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MECHANISTIC STUDY OF [2+2] PHOTOCYCLOADDITION OF NAPHTHALENE DERIVATIVES WITH ACETYLACETONE

by

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B.Sc.(EQUIVALENT) BEIJING INSTITUTE OF CHEMICAL ENGINEERING

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MECHANISTIC STUDY OF [2+2] PHOTOCYCLOADDITION OF NAPHTHALENE DERIVATIVES WITH ACETYLACETONE

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ABSTRACT

Photolysis of a solution containing a substituted naphthalene (NpR, R = 1- and 2-CO_2Me, 1- and 2-CO_2Et, 1- and 2-OMe and 1- and 2-CN) and acetylacetone (acacH) induces [2+2] photocycloaddition to give 1,5-diketone products. The electron donating quencher, tributylamine, that does not quench the excited state of acacH, intercepts the singlet excited state of 2-$NpCO_2Me$ giving k_q of 3.6×10^{10} $M^{-1}s^{-1}$ and retards the photocycloaddition giving k_q of 3.3×10^{10} $M^{-1}s^{-1}$, indicating that the singlet excited state of 2-$NpCO_2Me$ is reacting. An exciplex formation between ^{1}2-$NpCO_2Me$ and acacH is proposed and regiochemistry of addition products is discussed. The triplet sensitization by xanthone and benzophenone does not induce the photocycloaddition supporting the singlet mechanism. 1,3-Pentadiene (PD) enhances the quantum yield of compound **16** (1-acetyl-2-acetonyl-2-carbmethoxy-1,2-dihydronaphthalene) in the concentration range of 0-0.10 M probably via a termolecular mechanism, but retards it in the concentration range of 0.10-0.30 M due to the predominance of a competing reaction of PD and ^{1}2-$NpCO_2Me$.

The photocycloaddition of 2-NpR (R = CO_2Me and CO_2Et) with acacH is catalyzed by lithium acetylacetonate [Li(acac)], sodium acetylacetonate [Na(acac)] and potassium acetylacetonate [K(acac)]. The fluorescence of 2-NpR is quenched by Li(acac) giving k_q of 2.2×10^{10} M^{-1} s^{-1} ($k_q\tau_0$ of 205 M^{-1}) for R = CO_2Me and $k_q\tau_0$ of 209 M^{-1} for R = CO_2Et. The catalytic and non-catalytic processes coexist under the experimental conditions and the quantum yield dependence curve on concentration of Li(acac) from experimental data matches that from the calculated data in the Li(acac)

concentration range of 0.001-0.0045 M. The observations are interpreted as the interception of the singlet excited state of 2-NpR by Li(acac), followed by the addition of acacH to the naphthalene moiety of the exciplex giving the final product and Li(acac). In contrast, Li(acac) does not show a catalytic effect on the reaction systems of 2-NpOH and 2-NpOMe indicating the involvement of a different mechanism.

The photoaddition of NpR (R =1-CO_2Me or 2-CO_2Me) with acacH is catalyzed by sulfuric acid, phosphoric acid, hydrochloric acid and borontrifluoride. NpR fluorescence is quenched by H_2SO_4 giving k_q of 1.01 x 10^{10} M^{-1} S^{-1} ($k_q\tau$ of 35.3 M^{-1}) for R = 2-CO_2Me and $k_q\tau$ of 8.7 M^{-1} for R = 1-CO_2Me and a new broad emission at 470 nm is observed. This emission is assigned to emission from protonated ^{1}2-$NpCO_2Me$. The quenching of 2-$NpCO_2Me$ fluorescence in the presence of H_2SO_4 (0.0935 M) by acacH is accompanied by the quenching of the new broad emission giving $k_q\tau$ of 63.4 M^{-1} for the monomer quenching and $k_q\tau$ of 128 M^{-1} for the new broad emission quenching. The catalytic and non-catalytic processes coexist under the experimental conditions. The results are interpreted as the interception of the singlet excited state of 2-$NpCO_2Me$ by a proton, followed by the addition of the protonated ^{1}2-$NpCO_2Me$ to a ground state acacH giving the final product.

DEDICATION

TO MY PARENTS

TO LONGJIANG

TO XIAOJIANG

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

List of Abbreviations

1-$NpCO_2Me$	methyl 1-naphthoate
2-$NpCO_2Me$	methyl 2-naphthoate
1-$NpCO_2Et$	ethyl 1-naphthoate
2-$NpCO_2Et$	ethyl 2-naphthoate
PN	phenanthrene
1-NpOMe	1-methoxynaphthalene
2-NpOMe	2-methoxynaphthalene
1-NpCN	1-cyanonaphthalene
2-NpCN	2-cyanonaphthalene
AcacH	acetylacetone
Li(acac)	lithium acetylacetonate
Na(acac)	sodium acetylacetonate
K(acac)	potassium acetylacetonate
CD	1,3-cyclohexadiene
PD	1,3-pentadiene
HD	2,5-dimethyl-2,4-hexadiene
Φ_p	quantum yield based on product formation
Φ_{Np}	quantum yield based on naphthalene derivative disappearance.
DMA	N,N-dimethylaniline
TBA	tributylamine
NND	N,N-dimethylnitrosoamine
I.S.	internal standard
Rt	retention time

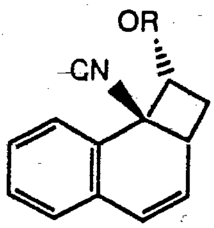
CHAPTER 1 INTRODUCTION

1.1 Photocycloaddition of aromatic compounds

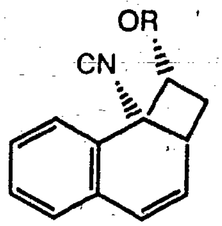
1.1.1 Naphthalene derivatives

[2+2] photocycloaddition is one of the most interesting photoreactions on theoretical,[1] mechanistic and synthetic grounds.[2,3] The reaction leads to the formation of four membered rings providing an important route for organic synthesis.[4]

The current active interests in photocycloadditions of naphthalene systems are still focused on the mechanistic aspects[5-7] such as the intermediates[8-11] in the reactions, and the factors controlling the stereospecificity.[10,12,13] No single mechanism has been proposed which is capable of explaining all of the observed results for the photocycloadditions involving aromatic compounds.[7,14-20] The photocycloaddition of unsaturated compounds to 1-cyanonaphthalene has been studied extensively. The stereoselectivity of the addition depends on the electronic nature of the olefin: more highly conjugated planar olefins such as phenyl vinyl ether and indene undergo *endo*-selective photocycloaddition.[21,22] Such stereoselectivity is lacking in the photocycloaddition of alkyl vinyl ethers, and both *endo*- and *exo*-cycloadducts **1** and **2** are formed in approximately equal amounts.[23]

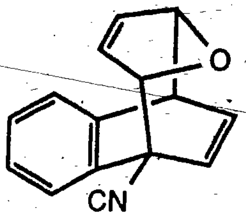


Endo **1**



Exo **2**

These observations have been interpreted in terms of differences in stability between exciplex configurations: the former type of olefin may be expected to form more stable exciplexes possessing a sandwich-type structure. However, the stereochemical course of photocycloadditions to naphthonitriles is also affected by the position of the cyano group: the addition of furan to 1-cyanonaphthalene gives [4+4] cycloadduct **3** with anti-configuration,[24] but that to 2-cyanonaphthalene occurs in the syn-direction to give eventually a cage-like compound **4**.[25] A negative temperature dependence for the quantum yield of addition was interpreted in terms of an exciplex intermediate.[26]



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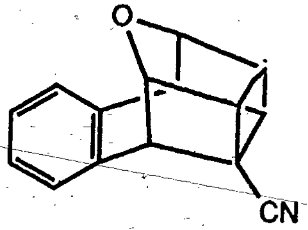
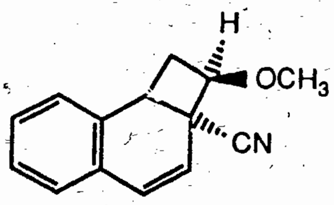


4

The distribution of products can depend on the wavelength of irradiation. For example,[6] photoaddition of 2-cyanonaphthalene and methyl vinyl ether gives a complex mixture of products. Irradiation at 313 nm affords mainly the cyclobutane **5**, but with light of shorter wavelengths (Hg arc, pyrex filtered) additional products **6-10** are formed. Although mechanistic details of this reaction have not been determined, it is likely that products **6-10** predominate with shorter wavelength light because they are more stable to irradiation than cyclobutane **5**. The cyclobutenes are undoubtedly formed by secondary photolysis of cyclooctadiene **6** and **8**. The additions of an olefin to naphthalene derivatives often occur at the substituted ring, but sometimes at the unsubstituted ring, in a manner which is still unpredictable.



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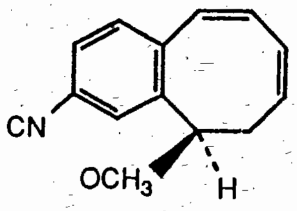

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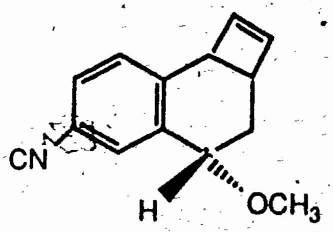

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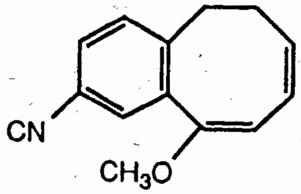

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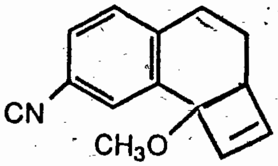

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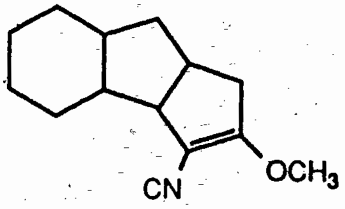


10

The reactions of naphthalene derivatives with alkenes involve the singlet excited states (^{1}S) of naphthalene derivatives and have been discussed in terms of exciplexes.[5,6,10,27-36] The exciplex fluorescences are observed for 1-cyanonaphthalene,[37-40] 2-methyl- or 4-methyl-1-cyanonaphthalene[27] and alkylethylene in nonpolar solvents. The photocycloaddition of olefin and furan derivatives to 1- and 2-cyanonaphthalenes are reviewed[9] in terms of the chemistry of exciplexes that are either totally non-emissive or very weakly emissive. Indirect and direct evidence for the intermediate of the exciplexes is described on the basis of kinetic data, involving an apparent temperature effect on kinetics, and the selective quenching of the exciplex by pyridine.

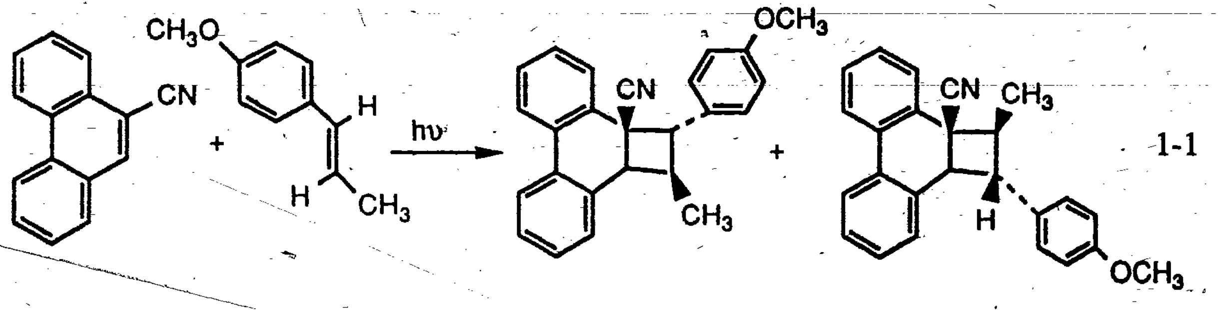
The photocycloadditions of naphthalene derivatives to 1,3-dienes also occur[41-43] and the major products are generally those from $4\Pi_s + 4\Pi_s$ additions.

Preliminary experiments in our laboratory[44,45] have shown that irradiation of a solution containing 2-methoxynaphthalene and acacH gives a 1,5-diketone product (equation 2-10, page 31).

1.1.2 Phenanthrene

On irradiation, phenanthrene (PN) adds to dimethyl fumarate, dimethyl maleate, maleic anhydride,[46-52] methyl vinyl ether, ethyl vinyl ether and 2,5-dimethyl-2,4-hexadiene.[53] Additions always occur at the 9,10-double bond and, except for the oxetane formation,[46-48] the products are cyclobutanes. The reactions occur both on direct and triplet sensitized irradiation, although oxetane formation is only observed on direct irradiation.[47]

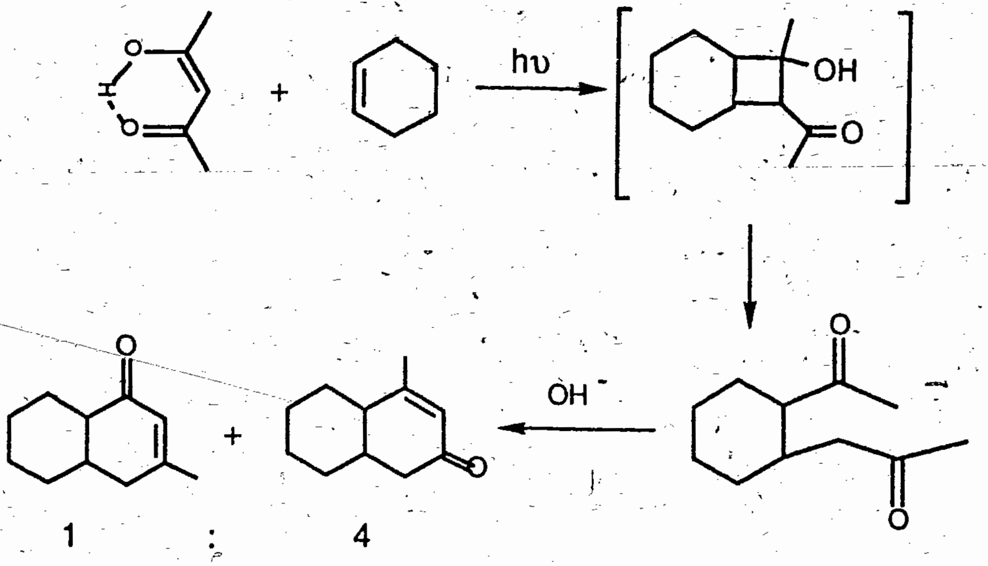
The photocycloaddition of 9-cyanonaphthalene (CN-PN) to substituted β-methylstyrenes (MST) (equation 1-1) is noteworthy in that it is the first case in which an emitting exciplex is shown to be the precursor of cycloaddition products.[54,55] An exciplex fluorescence from CN-PN and MST is observed at λ_{max} = 435 nm in benzene. This fluorescence is quenched by dimethylacetylenedicarboxylate (DAD) with $k_q\tau$ = 64 M^{-1}. The formation of the reaction products is quenched by DAD with $k_q\tau$ = 62 M^{-1}, indicating that exciplex formation precedes cycloaddition.



1-1

1.2 Photocycloaddition of acetylacetone to olefins

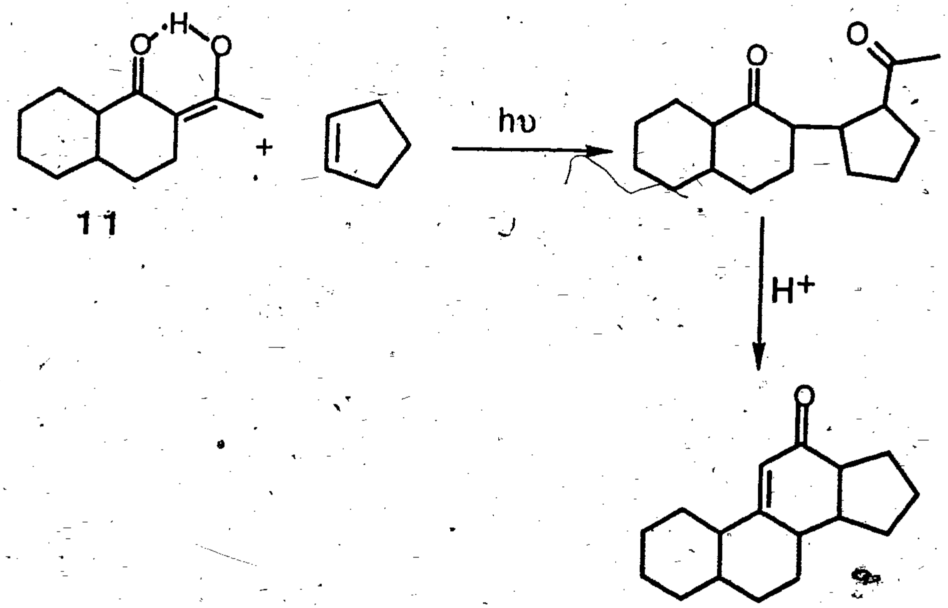
One of the earliest examples of the photoaddition of enones to alkenes was the reaction between acetylacetone (acacH) and several alkenes to give 1,5-diketones[56] as shown in equation 1-2. This reaction is often referred



1-2

to as the de Mayo reaction and it proceeds through the hydrogen bonded enol tautomer of acacH. The presence of acetophenone (E_T = 74 kcal/mol)[58] remarkably accelerates the de Mayo reaction (equation 1-2) indicating the triplet exited state of acacH is the reactive species. On the other hand, the presence of benzophenone does not show such rate enhancement, indicating the inefficiency of its triplet energy (E_T = 69 kcal/mol)[58] for sensitization of the reaction, and giving the lowest triplet energy of acacH to be in the range of 69 to 74 kcal/mol.[59] The reaction is always run in a non-polar solvent and is reported to be solvent dependent with the reaction rate decreasing in order of ether, ethyl acetate and acetonitrile.[57] Presumably such solvents lead to weakening of the intramolecular hydrogen bond in the more polar media.

The reaction of acacH with alkenes can be extended to 1,5-cycloocta-diene or 1,5,9-cyclododecatriene, but not to conjugated dienes.[59] For example, the photocycloaddition of acacH and cyclohexene is suppressed totally in the presence of 1,3-pentadiene. This fact is ascribed to the quenching effect of 1,3-pentadiene (E_T = 59.2 kcal/mol)[58] on the triplet state of acacH.[59] Reaction of cyclic 1,3-diketones with alkenes is also possible.[59-62] A major part of the synthetic interest in this reaction stems from the ready formation of cyclohexenones on exposure of the 1,5-diketone photoproducts to aldol condensation conditions (equation 1-2). The potential utility of this reaction is shown in a simple synthesis of the steriod skeleton[59] (equation 1-3).



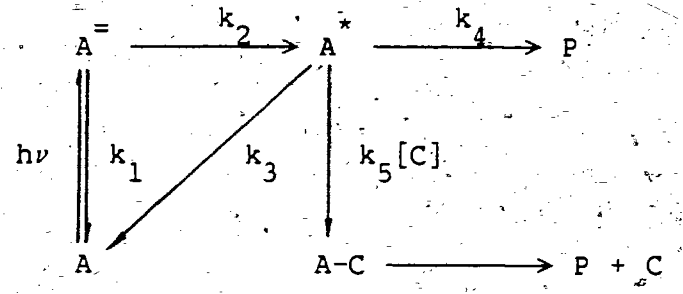
1-3

1.3 Catalysis of excited states

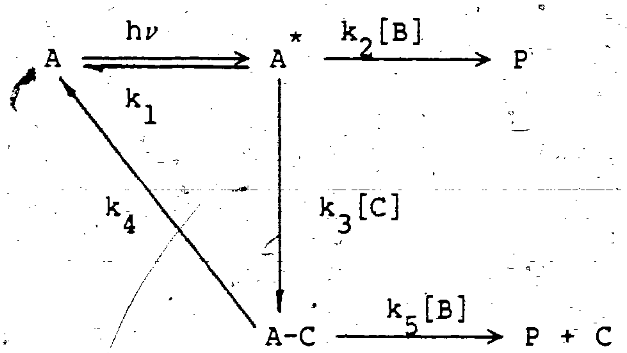
The increase of a reaction rate in the presence of a catalyst is due to the availability of a new reaction pathway involving an intermediate of which the catalyst is an ingredient. In a thermal reaction, a substance is said to act as a catalyst when it appears in the rate equation but not in the stoichiometric equation, or to put it in other words "when its concentration appears in the velocity expression to a higher power than it does in the stoichiometric equation."[63] Accordingly, Wubbles[64] proposed a definition of a catalyst in a photochemical reaction in 1981 for the first time by saying that "a photochemical catalyst is defined as a substance that appears in the quantum yield expression for the reaction from a particular excited state to a power greater than its coefficient in the stoichiometric equation."

Several reaction patterns are shown in the following schemes based on this definition of the photocatalysis reaction.[64,65]

Scheme 1-1



Scheme 1-2



Photochemical kinetic expressions can be derived by using the steady state assumption for excited states or reactive intermediates. The quantum yield (Φ) expression for Scheme 1-1 is shown in equation 1-4. Inversion of equation 1-4 gives a convenient working expression, equation 1-5. If $k_4 >> k_5[C]$, equation 1-5 becomes equation 1-6, which indicates that the quantum yield will not vary with changes in the concentration of catalyst; i.e. no catalytic effects. If $k_4 < k_5[C]$, equation 1-5 becomes equation 1-7, which indicates a linear relationship between $1/\Phi$ and $1/[C]$.

$$\Phi = \phi_i \left\{ \frac{k_4 + k_5[C]}{k_3 + k_4 + k_5[C]} \right\} \qquad 1\text{-}4$$

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left\{ 1 + \frac{k_3}{k_4 + k_5[C]} \right\} \qquad 1\text{-}5$$

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left\{ 1 + \frac{k_3}{k_4} \right\} \qquad 1\text{-}6$$

$$\frac{1}{\Phi} = \frac{1}{\phi_i} \left\{ 1 + \frac{k_3}{k_5[C]} \right\} \qquad 1\text{-}7$$

$$\Phi = \frac{k_2[B] + k_3[C] \dfrac{k_5[B]}{k_4 + k_5[B]}}{k_1 + k_2[B] + k_3[C]}$$

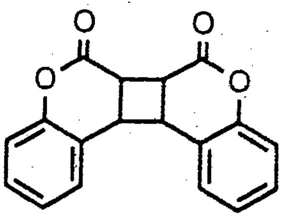
$$= \frac{k_2[B] + k_3[C]f}{k_1 + k_2[B] + k_3[C]} \qquad 1\text{-}8$$

$$\text{where} \quad f = \frac{k_5[B]}{k_4 + k_5[B]}$$

$$\frac{1}{\Phi} = \frac{1}{f}\left\{1 + \frac{k_1 + k_2[B]}{k_3[C]}\right\} \qquad 1\text{-}9$$

Scheme 1-2 represents a case in which the product-forming step is bimolecular and the catalyst complex A-C may decay to starting materials. The quantum yield expression is shown in equation 1-8. When $fk_3[C] \gg k_2[B]$, the inverted quantum yield expression is given by equation 1-9. When the concentration of B is fixed, the plot of $1/\Phi$ vs $1/[C]$ should be a straight line.

It is noteworthy that the key step for the catalysis of an excited state of a molecule is the interception of the excited state by the catalyst according to the definition by Wubble. A typical example is the photohydration of aromatic alkenes and alkynes[66-69] catalyzed by acid. Aromatic alkenes are significantly polarized in their singlet excited state and these undergo protonation by acids and hydration under general acid catalysis. The fluorescence of 2-vinyl-naphthalene is quenched by aqueous sulfuric acid giving a k_q value of $4.6 \times 10^6\ M^{-1}s^{-1}$ which is in a good agreement with the k_q value of $6.2 \times 10^6\ M^{-1}s^{-1}$ obtained from product quantum yield measurement of the reaction, thus indicating the catalysis of the excited state. On the other hand, in some cases,[70-74] a mechanism different from the catalysis of an excited state has a better chance to enhance the efficiency of the overall photochemical process. For example, Lewis acid complexes of methyl cinnamate[70-73] or coumarin[70,71,75] undergo efficient [2+2] photocycloaddition or dimerization. Irradiation of E-methyl cinnamic ester with simple alkenes results in inefficient formation of the [2+2] photocycloaddition product and Z-methyl cinnamic ester. In the presence of BF_3OEt_2 and after prolonged irradiation, a better yield of the [2+2] cycloaddition product is obtained.[70,71,73] The presence of the Lewis acid BF_3 causes a change in regiochemistry of coumarin photodimerization to give syn head-to-tail dimer **12** only (rather than a mixture of **12** and **13**) and enhancement of the quantum yields of **12** formation from 10^{-3} with no BF_3 to 0.16 with 0.125 equivalent of BF_3.



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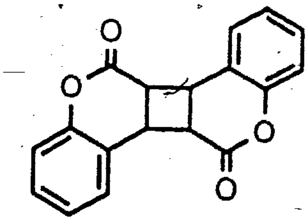


13

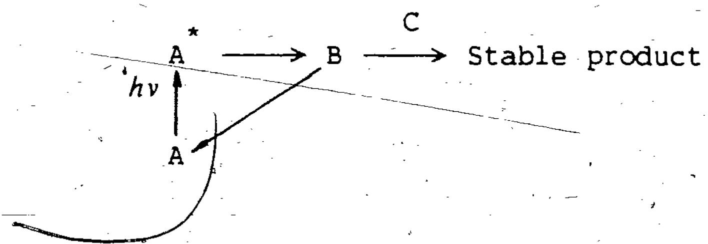
In these cases, the Lewis acid catalyst does not modify the reaction of an excited state of the original substrate, but forms a ground state complex with a different absorption spectrum. The ground state complex "A...B" is irradiated (Scheme 1-3).

Scheme 1-3

$$\begin{tikzcd} A^{*} & (A\ldots B)^{*} \arrow[r] & \text{Products} \\ A + B \arrow[u, "h\nu"] \arrow[r, shift left] \arrow[r, leftarrow, shift right] & (A\ldots B) \arrow[u, "h\nu'"] & \end{tikzcd}$$

Another possibility of accelerating the overall photochemical reaction is catalysis of the reaction of a primary photoproduct "B" rather than that of an excited state as shown in Scheme 1-4.

Scheme 1-4



1.4 Research proposal

Preliminary experiments carried out in this laboratory[44,45] showed that a novel photocycloaddition of naphthalene derivatives to acacH can occur (equation 2-10). In order to expand the reaction to other substrates and to gain more insight into the mechanism of the addition as well as the mechanism of catalysis, we have chosen acacH and a series of naphthalene derivatives (Table 1-1 and Table 1-2) to study for the following reasons:

1. Such photocycloadditions are still unexplored.
2. As different excited states of the starting materials could be involved, the photocycloaddition is mechanistically interesting.
3. Such photocycloaddition has considerable potential in synthesis (equation 2-10, page 31).
4. Catalysis of the photoreactions is remarkable and their mechanism is of great interest.

The aim of this research can be outlined as follows:

1. To synthesize new products from the photocycloaddition of naphthalene derivatives with acacH as well as from the photoproducts.

2. To investigate and differentiate the reactive species and to investigate the multiplicity of the reactive excited species involved in the photocycloaddition.
3. To establish the general reaction pattern of the photocycloaddition in the presence of dienes, electron donating quenchers and heavy atom solvents.
4. To investigate the kinetics of the photocycloaddition by using fluorescence quenching and quantum yield measurements.
5. To investigate and establish the mechanism of Li(acac) catalysis of the photocycloaddition by fluorescence quenching and quantum yield measurements.
6. To investigate the mechanism of sulfuric acid catalysis of the photocycloaddition by quantum yield measurement and absorption and emission spectral studies.

Table 1-1: The molar extinction coefficient ϵ ($cm^{-1}M^{-1}$) values of naphthalene derivatives and others

Compound	300 nm	310 nm	320 nm	330 nm	340 nm	350 nm	Solvent
acacH	990	166	39.2	6.6			CH_3CN^a
acacH	2222	463	49	5-7			CH_3OH^c
1-$NpCO_2Me$	6100	4350	2500	500			CH_3CN^a
1-$NpCO_2Me$	6280	4774	2889	625			$CH_2Cl_2{}^c$
2-$NpCO_2Me$	750	700	1050	1200	300	20	CH_3CN^a
2-$NpCO_2Me$	900	860	1300	1500	620	100	CH_3OH^c
1-$NpCO_2Et$	7000	500	2850	650	200	150	CH_3CN^b
2-$NpCO_2Et$	1000	920	1200	1430	270	80	CH_3CN^b
2-NpCN	655	328		1091			CH_3OH^b
1-NpCN	6010	4352					CH_3OH^b
1-NpOMe	3876	2558					CH_3OH^c
2-NpOMe	546	1008	1050	756			CH_3OH^c
Li(acac)	2000		500	40			CH_3OH^b
Na(acac)	1700			76			CH_3OH^b
2-NpOMe	800	1440	1380	700	28	10	CH_3CN^b

a. From Figure 2-2.
b. From Figure 2-24.
c. From experimental results.

Table 1-2: The first singlet and triplet excited-state energies (E_S and E_T) of naphthalene derivatives obtained from fluorescence and phosphorescence spectra[a]

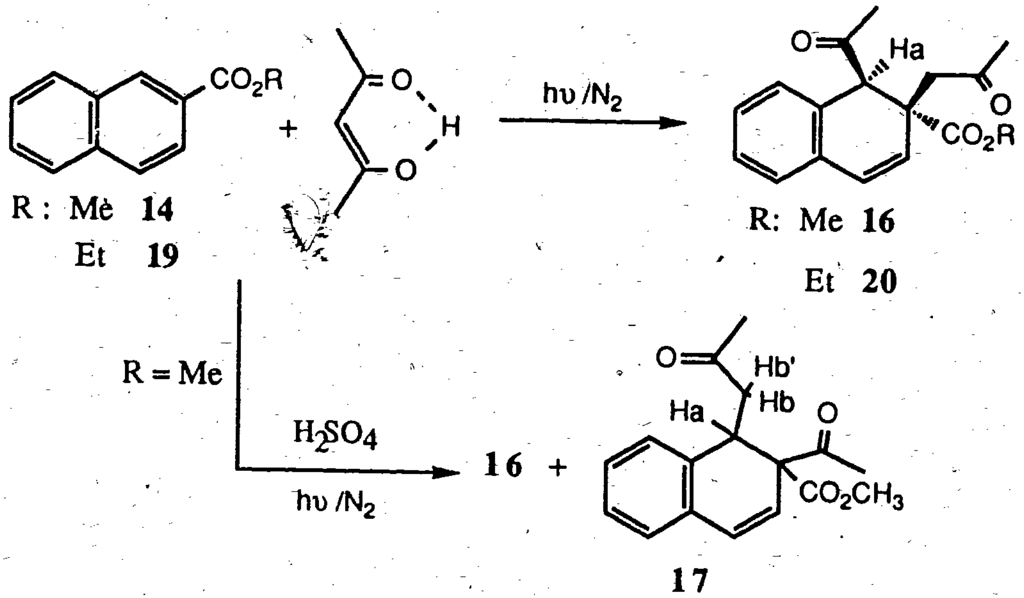
Compound	E_S[b] kcal/mol	(nm)	E_T[b] kcal/mol	(nm)	Solvent[c]	τ[d] ns
1-$NpCO_2Me$	85.9	333	57.2	500	1	
2-$NpCO_2Me$	84.5	338.5	59.3	482	1	3.5[g]
1-$NpCO_2Et$	84.9	337	57.7	496	2 and 3	
2-$NpCO_2Et$	83.6	342	58.8	486	2 and 3	
1-NpCN	86.9	329	56.7	504	1	4.4[h]
2-NpCN	85.9	333	58.4	490	1	12.6[h]
1-NpOMe	89.3[e]	320	59.7[e]	479		10[h]
2-NpOMe	84.6	338	60.9	470	2 and 3	
PD	90[f]		59[f]			
HD	103[e]	278	58.7[e]	487		
CD	97[e]	294	52.4[e]	545		

[a] Fluorescence spectra were taken at room temperature and phosphorescence spectra were taken at 77 K. Error: ± 1 kcal/mol. [b] Calculated from experimental results (Section 4.11). [c] 1 is methylcyclohexane, 2 is acetonitrile and 3 stands for isopropanol:ether 1:3. [d] The lifetime of the singlet excited state. [e] Cited from ref. 82. [f] Cited from ref. 58. [g] From Table 2-9. [h] Cited from ref. 138.

CHAPTER 2 RESULTS

2.1 [2+2] photocycloaddition of naphthalene derivatives and acetylacetone

Photolysis of methyl 2-naphthoate (2-NpCO$_2$Me, **14**) and acetylacetone (acacH, **15**) in acetonitrile at 300 nm (RPR lamps, for output of the relative energy, see Figure 4-1) for 15 hours led to a major product **16** (isolated yield of 33 %) and a trace amount of **17** (less than 2 % of **16**, ignored) as shown by equation 2-1. The structure of **16** was identified as 1-acetyl-2-acetonyl-2-carbmethoxy-1,2-dihydronaphthalene based on its

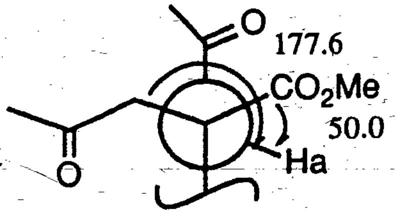


2-1

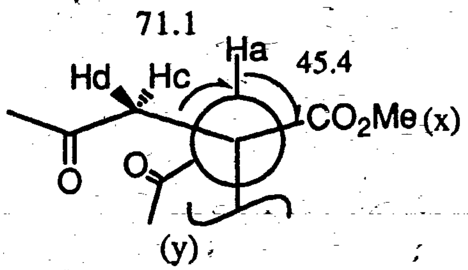
spectroscopic data (Tables 4-1 to 4-4). The ^{1}H NMR spectrum (in CDCl$_3$) shows an AB quartet at 5.81 ppm and 6.51 ppm with a coupling constant of 9.5 Hz indicating two adjacent olefinic protons conjugated to an aromatic ring, one singlet at 4.47 ppm for H$_a$, and an AB quartet at 3.19 ppm and 3.03 ppm (J = 18.5 Hz) for the diastereotopic methylene protons. The existence of unconjugated carbonyl groups is supported by resonances at

207.5 ppm and 205.8 ppm in the ^{13}C-NMR spectrum (Table 4-2) and a strong absorption at 1738 cm^{-1} in the infrared spectrum (Table 4-3).

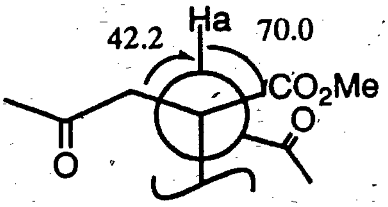
For **16**, there are two possible conformers in *cis* addition and two in *trans* addition. The Newman projections at C_1-$C_{2'}$ of these conformers are



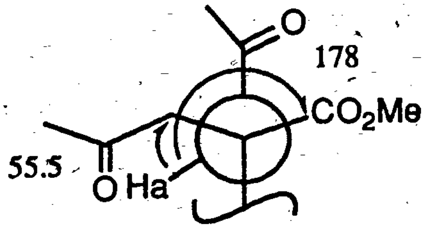
A: E = 47.0 kJ /mol



B: E = 39.7 kJ /mol



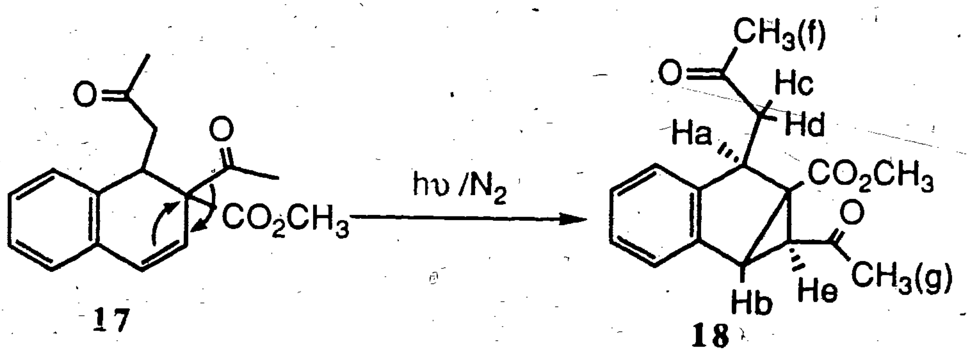
C: E = 85.2 kJ /mol



D: E = 39.6 kJ /mol

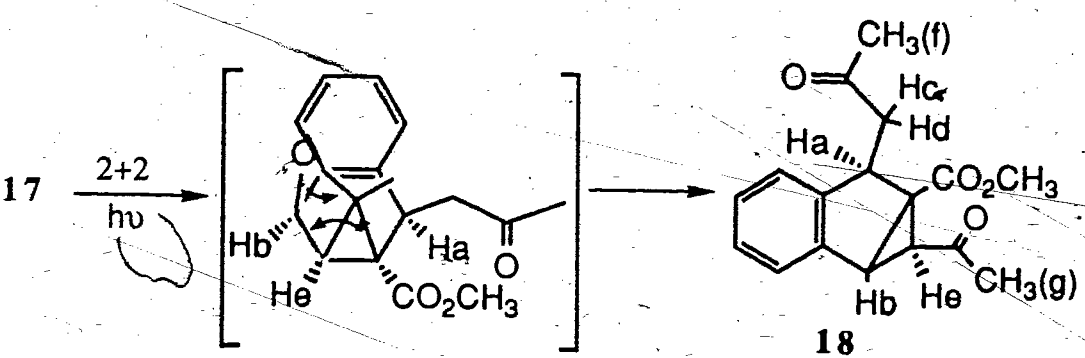
shown by A, B, C and D. Dihedral angles of H_a-C-C-CH_2COMe or H_a-C-C-CO_2Me were obtained by MM2 calculation from energy minimized conformers and are shown in the projections. NOE experiments of **16** showed that irradiation of H_a at 4.47 ppm caused enhancements of H_x (CH_3) at 3.59 ppm, H_y (CH_3) at 2.12 ppm and H_c at 3.19 ppm. Irradiation of H_c caused enhancements at H_d (3.03 ppm) and H_y. Irradiation of H_d caused enhancement at H_c. *Trans* addition could be ruled out due to the following reasons: i) the energy of conformer C is extremely high and ii) enhancement of H_x by irradiation of H_a is present. Conformer B is probably the most stable conformer for **16**. NOE experiments of **20** showed that irradiation of H_a at 4.46 ppm caused enhancement of H_x (CH_2 of Et) at 4.04 ppm and H_y at 2.11 ppm. Irradiation of H_x (CH_2 of Et) caused enhancement of H_a, H_c, H_d and H_x (CH_3 of Et). Since the structure of **20** is similar to that of **16**, a similar dihedral angles from MM2 calculation for **20** is assumed. *Trans* addition could be ruled out since enhancements of H_c and H_d by irradiation of H_a were absence.

Photolysis of 2-$NpCO_2Me$ (300 mg) and acacH (500 mg) in the presence of a trace amount of sulfuric acid in acetonitrile at 300 nm for 19 hours afforded not only the 1,5-diketone **16** (isolated yield of 8 %) but also the 1,5-diketone **17** (isolated yield of 16 %) as shown by equation 2-1.



17 **18**

2-2



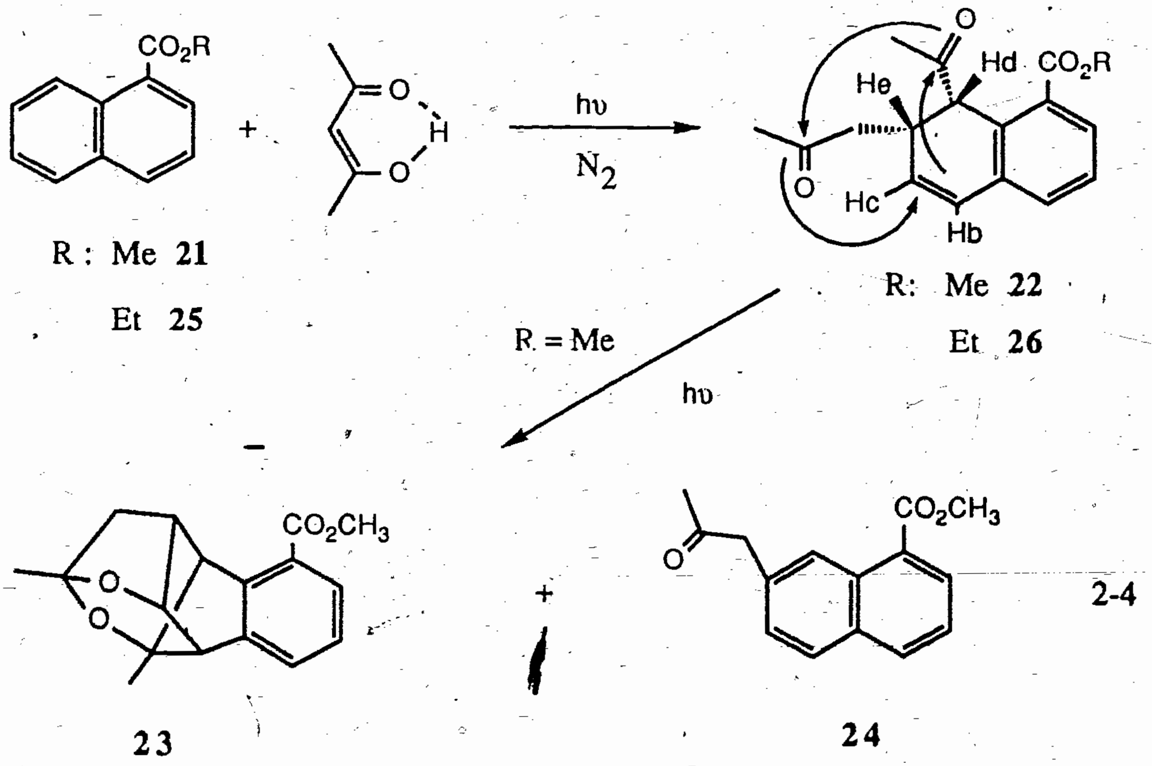
17 **18**

2-3

The ^1H NMR spectrum (in C_6D_6) of **17** shows an AB quartet (J = 10 Hz) at 6.41 ppm and 6.50 ppm indicating two olefinic protons conjugated with an aromatic ring, a ABX pattern at 4.71 ppm (J = 5.5, 7.5 and 1.5 Hz), at 2.28 ppm (J = 18 and 7.5 Hz) and 2.56 ppm (J = 18 and 5.5 Hz). The ABX pattern of these protons confirms **17** to have an addition pattern opposite to that of **16**. ^{13}C NMR, IR and GC-MS (both EI and CI) spectroscopy clearly indicated the functional groups similar to **16**. Prolonged irradiation of the above reaction solution gave two GC peaks at Rt 4.83 min (**17**) and at Rt 6.07 min (**18**) in addition to the peak of **16**. In an independent experiment, photolysis of **17** at 300 nm under comparable conditions led to the formation of **18** (61%) indicating **18** to be a secondary photochemical product (equation 2-2 or 2-3). The structure of **18** was determined by extensive studies of its spectroscopic data. Two signals with chemical shifts at 207.9 and 202.1 ppm assigned to carbonyl groups were observed in the ^{13}C NMR spectrum. Two methyl singlets at 1.99 and 2.28 ppm in the ^{1}H NMR spectrum (in $CDCl_3$) indicated that the two ketone side chains remained in **18**. The ^{1}H NMR spectrum showed the diastereotopic signals assigned to the methylene protons at 3.19 ppm (dd, J = 18 and 8 Hz) and at 3.15 ppm (dd, J = 18 and 4.5 Hz) as part of the ABX system. Decoupling experiments clearly established that H_b (d, 3.17 ppm, J = 9 Hz) was coupled with H_e (d, 3.06 ppm, J = 9 Hz). The NOE results revealed that irradiation of the signal at 2.28 ppm assigned to H_f (s) or the signal assigned to H_a (dd, 4.63 ppm, J = 8 and 4.5 Hz) caused enhancement of H_c and H_d, while irradiation of H_b and H_g (s, 1.99 ppm) resulted in the enhancement of H_e, supporting the assigned stereochemistry. Compound **18** may be formed via an oxa-di-π-methane rearrangment as shown in equation 2-2. On the basis of the structure-efficiency rules for the di-π-methane rearrangement,[58] the rearrangment is most probably induced by the singlet excited state of compound **17**. Alternatively, the oxetane formation followed by bond rearrangments may also explain the formation of compound **18** (equation 2-3).

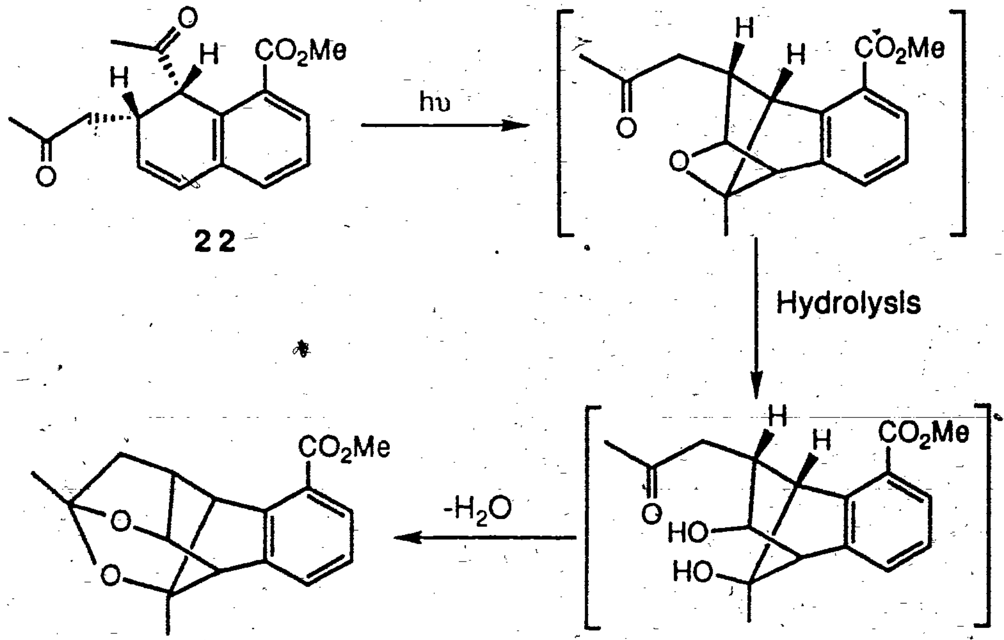
Photolysis of solutions (5 mL) containing 2-NpCO$_2$Me, (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol) and octadecane (as I.S., 0.005 M, 0.025 mmol) in various solvents using 300 nm lamps for 9 hours resulted in the yields of **16** to be 0% in cyclohexane, 10% in benzene, 9.3% in THF, 19.5% in acetonitrile and 19% in methanol. Compound **17** was not formed in these solvents.

Photolysis of the mixture of ethyl 2-naphthoate (2-NpCO$_2$Et, **19**) and acacH in acetonitrile at 350 nm (for the output of the relative energy, see Figure 4-1) for 13 hours led to a single product identified as 1-acetyl-2-acetonyl-2-carbethoxy-3,4-dihydronaphthalene **20** (isolated yield of 35%, equation 2-1) based on its spectroscopic data. The ^{1}H NMR and ^{13}C NMR spectra were very similar to those of **16** except the difference in the ester side chain and support the proposed structure (Tables 4-1 to 4-4).



2-4

Photolysis of the mixture of methyl 1-naphthoate (1-NpCO$_2$Me, **21**) and acacH in acetonitrile at 300 nm for 8 hours led to a single product (equation 2-4) identified as 1-carbmethoxy-7-acetonyl-8-acetyl-7,8-dihydronaphthalene (**22**, isolated yield of 30%) on the basis of the following spectroscopic data. The ^{1}H NMR spectrum showed three aromatic protons at 7.3-7.78 ppm indicating the addition to the unsubstituted ring. Decoupling experiments showed that H_c (dd, 5.78 ppm, J = 9.5 and 2.5 Hz) was coupled with H_b (dd, 6.51 ppm, J = 9.5 and 3 Hz) and H_e (m, 3.33 ppm), and the latter (H_e) with H_d (d, 4.32 ppm, J = 7 Hz) and H_c. NOE experiments supported the above results. The existence of two unconjugated carbonyl groups was indicated by resonances at 208.27 ppm and 206.97 ppm in the ^{13}C NMR spectrum (Table 4-2) and a strong broad absorption at 1736 cm^{-1} in the IR spectrum (Table 4-3). Prolonged photolysis of the above solution with 200 watt Hanovia medium pressure mercury lamp through a Pyrex filter resulted in a new caged compound **23**, 1,8-dimethyl-2,9-dioxa-5,6-[3'-carbomethoxybenzo]tetracyclo[5, 2, 2, $0^{3,11}$, $0^{4,8}$]undecane. In an independent experiment, photolysis of **22** through a Pyrex filter gave **23** (46%) and irradiation of **22** at 300 nm resulted in the formation of **23** (16%) and an unknown product **24** (39%). The latter compound showed a GC-MS (CI) pattern as follows: 243 (M+1, 475), 211 (100%) suggesting a 1-carbmethoxy-7-acetonyl-naphthalene structure as shown in equation 2-4. The spectroscopic data of **23** are given in Tables 4-1 to 4-4. The lack of characteristic peaks for ketones in the IR and ^{13}C NMR spectra and the absence of two methyl singlets adjacent to carbonyl group around 2 ppm in the ^{1}H NMR spectrum indicated that both carbonyl groups have disappeared as a consequence of photolysis. The ^{1}H NMR spectrum also showed the absence of olefinic protons around 5-6 ppm indicating the disappearance of the double bond in **23**. Two singlets in the ^{1}H NMR spectrum at 3.13 and 3.72 ppm were difficult to assign. Multiplicity sorting in the ^{13}C NMR spectrum showed six quaternary carbons indicating a caged structure. The structure could not be decided by spectroscopic data and was eventually determined by means of X-ray crystallography[45] (Figure 2-1). Compound **23** could be formed by a stepwise intramolecular cyclization from compound **22** (equation 2-4). Such a [2+2+2] cycloaddition involving two carbonyl groups has not been demonstrated before. It is also possible that the formation of **23** was mediated by water through an oxetane intermediate as shown in equation 2-5; this requires that the oxetane is readily hydrolyzed under the reaction conditions to open up a pathway for the formation of **23**. The possible pathway via the oxetane formation is supported by the formation of compound **34** (equation 2-7, page 27) and may be proved by exposure of compound **34** to hydrolysis conditions. It is still not clear why compound **33** did not give a caged compound under the same conditions as compound **22**. The *cis* orientation of H_d and H_e (with J = 7 Hz) in compound **22** is required for the formation of caged compound **23**.



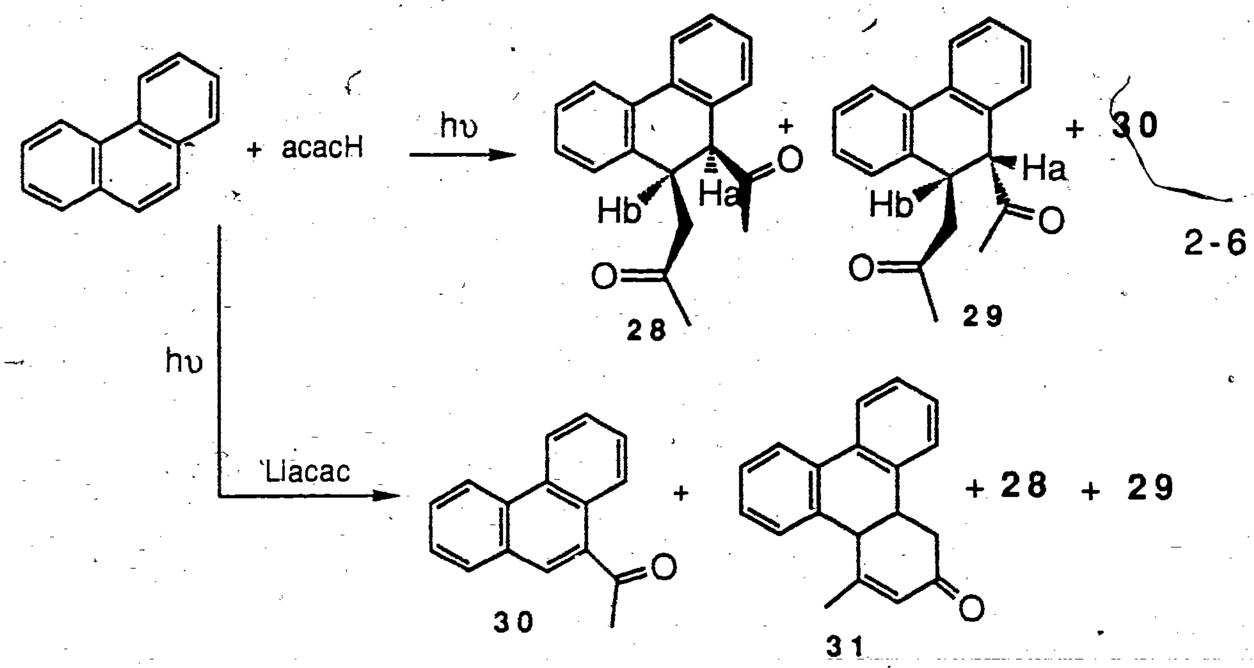
22

23

2-5

Photolysis of the mixture of ethyl 1-naphthoate (1-NpCO$_2$Et, **25**) and acacH in acetonitrile at 350 nm for 16 hours and at 300 nm for 6 hours led to a single product identified as 1-carbethoxy-7-acetonyl-8-acetyl-7,8-dihydronaphthalene (**26**) based on its spectroscopic data (equation 2-4). The ^{1}H NMR and ^{13}C NMR spectral data are similar to those of **22** (Tables 4-1 to 4-4).

Photolysis of a solution of phenanthrene (PN, **27**) and acacH in methanol at 350 nm for 10 hours resulted in two major products (equation 2-6) identified as *cis*-9-acetyl-10-acetonyl-9,10-dihydrophenanthrene (**28**, 27%) and *trans*-9-acetyl-10-acetonyl-9,10-dihydrophenanthrene (**29**, 22%) based on their spectroscopic data (Tables 4-1 to 4-4) and one minor product (**30**, 13%). The existence of the carbonyl groups in **29** was indicated by a strong



absorption at 1715 cm^{-1} in the IR spectrum (Table 4-3) and two methyl singlets at 1.40 ppm and 1.69 ppm in the ^{1}H NMR spectrum (table 4-1, in

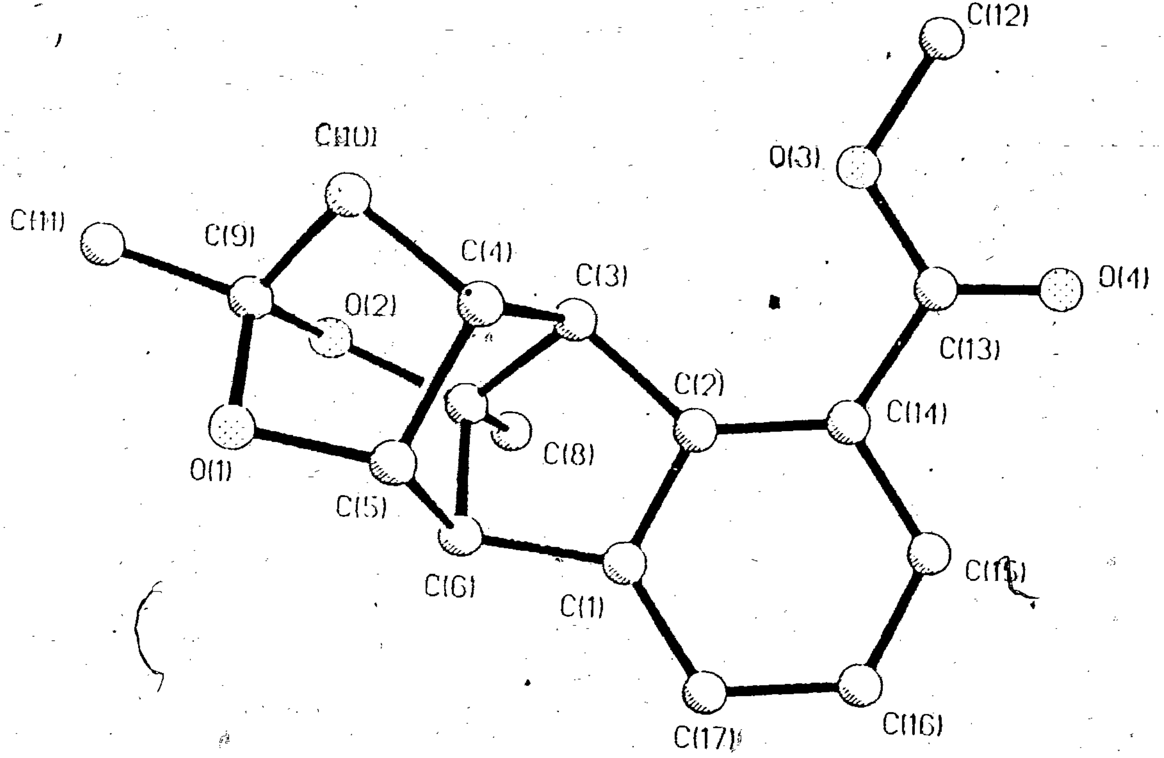


Figure 2-1: Structure of compound **23** determined by X-ray crystallography.[45]

C_6D_6). A doublet at 3.62 ppm (J = 1.7 Hz) for H_a and a doublet of doublets of doublets at 4.22 ppm for H_b (J = 8, 6 and 1.7 Hz) clearly indicated the 9,10-addition. Decoupling experiments showed that H_b was coupled with the methylene protons (dd, 2.10 ppm, J = 18 and 6 Hz; dd, 2.71 ppm, J = 18 and 8 Hz) and H_a. The ^1H NMR spectrum of **28** showed 9,10-addition based on a similar argument as above. Two sets of double doublets at 2.86 ppm (J = 18 Hz and 6 Hz) and 3.03 ppm (J = 18 and 6.5 Hz) were assigned to the diastereotopic methylene protons that were further coupled to H_b as a part of ABX system. Stereochemical assignments of **28** *(cis) and* **29** (*trans*) were made on the basis of a comparison of the vicinal coupling constants (Table 2-1) for protons of H_a and H_b with literature values[77] for 9,10-disubstituted 9,10-dihydrophenanthrenes. The assignments were also consistent with the fact that **28** underwent aldol condensation and dehydration in acidic medium while **29** did not.

Photolysis of PN (300 mg) and acacH (500 mg) in the presence of Li(acac) (53 mg) in methanol at 350 nm for 21 hours (overirradiated) showed 99% PN consumed and formation of four products: **28** (Rt 5.21 min, 9.4%), **29** (Rt 4.61 min, 27%), **30** (Rt 4.40 min, 36%) and **31** (Rt 6.72 min, 18.8%). The structures of the last two compounds were not firmly established. The GC-MS (CI) of **30** gave a parent peak at m/e = 221 (M+1, 100%) suggesting a 9-acetyl-phenanthrene structure. It is not likely that compound **30** still possesses an acetonyl group which is lost in the mass spectrometer by a McLafferty rearrangement. If it does, it should be identical to compound **28** or **29** and should not show its own GC peak. The GC-MS (CI) spectra of **28** and **29** clearly showed their parent peaks at m/e = 279 (M+1, 100% for **28**; M+1, 15% for **29**; Table 4-4) which are different from the parent peak of

Table 2-1: Vicinal coupling constants for 9,10-disubstituted 9,10-dihydrophenanthrenes

Compound	$J_{9,10}$Cis H_Z	$J_{9,10}$Trans H_Z
9-Carboxymethyl-10-methyl-9,10-dihydrophenanthrene[a]	5.2	2.8
9-Acetoxy-10-chloro-9,10-dihydrophenanthrene[b]	4.0	3.2
10-Methyl-9-phenyl-9,10-dihydrophenanthrene[c]	5.9	3.5
9-Acetyl-10-acetonyl-9,10-dihydrophenanthrene[d]	5.0	1.7

a. From Ref. 77.

b. From Ref. 78.

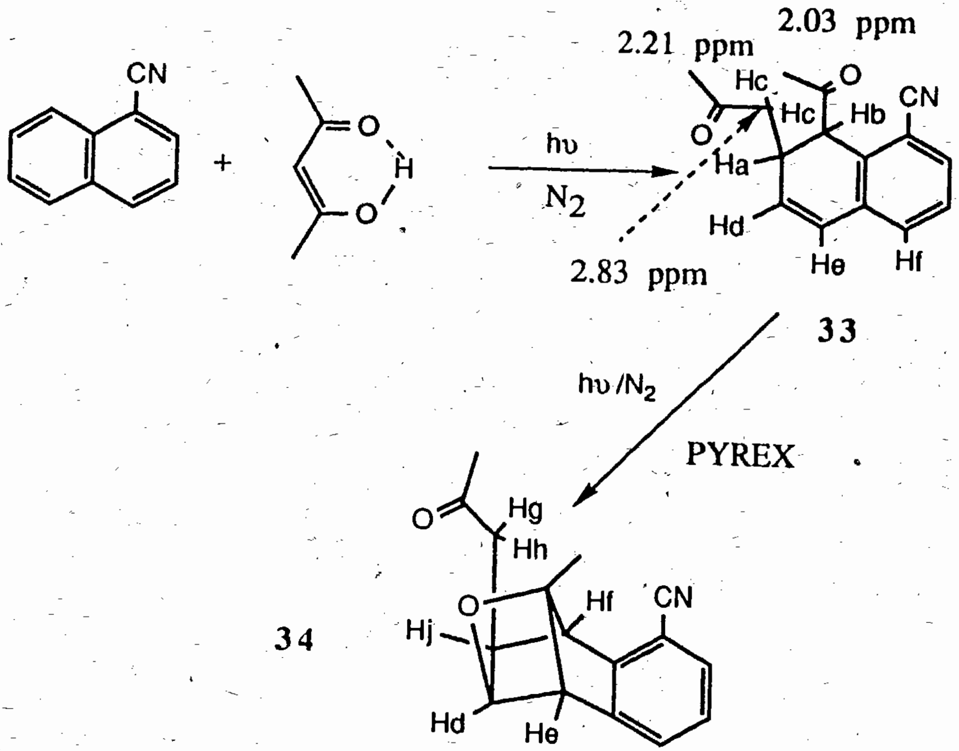
c. From Ref. 79.

d. From Table 4-1.

30. The GC-MS (CI) of **31** gave peaks at m/e = 261 (M+1, 100%) and at m/e = 178 (26%) suggesting an aldol condensation product as shown in equation 2-6. **31** was confirmed to be a secondary product by a treatment in dilute sulfuric acid of a mixture of **28**, **29**, **31** and PN in a ratio of 0.90, 0.16, 0 and 1. This gave the final ratio of 0.34, 0.16, 0.23 and 1 for these compounds using PN as the internal standard.

Photolysis of an acetonitrile solution containing PN (0.02 M) and **28** (0.01 M) at 350 nm for 5 hours showed that the ratio of PN over **28** (1 : 0.62 before and 1 : 0.64 after irradiation) did not change within the experimental error, and neither **29** nor **30** could be detected by GC analysis. In independent experiments, photolysis of **28** (0.01 M) in acetonitrile with 350 nm lamps for 5 hours did not show the formation of **29** and **30**, and photolysis of **29** (0.01 M) under the same conditions did not show the formation of **28** and **30**. These results indicate that compounds **28** and **29** were not interconvertible under the conditions used, and **30** was not a secondary product formed by Norish type II fragmentation. Further studies on the product distribution are required.

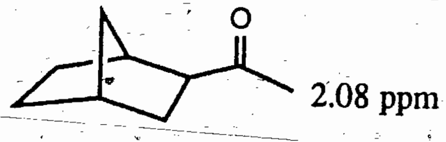
Photolysis of a solution of 1-cyanonaphthalene (1-NpCN, **32**) and acacH at RPR 300 nm for 18 hours in acetonitrile gave one major product identified as 1-cyano-7-acetonyl-8-acetyl-7,8-dihydronaphthalene (**33**, isolated yield of 14%, equation 2-7) as well as several small peaks which were not studied. The ^{13}C NMR signals at 206.3 ppm and 204.7 ppm (Table 4-2) and a strong IR absorption at 1715 cm^{-1} (Table 4-3) clearly indicated the existence of two carbonyl groups in **33**. The two ^{1}H NMR signals of conjugated olefinic protons appeared at 5.87 ppm (dd, J = 10 and 2 Hz) and 6.44 ppm (dd, J = 10 and 3 Hz) as expected. Decoupling experiments showed that H_b (d, 4.06 ppm, J = 6.5 Hz) was coupled with H_a (m, 3.43 ppm) which was coupled with H_c (m, 2.83 ppm, J = 2.5 Hz) and H_b. The two H_c protons



2-7

are magnetically equivalent by chance. NOE results were in agreement with structure **33** since the irradiation of H_e showed 15.4% enhancement for H_f and 15.7% enhancement for H_d. The irradiation of H_a showed 17.7% enhancement for H_b and 7.1% for H_d and the irradiation of H_b showed 13.4% enhancement for H_a. Similar to the case of compound **16** (page 16), there are two possible conformers in *cis* addition and two in *trans* for **33**. Coupling constants of H_a and H_b for these four conformers were obtained by MM2 calculation from energy minimized conformers. The coupling constants are 4.3 H_z (E = 51.71 kJ/mol) for *cis*/axial-H_b; 4.4 H_z (E = 58.88 kJ/mol) for *cis*/equatorial-H_b; 0.8 H_z (E = 50.03 kJ/mol) for *trans*/axial-H_b and 12.2 H_z (E = 64.17 kJ/mol) for *trans*/equatorial-H_b. The coupling constants of the two *cis* conformers are close to the experimental value (J_{ab} = 6.5 H_z) supporting a *cis* addition model. *Cis*/axial-H_b has a lower energy and is thus probably the most stable conformer of **33**.

Photolysis of **33** through a Pyrex filter gave an intramolecular photoaddition product **34**, 1-methyl-2-oxa-8-acetonyl-5,6-[3'-cyanobenzo] tricyclo [3, 2, $1^{3,7}$0] octane. A strong absorption at 1718 cm^{-1} in the IR spectrum, a 207.2 ppm signal in the ^{13}C NMR spectrum and single methyl resonance at 2.18 ppm in the ^{1}H NMR spectrum indicated only one carbonyl group in **34**. ^{1}H NMR decoupling experiments revealed that H_d (d, 4.67 ppm, J = 3.5 Hz) was coupled with H_e (dd, 3.91 ppm, J = 3.5 and 1.5 Hz), and that H_j (dd, 1.91 ppm, J = 5.5 and 9 Hz) was coupled with both H_g (dd, 3.02 ppm, J = 9 and 18.5 Hz) and H_h (dd, 2.87 ppm, J = 5.5 and 18.5 Hz). The acetonyl group in **34** was assigned based on the following arguments:



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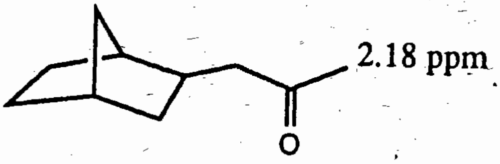
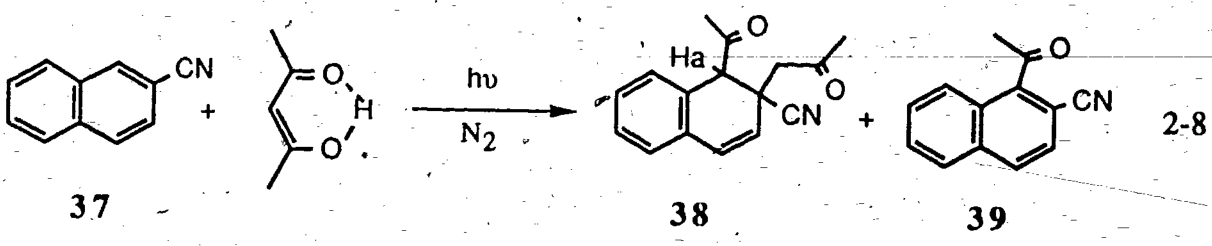


36

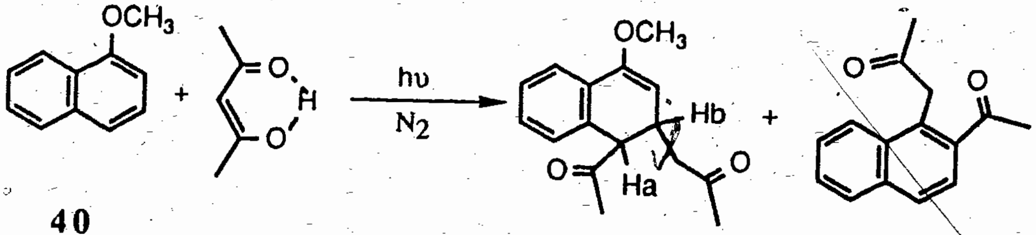
firstly, for **33**, the signal at 2.03 ppm in the ^{1}H NMR spectrum was assigned to a methyl resonance in the acetyl group with reference to **35**[80] and that at 2.21 ppm to the acetonyl group with reference to **36**[81]. The methyl group with 2.18 ppm in compound **34** was therefore assigned as acetonyl group. Secondly, the methylene protons in **34** have chemical shift at 2.87 ppm and 3.02 ppm which are very close to that in **33** (2.83 ppm, 2H) but far from that in the cage compound of **23** (1.87 and 2.05 ppm). The methylene protons are therefore most probably adjacent to the carbonyl group.



2-8

Photolysis of a solution of 2-cyanonaphthalene (2-NpCN, **37**) and acacH at 300 nm for 16 hours in methanol afforded one major product **38**, 1-acetyl-2-cyano-2-acetonyl-1,2-dihydronaphthalene (isolated yield of 10%) and a minor product **39** (**38** : **39** = 4 : 1) as shown in equation 2-8; in addition, several very small GC peaks were not studied. The existence of the two carbonyl groups in **38** was clearly indicated by the resonances at 204.38 ppm and 204.11 ppm in the ^{13}C NMR spectrum (Table 4-2), and a strong absorption at 1728 cm^{-1} in the IR spectrum (Table 4-3). The two methylene protons at 3.06 ppm (d, J = 17.5 Hz) and 3.46 ppm (d, J = 17.5 Hz) showed a typical AB quartet and were not coupled with any other protons. This data, together with a singlet proton at 4.49 ppm for H_a (Table 4-1), unambiguously indicated that addition occurred at the 1 and 2 positions as shown in **38**. Compound **39** was different from **38**, as showed by its own GC peak at Rt 5.88 min. The structure of **39** was not firmly established. The GC-MS spectrum of **39** showed peaks at m/e 195 (43%); 180 (100%); and 152 (51%), which is different from that of **38** suggesting a structure as shown by **39**. The photoaddition was proposed via a singlet mechanism, so the formation of a *trans* isomer of **38** did not likely happen. The possibility that **39** possesses an acetonyl group which is lost in the mass spectrometer by a McLafferty rearrangement is not likely. Alternatively, **39** may be a secondary product formed by the Norish type II fragmentation. These possibilities remain to be clarified.

Photolysis of 1-NpOMe (**40**) and acacH in acetonitrile at 300 nm for 48 hours resulted in one major product identified as 1-methoxy-3-acetonyl-4-acetyl-3,4-dihydronaphthalene (**41**, isolated yield of 15%) and one minor product identified as 1-acetonyl-2-acetylnaphthalene (**42**), as well as several small peaks which were not studied (equation 2-9). The ^{1}H NMR spectrum of **41** showed one proton of a conjugated olefin at 5.77 ppm (dd, J = 9.5 and 2.5 Hz) and four aromatic protons in the range 7.17-7.58 ppm (m) (Table 4-1), indicating that the addition had occurred at the 3,4-positions. The diastereotopic methylene protons appeared at 2.57 ppm (dd, J = 18 and 7 Hz) and 2.87 ppm (dd, J = 18 and 8 Hz) as a part of an ABX system. A doublet with J = 6.5 Hz at 3.78 ppm was assigned as H_a suggesting the *cis* orientation of H_a and H_b. A strong absorption at 1730 cm^{-1} in the IR spectrum (Table 4-3) as well as two methyl singlets at 2.01 ppm and 2.18 ppm in the ^{1}H NMR spectrum (Table 4-1) indicated the existence of two carbonyl groups. The ^{1}H NMR spectrum of **42** showed six aromatic protons around 7.58-8.03 ppm, and a singlet at 4.48 ppm for the methylene protons indicating a naphthalene type structure. The positions of the two side chains in **42** and **44** (*vide infra*) were indicated by the CH_2 ^{1}H NMR signals - 4.48 ppm in **42**, 3.87 ppm in **44**. The existence of the

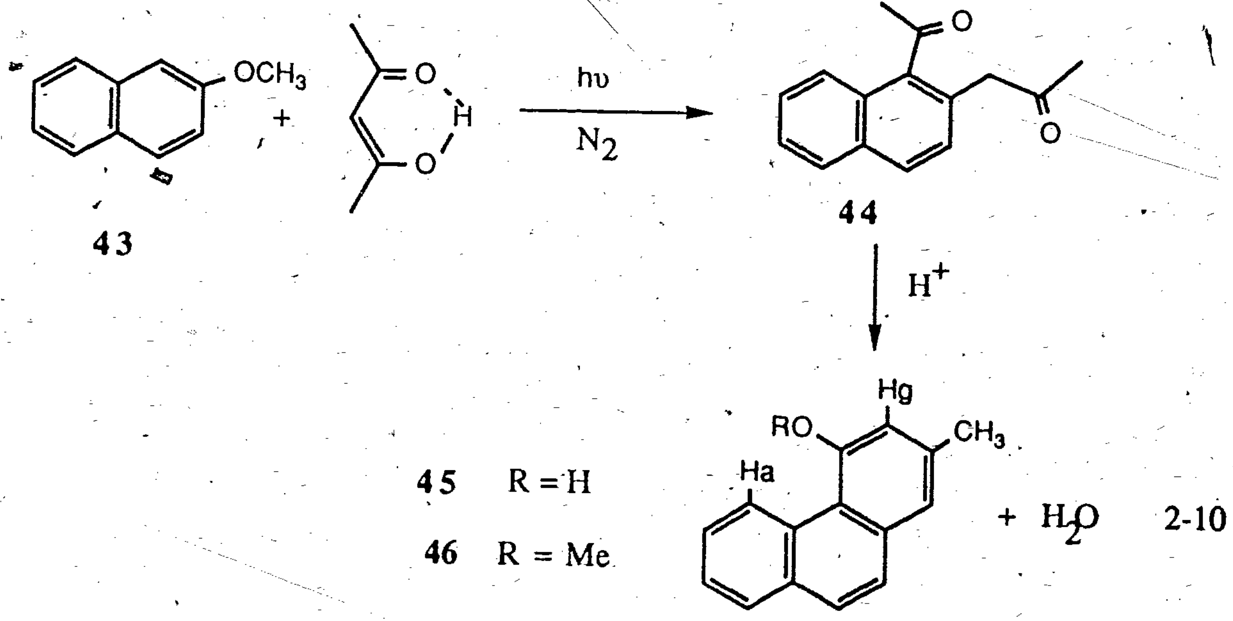


40 **41** **42**

2-9

functional groups of **42** was indicated by IR (Table 4-3) and ^{13}C NMR (Table 4-2) spectroscopy.

Photolysis of a solution of 2-methoxynaphthalene (2-NpOMe, **43**) and acacH at 300 nm for 15 hours in acetonitrile afforded one major product of 1-acetyl-2-acetonyl-naphthalene (**44**, isolated yield of 38%, equation 2-10) as well as some small GC peaks which were not studied. GC-MS (CI) of **44** showed a parent peak of 227 (M+1, 100%). The presence of the functional groups was clearly indicated by IR and ^{13}C NMR spectroscopy. Six aromatic protons between 7.28-7.87 ppm and the lack of conjugated olefinic protons revealed a naphthalene type structure for **44**. A singlet at 3.87 ppm was assigned as CH_2 which was at higher field than that of **42** (4.48 ppm).



43 **44**

45 R = H

46 R = Me

2-10

Heating of diketone **44** in the presence of a trace amount of an acid in acetonitrile led to an aldol condensation product, 1-hydroxy-3-methyl-phenanthrene (**45**). In methanol, the corresponding ether, 1-methoxy-3-methylphenanthrene (**46**, equation 2-10) was obtained. The ^{13}C NMR spectrum of **45** did not show any signal corresponding to ketone carbonyls, i.e. no signals in the 200-210 ppm region. NOE experiments showed that irradiation of H_a (dd, 9.58 ppm, J = 8.5 and 1 Hz) resulted in enhancement on the OH proton (s, 5.62 ppm) and irradiation of the OH proton caused enhancement of H_a and H_g (s, 6.81 ppm) indicating the location of hydroxy group instead of methyl group at position 1. The IR absorption at 3641 cm^{-1} indicated the OH functional group, and the MS gave a parent peak at m/e = 208, consistent with the given formulation. For **46**, the ^{1}H NMR spectrum was similar to that of **45**, except for the presence of an extra signal due to the methoxy group at 4.13 ppm (s), and the absence of the hydroxy group resonance. In NOE experiments, irradiation of the methyl protons of the methoxy group (s, 4.13 ppm) caused enhancement of the H_a (dd, 9.64 ppm, J = 8.5 and 1 Hz) and H_g (s, 7.0 ppm) signals, and irradiation of H_a showed enhancement of the methoxy protons. GC-MS showed a parent peak at m/e = 222 supporting the proposed structure (Table 4-4).

Acetonitrile solutions of acacH containing 1-acetyl- or 2-acetylnaphthalene and 1- or 2-naphthoic acid were irradiated with RPR 300 nm lamps but no new products were detected by GC analysis. The starting materials were recovered almost quantitatively in each case.

Photolysis of 1-methylnaphthalene and acacH in acetonitrile gave four major product peaks, with 69% (GC%) of 1-methylnaphthalene consumed after 18 hours of irradiation at RPR 300 nm. One of the peaks has GC-MS fragmantation pattern as follows: 242 (1%), 142 (100%), 115 (20%) and 43 (60%), suggesting an addition product of 1-methylnaphthalene and acacH.

Attempts to separate the products by flash chromatography and preparative GC failed.

After irradiation for 18 hours at 300 nm, the solutions of acacH containing 2,3-dihydroxy, 1,4-dihydroxy, 1,8-dihydroxy, 1-nitro or 1-aminonaphthalene turned brown and a large amount of starting materials (NpR) were lost with no new products detectable by GC analysis.

2.2 Sensitization and quenching of the photocycloaddition

2.2.1 Triplet sensitization

To investigate the possibility of a triplet pathway in photocycloaddition of 2-NpR (E_T = 59.3 kcal/mol for R = CO_2Me, 58.8 for R = CO_2Et, 60.9 for R = OMe and 58.4 for R = CN, Table 1-2) and acacH (E_T = 69-74 kcal/mol[59]), xanthone (E_T = 74.1 kcal/mol[82]) and benzophenone (E_T = 69.2 kcal/mol[82]) were used as triplet sensitizers. In these experiments, enough sensitizer (0.05 M) was added to an acetonitrile solution of 2-NpR (0.02 M) and acacH (0.08 M) to absorb more than 94% of incident light (350 nm). In all of the above reactions with sensitizer present, GC analysis of the photolysates showed no detectable cycloaddition products, while the corresponding control reactions (i.e. in the absence of a sensitizer) showed product formation of 18-40%.

2.2.2 Quenching of the photocycloaddition

It has been well established that electron donating quenchers, such as tributylamine (TBA), N,N-dimethylaniline (DMA), can quench the fluorescence of aromatic compounds or that of their exciplexes with alkenes; these have led to the suggestion that the photoreactions proceed via a singlet exciplex mechanism.[83,84]

The quantum yields of **16** in the photocycloaddition (at 350 nm) of $2\text{-NpCO}_2\text{Me}$ (0.02 M) and acacH (0.08 M) in acetonitrile were determined as a function of the concentration of TBA (0.0015-0.006 M). The reactions were repeated and the plots of $\Phi°/\Phi$ (the quantum yields of **16** without TBA over that with TBA) *vs* [TBA], based on equation 2-11, yielded straight lines with $k_{TBA}\tau$ of 237 M^{-1} and 230 M^{-1} for two sets experiments. k_{TBA} was calculated to be 3.3×10^{10} and 3.15×10^{10} M^{-1} (Table 2-2). The quantum yield of **16** in the presence (0.01 M) and absence of DMA was calculated to be 0.0008 and 0.0043. Similar experiments were carried out on the photocycloadditions of 2-NpR (R = CO_2Et, OMe and CN) with acacH with the quencher at a single concentration. The quantum yields of the product for the photocycloadditions in the presence (0.01 M) of the quenchers were smaller than that in the absence of the quenchers for all cases and are given in Table 2-3.

$$\Phi°/\Phi = 1 + \frac{k_{TBA}\ [TBA]}{k_a\ [acacH] + \Sigma k_d}$$

$$= 1 + k_{TBA}\tau[TBA] \qquad 2\text{-}11$$

where, $\tau = 1/(k_a\ [acacH] + \Sigma k_d)$, k_a represents k_q in Table 2-25.

The photocycloaddition of acacH (0.05 M) and cyclohexene (0.5 M) (i.e. the de Mayo reaction,[56,85,86]) was run (equation 2-12) at 300 nm in the presence of TBA and DMA at 0.01 M giving relative yield (GC% ratio of **47** over I.S.) of product **47** as follows: 11.8% without DMA or TBA; 9.4% with

Table 2-2: Quenching of photocycloaddition of 2-NpCO$_2$Me and acacH by TBA in acetonitrile[a]

[TBA] (M)	Φ_p[b]	Φ^o/Φ[b]	Φ[c]	Φ^o/Φ[c]
0	0.0043	1	0.0043	1
0.0015	0.0029	1.48	0.0027	1.59
0.003	0.0022	1.95	0.0023	1.87
0.0045	0.0019	2.26	0.0022	1.96
0.006	0.0018	2.39	0.0018	2.39
$k_q\tau$ (M^{-1})		237 ± 28.8		230 ± 30.6
k_q[d] (M^{-1} s^{-1})		3.3×10^{10}		3.15×10^{10}

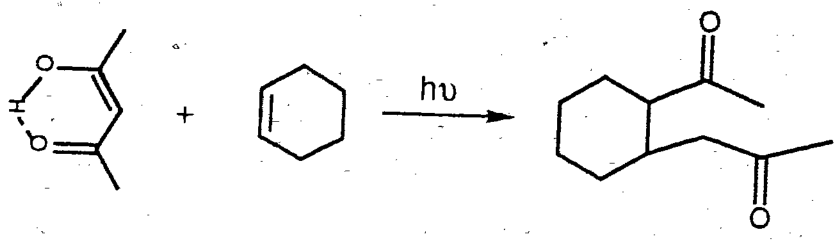
a. The solutions containing 2-NpCO$_2$Me (0.02 M), acacH (0.08 M), octadecane (as I. S., 0.005 M) and TBA (0-0.006 M) were irradiated (N$_2$ purged) at 350 nm for two hours in Apparatus II.

b. Results from the first run.

c. Results from the second run.

d. k_q was calculated by using τ of 7.3 ns which was obtained from equation 2-11 by adopting k_a of 2.47×10^8 M^{-1} s^{-1} (Table 2-25) and Σk_d of 1.18×10^8 M^{-1} s^{-1} ($1/\tau_0$, Section 2.3.3).

DMA and 10.7% with TBA. The slightly lower yield of the reaction with DMA was believed to be due to competing absorption of the incident light by DMA. The results indicated that DMA and TBA did not quench the excited state of acetylacetone.



47

2-12

Biacetyl, which has E_S = 65.3 and E_T = 57.2 kcal/mol[82] and is often energetically favorable for both singlet and triplet energy transfer, was used as a quencher for the photocycloaddition of 2-NpCO$_2$Me and acacH. Biacetyl suppressed the formation of **16** from 24% (control) to 20% at [biacetyl] = 0.002 M and from 17% (control) to 1% at [biacetyl] = 0.02 M. Oxygen also quenched the reaction: from a quantum yield of 0.0043 to 0.0013. Similarly, biacetyl (0.002 M) quenched the photocycloaddition of 2-NpR 4(R = CO$_2$Et and OMe) with acacH from 0.0033 and 0.036 to 0.0027 and 0.0026 as shown in Table 2-4. Oxygen showed similar quenching: from a quantum yield of 0.036 to 0.009 when R = 2-OMe and 0.030 to 0 when R = 2-CN.

The quenching of the photocycloaddition in acetonitrile by 1,3-pentadiene (PD, 0.02 M) in the presence of sulfuric acid (0.001 M) was attempted for the system of 2-NpCO$_2$Me (0.02 M)/acacH (0.08 M) at 300 nm. The yields of **17** and **16** were 38% and 18% without the diene and 34% and 17% with the diene. Similarly, the photoreactions were run in the presence and

Table 2-3: The effects of electron donating quenchers on quantum yields of photocycloaddition of 2-NpR and acacH in acetonitrile[a]

R	Φ_p[b] Control	DMA (0.01 M)	TBA (0.01 M)	t (Hour)
2-CO_2Me	0.0043	0.0008		4
2-CO_2Et	0.0033	0.0006	0.0013	4
2-OMe	0.036	0.029	0.031	1
2-CN	0.030	0.005	0.020	1

a. The solutions containing 2-NpR (0.02 M), acacH (0.08 M) and octadecane (as I.S., 0.005 M) with either DMA (N,N-dimethylaniline, 0.01 M) or TBA (tributylamine, 0.01 M) were irradiated (N_2 purged) against those solutions without a quencher in Apparatus II at 350 nm. Errors: ± 15%

b. The quantum yields of product formation were determined from Method II (section 4.3).

Table 2-4: The quantum yields of products of the photocycloaddition of NpR and acacH in the presence of quenchers[a]

		Φ^b		
R	Control	Oxygen[c]	Biacetyl	t (hour)
2-CO_2Me[d]	0.0043	0.0013		4
2-CO_2Et	0.0033		0.0027	6
2-OMe	0.036	0.009	0.0026	1
2-CN	0.030	0		35 min

a. Acetonitrile solutions containing NpR (0.02 M), acacH (0.08 M), biacetyl (0.002 M) and octadecane (0.005 M, as I.S.) were irradiated in Apparatus II at 31°C at 350 nm.

b. Errors: ± 15%.

c. The solution was purged with oxygen for 10 min.

d. The percentage yields for the reaction with (0.002 M) and without NND were 33% and 20% for 6 hours of irradiation. The percentage yields for the reaction with (0.002 M) and without biacetyl were 20% and 24% for 6 hours of irradiation at 300 nm. The percentage yields for the reaction with (0.02 M) and without biacetyl were 1% and 17% for 7 hours of irradiation at 300 nm.

absence of biacetyl (0.002 M). The yields of **17** and **16** were **48%** and 22% without biacetyl and 47% and 22% with biacetyl, indicating that biacetyl did not quench the reaction in the presence of sulfuric acid (0.001M). Experimental errors were estimated to be 5-10%.

2.3 The quenching of fluorescence of naphthalene derivatives

2.3.1 Acetylacetone quenching

Quenching of fluorescence of 2-NpCO$_2$Me (0.0005 M) by acacH (0.0005-0.006 M) in methylcyclohexane, acetonitrile and methanol was determined at room temperature (nitrogen purged). Since both 2-NpCO$_2$Me and acacH absorbed light around 300 nm (Figure 2-2), the percentage of light absorbed by 2-NpCO$_2$Me and fluorescence intensity were corrected according to equations 4-6 and 4-7 (Section 4.6). The Stern-Volmer correlations between $I°/I^*$ and [acacH], based on equation 2-13, were obtained from the slope of the plots and $k_q\tau_0$ were calculated (Table 2-5) from least square analysis: 75.5 M^{-1}(in methylcyclohexane, correlation coefficient γ = 0.993, monitoring at 352 nm), 28.7 M^{-1} (in acetonitrile, γ = 0.992, monitoring at 358 nm) and 24.4 M^{-1} (in methanol, γ = 0.997, monitoring at 363 nm).

$$\Phi^o_f / \Phi_f = (I°/I^*)_{max} = 1 + k_q\tau_0[\text{acacH}] \qquad 2\text{-}13$$

In equation 2-13, Φ^o_f and Φ_f are the fluorescence quantum yields of 2-NpCO$_2$Me in the absence and presence of various concentration of acacH; I° and I^* are the fluorescence intensities at the maximum emission wavelength of 2-NpCO$_2$Me in the absence and presence of acacH, corrected for the absorption of 2-NpCO$_2$Me according to equations 4-6 and 4-7. τ_0 is the

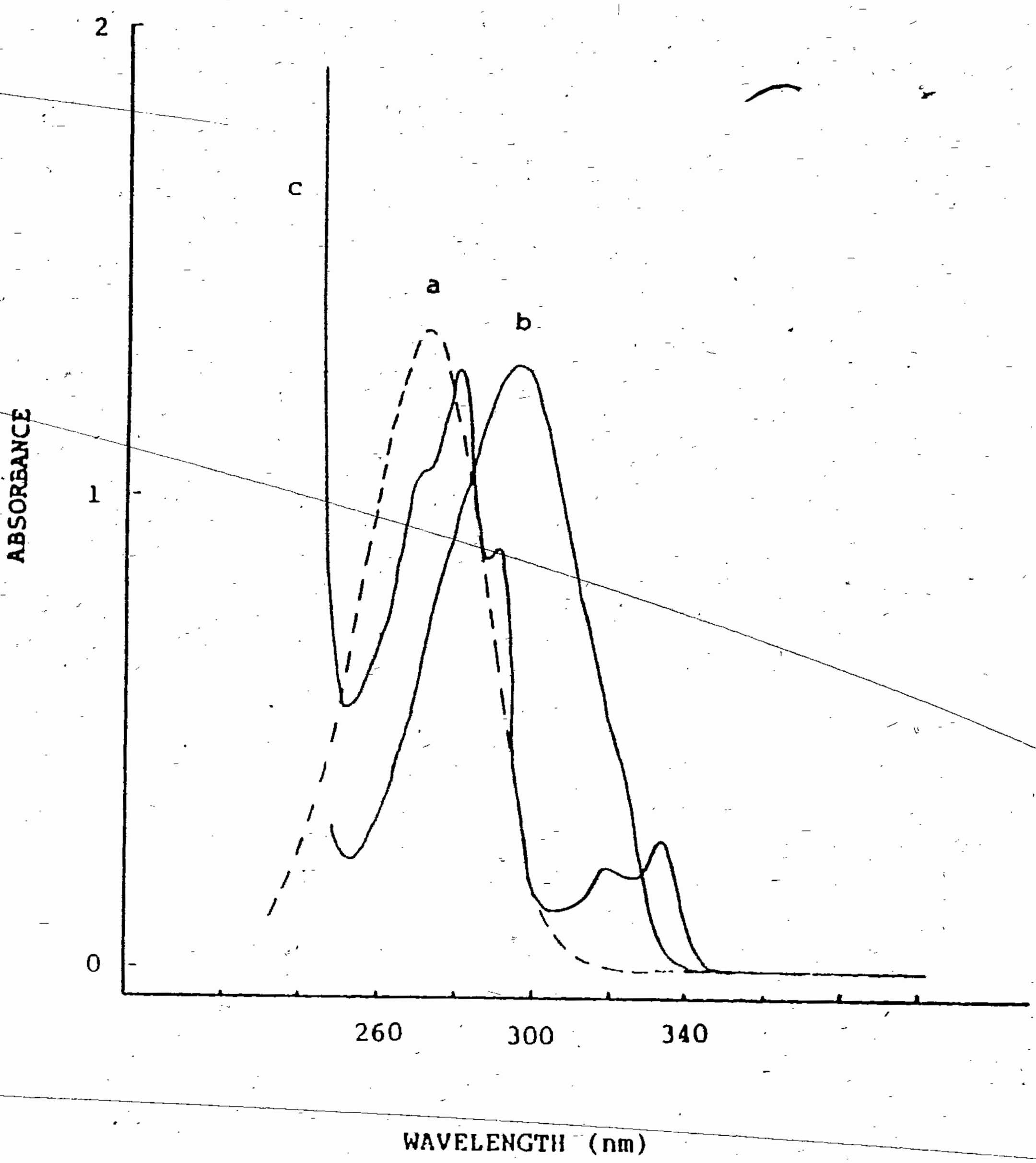


Figure 2-2: UV spectra of a) acacH (0.0002 M), b) 1-$NpCO_2Me$ (0.0002 M) in acetonitrile and c) 2-$NpCO_2Me$ (0.0002 M) in acetonitrile.

fluorescence lifetime of 2-NpCO$_2$Me without acacH and oxygen.

Quenching of fluorescence of 2-NpR (R = CO$_2$Me, CO$_2$Et, OMe and CN, 0.0005 M) by acacH (0.0005-0.006 M) in acetonitrile (nitrogen purged) was determined according to the above method to give $k_q\tau_0$: 28.7 M^{-1} for 2-NpCO$_2$Me with γ = 0.992, 28.4 M^{-1} for 2-NpCO$_2$Et with γ = 0.998, 38.6 M^{-1} for 2-NpOMe with γ = 0.96 and 57 for 2-NpCN with γ = 0.996 (Figure 2-3 and Table 2-6).

Quenching of 2-NpCO$_2$Me (0.0005 M) fluorescence by acacH (0.004-0.020 M) using various excitation wavelength (λ_{ex} = 330 nm, 340 nm and 350 nm) was examined in acetonitrile at room temperature (non-purged). The Stern-Volmer plots of $I°/I^*$ against [acacH] gave straight lines with $k_q\tau$: 11.8 M^{-1} for λ_{ex} = 330 nm (γ = 0.993), 14.3 M^{-1} for λ_{ex} = 340 nm (γ = 0.996 and 11.9 for λ_{ex} = 350 nm (γ = 0.994) (Table 2-7). τ is the fluorescence lifetime of 2-NpCO$_2$Me in the absence of acacH (not purged by N$_2$). Quenching of 2-NpCO$_2$Me (0.0005 M) fluorescence by acacH (0, 0.0027, 0.0053, 0.0079, 0.0106 and 0.0132 M) in methanol (not purged by N$_2$) at room temperature gave $k_q\tau$ of 10.1 M^{-1} with γ = 0.989.

2.3.2 Lithium acetylacetonate quenching

The absorption spectrum of 2-NpCO$_2$Me was not affected by Li(acac) or by sulfuric acid (Section 2.8), but its fluorescence was affected. Quenching of fluorescence of 2-NpR (R = CO$_2$Me, CO$_2$Et, OMe, CN and OH) in methanol by Li(acac) (0.0002, 0.0004, 0.0006, 0.0008, 0.0010 and 0.0012 M) were determined at room temperature under nitrogen purged conditions. The fluorescence intensity was corrected according to equation 4-7. The Stern-Volmer plots of $I°/I^*$ against [Li(acac)] yielded straight lines

Table 2-5: The quenching of methyl 2-naphthoate fluorescence by acacH[a]

[acacH] (M)	I°/I^*[b]		
	MCH[c]	CH_3CN	CH_3OH
0	1.0	1.0	1.0
0.0005M	1.04	1.03	1.02
0.001	1.10	1.04	1.03
0.002	1.16	1.08	1.06
0.003	1.25	1.11	1.08
0.004	1.35	1.13	
0.005	1.36	1.15	1.15
0.006	1.46	1.18	
$k_q\tau_0$ (M^{-1})	75.5 ± 3.69	28.7 ± 1.52	24.4 ± 0.866
γ:	0.993	0.988	0.997

a. Solutions of 2-$NpCO_2Me$ (0.0005 M) and acacH (0-0.006 M) were purged with nitrogen and their fluorescences were recorded with excitation wavelength at 330 nm at room temperature.

b. The intensity at 352 nm was used for calculation in MCH, that at 358 nm in CH_3CN and that 363 nm in CH_3OH.

c. Methylcyclohexane.

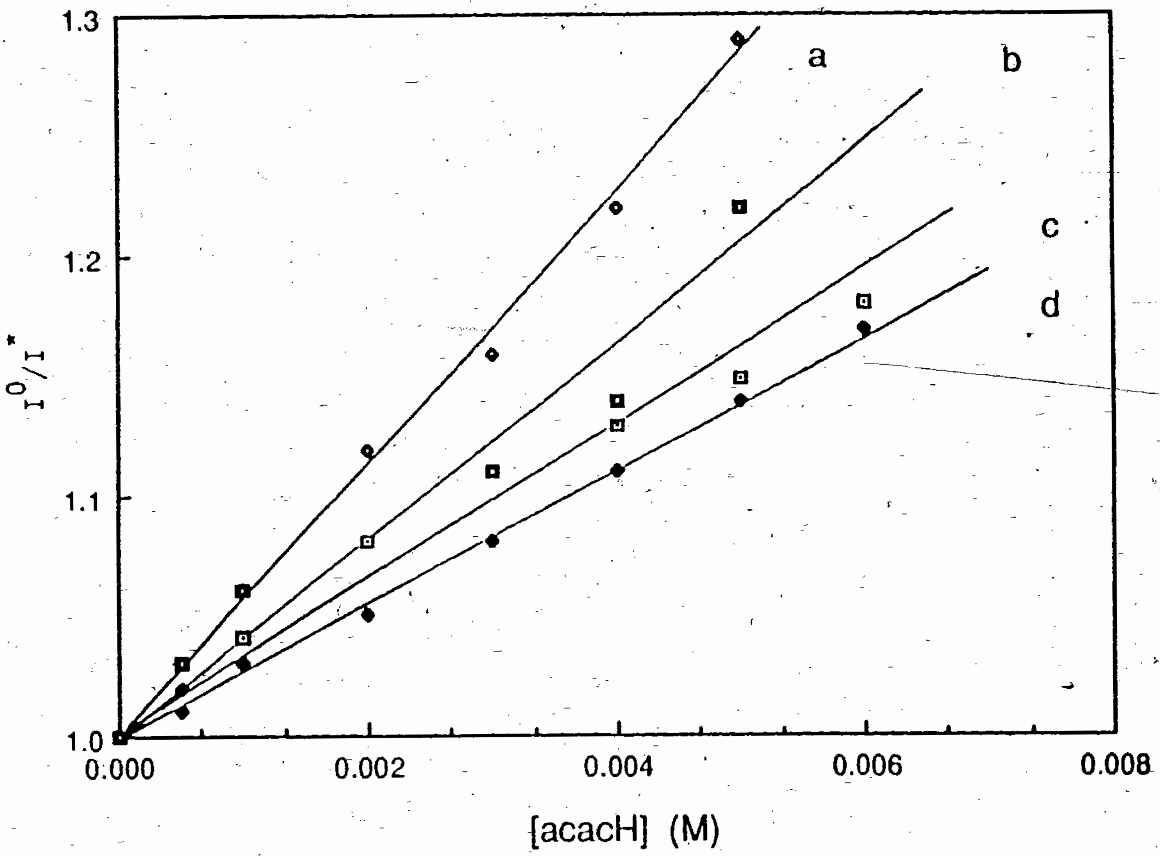


Figure 2-3: Fluorescence quenching of 2-NpR by acacH in acetonitrile (N_2 purged, Table 2-6) a) 2-NpCN, b) 2-NpOMe, c) 2-NpCO$_2$Me and d) 2-NpCO$_2$Et.

Table 2-6: The quenching of NpR fluorescence by acacH in acetonitrile at room temperature[a]

[acacH] (M)	I°/I^{*}			
	2-NpCO$_2$Me (330 nm)[b]	2-NpCO$_2$Et (330 nm)[b]	2-NpOMe (327 nm)[b]	2-NpCN (329 nm)[b]
0	1.0	1.0	1.0	1.0
0.0005	1.03	1.01	1.03	1.02
0.001	1.04	1.03	1.06	1.06
0.002	1.08	1.05		1.12
0.003	1.11	1.08	1.11	1.16
0.004	1.13	1.11	1.14	1.22
0.005	1.15	1.14	1.22	1.29
0.006	1.18	1.17		
$k_q\tau_0$ (M^{-1})	28.7[d] ± 1.52	28.4 ± 0.54	38.6 ± 3.93	57 ± 1.70
γ[c]	0.988	0.998	0.960	0.996

a. The solutions of 2-NpR (0.0005 M) and acacH (0-0.006 M) were purged with nitrogen for 10 min. b. The excitation wavelength.

c. Correlation coefficient of the Stern-Volmer plots.

d. k_q is calculated to be 3.4×10^9 M^{-1} by adopting τ_0 of 8.5 ns in acetonitrile (Section 2.3.3).

(Figure 2-4) giving $k_q\tau_0$: 205 M^{-1} for 2-$NpCO_2Me$, 209 M^{-1} for 2-$NpCO_2Et$, 80.4 M^{-1} for 2-NpOMe, 312 M^{-1} for 2-NpCN and 1100 M^{-1} for 2-NpOH (Table 2-8). In the 2-NpOH case, a new emission peaking at 500 nm appeared and increased in intensity with increasing concentrations of Li(acac), indicating that a different mechanism was involved (Figure 2-5). There was no new emission observed even with high concentration of Li(acac) (0.01, 0.02 and 0.04 M) in the 2-$NpCO_2Me$/Li(acac) case.

Quenching of 2-$NpCO_2Me$ fluorescence by sodium acetylacetonate [Na(acac), 0.0015, 0.003, 0.005, 0.008, 0.010 and 0.013 M] was determined in nitrogen purged methanol. The plots of $I°/I^*$ against [Na(acac)] showed curvature. This was most probably caused by an impurity in Na(acac) which was very difficult to purify.

2.3.3 Other quenchers

The fluorescence of non-purged solutions of 2-$NpCO_2Me$ (0.0005 M) in acetonitrile and methanol was quenched by biacetyl (0-0.00464), yielding Stern-Volmer plots with $k_q\tau$ of 95 M^{-1} (γ = 0.997, Table 2-9) and 70.8 M^{-1} (γ = 0.992, Table 2-9). The lifetime τ of the singlet excited state of 2-$NpCO_2Me$ was calculated to be 3.5 ns by adopting k_q of 2.7 x 10^{10} M^{-1} s^{-1} in acetonitrile[82] and 3.9 ns by adopting k_q of 1.8 x 10^{10} M^{-1} s^{-1} in methanol.[82] The lifetime τ_0 (N_2 purged) of the singlet excited state of 2-$NpCO_2Me$ was calculated to be 8.5 ns in acetonitrile according to equation 2-14.

Table 2-7: The quenching of methyl 2-naphthoate fluorescence by acacH in acetonitrile at various excitation wavelength[a]

[acacH]		I^o/I^{*b}	
(M)	330 nm[c]	340 nm[c]	350 nm[c]
0	1	1	1
0.004	1.06	1.07	1.04
0.008	1.08	1.12	1.10
0.012	1.14	1.18	1.14
0.016	1.19		1.20
0.020	1.24	1.29	1.23
$k_q\tau$ (M^{-1})	11.8 ± 0.59	14.3 ± 0.36	11.9 ± 0.47
γ^d:	0.993	0.996	0.994

a. The fluorescence of a solution containing 2-$NpCO_2Me$ (0.0005 M) and acacH (0-0.02 M) were measured under non-purged condition at room temperature.

b. I^* values were obtained from observed OD values by correction according to equation 4-6 and 4-7.

c. Excitation wavelength.

d. Correlation coefficient of the Stern-Volmer plots.

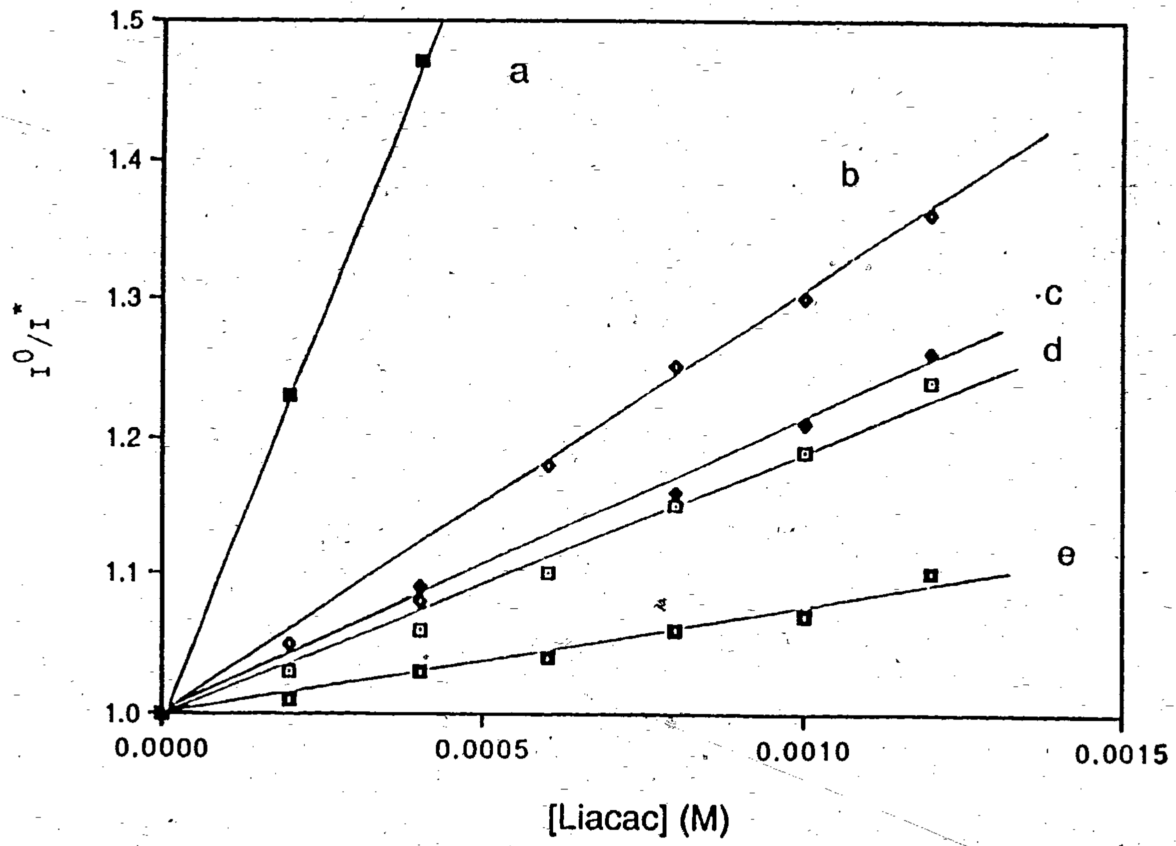


Figure 2-4: Fluorescence quenching of 2-NpR (0.0005 M) by Li(acac) in methanol (nitrogen purged) with excitation wavelength at 330 nm a) 2-NpOH, b) 2-NpCN, c) 2-NpCO$_2$Et, d) 2-NpCO$_2$Me and e) 2-NpOMe.

Table 2-8: The quenching of 2-NpR fluorescence by Li(acac)[a]

[Li(acac)](M)	$I°/I^{*}$ [b]				
R	CO_2Me	CO_2Et	OMe	CN	OH
0	1.0	1.0	1.0	1.0	1.0
0.0002	1.03	1.05	1.01	1.05	1.23
0.0004	1.06	1.09	1.03	1.08	1.47
0.0006	1.10		1.04	1.18	1.69
0.0008	1.15	1.16	1.06	1.25	1.89
0.0010	1.19	1.21	1.07	1.30	2.10
0.0012	1.24	1.26	1.10	1.36	2.23
$k_q\tau_0$ (M^{-1})	205[c]	209	80.4	312	1100
	± 8.41	± 6.58	± 4.99	± 15.79	±18.26
γ	0.99	0.996	0.996	0.998	0.999

a. The solutions containing 2-NpR (0.0005 M) and Li(acac) (0-0.0012 M) were purged with nitrogen for 10 min and their fluorescences were measured in methanol with excitation wavelength at 330 nm at room temperature.

b. I^{*} values were obtained from observed OD values by correction according to equation 4-6 and 4-7.

c. k_q is calculated to be 2.2×10^{10} M^{-1} s^{-1} by adopting τ_0 of 9.4 nm in methanol (Section 2.3.3).

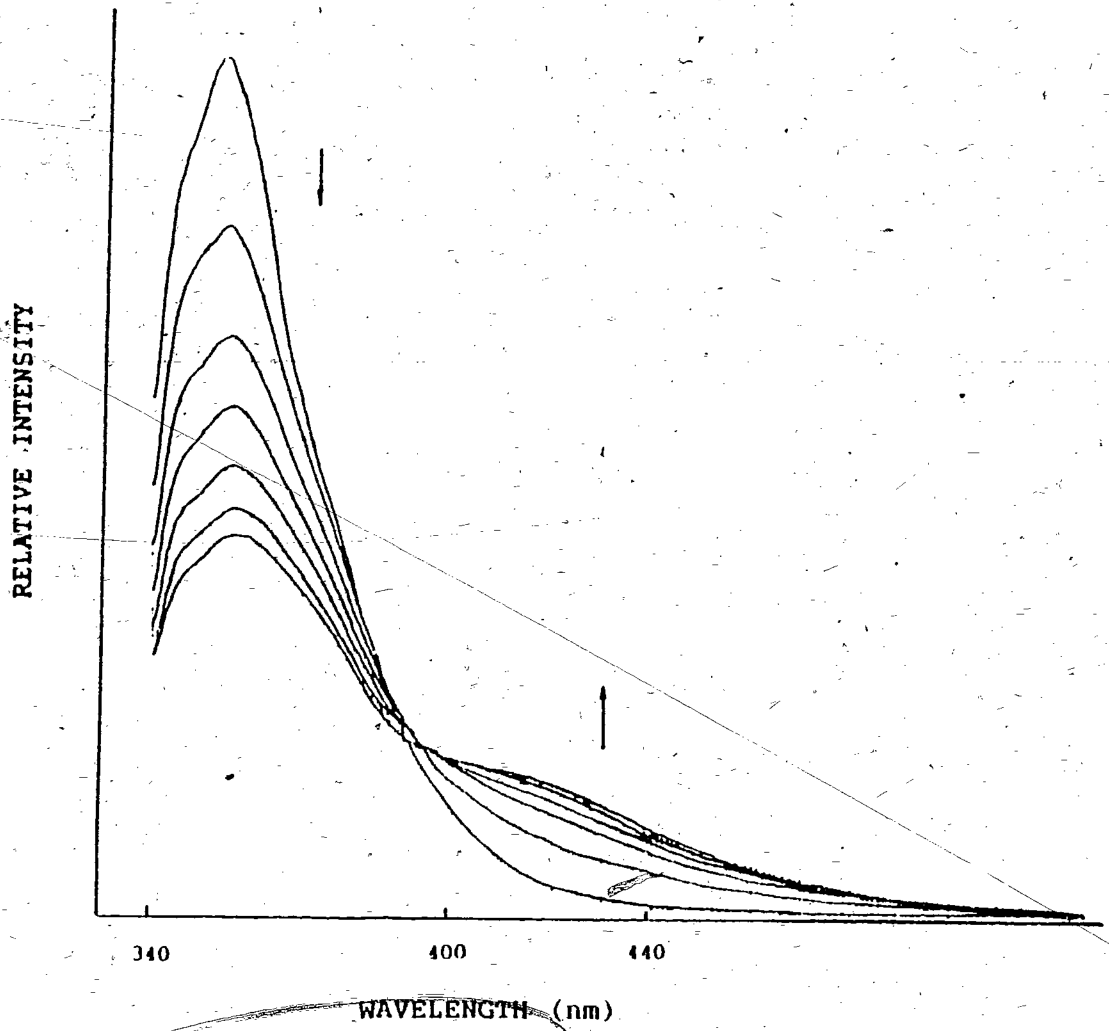


Figure 2-5: Fluorescence quenching (N_2 purged) of 2-NpOH (0.0005 M) by Li(acac) (a, 0; b, 0.0002; c, 0.0004; d, 0.0006; e, 0.0008; f, 0.001 and g, 0.0012 M) at room temperature in methanol with excitation wavelength at 330 nm.

$$k_q\tau_0/k_q\tau = 28.7/11.8$$

$$\tau_0 = (28.7/11.8)\,\tau \qquad 2\text{-}14$$

where 28.7 and 11.8 are values obtained from 2-$NpCO_2Me$ fluorescence quenching by acacH with N_2 purged and non-purged respectively (Table 2-7 and Figure 2-3), τ is the lifetime of the singlet excited state of 2-$NpCO_2Me$ (non-purged) obtained from biacetyl quenching (Table 2-9). Similarly, τ_0 (N_2 purged) in methanol was calculated to be 9.4 ns ($k_q\tau_0$ = 24.4 in Table 2-5; $k_q\tau$ = 10.1 in Section 2.3.1; τ = 3.9 ns in Table 2-9). The same quenching by biacetyl (0-0.006 M) in non-purged methylcyclohexane gave $k_q\tau$ of 65.3 M^{-1} (γ = 0.997, Table 2-10). The fluorescence of 2-$NpCO_2Me$ (0.0005 M) was quenched by oxygen after purging by O_2 for 10 min as shown in Figure 2-6. Quenching of 2-NpR (R = CO_2Me, CO_2Et, OMe and CN, 0.0005 M) fluorescence in acetonitrile by tributylamine (TBA, 0.0014-0.0084 M) was investigated in a similar manner (Table 2-11, non-purged) to afford $k_q\tau$: 127 M^{-1} (k_q of 3.6 x 10^{10} M^{-1} S^{-1} using τ of 3.5 ns in Table 2-9) for 2-$NpCO_2Me$ (γ = 0.991), 117 M^{-1} for 2-$NpCO_2Et$ (γ = 0.995), 26.8 M^{-1} for 2-NpOMe (γ = 0.991) and 177 M^{-1} for 2-NpCN (γ = 0.996, Figure 4-2). The fluorescence of 2-$NpCO_2Me$ (0.0005 M) was strongly quenched by N,N-dimethylaniline (DMA, 0.001-0.01 M, non-purged). $k_q\tau$ can not be calculated due to the overlap of the emissions from excited DMA and 2-$NpCO_2Me$. The 2-NpR (R = CO_2Me and CN, 0.0005 M) fluorescence was affected by iodomethane (CH_3I, 0.0053-0.0267 M, non-purged) and 1,2-dibromoethane (DBE, 0.0193-0.171 M, non-purged). The Stern-Volmer plots of I°/I against [CH_3I] or [DBE] yielded straight lines with $k_q\tau$ 39.9 M^{-1} for 2-$NpCO_2Me$/CH_3I

Table 2-9: Quenching of 2-NpCO$_2$Me (0.0005 M) fluorescence by biacetyl at room temperature (undegassed)

[Biacetyl][a] (M)	I°/I	[Biacetyl][b] (M)	I°/I	[Biacetyl][c] (M)	I°/I	
					470 nm[d]	359 nm[d]
0	1.0	0	1.0	0	1	1
0.00067	1.05	0.00067	1.04	0.00066	1.04	1.02
0.00133	1.11	0.00200	1.15	0.00132	1.09	1.06
0.00200	1.17	0.00332	1.20	0.00200	1.14	1.08
0.00266	1.23	0.00464	1.30	0.00331	1.24	
0.00332	1.30	0.00600	1.42	0.00396	1.29	1.16
0.00398	1.38	0.00737	1.53			
0.00464	1.43					
$k_q\tau$ (M^{-1})	95		70.8		74.0	41.4
	± 2.23		±2.79		± 1.12	± 1.78

a. The fluorescences were measured in non-purged acetonitrile with excitation wavelength at 330 nm. τ was calculated to be 3.5 ns ± 0.08 by adopting energy transfer rate constant of 2.7 x 10^{10} M^{-1} s^{-1} in acetonitrile from Ref. 82 as k_q.

b. The fluorescences were measured in non-purged methanol with excitation wavelength at 300 nm. τ was calculated to be 3.9 ns ± 0.15 by adopting energy transfer rate constant of 1.8 x 10^{10} M^{-1} s^{-1} in methanol from Ref. 82 as k_q.

c. The fluorescences were measured in the presence of H_2SO_4 (0.0935 M) with excitation wavelength at 330 nm (non-purged).

d. Monitoring wavelength.

Table 2-10 The quenching of methyl 2-naphthoate (0.0005 M) fluorescence (non-purged) at room temperature

[PD][a]	I°/I	[Na(acac)][b]	I°/I	[Biacetyl][c]	I°/I
0	1.0	0	1.0	0	1
0.0099	1.05	0.0015	1.14	0.0005	1.06
0.0231	1.18	0.003	1.37	0.001	1.08
0.0363	1.30	0.005	1.76	0.002	1.12
0.0495	1.42	0.008	2.51	0.003	1.22
0.0626	1.56	0.010	3.14	0.004	1.27
				0.005	1.33
				0.006	1.41
$k_q\tau$ (M^{-1})	9.08 ± 0.32		Curve	65.3 ± 2.39	

a. The fluorescences were taken in acetonitrile with excitation wavelength at 330 nm.

b. The fluorescences were taken in methanol with excitation wavelength at 330 nm.

c. The fluorescences were taken in cyclohexane with excitation wavelength at 300 nm.

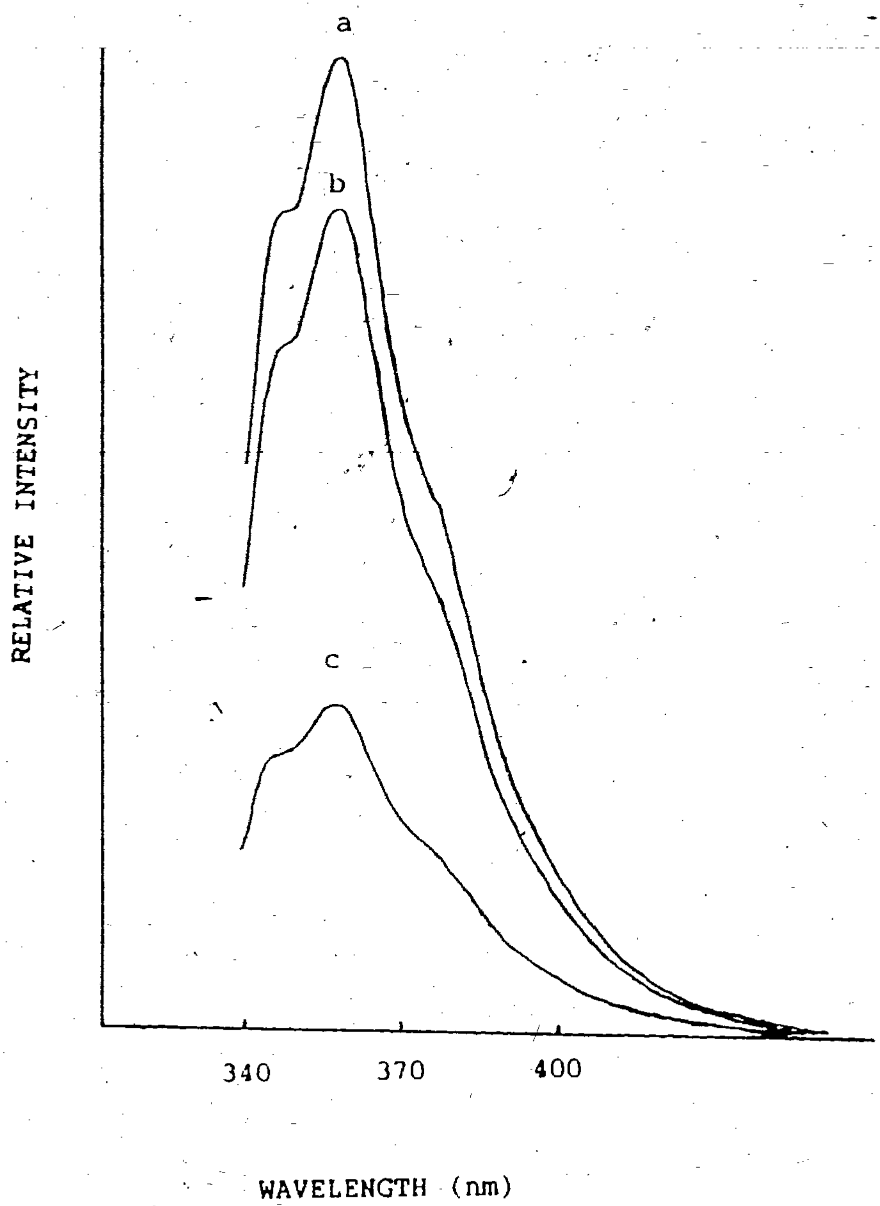


Figure 2-6: Fluorescence quenching of 2-$NpCO_2Me$ (0.0005 M) by oxygen in acetonitrile with excitation wavelength at 330 nm a) nitrogen purged for 10 min; b) non-purged and c) oxygen purged for 10 min.

Table 2-11: The quenching of 2-NpR fluorescence by tributylamine (TBA) in acetonitrile[a]

2-NpCO$_2$Me		2-NpOMe		2-NpCN		2-NpCO$_2$Et	
[TBA] (M)	I°/I	[TBA] (M)	I°/I	[TBA] (M)	I°/I	[TBA] (M)	I°/I
0	1.0	0	1.0	0	1.0	0	1.0
0.0014	1.15	0.0056	1.11	0.0028	1.43	0.0014	1.13
0.0028	1.34	0.0098	1.24	0.0042	1.69	0.0028	1.28
0.0042	1.51	0.014	1.36	0.0056	1.93	0.0042	1.45
0.0056	1.69	0.0195	1.47	0.007	2.18	0.0056	1.62
0.007	1.85	0.0251	1.68	0.0084	2.49	0.007	1.82
$k_q\tau$ (M^{-1})	127[b]		26.8		177		117
	±1.64		±1.25		± 5.27		±4.05
γ[c]	0.999		0.991		0.996		0.995
	330 nm[d]		320 nm[d]		330 nm[d]		330 nm[d]

a. The fluorescences of the solutions containing 2-NpR (0.0005 M) and TBA (0-0.0251 M) were measured non-purged at room temperature.

b. k_q was calculated to be 3.6 ± 0.083 x 10^{10} M^{-1} s^{-1} by adopting τ of 3.5 ns (Table 2-9).

c. Correlation coefficient.

d. Excitation wavelength.

Table 2-12: The quenching of NpR fluorescence by heavy atom solvents in acetonitrile[a]

2-NpCO$_2$Me		2-NpCN		2-NpCO$_2$Me	
[CH$_3$I] (M)	I°/I	[CH$_3$I] (M)	I°/I	[BrCH$_2$CH$_2$Br] (M)	I°/I
0	1.0	0	1.0	0	1.0
0.0053	1.20	0.0053	1.21	0.0193	1.02
0.0107	1.39	0.0107	1.51	0.0385	1.05
0.016	1.63	0.016	1.70	0.0577	1.09
0.0214	1.86	0.0214	1.93	0.0958	1.21
0.0267	2.05	0.0267	2.19	0.134	1.33
				0.171	1.43
$K_q\tau$ (M^{-1})	39.9 ± 0.75		44.4 ± 1.08	2.64 ± 0.15	
γ^b	0.999		0.998		0.984

a. The fluorescences of the solutions containing NpR (0.0005 M) and CH$_3$I (0-0.0267 M) or BrCH$_2$CH$_2$Br (0-0.171 M) were taken non-purged with excitation wavelength at 330 nm.

b. Correlation coefficient.

(γ = 0.998), 44.4 M^{-1} for 2-NpCN/CH_3I (γ = 0.998) and 2.64 M^{-1} for 2-$NpCO_2Me$/DBE (γ = 0.984, Table 2-12). 2-$NpCO_2Me$ fluorescence was quenched by 1,3-pentadiene (0.0099-0.0626 M) in non-purged acetonitrile yielding a straight line with $k_q\tau$ of 9.08 M^{-1} (γ = 0.995, Table 2-10).

The fluorescence of 2-$NpCO_2Me$ (0.0005 M) was quenched by sulfuric acid (0.0063-0.0375 M, non-purged) giving $k_q\tau$ of 35.3 M^{-1} (Table 2-13). k_q was calculated to be 1.01 x 10^{10} $M^{-1}S^{-1}$ using τ of 3.5 ns (Table 2-9). A new broad emission at 470 nm appeared with an isosbestic point at 414 nm and increased in intensity with increasing concentration of H_2SO_4 (Figure 2-7 and Figure 2-8). Similar quenching of 2-$NpCO_2Me$ (0.0005 M) fluorescence by H_2SO_4 (0-0.0562 M) in non-purged methanol occurred giving $k_q\tau$ of 6.5 M^{-1} (γ = 0.995) and a new broad emission at 470 nm (Figure 2-9). The fluorescence of 2-$NpCO_2Me$ (0.0005 M, at 359 nm) and the new band (at 470 nm) were quenched in non-purged acetonitrile at [H_2SO_4] of 0.0935 M by acacH (0-0.0081 M) yielding two straight lines with $k_q\tau$ = 63.4 M^{-1} for monitoring at 359 nm and $k_q\tau$ = 128 M^{-1} for monitoring at 470 nm (Table 2-14, Figure 2-10 and Figure 2-11).

The fluorescence of 2-$NpCO_2Me$ (0.0005 M, at 359 nm) and the new band (at 470 nm, [H_2SO_4] = 0.0935 M) were quenched in non-purged acetonitrile by biacetyl (0-0.00396 M) giving $k_q\tau$ of 74.0 M^{-1} (monitoring at 470 nm) and 41.4 M^{-1} (monitoring at 359 nm, Table 2-9). The quenching of 2-$NpCO_2Me$ (0.0005 M, non-purged) fluorescence by sulfuric acid (0.0124-0.0496 M) in the presence of acacH (0.08 M) gave $k_q\tau$ of 13.2 M^{-1} when monitoring at 359 nm in acetonitrile; the broad emission at 470 nm appeared when H_2SO_4 was added and increased in intensity with increasing concentration of H_2SO_4 (Table 2-13 and Figure 2-12). However, the same quenching in the presence of low concentrations of sulfuric acid (0.00017-0.00165 M) was not significant enough to be recorded. Similarly, the fluorescence of 1-NpCO$_2$Me (0.0005 M, at 362 nm) was quenched by H_2SO_4 (0-0.0562 M, non-purged giving $k_q\tau$ of 8.7 M^{-1} (Table 2-13). During the course of quenching, a new broad emission at 470 nm appeared with an isosbestic point at 423 nm and increased in intensity with increasing concentration of H_2SO_4 (Figure 2-13 and Figure 2-8). The fluorescence of 1-NpCO$_2$Me (0.0005 M) and the new band (at 470 nm) were quenched by acacH (0-0.0064 M) in non-purged acetonitrile/[H_2SO_4] (0.0935 M) solutions. Two curves were plotted (Table 2-14, Figure 2-14 and Figure 2-15). The fluorescence of 2-NpOMe (0.0005 M) in non-purged acetonitrile was not quenched by sulfuric acid (0.0063 and 0.0375 M)

2.3.4 Temperature [illegible]ect on the fluorescence quenching:

Quenching of 2-NpCO$_2$Me (0.0005 M) fluorescence intensity by acacH (0.003-0.015 M, N_2 purged) was examined at 7°C, 22°C and 50°C. The Stern-Volmer plots of $I°/I^*$ against [acacH] yielded straight lines (Figure 2-16). The $k_q\tau_0$ values, 31 M^{-1} for T = 7°C , 24 M^{-1} for T = 22°C and 8.5 M^{-1} for T = 50°C (Table 4-5), decrease with increasing temperature, consistent with the existence of a reversible exciplex[131,132]. The plot of Log k_q against 1/T yielded a straight line with a positive slope typical of a negative temperature effect[131,132] on the fluorescence quenching (Figure 2-16).

2.4 Heavy atom effect on the photocycloaddition

Table 2-13: Quenching of $NpCO_2Me$ (0.0005 M) fluorescence in acetonitrile (non-purged) by H_2SO_4 at room temperature

$[H_2SO_4]$ (M)	$I°/I^a$	$I°/I^b$	$[H_2SO_4]$ (M)	$I°/I^c$
0	1	1	0	1
0.0063	1.29	1.07	0.0124	1.15
0.0125	1.45	1.13	0.0248	1.33
0.0250	1.88	1.25	0.0372	1.51
0.0375	2.36	1.35	0.0496	1.64
0.0504				
0.0562		1.49		
$k_q\tau$	$35.3^d \pm 1.14$	8.7 ± 0.31		13.2 ± 0.41

a. Quenching of 2-$NpCO_2Me$ fluorescence intensity by H_2SO_4 (0-0.0375 M) with excitation wavelength at 300 nm.

b. Quenching of 1-$NpCO_2Me$ fluorescence intensity by H_2SO_4 (0-0.0562 M) with excitation wavelength at 320 nm.

c. Quenching of 2-$NpCO_2Me$ fluorescence intensity by H_2SO_4 (0-0.0496 M) in the presence of acacH (0.08 M) with excitation wavelength at 300 nm.

d. k_q was calculated to be $1.01 \pm 0.032 \times 10^{10}\ M^{-1}\ S^{-1}$ by adopting τ of 3.5 ns (Table 2-9).

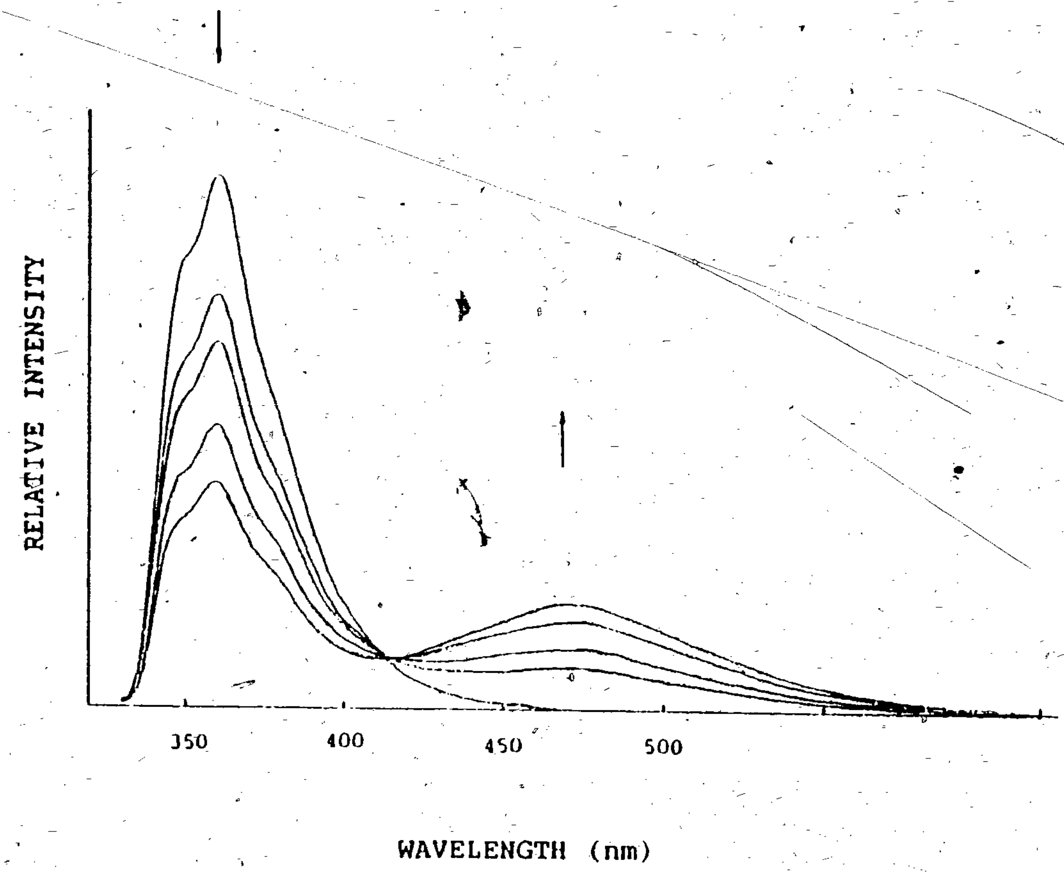


Figure 2-7: Quenching of fluorescence of 2-NpCO$_2$Me (0.0005 M) by sulfuric acid (0, 0.0063, 0.0125, 0.025 and 0.0375 M) in non-purged acetonitrile at room temperature with excitation wavelength at 300 nm.

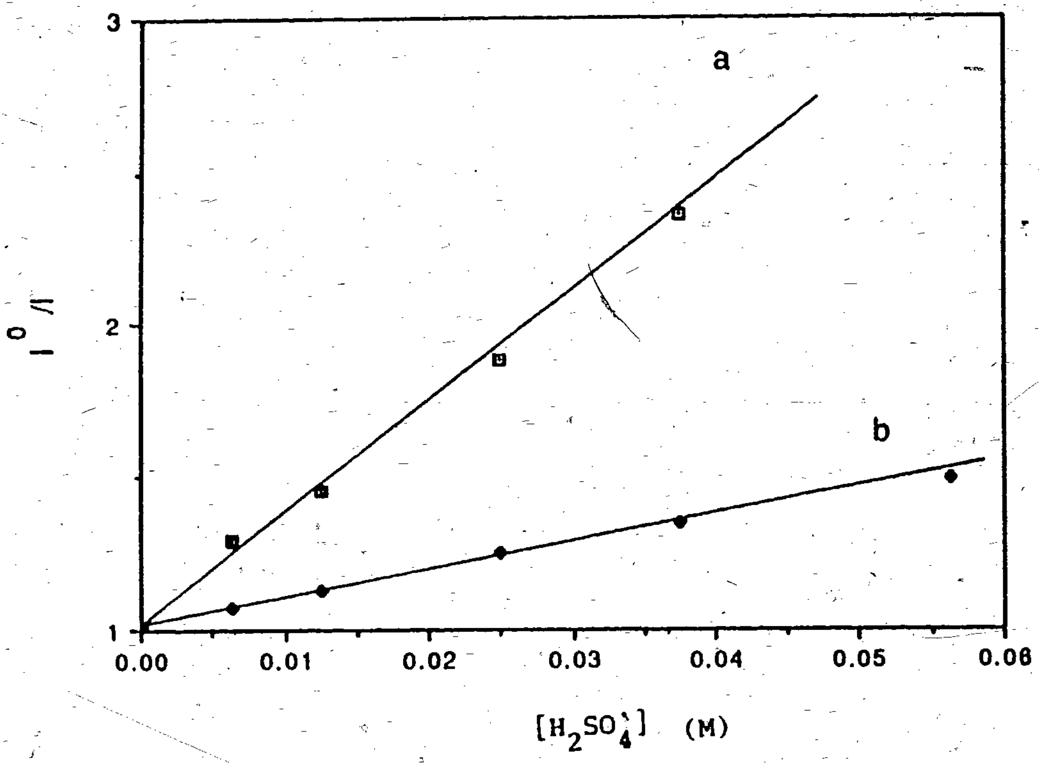


Figure 2-8: Quenching of $NpCO_2Me$ (0.0005 M) fluorescence by sulfuric acid (0-0.0562 M) in non-purged acetonitrile at room temperature a) 2-$NpCO_2Me$ with excitation wavelength at 300 nm and b) 1-$NpCO_2Me$ with excitation wavelength at 320 nm.

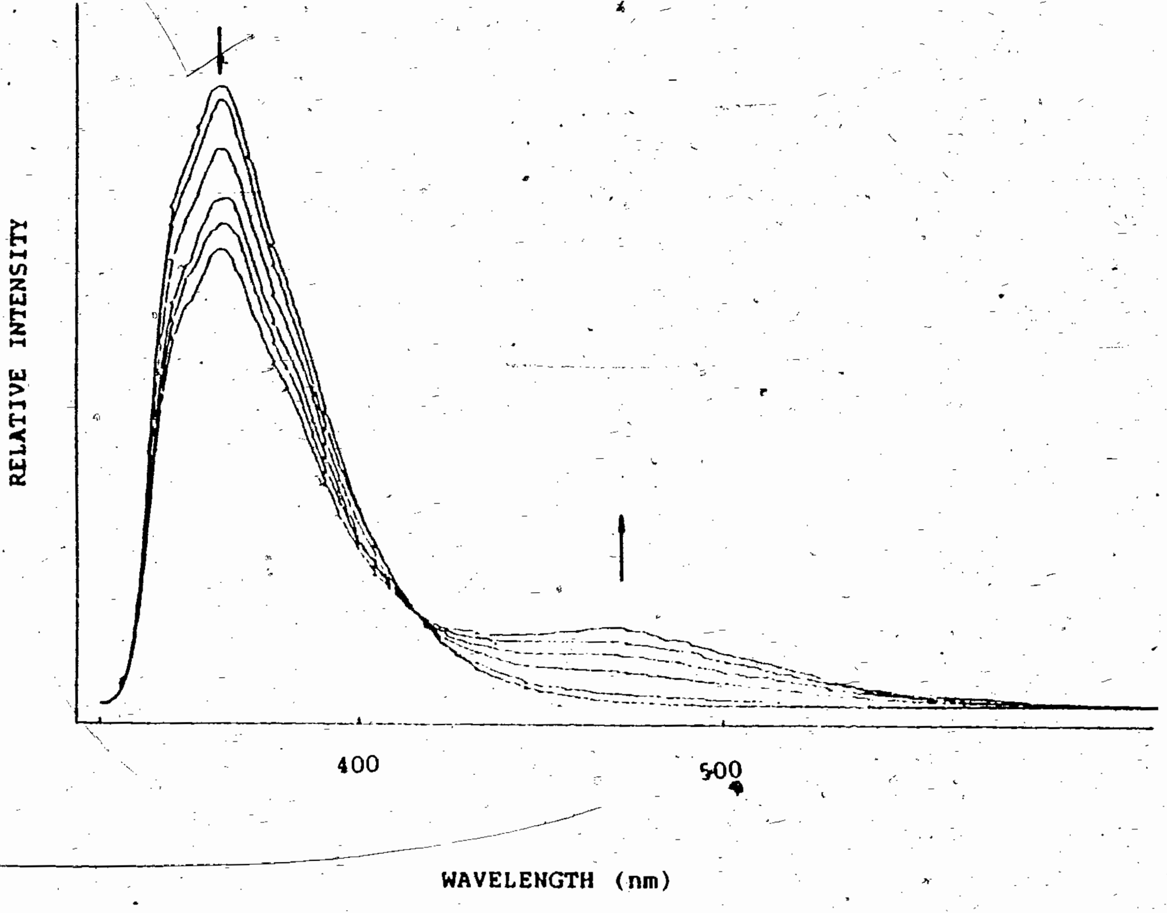


Figure 2-9: Quenching of fluorescence of 2-NpCO$_2$Me (0.0005 M) by sulfuric acid (0, 0.0063, 0.0188, 0.0313, 0.0437 and 0.0562 M) in non-purged methanol at room temperature with excitation wavelength at 300 nm.

Table 2-14: Quenching of $NpCO_2Me$ (0.0005 M) fluorescence in non-purged acetonitrile in the presence of H_2SO_4 (0.0935 M) by acacH at room temperature

[acacH] (M)	2-$NpCO_2Me$[a] I°/I		1-$NpCO_2Me$[b] I°/I	
	359 nm[c]	470 nm[c]	362 nm [c]	470 nm[c]
0	1	1	1	1
0.0016	1.10	1.18	1.28	1.24
0.0032	1.19	1.38	1.56	1.44
0.0048	1.30	1.57	2.00	1.78
0.0064	1.39	1.79	2.50	2.10
0.0081	1.52	2.04		
$k_q\tau$	63.4 ± 1.37	128 ± 3.08	232 ± 18.76	171 ±10.28

a. The fluorescences of solutions containing 2-$NpCO_2Me$, H_2SO_4 (0.0935 M) and acacH (0-0.0081 M) were measured with excitation wavelength at 330 nm.

b. The fluorescences of solutions containing 1-$NpCO_2Me$, H_2SO_4 (0.0935 M) and acacH (0-0.0064 M) were measured with excitation wavelength at 320 nm.

c. Monitoring wavelength.

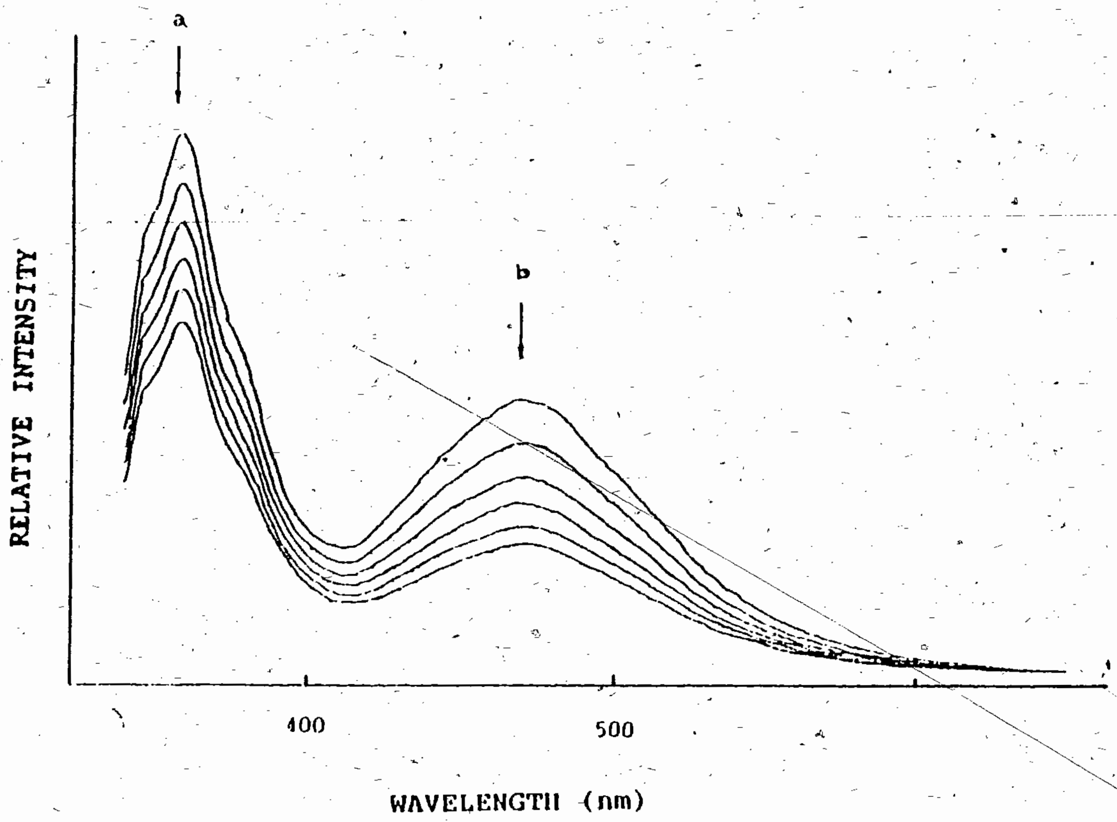


Figure 2-10: Quenching of 2-$NpCO_2Me$ (0.0005 M) fluorescence by acacH (0, 0.0016, 0.0032, 0.0048, 0.0064 and 0.0081 M) in the presence of H_2SO_4 (0.0935 M) at room temperature (non-purged) with excitation wavelength at 330 nm a) fluorescence of 2-$NpCO_2Me$ and b) emission of protonated ^{1}2-$NpCO_2Me$.

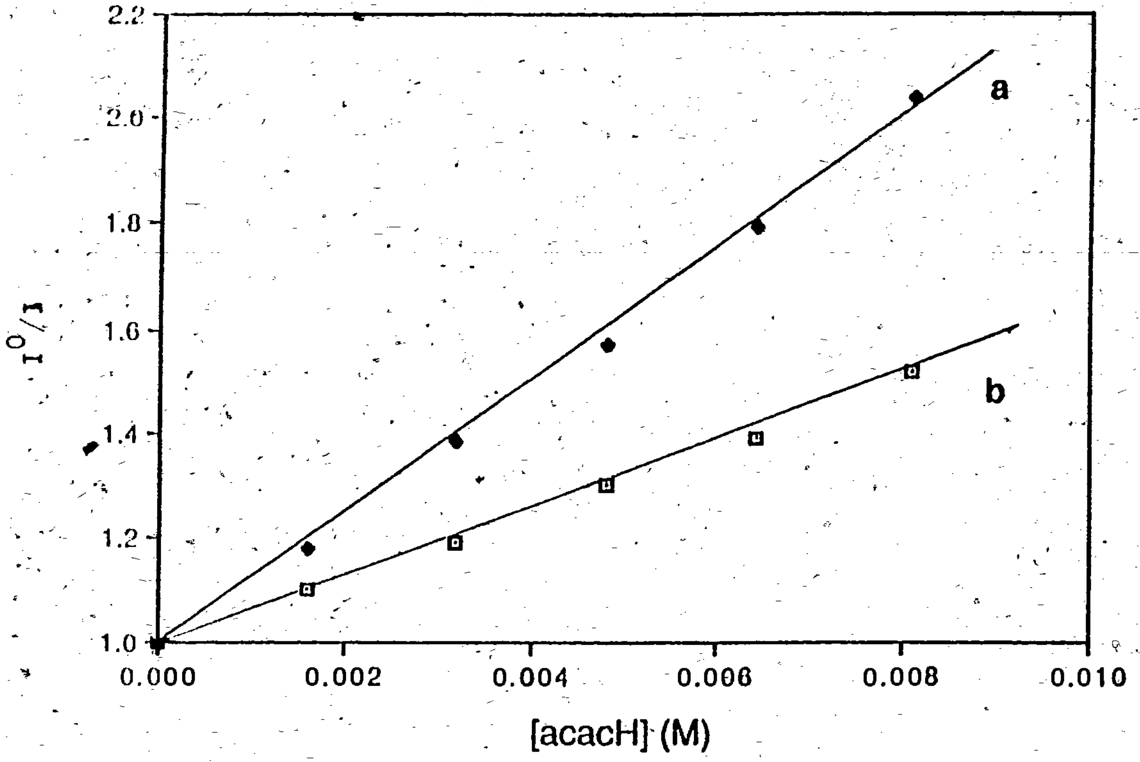


Figure 2-11: Quenching of 2-NpCO$_2$Me (curve b, 0.0005 M, monitoring at 359 nm) and protonated ^{1}2-NpCO$_2$Me (curve a, monitoring at 470 nm) fluorescence in the presence of sulfuric acid (0.0935 M) by acacH (0-0.0081 M) in non-purged acetonitrile at room temperature with excitation wavelength at 330 nm.

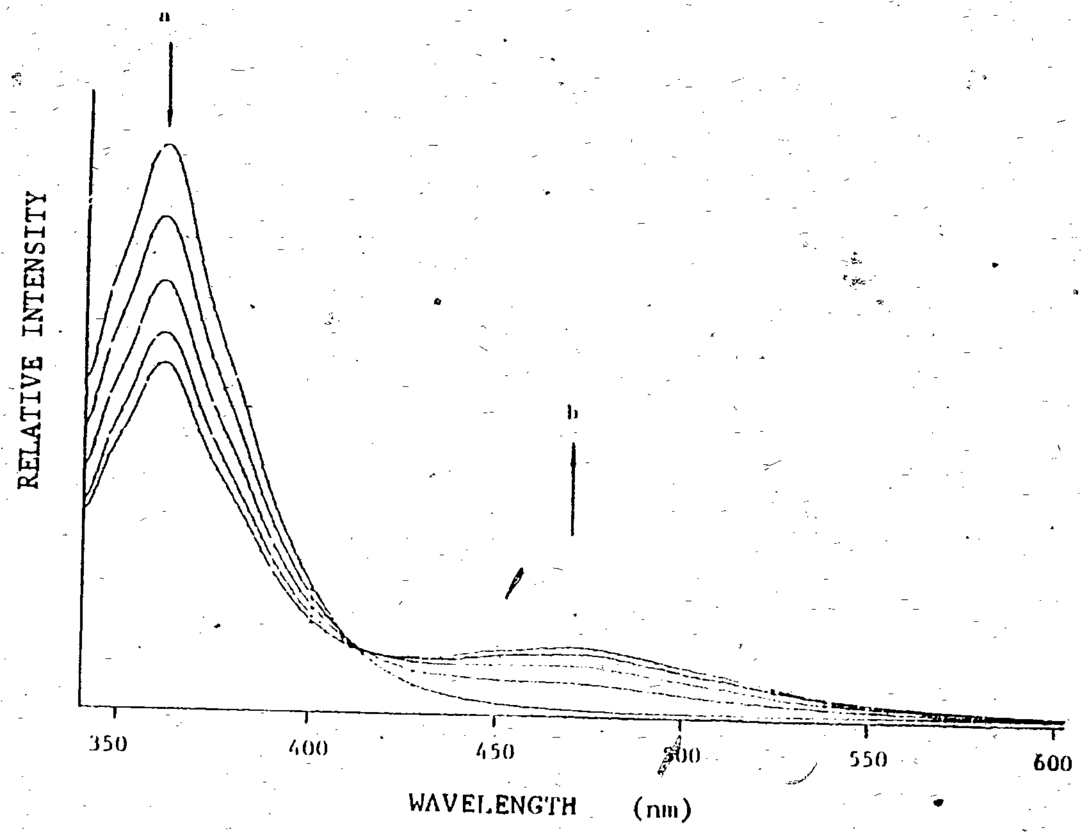


Figure 2-12: Quenching of fluorescence of 2-$NpCO_2Me$ (0.0005 M) in the presence of acacH (0.08 M) by sulfuric acid (0, 0.0124, 0.0248, 0.0372 and 0.0496 M) in non-purged acetonitrile at room temperature with excitation wavelength at 330 nm.

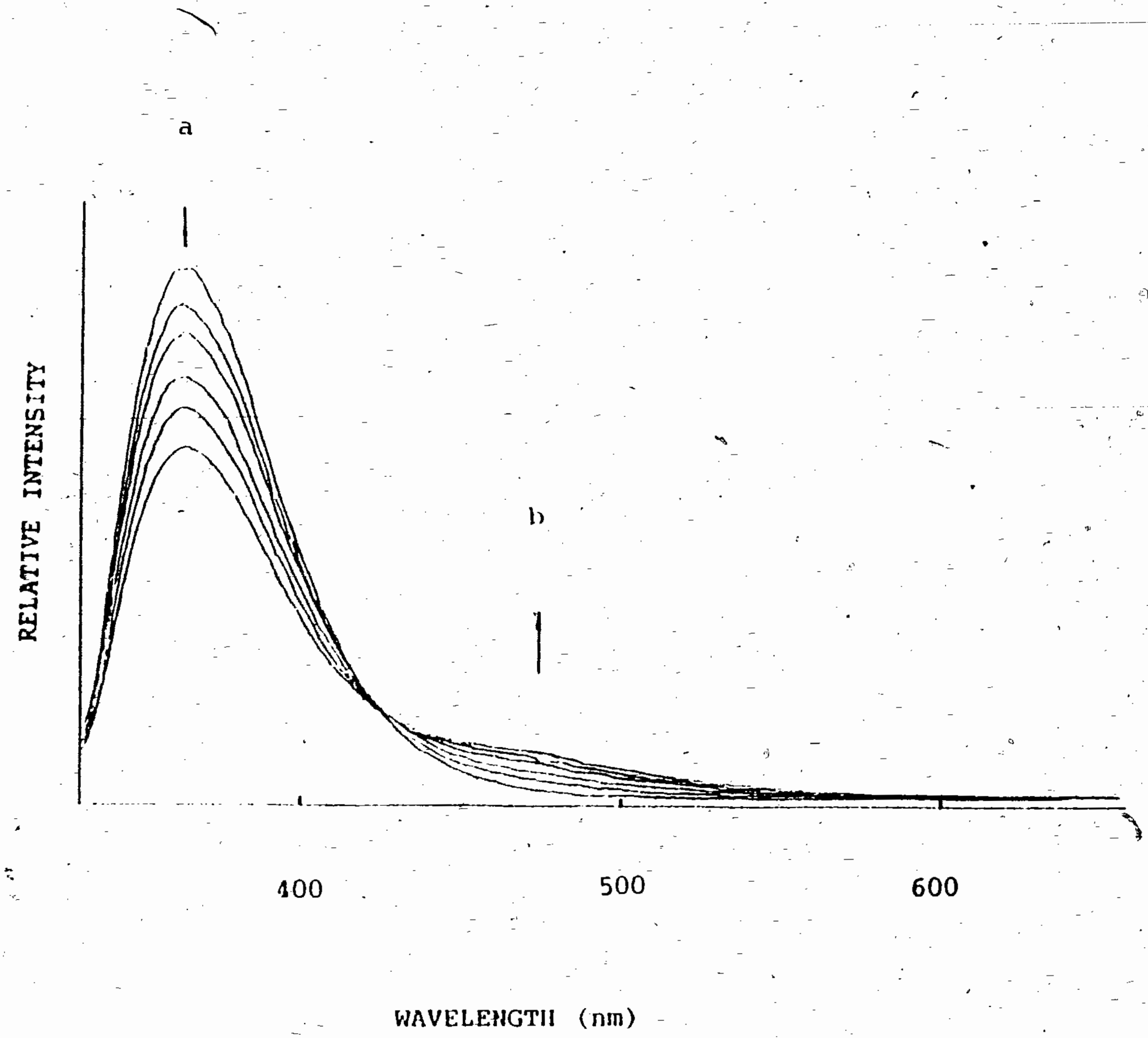


Figure 2-13: Quenching of 1-$NpCO_2Me$ (0.0005 M) fluorescence by sulfuric acid (0, 0.0063, 0.0125, 0.0250, 0.0375 and 0.0562 M) in non-purged acetonitrile at room temperature with excitation wavelength at 320 nm.

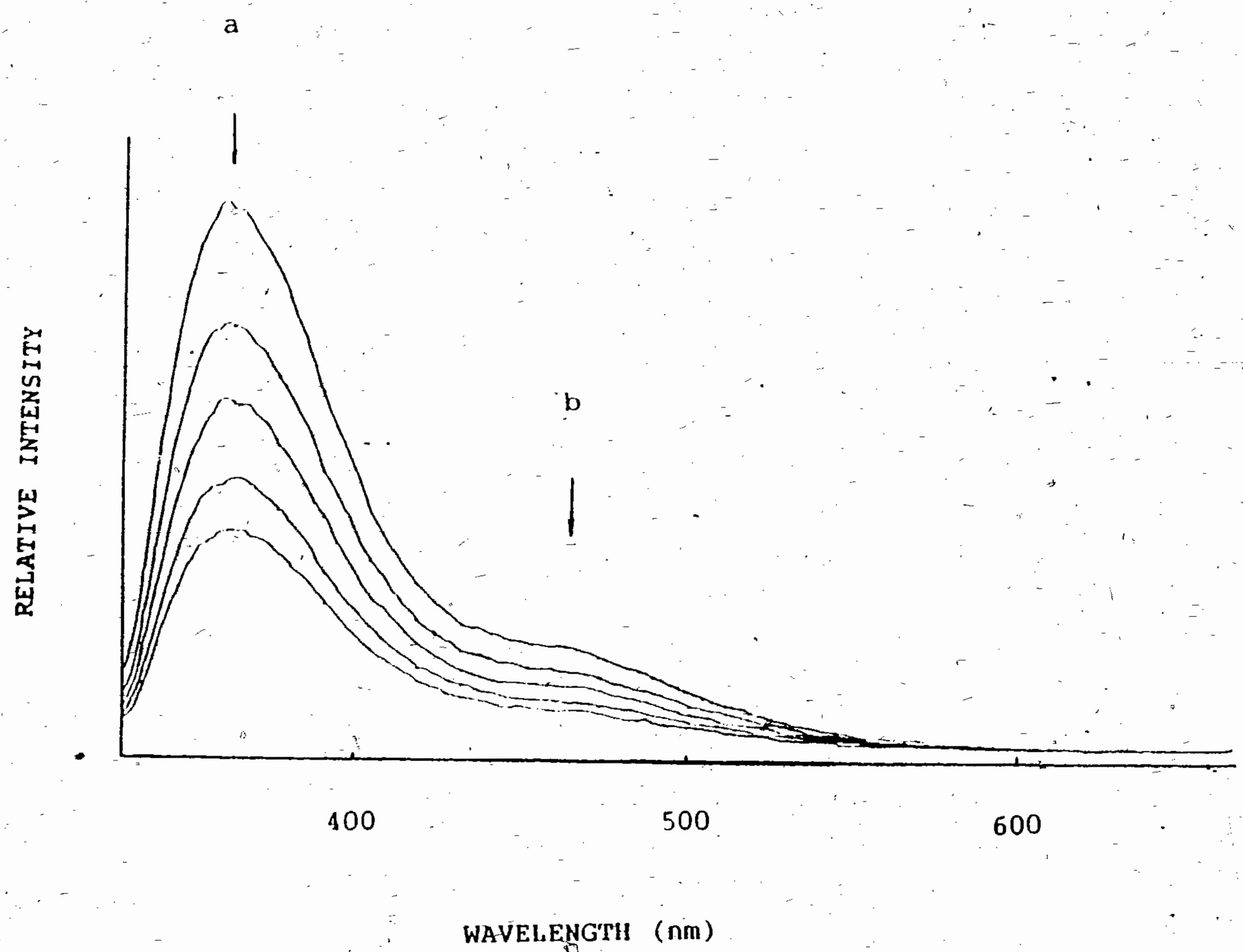


Figure 2-14: Quenching of 1-NpCO$_2$Me (0.0005 M) and protonated ^{1}1-NpCO$_2$Me fluorescence in the presence of sulfuric acid (0.0935 M) by acacH (0, 0.0016, 0.0032, 0.0048 and 0.0064 M) in non-purged acetonitrile at room temperature with excitation wavelength at 320 nm a) fluorescence of 1-NpCO$_2$Me and b) emission of protonated ^{1}1-NpCO$_2$Me.

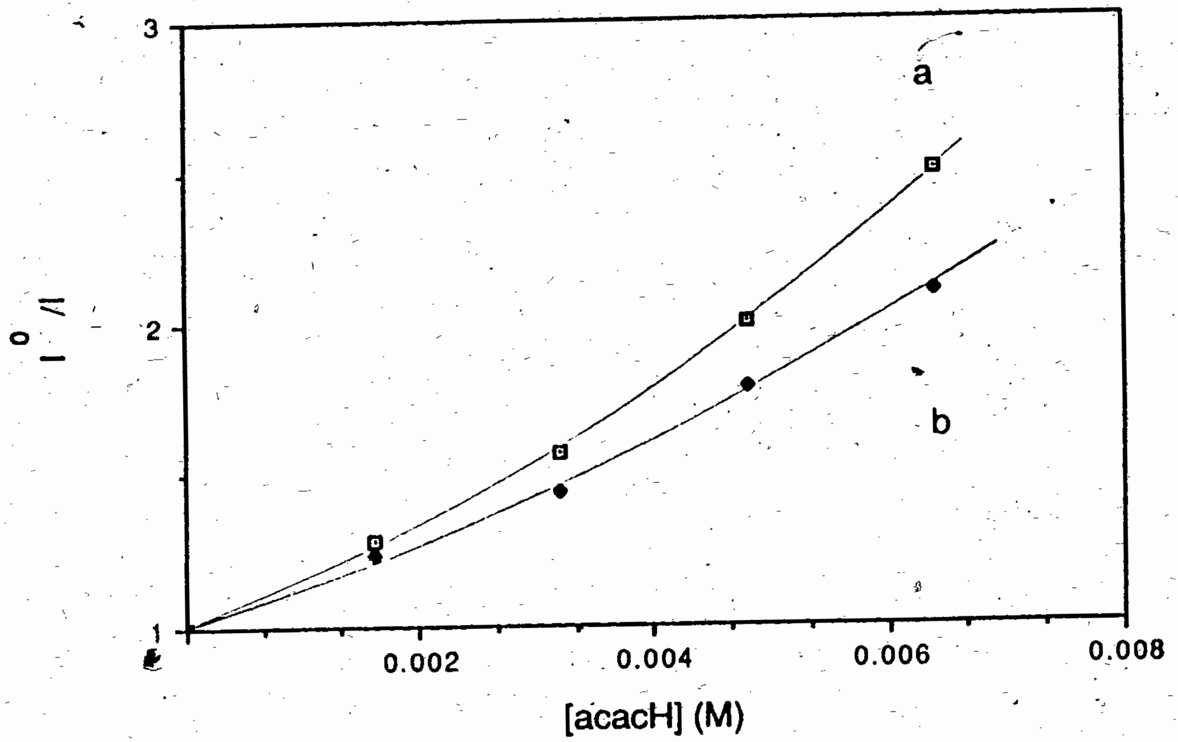


Figure 2-15: Quenching of 1-$NpCO_2Me$ (curve a, 0.0005 M, monitoring at 362 nm) and protonated ^{1}1-$NpCO_2Me$ (curve b, monitoring at 470 nm) fluorescence in the presence of sulfuric acid (0.0935 M) by acacH (0-0.0064 M) in non-purged acetonitrile at room temperature with excitation wavelength at 320 nm.

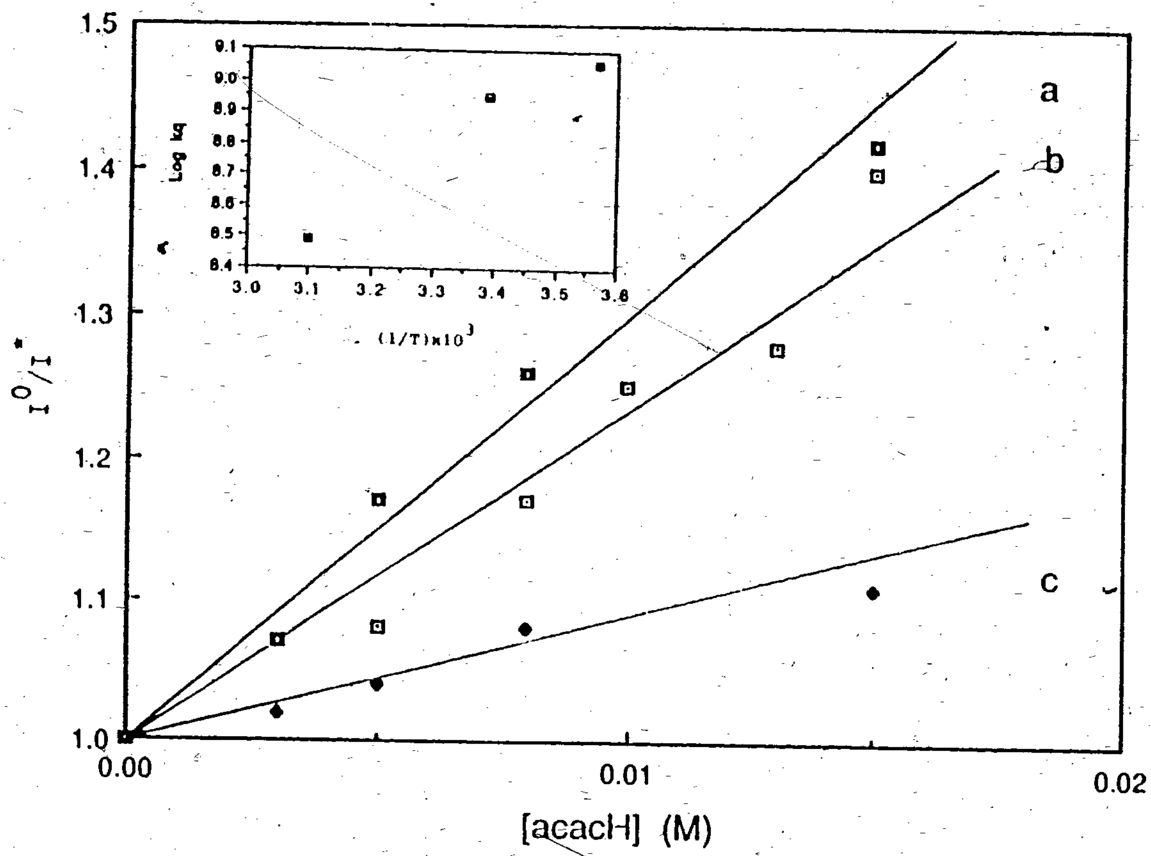


Figure 2-16: Fluorescence quenching of 2-NpCO$_2$Me (0.0005 M) by acacH in acetonitrile (nitrogen purged) at various temperatures with excitation wavelength at 330 nm a) at 7°C, b) at 22°C and c) at 50°C. The insert is the plot of Log k_q *vs* 1/T for quenching of 2-NpCO$_2$Me fluorescence by acacH in acetonitrile.

Table 2-15: The effects of methyl iodide on photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile[a]

$[CH_3I]$ (M)	Formation of **16** (%)[b]	Formation of **17** (%)[b]
0	17	1
0.001	14.5	1.5
0.002	14.3	4.8
0.003	13.9	5.2
0.004	13.5	5.5

a. The solutions containing 2-NpCO$_2$Me (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and CH_3I (0-0.004 M) were irradiated for 4 hours in apparatus II at 350 nm. Errors: ± 15%.

b. Reported in yield of formation of compound **16** and **17**. Conversion of 2-NpCO$_2$Me: 17-23%.

Table 2-16: Effects of 1,2-dibromoethane (DBE) on the photocycloaddition of methyl 2-naphthoate (14) and acacH in acetonitrile[a]

[DBE] (M)	[DBE]/[**14**]	Φ_p(**16**)[b]	Φ_p(**17**)[b]
0	0	0.0043	0.0002
0.001	0.05	0.0039	0.0002
0.002	0.10	0.0040	0.0002
0.004	0.20	0.0038	0.00025
0.005	0.25	0.0034	0.0002

a. The solution containing 2-NpCO$_2$Me (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and DBE (0-0.005 M) were irradiated (N$_2$ purged) for 4 hours using apparatus II at 350 nm.

b. Quantum yields of **16** and **17** were determined by method II (Section 4.3).

The dependence of the formation of **16** and **17** in the photocycloaddition of 2-NpCO$_2$Me (0.02 M) and acacH (0.08 M) on the concentration of the heavy atom compound, iodomethane (0.001-0.004 M), was examined at 350 nm in acetonitrile. The yield of **16** slightly decreased, within experimental error, when the concentration of CH$_3$I was increased. The yield of **17** increased from 1% to 5.5% when the concentration of CH$_3$I was increased (Table 2-15). After GC analysis, the irradiated solutions and ether (20 mL) were combined together and extracted with water (6 mL). The water layer showed a pH value of 4.5-5 by pH test paper indicating the formation of an acid during the irradiation.

Under the same conditions, the above reaction was run using 1,2-dibromoethane (0.001-0.005 M) instead of CH$_3$I as a heavy atom compound. The quantum yields of **17** were essentially constant, within experimental error, with the increasing concentration of DBE. The quantum yields of **16** showed a slight decrease from 0.0043 to 0.0034 with increasing concentration of DBE (Table 2-16).

Similarly, the photocycloaddition of 2-NpCN (0.02 M) and acacH (0.08 M) was examined in the presence of CH$_3$I (0.001-0.004 M). Product **38** was the only product obtained and the quantum yield slightly decreased from 0.030 to 0.025 with increasing concentration of CH$_3$I (Table 2-17).

2.5 Catalytic effects on the photocycloaddition

2.5.1 The effects of lithium and sodium acetylacetonate

Comparative photocycloadditions of 2-NpCO$_2$Me (0.02 M) in methanol were carried out under the same conditions in apparatus II; the first solution contained only acacH (0.05 M), the second only Li(acac) (0.05 M) and the third both Li(acac) (0.001 M) and acacH (0.05 M), in addition to 2-NpCO_2Me. Octadecane (0.005 M) was added as the internal standard in the beginning and the yields of **16** are listed in Table 2-18. Remarkably, Li(acac) did not undergo photocycloaddition with 2-NpCO_2Me at all, but it did assist or catalyze the photocycloaddition of 2-NpCO_2Me with acacH. Yield of the product was increased from 2% to 18%. A similar effect on the product yield of **16** was also observed in the presence of $Zn(acac)_2$ with increases from 8% to 41%.

The photocycloadditions of 2-NpCO_2Me (0.02 M) and acacH (0.08 M) at 350 nm were carried out in the absence (as a control) and in the presence of Li(acac) (0.001 M) in methanol. The quantum yields of **16** in the presence and in the absence of Li(acac) were 0.0235 and 0.0043 respectively, indicating the acceleration of the reaction by Li(acac). Similar experiments were carried out on systems of 2-NpR (R = CO_2Et, OMe, CN, OH and COMe)/acacH (Table 2-19).

Photolysis of solutions containing PN (0.02 M), acacH (0.08 M) and $C_{16}H_{34}$ (as I.S., 0.005 M) in the presence of Li(acac) (0, 0.001, 0.0003, 0.006 and 0.01 M) resulted in yields (GC%) of products **29**, **28** and **30** (**31** ignored) as follows: GC% of trans-fused **29** increased from 18% to 38% with increasing concentration of Li(acac) (0-0.01 M). At the same time, that of cis-fused **28** dropped from 14% to 7% and that of **30** increased from 4% to 16%. The conversion of PN increased from 59% to 79% (Table 2-20).

Solutions containing 2-NpR (0.02 M, R = 1-Me and H), acacH (0.08 M) with (0.01 M) and without (as a control) Li(acac) were photolyzed at 350 nm for 7 hours for the 1-NpMe system, 28 hours for the Np system and 6

Table 2-17: Effects of iodomethane on photocycloaddition of 2-NpCN and acacH in acetonitrile at room temperature[a]

$[CH_3I]$ (M)	$[CH_3I]/[NpCN]$	**38**[b]	Φ_p[c]
0	0	0.222	0.030
0.001	0.05	0.223	0.030
0.002	0.10	0.215	0.029
0.003	0.15	0.191	0.026
0.004	0.20	0.186	0.025

a. Acetonitrile solutions containing 2-NpCN (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and CH_3I (0-0.004 M) were irradiated in apparatus II for 3 hours at 350 nm.

b. Reported in relative yield which was the GC area ratio of the product over the I.S.

c. Quantum yields were determined by Method II (section 4.3) based on **38** formation.

Table 2-18: Metal acetylacetonate catalysis on photocycloaddition of methyl 2-naphthoate and acacH in methanol[a]

[acacH] (M)	[Li(acac)](M)	Yield%[b]
0.05	0	2
0	0.05	0
0.05	0.001	17.5
	$[Zn(acac)_2]$ (M)	
0.08	0	8.3
0	0.08	0
0.08	0.001	40.7

a. The solutions containing 2-$NpCO_2Me$ (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.05 M) or/and Macac (M = Li and Zn, 0.08 M or 0.001 M) were irradiated (N_2 purged) for 3 hours in apparatus II (at 300 nm for the Li(acac) case, and, at 350 nm for the $Zn(acac)_2$ case).

b. Concentrations of **16** were determined with the I.S. using equation 4-2 and yield % was calculated accordingly. Errors: ± 5-7%.

Table 2-19: The effects of lithium acetylacetonate on photocycloaddition quantum yields of 2-NpR and acacH in methanol[a]

R	Φ_p[b]		t
	[Li(acac)]=0	[Li(acac)]=0.001M	(hour)
$COCH_3$	0	0	4
OH[c]	(4%)	(0.5%)	19.5
CN	0.030	0.018	3
OMe	0.036	0.027	3
CO_2Et	0.0033	0.0124	4.5
CO_2Me	0.0043	0.0235	4

a. The solutions contained 2-NpR (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M); one also contained Li(acac) (0.001 M) and the other no Li(acac) served as a control were irradiated (N_2 purged) in apparatus II at 350 nm. Errors: ± 15%.

b. Quantum yields of **16** formation were determined by Method II (section 4.3).

c. Reported in GC % without I.S.

Table 2-20: Li(acac) catalytic effect on the photocycloaddition relative yields of phenanthrene (PN) and acacH in methanol[a]

Li(acac) (M)	**29**[b]	**28**[b]	**30**[c]	PN[d]
0	0.81	0.63	0.20	2.7
0.001	1.12	0.78	0.25	3.15
0.003	1.53	0.50	0.67	3.69
0.006	1.69	0.42	0.79	3.90
0.01	1.91	0.33	0.55	3.95

a. The solutions containing PN (0.02 M), acacH (0.08 M), $C_{16}H_{34}$ (as I.S., 0.005 M) and Li(acac) (0-0.06 M) were irradiated (N_2 purged) for 4 hours in apparatus II at 350 nm.

b. Reported in relative yield which was the GC area ratio of the product over the I.S. Errors: ± 5-7%.

c. Suggested structure: 9-acetylphenanthrene.

d. Relative yield of PN consumed.

hours for the 9-hydroxyphenanthrene system. No new products were detected by GC analysis of the control and sample solutions.

Solutions of 2-NpOMe (0.02 M) and acacH (0.05 M) in acetonitrile were irradiated at 300 nm in the absence (as a control) and in the presence of sodium hydroxide (0.001 M). The percentage yields of 1,5-diketone **44** were 21% and 26%, respectively, indicating little acceleration of the reaction by the base. In contrast, the photocycloaddition of 2-NpCO$_2$Me (0.02 M) and acacH (0.05 M) was accelerated by NaOH (0.001 M). The product **16** was the only product and its formation was 27% and 3% for the solutions with and without the base, respectively.

Solutions of 2-NpCO$_2$Me (0.02 M) and acacH (0.08 M) in 4:1 methanol:water were irradiated at 350 nm in the absence (as a control) and in the presence of sodium chloride (0.005 M). The yields of **16** were 13.3% and 13.5% respectively.

2.5.2 Acid effects

Photolysis (at 300 nm) of acetonitrile solutions of 2-NpCO$_2$Me (0.02 M) and acacH (0.08 M) containing: a) sulfuric acid (0.0003 M), b) phosphoric acid (0.0003 M), c) hydrochloric acid (0.0003 M), d) borontrifluoride in ether (0.0003 M) and e) trifluoroacetic acid (0.0005 M) were carried out for 3 hours (6 hours for trifluoroacetic acid). Compound **17**, in addition to **16** (equation 2-1) was formed in much higher yields (GC%, Table 2-21). The results showed that all the acids catalyzed the reaction no matter whether the acid was a Bronsted acid or Lewis acid. Among these acids, sulfuric acid enhanced the formation of **17** and **16** from 0% to 20.8% and 2% to 24.4%, respectively. Borontrifluoride enhanced the formation from 0% to 9.2% and

2% to 20.2%, respectively.

Photolysis (300 nm, 3 hours) of 1-NpCN (0.02 M) and acacH (0.05 M) in acetonitrile in the presence of sulfuric acid (0.0001, 0.0003, 0.0006 and 0.001 M) led to product **33** increasing from 7.7% (GC%) to 47.3% as shown in Table 2-22. Similarly, photolysis of 2-NpCN (0.02 M)/acacH (0.05 M) and 1-NpCO$_2$Me (0.02 M)/acacH (0.05 M) systems in the presence of sulfuric acid (0.0001, 0.0003, 0.0006 and 0.001 M) resulted in a similar trend of product distribution (GC%: 5% to 14% for 2-NpCN and 5% to 23% for 1-NpCO$_2$Me, Table 2-22).

Contrasting with the above observations, the photolysis (300 nm, 3 hours) of 2-NpOMe (0.02 M) and acacH (0.05 M) in acetonitrile in the presence of sulfuric acid (0.0001-0.001 M) showed a decrease of 1,5-diketone **44** from 21% to 5% (Table 2-22). Under the same conditions except that 350 nm lamps were used, the presence of sulfuric acid (0.02 M) also retarded the photocycloaddition of phenanthrene (0.02 M) and acacH (0.08 M) in methanol. The yields (GC%) of **29** and **28** dropped significantly from 22% and 27% to 4% and 3% respectively (Table 2-23). This results were obtained with H_2SO_4 at single concentration and need to be confirmed. The photolysis of 1-NpCH$_3$ (0.02 M)/acacH (0.08 M) and Np (0.02 M)/acacH (0.08 M) systems in methanol resulted in no product formation either in the presence or in the absence of sulfuric acid.

Photocycloadditions of 2-NpCO$_2$Me (0.02 M) and acacH (0.05 M) were carried out with 300 nm lamps in the presence of sulfuric acid (0, 0.0001, 0.0003, 0.0006 and 0.001 M) in acetonitrile and methanol, respectively. The acid accelerated the reaction in both solvents, but with more efficiency in acetonitrile (Table 2-24 and Figure 2-17).

Table 2-21: Acid catalysis on the photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile[a]

Acid (M)	Conversion of **14**	GC%[b] Formation of **17**	Formation of **16**
Control	2.06	0	2.06
H_2SO_4(0.0003)	66.6	20.8	24.4
H_3PO_4(0.0003)	12.6	4.4	8.2
HCl(0.0003)	22.0	7.2	10.6
BF_3OEt_2(0.0003)	37.4	9.2	20.2
CF_3COOH(0.0005)	13.7	2.9	10.5

a. The solutions containing 2-$NpCO_2Me$ (0.02 M), acacH (0.05 M) and one of above acids were irradiated (N_2 purged) for 3 hours (6 hours for CF_3COOH) in apparatus II at 300 nm.

b. The results were reported in GC% from print out without I.S. Errors: ± 5-7%.

Table 2-22: Acid effect on yield (GC%) of the photocycloaddition of NpR and acacH in acetonitrile[a]

$[H_2SO_4]$ (M)	**33**[b] 1-NpCN	**38**[b] 2-NpCN	**44**[b] 2-NpOMe	**22**[b] $1\text{-NpCO}_2\text{Me}$
0	5.6	4.8	24.4	0
0.0001	7.7	5.3	21.1	4.5
0.0003	37.5	10.0	14.8	16.4
0.0006	42.2	11.9	8.3	21.8
0.001	47.3	13.6	5.2	22.9
t (hour)	3	3	1	3

a. The solutions contained NpR (0.02 M), acacH (0.05 M) and H_2SO_4 (0.0001-0.001 M) were irradiated (N_2 purged) in Apparatus II with 300 nm lamps. Errors: ± 5-7%.

b. Reported in GC% from print out without I.S.

Table 2-23: Acid effect on yield (GC%)[a] of photocycloaddition of phenanthrene (PN) and acacH in acetonitrile[b]

	$[H_2SO_4]$ (M)	
	0	0.02 M
30	13	0
29	22	4
28	27	3
31	4	14
PN	25	77

a. Results were reported in GC% from print out without I.S. Errors: ± 5-7%.

b. The solutions contained PN (0.02 M), acacH (0.08 M) and H_2SO_4 (0 and 0.02 M) were irradiated (N_2 purged) for 7 hours in apparatus II at 350 nm.

Table 2-24: Sulfuric acid effects on yield (GC%)[a] of photocycloaddition of 2-$NpCO_2Me$ and acacH in acetonitrile and methanol[b]

$[H_2SO_4]$	**17**	**16**	**17**	**16**
(M)	(in CH_3CN)		(in CH_3OH)	
0	0	2.06	0	2.1
0.0001	8	23.8	trace	7.3
0.0003	28.7	30.7	13.4	20.7
0.0006	38.2	34.9	22.6	23.1
0.001	45.0	35.6	24.7	19.9

a. Results were reported in GC% from print out without I.S. Errors: ± 5-7%.

b. The solutions contained 2-$NpCO_2Me$ (0.02 M), acacH (0.05 M) and sulfuric acid (0-0.001 M) were irradiated (N_2 purged) for 3 hours in apparatus II at 300 nm.

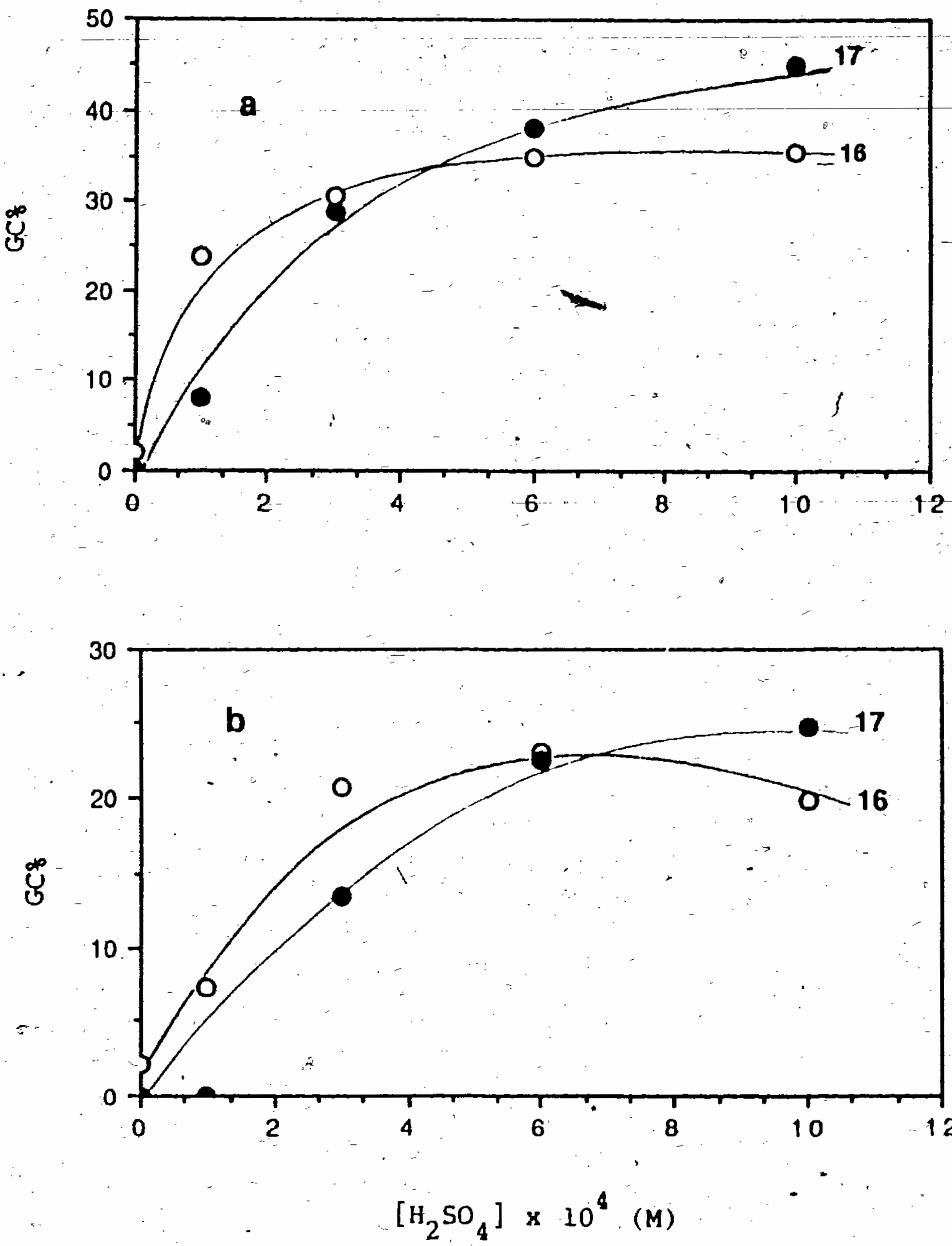


Figure 2-17: Sulfuric acid effects on yield (GC%) of photocycloaddition of 2-NpCO$_2$Me and acacH; a) in acetonitrile and b) in methanol.

2.6 Kinetic studies of the photocycloaddtion

2.6.1 In the absence of a catalyst

A basic reaction mechanism for the photocycloaddition of 2-NpR and acacH is proposed in Scheme 2-1 (2-NpCO$_2$Me will be used as a model compound) based on the findings which will be discussed in Discussion part.

Scheme 2-1

$$\text{2-NpCO}_2\text{Me} \xrightarrow{h\nu} {}^1\text{2-NpCO}_2\text{Me} \qquad \text{2-15}$$

$$^1\text{2-NpCO}_2\text{Me} \xrightarrow{k_f} \text{2-NpCO}_2\text{Me} + h\nu_f \qquad \text{2-16}$$

$$^1\text{2-NpCO}_2\text{Me} \xrightarrow{k_{ic}} \text{2-NpCO}_2\text{Me} + \Delta \qquad \text{2-17}$$

$$^1\text{2-NpCO}_2\text{Me} \xrightarrow{k_{isc}} {}^3\text{2-NpCO}_2\text{Me} \qquad \text{2-18}$$

$$^1\text{2-NpCO}_2\text{Me} + \text{acacH} \underset{k_q'}{\overset{k_q}{\rightleftharpoons}} {}^1\text{2-NpCO}_2\text{Me-acacH} \qquad \text{2-19}$$

$$^1\text{2-NpCO}_2\text{Me-acacH} \xrightarrow{k_p} \text{Product} \qquad \text{2-20}$$

$$^1\text{2-NpCO}_2\text{Me-acacH} \xrightarrow{k_b} \text{2-NpCO}_2\text{Me} + \text{acacH} \qquad \text{2-21}$$

$$^1\text{2-NpCO}_2\text{Me-acacH} \xrightarrow{k_p'} {}^3\text{2-NpCO}_2\text{Me-acacH} \qquad \text{2-22}$$

In Scheme 2-1, ^{1}2-NpCO$_2$Me-acacH is an exciplex assumed to be formed from the collisional interaction of $^1NpCO_2Me$ with acacH. It could dissipate primarily by four pathways, i.e., by collapsing to the final product (equation 2-20), to the starting materials (equation 2-21), to its triplet exciplex (equation 2-22) or back to ^1NpR and acacH (equation 2-19). The kinetic equations 2-23 and 2-25 were derived from Scheme 2-1 using steady state approximation for ^1NpR and $^12\text{-}NpCO_2Me\text{-}acacH$.

$$1/\Phi_p = 1/\beta + 1/\{\beta k_q\tau_0[\text{acacH}]\} \qquad 2\text{-}23$$

$$\text{Where, } \beta = \Phi_{\text{limiting}} = k_p/(k_p + k_p' + k_q' + k_b) \qquad 2\text{-}24$$

$$1/\Phi_{Np} = 1/\beta' + 1/\{\beta' k_q\tau_0[\text{acacH}]\} \qquad 2\text{-}25$$

$$\text{Where, } \beta' = \Phi'_{\text{limiting}} = (k_p + k_p')/(k_p + k_p' + k_q' + k_b)$$

If the proposed Scheme 2-1 is valid, a plot of either $1/\Phi_p$ (on product formation) or $1/\Phi_{Np}$ (on NpR disappearance) against 1/[acacH] should be linear based on equations 2-23 and 2-25. For each reaction, the $k_q\tau_0$ value and the limiting quantum yield Φ_{limiting} may be obtained.

The quantum yields Φ_p of **16** (Table 2-25) for the photocycloaddition of $2\text{-}NpCO_2Me$ (0.02 M) in acetonitrile were determined at 350 nm as a function of [acacH] (0.08-0.3 M). The plot (Figure 2-18) of $1/\Phi_p$ against 1/[acacH] yielded a straight line with slope and intercept of 14.2 and 30, respectively, from which $k_q\tau_0$ and Φ_{limiting} were calculated to be 2.1 (2.05 for the second run) M^{-1} and 0.033 (0.032 for the second run), based on equations 2-23 and 2-24.

The quantum yields Φ_p of **20** and **44** for the photocycloaddition of 2-NpR ($R = CO_2Et$ and OMe) and the Φ_{Np} of 2-NpCN disappearance for R = CN were determined as a function of [acacH] under similar conditions to those used in Table 2-25. The observed data are listed in Tables 4-6, 4-7 and 4-8 and the plots of $1/\Phi_p$ or $1/\Phi_{Np}$ against 1/[acacH] yielded straight lines with reasonably good correlations ($\gamma = 0.980$-0.997, Figure 2-18), indicating that the mechanism proposed in Scheme 2-1 can reasonably represent the reactions of these naphthalene derivatives. The calculated limiting quantum yield $\Phi_{limiting}$ and $k_q\tau_0$ are summarized in Table 2-26. The plots of $1/\Phi$ *vs* 1/[acacH] are shown in Figure 2-18.

2.6.2 In the presence of metal acetylacetonate

A basic mechanism for the photocycloaddition of NpR (2-NpCO_2Me is used as a model compound) and acacH catalyzed by Li(acac) is proposed in Scheme 2-2 (reaction 2-15, 2-16, 2-17, 2-21 and 2-22 should be included in the Scheme) based on the definition of a photocatalysis reaction[64,65] as well as the following findings: i) the photocycloaddition was catalyzed by Li(acac) and ii) 2-NpR fluorescence was quenched by Li(acac). In Scheme 2-2, $^12\text{-NpCO}_2Me$-Li(acac) is a catalytic intermediate and is formed by Li(acac) intercepting the lowest excited singlet state of 2-NpCO_2Me. $^12\text{-NpCO}_2Me$-Li(acac) could react by two pathways, i.e. by interaction with a ground state acacH to give the product and Li(acac) (equation 2-27) or by decay to the starting materials (equation 2-28). Further, it is assumed that the $^12\text{-NpCO}_2Me$-acacH complex does not react with the catalyst (Li(acac)) to give the product. The kinetic equation 2-29 was derived[64,65] from Scheme 2-2 using the steady state approximation for $^12\text{-NpCO}_2Me$ and $^12\text{-NpCO}_2Me$-Li(acac) (see Appendix). Equation 2-29 predicts a curve for

Table 2-25: Quantum yields of photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile[a]

[acacH]		Φ_p[b]		1/[acacH]		$1/\Phi_p$	
c	d	c	d	c	d	c	d
0.3	0.5	0.0138	0.0183	3.33	2	72.5	54.6
0.2	0.3	0.0112	0.0140	5.00	3.33	89.3	71.4
0.15	0.25	0.0087	0.0113	6.67	4	115.1	88.5
0.10	0.25	0.0055	0.0092	10.0	5	181.8	108.7
0.08	0.2	0.0043	0.0072	12.5	6.7	232.6	138.9
	0.12		0.0058		8.3		172.4
	0.1		0.0058		10		181.8
$k_q\tau_0$ (M^{-1})		2.1 ± 0.32[c,e]		2.05 ± 0.17[d]			
$\Phi_{limiting}$:		0.033 ± 0.0086[c]		0.032 ± 0.0042[d]			

[a] The solutions contained 2-$NpCO_2Me$ (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3-0.08 M) were irradiated (N_2 purged) for 2-4 hours in apparatus II at 350 nm.

[b] Quantum yields of **16** formation were determined by Method II (section 4.3).

[c] The first run with conversions of 2-$NpCO_3Me$ range of 16-22%.

[d] The second run with conversions of 2-$NpCO_3Me$ range of 7-17%.

[e] k_q was calculated to be 2.47 x 10^8 M^{-1} s^{-1} by adopting τ_0 of 8.5 ns in acetonitrile (N_2 purged, Section 2.3.3) and 2.2 x 10^8 M^{-1} s^{-1} by adopting τ_0 of 9.4 ns in methanol (N_2 purged, Section 2.3.3).

Table 2-26: Summary of kinetic data of photocycloaddition of 2-NpR and acacH

NpR	$k_q\tau_0$ (M^{-1})	$\Phi_{limiting}$	Intercept	Slope
2-CO_2Me[a]	2.1 ± 0.32	0.033 ± 0.0086	30 ± 7.8	14.2 ± 2.56
	2.05 ± 0.17	0.032± 0.0042	31 ± 4.03	15.1 ±1.49
2-CO_2Et[b]	2.32 ± 0.208	0.043 ± 0.0086	23.9 ± 4.84	10.3 ± 0.51
2-OMe[c]	18 ± 1.53	0.064 ± 0.0031	15.7 ± 0.75	0.88 ± 0.074
2-CN[d]	10 ± 0.75	0.065 ± 0.0049	15.5 ± 1.17	1.55 ± 0.116

a. From Table 2-25.

b. From Table 4-6.

c. From Table 4-7.

d. From Table 4-8.

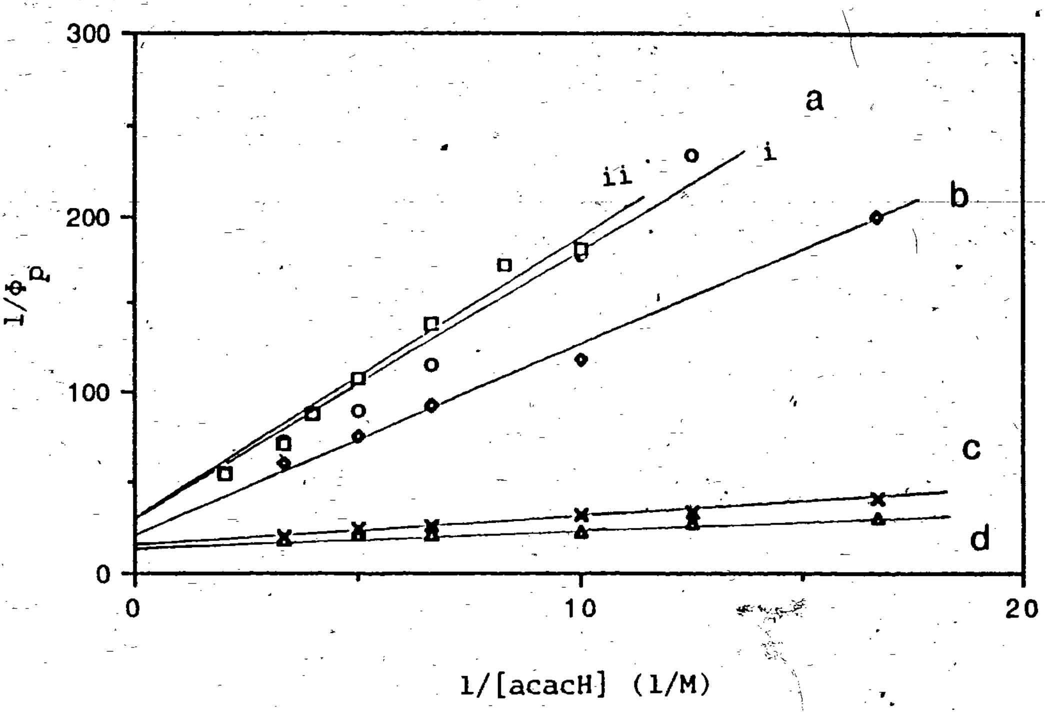


Figure 2-18: The plot of 1/Φ *vs* 1/[acacH] for photocycloaddition of 2-NpR (0.02 M) and acacH in acetonitrile (N_2 purged) a) 2-$NpCO_2Me$, (i: first run; ii: second run) b) 2-$NpCO_2Et$, c) 2-NpCN and d) 2-NpOMe.

Scheme 2-2

$$^{1}2\text{-NpCO}_2\text{Me} + \text{acacH} \underset{k_q'}{\overset{k_q}{\rightleftharpoons}} {}^{1}2\text{-NpCO}_2\text{Me-acacH} \qquad 2\text{-}19$$

$$^{1}2\text{-NpCO}_2\text{Me-acacH} \xrightarrow{k_p} \text{Product} \qquad 2\text{-}20$$

$$^{1}2\text{-NpCO}_2\text{Me} + \text{Li(acac)} \xrightarrow{k_c} {}^{1}2\text{-NpCO}_2\text{Me-Li(acac)} \qquad 2\text{-}26$$

$$^{1}2\text{-NpCO}_2\text{Me-Li(acac)} + \text{acacH} \xrightarrow{k_c'} \text{P} + \text{Li(acac)} \qquad 2\text{-}27$$

$$^{1}2\text{-NpCO}_2\text{Me-Li(acac)} \xrightarrow{k_b'} 2\text{-NpCO}_2\text{Me} + \text{Li(acac)} + \Delta \qquad 2\text{-}28$$

the dependence of quantum yield of product formation on [Li(acac)]. When k_c[Li(acac)]γ is much larger than k_q[acacH]x, the latter term may be omitted in 2-29. The inverted quantum yield expression is given by equation 2-32 under this provision. When the concentration of acacH is fixed, the plot of 1/Φ against 1/[Li(acac)] should be a straight line if the proposed Scheme 2-2 is valid, and if the above provision is met.

$$\Phi = \frac{k_q[\text{acacH}]x + k_c[\text{Li(acac)}]\dfrac{k_c'[\text{acacH}]}{k_c'[\text{acacH}] + k_b'}}{k_{ic} + k_f + k_q[\text{acacH}] + k_c[\text{Li(acac)}]}$$

$$= \frac{k_q[\text{acacH}]x + k_c[\text{Li(acac)}]\,\gamma}{k_{ic} + k_f + k_q[\text{acacH}] + k_c[\text{Li(acac)}]} \qquad 2\text{-}29$$

where: $\gamma = \Phi_{\text{limiting}}$

$$= \frac{k_c'[\text{acacH}]}{k_b' + k_c'[\text{acacH}]} \qquad 2\text{-}30$$

$$x = \frac{k_p}{k_p + k_q' + k_b + k_p'} \qquad 2\text{-}31$$

$$1/\Phi = 1/\gamma \left\{ 1 + \frac{k_{ic} + k_f + k_q[\text{acacH}]}{k_c[\text{Li(acac)}]} \right\} \qquad 2\text{-}32$$

The quantum yields of the photocycloadduct **16** from 2-$NpCO_2Me$ (0.02 M) and acacH (0.08 M) in methanol were determined as a function of [Li(acac)] (0.0001-0.001 M) at 350 nm. The dependence of the quantum yield of **16** on [Li(acac)] is given in Figure 2-19. The theoretical curve b in Figure 2-19 (based on equation 3-7) matches the experimental curve well over the Li(acac) concentration range of 0.0001-0.00045 M (for details, see Section 3.9, page 133). Under the same conditions, quantum yields of **16** from the photoaddition of 2-$NpCO_2Me$ (0.02 M) and acacH (0.08 M) were determined as a function of [K(acac)] (0.0001-0.001 M). The dependence of quantum yield of **16** on [K(acac)] is given in Figure 2-20. Similarly, Φ *vs* [M(acac)] (M = Na or K) correlations were studied by monitoring NpR disappearance at 300 nm in the following systems: 1-$NpCO_2Me$ (0.02 M)/acacH (0.05 M)/Na(acac) (0.0001-0.001 M) and 1-$NpCO_2Me$ (0.02 M)/acacH (0.05 M)/K(acac) (0.0001-0.001 M). The dependences of the quantum yield of **22** on [M(acac)] are given in Figure 2-20 and Table 2-27. The plot of 1/Φ *vs* 1/[M(acac)] is given in Figure 2-21 for above reactions.

2.6.3 In the presence of sulfuric acid

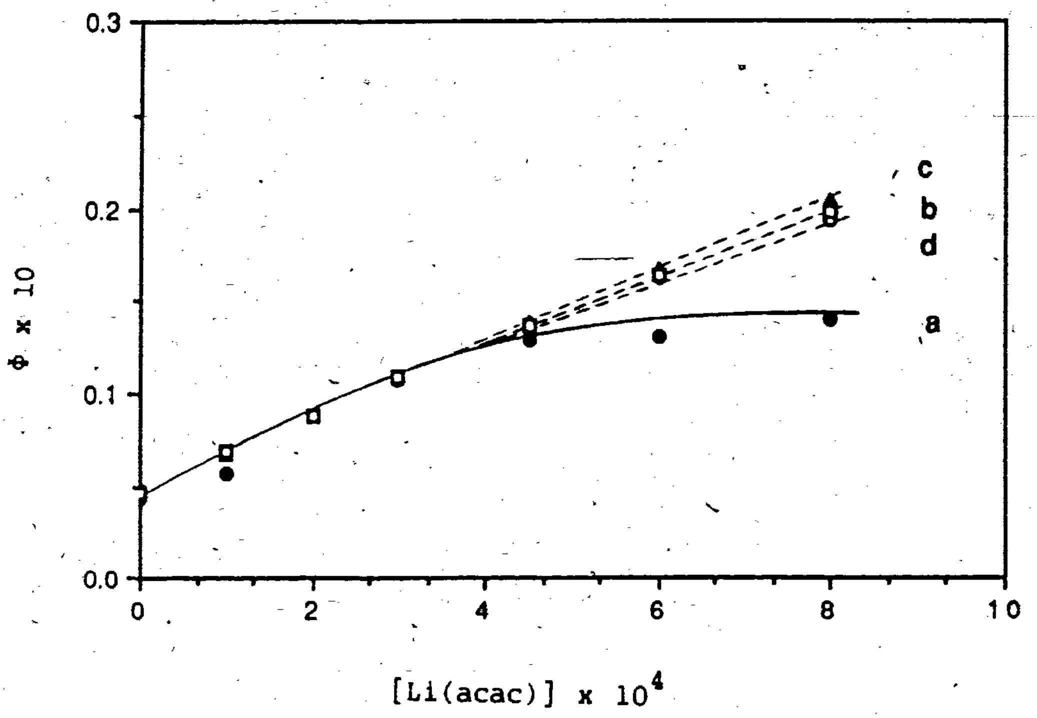


Figure 2-19: Plot of Φ_p(**16**) *vs* [Li(acac)] for photocycloaddition of 2-$NpCO_2Me$ (0.02 M) and acacH (0.08 M) in methanol in the presence of Li(acac) a) experimental results; b) calculated curve from equation 3-7; c) calculated curve from equation 3-8 and d) calculated curve from equation 3-9 (Section 3.9).

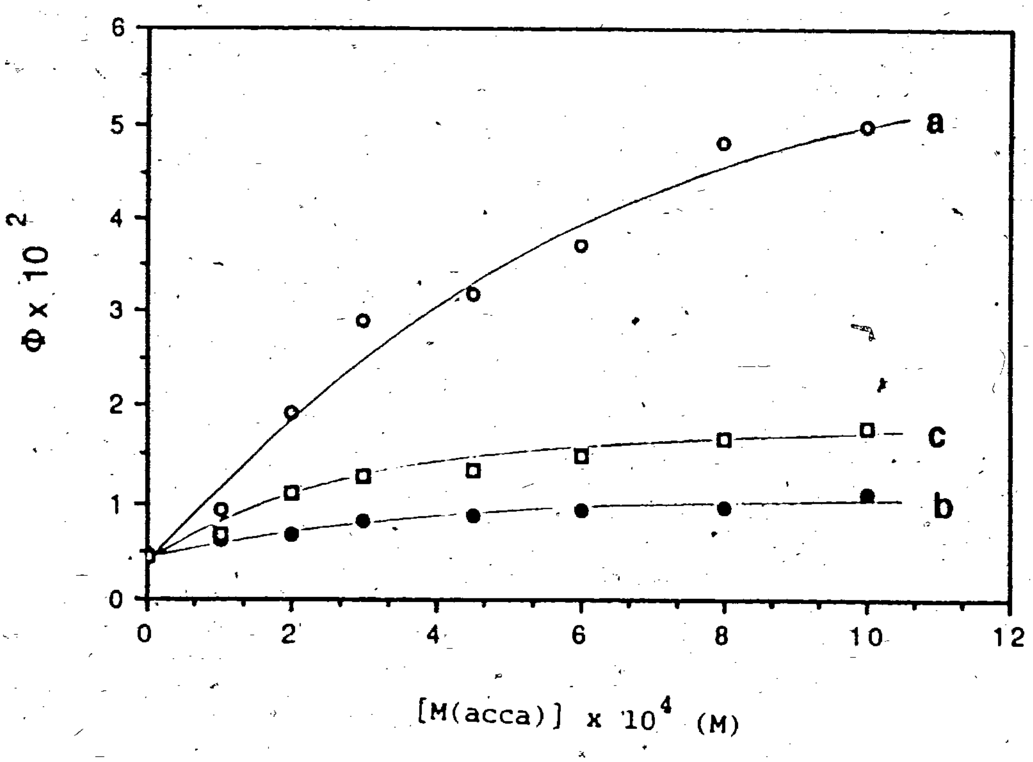


Figure 2-20: Plot of Φ_{Np} (the quantum yield NpR disappearance, curve a and b) or Φ_p (curve c, product **16** formation) *vs* [M(acac)] (M = Na and K) for the photocycloaddition of NpR (0.02 M) and acacH (0.05 M for a and b and 0.08 M for c) in methanol a)Na(acac)/1-NpCO$_2$Me; b) K(acac)/1-NpCO$_2$Me and c) K(acac)/2-NpCO$_2$Me.

Table 2-27: Quantum yield dependence of photocycloaddition of NpR and acacH on concentration of metal acetylacetonate in methanol[a]

[(acacM)] $\times 10^4$ (M)	Φ_{Np}[b] Na(acac) 1-$NpCO_2Me$[c]	K(acac) 1-$NpCO_2Me$[c]	Li(acac) 2-$NpCO_2Me$[d]	K(acac) 2-$NpCO_2Me$[d]
0	0.0047	0.0047	0.0043	0.0043
1	0.0093	0.0062	0.0057	0.0067
2	0.019	0.0066	0.0089	0.0109
3	0.029	0.0082	0.0109	0.0128
4.5	0.032	0.0086	0.0129	0.0134
6	0.037	0.0092	0.0130	0.0149
8	0.048	0.0095	0.0140	0.0166
10	0.050	0.0109	0.0145	0.0177
Conversion	5-19%	8-18%	7-30%	7-35%

a. The solutions contained NpR (0.02 M), acacH (0.05 M; 0.08 M in d cases) and M(acac) (0.0001-0.001 M) were irradiated (N_2 purged) in apparatus II. Errors: ± 10-15%.
b. Unless specified, the quantum yield of NpR disappearance was used.
c. For these two experiments, light source at 300 nm were used for 3 hours of irradiation.
d. For these two experiments, the quantum yield of **16** formation was used and irradiation was at 350 nm [100-180 min for Li(acac) case and 3 hour 20 min to 5 hour 30 min for K(acac) case].

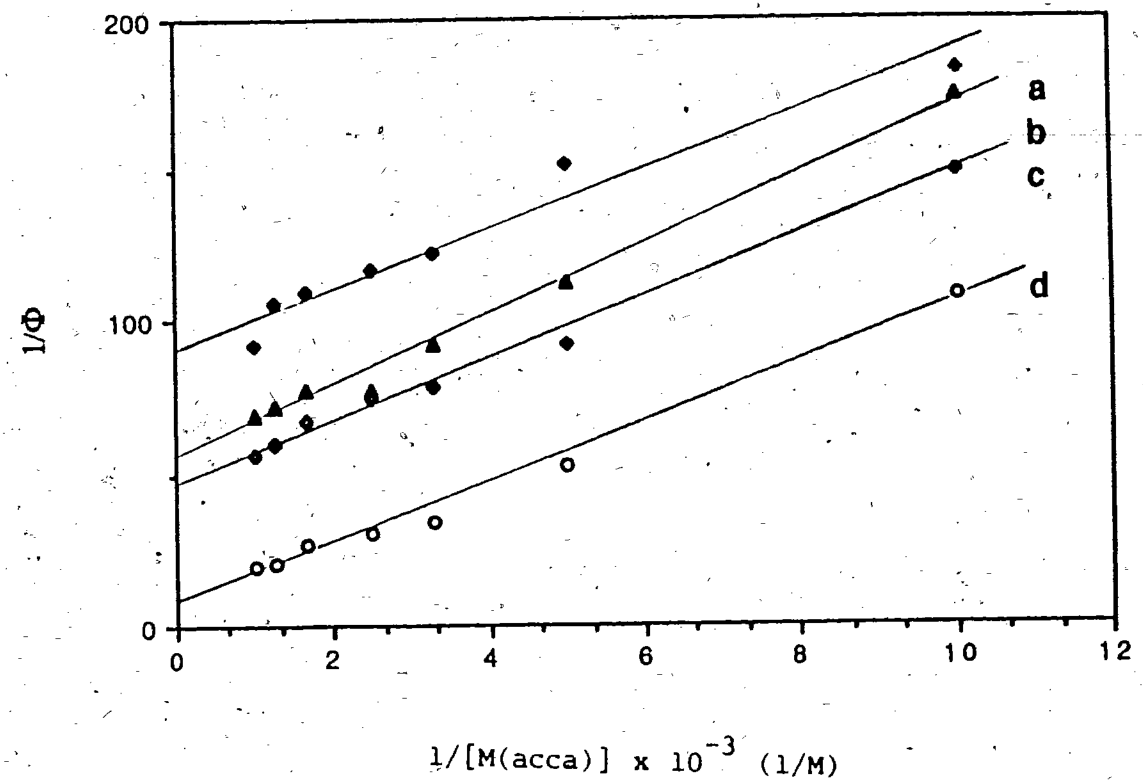


Figure 2-21: The plots of $1/\Phi_{Np}$ ($1/\Phi_p$ for c and d) *vs* 1/[M(acac)] (M = Li, Na and K) for photocycloaddition of NpR (0.02 M) and acacH (0.05 M for a and b and 0.08 M for c and d) in methanol a) Li(acac)/2-$NpCO_2Me$; b) K(acac)/1-$NpCO_2Me$; c) K(acac)/2-$NpCO_2Me$ and d) Na(acac)/1-$NpCO_2Me$.

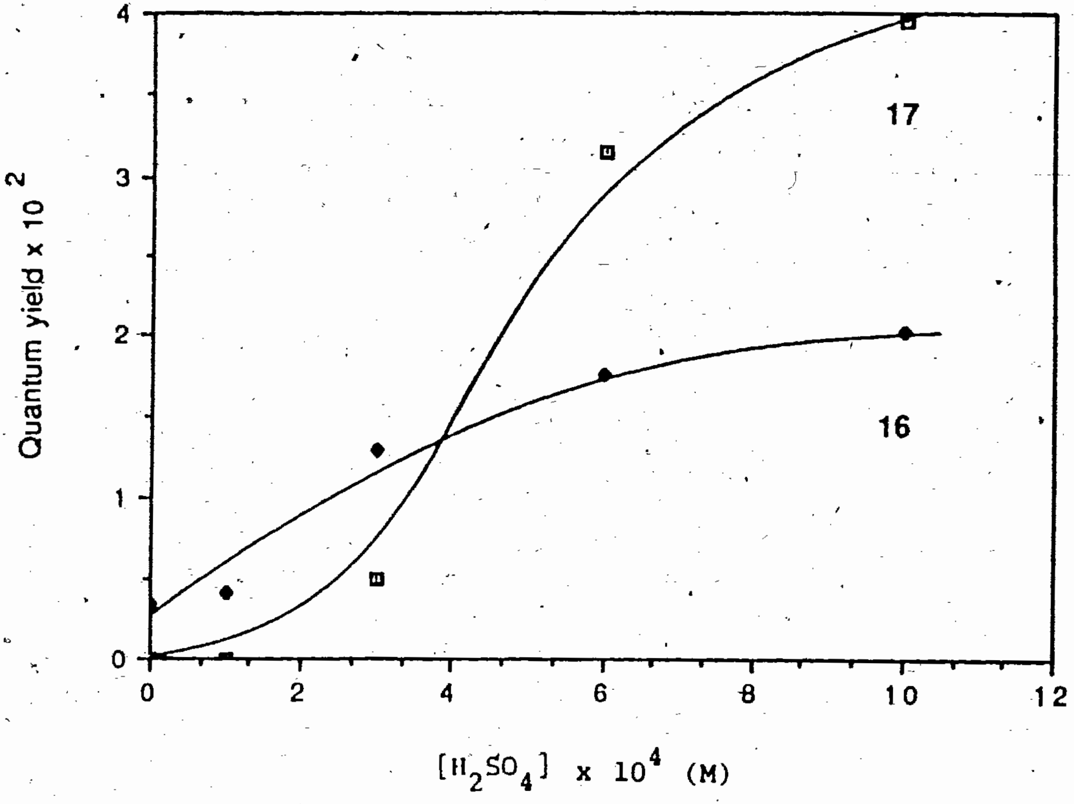


Figure 2-22: Plot of quantum yield of **16** and **17** *vs* [H_2SO_4] for photocycloaddition of 2-NpCO$_2$Me (0.02 M) and acacH (0.08 M) in acetonitrile at 350 nm.

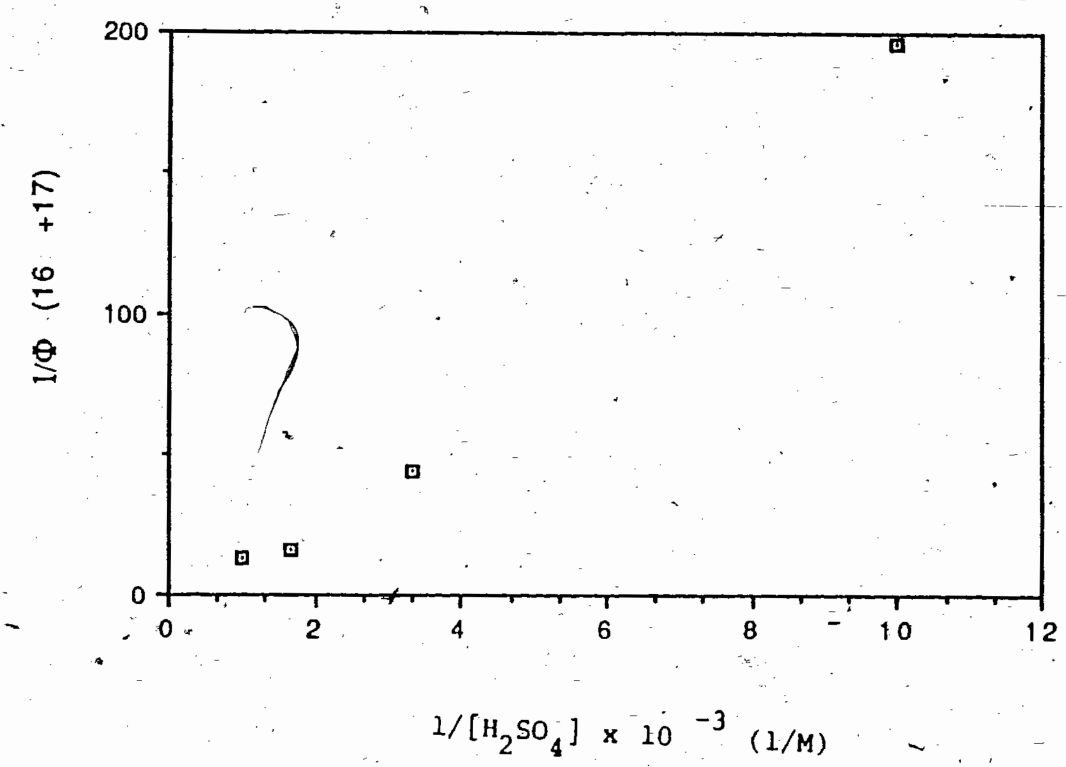


Figure 2-23: Plot of 1/Φ(**16** + **17**) *vs* $1/[H_2SO_4]$ for photocycloaddition of 2-$NpCO_2Me$ (0.02 M) and acacH (0.08 M) in acetonitrile at 350 nm.

The quantum yields of the formation of **16** and **17** for the photocycloaddition of 2-$NpCO_2Me$ (0.02 M) and acacH (0.08 M) at 350 nm were determined as a function of the concentration of sulfuric acid (0.0001-0.001 M). The dependence of the quantum yields of **16** and **17** on $[H_2SO_4]$ are given in Table 4-9 and Figure 2-22. The plot of $1/\Phi$(**16**+**17**) *vs* $1/[H_2SO_4]$ is given in Figure 2-23.

2.7 Effects of dienes on the photocycloaddition

The quantum yields of the photocycloaddition of 2-$NpCO_2Me$ (0.02 M) to acacH (0.08 M) were determined in acetonitrile at 350 nm in the presence (0.02 M) and absence (as a control) of dienes such as 1,3-pentadiene (PD), 2,5-hexadiene (HD) and 1,3-cyclohexadiene (CD). The results showed that the reaction was catalyzed by dienes to give quantum yields of **16** of 0.0077 with PD, 0.0059 with HD, 0.0051 with CD and 0.0043 for the control. Similar experiments were carried out on the photocycloadditions of 2-NpR (R = CO_2Et, OMe and CN) with acacH. The quantum yields of product formation in the presence of a diene were greater than in the absence of a diene for all cases, as shown in Table 2-28.

The quantum yield of **16** was investigated as a function of concentration of 1,3-pentadiene (0.02-0.1 M) under similar conditions at 350 nm. The relative yields and quantum yields of product **16** first increased in the PD concentration range of 0-0.02 M, then decreased with increasing PD concentration (0.02-0.1 M). The relative yields and quantum yields of **16** in the presence of PD were always greater than in the absence of PD (Table 2-29) except when [PD] = 0.10 M. In the photolysis, an addition product **48** of 2-$NpCO_2Me$ and PD was formed as shown by GC-MS (CI) with a parent peak at m/e = 255 (M+1, 100 %). The attempt to isolate this compound failed and its structure is not determined. The relative yields of the unknown product **48** increased with the increasing concentration of 1,3-pentadiene. The results suggested the existence of two competing processes between the addition of 2-NpCO$_2$Me with acacH and the addition of 2-NpCO$_2$Me with 1,3-pentadiene as well as a diene-catalyzed photoaddition of 2-NpCO$_2$Me with acacH, i.e. a termolecular process.[87-89]

Under the same conditions as above, the reaction of 2-NpCO$_2$Me with acacH was carried out using higher concentrations of 1,3-pentadiene (0.1-0.3 M). The quantum yield of product **16** decreased and the yield of product **48** increased rapidly with increasing concentration of 1,3-pentadiene (Table 2-30). The quantum yield of **16** in the presence of PD (0.1-0.3 M) were smaller than in the absence of PD, suggesting the existence of two competing processes, i.e. a 2-NpCO$_2$Me/acacH addition and a 2-NpCO$_2$Me/PD addition.

To investigate the possibility of a termolecular process in the 2-NpCO$_2$Me/PD addition reaction, the relative yields of **48** in the photoreaction of 2-NpCO$_2$Me (0.02 M) with 1,3-pentadiene (0.08 M) at 350 nm were determined as a function of the concentration of acacH (0.02-0.08 M). In the photolysis, **16** was also formed. No acceleration of the formation of **48** was observed, indicating the absence of effect due to acacH. The relative yield of **16** increased and that of **48** decreased with increasing concentration of acacH, indicating competing processes in the photoreactions of 2-NpCO$_2$Me with acacH and 1,3-pentadiene (Table 4-10).

2.8 Phosphorescence and UV studies

Table 2-28: The effects of diene on photocycloaddition of 2-NpR and acacH in acetonitrile[a]

2-NpR	Φ_p[b]			
	Control	[PD][c] (0.02M)	[HD][c] (0.02M)	[CD][c] (0.02M)
CO_2Me	0.0043	0.0077	0.0059	0.0051
CO_2Et	0.0033	0.0059		
OMe	0.036	0.053	0.042	
CN	0.030	0.038		

a. The solutions contained 2-NpR (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and also with (0.02 M) and without (as a control) a diene were irradiated in Apparatus II at 350 nm (4 hours for R = CO_2Me, 6 hours for R = CO_2Et, 1 hour for R = OMe and 35 min for R = CN).

b. Quantum yields of product formation were determined by Method II (Section 4.3). Errors: ± 15%.

c. PD stands for 1,3-pentadiene, HD for 2,5-dimethyl-2,4-hexadiene and CD for 1,3-cyclohexadiene.

Table 2-29: Concentration effects of 1,3-pentadiene (PD) on photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile[a]

[PD] (M)	**16**[b]	**48**[b]	Φ_p[c]	Φ/Φ^o[d]
0	0.384	0	0.0043	1
0.02	0.617	0.074	0.0070	1.62
0.04	0.547	0.096	0.0061	1.41
0.06	0.460	0.176	0.0052	1.21
0.10	0.388	0.226	0.0043	1

a. The solutions containing 2-$NpCO_2Me$ (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and PD (0.02-0.1 M) were irradiated (N_2 purged) for 4 hours in Apparatus II at 350 nm.

b. The results were reported in relative yield which was the GC area ratio of the product over the I.S. Errors: ± 5-7%.

c. Quantum yields of **16** formation were determined by Method II (section 4.3)

d. The quantum yield ratio (**16** formation) of above solutions with diene over that without diene.

Table 2-30: Concentration effects of 1,3-pentadiene (PD) on photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile[a]

[PD](M)	Φ_p[b]	**48**[c]	Φ/Φ_o[d]
0.3	0.0019	14	0.441
0.2	0.0029	13	0.676
0.15	0.0037	12	0.853
0.1	0.0043	11	1

a. The solutions contained 2-NpCO$_2$Me (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and PD (0.1-0.3 M) were irradiated (N_2 purged) for 5 hours in Apparatus II at 350 nm.

b. Quantum yields of **16** formation were determined by Method II (section 4.3). Error: ± 15%.

c. The results were reported in GC% from print out without I.S.

d. Same as that in d of Table 2-29.

To probe the possible existence of a ground state complex (GSC) between 2-NpCO_2Me and acacH, differential absorption spectra of solutions of acacH (0.1 M) and 2-NpCO_2Me (0.01, 0.001 and 0.0001 M) in acetonitrile were recorded against a double compartment reference cell, each compartment of which contained double the concentration of acacH and 2-NpCO_2Me as in the sample cell (see Figure 4-3, page 196). No new absorptions were observed, indicating the absence of a GSC between 2-NpCO_2Me and acacH. Differential absorption spectra were also recorded for the solution systems of acacH (3 M)/2-NpCO_2Me (0.01, 0.001 and 0.0001 M) and 2-NpCO_2Me (0.01 M)/acacH (1, 0.5 and 0.2 M), in acetonitrile. No new absorptions were observed for these systems.

The absorption spectra of NpR (R = 1-CO_2Me, 2-CO_2Me, 1-CO_2Et, 2-CO_2Et, 1-CN, 2-CN, 1-OMe and 2-OMe) and M(acac) (M = lithium or sodium) were measured at room temperature as shown in Figures 2-2, 2-24 and 2-25. The extinction coefficient values at various wavelengths are listed in Table 1-1.

The UV spectrum of 2-NpCO_2Me (0.0005 M) and that in the presence of sulfuric acid (0.0125, 0.0250 and 0.0375 M) were measured in acetonitrile at room temperature. No new absorptions were observed when sulfuric acid was added. Similar spectra were obtained in the presence of Li(acac) (0.01, 0.02 and 0.04 M) in methanol, again showing the absence of new absorptions under these conditions.

Phosphorescence of 2-NpCO_2Me (0.0005 M) in 1:3 2-propanol:ether at 77 K (as a solid solution) was not quenched by sulfuric acid (at concentrations of 0.003, 0.006 and 0.05 M).

The quenching of 2-$NpCO_2Me$ (0.0005 M) phosphorescence by acacH (at concentrations of 0.0005, 0.001, 0.005, 0.01, 0.05 and 0.1 M, Figure 2-26) and that of 2-$NpCO_2Me$ (0.02 M) phosphorescence by acacH (at concentrations of 0.01, 0.05 and 0.1 M, Figure 2-27) were attempted in 1:3 isopropanol:ether at 77 K, respectively. No quenching was observed in both cases. Since we have shown that 2-$NpCO_2Me$ fluorescence is quenched by acacH (Section 2.3.1), the absence of a change in phosphorescence must mean that the reverse triplet energy transfer also occurred; i.e. the third step in the following sequence: ^{1}2-$NpCO_2Me$ + acacH → ^{1}(2-$NpCO_2Me$-acacH) → (^{3}2-$NpCO_2Me$-acacH) → ^{3}2-$NpCO_2Me$ + acacH.

Phosphorescence of 2-$NpCO_2Me$ (0.01 M) was measured in the presence of iodomethane (0, 0.04 and 0.08 M). Intensity enhancements were observed, indicating the promotion of $S_1 \rightarrow T_1$ transition of 2-$NpCO_2Me$ by CH_3I (Figure 2-28).

2.9 Concentration dependence of the photocycloaddition

Because of the extensive overlap of the absorption spectra of NpR and acacH (Figures 2-2 and 2-24), it was difficult to determine which excited species was reacting, when mixtures of NpR (R = 1-CO_2Me, 2-CO_2Me, 1-OMe and 1-CN) and acacH were irradiated. Attempts at determining the reacting species were made by correlating quantum yields of NpR disappearance with the concentration of either NpR or acacH.

Quantum yields for 2-$NpCO_2Me$ disappearance in the photocycloaddition of 2-$NpCO_2Me$ (fixed at 0.05 M) and acacH at 300 nm were determined as a function of the concentration of acacH (0.05, 0.06, 0.07, 0.08 and 0.1 M). In addition, the quantum yields of the photocycloaddition of acacH (fixed

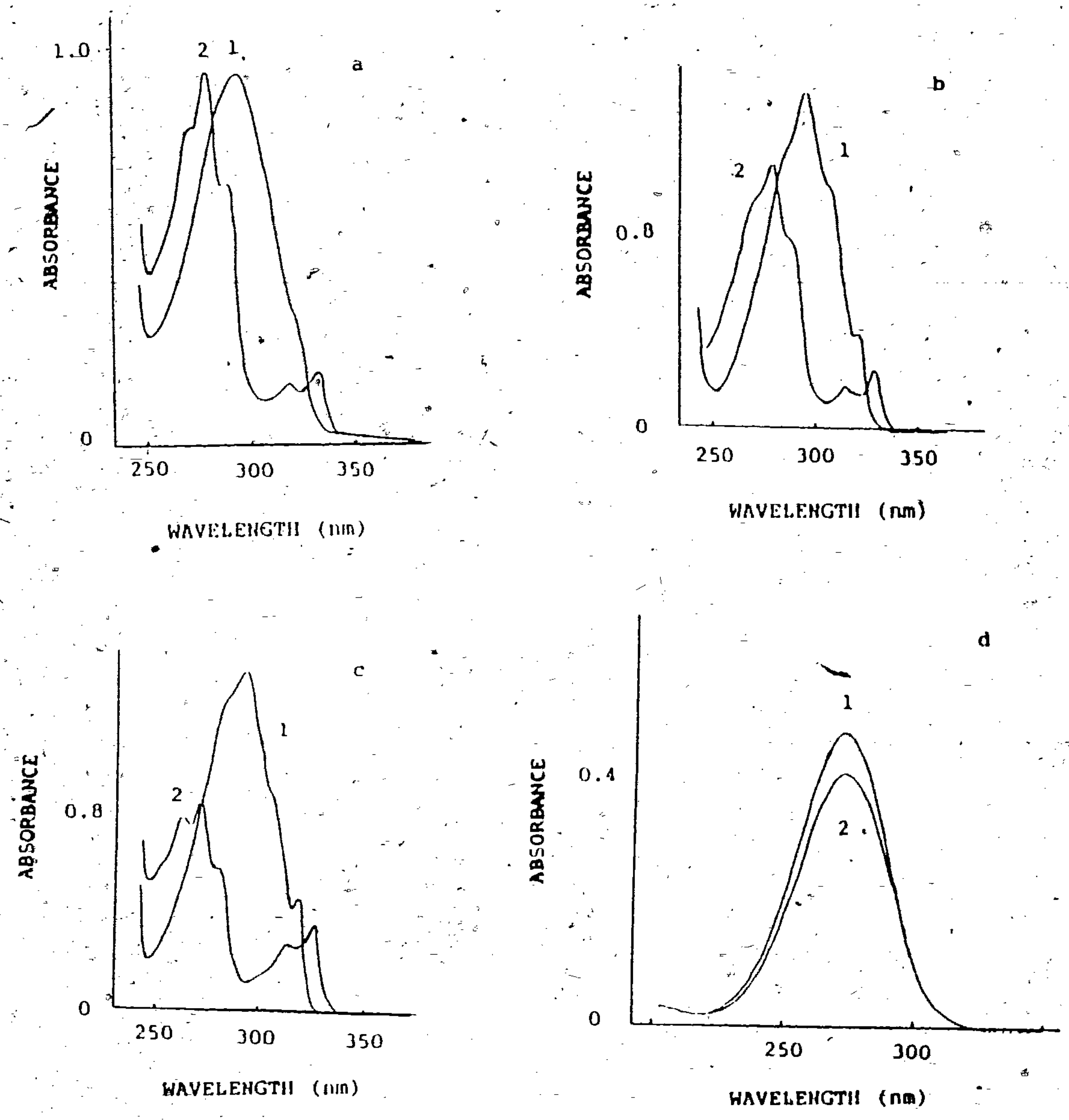


Figure 2-24: UV spectra a) 1-$NpCO_2Et$ (0.0004 M, curve 1) and 2-$NpCO_2Et$ (0.0004 M, curve 2) in acetonitrile; b) 1-NpCN (0.00093 M, curve 1) and 2-NpCN (0.000183 M, curve 2) in methanol; c) 1-NpOMe (0.000254 M, curve 1) and 2-NpOMe (0.000238 M, curve 2) in methanol and d) Na(acac) (0.000049 M, curve 1) and Li(acac) (0.00005 M, curve 2) in methanol.

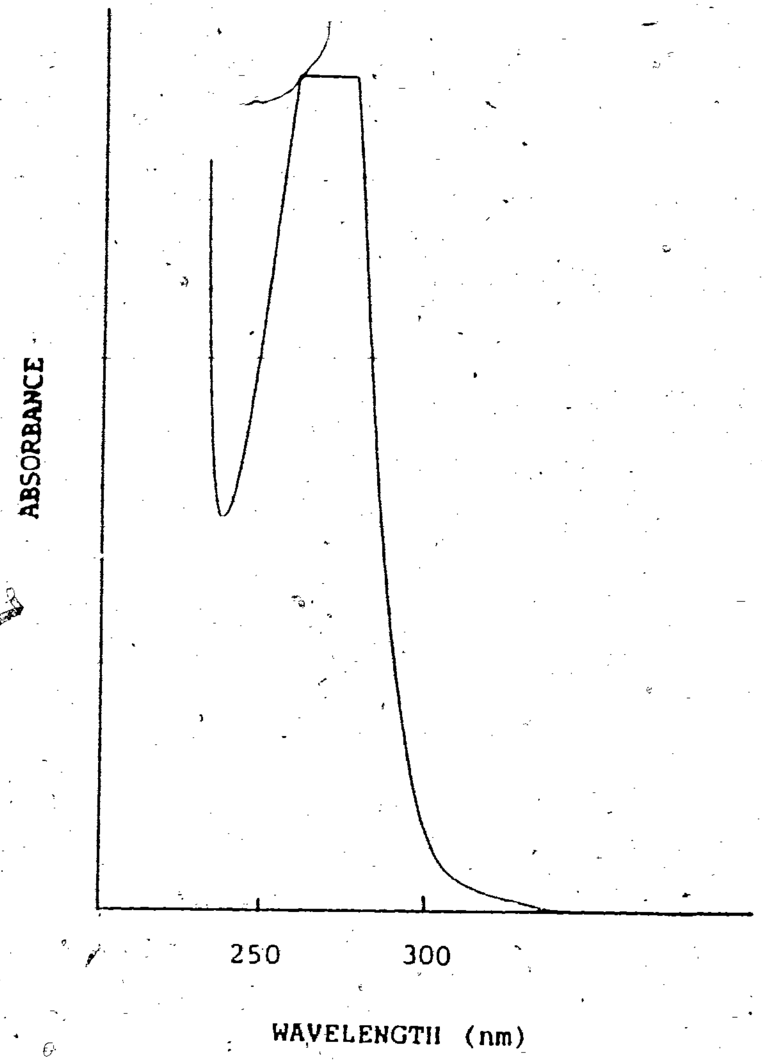


Figure 2-25: UV spectrum of compound **17** (0.0001 M) in methanol.

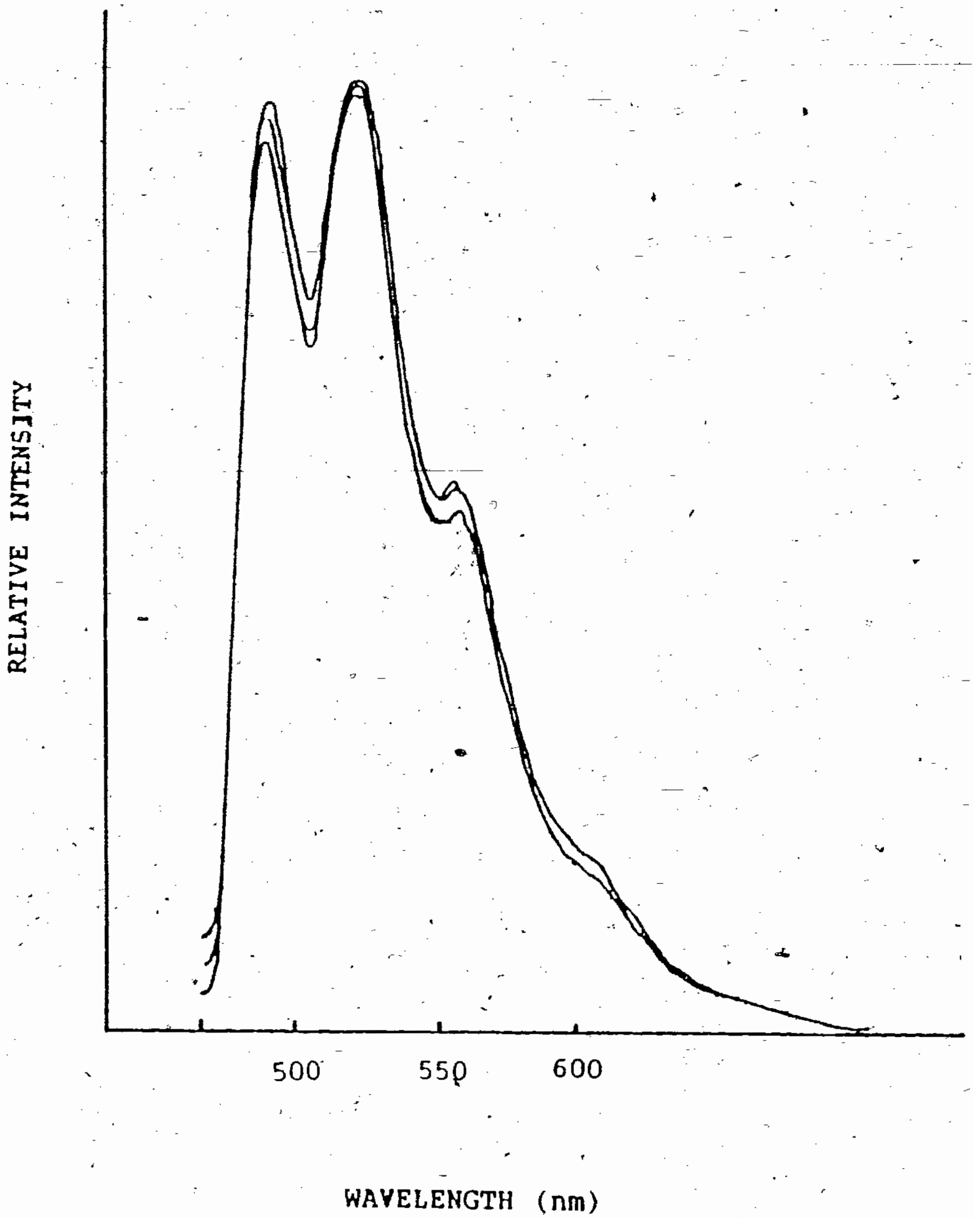


Figure 2-26: Phosphorescence quenching of 2-NpCO$_2$Me (0.0005 M) by acacH (0, 0.0005, 0.001, 0.005, 0.01, 0.05 and 0.1 M) at 77 K in 1:3 isopropanol:ether with excitation wavelength at 345 nm.

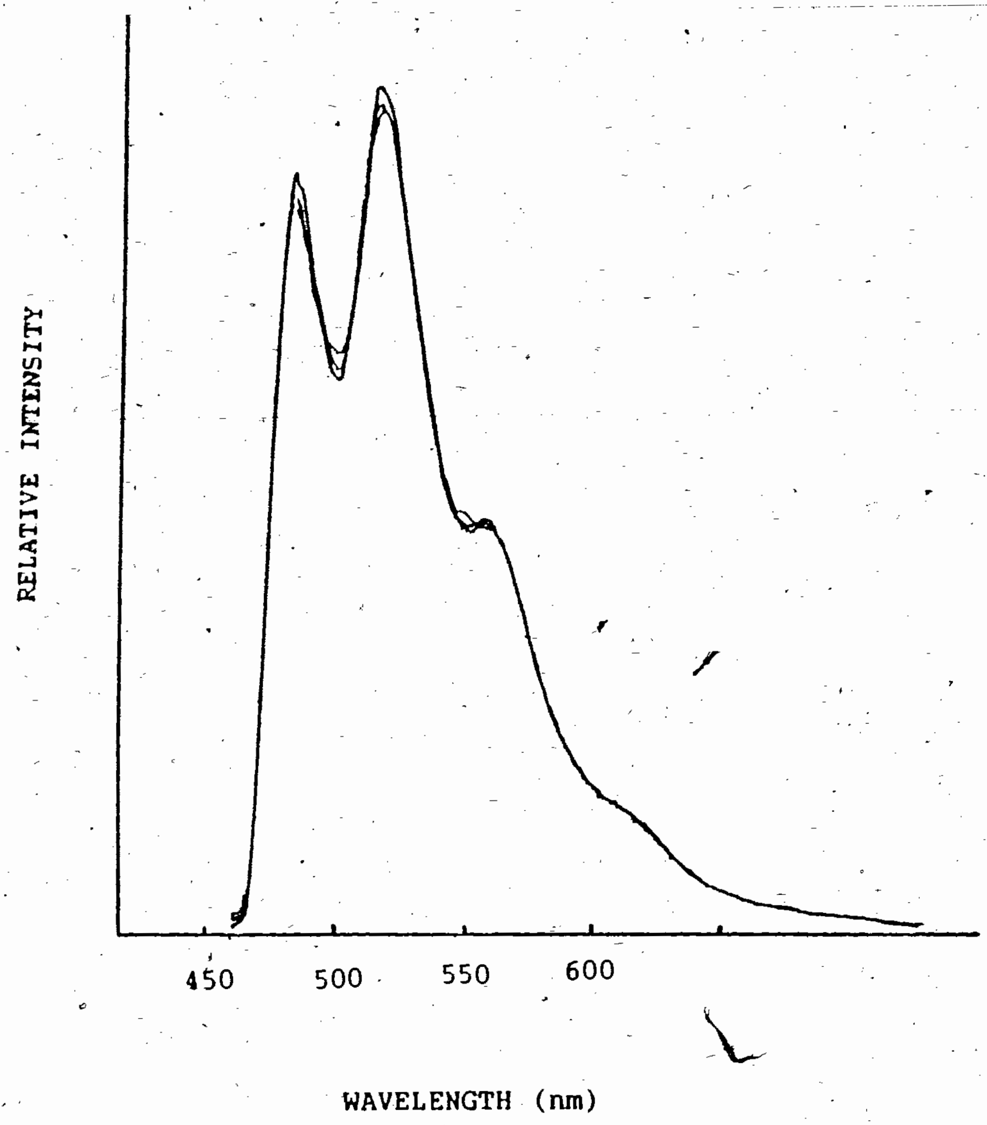


Figure 2-27: Phosphorescence quenching of 2-$NpCO_2Me$ (0.02 M) by acacH (0, 0.01, 0.05, 0.1 and 0.5 M) at 77 k in 1:3 isopropanol:ether with excitation wavelength at 350 nm.

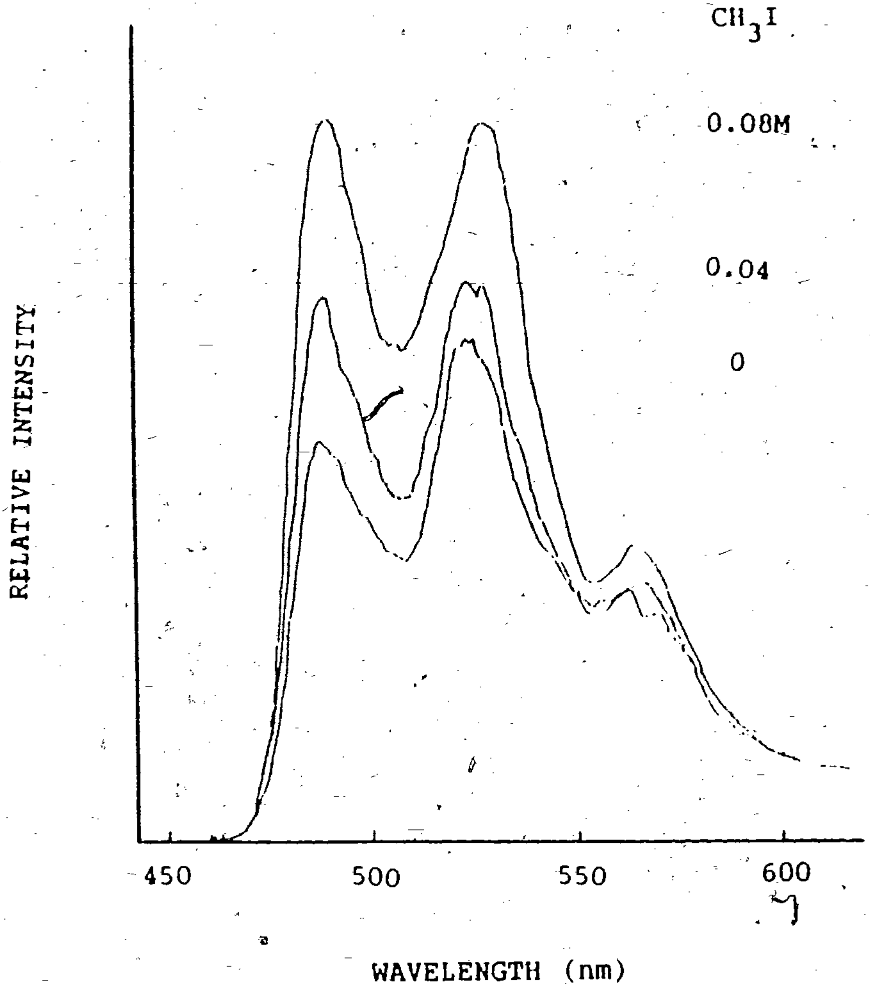


Figure 2-28: Phosphorescence enhancement of 2-NpCO$_2$Me (0.01 M) by CH$_3$I (0, 0.04 and 0.08 M) at 77 K in 1:3 isopropanol:ether with excitation wavelength at 330 nm.

at 0.05 M) and 2-$NpCO_2Me$ were determined as a function of the concentration of 2-$NpCO_2Me$ (0.05, 0.06, 0.07, 0.08 and 0.1 M). The light intensity absorbed by 2-$NpCO_2Me$ or acacH was calculated based on equation 4-4. At a fixed concentration of acacH but with increasing concentration of 2-$NpCO_2Me$, the quantum yields were essentially constant within experimental error (Table 2-31 and Figure 2-29, 0.0073-0.0078 if value of 0.005 was ignored). But at a fixed concentration of 2-$NpCO_2Me$ with increasing concentration of acacH, the quantum yields were increased (Table 2-31 and Figure 2-29, 0.015-0.059), suggesting that 2-$NpCO_2Me$ was the reacting species.

Similarly, the quantum yield dependence on the concentration of 1-$NpCO_2Me$ (0.05, 0.06, 0.07, 0.08 0.09 and 0.1 M) with a fixed concentration of acacH at 0.05 M and the quantum yield dependence on the concentration of acacH (0.04, 0.048, 0.056, 0.064, 0.072 and 0.08 M) with a fixed concentration of 1-$NpCO_2Me$ at 0.04 M were determined. Results similar to the above were obtained. At the fixed [acacH], the quantum yield of 1-$NpCO_2Me$ disappearance increased slightly as the concentration of 1-$NpCO_2Me$ increased (Table 2-32, 0.008-0.013). But with fixed [1-$NpCO_2Me$], the quantum yield increased markedly as the concentration of acacH increased (Table 2-32 and Figure 2-30, 0.001-0.026). Similar experiments were carried out with 2-NpOMe/acacH and 1-NpCN/acacH systems. The results (Table 4-11 and 4-12) were similar to those described above for the 1-$NpCO_2Me$/acacH system. Because of the complexity of the calculations and the large error margins, the results may not be used as solid proofs of the mechanism.

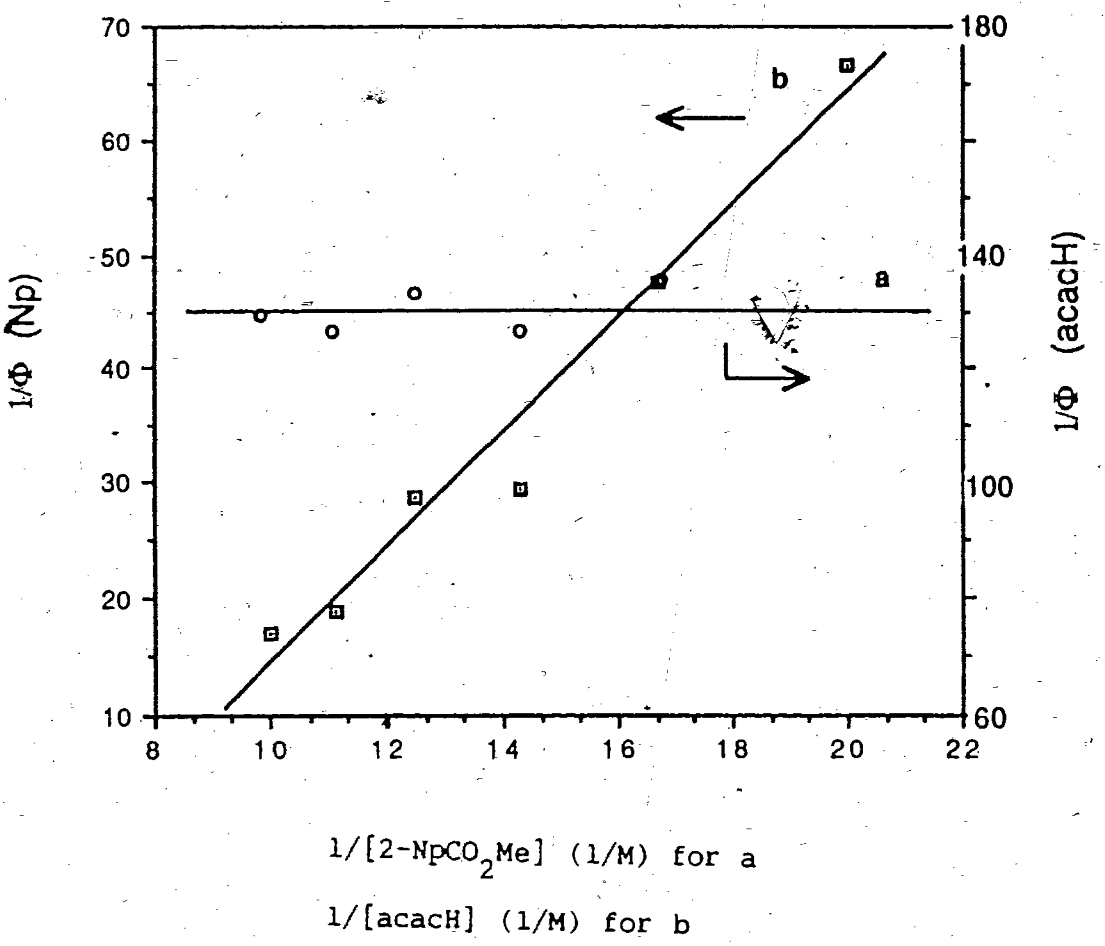


Figure 2-29: Concentration dependence of the photocycloaddition of 2-NpCO$_2$Me (0.05 M when fixed) and acacH (0.05 M when fixed) in acetonitrile at 300 nm irradiation.

Table 2-31: Concentration dependence of photocycloaddition of methyl 2-naphthoate and acacH in acetonitrile

$[2\text{-}NpCO_2Me]=0.05M^a$		$[acacH]=0.05\ M^c$	
[acacH] (M)	Φ_{Np}^{b}	$[2\text{-}NpCO_2Me]$ (M)	Φ_{acacH}^{d}
0.05	0.015	0.05	0.005
0.06	0.021	0.06	0.0073
0.07	0.034	0.07	0.0078
0.08	0.035	0.08	0.0074
0.09	0.053	0.09	0.0078
0.10	0.059	0.10	0.0077
Conversion	25-35%	13-17%	

a. The solutions containing $2\text{-}NpCO_2Me$ (0.05 M) and acacH (0.05-0.1 M) were irradiated for 5-10 hours in apparatus II at 300 nm using xanthone (mixed with resulting solution after irradiation) as I.S. Errors: ± 15%.

b. Quantum yields of $2\text{-}NpCO_2Me$ disappearance based on $2\text{-}NpCO_2Me$ absorbing light.

c. The solutions containing acacH (0.05 M) and $2\text{-}NpCO_2Me$ (0.05-0.1 M) were irradiated for 6-11 hours. For other conditions, see a.

d. Quantum yields of $2\text{-}NpCO_2Me$ disappearance based on acacH absorbing light.

Table 2-32: Concentration dependence of photocycloaddition of methyl 1-naphthoate and acacH in acetonitrile

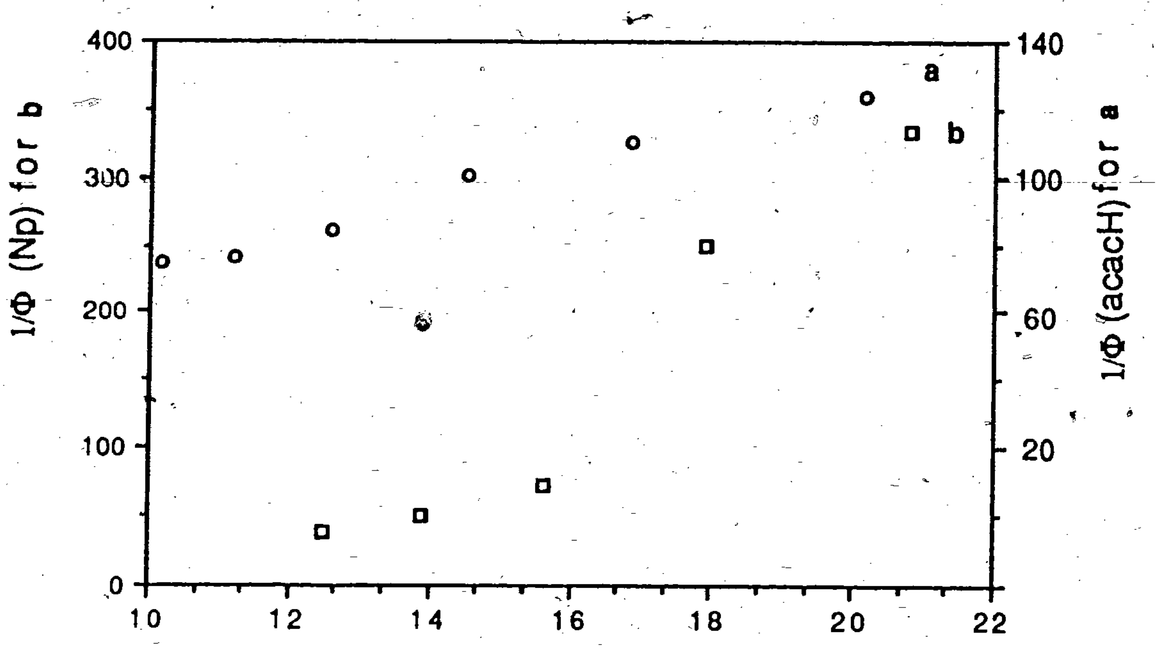
$[1\text{-NpCO}_2\text{Me}]=0.04\text{M}^a$		$[\text{acacH}]=0.05\ \text{M}^c$	
[acacH] (M)	$\Phi_{Np}{}^b$	$[1\text{-NpCO}_2\text{Me}]$ (M)	$\Phi_{acacH}{}^d$
0.04	0.001	0.05	0.008
0.048	0.003	0.06	0.009
0.056	0.004	0.07	0.01
0.064	0.014	0.08	0.012
0.072	0.020	0.09	0.013
0.08	0.026	0.10	0.013
Conversion>	4-28%		9-13%

a. The solutions containing $1\text{-NpCO}_2\text{Me}$ (0.04 M) and acacH (0.04-0.08 M) were irradiated for 6-8.5 hours in apparatus II at 300 nm. For GC analysis, see a of Table 2-31. Errors: ± 20%.

b. Quantum yield of $1\text{-NpCO}_2\text{Me}$ disappearance based on $1\text{-NpCO}_2\text{Me}$ absorbing light.

c. The solutions containing acacH (0.05 M) and $1\text{-NpCO}_2\text{Me}$ (0.05-0.1 M) were irradiated for 10-15 hours. For other conditions, see a.

d. Quantum yield of $1\text{-NpCO}_2\text{Me}$ disappearance based on acacH absorbing light.



1/[1-NpCO$_2$Me] (1/M) for a

1/[acacH] (1/M) for b

Figure 2-30: Concentration dependence of photocycloaddition of 1-NpCO$_2$Me (0.04 M when fixed) and acacH (0.05 M when fixed) in acetonitrile with 300 nm lamp irradiation.

CHAPTER 3 DISCUSSION

3.1 Concentration dependence

Irradiation of naphthalene derivatives (NpR; R = CO_2Me, CO_2Et, OME and CN) with acacH in acetonitrile gave 1,5-diketone products. The addition occurs at the 1,2-position of the naphthalene species when the substituent is at position 2 (equation 2-1, page 15; equation 2-8, page 29; equation 2-10, page 31) and occurs at the 7,8-position when the substituent is at position 1 (equation 2-4, page 19; equation 2-7, page 27) except for the 1-NpOMe case (equation 2-9, page 30). Naphthalene derivatives and acacH also undergo effective [2+2] photocycloaddition with simple olefines.[5-23,56,59] Their absorptions ranging from 240 nm to 340 nm overlap extensively (Figure 2-2, page 40 and 2-24, page 106). The excitation of both NpR and acacH is therefore unavoidable when the photoreaction is carried out with a light source at 300 nm, making it very difficult to determine which excited state is initiating the reaction. When a solution containing NpR and acacH is irradiated, there are four species in the solution, namely, ground state NpR and acacH and excited state NpR (*NpR) and acacH (*acacH). If the concentration of one of the starting materials is changed, then the concentrations of the rest are also changed, owing to changes in relative absorptions. There are three possible mechanisms which may lead to product, i.e. *NpR is reactive and adds to a ground state acacH; *acacH is reactive and adds to a ground state NpR; or both *acacH and *NpR are reactive giving the same products. The excitation of acacH probably does not generate singlet excited NpR. If the first mechanism is operating, the following kinetics should be observed. Firstly, according to equation 2-25, the plot of $1/\Phi_{Np}$ against 1/[acacH] should be linear with a positive slope when the concentration of NpR is fixed and the quantum yields are calculated based on NpR absorbing light (i.e. acacH as a quencher). Secondly, when the concentration of acacH is fixed and the quantum yields are calculated based on acacH absorbing light, the plot of $1/\Phi_{Np}$ against 1/[NpR] should produce a straight line with a slope of zero (i.e. $1/\Phi_{Np}$ does not change with the changing of NpR concentration). If the second mechanism is operating, the same argument will apply; the latter plot should be a straight line with a positive slope when the concentration of acacH is fixed and the former plot should have a slope of zero when the concentration of NpR is fixed.

The correlations of $1/\Phi_{Np}$ *vs* 1/[Q] (Q represents acacH when [NpR] is fixed and NpR when [acacH] is fixed; Figure 2-29, page 112) obtained from photocycloaddition of 2-$NpCO_2Me$ and acacH show that the quantum yield of 2-$NpCO_2Me$ disappearance remains unchanged with increasing concentration of 2-$NpCO_2Me$ when [acacH] is fixed (Table 2-31, page 113, 0.0073-0.0078 if the value of 0.005 is ignored), but the quantum yield increases with increasing concentration of acacH when [2-$NpCO_2Me$] is fixed (Table 2-31, 0.015-0.059). These results suggest that 2-$NpCO_2Me$ is the reactive species. The results from similar experiments on the photocycloaddition of 1-$NpCO_2Me$ and acacH are not as clear as above case. The quantum yield of 1-$NpCO_2Me$ disappearance increases slightly (Table 2-32, page 114, 0.008-0.013) with increasing concentration of 1-$NpCO_2Me$ when [acacH] is fixed, but increases markedly (Table 2-32, 0.001-0.026) with increasing concentration of acacH when [1-$NpCO_2Me$] is fixed (Figure 2-30, page 115). Taking into consideration the complexity of the system and the differences in quantum yield between the highest with the lowest concentrations (Φ = 0.008-0.013

when [acacH] is fixed and $\Phi = 0.001-0.026$ when [2-$NpCO_2Me$] is fixed), it is reasonable to suggest that the excited state of 1-$NpCO_2Me$ is initiating the reaction. Similar results are obtained from photoreactions of 2-NpOMe and 1-NpCN with acacH, which implys that the singlet excited 1-NpCN and 2-NpOMe are initiating the respective reactions.

3.2 Solvent effect on the photocycloaddition

Since the double bond of the enolic form of acacH is the bond that adds to the naphthalene derivatives, the existence of a certain amount of the enol form in a particular solvent is essential. Although acacH is more enolic in nonpolar solvents than in polar solvents,[90] the percentage of the enol form in either nonpolar or polar solvents is fortunately large enough to allow reaction. For example, 0.1 M acacH in hexane has 91.4-92%[90a] enol form, and in ethanol, 82.5-83.5%[90a] and in acetonitrile, 70%[90b]. The de Mayo reaction, i.e. [2+2] photocycloaddition of acacH and olefins, takes place only in a nonpolar solvent (e.g., cyclohexane) but not in a polar solvent.[57] The reaction is reported to be solvent dependent with the rate decreasing in the order of ether, ethyl acetate and acetonitrile.[57] However, the yield of **16** in the photocycloaddition of 2-$NpCO_2Me$ and acacH ranges from 0% to 19% in the increasing order of cyclohexane, benzene, THF and acetonitrile/methanol, just opposite to the trend observed in the de Mayo reaction. This strongly suggests that excited state acacH is not reactive in the photoaddition of 2-$NpCO_2Me$ and acacH.

It has been well established that two main factors are usually considered as the origin of bonding and stabilization in an exciplex.[5] These are excitation resonance between the monomer molecules, and charge transfer from one monomer to another, respectively. Solvent effect on exciplexes is therefore very important because the exciplex has charge-like character. Solvent molecules tend to reorient around the components in response to electronic changes. Polar solvent molecules are more effective because they can assist in the stabilization of the "new" charge of each reactant partner. In nonpolar solvents, such stabilization is weak. The above argument may be used to explain the solvent effect on the photoaddition of 2-NpCO_2Me with acacH, and may imply that the photoaddition occurs via an exciplex mechanism which is supported by other evidence as discussed in Section 3.7.

3.3 The effects of electron donating quencher

There are many reported examples[91-103] of the quenching of fluorescence of aromatic compounds by species which cannot function by simple transfer of electronic excitation energy because the quenchers do not have sufficiently low lying singlet manifolds. The quenching of 2-NpR (R = CO_2Me, CO_2Et, OMe and CN) fluorescence (Table 2-11, page 54) and the suppression of the photocycloaddition between 2-NpR with acacH (Table 2-2, page 35) by tributylamine (TBA) belong to this type. For example, the lowest singlet excited energy of TBA (>100 kcal/mole) is too high to quench that of 2-NpR (E_s = 83-86 kcal/mol, Table 1-2, page 14) by an energy transfer mechanism. On the other hand, it is well established that the lowest singlet excited states of aromatic hydrocarbons can be quenched by amines via an electron transfer mechanism.[104-106] The feasibility of an electron transfer pathway for a bimolecular quenching reaction is determined by the free energy changes (ΔG) evaluated from the Weller equation. The half-wave potential value ($E_{1/2}$) for TBA can be estimated to be around 1.05 v in acetonitrile by referring to that of tripropylamine

(1.12 v in acetonitrile), triethylamine (1.15 v in acetonitrile) and trimethylamine (1.29 v in acetonitrile).[107] The negative ΔG values (-39.8 kcal/mol for R = 2-CO_2Me, -16.5 kcal/mol for 2-CN and -0.43 kcal/mol for 2-OMe) of the pairs between NpR with TBA calculated from the Weller equation indicate a favorable electron transfer quenching pathway from TBA to ^{1}NpR. The fluorescence of 2-$NpCO_2Me$ was quenched by both TBA and DMA, indicating the interception of ^{1}2-$NpCO_2Me$ by TBA or DMA. The good agreement in rate constants obtained from fluorescence quenching of 2-$NpCO_2Me$ by TBA (k_q = 3.6 x 10^{10} M^{-1} s^{-1}, Table 2-11, page 54) and from quantum yield dependence of **16** formation for the photoaddition of 2-$NpCO_2Me$ and acacH on TBA (k_q = 3.3 x 10^{10} M^{-1} s^{-1}, Table 2-2, page 35) strongly support the view that the photocycloaddition is initiated by the singlet excited state of 2-$NpCO_2Me$. Similiar experiments with the quencher at a single concentration showed that the photoadditions of 2-NpR (R = CO_2Et, OMe and CN) and acacH were retarded in the presence of TBA (0.02 M) or DMA (0.02 M) (Table 2-3, page 37). The fluorescence of 2-NpR were also efficiently affected by TBA (Table 2-11, page 54). It is thus suggested that the interception of the ^{1}2-NpR by TBA is also responsible for the retardation of the photocycloaddition. Furthermore, the lack of quenching of the de Mayo reaction by TBA and DMA under comparable conditions clearly indicates that TBA and DMA do not quench the excited state of acacH, and confirms that ^{1}NpR is reacting in the photocycloaddition of NpR and acacH.

3.4 Diene effects

Energetically, dienes are good triplet quenchers in the NpR/acacH reaction system. This is because their singlet excited state is higher in energy, while the triplet excited state is lower in energy than the corresponding states of NpR (Table 1-2, page 14). The absence of quenching of the photocycloaddition by dienes appears to indicate that a triplet state mechanism is not involved. On the other hand, the presence of 1,3-pentadiene (PD), 2,5-dimethyl-2,4-hexadiene (HD) or 1,3-cyclohexadiene (CD) at a concentration of 0.02 M accelerates the photocycloaddition of 2-NpR (R = CO_2Me, CO_2Et, OMe and CN) to acacH. The quantum yields of product formation for the above photoreactions in the presence of diene were always greater than those in the absence of the diene (Table 2-28, page 101). A further concentration effect of PD on the photocycloaddition revealed that in a low [PD] range (i.e. [PD] = 0.02-0.1 M, Table 2-29, page 102), the addition product **48** increased with increasing concentration of PD. At the same time, the quantum yield (Φ_p) for the formation of **16** decreased, indicating that reaction 3-1 competes with reactions 3-2 and 3-3 (scheme 3-1). The $\Phi/\Phi°$ (the quantum yield ratio of **16** for reactions with

Scheme 3-1

$$^{1}\text{2-NpCO}_2\text{Me} + \text{acacH} \xrightarrow{k_1} {}^{1}(\text{2-NpCO}_2\text{Me-acacH}) \longrightarrow \mathbf{16} \qquad \text{3-1}$$

$$^{1}\text{2-NpCO}_2\text{Me} + \text{PD} \xrightarrow{k_2} {}^{1}(\text{2-NpCO}_2\text{Me-PD}) \qquad \text{3-2}$$

$$^{1}(\text{2-NpCO}_2\text{Me-PD}) \xrightarrow{k_3} \mathbf{48} \qquad \text{3-3}$$

$$^{1}(\text{2-NpCO}_2\text{Me-PD}) + \text{acacH} \xrightarrow{k_4} {}^{1}(\text{2-NpCO}_2\text{Me-acacH}) + \text{PD} \qquad \text{3-4}$$

$$^{1}(\text{2-NpCO}_2\text{Me-acacH}) \xrightarrow{k_5} \mathbf{16} \qquad \text{3-5}$$

and without diene) values show no correlation with concentrations of PD. The data presented here are most readily rationalized by the mechanism shown in Scheme 3-1. The key aspect of this scheme is the proposed exciplex formation between 2-$NpCO_2Me$ and PD (equation 3-2) and the interception of the exciplex by acacH (equation 3-4), perhaps via an exciplex-exciplex exchange reaction.[87-89,108-110] The quenching of the fluorescence of aromatic hydrocarbons (substituted naphthalene or phenanthrene) by 1,3-pentadiene has been interpreted in terms of exciplex formation between the lowest singlet excited state of the aromatic hydrocarbon and the diene.[111-116] Strong evidence for this mechanism is the observation of emission from the 1-cyanonaphthalene-diene exciplex.[117] The photocycloadditions of aromatic compounds with dienes have been reported to give 4+4 adducts via an exciplex mechanism.[41-43] The quenching of 2-$NpCO_2Me$ fluorescence by PD gives $k_q\tau$ of 9.08 M^{-1}, indicating that the singlet excited state of 2-$NpCO_2Me$ is indeed intercepted by PD, probably forming a non-fluorescing exciplex. Reactions 3-4 and 3-5 are analogous to the 'termolecular interaction' proposed by Liu[118,119] and Caldwell[120] to account for the catalytic effect of 1,3-pentadiene upon the dimerization of 9-phenylanthracene. Assuming that ^{1}(2-$NpCO_2Me$-PD) has a longer lifetime than ^{1}2-$NpCO_2Me$, in the low concentration range of PD, reactions 3-2 to 3-5 also occur in addition to reaction 3-1, due to the longer lifetime of ^{1}(2-$NpCO_2Me$-PD) contributing extra amount of **16**, and therefore enhancing the quantum yield of **16**. However, in the high concentration range of PD, ^{1}(2-$NpCO_2Me$-PD) is surrounded mostly by PD instead of acacH, reaction 3-4 is no longer important and the competition of reactions 3-1 and 3-2 dominates. Notice that they have close $k_q\tau$ values (under non-purged condition) obtained from fluorescence quenching, i.e. 11.8 M^{-1} for quenching by acacH (Table 2-7, page 46) and 9.08 M^{-1} for quenching by PD, (Table 2-10, page 52). This results in two competing reaction pathways, with no acceleration effect at all. The photoaddition of 2-NpCO$_2$Me with PD in the presence of various concentrations of acacH does not show any acceleration of the formation of **48**, indicating the absence of a termolecular process. The fact that the photocycloaddition of 2-NpCO$_2$Me with acacH is suppressed by the interception of ^{1}2-NpCO$_2$Me by PD (in high concentration range) combined with the absence of triplet sensitization of the reaction (Section 3.6) strongly suggests ^{1}2-NpCO$_2$Me as a reacting species in the photocycloaddition.

3.5 Heavy atom effects

In photochemistry, molecules with a heavy atom enhance yields of triplet derived products by promoting intersystem crossing.[89,121-125] Therefore, heavy atom effects on product distributions should provide good evidence on the multiplicity of reacting species. The photocycloaddition of 2-NpCO$_2$Me to acacH in the presence of CH_3I was examined. Since $k_q\tau$ (non-purged) of 39.9 M^{-1} (Table 2-12, page 55) for the 2-NpCO$_2$Me fluorescence quenching by CH_3I is considerably greater than that by acacH (11.8 M^{-1}, non-purged, Table 2-7, page 46), $[CH_3I]/[2\text{-NpCO}_2\text{Me}]$ was kept within 0-0.20 and $[CH_3I]/[\text{acacH}]$ within 0-0.05 so that the photoaddition of 2-NpCO$_2$Me to acacH would still predominate in the presence of CH_3I. The yield of **16** decreased slightly when the concentration of CH_3I was increased. At the same time, product **17** appeared and the yield of **17** increased when $[CH_3I]$ was increased (Table 2-15, page 70). The increased formation of **17** in the $[CH_3I]$ range of 0-0.004 M cannot be explained simply by the heavy atom effect, due to the fact that **17** was not formed under triplet sensitization (section 3.6). The acidity (pH = 4-4.5) of the resulting photolysate indicates the formation of an acid, most probably HI, during the irradiation. This acid is proposed to be responsible for the increase of **17** which was formed in the sulfuric acid catalyzed reaction (Section 3.10). The quenching of ^{1}2-NpCO$_2$Me by CH$_3$I may be responsible for the slight decrease of the yield of **16**. But since the changes in yields are quite small, the effect needs to be carefully reexamined using higher concentration of CH$_3$I.

The presence of CH$_3$I in the photocycloaddition between 2-NpCN and acacH simply caused a slight quantum yield decrease of compound **38** without an accompanying new product (Table 2-17, page 74). The same argument as above concerning the decrease of **38** applies. The absence of a new product is consistent with the results from the study of the effect of acid on the reaction (Section 2.5.2).

3.6 Reacting species

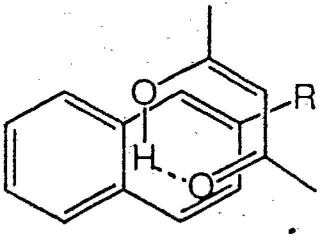
Another useful tool to determine the multiplicity of a photoreaction is selective quenching or selective sensitization. Thus, the absence of triplet quenching or sensitization indicates the possibility of a singlet mechanism. Xanthone (E_T = 74.1 kcal/mol)[82] and benzophenone (E_T = 69.2 kcal/mol)[82] failed to sensitize the photocycloaddition of 2-NpR (E_T = 58-61 kcal/mol, Table 1-2. R = CO$_2$Me, CO$_2$Et, OMe and CN) to acacH (E_T = 69-74 kcal/mol)[59], which indicates that neither the triplet state of 2-NpR nor that of acacH is involved in the photocycloaddition. Having a high efficiency of intersystem crossing (Φ_{isc} = 0.84)[18,82] from $S_1 \rightarrow T_1$, 2-acetonaphthalene fails to add to acacH, supporting the singlet mechanism.

At this stage, and based on the results of experiments to study (a) concentration dependencies, (b) solvent effects, (c) electron donating quencher effects, (d) diene effects, and (e) selective sensitization, it is concluded that the singlet excited state of 2-NpR is the reacting species in the photocycloaddition to acacH.

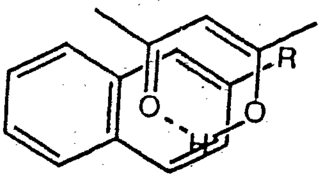
3.7 Discussion on the intermediate

Many photocycloadditions have been discussed in terms of exciplexes[5,6,10,27-35,126] which may be confirmed by the appearance of a unique fluorescence at longer wavelengths than the fluorescence of the precursors.[8,127,128] However, in some cases, exciplex emissions are totally absent so that the existence of postulated exciplexes remains speculative.[129,130] Pac has reported the negative temperature effect on both the fluorescence quenching and the photocycloaddition of 1-cyanonaphthalene to furan[9,26,131,132] and has proposed that an exciplex is the precursor of the addition product. The negative temperature effect is also observed with the 2-NpCO$_2$Me/acacH pair in fluorescence quenching of 2-NpCO$_2$Me by acacH. The $k_q\tau_0$ values decrease as the temperature is increased (Table 4-5, page 181) indicating that the dissociation of an exciplex into ^{1}2-NpCO$_2$Me and acacH is competing with the decay to ground state and to product. The plot of log k_q against 1/T gives a straight line with a positive slope (Figure 2-16, page 69) which is similar to that reported. Although there is no exciplex emission observed from the ^{1}2-NpCO$_2$Me-acacH pair in either polar (CH$_3$CN) or non-polar solvents (methylcyclohexane), the plot implies the existence of a reversible exciplex of ^{1}2-NpCO$_2$Me with acacH. It should be pointed out that the existence of an exciplex does not necessarily require the intermediacy of an exciplex in photoreactions, since exciplex formation may be independent of the photoreaction. Generally speaking, further evidence such as negative temperature effect on the photocycloaddition is needed to claim an exciplex intermediate in the reaction. Considering the observation of the negative temperature effect on the fluorescence quenching as well as the fact that exciplexes$^{5,6,10,27-36, 133,134}$ are quite commonly proposed in photocycloadditions, we assume that the photocycloaddition of 2-NpCO$_2$Me to acacH goes though an exciplex intermediate, on which the structures of the products will be discussed.

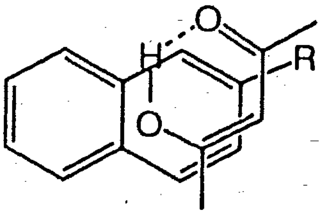
The photocycloadditions of 2-NpR (R = CO$_2$Me, CO$_2$Et, OMe and CN) to acacH are regioselective giving the orientation as shown in **16**, **20** (equation 2-1, page 15), **38** (equation 2-8, page 29) and **44** (equation 2-10, page 31) for the 1,2-addition products. The dependence of the regioselectivity on the electronic nature of 2-NpR can be ruled out due to the exclusive orientation of the 1,2-adducts regardless of the nature of an electron withdrawing group or an electron donating group at the 2-position.



E$_1$



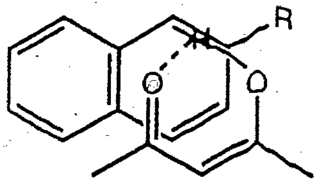
E$_2$



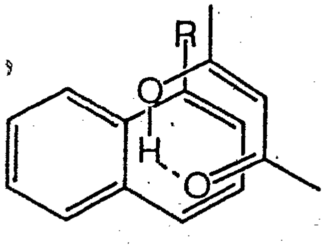
E$_3$

The regioselectivity may be explained in terms of exciplex geometry which is always in *endo* form. There are four kinds of exciplex conformation when the addition occurs at the substituted ring, i.e. 1) two 1,2-additions with respect to R as shown by E$_1$ and E$_2$; 2) two 3,4-additions with respect to the unsubstituted ring as shown by E$_3$ and E$_4$. The unfavorable interaction due to the methyl group of acacH lying above the unsubstituted ring in

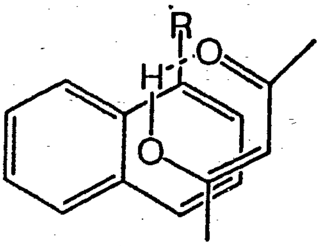
E_2 and E_4 may be responsible for the absence of the 1(or 4)-acetonyl-2(or 3)-acetyl-adduct. The same argument applies for 1-substituted naphthalene and these two types of conformations will not be discussed later. It seems that the steric hindrance in E_3 prevents the addition from occurring at the 3,4-position while E_1 does not show such crowding. The photocycloadditions of 1-NpR (R = CO_2Me, CO_2Et and CN) to acacH occur at the 7,8-position with the regiospecificity as shown in **22**, **26** (equation 2-4, page 19) and **33** (equation 2-7, page 27) except in the case of 1-NpOMe. Conformations such as E_5 and E_6 can explain the addition at the 3,4-position in 1-NpOMe case owing to unfavorable crowding in E_5. The preferred addition at the 7,8-position in the unsubstituted ring of other 1-NpR cases may imply a better activation of the unsubstituted ring by the substituents at carbon 1 position.



E_4



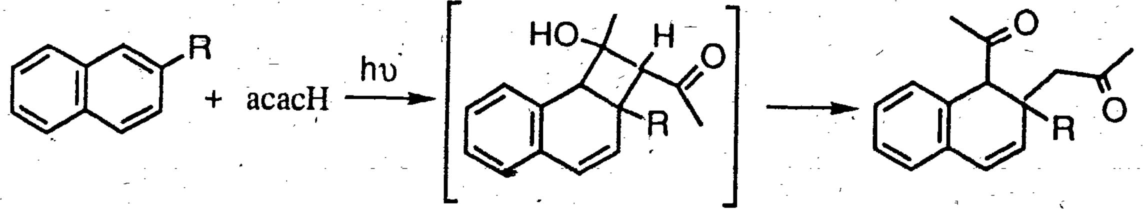
E_5



E_6

Part of stereochemistry of the addition products has been lost due to the ring opening as shown in equation 3-6. Considering i) the requirement of a *cis* orientation of H_d and H_e (J = 7 Hz) in compound **22** (equation 2-4, page 19) in order to undergo the secondary intramolecular addition resulting in a caged compound **23** (equation 2-4, page 19); ii) the corresponding protons of products such as **26** and **33** having coupling constant ranging 6.5-7.5 Hz which are very close to that of compound **22**; iii) the configuration requirement of the proposed exciplex intermediates

E_1 and E_6; and iv) the agreement of MM2 calculation with NOE experimental results on **16** and **33**, it is reasonable to assign the two ketone side chains in the *cis* orientation in all addition products from naphthalene derivatives.



3-6

Contrasting with above, the irradiation of phenanthrene with acacH under neutral condition gave a mixture of *cis*- and *trans*-9-acetyl-10-acetonyl-9,10-dihydrophenanthrene (**28** and **29**) plus a minor compound **30** (9-acetyl-9,10-dihydrophenanthrene, page 22). In independent experiments, irradiation of **28** did not give **29** and **30** and irradiation of **29** did not give **28** and **30**. These results indicate that compounds **28** and **29** are primary photoproducts and **30** is not a secondary product formed by Norish type II mechanism. A mechanistic study of phenanthrene addition was not carried out, but the formation of the *trans* product **29** as a primary product may imply a triplet mechanism which is consistent with reported[46-53] photoadditions of phenanthrene to olefins.

A preliminary photolysis study showed that in the presence of Li(acac), the ratio **28**/**29** becomes smaller (page 24) compared with that under neutral conditions. The amount of compound **30** increased sharply from 13% (page 22) to 36% (page 24) and an aldol condensation product **31** was also formed. Contamination of **28** by a small amount of **29** and contamination of **29** by a small amount of **28** made control experiments to determine thermal (acid or base catalyzed) epimerisation unreliable. The ratio of a mixture of **28, 29, 31** to PN changed from 0.90, 0.16, 0 and 1 to 0.34, 0.16, 0.23 and 1 after dilute sulfuric acid was added to the mixture. This observation indicates at least two possibilities. These are: a) **28** alone goes to only **31**; or b) **28** gives **29** under acidic or basic conditions, and both **28** and **29** undergo aldol condensation giving **31**. Conversion of PN increased when the concentration of Li(acac) increased (Table 2-20, page 77), showing an acceleration of the addition by Li(acac). Product distributions (Table 2-20) need to be reexamined, however due to an error in the detection of compound **31**. Further studies of the mechanism and the catalysis by Li(acac) are required.

3.8 Kinetic studies

Scheme 2-1 (page 85) is proposed as a basic reaction mechanism for the photocycloaddition of 2-$NpCO_2Me$ to acacH, based on the following findings: i) the photocycloaddition gives diketone product **16**; ii) quenching of 2-$NpCO_2Me$ fluorescence by acacH; iii) no triplet sensitization of the addition; iv) the lack of quenching of 2-$NpCO_2Me$ phosphorescence by acacH; v) a good agreement in rate constants obtained from 2-$NpCO_2Me$ fluorescence quenching by TBA and from quantum yield measurements in the presence of TBA. Generally speaking, a good agreement between $k_q\tau_0$ obtained from quantum yield measurement and that obtained independently from fluorescence quenching for the same photoreaction is required as a proof of the singlet mechanism.[58] However, for the photocycloaddition of 2-$NpCO_2Me$ with acacH, the discrepancy of the two $k_q\tau_0$ values (2.1 M^{-1} in Table 2-25, page 88 from quantum yield measurement and 28.7 M^{-1} in Table 2-6, page 44 from fluorescence quenching method) is considered too large to be due to experimental errors. A similar discrepancy also is observed for the photocycloaddition of 2-NpR (R = CO_2Et, OMe and CN) to acacH (Table 2-26, page 89; Table 2-6, page 44). Figures 2-2 (page 40) and 2-24 (page 106) show the extensive overlap of the absorption spectra of NpR and acacH. In the photoreactions, the simple correction made at one wavelength is certainly not adequate when the light sources have such a wide output (Figure 4-1, page 147). The discrepancies may also indicate that the photocycloaddition is much more complicated than by considering the quenching of 2-NpR fluorescence by acacH alone. The limiting quantum yield of 0.033 for the photoaddition of 2-$NpCO_2Me$ with acacH (Table 2-25, page 88) indicates a low quantum efficiency in photochemistry and hence high efficiency in the decay processes of ^{1}2-$NpCO_2Me$.

The conversion of 2-$NpCO_2Me$ in the photoaddition of 2-$NpCO_2Me$ to acacH was 16-22% for the first run and 7-17% for the second run (Table 2-25, page 88) The conversions of 2-NpR (R = CN, OMe and CO_2Et) were 14-30% (Tables 4-8, 4-7 and 4-6, page 188-190). The secondary photoproducts such as compound **18**, **23** and **34** were formed under irradiation at 300 nm or through a Pyrex filter (page 18, 20, 28). For quantum yield determinations, a light source at 350 nm was used (page 83). 1,5-diketone photoaddition products do not absorb at 350 nm (Figure 2-25, page 107;). Also, the concentration of the 1,5-diketone products was much lower than their starting materials, so even if there was some overlap of the 1,5-diketone and the light source band (350 ± 20 nm, Figure 4-1, Page 147), the absorption by the 1,5-diketone is negligible. For example, at 330 nm, 98% (calculated by equation 4-6, page 177, using ϵ=1200 for 2-$NpCO_2Me$ at 330 nm in Table 1-1 and ϵ=80 for the 1,5-diketone, estimated from Figure 2-25) of the incident light was absorbed by 2-NpCO$_2$Me when conversion was 22%. Thus, the change of quantum yield with conversion due to the secondary photoreaction may be neglected. When the dependence of 1/Φ_p on 1/[acacH] was examined, concentrations of acacH were 0.08-0.3 M (first run in Table 2-25, page 88). If considering the highest conversion (22%, 0.0044 M) of 2-NpCO$_2$Me in this reaction, the concentration of acacH would change from 0.08-0.3 M to 0.0756-0.296 M, then the highest errors brought in using starting concentrations (0.08-0.3 M) to plot 1/Φ_p *vs* 1/[acacH] will be 1-5.5%.

3.9 Metal acetylacetonate catalysis

We have discovered a novel catalytic effect of M(acac) (M = Li, Na and K) on the photocycloaddition of 2-NpCO$_2$Me to acacH. Adopting the definition of the catalysis of an excited state,[64,65] the essential step of the catalysis is the interception of the excited state by the catalyst (see Scheme 1-1 and 1-2, page 7). Generally, the reactions of excited states have very low activation energies (hence the usual temperature independence of photochemical reactions); otherwise, the photoreaction has no chance to compete with physical decay processes. Since the uncatalyzed process is fast, the interaction between the excited state with the catalyst must be equally fast to have a significant effect. This is why, on the whole, unambiguous examples of catalyzed reaction of excited states are rare. The comparative photoadditions of 2-NpCO$_2$R (R = Me and Et) to acacH with or without Li(acac) (0.001 M) give quantum yield values of 0.0235 and 0.0043 for R = Me and 0.0124 and 0.0033 for R = Et (Table 2-19, page 76), demonstrating the enhancement of the reaction in the presence of Li(acac). Furthermore, the results in Table 2-18 (page 75) indicate that Li(acac) only acts as a catalyst and does not add to 2-$NpCO_2Me$. The question of how Li(acac) affects the photoaddition is important. Li(acac) is found to quench the 2-NpR (R = CO_2Me, CO_2Et, OMe, OH and CN) fluorescences; that means that Li(acac) indeed intercepts the singlet excited state of 2-NpR. The $k_q\tau_0$ values obtained from 2-$NpCO_2Me$ fluorescence quenching (N_2 purged) by Li(acac) (205 $M^{-1}S^{-1}$, Table 2-8, page 48) and that by acacH (28.7 $M^{-1}S^{-1}$, Table 2-6, page 44) indicate that the former interaction is more effective than the latter. Although Li(acac) may be subject to minor dissociation to give Li^+ ion in solution,[135-137] the lack of catalytic effect on the reaction by addition of NaCl [notice that Na(acac) functions similarly to Li(acac) on the photocycloaddition, see 4.9.2] suggests that the metal ion was not likely to be the catalytic species. This suggestion is made under an assumption that the small amount of water added to dissolve NaCl in the reaction would not change the concentration of enolic acacH significantly.

A catalytic mechanism is proposed in Scheme 2-2 (Chapter 2) in which a new reaction pathway (reaction 2-26 and 2-27, page 91) accounts for the catalytic action. In thermal catalytic reactions, the new reaction pathway is always characterized by a lower activation energy. Similarly, since most photochemical reactions have activation barriers of less than 7 kcal/mole, the lowering of this barrier would give a larger rate constant. This is true for the Li(acac) catalysis on the photoaddition of 2-$NpCO_2Me$ to acacH. The rate constant k_c of the complexation of Li(acac) with ^{1}2-$NpCO_2Me$ is found to be 2.2×10^{10} M^{-1} s^{-1} (Table 2-8, page 48) which is much larger than the rate constant k_q of the complexation of acacH with ^{1}2-$NpCO_2Me$ (2.2×10^8 M^{-1} s^{-1}, Table 2-25, page 88). However, since the concentration of acacH (0.08 M) is much higher than that of Li(acac) (0.001-0.0001 M), reaction 2-19 is competitive with reaction 2-26 over a certain range of [Li(acac)]. In other words, the catalytic and uncatalytic processes coexist under the reaction conditions. Alternatively, it is also possible that the lifetime of the catalytic intermediate is longer than that of its precursor thus allowing the photochemical reaction to occur more efficiently than the photophysical decay process of the intermediate.

Equation 2-29 (for derivation, see Appendix) is based on Scheme 2-2 and predicts a curve for the dependence of quantum yield of product on [Li(acac)] under the experimental conditions. The reciprocal of the lifetime (9.4 ns, Section 2.3.3) of ^{1}2-NpCO$_2$Me indicates the sum of k_{ic} and k_f. The concentration of acacH (0.08 M) is fixed in the experiment. The rate constant k_q (2.2×10^{8} $M^{-1}s^{-1}$, Table 2-25, page 88) and k_c (2.2×10^{10} $M^{-1}s^{-1}$, Table 2-8, page 48) were obtained experimentally. By adopting x of 0.033 (Table 2-25, $\Phi_{limiting}$ in equation 2-24, which is identical to x in equation 2-31), equation 2-29 can be simplified as equation 3-7.

$$\Phi_p = \frac{5.8 \times 10^{5} + 2.2 \times 10^{10} [Li(acac)]\gamma}{1226 \times 10^{5} + 2.2 \times 10^{10} [Li(acac)]} \qquad 3\text{-}7$$

Based on the quantum yields measured at [Li(acac)] = 0.0002 and 0.0003 M, γ is calculated to be 0.125 using equation 3-7. The Φ_p as a function of [Li(acac)] thus calculated is shown by curve b in Figure 2-19 (page 93), which matches the experimental curve in the low concentration range of Li(acac) (0.0001-0.00045 M) well but deviates from the curve at high concentrations of Li(acac) (0.0006-0.001 M). γ values gradually decrease in [Li(acac)] range of 0.001-0.0006 M {0.090 at [Li(acac)] = 0.0006 M, 0.079

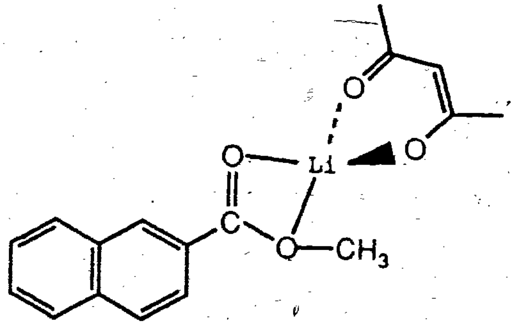
at [Li(acac)] = 0.0008 M and 0.069 at [Li(acac)] = 0.001 M}. This may suggest a relative large error in Φ_p in this concentration range, e.g. Li(acac) catalyzed aldol condensationof **16** may consume **16** significantly, bringing a large error. As indicated by γ of 0.125, the catalytic species, ^{1}2-NpCO$_2$Me-Li(acac), has a higher efficiency leading to the product compared with ^{1}2-NpCO$_2$Me-acacH (x = 0.033). As mentioned in Section 3.8, the discrepancy of $k_q\tau_0$ values obtained from fluorescence quenching and from quantum yield measurements may imply that the photocycloaddition has other complexities in addition to the quenching of 2-NpR fluorescence by acacH. The above calculated fitting was reexamined by assuming the lifetime of the reacting species of 2-NpCO$_2$Me as 5 ns and 12 ns respectively. The rate constant k_q is then calculated to be 4.2 x 10^8 M^{-1} s^{-1} (when τ_0 = 5 ns) and 1.75 x 10^8 M^{-1} s^{-1} (when τ_0 = 12 ns). Similarly, equation 2-29 can be simplified as equations 3-8 and 3-9. γ is calculated to be 0.228 (when τ_0 = 5 ns) and 0.10 (when τ_0 = 12 ns).

$$\Phi_p = \frac{11.1 \times 10^5 + 2.2 \times 10^{10} [\mathrm{Li(acac)}]\gamma}{2336 \times 10^5 + 2.2 \times 10^{10} [\mathrm{Li(acac)}]} \qquad 3\text{-}8$$

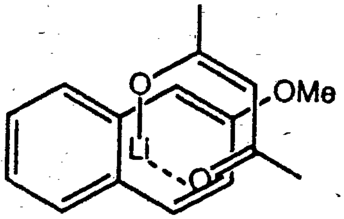
$$\Phi_p = \frac{4.62 \times 10^5 + 2.2 \times 10^{10} [\mathrm{Li(acac)}]\gamma}{970 \times 10^5 + 2.2 \times 10^{10} [\mathrm{Li(acac)}]} \qquad 3\text{-}9$$

It is found that the change of the lifetime does not change the calculated curves very much (Figure 2-19, page 93), but does change γ values; i.e. the shorter the lifetime is, the larger the γ value. It may be that there is electron migration from the aromatic ring into the electron-withdrawing group upon irradiation[138-140] which makes the group electron richer and facilitates the complexation of Li(acac) to it. The suggested structure of the complex of ^{1}2-NpCO$_2$Me-Li(acac) is shown by E$_7$.

Although the quenching of 2-NpOH fluorescence by Li(acac) gives the highest $k_q\tau_0$ value (1100 M^{-1}, Table 2-8, page 48), the presence of Li(acac) (0.001 M) in the photocycloaddition of 2-NpOH with acacH results in the suppression of the reaction (from 4% to 0.5%, Table 2-19, page 76). During the course of 2-NpOH fluorescence quenching by Li(acac), a new broad emission band, assigned to 2-NpO$^-$,[136] appears around 410-460 nm, with an isosbestic point at 397 nm (Figure 2-5, page 49), suggesting that a proton transfer occurs. As 2-NpO$^-$ does not undergo photocycloaddition, the occurrence of the proton transfer consumes ^{1}2-NpOH (notice the large $k_q\tau_0$ value) at the expense of the photocycloaddition of 2-NpOH with acacH (Table 2-19, page 76).



E$_7$



E$_8$

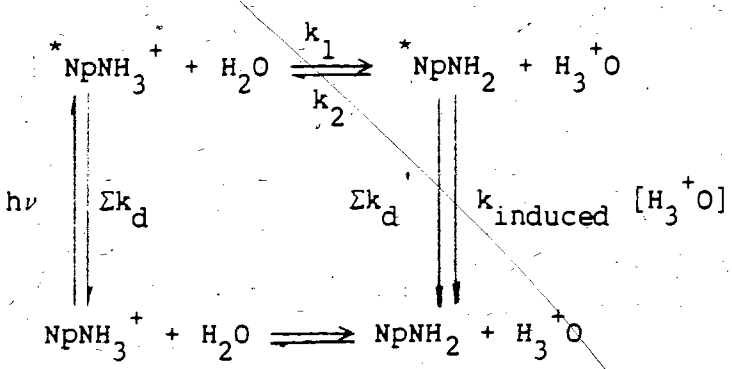
The absence of catalysis by Li(acac) of the photocycloaddition of 2-NpOMe to acacH (Table 2-19, page 76) may be explained by the structure of the complex. It has been proved that considerable electron migration from the electron donating substituent (e.g. OH and OMe) to the aromatic ring (the naphthalene, phenanthrene or anthracene) occurs in the excited state in polar media, and that the aromatic ring carrying high electron density is attacked by protons.[138-140] It is suggested that the complexation of Li(acac) with ^{1}2-NpOMe would prefer to occur at the aromatic ring as shown by E_8. The complexa- tion will either prevent the free acacH from attacking ^{1}2-NpOMe efficiently, or the lifetime of such a complex is short therefore the complexation consumes ^{1}2-NpOMe showing the retardation of the addition. However, the Li(acac)-catalytic mechanism of photocycloaddition of 2-NpCN to acacH seems to be more complicated. This contradiction that the fluorescence intensity of 2-NpCN is strongly quenched by Li(acac) ($k_q\tau_0$ of 312, Table 2-8, page 48) but the photoaddition is retarded in the presence of Li(acac) (Table 2-19, page 76) suggests that a different mechanism is involved which remains to be clarified. The lack of a catalytic effect by Li(acac) on the photoaddition of 2-NpCN with acacH indicates that the electronic nature of the substituents does not play an important role in the formation of a catalytic intermediate. It is obvious that an ester group on the naphthalene ring is essential for Li(acac) to function as a catalyst. The structure as shown by E_7 is therefore suggested as the catalytic intermediate.

3.10 Acid effects

The photocycloaddition of 2-$NpCO_2Me$ with acacH is also catalyzed by sulfuric acid. It was found that a Bronsted acid such as sulfuric acid, phosphoric acid, hydrochloric acid or an aprotic acid such as borontrifluoride (BF_3, in ether) catalyzes the photocycloaddition (Table 2-21, page 80). It has been demonstrated[141] that the enhancement in rate of the addition in the presence of BF_3 is caused by the excitation of a new complex between acacH and BF_3, followed by addition to naphthalene derivatives or olefins. In other words, the reacting species is different. Our study was focused on catalysis by sulfuric acid. Remarkably, the presence of a trace amount of sulfuric acid (10^{-4} to 10^{-3} M, Table 4-9, page 191, and Figure 2-22, page 97) not only enhances the quantum yield of [2+2] adduct **16** by about six fold, but also changes the product regiochemistry, giving a major product **17** in addition to **16**. The absorption spectrum of 2-$NpCO_2Me$ is not observed to change in acid solution (0.0125-0.0375 M, in non-purged acetonitrile, Section 2.8, page 104), but the fluorescence is quenched (k_H of 1.01×10^{10} $M^{-1}s^{-1}$) by moderate concentrations (0.0063-0.0375 M, Table 2-13, page 58). A new broad emission band around 470 nm was observed. This band was assigned to emission from the protonated ^{1}2-$NpCO_2Me$,[142] (isosbestic point at 414 nm, Figure 2-7, page 59, and 2-8, page 60). In other words, the singlet excited state of 2-$NpCO_2Me$ is intercepted by sulfuric acid to give an exciplex which emits at 470 nm; this emission also appears in the presence of acacH (0.08 M, Table 2-13, page 58; Figure 2-12, page 65). The acid-base properties of the excited states of aromatic compounds are closely related to their electronic structures,[138a,143-145] which are quite different from those of the ground states. A number of studies of acidity constants, $pK_a(S_1)$, have been reported showing that the values are dramatically different from those in the ground states, $pK_a(S_0)$. For example, the lowest singlet excited state of 2-naphthol is much more acidic than the ground state [$pK_a(S_0)$ = 9.5 and $pK_a(S_1)$ = 3.1] while the aromatic carbonyl compound e.g. 2-$NpCO_2Et$, becomes a stronger base in S_1 [$pK_a(S_0)$ = -8.2 and $pK_a(S_1)$ = -3.4].[146] The enhanced basicity of 2-$NpCO_2Me$ at the carbonyl group upon excitation is responsible for the protonation of the excited state of 2-$NpCO_2Me$. The fluorescence of ^{1}2-$NpCO_2Me$ (at 359 nm) and ^{1}(2-$NpCO_2Me$-H^+) (at 470 nm) are both quenched by acacH in the presence of H_2SO_4 (0.0935 M), giving $k_q\tau$ of 128 M^{-1} (at 470 nm) and 63.4 M^{-1} (at 359 nm). We propose that the protonated ^{1}2-$NpCO_2Me$ is the catalytic intermediate based on the observation of the quenching at 470 nm by acacH. Equation 2-29 should be applicable when Li(acac) is replaced by H_2SO_4. Similar to the Li(acac) catalysis, under the conditions employed in the photocycloaddition of 2-$NpCO_2Me$ to acacH in the presence of H_2SO_4, the catalytic process coexists with the uncatalytic process. For example, k_q[acacH]x = 6.6 x 10^5 (k_q = 2.5 x 10^8, x = 0.033 in Table 2-25, page 88, and [acacH] = 0.08 M) while $k_H\gamma[H_2SO_4]$ = 2.02 x 10^5 to 10^6 (k_q in Table 2-13, page 58, 1.01 x 10^{10} M^{-1}, $[H_2SO_4]$ = 0.001-0.0001 M) if assuming γ value as 0.2. Equation 2-29 predicts a curve for the dependence of quantum yield on $[H_2SO_4]$. The experimental results are shown in Table 4-9 (page 191) and Figure 2-22 (page 97). The redistribution of the electron density on the naphthalene moiety upon protonation on the singlet excited state of 2-$NpCO_2Me$ may be responsible for the change in regiochemistry of the products. This catalytic species is proposed to have a higher efficiency leading to products.

It is well known that pK_a^* values can be established by means of the Forster cycle[144,147-149], the fluorescence titration curve[144] and the triplet-triplet absorbance titration curve.[147] These methods involve the assumption that proton transfer in the excited state is very fast, resulting in establishment of an acid-base equilibrium during the lifetime in the excited state. Establishment of prototropic equilibrium has been reported in the case of 2-hydroxynaphthalene-6,8-disulfonate.[150] However, Shizuka[138] has reported recently that proton-induced fluorescence quenching ($k_{induced}$) competes with the proton transfer reaction (k_2) in the excited state of naphthylamines (Scheme 3-2). The protonation rate constant k_2 (1.2×10^8 M^{-1} s^{-1} for 1-$NpNH_2$) is smaller than that of $k_{induced}$ (8.9×10^9 M^{-1} s^{-1}), so the protonation process to 1-$NpNH_2{}^*$ is not fast enough to allow a complete acid-base equilibrium in the S_1 state. Shizuka also proved that

Scheme 3-2



the proton-induced quenching ($k_{induced}$) is only involved in the excited state of aromatic compounds having an intramolecular charge-transfer (CT) structure in the fluorescent state (e.g. 1-NpOMe, 1-NpOH and naphthylamines). In contrast, such proton-induced quenching is scarcely observed for aromatic compounds having no (or very weak) intramolecular CT character in the fluorescent state such as 2-NpOMe at moderate acid concentrations ($[H_3{}^+O]$ (0.1 M). Our result is consistent with the one published by Shizuka.[138] The failure of H_2SO_4 to quench 2-NpOMe fluorescence indicates the absence of protonation and the absence of proton-induced fluorescence quenching of the singlet excited state of 2-NpOMe. The retardation of the photoaddition of 2-NpOMe with acacH in the presence of H_2SO_4 indicates that a protonation process interferes with the catalytic process. On the basis of Shizuka's results,[138] it is not likely that there is a proton-induced quenching of 2-NpCO$_2$Me fluorescence by H$_2$SO$_4$, because of its substituted position (2-position) and the existence of an electron withdrawing group. The quenching of 2-NpCO$_2$Me fluorescence by H$_2$SO$_4$ could therefore be attributed to protonation process only. The value of the rate constant of unimolecular decay of ^{1}2-NpCO$_2$Me equals the reciprocal of its lifetime and is determined to be 2.9×10^8 s^{-1} (Table 2-9, page 51). The values of product of rate constant (1.01×10^{10} M^{-1} s^{-1}, Table 2-13, page 58) of protonation of ^{1}2-NpCO$_2$Me by H$_2$SO$_4$ and the concentrations of H$_2$SO$_4$ (0.0375-0.0063 M, Table 2-13) are determined and calculated to be from 6.4×10^7 to 3.8×10^8 s^{-1}. Since the rate of the decay is faster (or competitive) than (or with) the protonation process, it is likely that an acid-base equilibrium cannot be established during the lifetime of ^{1}2-NpCO$_2$Me.

3.11 Conclusions and further proposals

Our investigations of the mechanism of photocycloaddition of 2-NpR to acacH, and the catalysis of the reactions by Li(acac) and sulfuric acid, provide a good understanding of the reaction and catalysis of excited states. The following conclusions are drawn from the results.

1. [2+2] photocycloaddition occurs between NpR (R = 1-CO$_2$Me, 2-CO$_2$Me, 1-CO$_2$Et, 2-CO$_2$Et, 1-OMe, 2-OMe, 1-CN and 2-CN) and acacH in acetonitrile to give 1,5-diketones which have considerable potential in synthesis.
2. The photocycloaddition is initiated by the singlet excited state of 2-NpR.
3. Electron donating quenchers such as TBA and DMA intercept the singlet

excited state of 2-NpR and retard the photocycloaddition. A good agreement of rate constants obtained from fluorescence quenching of 2-NpCO_2Me by TBA (k_q of 3.6 x 10^{10} $M^{-1} s^{-1}$) and from quantum yield measurement (k_q of 3[illegible]3 x 10^{10} M^{-1} s^{-1}) was obtained.

4. 1,3-pentadiene (in the concentration range of 0.02-0.1 M) enhances the addition of 2-NpCO_2Me to acacH, probably by an exchange reaction.
5. The fluorescence of 2-NpCO_2Me is quenched by Li(acac) and the photocycloaddition of 2-NpCO_2Me and acacH is catalyzed by Li(acac); this is assumed to occur by the interception of ^{1}2-NpCO_2Me by Li(acac), followed by the addition of acacH to the Np moiety of the catalytic complex to give the final product and Li(acac).
6. The photocycloaddition of 2-NpCO_2Me with acacH is catalyzed by sulfuric acid. Protonation of the singlet excited state of 2-NpCO_2Me occurs giving its exciplex, ^{1}(2-NpCO_2Me-H^+), which emits at 470 nm. The emission from the exciplex is quenched by acacH and the exciplex is proposed to be responsible for the acid catalysis on the photocycloaddition. An acid-base equilibrium cannot be established during the lifetime of ^{1}2-NpCO_2Me.

[2+2] photocycloaddition of NpR to acacH provides a new branch in aromatic photochemistry, in which the addition takes place between NpR and a 1,3-diketone type compound. The catalysis of the addition by Li(acac) and sulfuric acid opens a new field, in which the catalytic mechanism and reacting intermediate are discussed. The extension of the photocycloaddition and further studies of the catalytic mechanism are proposed below.

1. It could be worthwhile to extend the photocycloaddition to phenanthrenes and anthracenes. In these cases, selective irradiation of the compounds can be achieved, since there is lesser overlap of their absorptions with that of acacH. Thus mechanistic studies would be easier.
2. The Li(acac) catalysis of the photocycloaddition could be extended to the addition between NpR and simple olefins such as alkyl vinyl ethers, tetramethylethylene and cyclohexene. In these cases, coirradiation of the starting materials can be avoided. Extension of catalytic studies to include Rb(acac), Cs(acac), $Cu(acac)_2$ and $Zn(acac)_2$ could also be attempted. The rate constants for the complexation of the $M(acac)_n$ with NpR could be obtained by fluorescence quenching. Studies of the interception of NpR by $M(acac)_n$ by means of the flash photolysis method could reveal details of the catalytic intermediate. A comparison of the rate of quenching of a transient spectrum from NpR with $M(acac)_n$ by an olefin with the rate of quenching of the corresponding photoreaction would provide evidence about the catalytic intermediate.
3. There have been some reports about the quenching of aromatic compound fluorescence by protons.[138-140,142,151] Shizuka has proved[140] that excited aromatic molecules having an intramolecular charge-transfer structure in the fluorescence state (e.g. 1-NpOMe, 1-NpOH...) are quenched effectively by protons and the protonation occurs at carbon 5 of 1-NpOMe. Aromatic compounds having no (or very weak) intramolecular CT character in the fluorescence state (2-NpOMe, Np and anthracene) are scarcely quenched, indicating the importance of the position of substituents on protonation. We have observed an exciplex, assigned as protonated ^{1}2-$NpCO_2Me$, from fluorescence quenching of ^{1}2-$NpCO_2Me$ by H_2SO_4; this is consistent with the results published by Xu *et al.*[142] A

systematic study of the proton-quenching of NpR fluorescence would be valuable and related to the study of the catalytic effects of H_2SO_4 on photocycloaddition. The study should involve the identification and the determination of the lifetime of the catalytic species, and the mechanism of reaction. Also, the potential catalytic effects of various acids on the addition of NpR to simple olefins may deserve further study.

CHAPTER 4 EXPERIMENTAL

4.1 General conditions

Unless otherwise specified, the following experimental conditions were used. Melting points (mp) were determined on a Fisher-Johns apparatus, and were uncorrected. Infrared spectra (IR) were recorded with a Perkin-Elmer 559B spectrophotometer using neat liquid film, Nujol mull or KBr pellet. Ultraviolet and visible spectra (UV) were taken with a Varian Cary 210 spectrophotometer. Mass spectra (MS) and gas-chromatography-mass spectra (GC-MS) were obtained on a Hewlett-Packard 5985 GC-MS system either by electron ionization or by chemical ionization. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded with a Bruker WM-400 spectrometer in $CDCl_3$ solution using tetramethylsilane (TMS) as an internal standard. Chemical shifts are reported in δ values in ppm and coupling constants (J) in Hz. The coupling patterns are presented as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). The chemical shifts of ^{13}C NMR spectra are also reported in ppm relative to TMS. Elemental analyses were carried out by Mr. M.K.Yang using a Carlo Erba Model-1106 Elemental Analyzer. Gas chromatography (GC) analyses were performed on a Hewlett-Packard 5790A chromatograph (FID), equipped with an OV-1 capillary column and a Hewlett-Packard 3390A chart integrator. Retention times (Rt) are reported in minutes (min). Phosphorescence and fluorescence spectra were taken with a Perkin-Elmer MPF 44B spectrophotometer and were uncorrected. Sample solutions for photoreactions were deaerated as follows: a sample solution in a test tube or a fluorescence cuvette was sealed with a septum and purged with nitrogen for 10 min. Chemical yields in preparative experiments were calculated based on the amount of the naphthalene derivatives present at the start of the reaction.

4.2 Chemicals and apparatus

For the preparative photochemical reactions, reagent grade solvents were distilled prior to use. Acetonitrile was distilled over P_2O_5. For spectroscopy, commercial spectroscopic grade solvents were used as supplied.

Methyl 1-naphthoate (1-$NpCO_2Me$), methyl 2-naphthoate (2-$NpCO_2Me$), ethyl 1-naphthoate (1-$NpCO_2Et$) and ethyl 2-naphthoate (2-$NpCO_2Et$) were prepared from the corresponding naphthoic acid by H_2SO_4 catalyzed esterfication.[152] The spectral data are listed in Tables 4-1 to 4-4. Lithium, sodium and potassium acetylacetonates were synthesized according to literature methods.[153-157]

Commercially available reagent grade 1-methoxynaphthalene (1-NpOMe, Aldrich), 2-methoxynaphthalene (2-NpOMe, Aldrich), 1-cyanonaphthalene (1-NpCN, Aldrich), 2-cyanonaphthalene (2-NpCN, Kodak), 2-naphthol (2-NpOH, Anachemia), 9-phenanthrol (Aldrich) and acetylacetone (acacH, BDH) were purified by recrystallization, vacuum sublimation or distillation prior to use. Benzophenone (Fisher), xanthone (Aldrich), benzhydrol (Matheson), and phenanthrene (Matheson) were used as supplied.

4.3 Photolysis apparatus and quantum yield determination

Three different types of photolysis apparatus were employed in the experiments.

Apparatus I

This apparatus consisted of a long cylindrical reaction vessel (180 ml, Pyrex glass) fitted with a side arm, into which a condenser was inserted. A Pyrex water-cooled lamp housing was inserted into the vessel. A nitrogen gas was bubbled into the photolysate through a gas inlet tube. The light source was a 200 watt Hanovia medium pressure mercury lamp (654A 36).

Apparatus II

This apparatus consisted of 8 quartz tubes (5 mL solution used for each one) which were placed in a Rayonet Photochemical Reactor (a "merry-go-round") equipped with RPR 300 nm lamps (16 x 21 watt, for output of the relative energy, see Figure 4-1) or RPR 350 nm lamps (16 x 24 watt, Figure 4-1) and a fan to circulate the air provided a constant temperature of 31±1°C.

Apparatus III

This apparatus consisted of a long cylindrical reaction vessel (3 x 20 cm, quartz glass) which was inserted into a quartz water cooled lamp housing. The vessel and lamp housing were inserted into the center of a Rayonet Photochemical Reactor equipped with RPR 300 nm lamps (16 x 21 watt) or 350 nm lamps (16 x 24 watt) and a fan to circulate the air provided a constant temperature of 31±1°C.

Unless otherwise specified, the following procedures were followed for preparation of actinometry solutions, light intensity determination and quantum yield determination.

The actinometer solution was prepared as follows. Benzophenone (456 mg, 2.50 mmol) and benzhydrol (921 mg, 5.0 mmol) were dissolved in benzene

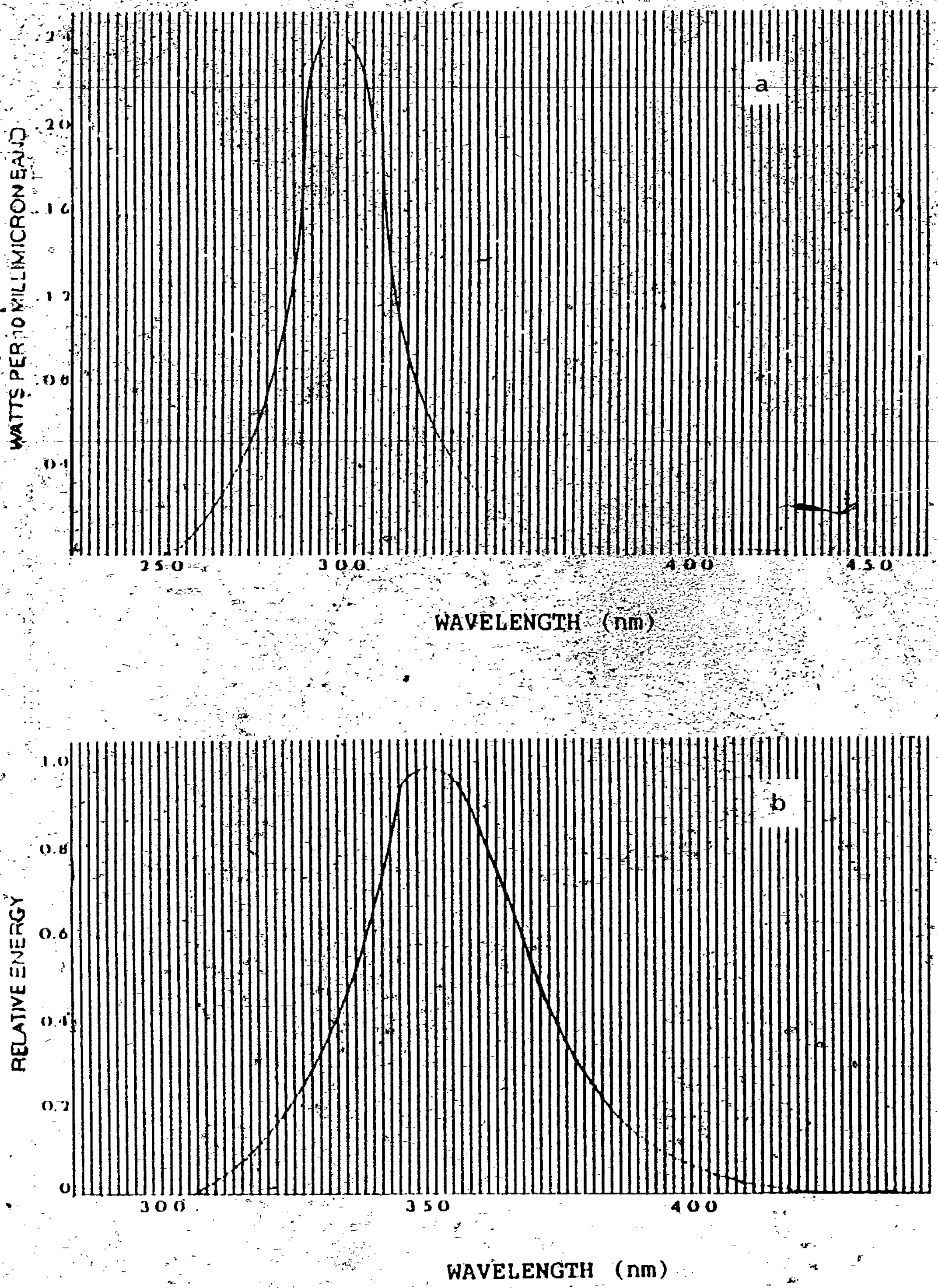


Figure 4-1: The output of light sources; a) RPR 300 nm lamp and b) RPR 350 nm lamp.

(25 mL). An aliquot (3 mL) from each of the above stock solutions were pipetted into a test tube. The actinometer solution (5 mL) containing 0.050 M benzophenone and 0.10 M benzhydrol was transferred into a quartz tube and purged with nitrogen for 10 min. The actinometer which is known to have the quantum yield of 0.74[158] was irradiated together with sample solutions in apparatus II for 5 min. The absorbance (A) at 342 nm of benzophenone was measured with 0.10 cm optical path cells before and after irradiation, respectively. The light intensity (I^0) was calculated by absorbance change (ΔA) from equation 4-1.

$$I^0 = \Delta A/(10^3\ \epsilon_{342}\ \Phi\ L\ \Delta t) \quad \text{Einstein/min.mL}$$

$$= (\Delta C\ V)/(\Phi\ \Delta t) \quad \text{Einstein/min.} \qquad 4\text{-}1$$

where $\epsilon_{342} = 140\ M^{-1}\ cm^{-1}$ is the extinction coefficient of benzophenone at 342 nm, t is the elapsed irradiation time in min., and L = 0.10 cm. V is volume in mL.

Quantum yields were determined as follows.

Method I

Photolysates were analyzed by G.C. with octadecane ($C_{18}H_{38}$, added into sample solution before irradiation) or xanthone (added after irradiation) as an internal standard (I.S.). The concentration of a product (P) or a starting material (Np) was calculated from equation 4-2 and the corresponding quantum yield Φ was calculated from equation 4-3.

$$[P] = R\ f\ [I.S.] \qquad 4\text{-}2$$

where, R is the GC area ratio of product : I.S. and f is response factor from calibration curves.

$$\Phi = (\text{Moles of P formed})/I^0\ \Delta t$$
$$= ([P]\ V)/I^0\ \Delta t \qquad 4\text{-}3$$

where I^0 is light intensity from equation 4-1, Δt is irradiation time and V is volume of reaction solution.

Since both NpR and acacH were irradiated when a 300 nm light source was used (Figures 2-2 and 2-24), the correction of the incident light absorbed by NpR (I^*) was made according to equation 4-4.

$$I^* = I^0[(\epsilon_{Np}\ C_{Np})/\ (\epsilon_{Np}\ C_{Np} + \epsilon_{acacH}\ C_{acacH})] \qquad 4\text{-}4$$

where I^0 is the light intensity measured, ϵ_{Np} and ϵ_{acacH} are the extinction coefficients of NpR and acacH at 300 nm, respectively, C_{Np} and C_{acacH} are concentrations of NpR and acacH, respectively. Similarly, the correction of the incident light absorbed by acacH was made by replacing the numerator term of $\epsilon_{Np}\ C_{Np}$ by $\epsilon_{acacH}\ C_{acacH}$ in equation 4-4.

Method II

For each reaction, a control solution (5 mL as a secondary actinometer) was prepared containing 2-NpR (0.02 M, R=CO_2Me, CO_2Et, OMe and CN), acacH (0.08 M) and octadecane (0.005 M, as I.S.) in acetonitrile and irradiated with an actinometer in apparatus II at 350 nm after being purged with nitrogen for 10 min. The quantum yields of the secondary actinometer Φ_{sec} for product formation were determined according to method I as 0.0043 for R = 2-CO_2Me, 0.0033 for R = 2-CO_2Et, 0.036 for R = 2-OMe and 0.030 for R = 2-CN (for its disappearance). When the secondary actinometer was used to determine quantum yield, sample solutions were irradiated together with the secondary actinometer and the photolysates were analyzed by GC to give R_{sec} (GC area ratio of product over I.S. from the secondary actinometer) and R_{sample} (GC area ratio of product over I.S. from the sample solution) that should be proportional to their quantum yields. The quantum yield Φ_{sample} of a sample solution based on product formation was calculated from equation 4-5.

$$\Phi_{sample} = \Phi_{sec} \,(R_{sample} / R_{sec}) \qquad 4\text{-}5$$

4.4 The [2+2] photocycloaddition of naphthalene derivatives with acetylacetone

4.4.1 General procedures

Unless otherwise specified, the following preparative procedures were followed. An acetonitrile solution of acetylacetone and a naphthalene derivative was placed in 8 quartz tubes. After the solution was sealed and purged with oxygen-free nitrogen for 10 min, the tubes were placed in Apparatus II to be irradiated with a light source at 300 nm or 350 nm. Reactions were monitored by GC. A zero hour sample was kept in the dark and analyzed by GC as a control. In order to avoid secondary photoreactions, the irradiation was stopped when the conversion of naphthalene derivative was around 50-60% as determined by GC. The residue was flash chromatographed to give product. The spectral data are listed in Tables 4-1 to 4-4.

4.4.2a Methyl 2-naphthoate

A solution of 2-NpCO$_2$Me (300 mg, 1.6 mmol) and acacH (1.6 g, 16 mmol) in acetonitrile (50 mL) was irradiated in apparatus II equipped with 300 nm lamps. After irradiation for 15 hours, the light yellow photolysate gave two GC (column at 200°C) peaks at Rt 2.73 min for 2-NpCO$_2$Me and at Rt 5.02 min for a product in the ratio of 1:1. A trace amount of a second product (Rt 4.83 min **17**, see 4.4.2b) was also detected but was ignored in all the mechanistic studies except in the studies of heavy atom and acid effects. The yellow residue was flash chromatographed using 30% ethyl acetate in hexanes as the eluant to give a yellow oily compound (152 mg, 33%) of 1-acetyl-2-acetonyl-2-carbmethoxy-1,2-dihydronaphthalene (**16**) and 2-NpCO$_2$Me (112.8 mg).

4.4.2b Methyl 2-naphthoate in the presence of sulfuric acid

A solution of 2-NpCO$_2$Me, (300 mg, 1.6 mmol), acacH (500 mg, 5 mmol) and a trace amount of sulfuric acid (about 0.0005 M) in acetonitrile (50 mL) was irradiated in apparatus II equipped with 300 nm lamps for 19 hours. The light brown photolysate showed three GC peaks (column at 200°C) at Rt 4.83 min. (45%), 5.02 min.(23%, **16**, see 4.4.2a) and 2.73 min (14.8%, 2-NpCO$_2$Me,). The residue was flash chromatographed using 30% ethyl acetate in hexanes as the eluant to give a yellow oily compound (36 mg, 8%) of **16** and a light yellow powder (72 mg, 16%) of 1-acetonyl-2-acetyl-2-carbmethoxy-1,2-dihydronaphthalene (**17**). The latter was further purified by recrystallization from cyclohexane to afford white crystals (70 mg, m.p. 81-82°C). The spectral data are listed in Tables 4-1 to 4-4.

A solution of 2-NpCO$_2$Me (300 mg, 1.6 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) with a trace amount of sulfuric acid (about 0.0005 M) was irradiated in apparatus II at 300 nm for over 20 hours (overirradiated). The GC analysis (column at 200°C) of the photolysate showed two major product peaks with Rt 6.07 min (31.2%) and 5.02 min (14.8%, **16**, see 4.4.2a). The products were flash chromatographed using 50% ethyl acetate in hexanes as eluant followed by preparative TLC separation using 50% ethyl acetate in hexanes as eluant to give a yellow oil of **17** (51 mg). The spectral data are listed in Tables **4-1** to **4-4**.

A solution of **17** (2.3 mg, 0.008 mmol) in acetonitrile (0.4 mL) in a quartz tube was irradiated in Apparatus II at 300 nm for 1 hour. The GC analysis (at 200°C) of the photolysate showed 3.5% of **17** left and 61.3% of **18** formed.

4.4.3 Methyl 1-naphthoate

A solution of 1-NpCO$_2$Me (300 mg, 1.6 mmol) and acacH (1.6 g, 16 mmol) in acetonitrile (50 mL) was irradiated in apparatus II equipped with 300 nm lamps. After irradiation for 8 hours, the GC analysis (column at 200°C) of the photolysate showed that 52% of 1-NpCO$_2$Me survived (Rt 2.62 min) and 34% of product (Rt 6.91 min) was formed. The yellow oily residue was flash chromatographed twice using 30% ethyl acetate in hexanes as eluant to give a pale yellow powder (139 mg, 30.4%) and 1-NpCO$_2$Me (120 mg). The former was further recrystallized from acetonitrile to afford white crystals of 1-carbmethoxy-7-acetonyl-8-acetyl-7,8-dihydronaphthalene (**22**, m.p. 107-107.5°C). The spectral data are listed in Tables **4-1** to **4-4**.

A solution of 1-NpCO$_2$Me (1 g, 5.6 mmol) and acacH (430 mg, 4.3 mmol) in methylene chloride (180 mL) was irradiated in apparatus I. After irradiation for 187 hours, GC analysis (column at 150-230°C at 10°C/min) of the photolysate showed that 62% of 1-NpCO$_2$Me (Rt 3.57 min) survived and two products were formed with Rt 6.31 min (30%) and 7.99 min (7%, **22**). The residue was flash chromatographed using 20% ethyl acetate in hexanes as eluant to give a crude product (66.5 mg, Rt 6.31 min) which was recrystallized from acetonitrile to give white crystals of 1,8-dimethyl-2,9-dioxa-5,6-[3'-carbomethoxybenzo]tetracyclo[5, 2, 2, $0^{3,11}$ $0^{4,8}$]-undecane (**23**, 31.1 mg, m.p. 117°C-117.5°C). Analysis: Calculated for $C_{17}O_4H_{18}$ (286), C, 71.33%; H, 6.29%; Found C, 71.42% and 71.23%; H, 6.47% and 6.34%. The spectral data are listed in Tables 4-1 to 4-4. The structure of **23** was ascertained by means of X-ray crystallography (Figure 2-1).

A solution of **22** (4.2 mg, 0.015 mmol) in methylene chloride (1 mL) in a quartz tube was irradiated in Apparatus II at 300 nm. A sample solution was withdrawn at one hour intervals and analyzed by GC. After 6 hours of irradiation, the GC analysis (150-230°C at 10°/min) of the photolysate showed three peaks at Rt 7.99 min for **22** (24%), Rt 6.31 min for **23** (16%) and an unknown product (**24** at Rt 7.33 min (39%). The unknown product showed GC-MS (CI) peak at m/e 243 (M+1, 47%) 211 (100%). No further study of this unknown compound was done.

A solution of **22** (4.7 mg, 0.016 mmol) in methylene chloride (1 mL) was irradiated through a Pyrex filter with a 200 Watt lamp. A sample solution was withdrawn at one hour intervals and analyzed by GC. After 6 hours of irradiation, GC (150°C-230°C at 10°/min) analysis of the photolysate showed three peaks at Rt 7.99 for **22** (22%), Rt 6.31 min for **23** (46%) and Rt 7.33 min for the unknown compound (14%).

4.4.4 Ethyl 2-naphthoate

A solution of 2-$NpCO_2Et$ (300 mg, 1.5 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) was irradiated in apparatus II equipped with 350 nm lamps. After 13 hours of irradiation, GC (column at 200°C) analysis showed that 47% of 2-$NpCO_2Et$ survived (Rt 3.08 min) and 45% of product was formed (Rt 5.74 min). The solvent was removed under reduced pressure. The yellow oily residue was flash chromatographed twice using 35% and 30% ethyl acetate in hexanes as eluant to give a yellow oil (123 mg, 35%) of 1-acetyl-2-acetonyl-2-carbethoxy-3,4-dihydronaphthalene (**20**) and 2-$NpCO_2Et$ (114 mg). The spectral data are listed in Tables 4-1 to 4-4.

4.4.5 Ethyl 1-naphthoate

A solution of 1-$NpCO_2Et$ (300 mg, 1.5 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) was irradiated in apparatus II equipped with 350 nm lamps. After 16 hours of irradiation, GC analysis (column at 200°C) showed only 20% of 1-$NpCO_2Et$ consumed. After another 6 hours of irradiation at 300 nm, 35% ethyl 1-naphthoate (Rt 2.95 min) was left and 26% product was formed (Rt 8.40 min). The photolysate gave two GC peaks at Rt 2.95 min for 1-$NpCO_2Et$ (35%) and Rt 8.40 min (26%). The residue was flash chromatographed using 30% ethyl acetate in hexanes as an eluant to give a yellow oil (16.3 mg) of 1-carbethoxy-7-acetonyl-8-acetyl-7,8-dihydro-naphthalene (**26**). The spectral data are listed in Tables 4-1 to 4-4.

4.4.6 1-Cyanonaphthalene

A solution of 1-NpCN (300 mg, 1.96 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) was irradiated in apparatus II at 300 nm for 18 hours. GC analysis (column at 200-230°C at 10°C/min) of the photolysate showed that 85% of 1-NpCN was consumed and one major product peak at Rt

4.34 min (47%) as well as several small peaks which were not studied. The residue was chromatographed twice using 42% and 30% ethyl acetate in hexanes as eluant to give white crystals (**33**, 66.9 mg, 14%) of 1-cyano-7-acetonyl-8-acetyl-7,8-dihydronaphthalene. The spectral data are listed in Tables 4-1 to 4-4. Analysis: Calculated for $C_{16}H_{15}O_2N$ (MW of 253), C, 75.87%; H, 5.97%; Found, C, 75.95%; H, 6.10%.

A solution of compound **33** (203 mg, 0.8 mmol) in acetonitrile (100 mL) was irradiated in apparatus I for 19 hours. GC analysis (column at 200-230°C at 10°C/min) of the photolysate showed two GC peaks at Rt 4.34 min (16%) for **33** and at Rt 3.77 min (41%). The residue was flash chromatographed using 40% ethyl acetate in hexanes as eluant to afford a yellow oil (40 mg) of **34**. The spectral data are listed in Tables 4-1 to 4-4.

4.4.7 2-Cyanonaphthalene

A solution of 2-NpCN (300 mg, 1.96 mmol) and acacH (300 mg, 3 mmol) in methanol (50 mL) was irradiated in Apparatus III equipped with 300 nm lamps for 16 hours. GC analysis (column at 150-230°C at 10°C/min) of the photolysate showed one major peak at Rt 7.93 min (29%) and one minor peak at 5.88 min [8%, GC-MS: 195(43%), 180(100%), 152(51%); the structure suggested for this product is **39**, see page 29] plus several more minor peaks (less than 3%) around Rt of 6-8 min which were not studied. The residue was flash chromatographed (30% ethyl acetate in hexanes) and recrystallized from ether to give white crystals (**38**, 50 mg) of 1-acetyl-2-acetonyl-2-cyano-3,4-dihydronaphthalene. The spectral data are listed in Tables 4-1 to 4-4. Analysis: Calculated for $C_{16}H_{15}O_2N$ (MW of 253), C, 75.87%; H, 5.97%; Found, C, 75.81%; H, 6.04%.

4.4.8 1-Methoxynaphthalene

A solution of 1-NpOMe (300 mg, 1.9 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) was irradiated in Apparatus III at 300 nm for 48 hours. GC analysis (column at 150-230°C at 10°C/min) showed two major product peaks at 7.48 min (33%) and 7.67 min (8%) plus several small peaks between 6-8 min which were not studied. The residue was flash chromatographed (20% ethyl acetate in hexanes) to afford white crystals (**41**, 73 mg) of 1-methoxy-3-acetonyl-4-acetyl-3,4-dihydronaphthalene as well as a tiny amount of 1-acetonyl-2-acetyl-naphthalene (**42**). The spectral data are listed in Tables 4-1 to 4-4. The GC-MS of the unknown **40** gave a parent peak of 258 (M^+, 10%) and 215 (50), 200 (80), 158 (100), 115 (35) and 43 (20) suggesting an addition product between 1-NpOMe and acacH. The GC-FT-IR of **40** showed a strong absorption at 1730 cm^{-1}.

4.4.9 2-Methoxynaphthalene

A solution of 2-NpOMe (300 mg, 1.9 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (50 mL) was irradiated in apparatus II at 300 nm for 15 hours. GC analysis (column at 200°) of the photolysate showed that 2-NpOMe (8%, Rt 2.25 min) survived and a major product peak at Rt 4.45 min (78%). The residue was flash chromatographed using 30% ethyl acetate in hexanes as eluant. The major fraction was recrystallized to afford white crystals (182 mg, 38%) of 1-acetyl-2-acetonylnaphthalene (**44**). The spectral data are listed in Tables 4-1 to 4-4. Analysis: Calculated for $C_{15}H_{14}O_2$ (MW of 226), C, 79.62%; H, 6.24%; Found, C, 79.80%, H, 6.26%. Compound **44** (100 mg) was dissolved in acetonitrile (12 mL) containing concentrated HCl (7 drops) and was refluxed for 5 hours. GC analysis (column at 200°C) showed **44** (4%) survived and a product with Rt 9.61 min was formed. The reaction solution was neutralized to pH = 7 with aqueous $NaHCO_3$ solution and extracted with ether (3 x 20 mL). The combined ether extracts were dried over magnesium sulphate, and the solvent was evaporated under reduced pressure. The residue was flash chromatographed using 20% ethyl acetate in hexanes as eluant to give brown crystals (23.4 mg, 25.4%) of 1-hydroxy-3-methyl-phenanthrene (**45**, m.p. 111-113°C). For spectral data, see Tables 4-1 to 4-4.

Compound **44** (148.6 mg) was dissolved in methanol (20 mL) containing concentrated HCl (6 drops) and was refluxed for 50 min. GC analysis (column at 200°C) showed **44** (2%) survived and a product (88%) at Rt 7.45 was formed. After work-up as described as above, some yellow oily crystals were obtained as crude product which was further recrystallized from cyclohexane to afford yellow crystals (59.5 mg, 40.8%) of 1-methoxy-3-methyl-phenanthrene (**46**, m.p. 73-74°C). For the spectral data, see Tables 4-1 to 4-4.

4.4.10a Phenanthrene (PN) in the presence of lithium acetylacetonate

A solution of PN (300 mg, 1.69 mmol), acacH (500 mg, 5 mmol) and lithium acetylacetonate [Li(acac), 53 mg, 0.5 mmol] in methanol (50 mL) was irradiated in apparatus II equipped with 350 nm lamps for 21 hours after which time GC analysis (column at 230°C) showed that all PN was consumed and four major products (including two secondary products) had been formed, with Rt 4.40 min (36%, **30**, unknown), 4.61 min (26.8%), 5.21 min (9.4%) and 6.72 min (18.8%). The residue was flash chromatographed using 15% ethyl acetate in hexanes as eluant to give a yellow oily compound (157 mg, 34%, Rt 4.61 min) of *trans*-9-acetyl-10-acetonyl-9,10-dihydro-phenanthrene (**29**). The spectral data are listed in Tables 4-1 to 4-4. The products with Rt

5.21 min and 6.72 min are described in section 4.4.10b. The GC-MS (CI) of **30** gave 221 (M+1, 100%) suggesting a 9-acetylphenanthrene structure.

4.4.10b Phenanthrene (PN)

A solution of PN (300 mg, 1.69 mmol) and acacH (500 mg, 5 mmol) in methanol (50 mL) was irradiated in apparatus II equipped with 350 nm lamps for 10 hours, after which time GC (column at 230°C) analysis showed that 25% of PN survived and two major products with Rt 4.61 min (22%, **29**, see 4.4.10a) and Rt 5.21 min (27%) and one minor product with Rt 4.40 (13%, **30**) had been formed. The residue was flash chromatographed using 12% and 15% ethyl acetate in hexanes as eluant, respectively, followed by recrystallization from ethyl acetate in hexanes to afford white crystals (198 mg, 42%, Rt 5.21) of *cis*-9-acetyl-10-acetonyl-9,10-dihydrophenanthrene (**28**). For spectral data, see Tables 4-1 to 4-4.

To a mixture of a solution containing **28** (41%), **29** (7%) and PN (as I.S., 46%), one drop of dilute sulfuric acid (in acetonitrile) was added. The resulting solution was analyzed by GC giving a mixture containing **28** (17%), **29** (8%), PN (51%) and an unknown compound **31** [12%, Rt 6.72 min, GC-MS (CI): 261 (M+1, 100%), 178 (26%)] suggesting an aldol condensation product. The calculated relative amounts of **28, 29** and **31** against I.S. are 0.90, 0.16 and 0 before acid was added and 0.34, 0.16 and 0.23 after acid was added.

4.4.11 Other naphthalene derivatives

A solution of 1-acetylnaphthalene (0.035 M) and acacH (1 M) in acetonitrile (5 mL) was irradiated in apparatus II equipped with 300 nm lamps for 17 hours. No product was detected by GC. Similar results were obtained for reactions of 2-acetylnaphthalene, 1-naphthoic acid or 2-naphthoic acid with acacH.

A solution of 1-methylnaphthalene (300 mg, 2.1 mmol) and acacH (500 mg, 5 mmol) in acetonitrile (45 mL) was irradiated for 18 hours in apparatus II at 300 nm. GC (column at 200°C) analysis of the photolysate showed that 1-methylnaphthalene (31%) survived and four major product peaks were formed at Rt 3.73 min (14.7%), 3.06 min (8.1%), 4.18 min (8.9%) and 4.73 min (5.2%). Attempts to separate the products by flash chromatography and preparative GC failed.

A solution of 2,3-dihydroxynaphthalene (0.02 M) and acacH (0.05 M) in acetonitrile (5 mL) was irradiated in apparatus II at 300 nm. After 18 hours of irradiation , the solution turned dark brown but no product could be detected by GC. Similar results were obtained for the reactions of 1,4-dihydroxynaphthalene, 1,8-dihydroxynaphthalene, 1-nitronaphthalene or 1-naphthylamine with acacH.

4.5 Sensitization and quenching of the photocycloaddition

Some results are reported in % yield; these were determined for photolysates by GC analysis. The concentrations of products and % yield were calculated. The former was calculated according to equation 4-2.

4.5.1 Triplet sensitization

Benzophenone and xanthone were employed as triplet sensitizers in photocycloaddition of 2-NpR (R = carbmethoxy, carbethoxy, methoxy and cyano groups) and acacH. Two tubes of acetonitrile solutions (5 mL) containing 2-NpR (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), octadecane (as I.S., 0.005 M, 0.025 mmol) were prepared; one tube also contained a sensitizer (0.05 M, 0.25 mmol) while the other served as the control. The solutions were irradiated in apparatus II at 350 nm.

Methyl 2-naphthoate: Three solutions were prepared in quartz tubes with No. 1 containing a solution (5 mL) without a sensitizer, No. 2 a solution (5 mL) with xanthone and No. 3 a solution (5 mL) with benzophenone. The above three solutions were irradiated for 6 hours. While from No. 1 solution, **16** was obtained (22%), no product could be detected by GC for No. 2 and No. 3 solutions.

2-NpR: The above procedures were repeated using 2-$NpCO_2Et$, 2-NpOMe and 2-NpCN for 6 hours, 1 hour and 35 min of irradiation, respectively. Products **20** (21.5%), **44** (39.5%) and **38** (17.5%) were obtained from the No. 1 solutions, no products could be detected by GC from the No. 2 or No. 3 solutions.

4.5.2 Quenching

4.5.2.1 By electron donating quenchers

Sample solutions which contained 2-NpR (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), octadecane (as I.S., 0.005 M, 0.025 mmol) were prepared in acetonitrile; one also contained TBA or DMA (0.01 M, 0.05 mmol) and the other served as a control. Quantum yields were determined by Method II (section 4.3). The sample solutions were irradiated in apparatus II at 350 nm. All results are summarized in Table 2-3.

Methyl 2-naphthoate and acacH: Five acetonitrile solutions (1 mL) containing 2-$NpCO_2Me$ (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005

Table 4-1: ^{1}H NMR data of products

Compound	Data (ppm in $CDCl_3$)	
22	1.87 (s, 3H)	2.23 (s, 3H)
	2.70 (dd, 1H, J=18Hz, J=7.5Hz)	3.33 (m, 1H)
	2.98 (dd, 1H, J=18Hz, J=7.5Hz)	3.88 (s, 3H)
	4.33 (d, 1H, J=7Hz)	7.3-7.78 (m, 3H)
	5.78 (dd, 1H, J=9Hz, J=2.5Hz)	
	6.52 (dd, 1H, J=9Hz, J=3Hz)	
23	1.87 (dd, 1H, J=7Hz,J=11Hz)	1.02 (s, 3H)
	2.05 (d, 1H, J=11Hz)	1.58 (s, 3H)
	2.55 (dd, 1H, J=5.5Hz, J=7Hz)	3.13 (s, 1H)
	4.48 (dd, 1H, J=5.5Hz, J=1Hz)	3.72 (s, 1H)
	7.2 (t, 1H, J=7Hz, J=8Hz)	3.95 (s, 3H)
	7.4 (d, 1H, J=7Hz)	7.78 (dd, 1H, J=8Hz)
17	1.94 (s, 3H)	2.23 (s, 3H)
	2.56 (d, 2H, J=6Hz)	3.63 (s, 3H)
	6.17 (dd, 1H, J=9.5Hz, J=1Hz)	4.34 (m, 1H)
	6.59 (d, 1H, J=9.5Hz)	7.05 (m, 1H)
	7.16 (m 3H)	
(in C_6D_6)	1.46 (s, 3H)	2.11 (s, 3H)
	2.28 (dd, 1H, J=18Hz, J=7.5Hz)	3.05 (s, 3H)
	2.56 (dd, 1H, J=18Hz, J=5.5Hz)	6.41 (d, 1H, J=10Hz)
	4.71(dd, 1H, J=5.5Hz, J=7.5Hz)	6.95 (m, 2H)
	6.5 (dd, 1H, J=10Hz, J=1.5Hz)	

Table 4-1 (Cont'd)

	6.83 (dd, 1H, J=7Hz, J=2Hz)	
	7.32 (dd, 1H, J=7Hz, J=1.5Hz)	
16	3.03 (d, 1H, J=18.5Hz)	2.12 (s, 6H)
	3.19 (d, 1H, J=18.5Hz)	3.59 (s, 3H)
	5.81 (d, 1H, J=9.5Hz)	4.47 (s, 1H)
	6.51 (d, 1H, J=9.5Hz)	7.07-7.24 (m, 4H)
20	1.07 (t, 3H, J=7Hz)	2.11 (s, 3H)
	2.12 (s, 3H)	3.04 (d, 1H, J=18Hz)
	3.17 (d, 1H, J=18Hz)	4.04 (q, 2H, J=7Hz)
	4.46 (s, 1H)	5.80 (d, 1H, J=9.5Hz)
	6.51 (d, 1H, J=9.5Hz)	7.07 (d, 1H, J=6.5Hz)
	7.12 (d, 1H, J=6.5Hz)	7.20 (m, 2H)
26	1.34 (t, 3H, J=7Hz)	1.83 (s, 3H)
	2.69 (dd, 1H, J=18Hz, J=7.5Hz)	2.18 (s, 3H)
	2.98 (dd, 1H, J=18Hz, J=8Hz)	3.31(m, 1H)
	4.32 (q, 2H, J=7Hz)	4.33 (d, 1H, J=7.5Hz)
	5.75 (dd, 1H, J=9.5Hz, J=2.5Hz)	7.26-7.34 (m, 2H)
	6.50 (dd, 1H, J=9.5Hz, J=3Hz)	
	7.74 (dd, 1H, J=7.5Hz, J=1.5Hz)	
29	1.96 (s, 3H)	2.0 (s, 3H)
	2.53 (dd, 2H, J=8Hz)	7.2-7.35 (m, 5H)
	3.70 (d, 1H, J=1.5Hz)	7.41 (td, 1H)
	4.0 (td, 1H, J=8Hz, J=1.5Hz)	7.73 (d, 1H, J=7.5Hz)
	7.80 (d, 1H,J=7.5Hz)	

Table 4-1 (Cont'd)

(in C_6D_6)	2.10 (dd, 1H, J=18Hz, J=6Hz)	1.40 (s, 3H)
	2.71 (dd, 1H, J=18Hz, J=8Hz)	1.69 (s, 3H)
	3.62 (d, J=1.7Hz)	7.58 (d, J=7Hz)
	4.22 (ddd, 1H, J=6, 8, 1.7Hz)	7.64 (d, J=7Hz)
	6.96 (dd, J=8, 1.7Hz)	7-7.3 (m, 5H)
28	1.95 (s, 3H)	2.19 (s, 3H)
	2.86 (dd, 1H, J=18Hz, J=6Hz)	3.83 (m, 1H)
	3.03 (dd, 1H, J=18Hz, J=6.5Hz)	7.24-7.43 (m, 5H)
	4.0 (d, 1H, J=5Hz)	7.18 (d, 1H, J=6.0)
	7.57 (d, 1H, J=6.5Hz)	7.63 (d, 1H, J=6.5Hz)
34	1.35 (s, 3H)	2.18 (s, 3H)
	1.91 (dd, 1H, J=5.5Hz, J=9Hz)	3.03 (s, 1H)
	2.87 (dd, 1H, J=18.5Hz, J=5.5Hz)	
	3.02 (dd, 1H, J=18.5Hz, J=9Hz)	
	3.91 (dd, 1H, J=3.5Hz, J=1.5Hz)	4.67 (d, 1H, J=3.5Hz)
	7.20 (dd, 1H, J=7.5Hz, J=8Hz)	7.34 (d, 1H, J=8Hz)
	7.40 (dd, 1H, J=7.5Hz, J=1.5Hz)	
18	3.06 (d, 1H, J=9Hz)	1.99 (s, 3H)
	3.15 (dd, 1H, J=18Hz, J=4.5Hz)	2.28 (s, 3H)
	3.19 (dd, 1H, J=18Hz, J=8Hz)	3.75 (s, 3H)
	3.17 8d, 1H, J=9Hz)	7.0 (d, 1H, J=7Hz)
	4.63 (dd, 1H, J=8Hz, J=4.5Hz)	7.12-7.24 (m, 3H)
45	7.56 (ddd, 1H, J=7.5Hz, J=7.5Hz, J=1Hz)	2.50 (s, 3H)

Table 4-1 (Cont'd)

	7.63 (ddd, 1H, J=8.5Hz, J=7.5Hz,	5.62 (s, 1H)
	J=1.5Hz)	
	7.62 (d, 1H, J=9Hz)	7.70 (d, 1H, J=9Hz)
	7.86 (dd, 1H, J=7.5Hz, J=1.5Hz)	6.81 (s, 1H)
	9.58 (dd, 1H, J=8.5Hz, J=1Hz)	7.31 (s, 1H)
46	7.57 (ddd, 1H, J=8Hz, J=8Hz, J=1Hz)	2.57 (s, 3H)
	7.63 (ddd, 1H, J=8.5Hz, J=8Hz,	4.13 (s, 3H)
	J=2Hz)	
	7.65 (d, 1H, J=9Hz)	7.0 (s, 1H)
	7.88 (dd, 1H, J=8Hz, J=2Hz)	7.33 (s, 1H)
	9.64 (dd, 1H, J=8.5Hz, J=1Hz)	7.73 (d, 1H, J=9Hz)
14	4.0 (s, 3H); 7.58 (m, 2H)	7.89 (d, 2H)
	7.97 (d, 1H); 8.07 (d, 1H)	8.62 (s, 1H)
21	4.0 (s, 1H); 7.52 (m, 2H)	7.62 (dd, 1H)
	7.88 (d, 1H); 8.03 (d, 1H)	8.19 (dd, 1H)
	8.91 (d, 1H)	
25	1.49 (t, 3H); 4.50 (q, 2H)	7.50 (t, 1H)
	7.54 (d, 1H); 7.62 (td, 1H)	7.88 (d, 1H)
	8.02 (d, 1H); 8.20 (dd, 1H)	8.93 (d, 1H)
19	1.45 (t, 3H); 4.45 (q, 2H)	7.53 (td, 1H)
	7.59 (td, 1H); 7.87 (d, 2H)	7.96 (d, 1H)
	8.07 (dd, 1H); 8.61 (s, 1H)	
Na(acac)	4.75 (s, 1H); 1.64 (s, 6H)	(in DMSO)
Lit.[159]	4.86 (s, 1H); 1.65 (s, 6H)	(in DMSO)

Table 4-1 (Cont'd)

K(acac)	1.72 (s, 6H); 4.58 (s, 1H)	(in DMSO)
Lit.^{159}	1.72 (s, 6H); 4.72 (s, 1H)	(in DMSO)
Li(acac)	1.6 (s, 6H); 5.0 (s, 1H)	(in DMSO)
Lit.^{159}	1.67 (s, 6H); 5.0 (s, 1H)	(in DMSO)
33	2.03 (s, 3H)	2.21 (s, 3H)
	4.06 (d, J = 6.5 Hz, 1H)	2.83 (m, 2H)
	5.87 (dd, J = 10 and 2 Hz, 1H)	3.43 (m, 1H)
	6.44 (dd, J = 10 and 3 Hz, 1H)	7.33 (m, 2H)
	7.49 (d, 1H)	
38	3.06 (d, J=17.5 Hz, 1H)	2.12 (s, 3H)
	3.46 (d, J=17.5 Hz, 1H)	2.22 (s, 1H)
	5.83 (d, J=10 Hz, 1H)	4.49 (s, 1H)
	6.58 (d, J=10 Hz, 1H)	7.18(m, 1H)
	7.31 (m, 3H)	
41	2.57 (dd, J=18 and 7 Hz, 1H)	2.01 (s, 3H)
	2.87 (dd, J=18 and 8 Hz, 1H)	2.18 (s, 3H)
	3.78 (d, J=6.5 Hz, 1H)	3.48 (m, 1H)
	5.77 (dd, 9.5 and 2.5 Hz)	3.85 (s, 3H)
	7.17-7.33 (m, 3H)	7.58 (m, 1H)
42	2.30 (s, 3H); 2.70 (s, 3H)	4.48 (s, 2H)
	7.58 (m, 2H); 7.8 (m, 3H)	8.03 (m, 1H)
44	2.23 (s, 3H); 2.66 (s, 3H)	3.87 (s, 2H)
	7.28 (d, 1H); 7.53 (m, 2H)	7.68 (d, 1H)
	7.87 (m, 2H)	

Table 4-2: ^{13}C NMR data of products

Compound		Data	(ppm in	CDCl$_3$)	
22	208.27	206.97	167.77	135.43	135.10
	132.78	130.59	129.99	129.44	127.57
	127.53	52.14	50.62	44.90	32.57
	30.44	29.95			
23	167.15(s)	147.17(s)	141.87(s)	127.97(d)	127.56(d)
	126.09(d)	124.70(s)	104.86(s)	94.04(s)	82.22(d)
	54.87(d)	54.60(d)	51.80(q)	42.28(d)	41.50(t)
	21.83(q)	18.24(q)			
17	206.4	203.6	170.2	137.0	130.8
	129.4	128.7	127.97	127.4	127.1
	124.6	65.0	52.7	44.4	37.8
	30.6	26.8			
16	207.5	205.8	173.7	132.2	131.8
	129.3	128.6	128.4	128.3	128.1
	127.3	56.4	52.4	47.6	47.3
	29.99	29.96			
20	207.6	205.9	173.0	132.0	131.8
	129.3	128.5	128.3	128.2	128.0
	127.2	61.3	56.3	47.6	47.1
	30.1	30.0	13.7		
34	207.2	156.1	138.4	129.8	128.0
	126.9	117.3	107.4	106.0	79.8

Table 4-2 (Cont'd)

	61.7	54.8	47.6	42.6	30.0
	15.4				
18	207.9	202.1	172.1	145.5	136.6
	127.8	126.9	124.2	123.9	52.5
	45.8	40.5	39.7	39.4	38.6
	31.4	30.1			
45	154.2	136.5	135.2	132.4	130.4
	128.3	128.2	128.1	126.8	126.5
	125.6	121.7	114.9	117.8	21.1
46	158.8	136.5	134.8	132.5	130.5
	128.3	128.2	128.0	126.9	126.3
	125.4	121.4	118.8	110.2	55.7
	21.6				
21	167.9	133.8	133.3	131.3	130.1
	128.5	127.7	127.1	126.1	125.8
	124.4	52.0			
25	167.7	133.9	133.2	131.4	130.1
	128.5	127.7	127.6	126.2	125.9
	124.5	61.0	14.4		
19	166.8	135.5	132.5	130.9	129.3
	128.1	128.0	127.7	127.7	126.5
	125.2	61.0	14.3		
33	206.3	204.7	136.9	135.9	135.3
	134.8	131.2	130.7	128.7	125.7
	117.5	112.6	52.9	44.6	32.3

Table 4-2 (Cont'd)

	30.2	29.5			
38	204.38	204.11	131.90	129.75	129.68
	129.15	129.08	129.01	127.76	126.49
	120.61	56.07	46.71	35.85	30.36
	29.49				
44	207.54	205.28	139.73	132.49	129.46
	129.12	128.48	128.11	127.32	127.09
	126.18	124.38	48.11	33.07	29.07

Table 4-3: IR data of products

Compound	V_{max} in cm^{-1}				
22	3044(w)	2961(w)	1736(s)	1439(m)	1362(m)
	1281(s)	1194(m)	1142(s)	756(m)	
23	3040(w)	1717(s)	1300(s)	1250(w)	1200(w)
	1150(s)	990(m)	960(m)	870(w)	840(m)
	765(m)	725(m)			
17	3072(w)	2959(w)	1728(s)	1437(w)	1364(m)
	1223	791	748		
16	3028(w)	2959(w)	1738(s)	1439(w)	1362(m)
	1194(s)	1084(m)	789(w)		
20	3000(m)	2950(w)	2940(w)	1720(s)	1495(w)
	1455(w)	1420(w)	1365(m)	1200(s)	1170(m)
	1090(w)	775(m)	740(w)	710(w)	
29	3000(m)	2960(w)	1715(s)	1495(w)	1370(s)
	1230(m)	1190(m)	1170(m)	965(w)	930(w)
	775(m)	752(m)			
34	2980(m)	2940(m)	2243(m)	1718(s)	1590(w)
	1440(m)	1165(m)	920(m)	860(m)	800(m)
	740(m)				
18	2940(m)	1703(s)	1430(m)	1350(m)	1240(m)
	1150(m)	755(m)			
45	3641(s)	3055(s)	2932(m)	1628(s)	1410(m)
	1227(s)	1177(m)	1128(m)	829(m)	744(s)

Table 4-3 (Cont'd)

46	3057(s)	2930(s)	1622(s)	1456(s)	1402(m)
	1306(m)	1217(m)	1142(s)	1084(s)	744(s)
14	3040(w)	1700(s)	1715(s)		
21	3070(w)	2970(m)	1720(s)	1600(m)	1582(m)
	1517(m)	1440(m)	1290(s)	1255(s)	1210(s)
	1143(s)	1080(m)	1045(m)	1025(m)	955(w)
	825(m)	793(s)			
25	3070(m)	3000(m)	2960(w)	2920(w)	1740(s)
	1600(m)	1585(m)	1518(s)	1285(s)	1250(s)
	1205(s)	1140(s)	1050(s)	790(s)	
Na(acac)	1670(m)	1630(m)	1515(m)	1455(m)	1415(m)
	1240(m)	1210(m)	1015(m)	920(m)	775(m)
K(acac)	2920(w)	2960(w)	1620(m)	1510(m)	1450(s)
	1410(s)	1240(w)	1200(w)	1010(m)	915(m)
	770(m)	660(m)			
Li(acac)	1608(s)	1524(s)	1455(s)	1410(s)	1350(w)
	1270(m)	1204(m)	1021(m)	927(s)	811(m)
	775(m)	670(w)			
26	3000(m)	2960(w)	1720(s)	1580(m)	1455(m)
	1420(m)	1370(s)	1280(s)	1190(s)	1160(s)
	1100(m)	1040(s)	970(m)	875(m)	840(m)
	770(s)	720(m)	680(w)		
33	2230(w)	1715(s)	1360(m)	1160(m)	910(m)
	820(m)				
38	2245(m)	1728(s)	1177(m)	1168(m)	

Table 4-3 (Cont'd)

39	1730(s)	1643(m)	1362(s)	1232(m)	1159(m)
(FT)	1101(m)	768(w)			
42	1730(m)	1703(s)	1666(w)	1360(m)	1234(s)
(FT)	1155(w)	1123(w)	808(m)	743(m)	
44	3065(m)	1713(s)	1508(m)	1427(w)	1360(m)
(FT)	1204(m)	1159(w)	957(W)	822(w)	746(w)

Table 4-4: Mass spectral data of products

Compound	Mode	m/e (%)			
22	EI	286(M$^+$, 0.5)	268(3)	244(2)	229(25)
		211(100)	186(45)	168(20)	155(50)
		141(28)	127(25)	115(20)	43(45)
23	CI	287(M+1, 100)			
17	EI	268(2)	186(100	155(80)	141(23)
		127(32)	43(25)		
	CI	287(M+1, 100)	269(38)	186(36)	
16	EI	286(M$^{+\cdot}$, 3.4)	227(1.5)	211(18.8)	186(100)
		167(20)	155(74)	141(62)	115(17)
	CI	287(M+1, 38)	269(69)	241(100)	227(9)
		186(26)			
20	EI	300(M$^+$, 5)	211(15)	200(100)	185(38)
		167(20)	155(25)	141(45)	115(15)
		43(35)			
	CI	301(M+1, 30)	255(100)	200(34)	185(10)
29	CI	279(M+1, 15)	221(100)		
28	CI	279(M+1, 100)	261(15)	221(28)	178(21)
34	EI	210(10)	196(5)	167(15)	153(28)
		43(100)			
	CI	254(M+1, 100)	236(19)		
18	EI	286(M$^+$, 2)	254(20	243(2)	229(1)

Table 4-4 (Cont'd)

		211(25)	186(50)	165(20)	155(70)
		141(65)	127(50)	115(55)	43(100)
	CI	287(M+1, 100)	269(30)	255(40)	227(80)
		186(37)			
45	EI	208(M^+, 100)	179(30)	165(32)	89(13)
		76(11)	63(3)		
46	EI	222(M^+,100)	207(45)	192(8)	179(40)
		178(40)			
	CI	223(M+1, 100)			
14	EI	186(M^+, 80)	155(100)	127(62)	
21	EI	186(M^+, 90)	155(100)	127(90)	115(7)
		101(10)	77(10)		
	CI	187(M+1, 100)			
25	EI	200(M^+, 30)	185(2)	172(10)	155(100)
		127(67)	77(12)	63(8)	
19	EI	200(M^+, 64)	185(10)	172(27)	155(100)
		127(52)			
38	EI	253(M^+, 2)	210(2)	196(7)	180(5)
		153(100)	141(40)	43(50)	
44	EI	226(M^+, 20)	211(24)	184(26)	169(100)
		141(33)	115(10)	43(22)	
33	EI	253(M^+, 1)	210(35)	196(50)	168(51)
		153(100)	43(75)		
26	EI	300 (1)	282 (1)	257 (15)	211 (100)
		200 (15)	185 (15)	167 (20)	155 (30)

Table 4-4 (Cont'd)

		141 (40)	127 (25)	115 (20)	43 (90)
	CI	301 (M+1, 32)	283 (28)	255 (41)	243 (100)
		227 (12)	201 (37)	185 (10)	
41	EI	258 (M^{+}, 10)	215 (80)	200 (100)	173 (45)
		158 (90)	141 (30)		128 (30)
		115 (39)	93 (35)		
42	EI	226 (M^{+}, 30)	211 (25)	184 (31)	169 (100)
		141 (35)	115 (12)	43 (8)	
39	EI	195 (43)	180 (100)	152 (51)	

M) and TBA (0, 0.0015, 0.003, 0.0045 and 0.006 M) were irradiated in Apparatus II at 350 nm for 2 hours. The reactions were repeated and the results are listed in Table 2-2. Two solutions (5 mL) were prepared in quartz tubes with No. 1 containing no DMA, No. 2 containing DMA (0.01 M). The solutions were irradiated for 4 hours (see Table 2-3).

Ethyl 2-naphthoate and acacH: Three solutions (5 mL) were prepared with No. 1 containing no DMA and TBA, No. 2 containing DMA (0.01 M) and No. 3 containing TBA (0.01 M). The solutions were irradiated for 4 hours (see Table 2-3).

2-Methoxynaphthalene and acacH: Three solutions were prepared and irradiated for 1 hour as described above except 2-NpOMe was used (see Table 2-3).

2-Cyanonaphthalene and acacH: Three solutions were prepared and irradiated for 1 hour as described above except 2-NpCN was used instead of 2-NpOMe (see Table 2-3).

de Mayo reaction: Three solutions (5 mL) in hexanes were prepared in quartz tubes, each of them containing acacH (0.05 M, 0.25 mmol), cyclohexene (0.5 M, 2.5 mmol) and decahydronaphthalene (as I.S., 0.004 M, 0.02 mmol); No. 2 tube also contained N,N-dimethylaniline (0.01 M, 0.05 mmol) and No. 3 tube tributylamine (0.01 M, 0.05 mmol) while No. 1 tube was used as a control solution. The solutions were irradiated in apparatus II at 300 nm for 4 hours. The relative yields (GC% ratio of **47** over I.S.) of product **47** (identified by coinjection with an authentic compound)[141] are 11.8% for No. 1 solution, 9.4% for No. 2 solution and 10.7% for No. 3 solution.

4.5.2.2 By others

The common conditions were the same as that in section 4.5.1 except that a quencher (0.002 M, biactyl, DMA or oxygen) was used. Quantum yields were determined by Method II (section 4.3). All the results are summarized in Table 2-4.

Methyl 2-naphthoate: Two solutions were prepared in quartz tubes with No. 1 containing no biacetyl and No. 2 solution with biacetyl (0.002 M). The solutions were irradiated in apparatus II at 300 nm for 6 hours. The above experiment was repeated with biacetyl at 0.02 M and 7 hours of irradiation. Two solutions (5 mL) without the quencher were prepared in quartz tubes. One of them was purged with nitrogen and the other with oxygen for 10 min. The above solutions were irradiated for 4 hours. Similarly, two solutions with (0.03 M) and without NND were irradiated at 300 nm for 6 hours. The results are shown in Table 2-4.

Ethyl 2-naphthoate: Two solutions were prepared in quartz tubes with (0.002 M) and without biactyl and irradiated for 6 hours (see Table 2-4).

2-Methoxynaphthalene: Three solutions were prepared in quartz tubes with No. 1 solution containing no quencher, No. 2 solution being purged with oxygen for 10 min and No. 3 solution containing biacetyl (0.002 M). The above solutions were irradiated for 1 hour (see Table 2-4).

2-Cyanonaphthalene: Two solutions without any quencher were prepared. One of them was purged with nitrogen and the other with oxygen for 10 min. They were irradiated for 35 min (see Table 2-4).

4.5.3 Quenching in the presence of sulfuric acid

Two acetonitrile solutions (5 mL) were prepared in quartz tubes containing 2-$NpCO_2Me$ (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), sulfuric acid (0.001 M, 0.005 mmol), octadecane (as I.S., 0.005 M, 0.025 mmol) with (0.02 M, 0.1 mmol) and without (as a control) 1,3-pentadiene. The two solutions were irradiated in apparatus II at 300 nm for 3 hours. The percentage yields of **17** and **16** were 38% and 18.5% without the diene and 33.5% and 17% with the diene.

Two solutions were prepared containing 2-$NpCO_2Me$ (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), sulfuric acid (0.001 M, 0.005 mmol), octadecane (as a I. S., 0.005 M, 0.025 mmol) with (0.002 M, 0.01 mmol) and without (as a control) biacetyl. The two solutions were irradiated in apparatus II at 300 nm for 3 hours. The percentage yields of **17** and **16** were 47.5% and 21.5% without biacetyl and 46.5% and 21.5% with biacetyl.

4.6 The quenching of fluorescence intensity of naphthalene derivatives

The fluorescence intensity ratio, $I°/I$, was determined at the maximum intensity wavelength. The Stern-Volmer correlation of $I°/I^*$ with respect to either [acacH] or [quencher], was carried out on the basis of equation 2-13. Light absorbed by NpR (% light) was calculated according to equation 4-6 and fluorescence intensities (I) were corrected to I^* by % light absorbed by NpR according to equation 4-7

$$\% \text{ light} = \epsilon_{Np}C_{Np} / (\epsilon_{Np}C_{Np} + \epsilon_{acacH} C_{acacH}) \times 100\% \qquad 4\text{-}6$$

where the definitions of terms in equation 4-6 are same as that in equation 4-4 (Section 4.3)

$I^* = I/(\%\ light)$

4.6.1 Acetylacetone quenching

The quenching of 2-NpCO_2Me fluorescence by acacH was measured (nitrogen purged for 10 min) in methylcyclohexane, acetonitrile and methanol with excitation wavelength at 330 nm (slit 3 nm). The intensity ratio was determined at 352 nm for methylcyclohexane, at 358 nm for acetonitrile and at 363 nm for methanol. Linearity of $I°/I^*$ *vs* [acacH] plots was established with a correlation coefficient of 0.992-0.997 as shown in Table 2-5.

Quenching of 2-NpR (R = carbmethoxy, carbethoxy, methoxy and cyano groups) fluorescence by acacH in acetonitrile (under nitrogen atmosphere) is shown in Figure 2-3 and results are listed in Table 2-6.

The results of quenching of 2-NpCO_2Me fluorescence by acacH at various excitation wavelength are listed in Table 2-7.

4.6.2 Other quencher quenching

NpR and lithium acetylacetonate (Li(acac)): The quenching of fluorescence of NpR (R = 2-CO_2Me, 2-CO_2Et, OMe, CN and OH groups) by Li(acac) are shown in Figure 2-4 and the results are summarized in Table 2-8. The conditions for these experiments are shown in these figure and table.

Methyl 2-naphthoate and biacetyl: The quenching of 2-NpCO_2Me fluorescence (non-purged) by biacetyl in methylcyclohexane and in acetonitrile were determined (Table 2-9). The results of the quenching of 2-NpCO_2Me fluorescence in the presence of H_2SO_4 and that of the quenching of its exciplex emission with H_2SO_4 (0.0935 M) by biacetyl (0-0.00396 M) are listed in Table 2-9 (non-purged).

Methyl 2-naphthoate and oxygen: See Figure 2-6.

NpR and sulfuric acid: The fluorescence of 2-NpOMe (at 0.0005 M) in acetonitrile was not quenched by sulfuric acid (0.0063 and 0.0375 M) while that of 2-$NpCO_2Me$ (at 0.0005 M) was quenched by sulfuric acid (0.0063-0.0375 M, Figure 2-7). The details of the quenching experiments of 2-$NpCO_2Me$ (0.0005 M) and of its exciplex emission with sulfuric acid (0.0935 M) by acacH (0-0.0081 M) are listed in Table 2-14, Figures 2-10 and 2-11. The results for the similar quenching experiments of 1-$NpCO_2Me$ (0.0005 M) are given in Table 2-14, Figures 2-8, 2-13, 2-14 and 2-15.

2-NpR and tributylamine: See Figure 4-2 and Table 2-11.

2-NpR and heavy atom solvent: The quenching of 2-NpR (R = CO_2Me and CN groups) fluorescence by iodomethane or 1,2-dibromoethane in acetonitrile (non-purged) were summarized Table 2-12.

Methyl 2-naphthoate and 1,3-pentadiene: See Table 2-10.

Methyl 2-naphthoate and sodium acetylacetonate [Na(acac)]: See Table 2-10.

4.6.3 Temperature effects on fluorescence quenching: Quenching of 2-$NpCO_2Me$ fluorescence by acacH (under nitrogen atmosphere) was determined in acetonitrile at 7°C, 22°C and 50°C, as shown in Table 4-5 and Figure 2-16.

4.7 Heavy atom effect on photocycloaddition

4.7.1 2-$NpCO_2Me$

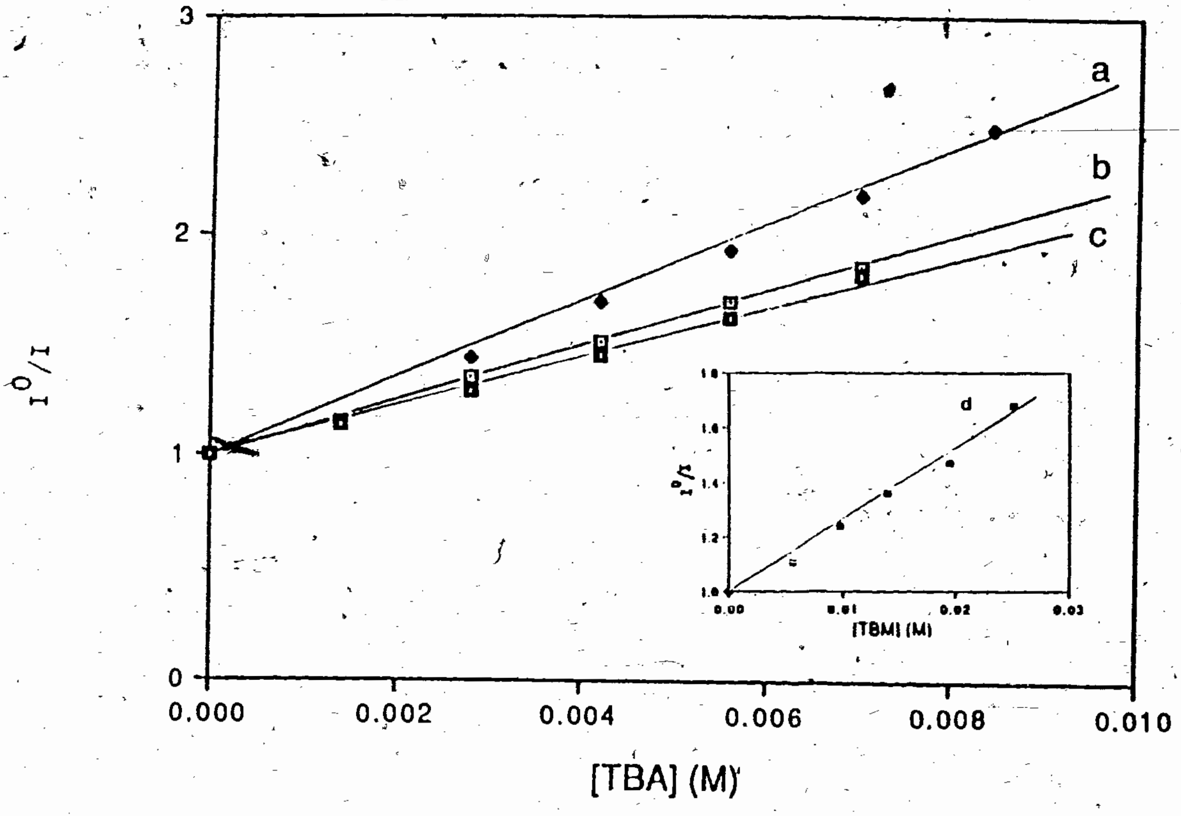


Figure 4-2: Fluorescence quenching (non-purged) of 2-NpR (0.0005 M) by tributylamine in acetonitrile with excitation wavelength at 330 nm (320 nm for 2-NpOMe) a) 2-NpCN; b) 2-NpCO$_2$Me; c) 2-NpCO$_2$Et and d) 2-NpOMe.

Table 4-5: The quenching of methyl 2-naphthoate fluorescence by acacH at various temperatures in acetonitrile[a]

[acacH] (M)	I°/I^{*} [b]		
	(at 7°C)	(at 22°C)	(at 50°C)
0	1.0	1.0	1.0
0.003	1.07		1.02
0.005	1.17	1.08	1.04
0.008	1.26	1.17	1.08
0.01		1.25	
0.013		1.28	
0.015	1.46	1.35	1.11
$k_q\tau_0$ (M^{-1})	31 ± 1.53	24 ± 1.75	8.5 ± 0.95

a. The solutions containing 2-NpCO$_2$Me (0.0005 M) and acacH (0-0.015 M) were purged with nitrogen for 10 min and their fluorescences were taken with excitation wavelength at 330 nm at room temperature.

b. I^{*} was obtained from observed OD values by correction according to equation 4-6 and 4-7.

Stock solution A (10 mL) containing 2-$NpCO_2Me$ (37.2 mg, 0.2 mmol), acacH (80 mg, 0.8 mmol) and octadecane (127 mg, 0.05 mmol) in acetonitrile was prepared. Solution B was prepared by mixing solution A (1 mL) and iodomethane (35.5 mg, 0.25 mmol). Then, 0-16 μL solution B was transferred into each of eight small Pyrex vials by a syringe followed by dilution to one mL with solution A to give five sample solutions containing 2-$NpCO_2Me$ (0.02 M), acacH (0.08 M), octadecane (0.005 M) and iodomethane (0-0.004 M). The vials were capped and purged with nitrogen for 5 min prior to irradiation. The samples were irradiated in apparatus II at 350 nm for 4 hours. The yields of **16** and **17** and other results are given in Table 2-15.

Five sample solutions containing 2-$NpCO_2Me$ (0.02 M), acacH (0.08 M), octadecane (as I.S., 0.005 M) and 1,2-dibromoethane (0-0.005 M) were prepared by a similar process. After 4 hours of irradiation, sample solutions were analyzed by GC (See Table 2-16).

4.7.2 2-Cyanonaphthalene

Five sample solutions containing 2-NpCN (0.02 M), acacH (0.08 M), octadecane (0.005 M, as I.S.) and iodomethane (0 0.004 M) were prepared in a similar way as shown in 4.7.1. After 3 hours of irradiation, the solutions were analyzed by GC. Quantum yields of product **38** are given in Table 2-17.

4.8 Catalytic effects on the photocycloaddition.

4.8.1 Lithium acetylacetonate effect

Li(acac): In quartz tubes, three methanol solutions (5 mL) containing 2-$NpCO_2Me$ (0.02 M, 0.1 mmol), octadecane (as I.S., 0.005 M, 0.025 mmol) were prepared; No. 1 tube also contained acacH (0.05 M, 0.25 mmol), No. 2 tube Li(acac) (0.05 M, 0.25 mmol) and No. 3 tube acacH (0.05 M, 0.25 mmol) and Li(acac) (0.001 M, 0.005 mmol). The solutions were irradiated in apparatus II for 3 hours at 300 nm. The % yields of **16** formation were calculated as described in section 4.5 and are listed in Table 2-18.

Zn(acac)$_2$: A similar experiment using Zn(acac)$_2$ was carried out (see Table 2-18).

2-Substituted naphthalene derivatives: The photoaddition of 2-NpR (R = carbmethoxy, carbethoxy, methoxy, cyano, hydroxy and acetyl groups) and acacH were carried out in the absence and in the presence of Li(acac). The common conditions were as follows. For each reaction, two methanol solutions (5 mL) were prepared containing 2-NpR (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol) octadecane (as I.S., 0.005 M, 0.025 mmol); one also contained Li(acac) (0.001 M, 0.005 mmol) and the other no Li(acac) (as control). The solutions were irradiated in apparatus II at 350 nm for 4 hours for 2-NpCO$_2$Me and 2-acetylnaphthalene systems, 4.5 hours for 2-NpCO$_2$Et, 3 hours for 2-NpOMe and 2-NpCN, and 19.5 hours for 2-NpOH systems, respectively. The quantum yields were calculated from GC analysis by Method II (section 4.3). The quantum yields of product formation in the absence and presence of Li(acac) are given in Table 2-19.

Phenanthrene: Five solutions (1 mL) containing PN (0.02 M, 0.02 mmol), acacH (0.08 M, 0.08 mmol), $C_{16}H_{34}$ (as I.S., 0.005 M, 0.005 mmol) and Li(acac) (0, 0.001, 0.003, 0.006 and 0.01 M) were prepared in methanol. The solutions were irradiated in apparatus II at 350 nm for 4 hours. The resulting solutions were analyzed by GC. The GC areas of the I.S. were controlled within 20-22%, so the GC% of the products **28**, **29** and **30** (**31**

ignored) are reported as relative yield as shown in Table 2-20.

4.8.2 Acid effects

Various acid catalysis: Six acetonitrile solutions (5 mL) in quartz tubes containing 2-NpCO$_2$Me (0.02 M, 0.1 mmol) and acacH (0.05 M, 0.25 mmol) were prepared; No. 1 tube also contained sulfuric acid (0.0003 M, 0.0015 mmol), No. 2 tube phosphoric acid (0.0003 M, 0.0025 mmol), No. 3 tube hydrochloric acid (0.0003 M, 0.0015 mmol), No. 4 tube borontrifluoride in ether (0.0003 M, 0.0015 mmol) and No. 5 tube trifluoroacetic acid (0.0005 M, 0.0015 mmol). The last tube (No. 6) was used as the control. The solutions were irradiated in apparatus II at 300 nm for 3 hours (but 6 hours for No. 5). The conversion of 2-NpCO$_2$Me and the formation of **17** and **16** (GC%) are given in Table 2-21.

Methyl 1-naphthoate: For the effect of H_2SO_4 on the photocycloaddition to acacH, see Table 2-22.

1-Cyanonaphthalene: For the effect of H_2SO_4 on the photocycloaddition to acacH, see Table 2-22.

2-Cyanonaphthalene: For the effect of H_2SO_4 on the photocycloaddition to acacH to yield **38**, see Table 2-22.

2-Methoxynaphthalene: For the effect of H_2SO_4 on the photocycloaddition to acacH to yield **44**, see Table 2-22.

Acid effects in various solvents: Two sets of solutions (5 mL) were prepared in acetonitrile and methanol containing methyl 2-naphthoate (0.02 M, 0.1 mmol), acacH (0.05 M, 0.025 mmol) and sulfuric acid (0, 0.0001, 0.0003, 0.0006 and 0.001 M). The solutions were irradiated in apparatus II at 300 nm for 3 hours. The results are reported in GC% in Table 2-24.

4.8.3 Base effects

2-Methoxynaphthalene: Two solutions (5 mL) were prepared in acetonitrile containing 2-NpOMe (0.02 M, 0.1 mmol), acacH (0.05 M, 0.25 mmol) and sodium hydroxide (0 and 0.001 M). The solutions were irradiated in apparatus II at 300 nm for 1 hour. The product **44** formation was 26% and 21% (GC%) for the solutions with and without sodium hydroxide, respectively.

Methyl 2-naphthoate: The above reactions were repeated for the 2-NpCO$_2$Me and acacH system except that the irradiation was for 3 hours. Formation of **16** was 27% and 3% for the solutions with and without sodium hydroxide, respectively.

Salt effects: Two solutions (5 mL) were prepared in 4:1 methanol:water containing 2-NpCO$_2$Me (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol) and sodium chloride (0 and 0.005 M; 0 and 0.025 mmol). The solutions were irradiated in apparatus II at 350 nm for 6 hours. The resulting solutions were analyzed by GC. Yields of **16** were 13.5% and 13.3% with and without sodium chloride, respectively.

4.9 Kinetic studies of the photocycloaddition

4.9.1 $k_q\tau_0$ determinations of the photocycloaddition

Methyl 2-naphthoate : A stock solution A (40 mL) containing 2-NpCO$_2$Me (148.8 mg, 0.8 mmol, 0.002 M) and octadecane (as I.S., 50.8 mg, 0.2 mmol, 0.003 M) in acetonitrile was prepared. Solution B was prepared by mixing A with acacH (600 mg, 6 mmol, 0.6 M) and diluting to volume of 10 mL. Exact amounts of solution B (2.5-0.67 mL) were pipetted into each of five volumetric flasks (5 mL) followed by dilution to 5 mL with solution A to give five sample solutions containing 2-NpCO$_2$Me (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3 M-0.08 M). The solution were capped and purged with nitrogen for 10 min. The deaerated samples and an actinometer solution were irradiated in apparatus II at 350 nm for 2-4 hours (but 5 min for the actinometer). The conversion of 2-NpCO$_2$Me ranged from 16% to 22%. The plot of $1/\Phi_p$ *vs* 1/[acacH] is given in Figure 2-18. The quantum yields are listed in Table 2-25. The above reactions were repeated and the results are listed in Table 2-25.

2-NpCO$_2$Et: Five sample solutions were prepared in a similar way as above and contained 2-NpCO$_2$Et (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3 M-0.06 M). The deaerated samples and an actinometer were irradiated in apparatus II at 350 nm for 2-5 hours (but 5 min for the actinometer). The conversion of 2-NpCO$_2$Et ranged from 20% to 30%. The plot of $1/\Phi_p$ *vs* 1/[acacH] is given in Figure 2-18. The quantum yields are listed in Table 4-6.

2-NpOMe: In similar manner to the above experiments, six sample solutions containing 2-NpOMe (0.02 M), octadecane (0.005 M, as I.S.) and acacH (0.3-0.06 M) were prepared and irradiated in apparatus II at 350 nm for 15-50 min. The conversion of 2-NpOMe ranged from 14% to 31%. The plot of $1/\Phi_p$ *vs* 1/[acacH] is given in Figure 2-18. Quantum yields are listed in Table 4-7.

2-NpCN: Six sample solutions containing 2-NpCN (0.02 M), octadecane (0.005 M, as I.S.) and acacH (0.3-0.06 M) were prepared in the same way as above and irradiated in apparatus II at 350 nm for 20-45 min. The conversion of 2-NpCN analyzed by GC ranged from 14% to 18%. The plot of

$1/\Phi_{Np}$ *vs* 1/[acacH] is given in Figure 2-18. Quantum yields are listed in Table 4-8.

4.9.2 Effects of metal acetylacetonate on the photocycloaddition

A methanol solution A containing 1-NpCO$_2$Me (186 mg, 1 mmol) and acacH (250 mg, 2.5 mmol) was prepared in a volumetric flask (50 mL). Sodium acetylacetonate [Na(acac), 3.1 mg] was dissolved with solution A in a volumetric flask (5 mL) to give solution B. To each of seven volumetric flasks (5 mL), solution B (0.1-1 mL) was transferred and diluted with solution A to afford 7 sample solutions containing 1-NpCO$_2$Me (0.02 M), acacH (0.05 M) and Na(acac) (0.0001-0.001 M). The sample solutions and an actinometer solution were irradiated in apparatus II at 300 nm for 3 hours. The disappearance of 1-NpCO$_2$Me was analyzed by GC using xanthone (0.02 M, mixed with sample solution after irradiation) as I.S. The plot of quantum yield against [Na(acac)] is given in Figure 2-20 and Table 2-27.

The above procedure was repeated using combinations of 1-NpCO$_2$Me/acacH/K(acac) (Figure 2-20), 2-NpCO$_2$Me/acacH/Li(acac) (Figure 2-19) and 2-NpCO$_2$Me/acacH/K(acac) (Figure 2-20). The plots of quantum yields against [metal acetylacetonate] and details of the conditions are given in Table 2-27.

4.9.3 Effects of sulfuric acid on the photocycloaddition

Sample solutions were prepared to contain 2-NpCO$_2$Me (0.02 M), acacH (0.08 M) and sulfuric acid (0.0001-0.001 M). The deaerated sample solutions and a secondary actinometer were irradiated in apparatus II at 350 nm for 100-240 min. Quantum yields of **16** and **17** were determined by GC and listed in Table 4-9. The plot of quantum yield against [sulfuric acid] is given

Table 4-6: Quantum yields of photocycloaddition of ethyl 2-naphthoate and acacH in acetonitrile[a]

[acacH] (M)	Φ_p[b]	1/[acacH] (M)	$1/\Phi_p$
0.3	0.0163	3.33	61.4
0.2	0.0132	5.00	75.8
0.15	0.0107	6.67	93.5
0.10	0.0084	10.0	119.3
0.06	0.005	16.7	200
$k_q\tau_0$ (M^{-1}):	2.32 ± 0.12	γ=0.997	
$\Phi_{limiting}$:	0.043 ± 0.0086		

a. The solutions containing 2-$NpCO_2Et$ (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3-0.6 M) were irradiated (N_2 purged) for 2-5 hours in apparatus II at 350 nm. Conversion of 2-$NpCO_2Et$: 20-30%.

b. Quantum yields were determined by Method I (section 4.3) and based on formation of **20**.

Table 4-7: Quantum yields of photocycloaddition of 2-methoxynaphthalene and acacH in acetonitrile[a]

[acacH] (M)	Φ_p[b]	1/[acacH] (M)	$1/\Phi_p$
0.3	0.0526	3.33	19.0
0.2	0.048	5.0	20.8
0.15	0.0485	6.67	20.6
0.10	0.0424	10.0	23.6
0.08	0.0367	12.50	27.3
0.06	0.0328	16.7	30.5
$k_q\tau_0$ (M^{-1}):		18 ± 1.53	
$\Phi_{limiting}$:		0.064 ± 0.0031	

a. The solutions containing 2-NpOMe (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3-0.06 M) were irradiated (N_2 purged) for 15-50 min in apparatus II at 350 nm. Conversion of 2-NpOMe: 14-31%.

b. Quantum yields were determined by Method I (section 4.3) and based on **44** formation.

Table 4-8: Quantum yields of photocycloaddition of 2-NpCN and acacH in acetonitrile[a]

[acacH] (M)	Φ_{Np} [b]	1/[acacH] (M)	$1/\Phi_{Np}$
0.30	0.051	3.33	19.6
0.2	0.041	5.0	24.4
0.15	0.039	6.67	25.6
0.10	0.031	10.0	32.3
0.08	0.030	12.5	33.3
0.06	0.024	16.70	41.7
$k_q\tau_0$ (M^{-1}):	10 ± 0.75	γ=0.978	
$\Phi_{limiting}$:	0.065 ± 0.0049		

a. The solutions containing 2-NpCN (0.02 M), octadecane (as I.S., 0.005 M) and acacH (0.3-0.06 M) were irradiated (N_2 purged) for 20-45 min in apparatus II at 350 nm. Conversion of 2-NpCN: 14-18%.

b. Quantum yields were determined by Method I (section 4.3) and based on 2-NpCN disappearance.

Table 4-9: Dependence of quantum yield for photocycloaddition of 2-NpCO$_2$Me and acacH on sulfuric acid in acetonitrile[a]

[H_2SO_4] x 10^4 (M)	Φ_p[b] **16**	**17**
0	0.0043	0
1	0.0051	trace
3	0.0164	0.0062
6	0.0223	0.0398
10	0.0256	0.0500

[a] The solution containing 2-NpCO$_2$Me (0.02 M), acacH (0.08 M), octadecane (0.005 M, as I.S.) and sulfuric acid (0.0001-0.001 M) were irradiated for 100-240 min in apparatus II at 350 nm. Errors: ± 15%.

[b] Quantum yields were determined based on **16** and **17** formation.

in Figure 2-22.

4.10 Effects of dienes on the photocycloaddition

4.10.1 2-Substituted naphthalene Photocycloadditions of 2-NpR (R = carbmethoxy, carbethoxy, methoxy and cyano groups) and acacH were carried out in the presence of dienes. Sample solutions contained 2-NpR (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), octadecane (as I.S., 0.005 M) in acetonitrile as the common ingredients and also with (0.02 M, 0.1 mmol) and without (as a control) a diene. A pair of the sample solutions (5 mL) were irradiated in apparatus II equipped with 350 nm lamps for a fixed time. The photolysates were analyzed by GC to provide quantum yields (Method II). The results are summarized in Table 2-28.

4.10.2 Concentration effect

Five sample solutions (5 mL) in acetonitrile containing 2-NpCO$_2$Me (0.02 M, 0.1 mmol), acacH (0.08 M, 0.4 mmol), octadecane (as I.S., 0.005 M, 0.025 mmol) and 1,3-pentadiene (0.1-0.3 M; 0.5-1.5 mmol) were prepared and irradiated in apparatus II at 350 nm for 5 hours. The quantum yields of **16** were determined by Method II (section 4.3). An unknown compound **48** (Rt 5.77 min at 200°C) was formed with a GC-MS (CI) pattern as follows: 255 (M+1, 100%), 223 (8%), 195 (11%), 187 (38%), 186 (41%) and 155 (15%) suggesting a product from photoaddition of 2-NpCO$_2$Me with 1,3-pentadiene. The attempt to isolate it failed. The results are given in Table 2-30.

Similarly, five solutions (1 mL) in acetonitrile were prepared containing 2-NpCO$_2$Me (0.02 M, 0.02 mmol), acacH (0.08 M, 0.08 mmol), octadecane (as I.S., 0.005 M, 0.005 mmol) and 1,3-pentadiene (0.02-0.1 M; 0.02-0.1 mmol). The solutions were irradiated for 4 hours in apparatus II at 350 nm. The quantum yields of **16** were determined by Method II (section 4.3). Quantum yields of **16** and GC% of **48** are given in Table 2-29.

Similarly, five sample solutions (1 mL) in acetonitrile were prepared containing 2-$NpCO_2Me$ (0.02 M, 0.02 mmol), 1,3-pentadiene (0.08 M, 0.08 mmol) octadecane (as I.S., 0.005 M, 0.005 mmol) and acacH (0.02-0.08 M; 0.02-0.02 mmol), and irradiated in apparatus II at 350 nm for 30 min. In addition to product **16**, two unknown addition products were detected as **50** and **48** [GC-MS (CI): for **48**: see above. For **50**: 255 (M+1, 100%), 223 (8%), 187 (18%), 186 (33%), 155 (10%)]. The results are given in Table 4-10.

4.11 Phosphorescence and UV spectroscopy studies

4.11.1 E_S and E_T determination

The first singlet and triplet excited state energies (E_S and E_T) of naphthalene derivatives (NpR, R = 1-carbmethoxy, 2-carbmethoxy, 1-carbethoxy, 2-carbethoxy, 1-cyano, 2-cyano, 1-methoxy and 2-methoxy groups) were determined from emission (fluorescence and phosphorescence) spectra. E_S was calculated according to equation 4-8[58] using the wavelength at which the fluorescence emission spectrum crossed the excitation spectrum. E_T was calculated according to equation 4-8 using the phosphorescence emission peak at the shortest wavelength.

$$E = (2.86 \times 10^4)/\lambda(nm) \qquad 4\text{-}8$$

E_S and E_T values for above compounds are listed in Table 1-2.

4.11.2 Attempted detection of ground state complexation

Table 4-10: Relative yields of photocycloaddition of methyl 2-naphthoate and 1,3-pentadiene in the presence of acacH in acetonitrile[a]

[acacH] (M)	**16**[b]	**48**[b]	**50**[b]	**50+48**	**16/(50+48)**
0	0	0.175	0.117	0.292	0
0.02	0.055	0.158	0.102	0.260	0.21
0.04	0.074	0.116	0.076	0.192	0.39
0.06	0.128	0.113	0.082	0.195	0.66
0.08	0.142	0.091	0.061	0.152	0.93

a. The solutions containing 2-NpCO$_2$Me (0.02 M), 1,3-pentadiene (0.08 M), octadecane (as I.S., 0.005 M) and acacH (0.02-0.08 M) were irradiated for 30 min in apparatus II at 350 nm. Error: ± 5-7%.

b. Reported in relative yield which was the GC area ratio of the product over the I.S.

A stock solution of acacH (0.1 M) and stock solutions of 2-NpCO$_2$Me (0.01, 0.001 and 0.0001 M) were prepared in acetonitrile and kept in the dark prior to use. Differential absorption spectra were recorded using a pair of double compartment cells. A typical run is shown in Figure 4-3. No new absorption was found. Similarly, differential absorption spectra were recorded with the solution systems of acacH (3 M)/2-NpCO$_2$Me (0.01, 0.001 and 0.0001 M) and 2-NpCO$_2$Me (0.01 M)/acacH (1, 0.5 and 0.2 M) in acetonitrile. No new absorption was detected.

4.12 Concentration dependence of the photocycloaddition

Quantum yields of NpR disappearance for photocycloaddition of NpR (R = 1-NpCO$_2$Me, 2-NpCO$_2$Me, 1-CN and 1-OMe groups) and acacH were measured as a function of concentration of NpR and acacH, respectively. GC analysis was performed using the mixture of xanthone solution (100 μL, as I.S., 0.05 M in acetonitrile) with sample solution (100 μL) before and after irradiation, respectively. One example is described below; other cases are summarized in Tables 2-32, 4-11 and 4-12.

Six acetonitrile solutions (5 mL) were prepared, containing 2-NpCO$_2$Me (0.05 M, 0.25 mmol) and acacH (0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 M). The solutions were irradiated in apparatus II at 300 nm for 5-10 hours. The conversions of 2-NpCO$_2$Me ranged 25-35%. The light intensity was adjusted, based on the 2-NpCO$_2$Me absorption (equation 4-4), and the quantum yields of 2-NpCO$_2$Me disappearance were calculated using equation 4-3 (Table 2-31).

In a similar manner as described above, six acetonitrile solutions (5 mL) were prepared, containing acacH (0.05 M, 0.25 mmol) and 2-NpCO$_2$Me

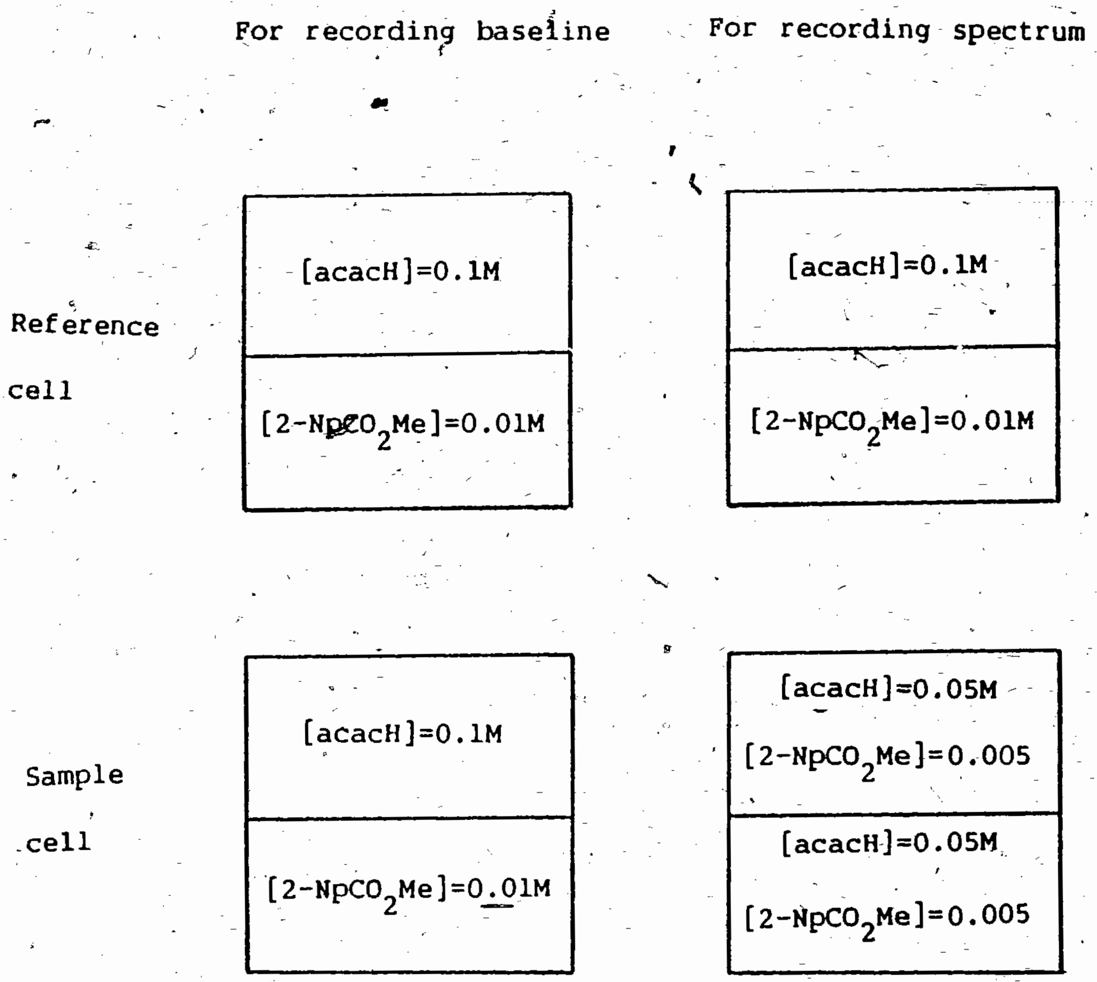


Figure 4-3: A pair of double compartment cells for the differential absorption spectra.

Table 4-11: Concentration dependence of photocycloaddition of 2-methoxynaphthalene in acetonitrile

[2-NpOMe]=0.05M[a]		[acacH]=0.053 M[c]	
[acacH] (M)	Φ_{Np}[b]	[2-NpOMe] (M)	Φ_{acacH}[d]
0.004	0	0.0053	0.076
0.016	0.044	0.0072	0.08
0.026	0.112	0.0092	0.076
0.039	0.179	0.011	0.10
0.061	0.315	0.021	0.13
		0.030	0.15
		0.053	0.13
Conversion	11-30%	14-21%	

a. The solution containing 2-NpOMe (0.05 M) and acacH (0.004-0.061 M) were irradiated for 2 hours in apparatus II at 300 nm. For GC analysis, see a of Table 2-31. Errors: ± 15%.

b. Quantum yield of 2-NpOMe disappearance based on 2-NpOMe absorbing light.

c. The solutions containing acacH (0.053 M) and 2-NpOMe (0.0053-0.053 M) were irradiated for 5-30 min. Other conditions were same as that in a.

d. Quantum yield of 2-NpOMe disappearance based on acacH absorbing light.

Table 4-12: Concentration dependence of photocycloaddition of 1-cyanonaphthalene and acacH in acetonitrile

[1-NpCN]=0.01M[a]		[acacH]=0.05 M[c]	
[acacH] (M)	Φ_{Np}[b]	[1-NpCN] (M)	Φ_{acacH}[d]
0.011	0.009	0.004	0.01
0.02	0.007	0.005	0.013
0.03	0.021	0.006	0.016
0.04	0.029	0.007	0.017
0.05	0.053	0.008	0.019
		0.009	0.024
		0.010	0.025
Conversion	18-30%		14-30%

a. The solutions containing 1-NpCN (0.01 M) and acacH (0.011-0.05 M) were irradiated for 1-3 hours and 40 min in apparatus II at 300 nm. Errors: ± 15%. For GC analysis, see a of Table 2-31.

b. Quantum yield of 1-NpCN disappearance based on 1-NpCN absorbing light.

c. The solutions containing acacH (0.05 M) and 1-NpCN (0.004-0.01 M) were irradiated for 30-100 min. Other conditions were same as that in a.

d. Quantum yield of 1-NpCN disappearance based on acacH absorbing light.

(0.05, 0.06, 0.07, 0.08, 0.09 and 0.10 M). The solutions were irradiated for 6-11 hours. The conversion of 2-$NpCO_2Me$ ranged 13-17%. The light intensity was adjusted based on the acacH absorption and the results are listed in Table 2-31.

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APPENDIX

Derivation of equations 2-29 from Scheme 2-2

The steady state approximation applied to the singlet excitate state 2-NpCO$_2$Me, to the exciplex, E, formed between ^{1}2-NpCO$_2$Me with acacH and to the catalytic intermediate, C, formed between ^{1}2-NpCO$_2$Me with Li(acac) gives the quantum yield of product formation (Φ_p):

$$\Phi_p = \Phi_E + \Phi_C \tag{1}$$

where Φ_E is the quantum yield of product formation through the uncatalyzed process; Φ_C is the quantum yield of product formation through the catalyzed process.

$$\Phi_E = \frac{M}{I} = \frac{k_p[E]}{I} \tag{2}$$

$$\frac{d[E]}{dt} = k_q[^1Np][acacH] - (k_q' + k_p + k_b + k_p')\ [E] = 0$$

$$[E] = \frac{k_q\ [^1Np][acacH]}{k_q' + k_p + k_b + k_p'} \tag{3}$$

$$I = \{k_q[acacH] + k_c[Li(acac)] + (k_f + k_{ic})\}\ [^1Np] \tag{4}$$

hence, the quantum yield Φ_E is given by

$$\Phi_E = \frac{k_q[\text{acacH}]x}{k_{ic} + k_f + k_q[\text{acacH}] + k_c[\text{Li(acac)}]} \qquad (5)$$

where: $x = k_p/(k_p + k_q' + k_p' + k_b)$

Similarly,

$$\Phi_C = \frac{M}{I} = \frac{k_c'[C][\text{acacH}]}{I} \qquad (6)$$

$$\frac{d[C]}{dt} = k_c[{}^1\text{Np}][\text{Li(acac)}] - (k_c'[C][\text{acacH}] - k_b'[C] = 0$$

$$[C] = \frac{k_c[{}^1\text{Np}][\text{Li(acac)}]}{k_c'[\text{acacH}] + k_b'}$$

hence, the quantum yield Φ_C is given by

$$\Phi_E = \frac{k_c[\text{Li(acacH)}]\gamma}{k_{ic} + k_f + k_q[\text{acacH}] + k_c[\text{Li(acac)}]} \qquad (7)$$

where: $\gamma = (k_c'[\text{acacH}])/(k_c'[\text{acacH}] + k_b')$

$$\Phi_p = \Phi_E + \Phi_C$$

$$= \frac{k_q[\text{acacH}]x + k_c[\text{Li(acac)}]\gamma}{k_{ic} + k_f + k_q[\text{acacH}] + k_c[\text{Li(acac)}]}$$ 2-29