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MECHANISTIC STUDIES ON THE PHOTOLYSIS OF NAPHTHYLMETHYL ESTERS OF CARBOXYLIC ACIDS

by

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Submitted in partial fulfillment of the requirements

for the Degree of Doctor of Philosophy

at

Dalhousie University

Halifax, Nova Scotia

August, 1990

ISBN 0-315-64547-4

To my parents, M. A. De Costa and

D. S. Kathriarachchi

for their wonderful understanding and

encouragement

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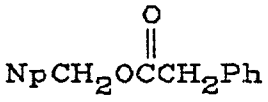
ABSTRACT

Four different ester series of substituted 1-naphthylmethanol, **16**, **20**, **29** and **35**, were synthesized. These esters were photolized in order to investigate the role of substituent effects on homolytic and heterolytic cleavage. The esters **16** and **20** behave similarly on photolysis but product partitioning is not explained by the "meta effect". However, the product ratios can be interpreted in terms of electron-transfer and decarboxylation of the in-cage radical pair resulting from homolytic cleavage. The free energy change and rate of electron-transfer of the in-cage naphthylmethyl/ phenylacetyloxy radical pair were estimated. The results obtained for the photolysis of esters, **16**, provide an excellent example of the Marcus theory of electron transfer including the "inverted region".



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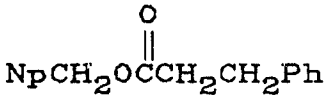

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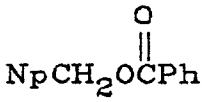

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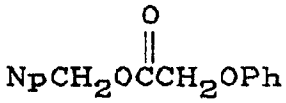

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The benzoate ester, **29**, formed an intramolecular charge transfer complex on excitation. The rate of this charge transfer process depends on the substituents both on the naphthalene and benzoate chromophores. The formation of exciplexes in these benzoate esters make them stable to the irradiation. The phenoxyacetate esters, **35**, behave unusually in that the excited state gives higher yields of products derived from the radical pair than expected. The results are interpreted by interaction between the two chromophores in the excited state.

LIST OF ABBREVIATION

A	acceptor
A	angstrom
Ac	acetic
aq.	aqueous
Ar	aromatic
cm	centimetre
D	donor
DMF	dimethylformamide
e	charge of electron
Et	ethyl
et	electron-transfer
eV	electron volt
E_S	energy of singlet state
E_T	energy of triplet state
$E_{1/2}^{ox}$	half-wave oxidation potential
$E_{1/2}^{red}$	half-wave reduction potential
g	gram
GC	gas chromatography
h	hours
HPLC	high pressure liquid chromatography
ir	infrared
J	nmr coupling constant
kcal	kilocalories
kJ	kilojoules

k_c	rate of decarboxylation
k_d	rate of diffusion
k_{et}	rate of electron-transfer
k_f	rate of fluorescence
k_I	rate of heterolytic cleavage
k_{ic}	rate of internal conversion
k_{isc}	rate of intersystem crossing
k_q	rate of quenching
k_R	rate of homolytic cleavage
LCAO	linear combination of atomic orbitals
Me	methyl
min	minutes
mg	milligram
mL	millilitre
MO	molecular orbital
MS	mass spectroscopy
nm	nanometre
nmr	nuclear magnetic resonance spectroscopy
ns	nanosecond
R	gas constant
R_t	retention time
s	second
T	temperature
uv	ultraviolet
V	Volt
ϕ_f	quantum yield of fluorescence

ϵ	extinction coefficient
λ_{max}	wavelength of maximum absorption
λ_i	inner-sphere reorganization energy
λ_o	outer-sphere reorganization energy
λ	reorganization energy
ΔG	free energy change
τ_S	singlet state lifetime

ACKNOWLEDGEMENT

I wish to express my heartfelt gratitude to my supervisor, Dr. J. A. Pincock, for helping me throughout this project regardless of his valuable time and his inspiration, encouragement and especilly for his kindness.

Thanks to Dr. P. R. Redden and Mr. J. W. Hilborn who worked with me in the laboratory.

I would like to thank Dr. D. L. Hooper and the Atlantic Regional Magnetic Resonance Center for their help in obtaining nmr spectra.

I also wish to thank Dr. D. D. M. Wayner for measuring oxidation potentials for the naphthylmethyl radicals.

I would like to thank all the people in the Dalhousie Chemistry Department who helped me in various way.

Last, but not least, I would to thank my wife Seetha for her help and understanding over the last four years.

CHAPTER 1

INTRODUCTION

Ground state solvolytic reactions involving both S_N^1 and S_N^2 mechanisms have been thoroughly studied and are quite well understood [1]. A simplified mechanism for the S_N^1 reaction involves rate-determining breaking of the σ-bond between a benzylic carbon (as an example) and a leaving group as shown below, eq. 1. According to ground state

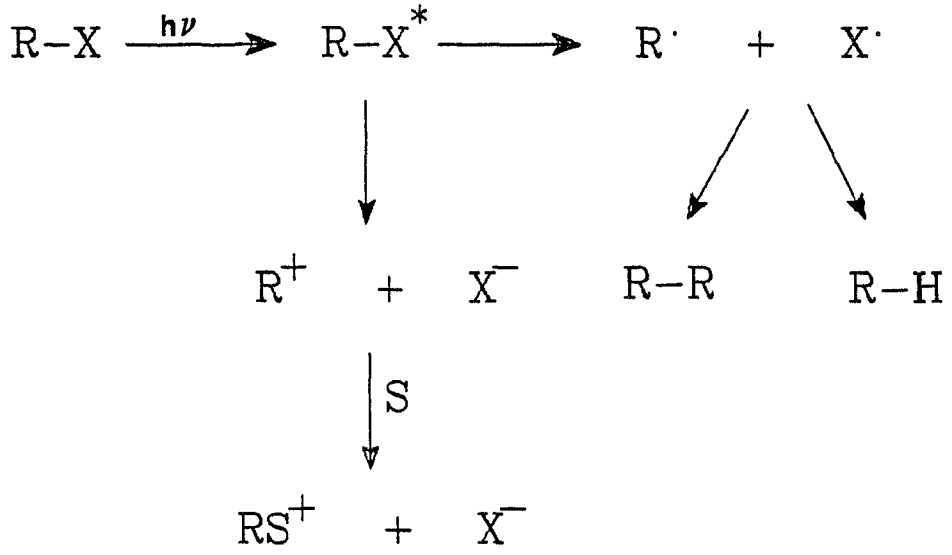
$$\begin{array}{l} ArCH_2\text{-}X + S \xrightarrow{\text{slow}} ArCH_2^+ + X^- + S \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \Big\downarrow \text{fast} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad ArCH_2S^+ + X^- \end{array} \qquad (1)$$

arguments, the rate of the reaction depends on, among other things, the substituents on the benzene ring, the nature of the leaving group and the solvent. Electron-donating groups such as a methoxy at the <u>ortho</u> or <u>para</u> positions of the benzene ring increase S_N^1 reaction rates. This is simply because there is a direct conjugative interaction between the electron-donating group on the ring with the developing positive charge on the benzylic carbon in the transition state. Such stabilization is not possible for <u>meta</u> substituents. Hammett correlations with σ^+ gave ρ^+ values that are negative and fairly large [2]. If the trapping

nucleophile is the solvent, S, these are called solvolysis reactions.

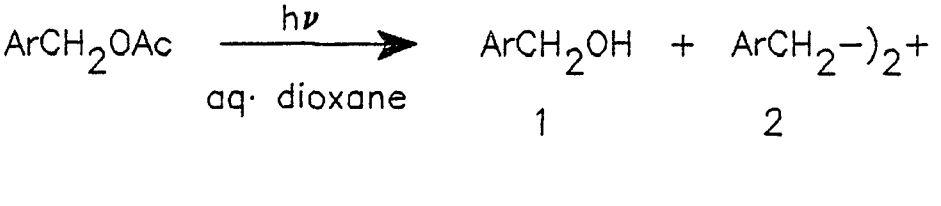
Excited states of some substrates also undergo solvolytic reactions, but in a more complicated manner [3]. In contrast to ground state chemistry, excited state S_N2 reactions have not been observed. In the excited state, the cleavage of the σ-bond can be either heterolytic to give ionic intermediates or homolytic to give radical intermediates. Moreover, these intermediates are often formed competitively in the same reaction. However, the products from each intermediate are different and therefore the two pathways can be monitored by analyzing the products. The heterolytic pathway gives a carbocationic intermediate which is usually trapped by the solvent, whereas the

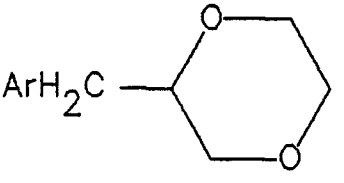
Scheme 1: General Mechanism for the Photolysis of R--X.



homolytic pathway gives radicals which undergo radical coupling or hydrogen-acom abstraction as shown in the Scheme 1. The relative proportions of these homolytic and heterolytic pathways depend on the structure of the group R, the leaving group X, the solvent S and the multiplicity of the reactive excited state. Non-nucleophilic solvents, such as benzene, enhance the proportion of the products derived from the homolytic pathway, whereas nucleophilic solvents, such as alcohols, increase the proportion of the heterolytic pathway.

Solvolysis in the excited state of benzylic compounds has been thoroughly studied beginning with the initial work of Zimmerman *et al.* [4]. Many of these studies have centered on the competition mentioned above between homolytic versus heterolytic cleavage of the σ-bond. This material has been reviewed by Cristol and Brindel [3]. In their studies of excited state benzylic cleavage, Zimmerman





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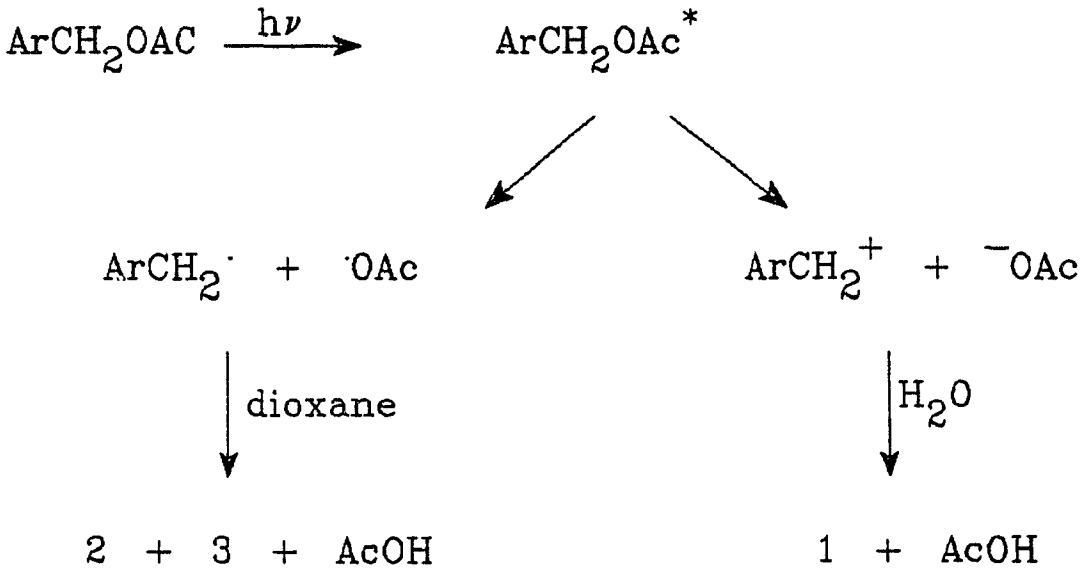
et al. [4] observed different reactivity of the excited state compared to that of the ground state. As shown in eq. 2, photolysis of benzyl acetate in aqueous dioxane gave three different products. The formation of the bibenzyl derivative, **2**, and benzyl dioxane, **3**, clearly results from formation of the benzyl radical followed by radical coupling. The formation of benzyl alcohol, **1**, result from heterolytic cleavage of the σ-bond followed by trapping of the benzyl cation by water. The proposed mechanism for these two processes is shown below in Scheme 2.

Scheme 2: Mechanism for the Photolysis of Benzylacetate.

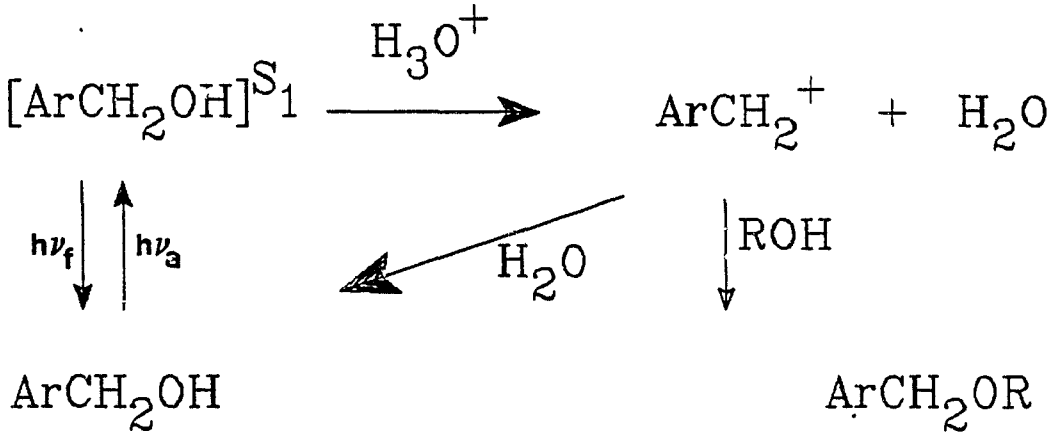


In contrast to ground state results, the observed photochemical reactivity was significantly enhanced by a

meta methoxy substituent. Also, the meta methoxy isomer gave exclusively the alcohol, 1, with high quantum yield (ϕ = 0.13) whereas the para isomer gave radical products, 2 and 3, with low quantum yields (ϕ = 0.016). The 3,5-dimethoxy compound also gave only solvolysis product. These results clearly indicate the higher reactivity of the meta-methoxy benzyl substrate relative to the para-methoxy benzyl substrate towards heterolytic σ-bond cleavage. This is the opposite of ground state reactivity. Zimmerman rationalized this enhanced excited state reactivity using Huckel LCAO-MO theory. The calculated first excited state electron density for methoxybenzene is concentrated in the ortho and meta position indicating that higher reactivity towards cation formation of the excited state of meta-methoxy benzylacetate would be expected. Zimmerman named this the "meta effect". Similar enhanced reactivity has been observed for photo-nucleophilic aromatic substitution of suitably substituted meta derivatives [5].

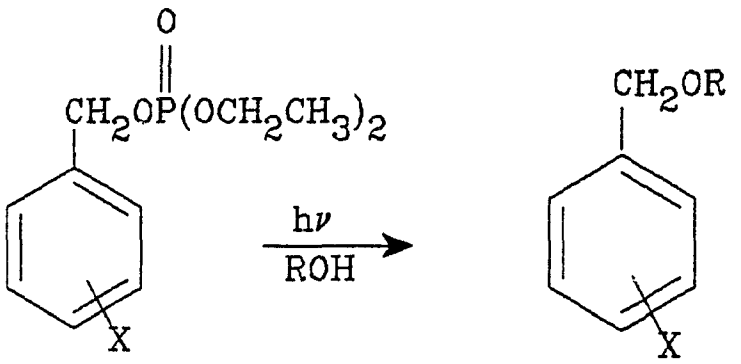
Since, that time there have been many examples of photosolvolysis results that support this idea as well as those that do not [6]. For instance, acid catalyzed fluorescence quenching and solvolysis of substituted benzyl alcohols has been observed by Wan and Turro [7]. Their proposed mechanism is given in the Scheme 3. The compounds with electron-donating substituents were found to have increased rates of fluorescence quenching. In a later

Scheme 3: Acid-Catalyzed Fluorescence Quenching of Benzyl Alcohol.



report on this work, Wan and Chak [8] have observed higher reactivity for the ortho and meta substituted methoxy compounds (ϕ = 0.01) compared to the para substituted compound (ϕ = 0.00). In these studies, Wan [9] has shown that the relative reactivities of several substituted benzyl alcohols follow the order 3,5-dimethoxy > ortho-methoxy > meta-methoxy > meta-methyl > meta-fluoro, and all of these are significantly more reactive than the para isomers.

There are, however, other closely related systems where the meta effect is not observed. For instance, Givens *et al.* [6] have observed a normal ground state order for photosolvolysis in the reaction of substituted benzyl phosphates, **4**, as shown in eq. 3. The observed quantum



(3)

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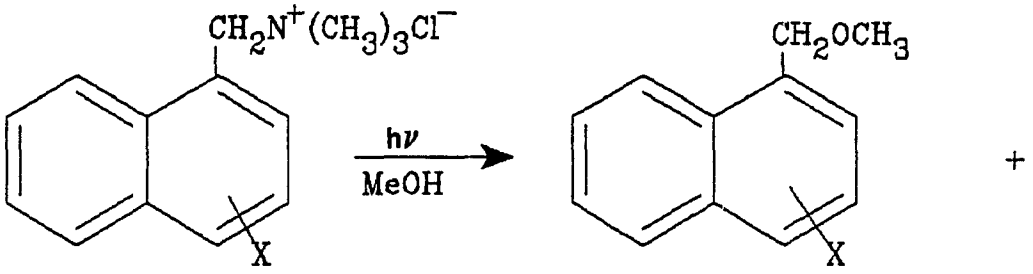
yields are 0.23, 0.18, 0.17, 0.16, 0.13, 0.063 and 0.012 for p-OCH_3, *m*-OCH_3, *p*-CH_3, H, *m*-CH_3, *p*-CF_3, and *m*-CF_3 respectively.

Pincock *et al.* [10], in their study of substituents effects in photosolvolysis reactions of 1-



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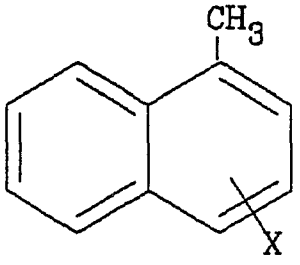

(4)

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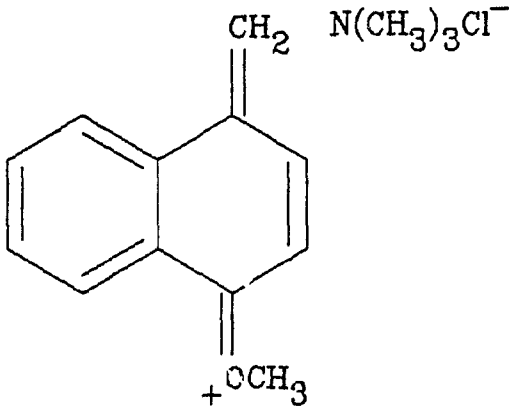
naphthylmethyltrimethylammonium chloride, **5**, eq. 4, have observed greater rates of reaction for the 4-methoxy isomer when compared to the 3-methoxy isomer. They have also observed higher yields of product **6**, derived from ionic cleavage for the 4-methoxy isomer. These results are of course not predicted by the "meta effect" argument. The authors explained this mechanistic change by considering the direct interaction between the electron-donating methoxy group and the positively charged leaving group in the ground state as shown in the structure, **8**. Therefore, internal charge transfer of this type may modify the nature of the electron density changes that occurs upon excitation and favour heterolytic cleavage. This preference should then depend on the structure of the leaving group.



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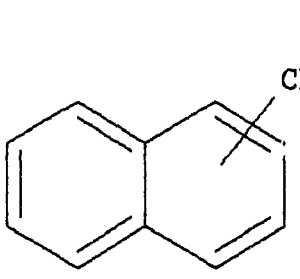
As described by Givens *et al.* [11], naphthyl derivatives absorbs above 300 nm and have triplet energies

of 57 - 62 kcal mol^{-1}. This make them suitable for studies of benzylic type photochemical reactions without interference from triplet state reactivity provided the benzylic carbon to leaving group bond strength is somewhat above 60 kcal mol^{-1}. This is true of the carbon oxygen bond of esters.

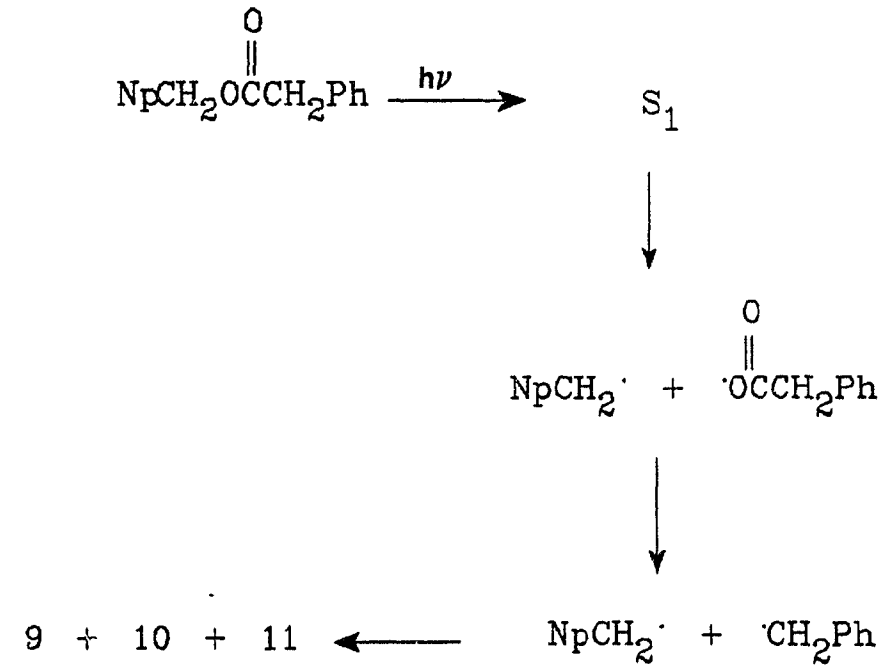
The photochemistry of naphthylmethyl esters has been studied by several authors. Ivanov *et al.* [12] have examined the photochemistry of naphthylmethyl acetates in water-acetonitrile. The major products are naphthylmethanol and acetic acid. They have confirmed that the singlet state is the reactive state by using flash photolysis and quenching studies. Givens *et al.* [11,13] have studied the photodecarboxylation of 1- and 2-naphthylmethyl phenylacetate esters in benzene as shown in eq. 5. They



$$\xrightarrow[C_6H_6]{h\nu} \underset{10}{NpCH_2CH_2Ph} + \underset{9}{NpCH_2-)_2} + \underset{11}{PhCH_2-)_2} \qquad (5)$$

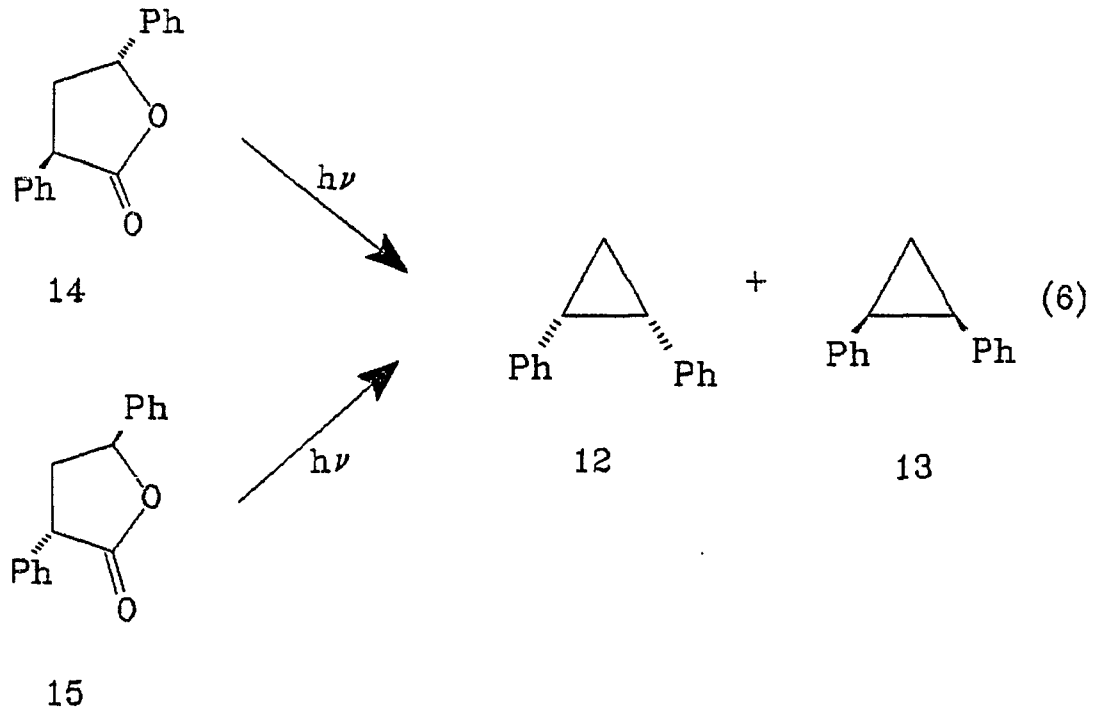
observed three products derived from the major photolysis pathway of homolytic photodecarboxylation. This is because, as mentioned before, products derived from heterolytic intermediates are not usually formed in non-nucleophilic solvents such as benzene. They have observed that **9**, **10**, and **11** were formed in a 1:10:1 ratio for both isomers. These results were rationalized by initial homolytic cleavage of the carbon-oxygen bond. Sensitization and quenching studies confirmed that the singlet state is the reactive state. The authors suggested a possible mechanism for the photodecarboxylation as shown in Scheme 4. This proposed mechanism involved the excitation of the

Scheme 4: Mechanism for the Photolysis of Naphthylmethyl Phenylacetate in Benzene.



naphthylmethyl chromophore followed by simultaneous or stepwise homolytic cleavage of the carbon-oxygen bond and expulsion of CO_2.

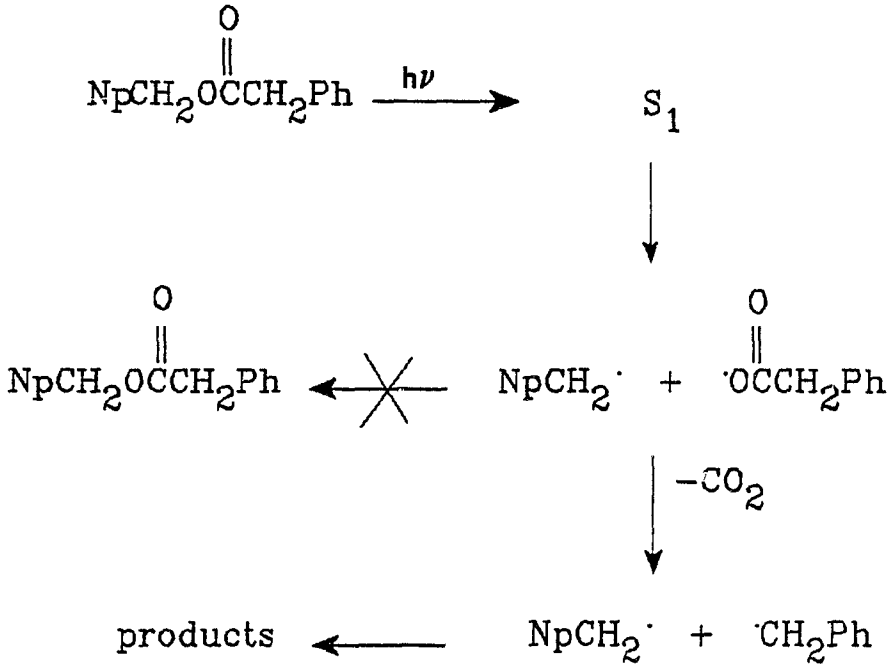
Earlier, Givens and Oettle [14] had shown that, with certain esters, photodecarboxylation could be a stepwise process. They have observed the isomeric cyclopropanes, **12** and **13**, as primary photoproducts of both **14** and **15** at low conversion, eq. 6. This suggested that CO_2 loss and C-C



bond formation could not be a totally concerted process. Furthermore,they concluded that the photodecarboxylation process occurs via discrete radical (diradical) intermediates which are formed by stepwise loss of CO_2 followed by recombination of the diradical to give the

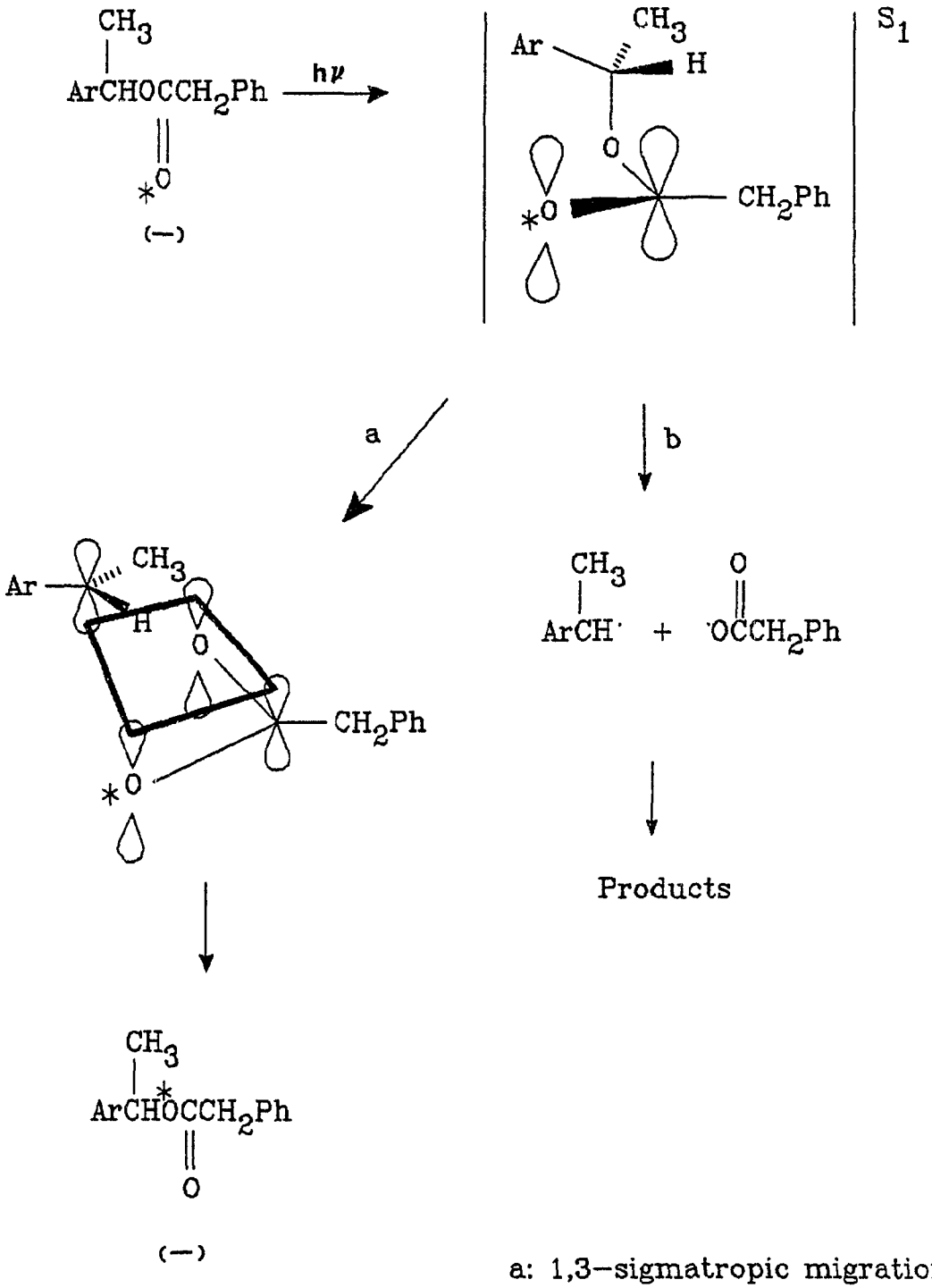
observed products. Recently, many examples have been found for the decarboxylation of phenylacetyloxy radicals within the solvent cage [15].

Scheme 5: Mechanism of Photodecarboxylation of Naphthylmethyl Esters.



Givens *et al.* [17] in their studies on photodecarboxylation of naphthylmethyl phenylacetate esters have discussed the reasons for the low efficiency of photodecarboxylation even though the loss of CO_2 should be rapid from the phenylacetyloxy radical. The possibility that the low efficiency of photodecarboxylation is due to internal return of the radical pair A, Scheme 5, has been excluded by studies on both ^{18}O labelled and optically pure

Scheme 6: Mechanism for ^{18}O Scrambling; 1,3-sigmatropic migration.



a: 1,3–sigmatropic migration

b: C–O bond cleavage

(+) or (-)-1-phenylethyl phenylacetate, Scheme 6. They observed 52% of ^{18}O scrambling of the ether oxygen, if the starting material was isolated after 30% conversion. This ^{18}O scrambling was explained by a 1,3-sigmatropic migration with retention of configuration of the migrating carbon. Essentially all the carbon-oxygen bond cleaved molecules lead to products as shown in the Scheme 5. The low efficiency for photodecarboxylation is due to the competing 1,3-sigmatropic migration of the singlet state without carbon-oxygen bond cleavage (Scheme 6).

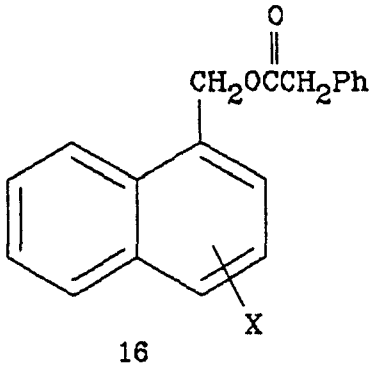
Similarly, Jaeger *et al.* [18] have photolyzed (+) and (-)-1-(3,5-dimethoxyphenyl)ethylacetate (labelled with ^{18}O in the ether oxygen) in methanol-water and obtained no racemization even though there is ^{18}O scrambling in the starting material. These results suggest that the ion-pair intermediate either does not return at all or does so before the two fragments get far enough apart to allow reorganization that would lead to loss of optical activity.

The previous work done by Givens *et al.* [11,13] as well as Pincock *et al.* [10,19] suggests that the naphthylmethyl group is better than the benzyl group for studies of photochemical benzylic cleavage reactions. Pincock *et al.* [19] have photolyzed a number of naphthylmethyl derivatives such as the chloride, bromide, trimethylammonium chloride, acetate and phosphate. From their studies they identified a

trimethylammonium chloride as the best group for a systematic study of substitution effects on benzylic cleavage reactions. However, later they found [10] that the 4-methoxy substituent behaved differently as mentioned above. This direct interaction between the electron-donating group and the positively charged leaving group in the ground state would not be possible for a neutral leaving group such as an ester group. However, Pincock *et al.* [19] have studied the photolysis of naphthylmethyl acetate in methanol and found it gave exclusively ionic products. Therefore, the acetate leaving group is not suitable for studying variation in the ionic versus radical cleavage processes. As mentioned above, Givens *et al.* [10,12] have observed photoproducts exclusively from homolytic cleavage for naphthylmethyl phenylacetates in benzene. Therefore, the proper solvent, leaving group, chromophore and multiplicity are the critical factors to consider in order to select the proper system for a study of substituent effects in benzylic cleavage photochemistry. In this regard, as mentioned before, the naphthylmethyl chromophore and methanol solvent are good choices. The next factor to consider is appropriate leaving group. The selection of the ester is important since proper monitoring of the two reaction pathways requires that both be occurring to a measurable extent. Moreover, the carboxylic acid

should not be too volatile or water soluble and should have an HPLC detectable chromophore.

This thesis will concentrate on four different ester series of 1-naphthylmethanols. They are phenylacetate, **16**, phenylpropanoate, **20**, benzoate, **29** and phenoxyacetate, **35**.



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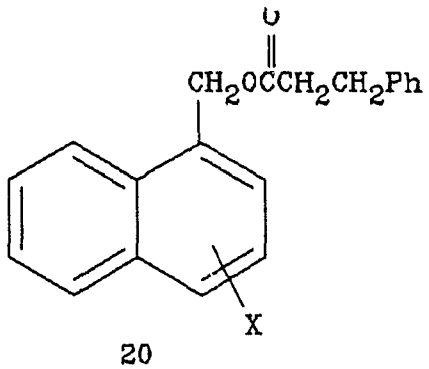

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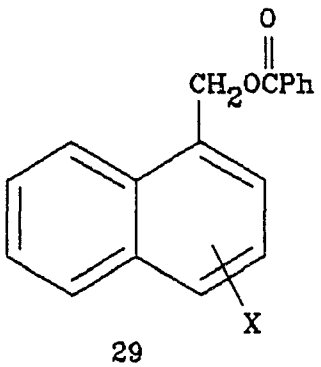

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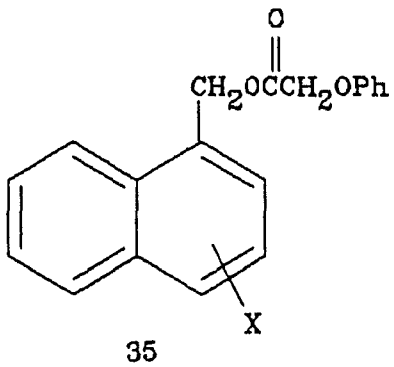

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The beginning objective was to identify a best ester group for the systematic study of substituent effects on benzylic cleavage. In fact these esters showed quite different photochemical behaviour. The phenylacetate, **16**, and phenylpropanoate, **20**, will be discussed in Chapters 2 and 3, the benzoates in Chapter 4 and the phenoxyacetate in Chapter 5.

CHAPTER 2

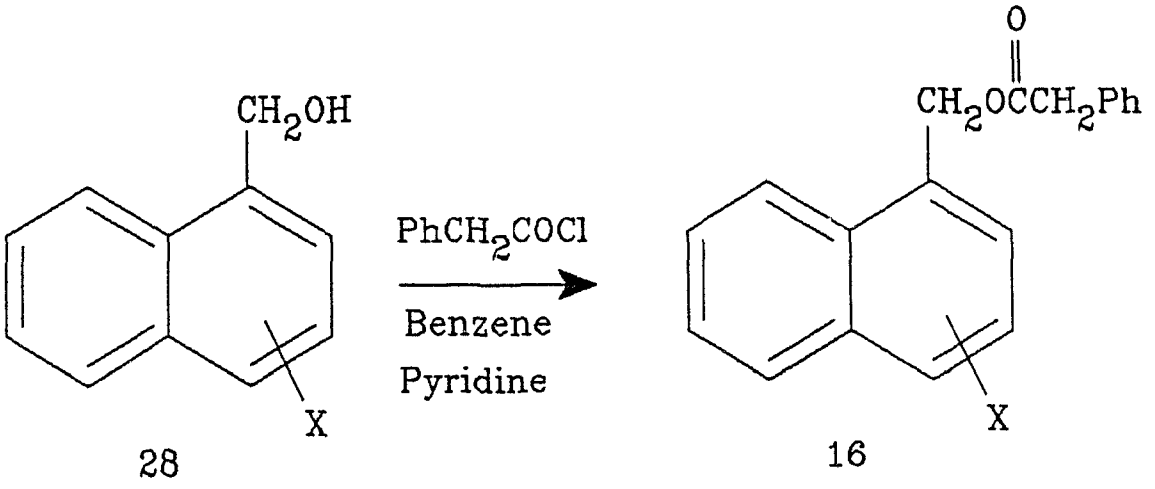
Results for the Photochemistry of Esters 16 and 20

As discussed in the introduction, the aim of this research was to study the mechanism of the photocleavage of substituted naphthylmethyl esters in a nucleophilic solvent, methanol. Four ester series of 1-naphthylmethyl alcohols were studied. The phenylacetate esters,**16**, and 3-phenylpropanoate esters,**20**, of 1-naphthylmethanol behaved similarly on photolysis and will be discussed in this and the next chapter.

2.1 GENERAL SYNTHESIS OF ESTERS 16, 20 AND 23:

The synthesis of 1-naphthylmethyl phenylacetates,**16**, 1'-naphthylmethyl 3-phenylpropanoates,**20**, and 1'-naphthylmethyl 9-methyl-9-fluorenyl carboxylates,**23**, were accomplished by a common method as outlined in Schemes 7, 8 and 9. These esters were purified either by distillation or by crystallization from hexane:dichloromethane. Details, spectra and elemental analyses are included in Chapter 6.

Scheme 7: Preparation of Phenylacetate Esters 16a - 16l.



a: X = H

b: X = 2-OCH_3

c: X = 3-OCH_3

d: X = 4-OCH_3

e: X = 4-CH_3

f: X = 4-CN

g: X = 4-OCH_2CH_3

h: X = 4-CO_2CH_3

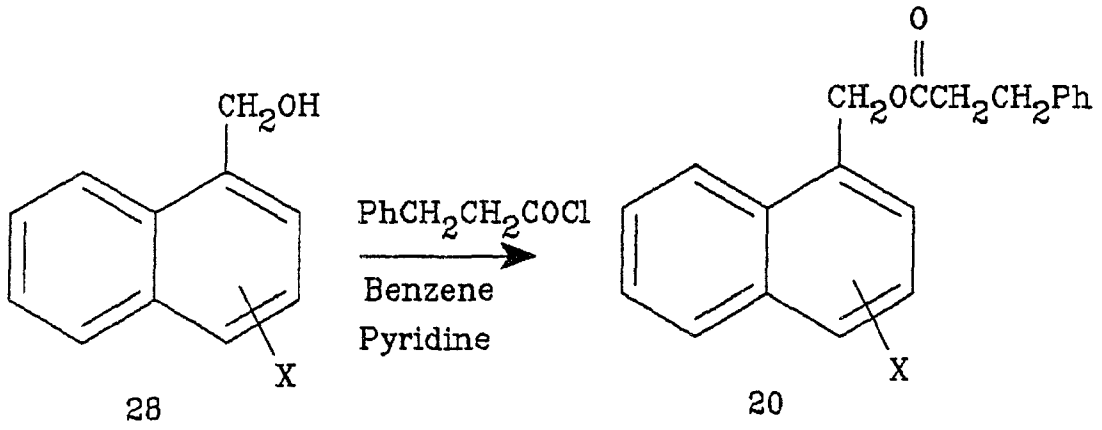
i: X = 4,5-diOCH_3

j: X = 4,7-diOCH_3

k: X = 4,8-diOCH_3

l: X = 4-F

Scheme 8: Preparation of Phenylpropanoate Esters 20a, 20c and 20d.

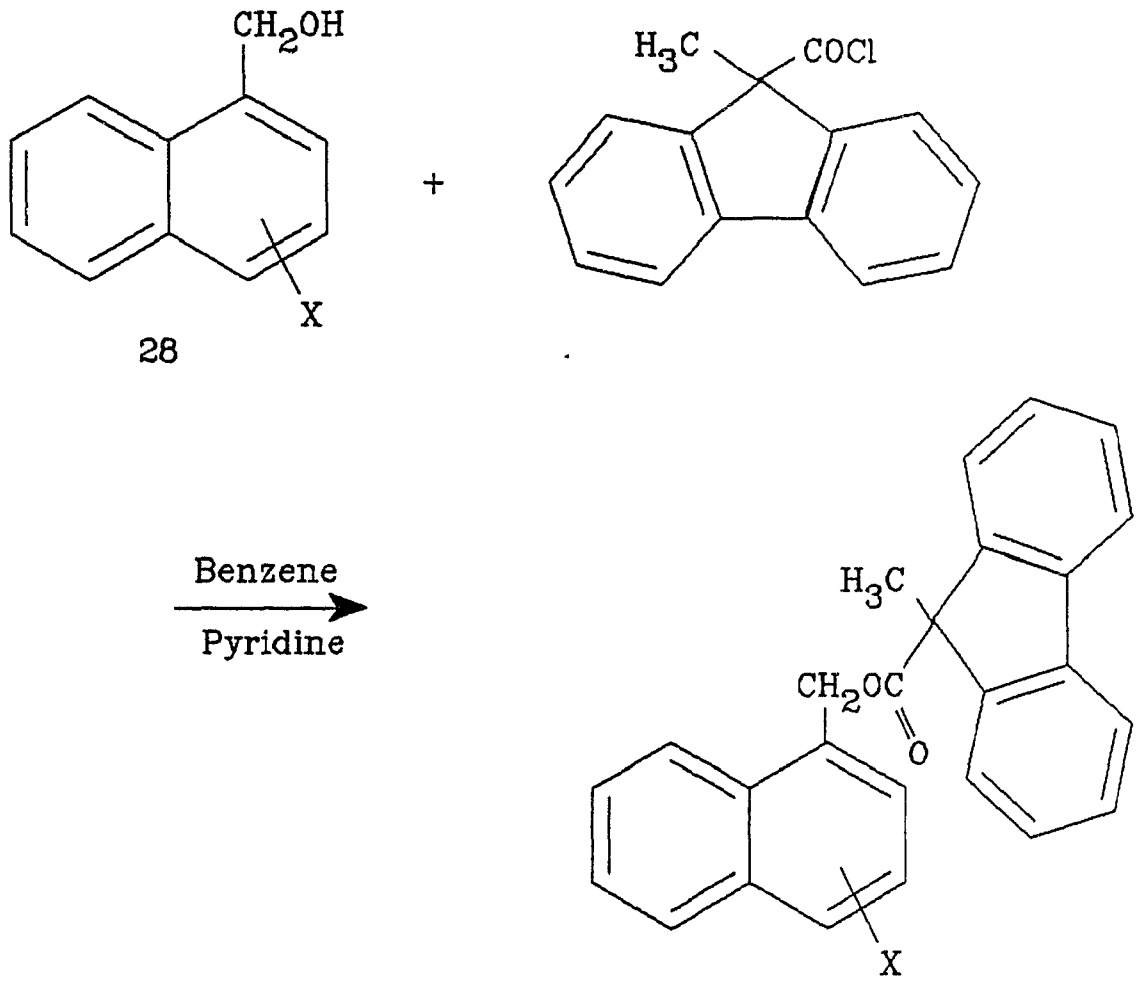


a: X = H

c: X = 3-OCH_3

d: X = 4-OCH_3

Scheme 9: Preparation of 9-methyl-9-fluorenyl carboxylate Esters **23d** and **23e.**



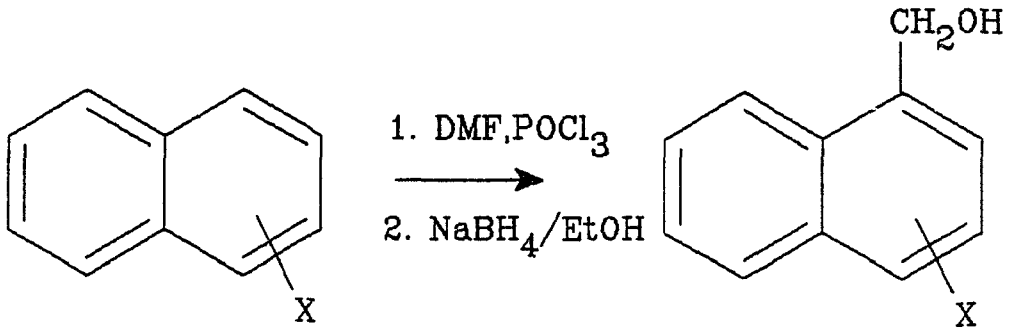
d: X = 4-OCH_3

e: X = 4-CH_3

2.2 PREPARATION OF 1-NAPHTHYLMETHANOLS:

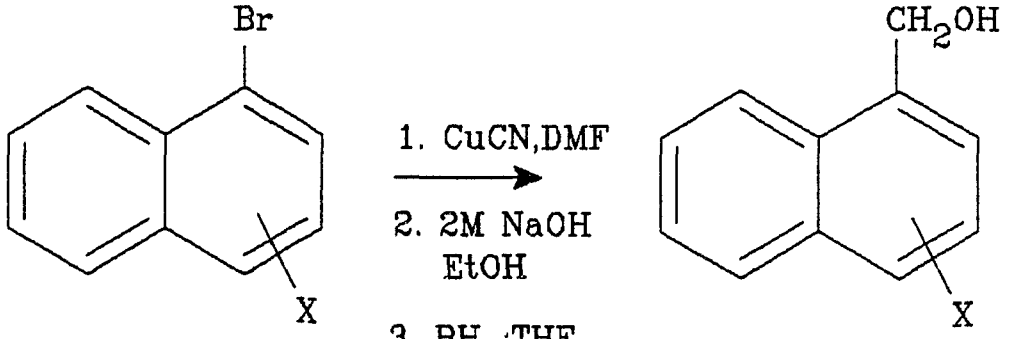
1-Naphthylmethanols **28b, 28d, 28g** and **28i-k** were synthesized by formylation of the corresponding ether followed by reduction of the aldehyde. 3-Methoxy-1-

Scheme 10: Preparation of 1-Naphthylmethanols **28b - 28e, 28g, 28i - 28l.**



28b, 28d, 28g

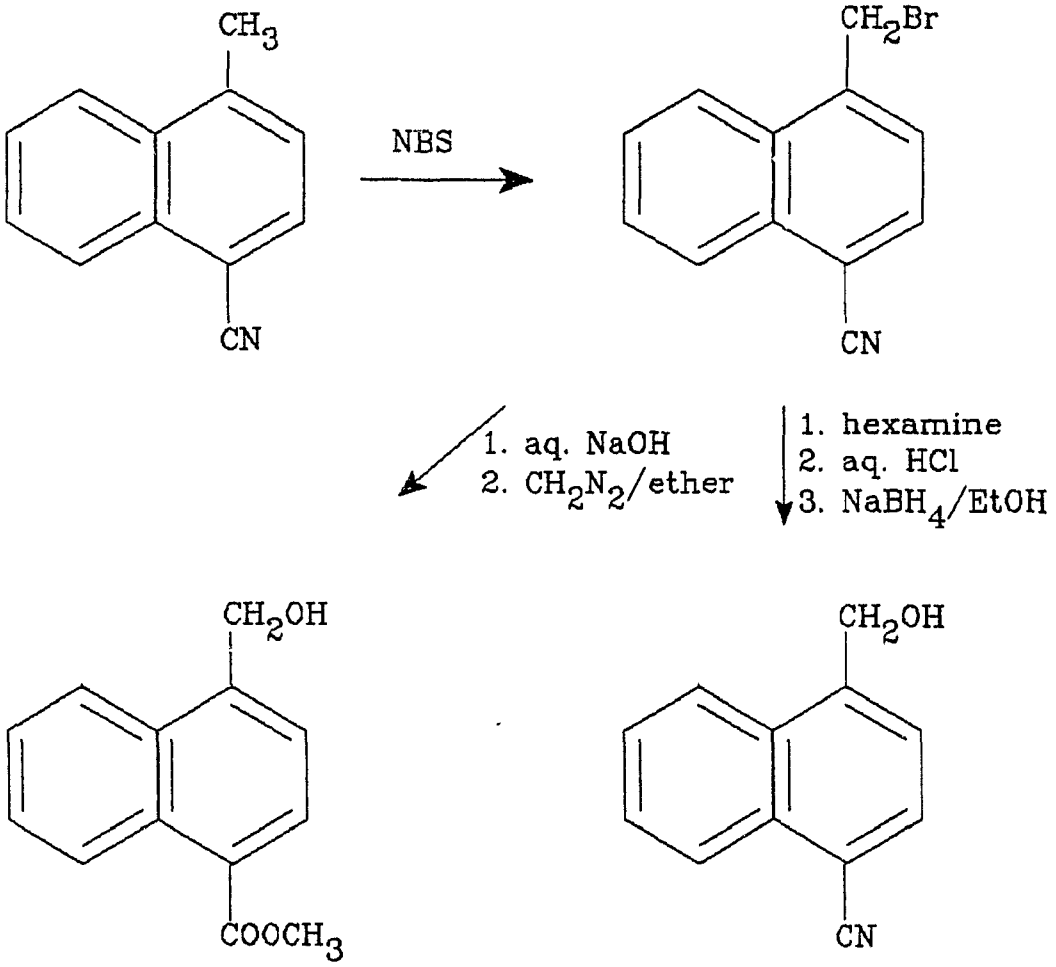
28i – 28k



28c, 28e, 28l

naphthylmethanol,**28c**, and 4-methyl-1-naphthylmethanol,**28e**, were prepared by cyanation of the corresponding bromo compound followed by hydrolysis and reduction. 4-Cyano-1-

Scheme 11: Preparation of 1-naphthylmethanol **28f** and **28h**.



28h 28f

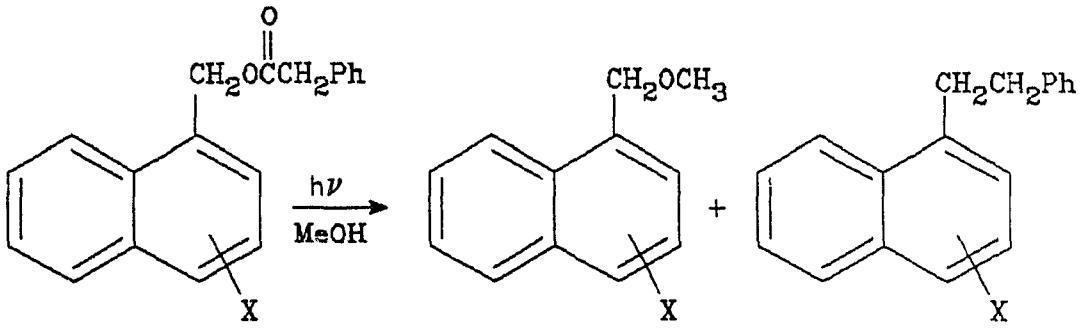
naphthylmethanol,**28f**, and 4-carbomethoxy-1-naphthylmethanol, **28h**, were prepared from 4-cyano-1-methylnaphthalene. 4-Fluoro-1-naphthylmethanol was prepared by reduction of the corresponding acid. These preparation are outlined in Schemes 10 and 11, and the details are in Chapter 6.

2.3 PREPARATIVE PHOTOLYSIS OF THE ESTERS 16, 20 AND 23:

Solutions of the esters in methanol were irradiated using a 200W medium pressure mercury lamp filtered with Pyrex. Solutions were purged with nitrogen before and during the irradiation. Reactions were monitored by hplc during the photolysis. The irradiations were continued until starting material had disappeared as indicated by hplc. The irradiation time varied from 14 h for the unreactive esters to 3 h for the reactive esters. Yields of the photoproducts of the reaction were determined by calibrated hplc with standard solutions of photoproducts.

Irradiation of esters **16** and **20** gave a mixture of three major products as shown in Scheme 12 and 13 whereas ester **23** on irradiation gave a mixture of five products, Scheme 14. Excellent mass balance was obtained for almost all cases. The results of the photolysis are given in Tables 1, 2 and 3. Trace amounts of the radical derived products, 1,2-dinaphthylethanes and 1-methylnaphthalenes were also formed as shown by GC/MS. However, the esters **16b**, **16c**, **16h**, **16j**, and **16k** gave larger amounts of the dimer and considerable amounts of 1-methylnaphthalenes.

Scheme 12: Photolysis of Esters **16a - 16l.**

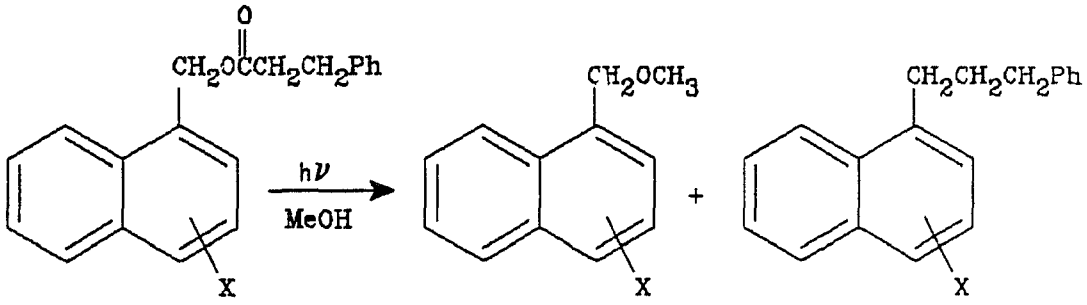


16a – 16l 17a – 17l 18a –18l

+ $PhCH_2CO_2H$

19

Scheme 13: Photolysis of Ester **20a, 20c** and **20d.**

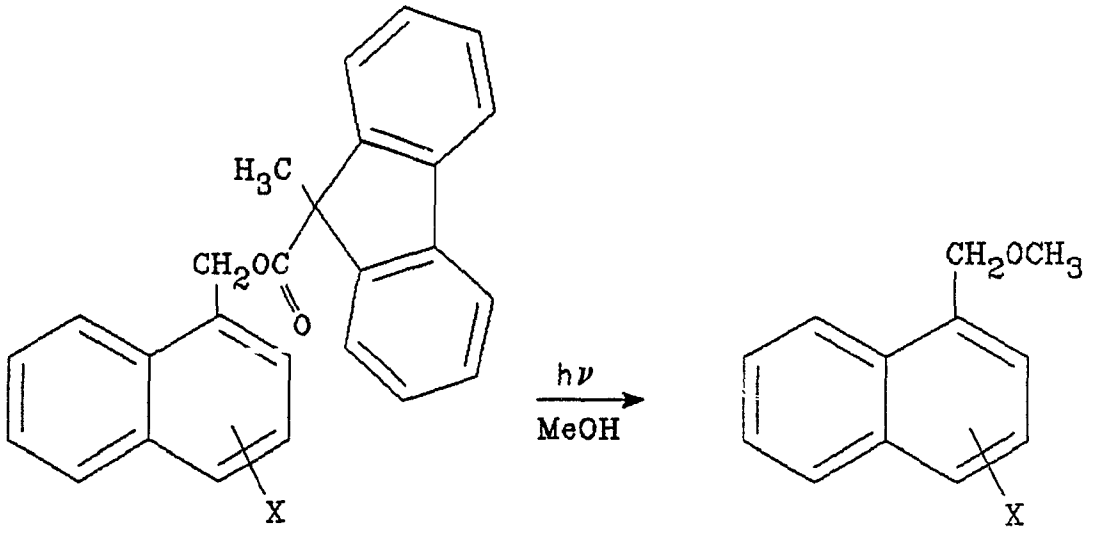


20a,20c,20d 17a,17c,17d 21a,21c,21d

+ $PhCH_2CH_2CO_2H$

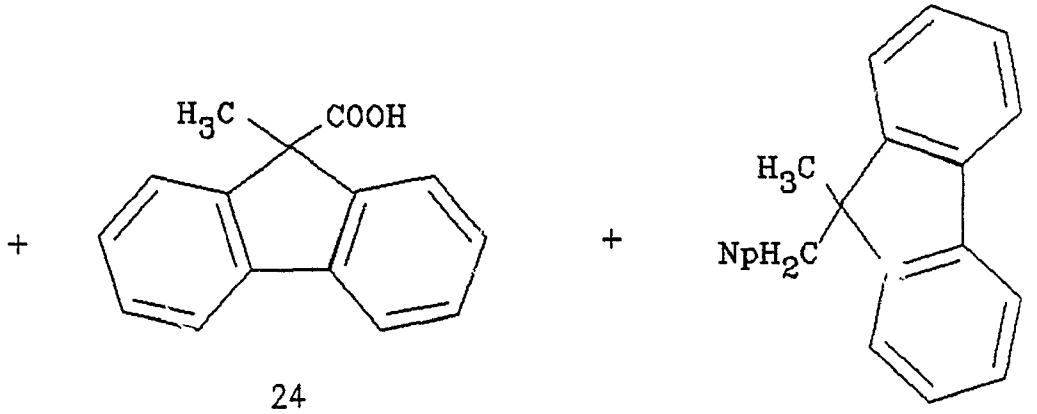
22

Scheme 14: Photolysis of Esters **23d** and **23e**.



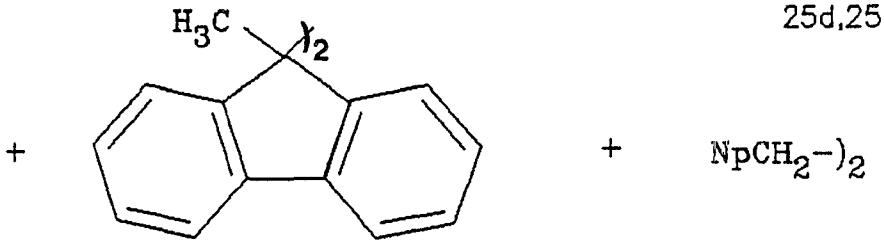
23 d, e

17a – 17l



24

25d,25e



27

26d,26e

Table 1: Percentage Yields[a] of Photoproducts from the Ester **16a - 16l.**

Ester **16**	X	Ether[b] **17**	Hydrocarbon[b] **18**	acid[c] **19**	Dimer[d]
a	H	84	16	60	trace
b	2-OCH_3	25	47	17	10
c	3-OCH_3	31	52	38	8
d	4-OCH_3	74	24	59	trace
e	4-CH_3	93	7	72	trace
f	4-CN	12	80	12	trace
g	4-OC_2H_5	80	22	60	trace
h	4-CO_2CH_3	10	52	11	20
i	4,5-diOCH_3	42	46	25	trace
j	4,7-diOCH_3	35	48	29	8
k	4,8-diOCH_3	47	33	51	7
l	4-F	83	12	74	trace

[a]Estimated analytical error, ±2%.

[b]By calibrated HPLC

[c]By weight of isolated product

[d]$NpCH_2CH_2Np$; by GC/MS and yields are less than 5% except where the values are given

Table 2: Percentage Yields[a] of Photoproducts from the Esters **20a, 20c** and **20d.**

Ester **20**	X	Ether[b] **17**	Hydrocarbon[c] **21**	Acid[d] **22**	Dimer[e]
a	H	96	6	83	trace
c	3-OCH_3	39	19	31	12
d	4-OCH_3	86	7	72	trace

[a]Estimated analytical error, ±2%

[b]By calibrated HPLC, [c]By nmr

[d]By weight of isolated acid

[e]By GC/MS and yields are less than 5% except where the values are given

Table 3: Percentage yields[a] of Photoproducts from the Esters **23d** and **23e.**

Ester **23**	X	Ether[b] **17**	Hydrocarbon[b] **25**	Acid[c] **24**	Dimers[b] **26**	**27**
a	4-OCH_3	42	33	41	17	18
e	4-CH_3	63	12[d]	40	7[d]	8[d]

[a]Estimated analytical error, ±2%

[b]By calibrated HPLC

[c]By weight of isolated acid, [d]by nmr

2.4 ABSORPTION, FLUORESCENCE AND PHOSPHORESCENCE MEASUREMENTS:

Extinction coefficients, fluorescence quantum yields, singlet state lifetimes and singlet and triplet state energies for all esters were obtained and tabulated in Tables 4 and 5. Details are included in Chapter 6.

Table 4: Absorption Properties of Esters **16**, **20** and **23**.

Ester	X	$\epsilon \times 10^{-3}$ (λ_{max}, nm)
16a	H	5.3(284), 7.4(275), 6.4(265)
16b	2-OCH_3	3.4(330), 3.1(318), 5.3(286), 6.4(274)
16c	3-OCH_3	2.7(325), 2.5(312), 4.8(279), 6.1(265)
16d	4-OCH_3	8.2(292)
16e	4-CH_3	5.7(292), 8.0(282)
16f	4-CN	2.9(321), 6.9(307), 9.2(294)
16g	4-OC_2H_5	7.9(294)
16h	4-CO_2CH_3	7.2(293)
16i	4,5-diOCH_3	6.3(327), 8.4(313)
16j	4,7-diOCH_3	2.6(326), 2.3(311), 5.2(290), 5.5(281)
16k	4,8-diOCH_3	5.2(326), 7.6(312), 10.2(295)
16l	4-F	4.4(290), 7.0(279), 6.2(267)
20a	H	4.5(285), 6.9(276), 5.4(266)
20c	3-OCH_3	2.6(328), 2.1(314), 5.0(282), 5.5(274)
20d	4-OCH_3	7.8(292)
23d	4-OCH_3	11(297), 12(287), 16(272), 18(258)
23e	4-CH_3	8.2(286), 20(262)

Table 5: Emission Properties of Esters **16, 20** and **23.**

Ester	X	E_S[a] kcal/mol (kJ/mol)	τ_S[b] ns	Φ_f[c]	E_T[b] kcal/mol (kJ/mol)
16a	H	91.9 (386)	49	0.14	60.0 (252)
16b	2-OCH_3	83.7 (352)	7.2	0.23	57.4 (241)
16c	3-OCH_3	84.8 (356)	10.9	0.24	57.4 (241)
16d	4-OCH_3	88.4 (371)	7.3	0.27	59.5 (250)
16e	4-CH_3	90.7 (381)	34	0.14	59.7 (251)
16f	4-CN	89.8 (377)	5.2	0.21	57.0 (239)
16g	4-OC_2H_5	88.1 (370)	7.0	0.28	57.2 (240)
16h	4-CO_2CH_3	84.8 (356)	4.0	0.20	59.4 (250)
16i	4,5-diOCH_3	86.2 (362)	6.1	0.16	59.4 (250)
16j	4,7-diOCH_3	84.1 (353)	7.1	0.21	57.7 (242)
16k	4,8-diOCH_3	86.2 (362)	4.8	0.10	59.2 (249)
16l	4-F	90.7 (381)	24	0.15	59.4 (250)
20a	H	91.9 (386)	41	0.14	60.2 (253)
20c	3-OCH_3	84.8 (356)	8.8	0.23	57.4 (241)
20d	4-OCH_3	88.2 (370)	7.6	0.27	59.4 (250)
23d	4-OCH_3	88.6 (372)	6.2	0.25	59.4 (250)
23e	4-CH_3	90.8 (382)	32	0.14	59.6 (251)

[a]Estimated error, ±1 nm; [b]Estimated error, ±5%

[c]Estimated error, ±0.01

CHAPTER 3

Discussion of the Photochemistry of Esters 16 and 20

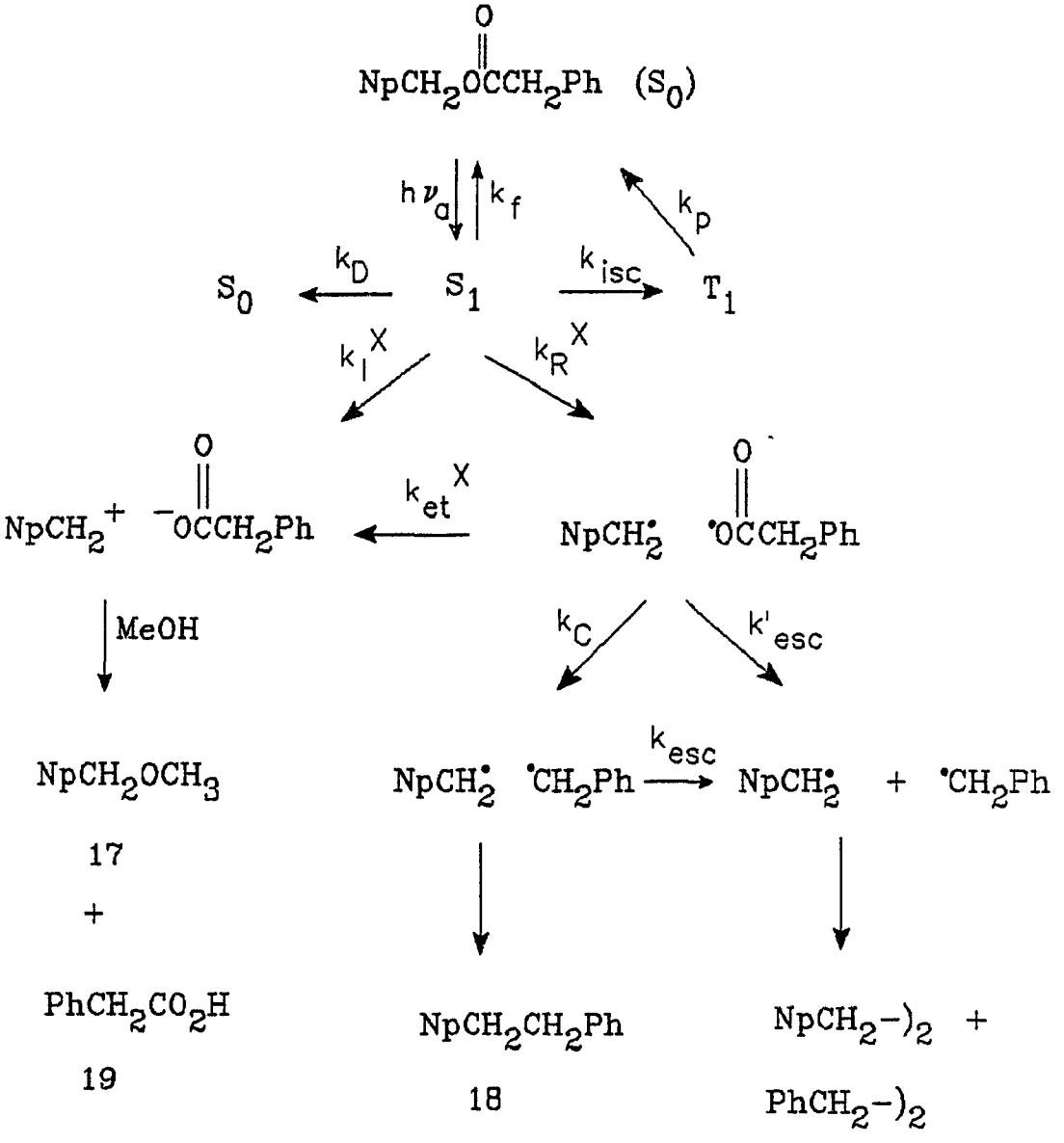
The ultraviolet spectra of the compounds **16a - 16l** are different depending on the position of substitution. As shown by Jaffe and Orchin [20] and discussed by Pincock *et al.* [10], there are two transitions above 250 nm for naphthalene derivatives. For naphthalene itself, these are a longitudinal polarized, ^1L_b band (λ_{max} = 312 nm, log ϵ = 2.4) and a transverse polarized ^1L_a band (λ_{max} = 286 nm, log ϵ = 3.6). Substitution in the 4,5 and 8 positions by conjugating methoxy or cyano groups causes bathochromic and hypochromic effects on ^1L_a so that the weaker ^1L_b band is often obscured. In contrast, substitution in the 2,3 and 7 positions has a similar effect on the ^1L_b band so that it is now readily observable although with a lower extinction coefficient. Due to this effect, the singlet energies for **16b, 16c** and **16j** are somewhat lower than the others, Table 5. The extinction coefficients at λ_{max} for the substrate with conjugating groups like 4-OCH_3 **(16d)**, 4-CN **(16f)** and 4-$COOCH_3$ **(16h)** are somewhat higher than for the unsubstituted ester, **16a**, Table 4. The absorption spectra of **16i** and **16k**, which have an additional methoxy group at the 5 and 8 position, respectively, show more vibrational structure than does the ester **16d**, which contains only one methoxy group at position 4, Table 4. The former two also have higher

extinction coefficients at λ_{max} and a slight bathochromic shift. The spectra of the phenyl propanoate esters, **20a**, **20c** and **20d**, are almost the same as those of the corresponding phenylacetate esters **16a**, **16c** and **16d** respectively.

As discussed in the introduction, Givens et al. [11,13] have confirmed that the singlet state is the reactive state in the photochemistry of 1- and 2-naphthylmethyl phenylacetates. The triplet energy of the naphthyl chromophore is 57 - 60 kcal mol^{-1}, Table 5, which is below the carbon-oxygen bond dissociation energies of 1-naphthylmethyl esters. An estimate of this bond strength in 1-naphthylmethyl acetate is 65 kcal mol^{-1}, based on a value of 68 kcal mol^{-1} [21] for benzyl acetate minus 3 kcal mol^{-1} [22] for the stabilization of the 1-naphthylmethyl radical relative to the benzyl radical. The singlet energy of the naphthyl residue is 84 - 91 kcal mol^{-1}, Table 5, which is well above this estimated bond energy. Therefore the reactive state should only be the high energy singlet state. In support of this, Pincock et al. [19] have noted that 1-naphthylmethyl acetate does not react from the triplet state.

In order to rationalize the results reported here, a consideration of the possible mechanisms for the reaction is required. As shown in Scheme 15, the absorption of light gives the reactive state, S_1. There are several competitive

Scheme 15: Mechanism for the Photolysis of 1-Naphthylmethyl phenylacetate Esters **16a - 16l.**



pathways available for this excited sate. Fluorescence is efficient (between 10 and 30%) Table 5, for all of the 1-naphthylmethyl phenylacetate esters, **16**, 1'-Naphthylmethyl 3-phenylpropanoate esters, **20**, and 1'-naphthylmethyl 9-methyl-9-fluorenyl carboxylate esters, **23**. The quantum yields of fluorescence are in the order 4-methoxy > 2-methoxy ≈ 3-methoxy ≈ 4-cyano > 4-methyl ≈ unsubstituted. This order is parallel to that observed for model compounds without the reactive ester group: 1-methoxynaphthalene, ϕ_f = 0.43 [23], 2-methoxynaphthalene, ϕ_f = 0.42 [24], 1-cyanonaphthalene, ϕ_f = 0.37 [25], 1-methylnaphthalene, ϕ_f = 0.22 [23] and naphthalene, ϕ_f = 0.21 [23]. This is probably due to the slower intersystem crossing rate for substituted esters compared to the unsubstituted one. However, intersystem crossing efficiencies are not known for these naphthyl derivatives. The same order for the quantum yield of fluorescence for the substituted 1-naphthylmethyl trimethylammonium chlorides has been observed previously [10]. The lifetimes of the singlet state are in the order of unsubstituted > 4-methyl > 2-, 3- and 4-methoxy> 4-cyano. This order is similar for naphthalene, τ_S = 96 ns [23], 1-methylnaphthalene, τ_S = 65 ns [23], 2-methoxynaphthalene, τ_S = 15 ns [24], 1-methoxynaphthalene, τ_S = 13 ns [23] and 1-cyanonaphthalene, τ_S = 4.4 [25].

Since all the compounds show phosphorescence in a rigid matrix at 77 K, intersystem crossing to the T_1 state does

occur. However, the triplet is not reactive as mentioned above and deactivates to the ground state. Since the spectral properties and photolysis results are similar for both phenylacetates,**16**, and 3-phenyl propanoates,**20**, the same mechanism for the photolysis is possible. This mechanism will be discussed next. In contrast, the observed spectroscopic results for the benzoate esters and phenoxyacetate esters are different. Therefore these will be discussed in separate chapters later in the thesis.

Since the spectroscopic properties of these esters are similar to those of corresponding methyl derivatives, the excitation energy must be principally localized in the naphthyl moiety. Therefore, the CH_2-OCO cleaves preferentially even though the bond strength of the CH_2-CO_2 bond is weaker (estimated as 55 kcal mol^{-1} for $C_6H_5CH_2$-CO_2H [26]) than the CH_2-OCO bond (estimated as 65 kcal mol^{-1} [21,22]). This fact has also been discussed by Givens *et al*. [11]. Therefore the formation of products results from excited state cleavage of the carbon-oxygen bond. Note that this is critical since any intervention of a pathway involving carbon-carbon bond cleavage would complicate the interpretation. It is clear that the ether product,**17**, and acid,**19**, are formed by trapping of the 1-naphthylmethyl carbocation and carboxylate ion by solvent methanol. In contrast, hydrocarbon product,**18**, is formed by homolytic cleavage of the carbon-oxygen bond followed by expulsion of

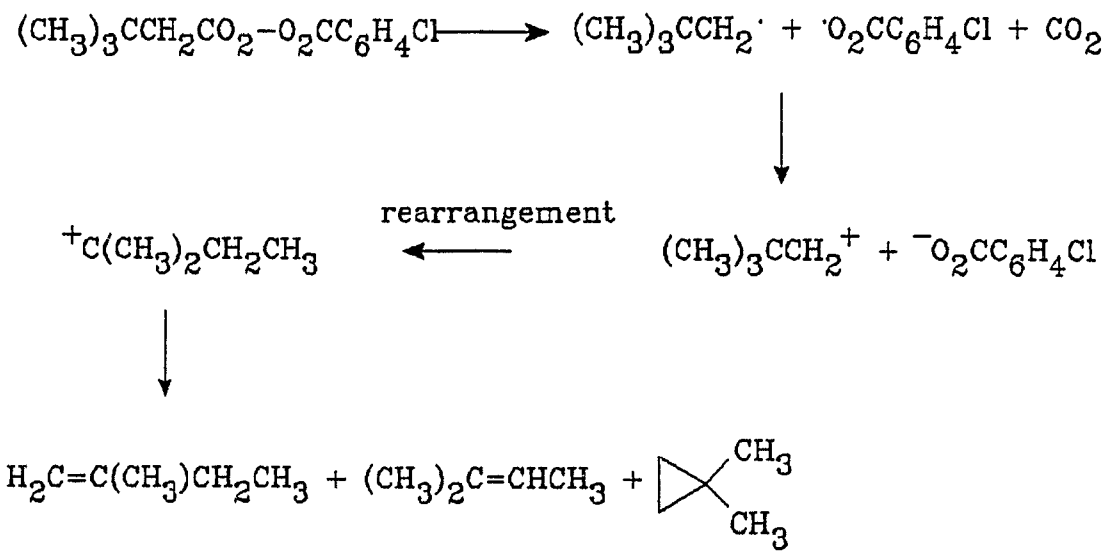
carbon dioxide and coupling of the two radicals. This is the only in-cage product observed by Givens et al. [11,13] in their studies on the photolysis of 1-naphthylmethyl phenylacetate in benzene. In contrast, for the photolysis reported here in the nucleophilic solvent, methanol, products from both radical and ionic intermediates are observed. Therefore the most critical intermediates in this photolysis are the two pairs: 1-naphthylmethyl radical / phenylacetyloxy radical and 1-naphthylmethyl carbocation / phenylacetate anion. The ionic products are derived from the ion-pair and radical products are derived from the radical-pair.

According to Zimmerman et al. [4], using the "meta effect" argument, the product partitioning in benzyl acetate photochemistry occurs at the initial photo cleavage of the carbon-oxygen bond. Therefore the ion-pair and radical-pair are formed directly from the excited substrate by either ionic cleavage or radical cleavage of the carbon-oxygen bond respectively. The greater electron donating ability of the 3-methoxy group in the excited state of the 3-methoxybenzyl acetate ester enhanced the efficiency of ion-pair formation so that only products obtained from ionic cleavage were observed. Homolytic cleavage was preferred for the unsubstituted and 4-methoxybenzyl acetate, and only products derived from the radical-pair were observed. Obviously, this explanation is unsatisfactory for the 1-naphthylmethyl

esters studied here. Both the unsubstituted and 4-methoxy compound,Table 3, give higher yields of the products **17** and **19** derived from the ion-pair than does the 3-methoxy substrate.

However the results can be explained by assuming that, independent of the substituent, the rate of homolytic cleavage (k_R) of the CH_2-OCO bond is much greater than the rate of heterolytic cleavage (k_I) of that bond, Scheme 15. The assumption is then made that the ion-pair is not formed directly from the excited state but rather by electron transfer in the initially formed radical-pair. The rate of this process will be substituent dependent as discussed below. There is precedence for this type of electron

Scheme 16: Thermal decomposition of 3,3-dimethylbutanoyl 3-chlorobenzoyl peroxide.



transfer in a radical-pair. During CIDNP studies on the thermal decomposition of 3,3-dimethylbutanoyl 3-chlorobenzoyl peroxide, Lower et al. [27] have demonstrated that initial homolytic cleavage of the peroxy bond initiates the reaction as shown in the Scheme 16. From CIDNP emission of the protons in the products, Lower et al. [27] concluded that an electron is transferred from the neopentyl radical to the m-chloro-benzoyloxy radical to form the neopentyl carbocation and the m-chlorobenzoate anion. Also, a similar electron-transfer mechanism has been proposed to account for the simultaneous appearance of typical radical and ionic products observed for the photolysis of alkyl halides by Kropp et el. [28].

Moreover, the free energy for the electron-transfer between the 1-naphthylmethyl radical and the phenylacetyloxy radical can be estimated from eq. 7. The oxidation potential of 1-naphthylmethyl radical is 0.47 V vs SCE [30]

$$\Delta G_{et} = 23.06\ (E^{ox}_{1/2} - E^{red}_{1/2}) + e^2/Dr \qquad (7)$$

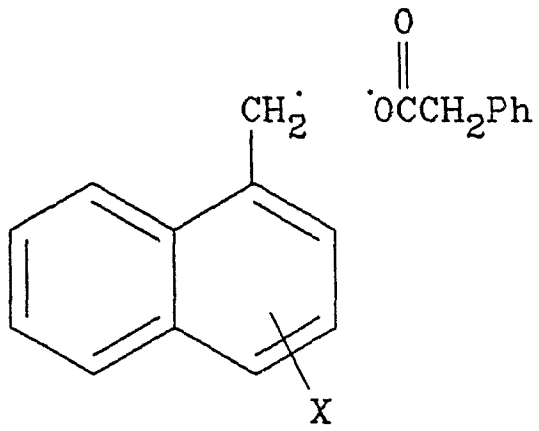
and the reduction potential of phenylacetyloxy radical is estimated at 1.80 V vs SCE [31] in acetonitrile. These values demonstrate that electron-transfer between the two radicals should be exoergonic by about 24 kcal mol^{-1} in acetonitrile. Although the photochemical results reported here are for methanol rather than acetonitrile, the above value should not change very much.

In competition with this electron-transfer process, the phenylacetyloxy radical can decarboxylate to give the more stable benzyl radical as shown by Givens et al. [11,13]. Bond strength calculations suggest this process should be exothermic by about 30 kcal mol^{-1} [32]. The incage coupling of the benzyl radical with the 1-naphthylmethyl radical accounts for the product, **18**.

In summary, there are two processes possible for the initially formed radical-pair that results from homolytic bond cleavage of the carbon-oxygen bond.

1. Electron-transfer from the 1-naphthylmethyl radical to the phenylacetyloxy radical to give the ion-pair with a rate constant, k_{et}. This ion-pair then reacts with solvent, methanol to give the ether,**17**, and acid,**19**.
2. Decarboxylation of phenylacetyloxy radical to give the benzyl radical with a rate constant, k_C. The benzyl radical and 1-naphthylmethyl radical then couple in the solvent cage to give the product, **18**.

For the phenylacetate ester series, **16a - 16l**, the rate of decarboxylation, k_C, will be a constant. Therefore the product composition is dependent only on changes in the rate of electron-transfer, k_{et}, between the 1-naphthylmethyl radical and phenylacetyloxy radical. This electron-transfer rate, k_{et}, should depend on the oxidation potential of 1-naphthylmethyl radical and the reduction potential of



phenylacetyloxy radical. In the series **16a - 16l**, the oxidation potential of the corresponding radical will vary with the substituents but the reduction potential of the phenylacetyloxy radical will be independent of the substituents. The ratio of the rates of electron-transfer and decarboxylation for the ester **16** can be given by eq. 8.

$$\frac{k_{et}^{X}}{k_C} = \frac{\text{Yield of } \mathbf{17}}{\text{Yield of } \mathbf{18}} \qquad (8)$$

$$k_{et}^{X} = \frac{\text{Yield of } \mathbf{17}}{\text{Yield of } \mathbf{18}} \times k_C \qquad (9)$$

Here the yield of **17** is a more reliable measure of the ionic pathway than the yield of **19**. Therefore, according to eq. 9, if k_C, the rate of decarboxylataion of the phenylacetyloxy radical were known, then the rate of electron transfer, k_{et}^{X}, could be determined. In other words, k_C, is serving as a "radical clock" [33] for the rate of electron-transfer, k_{et}^{X}. Unfortunately, the rate of

decarboxylation of the phenylacetyloxy radical is not known. However, this rate can be estimated as follows.

The spectral properties of 4'-methoxy-1-naphthylmethyl 9-methyl-9-fluorenyl carboxylate, **23d**, and 4-'methyl-1'-naphthylmethyl 9-methyl-9-fluorenyl carboxylate, **23e**, show that the excitation energy is localized mainly in the lower energy naphthyl chromophore in both esters, Table 5. Therefore, as discussed above, the photochemistry of these should be similar to the corresponding phenylacetate esters **16d** and **16e** respectively. The product partitioning of **23d** is controlled by the rate of electron-transfer, k'_{et}, from 4-methoxy-1-naphthylmethyl radical to the 9-methyl-9-fluorenoyloxy radical and by the rate of decarboxylation, k'_C, of the 9-methyl-9-fluorenoyloxy radical as given in eq. 10. Using the known rate of decarboxylation of

$$\frac{k'_{et}}{k'_C} = \frac{\mathbf{17d}}{\mathbf{25d + 27}} = 0.82 \qquad (10)$$

9-methyl-9-fluorenoyloxy radical, 1.8×10^{10} s^{-1} [34] and the yields of **17d**, **25d** and **27** in Table 3, gives k'_{et} as 1.5×10^{10} s^{-1}. Similarly, from the data of 4-methyl-1-naphthylmethyl 9-methyl-9-flourenyl carboxylate, **23e**, the rate of electron transfer from 4-methyl-1-naphthylmethyl radical to the 9-methyl-9-fluorenoyloxy radical, k''_{et}, can be estimated as 5.67×10^{10} s^{-1} as shown in eq. 11. If the

$$\frac{k''_{et}}{k'_{c}} = \frac{\textbf{17e}}{\textbf{25e + 27}} = 3.15 \qquad (11)$$

$$k''_{et} = 5.7 \times 10^{10}\ s^{-1} \qquad (12)$$

reasonable assumption is made that the rate of electron-transfer in the radical pair depends on the structure of the 1-naphthylmethyl radical but is independent of the carboxyl radical, then for the substrate **16d**, X = OCH_3 and **16e**, X = 4-CH_3 one can obtain eq. 13 and eq. 15 respectively.

$$\frac{\text{Yield of } \textbf{17d}}{\text{Yield of } \textbf{18d}} = 3.1 = \frac{k'_{et}}{k_C} = \frac{1.5 \times 10^{10}\ s^{-1}}{k_C} \qquad (13)$$

$$k_C = 4.8 \times 10^{9}\ s^{-1} \qquad (14)$$

$$\frac{\text{Yield of } \textbf{17e}}{\text{Yield of } \textbf{18e}} = 13 = \frac{k''_{et}}{k_C} = \frac{5.7 \times 10^{10}\ s^{-1}}{k_C} \qquad (15)$$

$$k_C = 4.4 \times 10^{9}\ s^{-1} \qquad (16)$$

Therefore the average for these two determinations of k_C is $4.6 \times 10^{9}\ s^{-1}$. As expected, this estimated value is within the relatively small range between $10^{9}\ s^{-1}$ estimated for the acetyloxy radical [35] and $1.8 \times 10^{10}\ s^{-1}$ estimated for the fluorenoyloxy radical [34]. Using this value, k_{et}^{X} values for the substrates **16a - 16l** can be estimated, Table 6.

Table 6: Estimated Values for log k_{et}^{X} and $E_{1\backslash 2}^{ox}$.

Ester 16	X	Yield of 17 / Yield of 18	log k_{et}^{X}	$E_{1\backslash 2}^{ox}$
a	H	5.3	10.40 (±0.13)	0.47
b	2-OCH_3	0.53	9.40 (±0.11)	0.13
c	3-OCH_3	0.60	9.44 (±0.11)	0.50[b]
d	4-OCH_3	3.1	10.15 (±0.12)	0.04
e	4-CH_3	13	10.78 (±0.20)	0.35
f	4-CN	0.15	8.84 (±0.16)	0.72
g	4-OC_2H_5	3.60	10.22 (±0.12)	0.04[c]
h	4-CO_2CH_3	0.19	8.94 (±0.17)	0.83
i	4,5-diOCH_3	0.91	9.62 (±0.11)	-0.05
j	4,7-diOCH_3	0.73	9.53 (±0.12)	-0.06
k	4,8-diOCH_3	0.96	9.65 (±0.11)	-0.05
l	4-F	6.9	10.50 (±0.14)	0.48[b]

[a]Error in brackets are estimated assuming ±2% in determination of product yields and ±10% in the value of k_c.

[b]not measured estimated from the Hammet relationship with $\rho^+ = 0.48$ mV/σ^+ [56].

[c]not measured but assumed equal to that for 4-OCH_3.

The free energy change, $\Delta G_{et}^{o\,X}$, for this electron-transfer process can be estimated from oxidation potential measurements according to eq. 17 where the last term is the electrostatic free energy. The known [30] values for the oxidation potentials of the naphthylmethyl radicals in

acetonitrile can be used, eq. 18, where A^X is an unknown solvent correction factor. Making the reasonable assumption

$$\Delta G_{et}^{o\,X} = E^{ox}(NpCH_2, CH_3OH) - E^{o}(PhCH_2CO_2, CH_3OH) - e^2/Dr_{12} \quad (17)$$

$$\Delta G_{et}^{o\,X} = E^{ox}(NpCH_2, CH_3CN) + A^X - E^{o}(PhCH_2CO_2, CH_3OH) - e^2/Dr_{12} \quad (18)$$

$$\Delta G_{et}^{o\,X} = E^{ox}(NpCH_2, CH_3CN) + B \quad (19)$$

that A^X is independent of the substituents X, eq. 18 simplifies to eq. 19 since the last three terms are all constants. The values obtained for log k_{et}^X and $E_{1/2}^{ox}$ are given in the Table 6.

Electron-transfer is one of the most fundamental and common reaction in many processes in chemistry and biology. The simplest definition of electron-transfer is a single electron transfer from one species to another. During this process one species is oxidized and the other is reduced. Usually electron-transfer processes in organic chemistry involve two neutral even-electron species and the result is a radical cation and radical anion. Usually, the oxidant and the reductant are referred to as the acceptor and donor, eq. 20. Many of the studies on electron-transfer involve

$$A + D \longrightarrow A^- + D^+ \quad (20)$$

processes with one of the species in electronically excited

state. This is because electron-transfer becomes more favourable since both the reduction and oxidation potentials are lowered in the excited states. The radical-ions that result from single electron transfer are often unstable and display further reaction. As an example, a radical cation may react with a nucleophile, with a base or undergo bond cleavage.

An important part of analyzing electron-transfer reactions is estimating the free energy change of the electron-transfer step. For the above example, eq. 20, the free energy change can be given by eq. 7. When one of the reactants is in it's first excited state as shown by eq. 21, the free energy change can be expressed as in eq. 22.

$$A \xrightarrow{h\nu} A^* \xrightarrow{D} A^- + D^+ \qquad (21)$$

$$\Delta G_{et} = E_{1/2}^{ox} - E_{1/2}^{red} + e^2/Dr - E_{oo}^{A} \qquad (22)$$

This thermodynamic approach to electron-transfer considers only the free energy difference between the initial and final state of the electron-transfer step. If the reaction is highly endergonic, the rate of electron-transfer should be slow or not take place at all. If the reaction is exoergonic then a low activation barrier might be expected. The rate would therefore be fast. However, this treatment is a simplistic approximation and more refined theoretical treatments have been developed to

estimate the free energy of activation for electron-transfer processes.

Although there are several theoretical treatments of electron-transfer rates, "Marcus theory" [36] is the simplest, most successful one. In the physical model of Marcus theory, the two species, acceptor and donor are approximated as two species of radii r_1 and r_2 with charges Z_1 and Z_2 and in a continuous medium of dielectric constant D. The two species diffuse together with rate constant, k_d, and form an encounter complex with the distance $r_{12} = r_1 + r_2$, as shown in eq. 23. Electron transfer then occurs.

$$A + D \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} A\,D \xrightarrow{k_{et}} A^- D^+ \qquad (23)$$

With several assumptions Marcus derived a parabolic expression for the free energy of activation, $\Delta G^{\#}$, for this electron-transfer process as given in eq. 24. In this

$$\Delta G^{\#} = \frac{Z_1 Z_2 e^2 f}{D r_{12}} + \frac{\lambda}{4}\left(1 + \frac{\Delta G^{0'}}{\lambda}\right)^2 \qquad (24)$$

Here, $\Delta G^{0'} = \Delta G^{0} + (Z_1 - Z_2 - 1)\dfrac{e^2 f}{D r_{12}}$

equation e is the electronic charge and f is a factor defining the effective ionic strength. The second term of this equation is the parabolic one, with the standard free energy change of the electron-transfer step. The

reorganization energy, λ, can be explained simply as follows. In order for the electron to be transferred from the donor to the acceptor, the energy of two species should be within $\pm RT$. This requirement is satisfied by increasing the energy of the system, by bond changes and solvent reorganization, until the energy levels match each other. The energy associated with these changes is called the reorganization energy.

With several assumptions, substitution of eq. 24 above into eq. 25 leads to the simplest version of the Marcus equation, eq. 26 [37]. Here A is the frequency factor.

$$k = KZ \exp.(-\Delta G^{\#}/RT) \qquad (25)$$

$$k_{et} = A \exp -[\frac{\lambda}{4} (1 + \frac{\Delta G^{0}}{\lambda})^{2}/RT] \qquad (26)$$

According to Marcus theory, a maximum for the rate of electron-transfer as a function of the change in free energy is predicted. Moreover, the rate of electron-transfer is predicted to decrease with increasing values of free energy of electron-transfer both in the endoergonic and exoergonic directions. The latter effect is not expected based on the prediction using thermodynamic factors. This is called the "Marcus inverted region". The value of the reorganization energy, λ, is the crucial factor for the inverted region. As mentioned before, the reorganization energy is the energy required by the system by reorganizing bonds and solvent in

order for electron-transfer to take place. The energy gained by reorganizing of bonds during the electron-transfer is named as bond or inner-sphere reorganization energy, λ_i. The energy gained by solvent reorganization is called outer-sphere or solvent reorganization energy, λ_o. The total

$$\lambda = \lambda_i + \lambda_o \qquad (27)$$

is given by eq. 27. Higher values of λ make the inverted region level off [37]. The higher values could be due to either large changes in λ_i or λ_o.

Photoinduced electron transfer processes have been very commonly observed in photochemistry for several years [38]. Much quantitative work has appeared beginning with the initial work of Weller [29]. Most of these studies do not show any evidence for the "Marcus inverted region", even though the free energy of electron-transfer can be as larger as 80 kcal/mol in the exoergonic direction [29]. The rate is dependent on thermodynamic factors and can be fitted to the Rehm-Weller equation [29], eq. 22. As the reaction becomes more favourable, the rate approaches and then levels off at the diffusional encounter rate. No decrease in rate is observed for highly exothermic cases.

Several explanations [39] have been put forward to account for the failure of experimental results to correctly fit the Marcus inverted region. One is the assumption that highly exoergonic processes can take place over longer

distances than the collision model implies. This will result in larger values for λ and the disappearance of the inverted region. A second explanation is that for strongly exoergonic processes electron-transfer to an electronically excited state is feasible. A third and perhaps most accepted explanation is that electron-transfer take place to vibrationally excited states of the product. For large molecules there is always close to a continuum of vibrational levels available so that the reaction still proceeds at maximum rate.

A forth explanation has recently been suggested by Mataga and Kikitani [40] using a different model from the Marcus frame work. In this model, they have distinguished between three different types of electron-transfer processes:

(i) a charge separation (CS)

two neutrals ----> two ions

(ii) a charge recombination (CR)

two ions ----> two neutrals

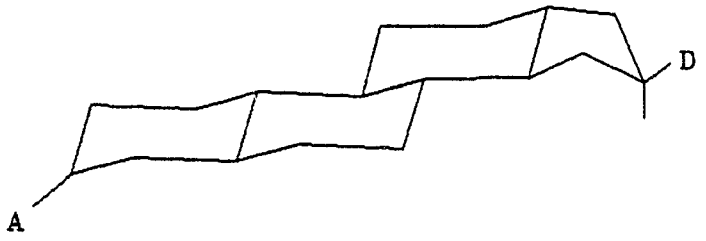
(iii) a charge shift (CSH)

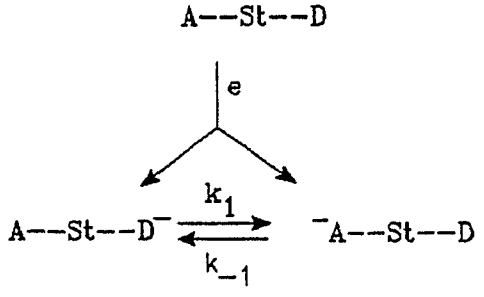
$A{-}{-}B^{+}$ ----> $A^{+}{-}{-}B$

In this model, they have postulated that in a charge separation reaction, where two neutral reactants yield two ions as a result of electron-transfer, a partial dielectric saturation occurs that would inhibit the observation of the inverted region. On the other hand, this partial dielectric

saturation model enhanced the inverted effect for the charge recombination and charge shift reactions [40].

Most results on electron-transfer processes published so far can be assigned to one of the above three categories. The most common examples for the charge separation process are photoinduced electron-transfer. Of course, these reactions do not show any evidence for the Marcus inverted region as predicted by the partial dielectric saturation model. On the other hand, there is experimental evidence for the Marcus inverted region for the charge recombination and charge shift reactions. Miller *et al.* [41] have studied the rate constants for intramolecular electron-transfer in a modified steroid molecule containing acceptor and donor groups on the ends. The derived rate constants for intramolecular electron-transfer show inverted





region behaviour. Of course, this is a charge shift reaction so this behaviour is predicted by the partial dielectric saturation model. However, this observation is also explained as mentioned above because, the distance between the donor and the acceptor is fixed and long distance electron-transfer is not possible.

Farid et al. [42] have studied the rate of back electron-transfer within the geminate radical pair formed in a photochemical charge transfer quenching processes and observed the Marcus inverted region. This is an example of a charge recombination reaction and, according to the partial dielectric saturation model, this observation is possible. However, this observation can again be explained as discussed above. Here long distance electron-transfer is prevented and only geminate pair electron-transfer is considered. Therefore the distance is short and the Marcus inverted region is possible due to a lower value of λ.

Recently, Tachiya [43] has published a series of papers strongly criticizing the Kakitani-Mataga model of electron-transfer. He has shown that the Kikitani-Mataga treatment of the dielectric saturation effect is incorrect and that even if one takes into account the dielectric saturation effect, the Marcus inverted theory is still valid. He concluded that the absence of the inverted region is not accounted for by the dielectric saturation model. Mataga and Kakitani [44] have since accepted that their basic

assumption in the dielectric saturation model has to be changed.

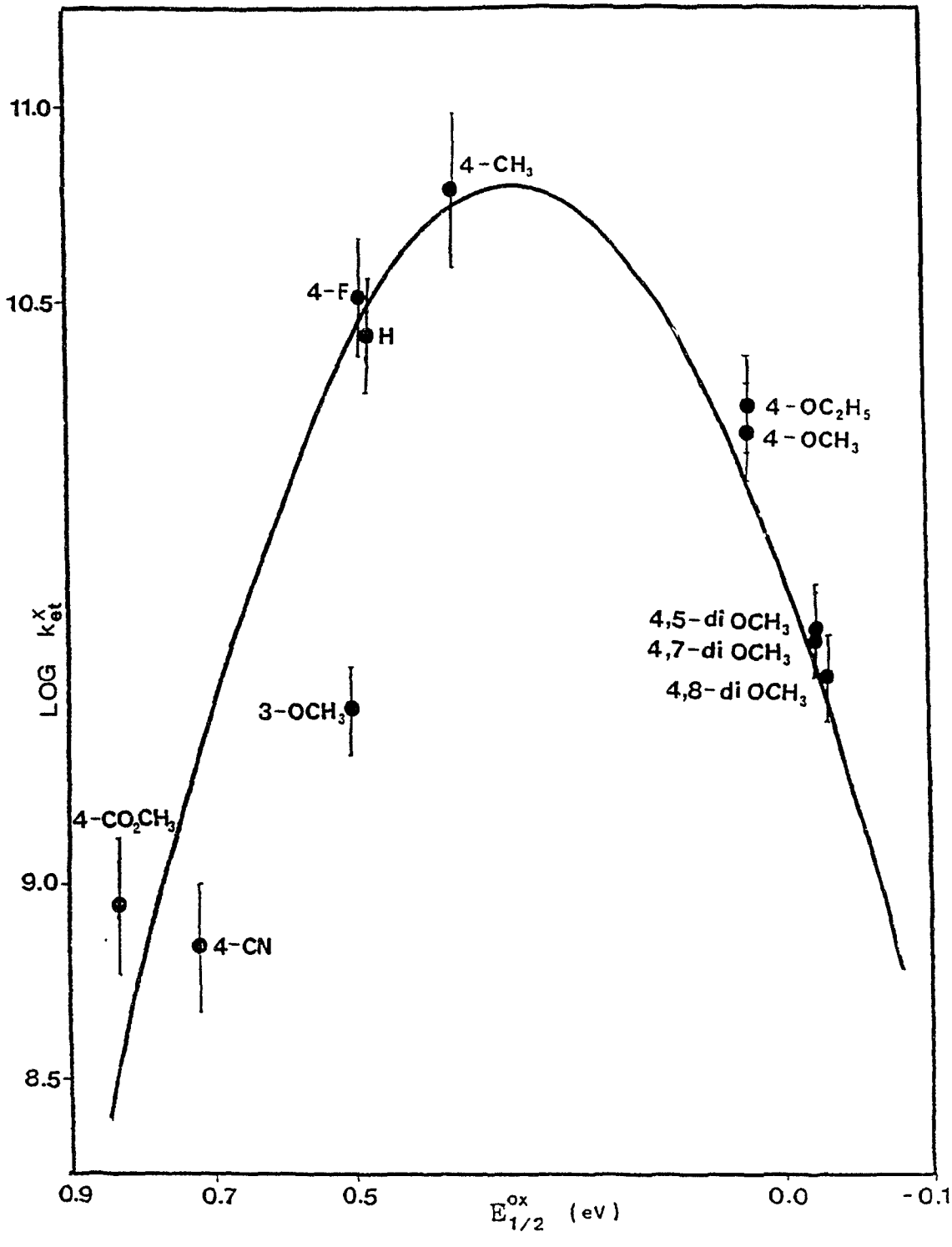
According to Eberson [39], the influence of structural and other factors upon the rates of non-bonded electron-transfer reactions can be summarized in the following way. The value of λ will be kept small in a system that has good possibilities for delocalization of the electron to be transferred. This can be done by using conjugated system which lead to smaller changes in local charge on transfer and smaller changes in bond lengths. Electron transfer over short distances will also lead to small λ values.

The results reported here for the photolysis of esters provide an excellent example to satisfy all of the above conditions. As discussed above, the electron-transfer between the 1-naphthylmethyl radical and phenylacetyloxy radical takes place in a solvent cage over a very short distance. Therefore, longer distance electron-transfer is not possible. Also, the electron to be transferred is delocalized over the naphthalene chromophore. In fact, the electron is being transferred from a non-bonding molecular orbital of the 1-naphthylmethyl radical to a non-bonding molecular orbital of the carboxyl radical so that bond length changes should be minimized. Furthermore, the resulting cation and anion are delocalized over the naphthalene ring and carboxylate group in the ion-pair.

Using the k_{et}^{X} and estimated values for $\Delta G_{et}^{0\,X}$, as obtained

above, one can plot the curve as shown in Fig. 1. As predicted the Marcus inverted region is observed. For this plot, the preexponential factor A in eq. 28, is set at 6 x 10^{10} s^{-1}. A value of λ = 0.60 eV gives a good fit (s = 0.14) to eq. 28 for all the data but a much better fit (s = 0.05) if the point for 3-methoxy is not included. Although, it is possible that 3-methoxy compound is behaving anomalously, there is no good reason for omitting it. The value of λ determines the width of the parabola, which is controlled by the magnitude of the change in k_{et} as a function of the change in ΔG^{o}_{et}. For these substrates, k_{et} changes by two powers of 10 as E^{o} changes from 0.72 V (4-cyano) to 0.35 V (4-methyl). The value of λ also determines, by definition, $-\Delta G^{o}_{et}$ at the maximum in Figure 1 and hence the constant B, eq. 19, since $\lambda = E^{o}_{max} + B$. However, reliable evaluation of any of the three unknowns that make up B, eq. 18, is not possible. The value λ is small, but there is precedent for low values for electron-transfer at short distances. A value of 0.48 eV has been reported for intramolecular electron-transfer over 5 Å in a radical ion [45].

Fig. 1: Plot of log k_{et}^{X} Versus E^{ox} of Electron-Transfer for the Conversion of the Radical-Pair to the Ion-Pair.



CHAPTER 4

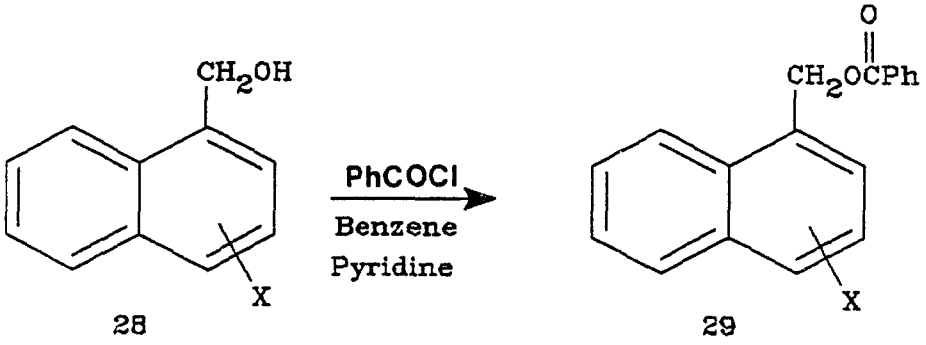
4.1 INTRODUCTION

As mentioned above the benzoate esters of 1-naphthylmethanols are photostable compared to the phenylacetates and phenylpropanoates of 1-naphthylmethanol. Moreover, these esters only gave products derived from the ion-pair intermediate. The results obtain for these esters will be discussed in this chapter.

4.2 PREPARATION OF BENZOATE ESTERS 29a - 29d:

As described above, these esters were prepared by the reaction of the acid chloride with the corresponding 1-naphthylmethanol in benzene at room temperature, Scheme 17.

Scheme 17: Preparation of Benzoate Esters **29a - 29d.**



28 29

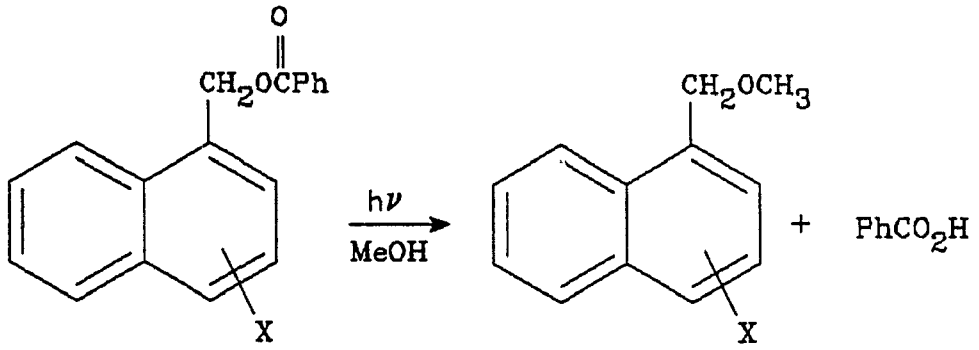
a: X = H
b: X = 2-OCH_3
c: X = 3-OCH_3
d: X = 4-OCH_3

All esters were purified by recrystallization from hexane:dichloromethane. Physical and chemical properties are given in the Chapter 6.

4.3 PREPARATIVE PHOTOLYSIS OF ESTERS 29b AND 29d:

Preparative scale photolysis were done only for the esters **16b** and **16d**. Solutions of the esters (20 mg) in methanol (20 ml) were irradiated in tubes (after degassing)

Scheme 18: Photolysis of Esters **29b** and **29d**.



29b, 29d 17a – 17l

using a 1000W Hg lamp. Irradiation of these esters gave a mixture of two major products as shown in the Scheme 18. Good mass balance was obtained as shown in Table 7.

Table 7: Product Yields[a] for the Photolysis of Esters **29b** and **29d**.

Ester **29**	X	Ether **17**[b]	Acid[c]
b	2-OCH_3	78	58
d	4-OCH_3	92	80

[a]Estimated error, ±2%

[b]By calibrated HPLC

[c]By weight of isolated product

4.4 SPECTRAL MEASUREMENTS OF ESTERS 29a - 29d:

Extinction coefficients, fluorescence quantum yields and singlet energies for all esters were obtained and are tabulated in Table 8. However, triplet energies could not be obtained due to the absence of phosphorescence even at 77K.

4.5 DISCUSSION

All phenylacetate esters,**16**, and phenylpropanoate esters,**20**, gave similar results on photolysis indicating that the same mechanism, as described in Chapter 3, takes place. However, the observed results for the benzoate esters are different. These compounds are relatively photostable and their quantum yields of fluorescence are

Table 8: Spectral Properties of Esters **29a - 29d** in Methanol.

Ester **29**	X	$\epsilon \times 10^{-3}$ (λ_{max}, nm)	E_S[a] kcal/mol (kJ/mol)	Φ_f[b]
a	H	8.0 (276)	92.0 (386)	0.005
b	2-OCH_3	5.0 (334), 4.5 (320), 7.8 (290), 10.3 (278), 7.7 (266)	84.0 (353)	0.015
c	3-OCH_3	3.2 (327), 2.4 (312), 6.0 (282), 7.0 (272), 7.0 (268), 6.0 (260)	85.5 (360)	0.015
d	4-OCH_3	8.1 (294)	88.1 (370)	0.005
d[c]	4-OCH_3	6.8 (293)		0.05

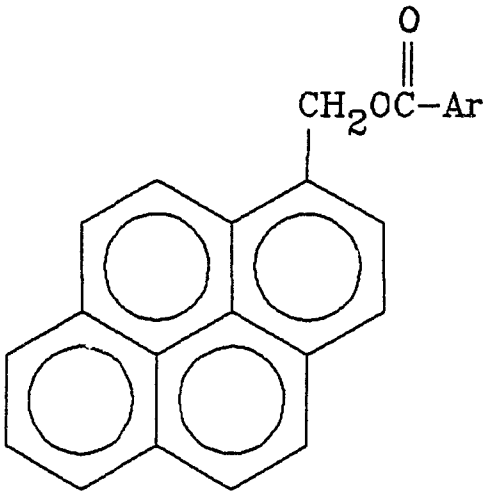
[a]Estimated error, ±0.01

[b]Estimated error, ±5%

[c]in hexane

very low, Table 8. A most revealing observation is that these esters showed a broad structureless very weak emission band ($\phi_f < 1.2 \times 10^{-3}$ for **29d**) at longer wavelength than the normal S_1 to S_0 emission. This is characteristic of the emission from an exciplex. This band, as well as the

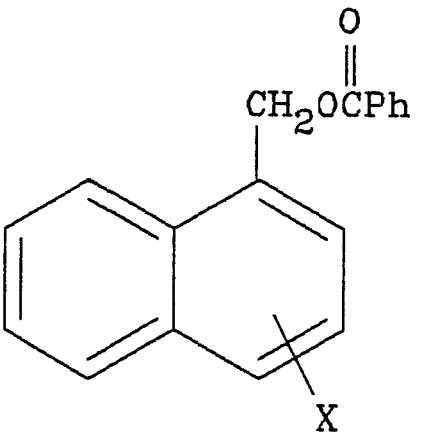
quantum yield for fluorescence of ester **29d** in methanol and hexane as shown in Table 8, provide evidence for the formation of a charge transfer complex in the excited state. The lower quantum yields of fluorescence of **29d** in methanol compared to hexane indicate that the formation of the charge transfer complex is more favoured in polar solvents such as methanol [46]. However, measurements of the lifetime of these exciplexes were not possible due to the weakness of the emission.



30· Ar = Ph

31· Ar = Np

32· Ar = An



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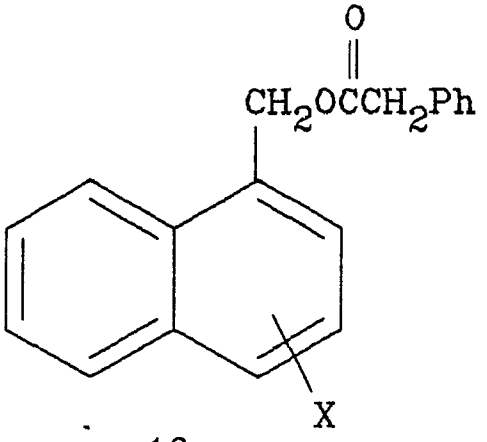
An example of the formation of a similar intramolecular exciplex with chromophores connected through the ester -C(=O)OC- linkage has been described by Iwamura *et al.* [47]. In this study on the photoreactivity of 1-pyrenylmethyl

esters, they observed that 1-pyrenylmethyl benzoate,**30**, 1-pyrenylmethyl naphthoate,**31**, and 1-pyrenylmethyl anthracene carboxylate,**32**, were photostable. The life times of the esters are: **30**, 97 ns; **31**, 0.85 ns; **32**, <1 ns. Ester **32** showed a broad structureless emission band at longer wavelength. They have studied the properties of this band in different solvents and assigned it as resulting from the formation of a charge transfer complex. However, this type of band was not observed for the esters **30** and **31**. Even though, the exciplexes of esters **30** and **31** do not emit, the shorter singlet lifetime and the stability of the esters on irradiation provide circumstantial evidence for the existence of exciplexes. Iwamura *et al.* explained that the absence of exciplex emission for the ester **30** and **31** could be due to non-radiative decay to the ground state. The same type of exciplex formation would rationalize the results obtained for the 1-naphthylmethyl benzoate ester studied here.

Intramolecular excimers between two chromophores connected through σ-bonds have been thoroughly studied by Hirayama [48] and others [49]. Most of these studies have been done on systems where two chromophores are connected by a hydrocarbon chain, $-(CH_2)_3-$, rather than ester linkage -C(=O)OC-. Exciplex emissions have been observed most often when the attached bridge contains three carbon atoms. The

phenylacetate esters,**16**, described in the previous chapters, do not show any evidence for the formation of exciplexes.



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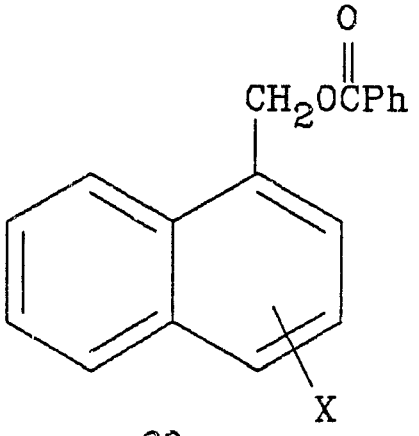


29

It is interesting that the two chromophores of the phenylacetate ester,**16**, are separated by four atoms instead of three atoms as in the benzoate esters,**29**.

However as described by Iwamura *et al.* [47], the -C(=O)OC- linkage is very different structurally from a $-(CH_2)_3-$ linkage. The s-*cis* conformation is necessary for intramolecular exciplex formation. The rotation around the carbon-ether oxygen bond of esters from s-*trans* to the conformations s-*cis* in the ground state has a very low activation energy [50]. According to Iwamura *et al.* [47] it

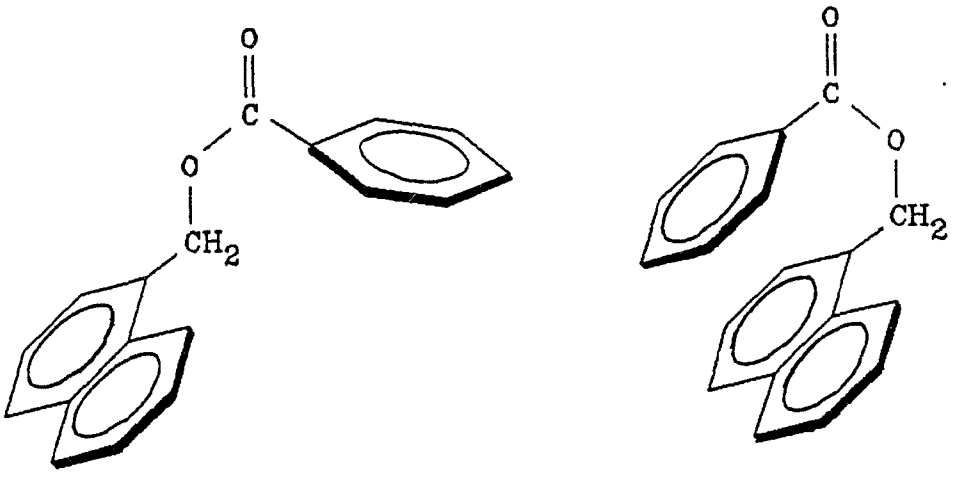
is possible to overcome this barrier for isomerization by columbic attraction forces between the two oppositely charged chromophores if intramolecular charge transfer occurs in the excited state. The following studies were done to confirm the existence of these charge transfer complex in the excited state.

4.6 FLUORESCENCE QUENCHING STUDIES:

The fluorescence quenching of 1-methoxynaphthalene by methyl benzoate in methanol was examined. The Stern-Volmer plot gives $k_q\tau_S$ = 13.7 ± 0.8 mol^{-1} which,along with the measured lifetime of 1-methoxynaphthalene of 13 ns [23], gave a fluorescence quenching rate constant as 1.1 x 10^9 mol^{-1} s^{-1}. Using the Weller equation, eq. 22, along with the oxidation potential of 1-methoxynaphthalene (1.38V vs SCE in CH_3CN [52]) and methylbenzoate (2.12V vs SCE in EtOH [51]), the singlet energy of 1-methoxynaphthalene (89.3 kcal/mol [23])and an assumed distance of 7 Å, predicts that electron-

$$\Delta G = 23.06(E_{1/2}^{ox} - E_{1/2}^{red}) - E_{o,o} + e^2/Dr \qquad (22)$$

transfer between the excited state of 1-methoxynaphthalene and the ground state of methyl benzoate is exothermic by 9 kcal/mol. The rate should, therefore, be diffusional. The fact that the quenching rate constant is a factor of ten too slow relative to rate of diffusion may be a result of the use of an incorrect potentials which have been measured in



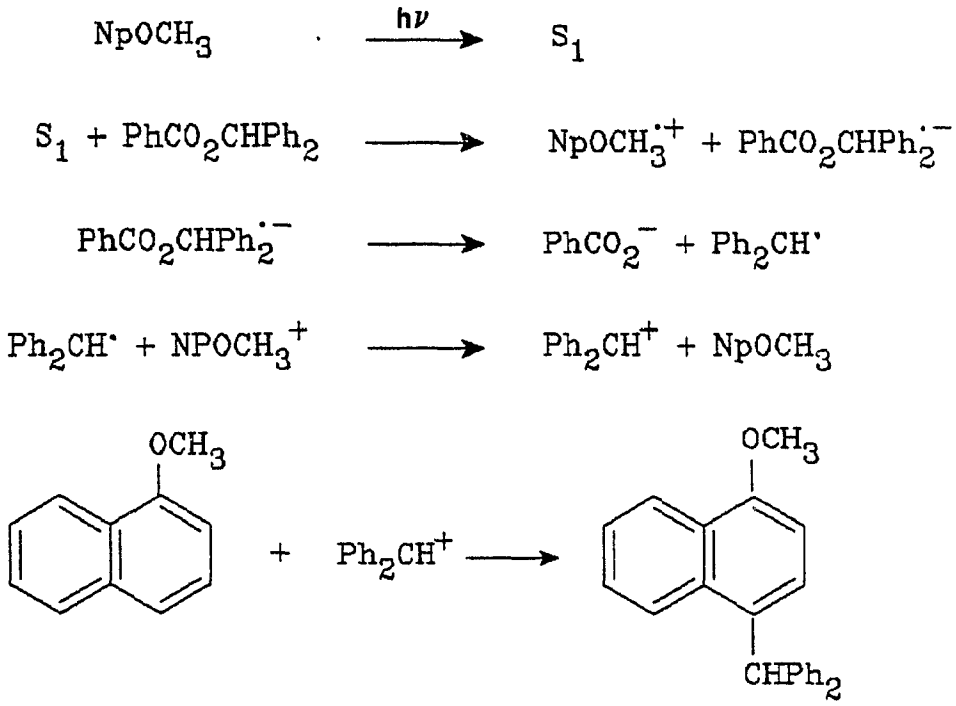
s–trans s–cis

acetonitrile for the oxidation and ethanol for the reduction. However, it is clear that the low fluorescence quantum yields for the benzoate esters could be due to internal charge transfer in the excited singlet state.

4.7 REACTIVITY OF RADICAL ANIONS GENERATED BY PHOTOINDUCED ELECTRON-TRANSFER

As mentioned above benzoate ester can accept an electron from electron donors such as the excited singlet state of 1-methoxynaphthalene. In this manner it is possible to generate the radical anion of the benzoate ester. To study the reactivity of ester radical anions, benzhydryl benzoate was prepared as described in the literature [53]. A solution of benzhydryl benzoate, 1-methoxynaphthalene, and $MgClO_4$ in methanol was irradiated with a 1000W mercury lamp. A product with long retention

Scheme 19: Mechanism of the Photolysis of Benzhydryl Benzoate in Acetonitrile in the Presence of 1-Methoxynaphthalene as Sensitiser.



33

time on reverse phase HPLC has observed and identified as diphenyl(4-methoxynaphthyl)methane, **33**, by ^{1}H nmr and mass spectrometry. Details are given in Chapter 6. The yield was about 20%. The suggested mechanism for the formation of this product is given in Scheme 19. The benzhydryl benzoate ester radical anion has been previously generated by pulse radiolysis by Masnovi *et al.* [54] in their studies on reactivity of ester radical anions. According to their results, benzoate ester radical anions decay to afford the

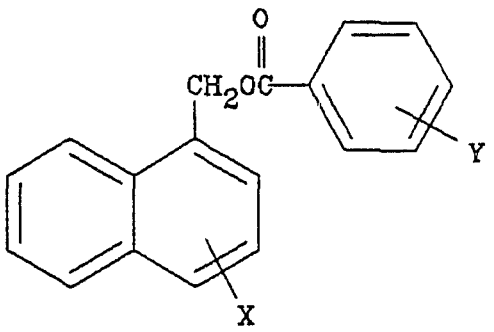
benzoate anion and an alkyl radical. The high stability of the benzhydryl radical lower the activation barrier of the ester C-OC(=O) bond cleavage. As outlined in the Scheme 19, the formation of diphenyl(4-methoxynaphthyl)methane, **33**, suggests the generation of the radical anion of the ester. This requires bimolecular electron-transfer from excited 1-methoxynaphthalene to the benzoate ester.

The preliminary results in this section clearly indicate that the photostability and low quantum yields of fluorescence of benzoate esters of 1-naphthylmethanol are due to the formation of a charge transfer complex in the excited state. The energy of this internal charge transfer complex is too low for efficient carbon-oxygen bond cleavage and deactivation to the ground state is the major pathway.

4.8 FURTHER STUDIES ON BENZOATE ESTERS

As mentioned above, both the photostability and the low quantum yields of the fluorescence of benzoate esters, **29a - 29d**, are due to the quenching of the singlet state, S_1, by intramolecular electron transfer. This different behaviour of the excited state of benzoates compared to the phenylacetates led to further investigation of benzoate esters. It is clear that this internal electron transfer takes place from the excited naphthalene chromophore to the benzoate chromophore. Therefore, for a given ester, the rate of this internal electron-transfer should depend on the

oxidation potential of the naphthalene chromophore and the reduction potential of the benzoate chromophore. The oxidation potential of the naphthalene chromophore can be varied by changing substituents. For instance, the oxidation potential of 1-methylnaphthalene is 1.54 V vs SCE in CH_3CN [55], whereas that of 4-cyano-1-methylnaphthalene is 2.34 V vs SCE in CH_3CN [56]. Similar changes will occur for the reduction potentials of the benzoate chromophore. Therefore, by changing the substituents in each ring one



29e – 29i

29e: X = 4–OCH_3, Y = 4–CN

29f: X = H , Y = 4–CN

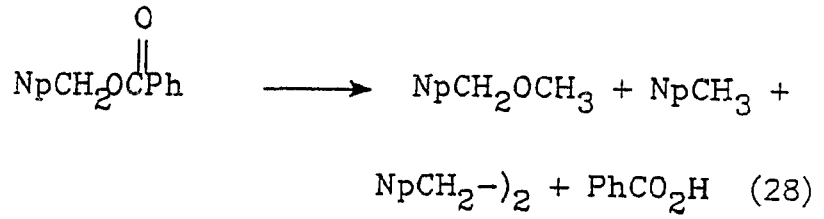
29g: X = H, Y = 4–OCH_3

29h: X = 4–CN, Y = 4–OCH_3

29i: X = 4–CN, Y = H

should change the rate of electron-transfer and hence the quantum yields of. fluorescence as well as reactivity. To demonstrate this idea, the following esters with different substituents on the naphthalene and/or the benzene

chromophore were prepared from the corresponding 1-naphthalenemethanol and benzoyl chloride. Preparative and analytical photolysis results, fluorescence quantum yields, singlet lifetimes and UV spectral measurements have been done as described in Chapter 6. The results are given in the Table 9, Table 10 and photolysis products are given in eq. 28.



$$NpCH_2OCPh \longrightarrow NpCH_2OCH_3 + NpCH_3 + NpCH_2-)_2 + PhCO_2H \quad (28)$$

Table 9: Spectral Properties of Esters **29e - 29i** in Methanol.

Ester 29	$\epsilon \times 10^{-3}$ (λ_{max})	E_S[a] kcal/mol	ϕ_f[b]	τ_S[c] ns
e	8.9 (292)		0.003	
f	5.3 (288), 7.4 (277) 6.2 (267)		0.004	
g	4.5 (288), 13(276)	93.5	0.030	7.6
h	3.1 (321), 6.9 (307) 9.1 (294)	87.2	0.195	5.0
i	3.0 (321), 7.1 (306) 9.3 (294)	87.2	0.16	5.2

[a]Estimated error, ±1nm; [b]Estimated error, ±0.001

[c]Estimated error, ±5%

Table 10: Product Yields for the Photolysis of Esters **29g** and **29i**, in Methanol.

Ester **29**	Ether[a] **17**	Acid[b]	Dimer[a]	methylnaphthalene[a]
g	83	70		
i[d]	66	55	22	5
i[c]	55	40	2	40

[a]By calibrated HPLC

[b]By weight of isolated acid

[c]Photolysis done with 300 mg of ester

[d]Photolysis done with 70 mg of ester

As mentioned above, benzoate esters have lower quantum yields of fluorescence relative to the phenylacetate esters. For comparison and convenience, the results obtained for the quantum yields of fluorescence of the benzoate esters and the corresponding phenylacetate esters are shown in Table 11. The quantum yields of fluorescence of the phenylacetate esters depend only on the substituents on the naphthalene ring and are independent of the substituents on the phenyl ring. This observation is supported by the work of Hilborn and Pincock [57]. They have measured quantum yields of fluorescence for a series of 1-naphthylmethyl phenylacetate esters having different substituents only on the phenyl

ring. The values obtained were almost constant at 0.14. Therefore, the comparison of the quantum yields of fluorescence of the benzoate esters can be done by considering only the substituents at the naphthalene ring. For instance, **16a** is useful model for **29a**, **29f** and **29g**.

Table 11: Comparison of Quantum Yields of Fluorescence of Benzoate and Phenylacetate Esters in Methanol.

Benzoate **29**	X	Y	ϕ_f^B	ϕ_f^{PA}	Phenylacetate **16**	X
a	H	H	0.005	0.14	**a**	H
c	3-OCH_3	H	0.015	0.24	**c**	3-OCH_3
d	4-OCH_3	H	0.005	0.27	**d**	4-OCH_3
e	4-OCH_3	4-CN	0.003	0.27	**d**	4-OCH_3
f	H	4-CN	0.004	0.14	**a**	H
g	H	4-OCH_3	0.030	0.14	**a**	H
h	4-CN	4-OCH_3	0.195	0.21	**f**	4-CN
i	4-CN	H	0.160	0.21	**f**	4-CN

It is clear that the quantum yields of fluorescence of the benzoate esters **29a - 29f** are diminished by more than 90% when compared to the corresponding phenylacetates. Also these esters are very unreactive photochemically. For instance, **16a** is 80% reacted after 15h of irradiation with

a 250W medium pressure Hg lamp, whereas **29a** has shown only 5% conversion. In contrast, the quantum yields of fluorescence of **29g - 29i** are relatively greater quenched. In agreement, **29h** is 80% reacted after 6h of irradiation with 250W medium pressure Hg lamp. Those esters having electron withdrawing substituents on the naphthalene chromophore, **29h** and **29i** or electron donating substituent in the benzoate chromophore have less efficient intramolecular

Table 12: Percentage of Quenching of Quantum Yields of the Fluorescence of Benzoate Esters Compare to Phenylacetates.

Ester 29	X	Y	$(1 - \phi_f^B/\phi_f^{PA}) \times 100^a$	$\sigma^+ - \sigma$
a	H	H	96 (±9)	0.00
c	3-OCH_3	H	94 (±7)	0.12
d	4-OCH_3	H	98 (±10)	-0.78
e	4-OCH_3	4-CN	99 (±12)	-1.44
f	H	4-CN	98 (±10)	-0.66
g	H	4-OCH_3	79 (±3)	0.27
h	4-CN	4-OCH_3	7 (±1)	0.93
i	4-CN	H	24 (±2)	0.66

[a]Errors in brackets are based on error of ±0.001 in ϕ_f.

electron-transfer. Hence, fluorescence emission is much more efficient. The ratio of fluorescence quantum yield for each benzoate ester, when compared to the corresponding phenylacetate ester is shown in Table 12.

An assumption can be made that the oxidation potential of the naphthalene chromophore and reduction potential of the benzoate group controls the ratio of the quantum yields. Making the reasonable assumption that these potentials vary with σ^+ for the oxidation and σ for the reduction gives the plot shown in Figure 2. This treatment can be made more quantitative as discussed next.

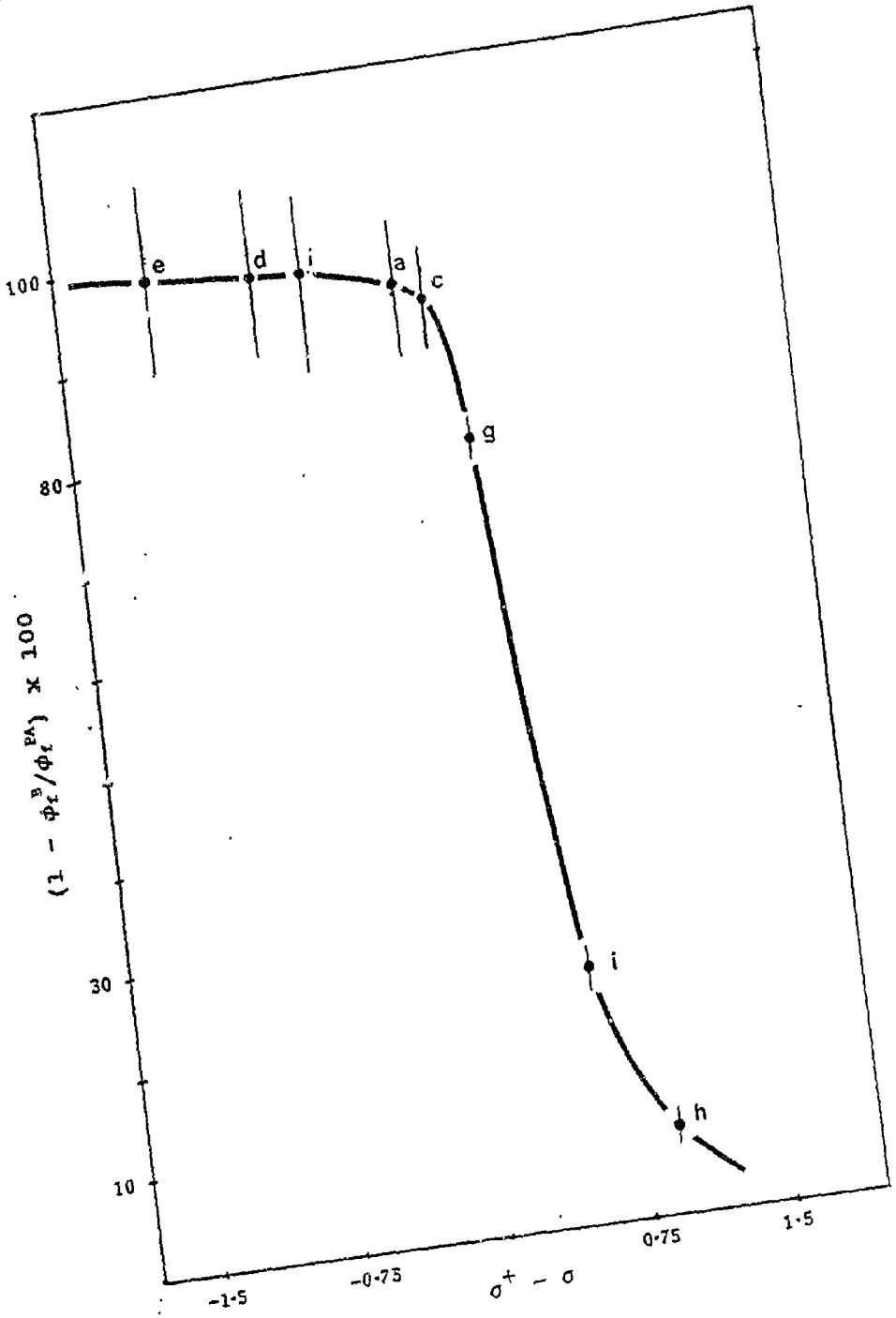
According to the mechanism outlined in Scheme 19, there are five different pathways for the disappearance of the excited state, S_1, of the benzoate esters with rate constants k_f, k_{isc}, k_{ic}, k_R and k_{et}. Eq. 29 can be easily derived for the quantum yield of fluorescence of these esters. For the phenylacetate esters, the corresponding derivation is eq. 30.

$$\phi_f^{B} = \frac{k_f}{k_f + k_{isc} + k_{ic} + k_R + k_{et}} \qquad (29)$$

$$\phi_f^{PA} = \frac{k_f}{k_f^{\circ} + k^{\circ}_{isc} + k^{\circ}_{ic} + k^{\circ}_R + k^{\circ}_{et}} \qquad (30)$$

Making the reasonable assumption that the rate of disappearance of the excited state of the phenylacetate and

Figure 2: Plot of $(1 - \phi_f^B/\phi_f^{PA}) \times 100$ Vs $\sigma^+ - \sigma$.



benzoate esters is similar except for the differences in the rate of electron-transfer and that there is no intramolecular electron-transfer for the phenylacetate, one can derive eq. 31.

$$\frac{\phi_f^{PA}}{\phi_f^{B}} = 1 + \tau^{PA} k_{et} \qquad (31)$$

$$\ln \left(\frac{\phi_f^{PA}}{\phi_f^{B}} - 1 \right) - \ln \tau^{PA} = \ln k_{et} \qquad (32)$$

Here, $\tau^{PA} = 1/(k^{o}_{f} + k^{o}_{isc} + k^{o}_{ic} + k^{o}_{R}) = 1/(k_f + k_{isc} + k_{ic} + k_R)$

The rate of electron-transfer should be a function of the oxidation potential of the naphthalene and the reduction potential of benzoate groups and hence, a function of σ^+ and σ. The values used for eq. 33 and are given in Table 13. By fitting $\ln(\phi_f^{PA}/\phi_f^{B} - 1) - \ln \tau^{PA}$ with σ^+ and σ as shown in Figure 3, one can obtain a best fit with $\rho_1 = -3.46$ and $\rho_2 = 2.17$ with $r^2 = 96\%$.

$$\ln\left[\frac{\phi_f^{PA}}{\phi_f^{B}} - 1 \right] - \ln \tau^{PA} = \rho_1 \sigma^+ + \rho_2 \sigma \qquad (33)$$

Although, the benzoate esters **29a - 29f** are photostable and have very low quantum yields of fluorescence, the esters, **29g - 29i** show higher quantum yields of fluorescence and are photoreactive. This observation can easily be explained by the less efficient intramolecular electron-transfer of esters **29g - 29i**. Therefore, the normal bond cleavage process discussed in Chapter 2 and 3 takes place. Irradiation of ester **29g** gave a mixture of photoproducts and

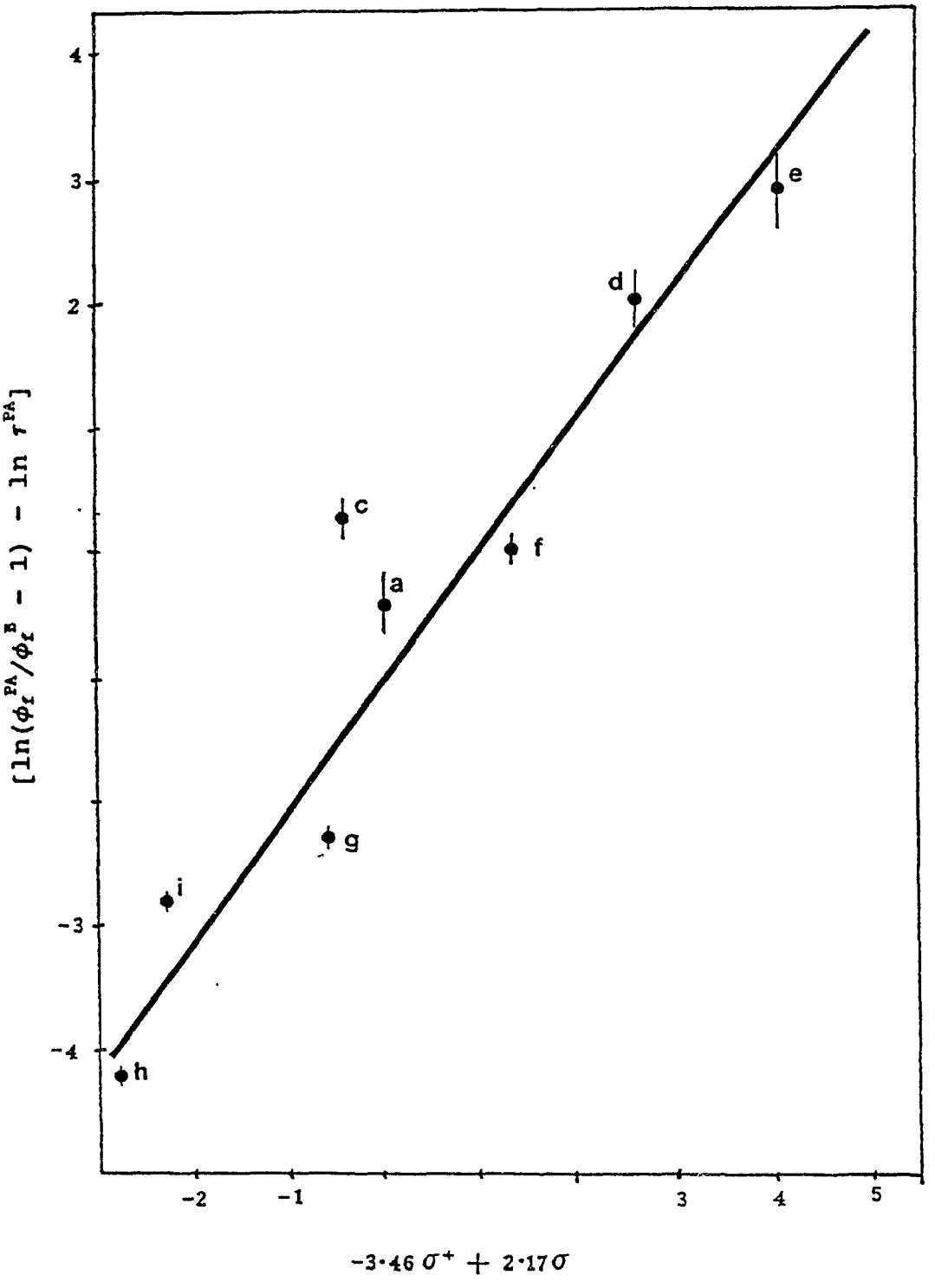
Table 13: Parameters of the Eq. 4 for Esters **29a - 29i.**

Ester 29	X	Y	σ^+	σ	ln $(\phi_f^{PA}/\phi_f^{B} - 1) - \ln \tau^{PA}$
a	H	H	0.00	0.00	-0.4 (±0.21)
b	3-OCH_3	H	0.12	0.00	0.3 (±0.14)
d	4-OCH_3	H	-0.78	0.00	2.0 (±0.21)
e	4-OCH_3	4-CN	-0.78	0.66	3.0 (±0.33)
f	H	4-CN	0.00	0.66	0.13 (±0.10)
g	H	4-OCH_3	0.00	-0.27	-2.38 (±0.05)
h	4-CN	4-OCH_3	0.66	-0.27	-4.17 (±0.01)
i	4-CN	H	0.66	0.00	-2.80 (±0.02)

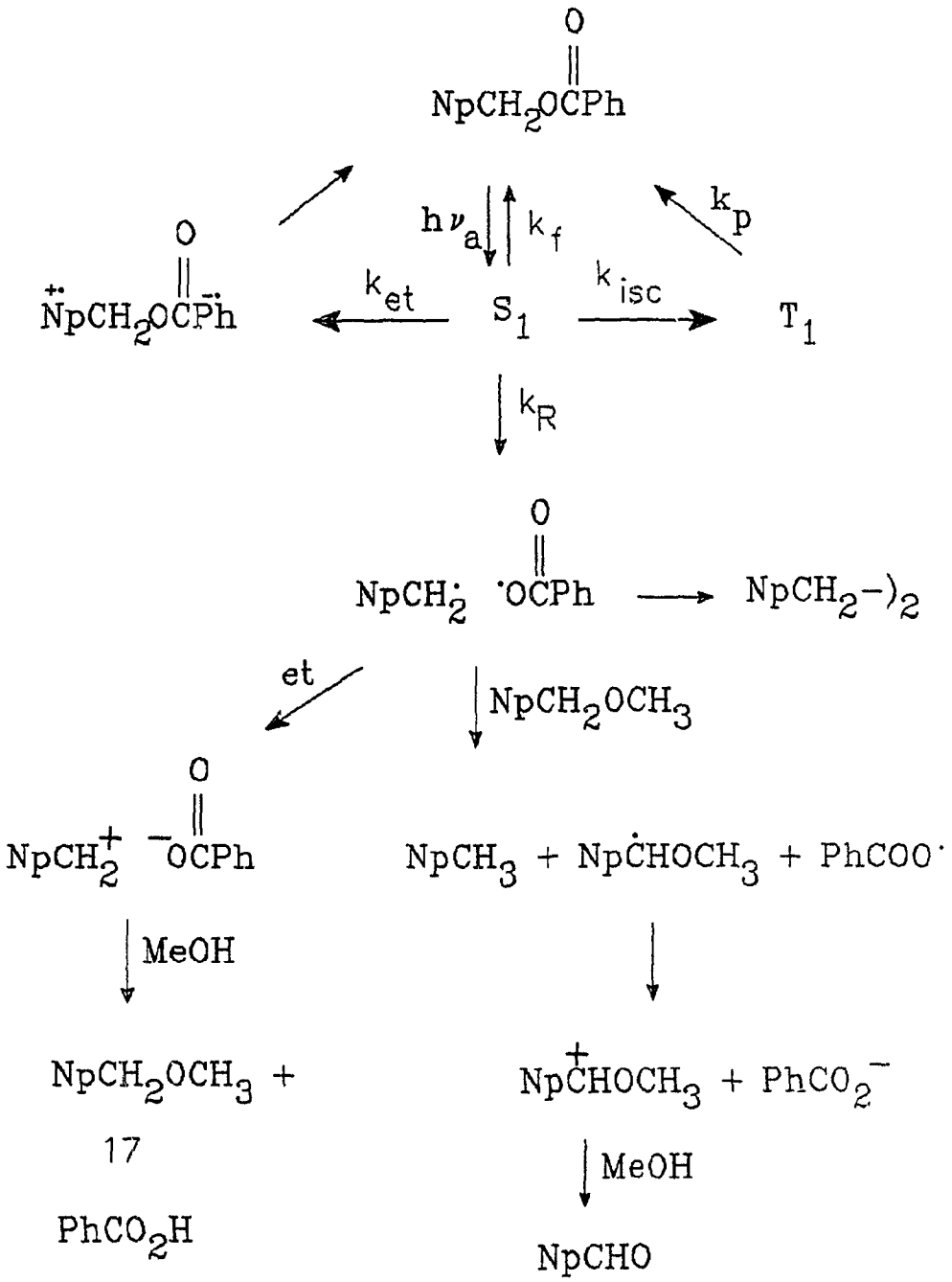
[a]Errors in brackets are based on error ±0.001 in ϕ_f and ±5% in τ.

a distribution that was dependent on the extent of conversion of the ester. The photoproducts of this ester given in eq. 28. The ether and the acid are probably obtained via pathways involving homolytic cleavage followed by electron-transfer and trapping of naphthylmethyl carbocation and benzoate anion with the solvent methanol, as shown in Scheme 20. The dimer is obtained from out-of-cage combination of two 1-naphthylmethyl radicals. Methyl-naphthalene and naphthaldehyde are obtained from the initially formed product ether, as shown in Scheme 20.

Figure 3: The Plot of $[\ln(\phi_t^{PA}/\phi_t^{B} - 1) - \ln r^{PA}]$ Vs σ^+ and σ.



Scheme 20: Mechanism for the Photolysis of Benzoate Esters **29.**



CHAPTER 5

UNUSUAL EXCITED STATE BEHAVIOUR OF PHENOXYACETATE ESTERS

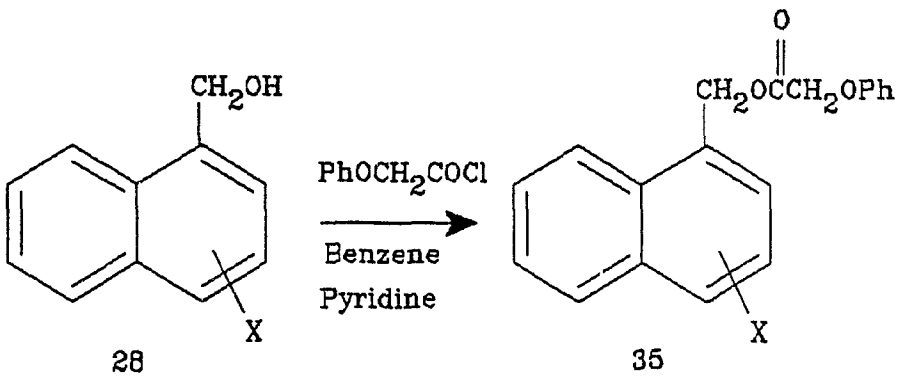
5.1 INTRODUCTION:

As indicated in chapter 3, phenoxyacetate esters, **35a - 35d**, are more photoreactive than their corresponding phenylacetate esters, **16a - 16d**, or phenylpropanoate esters, **20**. Moreover, the phenoxyacetate esters have lower quantum yields of fluorescence and shorter lifetimes of the singlet state when compared to the corresponding phenylacetate esters. However, the emission spectra of these esters do not show any evidence for exciplex formation as do the benzoate esters. The other major difference in the photochemistry of these phenoxyacetate esters is the higher yields of products derived from the radical pair compared to the corresponding phenylacetate esters. The results on these phenoxyacetate esters, **35a - 35d**, are discussed in this chapter.

5.2 PREPARATION OF PHENOXYACETATE ESTERS:

As described before, these esters were prepared by the reaction of the acid chloride with the corresponding 1-naphthylmethanol in benzene at room temperature. All these esters were purified by recrystallization from hexane. Physical and chemical properties are given in the Chapter 6.

Scheme 20: Preparation of Phenoxyacetate Esters, **35a - 35d.**

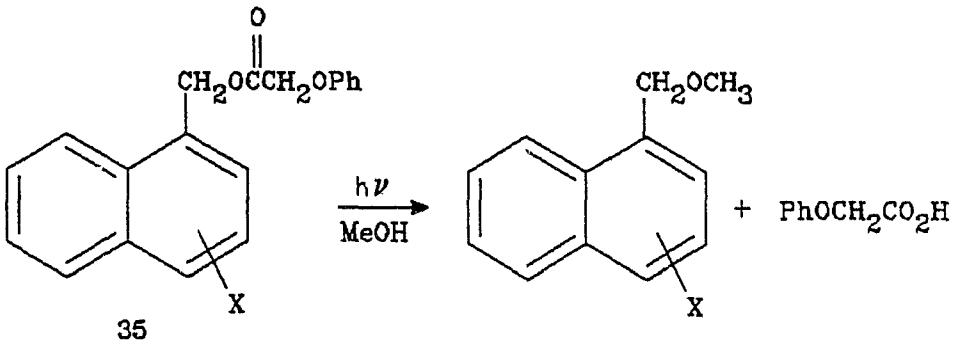


28 35

a: X = H
b: X = 2-OCH_3
c: X = 3-OCH_3
d: X = 4-OCH_3

5.3 PHOTOLYSIS OF ESTERS 35a - 35d:

The preparative photolysis were done with a 200W medium pressure mercury lamp filtered with Pyrex. Solutions were purged with nitrogen before and during the irradiation. Yields of photoproducts were determined by calibrated HPLC. Details are given in Chapter 6. Irradiation of these esters gave a mixture of three major products as shown in eq. 34. Good mass balance was obtained for all cases. The results of the photolysis are given in Table 14.



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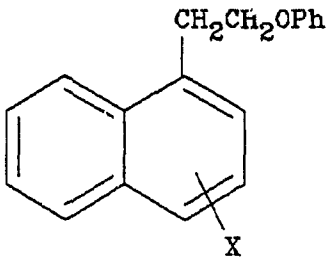
17a – 17l



(34)

36

Table 14: Percentage Yields of the Products from the Photolysis of Phenoxyacetate Esters in Methanol.

Ester	Methyl ether	Phenyl ether	Acid[b]
35	**17**	**36**	**37**
a	72 (84)	24 (15)	60
b	17 (25)	50 (47)	10
c	16 (31)	60 (52)	10
d	59 (74)	30 (24)	40

[a]By calibrated HPLC. Data obtained for phenylacetate esters **16a - 16d** are in brackets.

Table 15: Absorption Properties of Phenoxyacetate Esters **35a - 35d.**

Ester, 35	$\epsilon \times 10^{-3}$ (λ_{max}, nm)
a	..4 (288), 9.8 (276), 6.2 (267)
b	2.7 (327), 2.4 (312), 5.0 (280), 6.2 (274)
c	2.9 (328), 2.5 (314), 5.6 (282), 6.7 (273)
d	10.8 (293)

Table 16: Emission Properties of phenylacetate Ester **35a - 35d.**

Ester **35**	E_S[a] kcal/mol (kJ/mol)	E_T[a] kcal/mol (kJ/mol)	ϕ_f[b,d]	τ_f[c,d] ns
a	91.2 (383)	60.3 (253)	0.10 (0.14)	30 (39)
b	83.8 (352)	57.4 (241)	0.18 (0.23)	6.2 (7.2)
c	84.9 (357)	57.4 (241)	0.18 (0.24)	8.7 (11)
d	88.1 (370)	59.4 (249)	0.24 (0.27)	6.9 (7.3)

[a]Estimated error, ±1nm; [b]Estimated error, ±0.01.

[c]Estimated error, ±5%.

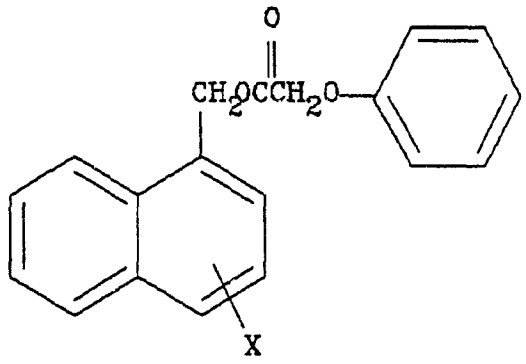
[d]Values obtained for the corresponding phenylacetate esters are given in brackets.

5.4 SPECTRAL MEASUREMENTS OF ESTERS 35a - 35d:

Extinction coefficients, fluorescence quantum yields, singlet and triplet energies and singlet lifetimes were measured and are reported in Tables 15 and 16.

5.5 DISCUSSION:

From Table 16, it is clear that the reactive singlet state of the phenoxyacetates is somewhat different from that of the phenylacetate esters. The differences are: nigher reactivity; higher yields derived from radical pair, Table 14; lower quantum yields of fluorescence; shorter lifetimes, Table 16. However, the only structural difference between these two ester series is the oxygen atom directly attached to the phenyl group in the phenoxyacetate esters as shown in structure 35.



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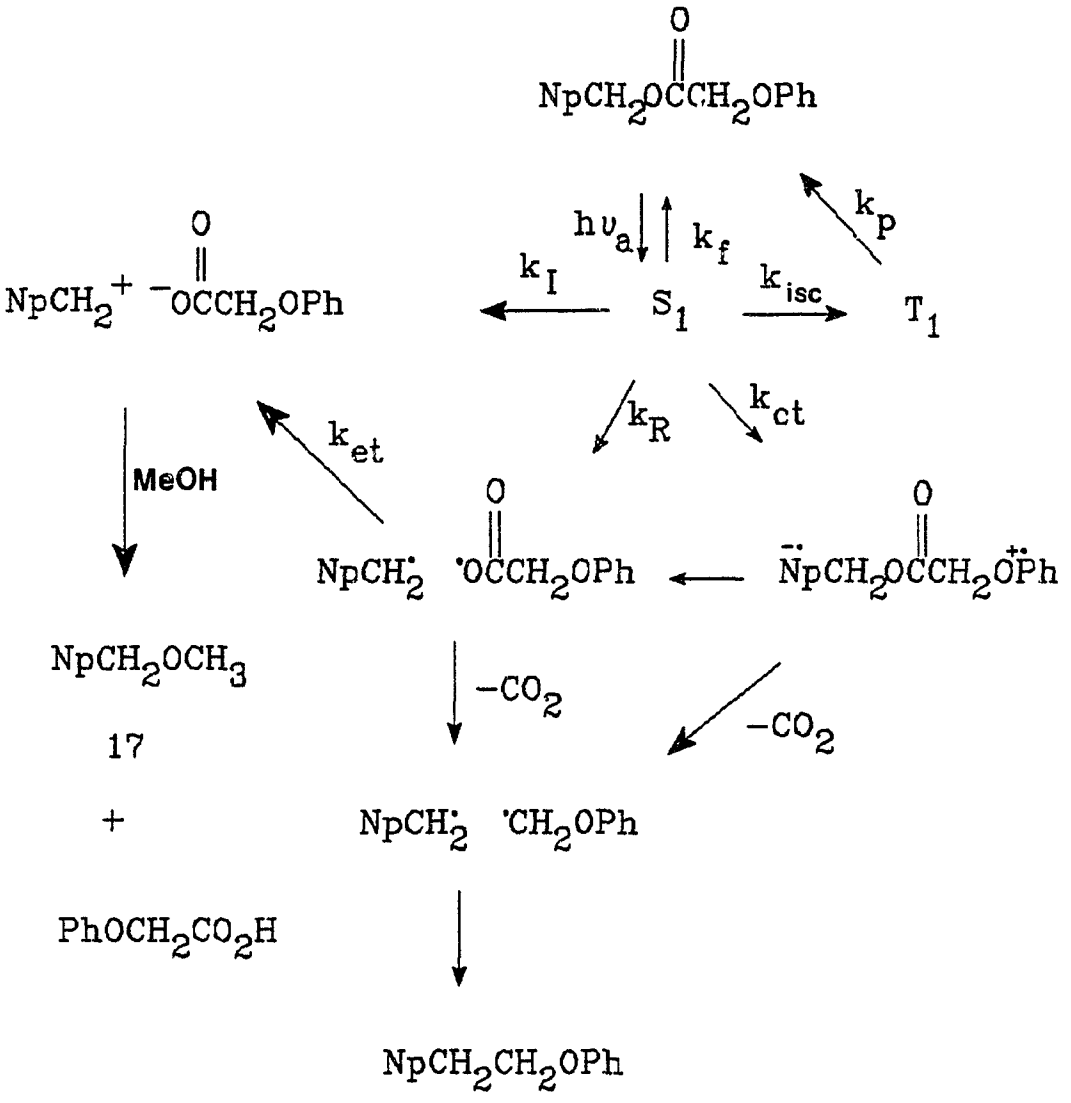
Pincock and Hilborn [57] have observed a similar reactivity change in studies of the photolysis of naphthylmethyl phenylacetate esters with different

substituents on the phenyl ring. They have observed higher yields of photoproducts derived from the radical pair for the 3- and 4-methoxy substituted esters when compared to the unsubstituted ester. This suggests that the different reactivity of the phenoxyacetate esters is due to the oxygen atom directly attached to the phenyl ring. The oxidation potential of benzene ($E_{1/2}^{ox}$ = 2.30 V vs SCE in CH_3CN [59]) is greatly lowered by methoxy substituents. As an example the oxidation potential of anisole is 1.76V vs SCE in CH_3CN [59]. So, it is possible that intramolecular electron transfer from the phenoxy ring to the naphthalene chromophore in the excited state is enhanced. Use of the Weller equation, along with the oxidation potential of anisole, the reduction potential of 1-methylnaphthalene ($E_{1/2}^{red}$ = -2.46V vs SCE in dioxane [51]) and an assumed distance of 7Å, predicts that ΔG = 6 kcal/mol for electron-transfer between excited 1-methylnaphthalene and the ground state of anisole. Even though this electron-transfer is endothermic by 6 kcal/mol, there is precedence for endothermic electron-transfer although at a relatively slow rate [60]. Assuming this electron-transfer is possible, the reported results can be explained.

As discussed in Chapter 3, phenylacetate esters give an in-cage coupling product by a pathway of homolytic cleavage, decarboxylation and finally coupling of the naphthylmethyl

radical with the benzyl radical. The coupling product **36** of the photolysis of phenoxyacetates can be explained in the same way as shown in Scheme 21. However, the higher yields of this in-cage coupling product suggest that another pathway is contributing to formation of the radical pair. As mentioned above, this pathway is probably the slow electron-transfer from the phenoxy chromophore to the excited naphthalene chromophore. If this is true, some of the in-cage coupling product would be formed from the charge transfer complex as shown in the Scheme 21. The bond dissociation energy of $OC(=O)--CH_2$ is 55 kcal/mol (2.3 eV) as estimated in Chapter 3. The energy of the charge transfer complex is 4.22 eV, so that the energy of charge transfer complex is strong enough to break the $OC(=O)--CH_2$ bond in the phenoxyacetate ester. Also, the higher reactivity for the photolysis of these phenoxy esters can be explained by the suggested electron-transfer between two chromophores. As mentioned above the energy of the charge transfer complex is high enough to allow efficient $OC(=O)-CH_2$ bond breaking and once this bond breaks, the coupling of two radicals gives the in-cage coupling product directly. However, if the excitation energy is concentrated on the naphthalene chromophore, the efficiency of the photolysis is reduced by a 1,3-sigmatrofic migration as explained in Chapter 1.

Scheme 21: Mechanism for the Photolysis of Phenoxyacetate Esters **35**.



CHAPTER 6

6.1 GENERAL EXPERIMENTAL

All melting points were determined on a Fisher-Johns melting point apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 237B ir spectrometer and are given in wavenumbers (cm^{-1}) calibrated against Nujol at 1458, 1378 cm^{-1}. Most ^1H nmr spectra were obtained on a Nicolet 360 instrument at 360 MHZ with chemical shift relative to TMS. The mass spectra were run on a CEC 21-104 mass spectrometer; all signals over 10% of the intensity of the base peak are reported as m/e(relative intensity). High pressure liquid chromatographic analysis was performed on a Waters System employing a model 6000A pump, a model 450 variable wavelength UV detector and model U6k injector. A Brownlee RP-8 analytical column was used with an 80% methanol-water mixture as the eluent and detection at 280 nm. Absorption spectra were obtained using a Varian Cary 219 spectrophotometer. GC/MS were done on a Hewlett-Packard capillary 5% phenyl silicone column using a HP 5970 Series Mass Selective Detector. C, H and N analyses were done by Canadian Microanalytical Service Ltd. 1-Naphthylmethanol, 1-methoxynaphthalene, 2-methoxy naphthalene, 1-aminonaphthalene, 1-methyl and 2-methylnaphthalene, 1,8-naphthalene sultone, 1,6-dihydroxynaphthalene, 1,7-dihydroxynaphthalene, 4-fluoro-1-naphthoic acid,

phenylacetyl chloride, 4-cyano-1-benzoyl chloride and 4-anisic acid were purchased from the Aldrich Chemical Co. The preparation of 4-methoxy-1-naphthylmethanol [77] and 2-methoxy-1-naphthylmethanol [80,81] were by literature procedures.

6.2 PREPARATION OF NAPHTHYLMETHANOLS

Preparation of 1-cyano-3-methoxynaphthalene : Starting from 1-aminonaphthalene, 1-bromo-3-methoxy naphthalene was prepared as described previously [61]. The cyanation procedure was that of Friedman and Schechter [62]. A solution of the bromide (2.37 g, 10 mmol) and CuCN (1.03 g,11.5 mmol) in 6 mL of DMF was refluxed for 6 h. The resulting mixture was poured into a solution of 6 mL of H_2O, 1 mL of conc. HCl and 4 g of $FeCl_3$, and the mixture heated at 65°C for 20 min. The mixture was extracted with 3 x 15 mL of toluene and the extracts were washed with 30 mL of 15% HCl, and 25 mL of 10% NaOH, dried over $MgSO_4$ and concentrated to give 1.7 g of crude product. Recrystallization from hexane gave 1.3 g (70%) of pure 1-cyano-3-methoxynaphthalene as colourless needles: mp 104-105°C (lit. [79] 103°C); ^1H nmr ($CDCl_3$) δ 8.3-8.1 (m, 1H), 8.0-7.8 (m, 1H), 7.7-7.5(m, 3H), 7.3(d, 1H, J = 2 Hz) 3.95 (s, 3H); ir (Nujol) 2200 cm^{-1}; mass spectrum,m/e 184 (17), 183 (100), 168 (39), 153 (37), 141 (39), 140 (100), 113 (68), 63 (46).

Preparation of 3-methoxy-1-naphthoic acid : The method of Amin *et al.* [63] was used with little change. A solution of the nitrile (1.4 g, 7.7 mmol) in 15 mL of hot ethanol was added to 20 mL of 2.5 M NaOH solution. The mixture was refluxed for 24 h followed by evaporation of most of the ethanol and filtration. The filtrate was washed with 2 x 20 mL of $CHCl_3$ and then acidified with conc. HCl to give 1.47 g (7.3 mmol, 95%) of the acid. Crystallization from ethanol-water gave the pure acid as fine colourless needles: mp 156-157°C; ir (nujol) 1685, 1220 cm^{-1}; ^1H nmr ($CDCl_3$) δ 9.05 (dd, 1H, J = 2.5, 8.5 Hz), 8.15 (d, 1H, J = 2.5 Hz), 8.0-7.8 (m, 1H), 7.65 (t, 1H, J = 7.8 Hz), 7.50 (t, 1H, J = 7.6 Hz), 7.40 (d, 1H, J = 2.2 Hz), 8.5 (broad singlet, 1H, exchangeable), 3.95 (s, 3H); mass spectrum,m/e 203 (13), 202 (100), 185 (12), 159 (16), 131(92), 127 (21), 115 (21), 114 (10).

Preparation of 3-methoxy-1-naphthylmethanol, **28c:** The method of Brown *et al.* [64] was used. To a solution of 3-methoxy-1-naphthoic acid (11.5 g, 57 mmol) in 25 mL of dry THF was added dropwise 76 mL of 1 M borane/THF solution at 0°C. The mixture was stirred for one hour at room temperature and excess hydride was destroyed by 80 mL of 1:1 water:THF. The mixture was then saturated with K_2CO_3 and extract with 2 x 100 mL of ether. The combined extracts

were washed with water, dried over $MgSO_4$ and concentrated to give 9.8 g (52 mmol, 92%) of crude product. Recrystallization from hexane yielded the pure alcohol: mp 87-88°C (lit. [10] 88-89°C)

Preparation of 4-methyl-1-naphthoic acid : Starting from 1-methylnaphthalene, 1-bromo-4-methylnaphthalene was prepared as described by Fieser and Bowen [67]. The cyanation method of Friedman and Schechter [62] was used. Recrystallization from dilute ethanol yielded pure 1-cyano-4-methylnaphthalene as colourless plates: mp 53-54°C (lit. [68] 53-54°C).

The nitrile was hydrolysed to the acid by the method described for 3-methoxy-1-naphthoic acid. Recrystallization from ethanol-water gave colourless needles: mp 178-179°C (lit. [69] 180°C).

Preparation of 4-methyl-1-naphthylmethanol, 28e: 4-Methyl-1-naphthoic acid was reduced to 4-methyl-1-naphthylmethanol by the method described for 3-methoxy-1-naphthoic acid. The yield of the alcohol was 90%, which is much better than yields obtained for the same reduction using $LiAlH_4$ [65]. This alcohol was crystallized from hexane to give fine colourless needles: mp 76-77°C (lit. 77°C [66]).

Preparation of 4-cyano-1-naphthylmethanol, 28f: 4-Cyano-1-naphthaldehyde was prepared from 4-cyano-1-methyl

naphthalene by the method of Dewar *et al.* [70]. This aldehyde was reduced to 4-cyano-1-naphthylmethanol with $NaBH_4$ in ethanol as described previously [10]. Recrystallization from ethanol yielded colourless crystals: mp 118-119°C (lit.[71] 118-119°C).

Preparation of 4-carbomethoxy-1-naphthylmethanol, **28h:** 1-Methyl-4-cyanonaphthalene was converted to 1-bromomethyl-4-cyanonaphthalene by the method of Dewar *et al.* [70]. This compound (5 g) was then refluxed in 30 mL of 20% aqueous NaOH for 5 days. The hot solution was filtered, diluted with 20 mL of water and washed with 25 mL of chloroform. Acidification of the aqueous layer and filtration yielded crude 4-hydroxymethyl-1-naphthoic acid (3 g, 72%). Recrystallization from ethanol water yielded colourless needles: mp 171-172°C; ^{1}H nmr ($CDCl_3$ + DMSO-d_6) δ 9.1-8.9 (m, 1H), 8.3-8.0 (m, 2H), 7.8-7.5 (m, 3H), 7.0 (broad singlet, exchangeable, 2H), 5.2 (s, 2H).

The ester was obtained from the acid using diazomethane in ether. Crystallization from ethanol gave colourless crystals: mp 59-60°C; ^{1}H nmr ($CDCl_3$) δ 9.0-8.8 (m, 1H), 8.1-7.8 (m, 2H), 7.6-7.3 (m, 3H), 5.2 (s, 2H), 5.0 (s, 2H), 3.9 (s, 3H), 3.0 (s, exchangeable, 1H).

Preparation of 4,8-dimethoxy-1-naphthylmethanol, **28k:** 4,8-

Dimethoxy-1-naphthaldehyde was prepared by the method of Buu-Hoi and Lavit [72]: mp 125-126°C (lit.[72] 126°C); ^{1}H nmr ($CDCl_3$) δ 11.17 (s, 1H), 8.13 (d, 1H, J = 8.1 Hz), 7.95 (d, 1H, J = 7.5 Hz), 7.47 (t, 1H, J = 8.0 Hz), 7.05 (d, 1H, J = 7.9 Hz), 6.90(d, 1H, J = 7.6 Hz), 4.07 (s, 3H), 4.00 (s, 3H).

This aldehyde was reduced to the 4,8-dimethoxy-1-naphthylmethanol,**28k**, with $NaBH_4$ in ethanol as described previously [10]. Recrystallization from ethanol yielded colourless crystals: mp 154-155°C; ^{1}H nmr ($CDCl_3$) δ 8.03 (d, 1H, J = 8.1 Hz), 7.40 (t, 1H, J = 7.95 Hz), 7.32 (d, 1H, J = 8.1 Hz), 6.95 (d, 1H, J = 8.1 Hz), 6.73 (d, 1H, J = 8.0 Hz), 4.95 (s, 2H), 4.05(s, 3H), 3.98 (s, 3H), 3.2 (s, 1H, exchangeable).

Preparation of 4,7-dimethoxy-1-naphthylmethanol, **28j**: 1,6-Dimethoxynaphthalene was obtained from the dihydroxy compound by the method of Buu-Hoi and Lavit [91]. This compound was formylated by the method of Buu-Hoi and Lavit [74]. Recrystallization from ethanol yielded colourless crystals: mp 78-79°C (lit.[73] 78-79°C); ^{1}H nmr ($CDCl_3$) δ 10.13 (s, 1H), 8.82 (d, 1H, J = 2.0 Hz), 8.20 (d, 1H, J = 8.4 Hz), 7.80 (d, 1H, J = 8.0 Hz), 7.17 (dd, 1H, J = 2.1, 8.2 Hz), 6.74 (d, 1H, J = 8.0 Hz), 4.03 (s, 3H), 3.95 (s, 3H).

The aldehyde was reduced to 4,7-dimethoxy-1-

naphthylmethanol,28j, with $NaBH_4$ in ethanol as described previously [10]: mp 78-79°C; ^1H nmr ($CDCl_3$) δ 8.23 (d, 1H, J = 7.9 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.55 (d, 1H, J = 7.9 Hz), 6.92 (d, 1H, J = 7.8 Hz), 6.78 (d, 1H, J = 7.9 Hz), 4.98 (s, 2H); 3.98 (s, 3H), 3.95 (s, 3H), 2.4 (s, 1H, exchangeable).

Preparation of 4,5-dimethoxy-1-naphthylmethanol, 28i: 1,8-Dimethoxynaphthalene was obtained from the sultone by the method of Parker and Iqbal [75]. This compound was formylated by the method of Buu-Hoi and Lavit [76]. Recrystallization from ethanol yielded colourless crystals: mp 94-95°C (lit. [76] 95°C); ^1H nmr ($CDCl_3$) δ 10.13 (s, 1H), 8.95 (d, 1H, J = 8.1 Hz), 7.9 (d, 1H, J = 8.0 Hz), 7.60 (d, 1H, J = 8.1 Hz), 6.98 (d, 1H, J = 8.0 Hz), 6.90 (d, 1H, J = 8.0 Hz), 3.98 (s, 3H), 3.90 (s, 3H).

The aldehyde was reduced to the 4,5-dimethoxy-1-naphthaylmethanol,28i, with $NaBH_4$ in ethanol as described previously [10]: mp 97-98°C; ^1H nmr ($CDCl_3$) δ 7.65 (d,1H, J = 7.9 Hz), 7.60 (t, 1H, J = 8.0 Hz), 7.55 (d, 1H, J = 7.9 Hz), 6.92 (d, 1H, J = 7.8 Hz), 6.78 (d, 1H, J = 7.9 Hz), 4.98 (s, 2H), 3.98 (s, 3H), 3.95 (s, 3H), 2.4 (s, 1H, exchangeable).

Preparation of 4-ethoxy-1-naphthylmethanol, 28q: 1-Ethoxynaphthalene was formylated by the method of Buu-Hoi and Lavit [77]. Recrystallization from acetic acid gave

colourless crystals: mp 74-75°C (lit. [78] 75°C). This aldehyde was reduced to 4-ethoxy-1-naphthylmethanol,28g, with $NaBH_4$ in ethanol as described previously [10]: mp 75-76°C; ^1H nmr ($CDCl_3$) δ 8.4-8.0 (m,2H), 7.6-7.4 (m, 2H), 7.3 (d, 1H, J = 8.0 Hz), 6.7 (d, 1H, J = 8.0 Hz), 5.0 (s, 2H), 4.2 (q, 2H, J = 7.6 Hz), 1.8 (s, 1H, exchangeable), 1.5 (t, 3H, J = 7.6 Hz).

Preparation of 4-fluoro-1-naphthylmethanol, **281:** 4-Fluoro-1-naphthoic acid was reduced to 4-fluoro-1-naphthylmethanol,**281**, by the method described for 3-methoxy-1-naphthoic acid. This alcohol was recrystallized from hexane to give colourless plates: mp 84-85°C; ^1H nmr ($CDCl_3$) δ 8.3-8.0 (m, 2H), 7.7-7.4 (m, 2H), 7.3 (dd, 1H, J = 7.5, 5.0 Hz), 7.0 (dd, 1H, J = 10.0, 7.5 Hz), 5.1 (s, 2H), 1.9 (s, 1H, exchangeable).

6.3 PREPARATION OF METHYLNAPHTHALENES FOR OXIDATION POTENTIAL MEASUREMENTS

3-methoxy-1-methylnaphthalene : This compound was prepared by the method of Bartoli *et al.* [83] and recrystallized from ethanol to give colourless crystals: mp 47-48°C (lit. [83] mp 48-49°C).

4-ethoxy-1-methylnaphthalene : This compound was prepared

by the method Buu-Hoi and Lavit [77] described for the 4-methoxy isomer. Recrystallization from ethanol gave colourless plates: mp 49-50°C; ^{1}H nmr ($CDCl_3$) δ 8.5-8.3 (m, 1H), 7.9-7.7 (m, 1H), 7.6-7.2 (m, 2H), 7.0 (d, J = 8.0 Hz, 1H), 6.4 (d, J = 8.0 Hz, 1H), 3.8 (q, J = 7.6 Hz, 2H), 2.5 (s, 3H), 1.3 (t, J = 7.6 Hz, 3H).

4,8-dimethoxy-1-methylnaphthalene : This compound was prepared by the method of Buu-Hoi and Lavit [72]. Recrystallization from ethanol gave colourless plates: mp 104-105°C (lit. [72] mp 105°C); ^{1}H nmr ($CDCl_3$) δ 8.0 (d, 1H, J = 8.5 Hz), 7.4 (t, 1H, J = 7.8 Hz), 7.15 (d, 1H, J = 8.2 Hz), 6.8 (d, 1H, J = 8.0 Hz), 6.6 (d, 1H, J = 8.0 Hz), 3.9 (s, 3H), 3.8 (s, 3H), 2.8 (s, 3H).

4,7-dimethoxy-1-methylnaphthalene : This compound was prepared by the method of Buu-Hoi and Lavit [91]. Recrystallization from ethanol gave colourless plates: mp 54-55°C (lit. [91] mp 54°C); ^{1}H nmr ($CDCl_3$) δ 8.2 (d, 1H, J = 8.5 Hz), 7.2-7.0 (m, 3H), 6.7 (d, 1H, J = 8.0 Hz), 3.95 (s, 3H), 3.9 (s, 3H), 3.9 (s, 3H), 2.7 (s, 3H).

4,5-dimethoxy-1-methylnaphthalene : This compound was prepared by the method of Buu-Hoi and Lavit [76]. Recrystallization from ethanol gave colourless plates: mp 64-65°C (lit [76] mp 65°C); ^{1}H nmr ($CDCl_3$) δ 7.4-7.2 (m, 2H),

7.1(d, 1H, J = 8.0 Hz), 6.8 (d, 1H, J = 8.0 Hz), 6.7 (d, 1H, J = 8.0 Hz), 3.9 (s, 3H), 3.85 (s, 3H), 2.6 (s, 3H).

4-Carbomethoxy-1-methylnaphthalene: 4-Methyl-1-naphthoic acid was esterified with methanol as usual to give the ester: bp 80-82°C at 0.05 Torr. Crystallization from hexane gave colourless plates: mp 30°C (lit. [84] bp 192-4°C at 12 Torr); ^{1}H nmr ($CDCl_3$) δ 9.1-8.9 (m, 1H), 8.0 (d, 1H, J = 8.0), 7.9-7.8 (m, 1H), 7.6 (t, 1H, J = 8.0 Hz), 7.5 (t, 1H, J =8.0 Hz), 7.2 (d, 1H, J = 8.0 Hz), 3.9 (s, 3H), 2.6 (s, 3H).

4-fluoro-1-methylnaphthalene : This compound was obtained by the method of Sauer *et al.* [92]: bp 64-66°C at 1 Torr (lit. [92] 107.5-109.5°C at 12 Torr).

2-methoxy-1-methylnaphthalene : This compound was prepared by the method of Buu-Hoi and Lavit [77]. Recrystallization from ethanol gave colourless plates: mp 41-42°C (lit. mp [93] 41-42°); ^{1}H nmr ($CDCl_3$) δ 8.1-7.5 (m, 3H), 7.4-7.2 (m, 2H), 7.1 (d, 1H, J = 8.0 Hz), 3.9 (s, 3H), 2.6 (s, 3H).

6.4 PREPARATION OF ACID CHLORIDE

Phenoxyacetyl chloride: This compound was prepared by refluxing a mixture of phenoxy acetic acid and thionyl

chloride followed by the distillation.

3-phenyl-1-propanoyl chloride: This compound was made by the same method as above from 3-phenylpropanoic acid.

9-methylfluorene-9-carbonyl chloride: Fluorene was converted to 9-methylfluorene-9-carboxylic acid as described by Bavin [88]. Recrystallization from water gave colourless needles: mp 170-171°C (lit. [88] 170-171°C). This acid was treated with PCl_5 to give the acid chloride as described by Boyd and Harms [89]. Recrystallization from petroleum ether gave colourless needles: mp 95-96°C (lit. [90] 95-96°C).

6.5 GENERAL METHOD FOR PREPARATION OF ESTERS

To a solution of the alcohol (20 mmol) in 75 mL of benzene and 1 mL of pyridine was added a solution of the acid chloride (22 mmol) in 20 mL of benzene. After 6 h the mixture was poured into 50 mL of water and the organic layer was separated. This layer was washed with 40 mL of 10% HCl, 5% NaOH and 40 mL of water, dried with $MgSO_4$ and evaporated to give an oil or solid. This crude material was chromatographed on silica gel with 30% CH_2Cl_2: hexane was employed as the eluent. The yields were 50-80%. The esters were purified either by crystallization from hexane or vacuum distillation. The boiling point or melting point, ^1H nmr ($CDCl_3$), ir, mass spectrum and analytical data are given.

1-naphthylmethyl phenylacetate, **16a:** bp 130-132°C at 0.05 Torr (lit [82] 212°C at 4-5 Torr); ^{1}H nmr ($CDCl_3$) δ 7.75-7.73 (m, 1H, H8), 7.68-7.62 (m, 2H, H4,5), 7.33-7.29 (m, 3H, H6,7,2), 7.22 (t, J = 7.8 Hz, 1H, H3), 7.12 - 7.05 (m, 5H, Ph), 5.39 (s, 2H, $NpCH_2$), 3.47 (s, 2H, $PhCH_2$); ir (neat) 3020, 2940, 1740, 1250, 1120 cm^{-1}; mass spectrum,m/e 277(7) 276(33), 142(13), 141(100), 115(10), 91(16).

2-methoxy-1-naphthylmethyl phenylacetate, **16b:** mp 90-91°C; ^{1}H nmr ($CDCl_3$) δ 7.87 (d, 1H, J = 9.1 Hz, H8), 7.86 (d, 1H, J = 8.5 Hz, H5), 7.79 (d, 1H, J = 8.1 Hz, H4), 7.44 (t, 1H, J = 8.4 Hz, H6), 7.37 (t, 1H, J = 7.9 Hz, H7), 7.28 (d, 1H, J = 7.6 Hz, H3), 7.28-7.24 (m, 5H, Ph), 5.68 (s, 2H, $NpCH_2$), 3.94 (s, 3H, OCH_3), 3.62 (s, 2H, $PhCH_2$); ir (Nujol) 1720, 1290, 1120 cm^{-1}; mass spectrum,m/e 307(13), 306(54), 171(15), 170(100), 141(7), 128(10), 115(10), 91(16); Anal calcd for $C_{20}H_{18}O_3$: C, 78.41; H, 5.92; Found: C, 78.26; H, 6.01.

3-methoxy-1-naphthylmethyl phenylacetate, **16c:** mp 60-67°C; ^{1}H nmr ($CDCl_3$) δ 7.81 (d, 1H, J = 8.4 Hz, H8), 7.76 (d, 1H, J = 8.1 Hz, H5), 7.44 (t, 1H, J = 7.6 Hz, H7), 7.36 (t, 1H, J = 7.5 Hz, H6), 7.33-7.26 (m, 5H, Ph), 7.19 (d, 1H, J = 2.6 Hz, H4), 7.11 (d, 1H, J = 2.6 Hz, H2), 5.53 (s, 2H, $NpCH_2$), 3.90 (s, 3H, OCH_3), 3.68 (s, 2H, $PhCH_2$). ir (Nujol) 1725,

1240, 1050 cm^{-1}; mass spectrum,m/e 307(20), 306(72), 188(40), 172(16), 171(100), 141(13), 128(13), 115(10), 92(18); Anal. calcd for $C_{20}H_{18}O_3$: C, 78,41; H, 5.92; Found: C, 78.37; H, 6.01.

4-methoxy-1-naphthylmethyl phenylacetate, **16d:** mp 51-52°C; ^1H nmr ($CDCl_3$) δ 8.32-8.30 (m, 1H, H8), 7.88-7.85 (m, 1H, H5), 7.55-7.49 (m, 2H, H6,7), 7.42 (d, 1H, J = 7.8 Hz, H2), 7.29-7.24 (m, 5H, Ph), 6.74 (d, 1H, J = 7.8 Hz, H3), 5.49 (s, 2H, $NpCH_2$), 3.99 (s, 3H, OCH_3), 3.63 (s, 2H, $PhCH_2$); ir (Nujol) 1728, 1220, 1085 cm^{-1}; mass spectrum,m/e 307(8), 306(40), 171(100), 141(10), 127(13), 115(10); Anal. calcd for $C_{20}H_{18}O_3$: C 78.41; H, 5.92; Found: C, 78.60; H, 5.91.

4-methyl-1-naphthylmethyl phenylacetate, **16e:** mp 50-51°C; ^1H nmr ($CDCl_3$) δ 8.03 (d, 1H, J = 8.1 Hz, H8), 7.92 (d, 1H, J = 8.1 Hz, H5), 7.53 (t, 2H, J = 8.1 Hz, H6, 7), 7.39 (d, 1H, J = 6.9 Hz, H2), 7.28-7.24 (m, 6H, Ph,H3), 5.55 (s, 2H, $NpCH_2$), 3.65 (s, 2H, $PhCH_2$), 2.70 (s, 3H, CH_3); ir (Nujol) 1745, 1240, 1060 cm^{-1}; mass spectrum,m/e 291(1), 290(9), 156(14), 155(100), 115(5), 92(9); Anal. calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25; Found: C, 82.95; H, 6.33.

4-cyano-1-naphthylmethyl phenylacetate, **16f:** mp 71-72°C; ^1H nmr ($CDCl_3$) δ 8.29 (d, 1H, J = 8.0 Hz, H5), 7.98 (d, 1H, J = 8.2 Hz, H8), 7.86 (d, 1H, J = 7.3 Hz, H3), 7.73 (t, 1H, J =

7.8 Hz, H6), 7.64 (t, 1H, J = 7.7 Hz, H7), 7.50 (d, 1H, J = 7.3 Hz, H2), 7.33-7.25 (m, 5H, Ph), 5.61 (s, 2H, $NpCH_2$), 3.70 (s, 2H, $PhCH_2$); ir (Nujol) 2025, 1745, 1250, 1120 cm^{-1}; mass spectrum,m/e 302(12), 3(53), 167(14), 166(95), 140(11), 93(13), 92(100); Anal. calcd for $C_{20}H_{15}O_2N$: C, 79.71; H, 5.02; N, 4.65; Found: C, 79.64; H, 5.01; N, 4.77.

4-ethoxy-1-naphthylmethyl phenylacetate, 16g: mp >15°C; ^1H nmr ($CDCl_3$) δ 8.36-8.32 (m, 1H, H8), 7.87-7.84 (m, 1H, H5), 7.50-7.45 (m, 2H, H6, 7), 7.37 (d, 1H, J = 7.8 Hz, H2), 7.28-7.22 (m, 5H, Ph), 6.69 (d, 1H, J = 7.9 Hz, H3), 5.47 (s, 2H, $NpCH_2$), 4.15 (t, 2H, J = 7.0 Hz, $O\underline{CH_2}CH_3Ph$), 3.60 (s, 2H, $Ph\underline{CH_2}CH_2$), 1.50 (t, 3H, J = 7.0 Hz, $OCH_2\underline{CH_3}$); ir (neat) 3060, 2960, 1730, 1270, 1060 cm^{-1}; mass spectrum,m/e Anal. calcd for $C_{21}H_{20}O_3$: C, 78.72; H, 6.29; Found: C, 79.52; H, 6.07.

4,8-dimethoxy-1-naphthylmethyl phenylacetate, 16k: mp 60-61°C; ^1H nmr ($CDCl_3$) δ 7.90 (d, 1H, J = 8.5 Hz, H5), 7.37 (t, 1H, J = 8.1 Hz, H6), 7.30 (d, 1H, J = 8.2 Hz, H2), 7.28-7.23 (m, 5H, Ph), 6.81 (d, 1H, J = 7.8 Hz, H7), 6.73 (d, 1H, J = 8.0 Hz, H3), 5.65 (s, 2H, $NpCH_2$), 3.96 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.64 (s, 2H, $PhCH_2$); ir (Nujol) 1725, 1270, 1060 cm^{-1}; mass spectrum,m/e 341(13), 340(54), 202(18), 201(100), 186(14), 185(9), 171(16), 128(17), 115(12), 91(27); Anal. calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99; Found:

C, 74.97; H, 5.81.

4,7-dimethoxy-1-naphthylmethyl phenylacetate, **16j:** mp 78-79°C; ^{1}H nmr ($CDCl_3$) δ 8.20 (d, 1H, J = 8.5 Hz, H5), 7.39 (d, 1H, J = 7.9 Hz, H2), 7.28-7.22 (m, 5H, Ph), 7.13 (d, 1H, J = 8.5 Hz, H6), 7.11 (s, 1H, H8), 6.61 (d, 1H, J = 8.7 Hz, H3), 5.46 (s, 2H, $NpCH_2$), 3.96 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.62 (s, 2H, $PhCH_2$); ir (Nujol) 1725, 1260, 1060 cm^{-1}; mass spectrum,m/e 341(8), 340(33), 202(15), 201(100), 158(8), 115(5), 91(11); Anal. calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99; Found: C, 74.96; H, 6.10.

4,5-dimethoxy-1-naphthylmethyl phenylacetate, **16i:** mp 76-77°C; ^{1}H nmr ($CDCl_3$) δ 7.46 (d, 1H, J = 7.8 Hz, H8), 7.42 (d, 1H, J = 7.9 Hz, H2), 7.40 (t, 1H, J = 7.7 Hz, H7), 7.28-7.25 (m, 5H, Ph), 6.91 (d, 1H, J = 7.7 Hz, H6), 6.78 (d, 1H, J = 8.0 Hz, H3), 5.45 (s, 2H, $NpCH_2$), 3.97 (s, 3H, OCH_3), 3.96 (s, 3H, OCH_3), 3.64 (s, 2H, $PhCH_2$); ir (Nujol) 1725, 1270, 1070 cm^{-1}; mass spectrum,m/e 341(14), 340(60), 202(16), 201(100), 157(6), 136(6), 91(26); Anal. calcd for $C_{21}H_{20}O_4$: C, 74.98; H, 5.99; Found: C, 74.89; H, 5.72.

4-carbomethoxy-1-naphthylmethyl phenylacetate, **16h:** mp 64-65°C; ^{1}H nmr ($CDCl_3$) δ 8.90 (d, 1H, J = 8.5 Hz, H5), 8.08 (d, 1H, J = 7.5 Hz, H3), 7.96 (d, 1H, J = 8.3 Hz, H8), 7.63 (dt, 1H, J = 1.6 Hz, 8.4 Hz, H6). 7.54 (dt, 1H, J = 1.6 Hz, 8.4

Hz, H7), 7.48 (d, J = 7.5 Hz, H2), 7.30 - 7.25 (m, 5H, Ph), 5.60 (s, 2H, $NpCH_2$), 3.99 (s, 3H, $COOCH_3$); 3.69 (s, 2H, $PhCH_2$); ir (Nujol) 1730, 1710, 1270, 1250, 1070 cm^{-1}; mass spectrum,m/e 335(11), 334(45), 200(16), 199(100), 171(14), 141(12), 140(11), 91(25); Anal. calcd for $C_{21}H_{18}O_4$: C, 75.43; H, 5.43; Found: C, 75,46; H, 5.49.

4-fluoro-1-naphthylmehtyl phenylacetate, 16l: mp 49-50°C; ^1H nmr ($CDCl_3$) δ 8.15-8.12 (m, 1H, H8), 7.91-7.88 (m, 1H, H5), 7.56 (t, 1H, J = 6.2 Hz, H6), 7.54 (t, 1H, J = 6.2 Hz, H7), 7.41 (dd, 1H, J_{H-H} = 7.7 Hz, J_{H-F} = 5.5 Hz, H2), 7.31-7.22 (m, 5H, Ph), 7.07 (dd, 1H, J_{H-F} = 10.2 Hz, J_{H-H} = 7.9 Hz, H3), 5.51 (s, 2H, $NpCH_2$), 3.64 (s, 2H, $PhCH_2$). ir (nujol) 1710, 1210, 1040 cm^{-1}; mass spectrum,m/e 295(7), 294(33), 160(13), 159(100), 133(8), 92(10), 34(15), 30(58). Anal. calcd for $C_{19}H_{15}FO_2$: C, 77.54; H, 5.14; Found: C, 77.53; H, 5.19.

4-methoxy-1-naphthylmethyl 9'-methyl-9'-fluorene carboxylate, 23d: mp 80-81°C; ^1H nmr ($CDCl_3$) δ 8.25 (d, 1H, J = 8.2 Hz, H8), 7.67 (d, 2H, J = 7.6 Hz, H1') 7.63 (d, 1H, J = 7.9 Hz, H4), 7.46 (t, 1H, J = 7.8 Hz, H6), 7.42 (d, 2H, J = 7.7 Hz, H4'), 7.39 (t, 1H, J = 7.8 Hz, H7), 7.34 (t, 2H, J = 7.5 Hz, H3'), 7.24 (d, 1H, J = 7.8 Hz, H3), 7.21 (t, 2H, J = 7.5 Hz, H2'), 6.65 (d, H, J = 7.9 Hz, H3), 5.39 (s, 2H, $NpCH_2$), 3.96 (s, 3H, OCH_3), 1.72 (s, 3H, CH_3); ir (Nujol)

1725, 1275, 1050 cm^{-1}; mass spectrum,m/e 395(2) 394(8), 222(25), 180(22), 179(54), 178(27), 172(14), 171(100), 165(19), 128(13); Anal. calcd for $C_{27}H_{20}O_3$: C, 82.21; H, 5.62; Found: C, 82.19; H, 5.53.

4-methyl-1-naphthylmethyl 9'-methyl-9'-fluorene carboxylate, **23e:** mp 98-99°C; ^1H nmr ($CDCl_3$) δ 7.98 (d, 1H, J = 8.6 Hz, H8), 7.70 (d, 1H, J = 8.2 Hz, H5), 7.68 (d, 2H, J = 6.8 Hz, H1'), 7.49 (t, 1H, J = 8.3 Hz, H7), 7.45 (d, 2H, J = 7.6 Hz, H4'), 7.39 (t, 1H, J = 8.3 Hz, H6), 7.35 (t, 2H, J = 6.8 Hz, H3'), 7.23 (t, 2H, J = 7.5 Hz, H2'), 7.17 (s, 2H, H2, 3), 5.44 (s, 2H, $NpCH_2$), 2.65 (s, 3H, CH_3) 1.74 (s, 3H, 9'-CH_3); ir (Nujol) 1720, 1230, 1050 cm^{-1}; mass spectrum,m/e 379(7), 378(23), 180(4), 179(23) 178(11), 156(15), 155(100), 153(4), 128(4), 115(4); Anal. calcd for $C_{27}H_{22}O_2$: C, 85.69; H, 5.85; Found: C, 85.63; H, 5.60.

1-naphthylmethyl 3-phenylpropanoate, **20a:** bp 137-139°C at 0.05 torr; ^1H nmr ($CDCl_3$) δ 7.91-7.89 (m, 1H, H8), 7.84-7.81 (m, 1H, H5), 7.79 (d, 1H, J = 8.2 Hz, H4), 7.45-7.36 (m, 4H, H2,3,6,7), 7.23-7.10 (m, 5H, Ph), 5.52 (s, 2H, $NpCH_2$), 2.29 (t, 2H, J = 7.8 Hz, $PhCH_2\underline{CH_2}$), 2.64 (t, 2H, J = 7.8 Hz, $Ph\underline{CH_2}CH_2$). ir (neat) 3010, 2920, 1735,1235, 1060 cm^{-1}; mass spectrum,m/e 291(8), 290(40), 142(14), 141(100), 115(11), 91(20); Anal. calcd for $C_{20}H_{18}O_2$: C, 82.73; H, 6.25; Found: C, 82.93; H, 6.32.

3'-methoxy-1'-naphthylmethyl 3-phenylpropanoate, 20c: mp 53-54°C; ^{1}H nmr ($CDCl_3$) δ 7.80 (d, 1H, J = 8.3 Hz, H8'), 7.73 (d, 1H, J = 8.1 Hz, H5'), 7.44 (t, 1H, J = 8.1 Hz, H7'), 7.36 (t, 1H, J = 8.3 Hz, H6'), 7.23 (d, 1H, J = 2.2 Hz, H4'), 7.21- 7.13 (m, 5H, Ph), 7.09 (d, 1H, J = 2.2 Hz, H2'), 5.49 (s, 2H, $NpCH_2$), 3.87 (s, 3H, OCH_3), 2.95 (t, 2H, J = 7.8 Hz, $PhCH_2\underline{CH_2}$), 2.67 (t, 2H, J = 7.8 Hz, $Ph\underline{CH_2}CH_2$); ir (nujol) 1740, 1280, 1050 cm^{-1}; mass spectrum,m/e 321(13), 320(50), 188(60), 186(61), 172(24), 171(72), 158(17), 129(28), 128(50), 127(25), 115(100), 106(17); Anal. calcd for $C_{21}H_{20}O_2$: C, 78.73; H, 6.29; Found: C, 78.53; H, 6.32.

4'-methoxy-1'-naphthylmethyl 3-phenylpropanoate, 20d: mp 45-46°C; ^{1}H nmr ($CDCl_3$) δ 8.29 (d, 1H, J = 8.0 Hz, H8'), 7.88 (d, 1H, J = 8.0 Hz, H5'), 7.52 (t, 1H, J = 7.8 Hz, H7'), 7.51 (t, 1H, J = 7.7 Hz, H6'), 7.42 (d, 1H, J = 7.8 Hz, H2'), 7.24-7.13 (m, 5H, Ph), 6.75 (d, 1H, J = 7.8 Hz, H3'), 5.43 (s, 2H, $NpCH_2$), 4.00 (s, 3H, OCH_3), 2.94 (t, 2H, J = 7.8 Hz, $PhCH_2\underline{CH_2}$), 2.65 (t, 2H, J = 7.8 Hz, $Ph\underline{CH_2}CH_2$); ir (nujol) 1735, 1270, 1100 cm^{-1}; mass spectrum,m/e 321(15), 320(63), 172(17), 171(100), 129(13), 128(10), 93(10); Anal. calcd for $C_{21}H_{20}O_2$: C, 78.73; H, 6.39; Found: C, 78.89; H, 6.25.

2-naphthylmethyl phenylacetate: mp 64-65°C (lit. 64-65°C (34)); ^{1}H nmr ($CDCl_3$) δ 7.84-7.77 (m, 3H, H8,5,4), 7.74 (d,

1H, J = 1.8 Hz, H1), 7.49-7.47 (m, 2H, H6,7), 7.39 (dd, 1H, J = 1.8 Hz, 8.4 Hz, H3), 7.33-7.26 (m, 5H, Ph), 5.28 (s, 2H, $NpCH_2$), 3.70 (s, 2H, $PhCH_2$). ir (nujol) 1727, 1225, 1123 cm^{-1}; mass spectrum,m/e 277(7), 276(35), 158(14), 142(13), 141(100), 115(11), 91(11).

1-naphthylmethyl benzoate, **29a**: mp 36-37°C; ^1H nmr ($CDCl_3$) δ 8.11 (d, 1H, J = 8.3 Hz, H8), 8.05 (d, 2H, J = 8.1 Hz, H2'), 7.85 (d, 1H, J = 8.0 Hz, H5), 7.86 (d, 1H, J = 8.5 Hz, H4), 7.63 (d, 1H, J = 6.7 Hz, H4'), 7.57-7.47 (m, 3H, H6,7,3), 7.45 (d, 1H, J = 7.0 Hz, H2), 7.39 (t, 2H, J = 7.7 Hz, H3'), 5.81 (s, 2H, $NpCH_2$). ir (neat) 3060, 2950, 1725, 1275, 1100 cm^{-1}; mass spectrum,m/e 263(15), 262(73), 141(67), 140(30), 139(12), 115(13), 105(100), 77(19); Anal. calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.34; Found; C, 82.43; H, 5.34.

2-methoxy-1-naphthylmethyl benzoate, **29b**: mp 87-88°C; ^1H nmr ($CDCl_3$) δ 8.03 (d, 1H, J = 8.8 Hz, H8), 8.00 (d, 2H, J = 7.8 Hz, H2'), 7.89 (d, 1H, J = 8.9 Hz, H5), 7.81 (d, 1H, J = 8.0 Hz, H4), 7.53-7.46 (m, 2H, H6,7), 7.39-7.30 (m, 4H, H3,3',4'), 5.91 (s, 2H, $NpCH_2$), 3.98 (s, 3H, OCH_3). ir (nujol) 1720, 1270, 1105 cm^{-1}; mass spectrum,m/e 293(20), 292(97), 186(62), 172(17), 171(100), 168(20), 141(11), 128(15), 115(15), 105(24), 78(23); Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52; Found: C, 78.29; H, 5.71.

3-methoxy-1-naphthylmethyl benzoate, **29c**: mp 53-54°C; ^1H

nmr ($CDCl_3$) δ 8.07 (d, 2H, J = 8.0 Hz, H2'), 7.99 (d, 1H, J = 8.3 Hz, H8), 7.79 (d, 1H, J = 8.2 Hz, H5), 7.55 (t, 1H, J = 7.5 Hz, H7), 7.48 (t, 1H, J = 7.7 Hz, H6), 7.42 (d, 1H, J = 7.6 Hz, H4'), 7.44 (t, 2H, J = 7.7 Hz, H3'), 7.33 (d, 1H, J = 2.6 Hz, H4), 7.15 (d, 1H, J = 2.6 Hz, H2), 5.77 (s, 2H, $NpCH_2$), 3.93 (s, 3H, OCH_3). ir (nujol) 1720, 1275, 1105 cm^{-1}; mass spectrum,m/e 293(12), 292(52), 186(68), 171(26), 158(14), 128(44), 115(100), 105(95), 77(38); Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52; Found: C, 77.86; H, 5.48.

4-methoxy-1-naphthylmethyl benzoate, **29d**: mp 77-78°C; ^1H nmr ($CDCl_3$) δ 8.32 (d, 1H, J = 8.2 Hz, H8), 8.06 (d, 1H, J = 8.3 Hz, H5), 8.01 (d, 2H, J = 7.4 Hz, H2'), 7.58-7.46 (m, 4H, H6,7,2,4'), 7.35 (t, 2H, J = 7.4 Hz, H3'), 6.76 (d, 1H, J = 7.8 Hz, H3), 5.72 (s, $NpCH_2$), 3.98 (s, 3H, OCH_3). ir (nujol) 1720, 1260, 1080 cm^{-1}; mass spectrum,m/e 293(14), 292(63), 172(14), 171(100), 136(17), 115(14); Anal. calcd for $C_{20}H_{18}O_3$: C, 78.06; H, 5.52; Found: C, 78.17; H, 5.66.

4'-methoxy-1'-naphthylmethyl 4-cyanobenzoate, **29e**: mp 112-113°C; ^1H nmr ($CDCl_3$) δ 8.33 (d, 1H, J = 8.0 Hz, H8), 8.07 (d, 2H, J = 7.6 Hz, H3'), 8.02 (d, 1H, J = 8.2 Hz, H4), 7.64 (d, 2H, J = 7.6 Hz, H2'), 7.57 (t, 1H, J = 7.5 Hz, H7), 7.52 (d, 1H, J = 7.9 Hz, H2), 7.51 (t, 1H, J = 7.5 Hz, H6), 6.77 (d, 1H, J = 8.0 Hz, H3), 5.74 (s, 2H, $NpCH_2$), 3.99 (s, 3H, OCH_3); ir(nujol) 2210, 1700, 1240, 1080 cm^{-1}; mass

spectrum,m/e 318(14), 317(65), 172(14), 171(100), 128(18), 102(10); Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41; found: C, 75.62; H, 4.93; N, 4.37.

1'-naphthylmethyl 4-cyanobenzoate, **29f**: mp 142-143°C; ^1H nmr ($CDCl_3$) δ 8.08 (d, 2H, J = 8.3 Hz, H3'), 8.05 (d, 1H, J = 8.3 Hz, H8), 7.88 (d, 1H, J = 7.6 Hz, H5), 7.86 (d, 1H, J = 7.6 Hz, H4), 7.63 (d, 2H, J = 8.4 Hz, H2'), 7.60 (d, 1H, J = 6.7 Hz, H2), 7.56 (t, 1H, J = 6.9 Hz, H6), 7.51 (t, 1H, J = 6.8 Hz, H7), 7.45 (t, 1H, J = 7.3 Hz, H3), 5.81 (s, 2H, $NpCH_2$); ir (nujol) 2205, 1710, 1270, 1100 cm^{-1}; mass spectrum,m/e 288(13), 287(60), 142(16), 141(100), 128(20), 115(15); Anal. calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88; found: C, 79.25; H, 4.47; N, 4.85.

1'-naphthylmethyl 4-methoxybenzoate, **29g**: mp 68-69°C; ^1H nmr ($CDCl_3$) δ 8.07 (d, 1H, J = 8.1 Hz, H8), 7.97 (d, 2H, J = 8.1 Hz, H2'), 7.84 (d, 1H, J = 8.4 Hz, H5), 7.81 (d, 1H, J = 8.5 Hz, H4) 7.58 (d, 1H, J = 7.0 Hz, H2), 7.51 (t, 1H, J = 8.0 Hz, H7), 7.49 (t, 1H, J = 8.0 Hz, H6), 7.42 (t, 1H, J = 7.1 Hz, H3), 6.81 (d, 2H, J = 7.4 Hz, H3'), 5.75 (s, 2H, $NpCH_2$), 3.73 (s, 3H, OCH_3); ir (nujol) 1695, 1240, 1010 cm^{-1}; mass spectrum,m/e 293(10), 292(46), 142(10), 141(80), 140(10), 136(10), 135(100), 115(11); Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52; Found: C, 77.69; H, 5.39.

4'-cyano-1'-naphthylmethyl 4-methoxybenzoate, **29h**: mp 140-141°C; ^{1}H nmr ($CDCl_3$) δ 8.29 (d, 1H, J = 8.2 Hz, H8), 8.15 (d, 1H, J = 8.2 Hz, H5), 8.02 (d, 2H, J = 8.9 Hz, H2'), 7.90 (d, 1H, J = 7.3 Hz, H3), 7.73 (t, 1H, J = 7.2 Hz, H6), 7.69 (t, 1H, J = 7.2 Hz, H7), 7.68 (d, 1H, J = 7.3 Hz, H2), 6.91 (d, 2H, J = 8.9 Hz, H3'), 5.81 (s, 2H, $NpCH_2$), 3.84 (s, 3H, OCH_3); ir (nujol) 2200, 1700, 1260, 1080 cm^{-1}; mass spectrum,m/e 318(4), 317(20), 166(35), 136(10), 135(100); Anal. calcd for $C_{20}H_{15}NO_3$: C, 75.70; H, 4.76; N, 4.41; found: C, 75.43; H, 4.89; N, 4.42.

4-cyano-1-naphthylmethyl benzoate, **29i**: mp 122-123°C; ^{1}H nmr ($CDCl_3$) δ 8.31 (d, 1H, J = 8.2 Hz, H8), 8.17 (d, 1H, J = 7.9 Hz, H5), 8.07 (d, 2H, J = 7.7 Hz, H2'), 7.92 (d, 1H, J = 7.4 Hz, H3), 7.74 (t, 1H, J = 6.6 Hz, H6), 7.70 (t, 1H, J = 7.3 Hz, H7), 7.70 (d, 1H, J = 7.4 Hz, H2), 7.58 (t, 1H, J = 7.3 Hz, H4'), 7.44 (t, 2H, J = 7.7 Hz, H3'), 5.86 (s, 2H, $NpCH_2$); ir (nujol) 2200, 1700, 1280. 1105 cm^{-1}; mass spectrum,m/e 288(7), 287(31), 166(32), 165(10), 140(11), 105(100), 77(24); Anal. calcd for $C_{19}H_{13}NO_2$: C, 79.43; H, 4.56; N, 4.88; Found: C, 79.00; H, 4.59; N, 4.86.

1-naphthylmethyl phenoxyacetate, **35a**: mp 51-52°C; ^{1}H nmr ($CDCl_3$) δ 7.96-7.93 (m, 1H, H8), 7.88-7.83 (m, 2H, H4,5), 7.53-7.49 (m, 3H, H6,7,4'), 7.42 (t, 1H, J = 7.6 Hz, H3), 7.22 (t, 2H, J = 7.6 Hz, H3'), 6.96 (t, 1H, J = 7.3 Hz, H2),

6.86 (d, 2H, J = 7.9 Hz, H2'), 5.63 (s, 2H, $NpCH_2$), 4.63 (s, 2H, $PhOCH_2$); ir (nujol) 1760, 1280, 1085 cm^{-1}; mass spectrum,m/e 293(7), 292(30), 142(13), 141(100), 115(9), 107(8), 78(11); Anal. calcd for $C_{19}H_{16}O_3$: C, 78.06; H, 5.52; Found: C, 78.13; H, 5.68.

2-methoxy-1-naphthylmethyl phenoxyacetate, **35b**: mp 91-92°C; ^1H nmr ($CDCl_3$) δ 8.11 (d, 2H, J = 7.9 Hz, H8,5), 8.02 (d, 1H, J = 8.1 Hz, H4), 7.71 (t, 1H, J = 7.6 Hz, H6), 7.59 (t, 1H, J = 7.6 Hz, H7), 7.51 (d, 1H, J = 8.1 Hz, H3), 7.47 (t, 2H, J = 8.0 Hz, H3'), 7.19 (t, 1H, J = 8.0 Hz, H4'), 7.09 (d, 2H, J = 7.9 Hz, H2'), 6.03 (s, 2H, $NpCH_2$), 4.84 (s, 2H, $PhOCH_2$), 4.11 (s, 3H, OCH_3). ir (nujol) 1750, 1260, 1085 cm^{-1}; mass spectrum,m/e 323(20), 322(91), 184(16), 171(44), 142(15), 141(100), 128(24), 115(23), 77(32); Anal. calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63; Found: C, 74.43; H, 5.70.

3-methoxy-1-naphthylmethyl phenoxyacetate, **35c**: mp 132-133°C; ^1H nmr ($CDCl_3$) δ 7.84 (d, 1H, J = 8.3 Hz, H8), 7.77 (d, 1H, J = 8.1 Hz, H5), 7.47 (t, 1H, J = 7.8 Hz, H7), 7.37 (t, 1H, J = 7.8 Hz, H6), 7.26 (t, 2H, J = 7.4 Hz, H3'), 7.23 (d, 1H, J = 2.6, H4), 7.14 (d, 1H, J = 2.6 Hz, H2), 6.98 (t, 1H, J = 7.6, H4'), 6.88 (d, 2H, J = 7.9 Hz, H2'), 5.65 (s, 2H, $NpCH_2$), 4.67 (s, 2H, $PhOCH_2$), 3.91 (s, 3H, OCH_3); ir (nujol) 1770, 1250, 1060 cm^{-1}; mass spectrum,m/e 323(13), 322(59), 172(14), 171(100), 141(10), 128(11), 78(11); Anal. calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63; Found: C, 74.56; H,

5.62.

4-methoxy-1-naphthylmethyl phenoxyacetate, **35d**: mp 110-111°C; ^{1}H nmr ($CDCl_3$) δ 8.31 (d, 1H J = 8.3 Hz, H8), 7.89 (d, 1H, J = 8.0 Hz, H5), 7.53-7.49 (m, 2H, H6,7), 7.46 (d, 1H, J = 7.8 Hz, H2), 7.23 (t, 2H, J = 7.2 Hz, H3'), 6.95 (t, 1H, J = 7.4 Hz, H4'), 6.85 (d, 2H, J = 8.1 Hz, H2'), 6.74 (d, 1H, J = 7.8 Hz, H3), 5.61 (s, 2H, $NpCH_2$), 4.61 (s, 2H, $PhOCH_2$), 3.99 (s, 3H, OCH_3). ir (nujol) 1760, 1265, 1080 cm^{-1}; mass spectrum,m/e 323(1), 322(5), 171(8), 152(92), 107(100), 94(26), 79(21), 77(100); Anal. calcd for $C_{20}H_{18}O_4$: C, 74.52; H, 5.63; Found: C, 74.68, H, 5.62.

6.6 PREPARATION OF PHOTOPRODUCTS

Photoproducts **17a - 17e, 17g** and **171** were prepared by the same method starting from the corresponding alcohols. To a solution of 5 mmol of alcohol in 10 mL of dry DMF was added washed NaH (0.12 g) in portions. After the mixture was stirred for 15 min., 1.9 mL of CH_3I was added and stirring was continued for 1 h at room temperature. A conventional work up yielded an oil which was chromatographed on silica gel eluting with 40% CH_2Cl_2 hexane to give the ether in 70-80% yield. All these compounds were purified by bulb-to-bulb distillation. The boiling points, ^{1}H nmr and mass spectra data are given below.

methyl 1-naphthylmethyl ether, **17a:** bp 108-110°C at 5 Torr (lit. [85] 133°C at 10 Torr); ^{1}H nmr ($CDCl_3$) δ 8.07 (d, ^{1}H, J = 8.37 Hz), 7.82 (d, 1H, J = 7.50 Hz), 7.77 (d, 1H, J = 8.09 Hz), 7.52-7.36 (m, 4H), 4.86 (s, 2H), 3.39 (s, 3H). mass spectrum,m/e 173(20), 172(100), 171(80), 157(10), 142(96), 129(79), 128(92), 127(50), 115(98).

methyl 2-methoxy-1-naphthylmethyl ether, **17b:** bp 102-103°C at 0.5 Torr; ^{1}H nmr ($CDCl_3$) δ 8.2-8.0 (m, 1H), 7.4-7.6 (m, 2H), 7.5-7.3 (m, 2H), 7.2 (d, 1H, J = 7.5 Hz), 5.0 (s, 2H), 4.0 (s, 3H), 3.4 (s, 3H); mass spectrum,m/e 203(15), 202(98), 172(48), 171(100), 144(23), 142(23), 141(100), 128(79), 127(47), 115(92).

methyl 3-methoxy-1-naphthylmethyl ether, **17c:** bp 96-100°C at 1 Torr; ^{1}H nmr ($CDCl_3$) δ 7.94 (d, 1H, J = 8.24 Hz), 7.69 (d, 1H, J = 8.03 Hz), 7.40 (t, 1H, J = 7.38 Hz), 7.33 (t, 1H, J = 7.07 Hz), 7.16 (d, 1H, J = 1.93 Hz), 7.02 (d, 1H, J = 1.93 Hz), 4.79 (s, 2H), 3.82 (s, 3H), 3.39 (s, 3H); mass spectrum,m/e 203(12), 202(86), 187(12), 172(25), 171(100), 141(30), 128(50), 115(47).

methyl 4-methoxy-1-naphthylmethyl ether, **17d:** bp 90-93°C at 2 Torr (lit. [10] 70-72°C at 0.2 Torr); ^{1}H nmr ($CDCl_3$) δ 8.28 (d, 1H, J = 8.47 Hz); 8.06 (d, 1H, J = 8.29 Hz), 7.54 (t,

1H, J = 7.55 Hz), 7.47 (t, 1H, J = 7.53 Hz), 7.34 (d, 1H, J = 7.78 Hz), 6.71 (d, 1H, J = 7.78 Hz), 4.80 (s, 2H), 3.76 (s, 3H), 3.39 (s, 3H); mass spectrum,m/e 203(5), 202(32), 172(70), 171(100), 157(43), 129(48), 128(67), 127(28), 115(29).

methyl 4-methyl-1-naphthylmethyl ether, 17e: bp 89-93°C at 0.2 Torr (lit. [86] bp 160-170°C at 13 Torr); ^{1}H nmr ($CDCl_3$) δ 8.13-8.10 (m, 1H), 8.02-7.99 (m, 1H), 7.55-7.51 (m, 2H), 7.35 (d, 1H, J = 7.05 Hz), 7.25 (d, 1H, J = 6.98 Hz), 4.86 (s, 2H), 3.41 (s, 3H), 2.67 (s, 3H), mass spectrum,m/e 187(23), 186(100), 172(24), (100), 156 (74), 155(100), 153(86), 141(85), 128(99), 115(99).

methyl 4-ethoxy-1-naphthylmethyl ether, 17g: mp 42-43°C; ^{1}H nmr ($CDCl_3$) δ 8.4-8.0 (m, 2H), 7.5-7.3 (m, 2H), 7.2 (d, 1H, J = 8.0 Hz), 6.7 (d, 1H, J = 8.0 Hz), 4.8(s, H), 4.1 (q, 2H, J = 7.4 Hz), 3.4 (s, 3H), 1.5 (t, 2H, J = 7.5 Hz).

methyl 4-fluoro-1-naphthylmethyl ether, 17l: bp 65-67°C at 0.1 Torr; ^{1}H nmr ($CDCl_3$) δ 8.109 (dd, 1H, J_{H-H} = 7.68 Hz, J_{H-F} = 5.98 Hz, H5), 8.081 (dd, 1H, J = 8.48 Hz, H8), 7.573 (t, 1H, J = 7.51 Hz, H7), 7.533 (t, 1H, J = 7.47 Hz, H6), 7.373 (dd, 1H, J_{H-F} = 5.48 Hz, J_{H-H} = 7.70 Hz, H2), 7.066 (dd, 1H, J_{H-H} = 7.80 Hz, J_{H-F} = 10.35 Hz, H3), 4.815 (s, 2H, $NpCH_2$), 3.417 (s, 3H, OCH_3); mass spectrum,m/e 191(8), 190(35), 160(30), 159(100), 156(25), 133(35), 128(10), 115(28).

methyl 4-cyano-1-naphthylmethyl ether, **17f:** This ether was prepared from 4-cyano-1-bromomethyl naphthalene [70] in the following manner. The bromo-cyano compound (10 mmol) was dissolved in 50 ml of methanol and NaOMe (100 mmol) was added. The mixture was stirred overnight, poured into water, extract with CH_2Cl_2, dried, filtered and evaporated to give crude ether. Chromatography on silica gel and crystallization with CH_2Cl_2 gave colourless needles. mp 74-75°C (lit. [69] 73-74°C). mass spectrum,m/e 198(9), 197(66), 196(48), 167(80), 166(100), 154(25), 140(25).

methyl 4-carbomethoxy-1-naphthylmethyl ether, **17h:** This ether was prepared from 4-cyano-1-bromomethyl naphthalene [70] in the following manner. The bromo-cyano compound (3g) was refluxed in 75 mL of methanol and 15 mL of 2 M NaOH for 5 days. The hot solution was filtered, diluted with 25 mL of water and washed with 25 mL of chloroform. Acidification of the aqueous layer and filtration yielded 2g (60%) of crude 4-methoxymethyl-1-naphthoic acid. Recrystallization from ethanol-water gave needles; mp 136-137°C (lit. [65] 136-137°C). The ether-acid was reacted with sulphuric acid/methanol in the usual manner to give the methyl ester as a colourless liquid: bp 171-174°C at 6 Torr; mass spectrum,m/e 231(9), 230(68), 183(30), 171(100), 139(50), 128(37), 127(28).

methyl 2-naphthylmethyl ether: bp 130-134°C at 4 Torr (lit. [87] bp 113°C at 1.3 Torr); ^{1}H nmr ($CDCl_3$) δ 7.80 (d, 3H, J = 7.96 Hz), 7.75 (s, 1H), 7.45-7.42 (m, 3H), 4.58 (s, 2H), 3.93 (s, 3H).

6.7 PREPARATIVE PHOTOLYSIS

The photolysis of each of the esters was carried out in the following manner. A solution was prepared consisting of 300-400 mg of the ester dissolved in a 300 mL of methanol. The solution was placed in a 300 mL Havonia immersion well and purged with nitrogen for 15 minutes before and during the irradiation. The light source was a Pyrex-filtered 200W medium-pressure Havonia mercury lamp. Irradition was continued until the starting ester was greater than 90% consumed.

Photolysis times varied from 3 hours for the more reactive esters to 16 hours for the less reactive ones. The photolyzed solution was then concentrated under vacuum and dissolved in 30 mL of CH_2Cl_2. This CH_2Cl_2 layer was extracted with 2 x 15 mL of 5% NaOH. Evaporation of the CH_2Cl_2 layer gave an oil which was subjected to silica gel chromatography using 20% CH_2Cl_2: hexane as eluent. The aqueous alkaline layer was acidified with conc. HCl, and extracted with 2 x 25 mL of CH_2Cl_2. Evaporation of this CH_2Cl_2 layer gave a solid which was identified as the corresponding acid. The photoproducts were characterized by

^{1}H nmr and GC/MS. The ^{1}H nmr and GC/MS data for the photoproducts **17i - 17k, 18a - 18k, 21a, 21c, 21d, 25d, 25e,** and **26** are given below:

methyl 4,8-dimethoxy-1-naphthylmethyl ether, **17k:** ^{1}H nmr ($CDCl_3$) δ 8.1 (d, J=8.0 Hz, 1H), 7.6 (d, J=8.0 Hz, 1H), 7.4 (t, J=8.0 Hz, 1H), 6.9 (d, J=7.9 Hz, 1H), 6.7 (d, J=7.9 Hz, 1H), 5.1 (s, 2H), 4.0 (s, 3H), 3.9 (s, 3H), 3.5 (s, 3H); GC/MS, R_t= 13.87 min, m/e 233(11), 232(90), 202(40), 201(100), 187(25), 186(26), 128(26), 115(26).

methyl 4,7-dimethoxy-1-naphthylmethyl ether, **17j:** ^{1}H nmr ($CDCl_3$) δ 8.2 (d, 1H, J=8.0 Hz), 7.4-7.0 (m, 3H), 6.6 (d, J=8.0 Hz, 1H), 4.8 (s, 2H), 3.9 (s, 3H), 3.8 (s, 3H), 3.3 (s, 3H); GC/MS, R_t = 13.80 min, m/e 233(19), 232(100, 202(64), 201(100), 158(43), 143(20), 115(37).

methyl 4,5-dimethoxy-1-naphthylmethyl ether, **17i:** ^{1}H nmr ($CDCl_3$) δ 7.8-7.2 (m, 3H), 6.9 (d, J=8.0 Hz, 1H), 6.8 (d, J=8.0; 1H), 4.8 (s, 2H), 4.0 (s, 3H), 3.95 (s, 3H), 3.4 (s, 3H); GC/MS R_t= 13.60 min, m/e 233(7), 232(50), 202(20), 201(100), 185(6), 171(5), 157(10), 128(13), 115(12).

1-(1-naphthyl)-2-phenylethane, **18a:** ^{1}H nmr ($CDCl_3$) δ 8.1-7.9 (m, 2H), 7.8-7.6 (m, 1H), 7.5-7.0 (m, 4H), 7.25 (s, 5H), 3.4-3.2 (m, 2H), 3.1-2.9 (m, 2H); GC/MS R_t = 14.58 min, m/e

233(10, 232(56), 142(25), 141(100), 128(12), 115(65), 91(20).

1-(2'-methoxy-1'-naphthyl)-2-phenylethane, **18b:** ^{1}H nmr ($CDCl_3$) δ 8.0-7.8 (m, 2H), 7.7-7.6 (m, 1H), 7.5-7.2 (m, 3H), 7.25 (s, 5H), 3.8 (s, 3H), 3.4-3.2 (m, 2H), 3.0-2.8 (m, 2H); GC/MS R_t = 16.27 min, m/e 263(6), 262(28), 172(16), 171(100), 141(49), 128(12), 115(22), 91(18).

1-(3'-methoxy-1'-naphthyl)-2-phenylethane, **18c:** ^{1}H nmr ($CDCl_3$) δ 8.1-7.9 (m, 1H), 7.8-7.6 (m, 1H), 7.5-7.1 (m, 3H), 7.2 (s, 5H), 7.0 (d, 1H, J=2.0 Hz), 3.9 (s, 3H), 3.4-3.2 (m, 2H), 3.0-2.8 (m, 2H); GC/MS R_t = 16.56 min, m/e 263(16), 262(79), 172(24), 171(100), 141(24), 128(39), 127(10), 115(24), 91(20).

1-(4'-methoxy-1'-naphthyl)-2-phenylethane, **18d:** ^{1}H nmr ($CDCl_3$) δ 8.5-8.3 (m, 1H), 8.1-7.9 (m, 1H), 7.7-7.7 (m, 3H), 7.2 (s, 5H), 6.7 (d, 1H), J=8.0 Hz), 3.8 (s, 3H), 3.4-3.2 (m, 2H), 3.0-2.8 (m, 2H); GC/MS R_t = 17.07 min, m/e 263(3), 262(17), 172(11), 171(100), 128(28), 127(13), 115(6).

1-(4'-methyl-1'-naphthyl)-2-phenylethane, **18e:** Since this product was only formed in trace amounts isolation was not done. It was identified by GC/MS R_t = 16.35 min, m/e 247(15), 246(68), 156(10), 155(100), 141(28), 127(12),

115(11).

1-(4'-cyano-1'-naphthyl)-2-phenylethane, **18f:** ^{1}H nmr ($CDCl_3$) δ 8.3-8.0 (m, 2H), 7.8-7.5 (m, 3H), 7.3 (d, 1H, J=7.8 Hz), 7.2 (s, 5H), 3.5-3.3 (m, 2H), 3.2-3.0 (m, 2H); GC/MS R_t = 18.41 min, m/e 258(6), 257(30), 166(23), 140(8), 91(100), 65(10).

1-(4'-ethoxy-1'-naphthyl)-2-phenylethane, **18g:** ^{1}H nmr ($CDCl_3$) δ 8.4-8.0 (m, 2H), 7.7-7.5 (m, 2H), 7.3-7.1 (m, 6H), 6.8 (d, J=7.9 Hz, 1H), 4.3 (q, 2H, J=7.8 Hz), 3.5-3.0 (m, 4H), 1.6 (t, J=7.8 Hz, 3H); GC/MS R_t = 17.82 min, m/e 277(5), 276(20), 186(20), 185(100), 171(21), 157(42), 128(19).

1-(4',8'-dimethoxy-1'-naphthyl)-2-phenylethane, **18k:** ^{1}H nmr ($CDCl_3$) δ 8.0 (d, 1H, J=8.0 Hz), 7.5 (d, J=8.0; 1H), 7.3 (s, 5H), 7.2 (t, J=7.8 Hz, 1H), 7.0 (d, 1H, J=8.0 Hz), 6.8 (d, J=8.0 Hz, 1H), 4.0 (s, 3H), 3.9 (s, 3H), 3.5-3.2 (m, 2H), 3.1-2.8 (m, 2H); GC/MS R_t= 20.14 min, m/e 293(6), 292(26), 202(13), 201(100), 171(11), 128(16), 115(10).

1-(4',7'-dimethoxy-1'-naphthyl)-2-phenylethane, **18j:** ^{1}H nmr ($CDCl_3$) δ 8.3 (d, 1H, J=8.0 Hz), 7.5-7.1 (m, 8H), 6.7 (d, J = 8.0 Hz, 1H), 4.0 (s, 3H), 3.9 (s, 3H), 3.3-2.9 (m, 4H); GC/MS R_t= 20.49 min, m/e 293(5), 292(20), 202(19), 201(100),

158(11), 128(6).

1-(4',5'-dimethoxy-1'-naphthyl)-2-phenylethane, 18i: ^{1}H nmr ($CDCl_3$) δ 7.5 (d, J = 8.0 Hz, 1H), 7.3-7.0 (m, 7H), 6.9 (d, J = 8.0 Hz, 1H), 6.7 (d, J = 8.0 Hz, 1H), 4.0 (s, 3H), 3.9 (s, 3H), 3.3-2.9 (m, 4H); GC/MS R_t= 19.91 min, m/e 293 (3), 292(19), 202(13), 201(100), 157(5), 128(10).

1-(4'-carbomethoxy-1'-naphthyl)-2-phenylethane, 18h: ^{1}H nmr ($CDCl_3$) δ 9.1-8.9 (m, 1H), 8.2-7.9 (m, 2H), 7.6-7.4 (m, 1H), 7.3-7.1 (m, 6H), 4.0 (s, 3H), 3.6-3.3 (m, 2H), 3.2-7.9 (m, 2H); GC/MS R_t= 20.04 min, m/e 291(11), 290(49), 199(100), 171(21), 139(12), 128(10).

1-(4'-fluoro-1'-naphthyl)-2-phenylethane, 18l: Since this compound was only formed in trace amounts isolation was not attempted. It was identified by GC/MS R_t = 14.33 min, m/e 251(5), 250(24), 160(14), 159(100), 133(18), 91(6).

9-methyl-9-(4'-methoxy-1'-naphthylmethyl)fluorene, 25d; ^{1}H nmr ($CDCl_3$) δ 8.4-8.2 (m, 1H), 7.9-7.0 (m, 12H), 6.7 (d, 1H, J=8.0 Hz), 4.0 (s, 3H), 3.4 (s, 2H), 1.5 (s, 3H); mass spectrum,m/e 350(2), 179(5), 178(5), 172(14), 171(100), 129(8).

Di 9-methyl-9-fluorene, 26: ^{1}H nmr ($CDCl_3$) δ 1.6-6.8 (m,

16H), 1.9 (s, 6H): mass spectrum,m/e 358(5), 180(16), 179(21), 178(21), 97(30).

9-methyl-9-(4'-methyl-1'-naphthylmethyl)fluorene, 25e: ^{1}H nmr ($CDCl_3$) δ 8.3-6.9 (m, 14H), 3.5 (s, 2H), 2.6 (s, 3H), 1.6 (s, 3H).

Compounds **21a**, **21c** and **21d** were formed in small amounts and isolation was not done. However these compounds were identified by GC/MS, and data is given below.

1-(1'-naphthyl)-3-phenyl propane, **21a**: GC/MS R_t = 15.76 min, m/e 247(8), 246(45), 142(22), 141(100), 128(12), 115(15).

1-(3'-methoxy-1'-naphthyl)-3-phenyl propane, **21c**: GC/MS R_t = 19.15 min, m/e 277(10), 276(50), 172(22), 171(100), 141(18), 128(10), 115(10).

1-(4'-methoxy-1'-naphthyl)-3-phenyl propane, **21d**: GC/MS R_t = 19.55 min, m/e 277(6), 276(40), 172(20), 171(100), 141(12), 128(30), 115(10).

phenyl 2-(1'-naphthyl)ethyl ether, **35a**: ^{1}H nmr ($CDCl_3$) δ 8.1-7.9 (m, 2H), 7.5-7.1 (m, 6H), 7.0-6.8 (m, 3H), 4.1-3.9 (m, 3H), 3.4-3.3 (m, 3H). GC/MS: R_t = 15.89 min,m/e

249(3), 248(16), 156(11), 155(100), 153(16), 141(16), 115(13).

phenyl 2-(2'-methoxy-1'-naphthyl) ethyl ether, **35b:** ^{1}H nmr ($CDCl_3$) δ 8.1 (d, 1H, J = 8.0 Hz), 7.9-7.7 (m, 2H), 7.6-7.2 (m, 5H), 7.1-6.8 (m, 3H), 4.2-4.0 (m, 2H), 3.9 (s, 3H), 3.4-3.2 (m, 2H); GC/MS R_t = 18.38 min, m/e 279(7), 278(34), 186(13), 185(100), 171(34), 170(24), 141(44), 128(12), 115(24).

phenyl 2-(3'-methoxy-1'-naphthyl ethyl ether, **35c:** ^{1}H nmr ($CDCl_3$) δ 8.1-7.9 (m, 1H), 7.8-7.6 (m, 1H), 7.6-7.4 (m, 3H), 7.3-6.9 (m, 6H), 4.4-4.2(m, 2H), 3.9 (s, 3H), 3.4-3.2 (m, 2H); GC/MS R_t = 19.24 min, m/e 279(15), 278(71), 185(100), 171(30), 170(27), 141(28), 115(23).

phenyl 2-(4'-methoxy-1'-naphthyl ethyl ether, **35d:** ^{1}H nmr ($CDCl_3$) δ 8.5-8.3 (m, 1H), 8.2-8.0 (m, 1H), 7.5-7.1 (m, 5H), 7.0-6.6 (m, 4H), 4.4-4.2 (m, 2H), 3.9 (s, 3H), 3.4-3.2 (m, 2H); GC/MS R_t = 19.49 min, m/e 279(10), 278(48), 186(10), 185(73), 172(12), 171(100), 14(12), 128(24), 115(14).

Diphenyl (4'-methoxy-1'-naphthyl) methane, **33:** ^{1}H nmr ($CDCl_3$) 8.3 - 8.1 (m, 1H), 8.0 - 7.8 (m, 1H), 7.4 - 7.0 (m, 13H), 6.7 (d, 1H, J = 8.0 Hz), 5.2 (s, 1H), 3.9 (s, 3H); mass spectrum,m/e 325(13), 324(49), 247(15), 183(55),

167(60), 166(100), 165(15), 164(30), 152(15), 143(11), 115(22).

6.8 ANALYSIS OF PHOTOLYSIS MIXTURE BY HPLC

The solutions were irradiated in the same way described under the preparative photolysis, but solutions were prepared with 70-90 mg of ester. Analyses were done with less than 50% 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 negligbly slow. Standard solutions containing authentic samples of each photoproduct in known amounts were prepared and used to determine the yields of photoproducts for the photolyses. 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.

6.9 FLUORESCENCE STUDIES

Fluorescence studies were done using a Perkin-Elmer MPF 66 fluorescence spectrometer 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 naphthalene. Singlet state energies were determined by

the position of 0,0 band using the overlap between the emission and excitation spectrum. Fluorescence lifetimes were measured using a PRA single photon counting apparatus with a hydrogen flash lamp of pulse width about 1 ns.

6.10 PHOSPHORESCENCE STUDIES

Phosphorescence spectra were done using an Aminco-Bowmann spectrophotometer at 77K. Solutions were prepared in 1:4 methanol: ethanol and degassed by freeze-pump-thaw cycles. Triplet state energies were found from the estimated position of the 0,0 band of the phosphorescence spectrum.

6.11 QUANTUM YIELD MEASUREMENTS

Absolute quantum yields for the chemical reactions of **34b - 34d** were determined using an optical bench equipped with 450 W Hg/Xe lamp, a SPEX minimatic monochromator at 300 nm, a beam splitter and reaction and reference cells. Calibration of light intensities and splitting ratios were done by ferrioxalate actinometry. Samples were purged with a stream of nitrogen, stirred and thermostatted at 25°C during the irradiation. Products and percentage conversions were determined by hplc.

Quantum yields for the chemical reaction of **16b - 16d** were determined on a merry-go-round apparatus with 200 W

lamp. The quantum yield of **16b**, **16c**, and **16d**, were obtained relative to the **34b**, **34c**, and **34d**, respectively by irradiating degassed samples simultaneously.

Table 17: Quantum Yields of the Photolysis Products of Esters **16b - d** and **35b - d.**

Ester	X	Quantum Yields		
		17	**18**	**36**
16b	2-OCH_3	0.024	0.027	
16c	3-OCH_3	0.008	0.013	
16d	4-OCH_3	0.017	0.006	
35b	2-OCH_3	0.028		0.082
35c	3-OCH_3	0.015		0.056
35d	4-OCH_3	0.018		0.014

CHAPTER 7

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