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**MECHANISTIC STUDIES OF THE PHOTOLYSIS
OF
SUBSTITUTED 1-NAPHTHYLMETHYL ESTERS
AND
SUBSTITUTED BENZYL ACETATES**

by

James W. Hilborn

**Submitted in partial fulfilment of the requirements
for the Degree of Doctor of Philosophy**

at

**Dalhousie University
Halifax, Nova Scotia
September, 1990**

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**To my family
for their love and support**

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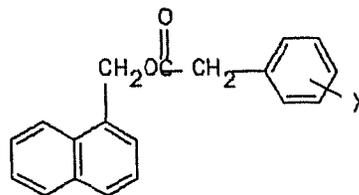
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ABSTRACT

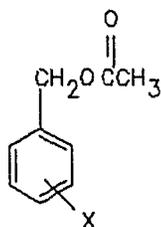
The photochemistry of four different ester series, was investigated in order to understand the mechanism of excited state cleavage reactions. Two of the ester series were substituted 1-naphthylmethyl alkanoates, **1a-h**, and phenylacetates, **2a-k**, and the other two being substituted benzyl acetates, **3a-e**, and 2,2-dimethylpropanoates, **4a-e**.



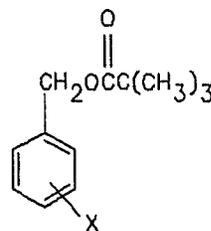
1a-h



2a-k



3a-e



4a-e

Esters **1a-h**, and **2a**, **2d-k**, were shown to behave similarly upon photolysis in methanol with constant fluorescence quantum yields (ϕ_f) and singlet lifetimes (τ_s). From the product ratios in the photolysis, the rates of decarboxylation of the acyloxy and aryloxy radicals were obtained. The results were rationalized using radical stability arguments. Esters **2b** and **2c** were shown to behave unusually since their fluorescence quantum yield and singlet lifetime were decreased markedly compared to the other esters. These unusual effects were rationalized by assuming that charge transfer or exciplex formation had occurred in the excited state.

The photochemistry of the benzylic esters, **3a-e** and **4a-e**, was examined in order to compare substituent effects in excited state benzene chemistry with those previously determined for naphthalene cases. The special effect of the *meta* methoxy compound was investigated. The importance of the electron transfer process converting radical pairs to ion pairs in determining product ratios was assessed.

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ABBREVIATIONS AND SYMBOLS

A	acceptor
Å	Ångström
Ac	acetyl
aq	aqueous
Ar	aromatic
CH ₂ Cl ₂	dichloromethane
cm	centimeter
CIDNP	chemically induced dynamic nuclear polarization
D	donor
DMF	dimethylformamide
e	charge of the electron
ϵ	molar extinction coefficient
Et	ethyl
ET	electron-transfer
Et ₂ O	diethyl ether
EtOH	ethanol
eV	electron volt
$E_{1/2}^{ox}$	half-wave oxidation potential
$E_{1/2}^{red}$	half-wave reduction potential

FMO	Frontier Molecular Orbital
g	gram
GLC	gas-liquid chromatography
GC/MS	gas chromatography / mass spectroscopy
h	hours
HCl	hydrochloric acid
H ₂ SO ₄	sulphuric acid
HMO	Hückel Molecular Orbital Theory
HOMO	highest occupied molecular orbital
HPLC	high performance liquid chromatography
I	ionic intermediate derived product
I ⁰ /I	fluorescence intensity quenching
ir	infrared
J	nmr coupling constant
kcal	kilocalories
kJ	kilojoules
k _c	rate constant of combination
k _{CO₂}	rate constant of decarboxylation
k _d	rate constant of diffusion
k _D	rate constant of disproportionation
k _H /k _D	kinetic isotope effects
k _{ET}	rate constant of electron transfer

k_f	rate constant of fluorescence
k_I	rate constant of heterolytic cleavage
k_{ic}	rate constant of internal conversion
k_{isc}	rate constant of intersystem crossing
k_q	rate constant of quenching
k_R	rate constant of homolytic cleavage
$LiAlH_4$	lithium aluminum hydride
LCAO	linear combination of atomic orbitals
LUMO	lowest occupied molecular orbital
M	mol/L
Me	methyl
$MgSO_4$	magnesium sulphate (anhydrous)
min	minutes
mg	milligram
mL	milliliter
MO	molecular orbital
MS	mass spectroscopy
MsCl	methanesulfonyl chloride
$NaBH_4$	sodium borohydride
$NaHCO_3$	sodium bicarbonate
NaOH	sodium hydroxide
nm	nanometer

Np	naphthalene
nmr	nuclear magnetic resonance spectroscopy
ns	nanosecond
R	radical intermediate derived product
R_t	retention time
s	second
S_0	ground state
S_1	singlet energy
S^*	first excited singlet state
T	temperature
THF	tetrahydrofuran
ϕ_f	quantum yield of fluorescence
λ_{max}	wavelength of maximum absorption
λ	reorganization energy
ΔG	free energy change
τ_s	singlet state lifetime

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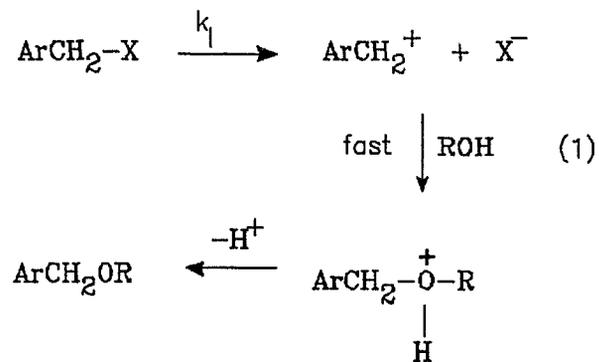
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General Introduction

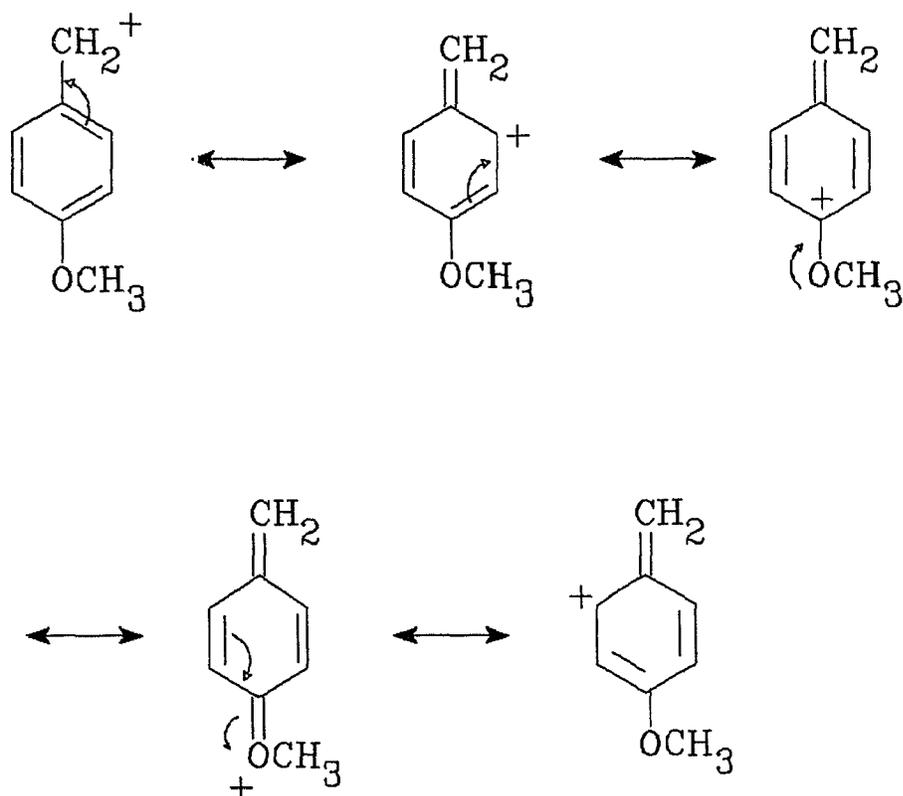
Solvolysis is the term used when the solvent participates in a reaction by combining with the substrate. Although many types of solvolytic displacements can be envisioned, the most common types occur when a leaving group is displaced by the solvent. For the most part, solvolytic reactions of organic molecules proceed by mechanisms which involve nucleophilic substitution on carbon, and usually occur at an alkyl group bonded to a leaving group. The two most common reactions are S_N1 and S_N2 . They are both quite well understood and are discussed in some detail in all introductory organic chemistry texts [1].

Substituent effects are known to have a profound effect on unimolecular nucleophilic substitution (S_N1) reactions. These effects are easily observed with benzylic ($ArCH_2-X$) substrates. Electron-donating substituents in the *ortho* and *para* positions accelerate, and electron-withdrawing substituents retard, the rate controlling heterolytic step (k_1) and, therefore, the measured rate, eq 1. These substituent effects were shown to be stronger when the substituent is acting from the *ortho* and *para*



positions, than when it is acting from the *meta* position. This observed rate difference can be rationalized by the fact that electron-donating groups in the *ortho* and *para* positions can stabilize the developing positive charge on the benzylic carbon by direct interactions, as shown in Figure 1. An electron-donating group in an *ortho* or *para* position will therefore help stabilize a positive charge by increasing the number of hybrid structures, due to the stability of the structure with the positive charge on oxygen. An electron-donating substituent in the *meta* position has little effect on the

Figure 1: Contributing Forms to the 4-Methoxybenzyl Cation Hybrid.

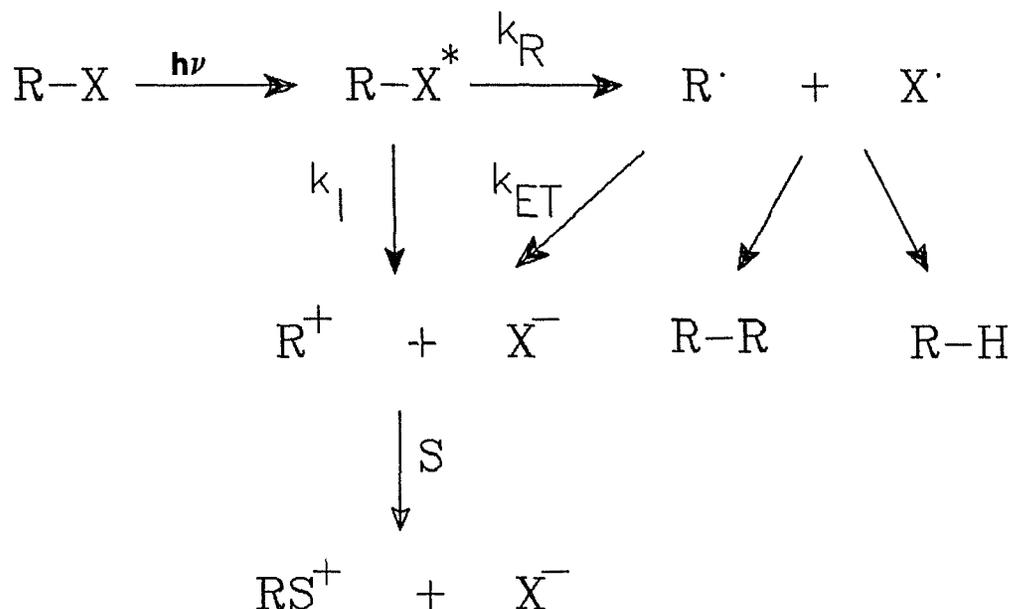


solvolysis rate since there is no direct interaction of charge with this group. These qualitative arguments are confirmed by quantitative Hammett $\rho^+\sigma^+$ correlations with ρ^+ values in the range of -4.5 [2].

Although the solvolysis of organic molecules in the ground state is quite well understood, the subject of solvolysis in the excited state has been given considerably less attention. There is an extensive review available [3]. Excited state solvolyses also can occur through cleavage of a σ bond between a leaving group and a benzylic carbon. Because the excited state lifetime of benzylic substrates is so short, bimolecular reactions are unlikely and excited state $S_1,2$ solvolysis reactions are not known. Moreover, the unimolecular reactions follow a more complex pathway than the ground state reactions. In the excited state, the σ bond can be broken in two ways, either heterolytically (analogous to the ground state S_N1 type mechanism) or homolytically (via radicals). These processes can occur competitively and the products which result from each pathway are different. Therefore, the two pathways can be monitored by analyzing the products. Heterolytic cleavage gives cationic intermediates which are trapped by the hydroxylic solvent, whereas homolytic cleavage gives radicals which may undergo radical coupling or hydrogen atom abstraction (Scheme 1).

Previous studies have indicated that the pathway by which a molecule undergoes photocleavage is controlled by factors such as the multiplicity of the reacting state, the solvent, the temperature the leaving group and the substituents. Non-nucleophilic solvents such as benzene are known to enhance the yield of the products derived from the homolytic pathway, while nucleophilic solvents such as

Scheme 1: General Mechanism for the Photochemistry of Benzylic Substrates.



alcohols enhance the yield of heterolytically derived products.

The solution photochemistry of benzylic substrates with leaving groups has been extensively studied in the last thirty years [4]. The mechanism usually involves the excitation of an aromatic chromophore. Upon excitation, the electronic energy is distributed among vibrational and rotational modes. This vibrational energy may then be sufficient to break bonds.

This thesis will examine some photochemical reactions of 1-naphthylmethyl and benzylic systems. Chapter 1 of this thesis will investigate the photochemistry of substituted 1-naphthylmethyl alkanoylates and substituted 1-naphthylmethyl phenylacetates in an attempt to obtain rates of decarboxylation of the alkanoyloxy radicals, $\text{R-CO}_2\cdot$; and of the substituted arylacetyloxy radicals, $\text{ArCH}_2\text{-CO}_2\cdot$. These

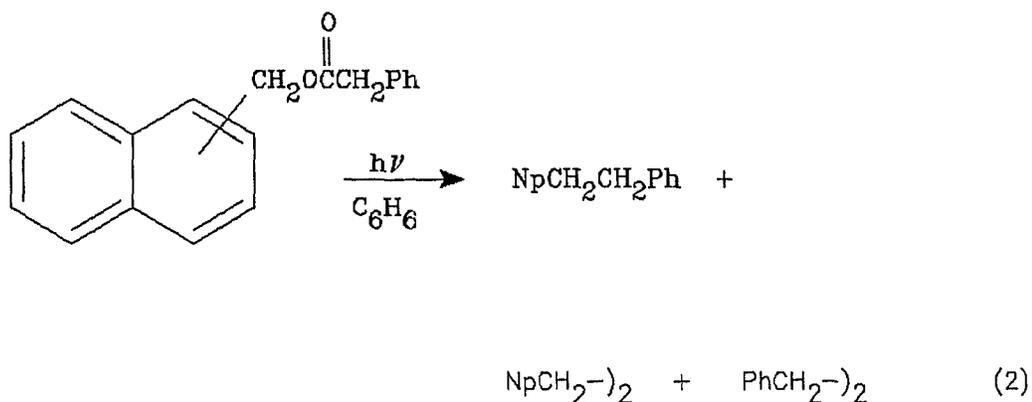
rates should contribute to the knowledge needed to understand the mechanistic photocleavage of esters. Chapter 2 will be directed at an attempt to understand the effect substituents on the aromatic ring have on the photocleavage of substituted benzyl acetates and benzyl 2,2-dimethylpropanoates. This study should also allow an investigation into the mechanism of the photocleavage and the extent to which electron transfer (k_{ET} , Scheme 1) converting the radical pair to the ion pair is important.

CHAPTER 1

The Photochemistry of the Substituted 1-Naphthylmethyl Esters 1a-h and 2a-k

1.1 Introduction

Givens *et al.* [5] have studied the photodecarboxylation of 1- and 2-naphthylmethyl phenylacetates in benzene as shown below in eq 2. In this study, they



observed three products derived from a homolytic decarboxylation pathway. The product ratios were not statistical in nature but reflected a much larger cross coupling of the radicals. The authors postulated that this ratio results from a solvent cage effect on the initially generated radical pair. Heterolytically derived products were not observed, but since benzene was the solvent this is not surprising.

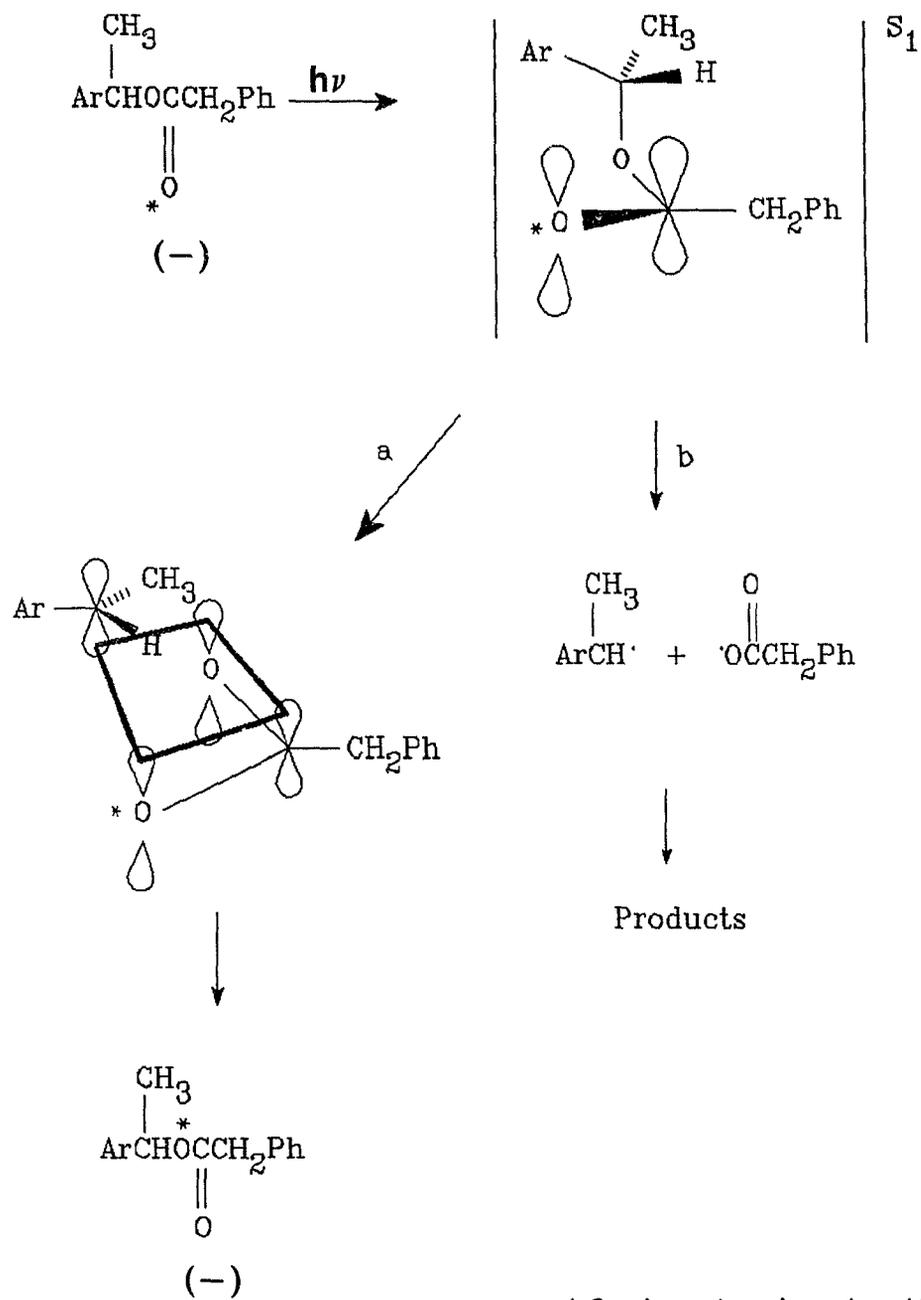
In this early study of the photochemistry of the 1-naphthylmethyl

phenylacetates by Givens *et al.* [5], they noted that for reaction to occur the alcohol C–O bond must be adjacent to the excited chromophore. They also deduced that there were no bichromophoric interactions between the two aromatic rings upon excitation. Finally, they concluded that the excitation energy remains in the naphthyl moiety and that C–O bond cleavage is favoured over C–C(=O)–O bond cleavage although bond strength arguments would favour the opposite order of reactivity.

Further research by Givens *et al.* [6] has shown that sensitization experiments were ineffective in promoting decarboxylation of 2-naphthylmethyl phenylacetate. Quenching studies on this substrate showed that the excited singlet state of the ester was intercepted at high concentration of the quencher but a chemical reaction occurred rather than physical quenching. Phosphorescence spectra indicated triplet energies of approximately 60 kcal/mol for these naphthyl substrates.

Further research [7] involving the mechanism of the photochemistry of an optically active 1-naphthyl-1-ethyl ester demonstrated that the ester remains optically pure when irradiated and reisolated. When a substrate with ^{18}O incorporated into the ether oxygen of the ester functional group was irradiated, the oxygen was shown to be scrambled in the recovered ester. The authors suggested that the oxygen scrambling in ester photochemistry occurs via a [1,3]-sigmatropic migration with retention of the configuration of the migrating carbon, as shown in Scheme 2. Jaeger *et al.* [8] in earlier work in the benzyl acetate system, dismissed this [1,3]-sigmatropic migration. Jaeger *et al.* in their study found no retention of the configuration at the chiral carbon which may indicate a different intermediary complex for the benzyl case. The

Scheme 2: Mechanism for ^{18}O Scrambling via [1,3]-Sigmatropic Migration.

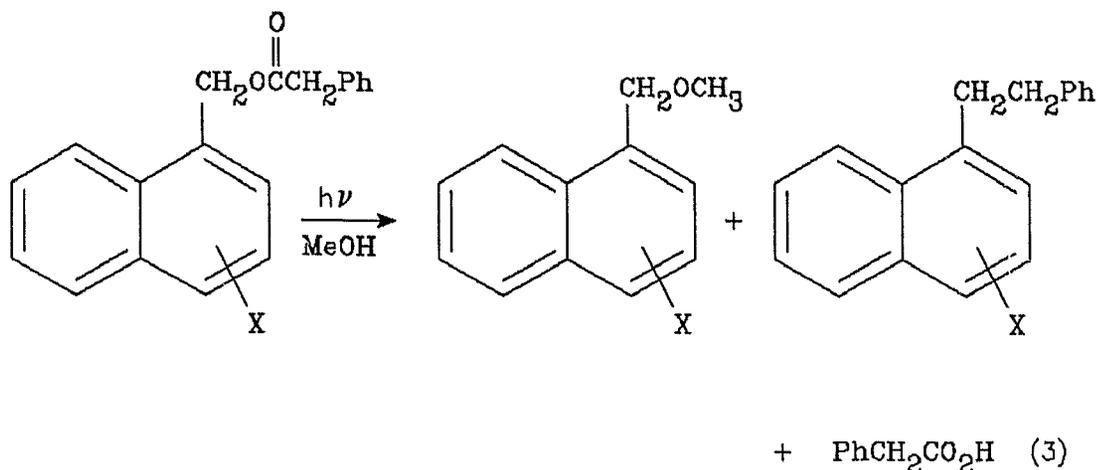


a: 1,3-sigmatropic migration

b: C-O bond cleavage

pathway shown in Scheme 2 allows for return of the intermediate to the starting ester, with the oxygen being scrambled between the ether and the carbonyl group of the ester functional group. This scrambling pathway is a competing reaction, and accounts for a significant fraction of excited state decay.

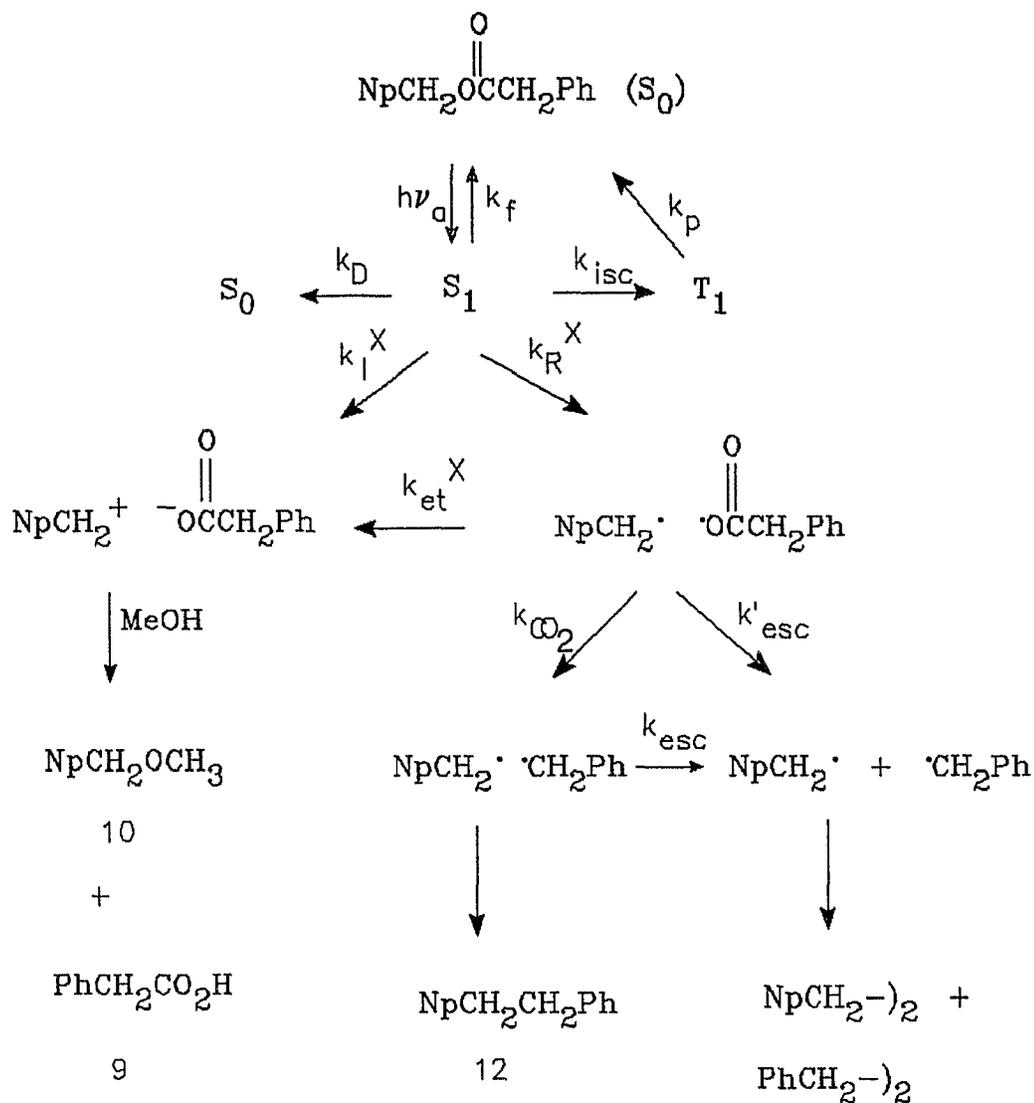
The work by Givens *et al.* [5,6] involving the 1-naphthylmethyl phenylacetate system was extended by De Costa and Pincock [9]. The esters were irradiated in the solvent methanol in order to understand the competition between ionic and radical pathways. Ionic products were not observed in the work by Givens since the experiments were done using the non-nucleophilic solvent benzene, and as mentioned earlier the solvent has a large effect on the products obtained from a photolysis. Givens *et al.* showed that ester photochemistry proceeds initially through homolytic cleavage of the O=CO-f-C alcohol bond. Once the two radicals are produced, electron transfer between the two fragments may be important. The importance of electron transfer in benzylic photochemistry was discussed in earlier work on the photochemistry of 1-naphthylmethyl trimethylammonium chloride salts [10]. In a nucleophilic solvents, such as methanol, ions can be trapped by the solvent. If, however, electron transfer is not important, then the radicals produced can undergo radical coupling reactions. The authors [9] found that direct irradiation of these esters in methanol resulted in the formation of three major products, eq 3. The ether results from trapping of the 1-naphthylmethyl cation, while the phenylacetic acid results from trapping of the phenylacetyloxy anion by methanol. The ethane derived product results from radical coupling after decarboxylation of the phenylacetyloxy radical. The



ether and acid product may be produced either by heterolytic cleavage from the singlet excited state or by homolytic cleavage followed by electron transfer. Determination of the product ratios obtained from photolysis as a function of substituents on the naphthalene ring gave an understanding into the favoured steps involved in the mechanism. The authors deduced that electron transfer was an important step in the photochemistry of these esters. From this study, a mechanism for the photolysis of 1-naphthylmethyl esters in methanol was proposed, shown in Scheme 3. It was deduced from the product yields that $k_{\text{R}}^{\text{x}} \gg k_{\text{I}}^{\text{x}}$ and that the competition must then occur between k_{ET}^{x} and k_{CO_2} . The authors evaluated many electron transfer rates (k_{ET}^{x}) for substituted 1-naphthylmethyl radicals. If the product distribution is a measure of the rate of electron transfer divided by the rate of decarboxylation, then evaluation of previously undetermined decarboxylation rates should be possible by this method.

Chapter 1 describes the synthesis of a series of substituted 1-naphthylmethyl acetates and 1-naphthylmethyl phenylacetates in order to study the rates of decarboxylation of the acyloxy radicals. The 1-naphthylmethyl derivatives were

Scheme 3: The Mechanism of Photolysis of 1-Naphthylmethyl Esters in Methanol.



chosen because their triplet energies lie below the C-O alcohol bond strength of the ester functional group. It is known that the triplet energy does not vary appreciably with substituents, and this allows for a detailed study of the singlet reaction only. The photochemistry of these esters will be examined in order to obtain ratios of the yields of ionic to the yields of decarboxylation products. Because the rate of electron transfer is a known value for the 1-naphthylmethyl radical/acyloxy radical pair, the

decarboxylation rates of the acyloxy radicals can then be determined.

1.2 Results

1.2.1 General Synthesis of the 1-Naphthylmethyl Esters 1a-h and 2a-k

The synthesis of the 1-naphthylmethyl esters was accomplished by a common method as outlined in Schemes 4 and 5. All esters were purified by column chromatography and then either by distillation or recrystallization from hexane. Spectral and elemental analyses are included in Chapter 3.

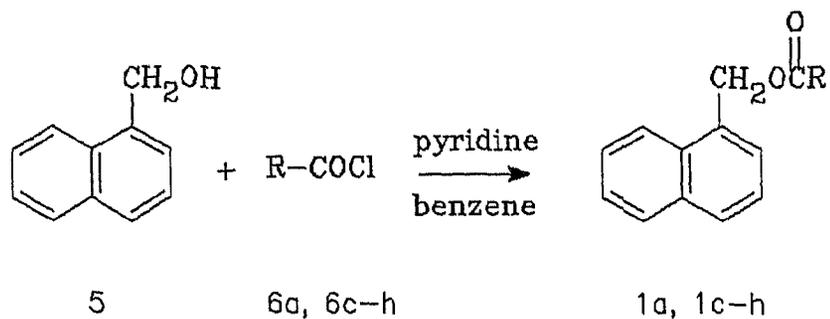
1.2.2 Spectral Properties of the 1-Naphthylmethyl Esters 1a-h and 2a-k

The emission properties of the substituted 1-naphthylmethyl acetate esters **1a-h** are summarized in Table 1 and those for esters **2a-k** are summarized in Table 3.

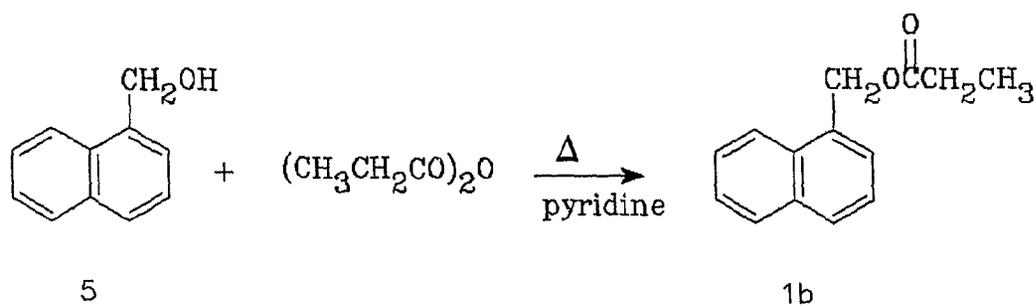
1.2.3 Photolysis Results of the 1-Naphthylmethyl Esters 1a-h and 2a-k

The photolysis results for the substituted 1-naphthylmethyl acetate esters **1a-h** and **2a** (Schemes 11 and 12) are summarized in Table 2 and those for esters **2a-k** are summarized in Table 4. The substituted 1-naphthylmethyl acetate esters were irradiated and the product yields of the ether and coupling product were determined by calibrated HPLC.

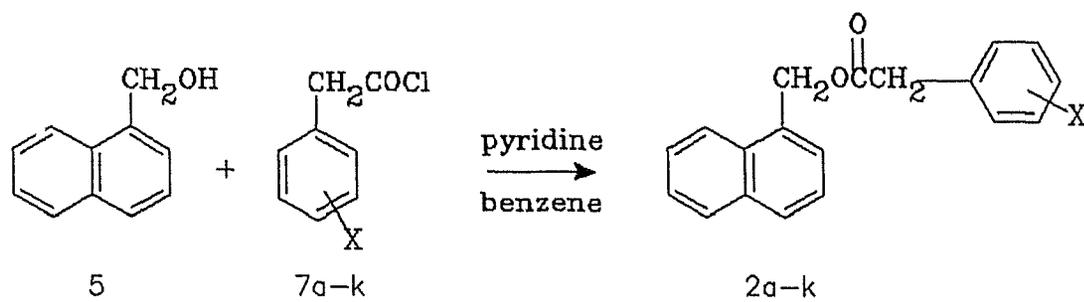
Scheme 4: Preparation of the Substituted 1-Naphthylmethyl Acetate Esters 1a-h.



- a : CH₃
- c : PhCH₂CH₂
- d : (CH₃)₂CH
- e : CH₂=CH-CH₂
- f : (CH₃)₃C
- g : CH₃OCH₂
- h : NCCH₂



Scheme 5: Preparation of the Substituted 1-Naphthylmethyl Phenylacetate Esters 2a-k.

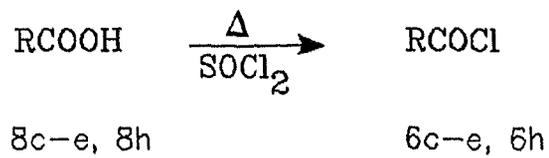


X

- a : H
- b : 4-OCH₃
- c : 3-OCH₃
- d : 4-CH₃
- e : 3-CH₃
- f : 4-F
- g : 3-F
- h : 4-CF₃
- i : 3-CF₃
- j : 4-CN
- k : 3-CN

Substituted acetyl chlorides **6c-e**, **6h** and substituted phenylacetyl chlorides **7b-k** were prepared by reaction of the corresponding acid with thionyl chloride as shown in Schemes 6 and 7.

Scheme 6: Preparation of the Substituted Acetyl Chlorides 6c-e and 6h.



R

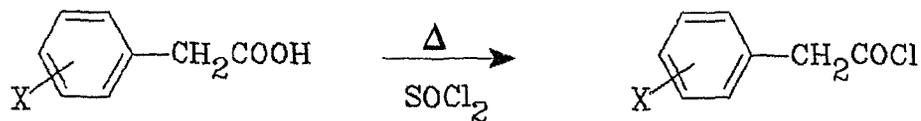
c : PhCH₂CH₂

d : (CH₃)₂CH

e : CH₂=CH-CH₂

h : NCCH₂

Scheme 7: Preparation of the Substituted Phenylacetyl Chlorides 7b-k.



9b-k

X

7b-k

b : 4-OCH₃

c : 3-OCH₃

d : 4-CH₃

e : 3-CH₃

f : 4-F

g : 3-F

h : 4-CF₃

i : 3-CF₃

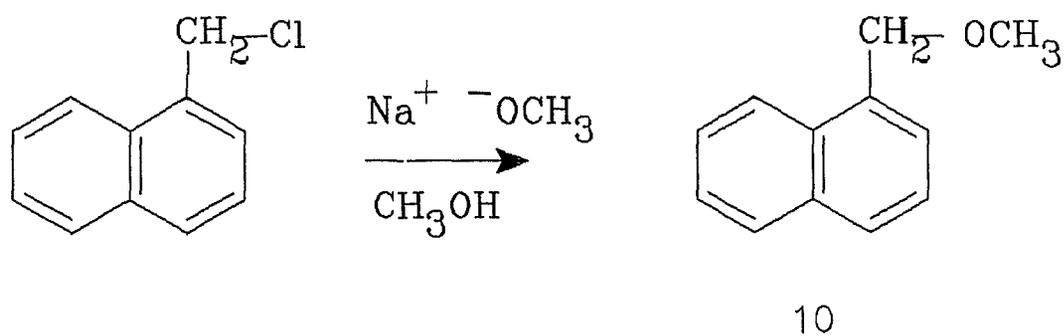
j : 4-CN

k : 3-CN

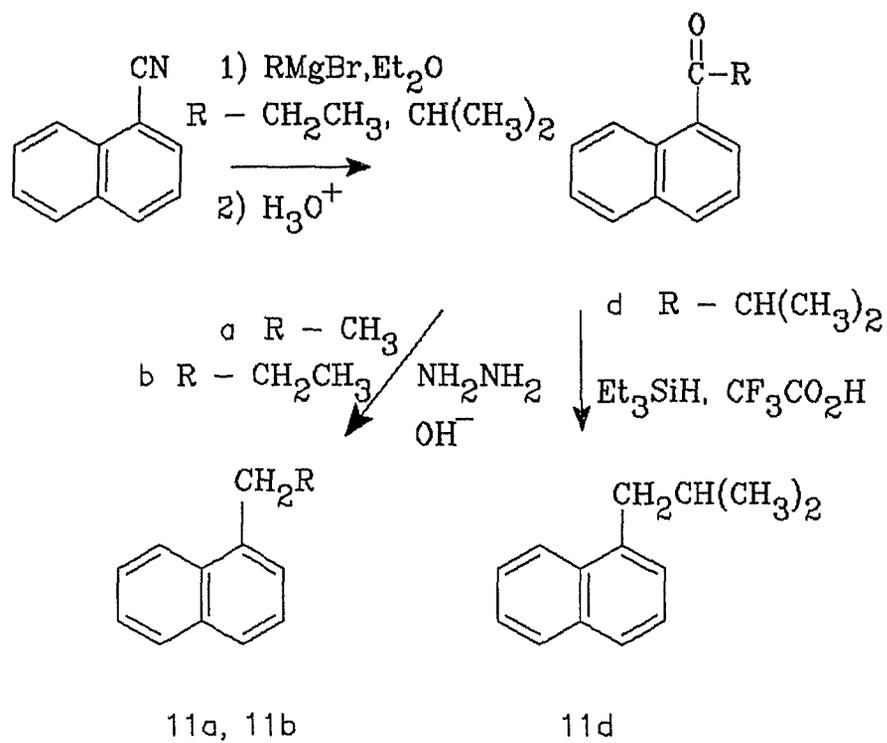
1.2.4 Preparation of the Photoproducts

The preparation of the photoproducts **10**, **11a**, **11b**, **11d** and **11h** are shown in Schemes 8-10.

Scheme 8: Preparation of 1-Methoxymethylnaphthalene **10**.



Scheme 9: Preparation of the Alkylnaphthalenes 11a-b and 11d.



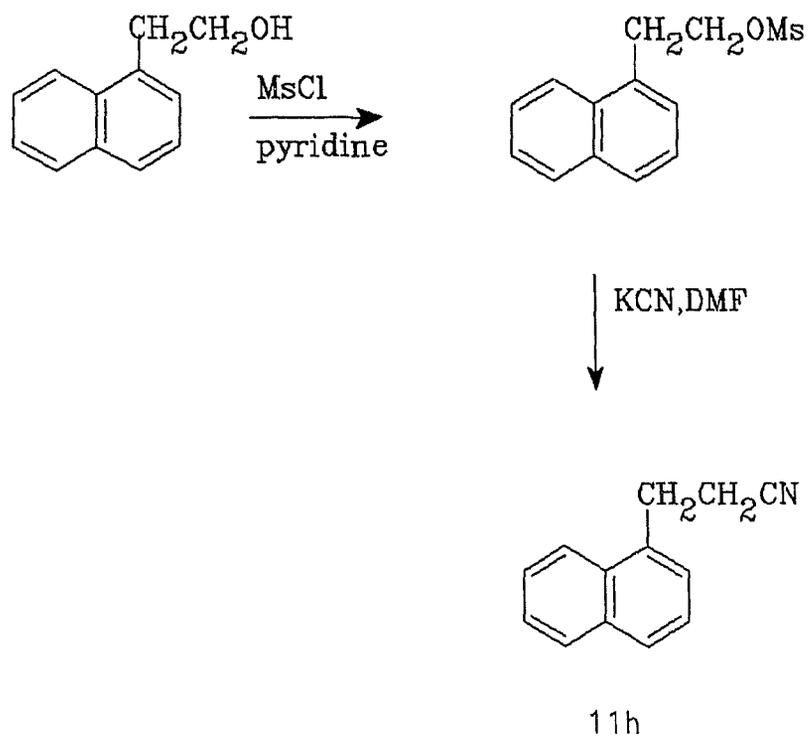
Scheme 10: Preparation of 3-(1'-Naphthyl)propionitrile 11h.

Table 1: Emission Properties of the Substituted 1-Naphthylmethyl Acetate Esters **1a-h** and **2a** in Methanol.

Ester	R	S_1 kcal/mol (kJ/mol)	τ_s ns	ϕ_F^a
1a	CH ₃	92.6 (387)	41	0.16
1b	CH ₃ CH ₂	92.0 (385)	40	0.14
1c	PhCH ₂ CH ₂	91.9 (384)	41	0.14
1d	(CH ₃) ₂ CH	91.7 (383)	40	0.16
1e	CH ₂ =CHCH ₂	91.4 (382)	39	0.16
1f	(CH ₃) ₃ C	92.1 (385)	39	0.14
1g	CH ₃ OCH ₂	92.6 (387)	39	0.15
1h	CNCH ₂	92.1 (385)	37	0.14
2a	PhCH ₂	92.1 (385)	39	0.14

a Quantum yields of fluorescence were determined using a value of 0.21 for 1-methylnaphthalene [11].

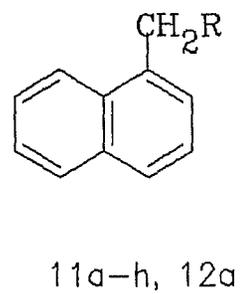
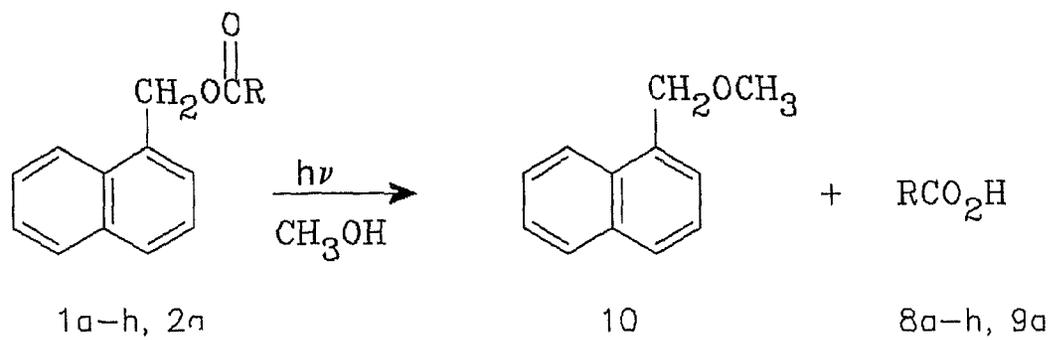
Scheme 11: Photolysis of Esters 1a-h and 2a.

Table 2: Percentage Yields of Photoproducts from Irradiation of the Substituted 1-Naphthylmethyl Acetate Esters **1a-h** and **2a** in Methanol.

Ester	R	10^a	11a-h, 12a^a	I/R	$k_{\text{CO}_2}^{\text{b,c}}$ ($\times 10^{-9} \text{ s}^{-1}$)	$\log k_{\text{CO}_2}$
1a	CH ₃	99	0 (1)	>20 ^d	<1.3 (± 0.2)	9.1 (± 0.6)
1b	CH ₃ CH ₂	93	6 (7)	13.3	2.0 (± 0.3)	9.3 (± 0.1)
1c	PhCH ₂ CH ₂ ^e	92	7 (8)	12	2.3 (± 0.4)	9.3 (± 0.2)
1d	(CH ₃) ₂ CH	80	6 (20)	4	6.4 (± 0.8)	9.8 (± 0.1)
1e	CH ₂ =CHCH ₂	77	14 (23)	3.3	7.7 (± 1.1)	9.9 (± 0.1)
1f	(CH ₃) ₃ C	71	19 (29)	2.5	10.5 (± 2.0)	10.0 (± 0.1)
1g	CH ₃ OCH ₂	89	10 (11)	8.1	3.2 (± 0.4)	9.5 (± 0.1)
1h	CNCH ₂	88	6 (12)	7.3	3.5 (± 0.5)	9.5 (± 0.1)
2a	PhCH ₂ ^f	84	16 (16)	5.2	5.0 (± 0.8)	9.7 (± 0.1)

a Estimated error $\pm 2\%$. Yields are corrected for unreacted starting material.

b By calibrated HPLC assuming $k_{\text{ET}}^{\text{H}} = 2.6 \times 10^{10} \text{ s}^{-1}$.

c Errors in brackets are calculated assuming $\pm 2\%$ in determination of product yields and 10% error in the measured rate of decarboxylation of 9-methyl-9-fluorenyl carboxylate radical.

d Assuming 5% of **11a** would have been detected.

e The yield of phenylpropanoic acid was 42% (isolated) D.P. De Costa and J.A. Pincock; To be published.

f The yield of phenylacetic acid was 34% (HPLC), 58% (isolated).

Table 3: Emission Properties of the Substituted 1-Naphthylmethyl phenylacetate Esters **2a-k** in Methanol.

Ester	X	S_1 kcal/mol (kJ/mol)	τ_s ns	ϕ_F^a
2a	H	92.1 (385)	39	0.14
2b	4-OCH ₃	93.3 (390)	15	0.08
2c	3-OCH ₃	93.4 (390)	18	0.07
2d	4-CH ₃	91.9 (384)	40	0.15
2e	3-CH ₃	92.1 (385)	37	0.12
2f	4-F	92.0 (385)	40	0.13
2g	3-F	92.2 (385)	40	0.13
2h	4-CF ₃	92.2 (385)	40	0.14
2i	3-CF ₃	92.2 (385)	39	0.15
2j	4-CN	92.2 (385)	37	0.12
2k	3-CN	92.4 (386)	38	0.14

^a Quantum yields of fluorescence were determined using a value of 0.21 for 1-methylnaphthalene [11].

**Scheme 12: Photolysis of the Substituted 1-Naphthylmethyl Phenylacetates
2a-k in Methanol.**

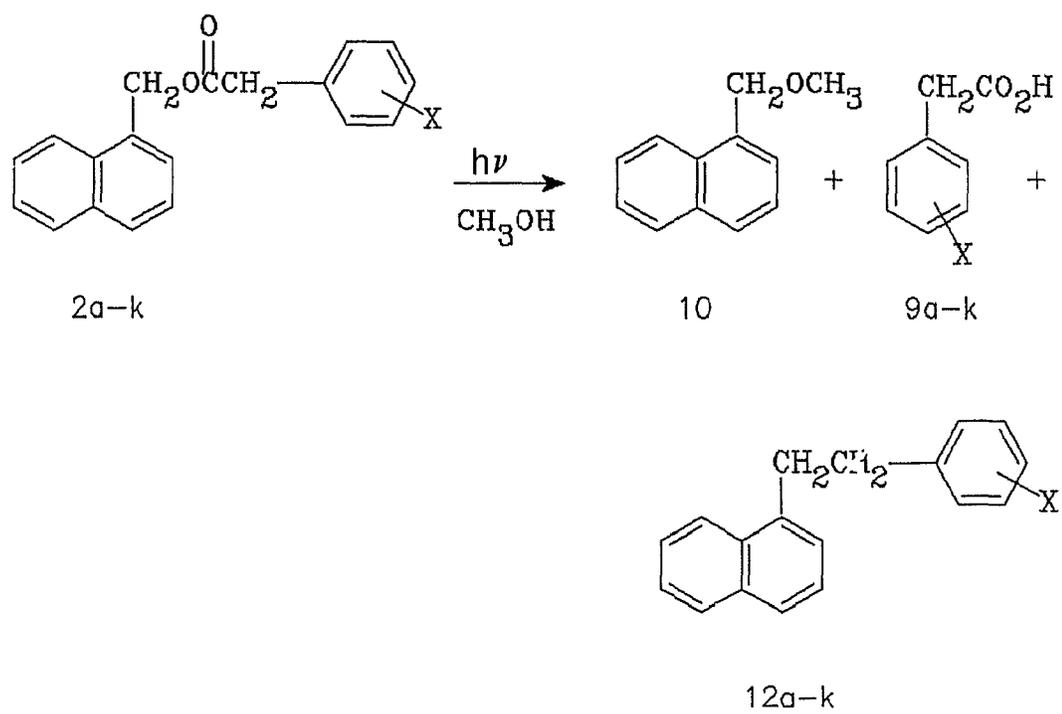


Table 4: Percentage yields of Photoproducts from Irradiation of the Substituted 1-Naphthylmethyl phenylacetate Esters **2a-k** in Methanol.

Ester	X	10^a	12 a-k^a	I/R	$k_{\text{CO}_2}^{\text{b,c}}$ ($\times 10^{-9} \text{ s}^{-1}$)	$\log k_{\text{CO}_2}$
2a	H	84	16 (16)	5.2	5.0 (± 0.8)	9.7 (± 0.1)
2b	4-OCH ₃	25	54 (75)	0.33	77.1 (± 10)	10.9 (± 0.1)
2c	3-OCH ₃	16	71 (84)	0.19	135.0 (± 19)	11.1 (± 0.1)
2d	4-CH ₃	76	23 (24)	3.17	8.1 (± 1.1)	9.9 (± 0.1)
2e	3-CH ₃	71	29 (29)	2.45	10.5 (± 1.5)	10.0 (± 0.1)
2f	4-F	72	25 (28)	2.57	10.0 (± 1.4)	10.0 (± 0.1)
2g	3-F	79	23 (21)	3.76	6.8 (± 0.9)	9.8 (± 0.1)
2h	4-CF ₃	72	24 (26)	2.85	9.0 (± 1.2)	9.9 (± 0.1)
2i	3-CF ₃	65	32 (35)	1.86	13.8 (± 2.0)	10.1 (± 0.1)
2j	4-CN	77	24 (23)	3.35	7.7 (± 1.1)	9.8 (± 0.1)
2k	3-CN	78	26 (12)	3.55	7.2 (± 1.0)	9.9 (± 0.1)

a Estimated error $\pm 2\%$. Yields are corrected for unreacted starting material.

b By calibrated HPLC assuming $k_{\text{ET}}^{\text{H}} = 2.6 \times 10^{10} \text{ s}^{-1}$.

c Errors in brackets are calculated assuming $\pm 2\%$ in determination of products yields and 10% error in the measured rate of decarboxylation of 9-methyl-9-fluorenyl carboxylate radical.

1.3 Discussion

1.3.1 The Discussion of the Photochemistry of 1-Naphthylmethyl Acetate Esters 1a-h in Methanol.

A series of substituted 1-naphthylmethyl esters, **1a-h** and **2a-k**, were synthesized and their behaviour upon photolysis in a nucleophilic solvent, methanol, was investigated. The substituted 1-naphthylmethyl acetate esters, **1a-h**, have similar ultraviolet spectra with wavelength maxima at approximately 265, 275 and 284 nm. Substitution on the carboxylic acid side of the molecule was shown to have little effect on the absorption characteristics and this can be seen in the values of the extinction coefficients of each ester (Section 3.6). They also all have very similar singlet energies, S_1 , singlet lifetimes, τ_s , and quantum yields of fluorescence, ϕ_F (Table 1).

Initial work by Givens *et al.* [5,6] on the photochemistry of the 1- and 2-naphthylmethyl phenylacetate systems was done in the solvent benzene. In benzene, the product mixture indicated the existence of the naphthylmethyl radical and the benzyl radical. The products obtained were either the in-cage or out-of-cage radical coupling products (eq 2). The importance of these experiments lies in the conclusion that the ether carbon-oxygen bond of the ester is homolytically broken upon excitation. The phenylacetyloxy radical produced by this cleavage decarboxylates to give the benzyl radical which then undergoes coupling reactions. For the 1-naphthylmethyl phenylacetate system, the implication of radical intermediates formed by homolytic cleavage from the singlet state is important, since the reaction from the triplet state can be ignored. This work confirms that the singlet state is the reactive state in the photochemistry of the 1- and 2-naphthylmethyl phenylacetates.

Pincock *et al.* [12] have examined 1-naphthylmethyl acetate and found no reaction from the triplet state. They concluded that direct irradiations must reflect singlet reactivity. The singlet energy of the 1-naphthylmethyl acetate residue is known to lie between 91.5 and 92.6 kcal/mol, which is well above the estimated bond energy. The triplet energy of the 1-naphthylmethyl group is known to be approximately 57–62 kcal/mol and does not vary appreciably with alkyl substitution [13]. This result was confirmed by De Costa and Pincock in their study of a variety of substituted 1-naphthylmethyl phenylacetate esters in which they found the triplet energy to lie between 57–60 kcal/mol [14]. The triplet energy is below the carbon-oxygen bond dissociation energy of the 1-naphthylmethyl esters, which is estimated at 65 kcal/mol for the 1-naphthylmethyl acetate ester. This estimated value is based on a value for benzyl acetate of 68 kcal/mol less 3 kcal/mol [15] for the stabilization of the 1-naphthylmethyl radical relative to the benzyl radical [16]. Therefore the singlet state should be the only reactive one since it has enough energy to overcome the bond dissociation energy while the triplet energy lies below the bond dissociation energy.

De Costa and Pincock in a recent study [9] undertook a study of the photochemistry of substituted 1-naphthylmethyl phenylacetates in the solvent methanol. The solvent methanol is significant because it has a high dielectric constant (32.66) and is able to stabilize, by solvation, ionic intermediates if produced. From this work the authors formulated a mechanism for the photolysis of substituted 1-naphthylmethyl phenylacetate esters which involves electron transfer. The proposed mechanism for the photolysis of these esters in methanol is given in Scheme 3. The

authors, in explaining the results from the photolysis, assumed that the rate of homolytic cleavage is much larger than the rate of heterolytic cleavage ($k_R^x \gg k_I^x$) for all substituents. The competition, then, occurs between the rate of electron transfer (k_{ET}^x) and the rate of decarboxylation (k_{CO_2}) of the phenylacetyloxy radical. Only the 1-naphthylmethyl side of the ester is substituted, and homolytic cleavage occurs on the ether carbon-oxygen bond. The decarboxylation of the phenylacetyloxy radical is serving as a "radical clock" for the rate of electron transfer.

Although the rate of decarboxylation of this particular "radical clock" is not known, a good estimate of this rate was obtained using the method described by De Costa and Pincock [9]. This method involves the photochemistry of 1-naphthylmethyl esters of 9-methyl-9-fluorene carboxylate. These esters upon photolysis give the intermediate (9-methyl-9-fluorenyl)carboxy radical which has a known rate of decarboxylation. Using this value of the rate of decarboxylation, they estimated the rate of electron transfer (k_{ET}^x) between a carboxyl radical and the 1-naphthylmethyl radicals in methanol. The product distribution from the photolysis of the substituted 1-naphthylmethyl esters of phenylacetic acid gave a ratio of ionic products (I) to the radical products (R), which is also the ratio of the rate of electron transfer (k_{ET}^x) to the rate of decarboxylation (k_{CO_2}). Since the rate of electron transfer of the 1-naphthylmethyl radical has now been determined, then the rate of decarboxylation for the phenylacetyloxy radical can be determined using the product ratio shown in eq 4. For other substituted 1-naphthylmethyl radicals, the I/R

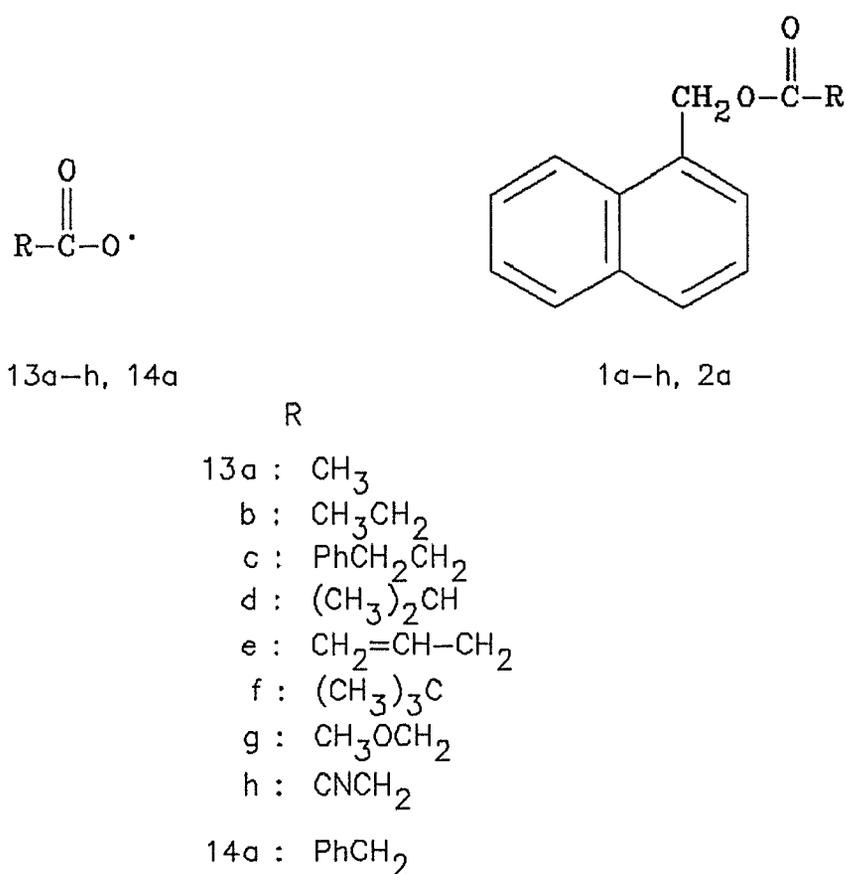
$$I/R = k_{ET}^x/k_{CO_2} \quad (4)$$

values are experimentally determined, and therefore estimates of electron transfer rates (k_{ET}^x) can be made by changing substituents on the naphthalene nucleus. A Marcus curve was obtained, giving a reorganization energy (λ) value of 0.60 eV. This curve clearly showed the Marcus inverted region, where the rate of electron transfer slows down as the reaction becomes progressively exergonic.

In contrast, if the rate of electron transfer is kept constant by keeping the substituents on the naphthalene ring unchanged, the product distribution (I/R) will be controlled by the rate of decarboxylation. From thermochemical estimates of the reduction potential of the acyloxy radical, it was shown that these potentials are very similar if the carboxyl group is not directly conjugated to a group which can provide resonance stabilization [17]. Changing the carboxylic acid side of the ester will therefore produce little change in the rate of electron transfer. The simplest way of dealing with the I/R values derived from the photolysis of the substituted 1-naphthylmethyl acetate esters, **1a-h** and **2a**, is therefore to consider the rate of electron transfer to be a constant and not dependent on the carboxylic acid side. The values for the rates of decarboxylation derived from such a method for alkanoyloxy radicals **13a-h**, **14a** (Figure 2) are summarized in Table 2. The rate constants reported are anchored to a single "radical clock" reaction: the rate of decarboxylation of the 9-methylfluorene-9-carboxylate radical. Any error in this value leads to an

error in all the other values but does not change the relative order of reactivity. The I/R values for the 1-naphthylmethyl alkanooate and phenylacetate esters were also determined experimentally. Again, assuming that the rate of electron transfer is a constant ($k_{ET}^H = 2.6 \times 10^{10} \text{ s}^{-1}$) allows a determination of the rates of decarboxylation by using eq 4. The rates for esters **1a-h** and **2a** are given in Table 2.

Figure 2: The Substituted Alkanoyloxy Radicals **13a-h**, **14a** Generated from the Photocleavage of the 1-Naphthylmethyl Esters **1a-h**, **2a**.



Few estimates of the rates of decarboxylation of acyloxy radicals are available since the process is extremely fast. This is not surprising since carbon dioxide is at the top of an extrusibility scale [18]. The loss of carbon dioxide from the acyloxy

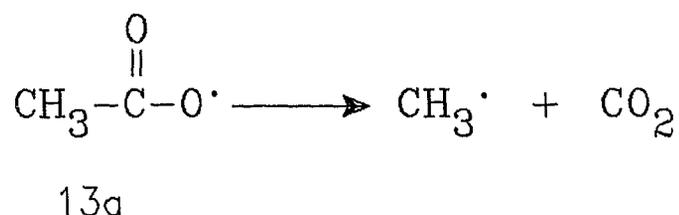
radical was calculated to be exothermic by 39 kcal/mol [19], and an earlier study suggests that the carbon-carbon bond of the C-CO₂ moiety had a negative dissociation energy of 17 kcal/mol [20]. Previous studies of the rate of the decarboxylation of the acyloxy radicals have made these values uncertain because only a lower limit to this rate can be set. Failure to trap the acetyloxy radical in chemical scavenging reactions and CIDNP studies on thermal decomposition of diacetyl peroxide allow an estimate for the rate of decarboxylation of $>10^9$ s⁻¹ [21,22]. Because the rate of decarboxylation of the acyloxy radicals is so fast, measurements have been done only on carboxylate radicals which do not decompose so rapidly. For Ph-CO₂, where the carbon-carbon bond dissociation energy is known to be higher, a value of 2×10^6 s⁻¹ in CCl₄ at 24°C has been obtained by laser flash photolysis [23]. From these early studies with the acyloxy radicals some researchers suggested that the acyloxy radicals upon generation decarboxylate via a concerted mechanism.

It was not until recently that Schuster [24], in a study of the 9-methylfluorene-9-carboxylate radical, obtained a rate of decarboxylation of 1.8×10^{10} s⁻¹. This value is much higher than previous estimations of decarboxylation rates which is undoubtedly due to a weaker carbon-carbon bond of the C-CO₂ moiety. Since there are few carbon-centred radicals that could be more highly stabilized than the 9-methylfluorenyl radical, this study demonstrates that presumably all acyloxy radicals will have a definite, if brief, lifetime. This result also disproves the idea about a concerted loss of carbon dioxide upon generation of the acyloxy radical [25].

The acetyloxy radical has been discussed extensively in the literature from both

an experimental and theoretical viewpoint [21,26a-c]. The rate of decomposition was shown to be first order with a rate constant of $1.6 \times 10^9 \text{ s}^{-1}$ at 60°C and an activation energy of 6.6 kcal/mol, shown in Scheme 13. From Table 2, the rate of decarboxylation of the acetyloxy radical, **13a**, generated by the photolysis of **1a** was determined to be $<1.3 \times 10^9 \text{ s}^{-1}$ assuming that the rate of electron transfer is 2.6×10^{10}

Scheme 13: The Decarboxylation of the Acetyloxy Radical **13a** at 60°C .



s^{-1} . The values obtained are for decarboxylation at 20°C . This value is quite close to the value obtained by Braun *et al.* [21], allowing for any decrease that results from decreasing the temperature. The decomposition of the acetyloxy radical is highly exothermic and authors have suggested that the transition state resembles the acetyloxy radical more than the methyl radical, which results from the decarboxylation of the acetyloxy radical. This result is supported by a study which estimated the α -secondary deuterium kinetic ($k_{\text{H}}/k_{\text{D}}$) isotope effect to be 1.03 [27]. This small value is consistent with the reaction being exothermic. This value is in contrast to the isotope effect observed for β -scission of cumyloxy radicals $k_{\text{H}}/k_{\text{D}} = 1.15$ [20]. Skell [26b] also investigated the acetyloxy radical by high level *ab initio* calculations and concluded that decarboxylation occurs by a pathway involving an early transition state, one in which there is little stretching of the carbon-carbon bond of the $\text{CH}_3\text{-CO}_2$

group. Skell also suggested two different states for the acetyloxy radical in an effort to understand the yields of products obtained by the trapping of $\text{CH}_3\text{CO}_2\cdot$. The two different states are labelled C_{σ_a} and C_{π} [26c]. Similar states were first suggested by Koenig and Wielesek from INDO calculations on the succinimidyl radical [28].

Kochi [29] has predicted that the rate of decarboxylation of the propanoyloxy radical, **13b**, should be greater than the rate obtained for the acetyloxy radical, **13a**. This proposal is consistent with ideas of increasing radical stability resulting from increased substitution on the radical centre. Therefore, the propanoyloxy radical should decarboxylate faster than the acetyloxy radical since the former gives a primary radical while the latter gives the methyl radical. The rate of decarboxylation of the propanoyloxy radical (Table 2) was determined to be $2.0 \times 10^9 \text{ s}^{-1}$. This is greater than the value obtained for the acetyloxy radical and supports radical stability arguments.

The value for the rate of decarboxylation of the β -phenylpropanoyloxy radical, **13c**, has been experimentally determined from this work to be $2.3 \times 10^9 \text{ s}^{-1}$. This value is very similar to that for the propanoyloxy radical which is consistent with the formation of a primary radical. Therefore, increased radical stability of the product alkyl radical seems to increase the rate of decarboxylation of the acyloxy radical. The increase in the rate of decarboxylation of the β -phenylpropanoyloxy radical over the propanoyloxy radical is not outside the limits of experimental error. The result of radical stability increasing the rate of decarboxylation is observed for the 2-methylpropanoyloxy radical, **13d**, as it decarboxylates more quickly than either the propanoyloxy radical or the β -phenylpropanoyloxy radical. The rate of

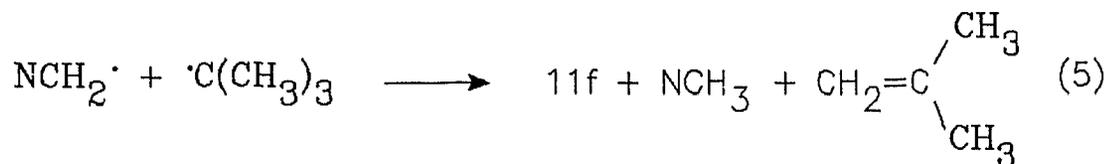
decarboxylation was determined to be $6.5 \times 10^9 \text{ s}^{-1}$. This higher value for the rate can be explained by the fact that upon decarboxylation, a secondary radical is generated by the photolysis of ester **1d**. The secondary radical is known from radical stability arguments to be more stable than the primary radicals produced from decarboxylation, such as propanoyloxy, **13b**, and β -phenylpropanoyloxy, **13c**, radicals.

The most rapid decarboxylation rate among the simple alkyl radicals studied occurred with the 2,2-dimethylpropanoyloxy radical, **13f**, generated from photolysis of ester **1f**. The radical produced upon decarboxylation was tertiary and by radical stability arguments this should be more stable than primary, secondary or methyl radicals. Therefore, this greater decarboxylation rate comes in the correct, predicted order. The value of the decarboxylation rate was experimentally determined to be $11 \times 10^9 \text{ s}^{-1}$. Traylor *et al.* [30] studied the factors which influence the rate of decarboxylation of acyloxy radicals. In this study, they determined that the carbon-carbon bond of the $\text{C}-\text{CO}_2\cdot$ group is very sensitive to hybridization, field and conjugation effects. They observed that, of the substrates studied, the most rapid decarboxylation occurred with the 2,2-dimethylpropanoyloxy radical. The authors concluded that this radical decarboxylated through a concerted carbon-carbon bond-breaking mechanism of the $(\text{CH}_3)_3\text{C}-\text{CO}_2\cdot$ group.

The 2,2-dimethylpropanoyloxy radical, **13f**, is sterically crowded because of the methyl groups. Decarboxylation of this radical produces a molecule of carbon dioxide and a *t*-butyl radical which has an increased C-C-C bond angle. The release of this steric crowding is explained by internal (I_s) strain arguments. Radical centres

adjacent to bulky substituents are susceptible to internal strain. This effect then enhances the reactivity of the 2,2-dimethylpropanoyloxy radical towards the formation of the tertiary radical. Skell and May [31] have concluded by trapping experiments that at low temperatures the 2,2-dimethylpropanoyloxy radical decarboxylates less quickly than even the acetyloxy radical. This observation contradicts those results obtained from radical stability including I_s strain arguments, as well as ones obtained in the present work. No explanation is offered for this discrepancy.

For esters **1d** and **1f**, the determination of the yield of products derived from the decarboxylation pathway (R) is not straightforward. The yield of the radical coupling product (R) is significantly lower for the highly branched aliphatic cases, because highly branched alkyl radicals give increased amounts of disproportionation (D) relative to combination (C), eq 5. For instance, for reaction with alkoxy radicals in decalin at 30°C, the relative values for D/C ratios are 1.0 (CH₃CH₂), 7.7



((CH₃)₂CH), 7.7 ((CH₃)₃C) [32]. As far as can be determined, values of D/C have not been determined for the specific radical pairs involved in this work (yields were not obtained). Disproportionation was not possible in the previous study [9] since the two radicals involved were substituted 1-naphthylmethyl and benzyl radicals.

The phenylacetyloxy radical, **14a**, has a rate of decarboxylation of $5.0 \times 10^9 \text{ s}^{-1}$ which is slower than the rate of decarboxylation for the 2-methylpropanoyloxy radical. This result does not agree with radical stability arguments since the phenylacetyloxy radical gives the benzyl radical while the 2-methylpropanoyloxy radical gives the isopropyl radical, a secondary radical. All estimations of bond dissociation enthalpies [33] and reaction rates predict that this value should be higher than that for **13f** ($\text{R}=(\text{CH}_3)_3\text{CCO}_2\cdot$). This result can, however, be explained by inductive and resonance stability arguments. The secondary radical produced from decarboxylation of the 2-methylpropanoyloxy radical is stabilized by inductive effects. The benzyl radical produced upon decarboxylation of the phenylacetyloxy radical is a primary radical that is stabilized by resonance. An explanation for this observation comes from results for the rates of decarbonylation of $\text{R}-\dot{\text{C}}\text{O}$ radicals. A plot [34] of the logarithm of these rates as a function of R versus calculated bond dissociation enthalpies is linear for alkyl groups except that benzyl derivatives fall significantly below the line. However, the frequency factors for these substrates are also somewhat lower, suggesting that there is an unfavourable entropy effect in the transition state for decarbonylation. This effect is a result of the requirement that the phenyl ring assume a conformation allowing overlap with the breaking σ bond and conjugation with the developing radical centre. For the case of the decarboxylation reactions where the process is more exothermic and the enthalpies of activation are undoubtedly very low, the energy of the transition state may be dominated by this entropic effect. The lowering of the rate now puts **14a** slower than **13d**.

The 3-butenyloxy radical, **13e**, has a rate of decarboxylation of $7.7 \times 10^9 \text{ s}^{-1}$. The decarboxylation rate of this 3-butenyloxy radical, generated by the photolysis of ester **1e**, should be fast because the allyl radical, stabilized by resonance, is produced. The 3-butenyloxy radical decarboxylates more rapidly than the secondary radical, but more slowly than the tertiary radical. The reason again for this apparent reversal of radical stability argument lies in the fact that the allyl radical, once formed by decarboxylation, must align itself with the π cloud, giving resonance stabilization.

The methoxyacetyloxy radical, **13g**, has a rate of decarboxylation of $3.2 \times 10^9 \text{ s}^{-1}$. This value indicates that the decarboxylation rate is much faster than what would be expected for a primary centred radical. The methoxymethyl radical produced upon decarboxylation of ester **1g** has special stabilization associated with it due to the oxygen adjacent to the radical centre. The stabilizing ability of a methoxy group α to a radical centre is well known and many methods for determining the magnitude of this effect have been reported [33]. The methoxy group by each of these methods has been shown to stabilize a radical relative to hydrogen. The radical is stabilized by the oxygen atom and the usual two atom–three electron resonance hybrid is given in Figure 3. This effect allows the methoxyacetyloxy radical to decarboxylate much

Figure 3: The Contributing Forms for the Stabilization of the Methoxymethyl Radical.



faster than the acetyloxy radical, **13a**. From the values obtained, the methoxyacetyloxy radical decarboxylates faster than the β -phenylpropanoyloxy radical (**13c**) which shows the effect of having a heteroatom next to a radical centre.

The rate of decarboxylation of the cyanoacetyloxy radical, **13h**, was determined to be $3.5 \times 10^9 \text{ s}^{-1}$. This value indicates a large increase in the rate of decarboxylation over the other primary centred radicals. The stabilizing effect of having a cyano group adjacent to the radical centre has also been determined and these values suggest that it has even a larger stabilizing effect than the α methoxy group [33]. These results suggest that the cyano group should stabilize the incipient radical even more than in the methoxy case. The cyanomethyl radical produced upon decarboxylation of ester **1h** also has special stabilization associated with it, as illustrated in Figure 4. The

Figure 4: The Contributing Forms for the Stabilization of the Cyanomethyl Radical.



possible resonance structure with the odd electron on the nitrogen atom is available to the cyanomethyl radical, increasing the rate of decarboxylation of the cyanoacetyloxy radical. From the values obtained, the cyanoacetyloxy radical decarboxylates more quickly than the β -phenylpropanoyloxy radical, **13c**, demonstrating again the large contribution this resonance structure has in stabilizing the radical centre. The fact that the methoxy substituent, **13g**, gives a slightly slower rate than the cyano substituent, **13h**, is in agreement with most scales of radical stabilizing effects. This may indicate

a slight amount of polar character in the transition state for decarboxylation with the carbonyl oxygen positive and the methylene carbon negative.

In conclusion, keeping in mind that these reactions are fast, and that any rate/substituent correlation will be small, the overall order for the rates of decarboxylation seems reasonable based on both radical stability and bond strength arguments.

1.3.2 The Discussion of the Photochemistry of 1-Naphthylmethyl Phenylacetate Esters 2a-k in Methanol.

The rate of decarboxylation of substituted 1-naphthylmethyl phenylacetates has been studied [9]. De Costa and Pincock investigated the role that substituents on the naphthalene ring have on the rate of electron transfer between the substituted 1-naphthylmethyl radical and the phenylacetyloxy radical. In this work, substitution of various functional groups on the phenyl ring, while keeping the naphthalene ring unchanged, was investigated. In order to understand the influence substituents have on the rate of decarboxylation of the various substituted arylacetyloxy radicals.

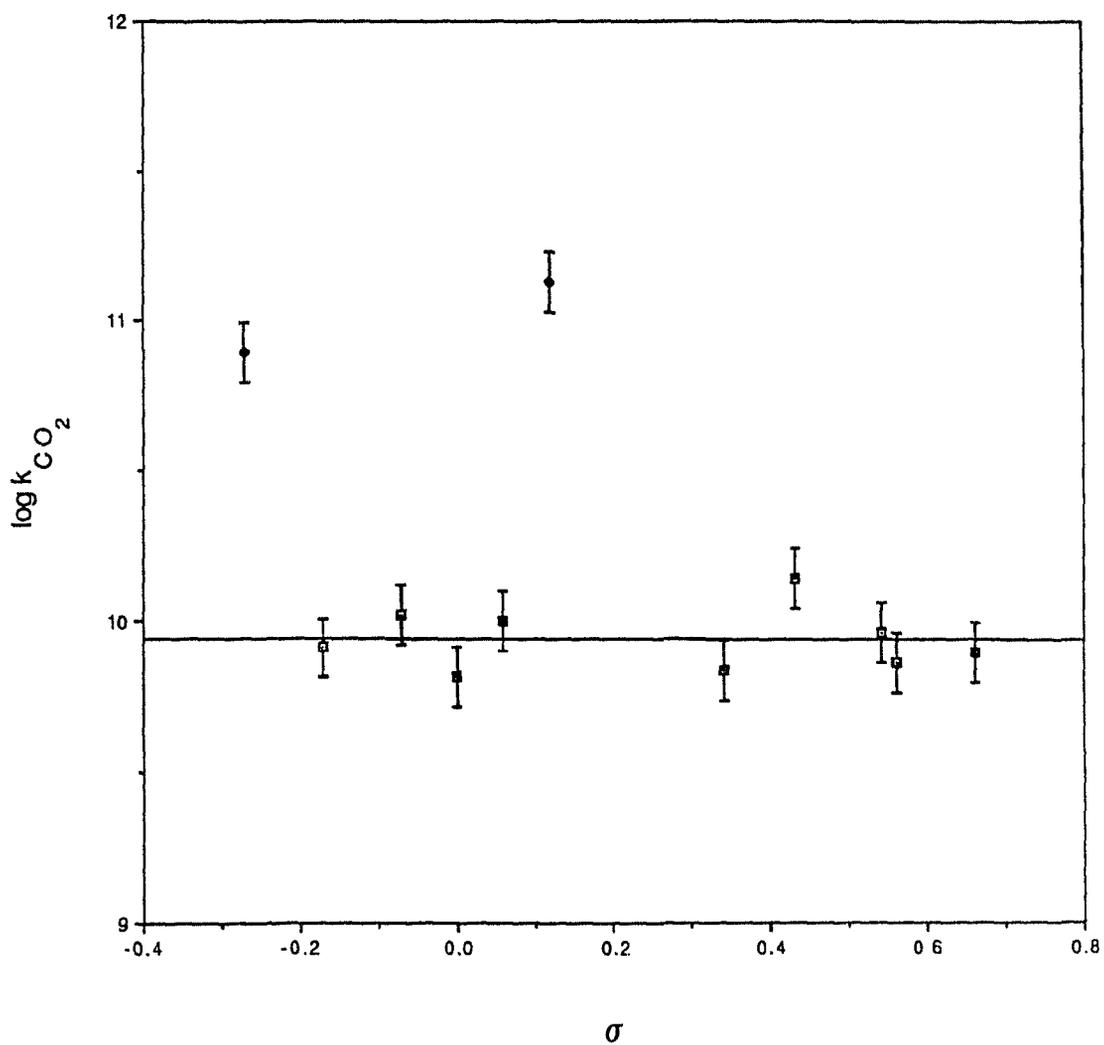
From earlier work, the rate of electron transfer between the 1-naphthylmethyl radical and the phenylacetyloxy radical is known: $2.6 \times 10^{10} \text{ s}^{-1}$. As mentioned earlier, the rate of electron transfer is dependent on the oxidation and reduction potentials of the donor and acceptor, respectively. Although, for the 1-naphthylmethyl phenylacetate esters (2a-k) the oxidation potential of the 1-naphthylmethyl radical is known the reduction potentials of the substituted arylacetyloxy radicals are not known.

The results for this series of substituted phenyl acetate esters were analyzed, as

The esters for this study, **2a–k**, were synthesized by the method given in Scheme 5 and their physical constants and spectral properties are given in the Experimental section. The singlet energy, lifetimes and quantum yields of fluorescence are recorded for these esters in Table 3. For esters **2a**, **2d–k** the values for each quantity are, within experimental error, identical and little difference in their photophysical nature is predicted. However, esters **2b** and **2c** have different lifetimes and quantum yields of fluorescence. The values of the extinction coefficients of the ultraviolet spectra for **2b** and **2c** are greater than those for **2a** and **2d–k**. These differences will be discussed in more detail later.

The substituted esters (**2a–k**) were irradiated in methanol and the product yields of ether **10** (I) and the coupling product **12a–k** (R) were monitored using HPLC (Scheme 12). The ratios of ionic products to radical products (I/R) were determined and are reported in Table 4. This value is also the ratio of the rate of electron transfer divided by the rate of decarboxylation. Using the rate of electron transfer of $2.6 \times 10^{10} \text{ s}^{-1}$ for each ester **2a–k** and determining the I/R ratio allows an evaluation of the rate of decarboxylation of each of the substituted arylacetyloxy radicals. These values are given in Table 4. A plot of $\log k_{\text{CO}_2}$ versus the σ constant for each of the substituents of the esters is shown in Figure 6, $\rho=0$ ($r=0.06$). The plot illustrates that there is essentially no change in the rate of decarboxylation, as a function of the substituents, if the rates of decarboxylation of esters **2b** and **2c** are disregarded. The average rate of decarboxylation of the substituted phenylacetyloxy radicals is $9.9 \times 10^9 \text{ s}^{-1}$. This observation may be explained by the fact that the benzyl radical produced is not

Figure 6: A Plot of $\log k_{\text{CO}_2}$ vs. Hammett σ Constant for Decarboxylation of Substituted 1-Naphthylmethyl Phenylacetates **2a-k**



stabilized by the benzene ring. This effect has been rationalized previously by Fischer [34] who suggested that the benzene ring must rotate in order to assume a conformation allowing overlap with the breaking σ bond and conjugation with the developing radical centre. Benzyl derivatives have been shown to fall below the line in a plot of the logarithm of rates of decarbonylation of R-CO as a function of R. The frequency factors for these substrates are lower than expected, suggesting that there is an unfavourable entropy effect in the transition state for decarbonylation. Therefore the rate of decarboxylation of the arylacetyloxy radicals is dominated by this entropic term (ΔS^\ddagger) which is substituent independent.

Esters **2b** and **2c** exhibit unusual photophysical and photochemical characteristics. They show lower values for both the quantum yield of fluorescence and singlet lifetime (Table 3), compared to esters **2a**, **2d-k**. Upon photolysis, these esters show a higher yield of radical derived products suggesting an enhanced rate of decarboxylation, in contrast to the results for all of the other esters (**2a**, **2d-k**). Both esters differ from esters **2a**, **2d-k** because they have methoxy groups attached to the phenyl ring. These methoxy groups allow the phenyl ring to have a marked bathochromic shift in the ultraviolet spectrum so that it now overlaps with the naphthalene chromophore. This effect also increases the extinction coefficients (ϵ) from 7400 at 275 nm for the unsubstituted compound to 8500 for the 4-CH₃O compound.

Many reports in the literature [35,36] have attempted to understand unusual effects occurring in the excited state, such as a decrease in quantum yield of fluorescence and singlet lifetimes. This decrease in quantum yield of fluorescence and

singlet lifetime has been associated with excited-state complex formation and electron transfer [37]. An abundance of experimental evidence shows that excited state processes can occur through the intervention of encounter complexes with charge or electron transfer characteristics [38]. For instance, the concentration dependence of pyrene fluorescence was interpreted in terms of complex formation between the singlet excited and ground state molecules [39]. This complex formation has been supported by other researchers [40–42] who referred to these excited homodimers as excimers. Excimers are characterized by monomer fluorescence self-quenching and a red-shifted dimer emission. These excimers are different from the excited states of ground state dimers since they are unassociated in the ground state, but form strongly associated complexes in the excited state.

Excited state complexation may also occur between two different species resulting in the formation of excited heterodimers, called exciplexes. Initial investigations [43,44] into the emitting exciplexes suggested that they are stabilized by charge transfer between excited donors and ground state acceptors or vice versa. This work has shown that usually it is the singlet state that is responsible for the quenching and emission characteristics attributed to exciplex formation and decay. The authors postulated that exciplex formation results from either partial or complete electron transfer, and this is substantiated by observations that show that the wavelength maxima for exciplex emission is dependent upon both the ionization potentials of the donors and electron affinities of acceptors in the pair, and the polarity of the medium.

One important aspect of exciplex chemistry as it pertains to chemical reactivity concerns the nature of the decay pathways available to the excited state complexes. The explanation above suggests that complex formation involves either partial or complete electron transfer from donors to acceptors and deactivation of the excited state occurs through emission and radiationless decay, which includes intersystem crossing. Thus exciplexes can serve as a source of radical ions. Accordingly, exciplex emission intensities are known to decrease in proceeding from solvents of low to high polarity, where the ions generated are stabilized. This decrease in exciplex lifetime is associated with complete electron transfer resulting in the production of radical ions. Importantly, the charged radical species formed in this way are capable of participating in a number of different chemical processes due to their high energy content.

If the reason for the decrease in the quantum yield of fluorescence and singlet lifetime for esters **2b** and **2c** is due to exciplex formation, then two mechanisms are possible. On the one hand, the intermolecular case may occur, in which the naphthalene ring of one molecule is quenched by the methoxyphenyl ring of another molecule. On the other hand, the interaction could be intramolecular, where the naphthalene ring is affected by the methoxyphenyl group on the same molecule. The intermolecular case was investigated initially. Solutions of 1-methylnaphthalene and methyl 4-methoxyphenylacetate were prepared with increasing concentrations of ester. From this experiment, no reduction in quantum yield of fluorescence of 1-methylnaphthalene was observed. Reduction in the intensity of fluorescence was

observed at high concentration of the ester (donor), due to competitive absorption at the excitation wavelength. This experiment would have shown much larger reduction of the quantum yield of fluorescence and singlet lifetime if intermolecular exciplex formation was occurring. In a study of the formation of intramolecular exciplexes, esters **2b** and **2c** did not show a long wavelength emission band, a characteristic of some exciplexes. The lack of a long wavelength emission band from the possible exciplex was possibly due to the solvent used for these studies, methanol. As mentioned previously in this section, polar solvents such as methanol are known to decrease the exciplex formation emission intensities. Therefore, solutions of esters **2b** and **2c** in cyclohexane were examined to determine if emission was evident in this nonpolar solvent. From this experiment, no emission was observed, suggesting that complete electron transfer was not occurring in the excited state of these esters or that the exciplex was very short-lived. If the exciplex is very weakly associated in the excited state then the complex may dissociate without emission but via some other mode of deactivation, such as intersystem crossing. Exciplex emission is known to give broad structureless bands, implying that these exciplexes have many rotational and vibrational levels associated with them and the number of levels may be so large as to allow another pathway for the exciplex to dissociate without emission. Therefore the exciplex formed in esters **2b** and **2c** must be loosely associated in the excited state and deactivate by vibrational and rotational modes. The energy of the vibrational modes may be large enough to allow for the deactivation of the exciplex by undergoing chemical reactions. This mode has been observed to occur for esters **2b**

and **2c**, since the photolysis times for these esters are approximately three hours while the other esters (**2a**, **2d-k**) usually require 20 hours. These lower photolysis times must be due to the formation of the charge transfer complex followed by cleavage of the bond by vibrational modes. This method of chemical reaction is not observed in Scheme 3 for the photolysis of 1-naphthylmethyl phenylacetates. The existence of the exciplex allows for another pathway for the generation of products. These intramolecular exciplexes are reactive and give products resulting from the equivalent of homolytic carbon-oxygen bond cleavage for the ester. Any product formed by this pathway would clearly decrease the yield of ether and lead to values for I/R that are not directly related to k_{ET}/k_{CO} , as in eq 4.

Frontier molecular orbital (FMO) theory was used to understand the changes substituents on the phenyl ring have on the photochemistry of these esters by determining if bichromophoric interactions are likely between the 1-methylnaphthalene orbitals and the substituted toluene orbitals. 1-Methylnaphthalene and substituted toluenes are used as a model in this work for the substituted 1-naphthylmethyl phenylacetates. Toluene and two substituted derivatives, 4-tolunitrile and 4-methylanisole, were chosen for this investigation.

1-Methylnaphthalene is known to absorb a photon ($S_0 \rightarrow S^*$) at 314 nm ($\epsilon = 338$, $E = 3.95$ eV) promoting an electron from the highest occupied molecular orbital (HOMO) to the lowest occupied molecular orbital (LUMO). With the 1-naphthylmethyl group in the excited state, the naphthalene chromophore can interact with the substituted toluene molecules intramolecularly. There exist two energetically

favourable types of frontier orbital interactions. The first involves the interaction between the singly occupied π^* orbital of the excited 1-methylnaphthalene molecule and the LUMO of the substituted toluene molecule in its ground state. The second involves the interaction between the singly occupied π orbital of the excited 1-methylnaphthalene molecule and the HOMO of the donor molecule which is in its ground state. For discussion in this thesis the interactions of the latter will be used.

The energy levels of the orbitals for 1-methylnaphthalene and the substituted toluene derivatives are available from their photoelectron spectra (PES) [45,46]. Therefore, a comparison can be made in order to determine if these interactions can occur in the excited state. Interactions are usually strong if the interacting orbitals are close in energy (ie. a small energy difference). Figures 7, 8 and 9 show the molecular orbitals of 1-methylnaphthalene with toluene, 4-tolunitrile and 4-methylanisole, respectively, with a comparison of the energy separation between the pairs in the ground state HOMO.

The energy separation between the pair of ground state HOMO's for the 1-methylnaphthalene and toluene pair (Figure 7) has been determined to be approximately 23.0 kcal/mol. No bichromophoric interactions can be expected for this couple, and thus for 1-naphthylmethyl phenylacetate (**2a**), these interactions are not possible. In fact, Givens *et al.* [5] have shown that no bichromophoric interactions occurred for ester **2a**. They showed that the energy difference is too large between the two rings and thus no interaction can occur.

Figure 7: Frontier Molecular Orbitals for Excited State
1-Methylnaphthalene and Toluene

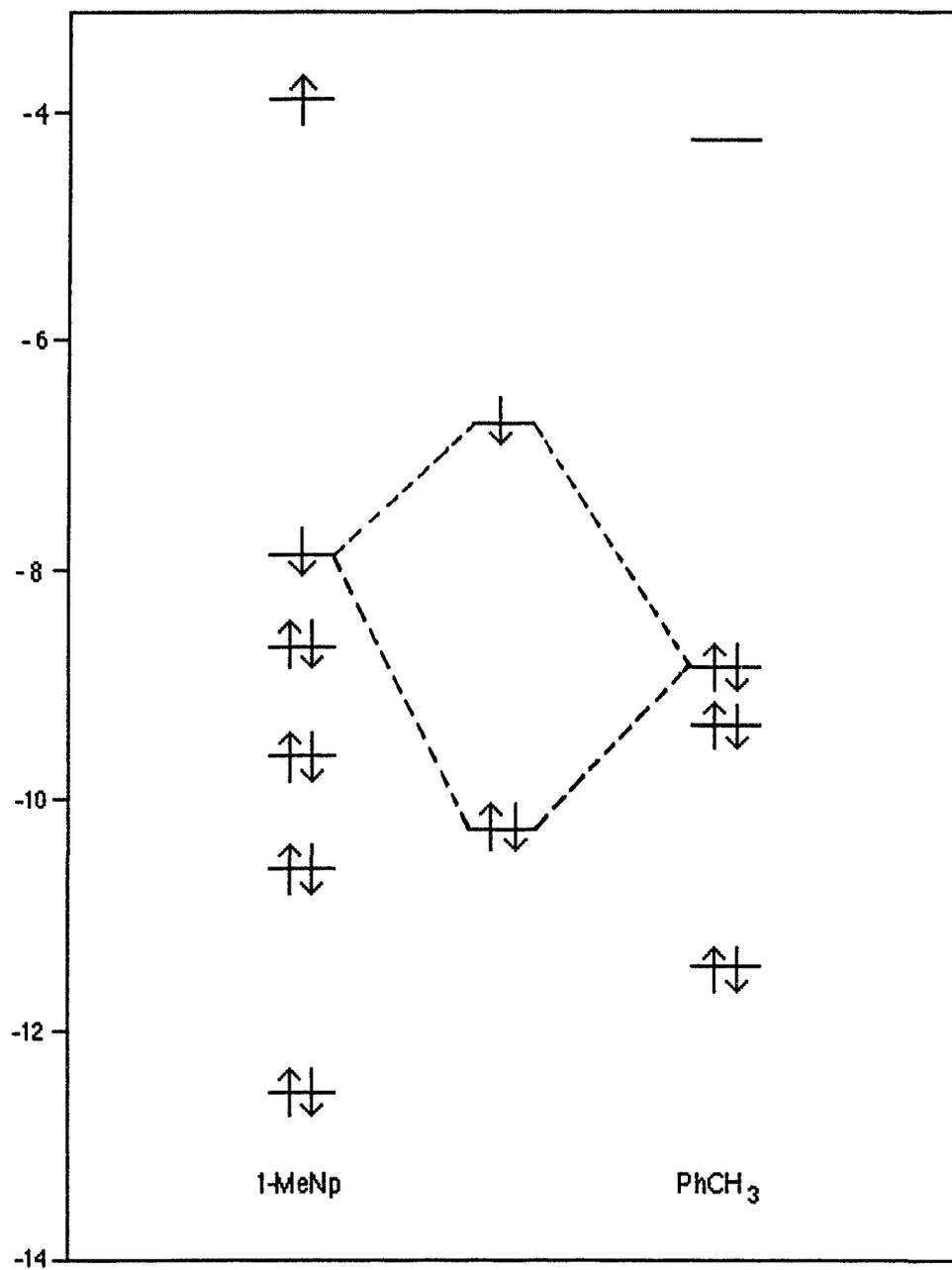


Figure 8: Frontier Molecular Orbitals for Excited State
1-Methylnaphthalene and p-Tolunitrile

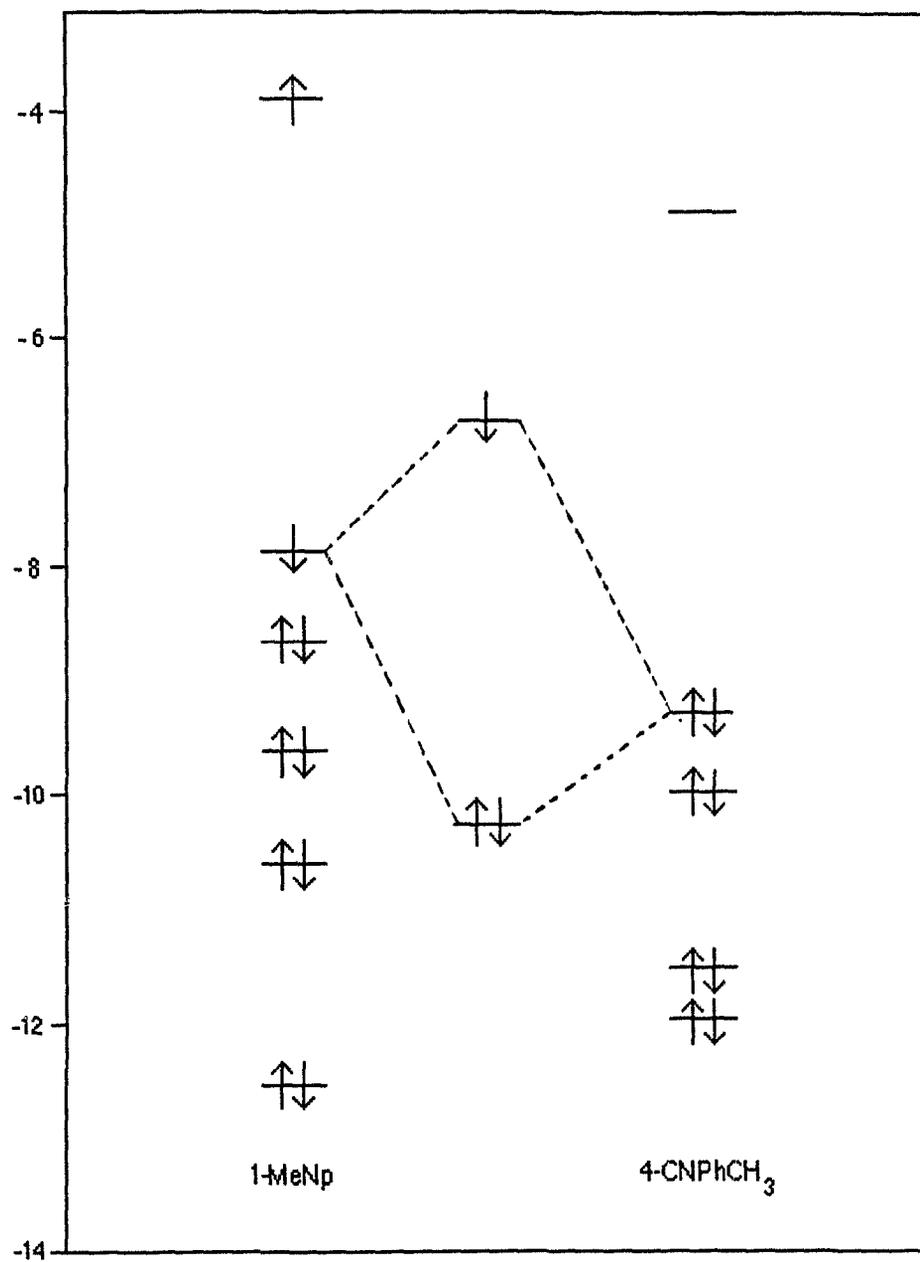
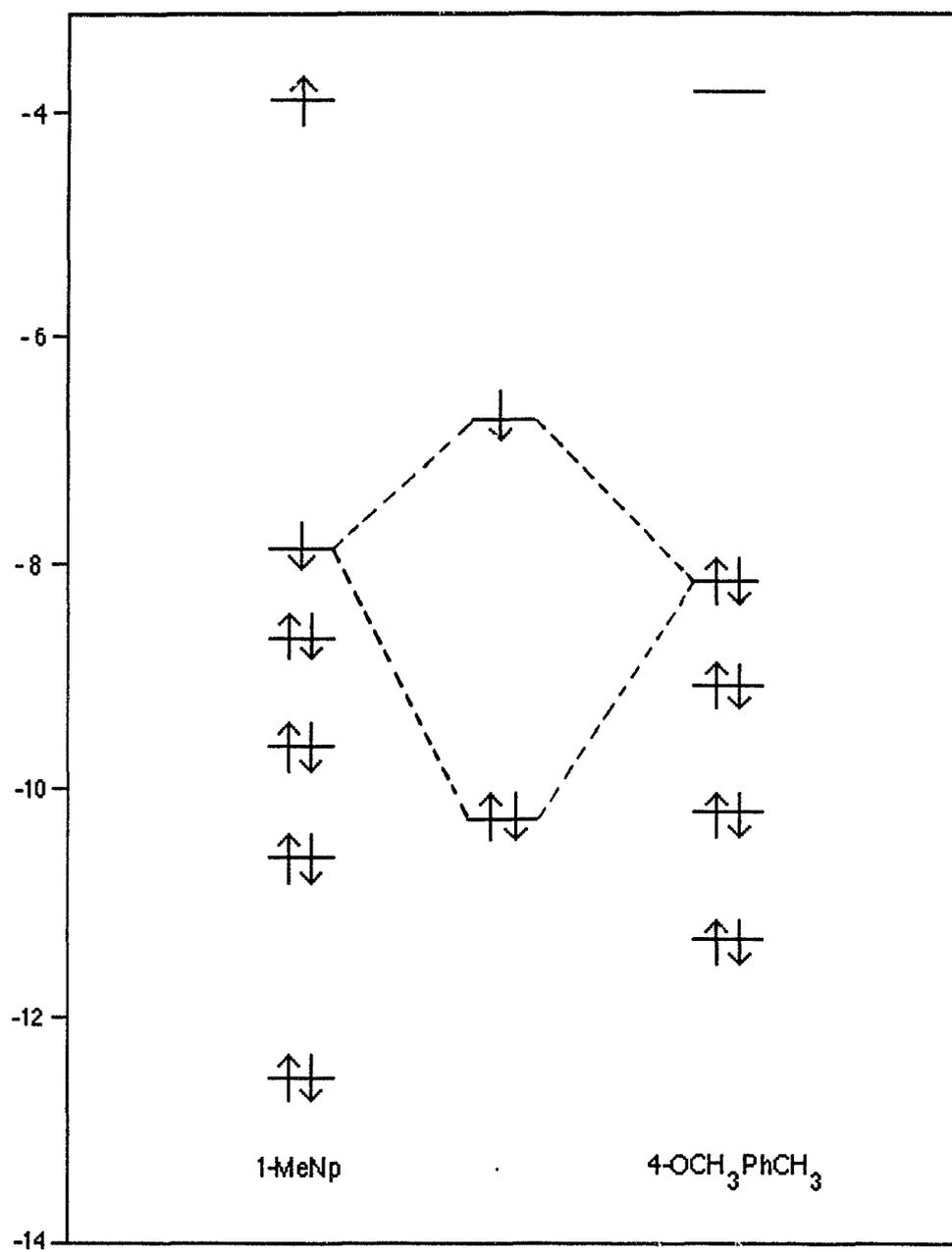


Figure 9: Frontier Molecular Orbitals for Excited State
1-Methylnaphthalene and p-Methylanisole



The energy separation for the 1-methylnaphthalene and p-tolunitrile pair (Figure 8) was determined to be 34.1 kcal/mol. This value is greater than the value for the 1-methylnaphthalene and toluene pair and thus no bichromophoric interactions are expected for the 1-naphthylmethyl 4-cyanophenyl acetate (**2k**) molecule. Since no unusual behaviour in the photochemistry of the molecule was observed, bichromophoric interactions are non-existent for this pair. No reduction in quantum yield of fluorescence and singlet lifetime was observed for this ester.

The energy separation for the 1-methylnaphthalene and 4-methylanisole pair (Figure 9) was determined to be 7.6 kcal/mol. This value is the smallest obtained for the three pairs studied. If a bichromophoric reaction were to occur, then it may occur for this pair. This is confirmed by the lower values for the quantum yield of fluorescence and the singlet lifetime for the 1-naphthylmethyl 4-methoxyphenyl acetate, **2b**, shown in Table 3. These bichromophoric interactions can create a situation in which the total energy is lower than when the two chromophores are considered separately, thus stabilizing the exciplex. This small difference allows the possibility of electron transfer occurring from the 4-methylanisole ring to the naphthalene ring as predicted by the Rehm-Weller relationship. The free energy change (ΔG_{ET}) of electron transfer for this system can be estimated by employing the oxidation and reduction potentials of 4-methylanisole and 1-methylnaphthalene, respectively. The oxidation potential of 4-methylanisole has not been measured. However, this value may be estimated by employing the value of anisole, which is +1.76 V versus SCE in CH₃CN [47]. The actual value for 4-methylanisole should be

smaller than the value for anisole since the radical cation will be more stable with the attached methyl group. The reduction potential for 1-methylnaphthalene has been measured at -2.46 V vs SCE in dioxane [47]. For this calculation, a distance of 7 \AA is assumed and the $E_{0,0}$ band for 1-methylnaphthalene is known to be 91.0 kcal/mol. A free energy change for this electron transfer is calculated to be 6 kcal/mol.

From this value for ΔG_{ET} , electron transfer is predicted to occur, even though the value is endothermic. Reports in the literature [48] have described small positive free energy changes resulting in electron transfer, although a rate constant of approximately 10^7 s^{-1} can be estimated. The use of the actual oxidation potential for p-methylanisole would predict a faster rate of electron transfer since the free energy change would be less than 6 kcal/mol. The reported results can therefore be explained by the electron transfer mechanism.

Efficient quenching of the quantum yield of fluorescence and the decrease in the singlet state lifetime by intramolecular exciplex formation for esters **2b** and **2c** imply one of three things. Firstly, a mechanism could be considered in which the esters **2b**, **2c** in the ground state are in the *s-cis* form. Although this is not the stable conformation of esters [49], the availability of exciplex formation allows for small interactions to occur in the ground state which may lower the overall energy of the molecule thereby favouring the *s-cis* form. Also the two aromatic rings in this molecule may have hydrophobic interactions in the polar solvent, methanol, which force the rings together. Therefore the *s-cis* form of the molecule may be favoured in polar solvents such as methanol. If this mechanism is occurring then electron transfer

may occur very quickly over the very short distance between the two rings.

Secondly, the reduction in singlet lifetime and quantum yield of fluorescence may, for the photolysis of esters **2b** and **2c**, be explained by assuming that the esters are in the *s*-*trans* form prior to excitation. Upon excitation, the methoxyphenyl group quickly rotates overtop of the charge transfer complex thereby quenching the singlet excited state. Although the rate of bond rotation for this particular system is not known, it would seem reasonable since the rate of rotation of the carbon-carbon bond in ethyl nitrate is approximately 10^{12} s^{-1} [50]. These very fast rotations would allow the methoxyphenyl group to position itself over the excited naphthalene ring during the lifetime of the excited state, $40 \times 10^{-9} \text{ s}$.

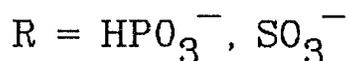
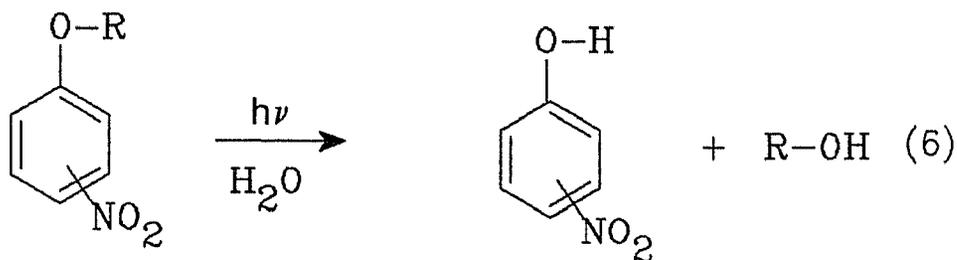
Finally, the last option is that the esters are in the more stable *s*-*trans* form and that the electron transfer occurs over the approximate 10 \AA from one ring to the other. Electron transfer over long distances has been shown to be quite rapid. In a recent study [51], the authors found that as the number of bonds separating the electron donor from the electron acceptor increased from four to twelve bonds the electron transfer rate constant decreased by a factor of a thousand. The separation by twelve bonds gave the slowest electron transfer rate constant on the order of 10^8 s^{-1} . This twelve bond value still is above the estimated value of 10^7 s^{-1} for the rate of fluorescence quenching. Therefore this mechanism of electron transfer through bonds is a possible way by which this charge transfer complex can form. Each of the above mechanisms are probable and more work must be done in order to determine which of the mechanisms is most likely.

CHAPTER 2

The Photochemistry of the Substituted Benzylic Esters 3a-e and 4a-e

2.1 Introduction

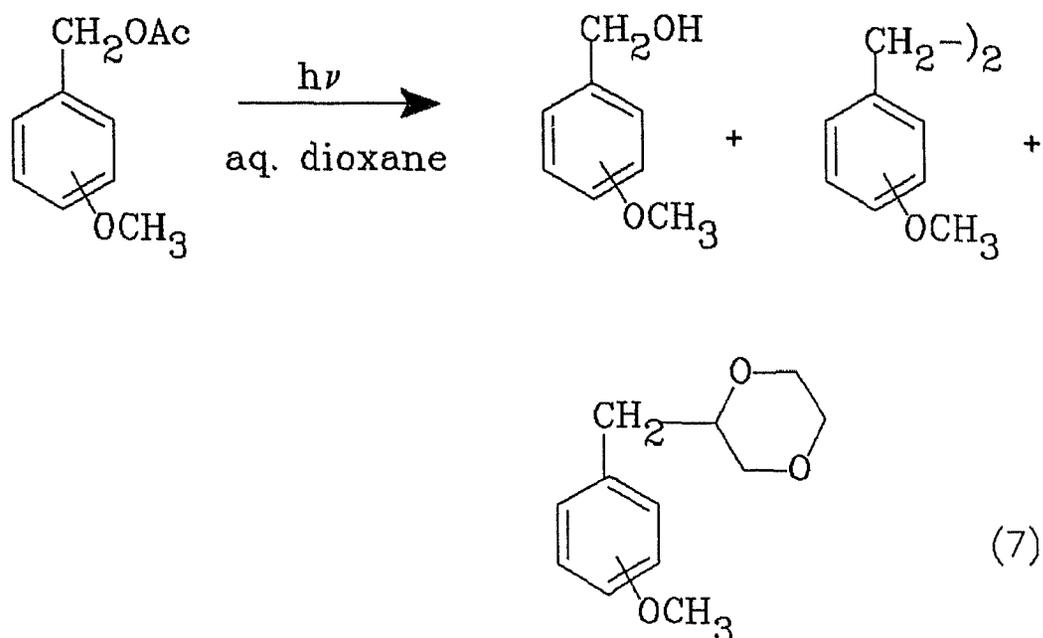
Initial results on aromatic substituent effects in photochemical cleavage reactions were reported by Havinga, DeJongh and Dorst [52], who investigated the photohydrolysis of isomeric nitrophenyl phosphate and sulfate esters (eq 6). They



found that the *meta*-substituted nitrophenol esters underwent the most efficient reaction. This result is contrary to what would be expected by ground state arguments, where the *para* substituent would have the greatest effect, while the *meta* substituent would have a relatively small effect on the reactivity.

In 1963, Zimmerman *et al.* [4] published a landmark paper pertaining to the photosolvolysis of benzylic compounds. The paper described the photolysis of *meta* and *para* methoxy substituted benzyl acetates which gave products that resulted from

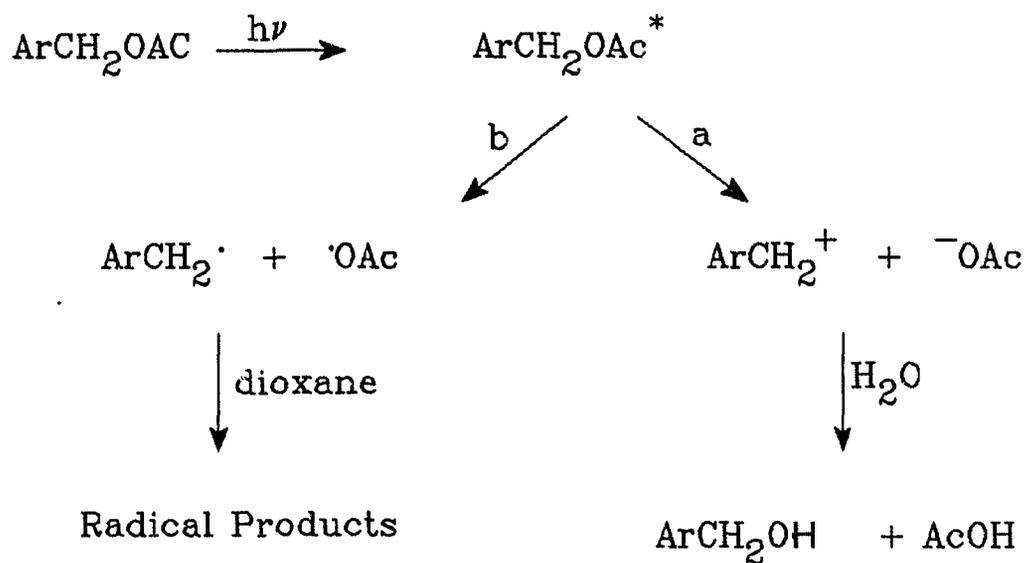
either ionic intermediates (alcohols) or radical intermediates (benzyl dimers and benzyl dioxane coupling products), as shown by eq 7. Zimmerman *et al.* found that the



observed photochemical reactivity was reversed from that of the ground state. The methoxy group in the *meta* position was shown to have a stronger activating effect than when it was in the *para* position. For instance, the *meta* methoxy isomer gave exclusively the alcohol (the product derived from the ionic intermediate) with a relatively high quantum yield of 0.13, while the *para* isomer gave products derived from the radical intermediate with a low quantum yield of 0.016. Zimmerman concluded that the 3-methoxy isomer underwent heterolytic cleavage of the σ bond to give the carbocation (pathway (a) of Scheme 14) which was then trapped by the

solvent, whereas the 4-methoxy isomer followed a homolytic pathway (pathway (b) of Scheme 14) giving increased yields of radical products. The proposed mechanism of these two processes is shown below in Scheme 14, where $\text{ArCH}_2\text{OAc}^*$ is an excited state.

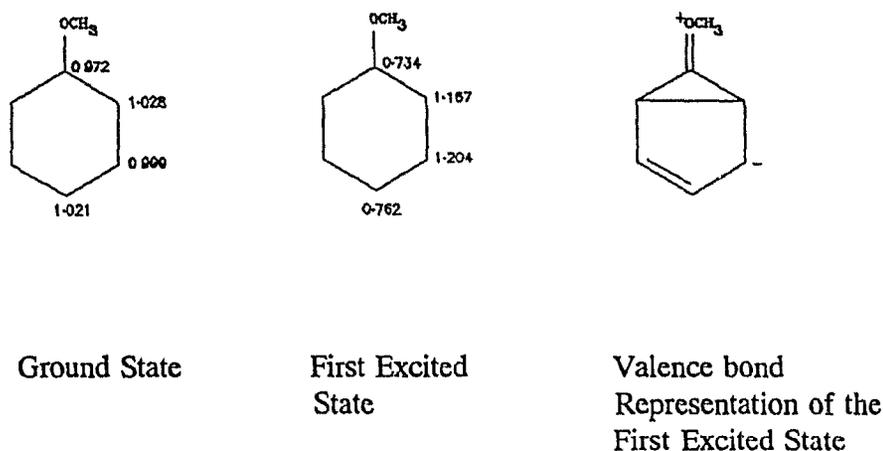
Scheme 14: The Proposed Mechanism for the Photolysis of 3- and 4-Methoxybenzyl Acetates.



Zimmerman *et al.* accounted for these altered excited state reactivities by calculating the π electron densities of the aryl ring carbons of anisole using Hückel molecular orbital (HMO) theory. The values of the π electron densities for the various states are given in Figure 10. These calculations show that, for the ground state, the *ortho* and *para* positions have the greatest electron density, as expected. In contrast, the calculated first excited-state electron density is concentrated in the *ortho* and *meta* positions, indicating higher reactivity with *meta* methoxy substituents, and therefore a

more efficient heterolytic cleavage (alcohols). This enhanced photosolvolysis of *meta* substituted benzyl acetates, which was named *meta* electron transmission by the

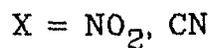
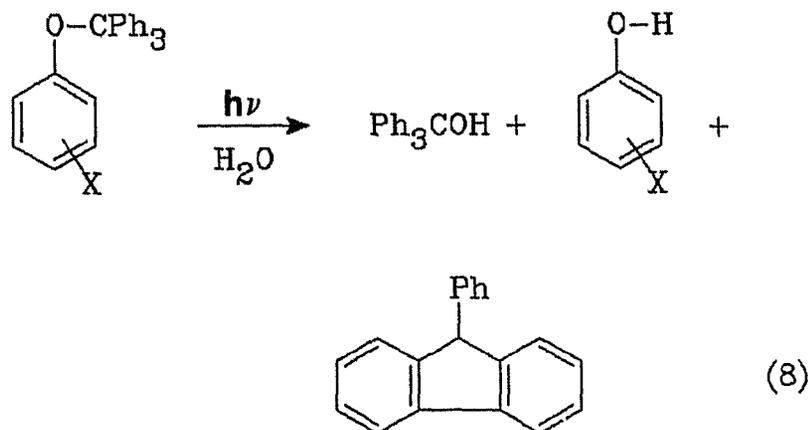
Figure 10: Ground and Excited State π Electron Density of Anisole.



authors, is now known commonly as the "*meta* effect".

In a subsequent paper, Zimmerman *et al.* [53] studied the effect of electron-withdrawing groups on photosolvolysis reactions, in which a negative charge develops during the reaction, by studying the substituted phenyl trityl ethers (eq 8). Again they observed an increase in reactivity and quantum yield for the electron-withdrawing groups which were in the *meta* position.

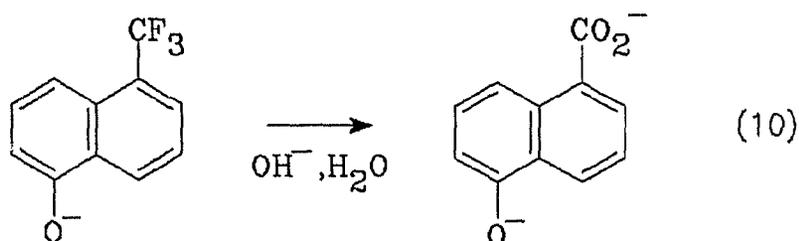
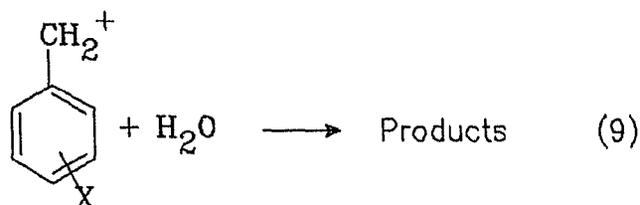
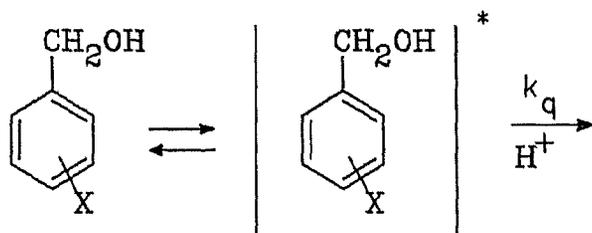
Other researchers have reported supporting evidence for the "*meta* effect". Kochi and Ratcliff [54] photolyzed a number of benzyltrimethylammonium salts and observed a large reduction in the photosolvolysis quantum yield for electron-withdrawing groups (i.e. cyano) in the *meta* position. Also, Barltrop and Schofield [55] irradiated several substituted benzyloxycarbonyl glycines and found a maximum



quantum yield for the *meta* methoxy substituent ($\phi = 0.28$).

Another important study which supports the "*meta* effect" argument was by Wan and Turro [56,57] who investigated the fluorescence quenching and photosolvolysis of various substituted benzyl alcohols. They observed that a decrease in the pH of the reaction solution led to a decrease in fluorescence and an increase in product formation, as outlined in eq 9. In acidic solution the fluorescence is quenched by protons more efficiently for *meta* substituents such as methoxy, methyl and fluorine. Unfortunately, a complete study of substituted examples was not possible due to the low reactivity of the *para* and unsubstituted compounds.

Probably the most definitive study of substituent effects of this type comes from the work of Seiler and Wirz [58,59] which provides very useful quantitative data. In their study, eight trifluoromethyl substituted naphthols were photohydrolyzed in alkaline media, as shown in eq 10. It was assumed that the reaction proceeds by an



initial rate determining ionic C-F bond cleavage from the first excited singlet state. The logarithm of the reaction rate for each of the compounds was plotted against the calculated charge density in the first excited state of the carbon α to the trifluoromethyl group. The result was a linear relationship.

In contrast to these observations supporting the "meta effect", a few opposing papers have appeared. Givens *et al.* [6] have shown that photolysis efficiencies of benzyl phosphates follow the normal ground state order. Also, McKenna and coworkers [60] report decreased yields of ionic cleavage for the photolysis of 3,5-dimethoxybenzylammonium salts in solvent.

Since these papers have been published, a great deal of photochemistry has

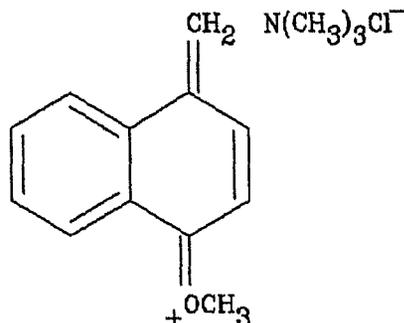
focused on the naphthalene compounds for the reasons explained by Givens *et al.* [6].

In a detailed study by Pincock *et al.* [10] of (1-naphthylmethyl) trimethylammonium chloride salts, the authors observed greater rates of reaction and higher yields of the cationic intermediates for the 4-methoxy isomer than predicted on the basis of the "meta effect". The authors, however, argued that this change in photocleavage results was related to a direct interaction in the ground state between the 4-methoxy group and the positively charged leaving group (Figure 11). Therefore, intramolecular charge transfer of this type may modify the nature of the electron density of the naphthalene nucleus upon excitation, which then favours heterolytic cleavage. This example suggests that the type of cleavage which occurs depends on the nature of both the substrate and the leaving group. The ester functional group was considered by Pincock *et al.* in an effort to determine a leaving group which would be more suitable than the trimethylammonium group. The ester group has the advantage of being a neutral leaving group and internal charge transfer of the kind seen in the trimethyl ammonium salts should no longer interfere.

The photochemistry of esters is a field of research going back approximately thirty years [3]. The majority of the cleavage reactions of esters involve the homolytic cleavage of the $O=C-O-C$ bond provided that the resulting carbon radical is stabilized, usually by conjugation.

Early work was done on the photochemistry of the benzyl acetate system [61] by Ivanov *et al.* The results suggested that solvolysis is the main photochemical reaction for these esters in polar hydroxylic solvents. In this work, the authors

Figure 11: Internal Charge Complex for (4-Methoxy-1-naphthylmethyl) Trimethylammonium Chloride.



measured the product yields derived from either direct irradiation (both singlet and triplet reactions) or sensitized reactions (triplet reactions only). Ivanov *et al.* concluded that in the photocleavage of substituted benzyl acetates, the solvolysis reaction proceeds for the unsubstituted case via the first excited singlet state and for electron donating groups from the triplet state. For the unsubstituted case the excited singlet state was thought to dissociate into ions (heterolytic cleavage) directly. However, the concept of homolytic cleavage to a radical pair followed by electron transfer to form the ion pair was not suggested. For the electron-donating substituents, the authors proposed that the photochemical solvolysis proceeded from the triplet state which then gave the ions. This mechanism seems unlikely since a triplet radical pair can only form the ion pair which is a singlet state by a process involving spin inversion.

The mechanism of a substituted benzyl acetate photosolvolysis was also investigated by Jaeger [8] by irradiation of optically active (-) 3,5-dimethoxybenzyl-1-d-acetate. The ester isolated after partial photolysis was found to be largely

racemized. This study also investigated oxygen-18 labelled benzyl acetate, which showed partial oxygen scrambling upon irradiation. The author, from this study, proposed a mechanism for the solvolysis of the benzyl acetate system in which the ionic and radical intermediates formed from the singlet state and sometimes recombined to give racemization and oxygen scrambling of the starting material. The author dismissed the mechanism of a concerted [1,3] suprafacial shift which would also account for the oxygen scrambling in the irradiations. McKenna *et al.* [60,62] have also investigated the photochemistry of benzyl acetate in methanol. Their results accounted for less than 50% of the material consumed. No authors have investigated the possible importance of electron transfer interconverting radical pair and ion pair.

Pincock *et al.* [10], in their investigation of the photochemistry of the (1-naphthylmethyl)trimethylammonium chloride salts, have raised the possible importance of electron transfer in the initially formed contact pair. It was later proposed [9] that esters first cleave homolytically, followed by electron transfer to give ionic intermediates. Thus, the final composition of the product mixture is not a direct measure of the initial excited-state bond cleavage process since electron transfer may allow interconversion between radical and ion pairs. The real rate constant for heterolytic cleavage is then not easily determined since the yield of products derived from ionic intermediates will be significantly affected by this alternative process, so much so that in any photocleavage the important process may be the electron transfer step.

Electron transfer theory has been a very important area of research in recent

years, and many reviews [17,63] are available on this subject. In 1964, Marcus derived a mathematical expression [64] for the free energy of activation (ΔG^\ddagger) for electron-transfer reactions. The expression is a quadratic (parabolic) equation and is given below in eq 11.

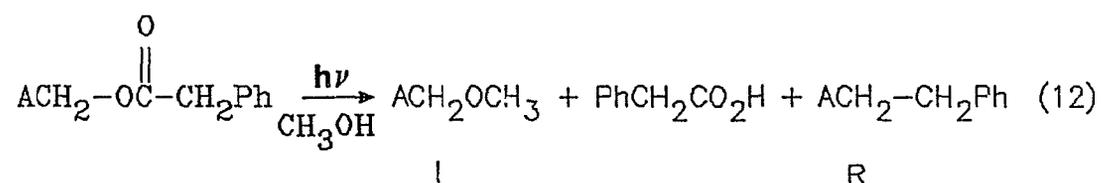
$$\Delta G^\ddagger = \frac{Z_1 Z_2 e^2 F}{D r_{12}} + \frac{\lambda}{4} \left(1 + \frac{\Delta G^{\circ i}}{\lambda} \right)^2 \quad (11)$$

The first term of this expression describes the loss or gain in electrostatic free energy as the precursor complex is formed. The $Z_1 Z_2$ values are the charges associated with the two precursors, r_{12} is the distance from infinity to collisional distance of the two precursors, e is the electronic charge, F is the factor defining the ionic strength, D is the dielectric constant for the pure solvent. If either of the species has zero charge, this first term will be zero. This is true for all the systems discussed in this thesis where the pair is a neutral caged pair. The second term is the parabolic one with λ being the reorganization energy and $\Delta G^{\circ i}$ being the corrected standard free energy change of the electron transfer step. The reorganization energy incorporates the energy changes necessary for the reaction to reach the transition state. These energy changes involve either bond lengthening or compression and/or torsional and bond angle changes, as well as the energy needed for the reorganization of the solvent molecules.

The development of Marcus theory allows an understanding of the factors which affect the rate of electron transfer between a donor molecule and an acceptor

molecule. The Marcus expression has been used extensively because of its simplicity and ability to produce qualitatively valid results. It also has the advantage of being easily handled mathematically, even though it leads to a quadratic free energy relationship. Indeed, a large body of evidence has accumulated, suggesting that a vast number of excited-state processes occur via the intervention of encounter complexes with charge or electron transfer characteristics.

In the study by De Costa and Pincock [9] the photochemistry of various substituted 1-naphthylmethyl phenylacetates had shown large variation in the product composition as a function of substituents (eq 12). In each case, the photolysis gave



varying amounts of the substituted methyl ether (I) and coupling product (R). The methyl ether was obtained by trapping of the substituted 1-naphthylmethyl cation by methanol and the coupling product was obtained by coupling of the benzyl radical with the substituted 1-naphthylmethyl radical. The benzyl radical was obtained by decarboxylation of the phenylacetyloxy radical generated by homolytic cleavage of the alcohol oxygen-carbon bond of the ester functional group.

De Costa and Pincock [9] did not see any unusual effects with the introduction of the *meta* methoxy substituent on the naphthalene ring. Because of this observation,

the authors proposed an alternate mechanism which accounted for the product yields of ionic and radical products by assuming that $k_R^x \gg k_I^x$. The mechanism which is given in Scheme 3 involves the excitation of the substituted 1-naphthylmethyl chromophore to the singlet state. From the singlet, the carbon-oxygen bond cleaves homolytically to give the substituted 1-naphthylmethyl radical and the phenylacetyloxy radical. Two competitive processes may occur from this radical pair. The phenylacetyloxy radical can decarboxylate to give the benzyl radical and coupling product (R). Electron transfer between the substituted 1-naphthylmethyl and the phenylacetyloxy radicals may also occur, giving the substituted 1-naphthylmethyl cation and phenylacetyloxy anion which are trapped as the methyl ether (I) and phenylacetic acid, respectively. The percentage of ionic product divided by radical product is equal to the rate of electron transfer divided by the rate of decarboxylation of the phenylacetyloxy radical. The variation in the product yields I and R is therefore dependent on the changes in the rate of electron transfer since in each case the rate of decarboxylation of the phenylacetyloxy radical is constant. A method for determining the rate of electron transfer was used which incorporates the known rate of decarboxylation of 9-methyl-9-fluorenyl carboxylate radical.

Marcus theory was applied to these electron transfer rates. Substituting eq 11 into eq 13 relates the rates of electron transfer to the free energy change at

$$k = A \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (13)$$

the transition state (ΔG^\ddagger) going from the radical pair to the ion pair. This free energy change can be related to the overall free energy change for the electron transfer (ΔG_{ET}°) which can be determined experimentally. ΔG_{ET}° is related to the oxidation and reduction potentials of the substituted 1-naphthylmethyl radicals and the phenylacetyloxy radical, respectively. Since in each case the reduction potential is that of the phenylacetyloxy radical and this value is constant, the rate of electron transfer is dependent only on the oxidation potential of the 1-naphthylmethyl radical. Recent advances in organic electrochemistry allow for the measurement of these oxidation potentials. ΔG_{ET}° may be incorporated into eq 13 to give eq 14. The pre-exponential A factor value has been set at $6 \times 10^{10} \text{ s}^{-1}$ [9] for electron transfer in the radical pair in

$$k_{ET} = 6 \times 10^{10} \exp - \left[\frac{\lambda}{4} \left(1 + \frac{\Delta G_{ET}^\circ}{\lambda} \right)^2 / RT \right] \quad (14)$$

ester photochemistry. The rate of electron transfer may be plotted against the oxidation potential of the substituted 1-naphthylmethyl radical giving a parabolic curve. This curve can be fitted by evaluation of the reorganization energy (λ). For this case a value of 0.60 eV was determined. This reorganization energy gives a good fit to the determined rates of electron transfer including the "inverted Marcus region".

Many experimental attempts have been made to find the "inverted region". In 1969, Rehm and Weller [48] measured the fluorescence quenching rate constants k_q and the free energy change ΔG_{ET}° for photoinduced electron transfer for some typical

electron-acceptors in acetonitrile. The correlation was in good agreement with the prediction of the Marcus treatment in the normal region (endergonic and slightly exergonic electron-transfer reaction) but there was no inverted region as predicted by Marcus theory in the highly exergonic region. Instead a diffusion-controlled rate was found. The prediction that k_{ET} should decrease with increasing negative ΔG_{ET}° is refuted for this case. Recently there have been several examples where the "inverted region" has been observed experimentally [65,66].

De Costa and Pincock [9] showed the importance of the process of electron transfer in the photochemistry of substituted 1-naphthylmethyl phenylacetate esters in methanol. In this thesis, electron transfer reactions in benzylic photocleavage of substituted benzyl acetate and benzyl 2,2-dimethylpropanoate esters will be studied. In these substrates, excitation of the benzene chromophore may also involve homolytic cleavage of the carbon-oxygen ether bond to give the substituted benzyl radical and the acetyloxy or the 2,2-dimethylpropanoyloxy radical. Electron transfer in the radical pair to give the ion pair or decarboxylation of the alkanoyloxy radical may occur to give radical derived products analogous to the mechanism derived for the 1-naphthylmethyl ester case. If this is true, then a systematic study of substrates that have varying oxidation potentials of the benzylic radical will assist in determining the mechanism for this photocleavage. This is most easily done by varying the substituents on the aromatic ring.

In Chapter 2, substituted benzyl acetates and substituted benzyl 2,2-dimethylpropanoates will be irradiated directly and with quencher in an attempt to

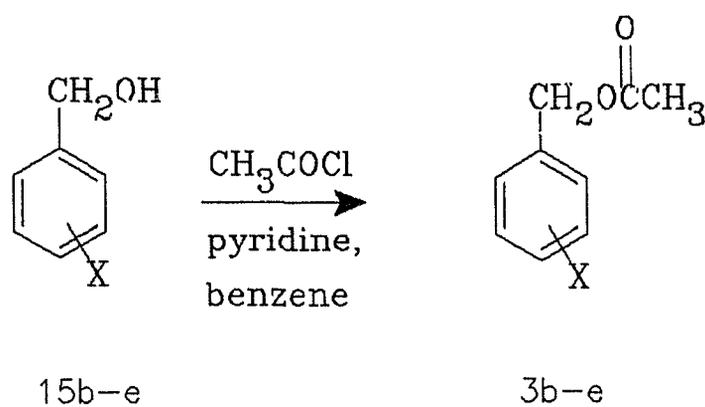
understand the reactive states involved. The product distribution, ionic versus radical, will be monitored and, by changing substituents, the electron transfer mechanism will be investigated. If the substituents change the rate of electron transfer, then the rates may be correlated with Marcus' theory of electron transfer and the reorganization energy determined for this system. The "*meta* effect" will also be investigated by changing the substituents on the aromatic ring. The results of this study should allow a greater understanding of the "*meta* effect" and the processes which govern benzylic ester photochemistry.

2.2 Results

2.2.1 General Synthesis of Esters 3a-e and 4a-e

The synthesis of the benzylic esters was accomplished by a common method as outlined in Schemes 15 and 16. All esters were purified by column chromatography

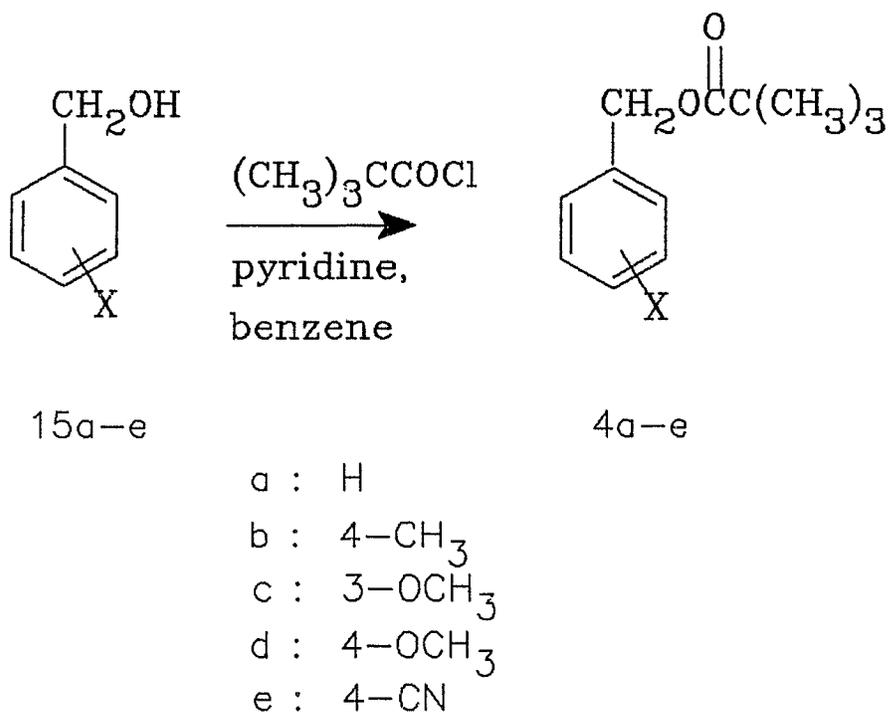
Scheme 15: Synthesis of the Substituted Benzyl Acetates 3b-e.



- b : 4-CH₃
- c : 3-OCH₃
- d : 4-OCH₃
- e : 4-CN

and further purified either by distillation or recrystallization from hexane. Spectral and elemental analyses are included in Section 3.6. The emission properties of these esters are summarized in Table 5.

Scheme 16: Synthesis of the Substituted Benzyl 2,2-dimethyl Propanoates 4a-e.



2.2.2 Preparation of Benzyl Alcohols 15b and 15e

4-methylbenzyl alcohol (15b) was synthesized by the reduction of 4-methylbenzoic acid using lithium aluminum hydride in diethyl ether shown in Scheme 17.

4-cyanobenzyl alcohol (15e) was synthesized by the reduction of 4-cyanobenzaldehyde with sodium borohydride in ethanol shown in Scheme 17.

2.2.3 Preparation of the Photoproducts

The preparation of photoproducts **16a-e** is shown in Scheme 18.

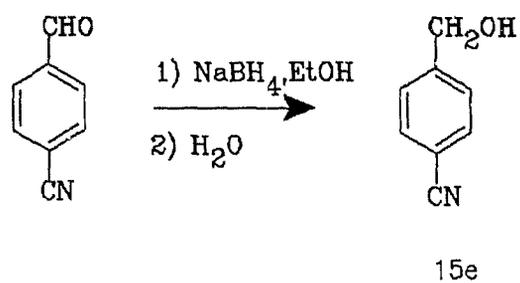
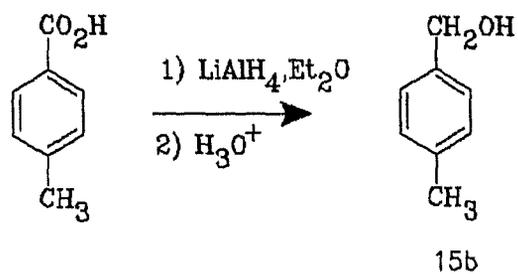
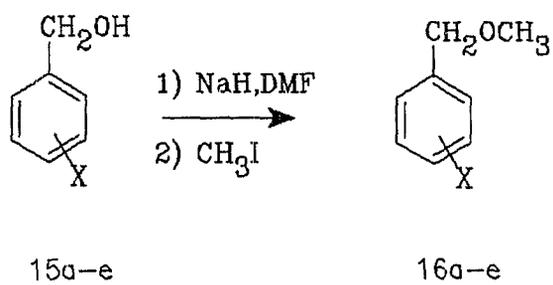
Scheme 17: The Synthesis of 4-methyl (15b) and 4-cyano (15e) Benzyl Alcohol.**Scheme 18:** Preparation of the Substituted Benzyl Methyl Ethers 16a-e.

Table 5: Emission Properties of the Substituted Benzyl Alcohols **15a–e** and Esters **3a–e** and **4a–e** in Methanol.

Alcohol or Ester	X	S_1^a kcal/mol (kJ/mol)	τ_s ns	ϕ_F^b
15a	H	105.8 (443)	21	0.07
3a		105.6 (442)	14	0.05
4a		105.5 (442)	12	0.03
15b	4-CH ₃	103.6 (434)	25	0.15
3b		103.9 (435)	25	0.12
4b		103.9 (435)	22	0.11
15c	3-OCH ₃	100.1 (419)	7	0.16
3c		100.1 (419)	–	0.01
4c		99.9 (418)	–	0.01
15d	4-OCH ₃	99.8 (418)	7	0.17
3d		100.9 (422)	6	0.17
4d		99.9 (418)	6	0.16
15e	4-CN	101.3 (424)	11	0.10
3e		101.0 (423)	11	0.10
4e		101.0 (423)	10	0.10

a From the 0,0 band determined by overlap of the emission and excitation spectra.

b Quantum yields of fluorescence were determined using a value of 0.13 for toluene in methanol [67].

2.2.4 Analytical Photolyses of Esters

2.2.4.1 Direct Irradiations of Esters 3a-e and 4a-e in Methanol.

The irradiation of the benzylic esters gave a mixture of six major products as shown in Scheme 19. The percentage yields of each product from the photolysis are given in Table 6.

Scheme 19: Direct Photolysis of the Benzylic Esters 3a-e and 4a-e in Methanol.

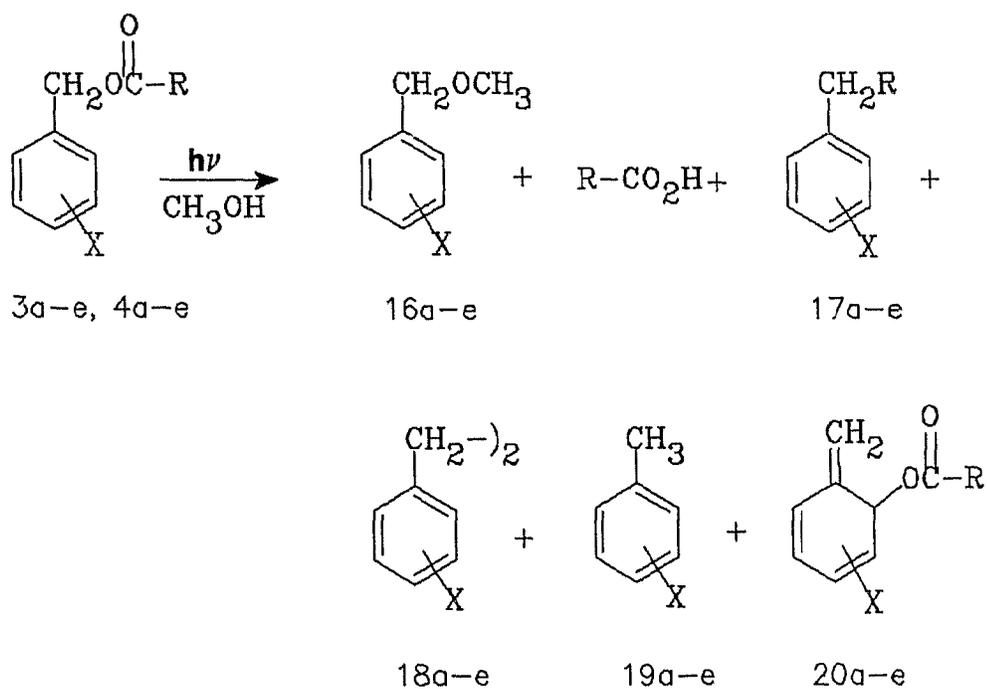


Table 6: Percentage Yields of Photoproducts from Irradiation of the Substituted Benzylic Esters **3a-e** and **4a-e** in Methanol.

Ester	X	Ether ^a Product 16a-e	Coupling ^a 17a-e	Dimer ^a 18a-e	Toluene ^a 19a-e	Photo- Fries ^a 20a-e
R=CH₃						
3a	H	19	18	21 [*]	2	15
3b	4-CH ₃	3	14	52 [*]	2	21
3c	3-OCH ₃	33	18	38 [†]	2	-
3d	4-OCH ₃	2	13	62 [†]	-	5
3e	4-CN	2	16	67 [†]	5	-
R=C(CH₃)₃						
4a	H	-	45	18 [*]	14	-
4b	4-CH ₃	-	53	31 [*]	14	-
4c	3-OCH ₃	7	58	13 [†]	17	-
4d	4-OCH ₃	-	41	36 [†]	10	2
4e	4-CN	-	43	32 [†]	16	-

a Estimated error $\pm 2\%$. Yields are corrected for unreacted starting material.

* by calibrated GLC

† by calibrated HPLC

- not present

2.2.4.2 Irradiation of Esters 3a-e and 4a-e in the Presence of the Quencher (2,3-Dimethyl-1,3-butadiene) in Methanol.

Solutions of the esters 3b-e (1×10^{-2} mol/L) in 100 mL of methanol were irradiated in the presence of 2,3-dimethyl-1,3-butadiene ($1.2-40.4 \times 10^{-3}$ mol/L). The conditions were identical to those used in the absence of quencher. The irradiations took place in a 100 mL quartz tube and were continually stirred. Prior to irradiation the solutions were degassed under a stream of nitrogen. The irradiation of the benzylic esters in the presence of the quencher gave a mixture of six major products as shown in Scheme 19. The percentage yields of each product from the photolysis are given in Table 7.

The concentration of the 2,3-dimethyl-1,3-butadiene to be used in each photolysis of esters 4b-e was determined from Stern-Volmer plots (Figure 12). Concentrations of the quencher that were used were those in which approximately 10% of the singlet had been quenched. The fluorescence intensity values used for the Stern-Volmer plots are given in Table 8.

Table 7: Percentage Yields of Photoproducts from Irradiation of the Substituted Benzylic Esters **3b-e** in the Presence of Quencher (2,3-Dimethyl-1,3-butadiene) in Methanol.

Ester	X	[Q] x10 ⁻³ M	%S	Ether ^a 16a-e	Coupling Product [†] 17a-e	Dimer ^a 18a-e	Toluene ^a 19a-e	Photo- ^a Fries [*] 20a-e
R=CH₃								
3b	4-CH ₃	2.01	8	7	11	64 ^a	2	14
3c	3-OCH ₃	40.2	12	48	27	- [†]	-	15
3d	4-OCH ₃	6.65	9	-	-	70 [†]	-	28
3e	4-CN	1.17	10	5	19	49 [†]	5	7

a Estimated error $\pm 2\%$. Yields are corrected for unreacted starting material.

* by calibrated GLC

† by calibrated HPLC

- not present

Figure 12: Stern-Volmer Quenching Plots by 2,3-Dimethyl-1,3-Butadiene of Esters **4b-e** in Methanol

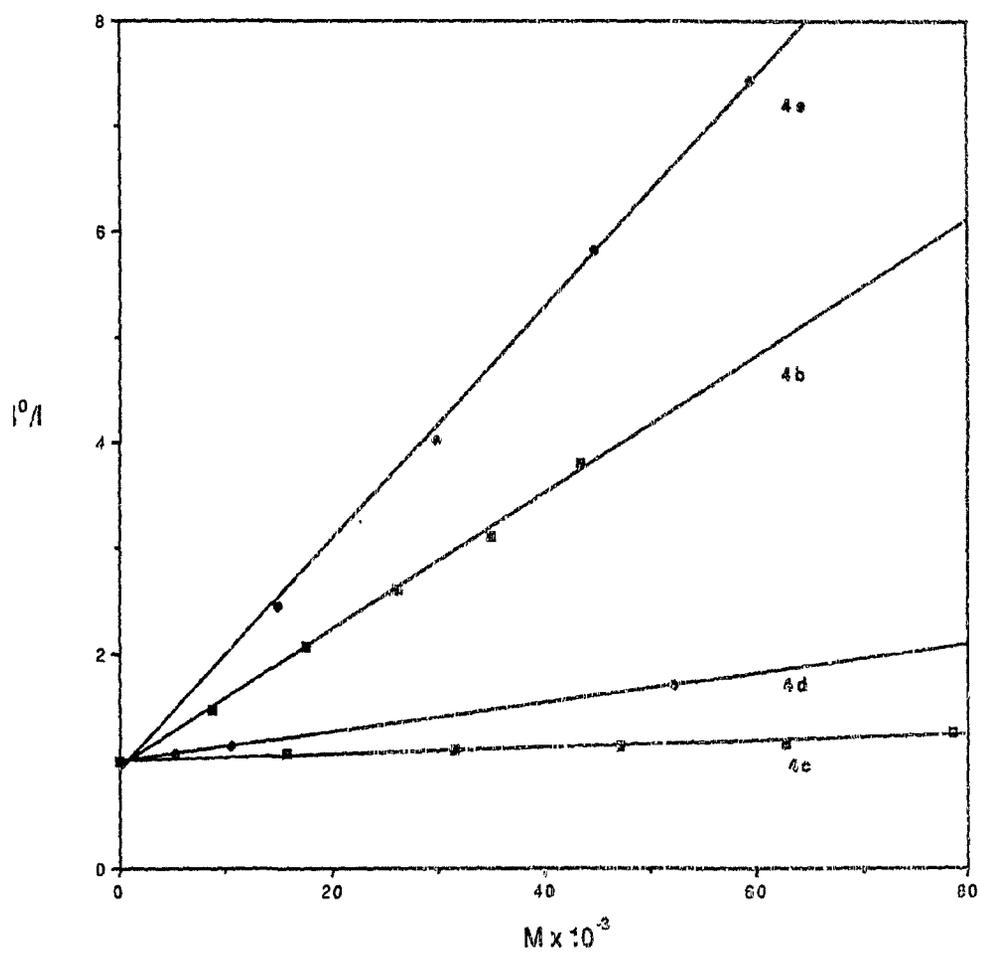


Table 8: Stern–Volmer Fluorescence Quenching of Esters **4b–e** with 2,3–Dimethyl–1,3–butadiene in Methanol.

Ester	[Q] x10 ⁻³ M	k _q τ _s M ⁻¹ s	I ⁰ /I	k _q x10 ⁻⁹ M ⁻¹ s ⁻¹
4b	0	0.064	1.00	2.9
	8.7	(r=1.00)	1.48	
	17.4		2.07	
	26.1		2.61	
	34.8		3.11	
	43.8		3.82	
4c	0	0.003	1.00	7.6
	15.7	(r=0.96)	1.07	
	31.4		1.10	
	47.1		1.14	
	62.8		1.17	
	78.5		1.27	
4d	0	0.014	1.00	2.3
	5.2	(r=1.00)	1.07	
	10.4		1.14	
	52.0		1.72	
4e	0	0.109	1.00	11.0
	14.8	(r=1.00)	2.45	
	29.7		4.03	
	44.6		5.82	
	59.4		7.42	
	74.2		11.10	

2.3 Discussion

2.3.1 General Discussion

In an effort to understand the photochemistry of benzylic substrates, esters **3a-e** and **4a-e** were synthesized and their behaviour upon photolysis in the nucleophilic solvent methanol was investigated. Esters **3a-e** and **4a-e** were prepared as shown in Scheme 15 and 16 in Section 2.2.1. A very important factor in the identification of a working mechanism is the composition of the product mixture obtained from the photolysis. For instance, the benzyl methyl ethers (**16a-e**) are formed by the trapping reaction of the substituted benzyl cation with methanol while the substituted 1,2-diphenylethane (dimer) product must come from coupling of the two benzyl radicals. The yields of each of the six major products from direct irradiation of esters **3a-e** and **4a-e** are given in Table 6.

The ultraviolet spectra of the compounds **3a-e** and **4a-e** differ depending on the position of the substitution on the ring. Benzene is a highly symmetric compound and substitution on the ring significantly changes the symmetry of the benzene molecule. Benzene has three principal transitions in the ultraviolet spectrum which include the symmetry forbidden transition band at long wavelength (254 nm), referred to as a secondary band, a forbidden band centred at 200 nm and an allowed band at 180 nm, associated with the vacuum ultraviolet region. Both of the short wavelength bands are referred to as the primary bands. The secondary band is the least intense of the benzene bands (ϵ 230). Substitution on the benzene ring does not produce large changes or new absorption bands, but only modifies the spectrum of the parent

substrate. The addition of most substituents to the benzene ring causes both a bathochromic and hyperchromic shift by conjugation. As well, the fine structure of the secondary band is lost and the band appears as a broad peak.

The photochemistry of the substituted benzyl acetates, **3a-e**, and benzyl 2,2-dimethylpropanoates, **4a-e**, is very dependent on the substituents on the benzene ring. For a systematic study of the photochemistry of these benzylic esters, **3a-e**, **4a-e**, the most accessible transition at which to irradiate is the secondary band. The availability of a wavelength from a low pressure mercury lamp (253.7 nm) which is close to this accessible band allows for the selective excitation of the benzene chromophore into the secondary forbidden band. The ultraviolet wavelength maximum (λ_{max}) values and molar extinction coefficients (ϵ) are given for each ester in section 3.6. The singlet energies, lifetimes and quantum yields of fluorescence for these esters are given in Table 5.

The simplest benzylic ester system is benzyl acetate. The photochemistry of benzylic systems is known to be complex, since both the singlet and triplet states have sufficient energy to break the O=C-O-C bond. The bond dissociation energy for the carbon-oxygen ether bond for benzyl acetate is 68 kcal/mol [15] and the singlet energy for these esters lies well above this value (Table 5). Although the triplet energies of the five substituted esters **3a-e** and **4a-e** have not been measured, they can be estimated from the triplet energies of the corresponding substituted toluene and benzene derivatives. The triplet energy of toluene, p-xylene, anisole and p-tolunitrile are known [67]. Based on these values, the estimated triplet energy of esters **3a**, **4a** is 83 kcal/mol, **3b**, **4b** is 80 kcal/mol, and **3e**, **4e** is 77 kcal/mol. The values for esters

3c, **4c** and **3d**, **4d** are estimated to be approximately 79 kcal/mol since the value for anisole is 81 kcal/mol and the addition of a methyl group decreases the triplet energy by approximately 2 kcal/mol [67]. All of these values are well above the carbon-oxygen bond strength. Thus direct irradiation of the benzylic esters **3a-e** and **4a-e** in methanol could lead to a product distribution which is due to the reactivity of both the singlet and triplet excited states. The different reactivity of these two states can be determined using quenching techniques.

Sensitization and quenching studies have been used previously in the investigation of benzylic photochemistry in attempts to determine the yields from each reactive state. Sensitization studies should allow for the investigation of the triplet excited state exclusively. However, these studies are difficult because the high triplet energy of the benzene chromophore makes it difficult to find a suitable sensitizer. This leads to ambiguous results. Therefore quenching studies are more common in mechanistic photochemistry of benzene substrates, and are discussed in detail in introductory photochemistry textbooks [68].

Quenching studies are performed in order to deconvolute the singlet and triplet reactions which can be occurring simultaneously so that only the singlet reaction is observed. The quencher is added to the solution in order to quench any triplet states which are produced from the singlet by intersystem crossing. The quenching process deactivates the triplet excited state back to the ground state. The triplet state reacts preferentially with the quencher, provided that the energetics for energy transfer are favourable, because it has a longer lifetime than the singlet state. In the benzyl acetate

system the approximate triplet energy of 77–83 kcal/mol is large enough to break the carbon–oxygen bond of the esters 3a–e, 4a–e. The addition of the quencher will allow the triplet state to become deactivated and return to the ground state without reaction. The reactivity of the singlet state should therefore be better understood.

In order to rationalize the results determined from the photolysis of these benzylic esters, a consideration of the possible mechanism for the photolysis is required. Zimmerman [4] suggested that product partitioning occurs at the initial photocleavage of the carbon–oxygen bond so both the ion pair (heterolytic) as well as the radical pair (homolytic) are formed from the excited singlet state. He argued that the greater electron–donating ability of the 3–methoxy group in the excited state gave rise to the enhanced quantum yield of photosolvolysis for 3–methoxybenzyl acetate (3c) and a rise in the efficiency of ion–pair formation. Knowledge of the redox potentials of the intermediate radicals has suggested the possible importance of electron transfer in the mechanism of photosolvolysis of substituted benzyl esters. Mechanisms that have been proposed for photocleavage all involve the initial absorption of light producing the excited singlet state which then gives the triplet state by intersystem crossing. Deactivation of both of these reactive states back to the ground state then competes with reaction. These deactivation processes include fluorescence, phosphorescence and internal conversion. The fluorescence quantum yields and singlet lifetimes for the esters 3a–e and 4a–e were measured and compared to their parent benzyl alcohols (15a–e) which are unreactive (Table 5). For esters 3a, 3b, 3d, 3e, 4a, 4b, 4d, 4e, small to negligible reduction in fluorescence quantum

yields and singlet lifetimes were observed relative to their parent alcohols (**15a**, **15b**, **15d**, **15e**). This result suggests that the quantum yield of reaction is very low for these esters because the values do not decrease significantly from those of the parent alcohol, which are unreactive. Large reductions in the fluorescence quantum yields and singlet lifetimes for esters **3c** and **4c** were observed when compared to the parent alcohol (**15c**) and this suggests the presence of another reactive pathway for the 3-methoxy isomers to form products. The quantum yield of reaction should therefore increase. This is observed since there is a reduction in photolysis time when the 3-methoxy isomer is compared to that of the 4-methoxy isomer. The results of these fluorescence quantum yields and singlet lifetimes suggest the presence of an additional reactive pathway for **3c** and **4c**. These observations will be discussed later.

2.3.2 Discussion of the Direct Photolysis of Esters **3a-e**

The product distributions from the direct photolysis of esters **3a-e** are shown in Table 6. The structure of the six major photoproducts is indicative of the excited state behaviour of the esters. Substituents are shown by these experiments to have a large effect on the product distribution.

The dimer (**18a-e**) is, in each photolysis, the major product of direct irradiation. The dimer is obviously formed by out-of-cage coupling of two benzyl radicals which are formed by homolytic cleavage of the carbon-oxygen bond of the ester. The radical pair can be either in a singlet state or a triplet state. The triplet radical pair can be formed either by direct cleavage of the excited triplet state of the

ester or by intersystem crossing in the originally formed singlet radical pair. Previous studies on other related systems have shown that this latter process is unimportant unless heavy atoms are present to increase spin-orbit coupling. The triplet radical pair is much more likely to escape from the solvent cage since it cannot undergo either recombination or electron transfer to form the ion pair. Therefore, a preliminary suggestion is that the high yield of dimer is a result of the intervention of triplet state reactivity in these benzylic esters. The fact that the yield of this product is very low in the related naphthyl esters supports this idea.

The singlet and triplet radical pairs have other competitive pathways which lead to products. If homolytic C-O bond cleavage occurs, the coupling product (17a-e) may be generated from either the singlet or the triplet radical pair. For the singlet radical pair, the initial homolytic cleavage generates the substituted benzyl radical and the acetyloxy radical. The decarboxylation rate for the acetyloxy radical has been determined ($<1.3 \times 10^9 \text{ s}^{-1}$ in methanol at 25°C [Chapter 1]). Once the decarboxylation takes place, in-cage or out-of-cage coupling may occur to give the coupling product. The triplet radical pair may decarboxylate ($<1.3 \times 10^9 \text{ s}^{-1}$ in methanol at 25°C) to give the substituted benzyl radical and the methyl radical triplet pair. Diffusion of these two radicals into the solvent and recombination may also give the coupling product. The yield of the coupling product is nearly constant (around 15%) when comparing esters 3a-e and, therefore, appears to be substituent independent. Again, quenching experiments may be useful in determining from which excited state the coupling product is generated.

The yield of the toluene products (19a-e) derived from hydrogen abstraction by the substituted benzyl radical was between 1% and 5% for esters 3a-e.

The ether products, 16a-e, may be produced by one of two pathways. They may be formed by heterolytic cleavage of the carbon-oxygen ether bond of the ester functional group directly into the ion-pair, or by homolytic cleavage of the carbon-oxygen bond followed by electron transfer converting the radical pair to the ion pair. The importance of this latter step for substituted 1-naphthylmethyl phenyl acetates has been demonstrated previously [9]. The yield of ether changes dramatically by changing the substituents on the aromatic ring. The largest change is observed with the photolysis of the 3-methoxybenzyl acetate, 3c. This compound gives, upon photolysis, approximately 33% of ether, which is close to the yield obtained by Zimmerman [4]. The peculiar behaviour of the 3-methoxy substituted aromatics has long been a point of interest in the photolysis of substituted benzyl substrates. McClelland [69] has recently obtained laser flash photolysis results which suggest unusual behaviour of 3-methoxy substituted substrates. His results suggest that two excited singlet states are formed with similar rates of decay. The observation of these two intermediates suggests the intervention of another process when these substrates are irradiated with light. This has been discussed previously with the reduction of the fluorescence quantum yield and singlet lifetime for these esters. Therefore the unusual photochemistry for the 3-methoxy substrates can possibly be explained by the intervention of another process. This explanation could account for "meta effect" results.

The direct photolysis of ester **3a** produced a considerable amount of ether product, indicating the possible importance of the electron transfer process with this substrate. Irradiations of esters **3b** and **3d-e**, however, showed little ionic product being produced. These results suggest that the heterolytic and/or homolytic cleavage followed by electron transfer is slow compared with the other processes by which the molecule forms product.

The free energy change of electron transfer converting radical pairs to ion pairs derived from esters **3a-e** may be calculated using the known oxidation potentials of the substituted benzyl radicals and the estimated reduction potential of the acetyloxy radical [70, 17]. These free energy changes of electron transfer for esters **3a-e** were calculated and were shown to be negative. Their free energy values are: -25 kcal/mol **3a**, -30 kcal/mol, **3b**, -36 kcal/mol, **3d**, and -17 kcal/mol, **3e**. Electron transfer converting radical pair to ion pair is therefore favourable for all cases.

The rates of electron transfer can be estimated using the benzylic oxidation potentials [70] and the curve derived by a previous study of electron transfer in 1-naphthylmethyl ester photochemistry [9] assuming the same reorganization energy (λ). These rates of electron transfer are given below: $7 \times 10^8 \text{ s}^{-1}$, **3a** and **4a**; $3 \times 10^9 \text{ s}^{-1}$, **3b** and **4b**; $1 \times 10^{11} \text{ s}^{-1}$ **3d** and **4d**; $1 \times 10^8 \text{ s}^{-1}$, **4e** and **5e**. These rates of electron transfer are small enough for all but **3d** and **4d** that diffusional cage escape, estimated at $3 \times 10^9 \text{ s}^{-1}$ [9], should be a dominant or competitive process. The high yield of out-of-cage dimers is therefore, not surprising.

The photo-Fries rearrangement reaction has been extensively studied and many

reviews are available [71, 72]. The majority of the reported esters that undergo the photo-Fries rearrangement are aryl esters; benzylic esters have not been investigated as thoroughly. Although the mechanism for formation of these photoproducts has not been clarified, the process is thought to occur from excited singlet states which undergo isomerization at a much higher rate than other experimentally observable photophysical processes such as emission. For aryl esters, it was deduced that rearrangement in the excited state proceeds from two or more excited singlets. Thus, the formation of photo-Fries products (20a-c) occurs from either an energetically higher excited state where dissociative isomerization can take place with cleavage of the ester, or from a lower excited state where non-dissociative rearrangement such as concerted [1,3]-shifts leads to *ortho* products. Upon photolysis, esters 3a, b and d gave photo-Fries products. The yield of the photo-Fries product seems to be affected by electron-donating groups on the ring. Esters 3c and 3e give no detectable yield of the rearrangement product. This result may be explained by the unusual behaviour of ester 3c in the excited state, as well as the electron-withdrawing substituent in the 3e case. Isolation of the photo-Fries products has been shown to be difficult [73]. Jaeger in the photosolvolysis of 3,5-dimethoxybenzyl acetate isolated the photo-Fries product and determined its structure by ^1H nmr. The presence of the photo-Fries product from the photolysis of ester 3b was confirmed by GC/MS. The photo-Fries product was not isolated but only the *ortho* substituted ester product could be formed in this case.

The carboxylic acid product was not quantified due to the low sensitivity of the

GLC detector.

2.3.3 Discussion of the Direct Photolysis of Esters 4a-e

The photochemistry of esters 4a-e were investigated and their product distributions were determined, as shown in Table 6. The dimer product was again produced in high yield, although it was not the major product as in the case of 3a-e. A trend can be seen upon comparison of the results from esters 3a-e and 4a-e. Firstly, the amount of dimer (18a-c) obtained by diffusional escape is dependent on the structure of the carboxylic acid side of the ester. In each case esters 4a-e gave less dimer product than esters 3a-e. This result may be rationalized by the fact that the benzyl radical undergoes in-cage chemistry with the *t*-butyl radical, in the singlet state, produced from decarboxylation of the 2,2-dimethylpropanoyloxy radical. The rate of decarboxylation of the 2,2-dimethylpropanoyloxy radical is known to equal $11 \times 10^{11} \text{ s}^{-1}$ [Chapter 1]. This faster alternate pathway of in-cage chemistry allows the benzyl radical to undergo reactions other than the diffusion of the benzyl radical into the solvent. The production of some dimer probably indicates that the dimer is again produced mainly via the triplet radical pair. The fact that some dimer is still produced may be used in the evaluation of the rate of diffusion of escape of the triplet radical pair in methanol.

The amount of ether, 16a-e, (heterolytic) produced upon direct irradiation of esters 4a-e is insignificant if one excludes the ether produced upon photolysis of the 3-methoxy substrate. Indeed, the amount is reduced from relatively small values in the 3a-e series to zero percent yield for esters 4a, 4b, 4d and 4e. For the 3-methoxy

case, the amount of ether, **6c**, produced from **3c** decreases by seventy-five percent in comparison with **4c**. This large reduction in the yield of ether produced by substitution on the carboxylic acid side is a strong argument that the faster rate of decarboxylation of the 2,2-dimethylpropanoyloxy radical versus that of the acetyloxy radical has an effect on the amount of ether produced. If this is valid, it follows that the ether is mainly produced for the 3-methoxy compounds by homolytic cleavage of the carbon-oxygen bond of the ester functional group, followed by electron transfer. The heterolytic cleavage (directly into the ions) mechanism should be little influenced by changing the carboxylic acid side of the ester, since it is the 3-methoxybenzyl chromophore that is being excited in each case. Therefore the reduction in yield of the ether must be due to a pathway not involving heterolytic cleavage. The homolytic pathway generates the substituted benzyl radical and the 2,2-dimethylpropanoyloxy radical. The free energy change of electron transfer may also be calculated using the known oxidation potentials of the substituted benzyl radicals and the reduction potential of the 2,2-dimethylpropanoyloxy radical. The reduction potential for the 2,2-dimethylpropanoyloxy radical was assumed to be equivalent to the acetyloxy value, which is reasonable since large changes occur only if the carboxylate group is attached directly to a conjugated group [17]. In each case the free energy change for esters **4a-e** was determined to be negative and thus electron transfer is predicted to be favourable. This is the first indication that an electron transfer step may be important in the photochemistry of phenylacetates. Quenching studies of this system may clarify the importance of an electron transfer step.

If the decarboxylation occurs before electron transfer, or before radical escape from the solvent cage, then a substituted benzyl radical and the *t*-butyl radical are generated. The subsequent reaction between the two radicals involves either disproportionation or combination reactions. The disproportionation step occurs when one radical in a pair of encountering radicals has a β -hydrogen adjacent to the radical centre. By abstracting the β -hydrogen, two stable molecules are formed, an unsaturated molecule and a molecule with a new carbon-hydrogen bond. The combination step is essentially a reaction which any radical pair may undergo by coupling in order to achieve termination. The disproportionation step has been shown to be exclusively a head-to-tail reaction between the two radicals, while the recombination step is a head-to-head process. Both of these processes are highly exothermic and only small changes in the k_D/k_C ratio are observed by changing the solvent or the temperature. Many quantitative k_D/k_C values have been determined in the gas phase, while solution work up until recently provided fewer valuable results.

The photochemical results for esters **3a-e** in methanol show a higher percentage of coupling products (**17a-e**) than disproportionation (**19a-e**, toluene) products. This result is not surprising since the substituted benzyl radical cannot abstract a hydrogen from the methyl radical produced from esters **3a-e**. Thus only coupling product is available to the radical pair in the solvent cage. Hydrogen abstraction (toluene) products that are observed are thought to be formed by the benzyl radical from the solvent (CH_3OH) or from the photoproducts. The elucidation of the process by which the toluene photoproduct is generated is difficult because it is

formed in such low yield. The large amount of dimer (out-of-cage) formed in the photolyses of esters **3a-e** is an indication of the slow rate of decarboxylation of the acetyloxy radical ($< 1.3 \times 10^9 \text{ s}^{-1}$, Chapter 1) relative to the rate of radical separation in methanol. The k_D/k_c ratios determined from the photolysis of esters **4a-e** in methanol range from 0.2 to 0.3. This is due to a large increase in both the yield of coupling product as well as the disproportionation product (toluene). The yield of the coupling product has increased, when the acetate series (**3a-e**) is compared to the 2,2-dimethylpropanoate series (**4a-e**). The increase in the combination (coupling) product, however, is not as large as the increase in the disproportionation (toluene) product. These large increases have been previously observed [74]. In general, the extent of disproportionation has been shown to increase with an increase in the number of β -hydrogens available for abstraction for simple alkyl radicals. This has been explained by considering a statistical effect [32]. This large increase can also be explained by assuming that the rate constant for combination becomes smaller as the radical becomes more sterically hindered. This explanation seems valid because the activation energy for combination of two methyl radicals is 0 kcal/mol, while the activation energy for combination of two ethyl radicals is 2 kcal/mol [75]. For more hindered pairs, these values for combination should increase, allowing for the disproportionation pathway producing toluene product to dominate.

Although the k_D/k_c ratios for the substituted benzyl radicals and the *t*-butyl radical have not been determined previously, other systems give values which are similar to the values presented by Boddy *et al.*[76]. Boddy *et al.* have found a k_D/k_c

value of 0.3 for a comparable reaction between the ethyl radical and the *t*-butyl radical in the gas phase. Solvent effects are known to be small, so the gas phase results can be compared to those in the solvent methanol. This idea has been confirmed by Mayo [77] who concluded that the competition between disproportionation and combination depends more on temperature than on reaction medium. He concluded that reactions in the gas phase and in condensed phases involve similar transition states with disproportionation being slightly favoured by low temperatures and solvent cages.

For the photolysis of esters **4a-e**, the amount of coupling product (**17a-e**) ranged between 41% and 58%. This range implies that the substituent may have an effect on the coupling reaction. The high yield of the coupling product, **17a-e**, in esters **4a-e** suggests that it is formed in-cage. The formation of the coupling product via the singlet radical pair is reasonable since decarboxylation of the 2,2-dimethylpropanoyloxy radical is extremely fast, and solvent separation would increase the amount of disproportionation. The yield of disproportionation (**19a-e**, toluene) product from the photolysis of esters **4a-e** does not vary significantly with change in substituent. The highest yield of toluene (17%) occurs for ester **4c**. The disproportionation product is possibly obtained from singlet radical pair hydrogen atom abstraction with the *t*-butyl radical produced adjacent to the substituted benzyl radical. The coupling product is obtained from the singlet radical pair. Determination of the pathway for formation of the disproportionation product is more difficult because it should be favoured by solvent-separated encounters. Out-of-cage as well as in-cage

disproportionation is possible and these processes could not be distinguished from this study.

The yield of the photo-Fries product, **20a-e** from photolysis of esters **4a-e**, becomes insignificant suggesting that the rearrangement can no longer compete with other processes occurring in these substrates. The decarboxylation rate of the 2,2-dimethylpropanoyloxy radical is much greater than the acetyloxy radical. Since the yields of coupling and disproportionation products are much larger for esters **4a-e**, the photo-Fries rearrangement must occur more slowly than the rate of decarboxylation for the 2,2-dimethylpropanoyloxy radical. This implies that the photo-Fries reaction is not concerted but occurs by a discrete radical pair.

In conclusion, esters containing the *meta* methoxy substituent (**3c** and **4c**) show unusual reactivity. This unusual effect may be due to the intervention of an unusually reactive excited state. However, even for these esters, the product yields of the photolyses suggest that electron transfer converting radical-pair to ion-pair is an important step in the mechanism. The photochemistry of esters **3a-e** and **4a-e** suggests that many different modes of reaction are available for these benzylic esters. Reaction from both the singlet and triplet states are complicating factors, but deconvolution of the two excited states is possible by quenching studies. Quenching studies of the substituted benzyl acetates (**3a-e**), should provide more information on the photochemistry of the singlet excited state allowing a better understanding of the mechanism. These results will be discussed next. Quenching studies of esters **4a-e** were not done.

2.3.4 Discussion of the Photolysis of Esters 3b–e in the Presence of 2,3-Dimethyl-1,3-butadiene

Prior to irradiating esters 3b–e in the presence of a quencher, information on excited state lifetimes was necessary to insure that only the singlet state was reacting. The quencher 2,3-dimethyl-1,3-butadiene with a known triplet energy of 60 kcal/mol [68] was used. This triplet energy is well below the estimated triplet energy of the esters and therefore should allow energetically favourable energy transfer to occur between the two substrates. Unfortunately, the triplet lifetimes of these esters are not yet known although the singlet lifetime is usually shorter than the triplet by two to three orders of magnitude. Concentrations of the diene for the photolysis were prepared in order that approximately 10% of the singlet for esters 4b–e was quenched (Table 7). At these concentrations an estimated > 99% of the triplet state should be quenched, assuming that the rate of triplet quenching is close to the diffusion controlled rate and that the triplet lifetimes are the same as the singlet lifetimes (determination of the triplet lifetimes is in progress [78]). This quenching study should allow for the deconvolution of the singlet from the triplet excited states since the reaction should now be occurring from the singlet state only. The singlet state quenching for benzylic esters by this diene is also rapid as shown in Table 8. A Stern–Volmer intensity quenching plot for esters 4b–e are shown in Figure 12. The $k_q\tau_s$ values from the slopes and the quenching rate constants (k_q) values calculated using τ_s from Table 5 are summarized in Table 8. The quenching rate constants (k_q) for the singlet state range between $2.9 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$ and $11 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$. The changing of

the substituent has a small effect on the quenching rate constants, k_q , as seen in Table 8. Ester **4e** has the highest k_q value and this may be explained by the formation of the exciplex involving electron transfer from the diene to the 4-cyanobenzyl ester substrate [79]. Examples of exciplex formation of this type have been discussed for other substrates with conjugated dienes [79]. The authors of this study suggest that the process occurs via exciplex formation between the excited molecule and the diene, followed by fast radiationless decay to the ground state. They found a correlation between the quenching rate constants for naphthalene substrates and the diene ionization potentials.

The results for photolysis of esters **3b–e** with specific diene concentrations and calculated percentage of singlet quenched at these diene concentrations are given in Table 7. Ester **3a** was not photolyzed in the presence of quencher since its extinction coefficient is low at the excitation wavelength of 253.7 nm. Competitive absorption of the diene was occurring.

The dimer (**18a–e**) was the major product for esters **3b**, **3d–e**, indicating that it is the singlet state which produces the dimer product. This result is surprising since it means that the singlet radical pair must diffuse efficiently into solution. This process must be competitive with other processes because the products resulting from electron transfer and other singlet pathways are not observed in high yield. The yields of dimer for esters **3c** and **3e** are lower than from the direct irradiations. The large drop in the yield of the dimer in the presence of quencher especially for ester **3c** indicates that, in direct irradiations, it is produced mainly from the longer lived triplet state.

The yields of the ethers (**16b-e**) from the photolysis of esters **3b-e** in the presence of quencher are very close to or slightly higher than those values obtained from the direct irradiations. These increases indicate that the ether is formed via the singlet state. Esters **3b** and **3e** show small enhancement in the amount of ethers **16b** and **16e**. These small increases suggest that electron transfer in the singlet pathway is important, although other processes such as diffusion into solution are dominant. Ester **3d** shows a slight reduction in the yield of ether in the quenching study. This indicates that the singlet radical pair formed from irradiation does not undergo electron transfer even though it is predicted to be favourable. Instead the radical pair undergoes radical escape and other termination reactions. Electron transfer can occur in the singlet radical pair and is predicted to be favourable.

The results from the photolysis of esters **3b-c** and **3e** each show either a small enhancement or no change in the yield of the coupling product (**17b-c** and **17e**). This result indicates that the singlet radical-pair is important in the generation of the coupling product. The 3-methoxy ester (**3c**) in the presence of quencher preferentially produces a large increase in the coupling product after decarboxylation of the acetyloxy radical in the solvent cage. Ester **3d** showed a decrease in yield of coupling product in the presence of quencher. This decrease must be due to combination of solvent separated methyl radicals and substituted benzyl radicals.

The lower product yields of the toluene derived products for the quenching studies in each case may be explained by the fact the substituted benzyl radical abstracts a hydrogen from outside the solvent cage. Little information can be obtained

about the excited state which gives rise to the toluene products, due to the low yields. From the reduction in yield of the toluene derived products one can conclude that the quencher is not acting as a source of hydrogen atoms.

The yield of photo-Fries product increases substantially in the presence of quencher for all esters except **3b**. This increase may be explained by intramolecular rearrangement which occurs in the singlet radical pair. It should be noted that for ester **3b**, out-of-cage products (dimer) are high in yield and the singlet radical pair probably separates quickly. Comparison of the photolysis of esters **3b-e** in the absence and presence of quencher suggests that irradiation in the absence of the quencher produces product mainly via the singlet state. Ester **3e**, from both irradiations, gave similar product yields as well as long reaction times. Because the product yields are so similar it may be postulated that the reaction occurs only from the singlet state for the irradiation in the absence of quencher. It is important that the 4-cyanobenzyl esters, **3e** and **4e**, have the lowest triplet energy of the studied esters. The estimated triplet energy is above the bond (C-O) dissociation energy by only 8 kcal/mol. This small difference suggests that reaction of the triplet state may be inefficient. It follows that irradiation in the absence of quencher may produce products via the singlet state only.

In conclusion, the photochemistry of the substituted benzyl acetates and 2,2-dimethylpropanoates has been investigated. The electron transfer step was shown to be an important pathway in the mechanism of these substrates, however, it is not a dominant pathway. The dominant step in this photochemistry is the diffusion of the

radical pair into solution where the radicals can undergo termination reactions. The importance of the "*meta* effect" was investigated and the introduction of another pathway which allows the ions to be obtained directly from the excited state is suggested.

CHAPTER 3

Experimental

3.1 General Experimental

Melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Ultraviolet (UV) spectra were obtained in methanol solution in 1 cm quartz cuvettes on a Varian Cary 219 spectrometer. Wavelength maxima (λ_{\max}) are reported in nanometers. Extinction coefficients (ϵ , $L \text{ mol}^{-1} \text{ cm}^{-1}$) were obtained from plots of absorbance vs concentration over a concentration range of 1×10^{-3} – 2×10^{-5} M. Proton (^1H) and carbon 13 (^{13}C) magnetic resonance spectra were obtained in CDCl_3 at 360 MHz and 90 MHz respectively on a Nicolet Magnetics Corporation NB-360 spectrometer. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (0.00) as an internal standard. Multiplicities are abbreviated as follows: s= singlet, d= doublet, dd = doublet of doublets, t= triplet, q= quartet, m= multiplet. GC/MS analyses were done on a Hewlett Packard 5890 A GC 5970 mass selective detector interfaced with a Hewlett Packard 9816 microcomputer. The column used was a 25 m x 0.2 mm 5% phenyl methyl silicone on fused silica with a film thickness of 0.25 μm . Masses are reported in units of mass over charge (m/z). Intensities are reported as a percent of the base peak intensity. The molecular ion is indicated by M^+ . Infrared spectra were determined on a Pye Unicam SP 1000 spectrophotometer and frequencies are reported in wavenumbers (cm^{-1}).

Silica gel T-6145 plates from Sigma were used for thin layer chromatography (TLC). Silica gel 60 Å (230–400 mesh) (Aldrich) was used for flash chromatography

while silica gel 60 Å (70–230 mesh) was used for normal column chromatography. Combustion analyses were carried out by Canadian Microanalytical Service Ltd., Delta, B.C. Canada.

HPLC analyses were performed on a Waters 6000 Solvent Delivery System with a Waters U6K injector under isocratic conditions (30:20 methanol:water) with a flow rate of 2 mL/min. A Brownlee Lab Spheri-10 10 µL reverse phase column (25 cm x 0.46 cm) and a Waters Model 450 Variable Wavelength Detector and UV detection was used at 280 nm for the 1-naphthylmethyl esters (1a–h, 2a–k) and 254 nm for the benzylic esters (3a–e, 4a–e) for monitoring the reaction.

GLC analyses were performed using a Hewlett Packard 5890 A gas chromatograph with a Hewlett Packard 7673 A controller and a Hewlett Packard 3396 A integrator using a Hewlett Packard 7673 automatic injector. A 1 m glass column was used with 10% Fluorad FC-431 and 1% H₃PO₄ on Chromosorb W HP 80/100 mesh.

A Perkin Elmer MPF 66 fluorescence spectrophotometer was used to determine the quantum yield of fluorescence (ϕ_f) and the singlet energy (S_1) of these esters.

A PRA System 3000 fluorescence lifetime instrument was used to determine the singlet lifetime (τ_s) of these esters.

1-Naphthylmethanol, 2-(1-naphthyl)ethanol, 1-(chloromethyl)naphthalene, benzyl acetate, 2,3-dimethyl-1,3-butadiene, phenylacetyl chloride, acetyl chloride, 2,2-dimethylpropanoyl chloride, cyanoacetic acid, 2-methylpropanoic acid, 3-butenic

acid, propanoic anhydride, 4-cyanobenzaldehyde, 3-methoxybenzyl alcohol, 4-methoxybenzyl alcohol, 4-methylbenzoic acid, methoxyacetyl chloride, 3-phenylpropanoic acid, 3-methoxyphenylacetic acid, 4-methoxyphenylacetic acid, 3-methylphenylacetic acid, 4-methylphenylacetic acid, 3-fluorophenylacetic acid, 4-fluorophenylacetic acid, 3- α,α,α -trifluoromethylphenylacetic acid, and 4- α,α,α -trifluoromethylphenylacetic acid and methanesulfonyl chloride were purchased from the Aldrich Chemical Company. All solvents were distilled prior to use.

3.2 The Synthesis of Benzyl Alcohols 15b and 15e

4-methylbenzyl alcohol (15b): 4-methylbenzoic acid was reduced with lithium aluminium hydride in diethyl ether as described below (Scheme 17). To 28.4 g (0.75 mol) of LiAlH_4 in 1 L of diethyl ether was added 40 g (0.29 mol) of 4-methylbenzoic acid in 300 mL of THF. The addition was continued so the ether was at a constant reflux. After the addition was complete, the solution was allowed to stir for 3 hours, water was slowly added (300 mL) and 30% H_2SO_4 in water (300 mL) was added. The solution was filtered and the ether layer was separated, dried and rotoevaporated to yield 29.4 g (0.24 mol, 83 %) of 4-methylbenzyl alcohol. The crude alcohol was recrystallized from heptane, mp 59–61°C (lit. [80] 61–62°C). The ^1H NMR of the purified alcohol was identical to that found in the literature [81].

4-cyanobenzyl alcohol (15e): 4-cyanobenzaldehyde, was reduced to 4-cyanobenzyl alcohol with sodium borohydride using the procedure described [10](Scheme 17).

Column chromatography of the crude alcohol gave the pure compound as a white solid: mp 131–133°C (lit. [82] 133–134°C).

3.3 General Method for the Synthesis of Acid Chlorides (6a, 6c–h, 7b–k)

Acid chlorides **6a**, **f**, **g** and **7a** are commercially available from the Aldrich Chemical Company and were used without further purification. Acid chlorides **6d** and **6h** were synthesized from the corresponding acid using the literature method [83, 84]. Acid chlorides **7b–k** were obtained from the corresponding acids **9b–k**. For acid chlorides **6c**, **6e** and **7b–k** the method below was used (Schemes 6 and 7).

The procedure involved dissolving the corresponding acid (0.01 mol) in 5 mL (0.03 mol) of thionyl chloride and refluxing for 1 hour. After 1 hour the excess thionyl chloride was removed by distillation at atmospheric pressure and the acid chloride was allowed to cool to room temperature. The flask was put under reduced pressure for 15 minutes to remove any residual thionyl chloride. The vacuum was removed and 30 mL of dry benzene was added and used for the synthesis of the esters.

The cyano acids **9j–k** are not commercially available and were synthesized using the method of Richter *et al.* [85] (Scheme 2). The esters generated were hydrolyzed in aqueous base to give the corresponding acids (**9j–k**).

3.4 Synthesis of Substituted 1-Naphthylmethyl Acetates

3.4.1 Synthesis of 1-Naphthylmethyl Acetates 1a, 1c-h and 1-Naphthylmethyl Phenylacetates 2a-k

To a well-stirred solution of 1-naphthylmethanol, **5**, (1.56 g, 0.01 mol) and 1 mL of pyridine in 50 mL of dry benzene was slowly added the corresponding acid chloride (0.01 mol) (**6a**, **6c-h** and **7a-k**) in 30 mL of benzene at room temperature. The pyridinium hydrochloride salt precipitated and after all of the acid chloride was added the solution was stirred overnight. Then 50 mL of water was added and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl, once with 5% aqueous NaOH and finally with water. The organic layer was dried (MgSO_4), filtered and rotoevaporated to yield the crude ester (Schemes 4 and 5).

3.4.2 Synthesis of 1-Naphthylmethyl propanoate 1b

To a 50 mL round bottom flask was added 1.56 g (0.01 mol) of 1-naphthylmethanol, **5**, and 20 mL of pyridine. Once the alcohol had dissolved 1.35 mL (0.01 mol) of propionic anhydride was introduced and the reaction mixture heated at 50°C for 1 day and allowed to stir at room temperature for 12 more hours. The solution was poured into 50 mL of diethyl ether and washed sequentially with 150 mL of a 20% aqueous solution of HCl, a 5% aqueous solution of NaHCO_3 and finally with water. The ether layer was dried over MgSO_4 , filtered and rotoevaporated to give a light yellow product (Scheme 4).

3.5 Synthesis of Substituted Benzyl Acetates and 2,2-Dimethylpropanoates (3a-e, 4a-e)

To a well-stirred solution of the corresponding benzyl alcohols **5a-e** (0.02 mol) and 1 mL of pyridine in 50 mL of dry benzene was slowly added the corresponding acid chloride **6a** and **6f** (0.02 mol) in 30 mL of dry benzene at room temperature. The pyridinium hydrochloride salt precipitated and after all of the acid chloride was added, the solution was stirred overnight. Then 50 mL of water was added and the two layers were separated. The benzene layer was washed twice with 10% aqueous HCl, once with 5% aqueous NaOH and finally with water. The organic layer was dried (MgSO₄), filtered and rotoevaporated to yield the crude ester (Schemes 16 and 17).

3.6 Isolation, Purification and Spectroscopic Identification of Esters 1a-h, 2a-k, 3a-e and 4a-e

The crude esters **1a-h**, **2a-k**, **3a-e** and **4a-e** were column chromatographed through silica gel (70-230 mesh) using 50:50 hexane:dichloromethane as the eluent. The ester fractions were identified by TLC, combined and concentrated. Those esters which were oils were distilled under vacuum and those which were solids were recrystallized from hexane before irradiation. The following is a summary of the characteristics of the esters prepared this way:

1-Naphthylmethyl acetate (1a): yield 63%; bp 55°C at 0.5 mm Hg [lit. [12] 65°C at 1 mm Hg]; The ^1H NMR was identical to that reported earlier [12].

1-Naphthylmethyl propanoate (1b): yield 65%; bp 86–88°C at 0.5 mm Hg; UV λ_{max} 265 (ϵ 6.56×10^3), 275 (7.26×10^3), 284 (5.10×10^3); IR (neat) 3015, 2950, 2915, 2870, 1735 (C=O), 1460, 1345, 1265, 1175 (C–O), 1070, 1000, 780, 760 cm^{-1} ; ^1H NMR δ 8.00 (d, 1H, $J=8.1$ Hz), 7.82–7.88 (m, 2H), 7.42–7.55 (m, 4H), 5.57 (s, 2H, CH_2O), 2.38 (q, 2H, $J=7.6$ Hz), 1.15 (t, 3H, $J=7.5$ Hz); ^{13}C NMR δ 174.3 (s, C=O), 133.6 (s), 131.5 (s), 129.1, 128.9 (s), 128.6, 127.3, 126.5, 125.9, 125.2, 123.5, 64.4 (t, CH_2O , $J=147.9$ Hz), 27.6 (t, CH_2CH_3 , $J=127.6$ Hz), 9.1 (q, CH_2CH_3 , $J=127.3$ Hz); GC/MS, 215 (8, $M+1$), 214 (48, M^+), 159 (12), 158 (96), 142 (18), 141 (100), 140 (64), 139 (37), 129 (43), 128 (24), 127 (24), 115 (49), 57 (46).

Anal. Calcd for $\text{C}_{14}\text{H}_{14}\text{O}_2$: C, 78.48; H, 6.59.

Found: C, 78.04; H, 6.59.

1-Naphthylmethyl 1-phenylpropanoate (1c): yield 52%; bp 133–137°C at 0.5 mm Hg; UV λ_{max} 267 (ϵ 8.14×10^3), 276 (9.30×10^3), 288 (5.98×10^3); IR (neat) 3050, 3030, 2920, 1740 (C=O), 1460, 1235, 1155, 790, 785, 770, 690 cm^{-1} ; ^1H NMR δ 7.90 (d, 1H, $J=8.5$ Hz), 7.82 (d, 1H, $J=7.6$ Hz), 7.79 (d, 1H, $J=8.2$ Hz), 7.36–7.48 (m, 4H), 7.12–7.22 (m, 5H), 5.52 (s, 2H, CH_2O), 2.93 (t, 2H, $J=7.8$ Hz, PhCH_2CH_2), 2.64 (t, 2H, $J=7.8$ Hz, PhCH_2CH_2); ^{13}C NMR δ 172.8 (s, C=O), 140.3 (s), 133.7 (s), 131.6 (s), 131.3 (s), 129.2, 128.7, 128.4, 128.2, 127.5, 126.5, 126.2, 125.9, 125.2, 123.5, 64.6

(t, CH₂O, J=147.2 Hz), 35.9 (t, C(=O)CH₂, J=128.8 Hz), 30.9 (t, CH₂Ph, J=128.1 Hz);
GC/MS 291 (6, M+1), 290 (32, M⁺), 142 (16), 141 (100), 115 (11).

Anal. Calcd for C₂₀H₁₈O₂: C, 82.73; H, 6.25.

Found: C, 82.93; H, 6.32.

1-Naphthylmethyl 2-methylpropanoate (1d): yield 50%; bp 115°C at 0.5 mm Hg [lit. [86] 127–128°C at 1 mm Hg]; UV λ_{\max} 266 (ϵ 5.37x10³), 276 (6.08x10³), 284 (4.40x10³); IR (neat) 3030, 2980, 2940, 2880, 1740 (C=O), 1465, 1195 (C–O), 1160, 965, 790, 775 cm⁻¹; The ¹H NMR was identical to that reported earlier [86]; ¹³C NMR δ 176.9 (s, C=O), 133.6 (s), 131.6 (s), 131.6 (s), 129.1, 128.6, 127.2, 126.4, 125.8, 125.2, 123.5, 64.5 (t, CH₂O, J=148.8 Hz), 34.1 (d, CH(CH₃)₂, J=129.7 Hz), 19.0 (q, CH₃, J=127.6 Hz); GC/MS 229 (10, M+1), 228 (49, M⁺), 159 (10), 158 (79), 142 (32), 141 (100), 140 (46), 139 (37), 129 (24), 128 (23), 127 (24), 115 (79), 71 (24).

1-Naphthylmethyl 1-butenolate (1e): yield 35%; bp 112–116°C at 0.5 mm Hg; UV λ_{\max} 265 (ϵ 6.56x10³), 275 (7.48x10³), 286 (5.09x10³); IR (neat) 3030, 2990, 2940, 1740 (C=O), 1325, 1250, 1170, 785, 765 cm⁻¹; ¹H NMR δ 7.96 (d, 1H, J=8.1 Hz), 7.78–7.84 (m, 2H), 7.38–7.53 (m, 4H), 5.88–5.95 (m, 1H, CH=CH₂), 5.55 (s, 2H, CH₂O), 5.08–5.15 (m, 2H, CH=CH₂), 3.11 (d, 2H, CH₂CH=C, J=6.9 Hz); ¹³C NMR δ 171.3 (s, C=O), 133.6 (s), 131.5 (s), 131.2 (s), 130.0, 129.2, 128.6, 127.4, 126.4, 125.8, 125.1, 123.4, 118.6 (t, CH=CH₂, J=156.8 Hz), 64.7 (t, CH₂O, J=147.8 Hz), 39.0 (t, C(=O)CH₂, J=129.2 Hz); GC/MS 227 (7, M+1), 226 (44, M⁺), 158 (21), 142 (13),

141 (100), 140 (15), 139 (10), 115 (15).

Anal. Calcd for $C_{15}H_{14}O_2$: C, 79.62; H, 6.24.

Found: C, 79.63; H, 6.25.

1-Naphthylmethyl 2,2-dimethylpropanoate (1f): yield 62%; bp 89–91°C at 0.1 mm Hg [lit. [87] 108–110°C at 0.2 mm Hg]; UV λ_{max} 265 (ϵ 5.54x10³), 275 (6.47x10³), 284 (4.60x10³); IR (neat) 3060, 2990, 2965, 2920, 2885, 1730 (C=O), 1485, 1285, 1730 (C=O), 1485, 1285, 1165, 800, 780 cm⁻¹; ¹H NMR identical to that reported earlier [88]; ¹³C NMR δ 178.3 (s, C=O), 133.7 (s), 131.8 (s), 131.6 (s), 129.0, 128.6, 126.9, 126.4, 125.8, 125.2, 123.6, 64.6 (t, CH₂O, J=150.0 Hz), 39.0 (s, C(CH₃)₃), 29.2 (q, CH₃, J=126.7 Hz); GC/MS 243 (6, M+1), 242 (32, M⁺), 142 (24), 141 (100), 139 (18), 127 (11), 115 (39).

1-Naphthylmethyl methoxyacetate (1g): yield 72%; bp 90–92°C at 0.5 mm Hg; UV λ_{max} 264 (ϵ 5.61x10³), 276 (6.73x10³), 286 (4.49x10³); IR (neat) 3070, 3010, 2960, 2840, 1760 (C=O), 1520, 1195, 1145, 805, 795, 780 cm⁻¹; ¹H NMR δ 8.00 (d, 1H, J=8.2 Hz), 7.87 (t, 2H, J=7.9 Hz), 7.42–7.58 (m, 4H), 5.66 (s, 2H, CH₂O), 4.06 (s, 2H, CH₂OCH₃), 3.43 (s, 3H, OCH₃); ¹³C NMR δ 170.1 (s, C=O), 133.6 (s), 131.5 (s), 130.8, 129.5, 128.7, 127.8, 126.6, 125.9, 125.2, 123.3, 69.7 (t, CH₂OCH₃, J=143.8 Hz), 64.7 (t, CH₂OC(=O), J=148.0 Hz), 59.4 (q, OCH₃, J=141.4 Hz); GC/MS 231 (6, M+1), 230 (46, M⁺), 142 (39), 141 (100), 139 (24), 128 (12), 127 (16), 115 (49).

Anal. Calcd for $C_{14}H_{14}O_3$: C, 73.03; H, 6.13.

Found: C, 72.78; H, 6.05.

1-Naphthylmethyl cyanoacetate (1h): yield 51%; mp 42–43°C; bp 110–112°C at 0.5 mm Hg; UV λ_{\max} 266 (ϵ 6.68x10³), 275 (7.22x10³), 286 (4.88x10³); IR (nujol) 3060, 2280 (C≡N), 1745 (C=O), 1520, 1340, 1230, 1210, 800, 790, 770 cm⁻¹; ¹H NMR δ 7.98 (m, 1H), 7.86–7.90 (m, 2H), 7.53–7.58 (m, 3H), 7.43–7.47 (m, 1H), 5.67 (s, 2H, CH₂O), 3.44 (s, 2H, CH₂CN); ¹³C NMR δ 162.9 (s, C=O), 133.6 (s), 131.4 (s), 129.9, 129.8 (s), 128.8, 128.1, 126.9, 126.1, 125.2, 123.2, 112.9 (s, C≡N), 66.7 (t, CH₂O, J=149.3 Hz), 24.7 (t, CH₂CN, J=136.8 Hz); GC/MS 226 (7, M+1), 225 (47, M⁺), 158 (17), 142 (13), 141 (10⁰), 140 (26), 129 (13), 128 (12), 127 (13), 115 (27).

Anal. Calcd for C₁₄H₁₁NO₂: C, 74.65; H, 4.92; N, 6.22.

Found: C, 74.60; H, 4.84; N, 6.19.

1-Naphthylmethyl phenylacetate (2a): yield 62%; bp 196–200°C at 0.5 mm Hg [lit. [89] bp 212°C at 4–5 mm Hg]; UV λ_{\max} 265 (ϵ 6.37x10³), 275 (7.39x10³), 284 (5.29x10³); IR (neat) 3010, 2930, 1740 (C=O), 1600, 1520, 1495, 1455, 1240, 1145, 940, 785, 765 cm⁻¹; ¹H NMR δ 7.73–7.75 (m, 1H), 7.62–7.68 (m, 2H), 7.30–7.33 (m, 3H), 7.22 (t, 1H, J=7.6 Hz), 7.09 (s, 5H), 5.39 (s, 2H, CH₂O), 3.47 (s, 2H, CH₂C(=O)); ¹³C NMR δ 171.4 (s, C=O), 133.8 (s), 133.6 (s), 131.5 (s), 131.2 (s), 129.2, 128.6, 128.5, 127.4, 127.0, 126.4, 125.9, 125.2, 123.5, 65.0 (t, CH₂O, J=147.8 Hz), 41.3 (t, CH₂C(=O), J=129.8 Hz); GC/MS 277 (7, M+1), 276 (39, M⁺), 142 (18), 141 (100), 115 (24), 91 (24).

1-Naphthylmethyl 4-methoxyphenylacetate (2b): yield 48%; bp 118–120°C at 0.5 mm Hg; UV λ_{max} 266 (ϵ 8.16x10³), 275 (8.52x10³), 286 (5.15x10³); IR (neat) 3080, 2980, 1740 (C=O), 1615, 1515, 1250, 1150, 1040, 980, 795, 780 cm⁻¹; ¹H NMR δ 7.89–7.91 (m, 1H), 7.79–7.85 (m, 2H), 7.46–7.49 (m, 3H), 7.40 (t, 1H, J=7.6 Hz), 7.16 (d, 2H, J=8.4 Hz), 6.81 (d, 2H, J=8.4 Hz), 5.55 (s, 2H, CH₂O), 3.74 (s, 3H, OCH₃), 3.57 (s, 2H, CH₂C(=O)); ¹³C NMR δ 171.4 (s, C=O), 158.8 (s), 133.7 (s), 131.6 (s), 131.4 (s), 130.1 (d, J=153.3 Hz), 129.1, 128.5, 127.1, 126.3, 126.0 (s), 125.7, 125.1, 123.5, 114.0 (d, J=158.7 Hz), 64.7 (t, CH₂O, J=148.2 Hz), 55.2 (q, OCH₃, J=143.5 Hz), 40.4 (t, CH₂C(=O), J=130.0 Hz); GC/MS 307 (6, M+1), 306 (29, M⁺), 142 (8), 141 (58), 121 (100), 115 (16), 78 (8).

Anal. Calcd for C₂₀H₁₈O₃: C, 78.41; H, 5.92.

Found: C, 78.16; H, 5.82.

1-Naphthylmethyl 3-methoxyphenylacetate (2c): yield 46%; bp 112°C at 0.5 mm Hg; UV λ_{max} 266 (ϵ 9.17x10³), 275 (9.25x10³), 286 (5.24x10³); IR (neat) 3020, 2930, 1735 (C=O), 1600, 1490, 1255, 1140, 1040, 970, 780, 760 cm⁻¹; ¹H NMR δ 7.89–7.91 (m, 1H), 7.79–7.85 (m, 2H), 7.46–7.48 (m, 3H), 7.39 (t, 1H, J=7.6 Hz), 7.18 (t, 1H, J=8.4 Hz), 6.77–6.84 (m, 3H), 5.55 (s, 2H, CH₂O), 3.67 (s, 3H, OCH₃), 3.60 (s, 2H, CH₂C(=O)); ¹³C NMR δ 171.3 (s, C=O), 159.6 (s), 135.2 (s), 133.6 (s), 131.5 (s), 131.2 (s), 129.5, 129.3, 128.6, 127.4, 126.5, 125.9, 125.2, 123.5, 121.6, 114.6, 112.9, 65.0 (t, CH₂O, J=147.7 Hz), 55.1 (q, OCH₃, J=143.8 Hz), 41.4 (t, CH₂C(=O), J=129.5 Hz); GC/MS 307 (9, M+1), 306 (42, M⁺), 142 (13), 141 (100), 121 (11), 115

(17), 91 (6), 78 (5).

Anal. Calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92.

Found: C, 78.67; H, 6.00.

1-Naphthylmethyl 4-methylphenylacetate (2d): yield 55%; mp 41–42°C; UV λ_{max} 265 (ϵ 5.49×10^3), 275 (7.54×10^3), 284 (4.46×10^3); IR (nujol) 1730 (C=O), 1505, 1285, 1250, 1125, 965, 785, 760 cm^{-1} ; 1H NMR δ 7.91–7.94 (m, 1H), 7.82–7.88 (m, 2H), 7.48–7.51 (m, 3H), 7.42 (t, 1H, $J=7.5$ Hz), 7.15 (d, 2H, $J=8.0$ Hz), 5.56 (s, 2H, CH_2O), 3.62 (s, 2H, $CH_2C(=O)$), 2.32 (s, 3H, CH_3); ^{13}C NMR δ 171.6 (s, C=O), 136.6 (s), 133.6 (s), 131.5 (s), 131.3 (s), 130.7 (s), 129.2, 128.6, 127.3, 126.4, 125.8, 125.1, 123.5, 64.9 (t, CH_2O , $J=148.4$ Hz), 40.9 (t, $CH_2C(=O)$, $J=129.9$ Hz), 21.0 (q, CH_3 , $J=126.0$ Hz); GC/MS 291 (12, $M+1$), 290 (49, M^+), 142 (20), 141 (100), 115 (24), 105 (49), 77 (11).

Anal. Calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25.

Found: C, 82.72; H, 6.21.

1-Naphthylmethyl 3-methylphenylacetate (2e): yield 41%; mp 30–31°C; UV λ_{max} 265 (ϵ 5.64×10^3), 275 (6.56×10^3), 284 (4.60×10^3); IR (nujol) 1730 (C=O), 1605, 1245, 1135, 970, 780, 760 cm^{-1} ; 1H NMR δ 7.90–7.93 (m, 1H), 7.81–7.87 (m, 2H), 7.48–7.50 (m, 3H), 7.41 (t, 1H, $J=7.9$ Hz), 7.04–7.06 (m, 3H), 5.57 (s, 2H, CH_2O), 3.61 (s, 2H, $CH_2C(=O)$), 2.28 (s, 3H, CH_3); ^{13}C NMR δ 171.5 (s, C=O), 138.1 (s), 133.7 (s), 131.5 (s), 131.3 (s), 130.0, 129.2, 128.9 (s), 128.6, 128.4, 127.8, 127.4,

126.4, 126.3, 125.9, 125.2, 123.6, 65.0 (t, CH₂O, J=126.6 Hz), 41.3 (t, CH₂C(=O), J=130.1 Hz), 21.3 (q, CH₃, J=125.1 Hz); GC/MS 291 (11, M+1), 290 (49, M⁺), 142 (12), 141 (100), 115 (20), 105 (12).

Anal. Calcd for C₂₀H₁₈O₂: C, 82.73; H, 6.25.

Found: C, 82.56; H, 6.29.

1-Naphthylmethyl 4-fluorophenylacetate (2f): yield 57%; mp 57–58°C; UV λ_{max} 265 (ε 6.10x10³), 275 (6.82x10³), 284 (4.68x10³); IR (nujol) 1735 (C=O), 1595, 1505, 1290, 1220, 1125, 970, 785, 760 cm⁻¹; ¹H NMR δ 7.83–7.92 (m, 3H), 7.48–7.52 (m, 3H), 7.42 (t, 1H, J=7.6 Hz), 7.19–7.24 (m, 2H), 6.97 (t, 2H, J=8.7 Hz), 5.57 (s, 2H, CH₂O), 3.62 (s, 2H, CH₂C(=O)); ¹³C NMR δ 171.2 (s, C=O), 162.0 (d, CF, J=245.2 Hz), 133.7 (s), 131.5 (s), 131.1 (s), 130.9, 129.5 (s), 129.3, 128.7, 127.5, 126.5, 125.9, 125.2, 123.5, 115.1 (dd, J_{CH}=162.1 Hz, J_{CCF}=21.3 Hz), 65.1 (t, CH₂O, J=148.4 Hz), 40.5 (t, CH₂C(-O), J=129.5 Hz); GC/MS 295 (6, M+1), 294 (30, M⁺), 142 (13), 141 (100), 115 (15), 109 (16).

Anal. Calcd for C₁₉H₁₅FO₂: C, 77.54; H, 5.14.

Found: C, 77.32; H, 5.24.

1-Naphthylmethyl 3-fluorophenylacetate (2g): yield 40%; mp 55–57°C; UV λ_{max} 264 (ε 6.49x10³), 276 (7.03x10³), 285 (4.97x10³); IR (nujol) 1730 (C=O), 1585, 1485, 1280, 1250, 1230, 1135, 970, 865, 790, 770 cm⁻¹; ¹H NMR δ 7.82–7.92 (m, 3H), 7.48–7.51 (m, 3H), 7.41 (t, 1H, J=7.6 Hz), 7.20–7.26 (m, 1H), 6.91–7.02 (m, 3H),

5.57 (s, 2H, CH₂O), 3.63 (s, 2H, CH₂C(=O)); ¹³C NMR δ 170.8 (s, C=O), 165.0 (d, CF, J=245.0 Hz), 133.7 (s), 131.5 (s), 131.1 (s), 130.0 (s), 129.9, 129.4, 128.7, 127.5, 126.5, 125.9, 125.2, 125.0, 123.5, 116.3 (dd, J_{CH}=162.8 Hz, J_{CCF}=21.7 Hz), 114.1 (dd, J_{CH}=162.9 Hz, J_{CCF}=20.8 Hz), 65.2 (t, CH₂O, J=148.1 Hz), 41.0 (t, CH₂C(=O), J=130.1 Hz); GC/MS 295 (23, M+1), 294 (100, M⁺), 158 (24), 142 (41), 141 (100), 128 (12), 127 (18), 115 (79), 109 (48), 83 (23).

Anal. Calcd for C₂₀H₁₅FO₂: C, 77.54; H, 5.14.

Found: C, 77.52; H, 5.15.

1-Naphthylmethyl 4-trifluoromethylphenylacetate (2h): yield 35%; mp 64–65°C; UV λ_{max} 265 (ε 5.61x10³), 275 (7.54x10³), 284 (4.33x10³); IR (nujol) 1730 (C=O), 1325, 1280, 1250, 1160, 1140, 1060, 970, 815, 790, 765 cm⁻¹; ¹H NMR δ 7.83–7.89 (m, 3H), 7.53 (d, 2H, J=8.1 Hz), 7.47–7.51 (m, 3H), 7.42 (t, 1H, J=7.6 Hz), 7.34 (d, 2H, J=8.1 Hz), 5.58 (s, 2H, CH₂O), 3.70 (s, 2H, CH₂C(=O)); ¹³C NMR δ 170.6 (s, C=O), 137.7 (s), 133.7 (s), 131.5 (s), 131.0 (s), 129.7, 129.4, 128.7, 127.7, 126.5, 126.3 (s), 126.0, 125.7, 125.4 (CF₃), 125.2, 123.4, 65.3 (t, CH₂O, J=147.8 Hz), 41.1 (t, CH₂C(=O), J=130.5 Hz); GC/MS 345 (18, M+1), 344 (84, M⁺), 159 (16), 158 (18), 142 (18), 141 (100), 139 (12), 115 (24), 109 (9).

Anal. Calcd for C₂₀H₁₅F₃O₂: C, 69.76; H, 4.39.

Found: C, 69.57; H, 4.64.

1-Naphthylmethyl 3-trifluoromethylphenylacetate (2i): yield 41%; mp 61–63°C; UV

λ_{\max} 265 (ϵ 6.61×10^3), 275 (7.24×10^3), 283 (5.17×10^3); IR (nujol) 1730 (C=O), 1325, 1290, 1245, 1170, 1105, 1065, 965, 790, 765 cm^{-1} ; ^1H NMR δ 7.87–7.90 (m, 1H), 7.79–7.84 (m, 2H), 7.46–7.51 (m, 5H), 7.32–7.41 (m, 3H), 5.56 (s, 2H, CH_2O), 3.66 (s, 2H, $\text{CH}_2\text{C}(=\text{O})$); ^{13}C NMR δ 170.6 (s, C=O), 134.7 (s), 133.7 (s), 132.7, 131.5 (s), 131.0 (s), 129.4, 128.9, 128.7, 127.6, 126.5, 126.3, 126.1, 126.0 (d, CF_3 , $J=281.8$ Hz), 125.5 (s), 125.2, 124.0, 123.4, 65.3 (t, CH_2O , $J=151.2$ Hz), 41.0 (t, $\text{CH}_2\text{C}(=\text{O})$, $J=129.7$ Hz); GC/MS 345 (37, $\text{M}+1$), 344 (100, M^+), 159 (46), 158 (42), 142 (43), 141 (100), 139 (25), 128 (16), 127 (19), 115 (77), 109 (21).

Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{O}_2$: C, 69.76; H, 4.39.

Found: C, 69.97; H, 4.50.

1-Naphthylmethyl 4-cyanophenylacetate (2j): yield 35%; mp 116–118°C; UV λ_{\max} 265 (ϵ 6.24×10^3), 275 (7.07×10^3), 284 (4.65×10^3); IR (nujol) 2120 (C \equiv N), 1740 (C=O), 1340, 1215, 1175, 1155, 945, 775 cm^{-1} ; ^1H NMR δ 7.84–7.91 (m, 3H), 7.38–7.54 (m, 5H), 7.16–7.26 (m, 1H), 7.12 (d, 2H, $J=8.3$ Hz), 5.57 (s, 2H, CH_2O), 3.60 (s, 2H, $\text{CH}_2\text{C}(=\text{O})$); ^{13}C NMR δ 170.1 (s, C=O), 139.1 (s), 133.7 (s), 132.2, 131.5 (s), 130.8 (s), 130.1, 129.5, 128.7, 127.8, 126.5, 126.0, 125.2, 123.4, 118.6 (s, C \equiv N), 111.2 (s, CCN), 65.5 (t, CH_2O , $J=145.8$ Hz), 41.3 (t, $\text{CH}_2\text{C}(=\text{O})$, $J=130.6$ Hz); GC/MS 302 (7, $\text{M}+1$), 301 (33, M^+), 142 (12), 141 (100), 116 (11), 115 (18).

Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_2$: C, 79.72; H, 5.02; N, 4.65.

Found: C, 79.36; H, 4.90; N, 4.69.

1-Naphthylmethyl 3-cyanophenylacetate (2k): yield 43%; mp 92–93°C; UV λ_{\max} 266 (ϵ 6.32×10^3), 275 (7.10×10^3), 284 (4.65×10^3); IR (nujol) 2100 (C≡N), 1730 (C=O), 1310, 1240, 1215, 1130, 970, 790, 760 cm^{-1} ; ^1H NMR δ 7.84–7.89 (m, 3H), 7.36–7.53 (m, 8H), 5.59 (s, 2H, CH_2O), 3.66 (s, 2H, $\text{CH}_2\text{C}(=\text{O})$); ^{13}C NMR δ 170.2 (s, C=O), 135.2 (s), 133.9, 133.7 (s), 132.8, 131.5 (s), 130.9, 129.5, 129.4 (s), 129.3, 128.7, 127.8, 126.6, 126.0, 125.2, 123.3, 118.5 (s, C≡N), 112.6 (s, CCN), 65.4 (t, CH_2O , $J=148.1$ Hz), 40.7 (t, $\text{CH}_2\text{C}(=\text{O})$, $J=130.6$ Hz); GC/MS 302 (7, $M+1$), 301 (35, M^+), 142 (15), 141 (100), 116 (12), 115 (26).

Anal. Calcd for $\text{C}_{20}\text{H}_{15}\text{NO}_2$: C, 79.72; H, 5.02; N, 4.65.

Found: C, 79.35; H, 4.95; N, 4.70.

Benzyl acetate (3a): This compound is commercially available and was distilled under reduced pressure and column chromatographed through silica gel before use. The ^1H , ^{13}C , UV and infrared spectra were identical to those in the literature [90, 91, 92, 93].

4-methylbenzyl acetate (3b): yield 39%; bp 65–67°C at 0.5 mm Hg [lit. [94] 137–138°C at 30 mm Hg]; UV λ_{\max} 253 (ϵ 230), 259 (270), 269 (220), 268 (180); IR (neat) 3040, 3020, 2960, 2920, 1750 (C=O), 1520, 1380, 1360, 1240, 1020, 800 cm^{-1} ; ^1H NMR δ 7.25 (d, 2H, $J=8.0$ Hz), 7.17 (d, 2H, $J=7.9$ Hz), 5.06 (s, 2H, CH_2O), 2.35 (s, 3H, CH_3), 2.08 (s, 3H, $\text{C}(=\text{O})\text{CH}_3$); ^{13}C NMR δ 170.8 (s, C=O), 138.0 (s), 132.8 (s), 129.1 (d, $J=157.6$ Hz), 128.3 (d, $J=158.3$ Hz), 66.2 (t, CH_2O , $J=147.2$ Hz), 21.1 (q, $\text{C}(=\text{O})\text{CH}_3$, $J=126.2$ Hz), 21.0 (q, CH_3 , $J=129.9$ Hz); GC/MS 165 (6, $M+1$), 164 (74,

M⁺), 123 (11), 122 (100), 107 (79), 105 (100), 104 (92), 103 (49), 93 (23), 91 (40), 79 (40), 78 (79), 77 (50), 65 (32).

3-methoxybenzyl acetate (3c): yield 49%; bp 86–89°C at 0.5 mm Hg [lit. [94] 165–167°C at 30 mm Hg]; UV λ_{\max} 271 (ϵ 1.93x10³), 277 (1.75x10³); IR (neat) 3000, 2940, 2820, 1750 (C=O), 1610, 1590, 1490, 1460, 1380, 1360, 1290, 1250, 1155, 1040, 775, 735, 685 cm⁻¹; ¹H NMR δ 7.27 (t, 1H, J=7.9 Hz), 6.85–6.94 (m, 3H), 5.07 (s, 2H, CH₂O), 3.80 (s, 3H, OCH₃), 2.10 (s, 3H, CH₃); ¹³C NMR δ 170.8 (s, C=O), 159.6 (s), 137.3 (s), 129.6 (d, J=159.1 Hz), 120.3 (d, J=160.1 Hz), 113.6 (d, J=158.5 Hz), 66.1 (t, CH₂O, J=147.8 Hz), 55.2 (q, OCH₃, J=143.8 Hz), 21.0 (q, CH₃, J=129.6 Hz); GC/MS 181 (5, M+1), 180 (47, M⁺), 139 (12), 138 (100), 121 (41), 109 (48), 107 (21), 92 (12), 91 (49), 78 (24), 77 (46), 65 (20).

4-methoxybenzyl acetate (3d): yield 44%; bp 92–95°C at 0.5 mm Hg [lit. [94] 180–181°C at 30 mm Hg]; UV: Identical to that found in the literature [95]; IR (neat) 3000, 2960, 2900, 2820, 1745 (C=O), 1620, 1590, 1520, 1470, 1380, 1360, 1300, 1250, 1175, 1030, 960, 820 cm⁻¹; ¹H NMR δ 7.28 (d, 2H, J=8.6 Hz), 6.87 (d, 2H, J=8.7 Hz), 5.02 (s, 2H, CH₂O), 3.77 (s, 3H, OCH₃), 2.05 (s, 3H, C(=O)CH₃); ¹³C NMR δ 170.8 (s, C=O), 159.5 (s), 130.0 (d, J=158.0 Hz), 127.9 (s), 113.8 (d, J=159.1 Hz), 66.0 (t, CH₂O, J=147.8 Hz), 55.2 (q, OCH₃, J=143.7 Hz), 21.0 (q, CH₃, J=129.4 Hz); GC/MS 181 (5, M+1), 180 (48, M⁺), 138 (24), 122 (11), 121 (100), 120 (42), 92 (11), 91 (37), 78 (20), 77 (33).

4-cyanobenzyl acetate (3e): yield 62%; mp 64–65°C [lit.[94] 64–65°C]; UV λ_{\max} 265 (ϵ 760), 270 (800), 276 (750); IR (nujol) 3100, 2260 (C \equiv N), 1750 (C=O), 1630, 1380, 1265, 1065, 940, 835 cm^{-1} ; ^1H NMR δ 7.67 (d, 2H, $J=8.2$ Hz), 7.46 (d, 2H, $J=7.9$ Hz), 5.16 (s, 2H, CH_2O), 2.14 (s, 3H, CH_3); ^{13}C NMR δ 170.4 (s, C=O), 141.2 (s), 132.3 (d, $J=173.8$ Hz), 128.3 (d, $J=163.8$ Hz), 118.5 (s, C \equiv N), 112.0 (s, CCN), 65.0 (t, CH_2O , $J=148.3$ Hz), 20.8 (q, CH_3 , $J=129.6$ Hz); GC/MS 176 (4, $M+1$), 175 (37, M^+), 134 (11), 133 (100), 132 (20), 116 (81), 115 (40), 114 (10), 89 (33), 77 (12), 76 (11), 75 (12), 63 (20).

Benzyl 2,2-dimethylpropanoate (4a): yield 65%; bp 63–65°C at 1.5 mm Hg [lit. [96] 67–70°C at 2 mm Hg]; UV λ_{\max} 246 (ϵ 158), 252 (198), 256 (158), 262 (99); IR (neat) 3050, 3020, 2960, 2940, 2920, 1735 (C=O), 1480, 1460, 1280, 1150, 1025, 740, 725, 690 cm^{-1} ; ^1H NMR δ 7.30 (s, 5H), 5.08 (s, 2H, CH_2O), 1.21 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR δ 178.2 (s, C=O), 136.4 (s), 128.4 (d, $J=160.2$ Hz), 127.6 (d, $J=158.0$ Hz), 66.0 (t, CH_2O , $J=147.4$ Hz), 38.8 (s, $\text{C}(\text{CH}_3)_3$), 27.2 (q, CH_3 , $J=127.8$ Hz); GC/MS 193 (5, $M+1$), 192 (40, M^+), 108 (20), 107 (11), 92 (37), 91 (100), 89 (21), 77 (37), 65 (82), 58 (24), 57 (100).

4-methylbenzyl 2,2-dimethylpropanoate (4b): yield 58%; bp 72–75°C at 1.5 mm Hg; UV λ_{\max} 254 (ϵ 215), 260 (265), 264 (210), 268 (180); IR (neat) 3040, 3020, 2960, 2920, 2850, 1735 (C=O), 1485, 1440, 1430, 1280, 1155, 1030, 795, 760 cm^{-1} ; ^1H NMR δ 7.22 (d, 2H, $J=7.9$ Hz), 7.15 (d, 2H, $J=7.9$ Hz), 5.06 (s, 2H, CH_2O), 2.34 (s, 3H, CH_3), 1.21 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR δ 178.3 (s, C=O), 137.6 (s), 133.4 (s),

129.1 (d, $J=157.4$ Hz), 127.8 (d, $J=157.9$ Hz), 66.0 (t, CH_2O , $J=146.9$ Hz), 38.7 (s, $\text{C}(\text{CH}_3)_3$), 27.2 (q, $\text{C}(\text{CH}_3)_3$, $J=128.7$ Hz), 21.2 (q, CH_3 , $J=127.2$ Hz); GC/MS 207 (3, $\text{M}+1$), 206 (23, M^+), 107 (10), 106 (37), 105 (100), 91 (16), 79 (23), 78 (19), 77 (39), 57 (99).

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$: C, 75.69; H, 8.80;

Found: C, 75.80; H, 8.60.

4-methoxybenzyl 2,2-dimethylpropanoate (4c): yield 53%; bp 85–87°C at 1.5 mm Hg; UV λ_{max} 272 (ϵ 1.90×10^3), 278 (1.70×10^3); IR (neat) 3000, 2980, 2940, 2880, 2840, 1740 (C=O), 1630, 1530, 1280, 1260, 1150, 1040, 820 cm^{-1} ; ^1H NMR δ 7.27 (d, 2H, $J=8.6$ Hz), 6.88 (d, 2H, $J=8.6$ Hz), 5.03 (s, 2H, CH_2O), 3.79 (s, 3H, OCH_3), 1.20 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR δ 178.4 (s, C=O), 159.3 (s), 129.5 (d, $J=158.8$ Hz), 128.5 (s), 113.8 (d, $J=159.2$ Hz), 65.8 (t, CH_2O , $J=146.9$ Hz), 55.2 (q, OCH_3 , $J=143.8$), 38.7 (s, $\text{C}(\text{CH}_3)_3$), 27.1 (q, CH_3 , $J=127.2$ Hz); GC/MS 223 (2, $\text{M}+1$), 222 (14, M^+), 122 (12), 121 (100).

Anal. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3$: C, 70.24; H, 8.16;

Found: C, 69.92; H, 8.00.

3-methoxybenzyl 2,2-dimethylpropanoate (4d): yield 49%; bp 80–82°C at 1.5 mm Hg; UV λ_{max} 271 (ϵ 1.93×10^3), 277 (1.74×10^3); IR (neat) 3020, 2980, 2910, 2880, 2830, 1735 (C=O), 1625, 1600, 1500, 1480, 1280, 1160, 1040, 770, 680 cm^{-1} ; ^1H NMR δ 7.25 (t, 1H, $J=7.9$ Hz), 6.81–6.91 (m, 3H), 5.08 (s, 2H, CH_2O), 3.78 (s, 3H,

OCH₃), 1.23 (s, 9H, C(CH₃)₃); ¹³C NMR δ 178.2 (s, C=O), 159.6 (s), 138.0 (s), 129.5 (d, J=159.1 Hz), 119.7 (d, J=161.0 Hz), 113.3 (d, J=158.2 Hz), 113.0 (d, J=157.3 Hz), 65.8 (t, CH₂O, J=147.6 Hz), 55.1 (q, OCH₃, J=144.0 Hz), 38.8 (s, C(CH₃)₃), 27.2 (q, CH₃, J=126.9 Hz); GC/MS 223 (11, M+1), 222 (79, M⁺), 138 (98), 137 (37), 136 (39), 122 (24), 121 (100), 109 (37), 107 (11), 91 (65), 78 (48), 77 (48), 65 (32), 57 (99).

Anal. Calcd for C₁₃H₁₈O₃: C, 70.24; H, 8.16;

Found: C, 69.91; H, 7.84.

4-cyanobenzyl 2,2-dimethylpropanoate (4e): yield 43%; bp 76–78°C at 1.5 mm Hg; UV λ_{max} 265 (ε 775), 270 (850), 277 (750); IR (neat) 2980, 2940, 2900, 2880, 2220 (C≡N), 1740 (C=O), 1620, 1485, 1460, 1400, 1370, 1280, 1150, 820 cm⁻¹; ¹H NMR δ 7.65 (d, 2H, J=8.2 Hz), 7.44 (d, 2H, J=7.9 Hz), 5.15 (s, 2H, CH₂O), 1.25 (s, 9H, C(CH₃)₃); ¹³C NMR δ 177.9 (s, C=O), 141.7 (s), 132.3 (d, J=164.8 Hz), 127.8 (d, J=162.7 Hz), 118.5 (s, C≡N), 111.7 (s, CCN), 64.8 (t, CH₂O, J=147.6 Hz), 38.8 (s, C(CH₃)₃), 27.1 (q, CH₃, J=126.9 Hz); GC/MS 217 (5, M⁺), 116 (33), 89 (13), 85 (14), 57 (100).

Anal. Calcd for C₁₃H₁₅NO₂: C, 71.87; H, 6.96; N, 6.45;

Found: C, 71.77; H, 6.76; N, 6.49.

3.7 Preparation of Photoproducts

Photoproduct **10** was prepared by the method by Wright *et al.* and the ^1H NMR was identical to that in the literature [97] (Scheme 8).

Decarboxylation photoproducts of the 1-naphthylmethyl acetate esters were synthesized independently. 1-Ethynaphthalene (**11a**) was synthesized by Wolff-Kishner reduction of 1-(1-naphthyl)ethanone using the Huang-Minlon modification [98] (Scheme 9). 1-Propylnaphthalene (**11b**) was produced from 1-(1-naphthyl)propanone by the method used by Kloetzel *et al.* [99]. The ketone was reduced by the Wolff-Kishner reduction using the Huang-Minlon modification [98] (Scheme 9). 2-Methyl-1-(1-naphthyl)propanone was synthesized by Grignard addition of isopropylmagnesium bromide to 1-cyanonaphthalene [99] followed by hydrolysis. The resulting ketone was reduced by triethylsilane in trifluoroacetic acid using the procedure of West *et al.* [100] (Scheme 9) giving 2-methyl-1-naphthylpropane (**11d**). 2,2-Dimethyl-1-naphthylpropane (**11f**) was synthesized by the procedure of Bullpit and Kitching [101]. 1-(2-Methoxyethyl) naphthalene methyl ether (**11g**) was obtained by the method of Todesco and Put [102]. 3-(1-Naphthyl)propionitrile (**11h**) was synthesized from 2-(1-naphthyl) ethanol. The alcohol was converted to the mesylate which was then subjected to potassium cyanide in DMF (Scheme 10). 1-(1-Naphthyl)-2-phenylethane (**12a**), 1-(1-naphthyl)-3-phenylpropane (**11c**) and 4-(1-naphthyl)-1-butene (**11e**) were isolated from the preparative photolysis by flash chromatography. The decarboxylation products had identical ^1H nmr to those in the literature [103, 104, 105, 101, 102, 106]. The

decarboxylation products from the 1-naphthylmethyl phenylacetates, **12a-k**, were identified by ^1H NMR and were consistent with their structure.

Photoproducts **16a-e** were prepared by the same method starting from the corresponding alcohols. To a solution of 5 mmol of the benzyl alcohol, **15a-e**, in 10 mL of dry DMF was added washed NaH (0.12 g, 5 mmol) in portions. After the mixture was stirred for 15 min., 1.9 mL (6 mmol) of CH_3I was added and stirring was continued for 1 hour at room temperature (Scheme 18). Conventional workup gave an oil which was chromatographed through silica gel and eluted with 40% CH_2Cl_2 :hexane to give the ether in 70–80% yield. The ethers were purified by distillation. The ^1H nmr were identical to those in the literature [107].

The substituted toluenes (toluene, p-xylene, 4-methylanisole, 3-methylanisole and p-tolunitrile) (**19a-e**) were obtained from the Aldrich Chemical Company. The ^1H NMR were identical to those in the literature [108].

Ethylbenzene (**17a**) was obtained from the Aldrich Chemical Company and was used without further purification. Ethylbenzene was used for determination of the product yields of the all the coupling products (**17a-e**).

1,2-Diphenylethane (**18a**) was obtained from trans-Stilbene by atmospheric hydrogenation over 10% palladium on carbon and was used for the determination of all the dimer products.

3.8 Preparative Photolysis

The photolysis of each of the 1-naphthylmethyl esters, **1a-h** and **2a-k**, was carried out in the following manner. A solution was prepared consisting of 300–400 mg of the ester dissolved in 300 mL of distilled methanol. The solution was placed in an immersion well and purged with nitrogen for 15 minutes before and during the irradiation. The light source was a Pyrex-filtered 200 W medium-pressure Hanovia mercury lamp. Irradiation was continued until the starting ester was greater than 90% consumed. Photolysis times varied from 3 hours for the more reactive esters (**2b**, **2c**) to 24 hours for the less reactive ones. The photolyzed solution was concentrated under vacuum to approximately 10 mL and then 30 mL of water and 30 mL of CH_2Cl_2 were added. The CH_2Cl_2 layer was separated and extracted with 2x15 mL of a 5% aqueous NaOH solution. The CH_2Cl_2 layer was dried (MgSO_4), filtered and rotoevaporated to give an oil which was subjected to flash chromatography through silica gel using 80:20 hexane: CH_2Cl_2 as the eluent. The aqueous alkaline layer was acidified with conc. HCl, and extracted with 2x25 mL of CH_2Cl_2 . Evaporation of the dried CH_2Cl_2 layer gave products which were identified as the corresponding acids **9a-k** except for esters **1a**, **1b**, **1d-h** which the corresponding acids **8a**, **8b**, **8d-h** are water soluble and were not isolated. Acid **8c** obtained from the photolysis of ester **1c** is not water soluble and was isolated from the extraction in 42% yield.

The photolysis of each of the benzyl esters **3a-e** and **4a-e** was carried out in the following manner. A solution was prepared consisting of 100–200 mg (0.01 M) of the ester dissolved in 100 mL of distilled methanol. For quencher irradiations, 2,3-

dimethyl-1,3-butadiene was also added. The solution was placed in a 100 mL quartz tube and purged with nitrogen for 15 minutes before and during the irradiation. In each case the light source was a Rayonet photochemical reactor using 16x75W 253.7 nm light. Photolysis times varied from 30 minutes for the more reactive esters to 12 hours for the less reactive ones. The composition of the photolyzed solution was determined by retention times using calibrated standards by GLC.

3.9 Analysis of Photolysis Mixture by HPLC

The 1-naphthylmethyl ester solutions, **1a-h** and **2a-k**, were irradiated the same as described under the preparative photolysis section, but in this case solutions were prepared with 70–90 mg of ester. Analyses were done with less than 70% of the starting ester consumed. Monitoring of the reactions indicated no change in product ratios as a function of extent of conversion. In all cases, dark reactions were found to be negligibly slow. Standard solutions containing authentic samples of each photoproduct in known amounts were prepared to determine the yields of photoproducts for the photolysis. This was done by comparing the peak heights in a sample of the completed reaction mixture to peak heights of a solution containing known amounts of photoproducts.

3.10 Analysis of Photolysis Mixture by GLC

The benzyl ester solutions, 3a-e and 4a-e, were irradiated using the method described under the preparative photolysis section. Analyses were done with less than 70% of the starting ester consumed. Monitoring of the reactions indicated no change in product ratios as a function of extent of conversion. In all cases, dark reactions were found to be negligibly slow. Standard solutions containing authentic samples of each photoproduct in known amounts were prepared to determine the yields of photoproducts for the photolysis. This was done by comparing the integrated values to the integrated values of a solution containing known amounts of photoproducts. For the quenching studies, the product yields were determined at ester concentrations of <20% converted to products.

3.11 Fluorescence Studies

Fluorescence studies were done using a Perkin Elmer MPF 66 fluorescence spectrophotometer at 25°C. Corrected spectra were obtained. All samples were degassed by three freeze-pump-thaw cycles. Fluorescence quantum yields were determined by comparison with the fluorescence quantum yield of 1-methylnaphthalene ($\phi_f=0.21$ [11]) for the 1-naphthylmethyl esters and toluene (assuming $\phi_f=0.13$ [67]) for the benzyl esters. Singlet state energies were determined by the position of the 0,0 band using the overlap between the emission and excitation spectra. Fluorescence lifetimes were measured using a PRA single photon counting apparatus with the hydrogen flash lamp of pulse width about 0.8 ns.

3.12 Fluorescence Quenching Studies

Fluorescence quenching studies were done using a Perkin Elmer MPF 66 fluorescence spectrophotometer at 25°C. All samples were degassed by three freeze-pump-thaw cycles except ester 4c. Fluorescence intensities were determined with increasing diene concentrations (Table 8). The concentration of the diene used was deliberately chosen to be high enough so that there was no ambiguity about quenching of essentially all the excited triplets. The percent of singlet excited states quenched at the concentration of the diene used (1.17×10^{-3} – 40.2×10^{-3} M) can be calculated (Table 7) and these values range from 8% to 12%.

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