DESIGNING FAST RADICAL CLOCKS

by

Sandra Marjorie Nevill

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for the degree of Doctor of Philosophy

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For Marcel and Jonah,
for their patience and understanding

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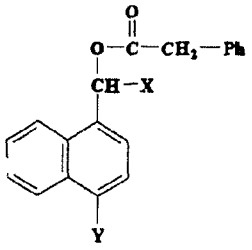
Abstract

Rate constants of radical reactions may be determined directly, using fast spectroscopic techniques such as laser flash photolysis, pulse radiolysis or esr, or indirectly, using product yield ratios. For indirect measurement, two competing reactions are required, one with a known rate constant called the radical clock. Radical clocks also may be used to investigate whether a reaction mechanism involves radical intermediates.

The photolysis of naphthylmethyl esters in nucleophilic solvents gives products derived from both ions and radicals. Initial studies on the photosolvolysis of benzylic esters suggested that the ions were formed by heterolytic cleavage from the excited state, and the radicals by homolytic cleavage. In contrast, DeCosta and Pincock suggested that only homolysis occurs, and then ions are produced by electron transfer in the initially-formed radical pair. The radicals that lead to products are produced by decarboxylation of the acyloxy radical. The rate constants determined from product yields for the electron transfer and decarboxylation steps fall in the range 10^9 to 10^{11} s^{-1}.

In this thesis, this mechanism was further investigated by synthesis of five naphthylmethyl esters, **1**. The rate constants for these radical clocks may be determined by product-yield ratios and the known rate constant of either the electron transfer or decarboxylation reactions.



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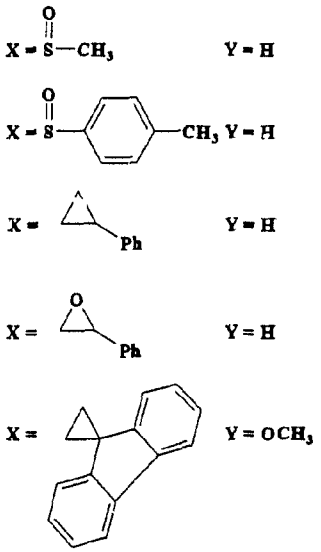

List of Abbreviations and Symbols

DMSO	dimethyl sulfoxide
g	gram
GC/MS	gas chromatography/mass spectroscopy
HPLC	High performance liquid chromatography
J	nmr coupling constant
k_β	rate constant for the β-cleavage reaction
k_{CO2}	rate constant for the decarboxylation reaction
k_{ET}	rate constant for the electron transfer reaction
k_R	rate constant for the rearrangement reaction
MS	mass spectroscopy
N	1-naphthyl
nmr	nuclear magnetic resonance
Ph	phenyl
s	second
tlc	thin layer chromatography

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1 INTRODUCTION

1.1 Radical Clocks

A radical is a chemical species having an unpaired electron. These unstable intermediates are known to be involved in a variety of reactions including inorganic, organic and enzymatic processes.[1] The products of these reactions are generally stable and isolable. Radicals are transient intermediates with an unpaired electron that are generated in chemical reactions using heat, light or a radical initiator, a compound which can undergo a facile reaction to form a radical. Radical reactions are defined as those that proceed by radical intermediates. Often radical reactions are chain reactions where a number of radical reaction steps occur consecutively, and considerable kinetic knowledge is required to be able to predict which radical reactions are preferred. Recent advances in synthetic organic chemistry using radical reactions are a result of advances in the knowledge of radical reaction rate constants.[2]

The rates of most chemical reactions are proportional to the concentrations of the reactant(s) which may be stable species or, in other cases, non-isolable intermediates. The change in concentrations as a function of time define the rate law of a reaction, and the order of a reaction is equal to th total of the exponents of the concentrations of the species in the rate law. For example, the rate of a first order reaction is proportional to the concentration of one species, and the rate of a second order reaction is proportional to the square of the concentration of one species or the sum of the concentrations of two species. The proportionality constant for the rate of the reaction, k, is called the rate constant. For every reaction, k will change with reaction conditions such as temperature

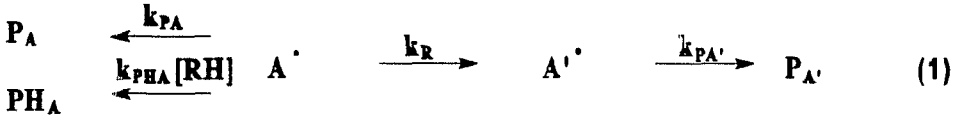
and solvent. Knowledge of rate constants of reactions aids in elucidating mechanisms. Reaction rates are obtained by measuring the changes over time in the concentration of a chemical species involved in the reaction. Various detection methods are available and the choice of one depends on the rate of the reaction. The detection method used must be faster than the change in concentration over time.

Radical reactions can be very fast, and therefore they require special methods of measurement. Rate constants of radical reactions may be determined directly, *i.e.*, absolutely, by rapid detection methods such as laser flash photolysis or electron spin resonance (esr) spectroscopy. In laser flash photolysis, molecules are excited photochemically and fast detectors are used to observe the transient species in the reaction pathway. The photochemical reactions of these molecules occur rapidly to form transient species and, to allow detection, the transient species' lifetimes must be slightly longer than the laser pulse duration. As a result of recent advances in lasers, transient species having picosecond or even femtosecond lifetimes can be observed, and therefore laser flash photolysis can now be applied to many photochemical reactions.

Alternatively the rate constants of some radical reactions can be determined by indirect chemical measurement. This can be accomplished using a "radical clock", a term first used by Ingold in 1980[3] who developed the first radical clock, the rearrangement by cyclization of the 5-hexenyl radical.[4]

By definition, a radical clock is a radical reaction having a known rate constant. There are two types of clocks in regular use: the first is a unimolecular reaction, either a fragmentation or a rearrangement; the second is a bimolecular reaction, usually a reaction

using a hydrogen-atom donor. For either of these radical-clock types, the determination of the rate constant is achieved by having two reactions in competition with each other; the rate constant of one reaction, which acts as the radical clock, must be known; the other rate constant then can be determined by the product ratios. In the example below, eq 1, radical A· may react in two ways; it can rearrange to give radical A′· or it can react to give product P_A. The rearranged radical A′ reacts to give product $P_{A'}$. The product ratio, $P_A/P_{A'}$ equals the ratio (k_{PA}/k_R) of the two rate constants, provided that the rearrangement reaction is irreversible. An irreversible reaction is a reaction in which the transition state is inaccessible from the product. Either of these rate constants (k_{PA} or k_R), if known, can act as the radical clock and, then the other rate constant can be determined.



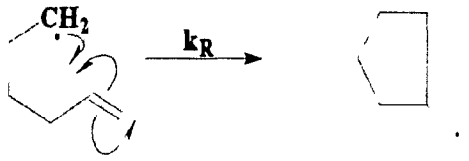
(1)

In the case where the radical clock is a bimolecular reaction, the concentration of the other reactant, usually a hydrogen-atom donor, must be included in the kinetic analysis. The rate of reaction then will equal $k_{PHA}[RH]$.

Radical clocks are examples of radical probes that can be used to determine whether a reaction involves radical intermediates. In addition, radical clocks can be used to determine specific rate constants of competing reactions.

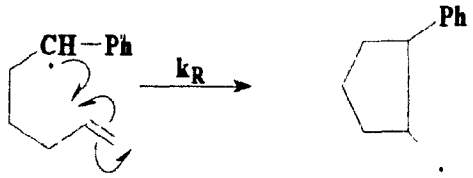
Certain conditions must be satisfied to use a radical clock. The radical clock must be competitive in rate with the other reaction, and the environment which the radical clock reaction is probing must not have been altered to a great extent from the one in which it

was initially measured. If the first condition is not met, *i.e.*, the two reactions are not competitive with each other, a product-yield ratio greater than that which can be measured experimentally will result. Most analytical techniques cannot easily be used if the product-yield ratio exceeds 100 to 1 because this would make reliable determination of the yields and rate constants very difficult. If the second condition is not met, *i.e.*, the two structures wherein the radical clock reaction rate constant is measured are not the same, then the previously measured rate constant for the radical clock reaction would not necessarily be the operative rate constant. The radical clock reaction then might have an operative rate constant faster or slower than the previously measured one. For example, incorporating the 5-hexenyl radical rearrangement, eq 2, into a system where the radical was benzylic, eq 3, would greatly affect the rate constant. Another example is the



(2)

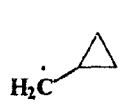
following series of substituted cyclopropyl carbinyl radicals The fastest radical clock of

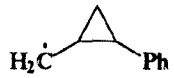


(3)

the series, the middle radical, differs from the other two only by a phenyl group, but the

rate constants for the radical clock reactions vary by at least three orders of magnitude.





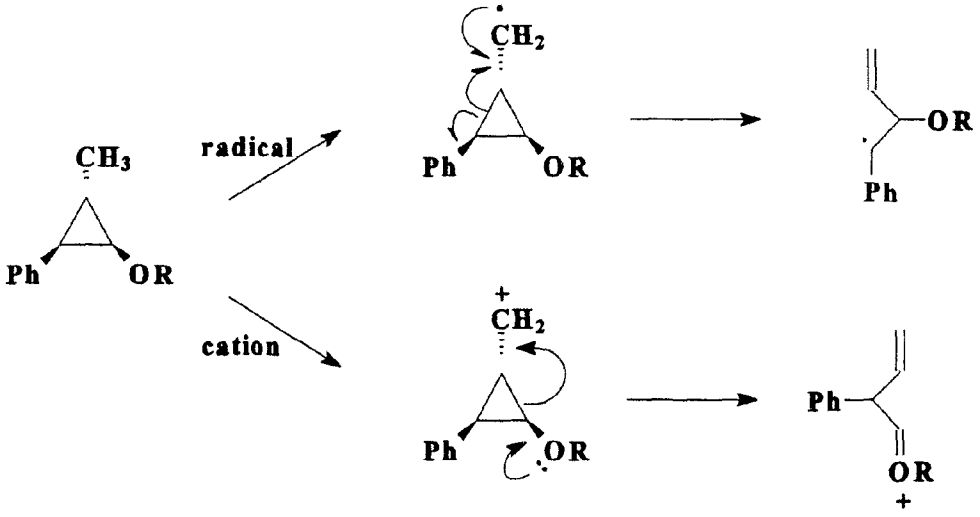
Currently there are many examples of unimolecular and bimolecular reactions used as radical clocks.[5] The rate constants of these radical clocks can be used to study radical reactions with rate constants from approximately 10^{-3} to 10^{12} s^{-1}.[6] They have been used to study mechanisms of such common organic reactions as Grignard reactions[7], the additions of carbon-centred radicals to alkenes, and other single-electron transfer processes,[8,9] and to determine both the mechanisms and the rate constants of some enzymatic reactions.[1,10,11,12]

The cyclopropylcarbinyl radical rearrangement was used as a radical clock to study the hydroxylation of hydrocarbons by cytochrome P450, a reaction which was believed to involve radical intermediates.[10, 11, 12] These radical clock studies have determined large variations in the rate constant for the hydroxylation reaction (1.4×10^{10} to 1.4×10^{13} s^{-1}). The latter value (1.4×10^{13} s^{-1}) is of the same order of magnitude as a molecular vibration.[13] The large variations in the measurement of the rate constant suggest that the

environment may alter the rate constant The sources of error in the measurement of the rate constant may be one or more of the following: under enzymatic conditions the radical clock reaction may be slower than when previously measured under non-enzymatic conditions; the mechanism may be either incomplete or incorrect; or there may be an error in the measurement of the product-yield ratios.

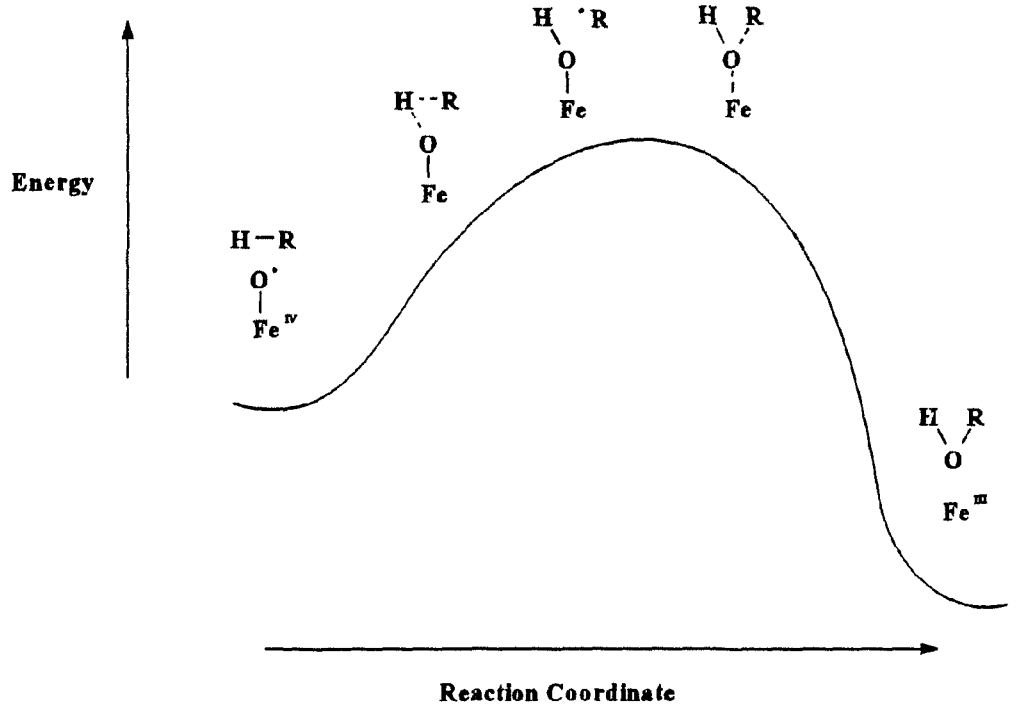
Traditional radical clocks, such as the cyclopropylcarbinyl radical rearrangement reaction or the 5-hexenyl radical cyclization reaction, are not able to differentiate between radical and ionic pathways when the same product results in both instances. A new type of radical clock was developed[14] to differentiate between these two pathways This clock contains a cyclopropyl ring which can open to give either a radical or a cation, Scheme 1. The phenyl ring stabilizes the radical when the ring is opened through a radical pathway, whereas the adjacent alkoxy group stabilizes the cation when the ring is opened through an ionic pathway.

Scheme 1 Mechanistic Probe



The mechanism for the hydroxylation of hydrocarbons by cytochrome P450 proposed before it was studied using the radical clock in Scheme 1, involved ionic intermediates. However, products were formed through the radical and cationic pathways. As well, a product with the cyclopropyl ring still intact was formed. Products formed by the ring-opening reaction of the radical were not formed by the conventional radical path but were instead formed by the radical that is present instantaneously during the nonsynchronous homolysis of the carbon-hydrogen bond and the formation of the carbon-oxygen bond, respectively. For a very short period of time, a carbon-centred radical exists during the hydroxylation reaction, Figure 1. The reaction coordinate in Figure 1 is incomplete, and further experimentation is required to complete the mechanism. Standard radical clocks, *e.g.*, the cyclopropylcarbinyl radical rearrangement, were not able to determine accurately the rate constant of the enzymatic reaction because the source of the radicals was not a conventional radical pathway.

Figure 1 **Reaction Coordinate for the Hydroxylation of Hydrocarbons by P450**

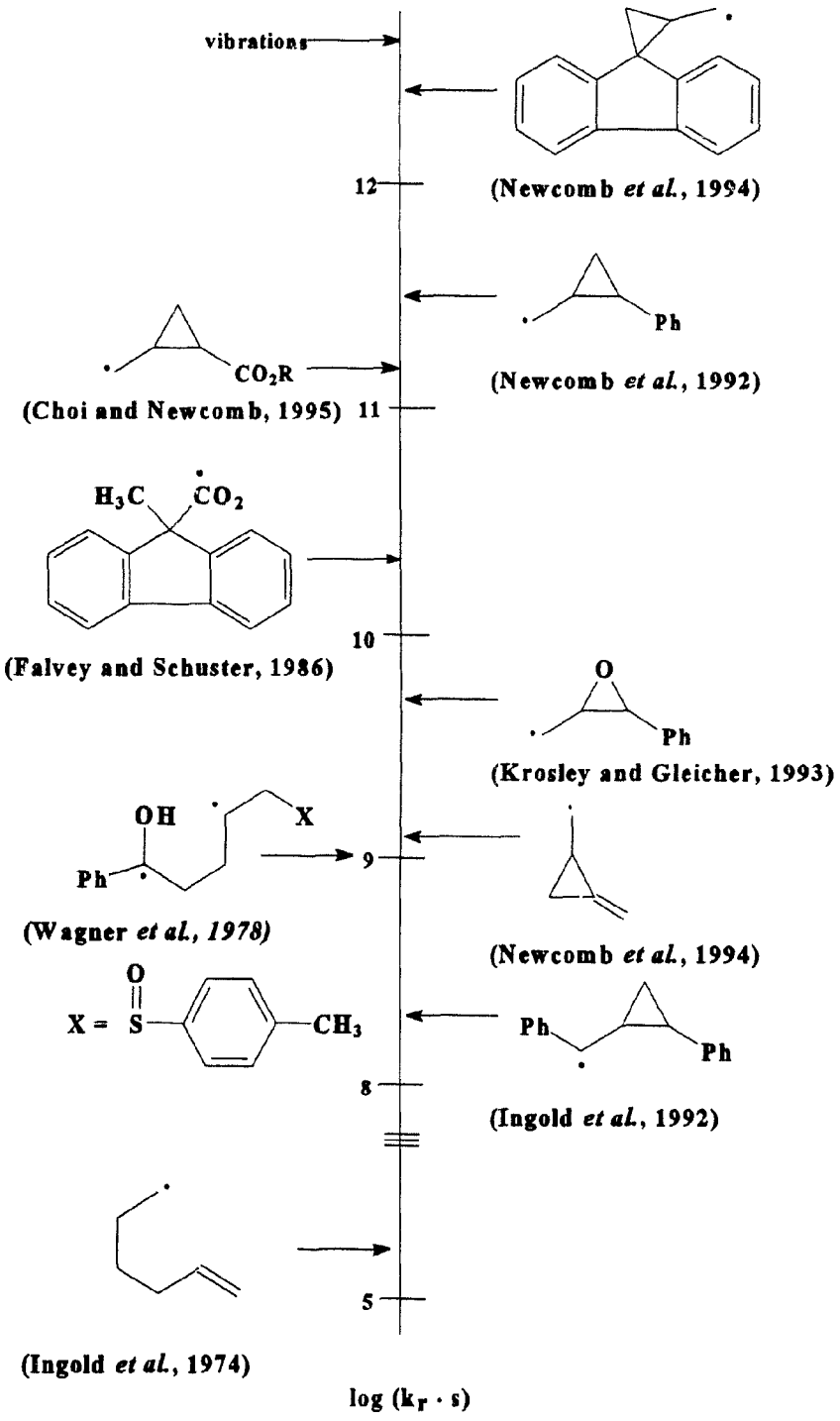


The following discussion describes some typical radical clocks, the relative rate constants of which are given in Scheme 2. Generally, the rate constants for the radical clocks in Scheme 2 were measured by competing bimolecular reactions using hydrogen-atom donors, such as tributyltin hydride or benzeneselenol. The well-established rate constants of these hydrogen-atom-donor reactio ·s make them prime candidates for usage as radical clocks. The fastest hydrogen-atom donor presently known, benzeneselenol, reacts with primary alkyl radicals with a rate constant of $2.1 \times 10^9\ M^{-1}s^{-1}$. This hydrogen-atom donor was calibrated using the cyclopropylcarbinyl radical clock. The concentration of the hydrogen-atom donor may be adjusted to increase or decrease as necessary the apparent rate in bimolecular reactions. This is in contrast to competing unimolecular

reactions.

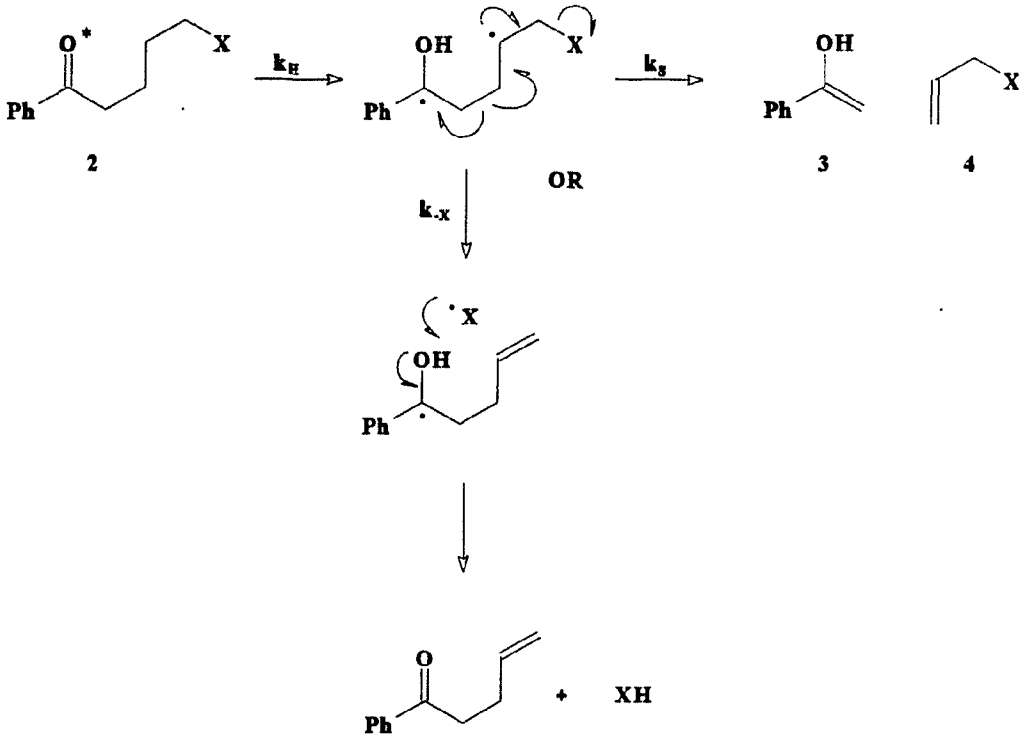
As mentioned previously, the first example of a radical clock, the cyclization of the 5-hexenyl radical,[4] eq 2, was calibrated by Ingold in the early 1970's. The 5-hexenyl radical underwent a ring-closing reaction to form the methylcyclopentyl radical. The rate constant of this reaction is $2.3 \times 10^5\ s^{-1}$ Much faster clocks have been developed since.

Scheme 2 **Relative Timescale of Some Very Fast Radical Clocks**



Results by Wagner *et al.*[15,16] in the photochemistry of δ-halovalerophenones, **2**, gave rate constants for β-cleavage reactions that were estimated to be as high as 10^9 s^{-1},

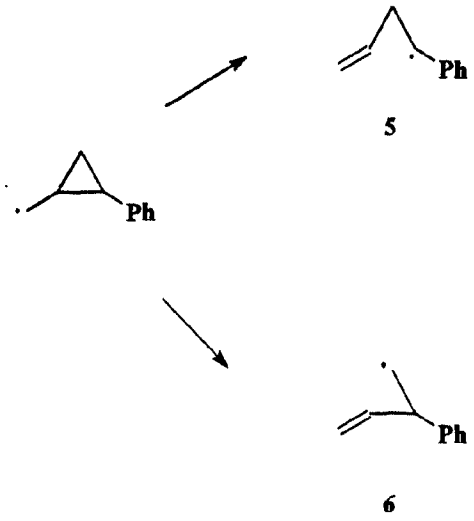
Scheme 3 The Photochemistry of δ-Halovalerophenones



Scheme 3. There are two potential reactions that can occur in this system; the β-cleavage reaction with loss of X, or cleavage of the biradical into the α,β-unsaturated alcohol, **3**, and the alkene, **4**. In the β-cleavage reaction, the radical adjacent to X forms a double bond with concurrent loss of either the radical or the atom, X.

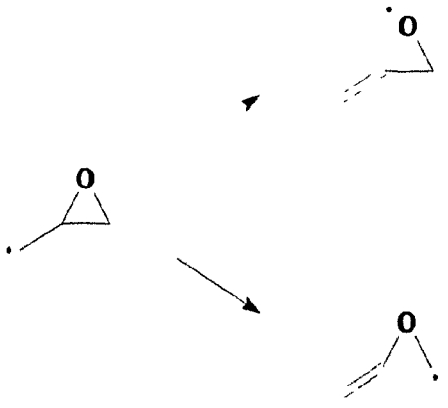
Radical clocks which contain cyclopropyl rings have very fast rate constants for their ring-opening reactions.[17,18,19] Either of two bonds in the cyclopropyl ring may break homolytically, and a double bond and a new radical are formed. In phenyl-substituted

cyclopropyl rings, the ring opens to form the benzylic radical, **5**, eq 4, and not the less stable methyl radical, **6**, the other possibility.



(4)

Krosley and Gleicher[20] compared the rate constants for the ring-opening reaction of the cyclopropylcarbinyl radical to that of the oxiranylcarbinyl radical. The ring-opening reaction of the oxiranylcarbinyl radical was faster by approximately an order of magnitude. There are two possible pathways for the oxiranylcarbinyl radical to ring open: the carbon-



(5)

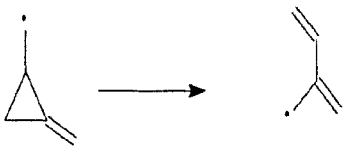
carbon bond cleaves to form the carbon-centred radical or the carbon-oxygen bond cleaves to form the oxygen-centred radical, eq 5. Substituents may alter the pathway preference. For example, a phenyl ring will enhance the rate constant for carbon-carbon bond cleavage.

Newcomb and Choi[21,22] have shown that ester-substituted cyclopropyl rings have rate constants for ring-opening reactions which are increased relative to those for the

(6)

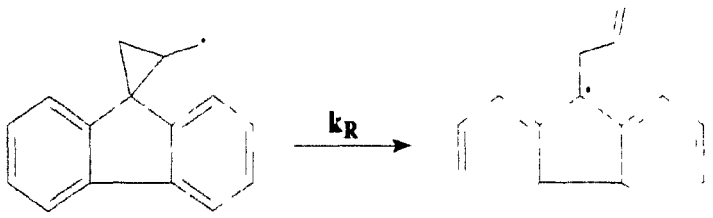
unsubstituted substrates, eq 6. The ring-opening reaction is the same for both the ester-substituted and the phenyl-substituted substrates.

Another example of a substituted cyclopropyl radical clock is the (methylenecyclopropyl)methyl radical reaction recently studied by Newcomb *et al.*[23] The ring-opening reaction of the cyclopropyl ring, eq 7, has a rate constant of 3-4 x $10^9 s^{-1}$.



(7)

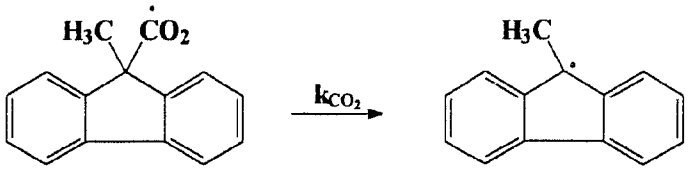
Currently the fastest measured[23,24] cyclopropylcarbinyl radical clock (10^{12} s^{-1}) is the ring opening of the spiro(cyclopropylfluorenyl)carbinyl radical to give the stable 9-fluorenyl radical, eq 8. The rate constant was measured using a hydrogen-atom-donor reaction with benzeneselenol. There is some uncertainty in the rate constant measured. Two reasons for the uncertainty are: first, the product-yield ratios measured were approximately 1000:1; second, the large concentrations of benzeneselenol required for competitive trapping might have interfered with the radical reaction. This might have decreased the



(8)

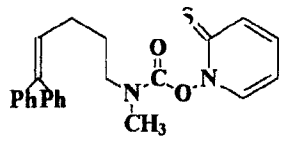
apparent rate constant of the trapping by the benzeneselenol so that the rate constant of the rearrangement reaction then would have been calculated to be greater than its correct value. Regardless of the source of the error, the rate constant for this radical clock reaction is not less than 10^{11} s^{-1}. Accurate determination of the actual value is not possible with this particular method. The rate constant of this radical clock should be measured independently, either directly or indirectly, before using it to time other reactions.

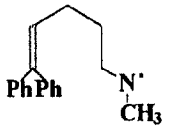
Falvey and Schuster[25] determined an absolute rate constant of 1.8×10^{10} s^{-1} for the decarboxylation of the 9-methylfluorenoyloxy radical to form the 9-methylfluorenyl radical, eq 9



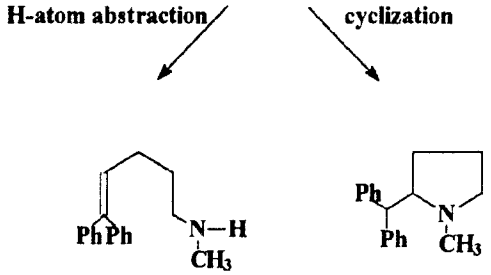
(9)

Newcomb *et al.*[26,27,28] also have investigated aminyl radical reactions in an attempt to develop new types of radical clocks, eq 10 They have not been included in Scheme 2 because the rate constant is dependent on the character and acidity of the solvent.



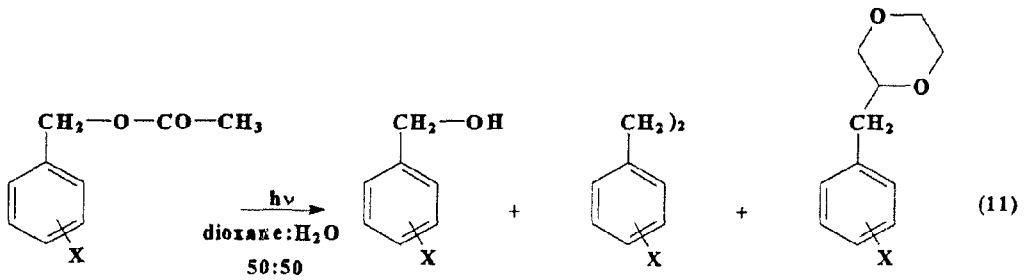


(10)



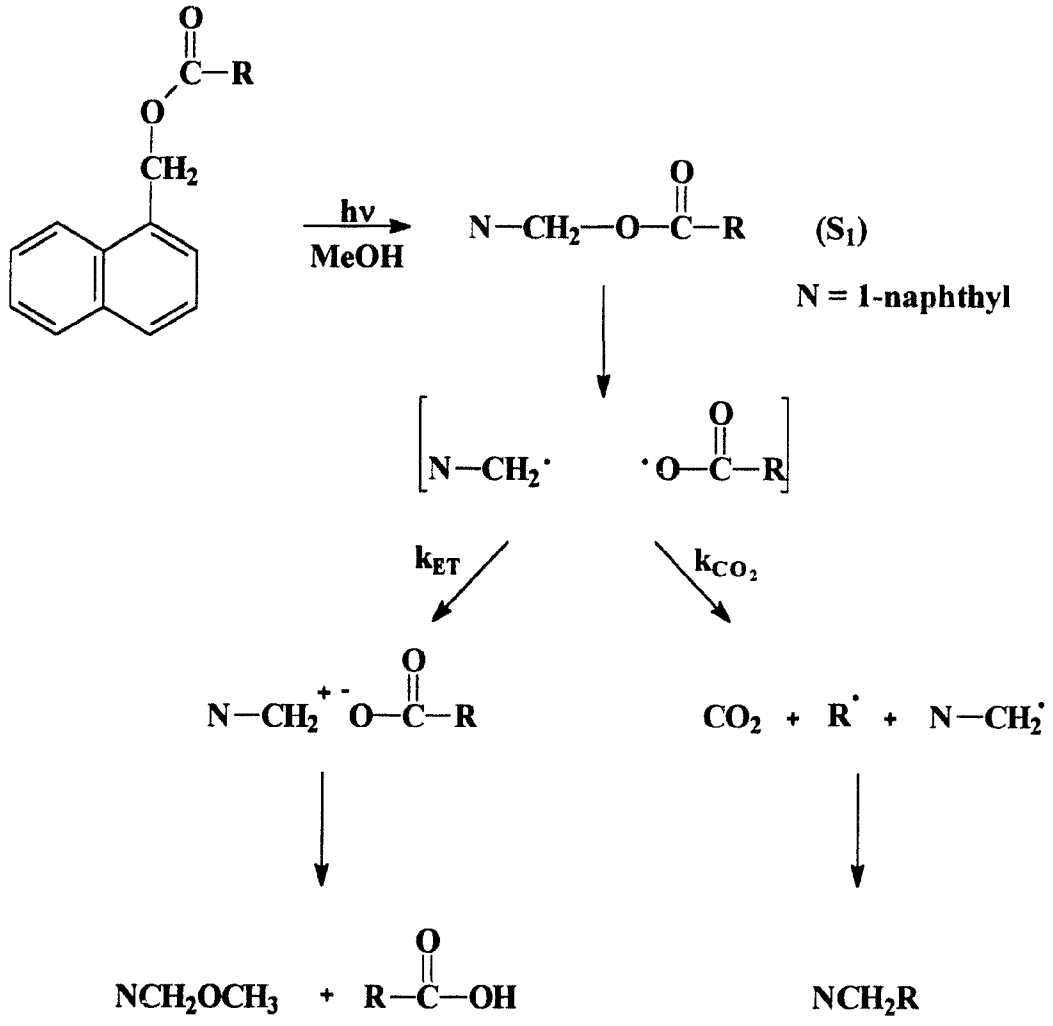
1.2 The Photochemistry of Arylmethyl Esters

Arylmethyl esters undergo photosolvolysis reactions in the presence of protic solvents such as methanol or water. In the early 1960's, Zimmerman and Sandel[29] examined the photochemistry of benzylic esters. Two types of products were observed: those formed through radicals and those formed through ions, eq 11. Their proposed mechanism involved an initial excited state carbon-oxygen bond cleavage, homolytic cleavage to form radicals and heterolytic cleavage to form ions The two pathways formed distinct products.



(11)

Scheme 4 The Photochemistry of Naphthylmethyl Esters



The mechanism proposed by Zimmerman and Sandel[29] was not challenged until the late 1980's, when DeCosta and Pincock[30] investigated the photochemistry of substituted 1-naphthylmethyl esters. Photolysis of naphthylmethyl esters in methanol forms methyl ethers and carboxylic acids from the ions, and hydrocarbon products from the radicals. The resulting product distributions as a function of X, the substituent on the aromatic ring, observed by DeCosta and Pincock[30] were explained without invoking heterolytic cleavage as a major pathway, even for substrates that had a preponderance of products resulting from ions. The mechanism proposed by DeCosta and Pincock involved homolytic ester carbon-oxygen bond cleavage from the singlet excited state; the initially-formed radical pair then partitions between two pathways: decarboxylation of the acyloxy radical, or electron transfer to form ions, Scheme 4. The other possible reaction which can occur is the radicals can escape from the solvent cage, a minor pathway with naphthylmethyl esters.

DeCosta and Pincock[30] were able to determine rate constants, as a function of X, for the two competing reactions, decarboxylation and electron transfer, using product-yield ratios The decarboxylation of the (9-methyl-9-fluorenoyl)oxy radical[25] was used as a radical clock (1.8×10^{10} s^{-1}) to determine the rate constant for electron transfer for the convertion of the radical pair to the ion pair based on the reported product-yield ratios.[30] The calculated rate constant for electron transfer between the (9-methyl-9-fluorenoyl)oxy radical and the 4-methoxynaphthyl radical[30] then was used as a radical clock to determine the rate constant (4.6×10^{9} s^{-1}) for the decarboxylation reaction of the phenylacetyloxy radical. This value was used as a radical clock to determine the rate constants for the

electron transfer reactions for the radical pairs generated by excitation and subsequent carbon-oxygen homolytic bond cleavage of substituted naphthylmethyl esters. The rate constant for the electron transfer reaction is dependent upon the oxidation potential of the naphthylmethyl radical, which is affected by substituents, X, on the naphthalene ring. In this way, DeCosta and Pincock[30] were able to measure electron-transfer rate constants for a number of electron-withdrawing and electron-donating substituents on the naphthalene ring.

An electron transfer reaction[30] was used later by Hilborn and Pincock[31] as a radical clock to determine the rate constants for decarboxylation of a number of acyloxy radicals, for example, the series $RCO_2\cdot$ for R equals methyl, ethyl, isopropyl and t-butyl. The rate constant for the decarboxylation reaction depends on the stability of the radical formed once decarboxylation has occurred. The rate constants for the electron transfer and decarboxylation reactions for the intermediates in the photolysis of 1-naphthylmethyl esters were calculated[30,31] to range from 10^9 to 10^{11} s^{-1}. The investigation by Pincock *et al.* into the photochemistry of arylmethyl esters has continued.[32,33,34,35] After a reinvestigation and extension of the work of Zimmerman and Sandel,[29] they concluded that the mechanism of benzylic ester photochemistry also may involve, as the major pathway, not direct heterolytic cleavage, but homolytic cleavage followed by electron transfer to produce ions.

The 5-hexenyl radical cyclization was used by Givens and Singh[36] to investigate the mechanism of phosphate ester photochemistry, and to determine whether heterolytic or homolytic cleavage of the carbon-oxygen bond was occurring. In general, the products of

the photolyses appeared to be ion-derived, and with the 5-hexenyl group incorporated, there were few products that resulted from the radical clock pathway From these results they concluded that the major pathway for cleavage of the carbon-oxygen bond was heterolytic, and that although homolysis occurred, it was a minor pathway An alternative explanation for this could be that the 5-hexenyl radical cyclization was not fast enough to compete with the other reactions With the assistance of very fast radical clocks, this mechanism might be revised to include homolysis followed by electron transfer to form ions

1.3 Project Objectives

The goal of this project was to design naphthylmethyl esters with radical clocks incorporated into them After excitation and carbon-oxygen homolytic bond cleavage, the radical clock reactions would occur and, then form distinct products For the rate constants of these radical reactions to be measured, they must be competitive with the rate constants for the electron transfer and decarboxylation reactions of the naphthylmethyl and phenylacetyloxy radical pair (10^9 to 10^{11} s^{-1}) In addition, the radical-clock reactions must be used in environments not unlike the environments in which the rate constants were initially measured

Two purposes would be served by incorporating these radical clocks into a naphthylmethyl ester first, the rate constants of these radical clocks could be determined from the known rate constants for the electron transfer and decarboxylation reactions, using the product yields, and second, the mechanism proposed, which does not include

heterolytic cleavage, could be further investigated. In this thesis, two types of radical clocks were incorporated into a naphthylmethyl ester: a β-cleavage reaction, and a three-membered ring-opening reaction.

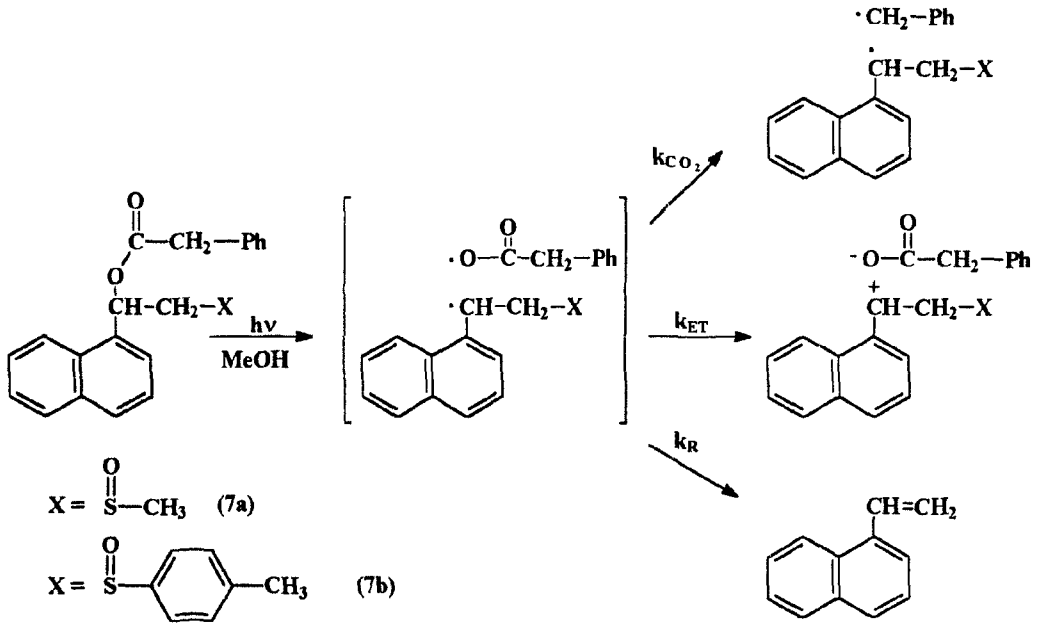
As mentioned earlier, Scheme 3, Wagner *et al.*[15, 16] studied two competing reactions after excitation of δ-halovalerophenones: hydrogen-atom abstraction and β-cleavage. The rate constants for the β-cleavage reaction in this system were of the right order of magnitude (10^9 s^{-1}) to compete with the radical processes (electron transfer and decarboxylation) occurring in naphthylmethyl ester photochemistry (10^9 - 10^{11} s^{-1}). The goal of this project, to incorporate radical clocks into naphthylmethyl esters, could be realized if a naphthylethyl ester were substituted at the β-carbon with a group able to undergo a β-cleavage reaction. Significant yields of product should come from the β-cleavage pathway if all three reactions, electron transfer, decarboxylation or β-cleavage, are competitive, and if the ions originated from homolytic cleavage followed by electron transfer.

Because the two systems, δ-halovalerophenones and naphthylethyl esters, are very different, the rate constants for the β-cleavage reactions in the two systems will not necessarily be the same. This project was expected to be able to provide a value for the rate constant for the β-cleavage reactions which would increase the confidence in the previously determined values.

Based on this hypothesis, the two esters in Scheme 5 with different X groups, methylsulfinyl and 4-tolylsulfinyl, were suggested as the substrates for this study. The idea was that the initially-formed radical pair generated from the excited-state carbon-oxygen

bond cleavage would follow one of three possible pathways: decarboxylation, electron transfer or β-cleavage. Rate constants k_{CO2}, k_{ET} and k_{β} then would be obtained by measurement of product-yield ratios. The syntheses of **7a,b** have been previously reported;[37] in this thesis the photolyses of **7a,b** will be discussed.

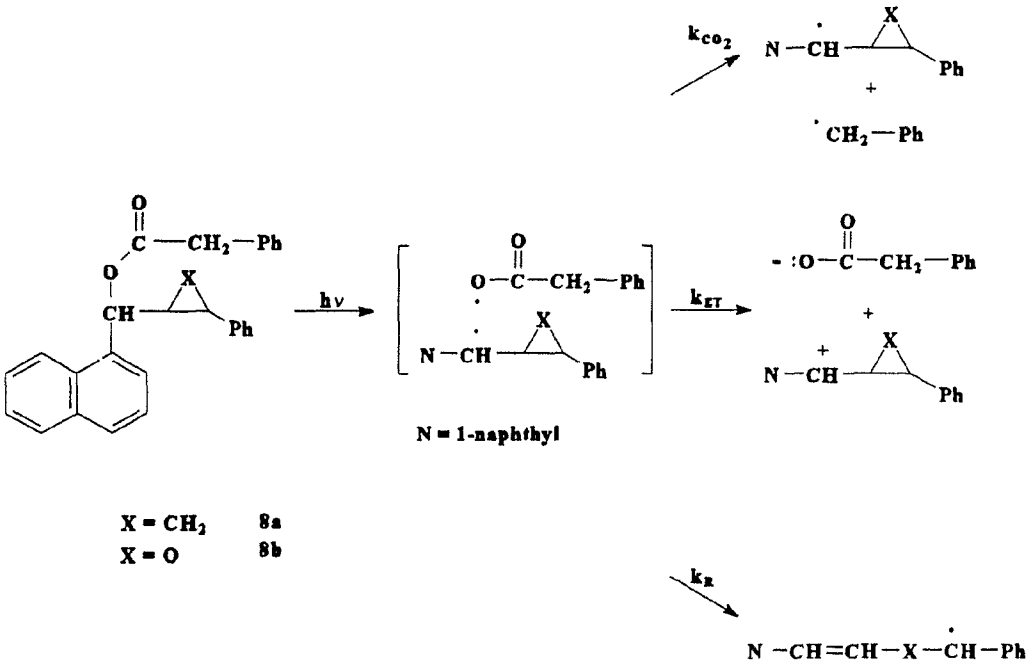
Scheme 5 Proposed Mechanism for the β-Cleavage Radical Clocks



As noted in Scheme 2, Newcomb *et al.*,[18] Ingold *et al.*,[17] and Lemieux and Beak[38] have shown that the rate constant for the ring-opening rearrangement of the phenyl cyclopropylcarbinyl radical is very fast (3×10^8 s^{-1}). Rate constants for the ring-opening reaction are greatly affected by substituents on the cyclopropyl ring. The phenyl cyclopropylcarbinyl radical clock reaction was proposed to be used because the ring-opening reaction should be fast enough to compete with the electron transfer and decarboxylation reactions.

Preliminary results[39] from the photolysis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate, **8a**, suggested that the ring-opening reaction of phenyl cyclopropylcarbinyl radical was not competitive with the electron transfer and decarboxylation reactions. Krosley and Gleicher[20] have compared the rate constants for the ring-opening reactions of the oxiranylcarbinyl radical and the cyclopropylcarbinyl radical and have found the former to be an order of magnitude faster. Therefore, incorporation of a phenyloxiranylcarbinyl radical clock into a naphthylmethyl ester might make the rate constant for the ring-opening reaction more competitive with the rate constants for the electron transfer and decarboxylation reactions.

Scheme 6 Proposed Mechanism for the Ring-Opening Radical Clock

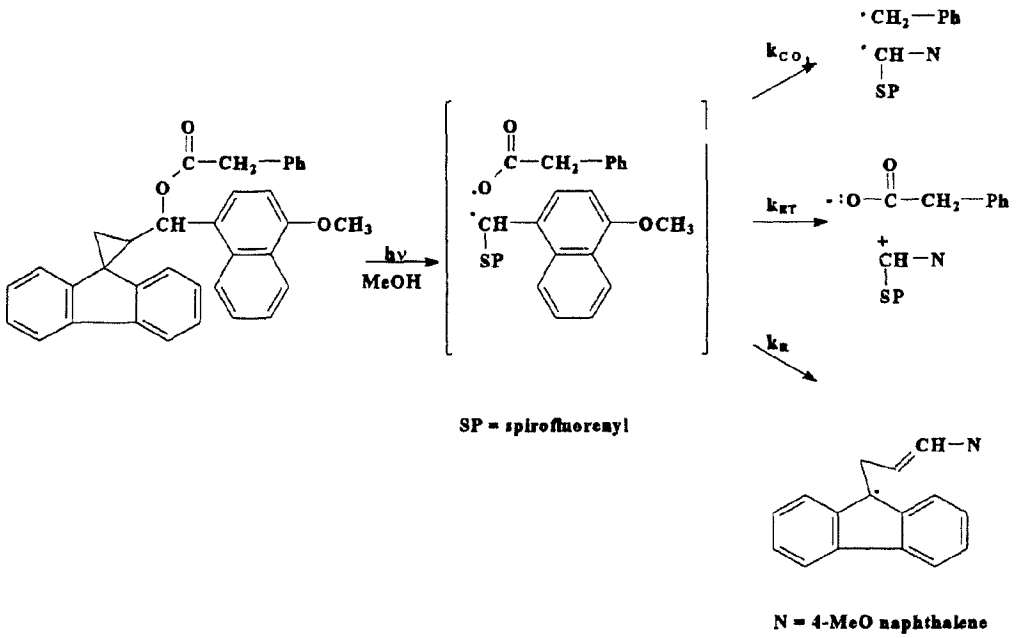


Based on these concepts, compounds **8a,b** were suggested for investigation, Scheme 6. Measurement of product-yield ratios would allow comparison of the rate constants k_{CO2}, k_{ET} and k_R. The synthesis and preliminary photolyses of **8a** were done previously.[39] A modified synthesis of **8a** is described in this thesis and an analysis of the products of the photolysis. The synthesis and photochemistry of **8b** is discussed.

The recent publication by Newcomb *et al.*[24] reported a radical clock, the spiro(fluorenylcyclopropyl)carbinyl radical reaction, which is too fast to be clocked by comparison with benzeneselenol in an hydrogen-atom-donor reaction. High concentrations of benzeneselenol (1.19 - 2.20 M) were required to make the two reactions, ring-opening and hydrogen-atom-trapping, competitive and that may have interfered with the rate constant measurement of approximately 10^{12} s^{-1}. This rate constant is considerably faster than the previously measured rate constants for the electron transfer and decarboxylation reactions of the radical pairs in naphthylmethyl ester photochemistry but is still competitive. This ring-opening reaction has great potential as a probe to investigate mechanisms because of its very fast rate constant of reaction but, as yet, the rate constant has not accurately been determined. Possibly the unimolecular rate constants of the electron-transfer and decarboxylation reactions will be fast enough to be used as radical clocks to determine the rate constant for the ring-opening reaction of the spiro(cyclopropylfluorenyl)carbinyl radical. Therefore, photochemistry of a naphthylmethyl ester with this radical clock incorporated would allow both the determination of the rate constant of the ring-opening reaction, and confirmation of the proposed mechanism suggested by Pincock and DeCosta,[30] if substantial amounts of

product results from the radical clock pathway. In this case, the naphthalene ring was substituted with a methoxy group to prevent competitive absorbance from the fluorenyl system, which absorbs in the same region as the unsubstituted naphthylmethyl ester. The molecule proposed to answer these questions is shown in Scheme 7. The competition again is among three reaction pathways from the initially-formed radical pair: electron transfer, decarboxylation and ring-opening. The three rate constants, k_{CO2}, k_{ET} and k_R then can be obtained using the product yield ratios. The synthesis of **9** and the photolysis will be discussed.

Scheme 7 **Proposed Mechanism for the Spiro(CyclopropylFluorenyl) Radical Clock**



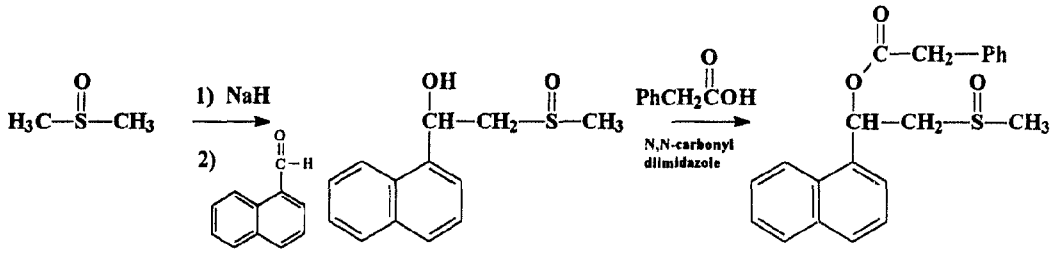
2 RESULTS AND DISCUSSION

2.1 Syntheses of Esters

2.1.1 Synthesis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a) and 2-(4-tolylsulfinyl)-1-(1-naphthyl)ethyl phenylacetate (7b)

These compounds were made previously,[37] see Schemes 8 and 9.

Scheme 8 Synthesis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)



7a

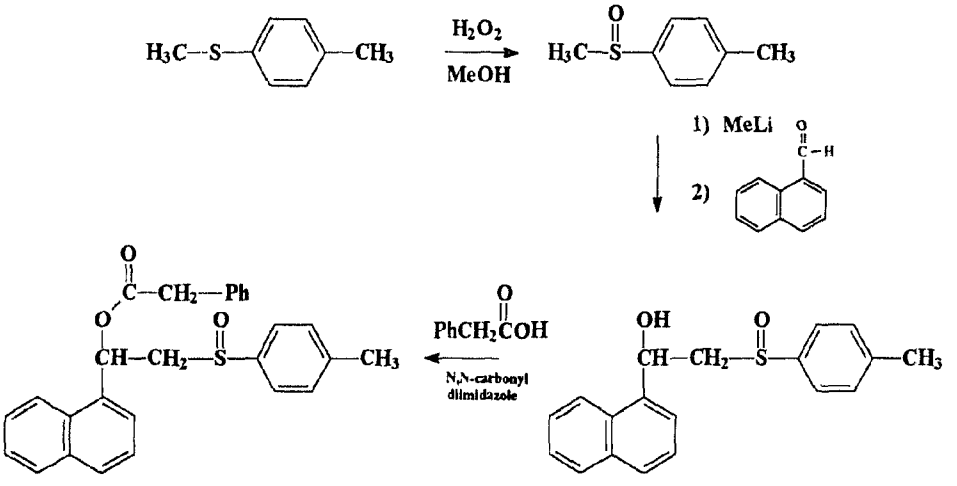
2.1.2 Synthesis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)

The original synthesis of **8a**, done in our laboratory, has been described elsewhere.[39] The synthesis has since been modified and, consequently, better yields of **8a** were obtained. Originally the cyclopropylmethyl alcohol was esterified by quenching the anion formed upon treatment with methyl lithium, with phenylacetyl chloride. This method was used because the cyclopropanated alcohol decomposed with the standard pyridine/acid chloride method. In the revised synthesis the alcohol was esterified with N,N-

carbonyldiimidazole and phenylacetic acid, conditions which resulted in higher yields.

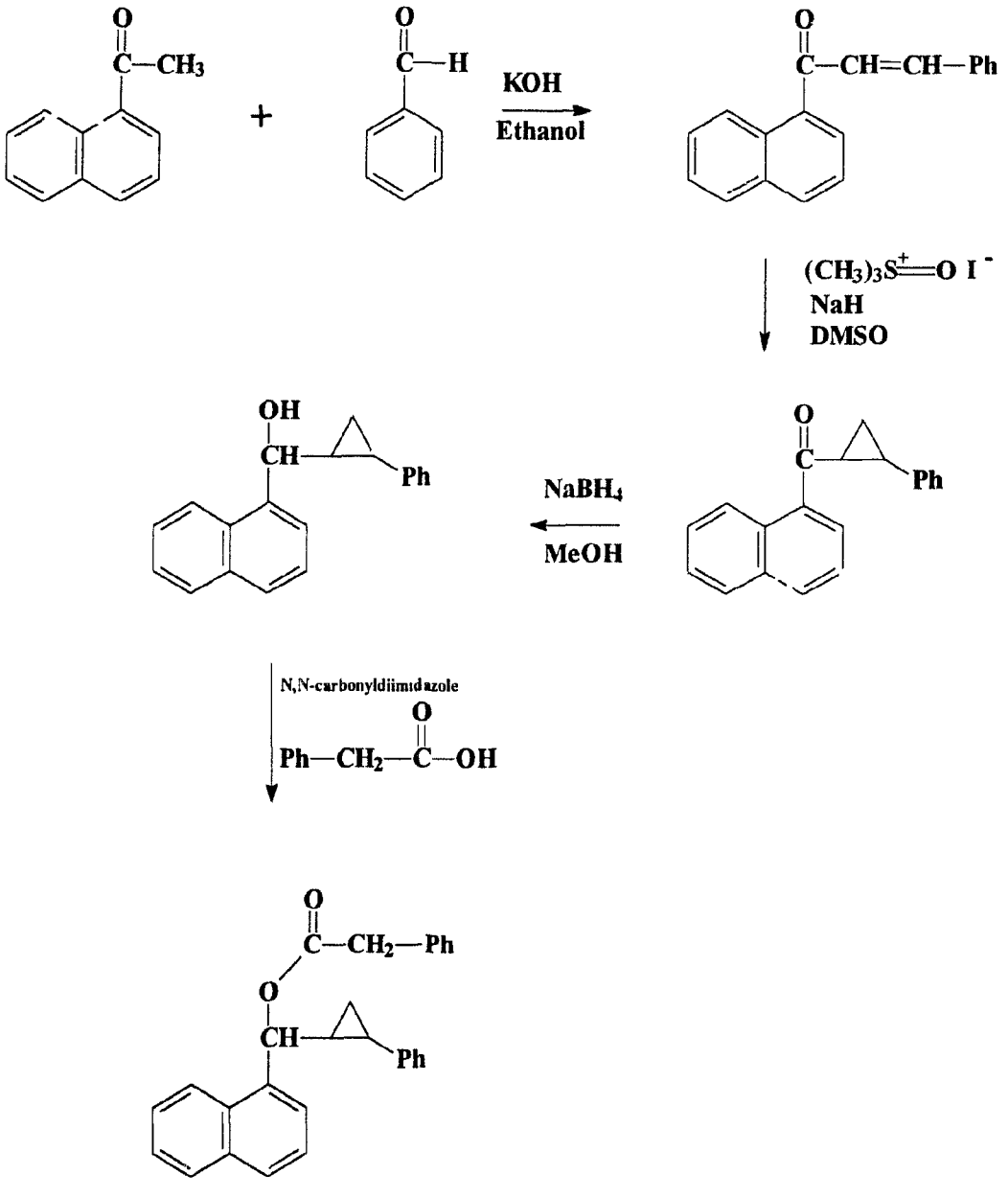
The first step in the synthesis is an aldol-type condensation of 1-acetonaphthone and benzaldehyde giving the *trans*-α,β-unsaturated ketone, Scheme 10 The α,β-unsaturated ketone was cyclopropanated according to the procedure of Prestwich *et al.*[40] of conjugate addition of a methylene group from trimethylsulfoxonium iodide using sodium hydride in dimethylsulfoxide. Next the cyclopropanated ketone was reduced to the alcohol with sodium borohydride. The resulting alcohol was esterified with N,N-carbonyldiimidazole and phenylacetic acid.

Scheme 9 Synthesis of 2-(4-tolylsulfinyl)-1-(1-naphthyl)ethyl phenylacetate (7b)



7b

Scheme 10 Synthesis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)



8a

There are three stereogenic carbons in [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate, and therefore eight possible stereoisomers. *Trans* stereochemistry is assumed for the hydrogens on the cyclopropyl ring because that isomer will be the most stable. Then only four stereoisomers are possible or two diastereomers, as enantiomeric pairs The *R,S,S* and the *S,S,S* diasteromers are shown The absolute stereochemistry of the *trans* isomers were not determined

The structure of the cyclopropyl ester was confirmed with proton and ^{13}C nmr spectra, and supported by mass spectral analysis The proton nmr spectrum shows three sets of multiplets at 2 10 ppm, 1 80 ppm and 0.90 ppm, which integrate for one, one and two protons, respectively. These multiplets are the protons on the cyclopropyl ring. Proton nmr coupling constants could not be used to determine stereochemistry in this instance Both *trans* and *cis* protons would be expected to have similar coupling constants of approximately 3-5 Hz. The singlet at 3 50 ppm, integrating for two protons, is the benzylic protons Both possible diastereomers are present because there are two doublets at 6 40 ppm and 6 20 ppm, in the ratio of 1 2, for the naphthylmethyl proton with coupling constants of 7 4 Hz and 8 2 Hz, respectively.

In the ^{13}C nmr spectrum, the presence of two diastereomers is confirmed by the doubling of all sp^3 hybridized signals The three peaks at 13 4 ppm, 23 1 ppm and 27 8 ppm are the cyclopropyl ring carbons in the major diastereomer. Those three carbons in

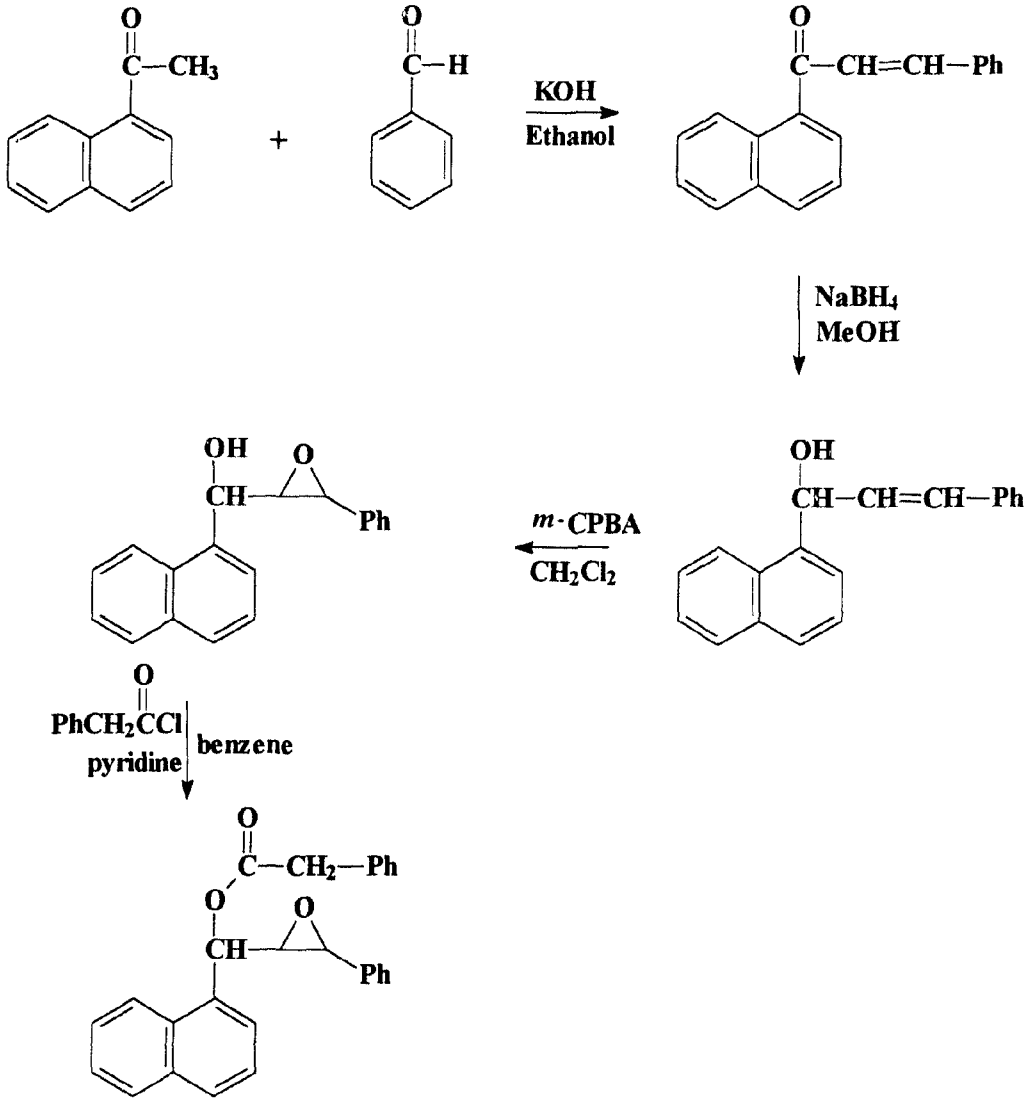
the minor diastereomer are at 14.5 ppm, 21.5 ppm and 27.1 ppm. The peaks at 171.3 ppm and 170.9 ppm are the ester carbon in the major and minor diastereomer, respectively. Some of the aromatic protons of the two diastereomers could not be assigned.

The mass spectrum gives a molecular ion at m/z 392.

2.1.3 Synthesis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)

The first step in the synthesis of **8b** is an aldol-type condensation of 1-acetonaphthone and benzaldehyde, the same reaction as described for **8a**. In the second step, the *trans*-α,β-unsaturated ketone was reduced using sodium borohydride, Scheme 11. The α,β-unsaturated alcohol was epoxidized with *m*-chloroperbenzoic acid (*m*-CPBA). Again there are three stereogenic carbons in the epoxy alcohol and the ester, but assuming *trans* stereochemistry only two diastereomers, as enantiomeric pairs, are possible. In this case, the stereochemistry of the ester was confirmed based on the observation of a small coupling constant of 1.5 Hz in the proton nmr spectrum between the two epoxy protons. This coupling constant is typical for *trans* epoxide hydrogens; whereas a typical coupling constant for *cis* epoxide protons is 4 Hz.[41]

Scheme 11 Synthesis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)



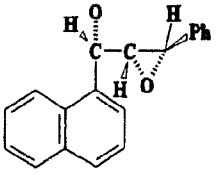
8b

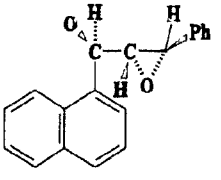
The proposed structure of the alcohol is supported by the proton nmr spectrum. There are two diastereomers present as indicated by the presence of two doublets at 5.70 ppm

and 5.40 ppm for the naphthylmethyl protons, which integrate for one hydrogen, in an approximately three to one ratio. The other protons in the molecule are assigned as follows. The hydroxyl protons are the broad singlet at 3.10 ppm. The protons on the epoxide ring are the multiplets at 4.10 ppm and 3.50 ppm. The coupling constants could not be determined for these protons. No attempts were made to separate this mixture.

The mixture of diastereomers of the epoxy alcohol then was esterified using phenylacetyl chloride and pyridine. The proton nmr spectrum was used to confirm that the ratio of diastereomers remained constant in converting the alcohol to the ester. The structure of the ester was confirmed using the proton nmr spectrum and the mass spectrum. The doublets at 6.60 ppm and 6.80 ppm, in a ratio of three to one, are the naphthylmethyl protons. The protons on the epoxide ring adjacent to the naphthylmethyl proton are the multiplets at 3.55 ppm and 3.46 ppm, in the major and minor diastereomer, respectively. Assignment of a particular diastereomer to specific peaks was not attempted. Column chromatography altered the proportion of diastereomers present in the mixture, but complete separation of the two diastereomers of the ester was not accomplished.

The mass spectrum gives a molecular ion at m/z 394.



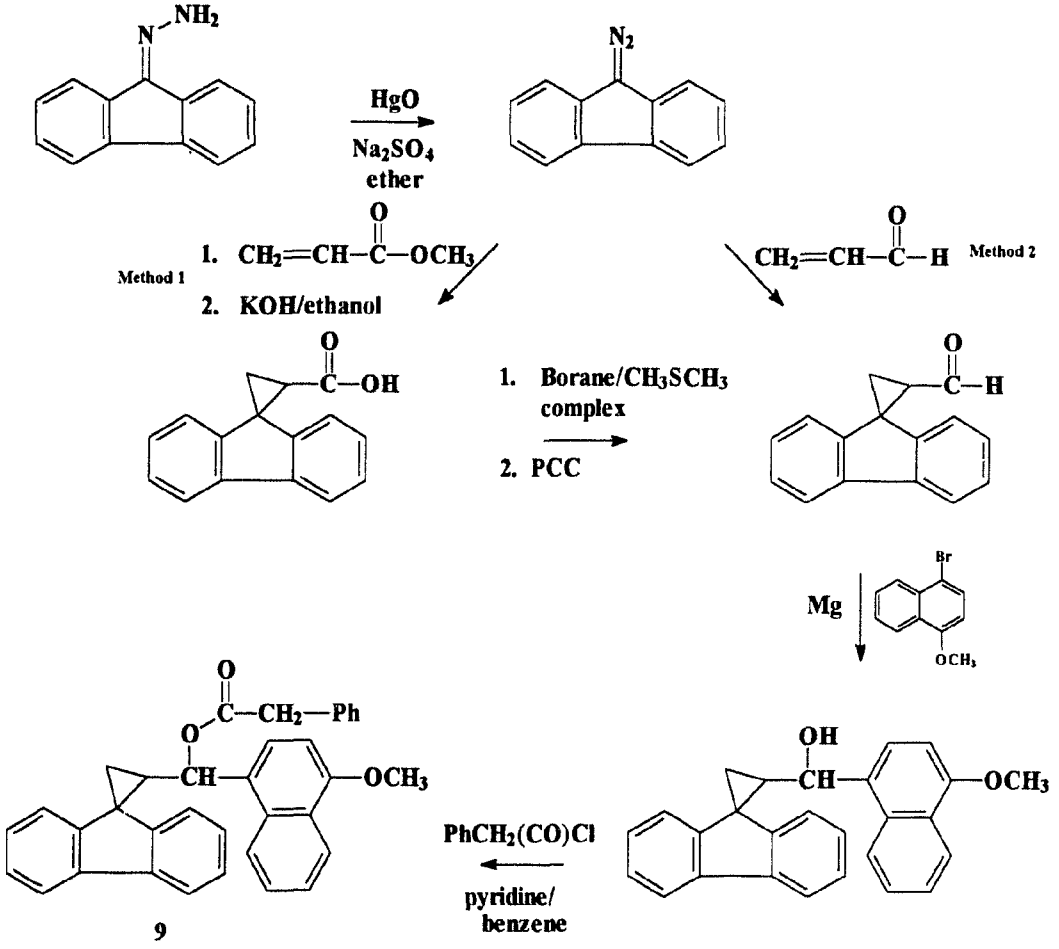


2.1.4 Synthesis of 1-(4-methoxynaphth-1-yl)-1-spiro[(fluorene-1,9'-cycloprop-2-

yl)]methyl phenylacetate (9)

The synthesis of **9** is shown in Scheme 12. The synthetic route was discussed with Professor Martin Newcomb from Wayne State University where his group had prepared the precursor compound to the aldehyde in the first method, the carboxylic acid. Professor Newcomb's group had spent considerable time working out ideal reaction conditions, and in particular, had found that the extrusion of nitrogen from the pyrazoline intermediate required specific reaction conditions. Moreover, the reaction seemed to work better on a smaller scale. Professor Newcomb's group had synthesized a similar aldehyde from a carboxylic acid using the borane-dimethylsulfide complex for the selective reduction and then pyridinium chlorochromate (PCC) for the oxidation. Professor Newcomb suggested that we attempt this reaction on this carboxylic acid.

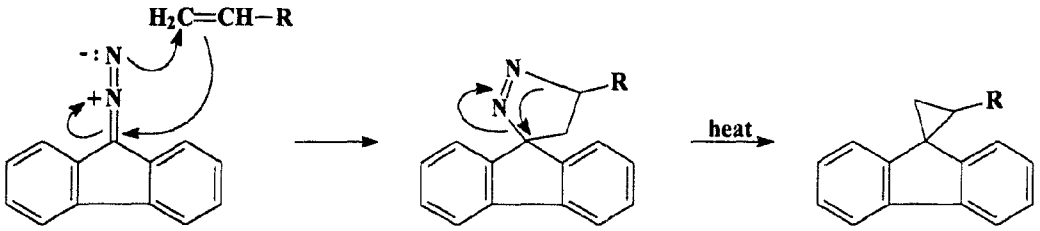
Scheme 12 Synthesis of 1-(4-methoxynaphth-1-yl)-1-spiro[fluorene-1,9'-cycloprop-2-yl]methyl phenylacetate



The first step was to assemble the spiro portion of the molecule. To do this, 9-fluorenone hydrazone was oxidized to 9-diazofluorene[42] using yellow mercuric oxide. Two different methods were used for the synthesis of 2-formyl-spiro(cyclopropane-1,9'-fluorene) from 9-diazofluorene.

In the first method, 9-diazofluorene was added to methyl acrylate. The mechanism involves two steps as shown in Scheme 13. First, a pyrazoline intermediate is formed in a 2+3 thermally allowed cycloaddition. These reactions, 1,3-dipolar cycloadditions to alkenes, are analogous to Diels-Alder reactions and have been extensively studied. The pyrazoline then was heated to the reflux temperature of methyl acrylate (80 °C) and nitrogen was extruded. The excess methyl acrylate was not removed before heating, and considerable polymerization occurred at this stage.

Scheme 13 Mechanism of Alkene Addition to 9-diazofluorene



An attempt was made to reduce the methyl ester to the alcohol with lithium aluminum hydride. The plan then was to selectively oxidize the alcohol to the aldehyde. However, no alcohol could be isolated from this reduction and, in fact, the crude proton nmr spectrum indicated that the cyclopropane ring had opened.

Because of this problem, Professor Newcomb suggested an alternative route involving initial hydrolysis of the ester, followed by reduction to the alcohol and then selective partial oxidation to the aldehyde. The hydrolysis was performed using potassium hydroxide in ethanol. The reduction of the carboxylic acid was performed using the borane-dimethyl sulfide complex to produce the borate ester which was oxidized to the

aldehyde using pyridinium chlorochromate without isolation of the alcohol. Professor Newcomb suggested that the alcohol would not be very stable, and that the borate ester might be preferred. This step in the synthesis formed the aldehyde in approximately 50% yield.

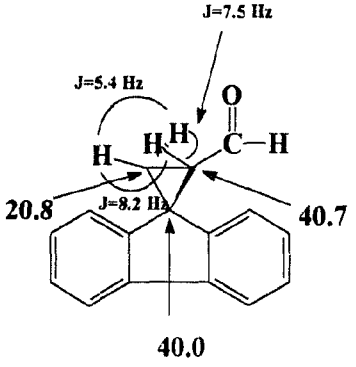
The polymerization of methyl acrylate and the hydrolysis reaction were responsible for large losses of material by this method Therefore, the cyclopropanation addition reaction was attempted with a different reagent alkene, acrolein. Using the vinyl aldehyde eliminated two steps in the reaction sequence, the reduction and the oxidation, because the spiro(cyclopropylfluorenyl) compound formed was already in the correct oxidation state at the exocyclic carbon. Although this switching of double bond substrates prevented some loss of material by eliminating the hydrolysis reaction, the acrolein still polymerized during heating.

By the second method, 9-diazofluorene was added to acrolein to give the pyrazoline intermediate. To prevent extensive polymerization from occurring, the excess acrolein was removed at room temperature using a vacuum pump. The residual acrolein spontaneously polymerized during the removal, but any of the pyrazoline that the polymer had absorbed was extracted with dichloromethane. Heating this pyrazoline intermediate in benzene (80°C) gave 2-formyl-spiro(cyclopropane-1,9'-fluorene) in 49% yield.

The aldehyde was identified by proton and ^{13}C nmr spectra. The doublet at 9.69 ppm with a coupling constant of 4.2 Hz is the aldehyde proton, coupled to the adjacent methine proton of the cyclopropyl ring. That methine proton is a triplet of doublets at 2.89 ppm, with coupling constants of 7.5 Hz and 8.2 Hz for the coupling to the adjacent methylene

protons in the cyclopropyl ring Although the other two protons on the cyclopropyl ring appear to have identical coupling constants to the methine proton, they are not isochronous and each appears as a doublet of doublets at 2 60 ppm and 2 30 ppm with a geminal coupling constant of 5 5 Hz As shown in Figure 2, the spectrum can be simulated[43] and the coupling constants obtained The proton *cis* to the aldehyde is at a lower field (δ 2 6) than the *trans* one (δ 2 3) and the *cis* coupling constant (8 2 Hz) is slightly larger than the *trans* one (7 5 Hz)

Figure 2 Proton and Carbon NMR Assignments in Aldehyde



In the ^{13}C nmr spectrum, the aldehyde carbon is at 197 8 ppm, and those of the three carbons of the cyclopropyl ring are at 40 7 ppm, 40 0 ppm and 20 8 ppm, and are the carbon adjacent to the aldehyde, the spiro carbon, and the methylene carbon, respectively The assignment of the spiro carbon was based on its lower intensity as would be expected for a quaternary carbon

Each of the above methods resulted in successful synthesis of the aldehyde for use in the Grignard reaction to form **9**, but only the second method gave the aldehyde in synthetically useful quantities Addition of 2-formyl-spiro(cyclopropyl-1,9'-fluorene) to

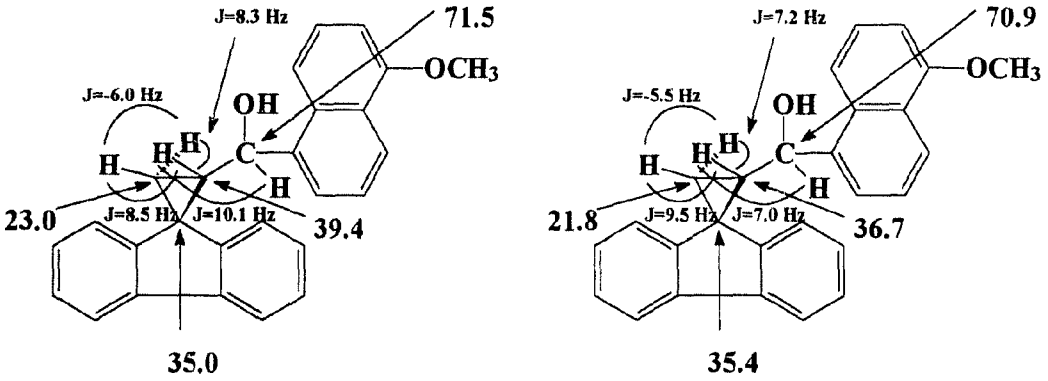
the Grignard reagent prepared from 1-bromo-4-methoxynaphthalene formed the alcohol. The crude proton nmr spectrum revealed two diastereomers of the alcohol, in an approximately 9:1 ratio as determined by comparison of the integration for the proton on the alcohol carbon. The alcohol contains two stereogenic centres, making the number of stereoisomers that are possible, four, or two diastereomers as enantiomeric pairs. The two diastereomers of the alcohol were completely separated on the chromatographic column. The minor diastereomer came off the column almost with the solvent front (5% ethyl acetate in hexane), whereas the major diastereomer appeared considerably later

The alcohol was identified using proton and ^{13}C nmr spectra. The proton nmr assignments for the major diastereomer are the following. The doublet at 5.65 ppm, with a coupling constant of 10.1 Hz, is the proton on the alcohol carbon. The singlet at 4.04 ppm is the methoxy protons. The multiplets at 2.67 and 1.98 ppm, which integrate for one and two protons respectively, are the three protons on the cyclopropyl ring. Again, as shown in Figure 3, this spectrum could be simulated. The large coupling constant of 10.1 Hz between the methine protons suggests that they are *anti* to each other. This will be confirmed in the ester because, from the X-ray crystal structure, we know the protons are *anti* and the coupling constant of 10.1 Hz suggests an *anti* conformation in solution for both. The broad singlet at 1.70 ppm is the hydroxyl proton.

The proton nmr assignments for the minor diastereomer are the following. The proton on the alcohol carbon is the doublet at 5.49 ppm with a coupling constant of 7.0 Hz. The methoxy protons are the singlet at 3.85 ppm, whereas the three protons on the cyclopropyl ring are the multiplets at 2.57 ppm, 2.27 ppm and 2.16 ppm, which integrate for one, one

and two protons, respectively. Simulation gives the coupling constants; the *cis* one (9.5 Hz) was assumed to be larger than the *trans* one (7.2 Hz). The hydroxyl proton signal is in the multiplet at 2.16 ppm.

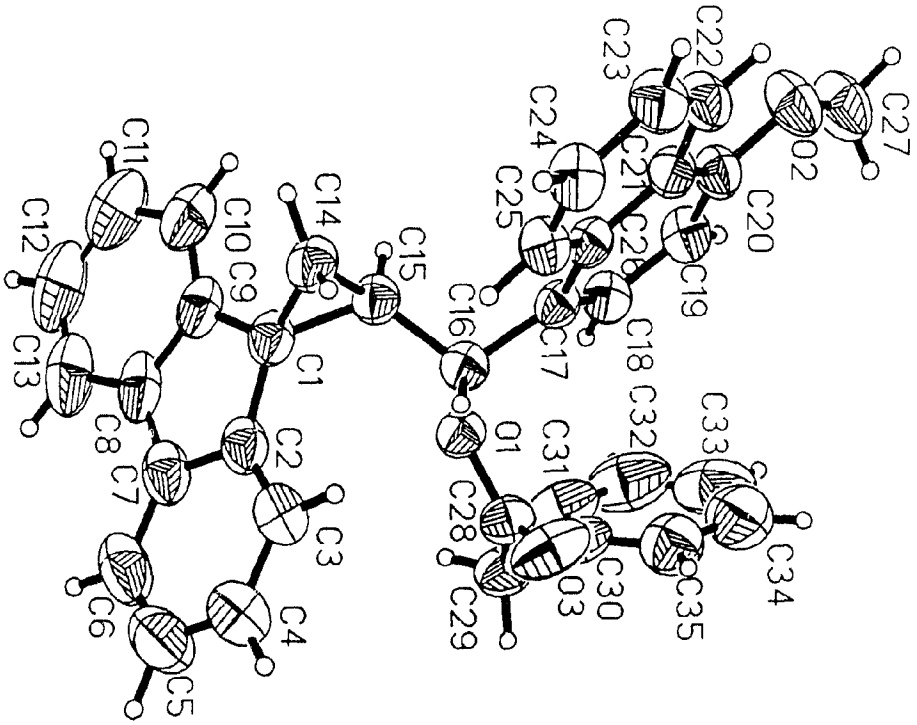
Figure 3 Proton and Carbon NMR Assignments in Alcohol



Minor **Major**

The assignments for the major diastereomer in the ^{13}C nmr spectrum are the following. The alcohol carbon is at 71.5 ppm, the methoxy carbon is at 55.6 ppm, and the three carbons on the cyclopropyl ring are at 39.4 ppm, 34.8 ppm and 23.0 ppm, with the first signal being the carbon adjacent to the alcohol and the second, the spiro carbon. The minor diastereomer assignments in the ^{13}C spectrum are as follows. The peak at 70.8 ppm is the alcohol carbon, the peak at 55.4 ppm is the methoxy carbon, and the three peaks at 36.7 ppm, 35.4 ppm and 21.8 ppm are the three carbons in the cyclopropyl ring; the peak at 36.7 ppm is the carbon adjacent to the alcohol and the peak at 35.4 ppm is the spiro carbon.

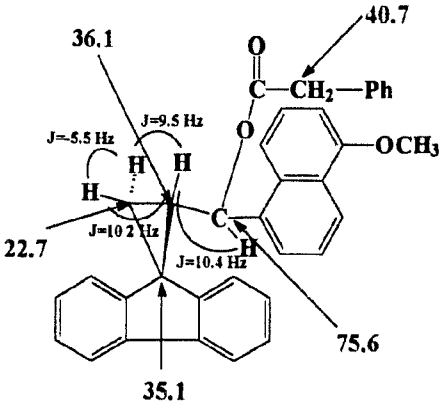
Figure 4 **X-Ray Crystallographic Structure of 9**



Only the major diastereomer of the alcohol was esterified with phenylacetyl chloride and pyridine, because the yield of the minor diastereomer of the alcohol was too small. The resulting ester was crystalline and its crystal structure was obtained (Figure 4) and the absolute stereochemistry was determined. The naphthylmethyl carbon has the *R,S* configuration and the adjacent stereogenic centre also has the *R,S* configuration. This confirmed the structure of the alcohol.

The ester was initially identified by proton and ^{13}C nmr spectra, with confirmation of the structure and absolute stereochemistry determined from a crystal structure. In the proton nmr spectrum of the ester, the naphthylmethyl proton is a doublet at 6.48 ppm with a coupling constant of 10.4 Hz This large *trans* coupling implies that the solution conformation is the same as that observed in the solid. The methoxy protons are the singlet at 4.03 ppm. At 3.14 ppm and 3.13 ppm, there are two very closely spaced doublets which integrate for a total of two protons, and are the benzylic protons. These protons are diastereotopic because of the stereogenic centres in the molecule, and thus have different chemical shifts. Their geminal coupling constant is 15.9 Hz. The multiplet at 2.70 ppm is the proton adjacent to the naphthylmethyl carbon. The rest of the spectrum is deceptively simple for an ABC system. Simulation gives the chemical shifts and coupling constants in Figure 5.

Figure 5 Proton and Carbon Assignments for 9



In the ^{13}C nmr spectrum, the ester carbon is at 170 2 ppm, and the naphthylmethyl carbon is at 75.7 ppm. The signal at 55.6 ppm is the methoxy carbon, whereas the signal at 40.7 ppm is the benzylic carbon. The remaining three signals at 36.1 ppm, 35.1 ppm and 22.7 ppm are the three carbons of the cyclopropyl ring, with the spiro carbon at 35 1 ppm.

The mass spectrum does not give a molecular ion but shows a base peak at m/z 360, which is the even electron cation resulting from loss of the phenylacetyloxy radical.

The ester, **9**, was designed to have the 4-methoxynaphthalene chromophore to avoid competitive excitation between the fluorenyl group, which is the clock, and the naphthylmethyl ester, which creates the radical pair Fluorene has its maximum absorbance at 265 nm with an extinction coefficient of 20,000, but at 286 nm where naphthalene has its maximum absorbance, the extinction coefficient for fluorene is still 4000. The extinction coefficient for naphthalene at 286 nm is 9300. A methoxy group on the naphthalene ring will shift the maximum absorbance to longer wavelength, and therefore at 310 nm, 1-methoxynaphthalene still has an extinction coefficient of 3200,

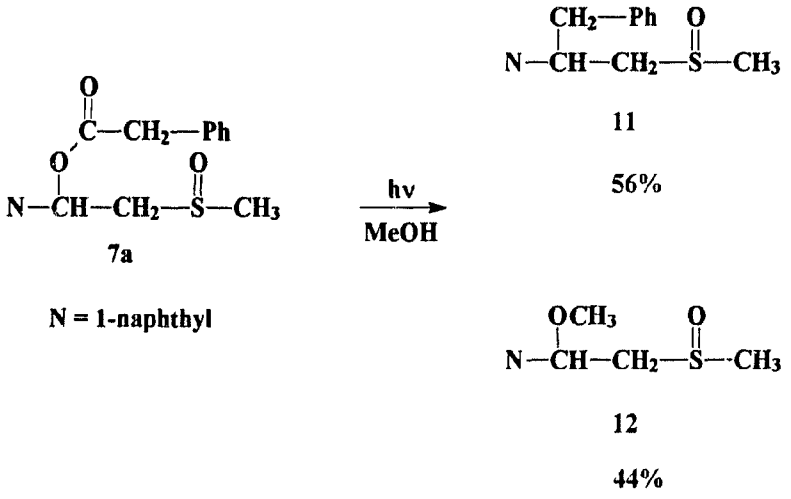
whereas fluorene's extinction coefficient at that wavelength is less than 300, ensuring that the naphthalene chromophore will absorb most of the energy. This is confirmed by ultraviolet and fluorescence spectra of the ester. The 0,0 band is at 326 nm (87.7 kcal/mol) and ϕ_F, the quantum yield of fluorescence, is 0 13. These values are similar to that observed for 4-methoxy-1-naphthylmethyl phenylacetate, 88.8 and 0.27, a compound that lacks the fluorenyl part.

2.2 Photolysis of Esters

2.2.1 Photolysis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)

The products obtained, and their yields, for the photolysis of **7a** in methanol are shown in Scheme 14. The isolated ether, **12**, was identified by comparison to a synthetic sample and confirmed by spectroscopic methods. The coupling product, **11**, was isolated from the photolysis mixture, and identified by spectroscopic methods. The yields were determined by assuming that the two products represented one hundred percent of the product, and then using the relative peak heights in the HPLC trace to determine the percentage of each product.

Scheme 14 Photolysis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)



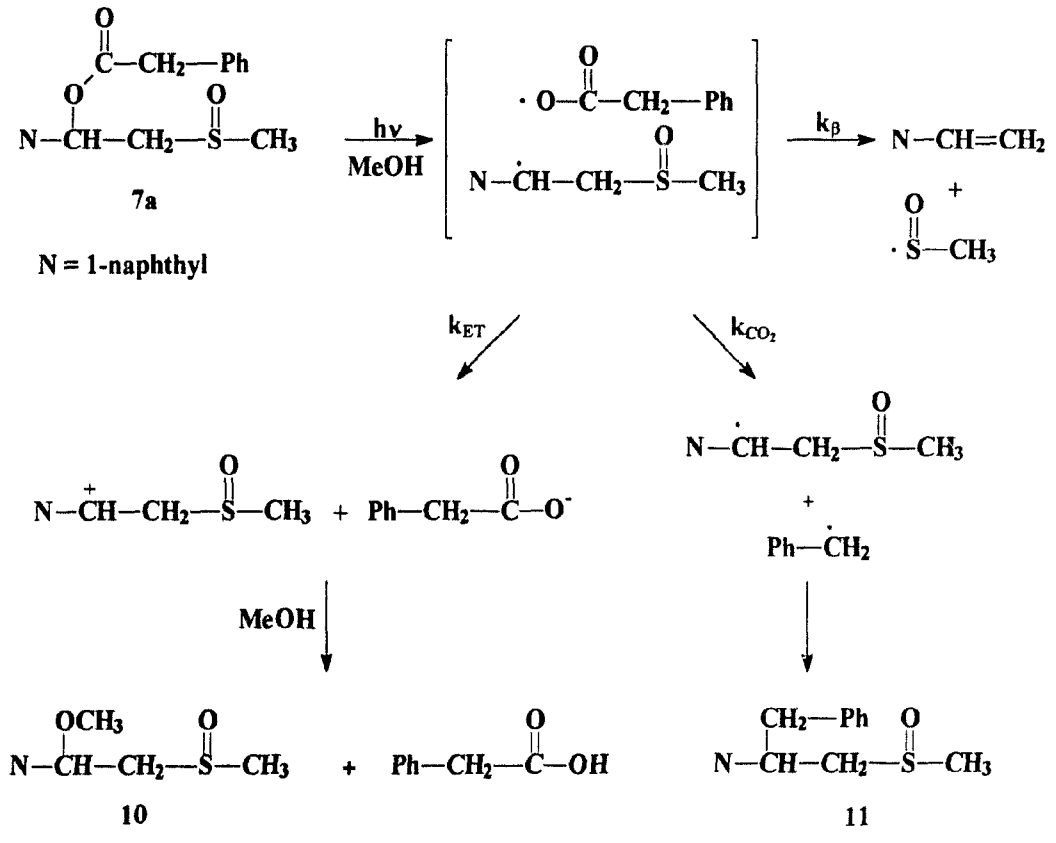
The ether, **12**, exhibits a characteristic SO stretching frequency at 782 cm^{-1} in the infrared spectrum. In the proton nmr spectrum, there is a doublet of doublets at 5.50 ppm, the naphthylmethyl proton. This proton couples to the adjacent methylene protons, the multiplet at 3.10 ppm. The two singlets, at 3.40 ppm and 2.60 ppm, both integrating for three hydrogens, are the methoxy protons and the methyl protons adjacent to the

sulfoxide group, respectively The mass spectrum gives a molecular ion at 248, and as well, a loss of 63, the methylsulfinyl group

The proton nmr spectrum of the coupling product, **11**, is complex, with three multiplets at 4 44 ppm, 3 29 ppm and 3 02 ppm, integrating for one, three and one protons, respectively These multiplets are not assigned to particular protons, and the coupling constants could not be determined The methyl protons adjacent to the sulfoxide group are the singlet at 2 42 ppm The peak at 60 1 ppm is the methylene carbon adjacent to the sulfoxide, and the peak at 40 4 ppm is the benzylic carbon A multiplicity experiment in the ^{13}C nmr spectrum was used to assign the particular peaks to particular carbons The methyl carbon is at 38 9 ppm, whereas the naphthylmethyl carbon is at 35 2 ppm The mass spectrum gives a molecular ion at m/z 308, with a loss of 63, the methylsulfinyl group

The two products of the photolysis are consistent with the general mechanism proposed by Pincock *et al* [30] The proposed mechanism for the photolysis of **7a** is outlined in Scheme 15

Scheme 15 **Mechanism of the Photolysis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)**



Upon photochemical excitation of **7a**, the singlet excited state of the ester is formed. The energy of this excited state (approximately 90 kcal mol^{-1}) is considerably higher than the carbon-oxygen bond dissociation energy (approximately 65 kcal mol^{-1}) of the ester. Therefore, homolytic carbon-oxygen bond cleavage occurs and an in-cage radical pair is formed. The radical pair then might undergo three competing reactions: electron transfer, decarboxylation or β-cleavage. The products obtained and the mass balance demonstrate that the latter possibility is not competitive with the former two.

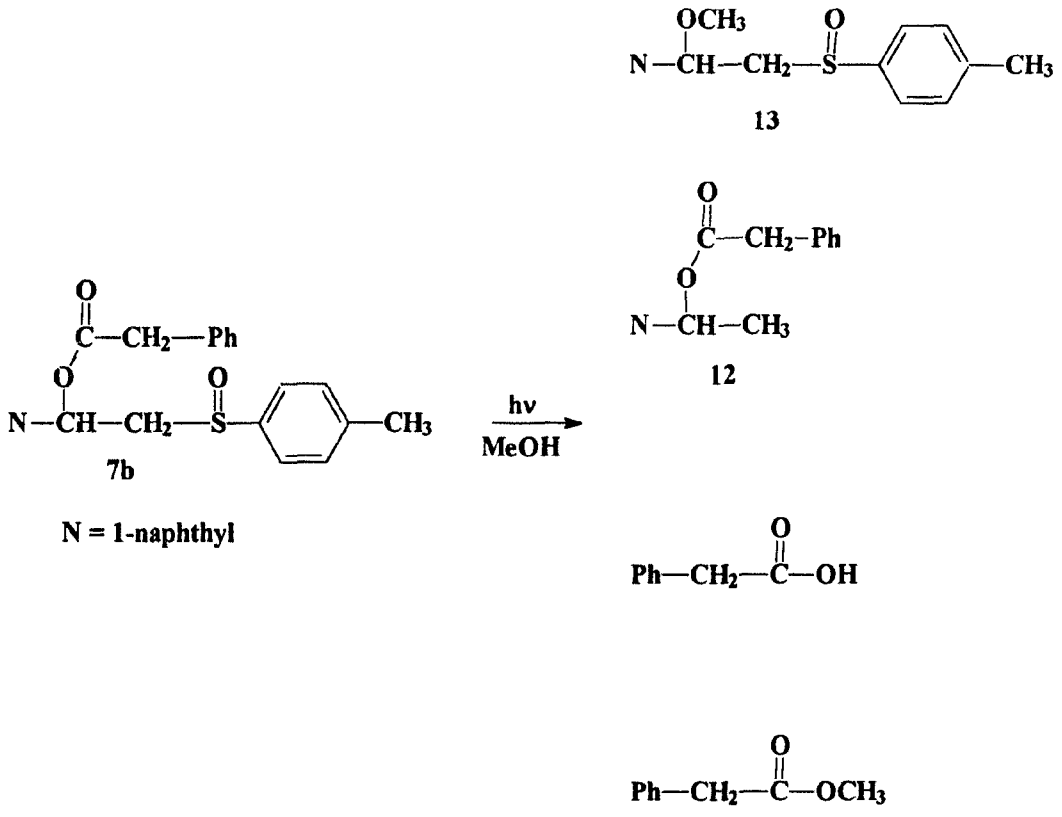
The ion pair, formed by the electron transfer reaction of the initial radical pair, reacted with methanol to form ether **10** and phenylacetic acid. The only other product detected in the photolysis was the coupling product, **11**, which results from the benzyl radical, formed by decarboxylation of the phenylacetyloxy radical, coupling with the 1-naphthylmethyl radical. A rate constant for the β-cleavage reaction at a non-benzylic alkyl radical was determined to be approximately 1×10^7 s^{-1} by Wagner *et al.*[15, 16] This value is two to three orders of magnitude slower than the values expected (10^9 to 10^{11} s^{-1}) for the electron transfer and decarboxylation reactions.[30,31] The lack, or at least very low yield, of product(s) obtained from the β-cleavage pathway is therefore consistent with expectations and demonstrate that faster radical clocks are necessary to probe the reactivity of these radical pairs.

2.2.2 Photolysis of 2-(4-tolylsulfinyl)-1-(1-naphthyl)ethyl phenylacetate (7b)

The products for the photolysis of **7b** are shown in Scheme 16. The two products obtained, the ether, **13**, and the ester, **12**, were identified by a proton nmr spectrum and a mass spectrum of the mixture. Complete separation of the two products was not

accomplished, and therefore, separate proton nmr spectra were not obtained. No quantitative yields could be determined because of the poor material balance obtained for this photolysis. All of the photolyses of **7b** resulted in the analytical recovery of less than 10% of the starting material mass even at conversions as low as 50%.

Scheme 16 Photolysis of 2-(4-tolylsulfinyl)-1-(1-naphthyl)ethyl phenylacetate (7b)



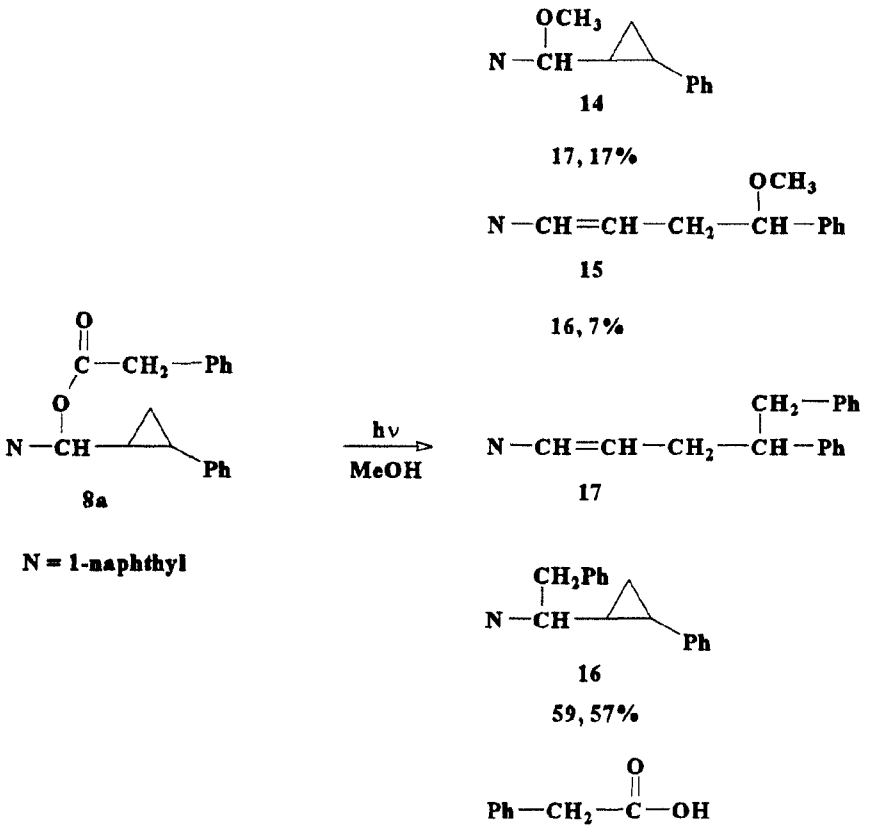
Compound **12**, resulted from direct photochemical cleavage of the carbon-sulfur bond β to the naphthylmethyl chromophore in the starting ester. There is precedence in the literature for the occurrence of this β-cleavage process.[44,45,46] The ether, **13**, was formed

by addition of methanol to the naphthylmethyl cation, which can be formed by one of two pathways: photochemical homolytic cleavage followed by electron transfer, or photochemical heterolytic cleavage. Ground state solvolysis in methanol was ruled out by controls in the dark. No products resulting from a β-cleavage reaction were detected. No further photochemistry of this compound was attempted, either to isolate products or to determine product yields, for two reasons: first, poor material balance was observed, and, second, one of the major products of the photolysis resulted from direct photochemical cleavage of the carbon-sulfur bond, **12**. This direct cleavage from the excited state makes the use of this compound as a probe for radical reactivity impossible. The radical clock method is based on the assumption that any product obtained from the radical comes only from the radical clock pathway The intervention of another pathway for formation of the same product makes assignment of product-yield ratios from the individual paths very difficult.

2.2.3 Photolysis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)

The identities and yields of the products of the photolysis of **8a** are given in Scheme 17. The structure of the ether, **14**, was determined by comparison with a synthetic sample. The structures of the other two products, **15** and **16**, were determined by spectroscopic methods. The yields were determined by comparing the peak heights of the products in an HPLC trace of a photolysis run to peak heights of samples of known concentration. The two values shown for the yields indicate the results from two separate analytical product-yield determinations.

Scheme 17 Photolysis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)



The proton nmr spectrum for the ether, **14**, indicates a mixture of diastereomers is present in the approximate ratio of 2 to 3, by integration of the two signals for the naphthylmethyl proton. These signals at 4.20 ppm and 4.58 ppm are completely separated, and the total integration of these two are for a single proton. Integrations for the other individual peaks did not resolve separate intensities for the two diastereomers. The methoxy protons are coincident, and are the singlet at 3 30 ppm. The complexity of the spectrum prohibits further identification of the remaining four multiplets. The simpler

^{13}C nmr spectrum allows identification of the carbons in both the major and the minor isomer A multiplicity experiment was used to identify the methylene carbon of the cyclopropyl ring For the major isomer, the methoxy carbon is at 56 9 ppm, and the naphthylmethyl carbon is at 84 2 ppm The three carbons of the cyclopropyl ring are at 28 3 ppm, 22 8 ppm and 12 8 ppm the first, the benzylic carbon, the second, the other methine carbon of the cyclopropyl ring, and the third, the methylene carbon In the spectrum of the minor isomer, the methoxy carbon is at 56 7 ppm, the naphthylmethyl carbon is at 83 3 ppm, and the three carbons of the cyclopropyl ring are at 28 1, 20 9 and 14 4 ppm, with the same assignments as in the major diastereomer There is a molecular ion at m/z 288 in the mass spectrum for both isomers

The structure of the coupling product, **16**, was determined, with some assumptions The mass spectrum gives a molecular ion at m/z 348, and partial assignment from the proton and ^{13}C nmr spectra was accomplished Once the molecular weight was known, this structure was assumed to be the coupling product, with the cyclopropyl ring either opened or closed The ring-opened coupling product, **17**, would have proton and ^{13}C nmr spectra with appropriate signals in the alkene region The ring-closed coupling product would have proton and ^{13}C nmr spectra with appropriate signals for the cyclopropyl ring A mixture of diastereomers is evident from the proton and ^{13}C nmr spectra The proton nmr spectrum is complex, with five multiplets, which could not easily be assigned There are no peaks in the olefin region of the spectrum, but there are peaks in the region generally assigned to cyclopropyl protons. The carbons in the ^{13}C nmr spectrum are slightly easier to assign, but not all of the carbons are identified in the spectrum, and each

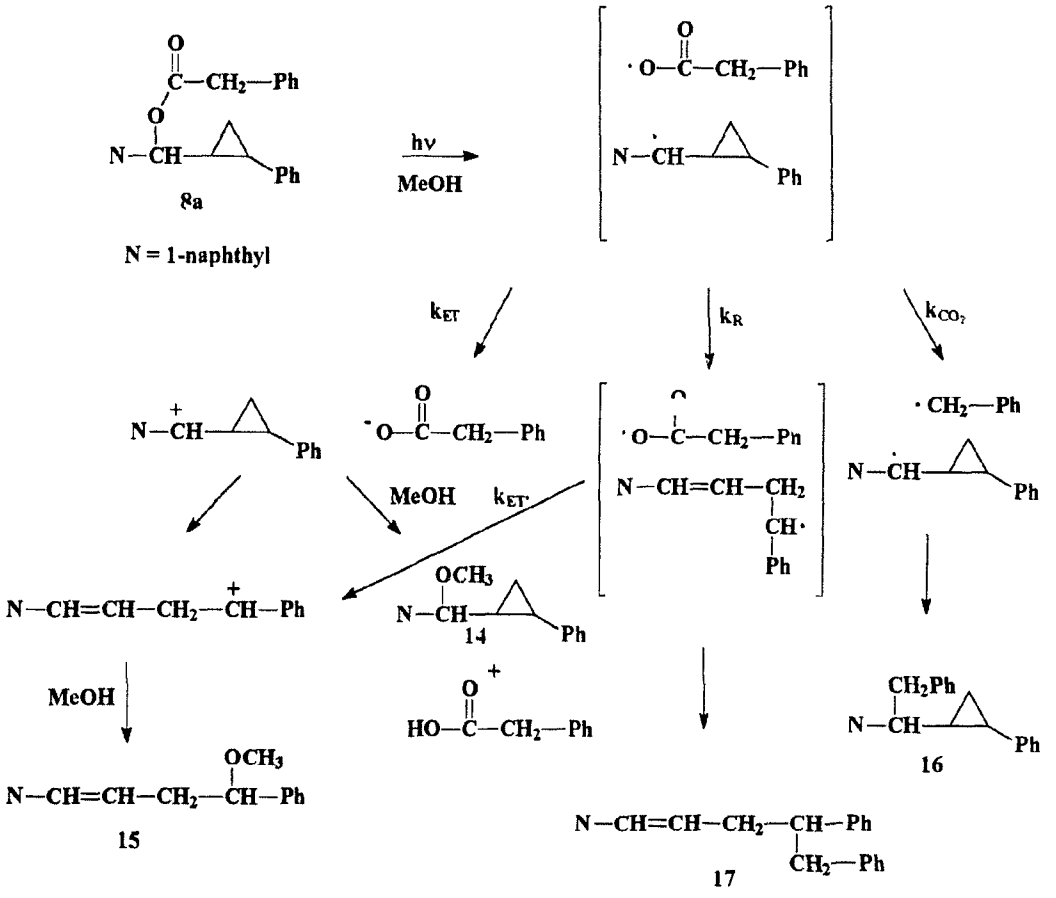
diastereomer is not assigned to particular peaks. There are no carbons that could be assigned to the olefinic region of the spectrum, but there are carbons in the region normally assigned to cyclopropyl carbons. From all of this information, the structure of the coupling product, **16**, as two diastereomers, was determined.

The structure of the third product of this photolysis, **15**, was determined from the proton nmr and ^{13}C nmr spectra, and a mass spectrum. In the proton nmr spectrum, only one alkene proton is assigned, the peak at 6.06 ppm. The peak representing the other alkene proton is in the aromatic signals. The multiplet for the aromatic protons integrates for thirteen, one more than expected by the number of aromatic protons. The triplet at 4.20 ppm is the benzylic proton, coupled to the adjacent methylene protons, that appear equivalent. They are not equivalent, and are the multiplet at 2.67 ppm which would be a doublet of doublets if they were equivalent. The methoxy protons are the singlet at 3.17 ppm.

In the ^{13}C nmr spectrum, the benzylic carbon is at 84.0 ppm, the methoxy carbon is at 56.8 ppm, and the methylene carbon is at 42.1 ppm. The mass spectrum gives a molecular ion at m/z 288.

The mechanism proposed for the formation of these products is shown in Scheme 18.

Scheme 18 Mechanism of the Photolysis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)



Photochemical excitation of **8a** into its singlet excited state results in homolytic carbon-oxygen bond cleavage. The radical pair then could undergo three competing reactions: electron transfer, decarboxylation or ring-opening of the cyclopropyl ring.

The ether, **14**, and phenylacetic acid result from the reaction of methanol with the ion pair formed by the electron transfer reaction. The ether, **14**, also could be produced by ground state solvolysis of the starting ester, **8a**, but this was ruled out by control experiments. Methanol also added to the cation formed after ring-opening of the cyclopropyl ring to form a second ether, **15**. This ring-opening can occur in two ways: first, through a radical pathway and second, through a cationic pathway. The first pathway would be ring-opening of the cyclopropylcarbinyl radical followed by electron transfer to form the cation. The second pathway would be electron transfer to form the ring-closed cation followed by ring-opening of that cation.

The hydrocarbon coupling product, **16**, results from the coupling of the benzyl radical, formed by decarboxylation of the phenylacetyloxy radical, with the 1-naphthylmethyl radical.

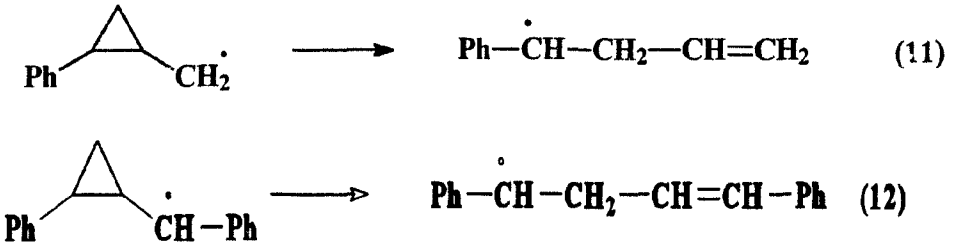
There were no products detected that resulted from the intermediate radical formed by the ring-opening of the radical clock. An example of a product resulting from the radical clock pathway is **17**, formed by coupling of the naphthylmethyl radical with the benzyl radical.

Results of the ground state solvolysis in methanol (24 hours at 65 °C) of **8a** showed formation of **14** and **15**, in a three to seven ratio. This differs from the photolysis results where an almost equal amount of both ethers were formed. This would not be the

expected result if **15** were produced in the photolysis through the radical clock pathway. In the photolysis, a larger ratio of **15** to **14** would be expected because there are two potential sources of the cation: the radical clock pathway, and rearrangement of the ring-closed cation. Perhaps the source of the ring-opened ether in the photolysis is through ring-opening of the cation formed by the electron transfer pathway, while the source of the ring-closed ether is through the electron transfer pathway. Methanol adds to both of these cations to give ethers. Probably the higher temperature (65°C) required for the ground state solvolysis also would increase the yield of the ring-opened cation.

The lack of products formed by the radical clock pathway was surprising based on the expected rate constant of the ring-opening reaction of the phenylcyclopropyl radical. Substituents on the cyclopropyl ring have large effects on rate constants. For example, in eq 11, a cyclopropylcarbinyl radical undergoes the ring-opening reaction to form a benzyl radical with a rate constant of approximately 4×10^{11} s^{-1}. In eq 12, a cyclopropylbenzyl radical undergoes the ring-opening reaction, and this change in the structure of the radical reduces the rate constant of the ring-opening reaction to 3×10^{8} s^{-1}. The radical formed from the photochemical reaction of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate, **8a**, is most similar to the cyclopropylbenzyl radical (eq 12), except for replacement of one of the phenyl rings with a naphthalene ring. Thus, we assume that the expected rate constant for ring-opening of the cyclopropyl ring in the naphthylmethyl radical is approximately 3×10^{8} s^{-1}. Therefore, only small amounts of product should have been formed by the radical clock pathway. One explanation for the complete lack of products formed through the radical clock pathway is that the

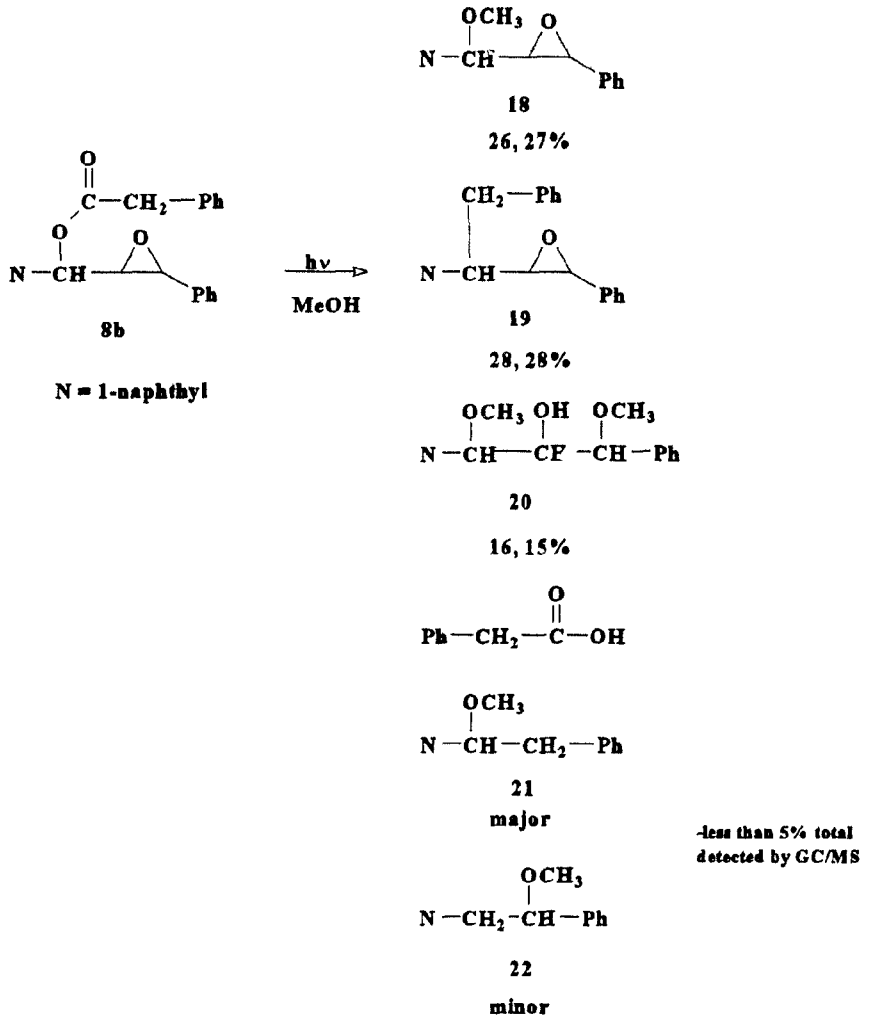
naphthalene ring would have slowed down the ring-opening reaction of the phenyl cyclopropylcarbinyl radical although the amount that this substitution might slow down this rate constant is unknown. Perhaps the rate constant for the ring-opening reaction is no longer competitive with the other possible reactions: electron transfer and decarboxylation.



2.2.4 Photolysis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)

The products and yields of the products for the photolysis of **8b**, are shown in Scheme 19. The two numbers indicate that two separate analytical determinations of product yields were made. The ether, **18**, was identified by comparison with a synthetic sample, whereas **19** and **20**, the coupling product and a secondary photolysis product, were identified and characterized using proton and ^{13}C nmr spectra, and mass spectra. The two minor products, **21** and **22**, were only identified by fragmentation patterns in the GC/MS because they were formed in yields too low for isolation.

Scheme 19 Photolysis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)



The proton nmr spectrum of **18** reveals a mixture of diastereomers. The peaks for each diastereomer are assigned as follows. The doublet at 5.10 ppm with a coupling constant of 3.3 Hz, and the doublet at 4.80 ppm with a coupling constant of 5.5 Hz, are assigned to the naphthylmethyl proton in the first diastereomer and second diastereomer, respectively. The doublets, with a coupling constant of 2.0 Hz, at 4.10 ppm and 3.80 ppm are the

benzyl protons of the epoxide ring, in the first and second diastereomer, respectively. The singlets at 3.39 ppm and 3.80 ppm, integrating for three protons each, are the methoxy protons in the first and second diastereomer, respectively. The doublet of doublets at 3.36 and 3.50 ppm are the other protons of the epoxide, in the first and second diastereomer, respectively.

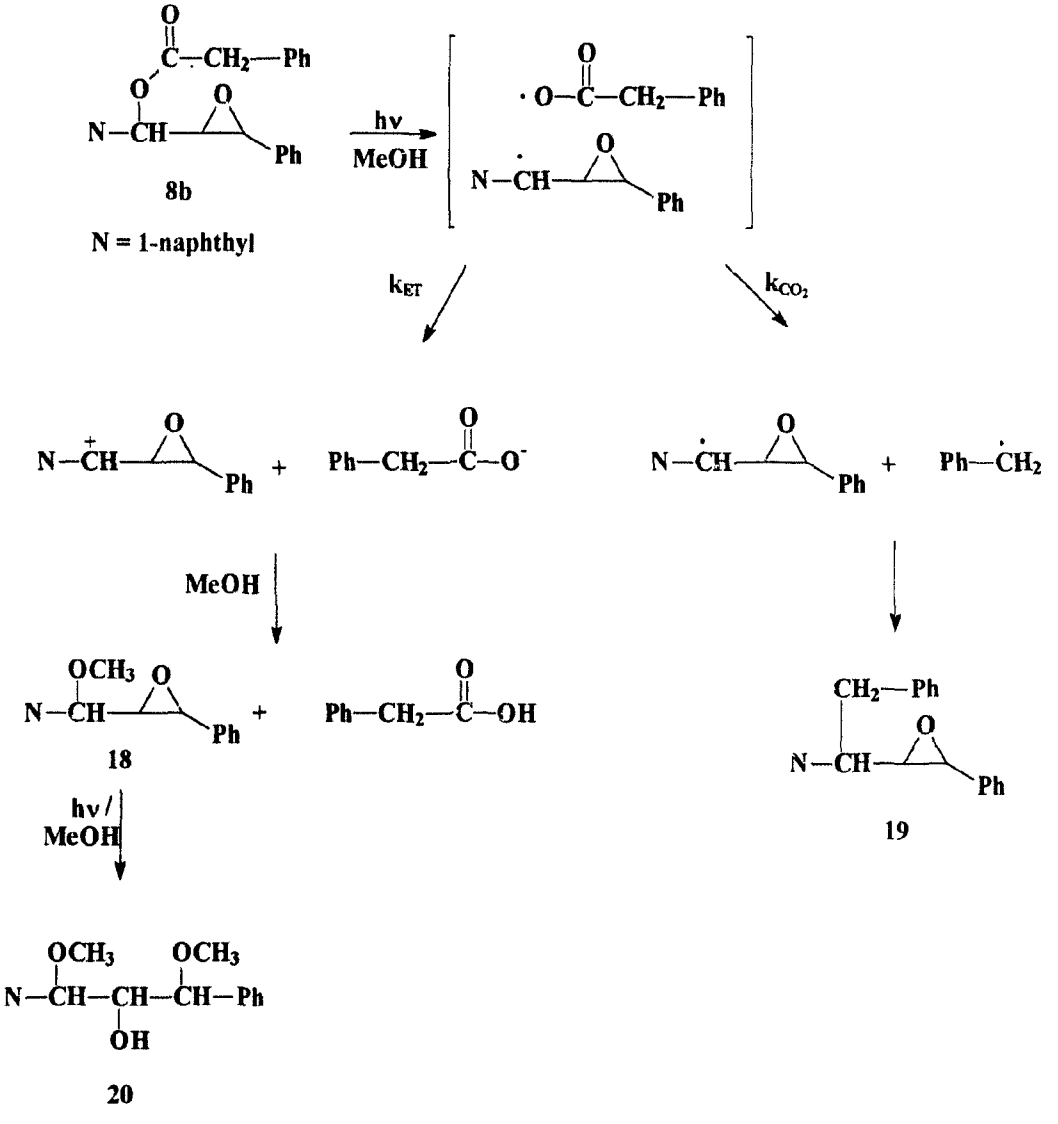
The coupling product, **19**, was isolated from the photolysis mixture as an oil, and gives a characteristic carbon-oxygen stretching frequency for oxiranes of 794 cm^{-1} in the infrared spectrum. The proton nmr spectrum is complex, and other than the aromatic region, shows two multiplets. Proton and ^{13}C nmr spectra, and a mass spectrum were used to identify this product As with the coupling product, **16**, formed in the photolysis of **8a**, this product was assumed to be a coupling product based on a molecular ion of m/z 350 in the mass spectrum. Again, the lack of protons and carbons in the alkene regions of the spectra is used to indicate that this coupling product still has the epoxide ring intact. The presence of two diastereomers is clear, and almost all peaks are assigned. The two diastereomers are identified as the major and the minor products on the basis of the ^{13}C spectrum, but because the proton nmr spectrum does not reveal the ratio of these diastereomers, the relative amount of each diastereomer is not known. The peaks at 65.6 ppm and 65.8 ppm are the benzyl carbon, in the major and minor diastereomer, respectively. The peak at 44.4 ppm is the naphthylmethyl carbons in both diastereomers. This peak shows a shoulder upon expansion, which was not labelled by the nmr spectrometer. The other carbons of the epoxide are at 59.1 ppm and 58.3 ppm, in the major and minor diastereomers, respectively. The methylene benzyl carbon is at 39 6 ppm

and 39.7 ppm, in the major and minor diastereomer, respectively. From this information, the structure of the coupling product was determined

The product, **20**, was identified using a proton nmr spectrum and a mass spectrum. In the proton nmr spectrum, the doublet at 5.40 ppm with a coupling constant of 2.0 Hz is the naphthylmethyl proton. The benzylic proton is the doublet at 4.34 ppm with a coupling constant of 7.9 Hz The multiplet at 3 93 ppm is the proton on the alcohol carbon, and the coupling constants could not be determined. The two singlets at 3 43 ppm and 3 30 ppm are each assigned to methoxy protons, though the similiarity in their environments prevents assigning particular methoxy protons to a particular signal The hydroxyl proton is the broad singlet at 2 00 ppm The mass spectrum of this compound gives a molecular ion at m/z 322

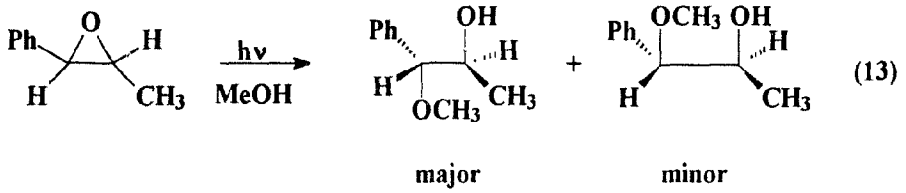
The suggested mechanism for the photochemical reaction of **8b** to form the three major products, **18**, **19**, and **20**, is shown in Scheme 20

Scheme 20 Mechanism of the Photolysis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)



After excitation of **8b** into its singlet excited state, homolytic carbon-oxygen bond cleavage to the radical pair occurs. Then there are three potential reactions: electron transfer, decarboxylation and a ring-opening of the oxiranylcarbinyl radical.

Reaction of methanol with the ion pair, formed by the electron transfer reaction, gives **18** and phenylacetic acid. Decarboxylation of the phenylacetyloxy radical forms the benzylic radical, which then couples with the 1-naphthylmethyl radical to give **19**. The third product, **20**, results from secondary photolysis of the ether, **18**. There is precedence in the literature for photochemical addition of methanol to epoxides.[47] Eq 13 illustrates the direction of addition; the epoxide ring opens to give the more stable cation, and methanol adds to this cation, the benzyl cation. Following the expected pathway for the ring-opening reaction, **18**, also gives the benzyl cation which reacts with methanol to form **20**.



(13)

major **minor**

The two minor products, **21** and **22**, no longer contain the epoxide functional group Although they were detected in the photolysis mixture, they were formed in such low yield that pure samples could not be isolated Their structures are assigned only by fragmentation patterns in the GC/MS. Both isomers have a molecular ion at m/z 262, but the major isomer, **21**, shows a loss of m/z 91, or a benzylic group, as the major fragmentation. The minor isomer, **22**, shows a loss of m/z 141, or the naphthylmethyl

group, as the major fragmentation. The structures of **21** and **22** were determined from this fragmentation. The major isomer, **21**, would be expected to lose a benzyl group, forming the stable naphthylmethyl cation, while the minor isomer, **22**, after losing a naphthylmethyl group, would form the stable benzyl cation. The mechanism for formation of **21** and **22** is not known, but must include a cleavage of the epoxide. In fact, the products look like those expected from photochemical addition of methanol to 1-phenyl-2-(1-naphthyl)ethene. However, which of the two phenyl groups of **8b** gets incorporated into the alkene is neither known nor obvious. They could possibly be formed from **19**. These products are of interest because they may be formed after cleavage of the epoxide ring in the radical intermediate. The low yields of these products prohibits the use of this radical clock to investigate naphthylmethyl ester photochemistry.

As discussed in the Introduction, the literature[20] suggested that the ring-opening reaction of the oxiranylcarbinyl radical would be competitive with the electron transfer and decarboxylation reactions of the 1-naphthylmethyl and phenylacetyloxy radicals. However, more recent results have estimated that the rate constant for the ring-opening reaction of the oxiranylcarbinyl radical to be approximately two orders of magnitude slower than the reverse reaction, ring-closing,[48,49] which may explain the results of the photolysis. The radical clock reaction in this photolysis, the ring-opening reaction of the oxiranylcarbinyl radical, did not lead to any of the major products. Although the recent literature results[48, 49] are applicable in this instance, they are not necessarily the only explanation for the lack of products derived from the ring-opening reaction. In the literature,[48, 49] the measurement for the rate constants of ring-opening and ring-closing of

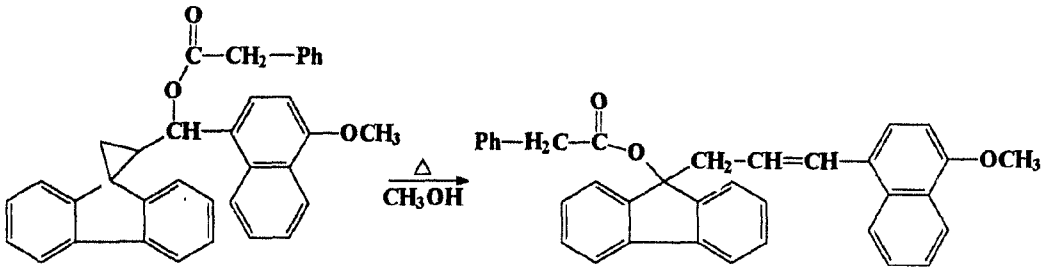
the oxiranylcarbinyl radical are for the ring-opening reaction leading to the oxygen-centred radical. In this photolysis, the oxiranylcarbinyl radical is phenyl-substituted and the radical clock reaction probably opened by homolytic cleavage of the carbon-carbon bond to give the benzyl radical. This is not the same pathway that was considered in the literature studies[48, 49] and the results from those studies may therefore not necessarily apply. An alternative explanation for the lack of products from the ring-opening pathway is that the rate constant for the ring-opening reaction of the phenyl oxiranylcarbinyl radical was not competitive with the rate constants for the electron transfer and decarboxylation reactions.

2.2.5 Photolysis of 1-(4-methoxynaphth-1-yl)-1-spiro[(fluorene-1,9'-cyclopro-2-yl)]methyl phenylacetate (9)

Preliminary photolysis of **9** in methanol, as revealed by HPLC, resulted in many products, four of which are believed to be hydrocarbons based on their long retention times on the reverse phase column. Attempts at isolation and identification of any of these products by chromatography on silica gel were unsuccessful.

In order to understand the reactivity of the expected ion pair for the photolysis in methanol, a ground state solvolysis of **9** was performed. Refluxing **9** in methanol resulted in quantitative conversion to a rearranged ester, **24**, Scheme 21. The first order process, as determined by HPLC, had a half life of 86 minutes.

Scheme 21 Ground State Solvolysis of 1-(4-methoxynaphth-1-yl)-1-spiro[(fluorene-1,9'-cycloprop-2-yl)]methyl phenylacetate (*9*)



9 **24**

The proposed structure of **24**, 3-[3-(9-fluorenyl)-1-(1-[4-methoxynaphthyl])]propenyl phenylacetate, was confirmed by proton and ^{13}C nmr spectra, and a mass spectrum. Infrared spectroscopy confirmed the presence of the ester carbonyl. The assignments in the proton nmr spectrum are as follows. The multiplet at 6.65 ppm, integrating for one hydrogen, is the olefinic hydrogen adjacent to the naphthalene ring. The other alkene proton is the multiplet at 5.75 ppm with coupling constants of 15.9 Hz for the coupling with the other alkene proton, and 7.3 Hz for the coupling with the adjacent methylene protons. The methoxy protons are the singlet at 3.89 ppm. The methylene protons on the carbon attached to the fluorene are the doublet at 3.04 ppm, with a coupling constant of 7.3 Hz, and the other methylene protons are the singlet at 2.86 ppm. In contrast to the starting ester, the absence of an AB doublet of doublets for these protons indicates a symmetric structure.

The ^{13}C nmr assignments are as follows. The methoxy carbon is at 55.5 ppm, the sp^2 carbon adjacent to the naphthalene ring is among the aromatic carbons and is not assigned,

whereas the other sp^2 carbon is at 120.0 ppm. The methylene carbon attached to the fluorene is at 51.6 ppm, and the other methylene carbon is at 44.0 ppm. Carbon 9 of the fluorene is at 88.1 ppm, and the ester carbon is at 177.6 ppm.

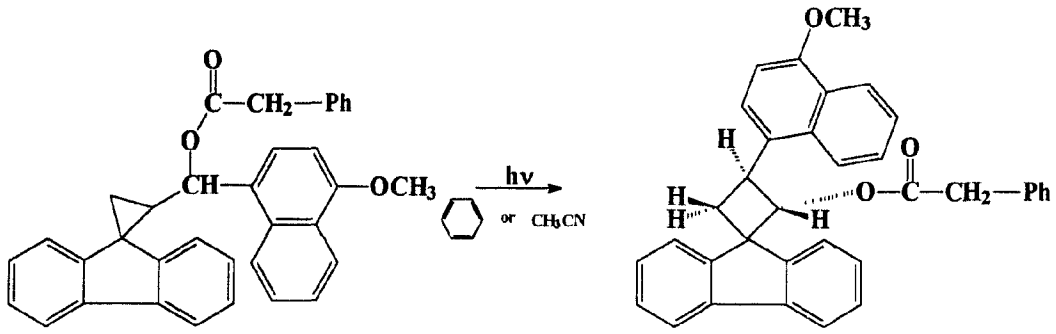
The mass spectrum does not give a molecular ion, but gives a weak signal at m/z 360, and the base peak at m/z 197 The signal at m/z 360 is the molecule after loss of the phenylacetyloxy group, whereas the base peak at m/z 197 is the naphthylpropene part.

The proposed mechanism for formation of **24** in the ground state solvolysis of **9** is through a very tight ion pair because there was no addition of methanol to the cation resulting in ether formation. The possibility that the reaction is concerted through a six-membered transition state was ruled out because the reaction does not occur in either refluxing hexane or acetonitrile

This reaction is in contrast to the ground state solvolysis reaction of **8a**, a compound similar in structure to **9**, which in refluxing methanol gave ethers The reason **9** does not also form ethers is unknown, and further investigation of this reaction is required to understand the mechanism

In order to understand the reactivity of the radical pair in the photolysis in methanol, a photolysis of **9** in benzene was performed, where there should only be products derived from radicals. By HPLC analysis, after 68% disappearance of **9**, one major product, **23**, was formed in about 50% yield (73% based on unreacted starting material), Scheme 22. Silica gel chromatography gave an 18% isolated yield of a pure sample of this compound plus later fractions that were mixtures with the starting ester

Scheme 22 Photolysis of 1-(4-methoxynaphth-1-yl)-1-spiro[(fluorene-1,9'-cycloprop-2-yl)]methyl phenylacetate (9)

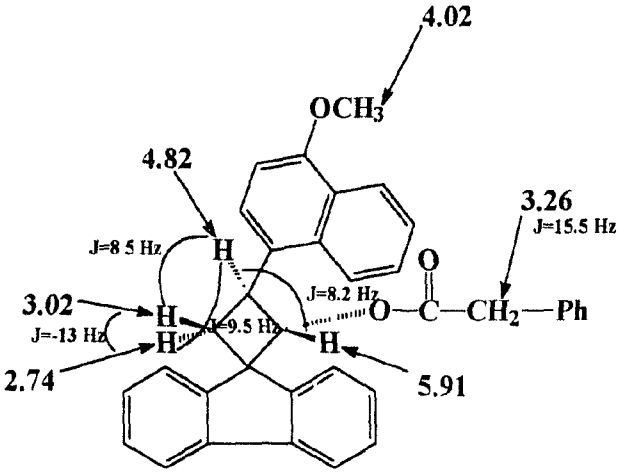


9 23

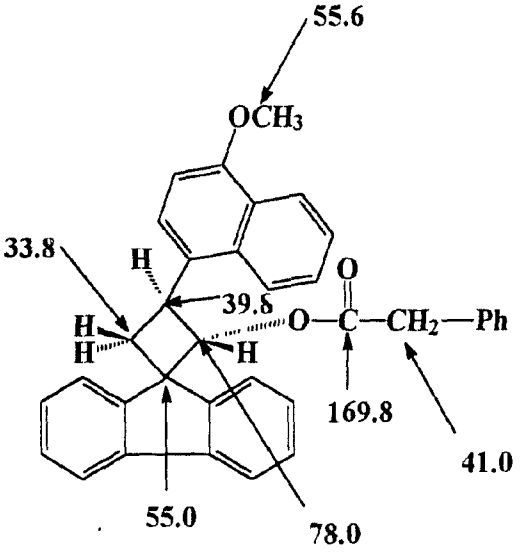
The structure of ester **23** was determined using proton and ^{13}C nmr spectra. A HETCOR experiment proved to be essential to assign the carbon chemical shifts. The assignments and the coupling constants in the proton nmr spectrum are based on a simulation of the spectrum, Figure 6. The methylene protons in the cyclobutane ring are at 3.02 ppm and 2.74 ppm. Although they appear as triplets in the spectrum, they are actually a doublet of doublets, with coupling constants of 8.5 Hz and -13 Hz, and 9 5 Hz and -13 Hz, respectively. This geminal coupling constant (-13 Hz) is too large for cyclopropanes (approximately -5 Hz) but is reasonable for cyclobutanes.[50] The proton on the same carbon of the cyclobutane ring as the 4-methoxynaphthalene ring is the signal at 4.82 ppm, with coupling constants of 8.5 Hz and 9.5 Hz for coupling with the methylene protons, and 8.2 Hz for coupling with the methine proton. The methine proton on the same carbon as the phenylacetyloxy group is at 5.91 ppm. The benzylic methylene protons are a very narrow doublet of doublets at 3.26 ppm with a coupling constant of 15.5 Hz

The methoxy protons are a singlet at 4 02 ppm.

Figure 6 Proton and Carbon NMR Assignments for 23



Proton Assignments



^{13}C Assignments

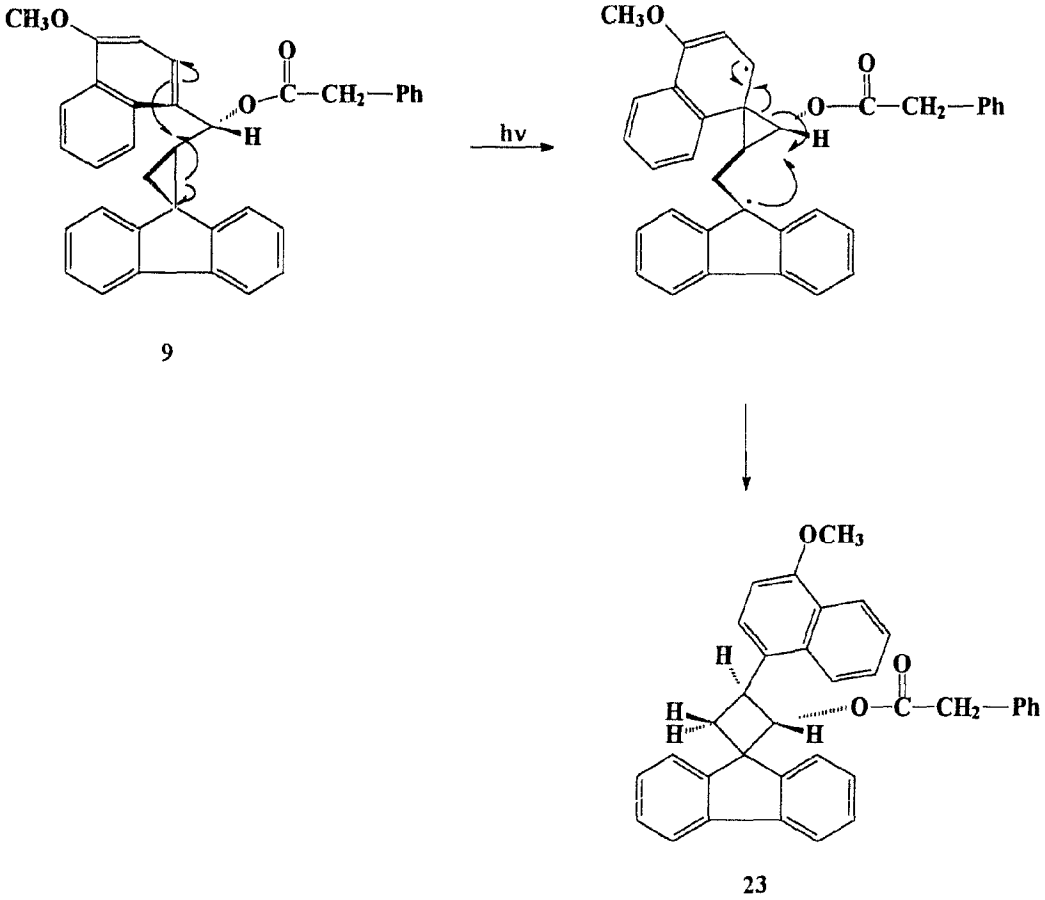
The assignments for the ^{13}C nmr spectrum are based on a HETCOR spectrum and are as follows In the cyclobutane ring, the spiro carbon is at 55 0 ppm, the methylene carbon

is at 33.8 ppm, the carbon with the naphthalene ring is at 39.8 ppm and the other methine carbon is at 78.0 ppm. The benzylic carbon is at 41.0 ppm, the methoxy carbon is at 55.6 ppm and the ester carbon is at 169.8 ppm.

At higher conversions, the yield of **23** drops and this ester slowly converts to a complex mixture of unidentified products. The result was the same for the photolysis of **9** in acetonitrile, although by HPLC analysis the yield of **23** never got as high as in benzene.

The mechanism for this photolysis is in Scheme 23.

Scheme 23 Mechanism for the Formation of 23



9

23

A rearrangement of this type has been considered previously although observed only in yields less than 1%.[50] The rearrangement is just the aromatic equivalent of the cyclopropyl-π-methane rearrangement, and another version of this, namely the di-π-methane rearrangement, is well known to occur photochemically.[51] The initial bond that cleaves homolytically is in a geometrically favourable position to overlap with the

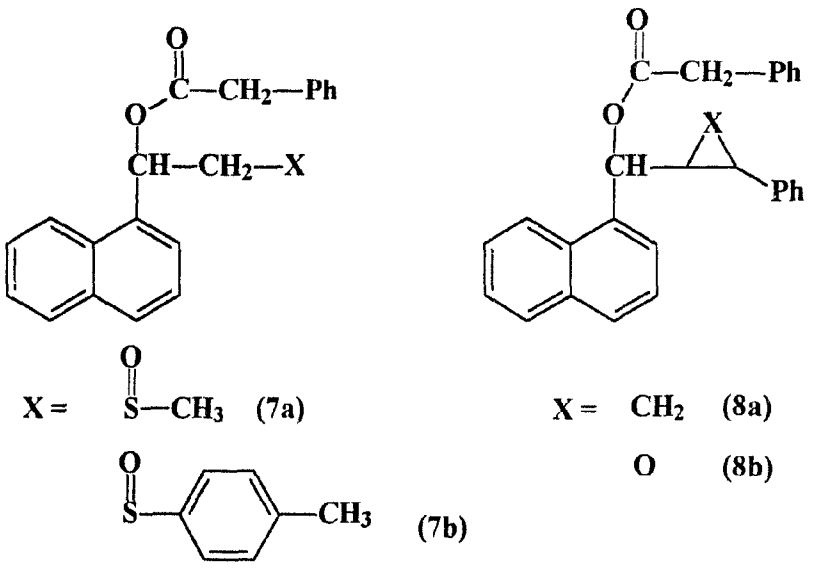
naphthalene ring based on the x-ray crystal structure. If the reaction is concerted, as is observed for the di-π-methane rearrangement, the stereochemistry of the cyclobutane will be *trans* as shown. Of course, this will be the more stable isomer anyway.

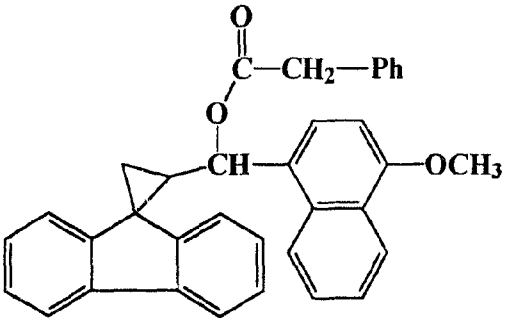
The conclusion from the photolysis of **9** is that it does not react like an arylmethyl ester at all but instead, a rearrangement, the aryl version of the cyclopropyl-π-methane rearrangement, is preferred. This unexpected observation probably results from two features in the x-ray crystal structure of **9**, assuming, as the proton nmr suggests, that the conformation in solution remains the same. First, the chromophore (4-methoxynaphthyl) is perfectly aligned to induce the cyclopropyl ring opening and second, it is very poorly aligned to induce ester cleavage. In the crystal structure, the dihedral angle between the plane of the aromatic ring and the carbon-oxygen bond is only 19°, and overlap will be poor.

3 CONCLUSIONS

The photochemistry of esters **7a,b, 8a,b**, and **9** (Figure 7) was studied in methanol. Although these esters were chosen and synthesized for the purpose of having their radical clock reactions compete with the other reactions occurring in naphthylmethyl ester photochemistry, this did not occur. The reasons for this varied with the ester. Ester **7a** was not suitable as a radical clock because the β-cleavage reaction was too slow to compete with the electron transfer and decarboxylation reactions. Although ester **7b** was predicted to be able to undergo a β-cleavage reaction in competition with the electron transfer and decarboxylation reactions, this did not happen, and instead, a direct photochemical cleavage of the carbon-sulfur bond occurred, making an analysis of the product-yield ratios impossible. The cyclopropylcarbinyl radical formed upon photolysis of **8a** ring-opened too slowly to compete with the electron transfer and decarboxylation reactions. Ester **8b**, after photolysis, did not undergo the ring-opening reaction of the oxiranylcarbinyl radical because the ring-opening reaction is reversible, as indicated by recent literature. Finally, **9** was not suitable as a radical clock because it did not react as a naphthylmethyl ester, and instead, reacted in a cyclopropyl-π-methane rearrangement.

Figure 7 Naphthylmethyl Esters That Were Studied





9

There is some evidence for the proposed mechanism of homolytic cleavage followed by electron transfer, by both independent measurements and direct picosecond laser sighting Recently, the carbon-oxygen bond cleavage in decarboxylation reactions has been observed.[52] Kochi *et al.* determined rate constants for decarboxylation reactions of acyloxy radicals, and their values agreed with those determined by Hilborn and Pincock [31] A recent picosecond kinetic study by Peters *et al.*[53,54] on the photoinduced homolysis and

heterolysis of diphenylmethylchloride also provided further evidence for the proposed mechanism. Both homolytic and heterolytic cleavage occurred in the case of diphenylmethylchlorides As well, the radical pair undergoes electron transfer to form the ion pair. With more advances and further development of radical clocks, there is a possibility of confirming this mechanism, and then perhaps applying this technique to other systems.

4 EXPERIMENTAL

4.' General Experimental

Melting points were determined on a Fisher-Johns Melting Point Apparatus and are uncorrected. Wavelength maxima (λ_{max}) are reported in nanometers. Proton (^1H) and carbon-13 (^{13}C) nuclear magnetic resonance (NMR) spectra were obtained in $CDCl_3$ on an AC 250 F NMR spectrometer in automation mode or on an AMX 400 NMR spectrometer. Some proton and carbon-13 NMR spectra were obtained in $CDCl_3$ on a Varian Gemini 200 as indicated. Chemical shifts are reported in parts per million (δ) relative to tetramethylsilane (0.00) as an internal standard. Multiplicities are abbreviated as follows: s=singlet, d=doublet, dd=doublet of doublets, ddd=doublet of doublet of doublets, t=triplet, q=quartet, m=multiplet.

Infrared spectra were obtained on a Nicolet 205 FTIR spectrophotometer and frequencies are reported in wavenumbers (cm^{-1}).

GC/MS analyses were done on a Hewlett Packard 5890 A GC 5970 with a mass selective detector. The column used was a 25-m x 0.2-mm 5% phenylmethyl silicone on fused silica with a film thickness of 0.25 μm. Masses are reported in units of mass over charge (m/z). Intensities are reported as a percent of the base peak intensity. The molecular ion is indicated by M^+.

HPLC analyses were done using a Waters 6000 solvent delivery system with a Waters U6K injector under isocratic conditions with a flow rate of 2 mL/min using a Brownlee Lab Spheri-10 10 μm reverse-phase column (25 x 0.46 cm) with a Waters Model 450 variable wavelength detector. UV detection for monitoring reactions was at 280 nm.

Combustion analyses were carried out by Canadian Microanalytical Service Ltd., Delta, B C., Canada.

Silica gel T-6145 plates from Sigma were used for thin layer chromatography (tlc) Silica gel 60Å (70-230 mesh), purchased from the Aldrich Chemical Co., was used for normal chromatography.

Accurate mass measurements were done by Dr. L. Ramaley on [1-(1-naphthyl)-1-(2-phenylcyclopropyl]methyl phenylacetate, **8a** and 2-phenyl-1-cyclopropyl(1-naphthyl)methyl methyl ether, **14**

Mass Spectra were done by Dr J H. Kim, Dalhousie University on a CEC 21-104 single focussing or a CEC 21-110B double focussing mass spectrometer run at 70 eV

The following compounds were purchased from the Aldrich Chemical Company: acetonaphthone, acrolein, benzaldehyde, N,N-carbonyldimidazole, *m*-chloroperbenzoic acid, dibromoethane, fluorenone hydrazone, magnesium metal, mercuric oxide (yellow), 1-methoxynaphthalene, methyl iodide, phenylacetic acid, phenylacetyl chloride, sodium borohydride, sodium hydride.

THF, previously dried from phosphorus pentoxide, was refluxed over sodium with benzophenone until the blue colour of the ketyl radical anion developed, before being distilled.

4.2 Syntheses

4.2.1 Synthesis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)

This was reported previously [37]

4.2.2 Synthesis of 2-(4-tolylsulfinyl)-1-(1-naphthyl)ethyl phenylacetate (7b)

This was reported previously.[37]

4.2.3 Synthesis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)

Trimethylsulfoxonium iodide was available in our laboratory. The ^{1}H nmr and necessary spectroscopic data of the compounds below has been previously described.[39]

To a solution of potassium hydroxide (16.64 g, 0.297 mol) in water (110 mL) was added ethanol (100 mL). The resulting solution was cooled and 1-acetonaphthone (53.6 mL, 0.357 mol) was added with stirring. While keeping the solution at room temperature, benzaldehyde (38 mL, 0.374 mol) was added. The reaction mixture was stirred at room temperature for one hour, and then stored for three hours at 0 °C. The oil which resulted was extracted from the aqueous solution with dichloromethane. The organic layer was washed with 10% HCl and water, then dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure, and the α,β-unsaturated ketone was fractionally distilled: yield 80.12 g (87%). The ^{1}H nmr was the same as that previously reported.[55]

The α,β-unsaturated ketone was cyclopropanated according to the procedure of Prestwich *et al.*[40] To a stirring solution of sodium hydride (56% in mineral oil) (3.25 g, 76 mmol) and trimethylsulfoxonium iodide (17.55 g, 80 mmol) in DMSO (75 mL) under nitrogen gas at 0 °C was added 1-naphthyl-3-phenylpropenone (15.36 g, 60 mmol) in DMSO (75 mL). The reaction was stirred under nitrogen for a further 16 hours at room temperature. The resulting reaction mixture was poured into water (100 mL), and extracted with ether (3 x 100 mL). The organic layers were combined, and washed with

brine and water The impure cyclopropyl ketone was isolated by drying the organic layer over anhydrous magnesium sulfate and removing the solvent under reduced pressure The ketone was purified by recrystallization from 100% ethanol yield 6 96 g (43%) The ^{1}H nmr was identical with that described previously [39] The cyclopropyl ketone was sufficiently pure to use in the next step

The cyclopropyl ketone was reduced according to the procedure of Murphy *et al* [56] To a solution of cyclopropyl ketone (9 57 g, 35 mmol) in methanol was added sodium borohydride (2 89 g, 70 mmol) in small portions After stirring the solution for one hour the solvent was removed under reduced pressure Ethyl acetate (25 mL) was added, and the organic layer was washed with water (2 x 25 mL) The solvent was dried over anhydrous magnesium sulfate, and rotoevaporated to give the crude alcohol as a pale yellow oil yield 10 8 g, ^{1}H nmr ($CDCl_3$) δ 8 1 - 7 0 (m, 12H), 5 06 (d, 1H), 2 36 (bs, 1H), 2 0 - 1 9 (m, 1H), 1 8 - 1 65 (m, 1H), 1 15 - 0 86 (m, 2H), ^{13}C nmr ($CDCl_3$) δ 142 4, 138 4, 133 9, 131 2, 128 8, 128 4, 126 1, 125 9, 125 6, 125 4, 123 9, 73 6, 29 4, 22 0, 14 0 The ^{1}H nmr was the same as that reported previously[39] for a chromatographed sample The alcohol was sufficiently pure to use in the esterification step

The ester was prepared using N,N-carbonyldiimidazole, phenylacetic acid and the cyclopropanated alcohol as described previously,[40] to give a pale yellow oil ^{1}H nmr ($CDCl_3$) δ 8 11 - 6 80 (m, 17H), 6 20 (d, 1H, J=8 2 Hz), 3 50 (s, 2H), 2 08 -2 04 (m, 1H), 1 80 - 1 75 (m, 1H), 0 93 - 0 83 (m, 2H), ^{13}C nmr ($CDCl_3$) δ 171 3, 142 1, 141 9, 135 3, 135 2, 134 3, 134 2, 131 1, 129 5, 129 1, 128 8, 128 6, 127 3, 126 6, 126 4, 126 1, 126 0, 125 5, 125 4, 125 0. 124 1, 123 8, 75 6, 53 7, 41 9, 27 8, 27 1, 23 1, 21 5, 14 5, 13 4, MS

392 (2, M^+), 288 (28), 257 (13), 256 (51), 171 (14), 170 (100), 167 (13), 165 (18), 152 (11), 141 (16), 91 (95); Accurate mass calcd for $C_{28}H_{24}O_2$· 392 1776, found 392 1804 Elemental analysis was not possible because the sample decomposed upon distillation

4.2.4 Synthesis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)

The procedure for the synthesis of the alcohol and the epoxy alcohol was that by Murphy *et al.*[56] The alcohol, 1-(1-naphthyl)-2-phenyl-1-prop-2-enol, was synthesized using the same method described in the synthesis of the cyclopropane ester, **8a** Yield 4.53 g, ^{1}H nmr ($CDCl_3$) δ 8 2-7 2 (m, 12H), 6.75 (d, 1H), 6 5 (dd, 1H), 6.0 (m, 1H), 2.9 (s, 1H). The ^{1}H nmr revealed the alcohol to be sufficiently pure to continue with the synthesis

A solution of *m*-chloroperbenzoic acid (57-86%) (7 44 g, 25 mmol) in dichloromethane (40 mL) was slowly added to a stirring solution of the alcohol (4 53 g, 17 mmol) in dichloromethane (30 mL). After stirring for three hours, the solution was washed with aqueous sodium sulphite (3 x 20 mL), saturated sodium bicarbonate (3 x 20 mL) and saturated sodium chloride solution (20 mL) The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed under reduced pressure The impure epoxy alcohol was chromatographed using 10 90 ethyl acetate hexane The epoxy alcohol, as a mixture of diastereomers, was isolated as a pale yellow oil yield 2.84 g (59%); ^{1}H nmr ($CDCl_3$) δ 8 1-7 1 (m, 12H), 5.7 (d, 1H), 5 4 (d, 1H), 4 1-4.0 (m, 1H), 3 5-3.4 (m, 1H), 3.1 (bs, 1H). The ^{1}H nmr spectrum showed the compound was sufficiently pure to continue to the next step.

To a stirring solution of the epoxy alcohol (2 84 g, 10 mmol) in benzene (50 mL) and

pyridine (1 mL) was added phenylacetyl chloride (1 73 g, 11 mmol) in benzene (10 mL) After stirring the reaction mixture overnight, water was added to destroy any excess acid chloride The organic layer was washed with 10% HCl solution (30 mL), 5% NaOH solution (30 mL) and water (30 mL), dried over anhydrous magnesium sulfate and rotoevaporated to dryness. The resulting ester was isolated as a colourless solid. yield 1 91 g (48%) Recrystallization from methanol water gave the ester, approximately 3 1 mixture of diastereomers, IR (neat) 1746 (C=O), 1142 (C-O) cm^{-1}, ^{1}H nmr ($CDCl_3$) δ (major) 8 2-7 1 (m, 17H, aromatic), 6 6 (d, 1H, N-CH), 3 84-3 77 (m, 3H), 3 55 (dd, 1H, J=1 5 Hz, N-CH-CH), (minor) 6 8 (d, 1H, N-CH), 3 46 (dd, 1H, N-CH-CH); ^{13}C nmr ($CDCl_3$) δ 170.5, 136 0, 133 8, 132 3, 129 4, 128 9, 128 6, 128 4, 127 2, 126 6, 125.9, 125 6, 125 2, 123 3, 73 0 (N-CH), 63 2 (CH-Ph), 56 9 (CH-CH-N), 41 4 (CH_2), MS 394 (6), 275 (28), 258 (12), 171 (22), 170 (50), 169 (11), 157 (14), 155 (14), 153 (13), 152 (14), 120 (12), 92 (10), 91 (100) Anal calcd for $C_{27}H_{22}O_3$ C, 82 21, H, 5 62 Found C, 81 92; H, 5 52

4.2.5 Synthesis of 1-(4-methoxynaphth-1-yl)-1-spiro[fluorene-1,9'-cycloprop-2-yl]methyl phenylacetate (9)

The procedure of Schoberg *et. al*[42] was used for the synthesis of 9-diazofluorene A mixture of fluorenone hydrazone (25g, 0 13 mol), mercuric oxide (43 75g, 0 20 mol) and anhydrous sodium sulfate (12 5 g, 8 8 x 10^{-2} mol) were ground together with a mortar and pestal, and then suspended in ether (200 mL) in a stoppered flask Approximately 1 mL of a concentrated solution of potassium hydroxide in ethanol, which had been freshly prepared, was added This suspension was then shaken on a wrist shaker for 35 minutes,

the solution was filtered, the solid particles washed with ether, and the solvent was removed under reduced pressure. Yield: 18.50 g (74%), mp 94 - 97 °C The melting point was the same as that reported in the synthetic reference.

The spirocyclopropylfluorenyl aldehyde was synthesized, with minor alterations, according to the procedure of Martin-Esker *et al.*[6] To a stirring solution of acrolein (350 mL) at 0°C was added 9-diazofluorene(35.00g, 0.208 mol) in one portion. After 15 minutes at 0°C, the solution was allowed to warm to room temperature. The excess acrolein was removed under reduced pressure. Some of the acrolein polymerized, and the resulting polymer was rinsed with dichloromethane to remove the aldehyde. The intermediate pyrazoline was then refluxed overnight in benzene. After removal of the benzene at reduced pressure, the aldehyde was chromatographed using 5:95 ethyl acetate:hexane. The aldehyde was a pale yellow oil: yield (19.90 g, 49%); ^{1}H nmr ($CDCl_3$) (Varian) δ 9.69 (d, 1H, J=4.2 Hz), 7 86-7.80 (m, 2H), 7.45-7.10 (m, 5H), 7 09-7.06 (m, 1H), 2.94-2.84 (td, 1H, J=4.0 Hz, J=7.5 Hz), 2.67-2.61 (dd, 1H, J=5 4 Hz, J=7.4 Hz), 2.31-2.24 (dd, 1H, J=5.5 Hz, J=8.2 Hz); ^{13}C nmr ($CDCl_3$) (Varian) δ 197 8, 146.2, 142.4, 141.5, 140.4, 127.9, 127.9, 127.5, 123.2, 120.8, 120.5, 119.3, 112.8, 40.7, 40.0, 20.9. The resulting aldehyde was sufficiently pure to be used in the Grignard reaction.

The alcohol was synthesized according to the procedure of Dickinson *et al.*[80] To a suspension of magnesium metal (0.63g, 26 mmol) in THF was added dibromoethane (0.15 g, 0.8 mmol) and a small amount of 1-bromo-4-methoxynaphthalene. Once the reaction started, the remainder of the 1-bromo-4-methoxynaphthalene was added dropwise. (Total 4.08 g, 16 mmol) The solution was then refluxed for 1 hour, and

then stirred at room temperature for 1 hour. To this stirring solution was then added spiro[2-(formaldehyde)cyclopropane-1,9'-fluorene] (0.868 g, 3.9 mmol) at 0°C. This solution was then stirred at 0°C for one hour, and then stirred overnight at room temperature. Saturated ammonium chloride solution was added to quench the reaction mixture. The aqueous solution was extracted with diethyl ether, and the organic layer was washed with water. After drying the ether layer with anhydrous magnesium sulfate, and filtering, the solvent was removed under reduced pressure. This mixture of alcohol diastereomers were chromatographed with 5:95 ethyl acetate:hexane to give the isolated diastereomers of the alcohol as green oils: Yield 0.923 g (63%); (major fraction of alcohol) ^{1}H nmr ($CDCl_3$) δ 8.39 - 8.33 (m, 2H), 7.96 - 7.86 (m, 2H), 7.71 - 7.25 (m, 8H), 7.03 (d, 1H, J=7.6 Hz), 6.86 (d, 1H, J=7.9 Hz), 5.65 (d, 1H, J=10.1 Hz), 4.04 (s, 3H), 2.73-2.62 (m, 1H), 2.04-1.93 (m, 2H), 1.70 (b.s., 1H); ^{13}C nmr ($CDCl_3$) δ 155.5, 148.1, 144.0, 141.4, 139.1, 131.9, 130.3, 127.2, 127.0, 126.78, 126.76, 126.3, 126.1, 125.1, 124.5, 123.8, 122.8, 121.1, 120.7, 120.0, 118.6, 103.2, 71.5, 55.6, 39.4, 34.8, 23.0; (minor fraction of alcohol) ^{1}H nmr ($CDCl_3$) δ 8.23-8.16 (m, 1H), 8.09-8.05 (m, 1H), 7.81-7.77 (m, 2H), 7.46-7.18 (m, 7H), 7.09-7.02 (m, 2H), 6.47 (d, 1H, J=8.0 Hz), 5.49 (d, 1H, J=7 Hz), 3.85 (s, 3H), 2.62-2.52 (m, 1H), 2.30-2.25 (m, 1H), 2.19-2.14 (m, 2H); ^{13}C nmr ($CDCl_3$) δ 155.3, 148.0, 144.3, 141.0, 139.4, 131.6, 131.1, 127.0, 126.6, 126.5, 126.2, 126.1, 125.0, 124.0, 123.8, 122.5, 121.8, 120.1, 119.7, 118.6, 102.8, 70.8, 55.4, 36.7, 35.4, 21.8. The alcohol was sufficiently pure to continue on to the next step.

To a stirring solution of the alcohol (major diastereomer) (2.95 g, 7.8 mmol) and

pyridine in benzene was added phenylacetyl chloride (1.1 mL, 8.6 mmol) in benzene dropwise. After stirring for 6 hours, water was added to destroy any excess acid chloride. The organic layer was washed with 5% HCl, 10% NaOH and water. The solution was dried over anhydrous magnesium sulfate, and the solvent was removed under reduced pressure. The resulting crude ester was chromatographed using 10% ethyl acetate: hexane: yield 3.0 g (80%); ^{1}H nmr ($CDCl_3$) 8.40-8.25 (m), 7.92 (t), 7.58-7.29 (m), 7.11-6.96 (m), 6.83-6.69 (m), 6.52 (d, 1H, J=10.4 Hz), 4.03 (s, 3H), 3.14 (s, 1H), 3.13 (s, 1H), 2.70 (m, 1H), 1.97 (dd, 2H); ^{13}C nmr ($CDCl_3$) δ 170.2, 155.8, 147.9, 143.9, 140.9, 131.4, 129.1, 128.3, 128.2, 127.0, 127.0, 126.8, 126.6, 126.5, 126.3, 126.1, 125.9, 125.2, 123.8, 122.9, 121.2, 120.3, 119.9, 118.6, 103.3, 75.7, 55.6, 40.7, 36.1, 35.1, 22.7; MS 360 ($M^{\cdot+}$ - 136), 136 (19), 92 (14), 91 (100), 65 (13). There was no molecular ion, but loss of 136 was phenyl acetic acid.

4.2.6 Synthesis of 1-bromo-4-methoxynaphthalene

The synthesis of 1-bromo-4-methoxynaphthalene was done according to the procedure of Konishi *et al.*[57] To a solution of 1-methoxynaphthalene (50 g, 0.316 mol) in CCl_4 was added N-bromosuccinimide (67.75 g, 0.381 mol) and silica gel (181.16 g). After stirring for two hours at room temperature, the mixture was filtered to remove any insoluble particles, and the organic layer was washed with aqueous sodium thiosulfate. The organic layer was dried over anhydrous magnesium sulfate, and rotoevaporated to remove the solvent. The impure 1-bromo-4-methoxynaphthalene was distilled at reduced pressure to give: Yield (54.4 g, 73 %). The ^{1}H NMR was the same as that reported in the synthetic reference.

4.2.7 General Synthesis of Ethers

To a stirred solution of the alcohol (15 mmol) in dimethylsulfoxide (15 mL) was added sodium hydride (57% by weight in mineral oil) (25 mmol) under nitrogen gas. After stirring for one hour, methyl iodide (50 mmol) in DMSO (10 mL) was added. After stirring for an additional hour, the reaction mixture was poured into water (10 mL), and the product was extracted with dichloromethane (15 mL). The organic layer was then washed with water and brine solution several times to remove any excess DMSO. The solvent was dried over anhydrous magnesium sulfate and then removed under reduced pressure. The resulting ethers were purified using column chromatography with ethyl acetate:hexane as eluant. The spectra of these compounds are described later.

4.3 Photolyses

4.3.1 Preparative Photolysis of 2-methylsulfinyl-1-(1-naphthyl)ethyl phenylacetate (7a)

The photolysis of this compound was done using 1.97 grams.

Methyl 2-methoxy-2-(1-naphthyl)ethyl sulfoxide (12)

Yield 0.095 g (6%); IR (neat) 1100 (C-O), 1040 (C-O), 782 (SO) cm^{-1}; ^1H nmr ($CDCl_3$) δ 8.2-7.5 (m, 7H), 5.5 (dd, 1H), 3.4 (s, 3H, OCH_3), 3.1-3.09 (m, 2H), 2.6 (s, 3H, $CH_3(SO)$); ^{13}C nmr ($CDCl_3$) δ 134.7, 134.0, 130.5, 129.1, 128.8, 126.7, 125.9, 125.5, 123.8, 122.7, 74.6, 62.9, 57.4, 39.4; MS 248 (6, M^+),185 (14), 184 (66), 183 (13), 171 (29), 155 (10), 154 (20), 153 (100), 152 (16), 141 (27), 128 (11), 127 (11). An independently synthesized sample of this ether showed an identical ^1H

nmr spectrum.

Methyl 2-(1-naphthyl)-3-phenylpropyl sulfoxide (11)

Yield 0.076 g (4%); ^{1}H nmr ($CDCl_3$) δ 8.14 (d, 1H), 7.85-7.73 (m, 2H), 7.53-7.04 (m, 9H), 4.44 (m, 1H), 3 38-3.20 (m, 3H), 3.02 (m, 1H), 2.42 (s, 3H, CH_3(SO)); ^{13}C nmr ($CDCl_3$) δ 138.4, 137.6, 134.0, 131.1, 129.3, 129.0, 128.6, 128.2, 127.7, 126.44, 126.38, 126.0, 125.7, 125.1, 124.2, 122.6, 60.1 (CH_2(SO)), 40.4 (CH_2Ph), 38.9 (CH_3), 35.2 (CH); MS 308 (13, M^+), 245 (23), 244 (81), 167 (14), 154 (56), 153 (100), 152 (33), 141 (12), 117 (15), 115 (11), 91 (88), 43 (16).

4.3.2 Preparative Photolysis of [1-(1-naphthyl)-1-(2-phenylcyclopropyl)]methyl phenylacetate (8a)

2-phenyl-1-cyclopropyl(1-naphthyl)methyl methyl ether (14)

(mixture of diastereomers 24:66) ^{1}H nmr ($CDCl_3$) δ 8.35-7.00 (m), 4.70 (d), 4.58 (d), 3.30 (s), 1.97-1.94 (m), 1.79-1.78 (m), 1.10-1.00 (m), 0.94-0.87 (m); ^{13}C nmr ($CDCl_3$) δ 142.5, 136.3, 134.0, 131.5, 128.9, 128.3, 126.0, 126.0, 125.6, 125.4, 125.0, 124.8, 124.1, 124.0; major 84.2, 56.9, 28.3, 22.8, 12.8 (CH_2); minor 83.3, 56.7, 28.1, 20.9, 14.4 (CH_2); MS 288 (1, $M^{\cdot+}$), 185 (14), 184 (100), 171 (12), 141 (16), 134 (25), 128 (11); Accurate mass calcd for $C_{21}H_{20}O$: 288.1514; found 288.1513.

1-(1-naphthyl)-1-(2-phenylcyclopropyl)-2-phenylethane (16)

(mixture of diastereomers) ^{1}H nmr ($CDCl_3$) δ 8.13-6.83 (m), 3.41-2.90 (m), 1.54 (m), 1.27 (s), 1.07-1.00 (m), 0.94-0.86 (m), 0.75-0.65 (m); ^{13}C nmr ($CDCl_3$) δ 143.2, 140.7, 140.4, 140.3, 140.2, 134.0, 131.9, 129.6, 129.4, 129.1, 128.2, 128.1, 128.0,

126.9, 126.8, 126.0, 125.7, 125.6, 125.4, 124.7, 124.5, 123.2, 46.6, 43.4, 43.2, 29.8, 28.8, 27.4, 25.0, 21.9, 17.1, 14.4; MS 348 (0.2, $M^{\cdot+}$), 334 (25), 244 (17), 243 (75), 230 (11), 203 (11), 168 (32), 166 (27), 153 (10), 152 (16), 151 (33), 140 (12), 139 (43), 138 (12), 127 (32), 115 (20), 77 (100).

4-methoxy-1-(1-naphthyl)-4-phenyl-1-butene (15)

^{1}H nmr ($CDCl_3$) δ 7.72-6.94 (m, 13H), 6.12-6.00 (m, 1H), 4.20 (t, 1H), 3.17 (s, 3H), 2.81-2.52 (m, 2H); ^{13}C nmr ($CDCl_3$) δ 141.7, 135.5, 133.6, 131.1, 129.7, 129.6, 128.5, 128.4, 127.7, 127.5, 126.9, 125.8, 125.7, 124.1, 123.7, 84.0, 56.8, 42.1; MS 288 (3, $M^{\cdot+}$), 181 (12), 171 (13), 165 (23), 152 (12), 128 (13), 127 (12), 121 (100), 105 (11), 91 (35), 77 (15).

4.3.3 Preparative Photolysis of [1-(1-naphthyl)-1-(2-phenyloxiranyl)]methyl phenylacetate (8b)

Photolysis was done using 1.65 g.

1,3-dimethoxy-1-(1-naphthyl)-3-phenyl-2-propanol (20)

Yield 0.11 g (9%); ^{1}H nmr ($CDCl_3$) δ 8.1-7.2 (m, 12H, aromatic), 5.4 (d, 1H, J=2.0 Hz, N-CH), 4.34 (d, 1 H, J=7.9 Hz, CH-Ph), 3.93 (m, 1H, J=7.9 Hz, CH-OH), 3.43 (s, 3H, OCH_3), 3.3 (s, 3H, OCH_3), 2.0 (br.s, 1H, OH); ^{13}C nmr ($CDCl_3$) δ 139.2, 134.2, 134.0,131.1, 129.0, 128.3, 128.1, 128.07, 128.04, 126.1, 125.5, 125.4, 124.6, 122.9, 83.9, 78.3, 76.6, 57.7, 56.9; MS 322 (5, M^+), 172 (63), 171 (100), 141 (10), 128 (13), 122 (11), 121 (35).

1-(1-naphthylmethoxymethyl)-2-phenyloxirane (18)

Yield 0.28 g (23%); ^{1}H nmr ($CDCl_3$) (1st diastereomer) 8.3-7.1 (m, 12H,

aromatic), 5.1 (d, 1H, J=3.3 Hz), 4.1 (d, 1H, J=1.9 Hz), 3.39 (s, 3H), 3.36 (dd, 1H, J=3.3 Hz, J=2.1 Hz); (2nd diastereomer) 8.3-7.1 (m, 12H), 4.8 (d, 1H, J=5.5 Hz), 3.8 (d, 1H, J=2.0 Hz), 3.42 (s, 3H), 3.5 (dd, 1H, J=5.5 Hz, J=2.1 Hz); ^{13}C ($CDCl_3$) δ 137.0, 136.7, 134.1, 134.0, 133.6, 131.4, 129.1, 129.0, 128.5, 128.2, 126.4, 125.8, 125.7, 125.6, 125.5, 125.46, 123.7, 123.5, 82.0, 80.1, 64.8, 64.3, 57.6, 57.2, 56.5, 56.4; MS 290 (5, M^+), 199 (18), 186 (12), 184 (11), 172 (13), 171 (100), 141 (12), 128 (16). The ^1H nmr spectrum of the independently synthesized ether was found to be identical to that of the photoproduct.

1-(1-(1-naphthyl)-2-phenylethyl)-2-phenyloxirane (19)

Yield 0.096 g (7%); IR (neat) 1598, 1495, 1455 (aromatic), 794 (C-O) cm^{-1}; ^1H nmr ($CDCl_3$) δ 8.1-6.9 (m), 3.9-3.8 (m), 3.4-3.1 (m); ^{13}C nmr ($CDCl_3$) δ (major) 139.8, 137.4, 137.2, 134.0, 132.0, 129.2, 129.0, 128.6, 128.2, 127.9, 127.5, 125.54, 125.45, 123.1, 65.6(CH-Ph), 59.1(*C*H-CH-N), 44.4(N-CH), 39.6(CH_2); (minor) 139.0, 137.1, 137.0,133.9, 131.7, 129.3, 128.1, 128.0,127.4, 126.4, 126.2, 126.14, 126.12, 125.6, 125.03, 124.8, 124.2, 123.0, 65.8 (CH-Ph), 58.3(*C*H-CH-N), 44.4 (N-CH), 39.7(CH_2). Accounting for all the methine aromatic carbons in the two diastereomers was not possible because some peaks were coincident. As well, the signal at δ 44.4 showed a shoulder upon expansion indicating two peaks but the instrument did not assign a chemical shift to this shoulder. MS 350 (9, M^+), 259 (34), 241 (12), 231 (11), 229 (10), 217 (13), 171 (24), 156 (13), 155 (23), 154 (14), 153 (100), 152 (40), 151 (10), 141 (13), 128 (22), 127 (26), 121 (60), 115 (13), 105 (11), 91 (51), 77 (23). The following two products represent less than 5% of the total mass

isolated and the composition of the mixture of etners is indicated as minor and major. Thes. products were not separated from each other.

1-naphthyl-2-phenylethyl methyl ether (21)

(major) GC/MS 262 (0.3, M^+), 172 (13), 171 (100), 128 (24), 127 (12).

2-naphthyl-1-phenylethyl methyl ether (22)

(minor) GC/MS 262 (2, M^+), 121 (100), 91 (10), 77 (14).

MS (of both isomers) 262 (4), 172 (14), 171 (100), 128 (15), 121 (33).

4.3.4 Preparative Photolysis of 1-(4-methoxynaphth-1-yl)-1-spiro[fluorene-1,9'-cycloprop-2-yl]methyl phenylacetate (9)

3-(4-methoxy-1-naphthyl)-2-phenylacetate-spiro(fluorene-1,9'-cyclobut-2-ane) (23)

^{1}H nmr ($CDCl_3$) δ 8.37 - 6.70 (m, 19H), 5.91 (d, 1H, J=8.2 Hz), 4.82 (m, 1H, J=8.2 Hz, J=8.5 Hz, J=9.5 Hz), 4.02 (s, 3H), 3.26 (dd, 2H, J=15.5 Hz), 3.02 (m, 1H, J=8.5 Hz, J=-13 Hz), 2.74 (m, 1H, J=9.5 Hz, J=-13 Hz); ^{13}C nmr ($CDCl_3$) δ 169.8, 154.8, 149.0, 145.6, 141.4, 139.6, 133.6, 132.5, 129.3, 129.2, 128.5, 127.8, 127.7, 127.1, 126.9, 126.7, 126.1, 125.3, 124.7, 123.8, 122.9, 122.8, 120.1, 119.7, 103.3, 78.0, 55.6, 55.0, 41.0, 40.0, 33.9.

4.3.5 Ground State Solvolysis of 1-(4-methoxynaphth-1-yl)-1-spiro[fluorene-1,9'-cycloprop-2-yl]methyl phenylacetate (9)

9-fluorenyl-3-(1-[4-methoxynaphthyl])-2-propene phenylacetate (24)

^{1}H nmr ($CDCl_3$) δ 8.20 (m, 1H), 7.60 - 7.18 (m, 18H), 6.65 (m, 1H), 5.75 (m, 1H, J=7.3 Hz, J=15.9 Hz), 3.89 (s, 3H), 3.04 (d, 2H, J=7.3 Hz), 2.86 (s, 2H); ^{13}C nmr ($CDCl_3$) δ 154.8, 145.1, 140.8, 131.9, 131.1, 129.6, 129.0, 128.8, 128.3, 127.7,

127.1, 126.2, 126.2, 125.3, 125.0, 124.5, 124.1, 123.9, 122.2, 120.0, 103.7, 88.2, 55.5, 51.7, 49.2, 44.0.

4.3.6 General Procedure for Preparative Photolyses

A solution of the ester (approximately 6 x 10^{-3} mol) in sodium distilled methanol (420 mL) was purged with nitrogen for fifteen minutes. The solution was irradiated in an immersion well using a Pyrex-filtered 200W medium pressure Hanovia mercury lamp. The progress of the reaction was monitored by HPLC, and the reaction was stopped when the ester was greater than 90% consumed. The compounds were isolated and purified using column chromatography.

4.3.7 Quantitative Photolyses

The procedure followed was the same as that described in the preparative photolysis section except the solutions contained only 100 - 200 mg of the ester and analyses were done with approximately 50% conversion of the ester to products. The yields of the photoproducts were determined by comparing the peak heights of the various components in the photolysis mixture in an HPLC trace to the peak heights of the standard solutions of known concentration under identical HPLC conditions.

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