EXPLORATORY STUDIES AND CHEMISTRY OF PHOTOGENDERED CARBANIONS AND CARBOCATIONS FROM DIBENZANNELATED SYSTEMS

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Abstract

Photochemical reactivity of several dibenzannelated systems has been investigated to demonstrate that the driving force inherent in many of their reactions is the attainment of a $4n\pi$-electron system or intermediate in $S_1$. It has been shown that the inherent driving force for the benzylic C-H bond ionization in $9H$-xanthene (125) and $9H$-thioxanthene (136) is the formation of $8\pi$-electron cyclically conjugated carbanion intermediates 130 and 137, respectively, in $S_1$. Formation of deuterium incorporated products when 125 and 136 are photolyzed in NaOD-EtOD solutions and protium incorporation in products when photolysis of 123 and 134 is carried out in NaOH-EtOH is consistent with the intermediacy of carbanions in these reactions. Fluorescence quenching of 123 and 125 by ethanolamine in CH$_3$CN gave linear Stern-Volmer plots, with $k_q = (2.16 \pm 0.05) \times 10^7$ M$^{-1}$ s$^{-1}$ for 125 and $(1.12 \pm 0.05) \times 10^7$ M$^{-1}$ s$^{-1}$ for 123, which corresponds to an isotope effect for quenching by ethanolamine, of $k_H/k_D = 1.92 \pm 0.04$. Enhanced stability of $8\pi$ carbanions in $S_1$ is further evidenced in the photodecarboxylation of xanthene-9-carboxylic acids (142 and 145) and thioxanthene-9-carboxylic acids (147 and 148) in aqueous solution. The intermediacy of carbanions has been demonstrated in the product studies carried out in 80% D$_2$O-CH$_3$CN solution. A mechanism has been proposed which involves heterolytic bond cleavage of the carboxylate ion in $S_1$ to give intermediate carbanions. Additional support for the excited state stability of $4n$ systems comes from the studies of 155.
Photoexcitation of bent 155 results in its planarization to give planar 155 in $S_1$. The driving force for this change of conformation of 155 is believed to be the attainment of a conjugated $8\pi$-electron internal cyclic array in $S_1$.

Photolysis of substituted suberenes in aqueous CH$_3$CN results in benzylic C-H bond cleavage in these systems in $S_1$, the efficiency of which is greatly affected by the nature of substituent present. Results obtained in this study are consistent with benzylic C-H bond cleavage, with H$_2$C acting as the base, to give intermediate carbanions in $S_1$. Quantum yields of exchange in L$_2$O-CH$_3$CN (L = H or D) and in a variety of other solvent mixtures have been measured.

The photochemistry of xanthenium (99 and 114) and thioxanthenium (219) cations has been studied in aqueous H$_2$SO$_4$ in the presence of di- and trimethoxybenzenes. It has been shown that the primary photochemical step is electron transfer from methoxybenzenes to singlet excited 99 and 114. The radical intermediates thus generated subsequently react with O$_2$ to give peroxy compounds as final products.

These and other results of the photochemistry of dibenzannelated systems show that there is much interesting photochemistry to be discovered in these molecules.
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Dedicated To My Parents
CHAPTER ONE
INTRODUCTION

1.1 Prologue

Photochemical reactions are fundamentally different from ground state reactions since they involve the participation of an electronically excited state. As a consequence, photochemical reactions can occur via entirely different pathways from those encountered for ground state reactions. Consequently, the products formed in photochemical reactions often differ from ground state reactions, and can not usually be achieved even if ground state reactions were carried out at a temperature "equivalent" to the energy of the electronically excited state. The reason for this lies in the fact that the electronic configuration of an electronically excited molecule may never be achieved thermally, because in the latter case a variety of other reactions paths requiring much less energy are available, and these paths are utilized before the molecule can reach the desired state.1

The ground state electronic configuration of organic molecules consists of electrons in bonding molecular orbitals (MOs) with the antibonding MOs unoccupied. The absorption of light causes excitation of an electron from the highest occupied MO (HOMO) to the lowest unoccupied MO (LUMO), thereby creating an electronically excited state. Therefore, excited states of molecules possess excess energy which could be dissipated via a number of processes (radiative and non-radiative). Unimolecular processes such as bond
fragmentation and molecular isomerization are common. In the presence of an appropriate second molecule, bimolecular photochemical reactions, such as electron transfer to or from the excited species, can also occur. As this report mainly deals with excited state bond cleavage reactions, it is appropriate here to briefly dwell on the mechanistic possibilities for these processes.

The three most commonly cited bond fragmentation processes in the literature are (i) homolysis, where the bonding electron pair is equally apportioned between the two departing fragments; (ii) heterolysis, where the bonding electron pair remains with one fragment; and (iii) mesolytic cleavage, which involves the fragmentation of radical ions, formed as a result of electron transfer or charge transfer. The particular pathway followed by a given molecule is governed by a number of factors including the nature of the leaving group, the solvent, and the nature of the excited state (singlet versus triplet) from which the reaction is taking place.

Heterolytic bond cleavage reactions, in general, are not commonly encountered processes in organic photochemistry. This is mainly due to the fact that much of the earlier work in organic photochemistry was carried out in non-polar solvents where bond homolysis is energetically more favourable than bond heterolysis. Indeed it has been estimated that in the absence of stabilizing solvent effects, heterolysis of a carbon-chlorine bond requires ≈170 kcal mol\(^{-1}\), whereas the homolytic bond dissociation energy is about 80 kcal mol\(^{-1}\). As a result much of the earlier work in the organic photochemical literature involved
intermediates derived from bond homolysis (radical and radical pairs) and electron transfer (radical ions). On the other hand, the situation changes when solvent effects are taken into consideration. In polar solvents, where ions and ion pairs can be solvated, heterolytic cleavage may become energetically favourable and photoactivation could lead to bond heterolysis rather than homolysis.

1.2 Photogeneration of Carbanions

1.2.1 o-Nitrobenzyl Carbanions

Nitrobenzyl carbanions were the first and at present the only kind of carbanion intermediates to be generated and spectroscopically observed in photochemical reactions. The mechanism of the overall C-H bond heterolysis, in the case of nitrotoluenes containing a nitro group ortho to the methyl group, is now well understood.\textsuperscript{14} For example, photoexcitation of o-nitrotoluene (1) results in hydrogen transfer from the benzylic methyl group of 1 to the nitro group, to generate aciquinoid isomer 2 (Scheme 1.1). The hydrogen transfer process is found to be reversible in the case of 1, and the overall process does not result in any net chemical change. However, in aqueous solutions of pH > 3, deprotonation of the aciquinoid hydroxyl group (pK\textsubscript{s} = 1-4)\textsuperscript{9} competes effectively giving rise to o-nitrobenzyl carbanion (3), which in general are long-lived ( > 100 μs) and have strong absorption in the visible region.\textsuperscript{314} Irradiation of 1 in D\textsubscript{2}O results in deuterium incorporation\textsuperscript{9,15} at the benzylic carbon, consistent with the intermediacy of a carbanion.
Most of the studies in photogeneration of nitrobenzyl carbanions have concentrated on 2,4- and 2,6-dinitrotoluenes, which on irradiation generate long-lived carbanions in aqueous solutions. Atherton and Craig\textsuperscript{11} have carried out detailed mechanistic studies of these systems using nano and picosecond laser flash photolysis (LFP) methods. Thus photoexcitation of 2,6-dinitrotoluene (4) in aqueous solutions results in the formation of the aciquinoid isomer 5 (\(\lambda_{\text{max}} = 400-420\) nm) formed via initial intramolecular hydrogen transfer. The latter then undergoes deprotonation (\(k_{\text{MeOH/OH}} = 5 \times 10^4\) s\(^{-1}\)) to give 2,6-dinitrobenzyl carbanion (6) (\(\lambda_{\text{max}} = 490-550\) nm). This result was supported by McClelland and Steenken,\textsuperscript{13} who by conductivity measurements have shown that photoexcited 4 undergoes rapid hydrogen transfer to form 5 as a nonconductive transient. The excited state responsible for the reaction has been shown to be the lowest \(n,n^*\)
triplet state, which undergoes intramolecular hydrogen atom transfer with a very fast rate \( k = 0.5 \times 10^9 \text{ s}^{-1} \).

In the case of 2,4-dinitrotoluene (7), McClelland and Steenken\(^{13}\) have shown that the assignment of the absorption due to 2,4-dinitrobenzyl carbanion is not straightforward due to large solvent-induced spectral shifts. In water, the carbanion exists in the hydrogen bonded form and exhibits \( \lambda_{\text{max}} \) at 350 and 500 nm whereas in CH\(_3\)CN, where the nature of solvated species is unspecified, it has \( \lambda_{\text{max}} \) at 400 and 600 nm. Similar spectral shifts have been reported for \( p \)-nitrobenzyl carbanion.\(^{16}\)

1.2.2 Photodecarboxylation

Since the early report by Farkas and Wansbrough-Jones\(^{17}\) in 1932 of the
photodecomposition of acetic acid in aqueous solution to yield methane and CO₂, photodecarboxylation (PDC) has been shown to occur for a variety of other carboxylic acids. The mechanisms of PDC have been extensively investigated and three primary mechanistic modes have been proposed based on the nature of the C-C bond cleavage step, viz., homolytic, mesolytic and heterolytic cleavages (*vide supra*). These mechanistic possibilities have been summarized in a recent review¹⁸ and will not be dealt with in this report. However, PDC occurring via the heterolytic mode and where there is conclusive evidence for the involvement of carbanion intermediates is relevant to the present discussion and will be discussed in some detail below.

Arylacetic acids are the most commonly studied acids in PDC reactions¹⁹-²⁵ for the simple reason that the carbanion intermediates generated in these systems can be stabilized by the aryl group. The simplest arylacetic acid, viz., phenylacetic acid (8), has been studied by a number of groups. Thus photolysis of 8 in methanol results in the formation of bibenzyl and an unidentified polyacid (eq 1.1).²⁶ The process was shown to occur via a homolytic pathway but the

\[
\begin{align*}
\text{CH}_2\text{CO}_2\text{H} & \quad \xrightarrow{\text{hu}, \text{CH}_3\text{OH}} \quad \begin{pmatrix}
\text{CH}_2 \\
\text{CH}_2\text{CO}_2\text{H}
\end{pmatrix} \\
\text{CH}_2 = \text{CH}_2 \quad + \quad \text{CO}_2\text{H} \\
\text{8} & \quad \xrightarrow{\text{hu}, \text{CH}_3\text{OH}} \quad \begin{pmatrix}
\text{CH}_2 \\
\text{CH}_2\text{CO}_2\text{H}
\end{pmatrix} \\
& \quad \xrightarrow{\text{hu}, \text{CH}_3\text{OH}} \quad \text{bibenzyl} + \text{Polyacid}
\end{align*}
\]

(1.1)
detailed quantitative studies were encumbered by low quantum efficiency ($\Phi < 0.03$) of the process. However, recent studies\textsuperscript{21} have indicated that at least some portion of the PDC of 8 occurs via the heterolytic pathway (i.e., benzyl carbanion intermediate), by measuring the amount of deuterium incorporation in products obtained from photolysis in solvents such as MeOD and $(\text{Me}_2\text{CH})_2\text{O-MeOD}$.

Some deuterium incorporation was observed but it was noted that the major amount of PDC in 8 was via homolytic C-C bond cleavage. Substitution of a hydroxyl group or an equivalent electronegative substituent at the $\alpha$-position to the carboxyl group of phenylacetic acid increases the propensity of these acids to photodecarboxylate via arylmethyl carbanion intermediates.\textsuperscript{27} Wan and Xu\textsuperscript{27} have shown that photolysis of mandelic acid (9) and $\alpha$-hydroxy-2-naphthylacetic acid (10) in aqueous solutions results in PDC, to yield benzyl alcohol (11) and
2-naphthylmethanol (12) (eq 1.2), respectively, with high quantum yields (Φ = 0.4). On the other hand, the parent naphthylacetic acid (13) (with no substituent at the α-position), photodecarboxylates via a homolytic mechanism with a much lower quantum yield (Φ < 0.02). The intermediacy of carbanions in the PDC of 9 and 10 was shown by the deuterium incorporation in products (viz., 11 and 12) obtained from photolyses in D$_7$O. Further evidence for the involvement of a carbanion intermediate in these PDCs was in the low reactivity of α-hydroxy-3-methoxyphenylacetic acid (14) (Φ < 0.01). Such low reactivity of 14 indicates that the electron donating (in the excited state) meta-methoxy group destabilizes the intermediate α-hydroxyaryl methyl carbanion 15 formed after the loss of CO$_2$. It was also shown that the PDC does not take place at pH < pK$_a$, indicating that only the carboxylate ion was the reactive species. This was also confirmed by the lack of reactivity in the ester 16.
The \( m \)- and \( p \)-nitrophenylacetic acids (17 and 18) are, perhaps, the best characterized PDC reactions via carbanion intermediates.\textsuperscript{16,19,22} Photolysis of 18 in aqueous solutions results in the formation of \( p \)-nitrotoluene (20) and \( p,p' \)-dinitrobibenzyl (21) (eq 1.3). Electron ejection from the carbanion 19 gives benzyl radical, which subsequently dimerizes to give 21. Three LFP studies\textsuperscript{16,19,22} of these systems have been reported which give considerable insights into the mechanism of PDC. Employing conventional lamp flash photolysis, Margerum and Petrusis\textsuperscript{19} reported, for the first time, the observation of a long-lived transient (\( t = 53 \) s) at 358 nm which was assigned to the \( p \)-nitrobenzyl carbanion (19) derived from \( p \)-nitrophenyl acetate (18) in aqueous solution, with a high quantum yield of decarboxylation (\( \Phi = 0.6 \)). The \( m \)-isomer 17 also underwent an efficient decarboxylation but no transient assignable to the corresponding carbanion was observed, indicating that the corresponding \( m \)-nitrobenzyl carbanion was very
short-lived. More recent pico- and nanosecond LFP studies of 18 in aqueous

solution by Craig and coworkers\textsuperscript{16,22} have provided a detailed mechanistic picture

of PDC. It has been shown that PDC occurs from the lowest triplet state, which

in a primary adiabatic step generates 19 in its triplet state ($\lambda_{\text{max}} \approx 290$ nm; $\tau = 90$

ns at pH > 5.0) (Scheme 1.2). The kinetics of the decay of triplet 19 has also been

\begin{center}
\begin{tikzpicture}
\node at (0,0) {18 \xrightarrow{\text{hv}} \text{ISC} \rightarrow \text{ISC} \downarrow \text{-CO}_2 \quad \text{21} + \text{20} \xleftarrow{\text{ISC}} \text{19 (S\text{\textsubscript{0}})} \quad \text{19 (T\text{\textsubscript{1}})}
\end{tikzpicture}
\end{center}

\textbf{Scheme 1.2}
studied in detail. Wan and Muralidharan have also proposed the involvement of nitrobenzyl carbanion intermediates from the triplet excited state in the photo-retro-Aldol type reactions of several nitrobenzyl derivatives and also in the PDC of 17 and 18 (vide infra).

Arylacetic acids such as 2-, 3- and 4-pyridylacetic acids (22) have been reported to undergo PDC via heterolytic cleavage. Stermitz and Huang have shown that irradiation of these acids in aqueous solution results in efficient PDC (φ = 0.20-0.50) to yield corresponding methylpyridines (eq 1.4). The reactions of these acids are most efficient at pH = pI (isoelectric point), indicating that the

\[
\begin{align*}
22 & \leftrightarrow 23 & \text{hu} & \rightarrow 24 \\
\end{align*}
\]

(zwitterion 23 is the reactive species in the PDC. A discrete carbanion intermediate may not be involved in these reactions and a quinoid species (at least for the 2- and 4-isomers) of the type 24 might be involved in the reaction mechanism.)
The PDC of benzoylformic acid (25) in aqueous solution (pH < 2.0) proceeds with high quantum efficiency to yield benzaldehyde (27). The reaction is of interest because of its high quantum efficiency and lack of any side products. It has been suggested to be of possible use as an actinometer for 250-400 nm region. Kuhn and Gorner, using LFP, have proposed that the excited triplet state of carboxylate 25 was the reactive state, which upon loss of CO₂ (in H₂O) gives the transient acyl anion 26, which subsequently undergoes protonation to give benzaldehyde (27) (Scheme 1.3). However, there does not seem to be any apparent driving force for the triplet excited state (T₁) of carboxylate 25 to
decarboxylate, to produce a highly unfavourable species, viz., the acyl anion 26. It is possible that the reaction mechanism in this case is analogous to the mechanism of PDC suggested for mandelic acid (9) (vide supra). Since slightly acidic solution is required for reaction of 25, it is possible that the hydrated form of 25, i.e., 27 is the actual reactive species. It must be noted that 27 is structurally similar to mandelic acid (9), which has been shown to undergo facile PDC via a carbanion intermediate.

Wan and coworkers$^{31,32a,b}$ have demonstrated that the presence of a nitro substituent is not imperative to observe efficient PDC in diarylacetic acids. These authors have studied PDC in aqueous solutions of a series of compounds related to diphenylacetic acid (e.g., 28-31), differing only in the structure of the central
ring. Thus photolysis of 28 and 29 in deaerated 60% H$_2$O-CH$_3$CN at various pHs produced the corresponding hydrocarbons 36 and 37, respectively (eqs 1.5 and 1.6). Photolysis of esters 31 and 32 did not result in any reaction. It was also shown that PDC decreased at pH < pK$_a$ of the acid, indicating that only carboxylate ion was the reactive species. Comparison of the ground state reactivity of these acids revealed that fluorene-9-carboxylic acid (28) was most easily decarboxylated via an aromatic 6π-electron 9-fluorenyl carbanion (34) intermediate, whereas suberene-5-carboxylic acid (29) was reluctant to decarboxylate even on prolonged reflux. This is not surprising since the ionic decarboxylation of 29 proceeds through an incipient 8π-electron (antiaromatic) carbanion intermediate 35, which would require a very high activation energy.
On the other hand, of all the systems investigated, 29 was the most reactive photochemically ($\Phi = 0.60; k(\text{decarboxylation}) = 6 \times 10^9 \text{ s}^{-1}$), whereas 28 was the least reactive ($\Phi = 0.042; k(\text{decarboxylation}) = 8.8 \times 10^6 \text{ s}^{-1}$). The intermediacy of carbanions in these PDCs was supported by the following facts: (i) the carboxylate ion is the more reactive than the acid form; (ii) deuterium incorporation in products when photolyses were carried out in D$_2$O; and (iii) lack of any radical-derived coupling products. It was further noted that the relative reactivity of 28 vs 29 was explicable in terms of the electron count in the central ring, called the internal cyclic array (ICA), of the carbanion intermediates derived from these systems (*vide infra*).

### 1.2.3 Photoretro-Aldol Reactions

Carbanions have been proposed as intermediates in several photoretro-Aldol reactions.$^{33-39}$ The retro-Aldol reaction is mechanistically akin to decarboxylation and, in general, exhibits base catalysis. Several appropriately substituted nitroaromatic compounds have been shown to undergo this type of reaction. Wan and Muralidharan$^{33}$ have shown that the photolysis of 38 in

$$
\text{PhCHO} + \text{HNO}_2 
$$

(1.7)
aqueous solution results in the formation of $p$-nitrobenzyl carbanion 19 (eq 1.7). The proposed mechanism is similar to the PDC of $m$- and $p$-nitrophenylacetates (17 and 18) as discussed above and involves the excited triplet state mediated heterolytic cleavage of the benzylic bond as the primary photochemical step to produce the $p$-nitrobenzyl carbanion 19 (eq 1.7). Steerken and McClelland,\textsuperscript{34} using LFP, have shown that the analogous reaction reported for the acetal 39 gave

$$\text{Ph} \text{CH}_2 \text{CH}_2 \text{NO}_2 \xrightarrow{\text{hv}} \text{Ph}^+ \frown \text{CH}_2 \text{CH}_2 \text{OH} + \text{19}$$

$$\text{+H}_2\text{O} \rightarrow \text{20} + \text{21}$$

Scheme 1.4
both \( p \)-nitrobenzyl carbanion (19; \( \lambda_{\text{max}} \) 355 nm) and the 2-phenyl-1,3-dioxolan-2-ylium ion (40) (\( \lambda_{\text{max}} \) 260 nm) (Scheme 1.4). Related photoretro-Aldol reaction have also been observed for \( m \)- and \( p \)-nitrobenzylphosphonates 41.\(^{35-37}\)

Wayner and Gravelle\(^ {38} \) have reported a photoretro-Aldol reaction for amine 42 in MeOH proceeding via the diphenylmethanyl carbanion 43 as the intermediate (eq 1.8). However, in cyclohexane the radical fragmentation pathway was found to be dominant. The triphenylmethyl carbanion has been photogenerated via a photoretro-Aldol reaction of 1,1,1-triphenylphosphonate (44), which eliminates the metaphosphate ion on irradiation in basic solution.\(^ {39} \)

\[ \begin{align*}
\text{Ph-CHCH}_2\text{NMe}_2 & \xrightarrow{\text{hv, MeOH}} \text{Ph-CHPh} + \text{H}_2\text{C}==\text{NMe}_2 \\
\text{Ph} & \xrightarrow{\text{CH}_2\text{Ph}} \\
\text{Ph-C-PO(O)}_2 & \\
\end{align*} \]  

(1.8)
1.2.4 Excited State Carbon Acids

In the ground state carbanions are generated most commonly via deprotonation of the corresponding carbon acid precursor, by the action of a base of appropriate strength. A similar reaction for electronically excited states has not been very successful until very recently. Attempts have been made at deprotonating diarylmethanes such as fluorene (36) without any success.\textsuperscript{6,40} Förster cycle calculations show that 36 and related compounds are much more acidic in $S_1$ ($pK(S_1) \approx -8$ to -12)\textsuperscript{40} than in the ground state. However, photoexcitation of 36 and related hydrocarbons with a benzyl moiety in $D_2O$ failed to result in proton exchange, though a claim\textsuperscript{41} has been made recently that 36 and two other derivatives undergo benzylic proton dissociation in $S_1$ in very basic medium. However, conclusive evidence such as deuterium exchange was not reported. It has been shown that the azulinium cation 45 is much more acidic in $S_1$ than in the ground state.\textsuperscript{42} Thus flash photolysis of 45 (in strong acid) resulted in deprotonation of the excited state and transient formation of azulene (46) could be detected (eq 1.9). However, although this reaction is formally C-H deprotonation, it does not lead to or involve a carbanion intermediate.
In the ground state, C-H deprotonations are typically very slow because of lack of hydrogen bonding to solvent and the substantial geometrical and solvation changes generally required on deprotonation of carbon acids. If this also holds true for the excited state, such slow deprotonation rates would not be able to compete with the fast rates of decay generally available for $S_1$.

The cyclooctatetraene dianion (47) has been reported to undergo facile protonation in the excited state in a medium where it could not be protonated in the ground state (eq 1.10). This result suggests that 47 is much more basic in the

\[ \text{47} \xrightarrow{\text{hv}} \text{46} \]

$S_1$ than in the ground state. It could also be interpreted as evidence that ground state carbanion systems containing $4n + 2$ $\pi$-electrons (e.g., 47) are less favoured
in the excited state. The reverse reaction, i.e., photochemical deprotonation of a carbon acid to form the conjugate carbanion, has been shown to be unfavourable for systems such as fluorene (36) \((\text{vide supra})\). These results suggest that systems that generate \(4n + 2\) \(\pi\)-electron carbanions are less favoured on the excited state surface. Perhaps a hydrocarbon system which could generate a carbanion containing \(4n\) \(\pi\)-electrons upon deprotonation would better be able to exhibit carbon acid behavior in the excited state. This is indeed the necessary requirement as was shown by the following studies.

The first example of an excited state carbon acid was reported by Wan and coworkers\(^{47,48}\), who showed that suberene (37) is much more acidic in the \(S_1\) state compared to the ground state (pK(S\(_1\)) \(-1\); pK(S\(_0\)) \(-31-38\)). Thus, photolysis of suberene (37) in D\(_2\)O-CH\(_3\)CN resulted in exchange of the benzylic protons with deuterons \(\Phi = 0.030\) to give 37-\(d\) (eq 1.11). Photolysis of 5,5-dideuterosuberene (37-\(d\)) in H\(_2\)O-CH\(_3\)CN resulted in exchange of the deuterons at the benzylic

![Chemical structure and reactions](image)
position (C-5) with the proton from the solvent ($\Phi = 0.035$), also giving 37-$d$. The proposed mechanism of the reaction involves initial C-H bond heterolytic cleavage, with water acting as the general base, to generate the suberenyl carbanion (35), which undergoes reprotonation exclusively at the 5-position (eq 1.11). The mechanism is further supported by the fact that the fluorescence emission of 37 was efficiently quenched by H$_2$O in CH$_3$CN solution ($k_q = 1.68 \times 10^8$ M$^{-1}$ s$^{-1}$) and that the corresponding fluorescence quenching rate for 5,5-dideuterosuberene (37-$d_2$) was lower, giving a primary isotope effect ($k_{H}/k_{D}$) of 2.8. Since related compounds such as fluorene (36), diphenylmethane (48) and suberane (49) do not exhibit C-H bond cleavage in the S$_1$, it was proposed that the photogeneration of a 4n $\pi$-electron cyclically conjugated carbanion was a necessary requirement to observe carbon acid behavior in S$_1$.

In a related study, Wan and co-workers$^{49}$ have shown that 5-suberenol (50) undergoes photoketization to give dibenzosuberone (52) via a carbanion mechanism (eq 1.12). The key step in this reaction is C-H bond heterolysis on photoexcitation, to generate the 4n $\pi$-electron carbanion 51. Intermediacy of this carbanion in the reaction was further confirmed by the photolysis of 50 in D$_2$O.
which resulted in the formation of 5-deuterio-5-suberenol (50-d), and
dibenzosuberone (52-d₂) in which each of the 9- and 10-positions were
monodeuterated. Fluorescence quenching rates of 50 and 5-deuterio-5-suberenol
(50-d) by H₂O in CH₃CN again showed a substantial primary isotope effect (k₉/k₀
= 2.9). These results support a mechanism in which H₂O deprotonates the
benzylic C-H bond of 50 in the primary step to generate carbanion 51.

These studies present compelling evidence that there is an enhanced
driving force for the photogeneration of intermediates which contain cyclically
conjugated $4n\pi$-electrons in the excited state, compared to systems which are not cyclically conjugated or generate $4n + 2\pi$-electron intermediates.

Wan, Yates and coworkers\textsuperscript{50-52} have proposed that the photochemistry observed for $m$- and $p$-nitrobenzyl alcohols and related compounds may be rationalized by proposing that the primary photochemical step is benzylic C-H bond heterolytic cleavage from the triplet excited state, to generate a delocalized anion, which subsequently reacts to give the observed redox-type products. For example, in the reaction for $p$-nitrobenzyl alcohol (53), the initially generated carbanion 54 reacts via an overall redox reaction to give $p$-nitrosobenzaldehyde (55) (eq 1.13). The reaction was shown to be catalyzed by hydroxide ion

\[
\begin{align*}
\text{O}_2\text{N-CH}_2\text{OH} &\xrightarrow{\text{h}u} \text{O}_2\text{N-CHOH} \\
\text{53} &\rightarrow \text{54} \\
\end{align*}
\]

consistent with a carbanion mechanism. However, photolysis in D$_2$O/OD resulted in no observable deuterium incorporation in the substrate, suggesting
that every photogenerated carbanion leads to the product. A significant primary α-deuterium (at the benzylic position) isotope effect ($\Phi_H/\Phi_D > 4$) was observed which is indicative of abstraction of these protons in the product forming step.

The mechanism of reaction for m-nitrobenzyl alcohol is similar to that proposed for 53, i.e., initial formation of α-hydroxy-m-nitrobenzyl carbanion (56). However, simple redox chemistry was not observed and an electron transfer from the photogenerated carbanion to the substrate was proposed, giving rise to a more complex product mixture.52,53

![Structure of 56](image)

1.3 Photogeneration of Carbocations

Carbocations are important intermediates in organic chemistry, and as such have been extensively studied.54,55 Their existence and role in a variety of ground state (thermal) reactions such as rearrangement, nucleophilic substitution and elimination are well established and a number of reviews dealing with different facets of ground state carbocation chemistry are now available.54-57

In recent years, the generation of carbocation intermediates by photochemical methods has attracted considerable attention.58,59 In general the four most commonly employed methods to generate carbocation intermediates
are, (i) photoheterolysis or photosolvolysis, which involves formal heterolytic cleavage of a σ bond between a carbon atom and a hetero atom, such as oxygen, nitrogen, etc.; (ii) photoprotonation of a carbon-carbon double or triple bond; (iii) photoheterolysis of a radical cation; and (iv) light induced one electron oxidation of a radical (R). The following discussion is not aimed to be an exhaustive account of carbocation photogeneration, since Cristol and Bindel’s review on the subject is still an authoritative source of information in this area. More recently Das has reviewed the progress made in the photogeneration and study of transient carbocations and carbanions by laser flash photolysis methods.

1.3.1 Photosolvolysis

The photosolvolysis of organic molecules involves formal heterolytic cleavage of a σ bond, R-X, on irradiation. The carbocationic species thus generated can then be trapped by the nucleophilic solvent to give the solvolysis product (eq 1.14).

\[
R-X \xrightarrow{\text{hu}} R^+ X^- \xrightarrow{\text{Sol}^H} R-\text{Sol} + HX \quad (1.14)
\]

One of the earliest examples of photogeneration of carbocation was reported by Lifschitz and Joffe in 1919. Irradiation of triarylmethyl (TAM) leuco dye 57 in EtOH results in the efficient loss of cyanide ion to generate cation 58, which in the absence of light recombines with the cyanide ion to regenerate 57 (eq 1.15). This reaction was later shown to be highly solvent dependent, and in polar
solvents (e.g., EtOH) the quantum efficiency of formation of 58 was close to unity.\textsuperscript{61} Holmes\textsuperscript{62a,b} later showed that photolysis of 57 in aqueous ethanol results in the formation of the corresponding solvolysis products 60a and 60b via a carbocation intermediate. Herz\textsuperscript{63} in LFP studies of these systems showed that the S\textsubscript{1} state of 57 was the precursor to the cation 58. Triphenylmethane derivative 61 and other TAM derivatives have also been studied by picosecond LFP methods.
in both polar and non-polar solvents. In non-polar solvents like cyclohexane, homolytic bond cleavage generating radical intermediates is the common reaction pathway. However, in polar solvents like MeOH and CH₃CN heterolytic cleavage leading to carbocationic intermediates is the predominant pathway. These studies also delineated the effect of leaving groups (e.g., Cl, OH, OCH₃, etc.) on the ease of photoheterolysis. For example, in 61, photoheterolytic cleavage to form the corresponding carbocation for X = OH is much more faster than X = OCH₃; no carbocation formation occurs for X = H. These relative rates of heterolytic cleavages in 61 have been correlated to the higher electron affinity of HO⁻ (1.83 eV) compared to CH₃O⁻ (1.57 eV) and H⁻ (0.80 eV). Argument that the electron affinity of a leaving group is correlates with the ease with which it can undergo heterolytic cleavage in S₁ is strengthened by the fact that the PhCH₂-OCH₃ bond (68-70 kcal/mol) is actually weaker than the PhCH₂-OH bond (78 kcal/mol). Employing LFP, the temporal changes in hybridization (from sp³ to sp²) at the central carbon atom of TAM systems during carbocation formation in the S₁ state has also been studied. However, in a later study Peters and Manring showed that these results are attributable to solvents (EtOH and glycerol) used in the study and not due to changes in hybridization at the central carbon.

Using LFP studies Scaiano and coworkers have shown that photolysis of phosphonium chloride 62 results in the formation of the corresponding
carbocation ($\lambda_{\text{max}} \sim 360$ and $\lambda_{\text{max}} \sim 500$ nm; $\tau = 2.5$ µs). The bimolecular rate constants of reaction for the photochemically generated cation with added nucleophiles are near the diffusion controlled limit (e.g., $k(\text{N}_3^-) = 1.8 \times 10^{10}$ M$^{-1}$ s$^{-1}$ and $k(\text{Cl}^-) = 2.2 \times 10^9$ M$^{-1}$ s$^{-1}$).

McClelland, Steenken and coworkers$^{67,68}$ in extensive LFP studies of TAM and diarylmethyl systems in aqueous CH$_3$CN solution, have measured the quantum efficiencies of photohomolysis and photoheterolysis in these systems. In CH$_3$CN, the quantum yield for homolysis ($\Phi = 0.2-0.4$) are shown to be essentially independent of the nature of substituent on the benzene ring, while the efficiency of heterolysis increases with increasing electron donating ability of the substituent ($\Phi < 0.07$ for CF$_3$ and $\Phi < 0.3$ for OMe). Furthermore, the yield of the photogenerated cation has been shown to correlate with the $\sigma^*$ value of the para-substituent and on the $pK_{R^*}$ value (measure of cation stability in solution) of the cation.$^{68}$ The efficiency and yield of cation formation has also been shown to depend on the nature of the leaving group. For example, in the halides, the
observed heterolysis to homolysis ratio correlates with the pKₐ value of the conjugate acid HX and not with the electron affinity of the halide radical.⁶⁸

1.3.2 Photosolvolysis of Benzyl Derivatives

Although the early work on the photosolvolysis of TAM derivatives generated considerable interest, it was not until many years later that photosolvolysis reactions were extended to simple organic compounds. In this respect, photosolvolyses of benzyl derivatives have been a subject of numerous studies.⁵⁹ The interest in these systems is partly due to the inherent simplicity of these systems and the significant contributions made by Zimmerman and coworkers⁶⁹,⁷⁰ in the early 1960's. In their pioneering work Zimmerman and Sandel⁶⁹ correctly predicted the enhanced photoreactivity of meta-methoxybenzyl acetate (63) compared to the para- isomer 64, by calculating the electron density distribution for the S₁. The meta- isomer 63 which is most resistant to solvolysis in the ground state has a quantum yield of photosolvolysis nearly ten times (Φ = 0.13) that of para- isomer 64 (Φ = 0.016). This reversal in reactivity was shown to be due to the enhanced electron density at meta position in 63 in the S₁ state. The placement of acetoxymethylene group at the meta- position thus leads to the loss of acetate ion following excitation. This so called "meta- electron transmission" effect was explained with the aid of non-Kekulé structure 65 (eq 1.16). The structure 65 could be envisioned as the excited state of the benzyl cation which could react with a nucleophile such as water to give benzyl alcohol.
Besides solvolysis products, radical-derived products, via benzylic C-OAc bond homolysis, are also formed in these reactions. Since the early reports by Zimmerman and coworkers, the involvement of carbocations in the photosolvolysis of benzyl compounds has been supported by several other studies. For example, Cristol and Schloemen have shown that photosolvolysis of 67 results in the formation of isomeric deuterium labelled alcohols 68 and 69 (eq 1.17). The formation of 69 is envisioned as arising from the Wagner-Meerwein rearrangement of the initially formed carbocation 70, followed by solvolysis by water.
In the photosolvolysis of optically active (-)-1-phenylethyltrimethylammonium iodide (71) in water, McKenna and coworkers\textsuperscript{72a,b} have shown that the recovered 71 undergoes little racemization, indicating that internal return in the initially formed ion-pair is not significant. Similarly, Jaeger\textsuperscript{73a,b} has shown the involvement of carbocation in the photosolvolysis of 72.

Photolysis of $^{18}$O labelled 72 in aqueous methanol results in the formation of corresponding methyl ether. Besides solvolysis products, some radical derived products are also formed in this reaction. Interestingly, the recovered 72 shows complete scrambling of $^{18}$O's, which by photolysis of optically active 73 is shown
to be via internal return of the initially formed ion-pair. Thus, photolysis of optically active 73 in aqueous methanol yields the corresponding completely racemized methyl ether. However, the recovered 73 shows $^{18}$O scrambling, but no loss in optical activity. These results are consistent with the mechanism in which the initially formed ion-pair can either dissociate, to yield solvolysis product, or collapse to give back the $^{18}$O scrambled 73 with total retention of configuration. The proposed unifying gross mechanism involving the benzyl cation is shown in Scheme 1.5.

![Scheme 1.5](image)

Scheme 1.5
Photosolvolysis of benzyl compounds with a variety of leaving groups has been extensively investigated. For example, both benzylsulfonyl tetrafluoroborate salt 74 and phenylethyltrimethylammonium salt 71 have been shown to undergo photosolvolysis in aqueous solution via the corresponding intermediate benzyl carbocations.\textsuperscript{72,74,75} Furthermore, McKenna and coworkers\textsuperscript{77,75} have demonstrated that the efficiency of photosolvolysis in 71 is greatly affected by the nature of the substituents present on the benzene ring. For example, the quantum yields of photosolvolyses of 71 remains more or less (\(\Phi \approx 0.31\) to 0.39) constant for a variety of substituents (for e.g., \(\text{CH}_3\), \(\text{OCH}_3\)). However, for \textit{meta}-cyano (CN) substitution the quantum yield is very low (\(\Phi \approx 0.005\)), presumably due to the lower electron density at the carbon \textit{meta}- to the CN group ("\textit{meta} effect"). McKenna and coworkers\textsuperscript{76} have also shown that benzyl halides (chloride, bromide and iodide) undergo photosolvolysis from both \(S_1\) and \(T_1\) states.

Arnold and coworkers\textsuperscript{77} in the photosolvolysis of 1-naphthylmethyl derivatives 75 have developed a semi-quantitative scale of leaving group abilities of various groups in the excited state. The photosolvolysis of 75 in methanol
affords products derived both from heterolytic and homolytic cleavage of NpCH₂-X bond. The quantum yields of products derived from both heterolytic and homolytic cleavage are dependent on the nature of the leaving group (X). Using fluorescence quenching rates and quantum yields of solvolysis products, a scale of leaving group abilities of various groups has been proposed:

\[
S(CH_3)_2 > Cl = N(CH_3)_2 > O_2P(OEt)_2 > O_2CCH_3 > SO_2CH_3
\]

The case for X = I has been omitted because a study by Schuster and coworkers has shown that this substrate reacts by a pathway quite different from that of the other X groups and involves the radical anion of molecular iodine.

A considerable amount of work has been reported by Cristol and coworkers and Morrison on the photosolvolytic behavior of bridged systems such as 76 and 77. Photolysis of these systems in general gives both the
solvolyis and Wagner-Meerwien rearrangement products. A major part of this work on the photosolvolyis of these systems deals with the stereochemical requirements for both the leaving group and migrating group. Cristol and coworkers\(^79\) have proposed a mechanism (Scheme 1.6) for the observed photobehaviour of these systems which involves initial electron transfer from the aromatic ring to the remote leaving group forming a zwitterionic biradical species. Loss of the leaving group from the zwitterionic biradical species then leads to the formation of cation biradical, which may then undergo rearrangement or decay to the bridged phenonium ion. A similar mechanism has also been proposed by Jaeger\(^81\) to account for the products observed in the photosolvolyis of \(\beta\)-aryl ethyl (homobenzyl) system \(78\). Irradiation of \(78\) in aqueous methanol results in the
the formation of photosolvolysis product 79, as well as a minor amount of the rearrangement product 80. The proposed mechanism which explains the formation of observed products is shown in Scheme 1.6. This mechanism is further supported by results of irradiation of α,α'-dideutério analog of 78 which gives solvolysis products with completely scrambled deuteriums, and the recovered starting material with partial scrambling of deuteriums.81

Miller and coworkers82 have reported an interesting case of photosolvolysis of 3,4-dichloroaniline (81) in water to yield 83 (eq 1.18). To rationalize the formation of 83, authors have proposed the intermediacy of aryl cation 82

(eq 1.18). Due to large electron density at carbon meta- to the NH₂ group ("meta-effect"), the C-Cl bond is polarized in the excited state and cleaves heterolytically to yield cation 82, which is subsequently trapped by water to give 83.

1.3.3 Photodehydroxylation

The hydroxide ion (HO⁻) is considered a very poor leaving group in the ground state solvolysis reactions. However, there are a number of examples
where it has been shown that HO⁻ behaves as a good leaving group in the photosolvolysis reactions. The first example of a light induced heterolytic cleavage of a C-OH bond was reported for all-trans-retinol (84) by Rosenfeld and coworkers. Nanosecond LFP of 84 at 337 nm results in the C-OH bond heterolytic cleavage in the S₁ state, thereby generating the retinylic cation 85 (λₘₐₓ, 590 nm) (eq 1.19). A picosecond LFP study by Pienta and Kesseler provides a more detailed mechanistic picture of this process. Laser excitation of 84 results in rapid formation of contact ion-pair over a picosecond time scale following the formation of the cation 85, and before the appearance of free ions observed over several nanoseconds.

Benzyl alcohol derivatives are by far the most widely studied systems in photodehydroxylation reactions. Lin and coworkers first reported that
irradiation of bichromophoric benzyl alcohol 86 in methanol, results in the heterolytic C-OH bond cleavage generating the benzyl cation 87, which undergoes fragmentation to yield alkene 88 and triarylmethyl cation 89 (eq 1.20).

\[
\text{Ar} = \text{p-}\, \text{N(CH}_3\rangle_2\, \text{C}_6\text{H}_4
\]

Fragmentation of the cation 87 only occurs when the departing carbocation could be stabilized by one or more electron donating groups, such as dimethylaminophenyl groups in the cation 89. It was further shown that irradiation of alcohols 90 and 91 does not result in any observable reaction suggesting that both an electron accepting (phenyl) and donating (dimethylamino) moieties are required to observe an efficient photodehydroxylation reaction. However, these donor and acceptor moieties do not necessarily have to be on the
same molecule as shown by the efficient photosolvolysis of benzyl alcohol (93) in the presence of N,N-dimethylaniline (92). A charge transfer mechanism has been proposed to explain these observations (Scheme 1.7). In this mechanism,

Scheme 1.7

photoexcitation results in the charge transfer from the electron donor (D) to the
acceptor (A) moiety. The radical anion thus formed presumably expels the hydroxide ion to give the benzyl radical, which is then reoxidised by the radical cation of the electron donor to give a ground state benzyl cation, which can undergo fragmentation or nucleophilic attack.

In recent years Wan and coworkers\textsuperscript{87-91} have proposed an entirely different mechanism for the photosolvolysis of benzyl alcohols. Turro and Wan\textsuperscript{91} have shown that the proton assisted photodehydroxylation of methoxy substituted benzyl alcohols in aqueous solution proceeds via a benzyl cation (PhCH\textsubscript{2}⁺) intermediate. For example, photolysis of ortho-methoxybenzyl alcohol (94) in aqueous methanol results in the formation of the corresponding methyl ether (eq 1.21). Small amounts (≤ 5\%) of dimeric products 95 and 96, resulting from the benzylic C-OH bond homolysis, are also observed. This reaction has been shown to be acid catalyzed as the efficiency of formation of photosolvolysis products increases with decreasing pH.\textsuperscript{91} Acid catalysis is further manifested in the fluorescence emission quenching of alcohol 94 by added acid, in the same pH
region where acid catalysis of photosolvolysis is observed. Comparison of fluorescence emission quenching rates showed that ortho-methoxybenzyl alcohol (94) is at least 3 times more reactive than the corresponding meta-isomer 97. Although this result is contrary to the predictions made by Zimmerman and Sandel, it must be noted that in the case of 94 and 97 photosolvolysis was carried out in the presence of an added acid, which is the required catalyst to observe photodehydroxylation. A mechanism has been proposed in which the primary photochemical step involves proton assisted cleavage of the ArCH$_2$OH bond to generate the ArCH$_2^+$ cation (Scheme 1.8). An alternative mechanism involving the benzylic C-OH bond homolysis was ruled out since it could not fully account for the observed acid catalysis. Other studies have been carried out which delineate the effect of substituents in photosolvolysis of benzyl...
alcohols. The results obtained in these studies are in accord with the "meta
electron transmission" effect proposed by Zimmerman and Sandel.69,70

In a study of structurally rigid benzyl alcohol derivatives, Wan and
coworkers92 have reported the adiabatic photodehydroxylation of 9-
phenylxanthen-9-ol (98) to generate the 9-phenylxanthenium carbocation 99 in the
S1 state (Scheme 1.9). The adiabatic nature of this process was established by
steady-state fluorescence studies. A single step water assisted
photodehydroxylation mechanism has been proposed (Scheme 1.10). This

\[
\begin{align*}
\text{HO} & \quad \text{Ph} \\
\text{Ph} & \quad \text{OH} \\
\text{hv} & \quad \text{hv}' \\
\text{hv''} & \quad \text{H}^+ \\
\text{Ph} & \quad \text{OH}^{-} \\
\text{Ph} & \quad \text{H}_2\text{O} \quad \text{98} \\
\text{Ph} & \quad \text{99} \\
\end{align*}
\]

Scheme 1.9

mechanism is supported by the solvent isotope effect observed on the emission
yields of 98 and 99 in H2O and D2O solutions. The emission yield (Φ) of 98
increases by = 16% on going from 20% CH3CN-H2O to 20% CH3CN-D2O, whereas
the emission yield of cation 99 exhibits a concomitant decrease of similar extent. This is consistent with the water assisted dehydroxylation in the $S_1$ state. Recent LFP studies by Das and Minto, McClelland and coworkers, and Okuyama and coworkers confirm that the primary photochemical step in photodehydroxylation of 98 is the loss of hydroxide ion. However, it is also shown that only a small fraction of the photodehydroxylation (= 1% in 1:1 H$_2$O-CH$_3$CN) occurs via the adiabatic route.

Other rigid benzylic alcohols have also been shown to undergo efficient photodehydroxylation. Wan and Krogh have shown that 9-fluorenol (100) undergoes efficient photosolvolysis in aqueous methanol via the intermediate 9-fluorenyl cation 101, to give the corresponding methyl ether (eq 1.22). The LFP studies of 100 have shown that not only the cation 101, but radical 102 (via C-OH bond homolysis) is also formed in this reaction. The propensity of 100 to
undergo efficient photosolvolyis is attributed to the formation of an antiaromatic 4π-electron 9-fluorenyl cation 101 which may possess an aromatic character on the excited state surface. This contention is further supported by the observed lower photochemical reactivity of several dibenzosuberenyil alcohols which form 6π (4n+ 2) electron carbocations (e.g., 103) under conditions where 100 and other 9-fluorenol derivatives (e.g., 104) react much more efficiently.

2) electron carbocations (e.g., 103) under conditions where 100 and other 9-fluorenol derivatives (e.g., 104) react much more efficiently.

1.3.4 Photoinduced Electron Transfer (PET) Reactions of Carbocations

The initial step of producing a photochemically excited state often provides the driving force for electron transfer reactions that are not thermodynamically favourable when both electron donor and electron acceptor are in the ground electronic state. Excitation of an electron from the HOMO to the LUMO reduces the ionization potential and increases the electronic affinity of a molecule, as shown in Fig 1.1. Thus, an electronically excited molecule can function both as a powerful one-electron reducing agent (electron donor, D) and a one-electron oxidizing agent (electron acceptor, A). The feasibility of PET reaction between an excited state donor and acceptor is dictated by overall change in free energy ΔG
Figure 1.1 Electron transfer energetics of excited states

which accompanies the reaction. In polar solvents, it can be predicted on the basis of the simple equation derived by Weller and co-workers\textsuperscript{100} (eq 1.23)

\[
\Delta G \text{ (kcal/mol) } = 23.06(E_{D/D^*} - E_{A/A^*} - e^2/\alpha\chi) - \Delta E_{0,0} \\
(1.23)
\]

where: \(E_{D/D^*}\) and \(E_{A/A^*}\) are the oxidation and reduction potentials of the donor and acceptor respectively; \(e^2/\alpha\chi\) is the energy gained by bringing the two reacting species to the encounter distance in a medium of dielectric constant \(\chi\); and \(\Delta E_{0,0}\) is the electronic excitation energy of the donor.

Once the electron transfer has taken place the subsequent ability of the intermediates, viz., radicals or radical ions, to undergo further chemistry depends on several factors including the lifetimes of the singlet contact or solvent
separated ion pairs, and the rate of back electron transfer.

Unlike the photochemistry of carbanions, which has been reasonably well-studied, the photochemistry of carbocations has received considerably less attention. In the early 1970's van Tamelen and coworkers reported the steady state photolysis of several stabilized carbocations. The reactions were often complex and very solvent dependent. Although no electron donors were deliberately added, the nature of the products occasionally suggested an electron transfer had taken place. For example, photolysis of triphenylcyclopropenium bromide (105) in 10% aqueous H₂SO₄ affords hexaphenylbenzene (106) in 50% yield (eq 1.24). The efficiency of this reaction increases when methanol is used as a co-solvent.

\[
\begin{align*}
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
  &\text{Ph} \quad \text{Ph} \quad \text{Ph} \\
\end{align*}
\]

(1.24)

More recently, Al-Ekabi and coworkers have reported that irradiation of 1,1'-(di-p-anisylmethyl)ethyl cation (108) in benzene-trifluoroacetic acid solution results in electron transfer from the neutral precursor 107 to the cation 109.
(Scheme 1.10). The quantum yields of the photoproducts are very low ($\Phi = 0.001$), presumably due to an efficient back electron transfer process. The nature of the final products strongly suggests the intermediacy of the radical 109 and the radical cation 110. In the presence of a better electron donor such as 1,2,3-trimethoxybenzene (TMB), the yields of products derived from radical cation 110 is suppressed because of the competitive interception of the excited 108* by the TMB. The presence of TMB also quenches the dimerization of radical 109, indicating that the back electron transfer reaction is more facile with TMB than with 107. The radical cation 110 has been directly observed in the course of microsecond flash photolysis studies. When dicyanoanthracene is used as the excited state electron acceptor in presence of 107, same transient absorption assignable to 110 is observed. However, in the presence of TMB this transient is
completely quenched.\textsuperscript{103} 

Takahashi and coworkers\textsuperscript{104} have studied the photochemistry of charge transfer (CT) complexes of the tropylium cation (111) and a series of substituted arenes in CH\textsubscript{3}CN solutions. Photoexcitation of these CT complexes leads to an electron transfer from the arene donor to the tropylium cation acceptor (eq 1.25).

\[
\begin{align*}
\text{Ar} = \text{substituted benzenes, naphthalenes} \\
\text{Br}^+ + \text{Ar} & \rightleftharpoons [\text{Ar} \text{Br}^+] & \hnu_{\text{CT}} & \text{Ar}^+ \text{Br}^- \frac{k_{\text{BET}}}{k_{\text{BET}}} (1.25)
\end{align*}
\]

The arene radical cations thus formed (within 30 ps laser pulse) have been detected by time resolved spectroscopic techniques. The subsequent decay of the radical cation and the concomitant regeneration of the ground state CT complex occurs with a rate constant, \(k_{\text{BET}} > 4 \times 10^{10} \text{ s}^{-1}\) (eq 1.25). No further chemical reactions are observed from the excited state CT complex because of short lifetime of the arene radical cation (\(\tau = 15 \text{ ps}\)), and the fast rate (\(k_{\text{BET}}\)) of back electron transfer. Hence, prolonged photolysis of the CT complexes of substituted benzenes, naphthalenes, and anthracenes fails to yield any detectable photoproducts. However, unimolecular processes are quite rapid and can effectively compete with back electron transfer. For example, isomerization of hexamethyl Dewar benzene 112 is photoinduced via excited CT complex (eq 1.26).\textsuperscript{104}
A number of xanthenium and thioxanthenium cations in their singlet excited states have been found to be efficiently quenched by a variety of aromatic donors.\textsuperscript{105a} For example, the emission of 9-phenylxanthenium cation (99) is quenched by a number of electron donors with rates varying from $4.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (for benzene) to $2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (for anthracene). The products derived from electron transfer, viz., arene radical cation and 9-phenylxantheryl radical (113) have been detected by transient spectroscopic methods. Azarani and coworkers\textsuperscript{106} have shown that the fluorescence quenching rates of dibenzosuberenyl (103), xanthenium (114) and 9-phenylxanthenium (99) cations by electron donors (e.g., substituted benzenes) can be correlated to their oxidation potentials. Johnston and coworkers\textsuperscript{105b} have shown that the ground state of cation 115 acts as an
electron acceptor from the triplet of 1-methoxynaphthalene (116) \( (k_q = 1 \times 10^9 \text{ M}^{-1}\text{s}^{-1}) \text{ in trifluoroethanol} \). The transient absorption spectra resulting from LFP of 116 in the presence of the cation 115 shows the formation of the naphthalene radical cation \( 116^+ \) and radical 115 (eq 1.27).

\[ \text{MeO-} + \text{CH-} + \text{OMe} \quad \text{115} \quad \text{116} \quad \text{OMe} \]

1.4 Excited States of Aromatic and Antiaromatic Systems

Since the discovery of benzene by Faraday\(^{107}\) in 1825, the chemistry of aromatic compounds has attracted considerable attention. It was Kekulé who first proposed the term ‘aromatic compounds’ as a name for describing benzene and its derivatives because of their odour.\(^{108}\) A variety of chemical and physical phenomena are interpreted as caused by, or directly related to, the aromatic nature of substances. The predisposition to electrophilic substitutions vs low proclivity towards addition reactions of benzene and the unusual tendency of a molecule to release a positive or negative group (for e.g., cyclopentadiene, cycloheptatriene) are some known examples of how significantly aromatic
character and the tendency of species to acquire such character influences chemical behaviour. Important physical properties, such as diamagnetic ring current and characteristic electronic transitions, as expressed by NMR and UV patterns, are also associated with the aromaticity in the molecule under consideration. However, an unambiguous criterion which could be used to classify particular compounds as aromatic or antiaromatic does not exist. The criteria based on the reactivity data characterizes the kinetic stability and are determined by the properties not only of the ground state of the molecule, but also those of the transition state of the reaction being considered. In their monograph "Facts and Theories of Aromaticity", Lewis and Peters\textsuperscript{109} concluded on the basis of a detailed discussion of various interpretations of the term "aromaticity" that the most general definition reduces to the following: "an aromatic molecule is a molecule which resembles benzene".

The connection between electronic make-up of aromatic molecules and their unusual stability was noticed as early as 1922. It was suggested that a sextet of electrons in a molecule like benzene confer reduced unsaturation and a tendency to be inert. In 1928 the marked stability of the cyclopentadienide anion was attributed to the presence of a sextet of electrons. The first quantum mechanical explanation of the phenomenon of aromaticity was provided by Hückel's molecular orbital (HMO) theory in 1931.\textsuperscript{110} Hückel predicted that a planar molecule containing a cyclic array of \( \pi \) electrons is stabilized when the bonding \( \pi \)-orbitals are completely filled with the electrons and, the non-bonding
and antibonding molecular orbitals are unoccupied. The fulfilment of these conditions leads to the familiar \(4n + 2\) \((n = 0, 1, 2, \ldots)\) rule for the number of \(\pi\)-electrons in an aromatic compound. Since each orbital can contain two electrons, only cyclic molecules having \((4n + 2)\) \(\pi\) electrons \((n = 0, 1, 2, \ldots)\) will have a closed shell configuration and therefore will be extra stable. This is analogous to the "closed shell" arrangement of electrons about atoms of the inert elements \((2n^2)\) electrons) which exhibit marked stability. In contrast, cyclic conjugated systems with \(4n\) \(\pi\)-electrons have an open shell electronic configuration and hence do not exhibit any extra stability. This Hückel \(4n + 2\) aromaticity rule has now been experimentally verified for a large number of neutral and charged cyclic systems.

The contribution of cyclic conjugation of electrons to the energy of a molecule is characterized by the Hückel resonance energy (RE), which in terms of the Hückel approximation is defined as the difference between the total \(\pi\)-electron energies of the conjugated molecule and a reference system consisting of same number of isolated double bonds. In aromatic systems, the cyclic \(\pi\)-electron delocalization reduces the energy content of the system relative to the corresponding model compound which lacks such cyclic delocalization. On the other hand, cyclic delocalization of \(\pi\)-electrons in \(4n\) antiaromatic systems raises its energy compared to the reference compound which is not cyclically conjugated. The resonance energy has been shown to be an excellent aromaticity index for a number of monocyclic conjugated compounds. The RE as an index of aromaticity has also been used to predict the extent of aromaticity in a number
Electronic excitation of aromatic as well as antiaromatic molecules results in redistribution of electrons which affects both their physical and chemical properties. One way to understand changes that accompany electronic excitation is to examine the nodal properties of the HOMO and the LUMO of the molecule. In aromatic (4n + 2) systems the nodal properties of molecular orbitals are such that the LUMO always contains one more nodal plane than the HOMO. Thus when an electron is excited from the HOMO to the LUMO it results in the weakening of bonds (decrease in the net bond order). For example, the ring bond lengths of benzene increases from 1.393 Å to 1.434 Å in the $S_1$ state and the aromatic character (and RE) is significantly reduced. On the contrary, in the antiaromatic systems containing 4n π-electrons, the HOMO and the LUMO have equal number of nodal planes. When the HOMO contributes local bonding between two neighbouring atoms, the LUMO provides antibonding of equal magnitude and vice versa. For example, in cyclobutadiene (119) the HOMO has bonding character between atoms 1 and 3, 2 and 4, whereas the LUMO has
antibonding character between these centres (Fig 1.2). Thus, excitation of an electron in \( \textbf{119} \) from the HOMO to the LUMO reduces the bond alternating effect of HOMO and the \( \pi \)-electrons evenly localize in the four membered ring. As a direct consequence of this uniform delocalization of \( \pi \) electrons in the entire ring, the aromatic character of \( \textbf{119} \) (and similar \( 4n \) systems) is enhanced in the excited state. This reversal of aromatic character of \( 4n + 2 \) vs \( 4n \) systems has also been predicted by a number of theoretical calculations. Aihara's calculation\(^{114} \) of delocalization energies for a number of Hückel aromatic and antiaromatic systems show that excitation of an electron in a cyclic aromatic \( (4n+2) \) systems results in an overall decreased electron delocalization whereas electrons in antiaromatic \( (4n) \) systems on excitation become more delocalized. For example, the resonance energy of benzene (0.273 \( \beta \)) is greatly reduced in the excited state (-0.692 \( \beta \)); whereas the resonance energy of \( \textbf{119} \) increases on excitation (-1.226 \( \beta (T_1) \)) to 0.305 \( \beta (S_1) \)).\(^{114} \) Experimentally such a situation is best represented by a high reactivity
of benzene in the excited state forming benzvalene (120), Dewar benzene (121),
and prismane (122) on irradiation, whereas 119 appears to be relatively stable,
decomposing to acetylene on extended irradiation. Similar conclusions were
reached by Jug and coworkers\textsuperscript{115} in their calculations on the number of $4n + 2$ and
$4n \pi$-electron systems at the SINDO1 level using the bond order as a measure of
aromaticity. The bonds are significantly elongated and the bond alternation is
increased in number of $6\pi$ electron systems in the excited $S_1$ and $T_1$ states,
indicating aromatic character of these systems is reduced in the excited states. In
contrast, the optimized geometries of some $4n \pi$-electron systems in the excited
states exhibit increased aromatic character as indicated by bond equalization or
reduced bond alternation.

Chak and Dingle\textsuperscript{116} have performed PPP $\pi$-SCF calculations on the
cyclopentadienyl and cycloheptatrienyl systems as well as their dibenzo
derivatives. The calculations on the dibenzo $4n \pi$-systems indicate that the
strong bond alternation in bond lengths and charge distribution in the ground
state ($S_0$) becomes weaker in the $S_1$ state. For example, in 9-fluorenyl cation 101
most of the positive charge in $S_0$ tends to localize in the central five-membered
ring, and only a small amount is delocalized into benzene rings. However, calculations on the $S_1$ of 101 show the weakening of bond alternation indicating that there is enhanced charge delocalization of electrons. This is also supported by the observed efficient photosolvolysis of 9-fluorenol (100) in 1:1 MeOH-H$_2$O (vide supra), a medium in which diphenylmethanol (no cyclic delocalization of charge possible) does not show any reaction.$^{96}$ Similar calculations on the systems with aromatic electron count (4n+2), showed that they also experience extensive electron distribution in the $S_1$ state. For example, in 8π-electron dibenzosuberenyl carbanion 35, the delocalization of electrons in the central seven member ring has been shown to be enhanced in the $S_1$ state, and hence 35 is predicted to be more stable in the $S_1$ state.$^{116}$ Experimentally this is manifested in the benzylic C-H bond cleavage of suberene 37 in the $S_1$ state to give intermediate carbanion 35. In contrast fluorene (36) which forms 6π-electron 9-fluorenyl carbanion does not undergo C-H bond cleavage in the $S_1$ state (vide supra). The efficient PDC of suberene carboxylic acid (29) via 8π-electron suberenyl carbanion (35), compared to fluorene carboxylic acid (28) and diphenylcarboxylic acid (30), is also in accord with the enhanced stability of 8π carbanions in the excited state.

1.5 Proposed Research

It has been demonstrated that in dibenzannelated systems the photogeneration of carbocation and carbanion intermediates that consist of 4n π-electrons in an internal cyclic array (ICA) is favoured on the excited state.
The facile photodecarboxylation of several dibenzannelated acetic acids (e.g., 29) and unique carbon acid behaviour of suberene (37) (vide supra), have been attributed to the photogeneration of a cyclically conjugated 8π (4n) electron carbanion intermediate in these reactions. The efficient photosolvolysis of fluorenols (e.g., 100) via 4π-electron carbocation intermediates further supports this notion. In contrast, reactions that give rise to 4n + 2 π-electron intermediates (carbanions and carbocations) are less favoured in the excited states. Thus, assuming that the Hammond’s postulate applies to the excited state surface, it would appear that the activation barrier (∆G°) encountered for the formation of 4n π-electron intermediates on the excited surface is lower than for the corresponding 4n + 2 π-electron intermediates. In other words, reactions that give rise to cyclically conjugated 4n π-electron intermediates are favoured, because such species are more stabilized on the excited state surface relative to their 4n + 2 counterparts. There is some theoretical justification behind this proposal as well. Calculations carried out on a number of aromatic (4n + 2) and antiaromatic (4n) systems have shown that excitation results in reversal of their respective stabilities. That is, ground state stable aromatic (4n + 2) systems are destabilized, whereas antiaromatic (4n) systems are stabilized on the excited state surface (vide supra).

This argument is true only if the reaction which gives rise to such intermediates takes place (at least partially) on the excited state surface, that is, the reaction is adiabatic. However, so far there has been no proof for the
adiabaticity of such reactions and hence, no direct evidence for the formation of such 4n n-electron intermediates (carbanions or carbocations) on the excited state surface is available.

The present work is a continuing effort to obtain a better understanding of this unique phenomenon of enhanced reactivity of 4n systems on the excited state surface. In this dissertation, attempts will be made to show the generality of this process, and to address the question of structure-reactivity. The dibenzannelated systems 125, 136, 142 and 147 were chosen as progenitors of carbanion intermediates by way of C-H bond photoheterolysis and photodecarboxylation reactions. These systems are isoelectronic to suberene (37) and give rise to carbanion intermediates which consist of 8π-electrons in an ICA. However, carbanions derived from these systems (125 or 136) are expected to be less stable than the corresponding suberenyl carbanion (35), because the presence of bridge hetero atoms (O and S), which reduces the extent of negative charge delocalization (compared to the suberenyl carbanion 35). This difference in
relative stabilities of carbanion intermediates should be manifested in reduced reactivity (carbon acid behaviour) of 125 and 136 compared to 37. For similar reasons, the photodecarboxylation efficiencies of 142 and 147 are expected to be lower than that of 29. The related isoelectronic system 140 is shown not to exhibit carbon acid behaviour in the excited state because of a competing electron transfer process. The mechanism of this process has been investigated in detail by employing LFP.

The enhanced stability of 4π electron systems in the excited state is further manifested in the unprecedented photophysical properties of 155 discovered during the course of this work. The driving force behind the excited state planarization of 155 is shown to be the attainment of an 8π-electron ICA in $S_1$.

The question of structure-reactivity in the excited state carbon acid behaviour of suberene (37) is addressed by investigating the reactivity of various substituted suberenes. The substituted suberene derivatives 180, 185 and 189 were synthesized to examine the effects of electron donating and electron withdrawing substituents on the efficiency of benzylic C-H bond ionization in $S_1$. 

![chemical structures](image-url)
The results obtained in these studies support the intermediacy of 8π-electron suberenyl carbanions in these reactions. Highly annelated systems 193 and 196 undergo C-H bond ionization in the S₁ only in the presence of an added base (e.g., ethanolamine). This difference in reactivity of 193 (or 196) vs 37 underscores the differences in the stability of corresponding carbanion intermediates.

The second part of the dissertation deals with the photogeneration and
photochemistry of dibenzannelated carbocations. Previous studies have shown that, in the presence of a variety of electron donors, 9-phenylxanthenium cation (99) and 9-xanthenium cation (114) act as very good electron acceptors in the $S_1$ state. However, no attempts were made to identify the products that are formed once the electron transfer has taken place. In the present study it is shown that these cations, 99 and 114, in the $S_1$ state accept an electron from di- and trimethoxybenzenes to give the corresponding radical intermediates. The radical intermediates subsequently react with oxygen present in the reaction mixtures to give dialkyl peroxy compounds as the final product.

Finally, it is shown that irradiation of 9-thioxanthenols (e.g., 226, 228 etc.) in aqueous solution (pH 7) results in adiabatic photodehydroxylation to give the corresponding thioxanthenium carbocations in the $S_1$ state. The adiabaticity of the process is investigated by steady-state fluorescence studies. The reactivity of photogenerated thioxanthenium cations with added nucleophiles is also studied.

1.6 Experimental Approach

The rates of reaction of the various excited states either towards C-H
heterolytic cleavage, decarboxylation, electron transfer and dehydroxylation are of primary interest. Since these rate constants are not themselves directly measurable, use is made of directly measurable parameters, viz., the product quantum yields ($\Phi_P$), fluorescence quantum yields ($\Phi_F$) and fluorescence lifetimes ($\tau_F$).

The results presented in this thesis were obtained in a systematic manner as follows. Initially, product studies were carried out to accumulate evidence for a working mechanism of the photoreaction being investigated. The photoproducts formed in a given reaction were identified and characterized by NMR, UV and GC/MS analyses. The product quantum yields, $\Phi_P$, were determined to measure the efficiency of the photoreaction. The amount of photoproduct(s) formed was measured by GC-MS analyses or occasionally by $^1$H NMR integrations. The light intensity at the wavelength of irradiation was monitored using chemical actinometry and quantified by either potassium ferrioxalate actinometry or GC/$^1$H NMR (in case of secondary photochemical actinometers). The mechanism was further probed by investigating the effect of solvent and isotopic substitution on the photoprocess. Whenever possible, steady-state fluorescence quenching studies were employed to measure the excited rate constants. The fluorescence lifetimes ($\tau_F$) were measured by single photon counting. Finally, a mechanism of the photoprocess is proposed which is consistent with all the accumulated experimental data.
CHAPTER TWO

PHOTOCHEMICAL PHOTOGENERATION OF ANTIAROMATIC 8π CARBANIONS FROM OXYGEN AND SULFUR-CONTAINING DIBENZANNELATED SYSTEMS

2.1 Excited State Carbon Acid Behaviour of 9H-Xanthene (125) and 9H-Thioxanthene (136): Photogeneration of 8π-Electron Cyclically Conjugated Carbanions via Benzylic C-H Bond Heterolysis

2.1.1 Product Studies

2.1.1.1 Photolysis of 9D-Xanthene (123) in Aqueous Solution

Photolysis of a 10^{-3} M solution of 9D-xanthene (123) in 50% H_{2}O-CH_{3}CN at 300 nm (Rayonet RPR 100 photochemical reactor; = 15-17 °C; Ar purged) for 1 hour did not result in any residual exchange of deuterium, and the starting material was recovered with some photodecomposition to give 126-129 (< 20%) (eq 2.3). However, photolysis of 123 in an aqueous NaOH solution resulted in the deuterium exchange at the benzylic position. Thus, photolysis of a 10^{-3} M solution of 123 in 50% 1M NaOH-EtOH (ca. 75 min), upon work up gave a mixture which was analyzed by $^1$H NMR and GC/MS. The $^1$H NMR (250 MHz) of the product mixture showed the appearance of a new unresolved triplet at $\delta$ 4.05 (J = 1-2 Hz) (Figure 2.1). This peak was assigned to 9D,9H-xanthene (124) by comparison with the $^1$H NMR spectra of an authentic sample. The aromatic proton signals did not change in the photolyzed sample. The amount of 124 formed was calculated to be =8%, by integrating the area under the peak at $\delta$ 4.05.
However, the mass spectral analysis of the same product mixture showed the presence of both 124 (10%) and 125 (3%) (eq 2.1). It was not possible to accurately determine the amount of 125 by $^1$H NMR spectral analysis, because the triplet due to 124 at $\delta$ 4.05 overlaps the singlet due to 125 at $\delta$ =4.09 (Figure 2.1).
Photolysis of 9H-xanthene (125) in 50% 1 M NaOD-EtOD also resulted in the exchange of benzylic protons with the deuterons from the solvent to yield 124 (12%) and 123 (4%), as indicated by GC/MS analysis of the product mixture (eq 2.2).

![Diagram](image)

The possibility that a residual amount of deuterium might be incorporated into the benzene ring positions 125 was examined by $^2$H NMR. A solution of 125 in 50% 1 M NaOH-EtOH was irradiated for 1 hour and the reaction mixture, after work-up, was examined by $^2$H NMR in CD$_2$Cl$_2$ with acetone-$d_6$ as internal standard. The spectrum of the product mixture showed a strong peak at $\delta = 4.1$, indicative of mono- and dideuteration (i.e., formation of 123 and 124) at the benzylic position. No peak was observed in the aromatic region of the $^2$H spectrum, clearly showing that the deuterium exchange takes place exclusively at the C-9 position of 125.

The deuterium exchange of 123 with the solvent takes place only on irradiation. A control experiment where a solution of 123 in 50% 1 M NaOH-EtOH was left stirring in the dark for 1 hour did not result in deuterium exchange at the benzylic position. Increasing the concentration of NaOH (ca. 5 M) also did
not promote deuterium exchange in dark, and the unchanged starting material could be recovered after work-up.

The kinetics of exchange was followed by irradiating a solution of 123 in 50% 1 M NaOH-EtOH, and removing aliquots after set periods of time. The aliquots upon work-up were examined by $^1$H NMR and GC/MS to determine the yields of products, viz., 124 and 125, and starting material. The resulting plot of such an experiment is shown in Figure 2.2. It is clear from the plot that at short

![Figure 2.2](image)

**Figure 2.2** Plot of percent recovered 123 and yields of exchange photoproducts 124 and 125 vs photolysis time in 50% 1 M NaOH-EtOH.
photolysis times the only product observed is 124, indicating that it is the primary photoproduct, which reacts via a secondary photoreaction to give 125. This shows that the proton exchange in 123 is a sequential process.

Previous results obtained in our laboratories have shown that photolysis of 125 in 100% CH₃CN for 1-2 hours results in its photoisomerization to yield 6H-dibenzo[b,d]pyran (126) as a major product.¹⁷ In addition to 126, 2-benzylphenol (127), 9,9'-bisxanthene (128), and 2-(2'-hydroxyphenyl)benzyl (129) alcohol are also observed as minor products (eq 2.3). However, photolysis of 125 in 50% 1 M NaOH-EtOH for the same period of time did not give any isomerized product. This suggests that under these reaction conditions, benzylic proton exchange of 125 competes efficiently with its isomerization.

When 123 was photolyzed in 100% EtOH, in the absence of aqueous
NaOH, no protium incorporation at the benzylic position (to give 124) was observed. This suggests that NaOH is the deprotonating base which abstracts deuteron from the excited 123 to form the intermediate 9-xanthenide carbanion (130), which is subsequently protonated by the solvent to give the overall deuterium exchanged product 124. The proposal that NaOH is the deprotonating base is further supported by the fact that when the concentration of NaOH in the photolyses of 123 in 50% NaOH-EtOH was increased, the yields of the exchanged products, viz., 124 and 125, also increased (Table 2.1).

![Diagram of 130]

Table 2.1 Conversions to Exchange Photoproducts 124 and 125 in the Photolysis of 9D-Xanthene (123) in 50% NaOH-EtOH.

<table>
<thead>
<tr>
<th>[NaOH](^\text{a})</th>
<th>% 124(^b)</th>
<th>% 125(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>2 M</td>
<td>16</td>
<td>5</td>
</tr>
<tr>
<td>3 M</td>
<td>23</td>
<td>7</td>
</tr>
<tr>
<td>4 M</td>
<td>33</td>
<td>11</td>
</tr>
<tr>
<td>5 M</td>
<td>40</td>
<td>14</td>
</tr>
</tbody>
</table>

a) A 10\(^{-3}\) M solution of 123 in 50% NaOH-EtOH photolysed at 300 nm for 75 min.
b) Product distribution analyzed by \(^1\)H NMR (250 MHz) integration and GC/MS analyses; errors in calculated percentages are estimated to be ≤ 3%.
An alternative possibility which could account for the protium incorporation in 123 involves initial homolysis of the benzylic C-D bond to generate 9-xanthenyl radical (131), which subsequently abstracts hydrogen from the solvent to give deuterium exchange product 124. However, deuterium exchange via C-H(D) homolysis can be ruled out since no deuterium/protium incorporation is observed when 123/125 was photolyzed in 100% CH₃CN (or 100% 2-PrOH), a better hydrogen donating solvent than H₂O or EtOH. In addition, any photogenerated 9-xanthenyl radical (131) would be expected to dimerize efficiently to give 128, which was not observed in these photolyses.

### 2.1.1.2 Photolysis of 123 in the Presence of Ethanolamine

Photolysis of a 10⁻³ M solution of 123 in 100% CH₃CN in the presence of 5.0 M ethanolamine (ca. 10 min) resulted in the formation of 125 (≥ 98%) as the only observable product by ¹H NMR. However, when a similar solution was irradiated for a shorter period of time (ca. 5.0 min) both 124 (=60%) and 125 (=24%) were observed in the ¹H NMR spectrum of the reaction mixture (eq 2.4). No deuterium exchange took place when a solution of 123 in 100% CH₃CN was irradiated (however efficient isomerization of 123 was observed (vide supra)).
suggesting that ethanolamine acts as the deprotonating base. This is further supported by the increase in quantum yields (Φ's) of deuterium exchange (to give 124) as the concentration of ethanolamine is increased (vide infra). Control experiments showed that deuterium exchange of 123 does not take place in the dark, clearly demonstrating that the observed deuterium exchange in the presence of ethanolamine is a photochemical process.

A comparison of the amounts of monodeuterium exchange product 124 formed in the photolyses of 123 in the presence of aqueous NaOH and ethanolamine indicates that ethanolamine in CH₃CN is a much better base at promoting deuterium exchange than aqueous NaOH in 95% EtOH. The possible reason(s) for these differences are not clear at this stage.

Photolyses of related system 9-phenyl-9D-xanthene (132) and 9-phenyl-9H-xanthene (133) were also carried out to investigate the effect of substituent on the
exchange process. However, photolysis of 133 in 50% NaOH-EtOH \((\text{ca. 2 h})\) or in the presence of ethanolamine in CH\(_3\)CN did not result in deuterium exchange at the benzylic position. Instead, efficient isomerization of 133 (possibly similar to the isomerization of 125 in 100% CH\(_3\)CN\(^{117}\)) was observed. However, repeated attempts to determine the structure of the isomerized product were of no avail. Increasing the concentration of bases (NaOH or ethanolamine; \(\text{ca. 5 M}\)) also did not promote exchange in 133, and only isomerization of 133 was observed.

2.1.1.3 Photolysis of 9D-Thioxanthene (134) in Aqueous Solution

Photolysis of 9D-thioxanthene (134) in 50% H\(_2\)O-CH\(_3\)CN (\(\lambda\_\text{ex} = 300 \text{ nm}\)) also did not result in deuterium exchange at the benzylic position. However, irradiation of a \(10^{-3} \text{ M}\) solution of 134 in 50% 1 M NaOH-EtOH (\(\text{ca. 30 min}\)) resulted in deuterium exchange at the benzylic position with the solvent. The \(^1\text{H}\) NMR (250 MHz) spectrum of the reaction mixture showed the appearance of a new unresolved triplet at \(\delta 3.82 \ (J \approx 1-2 \text{ Hz})\) (Figure 2.3) due to monodeuterated 135 and a singlet at \(\delta 3.85\) due to 9H-thioxanthene (136) (eq 2.5). The assignments of the photoproducts were based on the comparison with the \(^1\text{H}\) NMR spectra of authentic materials. Based on the \(^1\text{H}\) NMR integration the
amounts of 135 and 136 present in the reaction mixture were calculated to be ≈18% and ≈7% respectively, (eq 2.5). No reaction took place when 134 was photolyzed in 100% EtOH, and the starting material was recovered quantitatively. No deuterium exchange at the benzylic position of 134 takes place in the absence of irradiation, clearly showing that the deuterium exchange is a photochemical process.

Photolysis of 9H-thioxanthene (136) in 50% 1 M NaOD-EtOD also resulted in the formation of monodeuterated 135 (≈21%) and dideuterated 134 (≈9%) (eq 2.6). No deuterium incorporation takes place in the benzene ring proton positions. The ²H NMR (CH₂Cl₂ with acetone-d₆ as internal standard) of the reaction mixture showed a strong peak at δ = 3.85, indicative of mono- and dideuteration at the benzylic position; no peak was observed in the aromatic region (between δ 7.0-7.5).

The extent of proton exchange in photolysis of 134 in 50% NaOH-EtOH increased with the increasing NaOH concentration. The results obtained in the photolysis of 134 at varying NaOH concentrations are presented in Table 2.2. The amount of exchange products formed (viz., 135 and 136) were calculated by ¹H NMR and GC/MS analyses. In general, good agreements, between the ¹H NMR
and MS data, for the calculated percentages of 135 and 136 were observed.

Table 2.2 Conversions to Exchange Photoproducts 135 and 136 in the Photolysis of 9D-Thioxanthene (134) in 50% NaOH-EtOH.

<table>
<thead>
<tr>
<th>[NaOH]a</th>
<th>% 135b</th>
<th>% 136b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M</td>
<td>18</td>
<td>7</td>
</tr>
<tr>
<td>2 M</td>
<td>22</td>
<td>9</td>
</tr>
<tr>
<td>3 M</td>
<td>29</td>
<td>11</td>
</tr>
<tr>
<td>4 M</td>
<td>35</td>
<td>13</td>
</tr>
<tr>
<td>5 M</td>
<td>43</td>
<td>15</td>
</tr>
</tbody>
</table>

a) A 10⁻³ M solution of 134 in 50% NaOH-EtOH photolysed at 300 nm for 30 min each.

b) Product distribution analyzed by ¹H NMR (250 MHz) integration and GC/MS; errors in calculated percentages are estimated to be ≤ 3%.

The kinetics of exchange was followed by ¹H NMR using 134 as the starting material. Thus a solution of 250 mg of 134 in 50% 1 M NaOH-EtOH was irradiated and aliquots removed after set periods of irradiation, and yields of products 135, 136 and starting material were calculated by ¹H NMR spectral analyses. The production of monodeuterated 135 and 9H-thioxanthene (136) with photolysis time was monitored by the growth of ¹H NMR peaks at δ 3.82 and 3.85 respectively (Figure 2.3). The resulting plot of percentages yields vs photolysis
Figure 2.3 $^1$H NMR (250 MHz) spectrum of 134 before and after (inset) photolysis in 50% 1 M NaOH-EtOH, showing formation of monodeuterated 135 and 136.

Figure 2.4 Plot of percent recovered 134 and yields of exchange photoproducts 135 and 136 vs photolysis time in 50% 1 M NaOH-EtOH.
time is shown in Figure 2.4. It is evident from this plot that the primary exchange product is monodeuterated 135, which reacts via a secondary photoreaction to yield 136.

The results obtained in the photochemical exchange studies of 134 (and 136) strongly implicate the intermediacy of 9-thioxanthenide carbanion (137). The deuterium incorporation in 136 on photolysis in 50% NaOD-EtOD and protium incorporation in 134 on photolysis in 50% NaOH-EtOH are consistent with the 9-thioxanthenide carbanion (137) intermediate. Furthermore, the absence of protium/deuterium exchange when photolysis was carried out in 100% EtOH(D) suggests that NaOH(D) is the deprotonating base which abstracts proton (or deuteron) from the benzylic position of excited 136 to give the intermediate carbanion 137. Increase in the exchange product (viz., 135 and 136) yields with increasing NaOH concentration (Table 2.2) also supports the notion that NaOH is the deprotonating base.

2.1.1.4 Photolysis of 134 in the Presence of Ethanolamine

Photolysis of a 10^3 M solution of 134 in the presence of 0.5 M ethanolamine in CH₃CN (ca. 1 h) resulted in the formation of monodeuterated 135.
(11%) and 136 (=4%) (eq 2.7). The reaction of 134 in the presence of ethanolamine was sluggish (unlike 123) compared to its reaction in the presence of aqueous NaOH, as calculated by the amount of photoproducts (135 and 136) formed in these reactions. However, as the concentration of ethanolamine in CH$_3$CN was increased the yields of exchange products (135 and 136) increased, suggesting that ethanolamine was acting as the deprotonating base (vide infra).

Photolyses of related systems, 9-phenyl-9D-thioxanthene (138) and 9-phenyl-9H-thioxanthene (139) were also carried out. However, photolysis of 138 at various concentrations of NaOH and ethanolamine failed to result in any observable deuterium exchange. A possible reason for this behaviour could be the presence of phenyl group at the C-9 position which hinders the approach of the base thereby preventing it from abstracting the proton, which is the key step to observe exchange.
Photolysis of the isoelectronic system N-methylacridan (140) was also carried out to investigate the possibility of benzylic C-H bond heterolysis. However, photolysis of 140 in 50% D₂O-CH₃CN or in the presence of ethanolamine did not result in deuterium exchange at the benzylic position. Instead, a new product, viz., bis(N-methylacridyl) (141) was formed in these photolyses. Results of the photolyses of 140 and the mechanism of the formation of 141 will be discussed separately in de-nil (vide infra).

2.1.2 Quantum Yields

The efficiency with which the supplied light converts the starting material to product is measured by the quantum yield of product formation. The quantum yield (Φ) for formation of a particular product is given by eq 2.8.

$$\Phi = \frac{\text{moles of product formed}}{\text{moles of light absorbed}}$$  

Quantum yields (Φ's) for mono deuterium incorporation in 125 and 136 and mono protium incorporation in 123 and 134 were measured on an optical bench using the output of an Oriel 200-W Hg arc lamp with the monochromator set at λ₀ = 280 nm. Potassium ferrioxalate actinometry was employed to measure the lamp intensity at this excitation wavelength. In general, 10⁻³-10⁻⁴ M solutions of the substrates in an appropriate solvent mixture were irradiated with continuous purging with a stream of argon prior to and during the photolysis,
which served to deaerate as well as stir the reaction mixtures. The conversions to exchange products were kept between 15-20%, and the amount of deuterium incorporation in products was measured by GC/MS analyses.

Table 2.3 presents the Φ's of monodeuterium incorporation in 125 and 136 in 50% 1 M NaOL-EtOL (L = H and D) mixture. No deuterium incorporation

Table 2.3  Quantum Yields (Φ's) of Formation of 124 and 135 on Photolysis in 50% NaOL-EtOL (L = H and D).

<table>
<thead>
<tr>
<th></th>
<th>50% 1 M NaOD-EtOD</th>
<th>50% 1 M NaOH-EtOH</th>
<th>50% 1 M NaOH-EtOH</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΦH</td>
<td>0.00019 ± 0.00004</td>
<td>0.0021 ± 0.0002</td>
<td>0.90 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>(from 125)</td>
<td>(from 123)</td>
<td>ΦH/ΦD = 0.90 ± 0.10</td>
</tr>
<tr>
<td>ΦD</td>
<td>0.020 ± 0.005</td>
<td>0.018 ± 0.004</td>
<td>1.11 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>(from 136)</td>
<td>(from 134)</td>
<td></td>
</tr>
</tbody>
</table>

a) Photolysis of 10⁻³ M solutions of 125 and 136.
b) Photolysis of 10⁻³ M solutions of 123 and 134.
c) Errors quoted are the standard deviation of three independent runs.

takes place in the absence of NaOL. In addition, the quantum yields for exchange (Φ's) obtained in NaOL-EtOL. (L = H or D) showed no significant isotope effect (ΦH/ΦD = 1.00 ± 0.10 (Table 2.3)), even though the initial process required for exchange involves C-H vs C-D bond cleavage. Quantum yields (Φ's) of protium incorporation in 123 and 134 in 50% NaOH-EtOH at various concentrations of NaOH were also measured and are presented in Table 2.4. Consistent with the
results of product studies, the $\Phi$'s of exchange photoproducts, viz., 124 and 135, increase with the increasing concentration of NaOH.

Table 2.4  Quantum Yields ($\Phi$) for Monoprotium Incorporation into 123 and 134 at Various Concentrations of NaOH in 50% NaOH-EtOH Solutions.$^{ab}$

<table>
<thead>
<tr>
<th>[NaOH]</th>
<th>$\Phi'$ (123)</th>
<th>$\Phi'$ (134)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M NaOH</td>
<td>0.00021 ± 0.00002</td>
<td>0.018 ± 0.0005</td>
</tr>
<tr>
<td>2 M NaOH</td>
<td>0.00026 ± 0.00003</td>
<td>0.022 ± 0.002</td>
</tr>
<tr>
<td>3 M NaOH</td>
<td>0.00035 ± 0.00003</td>
<td>0.026 ± 0.003</td>
</tr>
<tr>
<td>4 M NaOH</td>
<td>0.00181 ± 0.00005</td>
<td>0.028 ± 0.003</td>
</tr>
<tr>
<td>5 M NaOH</td>
<td>0.00350 ± 0.0005</td>
<td>0.032 ± 0.002</td>
</tr>
<tr>
<td>50% H$_2$O-CH$_3$CN</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>100% EtOH</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses of 2-3 independent runs.  
b) For solubility reasons 50% EtOH (v/v) used as co-solvent.  
c) Errors quoted are standard deviations of 3 independent measurements.

Quantum yields ($\Phi$'s) of deuterium exchange for 123 and 134 were also measured in the presence of ethanolamine in dry CH$_3$CN. Table 2.5 presents the $\Phi$'s of monodeuterium exchange of 123 and 134 at various concentrations of ethanolamine. Comparisons of $\Phi$'s of monodeuterium incorporation from Tables
Table 2.5 Quantum Yields ($\Phi$) for Monoprotium Incorporation into 123 and 134 at Various Concentrations of Ethanolamine.$^{ab}$

<table>
<thead>
<tr>
<th>[Ethanolamine]</th>
<th>$\Phi^e$ (123)</th>
<th>$\Phi^e$ (134)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 M</td>
<td>0.0074 ± 0.0002</td>
<td>0.0056 ± 0.0005</td>
</tr>
<tr>
<td>2 M</td>
<td>0.0098 ± 0.0004</td>
<td>0.0074 ± 0.0003</td>
</tr>
<tr>
<td>3 M</td>
<td>0.0141 ± 0.0002</td>
<td>0.0090 ± 0.0004</td>
</tr>
<tr>
<td>4 M</td>
<td>0.0173 ± 0.0002</td>
<td>0.0100 ± 0.0020</td>
</tr>
<tr>
<td>5 M</td>
<td>0.0193 ± 0.0003</td>
<td>0.0140 ± 0.0003</td>
</tr>
<tr>
<td>6 M</td>
<td>0.0250 ± 0.003</td>
<td>0.0173 ± 0.0004</td>
</tr>
<tr>
<td>100% CH$_3$CN</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses of 2-3 independent runs.
b) Ethanolamine solutions made in dry CH$_3$CN.
c) Errors quoted are standard deviations of 3 independent measurements.

2.4 and 2.5 reveals that ethanolamine (in CH$_3$CN) is a better base at promoting exchange of 123 than aqueous NaOH; whereas, in the case of 134 aqueous NaOH appears to be a better base at promoting exchange than ethanolamine. These results corroborate those obtained in the preparative scale photolyses of these compounds.

2.1.3 Steady-State Fluorescence and Lifetime Studies

Steady-state fluorescence quenching studies provide a crucial way to investigate the reactivity of excited singlet ($S_1$) states. For molecules with
fluorescent $S_
u$, quenching is observed as a diminution of the intensity of light emission. A variety of processes can result in quenching including excited state reactions, energy transfer, complex formation, and collisional quenching. In the present context we are primarily concerned with quenching resulting from collisional encounters between the fluorophore and quencher, which is called collisional or dynamic quenching. Collisional quenching of fluorescence is described by the Stern-Volmer relationship\textsuperscript{19} (eq 2.9).

\[
\frac{F_0}{F} = 1 + k_q\tau_0 [Q] = 1 + K_{SV}[Q]
\] (2.9)

In eq 2.9, $F_0$ and $F$ are the fluorescence intensities in the absence and presence of quencher, respectively, $k_q$ is the bimolecular quenching constant, $\tau_0$ is the lifetime of fluorophore in the absence of quencher, $[Q]$ is the concentration of quencher, and $K_{SV} = k_q\tau_0$ is the Stern-Volmer quenching constant. A plot of $F_0/F$ vs $[Q]$ yields an intercept of one on the $y$ axis and a slope equal to $K_{SV}$. Alternatively, since collisional quenching is a rate process which depopulates the $S_1$, the lifetimes of fluorophore in the absence ($\tau_0$) and presence ($\tau$) of quencher can be used to investigate the collisional quenching phenomenon. The Stern-Volmer equation which describes the lifetimes quenching is given by eq 2.10.

\[
\frac{\tau_0}{\tau} = 1 + k_q\tau_0 [Q]
\] (2.10)
Eq 2.10 illustrates an important characteristic of collisional quenching, which is an equivalent decrease in fluorescence intensity and lifetime (eq 2.11),

\[ \frac{F_0}{F} = \frac{\tau_0}{\tau} \]  \hspace{1cm} (2.11)

The decrease in lifetime occurs because quenching is an additional rate process which depletes the \( S_1 \). The diminution in fluorescence intensity occurs because the quenching rate depopulates the \( S_1 \) without fluorescence emission. A good agreement between the quenching rates, \( k_q \), obtained by fluorescence intensity and lifetimes quenching methods is indicative of collisional or dynamic quenching. Sometimes fluorescence intensity diminution is also observed when the fluorophore and quencher form a complex in the ground state (called static quenching). Fluorescence quenching data, obtained by intensity measurement alone, can be explained by either dynamic or static processes. The measurements of fluorescence lifetimes is the most definitive method to distinguish between static and dynamic quenching. Static quenching removes a fraction of fluorophores from observation. The complexed fluorophores are nonfluorescent and the only observed fluorescence is from the uncomplexed fluorophore. The uncomplexed fraction of fluorophores is unperturbed, and hence the lifetime is \( \tau_0 \). Therefore, for static quenching \( \frac{\tau_0}{\tau} = 1 \). In contrast, for dynamic quenching, \( \frac{F_0}{F} = \frac{\tau_0}{\tau} \).\(^{119}\)

In the present study the kinetics of proton/deuteron exchange was
investigated by both fluorescence emission intensity and lifetime quenching methods. The fluorescence emission and excitation spectra of 125 in dry CH$_3$CN are shown in Figure 2.5. Addition of ethanolamine quenched the emission intensity of 125 in CH$_3$CN. The deuterated analogue 123 also displayed similar fluorescence emission quenching. However, the emission of 9-phenyl-9H-xanthene (133) in CH$_3$CN was not quenched by added ethanolamine. Stern-Volmer analyses of fluorescence emission quenching of 123 and 125 by ethanolamine resulted in good linear plots. The calculated steady-state fluorescence quenching rate constants ($k_q$) are shown in Table 2.7 (vide infra).
Fluorescence lifetimes ($\tau$'s) of 123 and 125 measured at different

<table>
<thead>
<tr>
<th>[Ethanolamine]a</th>
<th>Lifetimes ($\tau$)b</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>125 (ns)</td>
</tr>
<tr>
<td>100% CH$_3$CN</td>
<td>7.59 ± 0.03</td>
</tr>
<tr>
<td>0.30 M</td>
<td>7.28 ± 0.02</td>
</tr>
<tr>
<td>0.60 M</td>
<td>7.09 ± 0.03</td>
</tr>
<tr>
<td>0.90 M</td>
<td>6.81 ± 0.04</td>
</tr>
<tr>
<td>1.20 M</td>
<td>6.44 ± 0.04</td>
</tr>
<tr>
<td>1.50 M</td>
<td>6.09 ± 0.05</td>
</tr>
<tr>
<td>2.00 M</td>
<td>5.75 ± 0.04</td>
</tr>
</tbody>
</table>

a) Freshly made ethanolamine solutions in dry CH$_3$CN.  
b) Lifetimes ($\tau$) obtained via Single Photon Counting; $\lambda$$_{ex}$ 260 nm and $\lambda$$_{em}$ 320 nm; all decays were single exponential with fitting parameter $\chi^2 < 1.30$.

ethanolamine concentrations in CH$_3$CN are presented in Table 2.6. It can be seen that lifetimes ($\tau$'s) of both 123 and 125 decrease with increasing ethanolamine concentration. However, the lifetime of 125 is quenched faster than the lifetime of 123. A Stern-Volmer analysis of the lifetime quenching of 123 and 125 by ethanolamine resulted in good linear plots (Figure 2.6). The $k_q$’s calculated from
Figure 2.6 Representative Stern-Volmer plot of lifetime (τ) quenchings of 123 and 125 in CH₃CN by added ethanolamine.

Table 2.7 Fluorescence Quenching Rate Constants (kₚ's) for 9H-Xanthene (125) and 9D-Xanthene (123) by Ethanolamine in CH₃CN.

<table>
<thead>
<tr>
<th></th>
<th>k₀ (M⁻¹ s⁻¹)</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Steady-State</td>
<td>Lifetimes</td>
<td></td>
</tr>
<tr>
<td>123</td>
<td>(1.18 ± 0.04) x 10⁷</td>
<td>(1.12 ± 0.05) x 10⁷</td>
<td></td>
</tr>
<tr>
<td>125</td>
<td>(2.52 ± 0.05) x 10⁷</td>
<td>(2.16 ± 0.05) x 10⁷</td>
<td></td>
</tr>
<tr>
<td>kₚ/k₀</td>
<td>2.18 ± 0.05</td>
<td>1.92 ± 0.04</td>
<td></td>
</tr>
</tbody>
</table>

a) By standard Stern-Volmer analyses of quenching.
b) Steady-state fluorescence spectra obtained by excitation of an argon purged (ca. 5.0 min) 10⁻⁷ M solutions of 123 and 125 at λₑ = 260 nm.
c) Lifetimes (τ) obtained via single photon counting; λₑ = 260 nm, λₘ = 320 nm; all decays were single exponential with fitting parameter χ² ≤ 1.3.
the Stern-Volmer analyses of lifetimes quenching of 123 and 125 by ethanolamine are presented in Table 2.7. It can be seen that there is a good agreement, within experimental errors, between the \( k_q \)'s obtained by steady-state fluorescence quenching \( (k_q^{sp}) \) and lifetime quenching \( (k_q^*) \) methods, indicating that the observed fluorescence quenching is a dynamic phenomenon \( (\text{vide supra}) \). A significant primary isotope effect, \( (k_{H}/k_{D})_q = 2.00 \pm 0.05 \), is observed in the fluorescence quenching rates of 123 and 125 (Table 2.7). This result is consistent with \( C-I. \) \( (I. = H \text{ and } D) \) bond heterolytic cleavage in the \( S_1 \) state with ethanolamine acting as the deprotonating base.

Attempts were also made to investigate the fluorescence quenching of 123 and 125 in 95% ethanol by aqueous NaOH. At low concentrations of NaOH \( (\text{ca. } 0.025 \text{ M}) \) the emission of 123 in ethanol was quenched. However, at higher concentrations of NaOH the emission spectrum of 123 (and 125) was distorted, which prevented a systematic fluorescence quenching study.

The fluorescence quenching studies of 9H-thioxanthene (136) (and 134) were hampered due to its weak fluorescence \( (\Phi_t = 0.020 \pm 0.005 \text{ in } \text{CH}_3\text{CN}; \) relative to suberene \( (37)^{th} \Phi_t = 0.86) \). This is presumably due to the presence of the sulfur atom which promotes the intersystem crossing (ISC) rate of excited 136. It is well known that presence of a heavy atom \( (\text{e.g., sulfur}) \) in molecules promotes the rate of ISC via spin-orbit interactions \( (\text{"heavy atom effect"}) \).\textsuperscript{120} The excitation and emission spectra of 136 in dry CH\(_3\)CN are presented in Figure 2.7.
Although fluorescence emission of 136 in CH$_3$CN was quenched by added ethanolamine, estimates of the quenching rate constant ($k_q$) from these data were not reproducible due to the weak fluorescence.

In previous studies it has been shown that molecules like fluorene (36) and divenzosuberane (49) (which do not undergo deuterium exchange at the benzylic position on irradiation in 50% D$_2$O-CH$_3$CN) do not exhibit fluorescence quenching by H$_2$O. In contrast, the fluorescence emission of suberene (37) in CH$_3$CN, which undergoes deuterium exchange via suberenyi carbanion (35) on irradiation in 50% D$_2$O-CH$_3$CN, is efficiently quenched by added H$_2$O ($k_q = 1.71 \pm 0.04 \times 10^8$ M$^{-1}$ s$^{-1}$). It has been proposed that the emission of suberene (37) is quenched via deprotonation of benzylic protons by H$_2$O in S$_i$. In the present
study. The fluorescence emission of both 9D-xanthene (123) and 9D-thioxanthene (134) in CH$_2$CN are quenched by added ethanolamine - a solvent system in which these molecules exhibit deuterium exchange at the benzylic position (vide supra). That is, the singlet excited states of 123 and 134 are quenched via deprotonation of benzylic protons by ethanolamine. On the other hand, the 9-phenyl analogues, 132 and 138, which do not undergo deuterium exchange with ethanolamine, do not exhibit fluorescence quenching by added ethanolamine.

2.1.4 Mechanism of Exchange: Excited State Carbon Acids

In principle any organic compound that contains a C-H bond can function as a carbon acid in the classical sense by donating a proton to a suitable base. However, deprotonation rates from C-H acids in the ground state are typically slow because of the lack of hydrogen bonding to the solvent and the substantial geometrical and solvation changes generally required on deprotonation of carbon acids. If this holds true for electronically excited states as well, then such intrinsically slow rates for deprotonating C-H bonds would not compete favourably with the fast rates of decay intrinsic to an excited molecule.

Many organic molecules become more acidic or basic in the singlet excited state. This has been predicted based on Förster cycle calculations. The Förster cycle combines thermodynamic and spectroscopic data to predict the chemical equilibrium constants in the excited state. For a simple deprotonation of the acid AH shown by the equilibrium of eq 2.12, it is possible to visualize both
ground and excited state process, as shown in Figure 2.8, with the appropriate energies connecting the various levels.

\[ \text{AH}^* \rightleftharpoons A + \text{H}^* \]  

(2.12)

Figure 2.8 Förster cycle for the acid-base equilibrium given in equation 2.12.

The Förster cycle gives rise to eq 2.13,

\[ \Delta \text{H}^* - \Delta \text{H} = N \hbar (v_A + v_{AH^-}) \]  

(2.13)
where, $\Delta H^*$ and $\Delta H$ are the enthalpy changes in the excited and the ground states, $v_A$ and $v_{AH}$ are the frequencies of the lowest absorption bands of A and AH*, $h$ is the Planck's constant and $N_A$ is the Avogadro number. Assuming,

$$\Delta H^* - \Delta H = \Delta G^{\circ} - \Delta G^0$$  \hspace{1cm} (2.14)

then,

$$\Delta pK = \frac{N_A h(v_A + v_{AH})}{2.303RT}$$  \hspace{1cm} (2.15)

The derivation of eq 2.15 assumes that: (a) the entropy of protonation, $\Delta S^0$, is the same in the ground and excited states; (b) the 0-0 bands of either emission or absorption are accurately known.

Based on Förster cycle calculations, fluorene (36) ($pK(S_0)$ of benzylic protons $\sim$21-23 in DMSO) has been predicted to become vastly more acidic in the $S_1$ state ($pK(S_1) = -8.5$). However, photoexcitation of fluorene (36) in $D_2O$ does not result in deuterium exchange of the benzylic protons. That is, fluorene (36) does not function as an excited state carbon acid. Failure to observe any proton exchange on excitation of 36 may be due to the intrinsically short lifetimes of the $S_1$, which competes favourably with the slow deprotonation rate of C-H bond. However, photoexcitation of suberene (37) ($pK(S_0)$ $\sim$30; $pK(S_1) = -7$) in 50% $D_2O-CH_2CN$ results in exchange of benzylic protons to give deuterium incorporated product (eq 1.11). The proposed mechanism of the deuterium exchange involves benzylic C-H bond cleavage in $S_1$ to give the intermediate suberenyl carbanion 35,
which on subsequent deuteration from the solvent D$_2$O gives the overall exchange product. That is, suberene (37) acts like a carbon acid in the $S_1$ state.

The isoelectronic systems 9H-xanthene (125) and 9H-thioxanthene (134) also act as carbon acids in $S_1$. The results obtained in the product and steady-state fluorescence studies of 123 and 134 are suggestive of an ionic mechanism for the observed deuterium exchange from $S_1$. A mechanism consistent with all available data is presented in Scheme 2.1. In this mechanism, the base ethanolamine abstracts the deuteron at the benzylic position of 123 in $S_1$ to give the intermediate.
9-xanthenide carbanion (130). The carbanion 130 may be partially hydrogen bonded to the departing RNH₂D⁺. Hence, the deuteron which is abstracted may rebond to the carbanion 130 thereby resulting in no net exchange (internal return). However, exchange of the departing deuteron with a proton from ethanolamine, and subsequent protonation of the carbanion 130 results in an overall exchange at the benzylic position of 123, to give monodeuterated product (i.e., 124).

The primary kinetic isotope effect, \((k_H/k_D)_q = 2.00\) (Table 2.7), observed in the fluorescence quenching rates of 123 and 125 respectively, by ethanolamine is consistent with the proposed ethanolamine assisted benzylic C-H vs C-D bond cleavage in the primary step in the \(S_1\) state to give the intermediate carbanion 130. Since internal return of abstracted deuteron or proton is possible, the isotope effect on the overall exchange quantum yields would be expected to be relatively small. This argument is supported by the following observations. The fluorescence quantum yield \((\Phi_f)\) of 123 in the nonreactive solvent CH₃CN is 0.23 ± 0.02 (relative to dibenzofuran). In the presence of 2.0 M ethanolamine the \(\Phi_f\) of 123 in CH₃CN is quenched by ~15% \((\Phi_f = 0.195)\). However, the observed monodeuterium exchange quantum yield in this solvent is 0.0098 ± 0.0004. If it is assumed that the decrease in \(\Phi_f\) is mostly due to the reaction of excited 123 via heterolytic deuteron abstraction from the benzylic C-D position, then out of about 35 deprotonated molecules only 10 exchange. This suggests that internal return of the deuteron is the major reaction pathway of carbanion 130 photogenerated via C-D ionization by ethanolamine.
The mechanism presented in Scheme 2.1 also explains the exchange in the presence of NaOH. The hydroxide ion abstracts deuteron from 123 in S₁ to give the intermediate 9-xanthenide carbanion (130) (which is possibly hydrogen bonded to the departing HOD), which is subsequently protonated by the solvent to give overall deuterium exchanged product, viz., 124. Once again, internal return of the deuteron to the carbanion is a distinct possibility, in that case, no net exchange will result. The exchange quantum yields of 123 and 125 in NaOL-EtOL (L = H or D) (Table 2.3) do not exhibit isotope effect. Assuming the proposed carbanion mechanism in Scheme 2.1 is true, the primary isotope effect which arises from bond cleavage of C-H vs C-D is not manifested in exchange quantum yields (Φₜ/Φₜ = 1.0 ± 0.1). This is not unexpected since the overall exchange requires the reprotonation of the photogenerated carbanion 130. This second step has associated with it a primary isotope effect (protonation from Lₒ) which compensates for the initial isotope effect. An estimate of the kinetic isotope effect using NaOH for the rates of C-D vs C-H bond cleavages in 123 and 125, respectively, could not be made because of difficulties encountered in fluorescence quenching studies of these systems in ethanol in the presence of aqueous NaOH.

The mechanism shown in Scheme 2.1 also explains the observed proton (or deuteron) exchange in 134 in the presence of ethanolamine or NaOH. Consistent with the proposed ethanolamine assisted benzylic C-L (L = H and D) bond cleavage in S₄, the fluorescence of 134 in CH₃CN is quenched by added ethanolamine. However, an accurate estimate of fluorescence quenching rate
constants (and hence the kinetic isotope effect) is not available due to the weak fluorescence of 134 and 136.

The derivative 9-phenylxanthene (133), did not exhibit excited state carbon acid behaviour, possibly because of a competing isomerization process. Consistent with the lack of carbon acid behaviour, the fluorescence emission of 133 is not quenched by NaOH or ethanolamine. Similarly, 9-phenylthioxanthene (139) also does not exhibit C-H bond cleavage in $S_1$. However, no competing photoisomerization of 139 is observed. It is possible that the presence of the phenyl group in both 133 and 139 hinders the approach of the base thereby preventing it from abstracting the proton (or deuteron), the key step required to observe exchange.

2.1.5 Discussion: Stabilized $8\pi$ Carbanions in $S_1$

The enhanced carbon acid behaviour of suberene (37) in the excited state is of fundamental interest because in the ground state it is very difficult to deprotonate the same benzylic protons of 37 ($pK \geq 35$), and requires the use of very strong bases (e.g., $n$-BuLi). In contrast, 100% exchange of the dibenzylic protons of fluorene (36) with deuterons can be accomplished by refluxing in 50% D$_2$O-dioxane ($pD = 13$). The difference in the ground state reactivities of fluorene (36) vs suberene (37) is understandable in terms of the relative stabilities of respective carbanion intermediates. Deprotonation of Fluorene (36) in the ground state is energetically favourable because of the incipient formation of a highly
stabilized aromatic 6π-electron fluorenly carbanion 34, whereas suberene (37) gives rise to a highly destabilized antiaromatic 8π-electron suberenyl carbanion 35. However, photoexcitation results in reversal of reactivities: 37 in $S_1$ undergoes facile benzylic C-H deprotonation to give the intermediate 8π-electron suberenyl carbanion 35, whereas 36 is unreactive. Since related systems such as diphenylmethane (48) and dibenzosuberene (49), which cannot form cyclically conjugated carbanions, do not exhibit benzylic C-H bond deprotonation in $S_1$, it has been suggested that the excited state carbon acid behaviour of 37 is due to the enhanced stability of 8π-electron carbanion intermediate 35 in $S_1$. Results obtained in other related studies also support the notion that formation of 4π-electron intermediates (carbanion and carbocations) is favoured in $S_1$. The excited state carbon acid behaviour of 9H-xanthene (125) and 9H-thioxanthene (136) is also consistent with this notion. That is, the driving force behind the facile benzylic C-H bond ionization in 125 and 136 is the photogeneration of antiaromatic 8π-electron cyclically conjugated carbanions 130 and 137, respectively. In the ground state, because of the antiaromatic nature of carbanions (8π-electrons in the central ring) 130 and 137, these carbanions are difficult to form and strongly basic conditions are required to generate them. For example, 9-xanthenide (130) and 9-thioxanthenide (137) carbanions have been generated in the ground state via deprotonation of 125 ($pK(S_0) = 29$) and 136 ($pK(S_0) = 30$), respectively, by employing KNH$_2$ in liquid ammonia at -30 °C. The antiaromatic nature of carbanions 130 and 137 has been shown by the upfield
shift of the "benzenoid" protons in the $^1$H NMR spectra. For example, the benzene ring protons of 125 appear in the aromatic region, $\delta$ 7-8, of the spectrum, whereas in the 9-xanthenide carbanion (130) these proton shift more upfield than could be accounted for by the presence of the negative charge (indicative of increased shielding) and appear between $\delta$ 5-6. Furthermore, the $^{13}$C NMR spectral analyses of the 9-xanthenide carbanion (130) reveals that the negative charge is mostly localized at the carboxylic carbon (C-9), indicating that there is very little charge delocalization consistent with the antiaromatic nature of the species. In contrast, the negative charge in 9-thioxanthenide carbanion (137) is more delocalized primarily because of the ability of the bigger sulfur atom to stabilize the negative charge ($d\pi-p\pi$ interaction).

In $S_1$, 125 and 136 are deprotonated under relatively mild reaction conditions to give intermediate carbanions 130 and 137, respectively (vide supra). Based on Förster cycle calculations, the $S_1$ state of these molecules would be expected to be much more acidic (lower pK) than the $S_0$ state. Using Förster cycle calculations (eq 2.15), an estimate of pK($S_1$) of 125 was made. The main difficulty in using Förster cycle calculation for 125 lies in estimating the $\Delta E_{0,0}$ energy for the 9-xanthenide carbanion (132) because of its instability (antiaromatic). The 9-xanthenide carbanion (130) was generated under N$_2$ in dry THF using n-BuLi as the deprotonating base. The absorption spectrum of 130, recorded immediately, showed a broad long wavelength band at $\lambda_{max} = 590$ nm. Based on this absorption band at 590 nm, our best estimate of $\Delta E_{0,0}$ for 130 is $\approx 44$ kcal/mol.
Thus, using \( pK(S_0) \) of 30 for 125, the excited singlet state \( pK(S_1) = -2 \) for 125 was calculated. It is clear that based on this calculation, 125 is vastly more acidic in \( S_1 \) compared to the ground state. Fluorene (36; \( pK(S_0) = -8.5 \)) and its derivatives have also been predicted to become highly acidic in \( S_1 \). However, fluorene (36) does not undergo deuterium exchange on irradiation in D\(_2\)O. That is, kinetically it is not an excited state carbon acid although Förster cycle calculations predict it to be a very strong acid in \( S_1 \) if equilibrium can be attained. These observations are consistent with the proposal that only systems that give carbaniions with 4n π-electrons in an internal cyclic array (e.g., 130) have observable excited state carbon acid behaviour.

To understand the enhanced reactivity of molecules that give rise to antiaromatic 4n π-electron carbaniions in \( S_1 \), it is useful to invoke the same arguments that are used for ground state reactions. It is well known that transformations in the ground state that lead to the formation of the highly destabilized (higher \( AG^0 \)) antiaromatic 4n π-electron intermediates have large activation barriers (\( AG^1 \)) compared to those that generate relatively stable aromatic 4n+2 π-electron intermediates. This argument is based on the Hammond postulate, which relates thermodynamic features of an elementary reaction to the structure and energy of the transition state, and hence kinetic behaviour. This approach is presented diagrammatically in Figure 2.9.
Figure 2.9 Illustration of the Hammond postulate as applied to $S_0$ and $S_1$ surfaces.

Previous studies have shown that photoreactions of dibenzannelated systems that give rise to intermediates containing $4n\pi$-electrons ICA are favoured in the $S_1$ state, compared to their $4n+2$ counterparts. Photogeneration of 9-xanthenide (130) and 9-thioxanthenide (137) carbanions, both consisting of an $8\pi$-electron ICA, is consistent with this notion. If the preferential formation of these carbanions, 130 and 137, is taken to imply a lower activation barrier ($\Delta G^+$) on the $S_1$ surface, then extension of Hammond’s postulate would suggest that in the $S_1$ state carbanions 130 and 137 are indeed more stabilized than their $4n+2$ counterparts (e.g., the fluorenyl carbanion 34). This argument is true assuming that, (a) the Hammond postulate applies to the $S_1$ surface and, (b) the C-H bond
cleavage takes place on the $S_1$ surface. There is no apparent reason to doubt the applicability of Hammond's postulate to the $S_1$ surface. However, there is no direct evidence for the adiabatic formation of carbanions 130 and 137 on the $S_1$ surface.

If the excited 125 and 134 funnel down from the $S_1$ to the $S_0$ potential energy surface, rather than proceeding or to react completely on the $S_1$ surface, then an enhanced stability of $8\pi$ carbanions 130 and 137 is not required to explain the enhanced reactivity of 125 and 134, compared to fluorene (36), on photoexcitation (Figure 2.10a). Instead, it could be envisaged that C-H bond photoionization of 125 (or 134) to give the intermediate carbanions 130 (or 137) is preferred simply because the higher thermal activation barriers (to form these carbanions) brings the $S_0$ and the $S_1$ surfaces much closer together and hence increases the rate of internal conversion (adiabatic return) (Figure 2.10a). In such a case the preferential formation of 130 or 137 is not due to the low activation barrier encountered on the $S_1$ surface, but rather due to small $S_0$-$S_1$ gap at some point on the reaction coordinate. However, since the transition state for formation of carbanions 130 and 137 occurs late on the $S_0$ surface (endothermic reaction) and rather early on the $S_1$ surface (exothermic reaction), it is not clear why internal conversion from $S_1$ to $S_0$ should occur prior to the activated complex formation on $S_1$. In order for diabatic return to the $S_0$ surface to be product forming, it must occur late enough to intercept the $S_0$ transition state. Thus as long as internal
Figure 2.10 Generalized potential energy surface for two possibilities for excited state carbon acid dissociations, (a) Diabatic Process: internal return to the $S_0$ surface; (b) Adiabatic Process: excited state cleavage step followed by deactivation to the ground state ionic intermediates.
conversion to $S_0$ follows the rate limiting cleavage step, the excited state reactivity will reflect the $S_1$ energy barrier.

On the other hand if the reaction is adiabatic in nature, then the C-H bond photoionization step occur on the $S_1$ surface and the intermediate carbanions 130 and 137 are formed on the $S_1$ surface (Figure 7.10b). In this case, deactivation to the $S_0$ occurs at the carbanion stage. Interactions of these carbanions with the solvent molecules then deactivates them to the $S_0$ surface, and the rest of the reaction then proceeds along the $S_0$ surface. However, fluorescence emission from such photogenerated $4n$ ($8\pi$) carbanions has not been observed. In contrast, photochemical reactions which give rise to $4n+2$ $\pi$-electron carbocation intermediates (e.g., 99) have been shown to be adiabatic, by observation of their fluorescence emission. This difference in emissive behaviour of $4n$ vs $4n+2$ systems is understandable if the energy differences between $S_0$-$S_1$ for the two systems is taken into consideration. The $S_0$-$S_1$ energy gap for $4n+2$ systems is larger compared to the $4n$ systems. For example, the 9-fluorenyl carbanion (34; 6$\pi$-electrons, $4n+2$ system) is known to be fluorescent, and has a $S_0$-$S_1$ gap of 54-56 kcal mol$^{-1}$. Unfortunately, electronic spectra of antiaromatic ions are less well defined. Calculations carried out by Jug and Padma Malar and Aihara suggest that antiaromatic ($4n$) systems have low lying excited states. For example, in the case of the suberenyl carbanion (35) it has been estimated that the energy difference between $S_0$ and $S_1$ is at least 20 kcal mol$^{-1}$ smaller than the gap for the corresponding $4n+2$ ion. Hence, although no emission from the photogenerated
carbanions 130 or 137 has been observed, their efficient formation would suggest that these antiaromatic carbanions are indeed more stabilized in the excited state and can be generated adiabatically.

The excited state benzylic C-H deprotonation of 125 and 134 is clearly supported by both product and fluorescence quenching studies. It seems reasonable that the measured $k_q$'s for fluorescence quenching of 123 and 125 by ethanolamine can be equated to the rates ($k_{H}$) of benzylic C-L (L = H or L') bond ionization in $S_1$ with ethanolamine acting as the base. These C-H bond ionization rates for 125 are an order of magnitude smaller than those obtained for suberen (37). This difference in reactivity of 125 vs 37 may be reflective of the relative stabilities of the intermediate 8π-electron carbanions 130 and 35. In terms of resonance energy, in the ground state, it is well known that aromatic systems with a hetero atom (e.g., pyridine) are not as stable as their hydrocarbon analogue (e.g., benzene). In the present context, the negative charge in the 9-xanthenide carbanion (130) cannot be delocalized as much as it can be compared to the corresponding suberenyl carbanion 35. Because of the reduced negative charge delocalization, 130 would be expected to be less stable than 35. This difference in stabilities of these carbanions (130 vs 35) is reflected in the reduced carbon acidity of 125 compared to 37.

Dewar-Zimmerman and Woodward-Hoffmann rules predict that photochemical pericyclic reactions take place preferentially through excited forms of antiaromatic transition states. That is, an antiaromatic cyclic transition state is
more stable in the excited state than the corresponding aromatic transition state. Although the reaction investigated (C-H bond ionization) in the present study is not formally a pericyclic reaction, these rules still work in predicting the outcome of these reactions. That is, there is an inherent stabilizing effect of a 4n array of electrons on the excited state surface, analogous to the aromatic stabilization associated with 4n + 2 systems in the ground state. Further support for this proposal comes from the following photodecarboxylation studies of xanthene and thioxanthene carboxylic acid derivatives in aqueous solution (vide infra).

2.2 Photodecarboxylation of Xanthene and Thioxanthene Carboxylic Acids in Aqueous Solution: Photogeneration of 8π Electron Carbanion Intermediates

2.2.1 Product Studies

Photolysis of the diaryl acetic acids (Rayonet RPR 100 reactor; 254 nm lamps; quartz vessel; solution cooled with a cold finger to -15 °C; argon-purged solutions; photolysis time 1-10 min.) were carried out using -10⁻³ M solutions of substrates dissolved in 200 mL aqueous CH₃CN (typically 80% (v/v) H₂O-CH₃CN), and the pH adjusted using a pH meter, to ≥ 8 by adding an appropriate amount of a stock NaOH solution. Photolysis of all diarylacetic acids resulted in the formation of the corresponding decarboxylated products in moderately high yields. Photolysis in D₂O-CH₃CN resulted in the formation of the corresponding monodeuterated products, whereas photolysis in 100% CH₃CN resulted in no
2.2.1.1 Photolysis of Xanthene-9-Carboxylic Acid (142)

Photolysis of an argon purged solution of 142 in 80% H$_2$O-CH$_3$CN (pH $\geq 8$) for 10 min resulted in efficient decarboxylation to yield 9H-xanthene (125) and 9,9'-bisxanthene (128) (eq 2.16) as indicated by $^1$H NMR spectral analysis of the reaction mixture. The assignments of the photoproducts were based on comparison with the $^1$H NMR spectra of the authentic samples.

In a previous study it has been shown that photolysis of 125 in aqueous CH$_3$CN solution in the presence of p-nitrobenzoic acid resulted in the formation of 128. The proposed mechanism of this dimerization involves electron transfer from 125 to p-nitrobenzoic acid to form the radical cation 125$^+$, followed by
deprotonation, to give xanthenyli radical 131, which subsequently dimerizes to form 128 (eq 2.17). To test for the possibility that 128 of eq 2.16 might be formed via secondary photolysis of 125, a solution of 125 in 80% H₂O-CH₃CN (pH = 9) was photolyzed for the same duration as used for 142 (ca. 10 min). Dimer 128 was not formed under these reaction conditions, ruling out the possibility that 128 was formed via secondary photolysis of 125. Furthermore, a kinetic study found that both 125 and 128 were present even at short photolysis times (ca. 30 seconds) (Figure 2.11). These results clearly demonstrate that both 125 and 128 are primary photoproducts of 142.
Figure 2.11 Plot of yields of photoproducts 125 and 128 vs photolysis time in 80% H₂O-CH₃CN (pH = 7).

When the photolysis of 142 was carried out in 80% D₂O-CH₃CN solution (pD = 8), it resulted in the formation of 9D,9H-xanthene (124) and 128 (eq 2.18). The 'H NMR and mass spectral analyses of the photoproducts indicated that no deuterium was incorporated in 9,9'-bisxanthene (128). To rule out the possibility that the proton at C₉ of 142 was undergoing photoexchange with the solvent D₂O prior to the decarboxylation, 9-deuterio-9-xanthenecarboxylic acid (143) was photolyzed in 80% H₂O-CH₃CN. The recovered 143 showed no sign of having exchanged at this position at these short irradiation times. Furthermore, photolysis of 125 in 80% D₂O-CH₃CN did not result in deuterium exchange at
the benzylic position (a reaction that has been observed in more basic solution, *vide supra*). This rules out the possibility that deuterated 124 could have arisen from secondary photolysis of 125. A dark reaction of 142 carried out in 80% D₂O-CH₃CN (pD = 10) for 30 min did not result in any decarboxylation or proton exchange at the C₅ position with solvent D₂O. These results clearly indicate that the deuterium incorporated in 124 is via photodecarboxylation of 142. This strongly implicates the intermediacy of 9-xanthenide carbanion (130). However, formation of 9,9'-bisxanthene (128) is consistent with the intermediacy of the 9-xanthenyl radical (131). Since it was shown above that both 124 and 128 are primary photoproducts (Fig. 2.11), it is possible that both C-C bond homolysis (to give radical 131) and heterolysis (to give carbanion 130) takes place on irradiation of 142. One possible way to check for this possibility is to investigate the effect
of solvent on the photodecarboxylation of 142. Solvent effects on reactions can be used to distinguish between ionic and radical mechanisms. Whereas reactions proceeding through ionic intermediates are greatly affected by the nature of solvent, radical reactions are generally unaffected. Hence, if C-C bond homolysis is taking place then photolysis of 142 in 100% CH$_3$CN should result in the exclusive formation of 128. However, photolysis of 142 in 100% CH$_3$CN did not result in any observable reaction (eq 2.19), indicating that photodecarboxylation of 142 via C-C bond homolysis does not take place. Alternatively, the radical 131 could arise via electron ejection from the intermediate carbanion 130 (Scheme 2.2). Carbanions are known to be good electron sources.$^{101p}$ In a related study it has been shown that photolysis of 142 in the presence of p-nitrobenzoic acid results in the formation of p-nitrobenzoate (PNB) radical dianion, as detected by ESR spectroscopy. The formation of PNB radical dianion is presumed to be via electron transfer from the photogenerated 130 to the p-nitrobenzoate. No ESR signal due to PNB radical anion was observed in the dark or on photolysis of PNB alone. These results support the notion that 130 is the precursor to both radical 131 and 125.
Photolysis of 142 in oxygen saturated solutions under conditions where extensive decarboxylations occurred resulted in formation of 125, 128 and 9-xanthone (144) (eq 2.20). Products obtained on photolysis under argon and under oxygen are presented in Table 2.8. Control experiments in which both 125 and 128 were independently photolyzed in O₂ saturated aqueous CH₃CN solutions (ca. 90 min) resulted in only trace amounts (< 1%) of 144. Thus, photooxygenation
Table 2.8  Conversions and Product Distributions in the Photolysis of 9H-Xanthene-9-Carboxylic Acid (142) in O₂ and Ar Saturated 80% H₂O-CH₃CN (pH > 8) Solutions. 

<table>
<thead>
<tr>
<th></th>
<th>% 125</th>
<th>% 128</th>
<th>% 144</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂b Saturated</td>
<td>- 63%</td>
<td>- 4%</td>
<td>- 11%</td>
</tr>
<tr>
<td>Arb Saturated</td>
<td>- 63%</td>
<td>- 11%</td>
<td>- 4%</td>
</tr>
</tbody>
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a) Product distribution analyzed by ¹H NMR integration.
b) - 80 mg of substrate dissolved in 80% H₂O-CH₃CN (200 mL; pH ~ 8) solution and irradiated with continuous bubbling of O₂ or Ar, at λₑ. 254 nm for 5.0 min.

of the initially formed photoproducts, viz., 125 and 128, can be ruled out. It is evident from Table 2.8 that the conversion to 125 in both photolyses (in presence and absence of O₂) remains unaffected, whereas the amount of 144 formed in O₂ saturated solution is approximately equal to the amount of 128 formed in argon saturated solution. These observations suggest that both 128 and 144 have a common precursor, viz., 9-xanthenyl radical (131). In the absence of oxygen most of the radical 131 formed dimerizes to give 128. However, in the presence of oxygen the bimolecular trapping of the 9-xanthenyl radical (131) by oxygen leads to the hydroperoxide which is known to break down to yield the ketone 144 (Scheme 2.2).

Table 2.9 summarizes the results obtained in photolysis of 142 in aqueous solutions of varying acidities. In general, both aryl and diarylacetic acids
decarboxylate only in their carboxylate ion forms.\textsuperscript{19,27,28} Consistent with this prediction, 142 failed to photodecarboxylate at pH < pK\textsubscript{a} (pK\textsubscript{a} of 142 = 4), indicating that only the carboxylate ion of 142 is the reactive species. The lack of reactivity of 142 in 100% CH\textsubscript{3}CN is also consistent with this observation.

Preparative scale photolysis were also carried out with 9-phenylxanthene-9-carboxylic acid (145), to investigate the effect of the phenyl group on the

\begin{table}[h]
\centering
\begin{tabular}{|c|c|c|c|}
\hline
pH & \% 125\textsuperscript{b} & \% 128\textsuperscript{b} & \% 142\textsuperscript{b} \\
\hline
1.0 & 0.00 & 0.00 & 100 \\
3.0 & 23 & 7 & 70 \\
4.0 & 63 & 12 & 24 \\
7.0 & 61 & 15 & 24 \\
8.0 & 63 & 15 & 22 \\
10.0 & 65 & 16 & 18 \\
12.0 & 64 & 14 & 21 \\
100% CH\textsubscript{3}CN & 0.00 & 0.00 & 100% \\
\hline
\end{tabular}
\caption{Photoproduction Distribution in the Photolysis of Xanthene-9-Carboxylic Acid (142) in 80\% H\textsubscript{2}O-CH\textsubscript{3}CN at Various pHs.}
\end{table}

\textsuperscript{a} pH of the aqueous portion of the solution; each solution contained \textasciitilde75 mg of the substrate dissolved in 80\% H\textsubscript{2}O-CH\textsubscript{3}CN (200 mL); pH of the solution was adjusted using a pH meter with dropwise addition of a standard solution of HCl or NaOH; \lambda\textsubscript{ex} 254 nm; photolysis time 5.0 min.

\textsuperscript{b} Photoproduct distribution analyzed by \textsuperscript{1}H NMR integration; errors in percentage conversions are estimated to be \pm 8-10\% of the quoted values.
efficiency of the photodecarboxylation. Thus, photolysis of 145 in 80% H₂O-CH₃CN (pH ≥ 8) resulted in efficient reaction, to give 9-phenyl-9H-xanthene 9-phenyl-xanthenide carbanion (140). No radical derived products were isolated in these photolyses. When 145 was photolyzed in oxygen saturated aqueous CH₃CN solution, only 133 was observed.

Table 2.10 summarizes the results of photolyses of 145 in solutions of various pHs (pKₐ of 145 = 4.5).
Table 2.10  Conversions to 133 in the Photolysis of 9-Phenylxanthene-9-Carboxylic Acid (145) in 80% H₂O-CH₃CN Solutions of Various pHs.

<table>
<thead>
<tr>
<th>pH</th>
<th>% 133b</th>
<th>% 145b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>2.0</td>
<td>0.00</td>
<td>100</td>
</tr>
<tr>
<td>4.0</td>
<td>5</td>
<td>12</td>
</tr>
<tr>
<td>7.0</td>
<td>21</td>
<td>78</td>
</tr>
<tr>
<td>8.0</td>
<td>23</td>
<td>77</td>
</tr>
<tr>
<td>10.0</td>
<td>30</td>
<td>70</td>
</tr>
<tr>
<td>12.0</td>
<td>33</td>
<td>66</td>
</tr>
<tr>
<td>100% CH₃CN</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a) Quoted pH is of the aqueous portion of the solvent system; each solution contained 75 mg of 145 dissolved in 80% H₂O-CH₃CN (200 mL) and pH adjusted using a pH meter with dropwise addition of a standard solution of HCl or NaOH; λₚ, 254 nm; photolysis time ca. 2.0 min.
b) Conversion to product calculated by ¹H NMR integration using suberene (37) as external standard; errors in percentage conversions are estimated to be ± 10% of the quoted values.

A preliminary comparison of the relative reactivity of 142 and 145, based on the conversion to the respective photoproducts 125 and 133, shows that the presence of the bulky phenyl group at C-9 does not have any significant effect on the photodecarboxylation efficiency. This result is interesting considering the fact that photodecarboxylation of 145 generates a tertiary triphenylmethane carbanion, viz., 146, whereas 142 gives a secondary carbanion, viz., 130. Thermally, the formation of a tertiary carbanion is energetically less favourable compared to a
secondary carbanion, because of the lower stability of the former.\textsuperscript{127}

2.2.1.2 Photolysis of Thioxanthene-9-carboxylic Acid (147)

Photolysis of 147 in 80\% H\textsubscript{2}O-CH\textsubscript{3}CN (pH ≥ 8) led cleanly to the formation of 9H-thioxanthene (136) (eq 2.23). However, the yields of photoproduct 136 were significantly lower than those obtained from 142 under similar reaction conditions.

Photolysis of 147 in a 80\% D\textsubscript{2}O-ACN (pD ≥ 9) resulted in clean formation

\[
\text{Ph} \\
\begin{array}{c}
\text{146} \\
\end{array}
\]

\[
\begin{array}{c}
\text{H} \\
\text{130}
\end{array}
\]

significant lower than those obtained from 142 under similar reaction conditions.
of the corresponding mono-deuterated product 135 (eq 2.24).

It was shown earlier that photolysis of 136 in basic solution results in deuterium exchange at the benzylic position, to give monodeuterated 135 (vide supra). However, photolysis of 136 under conditions employed for the photodecarboxylation did not result in any observable deuterium exchange at the benzylic position. This precludes the possibility that the observed deuterium incorporation in 135 could have resulted from a secondary photolysis of 136. Photolysis of 147 in 100% CH$_3$CN did not lead to any product and the unchanged starting material was recovered (eq 2.25). In addition, no radical derived products were observed on photolyses of 147 in aqueous solution. Photolysis in O$_2$ saturated aqueous solution also resulted in the formation of 136 as the only product.

The deuterium incorporation in photoprodut (viz., 135) on photolysis of 147 in D$_2$O and the absence of radical derived product(s) strongly implicates the
intermediacy of the 9-thioxanthenide carbanion (137). Furthermore, the lack of reactivity in aqueous solutions of pH's < pKₐ (estimated pKₐ of 147 = 3.3) indicates that only the carboxylate ion is the reactive species.

Photolysis of 9-phenylthioxanthen-9-carboxylic acid (148) in 80% H₂O-CH₃CN (pH ≥ 8) solution also resulted in the formation of corresponding decarboxylated product 139 (eq 2.26). The presence of the phenyl group had no apparent effect on the reactivity of 148 as it decarboxylated with similar facility as the parent system 147. Consistent with the intermediacy of carbanion 149 in

![Diagram](149)

the photodecarboxylation, photolysis in 80% D₂O-CH₃CN (pD = 9) resulted in the formation of deuterated 138 (eq 2.27).
Photolyses of esters 150, 151, 152 and 153 in 80% H$_2$O-CH$_3$CN, conditions under which the corresponding acids react extensively, did not result in any observable reaction, and the starting materials were recovered unchanged. This is consistent with the notion that only the carboxylate ion is the reactive species.

2.2.2 Product Quantum Yields

Quantum yields for photodecarboxylation ($\Phi_P$'s) of 142, 145, 147 and 148 were measured in deaerated 80% H$_2$O-CH$_3$CN solutions at various pH's. The solvent isotope effect and the effect of solvent on the efficiency of photodecarboxylation were also investigated in quantitative detail.

2.2.2.1 Quantum Yields at pH 7

The quantum yields ($\Phi_P$'s) for the photodecarboxylation (formation of product) were measured in aqueous solution (pH 7 buffer) using 20% (v/v) CH$_3$CN as cosolvent (Table 2.11). The measurements for all the acids were
carried out on an optical bench ($\lambda_{\text{max}} = 280 \text{ nm}$) under a fine stream of argon, which served to deaerate and stir the solutions ($\alpha_i = 1 \times 10^{-3} \text{ M}$). Potassium ferrioxalate was employed to monitor the light intensity. Conversions of the diarylacetic acids to the corresponding photoproducts were determined by GC analyses employing appropriate external standards. The GC results were corrected for differences in the detector response of the photoproduct and the external standard in each case. In the case of 142, $\Phi_p$ refers to the formation of 125 (and 124) only, since dimer 128 was not readily analyzable because of its long retention time on GC column.

Table 2.11 Product Quantum Yields ($\Phi_p$) for Photodecarboxylation of Diarylacetic Acids in 80% $L_2O$-$CH_3CN$ ($L = H$ or $D$) at pH 7/pD ~8.

<table>
<thead>
<tr>
<th></th>
<th>$\Phi_p$ (142)$^d$</th>
<th>$\Phi_p$ (145)</th>
<th>$\Phi_p$ (147)</th>
<th>$\Phi_p$ (148)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_2O$ (pH = 7)$^b$</td>
<td>0.30 ± 0.03</td>
<td>0.28 ± 0.03</td>
<td>0.18 ± 0.02</td>
<td>0.22 ± 0.02</td>
</tr>
<tr>
<td>$D_2O$ (pD = 8)$^c$</td>
<td>0.24 ± 0.004</td>
<td>0.22 ± 0.02</td>
<td>0.14 ± 0.02</td>
<td>0.17 ± 0.03</td>
</tr>
</tbody>
</table>

a) Quantum Yields ($\Phi_p$) refers to the photoproduct formation, measured by GC using an appropriate external standard; the mass balance in each case was > 90%; the errors quoted are the standard deviations of 2-3 independent measurements.
b) 20% CH$_3$CN as co-solvent; pH 7 phosphate buffer used; $\lambda_{\alpha_i} = 280 \text{ nm}$; Ar purged.
c) 20% CH$_3$CN used as co-solvent; pD adjusted by addition of standard 1 M NaOD solution; Ar purged.
d) In the case of 142, $\Phi_p$ refers to the formation of 123 and 124 only; $\Phi$ for the formation of dimer 128 was not directly measureable because of its long retention time on GC column.
2.2.2.2 Solvent and pH Effects

The photodecarboxylation efficiency of all the acids displayed considerable solvent and pH dependency. In 100% CH$_3$CN none of the acids studied showed any reactivity. In general, the acids were less reactive in acidic solutions. These results are consistent with the preparative scale product studies described earlier.

Table 2.12 Product Quantum Yields ($\Phi_p$'s) for Photodecarboxylation of Diarylacetic Acids in Aqueous Solutions* at Various pHs.

<table>
<thead>
<tr>
<th>pH$^b$</th>
<th>142$^d$</th>
<th>145</th>
<th>147</th>
<th>148</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>2.0</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>4.0</td>
<td>0.074</td>
<td>0.060</td>
<td>0.038</td>
<td>0.046</td>
</tr>
<tr>
<td>9.0</td>
<td>0.33</td>
<td>0.30</td>
<td>0.20</td>
<td>0.23</td>
</tr>
<tr>
<td>10.0</td>
<td>0.33</td>
<td>0.32</td>
<td>0.22</td>
<td>0.26</td>
</tr>
<tr>
<td>12.0</td>
<td>0.34</td>
<td>0.33</td>
<td>0.23</td>
<td>0.26</td>
</tr>
</tbody>
</table>

a) 20% (v/v) CH$_3$CN used as co-solvent; Argon purged; $\lambda_{ex} = 280$ nm.
b) Standard buffer solutions used to get the desired pH; solutions of pH 10 and 12 prepared using a pH meter with dropwise addition of a standard solution of NaOH.
c) $\Phi_p$'s measured by GC using appropriate external standard in each case; the mass balance was > 90% in each case; the errors in the measurements are ±10% of the quoted values.
d) $\Phi_p$ refers to the formation of 125 only.
The quantum yields of photodecarboxylation ($\Phi_p$; product formation) of diarylacetic acids at various pH's are presented in Table 2.12. A cursory comparisons of $\Phi_p$'s reveals that xanthene carboxylic acids (142 and 145) photodecarboxylate more efficiently than the corresponding thioxanthene carboxylic acids (147 and 148) at all pHs.

2.2.2.3 Solvent Isotope Effects

Quantum yields ($\Phi_p$'s) of diarylacetic acids were also measured in D$_2$O (20% CH$_3$CN co-solvent) to measure the solvent isotope effect. The solutions were adjusted to pD $\geq$ 8 by adding NaOD (Table 2.13). Comparison of quantum yields ($\Phi_p$'s) obtained in H$_2$O and D$_2$O shows that product yields are lower in D$_2$O, corresponding to a normal solvent isotope effect, $\Phi_{H2O}/\Phi_{D2O} = 1.2-1.3$, and are consistent with a solvent assisted heterolytic mechanism of photodecarboxylation.

Table 2.13 Solvent Isotope Effect on Photodecarboxylation Quantum Yields of the Diarylacetic Acids.

<table>
<thead>
<tr>
<th></th>
<th>142</th>
<th>145</th>
<th>147</th>
<th>148</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Phi_{H2O}/\Phi_{D2O}$</td>
<td>$1.25 \pm 0.03$</td>
<td>$1.27 \pm 0.03$</td>
<td>$1.28 \pm 0.04$</td>
<td>$1.30 \pm 0.05$</td>
</tr>
</tbody>
</table>

a) Reactions carried out with 20% (v/v) CH$_3$CN cosolvent at pH 7 or pD $\geq$ 8.
2.2.3 Steady-State Fluorescence Studies

2.2.3.1 General Spectral Characteristics

The fluorescence emission spectra of carboxylic acids 142 and 145 had a similar appearance to the spectra of the corresponding xanthene chromophore. However, their fluorescence quantum yields ($\Phi_f$ of 142 and 145) in CH$_3$CN were considerably lower. The reason for this could be the presence of the carboxyl group which opens up additional radiationless decay pathways. Fluorescence emissions of 147 and 148 were extremely weak ($\Phi_f < 0.0001$ in CH$_3$CN relative to biphenyl ether ($\Phi_f = 0.03$ in cyclohexane)$^{135}$), possibly due to the presence of sulfur atom, which promotes the rate of intersystem crossing, thereby reducing the fluorescence emission ("heavy atom effect").$^{120}$ Because of this no attempts were made to study their fluorescence behaviour as probe of mechanism.

2.2.3.2 Solvent and pH Effects on Fluorescence Quantum Yields

The fluorescence behaviour of acids 142 and 145 was strongly solvent and pH dependent. The parent acid 142 was moderately fluorescent in 100% CH$_3$CN ($\Phi_f = 0.022 \pm 0.005$, relative to biphenyl ether ($\Phi_f = 0.03$ in cyclohexane)$^{135}$), whereas the corresponding 9-phenyl analogue 145 was weakly fluorescent ($\Phi_f = 0.0082 \pm 0.0005$, relative to biphenyl ether). The weak emitting behaviour of 145 is probably due to the presence of phenyl group which opens up additional deactivation pathways competing with fluorescence.

It has been observed that the carboxylate forms of arylacetic acids are more
fluorescent than their protonated counterparts.\textsuperscript{27,31a,b} However, in the present study the carboxylate form of the acids was found to be less fluorescent than their protonated counterparts which was consistent with their photoreactivity. For example, the fluorescence quantum yield of 142 in 100\% CH\textsubscript{3}CN was $\Phi_f = 0.022 \pm 0.002$, a solvent in which it does not exhibit any reactivity ($\Phi_p = 0.00$), whereas in 80\% H\textsubscript{2}O-CH\textsubscript{3}CN (pH 7.0), a solvent system in which 142 efficiently photodecarboxylates ($\Phi_p$ at pH 7 = 0.30), the $\Phi_f$ was $0.0062$.

The fluorescence emission intensities of 142 and 145 were progressively quenched as the pH of the aqueous portion in 80\% H\textsubscript{2}O-CH\textsubscript{3}CN was increased, following an opposite trend in their photochemical reactivity. The pH dependence of fluorescence quantum yields ($\Phi_f$) and product quantum yields ($\Phi_p$) of 142 and 145 are presented in Figures 2.12 and 2.13, respectively. The drop in fluorescence intensity at higher pH's is due to the enhanced reactivity of the carboxylate ion form (higher $\Phi_p$'s) which provides an additional deactivational pathway for $S_1$ of the acids. These results are consistent with the results obtained in product studies; that is, only the carboxylate ion form is reactive.
Figure 2.12 Fluorescence ($\Phi_f$) and product ($\Phi_p$) quantum yields for 142 as a function of the pH of the aqueous portion in 80% H$_2$O-CH$_3$CN.

Figure 2.13 Fluorescence ($\Phi_f$) and product ($\Phi_p$) quantum yields for 145 as a function of the pH of the aqueous portion in 80% H$_2$O-CH$_3$CN.
2.2.4 Mechanism of Photodecarboxylation: Photogeneration of $8\pi$-Electron Cyclically Conjugated Carbanions

The mechanism of photodecarboxylation of carboxylic acids and esters has been a subject of numerous studies. The generality of this process is now well established and a variety of mechanisms have been proposed. For instance, Miller and coworkers have outlined 25 possible cleavage modes for the carboxyl group. Most of these possible modes could be eliminated in the present study on the basis of the results obtained in this work. However, there still remain three possible primary photochemical pathways which can account for the observed results in the present study (eqs 2.28-2.30).

$$\begin{align*}
R-\text{CO}_2^- & \xrightarrow{k_{dc}} R^- + \text{CO}_2 & (2.28) \\
R-\text{CO}_2^- & \xrightarrow{k_h} R^- + \text{CO}_2^\cdot \xrightarrow{k_{ET}} R^- + \text{CO}_2 & (2.29) \\
R-\text{CO}_2^- & \xrightarrow{k_{eo}} R-\text{CO}_2 \quad \xrightarrow{k_h'} R^- + \text{CO}_2 & (2.30)
\end{align*}$$

In the first (eq 2.28) and the simplest mechanism, photoexcitation of the carboxylate ion results in the loss of CO$_2$ via heterolytic C-C bond cleavage from $S_1$ to give the corresponding carbanion. The second process (eq 2.29) involves homolytic C-C bond fragmentation of the carboxylate, to generate the alkyl radical and the carbon dioxide radical anion. This initially formed radical-radical anion
pair then undergoes electron transfer, to generate the alkyl carbanion. Although the exact redox potentials of the various couples are not known for the xanthene and thioxanthene systems, electron transfer ($k_{\text{ET}}$) would form ground state antiaromatic carbanions, viz., 130 and 137, respectively, and should not be favoured. Furthermore, the lack (except in the case of 142) of radical derived products as well as observed solvent isotope effects are inconsistent with this mechanism (eq 2.29). The final possible mechanism (eq 2.30) for photodecarboxylation involves electron ejection from the excited carboxylate ion, followed by homolytic C-C bond cleavage to yield the corresponding radical intermediates. If these radicals are to be converted into the carbanions, as the product studies require, they must recapture the initially ejected electron, which is not reasonable since solvated electrons are efficiently scavenged by oxygen and other dissolved impurities or solutes.

Previous results obtained in our laboratories have clearly demonstrated that dibenzannelated acetic acids undergo photodecarboxylation from $S_1$ via eq 2.28, the details of which are shown in Scheme 2.3. In this simple mechanism photoexcitation of the carboxylate ion leads to the loss of CO$_2$ from $S_1$ in a heterolytic manner, to generate the corresponding carbanion. The intermediate carbanions produced in the decarboxylation step are many orders of magnitude more basic than H$_2$O, and are protonated promptly or even concertedly with their formation, to give the hydrocarbon photoproducts. In the present study, the following observations support this ionic mechanism: (1) The incorporation of
deuterium in the photoproducts when the reactions are carried out in D₂O is consistent with the intermediacy of carbanions. The general lack of radical coupling products, further supports an ionic mechanism for photodecarboxylation. The only exception to this is 142, which gave a radical coupling product, viz., 9,9'-bisxanthene (128). However, this does not imply that radical 131 is formed via a primary C-C bond homolysis of the carboxylate ion. Product studies of 142 indicate that 131 is formed via electron ejection from the initially generated 9-xanthenide carbanion 130. This is further supported by the fact that when 142 is photolyzed in the presence of an electron acceptor p-nitrobenzoic acid (PNB), formation of PNB radical dianion has been detected by ESR spectroscopy, which is indicative of an electron transfer reaction.31 No ESR signals are observed in the dark or on photolysis of PNB alone. The propensity of 130 to act as an one
electron reducing agent is compatible with it being a "π-excessive" antiaromatic system. (2) Fluorescence emissions of 142 and 145 display a strong dependence on the pH of solution, which is consistent with an ionic mechanism of photodecarboxylation via the carboxylate form. (3) Solvent isotope effects observed in the product quantum yields (Φp) when photolyses of these acids were carried out in H2O and D2O are consistent with the proposed ionic mechanism.

In the transition state the excited carboxylate ion is surrounded by water molecules which assist the photodecarboxylation, by stabilizing the developing negative charge at the carbon center via hydrogen bonding interactions. The solvent isotope effects (ΦH/ΦD; Table 2.13) observed in product quantum yields also suggest that heterolytic C-C bond cleavage step is associated with solvent interactions in the transition state. However, these interaction between the excited carboxylate ion and the solvent are probably not very strong ("loose transition state") since the observed solvent isotope effects are not very large (ΦH/ΦD = 1.30).

In ionic ground state decarboxylation reactions it is recognized that electron withdrawing groups that can stabilize the intermediate carbanions accelerate the reaction. However, Wan and Krogh 32a,b have shown that the presence of such groups is not necessary to observe efficient photodecarboxylation in diarylacetic acids. In a study of series of compounds related to diphenylacetic acid (e.g., 28-31), differing only in the structure of the central ring, Wan and Krogh 32a,b have shown that in the ground state fluorene-9-carboxylic acid (28) is most easily decarboxylated whereas suberene-5-carboxylic acid (29) is reluctant to
decarboxylate even on prolonged reflux. This is not surprising since ionic decarboxylation of 29 would form an 8π-electron (antiaromatic) carbanion intermediate 34, which requires a very high activation energy. However, photochemically, 29 is the most reactive ($\Phi = 0.60$; $k$ (decarboxylation) = $6 \times 10^9$ s$^{-1}$), whereas 28 is the least reactive ($\Phi = 0.042$; $k$ (decarboxylation) = $8.8 \times 10^6$ s$^{-1}$) acid. The unconjugated systems 30 and 31 are about an order of magnitude more reactive than 28.

An estimate of the rate constant ($k_{dc}$) for photodecarboxylation, assuming the applicability of mechanism shown in Scheme 2.3, can be made by combining the product quantum yields ($\Phi_p$) and fluorescence lifetimes ($\tau_f$) (in 80% H$_2$O-CH$_3$CN) according to equation 2.31. These rate constants for 142 and 145 are

$$\Phi_p = k_{dc} \tau \text{ or } k_{dc} = \frac{\Phi_p}{\tau}$$

(2.31)

presented in Table 2.14. Estimate of the photodecarboxylation rate constants of

<table>
<thead>
<tr>
<th></th>
<th>$\tau$ (ns)$^a$</th>
<th>$k_{dc}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>142</td>
<td>0.40 ± 0.05</td>
<td>7.5 x 10$^6$</td>
</tr>
<tr>
<td>145</td>
<td>0.35 ± 0.05</td>
<td>8.0 x 10$^6$</td>
</tr>
<tr>
<td>29$^a$</td>
<td>&lt; 0.10$^b$</td>
<td>-6.0 x 10$^9$</td>
</tr>
</tbody>
</table>

a) Lifetimes measured in 80% H$_2$O-CH$_3$CN via single photon counting.
b) Taken from ref. 32a.
147 and 148 could not be made because their short fluorescence lifetimes in aqueous solution ($\tau < 0.1$ ns) could not be measured with the instrument available.

Comparison of these $k_d$'s for 142 and 145 shows that presence of phenyl group has no significant effect on the photodecarboxylation rate. However, these rates are approximately an order of magnitude lower than for of suberene carboxylic acid$^{32a,b}$ (29; $k_d = 6 \times 10^9$ s$^{-1}$).

Attainment of a 4$n$-electron internal cyclic array (4$n$) in $S_1$ is not restricted to only charged intermediates. In the next section, photophysical studies of dibenz[b,f]oxepin (155) show that photoexcitation of this non-planar molecule in $S_0$ results in a planar fluorescent $S_1$ state. The driving force behind this conformational change is believed to be the attainment of a 8$n$-electron ICA in $S_1$ (vide infra).

2.3 Conformational Studies of Dibenz[b,f]oxepin (155) and Related Systems by Steady-State Fluorescence Spectrophotometry: Evidence for an Excited State 8$n$ Internal Cyclic Array$^{32a}$

2.3.1 Syntheses

2.3.1.1 Dibenz[b,f]oxepin (155)

The strategy utilized in the synthesis of dibenz[b,f]oxepin (155) is shown

\[
\begin{align*}
&\text{CH}_2\text{OH} \\
\text{154} &\xrightarrow{\text{P}_2\text{O}_5,\text{Benzene reflux, 15 min}} \sim 88\% \\
\text{155}
\end{align*}
\]
in eq 2.32. An acid catalyzed rearrangement of xanthene-9-methanol (154) with phosphorus pentoxide (P$_2$O$_5$) in boiling benzene readily afforded 155 in ~ 85% yield. Purification of the crude material by recrystallization from 95% EtOH afforded pure 155.

2.3.1.2 10,11-Dihydrodibenz[b,f]oxepin (156)

Reduction of 155 over 5% palladium-on-charcoal catalyst gave 10,11-dihydrodibenz[b,f]oxepin (156) in ~ 90% yield (eq 2.33). The crude material was purified by distillation to afford pure 156 as a colourless viscous oil.

$$\begin{align*}
\text{155} & \xrightarrow{\text{H}_2/\text{Pd-C}} \text{100\%} \quad \text{156} \\
\end{align*}$$

2.3.1.3 10-Hydroxy-dihydrodibenz[b,f]oxepin (157)

Following the general procedure of Zweifel and Brown treatment of 155 with a solution of BH$_3$ in dry THF followed by oxidation with H$_2$O$_2$ in the

$$\begin{align*}
\text{155} & \xrightarrow{i) \text{BH}_3/\text{THF}} \xrightarrow{\text{ii) } \text{H}_2\text{O}_2/\text{NaOH}} \text{65\%} \quad \text{157} \\
\end{align*}$$
presence of 3 M NaOH afforded the crude 157 in ~72% yield (eq 2.34). The crude material was purified by bulb-to-bulb distillation to obtain pure 157 as a colourless viscous oil.

2.3.1.4 10-Hydroxysuberane (158)

Treatment of suberene (37) with BH₃ in dry THF followed by oxidation with H₂O₂/NaOH afforded the crude 158 as an oil (eq 2.35). The crude oil could not be purified by bulb-to-bulb distillation because of its facile thermal dehydration to give starting material, viz., suberene (37). Column chromatography (neutral Al₂O₃; CH₂Cl₂) was employed to obtain pure 158.

2.3.1.5 Dibenz[b,f]thiepin (160)

Treatment of thioxanthene-9-methanol (159) with P₂O₅ in boiling benzene readily afforded dibenz[b,f]thiepin (160) in ~43% yield (eq 2.36). The crude
material was purified by recrystallization from 95% EtOH and characterized by 
$^1$H NMR (250 MHz) and mass spectrometry.

2.3.1.6 Dibenzocyclooctatetraene (163)

The synthesis of dibenzocyclooctatetraene (163) was achieved by the Wittig condensation of o-phthaldehyde (162) with the bis-phosphonium salt 161 in DMF using LiOEt as the base (eq 2.37).

\[ \text{CHO} \quad \text{EtO}_2\text{Li/DMF} \quad 90^\circ\text{C}; 48\text{ h} \quad 10\% \]

\[ \text{161} + \text{CHO} \quad \text{EtO}_2\text{Li/DMF} \quad 90^\circ\text{C}; 48\text{ h} \quad 10\% \quad \text{163} \]

2.3.2 Product Studies

2.3.2.1 Photolysis of 10,11-Dihydrodibenz[b,f]oxepin (156)

When a $10^{-3}$ M solution of 156 in 100% CH$_3$CN was photolyzed at 254 nm (Ar purged; − 14 °C; 15-30 min) the colour of the reaction mixture changed immediately (ca. 1 min) to yellow. After 10 min of photolysis the CH$_3$CN was evaporated to obtain a yellow mixture. The $^1$H NMR (90 MHz) spectrum of the product mixture, besides showing signals due to starting material 156, showed appearance of new signals between 8 7-6 and 8 2-4, indicating the formation of photoproduct(s). Thin layer chromatographic analysis of the product mixture
(silica plates; CH₂Cl₂) also showed the presence of several new spots, only one of which was a significant (Rᵥ = 0.14). Separation of this spot from the product mixture by preparative scale thin layer chromatography afforded a yellow solid. The ¹H NMR (250 MHz) spectrum of the isolated product showed complex sets of multiplets between δ 2-4 and δ 6-7, along with signals due to aromatic protons between δ 7.1-8.2 (see Experimental). The ¹³C NMR spectrum (see Experimental) showed the presence of 28 distinct carbons. It was not possible to assign a structure to this product with any degree of confidence due to the complex nature of the ¹H and ¹³C spectra. Attempts were made to solve the structure of the product by X-ray crystallography. The solid was crystallized from CH₂Cl₂/hexanes to give pale yellowish crystals. The ¹H and ¹³C NMR of this

Figure 2.14 X-Ray crystal structure (preliminary) of 166.
material were identical to the spectra observed before re-crystallization. A preliminary X-ray crystal structure showed the material to be a spiro adduct 166 (Figure 2.14). Difficulties were encountered in refining the structure to acceptable limits. Work will continue by other members of the group to improve this.

Previous studies of 9H-xanthene (125) photochemistry have shown that irradiation of 125 in aqueous CH₃CN solution results in its photoisomerization to yield the 6H-dibenzo[b,d]pyran (126). The proposed mechanism of this isomerization involves initial aryl-oxygen bond homolysis from $S_1$ to give a biradical (Scheme 2.4). Trivial recombination of the biradical gives back

Scheme 2.4

9H-xanthene (125). However, recombination of the biradical at the ipso benzylic position (ortho to the phenol) gives a spiro ketone intermediate. Subsequent
The homolysis of the C-C bond of the spiro ketone shown gives a biphenyl o-quinone methide, which undergoes electrocyclic ring closure to give the observed pyran 126 (Scheme 2.4). The high reactivity of the spiro ketone is obviously due to the presence of a highly strained fused four-membered ring in the molecule. The formation of 166 can also be explained by invoking a similar mechanism for 156. That is, photoexcitation of 156 results in aryl-oxygen bond homolysis, to generate biradical 164 (eq 2.38). Subsequent coupling of biradical 164 by ipso attack of the phenyl radical to the ortho position of the phenoxy ring forms the spiro ketone 165. Thermal [4+2] cycloaddition reaction of 165 with a second molecule yields the observed adduct 166. This cycloaddition of 165 was unexpected; repeated attempts to isolate only the spiro ketone 165 were of no avail. However, based
on the structure of the final product 166 it is clear that 165 was formed. Thus, although 165 does not fragment as observed for the cyclobutene analog (vide supra), the presence of the cyclohexadienyl system makes it exceptionally reactive towards [4+2] cycloaddition.

2.3.2.2 Photolysis of Dibenz[b,f]oxepin (155)

Photolysis of a solution of 155 in 100% CH₃CN at 300 nm for 30 min did not result in any observable reaction. Even at longer irradiation times (ca. 60-90 min), 155 remained photochemically inert. This was surprising because under similar reaction conditions 156 reacted extensively to form the adduct 166. Although the extended conjugation present in 155 (cis-stilbene like chromophore) lowers its $S_1$ energy relative to 156, the complete lack of aryl-oxygen bond homolysis was unexpected. Steady-state fluorescence studies of 155 provided some remarkable insights of the nature of the excited state of 155 (vide infra).

2.3.2.3 Photolysis of Dibenz[b,f]oxepin (155) in the Presence of Et₃N

Photolysis of a 10⁻³ M solution of suberene (37) in the presence of ~5 M Et₃N in CH₃CN ($\lambda_{ex} = 300$ nm; Ar purged; 30 min) resulted in the reduction of the
vinylic C=C bond to yield suberane (49) (ca. 87%) (eq 2.39). The mechanism of this reduction is believed to be via an initial electron transfer from Et$_3$N to photoexcited 37, to form the radical-ion pair (167) (Scheme 2.5). Subsequent hydrogen abstraction by the radical anion followed by protonation (or vice versa) results in the overall reduction of the C=C bond, to give 49. A similar photolysis of 155 in a solution of ~5 M Et$_3$N in CH$_3$CN resulted in a substantially lower yield of the corresponding reduced product 156 (ca. 27%) (eq 2.40). This suggests that the vinylic C=C bond of 155 is less prone to photoreduction compared to that in 37. The lower photoreactivity of the vinylic
C=C of 15 was further evidenced in photohydration reactions of 37 and 155 in aqueous acid discussed below.

2.3.2.4 Photolysis of 155 and 37 in Aqueous Acid

Photolysis of 155 in 50% CH₃CN-10% (w/w) H₂SO₄ at 300 nm (ca. 30 min) resulted in very inefficient photohydration of the C=C bond, to yield 157 (< 2%, by ¹H NMR integration) (eq 2.41). However, a similar photolysis of 37 resulted in an efficient reaction, to yield 158 (29%) (eq 2.42). Although, the reasons for the lower reactivity of 155 vs 37 are not clear at this stage, it is clear that the vinylic C=C bond of 155 behaves differently compared to its counterpart in 37.
Photolysis of 157 and 158 in Aqueous Acid

Photolysis of 157 in 50% CH₃CN-20% H₂SO₄ at 254 nm (ca. 30 min) resulted in the efficient formation of 155 (ca. 50%, by ¹H NMR integration) (eq 2.43). A similar photolysis of 158 resulted in a much lower yield of 37 (~ 9%) (eq 2.44).

In contrast, thermal acid catalyzed dehydration of 158 was very efficient to yield 37 (ca. 100%) (eq 2.45) whereas, it was difficult to dehydrate 157, even in refluxing aqueous acid (ca. 50% CH₃CN-20% (w/w) H₂SO₄ solution) (eq 2.46).
Photochemical dehydration of 157 (to give 155) was so favourable that it could be readily achieved even in dilute acid solutions. Thus, photolysis of 157 in 50% CH$_2$OH-H$_2$O (pH ~ 1) resulted in the formation of 155 (~ 45%) as the only product. In contrast, photolysis of 158 under similar conditions resulted in the formation of the corresponding methyl ether 168 (~ 30%) (eq 2.47). These results suggest that there is an enhanced driving force for the formation of the vinylic C=C in 155 on photolysis which is absent in 37. Conversely, it is photochemically difficult to remove the vinylic C=C of 155 compared to 37.

2.3.3 Steady-state and Transient Fluorescence Studies

The fluorescence and absorption characteristics of an aromatic molecule can often provide qualitative information concerning the conformation of the molecule in the ground and first excited states.$^{134}$ The theoretical basis for such studies lies in the Franck-Condon (FC) principle. The basis of which lies in the fact that electronic motion (~ $10^{-15}$ sec) is much faster than the nuclear motion (~ $10^{-13}$ to $10^{-11}$ sec). Thus immediately after excitation, the excited state of the molecule retains the ground state geometry and solvent cage. This is called the FC excited state. From this state, the molecule can rapidly ($10^{14}$ to $10^{13}$ sec) lose excess vibrational
energy by thermal relaxation and end up in the lowest vibrational level ($v_0$) of $S_1$. Fluorescent molecules in solution usually have a singlet lifetimes of $10^9$ to $10^4$ s.

Figure 2.15 Four-state diagram illustrating the Franck-Condon principle.

Since solvent relaxation and changes in molecular geometry are governed by the speed of nuclear motion ($10^{-13}$ to $10^{-15}$ sec), there is usually sufficient time for the excited state molecule to acquire a geometry and solvent cage more compatible with its electron density distribution. This lower energy state is called the equilibrium (EQ) excited state and it lies lower in energy than the FC excited state owing to the stabilization resulting from the change in geometry and solvent cage. Emission from the EQ excited state produces the FC ground state which has the
same geometry and solvent cage as the EQ excited state. Subsequently, thermal relaxation occurs and the molecule reaches the lower energy EQ ground state. These processes are diagrammatically presented in Figure 2.15. The emitting EQ excited state always lies lower in energy from the FC excited state. Therefore, amount of energy lost between the absorption and emission processes is related to the extent of geometrical and solvation changes that accompany the excitation process, and is known as the Stokes loss. As the difference in $S_0$ and $S_1$ geometries and solvation becomes greater, so does the extent of Stokes loss. Rigid molecules (e.g., anthracene) undergo little geometrical and solvation changes on excitation and exhibit small Stokes loss. These systems exhibit a mirror image relationship between their absorption and emission spectra. The presence of a mirror image relationship between the absorption and emission spectra indicates that the vibrational level spacings in the FC and EQ states of such molecules are similar. In contrast, if a molecule undergoes a large geometrical change on photoexcitation, a large Stokes loss and absence of mirror image relationship between the absorption and emission spectra are usually observed.

The fluorescence excitation and emission spectra of 156 in cyclohexane is shown in Figure 2.16. The broad structureless excitation spectrum was identical to its absorption spectrum. The emission spectrum of 156 ($\lambda_{\text{max}} = 300$ nm) was also structureless and showed no significant Stokes shift (Figure 2.16). In contrast,
Figure 2.16 Fluorescence excitation and emission spectra of dihydrodibenz[b,f]oxepin (156) in CH₃CN.

The emission spectrum of 155 (λ_max = 478 nm in cyclohexane) was highly Stokes shifted (4720 cm⁻¹; Stokes-shift was calculated according to the definition given by Berlman) and showed well defined vibronic structure (progression ≈1500 cm⁻¹) (Figure 2.17). The structureless excitation spectrum of 155 was essentially identical to its absorption spectrum. The shape and vibronic structure in the emission spectrum of 155 were not affected by the polarity of the solvent, suggesting that the observed Stokes-shift is not due to solvation changes experienced by 155 in the S₁ state. In fact, albeit a little more diffused, the vibronic structure was evident even in H₂O. Some photophysical parameters for
Figure 2.17 Fluorescence excitation and emission spectra of dibenz[b,f]oxepin (155) in CH₃CN.

155 and related systems are presented in Table 2.15.

Table 2.15 Photophysical Parameters for 155, 156 and 160 in CH₃CN.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Φᵢ</th>
<th>τᵢ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>155</td>
<td>0.14 ± 0.02ᵃ</td>
<td>8.36 ± 0.04</td>
</tr>
<tr>
<td>156</td>
<td>0.08 ± 0.03ᵇ</td>
<td>2.50 ± 0.03</td>
</tr>
<tr>
<td>160</td>
<td>0.0012 ± 0.0002ᶜ</td>
<td>&lt; 0.2</td>
</tr>
</tbody>
</table>

ᵃ) Measured relative to quinine bisulfate (Φᵢ = 0.55 in 1 N H₂SO₄)⁷⁷.  
b) Measured relative to xanthene (125) (Φᵢ = 0.24 in CH₃CN; vide supra).  
c) Measured relative to 155.  
d) Measured by single photon counting; all good first order decays; 155: λₑ 290 nm/λₑ 490 nm; 156: λₑ 260 nm/λₑ 320 nm; 160: λₑ 300 nm/λₑ 550 nm.

The emission spectrum of the related system dibenz[b,f]thiepin (160) also...
displayed a similar large Stokes-shift. However, vibronic structure in the

emission of 160 was not evident (Figure 2.18). Its weak emission is probably due
to the presence of the sulfur atom which increases the rate of intersystem crossing
to the triplet state ("heavy atom effect").120

Suberene (37) also possesses the cis-stilbene chromophore like 155 and 160
but lacks possible conjugation through the methylene carbon. The emission
spectrum of suberene48 does not exhibit the large Stokes shift or enhanced
vibronic structure observed for 155. However, suberene is highly fluorescent ($\Phi_t$
$= 0.86 \pm 0.05; \tau_t = 5.04 \pm 0.04$ (in CH$_3$CN))$^{48}$, which is a general characteristic of

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fluorescence_spectra.png}
\caption{Fluorescence excitation and emission spectra of dibenz[b,f]thiapin (160) in CH$_3$CN.}
\end{figure}
"locked" stilbenes.\textsuperscript{120}

The spectral characteristics of 155 suggest that its excited state geometry is different from that in the ground state. The ground state structure, as determined by X-ray crystallography,\textsuperscript{136} resembles that of a "butterfly" (saddle-shaped), with its "wings" highly bent backwards (Bent 155). Non-planar 155 is torsionally free around aryl-O and aryl-CH bonds and can therefore acquire a number of different conformations which are all energetically very similar. At room temperature, the $S_0$ state of 155 can thus be visualized as an ensemble of all such possible conformers. Since the energy difference between these various conformations is very small, electronic transition from $S_0$ results in a structureless absorption spectrum. On the other hand, transitions originating from a planar electronic state should produce highly structured spectra,\textsuperscript{134} because planar rigid molecules do not have rotational freedom possessed by non-planar molecules. As a consequence the vibrational levels of planar molecule in a given electronic state are discrete. The highly structured emission spectrum of 155 indicates that the geometry of $S_1$ is planar and rigid.

A change from a non-planar $S_0$ state to a more planar fluorescent $S_1$ state has been well documented for biphenyl and related compounds.\textsuperscript{134,135} The rationale commonly accepted for this behaviour of biphenyl is that there is enhanced double bond character in the bond joining the two phenyl rings in $S_1$ which is absent in $S_0$.\textsuperscript{127} A similar geometrical change is proposed to occur on photoexcitation of 155. That is, bent 155 in $S_0$ becomes planar 155 in $S_1$. The high
degree of non-planarity of 155 in the ground state is not surprising since simple Hückel-type arguments would predict that a planar structure would be unfavourable due to the antiaromatic nature of a planar 8\pi-electron cyclic array in the internal ring. More sophisticated MO calculations confirm this. However, fluorescence studies indicate that the EQ excited state geometry of 155 is that of a rigid planar system (Planar 155), allowing for complete conjugation of the internal cyclic array. Indeed, the emission of 155, with its associated fine structure, could be mistaken for the fluorescence emission of anthracene (which has a similar overall appearance but is about 80 nm blue-shifted), a classic example of a strongly emitting rigidly planar (in both S₀ and S₁) aromatic molecule.

Another possibility for the observed emission spectrum of 155 which was
considered but ruled out is the formation of the valence isomer 169 via electrocyclic 6π ring closure. Adiabatic extrusion of the oxygen atom in a subsequent step then forms phenanthrene in S1. However, the known fluorescence emission of phenanthrene is ≈ 110 nm blue-shifted compared to that observed for 155. On the other hand, the observed emission might be due to the valence isomer 169 itself. This is unlikely since this would be equally possible in the case of suberene (37). However, 37 does not show any spectral characteristics that are observed for 155. The fluorescence spectra of two related systems 163 and iminostilbene (170) were also studied. The absorption and emission spectra of 163 were found to be structureless and did not exhibit a significant Stokes loss. These spectral characteristics suggest that 163 does not undergo geometrical changes (i.e., does not become planar) in S1. This is presumably due to the unfavourable interactions experienced by the peri hydrogens preventing 163 from acquiring a planar structure. Emission studies of 170 proved to be extremely difficult because of its very weak emission. However, no significant Stokes loss was observed in the emission spectrum.

Corroborating chemical evidence for the above proposal of a "stabilized" planar geometry of 155 in S1 comes from the reactivity data obtained in product
studies. Resistance of the vinylic C=C bond of 155 compared to 37 to undergo photoreduction (by Et$_3$N) and photohydration points towards the special nature of this bond in 155. Thermal acid-catalyzed dehydration of 158 to form 37 is readily achievable (eq 2.45), whereas 157 is inert to dehydration, even in refluxing aqueous acid (eq 2.46). On the other hand, photodehydration of 157 to form 155 in 50% H$_2$O-MeOH is readily accomplished even in dilute acid solutions (pH 1-3), whereas 158 results largely in the formation of the corresponding methyl ether 168 (eq 2.47), indicating that there is an enhanced driving force for formation of 155 in the excited state which is absent in 158.

The results of $\pi$-SCF PPP calculations$^{129b}$ of planar 155 in both $S_1$ and $S_0$ show that there is a greater degree of delocalization of the oxygen lone pair to the rest of the $\pi$-system in $S_1$ than in $S_0$. Moreover, the electron density from the oxygen is distributed more in the central ring in $S_1$ than in $S_0$, consistent with the proposal that there is an inherent driving force for this ring to achieve delocalization of 8$\pi$ electrons (which is achieved only when 155 becomes planar in $S_1$).

These results unambiguously support the proposal that photoexcitation of bent 155 results in a planar fluorescent state. The energetics of this process are illustrated in Figure 2.18. The potential energy curves in Figure 2.18 show that a large energy barrier exists for the planarization of bent 155 in $S_0$. In $S_1$, bent 155 undergoes fast torsional twisting to acquire the planar fluorescent $S_1$(EQ) conformation. Emission from planar 155 produces the $S_0$(FC) which has the same
Figure 2.18 Potential energy surface for torsional twisting of 155 in $S_0$ and $S_1$ (energies not drawn to scale).

geometry as the $S_1$(EQ). Since no emission from the bent 155 ($S_1$(FC)) was observed, it suggests that there is no (or very small) energy barrier for the planarization of 155 on $S_1$ surface.

It was pointed out earlier that photolysis of N-methylnorlan (140) in 50% H$_2$O-CH$_3$CN resulted in its dimerization, to form 141. This process was investigated in more detail and is presented below.
2.4 Photoionization of N-methylacridan (140) in Aqueous Solution

2.4.1 Product Studies

N-methylacridan (140) was prepared from NaBH₄ reduction of N-methylacridinium iodide, adapted from the reported procedure of Colter and coworkers (eq 2.48). The crude white crystalline material was recrystallized several times from 95% EtOH until GC analysis showed no detectable traces of impurities.

Photolysis of 140 in 50% H₂O-CH₂CN at 254 nm (ca. 10-60 min) yielded very small amounts (< 5%) of 9,9'-bis(N-methylacridyl) (141), as detected by ¹H NMR of the product mixture. The solution after photolysis was of deep orange colour. However, photolysis of the above solution at 300 nm for the same length of time resulted in efficient formation of an off-white precipitate. Analysis of the ¹H NMR spectrum of the product mixture obtained in the 300 nm photolysis showed a much higher yield (= 50%) of 141 (by ¹H NMR integration) (eq 2.49).
The pronounced change in the yield of 141 by simply changing the wavelength of irradiation from 254 nm to 300 nm was not expected since organic compounds in solution generally do not exhibit wavelength-dependent photochemistry.

Photolysis of 140 in 50% H₂O-CH₃CN (Ar purged) also leads to the formation of trace amounts of N-methylacridone (171) and N-methylacridinium ion (172) (vide infra), in addition to 141, which is the only observable product by ¹H NMR. Both of 171 and 172 have intense (ε ≥ 40,000 M⁻¹ cm⁻¹) absorption at 254 nm where 140 has very little absorption (its λₘₐₓ is at 286 nm). The observed "low" reactivity of 140 at 254 nm is therefore due to preferential absorption of
light by traces of 170 and 172 which are formed in the course of photolysis. The situation is very different at 300 nm. Here, both 171 and 172 have much lower molar extinction coefficients (e) and all the light is absorbed by 140 (λ_{max} ~ 286 nm).

To investigate the effect of solvent polarity, photolysis of 140 was carried out in several polar and non-polar solvents. Yields of 141 obtained on photolysis of 140 at 300 nm in a variety of solvents are shown in Table 2.16. It is evident that the yields of 141 are enhanced in more polar solvents, and are especially favourable in H_{2}O-CH_{3}CN.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>% Yield of 141^{b}</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH_{3}CN</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>100% Et_{2}O</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>95% EtOH</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>100% hexane</td>
<td>5 ± 2</td>
</tr>
<tr>
<td>50% H_{2}O-CH_{3}CN</td>
<td>18 ± 3</td>
</tr>
</tbody>
</table>

a) A solution 50 mg of 140 in 100 mL of solvent irradiated for 15 min at 300 nm. b) Due to the fact that 141 has a very long retention time on the GC column, yields were calculated by ^{1}H NMR integration of the product mixture after work-up.

In a related study Fukuzumi and coworkers have shown that photolysis
of 140 in the presence of O₂ results in the formation of N-methylacridinium ion (172). The key step in the proposed mechanism of this reaction involves electron transfer from the photoexcited 140 to O₂, to generate a radical cation/anion pair (140⁺/O₂⁻). Subsequent transformation of this species depended on whether the solvent was pure CH₃CN or aqueous CH₃CN with added H⁺, but in each case involving the formation of N-methylacridan radical (140) from the decomposition of 140⁺/O₂⁻.¹⁴¹ In the present study photolysis of an O₂ purged solution of 140 in 50% H₂O-CH₃CN also resulted in the formation of 172. However, 140 was found to be reactive even in the absence of O₂, in both 100% CH₃CN and aqueous CH₃CN solutions. Results of the photolyses of 140 in the presence and absence of oxygen and/or water are shown in Table 2.17.

Table 2.17  Yields of Products from Photolysis of 140 under Various Conditions at 300 nm.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Product (%) yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH₃CN (O₂ purged)</td>
<td>171 (= 55%)b</td>
</tr>
<tr>
<td>50% H₂O-CH₃CN (O₂ purged)</td>
<td>172'</td>
</tr>
<tr>
<td>50% H₂O-CH₃CN (Ar purged)</td>
<td>141 (= 50%)b,d</td>
</tr>
</tbody>
</table>

a) ~100 mg of 140 in 200 mL of solvent irradiated at 300 nm for 30 min.
b) Product identified by comparison with ¹H NMR of authentic sample; yields calculated by integration of appropriate peaks.
c) Detected by UV-Vis absorption spectrum by comparison to an authentic sample; yield not quantified but 172 is the only product observed under these conditions (Φ = 0.022 ± 0.004 using 10⁻³ M of 140 with λₑᵣ = 302 nm; oxygenated 50% H₂O-CH₃CN; steady-state irradiation); no 141 formed according to ¹H NMR of reaction mixture.
d) Photolysis was done for 120 min, because the formation of precipitate of 141 blocks light.
2.4.2 Quantum Yields for Formation of 141 in Various Solvents

Since 141 was not readily analyzable using GC because of its long retention time and possible decomposition on the column, quantum yields for the loss of substrate 140 (Φₜ) were measured instead (Table 2.18), using 9H-xanthene (125).

Table 2.18 Quantum Yields for Loss (Φₜ) of 140 and Fluorescence Lifetimes (τ) in Deaerated Solvents.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Φₜ⁺</th>
<th>τ nsᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% Et₂O</td>
<td>0.0060 ± 0.0006</td>
<td>3.7 ± 0.2</td>
</tr>
<tr>
<td>100% Hexane</td>
<td>0.0060 ± 0.0006</td>
<td>4.3 ± 0.2</td>
</tr>
<tr>
<td>100% CH₃CN</td>
<td>0.022 ± 0.002</td>
<td>7.0 ± 0.2</td>
</tr>
<tr>
<td>95% EtOH</td>
<td>0.0080 ± 0.0005</td>
<td>5.6 ± 0.2</td>
</tr>
<tr>
<td>50% H₂O-CH₃CN</td>
<td>0.085 ± 0.004</td>
<td>6.5 ± 0.2</td>
</tr>
<tr>
<td>100% H₂O</td>
<td></td>
<td>3.0 ± 0.2</td>
</tr>
</tbody>
</table>

a) Measured by GC using 125 as external standard; λₑm = 302 nm.
b) Measured by single photon counting; λₑm 300 nm/λₑm 360 nm; all decays were single exponential (χ² ≤ 1.30).
c) < 2% CH₃CN used as a cosolvent.

as external standard. The GC results were corrected for differences in the detector response of xanthene (125) and the starting material 140. Because 141 was the only isolable product in these experiments, where mass balances were excellent (> 90%), Φₜ when divided by a factor of two should be a good measure of the quantum yield for formation of 141. Products 171 and 172 were formed in only trace amounts (< 1%) in argon purged solutions. The higher Φₜ in 50% H₂O-
CH₃CN compared to 100% CH₃CN, 95% EtOH and the other solvents used is consistent with the results of the product studies followed by ¹H NMR.

2.4.3 Steady-State and Transient Fluorescence Measurements

As has been already stated, photolysis of N-methylacridan (140) in 50% H₂O-CH₃CN at 254 nm results in the formation of trace amounts of N-methylacridone (171) and N-methylacridinium ion (172). These compounds have higher ε at 254 nm than 140, and once formed then absorb light preferentially, slowing down the reaction of 140. However, 171 and 172 could not be detected by ¹H NMR of the reaction mixture. Steady-state fluorescence studies of the photolysis of 140 conclusively demonstrate that trace amounts of 171 and 172 are indeed formed on irradiation at 254 nm. Fluorescence spectra of 140 were recorded using 10⁻⁴ M deaerated 50% H₂O-CH₃CN solutions at excitation wavelengths of 254 and 300 nm. Excitation of 140 at 254 nm gave an intense emission centered at 480 nm and two much weaker emissions centered at 425 nm and 360 nm. The emission at 480 nm was assigned to N-methylacridinium ion (172) by comparison with the emission spectrum of the authentic material. This emission band increased in intensity as more and more of 172 is formed with increasing photolysis time. The weak emission bands at 425 nm and 360 nm were assigned to N-methylacridone (171) and N-methylacridan (140), respectively, by comparison with the emission spectra of the authentic samples. However, when 140 was excited at 300 nm only one emission band at 360 nm (due to 140) was
observed. The intense emission observed from 172 on excitation at 254 nm is due to the fact that this ion has an intense absorption at this wavelength as well as being a strongly emitting chromophore. Ketone 171 also has an intense absorption here but it is not formed to the same extent as 172 in aqueous CH$_3$CN solutions (vide supra). These steady-state fluorescence measurements clearly demonstrate the formation of both 171 and 172 on photolysis of 140 in deaerated aqueous CH$_3$CN.

Fluorescence lifetimes of 140 were measured using single photon counting ($\lambda_{en} = 300$ nm; $\lambda_{em} = 360$ nm) using deoxygenated solutions. Lifetimes of 140 in various solvents are shown in Table 2.18. All observed decays were single exponential. A decrease in lifetime ($\tau$) is observed going from 100% CH$_3$CN to 100% H$_2$O with a concomitant increase in $\Phi_L$. However, lifetimes of 140 in both 100% Et$_2$O and 100% hexane are shorter than expected based on the measured $\Phi_L$ in these two solvents. Hence, it seems that there is no simple correlation between fluorescence lifetime and the quantum efficiency of formation of 141 in a given solvent. Using fluorescence quenching data, Fukuzumi and coworkers$^{141}$ have found that the photoredox chemistry of 140 (in the presence of O$_2$) originates from $S_1$. The lifetime data in the present study are not completely consistent with $S_1$ reactivity but does not rule out $S_1$ reaction either. To investigate the nature of the excited state ($S_1$ vs $T_1$) involved in the reaction of 140 triplet quenching experiments were carried out.
2.4.4 Triplet Quenching of 140

The excited state responsible for a photochemical reaction is often, though not always, either the lowest excited singlet state \( (S_\text{r}) \) or the lowest triplet state \( (T_\text{r}) \) of a molecule. To find out which is involved, sensitization and quenching methods are employed. Most studies use triplet sensitizers or triplet quenchers, partly because the results of such studies are more easily interpreted than those involving the use of singlet sensitizers and quenchers.\(^{142}\)

Triplet quenching experiments involve selectively exciting the molecule in presence of an appropriate triplet \( (T_\text{r}) \) quencher. The logic of triplet quenching is that if the quencher inhibits the reaction, then reaction is deduced to occur from \( T_\text{r} \). A negative result implies that reaction occurs from \( S_\text{r} \). In the choice of a suitable triplet quencher it is imperative that the \( T_\text{r} \) energy of the quencher must be lower than the \( T_\text{r} \) energy of the molecule under investigation for efficient energy transfer to take place. Furthermore, the quencher must not have a significant absorption in a region of the spectrum where the molecule is being excited.\(^{142}\)

The triplet energy of 140 has not been measured. However, it would be expected to be close to that of \( \text{N,N-dimethylaniline (173)} \) and \( \text{diphenylamine (174)} \)

\[
\begin{align*}
\text{173} & & \text{174} \\
E_T &= 72\text{-}75 \text{ kcal mol}^{-1} & E_T &= 53 \text{ kcal mol}^{-1}
\end{align*}
\]
(E<sub>f</sub>'s = 72-75 kcal mol<sup>-1</sup>)<sup>143</sup>, if not lower. Use of 1,3-cyclohexadiene (175) (E<sub>f</sub> = 53 kcal mol<sup>-1</sup>) as triplet quencher would be appropriate.<sup>142</sup> Since the triplet lifetime of 140 was found to be ≥ 2 µs from laser flash photolysis experiments (<em>vide infra</em>) use of a 10<sup>-3</sup> M solution of triplet quencher should quench all triplet states and hence also reaction of 140 to form 141 if the triplet state was indeed responsible for the observed chemistry. Photolysis of a 10<sup>-3</sup> M solution of 140 in the presence of 0.003 M solution of 1,3-cyclohexadiene (175) in 100 mL CH<sub>3</sub>CN at 300 nm gave the same yield of 141 as without added quencher. This shows that the lowest triplet is not the reactive state in the reaction of 140.

2.4.5 Mechanism of Photodimerization of 140

Extensive studies by Fukuzumi and coworkers<sup>144</sup> have shown that 140 is a modest reducing agent, in both ground and excited states. For example, photolysis of 140 in the presence of phenacyl bromide results in the formation of N-methylacridinium bromide and acetophenone via an overall redox process initiated by light.<sup>144a</sup> This same reaction could be sensitized with [Ru(bpy)<sub>3</sub>]<sup>2+</sup> by irradiation at 452 nm, where 140 does not absorb.<sup>144a</sup> Use of photoexcited benzophenone with 140 has been reported by Peters and coworkers<sup>145</sup> to result in electron transfer from 140 to triplet benzophenone, to generate the corresponding radical anion/radical cation pair which subsequently collapse to the radical pair after proton transfer from 140<sup>+</sup> to benzophenone radical anion. In all these studies, 140 has been used for redox or photoredox chemistry in conjunction with
an electron acceptor of some kind. However, results obtained in the present study clearly show that 140 is reactive even in the absence of any added electron acceptor, to produce 141 in modest yields.

The formation of 141 suggests the intermediacy of N-methylacridan radical (140). Based on the knowledge of redox behaviour of 140, one can envision that the photoexcitation of 140 results in the one-electron transfer (solvent acting as an electron sink) to generate the N-methylacridan radical cation (140\(^+\)) which upon deprotonation gives the radical 140. A working mechanism for the formation of 141 is presented in the Scheme 2.6.

![Scheme 2.6](image-url)
To investigate the details of this proposed mechanism (Scheme 2.6) laser flash photolysis studies of 140, in collaboration with Dr. L. J. Johnston (National Research Council (NRC) at Ottawa) were carried out at NRC.

Laser excitation of 140 at \( \lambda_{ex} = 308 \text{ nm} \) in CH\(_3\)CN gave a transient species absorbing at \( \lambda_{max} = 520 \text{ nm} \) (\( \tau = 3 \mu \text{s} \)). This transient was assigned to the triplet-triplet \( (T_1-T_1) \) absorption of 140 based on its efficient reaction with 1,3-cyclohexadiene \( (175; 1.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}) \) and oxygen. A similar laser excitation of 140 in aqueous CH\(_3\)CN gave two transient species, absorbing between 600-700 nm and at \( \lambda_{max} = 355 \text{ nm} \). The transient absorbing between 600-700 nm decayed in 70 \( \mu \text{s} \), leaving a species with a sharp absorption at 355 nm and a weak shoulder at \( \approx 420 \text{ nm} \). The 420 nm band was assigned to the \( N \)-methylacridinium ion \( (172) \), based on comparison with the spectrum of an authentic sample. The transient species absorbing in long wavelength region between 600-700 nm region also had a UV band at \( \approx 330 \text{ nm} \) (\( \tau = 50 \mu \text{s} \)). This transient (between 600-700 nm) was not affected by oxygen or 1,3-cyclohexadiene and was assigned to \( N \)-methylacridan radical cation \( (140^+) \), based on the comparison with the previously reported spectrum for \( 140^+ \) by Peters and coworkers\(^{145} \), and to the reported transient spectrum of diphenylamine radical cation.\(^{146} \). The transient due to \( 140^+ \) (\( \lambda_{max} = 630 \text{ nm} \)) was quenched by bases such as hydroxide \( (k(\text{HO}^-) = 2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}) \) and pyridine \( (k = 7.3 \times 10^5 \text{ M}^{-1} \text{ s}^{-1}) \). The rate constant obtained for the reaction of pyridine with \( 140^+ \) was in good agreement with that obtained for deprotonation of \( 140^+ \) in CH\(_3\)CN (+ 0.6 M Et\(_4\)N\(^+\)BF\(_4^-\)) from simulation of electrochemical data.
(k = 3.1 \times 10^6 \text{ M}^{-1} \text{s}^{-1})^{147}. Time resolved conductance measurements further confirmed the formation of an ionic species, viz., 140⁺.

The laser flash photolysis experiments of 140 in aqueous \text{CH}_3\text{CN} showed that the transient signals due to T₁ (λ_{max} = 520 nm) and 140⁺ (λ_{max} = 630 nm) were formed rapidly within the duration of the laser pulse. However, the signal due to cation 172 (λ_{max} 420 nm) showed readily resolvable growth over a time-scale which agreed with the decay of 140⁺ (λ_{max} 630 nm), suggesting that the radical cation 140⁺ was the precursor of cation 172.

Two laser experiments in which triplet 140 was generated in aqueous \text{CH}_3\text{CN} and then re-excited = 100 ns later with a 530 nm Nd:YAG laser pulse, indicated that the photoionization of 140 can occur from a triplet state. However, the lowest energy triplet was not responsible for the one laser photoionization of 140 since all the radical cation 140⁺ was formed within the duration of the laser pulse, whereas the triplet absorption decayed over a period of several microseconds.

Laser excitation of 140 in aqueous \text{CH}_3\text{CN} in the presence of 0.038 M \text{NaOH}, shortened the lifetime of the radical cation 140⁺ (τ = 1.5 μs), and showed the formation of a new species absorbing at λ_{max} 510 nm. However, this species was not particularly long lived (5-10 μs) and was not easily separable from the T₁ of 140, which also absorbs in the 500 nm region. However, when the experiment was repeated in the presence of both hydroxide (to reduce 140⁺ lifetime) and 0.0025 M 1,3-cyclohexadiene (175) (to quench T₁ of 140), the transient
species absorbing at $\lambda_{\text{max}} = 510 \text{ nm}$ was clearly observed. This transient was assigned to 140 based on comparison with the reported spectrum.\textsuperscript{148,151}

Furthermore, in the presence of hydroxide the rate of growth of signal due to 140 at 510 nm agreed well with the rate of decay of 140\textsuperscript{+} indicating that it was the precursor of radical 140\textsuperscript{+}.

In the absence of added base the kinetics of decay of 140\textsuperscript{+} agreed well with those for the growth of cation 172. However, the lifetime of radical 140\textsuperscript{+} was substantially shorter than that of 140\textsuperscript{+} under these conditions, suggesting either 140\textsuperscript{+} or 140\textsuperscript{+} could be the precursor for cation 172. In the presence of base and diene (to quench T\textsubscript{1}), the growth of signal due to cation 172 occurred more slowly than the decay of 140\textsuperscript{+} but was in reasonable agreement with the decay of radical 140\textsuperscript{+} monitored at 510 nm. Addition of small amounts of air to the sample resulted in a more rapid decay of the radical and a concomitant increase in the rate of production of cation 172. However, addition of air did not decrease the yield of 172; similarly, either oxygen or nitrogen purged samples gave the same yield of 172. These results indicate that most of cation 172 is formed from radical 140, at least under these conditions.

The results of laser flash photolysis experiments demonstrate that excitation of 140 in aqueous CH\textsubscript{3}CN results in its photoionization from $S_1$, to generate N-methylacridyl radical cation (140\textsuperscript{+}), which on subsequent deprotonation generates N-methylacridyl radical (140), which dimerizes to give 141. The detailed mechanism of photodimerization of 140 is presented in Scheme 2.7.
In this mechanism photoionization of 140 from S₁ results in the formation of N-methylacridan radical cation (140⁺). The major reaction pathway for 140⁺ is deprotonation, to give the corresponding radical 140⁻; the intermediacy of 140⁻ is demonstrated by both isolation of dimerization product 141 in preparative scale product studies and its direct detection in the laser flash photolysis experiments.
Intersystem crossing to $T_1$ of 140 does occur but leads to no chemistry. The lifetime of 140$^-$ is shortened in the presence of added hydroxide which is consistent with the enhancement in deprotonation of 140$^-$ to form 140$^\circ$. However, no overall increase in the yield of 141 was observed on increasing the pH suggesting that the product-limiting step is ionization of 140 which is probably irreversible. The radical 140 can be trapped by residual oxygen present in the solution (to give cation 172) which competes with its dimerization. This notion is not unreasonable since, the product studies have shown that photolysis of 140 in oxygen purged solution results in the exclusive formation of 172.
CHAPTER THREE

EXCITITED STATE CARBON ACID BEHAVIOUR OF SUBSTITUTED SUBERENES: PHOTOGENERATION OF CYCLICALLY CONJUGATED \(8\pi\) ELECTRON CARBANIONS

3.1 Syntheses

3.1.1 2,8-Dimethoxysuberene (180)

2,8-Dimethoxysuberene (180) was synthesized according to the method outlined in Scheme 3.1. The ketone 178 was synthesized following reported procedures\(^{149}\) via the Parham cyclization\(^{150}\) of the lithium salt of carboxylic acid 177 generated in situ by the treatment of 176 with one equivalent of \(n\)-BuLi followed by the addition of \(CO_2\) (g) at -100 °C. Treatment of 177 with \(n\)-BuLi at -100 °C induced halogen-metal exchange followed by cyclization to yield the desired ketone 178. The double bond of 179 was introduced by treating it with NBS to give corresponding 10-bromo substituted ketone which upon dehydrobromination with 2,4,6-collidine afforded the ketone 179. Reduction of ketone 179 with the mixed hydride reagent\(^{151}\) LiAlH\(_4\)/AlCl\(_3\) in dry THF afforded 2,8-dimethoxysuberene (180) which was purified by recrystallization from EtOH/H\(_2\)O. The \(^1\)H NMR and mass spectral analyses were consistent with the structure of 180. The corresponding dideuterated 181 was similarly prepared by reducing ketone 179 with LiAlD\(_4\)/AlCl\(_3\) in dry THF. The mass spectrum and \(^1\)H NMR of 181 were consistent with the incorporation of two deuteriums at the indicated bibenzylic position.
Scheme 3.1

3.1.2 10-Methoxysuberene (185)

10-Methoxysuberene (185) was synthesized by following Scheme 3.2. Dehydrobromination of 182 to give 183 had been earlier accomplished by using NaOH/MeOH, but it was found to result in low yields of 183. Treatment of 185 in refluxing 3 M methanolic solution of KOH for one hour was found to result in much higher yields (ca. > 90%) of 183. Subsequent reflux of 183 in methanolic KOH solution (ca. 3 M) for 4 hours, followed by cooling the reaction
mixture to -4 °C (18 h) afforded 10-methoxysuberone 184 as a yellow crystalline solid. Reduction of ketone 184 with LiAlH₄/AlCl₃ in dry THF afforded the

![Chemical structures showing the transformation of 182 to 184, and 184 to 185 and 186.]

Scheme 3.2

crude 185 which was purified by recrystallization from methanol. The ¹H NMR and mass spectral analyses of 185 were consistent with the indicated structure. The corresponding dideuterated 186 was similarly prepared by reducing 184 with LiAlD₄/AlCl₃ in dry THF. The ¹H NMR spectrum of 186 was similar to 185 except for the absence of the bibenzyllic protons. The mass spectral analysis of 186 also indicated the presence of two deuteriums in the molecule.
3.1.3 10-Bromosuberene (187)

10-Bromosuberene (187) was prepared by reducing ketone 183 with LiAlH₄/AlCl₃ in dry THF (eq 3.1). The crude 187 was purified by column chromatography (silica gel; CH₂Cl₂) and recrystallized from petroleum ether. The ¹H NMR and mass spectrum of 187 were consistent with its indicated structure. The corresponding dideuterated 188 was similarly prepared by the reduction of 183 by LiAlD₄/AlCl₃ in dry THF and characterized by ¹H NMR and mass spectral analysis.

3.1.4 10-Cyanosuberene (189)

The strategy utilized for the synthesis of 10-cyanosuberene (189) is shown in eq 3.2. Treatment of the 10-bromosuberene (187) with CuCN in refluxing 1-
methyl-2-pyrrolidone\textsuperscript{153} afforded a white solid which on further purification by column chromatography (silica gel; hexanes) and recrystallization from 100% EtOH afforded pure 189. The 'H NMR and mass spectrum of 189 were consistent with its indicated structure. The corresponding didideuterated 190 was similarly prepared by treating 188 with CuCN.

3.1.5 Tribenzosuberene (193)

Tribenzosuberene (193) was synthesized according to Scheme 3.3. Treatment of ketone 183 with potassium t-butoxide in the presence of furan afforded the adduct 191.\textsuperscript{152} Deoxygenation of 191 with Fe\textsubscript{2}(CO)\textsubscript{9}\textsuperscript{154} in refluxing benzene yielded tribenzosuberenone (192) as a yellow crystalline solid. Reduction

\begin{center}
\begin{tikzpicture}
\node at (0,0) {183 \(\xrightarrow{\text{t-BuO}^+ \text{K}^+ \text{Furan}}\) 191 \(\xrightarrow{\text{Fe}_2(\text{CO})_9 \text{benzene}}\) 192}
\node at (0,-2) {183 \(\xrightarrow{\text{LiAlH}_4 \text{or LiAID}_2/\text{AlCl}_3}\) 193 or 194}
\end{tikzpicture}
\end{center}

Scheme 3.3
of 192 with LiAlH<sub>4</sub>/AlCl<sub>3</sub> in THF afforded the crude tribenzosuberene (193), which was purified by column chromatography (silica gel; CH<sub>2</sub>Cl<sub>2</sub>) and recrystallized from EtOH/H<sub>2</sub>O. The mass spectral and <sup>1</sup>H NMR analyses of 193 were consistent with its indicated structure of 193. The dideuterated analogue 194 was similarly prepared by reduction of ketone 192 with LiAlD<sub>4</sub>/AlCl<sub>3</sub>.

3.1.6 8H-Furo[3,4-d]dibenzo[b,f]suberene (196)

Treatment of adduct 191 with 3,6-di(pyridin-2'-yl)-s-tetrazine<sup>155</sup> (TZ) in CHCl<sub>3</sub> afforded ketone 195 in > 98% yield. Ketone 195 was reduced with LiAlH<sub>4</sub>/AlCl<sub>3</sub> in THF to afford the target molecule 196 (Scheme 3.4).
1H NMR analysis and mass spectrum of 196 were consistent with its indicated structure. The dideuterated 197 was similarly prepared by reduction of ketone 195 with LiAlD₄/AlCl₃.

3.1.7 3,4-Benzotropilidene (201) and 1,2-Benzotropilidine (202).

3,4-Benzotropilidene (201) was made from 1-benzosuberone (198) using the procedure of Burdett and coworkers. Treatment of 198 with NBS in refluxing CCl₄ afforded 199 which on refluxing with 2,4,6-collidine yielded 200. In subsequent steps 200 was converted to the corresponding tosylhydrazone, followed by treatment with MeLi in dry THF afforded 201 as an oil which was purified by distillation under reduced pressure to obtain pure 201 (Scheme 3.5).

![Scheme 3.5](image)

Conversion of 201 to the isomer 1,2-benzotropilidine (202) was accomplished by
isomerization with potassium t-butoxide (Scheme 3.5).  

3.2 Product Studies

3.2.1 Photolysis of 2,8-Dimethoxysuberene (180)

Photolysis of 180 in 50% D₂O-CH₃CN for 2 hours gave a reaction mixture which showed the appearance of a new unresolved triplet at δ 3.58 (J = 1-2 Hz) along with a decrease in signal intensity (relative to the vinyl protons) of the methylene signal of 180 at δ 3.60. The appearance of the triplet at δ 3.58 is consistent with the formation of 203 (= 25% based on ¹H NMR integration) in which the monobenzylic proton is coupled to the geminal deuterium. The aromatic and vinyl signals in the photolyzed sample remain unchanged. However, GC/MS analysis of the product mixture indicated formation of both 203 (~21%) and 181 (~3%) (eq 3.3).

Previous results have demonstrated that photolysis of suberene (37) in 50% D₂O-CH₃CN results in deuterium incorporation at the 5-position to form
monodeuterated 37-d (eq 1.11).\textsuperscript{46} The \(^1\)H and \(^{13}\)C NMR spectra of the photoproducts obtained in the photolysis of 37 clearly showed that the deuteriums were incorporated at the benzylic position (C-5 position). The possibility that a residual amount of deuterium might be incorporated into other positions, viz., the vinylic or benzene ring positions, was ruled out since the \(^2\)H NMR of the photoproducts showed \(< 2\%\) deuterium incorporation at other positions of 37. Results obtained in the photolysis of 180 were consistent with these findings. That is, \(^2\)H NMR of the product mixture obtained after photolysis of 180 showed a strong signal at \(\delta 3.60\), indicating the formation of 203 and 181, with no signals between \(\delta 5.0-8.0\).

Deuterium incorporation in 180 takes place only on irradiation. A solution of 180 in 50\% \(\text{D}_2\text{O}\)-\(\text{CH}_3\text{CN}\) (pD 7-14) left stirring in the dark (at \(\approx 22 \pm 2 \, ^\circ\text{C}\)) for 2 hours did not result in deuterium incorporation.

Photolysis of dideuterated 181 in 50\% \(\text{H}_2\text{O}\)-\(\text{CH}_3\text{CN}\) (ca. 2 h) at 300 nm also resulted in the formation of 203 \(12\%\) and 180 \(2\%\) (eq 3.4). In general, good agreement was observed between the calculated amounts of deuterium exchange by \(^1\)H NMR and GC/MS. The kinetics of deuterium exchange was followed by
irradiating ~ 60 mg of 181 in 50% \( H_2O-CH_3CN \) and removing aliquots after set period of times. These aliquots were then examined by GC/MS (after work-up) to determine the yields of 203 and 180. The results are presented in Figure 3.1. It is evident from the plot that the initially exchanged product is 203 (primary photoproduct), which subsequently reacts via a secondary photoreaction to give 181.

![Graph showing the percentage yield of 203, 180, and 181 over photolysis time.](image)

**Figure 3.1** Plot of percent recovered 181 and yields of exchange photoproducts 203 and 181 vs photolysis time in 50% \( H_2O-CH_3CN \).
Deuterium incorporation in 180 on irradiation in 50% D₂O-CH₃CN, and protium incorporation in 181 on photolysis in 50% H₂O-CH₃CN is consistent with the intermediacy of carbanion 204. That is, photoexcitation of 180 results in the benzylic C-H bond ionization, with H₂O acting as the deprotonating base, to give the intermediate 8π-electron carbanion 204. The photogenerated carbanion 204 is subsequently deuterated by the solvent to give overall exchange product (viz., 203). Another mechanistic possibility that might explain the deuterium incorporation in 180 involves the initial homolysis of the benzylic C-H bond to generate radical 205 which subsequently abstracts deuteron from the solvent. However, this possibility can be ruled out since when 180 was photolyzed in 100% CD₃CN no deuterium incorporated product was isolated. If radical 205 was indeed formed then it should have abstracted deuterium from CD₃CN, which is a better deuterium source than D₂O. In addition, if any radical were formed it would be expected to dimerize efficiently, to give the corresponding dimer of 180, which was not observed.

To investigate the qualitative effect of methoxy groups in 180 on the efficiency of C-H bond heterolysis, photolysis of 180 and 37 was carried out under
identical conditions. Thus, photolysis of suberene (37) in 50% D₂O-CH₃CN resulted in substantially higher amounts of deuterium incorporated products, viz., 37-d (53%) and 37-d (9%), compared to a similar photolysis of 180 which resulted in significantly lower amounts of deuterium incorporated products, viz., 203 (-12%) and 181 (-3%). This result is in accord with the intermediacy of carbanion 204 in the deuterium exchange reaction of 180. The presence of methoxy groups destabilizes the negative charge of the incipient carbanion 204 in the transition state which retards the C-H bond photoheterolysis in 180. The effects of other substituents on the efficiency of excited state C-H bond ionization in suberene were also investigated, and are described below.

3.2.2 Photolyses of 10-Methoxysuberene (185) and 10-Cyano-suberene (189)

Photolysis of 185 in 50% D₂O-CH₃CN resulted in the formation of monodeuterated 206 (9%) (eq 3.5) as indicated by GC/MS analysis of the reaction mixture. At such short photolysis time (ca. 5 min) no dideuterated 186 was observed. Thermally, 185 in aqueous CH₃CN solution undergoes hydrolysis to yield 207 (eq 3.6). Because of this competing thermal reaction photolysis of 185
for longer durations could not be carried out. Consistent with the intermediacy of carbanion a similar photolysis of 186 in 50%H₂O-CH₃CN also resulted in the formation of 206 (~6%) (eq 3.7).

Photolysis of 189 in 50% D₂O-CH₃CN gave monodeuterated 208 (42%) and 190 (8%) (eq 3.8). A similar photolysis of suberene (37) resulted in significantly
lower amounts of deuterium incorporated photoproducts, viz., monodeuterated 37-d (35.5%) and dideuterated 37-d_2 (5%). The increased amount of deuterium incorporation in 189 suggests that the presence of the cyano group at the 10-position increases the C-H ionization rate of 189. This is understandable since the intermediate carbanion 209 is stabilized by the cyano group which will enhances the C-H bond ionization rate. This observation further supports the intermediacy of carbanion intermediates in the deuterium exchange reactions of suberene (37) and its derivatives.

![Diagram of molecule 209](image)

3.2.3 Photolysis of 10-Bromosuberene (187)

Deuterium exchange studies of 187 proved to be difficult because of its efficient photodebromination and photohydrolysis in aqueous CH_3CN. Thus, photolysis of 187 in 50% H_2O-CH_3CN resulted in the formation of 37 (~12%) and ketone 207 (~15%) (eq 3.9). In the absence of irradiation, a very slow thermal solvolysis of 187 (to give ketone 207) was observed. It has been shown that photolysis of vinyl bromides results in the C-Br bond homolysis to generate a radical pair.\(^6\) Rapid electron transfer within the radical pair results in the
formation of vinyl cation which is subsequently trapped by solvent to give solvolysis products. A similar mechanism is proposed to operate in the case of 187. That is, photolysis of 187 results in the vinylic C-Br bond homolysis, to give

\[
\text{hv} (300 \text{ nm}) \rightarrow [\text{radical pair}] \rightarrow [\text{solvolysis products}]
\]

the radical pair 210 in a solvent cage. Electron transfer (ET) within the caged
radical pair 210 generates the ion pair 211, which is subsequently trapped by water to yield ketone 207 (Scheme 3.6). Escape of radical pair 210 from the solvent cage followed by hydrogen abstraction from the solvent generates 37. Formation of carbocation 211 was shown by photolyzing 187 in 100% MeOH which resulted in the formation of the corresponding methyl ether 185 (~30%) (eq 3.10). The notion that the primary photochemical event is the vinylic C-Br bond homolysis is supported by the fact that when 187 was photolyzed in 100% CH₃CN (dry), only 37 was formed (eq 3.11).

\[
\begin{align*}
187 & \xrightarrow{\text{hv (300 nm)}} 185 \\
\text{100% MeOH} & \\
\end{align*}
\]

\[
\begin{align*}
187 & \xrightarrow{\text{hv (300 nm)}} 37 \\
\text{100% CH₃CN} & \\
\end{align*}
\]

3.2.4 Photolysis of Tribenzosuberene (193) and 6H-Furo[3,4d]-dibenzo[b,f]suberene (196)

Photolysis of 193 and 196 in 50% D₂O-CH₃CN did not result in deuterium
exchange and the starting materials were recovered. However, photolysis of 193 in 50% 1 M NaOD-EtOD resulted in the formation of 212 (-15%) and 194 (-3%) (eq 3.12). A similar photolysis of 193 in 100% EtOD did not result in any reaction. The amount of exchange photoproduct 212 increased with the concentration of NaOD suggesting that it was the deprotonating base.

Photolysis of 194 in the presence of amine bases resulted in substantially higher amount of exchange. Thus, photolysis of 194 in the presence of 1 M ethanolamine solution in CH₃CN resulted in the formation of 212 (26%) and 193 (7%) (eq 3.13). Similarly, photolysis of 197 in the presence of 0.5 M ethanolamine
solution in CH$_3$CN also resulted in the deuterium exchange to give monodeuterated 214 (-23%) and 196 (-7%) (eq 3.14). Photolysis of 194 and 197 in 100% CH$_3$CN did not result in any observable exchange, suggesting that ethanolamine was the deprotonating base. This is further supported by the fact that when the concentration of ethanolamine in CH$_3$CN was increased, the amount of exchange product 212 also increased.

3.2.5 Photolyses of 3,4-Benzotropolidine (201) and 1,2-Benzotropolidine (202)$^{15b}$

Possibility of deuterium exchange in less rigid systems (compared to suberene) 201 and 202 was also explored. It has been shown earlier that photexcitation of 201 and 202 in cyclohexane results in the formation of
benzonorcaradiene (215) (eq 3.15). The mechanism of the rearrangement has been shown to involve initial 1,7-hydrogen shift followed by electrocyclic ring closure to give 215. Photolysis of both 201 and 202 in 100% CH$_3$CN or 50-70% D$_2$O-CH$_3$CN gave 215 as the only product (eq 3.15), with no evidence for deuterium incorporation in recovered substrates or 215 as determined by $^1$H NMR and GC/MS analyses. The rearrangement to 215 was a very efficient process and only short photolysis times were required to convert 201 or 202 to 215. Thus it would appear that in the excited state C-H bond ionization cannot compete with efficient molecular rearrangement for these more flexible systems, although they possess the correct incipient 8π electron carbanion ring system to undergo C-H bond ionization.

3.3 Quantum Yields

Quantum yields (Φ) for deuterium incorporation in 180 (i.e., formation of 203) and protium incorporation in 181 (i.e., formation of 203) were measured on an optical bench at $\lambda_{\text{ex}} = 280$ nm. Quantum yields of deuterium/protium incorporation in other substituted suberene derivatives viz., 185, 186, 189, 190, 193, 194, 197, were also measured. Conversions to exchange photoproducts were kept between 12-20% and measured by GC/MS analyses.

Table 3.1 shows the quantum yields (Φ's) of deuterium incorporation in 180 on photolysis in deuterated solvents. For the purpose of comparisons, the quantum yields of deuterium incorporation into 37 are also presented in Table 3.1.
Table 3.1  Quantum Yields (Φ) for Monodenterium Incorporation into 180 in Various Solvents.a

<table>
<thead>
<tr>
<th>Solvent Mixtureb</th>
<th>180</th>
<th>37d</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CD3CN</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>70% D2O-CH3CN</td>
<td>0.0079±0.0005</td>
<td>0.029±0.004</td>
</tr>
<tr>
<td>50% D2O-CH3CN</td>
<td>0.0071±0.0004</td>
<td>0.030±0.004</td>
</tr>
<tr>
<td>20% D2O-CH3CN</td>
<td>0.0046±0.0002</td>
<td>0.021±0.001</td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses; errors quoted are standard deviation in amounts of deuterium incorporation calculated by 2-3 independent mass spectral analyses.
b) For solubility reasons CH3CN was used as cosolvent.
c) NMR solvent used without further treatment.
d) Obtained from ref. 48.

Table 3.2 presents the quantum yields (Φ's) of monoprotium incorporation in 181 in a variety of solvent mixtures. It is clear from Table 3.1 that aqueous CH3CN is the best solvent mixture to observe exchange. Furthermore, Φ's of exchange in H2O-CH3CN and D2O-CH3CN for 180 and 181, respectively (Tables 3.1 and 3.2), were essentially same (no significant isotope effect), even though the initial process required to observe exchange involves C-H bond ionization in 180 vs. C-D bond ionization in 181.
Quantum yields (Φ) for exchange of 181 were also measured in aqueous EtOH or CH₃CN solutions where the acidity or basicity of the aqueous portion was varied (Table 3.3). It was found that the exchange efficiency was reduced in acidic solutions and enhanced in aqueous NaOH solutions.

The quantum yields (Φ's) of deuterium incorporation (Table 3.1) in 180 are lower compared to suberene (37). This is in accord with the destabilizing effect

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>181</th>
<th>37-d₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH₃CN</td>
<td>0.000</td>
<td>0.000</td>
</tr>
<tr>
<td>70% H₂O-CH₃CN</td>
<td>0.011 ± 0.002</td>
<td>0.045 ± 0.006</td>
</tr>
<tr>
<td>50% H₂O-CH₃CN</td>
<td>0.0076 ± 0.0004</td>
<td>0.035 ± 0.006</td>
</tr>
<tr>
<td>20% H₂O-CH₃CN</td>
<td>0.0050 ± 0.0004</td>
<td>0.024 ± 0.003</td>
</tr>
<tr>
<td>70% MeOH-CH₃CN</td>
<td>0.0023 ± 0.0004</td>
<td>0.012 ± 0.002</td>
</tr>
<tr>
<td>70% EtOH-CH₃CN</td>
<td>0.0012 ± 0.0004</td>
<td>0.008 ± 0.001</td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses; errors quoted are standard deviation in amounts of deuterium calculated by 2-3 independent mass spectral analyses.
b) For solubility reasons CH₃CN was used as co-solvent.
c) Dry CH₃CN used without further treatment.
d) Obtained from ref. 48.
Table 3.3  Quantum Yields (Φ) for Protium Incorporation into 181 in Acidic and Basic Solutions.

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>Φ 181</th>
</tr>
</thead>
<tbody>
<tr>
<td>70% H₂O-CH₃CN</td>
<td>0.012 ± 0.004</td>
</tr>
<tr>
<td>70% 1.25 M H₂SO₄-EtOH</td>
<td>0.0028 ± 0.0003</td>
</tr>
<tr>
<td>70% 2.5 M H₂SO₄-EtOH</td>
<td>0.0012 ± 0.0004</td>
</tr>
<tr>
<td>50% 0.5 M NaOH-EtOH</td>
<td>0.0124 ± 0.0004</td>
</tr>
<tr>
<td>50% 1.0 M NaOH-EtOH</td>
<td>0.017 ± 0.003</td>
</tr>
<tr>
<td>50% 2.0 M NaOH-EtOH</td>
<td>0.020 ± 0.002</td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses; errors quoted are standard deviation in amounts calculated by mass spectral analyses.
b) For solubility reasons CH₃CN and EtOH were used as cosolvents.

of methoxy groups on the incipient carbanion intermediate 204. In contrast, the cyano group stabilizes the carbanion intermediate 209. This is manifested in the higher quantum yields of exchange for 189 and 190 compared to 37 (Table 3.4).

Table 3.4  Quantum yields of deuterium incorporations in 185 and 189 and protium incorporation in 186 and 190.

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>Φ¹</th>
<th>Φ⁵</th>
<th>Φ⁹</th>
<th>Φ₁⁰</th>
</tr>
</thead>
<tbody>
<tr>
<td>70% D₂O-CH₃CN</td>
<td>0.036</td>
<td>0.035</td>
<td></td>
<td></td>
</tr>
<tr>
<td>70% H₂O-CH₃CN</td>
<td>0.027</td>
<td>0.046</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a) Determined by mass spectral analyses.
b) errors are ± 10% of the quoted values.
Quantum yields ($\Phi$'s) of protium incorporation for 194 and 197 were measured in NaOH-EtOH solution and in the presence of ethanolamine in CH$_3$CN (Table 3.5). The exchange process in 194 and 197 was sluggish at lower ethanolamine concentrations and no exchange took place in the absence of the base (NaOH or ethanolamine).

Table 3.5 Quantum Yields for Protium Incorporation in 194 and 197 in Various Solvents.

<table>
<thead>
<tr>
<th>Solvent Mixture</th>
<th>$\Phi$' $\Phi$'</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>194</td>
</tr>
<tr>
<td>1.0 M Ethanolamine$^b$</td>
<td>0.0086</td>
</tr>
<tr>
<td>2.0 M Ethanolamine$^b$</td>
<td>0.016</td>
</tr>
<tr>
<td>50% 3.0 M NaCH$_3$-EtOH</td>
<td>0.0015</td>
</tr>
<tr>
<td>70% H$_2$O-CH$_3$CN</td>
<td>0.000</td>
</tr>
<tr>
<td>100% CH$_3$CN</td>
<td>0.000</td>
</tr>
<tr>
<td>95% EtOH</td>
<td>0.000</td>
</tr>
</tbody>
</table>

a) Measured by GC/MS analyses of reaction mixtures.
b) Ethanolamine solutions in dry CH$_3$CN
c) Errors are $\pm$ 10% of the quoted values.

The quantum yield ($\Phi$) for rearrangement of 201 has been measured by Swenton and coworkers$^{15a}$ to be $\sim$0.9 in cyclohexane ($\lambda_{\max} = 330$ nm). Using this reaction as the secondary actinometer, quantum yields for rearrangement of 201 and 202 (to 215) were measured in a number of additional solvents (Table 3.6).
In all cases, the rearrangement quantum yields were very high, with no apparent retarding effect by added water.

Table 3.6 Quantum Yields of Rearrangement of 201 and 202 in Various Solvents.

<table>
<thead>
<tr>
<th></th>
<th>201*</th>
<th>202*</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% CH₃CN</td>
<td>0.84</td>
<td></td>
</tr>
<tr>
<td>95% EtOH</td>
<td>≥ 0.7</td>
<td></td>
</tr>
<tr>
<td>50% H₂O-CH₃CN</td>
<td>≥ 0.7</td>
<td>=0.7</td>
</tr>
<tr>
<td>C₆H₁₂</td>
<td>0.87⁵</td>
<td>0.7 ± 0.1</td>
</tr>
</tbody>
</table>

a) Measured relative to the known quantum yield of 201 in C₆H₁₂ (Φ = 0.87), λₒ = 254 nm.
b) From ref. 156.

3.4 Steady-State Fluorescence Studies

3.4.1 General Spectral Characteristics and Fluorescence Quantum Yields

The fluorescence emission spectra of all suberene derivatives, viz., 180, 185 and 189, displayed spectral characteristics similar to the parent suberene⁴⁸ (37). The absorption and emission spectra of tribenzosuberene (193) and 8/i-furo[3,4d]dibenzo[b,f]suberene (196) however, were blue shifted compared to the parent system.

The fluorescence quantum yields (Φ's) of substituted suberenes were measured in 100% CH₃CN, relative to the parent suberene (37) (Φ = 0.86 ± 0.05
in \( \text{CH}_3\text{CN} \), and are presented in Table 3.7. The fluorescence quantum yields

Table 3.7 Photophysical Parameters of Substituted Suberenes in CH\(_3\)CN.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>( \Phi_f )</th>
<th>( \tau ) (ns)</th>
<th>( \lambda_{\text{max}} ) (emission)</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>0.47 ± 0.05( ^b )</td>
<td>5.10 ± 0.05( ^c )</td>
<td>410 nm</td>
</tr>
<tr>
<td>185</td>
<td>0.0051 ± 0.0004( ^b )</td>
<td>3.55 ± 0.05( ^c )</td>
<td>390 nm</td>
</tr>
<tr>
<td>18( ^{\text{n}} )</td>
<td>0.0048 ± 0.0005( ^b )</td>
<td>4.36 ± 0.05( ^c )</td>
<td>385 nm</td>
</tr>
<tr>
<td>193</td>
<td>0.18 ± 0.02( ^c )</td>
<td>3.21 ± 0.04( ^f )</td>
<td>325 nm</td>
</tr>
<tr>
<td>196</td>
<td>0.24 ± 0.03( ^c )</td>
<td>2.21 ± 0.05( ^f )</td>
<td>340 nm</td>
</tr>
</tbody>
</table>

a) Errors are ± 10% of the quoted values.
b) Measured relative to suberene (37) (\( \Phi_f = 0.86 \) in \( \text{CH}_3\text{CN} \)).
c) Measured relative to biphenyl ether (\( \Phi_f = 0.03 \) in cyclohexane).
d) Measured by single photon counting.
e) \( \lambda_{\text{ex}} = 280 \) nm.
f) \( \lambda_{\text{ex}} = 260 \) nm.

(\( \Phi_f \)'s) of the substituted suberenes were considerably lower than the parent 37 (Table 3.7). The reduced emission yields (\( \Phi_f \)'s) of substituted suberenes is due to the presence of substituents which open additional pathways for radiationless deactivation of \( S_1 \).

3.4.2 Fluorescence Quenching.

The emissions of suberene derivatives 180, 185 and 189 and their deuterated analogues, viz., 181, 186 and 190, in \( \text{CH}_3\text{CN} \) were quenched on addition of \( \text{H}_2\text{O} \). A representative case of emission quenching of 185 in \( \text{CH}_3\text{CN} \)
by added H$_2$O is shown in Figure 3.2.

Figure 3.2 Fluorescence quenching of 185 in CH$_3$CN by added H$_2$O.

Quenching rate constants ($k_q$'s) were calculated by standard Stern-Volmer analysis and are presented in Table 3.8. For the sake of comparison the fluorescence quenching rate constants for parent 37 and 37-$d_2$ are also presented in Table 3.8. The fluorescence quenching rate ($k_q$) of 180 by H$_2$O was lower than the suberene (37), whereas the cyano substituted 190 was quenched at a slightly higher rate (Table 3.8). The fluorescence quenching rate constants ($k_q$'s) for dideuterated 181, 186 and 191 were smaller than the diprotiated molecules, viz., 180, 185 and 190, corresponding to a primary kinetic isotope effect of ($k_H/k_D)_q = 2.20-3.00$ (Table 3.8). These isotope effects are consistent with the C-H vs C-D bond ionization in $S_t$, with H$_2$O acting as the deprotonating base.
Table 3.8 Fluorescence Quenching Rate Constants ($k_q$'s) of Substituted Stibenes in CH$_3$CN by Added H$_2$O.$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$k_q$(H$_2$O) M$^{-1}$ s$^{-1}$</th>
<th>$k_{H2O}/k_D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>$(1.53 \pm 0.06) \times 10^7$</td>
<td></td>
</tr>
<tr>
<td>181</td>
<td>$(0.51 \pm 0.05) \times 10^7$</td>
<td>$3.00 \pm 0.40$</td>
</tr>
<tr>
<td>185</td>
<td>$(1.81 \pm 0.07) \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>186</td>
<td>$(0.72 \pm 0.05) \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>189</td>
<td>$(2.05 \pm 0.08) \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>190</td>
<td>$(0.83 \pm 0.04) \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>37$^b$</td>
<td>$(1.68 \pm 0.08) \times 10^6$</td>
<td></td>
</tr>
<tr>
<td>37-$d_2$$^b$</td>
<td>$(0.61 \pm 0.06) \times 10^6$</td>
<td>$2.75 \pm 0.40$</td>
</tr>
</tbody>
</table>

a) Rate constants ($k_q$'s) obtained by standard Stern-Volmer analysis of quenchings; $\lambda_{ex} = 280$ nm.
b) Obtained from ref. 48.

To study the effect of medium acidity or basicity on fluorescence efficiency, the fluorescence emission intensity of 180 was monitored by varying the aqueous portion of the solution from 1 M NaOH (pH 14) to ca. 10% H$_2$SO$_4$ (Figure 3.3). The emission intensity of 180 stays relatively constant over the pH 7-10 region. However, the emission intensity of 180 was substantially enhanced on increasing the acidity, from pH 6 to pH 4. In solutions of higher acidities, the fluorescence intensity drops off. This intensity drop off in stronger acids is probably due to some thermal reaction of substrate since, 180 could not be recovered unchanged from these solutions of higher acidities. However, emission behaviour of 180 in
acidic solutions of pH < 5 suggests that we are observing fluorescence titration of the excited state carbon acid 180 (Figure 3.3). That is, on increasing the

![Figure 3.3 Fluorescence emission intensity of 180 vs pH or H_0 (30% EtOH co-solvent).](image)

Figure 3.3 Fluorescence emission intensity of 180 vs pH or H_0 (30% EtOH co-solvent).

solution acidity, the medium basicity is decreased, thus reducing the rate of deprotonation. This argument is further supported by the fact that the quantum yields of exchange of 180 decrease in the same acidity region. Similar behaviour has also been observed for the superene (37).\(^{48}\) Fluorescence of 180 was quenched in basic (pH > 12) aqueous solutions which suggests the base catalysis of deprotonation process. The enhanced quantum yields (\(\Phi\)'s) for exchange measured for 180 in basic aqueous solutions also support this notion (Table 3.3).
Consistent with their reactivity, fluorescence emission of tribenzosuberene (193) and 196 in CH₃CN was not quenched by added H₂O. However, the emission of 193, 194 and 196 in CH₃CN was quenched by added ethanolamine. A representative case of fluorescence quenching of 193 in CH₃CN by added ethanolamine is shown in Figure 3.4. The calculated fluorescence quenching rate constants (k_q's) for 193, 194 and 197 are shown in Table 3.9.

![Figure 3.4 Fluorescence excitation and emission spectra of 193 in 100% CH₃CN, with overlay of fluorescence quenching of 193 by ethanolamine in CH₃CN.](image-url)
Table 3.9  Fluorescence Quenching Rate Constants ($k_q$'s) of 193, 194 and 196 in CH$_3$CN by Added Ethanolamine.$^a$

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$k_q$ M$^{-1}$ s$^{-1}$</th>
<th>$k_H^0/k_D^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>193</td>
<td>$3.50 \pm 0.07 \times 10^8$</td>
<td></td>
</tr>
<tr>
<td>194</td>
<td>$2.12 \pm 0.05 \times 10^8$</td>
<td>$1.65 \pm 0.20$</td>
</tr>
<tr>
<td>196</td>
<td>$9.09 \pm 0.09 \times 10^8$</td>
<td></td>
</tr>
</tbody>
</table>

$^a$) Quenching rate constants ($k_q$'s) obtained by standard Stern-Volmer analyses of quenchings; $\lambda_{\text{ex}} = 260$ nm.

3.5  Mechanism of Proton and Deuteron Exchange in Suberenes

The results of the product and fluorescence studies are consistent with an ionic mechanism of exchange in $S_1$. The proposed mechanism for exchange in the case of 180 is shown in Scheme 3.7. In this simple carbon acid mechanism, 180 is deprotonated by D$_2$O in $S_1$, to give the intermediate carbanion 204 (which is presumed to be hydrogen bonded to the departing hydronium ion). The deprotonated proton may rebond to the carbanion 204, thus resulting in no net exchange (internal return). However, exchange of the departing proton with deuterons from D$_2$O, and subsequent deuteration of the carbanion 204 results in an overall exchange at the 5-position. An estimate of the percentage internal return can be made as follows. The fluorescence quantum yield ($\Phi_f$) of 180 in the nonreactive solvent CH$_3$CN is $0.47 \pm 0.05$. In 70% D$_2$O-CH$_3$CN, $\Phi_f$ drops to $\sim 0.16$. 
The observed exchange quantum yield in this solvent is $0.0079 \pm 0.0005$. Assuming that the decrease in $\Phi_i$ is mostly due to reaction via deprotonation of the benzylic C-H bond, then out of about 30 deprotonated molecules only 1 undergoes exchange.

Scheme 3.7
Fluorescence quenching rates of 180 and 181 by H_2O in CH_3CN show a significant isotope effect, \((k_H/k_D)_q = 3.00 \pm 0.40\), which is consistent with the cleavage of C-H vs C-D bond in the key primary step in S_1. However, primary isotope effect on the exchange quantum yields in L_2O-CH_3CN (L = H or D) (Tables 3.1 and 3.2) is significantly smaller \((\Phi_H/\Phi_D = 1.1-1.4)\). That is, the primary isotope effect which arises from C-H vs C-D bond cleavage is not manifested in exchange quantum yields. This is understandable, since the overall exchange requires the protonation of the intermediate carbanion 204 in a second step (Scheme 3.7). This second step has associated with it a primary isotope effect (protonation from L_2O) which compensates for the initial isotope effect (due to C-H vs C-D bond cleavage). The small isotope effect observed for the exchange quantum yields further underscores the significance of internal return in these photogenerated carbanions. Because, if every deprotonation resulted in exchange, a large isotope effect (equal to \((k_H/k_D)_q\)) would have been observed in the exchange quantum yields. Results obtained for other suberene derivatives, viz., 185 and 189, are also consistent with the mechanism presented in the Scheme 3.7.

Scheme 3.7 also explains the observed exchange of 193 and 196 in the presence of base (NaOH or ethanolamine). Increase in exchange quantum yields (Table 3.5) of 194 and 197 with increasing ethanolamine concentration is consistent with the notion that ethanolamine acts as the deprotonating base in S_1. Furthermore, the fluorescence quenching rates for 193 and 194 in CH_3CN by ethanolamine exhibits a moderate isotope effect, \((k^H/k^D)_q = 1.65 \pm 0.20\), which is
consistent with the C-H vs C-D bond ionization in $S_1$.

The excited state carbon acid behaviour of substituted suberenes (180, 185 and 189) is similar to the parent suberene 37. However, the stability of the intermediate carbanions, viz., 204 and 207, is significantly different from the parent suberenyl carbanion 35. The fluorescence titration of 180 indicates $pK(S_1) = 4$ (Figure 3.3), which is significantly higher than that of 37 ($pK(S_1) = -1$) obtained by similar method. This reduced acidity of 180 in $S_1$ is attributable to the reduced stability of carbanion 204. The lower exchange quantum yield ($\Phi$) of 180 compared to suberene (37) (Tables 3.1 and 3.2), is consistent with the notion that the reduced stability of intermediate carbanion 204 retards the rate of C-H bond cleavage of 180 in $S_1$. This is manifested in the lower fluorescence quenching rate ($k_q$) of 180 ($1.53 \pm 0.06 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$) by H$_2$O compared to 37 ($1.68 \pm 0.08 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$). Assuming that these measured $k_q$'s for fluorescence quenching of 180 by H$_2$O are equatable to the rates of C-H bond ionization in $S_1$, the difference in reactivity of 180 vs 37 are easily understood by application of the Hammond postulate to $S_1$. Thus, the lower rate of deprotonation of 180 implies that the transition state of C-H bond cleavage in $S_1$ occurs late along the C-H stretch reaction coordinate compared to 37. That is, the activation energy required to cleave C-H bond of 180 is higher than that of suberene (37). This is because the methoxy groups destabilize the developing negative charge on the incipient carbanion intermediate 204 in the transition state. This situation is diagrammatically presented in the Figure 3.5. On the other hand, the cyano
The requirement of a stronger base (viz., ethanolamine) to induce the C-H bond cleavage in 193 implies that it is less acidic than simple suberenes in $S_1$. The
MMX (PCMODEL force field) calculations indicate that in S_0 193 has a highly bent structure ("saddle shape") (Figure 3.6) which prevents an extensive \( \pi \)-orbital overlap. As a consequence, the negative charge in the incipient tribenzosuberenyl carbanion 213 in the transition state is less stabilized compared to simple suberenyl carbanions (e.g., 35).

Figure 3.6 Minimum energy structure for 193 predicted from PCMODEL.
CHAPTER FOUR

PHOTOGENERATION AND REACTIONS OF THIOXANTHENIUM AND XANTHENIUM CATIONS

4.1. Product Studies of Electron Transfer to Photoexcited Xanthenium and Thioxanthenium cations in \( S_i \) in Aqueous Acid Solution

4.1.1 Product Studies

9-Phenylxanthen-9-ol (98), and 9-xanthenol (216) were purchased from Aldrich and purified by recrystallization from hexane. 9-Phenylthioxanthen-9-ol (219) was prepared by adaption of reported procedures.\(^\text{159}\) 9,9'-Bisxanthene (128) was made according to a literature method, by photolysis of 9H-xanthene (125) followed by purification using preparative thin layer chromatography (eq 2.9).\(^\text{117}\) 9-Phenylxanthene (133), 9-phenylthioxanthene (139) and 9H-thioxanthene (136) were prepared via \( \text{LiAlH}_4/\text{AlCl}_3 \) reduction of the corresponding alcohols and purified by recrystallization from EtOH/H\(_2\)O. Bis(xanthen-9-yl)peroxide (217) was made by adaptation of reported method,\(^\text{160}\) via the oxidation of 216 with H\(_2\)O\(_2\) and purified by recrystallization from petroleum ether (eq 4.1).

\[ \begin{align*}
\text{H} & \quad \text{OH} \\
\text{216} & \xrightarrow{\text{H}_2\text{O}_2/\text{AcOH}} \\
\text{217} & 
\end{align*} \]
4.1.1.2 Photolysis of 9-Phenylxanthenium Cation (99)

Acidification of a CH₃CN solution of 9-phenylxanthenol (98) (pKᵢ⁺ = 1.0 ± 0.5 in aq. H₂SO₄) by 10% (w/w) H₂SO₄ readily afforded the cation 99 (eq 4.2).

\[
\begin{align*}
\text{Ph} & \quad \text{OH} \\
\text{O} & \quad \text{O} \\
\text{98} & \quad \text{CH₃CN-10% H₂SO₄} \\
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{99} \\
\text{O} & \quad \text{O} \\
\lambda_{\max} = & \ 375, 450 \text{ nm} \\
\end{align*}
\]

The cation 99 had a strong absorption band at approximately 375 nm and a broad weaker band at 450 nm giving rise to a characteristic yellow solution. Photolysis of 10⁻² M solutions of 99 for 30-60 min at 350 nm in 1:1 CH₃CN-10% (w/w) H₂SO₄ resulted in no significant reaction and the alcohol precursor 98 could be recovered after neutralizing the solution. However, when the above solution of 99 was photolyzed in the presence of 10⁻² M 1,3-dimethoxybenzene (1,3-DMB), a brown precipitate was observed to be forming after only 2 min of photolysis. After 30 min photolysis, the precipitate was filtered, washed with water and dried (yield = 10 mg). The ¹H NMR of the precipitate was not very informative and showed no significant peaks between δ 1-7 region indicating that the precipitate contained no 1,3-DMB fragment. The mass spectrum (CI) of this precipitate showed a significant peak at m/z 257 which corresponded to the 9-phenylxanthenyl fragment. On the other hand, when the filtrate was neutralized and extracted with CH₂Cl₂ it yielded recovered 98 and 1,3-DMB.
Only the cation 98 absorbs at the irradiation wavelength of 350 nm. In addition, there was no reaction observed when the reaction mixture was left in the dark or when irradiated in the absence of 1,3-DMB. Thus it is clear that the chemistry observed is due to photoexcited 99 in the presence of 1,3-DMB. Formation of precipitate was also seen when irradiation was carried out in the presence of 1,2-, 1,4-DMB and 1,3,5-TMB instead of 1,3-DMB. However, irradiation of 99 in the presence of benzonitrile did not result in the formation of the precipitate and 98 was recovered unchanged after photolysis.

Since the $^1$H NMR and mass spectral analyses of the precipitate were not particularly informative it was decided to make the use of X-ray crystallography to elucidate the nature of the precipitate. The precipitate was crystallized from CH$_2$Cl$_2$/hexanes to obtain yellowish crystals. The $^1$H NMR of the re-crystallized material was identical to the spectrum observed before re-crystallization reassuring that crystallization process did not change the structure of the photoprodut, or at least any change that could be detected by $^1$H NMR. The structure of the crystal was solved by X-ray crystallography (Table 4.1 and Figure 4.1) and found to be bis(9-phenylxanthen-9-yl) peroxide (218) (eq 4.3). It is

$\text{Ph}$

\[
\text{99} \xrightarrow{\text{hu (350 nm)}} \text{218}
\]

\[
\frac{50\% \text{CH}_3\text{CN}-10\% \text{H}_2\text{SO}_4}{1,3\text{-DMB}} 30 \text{ min}
\]
Figure 4.1 X-Ray structure of 218.

Table 4.1 Summary of Crystallographic Data for 218.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>C_{38}H_{36}O_{4}</td>
</tr>
<tr>
<td>mol wt</td>
<td>546.62</td>
</tr>
<tr>
<td>crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>p2\textsubscript{1}/n</td>
</tr>
<tr>
<td>cell dimensions</td>
<td></td>
</tr>
<tr>
<td>a, Å</td>
<td>8.461(1)</td>
</tr>
<tr>
<td>b, Å</td>
<td>16.870(4)</td>
</tr>
<tr>
<td>c, Å</td>
<td>19.847(3)</td>
</tr>
<tr>
<td>α, deg</td>
<td>90</td>
</tr>
<tr>
<td>β, deg</td>
<td>95.80(1)</td>
</tr>
<tr>
<td>γ, deg</td>
<td>90</td>
</tr>
<tr>
<td>V, Å\textsuperscript{3}</td>
<td>2822.3</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>T</td>
<td>20 °C</td>
</tr>
<tr>
<td>λ</td>
<td>Mo Kα(0.71069)</td>
</tr>
<tr>
<td>ρ\textsubscript{obsd} g cm\textsuperscript{-1}</td>
<td>1.281</td>
</tr>
<tr>
<td>ρ\textsubscript{calc} g cm\textsuperscript{-1}</td>
<td>1.286</td>
</tr>
<tr>
<td>R(F\textsubscript{0})</td>
<td>0.0753</td>
</tr>
<tr>
<td>R\textsubscript{w}(F\textsubscript{0})</td>
<td>0.0707</td>
</tr>
</tbody>
</table>
evident from the structure of 218 the anti arrangement of the xanthene and phenyl rings with respect to the O-O bond, relieves a significant amount of the steric interaction. The compound 218 has been previously reported in the literature. It has been made via the oxidation of 9-phenylxanthene (133)\(^{161}\) and via reduction of 99 with VCl\(_2\)\(^{162}\) but its crystal structure has not been reported.

The formation of 218 suggests the formation of 9-phenylxanthenyl radical (113) which, in principle, could either react with another radical to give rise to a dimer or, undergo a bimolecular reaction with O\(_2\) to yield 218. The presence of bulky phenyl groups induces unfavourable steric interactions and prevents the possibility of dimerization of radical 113 and hence the only observed photoproduct is 218. The possibility that the excited carbocation 99 itself could react with O\(_2\) to give rise to 218 is ruled out since the photolysis of 99 in the absence of 1,3-DMB did not lead to any reaction (eq 4.4). Moreover, it has been shown that 99 reacts slowly (compared to aromatic donors) with O\(_2\) \((k_{99-O2} \approx 10^{-7} \text{ M}^{-1} \text{s}^{-1})\)\(^{163}\). This is mainly because the cation 99 being electron deficient, the charge transfer interaction with O\(_2\) is absent. Additionally, the fact that an incipient dication-anion pair would be formed in the course of charge-transfer makes the latter unfavourable on the basis of intramolecular coulombic attraction.\(^{163}\)

Formation of 9-phenylxanthenyl radical 113 was further evident in the

\[
\begin{align*}
99 + O_2 & \overset{hv}{\longrightarrow} \text{no reaction} \\
& \text{1:1 H}_2\text{SO}_4-\text{CH}_3\text{CN}
\end{align*}
\]
course of photolysis of 99 in 2-propanol. Photolysis of 99 in 1:1 2-ProOH-10% (w/w) H$_2$SO$_4$ for 60 min failed to give any precipitate and 98 could be recovered after work up of the reaction mixture (eq 4.5). However, when the photolysis of such a solution was carried out in the presence of 1,3-DMB, the only product observed was 9-phenylxanthene (133) (≈ 30%), by comparison with an authentic sample (eq 4.6). These observations are consistent with the formation of the 9-phenylxanthenyl radical (113) as an intermediate in the photoreaction.

Moreover, 133 was only formed in the presence of dimethoxy benzenes, viz., 1,2-, 1,4- and 1,3-DMB.
The parent xanthenium cation (114) was generated from 9-xanthen-9-ol (216) in 1:1 CH$_3$CN-30% (w/w) H$_2$SO$_4$ (eq 4.7). Lower H$_2$SO$_4$ concentration failed to produce the cation on dissolution of the alcohol 216 signifying that the pK$_{a}$ is significantly lower (= -0.84 in aq H$_2$SO$_4$). The cation 114, similar to 99, had a strong absorption band at $\approx$ 374 nm and a much weaker broad band at $\approx$ 450 nm giving rise to its characteristic yellow colour.

Photolysis of a solution 114 in 1:1 CH$_3$CN-30% (w/w) H$_2$SO$_4$ in the presence of 1,3-DMB produced a yellow precipitate. This yellow precipitate upon isolation gave an $^1$H NMR spectrum with singlets at $\delta$ 5.8 and 4.2 indicative of two methine signals as well as aromatic signals characteristic of xanthone (144). In the absence of 1,3-DMB, photolysis of 114 did not yield any precipitate. However, upon work up of such a solution, the $^1$H NMR spectrum of the reaction mixture showed formation of an equal amount of 9-xanthone (144) and 9$_H$-xanthene (125). This mixture was also observed in a dark control reaction and therefore is attributed to a thermal reaction: a hydride transfer from the methine of 216 to the carbocationic centre of 114 (eq 4.8).
It was not possible to grow crystals from the photochemical product mixture that were suitable for X-ray crystallography. Therefore, the structure of the products, obtained on the photolysis of 114 in the presence of 1,3-DMB, were assigned by comparison with $^1$H NMR spectra of authentic samples. The singlet at $\delta$ 4.2 was assigned to 9,9'-bisxanthene (128), by comparison to an authentic sample prepared independently. The other singlet at $\delta$ 5.8 was assigned to
bis(xanthen-9-yl) peroxide (217), by comparison with an authentic sample made via \( \text{H}_2\text{O}_2 \) oxidation of 216 (eq 4.9). In a separate experiment when 217 was dissolved in aqueous \( \text{H}_2\text{SO}_4 \) (= 5% (w/w)) it readily decomposed to yield 9-xanthone (144). Thus, 9-xanthone (144) observed in the reaction mixture is probably due to reaction of 217 in water. Because, if 144 were formed in a thermal reaction, an equal amount of 125 should also have been observed (vide supra).

4.1.1.4 Photolysis of 9-Phenylthioxanthenium Cation (220)

The 9-phenylthioxanthenium cation (220) was generated by acidifying acetonitrile solution of the precursor 9-phenylthioxanthene-9-ol (219) with 30% (w/w) \( \text{H}_2\text{SO}_4 \) (eq 4.10). The cation 220 showed strong absorption band at ~385 nm as well as a weak long wavelength band at 500 nm, giving it a characteristic orange-red colour. Photolysis of a solution of 220 in 1:1 \( \text{CH}_3\text{CN-30\% H}_2\text{SO}_4 \) (\( \lambda_{\text{on}} \), 350 nm) did not result in any observable reaction and alcohol 219 could be recovered unchanged after work-up of the reaction mixture. Photolysis as above but in the presence of 1,3-DMB also did not show any reaction and 219 could be
recovered unchanged after work-up (eq 4.11). Use of 1,2-, 1,4-DMB and 1,3,5-
TMB also did not result in any observable reaction. This apparent lack of

![Chemical structure](image)

reactivity of cation 220 was intriguing because under similar conditions photolysis
of 9-phenylxanthenium cation (99) results in the formation of peroxy compound
218 via 9-phenylxantheny1 radical 113. It is possible that in the case of 220 the

![Chemical structure](image)

the corresponding radical 221 is formed but does not undergo any further
reaction with O₂. If the radical 221 is formed it could be reduced in the presence
of a good hydrogen donating solvent like 2-propanol to yield the hydrocarbon
139. However, when a solution of 220 in 1:1 2-propanol-30% H₂SO₄ along with
1,3-DMB was irradiated as above, it did not result in the formation of 9-phenyl-
9H-thioxanthene (139).
4.2 Quantum Yield Measurement

Since it was not possible to directly monitor the appearance of 218 in any quantitative fashion (GC, NMR), quantum yields for the loss of 99 (Φ<sub>L</sub>) in 8:2 1.25 M H<sub>2</sub>SO<sub>4</sub>-CH<sub>3</sub>CN were measured instead. The measurements were carried out in the presence of 10<sup>2</sup> M 1,3-DMB and followed by UV-Vis spectrophotometry (λ<sub>ex</sub> = 375 nm). Potassium ferrioxalate actinometry was employed to monitor the light intensity. Both the substrate and actinometer solutions were purged with a stream of argon prior to and during the photolysis. The Φ<sub>L</sub> = 0.0007 was obtained for the loss of 99. The low Φ<sub>L</sub> indicates that the reaction of excited 99 is extremely inefficient.

4.3 Steady-state Fluorescence and Lifetime Quenching Studies

The fluorescence behaviour of variety of xanthenium and thioxanthenium cations has been previously examined by several groups. Most of these cations fluoresce strongly and have relatively long (except 220) singlet lifetimes. Relevant fluorescence lifetimes (<i>τ</i>s) and quantum yields (Φ<sub>r</sub>) data in 8:2 1.25 M H<sub>2</sub>SO<sub>4</sub>-CH<sub>3</sub>CN for the cations examined in this work are collected in Table 4.2.
Table 4.2  Photophysical Parameters of Carbocations in Aqueous H$_2$SO$_4$ Solution.

<table>
<thead>
<tr>
<th>Carbocation</th>
<th>$\Phi_i^b$</th>
<th>$\tau_i$ (ns)</th>
<th>$\varepsilon_{\text{max}}$ (10$^3$ M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>99</td>
<td>0.077 ± 0.004</td>
<td>4.25 ± 0.02$^c$</td>
<td>39.00 ± 0.07$^f$</td>
</tr>
<tr>
<td>114</td>
<td>0.057 ± 0.003</td>
<td>6.22 ± 0.02$^d$</td>
<td>21.80 ± 0.05$^g$</td>
</tr>
<tr>
<td>221</td>
<td>0.015 ± 0.003</td>
<td>0.85 ± 0.05$^e$</td>
<td>16.50 ± 0.05$^h$</td>
</tr>
</tbody>
</table>

a) Standard 2.5 N H$_2$SO$_4$ solutions with 20% CH$_3$CN (v/v) as co-solvent.
b) $\Phi_i$’s measured relative to quinine bisulfate ($\Phi_i = 0.55$ in 1 N bH$_2$SO$_4$)$^{127}$.
c) $\lambda_{\text{ex}}$ 372 nm/$\lambda_{\text{em}}$ 520 nm. d) $\lambda_{\text{ex}}$ 370 nm/$\lambda_{\text{em}}$ 540 nm. e) $\lambda_{\text{ex}}$ 385 nm/$\lambda_{\text{em}}$ 580 nm.
f) At $\lambda_{\text{max}} = 374$ nm. g) At $\lambda_{\text{max}} = 375$ nm. h) At $\lambda_{\text{max}} = 384$ nm.

The fluorescence of 9-phenylxanthenium cation (99) and xanthenium cation (114) in 8:2 H$_2$SO$_4$-CH$_3$CN were found to be easily quenched by di- and trimethoxybenzenes. This was evident in terms of both progressive decrease in steady-state emission intensity and gradual shortening of observed lifetimes. A representative case of steady-state fluorescence quenching of emission of 99 by added 1,3-DMB is shown in Figure 4.2. Figure 4.3 shows the effect of added benzonitrile on the emission of 99.
Figure 4.2 Fluorescence quenching of cation 99 by added 1,3-DMB in 8:2 1.25 M H\textsubscript{2}SO\textsubscript{4}-CH\textsubscript{3}CN solution (\(\lambda_{ex} = 375\) nm).

Figure 4.3 Fluorescence quenching of cation 99 by added benzonitrile in 8:2 1.25 M H\textsubscript{2}SO\textsubscript{4}-CH\textsubscript{3}CN solution (\(\lambda_{ex} = 375\) nm). Note the lack of any significant quenching using the same concentration of benzonitrile as 1,3-DMB used in Fig. 4.2.
The quenching rate constants from steady-state fluorescence quenching ($k_{q8}$) and lifetime quenching ($k_{q8}^*$) were calculated by standard Stern-Volmer analyses of the quenching process and are presented in Table 4.3. The good agreement seen between the two rate constants (steady-state and lifetimes) signifies that the quenching is a dynamic process, and that the fluorescence quenching observed is not due to some ground state complexation of the cation and the quencher. Moreover, no ground state complexation between carbocations and the quencher(s) was indicated in the absorption spectra of the carbocations in the presence of the quenchers at the highest concentrations used.

Previous studies have shown that the fluorescence of cations 99, 114 and

<table>
<thead>
<tr>
<th>Quencher</th>
<th>Steady-State</th>
<th>Lifetimes</th>
<th>Steady-State</th>
<th>Lifetimes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,2-DMB</td>
<td>$7.0 \times 10^9$</td>
<td>$1.4 \times 10^{10}$</td>
<td>$6.3 \times 10^9$</td>
<td>$6.18 \times 10^9$</td>
</tr>
<tr>
<td>1,3-DMB</td>
<td>$5.0 \times 10^9$</td>
<td>$4.9 \times 10^9$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,4-DMB</td>
<td>-</td>
<td>$1.4 \times 10^{10}$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,3,5-TMB</td>
<td>$7.9 \times 10^9$</td>
<td>$7.8 \times 10^9$</td>
<td>$7.3 \times 10^9$</td>
<td>$7.12 \times 10^9$</td>
</tr>
</tbody>
</table>

a) Calculated by standard Stern-Volmer analysis of quenching.
b) Errors in $k_q$'s are ± 10% of the quoted values.
c) Measured by single photon counting.
220 is readily quenched by aromatics (e.g., benzene) by predominantly electron-
transfer mechanism in which the excited carbocations act as electron
acceptors. The products derived from electron transfer, viz., radical cations
(from aromatic quenchers) and radicals (from carbocations) have also been
observed in nanosecond laser flash photolysis studies. The thermodynamics of
photochemical electron transfer are governed by the Rhem-Weller equation (eq
4.12). Using eq 4.12, the electron transfer from variety of substituted benzenes

\[ \Delta G_{\text{ET}} = -E_r - E_{\text{red}_{1/2}} \text{(carbocation)} + E_{\text{ox}_{1/2}} \text{(donor)} \]  

\[ (4.12) \]

to these cations has been shown to be an exothermic process. For example, the
free energy of electron transfer (\( \Delta G_{\text{ET}} \)) from anthracene \((E_{1/2} = 0.84 \text{ V})\) to \(S_1\) of 99
\((E_{1/2} = -0.374 \text{ V}; \text{in sulfolane/3-methylsulfolane vs silver/silver nitrate; glassy}
\text{carbon electrode})\) has been calculated to be -32 kcal/mol. Although the \(E_{1/2}\)
values of the various quenchers (e.g., 1,2- and 1,3-DMB) used in this work are not
known, the results of steady-state emission quenching and product studies
strongly indicate that di- and trimethoxybenzenes quench \(S_1\) of carbocations via
electron transfer with rates indicated by the fluorescence quenching rates \(k_q\)'s).
Laser flash photolysis studies of electron transfer from aromatic donors to 99 have
revealed that the yield of such electron transfer as a result of \(S_1\) quenching is very
small ca. \(0.02\). These low yields suggest that the back electron transfer in the
photogenerated singlet radical-ion/radical pairs is predominant over their
dissociation. This small yield of electron transfer also explains the low yield for loss (Φe) of 99 obtained in the product studies.

4.1.4 Mechanism of Formation of Peroxy Products

A mechanism for the reaction of 99 in the presence of electron donor 1,3-DMB is shown in Scheme 4.1. Electron transfer from 1,3-DMB gives the radical 113/1,3-DMB radical ion pair, most of which reverts back to regenerate 99 (and 1,3-DMB) via back electron transfer. In the presence of 2-propanol (2-PrOH), reduction of 113 to give 133 is the only observed reaction in competition with the back electron transfer. In the absence of 2-PrOH, 113 reacts with the residual
oxygen in the solution to generate 218. Alternatively, dimerization of radical 113 gives bis(9-phenylxanthen-9-yl) (222), which is unstable and known to react with oxygen to give 218. The possibility that the initial precipitate observed on the photolysis of 99 is in fact 222 (or an isomer), which upon subsequent crystallization and contact with air gives 218 has not been ruled out. There is literature precedent to indicate that this pathway is plausible. In fact, it has been reported that bis(9-phenylfluoren-9-yl) dimer (223) slowly absorbs oxygen to give the corresponding peroxide. In any event, results of this study clearly indicate that 9-phenylxanthenyl radical (113) is the primary intermediate formed on photolysis of 99 in the presence of an electron donor.

In the case of reaction of 114, a similar mechanistic scheme applies. However, there is an important subtle difference: dimer 128 is formed and more significantly, 128 is not a precursor to peroxide 217 as indicated by an independent photolysis of 128. This implies that 217 is formed via reaction of the free radical or the radical/radical ion pair with oxygen. The lack of reactivity of 9-bisxanthene (128) suggests that the photogenerated radical pair from this dimer preferentially undergoes geminate recombination as opposed to reaction with
oxygen or escape out of the solvent cage.

The steady-state fluorescence quenching of 220 by 1,3 DMB ($k_q = (1.92 \pm 0.04) \times 10^{10} \text{M}^{-1} \text{s}^{-1}$) indicates that the electron transfer to the cation 220 in $S_1$ is thermodynamically allowed and does take place. The observation of 9-phenylthioxanthenyl radical (221) in the LFP of 220 in the presence of other aromatic donors (e.g., benzene, naphthalene) confirms this. However, as indicated by the results obtained in the product studies, further reaction of the radical does not take place to yield any observable product. An efficient back electron transfer in the photogenerated radical/radical ion pair to regenerate 220 seems to be the dominant reaction pathway.

4.2 Adiabatic Photogeneration of Thioxanthenium Cations in Neutral Aqueous Solution

4.2.1 Product Studies

Thioxanthenols 226-229 and 219 were prepared from the corresponding commercially available ketones 224 and 225 (Aldrich), by NaBH₄ reduction or by reaction with the appropriate Grignard reagent. The alcohols were purified by recrystallization from warm (~ 35 °C) hexanes/ether. The $^1$H NMR spectra were all consistent with their assigned structures. The alcohols slowly decomposed via
a disproportionation pathway, to give the corresponding thioxanthone 224 (or 225), and the corresponding 9,9'-disubstituted (with R) thioxanthene. This decomposition pathway was most significant when R = H and CH₃ (i.e., alcohols 226, 227, and 228). The purified alcohols were used as soon as possible after recrystallization or stored in the cold under an inert atmosphere. Because these alcohols also decomposed on the GC column (via the same pathway described above), purity checks were carried out by high field (250 MHz) ¹H NMR. The absence of characteristics peaks of 224 and 225 at δ 8.7 (peri protons on the ring) was used as an indication of alcohol purity.

Photodehydroxylation of the thioxanthenols was carried out in aqueous MeOH (typically 50% (v/v) MeOH-H₂O; pH 7) and 100% MeOH solutions. On
photolysis many of these alcohols were converted to their corresponding methyl ethers, thus the overall process is photosolvolysis. The methyl ethers thus produced were themselves photochemically reactive, producing secondary photoproducts, particularly at higher conversions.

4.2.1.1 Photolysis of Thioxanthen-9-ol (226) in Aqueous Methanol

Photolysis of 226 in 50% H₂O-CH₂OH (pH 7) at 254 nm resulted in the formation of corresponding methyl ether 230 (≈40%) (eq 4.13), as indicated by

\[
\text{hv (254 nm)} \quad \frac{50\% \text{MeOH-H₂O}}{5 \text{ min}} \quad 226 \rightarrow 230
\]

the characteristic methoxy resonance at δ 3.2 in 'H NMR spectra of the reaction mixture. The formation of methyl ether 230 in the photosolvolysis of 226 is consistent with the intermediacy of carbocation 231. However, the yield of methyl ether 230 is only a lower limit of the yield of carbocation formation, because a certain portion of carbocation is trapped by H₂O and therefore
regenerates the starting material. Previous studies have shown that the photodehydroxylation of aryl and diaryl alcohols is catalyzed by acids.\textsuperscript{87,88,90,96} In the case of photodehydroxylation of 226 it was not possible to address the question acid catalysis because of efficient thermal dehydroxylation of 226 even in mildly acidic solutions (ca. pH 6).

4.2.1.2 Photolysis of 226 with External Nucleophiles

In order to substantiate the intermediate 9-thioxanthenium cation 231, attempts were made to trap it using nucleophiles other than solvent (MeOH). Previous studies in our laboratory have shown that cyanide ion (0.25 M NaCN in aqueous CH\textsubscript{3}CN) is capable of trapping the incipient cation generated in the photolysis of 2,6-dimethoxybenzyl alcohols.\textsuperscript{88} Thus, photolysis of 226 in 50% CH\textsubscript{3}CN-H\textsubscript{2}O (0.2 M NaCN) for 10 min resulted in the formation of two trapping products, 9-cyanothioxanthene (232) (=30%), and a ring substituted cyanothioxanthene 233 (=10%) (eq 4.14).
4.2.1.3 Photolysis of Alcohols 227, 228, 229 and 219 in Aqueous Methanol

Photolysis of alcohols 227, 228 and 219 in 50% MeOH-H\textsubscript{2}O (pH 7) also resulted in the formation of the corresponding methyl ethers (yields 25-35%) as indicated by the \textsuperscript{1}H NMR spectra of the reaction mixtures (eq 4.15). However, a

\begin{equation}
\text{hv (254 nm)} \quad 50\% \text{ MeOH-H}_2\text{O} \\
\quad 5 \text{ min}
\end{equation}

\begin{align*}
228 & \quad R = \text{CH}_3 \\
219 & \quad R = \text{Ph}
\end{align*}

similar photolysis of 229 gave only a trace of methyl ether, the major product being alkene 234 (=20%) (eq 4.16). The alkene 234 is believed to arise by the loss

\begin{equation}
\text{hv (254 nm)} \quad 50\% \text{ MeOH-H}_2\text{O} \\
\quad 5 \text{ min}
\end{equation}

\begin{align*}
229 & \\
234 & \quad \text{Ph}
\end{align*}

of proton from the intermediate cation via a formal E1 elimination.

4.2.2 Steady-State and Transient Fluorescence Studies

Fluorescence emission spectra of alcohols 219 and 226-229 recorded in dry
CH$_3$CN gave only emission from the corresponding alcohols ($\lambda_{\text{max}} = 340$-$350$ nm), with no longer wavelength emitting species. A representative fluorescence excitation and emission spectra of 226 in CH$_3$CN (dry) is shown in Figure 4.4.

![Fluorescence excitation and emission spectra of 226 in CH$_3$CN.](image)

**Figure 4.4** Fluorescence excitation and emission spectra of 226 in CH$_3$CN.

However, emission spectra recorded in aqueous solutions (100% H$_2$O; pH 7 buffer), showed two additional bands at 450 and 550 nm. The relative intensity of these two new emission bands depended on the nature of the alkyl group in alcohols 226-229. Figure 4.5 shows such an emission spectrum for 226 ($\lambda_{\text{em}} = 250$ nm). The emission band at 450 nm was identified to be due to ketone 224, by comparison with its authentic emission. The excitation spectrum of 450 nm band
resembled the absorption spectrum of the ketone 224 indicating that it arises from the trace quantities of 224 present in the sample and it is not generated via excitation of the alcohol precursor. The ketone 224 is believed to be formed thermally via a disproportionation pathway described above, which takes place to some extent upon dissolution of alcohol in aqueous solutions.

The emission band at 550 nm had the same excitation spectrum as the emission at 340 nm and was identical in appearance to the authentic emission of thioxanthenium cation 231 (generated in 10% H$_2$SO$_4$). Therefore, this band at 550 nm was assigned to adiabatically generated 231 (Scheme 4.2). There is essentially
no cation present in the ground state at pH 7. To further confirm this, excitation of the sample at 375 or 450 nm (where only the cation absorbs strongly) gave no detectable emission peaks. Similar observations were made for alcohols 227-229 and 219. However, in the cases of alcohols 229 and 219 much less emission was observed from the ketone 224. These two compounds also gave the weakest emission due to the corresponding adiabatically generated cations. Figure 4.6 shows the excitation and emission spectra of 219 recorded in aqueous solution (pH 7 buffer).
Figure 4.6 Fluorescence excitation and emission spectra of 219 in pH 7 buffer (inset x 50).

Figure 4.7 presents a generalized look at the potential energy surfaces for the adiabatic photodehydroxylation of thioxanthenols. These energy surfaces give

Figure 4.7 Generalized excited state potential energy surface, relative to the ground state, for the adiabatic photodehydroxylation of thioxanthenols (e.g., 226) in H₂O.
us a clue regarding the nature of the excited state energy surface in relation to the ground state energy surface for photodehydroxylation process. Since the photogenerated thioxanthenium cations exhibit fluorescence emission the energy minimum for excited cation (R*) must be nearly or directly situated above the energy minimum for R* of the ground state surface.

The relative emission intensities of 345 nm and 550 nm bands were affected by use of H$_2$O/D$_2$O. For the 345 nm emission (due to alcohol 226), the ratios of emission intensities in H$_2$O vs D$_2$O ((\(\Phi^H_\text{345}/\Phi^D_\text{345}\)) was 0.82 ± 0.06. For the 550 nm emission (due to cation 231) an inverted ration ((\(\Phi^H_\text{550}/\Phi^D_\text{550}\)) = 1.38 ± 0.04) was observed. Both of these experiments were carried out in 100% L$_2$O (L = H and D) at a pH of 7.0 ± 0.2), without any added buffer. These isotope effects are consistent with a reaction mechanism involving product-determining proton transfer from the solvent to the incipient leaving hydroxide ion of photoexcited 226, to give thioxanthenium cation 231. It also suggests that the protonation of excited 226 is irreversible. That is, since the rate of photodehydroxylation is greater in H$_2$O than in D$_2$O (due to primary solvent isotope effect), a proportionately larger amount of cation 231 is formed in H$_2$O than in D$_2$O, thus resulting in the observed decrease in fluorescence emission intensity relative to D$_2$O at 345 nm (due to photoexcited 226). Because the rate of reaction is faster in H$_2$O, (\(\Phi^H_\text{550}/\Phi^D_\text{550}\)) = 1.38 ± 0.04 is found for the 550 nm emission of the carbocation 231. Furthermore, this latter observation supports the photodehydroxylation mechanism involving product determining proton transfer from the solvent (H$_2$O).
in the primary step of the reaction. Catalysis of photodehydroxylation process by added hydronium ions could not be tested because 226 (and other alcohols as well) ionizes in the ground state even in solutions of moderate acidity (pH 6.0).

Adiabatic reactions of large organic molecules are in general not common. Concerted or stepwise structural isomerization reactions are known to take place adiabatically. However, adiabatic photoreactions involving heterolytic bond cleavages are not common. The most common adiabatic reactions are simple excited state proton transfer reactions. The first example of adiabatic photodehydroxylation was shown in the case of 9-phenylxanthenol (98). It has been shown that 9-phenylxanthenol (98) undergoes adiabatic photodehydroxylation in aqueous solution to give 9-phenylxanthenium cation (99) in S1. Laser flash photolysis of this reaction confirm that the primary photochemical step in this reaction is the loss of the hydroxide ion. However, it was also noted that only a small fraction (= 1%) of the photodehydroxylation occurs adiabatically.

Fluorescence quantum yields (Φf's) of the adiabatically generated thioxanthenium cations in H2O (pH 7 buffer) were measured using quinine bisulphate as a secondary standard and are presented in Table 4.4. Corrected fluorescence spectra of thioxanthenols and quinine bisulfate were utilized for the measurement of Φf's. These fluorescence quantum yields are the lower limits for
Table 4.4 Photophysical Parameters of Adiabatically Photogenerated Thioxanthenium Cations.*

<table>
<thead>
<tr>
<th>Alcohol</th>
<th>$\lambda_{\text{max}}$ (emission)</th>
<th>$\Phi_i^b$</th>
<th>$\tau^c$ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>226</td>
<td>549 nm</td>
<td>0.038 ± 0.004</td>
<td>21.20 ± 0.04</td>
</tr>
<tr>
<td>227</td>
<td>549 nm</td>
<td>0.014 ± 0.002</td>
<td>16.40 ± 0.04</td>
</tr>
<tr>
<td>228</td>
<td>555 nm</td>
<td>0.035 ± 0.002</td>
<td>18.70 ± 0.05</td>
</tr>
<tr>
<td>229</td>
<td>550 nm</td>
<td>0.0015 ± 0.0004</td>
<td>=0.3</td>
</tr>
<tr>
<td>220</td>
<td>555 nm</td>
<td>0.0014 ± 0.0004</td>
<td>0.80 ± 0.04</td>
</tr>
</tbody>
</table>

a) In wholly aqueous solutions (pH 7 phosphate buffers); $\lambda_{\text{ex}} = 250$ nm.

b) Measured relative to quinine bisulfate ($\Phi_i = 0.546$ in 0.05 M H$_2$SO$_4$)$^{177}$.

c) Measured via single photon counting; $\lambda_{\text{ex}} = 260$ nm.

The quantum yield of the adiabatic step for each substrate. For example, substrate 226 reacts via the adiabatic pathway with at least 0.038 quantum efficiency. This is in contrast to the results obtained for 9-phenylxanthenol (98) which reacts with about 1% efficiency via the same pathway.$^{93,95}$ Also presented in Table 4.4 are the fluorescence lifetimes ($\tau$'s) in H$_2$O of adiabatically generated thioxanthenium cations. Unlike adiabatically photogenerated xanthenium cations, all of the thioxanthenium cations have lifetimes that were measurable using single photon counting (H$_2$ lamp). The parent (226) and methyl substituted (228) alcohols exhibited the highest adiabatic fluorescence emissions, with significant quantum yields. Phenyl or benzyl groups, 219 and 229, lower the emission quantum yields and lifetimes, probably due to enhanced internal conversion rates due to the
bulkier groups at the 9-position.

The possible factor responsible for the enhanced adiabatic fluorescence emission yields (Φ's) of the thioxanthenols systems is that the corresponding excited state thioxanthenium cations are less prone to the nucleophilic attack by water, and hence are not deactivated as readily as the xanthenol systems. Boyd and coworkers have shown that the fluorescence lifetimes of xanthenium cations are very sensitive to the presence of H₂O in acid solutions, indicating that they are probably efficiently quenched by nucleophilic attack by H₂O. To test the proposal that the present thioxanthenium cation excited singlet states are less prone to nucleophilic attack by H₂O, fluorescence lifetimes of 231 were measured in a range of acidities (Table 4.5). Interestingly, the lifetime (τ = 21.25 ns) of

<table>
<thead>
<tr>
<th>Solvent</th>
<th>τ (ns)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O (pH 7 buffer)</td>
<td>21.25 ± 0.04</td>
</tr>
<tr>
<td>10% H₂SO₄</td>
<td>22.07 ± 0.04</td>
</tr>
<tr>
<td>20% H₂SO₄</td>
<td>22.12 ± 0.04</td>
</tr>
<tr>
<td>30% H₂SO₄</td>
<td>22.61 ± 0.05</td>
</tr>
<tr>
<td>CF₃CH₂OH</td>
<td>28.42 ± 0.05</td>
</tr>
</tbody>
</table>

a) Measured by single photon counting.
b) Adiabatically generated; λₑx 250 nm/λₑm 540 nm.

adiabatically photogenerated cation 231 in pH 7 is not very different from the
lifetimes ($\tau \pm 1\) ns) of cation 231 generated thermally in 10-30% $\text{H}_2\text{SO}_4$
solutions. In the $\text{H}_2\text{SO}_4$ solutions, the lifetimes were measured by direct excitation
of the cation 231 at 375 nm. In the highly ionizing medium 100% $\text{CF}_3\text{CH}_2\text{OH}$, the
lifetime of adiabatically generated 231 was 28.42 ns. Thus it is clear from the
lifetimes (Table 4.4) that the excited state of 231 is not prone to quenching by
$\text{H}_2\text{O}$. For the same reasons the adiabatically photogenerated thioxanthenium
cations exhibit relatively strong emissions (high $\Phi_r$'s) in $\text{H}_2\text{O}$ (pH 7 buffer).

Though the emission from photogenerated thioxanthenium cations is not
greatly affected by $\text{H}_2\text{O}$, interestingly, addition of MeOH quenched the
fluorescence emission when added to the aqueous samples. Stern-Volmer
analysis of fluorescence quenching of adiabatically generated 231 by MeOH gave

\begin{table}
\begin{tabular}{|c|c|}
\hline
$[\text{NaN}_3]$, M & \\
\hline
1 & $6.6 \times 10^{-1}$ \\
2 & 13 \\
3 & 19 \\
4 & 76 \\
5 & 33 \\
6 & 39 \\
\hline
\end{tabular}
\end{table}

\begin{figure}
\centering
\includegraphics{figure4.8.png}
\caption{Quenching of adiabatically photogenerated cation 231 by $\text{NaN}_3$ in pH 7 buffer ($\lambda_{ex} = 270$ nm; 20\% (v/v) $\text{CH}_2\text{CN}$ used as co-solvent).}
\end{figure}
rate constant $k_q = (4.10 \pm 0.07) \times 10^7$ M$^{-1}$ s$^{-1}$, suggesting that MeOH is more nucleophilic towards 231 in H$_2$O than water itself. Addition of other nucleophiles, viz., N$_3^-$ and 'CN also quenched the emission of cation 231 in H$_2$O. Figure 4.8 shows the fluorescence emission quenching of adiabatically photogenerated 231 in H$_2$O by added N$_3^-$ . Note that the emission due to ketone 224 (450 nm) is not significantly quenched. Quenching rate constants ($k_q$'s) for 231 by N$_3^-$ and 'CN were obtained by standard Stern-Volmer analyses of quenching processes and are collected in Table 4.6.

Table 4.6 Fluorescence Quenching Rate Constants ($k_q$'s) for Adiabatically Photogenerated Thioxanthenium Cation (231) in Water (pH 7 buffer).

<table>
<thead>
<tr>
<th>Quencher</th>
<th>$k_q$ M$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>MeOH$^b$</td>
<td>$4.10 \pm 0.07 \times 10^7$</td>
</tr>
<tr>
<td>'CN$^c$</td>
<td>$1.34 \pm 0.05 \times 10^9$</td>
</tr>
<tr>
<td>N$_3^-$</td>
<td>$1.47 \pm 0.05 \times 10^{10}$</td>
</tr>
</tbody>
</table>

a) Rate constants ($k_q$'s) obtained by standard Stern-Volmer analysis of quenching.
b) $k_q$ obtained by lifetimes ($\tau$) quenching of cation 231 by added MeOH.

The possibility that the observed quenching is due to initial electron transfer from nucleophile to the excited state carbocation needs to be addressed. It has been shown earlier that excited state of xanthenium and thioxanthenium cations act as very good electron acceptors in the presence of variety of
Donors. Direct evidence for an electron transfer mechanism would be isolation of radical coupling products such as 9,9'-bis(thioxanthene), which were not observed in this study. Furthermore, attempts to trap any photogenerated 9-thioxantheny1 radical with 2-propanol were of no avail. Thus, if any electron transfer mechanism was operative, the subsequent coupling of the geminate radicals pairs is very fast. In such a case, it would be mechanistically indistinguishable from simple direct nucleophilic attack, at least with the probes at our disposal.
CHAPTER FIVE

SUMMARY AND CONCLUSIONS

In photoreactions of a series of structurally related dibenzannelated systems, it was demonstrated that the driving force inherent in many of their reactions is the attainment of an 4n π-electron system or intermediate in $S_1$. For example, in the photolysis of 9H-xanthene (125) and 9H-thioxanthene (136) in basic solution, it was demonstrated that the driving force for the C-H bond cleavage in $S_1$ was the formation of 8π-electron cyclically conjugated carbanions 130 and 137, respectively. Intermediacy of carbanions in these reaction was demonstrated by deuterium incorporation in photoproducts when these compound were irradiated in deuterated solvents. Additional support for the C-H bond cleavage in $S_1$ was provided by the fluorescence studies of these molecules. Fluorescence quenching of 125 in CH$_3$CN by added ethanolamine gave a linear Stern-Volmer plot, with $k_q = (2.52 \pm 0.04) \times 10^7$ M$^{-1}$ s$^{-1}$. The calculated $k_q$ was equated to the rate by which ethanolamine deactivates $S_1$ of 125 via C-H bond ionization. Consistent with this, the fluorescence quenching rates ($k_q's$) of 125 and 123 by ethanolamine in CH$_3$CN showed a substantial kinetic isotope effect. A systematic quenching study of 135 was not possible because of its very weak fluorescence. The 9-phenyl analogue 139 did not exhibit excited state C-H bond ionization, possibly because of the presence of phenyl group which prevents the C-H bond ionization by the base.

The enhanced stability of 8π-electron carbanions was further evident in the
efficient photodecarboxylation of diarylacetic acids 142, 145, 147 and 148. Photolysis of these acids in aqueous solution led to the photogeneration of the corresponding carbanion intermediates. The involvement of carbanions in these reactions was demonstrated by deuterium incorporation experiments. Fluorescence behaviour of the diarylacetic acids showed considerable solvent and pH dependency, which is consistent with reaction via the carboxylate ion. Interestingly, the presence of a 9-phenyl group in 145 and 148 had no significant effect on the reactivity of these acids, and they decarboxylated with the same facility as the parent acids.

Additional support for the excited state stability of 4n systems came from the studies of 155. The steady-state fluorescence studies of 155 demonstrated that photoexcitation of bent 155 results in the change of its conformation to give planar 155 in S1. The driving force for the planarization of 155 in S1 was shown to be the attainment of a 8π-electron internal cyclic array.

Product studies of 140 showed that it does not exhibit excited state C-H bond ionization even though it is isoelectronic to 125 and 136. However, it was shown that photolysis of 140 in aqueous solution results in its dimerization, to give 141. The mechanism of this process was investigated in detail by laser flash photolysis studies and was shown to involve one-electron ionization of 140 in S1, to form radical cation 140+. The major pathway for the reaction of photogenerated 140+ was shown to be deprotonation of one of the benzylic protons, to generate radical 140, which subsequently dimerizes to give 141.
The question of structure-reactivity in the excited state carbon acid behaviour of suberene (37) was also addressed. Results obtained in the photolysis of substituted suberene derivatives showed that the efficiency of C-H bond cleavage in S₁ was greatly affected by the nature of the substituent present in the molecule. The results of these studies were consistent with the involvement of carbanions in the C-H bond ionization in S₁. The methoxy groups in 180 retarded the C-H bond ionization in S₁, whereas the cyano substituted 189 was shown to react more efficiently than the parent suberene (37). These differences in reactivities of 180 and 189 compared to 37 were correlated to the differences in the relative stabilities of the photogenerated carbanion intermediates 204 and 209 vs 35 in S₁. It was also shown that the highly annelated molecules 193 and 197 exhibit reduced carbon acid behaviour in S₁, because of the lower stability (due to non-planarity) of the photogenerated carbanion intermediates.

In the study of 9-phenylxanthenium (99) and xanthenium (114) cations it was shown that S₁ of these cations acts as an excellent electron acceptor from di- and trimethoxybenzenes. The kinetics of electron transfer to excited 99 and 114 was followed by steady-state fluorescence quenching of 99 and 114 in aqueous H₂SO₄ solution by added di- and trimethoxybenzenes. It was also shown that the radical intermediates formed in these reactions undergo an irreversible reaction with dissolved oxygen to give isolable peroxides, viz., 217 and 218 respectively.

Lastly it was shown that thioxanthenols undergo efficient adiabatic photodehydroxylation in aqueous solution to give thioxanthenium carbocations
in the $S_1$ state. The adiabaticity of this process was demonstrated by the steady-state fluorescence studies. A lower limit of 5% adiabatic efficiency was observed for the more reactive derivatives, although it is believed that the carbocation is still generated predominantly via a diabatic step. The adiabatically generated thioxanthenium cations exhibited substantially higher emission yields than the corresponding xanthenium cations. This is believed to be due to the low reactivity of the excited thioxanthenium cations with water, as demonstrated by the lack of fluorescence quenching by water.
6.1 Instrumentation

'H NMR spectra were recorded on a Perkin-Elmer R32 (90 MHz), Bruker WM-250 (250 MHz), or Bruker AMX (360 MHz) instrument in CDCl₃ unless otherwise noted. Tetramethylsilane was used as an internal standard in the recording of 90 MHz spectra. UV spectra were recorded on a Perkin-Elmer Lambda 4B or a Pye-Unicam 800 spectrophotometer. IR spectra were recorded on a Perkin-Elmer 283 instrument. Mass spectra were obtained on a Finnigan 3300 instrument. High resolution mass spectra (HRMS) were recorded on a Kratos Concept 1H instrument. Melting points were determined on a Koefler hot stage microscope and are uncorrected. Gas chromatography was performed on a Varian 3700 instrument with a Hewlett Packard 3390A integrator. Measurements of pHs were carried out on a Coming pH meter 140. Photolyses were carried out in Suprasil quartz cuvettes or 100/200/600 ml quartz tubes using a Rayonet RPR 100 photochemical reactor (254, 300, or 350 nm lamps). An Oriel 200 W Hg light source and an Applied Photophysics monochromator on an optical bench were employed in the quantum yield determinations. Fluorescence lifetimes were measured using time correlated single photon counting on a Photon Technology International (PTI) LS-1 instrument in lifetime mode.
6.2 Common Laboratory Reagents

Dichloromethane (Van Waters and Rogers Ltd.) was distilled before use. Other solvents (A.C.S. reagent grade) were used in reactions, for extraction or for column chromatography without further purification. Deuterated solvents used for NMR spectroscopy were CDCl₃ (Aldrich gold label) and acetone-d₆ (MSD Isotopes). The D₂O used for solvent isotope studies, preparatory photolysis and NMR spectroscopy was 99.9% D (MSD Isotopes). Standard buffer solutions (Fisher Scientific), were used for product quantum yield experiments and fluorescence spectrophotometry work. Solvents for fluorescence studies were of the highest available purity and checked for spurious emission before use.

6.3 Materials

The following compounds were purchased from Aldrich Chemical Co. for use in synthetic preparations: benzosuberone (198); m-methylanisole; 1,2-dimethoxy benzene (1,2-DMB); 1,3-dimethoxybenzene (1,3-DMB); 1,4-dimethoxy benzene (1,4-DMB); 1,3,5-trimethoxybenzene (1,3,5-TMB); benzonitrile; 9-xanthone (144); 9-phenylxanthen-9-ol (98); thioxanth-9-one (224); xanthene-9-ol (216); xanthene-9-carboxylic acid (142); trans-10,11-dibromodibenzosuberone (182); N-methylacridone; N-methylacridinium iodide (172); iminostilbine (170). The following compounds were used as secondary standards for fluorescence quantum yield experiments: quinine bisulfate (recrystallized); biphenvlether (recrystallized); dibenzofuran; fluorene (36); and suberene (37; recrystallized).
6.3.1 9D-Xanthene (123)

To a stirred suspension of LiAlD₄ (0.047 g; 1.3 mmol) in diethyl ether (200 mL; dry) at -4 °C, AlCl₃ (0.35 g; 2.6 mmol) was slowly added under an inert atmosphere. The mixture was stirred for 10 min at 0 °C and then 9-xanthone (144) (0.2 g; 0.7 mmol) was introduced into the cold reaction mixture. The reaction mixture was allowed to attain the room temperature and then refluxed for 12 hours. At the end of reflux, the reaction was cooled in an ice bath and carefully quenched with water (100 mL) followed by the addition of sufficient amount of 10% HCl solution to dissolve the suspension. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 100 mL). The combined organic layers were dried over anhydrous MgSO₄ and CH₂Cl₂ removed to yield 0.18 g of the crude 123 as a white solid (yield > 95%), which was purified by recrystallization from 95% EtOH/H₂O; mp 102-104 °C; ¹H NMR (90 MHz, CDCl₃) δ 7.10-7.50 (m, 8H, arom.); mass spectrum (Cl) (m/z) 185 (M⁺+1).

6.3.2 9D,9H-Xanthene (124)

Treatment of xanthen-9-ol (216) with LiAlD₄/AlCl₃ in dry THF afforded a white solid which was purified by recrystallization from EtOH/H₂O to obtain pure 124; mp 103 °C; ¹H NMR (250 MHz, CDCl₃) δ 4.05 (t, 1H, J = 1.6 Hz, Ar₂CHD), 7.0-7.4 (m, 8H, arom.); mass spectrum (Cl) (m/z) 184 (M⁺+1).
6.3.3 9H-Xanthene (125)

Treatment of 9-xanthone (144) (0.4 g; 0.14 mmol) with LiAlH₄ (0.094 g; 2.6 mmol)/AlCl₃ (0.70 g; 5.2 mmol) in dry THF (200 ml) at -4 °C in a manner described earlier afforded 9H-xanthene (125) as a white solid (yield > 95%), which was purified by recrystallization from EtOH/H₂O; mp 100-101 °C [lit.¹⁶⁸ mp 100.5 °C]; ¹H NMR (90 MHz, CDCl₃) δ 4.0 (s, 2H, ArCH₂Ar), 7.10-7.50 (m, 8H, arom.); mass spectrum (Cl) (m/z) 183 (M⁺+1).

6.3.4 9-Phenyl-9H-xanthene (132)

A solution of commercially available 9-phenylxanthen-9-ol (98) in dry THF on treatment with LiAlD₄/AlCl₃, in a manner described earlier, afforded crude 132 as a white solid (yield > 95%), which was purified by recrystallization from 95% EtOH/H₂O; mp 144-145 °C; ¹H NMR (90 MHz, CDCl₃) 6.95-7.30 (m, 13H, arom.); mass spectrum (El) (m/z) 259 (M⁺).

6.3.5 9-Phenyl-9H-xanthene (133)

Treatment of 9-phenylxanthen-9-ol (98) with LiAlH₄/AlCl₃ in dry THF in usual manner afforded crude 147 which was purified by recrystallization from EtOH/H₂O to obtain 147 as a white crystalline solid (yield > 95%); mp 144 °C [lit.¹⁶⁹ mp 145 °C]; ¹H NMR (90 MHz, CDCl₃) δ 5.25 (s, 1H, ArCH), 6.95-7.30 (m, 13H, arom.); mass spectrum (El) (m/z) 258 (M⁺+1).
6.3.6 9D-Thioxanthene (134)

Treatment of 9-thioxanthone (224) with LiAlD₄/AlCl₃ in dry THF afforded 134 as a white solid (yield > 93%), which was purified by recrystallization from EtOH/H₂O; mp 147-148 °C; 'H NMR (90 MHz, CDCl₃) δ 7.10-7.50 (m, 8H, arom.); mass spectrum (Cl) (m/z) 201 (M⁺+1).

6.3.7 9D,9H-Thioxanthene (135)

Treatment of thioxanthen-9-ol (226) with LiAlH₄/AlCl₃ in dry THF afforded 135 which was further purified by recrystallization from EtOH/H₂O; mp 146 °C; 'H NMR (250 MHz, CDCl₃) δ 3.82 (t, 1H, J = 2 Hz, Ar₂CHD), 7.1-7.5 (m, 8H, arom.); mass spectrum (Cl) (m/z) 200 (M⁺+1).

6.3.8 9H-Thioxanthene (136)

Treatment of 9-thioxanthone (224) with LiAlH₄/AlCl₃ in dry THF in the procedure described earlier afforded a white solid (yield > 90%), which was purified by recrystallization from EtOH/H₂O; mp 127-128 °C [lit.¹⁷⁰ mp 128 °C]; 'H NMR (90 MHz, CDCl₃) δ 3.85 (s, 2H, ArCH₂Ar), 7.10-7.50 (m, 8H, arom.); mass spectrum (Cl) (m/z) 199 (M⁺+1).

6.3.9 9-Phenylthioxanthene-9-ol (219)

To the stirred solution of 9-thioxanthone (224) (1.0 g, 4.72 mmol) in dry THF (125 mL) at 0 °C, 2.0 M solution of PhLi (2.5 M, 5.0 mmol; Aldrich) was
introduced slowly with the aid of a syringe. The reaction mixture was stirred at room temperature for 12 hours and then carefully quenched with water. The organic layer was separated out and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 75 mL). The combined organic layers were washed with water (3 x 75 mL), dried over MgSO$_4$ and CH$_2$Cl$_2$ removed to afford a pale yellow solid which was recrystallized from warm hexane/ether mixture to give 219 as a white crystalline solid; mp 107 °C [lit. $^{19}$ mp 109 °C]; $^1$H NMR (90 MHz, CDCl$_3$) δ 2.30 (s, 1H, -OH), 6.90-7.50 (m, 11H, arom.), 7.90-8.10 (m, 2H, peri arom. Hs); mass spectrum (Cl) (m/z) 291 (M$^+$+1).

6.3.10 9-Phenyl-9D-thioxanthene (138)

Treatment of 9-phenylthioxanthen-9-ol (219) (2.0 g, 6.9 mmol) with LiAlD$_4$/AlCl$_3$ in dry THF (175 mL) in a manner described earlier afforded a white solid (1.8 g; yield > 93%), which was purified by recrystallization from EtOH/H$_2$O to obtain 138 as a white crystalline solid; mp 100-101 °C; $^1$H NMR (90 MHz, CDCl$_3$) 7.90-7.55 (m, 13H, arom.); mass spectrum (Cl) (m/z) 276 (M$^+$+1).

6.3.11 9-Phenyl-9H-thioxanthene (139)

Treatment of 9-phenylthioxanthen-9-ol (98) (2.0 g, 6.9 mmol) in usual manner with LiAlH$_4$/AlCl$_3$ in dry THF yielded 150 as a white solid (1.8 g; yield > 93%), which was purified by recrystallization from EtOH/H$_2$O; mp 99-100 °C [lit.$^{17}$ mp 99 °C]; $^1$H NMR (90 MHz, CDCl$_3$) δ 5.25 (s, 1H, Ar$_3$CH), 6.90-7.55 (m,
6.3.12 9-Phenylxanthen-9-carboxylic Acid (145)

To a stirred solution of 9-phenyl-9H-xanthene (147) (2.0 g, 7.76 mmol) in dry THF at -100 °C (diethyl ether/dry ice), a solution of n-BuLi (2 M, 8 mL, 16 mmol) was slowly added under an inert atmosphere. The colour of the reaction mixture turned to dark brown immediately after the addition of n-BuLi. The reaction mixture was allowed to warm up to the room temperature (ca. 22-25 °C) and refluxed for an additional 4 hours. The reaction mixture was cooled down to -100 °C and a stream of dry CO₂ gas was bubbled into it for approximately 1 hour. The reaction was warmed up to the room temperature and refluxed with continuous bubbling of CO₂ gas for another 5 hours. The reaction was cooled down in an ice bath and carefully quenched by adding a 15% HCl solution (200 mL). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 100 mL). The organic layers were combined and extracted with a 1 M NaOH solution (5 x 50 mL). Careful neutralization of the combined base extract with conc. HCl solution (= 10 M) afforded a white precipitate. The precipitate was filtered out and recrystallized from 95% EtOH to yield 145 as a white crystalline solid (1.2 g; yield 55%); mp 168-169 °C; ¹H NMR (90 MHz, acetone-ｄ₆) δ 5.35 (s, 1H, -CO₂H), 7.0-7.40 (m, 13H, arom.); IR (KBr, cm⁻¹) ν 3450 (broad, O-H str.), 1690 (strong, C=O str.), 1266 (strong, C-O str.); mass spectrum (Cl) (m/z) 303 (M⁺+1); HRMS (El) 302.3321 (calc. 302.3323).
6.3.13 9H-Thioxanthen-9-carboxylic Acid (147)

Treatment of 9H-thioxanthene (136) (2.0 g; 10 mmol) in dry THF (175 mL) with n-BuLi (2 M, 7 mL, 14 mmol) and CO₂, in a manner described earlier, yielded crude 148 as a white solid (1.64 g; yield > 65%). The crude material was purified by recrystallization from 95% EtOH to afford 147 as a white crystalline material; mp 224-226 °C [lit. 180 mp 227 °C]; ¹H NMR (90 MHz, acetone-d₆) δ 5.10 (s, 1H, Ar-CH), 5.20 (s, 1H, -CO₂H), 7.20-7.60 (m, 8H, arom.); IR (KBr, cm⁻¹) v 3400-3200 (broad, O-H str.), 1698 (strong, C=O str.), 1254 (strong, C-O str.); mass spectrum (Cl) (m/z) 243 (M⁺+1).

6.3.14 n-Phenylthioxanthen-9-carboxylic Acid (148)

Treatment of 9-phenyl-9H-thioxanthene (139) (3.0 g, 10.1 mmol) in dry THF (200 mL) with n-BuLi (2 M, 7 mL, 14 mmol) and CO₂(g), in a manner described earlier, afforded crude 149 as a light pink solid (1.75 g, yield > 50%), which on recrystallization from 95% EtOH yielded pure 149 as a white crystalline solid; mp 162 ± 1 °C; ¹H NMR (90 MHz, acetone-d₆) δ 4.85 (s, 1H, -CO₂H), 6.95-7.60 (m, 13H, arom.); IR (KBr, cm⁻¹) v 3400-3200 (broad, O-H str.), 1698 (strong, C=O str.), 1260 (strong, C-O str.); mass spectrum (Cl) (m/z) 319 (M⁺+1); HRMS 318.3967 (calc. 318.3969).

6.3.15 Xanthene-9-methanol (154)

To a stirred solution of xanthene-9-carboxylic acid (142; Aldrich) (5.0 g,
22.12 mmol) in dry THF (250 mL) at 0 °C, LiAlH₄ (0.84 g, 22.0 mmol) was slowly added under an inert atmosphere. The reaction was warmed up to the room temperature and refluxed for 12 hours. At the end of reflux, the reaction was quenched with cold saturated NH₄Cl solution and the organic layer was separated out. The aqueous layer was extracted with CH₂Cl₂ (3 x 75 mL) and the combined organic layers were washed with water, dried over MgSO₄ and solvent removed on a rotary evaporator to afford a yellow coloured oil, which on trituration with cold hexanes gave a white solid. The crude product was recrystallized from hexanes to yield 154 as a white crystalline material (3.5 g; yield = 75%); ¹H NMR (90 MHz, CDCl₃) δ 1.52 (s, 1H, -OH), 3.6 (d, 2H, J = 2.7 Hz, -CH₂-), 4.0 (t, 1H, J = 2.7 Hz, Ar₂CH-), 6.95-7.40 (m, 8H, arom.).

6.3.16 Dibenz[b,fl]oxepin (155)¹³⁰

To a stirred solution of 154 (4.0 g, 19.0 mmol) in benzene (200 mL), P₂Os (30 g, 22.0 mmol) was slowly added and the reaction mixture was boiled under reflux for 15 minutes. The reaction mixture was cooled and filtered through a sintered funnel and the residual solid washed with benzene (2 x 20 mL). The combined benzene extracts were washed with saturated brine solution, dried over MgSO₄ and benzene removed to afford a white solid (3.0 g; yield = 85%), which upon recrystallization from 95% EtOH gave 155 as a white crystalline solid; mp 107-108 °C [lit.¹³⁰ mp 107 °C]; ¹H NMR (90 MHz, CDCl₃) δ 6.65 (s, 2H, -CH=CH-), 7.0-7.32 (m, 8H, arom.); mass spectrum (EI) (m/z) 194 (M⁺).
6.3.17 10,11-Dihydrodibenzo[b,f]oxepin (156)

A mixture of 155 (2.0 g, 10.21 mmol) and 5% palladium-on-charcoal (0.30 g) in 100 mL ethyl acetate was hydrogenated at 25 psi H₂ pressure. When the hydrogen uptake was complete, the solution was filtered and solvent removed to afford a colorless oil (1.8 g; yield = 89%). Distillation under reduce pressure gave 156 as colourless viscous oil (Caution: this material is extremely light sensitive; store in a cool dark place); ¹H NMR (90 MHz, CDCl₃) δ 3.1 (s, 4H, -CH₂CH₂-), 7.0-7.3 (m, 8H, arom.) [lit. ¹H NMR δ 3.1 (s, 4H, -CH₂CH₂-), 7.0-7.3 (m, 8H, arom.); mass spectrum (EI) (m/z) 196 (M⁺)].

6.3.18 10-Hydroxy-10,11-dihydrodibenzo[b,f]oxepin (157)

To a cold stirred solution of 155 (1.5 g, 7.73 mmol) in THF (dry; 100 mL) at ~ -4 °C (dry ice/acetone), a solution of BH₃-THF (2.5 M) was slowly added (ca. 30 min) under an inert atmosphere. The reaction was allowed to stir for an additional 15 minutes at -4 °C and then warmed to room temperature and refluxed for 4 hours. At the end of reflux the reaction mixture was cooled to -4 °C and 100 mL of water was added dropwise into it (CAUTION: some foaming occurs at this stage which could be avoided by changing the rate of addition of water). The reaction was stirred for 15 minutes and then 40 mL of 30% H₂O₂ followed by 40 mL of 3 M NaOH solution was introduced into the reaction mixture.¹³¹ The reaction was stirred for another 3 hours at 30-40 °C and then quenched by pouring it over crushed ice (500 g). The organic layer was separated out and the
aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 50 mL). The combined organic layers were washed with water, dried over MgSO$_4$ and CH$_2$Cl$_2$ removed to afford a pale yellow oil (yield ≥ 90%), which on distillation under reduced pressure yielded 157 as a colourless viscous oil; $^1$H NMR (90 MHz, CDCl$_3$) δ 2.0-2.2 (s, 1H, OH), 3.3 (q, J = 6Hz; 2H, -CH$_2$-), 5.03 (dd, J = 2 Hz, 1H, -CH-), 6.9-7.5 (m, 8H, arom.); mass spectrum (Cl) (m/z) 213 (M$^+$+1).

6.3.19 10-Hydroxysuberane (10-Hydroxydibenz[a,d]cycloheptene) (158)

Treatment of a solution of suberene (37) in dry THF with a solution of BH$_3$-THF, followed by addition of 30% H$_2$O$_2$ and 3 M NaOH solutions, in a manner described earlier, yielded a colorless oil (yield = 90%), which on purification by column chromatography (neutral alumina, CH$_2$Cl$_2$) gave 158 as a colourless viscous oil; $^1$H NMR (90 MHz, CDCl$_3$) δ 3.65 (m, 2H, -CH$_2$-), 2.65 (s, 1H, -OH), 4.05 (q, J = 10 Hz; 2H, Ar$_2$CH$_2$), 5.0-5.2 (m, 1H, -CH-), 7.1-7.6 (m, 8H, arom.); mass spectrum (Cl) (m/z) 211 (M$^+$+1).

6.3.20 Thioxanthene-9-methanol (159)

To a stirred solution of 9H-thioxanthene-9-carboxylic acid (148) (1.0 g 4.2 mmol) in 150 mL dry THF at 0 °C, a cold solution of BH$_3$-THF was slowly added under an inert atmosphere. The reaction mixture was refluxed for 18 hours and then quenched with water. The organic layer was separated out and the aqueous layer was extracted with CH$_2$Cl$_2$ (2 x 75 mL). The combined organic layers were
washed with water, dried over MgSO₄, and removed to afford a white solid (yield ~ 80%), which on recrystallization from hexanes gave 159 as a white crystalline solid; ¹H NMR (90 MHz, CDCl₃) δ 1.75 (s, 1H, -OH), 3.7 (d, 2H, J = 2.7 Hz, -CH₂-), 4.2 (t, 1H, J = 2.7 Hz, Ar₂CH-), 7.1-7.5 (m, 8H, arom.); mass spectrum (Cl) (m/z) 229 (M⁺+1).

6.3.21 Dibenzo[b,j]thiepin (160)

Treatment of 159 in benzene with P₂O₅, in a manner described earlier, yielded a white solid (yield 90%), which upon recrystallization from hexanes afforded 160 as a white crystalline material; mp 76 °C [lit. mp 73-75 °C]; ¹H NMR (90 MHz, CDCl₃) δ 7.0 (s, 2H, -CH=CH-), 7.2-7.6 (m, 8H, arom.); mass spectrum (EI) (m/z) 210 (M⁺).

6.3.22 Dibenzocyclooctatetraene (163)¹³²

A mechanically stirred mixture of ortho-xylylene bis(triphenylphosphonium bromide) (162) (18.1 g, 23 mmol) and ortho-phthaldehyde (161) (3.0 g, 22 mmol) in 400 mL of dry DMF was heated to 90 °C under an atmosphere of N₂. A solution of lithium ethoxide (59 mmol) in 100 mL absolute ethanol was added to the reaction mixture with rapid stirring over a period of 30 hours. Addition of the base gave a deep orange solution which persisted for 20 hours. After the addition of base was complete, the reaction mixture was diluted with 500 mL water. A precipitate came out of the solution which was separated by decantation. The precipitated material was extracted with diethyl ether (5 x
50 mL) and the ethereal extracts were washed with water, dried over MgSO₄ and removed to obtain a dark brown oil. The oil was extracted with boiling petroleum ether to effect separation of triphenylphosphine oxide. Evaporation of petroleum ether gave ~5.0 g of an orange coloured oil which was chromatographed on a silica gel column (2.5 cm diameter, 20 cm long, first 10 fractions 25 mL each). Elution with petroleum ether gave 1.0 g of a pale yellow oil which was again chromatographed on silica gel column (1.0 cm diameter, 40 cm long) using petroleum ether. The first six fractions were collected and the solvent was removed to afford 163 as a white solid (yield ~ 1%); mp 107-108 °C [lit.¹³² 106.8-108.1 °C]; 'H NMR (250 MHz, CDCl₃) δ 6.74 (s, 4H, -CH=CH-), 7.03 (m, 4H, arom), 7.12 (m, 4H, arom.) [lit.¹³³ δ 6.74 (s, 4H, -CH=CH-), 7.03 (m, 4H, arom.), 7.12 (m, 4H, arom.)]; mass spectrum (Cl) (m/z) 205 (M⁺+1).

6.3.23 N-methylacridan (140)¹⁴⁰

To a stirred solution of N-methylacridinium iodide (4 g, 12.5 mmol) in 150 mL 2-propanol, NaBH₄ (0.5 g, 15.0 mmol) was added at room temperature. The reaction was refluxed for 6 hours and worked up by pouring into a dilute NaHCO₃ solution (200 mL) to obtain a white precipitate (yield ≥ 90%), which was recrystallized from 95% EtOH to afford 140 as white crystalline solid; mp 93-94 °C [lit.¹⁴⁰ mp 94 °C]; 'H NMR (90 MHz, CDCl₃) δ 3.3 (s, 3H, N-CH₃), 3.85 (s, 2H, Ar₂CH₂), 6.75-7.3 (m, 8H, arom.); mass spectrum (Cl) (m/z) 196 (M⁺+1).
6.3.24 *m*-Bromomethyl-\(p\)-bromoanisole (176)\textsuperscript{174}

A mixture of \(m\)-methylanisole (15 g, 122.95 mmol) and \(N\)-bromosuccinimide (13.3 g, 75.59 mmol) in 50 mL \(\text{CCl}_4\) was stirred under reflux for 24 hours. The mixture was cooled, filtered and \(\text{CCl}_4\) was removed to yield crude \(p\)-bromo-\(m\)-methylanisole\textsuperscript{174} as a red coloured oil which was taken to the next step without further purification (yield 23 g, 93%).

Treatment of \(p\)-bromo-\(m\)-methylanisole (20 g, 99.50 mmol), with \(N\)-bromosuccinimide (20.2 g, 114.77 mmol) and benzoyl peroxide (0.20 g) in refluxing \(\text{CCl}_4\) (ca. 20 hours), yielded crude 176 as a reddish brown solid. Recrystallization of crude material from boiling petroleum ether (30-60°) yielded pure 176 as yellow needle shaped crystals (yield 15 g, 54%); mp 91 °C [lit.\textsuperscript{174} mp 91-92 °C]; \(^1\text{H NMR} (90 \text{ MHz, CDCl}_3)\delta 7.5 - 6.6\ (\text{m, 3 H, arom.}); 4.52\ (s, 2\ H, \text{Ar-CH}_2); 3.74\ (s, 3\ H, \text{-OCH}_3)\)

6.3.25 2,8-Diethoxydibenzosuberone (178)\textsuperscript{149}

\(\text{m}\)-Bromomethyl-\(p\)-bromoanisole (14 g, 50 mmol) was dissolved in dry THF (325.0 mL) and hexane (100 mL, dry) in a 1 L two necked flask and was cooled to -100° (\(\text{CO}_2\)-\(\text{Et}_2\text{O}\) slurry). \(n\)-BuLi (50 mmol) was added at such a rate that the temperature of the reaction mixture did not rise above -99°. After 1 hour at -100°, a stream of \(\text{CO}_2\) gas was bubbled through the reaction mixture for 1.5 hours at -100° to -80°. After this, the cooling bath was removed and the temperature was allowed to rise to 25° (approx. 2 h). A stream of argon was bubbled through the
reaction mixture for -1.5 hours to get rid of the excess of CO\textsubscript{2}. The reaction mixture was again cooled to -100° and n-BuLi (30 mmol, 30% excess) added into it at such a rate that the temperature never exceeded -98°. The reaction mixture was stirred for 30 min at -100°, then allowed to warm to 25°, and stirred for 6 hours at 25°. The reaction was quenched by pouring into 5% HCl solution and the organic layer was separated and the aqueous layer was extracted with CH\textsubscript{2}Cl\textsubscript{2} (3 x 150 mL). The combined organic layers were washed with 5% NaOH (w/w) solution and dried over anhydrous MgSO\textsubscript{4}. Removal of CH\textsubscript{2}Cl\textsubscript{2} yielded 2.0g of the crude product which upon recrystallization from CH\textsubscript{2}Cl\textsubscript{2}/MeOH (1:1) afforded slightly yellow needle like crystals of 178 (yield 1.3g); mp 121 °C (lit.\textsuperscript{14} mp 119-121 °C); \textsuperscript{1}H NMR (CDCl\textsubscript{3}) δ 3.12 (s, 4H, -CH\textsubscript{2}.CH\textsubscript{2}.); 3.85 (s, 6H, -OCH\textsubscript{3}); 6.60- 8.20 (m, 6H, arom.).

6.3.26 2,8-Dimethoxydibenzosuberenone (179)

A mixture of 2,8-dimethoxydibenzosuberone (178) (1.3 g, 4.80 mmol), N-bromosuccinimide (0.87 g, 5.0 mmol) and benzoyl peroxide (0.1 g) in CCl\textsubscript{4} (50 mL) were stirred with reflux for 36 hours. The reaction mixture was cooled to room temperature and filtered through a sintered funnel and filtrate washed with water (2 x 100 mL). The combined organic layers were dried over anhydrous MgSO\textsubscript{4} and CCl\textsubscript{4} removed to afford 1 g of the crude product. This crude product was analyzed to be a mixture of 10,11-dibromo-2,8-dimethoxydibenzosuberone and 10,10'-dibromo-2,8-dimethoxydibenzosuberenone by \textsuperscript{1}H 90 MHz NMR. The
mixture was separated by competitive recrystallization from 95% EtOH/ H₂O (1:1). The dibromo compound crystallized out first as long yellow crystals and were filtered out. On further cooling of the filtrate white crystals of 10,10'-dibromo-2,8-dimethoxydibenzosuberone came out of the solution.

The dibromo compounds (0.4 g) were dissolved in 15 mL of 2,4,6-trimethylpyridine (collidine) and refluxed for 24 hours. The reaction mixture was cooled in an ice bath and quenched with an excess of 20% HCl and extracted with CH₂Cl₂ (2 x 100 mL). The combined CH₂Cl₂ layers were washed with water (2 x 50 mL), dried over anhydrous MgSO₄ and removed to yield 0.25g of 180; mp 119-121 °C; ¹H NMR (90 MHz, CDCl₃) δ 3.75 (s, 6H, -OCH₃); 6.90 (s, 2H, -CH=CH-); 6.8-7.25 (m, 6H, arom.); IR (KBr, cm⁻¹) v 1690 (strong, C=O stretch), 1645 (medium, vinylic C=C stretch), 1600 and 1460 (medium, arom. C=C stretch); mass spectrum (EI) (m/z) 266 (M⁺).

6.3.27 2,8-Dimethoxydibenzosuberene (180)

To a stirred suspension of LiAlH₄ (0.047 g; 1.3 mmol) in diethyl ether (200 mL; dry) at -4 °C, AlCl₃ (0.35 g; 2.6 mmol) was slowly added under an inert atmosphere. The mixture was allowed to stir for additional 10 min at 0 °C and then 17⁹ (0.2 g; 0.7 mmol) was introduced into it. The reaction mixture was allowed to attain the room temperature and refluxed for 4 hours. At the end of reflux the reaction was cooled in an ice bath and carefully quenched by addition of water (~ 75 mL), followed by the addition of a sufficient amount of 10% HCl...
to dissolve the suspension. The organic layer was separated and the aqueous
layer was extracted with CH₂Cl₂ (2 x 100 mL). The combined organic layers were
washed with water, dried over anhydrous MgSO₄, and CH₂Cl₂ removed to yield
0.18g of the crude product. Recrystallization of crude material from 50% EtOH/
H₂O afforded 0.17g of pure 180 as white crystalline solid; mp 185-187 °C; ¹H NMR
(90 MHz; CDCl₃) δ 3.75 (s, 6H, -OCH₃), 3.60 (s, 2H, Ar·CH₂·Ar), 6.90 (s, 2H, -
CH=CH-); 6.8-7.25 (m, 6H, arom.); mass spectrum (El) (m/z) 252 (M⁺); HRMS
252.3153 (calc. 252.3154).

6.3.28 5-Deuterio-2,8-Dimethoxydibenzosuberone (181)

Treatment of 179 with LiAlD₄/AlCl₃ in dry THF afforded 181, which was
purified by recrystallization from EtOH/H₂O to give pure 181 as a white
crystalline solid (yield > 93%); mp 188-189 °C; ¹H NMR (90 MHz; CDCl₃) δ 3.75
(s, 6H, -OCH₃), 6.90 (s, 2H, -CH=CH-), 6.80-7.25 (m, 6H, arom.); mass spectrum
(El) (m/z) 254 (M⁺);

6.3.29 10-Bromodibenzo[a,e]cyclohepten-5-one (183)

trans-10,11-dibromodibenzo[a,e]cyclohepten-5-one (182) (5 g, 13.6 mmol;
Aldrich) was dissolved in a 3 M methanolic solution of KOH (22.25 g KOH in
125.0 ml CH₃OH) and refluxed with stirring for one hour (Caution: only one hour!
longer reflux results in much lower yields) to give a yellow coloured solution. The
hot reaction mixture was filtered through a sintered funnel (to remove the
precipitated KBr) and the filtrate cooled in an ice bath for 2 hours to afford crude 183. The crude product was recrystallized from warm hexanes to yield 10-
bromodibenz[a,e]cyclohepten-5-one (183) as pale yellow crystalline solid (yield
80%); mp 116-117 °C [lit.\textsuperscript{152} 117 °C]; \textsuperscript{1}H NMR (90 MHz, CDCl\textsubscript{3}) δ 7.8 (s, ArCH=CB=), 7.0-7.7 (m, 8H, arom.); mass spectrum (Cl) (m/z) 286 (M\textsuperscript{+}+1).

6.3.30 10-Methoxydibenz[a,e]cyclohepten-5-one (184)

A mixture of 10-bromodibenz[a,e]cyclohepten-5-one (183) in a methanolic
solution of KOH (3 M, 250 mL) was refluxed with stirring for 16 hours. At the
end of reflux the reaction mixture was allowed to stand at 0 °C for 24 hours to
afford yellow crystals of 184; mp 132 °C; \textsuperscript{1}H NMR (90 MHz, CDCl\textsubscript{3}) δ 3.9 (s, 3H, -OCH\textsubscript{3}), 6.4 (s, 1H, -CH=), 7.4-8.2 (m, 8H, arom.); mass spectrum (Cl) (m/z) 237 (M\textsuperscript{+}+1).

6.3.31 10-Methoxysuberene (10-Methoxy-5H-dibenz[a,i']cycloheptene) (185)

Reduction of 184 with LiAlH\textsubscript{4}/AlCl\textsubscript{3} in dry THF, in a manner described
earlier, yielded 185 which was purified by recrystallization from hexanes to afford
pure 185 as a white crystalline solid; mp 146 °C; \textsuperscript{1}H NMR (90 MHz, CDCl\textsubscript{3}) δ 3.9 (s, 3H, -OCH\textsubscript{3}), 3.7 (s, 2H, ArCH\textsubscript{2}Ar), 6.3 (s, 1H, -CH=C-), 7.2-7.8 (m, 8H, arom.); mass spectrum (Cl) (m/z) 223 (M\textsuperscript{+}+1).
6.3.32 10-Methoxy-5D-suberene (10-Methoxy-5D-dibenz[a,e]cycloheptene) (186)

Reduction of 184 with LiAlD₄/AlCl₃ in dry THF, in a usual manner, yielded crude 186 which was purified by recrystallization from hexanes to afford pure 186 as white crystalline solid; mp 147 °C; ¹H NMR (90 MHz, CDCl₃) δ 3.9 (s, 3H, -OCH₃), 6.3 (s, 1H, -CH=CR-), 7.2-7.8 (m, 8H, arom.); mass spectrum (Cl) (m/z) 225 (M⁺+1).

6.3.33 10-Bromo-5H-suberene (10-Bromo-5H-dibenz[a,e]cycloheptene) (187)

Reduction of 10-bromosuberone (183) with LiAlH₄/AlCl₃ in dry THF afforded 187 which was purified by column chromatography (silica gel, hexanes) and recrystallized from 95% EtOH to afford 187 as white crystalline solid; mp 62 °C; ¹H NMR (90 MHz, CDCl₃) δ 3.70 (s, 2H, ArCH₂Ar), 7.10-7.35 (m, 7H, arom.), 7.65 (s, 1H, -CH=CBr-), 7.70-7.85 (m, 1H, ArH next to Br); mass spectrum (El) (m/z) 271 (M⁺); (Cl) (m/z) 272 (M⁺+1).

6.3.34 10-Bromo-5D-suberene (10-Bromo-5D-dibenz[a,e]cycloheptene) (188)

Reduction of 10-bromodibenzosuberone (183) with LiAlD₄/AlCl₃ in dry THF afforded crude 188 which was purified by column chromatography (silica gel, hexanes) and recrystallized from 95% EtOH to give pure 188 as white solid; mp 55-58 °C; ¹H NMR (90 MHz, CDCl₃) δ 7.10-7.35 (m, 7H, arom.), 7.65 (s, 1H, -CH=CBr-), 7.70-7.80 (m, 1H, ArH closest to Br); mass spectrum (Cl) (m/z) 274 (M⁺+1).
6.3.35 10-Cyano-5H-suberene (10-Cyano-5H-dibenzo[1,e]cycloheptene) (189)

A stirred mixture of 10-bromosuberene (187) (0.2 mmol) and CuCN (0.4 g, 6 mmol) were dissolved in 1-methyl-2-pyrrolidinone (100 mL) and refluxed for 36 hours at 180 °C. The reaction mixture was cooled to 100 °C and poured into a 1:1 NH₃/H₂O solution (300 mL) and stirred at room temperature for 12 hours. The solution was then filtered through a celite pad, and the filtrate was extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were dried over MgSO₄ and evaporated to yield a yellow oil. The oil was dissolved in 1:2 Et₂O/H₂O (500 mL) mixture and stirred overnight at room temperature. The ether layer was separated, dried and removed to yield the crude 189 which on purification by column chromatography (silica gel, CH₂Cl₂) afforded pure 189 as a white solid; mp 97-99 °C; ¹H NMR (90 MHz, CDCl₃) δ 3.80 (s, 2H, ArCH₂Ar), 7.10-7.75 (m, 8H, arom.), 7.80 (s, -CH=C-); IR (KBr, cm⁻¹) ν 2220 (medium, CN str.), 1606 (strong, vinyl C=C str.), 1480 (medium, arom. C=C str.); mass spectrum (Cl) (m/z) 218 (M⁺+1); HRMS 217.2723 (calc. 217.2724).

6.3.36 10-Cyano-5D-suberene (10-Cyano-5D-dibenzo[1,e]cycloheptene) (190)

Treatment of 10-bromo-5D-dibenzo:uberene (188) with CuCN in 1-methyl-2-pyrrolidinone, afforded 190 as white solid which was purified by column chromatography (silica gel; CH₂Cl₂); mp 98-100 °C; ¹H NMR (90 MHz, CDCl₃) δ 7.10-7.75 (m, 8H, arom.), 7.80 (s, -CH=C-); mass spectrum (Cl) (m/z) 220 (M⁺+1).
6.3.37 10,13-Epoxy-10,13-dihydro-tribenzo[a,c,e]cyclohepten-5-one (191){152}

To a stirred mixture of 10-bromodibenz[a,c]cyclohepten-5-one (183) (3.8 g, 13.33 mmol) and potassium t-butoxide (3 g, 13.33 mmol) in THF (150 ml, dry) at 0 °C, freshly distilled furan (50 mL) was added under an inert atmosphere. The reaction mixture immediately turned to a brick-red colour. The reaction was allowed to stir at room temperature for additional 18 hours after which it was poured over an ice cold solution of 10% HCl. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (4 x 75 mL). The combined organic layers were washed with water, dried over MgSO₄ and the solvent was removed to yield a yellow coloured solid. The crude material was recrystallized from petroleum ether (40-60 °C) to yield 191 as yellow coloured prism like crystals (yield 2.86 g, 79%); mp 205-206 °C [lit.152 mp 203-207 °C]; ¹H NMR (90 MHz, CDCl₃) δ 6.0 (s, 2H, -CH=CH-), 7.35 (s, 2H, -CH-O-CH-), 7.42-8.25 (m, 8H, arom.); mass spectrum (Cl) (m/z) 273 (M+ +1).

6.3.38 Tribenzosuberone (Tribenzo[a,c,e]cyclohepten-5-one) (192)

To a stirred solution of 191 (1.5 g, 5.86 mmol) in benzene (70 mL), Fe₂(CO)₉ (9.0 mmol) was added and the mixture was refluxed for 4 hours. The reaction was cooled and filtered through a celite pad. The filtrate was washed with brine solution (2 x 50 mL), dried over MgSO₄ and benzene was evaporated to yield a pale yellow solid which on recrystallization from hexanes afforded 192 as yellow crystalline solid; mp 175-176 °C [lit.152 mp 176.5-177.5 °C]; ¹H NMR (90 MHz,
CDCl$_3$ δ 7.32-7.80 (m, 12 H, arom.); mass spectrum (Cl) (m/z) 257 (M$^+$+1); (EI) (m/z) 228 (M$^+$).

6.3.39 Tribenzosuberene (5H-Tribenzo[a,c,e]cycloheptene) (193)

To a stirred suspension of LiAlH$_4$ (0.06 g; 1.5 mmol) in THF (dry; 150 mL) at -4 °C (CO$_2$/acetone), AlCl$_3$ (0.4 g, 3.0 mmol) was slowly added under an inert atmosphere. Tribenzosuberone (192) (1.0 g, 4.4 mmol) was introduced into the reaction mixture at -4 °C and the reaction was allowed to warm up to the room temperature and refluxed for 5 days. The reaction was carefully quenched with an ice cold 5% HCl solution and the aqueous layer was extracted with CH$_2$Cl$_2$ (4 x 50 mL). The combined organic layers were washed with water (2 x 100 mL), dried over MgSO$_4$ and solvent evaporated to yield a white solid. The crude solid was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to afford pure 193 which on recrystallization from EtOH gave 193 as a white crystalline solid; mp 107-108 °C [lit.$^{76}$ mp 105-115 °C]; $^1$H NMR (90 MHz, CDCl$_3$) δ 3.65 (s, 2 H, ArCH$_2$Ar), 7.1-7.8 (m, 12 H, arom.); mass spectrum (Cl) (m/z) 243 (M$^+$+1); (EI) (m/z) 242 (M$^+$).

6.3.40 5D-Tribenzosuberene (5D-Tribenzo[a,c,e]cycloheptene) (194)

Reduction of 192 with LiAlD$_4$/AlCl$_3$ in dry THF (7 days) afforded crude 194 which was purified by column chromatography (silica gel, CH$_2$Cl$_2$) to obtain pure 194 as a white solid; mp 108 °C; $^1$H NMR (90 MHz, CDCl$_3$) δ 7.1-7.8 (m, 12 H, arom.)
H, arom.); mass spectrum (Cl) (m/z) 245 (M^+1); (El) (m/z) 244 (M^+).

5.3.41 Furo-[3,4d]dibenzo[b,f]suberone (195)

To a well stirred solution of adduct 191 (0.5 g, 1.84 mmol) in CHCl₃ (70 mL), an equivalent amount of 3,6-di(pyridin-2'-yl)-s-tetrazine¹⁵⁵ was added at room temperature. The reaction was stirred for 12 hours (22-25 °C) and CHCl₃ removed to obtain a orange coloured crude product. The crude material was purified by column chromatography (silica gel, CH₂Cl₂) to get pure 195 as yellow crystalline solid; mp 153-155 °C; 'H NMR (250 MHz, CDCl₃) δ 7.37-7.63 (m, 6H, arom.), 7.81 (m, 2H, peri arom. Hs), 7.89 (s, 2H, -CH-O-CH-); mass spectrum (Cl) (m/z) 247 (M^+1); HRMS 246.2680 (calc. 246.2680).

6.3.42 8H-Furo[3,4d]dibenzo[b,f]suberene (196)

Reduction of ketone 195 with LiAlH₄/AlCl₃ in THF (dry) in usual manner afforded 196 which was purified by column chromatography (silica gel, CH₂Cl₂); mp 76-77 °C; 'H NMR (250 MHz, CDCl₃) δ 3.86 (s, 2H, ArCH₂Ar), 7.2-7.44 (m, 8H, arom.), 7.76 (s, 2H, -CH-O-CH-); mass spectrum (Cl) (m/z) 233 (M^+1); HRMS 232.2844 (calc. 232.2846).

6.3.43 8D-Furo[3,4d]dibenzo[b,f]suberene (197)

Treatment of ketone 195 with LiAlD₄/AlCl₃ in THF afforded 197 which was purified by column chromatography (Caution: light sensitive!); mp 75-77 °C; 'H
NMR (250 MHz, CDCl₃) 7.2-7.44 (m, 8H, arom.), 7.76 (s, 2H, -CH-O-CH-); mass spectrum (Cl) (m/z) 235 (M⁺+1).

6.3.44 5-Bromobenzosuberone (199)

A well stirred mixture of benzosuberone (198) (10 g, 60.0 mmol), N-bromosuccinimide (12.0 g, 66.0 mmol) and benzoylperoxide (0.025 g) in CCl₄ (200 mL) was refluxed for 8 hours. At the end of reflux the reaction mixture was cooled and filtered through a sintered funnel. The filtrate was washed successively with water (2 x 100 mL) and brine solution (1 x 100 mL) and CCl₄ was evaporated to yield 5-bromo-benzosuberone (199) as a yellow coloured oil, which was taken to the next step without any further purification.

6.3.45 2,3-Benzocyclohepta-2,4-dienone (200)

5-Bromobenzosuberone (199) (12.8 g; 53.0 mmol) was dissolved in 2,4,6-collidine (30 mL) and stirred under reflux for 18 hours. The reaction was cooled and quenched by pouring into ice-cold 5% HCl solution (150 mL) and extracted with CH₂Cl₂ (3 x 75 mL). The combined CH₂Cl₂ layers were washed with 10% HCl (2 x 50 mL), dried over MgSO₄ and CH₂Cl₂ was evaporated to yield crude 200 as a dark red coloured oil. The crude product was distilled under reduced pressure to yield pure 200 (yield > 50%); bp 85-87 °C, 5 mm Hg [lit.¹⁵⁶ bp 83-86 °C; 5 mm Hg].
6.3.46 3,4-Benzotropilidine (201)\(^{156}\)

A mixture of 200 (4.33 g, 27.4 mmol), tosylhydrazide (5.9 g, 32.8 mmol) in methanol (100 mL) in the presence of a catalytic amount of conc. HCl (1.0 mL) was refluxed for 2 hours. The solvent was evaporated to yield a yellow oil which solidified on trituration with Et\(_2\)O. The solid was recrystallized from C\(_2\)H\(_5\)OH-H\(_2\)O to yield the corresponding hydrazone of 200 as yellow crystalline material; mp 155 °C [lit.\(^{156}\) 155-156 °C].

To a stirred solution of the hydrazone (3.0 g) in THF (dry; 150 mL) at 0 °C, CH\(_3\)Li (1.2 M, 20 mL) was slowly added for over 30 minutes under an inert atmosphere. The reaction mixture was allowed to attain the room temperature, and stirred for an additional 1 hour. The reaction was quenched by water and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (3 x 75 mL). The combined organic layers were washed with water (150 mL), dried over MgSO\(_4\) and solvent was removed to yield a dark red oil. The crude oil was distilled under reduced pressure to afford 3,4-benzotropilidine (201) as a colourless oil; \(^1\)H NMR (90 MHz, CDCl\(_3\)) \(\delta\) 2.5 (t, J = 7 Hz, -CH\(_2\)-), 5.85 (dt, J = 10, 7 Hz, ArCH=CHCH\(_2\)-), 6.6 (d, J = 10 Hz, ArCH=), 7.1-7.5 (m, 4 H, arom.); mass spectrum (EI) (m/z) 142 (M\(^+\)).

6.3.47 1,2-Benzotrplidene (202)\(^{157}\)

3,4-Benzotropilidine (201) (0.28 g, 2.0 mmol) was dissolved in a mixture of t-BuOH-t-BuOK\(^+\) and refluxed for 3 hours. The reaction was quenched with water and extracted with CH\(_2\)Cl\(_2\) (3 x 50 mL). The combined organic layers were
washed with 10% HCl solution, dried over MgSO_4 and solvent evaporated to afford 1,2-benzotropolidene (202) as a colorless oil which was further purified by distillation under reduced pressure; ^1H NMR (90 MHz, CDCl_3) δ 3.05 (d, J = 7 Hz, ArCH_2), 5.6-6.2 (m, 2 H, ArCH=CHCH_2), 6.5 (dd, J = 7, 10 Hz, ArCH=CH-), 7.1 (d, J = 10 Hz, ArCH=), 7.1-7.4 (m, 4 H, arom.); mass spectrum (EI) (m/z) 142 (M^+).

6.3.48 Bis(xanthen-9-yl)peroxide (217)

A solution of xanthene-9-ol (216) (1.0 g) in diethyl ether (20 mL), was stirred for 4 hours with 30% hydrogen peroxide (20 mL). Addition of petroleum ether to the reaction mixture gave a precipitate which was recrystallized from a mixture of Et_2O/petroleum ether yielded xanthene hydroperoxide as colorless crystalline solid (mp 122 °C [lit.^{160a} mp 123-124 °C]); ^1H NMR (90 MHz) δ 6.0 (s, 1H, ArCH), 7.1-7.7 (m, 8H, arom.).

A stirred solution of xanthene hydroperoxide (0.5 g), obtained above, in glacial acetic acid (10 mL) was warmed in a water bath to 50 °C for 1 hour. The reaction mixture was poured over crushed ice (50 g) to afford crude 217 as a white solid which was recrystallized from 95% EtOH; mp 152 °C [lit.^{160b} mp 152-153 °C]; ^1H NMR (90 MHz) δ 5.71 (s, 2H, ArCH-O-O-CHAr), 7.0-7.7 (m, 16H, arom.).
6.3.49 Thioxanthen-9-ol (226)

A stirred mixture of thioxanthen-9-one (224) (5.0 g, 23.6 mmol) and NaBH₄ in 2-propanol (200 mL) was refluxed for 5 hours. The reaction was cooled down to room temperature and poured over 500 g of crushed ice and allowed to stand for 30 minutes. A white precipitate was obtained, which was recrystallized from warm hexane/ether to get pure 226; mp 91 °C; ¹H NMR (90 MHz, CDCl₃) δ 2.41 (d, J = 8 Hz, 1H, -OH), 5.48 (d, J = 8 Hz, 1H, ArCH-), 7.2-7.7 (m, 8H, arom.); mass spectrum (Cl) (m/z) 215 (M⁺+1).

6.3.50 2-Chlorothioxanthen-9-ol (227)

A mixture of 2-chlorothioxanthen-9-one (225) (1.0 g, 4.1 mmol) and NaBH₄ (5.0 mmol) in 2-propanol was refluxed for 5 hours and then cooled to room temperature. The cold reaction mixture was poured over 500 g of crushed ice to afford a white precipitate (yield ~ 78%), which was recrystallized from warm hexane/ether to give pure 227; mp 90-91 °C; ¹H NMR (90 MHz, CDCl₃) δ 2.41 (d, J = 8 Hz, 1H, -OH), 5.45 (d, J = 8 Hz, 1H, ArCH-), 7.1-7.7 (m, 7H, arom.); mass spectrum (Cl) (m/z) 249 (M⁺+1).

6.3.51 9-Methylthioxanthen-9-ol (228)

To a cold (0 °C) stirred solution of thioxanthen-9-one (244) (1 g, 4.7 mmol) in THF (dry, 100 mL), CH₃MgCl was slowly (ca. 5 min) introduced with the aid of a syringe. The reaction was allowed to warm to the room temperature and
refluxed for 6 hours. The reaction was cooled and quenched with cold water and aqueous layer extracted with CH₂Cl₂ (2 x 75 mL). The combined CH₂Cl₂ layers were washed with water, dried over MgSO₄, and CH₂Cl₂ removed to afford a pale yellow solid (yield = 65%), which upon recrystallization from warm hexane/ether mixture gave 228 as a white crystalline solid; mp 88 °C; ¹H NMR (90 MHz, CDCl₃) δ 1.52 (s, 3H, -CH₃), 2.35 (s, 1H, -OH), 7.1-7.45 (m, 6H, arom.), 7.8-8.0 (m, 2H, peri Hs); mass spectrum (Cl) (m/z) 227 (M⁺+1).

6.3.52 9-Benzylthioxanthen-9-ol (229)

To a stirred solution of thioxanthen-9-one (224) (3.0 g, 14 mmol) in THF (dry, 150 mL) benzyl magnesium chloride (15.5 mmol) was introduced, with the aid of a syringe, at room temperature. The reaction was refluxed for 12 hours then quenched by pouring into 200 mL of ice cold water. The organic layer was separated out and the aqueous layer extracted with CH₂Cl₂ (3 x 50 mL). The combined organic layers were washed with water, dried, and CH₂Cl₂ removed to afford a white solid (yield ~ 85%), which was recrystallized from hexanes; mp 113 °C; ¹H NMR (90 MHz, CDCl₃) δ 2.5 (s, 1H, -OH), 3.05 (s, 2H, PhCH₂), 6.6-7.7 (m, 13H, arom.); mass spectrum (Cl) (m/z) 305 (M⁺+1).

6.3.53 9-Benzylidienethioxanthene (234)

A solution of 9-benzylthioxanthen-9-ol (0.20 g, 0.66 mmol) dissolved in acetonitrile (50 mL) was treated with an equal volume of 20% (v/v) H₂SO₄ and
stirred at room temperature for 2 hours. The reaction was quenched by pouring into 100 mL water (pH ~ 12) and extracted with CH₂Cl₂ (3 × 50 mL). The organic layers were combined, washed with water, dried, and CH₂Cl₂ removed to afford a white solid (yield ≥ 90%), which was recrystallized from 95% EtOH-H₂O mixture; mp 109 °C; ¹H NMR (90 MHz, CDCl₃) δ 6.9 (s, 1H, Ph-CH=C-), 7.0-7.8 (m, 13H, arom.); mass spectrum (CI) (m/z) 287 (M⁺+1).

6.4 Excited State Carbon Acid Behaviour of 9H-Xanthene (125) and 9H-Thioxanthene (136)

6.4.1 Product Studies

6.4.1.1 Dark Reactions of Xanthenes 123, 125, 133 and thioxanthenes 134, 136 and 138 in Various Solvents

None of the xanthenes (123 and 125) and thioxanthenes (134 and 136) or their 9-phenyl analogues (132 and 138) exhibited any tendency to undergo deuterium/protium exchange thermally (22 ± 2 °C) with the solvent L₂O (L = H or D), under the reaction conditions where their photochemical behaviour was being investigated. Thermally, these compounds did not show any sign of deuterium and/or protium exchange even at higher basicities (ca. up to 6.0 M NaOH and 5.0 M ethanolamine). In preparative scale dark reactions, ~70 mg of substrate was dissolved in an appropriate solvent mixture, viz., 50% (v/v) 1-4 M NaOH-EtOH (175 mL) or in a 1-2 M solution of ethanolamine in CH₃CN, and left stirring in dark for 1-2 hours. The reaction mixture was then worked up in an appropriate manner and samples were analyzed by GC/MS and ¹H NMR.
6.4.1.2 Photolysis of 123/125 and 134/136 in Aqueous Solutions

In a typical preparative scale photolysis ~70 mg of the substrate was dissolved in 75 mL of CH₃CN and diluted by adding 75 mL of H₂O or D₂O to a total volume of 150 mL. The solution was then transferred into a quartz tube equipped with a cooling finger and deaerated with a continuous stream of argon. The solution was then irradiated at 300 nm in a Rayonet RPR 100 photochemical reactor for an appropriate period of time. After photolysis the reaction was worked up by adding a saturated solution of NaCl, and extracting with CH₂Cl₂ (3 x 30 mL). The combined organic layers were washed with water, dried over MgSO₄, and CH₂Cl₂ removed on a rotary evaporator. The photolysate was examined by ¹H NMR (250 MHz) and GC/MS analyses. The photoproducts were identified by comparisons with the ¹H NMR spectra of the authentic materials and conversions to photoproducts calculated by ¹H NMR integration and GC/MS.

Photolysis of 125 and 134 in 50% D₂O-CH₃CN (ca. 60 min) did not result in the formation of deuterium incorporated products as determined by the GC/MS (CI mode) analyses of the reaction mixtures. However, photolysis of 125 (λₓ 300 nm; 60 min) in 50% H₂O-CH₃CN results in its isomerization to yield 126, 127, 128 and 129. These products were identified by comparison with the ¹H NMR spectra of the authentic samples. The GC/MS analysis of the recovered 125 did not show any sign of deuterium incorporation. Photolysis of 135 under similar conditions also did not result in the formation of deuterium exchanged products. No isomerization of 135 takes place under these reaction conditions.
6.4.1.3 Photolysis of 123/125 and 134/136 in Aqueous Ethanol Solutions

Photolysis of 123 and 134 in 50% NaOH-EtOH solution resulted in deuterium incorporation at the benzylic position to yield monodeuterated 124 and 135 respectively. A similar photolysis of 125 and 136 in 50% NaOD-EtOD also resulted in the formation of 124 and 135. The preparative scale photolysis were carried out by dissolving ~75 mg of substrate in 75 mL of 95% EtOL (L = H or D) and diluted by 75 mL of aqueous 1 M NaOL (L = H or D) solution. The solution was then irradiated at 300 nm in a quartz vessel for an appropriate period of time. After photolysis the reaction mixture was worked up by saturating with NaCl and neutralizing it by a careful addition of 10% HCl solution. The aqueous layer was then extracted with CH$_2$Cl$_2$ (3 x 75 mL), and the combined organic layers were washed with saturated brine solution (2 x 50 mL), followed by water and dried over MgSO$_4$. The photolyate was analyzed by $^1$H NMR (250 MHz) and photoproducts identified by comparison with the $^1$H NMR spectra of the authentic samples prepared separately (vide supra). The conversions to exchange photoproducts were determined both by $^1$H NMR integration and GC/MS (Cl mode) analyses. For example, photolysis of 134 in 50% 1 M NaOH-EtOH for 30 min results in the formation of 135 (~18%) and 136 (~7%) as calculated by the integration of $^1$H NMR (250 MHz) spectrum of the photolyate (Figure 2.3). No attempts were made to isolate these photoproducts.
6.4.1.4 Photolyses of 123 and 133 in Solutions of Ethanolamine in CH$_3$CN

Photolyses of 123 and 133 in the presence of ethanolamine in CH$_3$CN also resulted in the formation of exchange products. In general, 75-80 mg of the substrate was dissolved in 175 mL solution of ethanolamine in CH$_3$CN (0.5-2 M concentration) and irradiated in a quartz tube at 300 nm. The reaction mixture, after photolysis, was poured into a flask and cooled in an ice bath, and carefully quenched with 10-15% HCl solution. The aqueous layer was then extracted with CH$_2$Cl$_2$ (3 x 50 mL), and the combined CH$_2$Cl$_2$ layers were washed successively with 5% HCl solution and water, dried over MgSO$_4$, and removed to obtain the product mixture. Photolysis of both 123 and 134 in the presence of ethanolamine in CH$_3$CN resulted in the deuterium incorporation at the benzylic position. The photoproducts (124 and 135) were identified by comparison with the $^1$H NMR spectra of authentic samples. The percentage exchanged product was calculated by $^1$H NMR and GC/MS (CI mode) analyses.

6.4.2 Thermal Generation of 9-Xanthenide Carbanion (130)

The ground state 9-xanthenide carbanion (130) was generated in THF solution by deprotonating 9H-xanthene (125) with excess of n-BuLi under N$_2$. The reaction was slow and required heating to reflux for 10-30 min, which gave a deep orange black solution. That the carbanion was indeed generated was shown by quenching the solution with CO$_2$(g), which gave xanthene-9-carboxylic acid (142) in >75% yield. The absorption spectrum of 130 was obtained by transferring...
a portion (200-500 µL) of the solution to a quartz cuvette containing 2.5 mL of dry THF in a glove bag. The absorption spectrum showed a strong band at $\lambda_{\text{max}} \approx 590$ nm. This band disappears on exposure of the solution to moisture.

6.4.3 Quantum Yields Measurements

Quantum yields ($\Phi$'s) of monodeuterium incorporation in 123, 125, 133, and 136 were measured in a variety of solvent mixtures on an optical bench using an Oriel 200W Hg lamp and an Applied physics monochromator set at $\lambda_{\text{exc}} = 280$ nm with slits of 7.0 nm. Samples were prepared by taking 50 µL of stock solution (= $10^{-4} - 10^{-3}$ M) of substrate and diluting it to 3.90 mL with the appropriate solvent mixture in a suprasil quartz cuvette. The concentration of each substrate in the cuvette solutions were such that they had an absorbance $\geq 2.0$ at the excitation wavelength ($\lambda_{\text{exc}} = 280$ nm). The solutions were purged with a stream of argon for 5 min prior to and during the photolysis (usually 30-45 min). The irradiation time was so adjusted as to keep the conversions to photoproducts between 10-15% in all cases. After irradiation the photolysate was transferred to a test tube, saturated with NaCl, acidified to pH = 7 by adding 5% HCl, and extracted with CH$_2$Cl$_2$ (4 x 5 mL). The organic fractions were combined and washed with H$_2$O (pH = 1; 2 x 10 mL), dried over MgSO$_4$, and evaporated to yield the photolysate. The photolysate was then analyzed by GC/MS (CI mode) to determine the percent deuterium/protium exchanged products formed. For example, photolysis of 134 (1.5 x $10^6$ moles) in 50% i M NaOH-EtOH for 30 min upon work up gave
a mixture whose mass spectrum (CI mode) showed molecular ion peaks at $M^* = 201$ (due to 134), $M^* = 200$ (due to 135) and $M^* = 199$ (due to 136). The percentage 135 (16.8%) formed was calculated from the mass spectrum after correcting for the natural abundance of D and $^{13}$C. Only trace amount of 136 (< 1%) was formed in this photolysis. The percentage conversion to 135 in conjunction with the knowledge of number of moles of starting material used and the intensity of light at 280 nm (vide supra) gave the quantum yield of exchange. Similar method was employed to measure the quantum yields of exchange for 123,125, and 136 in other solvent mixtures.

Since all photolysis were carried out on 3.0 mL of solution, the light intensity in einstein/min was measured before each photolysis by employing potassium ferrioxalate ($K_3Fe(C_2O_4)_3$; PF) actinometry. When solutions of PF in dilute $H_2SO_4$ are irradiated, Fe$^{3+}$ is efficiently reduced to Fe$^{2+}$ with the simultaneous oxidation of oxalate ion. Quantum yields for this reaction range from 1.25 to 0.90 over the wavelength range 250-500 nm. The relatively small dependence of these quantum yields on reactant and product concentration, intensity of the incident light, and temperature makes this a convenient actinometer. The Fe$^{2+}$ is transparent to the incident radiation and is analyzed by forming the highly coloured Fe(phen)$^{2+}$ complex (where phen = 1,10-phenanthroline).

A solution of 0.0060 M PF in 0.05 M $H_2SO_4$ (250 mL) was prepared in the dark along with a 2% by weight solution of 1,10-phenanthroline in distilled water
(to be used later). All subsequent solution transfers were carried out under a red photographic light. To determine the light intensity at 280 nm, 3.0 mL ($V_1$) solution of PF was pipetted into two quartz cuvettes. One of these was then irradiated on the optical bench at 280 nm for the appropriate time ($\Delta t$ was typically 5 min at this wavelength) under a stream of argon purging which served to stir and purge the solution. The other cell was handled under the safelight for the same duration and served as a blank. Both solutions were the worked up as follows: 1.0 mL ($V_2$) of reaction mixture was pipetted from the cuvette into a 10 mL ($V_3$) volumetric flask. To this was added 2.0 mL of a 2% (weight) solution of 1,10-phenanthroline in water and 0.5 mL of a buffer solution (prepared from 41.0 g NaOAc·3H₂O and 5.0 mL H₂SO₄ in 1 L). The volume was adjusted to 10 mL with distilled water and the solutions were mixed and allowed to stand in dark for 30 min. The absorbance of the irradiated and blank solutions was then measured at 510 nm and the difference ($\Delta A$) was used in eq 6.1 to calculate the number of Einsteins of incident light (where $\varepsilon = 1.11 \times 10^4$ M⁻¹ cm⁻¹ and $\Phi(Fe^{2+})$)

$$\text{einstein/min} = \Delta A \frac{V_1}{V_2} \frac{1}{\varepsilon} \Phi(Fe^{2+}) \frac{V_3}{V_2} \Delta t$$

(6.1)

$= 1.25$ at 250 nm). The absorbance of the blank (O.D at 510 nm < 0.05) was used to check the quality of the stock solution of PF with respect to photodecomposition. Using this procedure the average intensity of light at 280 nm (7 nm slit width) was measured to be $4.67 \times 10^7$ einstein/min.
6.4.4 Steady-state Fluorescence and Lifetime Measurements

Steady-state fluorescence spectra (uncorrected, including those used for measuring $\Phi$) were taken in 3.0 mL Suprasil quartz cuvettes at $=10^4$ M using a Perkin Elmer MPF-66 spectrophotometer at ambient temperature. Solutions were purged for 5.0 min with a stream of argon prior to measurements. Lifetimes were measured using a Photon Technology International (PTI) LS-1 instrument with a H$_2$ lamp. All decays were first-order by analysis using software supplied by PTI. Figure 6.1 shows a representative lifetime decay of 125 in 100% CH$_3$CN. The

Figure 6.1 Representative fluorescence lifetime decay curve of 125 in 100% CH$_3$CN, $\tau = 7.59$; $\chi^2 = 1.24$. 
lifetime (τ) was generated by mathematical deconvolution procedure that separates the lamp profile from the sample (125) decay function. The value of χ², was taken as a measure of agreement between the calculated line and experimental data. The weighted residual and autocorrelation functions were also utilized in judging the quality of the calculated curve (in other words τ), and are shown in Figure 6.1.

Fluorescence quantum yields (Φᵣ) were determined by comparing the integrated emission bands of the substrates with those of a secondary standards according to eq 6.2.¹⁷⁷

\[
Φᵣ' = Φᵣ' \left( \frac{Iᵣ'}{Iᵣ} \frac{η₀^{2}}{ηᵣ^{2}} \right)
\]

(6.2)

where \(Iᵣ'\) and \(Iᵣ\) are the total fluorescence intensities of the unknown samples and a standard, \(η\) is the refractive index of the solvent, and \(Φᵣ'\) is the fluorescence quantum yield of the standard. In measuring the fluorescence quantum yields the solutions (O.D. < 0.1) of substrate and standard were absorption matched at the exciting wavelength. Standards were chosen to maximize their spectral overlap with the emission band of the samples. Dibenzofuran was the standard of choice for 9:9'-xanthene (125) whereas suberene (17) provided a better spectral overlap with the emission band for 9H-thioxanthene (136). All solutions were purged with argon for at least 5 min prior to measurements.
6.5 Photodecarboxylation of Xanthene and Thioxanthene Carboxylic Acids in Aqueous Solution

6.5.1 Product Studies

6.5.1.1 Dark Reactions

None of the xanthene- and thioxanthene-9-carboxylic acids studied in this work showed any tendency to decarboxylate thermally under the conditions employed to investigate their photochemistry. In preparative scale dark reactions a solution of ~100 mg of acid was dissolved in 30 mL CH3CN and diluted with 70mL H2O. The pH of the solution was adjusted to pH ≥ 8 by adding a stock solution of 1 M NaOH and using a pH meter. The reaction mixture was then stirred at room temperature (22 ± 3 °C) in dark for one hour. The reaction mixtures were quenched with dilute acid (~ 5% HCl solution) and extracted with CH2Cl2. After removal of solvent, analysis of the reaction mixtures by 1H NMR (90 MHz) did not show any sign of reaction (i.e., no new product was formed).

6.5.1.2 Preparative photolyses of 142, 145, 147 and 148 in CH3CN-H2O mixtures

In preparative scale studies, ~70 mg of the acid was dissolved in 30 mL CH3CN and then diluted with 70 mL H2O. The solutions were adjusted to pH ≥ 8 with the aid of a pH meter, by dropwise addition of a stock solution of ~ 1 M NaOH. The solution was then transferred to a quartz vessel fitted with a cooling finger and deaerated with a continuous stream of argon. The solution was irradiated at 254 nm in a Rayonet RPR 100 photochemical reactor for an
appropriate period of time. After photolysis the solution was worked up by saturating with NaCl, acidifying to pH = 1 with 10% HCl, and extracting with CH₂Cl₂ (3 x 75 mL). The photoproducts formed in each case were characterized by comparison with the ¹H NMR spectra of authentic samples, and conversions to products determined by the ¹H NMR integration (relative to the benzylic proton of the starting material). In the case of 145 (and 148), the percentage conversion to product was determined by ¹H NMR using suberene (37) as an external standard. All acids investigated in this study photodecarboxylated cleanly giving rise to only one photoproduct (except 142 which gave two products, viz., 125 and the dimer 128).

6.5.1.3  Preparative Photolyses of 142, 145, 147 and 148 in CH₃CN-D₂O mixtures

In preparative scale studies, ~55 mg of the acid was dissolved in 30 mL CH₃CN and diluted with 80 mL of D₂O. After adjusting the pH ≥ 8 with ~1 M NaOD, the solutions were photolyzed at 254 nm and worked up in the usual manner. Conversions to monodeuterated products were determined by ¹H NMR (90 MHz) integrations (in the case of 142 and 147) and mass spectral analyses (in the case of 145 and 148). The monodeuterated products, viz., 124, 132, 135 and 138 were isolated by extracting the crude reaction mixtures with bicarbonate solution, and characterized by comparison of their ¹H NMR and mass spectra with the authentic samples.
6.5.1.4 Preparative photolysis of 142, 145, 147 and 148 in oxygen saturated solutions

Photolysis were carried out as before but under continuous stream of oxygen instead of argon. The conversions were determined by \(^1\text{H} \text{ NMR analysis of the crude reaction mixtures. In all cases, except 142, only the corresponding decarboxylated product was formed. The ketone 144 formed in the case of 142 was identified by comparison of its \(^1\text{H} \text{ NMR and GC retention time with an authentic sample. The ratios of ketone 144 to 125 were determined by integration of appropriate \(^1\text{H} \text{ NMR signals (144: } \delta \text{ 8.4 and 125: } \delta \text{ 4.0).}}\)

6.5.2 Steady-State and Transient Fluorescence Behaviour

Fluorescence quantum yields were measured on a MPF-66 instrument employing appropriate secondary standard of known fluorescence quantum yield (eq 6.2). Biphenyi ether\(^{135}\) was employed as a secondary standard for xanthene carboxylic acids 142 and 145. Solutions (\(\approx 10^{-5} \text{ M}\)) of acids and the reference were matched for the absorbance (O.D. < 0.08) at \(\lambda_{\text{ex}} = 260 \text{ nm}\) and deaerated with a fine stream of argon for 5 min prior to measurements. Because of the better spectral overlap suberene (37) was chosen as the fluorescence standard for acids 147 and 148. Fluorescence lifetimes of 142 and 145 were measured in 80% H\(_2\)O-CH\(_3\)CN (pH 7) by time correlated single photon counting method on a PTI LS-1 instrument. Solutions of the substrate (O.D. < 0.2) were deaerated with argon before measurements. Lifetimes of 147 and 148 in 80% H\(_2\)O-CH\(_3\)CN could not be measured accurately because of their weak fluorescence.
6.5.3 Ground State pKₐ Estimation of 142, 145, and 147

The pKₐ's of diarylacetonic acids were estimated under an inert (N₂) atmosphere by titrating a 10⁻³ M solution of substrate dissolved in 80% H₂O-CH₃CN (deionized H₂O) with a standardized NaOH solution (1.0070 M). A standard glass electrode with Ag/AgCl reference was employed for the hydronium ion concentrations. End points were determined by a curve-fitting procedure, and the pKₐ was taken as the pH at half-neutralization.

6.5.4 Product Quantum Yields

Quantum yields of formation of the corresponding decarboxylated products for 142, 145, 147, and 148 were measured in a variety of solvent mixtures on an optical bench (λₑₓ = 280 nm). In general, 0.6 mL of a stock solution of substrate in CH₃CN (5 x 10⁻⁴ M) was transferred to a quartz cuvette and diluted with 2.4 mL of H₂O (of appropriate pH). The concentration of the each substrate in the cuvette solutions were such that they had an absorbance ≥ 2.0 at the excitation wavelength. The solutions were purged with a stream of argon for 5 min prior to and during the photolysis (usually 1-10 min). The irradiation time was so adjusted as to keep the conversions to products between 10-15% in all cases. After irradiation the photolysate was transferred to a test tube, saturated with NaCl, acidified to pH = 1 by adding 5% HCl, and extracted with CH₂Cl₂ (4 x 5 mL). The organic fractions were then combined and washed with H₂O (pH ~ 1; 2 x 10 mL), dried over MgSO₄ and filtered. Each solution was then injected with
50 μL of a stock solution of an external standard of appropriate molarity (viz., suberene (37) in the case of 142 and 147; 9-phenyl-9H-thioxanthene (139) in the case of 9-phenylxanthene carboxylic acid (145); and 9-phenyl-9H-xanthene (133) in the case of 9-phenylthioxanthene carboxylic acid (148)) and evaporated to ca. 200 μL before being injected into a GC capillary column (programmed with initial temperature at 150 °C with temperature increment of 10 °C/min up to 250 °C) for analyses. The number of moles of product (125, 133, 136 and 139) formed were determined by comparing integrated peak areas of the product and the external standard and employing a correction factor to compensate for the GC detector response. Correction factor in each case were generated by injecting solution of the authentic sample of photoproduct and external standard in known molar ratios and checking the responses. In the case of 142 both 125 and 128 are formed however, the measured product quantum yields (Φp) of this substrate refer to the formation of 125 only. This was because of the long retention time of 128 on the GC column which prevented the determination of the percentage 128 formed. Light intensity at 280 nm was determined to be $1.0687 \times 10^7$ Einstein/min/3 mL according to the method of Hatchard and Parker described earlier (vide supra).

6.6 Conformational Studies of Dibenzo[b,f]oxepin (155) and Related Systems

6.6.1 Product Studies

6.6.1.1 Photolysis of Dihydrodebenzo[b,f]oxepin (156) in CH$_3$CN

In a preparative scale photolysis, 100 mg of 156 was dissolved either in
100% CH$_3$CN or 50% CH$_3$CN-H$_2$O and the colourless solution was then transferred into a quartz tube fitted with a cooling finger and deaerated with continuous stream of argon and irradiated at 254 nm (Rayonet RPR 100 photochemical reactor) for 10 min. After irradiation the yellow reaction mixture was worked-up and photolysate analyzed by $^1$H NMR (90 and 250 MHz) and TLC. The $^1$H NMR spectrum of the reaction mixture showed a complicated set of multiplets between $\delta$ 2.0-3.0 and 6.0-7.0. The TLC (silica gel, CH$_2$Cl$_2$) of the reaction mixture showed the formation of one major product ($R_f = 0.14$). Preparative thin layer chromatography was employed to isolate this material as a yellow solid. The $^1$H and $^{13}$C NMR spectra of the purified material are shown in Figure 6.2. Crystals of the pale yellow solid were grown in CH$_2$Cl$_2$/hexanes. The results of preliminary X-ray crystallographic analysis indicated that this solid was adduct 166. The $^{13}$C NMR which showed the presence of 28 distinct carbons was consistent with the structure of 166.
Figure 6.2 $^1$H (360 MHz) (a) and $^{13}$C (b) NMR spectra of 166.
6.6.1.2 Preparative scale photolyses of 155 and 37 in CH$_3$CN solution of Et$_3$N

In a typical run ~80 mg of 155 or 37 was dissolved in 0.5 M solution of Et$_3$N in CH$_3$CN and irradiated at 254 nm (ca. 30 min). After irradiation the reaction mixture was quenched by adding a cold aqueous solution of 15% (v/v) HCl, and extracted with CH$_2$Cl$_2$ (3 x 40 mL). The organic layers were combined and washed with 10% HCl solution and water, dried over MgSO$_4$, and CH$_2$Cl$_2$ was removed and the photolysate examined by $^1$H NMR. In each case the only product formed was the corresponding reduced hydrocarbon, viz., 156 and 49. Preparative scale thin layer chromatography (silica gel, CH$_2$Cl$_2$) was employed to isolate these photoproducts from the reaction mixture and identified by comparison with the $^1$H NMR spectra of authentic samples.

6.6.1.3 Preparative Scale Photolyses of 155 and 37 and 157 and 158 in Aqueous CH$_3$CN Solution

In preparative scale experiments the substrate (~80 mg) was dissolved in 80 mL of CH$_3$CN and diluted with an equal amount of buffer solution of appropriate pH. In the case of photolysis in the presence of sulfuric acid, the CH$_3$CN solution of the substrate (75 mL) was diluted with an equal amount of 10-20% (w/w) H$_2$SO$_4$ solution. After irradiation of these solutions at 300 nm (in the case of 155 and 37) or 254 nm (in the case of 157 and 158) for an appropriate period of time the reaction mixture was worked up by adding a saturated brine solution, neutralizing with an aqueous NaOH solution and extracting the aqueous
layer with CH₂Cl₂ (3 x 30 mL). The organic layers were combined and washed with water, dried over MgSO₄ and CH₂Cl₂ removed. The photolysate was examined by ¹H NMR (90 MHz) and photoproducts identified by comparison with the ¹H NMR spectra of the authentic materials.

6.6.2 Steady-State Fluorescence Studies

Fluorescence spectra were measured in 1.00 cm Suprasil quartz cuvettes at 10⁻⁵-10⁻⁴ M after 10 min of argon purging. Fluorescence lifetimes were measured by single photon counting at optical densities of 0.03-0.08 at the exciting wavelength (details of the single photon counting discussed later, vide infra). Fluorescence quantum yield (Φ₁) of 155 was measured relative to quinine bisulfate (Φ₁ = 0.55 in 1 N H₂SO₄)¹⁷⁷ according to eq 6.² (vide supra).

6.7 Photoionization of N-methylacridan (140)

6.7.1 Product Studies

6.7.1.1 Dark Reactions of 140

N-methylacridan (140) did not show any reactivity in the dark under the conditions employed to study its photochemistry. Control experiments were performed by treating = 60 mg of substrate in exactly the same manner as the photolyzed sample except that they were stirred in dark for 30-60 min. The samples were then worked up in a usual manner and analyzed by ¹H NMR (90 MHz).
6.7.1.2 Preparative Scale Photolysis of N-methylacridan (140)

In a typical preparative study 100 mg of 140 was dissolved in 200 mL of solvent (e.g., CH$_3$CN, Et$_2$O etc.) and irradiated at 254/300 nm for 60 min. The solvent was then evaporated on a rotary evaporator and photolysate analyzed by $^1$H NMR (90 MHz, CDCl$_3$) for the product bis(N-methylacridyl) (141) formed. The percentage conversion to bis(N-methylacridyl) (141) (mp 238 ± 2 °C) was determined by integrating the N-CH$_3$ signals of the product 141 (δ 2.95 (s, 6H)) with respect to that of starting material 140 (δ 3.31 (s, 3H)).

6.7.2 Product Quantum Yields

Quantum yields ($\Phi_Q$) for loss of 140 were measured in number of solvents on an optical bench ($\lambda_{ex} = 302$ nm). In a typical experiment 0.5 mL of a stock solution of 140 in CH$_3$CN (2 x 10$^{-3}$ M) was transferred to a quartz cuvette and diluted with 2.5 mL of the appropriate solvent in which the quantum yield was being measured. The solutions were purged with a stream of argon for 10 min prior to and during the photolysis (usually 1-10 min). Conversions to product were kept below 15% in all solvents. After irradiation the photolysate was transferred into a round bottomed flask and solvent was evaporated under reduced pressure to ca. 100 μL. In case of photolysis in 1:1 CH$_3$CN-H$_2$O, the photolysate was transferred to a test tube, saturated with NaCl, and extracted with CH$_2$Cl$_2$ (3 x 5 mL). The organic fractions were combined, dried over MgSO$_4$ and filtered, and solvent removed to ca. 100 μL. Each solution was then injected.
with 50 µL of a stock solution of 9H-xanthene (125) before being injected into the GC capillary column (180 °C) for analysis. Since the retention time of the product bis(N-methylacridyl) (141) was very long, loss of starting substrate 140 was measured instead to measure the number of moles of products formed. This was achieved by comparing the integrated peak areas of external standard xanthene (125) and N-methylacridan (140). The respective peak areas were corrected for the differences in the GC detector response. Correction factors were generated independently by injecting solutions of the 125 and 140 in known molar ratios and checking the response. Light intensity measurement were made by employing potassium ferrioxalate actinometry according to the method of Hatchard and Parker described earlier (vide supra).¹¹⁸

6.8 Excited State Carbon Acid Behaviour of Substituted Suberenes

6.8.1 Product Studies

6.8.1.1 Preparative Scale Photolyses of 180, 181, 185, 186, 187, 188, 189, 190, 193, 194, 196 and 197 in Aqueous CH₃CN

In general ~ 60-75 mg of substrate was dissolved in the 75 mL of CH₃CN and then diluted with an equal amount of L₂O (L = H or D), and transferred to a 200 mL quartz tube. The solution was cooled to ~ 14 °C with an internal cooling finger and purged with a stream of argon for 5 min before photolysis at 300 nm inside a Rayonet RPR 100 photochemical reactor. Photolyzed solutions were worked up by first saturating the solution with NaCl, extracting with CH₂Cl₂ (3 x 50 mL), and then evaporating the solvent on a rotary evaporator. The
photoproducts formed in each case were identified by $^1$H NMR (250 MHz) and conversion to deuterium/protium exchange photoproducts were calculated by $^1$H NMR integration and GC/MS analyses.

6.8.1.2 Preparative scale photolysis of 194 and 197 in Ethanolamine solution

In these experiment ~ 50 mg of the substrate (194 or 197) was dissolved in 100 mL solution of ethanolamine (ca. 0.2-0.5 M) in CH$_3$CN. The solution was transferred into a quartz tube and purged with argon for 5 min, and it radiated at 254 nm. After photolysis, the reaction mixture was carefully quenched with a 10% HCl solution and extracted with CH$_2$Cl$_2$ (3 x 30 mL). The CH$_2$Cl$_2$ layers were combined and washed with water, dried over MgSO$_4$ and evaporated on a rotary evaporator. The photolysate was then examined by $^1$H NMR (250 MHz) and conversions to deuterium exchanged photoproducts were calculated by GC/MS.

6.8.2 Quantum Yields Measurements

Quantum yields ($\Phi$'s) of monodeuterium and monoprotium incorporation were measured in a variety of solvent mixtures on an optical bench ($\lambda_{\text{ex}}$ = 280 nm). Potassium ferrioxalate actinometry was employed to determine the light intensity at 280 nm (4.7632-4.7732 x $10^{-7}$ Einstein/min/3 mL) (vide supra). In general, 3 mL solution (~ $10^3$ - $10^4$ M) of substrate in an appropriate solvent mixture was transferred to a quartz cuvette. The concentrations of the each
substrate in the cuvette solutions were such that they had an absorbance ≥ 2.2 at
the excitation wavelength (λex = 280 nm). The solutions were purged with a
stream of argon for 5 min prior to and during the photolysis (usually 30-60 min).
The irradiation time was so adjusted as to keep the conversions to photoproducts
between 10-12% in all cases. After irradiation the photolysate was transferred to
a test tube, saturated with NaCl, acidified to pH = 7 by adding 5% HCl, and
extracted with CH2Cl2 (4 x 5 mL). The organic fractions were then combined and
washed with H2O (pH ~ 1; 2 x 10 mL), dried over MgSO4 and filtered. The
photolysate was then analyzed by GC/MS (CI mode) to calculate the percentage
deuterium incorporation (after correcting for the natural abundance of D and 13C)
in photoproducts. A representative case of percentage conversion of 181 to 203
in various solvent mixtures is shown in Table 6.1.

Table 6.1 Percentage Conversion to 203 in the Photolysis of 181 at 280 nm
in Various Solvent Mixtures

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solvent Mixture</th>
<th>Photolysis Time</th>
<th>% 203</th>
</tr>
</thead>
<tbody>
<tr>
<td>181</td>
<td>70% H2O-CH3CN</td>
<td>30 min</td>
<td>10.74 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>70% 1.25 M H2SO4-EtOH</td>
<td>120 min</td>
<td>8.87 ± 0.04</td>
</tr>
<tr>
<td></td>
<td>50% H2O-CH3CN</td>
<td>45 min</td>
<td>10.47 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>50% 1.0 M NaOH-EtOH</td>
<td>30 min</td>
<td>13.96 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>50% 2.0 M NaOH-EtOH</td>
<td>20 min</td>
<td>11.50 ± 0.05</td>
</tr>
</tbody>
</table>

a) Number of moles of 181 photolyzed: 1.60 x 10⁴; light intensity at 280 nm:
4.77 x 10⁷ einstein/min.
b) Number of moles of 181 photolyzed: 1.74 x 10⁴; light intensity at 280 nm:
7.76 x 10⁷ einstein/min.
Table 6.2 shows the conversion of 180 to 203 on photolysis in D$_2$O-CH$_3$CN solutions. Only trace amounts of 181 (< 1%) were formed in these photolysis.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Solvent Mixture</th>
<th>Photolysis Time</th>
<th>% 203</th>
</tr>
</thead>
<tbody>
<tr>
<td>180</td>
<td>70% D$_2$O-CH$_3$CN</td>
<td>45 min</td>
<td>9.73 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>50% D$_2$O-CH$_3$CN</td>
<td>60 min</td>
<td>11.33 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>20% D$_2$O-CH$_3$CN</td>
<td>75 min</td>
<td>9.85 ± 0.03</td>
</tr>
<tr>
<td></td>
<td>CD$_3$CN</td>
<td>60 min</td>
<td>0.00</td>
</tr>
</tbody>
</table>

a) Number of moles of 180 photolyzed: 1.74 x 10$^6$; light intensity at 280 nm: 4.76 x 10$^7$ einstein/min.

6.8.3 Steady-State Fluorescence Studies

Fluorescence quenching studies of 180, 181, 185, 186, 189, and 190 were performed on a Perkin-Elmer MPF-66 spectrophotometer using H$_2$O as the quencher. A dilute sample (=10$^{-5}$ M) of the substrate in CH$_3$CN (dry) was prepared and its fluorescence spectrum recorded. No fluorescence was observed from the distilled H$_2$O or CH$_3$CN used in these experiments. The photostability of the samples over time was determined by monitoring the samples' fluorescence intensity for ~30 min. Little variation in the fluorescence intensity was observed.
For systematic fluorescence quenching studies, a series of substrate solutions in CH$_3$CN (dry) with varying concentration of H$_2$O were prepared in Suprasil quartz cuvettes. Three samples were prepared at each concentration of H$_2$O. The fluorescence intensity was measured for each and an average of three values was taken. These values of fluorescence intensities over the range of H$_2$O concentration were then used in Stern-Volmer analysis to obtain quenching rate constants (k$_q$). Fluorescence of 194 and 197 in CH$_3$CN was not quenched by added H$_2$O. However, fluorescence of these molecules was efficiently quenched by added ethanolamine. A representative case of such fluorescence quenching of 193 in CH$_3$CN by ethanolamine is shown in Figure 3.4 (Chapter Three).

Fluorescence quantum yields ($\Phi_f$) of various suberene derivatives, viz., 180, 185 and 189, in CH$_3$CN were measured relative to suberene (37) using eq 6.2. For these purposes each set of solution (sample and 37) were absorption matched at $\lambda_{ex} = 280$ nm (O.D. = 0.019-0.025). Excitation of each compound was then done at 280 nm and the resulting fluorescence spectrum recorded. The area of the integrated emission band of sample relative to 37 was then used in eq 6.2 to calculate the $\Phi_f$ of the substrate. Because of the better spectral overlap biphenyl ether was chosen as the secondary fluorescence standard for 193 and 196.

6.9 Product Studies of Electron Transfer to Photoexcited Xanthenium and Thioxanthenium Cation in S$_1$ in Aqueous Acid Solution

6.9.1 Product Studies

6.9.1.1 Photolysis of 99 in aqueous H$_2$SO$_4$
The cation 99 was generated by dissolving ≈ 250 mg of 9-phenylxanthenol (98) in 100 mL of CH₂CN and diluting the solution with 100 mL of 10% (w/w) H₂SO₄. A bright yellow solution was obtained indicating the formation of cation 99. The solution was transferred into a pyrex tube and purged with Argon for 5 min prior to its photolysis at 345 nm (Rayonet RPR 100 photochemical reactor; ≈ 14 °C) for 30 min. The reaction was worked up by neutralizing it with a solution of NaOH (ca. 0.5 M) and extracting several times with CH₂Cl₂. The combined CH₂Cl₂ layers were washed with water and CH₂Cl₂ was removed on a rotary evaporator. The photolysate was then examined by ¹H NMR (90 MHz).

6.9.1.2 Photolysis of 99 in aqueous H₂SO₄ in the presence of 1,3-DMB

The cation 99 was generated in 1:1 CH₂CN-10% (w/w) H₂SO₄ and ≈ 300 mg of 1,3-DMB was added into the solution. Irradiation of such a solution at 345 nm for 30 min resulted in the formation of a off-white precipitate. The precipitate was filtered out and washed with water. The filtrate was then neutralized and extracted with CH₂Cl₂. The ¹H NMR analysis of the filtrate showed it to be the mixture of 98 and 1,3-DMB. The crystals of the precipitate were grown in CH₂Cl₂/hexane and its structure was solved by X-Ray crystallography (Figure 4.1).

6.9.1.3 Photolysis of 99 in 2-PrOH in the presence of 1,3-DMB

In preparative scale experiment the cation 99 was generated in 1:1 2-PrOH-
10% H₂O₂ and ~200 mg of 1,3-DMB was added into it. The solution was photolyzed at 345 nm for 30 min and the reaction mixture worked up by neutralizing with an aqueous solution of NaOH and extraction with CH₂Cl₂. The photolysate was then examined by ¹H NMR (90 MHz) and the photoproduct 133 formed characterized by comparison with the ¹H NMR spectrum of an authentic sample. A similar photolysis of 99 in the presence of 1,2- and 1,4-DMB also resulted in the formation of 133 as indicated by the ¹H NMR spectrum of the reaction mixtures. In the absence of 1,3-DMB (or 1,2- and 1,4-DMB) no 133 was formed.

6.9.1.4 Photolysis of 114 in aqueous H₂SO₄ in the presence of 1,3- and 1,4-DMB

The cation 114 was generated by dissolving ~200 mg of xanthenol in 100 mL of CH₃CN and diluting the resulting solution with an equal amount of 30% (w/w) H₂SO₄. A deep yellow coloured solution of cation 114 was formed. To this solution of cation 114, ~200 mg of 1,3-DMB was added and the solution was transferred into a pyrex tube and irradiated at 345 nm for 30 min. A yellow coloured precipitate was formed after the photolysis. The precipitate was filtered out and washed with water. The ¹H NMR (90 MHz) of the precipitate showed it be a mixture of 128 (δ 4.20) and 217 (δ 5.71) by comparison with the ¹H NMR spectra of the authentic samples. Same products (128 and 217) were obtained when 1,4-DMB was used instead of 1,3-DMB.
6.9.5 Quantum Yield Measurement

Quantum yield for the loss of cation 99 in the presence of electron donors, viz., 1,3-, 1,2-, and 1,4-DMB was measured using UV-visible spectrophotometry. In a typical experiment the cation 99 was generated in 8:2 1.25 M H₂SO₄-CH₃CN and a solution of 1,3-DMB (10⁻² M) was into it. The solution was transferred into a quartz cuvette and the absorbance of the cation 99 measured at 375 nm (ε = 39000 M⁻¹ cm⁻¹). The solution was then irradiated on an optical bench at 358 nm under a fine stream of argon for 30-45 min. At the end of photolysis, the absorbance of the cation 99 at 375 nm was measured again. The change in the absorbance (ΔA) of cation 99 at 375 nm before and after photolysis was noted, and the quantum yield for loss of substrate was calculated using eq 6.3,

\[ \Phi_L = \frac{\Delta A_\lambda}{10^4 \epsilon_\lambda \Delta I_x} \]  

(6.3)

where \( \Delta A_\lambda \) is the change in absorbance at 375 nm, \( \epsilon_\lambda \) is the corresponding extinction coefficient and \( \Delta I_x \) is the moles of photons absorbed during the photolysis time. The concentration of 99 so set that its absorbance at irradiation wavelength (358 nm) was greater than 1.75, ensuring absorption of more than 95% of the exciting light.

6.10 Adiabatic Photogeneration of Thioxanthenium Cations in pH 7 Buffer

6.10.1 Product Studies
6.10.1.1 Preparative Scale Photolysis in Methanol

In a typical experiment 75 mg of alcohol was dissolved in 75 mL of MeOH and then diluted with an equal amount of H$_2$O (pH ~7). The solution was transferred to a quartz tube and purged with argon for 5 min prior to photolysis. The solution was then irradiated at 254 nm (Rayonet RPR 100 photochemical reactor; = 15 °C; 5-10 min). After photolysis, the solution was saturated with NaCl, and extracted with CH$_2$Cl$_2$ (3 x 40 mL). The combined CH$_2$Cl$_2$ layers were washed with water, dried over MgSO$_4$ and evaporated on a rotary evaporator. The photolysate was then examined by $^1$H NMR. Photolysis of 226, 219, 227 and 228 alcohols in 50% MeOH-H$_2$O resulted in the formation of corresponding methyl ethers. The $^1$H NMR data of the corresponding methyl ethers formed are presented below:

9-Methoxythioxanthene

$^1$H NMR (90 MHz, CDCl$_3$) δ 3.28 (s, 3H, OCH$_3$), 5.10 (s, 1H, Ar$_2$CH), 7.1-7.7 (m, 8H, arom.).

9-Methoxy-9-phenylthioxanthene

$^1$H NMR (90 MHz, CDCl$_3$) δ 3.10 (s, 3H, OCH$_3$), 6.9-8.1 (m, 13H, arom.).

9-Methoxy-2-Chlorothioxanthene

$^1$H NMR (90 MHz, CDCl$_3$) δ 3.3 (s, 3H, OCH$_3$), 5.15 (s, 1H, Ar$_2$CH), 7.1-7.7 (m, 7H, arom.).

9-Methoxy-9-Methylothioxanthene

$^1$H NMR (90 MHz, CDCl$_3$) δ 2.45 (s, 3H, CH$_3$), 3.0 (s, 3H, OCH$_3$), 7.1-7.9 (m, 8H,
6.10.1.2 Preparative scale photolysis of 226 in aqueous NaCN

60 mg of 226 was dissolved in 50 mL of CH$_3$CN and diluted with an equal amount of 0.2 M aqueous NaCN solution. The solution was transferred into a quartz tube and photolyzed at 254 nm with continuous purging with argon. The reaction was worked up by saturating with NaCl, and extracting the aqueous layer with CH$_2$Cl$_2$ (4 x 40 mL). The photolysate was examine by $^1$H NMR and GC/MS. The GC/MS analyses indicated the formation of two isomeric cyano substituted thioxanthenes, viz., 232 and 233. Thioxanthenes 232 and 233 were separated by preparative thin layer chromatography (Silica gel; CH$_2$Cl$_2$), and characterized by $^1$H NMR:

9-Cyano-9H-thioxanthene (232)

$^1$H NMR (90 MHz, CDCl$_3$) $\delta$ 4.80 (s, 1H, Ar CH$_2$), 7.2-7.8 (m, 8H, arom.); IR (Nujol) 2250 cm$^{-1}$ (weak, CN stretch); GC-mass spectrum (Cl) (m/z) 224 (M$^+$+1).

9H-Cyanothioxanthene 233

$^1$H NMR (90 MHz, CDCl$_3$) $\delta$ 4.10 (s, 2H, Ar$_2$CH$_2$), 7.3-7.8 (m, 8H, arom.); IR (Nujol) 2235 cm$^{-1}$ (weak, CN stretch); GC-mass spectrum (Cl) (m/z) 224 (M$^+$+1).

6.10.2 Steady-state Fluorescence Studies of Thioxanthenols

Fluorescence excitation and emission spectra of thioxanthenols were recorded on a Perkin-Elmer MPF-66 instrument at room temperature (22 ± 3 °C).
and are uncorrected. Solutions of thioxanthenols were prepared in pH 7 buffer (ca. 10^{-4} M) in a quartz cuvette, by injecting a known volume (ca. 50 μL) of the substrate dissolved in 100% CH₃CN (dry). The solution in the cuvette was vigorously shaken and purged (ca. 3-5 min) with a fine stream of Argon prior to recording of the fluorescence spectrum. Because the adiabatically generated thioxanthenium cations in pH 7 buffer fluoresce between 400-700 nm region, second-order effects (i.e., 2 x excitation wavelength) become important. To eliminate these, a 290 nm band-pass filter was placed in front of the excitation monochromator. This effectively cuts-out the 2 x 260 nm (= 520 nm) second-order scattering due to the exciting wavelength. It also eliminates the second-order band of the Raman scattering peak of the excitation wavelength. The fluorescence quantum yields (Φ')s of the cations were measured using emission of quinine bisulfate in 1 N H₂SO₄ as the reference (Φ = 0.55)^177 (eq 6.2 vide supra). For these purposes, the corrected fluorescence spectra of thioxanthenols and quinine bisulfate were utilized.

6.10.3 Fluorescence Lifetime Measurement of Thioxanthenium Cations

Fluorescence lifetimes of thioxanthenium cations (ground state and adiabatically photogenerated) were measured by time-correlated single photon counting (SPC) (PTI LS-1 instrument) in argon saturated solutions with optical densities of 0.20-0.30 at the exciting wavelength.

The time correlated SPC method measures the time delay between the
absorption and emission of individual photons in a fluorescent sample. The key components of a SPC consists of a high repetition rate, low intensity pulsed excitation source (e.g., low pressure H₂ lamp), a start photomultiplier tube (PMT), a stop PMT, a time-to-amplitude converter (TAC), and a multichannel analyzer (MCA). The triggering of the excitation source is detected optically by start PMT that generates an electrical signal correlated to the excitation pulse. This signal travels to a discriminator and then to TAC, thus initiating the charging of a capacitor resulting in a voltage ramp which is linear with time. On detection of the emitted photon (by stop PMT) the ramp is halted and the voltage output of the TAC is given a value by the analog to digital convertor and a count is stored in the appropriate channel of the MCA corresponding to the delay of the emitted photon with respect to the excitation pulse. With the high frequency of detected events a statistical distribution of the fluorescence emission is quickly accumulated that corresponds to the time dependence of the intensity of fluorescence from which the lifetime information can be obtained.

The SPC traces are generally recorded using the semilogarithmic graphics. A representative case of such a fluorescence decay of thioxanthinenium cation 231 in CF₃CH₂OH recorded on LS-1 SPC instrument is presented in Figure 6.3. Note that the ordinate is logarithmic such that the single exponential decay function give rise to a straight line. The LS-1 SPC instrument also records the instrument response function (or the lamp profile). The IRS was collected by using a scattering solution (milk/water solution) and recording the temporal data as it
was done for the sample. The LS-1 SPC automatically alternates between the sample and scattering solutions during the course of the data acquisition. Both the observed decay and IRF are down-loaded and stored on a microcomputer.

![Graph](image)

**Figure 6.3** Representative fluorescence lifetime decay curve of adiabatically photogenerated thioxanthenium cation 231 in CF$_3$CH$_2$OH. $\tau = 28.42$; $\chi^2 = 1.23$.

(NEC 8086 processor). The lifetime of the sample is then extracted from the above data by an iterative reconvolution procedure. In this method the measured IRF, described by $R(t)$ is fixed and convoluted along with a variable
G(t) function to give a simulated decay function \( S(t) \) (eq 6.4).

\[
S(t) = \int_0^t R(t') G(t-t')dt
\]  

(6.4)

The simulated decay, \( S(t) \), is then compared to the measured decay, \( I(t) \), and the chi-squared \( (\chi^2) \) value is calculated using eq 6.5

\[
\chi^2 = \sum_{i=1}^{n_1} \frac{(I(t_i) - S(t_i))^2}{I(t_i)}
\]  

(6.5)

where \( n_1 \) (channel with maximum counts) and \( n_2 \) (channel where the count reach a background level) are the limits of the analysis range. In the iterative reconvolution process the parameters in \( G(t) \) are varied and optimized to achieve a minimum value in \( \chi^2 \), the point by point deviation between experimental and simulated decay curves. For correct calculated function \( \chi^2 \) value between 0.9-1.3 is acceptable (e.g., in Figure 6.3 \( \chi^2 = 1.23 \)). The \( \chi^2 \) parameter, however, contains no information on the error distribution within the analyzed range of data points. A plot of the weighted residuals \( r(t) \) (eq 6.6) may be used to visualize the error distribution where,

\[
r(t_i) = \frac{I(t_i) - S(t_i)}{\sqrt{I(t_i)}}
\]  

(6.6)

In this context the autocorrelation function, \( C(j) \), is useful. It describes the correlation between the residuals \( r(t_i) \) and \( r(t_{i+j}) \) and is defined by eq 6.7,
where \( n_3 = n_2 + n_1 + 1 \), \( j = n_3 / 2 \), and \( m = n_3 - j \). For good fits, the autocorrelation plots should show an initial value of 1.0 and random dispersion of the residuals around the \( C(j) = 0 \) line (see at the bottom of Figure 6.3). A poor fit is demonstrated by sigmoidal distribution around \( C(j) = 0 \) or a plot that fails to cross this line.
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