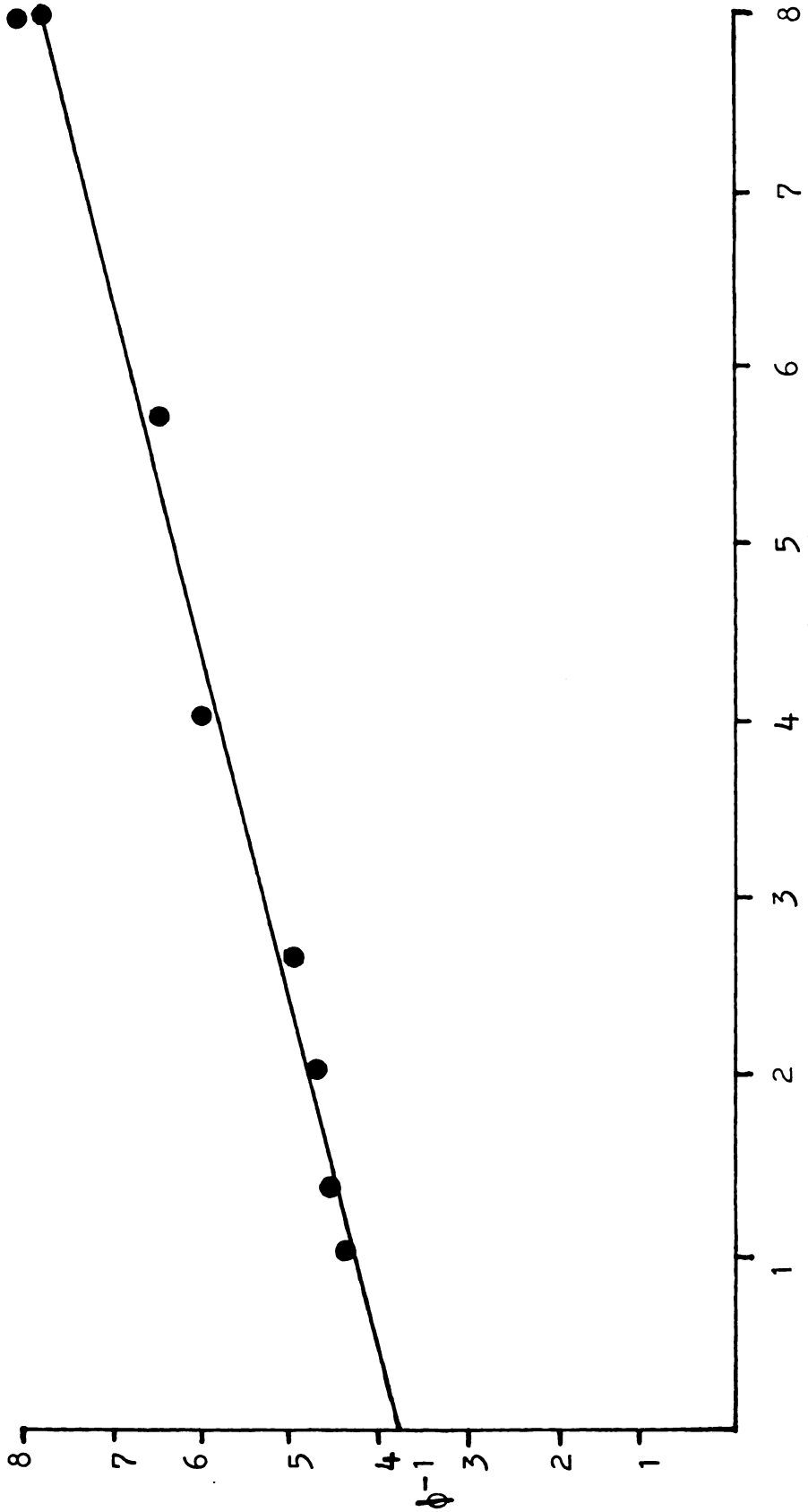


Figure 46. Double Reciprocal Plot: Photoreduction of BP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

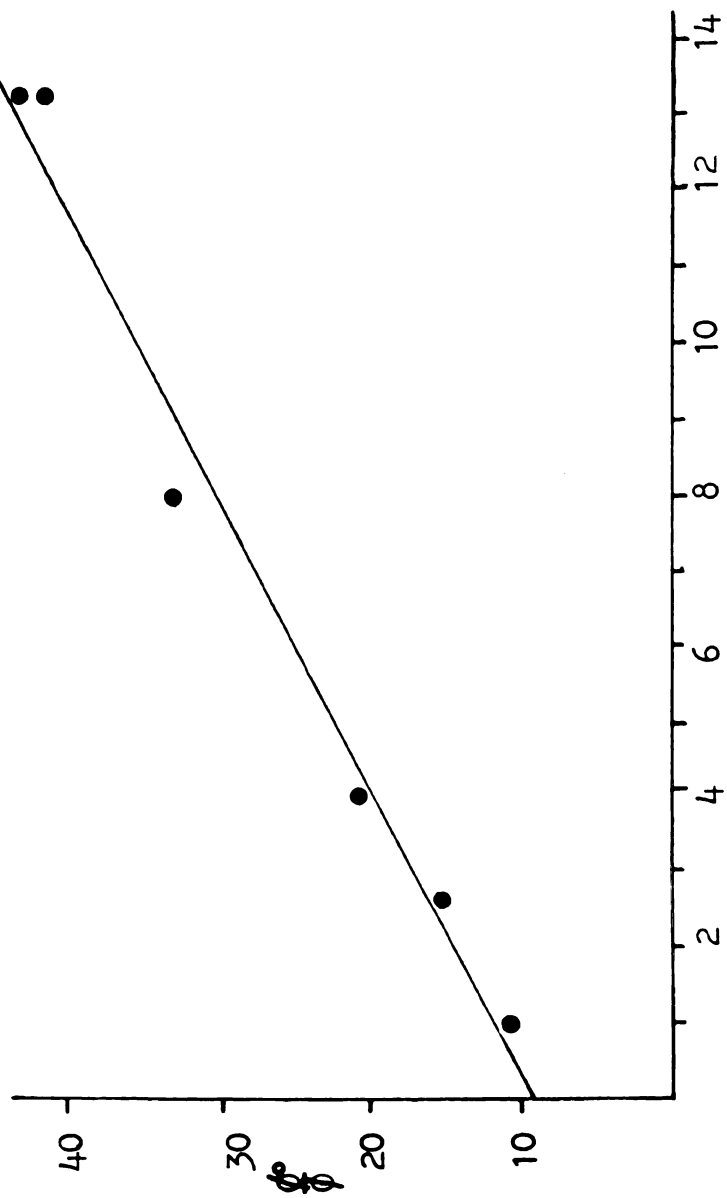


Figure 47. Double Reciprocal Plot: Photoreduction of 4,4'-Me-BP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

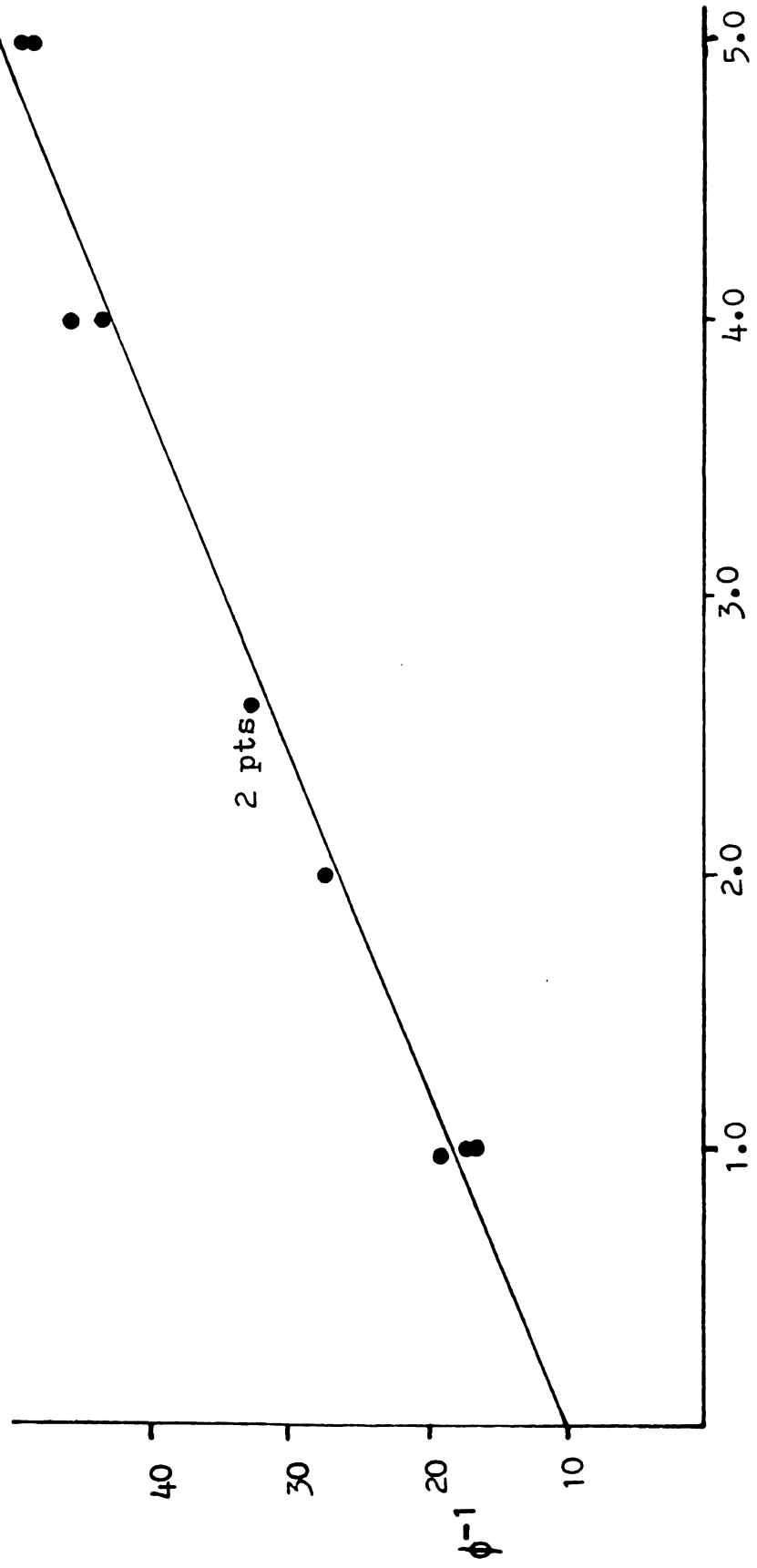


Figure 48. Double Reciprocal Plot: Photoreduction of 4,4'-Me-BP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

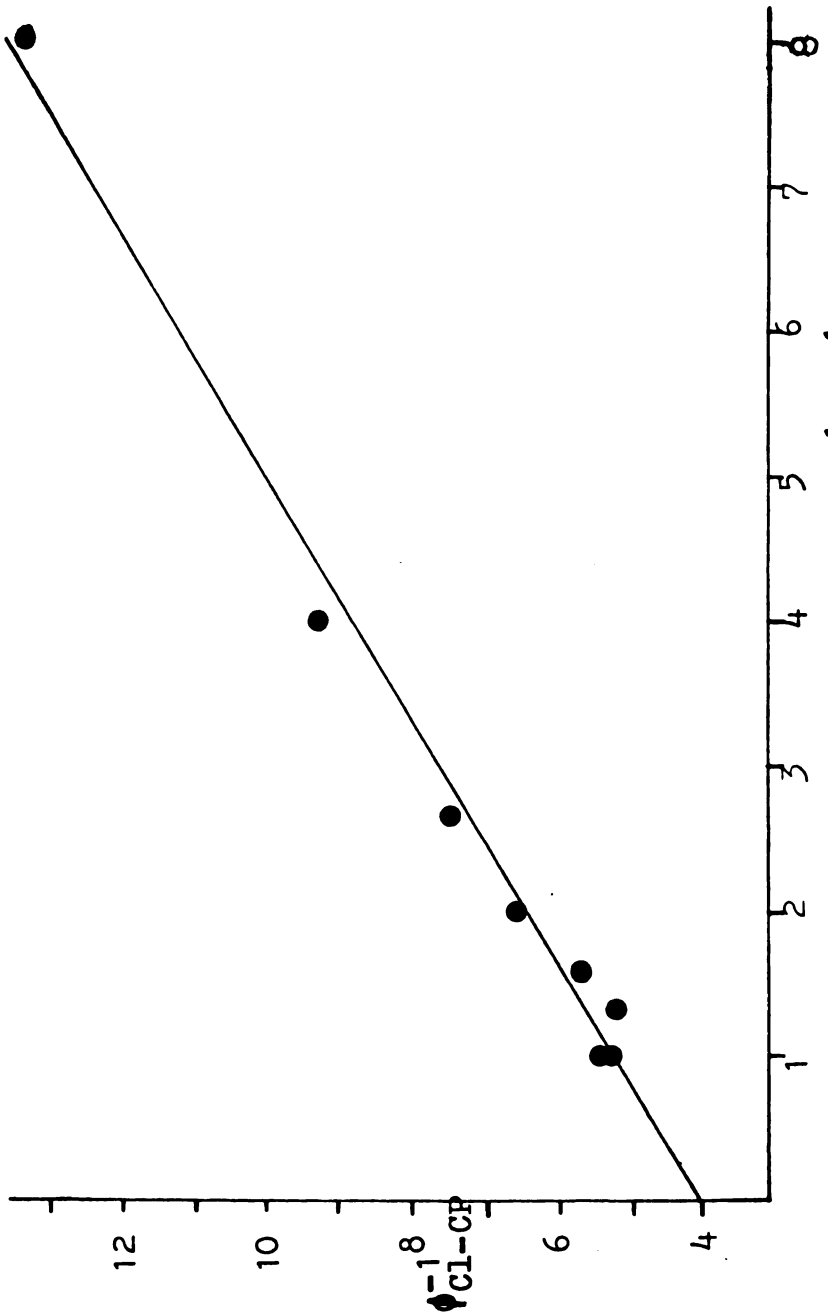


Figure 49. Double Reciprocal Plot: Photoreduction of TFA by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

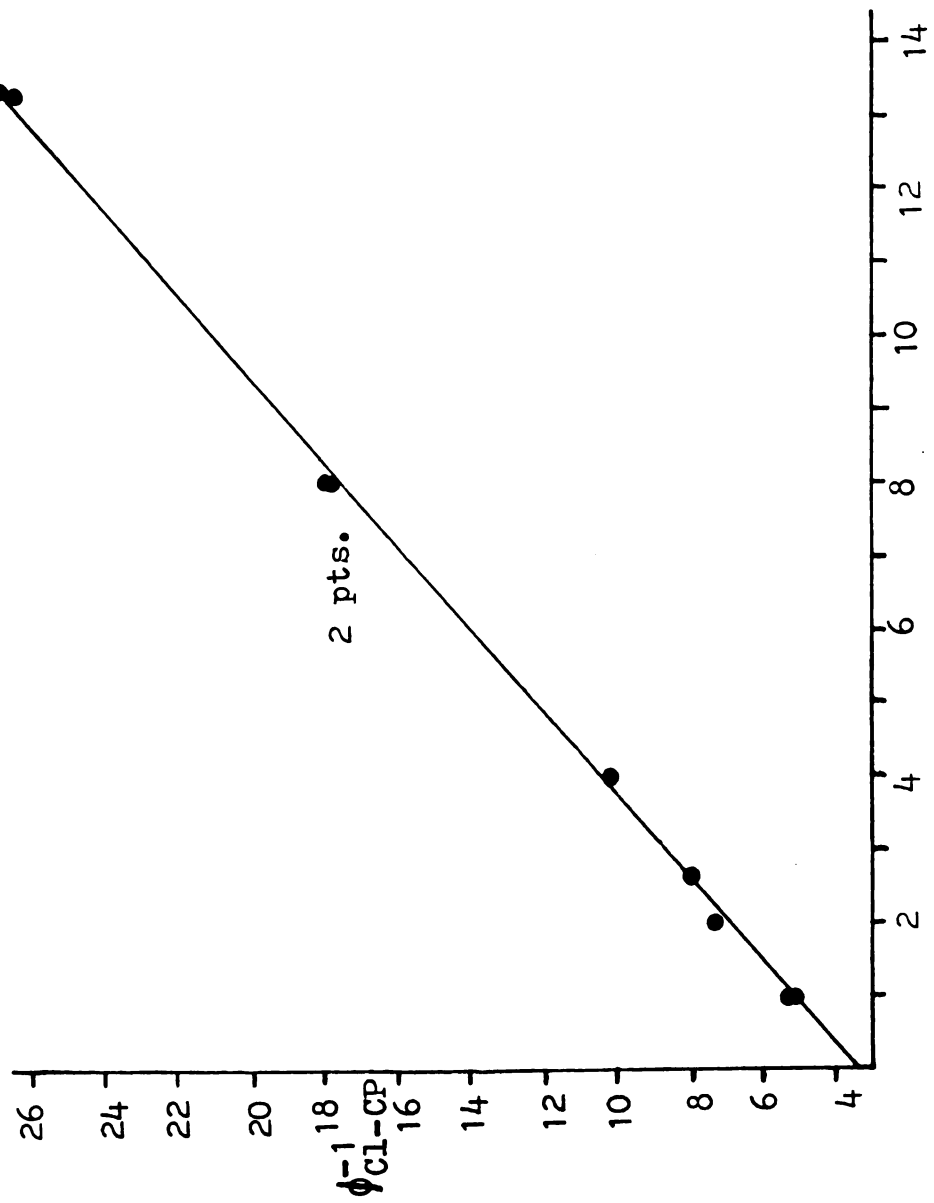


Figure 50. Double Reciprocal Plot: Photoreduction of m-Cl-TFA by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

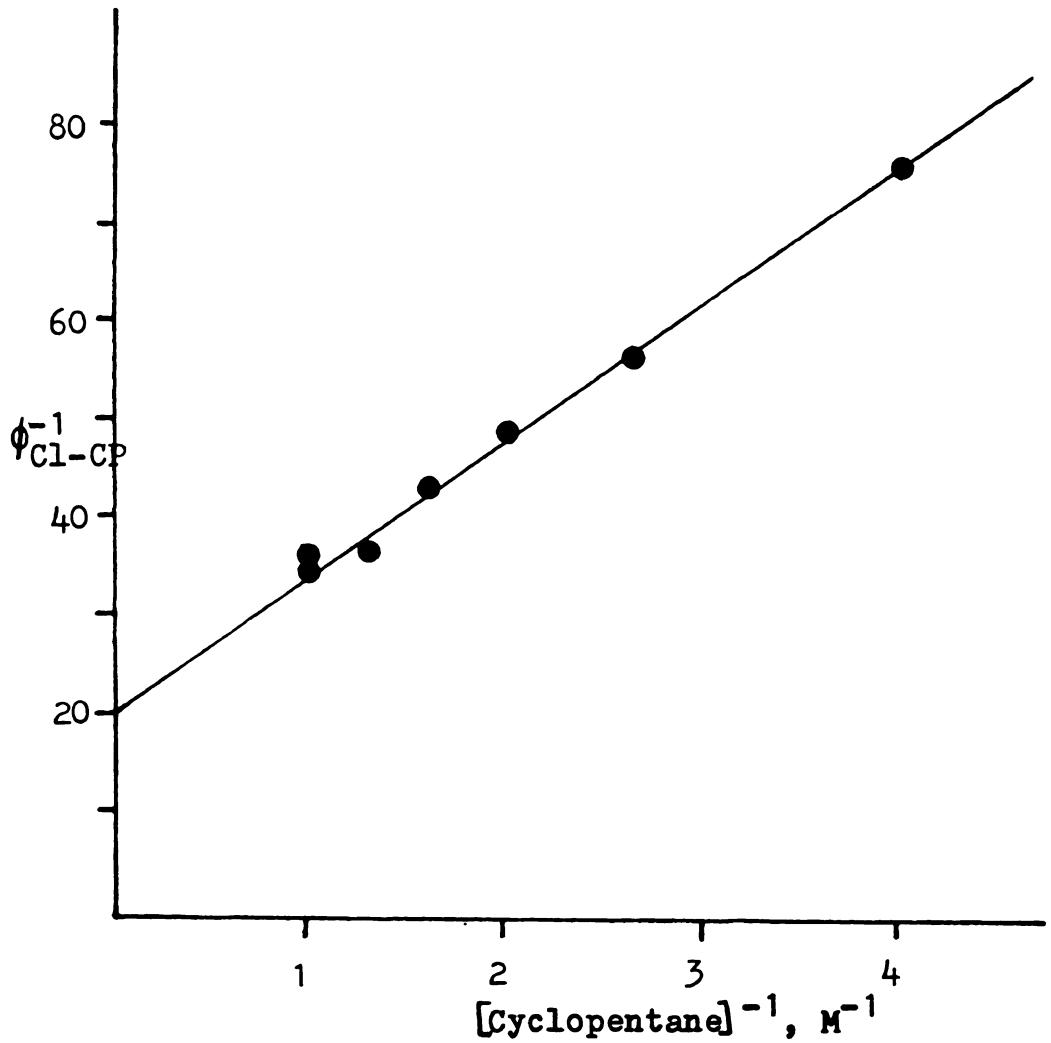


Figure 51. Double Reciprocal Plot: Photoreduction of p-MeO-TFA by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

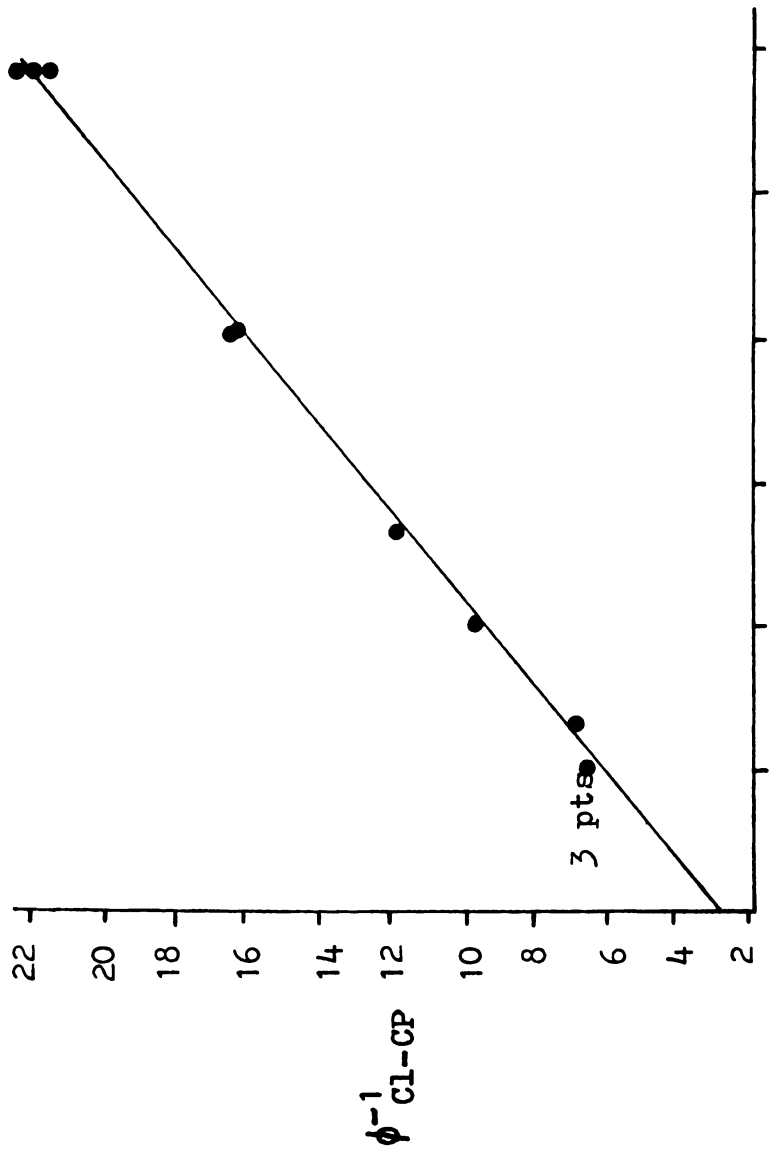


Figure 52. Double Reciprocal Plot: Photoreduction of ACP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

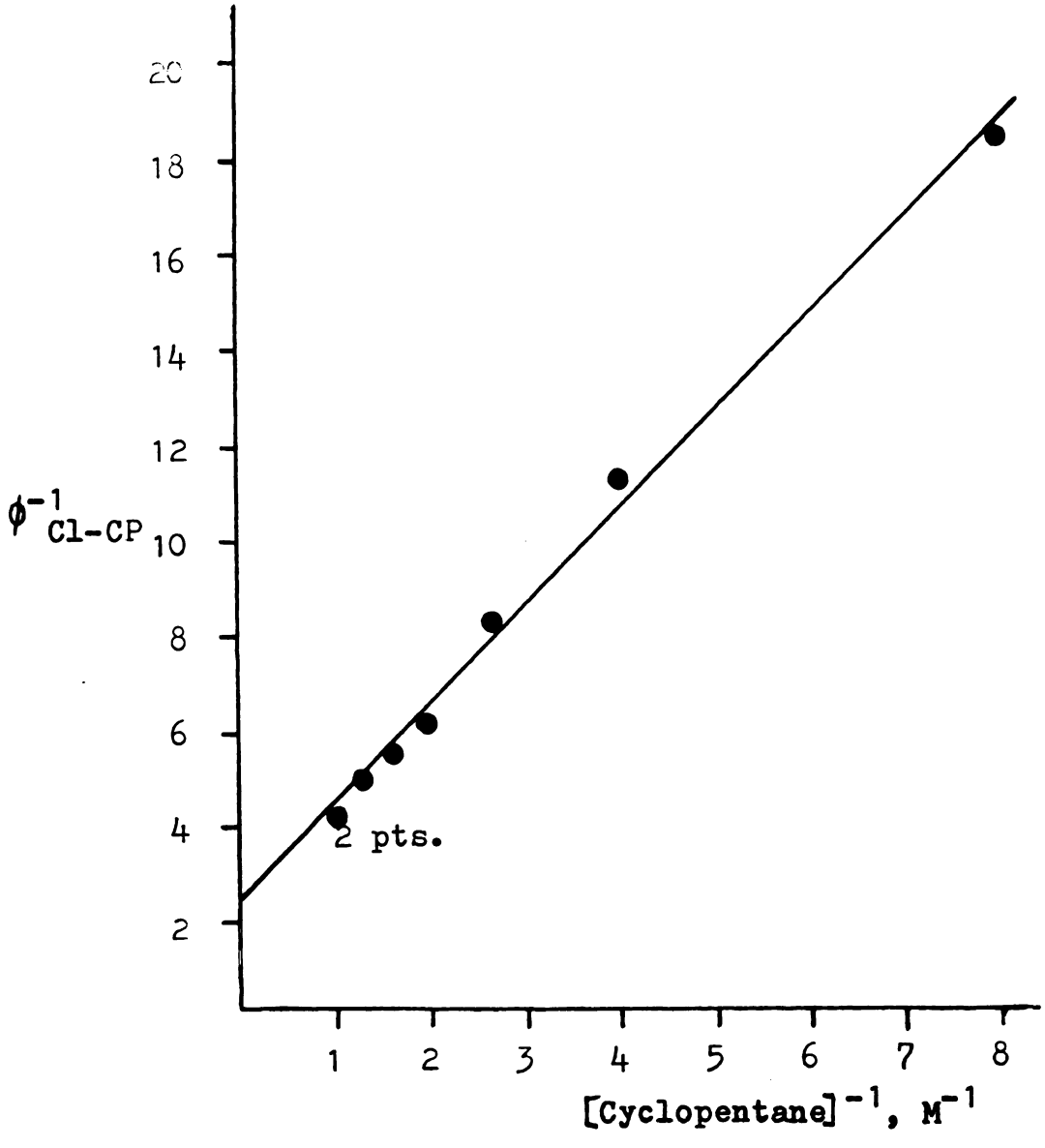


Figure 53. Double Reciprocal Plot: Photoreduction of p-Me-TFA by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

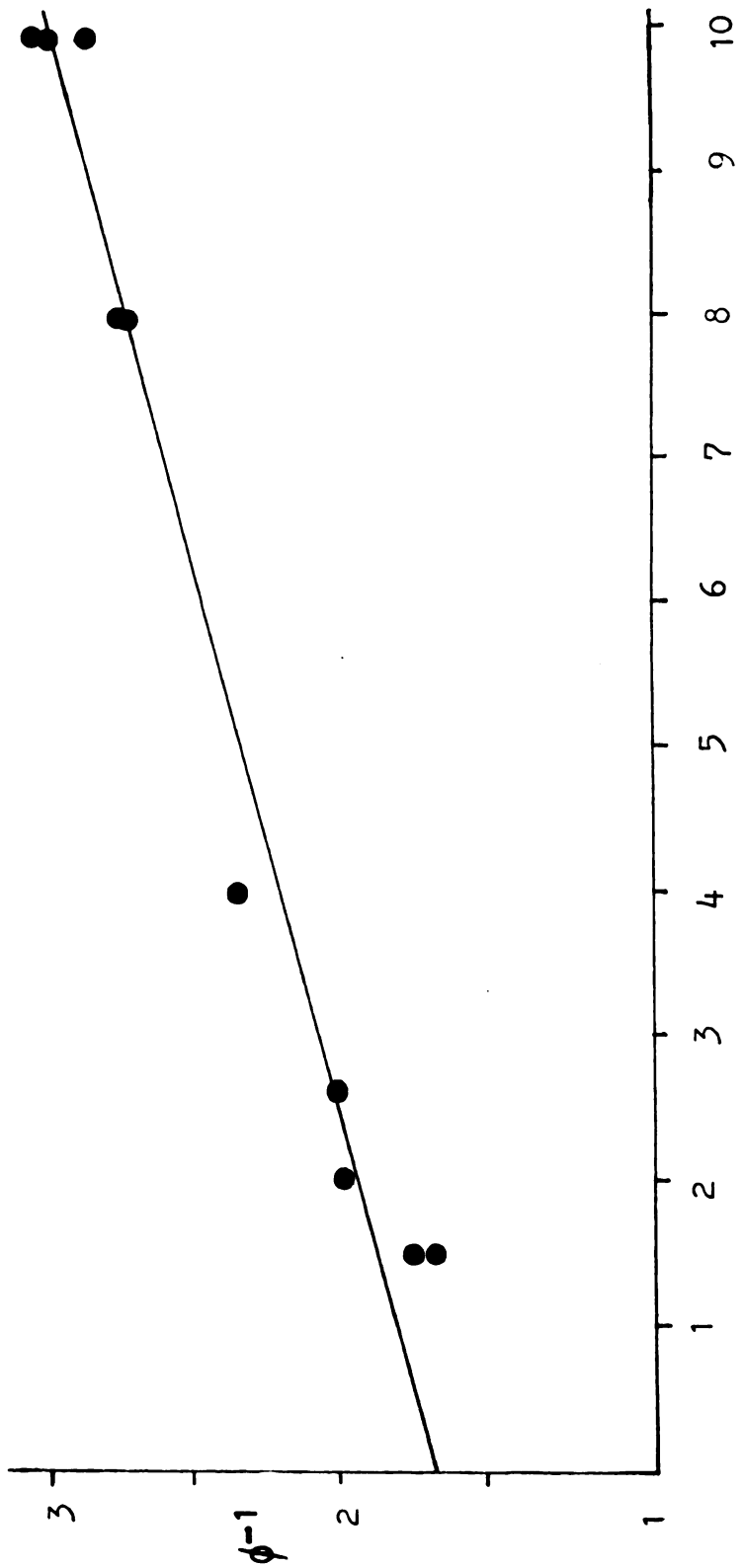


Figure 54. Double Reciprocal Plot: Photoreduction of p-CF_3-ACP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

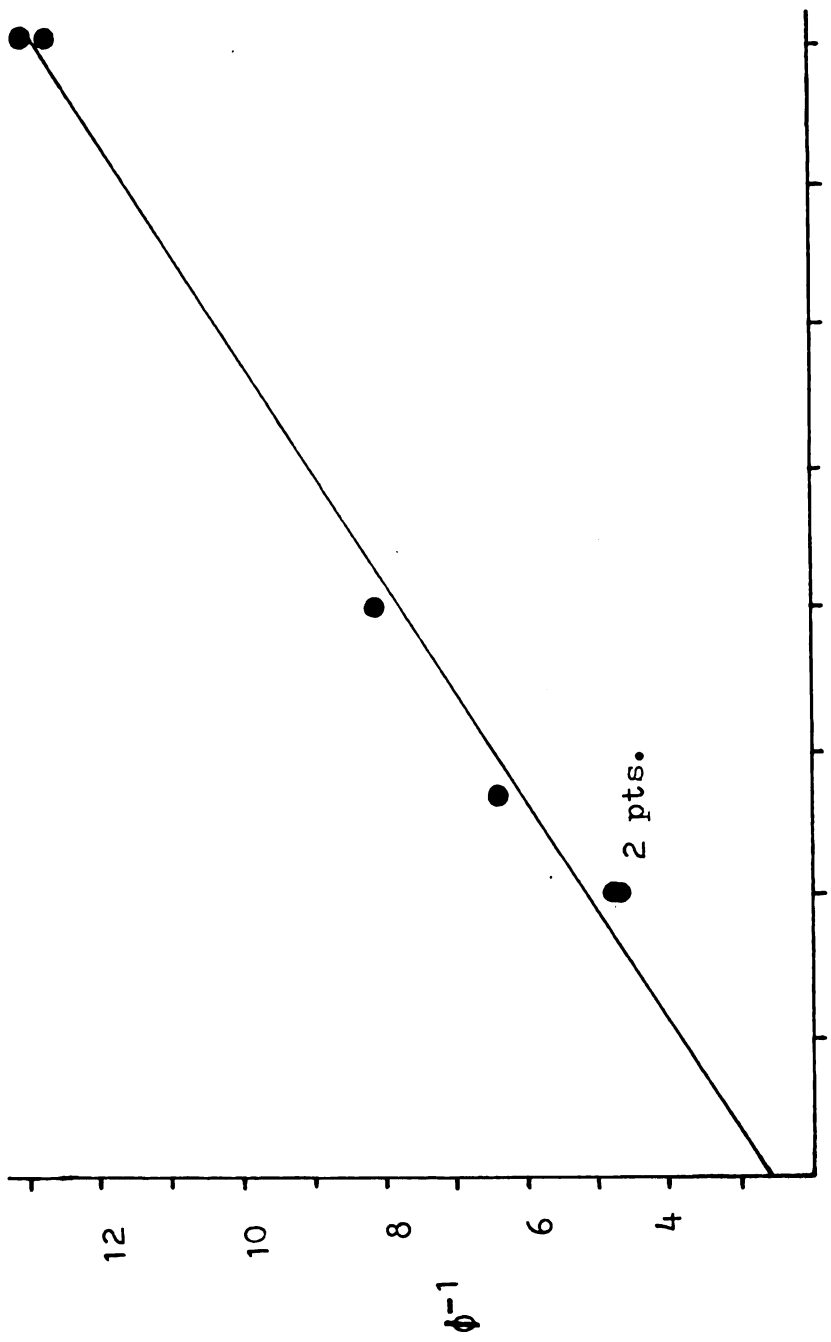


Figure 55. Double Reciprocal Plot: Photoreduction of p-Me-ACP by Cyclopentane in CCl_4. Chlorocyclopentane Monitored.

Table XXVII. Photoreduction of 0.1 M BP in CCl_4 by 1 M Cyclopentane: Quantum Yield of Chlorocyclopentane as a Function of Light Absorbed.

Cl-CP/PhCl[a]	[Cl-CP](10^{-3}), M[b]	I_a,E/l	ϕ_{Cl-CP}
0.502;0.506	4.60	0.0135	0.340
0.983	8.96	0.0255	0.351
2.13	19.4	0.0585	0.332
3.00	27.4	0.0903	0.303
4.45;4.77	42.1	0.137	0.318

[a]Cl-CP-chlorocyclopentane.

[b]SF=1.20; [PhCl]=0.00760 M.

Table XXVIIII. Photoreduction of 0.1 M BP in CCl_4 by 1 M Cyclopentane: Product Quantum Yields as a Function of Light Intensity.

Path, cm[a]	[Cl-CP](10^{-2}), M[b]	[KP](10^{-4}), M[c]	ϕ_{Cl-CP}	ϕ_{KP}
1.5	2.65	7.52	0.176	0.0047
1.5	2.59	6.40		
3.0	3.68	8.21	0.150	0.0032
3.0	3.25	6.45		
4.5	3.49	9.82	0.151	0.0046
4.5	3.38	11.3		

[a]Pathlength of the filter solution. A = log (I°/I); the absorbance at 335 nm, was measured in a 1 cm cell using air as reference: A = 0.495.

[b]Cl-CP=chlorocyclopentane.

[c]KP=ketyl-cyclopentane cross-coupling product.

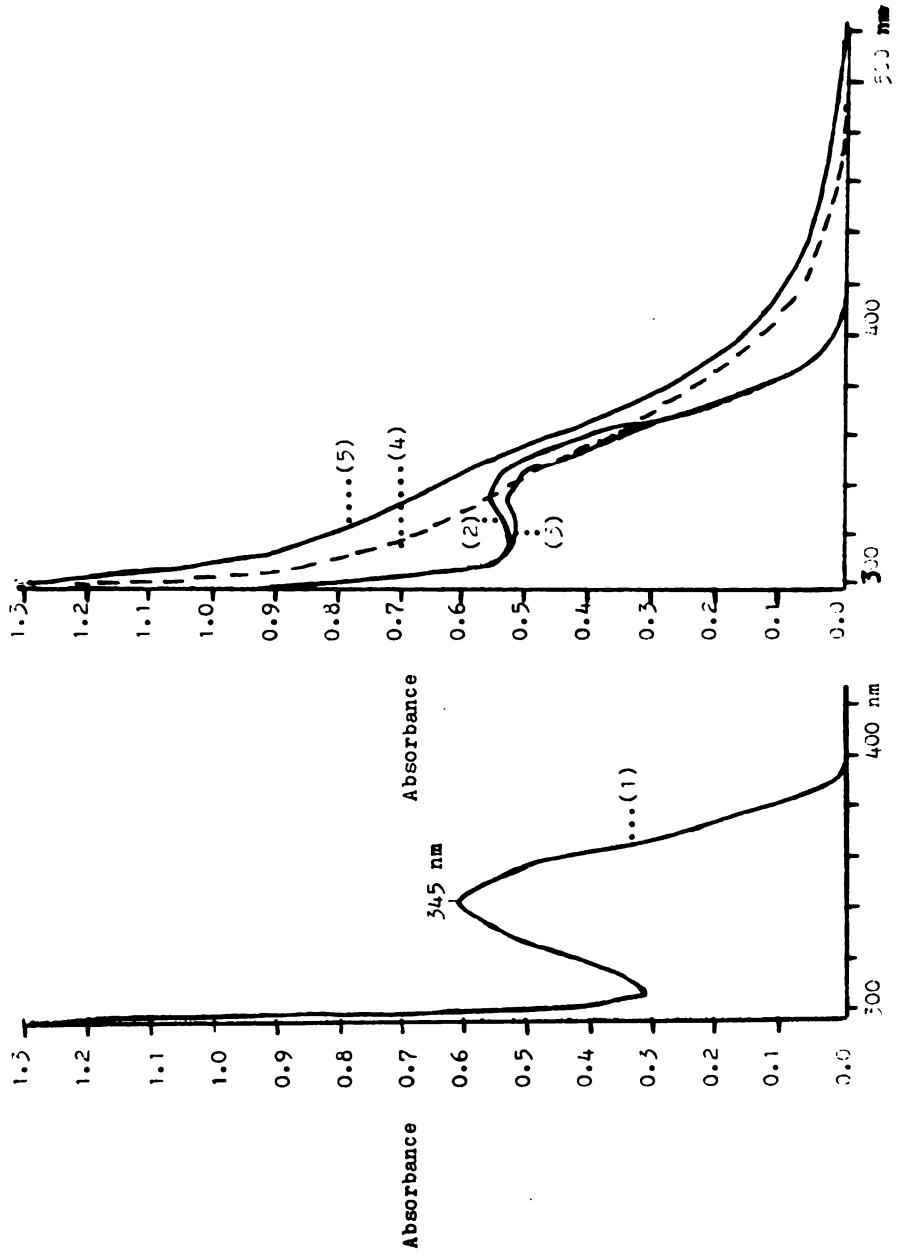


Figure 56. Photolysis at 313 nm of Degassed 0.02 M BP solutions in CCl_4 Containing 1 M Cyclopentane: (1) 0 hours; (2) 3 hours; (3) 5 hours; (4) 36 hours; (5) 48 hours.

The quantum yields of bicyclopentyl and the cross-coupling product from the photoreduction of TFA in neat cyclopentane were measured as a function of conversion. From Table XXIX it is apparent that product quantum yields decrease with conversion.

The photoreduction of TFA by neat cyclopentane produced cyclopentene as a major photoproduct (Table XXX). The concentrations of all the major photoproducts were determined by vpc.

When TFA was photoreduced in CCl_4 in the presence of 1 M cyclopentane, cyclopentene was also observed by vpc, but the concentration was too small to analyze.

Since cyclopentene was formed by irradiating phenyl ketones in the presence of cyclopentane, the effectiveness of cyclopentene as a quencher was examined (Table XXXI, Figure 57).

It was suspected that a chloromethyl radical produced photochemically may abstract hydrogen from cycloalkanes. The concentration of chloroform produced from the photoreduction of several ketones by cyclohexane is presented in Table XXXII.

H. Quenching Kinetics for Ring-Substituted Valerophenone

Lifetimes and product quantum yields of p-Me-VP and p-t-Bu-VP were measured, and the results are presented in Table XXXIII. It is observed that p-Me-VP has a longer

Table XXIX. Photoreduction of 0.1 M TFA by Neat Cyclopentane: Quantum Yields as a Function of Light Absorbed.

[BCP][a]	[KP][b]	I_a,E/l[c]	ϕ_{BCP}[d]	ϕ_{KP}[d]
2.39	9.50	1.21	2.0	7.9
4.05	16.2	2.36	1.7	6.8
8.98	37.2	6.58	1.4	5.7
13.6	57.2	10.5	1.3	5.4

[a] $X10^{-4}$ M; BCP=bicyclopentyl photoproduct. Average of two experiments.

[b] $X10^{-4}$ M; KP=ketyl-pentyl cross product. Average of two experiments.

[c] $X10^{-2}$; light absorbed, determined by valerophenone actinometry.

[d] $X10^{-2}$.

Table XXX. Photoreduction of TFA by Neat Cyclopentane: Concentration of the Major Photoproducts.

[CP] M[a]	[BCP, M[b]	[KP], M[c]	[TFPE], M[d]	[K-K], M[e]
0.0147	0.00283	0.00995	0.00283	0.0128

[a]CP=cyclopentene.

[b]BCP=bicyclopentyl.

[c]KP=ketyl-pentyl cross-coupling product.

[d]TFPE=1,1,1-trifluoro-2-phenyl-2-ethanol.

[e]K-K=the pinacol photoproduct.

Table XXXI. Photoreduction of 0.05 M p-MeO-TFA in CCl_4 1.3 M Cyclopentane: Stern-Volmer Quenching by Cyclopentene.

Slope	I_a,E/l	$\phi_{Cl\text{-}CP}$[a]
37.3	0.0936	0.0502

[a]Cl-CP=chlorocyclopentane; irradiation at >335 nm.

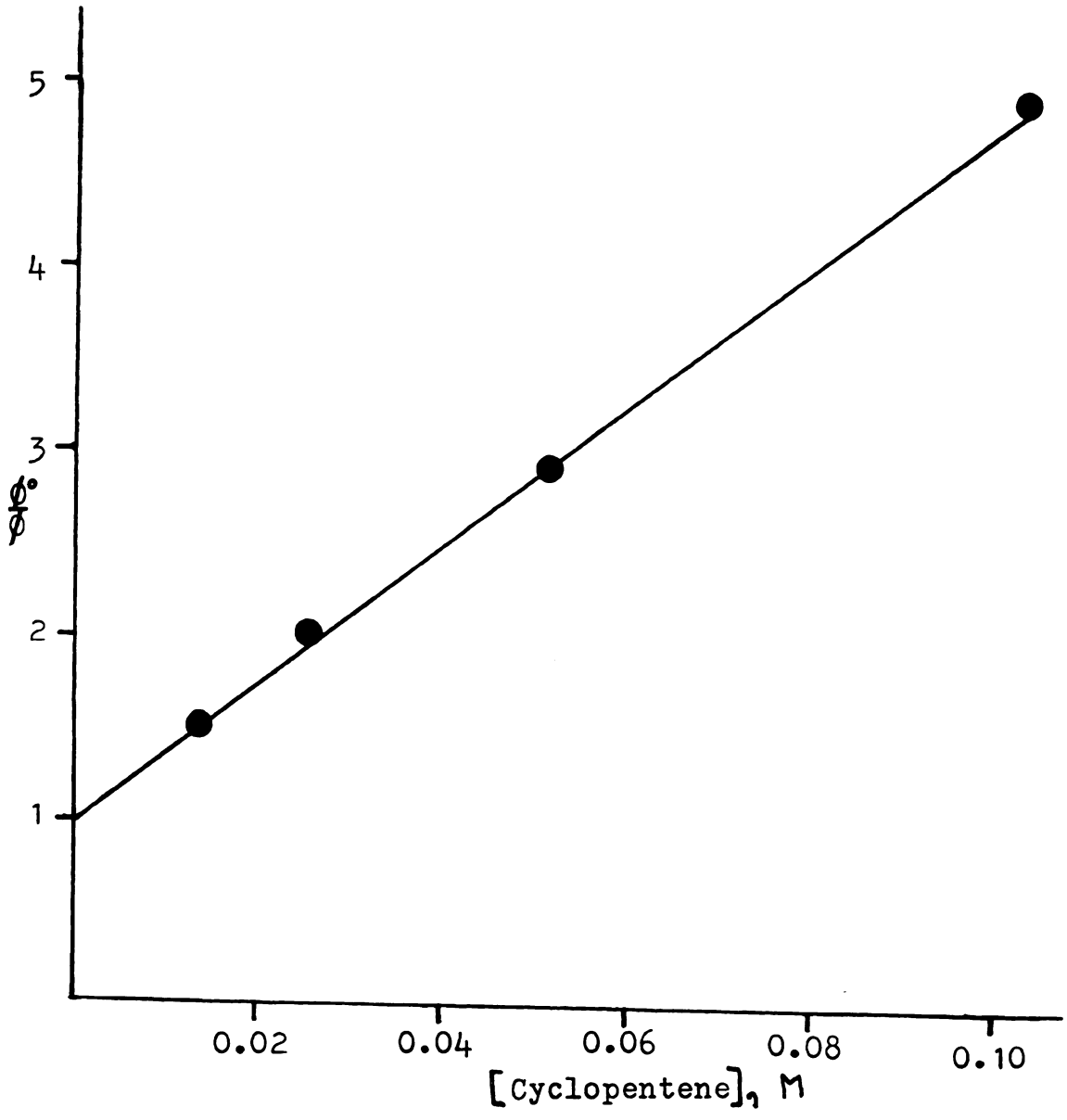


Figure 57. Stern-Volmer Plot: Photoreduction of p-Me-TFA by 1 M Cyclopentane in CCl_4, Quenched by Cyclopentene. Chlorocyclopentane Monitored.

Table XXXII. Photoreduction of Several Ketones by Cyclohexane: Concentration of Chloroform and Chlorocyclohexane Produced.

Ketone[a]	$[HCCl_3]$, M	[Cl-CH], M[b]	$[HCCl_3]$ / [Cl-CH]
ACP	0.10;0.093	0.251;0.245	0.38
BP	0.0370;0.0501	0.149;0.451	0.29
p-MeO-TFA	0.0272;0.0242	0.149;0.149	0.26
TFA	0.0074;0.0318	0.0483;0.165	0.17
3,4-di-Me-TFA	0.0218;0.0141	0.121;0.113	0.18
p-Me-TFA	0.0349;0.0365	0.137;0.134	0.17

[a] ACP=acetophenone; BP=benzophenone; TFA=α,α,α-trifluoroacetophenone. 0.2 M ketone, 1 M Cyclohexane.

[b] Cl-CH=chlorocyclohexane.

Table XXXIII. Stern-Volmer Quenching of the Type II Reaction of Valerophenones in Various Solvents.

Subst.[a]	Solvent	ϕ_{Max}	$k_q\tau$[b]	k_q[c], $M^{-1}s^{-1}$
H	Benzene	1.0[d]	44(40)[d]	$5x10^9$
H	CCl_4	1.0[d]	49	$5x10^9$
H	CH_3CN	1.0[d]	103	$1x10^{10}$
p-MeO	Benzene	0.26[e]	2250[e]	$5x10^9$
p-MeO	CH_3CN	0.26	6567	$1x10^{10}$
p-Me	CH_3CN	0.22[f]±0.006	687[g]±17	$1x10^{10}$
p-Me	Benzene	----	272[d]	$5x10^9$
p-t-Bu	CH_3CN	0.34[f]±0.006	397[g]±30	$1x10^{10}$

[a] 0.05 M ketone solutions.

[b] Single experiment.

[c] in CCl_4 and PhH assumed to be very similar.

[d] From Reference 27.

[e] From Reference 27 and 191.

[f] $\phi_{ACP} + \phi_{cyclobutanol}$.

[g] Average of 2 experiments.

lifetime and lower product quantum yield than does p-t-Bu-VP.

Stern-Volmer quenching studies were performed on VP and p-MeO-VP in various solvents (Table XXXIII). It is observed that the $k_q\tau$ values measured for VP in CCl_4 and benzene are quite similar.

I. Relative Quenching Rate Constants, k_q, for Various Quenchers

The photoreduction of several ketones by toluene was quenched by various quenchers. The results from Stern-Volmer plots of bibenzyl concentrations are shown in Table XXXIV. It is observed that the same $k_q\tau$ values were obtained when using naphthalene and pentadiene.

J. Photoreduction of p-Acetyl-α,α,α-Trifluoroacetophenone

Experiment A. - A solution of 0.2 M p-Ac-TFA and 1.0 M 2-propanol in CD_3CN was introduced into an NMR tube, and then degassed by bybbling nitrogen gas through a rubber stopper into the solution. A rubber stopper kept the solution airtight at all times.

A proton NMR spectrum was run at 250 MHz (Figure 91), and the following peaks were found: δ8.2 (d, J=3.8 Hz), 7.9 (d, J=3.8 Hz), 2.65 (s). This sample was then irradiated at 313 nm for 8 hours. The ^1H NMR spectrum of

Table XXXIV. Photoreduction of Several Phenyl Ketones by Toluene: $k_q\tau$ Values Using Various Quenchers.

Ketone	Quencher[a]	[Toluene], M	$k_q\tau$[b]	# Runs
TFA	Pentadiene	1.07	826±10	2
TFA	Naphthalene	1.00	795±39	2
TFA	Hexadiene	1.00	722	1
TFA	Ethyl Sorbate	1.00	398±30	2
TFA	Fumaronitrile	1.00	480	1
p-CF_3-TFA	Pentadiene	0.108	122±6	2
p-CF_3-TFA	Naphthalene	0.100	161	1
p-Cl-TFA	Pentadiene	1.12	1790±26	2
p-Cl-TFA	Naphthalene	1.10	1750	1
m-Cl-TFA	Pentadiene	1.11	211	1
m-Cl-TFA	Naphthalene	1.00	233	1

[a]Runs with naphthalene quencher were irradiated at 366 nm; all other quenchers were irradiated at 313 nm. E_T values, in non-polar solvent (Reference 122): Pentadiene = 58.3 kcal; naphthalene = 60.9 kcal; hexadiene = 58.7 kcal.

[b]Average deviation reported.

the photolyzed sample (Figure 92) was run at 250 MHz, and some new small peaks appeared in the aromatic region; in addition a new peak showed up at 2.1 (s) (acetone). G.c. analysis using a 5% SE-30 column confirms that a new photoproduct has formed, with a retention time (at 250°C) that is much greater than that of the starting ketone.

Experiment B. - The experiment just described was repeated but 2-propanol was replaced by toluene-d_8, The ^1H NMR spectrum was run at 250 MHz (Figure 93), and the following peaks were found: δ8.1 (d, J = 3.8 Hz), 7.85 (d, J = 3.8 Hz), and 2.6 (s). The degassed solution was irradiated at 313 nm for 15 hours, and the ^1H NMR spectrum was taken again at 250 MHz (Figure 94). The aromatic region was too complicated to interpret, but it does inform us that a photoreaction has indeed occurred. The methyl protons still appear intact at 2.6 (s), and no new peaks were found.

Further irradiation of the above sample for a total of 33 hours still left the original methyl protons intact and no new peaks were found (Figure 95).

DISCUSSION

As discussed in the Introduction, the photoreduction mechanism of triplet ketones is composed of two key steps: the quenching interaction of substrate with the triplet ketone (with rate constant k_r); and the formation of stable products from the initially formed metastable intermediates (efficiency α; $\phi_{Max} = \alpha\phi_{isc}$). Assuming that $\phi_{isc} = 1$[8,62 81,123,124], the efficiencies of both steps determine the overall product yield. As is apparent from the kinetic scheme presented in the Introduction, the hydrogen transfer step from donor compound to ketone will be incorporated into the k_r term or as part of α, depending on whether the initial interaction involves direct hydrogen abstraction or exciplex formation (or a mixture of both).

Using $k_q = 1.0 \times 10^{10}$ $M^{-1}s^{-1}$[81], the experimental results from Tables I and II, III and IV were used to calculate k_r, k_d and ϕ_{Max} ($=\alpha$), which are summarized in Tables XXXV and XXXVI for the photoreduction of substituted α,α,α-trifluoroacetophenones in the presence of toluene and p-xylene, respectively. The data from Tables VII and VIII for the photoreduction of substituted acetophenones by p-xylene led to the values reported in Table XXXVII. The data from Tables XIV and XV for the photoreduction of

Table XXXV. Photoreduction of α,α,α-Trifluoroacetophenones by Toluene in CH_3CN

Subst.[a]	$k_r(10^7)$, $M^{-1}s^{-1}$[c]		$k_d(10^7)$, s^{-1}		ϕ_{Max}^{BB}[b]	
m-CF_3	78	(100)	1.6	(3.0)	0.016	(0.05)
p-CF_3	44	(72)	2.9	(3.6)	0.063	(0.10)
m-Cl	4.7	(4.9)	0.30	(0.6)	0.049	(0.067)
p-CH_3CO	3.2		0.81		0.026	
p-F	1.5		0.031		0.060	
H	0.93	(1.1)	0.29	(0.2)	0.024	(0.04)
p-Cl	0.42	(0.49)	0.10	(0.14)	0.054	(0.075)
p-t-Bu	0.36		0.28		0.030	
p-CH_3	0.074	(0.09)	0.053	(0.09)	0.056	(0.07)
m-CH_3	0.068	(0.23)	1.1	(0.41)	0.039	(0.032)
3,4-di-Me	0.023[d]		0.39		0.047	
p-MeO	0.0080	(0.0048)	0.038	(0.035)	0.064	(0.06)

[a] 0.05 M ketone solutions, irradiated at 313 or 366 nm. Formation of BB monitored. Values in parenthesis taken from Reference 81, work also in acetonitrile.

[b] From the reciprocal of the intercept from the double reciprocal plots.

[c] Error boundary within 15%.

[d] ±50%.

Table XXXVI. Photoreduction of Substituted α,α,α-Trifluoroacetophenones by p-Xylene in CH_3CN.

Subst.	$k_r(10^8)$, M^{-1} s^{-1} [a,b]	$k_d(10^6)$, s^{-1}	ϕ_{Max}^{DTE} [b,c]
p-CF_3	31		
p-CH_3CO	5.1	5.7	0.093
H	2.2	7.5	0.11
m-CH_3	0.29	3.9	0.11
p-MeO	0.0021	0.46	0.092

[a] 0.05 M ketone solutions, irradiated at 313 or >335 nm. Formation of BB monitored.

[b] Taken from the inverse of the intercept of the double reciprocal plots.

[c] Error boundary within ±10%.

Table XXXVII. Photoreduction of Substituted Acetophenones by p-Xylene in CH_3CN.

Subst.[a]	$k_r(10^6)$, $M^{-1}s^{-1}$	$k_d(10^5)$, s^{-1}	ϕ_{Max}^{DTE}[b]
m-CN	15	10	0.0317
m-CF_3	6.4	5.7	0.139
p-CF_3	4.7	3.0	0.206
m-Cl	2.8	5.2	0.105
p-CN	1.8	1.3	0.130
p-$COCH_3$	1.8	4.1	0.057
H	0.70	2.3	0.280
m-Ho	0.27	6.3	0.158
p-t-Bu	0.20	2.2	0.047
p-Cl	0.20[c]	0.73	0.152
p-Me	0.081[c]	4.5	0.107
3,4-di-Me	0.034[c]	3.3	0.023
p-MeO	0.034	1.8	0.039

[a] 0.01-0.03 M ketone solutions, irradiated at 313, 335, or >366 nm. Formation of DTE monitored. Error boundary within ±15%.

[b] Taken from the reciprocal of the intercepts from the double reciprocal plots.

[c] ±50%.

substituted benzophenones led to the parameters reported in Table XXXVIIII. As mentioned earlier, the goal in this project was to determine whether there is an inherent reactivity difference between n,π* and π,π* triplets, and the series of compounds studied were chosen to allow one to examine the behavior of separate n,π*, π,π* or energetically proximate triplets. Before examining this key question, two preliminary topics will be addressed. (a) A few of the triplet α,α,α-trifluoroacetophenones were quenched by pentadiene, whereas naphthalene was used in all the other Stern-Volmer experiments reported in this thesis. One must establish that both quenchers give similar k_q values. (b) If self-quenching rates are sizeable, then large k_d values will be observed. This would lead to steep slopes in the double reciprocal plots (since slope/intercept = k_d/k_r) and large experimental errors. Self-quenching can be minimized by working with dilute ketone concentrations.

Relative Quenching Rate Constants, k_q for Various Quenchers

The quenching of triplet ketones by exothermic energy transfer was thought at one time to be diffusion controlled[7,125-127], such that transfer of energy occurs on every collision[128]. Hammond[129] examined the photoreduction of benzophenone by benzhydrol in the presence of naphthalene and 1,3-pentadiene, and found k_q/k_r ratios of 750 for <u>both</u>

Table XXXVIII. Photoreduction of Substituted Benzophenones by p-Xylene in CH_3CN.

Subst.	$k_r(10^6)$, M^{-1} s^{-1} [a]	$k_d(10^5)$, s^{-1}	ϕ_{Max}^{DTE} [b]
m-CF_3	30	13	0.0407
p-CN	30	3.8	0.12
m-Cl	28	8.8	0.0526
p-CF_3	26	4.8	0.0559
4,4'-Cl	8.3	2.6	0.13
4,4'-F	7.6	4.3	0.0909
p-Cl	7.2	3.7	0.0917
H	6.9	3.9	0.0645
4,4'-t-Bu	2.4	9.3	0.24
4,4'-Me	1.7	7.5	0.21
4,4'-MeO	0.84	12	0.20

[a] 0.05 M ketone solutions, irradiated at 313, >335 or 366 nm. Formation of BB monitored. Error boundary within ±10%.

[b] Taken from the inverse of intercept of the double reciprocal plots.

quenchers. However, in this work a benzyl radical is produced, and it is possible that addition to the double bond[130,131] of the diene may consume the quencher. To examine this question, the photoreduction of several α,α,α-trifluoroacetophenones by toluene was quenched by 1,3 pentadiene and other compounds. The Stern-Volmer experiments (Table XXXIV) gave the same $k_q\tau$ values for naphthalene, pentadiene and hexadiene, and straight lines were obtained in these experiments. These results indicate that the dienes have not been consumed to an appreciable extent. Apparently the diffusion-controlled coupling of benzyl radicals is much faster than addition to the low concentrations ($\sim 10^{-3}$ M) of the dienes. These dienes are an attractive alternative to naphthalene as a quencher, which absorbs light at 313 nm but these compounds do not[132]. To prevent internal filtering by naphthalene, filters must be used to eliminate all the light at λ <335 nm. Since many ketones absorb weakly at these longer wavelengths, long irradiation times are required, which can be avoided by using a quencher like pentadiene or hexadiene at 313 nm. However, to ensure that radical addition does not occur appreciably at higher diene concentrations one needs to know the rate constant for such a process.

When ethyl sorbate and fumaronitrile were used as quenchers (Table XXXIV), the $k_q\tau$ values measured were about half as large as found for pentadiene, hexadiene,

and naphthalene. This is a puzzling observation. There should be no steric hindrance to energy transfer, and the only unusual feature appears to be the fact that electron-withdrawing groups are present. It is possible that the energy transfer process may be different for these compounds, and not truly diffusion-controlled. Turro[134] and Caldwell point out that energy transfer may occur via a concerted exchange of electrons between donor and acceptor, or a charge transfer exchange of electrons. It is possible that the former mechanism may occur in the case of naphthalene, pentadiene, and hexadiene, but that the electron-deficient fumaronitrile and ethyl sorbate may exchange electrons in a stepwise manner, leading to an overall slower quenching rate. As mentioned earlier, triplet ketones are known to form charge-transfer exciplex[76,133] with ground state olefins.

Self-Quenching

As discussed in the Introduction, ground state ketones may deactivate excited state ones[108-110]. From the experiments reported in Tables X and XI it is apparent that the quantum yields of di-tolylethane (DTE) and bibenzyl (BB) formation are not affected by the concentration of substituted α,α,α-trifluoroacetophenones and benzophenones, but are very sensitive in the case of substituted acetophenones, Table IX. Self-quenching rate

constants for these acetophenones must be competitive with k_r values.

The effect of k_{sq} values on triplet lifetimes are given by Equation (37).

$$\tau^{-1} = k_r[\text{Donor}] + k_d + k_{sq}[\text{Ketone}] \qquad (37)$$

From Equation (37) one sees that a plot of τ^{-1} vs [ketone] at a fixed donor concentration gives a slope = k_{sq}. Values of τ^{-1} as a function of ACP concentration were taken from Table XII and are plotted in Figure 58. Values of k_{sq} = 8.2 x 10^6 and 4.6 x 10^6 $M^{-1}s^{-1}$ were found at [p-xylene] = 1.44 and 0.15 M, respectively (Table XXXIX). The discrepancy between these two experimental values is not surprising since τ^{-1} values did not vary much for ACP concentrations of 0.2 and 0.01 M. (Notice the narrow slopes in Figure 58). Steel[110] measured a k_{sq} value of 1.9 x 10^7 x 10^7 $M^{-1}s^{-1}$ by flash photolysis.

Comparing the k_{sq} just calculated with the k_r reported in Table XXXVII indicates that k_{sq}/k_r = 10. At large ketone concentrations, the self-quenching term leads to short lifetimes, τ.

Low ketone concentrations (ca. 0.05 M) were used in all the experiments used to calculate the rate constants reported in Tables XXXV-XXXVIIII, especially for the acetophenones ($\leq$0.03 M).

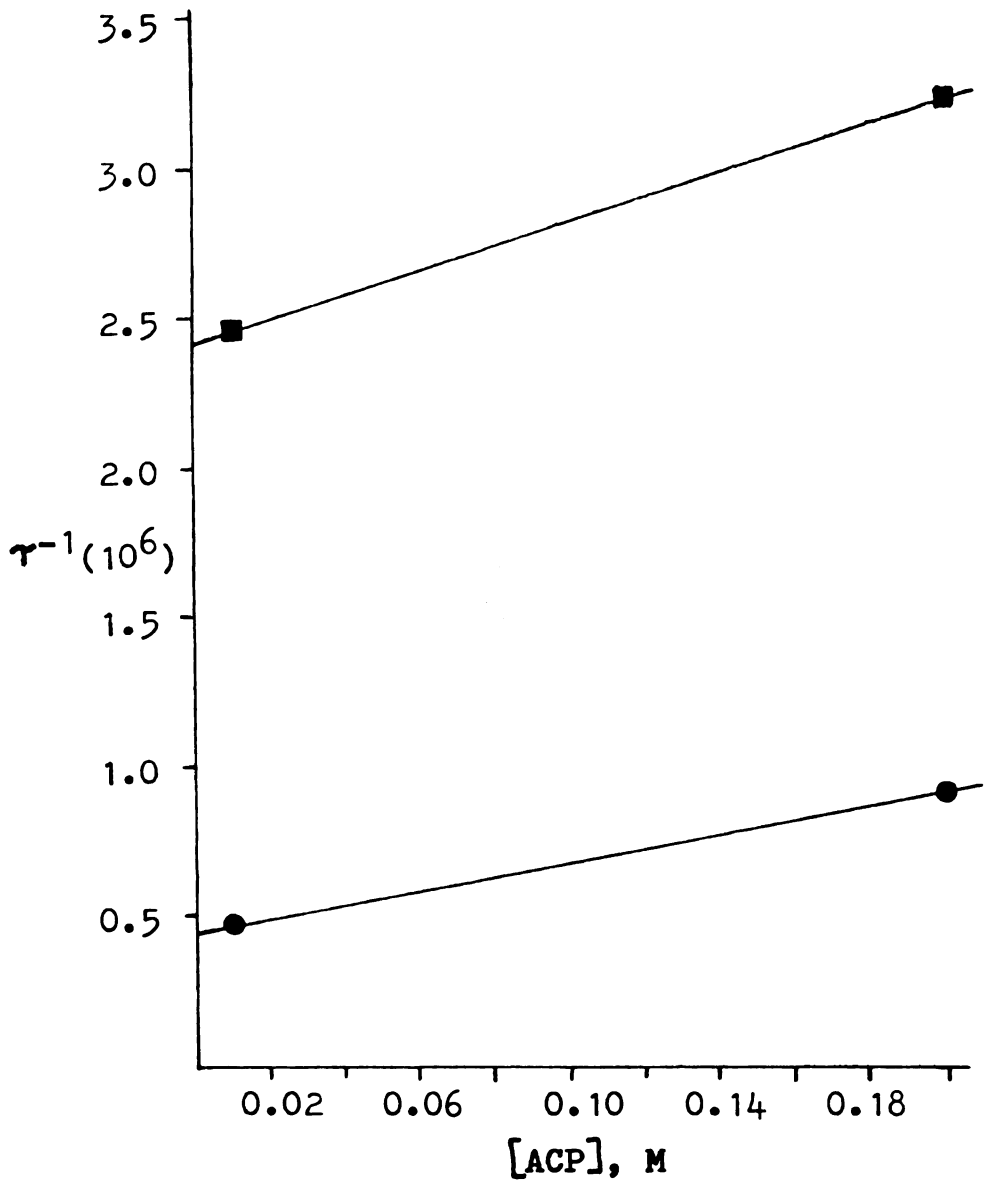


Figure 58. τ^{-1} vs ACP: ■, [p-Xylene]=1.44 M; ●, [p-Xylene]=0.15 M, in CH_3CN.

Table XXXIX. Self-Quenching of Acetophenone in CH_3CN.

[p-Xylene],M	$k_{sq}(10^6)$, $M^{-1}s^{-1}$	[ACP],M	$k_d^{obsd}(10^5)$ s^{-1}[b]
1.44	8.2[c]	0.01	2.4
0.15	4.6[d]	0.2	6.4
----	19[a]	---	---

[a]From Reference .

[b]Sum of unimolecular and self-quenching processes.

[c]From Equation 37: $k_{sq} = \Delta\tau^{-1}/\Delta[\text{ketone}]$; from Table XII: $(6.44-4.88)\ 10^6/(0.2-0.01)$

[d]From Equation 37: $k_{sq} = \Delta\tau^{-1}/\Delta[\text{ketone}]$; from Table XII: $1.82-0.937)\ 10^6/(0.2-0.01)$

The effect of self-quenching on observed k_d values is shown in Equation (38)

$$\tau^{-1} = k_r[\text{Donor}] + k_d^{obsd} \quad , \qquad (38)$$

$$k_d^{obsd} = k_d + k_{sq}[\text{ketone}]$$

where k_d^{obsd} is now the sum of all unimolecular and bimolecular decay processes. In Figure 59, τ^{-1} is plotted against [p-Xylene], using values from Table XII. The k_d^{obsd} values, taken from the intercepts, are given in

Table XXXIX: at [ACP] = 0.01 M, k_d^{obsd} = 2.4 x 10^5, at [ACP] = 0.2 M, k_d^{obsd} = 6.4 x 10^5 s^{-1}, once again confirming that a sizeable amount of self-quenching is occurring. This can lead to large slopes in double reciprocal plots, k_d/k_r = slope/intercept. Similar experiments could be performed to determine the effect of ring-substitution on k_{sq} and hence k_d^{obsd} values.

With these preliminary comments taken care of we are ready to discuss the rate constants in Tables XXXV-XXXVIII. The measured k_r values in these tables include all quenching interactions of the triplet ketone and a ground state donor molecule. The components that may be involved in the observed k_r values are indicated in Equation (39)[62].

$$k_r^{obsd} = \chi_n k_H^n + \chi_n k_{CT}^n + \chi_\pi k_{CT}^\pi \qquad (39)$$

where χ_n and χ_π represent the fractional population of the $^3n,\pi^*$ and $^3\pi,\pi^*$ states, with their sum = 1.0; k_{CT}^n and k_{CT}^π represent the rate constants for exciplex formation. Direct hydrogen abstraction by the π,π^* triplet can probably be neglected[58], so no $\chi_\pi k_H^\pi$ term has been included in Equation (39).

The small ϕ_{Max} values observed (ca. 0.1) in Tables XXXV-XXXVIIII are consistent with the notion that the photoreductions proceed almost entirely via an exciplex mechanism, as discussed in the Introduction[61,97,81].

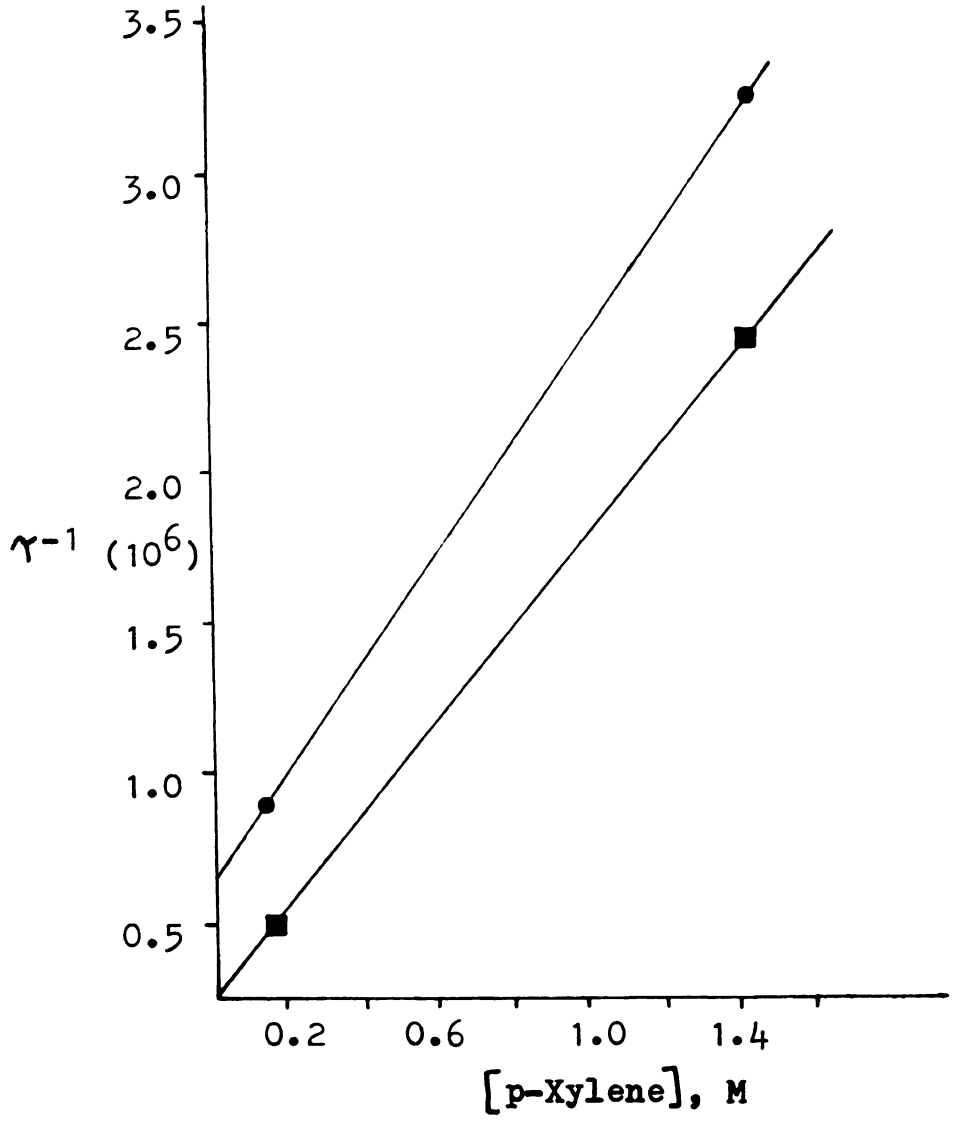


Figure 59. τ^{-1} vs p-Xylene : ● ACP =0.2 M; ■ ACP =0.01 M, in CH_3CN.

Since we are interested in the question of the amount of charge-transfer involved in these reactions, log k_r values were plotted against E^*_{red}, taken from Tables VI, XIII and XVI (Figures 60-63).

The three classes of compounds all showed negative slopes, such that the ketones with more negative E^*_{red} have the larger k_r values. Qualitatively, a good correlation between log k_r values and E^*_{red} indicates that CT must be involved in the quenching interaction.

The isotope effect studies from Table XVII were used to calculate the parameters reported in Table XL. Sizeable k^H/k^D ratios were found when BP and 4,4'-di-Me-BP were photoreduced by toluene and toluene-d_8. This could be interpreted to mean that such compounds are photoreduced primarily via a direct hydrogen-atom abstraction mechanism[62] when toluene is the donor, or alternatively, that exciplex formation is partially reversible, such that k_r values are expressed by Equation (40).

$$k_r = k_{CT}(k_{pt} + k_e)/(k_{-CT} + k_{pt} + k_e)^{62} \qquad (40)$$

where k_{pt} is the proton transfer step, k_e exciplex deactivation, and k_{-CT} reversible exciplex formation, as was shown in Scheme 2. Small k^H/k^D ratios were found for p-MeO-TFA and p-CF_3-TFA, which have lower E^*_{red} values than the preceeding benzophenones. For these latter

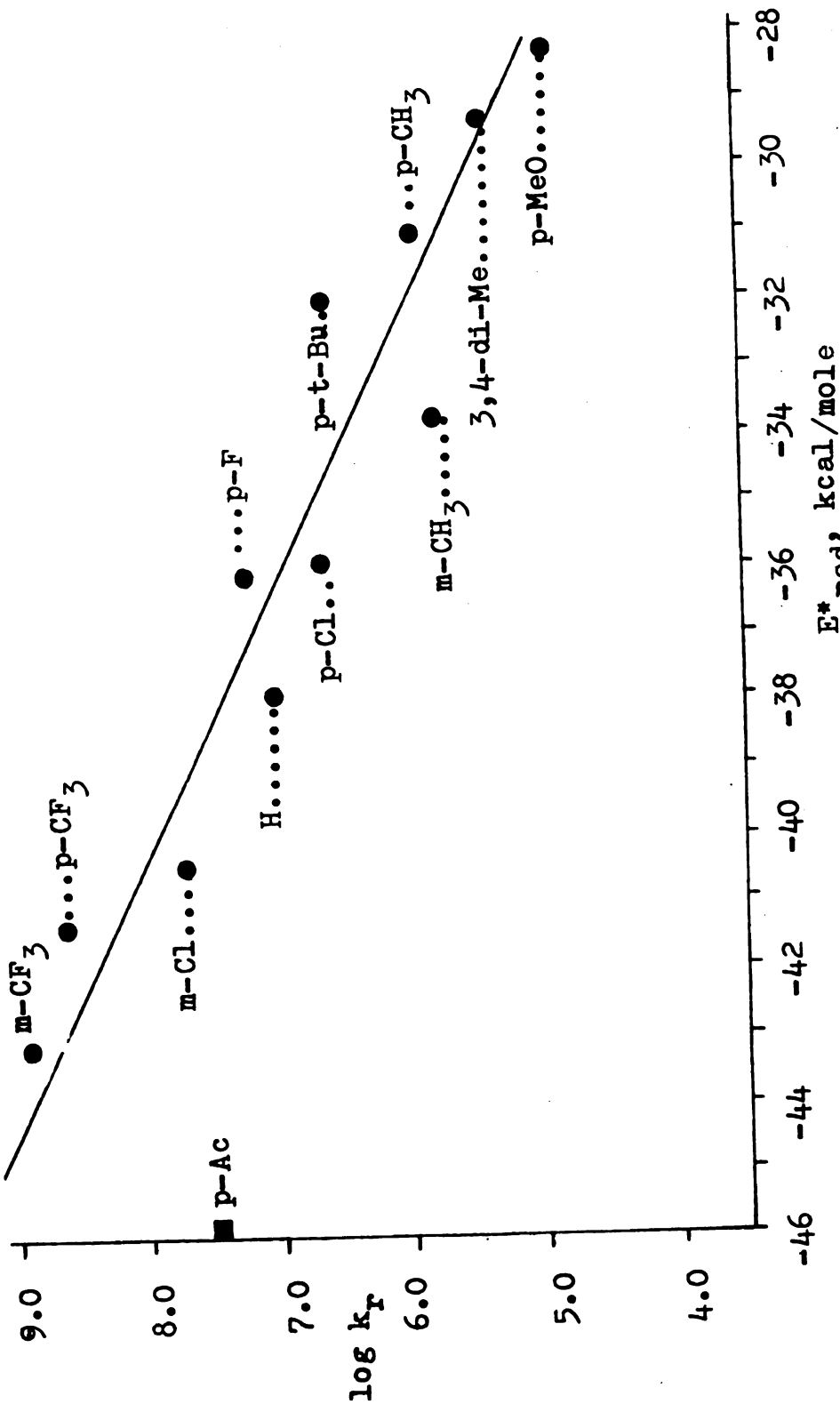


Figure 60. Photoreduction of Substituted α,α,α-Trifluoroacetophenones by Toluene in CH_3CN. Dashed line: the Predicted Slope of -0.163/kcal for $^3\pi,\pi^*$ States.

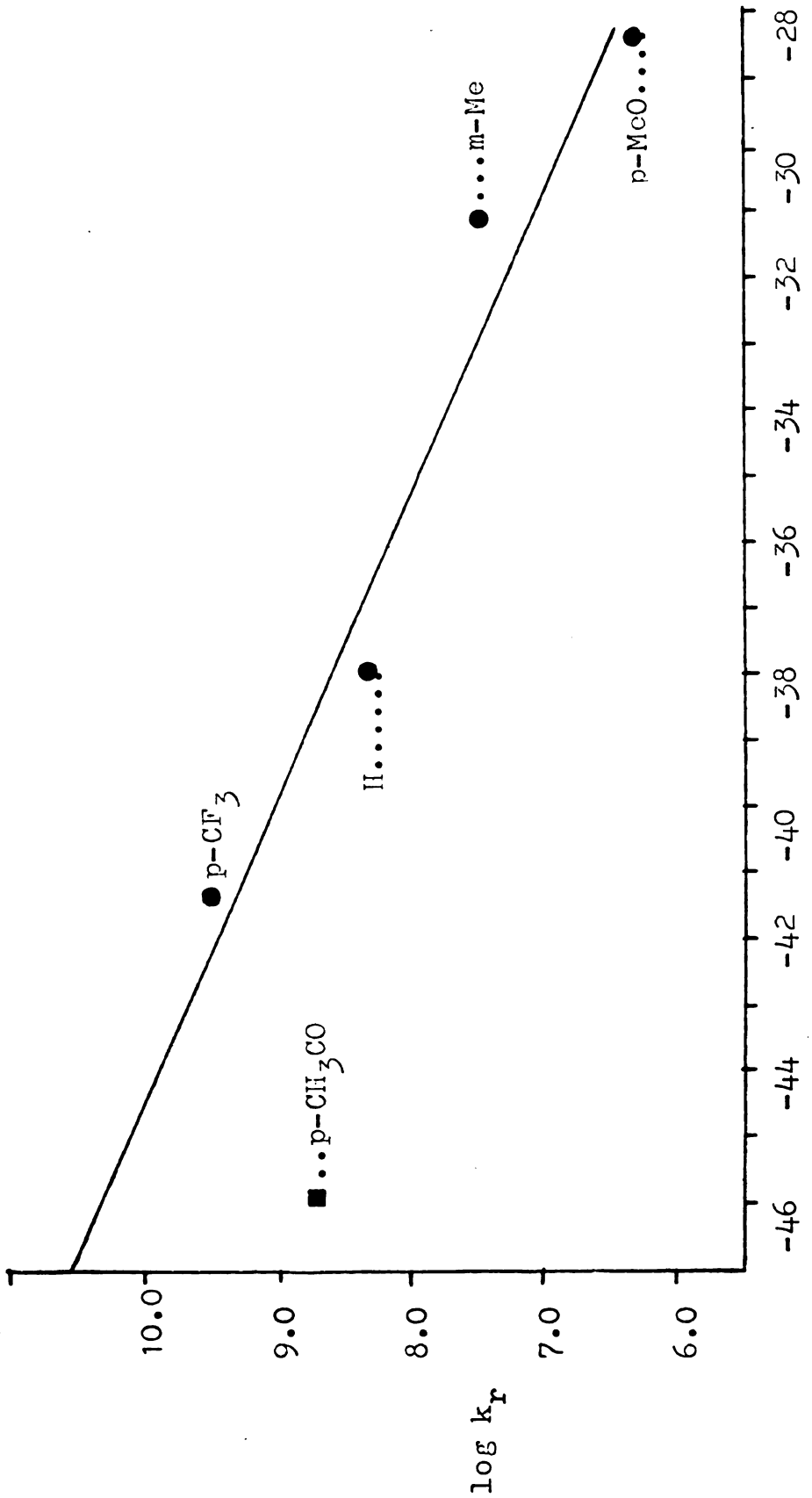


Figure 61. **Photoreduction of α,α,α-Trifluoroacetophenones by p-Xylene in CH_3CN.**

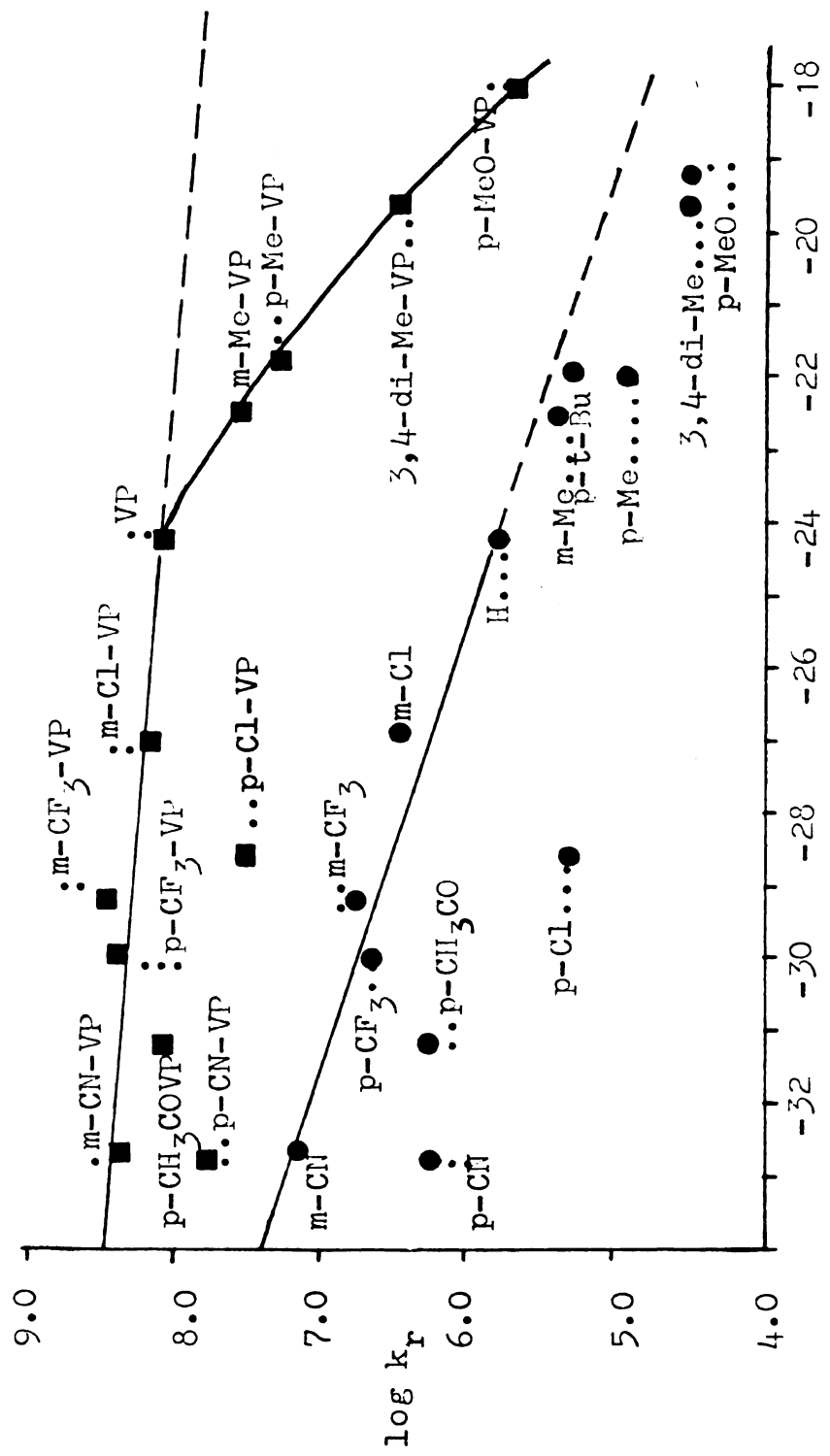


Figure 62. **Photoreduction of Acetophenones (●) by p-Xylene in CH_3CN, and the Type II Reaction of Valerophenones in Benzene (■).**

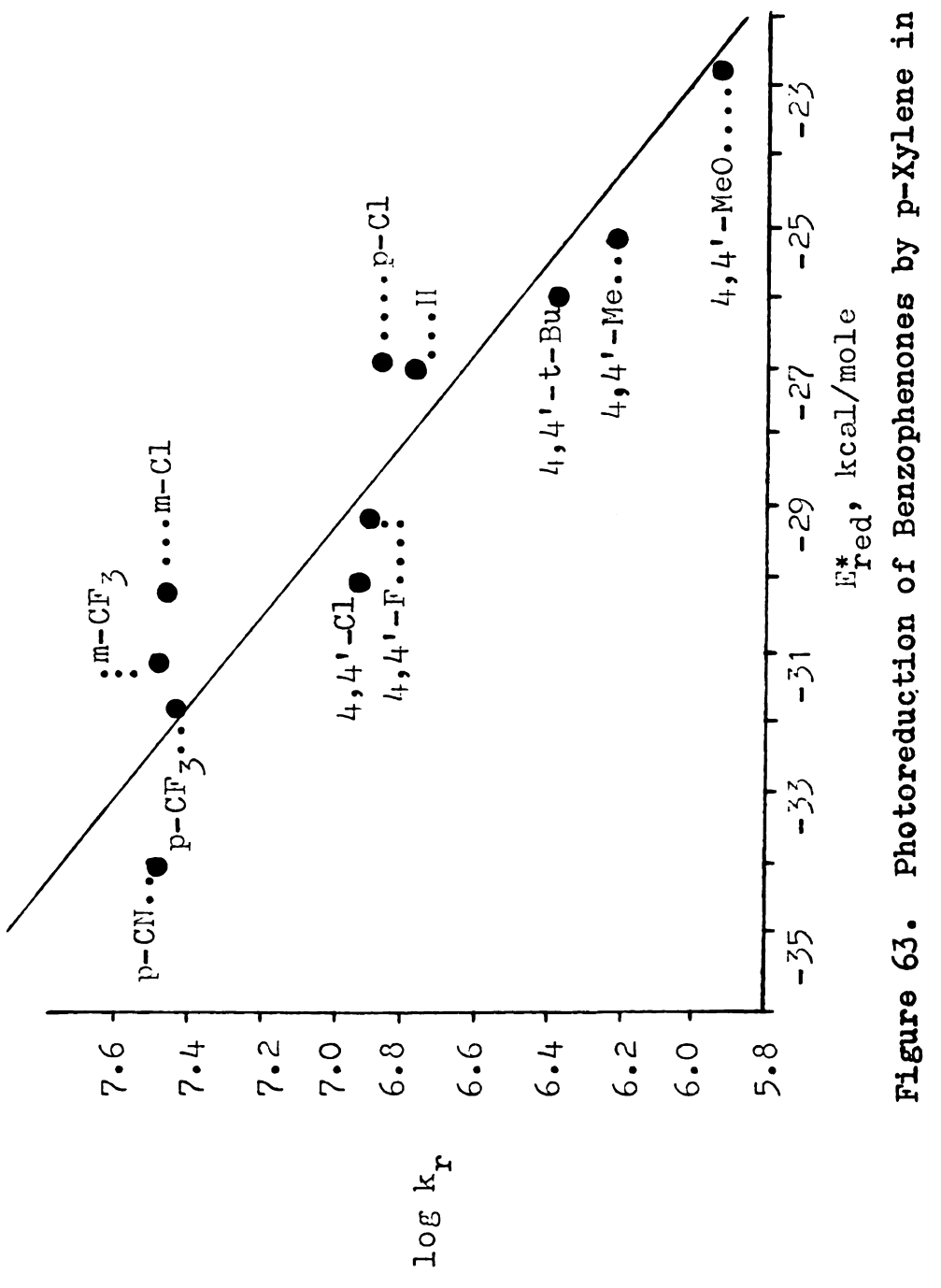


Figure 63. Photoreduction of Benzophenones by p-Xylene in CH_3CN.

Table XL. Photoreduction of Ketones by Toluene and Toluene-d_8 in CH_3CN.

Ketone	$k_r(10^4)$, $M^{-1}s^{-1}$	Donor	ϕ^{BB}_{Max} [a]	k^H/k^D
p-MeO-TFA	7.9	Toluene	0.0641	1.1
p-MeO-TFA	7.1	Toluene-d_8	0.0490	
BP	33	Toluene	0.0926	3.3
BP	10	Toluene-d_8	0.0775	
p-CF_3-BP	78	Toluene	0.220	1.4
p-CF_3-BP	55	Toluene-d_8	0.0649	
4,4'-di-Me-BP	7.5[c]	Toluene	0.694[d]	(6.3)
4,4'-di-Me-BP	1.2[c]	Toluene-d_8	----	
4,4'-di-Me-BP k_r	= 2.4[b]	Toluene		2.4
4,4'-di-Me-BP k_r	= 1.0[b]	Toluene-d_8		

[a] Inverse of the intercept from double reciprocal plots.

[b] By phosphorescence quenching; benzene used as solvent.

[c] Assuming the correct intercept=4, the lowest possible value; the calculated k_r is the minimum value.

[d] Large error expected, due to the very steep slope.

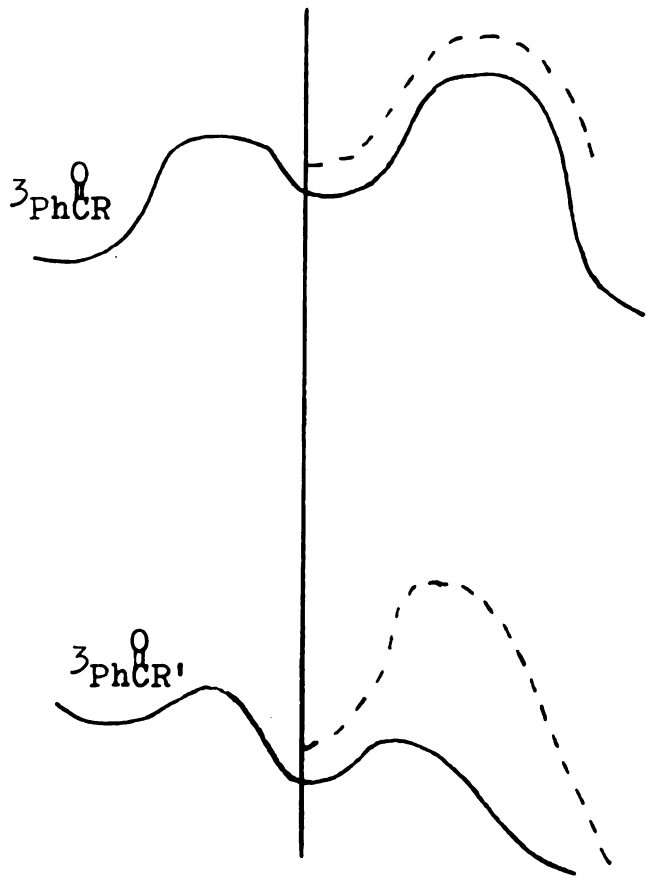
compounds very stable exciplexes may form irreversibly. The two cases are illustrated in Scheme 5[96]. The reaction coordinate on the left corresponds to CT complexation (Scheme 5), on the right to hydrogen-transfer to the carbonyl. The top case refers to an exciplex in which little CT has occurred, which may be partially (or completely reversible).

As will be discussed latter, the reversible exciplex explanation for the large k^H/k^D ratios is consistent with large ϕ_{Max} values, but a direct hydrogen atom abstraction mechanism is not.

All the evidence presented so far, low ϕ_{Max} values and good correlations in log k_r vs E^*_{red} plots, suggests that the exciplex mechanism accounts for most of the photoreactivity summarized in Tables XXXV-XXXVIII. The relative rates for which n,π* and π,π* triplets form exciplexes with toluene and p-xylene will be discussed next. Whether direct hydrogen atom abstraction can also occur will be discussed later.

The Charge-Transfer Exciplex Mechanism

The discussion that follows will be broken into three sub-sections: (a) The behavior of ketones with n,π* lowest triplets: (b) Ketones with π,π* lowest triplets; and (c) Ketones with proximate triplets.



Scheme 5. Triplet-State Hydrogen Abstraction; ——Proton Transfer, ---Direct Hydrogen Atom Abstraction.

(a) Ketones with n,π^* Lowest Triplet States

All the benzophenones in Table XXXVIII have n,π^* lowest triplets[56,99,100-102] as do the acetophenones with non-conjugating electron-withdrawing ring substituents[11,24,100]. Thus, log k_r *vs* E^*_{red} plots for these compounds illustrate the response of k^n_{CT} toward the ketone excited state reduction potential. For the benzophenones (Figure 63), a slope = -0.162/kcal (corr. = 0.93; 11 points) was found, and for the acetophenones with electron-withdrawing substituents (Figure 62), slope = -0.163/kcal (corr. = 0.98, 5 points). The slopes are quite different from that found for analogous valerophenones with electron-withdrawing substituents (Figure 62). The flat line and poor correlation contrasts strongly with the preceding plots, and confirm the notion that the k_r values measured are composed primarily by k^n_{CT}.

One is probably justified in extrapolating the line for the substituted acetophenones just described to predict k^n_{CT} values for those acetophenones with electron-donating substituents (Figure 62), since no breaks are found in the plot involving similar substituents on BP. These predicted k^n_{CT} values will be used later to estimate the relative contributions from $\chi_n k^n_{CT}$ and $\chi_\pi k^\pi_{CT}$ terms for proximate triplets.

The triplet energies, E_T, used in the E^*_{red} term are those measured directly by phosphorescence emission at 77°K in 2-methyltetrahydrofuran glass (Tables VI, XIII

and XVI). This polar solvent was chosen to mimic the polarity of CH_3CN in which the photoreductions were performed. The actual room temperature E_T values in fluid CH_3CN should be a little lower than measured: the n,π^* triplet energies in frozen media are about 2 kcal greater than in fluid solvents[28], since the excited state is locked in an unfavorable ground state geometry. Addition is iso-pentane would soften the glass, allowing the excited molecule some freedom to rearrange into a stabler excited state geometry. However, addition of iso-pentane would change the polarity of the glass. A second correction involves the difference between the absorption and emission energy measured. This Stoke's shift of ca. 1 kcal[28] would raise the E_T values calculated. However, it is not necessary to use the exact values since the correction term for each compound should be small and similar from compound to compound, so no corrections were made in plotting k_r values against E^*_{red}.

(b) Ketones with π,π^* Lowest Triplet States

Several of the acetophenones studied have lowest π,π^* triplets. From Figure 62, p-Cl-ACP, p-CN-ACP, p-Ac-ACP, and p-MeO-ACP are photoreduced by p-xylene with rate constants, k_r, about an order of magnitude smaller than predicted from the line correlating those acetophenones with lowest n,π^* triplets. This is an important observation,

since it allows one to estimate the difference in reactivity between triplet π,π^* and n,π^* states toward an aromatic donor.

All the substituted α,α,α-trifluoroacetophenones have lowest π,π^* triplets[81]. A log k_r *vs* E^*_{red} (Figure 61, donor = p-xylene) gave a slope of -0.209/kcal, and -0.244/kcal using toluene as the donor (Figure 60). This later value agrees reasonably well with a previous study[81] (slope = -0.30/kcal). The difference in slopes found when using toluene *vs* p-xylene, though not very great, does argue against the view that slopes from log k_r *vs* E^*_{red} and log k_r *vs* IP plots represent the amount of charge transferred in forming an exciplex, as discussed in the Introduction. This view would require the same slopes. Qualitatively, one can state that good correlations between log k_r and E^*_{red} values do indicate that CT occurs in triplet state quenching. Assuming a proportionality between $\Delta G^{\neq}$ and ΔG_{CT}, more CT would stabilize the exciplex, lower $\Delta G^{\neq}$ and accelerate the observed k_r values. The steepness of the slope from a log k_r *vs* E^*_{red} may only indicate how well a given excited state can accept CT from a particular donor.

(c) Ketones with Proximate Triplet States

The relative contribution of $\chi_n k^n_{CT}$ and $\chi_\pi k^\pi_{CT}$ terms to the observed k_r values for ketones with proximate triplets

states will be examined in this section. The following steps will be taken. (i) ΔE_T values will be estimated to calculate the relative population of both excited states; (ii) k_{CT}^n values will be estimated by extrapolating log k_r vs E_{red}^* plots, for those compounds with lowest n,π* triplets; (iii) Finally, estimates of $\chi_\pi k_{CT}^\pi$ will be made by comparing observed k_r values (k_r^{obsd}) with calculated $\chi_n k_{CT}^n$ values: $\chi_\pi k_{CT}^\pi = k_r = \chi_n k_{CT}^n$ (see Equation (39)).

Relative Triplet Energy Spacings, ΔE_T. Calculated ΔE_T values have been published for substituted valerophenones in benzene. Since the k_r values in this thesis were almost all measured in CH_3CN, it must be determined whether these ΔE_T values can be applied to the present work.

If CH_3CN significantly stabilizes the π,π* triplet state (compared to benzene), k_H values measured in the more polar solvent would be significantly lower. Wagner and Siebert[29] found similar k_H values for substituted valerophenones in both solvents. In addition, the absolute and relative k_H values of valerophenone (VP), p-Me-VP, and p-MeO-VP can be calculated from the experiments summarized in Table XXXIII, as shown in Table XLI.

The results from Table XLI suggest that the rate constants for direct hydrogen abstraction are about the same in CH_3CN and benzene, and the ΔE_T values are probably similar in both solvents, since $k_H \alpha e^{-\Delta E/RT}$[28].

Table XLI. Type II Reaction in CH_3CN and Benzene.[a]

Ketone	Solvent	$\tau^{-1}(10^7)$ s^{-1}	$k_H(10^7)$ s^{-1}	$k_H(VP)$ $k_H(X\text{-}VP)$
VP	CH_3CN	9.7	9.7	
VP	Benzene	11.4	11.4(12.5)[b]	
p-Me-VP	CH_3CN	1.5	1.5	6.5
p-Me-VP	Benzene	1.8	1.8[b]	6.3
p-t-Bu-VP	CH_3CN	2.5	2.5	---
p-MeO-VP	CH_3CN	0.15	0.039[c]	249
p-MeO-VP	Benzene	0.22[b]	0.057[c]	200

[a]This work, unless otherwise indicated.

[b]From Reference 27.

[c]$k_H = \phi_{Max}\tau^{-1}$, ϕ_{Max} = 0.26 from Reference 27, and assumed to be similar in benzene and dry CH_3CN.

Table XLII summarizes ΔE_T values for several substituted acetophenones. It has been assumed that substituents will affect the ΔE_T spacings of acetophenones and valerophenones[28] in an identical manner. If the substituents shown affect the α,α,α-trifluoroacetophenones in a parallel manner, then the E_T values for these compounds can be calculated. The ΔE_T of TFA is not known exactly, but it is probably a few hundred calories/mole[81].

Table XLII. Estimated ΔE_T Values for Substituted Acetophenones and α,α,α-Trifluoroacetophenones.

Ketone	ΔE_T[a], kcal	Substituent Effect (kcal)	Ketone	ΔE_T, kcal
ACP	-2.1	----	TFA	∿ 0[b]
m-Me-ACP	0.4	2.5	m-Me-TFA	∿2.5
p-t-Bu-ACP	0.6[c]	2.7	p-t-Bu-TFA	∿2.7
p-CN-ACP	0.67[d]	2.77	p-CN-TFA	∿2.8
p-Cl-ACP	0.87[e]	3.0	p-Cl-TFA	∿3.0
p-Me-ACP	1.0	3.1	p-Me-TFA	∿3.1
p-Ac-ACP	1.3[d]	3.4	p-Ac-TFA	∿3.4
3,4-di-Me	1.8	3.9	3,4-di-Me	∿3.9
p-MeO-ACP	2.8	4.9	p-MeO-TFA	∿4.9

[a] $\Delta E_T = E(^3n,\pi^*-^3\pi,\pi^*)$; values in benzene at room temperature[28]; acetophenones and valerophenones assumed to have the same ΔE_T values.

[b] From Reference 81: actual value estimated as a few tenths kcal/mole.

[c] ΔE_T for p-t-Bu-ACP calculated from the extrapolation of log k_H vs σ[28,29]; $k_n^{rel} = 0.75$, $k_H^n = 9.4 \times 10^7\ s^{-1}$; $\chi_N = k_H^{obsd}/k_H^n = 2.5 \times 10^7/9.4 \times 10^7 = 0.27$; $\Delta E_T = RT \ln(\chi_n^{-1}) = 0.60$.

[d] From Reference 28.

[e] Calc. as in c; $k_n^{rel}=1.3$, $k_H^n=1.6 \times 10^8\ s^{-1}$; $\chi_n=k_H^{obsd}/k_H^n=3.0\times10^7/1.6\times10^8=0.19$; $\Delta E_T=0.87$.

Thermal equilibration can populate an upper n,π^* triplet state[28]. The relative importance of the $\chi_n k_{CT}^n$ and $\chi_\pi k_{CT}^\pi$ terms in Equation (39) can be estimated if one can calculate k_{CT}^n values for those acetophenones with lowest π,π^* triplets. These can be estimated from the extrapolation of a log k_r vs E^*_{red} plot (Figure 62), shifted ΔE_T units (taken from Table XLII) to correct for the true E^*_{red} of the n,π^* state. The relevant parameters are summarized in Table XLIII.

Direct hydrogen atom abstraction probably makes only a negligible contribution to the observed k_r values for acetophenones with lowest π,π^* triplets: From Figure 62 the observed k_H values for the Type II reaction of analogous valerophenones drop off rapidly with triplet state inversion. In addition, the low ϕ_{Max}^{DTE} values found in Table XXXVII are inconsistent with a direct hydrogen abstraction mechanism.

From Table XLIII one sees that the observed k_r values are too large to be accounted for on the basis of thermal equilibration and reaction from only upper n,π^* triplets. This suggests that the lower π,π^* triplets are also involved: $k_r^{obsd} - \chi_n k_{CT}^n \doteq \chi_\pi k_{CT}^\pi$. For several of the compounds, $\chi_n k_{CT}^n \doteq \chi_\pi k_{CT}$; these tend to be those compounds with proximate triplet levels, which probably mix such that it is not possible to consider the contributions from discrete states. Other compounds (p-CN-ACP, p-Cl-ACP, p-Ac-ACP, 3,4-di-Me-ACP, and p-OCH_3-ACP) have $\chi_\pi k_{CT}^\pi >> \chi_n k_{CT}^n$. A sizeable decrease in observed k_r values was

Table XLIII. Predicted Values for $\chi_n k_{CT}^n$ and $\chi_\pi k_{CT}^\pi$ for Substituted Acetophenones with Lowest π,π^* Triplets.

Subst.	χ_n [a]	log k_{CT}^n [b]	k_{CT}^n [d]	$\chi_n k_{CT}^n$ [d]	k_r^{obsd} [d,e]	$\chi_\pi k_{CT}^\pi$ [d]
H	1.0	5.85	7.0	7.0	7.0	----
m-Me	0.34	5.65	4.5	1.5	2.7	1.2
p-t-Bu	0.27[c]	5.6	4.0	1.1	2.0	0.9
p-CN	0.25[f]	7.25	18	4.5	18	14
p-Cl	0.19[c]	6.6	4.0	0.76	2.0	1.2
p-Me	0.15	5.65	4.5	0.68	0.81	0.13
p-Ac	0.10[f]	7.1	13	1.3	18	17
3,4-di-Me	0.048	5.4	2.5	0.12	0.31	0.19
p-MeO	0.0090	5.5	3.2	0.029	0.31	0.28

[a] Reference 28. $\chi_n + \chi_\pi = 1$.

[b] Extrapolated from Figure 62 (see text); E_T values taken from Table XLII.

[c] From Table XLII.

[d] x 10^5, $M^{-1}s^{-1}$.

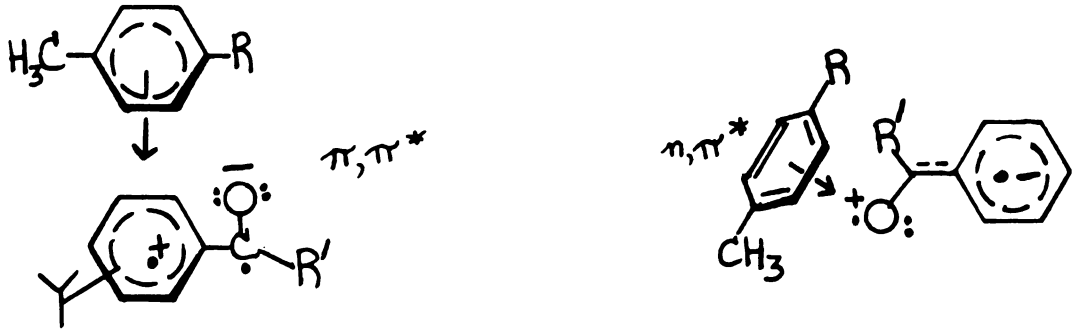
[e] From Table XXXVII.

[f] From Reference 29.

found for these compounds (Figure 62) when compared to those acetophenones with lowest n,π* triplets. It seems likely that virtually all the reactivity arises from the lowest $^3\pi,\pi^*$ states in spite of the relatively small ΔE_T values reported[29] for p-CN-ACP (0.67 kcal) and p-Ac-ACP (1.3 kcal). It is possible that for reasons not understood, the k_H values measured for p-CN-VP and p-Ac-VP are unusually large, leading to calculated ΔE_T values that are too small. By using model compounds possessing pure n,π* or π,π* triplets, Siebert[29] examined the effect of p-CN and p-CO_nBu on triplet energies. Predicted values in benzene at 25°C are 1.9 and 3.3 kcal, respectively. Though the error boundaries are sizeable in these studies, these large ΔE_T values do suggest low Boltzmann equilibrium populations of upper n,π* triplets such that $k_r \doteq \chi_\pi k_{CT}^\pi$. In any event, the decrease in observed k_r values for the acetophenones with low-lying π,π* triplets suggests that $k_{CT}^\pi \doteq 0.1\ k_{CT}^n$.

The two kinds of exciplexes discussed are depicted in Scheme 6.

As was discussed in the Introduction, if R_N (the inherent thermodynamics-independent k_{CT}^n/k_{CT} value[81]) is only about 10, then it will be difficult to see an S-shaped curve in the log k_r vs E_{red}^* plot for α,α,α-trifluoroacetophenones, which possess only lowest π,π* triplets. Figures 60 and 61 show that a straight line correlates all the



Scheme 6. Valence Bond Representations for n,π* and π,π* Exciplexes.

experimental points. However, the acetophenones can possess lowest n,π* or π,π* triplets, and from Equation (12) and (14) in the Introduction[81] three separate regions should be seen in the log k_r vs E^*_{red} plot: ketones with large $|\Delta E|$ should determine two lines, and ketones with both triplets populated would give a roughly S-shaped curve between the two lines. This prediction is shown for the first time to be true. From Figure 62, ACP with non-conjugated electron-withdrawing substituents (lowest n,π* triplets) are correlated by a good line, whereas 3,4-di-Me-ACP and p-MeO-ACP (low-lying π,π* triplets) fall below this line and may begin a second line. The compounds with proximate triplets fall between these two regions, as predicted. Compounds such as p-Ph-ACP and 3,4,5-tri-Me-ACP

could be examined to clarify the trend in the low-lying π,π^* region.

Having established that the π,π^* triplets are about an order of magnitude less reactive than n,π^* triplets, it seemed of interest to see how bulky substituents affect the behavior of these states.

Effect of Bulky Substitution on Photoreactivity

The effect of replacing a p-Me with a p-t-Bu group on k_r and ϕ_{Max} values was examined for several ketones.

From Table XLIV the following observations can be made: (i) The k_H values for the Type II reaction of p-t-Bu-VP and p-Me-VP are similar, with the former being a little greater. Apparently the p-t-Bu group does not stabilize the π,π^* triplet as much as p-Me does, suggesting that inductively it may be less electron-donating[146] in the excited state. (ii) The k_r value of 4,4'-di-t-Bu-BP is greater than that of 4,4'-di-Me-BP, and the ϕ_{Max} values are the same. Little steric interference can be involved in the initial interaction and in the subsequent proton-transfer step. This confirms the notion that the chemical reactivity of a lowest n,π^* state is localized tightly about the carbonyl oxygen[18]. (iii) The ϕ_{Max} values measured for p-t-Bu-ACP and p-t-Bu-TFA are lower than were found for p-Me-ACP and p-Me-TFA, respectively. This

Table XLIV. Kinetic Parameters for the Photoreduction of Phenyl Ketones Substituted by p-Methyl and p-tert-Butyl Groups in Acetonitrile.

Ketone	$k_r(10^6)$, $M^{-1}s^{-1}$	Φ_{Max}[d]
4,4'-di-Me-BP[a]	1.7[b]±10%	0.21±0.031
4,4'-di-t-Bu-BP[a]	2.4[c]±10%	0.24
p-Me-ACP[e]	0.081[h]±15%	0.107[f]±0.061
p-t-Bu-ACP[e]	0.20[b]±15%	0.052±0.015
p-Me-TFA[g]	0.74[b]±15%	0.056±0.003
p-t-Bu-TFA[g]	3.6[b]±15%	0.030
p-Me-VP[i,l]	15[j]±2%	0.22[k]±0.006
p-t-Bu-VP[i]	25[i]±8%	0.34[k]±0.006

[a] 0.05 M ketone, donor = p-xylene; from Table XXXVIII.
[b] Average from two Stern-Volmer and two double reciprocal plots.
[c] Single Stern-Volmer and double reciprocal plot.
[d] Inverse of the intercept from the double recip. plots.
[e] 0.02 M ketone, donor = p-xylene. Table XXXVII.
[f] Wide scatter in the experimental values.
[g] 0.05 M ketone, donor = toluene. Table XXXV.
[h] Average of 3 Stern-Volmer, 5 double reciprocal plots.
[i] 0.05 M ketone in benzene, average of two runs; from Table XXXIII.
[j] $k_r = \tau^{-1}$ from the Stern-Volmer plots.
[k] $\Phi_{Max} = \Phi_{II} = \Phi_{ACP} + \Phi_{butanol}$.
[l] Lit.: $\tau^{-1} = 1.8 \times 10^7$, $\Phi_{II} = 0.39$[25], in benzene.

suggests that the lowest π,π^* triplets of these compounds must be involved to a significant extent in the photoreduction, with bulky substituents preventing good orbital overlap in the exciplex. If the photoreactivity arises only from equilibrium populations of the upper n,π^* triplets, then the ϕ_{Max} values would be the same, as was found in the case of the substituted benzophenones (lowest $^3n,\pi^*$ states). As was discussed in the Introduction, steric hindrance in an exciplex can lead to energy wastage[113] instead of a photoreaction. In the present case, proton transfer (k_{pt}) may be hindered but not back charge-transfer (k_e) (Scheme 2). Since the k_r value of p-t-Bu-ACP is larger than that of p-Me-ACP, and p-t-Bu-TFA greater than for p-Me-TFA, the tertbutyl group must not be offering much steric hindrance to exciplex formation. The interpretation of this effect is complicated by the fact that both triplets seem to be photoreactive: for p-t-Bu-ACP, $\chi_\pi k^\pi_{CT} \doteq \chi_n k^n_{CT}$ (Table XLIII).

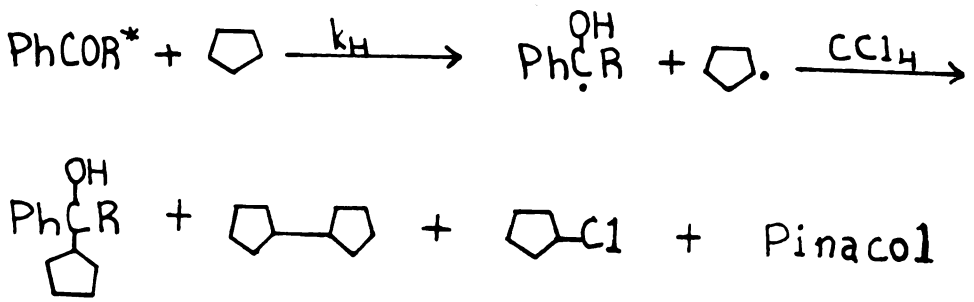
Direct Hydrogen Abstraction

The small ϕ_{Max} values and large substituent effect on k_r values (Tables XXXV-XXXVIII) indicate that the photoreductions examined proceed via a CT mechanism. The

amount of direct hydrogen atom abstraction (the $\chi_n k_H^n$ term in Equation (39)) competing with this mechanism is examined next.

Photoreduction Using Cyclopentane

It was anticipated that absolute k_H values would clarify how ring substituents affect the rate of direct hydrogen abstraction for ketones with lowest n,π* and π,π* triplets and what fraction of the observed k_r values may be assigned to this process. Photoreductions by chclopentane in CCl_4 were studied, Equation (41).



(41)

Unfortunately, these studies led to some difficulties, as will be discussed.

From Table XXIII, the photoreduction of TFA by cyclopentane in CCl_4 led to a ratio of chlorocyclopentane to cross-coupling product of 10:1. The photoreduction of BP also showed (Table XXII) that chlorocyclopentane accounts for almost all of the cyclopentane consumed. These studies suggest that almost all of the cyclopentyl radical formed is trapped by CCl_4. Since a few reports can be found in the literature in which cyclohexane is used as a donor,

the relative reactivity of cyclopentane and cyclohexane were compared by a competitive study, as shown in Table XXIV. The same chlorocycloalkane concentrations were found.

The usual Stern-Volmer and double reciprocal experiments were performed by analyzing chlorocyclopentane in most cases, Tables XXV and XXVI, and the kinetic parameters are summarized in Table XLV. The k_r values from flash photolysis studies reported in the literature are about an order of magnitude smaller than those calculated in this project. In addition, the k_d values reported in Table XLV are all larger than those measured in previous photoreductions using toluene or p-xylene as donors in CH_3CN (Tables XXXV-XXXVIII) for the same ketones. Clearly, the results for these studies must be treated with suspicion.

In an earlier report, Wagner and Leavitt[62] examined the photoreduction of TFA by cyclohexane in benzene. The reported k_H value (4.7×10^6 $M^{-1}s^{-1}$) agrees well with the value measured in CCl_4 (6.0×10^6 $M^{-1}s^{-1}$, this work), which indicates that the rate constants are reproducible, but it is not apparent why flash photolysis studies give lower values. The cyclopentane/CCl_4 system was explored in some detail, since no systematic study has been reported on how various ring substituents affect bimolecular k_H values.

The first difficulty addressed was why such large k_d values are obtained. Quenchers may be present in the solvent or may be formed photochemically.

Table XLV. Photoreduction of Some Phenyl Ketones by Cyclopentane in CCl_4.

Ketone[e]	$k_H(10^6)$ M^{-1} s^{-1}	$k_d(10^6)$ s^{-1}	ϕ_{Max}^{Cl-CP}[a]
ACP	1.8[b]	1.6	0.45
p-CF_3-ACP	5.1	0.41	0.60
p-CH_3-ACP	3.0	3.0	0.38
BP	6.2[c]	0.82	0.26
4,4'-di-Me-BP	6.3	1.8	0.110
4,4'-di-MeO-BP	11	8.6	0.0990
TFA	6.0[d]	1.8	0.252
m-Cl-TFA	3.4	1.7	0.282
p-MeO-TFA	0.87	0.51	0.535
p-Me-TFA	0.69	0.77	0.336

[a] Cl-CP=chlorocyclopentane; values are the inverse of the intercepts from the double reciprocal plots.

[b] k_H (neat cyclohexane) = 4.8×10^5 $M^{-1}s^{-1}$, by flash photolysis, Reference 135, 136; also, $k_H \pm 3.5 \times 10^5$ M^{-1} s^{-1} (cyclohexane in CH_3CN)[110].

[c] k_H (neat cyclohexane) = 3.6×10^5 $M^{-1}s^{-1}$, by flash photolysis; Reference 135, 138; k_H (cyclopentane, in PhH) = 5.0×10^5 $M^{-1}s^{-1}$, by phosphorescence quenching[137].

[d] k_H(cyclohexane, in PhH) = 4.7×10^6 $M^{-1}s^{-1}$, by a double redouble reciprocal plot, assuming that $k_d = 8.8 \times 10^6$ s^{-1}.[62]

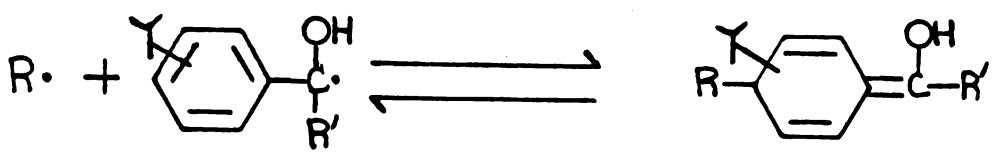
[e] Rate constants were calculated from Stern-Volmer and double reciprocal plots (Tables XXV, XXVI).

Formation of Cyclopentene. The photoreduction of TFA by neat cyclopentane led to the formation of cyclopentene as the major photoproduct (Table XXX). However, the photoreduction in the presence of 1 M cyclopentane in CCl_4 led to only very small concentrations of cyclopentene, too small to measure by vpc, indicating that in CCl_4 solvent, most of the cyclopentyl radical is trapped as soon as it is formed. Apparently very little in-cage hydrogen transfer from cyclopentyl radical to ketyl radical occurs.

Since at least a small amount of cyclopentene is formed, its effectiveness as a quencher was examined, using a ketone with a fairly long-lived triplet. Triplet p-MeO-TFA was quenched by 1.3 M cyclopentane in CCl_4 in the presence of various concentrations of cyclopentene. A Stern-Volmer plot (Figure 57, Table XXXI) gave a $k_q\tau$ value of 37.3. The same ketone, solvent and donor (1.03 M cyclopentane) with naphthalene as the quencher gave a $k_q\tau$ value of 3,500 (Table XXV). Ignoring the small differences in donor concentrations, one finds a ratio of $k_q\tau$ (pentene)/$k_q\tau$(naphthalene) $\doteq$ 0.01. Since it was already shown that similar $k_q\tau$ values are obtained for the quenching of the Type II reaction of valerophenone in benzene and CCl_4 (Table XXXIII, this work), then one can assume that the rate of diffusion of naphthalene is about the same, 5×10^9 s^{-1}, in both solvents. This indicates that the k_q of cyclopentene in CCl_4 is about 0.01 times the k_q of naphthalene, or ca

5×10^7 s^{-1}. Only if sizeable amounts of cyclopentene were to form photochemically could quenching of triplet ketone be competitive with the photoreduction in the presence of 1 M cyclopentane. Since very little cyclopentene forms in CCl_4, such quenching is probably negligible.

Other Quenching Products. Para-addition of radicals to a benzylic radical can generate highly conjugated quenching products[139-144] (Scheme 7).



R· = any radical found in the solution.

Scheme 7. Generation of Quenching Photoproducts.

Such products may be seen by UV spectroscopy. Identical degassed solutions of 0.02 M BP with 1 M cyclopentane in CCl_4 were irradiated at 313 nm for various lengths of time (Figure 56). Irradiations of 3 and 5 hours (the usual time required for Stern-Volmer and double reciprocal experiments) gave spectra resembling a non-photolyzed sample, whereas longer irradiation time (36 and 48 hrs) led to strong absorption beginning around λ = 500 nm. As irradiation time increased, the sample solutions turned a

darker yellow. Apparently quenchers can form photochemically, but the concentrations may be low for short irradiation times since new absorptions were not found in the UV spectra after relatively short irradiation times.

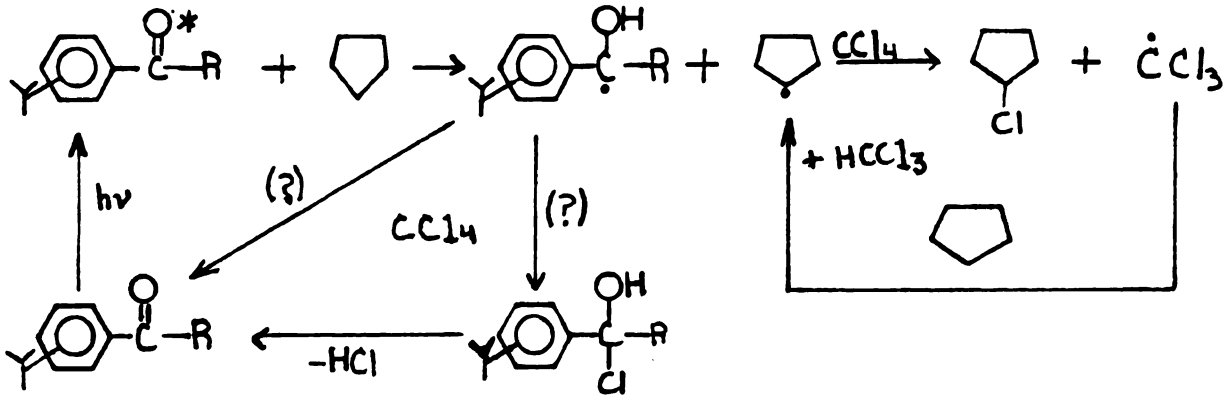
As another test for the formation of quenching products the concentrations of the major products from the photoreduction of BP by cyclopentane in CCl_4 were examined as a function of light intensity (Table XXVIII). Since the product quantum yields did not decrease very much at higher light intensity, it would seem that, at least for BP, only low steady state equilibrium concentrations of quenchers form. On the other hand, when the photoreduction of triplet TFA in neat cyclopentane was carried out to various conversions (Table XXIX), product quantum yields decreased steadily as conversion increased, confirming that quenchers can indeed be produced photochemically. But these quenchers may be produced in only low concentrations when the photoreaction is carried out in CCl_4 (Table XXVII). Apparently CCl_4 intercepts an intermediate radical such as cyclopentyl, which could otherwise form quenching products.

All these experiments suggest that sizeable amounts of quenchers are not formed when CCl_4 is used as a solvent and radical trap at relatively short irradiation times. The quenching observed in neat cyclopentane may include contributions from cyclopentane and highly conjugated products (Scheme 7). However, if <u>para</u>-coupling of

the radicals occurs to a sizeable extent, it would also occur when toluene or p-xylene are used as donors. It is possible that the large k_d values measured may be due to quenchers already present in CCl_4.

Another difficulty encountered when using cyclopentane as a hydrogen donor was that the substituted α,α,α-trifluoroacetophenones gave curved Stern-Volmer plots (Figure 36-42). Such behavior is typical of systems in which two excited states are involved in a photoreaction. Since it is conceivable that both the n,π* and π,π* triplets may be reacting, the quenching of p-MeO-TFA and p-Me-TFA were re-examined by analyzing the cross-coupling product. The Stern-Volmer plots no longer curve (Figure 39,40), and a $k_q\tau$ (for p-MeO-TFA) almost 40 times greater (Table XXV) was found than when chlorocyclopentane concentrations were monitored. If two excited states of very different reactivities were involved, then the curved behavior should be seen when either of these photoproducts are used in the Stern-Volmer plots. From Table XXV, the photoreduction of BP by cyclopentane in CCl_4 led to similar $k_q\tau$ values when monitoring chlorocyclopentane, the cross-coupling product, or the bi-cyclopentyl product for the Stern-Volmer analysis. The unusual behavior of the substituted α,α,α-trifluoroacetophenones is not understood at this time. The question arises whether chlorocyclopentane could be formed by any other pathway than the process shown, Equation (41). One possibility is

outlined in Scheme 8. If a chain reaction occurs, such that a trichloromethyl radical abstracts hydrogen from cyclopentane, then there exists a second process to generate



Scheme 8. Formation of Chloroform Photochemically.

chlorocyclopentane. The formation of sizeable amounts of chloroform (Table XXXII) confirms that this indeed occurs. The ratios of chloroform to chlorocyclohexane (0.17-0.38) are sizeable, though no pattern is apparent. It is not clear how the chain reaction outlined in Scheme 8 would lead to curved plots for the substituted α,α,α-trifluoroacetophenones, especially since greater amounts of chloroform were found for ACP and BP, which showed no curved behavior.

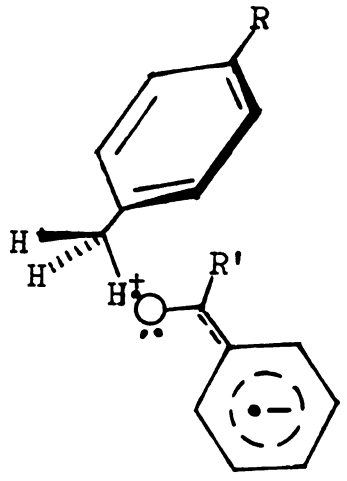
In Scheme 8 the ketyl radical is shown to regenerate starting ketone. The mechanism has not been examined, but a gas is formed photochemically which turns litmus red, and is presumably HCl. (Walling[53] has reported that the photoreduction of benzophenone by 2,3-dimethylbutane in CCl_4 produces HCl). It was shown (Table XXIII) that the amount of ketone consumed is far less than expected on the basis of photoproduct concentrations. Though some cross-coupling product does form, possibly in the original solvent cage, very little pinacol was found, suggesting that only low free ketyl radical concentrations are formed. Regeneration of starting ketone may explain why CCl_4 is such a good solvent for phosphorescence studies: the low concentration of free ketyl radical prevents sizeable amounts of quenching products involving this radical from forming.

In summary, hydrogen abstraction rate constants (k_H) measured by monitoring product formation were found to be significantly larger than the k_H values measured by flash photolysis studies. This latter technique may be a better method, as the very low conversions prevent the build-up of quenching products. On the other hand, it will be shown in a few pages that the k_r values measured by flash photolysis studies using toluene as the donor agree with the values calculated by product analysis studies. It is clear from the brief comments in this section that the cyclopentane in CCl_4 system needs to be examined in more

detail if trustworthy bimolecular k_H values are to be measured.

The tert-butoxy radical has been used as a model for direct hydrogen atom abstraction to compare the relative reactivity of various donors[53]. Scaiano[145] measured absolute k_H values for hydrogen abstraction by this radical from cyclopentane (k_H = 8.8 x 10^5 $M^{-1}s^{-1}$) and toluene (k_H = 2.3 x 10^5 $M^{-1}s^{-1}$). Direct hydrogen abstraction from cyclopentane is almost four times faster than from toluene, and slightly faster than from p-xylene[53]. By comparing literature k_H values for direct hydrogen atom abstraction by triplet phenyl ketones from cyclopentane and cyclohexane and comparing these k_H values with the k_r values measured using toluene and p-xylene as donor (Tables XXXV-XXXVIIII), one can estimate rate constants for direct hydrogen atom abstraction (k_H) by the triplet ketones from toluene and p-xylene. As indicated by Equation (39), the observed k_r values may include a $\chi_n k_H^n$ term, and this question will be addressed in the next few pages. But before discussing this matter, one should consider whether discrete pathways for triplet state quenching can actually exist, as implied by Scheme 2 in the Introduction. If k_H^n is competitive with k_{CT}^n, then both processes should be possible if the geometry for direct hydrogen abstraction doesn't allow a simultaneous CT interation between the ketone carbonyl and the donor aromatic ring. Scheme 6 illustrated the geometry of the n,π^* exciplex: the

carbonyl oxygen lies perpendicular to the donor aromatic ring. Though the geometry for direct hydrogen atom abstraction (Scheme 9) also places the carbonyl oxygen perpendicular to the donor aromatic ring, the carbonyl oxygen



Scheme 9. Geometry for Direct Hydrogen Atom Abstraction by an n,π* State.

may be too far away to interact to a significant extent simultaneously with the benzylic hydrogen and the ring. As will be shown in the next pages, the only ketones that may possess sizeable $\chi_n k_H^n$ terms are those with small $-E^*_{red}$ values, and it seems unlikely that such compounds would interact appreciably with the aromatic ring from the geometry shown in Scheme 9. So tentatively, it will be assumed that discrete pathways for triplet quenching exists, as illustrated in Scheme 2.

Direct Hydrogen Abstraction by α,α,α-Trifluoroacetophenone

Wagner and Leavitt[62] found the same k_r values when photoreducing TFA by toluene and toluene-α-d_3 in benzene. This suggests that direct hydrogen abstraction probably represents almost a small fraction of the observed k_r value, about 5% according to the authors. From Table XL one also finds almost identical k_r values for the photoreduction of p-MeO-TFA when using toluene and toluene-d_8 as donors, in CH_3CN. Since electron-withdrawing ring substituents on TFA dramatically increase the k_r values (Table XXXV) with respect to the unsubstituted TFA, these studies indicate that the observed k_r values for these compounds include virtually no contribution from direct hydrogen abstraction.

From Table XLV direct hydrogen abstraction from cyclopentane by triplet TFA in CCl_4 has a value of $k_H = 6.0 \times 10^6$ $M^{-1}s^{-1}$. Leavitt[62] reported a value of $k_H = 4.7 \times 10^6$ $M^{-1}s^{-1}$ for the same ketone and cyclohexane in benzene. In both these studies rate constants were obtained from product analysis, which may not be very accurate, as was discussed. In any event, from Tables XXXV and XXXVI, k_r = 9.3×10^6 $M^{-1}s^{-1}$ (TFA + toluene) and 2.2×10^8 $M^{-1}s^{-1}$ (TFA + p-xylene), in CH_3CN. As pointed out above[145], cyclopentane is a much better donor than is toluene, and comparable with p-xylene, in hydrogen atom abstraction reactions. These rate constants are consistent with the

view that the photoreductions of TFA and substituted TFA by alkylbenzenes proceed with rate constants $k_r >> k_H$.

Direct Hydrogen Abstraction by Acetophenone

Steel et al.[110] examined the quenching of triplet ACP by toluene (k_r = 2.2 x 10^5 $M^{-1}s^{-1}$) and cyclohexane (k_H = 3.5 x 10^5 $M^{-1}s^{-1}$) in CH_3CN. This last value agrees with a later study by Yip and Siebrand[135,136]: k_H = 4.8 x 10^5 $M^{-1}s^{-1}$ in neat cyclohexane. These two studies agree well with each other, but not very well with work reported in this thesis: by analyzing the concentrations of chlorocyclopentane in CCl_4 (Table XLV), a k_H value of 1.8 x 10^6 $M^{-1}s^{-1}$ was obtained.

The literature k_H values[135,136,110] can be compared with the rate constant found when using p-xylene as the donor, from Table XXXVII: k_r = 7.0 x 10^5 $M^{-1}s^{-1}$, in CH_3CN. Since hydrogen abstraction should be about equally facile from cyclohexane and from p-xylene, then direct hydrogen atom abstraction may represent about half the observed k_r value, which is consistent with the large ϕ_{Max}^{DTE} value (0.28) measured.

A kinetic isotope effect has been reported[62] for the photoreduction of ACP by toluene-α-d_3 (compared to toluene). Severe curvature in the double reciprocal plot complicated the interpretation of this experiment, but the authors suggested that if one assumes that both donors give the same

intercept (i.e., that only direct hydrogen atom abstraction is occurring, and α values are the same), then $k_H/k_D > 5$. It is certainly possible that the photoreduction of ACP by toluene proceeds entirely via direct abstraction, but that p-xylene photoreduces by direct hydrogen atom abstraction and exciplex formation followed by hydrogen ("proton") transfer (Scheme 2). Though k_H using p-xylene is expected to be larger than for toluene[53], the rate of exciplex formation, k_{CT}, may increase at a relatively greater rate. This question could be examined by measuring k_r and ϕ_{Max} values for p-xylene-α-d_6.

Direct Hydrogen Abstraction by Benzophenone

The photoreduction of triplet BP by neat cyclohexane has been measured by flash photolysis[135,138]: $k_H = 3.6 \times 10^5\ M^{-1}s^{-1}$. A similar value, $k_H = 5.0 \times 10^5\ M^{-1}s^{-1}$ was obtained[137] by phosphorescence quenching in benzene. Steel[110] reports $k_H = 7.2 \times 10^5\ M^{-1}s^{-1}$ for cyclohexane in CH_3CN by flash photolysis. These values are about an order of magnitude smaller than was found in this work by product analysis studies: $k_H = 6.2 \times 10^6\ M^{-1}s^{-1}$ (Table XLV). Though this discrepancy is puzzling, the rate constants measured by flash photolysis studies do agree with those measured in this work for an alkylbenzene donor. Steel[110] reports that BP is photoreduced by toluene in CH_3CN with a rate constant, $k_r = 4.1 \times 10^5\ M^{-1}s^{-1}$, which

agrees with the value reported in Table XL: k_r = 3.3 x 10^5 $M^{-1}s^{-1}$. Steel also reports[110] that ACP is photoreduced by toluene with rate constant, k_r = 2.2 x 10^5 $M^{-1}s^{-1}$ in reasonable agreement with Leavitt's[62] value, k_r = 1.2 x 10^5 $M^{-1}s^{-1}$, measured by product analysis studies as in this work.

The literature rate constants[110,135,137,138] using cyclohexane as donor are over an order of magnitude lower than the value measured using p-xylene in this work: k_r = 6.9 x 10^6 $M^{-1}s^{-1}$ (Table XXXVIII). If one assumes similar k_H values for p-xylene and cyclohexane[53], then direct abstraction by triplet BP from p-xylene may represent about 5-10% of the observed k_r value. The low ϕ_{Max}^{DTE} value (0.0645) (Table XXXVIII) measured is consistent with an exciplex mechanism.

The kinetic isotope effect found (Table XL) when comparing toluene and toluene-d_8 (k_H/k_D = 3.3) may indicate that a sizeable amount of direct hydrogen atom abstraction occurs when toluene is the donor, but may also mean that formation of the BP-toluene exciplex is partially reversible.

The k_H value for hydrogen transfer from toluene to triplet BP cannot be greater than the observed k_r value of 3.3 x 10^5 $M^{-1}s^{-1}$ (Table XLV). If one estimates that a p-methyl group on toluene will increase k_H by a factor of about 3[53], then one predicts a k_H value for direct

hydrogen atom abstraction by triplet BP from p-xylene that is less than 15% of the observed k_r (Table XXXVIII).

From Tables XIII and XVI, a 7.2 kcal difference in reduction potential is found for BP and ACP. This factor explains why for BP $k_{CT}^n >> k_H^n$, whereas for ACP $k_{CT}^n \approx k_H^n$ when the donor is p-xylene.

Direct Abstraction by Ring-Substituted Phenyl Ketones

Since the rate constants, k_H, for the photoreduction of substituted ketones by cyclopentane in CCl_4 are untrustworthy (Table XLV), the type II reaction of substituted valerophenones will be used as a model for the effect of various substituents on these rate constants. The relative k_H values from this reaction and the relative k_r values from the photoreduction of substituted acetophenones and benzophenones by p-xylene are given in Table XLVI. The following observations can be made: (i) Electron-withdrawing conjugated substituents like p-Cl, p-CN, and p-Ac slow down the rate constants in the VP and ACP series. In Figure 62, log k_r values were plotted against E^*_{red} and again one sees that compounds with p-Cl, p-CN, and p-Ac substituents show decreased reactivity (such a plot assumes that a sizeable fraction of k_r is due to formation of CT exciplexes). The observed decrease in reactivity apparently reflects the reduced reactivity of the π,π^* triplets[29]. From Table XLVI, p-CN-VP, p-Ac-VP, and p-Cl-VP are all less

Table XLVI. Rate Constants for Phenyl Alkyl Ketones.

VP	k_H[a]	Relat. k_H[e]	ACP	k_r[b]	Relat. k_r[e]	BP	k_r[b]	Relat. k_r[e]
m-CN[c]	26	2.1	m-CN	15	21.4	----	----	----
m-CF_3	32	2.6	m-CF_3	6.4	9.1	m-CF_3	30	4.3
p-CF_3	28	2.2	p-CF_3	4.7	6.7	p-CF_3	26	3.8
m-Cl	16	1.3	m-Cl	2.8	4.0	m-Cl	28	4.1
p-CN[c]	6.8	0.54	p-CN	1.8	2.6	p-CN	30	4.3
p-CH_3CO[c]	12	0.96	p-CH_3CO	1.8	2.6	----	----	----
p-F	15	1.2	p-F	----	----	4,4'-F	6.8	0.99
H	12.5	1.0	H	0.70	1.0	H	6.9	1.0
m-Me	3.9	0.31	m-Me	0.27	0.39	4,4'-Cl	8.3	1.2
p-Cl	3.0	0.24	p-Cl	0.20	0.29	p-Cl	7.2	1.0
p-Me	1.8	0.14	p-Me	0.081	0.12	4,4'-Me	1.7	0.25
3,4-di-Me[d]	0.34	0.027	3,4-di-Me	0.034	0.049	----	----	----
p-MeO	0.05	0.0040	p-MeO	0.034	0.049	4,4'-MeO	0.84	0.12

[a] $x10^7$, s^{-1}. Type II reaction of substituted valerophenone in PhH. Ref. 27.

[b] $x10^6$, $M^{-1}s^{-1}$. Photoreduction in the presence of p-xylene in CH_3CN.

[c] Reference 29; τ^{-1} values were reported.

[d] Reference 28, in benzene solvent.

[e] Relative to the rate constant of the unsubstituted compound.

reactive than the unsubstituted VP. In contrast, the k_r values of p-CN-ACP and p-Ac-ACP are greater and p-Cl-ACP smaller than the unsubstituted ACP. This suggests that triplet state inversion, such that the π,π^* triplet is lowest, significantly lowers the rate of direct hydrogen abstraction. However, another process can still lead to the photoreduction of these acetophenones: The CT exciplex mechanism. This process seems to be especially effective when the conjugated substituents are strongly electron-withdrawing. From Table XXXVII, relatively small ϕ_{Max}^{DTE} values were reported for p-CN-ACP (0.130) and p-Ac-ACP (0.057), and a little greater for p-Cl-ACP (0.152), which are consistent with the view that an intermediate exciplex forms.

Since BP has a very low-lying n,π^* state[56,99,101,102,137], the conjugated substituents are not able to invert the excited states. However, it is observed that 4,4'-di-Cl-BP and p-CN-BP are a little less reactive (Figure 63) than is expected by the line connecting all the benzophenones (4,4'-di-Ac-BP has not been examined). In addition, the triplet energy, E_T, measured for p-CN-BP is about 2 kcal lower than expected from comparison with other electron-withdrawing substituents (Table XVI). It is possible that conjugation does have a small effect on the reactivity of the n,π^* triplet state of benzophenones.

(ii) Electron-withdrawing substituents other than p-Cl,

p-CN, and p-Ac increase slightly the relative k_H values for the valerophenones, but the relative k_r values of substituted benzophenones and acetophenones are much greater. It is unfortunate that k_H values for these compounds are not available, but the trend observed in Table XLVI suggests that the observed k_r values for the photoreductions by p-xylene cannot be accounted for by direct hydrogen atom abstraction. Non-conjugated electron-withdrawing substituents must accelerate the formation of exciplexes, k_{CT}, faster than k_H, especially for the aceto-phenones: from Table XLVI, the k_H value measured for m-CN-VP is twice that of VP, but the k_r measured for m-CN-ACP (in the presence of p-xylene) is >20 times that of ACP. The huge increases in k_r^{rel} are strong evidence that the dominant component of the observed k_r values are k_{CT}^n terms.

The kinetic isotope study using p-CF_3-BP (Table XL) showed a small effect on k_r values when comparing toluene and toluene-d_8 (k_H/k_D = 1.4), but a sizeable effect on ϕ_{Max}^{BB} ratios (3.4). These facts are consistent with exciplex formation being essentially irreversible and the view that little direct hydrogen atom abstraction is occurring.

(iii) From Table XLVI electron-donating ring substituents decrease the relative k_H values of the valerophenones dramatically[24-28] due to inversion of the triplet states. As discussed earlier, the analogous acetophenones did not show this rapid drop-off as the π,π^* triplets of these compounds can react via the exciplex mechanism.

The decrease in k_r^{rel} values for benzophenones with electron-donating substituents is smaller than was found with the acetophenones and valerophenones, since no triplet state inversion has occurred. These compounds offer a unique model for the effect of electron-donating substituents on the reactivity of an n,π* state, though the measured reactivity may include both direct hydrogen atom abstraction and exciplex formation. Rate constants, k_H^n, for benzophenones with electron-donating substituents are not available. Extrapolation of log k_H^{rel} versus values for valerophenones with electron-withdrawing ring substituents would indicate[28] that electron-donating ring substituents decrease k_H^n values very little, but one cannot be sure that ground state inductive effects are meaningful in the excited state. A priori, one simply does not know the relative importance of the k_H^n term in the observed k_r values of these benzophenones. Good kinetic isotope effect studies on the photoreduction of such ketones by p-xylene and p-xylene-α-d_6 may clarify which pathway predominates. The studies that were performed, using 4,4'-di-Me-BP with toluene and toluene-d_8 reported in Table XL shed little light on this question. The very steep slopes and long extrapolations to the intercept in the double reciprocal plots (Figure 29) prevent one from obtaining reliable k_d/k_r (slope/intercept) values.

The quenching of 4,4'-di-Me-BP by toluene and toluene-d_8

was re-examined by a phosphorescence quenching study. From Table XVII, quenching by toluene in benzene gave a $k_r\tau$ = 2.4, and by toluene-d_8, $k_r\tau$ = 1.0. This factor of 2.4 may indicate that a sizeable amount of direct hydrogen atom abstraction (k_H^n) is occurring from toluene. This could be clarified by accurate ϕ_{Max}^{BB} measurements. It is possible that the k_H^n term also represents a sizeable component of the observed k_r values measured using p-xylene, as a large ϕ_{Max}^{DTE} (0.21, Table XXXVIII) was measured. In fact, the ϕ_{Max}^{DTE} values of 4,4'-di-t-Bu-BP (0.21), 4,4'-di-Me-BP (0.21), and 4,4'-di-MeO-BP (0.20) are all near the maximum value of 0.25 expected if ketyl and benzylic radicals couple randomly and do not undergo disproportionation.

To summarize, direct hydrogen atom abstraction from p-xylene may represent a sizeable component of the observed k_r values in the case of ACP and benzophenones with electron-donating substituents.

Photoreduction by p-Cymene in Acetonitrile

In a previous study[96], Wagner and Puchalski examined the photoreduction of several substituted acetophenones, benzophenones, and α,α,α-trifluoroacetophenones by p-cymene and found a trend in which electron-withdrawing ring substituents raise the P/T ratio, and electron-donating substituents lower this ratio, with the α,α,α-trifluoroacetophenones showing the greatest variation. This study was repeated and

many more compounds were examined to test the generality of this effect.

As discussed in the Introduction, the P/T ratios have been interpreted as reflecting the amount of charge-transfer[95,96] involved in the intermediate exciplexes. More CT preferentially accelerates the rate constant, k_{pt}, for primary proton transfer from p-cymene to the ketone, increasing the fraction of primary over tertiary intermediate radicals formed.

In the studies that have been discussed up to this point, the rates of formation of an intermediate between triplet ketones and various donors have been examined. In these next studies we will be examining what happens after the intermediates form.

a) Photoreduction of α,α,α-Trifluoroacetophenones by p-Cymene

The experimental results in Table XVIII were used to calculate P/T ratios according to expression (42):

$$\frac{P}{T} = \frac{2[PP] + [PT]}{2[TT] + [PT]} , \qquad (42)$$

where PP represents the product obtained when primary benzylic radicals couple; TT when the tertiary radicals couple; and PT the cross coupling product.

The log of the P/T ratios from Table XLVII have been plotted against log k_r, the rate constants for the photoreduction of substituted α,α,α-trifluoroacetophenones by toluene, taken from Table XXXV (Figure 64). A fairly good correlation is observed. The most reactive ketones, those with electron-withdrawing substituents, clearly display the largest P/T values.

The P/T values measured when photoreducing m-CF_3-TFA (3.9) and p-F-TFA (3.4) are noteworthy as these ratios demonstrate that the trend observed is not due merely to loss of selectivity. Ratios greater than 3 imply a non-radical-like hydrogen transfer step, which probably resembles proton transfer.

It was concluded in this thesis that direct hydrogen abstraction by substituted α,α,α-trifluoroacetophenones accounts for a negligibly small amount of the observed k_r values. Wagner and Puchalski[96] estimated a maximum of 3% direct hydrogen abstraction by these compounds from p-cymene. The P/T ratios can probably be interpreted in terms of only the behavior of a CT exciplex intermediate. As more CT occurs, more selectivity toward the primary C-H benzylic bond results, since the proton becomes more acidic. If less charge separation occurs, then this proton transfer step becomes more radical-like, and the C-H bond strength becomes relatively more important, leading to increasing hydrogen abstraction from the tertiary center.

Table XLVII. Photoreduction of Substituted α,α,α-Trifluoroacetophenones by p-Cymene in acetonitrile.

Ketone	P/T Ratio[a]	ln P/T	P/T Ratio[b]	$k_r(10^6)$, M^{-1} s^{-1}[c]	log k_r
m-CF_3-TFA	3.9[d]	1.4	---	780	8.9
p-CF_3-TFA	2.8[d]	1.0	4.7	440	8.6
m-Cl-TFA	2.8	1.0	---	47	7.7
p-CH_3CO-TFA	0.57	-0.56	---	32	7.5
p-F-TFA	3.4[d]	1.2	---	15	7.2
TFA	2.6	0.96	3.4	9.3	7.0
p-Cl-TFA	2.1	0.74	---	4.2	6.6
p-t-Bu-TFA	1.3	0.26	---	3.6	6.6
p-Me-TFA	1.7	0.53	1.7	0.74	5.9
3,4-di-Me-TFA	1.2	0.18	---	0.23	5.4
p-MeO-TFA	1.2	0.18	1.1	0.0080	4.9

[a]This work, in CH_3CN; [p-cymene] = 1 M. Almost all values reproducible to ±3% from the average.
[b]From Reference 120, in benzene.
[c]k_r measured in CH_3CN, using toluene.
[d]5% SE-30 column used. Others: 5% QF-1, 1.25% carbowax.

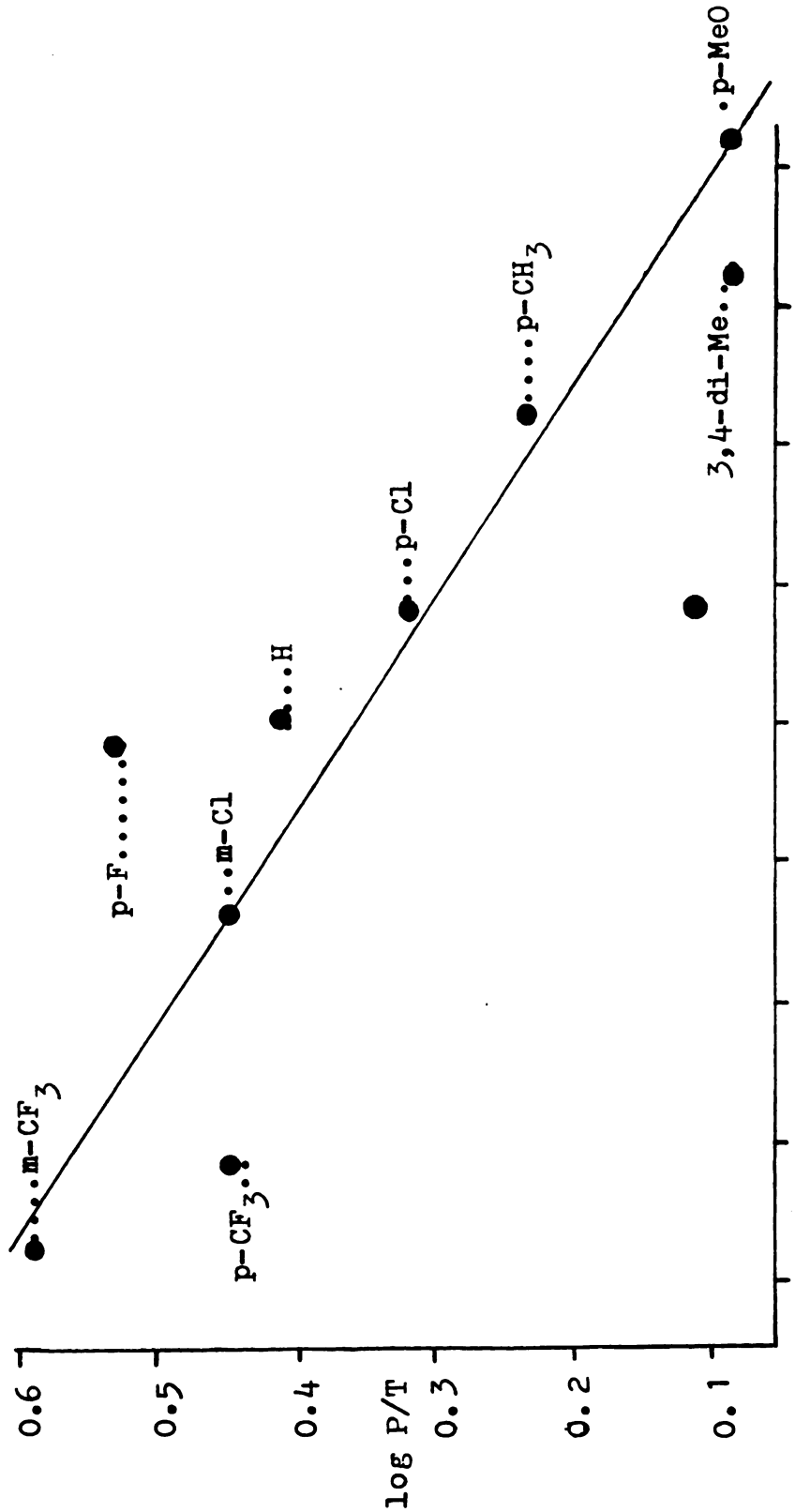


Figure 64. Correlation Between P/T Product Ratios from the Photoreduction of α,α,α-Trifluoroacetophenones by p-Cymene with the k_r Values from the Photoreduction by Toluene, in CH_3CN.

The unusual ratio found when using p-acetyl-α,α,α-trifluoroacetophenone deserves some comment. The P/T ratio, 0.57, would be fairly reasonable if it is the acetyl carbonyl that is reacting, as can be seen from the values found in Table XLVIII. In addition, the unusually high E_T value, 72.4 kcal, (Table VI) is higher than any of the α,α,α-trifluoroacetophenones examined, even though conjugation of the acetyl groups is expected to lower the triplet energy[29] significantly. On the other hand, an E_T value of 72.4 kcal is a little more reasonable if it is the acetyl carbonyl that is phosphorescing. However, the ^1H NMR study described in the Experimental section indicates that the acetyl carbonyl is not undergoing photoreduction. In the first experiment, irradiation of p-Ac-TFA in the presence of 2-propanol produced acetone (δ2.1, s; Figure 92), but no other new peaks appeared. Equation (43) shows the expected photoreaction.[36]

$$\underset{\text{R = CH}_3 \text{ or CF}_3}{\text{PhCR} + \text{2-propanol}} \xrightarrow{h\nu} (\text{PhC}(\text{OH})\text{R}-)_2 + \text{CH}_3\text{CCH}_3 \qquad (43)$$

If the acetyl group were to react, the pinacol product would show a methyl proton peak at around δ1.4 (Figure 96 shows that the methyl protons of acetophenone pinacol appear at δ1.4). The only way acetone could form without showing new methyl protons is if it is the trifluoroacetyl carbonyl that reacts.

Table XLVIII. Photoreduction of Substituted Acetophenones by p-Cymene in Acetonitrile.

Ketone	P/T Ratio[a]	ln P/T	P/T Ratio[b]	$k_r(10^6)$, M^{-1} s^{-1}[c]	log k_r
α,α-F_2-ACP	2.8	1.0	1.8	---	---
p-Cl-ACP	0.98	-0.020	---	0.2	5.3
p-CN-ACP	0.96	-0.041	---	1.8	6.3
3,4-di-Cl-ACP	0.91	-0.094	---	---	---
m-CN-ACP	0.74	-0.30	---	15	7.2
m-CF_3-ACP	0.71	-0.34	0.53	6.4	6.8
m-Cl-ACP	0.69	-0.37	---	2.8	6.5
p-CF_3-ACP	0.68	-0.39	---	4.7	6.7
α-F-ACP	0.65	-0.43	---	---	---
p-F-ACP	0.60	-0.51	0.59	---	---
p-MeO-ACP	0.61	-0.49	---	0.034	4.5
m-Me-ACP	0.54	-0.62	---	0.27	5.4
p-Me-ACP	0.51	-0.67	0.30	0.081	4.9
p-t-Bu-ACP	0.47	-0.71	---	0.20	5.3
3,4-di-Me-ACP	0.49	-0.71	---	0.034	4.5
ACP	0.47	-0.76	0.36	0.70	5.8
p-CH_3CO	0.19	-1.7	---	1.8	6.3

[a]This work, acetonitrile, [p-cymene]=1M. All values reproducible to within ~±10% from the average. [b]From Reference 97, in benzene. [c]k_r measured in CH_3CN, using p-xylene as the donor.

This experiment was repeated using toluene-d_8 instead of 2-propanol as the donor. G.C. analysis and the complex aromatic region of the ^1H NMR spectrum (Figures 94, 95) confirm that the expected photoreaction has occurred, but once again, no new protons appeared near δ1.4. In conclusion, the photoreduction of p-Ac-TFA must involve the trifluoroacetyl carbonyl. This conclusion is not surprising in view of the fact that the quenching of triplet TFA by p-xylene (Table XXXVI) occurs with a k_r value over 300 times greater than of triplet ACP (Table XXXVII).

It would be possible to carry out further studies using the same principles just used, but analyzing the photoproducts by ^{13}C NMR, or ^{19}F. One should use donors that prevent the formation of a large number of different photoproducts or the analysis will become intractable.

Some speculation as to why the P/T ratio is so low will follow in a few pages.

b) Photoreduction of Substituted Acetophenones by p-Cymene

From Table XLVIII the P/T ratios, calculated from the data found in Table XIX, qualitatively parallel the trend just described for the α,α,α-trifluoroacetophenones. The correlation between the k_r values and the P/T ratios is not

obvious, and the variations of P/T ratios with various substituents are not as great (Figure 65).

Unsubstituted ACP and all the substituted acetophenones have values greater than 0.37, the ratio reported for direct hydrogen abstraction by t-butoxy radical[47], even those compounds that are less reactive than the t-butoxy radical. The implication is that direct hydrogen abstraction alone cannot account for the photoreduction of these ketones by p-cymene or similar alkyl benzene donors. One can also suggest that the amount of CT in the intermediate cannot be as great as was found in the α,α,α-trifluoroacetophenone series of compounds.

Included in Figure 65 are values taken from the α,α,α-trifluoroacetophenone series. It is observed that a good correlation exists between those compounds with lowest π,π* triplet states: p-MeO-ACP, 3,4-di-Me-ACP, p-Cl-ACP, p-CN-ACP, p-MeO-TFA, TFA, and p-CF_3-TFA (such compounds presumably undergo negligible direct hydrogen abstraction, as already discussed). The same thermodynamic factors which influence the k_r values also lead to greater P/T ratios. The common link appears to be the amount of CT involved in the exciplexes.

From Figure 65 p-acetyl substituent leads to unusually low P/T ratios for both the TFA and ACP series of compounds. In addition, p-Ac-TFA has a P/T value lower than the line connecting the other α,α,α-trifluoroacetophenones by a

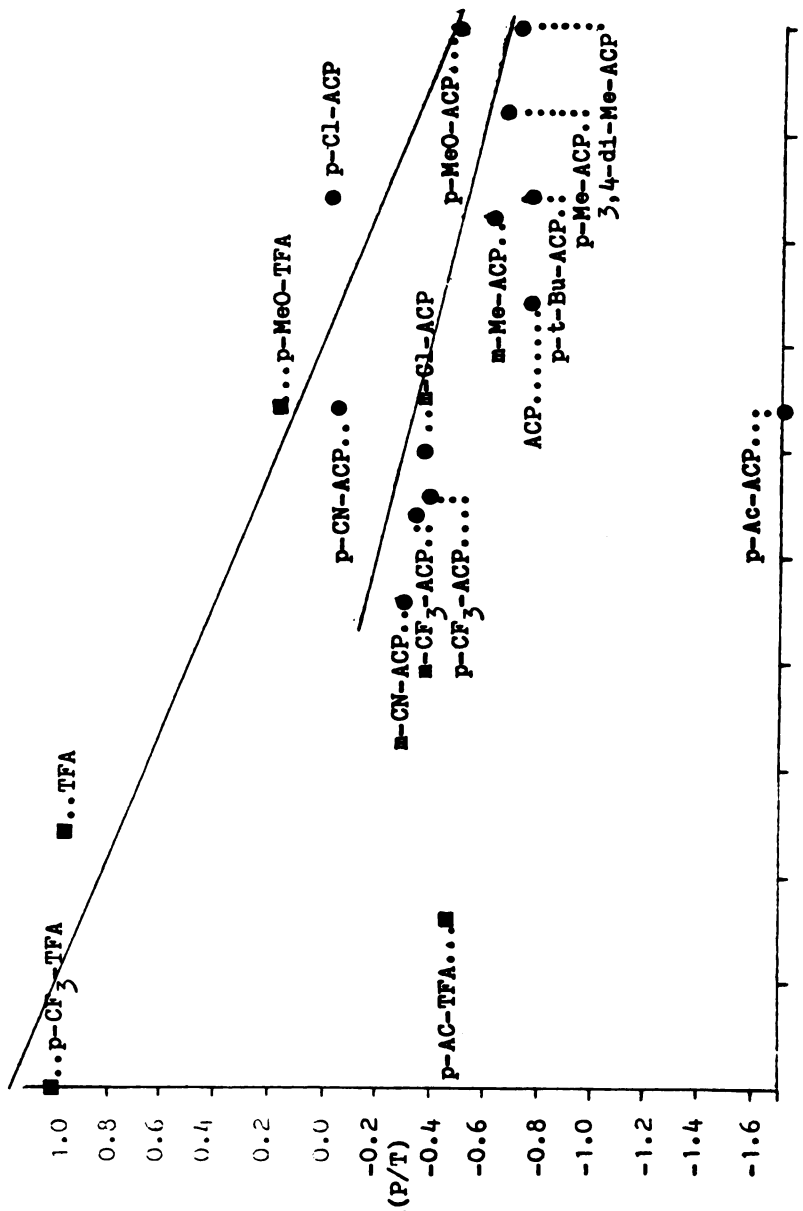


Figure 65. Correlation Between P/T Product Ratios from the Photoreduction of Acetophenones and α,α,α-Trifluoroacetophenones by p-Cymene with the k_r Values from the Photoreduction by p-Xylene, in CH_3CN.

similar amount as does p-Ac-ACP from the line correlating the acetophenones. Further exploratory work is needed to elucidate this unusual behavior. A compound like 4,4'-di-Ac-BP could be examined to see the effect on the P/T ratio for a compound possessing a low-lying n,π^* triplet state.

c) Photoreduction of Substituted Benzophenones by p-Cymene

The natural log of the P/T values taken from Table XLIX was plotted against log k_r (from Table XXXVIII) in Figure 66. The correlation is poor. However, it is instructive to contrast the very shallow negative slope obtained with the results of the photoreduction of several substituted benzophenones by 2,3-di-methylbutane in CCl_4 (Table XX, Figure 67). Clearly, the trends observed are in opposite directions. Once again, direct hydrogen abstraction alone cannot account for the behavior observed. As discussed earlier, direct hydrogen atom abstraction from p-xylene by triplet BP and BP with electron-withdrawing substituents contribute very little to the photoreduction process, but the contribution may be sizeable when electron-donating substituents are present.

A good correlation does exist (Figure 66) between BP and all the para-substituted BP compounds, suggesting that steric effects may be involved for meta-substituted benzophenones.

Table XLIX. Photoreduction of Substituted Benzophenones by p-Cymene in Benzene.

Ketone	P/T Ratio[a]	ln P/T	P/T Ratio[c]	$k_r(10^6)$, M^{-1} s^{-1}[b]	log k_r
p-CN-BP	0.66	-0.42	---	30	7.47
3,4-di-Cl-BP	0.60	-0.51	---	---	---
m-CF_3-BP	0.37	-0.99	---	30	7.47
m-Cl-BP	0.43	-0.84	---	28	7.45
p-CF_3-BP	0.56	-0.58	---	26	7.42
4,4'-Cl-BP	0.57	-0.56	0.59	8.3	6.92
4,4'-F-BP	0.50	-0.69	---	7.6	6.88
p-Cl-BP	0.45	-0.80	---	7.2	6.85
BP	0.42	-0.87	0.42	6.9	6.77
4,4'-t-Bu-BP	0.26	-1.3	---	2.4	6.37
4,4'-Me-BP	0.39	-0.94	0.19	1.7	6.27
3,3'-Me-BP	0.32	-1.1	---	---	---
4,4'-MeO-BP	0.30	-1.2	0.33	0.84	5.92

[a] This work, in CH_3CN, [p-cymene] = 1 M. Almost all values reproducible to ±5% from the average.

[b] k_r values measured using p-xylene in CH_3CN.

[c] From Reference 97, in benzene.

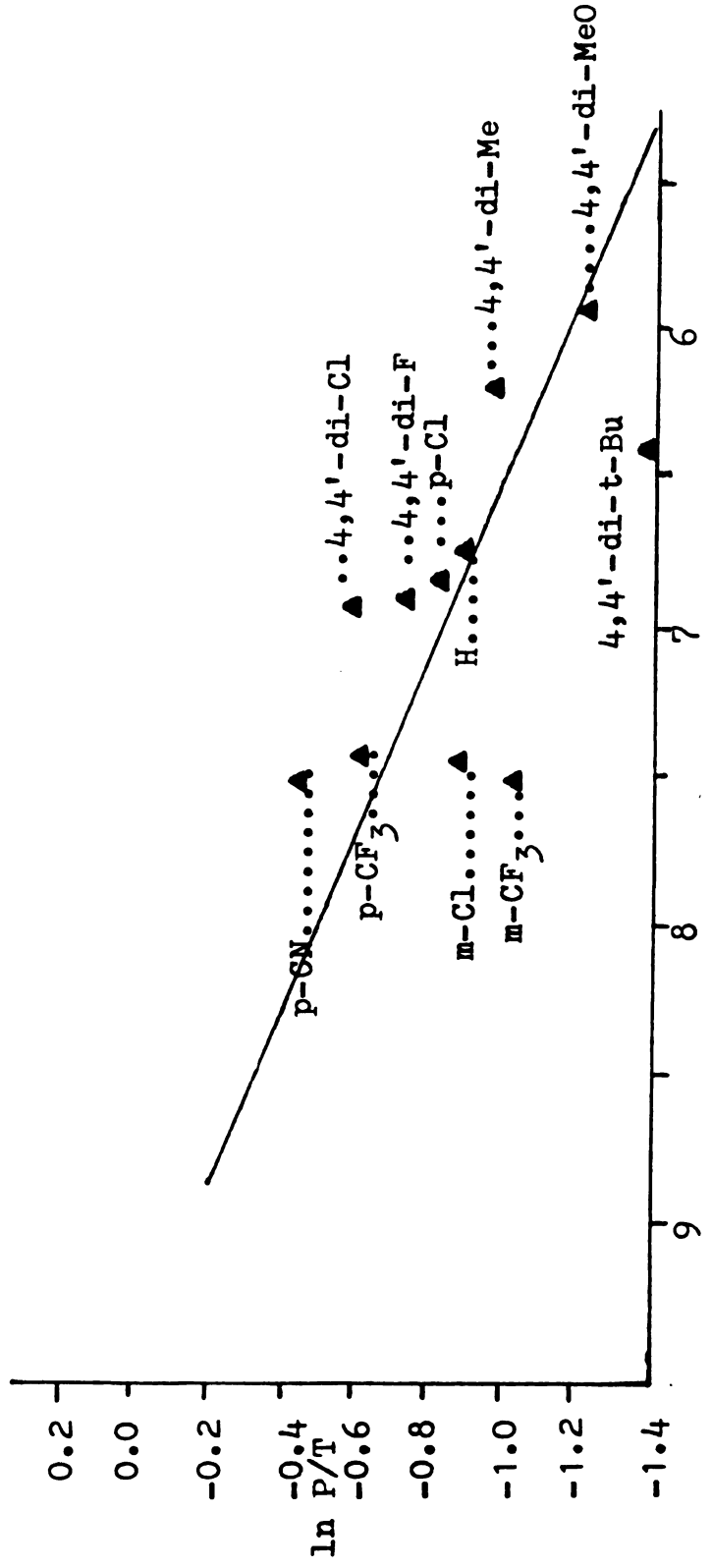


Figure 66. Correlation Between P/T Product Ratios from the Photoreduction of Benzophenones by p-Cymene with the k_r Values from the Photoreduction by p-Xylene, in CH_3CN.

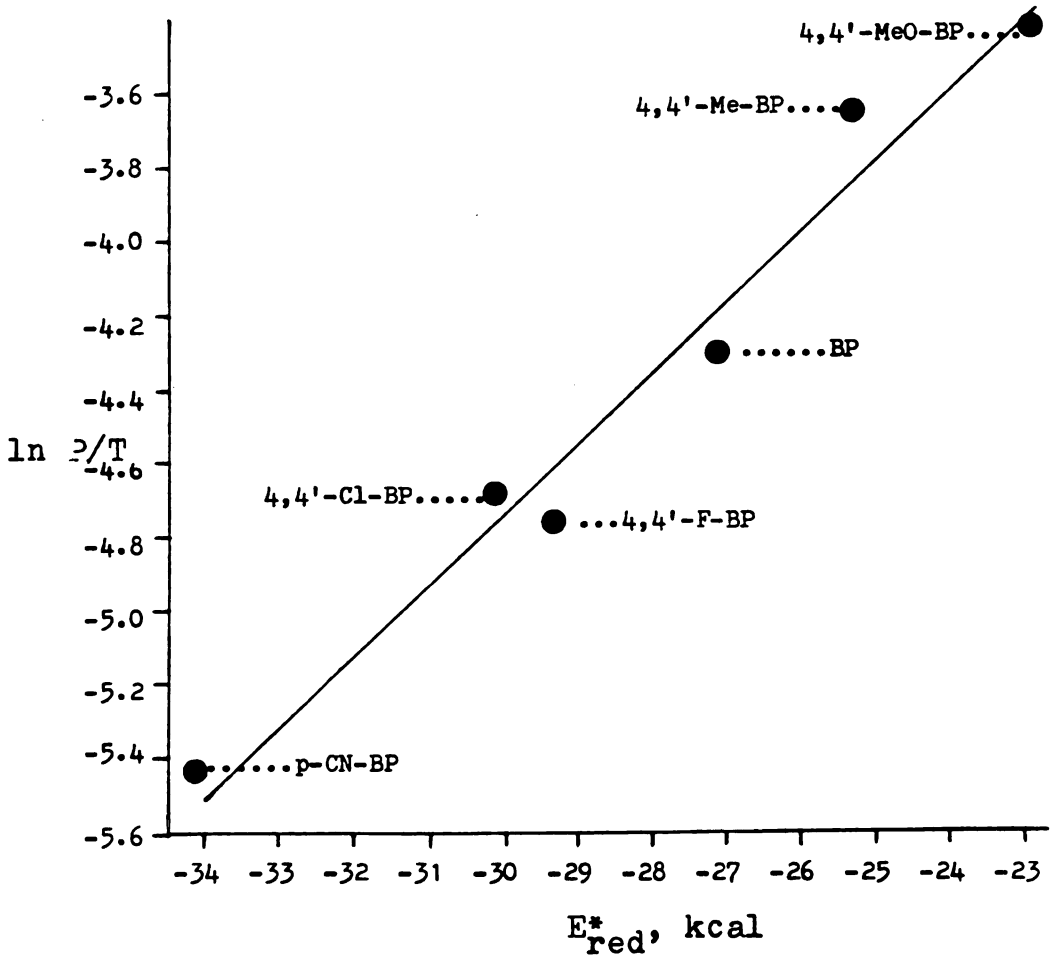


Figure 67. Photoreduction of Benzophenones by 2,3-di-Methylbutane in CCl_4.

d) Overall Selectivity Pattern

The natural log of all the P/T values is plotted against E^*_{red} in Figure 68. Examining those ketones with π,π^* lowest triplets reveals that a good correlation exists between these compounds (slope = 0.088, corr. 0.96). These compounds have an electron-deficient aromatic ring and electron-rich carbonyl oxygen, as discussed in the Introduction. This electronic distribution is well suited for a proton transfer process, as shown in Scheme 10.

It is clear from Scheme 10 that more CT from the p-cymene ring to the ketone ring increases the acidity of the proton.

Compounds with lowest n,π^* triplets probably form exciplexes in which the electrophilic carbonyl oxygen overlaps with the p-cymene ring (Scheme 11).

As already discussed, the compounds with lowest n,π^* triplets correlate poorly with k_r values and show little sensitivity toward variation in E^*_{red} values. Photoreduction of such ketones by direct hydrogen abstraction from non-complexed p-cymene can obscure the P/T ratios observed, but as already discussed, for most of these compounds $k^n_{CT} >> k^n_H$ when p-xylene is the donor. This should also be true when p-cymene is the donor.

The compounds with n,π^* triplets showed unusually low P/T ratios. This can be illustrated by comparing the ratios found for p-CF_3-BP (0.56) and 3,4-di-Me-TFA (1.2),

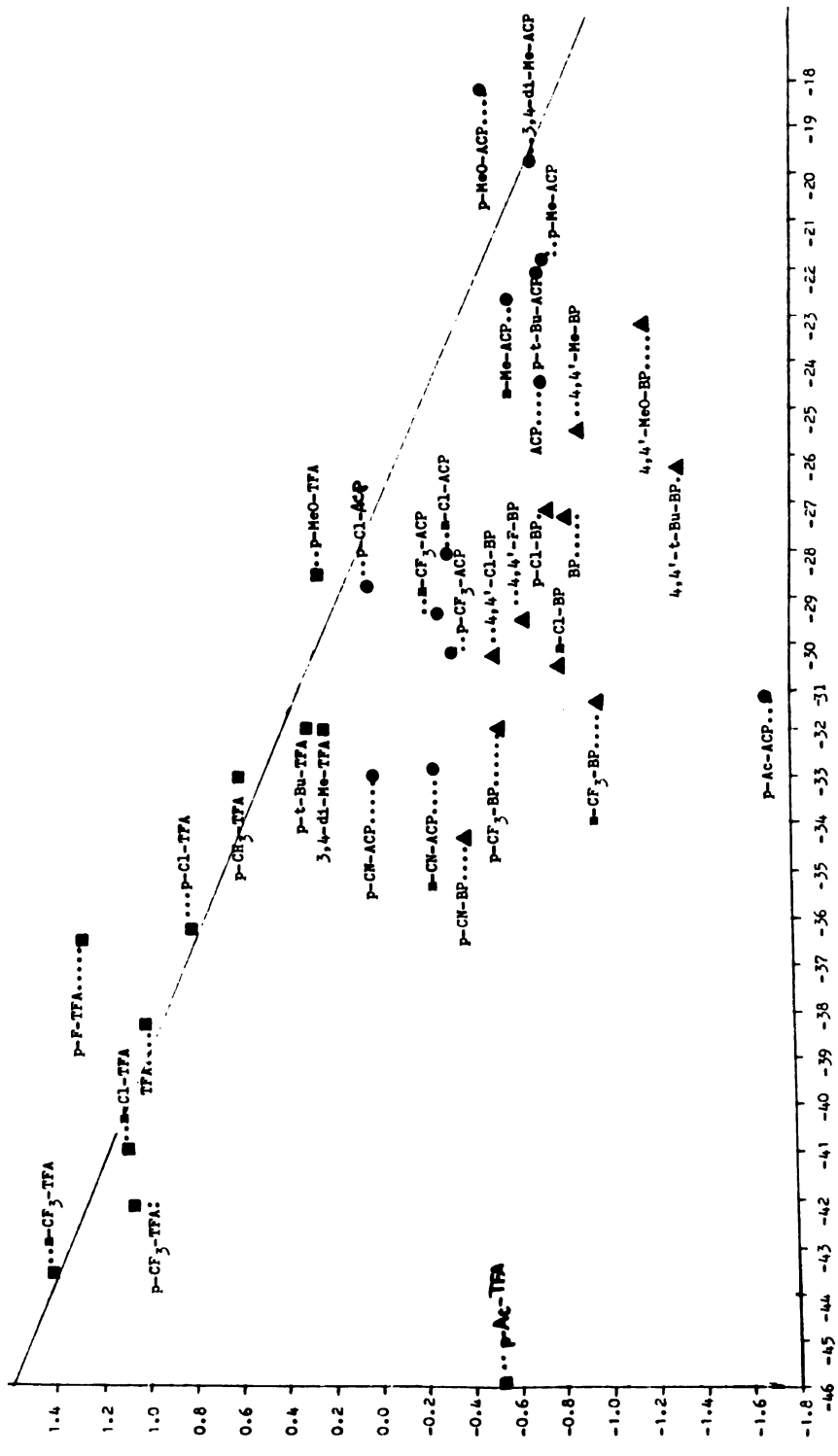
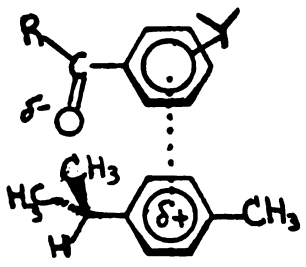
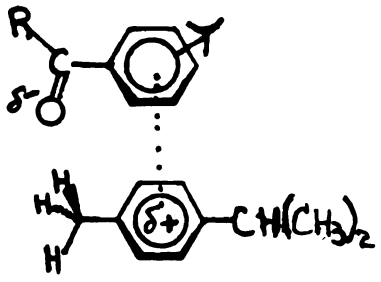


Figure 68. Correlation between P/T Ratios and E^*_{red}.

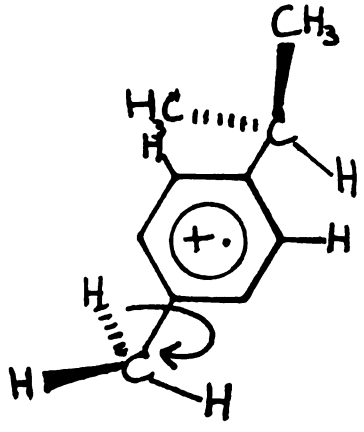


VII

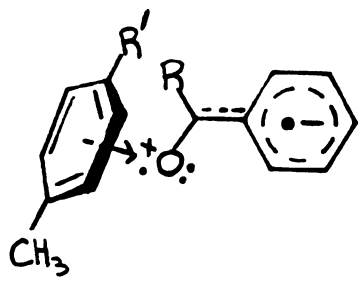


VIII

Scheme 10. Geometries of the Exciplexes for the Photoreduction of a π,π^* State by p-Cymene.



Scheme 12. Preferred Geometry of p-Cymene.



Scheme 11. Transition State for the Photoreduction of an n,π* State.

as both compounds have the same E^*_{red} values. The absence of a kinetic isotope effect on k_r for p-CF_3-BP and p-MeO-TFA (Table XVII) also indicates that direct hydrogen abstraction can only be occurring to a negligible extent. The lower P/T value found for p-CF_3-BP seems to indicate that less CT has occurred in the exciplex involving its n,π* triplet. This could be interpreted in two ways. a) The overlap between electrophilic carbonyl and the π system of p-cymene allows less CT to occur than does an interaction between electrophilic ring (i.e., the π,π* triplet state) with the same p-cymene ring; or, b) The carbonyl oxygen of an n,π* triplet cannot abstract a proton from the favored geometry. For the carbonyl to approach one of the benzylic hydrogens, orbital overlap with the π system would decrease (back CT), decreasing the acitity of the primary proton at the time of proton transfer. Both views imply a proportionality between P/T ratios and the amount of CT <u>at the time of proton transfer</u>.

The small isotope effect on the intercept value of p-MeO-TFA and the large effect found in the case of p-CF_3-BP (Table XVII) are consistent with facile proton transfer in the former case, but not in the latter.

Whether the oxygen can reach a benzylic proton from the exciplex geometry could be determined by model studies involving rigid systems restricting how close the carbonyl may approach a benzylic proton, but still interact with the aromatic ring.

The very low P/T values measured for p-Ac-substituted TFA and ACP are puzzling. Both compounds are expected to have very low-lying π,π^* triplets, though as pointed out, the high E_T values of p-Ac-TFA seems more consistent with a lowest n,π^* triplet. As just discussed, ketones with lowest π,π^* triplets consistently gave the highest P/T ratios. Other electron-withdrawing substituents, p-CN and p-Cl, did not give these low P/T values. The only unique feature seems to be the fact that there are <u>two</u> carbonyls present. Perhaps these carbonyls are less electron rich in a triplet π,π^* state than a single carbonyl would be, causing the proton transfer step to be more difficult and radical-like. Further studies could be carried out by examining tri-acetyl compounds, di-aldehydes, or compounds with multiple carbonyls not in conjugation with each other, like m-di-acetylbenzene.

Steric Effects on Selectivity

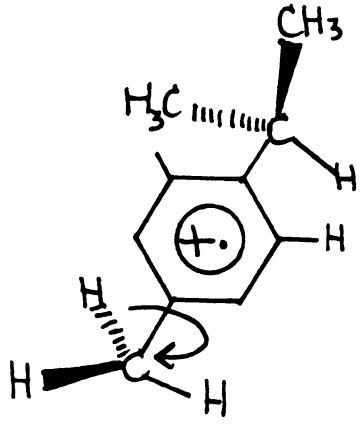
The geometry of the exciplexes involving triplet π,π^* states (shown in Figure 10) would suggest that bulky ring substituents would favor tertiary hydrogen transfer on the basis of only steric considerations. It is clear that for the α,α,α-trifluoroacetophenones (Figure 64 and 68) the P/T ratios are not determined by steric effects, e.g., p-CF_3-TFA gave a much greater P/T ratio than did p-CH_3O-TFA. The few examples of acetophenones with lowest π,π^* triplets studied do not allow the steric effects to be examined (Figure 65 and 68). It is observed, however, that p-t-Bu does appear to affect the selectivities: P/T ratios for p-Me-TFA > p-t-Bu-TFA and also for p-Me-ACP > p-t-Bu-ACP were measured.

The geometry of the exciplexes involving triplet n,π^* states (shown in Figure 11) would suggest that meta-substituents or very large para ones would enhance tertiary hydrogen transfer on steric grounds. From Figure 66 and 68, the P/T ratios of meta-substituents do show decreased values, and the ratio is also greater for 4,4'-di-Me-BP than for 4,4'-di-t-Bu-BP. The relatively small E^*_{red} values of these compounds allow the steric effects to become meaningful.

To summarize, proton transfer is controlled by stereoelectronic factors and not by the thermodynamic stability of the radical formed, though steric effects can play

a small role in the selectivity. As discussed in the Introduction, in the preferred geometry[91] of the p-cymene radical cation, the tertiary hydrogen of the isopropyl group is located in the nodal plane of the ring, as shown in Scheme 12, where there is little interaction with the π system in the transition state. On the other hand, the methyl group rotates freely, allowing these protons to be preferentially transferred. The implication in these studies is that as the amount of charge-transfer in the intermediate exciplexes increases, the acidity of the primary proton also increases. Whether the amount of CT affects the acidity of the tertiary proton could be explored by isotope effect studies on k_r and ϕ_{Max} using cymene and cumene-α-d_1 as the donor, and a series of ketones with varying E^*_{red} values.

The overall trend in the P/T values seem to imply that if much CT occurs in the intermediate ketone-donor interaction, then the acidity of the primary proton determines which hydrogen is abstracted, whereas if little CT occurs, then it is the relative C-H bond strength that determines which hydrogen is transferred to the ketone.



Scheme 12. Preferred Geometry of the p-Cymene Radical Cation.



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CONCLUSIONS

The log k_r *vs* E^*_{red} plot for the substituted acetophenones showed that those compounds with low-lying π,π^* triplet states fall below a line correlating the acetophenones with lowest n,π^* triplets. From this plot it was concluded that the n,π^* triplet states are quenched by aromatic donors about ten times faster than are the π,π^* triplet states. The acetophenones with proximate triplets showed intermediate reactivities, confirming Lam's[81] prediction for an S-shaped curve if equilibrating triplets of different reactivities are involved. No such curve could be seen for the α,α,α-trifluoroacetophenones, all of which possess only lowest π,π^* triplets. A ten-fold reactivity difference would not be large enough to allow an S-shaped curve to be observed for the α,α,α-trifluoroacetophenones unless one had more compounds possessing proximate and lowest n,π^* triplets to study.

The t-butyl group does not slow down k_r values with respect to the analogous p-methyl-substituted compound and does not prevent the formation of an exciplex. Inductively, a p-t-butyl group is less electron-releasing[146] than is a p-methyl group, and the compounds with the former substituent should possess triplets with more

n,π^* character.

Assuming that direct hydrogen atom abstraction can occur independently from exciplex formation, the k_H^n values may account for 50% or more of the observed k_r value (for quenching by p-xylene) of ACP, 4,4'-di-Me-BP, 4,4'-di-t-Bu-BP, and 4,4'-di-OMe-BP. All the other triplet acetophenones, benzophenones, and α,α,α-trifluoroacetophenones are quenched by p-xylene primarily via a CT exciplex pathway. This is also true for the quenching of triplet α,α,α-trifluoroacetophenones by toluene.

The small ϕ_{Max} values and isotope effect studies suggest that the proton transfer step following exciplex formation is not very efficient, and that exciplex decay significantly lowers the overall quantum yields of product formation.

The P/T product ratios correlate with log k_r and E^*_{red} values, suggesting that the amount of CT involved in the various exciplexes varies according to the thermodynamic demand. The ketones with lowest π,π^* triplets give larger P/T ratios than those with lowest n,π^* triplets at the same E^*_{red} values. This observation is not understood at this time.

Steric effects may play a role in determining P/T ratios for ketones with low E^*_{red} values. All the p-t-butyl-substituted ketones gave lower P/T values than the corresponding p-methyl-substituted ketones, and meta-substituted benzophenones gave lower P/T ratios than the p-substituted ones.

FURTHER WORK

1) The acetophenones examined with electron-donating substituents have proximate triplet states. To clarify the trend observed in the log k_r vs E^*_{red} plot, more compounds could be added to the series. In particular, the extreme end (very low-lying π,π^* triplets) can be explored by adding more electron-donating substituents to the ring or more powerful ones such as p-phenyl or O^-. A better donor, such as p-methyl anisole could be used to avoid having to work with very low k_r values (and thus very steep slopes in the double reciprocal plots).

2) A class of compounds with very low-lying π,π^* triplets but a favorable E^*_{red} should be sought to examine the behavior of this state, even as the substituted benzophenones provide a good model for the behavior of the n,π^* state. The α,α,α-trifluoroacetophenones with electron withdrawing substituents possess proximate triplet levels such that the k_r values observed include contributions from both the n,π^* and π,π^* states.

3) The TFA series could be extended by adding more electron-withdrawing substituents to the ring, or cations, to see if there is curvature in the log k_r *vs* $E^*_{red.pot}$ plot for those compounds with lowest n,π^* triplets. A new donor, such as m-chlorotoluene, may have to be used

to prevent k_r from approaching $k_{diffusion}$.

4) Model studies for direct hydrogen atom abstraction behavior could be carried out by flash photolysis, using representative acetophenones, benzophenones, and α,α,α-trifluoroacetophenones with cyclopentane as donor.

5) A thorough study of the photoreduction of phenyl ketones by cyclopentane in CCl_4 could be undertaken, to find all the quenchers formed, explain the meaning of the chloroform produced and explain the curvature found in several Stern-Volmer plots.

6) The effect of size of an acceptor π,π* molecular orbital on k_{CT} rates, extrapolated to the same $E^*_{red.pot}$ values could be investigated. Large π,π* systems, such as in naphthyl ketones, should offer less steric constraints, but may also form weaker interactions with the donor orbital.

7) An isotope effect study could be carried with several phenylketones using p-xylene and p-xylene-d_{10} as donors.

The involvement of direct hydrogen atom abstraction may be determined by k_r^H/k_r^D values. The efficiency of the proton-transfer step (k_{pt}) as a function of E^*_{red} may be examined from the ϕ^{DTE}_{Max} values. A variation of this concept could use p-xylene-α-d_3 as donor. The selectivity of hydrogen versus deuterium may vary as a function of the amount of CT in the exciplex. Of course, a good analytical method is needed to determine whether hydrogen or deuterium is abstracted.

8) The P/T ratios were interpreted as reflecting the amount of CT occurring in the various exciplexes. More CT increases the acidity of the primary benzylic proton, but the effect on the tertiary proton isn't known. Since this C-H bond is presumably in the nodal plane of the ring[91], changes in CT should affect its acidity very little. One could examine k_r and ϕ_{Max} values using cumene and cumene-α-d_1 as donors for several ketones over a wide range of E^*_{red} values.

9) The unusually low P/T ratios found for p-Ac-ACP and p-Ac-TFA could be explored by using tri-acetylbenzene and other compounds with multiple reactive conjugated and non-conjugated carbonyl groups. One could also prepare 4,4'-di-Ac-BP to see what P/T value is obtained.

EXPERIMENTAL

A. Preparation and Purification of Chemicals

1. Solvents

Benzene. Analytical reagent grade benzene was obtained from Mallinckrodt Co. and purified by stirring over concentrated sulfuric acid (about 1:10 acid:benzene) several times. When the acid layer no longer turned yellow, the benzene was washed three times with H_2O, twice with a concentrated sodium bicarbonate solution, then twice again with H_2O. This benzene was dripped through anhydrous magnesium sulfate into a 5-liter round bottom flask containing phosphorus pentoxide then refluxed overnight up a 95 cm column packed with glass helices. A central cut of about 70% was collected (bp 80.0 °C; lit.[99], 80.1 °C).

Acetonitrile. Analytical reagent grade acetonitrile was obtained from Mallinckrodt Co. To about 4 liters the following steps were performed[74]: a) 55 ml benzoyl chloride was added, then distilled almost to dryness using a 14 inch Vigreaux column; b) 55 ml H_2O and 100 gm anhydrous sodium carbonate were added, the solution refluxed 2 hours, then distilled; c) 50 gm anhydrous sodium

carbonate and 75 gm potassium permanganate were added, and the solution distilled; d) about 5 ml of concentrated sulfuric acid and a boileezer were added, the solution refluxed overnight on a 92 inch column, and a central cut (∿90%) was collected. The distillation was repeated on this central cut. A forecut was discarded (∿10%) and a central cut (∿90%) collected (bp 81.5°C; lit.[99], 81.6°C).

2. Donor Compounds

Toluene (Mallinckrodt). Same purification method as benzene, on a smaller scale. bp 110.5°C, lit.[99], 110.6°C.

p-Xylene (Mallinckrodt). See toluene. bp 137.5°C, lit.[99], 137-138°C.

p-Diisopropylbenzene (Mallinckrodt). See toluene. bp 210°C, lit.[100], 210.3°C.

p-Cymene (Aldrich). See toluene. bp 177°C, lit.[99], 177.1°C.

2,3-Dimethylbutane (Phillips Petroleum Co.). See toluene. bp 58°C, lit.[100], 58°C.

Cyclopentane (Mallinckrodt). See toluene. bp 49°C, lit.[99], 49.3°C.

Cyclohexane (Mallinckrodt). See toluene. bp 81°C, lit.[99], 80.7°C.

Carbon tetrachloride (Mallinckrodt). See toluene. bp 76.5°C, lit.[99], 76.7°C.

3. Standards

n-Hexane (Aldrich). Purified by Dr. P. J. Wagner the way benzene was, then distilled under reduced pressure. bp 69°C, lit.[99], 69°C.

Chlorobenzene (MC/B). Purified by distillation under reduced pressure using a 14 inch Vigreaux column.

n-Dodecane (Aldrich). Purified already by distillation under reduced pressure.

n-Tridecane (Aldrich). Purified already by distillation under reduced pressure.

Methylbenzoate (MC/B). Distilled under reduced pressure. bp 199°C, lit.[99], 198°C.

n-Ethylbenzoate. Prepared by reaction of benzoyl chloride (MC/B) with ethanol (Aldrich); m/e 150 (H^+). This and the following benzoates were prepared as follows. A 10% excess of the appropriate alcohol was added to benzoyl chloride in ethyl ether, ca. 1:5 by volume. The rapidly stirred solution was refluxed overnight, cooled, washed with water, extracted with ethyl ether several times, then dried by passing over anhydrous sodium sulfate. Concentration in vacuo gave a clear liquid in quantitative yield.

Distillation under reduced pressure using a spinning band distillation apparatus resulted in 100% pure product. All NMR spectra confirmed the expected structure. bp 213°C, lit.[101], 100-102°C/20 mm.

n-Propyl benzoate (Eastman). Distilled using a spinning band distillation apparatus, collecting a central cut. m/e 164 (M^+). bp 236°C, lit.[100], 231°C.

n-Butyl benzoate (Eastman). See n-Propyl benzoate. m/e 178 (M^+). bp 248°C, lit.[100], 250.3°C.

n-Pentyl benzoate. Prepared as n-ethyl benzoate, using n-pentyl alcohol (MC/B). m/e 192 (M^+). bp 260°C.

n-Hexyl benzoate. Prepared as n-ethyl benzoate, using n-hexyl alcohol (MC/B). m/e 206 (M^+). bp 177-177.5°C/ 15 mm.

n-Heptyl benzoate. Prepared as n-ethyl benzoate, using n-heptyl alcohol (Eastman). m/e 220 (M^+). bp 181-185°C/ 15 mm.

n-Octyl benzoate. Prepared as n-ethyl benzoate, using n-octyl alcohol (MC/B). m/e 234 (M^+). bp 197-198°C/ 15 mm.

n-Nonyl benzoate. Prepared as n-ethyl benzoate, using n-nonyl alcohol (Eastman). m/e 248 (M^+). bp 200-204°C/ 15 mm.

n-Decyl benzoate. Prepared as n-ethyl benzoate, using n-decyl alcohol (Eastman). m/e 262 (M^+). bp 210-215°C/ 15 mm.

4. Quenchers

Naphthalene (Aldrich). Had been recrystallized several times from ethanol. mp 79.0-80.0°C, lit.[99], 80.2°C.

2,5-Dimethyl-2,4-hexadiene (Chemical Samples Co.). Distilled under reduced pressure by Dr. T. Hasegawa. Only sublimed sample was used.

Cis and trans 1,3-pentadiene (Chemical Samples Co.). Used as received.

5. Ketones

The purity of all the following ketones was determined to be 99.4% by vpc).

α,α,α-Trifluoroacetophenone. A modification of the method of Dishart and Levine (Reference 75) was used. 1. - CF_3COOLi was prepared[76] by adding trifluoroacetic acid (Aldrich; 200 gm, 1.75 mole) dropwise into a rapidly stirring $LiOH \cdot H_2O$ (Aldrich; 73 gm, 1.74 mole/200 ml H_2O) solution in a 1 liter beaker. The end point was reached when Bromcresol Green indicator went from yellow to blue. Water was removed using first an aspirator and steam bath,

then under high vacuum in a desiccator at over 100°C in the presence of P_2O_5. About 200 gm of white powder was obtained.

Mg turnings (MC/B; 3.4 gm, 0.14 mole) were placed in a 500-ml 3-neck flask, connected to a water-cooled coil condenser, mechanical stirrer and addition funnel. The whole system was flame dried while forcing N_2 gas over the glassware and out of a mineral oil bubbler. The N_2 pressure was adjusted such that a slow, steady stream of bubbles escaped out of the bubbler, maintaining an air-tight system.

2. - Phenyl magnesium bromide was prepared by adding bromobenzene (Aldrich; 15.7 gm, 0.10 mole) in 200 ml ethyl ether to Mg turnings (3.4 gm, 0.14 mole) covered with ether. A crystal of I_2 was added, the mixture warmed with a heating mantle, and the halide added with stirring. After refluxing 2 hours, the cooled solution was dumped into H_2O made slightly acidic with HCl, stirred, extracted 4 times with ether, and the combined ether layers concentrated <u>in vacuo</u>. The yellow oil was distilled under vacuum, and a clear liquid product obtained (6.3 gm, 0.033 mole). (Higher yields were obtained by using THF instead of ether). Spinning band distillation afforded a central cut over 99.5% pure. MS (70 eV) m/e 174, 105, 78; NMR ($CDCl_3$) δ7.9 (m, 3H), 7.4 (m, 2H); IR (neat) 3400 cm^{-1}, 3080, 1730, 1600, 1450; clear liquid; ε(313 nm) = 155; bp 146.5°C; lit.[42], 65-70°C/22 mm.

p-Fluoro-α,α,α-trifluoroacetophenone. Prepared from p-bromofluorobenzene (Aldrich; 15.0 gm, 0.0857 mole) and lithium trifluoroacetate (12.0 gm, 0.70 ml) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 192, 173, 123; NMR ($CDCl_3$) δ8.0 (m, 2H), 7.1 (m, 2H); IR (neat) 2950 cm^{-1}, 2920, 2850, 1710, 1595, 1450; crystallizes ca. room temperature; ε(313 nm) = 88, ε(366 nm) = 2.2; bp 152.0°C.

m-Methyl-α,α,α-trifluoroacetophenone. Prepared from m-tolylbromide (Eastman; 61.0 gm, 0.357 mole) and lithium trifluoroacetate (54.0 gm, 0.45 mole) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 188, 119, 91; NMR ($CDCl_3$)δ7.2-7.7 (m, 4H), 2.4 (s, 3H); IR (neat) 3100-2900 cm^{-1}; 1710, 1600, 1480, 1140; liquid at room temperature; ε(313 nm) = 85.9; bp 172.5°C, lit.[42], 60-63/ 13 mm.

p-Methyl-α,α,α-trifluoroacetophenone. Prepared from p-tolylbromide (Aldrich; 61.0 gm, 0.357 mole) and lithium trifluoroacetate (54.0 gm, 0.45 mole) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 188, 119, 91; NMR ($CDCl_3$)δ7.8 (d, 2H, J = 8.0 Hz), 7.15 (d, 2H, J = 8 Hz), 2.35 (s, 3H); IR (neat) 3400 cm^{-1}, 2900-3050, 1700, 1600, 940-1225; liquid at room temperature, ε(313) = 227; bp 174.0°C.

m-Methoxy-α,α,α-trifluoroacetophenone. Prepared from m-bromoanisole (Aldrich; 46 gm, 0.25 mole) and lithium trifluoroacetate (50 gm, 0.42 mole) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 204, 135, 107, 92, 77; NMR ($CDCl_3$) δ7.0-7.6 (m, 4H), 3.8 (s, 3H); bp 181.0°C, lit.[42], 55-59°C/3 mm.

p-Methoxy-α,α,α-trifluoroacetophenone. Prepared from p-bromoanisole (Aldrich; 150 gm, 0.80 mole) and lithium trifluoroacetate (131.9 gm, 1.20 mole) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 204, 135, 107, 92, 77; NMR ($CDCl_3$) δ7.9 (d, 2H, J = 9 Hz), 6.9 (d, 2H, J = 9 Hz), 3.8 (s, 3H); IR (neat) 3410 cm^{-1}, 2850-3100, 1710, 1600, 1595; liquid at room temperature; ε(313 nm) = 4708, ε(366) = 72; bp 183, lit.[42], 72-73/2mm.

m-Chloro-α,α,α-trifluoroacetophenone. Prepared from m-chlorobromobenzene (Aldrich, 28.7 gm, 18.2 ml) and lithium trifluoroacetate (22.5 gm, 0.188 mole) as described for α,α,α-trifluoroacetophenone. Isolated product, 14.0 gm, 0.067 mole. MS (70 eV) m/e 209, 208, 139, 111; NMR ($CDCl_3$) δ7.1-8.0 (m); IR (neat) 3400 cm^{-1}, 3050, 1720, 1595, 1460, 1420; liquid at room temperature; ε(313 nm) = 630; bp 164.0°C, lit.[42], 75-78°C/20 mm.

p-Chloro-α,α,α-trifluoroacetophenone. Prepared from p-chlorobrobromobenzene (Aldrich; 57.4 gm, 0.30 mole) and lithium trifluoroacetophenone (54 gm, 0.45 mole) as described

for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 209, 208, 139, 111; NMR ($CDCl_3$) δ7.85 (d, 2 H, J = 1) 7.25 (d, 2H, J = 9 Hz); IR (neat) 3400 cm^{-1}, 3050, 1740, 1600, 1500, 1420; ε(313 nm) = 148; bp 185°C, lit.[42], 83-84/24 mm.

p-Trifluoromethyl-α,α,α-trifluoroacetophenone. Prepared from p-bromobenzotrifluoride (Aldrich, 42.7 gm, 0.19 mole) and lithium trifluoroacetate (30 gm, 0.25 mole) as described for α,α,α-trifluoroacetophenone. Isolated product, 20.3 gm, 0.084 mole. MS (70 eV) m/e 242, 223, 174, 173, 146, 145, 125; NMR ($CDCl_3$) δ8.1 (d, 2H, J = 8 Hz), 7.7 (d, 2H, J = 8 Hz); IR (neat) 3420-3600 cm^{-1}, 1730, 1510, 1410; liquid at room temperature, ε(313) = 101; bp 155.5°C, Lit.[42], 65-70/22 mm.

m-Trifluoromethyl-α,α,α-trifluoroacetophenone. Prepared from m-bromobenzotrifluoride (Aldrich; 11.5 gm, 0.05 mole) and lithium trifluoroacetate (12 gm = 0.10 mole) as described for α,α,α-trifluoroacetophenone. MS (70 eV) m/e 242, 223, 174, 173, 146, 145, 125; NMR ($CDCl_3$) δ7.5-8.2 (m); IR (neat) 3410 cm^{-1}, 1730, 1605, 1440; liquid at room temperature; ε(313) = 50; bp = 153.0°C, lit.[42], 68-71/22 mm.

p-Thiomethyl-α,α,α-trifluoroacetophenone. Prepared from p-bromothioanisole (Aldrich; 20 gm, 0.10 mole) and lithium trifluoroacetate (19.2 gm, 0.16 mole) as described for

α,α,α-trifluoroacetophenone. MS (70 eV) m/e 151, 136, 123, 108; NMR ($CDCl_3$) δ7.9 (d, 2H, J = 7 Hz) 7.2 (d, 2H, J = 7 Hz), 2.5 (s, 3H); IR (Nujol) 1725 cm^{-1}, 1600; solid at room temperature; mp 49.5-49.6°C.

p-Acetyl-α,α,α-trifluoroacetophenone. p-Bromoacetophenone (Aldrich; 50 gm, 0.25 mole) and ethylene glycol (21.7 gm, 0.35 mole) were stirred in 200 ml benzene with 0.5 gm p-toluenesulfonic acid and refluxed 3 days in a Dean Start apparatus. The solution was neutralized with sodium bicarbonate, then dried by passing over anhydrous sodium sulfate. Concentration in vacuo gave pure ketal by vpc (52 gm, 0.21 mole). NMR ($CDCl_3$) δ7.3 (4H), 3.9 (m, 2H), 3.7 (m, 2H), 1.5 (s, 3H). The Grignard of this ketal was added to lithium trifluoroacetate as described for α,α,α-trifluoroacetophenone (65% yield). The 1,3 dioxalan was hydrolyzed (Reference 77) by dissolving in 200 ml acetone, adding 1 gm p-toluene sulfonic acid and 2 ml concentrated H_2SO_4, then refluxing 6 hours. After concentrating in vacuo, ethyl ether was added, the combined layer was washed with $NaHCO_3$ solution, then concentrated in vacuo, giving a yellow oil. Decanting from hot methanol removed yellow polymeric impurity. Recrystallization from methanol afforded 100% pure product. MS (70 eV) m/e 216, 201, 173; NMR (CD_3CN) δ8.0 (d, 2H, 8 Hz), 7.8 (d, 2H, 8 Hz), 2.6 (s, 3H); mp 98.9-99.0°C; IR (Nujol) 1630 cm^{-1}.

3,4-Dimethyl-α,α,α-trifluoroacetophenone. Prepared by Friedel-Crafts acylation of o-xylene (MC/B; 114.5 gm, 1.1 mole) by trifluoroacetic anhydride (MC/B; 132.7 gm, 0.63 mole) with $AlCl_3$ (87.3 gm, 0.65 mole) catalyst in 1 liter CS_2 solvent. The apparatus used was described in the preparation of TFA above. The anhydride was added over 6 hours, stirred overnight, refluxed at 46°C 3 hrs, cooled, dumped into icy H_2O, extracted 4 times with ether, neutralized with $NaHCO_3$ solution, washed with H_2O, dripped through anhydrous sodium sulfate, concentrated in vacuo, resulting in a yellow oil (ca. 60% based on the anhydride). Spinning band distillation afforded a central cut 99.9% pure. MS (70 eV) m/e 203 (H^+), 133, 105, 77; NMR ($CDCl_3$) δ7.0-7.8 (m, 3H), 2.25 (s, 6H); IR (neat) 2775-3100 cm^{-1}, 1710, 1600; clear liquid; ε(313 nm) = 1008; bp. 203°C.

p-tert-Butyl-α,α,α-trifluoroacetophenone. Prepared by Friedel-Crafts acylation of tert-butyl benzene (Aldrich; 10 gm, 0.075 mole) by trifluoroacetic anhydride (MC/B; 15.6 gm, 0.074 mole) with $AlCl_3$ (21.8 gm, 0.16 mole) catalyst in 350 ml CS_2 solvent. Procedure and workup follows that of 3,4-dimethyl-α,α,α-trifluoroacetophenone. NMR ($CDCl_3$) δ7.95 (d, 2H, J = 8 Hz), 7.5 (d, 2H, J = 8 Hz) 1.4 (s, 9H); clear crystals; ε(313 nm) = 320, ε(366 nm) = 0.4; mp 41-44°C.

Acetophenones

Acetophenone (MC/B) Purified by distillation. MS (70 eV) m/e 120, 105; NMR ($CDCl_3$) δ7.8-8.0 (m, 2H), 7.4-7.5 (m, 3H), 2.6 (s, 3H); IR (Nujol) 1700 cm^{-1}, 1580, 1260; liquid at room temperature; ε(313 nm) = 52; ε(366 nm) = 0.0; bp 197.5°C, lit.[100], 232°C.

m-Chloroacetophenone (Eastman Organic Chemicals). Purified by distillation. MS (70 eV), m/e 154, 139, 105; NMR ($CDCl_3$) δ7.3-7.9 (m, 4H), 2.6 (s, 3H); IR (neat) 3065 cm^{-1}, 3000, 1680, 1570, 1440, 1300; liquid at room temperature; ε(313 nm) = 47, ε(366 nm) = 0.04; bp 211°C, lit.[100], 227-229.

p-Methylacetophenone. Prepared by Friedel-Crafts acylation of toluene (80 gm. 0.76 mole) by acetic anhydride (102.1 gm, 1.0 mole) using $AlCl_3$ (133.3 gm, 1.0 mole) as catalyst in 1.2 liters dichloroethane solvent. Procedure and purification parallels that of 3,4-dimethyl-α,α,α-trifluoroacetophenone (60% yield; polymeric material also formed). MS (70 eV) m/e 134, 119, 105; NMR ($CDCl_3$) δ7.7 (d, 2H, J = 8 Hz), 7.05 (d, 2H, J = 8 Hz), 2.7 (s, 3H), 2.4 (s, 3H); IR (neat) 3000 cm^{-1}, 1680, 1420; ε(313 nm) = 68; bp 224°C, lit.[100], 226°C.

m-Methylacetophenone (Aldrich). Purified by distillation. MS (70 eV) m/e 134, 119, 105, 91; NMR ($CDCl_3$)

δ7.7 (m, 4H), 2.7 (s, 3H), 2.4 (s, 3H); liquid at room temperature; ε(313 nm) = 57; bp 217°C, lit.[100], 220°C.

p-Methoxyacetophenone (Aldrich). Purified by distillation. MS (70 eV) m/e 150, 135, 121, 107, 92; NMR ($CDCl_3$) δ7.8 (d, 2H, J = 8 Hz), 6.9 (d, 2H, J = 8 Hz), 3.7 (s, 3H), 2.4 (s, 3H); IR (Nujol) 1690 cm^{-1}, 1600, 1375, 1250; solid white crystals at room temperature; ε(313) = 138; mp 37.0-37.5, lit.[100], 38-39°C.

3,4-Dimethylacetophenone. Prepared by Friedel-Crafts acylation of o-xylene (MC/B; 100 gm, 0.94 mole) by acetyl chloride (73.8 gm, 0.94 mole) with $AlCl_3$ (140 gm, 1.05 mole) as catalyst in 1.2 liters CS_2 solvent as outlined for 3,4-dimethyl-α,α,α-trifluoroacetophenone. MS (70 eV) m/e 148, 133, 105, 91, 77; NMR ($CDCl_3$) δ7.7 (m, 1H), 7.6 (m, 1H), 7.2 (s, 1H), 2.5 (s, 3H), 2.3 (s, 6H); IR (neat) 2850-2950 cm^{-1}, 1700, 1625, 1275; liquid at room temperature; ε(313) = 79; bp 244°C, lit.[100], 246-247°C.

p-t-Butylacetophenone. Prepared by Friedel-Crafts acylation of t-butyl benzene (Aldrich; 32.2 gm, 0.24 mole) by acetyl chloride (18.8 gm, 0.24 mole) using $AlCl_3$ (37.3 gm, 0.28 mole) as catalyst in 150 ml CS_2 solvent, as outlined for 3,4-dimethyl-α,α,α-trifluoroacetophenone. MS (70 eV) m/e 161, 146, 139, 115, 105, 91; NMR ($CDCl_3$) δ7.85 (d, 2H, J = 8 Hz), 7.4 (d, 2H, J = 8 Hz), 2.6 (s, 3H), 1.2 (s, 9H); IR (neat) 2850-2950 cm^{-1}, 1680, 1600, 1260; clear

liquid, bp 239°C, lit.[103], 136-138/20 mm.

p-Trifluoromethylacetophenone. p-Trifluoromethylphenylmagnesium bromide was prepared by adding 4-bromobenzotrifluoride (Aldrich; 14.2 gm, 0.063 mole) in 60 ml ether to Mg turnings (3.8 gm, 0.156 mole) covered with ether, using an I_2 crystal and a heating mantle to initiate the reaction as discussed in the preparation of α,α,α-trifluoroacetophenone. After refluxing 30 minutes with stirring, benzaldehyde (Mallinckrodt; 12.4 gm, 0.20 mole) in 50 ml ether was added slowly to the cooled Grignard reagent. When the reaction had subsided, it was refluxed 15 minutes, cooled, dumped into icy dilute HCl solution, extracted 3 times with ethyl ether, washed with a $NaHCO_3$ aqueous solution, then concentrated in vacuo. The crude alcohol was dissolved in 50 ml acetone, cooled, and a mixture of $Na_2Cr_2O_7 \cdot H_2O$ (23.8 gm, 0.08 mole), H_2SO_4 (26.1 gm, 0.27 mole), acetone (50 ml) and water (125 ml)[78] added slowly with rapid stirring. After stirring 1.5 hours at room temperature, the product was extracted with ethyl ether, washed with $NaHCO_3$ solution, then water, and then concentrated in vacuo. The oily product was distilled under reduced pressure giving a central cut over 99.5% pure. MS (70 eV) m/e 188, 173, 169, 145, 127; NMR ($CDCl_3$) δ8.0 (d, 2H, J = 8 Hz), 7.7 (d, 2H, J = 8 Hz), 2.6 (s, 3H); IR (Nujol) 1680 cm^{-1}, 1500; solid, clear crystals at room temperature; ε(313 nm) = 42; ε(366 nm) = 0.08; mp 29°C; bp 199.0, lit.[102], 198-200°C.

m-Trifluoromethylacetophenone. The procedure outlined for p-trifluoromethylacetophenone was followed, using 3-bromobenzotrifluoride (Aldrich; 40 gm, 0.18 mole) and benzaldehyde (Mallinckrodt; 12.4 gm, 0.20 mole). MS (70 eV) m/e 188, 173, 145, 127; NMR ($CDCl_3$) δ7.4-8.15 (m, 4H), 2.5 (s, 3H); IR (neat) 3060 cm^{-1}, 2900-2970, 1670, 1600, 1440, 1330; solid at room temperature; ε(313 nm) = 3.7; ε(366 nm) = 0.04; mp, 30.5-31.0°C; bp 200.0, lit.[102], 79-80°C/8mm.

p-Acetylacetophenone (Aldrich). The yellow color was removed by dissolving in acetone and stirring with Norit. Recrystallization 3 times from hot methanol gave white crystals. MS (70 eV) m/e 162; NMR ($CDCl_3$) δ8.0 (s, 4H), 2.6 (s, 6H); mp 111.0-111.5°C, lit.[102], 111-113°C.

m-Cyanoacetophenone. Synthesized and purified by Dr. E. Siebert, and used as found. MS (70 eV) m/e 145, 130, 102, 75; NMR ($CDCl_3$) δ7.4-8.2 (m, 4H), 2.6 (s, 3H); IR (Nujol) 2200 cm^{-1}, 1695; solid white crystals; ε(313 nm) = 68, ε(366 nm) = 4.8; mp 97.0-97.2°C lit.[104], 98-99°C.

p-Cyanoacetophenone. Sodium cyanide (Baker; 3.5 gm, 0.071 mole) was suspended in 70 ml DMSO and warmed to 110°C. To this rapidly stirring solution p-fluoroacetophenone (Aldrich; 6.0 gm, 0.043 mole) in 10 ml DMSO was added. After refluxing 5 hours and cooling, water and benzene

were added. The organic layer was washed twice with H_2O then concentrated in vacuo. G.C. analysis (5% SE-30) showed 74% of the p-F-ACP was converted to p-CN-ACP. Recrystallization from ethanol gave pure white crystals. MS (70 eV) m/e 145, 130, 102, 75; NMR ($CDCl_3$) δ8.0 (d, 2H, J = 8 Hz), 7.7 (d, 2H, J = 8 Hz), 2.6 (s, 3H); IR (Nujol) 2200 cm^{-1}, 1670, 1460; ε(313 nm) = 71, ε(366 nm) = 3.8; mp 59.0-59.5°C, lit.[102], 57-58°C.

Benzophenones

Benzophenone (Aldrich). Recrystallized from ethanol; MS (70 eV) m/e 182, 105, 77; NMR ($CDCl_3$) δ7.8 (m, 2H), 7.5 (m, 3H); IR (Nujol) 1670 cm^{-1}, 1605, 1370; solid white crystals; ε(313 nm) = 93, ε(366 nm) = 26; mp 48.0-48.2°C, lit.[99], 48.5°C.

4,4'-Di-tert-butylbenzophenone. To a rapidly stirring mixture of CCl_4 (23.2 gm, 0.15 mole) and $AlCl_3$ (20.0 gm, 0.15 moles) in 300 ml CS_2 t-butylbenzene was added (Aldrich; 40.0 gm, 0.30 mole) dropwise, then stirred 36 hours. The solution was dumped into icy H_2O, extracted 3 times with ethyl ether, neutralized with $NaHCO_3$ solution, washed with H_2O, then concentrated in vacuo, yielding dichlorodiphenyl methane as a yellow oil. Refluxing this oil 12 hours with 300 ml H_2O gave the desired ketone as a dark oil. Filtering this product dissolved in n-heptane

removed most of the color. Recrystallization from ethanol gave pure white crystals. MS (70 eV) m/e 294, 279, 161; NMR ($CDCl_3$) δ7.7 (d, 4H, J = 9 Hz), 7.4 (d, 4H, J = 9 Hz), 1.3 (s, 18H); ε(313 nm) = 174, ε(366 nm) = 31; mp 132-133°C, lit.[107], 134.6-134.9°C.

m-Chlorobenzophenone. Prepared by Friedel-Crafts acylation of benzene (200 ml) by m-chlorobenzoyl chloride (Aldrich; 20.0 gm, 0.11 mole), using $AlCl_3$ (21.3 gm, 0.16 mole) as catalyst, as outlined for 4,4'-di-tert-butylbenzophenone. MS (70 eV) m/e 216, 181, 105, 77; NMR ($CDCl_3$) δ7.3-7.8 (M); IR (Nujol) 1640 cm^{-1}, 1630, 1600, 1575; fluffy white crystals; ε(313 nm) = 105, ε(366 nm) = 33; mp 79.0-80.5°C, lit.[100], 82-83°C.

p-Chlorobenzophenone. Prepared by Friedel-Crafts acylation of benzene (700 ml) by p-chlorobenzoyl chloride (Aldrich; 59.5 gm, 0.34 mole), using $AlCl_3$ (54 gm, 0.40 mole) as catalyst, as outlined for 4,4'-di-tert-butylbenzophenone. MS (70 eV) m/e 216, 181, 105, 77; NMR ($CDCl_3$) δ7.2-7.8 (m): IR (Nujol) 1660 cm^{-1}, 1620; solid white crystals; ε(313 nm) = 121, ε(366 nm) = 36; mp 72.0-73.0, lit.[102], 75-77°C.

3,4-Dichlorobenzophenone. Prepared by Friedel-Crafts acylation of benzene (600 ml) by 3,4-dichlorobenzoyl chloride (Aldrich; 70 gm, 0.33 mole) using $AlCl_3$ (54 gm, 0.40 mole) as catalyst as outlined for 4,4'-di-tert-butylbenzophenone. MS (70 eV) m/e 250, 215, 173, 145, 105, 77;

NMR ($CDCl_3$) δ7.1-7.7 (m); IR (Nujol) 1650 cm^{-1}, 1570; fluffy white crystals; mp 101.5-102.0°C, lit.[105], 102°C.

4,4'-Dichlorobenzophenone (Aldrich). Recrystallized from ethanol; MS (70 eV) m/e 250, 215, 139, 111, 75; NMR ($CDCl_3$) δ7.7 (d, 4H, J = 8 Hz), 7.4 (d, 4H, J = 8 Hz); IR (Nujol) 1630 cm^{-1}, 1595; white crystals; ε(313 nm) = 122, ε(366 nm) = 31; mp 145.0-145.5°C, lit.[102], 144-146°C.

4,4'-Dimethylbenzophenone (Eastman). Recrystallized from ethanol. MS (70 eV) m/e 210, 195, 119, 91; NMR ($CDCl_3$) δ7.7 (d, 4H, J = 8 Hz), 7.2 (d, 4H, J = 8 Hz), 2.45 (s, 3H); IR (Nujol) 1630 cm^{-1}, 1605; white crystals; mp 92.0-92.2°C, lit.[100], 95°C.

4,4'-Dimethoxybenzophenone (Aldrich). Recrystallized from ethanol. MS (70 eV) m/e 242, 211, 135, 107, 92, 77; NMR ($CDCl_3$) δ7.8 (d, 4H, J = 8 Hz), 6.9 (d, 4H, J = 8 Hz), 3.8 (s, 3H). White crystals; mp 142.0-142.2°C, lit.[100], 144°C.

4,4'-Di-fluorobenzophenone. Prepared by adding fluorobenzene (Aldrich; 40.0 gm, 0.42 mole) to a mixture of CCl_4 (27.7 gm, 0.21 mole) and $AlCl_3$ (30.0 gm, 0.20 mole) in 80 ml CS_2 solvent, then refluxing in the presence of H_2O as outlined for 4,4'-di-tert-butylbenzophenone. MS (70 eV) m/e 218, 123, 95, 75; NMR ($CDCl_3$) δ7.8 (m, 2H), 7.2 (m, 2H); IR (Nujol) 1600 cm^{-1}, 1500;

white crystals; ε(313 nm) = 116, ε(366 nm) = 10.5; mp 107.0-107.5, lit.[102], 102-105°C.

p-Trifluoromethylbenzophenone. p-Trifluoromethylphenyl magnesium bromide was prepared by adding p-bromobenzotrifluoride (Aldrich; 45.0 gm, 0.20 mole) in 200 ml ethyl ether to Mg turnings (6.3 gm, 0.26 mole) with a crystal of I_2. After refluxing 2 hours, the solution was cooled and benzaldehyde (24.4 gm, 0.23 mole) in 50 ml ether added dropwise with rapid stirring. The solution was refluxed 1 hr, dumped into a dilute icy HCl solution, extracted 5 times with ether, and the combined organic layers concentrated in vacuo, yielding brown polymeric material. This alcohol was dissolved in 50 ml acetone and a mixture of $NaCr_2O_7 \cdot 2H_2O$ (Fisher; 23.8 gm, 0.08 mole), conc. H_2SO_4 (26.1 gm, 0.27 mole) and H_2O (125 ml) was added slowly[79]. After stirring 30 minutes at room temperature, the aqueous solution was extracted 4 times with ether, washed with a $NaHCO_3$ solution, then H_2O, and concentrated in vacuo. The crude product was recrystallized 4 times from hot ethanol then passed through a column packed with silica gel, eluting with pentane. A final recrystallization from ethanol afforded pure white fluffy crystals. MS (70 eV) m/e 250, 231, 181, 173, 145, 105; NMR ($CDCl_3$) δ7.3-7.8 (m); IR (Nujol) 1640 cm^{-1}; 1380; white crystals; ε(313 nm) = 84, ε(366 nm) = 36; mp = 113.0-113.5°C, lit.[102] 116-118°C.

m-Trifluorobenzophenone. Prepared from m-bromobenzotrifluoride (Aldrich; 32.8 gm. 0.15 mole) and benzaldehyde (15.5 gm, 0.15 mole) as outlined for p-trifluorobenzophenone. MS (70 eV) m/e 251, 231, 182, 173, 145, 105; NMR ($CDCl_3$) δ7.4–8.0 (m); IR (Nujol) 1630 cm^{-1}, 1605, 1370; white crystals at room temperature; ε(313 nm) = 103, ε(366) = 28; mp 4.90-52.0, lit.[108], 51.5-53°C.

p-Cyanobenzophenone. p-Cyanobenzoyl chloride was pre-prepared by chlorinating p-cyanobenzoic acid (Aldrich; 4.4 gm, 0.03 mole) with thionyl chloride (50 ml). After refluxing 1 hour, the excess thionyl chloride was removed under vacuum. NMR ($SOCl_2$) δ7.8-8.2 (d, 2H). Friedel-Crafts acylation of benzene (90 ml) by the crude p-cyanobenzoyl chloride just prepared with $AlCl_3$ (4.0 gm, 0.030 mole) led to crude p-cyanobenzophenone. The mixture was stirred 30 minutes at room temperature, then refluxed gently 3.5 hrs, cooled, dumped into icy H_2O, then extracted with ether. The combined ether layers was neutralized with an $NaHCO_3$ aqueous solution, washed with water, concentrated in vacuo, yielding a brown solid product. Recrystallizing from hot ethanol produced the pure, white, solid p-cyanobenzophenone. MS (70 eV), m/e 207, 130, 105, 77; NMR ($CDCl_3$) δ7.4-7.8 (m); ε(313 nm) = 103, ε(366 nm) = 48; mp 110.0-110.5°C, lit.[106], 107-108°C.

Valerophenones

p-Methylvalerophenone. Valeryl chloride was prepared by adding thionyl chloride (107.1 gm, 0.90 mole) to valeric acid (Eastman: 80.0 gm, 0.78 mole). The solution was refluxed 2 hours and the thionyl chloride removed in vacuo. The resulting valeryl chloride was added dropwise to a rapidly stirring, chilled mixture of toluene (143.3 gm, 1.56 mole) and $AlCl_3$ (106.6 gm, 0.80 mole) in 150 ml CS_2 solvent. After addition was complete, the solution was stirred 1 hr at room temperature, refluxed 2 hrs, dumped into icy H_2O, then extracted 3 times with ether. The combined organic layers were neutralized with a $NaHCO_3$ solution, washed with H_2O, and concentrated in vacuo, giving a brown liquid. Distillation of this liquid with a 14 inch Vibreaux column gave p-methylvalerophenone in over 99.5% purity. MS (70 eV) m/e 176, 134, 119, 91; NMR ($CDCl_3$) δ7.8 (d, 2H, J = 8 Hz), 7.2 (d, 2H, J = 8 Hz), 2.9 (t, 2H, J = 7 Hz), 2.4 (s, 3H), 0.9-1.9 (m); clear liquid; mp 18.5-19.0°C, lit.[21d], 19-20°C.

p-tert-butylvalerophenone. Prepared by Friedel-Crafts acylation of tertbutylbenzene (Aldrich; 18.9 gm, 0.14 mole) by valeryl chloride (17.0 gm, 0.14) as outlined for p-methylvalerophenone. MS (70 eV) m/e 219, 203, 176, 161, 146, 118; NMR ($CDCl_3$) δ7.9 (d, 2H, J = 8 Hz), 7.5 (d, 2H, J = 8 Hz), 2.9 (t, 2H, J = 7 Hz), 1.3 (s, 9H), 0.9-1.9 (m); clear liquid; bp 290°C.

p-Methoxyvalerophenone. Synthesized by Dr. A. Kemppainen. Recrystallized from ethanol. MS (70 eV) m/e 192, 176, 161, 150, 135; NMR ($CDCl_3$) δ7.9 (d, 2H, J = 8 Hz), 6.9 (d, 2H, J = 8 Hz), 3.8 (s, 3H), 2.9 (t, 2H, J = 7 Hz), 0.9-1.9 (m, 7H); bp 282.0°C, lit.[21d], 143°C/6 mm; mp 24.0-24.3°C.

B. Photokinetic Techniques

1. Glassware

All glassware used in the kinetic experiments (class A volumetric flasks and pipets, Pyrex culture tubes and 5 cc syringes) were washed twice with acetone then soaked in hot distilled water containing Alconox (Alconox, Inc.) detergent for a day. Then the equipment was rinsed 5 times with distilled water and soaked 12 hours in hot distilled water. This last cycle was repeated four times. All glassware was dried at 150°C in an oven used solely for this purpose.

The Pyrex culture tubes (13 x 100 mm) were drawn out to 15 cm by heating with an oxygen torch about 4 cm from the top.

2. Preparation of Samples

Solutions were prepared by weighing samples directly into volumetric flasks and diluting to the mark or by

pipeting aliquots from a stock solution prepared in the same manner into volumetric flasks and then adding various amounts of quencher or donor stock solution to each flask before diluting. 2.8 ml of the final solutions were syringed into the constricted culture tubes.

3. Degassing Technique

The culture tubes, each filled with 2.8 ml of sample solution, were attached to a vacuum line (10^{-4} Torr) by means of rubber stoppers (size 00) connected to a manifold containing 12 glass stopcocks, built in this department's glass-shop. The samples were frozen in liquid nitrogen, the stopcocks opened for 10 minutes, then closed, and the samples thawed with a bucket of cold water. This freeze-pump-thaw cycle was repeated 3 times and the tubes sealed while still frozen using an oxygen torch.

4. Irradiation Procedure

Quantum yield and Stern-Volmer quenching studies were performed by parallel irradiation of degassed samples in a merry-go-round apparatus immersed in a water bath at ambient temperature. A water-cooled Hanovia medium-pressure mercury lamp supplied the UV light needed. One of three filter systems was used to isolate the desired wavelength region: at 313 nm, by an alkaline potassium

chromate (0.002M K_2CrO_4 and 1% K_2CO_3); b) 366 nm, with Corning #7-83 filters; c) 335 nm and longer wavelength, by $Pb(NO_3)_2$ (0.025 M) dissolved in distilled water and saturated with $NaBr^{80}$.

5. Analysis

All analyses were done by gas chromatography on a Varian Aerograph series 1400 gas chromatograph, employing a flame ionization detector. Peaks were recorded on a Leeds and Northrup recorder and areas measured on an Infratronics CRS 309 digital integrator. Columns of various packing materials allowed separation of those components of interest. Optimum temperatures and nitrogen carrier gas (usually ca. 30 ml/min) were determined by trial-and-error.

GC standardization factors (SF) were determined by measuring the relative peak areas of products and standards whose concentrations are known.

$$\frac{[\text{Compound}]}{[\text{Standard}]} = SF \left(\frac{\text{Compound}}{\text{Standard}}\right) \text{ by GC}$$

$$SF = \frac{[\text{Compound}]}{[\text{Standard}]} \times \left(\frac{\text{Standard}}{\text{Compound}}\right) \text{ by GC,}$$

where the concentrations are determined by weighing out the samples and using their molecular weights.

A very good approximation is given by:

$$SF \quad \frac{\text{\# C atoms in standard}}{\text{\# C atoms in compound}} ,$$

where one counts single and double C-O bonds as 1/2 a C atom.

The SF used are given below.

Standard/Compound	SF
n-hexadecane/acetophenone	1.96
bibenzyl/n-pentylbenzoate	0.768
bibenzyl/n-hexybenzoate	0.807
bibenzyl/n-heptylbenzoate	0.945
p-ditolylethane/n-heptylbenzoate	0.813
p-ditolylethane/n-octylbenzoate	0.871
p-ditolylethane/n-nonylbenzoate	0.768
cyclopentyl chloride/phenylchloride	1.20*
cyclopentene/cyclopentane	1.00*
bicyclopentyl/tetradecane	1.40*
diisopropyl benzene/n-decylbenzoate	0.667*
p-methylacetophenone/n-butylbenzoate	1.18*
p-t-butylacetophenone/n-hexylbenzoate	1.04*
p-methoxyacetophenone/n-octylbenzoate	1.75*

*Based on relative number of C atoms.

Occasionally the usual column and conditions to analyze one of these photoproducts could not be employed, and the SF used was measured under <u>these</u> conditions.

The concentration of any compound analyzed by GC is given by:

$$[\text{Compound}] = SF[\text{Standard}] \left(\frac{\text{area compound peak}}{\text{area standard peak}}\right) \text{ by GC.}$$

6. Calculations of Quantum Yields

The amount of light absorbed, I_a, in einstein/liter was determined by valerophenone actinometers. Stock solutions of 0.10 M valerophenone in benzene with hexadecane standard were prepared. 2.8 ml samples in culture tubes were co-irradiated with the samples to be analyzed. The acetophenone concentration was calculated in the usual manner:

$$[\text{acetophenone}] = \text{SF hexadecane} \left(\frac{\text{area acetophenone peak}}{\text{area hexadecane peak}}\right) \text{ by GC}$$

From the concentration of acetophenone, the amount of light can be calculated:

$$I_a = \text{light absorbed} = [\text{acetophenone}]/0.33$$ [21b]

C. Spectra

1. Phosphorescence Emission Spectra

Phosphorescence spectra were recorded on a Perkin-Elmer MPF-44A Fluorescence Spectrophotometer equipped with a Differential Corrected Spectra Unit and Hitachi Phosphorescence Accessory. Samples were run at 10^{-4} M ketone using a quartz dewar with liquid nitrogen and 5 mm quartz tubes. The corrected emission scan mode, DC photometric

mode and ratio measurement mode were used. Excitation and emission slit widths were always 12 nm, and the spectra were run at a scan rate of 60 nm/min. Sample sensitivity varied with sample, and an excitation wavelength of 290 nm was used.

2. Infrared Spectra

IR spectra were recorded on a Perkin-Elmer Model 237 B grating infrared spectrophotometer. Samples were run neat, diluted in CCl_4, or dispersed in Nujol, using polystyrene (1601 cm^{-1}) to calibrate each spectrum.

3. ^1H NMR Spectra

A Varian T-60 spectrometer was used, with most samples dissolved in $CDCl_3$ and TMS used as a reference.

4. Mass Spectra

Mass spectra were run on a Finnigan 4000 GC/MS owned by the Chemistry Department. Pure samples were introduced directly into the inlet mode. Mixtures were first separated with a 5% SE-30 column.

5. Cyclic Voltammetry

Reduction potentials were measured for all ketones examined in Aldrich gold label acetonitrile or

propionitrile, 10^{-4} M ketone and 0.1-1 M TEAP, relative to SCE. Sweep rates of 200-400 mV/sec were used. Most of the ketones were reversible or at least semi-reversible. The equipment used belongs to Dr. C. K. Chang.

6. Extinction Coefficients

Molar extinction coefficients, ε, were determined by rearranging Beer's Law:

$$\log I_0/I = \varepsilon bc \ ,$$

where the absorbance, $\log I_0/I$, was measured on a Gilford Optical Density Converter Model 220, using the empty cuvettes as reference.

The pathlength, b, was 1.0 cm, and concentration, c, measured in moles/liter (sample in acetonitrile).

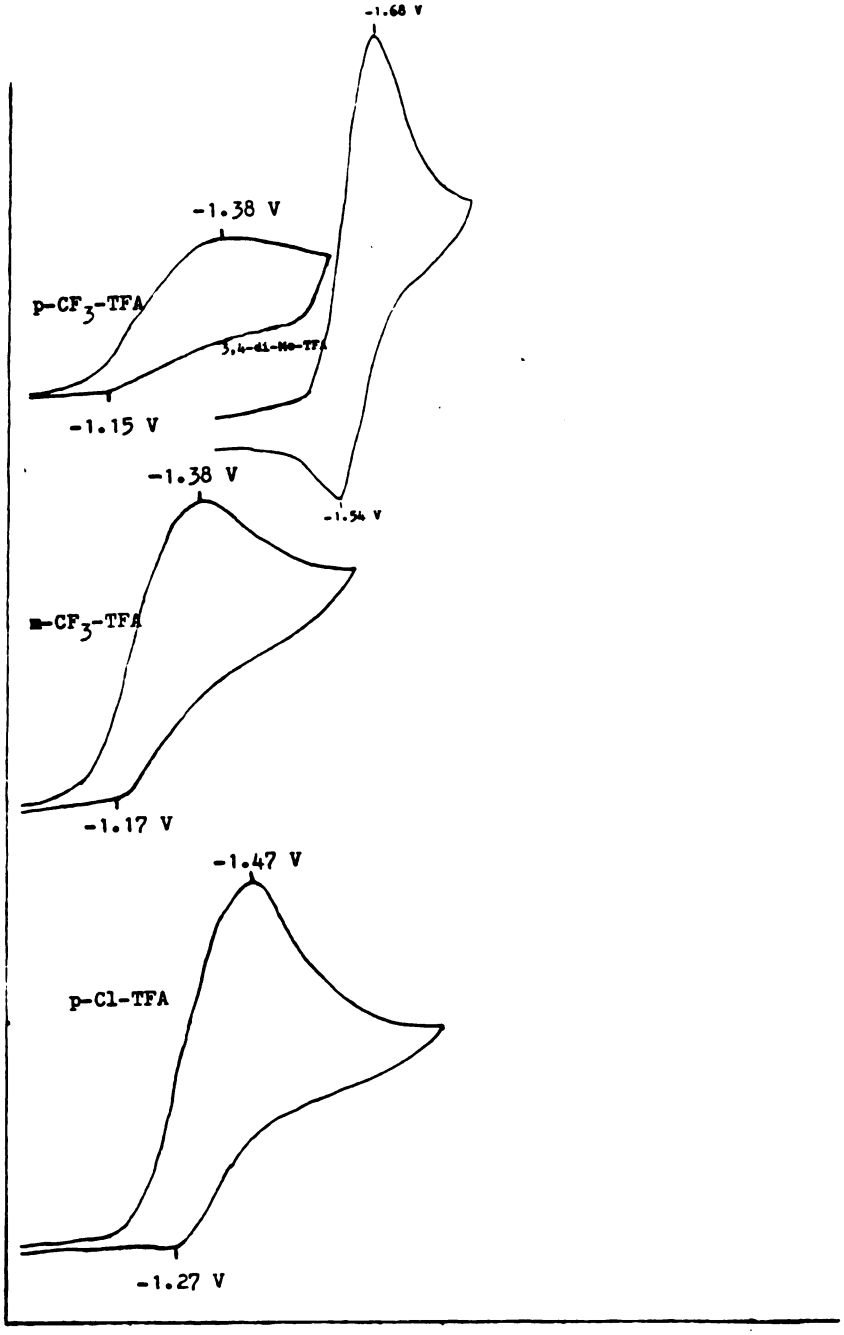


Figure 69. Cyclic Voltammagrams for 10^{-4} M α,α,α-Trifluoroacetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

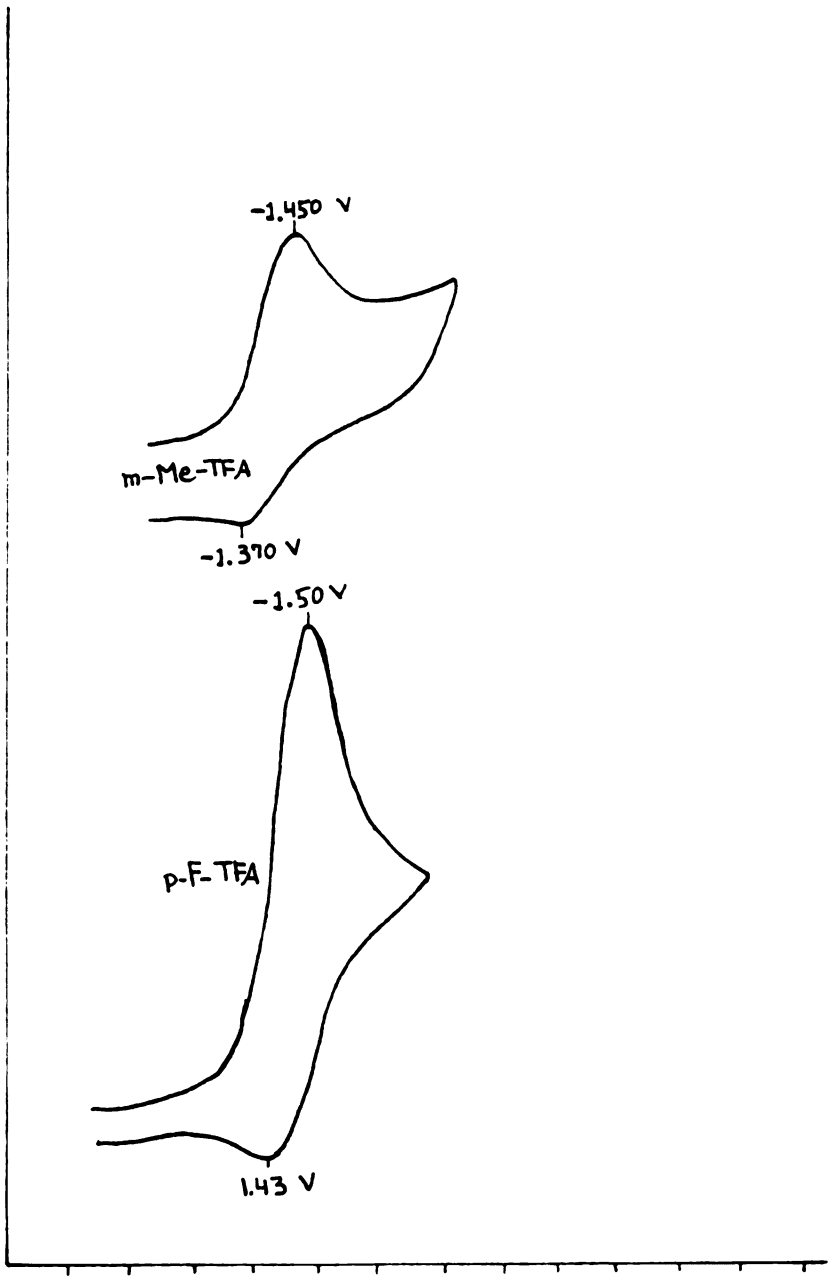


Figure 70. Cyclic Voltammagrams for 10^{-4} M , , -Trifluoro-acetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

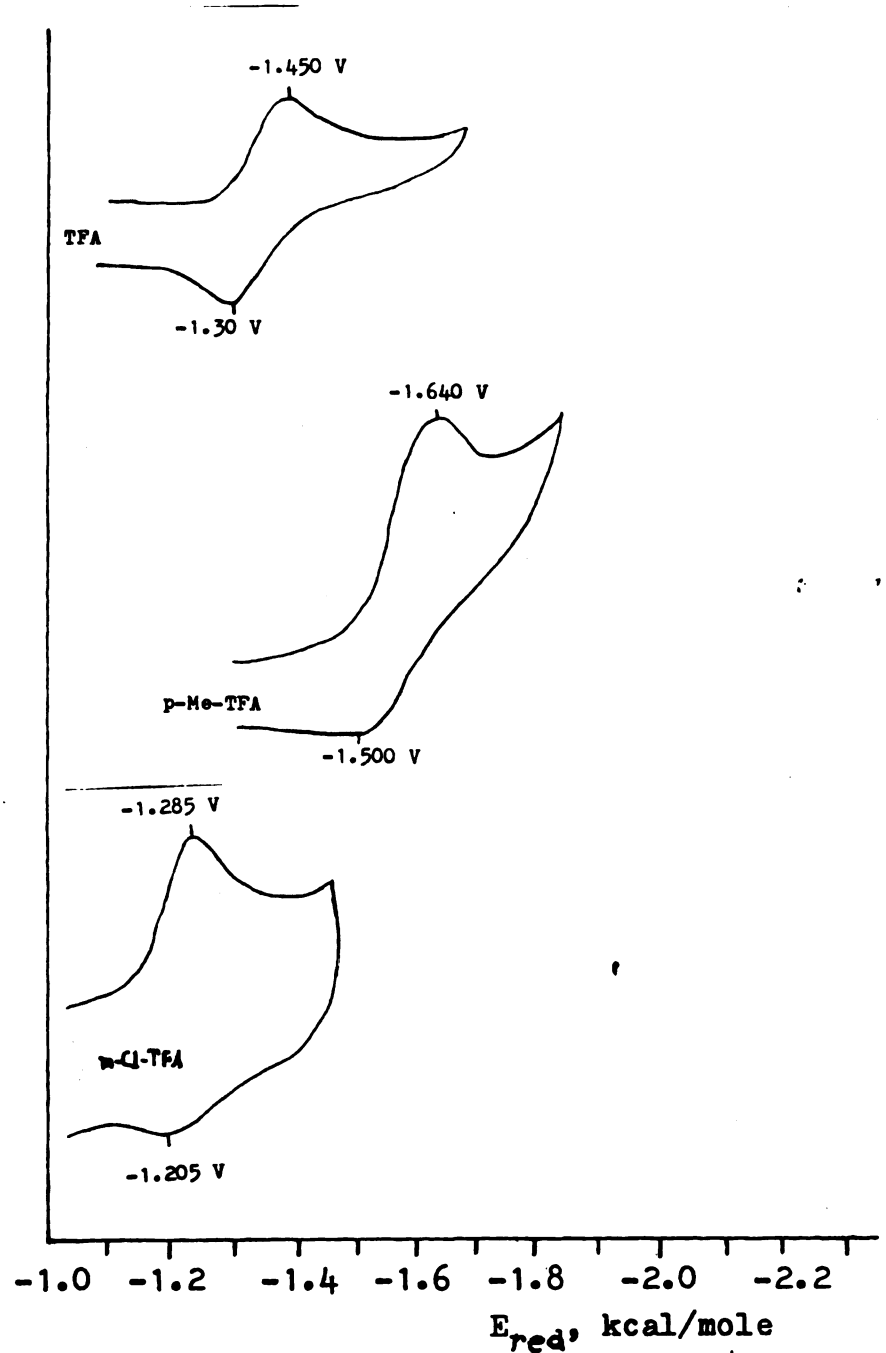


Figure 71. Cyclic Voltammagrams for 10^{-4} M α,α,α-Trifluoroacetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

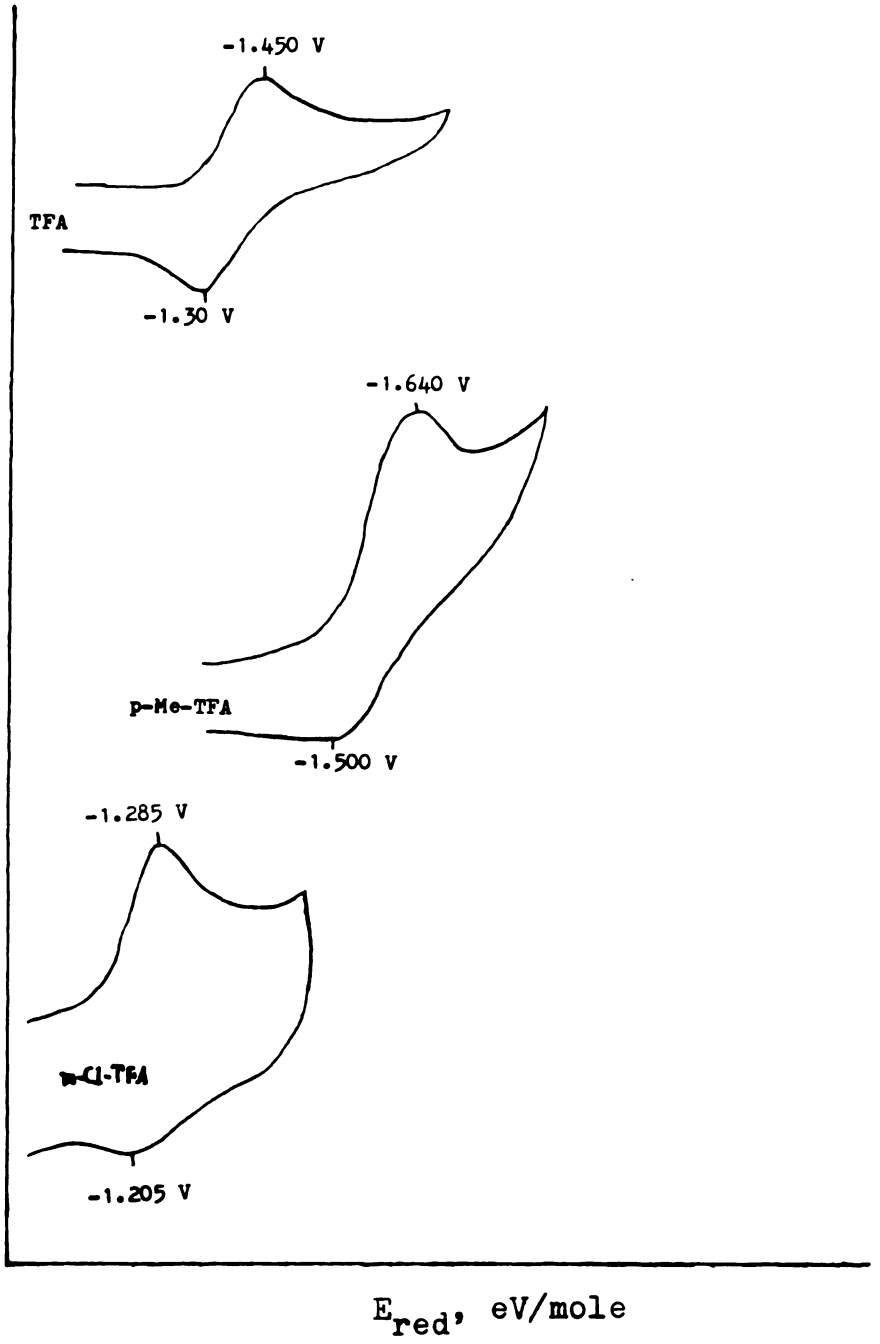


Figure 72. Cyclic Voltammagrams for 10^{-4} M α,α,α-Trifluoroacetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

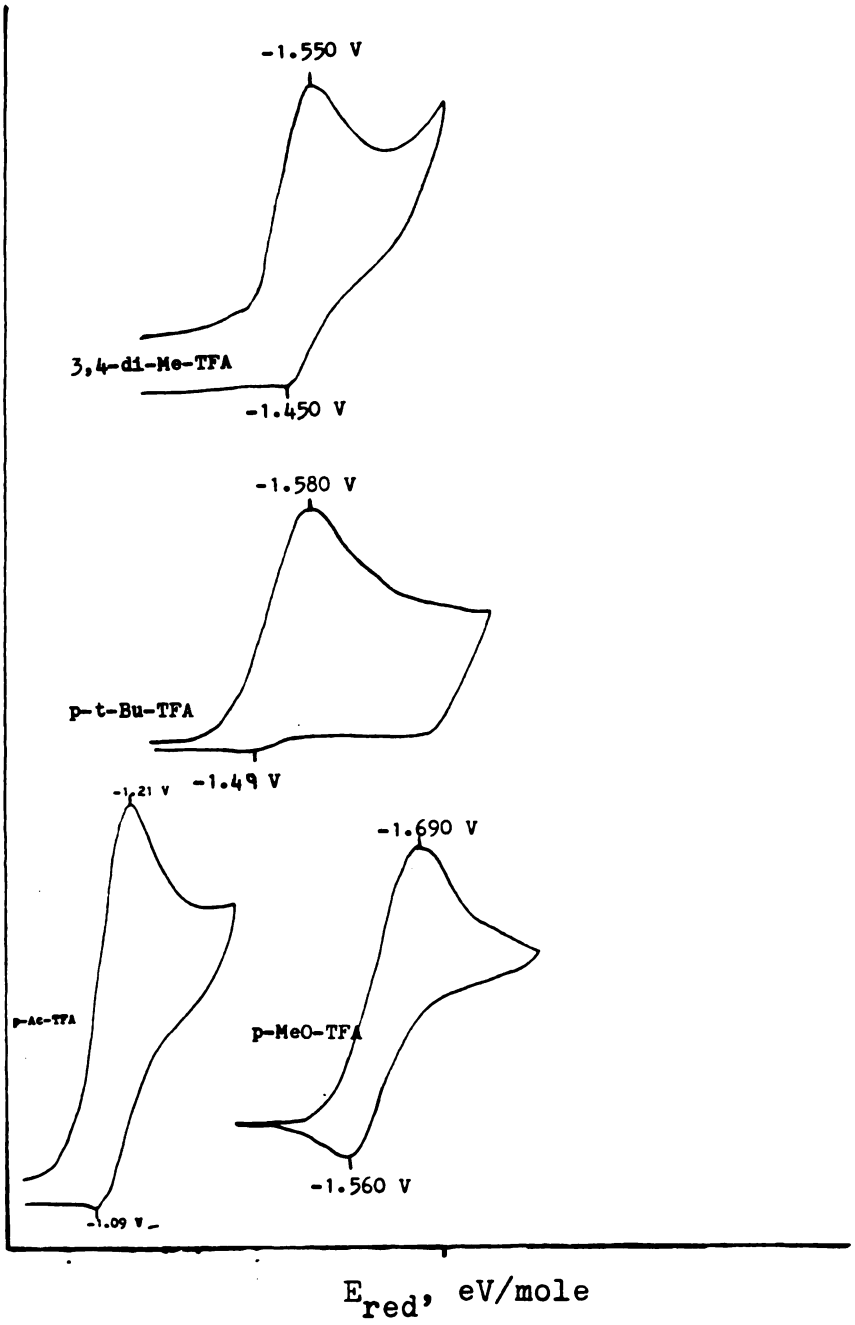


Figure 73. Cyclic Voltammagrams for 10^{-4} M α,α,α-Trifluoroacetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

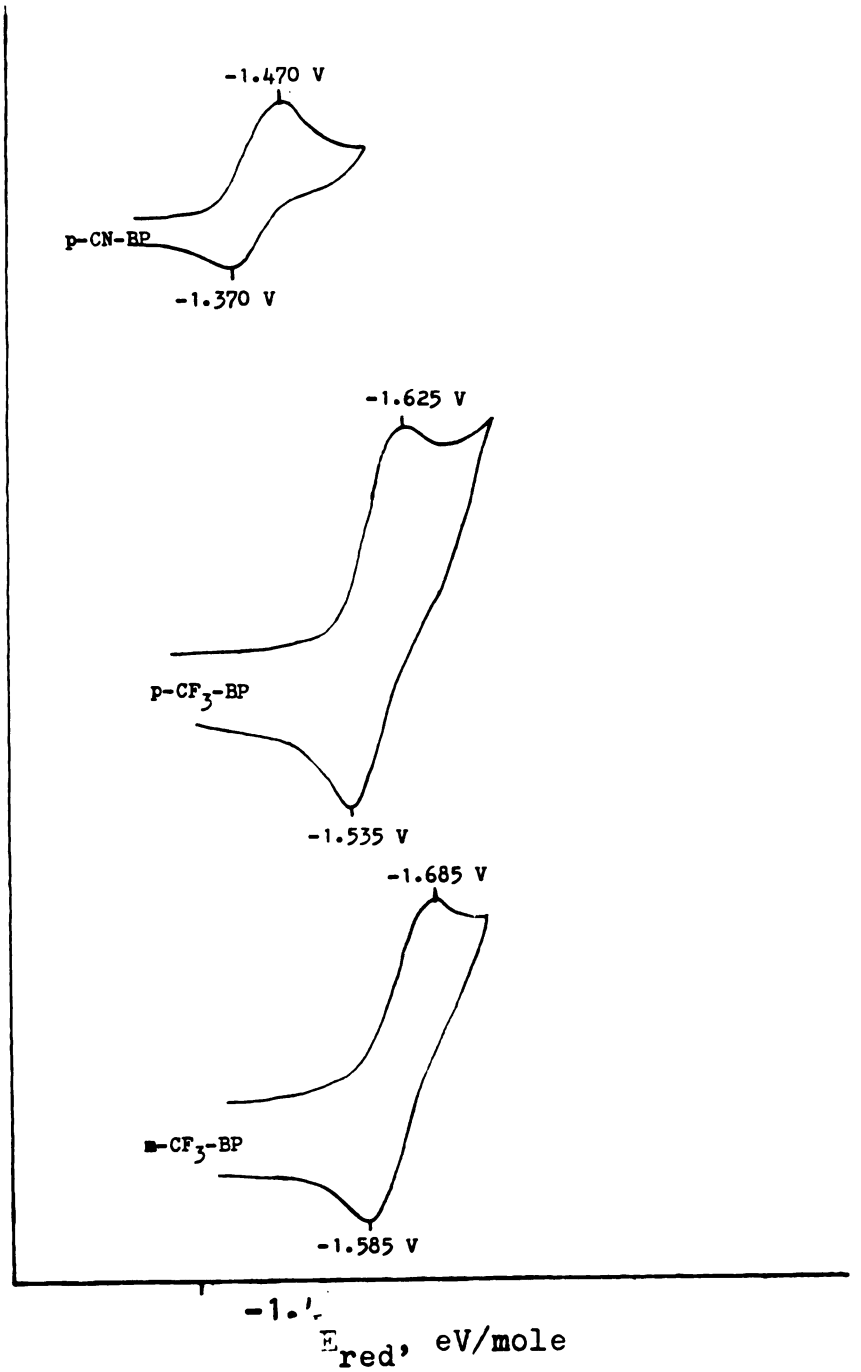


Figure 74. Cyclic Voltammagrams for 10^{-4} M Benzophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

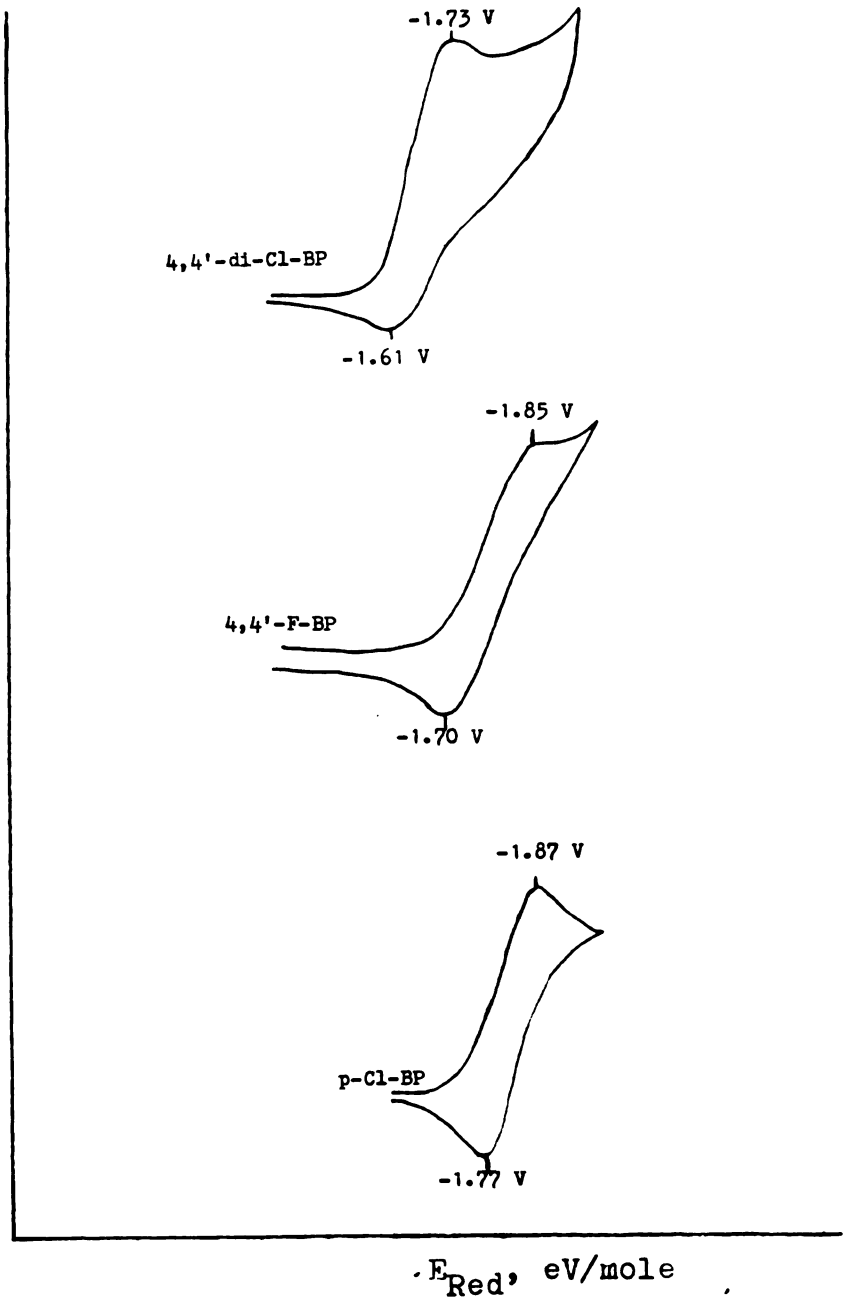


Figure 75. Cyclic Voltammagrams for 10^{-4} M Benzophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

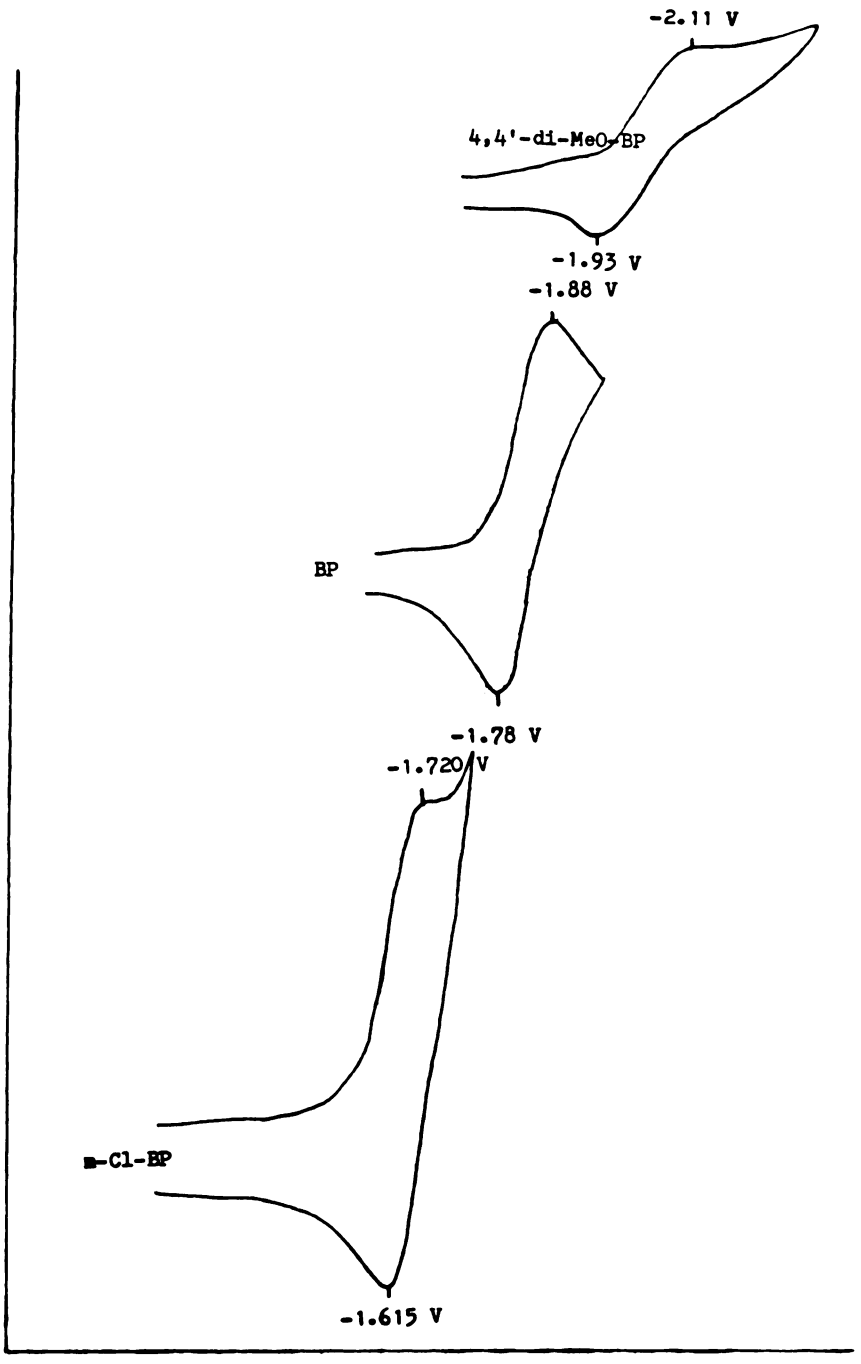


Figure 76. Cyclic Voltammagrams for 10^{-4} M Benzophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

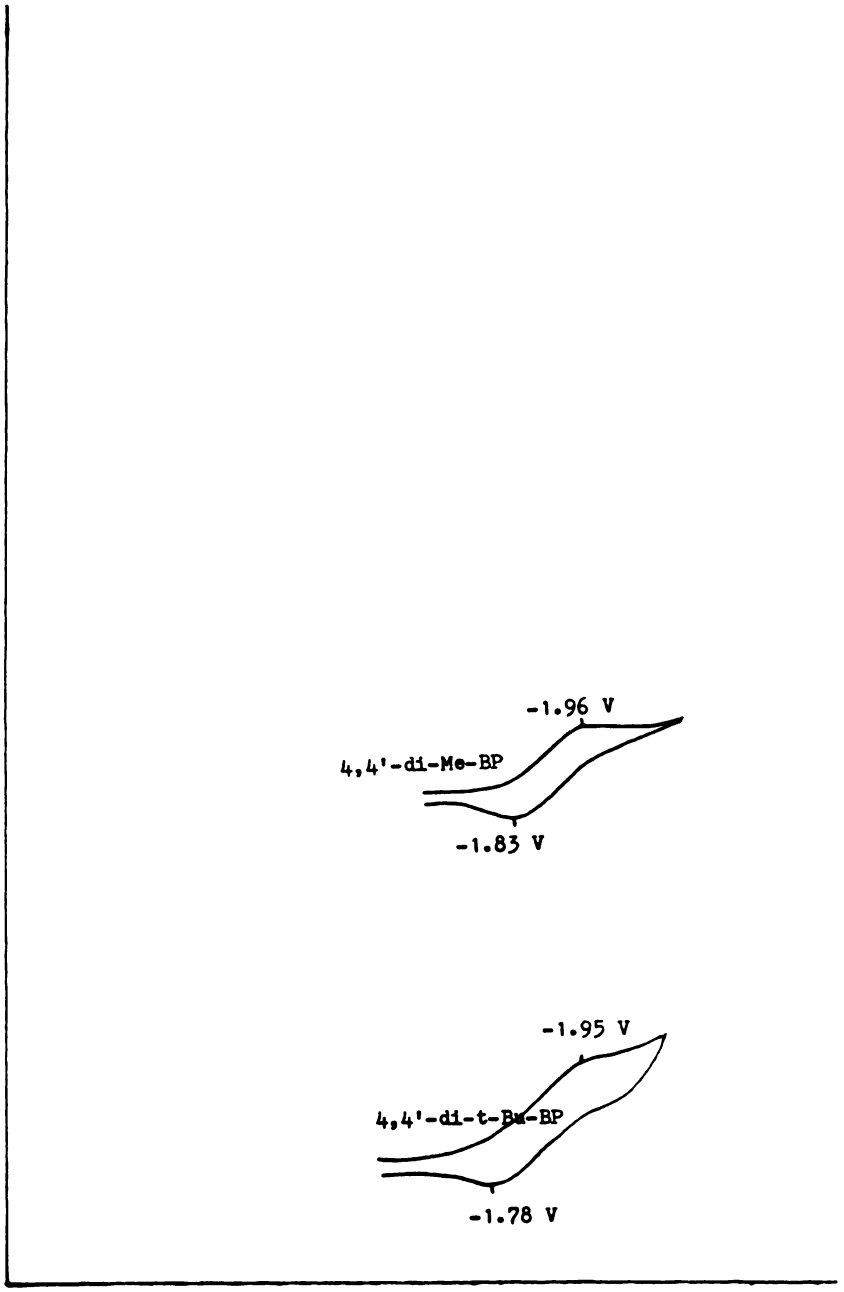


Figure 77. Cyclic Voltammagrams for 10^{-4} M Benzophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

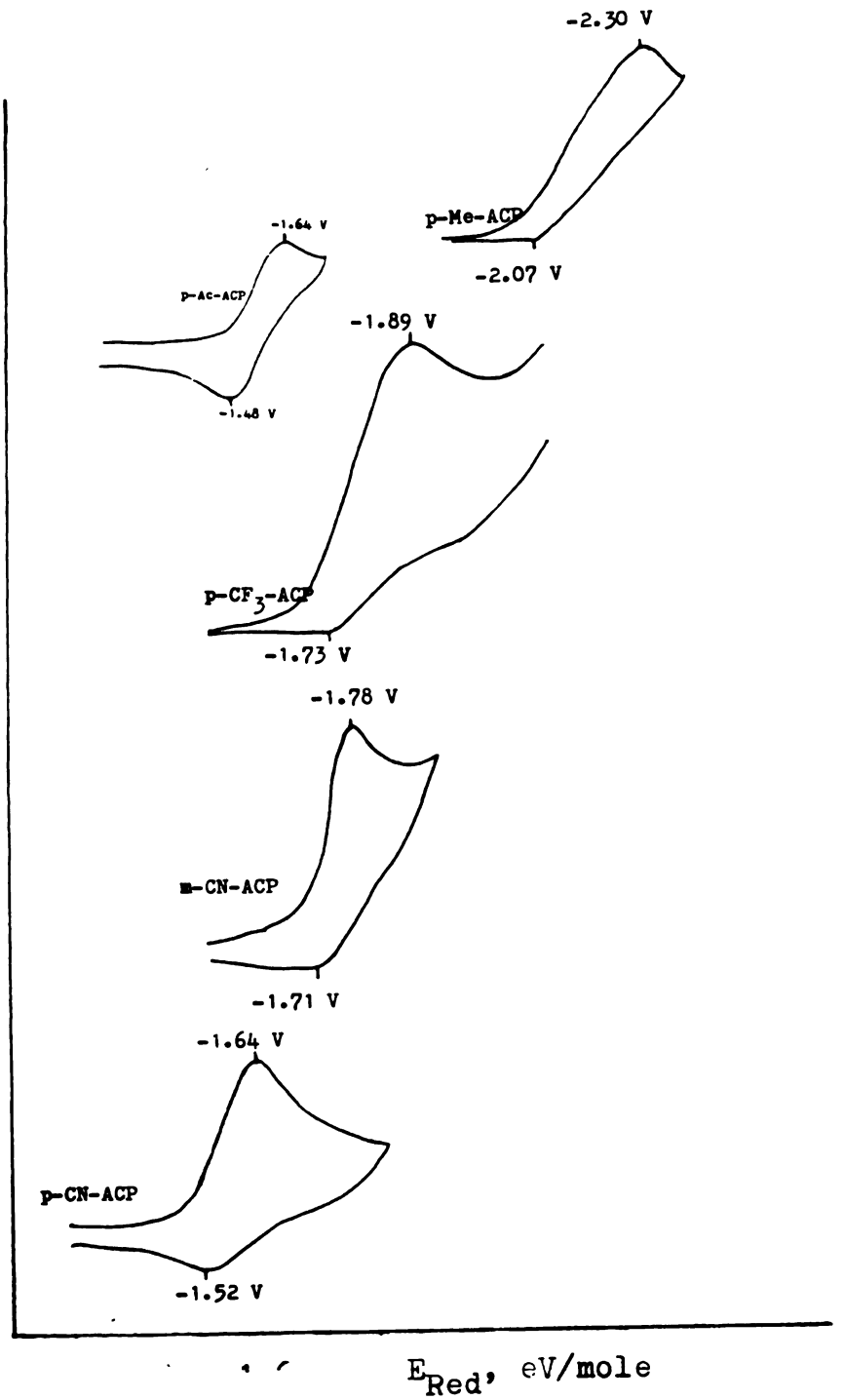


Figure 78. Cyclic Voltammagrams for 10^{-4} M Acetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

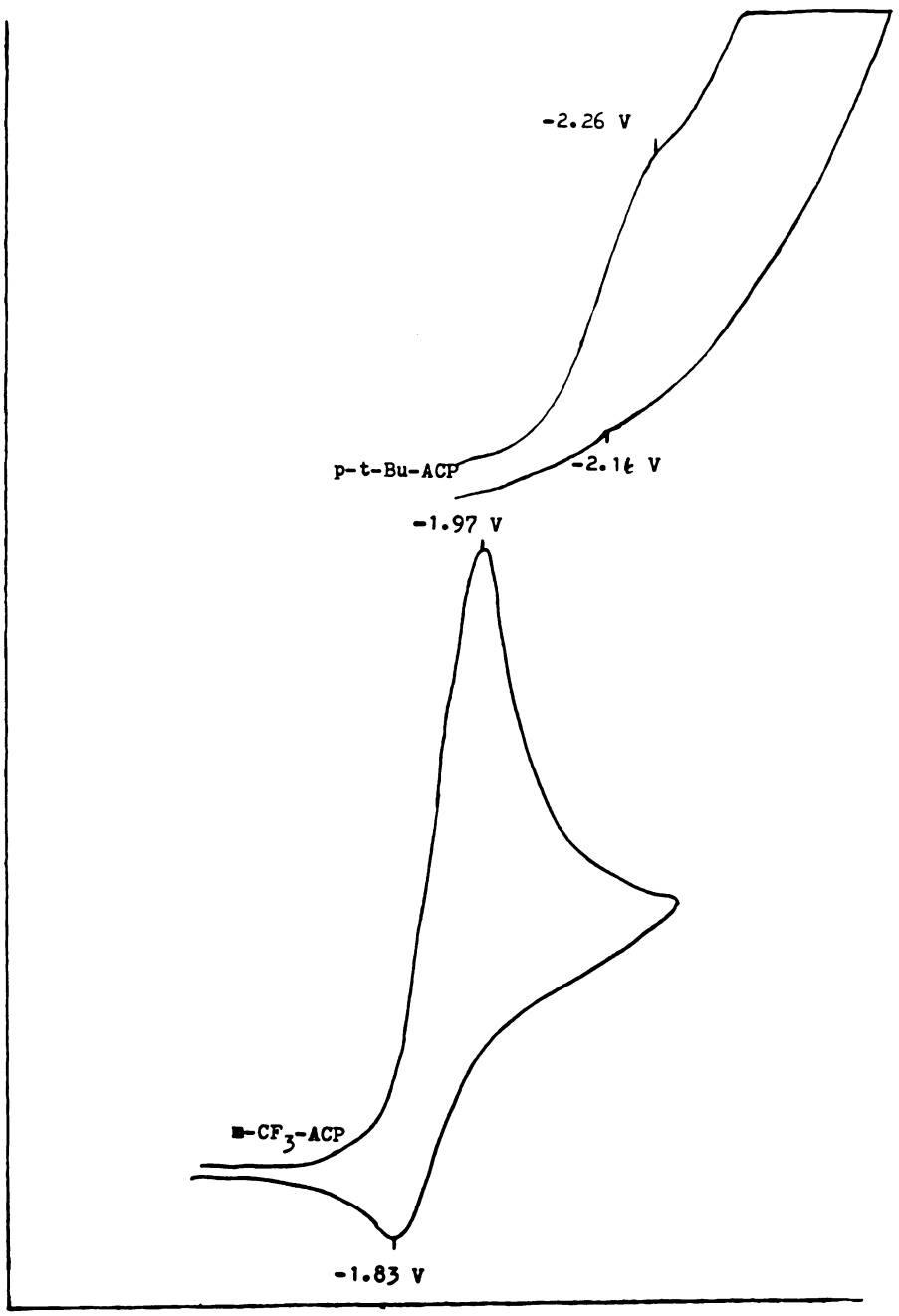


Figure 79. Cyclic Voltammagrams for 10^{-4} M Acetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

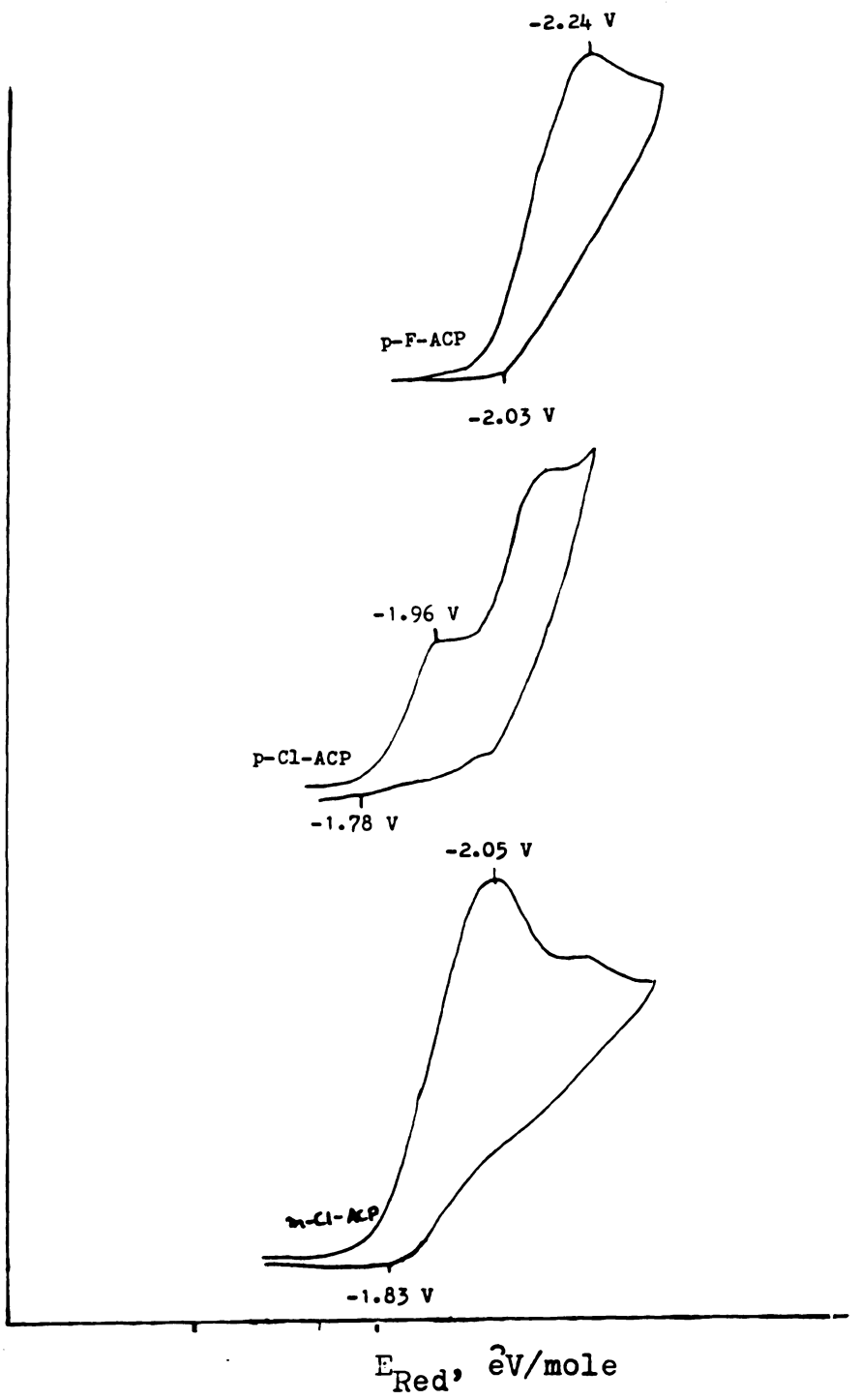


Figure 80. Cyclic Voltammagrams for 10^{-4} M Acetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

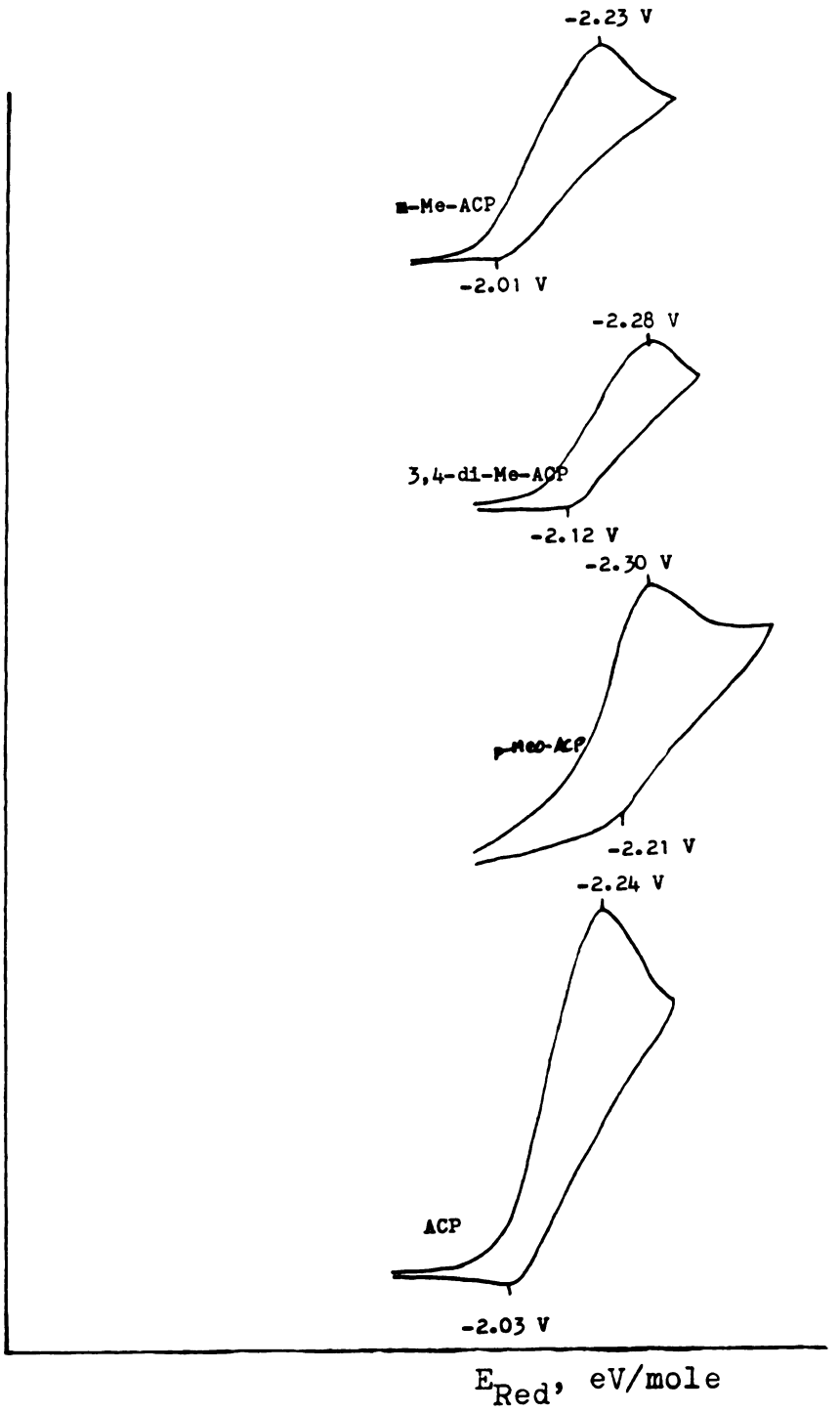


Figure 81. Cyclic Voltammagrams for 10^{-4} M Acetophenones in Acetonitrile (0.1 M TEAP) versus SCE (500 mV/sec).

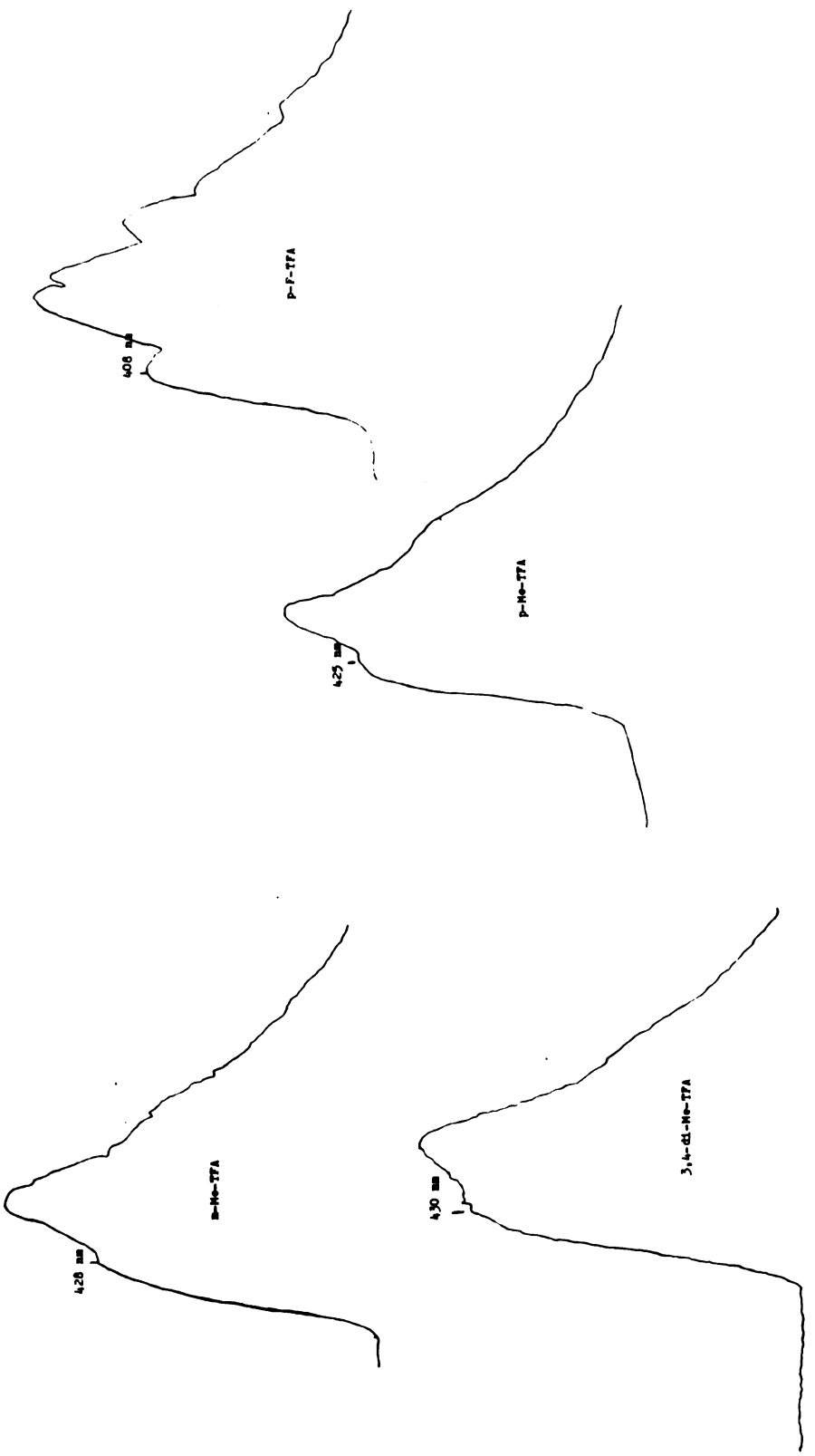


Figure 82. Phosphorescence Spectra, α,α,α-Trifluoroacetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

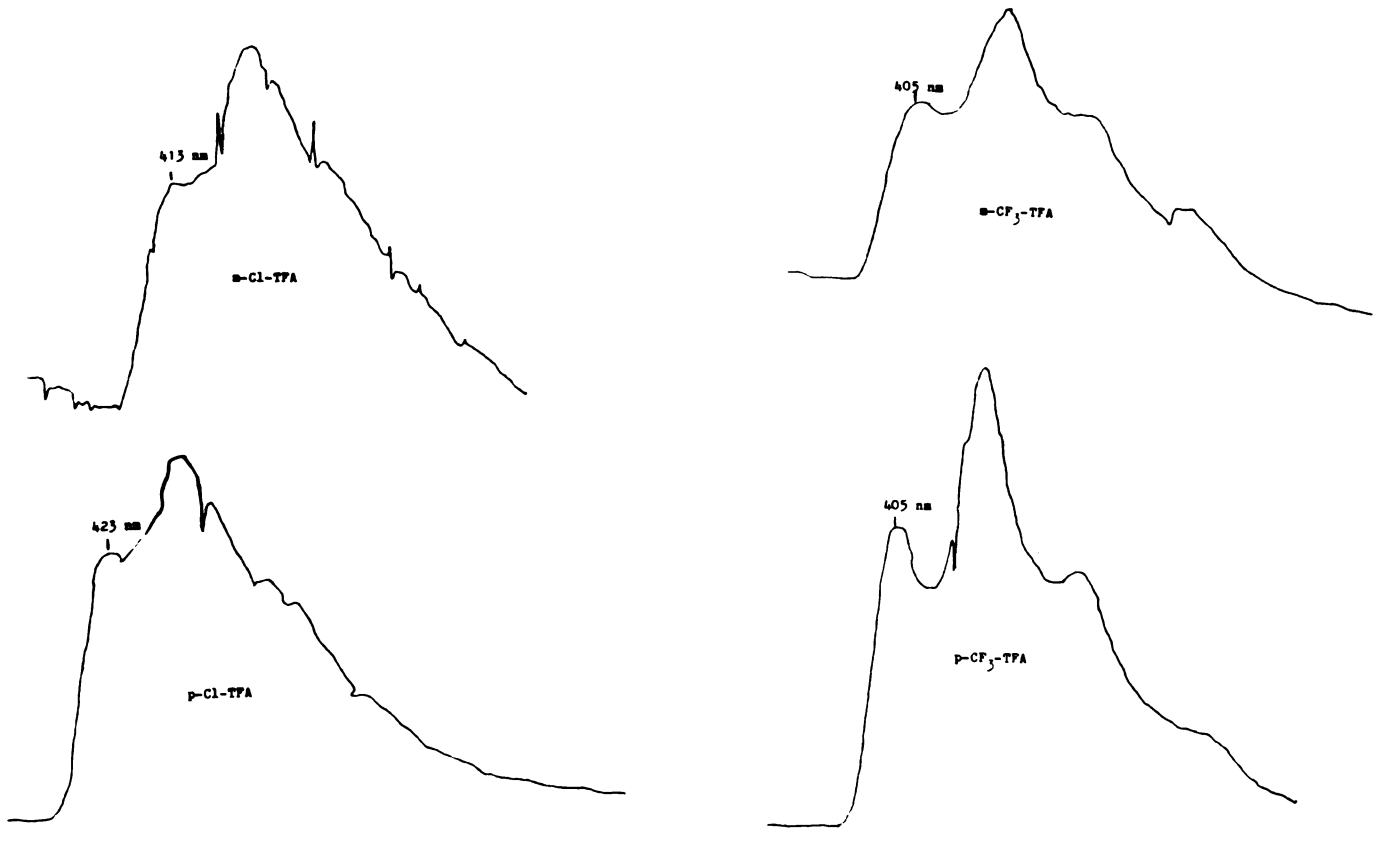


Figure 83. Phosphorescence Spectra, α,α,α-Trifl oacetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

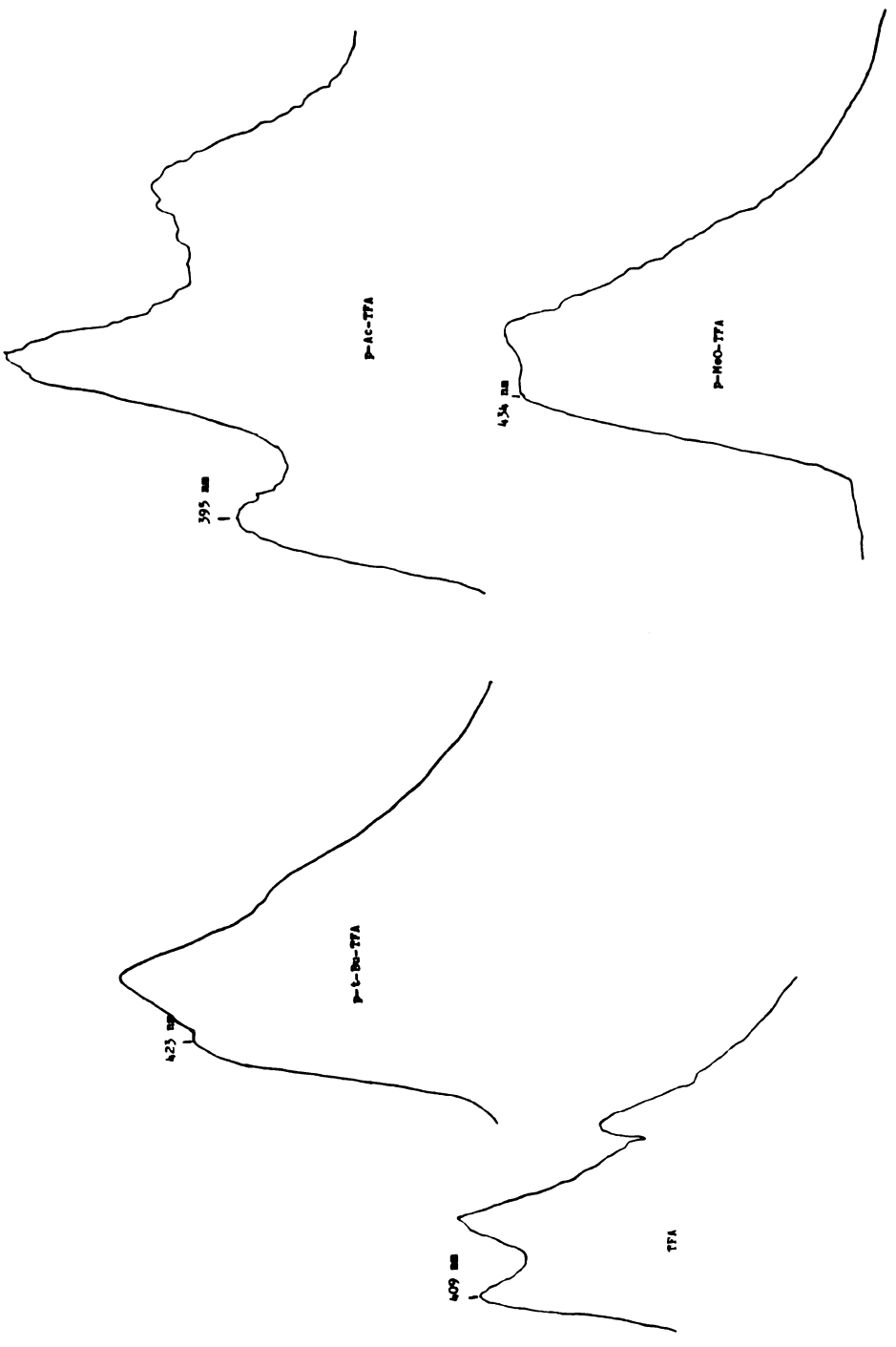


Figure 84. Phosphorescence Spectra, α, α, α-Trifluoroacetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

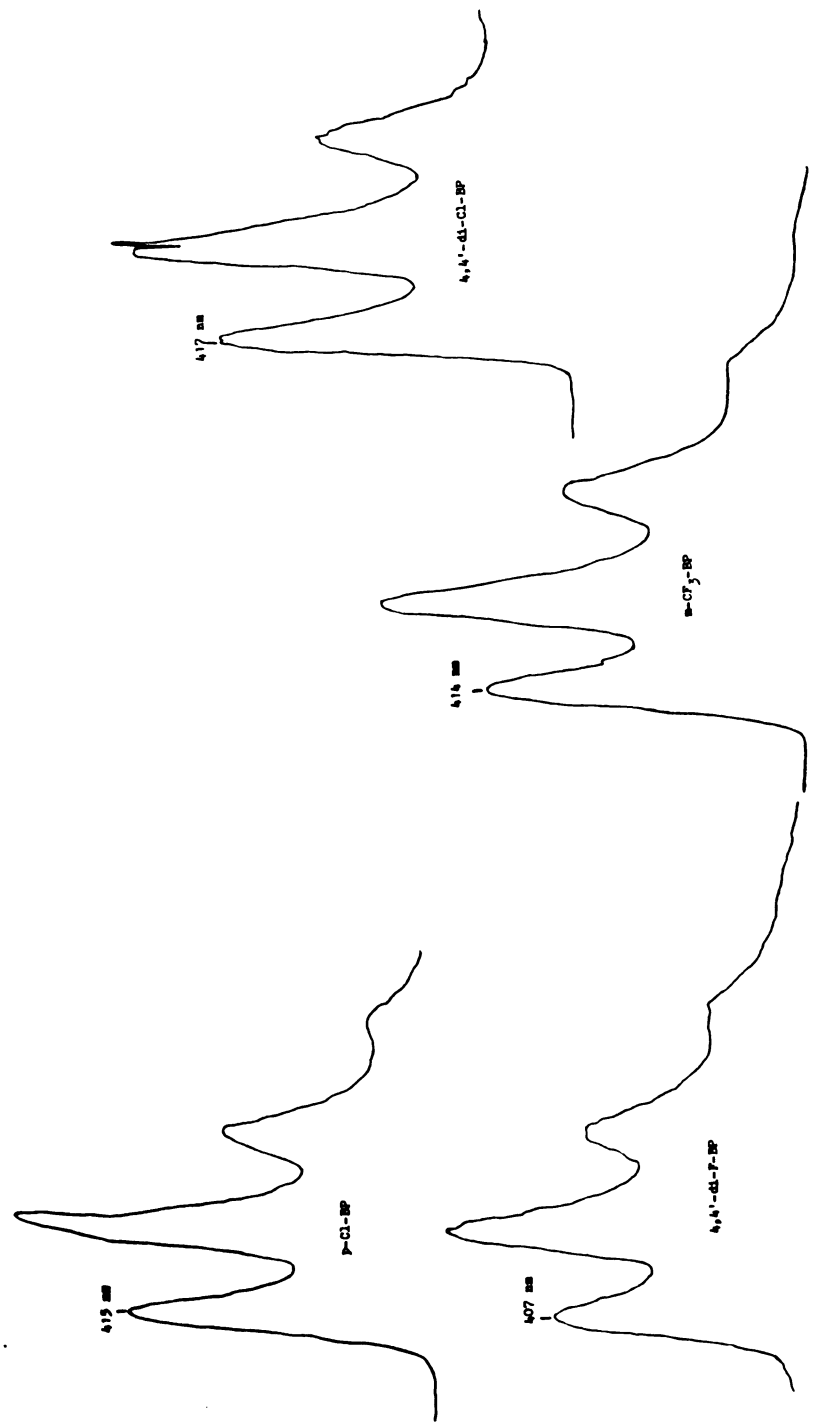


Figure 85. Phosphorescence Spectra of Benzophenones in 2-Methyl-Tetrahydrofuran at 77°K.

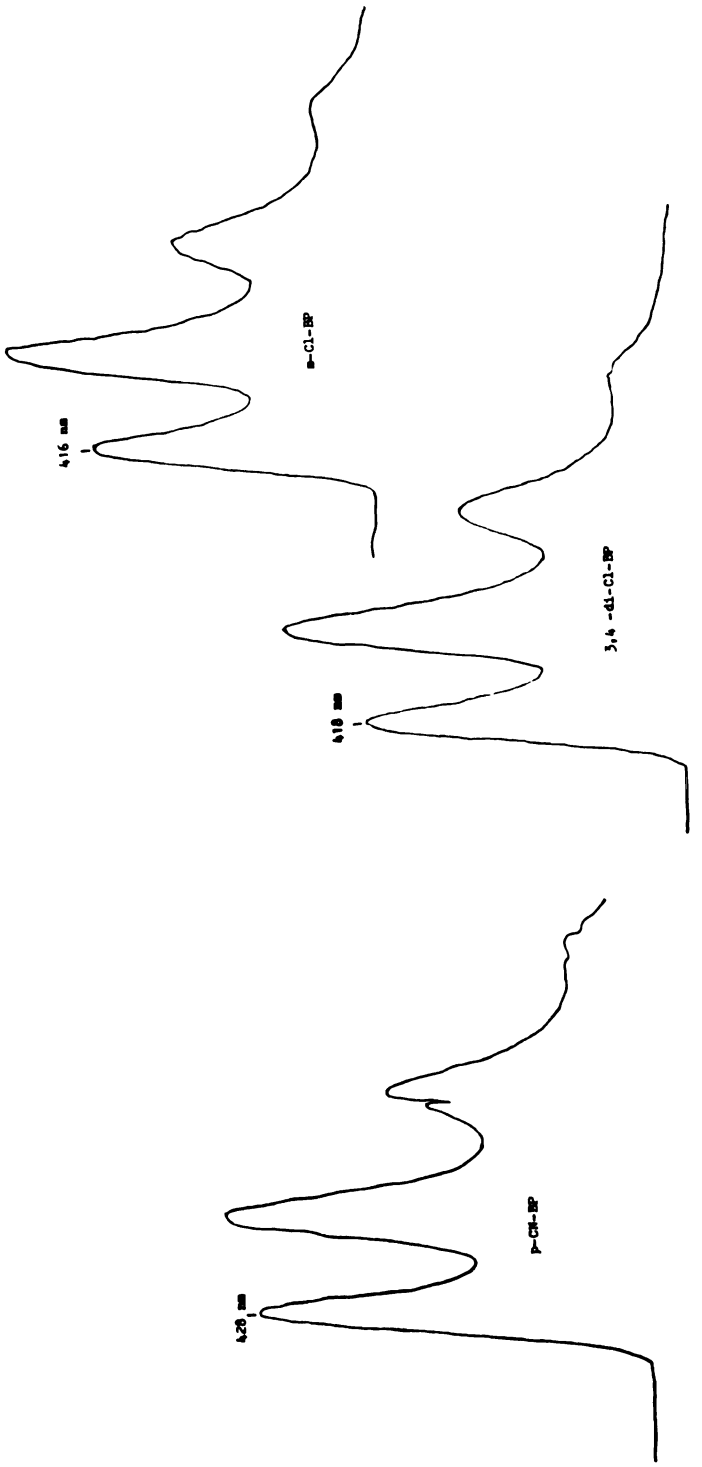


Figure 86. Phosphorescence Spectra of Benzophenones in 2-Methyl-Tetrahydrofuran at 77°K.

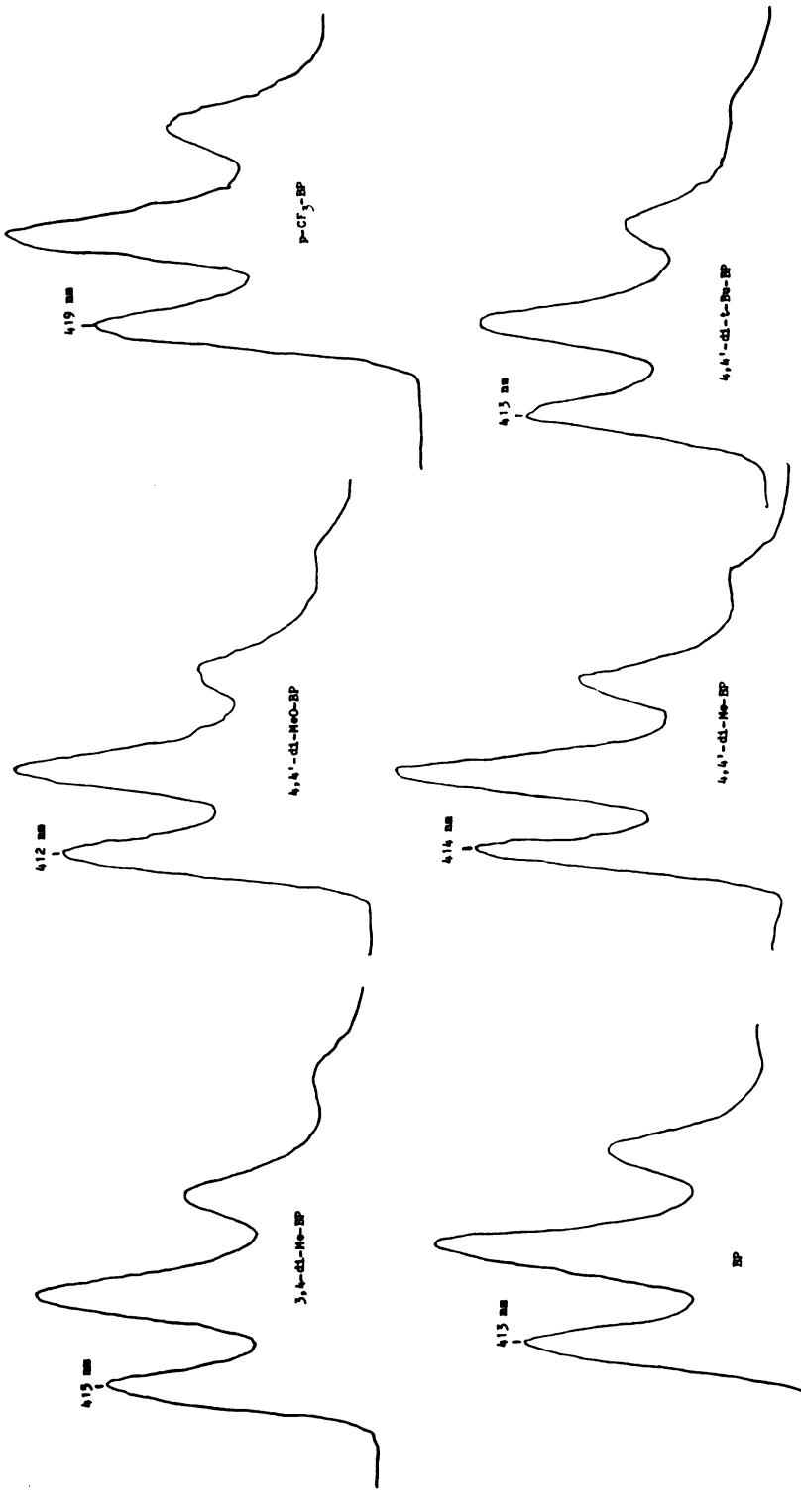


Figure 87. Phosphorescence Spectra of Benzophenones in 2-Methyl-Tetrahydrofuran at 77 °K.

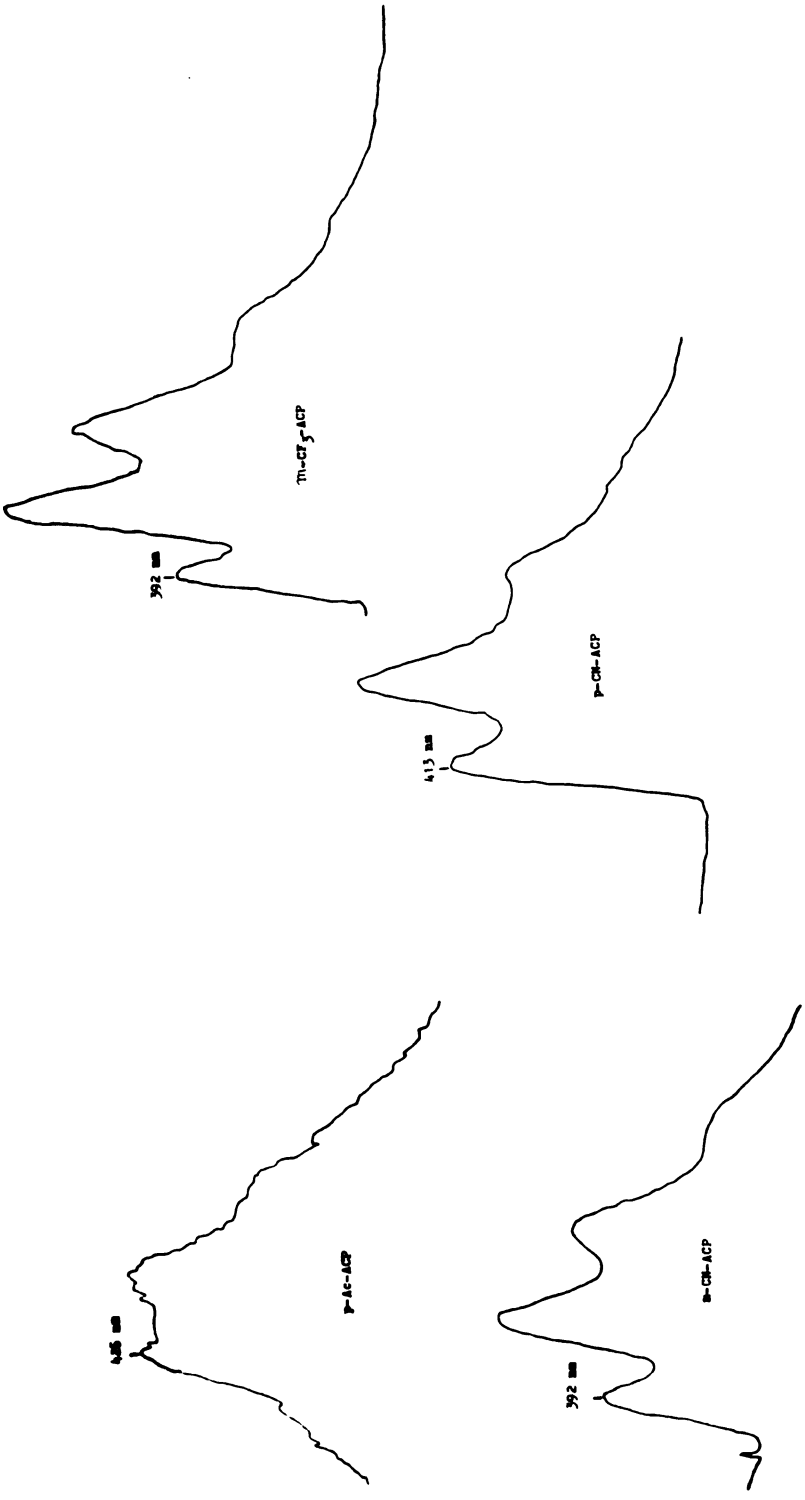


Figure 88. Phosphorescence Spectra of Acetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

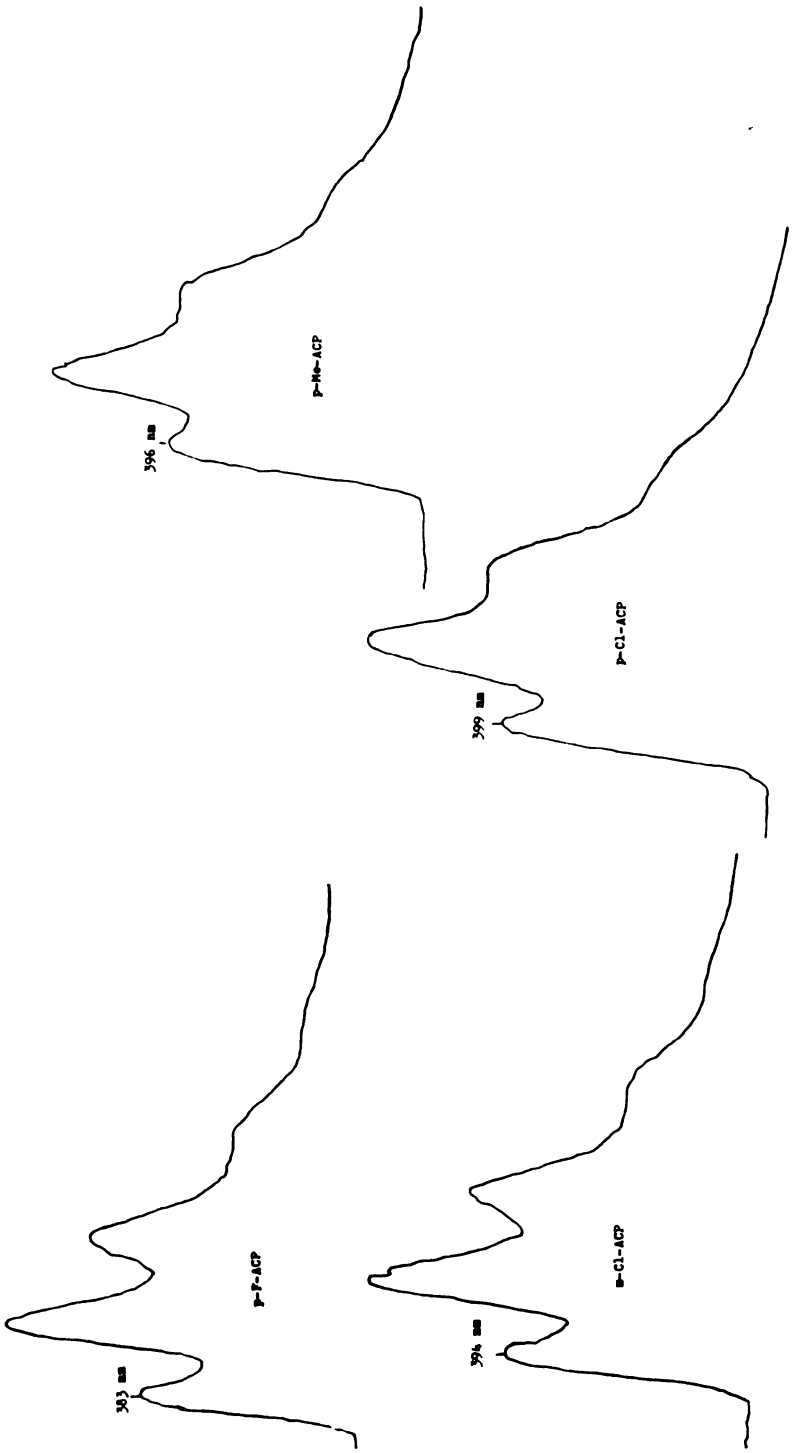


Figure 89. Phosphorescence Spectra of Acetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

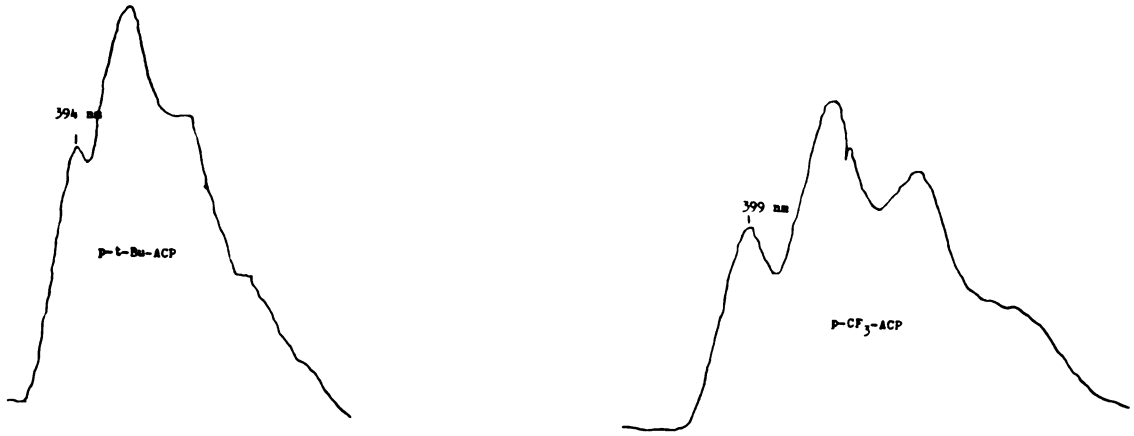


Figure 90. Phosphorescence Spectra of Acetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

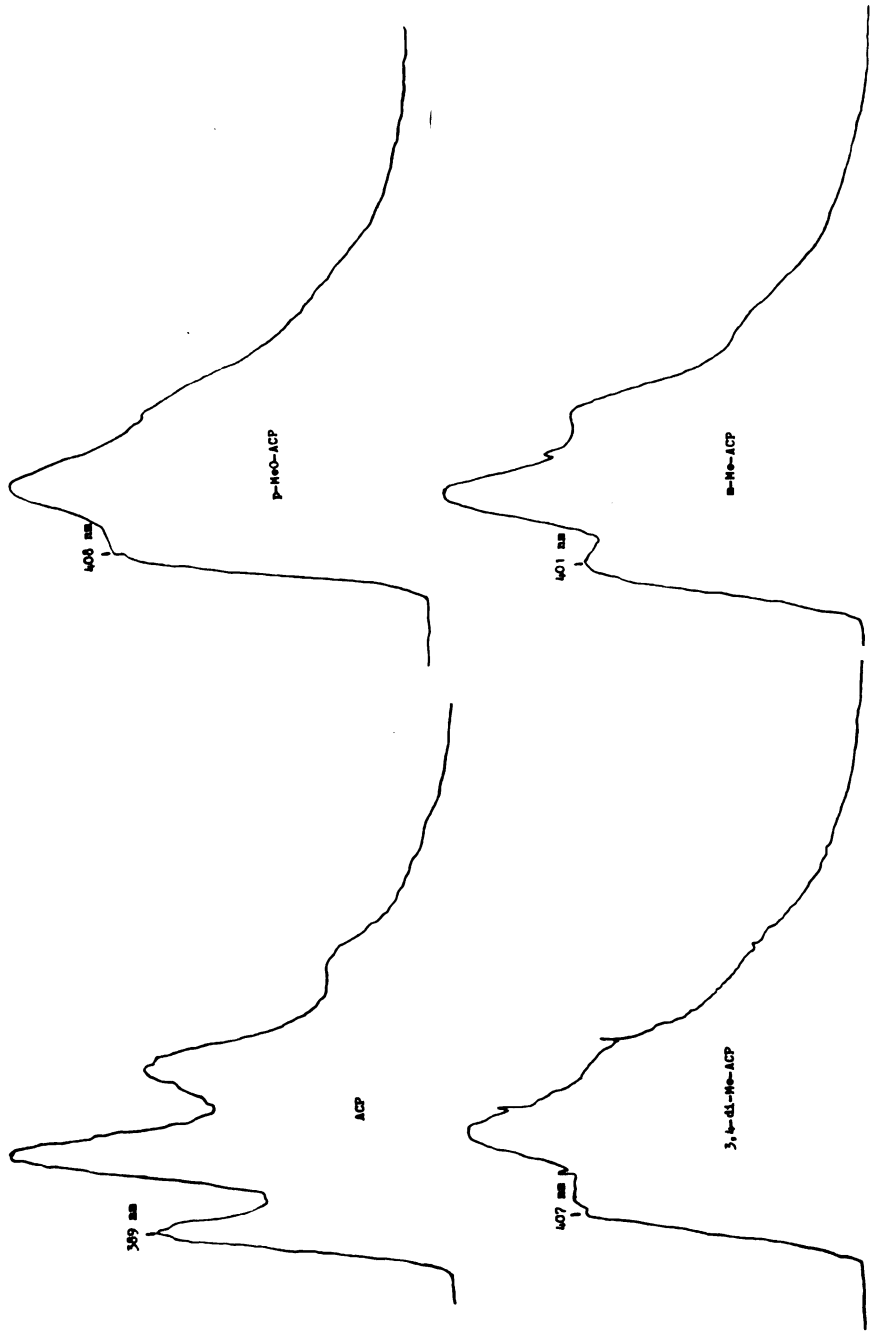


Figure 91. Phosphorescence Spectra of Acetophenones in 2-Methyl-Tetrahydrofuran at 77°K.

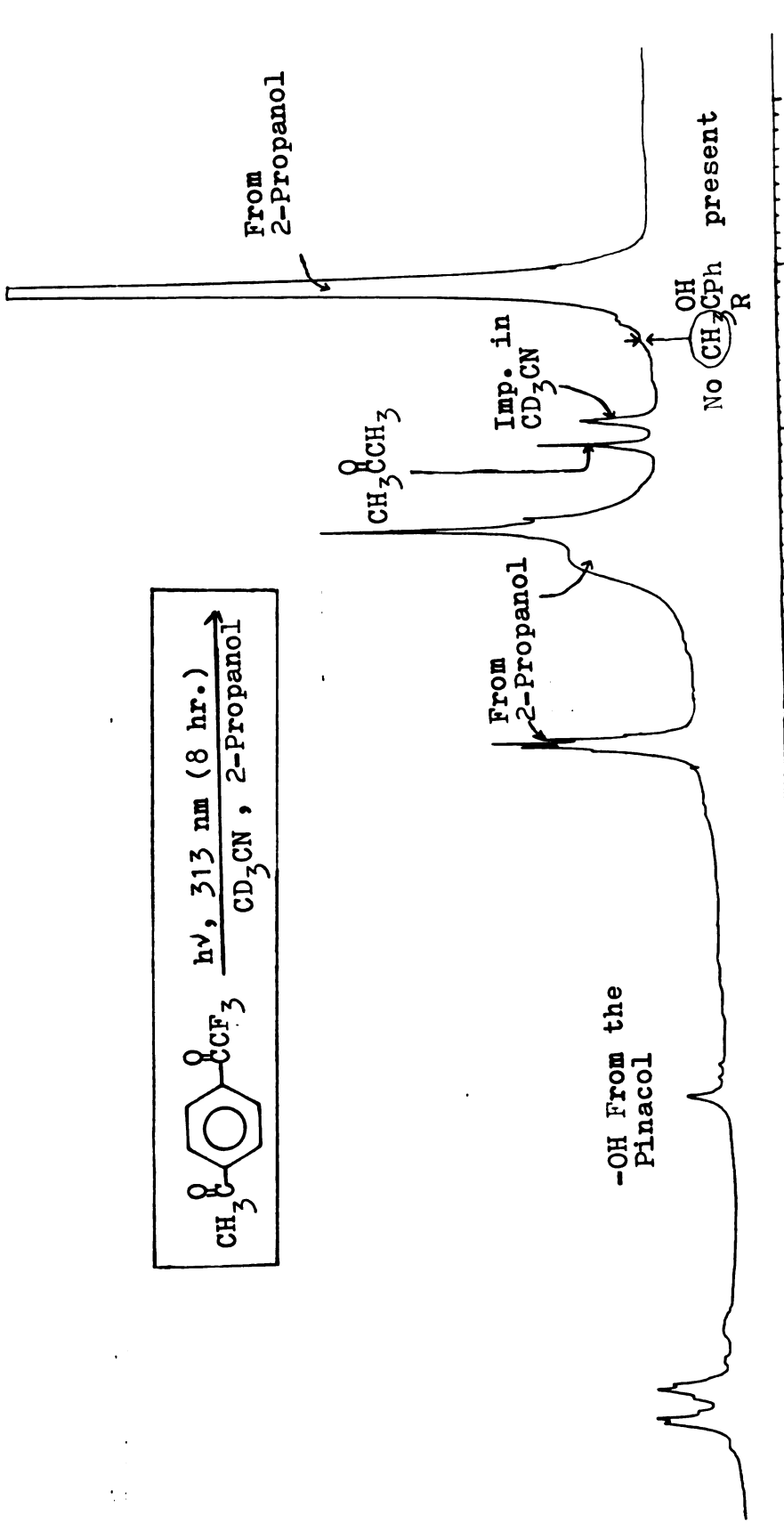


Figure 92. NMR Spectrum of p-Acetyl-α,α,α-Trifluoroacetophenone in CD_3CN with 2-Propanol Irradiated 8 hr. at 313 nm (250 MHz).

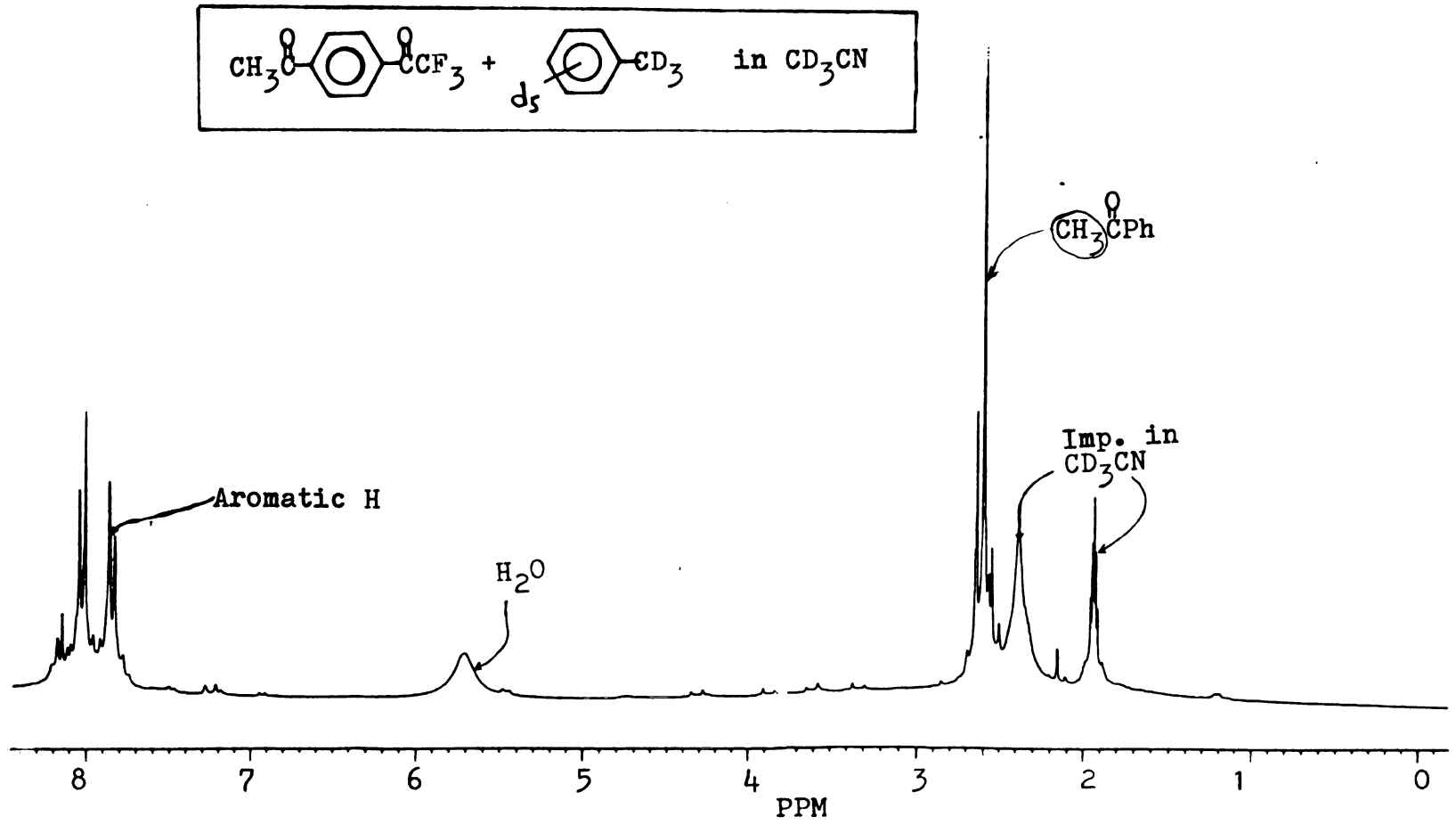


Figure 93. 250 MHz ^{1}H NMR of p-Acetyl-α,α,α-Trifluoroacetophenone and Toluene-d_8 in CD_3CN.

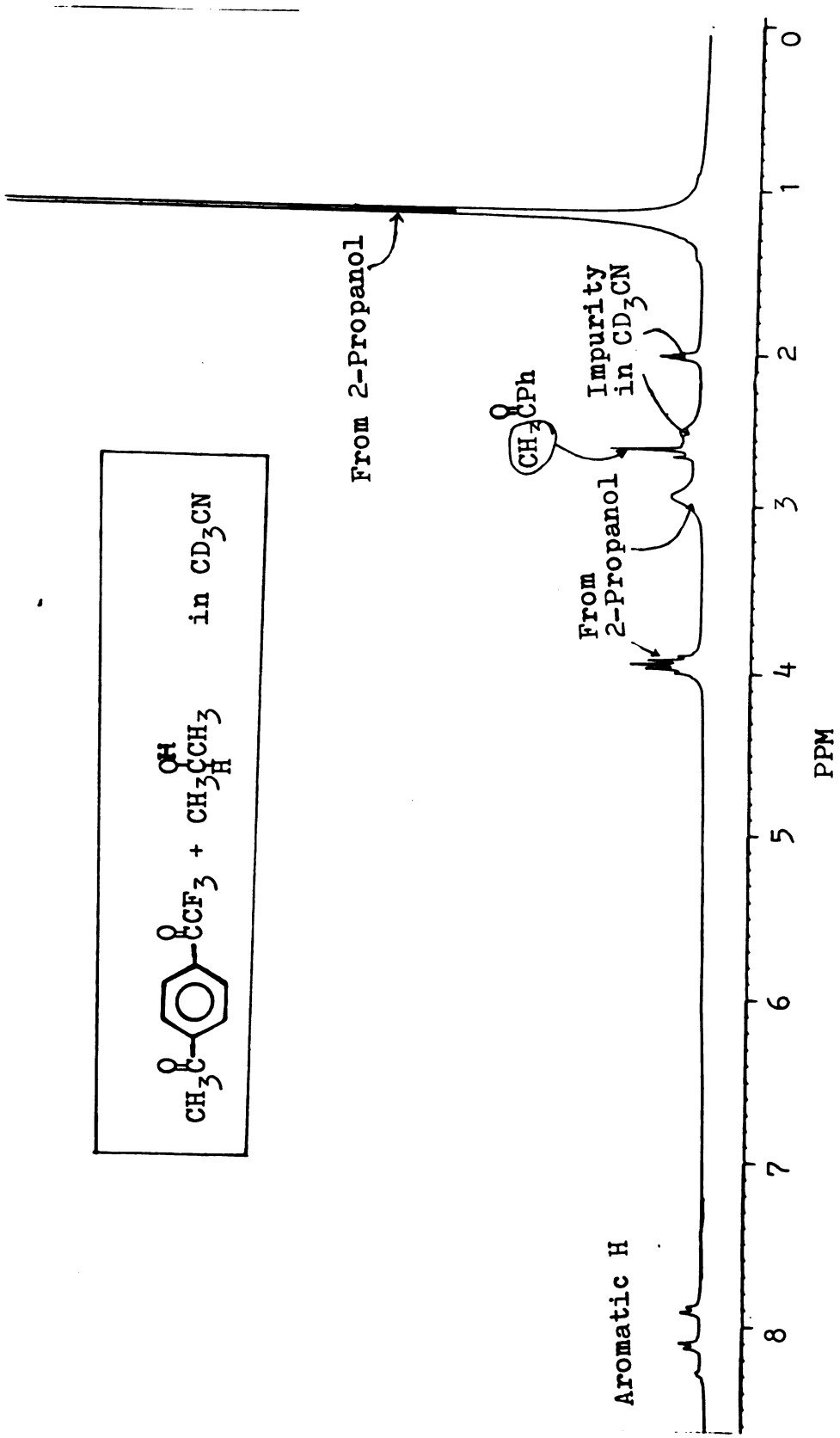


Figure 94. 250 MHz ^{1}H NMR of p-Acetyl-α,α,α-Trifluoroacetophenone and 2-Propanol in CD_3CN.

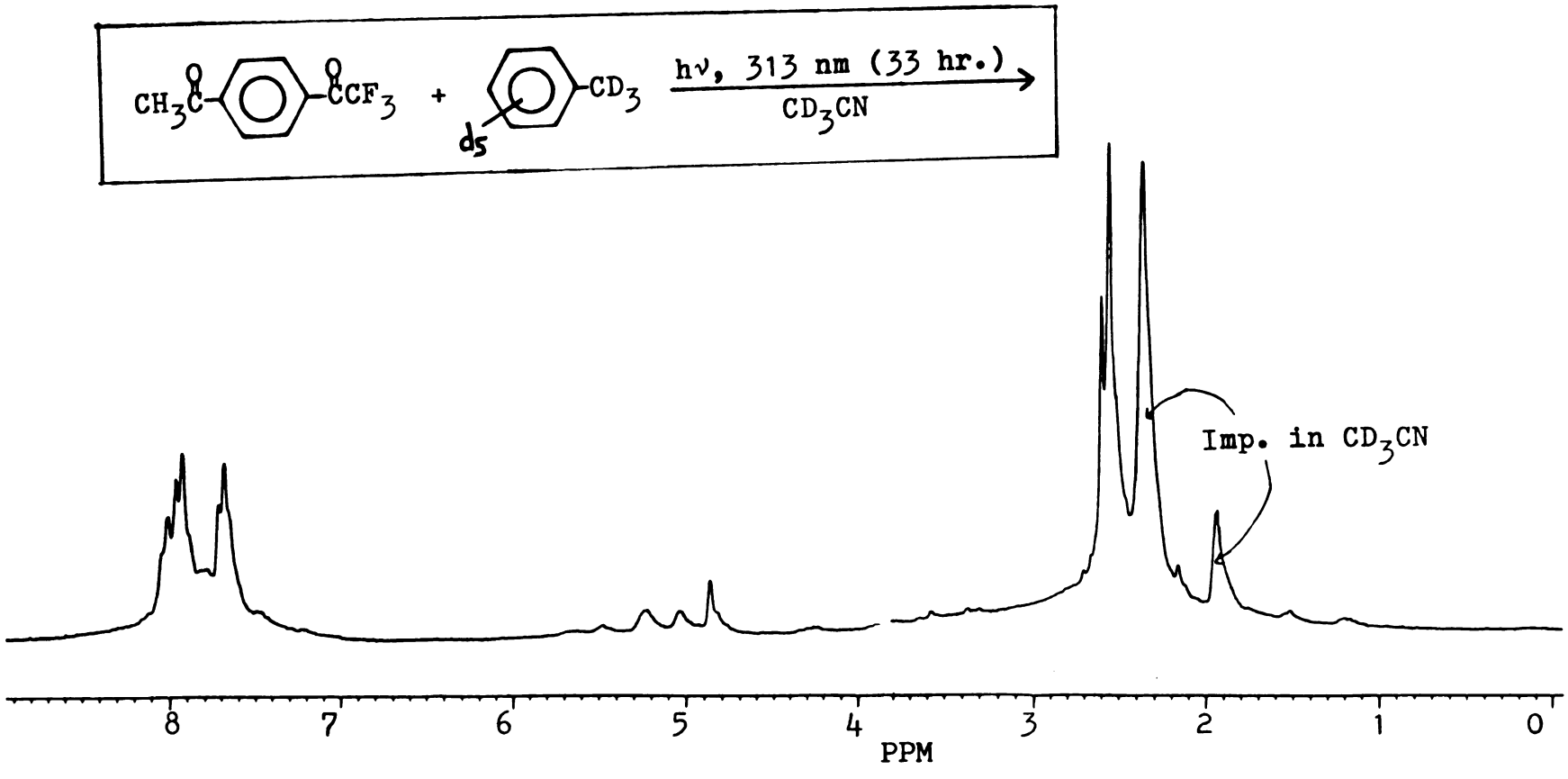


Figure 95. 250 MHz ^{1}H NMR of p-Acetyl-α,α,α-Trifluoroacetophenone and Toluene-d_8 in CD_3CN, Irradiated at 313 nm for 33 hr.

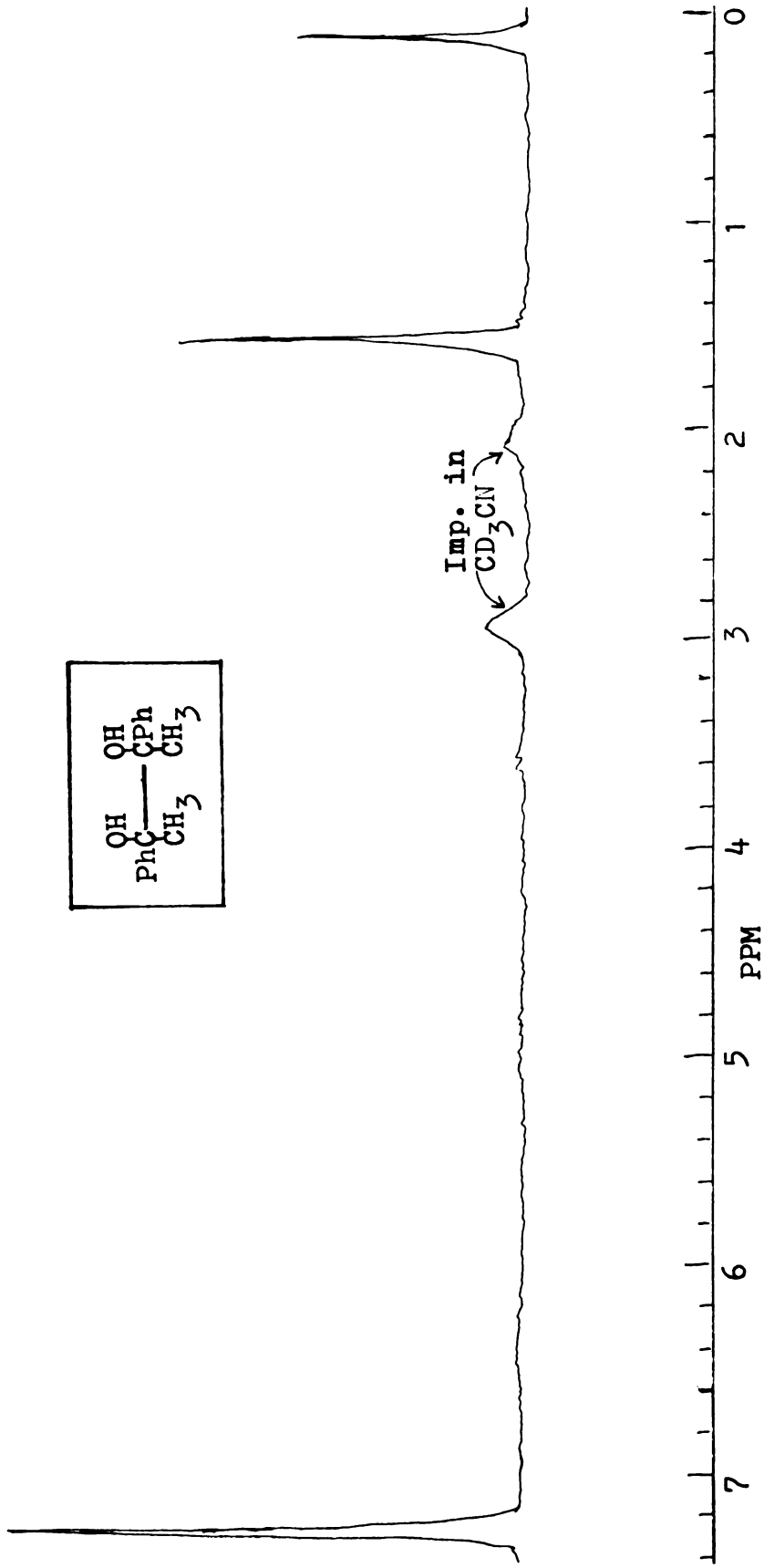


Figure 96. 60 MHz ^{1}H NMR of Acetophenone Pinacol in CD_3CN:$CDCl_3$ (1:5).

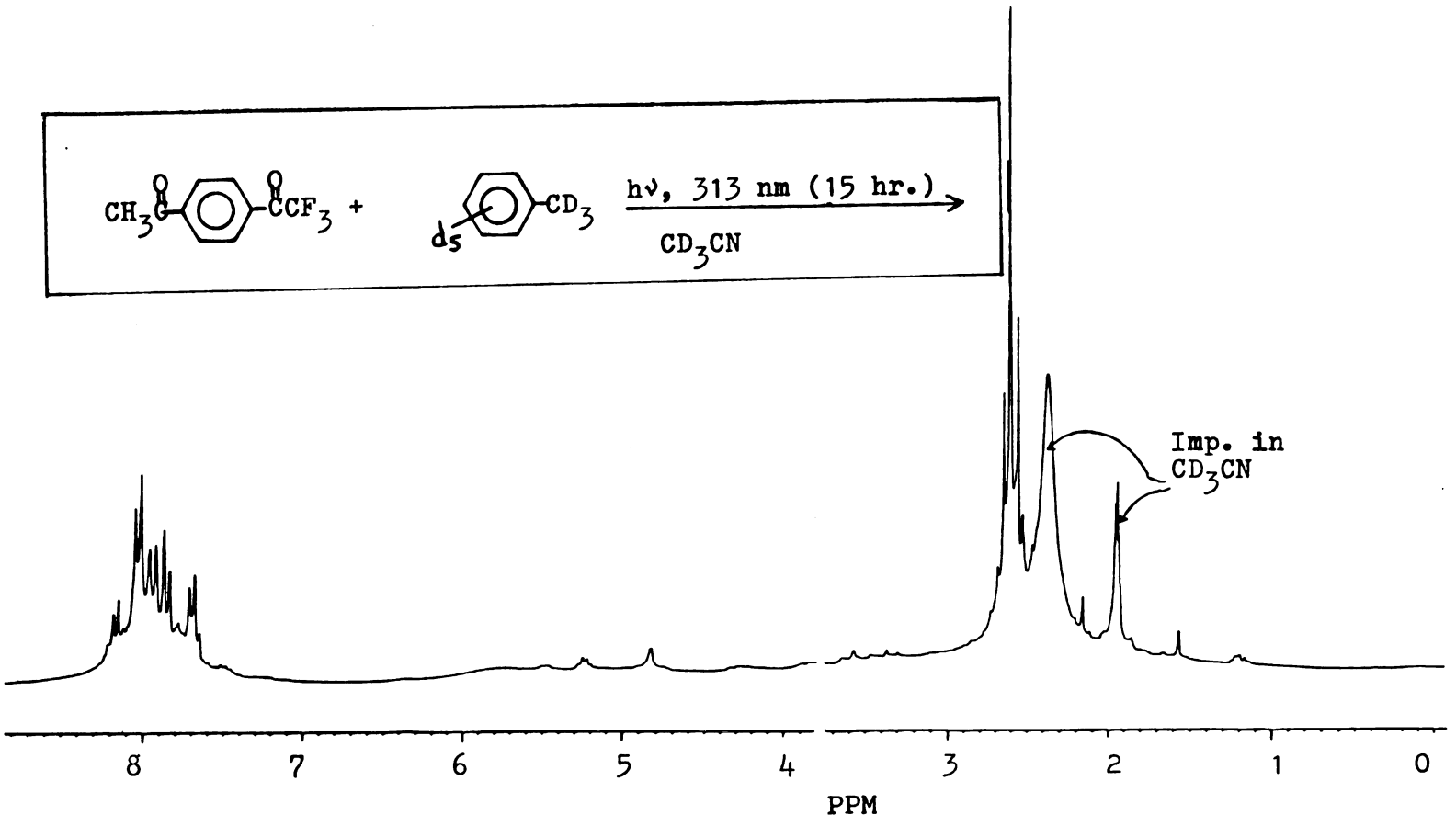


Figure 97. 250 MHz ^{1}H NMR of p-Acetyl-α,α,α-Trifluoroacetophenone and Toluene-d_8 in CD_3CN, Irradiated at 313 nm for 15 hr.

RAW DATA

This section contains the raw experimental data. The concentration of reactants, standards, and product to standard peak ratios (by vpc) were recorded. The pressure of the nitrogen carrier gas was 20-30 psi (always ca. 20 ml/min), with the temperature indicated in the tables. The following gc columns were used:

Column A: 8 ft x 1/8" 5% AQ-1, 1.25% carbowax 20M on chromsorb G DMSC.

Column B: 5 ft x 1/8" 5% SE-30 on chromosorb W (HP).

Column C: 7 ft x 1/8" 20% SE-30 on chromosorb G (AW, DMCS) 60/80.

Column D: 40 ft x 1/8", column.

Column E: 8 ft x 1/8", 25% carbowax 20M on chromosorb W (AW, DMCS).

Column F: 2 ft x 1/8", 10% FFAP on chromosorb P.

All valerophenone actinometry was performed on column A at 112 °C.

The given product concentrations are calculated from the vpc peak area ratios, appropriate standardization factor and concentration of standard, as shown in the experimental section. From the product concentrations and the amount of light absorbed (I_a), as determined by valerophenone actonometry, the quantum yields were determined.

Table 1. Stern-Volmer Data for α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4}M)$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.276		14.9	
0.0	0.264	0.267±0.006	14.2	
0.0	0.260		14.0	1.00
8.17	0.168			1.59
12.3	0.137			1.95
16.4	0.116			2.30
20.4	0.101			2.64
24.5	0.086			3.10
32.7	0.069			3.87

[TFA]=0.07 M pentadiene quencher, $[PhCOOC_7]=5.39 \times 10^{-3}$M, 313 nm, 3.5 hrs. irradiation, [Toluene] = 1.06 M, SF = 1.00 G.C. Column A, 132°C. $k_q\tau$ = 835.

		EXP #2		
0.0	0.289		16.0	
0.0	0.249	0.269±0.020	13.8	1.00
8.17	0.177			1.52
12.3	0.148			1.82
16.3	0.129			2.09
24.5	0.092			2.92

[TFA]=0.06 M pentadiene quencher, $[PhCOOC_7]=5.53 \times 10^{-3}$ M, 313 nm, 3.5 hrs. irradiation time, [Toluene] = 1.07 M, SF = 1.00 G.C. Column A, 132°C. $k_q\tau$ = 816.

Table 1. Continued.

$[Q](10^{-4}M)$	$BB/PhCOOC_n$		$[BB](10^{-3})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	0.0854		5.39	1.00
0.0	0.0824	0.0839±0.0015	5.20	1.00
4.01	0.0632			1.33
8.02	0.0514			1.63
16.0	0.0365			2.30
24.1	0.0268			3.13
32.1	0.0187			4.49

[TFA]=0.05, naphthalene quencher, $[PhCOOC_7]=6.31 \times 10^{-2}$ M, 366 nm, 16 hrs. irradiation time, [Toluene]=1.00 M, SF=1.00. G.C. Column A, 132°C. $k_q\tau=833$.

		EXP #4		
0.0	0.684		5.86	
0.0	0.685	0.685±0.001	5.87	1.00
7.93	0.436			1.57
11.9	0.355			1.93
16.0	0.302			2.27
19.8	0.272			2.52
23.8	0.243			2.82
27.8	0.226			3.03
31.7	0.195			3.51

[TFA]=0.05 M, naphthalene quencher, $[PhCOOC_6]=9.99 \times 10^{-4}$M, 366 nm, [Toluene]=1.00 M, SF=0.857. G.C. Column A, 135°C. $k_q\tau=756$.

Table 2. Reciprocal Plot, α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene] M	[Toluene]$^{-1}$ M^{-1}	BB/ $PhCOOC_7$	[BB] (10^{-3}M)	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}
		EXP#1			
0.250	4.00	0.164	1.01	1.98	50.5
0.376	2.66	0.211	1.30	2.55	39.2
0.501	2.00	0.225	1.38	2.71	36.9
0.751	1.33	0.262	1.61	3.16	31.6
1.00	1.00	0.292	1.80	3.53	28.3
1.50	0.667	0.321	1.98	3.88	25.8
2.00	0.500	0.341	2.10	4.12	24.3

I_a=0.0510E/l, [TFA]=0.05M, [$PhCOOC_7$]=6.15 x 10^{-3}M, SF=1.00, 313 nm, 3.5 hrs. irradiation. G.C. Column A, 132°C. Slope =7.28 intercept-21.2, slope/intercept=0.343.

		EXP#2			
0.125	8.00	0.0782	0.524	1.67	59.9
0.250	4.00	0.120	0.804	2.55	39.2
0.376	2.66	0.139	0.931	2.97	33.7
0.501	2.00	0.160	1.07	3.41	29.3
0.799	1.25	0.191	1.28	4.07	24.5
1.07	0.935	0.206	1.38	4.40	22.7
1.33	0.752	0.218	1.46	4.65	21.5
1.60	0.625	0.227	1.52	4.84	20.7
2.13	0.469	0.255	1.71	5.45	18.3

I_a=0.0314, [TFA]=0.05, [$PhCOOC_7$]=6.70 x 10^{-3} M, SF=1.00, 313 nm, 3.5 hrs. irradiation. G.C. Column A, 132°C. Slope =5.38, intercept=17.6, slope/intercept=0.306.

Table 2. Continued.

[Toluene] M	$[Toluene]^{-1}$ M^{-1}	BB/ $PhCOOC_7$	[BB] (10^{-3}M	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}
		EXP#3			
0.250	4.00	0.451	0.871	2.68	37.3
0.750	1.33	0.705	1.36	4.18	23.9
1.25	0.800	0.748	1.44	4.43	22.6
1.50	0.667	0.911	1.76	5.42	18.5
1.75	0.571	0.916	1.77	5.45	18.3

I_a=0.0325E/1, [TFA]=0.05M, $[C_{20}]$=1.35 x 10^{-3}M, SF=1.43, 313 nm, 7 hrs. irradiation. G.C. Column A, 135°C. Slope= 5.40, intercept=16.1, slope/intercept=0.335.

		EXP#4			
0.251	3.98	0.531	5.06	1.79	55.9
0.451	2.22	0.670	6.39	2.27	44.1
0.501	2.00	0.715	6.87	2.41	41.5
0.627	1.59	0.775	7.39	2.62	38.2
1.00	1.00	0.856	8.16	2.89	34.6
1.50	0.667	0.936	8.92	3.16	31.6
2.00	0.500	0.965	9.20	3.26	30.7

I_a=0.0282E/1, [TFA]=0.05, $[PhCOOC_7]$=9.53 x 10^{-4}M, SF=1.00, 313 nm, 3 hrs. 15 min irradiation. G.C. Column A, 132°C. Slope=7.68, intercept=28.6, slope/intercept=0.269.

Table 3. Stern-Volmer Data for p-Trifluoromethyl-α,α,α-Trifluoroacetophenone and 0.1 M Toluene in CH_3CN.

$[Q](10^{-3}M)$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.225		13.3	
0.0	0.225	0.229±0.006	13.3	
0.0	0.238		14.1	1.00
7.88	0.131			1.75
11.8	0.102			2.25
15.8	0.078			2.94
23.6	0.049			4.67

$[p\text{-}CF_3\text{-}TFA]$=0.05, pentadiene quencher, $[PhCOOC_7]$=5.89 x 10^{-3} M, 313 nm, 6.0 hrs. irradiation, [Toluene]=0.101 M, SF=1.00. Column A, 100°C, $k_q\tau$=116.

		EXP #2		
0.0	0.227		14.0	1.00
3.98	0.197			1.15
7.96	0.153			1.48
11.9	0.116			1.96
31.8	0.042			5.40

$[p\text{-}CF_3\text{-}TFA]$=0.05 M, pentadiene quencher, $[PhCOOC_7]$=6.15 x10^{-3} M, 313 nm, [Toluene]=0.107 M, SF=1.00. Column A, 100°C, $k_q\tau$=127.

Table 3. Continued.

$[Q](10^{-3}M)$	$BB/PhCOOC_7$		$[BB](10^{-3})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	17.1	17.1	36.6	1.00
5.21	8.74			1.96
7.82	8.17			2.09
10.4	6.59			2.59
13.0	4.98			3.43
15.6	4.81			3.56
18.2	4.58			3.73
20.8	3.75			4.56

$[p\text{-}CF_3\text{-TFA}]$=0.05 M, naphthalene quencher, $[PhCOOC_6]$=2.50 x 10^{-3} M, 366 nm, 47 hrs. irradiation, [Toluene]=0.101 M, SF=0.857. Column A, 100°C. $k_q\tau$=161.

Table 4. Reciprocal Plot, p-Trifluoromethyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene] M	$[Toluene]^{-1}$ M^{-1}	BB/ $PhCOOC_7$	[BB] (10^{-3}M)	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}
0.0105	95.2	0.0854	0.534	0.902	111
0.0157	63.7	0.130	0.813	1.37	73.0
0.0210	47.6	0.168	1.05	1.77	56.5
0.0262	38.2	0.202	1.26	2.13	46.9
0.0426	23.5	0.260	1.63	2.75	36.4
0.0533	18.8	0.293	1.83	3.09	32.4
0.0639	15.6	0.308	1.93	3.26	30.7

[p-CF_3-TFA]=0.05 M, [$PhCOOC_7$]=6.25 x 10^{-3} M, SF=1.00, 313 nm, 7.5 hrs. irradiation, I_a=0.0592 E/1. G.C. Column A, 100°C. Slope=1.22, intercept=14.7, slope/intercept=0.0830.

EXP #2

0.0322	31.1	0.195	1.28	2.05	48.8
0.0429	23.3	0.237	1.55	2.48	40.3
0.0536	18.7	0.307	2.01	3.22	31.1
0.0643	15.6	0.309	2.02	3.24	30.9
0.0857	11.7	0.332	2.17	3.48	28.7

[p-CF_3-TFA]=0.05 M, [$PhCOOC_7$]=6.55 x 10^{-3} M, SF=1.00, 313 nm, 4.0 hrs. irradiation, I_a=0.0624 E/1. G.C. Column A, 100°C. Slope=1.09, intercept=17.0, slope/intercept=0.0641.

Table 4. Continued.

[Toluene] M	$[Toluene]^{-1}$ M^{-1}	BB/ $PhCOOC_7$	[BB] (10^{-3}M)	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}
		EXP #3			
0.0172	58.1	0.150	0.911	1.67	59.9
0.0229	43.7	0.187	1.14	2.09	47.8
0.0344	29.1	0.265	1.61	2.95	33.9
0.0458	21.8	0.305	1.85	3.39	29.5
0.0573	17.5	0.347	2.11	3.86	25.9
0.0688	14.5	0.364	2.21	4.05	24.7
0.0917	10.9	0.377	2.29	4.19	23.9

[p-CF_3-TFA]=0.05 M, 2% aq. CH_3CN, [$PhCOOC_7$]=6.07 x 10^{-3} M, SF=1.00, 313 nm, I_a=0.0546 E/l. G.C. Column A, 100°C. Slope=0.794, intercept=15.7, slope/intercept=0.0506.

		EXP #4			
0.115	8.70	0.500	0.514	2.28	43.9
0.229	4.37	0.690	0.710	3.16	31.6
0.344	2.91	0.780	0.802	3.56	28.1
0.459	2.18	0.911	0.936	4.16	24.0
0.574	1.74	0.893	9.18	4.08	24.5
0.688	1.45	0.971	0.999	4.44	22.5
0.803	1.25	0.979	1.01	4.49	22.3
0.918	1.09	1.01	1.04	4.62	21.6

I_a=0.0225 E/l, [p-CF_3-TFA]=0.05 M, [$PhCOOC_6$]=1.20 x 10^{-3} M, SF=0.857, 313 nm, 1.0 hr. irradiation. G.C. Column A, 100°C, Slope=2.90, intercept=18.7, slope/intercept=0.155.

Table 5. Stern-Volmer Data, p-Methoxy-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-5}M)$	$BB/PhCOOC_7$		[DTE](10^{-4})	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.173		11.5	
0.0	0.169	0.171±0.002	11.2	1.00
3.13	0.0870			1.97
6.27	0.0636			2.69
7.83	0.0471			3.63
9.40	0.0438			3.90
11.0	0.0342			5.00
12.5	0.0341			5.01

[p-MeO-TFA]=0.05 M, SF=1.00, pentadiene quencher, $[PhCOOC_7]$ $=6.62 \times 10^{-3}$ M, 313 nm, [Toluene] = 1.07 M, G.C. Column A, 100°C, $k_q\tau=32,000$.

		EXP #2		
0.0	0.354	0.354	23.7	1.00
3.62	0.208			1.70
7.23	0.163			2.17
9.04	0.157			2.25
10.9	0.139			2.55
12.7	0.113			3.13

[p-MeO-TFA]=0.05 M, SF=1.00, pentadiene quencher, $[PhCOOC_7]$ $=6.69 \times 10^{-3}$ M, 313 nm, [Toluene] = 1.08 M. G.C. Column A 100°C, $k_q\tau=14,600$.

Table 5. Continued.

$[Q](10^{-5}M)$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	0.136		12.6	
0.0	0.126	0.137±0.005	11.7	1.00
3.78	0.0842			1.56
5.67	0.0669			1.96
7.56	0.0543			2.41
9.45	0.0450			2.91
11.3	0.0383			3.43
15.1	0.0320			4.09

[p-MeO-TFA]=0.05M, pentadiene quencher, $[PhCOOC_7]$=9.30 x 10^{-3} M, 313 nm, [Toluene]=1.07 M, SF=1.00. G.C. Column A, 100°C. $k_q\tau$=17,300.

Table 6. Reciprocal Plot, p-Methoxy-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	BB/$PhCOOC_7$	[BB](10^{-3}M)	I_a E/l	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}
			EXP #1			
0.795	1.26	0.130	0.786	0.0804	9.78	102
1.06	0.943	0.163	0.986	0.0804	12.2	82.0
1.59	0.629	0.219	1.32	0.0804	16.4	61.0
2.12	0.472	0.227	1.37	0.0655	20.9	47.8
2.65	0.377	0.267	1.61	0.0655	24.6	40.7
3.18	0.314	0.275	1.66	0.0655	25.3	39.5
4.24	0.236	0.313	1.89	0.0655	28.9	34.6

[p-MeO-TFA]=0.05 M, [$PhCOOC_7$]=6.40 x 10^{-3} M, SF=0.945, 313 nm. Gc column A, 100°C.
Slope=67.9, intercept=17.2, slope/intercept=3.95.

			EXP #2			
1.06	0.943	0.0965	0.570	0.0638	8.93	112
1.59	0.629	0.165	0.975	0.0638	15.3	65.4
1.85	0.541	0.192	1.13	0.0638	17.7	56.5
2.12	0.472	0.112	0.662	0.0375	17.7	56.5
3.18	0.314	0.165	0.975	0.0375	26.0	38.5
3.71	0.270	0.169	0.998	0.0375	26.6	37.6
4.24	0.236	0.195	1.15	0.0375	30.7	32.6

[p-MeO-TFA]=0.05 M, [$PhCOOC_7$]=6.25 x 10^{-3} M, SF=0.945, 313 nm. Gc column A, 100°C.
Slope=82.6, intercept=14.0, slope/intercept=5.90.

Table 7. Reciprocal Plot, p-Methoxy-α,α,α-Trifluoroacetophenone and $Toluene_{d-8}$ in CH_3CN.

$[Tol_{d-8}]$	$[Tol_{d-8}]^{-1}$	$BB/PhCOOC_7$	$[BB]10^{-3}$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
2.08	0.481	0.715	1.32	1.33	75.2
2.08	0.481	0.763	1.40	1.41	70.9
3.12	0.321	0.975	1.79	1.81	55.2
3.12	0.321	0.980	1.80	1.82	54.9
4.16	0.240	1.16	2.13	2.15	46.5
4.16	0.240	1.14	2.10	2.12	47.2

[p-MeO-TFA]=0.05 M, $[PhCOOC_7]$=0.00153 M, SF=0.945, 313 nm. G.C. Column A, 180°C. Slope=109, intercept=20.4, slope/intercept=5.34.

Table 8. Stern-Volmer Data for p-Chloro-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4}M)$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.114		6.40	
0.0	0.117		6.56	
0.0	0.114	0.115±0.001	6.40	1.00
8.14	0.0452			2.54
12.2	0.0364			3.16
16.3	0.0285			4.04
20.3	0.0244			4.71
24.4	0.0194			5.93

[p-Cl-TFA]=0.05 M, pentadiene quencher, $[PhCOOC_7]=5.61 \times 10^{-3}$ M, 313 nm, 5 hrs. irradiation, [Toluene]=1.12 M, SF=1.00. G.C. Column A, 128°C. $k_q\tau=1.814$.

		EXP #2		
0.0	0.141		7.91	
0.0	0.149		8.36	
0.0	0.145	0.145±0.003	8.14	1.00
8.14	0.0584			2.48
12.2	0.0460			3.15
16.3	0.0384			3.78
20.3	0.0314			4.62
24.4	0.0270			5.37

[p-Cl-TFA]=0.05, pentadiene quencher, $[PhCOOC_7]=5.61 \times 10^{-3}$ M, 313 nm, 5 hrs. irradiation, [Toluene]=1.12 M, SF=1.00. G.C. Column A, 128°C. $k_q\tau=1,762$.

Table 8. Continued.

$[Q](10^{-4}M)$	$BB/PhCOOC_7$	Average	$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	0.859		6.85	
0.0	0.882	0.871±0.011	7.04	1.00
0.737	0.748			1.16
1.10	0.714			1.22
1.47	0.662			1.32
1.84	0.680			1.28
2.21	0.643			1.35
2.58	0.617			1.41
2.95	0.612			1.42

[p-Cl-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_6]=9.31 \times 10^{-4}$ M, 366 nm, 6.5 hrs. irradiation, [Toluene]=1.12 M, SF=0.857. G.C. Column A, 128°C. $k_q\tau$ = 1,750.

Table 9. Reciprocal Plot, p-Chloro-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene]M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	$[BB](10^{-4})M$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #1			
0.216	4.63	4.12	3.06	3.26	30.7
0.324	3.09	4.63	3.43	3.65	27.4
0.432	2.31	5.39	4.00	4.26	23.5
0.534	1.87	6.53	4.84	5.15	19.4
1.07	0.935	6.71	4.98	5.30	18.9
1.60	0.625	7.32	5.43	5.78	17.3
2.14	0.461	7.73	5.73	6.10	16.4
[p-Cl-TFA]=0.05 M, $[PhCOOC_7]=7.85 \times 10^{-3}$ M, $I_a=9.39 \times 10^{-3}$ E/l, SF=0.945, 313 nm, 3 hrs. irradiation. Gc column A, 128°C. Slope=3.53, intercept=18.1, slope/intercept=0.195.					
		EXP #2			
0.108	9.26	4.40	2.49	2.62	38.2
0.216	4.63	6.97	3.95	4.15	24.1
0.324	3.09	8.56	4.85	5.09	19.6
0.432	2.31	8.23	4.67	4.91	20.4
0.534	1.87	8.49	4.81	5.05	19.8
1.07	0.935	1.08	6.12	6.43	15.6

Table 9. Continued.

[Toluene]M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	$[BB](10^{-4}M)$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
1.60	0.625	1.09	6.18	6.49	15.4
2.14	0.467	1.15	6.52	6.85	14.6

[p-Cl-TFA]=0.05 M, $[PhCOOC_7]=6.00 \times 10^{-3}$ M, $I_a=9.52 \times 10^{-3}$ E/l, SF=0.945, 313 nm, 3 hrs irradiation. Gc column A, 128°C. Slope=2.52, intercept=16.7, slope/intercept=0.151

EXP #3

0.107	9.35	2.13	1.27	1.49	67.1
0.215	4.65	3.41	2.03	2.38	42.0
0.322	3.11	4.73	2.82	3.31	30.3
0.429	2.33	5.59	3.33	3.91	25.6
1.07	0.935	7.17	4.27	5.01	20.0
1.60	0.627	8.44	5.02	5.89	17.0
2.14	0.467	8.80	5.24	6.15	16.3

[p-Cl-TFA]=0.05 M, $[PhCOOC_7]=6.30 \times 10^{-3}$ M, $I_a=8.52 \times 10^{-3}$ E/l, SF=0.945, 313 nm, 3 hrs irradiation. Gc column A, 128°C. Slope=5.72, intercept=16.5, slope/intercept=0.347.

Table 9. Continued.

[Toluene]M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7(10^{-2})$	$[BB](10^{-4}M)$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #4			
0.107	9.35	0.223	0.140	1.15	87.0
0.161	6.21	0.313	0.197	1.61	62.1
0.215	4.65	0.349	0.219	1.80	55.6
0.322	3.11	0.421	0.265	2.17	46.1
0.429	2.33	0.471	0.296	24.3	41.2
0.535	1.87	0.553	0.348	2.85	35.1
1.07	0.935	0.611	0.384	4.68	21.4
2.14	0.467	0.749	0.471	3.86	25.9

[p-Cl-TFA]=0.05 M, $[PhCOOC_7]=6.65 \times 10^{-3}$ M, I_a=0.122 E/l, SF=0.945, 313 nm, 3 hrs. 45 min. irradiation. Gc column A, 128°C. Slope=6.26, intercept=22.8, slope/intercept= 0.275.

Table 10. Stern-Volmer Data, p-Fluoro-α,α,α-Trifluoroacetophenone and 0.05 M Toluene in CH_3CN.

$[Q](10^{-4}M)$	$BB/PhCOOC_6$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.924		6.60	
0.0	1.05		7.51	
0.0	0.884	0.953±0.065	6.32	1.00
3.78	0.239			3.99
7.56	0.121			7.88

[p-F-TFA]=0.05 M, Naphthalene quencher, $[PhCOOC_6]=8.34 \times 10^{-4}M$, 366 nm, 8 days irradiation, [Toluene]=0.0459 M, SF =0.857. G.C. Column A, 128°C. $k_q\tau=12,000$.

		EXP #2		
0.0	0.796		11.5	
0.0	0.742	0.769±0.027	10.7	1.00
1.94	0.321			2.40
3.88	0.200			3.85
4.85	0.151			5.09
5.82	0.129			5.96

[p-F-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_6]=1.68 \times 10^{-3}$ M, 366 nm, 6 days irradiation, [Toluene]=0.0458 M, SF=0.857. G.C. Column A, 128°C. $k_q\tau=7,929$.

Table 11. Reciprocal Plot, p-Fluoro-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	BB-$PhCOOC_6$	[BB]M(10^{-4})	ϕ_{BB}(10^{-2})	ϕ_{BB}^{-1}
		EXP #1			
0.0435	23.0	1.06	7.30	2.89	34.6
0.0435	23.0	1.09	7.50	2.96	33.8
0.0435	23.0	1.09	7.50	2.96	33.8
0.0871	11.5	1.32	9.09	3.59	27.9
0.0871	11.5	1.20	8.26	3.26	30.7
0.174	5.74	1.29	8.88	3.51	28.5
0.349	2.87	1.42	9.78	3.87	25.8
0.698	1.43	1.47	1.01	3.99	25.1
1.40	0.714	1.54	1.06	4.19	23.9

I_a=0.0253 E/l, [pFTFA]=0.05 M, [$PhCOOC_6$]=8.53 x 10^{-4} M, SF=0.807, 313 nm, 1.0 hr. irradiation. Gc column A, 170°C. Slope=0.478, intercept=23.7, slope/intercept=0.0202.

		EXP #2			
0.0348	28.7	0.317	2.79	4.29	23.3
0.0348	28.7	0.311	2.74	4.21	23.8
0.0348	28.7	0.319	2.81	4.32	23.1
0.0522	19.2	0.355	3.12	4.79	20.9

Table 11. Continued.

[Toluene],M	$[Toluene]^{-1}$,M^{-1}	$BB/PhCOOC_6$	$[BB]M(10^{-4})$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #2 (Cont)			
0.0522	19.2	0.353	3.11	4.78	20.9
0.139	7.19	0.392	3.45	5.30	18.9
0.435	2.30	0.464	4.08	6.27	15.9
0.74	0.575	0.482	4.28	6.57	15.2
$I_a=6.51 \times 10^{-3}$ E/l, [pFTFA]=0.05 M, $[PhCOOC_6]=1.09 \times 10^{-3}$ M, SF=0.807, 313 nm, 51 min. irradiation. Gc column A, 170°C. Slope=0.267, intercept=15.9, slope/intercept=0.0168.					
		EXP #3			
0.0262	38.2	0.527	6.81	4.20	23.8
0.0262	38.2	0.601	7.76	4.79	20.9
0.0262	38.2	0.539	6.96	4.30	23.3
0.0393	25.4	0.687	8.87	5.48	18.2
0.0523	19.1	0.800	10.3	6.36	15.7
0.451	2.22	1.08	13.9	8.58	11.7
$I_a=0.0162$ E/l, [pFTFA]=0.05 M, $[PhCOOC_6]=1.60 \times 10^{-3}$ M, SF=0.807, 313 nm, 2.5 hr. irradiation. Gc column A, 170°C. Slope=0.308, intercept=10.5, slope/intercept=0.0293.					

Table 12. Stern-Volmer Data, m-Chloro-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4})$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.271		16.0	
0.0	0.263	0.267±0.004	15.5	1.00
5.71	0.255			1.05
11.4	0.239			1.12
14.3	0.229			1.17
17.1	0.216			1.24
22.8	0.201			1.33

[m-Cl-TFA]=0.05 M, $[PhCOOC_7]=6.24 \times 10^{-3}$ M, pentadiene quencher, 313 nm, 2 hr. irradiation time, [Toluene]=1.22 M, SF=0.945. G.C. Column A, 128°C $k_q\tau$ = 127.

		EXP #2		
0.0	0.162		8.82	
0.0	0.165		8.98	
0.0	0.162	0.163±0.001	8.82	1.00
5.71	0.150			1.09
8.56	0.137			1.19
11.4	0.129			1.26
14.3	0.124			1.31
17.1	0.116			1.41
22.8	0.108			1.51

[m-Cl-TFA]=0.05 M, pentadiene quencher, $[PhCOOC_7]=5.76 \times 10^{-3}$, 313 nm, [Toluene]=1.11 M, SF=0.945. GC Column A, 128°C. $k_q\tau$=211.

Table 12. Continued.

$[Q](10^{-3}M)$	$BB/PhCOOC_7(10^{-2})$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	20.4		7.83	
0.0	19.6	20.0±0.4	7.52	1.00
2.83	11.6			1.72
5.66	8.29			2.41
11.3	5.50			3.64
14.1	4.46			4.48

[m-Cl-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]=4.06 \times 10^{-3}$ M, 366 nm, [Toluene]=1.00 M, SF=0.945. G.C. Column A, 128°C. $k_q\tau=233$.

Table 13. Reciprocal Plot, m-Chloro-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7(10^{-2})$	$[BB],M(10^{-4})$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
0.108	9.26	3.70	2.57	3.01	33.2
0.162	6.17	3.95	2.74	3.21	31.2
0.217	4.61	4.58	3.18	3.73	26.9
0.325	3.02	4.94	3.43	4.02	24.9
0.433	2.31	5.14	3.57	4.19	23.9
0.535	1.87	5.57	3.86	4.53	22.1
1.07	0.935	5.72	3.97	4.65	21.5
1.60	0.625	5.96	4.13	4.84	20.7
2.14	0.467	6.16	4.27	5.01	20.0

$I_a=8.53 \times 10^{-3}$ E/l, [mClTFA]=0.05 M, $[PhCOOC_7]=7.34\times10^{-3}$ M, SF=0.945, 313 nm, 41 min. irradiation. Gc column A, 128°C. Slope=1.58, intercept=24.1, slope/intercept=0.0656.

Table 13. Continued.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7(10^{-2})$	$[BB],M(10^{-4})$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #2			
0.109	9.17	4.88	3.15	3.84	26.0
0.163	6.13	5.92	3.82	4.65	21.5
0.217	4.61	6.61	4.26	5.19	19.3
0.326	3.07	7.20	4.64	5.65	17.7
0.434	2.30	7.37	4.75	5.79	17.3
0.536	1.87	7.97	5.14	6.26	16.0
1.07	0.935	8.65	5.57	6.78	14.7

$I_a=8.21 \times 10^{-3}$ E/l, [mClTFA]=0.05 M, $[PhCOOC_7]$=0.0682 M, SF=0.945, 313 nm, 46 min. irradiation. Gc column A, 128°C. Slope=1.21, intercept=17.5, slope/intercept=0.0691.

Table 14. Stern-Volmer Data, p-Methyl-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4}M)$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.245		8.73	
0.0	0.257	0.251±0.006	9.16	1.00
0.559	0.189			1.33
1.12	0.152			1.65
1.68	0.125			2.01
4.47	0.0648			3.87

[p-Me-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]=3.77 \times 10^{-3}$ M, 366 nm, 21 hrs. irradiation, [Toluene]=1.09 M, SF=0.945. G.C. Column A, 150°C. $k_q\tau=6,250$.

		EXP #2		
0.0	0.483		8.26	1.00
0.558	0.331			1.46
1.12	0.247			1.96
1.67	0.205			2.36
2.23	0.164			2.95
2.79	0.138			3.50
3.35	0.119			4.04

[p-Me-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_6]=1.81 \times 10^{-3}$ M, 366 nm, 45 hrs. irradiation, [Toluene]=1.09 M, SF=0.945. G.C. Column A, 150°C, $k_q\tau=8,743$.

Table 15. Reciprocal Plot, p-Methyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	BB/$PhCOOC_7$	[BB],M(10^{-4})	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #1			
0.515	1.94	0.115	6.75	2.11	47.4
0.773	1.29	0.153	8.98	2.81	35.6
1.03	0.971	0.176	10.3	3.22	31.1
1.55	0.645	0.203	11.9	3.72	26.9
2.08	0.481	0.221	13.0	4.06	24.6
2.60	0.385	0.233	13.7	4.28	23.4
3.12	0.321	0.238	14.0	4.38	22.8
4.16	0.240	0.252	14.8	4.63	21.6
I_a=0.0320 E/l, [pMeTFA]=0.05 M, [$PhCOOC_7$]=6.21 x 10^{-3} M, SF=0.945, 313 nm, 3.5 hrs. irradiation. Gc column A, 150°C. Slope=13.1, intercept=18.5, slope/intercept=0.708.					
		EXP #2			
0.515	1.94	0.140	8.22	2.44	41.0
0.773	1.29	0.175	10.3	3.06	32.7
1.03	0.971	0.203	11.9	3.53	28.3
1.55	0.645	0.233	13.7	4.07	24.6
2.08	0.481	0.248	14.6	4.33	23.1

Table 15. Continued.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	[BB],M(10^{-4})	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #2 - Cont.			
2.60	0.385	0.265	15.6	4.63	21.6
3.12	0.321	0.275	16.1	4.78	20.9
4.16	0.240	0.289	17.0	5.04	19.8

I_a=0.0337 E/l, [pMeTFA]=0.05 M, $[PhCOOC_7]=6.21 \times 10^{-3}$ M, SF=0.945, 313 nm. Gc column A, 150°C. Slope=12.3, intercept=16.9, slope/intercept=0.728.

Table 16. Stern-Volmer Data, m-Trifluoromethyl-α,α,α-Trifluoroacetophenone and 0.1 M Toluene in CH_3CN.

$[Q](10^{-3}M$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.130		7.79	
0.0	0.128	0.129±0.001	7.67	1.00
4.00	0.0856			1.51
8.00	0.0658			1.96
12.0	0.0515			2.50
16.0	0.0404			3.19

[m-CF_3-TFA]=0.05 M, pentadiene quencher, [$PhCOOC_7$]=6.34 x 10^{-3} M, 313 nm, 5 hrs. irradiation, [Toluene]=9.99 x 10^{-2} M. SF=0.945. G.C. Column A, 153°C. $k_q\tau$= 125.

		EXP #2		
0.0	0.121		7.50	
0.0	0.130	0.126±0.005	9.75	1.00
2.28	0.106			1.19
4.55	0.0905			1.39
9.10	0.0702			1.79
11.4	0.0629			2.00
13.7	0.0546			2.31

[m-CF_3TFA]=0.05 M, naphthalene quencher, [$PhCOOC_7$]=6.56 x 10^{-3} M, 366 nm, 7 days irradiation, [Toluene] = 9.97 x 10^{-2}M, SF=0.945. G.C. Column A, 153°C. $k_q\tau$=89.4.

Table 17. Reciprocal Plot, m-Trifluoromethyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	[BB],M(10^{-4})	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}
		EXP #1			
0.0115	87.0	0.0439	0.0221	4.67	214
0.0172	58.1	0.0660	3.02	6.38	157
0.0229	43.7	0.0766	3.86	8.16	123
0.0344	29.1	0.0886	4.46	9.43	106
0.0458	21.8	0.0807	4.07	8.60	116
0.0573	17.4	0.0897	4.52	9.56	105
0.0688	14.5	0.0907	4.57	9.66	104
0.0917	10.9	0.0941	4.74	10.0	100

I_a=0.0473 E/1, [m-CF_3-TFA]=0.05 M, [$PhCOOC_7$]=5.33 x 10^{-3} M, SF=0.945, 313 nm, 5 hrs. irradiation. Gc column A, 153°C. Slope=1.15, intercept=61.8, slope/intercept=0.0186.

		EXP #2			
0.0115	87.0	0.0634	2.88	5.35	187
0.0172	58.1	0.0817	3.71	6.90	145
0.0230	43.5	0.0987	4.48	8.33	120
0.0287	34.8	0.104	4.72	8.78	114
0.0344	29.1	0.112	5.08	9.44	106
0.0574	17.4	0.131	5.94	11.0	90.9

I_a=0.0538 E/1, [m-CF_3-TFA]=0.05 M, [$PhCOOC_7$]=4.80 x 10^{-3} M, SF=0.945, 313 nm, 5 hrs. irradiation. Gc column A, 153°C. Slope=1.39, intercept=64.5, slope/intercept=0.0216.

Table 18. Stern-Volmer Data, m-Methyl-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4})$	$BB/PhCOOC_7$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.22		8.46	
0.0	0.246	0.234±0.012	9.37	1.00
0.559	0.179			1.31
1.12	0.154			1.52
1.68	0.122			1.92
2.24	0.106			2.21
2.80	0.0939			2.49
3.36	0.0822			2.85
4.47	0.0661			3.54

$[m\text{-}CH_3TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=4.03 x 10^{-3} M, 366 nm, 6 days irradiation, SF=0.945, [Toluene]= 1.08 M. G.C. Column A, 155°C. $k_q\tau$ = 5,333.

		EXP #2		
0.0	0.922		12.5	
0.0	0.995	0.959±0.036	13.5	1.00
1.31	0.622			1.54
1.97	0.535			1.79
3.28	0.343			2.80
3.93	0.244			3.93

$[m\text{-}CH_3TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=1.44 x10^{-3} M, 366 nm, 47 hrs. irradiation, SF=0.945, [Toluene]= 1.08 M. G.C. Column A, 155°C. $k_q\tau$=5,889.

Table 19. Reciprocal Plot, m-Methyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}$,M^{-1}	$BB/PhCOOC_7$	$[BB]M(10^{-4})$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #1			
0.500	2.00	0.0740	5.68	0.879	114
0.750	1.33	0.101	7.75	1.20	83.3
1.00	1.00	0.117	8.98	1.39	71.9
1.50	0.667	0.154	11.8	1.83	54.6
2.00	0.500	0.182	14.0	2.16	46.3
2.50	0.400	0.188	14.4	2.23	44.8
3.00	0.333	0.207	15.9	2.46	40.7
4.00	0.250	0.226	17.3	2.68	37.3
I_a=0.0646 E/l, $[m\text{-}CH_3\text{-}TFA]$=0.05 M, $[PhCOOC_7]$=8.12 x 10^{-3} M, SF=0.945, 313 nm, 6 hrs. irradiation. Gc column A, 155°C. Slope=43.9, intercept=25.9, slope/intercept=1.69.					
		EXP #2			
0.500	2.00	0.144	8.48	1.15	87.0
0.750	1.33	0.176	10.4	1.41	70.9
1.00	1.00	0.212	12.5	1.70	58.8
1.25	0.800	0.242	14.2	1.93	51.8

Table 19. Continued.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	[BB],M(10^{-4}	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
		EXP #2 - Cont.			
1.50	0.667	0.271	16.0	2.17	46.1
2.00	0.500	0.296	17.4	2.36	42.4
2.50	0.400	0.311	18.3	2.48	40.3

I_a=0.0737 E/l, [m-CH_3-TFA]=0.05 M, [$PhCOOC_7$]=6.23 x 10^{-3} M, SF=0.945, 313 nm. Gc column A, 155°C. Slope=34.1, intercept=24.9, slope/intercept=1.37.

Table 20. Stern-Volmer Data, 3,4-dimethyl-α,α,α-Trifluoroacetophenone and 1.6 M Toluene in CH_3CN.

$[Q](10^{-5})$	$BB/PhCOOC_7(10^{-2})$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	13.2		7.26	
0.0	13.6	13.4±0.27	7.48	1.00
2.75	9.77			1.37
3.66	8.50			1.58
5.50	7.46			1.80
6.41	6.98			1.92

[3,4-Di-Me-TFA]=0.05 M, pentadiene quencher, $[PhCOOC_7]=5.8\times10^{-3}$M, 313 nm, [Toluene]=1.60 M, SF=0.945. G.C. Column A, 140°C. $k_q\tau$=14,615.

		EXP #2		
0.0	10.2		5.62	
0.0	9.92	10.1±0.1	5.47	1.00
1.33	8.57			1.18
2.65	7.41			1.36
3.98	6.88			1.47
5.31	6.24			1.62
7.96	5.23			1.93
9.29	4.58			2.21
10.6	4.52			2.23

[3,4-Di-Me-TFA]=0.05 M, pentadiene quencher, $[PhCOOC_7]=5.83\times10^{-3}$M, 313 nm, [Toluene]=1.60 M, SF=0.945. G.C. Column A, 140°C. $k_q\tau$=12,091.

Table 20. Continued.

$[Q](10^{-5}M)$	$BB/PhCOOC_7$		$[BB](10-4)$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #3		
0.0	0.579		10.3	
0.0	0.560	0.570±0.010	10.0	1.00
1.34	0.431			1.32
4.01	0.284			2.01
5.34	0.305			1.87
6.68	0.242			2.36
8.02	0.227			2.51
10.7	0.180			3.17
[3,4-Di-Me-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]$= 1.89×10^{-3} M, 366 nm, 50 hrs. irradiation, [Toluene]= 1.04 M, SF = 0.945. G.C. Column A, 140°C. $k_q\tau$ = 20,000.				
		EXP #4		
0.0	0.779		5.89	
0.0	0.799		6.04	
0.0	0.819	0.799±0.013	6.19	1.00
2.72	0.595			1.34
5.44	0.456			1.75
6.81	0.394			2.03
8.17	0.365			2.19
9.53	0.335			2.39
[3,4-Di-Me-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_6]$= 8.82×10^{-4} M, 366 nm, 18 hrs. irradiation, [Toluene]= 1.04 M, SF=0.857. G.C. Column A, 140°C. $k_q\tau$=15,895.				

Table 21. Reciprocal Plot, 3,4-di-Methyl-α,α,α-Trifluoroacetophenone in Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	$[BB](10^{-4})$	I_a E/l	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}
			EXP #1			
0.250	4.00	0.0679	4.49	0.0458	9.80	102
0.500	2.00	0.114	7.53	0.0458	16.4	61.0
1.00	1.00	0.143	9.45	0.0458	20.6	48.5
1.50	0.667	0.195	1.29	0.0458	28.2	35.5
1.75	0.571	0.126	8.32	0.0245	34.0	29.4
2.00	0.500	0.128	8.46	0.0245	34.5	29.0
4.00	0.250	0.161	10.6	0.0245	43.3	23.1
[3,4-Di-Me-TFA]=0.05 M, $[PhCOOC_7]=6.99 \times 10^{-3}$ M, SF=0.945, 313 nm. Gc column A, 140°C						
Slope=20.6, intercept=20.4, slope/intercept=1.01.						
			EXP #2			
0.500	2.00	0.0694	3.75	0.0217	17.3	57.8
1.00	1.00	0.102	5.51	0.0217	25.4	39.4
1.50	0.667	0.123	6.65	0.0217	30.8	32.5
2.00	0.500	0.131	7.08	0.0217	32.7	30.6
2.50	0.400	0.0904	4.89	0.0141	34.7	28.8
3.00	0.333	0.103	5.57	0.0141	39.3	25.4
4.00	0.500	0.107	5.78	0.0141	41.2	24.3

Table 21. Continued.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_7$	$[BB](10^{-4})$	I_a E/l	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}
EXP #2 - Footnotes: [3,4-Di-Me-TFA]=0.05 M, $[PhCOOC_7]=5.72 \times 10^{-3}$ M, SF=0.945, 313 nm. Gc column A, 140°C. Slope=18.9, intercept=20.2, slope/intercept=0.936.						
			EXP #3			
0.500	2.00	0.169	1.45		5.03	199
1.00	1.00	0.327	2.80		9.72	103
1.50	0.667	0.417	3.57		12.4	80.6
2.00	0.500	0.480	4.10		14.2	70.4
2.50	0.400	0.550	4.71		16.4	61.0
4.00	0.500	0.694	5.94		20.6	48.5
I_a=0.0288, [3,4-Di-Me-TFA]=0.05 M, $[PhCOOC_6]=9.99 \times 10^{-4}$ M, SF=0.857. Gc column A, 140 °C. Slope=77.5, intercept=25.2, slope/intercept=3.08.						
			EXP #4		$\phi_{BB}(10^{-2})$	
1.00	1.00	0.217	3.90		1.82	54.9
1.50	0.667	0.265	4.75		2.22	45.0
4.00	0.250	0.445	7.97		3.72	26.9
I_a=0.0214 #/l, [3,4-Di-Me-TFA]=0.05 M, $[PhCOOC_6]=2.09 \times 10^{-3}$ M, SF=0.857, 313 nm. 2.5 hrs. irradiation. Gc column A, 140°C. Slope=37.8, intercept=18.1, slope/intercept=2.09.						

Table 21. Continued.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_6$	$[BB](10^{-4})$	$\phi_{BB}(10^{-2})$	ϕ_{BB}^{-1}
			EXP #5		
1.00	1.00	0.236	4.25	1.99	50.3
1.50	0.667	0.301	5.42	2.53	39.5
2.00	0.500	0.336	6.05	2.83	35.3
4.00	0.250	0.397	7.15	3.34	29.9

I_a=0.0214 E/1, [3,4-Di-Me-TFA]=0.05 M, $[PhCOOC_6]=2.10 \times 10^{-3}$ M, SF=0.857, 313 nm. 2.5 hrs. irradiation. Gc column A, 140°C. Slope=27.4, intercept=22.3, slope/intercept=1.23.

Table 22. Stern-Volmer Data, p-tert-Butyl-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-4})$	$BB/PhCOOC_6$		$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	0.725		6.21	
0.0	0.751	0.738±0.013	6.44	1.00
1.41	0.576			1.28
2.82	0.491			1.50
4.23	0.391			1.89
5.63	0.364			2.03

[p-t-Bu-TFA]=0.035 M, $[PhCOOC_6]=1.00 \times 10^{-3}$, naphthalene quencher, 36 hrs. irradiation, SF=0.857, [Toluene]=1.08 M. G.C. Column A, 155°C. $k_q\tau=1,850$.

Table 23. Reciprocal Plot, p-tert-Butyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene],M	$[Toluene]^{-1}M^{-1}$	$BB/PhCOOC_5$	$[BB](10^{-4})$	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}
0.225	4.44	0.203	5.97	6.77	148
0.450	4.44	0.198	5.82	6.60	152
0.562	1.78	0.370	11.1	12.6	79.4
0.674	1.48	0.402	11.8	13.4	74.6
0.899	1.11	0.491	14.4	16.3	61.3

I_a=0.0882 E/l, [p-t-Bu-TFA]=0.035 M, $[PhCOOC_5]$=4.12 x 10^{-3} M, SF=0.714, 313 nm, 4 hrs. irradiation. Gc column A, 155°C. Slope=26.3, intercept=33.3, k_d/k_r=0.790.

Table 24. Stern-Volmer Data, p-Acetyl-α,α,α-Trifluoroacetophenone and 1 M Toluene in CH_3CN.

$[Q](10^{-3})$	BB/PhC_7		$[BB](10^{-3})$	$\phi^{\circ}_{BB}/\phi_{BB}$
		EXP #1		
0.0	2.16		3.33	
0.0	2.21		3.40	
0.0	2.14	2.17±0.03	3.30	1.00
1.25	1.57			1.38
2.09	1.43			1.52

[p-CH_3CO-TFA]=0.03 M, naphthalene quencher, [PhC_7]=0.00163 M, SF=0.945, 335 nm, 9.5 hrs. irradiation time, [Toluene] =1.02 M. G.C. Column A, 185°C. $k_q\tau$=272.

		EXP #2		
0.0	2.67		3.60	
0.0	2.73	2.70±0.03	3.69	1.00
1.85	2.06			1.31
5.56	1.17			2.31

[p-CH_3CO-TFA]=0.03 M, naphthalene quencher, [PhC_7]=0.00143 M, SF=0.945, 335 nm, 8.5 hrs. irradiation time, [Toluene]= 1.03 M. G.C. Column A, 185°C. $k_q\tau$=220.

Table 25. Reciprocal Plot, p-Acetyl-α,α,α-Trifluoroacetophenone and Toluene in CH_3CN.

[Toluene]	$[Toluene]^{-1}$	BB/PhC_7	$[BB](10^{-4})$	$\phi_{BB}(10^{-3})$	ϕ_{BB}^{-1}	Average
			EXP #1			
0.250	4.00	0.443	6.42	8.62	116	
0.250	4.00	0.436	6.32	8.48	118	117
1.00	1.00	0.728	10.6	14.2	70.4	
1.00	1.00	0.776	11.3	15.2	65.8	
1.00	1.00	0.704	10.2	13.7	73.0	69.7

I_a=0.745 E/l, [p-CH_3CO-TFA]=0.03 M, CH_3CN, [PhC_7]=0.00153 M, SF=0.945, 6 hrs. irradiation time. Gc column A, 167°C. Slope=15.8, intercept=54.0, slope/intercept=0.293.

			EXP #2			
0.250	4.00	1.02	15.2	26.8	37.3	
0.250	4.00	0.967	14.4	25.4	39.4	
0.250	4.00	0.978	14.6	25.7	38.9	38.5
1.00	1.00	1.45	21.6	38.1	26.2	
1.00	1.00	1.39	20.7	36.5	27.4	
1.00	1.00	1.46	20.9	36.9	27.1	26.9

I_a=0.0567 E/l, [p-CH_3CO-TFA]=0.02 M, CH_3CN, [PhC_7]=0.00158 M, SF=0.945, 4 hrs. irradiation time. Gc column A, 167°C. Slope=3.87, intercept=23.0, slope/intercept=0.168.

Table 26. Stern-Volmer Data, p-Trifluoromethyl-α,α,α-Trifluoroacetophenone and 1 M p-xylene in CH_3CN.

$[Q](10^{-2}, M$	DTE/PhC_7		[DTE] $(10^{-3}),M$	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	1.71		1.78	
0.0	1.71		1.78	
0.0	1.67	1.70±0.02	1.73	1.00
4.98	1.47			1.16
7.47	1.40			1.21
9.96	1.35			1.26
9.96	1.35			1.26
14.9	1.21			1.40
19.9	1.05			1.62

$[p\text{-}CF_3\text{-}TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00133 M, 335 nm, [p-Xylene]=1.00 M, SF=0.781. G.C. Column A, 195°C. $k_q\tau$=2.95.

		EXP #2		
0.0	1.63		1.85	
0.0	1.63		1.85	
0.0	1.62	0.63±0.003	1.83	1.00
19.4	1.06			1.54
25.9	0.942			1.73
38.8	0.729			2.24
51.8	0.561			2.91
51.8	0.556			2.93

$[p\text{-}CF_3\text{-}TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00145 M, 335 nm, [p-Xylene]=1.01 M, SF = 0.781. G.C. Column A, 195°C. $k_q\tau$=3.35.

Table 27. Stern-Volmer Data, α,α,α-Trifluoroacetophenone and 1 M p-Xylene in CH_3CN.

$[Q](10^{-3})$,M	DTE/PhC_7		$[DTE](10^{-3})$	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	0.704		1.97	
0.0	0.694		1.94	
0.0	0.658		1.84	
0.0	0.683	0.685±0.019	1.91	1.00
7.35	0.529			1.29
11.0	0.468			1.46
14.7	0.421			1.63
22.1	0.346			1.98
25.7	0.311			2.21
29.4	0.309			2.22

[TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]=3.40 \times 10^{-3}$ M, 335 nm, [p-Xylene]=1.07 M, SF=0.813. G.C. Column A, 195° C. $k_q\tau=43.3$.

		EXP #2		
0.0	2.47		2.57	
0.0	2.45		2.54	
0.0	2.44	2.45±0.01	2.53	1.00
12.2	1.70			1.44
18.2	1.44			1.70
24.3	1.25			1.96
36.5	0.996			2.46
48.6	0.815			3.01
48.6	0.810			3.02

[TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]=1.33 \times 10^{-3}$ M 335 nm, [p-Xylene]=1.08 M, SF = 0.813. G.C. Column A, 195°C. $k_q\tau=40.0$.

Table 28. Reciprocal Plot, α,α,α-Trifluoroacetophenone and p-Xylene in CH_3CN.

[Xyl],M	$[Xyl]^{-1}$ M^{-1}	DTE/PhC_9	[DTE] M(10^{-3})	ϕ_{DTE}	ϕ_{DTE}^{-1}	Av.
			EXP #1			
0.125	8.00	0.527	1.00	0.0870	11.5	
0.125	8.00	0.567	1.08	0.0939	10.6	11.05
2.00	0.500	0.548	1.04	0.0904	11.1	
2.00	0.500	0.569	1.08	0.0939	10.6	10.85
I_a=0.0115 E/l, [$PhCOOC_7$]=2.34 x 10^{-3} M, 313 nm, 1 hr. irradiation time, SF = 0.813, [TFA]=0.05 M, Xyl=p-xylene. G.C. Column A, 195°C. Intercept=10.8.						
			EXP #2			
0.0501	20.0	0.086	1.04	0.0703	14.2	
0.0501	20.0	0.739	0.952	0.0643	15.6	
0.0501	20.0	0.746	0.961	0.0649	15.4	
0.0501	20.0	0.776	1.00	0.0679	14.8	15.0
0.125	8.00	1.09	1.40	0.0946	10.6	
0.125	8.00	1.06	1.37	0.0926	10.8	
0.125	8.00	1.05	1.35	0.0912	11.0	10.8
2.00	0.500	1.26	1.62	0.109	9.17	
2.00	0.500	1.24	1.60	0.108	9.26	
2.00	0.500	1.24	1.60	0.108	9.26	9.23
I_a=0.0148 E/l, [$PhCOOC_7$]=1.65 x10^{-3} M, 313 nm, 1 hr. irradiation time, SF = 0.813, [TFA]=0.05 M, Xyl = p-Xylene. G.C. Column A, 195°C. Slope = 0.301, intercept = 8.82, slope/intercept = 0.0341.						

Table 29. Stern-Volmer Data, m-Methyl-α,α,α-Trifluoroacetophenone and 1 M p-Xylene in CH_3CN.

$[Q](10^{-3})$	DTE/PhC_7	Av.	$[DTE](10^{-3})$	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	1.66		2.14	1.00
0.0	1.61		2.07	
0.0	1.63	1.63±0.02	2.10	1.00
2.40	0.921			1.77
3.61	0.775			2.10
4.81	0.679			2.40
6.01	0.583			2.80
9.62	0.484			3.37

$[m\text{-}CH_3\text{-}TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00165 M, 335 nm, [p-Xylene]=1.01 M, SF=0.813. G.C. Column A, 195°C. $k_q\tau$=300.

		EXP #2		
0.0	2.56		2.44	
0.0	2.54		2.42	
0.0	2.48	2.53±0.03	2.36	1.00
2.47	1.40			1.81
3.71	1.17			2.16
4.94	1.04			2.43
7.42	0.788			3.21
9.89	0.681			3.72

$[m\text{-}CH_3\text{-}TFA]$=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00122 M, 335 nm, [p-Xylene]=1.02 M, SF=0.813. G.C. Column A, 195°C. $k_q\tau$=292.

Table 30. Reciprocal Plot, m-Methyl-α,α,α-Trifluoroacetophenone and p-Xylene in CH_3CN.

[Xyl],M	$[Xyl]^{-1}$	DTE/PhC_7	[DTE] (10^{-3}),M	$\phi_{DTE}(10^{-2})$	ϕ_{DTE}^{-1}
0.0753	13.3	0.863	1.00	3.82	26.2
0.0753	13.3	0.841	0.979	3.74	26.7
0.0753	13.3	0.846	0.985	3.76	26.6
0.126	7.94	1.16	1.35	5.15	19.4
0.351	2.85	1.77	2.06	7.86	12.7
0.502	1.99	1.97	2.29	8.74	11.4
2.01	0.498	2.07	2.40	9.20	10.9
2.01	0.498	2.09	2.43	9.27	10.8

I_a=0.0262 E/l, CH_3CN, $[PhCOOC_7]$=0.00149 M, 2 hr. irradiation time, SF=0.781, [TFA]=0.05 M, Xyl=p-xylene. G.C. Column A, 195°C. Slope=1.27, intercept=9.44, slope/intercept= 0.135.

Table 31. Stern-Volmer Data, p-Methoxy-α,α,α-Trifluoroacetophenone and 1 M p-Xylene in CH_3CN.

$[Q](10^{-4})$,M	DTE/PhC_7		$[DTE](10^{-4})$	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	1.17		15.0	
0.0	1.28		16.4	
0.0	1.31	1.25±0.06	16.8	1.00
7.24	0.342			3.64
10.9	0.257			4.86
14.5	0.202			6.19
21.7	0.163			7.67

[p-MeO-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00164 M, 335 nm, [p-Xylene]=1.01 M, SF=0.781. G.C. Column A, 195°C. $k_q\tau$=3,409.

		EXP #2		
0.0	1.98		22.7	
0.0	1.95		22.4	
0.0	2.01	1.98±0.02	23.1	1.00
3.25	0.808			2.45
6.49	0.518			3.82
9.74	0.385			5.14
13.0	0.310			6.39
13.0	0.319			6.21
19.5	0.245			8.08

[p-MeO-TFA]=0.05 M, naphthalene quencher, $[PhCOOC_7]$=0.00147 M, 335 nm, [p-Xylene]=1.01 M, SF=0.781. G.C. Column A, 195°C. $k_q\tau$=4,154.

Table 32. Reciprocal Plot, p-Methoxy-α,α,α-Trifluoroacetophenone and p-Xylene in CH_3CN.

[Xyl],M	$[Xyl]^{-1}M^{-1}$	DTE/PhC_7	[DTE] (10^{-3}),M	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.126	7.94	0.309	0.883	0.0310	32.3
0.126	7.94	0.315	0.900	0.0316	31.6
0.126	7.94	0.320	0.914	0.0321	31.2
0.201	4.98	0.395	1.13	0.0396	25.3
0.201	4.98	0.396	1.13	0.0396	25.3
0.351	2.85	0.522	1.49	0.0523	19.1
0.753	1.33	0.663	1.90	0.0667	15.0
1.00	1.00	0.744	2.13	0.0747	13.4
2.01	0.498	0.816	2.33	0.0818	12.2
2.01	0.498	0.828	2.37	0.0832	12.0
I_a = 0.0285 E/l, $[PhCOOC_7]$=3.66 x 10^{-3} M, 313 nm, 3 hr. irradiation time, SF=0.781, [p-MeO-TFA]=0.05 M. G.C. Column A, 195°C. Slope=2.66, intercept=11.2, slope/intercept=0.238.					
		EXP #2			
0.126	7.94	0.868	1.19	0.0389	25.7
0.126	7.98	0.853	1.17	0.0382	26.2
0.126	7.94	0.804	1.10	0.0359	27.9
0.201	4.98	1.03	1.41	0.0461	21.7
0.201	4.98	1.04	1.42	0.0464	21.6
0.351	2.85	1.32	1.80	0.0588	17.0
0.502	1.99	1.50	2.05	0.0670	14.9
0.753	1.33	1.73	2.36	0.0771	13.0
2.01	0.498	2.01	2.75	0.0899	11.1
2.01	0.498	2.02	2.76	0.0902	11.1
I_a=0.0306 E/0, $[PhCOOC_7]$=1.75 x 10^{-3} M, 313 nm, 4.5 hr. irradiation time, SF=0.781, [p-MeO-TFA]=0.05 M. G.C. Column A, 195°C. Slope=2.10, intercept=10.5, slope/intercept=0.200.					

Table 33. Stern-Volmer Data, p-Acetyl-α,α,α-Trifluoroacetophenone and 1 M p-Xylene in CH_3CN.

[Q]	DTE/$PhCOOC_7$		[DTE] (10^{-3})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	0.764		1.25	
0.0	0.725	0.745±0.021	1.19	1.00
0.109	0.232			3.21
0.218	0.135			5.52
[p-CH_3CO-TFA]=0.02 M, naphthalene quencher, [$PhCOOC_7$]= 0.00202 M, SF=0.813, 335 nm, 3 hr, 15 min. irradiation time, [p-xylene]=1.01 M. G.C. Column A, 185°C. $k_q\tau$=20.5.				
		EXP #2		
0.0	2.35		2.94	
0.0	2.37		2.90	
0.0	2.16	2.28±0.09	2.70	1.00
0.0819	0.946			2.41
0.109	0.762			2.99
0.164	0.593			3.84
[p-CH_3CO-TFA]=0.02 M, naphthalene quencher, [$PhCOOC_7$]= 0.00154 M, SF=0.813, 335 nm, 3 hr. irradiation time, [p-xylene]=1.02 M. G.C. Column A, 185°C. $k_q\tau$ =17.6.				
		EXP #3		
0.0	1.87		2.24	
0.0	1.87		2.24	
0.0	1.91	1.88±0.02	2.29	1.00
0.114	0.961			1.96
0.172	0.795			2.36
[p-CH_3CO-TFA]=0.02 M, naphthalene quencher, [$phCOOC_7$]= 0.00147 M, SF=0.813, 335 nm, 1.5 hr. irradiation time, [p-xylene]=1.02 M. G.C. Column A, 185°C. $k_q\tau$=8.1.				

Table 34. Reciprocal Plot, p-Acetyl-α,α,α-Trifluoroacetophenone and p-Xylene in CH_3CN.

[Xyl]	$[Xyl]^{-1}$	DTE/PhC_7	[DTE] (10^{-4})	DTE (10^{-2})	ϕ_{DTE}^{-1}
0.126	7.94	0.690	8.56	8.59	11.6
0.126	7.94	0.682	8.46	8.49	11.8
0.126	7.94	0.686	8.51	8.54	11.7
2.01	0.498	0.735	9.11	9.14	10.9
2.01	0.498	0.766	9.50	9.53	10.5
2.01	0.498	0.731	9.06	9.09	11.0

I_a=0.00997 E/l, $[pCH_3COTFA]$=0.03 M, $[PhC_7]$=0.00153 M, SF= 0.813, 1 hr. irradiation time. G.C. Column A, 185°C.

Slope=0.121, intercept=10.8, slope/intercept=0.0112.

Table 35. Stern-Volmer Plot, α,α,α-Trifluoroacetophenone and p-di-iso-Propylbenzene in CH_3CN.

$[Q](10^{-4})$	HdC/C_{24}		$[HdC](10^{-3})$	$\phi°/\phi$
0.0	0.509		7.99	
0.0	0.492		7.72	
0.0	0.484	0.495±0.009	7.60	1.00
7.74	0.467			1.06
19.4	0.416			1.19
31.0	0.371			1.33

[TFA]=0.05 M, naphthalene quencher, $[C_{24}]$=0.0157 M, 366 nm, [p-diisopropylbenzene]=1.02 M, SF=1.00, HdC=the bibenzyl coupling product. G.C. Column B, 220°C. $k_q\tau$= 100.

Table 36. Reciprocal Plot, α,α,α-Trifluoroacetophenone and p-di-iso-Propylbenzene in CH_3CN.

[DIPB]	$[DIPB]^{-1}$	HdC/C_{24}	[HdC] (10^{-4})	$\phi(10^{-2})$	ϕ_{HdC}^{-1}
0.0250	40.0	0.155	9.15	1.82	54.9
0.0250	40.0	0.166	9.79	1.95	51.3
0.0250	40.0	0.163	9.62	1.91	52.4
0.0750	13.3	0.304	1.79	3.56	28.1
0.250	4.00	0.456	2.69	5.35	18.7
0.500	2.00	0.467	2.76	5.49	18.2
1.00	1.00	0.572	3.37	6.70	14.9
2.00	0.500	0.517	3.05	6.06	16.5
2.00	0.500	0.501	2.96	5.88	17.0

I_a=0.0503 E/l, [TFA]=0.05 M, $[C_{24}]$=0.0059 M, 313 nm, SF= 1.00, 5 hrs. irradiation time, DIPB=p-diisopropylbenzene, HdC=the bibenzyl coupling product. G.C. Column A,176°C. Slope=0.938, intercept=15.4, slope/intercept=6.09.

Table 37. Concentrations of the Major Products from the Photoreduction of ACP by p-Xylene.

EXP	[ACP][a]	[PhC_{10}][b]	[Xyl][c]	ACP/PhC_2[d]	SF[e]	ACP/PhC_2[f]	[ACP][g]	DTE/PhC_{10}	[DTE][h]
1	5.410	4.116	2.003	1.203	0.976	0.5888	2.648	1.541	7.250
2	6.042	3.964	0.519	1.331	0.985	0.7799	3.540	1.254	5.682
3	6.109	3.811	0.168	1.326	0.821	0.8211	3.783	1.238	5.393

EXP	KP/PhC_{10}	[KP][i]	Pinacol/PhC_{10}	[Pinacol][j]
1	2.668	1.133	1.368	5.535
2	2.519	1.030	1.270	4.949
3	2.136	0.8401	1.386	5.192

[a] x 10^{-2} M, the initial conc. weighed out.

[b] x 10^{-3} M.

[c] Conc. of p-xylene, M.

[d] [PhC_2]=0.04608 M stock soln.; mixed 1:1 with ketone solution. GC ratio, non photolyzed.

[e] $SF = \frac{[ACP]}{[PhC_2]} \left(\frac{PhC_2}{ACP}\right)$ by GC.

[f] GC ratio, after photolysis.

[g] x 10^{-2} M; final conc.:=SF(ACP/PhC_2[PhC_2]. [h] x 10^{-3}; SF≐16C atoms/14C atoms=1.143.

[i] x 10^{-2}; SF≐1.032, based on the relative number of C atoms. The cross-coupled product.

[j] x 10^{-3} M; SF=0.983, determined experimentally.

Gc column A, 170°C, 210°C.

Table 38. Stern-Volmer Data, Acetophenone and 1.6 M p-Xylene in CH_3CN.

[Q], M(10^{-4})	DTE/$PhCOOC_8$		[DTE] (10^{-4})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	0.366		2.72	
0.0	0.349		2.59	
0.0	0.360	0.358±0.006	2.67	1.00
2.63	0.192			1.86
5.26	0.135			2.65
7.88	0.0967			3.70

[ACP]=0.01 M, naphthalene quencher, [$PhCOOC_8$]=9.47 x 10^{-4} M, 366 nm, 19 hrs. irradiation, [p-Xylene]=1.61 M, SF=0.784. G.C. Column A, 136°C. $k_q\tau$=3,300.

		EXP #2		
0.0	0.352		2.71	
0.0	0.337		2.59	
0.0	0.367	0.352±0.010	2.82	1.00
0.865	0.296			1.19
2.59	0.193			1.82
3.46	0.168			2.10
5.19	0.132			2.67

[ACP]=0.01 M, naphthalene quencher, [$PhCOOC_8$]=9.81 x 10^{-4} M, 366 nm, 20 hrs. irradiation, [p-Xylene]=1.61 M, SF=0.784. G.C. Column A, 136°C. $k_q\tau$=3,050.

Table 38. Continued.

[Q],M(10^{-4})	DTE/$PhCOOC_8$		[DTE] (10^{-4})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #3		
0.0	0.356		2.67	
0.0	0.382		2.86	
0.0	0.359	0.366±0.011	2.69	1.00
2.30	0.233			1.57
4.66	0.173			2.12
6.13	0.147			2.49

[ACP]=0.01 M, hexadiene quencher, $[PhCOOC_8]=9.56 \times 10^{-4}$M, 313 nm, 1 hr. 40 min. irradiation, SF=0.784, [p-Xylene]= 1.61 M. G.C. Column A, 136°C. $k_q\tau=2,433$.

Table 39. ·Reciprocal Plot, Acetophenone and p-Xylene in CH_3CN.

[p-Xyl],M	$[p\text{-Xyl}]^{-1}$,M^{-1}	DTE/PhC_8	DTE*	A	$I_a(1-10^{-A})$ (10^{-3})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
			EXP #1				
0.625	1.60	0.20	1.39	0.510	2.97	4.68	21.4
0.938	1.07	0.283	1.97	0.504	2.95	6.68	15.0
1.25	0.800	0.348	2.42	0.499	2.94	8.23	12.2
1.56	0.641	0.379	2.64	0.497	2.93	9.01	11.1
1.88	0.532	0.433	3.01	0.493	2.92	10.3	9.71

*(10^{-4}), $I_a=4.30 \times 10^{-3}$ E/l, $[ACP]=1.004 \times 10^{-2}$ M, $[PhCOOC_8]=8.876 \times 10^{-4}$ M, SF=0.784, 313 nm, 51 min. irradiation. Gc column A, 136°C. Slope=10.8, intercept=3.82, slope/intercept=2.83.

			EXP #2				
0.625	1.60	0.132	0.865	0.526	2.78	4.16	24.1
0.756	1.33	0.210	1.38	0.520	2.76	4.99	20.1
0.938	1.07	0.260	1.71	0.517	2.76	6.19	16.2
1.06	0.943	0.321	2.11	0.512	2.74	7.66	13.0
1.25	0.800	3.44	2.26	0.511	2.74	8.23	12.2
1.56	0.641	0.356	2.33	0.510	2.74	8.51	11.7
1.88	0.532	0.410	2.69	0.507	2.73	9.85	10.2
2.50	0.400	0.448	2.94	0.504	2.72	1.08	9.27

$I_a=3.96 \times 10^{-3}$ E/l, $[ACP]=0.01024$ M, $[PhCOOC_8]=8.364 \times 10^{-4}$ M, SF=0.784, 313 nm. 1 hr. 10 min. irradiation, Slope=12.4, intercept=3.25, slope/intercept=3.82.

Table 40. Stern-Volmer Data, p-Methylacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q],M(10^{-5})	DTE/$PhCOOC_8$		[DTE] (10^{-4})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	0.438		2.26	
0.0	0.447	0.443±0.004	2.30	1.00
4.62	0.354			1.25
6.16	0.314			1.25
6.16	0.314			1.41
9.23	0.290			1.53
12.3	0.281			1.58

[p-Me-ACP]=0.01 M, hexadiene quencher, [$PhCOOC_8$]=6.57 x 10^{-4} M, 313 nm, 4 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.784. G.C. Column A, 180°C. $k_q\tau$=13,200.

		EXP #2		
0.0	0.669		4.79	
0.0	0.723		5.18	
0.0	0.783	0.725±0.039	5.60	1.00
0.555	0.559			1.30
1.11	0.491			1.48
2.22	0.392			1.85
3.33	0.340			2.13
4.44	0.276			2.63

[p-Me-ACP]=0.01 M, hexadiene quencher, [$PhCOOC_8$]=9.13 x 10^{-4} M, 313 nm, 4 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.784. G.C. Column A, 180°C. $k_q\tau$=18,125.

Table 40. Continued.

[Q],M(10^{-5})	DTE/$PhCOOC_8$		[DTE] (10^{-4})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #3		
0.0	0.671		4.45	
0.0	0.707		4.68	
0.0	0.742		4.92	
0.0	0.781	0.725±0.036	5.17	1.00
1.14	0.473			1.57
1.71	0.384			1.89
2.28	0.338			2.14
3.99	0.256			2.83

[p-Me-ACP]=0.01 M, hexadiene quencher, $[PhCOOC_8]$=8.45 x 10^{-4} M, 313 nm, 4 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.784 G.C. Column A, 180°C. $k_q\tau$=20,182.

Table 41. Reciprocal Plot, p-Methylacetophenone and p-Xylene in CH_3CN.

[p-Xyl],M	$[p\text{-Xyl}]^{-1}$, M^{-1}	DTE/PhC_8	[DTE]*, M	A_{313}	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #1			
1.00	1.00	0.221	1.54	0.723	0.0304	32.9
1.00	1.00	0.195	1.36	0.725	0.0269	37.2
1.50	0.667	0.278	1.94	0.737	0.0383	26.1
1.50	0.667	0.280	1.95	0.717	0.0385	26.0
2.00	0.500	0.349	2.43	0.711	0.0480	20.8
2.00	0.500	0.354	2.47	0.710	0.0488	20.5
A(aver)=0.720, I_a=6.26 x 10^{-3} E/l, $I_a(1-10^{-A})$=5.06 x 10^{-3} E/l, $[PhC_8]$=8.88 x 10^{-4} M, 313 nm, SF=0.784. Gc column A, 180°C. Slope=33.6, intercept=3.84, slope/intercept=8.75.						
			EXP #2			
1.25	0.800	0.240	1.41	0.740	0.0293	34.1
1.56	0.641	0.291	1.70	0.736	0.0353	28.3
1.88	0.532	0.358	2.09	0.730	0.0435	23.0
2.50	0.400	0.428	2.49	0.725	0.0518	19.3
A(aver)=0.733, I_a=5.90 x 10^{-3} E/l, $I_a(1-10^{-A})$=4.81 x 10^{-3} E/l, $[PhC_8]$=7.43 x 10^{-4} M, 313 nm, SF=0.784. Gc column A, 180°C. Slope=38.5, intercept=3.38, slope/intercept=11.4.						

Table 41. Continued.

[p-Xyl],M	$[p\text{-Xyl}]^{-1}$, M^{-1}	DTE/PhC_8	[DTE]*, M	A_{313}	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #3			
1.25	0.800	0.248	1.43	0.724	0.0300	33.3
1.56	0.641	0.310	1.78	0.719	0.0373	26.8
1.88	0.532	0.345	1.99	0.717	0.0417	24.0
2.50	0.400	0.420	2.42	0.711	0.0507	19.7

A(aver)=0.718, I_a=5.90 x 10^{-3} E/1, I_a(1-10-A)=4.77 x 10^{-3} E/1, [PhC_8]=7.34 x 10^{-4} M, 313 nm, SF=0.784. Gc column A, 180°C. Slope=34.2, intercept=4.71, slope/intercept=5.99.

[Xyl], M	$[Xyl]^{-1}$, M^{-1}	DTE/PhC_8	[DTE]*, M	A_{313}	ϕ_{DTE} (10^{-3})	ϕ_{DTE}^{-1}
			EXP #4			
0.250	4.00	0.524	3.76		3.55	282
0.250	4.00	0.486	3.49		3.29	304
0.334	2.99	0.596	4.28		4.04	248
0.500	2.00	1.01	7.25		6.84	146
0.667	1.50	1.33	9.54		9.00	111
1.00	1.00	1.63	11.7		11.0	90.9
1.33	0.752	1.82	13.1		12.4	80.6

Table 41. Continued.

[Xyl], M	$[Xyl]^{-1}$, M^{-1}	DTE/PhC_8	[DTE]*, M	A_{313}	ϕ_{DTE} (10^{-3})	ϕ_{DTE}^{-1}

Footnotes to Exp #4: I_a=0.106 E/l, [$PhCOOC_9$]=9.34 x 10^{-4} M, SF=0.768, 313 nm, 9 hrs. irradiation. Gc column A, 180°C. Slope=7.11, intercept=15.4, slope/intercept=4.62.

EXP #5

0.250	4.00	0.625	3.94		3.72	269
0.333	3.00	0.737	4.65		4.39	228
0.500	2.00	1.26	7.95		7.50	133
1.33	0.752	2.83	17.8		16.8	59.5

I_a=0.106 E/l, [$PhCOOC_9$]=8.21 x 10^{-4} M, SF=0.768, 313 nm, 9 hrs. irradiation. Gc column A, 180°C. Slope=70.0, intercept=19.1, slope/intercept=3.66.

EXP #6

1.00	1.00	0.0976	0.627	0.762	11.7	85.5
1.50	0.667	0.130	0.835	0.760	15.6	64.1
2.00	0.500	0.163	1.05	0.757	19.6	51.0
3.00	0.333	0.212	1.36	0.752	25.4	39.5
4.00	0.250	0.256	1.64	0.749	30.7	32.6

A(aver)=0.756, I_a=6.49 x 10^{-3} E/l, I_a ($1-10^{-A}$)=5.35 x 10^{-3} E/l, [PhC_8]=8.19 x 10^{-4} M, 313 nm, SF=0.784. Gc column A, 180°C. Slope=67.3, intercept=8.40, slope/intercept=8.01.

Table 42. Stern-Volmer Data, m-Methylacetophenone and 1.6 M. p-Xylene in CH_3CN.

$[Q], M(10^{-5})$	DTE/$PhCOOC_8$		$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1	
0.0	0.494		
0.0	0.549		
0.0	0.509		
0.0	0.537	0.522±0.021	1.00
9.32	0.374		1.40
12.4	0.328		1.59
18.6	0.261		2.00

[m-Me-ACP]=0.01 M, [$PhCOOC_8$]=8.53 x 10^{-4} M, hexadiene quencher, 313 nm, 4 hrs. irradiation, [p-Xylene]=1.60 M, G.C. Column A, 155°C. $k_q\tau$=8,684.

		EXP #2	
0.0	0.948		
0.0	0.908		
0.0	0.873		
0.0	1.04	0.942±0.052	1.00
8.91	0.746		1.26
17.8	0.539		1.75
22.3	0.459		2.05
26.7	0.444		2.12

[m-Me-ACP]=0.01 M, [$PhCOOC_8$]=1.20 x 10^{-3} M, hexadiene quencher, 313 nm, 3 hrs. irradiation, [p-Xylene]=1.60 M. G.C. Column A, 155°C. $k_q\tau$=10,263.

Table 43. Reciprocal Plot, m-Methylacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}, M^{-1}$	DTE/$PhCOOC_8$	[DTE] (10^{-4})	A_{313}	$I_a(1-10^{-A})$*	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #1				
1.25	0.800	0.390	2.69	0.625	5.64	0.0477	21.0
1.25	0.800	0.380	2.62	0.625	5.65	0.0464	21.6
1.25	0.800	0.344	2.37	0.628	5.66	0.0419	23.9
1.38	0.725	0.394	2.72	0.624	5.64	0.0482	20.7
1.69	0.592	0.441	3.04	0.621	5.63	0.0540	18.5
1.88	0.532	0.477	3.29	0.618	5.62	0.0585	17.1
2.19	0.457	0.551	3.80	0.612	5.59	0.0680	14.7
2.50	0.400	0.559	3.85	0.612	5.59	0.0689	14.5

I_a=0.00740 E/l, [m-Me-ACP]=0.01 M, [$PhCOOC_8$]=8.79 x 10^{-4} M, SF=0.784, 313 nm, 13 hrs. irradiation. Gc column A, 155°C. Slope=20.0, intercept=6.26, slope/intercept=3.20.

			EXP #2				
0.938	1.07	0.285	1.60	0.602	4.90	0.0339	29.5
1.25	0.800	0.325	1.89	0.600	4.89	0.0387	25.8
1.25	0.800	0.350	2.04	0.598	4.89	0.0417	24.0
1.38	0.725	0.367	2.14	0.597	4.88	0.0439	22.8
1.56	0.641	0.421	2.45	0.594	4.87	0.0503	19.9
1.69	0.592	0.435	2.53	0.593	4.86	0.0520	19.2
1.88	0.532	0.436	2.54	0.592	4.86	0.0523	19.1
2.19	0.457	0.476	2.77	0.590	4.85	0.0571	17.5
2.50	0.400	0.509	2.97	0.588	4.84	0.0614	16.3

I_a=0.00653 E/l, [m-Me-ACP]=0.01 M, [$PhCOOC_8$]=7.43 x 10^{-4} M, SF=0.784, 313 nm. *10^{-3}M. Gc column A, 155°C. Slope=19.8, intercept=8.19, slope/intercept=2.41.

Table 43. Continued.

[Xylene]	$[Xylene]^{-1}, M^{-1}$	$DTE/PhCOOC_9$	$[PhC_9]^*$	[DTE]	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #3			
0.350	2.86	1.14	2.39	2.92	0.0442	22.6
0.350	2.86	1.09	2.39	2.79	0.0423	23.6
1.00	1.00	0.715	6.83	5.23	0.0792	12.6
1.25	0.800	0.713	8.54	6.52	0.0988	10.1
1.50	0.667	0.641	10.2	7.00	0.106	9.43
1.75	0.571	0.589	11.9	7.50	0.114	8.77
2.00	0.500	0.609	13.7	8.93	0.135	7.41

I_a=0.00706 E/l, A_{313} nm (aver) = 1.189, $I_a(1-10^{-A})$=0.00660 E/l, [m-Me-ACP]=0.02 M, 313 nm. *x 10^{-4} M, SF=1.07, 1 hr. irradiation. Gc column A, 155°C. Slope=6.40, intercept=5.09, slope/intercept=1.20.

			EXP #4			
0.167	5.99	0.145		1.41	0.0125	80.0
0.234	4.27	0.215		2.09	0.0185	54.1
0.234	4.27	0.220		2.14	0.0189	53.9
0.234	4.27	0.192		1.87	0.0165	60.6
0.334	2.99	0.308		3.00	0.0265	37.7
0.500	2.00	0.437		4.26	0.0377	26.5
0.667	1.50	0.554		5.39	0.0477	21.0
1.00	1.00	0.594		5.78	0.0512	19.5
1.33	0.752	0.612		5.96	0.0527	19.0

I_a=0.0123 E/l, A_{313} (Aver) = 1.112, $I_a(1-10^{-A})$=0.0113 E/l, [m-Me-ACP]=0.02 M, 313 nm, $[PhCOOC_9]$=9.10 x 10^{-4} M, SF=1.07, 1 hr. irradiation. Gc column A, 155°C. Slope=11.9, intercept=5.68, slope/intercept=2.10.

Table 44. Stern-Volmer Data, 3,4-di-Methylacetophenone and 1.6 M in CH_3CN.

[Q] (10^{-4}), M	DTE/ $PhCOOC_7$		[DTE]	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.42		0.231	
0.0	1.43	1.43±0.00	0.233	1.00
0.879	0.463			3.09
1.70	0.278			5.14
2.17	0.237			6.03
2.55	0.219			6.53
2.55	0.205			6.98

[3,4-Di-Me-ACP]=0.02 M, [$PhCOOC_7$]=0.00200 M, naphthalene quencher, 335 nm, 1 week irradiation time, [p-Xylene]= 1.59 M, solvent, SF=0.813. G.C. Column F, 215°C. $k_q\tau$= 23,077.

		EXP #2		
0.0	1.16		0.160	
0.0	1.05		0.145	
0.0	1.06	1.09±0.005	0.147	1.00
0.297	0.606			1.80
0.593	0.370			2.95
1.19	0.247			4.41
1.19	0.251			4.34
1.48	0.205			5.30

[3,4-Di-Me-ACP]=0.02 M, [$PhCOOC_7$]=0.00170 M, naphthalene quencher, 335 nm, 4 1/2 days irradiation time, [p-xylene] =1.60 M, SF=0.813. G.C. Column F, 215°C. $k_q\tau$=29,000.

Table 45. Reciprocal Plot, 3,4-di-Methylacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_7	[DTE]*	ϕ_{DTE} (10^{-3})	ϕ_{DTE}^{-1}
		EXP #1			
0.167	5.99	0.0877	1.18	4.18	2,392
0.167	5.99	0.0941	1.26	4.47	2,237
0.234	4.27	0.119	1.59	5.64	1,773
0.334	2.99	0.169	2.26	8.01	1,248
0.501	2.00	0.295	2.95	10.5	952
1.34	0.746	0.926	12.6	44.0	227

*x 10^{-4} M, I_a=0.282 E/l, [3,4-Di-Me-ACP]=0.02 M, [PhC_7]= 0.00134 M, SF=0.800, 313 nm, 29 hrs. irradiation time, [Xylene]=1.6 M. G.C. Column F, 215°C. Slope=389, intercept-57.3, slope/intercept=6.8.

		EXP #2			
0.336	2.98	0.0807	1.78	0.748	1,337
0.672	1.49	0.160	3.54	1.49	671
0.840	1.19	0.217	4.80	2.02	495
1.01	0.990	0.239	5.28	2.22	450
1.34	0.746	0.296	6.54	2.75	364
1.34	0.746	0.313	6.92	2.91	344

I_a=0.238 E/l, [3,4-Di-Me-ACP]=0.02 M, [PhC_7]=0.00276 M, SF=0.800, 313 nm, 22 hrs. irradiation, [xylene]=1.6 M. G.C. Column F, 215°C. Slope=407, intercept=43.6, slope/intercept=9.3.

Table 45. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_7	[DTE]*	ϕ_{DTE} (10^{-3})	ϕ_{DTE}^{-1}
		EXP #3			
0.335	2.99	0.176	1.66	0.697	1,435
0.335	2.99	0.179	1.69	0.710	1,408
0.402	2.49	0.210	1.98	0.832	1,202
0.502	1.99	0.266	2.51	1.05	952
0.837	1.19	0.515	4.86	2.04	490
1.34	0.746	0.594	5.61	2.36	424
1.34	0.746	0.638	6.02	2.53	395

I_a=0.238 E/l, [3,4-Di-MeACP]=0.02 M, $[PhC_7]$=0.00118 M, SF=0.800, 313 nm, 22 hrs. irradiation time, [Xylene]=1.6 M. G.C. Column F, 215°C. Slope=464, intercept=28.3, slope/intercept=16.4.

Table 46. Stern-Volmer Data, p-Methoxyacetophenone and 1.6 M p-Xylene in CH_3CN.

$[Q]$ (10^{-5}),M	DTE/ $PhCOOC_9$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	0.549		8.50	
0.0	0.586		9.07	
0.0	0.541	0.559±0.018	8.37	1.00
0.590	0.432			1.29
1.18	0.350			1.60
1.77	0.312			1.79
3.54	0.247			2.26
4.72	0.150			3.73

[p-MeO-ACP]=0.02 M, $[PhCOOC_9]=1.65 \times 10^{-3}$M, naphthalene quencher, 335 nm, 2 weeks irradiation time, [p-xylene]= 1.59 M, SF=0.938. Column A, 195°C. $k_q\tau$=47,368.

		EXP #2		
0.0	0.595		9.38	
0.0	0.544	0.570±0.026	8.57	1.00
0.590	0.416			1.37
1.18	0.380			1.50
1.77	0.317			1.80
2.36	0.318			1.79
4.72	0.200			2.83

[p-MeO-ACP]=0.02 M, $[PhCOOC_9]=1.68 \times 10^{-3}$ M, naphthalene quencher, 335 nm, [p-xylene]=1.60 M, SF=0.938. Column A, 195°C. $k_q\tau$=39,579.

Table 47. Reciprocal Plot, p-Methoxyacetophenone and p-Xylene in CH_3CN.

[Xyl]	$[Xyl]^{-1}$	DTE/PhC_8	[DTE]*	A_{313}	$I_a(1-10^{-A})$	$\phi_{DTE}(10^{-3})$	ϕ_{DTE}^{-1}
			EXP #1				
0.625	1.60	0.226	1.51	1.40	0.0260	5.81	172
0.625	1.60	0.207	1.38	1.41	0.0260	5.31	188
0.625	1.60	0.153	1.02	1.42	0.0260	3.92	255
1.25	0.800	0.336	2.25	1.38	0.0259	8.69	115
1.69	0.592	0.447	2.99	1.36	0.0259	11.5	87.0
1.88	0.532	0.464	3.10	1.36	0.0259	12.0	83.3
2.19	0.457	0.577	3.86	1.34	0.0258	15.0	66.7
2.50	0.400	0.613	4.10	1.33	0.0258	15.9	62.9

*x 10^{-4}, I_a=0.0270 E/l, [p-Me-ACP]=0.01 M. [$PhCOOC_8$]=8.53 x 10^{-4} M, SF=0.784, 313 nm, 6.5 hrs. irradiation. Gc column A, 114°C, slope=118.3, intercept=16.95, slope/intercept=6.98.

			EXP #2				
0.625	1.60	0.178	1.26	1.41	0.0260	4.85	206
0.625	1.60	0.193	1.37	1.41	0.0260	5.27	190
0.625	1.60	0.188	1.33	1.41	0.0260	5.12	197
1.25	0.800	0.350	2.48	1.38	0.0259	9.58	104
1.88	0.532	0.429	3.04	1.36	0.0259	11.7	85.5
2.19	0.457	0.497	3.53	1.35	0.0258	13.7	73.0
2.50	0.400	0.687	4.87	1.31	0.0257	18.9	52.9

I_a=0.0270 E/l, [p-Me-ACP]=0.01 M, [$PhCOOC_8$]=9.05 x 10^{-4} M, SF=0.784, 313, 6.5 hrs. irradiation. Gc column A, 114°C. Slope=112.6, intercept=17.36, slope/intercept=6.49.

Table 47. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	$[DTE](10^{-4})$	$\phi_{DTE}(10^{-3})$	ϕ_{DTE}^{-1}
			EXP #3		
0.234	4.27	0.171	1.19	1.28	781
0.234	4.27	0.177	1.23	1.32	758
0.334	2.99	0.232	1.61	1.73	5.78
0.501	2.00	0.332	2.30	2.48	403
0.668	1.50	0.423	2.93	3.15	317
1.00	1.00	0.669	4.63	4.98	201
1.34	0.746	0.941	6.52	7.02	142

I_a=0.0929 E/l, [p-Me-ACP]=0.02 M, $[PhCOOC_9]$=9.02 x 10^{-4} M, SF=0.768, 313 nm, 8 hrs. irradiation. Gc column A, 115°C. Slope=169.9, intercept=42.85, slope/intercept=3.96.

Table 48. Stern-Volmer Data, p-Cyanoacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q],M(10^{-4})	DTE/$PhCOOC_5$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.12		7.23	
0.0	1.09		7.04	
0.0	1.11	1.11±0.01	7.17	1.00
5.99	0.406			2.46
8.99	0.280			3.96
12.0	0.217			5.12
18.0	0.142			7.82
24.0	0.114			9.74

[p-CN-ACP]=0.02 M, naphthalene quencher, [$PhCOOC_5$]=1.10 x 10^{-3} M, 366 nm, 4.5 hrs. irradiation, [p-Xylene]=1.59 M, SF=0.587. G.C. Column A, 190°C. $k_q\tau$=3,500.

		EXP #2		
0.0	1.29		8.10	
0.0	1.22		7.66	
0.0	1.15		7.22	
0.0	1.12	1.16±0.06	7.03	1.00
3.06	0.721			1.61
4.60	0.546			2.12
6.13	0.380			3.05
9.19	0.275			4.22
10.7	0.244			4.75
12.3	0.247			4.70

[p-CN-ACP]=0.02 M, naphthalene quencher, [$PhCOOC_5$]=1.07 x 10^{-3} M, 366 nm, 4.5 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.587. G.C. Column A, 190°C. $k_q\tau$=3,208.

Table 49. Reciprocal Plot, p-Cyanoacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_5	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0754	13.3	0.515	3.60	6.87	14.6
0.0754	13.3	0.502	3.51	6.70	14.9
0.0754	13.3	0.497	3.47	6.62	15.1
0.113	8.85	0.587	4.10	7.82	12.8
0.113	8.85	0.579	4.04	7.71	13.0
0.113	8.85	0.604	4.22	8.05	12.4
0.151	6.62	0.696	4.86	9.27	10.8
0.301	3.32	0.781	5.46	10.4	9.62
0.452	2.21	0.812	5.61	10.7	9.35
0.667	1.50	0.907	6.34	12.1	8.26
1.33	0.752	0.983	6.87	13.1	7.63

I_a=0.00524 E/l, [p-CN-ACP]=0.02 M, [PhC_5]=0.00119 M, SF= 0.587, 313 nm, 40 min. G.C. Column A, 190°C. Slope=0.558, intercept=7.58, slope/intercept = 0.0736.

Table 49. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_5	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #2			
0.0754	13.3	0.464	2.86	5.46	18.3
0.0754	13.3	0.547	3.37	6.43	15.6
0.0754	13.3	0.534	3.29	6.28	15.9
0.113	8.85	0.638	3.93	7.50	13.3
0.113	8.85	0.630	3.88	7.40	13.5
0.113	8.85	0.613	3.78	7.21	13.9
0.226	4.42	0.730	4.50	8.59	11.6
0.453	2.21	0.928	5.72	10.9	9.17
0.667	1.50	0.986	6.07	11.6	8.62
1.33	0.752	1.01	6.23	11.9	8.40

I_a=0.00524 E/l, [p-CN-ACP]=0.02 M, [PhC_5]=0.00105 M, SF= 0.587, 313 nm, 25 min. G.C. Column A, 190°C. Slope=0.605, intercept=8.00, slope/intercept=0.0756.

Table 50. Stern-Volmer Data, m-Cyanoacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q], (10^{-4})	DTE/ $PhCOOC_5$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	0.218		1.50	
0.0	0.231		1.59	
0.0	0.217	0.222±0.006	1.49	1.00
5.13	0.181			1.23
6.84	0.169			1.31
10.3	0.154			1.44
13.7	0.133			1.67
13.7	0.139			1.60

[m-CN-ACP]=0.02 M, naphthalene quencher, $[PhCOOC_5]$=0.00117 M 313 nm, 5.5 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.587. G.C. Column A, 185°C. $k_q\tau$=455.

		EXP #2		
0.0	0.840		5.28	
0.0	0.971		6.10	
0.0	1.05	0.954±0.076	6.59	1.00
22.0	0.602			1.58
33.1	0.475			2.01
44.1	0.403			2.37
66.1	0.314			3.04
8.82	0.250			3.82

[m-CN-ACP]=0.02 M, naphthalene quencher, $[PhCOOC_5]$=0.00107 M, 313 nm, 48 hrs. irradiation, [p-Xylene]=1.59 M, SF=0.587. G.C. Column A, 185°C. $k_q\tau$=336.

Table 51. Reciprocal Plot, m-Cyanoacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_5	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.0754	13.3	0.383	2.25	0.0167	59.9
0.0754	13.3	0.370	2.17	0.0161	62.1
0.0754	13.3	0.367	2.15	0.0159	62.9
0.113	8.85	0.441	2.59	0.0192	52.1
0.113	8.85	0.460	2.70	0.0200	50.0
0.151	6.62	0.500	2.93	0.0217	46.1
0.226	4.42	0.566	3.32	0.0246	40.7

I_a=0.135 E/l, [m-CN-ACP]=0.02 M, $[PhCOOC_5]$=9.99 x 10^{-4} M, SF=0.587, 313 nm, 1 hr. G.C. Column A, 185°C. Slope=2.21, intercept-29.0, slope/intercept=0.076.

		EXP #2			
0.0753	13.3	0.329	2.16	0.0160	62.5
0.0753	13.3	0.332	2.18	0.0161	61.1
0.0753	13.3	0.338	2.22	0.0164	61.0
0.113	7.52	0.373	2.45	0.0181	35.2
0.113	7.52	0.408	2.68	0.0200	50.0
0.113	7.52	0.394	2.59	0.0199	50.3
0.151	6.62	0.427	2.81	0.0208	48.1
0.226	4.42	0.477	3.14	0.0233	42.9
0.452	2.21	0.574	3.77	2.79	35.5

I_a=0.0135 E/l, [m-CN-ACP]=0.02 M, $[PhCOOC_5]$=0.00112 M, SF=0.587, 313 nm, 1 hr. G.C. Column A, 185°C. Slope=2.04, intercept=34.0, slope/intercept=0.061.

Table 52. Stern-Volmer Data, p-Chloroacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q], $[10^{-4})$	DTE/ $PhCOOC_9$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.17		8.39	
0.0	1.15		8.25	
0.0	1.23	1.18±0.03	8.82	1.00
1.15	0.575			2.05
2.31	0.206			5.73
3.46	0.152			7.76
4.62	0.0984			12.0
[p-Cl-ACP]=0.02 M, hexadiene quencher, $[PhCOOC_9]=9.34 \times 10^{-4}$ M, [Xylene]=1.59 M. SF=0.768. G.C. Column A, 150°C. $k_q\tau=23,391$.				
		EXP #2		
0.0	1.03		5.99	
0.0	1.08		6.28	
0.0	1.17	1.09±0.05	6.80	1.00
1.40	0.244			4.47
2.80	0.132			8.26
3.50	0.0949			11.5
[p-Cl-ACP]=0.02 M, naphthalene quencher, $[PhCOOC_9]=7.57 \times 10^{-4}$ M, [Xylene]=1.60 M. SF=0.768. Column A, 150°C. $k_q\tau=25,000$.				

Table 52. Continued.

[Q], (10^{-5})	DTE/ $PhCOOC_9$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
0.0	0.944	EXP #3	5.60	
0.0	1.01		6.00	
0.0	0.992	0.982±0.025	5.90	1.00
7.02	0.350			2.81
11.7	0.236			4.16
14.1	0.184			5.34
18.7	0.143			6.87

[p-Cl-ACP]=0.02 M, naphthalene quencher, $[PhCOOC_9]$=7.73 x 10^{-4} M, 366 nm, 10 hrs. irradiation, [p-Xylene]=1.60 M; SF=0.768. G.C. Column A, 150°C. $k_q\tau$=29,474.

Table 53. Reciprocal Plot, p-Chloroacetophenone and p-Xylene in CH_3CN.

[Xylene],M	$[Xylene]^{-1}$	DTE/PhC_8	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #3			
0.169	5.92	0.670	4.29	0.0425	23.5
0.169	5.92	0.565	3.62	0.0358	27.9
0.169	5.92	0.653	4.18	0.0414	24.2
0.226	4.42	0.666	4.26	0.0422	23.7
0.226	4.42	0.644	4.12	0.0408	24.5
0.452	2.21	0.945	6.05	0.0599	16.7
0.678	1.47	1.09	6.98	0.0691	14.5
0.903	1.11	1.36	8.70	0.0861	11.6
0.903	1.11	1.22	7.81	0.0773	12.9

I_a=0.0101 E/l, [p-Cl-ACP]=0.02 M, $[PhCOOC_8]=8.79 \times 10^{-4}$ M, SF=0.728, 313 nm, 1 hr. G.C. Column A, 150°C. Slope= 2.75, intercept=10.2, slope/intercept=0.270.

		EXP #2			
0.113	8.85	0.584	4.23	0.0341	29.3
0.170	5.88	0.797	5.77	0.0465	21.5
0.452	2.21	1.73	1.25	0.101	9.90
0.678	1.47	2.12	1.53	0.123	8.13
0.904	1.11	2.41	1.74	0.140	7.14
0.904	1.11	2.31	1.67	0.135	7.41

I_a=0.0124 E/l, [p-Cl-ACP]=0.02 M, $[PhCOOC_9]=9.42 \times 10^{-4}$ M, SF=0.768, 313 nm, 1 hr. G.C. Column A, 150°C. Slope= 2.91, intercept=3.85, slope/intercept=0.756.

Table 53. Continued.

[Xylene],M	$[Xylene]^{-1}$	$DTE/PhC_{\hat{o}}$	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #3			
0.0945	10.6	1.03	6.37	0.0453	22.1
0.113	8.85	1.06	6.55	0.0466	21.5
0.151	6.62	1.28	7.91	0.0563	17.8
0.302	3.31	2.13	1.32	0.0939	10.6
0.302	3.31	2.13	1.32	0.0939	10.6

I_a=0.0136 E/l, A_{313} (aver)=1.477, I_a $(1-10^{-A})$=0.0132 E/l, [p-Cl-ACP]=0.02M, $[PhCOOC_9]$=8.05 x 10^{-4}M, 1 hr. irradiation G.C. Column A, 150°C. Slope=1.52, intercept=5.62, slope/intercept=0.270.

Table 54. Stern-Volmer Data, m-Chloroacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q],M (10^{-3})	DTE/ $PhCOOC_8$		[DTE] (10^{-4})	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	0.886		5.84	
0.0	0.890	0.888±0.002	5.86	1.00
1.28	0.271			3.28
3.83	0.0993			8.94
5.11	0.0756			11.7

[m-Cl-ACP]=0.02 M, hexadiene quencher, [$PhCOOC_8$]=9.05 x 10^{04}M, 313 nm, 1 hr. 40 min. irradiation, [p-Xylene]=1.60 M, SF=0.728. G.C. Column A, 160°C. $k_q\tau$=2,040.

		EXP #2		
0.0	0.853		6.81	
0.0	0.833	0.843±0.001	6.65	1.00
0.0492	0.797			1.06
0.148	0.713			1.18
0.197	0.662			1.27

[m-Cl-ACP]=0.02 M, hexadiene quencher, [$PhCOOC_9$]=1.04 x 10^{-3} M, 313 nm, 1 hr. 50 min. irradiation, [p-Xylene]= 1.59 M, SF=0.768. G.C. Column A, 160°C. $k_q\tau$= 1,300.

Table 54. Continued.

[Q],M (10^{-3})	DTE/ $PhCOOC_8$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #3		
0.0	1.53		9.74	
0.0	1.65		10.5	
0.0	1.56	1.58±0.05	9.93	1.00
1.05	0.555			2.85
1.57	0.397			3.98
2.10	0.311			5.08
[m-Cl-ACP]=0.02 M, hexadiene quencher, [$PhCOOC_9$]=8.29 x 10^{-4} M, 313 nm, 2.5 hrs. irradiation, [p-Xylene]=1.60 M, SF= 0.768. G.C. Column A, 160°C. $k_q\tau$=1,905.				
		EXP #4		
0.0	2.01		1.36	
0.0	2.50		1.69	
0.0	2.58		1.74	
0.0	2.43		1.64	
0.0	2.22	2.35±0.31	1.59	1.00
3.85	1.11			2.12
11.6	0.514			4.57
15.4	0.405			5.80
[m-Cl-ACP]=0.02 M, naphthalene quencher, [$PhCOOC_9$]=8.78 x 10^{-4} M, 366 nm, 5.5 days irradiation, [p-Xylene]=1.60 M, SF=0.768. G.C. Column A, 160°C. $k_q\tau$=3,000.				

Table 54. Continued.

[Q],M [10^{-3})	[DTE] $PhCOOC_8$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #5		
0.0	0.612		8.55	
0.0	0.586		8.19	
0.0	0.598	0.599±0.009	8.36	1.00
2.71	0.420			1.43
4.06	0.406			1.48
5.42	0.325			1.84
8.12	0.245			2.43
10.8	0.220			2.72
10.8	0.249			2.41

[m-Cl-ACP]=0.02 M, naphthalene quencher, $[PhC_9]=1.82 \times 10^{-3}$ M, SF=0.768, [p-Xylene]=1.60 M. G.C. Column A, 160°C. $k_q\tau=1,564$.

Table 55. Reciprocal Plot, m-Chloroacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.113	8.85	0.210	1.87	0.0403	24.8
0.113	8.85	0.204	1.82	0.0392	25.5
0.170	5.88	0.262	2.33	0.0502	19.9
0.170	5.88	0.254	2.26	0.0487	20.5
0.226	4.42	0.274	2.44	0.0526	19.0
0.453	2.21	0.358	3.19	0.0688	14.5
0.679	1.47	0.408	3.64	0.0784	12.8
0.906	1.10	0.433	3.86	0.0832	12.0

I_a=0.00464 E/l, [m-Cl-ACP]=0.02 M, SF=0.768, $[PhCOOC_9]$= 1.16×10^{-3} M, 313 nm, 48 min. irradiation. G.C. Column A, 160°C. Slope=1.72, intercept=8.45, slope/intercept=0.204.

		EXP #2			
0.113	8.85	0.309	1.95	0.0420	23.8
0.113	8.85	0.314	1.98	0.0427	23.4
0.113	8.85	0.292	1.84	0.0397	25.2
0.170	5.88	0.442	2.79	0.0601	16.6
0.170	5.88	0.407	2.57	0.0554	18.1
0.170	5.88	0.385	2.43	0.0524	19.1
0.452	2.21	0.607	3.83	0.0825	12.1
0.678	1.47	0.643	4.05	0.0873	11.5
0.904	1.11	0.703	4.43	0.0955	10.5
0.904	1.11	0.719	4.53]	0.0976	10.2

I_a=0.00464 M [m-Cl-ACP]=0.02 M, SF=0.768, $[PhCOOC_9]$=8.21 x 10^{-4}M, G.C. Column A, 160°C. Slope=1.68, intercept= 10.57, slope/intercept=0.159.

Table 56. Stern-Volmer Data, m-Trifluoromethylacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q], M (10^{-3})	$PhCOOC_9$		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.75		11.1	
0.0	1.75		11.1	
0.0	2.31	1.94±0.25	14.7	1.00
2.59	0.564			3.44
5.18	0.289			6.71
7.77	0.242			8.02

[m-CF_3-ACP]=0.02 M, naphthalene quencher, [$PhCOOC_9$]=8.29 x 10^{-4} M, 366 nm, 27.5 hrs. irradiation, [p-Xylene]=1.60, SF=0.768. G.C. Column A, 155°C. $k_q\tau$=975.

		EXP #2		
0.0	0.844		7.32	
0.0	0.848		7.36	
0.0	0.899	0.864±0.024	7.80	1.00
8.18	0.553			1.56
16.4	0.393			2.20
24.5	0.282			3.06
32.7	0.201			4.30

[m-CF_3-ACP]=0.02 M, naphthalene quencher, [$PhCOOC_9$]=1.13 x 10^{-3} M, 366 nm, 25 hrs. irradiation, [p-Xylene]=1.60 M, SF=0.768. G.C. Column A, 155°C. $k_q\tau$=872.

Table 57. Reciprocal Plot, m-Trifluoromethylacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.0341	29.3	0.387	2.63	0.0353	28.3
0.0341	29.3	0.405	2.76	0.0370	27.0
0.0681	14.7	0.596	4.06	0.0544	18.4
0.136	7.35	0.974	6.63	0.0889	11.2
0.335	2.99	1.11	7.55	0.101	9.90
1.34	0.746	1.16	7.89	0.106	9.43
1.34	0.746	1.55	1.05	0.141	7.09

I_a=0.00746 E/l, [m-CF_3-ACP]=0.02 M, SF=0.768, [PhC_9]=8.86 x 10^{-4} M, 313 nm, 4.5 hrs. irradiation. G.C. Column A, 155°C. Slope=0.693, intercept=7.47, slope/intercept=0.0928.

		EXP #2			
0.0454	22.0	0.560	3.74	0.0501	20.0
0.136	7.35	1.02	6.82	0.0914	10.9
0.335	2.99	1.28	8.55	0.115	8.70
0.134	7.46	1.45	9.69	0.130	7.70
0.134	7.46	1.39	9.29	0.125	8.00
0.134	7.46	1.64	11.0	0.147	6.80

I_a=0.00746 E/l, [m-CF_3ACP]=0.02 M, SF=0.768, [PhC_9]=8.70 x 10^{-4} M, 313 nm, 4.5 hrs. irradiation. G.C. Column A, 155° C. Slope=0.585, intercept=6.96, slope/intercept=0.0841.

Table 58. Stern-Volmer, p-Trifluoromethylacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q], M (10^{-4})	DTE/PhC_9		[DTE], M (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.21		7.26	
0.0	1.17		7.02	
0.0	1.12		6.72	
0.0	1.29	1.20±0.05	7.74	1.00
6.93	0.767			1.56
9.24	0.709			1.69
9.24	0.725			1.66
9.24	0.643			1.87

[p-CF_3-ACP]=0.02 M, naphthalene quencher, [PhC_9]=7.81 x 10^{-4} M, 366 nm, [p-Xylene]=1.60 M, 8.5 hrs. irradiation, SF=0.768. G.C. Column A, 152°C. $k_q\tau$=811.

		EXP #2		
0.0	1.12		7.34	
0.0	1.04		6.81	
0.0	0.961	1.04±0.05	6.30	1.00
20.1	0.273			3.81
30.1	0.192			5.42
40.2	0.130			8.00

[p-CF_3-ACP]=0.02 M, naphthalene quencher, [PhC_9]=8.53 x 10^{-4} M, 366 nm, [p-Xylene]=1.60 M, 4.5 hrs. irradiation, SF=0.768. G.C. Column A, 152°C. $k_q\tau$=1,600.

Table 58. Continued.

[Q], M (10^{-4})	DTE/PhC_9		[DTE], M (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #3		
0.0	1.16		6.67	
0.0	0.996		5.73	
0.0	1.04		5.98	
0.0	1.08	1.07±0.05	6.21	1.00
1.29	0.409			2.62
1.61	0.338			3.17
1.93	0.279			3.84
2.57	0.264			4.05
2.57	0.193			5.54

$[p\text{-}CF_3\text{-}ACP]$=0.02 M, naphthalene quencher, $[PhC_9]$=7.49 x 10^{-4} M, 366 nm, [p-Xylene]=1.60 M, 4.0 hrs. irradiation, SF=0.768. G.C. A, 152°C. $k_q\tau$=1,404.

Table 59. Reciprocal Plot, p-Trifluoromethylacetophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0454	22.0	1.03	6.82	7.26	13.8
0.0454	22.0	1.06	7.02	7.48	13.4
0.0454	22.0	1.05	6.95	7.40	13.5
0.0682	14.7	1.35	8.94	9.52	10.5
0.0909	11.0	1.60	1.06	11.3	8.85
0.114	0.772	1.64	1.09	11.6	8.62
0.136	7.35	1.77	1.17	12.5	8.00
0.182	5.49	1.96	1.30	13.8	7.25
0.182	5.49	1.82	1.20	12.8	7.81
0.182	5.49	2.00	1.32	14.1	7.09

A_{313} (Aver.)=0.858, I_a=0.0109, I_a $(1-10^{-A})$=0.00939 E/1, [p-CF_3-ACP]=0.02 M, SF=0.768, [PhC_9]=8.62 x 10^{-4} M, 313 nm, 1 hr. 40 min. irradiation. C.G. Column A, 152°C. Slope= 0.366, intercept=5.33, slope/intercept=0.0687.

		EXP #2			
0.0343	29.2	1.10	6.67	7.13	14.0
0.0343	29.2	0.947	5.74	6.14	16.3
0.0457	21.9	1.23	7.45	7.97	12.5
0.0457	21.9	1.21	7.33	7.84	12.8
0.0913	11.0	1.64	9.94	10.6	9.43
0.114	8.77	1.79	10.8	11.6	8.62
0.137	7.30	1.89	11.5	13.2	7.58
0.183	5.46	1.93	11.7	13.5	7.41

A_{313} (Aver.)=0.849, I_a=0.0109 E/1, I_a $(1-10^{-A})$=0.00935 E/1, [p-CF_3-ACP]=0.02 M, SF=0.768, [PhC_9]=7.89 x 10^{-4} M, 313 nm, 1 hr. 40 min. irradiation. G.C. Column A, 152°C. Slope= 0.330, intercept=5.56, slope/intercept=0.0594.

Table 59. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #3			
0.0346	28.9	0.480	3.18	9.01	11.0
0.0346	28.7	0.530	3.50	9.92	10.1
0.0461	21.7	0.655	4.34	12.3	8.13
0.115	8.70	0.888	5.88	16.7	5.99
0.138	7.25	0.993	6.57	18.6	5.38
0.184	5.43	1.12	7.42	21.0	4.76

I_a=0.00353 E/l, [p-CF_3-ACP]=0.02 M, SF=0.768, [PhC_9]= 8.62×10^{-4} M, 313 nm, 32 min. irradiation. G.C. Column A, 152°C. Slope=0.228, intercept=3.70, slope/intercept= 0.0616.

Table 60. Stern-Volmer Data, p-tert-Butylacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q] (10^{-4})	DTE/PhC_9		[DTE] (10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
0.0	1.88		15.2	
0.0	1.84		14.8	
0.0	1.79	1.84±0.03	14.4	1.00
1.42	0.494			3.72
2.85	0.310			5.94
3.56	0.232			7.93

[p-t-Bu-ACP]=0.02 M, naphthalene, [PhC_9]=0.00105 M, 335 nm, [p-Xylene]=1.58 M, SF=0.768. G.C. Column A, 163°C. $k_q\tau$= 18,333.

Table 61. Reciprocal Plot, p-tert-Butylacetophenone and p-Xylene in CH_3CN.

[Xyl]	$[Xyl]^{-1}$	DTE/PhC_9	$[DTE](10^{-3})$	A_{313}	$(1-10^{-A})I_a$	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #1				
0.335	3.00	0.864	1.13	1.425	0.0717	0.0157	63.7
0.502	1.99	0.846	1.11	1.419	0.0717	0.0154	64.9
0.669	1.49	1.49	1.95	1.28	0.0706	0.0275	36.4
0.847	1.19	1.86	2.43	1.23	0.0701	0.0346	28.9
1.00	1.00	1.91	2.49	1.201	0.0698	0.0357	28.0
1.34	0.746	1.73	2.26	1.242	0.0702	0.0322	31.1

I_a=0.0745 E/1, [p-t-Bu-ACP]=0.02 M, $[PhC_9]$=0.00170 M, SF=0.768, 313 nm, 3 hrs. irradiation time. Gc column A, 163°C. Slope=16.3, intercept=15.8, slope/intercept=1.03.

			EXP #2				
0.334	2.99	1.03	1.31	1.365	0.151	0.0829	121
0.501	2.00	1.72	2.19	1.261	0.149	0.139	71.9
0.668	1.50	1.66	2.11	1.247	0.149	0.134	74.6
0.835	1.20	1.70	2.16	1.232	0.149	0.137	73.0
1.00	1.00	2.40	3.06	1.217	0.148	0.194	51.5
1.34	0.746	2.43	3.09	1.141	0.147	0.196	51.0

I_a=0.158 E/1, [p-t-Bu-ACP]=0.02 M, $[PhC_9]$=0.00168 M, SF=0.768, 313 nm. 6 hrs. irradiation time. Gc column A, 163°C.

Note: A_{313} is the average of initial (pre-irradiation) and final A_{313} nm. Slope=31.6, intercept=27.2, slope/intercept=1.16.

Table 61. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/PhC_9	$[DTE](10^{-4})$	A_{313}	$I_a(1-10^{-A})$	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #3				
0.334	2.99	0.384	0.319	1.483	0.0237	0.0134	74.6
0.334	2.99	1.36	1.13	1.316	0.0741	0.0152	65.8
1.00	1.00	2.62	2.17	1.214	0.0731	0.0297	33.7
1.34	0.746	3.28	2.72	1.079	0.0714	0.0381	26.2
1.34	0.746	2.93	2.43	1.120	0.0720	0.0338	29.6

I_a=0.0779 E/l, [p-t-Bu-ACP]=0.02 M, $[PhCOOC_9]$=0.00108 M, SF=0.768, 313 nm, 3.5 hrs. irradiation time. Gc column A, 163°C. Slope=18.7, intercept=14.5, slope/intercept= 1.29.

Table 62. Stern-Volmer Data, p-Acetylacetophenone and 1.6 M p-Xylene in CH_3CN.

[Q] (10^{-4})	DTE/ $PhCOOC_7$		[DTE] (10^{-3})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	5.98		7.59	
0.0	5.45		6.92	
0.0	5.27	5.57±0.28	6.69	1.00
2.78	3.16			1.76
5.56	1.94			2.26
11.1	1.04			4.22
[p-CH_3CO-ACP]=0.03 M, naphthalene quencher, [$PhCOOC_7$] =0.00156 M, SF=0.813, 335 nm, 6 hrs. irradiation time, [p-Xylene]=1.59 M. G.C. Column A, 180°C. $k_q\tau$=2,727.				
		EXP #2		
0.0	5.42		5.85	
0.0	5.25		5.67	
0.0	5.14	5.27±0.10	5.55	1.00
2.76	2.94			1.66
5.52	1.72			2.83
5.52	1.76			2.77
8.27	1.21			4.02
11.0	0.869			5.61
11.0	0.920			5.30
[p-CH_3-CO-ACP]=0.03 M, naphthalene quencher, [$PhCOOC_7$] =0.00133 M, SF=0.813, 335 nm, 3 hrs. irradiation time, [p-Xylene]=1.58 M. G.C. Column A, 180°C. $k_q\tau$=3,455.				

Table 63. Reciprocal Plot, p-Acetylacetophenone and p-Xylene in CH_3CN.

[Xyl]	$[Xyl]^{-1}$	DTE/ PhC_7	[DTE] (10^{-3})	ϕDTE (10^{-2})	ϕ_{DTE}^{-1}
0.313	3.19	1.76	1.04	3.33	30.0
0.313	3.19	1.77	1.04	3.33	30.0
0.470	2.13	2.01	1.19	3.81	26.2
0.470	2.13	2.04	1.20	3.85	26.0
6.26	1.60	2.22	1.31	4.20	23.8
0.940	1.06	2.49	1.46	4.71	21.2
1.25	0.800	2.54	1.50	4.81	20.8
2.51	0.398	2.49	1.47	4.71	21.2

I_a=0.0312 E/l, [p-CH_3CO-ACP]=0.013 M, [PhC_7]=7.26 x 10^{-4} M, SF=0.813, 2 hrs. irradiation time, xyl=p-xylene. G.C. Column A, 180°C. Slope-3.98, intercept=17.4, slope/intercept=0.229.

Table 64. Stern-Volmer Data, Acetophenone and 1.3 M Toluene in CH_3CN.

$[Q](10^{-5})$	BB/PhC_7	$[BB](10^{-4})$	$\phi^{\circ}_{BB}/\phi_{BB}$
	EXP #1		
0.0	0.189	7.39	1.00
4.24	0.115		1.64
8.49	0.0926		2.04
12.7	0.0863		2.19
17.0	0.0702		2.69
21.2	0.0602		3.14
25.5	0.0550		3.44

[ACP]=0.05 M, 2% aq. CH_3CN, naphthalene quencher, $[PhC_7]$= 4.14×10^{-3} M, 366 nm, [Toluene]=1.26 M, SF=0.945. G.C. Column A. $k_q\tau$=9,804.

Table 65. Stern-Volmer Data, Acetophenone and 1 M p-di-iso-Propylbenzene in CH_3CN.

[Q] (10^{-4})	HdC/PhC_{10}		[HdC](10^{-3})	$\phi°/\phi$
		EXP #1		
0.0	4.45		1.97	
0.0	4.64	4.55	2.05	1.00
3.44	3.70		1.64	1.23
8.61	3.01		1.33	1.51
10.3	2.78		1.23	1.64
13.8	2.65		1.17	1.72

[ACP]=0.02 M, hexadiene quencher, $[PhC_{10}]=6.63 \times 10^{-4}$ M, 313 nm, SF=0.667, 10.5 hrs. irradiation time, [Diisopropylbenzene]=1.04 M, HdC=the bibenzyl coupling product. G.C. Column A, 176°C. $k_q\tau=571$.

		EXP #2		
0.0	1.12		0.508	
0.0	1.12	1.12	0.508	1.00
10.4	0.746		0.339	1.50
15.6	0.648		0.294	1.73
20.8	0.548		0.249	2.04
26.0	0.541		0.246	2.07
41.5	0.369		0.168	3.04

[ACP]=0.02 M, hexadiene quencher, CH_3CN solvent, $[PhC_{10}]=6.71 \times 10^{-4}$ M, 313 nm, SF=0.667, 4 hrs. 15 min. irradiation time, [Diisopropyl benzene]=1.05 M, HdC=the bibenzyl coupling product. G.C. Column A, 176°C. $k_q\tau=471$.

Table 66. Reciprocal Plot, Acetophenone and p-di-iso-propylbenzene in CH_3CN.

[DIPB]	$[DIPB]^{-1}$	Prod/ PhC_{10}	[Prod] (10^{-4})	$\phi(10^{-3})$	ϕ^{-1}
0.0500	20.0	0.719	3.62	7.39	135
0.0500	20.0	0.723	3.64	7.43	135
0.0500	20.0	0.709	3.57	7.29	137
0.100	10.0	0.816	4.11	8.39	119
0.100	10.0	0.748	3.77	7.69	130
0.125	8.00	0.810	4.08	8.33	120
1.00	1.00	0.938	4.72	9.63	104
2.00	0.500	1.04	5.24	10.7	93.5
2.00	0.500	0.995	5.01	10.2	98.0

I_a=0.0490 E/l, [ACP]=0.0212 M, $[PhC_{10}]=7.55 \times 10^{-4}$ M, SF= 0.667, 313 nm, 6 hrs. irradiation, DIPB=diisopropylbenzene, Prod=the bibenzyl. G.C. Columb A, 192°C. Slope=1.94, intercept=100.7, slope/intercept=0.0193.

Table 67. Stern-Volmer Data, Benzophenone and 0.5 M p-Xylene in CH_3CN.

[Q],M(10^{-4})	DTE/PhC_8		[DTE](10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.12		7.49	
0.0	1.12		7.49	
0.0	1.04	1.09±0.04	6.96	1.00
1.87	0.670			1.63
3.73	0.502			2.17
5.60	0.410			2.66
7.47	0.354			3.08
1.12	0.264			4.13
1.49	0.215			5.07

[Benzophenone]=0.05 M, naphthalene quencher, [PhC_8]=7.68 x 10^{-4}M, 366 nm, 3.5 hrs. irradiation, [p-Xylene]=0.500 M, SF=0.871. G.C. Column A, 115°C. $k_q\tau$=2,900.

		EXP #2		
0.0	0.951		6.36	
0.0	0.971		6.50	
0.0	1.01		6.76	
0.0	0.947	0.970±0.02	6.34	1.00
1.75	0.652			1.49
3.50	0.472			2.06
5.24	0.375			2.59
6.99	0.319			3.04
10.5	0.255			3.80
14.0	0.188			5.16

[Benzophenone]=0.05 M, naphthalene quencher, [PhC_8]=1.24 x 10^{-3} M, 366 nm, 4 hrs. irradiation. [p-Xylene]=0.500 M, SF=0.871. G.C. Column A, 115°C. $k_q\tau$=3,000.

Table 68. Reciprocal Plot, Benzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.188	5.32	1.35	8.33	0.0471	21.2
0.282	3.53	1.51	9.31	0.0526	19.0
0.376	2.66	1.51	9.31	0.0526	19.0
0.470	2.13	1.55	9.56	0.0540	18.5
0.564	1.77	1.64	10.1	0.0571	17.5
I_a=0.0177 E/l, [BP]=0.0500 M, SF=0.871, $[PhC_8]$=7.08 x 10^{-4} M, 313 nm. G.C. Column A, 115°C. Slope = 0.97, intercept= 15.8, slope/intercept=0.0530.					
		EXP #2			
0.0250	40.0	0.374	2.89	0.0151	66.2
0.0500	20.0	0.628	4.86	0.0253	39.5
0.100	10.0	0.915	7.08	0.0369	27.1
0.150	6.67	1.02	7.89	0.0410	24.4
0.250	4.00	1.19	9.20	0.0479	20.9
0.500	2.00	1.30	10.1	0.0526	19.0
0.752	1.33	1.38	1.07	0.0557	18.0
1.00	1.00	1.40	1.08	0.0563	17.8
I_a=0.0192 E/l, [BP]=0.05 M, SF=0.871, $[PhC_8]$=8.88 x 10^{-4} M, 313 nm, 1 hr. irradiation. G.C. Column A, 115°C. Slope = 1.23, intercept=16.2, slope/intercept=0.0759.					

Table 68. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #3			
0.0250	40.0	0.116	1.21	0.0215	46.5
0.0250	40.0	0.113	1.18	0.0210	47.6
0.0500	20.0	0.178	1.86	0.0331	30.2
0.0750	13.3	0.209	2.18	0.0388	25.8
0.100	10.0	0.236	2.47	0.0440	22.7
0.150	6.66	0.252	2.63	0.0468	21.4
0.200	5.00	0.275	2.87	0.0511	19.6
0.501	2.00	0.345	3.61	0.0642	15.6
1.00	1.00	0.392	4.10	0.0732	13.7

I_a=0.00562 E/l, [BP]=0.05 M, SF=0.871, $[PhC_8]=1.20 \times 10^{-3}$ M, 313 nm, 1 hr. irradiation. G.C. Column A, 115°C. Slope= 0.81, intercept=14.4, slope/intercept=0.0563.

Table 69. Reciprocal Plot, Benzophenone and Toluene in CH_3CN.

[Tol]	$[Tol]^{-1}$	BB/ $PhCOOC_7$	[BB] (10^{-3})	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}	Aver.
0.218	4.59	1.88[a]	1.71	1.45	69.9	69.0
0.261	3.83	2.17[a]	1.97	1.67	59.9	59.6
0.261	3.83	2.19[a]	1.99	1.69	59.2	
0.348	2.87	2.68[a]	2.44	2.07	48.3	48.1
0.348	2.87	2.72[a]	2.47	2.09	47.8	
1.30	0.769	1.52[b]	1.25	5.21	19.2	19.1
1.30	0.769	1.54[b]	1.27	5.29	18.9	
1.96	0.510	1.72[b]	1.42	5.92	16.9	17.3
1.96	0.510	1.67[b]	1.37	5.71	17.5	
2.61	0.383	1.75[b]	1.44	6.00	16.7	16.8
2.61	0.383	1.72[b]	1.42	5.92	16.9	

[a] $[PhCOOC_7]=9.62 \times 10^{-4}$ M; $I_a=0.118$ E/l.

[b] $[PhCOOC_7]=8.71 \times 10^{-4}$ M; $I_a=0.0240$ E/l.

[BP]=0.05 M, SF=0.945, 313 nm. G.C. Column A, 190°C.
Slope=12.7, intercept=10.8, slope/intercept-1.18.

Table 70. Reciprocal Plot, Benzophenone and $Toluene_{d-8}$ in CH_3CN.

$[Tol_{d-8}]$	$[Tol_{d-8}]^{-1}$	BB/ $PhCOOC_7$	[BB] (10^{-3})	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}	Aver.
0.785	1.27	2.30	1.38	1.31	76.3	75.8
0.785	12.7	2.33	1.40	1.33	75.2	
1.05	0.952	2.92	1.75	1.67	59.9	59.0
1.05	0.952	3.02	1.81	1.72	58.1	
3.06	0.327	4.04	2.42	2.30	43.5	42.7
3.06	0.327	4.18	2.51	2.39	41.8	
1.56	0.641	5.70	3.42	3.26	30.7	30.1
1.56	0.641	5.94	3.56	3.39	29.5	

[BP]=0.067 M, $[PhCOOC_7]=6.35 \times 10^{-4}$M, SF=0.945, 313 nm, 10 hrs. irradiation. G.C. Column A, 180°C. Slope=48.9, intercept=12.9, slope/intercept=3.79.

Table 71. Stern-Volmer Data, p-Chlorobenzophenone and 0.5 p-Xylene in CH_3CN.

[Q],M(10^{-4})	DTE/PhC_8		[DTE](10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	0.924		7.35	
0.0	0.890		7.08	
0.0	0.863		6.86	
0.0	0.955	0.908±0.032	7.59	1.00
1.41	0.635			1.43
2.82	0.508			1.79
4.22	0.421			2.16
5.63	0.374			2.43
8.45	0.301			3.02
11.3	0.234			3.88

[p-Cl-BP]=0.05 M, naphthalene quencher, [PhC_8]=9.13 x 10^{-4} M, 366 nm, 1 hr. irradiation, [p-Xylene]=0.502 M, SF=0.871. G.C. Column A, 147°C. $k_q\tau$=2,500.

		EXP #2		
0.0	1.01		7.50	
0.0	1.04		7.73	
0.0	0.985	1.01±0.01	7.32	1.00
1.47	0.728			1.39
2.93	0.573			1.76
4.40	0.489			2.07
5.87	0.414			2.44
8.80	0.324			3.12
11.7	0.261			3.87

[p-Cl-BP]=0.05 M, naphthalene quencher, [PhC_8]=8.53 x 10^{-4} M, 366 nm, 1 hr. 44 min. irradiation [p-Xylene]=0.508 M, SF=0.871. G.C. Column A, 147°C. $k_q\tau$=2,470.

Table 72. Reciprocal Plot, p-Chlorobenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0251	39.8	0.157	2.12	2.75	36.4
0.0251	39.8	0.169	2.28	2.96	33.8
0.0251	39.8	0.161	2.17	2.81	35.6
0.0502	19.9	0.257	3.47	4.50	22.2
0.0753	13.3	0.288	3.89	5.05	19.8
0.100	10.0	0.320	4.32	5.60	17.9
0.151	6.62	0.357	4.82	6.25	16.0
0.201	4.98	0.391	5.28	6.85	14.6
0.500	2.00	0.494	6.67	8.65	11.6
1.00	1.00	0.530	7.16	9.23	10.8
I_a=0.00771 E/l, [p-Cl-BP]=0.05 M, SF=0.871, $[PhC_8]$=1.55 x 10^{-3}M, 313 nm, 40 min. irradiation. Gc column A, 147°C. Slope=0.61, intercept=11.1, slope/intercept=0.0548.					
		EXP #2			
0.0248	40.3	0.211	1.37	3.33	30.0
0.0248	40.3	0.206	1.33	3.23	31.0
0.0248	40.3	0.201	1.30	3.16	31.6
0.0497	20.1	0.293	1.90	4.61	21.7
0.0745	13.4	0.348	2.25	5.46	18.3
0.0993	10.1	0.378	2.45	5.95	16.8
0.149	6.71	0.433	2.80	6.80	14.7
0.199	5.03	0.483	3.13	7.60	13.2
0.500	2.00	0.576	3.73	9.05	11.0
1.00	1.00	0.643	4.16	1.01	9.90
I_a=4.12 x 10^{-3} E/l, [p-Cl-BP]=0.05 M, SF=0.871, $[PhC_8]$= 7.43 x 10^{-4} M, 313 nm. Gc column A, 147°C. Slope=0.51, intercept=10.7, slope/intercept=0.0474.					

Table 73. Stern-Volmer Data, p-Trifluoromethylbenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_8		$[DTE](10^{-4})$	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
0.0	1.06	EXP #1	7.72	
0.0	1.16		8.45	
0.0	1.10	1.11±0.04	8.01	1.00
3.35	0.910			1.22
5.03	0.881			1.26
6.70	0.797			1.39
10.1	0.652			1.70
13.4	0.544			2.04

$[p\text{-}CF_3\text{-}BP]$=0.05 M, $[PhC_8]$=8.36 x 10^{-4}M, naphthalene quencher, 366 nm, 5 hrs. 43 min. irradiation, [p-Xylene]=0.501 M, SF=0.871. G.C. Column A, 180°C. $k_q\tau$=678.

		EXP #2		
0.0	0.996		7.85	
0.0	1.11		8.75	
0.0	1.02		8.04	
0.0	0.974	1.03±0.05	7.68	1.00
0.790	0.686			1.50
1.58	0.448			2.30
2.37	0.367			2.81
3.16	0.277			3.72

$[p\text{-}CF_3\text{-}BP]$=0.05 M, $[PhC_8]$=9.05 x 10^{-4} M, naphthalene quencher, 366 nm, 5 hrs. 45 min. irradiation, [p-Xylene]=0.501 M, SF=0.871. G.C. Column A, 180°C. $k_q\tau$=789.

Table 74. Reciprocal Plot, p-Trifluoromethylbenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.0126	79.4	0.364	2.90	2.25	44.5
0.0126	79.4	0.364	2.90	2.25	44.5
0.0251	39.8	0.531	4.22	3.27	30.6
0.0377	26.5	0.605	4.81	3.73	26.8
0.0502	19.9	0.664	5.28	4.09	24.4
0.0754	13.3	0.719	5.72	4.43	22.6
0.100	10.0	0.745	5.92	4.59	21.8
0.250	4.00	0.836	6.65	5.16	19.4
0.500	2.00	0.884	7.03	5.45	18.3
I_a=0.0129 E/l, [p-CF_3-BP]=0.05 M, [PhC_8]=9.13 x 10^{-4} M, SF=0.871, 2 hrs. irrad. Gc column A, 180°C. Slope=0.33, intercept=18.8, slope/intercept=0.0183.					
		EXP #2			
0.0127	78.7	0.232	2.71	2.24	44.6
0.0127	78.7	0.238	2.78	2.30	43.5
0.0254	39.4	0.344	4.01	3.31	30.2
0.0381	26.2	0.397	4.63	3.83	26.1
0.0508	19.7	0.440	5.14	4.25	23.5
0.0762	13.1	0.467	5.45	4.50	22.2
0.102	9.80	0.501	5.85	4.82	20.7
0.249	4.02	0.508	5.93	4.90	20.4
0.498	2.01	0.572	6.68	5.52	18.1
I_a=0.0121 E/l, [p-CF_3-BP]=0.05 M, [PhC_8]=1.34 x 10^{-4}, SF =0.871, 2 hrs. irradiation. Gc column A, 180°C. Slope= 0.33, intercept=17.7, slope/intercept=0.0186.					

Table 75. Reciprocal Plot, p-Trifluoromethylbenzophenone and Toluene in CH_3CN.

[Tol]	$[Tol]^{-1}$	BB/ $PhCOOC_7$	[BB] (10^{-4})	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}	Aver.
0.0652	15.3	0.318[a]	4.36	2.10	47.6	47.5
0.0652	15.3	0.320[a]	4.38	2.11	47.4	
0.0869	11.5	0.373[a]	5.11	2.46	40.5	
0.0869	11.5	0.433[a]	5.93	2.85	35.1	35.8
0.0869	11.5	0.482[a]	6.60	3.17	31.5	
0.348	2.87	1.05[a]	14.4	6.92	14.5	
0.348	2.87	0.840[a]	11.5	5.53	18.1	16.7
0.348	8.87	0.860[a]	11.8	5.67	17.6	
0.392	2.55	0.930[b]	9.49	10.1	9.90	9.63
0.392	2.55	0.994[b]	10.1	10.7	9.35	
0.522	1.92	1.25[b]	12.8	13.6	7.35	7.68
0.522	1.92	1.16[b]	11.8	12.5	8.00	
1.04	0.962	1.21[b]	12.3	13.1	7.63	7.66
1.04	0.962	1.20[b]	12.2	13.0	7.69	

[a] $[PhCOOC_7]=1.45 \times 10^{-3}$ M; $I_a=0.0208$ E/1.

[b] $[PhCOOC_7]=1.08 \times 10^{-3}$ M; $I_a=0.00942$ E/1.

$[pCF_3BP]=0.05$ M, SF=0.945, 313 nm. Gc column A, 180°C. Slope=2.78, intercept=4.54, slope/intercept=0.612.

Table 76. Reciprocal Plot, p-Trifluoromethylbenzophenone and Toluene-d_8 in CH_3CN.

[Tol-d_8]	[Tol-d_8]$^{-1}$	BB/ $PhCOOC_7$	[BB] (10^{-4})	ϕ_{BB} (10^{-3})	ϕ_{BB}^{-1}	Av.
0.0875	11.4	0.102[a]	1.20	5.77	173	
0.0875	11.4	0.105[a]	1.24	5.96	168	169
0.0875	11.4	0.107[a]	1.26	6.06	165	
0.350	2.86	0.331[a]	3.91	18.8	53.2	
0.350	2.86	0.336[a]	3.96	19.0	52.6	53.5
0.350	2.86	0.323[a]	3.81	18.3	54.6	
0.523	1.91	0.868[b]	8.85	26.3	38.0	37.9
0.523	1.91	0.874[b]	8.91	26.5	37.7	
0.916	1.09	0.980[b]	10.0	29.8	33.6	33.4
0.916	1.09	0.993[b]	10.1	30.1	33.2	
1.05	0.952	1.17[b]	11.9	35.4	28.2	

[a] $[PhCOOC_7]=1.25 \times 10^{-3}$ M; $I_a=0.0208$ E/l.

[b] $[PhCOOC_7]=1.08 \times 10^{-3}$ M; $I_a=0.0336$ E/l.

[p-CF_3BP]=0.05 M, SF=0.945, 313 nm. Gc column A, 180°C. Slope=13.4, intercept=15.4, slope/intercept=0.870.

Table 77. Stern-Volmer Data, m-Trifluoromethylbenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_8		$[DTE](10^{-4})$	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.08		7.15	
0.0	1.17		7.75	
0.0	1.11		7.35	
0.0	1.13	1.12±0.03	7.48	1.00
9.86	0.664			1.69
14.8	0.573			1.95
19.7	0.557			2.01
29.6	0.414			2.71
34.5	0.352			3.18
39.4	0.362			3.09

$[m\text{-}CF_3\text{-}BP]$=0.05 M, naphthalene quencher, $[PhC_8]$=7.60 x 10^{-4} M, 366 nm, 3.5 hrs. irradiation, [p-Xylene]=0.501 M, SF= 0.871. G.C. Column B, 150°C. $k_q\tau$=589.

		EXP #2		
0.0	0.785		5.96	
0.0	0.748		5.68	
0.0	0.744		5.64	
0.0	0.721	0.750±0.04	5.47	1.00
13.4	0.410			1.83
26.8	0.278			2.70
47.0	0.183			4.10

$[m\text{-}CF_3\text{-}BP]$=0.05 M, naphthalene quencher, $[PhC_8]$=8.71 x 10^{-4} M, 366 nm, 5 hrs. irradiation, [p-Xylene]=0.500 M, SF= 0.871. Column B, 150°C. $k_q\tau$=630.

Table 78. Reciprocal Plot, m-Trifluoromethylbenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE} (10^{-3})	ϕ_{DTE}^{-1}
		EXP #1			
0.0126	79.4	0.432	2.77	9.39	107
0.0126	79.4	0.434	2.79	9.46	106
0.0126	79.4	0.412	2.65	8.98	111
0.0253	39.5	0.708	4.55	15.4	64.9
0.0379	26.4	0.947	6.08	20.6	48.5
0.0506	19.8	1.07	6.87	23.3	42.9
0.0759	13.2	1.25	8.03	27.2	36.8
0.101	9.90	1.38	8.86	30.0	33.3
0.251	3.98	1.64	10.5	35.6	28.1
0.502	1.99	1.74	11.2	38.0	26.3

I_a=0.0295 E/l, [m-CF_3-BP]=0.05 M, [PhC_8]=8.19 x 10^{-4} M, SF=0.784, 3 hrs. irradiation. Gc column A, 118°C. Slope= 1.03, intercept=24.1, slope/intercept=0.0427.

		EXP #2			
0.0126	79.4	0.323	2.40	9.27	108
0.0126	79.4	0.325	2.41	9.31	107
0.0126	79.4	0.319	2.37	9.15	109
0.0253	39.5	0.502	3.73	14.4	69.4
0.0379	26.4	0.647	4.80	18.5	54.1
0.0506	19.8	0.775	5.75	22.2	45.0
0.0759	13.2	0.882	6.55	25.3	39.5
0.101	9.90	0.967	7.18	27.7	36.1
0.251	3.98	1.20	8.91	34.4	29.1
0.503	1.99	1.38	10.2	39.4	25.4

I_a=0.0259 E/l, [m-CF_3-BP]=0.05 M, [PhC_8]=9.47 x 10^{-4} M, SF=0.784, 2.5 hr. irradiation. Gc column A, 118°C. Slope= 1.06, intercept=25.0, slope/intercept=0.0422.

Table 79. Stern-Volmer Data, m-Chlorobenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_8		$[DTE](10^{-4})$	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.24		7.83	
0.0	1.16		7.33	
0.0	1.16		7.33	
0.0	1.20	1.19±0.03	7.58	1.00
4.40	0.915			1.30
5.87	0.829			1.44
8.80	0.694			1.71
10.3	0.683			1.74
11.7	0.639			1.86

[m-Cl-BP]=0.05 M, naphthalene quencher, $[PhC_8]=7.25 \times 10^{-4}$ M, 366 nm, 8 hrs. irradiation, [p-Xylene]=0.508 M, SF= 0.871. G.C. Column A, 115°C. $k_q\tau=720$.

		EXP #2		
0.0	0.832		5.94	
0.0	0.856		6.11	
0.0	0.831	0.840±0.011	5.93	1.00
2.99	0.715			1.17
4.48	0.729			1.15
5.98	0.602			1.40
8.97	0.583			1.44
10.5	0.462			1.82
12.0	0.501			1.68

[p-Cl-BP]=0.05 M, naphthalene quencher, $[PhC_8]=8.19 \times 10^{-4}$ M, 366 nm, 6 hrs. irradiation, [p-Xylene]=0.508 M, SF=0.871. G.C. Column A, 115°C. $k_q\tau=600$.

Table 80. Reciprocal Plot, m-Chlorobenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_8	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0250	40.0	0.227	1.46	3.00	33.3
0.0748	13.4	0.418	2.68	5.51	18.1
0.0997	10.0	0.390	2.50	5.14	19.5
0.150	6.67	0.469	3.01	6.19	16.2
0.199	5.03	0.449	2.88	5.93	16.9
0.501	2.00	0.593	3.81	7.84	12.8
1.00	0.500	0.858	5.51	1.13	8.85
I_a=0.00486 E/l, [m-Cl-BP]=0.05 M, $[PhC_8]$=8.19 x 10^{-4} M, SF=0.784, 45 min. irradiation. Gc column A, 115°C. Slope=0.70, intercept=18.0, slope/intercept=0.0372.					
		EXP #2			
0.0250	40.0	0.307	2.03	2.52	39.7
0.0250	40.0	0.308	2.04	2.54	39.4
0.0250	40.0	0.304	2.01	2.50	40.0
0.0500	20.0	0.393	2.60	3.23	31.0
0.0751	13.3	0.438	2.90	3.61	27.7
0.100	10.0	0.490	3.25	4.04	24.8
0.150	6.67	0.533	3.53	4.39	22.8
0.200	5.00	0.566	3.75	4.66	21.5
I_a=0.00804 E/l, [m-Cl-BP]=0.05 M, $[PhC_8]$=8.45 x 10^{-4} M, SF=0.784, 313 nm. Gc column A, 115°C. Slope=0.50, intercept=19.9, slope/intercept=0.0250.					

Table 81. Reciprocal Plot, 4,4'-di-Methylbenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0506	19.8	0.395	2.30	1.83	54.6
0.0759	13.2	0.641	3.73	2.96	33.8
0.101	9.90	0.833	4.84	3.84	26.0
0.152	6.58	1.18	6.86	5.44	18.4
0.202	4.95	1.40	8.14	6.46	15.5
I_a=0.0126 E/l, [4,4'-Me-BP]=0.05 M, SF=0.768, [PhC_9]= 7.57 x 10^{-4}M, 313 nm, 7 hrs. irradiation. Gc column A, 200°C. Slope=2.16, intercept=3.99; slope/intercept=0.541.					
		EXP #2			
0.0999	10.0	0.747	5.31	4.35	23.0
0.0999	10.0	0.643	4.53	3.75	26.7
0.0999	10.0	0.670	4.77	3.91	25.6
0.125	8.00	0.852	6.06	4.97	20.1
0.125	8.00	0.825	5.87	4.81	20.8
0.125	8.00	0.828	5.89	4.83	20.8
0.150	6.67	0.895	6.37	5.22	19.2
0.200	5.00	1.14	8.11	6.65	15.0
0.250	4.00	1.31	9.32	7.64	13.1
0.300	3.33	1.42	10.1	8.28	12.1
0.400	2.50	1.65	11.7	9.59	10.4
I_a=0.0122 E/l, [4,4'-Me-BP]=0.05 M, SF=0.768, [PhC_9]=9.26 x 10^{-4} M, 313 nm, 5 hrs. irradiation. Gc column A, 200°C. Slope=1.96, intercept=5.36, slope/intercept=0.366.					

Table 82. Reciprocal Plot, 4,4'-di-Methylbenzophenone and Toluene in CH_3CN.

[Tol]	$[Tol]^{-1}$	BB/ $PhCOOC_7$	[BB] (10^{-4})	ϕ_{BB} (10^{-2})	ϕ_{BB}^{-1}	Av.
0.457	2.19	0.404	5.42	1.05	95.2	95.7
0.457	2.19	0.401	5.38	1.04	96.2	
0.653	1.53	0.606	8.13	1.57	63.7	63.3
0.653	1.53	0.613	8.23	1.59	62.9	
0.979	1.02	0.915	12.3	2.37	42.2	42.2
0.979	1.02	0.916	12.3	2.37	42.2	
1.31	0.763	1.26	16.9	3.26	30.7	31.0
1.31	0.763	1.23	16.5	3.19	31.3	
2.61	0.383	2.17	29.1	5.62	17.8	17.6
2.61	0.383	2.23	29.9	5.77	17.3	

[4,4'-MeBP]=0.05 M, [$PhCOOC_7$]=0.00142 M, SF=0.945, 313 nm. Gc column A, 187°C. Slope=12.7, intercept=10.8, slope/intercept=1.18.

Table 83. Reciprocal Plot, 4,4'-di-Methylbenzophenone and Toluene-d_8.

[Tol-d_8]	[Tol-d_8]	BB/ $PhCOOC_7$	[BB] (10^{-3})	I_a E/l	ϕ_{BB}	ϕ_{BB}^{-1}
1.29	0.775	0.927	1.24	0.211	5.88	170
1.29	0.775	0.866	1.16	0.211	5.50	182
2.63	0.380	0.572	0.768	0.0573	13.4	74.6
2.63	0.380	0.547	0.734	0.0573	12.8	78.1

[4,4'-Me-BP]=0.05 M, [$PhCOOC_7$]=1.42 x 10^{-3} M, SF=0.945, 313 nm. Gc column A, 190°C. Slope=252, intercept=-19.4.

Table 84. Stern-Volmer Plot, Room Temperature Quenching of Triplet 4,4'-di-Me-BP by Toluene.

[Q], M	Height of 0,0 Band, inches[a]			$\phi°/0$
0.0	3.7			
0.0	4.4			
0.0	4.1			
0.0	4.3	Aver.	4.13 ± 0.23	1.00
1.00	2.1			1.97
1.22	1.9			2.17
1.44	1.6			2.58

[4,4'-Me-BP]=2.00 x 10^{-4} M, Q=toluene$_{d-8}$, excitation wavelength (emission and excitation)=12 nm, sensitivity setting= 12 nm in benzene. Slope = k_r/k_d.

[a]Average of 4 measurements: each tube was rotated 90 degrees and the emission height recorded.

Slope = k_r/k_d = 1.0.

Table 85. Stern-Volmer Plot, Room Temperature Quenching of Triplet 4,4'-di-Me-BP by Toluene in Benzene.

[Q], M	Height of 0,0 Band, inches[a]	$\phi°/0$
0.0	3.7	
0.0	3.5	
0.0	4.6	
0.0	3.2 Average 3.75±0.43	1.00
0.12	3.25	1.15
0.18	2.83	1.33
0.30	2.15	1.74
0.56	1.48	2.53

[4,4'-Me-BP]=2.00 x 10^{-4} M, Q=toluene, excitation wavelength =345 nm, slit width (emission and excitation)=12 nm, sensitivity=10.

[a]Average of 4 measurements: each tube was rotated 90 degrees and the emission height recorded.

Slope = k_r/k_d = 2.4.

Table 86. Stern-Volmer Data, 4,4'-di-Methoxybenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_7		$[DTE](10^{-4})$	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.05		7.93	
0.0	1.26	1.16±0.10	9.52	1.00
1.44	0.571			2.01
2.87	0.442			2.60
3.59	0.367			3.13
4.31	0.303			3.80
5.02	0.269			4.28
5.74	0.240			4.80

[4,4'-MeO-BP]=0.05 M, naphthalene quencher, $[PhC_7]=9.44 \times 10^{-4}$ M, 366 nm, 25 hrs. irradiation, [p-Xylene]=0.500, SF= 0.800. G.C. Column A, 197°C. $k_q\tau=6,372$.

Table 87. Reciprocal Plot, 4,4'-di-Methoxybenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0998	10.0	0.652	4.03	0.931	107
0.0998	10.0	0.709	4.38	1.01	99.0
0.0998	10.0	0.653	4.04	0.933	107
0.125	8.00	0.780	4.82	1.11	90.0
0.200	5.00	1.35	8.35	1.93	51.8
0.250	4.00	1.73	10.7	2.47	40.5
0.300	3.33	1.52	9.40	2.17	46.1
0.400	2.50	2.22	13.7	3.16	31.6

I_a=0.0433 E/l, [4,4'-MeO-BP]=0.02 M, $[PhC_9]=8.05 \times 10^{-4}$ M, SF=0.768, 313 nm, 4 hrs. irradiation. Gc column A, 197°C. Slope=9.89, intercept=6.50, slope/intercept=1.52.

		EXP #2			
0.0999	10.0	0.247	1.67	1.40	71.4
0.0999	10.0	0.294	1.98	1.66	60.2
0.0999	10.0	0.398	2.68	2.25	44.5
0.125	8.00	0.452	3.05	2.56	39.1
0.125	8.00	0.439	2.96	2.49	40.2
0.125	8.00	0.467	3.15	2.65	37.7
0.150	6.67	0.412	2.78	2.34	42.7
0.200	4.00	0.615	4.15	3.49	28.7
0.300	3.33	0.881	5.94	4.99	20.0
0.400	2.50	0.875	5.90	4.96	20.2

I_a=0.0119 E/l, [4,4'-MeO-BP]=0.02 M, $[PhC_9]=8.78 \times 10^{-4}$ M, SF=0.768, 313 nm, 5 hrs. irradiation. Gc column A, 197°C. Slope=5.06, intercept=5.01, slope/intercept=1.01.

Table 87. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #3			
0.0998	10.0	0.209	1.49	1.58	63.3
0.0998	10.0	0.207	1.47	1.56	64.1
0.149	6.71	0.283	2.01	2.13	46.9
0.200	5.00	0.386	2.75	2.92	34.2
0.250	4.00	0.585	4.16	4.42	22.6
0.300	3.33	0.584	4.15	4.41	22.7
0.399	2.51	0.680	4.84	5.14	19.5

I_a=0.00942 E/l, [4,4'-MeO-BP]=0.02 M, $[PhC_9]=9.26 \times 10^{-4}$ M, SF=0.768, 313 nm, 5 hrs. irradiation. Gc column A, 197°C. Slope=6.09, intercept=3.84, slope/intercept=1.59.

Table 88. Stern-Volmer Data, 4,4'-di-Fluorobenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_7		$[DTE](10^{-4})$	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	0.842		5.20	
0.0	0.813		5.02	
0.0	0.824		5.09	
0.0	0.868	0.837±0.014	5.36	1.00
4.44	0.419			2.00
8.88	0.293			2.86
13.3	0.191			4.38
[4,4'-FBP]=0.02 M, hexadiene quencher, $[PhC_7]=7.72 \times 10^{-4}$ M, 366, 32 min. irradiation, [p-Xylene]=0.519 M, SF=0.800. G.C. Column A, 158°C. $k_q\tau=2,321$.				
		EXP #2		
0.0	2.09		14.3	
0.0	2.19		14.9	
0.0	1.95	2.08±0.08	13.3	1.00
7.49	0.733			2.84
11.2	0.477			4.36
[4,4'-FBP]=0.02 M, naphthalene quencher, $[PhC_7]=8.53 \times 10^{-4}$ M, 366 nm, 24 hrs. irradiation, [p-Xylene]=0.519 M. G.C. Column A, 158°C. $k_q\tau=2,750$.				

Table 89. Reciprocal Plot, 4,4'-di-Fluorobenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_7	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #1			
0.0765	13.1	0.631	3.85	1.77	56.5
0.00765	13.1	0.527	3.22	1.48	67.7
0.00765	13.1	0.534	3.26	1.50	66.7
0.0153	65.4	1.19	7.26	3.33	30.0
0.0306	32.7	2.45	1.50	6.88	14.5
0.0535	18.7	3.86	2.36	10.8	9.26
0.214	4.67	4.97	3.03	13.9	71.9
0.214	4.67	5.55	3.39	15.6	6.41
I_a=0.0218 E/l, [4,4'-F-BP]=0.02 M, $[PhC_7]=7.63 \times 10^{-4}$ M, SF=0.800, 313 nm, 3.5 hrs. irradiation. Gc column A, 158°C Slope=0.431, intercept=4.89, slope/intercept=0.0881.					
		EXP #2			
0.0209	47.8	0.346	2.54	1.15	87.0
0.0209	47.8	0.321	2.36	1.07	93.5
0.0209	47.8	0.365	2.68	1.21	82.6
0.0314	31.8	0.510	3.74	1.69	59.2
0.0314	31.8	0.469	3.44	1.56	64.1
0.0314	31.8	0.478	3.51	1.59	62.9
0.0418	23.9	0.542	3.98	1.80	55.6
0.0523	19.1	0.615	4.51	2.04	49.0
0.0628	15.9	0.653	4.79	2.17	46.1
0.0837	11.9	0.671	4.92	2.23	44.8
I_a=0.0221 E/l, [4,4'-F-BP]=0.02 M, $[PhC_7]=9.17 \times 10^{-4}$ M, SF=0.800, 313 nm, 34 min. irradiation. Gc column A, 158°C. Slope=1.40, intercept=23.7, slope/intercept=0.0591.					

Table 89. Continued.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_7	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
		EXP #3			
0.0209	47.8	0.948	6.82	6.14	16.3
0.0209	47.8	1.05	7.55	6.80	14.7
0.0209	47.8	1.01	7.26	6.54	15.3
0.0314	31.8	1.22	8.77	7.90	12.7
0.0314	31.8	1.21	8.70	7.84	12.8
0.0418	23.9	1.52	10.9	9.82	10.2
0.0523	19.1	1.71	12.3	11.1	9.01
0.0837	11.9	2.22	1.60	14.4	6.94
0.0837	11.9	2.24	16.1	14.5	6.90

I_a=0.0111 E/l, [4,4'-F-BP]=0.02 M, $[PhC_7]=8.99 \times 10^{-4}$ M, SF=0.800, 313 nm, 1 hr. irradiation. Gc column A, 158°C. Slope=0.239, intercept=4.42, slope/intercept=0.0541.

Table 90. Stern-Volmer Data, 4,4'-di-Chlorobenzophenone and 0.5 M p-Xylene in CH_3CN.

[Q] (10^{-4})	DTE/PhC_9		[DTE](10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.27		8.01	
0.0	1.23	1.25±0.02	7.76	1.00
3.00	0.738			1.69
6.00	0.549			2.28
8.99	0.418			2.99
12.0	0.360			3.47
12.0	0.327			3.82

[4,4'-Cl-BP]=0.02 M, naphthalene quencher, [PhC_9]=8.21 x 10^{-4} M, 366 nm, 1.5 hr. irradiation, [p-Xylene]=0.508 M, SF=0.768. G.C. Column A, 152°C. $k_q\tau$=2,233.

Table 91. Reciprocal Plot, 4,4'-di-Chlorobenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_9	[DTE] (10^{-4})	[PhCo] (10^{-3})	ϕ_{DTE}	ϕ_{DTE}^{-1}
			EXP #1			
0.0117	85.5	0.0675	2.09	4.03	0.0346	28.9
0.0176	56.8	0.0901	3.18	4.59	0.0526	19.0
0.0176	56.8	0.0841	2.96	4.59	0.0490	20.4
0.0470	21.3	0.143	4.87	4.43	0.0806	12.4
0.0470	21.3	0.134	4.56	4.43	0.0755	13.2
0.0939	10.6	0.147	5.77	5.11	0.0955	10.5
0.519	1.93	0.216	7.36	4.43	0.122	8.20

I_a=0.00604 E/l, [4,4'-Cl-BP]=0.05 M, SF=0.768, 313 nm, 3.5 hrs. irradiation. Gc column A, 152°C. Slope=0.240, intercept=7.61, slope/intercept=0.0315.

Table 92. Stern-Volmer Data, p-Cyanobenzophenone and 0.5 M p-Xylene in CH_3CN.

[Q] (10^{-3})	DTE/PhC_9		[DTE](10^{-4})	$\frac{\phi^{\circ}_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.05		6.17	
0.0	1.31		7.70	
0.0	1.19	1.18±0.09	6.99	1.00
3.11	0.357			3.31
4.66	0.263			4.49
6.22	0.228			5.18
6.22	0.242			4.88

[p-CN-BP]=0.02 M, naphthalene quencher, [PhC_9]=7.65 x 10^{-4} M, 366 nm, 3 hrs. irradiation, SF=0.768, [p-Xylene]=0.50 M. G.C. Column A, 155°C. $k_q\tau$=708.

		EXP #2		
0.0	0.583		4.04	
0.0	0.638		4.42	
0.0	0.682		4.72	
0.0	0.623	0.632±0.029	4.32	1.00
2.73	0.211			3.00
4.10	0.177			3.57
5.47	0.154			4.10
5.47	0.153			4.13

[p-CN-BP]=0.02 M, naphthalene quencher, [PhC_9]=9.02 x 10^{-4} M, 366 nm, 3 hrs. irradiation, SF=0.768, [p-Xylene]=0.50 M. G.C. Column A, 155°C. $k_q\tau$=609.

Table 93. Reciprocal Plot, p-Cyanobenzophenone and p-Xylene in CH_3CN.

[Xyl]	$[Xyl]^{-1}$	DTE/PhC_9	[DTE] (10^{-4})	ϕ_{DTE}	ϕ_{DTE}^{-1}
		EXP #1			
0.0128	78.1	0.288	1.91	0.0640	15.6
0.0128	78.1	0.239	1.58	0.0530	18.9
0.0128	78.1	0.273	1.81	0.0607	16.5
0.0191	52.4	0.293	1.94	0.0651	15.4
0.0383	26.1	0.344	2.28	0.0763	13.1
0.0765	13.1	0.429	2.84	0.0953	10.5
0.125	8.02	0.492	3.26	0.109	9.16
0.499	2.00	0.518	3.43	0.115	8.69
0.499	2.00	0.604	4.00	0.134	7.46
I_a=0.00298 E/l, [pCNBP]=0.02 M, [PhC_9]=8.62 x 10^{-4} M, SF= 0.768, 313 nm, 2 hr. irradiation time. Gc column A, 155°C. Slope=0.120, intercept=8.51, slope/intercept=0.014.					
		EXP #2			
0.0127	78.7	0.287	1.84	0.0619	16.2
0.0127	78.7	0.256	1.65	0.0552	18.1
0.0127	78.7	0.281	1.81	0.0606	16.5
0.0190	52.6	0.297	1.91	0.0642	15.6
0.0761	13.1	0.410	2.63	0.0884	11.3
0.125	8.00	0.448	2.88	0.0966	10.4
0.498	2.01	0.537	3.46	0.116	8.62
0.498	2.01	0.524	3.37	0.113	8.85
I_a=0.00298 E/l, [p-CN-BP]=0.02 M, @PhC_9]=8.38 x 10^{-4} M, SF=0.768, 313 nm, 2 hr. irradiation time. Gc column A, 155°C. Slope=0.103, intercept=9.39, slope/intercept= 0.011.					

Table 94. Stern-Volmer Data, 4,4'-di-tert-Butylbenzophenone and 0.5 M p-Xylene in CH_3CN.

[Q] (10^{-4})	DTE/PhC_9		[DTE](10^{-4})	$\frac{\phi_{DTE}}{\phi_{DTE}}$
		EXP #1		
0.0	1.74		10.9	
0.0	1.73		10.8	
0.0	1.74	1.74±0.00	10.9	1.00
1.66	1.08			1.61
3.31	0.761			2.29
4.14	0.634			2.74
4.97	0.476			3.66
6.62	0.375			4.64

[4,4'-t-Bu-BP]=0.02 M, hexadiene quencher, [PhC_9]=8.13 x 10^{-4} M, 313 nm, 1 hr. irradiation, [p-Xylene]=0.504 M, SF=0.768. G.C. Column A, 161°C. $k_q\tau$=4,771.

Table 95. Reciprocal Plot, 4,4'-di-tert-Butylbenzophenone and p-Xylene in CH_3CN.

[Xylene]	$[Xylene]^{-1}$	DTE/ PhC_9	[DTE] (10^{-4})	ϕ_{DTE} (10^{-2})	ϕ_{DTE}^{-1}
0.100	10.0	0.663	3.89	4.89	20.4
0.100	10.0	0.615	3.60	4.52	22.1
0.100	10.0	0.613	3.59	4.51	22.2
0.120	8.33	0.819	4.79	6.02	16.6
0.200	5.00	1.16	6.79	8.53	11.7
0.250	4.00	1.35	7.90	9.92	10.1
0.300	3.33	1.32	7.72	9.70	10.3
0.401	2.49	1.54	9.01	0.113	8.85

I_a=0.00796 E/l, [4,4'-t-Bu-BP]=0.02 M, $[PhC_9]=7.65 \times 10^{-4}$ M, SF=0.768, 313 nm, 1 hr. irradiation. Gc column A, 161°C. Slope=1.62, intercept=4.20, slope/intercept=0.386.

Table 96. Photoreduction of Several Substituted α,α,α-Trifluoroacetophenones by p-Cymene: Relative Hydrocarbon Concentration.

Subst.[a]	PT/$PhCOOC_8$[c]	TT/$PhCOOC_8$[d]	PP/$PhCOOC_8$[e]	%PT	%TT	%PP
mCF_3[b]	41.6;40.7%[f]	0.0%	58.5;59.4%	41	0	59
pCF_3[b]	52.2%[f]	0.0%	47.9%	52	0	48
mCl	35.3;38.2%[f]	7.8;8.0	57.0;53.8%	37	8	56
pF[b]	34.8;35.0%[f]	5.0;5.0%	60.2;62.0%	35	5	60
H	29.2%[f]	12.6%	58.2%	29	13	58
pCl	2.34;1.13	0.496;0.304	2.35;1.28	43	11	47
ptBu	44.1%[f]	20.7%	35.2%	44	21	35
pCH_3	2.30	0.849	2.34	42	16	43
mCH_3	0.396;0.890	0.108;0.193	0.667;1.42	35	8	59
3,4-Di-MeO	0.335;0.843	0.193;0.392	0.225;0.607	46	22	33
pMeO	0.439	0.118	0.167	46	23	32

[a] 0.1 M ketone/CH_3CN, 1 M p-cymene; Gc column A, 160°C, unless noted.

[b] Gc column B, 145°C.

[c] PT, the primary-tertiary coupling product. $PhCOOC_8$=n-octylbenzoate standard.

[d] TT, the tertiary-tertiary coupling product.

[e] PP, the primary-primary coupling product.

[f] No internal standard was used.

Table 97. Photoreduction of Substituted Acetophenones by p-Cymene: Relative Hydrocarbon Concentration.

Subst.[a]	PT/$PhCOOC_8$[b]	TT/$PhCOOC_8$[c]	PP/$PhCOOC_8$[d]	%PT	%TT	%PP
$\alpha,\alpha F_2$	1.87;1.66	0.350;0.283	2.63;2.36	39	7	55
pCN[e]	43.9%	29.2%	26.9%	52	25	24
pCl	3.15;4.11	1.25;2.29	1.52;1.85	44	29	27
3,4-Di-Cl	1.09	0.656	0.538	48	29	24
mCN[e]	45.1%	34.6%	20.4%	45	35	20
mCF_3	0.279	0.223	0.119	45	36	19
mCl	0.977	0.822	0.423	44	37	19
pCF_3[e]	43.6%	37.6%	18.9%	44	38	19
αF	2.20	1.84	0.814	45	38	17
pF	1.09	1.05	0.408	43	41	16
pMeO	0.155	0.153	0.0617	42	41	17
mCH_3	0.662;0.317	0.758;0.341	0.240;0.111	41	45	15
pCH_3	0.415;3.45; 0.105	0.0476;3.99; 0.126	0.147;1.22; 0.0349	40	47	14
ptBu[e]	40.6%	48.0%	11.5%	41	48	12
3,4-Di-MeO	0.286;39.8%[e]	0.353;48.7%[e]	0.0986;11.5%[e]	40	48	13
ACP	1.48;1.17; 0.0460	1.68;1.34; 0.0291	0.404;0.387; 0.0278	41	47	11

[a]0.1 M ketone/CH_3CN, 1 M p-cymene. Gc column A, 160°C. [b]PT, the primary-tertiary coupling photoproduct; $PhCOOC_8$=n-octyl benzoate standard. [c]TT, the tertiary-tertiary coupling photoproduct. [d]PP, the primary-primary coupling photoproduct. [e]No standard used.

Table 98. Photoreduction of Substituted Benzophenones by p-Cymene: Relative Hydrocarbon Concentration.

Subst.[a]	PT/$PhCOOC_8$[b]	TT/$PhCOOC_8$[c]	PP/$PhCOOC_8$[d]	%PT	%TT	%PP
pCN[e]	40.8;42.1%	40.3;39.1%	19.1;18.9%	42	40	19
mCF_3	0.798	1.31	0.233	34	56	10
mCl	1.50	1.96	0.419	39	51	11
pCF_3	0.225	0.227	0.0827	42	43	15
4,4'Cl	0.982	1.03	0.373	41	43	16
4,4'F	40.7;41.1%	46.3;45.6%	13.1;13.1%	41	46	13
pCl	1.58	1.82	0.373	42	48	10
H[f]	1.24;8.07;1.36	1.39;8.59;1.61	0.216;1.26;0.255	44	49	8
4,4'tBu[e]	31.2%	64.1%	4.49%	31	64	5
4,4'Me	0.761	1.36	0.178	34	59	8
4,4'OMe	0.385	0.729	0.0803	33	59	8
3,4-Di-Cl	0.353	0.356	0.138	32	61	7
3,3'Me	0.663	1.18	0.152	41	42	17

[a] 0.1 M ketone/CH_3CN, 1 M p-xylene. Gc column A, 160°C unless otherwise noted.
[b] PT, the primary-tertiary coupling product. $PhCOOC_8$=n-octylbenzoate standard.
[c] TT, the tertiary-tertiary coupling product.
[d] PP, the primary-primary coupling product. [e] No standard used. [f] Gc column B, 145°C.

Table 99. Stern-Volmer Data, α,α,α-Trifluoroacetophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-3})$	Cl-CP/ϕBr		$[Cl\text{-}CP](10^{-2})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	0.672		0.0629	
0.0	0.675		0.0632	
0.0	0.688	0.678±0.006	0.0644	1.00
2.77	0.207			3.28
5.54	0.137			4.95
6.93	0.129			5.26
8.32	0.117			5.79
8.32	0.106			5.79
11.1	0.117			6.40

[TFA]=0.05 M, naphthalene, [ϕBr]=0.0780 M, 335 nm, [cyclopentane]=1.01 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C. $k_q\tau$=644.

		EXP #2		
0.0	5.21		2.37	
0.0	4.90		2.23	
0.0	4.90	5.00±0.14	2.23	1.00
6.65	0.963			5.19
9.98	0.672			7.44
13.3	0.582			8.59

[TFA]=0.05 M, naphthalene, [ϕBr]=0.00379 M, 335 nm, [cyclopentane]=1.01 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C. $k_q\tau$=614.

Table 99. Continued.

$[Q](10^{-3})$	Cl-CP/PhC_6		$[Cl\text{-}CP](10^{-2})$	$\frac{\phi^{o}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #3		
0.0	0.813		7.82	
0.0	0.826	0.820±0.007	7.94	1.00
6.52	0.180			4.6
9.78	0.126			6.5

[TFA]=0.05 M, neat cyclopentane=10.2 M, naphthalene quencher, $[PhC_6]$=0.00769 M, SF=1.02 M, 335 nm, Cl-CP=chlorocyclopentane. G.C. Column C, 205°C. $k_q\tau$=550.

Table 100. Reciprocal Plot, α,α,α-Trifluoroacetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhBr	[Cl-CP] (10^{-3})	$\phi(10^{-2})$	ϕ^{-1}
0.125	8.00	0.410	3.11	7.55	13.2
0.125	8.00	0.412	3.13	7.60	13.2
0.125	8.00	0.406	3.08	7.48	13.4
0.250	4.00	0.587	4.46	10.8	9.26
0.376	2.66	0.732	5.56	13.5	7.41
0.501	2.00	0.842	6.40	15.5	6.45
0.626	1.60	0.977	7.42	18.0	5.56
0.751	1.33	1.05	7.98	19.4	5.15
1.00	1.00	1.03	7.82	19.0	5.26
1.00	1.00	1.03	7.82	19.0	5.26

I_a=0.0412 E/1, [TFA]=0.05 M, [PhBr]=0.00633 M, SF=1.20, 313 nm, 3.5 hrs. irradiation, Cl-CP=chlorocyclopentane, CCl_4 solvent, CP=cyclopentane. Gc column C, 135°C. Slope= 1.19, intercept=3.97, slope/intercept=0.300.

Table 101. Stern-Volmer Data, m-Chloro-α,α,α-Trifluoroacetophenone and 1 M Cyclopentane in CCl_4.

[Q] (10^{-3})	Cl-CP/ϕCl		[CP](10^{-3})	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	4.31		16.7	
0.0	4.43		17.2	
0.0	4.35	4.36±0.04	16.9	1.00
1.46	1.49			2.93
2.19	1.21			3.60
2.92	0.978			4.46
5.84	0.611			7.14

[m-Cl-TFA]=0.05 M, naphthalene, [ϕCl]=0.00323 M, 335 nm, 2.0 hrs. irradiation time, [cyclopentane]=1.05 M, Cl-CP= chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=1,158.

		EXP #2		
0.0	6.39		24.8	
0.0	6.11		23.7	
0.0	6.34	6.28±0.11	24.6	1.00
9.44	0.731			8.59
11.8	0.617			10.2
14.2	0.538			11.7
18.9	0.471			13.3

[m-Cl-TFA]=0.05 M, naphthalene quencher, [ϕCl]=0.00323 M, 335 nm, 4.0 hrs. irradiation, [cyclopentane]=1.05 M, Cl-CP= chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=771.

Table 102. Reciprocal Plot, m-Chloro-α,α,α-Trifluoroacetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhCl	[Cl-CP] (10^{-3})	$\phi(10^{-2})$	ϕ^{-1}
0.0752	13.3	0.159	0.861	3.70	27.0
0.0752	13.3	0.162	0.877	3.76	26.6
0.0752	13.3	0.164	0.888	3.81	26.2
0.125	8.00	0.240	1.30	5.58	17.9
0.125	8.00	0.244	1.32	5.67	17.6
0.251	3.98	0.421	2.28	9.79	10.2
0.376	2.66	0.539	2.92	12.5	8.00
0.502	1.99	0.583	3.16	13.6	7.35
1.00	1.00	0.798	4.32	18.5	5.41
1.00	1.00	0.862	4.67	20.0	5.00

I_a=0.0233 E/l, [m-Cl-TFA]=0.05 M, [PhCl]=0.00451 M, SF= 1.20, 313 nm, 2 hrs. irradiation, Cl-CP=chlorocyclopentane, CP=cyclopentane. Gc column C, 135°C. Slope=1.75, intercept= 3.54, slope/intercept=0.494.

Table 103. Stern-Volmer Plot, p-Methoxy-α,α,α-Trifluoroacetophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-3})M$	Cl-CP/ϕCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	0.938		4.50	
0.0	0.952		4.57	
0.0	0.936	0.942±0.007	4.49	1.00
1.97	0.776			1.21
3.94	0.670			1.41
4.93	0.617			1.53
5.92	0.573			1.64
7.89	0.508			1.85

[p-MeO-TFA]=0.05 M, naphthalene quencher, [ϕCl]=0.00400 M, 335 nm, 10 hrs. irradiation, SF=1.20, [cyclopentane]=1.02 M, Cl-CP=chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=106.

		EXP #2		
0.0	1.58		5.82	
0.0	1.57	1.58±0.01	5.78	1.00
6.65	0.919			1.72
9.98	0.818			1.93
13.3	0.730			2.16

[p-MeO-TFA]=0.05 M, naphthalene, [ϕCl]=0.00307 M, 335 nm, 12 hrs. irradiation time, SF=1.20 [cyclopentane]=1.02 M, Cl-CP=chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=91.

Table 103. Continued.

$[Q](10^{-3})M$	Cl-CP/ϕCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #3		
0.0	1.596		5.92	
0.0	1.565		5.80	
0.0	1.592	1.58±0.01	5.90	1.00
1.72	1.37			1.15
2.58	1.25			1.26
3.45	1.18			1.34
4.31	1.13			1.40
5.17	1.07			1.48
6.89	1.00			1.58

[p-MeO-TFA]=0.05 M, naphthalene, [ϕCl]=0.00309 M, 335 nm, 12 hrs. irradiation, SF=1.20, [cyclopentane]=1.02 M, Cl-CP= chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=90.

$[Q](10^{-4})$	KP/PhC_{10}		$[KP](10^{-4})M$	$\frac{\phi^{\circ}_{KP}}{\phi_{KP}}$
		EXP #4		
0.0	0.461		5.90	
0.0	0.477	0.469±0.008	6.10	1.00
4.81	0.182		2.33	2.58
9.62	0.107		1.37	4.38
14.4	0.0785		1.00	5.97
24.1	0.0518		0.739	8.67
28.9	0.0424		0.542	11.1

[p-MeO-TFA]=0.05 M, naphthalene, $[PhC_{10}]=9.99 \times 10^{-4}$ M, 335 nm, [cyclopentane]=1.02 M, SF=1.28, 50 hrs irradiation, KP=cross product. G.C. Column B, 160°C. $k_q\tau$=3,467.

Table 104. Reciprocal Plot, p-Methoxy-α,α,α-Trifluoroacetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/PhCl	[Cl-CP] (10^{-3})	$\phi(10^{-2})$	ϕ^{-1}
		EXP #1			
0.250	4.00	0.512	3.20	1.58	63.3
0.376	2.66	0.682	4.26	2.11	47.4
0.501	2.00	0.788	4.93	2.44	41.0
0.626	1.60	0.898	5.61	2.78	36.0
0.751	1.33	1.07	6.69	3.31	30.2
1.00	1.00	1.06	6.63	3.28	30.5
1.00	1.00	1.07	6.69	3.31	30.2

I_a=0.202 E/l, [p-MeO-TFA]=0.05 M, [PhCl]=0.00512 M, SF= 1.20, 313 nm, 22 hrs. irradiation, CP=cyclopentane, Cl-CP= chlorocyclopentane. Gc column C, 135°C. Slope=13.7, intercept=20.9, slope/intercept=0.656.

		EXP #2			
0.251	3.98	0.391	2.45	1.99	50.3
0.251	3.98	0.404	2.53	2.06	48.5
0.301	3.32	0.443	2.77	2.25	44.4
0.376	2.66	0.481	3.01	2.45	40.8
0.501	2.00	0.600	3.76	3.06	32.7
0.627	1.59	0.672	4.21	3.42	2.92
0.752	1.33	0.736	4.61	3.75	26.7
1.00	1.00	0.763	4.78	3.89	25.7

I_a=0.123 E/l, [p-MeO-TFA]=0.05 M, [PhCl]=0.00522 M, SF= 1.20, 313 nm, 1 hr. irradiation, Gc column C, 135°C. Slope =8.43, intercept=16.5, slope/intercept=0.511.

Table 105. Stern-Volmer Data, p-Methyl-α,α,α-Trifluoroacetophenone and 1 M Cyclopentane in CCl_4.

[Q] (10^{-3})M	Cl-CP/ϕCl		[Cl-CP](10^{-3})	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	3.53		16.8	
0.0	3.63		17.2	
0.0	3.76	3.64±0.08	17.9	1.00
0.630	1.52			2.39
1.26	1.10			3.31
1.83	0.905			4.02
2.52	0.814			4.47
3.78	0.724			5.03

[p-Me-TFA]=0.05 M, naphthalene, [ϕCl]=0.00396 M, 335 nm, [cyclopentane]=1.02 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C.

		EXP #2		
0.0	4.00		15.7	
0.0	4.12	4.06±0.06	16.2	1.00
0.133	2.87			1.41
0.265	1.96			2.07
0.530	1.68			2.42
0.796	1.46			2.78
1.06	1.28			3.17

[p-Me-TFA]=0.05 M, naphthalene, [ϕCl]=0.00327 M, 335 nm, [cyclopentane]=1.03 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C.

Table 105. Continued.

$[Q](10^{-3})M$	Cl-CP/ϕCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #3		
0.0	1.22		7.14	
0.0	1.22		7.17	
0.0	1.19	1.21±0.01	6.99	1.00
1.16	0.357			3.38
2.31	0.326			3.71
2.89	0.308			3.92
3.46	0.282			4.28
3.46	0.284			4.25
4.62	0.257			4.70
[p-Me-TFA]=0.05 M, CCl_4 solvent, naphthalene, [ϕCl]=0.00490 M, 335 nm, [cyclopentane]=1.02 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C.				
		EXP #4		
0.0	0.974		6.50	
0.0	0.950		6.34	
0.0	1.01	0.978±0.021	6.74	1.00
0.323	0.442			2.21
0.485	0.382			2.55
0.647	0.342			2.86
0.809	0.327			2.99
0.970	0.312			3.13
1.29	0.278			3.52
[p-Me-TFA]=0.05 M, naphthalene, [ϕCl]=0.00556 M, 335 nm, [cyclopentane]=1.02 M, SF=1.20, irradiation time=4 hrs. G.C. Column C, 135°C.				

Table 105. Continued.

$[Q](10^{-3})$	Cl-CP/ϕCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #5		
0.0	2.32		2.81	
0.0	2.34		2.83	
0.0	2.30		2.78	
0.0	2.30	2.32±0.03	2.78	1.00
0.187	1.43			1.62
0.373	1.02			2.27
0.560	0.772			3.01
0.933	0.525			4.42
1.12	0.476			4.87
1.49	0.239			9.71

[p-Me-TFA]=0.05 M, naphthalene, $[PhC_6]$=0.00136 M, 335 nm, [cyclopentane]=1.03 M, Cl-CP=cross product, SF=0.889, 10.5 hrs. irradiation, I_a=0.206. G.C. Column B, 150°C.

EXP #1-4: The plots curve then level off. EXP #5: $k_q\tau$=4,444.

$[Q](10^{-3})$	Cl-CP/PhCl		$[Cl\text{-}CP](10^{03})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #6		
0.0	1.79		14.0	
0.0	1.77		13.8	
0.0	1.71	1.76±0.03	13.4	1.00
3.50	1.63			1.08
6.99	1.53			1.15
10.5	1.40			1.26
14.0	1.30			1.35
21.0	1.21			1.45
28.0	1.14			1.54

[p-Me-TFA]=0.026 M, [cyclopentane]=1.06 M, naphthalene quencher, [PhCl]=0.00652 M, SF=1.20, 335 nm, Cl-CP=chlorocyclopentane. G.C. Column C, 135°C. $k_q\tau$=2,375.

Table 106. Reciprocal Plot, p-Methyl-α,α,α-trifluoroacetophenone and Cyclopentane in CCl_4.

[CP]M	$[CP]^{-1}$	Cl-CP/ ϕCl	[Cl-CP] (10^{-3})	$\phi_{Cl\text{-}CP}$ (10^{-2})	$\phi^{-1}_{Cl\text{-}CP}$
0.175	5.71	0.159	1.02	4.57	21.9
0.175	5.71	0.155	0.992	4.45	22.5
0.175	5.71	0.162	1.04	4.66	21.5
0.250	4.00	0.210	1.34	6.01	16.6
0.250	4.00	0.212	1.36	6.10	16.4
0.375	2.67	0.294	1.88	8.43	11.9
0.500	2.00	0.360	2.30	10.3	9.71
0.751	1.33	0.501	3.21	14.4	6.94
1.00	1.00	0.526	3.37	15.1	6.62
1.00	1.00	0.520	3.33	14.9	6.71
1.00	1.00	0.519	3.32	14.9	6.71

I_a=0.0223 E/l, [pMeTFA]=0.05 M, [ϕCl]=0.00533 M, 313 nm, 4 hrs. irradiation time, Cl-CP=chlorocyclopentane, CP=cyclopentane. Gc column C, 135°C. Slope=3.34, intercept=2.98, slope/intercept=1.12.

Table 107. Stern-Volmer Data, 3,4-di-Methyl-α,α,α-Trifluoroacetophenone in 1 M Cyclopentane.

$[Q](10^{-4})M$	Cl-CP/ϕCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi Cl\text{-}CP}$
0.0	1.48		10.5	
0.0	1.44		10.2	
0.0	1.52		10.8	
0.0	1.65	1.52±0.06	11.7	1.00
7.99	0.688			2.21
11.2	0.633			2.40
15.0	0.650			2.34
18.7	0.627			2.42
30.0	0.568			2.68

[3,4-Di-Me-TFA]=0.05 M, naphthalene, [ϕCl]=0.00592 M, 335 nm, [cyclopentane]=1.02 M, Cl-CP=chlorocyclopentane, SF=1.20. G.C. Column C, 135°C. $k_q\tau$: the plot curves then levels off.

Table 108. Stern-Volmer Data, Acetophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-4})$	Cl-CP/ϕBr	Aver.	$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
0.0	0.491		12.6	
0.0	0.468		13.0	
0.0	0.491		12.6	
0.0	0.494	0.486	12.6	1.00
6.24			6.31	1.97
12.5			4.55	2.73
12.5			4.27	2.91
15.6			3.48	3.57
18.7			3.45	3.60
25.0			2.66	4.67

[ACP]=0.05 M, naphthalene, [ϕBr]=0.0213 M, 335 nm, 6 hrs. irradiation time, [cyclopentane]=1.01 M, SF=1.20, Cl-CP= chlorocyclopentane. G.C. Column C, 165°C. $k_q\tau$=1,481.

Table 109. Reciprocal Plot, Acetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhCl	[Cl-CP] (10^{-3})	$\phi(10^{-2})$	ϕ^{-1}_{Cl-CP}
0.125	8.00	0.512	1.87	5.86	17.1
0.125	8.00	0.463	1.69	5.30	18.9
0.125	8.00	0.539	1.97	6.18	16.2
0.250	4.00	0.782	2.85	8.93	11.2
0.375	2.67	1.06	3.87	12.1	8.26
0.500	2.00	1.44	5.25	16.5	6.06
0.626	1.60	1.62	5.91	18.5	5.41
0.751	1.33	1.83	6.68	20.9	4.78
1.00	1.00	2.14	7.81	24.5	4.08
1.00	1.00	2.24	8.17	25.6	3.91

I_a=0.0319 E/1, [ACP]=0.02 M, [PhCl]=3.04 x 10^{-3} M, SF=1.20, 313 nm, 3 hrs. irradiation, Cl-CP=chlorocyclopentane, CP= cyclopentane. Gc column C, 165°C. Slope=2.06, intercept= 2.23, slope/intercept=0.924.

Table 110. Stern-Volmer Data, p-Trifluoromethylacetophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-3})$	Cl-CP/PhCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
0.0	3.09		17.5	
0.0	2.86		16.2	
0.0	3.14	3.03±0.11	17.8	1.00
1.55	1.25			2.42
3.10	0.749			4.05
4.65	0.605			5.01
6.20	0.461			6.57
9.31	0.365			8.30

$[p\text{-}CF_3\text{-}ACP]$=0.03 M, naphthalene quencher, [PhCl]=0.00473 M, 335 nm, [cyclopentane]=1.00 M, 2 hr. irradiation time, SF=1.20, Cl-CP=chlorocyclopentane. G.C. Column C, 130°C. $k_q\tau$=908.

Table 111. Reciprocal Plot, p-Trifluoromethylacetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhCl	[Cl-CP] (10^{-3})	Φ_{Cl-CP}	Φ^{-1}_{Cl-CP}
0.101	9.90	0.775	5.93	0.353	2.83
0.101	9.90	0.725	5.55	0.330	3.03
0.101	9.90	0.729	5.58	0.332	3.01
0.126	7.94	0.800	6.12	0.364	2.75
0.126	7.94	0.821	6.29	0.374	2.67
0.252	3.97	0.938	7.18	0.427	2.34
0.378	2.65	1.09	8.35	0.497	2.01
0.504	1.98	1.12	8.57	0.510	1.96
1.01	0.990	1.27	9.72	0.579	1.73
1.01	0.990	1.30	10.1	0.601	1.66

I_a=0.0168 E/l, [pCF_3ACP]=0.03 M, [PhCl]=0.00638 M, SF=1.20, 3.3 nm, 1.5 hr. irradiation time, Cl-CP=chlorocyclopentane, CP=cyclopentane. Gc column C, 130°C. Slope=2.58, intercept=2.61, slope/intercept=0.989.

Table 112. Stern-Volmer Data, p-Methylacetophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-4})$	Cl-CP/PhCl		$[Cl\text{-}CP](10^{-2})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	1.40		1.41	
0.0	1.50		1.51	
0.0	1.54		1.55	
0.0	1.48	1.48±0.04	1.49	1.00
3.73	1.26			1.17
7.46	0.949			1.55
9.33	0.901			1.64
11.2	0.805			1.83
13.1	0.672			2.19
14.9	0.653			2.26

[p-Me-ACP]=0.03 M, naphthalene quencher, [PhCl]=0.00837 M, SF=1.20, Cl-CP=chlorocyclopentane, 9.5 Hr. irradiation, [cyclopentane]=1.03 M, 335 nm, G.C. Column C, 130°C. $k_q\tau$=880.

		EXP #2		
0.0	2.67		1.80	
0.0	2.77		1.87	
0.0	2.62	2.69±0.06	1.77	1.00
10.2	1.57			1.71
20.5	1.04			2.59
25.6	0.886			3.04
30.7	0.761			3.53
35.8	0.687			3.92
40.9	0.619			4.35

[p-Me-ACP]=0.03 M, naphthalene quencher, [PhCl]=0.00563 M, SF=1.20, Cl-CP=chlorocyclopentane, 9.5 hr. irradiation, [cyclopentane]=1.03 M, 335 nm. G.C. Column C, 130°C. $k_q\tau$=800°C.

Table 113. Reciprocal Plot, p-Methylacetophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhCl	[Cl-CP] (10^{-3})	$\phi_{Cl\text{-}CP}$ (10^{-2})	$\phi^{-1}_{Cl\text{-}CP}$
0.250	4.00	0.282	2.25	7.68	13.0
0.250	4.00	0.290	2.32	7.92	12.6
0.499	2.00	0.453	3.02	12.4	8.06
0.749	1.34	0.570	4.56	15.6	6.41
0.998	1.00	0.789	6.31	21.5	4.65
0.998	1.00	0.772	6.17	21.1	4.74

I_a=0.0297 E/l, [pMeACP]=0.03 M, [PhCl]=0.00666 M, SF=1.20, 313 nm, CP=cyclopentane, Cl-CP=chlorocyclopentane, 3 hr. irradiation time. Gc column C, 130°C. Slope=2.58, intercept=2.61, slope/intercept=0.989.

Table 114. Stern-Volmer Data, Benzophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-4}$	Cl-CP/ϕCl		[Cl-CP], M	$\phi^{\circ}_{Cl\text{-}CP}/\phi_{Cl\text{-}CP}$
		EXP #1		
0.0	1.97	0.0148	0.0148	
0.0	1.90		0.0143	
0.0	1.99	1.95±0.04	0.0150	1.00
9.11			0.00745	1.93
13.7			0.00604	2.42
18.2			0.00520	2.82
27.3			0.00418	3.51
36.4			0.00330	4.44

[BP]=0.05 M, naphthalene, [ϕCl]=6.27 x 10^{-3} M, 335 nm, [cyclopentane]=1.03 M, Cl-CP= chlorocyclopentane, SF=1.20, 2.5 hrs. irradiation time. Gc column C, 147°C. $k_q\tau$=961.

EXP #2

[Q] (10^{-3})	KP/ PhC_{10}		[KP] (10^{-3})	$\phi^{\circ}_{KP}/\phi_{KP}$	Cl-CP/Cl		[Cl-CP]	$\phi^{\circ}_{Cl\text{-}CP}/\phi_{Cl\text{-}CP}$
0.0	2.84		3.77		2.91		0.0415	
0.0	2.93		3.89		2.75		0.0392	
0.0	2.80	2.86±0.05	3.72	1.00	2.79	2.82±0.06	0.0398	1.00
0.506	2.35		3.12	1.22	2.37		0.0338	1.14
1.01	1.87		2.48	1.53	1.88		0.0268	1.50
1.52	1.57		2.09	1.82	1.74		0.0248	1.62
2.53	1.13		1.50	2.53	1.23		0.0175	2.29
3.03	0.995		1.32	2.87	1.12		0.0160	2.52
4.04	0.707		0.939	4.05	1.10		0.0157	2.56

Table 114. Continued.

Exp. #2 Footnotes: [BP]=0.05 M, naphthalene quencher, [PhC_{10}]=1.46 x 10^{-3} M, SF=0.91, [ϕCl]=0.0119 M, SF'=1.20, [cyclopentane]=1.09 M, Cl-CP=chlorocyclopentane, KP=cross product, 7 hrs. irradiation time. Gc column C, 147°C, 200°C. $k_q\tau$=484 (Cl-CP); $k_q\tau$=547 (KP).

EXP #3

[Q](10^{-4})	KP/PhC_{10}		[KP(10^{-3})	$\frac{\phi^\circ_{KP}}{\phi_{KP}}$	Cl-CP/ϕCl		[Cl-CP]	$\frac{\phi^\circ_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
0.0	1.96		3.50		3.36		3.64×10^{-2}	
0.0	2.09		3.73		3.45		3.74	
0.0	2.00		3.57		3.52		3.81	
0.0	2.29	2.09±0.11	4.08	1.00	3.27	3.40±0.09	3.54	1.00
0.577	1.68			1.24	2.52			1.35
1.15	1.28			1.63	2.15			1.58
1.73	1.00			2.09	1.76			1.93
2.89	0.641			3.26	1.29			2.64
3.46	0.532			3.93	1.22			3.04
4.62	0.394			5.30	0.895			3.80

[BP]=0.05 M, naphthalene quencher, [ϕCl]=9.03 x 10^{-3} M, SF=1.20, [PhC_{10}]=1.96 x 10^{-3}M, SF'=0.91, 335 nm, [cyclopentane]=1.06 M, Cl-CP=chlorocyclopentane, KP=cross product, 6 hrs. irradiation time. Column C, 147°C. $k_q\tau$(Cl-CP)=578.

Table 114. Continued.

$[Q](10^{-4})$	BCP/C_{14}		$[BCP](10^{-3})$	ϕ_{BCP}	$\phi^{\circ}_{BCP}/\phi_{BCP}$
			EXP #4		
0.0	0.982		2.98	0.0247	
0.0	0.942	0.962±0.02	2.85	0.0234	1.00
3.26	0.581		1.76		1.66
6.52	0.310		0.939		3.10
16.3	0.123		0.373		7.87
19.6	0.107		0.324		8.99

[BP]=0.03 M, naphthalene quencher, $[C_{14}]$=0.00216 M, SF=1.40, BCP=bicyclopentyl, [cyclopentane]=10.4 M, I_a=0.122 E/l, 7 hr. irradiation time. Column C, 220°C. $k_q\tau$=375.

			EXP #5		
0.0	0.572		1.21		
0.0	0.592		1.25		
0.0	0.592	0.585±0.009	1.25		1.00
13.5	0.265		0.560		2.21
20.2	0.214		0.452		2.73
27.0	0.148		0.313		3.95

[BP]=0.05 M, benzene solvent, naphthalene quencher, $[C_{14}]$=0.00151 M, SF=1.40, BCP=bicyclopentyl, [cyclopentane]=1.06 M, 9.5 hr. irradiation. Gc column C, 220°C. $k_q\tau$=933.

Table 115. Reciprocal Plot, Benzophenone and Cyclopentane in CCl_4.

[CP],M	$[CP]^{-1}$	Cl-CP/ϕCl	[Cl-CP](10^{-3})	ϕ_{Cl-CP}	ϕ^{-1}_{Cl-CP}
			EXP #1		
0.126	7.94	0.463	3.45	0.126	8.00
0.126	7.94	0.478	3.57	0.130	7.69
0.126	7.94	0.577	4.30	0.156	6.41
0.176	5.68	0.618	4.61	0.168	5.95
0.251	3.98	0.749	5.59	0.203	4.93
0.377	2.65	0.786	5.86	0.213	4.69
0.502	1.99	0.809	6.04	0.220	4.55
0.754	1.33	0.837	6.24	0.227	4.41
1.00	1.00	0.850	6.34	0.231	4.33

I_a=0.0275 E/l, [BP]=0.05 M, naphthalene, [ϕCl]=0.00622 M, 335 nm, CP=cyclopentane, Cl-CP=chlorocyclopentane, 1.5 hr. irradiation time, SF=1.20. Gc column C, 120°C. Slope=0.497, intercept=3.79, slope/intercept=0.131.

Table 115. Continued.

[CP]	$[CP]^{-1}$	KP PhC_{10}	[KP] (10^{-3})	$\phi(10^{-3})$	ϕ_{KP}^{-1}	$\frac{Cl\text{-}CP}{\phi Cl}$	[Cl-CP]	$\phi(10^{-2})$	$\phi_{Cl\text{-}CP}^{-1}$
				EXP #2					
0.126	7.94	0.589	8.84	7.07	141	0.771	8.09	6.47	15.5
0.251	3.98	0.763	11.5	9.20	109	1.07	11.2	8.96	11.2
0.377	2.65	0.861	12.9	10.3	97.1	1.25	13.1	10.5	9.52
0.629	1.59	1.02	15.3	12.2	82.0	1.61	16.9	13.5	7.41
0.754	1.33	1.06	15.9	12.7	78.7	1.81	19.0	15.2	6.58
1.01	0.990	1.26	18.9	15.1	66.2	2.18	22.9	18.3	5.46

I_a=0.125 E/1, [BP]=0.10 M, naphthalene, [ϕCl]=0.00874 M, 335 nm, CP=cyclopentane, Cl-CP=chlorocyclopentane, SF=1.20, KP=cross product, [PhC_{10}]=0.00165 M, SF'=0.91. Gc column C, 120°C, 222°C.

Slope=1.38, intercept=5.02, slope/intercept=0.275 (using Cl-CP).

Slope=10.0, intercept=64.8, slope/intercept=0.154 (using KP).

Table 116. Stern-Volmer Data, 4,4'-di-Methylbenzophenone and 1 M cyclopentane in CCl_4.

$[Q](10^{-3})$	Cl-CP/PhCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{o}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	1.72		29.1	
0.0	1.70		28.8	
0.0	1.77	1.73±0.03	29.9	1.00
1.40	1.18			1.47
2.10	0.848			2.04
2.80	0.715			2.42
4.19	0.588			2.94
5.59	0.485			3.57

[4,4'-Me-BP]=0.05 M, naphthalene quencher, [PhCl]=0.0141 M, SF=1.20, 335 nm, [cyclopentane]=1.05 M, 11 hr. irradiation, Cl-CP=chlorocyclopentane. G.C. Column C, 185°C. $k_q\tau$=470.

		EXP #2		
0.0	3.78		13.9	
0.0	3.76		13.8	
0.0	3.73	3.76±0.02	13.7	1.00
1.60	1.55			2.43
2.40	1.19			3.16
3.20	1.05			3.58
4.79	0.841			4.47
6.39	0.732			5.14
6.39	0.728			5.16

[4,4'-Me-BP]=0.05 M, naphthalene quencher, [PhCl]=0.00306 M, SF=1.20, 335 nm, [cyclopentane]=1.05 M, 4 hr. irradiation time, Cl-CP=chlorocyclopentane. G.C. Column C, 185°C. $k_q\tau$=723.

Table 117. Reciprocal Plot, 4,4'-di-Methylbenzophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl-CP/ PhCl	[Cl-CP] (10^{-3})	$\phi_{Cl\text{-}CP}$ (10^{-2})	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
0.0757	13.2	0.166	2.13	2.31	43.3
0.0757	13.2	0.173	2.27	2.41	41.5
0.126	7.94	0.217	2.79	3.03	33.0
0.126	7.94	0.219	2.81	3.05	32.8
0.252	3.97	0.347	4.46	4.84	20.7
0.378	2.65	0.471	6.05	6.57	15.2
0.378	2.65	0.471	6.05	6.57	15.2
1.01	0.990	0.683	8.77	9.52	10.5
1.01	0.990	0.672	8.63	9.37	10.7

I_a=0.0921 E/0, [4,4'-MeBP]=0.05 M, [PhCl]=0.0107 M, SF= 1.20, 313 nm, 8 hr. irradiation time, CP=cyclopentane, Cl-CP =chlorocyclopentane. Gc column C, 185°C. Slope=2.65, intercept=9.13, slope/intercept=0.290.

Table 118. Stern-Volmer Data, 4,4'-di-Methoxybenzophenone and 1 M Cyclopentane in CCl_4.

$[Q](10^{-3})$	Cl-CP/PhCl		$[Cl\text{-}CP](10^{-3})$	$\frac{\phi^{\circ}_{Cl\text{-}CP}}{\phi_{Cl\text{-}CP}}$
		EXP #1		
0.0	0.752		6.91	
0.0	0.796		7.32	
0.0	0.786	0.778±0.017	7.22	1.00
2.22	0.534			1.46
3.37	0.468			1.66
4.43	0.460			1.69
6.65	0.339			2.29
7.76	0.314			2.48
8.86	0.277			2.81
[4,4'-MeO-BP]=0.025 M, naphthalene quencher, [PhCl]=0.00766 M, SF=1.20, Cl-CP=chlorocyclopentane, [Cyclopentane]=1.03 M, 6 hr. irradiation time. G.C. Column C, 185°C. $k_q\tau$=200.				
		EXP #2		
0.0	0.698		3.74	
0.0	0.684		3.66	
0.0	0.705		3.77	
0.0	0.717	0.701±0.012	3.84	1.00
2.78	0.380			1.84
3.71	0.300			2.34
5.56	0.270			2.60
6.49	0.250			2.80
[4,4'-MeO-BP]=0.026 M, [PhCl]=0.00446 M, SF=1.20, Cl-CP= chlorocyclopentane, [cyclopentane]=1.03 M, 3 hr. irradiation time. G.C. Column C, 185°C. $k_q\tau$=298.				

Table 119. Reciprocal Plot, 4,4'-di-Methoxybenzophenone and Cyclopentane in CCl_4.

[CP]	$[CP]^{-1}$	Cl/CP/ PhCl	[Cl-CP] (10^{-3})	ϕ_{Cl-CP} (10^{-2})	ϕ^{-1}_{Cl-CP}
0.0757	13.2	0.108	1.02	1.05	95.2
0.0757	13.2	0.108	1.02	1.05	95.2
0.0757	13.2	0.105	0.989	1.02	98.0
0.126	7.94	0.126	1.19	1.23	81.3
0.126	7.94	0.143	1.35	1.39	71.9
0.202	4.94	0.175	0.65	1.70	58.8
0.379	2.64	0.302	2.84	2.93	34.1
0.379	2.64	0.279	2.63	2.71	36.9
1.01	0.990	0.580	5.46	5.63	17.8
1.01	0.990	0.603	5.68	5.86	17.1

I_a=0.0970 E/l, [4,4'-MeOBP]=0.015 M, [PhCl]=0.00785 M, SF= 1.20, 313 nm, 9 hr. irradiation time, CP=cyclopentane, Cl-CP=chlorocyclopentane. Gc column C, 185°C. Slope=8.52, intercept=11.9, slope/intercept=0.716.

EXP #2

0.200	5.00	0.330	1.32	2.08	48.1
0.200	5.00	0.331	1.30	2.04	49.0
0.200	5.00	0.315	1.24	1.95	51.3
0.250	4.00	0.375	1.47	2.31	43.3
0.250	4.00	0.353	1.39	2.19	45.7
0.345	2.67	0.497	1.95	3.07	32.6
0.375	2.67	0.489	1.92	3.02	33.1
0.500	2.00	0.589	2.31	3.63	27.5
1.00	1.00	0.989	3.88	6.10	16.4
1.00	1.00	0.941	3.69	5.80	17.2

I_a=0.0636 E/0, [4,4'-MeOBP]=0.016 M, [PhCl]=0.00327 M, SF= 1.20, 313 nm, 6 hr. irradiation time. Gc column C, 185°C. Slope=8.21, intercept=10.1, slope/intercept=0.813.

Table 120. Photoreduction of α,α,α-Trifluoroacetophenone by Cyclopentane in CCl_4. Mass Balance and Concentration of Photoproducts.

EXP #	$[TFA]_i$[a]	[PhBr] (10^{-3})[a]	$(PhBr/TFA)_i$[b]	SF[c]	$(TFA/PhBr)_f$[b]
1	0.1033	5.413	0.04478	0.855	17.01
2	0.1027	12.10	0.1042	0.884	2.549
3	0.1038	10.25	0.09523	0.964	2.297
4	0.1012	11.34	0.1123	1.00	2.792

EXP #	Cl-CP/PhBr[d]	SF'[e]	KP/C_{13}	$[C_{13}](10^{-3})$[a]
1	5.195	1.20	0.907	4.177
2	2.549	1.20	0.909	4.448
3	7.938	1.20	2.59	3.309
4	6.994	1.20	2.34	4.177

[a] Concentration weighed out.

[b] Ratio measured by vpc.

[c] $SF = \frac{[TFA]\ (\text{weighed})}{[PhBr]\ (\text{weighed})} \left(\frac{PhBr}{TFA}\right)_{GC}$

[d] Cl-CP=chlorocyclopentane; ratio measured by gc.

[e] $SF' = \frac{\#C \text{ in PhBr}}{\#C \text{ in PentCl}} = \frac{6}{5} = 1.20.$

[f] KP = ketyl-cyclopentyl cross product. SF" used was based on the number of C atoms:

$SF'' = \frac{\#C \text{ in Cl3}}{\#C \text{ in CP}} = \frac{13}{12.5} = 1.04$, counting C-O as 1/2.

Gc column C', 175°C (TFA, Cl-CP); 250°C (KP).

Table 121. Photoreduction of Benzophenone by Cyclopentane in CCl_4: Ratio of Chlorocyclopentane Produced to Cyclopentane Consumed.

EXP #	$[CP]_i$[a]	$(PhCl/CP)_{i,GC}$	SF[a]	$(CP/PhCl)_f$	Cl-CP/PhCl[c]	[Cl-CP][d]
1	0.1099	0.5286	1.178	1.371	0.5168	0.03058
2	0.1099	0.5286	1.178	1.136	0.7201	0.04261

[a]Concentration of cyclopentane weighed out.

[b]$SF \doteq \frac{[Pent]}{[PhCl]}$ (weighed) x $(\frac{PhCl}{Pent})_{GC}$; [PhCl]=0.04931 M.

[c]Ratio of cyclopentylchloride to phenyl chloride, determined by vpc.

[d]$SF \doteq \frac{\#C\ PhCl}{\#C\ PentCl} = \frac{6}{5} = 1.20$.

[Benzophenone] = 0.1 M, 313 nm. Gc column C, 119°C.

Table 122. Photoreduction of α,α,α-Trifluoroacetophenone by Cyclopentane and Toluene in Parallel: Relative Product Yields.

EXP #	$[CP]_i$[a]	Cl-CP/C_{13}[b]	$[Cl\text{-}CP](10^{-2})$
1	1.015	2.51	4.95
2	1.015	2.52	4.97

EXP #	$[Tol]_i$[c]	BB/C_{13}[d]	$[BB](10^{-2})$	KB/C_{13}[e]	$[KB](10^{-2})$[f]	$PhCH_2Cl/C_{13}$[g]
1	2.048	0.870	0.644	1.66	1.19	0.0
2	2.048	0.917	0.679	1.71	1.22	0.0

[a] CP=cyclopentane; concentration weighed out.

[b] Cl-CP=chlorocyclopentane; $[C_{13}]=7.593 \times 10^{-3}$ M;

$$SF = \frac{\#\ C\ Cl3}{\#\ C\ Cl\text{-}CP} = \frac{13}{5} = 2.60.$$

[c] Tol=toluene weighed out.

[d] BB = bibenzyl produced; $[C_{13}]=7.973 \times 10^{-3}$ M; $SF = \frac{\#C\ Cl3}{\#C\ BB}$

$$= \frac{13}{14} = 0.929.$$

[e] KB = ketyl-benzyl radical cross product.

[f] $SF = \frac{\#C\ Cl3}{\#C\ KB} = \frac{13}{14.5} = 0.897$, counting C-O as 1/2.

[g] No product found.

[TFA]=0.1 M, CCl_4 solvent. Gc column C, 120°C.

Table 123. Photoreduction of Benzophenone by Cyclopentane in CCl_4. Effect of Light Intensity on Photoproduct Quantum Yields.

Path, cm[a]	Cl-CP/PhCl[b]	[Cl-CP] (10^{-2}),M	KP/C_{22}[c]	[KP](10^{-4})M	I_a E/l[d]	ϕ_{Cl-CP}	$\phi_{KP}(10^{-3})$
1.5	2.21;2.16	2.65;2.59	0.0980; 0.0834	7.52;6.40	0.149	0.176	4.7
3.0	3.07;2.71	3.68;3.25	0.107; 0.0841	8.21;6.45	0.232	0.150	3.2
4.5	2.91;2.82	3.49;3.38	0.128; 0.147	9.82;11.3	0.228	0.151	4.6

[a]Pathlength of the filter solution. A=log I°/I, the absorbance at 335 nm, was measured in a 1 cm cell using air as reference. A=0.495. [Benzophenone]=0.05 M. Cyclopentane= 1.1 M.

[b]Cl-CP=chlorocyclopentane; PhCl=phenyl chloride=0.0100 M; SF=1.20, based on the relative number of C atoms: #C in PhCl/# C in Cl-CP=6/5 = 1.20.

[c]KP=ketyl-pentyl cross product. C_{22}=n-docosane=0.00609 M; SF'=1.26, based on relative number of C atoms: #C_{22}/#C in KP=22/17.5=1.26.

[d]Light absorbed, by valerophenone actinometry. [Benzophenone]=0.1 M, 335 nm. Gc column C, 130°C (Cl-CP) Column B, 240°C (KP).

Table 124.· Photoreduction of α,α,α-Trifluoroacetophenone by Cyclopentane: Quantum Yields as a Function of Conversion.

	BCP/C_{12}[a]	[BCP](10^{-4})	KP/C_{16}[b]	[KP](10^{-2})	I_a	ϕ_{BCP}(10^{-2})	ϕ_{KP}(10^{-2})
A	0.0419; 0.0417	2.39	0.176; 0.189	9.50	0.0121	2.0	7.9
B	0.0699; 0.0713	4.05	0.311; 0.308	16.2	0.0236	1.7	6.8
C	0.155; 0.158	8.98	0.714; 0.718	37.2	0.0658	1.4	5.7
D	0.231; 0.243	13.6	1.10; 1.09	57.2	0.105	1.3	5.4

[a]BCP=bicyclopentyl; C_{12}=n-dodecane=0.00477 M; SF=1.20 by the relative number of C atoms: #C atoms in C_{12}/#C atoms in BCP=12/10=1.20. Analysis carried out on a 10% FFAP gc column.

[b]KP=ketyl-pentyl cross product; C_{16}=n-hexadecane=0.00392 M; SF'=1.33 by the relative number of C atoms: #C atoms in C_{16}/#C atoms in KP=16/12.5=1.28, counting a C-O single bond as 1/2 a C atom. Analysis on a 5% SE-30 gc column.

[c]The amount of light absorbed was determined by valerophenone actinometry.

[TFA]=0.109 M, [cyclopentane]=10.4 M. Irradiation times: A=1.0 hr.; B=2 hr., 13 min.; C=6 hr., 10 min.; D=11 hr., 10 min. Gc column C, 190° (BCP), 255°C (KP).

Table 125. Photoreduction of α,α,α-Trifluoroacetophenone by Neat Cyclopentane: Concentration of Major Photoproducts.

CP/C_5[a]	[CP], M	BCP/C_{12}[b]	[BCP], M	KP/C_{16}[c]
0.00141	0.0147	0.860	0.00283	2.47

[KP], M	TFPE/C_{12}[d]	[TFPE], M	Pinacol/C_{16}
0.00995	0.926	0.00283	3.72

[Pinacol], M[e]	$(C_{12}/TFA)_i$	$(TFA/C_{12})_f$	[TFA], M(final)
0.0128	0.0956	0.0359	0.0359

[TFA], M (consumed)
0.0597

[a] CP=cyclopentene; C_5=cyclopentane=10.4 M. Gc column D, 25°C N_2 flow rate = 20 ml/min. SF=1.00.

[b] BCP=bicyclopentane; C_{12}=dodecane=0.00274 M. Gc column C, 177°C, SF=1.20, based on # of C atoms: #C in C_{12}/#C in BCP=12/10=1.20.

[c] KP ketyl-pentyl cross product; C_{16}=hexadecane=0.00303 M; SF=1.33, based on # of C atoms; #C in C_{16}#C KP=16/12=1.33, counting C-O and CF_3 as 1/2 a C atom. Gc column C, 240°C.

[d] TFPE=1,1,1-trifluoro-2-phenyl-2-ethanol; SF=1.60, based on the # of C atoms: #C in C_{12}/#C in TFPE=12/7.5=1.60, counting C-O as 1/2 a C. Gc column C, 177°C.

[e] SF=1.14 based on the number of C atoms: #C in C_{16}/C atom. Gc column C, 240°C.

[f] [TFA] as weighed: 0.0490 M; SF=[TFA]/[C_{12}](weighed) x $(C_{12}/TFA)_{gc}$=0.0490/0.00274) x (0.0956) = 1.71. Gc column C, 169°C.

Table 126. Stern Volmer Quenching Data of p-Methoxy-α,α,α-Trifluoroacetophenone by Cyclopentene in CCl_4.

[Pentene][a]	Cl-CP/PhCl[b]	[Cl-CP](10^{-3})	ϕ_{Cl-CP}	$\phi°/\phi$
0.0	0.562	4.63	0.0495	
0.0	0.629	5.18	0.0553	
0.0	0.521	4.29	0.0458	1.00
0.0127	0.378	3.11	0.0332	
0.0127	0.380	3.13	0.0334	1.51
0.0254	0.286	2.35	0.0251	2.00
0.0508	0.196	1.61	0.0172	2.92
0.102	0.113	0.930	0.994	4.92
0.102	0.114	0.938	0.0100	
0.102	0.120	0.988	0.0106	4.87

[a]Pentene=cyclopentene.

[b]Cl-CP=chlorocyclopentane.

I_a=0.0936 E/l, Cyclopentane = 1.34 M, 12 hours irradiation 335 nm, SF=1.20, PhCl=0.00686 M. Gc column C, 140°C. $k_q\tau$=37.3.

Table 127. Photoreduction of Several Ketones by Cyclohexane in CCl_4: Concentration of Chloroform and Chlorocyclohexane Produced.

Ketone	$\frac{HCCl_3}{PhH_i}$	$HCCl_3/PhH_f$	$[HCCl_3]^a$	$\frac{Cl\text{-}CH}{PhH}^b$	[PhH]	$[Cl\text{-}CH]^c$	$[HCCl_3]/[Cl\text{-}CH]$
Acetophenone	0.149	0.775;0.722	0.101; 0.093	12.7; 12.4	0.0204	0.251; 0.245	0.38
Benzophenone	0.152	0.381;0.464	0.0370; 0.0504	7.52; 7.61	0.0202	0.149; 0.151	0.29
pMeOTFA	0.102	0.212;0.200	0.0272; 0.0242	4.91; 4.91	0.0307	0.149; 0.149	0.26
TFA	0.145	0.191;0.342	0.0074; 0.0318	2.44; 8.34	0.0200	0.0483; 0.165	0.17
3,4-Di-Me-TFA	0.120	0.209;0.178	0.0218; 0.0141	3.99; 3.73	0.0307	0.121; 0.113	0.18
p-Me-TFA	0.122	0.256;0.262	0.0349; 0.0365	4.30; 4.21	0.0323	0.137; 0.134	0.17

[a] SF determined experimentally: 0.807.

[b] Cl-CH = cyclohexylchloride.

[c] SF=0.989, determined experimentally.

Gc column E, 135°C. 0.2M Ketone, CCl_4 solvent.

Table 128. Stern-Volmer Data, Valerophenone in Acetonitrile.

$[Q](10^{-2})$	$\frac{ACP}{PhCOOC_3}$		[ACP]	ϕ_{ACP}	$\frac{\phi^{\circ}_{ACP}}{\phi_{ACP}}$
0.0	5.07				
0.0	5.29				
0.0	5.23	5.20±0.08	0.0339	0.848	1.00
3.22	1.90				2.74
4.04	1.22				4.26
4.83	1.02				5.10

[VP]=0.05 M, naphthalene quencher, $[PhCOOC_3]$=0.00543 M, SF=1.20, 313 nm, 2 hrs. 45 min. Gc column A, 139°C. $k_q\tau$= 103.

Table 129. Stern-Volmer Data, Valerophenone in Benzene and CCl_4.

$[Q](10^{-2})$	ACP/C_{14}		$[ACP](10^{-2})$	$\frac{\phi^{\circ}_{ACP}}{\phi_{ACP}}$
		EXP #1		
0.0	2.08		2.75	
0.0	2.04		2.70	
0.0	2.12	2.08±0.03	2.81	1.00
1.26	1.35			1.54
2.52	1.01			2.06
3.78	0.748			2.18
6.30	0.560			3.71
7.56	0.455			4.57
[VP]=0.100 M, ϕH, naphthalene quencher, $[C_{14}]$=0.00708 M, SF=1.87, 335 nm, 3 hrs. irradiation time. G.C. Column A, 134°C. $k_q\tau$=44.				
		EXP #2		
0.0	2.19		2.90	
0.0	2.28		3.02	
0.0	2.23	2.23±0.03	2.95	1.00
1.27	1.40			1.59
2.54	0.960			2.32
3.81	0.770			2.90
6.35	0.550			4.05
7.62	0.472			4.72
10.2	0.364			6.13
[VP]=0.100 M, CCl_4, naphthalene quencher, $[C_{14}]$=0.00708 M, SF=1.87, 335 nm, 2.5 hrs. irradiation time. G.C. Column A, 134°C. $k_q\tau$=49.				

Table 130. Stern-Volmer Data, p-Methylvalerophenone in CH_3CN.

$[Q](10^{-3})$	p-MeACP/PhC_4		$[p\text{-MeACP}](10^{-2})$	$\frac{\phi^{\circ}_{pMeACP}}{\phi_{pMeACP}}$
		EXP #1		
0.0	0.973		1.48	
0.0	0.993		1.51	
0.0	1.05	1.01±0.03	1.60	1.00
2.76	0.372			2.72
5.52	0.204			4.95
6.90	0.172			5.87
8.27	0.149			6.78
11.0	0.106			9.53

I_a=0.0744 E/l, [p-Me-VP]=0.05 M, naphthalene, CH_3CN solvent, [PhC_4]=0.0129 M, 335 nm, SF=1.18; [p-tolyl-2-methylcyclobutanol]=1.06 x 10^{-4} M. G.C. Column F, 120°C. $k_q\tau$=704.

		EXP #2		
0.0	3.33		15.5	
0.0	3.42		15.9	
0.0	3.56	3.44±0.08	16.6	1.00
3.95	1.00			3.44=
7.91	0.561			6.13
9.89	0.423			8.13
11.9	0.233			14.8
15.8	0.265			13.0

I_a=0.0733 E/l, [p-Me-VP]=0.05 M, CH_3CN, naphthalene, [PhC_4] =0.00395 M, 335 nm, SF=1.18. G.C. Column F, 120°C. $k_q\tau$=670.

Table 131. Stern-Volmer Data, p-tert-Butylvalerophenone in CH_3CN.

$[Q](10^{-3})$	p-tBuACP/PhC_6		[p-tBuACP](10^{-2})	ϕ°/ϕ
		EXP #1		
0.0	1.30		1.41	
0.0	1.32		1.43	
0.0	1.30	1.31±0.01	1.41	1.00
2.61	0.603			2.17
5.22	0.394			3.32
6.53	0.355			3.69
7.83	0.308			4.25
10.4	0.239			5.48
10.4	0.242			5.41

I_a=0.0444 E/l, [p-tBuVP]=0.05 M, naphthalene, $[PhC_6]$= 0.0104 M, 335 nm, SF=1.04, 3 hr. irradiation time; [1-p-tButylphenyl-2-methylcyclobutanol]=1.10 x 10^{-3} M, average of tubes without quencher. G.C. Column F, 150°C. $k_q\tau$= 427.

		EXP #2		
0.0	6.32		2.25	
0.0	6.31		2.24	
0.0	6.36		2.26	
0.0	6.30	6.32±0.02	2.24	1.00
3.95	2.44			2.59
7.91	1.56			4.05
9.89	1.39			4.55
11.9	1.16			5.45
15.8	0.960			6.58
15.8	0.945			6.69

I_a=0.0744 E/l, [p-tBuVP]=0.05 M, naphthalene, $[PhC_6]$=0.00342M, 335 nm, SF=1.04, 2.5 hr. irradiation time; [1-p-tButylphenyl-2-methylcyclobutanol]=2.31 x 10^{-3} M, average of tubes without quencher. G.C. Column F, 150°C. $k_q\tau$=366.

Table 132. Stern-Volmer Data, p-Methoxyvalerophenone in CH_3CN.

$[Q](10^{-4})$	$\frac{pMeOACP}{PhCOOC_8}$		$\frac{[pMeOACP]}{(10^{-3})}$	$\phi_{pMeOACP}$	$\frac{\phi^{\circ}_{pMeOACP}}{\phi pMeOACP}$
0.0	1.50		4.34	0.187	
0.0	1.44		4.16	0.179	
0.0	1.50	1.48±0.03	4.34	0.187	1.00
2.68	0.559			(Aver=.184)	2.65
5.36	0.335				4.42
6.70	0.268				5.52
8.04	0.229				6.46

[p-MeOVP]=0.021 M, naphthalene quencher, $[PhCOOC_8]$=0.00165 M, SF=1.75, 313 nm, 2.5 hrs. irradiation time. G.C. Column A, 180°C. $k_q\tau$=6,562.

Table 133. Photoreduction of Substituted Benzophenones by 1.4 M 2,3-Dimethylbutane in CCl_4.

Ketone[a]	2-Cl-B/1-Cl-B[b]	C_2Cl_6/2-Cl-B[c]	$[C_2Cl_6]/[2\text{-Cl-B}]$[d]
4,4'-MeO-BP	30.4		
4,4'-Me-BP	38.6	0.082	0.25
BP	74.5	0.11	0.34
4.4'-Cl-BP	108		
4,4'-F-BP	117		
4-CN-BP	228	0.11	0.34

[a] 0.1 M ketone.

[b] 1-Cl-B=1-chloro-2,3-dimethylbutane; 2-Cl-B=2-chloro-2,3-dimethylbutane. Ratio reported is that taken directly from vpc analysis. Gc column: 6 ft, 20% SE-30, 120°C.

[c] Relative area by vpc.

[d] SF measured using C_2Cl_6 and chlocyclohexane (Cl-H) under identical conditions: 6 ft gc column, 20% SE-30, 120 and 240°C.

$$SF = \frac{[C_2Cl_6]}{[Cl\text{-}H]} \times \frac{Cl\text{-}H}{C_2Cl_6} \text{ (by gc)} = \frac{0.0296}{0.0441} (4.60) = 3.1.$$

Table 134. Photoreduction of Substituted Acetophenones in CH_3CN by p-Xylene: Quantum Yield of p-di-Tolyl-ethane as a Function of Ketone Concentration.[a]

[ACP], M	DTE/$PhCOOC_7$	[DTE](10^{-4}), M[b]
0.01	0.295	2.65[c]
0.01	0.301	2.71[c]
0.05	0.317	2.85
0.10	0.271	2.43
0.15	0.222	1.99
0.22	0.171	1.54
0.22	0.165	1.48
[p-Me-ACP]	**DTE/$PhCOOC_7$**	**[DTE](10^{-4}, M[d])**
0.018	0.281	9.75[e]
0.018	0.278	9.65[e]
0.10	0.0210	7.29
0.20	0.0125	4.34
0.20	0.0100	3.46
[3,4-di-Me-ACP]	**DTE/$PhCOOC_9$**	**[DTE](10^{-4}, M[f])**
0.00857	1.89	4.70[g]
0.00857	1.65	4.10[g]
0.106	1.75	4.35[h]
0.106	1.25	3.11[h]
[p-MeO-ACP]	**DTE/$PhCOOC_9$**	**[DTE](10^{-4}), M[i]**
0.0106	1.15	2.86[j]
0.0106	1.55	3.84[j]
0.104	1.19	2.96[k]
0.104	1.49	3.70[k]

Table 134. Continued.

[p-t-Bu-ACP], M	DTE/$PhCOOC_9$	[DTE](10^{-3}), M[l]
0.012	0.393	1.36
0.012	0.433	1.50
0.074	0.485	1.68
0.074	0.427	1.48
0.15	0.263	0.913
0.15	0.256	0.888

[a]Irradiated at 313. Column A, 150°C.

[b]$[PhCOOC_7]$=0.001198 M, SF=0.75, [p-xylene]=0.15 M, I_a= 0.0110 E/l.

[c]Average absorbance before and after photolysis: A=0.524.

[d]$[PhCOOC_9]$=0.00452 M, SF=0.768, [p-xylene]=0.15 M, I_a= 0.224 E/l.

[e]Average absorbance before and after photolysis: A=1.22.

[f]$PhCOOC_9=3.237 \times 10^{-4}$ M, SF=0.768, [p-xylene]=0.17 M.

[g]I_a=0.0350 E/l.

[h]I_a=0.0748 E/l.

[i]$[PhCOOC_9]=3.237 \times 10^{-4}$ M, SF=0.768, [p-xylene]=0.15 M.

[j]I_a=0.0350 E/l.

[k]I_a=0.0748 E/l.

[l]$[PhCOOC_9]$=0.00452 M, SF=0.768, [p-xylene]=0.15 M, I_a= 0.224 E/l.

Table 135. Photoreduction of Benzophenones in CH_3CN by p-Xylene: Quantum Yield of p-di-Tolylethane as a Function of Ketone Concentration.[d]

[BP]	DTE/$PhCOOC_7$	[DTE](10^{-4})[a]
0.01	0.476	5.22[b]
0.01	0.514	5.63[b]
0.05	0.539	5.91
0.10	0.528	5.79
0.15	0.534	5.85
0.20	0.548	6.01
0.20	0.527	5.78
[4,4'-di-MeO-BP]	**DTE/$PhCOOC_7$**	**[DTE](10^{-4})[c]**
0.01	0.530	5.81
0.03	0.464	5.08
0.03	0.437	4.79
0.05	0.500	5.44
0.05	0.468	5.13

[a] $[PhCOOC_7]$=0.00137 M, SF=0.800, I_a=0.0124 E/l, [p-xylene] =0.15 M.

[b] I_a must be multiplied by $(1-10^{-A})$, where the absorption, A=0.768.

[c] $[PhCOOC_7]$=0.00137 M, SF=0.800, I_a=0.0358 E/l.

[d] Irradiated at 313 nm. Column A, 140°C.

Table 136. Photoreduction of α,α,α-Trifluoroacetophenones in CH_3CN by Toluene: Quantum Yield of Bibenzyl as a function of Ketone Concentration.[c]

[TFA], M	BB/$PhCOOC_7$	[BB](10^{-4}), M[a]
0.02	0.441	4.83
0.02	0.433	4.75
0.10	0.323	3.54
0.20	0.313	3.43
0.20	0.304	3.34
[p-CF_3-TFA], M	**BB/$PhCOOC_7$**	**[BB](10^{-4}), M[b]**
0.02	0.392	4.30
0.10	0.446	4.89
0.10	0.412	4.52
0.20	0.423	4.64
0.20	0.427	4.68

[a] [$PhCOOC_7$]=1.16 x 10^{-3} M, SF=0.945, I_a=0.0143 E/l, [toluene]=0.15 M.

[b] [$PhCOOC_7$]=1.16 x 10^{-3} M, SF=0.945, I_a=0.00706 E/l, [toluene]=0.15 M.

[c] Irradiated at 313 nm. Column A, 140°C.

Table 137. Stern-Volmer Data, 4,4'-di-Methylbenzophenone and 0.5 M p-Xylene in CH_3CN.

$[Q](10^{-4})$	DTE/PhC_7		$[DTE](10^{-4})$	$\phi^{\circ}_{DTE}/\phi_{DTE}$
		EXP #1		
0.0	1.16		9.37	
0.0	1.20		9.70	
0.0	1.34	1.23±0.07	10.8	1.00
2.05	0.497			2.47
4.09	0.359			3.43
5.12	0.294			4.18
6.14	0.229			5.37
7.17	0.225			5.47
8.19	0.212			5.80

[4,4'-Me-BP]=0.05 M, naphthalene quencher, $[PhC_7]=1.01 \times 10^{-3}$ M, 366 nm, 6 hrs. irradiation, [p-Xylene]=0.500 M, SF=0.800. Gc column A, 200°C. $k_q\tau=5,556$.

		EXP #2		
0.0	0.978		4.84	
0.0	1.00		4.95	
0.0	0.938	0.972±0.023	4.64	1.00
1.68	0.477			2.04
3.37	0.284			3.42
4.21	0.260			3.74
5.05	0.229			4.24
6.74	0.165			5.89
6.74	0.167			5.82

[4,4'-Me-BP]=0.02 M, hexadiene quencher, $[PhC_9]=8.05 \times 10^{-4}$ M, 313 nm, 50 min. irradiation, [p-Xylene]=0.500 M, SF=0.768. Gc column A, 200°C, $k_q\tau=6,700$.

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