This is to certify that the

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Stereoselectivity in the Intramolecular Cycloaddition of Double Bonds to Triplet Benzenes

presented by

Kung-Lung Cheng

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Ph.D. degree in Organic Photochemistry

Peter J. Wagner
Major professor

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STEREOSELECTIVITY IN THE INTRAMOLECULAR CYCLOADDITION OF DOUBLE BONDS TO TRIPLET BENZENES

By

Kung-Lung Cheng

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ABSTRACT

STEREOSELECTIVITY IN THE INTRAMOLECULAR CYCLOADDITION OF DOUBLE BONDS TO TRIPLET BENZENES

By

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The diastereoselectivty with which *o*- and *p*-butenoxy acetophenones undergo intramolecular triplet [2 + 2] photocycloadditions has been measured. Alkyl groups originally on the tether or the double bond show high selectivity with regard to the configuration of the bridgehead stereocenters. The five- and four-membered rings of the tricyclo[7.2.0.$0^{5,9}$]undecadiene photoproducts are always *anti* to each other and all-*cis* with respect to the six-membered ring. This fact indicates that the photoinduced electrocyclization to a cyclobutene of one diene unit of the bicyclo[6.3.0]undecatriene intermediate puckers in only one of two possible ways.

The intermediacy of a 1,4-biradical in this photocycloaddition was confirmed by the means of a "Free Radical Clock": the cyclopropylcarbinyl radicals to allylcarbinyl radicals rearrangement. Product analyses showed that the biradical cyclizes slowly but cleaves very rapidly, and undergoes a rare tandem *biradical* cyclization process. Both the large cleavage/coupling rate ratio

and assistance by rearomatization may explain the modest quantum yields (Φ = 0.07 - 0.25) normally observed in this cyclization reaction.

The processes of photoreversion of cyclohexadienes and secondary photoelectrocyclizations for cyclobutenes have also been examined. Efficient photoreversion (Φ = 0.70 - 0.78) of the thermally stable cyclohexadiene to phenyl ketone was observed. Low quantum efficiency of the cyclobutene formation (Φ = 0.05 - 0.21) in secondary photoelectrocyclizations is probably due to an intensely efficient *cis* and *trans* photoisomerization of cycloöctatrienes.

ACKNOWLEDGMENTS

I wish to thank Professor Peter J. Wagner for his guidance and encouragement throughout the course of this research. I would like to thank the Chemistry Department at MSU for financial support and use of its facilities and the National Science Foundation and the National Institute of Health for the research assistantships administrated by Professor Wagner. I would also like to thank my friends in the Wagner group who made my stay at MSU an enjoyable one.

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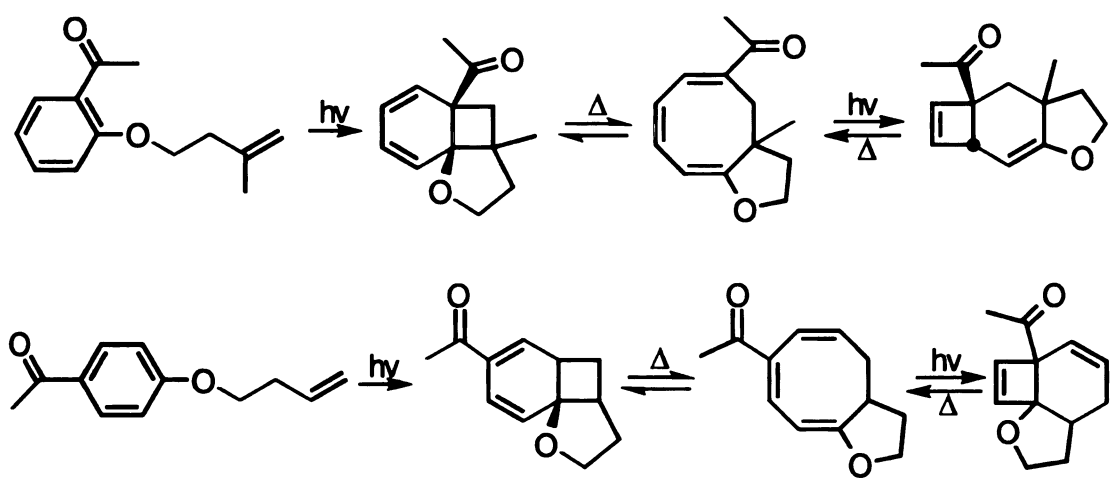
INTRODUCTION

I. Preliminary Studies

Wagner and Nahm reported the first intramolecular [2+2] *ortho* cycloaddition of *ortho*- and *para*-alkenoxyphenyl ketones via π, π^* lowest triplets. Addition to the remote double bond yields bicyclo[4.2.0]octadienes that quickly convert thermally to cycloöctatrienes. The cycloöctatrienes undergo subsequent photochemical diene-to-cyclobutene interconversion to form linear or angular bicyclooctadienes different from the initial photoadducts (Scheme 1).[1,2]

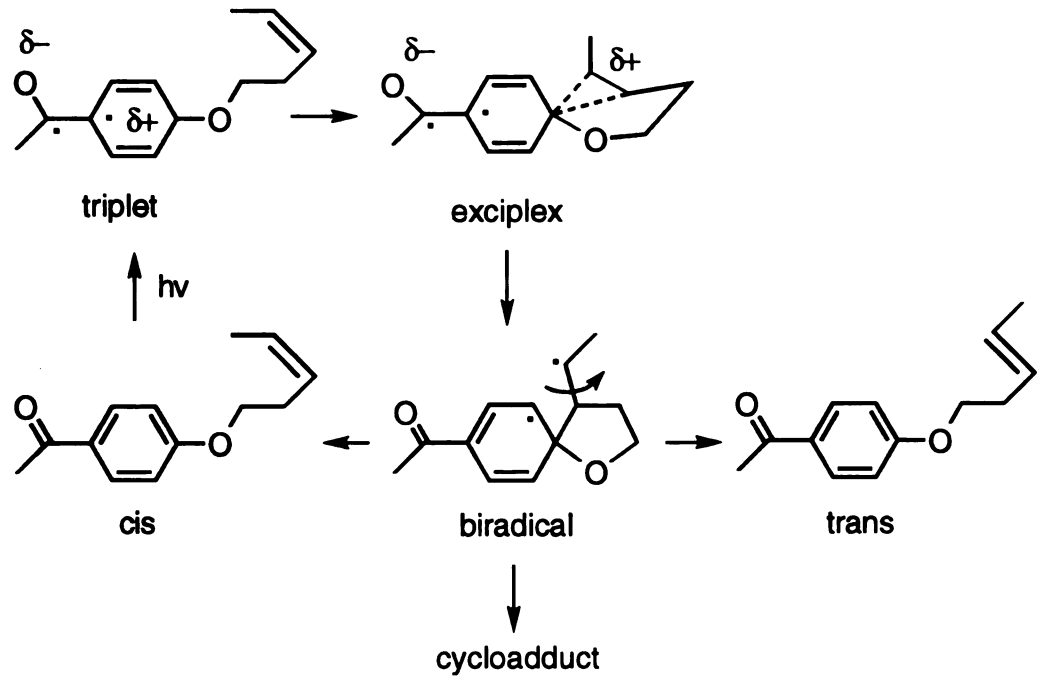
Scheme 1



The mechanism of this reaction was proposed to proceed via a triplet state in contrast to an excited singlet. The π, π^* lowest triplet state of the *p*-alkoxyphenyl ketone undergoes intramolecular charge *trans*fer with the donor double bond to generate an exciplex, followed by 1,4-biradical formation. This biradical may either give *cis-trans* isomerization or couple to produce the

cycloadducts. Facile *cis-trans* isomerization of the remote double bond ($\Phi = 0.27$) strongly implicates a biradical intermediate (Scheme 2).

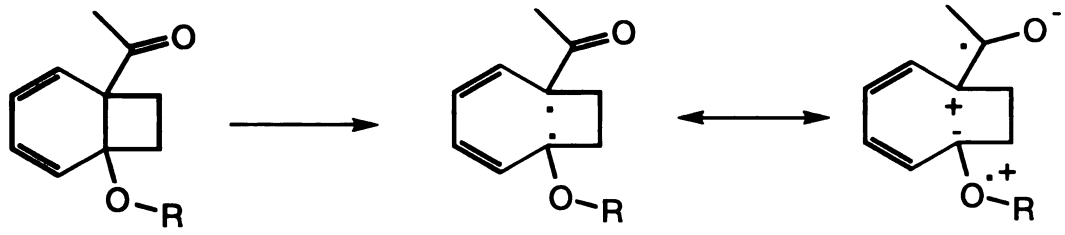
Scheme 2



The suprafacial [2+2] cycloadduct containing a cyclohexadiene subunit, undergoes rapid thermal disrotatory opening to give the all *cis*-cycloöctatriene. Secondary photolysis of the cycloöctatriene gives a photostable cyclobutene, by disrotatory closure in accordance with orbital-symmetry rules.[3]

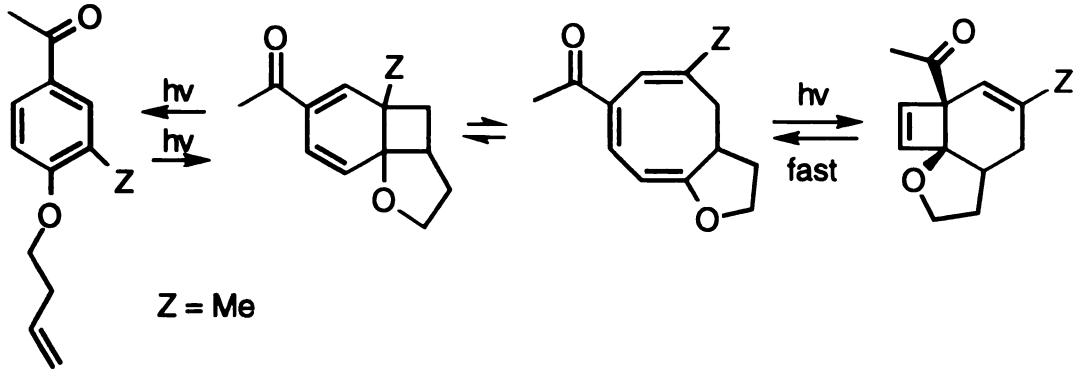
Cyclobutenes, which are thermally unstable, open easily to cycloöctatrienes. This ring opening is proposed to occur, not via a concerted electrocyclic reaction, but by cleavage of the weakened central C-C bond due to donor-acceptor conjugation (Scheme 3).[4]

Scheme 3



High regioselectivity promoted by ring substituents *ortho* to the tether has also been reported.[5,6] This selectivity appears to reflect inductive effects by the ring substituents on the triplet state cycloaddition. Strong electron-donating substituents, e.g., OMe and SMe, favor cycloaddition away from the *ortho* substituents. In contrast, strong electron-withdrawing substituents, e.g., CN and $CONH_2$, favor cycloaddition toward the substituents. Ketones containing an *ortho* methyl group also favor cycloaddition toward the alkyl substituent. Exciplex orientational preferences cannot totally explain the observed regioselectivity (Scheme 4).

Scheme 4

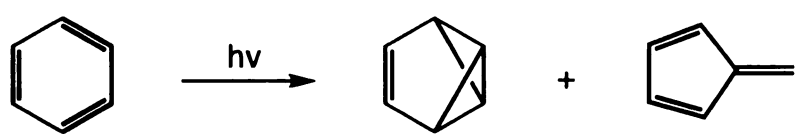


Irradiation of the above acylbenzenes generated either angular or linear cyclobutenes, except for the methoxy-substituted case. Irradiation to 20 % conversion of the latter gave only methoxy-substituted cyclohexadiene in >80 % yield even after workup. Irradiation of the methoxy-substituted cyclohexadiene produced mainly starting acylbenzene. The same behavior has been observed for a derivative in which the anchoring oxygen is replaced with a methylene group.[7] This suggests that back photocleavage of the cyclohexadiene is efficient.

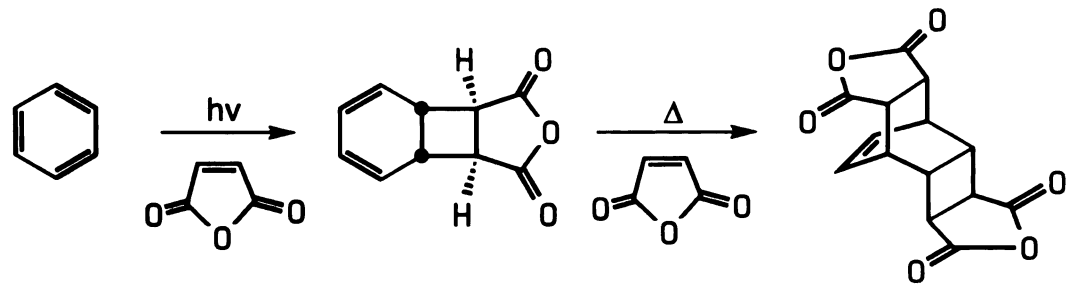
II. Historical Perspective

Photochemistry covers all processes by which chemical change occurs by the action of visible or ultraviolet radiation. These processes normally involve direct participation of an electronically excited state. Excited states are produced by electron movement from the lower to higher energy levels. Excited states have properties and electron distribution which are very different from ground states, and therefore exhibit reactions not accessible from the ground states.[8]

Benzene can be used as an example. With few exceptions, benzene is structurally rigid in the ground state but becomes extremely flexible and chemically labile when irradiated with light. Since the discovery of benzene's photoisomerization to fulvene, its unexpected photolability has aroused considerable research interest.[9] During the last three decades, there has been great progress made on its versatile transformations, such as isomerization, addition, substitution and cycloaddition.[10-13]

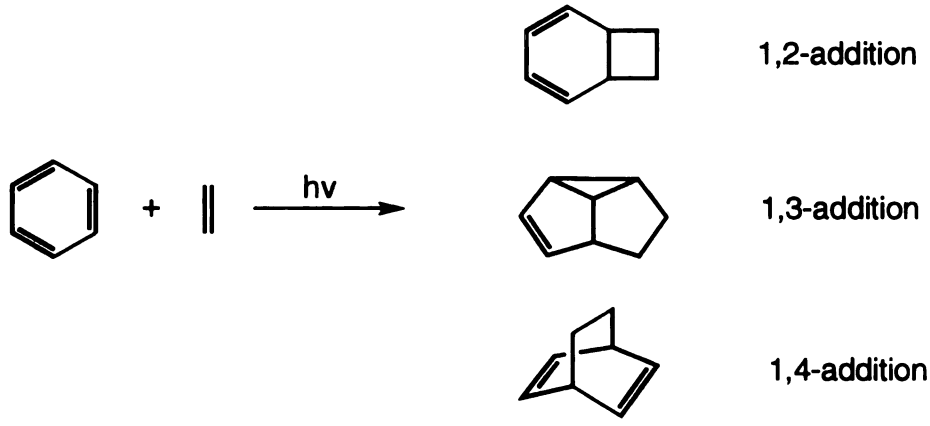


The first reports of photocycloaddition, reactions of double bonds with aromatic rings, appeared soon after the discovery of benzene photorearrangements. Angus and Bryce-Smith attempted to trap fulvene by addition of a dienophile, maleic anhydride.[14] Product analysis indicated the reaction proceeded via initial [2+2] photocycloaddition of maleic anhydride to benzene, followed by a Diels-Alder cycloaddition.



Photocycloaddition between benzene and a double bond has become a versatile and synthetically useful reaction. There are three modes of addition in photocycloaddition of benzene with an alkene; 1,2 (*ortho*), 1,3 (*meta*) and to a lesser extent 1,4 (*para*) to form bicyclo-[4.2.0]octa-2,4-dienes, tricyclo-[3.3.0.$0^{4,6}$]oct-2-enes and bicyclo-[2.2.2]octa-2,5-dienes, respectively (Scheme 5).

Scheme 5



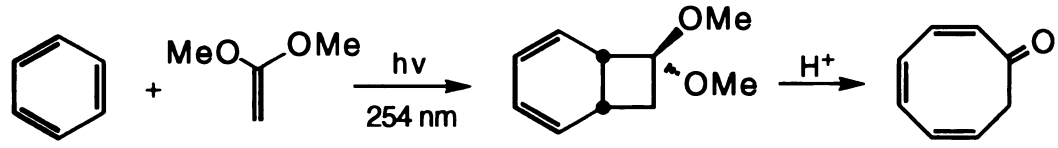
Such a bichromophoric reaction may proceed inter- or intramolecularly. In intramolecular systems, the addition pattern and the efficiency of the reaction is dependent on chain length and type of tether. Generally, intramolecular interactions are more efficient. The stereoselectivity of intramolecular reactions,

as a consequence of geometric restriction, will be discussed in greater detail later.

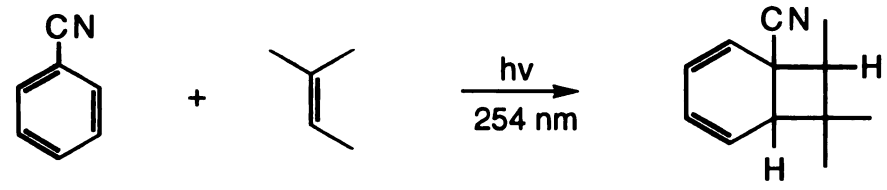
Ortho photocycloaddition of benzene and alkenes

Intermolecular

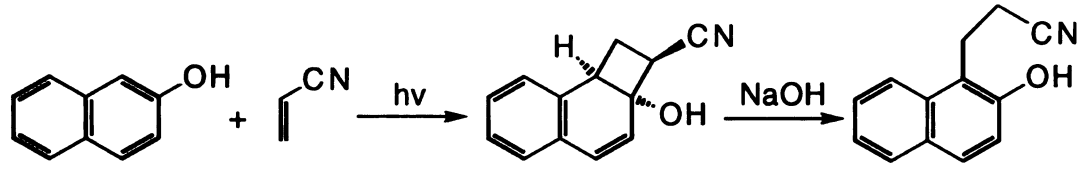
The earliest example of intermolecular *ortho* photocycloaddition was discovered by Gilbert et. al.[15] Direct irradiation of benzene in the presence of 1,1-dimethoxyethylene provided 7.7-dimethoxybicyclo-[4.2.0]octa-2,4-diene; acid treatment gave the cyclooctatrienone. *Ortho* photocycloadditions were also observed in irradiation of benzene with maleimide,[16] methyl vinyl ketone,[17] methyl vinyl sulfide,[11] methacrylonitrile, methyl acrylate,[18] or 1,4-dioxene.[15]



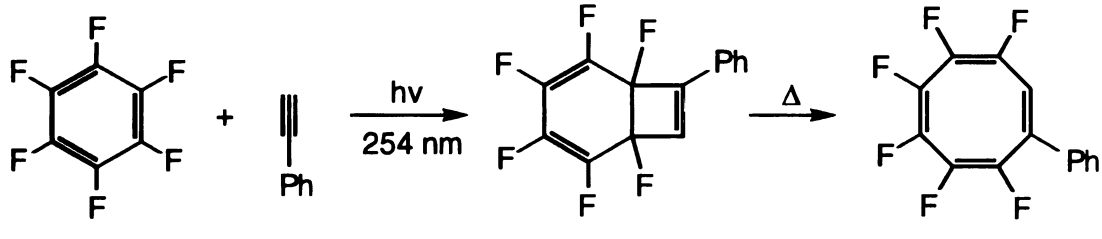
Irradiation of benzonitrile and 2-methyl-2-butene produced a 1:1 adduct which was identified as 7,7,8-trimethylbicyclo[4.2.0]octa-2,4-diene-1-carbonitrile. This compound is not stable to ultraviolet light and readily reverted to benzonitrile and olefin. Dialkylacetylenes could also added to benzonitrile photochemically and cycloöctatetraene-carbonitrile was isolated.[19]



Similar reactions have also been reported in the photochemistry of naphthalene derivatives. Photocycloaddition of 2-naphthol with acrylonitrile in a 1:1 isopropyl alcohol-tert-*butyl* alcohol mixture afforded the head-to-head cyclobutanol product, 7-cyano-2,3-benzobicyclo[4.2.0]octa-2,4-dien-6-ol. Further treatment with NaOH gave 1-(2-cyanoethyl)-2-naphthol, via a retroaldol reaction.[20]



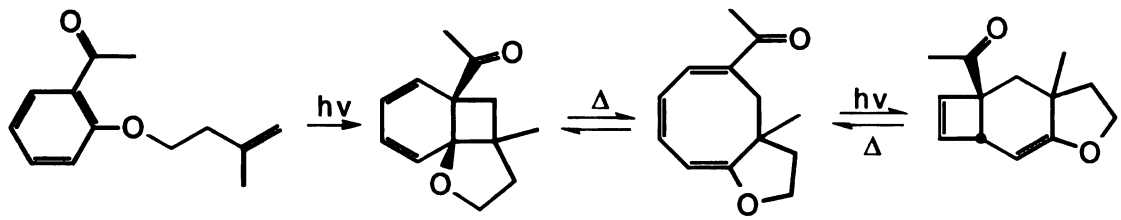
Irradiation of hexafluorobenzene and phenylacetylene gave phenyl-hexafluorobicyclo[4.2.0]octatriene which was thermally converted to hexafluorocycloöctatetraene.[21]



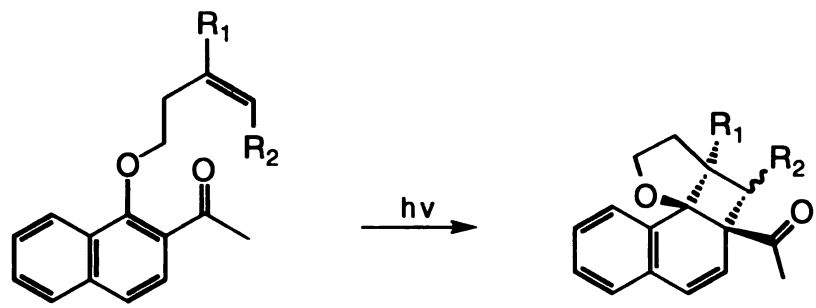
Intramolecular

Wagner and Nahm discovered that phenyl ketones with π, π^* lowest triplets undergo intramolecular [2+2] *ortho* cycloaddition to remote double bonds to generate tricycloundecadienes, and this are thermally converted to an isomeric cycloöctatriene.[1] Such cycloöctatrienes underwent a subsequent photochemical

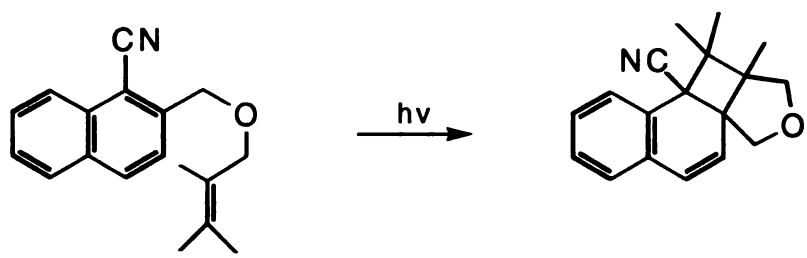
diene-to-cyclobutene interconversion to form isomeric tricycloundecadienes which are different from the initial photoadducts.[2]



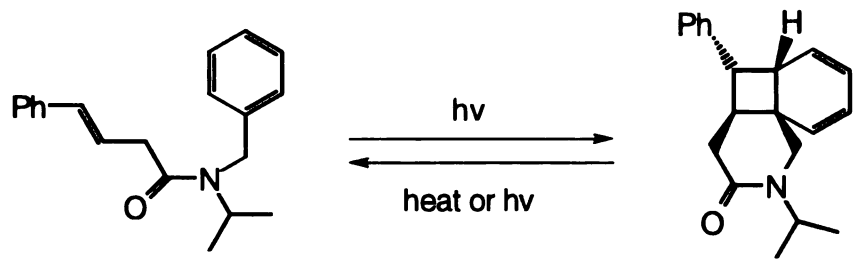
The first example of intramolecular 1,2-addition of simple alkenes to triplet naphthalenes was achieved by Wagner and Sakamoto.[22] Both 1-butenoxy-2-acetonaphthones and 2-butenoxy-1-acetonaphthones undergo [2+2] cycloadditions from their triplet states with high chemical yield. The results were similar to the [2+2] photocycloadditions of 2-, 4- and 6-(2-oxa-4,5-dimethyl-4-hexenyl)-1-cyanonaphthalenes but the latter are known to proceed from singlet exciplexes with high quantum yield (0.69).[23]



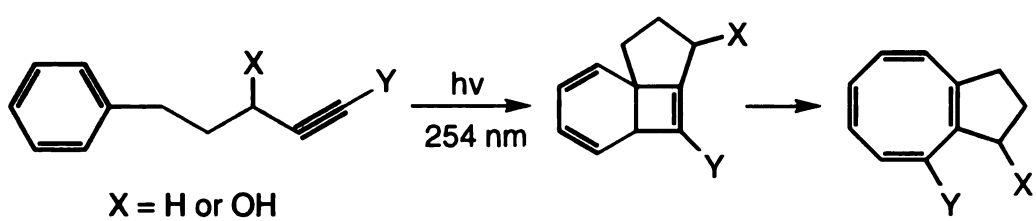
R_1=R_2=H or
R_1=Me, R_2=H or
R_1=H, R_2=Et



Irradiation of N-benzylstyrylacetamides provides tricyclic amide products via cycloaddition between the styryl and benzene groups. The photoproducts quantitatively revert to starting material on heating or photolysis.[24]



Morrison and coworkers had previously examined the intramolecular *ortho* photocycloaddition of benzene to triple bonds.[25] The initial cycloadducts rearranged inefficiently to cyclooctatetraenes. Placement of a trimethylsilyl group on the triple bonds provides cyclooctatetraenes in high chemical yield.[26]



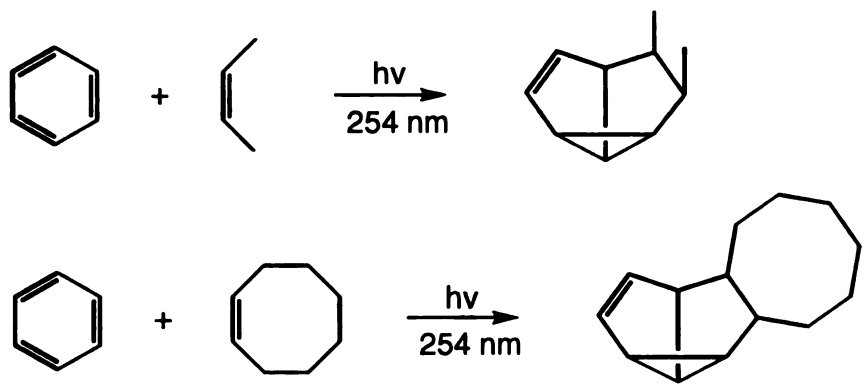
X = H or OH
Y = Me or TMS

Meta photocycloaddition of benzene and alkene

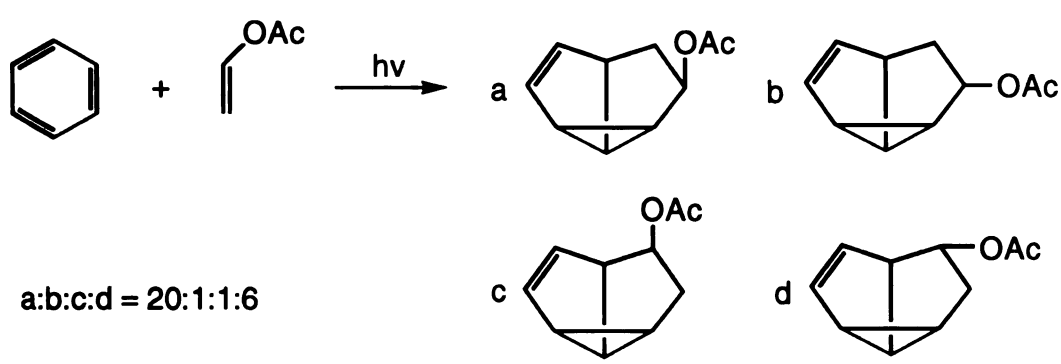
Intermolecular

Wilzbach and Kaplan reported the first meta photocycloaddition in 1966. Photolysis of a solution of *cis*-but-2-ene in benzene at 254 nm provided 6,7-dimethyl-tricyclo[3.3.0.$0^{2,8}$]oct-3-ene.[27] In addition, Bryce-Smith, Gilbert and

Orger also reported that irradiation of an equimolar mixture of benzene and *cis*-cyclooctene led to a 1:1 adduct , identified as tetracyclo[6.6.0.$0^{2,4}$.$0^{3,7}$]tetradec-5-ene.[28]

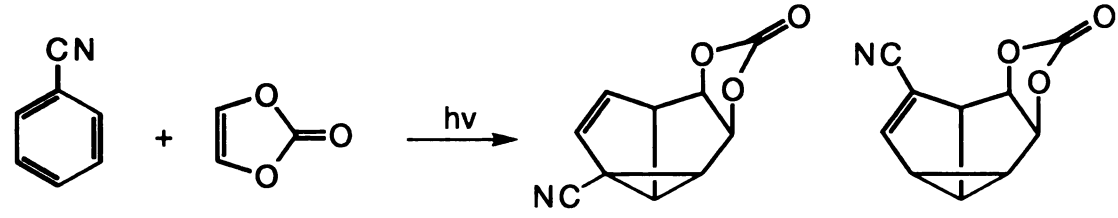


Different combinations of benzene and various alkenes have been photolyzed and the observed isomeric adducts of *meta* addition isolated; for example, mono-, di-, tri-, tetra- alkyl-substituted alkenes, cycloalkenes[17] (3-, 4-, 5-, 6-, 7-, 9-membered ring) and alkenes with electron donating groups (-Ot-Bu) or withdrawing groups (-Cl, -OAc).[12] Minor *ortho* cycloadducts are also obtained in some of the above examples.



Meta photocycloadditions of mono-, di-, tri- and hexa-substituted benzenes to various alkenes have been studied. Substituents on the benzene

ring appear to have a pronounced directing effect (regioselectivity) on the addition, but complicate product analysis. In general, *ortho* cycloaddition involving charge *trans*fer between an electron poor benzene and electron rich double bond has been predicted by Bryce-Smith. However, an exception, the photocycloaddition of an electron poor benzene (benzonitrile) and electron rich double bond (1,3-dioxol-2-one) yields exclusively *meta* adducts.[29]

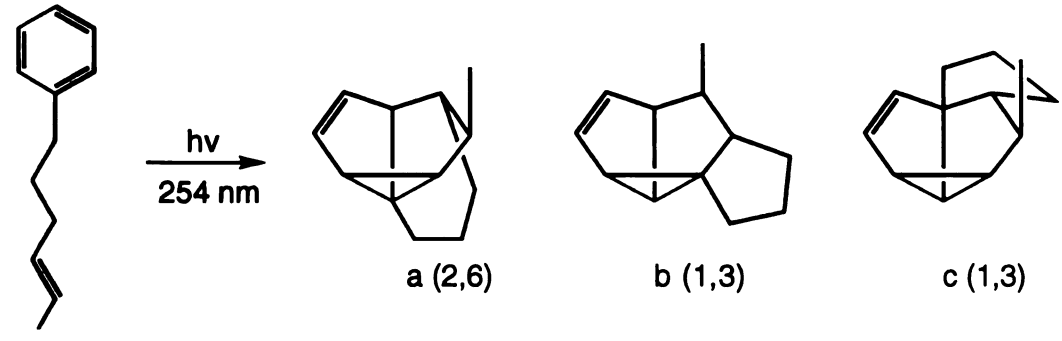


a b

a:b = 45 : 55

Intramolecular

Morrison and Ferree reported that photolysis of *trans*-6-phenylhex-2-ene leads to the formation of 2,6 and 1,3 diastereomeric cycloadducts via a singlet process.[30]



a (2,6) b (1,3) c (1,3)

a : (b + c) = 91 : 9

Other intramolecular *meta* cycloadditions of benzenes with various alkyl-substituted tether are summarized in Table 1.

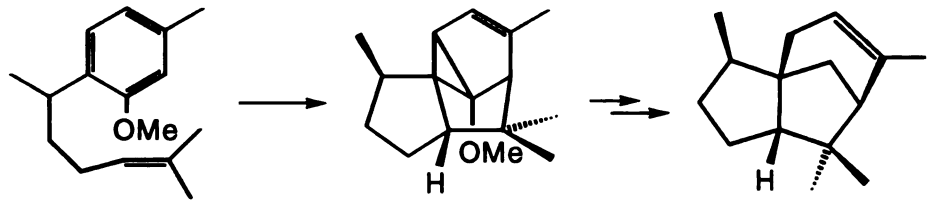
Table 1 Intramolecular Cycloadditions of Arenes to Alkenes

starting material	orientation	product ratio and Φ	ref.
$Ph(CH_2)_3CH=CH_2$	2,6 / 1,3	$\Phi_{2,6} = 0.11$, $\Phi_{1,3} = 0.04$	31
$Ph(CH_2)_3CH=CHMe$ (*cis*)	1,3	$\Phi_{1,3} = 0.26$	30
$Ph(CH_2)_3CMe=CH_2$	2,6 / 1,3	1 : 1.6, $\Phi_{tot} = 0.65$	11
$Ph(CH_2)_3CH=CMe_2$	1,3	a	12
$PhCHMe(CH_2)_2CH=CH_2$	2,6 / 1,3	1.7 : 1, $\Phi_{tot} = 0.055$	11
$PhCH_2CHMeCH_2CH=CH_2$	2,6	$\Phi_{tot} = 0.035$	11
$Ph(CH_2)_2CHMeCH=CH_2$	2,6 / 1,3 / 2,4	2.2 : 1.3 : 1, $\Phi_{tot} = 0.055$	11
$PhO(CH_2)_2CH=CH_2$	2,4	very inefficient	31
o-$MePh(CH_2)_3CH=CH_2$	1,3 / 1,4	5.9 : 1, $\Phi_{tot} = 0.60$	32
o-$MePh(CH_2)_3CH=CHMe$ (*trans*)	2,6 / 1,3	1 : 1 (with other isomers)	12
o-$MePh(CH_2)_3CH=CHMe$ (*cis*)	1,3	a	12
o-$MePhCHMe(CH_2)_2CH=CMe_2$	1,3	1 : 1 isomers	33
o-$MePhCHMe(CH_2)_2CMe=CHMe$	1,3	1 : 1 isomers	34
p-$AcPh(CH_2)_3CH=CH_2$		no meta cycloaddition	32

a. Φ not determined.

The versatility of *meta* cycloaddition has led to the development of very elegant synthetic approaches to a wide variety of natural products. Wender and Howbert reported the first application of an arene-alkene photocycloaddition as the key step in the total synthesis of (±)-cedrene (Scheme 6).[35]

Scheme 6

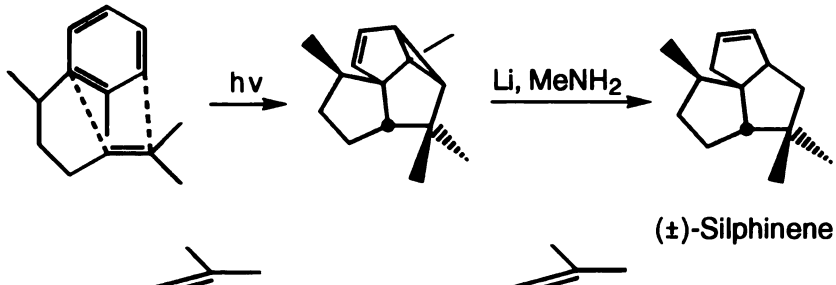


(±)Cedrene

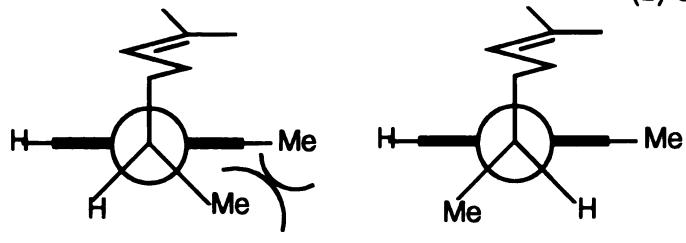
Stereoselectivity

Exo / *endo* selectivity in photocycloaddition for the synthesis of (±)-silphinene is controlled by steric hindrance; orbital overlap leading to the *endo* complex can not be achieved without introducing strain, resulting in an *exo*-selective reaction. Formation of the β-methyl stereoisomer is a consequence of non-bonding interactions in the *trans*ition state (Scheme 7).[33]

Scheme 7



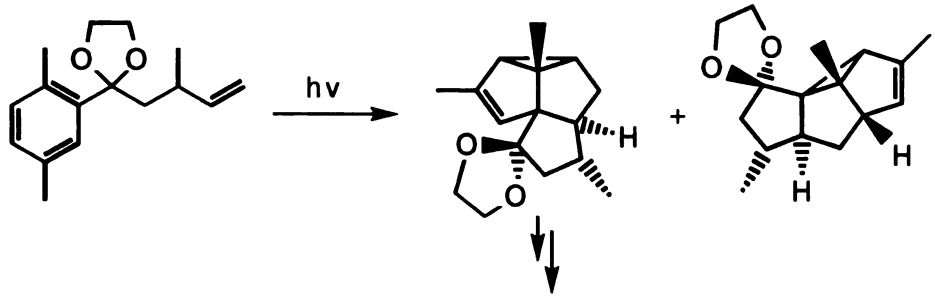
(±)-Silphinene



exo favored

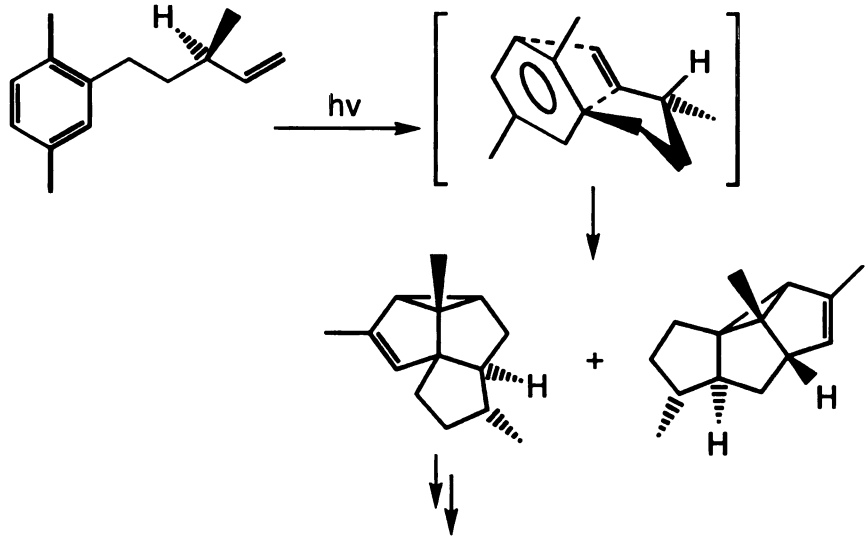
Recently, *meta* cycloaddition has been used to synthesize (±)-subergorgic acid,[36] (-)-retigeranic acid,[37] and grayanotoxin II.[11] The stereospecificity, induced by *ortho*-substituents on benzene, has been obtained by pre-existing stereogenic centers on the tethers at the benzylic, allylic, homobenzylic position or combinations of all three. (Scheme 8-10) Less attention has been paid to the diastereoselectivity exhibited by the tether itself during cyclization. This topic forms the central core of the research discussed in this thesis, and will be expanded upon later.

Scheme 8



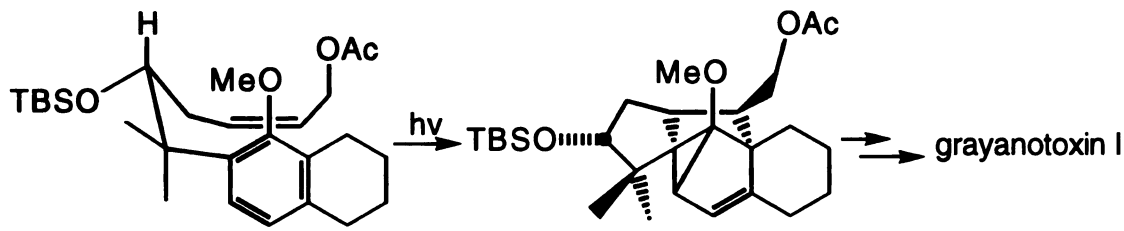
(±)-subergorgic acid

Scheme 9



(-)-retigeranic acid

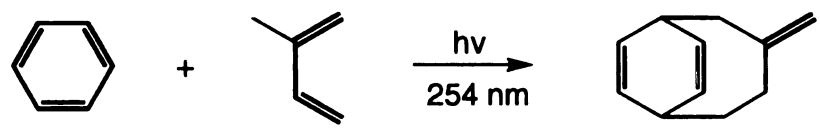
Scheme 10



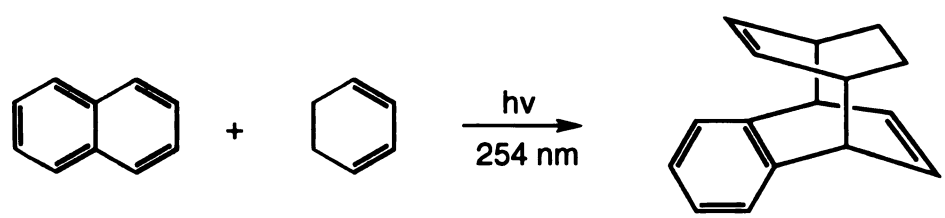
Para photocycloaddition of benzene and alkene

Intermolecular

Para photocycloaddition occurs primarily when benzene rings are photolyzed in the presence of dienes or allenes. Irradiation of isoprene and benzene gave the initial 1:1 photoadduct which undergoes a 1,3-hydrogen shift to afford the observed product; 3-methylenebicyclo[4.2.0]deca-7,9-diene.[38]

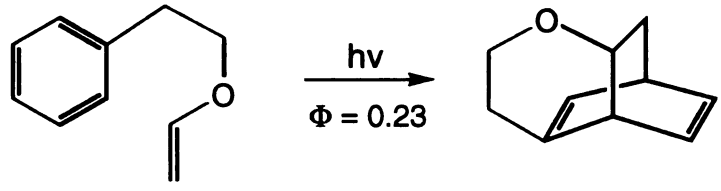


Yang extended the *para* photocycloaddition to naphthalene with cyclohexadiene and isolated the polycyclic hexaprismanes in moderate yield.[39]



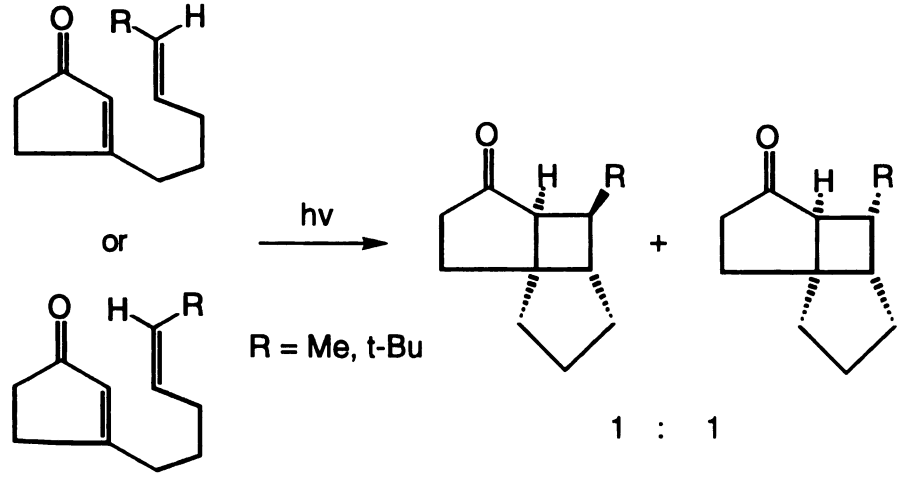
Intramolecular

Not many examples have been reported for intramolecular *para* photocycloaddition, due largely to the ring strain in the photoproducts. An interesting example, reported by Gilbert and coworkers, is that photolysis of the enol ether below afford the tricyclic ether in high chemical yield and quantum yield.[38]

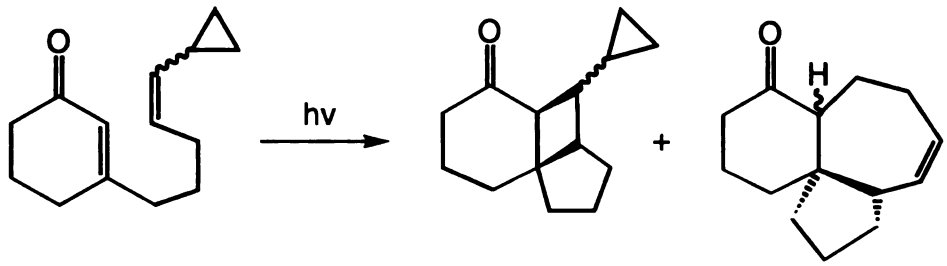


Other [2+2] photocycloadditions

Becker has investigated the stereochemistry of intramolecular photocycloaddition of enones with tethered alkenes. The identical low stereoselectivity (around 1 : 1) of the cycloadducts was found when β-alkenylcyclopentenones (either *cis* or *trans*) were irradiated. It was concluded that steric effects might not influence the course of reaction.[40,41]

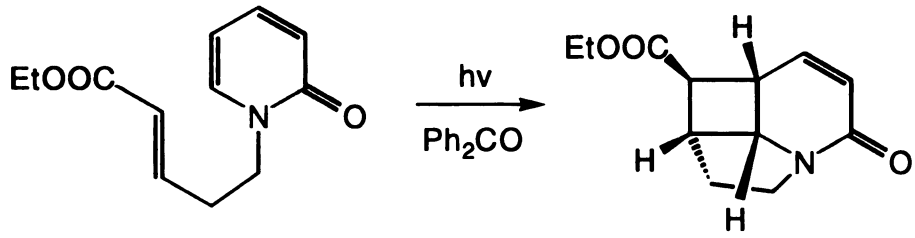


A 1,4-biradical intermediate was found to be involved in this reaction. The enone with a cyclopropyl group at the end of the double bond was photolyzed and gave the normal [2+2] cycloadducts as well as rearrangement products in a ratio of 2:1.[42]

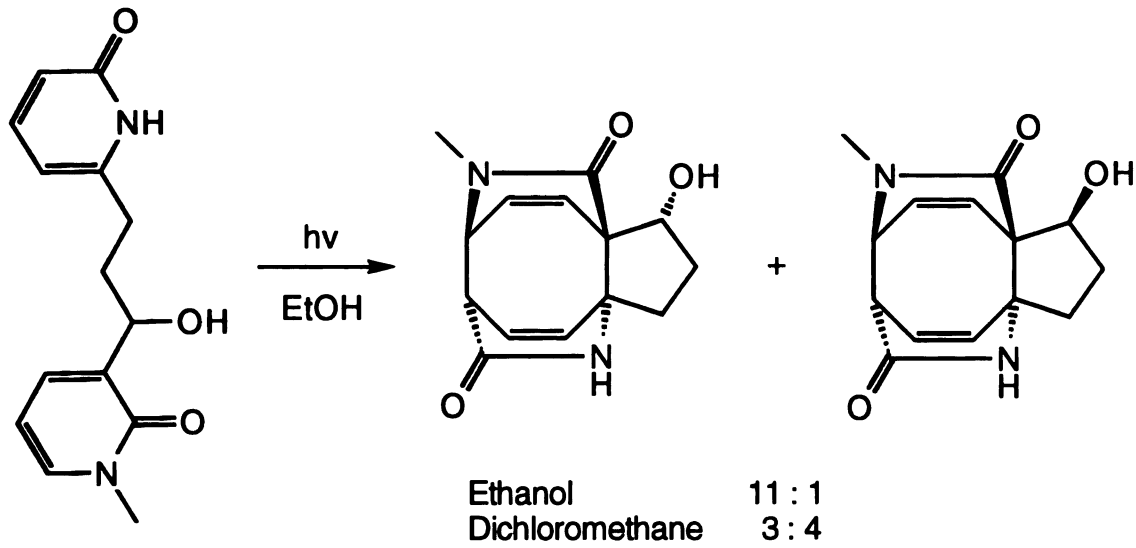


2 : 1

Photosensitized cycloaddition of 1-(ω -alkenyl)-2-pyridone afforded an intramolecular [2+2] cycloadduct across the 5,6-bond of the 2-pyridone to give a tricyclic lactam which contains a *cis*-ring junction in 95 % yield. The addition was regio- and stereospecific.[43]



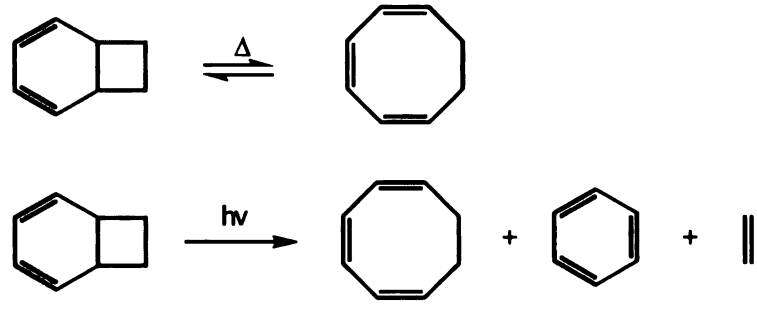
The intramolecular [4+4] photocycloaddition of tethered bis-pyridone provides an 8-5 bicyclic carbon skeleton. It is interesting that the stereoselectivity of the hydroxy group is reversed in dichloromethane. This solvent effect on stereoselectivity for the hydroxy-substituted tethers was explained by hydrogen bonding of the hydroxy group to the solvent, methanol.[44-46]



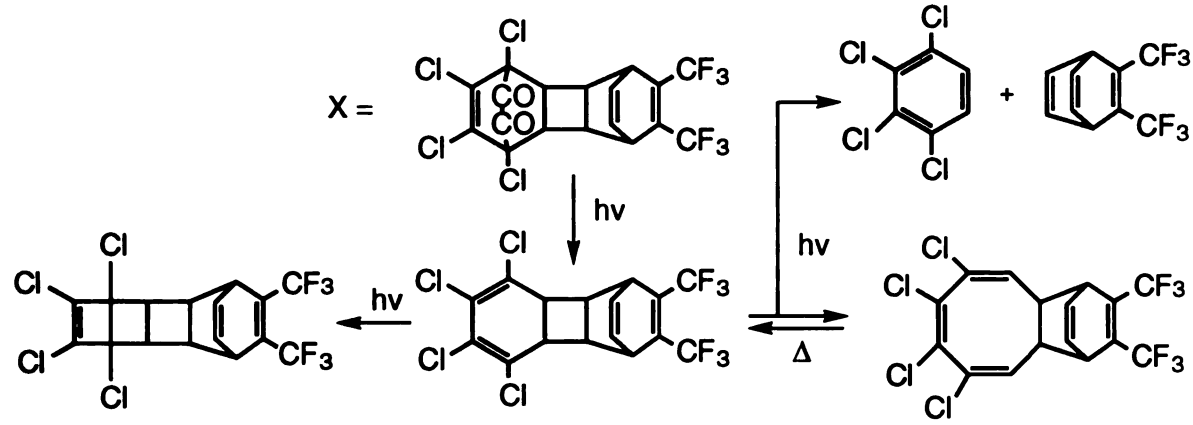
Ethanol	11 : 1
Dichloromethane	3 : 4

Equilibrium of cyclohexadiene and cycloöctatriene

1,3,5-Cycloöctatriene has been found to exist in equilibrium with its valence tautomer, bicyclo[4.2.0]octa-2,4-diene.[47] Such an equilibrium was also observed in our system. From orbital symmetry rules, bicyclo[4.2.0]octa-2,4-diene should be converted thermally to 1,3,5-cycloöctatriene by a disrotatory process.[48] This was observed at 100 °C experimentally. However, direct photolysis of bicyclo[4.2.0]octa-2,4-diene in the gas phase at 280-300 nm produced mainly 1,3,5-cycloöctatriene and benzene plus ethylene.[49]



Warrener and co-workers offered another example of photoisomerization of a bicyclo[4.2.0]octa-2,4-diene. Irradiation of compound X generated a cycloöctatriene, benzene plus ethylene and tricyclo[4.2.0.$0^{2,5}$]octene in either THF or benzene.[50]



III. Mechanistic Considerations

The mechanisms of photocycloadditions between benzene and double bonds and the various factors influencing the modes of cycloaddition have been subjects of longstanding interest. The first question that arises is, does the reaction proceed in a concerted or stepwise fashion, from the singlet or triplet state. Previously reported cycloadditions involved the singlet excited states of benzene except the examples using phenyl ketones recently found by the Wagner group.[1]

Due to deuterium labeling studies[51] and regio- and stereo-selectivity analysis of products,[17] the mechanism for photocycloadditions between benzene and double bonds is proposed to proceed via the formation of an exciplex followed by bond formation. Mattay has reported long wavelength emission attributable to an exciplex. Quenching of this emission and of product formation have identical rate constants ($k_q\tau$).[52]

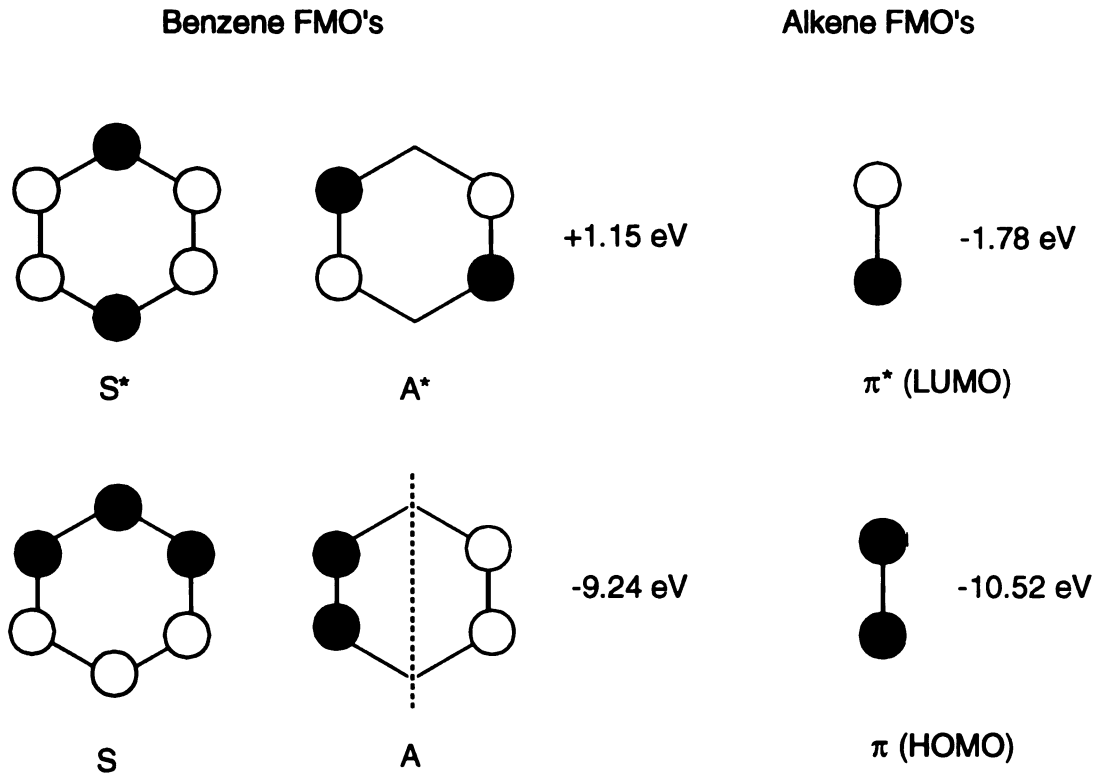
Bryce-Smith and Longuet-Higgins provided the first theoretical treatment. From an orbital symmetry viewpoint, they proposed that *ortho* and *para* cycloadditions of double bonds to benzene are forbidden from the $^1B_{2u}$ (S_1) state, unless they involve charge *trans*fer.[53] *Meta* cycloadditions are considered to be symmetry allowed from this state. The ionization potential difference rule (Δ I.P. between benzene and double bond) can be used to predict the modes of cycloaddition. Reactions of benzene (I.P. = 9.24 eV) with alkenes having I.P. between 8.6 and 9.6 eV generally proceed with *meta*-mode selectivity. On the other hand, when the Δ I.P. is larger than this range (± 0.5 eV), charge *trans*fer and *ortho*-modes are favored.[17]

Since the ionization potential difference rule (Δ I.P.) is based solely on the energies of filled orbitals, the consideration of both energies of filled orbitals and

singly occupied molecular orbitals was further studied. Houk provided a frontier molecular orbital (FMO) analysis for rationalizing the partitioning of these photocycloaddition modes.[54] The actual frontier orbitals of benzene are the combinations of configurations: the lowest excited singlet B_{2u} (SA*-AS*); the lowest triplet B_{1u} (SS*+AA*). The analysis indicated that the alkene's HOMO can mix with the benzene S orbital to stabilize a *meta* cycloaddition and with the benzene A orbital to stabilize an *ortho* cycloaddition. Alkene π^* orbital mixing with the benzene A* is possible in both cases. A *para*-approach is only weakly stabilized by interaction of the benzene S and alkene π orbital. From this analysis, it could be predicted that *ortho* cycloaddition is stabilized by an A -> S* *trans*ition, but *meta* cycloaddition is stabilized by an S -> A* *trans*ition (Figure 1).

However, substituents on the benzene and/or the double bond would remove the degeneracy of the HOMOs and of the LUMOs. An electron withdrawing group, such as acetyl or cyano, would stabilize both the S and S* orbitals of benzene, so that the HOMO is the A orbital and LUMO the S* orbital. *Ortho* cycloaddition is favored over the *meta* mode due to stabilization of the A -> S* *trans*ition (Figure 2).[55]

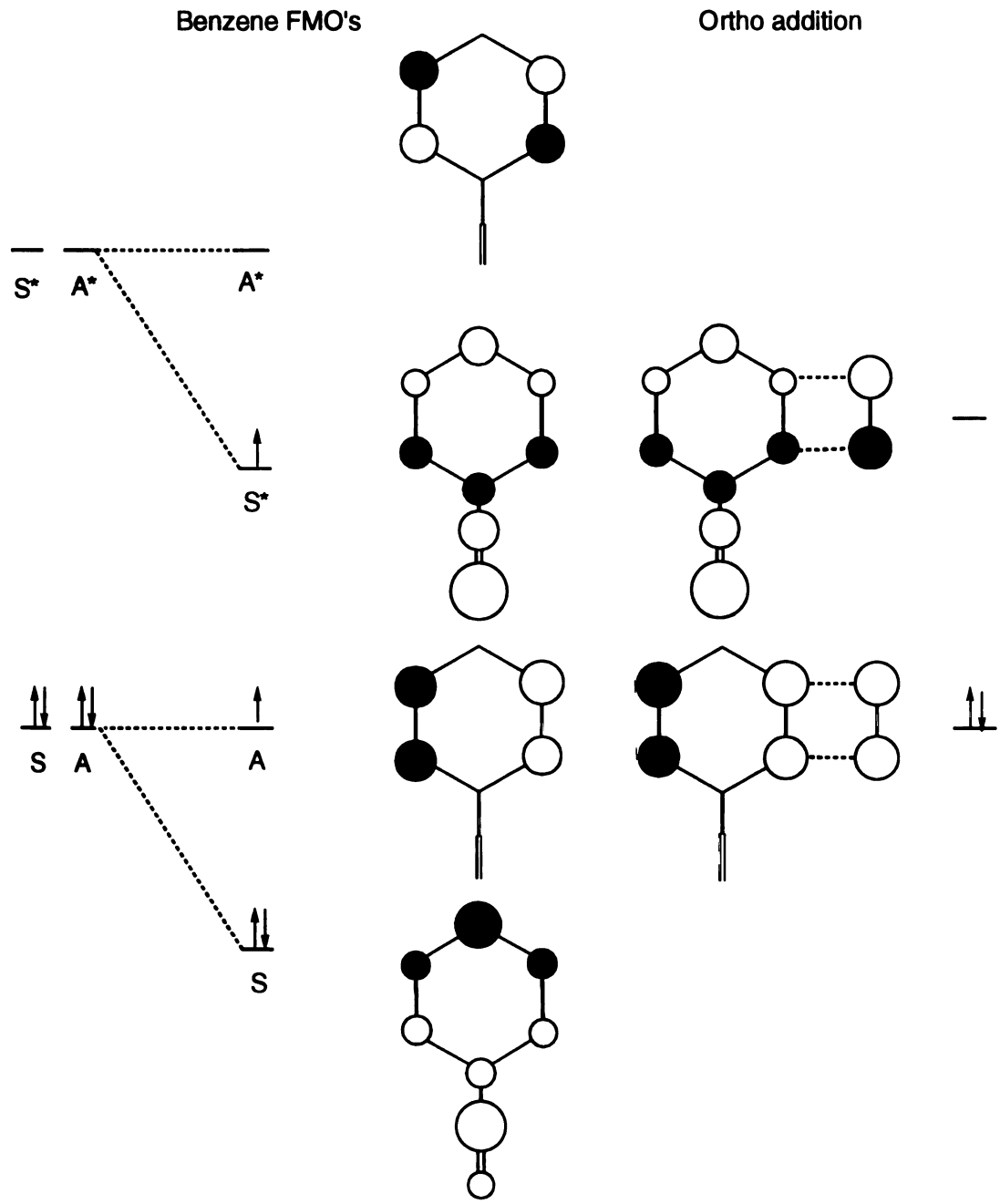
Figure 1. Frontier molecular orbitals (FMO) and excited states of benzene (mirror plane)



B_{2u} (SA* - AS*) lowest excited singlet state

B_{1u} (SS* + AA*) lowest triplet state

Figure 2. Orbital energies of triplet electron-deficient benzene with electron withdrawing groups, such as acetyl or cyano group, and alkene for *ortho* addition



IV. Quantum yields and kinetics

Equation 1 describes the rate of a photochemical reaction as a function of I_a, the total light intensity (photons/s or einsteins/s) absorbed by the sample during photolysis. It is important to distinguish among light incident upon the sample, total absorbed light, and light absorbed by the reacting compound. Most actinometry determines light incident upon the sample. When the optical density (A) of the sample, as described by Beer's law, is 2 or larger, then effectively all of the incident light (>99%) is absorbed.

$$\text{Rate} = \Phi \times I_a \tag{1}$$

The proportionality constant Φ that relates rate to light intensity is the observed quantum yield. It can also be defined independently as the ratio of molecules reacted to photons absorbed, in equation 2.

$$\Phi_{product} = \frac{\text{no. of molecules of product formed}}{\text{no. of photons absorbed}} \tag{2}$$

The triplet lifetimes of the ketones in this thesis were measured by the Stern-Volmer quenching technique.[56] 2,5-Dimethyl-2,4-hexadiene or sorbic acid was used to quench the triplet ketones by energy *trans*fer. The mathematical expression of this process is given in equation 3.

$$\Phi_0 = \Phi_{isc} k_r \tau_T$$
$$\Phi = \frac{\Phi_{isc} k_r}{1/\tau_T + k_q[Q]}$$
$$\frac{\Phi_0}{\Phi} = 1 + k_q \tau_T [Q] \tag{3}$$

where Φ_0, Φ = quantum yield in the absence and the presence of a quencher, respectively

$\tau_T = 1 / \Sigma ki$, triplet lifetime

k_q : rate constant for quenching by the quencher

k_r : rate constant for the product formation

[Q] : concentration of a quencher

A plot of Φ_0 / Φ vs. [Q] provides a straight line with an intercept of 1 and a slope of $k_q\tau_T$. The quenching rate of either 2,5-dimethyl-2,4-hexadiene or sorbic acid is usually close to the diffusion controlled rate 7.5×10^9 $M^{-1}s^{-1}$ in methanol at 25 °C.[62] The triplet lifetime can be calculated from the slope of the Stern-Volmer plot.

V. Research goals

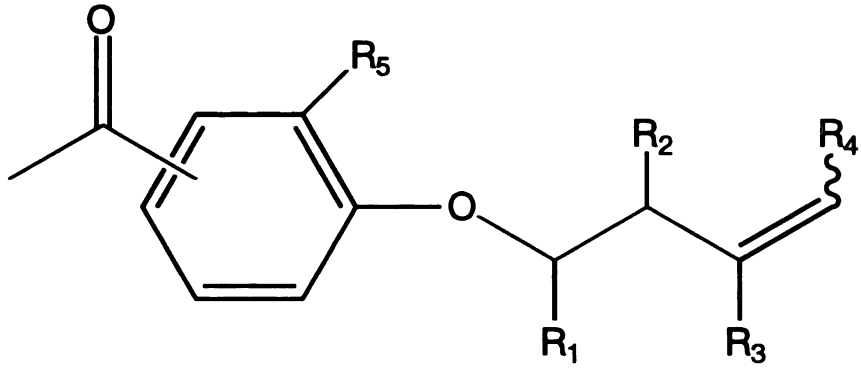
In this dissertation, the stereochemistry of intramolecular cycloaddition of double bonds to triplet benzenes will be discussed. Since there are four potential stereocenters on the tether and at least two more stereocenters generated from the secondary photochemical electrocyclic rearrangement, the diastereoselectivity of thermally stable cycloadducts and photostable cyclobutenes were explored. The biradical intermediacy of this photocycloaddition was confirmed by incorporating a radical clock (cyclopropylcarbinyl radical rearranging to allylcarbinyl radical).[57] Quantum yields for each process were measured independently.

RESULTS

I. Alkenoxyphenyl Ketones

In order to investigate the stereoselectivity of the [2+2] photocycloaddition of triplet benzene to double bonds, alkyl-substituted alkenoxyphenyl ketones were employed as reactants. These ketones were prepared by the S_N2 reaction between the phenolates of *para-* or *ortho-* hydroxyacetophenones and alkyl-substituted alkenyl tosylates in dry dimethyl formamide (DMF) or acetone. Alkyl-substituted alkenyl tosylates were prepared from the corresponding alcohols by standard tosylation in pyridine. Alcohols were purchased from the Aldrich Company or made by either Grignard or Wittig reactions.

Table 2 Alkenoxyphenyl Ketones



* *para-* or *ortho–* alkenoxyacetophenones

* **M** = methyl, **I** = isopropyl, **C** = cyclopropyl group and **K** = ketone

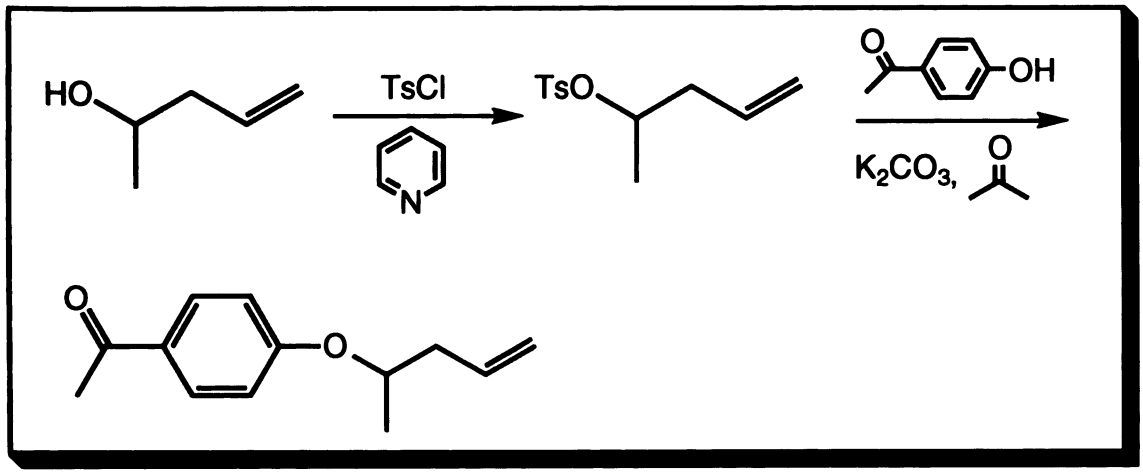
* The shorthand is also applied to **CH** = cyclohexadiene, **COT** = cyclooctatriene and **CB** = cyclobutene

p-M_0K	*para* butenoxyacetophenone without substituent
p-M_1K	*para* R_1 = Me
p-I_1K	*para* R_1 = i-Pr
p-M_1M_3K	*para* R_1 = R_3 = Me
p-I_1M_3K	*para* R_1 = i-Pr, R_3 = Me
p-M_2M_3K	*para* R_2 = R_3 = Me
p-M_3M_4K	*para* R_3 = R_4 = Me
p-$M_1M_3M_4$K	*para* R_1 = R_3 = R_4 = Me
p-M_4K	*para* R_4 = Me
p-$M_3M_4M_5$K	*para* R_3 = R_4 = R_5 = Me
p-$M_1M_3M_4M_5$K	*para* R_1 = R_3 = R_4 = R_5 = Me
p-M_4M_5K	*para* R_4 = R_5 = Me
p-C_4K	*para* R_4 = cyclo-Pr
p-I_4K	*para* R_4 = iso-Pr
o-I_1K	*ortho* R_1 = iso-Pr
o-I_1M_3K	*ortho* R_1 = iso-Pr, R_3 = Me

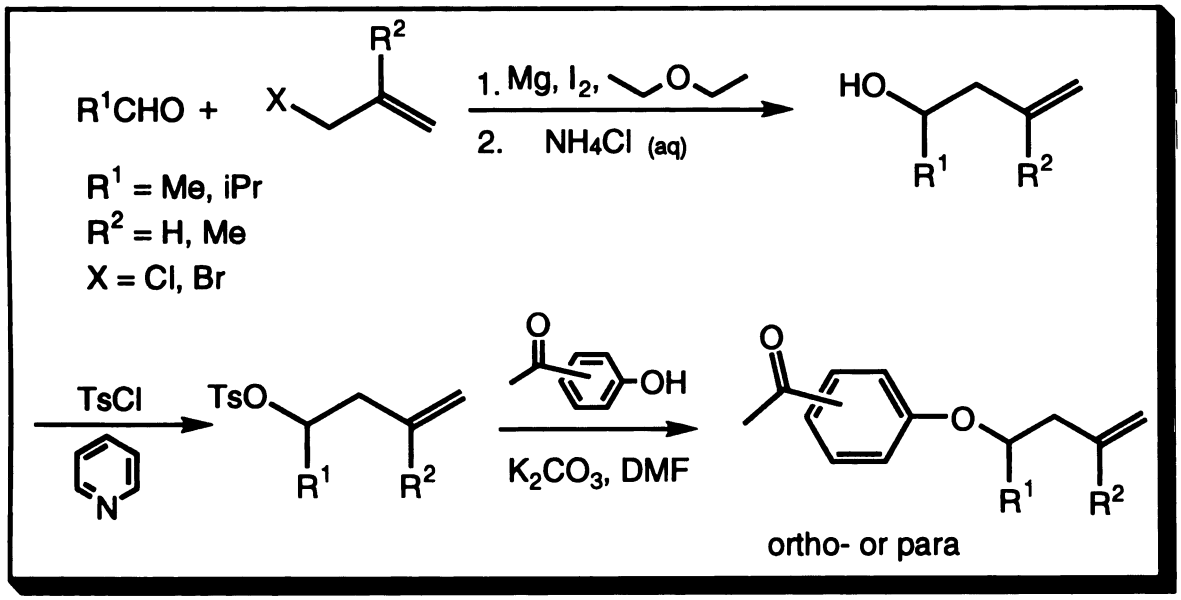
The synthesis of **p-M_1K** is outlined in Scheme 11.

Alcohols used to make **p-I_1K, p-M_1M_3K, p-I_1M_3K, o-I_1K and o-I_1M_3K** were prepared by reaction between acetaldehyde or isobutyraldehyde and allyl Grignard reagents, followed by tosylation at 0°C in pyridine. The standard coupling method was carried out in DMF (Scheme 12).

Scheme 11



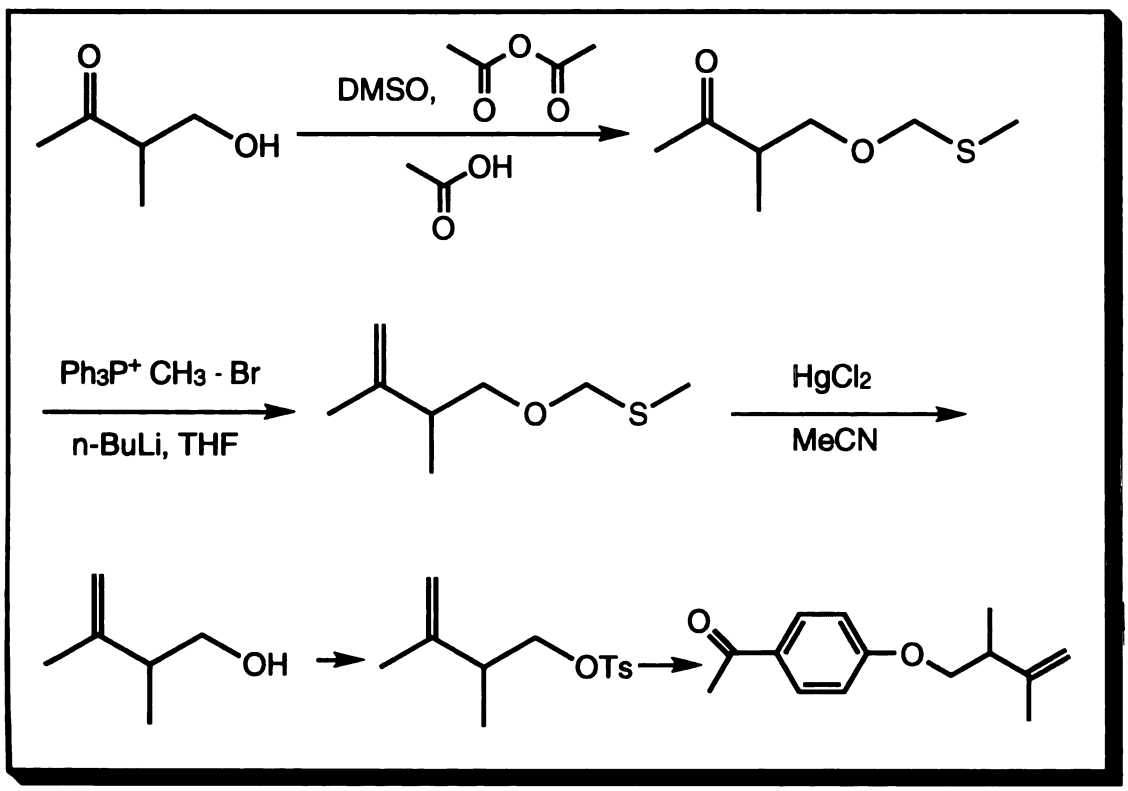
Scheme 12



1-Hydroxy-2-methyl-3-butanone was used as the precursor of **p-M_2M_3K**. After protection using the methylthiomethyl group (MOM), a Wittig reaction using methyl triphenylphosphonium bromide, followed by removal of the MOM group by

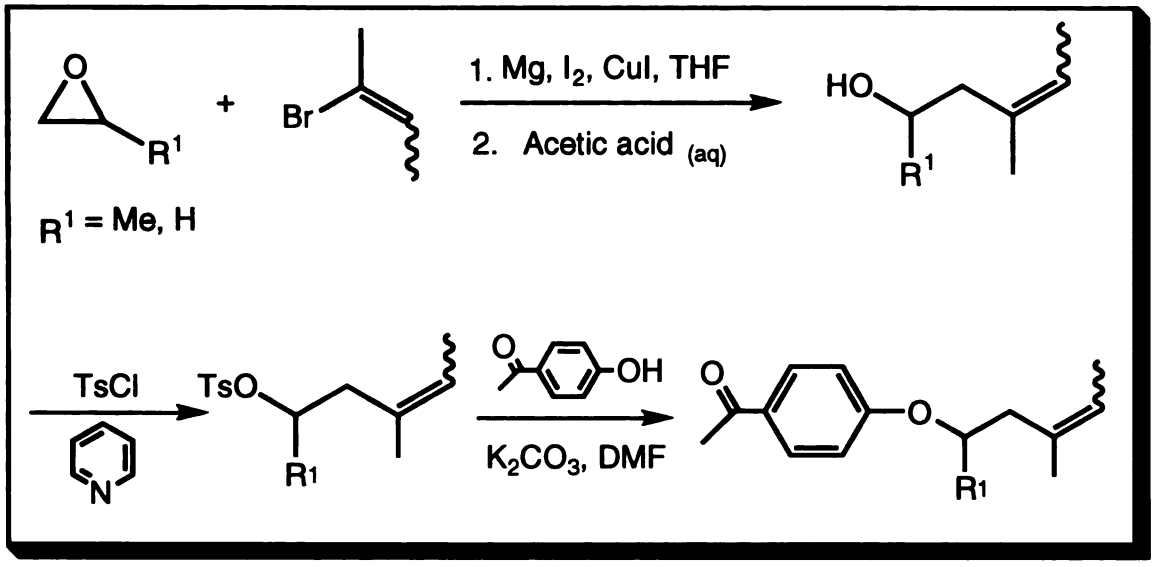
mercury chloride, gave the corresponding alcohol. Tosylation and coupling provided the ketone **p-M_2M_3K** (Scheme 13).

Scheme 13



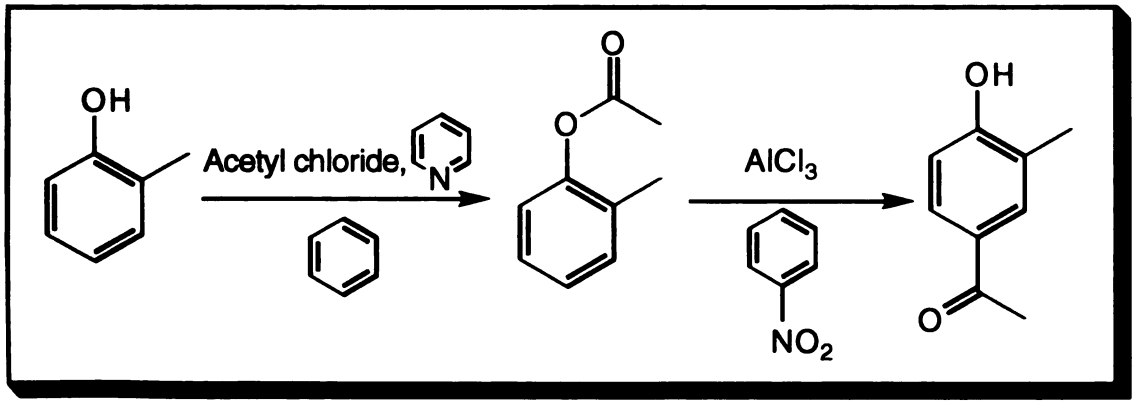
The alcohols for **p-M_3M_4K** and **p-$M_1M_3M_4K$** were prepared by reaction of ethylene oxide or propylene oxide and vinyl cuprate reagents (Scheme 14).

Scheme 14



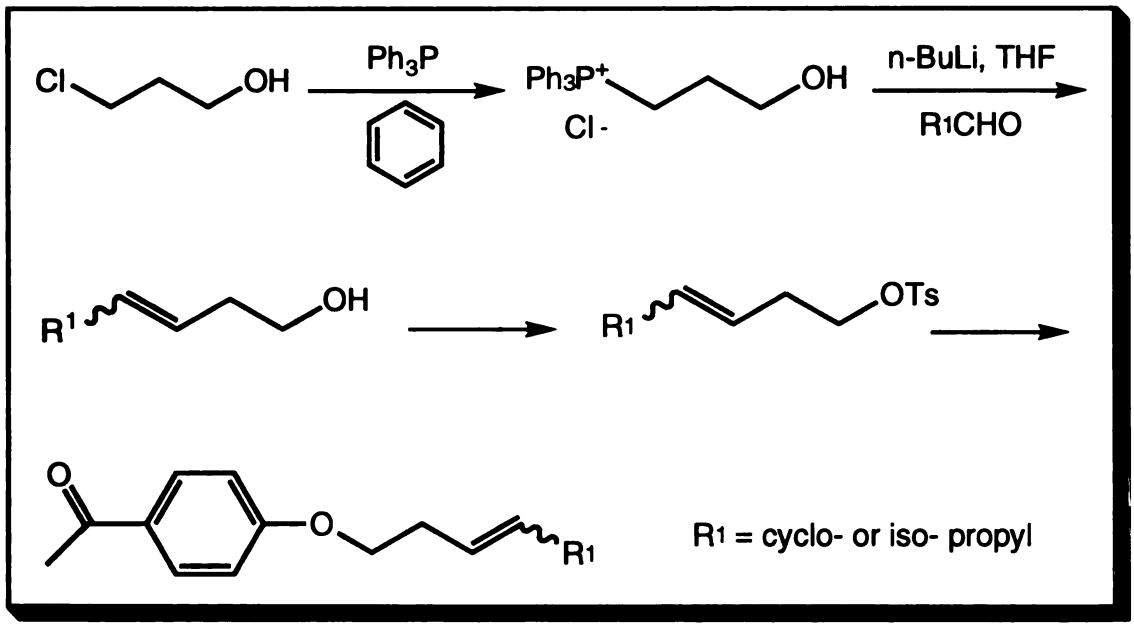
The methyl-substituted hydroxyacetophenones were prepared by a thermal Fries rearrangement method. The hydroxyl group of *o*-cresol was protected by an acetyl group. Stirring in the presence of aluminum chloride in nitrobenzene at room temperature generated the rearranged 4-hydroxy-3-methylacetophenone (Scheme 15). This compound was used for the syntheses of **p-$M_3M_4M_5K$**, **p-$M_1M_3M_4M_5K$** and **p-M_4M_5K**.

Scheme 15



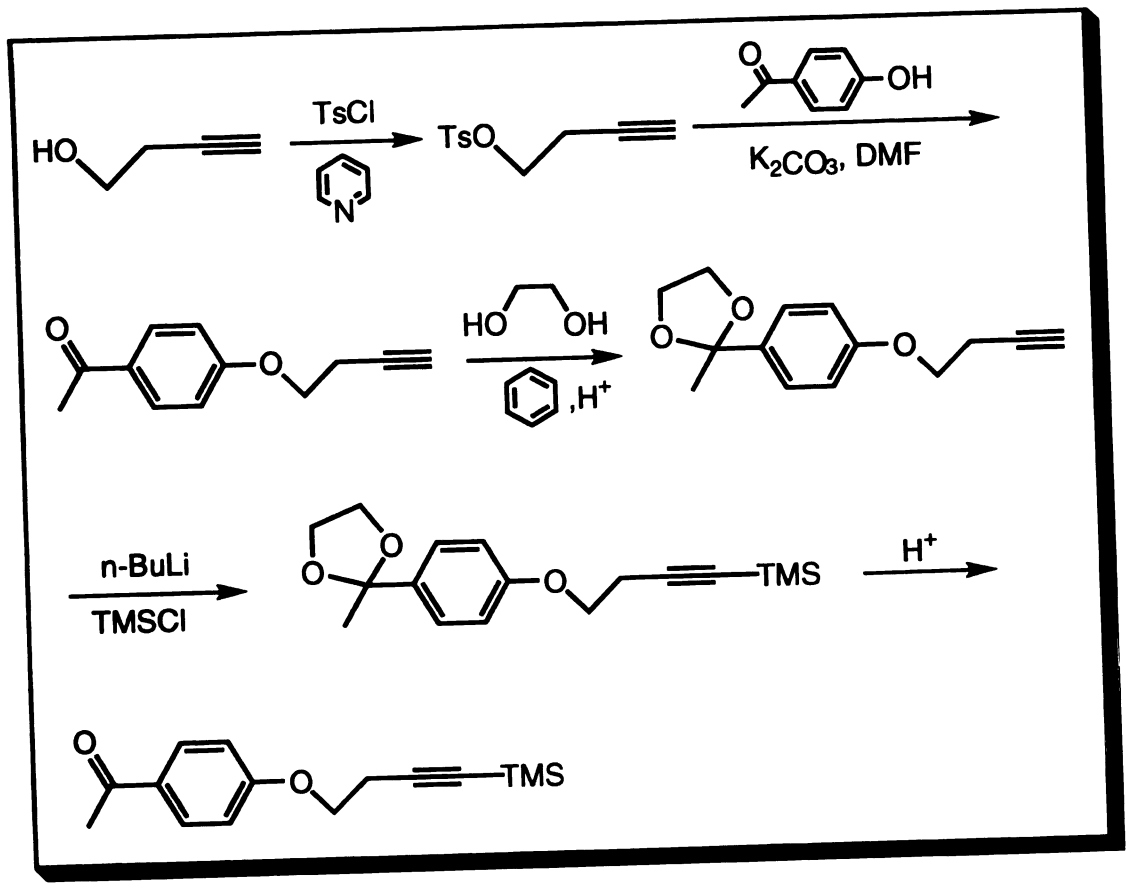
Alcohols used to prepare **p-C_4K** and **p-I_4K** were prepared by Wittig reaction between 3-hydroxypropyltriphenylphosphonium chloride and cyclopropane-carboxaldehyde or isobutyraldehyde (Scheme 16).

Scheme 16



4'-(3-Butyn-1-oxy)acetophenone was prepared by the coupling method and then protected by ethylene glycol. A trimethylsilyl group was added to the end the triplet bond, and final deprotection was performed in aqueous HCl solution (Scheme 17).

Scheme 17



II. Photocycloadditions and Identification of Photoproducts

a. General

All photoproducts were identified by nuclear magnetic resonance spectroscopy (^{1}H-NMR and ^{13}C-NMR).

For small scale photolysis, 0.7 mL argon-bubbled methanol solutions of various alkyl-substituted alkenoxyacetophenones (0.01 to 0.03 M) were irradiated with a medium pressure mercury arc filtered so as to isolate the 313 nm band or filtered only by Pyrex glass filter (> 290 nm). Time-resolved NMR analysis indicated clean conversion of each reactant into a mixture of two diastereomers of 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-dienes (from *para* ketones) or 9-acetyl-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-dienes (from *ortho* ketones). Diastereomeric product ratio was determined by integration of olefinic and/or methyl group signals observed in high resolution ^{1}H-NMR spectra. Chemical yields were measured by integration of methyl group signals in the ^{1}H-NMR spectra relative to an internal standard (methyl benzoate). The stereochemistry of photoproducts was determined by nuclear Overhauser effect experiments (nOe).

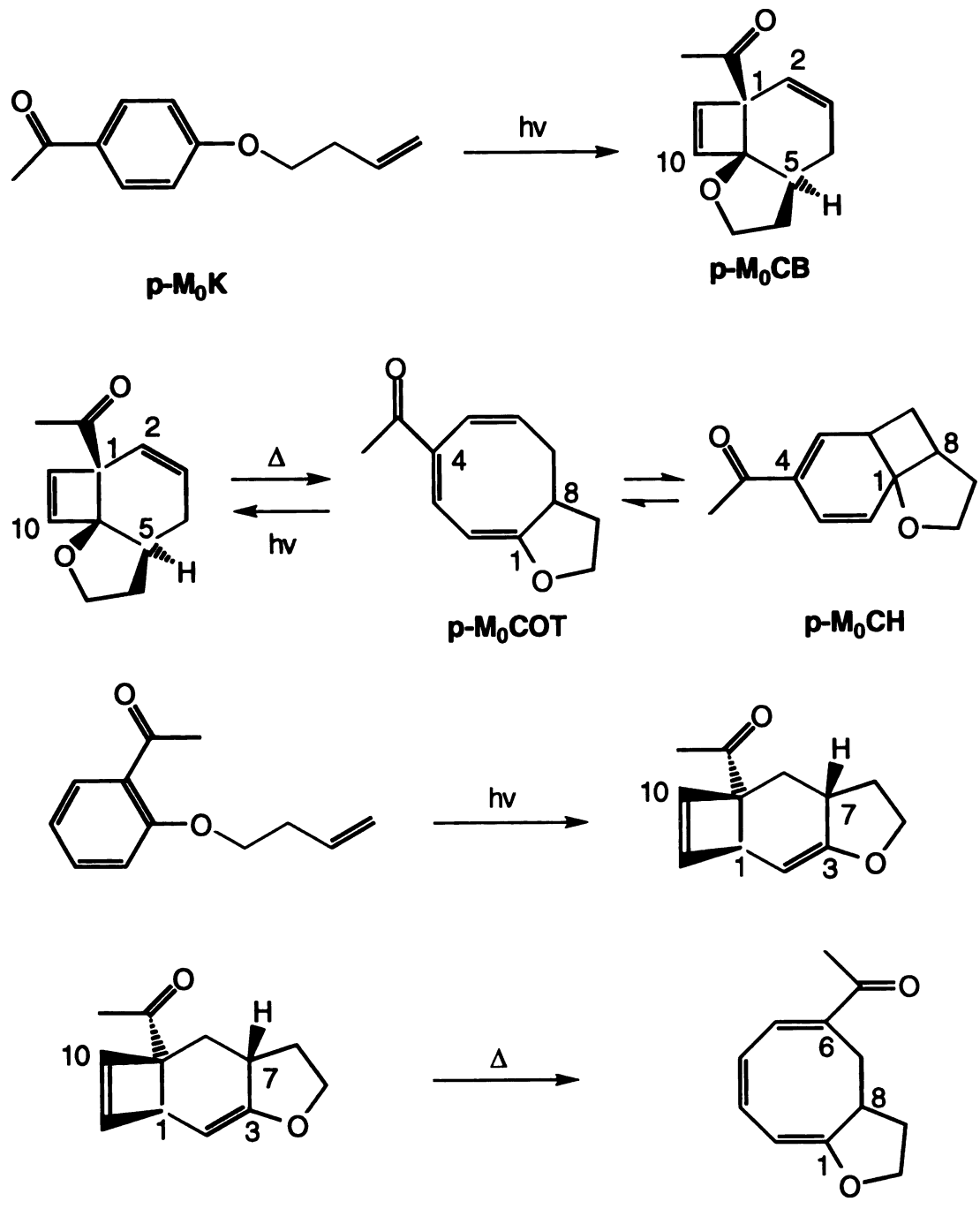
These 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undec-2,10-dienes (henceforth abbreviated as **CB**, cyclobutenes) were then converted thermally (either standing at room temperature for a few days or heated at 40°C overnight) to equilibrium mixtures of 4-acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (henceforth abbreviated as **COT**, cycloöctatriene) and/or 4-acetyl-11-oxatricyclo[6.3.0.0] undeca-2,4-diene (refer to the **CH**, cyclohexadiene). Similarly, 9-acetyl-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-dienes were converted to 6-acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (refer to the **COT**, cycloöctatriene). Again, isomer ratios were determined by ^{1}H-NMR, while the stereochemistry was confirmed by nOe experiments of isolated products .

For the purpose of isolation, large scale photolyses were performed in 100 mL Pyrex test tubes or Pyrex reactors. Argon-bubbled methanol solutions 0.01-0.02 M in various alkyl-substituted alkenoxyacetophenones (ca. 0.2 g in 120 mL methanol) were irradiated above 290 nm and the progress of irradiation was checked with TLC, GC or HPLC by removal of a small aliquot by syringe. After > 95% conversion, the solvent was evaporated and the residue was purified by alumina or silica gel column chromatography. The isolated products were re-identified as cyclohexadienes, cycloöctatrienes or cyclobutenes, depending on how stable the cyclobutenes are after chromatography at room temperature. The isolated yield was also measured and the isolated products (**COT** or **CH**) could be used for quantum yield determination. Also, the isolated products (**COT** or **CH**) were irradiated again to confirm the formation of cyclobutenes (**CB**). Scheme 18 describes briefly the observed photoreactions and subsequent thermal rearrangements.

The diastereoselectivity of the reaction is characterized by the diastereomeric excess (de) as defined in eq. (4); where c and c' are the concentration of the major and minor isomers ,respectively, of cyclohexadienes, cycloöctatrienes or cyclobutenes in the mixture.[58]

$$\% \text{ de} = (c - c' / c + c') \times 100 \qquad (4)$$

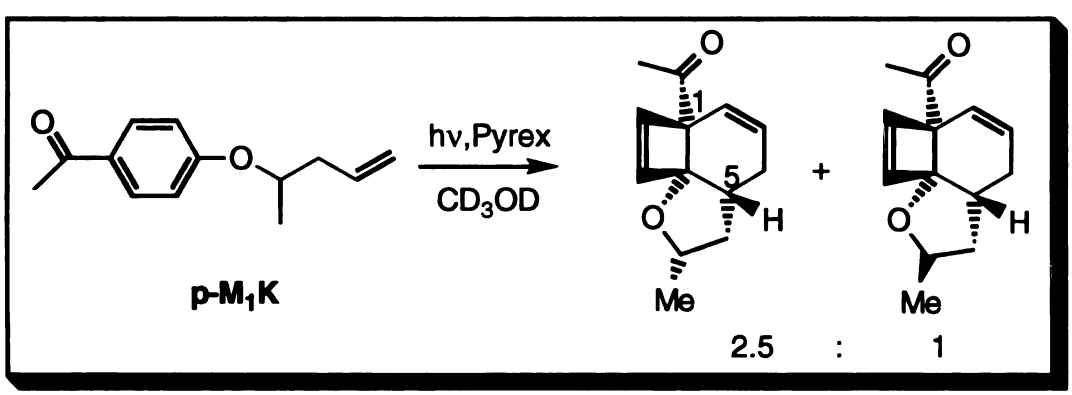
Scheme 18



b. **p-M_0K**

An NMR tube containing 2.0 x 10^{-2} M **p-M_0K** in CD_3OD was irradiated with a Pyrex-filtered mercury arc, following Nahm's procedures.[59] 1-Acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene and a small amount of 4-acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene were identified by ^{1}H-NMR spectroscopy at low conversion but only 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene was obtained after completion. NOe showed the bridgehead proton H_5 and cyclobutene ring *cis* to each other. The 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene converted totally to 4-acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene in 2 days at room temperature, whereas Nahm performed the conversion at 200°C.[59]

c. **p-M_1K**

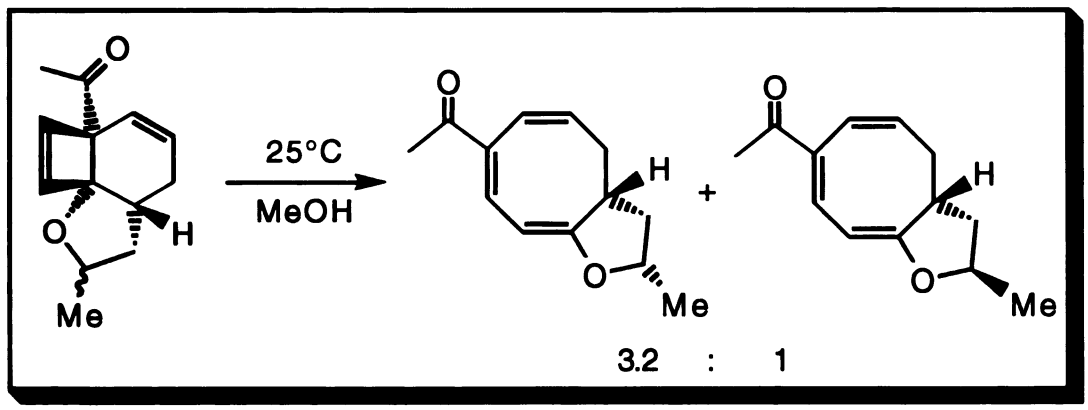


An NMR tube containing 3.4 x 10^{-2} M **p-M_1K** and 3.3 mg methyl benzoate in CD_3OD was degassed with argon and irradiated by Pyrex-filtered mercury arc. After 100 % conversion, two photoproducts were identified by ^{1}H-NMR as diastereomers of 1-acetyl-7-methyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene. The chemical yield was 85%, which was measured by NMR integration of the

methyl group of methyl benzoate (δ 3.99) and the products' acetyl groups (δ 2.183 and δ 2.185). A diastereomeric excess (de) of 41% was determined by integration of the 7-Me doublets (δ = 1.05 vs. δ 1.14 in a ratio 2.5 : 1). Two AB quartet patterns at δ 6.29, 6.42 (J = 2.8 Hz) and δ 6.28, 6.34 (J = 2.9 Hz) represent the isomeric pair of cyclobutene hydrogens. It is interesting that $H_{4\alpha}$ is coupled to H_2 through allylic coupling (J = 2.3 Hz) in this rigid structure but $H_{4\beta}$ isn't. The stereochemistry of $H_{4\alpha}$ and $H_{4\beta}$ was assigned from the nOe experiments.

The nOe results indicated that the major photoproduct has the bridgehead proton H_5 and 7-Me *trans* to each other, but H_5 and cyclobutene ring *cis* to each other. The minor photoproduct also has H_5 and the cyclobutene ring *cis* to each other, but the bridgehead proton H_5 and 7-Me are also *cis* to each other.

When the reaction was performed at 313 nm, it gave identical results. In addition, there were only slight differences in diastereomeric excess (de) when this compound was irradiated in either benzene or acetonitrile.



A dry methanol solution (210 mL) of **p-M_1K** (8×10^{-3} M) was bubbled with argon and monitored by TLC or GC during irradiation (Pyrex filter) until 100 % conversion. The solvent was evaporated at 45°C and the residue changed from

colorless to yellow. The product mixture was passed through a silica gel column and the isolated yield was 63 %. The structures were identified as diastereomers of 4-acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene from the following spectroscopic data: Pairs of resonances were observed in both the olefinic and aliphatic regions of ^{1}H-NMR spectra, 10-Me (δ 1.33 vs. δ 1.34) and COMe (δ 2.31 vs. δ 2.35). The well-resolved pattern of olefinic peaks was assigned to two cycloöctatriene skeletons; the major has δ 5.36 (dd), 6.02 (dt), 6.36 (d), 6.99 (d), and the minor has δ 5.41 (dd), 5.89 (dt), 6.25 (dt), 7.06 (d), with only slight difference in coupling constants: $J_{2,3}$ = 8.0 Hz, $J_{5,6}$ = 11.3 Hz (major) and $J_{2,3}$ = 6.3 Hz, $J_{5,6}$ = 13.1 Hz (minor). A diastereomeric excess (de) of 56 % was determined by integration of H_{10} signals (δ = 4.41 vs. 4.71 in a ratio of 3.2 : 1 in Figure 3). The discrepancy in the ratio of diastereoselectivity between **COT** (56%) and **CB** (41%) is probably due to limitations in the integration of NMR spectroscopy. Another possibility is a little decomposition of **COT** during the interconversion from **CB** to **COT**.

The UV-Visible spectrum showed a λ_{max} at 344 nm and IR spectrum had a peak at 1682 cm^{-1} indicative of a highly conjugated carbonyl compound. An identical molecular ion peak to the starting ketone was found in the mass spectrum.

The cycloöctatriene diastereomers were irradiated in methanol to gave the same 3.2:1 ratio of diastereomeric 1-acetyl-7-methyl-8-oxatricyclo-[7.2.0.0^{5,9}]undec-2,10-dienes. (Figure 3,4) The cycloöctatriene diastereomers were separated by neutral alumina chromatography. Since the stereoselectivity observed for the cycloöctatrienes is the same as for cyclobutene formation, the bridgehead proton H_8 and Me_{10} are assigned *trans* to each other in the major cycloöctatriene and *cis* in the minor. This was confirmed by nOe experiments.

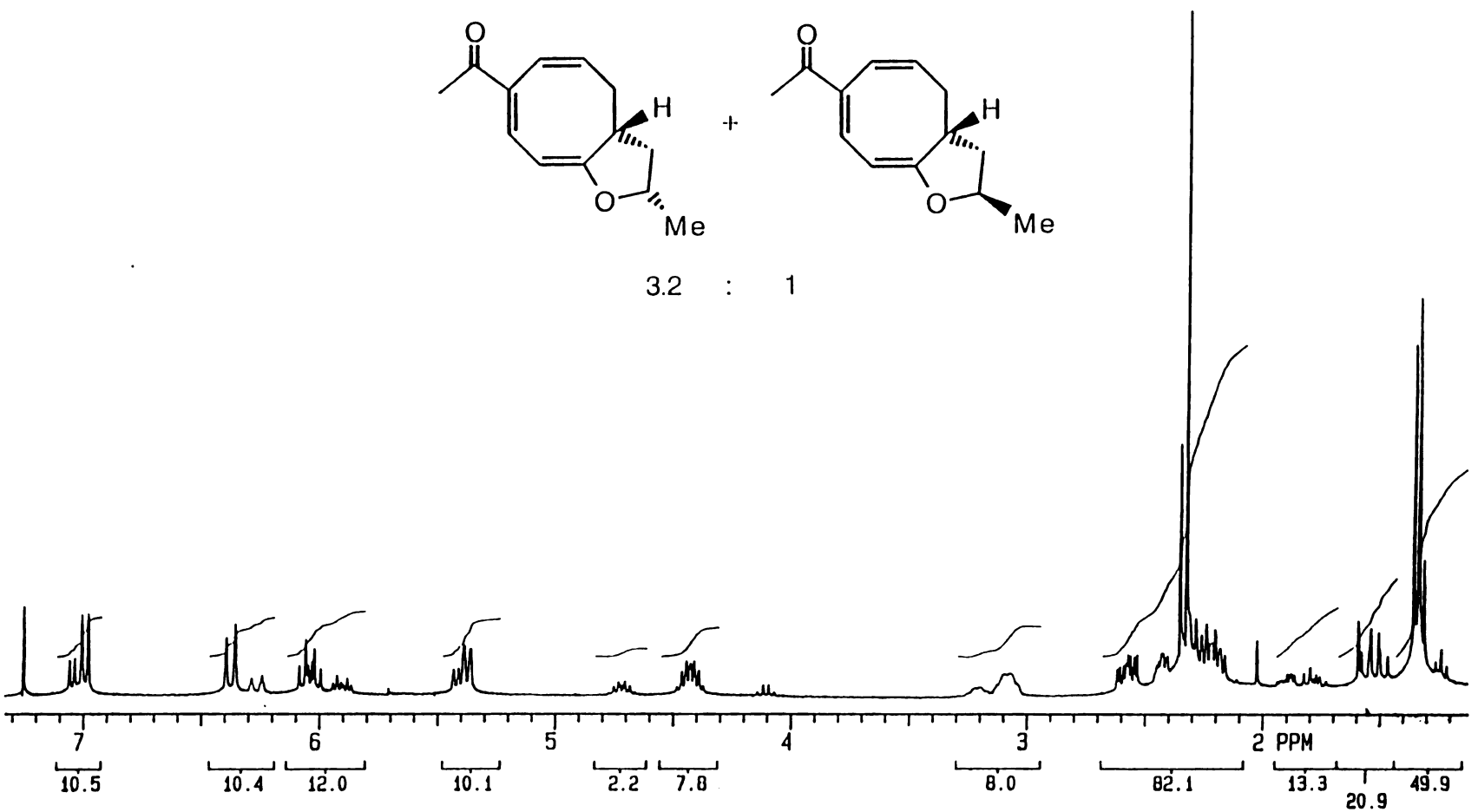


Figure 3. ^{1}H-NMR spectrum of 4-acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**p-M_1COT**) in $CDCl_3$

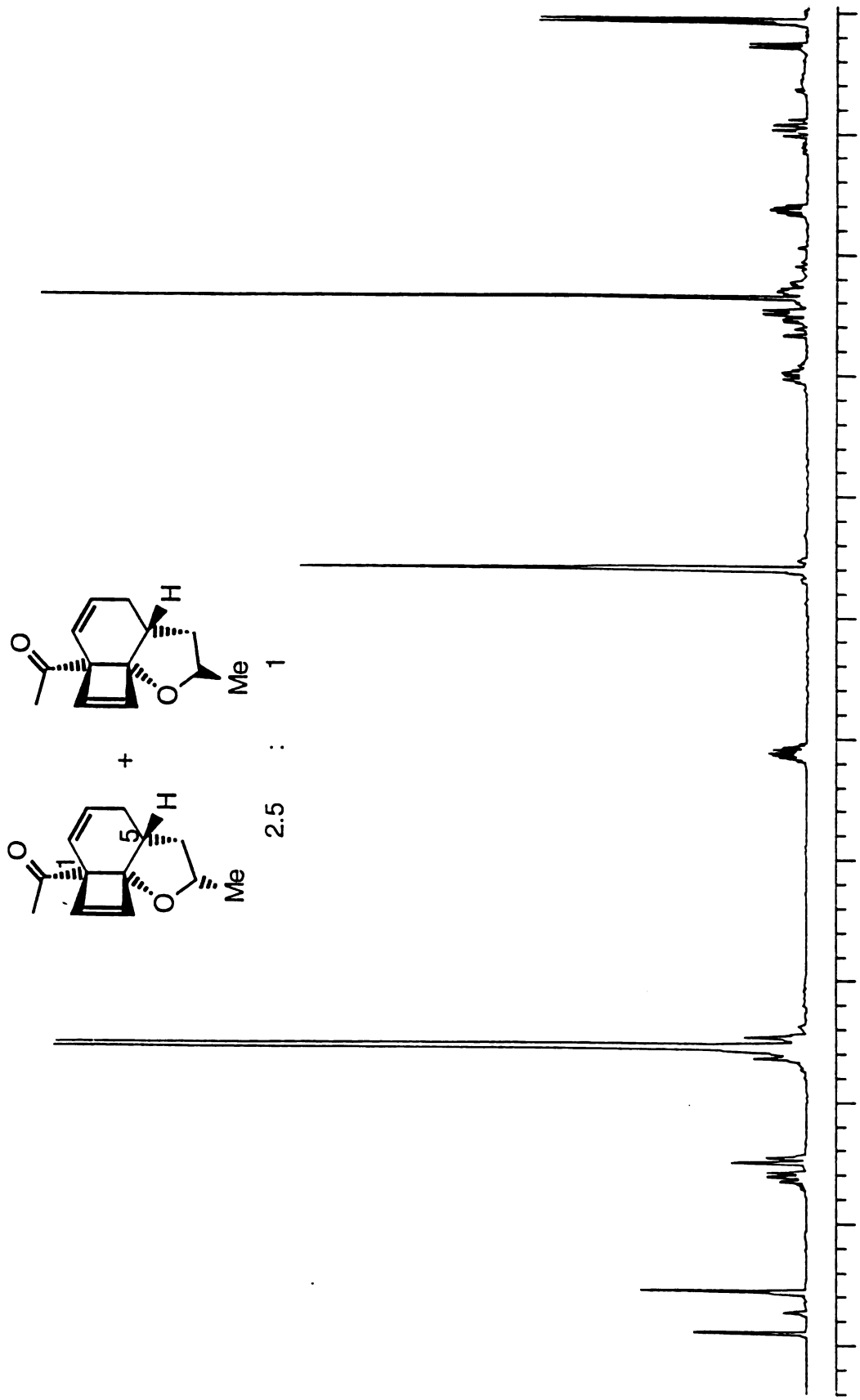
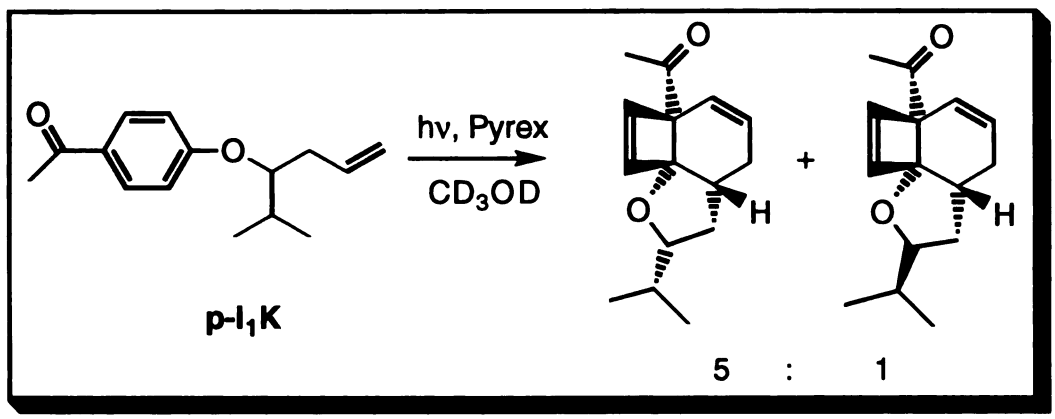


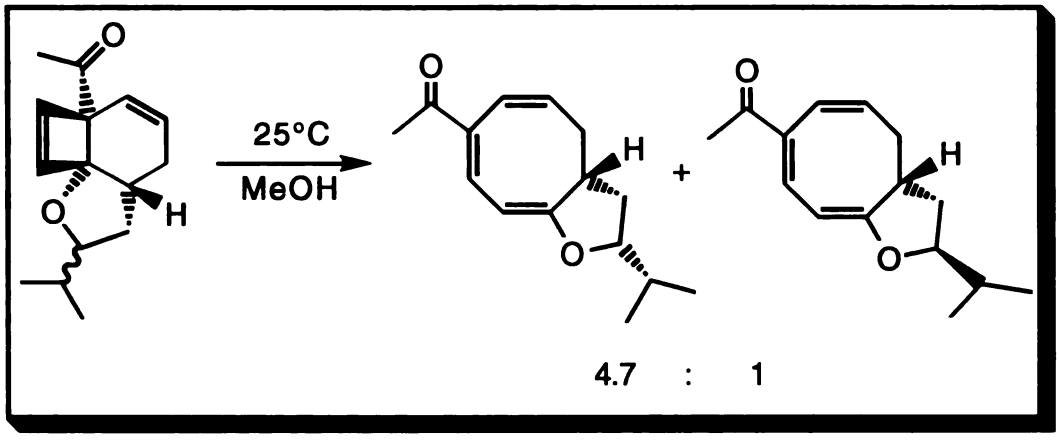
Figure 4. ^{1}H-NMR spectrum of 1-acetyl-7-methyl-8-oxatricyclo-[7.2.0.0^{5,9}]undec-2,10-dienes (**p-M$_1$CB**) in CD_3OD, obtained by irradiation of **p-M$_1$COT**

d. **p-I_1K**



A mixture of 2.0 mg of **p-I_1K** and 4.3 mg internal standard (methyl benzoate) in a 0.6 mL CD_3OD (0.015 M) was degassed and irradiated by mercury arc with a Pyrex filter. Photoreactions were followed by ^{1}H-NMR spectroscopy from 100 % of reactant to 0 %. Photoproducts were characterized as a pair of 1-acetyl-7-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene diastereomers, as in the previous example. Two sets of peaks were obtained in ^{1}H-NMR spectrum. A pair of AB quartets at δ 6.25, 6.45 and δ 6.27, 6.35 were assigned to two cyclobutenes. Two multiplets (dd) at δ 0.47, 0.88 and δ 0.83, 0.90 represented two non-equivalent methyls in each isopropyl group due to an adjacent chiral center. Integration of the two H_{10} signals (δ 6.45 vs. δ 6.35) indicated 90% chemical yield and 67% diastereomeric excess.

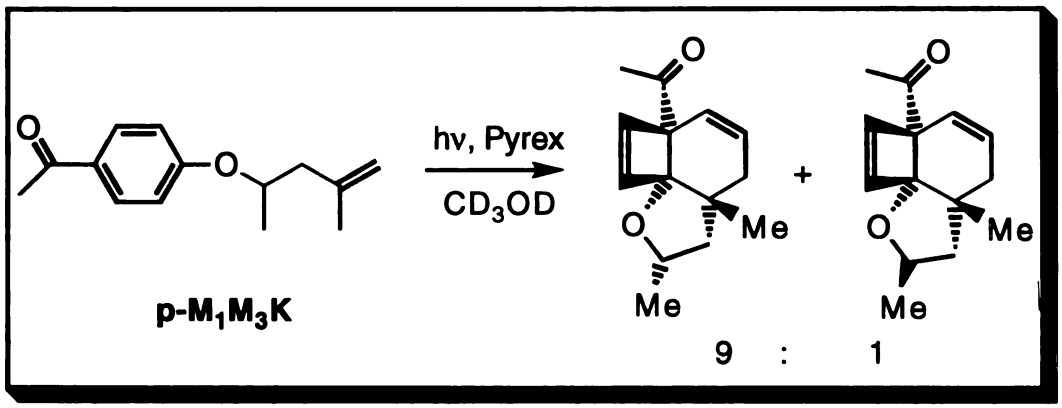
The major diastereomer has the bridgehead proton H_5 and i-Pr_7 *trans* to each other, and H_5 is *cis* to the cyclobutene ring. The minor product had the bridgehead proton H_5 and i-Pr_7 *cis* to each other and the cyclobutene ring.



A solution of 0.10 g **p-H_1K** in a MeOH (60 mL), was degassed and irradiated at >290 nm. The reaction was monitored by TLC or GC to 100 % conversion. After removal of solvent, the residue was purified by silica gel column chromatography to give two products in 68% isolated yield. The structures were identified as the two diastereomers of 4-acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene from the following spectroscopic results: ^{1}H-NMR spectrum showed two sets of four vinyl protons; δ 5.37 (dd, J = 8.4, 2.2 Hz, H_2), 6.05 (dt, J = 10.8, 8.1 Hz, H_6), 6.32 (d, J = 10.8 Hz, H_5) and 7.09 (d, J = 8.4 Hz, H_3) for the major and δ 5.40 (d, J = 6.3 Hz, H_2), 5.86 (dt, J = 13.2, 4.3 Hz, H_6), 6.20 (dt, J = 13.2, 2.2 Hz, H_5) and 7.17 (d, J = 6.3 Hz, H_3) for the minor. The diastereomeric excess, determined by integration of the two H_3 signals , is 65%. In addition, there are two acetyl groups at δ 2.31 and 2.34 and two sets of doublets (δ 0.90, 1.00 and δ 0.89, 0.99) representing the isopropyl group of each diastereomer. There are also two peaks (δ 199.1 and 199.5) due to the carbonyl group in the ^{13}C-NMR spectrum. The conjugated carbonyl group was confirmed by IR (1682 cm^{-1}) and UV (346 nm) spectra . Both high- and low- resolution Mass spectra gave the identical molecular ion for starting ketone and product mixture. Separation of the diastereomers was unsuccessful.

Because the diastereomeric ratios of 1-acetyl-7-isopropyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene and 4-acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene are nearly identical, the major product of 4-acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-trienes are assigned with the bridgehead proton H_8 and i-Pr_{10} *trans* to each other. The minor product has the bridgehead proton H_8 and i-Pr_{10} *cis* to each other.

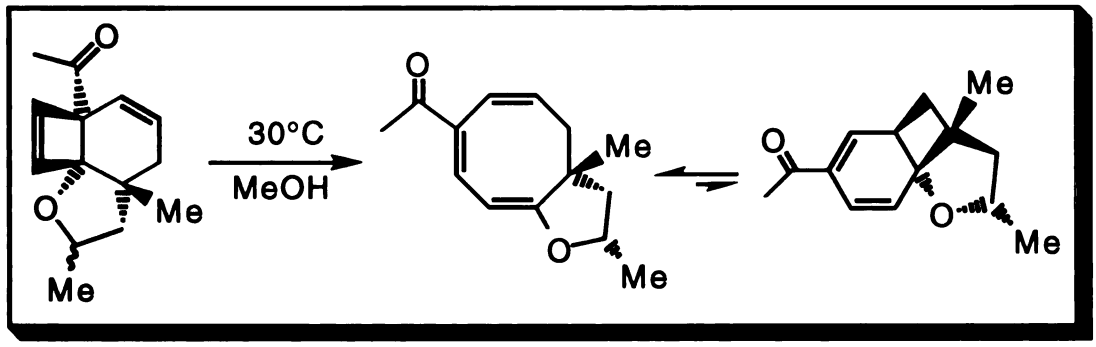
e. **p-M_1M_3K**



A 0.024 M argon-degassed CD_3OD solution of **p-M_1M_3K** and internal standard (methyl benzoate) was photolyzed in a NMR tube through a Pyrex filter. The reaction was monitored by ^{1}H-NMR spectra to 100% conversion. The products were characterized as two diastereomers of 1-acetyl-5,7-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene. Integration of the two 10-Me signals determined a diastereomeric excess of 80 % and chemical yield 78%. Due to the higher selectivity, the minor product was difficult to observe by ^{1}H-NMR spectroscopy. The major cyclobutene had an AB quartet (δ 6.35 and 6.45, J = 2.9 Hz, H_{10} and H_{11}) and two olefinic protons (δ 5.75 ,dd, J = 10.0, 2.9 Hz, H_2 and δ 5.77, ddd, J = 10.0, 6.1, 1.7 Hz, H_3) and a bridgehead methyl group (δ

1.08, 5-Me), instead of a proton. This simplified the interpretation of the ^{1}H-NMR spectrum. When the reaction was carried out in either C_6D_6 or CD_3CN, identical selectivity was observed.

NOe measurements showed that the major product had a bridgehead methyl group, 5-Me, *cis* to the cyclobutene group but *trans* to the 7-Me.

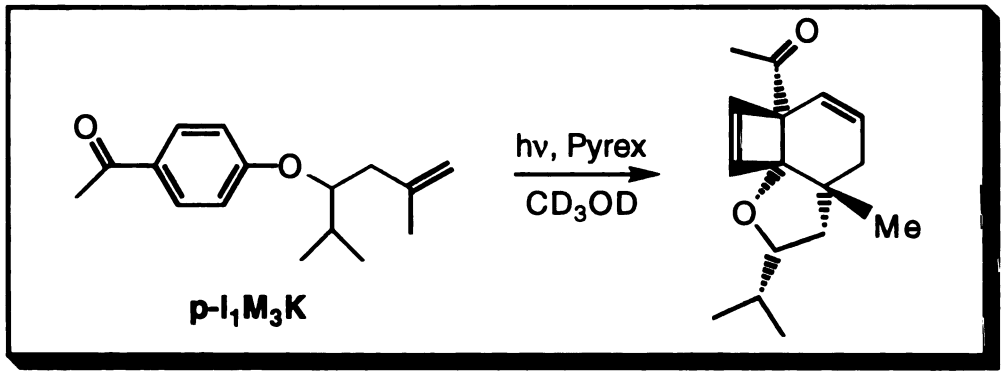


A degassed methanol solution of **p-M_1M_3K** (0.01 M) was irradiated at > 290 nm. After completion, the solution was heated at 30°C in warm water for 24 h until the solution color turned to yellow. After silica gel column chromatography, the products were identified as an equilibrium of 4-acetyl-8,10-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene and 4-acetyl-8,10-dimethyl-11-oxatricyclo-[6.3.0.0^{1,6}]undeca-2,4-diene in a 3 : 1 ratio at room temperature. The major product had olefinic proton signals typical of cycloöctatriene; δ 5.17 (d, J = 6.6 Hz, H_2), 6.19 (ddd, J = 10.8, 9.1, 7.1 Hz, H_6), 6.36 (d, J = 10.8 Hz, H_5) and 7.17 (d, J= 6.6 Hz, H_3), but the minor isomer had olefinic signals characteric of a cyclohexadiene; δ 5.59 (d, J = 10.2 Hz, H_2), 6.68 (dd, J = 10.2, 1.6 Hz, H_3) and 7.01 (dd, J = 6.5, 1.6 Hz, H_5). In particular, the spectrum indicated an allylic proton at δ 3.14 (dt, J = 10.4, 6.5, Hz) which was assigned to H_6 of cyclohexadiene. The 3 : 1 ratio was measured by integration of the acetyl methyl group in cycloöctatriene (δ 2.32) and cyclohexadiene(δ 2.30). A small amount of

the other cyclohexadiene diastereomer was detected by its characteristic vinyl proton signals.

Since only one major stereoisomer of the cycloöctatriene was detected in ^{1}H-NMR spectrum, the stereochemistry was assigned as in the 1-acetyl-5,7-dimethyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene example. This fact determined that the major product has the bridgehead methyl group, 5-Me, *trans* to the 7-Me group.

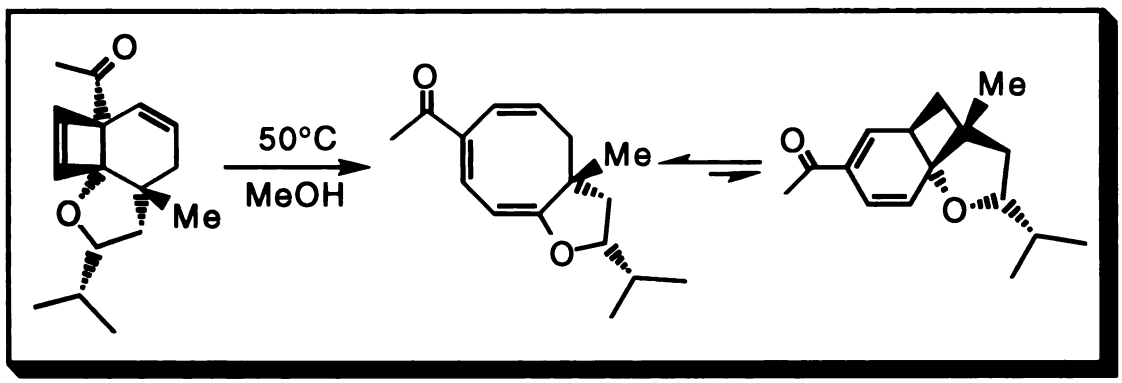
f. **p-I$_1$M$_3$K**



An oxygen-free CD_3OD solution of **p-I$_1$M$_3$K** (0.016 M) containing methyl benzoate was irradiated through a Pyrex filter for 1 h. The product detected by ^{1}H-NMR spectroscopy was identified as 1-acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene in 75% chemical yield and >95% diastereomeric excess. The ^{1}H-NMR spectrum is similar to 1-acetyl-5,7-dimethyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene except for two new doublets at δ 0.71 (J = 6.6 Hz) and δ 0.88 (J = 6.6 Hz) attributed to the 7-iPr group. The bridgehead methyl (5-Me) facilitated interpretation of the ^{1}H-NMR spectrum. The ^{13}C-NMR spectrum was obtained at -20°C to prevent thermal rearrangement. The chemical

shift at δ 214.9 was assigned to the cyclobutene carbonyl substituent, which is nonconjugated.

An nOe experiment indicated that the product has a bridgehead methyl group , 5-Me, *cis* to the cyclobutene group but *trans* to the 7-iPr group.



Ketone **p-I_1M_3K** (0.008 M) was photolyzed in methanol in a manner similar to **p-M_1M_3K**. After heating at 50°C overnight, the products were purified by silica gel column chromatography and identified as an equilibrium mixture of 4-acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene and 4-acetyl-10-isopropyl-8-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene in a ratio of 3 : 1 at room temperature This is similar to the previous example (**p-M_1M_3K**). No other diastereomer could be detected.

^{1}H-NMR showed different sets of peaks for each isomer; δ 1.14 (8-Me), δ 5.23 (d, J = 6.6 Hz, H_2), 6.18 (ddd, J = 10.6, 9.4, 7.2 Hz, H_6), 6.41 (d, J = 10.6 Hz, H_5) and 7.08 (d, J= 6.6 Hz, H_3) for the cycloöctatriene and δ 1.13 (8-Me), δ 5.61 (d, J = 10.3 Hz, H_2), 6.74 (dd, J = 10.3, 1.6 Hz, H_3) and 6.80 (dd, J = 6.2, 1.6 Hz, H_5) for the cyclohexadiene. The IR spectrum indicated two carbonyl group absorptions (1676 cm^{-1} and 1647 cm^{-1}), confirmed by ^{13}C-NMR spectroscopy (δ 198.6 vs. δ 196.7). 2D-COSY spectroscopy also showed the equilibrium of cycloöctatriene and cyclohexadiene. UV-visible spectra had an absorption at 344

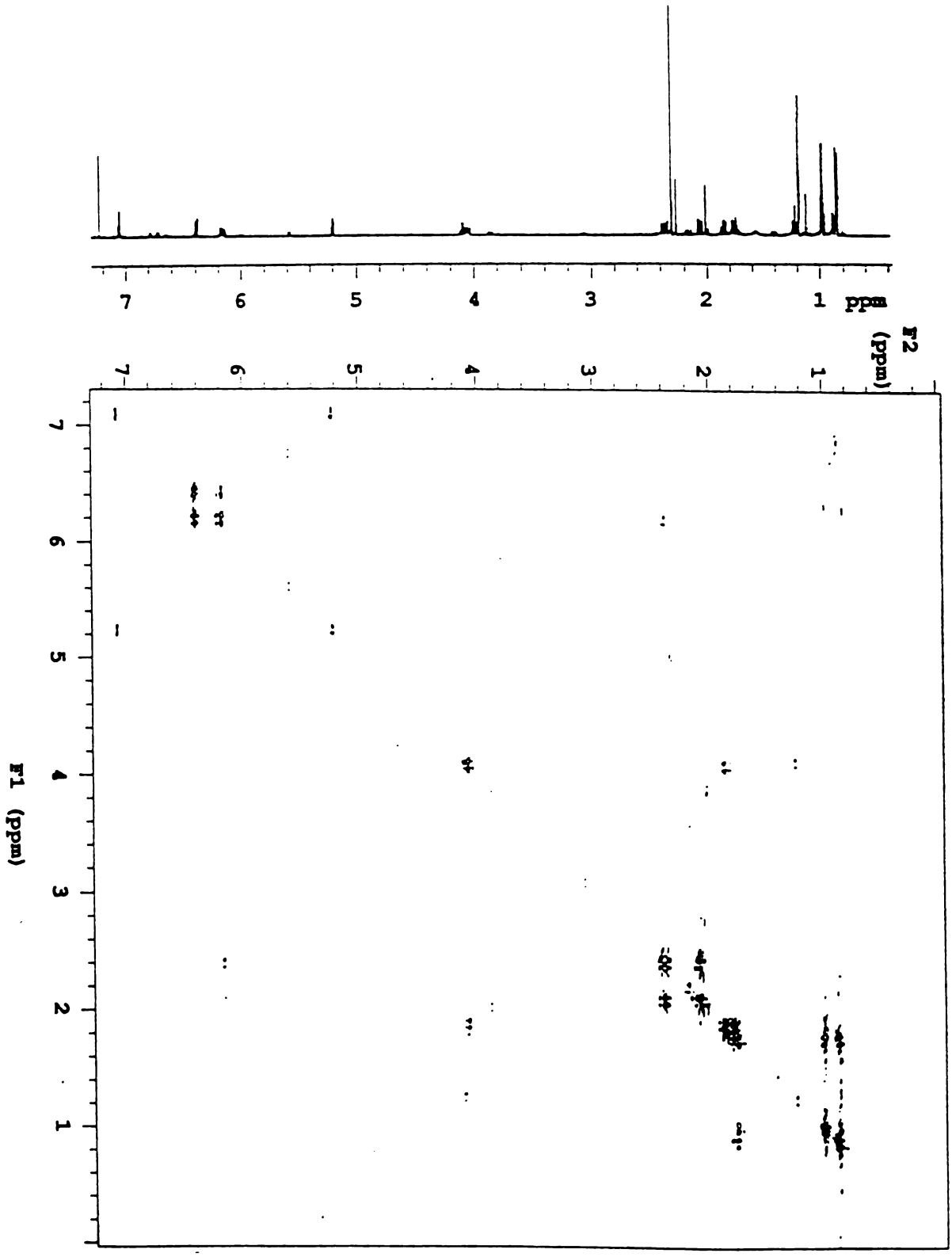


Figure 5. 2D COSY spectrum of the equilibrium of 4-acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**p-I_1M_3COT**) and 4-acetyl-10-isopropyl-8-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene (**p-I_1M_3CH**) in $CDCl_3$

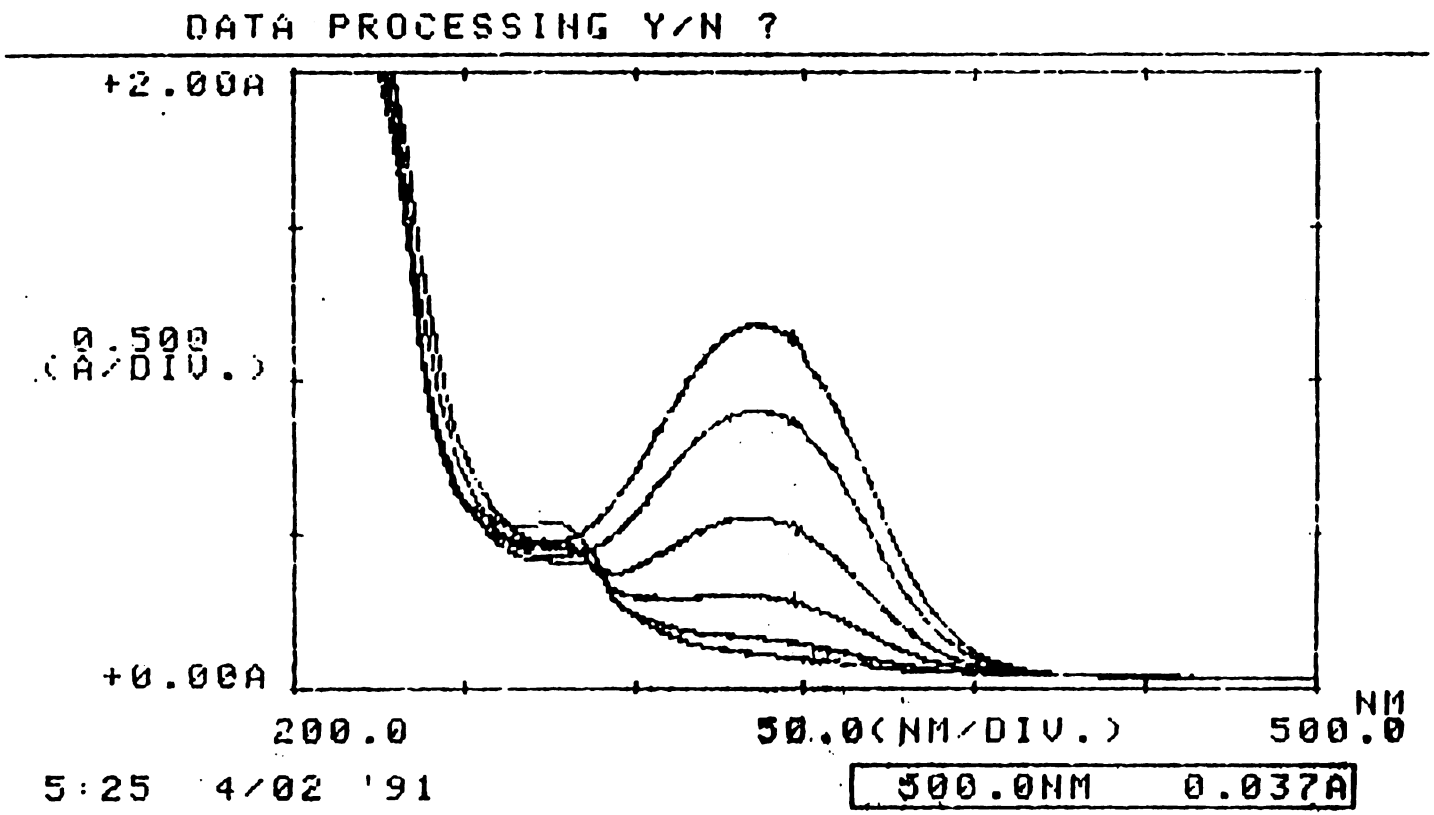
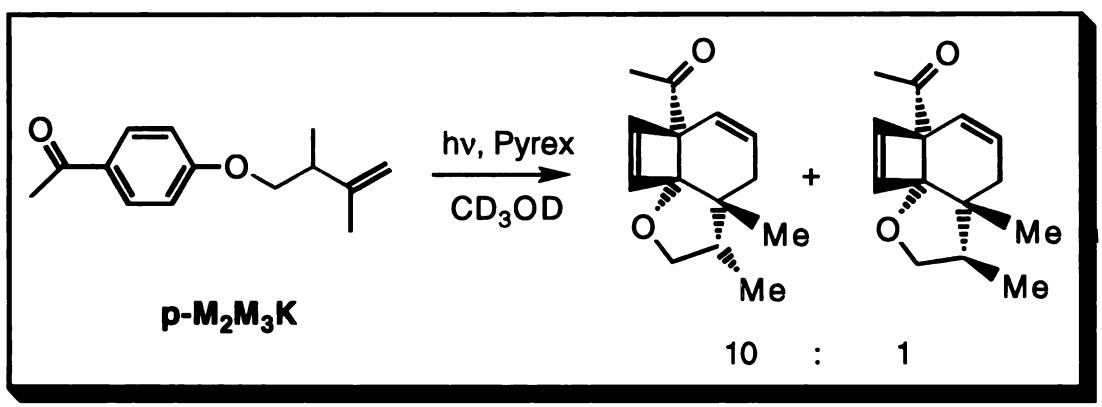


Figure 6. Time-resolved UV-Visible spectra of 4-acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**p-I_1M_3COT**) at 313 nm irradiation in methanol (1.70 x 10^{-4} M).

nm due to the cycloöctatriene chromophore (Figure 5,6), and the mass spectrum indicated a parent ion isomeric with the starting ketone **p-I_1M_3K**. Reirradiation of the equilibrium mixture yielded the same 1-acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene obtained in the initial cycloaddition.

Furthermore, an nOe experiment showed that the bridgehead 8-Me is *trans* to the 10-iPr group just as it is in the cyclobutene.

g. **p-M_2M_3K**



A solution of **p-M_2M_3K** and methyl benzoate in CD_3OD was irradiated at > 290 nm for 12 h. The photoproducts were determined to be a pair of diastereomers of 1-acetyl-5,6-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene in 82 % diastereomeric excess and 76 % chemical yield. The singlet at δ 0.92 and doublet at δ 0.97 (J = 6.9 Hz) could be assigned to 5-Me and 6-Me of the major diastereomer, respectively. An AB quartet at δ 6.21, 6.33 (J = 3.0 Hz) is characteristic of a cyclobutene ring (Figure 7).

An nOe experiment on this cyclobutene couldn't be carried out due to the close proximity of the two methyls. However, the stereochemistry of the major product could be determined as having the 5-Me and 6-Me *trans* to each other from nOe experiments involving the thermally rearranged cyclohexadiene isomer.

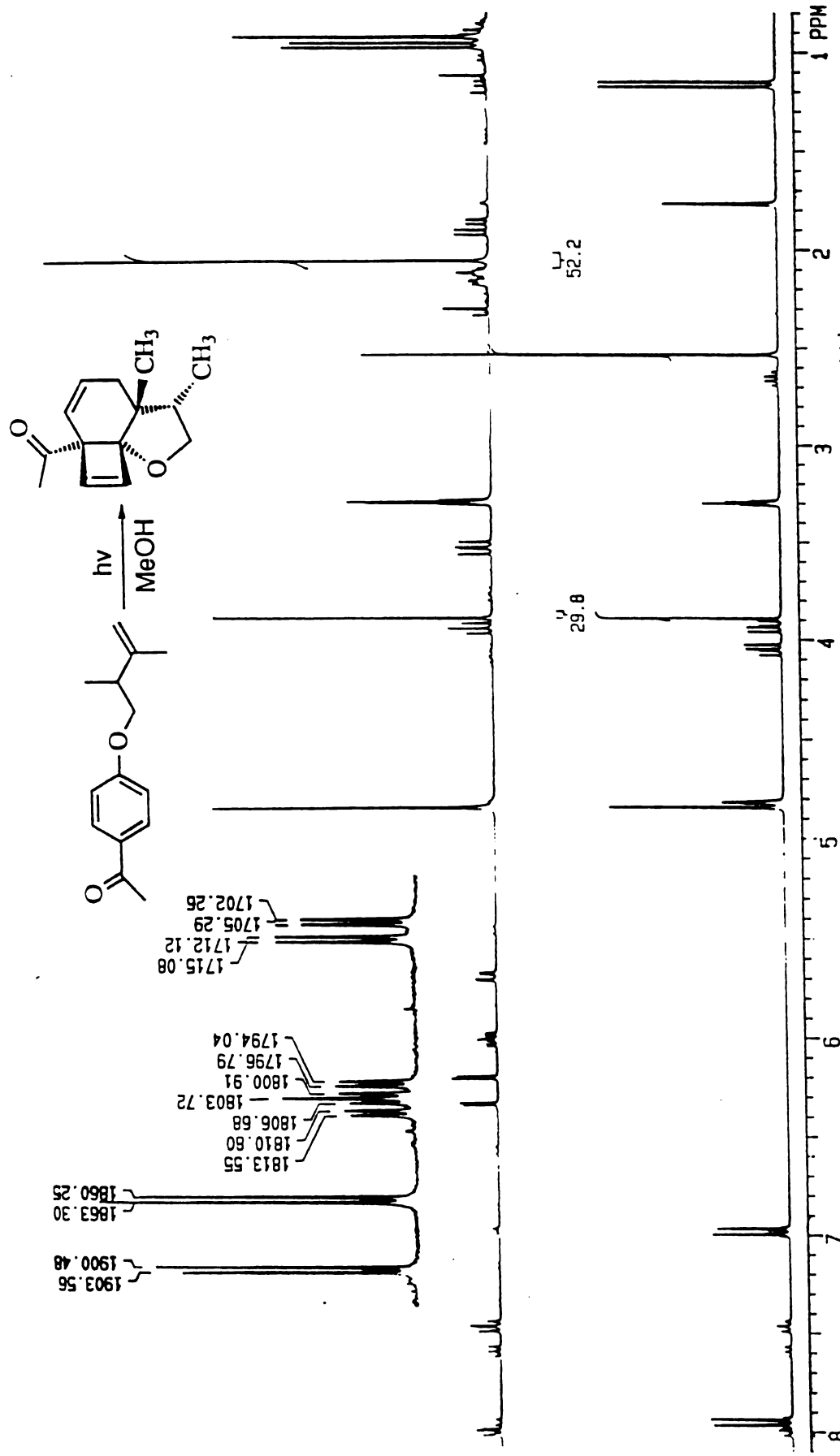
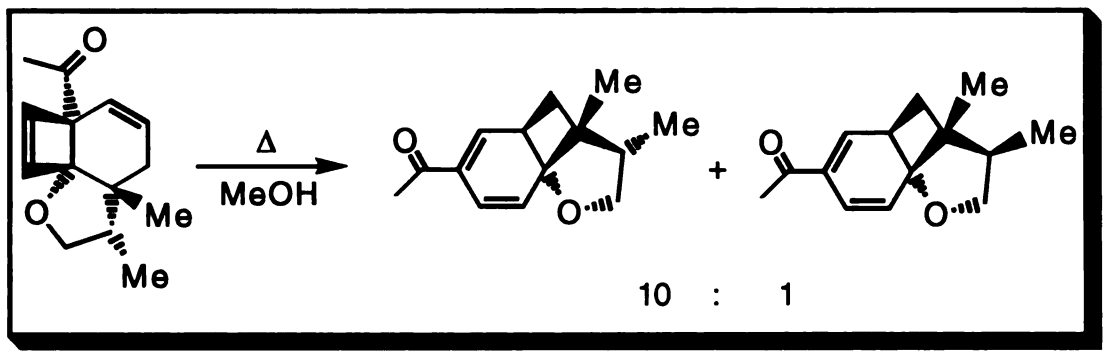


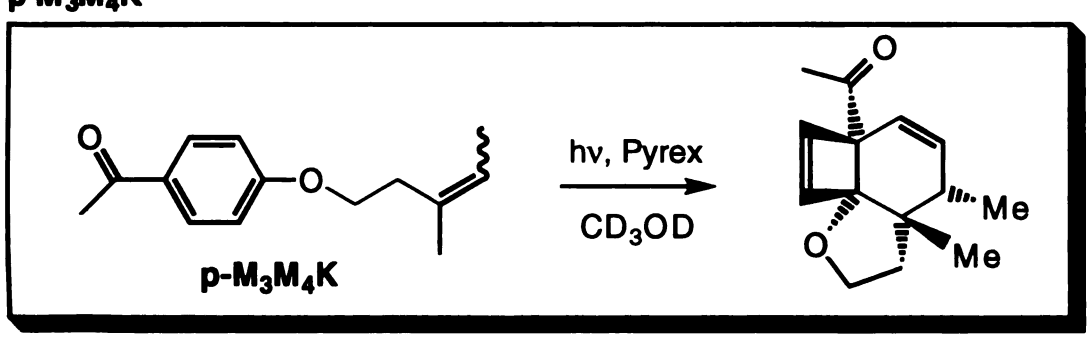
Figure 7. Before and after irradiation ^{1}H-NMR spectra of 4'-(2,3-dimethyl-3-buten-1-oxy)acetophenone (**p-M_2M_3K**) and its chemical yield determination .



A large scale photolysis of **p-M$_2$M$_3$K** (100 mL) was undertaken. Photoproducts were allowed to stand in solution at room temperature for two days Purification by silica gel column chromatography gave a diastereomeric mixture of 4-acetyl-8,9-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-dienes in 85 % diastereomeric excess. The peaks at δ 5.46 (dd, J = 10.2, 1.0 Hz, H_2), 6.59 (dd, J = 10.2, 1.6 Hz, H_3) and 6.74 (dd, J = 5.5, 1.0 Hz, H_5) and at δ 5.20 (dd, J = 8.2, 1.1 Hz, H_2), 6.60 (dd, J = 8.2, 1.5 Hz, H_3) and 6.75 (dd, J = 4.5, 1.1 Hz, H_5) represented the major and minor cyclohexadiene, respectively. Only a very small amount of the minor cycloöctatriene could be detected by ^{1}H-NMR spectroscopy, e.g. δ 5.20 (dd, J = 6.5, 1.1 Hz, 1H) 5.95-6.10 (m) 7.02 (d, J = 6.5 Hz, 1H).

An nOe experiment showed that 8-Me and 9-Me of the major product are *trans* to each other and that cyclobutane ring has a *cis*-fused to the cyclohexadiene.

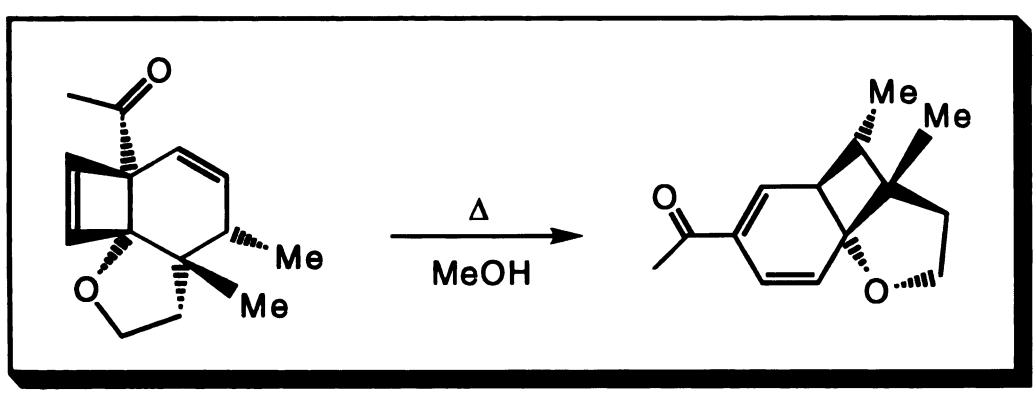
h. **p-M$_3$M$_4$K**



An NMR tube containing 3.0 mg **p-M_3M_4K** (95 % *trans* and 5 % *cis*) and 4.4 mg methyl benzoate dissolved in CD_3OD was irradiated at > 290 nm for 1.5 h. 1-Acetyl-4,5-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene was the only photoproduct (> 95 % diastereomeric excess and 45 % chemical yield) determined by ^{1}H-NMR spectroscopy.

Since this cyclobutene is stable in contrast to the previous examples, isolation could be undertaken by silica gel column chromatography. Mass spectroscopy indicated an identical molecular ion for the starting ketone **p-M_3M_4K** (M.W. = 218) and this compound. The peak at δ 209.8 in ^{13}C-NMR spectrum and the stretching frequency at 1703 cm^{-1} in IR spectrum corresponds to a nonconjugated carbonyl group. Two methyl groups at δ 0.93 (s) and 1.04 (d, J = 7.4 Hz) represented 5-Me and 4-Me, respectively. The cyclobutene ring was evident from an AB quartet at δ 6.33 ,6.44 (J = 2.9 Hz, H_{10}, H_{11}). UV-visible spectrum showed a $\pi\ \pi^*$ absorption at 280 nm which had a much smaller extinction coefficient (ε = 875) compared with starting ketone (ε = 16500).

The bridgehead 5-Me was *cis* to the cyclobutene ring but *trans* to 4-Me determined by nOe experiments.



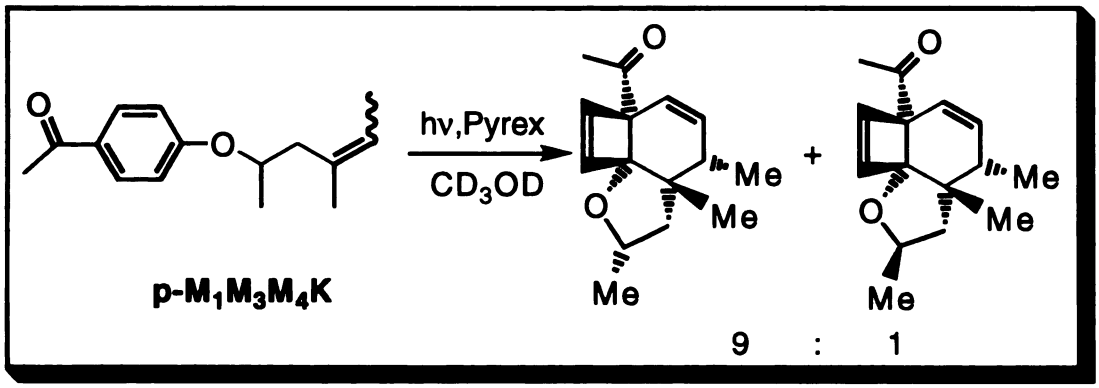
The cyclobutene product from the previous experiment was heated in methanol at 40°C for 24 h, until conversion to 4-acetyl-7,8-dimethyl-11-

oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene was completed. This compound was purified by silica gel chromatography then recrystallized from hexane-ethyl acetate mixture in the refrigerator.

Identical molecular ions for the starting ketone **p-M_3M_4K** and its **CB** (M.W. = 218) were obtained by Mass spectroscopy. The signal at δ 196.3 in ^{13}C-NMR spectrum was interpreted as that of a conjugated carbonyl carbon. Two methyl groups at δ 0.95 (d, J = 7.5 Hz) and 1.03 (s) represented 7-Me and 8-Me, respectively. Olefinic peaks at δ 5.45 (d, J = 9.7 Hz, H_2), 6.59 (d, J = 9.7 Hz, H_3) and 6.61 (d, J = 5.8 Hz, H_5) were characteric of the cyclohexadiene unit. UV-visible spectrum showed a $\pi\,\pi^*$ band at 295 nm which had a medium extinction coefficient (ε = 2200).

The methyls at C-7 and C-8 were determined by nOe to be *trans* to each other.

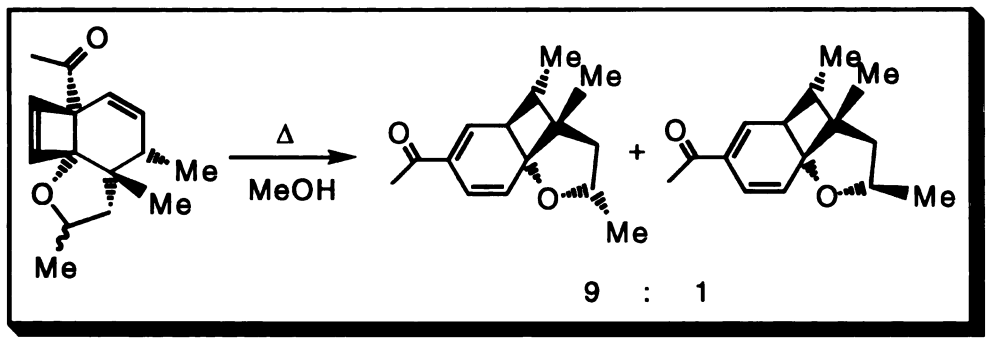
i. **p-$M_1M_3M_4K$**



The NMR scale photolysis of a *cis* + *trans* mixture of **p-$M_1M_3M_4K$** with methyl benzoate in CD_3OD (0.022 M) at > 290 nm provided a diastereomeric mixture of 1-acetyl-4,5,7-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-dienes in 80 % diastereomeric excess and 49 % chemical yield. Three signals at δ 0.98 (s),

1.05 (d, J = 7.4 Hz) and 1.11 (d, J = 6.1 Hz) were characterized as 5-Me, 4-Me and 7-Me, respectively. An AB quartet at δ 6.47, 6.50 (AB q, J = 3.0 Hz, H_{10}, H_{11}) was assigned to olefinic protons of the cyclobutene ring.

NOe experiments verified that the major diastereomer had bridgehead 5-Me *cis* to the cyclobutene ring but *trans* to both 4-Me and 7-Me. The minor had R_1 and R_3 *cis* to each other and R_3 and R_4 *trans* .

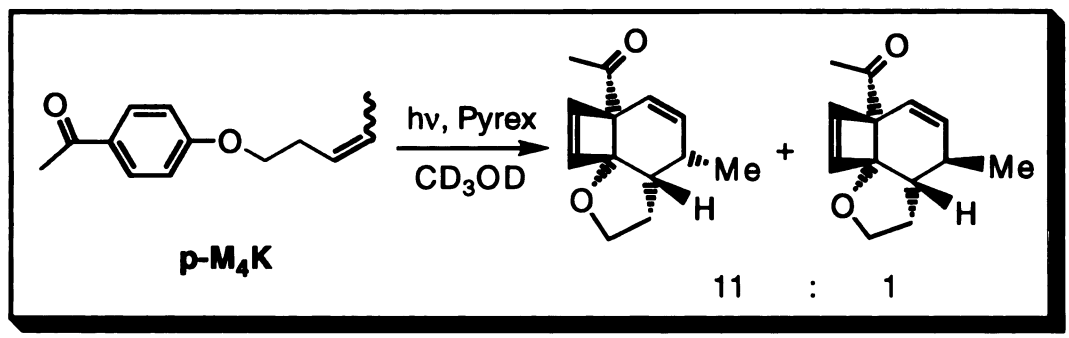


A solution of **p-$M_1M_3M_4K$** (*cis* and *trans* mixture, 0.014 M) in methanol was irradiated at > 290 nm and then heated at 40°C for 24h. After purification by silica gel column chromatography, photoproducts were identified as a pair of diastereomers of 4-acetyl-7,8,10-trimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene with 80 % diastereomeric excess. Three methyl groups at δ.0.89 (d, J = 7.5 Hz), 1.04 (s) and 1.32 (d, J = 5.9 Hz) were assigned to 7-Me, 8-Me and 10-Me, respectively. The peaks at δ 3.42 (dd, J = 10.0, 6.3 Hz, H_6), 5.62 (d, J = 10.2 Hz, H_2), 6.61 (dd, J = 10.2, 1.5 Hz, H_3) and 6.83 (dd, J = 6.3, 1.5 Hz, H_5) constituted the cyclohexadiene skeleton.

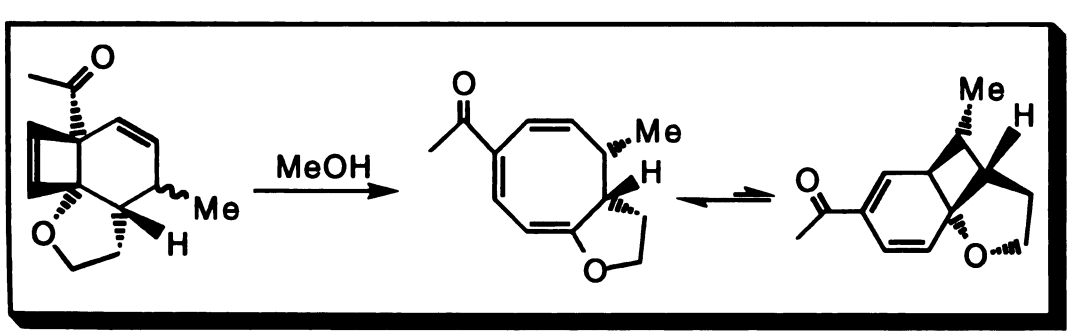
The stereochemistry of this compound has a bridgehead 8-Me group *trans* to both 7-Me and 10-Me. Isolated 4-acetyl-7,8,10-trimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene could regenerate starting material **p-**

$M_1M_3M_4K$ at low conversion, however, after longer irradiation the 1-acetyl-4,5,7-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene was again found.

j. **p-M_4K**

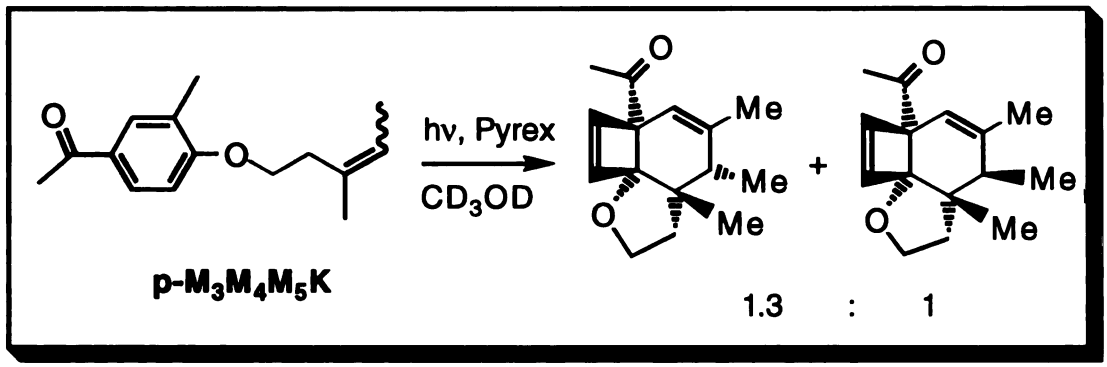


A 0.02 M solution of pure *trans* **p-M_4K** (purified from a *trans* and *cis* mixture by silica gel column chromatography or HPLC) and 2.2 mg methyl benzoate in CD_3OD was irradiated. At low conversion (7 % in 50 min), a signal due to *cis* **p-M_4K** was detected by ^{1}H-NMR spectrum and HPLC. After high conversion (> 95 % in 18 h), a diastereomeric mixture (11 : 1) of 1-acetyl-4-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-dienes was isolated in 41 % chemical yield. A doublet in the ^{1}H-NMR spectrum at δ 1.13 (J = 7.2 Hz) was assigned to the 4-Me. There were also two sets of AB quartet olefinic peaks characteristic of cyclobutenes.



Ketone **p-M_4K** (0.2 g) was irradiated in methanol at > 290 nm for 16 h. After a few days in the refrigerator, the colorless solution had turned yellow. The mixture was purified by silica gel column chromatography. Products were identified as a diastereomeric mixture (5 : 1) of two 4-acetyl-7-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-trienes and small amount (< 15 %) of 4-acetyl-7-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene. The overall isolated yield was 34 %. This mixture was decomposed gradually even in the refrigerator.

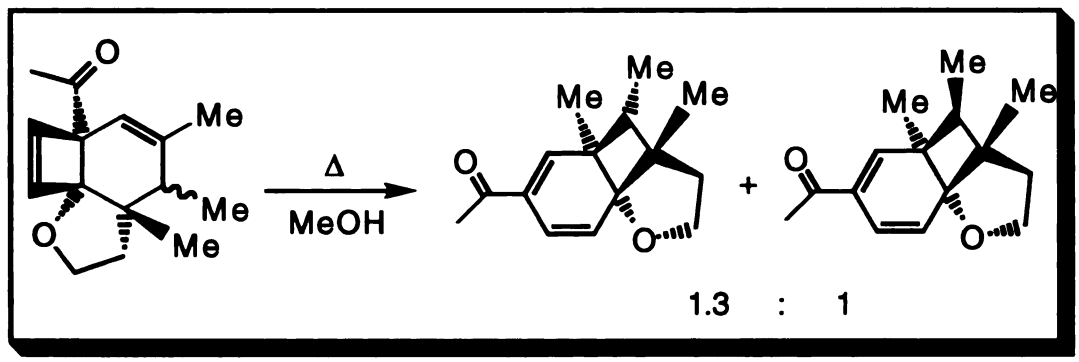
k. **p-$M_3M_4M_5$K**



Irradiation of a methanol solution of a *cis/trans* mixture of **p-$M_3M_4M_5$K** at > 290 nm provided a diastereomeric mixture of 1-acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene. The reaction is highly regioselective; addition occurs toward the methyl group on the phenyl ring with a lower diastereomeric excess (13 % in R_4/R_5) than previously observed.

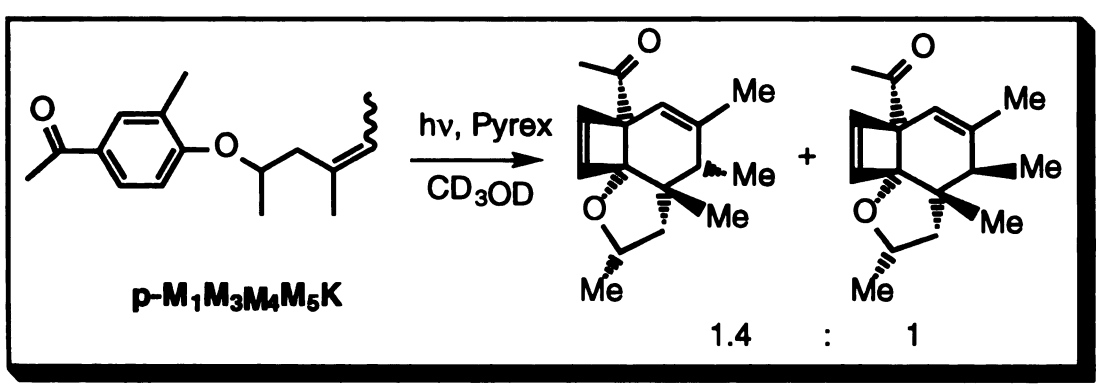
Two similar sets of patterns were observed in the ^{1}H-NMR spectrum, except for H_2. The major isomer has a quartet (J = 1.4 Hz) at δ 5.37 which coupled only to 3-Me. However, the minor product has a quintet (J = 1.4 Hz) at δ 5.45 which is coupled to both 3-Me and $H_{4\alpha}$ The major photoproduct was

assigned with 4-Me and 5-Me *trans* to each other, while the minor had 4-Me and 5-Me *cis*.



A mixture of 1-acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene diastereomers obtained from above experiment was heated in methanol to give two 4-acetyl-6,7,8-trimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-dienes with the same diastereomeric excess (13 %). The singlets at δ 6.70 and δ 6.76 were assigned to the methyls at C-5 for each diastereomer.

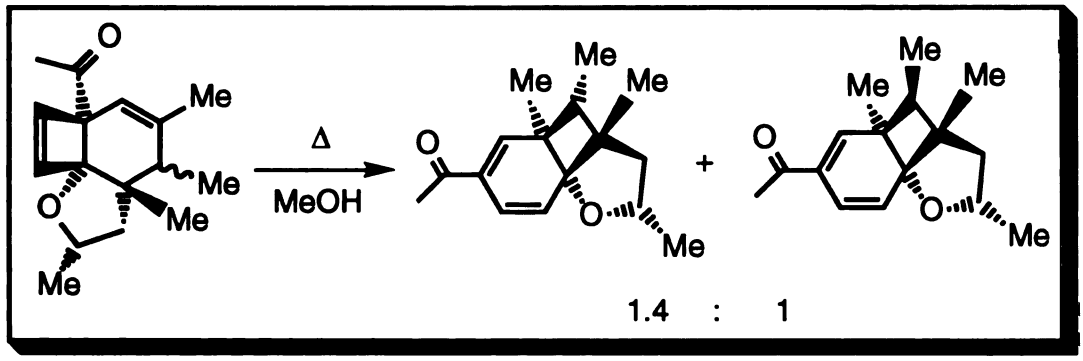
l. **p-$M_1M_3M_4M_5$K**



A 0.021 M methanol solution of a *cis/trans* mixture of **p-$M_1M_3M_4M_5$K** was photolyzed at > 290 nm for 8 h. Photoproducts were characterized as two

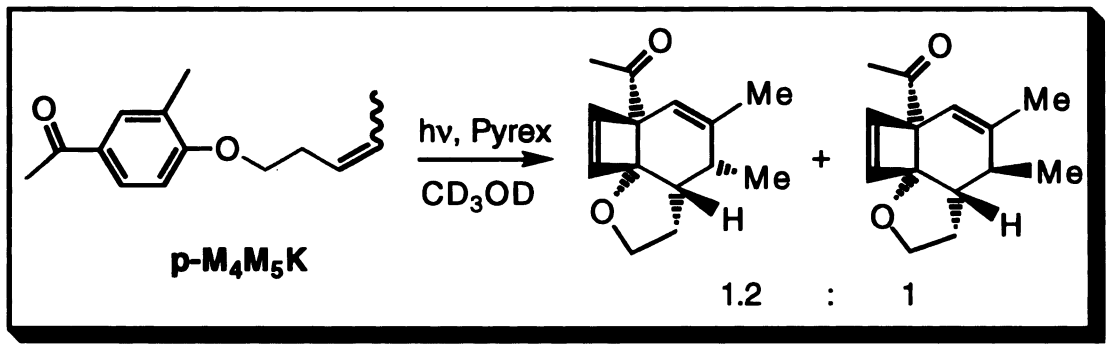
diastereomers of 1-acetyl-3,4,5,7-tetramethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene with diastereomeric excess (16 %) and chemical yield (55 %).

The ^{1}H-NMR spectrum was similar to 1-acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene except for one more methyl group at C-10. Regioselectivity occurred only toward the methyl group during cycloaddition with low diastereomeric excess (10 % in R_4/R_5). The major product was assigned by nOe experiments with 4-Me and 7-Me *trans* to 5-Me. The minor product was 4-Me *cis* to 5-Me but 7-Me *trans* to 5-Me. There were other minor signals in ^{1}H-NMR spectrum which were not identified.



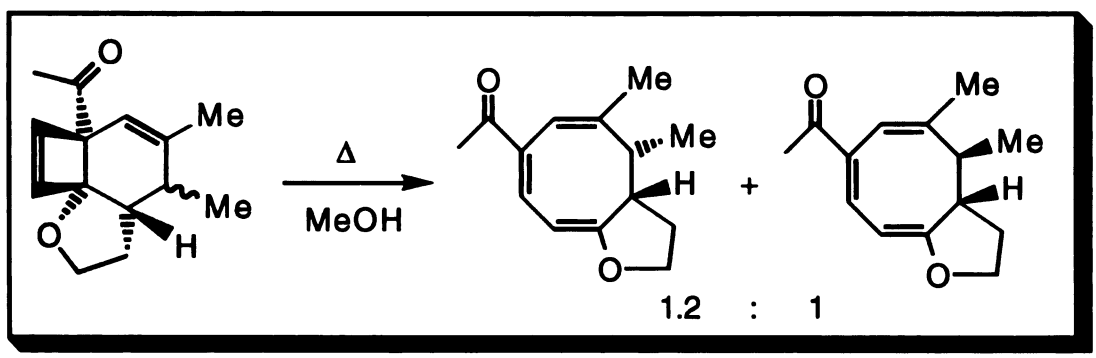
A mixture of the above 1-acetyl-3,4,5,7-tetramethyl-8-oxatricyclo[7.2.0.0^{5,9}]-undeca-2,10-diene diastereomers was heated in methanol at 40°C for 36 h. Identical diastereoselectivity was obtained for the new 4-acetyl-6,7,8,10-tetramethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-dienes. Again, the ^{1}H-NMR spectrum was comparable with 4-acetyl-6,7,8-trimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-dienes excluding the 10-H_α which is replaced with 10-Me_α. The nOe results indicated that the major product has its 6-Me, 7-Me and 10-Me groups *trans* to its 8-Me. The minor product has its 7-Me *cis* to 8-Me, but 6-Me and 10-Me *trans* to 8-Me.

m. **p-M_4M_5K**



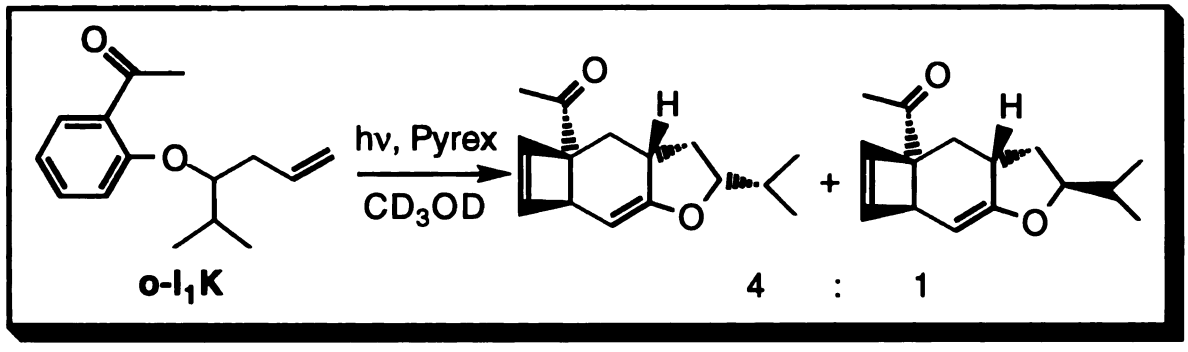
p-M_4M_5K

The same photolysis procedures used for **p-$M_3M_4M_5K$** were followed. Two diastereomers of 1-acetyl-3,4-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene in 61 % chemical yield and 10% diastereomeric excess were obtained. This is similar to the two previous examples. All three ^{1}H-NMR spectra were similar except the bridgehead substituent, which was hydrogen (H_5) in this case. The major product was assigned to the structure with H_5 *trans* to 4-Me.

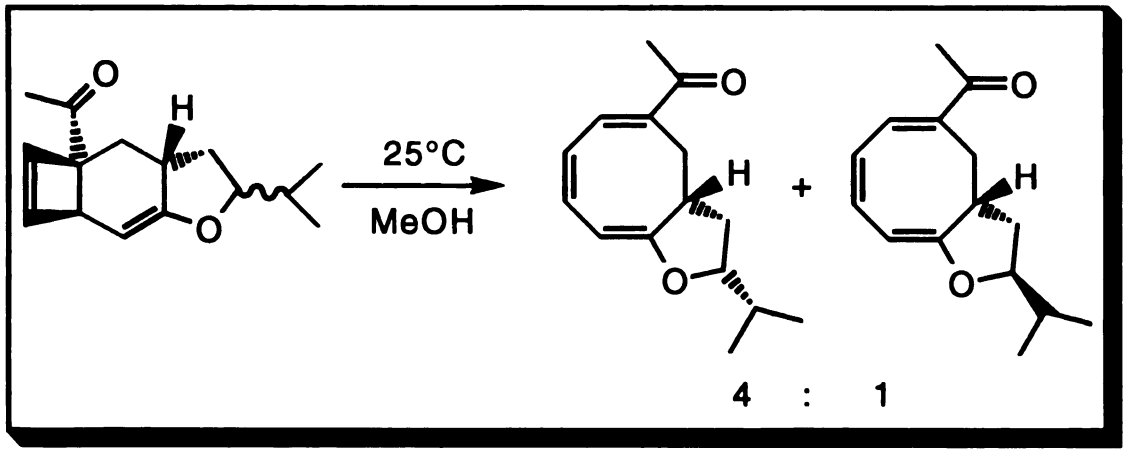


Two diastereomers of 1-acetyl-3,4-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]-undeca-2,10-diene were heated in methanol to give diastereomers of 4-acetyl-6,7-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene in the same ratio. It is noteworthy that cycloöctatrienes (λ_{max} = 337 nm) were obtained instead of cyclohexadienes in this case.

n. **o-I_1K**



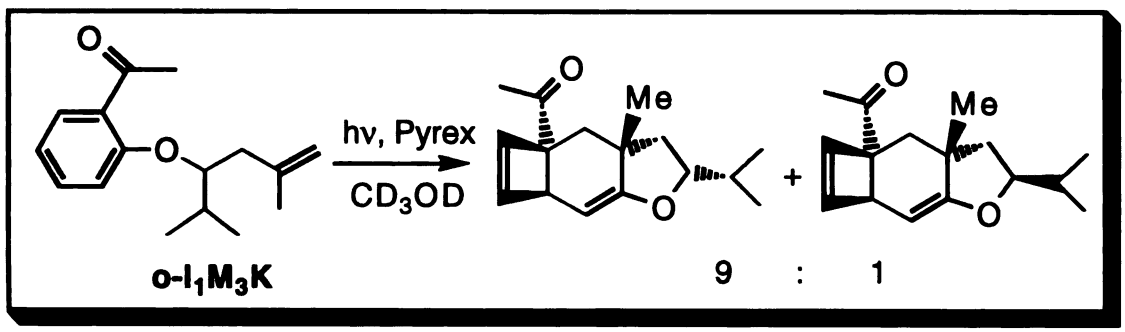
An NMR-scale solution of **o-I_1K** (1.8 mg) and 1.6 mg methyl benzoate in CD_3OD (0.013 M) was irradiated at > 290 nm (Pyrex) for 1 h. The photoproducts were two diastereomers of 9-acetyl-5-isopropyl-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene obtained in 71 % chemical yield. The ^{1}H-NMR results were, therefore, similar to the angular 1-acetyl-7-isopropyl-8-oxatricyclo-[7.2.0.$0^{5,9}$]undeca-2,10-dienes obtained from **p-I_3K**, except the partial protons; H_1 δ 3.42 (dd, J = 6.6, 1.7 Hz), H_2 δ 4.72 (dd, J = 6.6, 2.5 Hz). The structure was assigned as a linear 4-6-5 ring system. The diastereomeric excess of 60 % is close to that observed in **p-I_3K** case (67 %). Stereochemistry about the ring junction was assigned to be similar to the angular case: that is, bridgehead H_7 is *trans* to 5-iPr but *cis* to cyclobutene ring for the major product.



A methanol solution of **o-I_1K** (0.015 M) was irradiated at > 290 nm for 5 h. The yellow product was purified by silica gel column chromatography to give diastereomers of 6-acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene in 52% chemical yield and 60% diastereomeric excess. The splitting patterns of these compounds were similar to those of the 4-acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-trienes. The most significant difference between them was the olefinic protons of cycloöctatrienes. These protons were coupled to each other, for example, δ 5.33 (dd, J = 9.4, 2.5 Hz, H_2), 5.73 (dd, J = 13.2, 6.1 Hz, H_4), 6.01 (dd, J = 13.2, 9.4 Hz, H_3) and 7.05 (d, J = 6.1 Hz, H_5) for the major isomer. The extra double bond between oxygen and carbonyl shifted the UV-visible absorption λ_{max} to longer wavelength (377 nm).

Stereochemistry of the cycloöctatrienes was determined from the cyclobutene, since both showed the same diastereoselectivity. The bridgehead H_8 was *trans* to 10-iPr in the major product but H_8 was *cis* to 10-iPr in the minor.

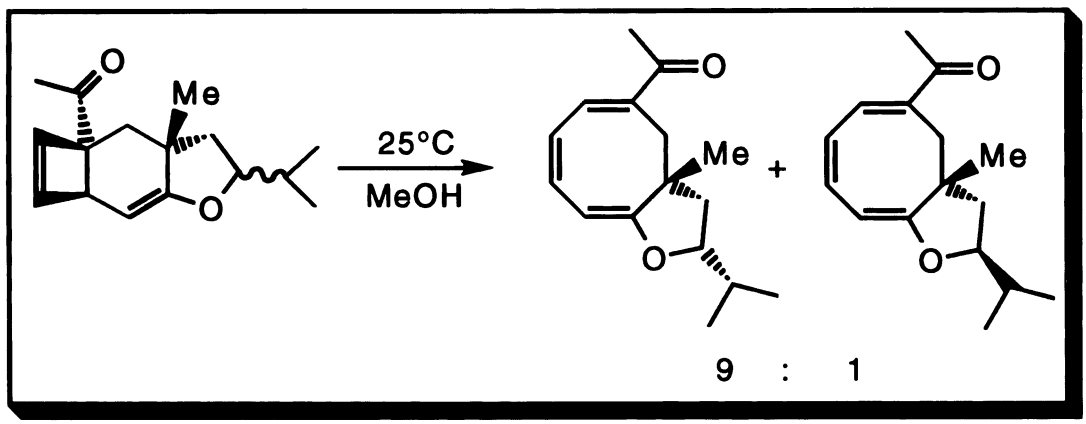
o. **o-I_1M_3K**



Irradiation of **o-I_1M_3K** in CD_3OD provided one major product which was characterized as 9-acetyl-5-isopropyl-7-methyl-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene with a small amount of a second diastereomer in a 9 : 1 ratio with

chemical yield 67%. The product mixture contained a linear cyclobutene skeleton with ^{1}H-NMR signals at δ 6.24 (d, J = 2.8 Hz, H_{10}) and 6.36 (dd, J = 2.8, 0.9 Hz, H_{11}) and a bridgehead methyl group at δ 1.28 (s, 7-Me) instead of a proton.

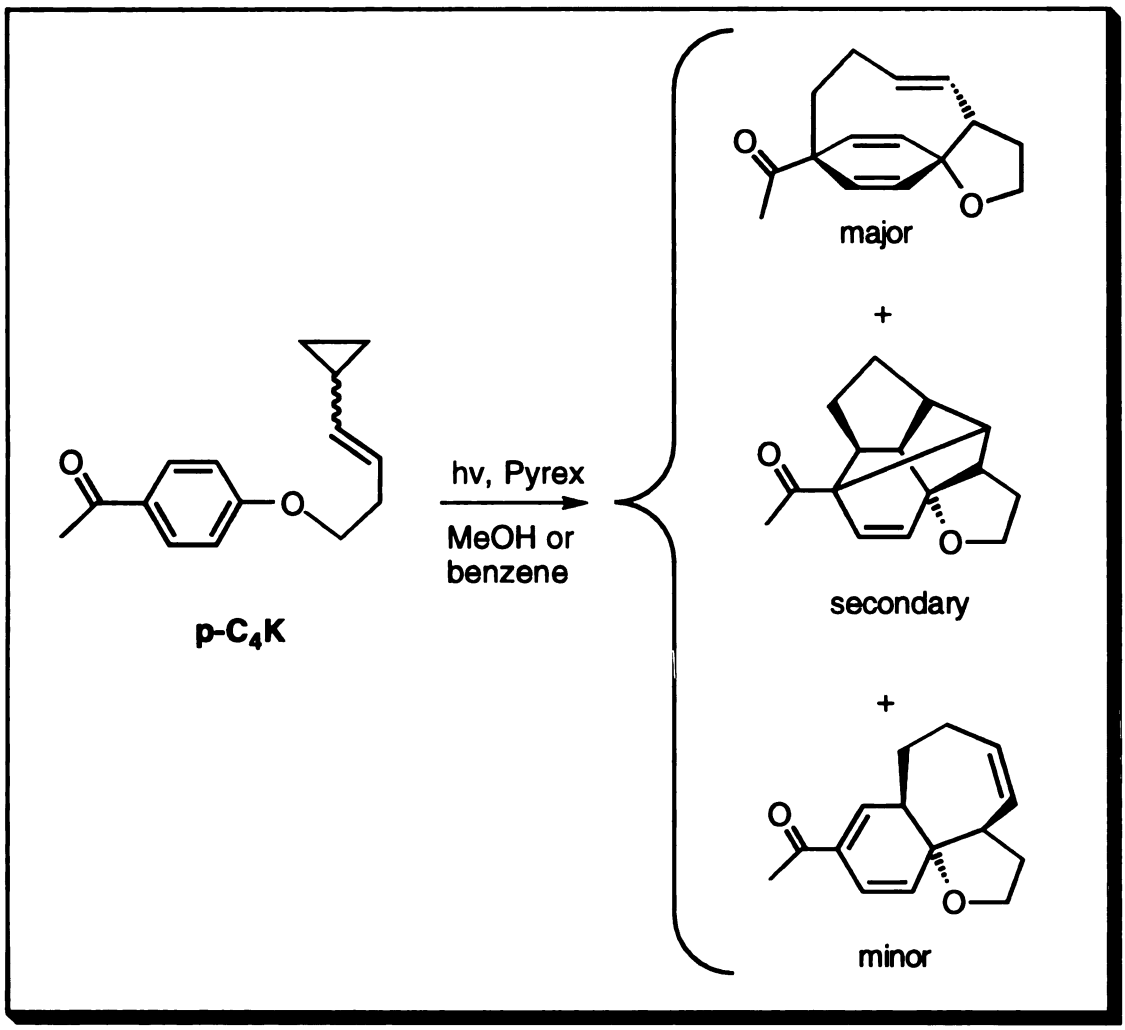
Stereochemistry of the major product was shown by an nOe experiment at -20°C. Results indicated that the major product had a bridgehead methyl group, 7-Me, *cis* to the cyclobutene group but *trans* to the 5-iPr.



Large scale photolysis (0.2 g of **o-I_1M_3K**) followed by silica gel column chromatography gave a diastereomeric mixture of 6-acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene in 60 % isolated yield and 80 % diastereomeric excess. UV absorption of the yellow mixture had λ_{max} 388 nm. Bridgehead methyl group at δ 1.03 (s, 8-Me) made interpretation of the ^{1}H-NMR spectrum easier. There were 4 sets of olefinic protons δ 5.13 (d, J = 8.2 Hz, H_2), 5.88 (dd, J = 12.9, 5.9 Hz, H_4), 6.15 (dd, J = 12.9, 8.2 Hz, H_3) and 7.29 (d, J = 5.9 Hz, H_5) corresponding to the cycloöctatriene structure.

Diastereomeric excess of cycloöctatrienes was identical to that for the cyclobutenes. This indicated the major cycloöctatriene had 10-iPr group *trans* to 8-Me. Results from nOe studies support the above observation.

p. **p-C_4K**



A methanol (or benzene) solution of **p-C_4K** (0.017 M) as a *cis/trans* (=1/1.7) mixture was irradiated at wavelengths >290 nm (or 313 nm). ^{1}H-NMR analysis showed no trace of residual cyclopropyl resonances and indicated the formation of three isomers. They were assigned the followed structures: the 1,4-adduct (major), the polycyclic ketone (secondary) and the 1,2-adduct (minor). They were produced in the proportion of 5 : 3 : 1, respectively, as determined by NMR, although the ratio differed in different experiments. The isolated secondary and minor products have the same molecular weight (230), determined by MS spectroscopy.

A typical *trans* vinyl proton coupling constant (16.0 Hz, see Table 33),[60] a pair of *cis* vinyl proton coupling constants (11.1 and 10.2 Hz) typical of 6-membered rings, and a pair of W-proton coupling constants (2.4 and 2.1 Hz) identify the major product as a tricyclic ketone with a cyclohexa-1,4-diene skeleton and a ring containing a *trans* double bond. Unfortunately, the isolation of this compound was unsuccessful because it decomposed during chromatography and generated a non-identifiable rearranged isomer with only one vinyl proton ; so the structure determination of the major product was based on the NMR spectrum of the mixture of products (Figure 8).

The secondary product, after purification by column chromatography and recrystallization, was identified by its simple AB quartet at δ 5.52 (dd, J = 9.9, 1.6 Hz, 1H), 5.86 (dd, J = 9.9, 0.9 Hz, 1H) due to its two vinyl protons. It was further confirmed by its distinct ^{13}C-NMR DEPT spectrum, with δ 128.2 and 134.0 for olefinic carbons and δ 210.2 of the non-conjugated carbonyl group (Figure 9). The non-conjugated carbonyl group was also confirmed by its IR spectrum, with an absorption at 1693 cm^{-1}.

The minor product was assigned as the seven-six-five-fused tricyclic triene from its five vinyl resonances, especially J values (10.5 Hz and 10.3 Hz) characteristic only of *cis* double bonds.[61] No product with a cyclopropyl group was detected or isolated.

A C_6D_6 solution of **p-C_4K** and methyl benzoate (ratio = 1.5:1 in comparison with the acetyl and methoxy groups, measured by ^{1}H-NMR) was irradiated at 313 nm and room temperature. ^{1}H-NMR showed that 1.5:1 ratio by comparing the integrations of four acetyl groups of **p-C_4K** and three photoproducts to methoxy group of methyl benzoate is remained at 40% conversion . This indicated that the material balance of this photoreaction was maintained at low conversion.

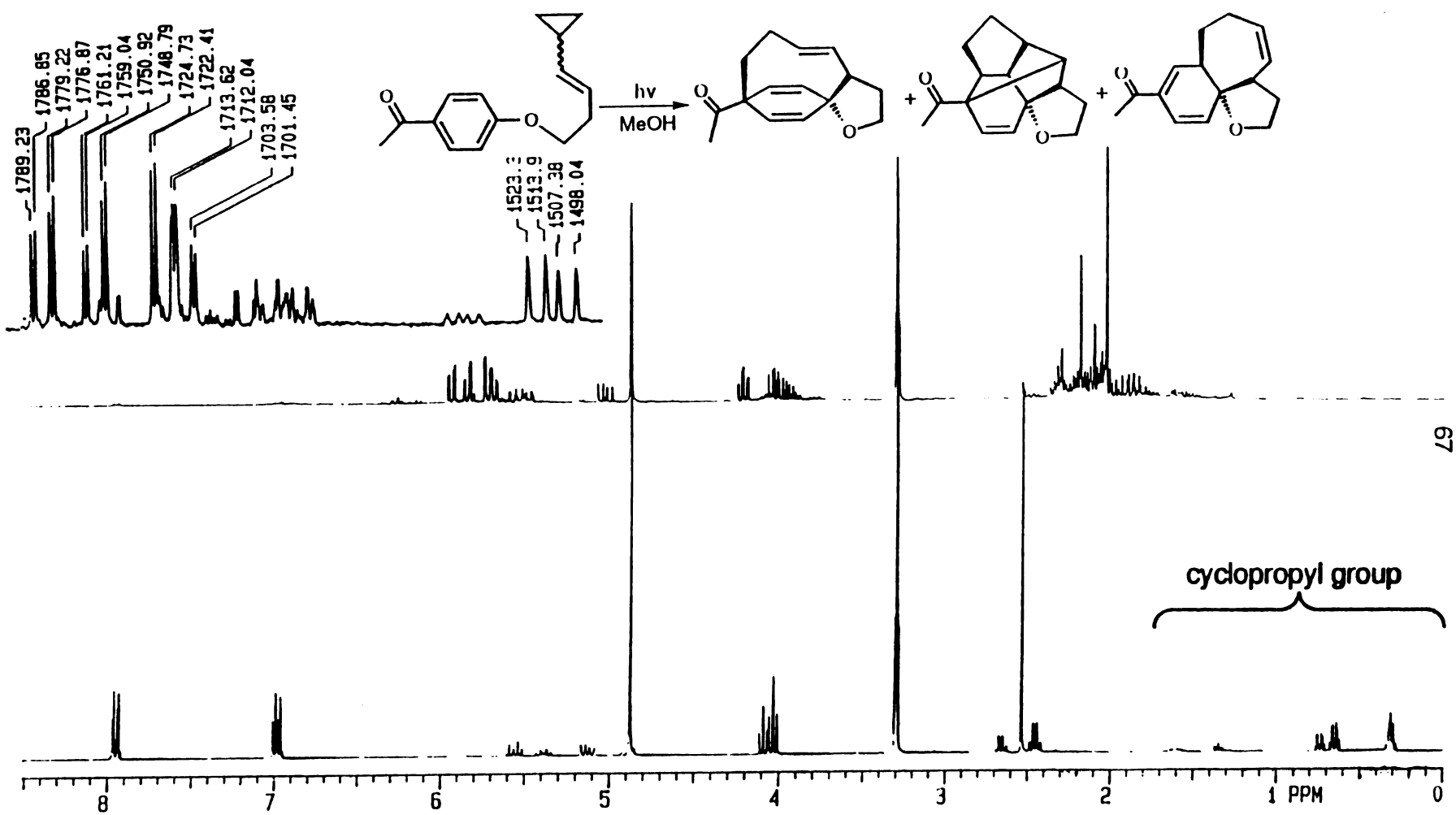


Figure 8. Before and after irradiation of ^{1}H-NMR spectra of *cis+trans*- 4'-(4-cyclopropyl-3-buten-1-oxy)acetophenone (**p-C_4K**) in CD_3OD.

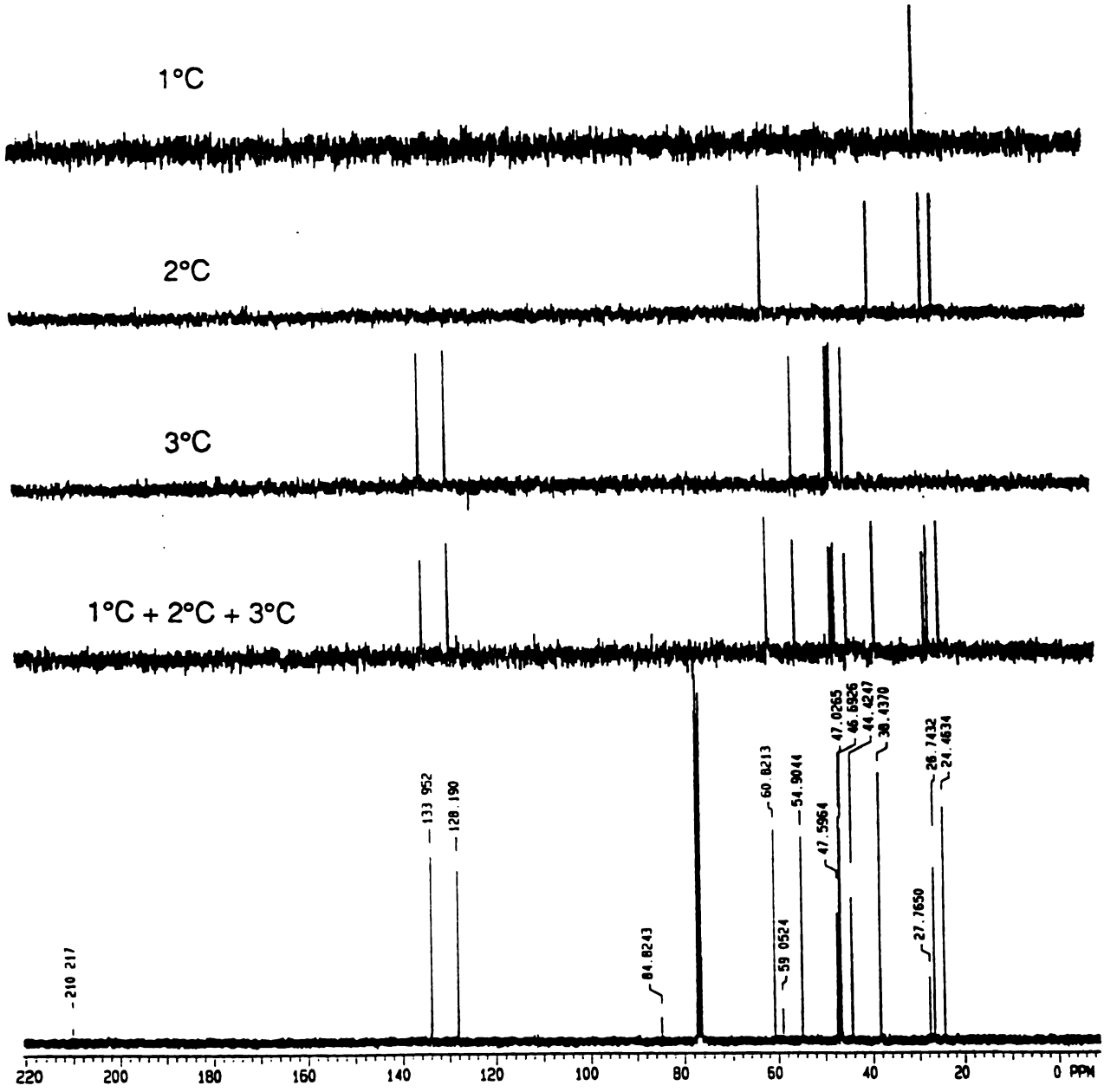
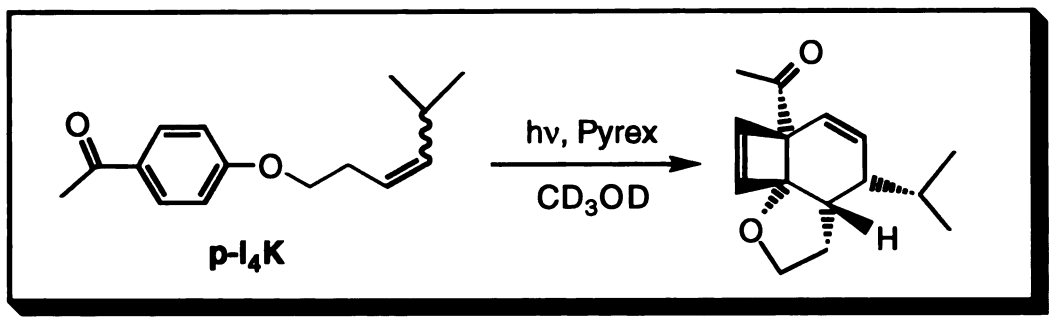
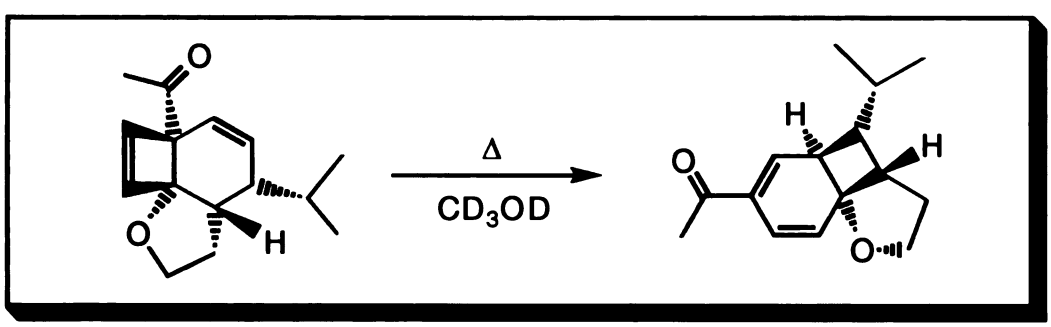


Figure 9. DEPT spectra of polycyclic ketone in $CDCl_3$.

q. **p-I$_4$K**



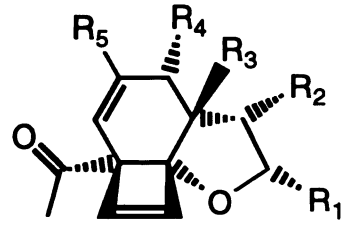
A 0.02 M CD_3OD solution of **p-I$_4$K** (1/1.7 = *cis/trans* mixture) in an NMR tube was photolyzed at >290 nm. The photoreaction was inefficient and could not be carried to completion. The product was identified as 1-acetyl-4-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene but decomposed gradually during the irradiation. It could, however, be characterized after 10 h irradiation at 50% conversion. There was exclusively one diastereomer in 38 % chemical yield which was assigned with the bridgehead proton *trans* to 4-iPr.



The above photoproduct was heated and 4-acetyl-7-isopropyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene was characterized. Only certain peaks, such as, δ 3.17 (ddd, J = 7.7, 5.5,2.2 Hz, H_6), 6.26 (d, J = 10.1 Hz, H_2), 6.45 (d, J = 10.1 Hz, H_3) and 6.70 (d, J = 7.7 Hz, H_5), could be found in ^{1}H-NMR spectrum. These were assigned to the typical cyclohexadiene structure.

III. Diastereoselectivity and Chemical Yields of Photoproducts

Table 3 Diastereomeric Excess (de) and Chemical Yields of Various 1-Acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-dienes



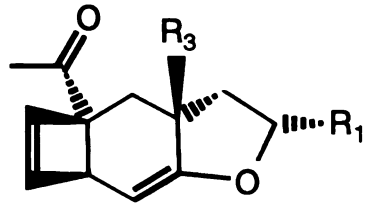
Reactants	Ratio	de	Chemical yield [a]
p-M$_1$K	2.5 / 1	41 % (R_1 / R_3)	85 %
p-I$_1$K	5 / 1	67 % (R_1 / R_3)	90 %
p-M$_1$M$_3$K	9 / 1	80 % (R_1 / R_3)	78 %
p-I$_1$M$_3$K	b	> 95 % (R_1 / R_3)	75 %
p-M$_2$M$_3$K	10 / 1	82 % (R_2 / R_3)	76 %
p-M$_3$M$_4$K	b	> 95 % (R_3 / R_4)	45 %
p-M$_1$M$_3$M$_4$K	9 / 1	80 % (R_1 / R_3), > 95 % (R_3 / R_4)	49 %
p-M$_4$K	11 / 1	83 % (R_3 / R_4)	43 %
p-M$_3$M$_4$M$_5$K	1.3 / 1	13 % (R_3 / R_4)	45 %
p-M$_1$M$_3$M$_4$M$_5$K	1.4 / 1	80 % (R_1 / R_3), 16 % (R_3 / R_4)	55 %
p-M$_4$M$_5$K	1.2 / 1	10 % (R_3 / R_4)	61 %
p-I$_4$K	b	> 95 % (R_3 / R_4)	38 %[c]

a: Z+E yields, determined by internal standard (methyl benzoate) on ^{1}H-NMR spectra to > 95% conversion except c.

b: Single diastereomer obtained from ^{1}H-NMR spectrum.

c: 50% conversion.

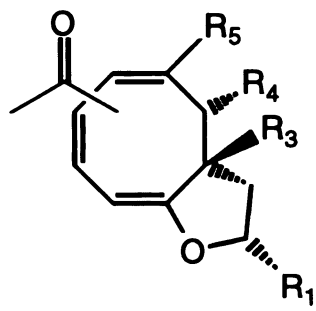
Table 4 Diastereomeric Excess of Various 9-Acetyl-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-dienes



Reactants	**Ratio**	**de**	**Chemical yield** [a]
o-I$_1$K	4 / 1	60 % (R$_1$ / R$_3$)	71 %
o-I$_1$M$_3$K	9 / 1	80 % (R$_1$ / R$_3$)	67 %

a: Z+E yields, determined by internal standard (methyl benzoate) on ^{1}H-NMR spectra to > 95% conversion.

Table 5 Diastereomeric Excess of Various 4- or 6-Acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene

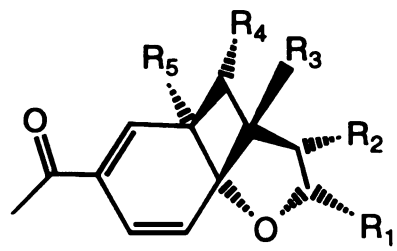


Reactants	Ratio	de	Isolated yield [a]
p-M_1K	3.2 / 1	56 % (R_1 / R_3)	63 %
p-I_1K	4.7 / 1	65 % (R_1 / R_3)	68 %
p-M_1M_3K	9 / 1	80 % (R_1 / R_3)	48 %
p-I_1M_3K	b	> 95 % (R_1 / R_3)	46 %
p-M_4K	9 / 1	80 % (R_3 / R_4)	41 %
p-M_4M_5K	1.2 / 1	10 % (R_3 / R_4)	44 %
o-I_1K	4 / 1	60 % (R_1 / R_3)	52 %
o-I_1M_3K	9 / 1	80 % (R_1 / R_3)	60 %

a: Z+E yields

b: Single diastereomer obtained from ^{1}H-NMR spectrum.

Table 6 Diastereomeric Excess of Various 4-Acetyl-11-oxatricyclo[6.3.0.0^{1,6}] undeca-2,4-diene



Reactants	**Ratio**	**de**	**Isolated yield** [a]
p-M_2M_3K	10 / 1	85 % (R_2 / R_3)	58 %
p-M_3M_4K	b	> 95 % (R_3 / R_4)	45 %
p-$M_1M_3M_4K$	9 / 1	80 % (R_1 / R_3), > 95 % (R_3 / R_4)	50 %
p-$M_3M_4M_5K$	1.3 / 1	13 % (R_3 / R_4)	47 %
p-$M_1M_3M_4M_5K$	1.4 / 1	80 % (R_1 / R_3), 16 % (R_3 / R_4)	48 %
p-I_4K	b	> 95 % (R_3 / R_4)	38 % [c]

a: Z+E yields.

b: Single diastereomer obtained from ^{1}H-NMR spectrum.

c: Chemical Yield.

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V. Quantum Yields and Kinetic Results

Quantum yields of [2+2] cycloadduct formation were measured at low conversion (5-15 %) by means of GC or HPLC. The **COT** and **CH** were isolated from silica gel chromatography after large scale irradiation. The response factors of ketones, **COT** and **CH** were measured by either GC or HPLC. About 0.01 M solution of starting ketones in methanol was degassed by the freeze-and-thaw method and irradiated at 313 nm with valerophenone actinometer ($\Phi_{AP} = 0.33$)[62] in a merry-go-round apparatus at room temperature (see experimental section). The concentrations of **COT** and **CH** were measured.

Table 7 Quantum Yields of Various Cycloöctatrienes or Cyclohexadienes

Reactants	Quantum yield Φ
p-M_0K [a]	0.20 [b]
p-M_1K	0.10 [b]
p-I_1K	0.12 [b]
p-I_1M_3K	0.19 [b]
o-I_1K	0.25 [b]
o-I_1M_3K	0.15 [b]
p-M_3M_4K	0.07 [c]
p-I_4K	0.08 [b]

a: 4'-(3-Buten-1-oxy)acetophenone

b: **COT** determined by GC

c: **CH** determined by HPLC

Quantum yields of photocyclization of **COT**'s were measured at moderate conversion (30-60 %) by means of UV. About 10^{-4}-10^{-5} M solution of cycloöctatrienes (optical density < 2.5), which could be detected by UV in methanol was degassed by the freeze-and-thaw method and irradiated at 313 nm with valerophenone actinometer (Φ_{AP} = 0.33) or at 366 nm of light with benzophenone and benzhydrol actinometer (Φ = 0.78)[63] in a merry-go-round apparatus at room temperature (see experimental section). The disappearance of **COT** was measured. The sensitized reaction by adding 0.05 M 4-methoxy-acetophenone in above **COT** solution was performed in parallel with the original photocyclization of **COT**. The concentration of **COT** in sensitized reaction had no change after irradiation since the 4-methoxy-acetophenone absorbed all the light.

Table 8 Quantum Yields of Various Cyclobutenes

Reactants	**Quantum yield Φ**
p-M_0COT [a]	0.14 [b]
p-M_1COT	0.05 [b]
p-I_1COT	0.08 [b]
p-I_1COT	0.10 [b, c]
p-I_1M_3COT	0.11 [b]
p-I_1M_3COT	0.11 [d]
o-I_1COT	0.10 [b]
o-I_1M_3COT	0.21 [b]

a: 4-Acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene

b: At 313 nm

c: No significant change on COT concentration after irradiation by adding 4-methoxy-acetophenone

d: At 366 nm

Quantum yields of reversed [2+2] cycloaddition for recovery of starting ketone were measured at low conversion (15 %) by means of HPLC. About 0.005 M solution of cyclohexadienes in methanol with different amount of quencher was degassed by the freeze-and-thaw method and irradiated at 313 nm with valerophenone actinometer (Φ_{AP} = 0.33) in a merry-go-round apparatus at room temperature. The concentrations of starting ketones were measured.

Table 9 Quantum Yields and Kinetic Data of Starting Ketones

Reactants	**Quantum yield Φ**	**$k_q\tau$**
p-M_3M_4CH	0.78	5.0 [a]
p-M_3M_4CH	0.70	4.1 [b]

a: Quencher = 2,5-dimethyl-2,4-hexadiene

b: Quencher = sorbic acid

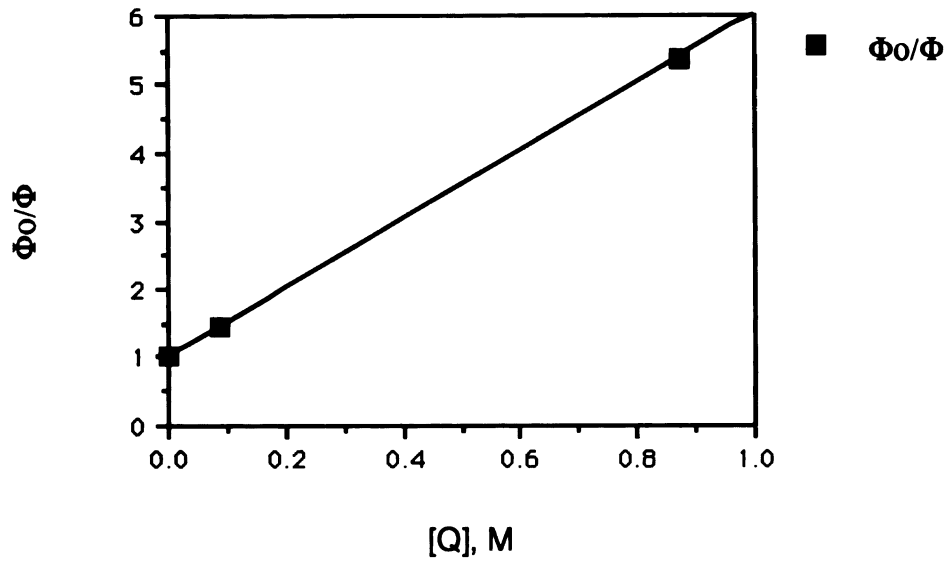


Figure 10. Stern-Volmer plots of 4'-(3-methyl-3-penten-1-oxy)acetophenone (**p-M_3M_4K**) with 2,5-dimethyl-2,4-hexadiene in methanol, $k_q\tau = 5.0$.

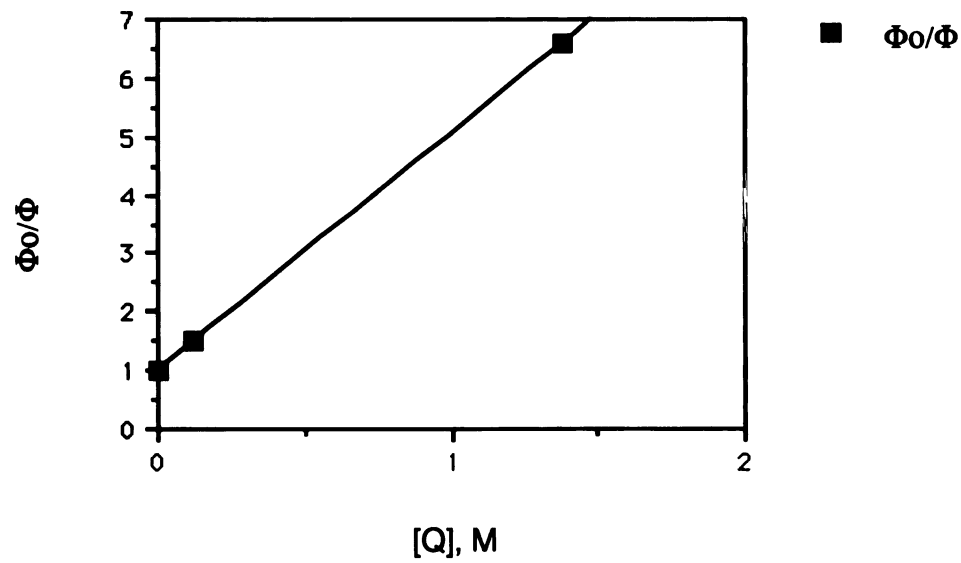


Figure 11. Stern-Volmer plots of 4'-(3-methyl-3-penten-1-oxy)acetophenone (**p-M_3M_4K**) with sorbic acid in methanol, $k_q\tau = 4.1$.

Quantum yields of the formation of polycyclic ketone and 1,2-adduct from 4'-(4-cyclopropyl-3-buten-1-oxy)acetophenone were measured at 313 nm three times at low conversion by the means of GC. Procedures as for the previous starting ketones were followed. The quantum yields were 0.21, 0.15 and 0.16, respectively. Since the major product wasn't stable on GC column and the ratio between the major product and overall product mixture is 4/9 from the determination of NMR spectroscopy, the above values only represented about 4/9 of the overall quantum yield.

V. Conformation Analysis

The Karplus equations are some of the most powerful theoretical rules for solving the structural and conformational problems in organic chemistry. They predict an approximate relation between the dihedral angle ϕ and the vicinal coupling constant $J_{H\text{-}C\text{-}C\text{-}H'}$. Vicinal coupling is defined as the interaction between nuclei bound to contiguous atoms, i.e. a coupling across three bonds. The Karplus rule is usually expressed by the following equations. In general, *trans* vicinal coupling constants are larger than *cis*.[64]

$$J_{H\text{-}C\text{-}C\text{-}H'} = 8.5 \cos^2 \phi - 0.3 \qquad 0° < \phi < 90°$$

$$J_{H\text{-}C\text{-}C\text{-}H'} = 9.5 \cos^2 \phi - 0.3 \qquad 90° < \phi < 180°$$

The photoproduct structure was firstly minimized by molecular mechanics (MM2),[65,66] then further optimized at the semi-empirical level (AM1).[67,68] All calculations were performed using unrestricted Hartree-Fock (UHF) treatment. The structure of the secondary polycyclic photoproduct from **p-C$_4$** was calculated to give the best geometry (Figure 12) and dihedral angles (Table 10). From dihedral angles, vicinal coupling constants $J_{H\text{-}C\text{-}C\text{-}H'}$ were calculated by the Karplus equations. Theoretical vicinal coupling constants correlate well with the experimental vicinal coupling constants obtained experimentally.

The best geometry and dihedral angles of other **CB**, **CH** and **COT** were also obtained and shown in the following pages.

Figure 12. Best geometry of polycyclic ketone

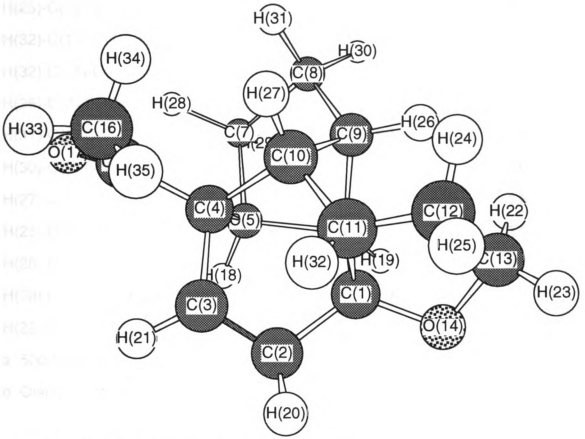


Table 10 Coupling Constants of Polycyclic Ketone

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(5)-C(6)-H(19)	49.076	3.4	6.5
H(18)-C(5)-C(7)-H(28)	82.079	0.0	0.0
H(18)-C(5)-C(7)-H(29)	-44.255	4.1	7.1
H(19)-C(6)-C(9)-H(26)	-62.414	1.4	1.0
H(20)-C(2)-C(3)-H(21)	-0.633	b	9.9
H(24)-C(12)-C(13)-H(22)	-27.406	6.4	6.5
H(25)-C(12)-C(13)-H(22)	-154.780	6.7	6.7

H(24)-C(12)-C(13)-H(23)	102.147	0.1	0.0
H(25)-C(12)-C(13)-H(23)	-25.224	6.7	6.7
H(32)-C(11)-C(12)-H(24)	-120.335	1.8	1.9
H(32)-C(11)-C(12)-H(25)	7.040	8.0	9.1
H(26)-C(9)-C(10)-H(27)	85.582	0.0	0.0
H(31)-C(8)-C(9)-H(26)	37.497	5.1	6.2
H(30)-C(8)-C(9)-H(26)	-89.028	0.0	0.0
H(27)-C(10)-C(11)-H(32)	65.621	1.1	1.6
H(28)-C(7)-C(8)-H(30)	-121.841	2.0	3.0
H(28)-C(7)-C(8)-H(31)	4.684	8.1	9.1
H(29)-C(7)-C(8)-H(30)	4.500	8.1	9.2
H(29)-C(7)-C(8)-H(31)	131.031	3.8	7.1

a. 500 MHz ^{1}H-NMR

b. Olefinic protons

Figure 13. Best geometry of **p-I$_4$CB**

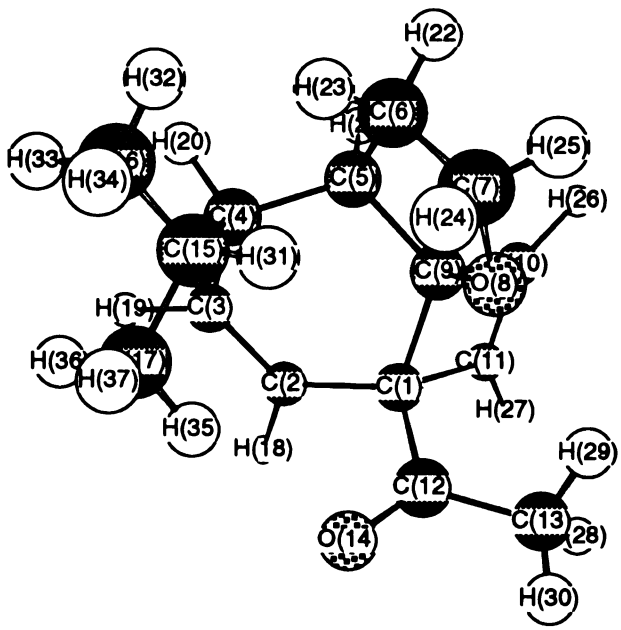


Table 11 Coupling Constants of **p-I_4CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(19)-C(10)-C(11)-H(18)	-2.742	b	2.9
H(20)-C(2)-C(3)-H(21)	-0.316	b	10.3
H(21)-C(3)-C(4)-H(22)	-33.703	5.5	4.4
H(22)-C(4)-C(5)-H(23)	-38.941	4.8	7.3
H(22)-C(4)-C(15)-H(31)	-129.253	3.5	6.3
H(23)-C(5)-C(6)-H(24)	-11.164	7.9	10.5
H(23)-C(5)-C(6)-H(25)	108.570	1.6	5.0
H(24)-C(6)-C(7)-H(26)	131.035	3.8	3.6
H(24)-C(6)-C(7)-H(27)	6.326	8.1	7.5
H(25)-C(6)-C(7)-H(26)	11.979	7.9	7.5
H(25)-C(6)-C(7)-H(27)	-112.731	1.2	1.6
H(31)-C(15)-C(16)-H(32)	67.135	c	6.7
H(31)-C(15)-C(16)-H(33)	-172.849	c	6.7
H(31)-C(15)-C(16)-H(34)	-53.162	c	6.7
H(31)-C(15)-C(17)-H(35)	-58.334	c	6.7
H(31)-C(15)-C(17)-H(36)	-179.368	c	6.7
H(31)-C(15)-C(17)-H(37)	61.184	c	6.7

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 14. Best geometry of **p-M_1CB**

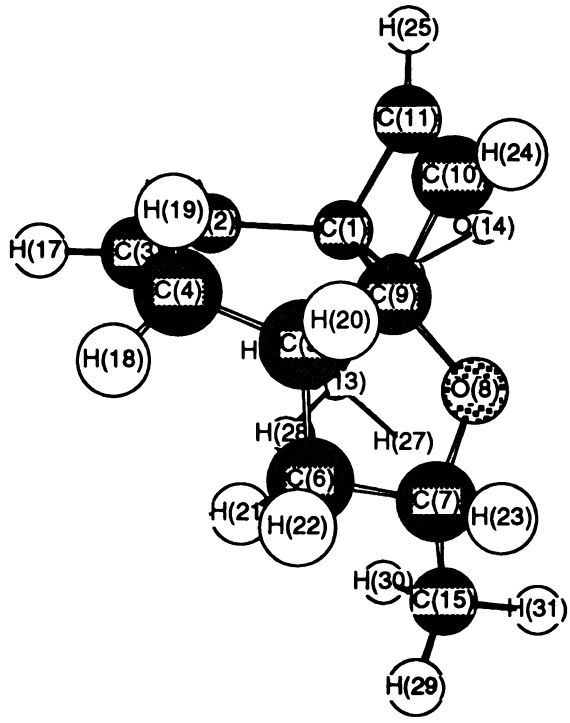


Table 12 Coupling Constants of **p-M_1CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(16)-C(2)-C(3)-H(17)	2.969	b	10.1
H(17)-C(3)-C(4)-H(19)	-82.340	0.0	2.3
H(17)-C(3)-C(4)-H(18)	33.254	5.6	6.6
H(18)-C(4)-C(5)-H(20)	-88.309	0.0	2.1
H(19)-C(4)-C(5)-H(20)	27.426	6.4	8.0
H(20)-C(5)-C(6)-H(21)	154.009	7.4	12.8
H(20)-C(5)-C(6)-H(22)	32.825	5.5	6.0
H(21)-C(6)-C(7)-H(23)	-148.090	6.8	11.3
H(22)-C(6)-C(7)-H(23)	-27.223	6.5	5.1
H(23)-C(7)-C(15)-H(29)	63.185	c	6.0

H(23)-C(7)-C(15)-H(30)	-176.337	c	6.0
H(23)-C(7)-C(15)-H(31)	-56.659	c	6.0
H(24)-C(10)-C(11)-H(25)	-3.917	b	2.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 15. Best geometry of **p-M_1M_3CB**

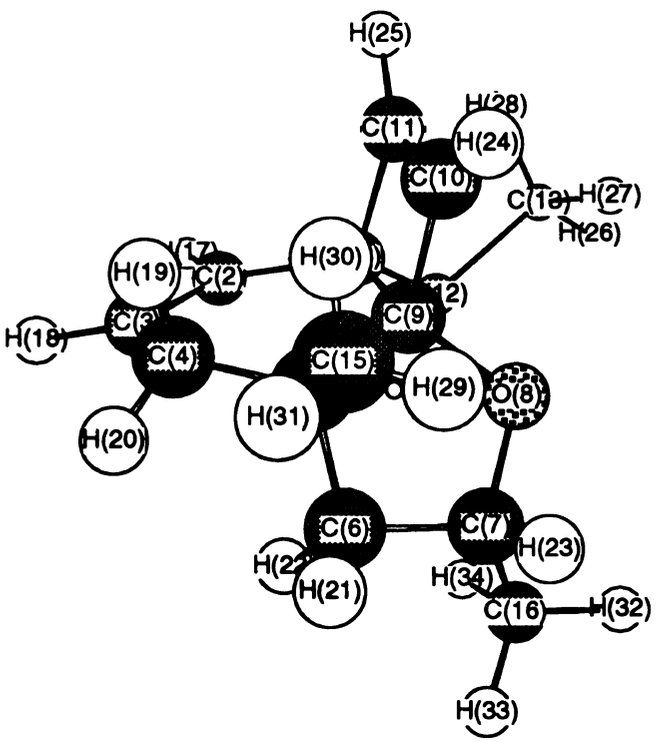


Table 13 Coupling Constants of **p-M_1M_3CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(17)-C(2)-C(3)-H(18)	1.675	b	10.0
H(18)-C(3)-C(4)-H(19)	-82.420	0.0	1.7
H(18)-C(3)-C(4)-H(20)	33.017	5.7	6.1

H(21)-C(6)-C(7)-H(23)	-24.951	6.7	10.4
H(22)-C(6)-C(7)-H(23)	-145.252	6.1	5.7
H(23)-C(7)-C(16)-H(32)	-52.006	c	6.2
H(23)-C(7)-C(16)-H(33)	68.046	c	6.2
H(23)-C(7)-C(16)-H(34)	-171.440	c	6.2
H(24)-C(10)-C(11)-H(25)	-3.876	b	2.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 16. Best geometry of **p-I_1M_3CB**

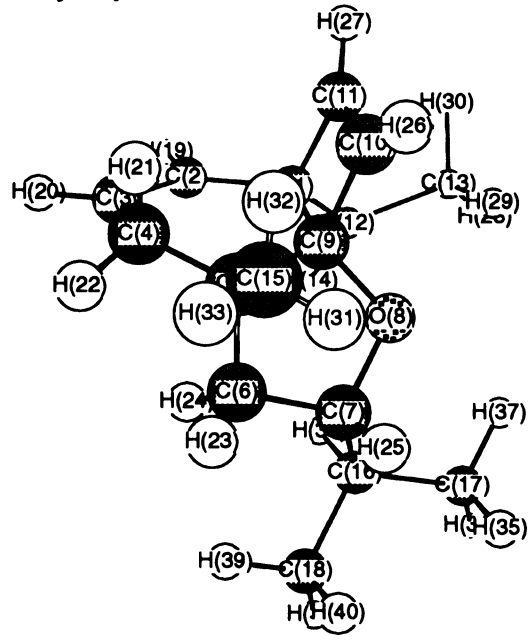


Table 14 Coupling Constants of **p-I_1M_3CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(19)-C(2)-C(3)-H(20)	0.949	b	10.2

H(20)-C(3)-C(4)-H(21)	-83.541	0.0	1.6
H(20)-C(3)-C(4)-H(22)	32.692	5.8	5.8
H(23)-C(6)-C(7)-H(25)	-23.567	6.8	10.4
H(24)-C(6)-C(7)-H(25)	-144.367	6.0	5.7
H(25)-C(7)-C(16)-H(34)	-174.130	9.0	5.7
H(34)-C(16)-C(17)-H(35)	-178.210	c	6.6
H(34)-C(16)-C(17)-H(36)	-58.016	c	6.6
H(34)-C(16)-C(17)-H(37)	61.952	c	6.6
H(34)-C(16)-C(18)-H(38)	61.202	c	6.6
H(34)-C(16)-C(18)-H(39)	-58.663	c	6.6
H(34)-C(16)-C(18)-H(40)	-179.163	c	6.6
H(26)-C(10)-C(11)-H(27)	-3.759	b	2.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 17. Best geometry of **p-M_2M_3CB**

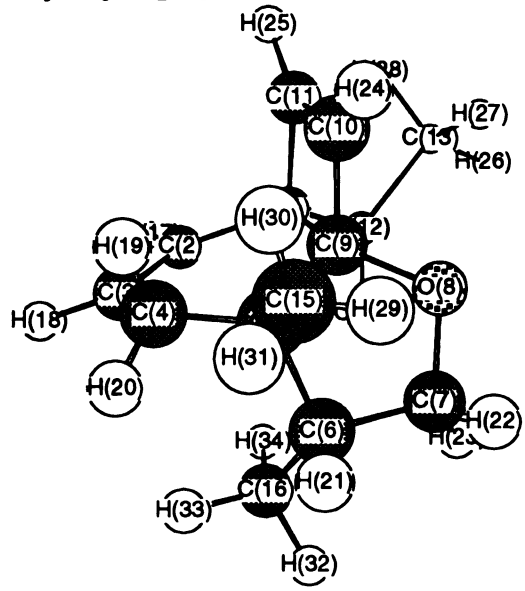


Table 15 Coupling Constants of **p-M_2M_3CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(17)-C(2)-C(3)-H(18)	-0.316	b	9.8
H(18)-C(3)-C(4)-H(19)	-84.417	0.0	2.6
H(18)-C(3)-C(4)-H(20)	31.292	5.9	6.8
H(21)-C(6)-C(7)-H(22)	-12.220	7.8	8.1
H(21)-C(6)-C(7)-H(23)	112.857	1.2	4.0
H(21)-C(6)-C(16)-H(32)	-59.502	c	6.9
H(21)-C(6)-C(16)-H(33)	60.314	c	6.9
H(21)-C(6)-C(16)-H(34)	-179.368	c	6.9
H(24)-C(10)-C(11)-H(25)	-2.866	b	3.0

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 18. Best geometry of **p-M_3M_4CB**

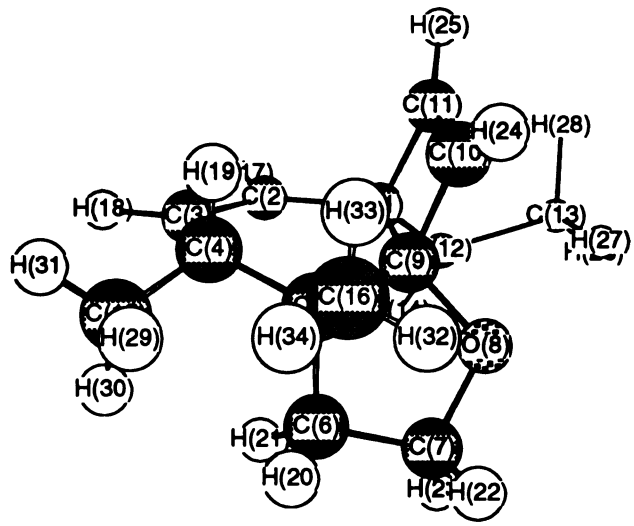


Table 16 Coupling Constants of **p-M_3M_4CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(17)-C(2)-C(3)-H(18)	-0.346	b	10.0
H(18)-C(3)-C(4)-H(19)	-88.876	0.0	4.1
H(19)-C(4)-C(15)-H(29)	-63.508	c	7.4
H(19)-C(4)-C(15)-H(30)	175.935	c	7.4
H(19)-C(4)-C(15)-H(31)	56.019	c	7.4
H(20)-C(6)-C(7)-H(22)	-17.157	7.5	7.7
H(20)-C(6)-C(7)-H(23)	108.181	0.6	5.9
H(21)-C(6)-C(7)-H(22)	-138.261	4.9	6.9
H(21)-C(6)-C(7)-H(23)	-12.923	7.7	8.3
H(24)-C(10)-C(11)-H(25)	-3.350	b	2.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 19. Best geometry of **p-$M_1M_3M_4$CB**

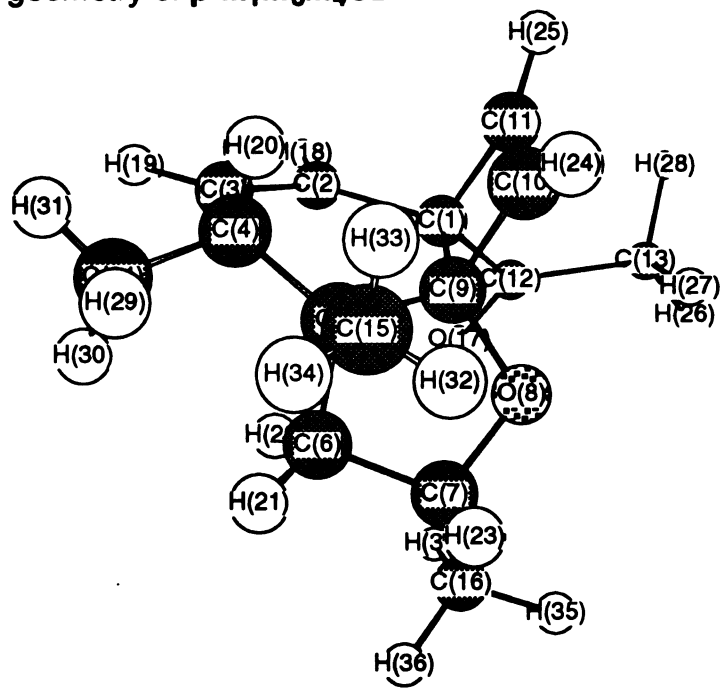


Table 17 Coupling Constants of **p-$M_1M_3M_4$CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(2)-C(3)-H(19)	1.343	b	10.0
H(19)-C(3)-C(4)-H(20)	-91.422	0.0	4.3
H(20)-C(4)-C(14)-H(29)	-68.300	c	7.4
H(20)-C(4)-C(14)-H(30)	174.984	c	7.4
H(20)-C(4)-C(14)-H(31)	55.245	c	7.4
H(21)-C(6)-C(7)-H(23)	-36.833	5.1	7.3
H(22)-C(6)-C(7)-H(23)	-157.735	7.9	7.3
H(23)-C(7)-C(16)-H(35)	-58.380	c	6.1
H(23)-C(7)-C(16)-H(36)	61.550	c	6.1
H(23)-C(7)-C(16)-H(37)	-178.551	c	6.1
H(24)-C(10)-C(11)-H(25)	-3.824	b	3.0

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 20. Best geometry of **p-M_4CB**

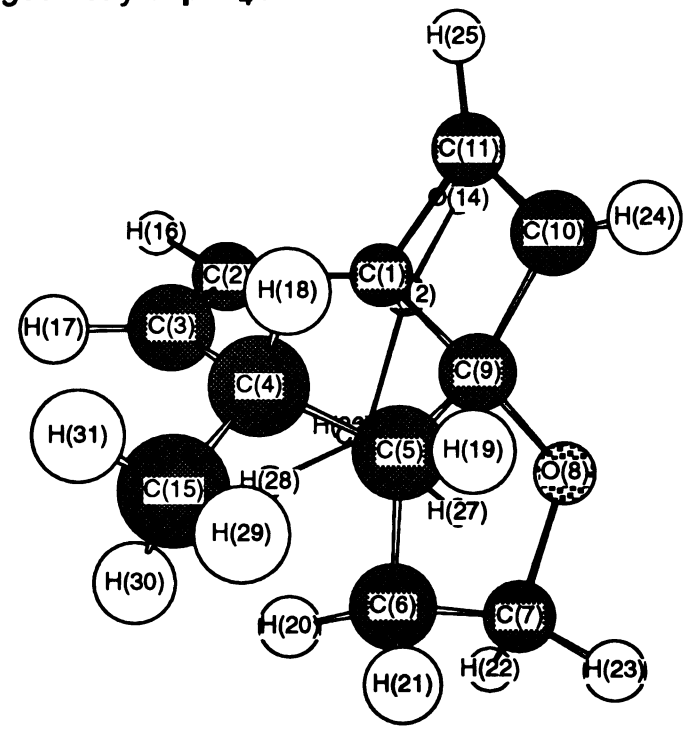


Table 18 Coupling Constants of **p-M_4CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(16)-C(2)-C(3)-H(17)	1.380	b	10.1
H(17)-C(3)-C(4)-H(18)	-92.681	0.0	3.7
H(18)-C(4)-C(5)-H(19)	41.148	4.5	7.2
H(18)-C(4)-C(15)-H(29)	-64.545	c	7.2
H(18)-C(4)-C(15)-H(30)	175.337	c	7.2
H(18)-C(4)-C(15)-H(31)	55.318	c	7.2
H(19)-C(5)-C(6)-H(20)	153.592	7.3	9.3
H(19)-C(5)-C(6)-H(21)	32.830	5.7	5.2

H(20)-C(6)-C(7)-H(22)	-15.459	7.6	7.5
H(20)-C(6)-C(7)-H(23)	-140.000	5.3	6.7
H(21)-C(6)-C(7)-H(22)	105.261	0.3	3.4
H(21)-C(6)-C(7)-H(23)	-19.278	7.3	7.5
H(24)-C(10)-C(11)-H(25)	-4.443	b	2.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 21. Best geometry of **p-$M_3M_4M_5$CB**

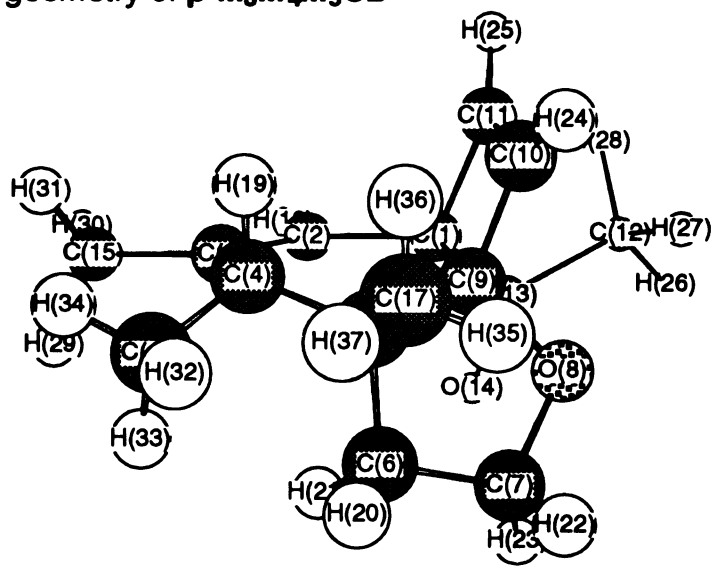


Table 19 Coupling Constants of **p-$M_3M_4M_5$CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(19)-C(4)-C(16)-H(32)	-68.158	c	7.2
H(19)-C(4)-C(16)-H(33)	171.483	c	7.2
H(19)-C(4)-C(16)-H(34)	51.150	c	7.2
H(20)-C(6)-C(7)-H(22)	-15.681	7.6	7.4

H(20)-C(6)-C(7)-H(23)	109.836	0.8	3.9
H(21)-C(6)-C(7)-H(22)	-137.088	4.8	6.5
H(21)-C(6)-C(7)-H(23)	-11.568	7.8	7.6
H(24)-C(10)-C(11)-H(25)	-3.196	b	3.0

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 22. Best geometry of **p-$M_1M_3M_4M_5$CB**

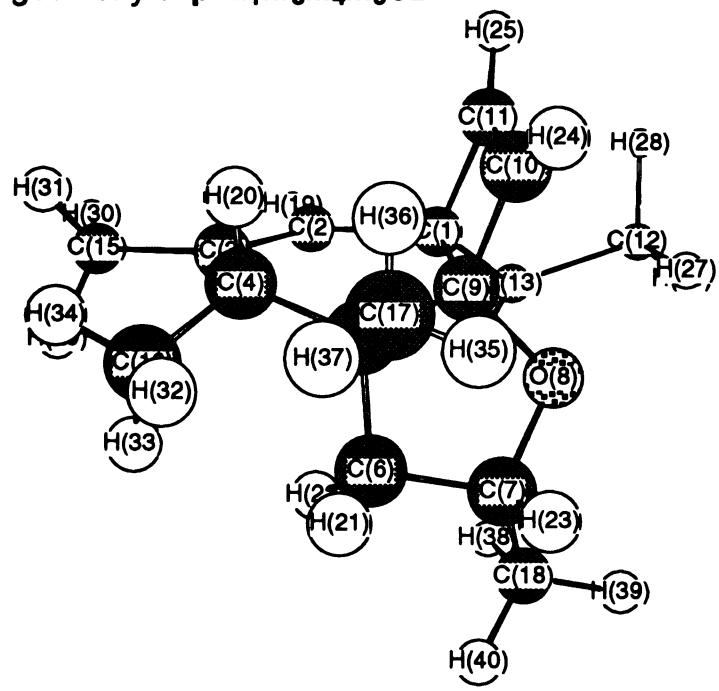


Table 20 Coupling Constants of **p-$M_1M_3M_4M_5$CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(20)-C(4)-C(16)-H(32)	-69.326	c	7.4
H(20)-C(4)-C(16)-H(33)	170.212	c	7.4
H(20)-C(4)-C(16)-H(34)	49.948	c	7.4

H(21)-C(6)-C(7)-H(23)	-24.707	6.7	10.2
H(22)-C(6)-C(7)-H(23)	-145.112	6.0	5.8
H(23)-C(7)-C(18)-H(38)	-171.226	c	6.2
H(23)-C(7)-C(18)-H(39)	-51.634	c	6.2
H(23)-C(7)-C(18)-H(40)	68.339	c	6.2
H(24)-C(10)-C(11)-H(25)	-3.637	b	2.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 23. Best geometry of **p-M_4M_5CB**

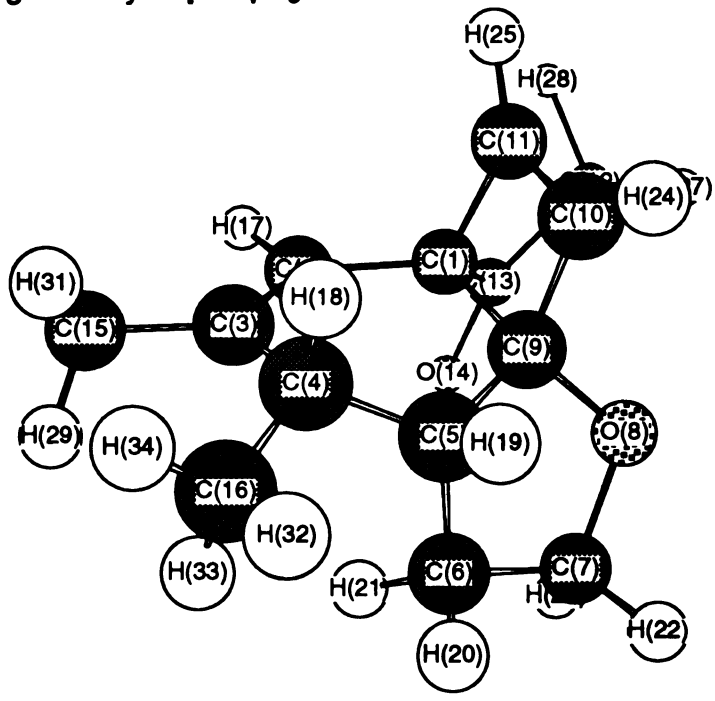


Table 21 Coupling Constants of **p-M_4M_5CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(4)-C(5)-H(19)	44.236	4.1	2.6
H(18)-C(4)-C(16)-H(32)	-66.748	c	6.4
H(18)-C(4)-C(16)-H(33)	173.426	c	6.4
H(18)-C(4)-C(16)-H(34)	52.935	c	6.4
H(19)-C(5)-C(6)-H(20)	31.323	5.9	7.7
H(19)-C(5)-C(6)-H(21)	152.078	7.1	10.2
H(20)-C(6)-C(7)-H(22)	-13.035	7.7	7.2
H(20)-C(6)-C(7)-H(23)	112.322	1.0	4.1
H(21)-C(6)-C(7)-H(22)	-133.624	4.2	6.0
H(21)-C(6)-C(7)-H(23)	-8.267	8.0	6.9
H(24)-C(10)-C(11)-H(25)	-3.467	b	2.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 24. Best geometry of **o-I_1CB**

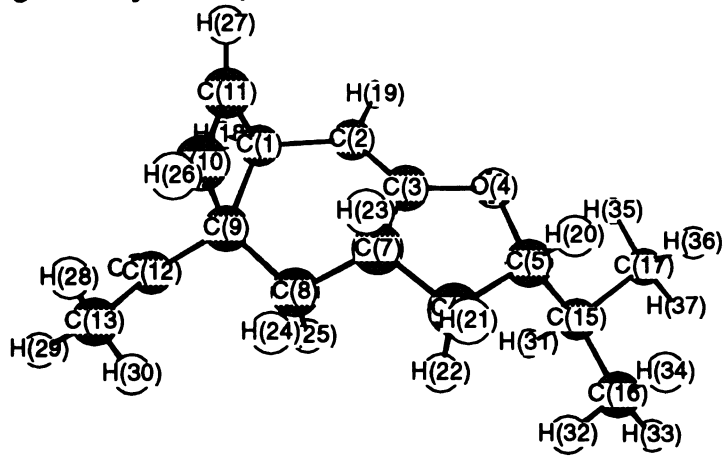


Table 22 Coupling Constants of **o-I_1CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(1)-C(2)-H(19)	33.121	5.7	6.6
H(20)-C(5)-C(6)-H(21)	-14.167	7.7	12.4
H(20)-C(5)-C(6)-H(22)	-134.175	4.3	4.9
H(20)-C(5)-C(15)-H(31)	-178.621	9.2	6.7
H(21)-C(6)-C(7)-H(23)	19.510	7.3	9.8
H(22)-C(6)-C(7)-H(23)	140.092	5.3	3.8
H(23)-C(7)-C(8)-H(24)	-55.675	2.5	5.2
H(23)-C(7)-C(8)-H(25)	-173.328	9.0	8.7
H(31)-C(15)-C(16)-H(32)	-59.453	c	6.7
H(31)-C(15)-C(16)-H(33)	60.534	c	6.7
H(31)-C(15)-C(16)-H(34)	-180.000	c	6.7

H(31)-C(15)-C(17)-H(35)	61.178	c	6.7
H(31)-C(15)-C(17)-H(36)	-179.051	c	6.7
H(31)-C(15)-C(17)-H(37)	-58.962	c	6.7
H(26)-C(10)-C(11)-H(27)	-3.259	b	2.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 25. Best geometry of **o-I_1M_3CB**

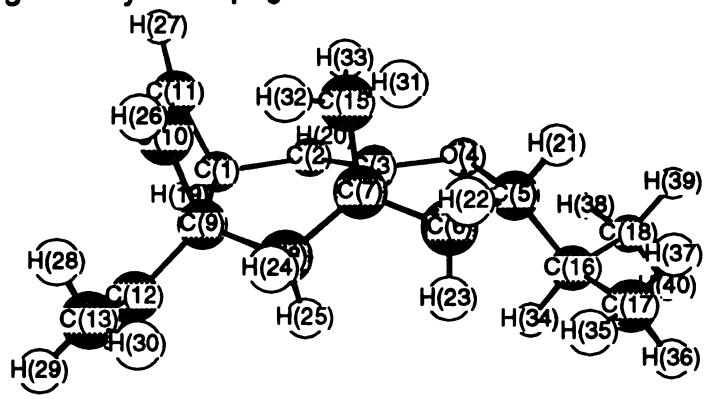


Table 23 Coupling Constants of **o-I_1M_3CB**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(19)-C(1)-C(2)-H(20)	31.858	5.8	6.6
H(21)-C(5)-C(6)-H(22)	-9.117	8.0	11.0
H(21)-C(5)-C(6)-H(23)	-130.568	3.7	5.0
H(21)-C(5)-C(16)-H(34)	176.636	9.1	6.9
H(34)-C(16)-C(17)-H(35)	-59.684	c	6.8
H(34)-C(16)-C(17)-H(36)	60.314	c	6.8
H(34)-C(16)-C(17)-H(37)	-180.000	c	6.8

H(34)-C(16)-C(18)-H(38)	61.741	c	6.8
H(34)-C(16)-C(18)-H(39)	-178.296	c	6.8
H(34)-C(16)-C(18)-H(40)	-58.259	c	6.8
H(26)-C(10)-C(11)-H(27)	-3.182	b	2.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 26. Best geometry of **p-M_2M_3CH**

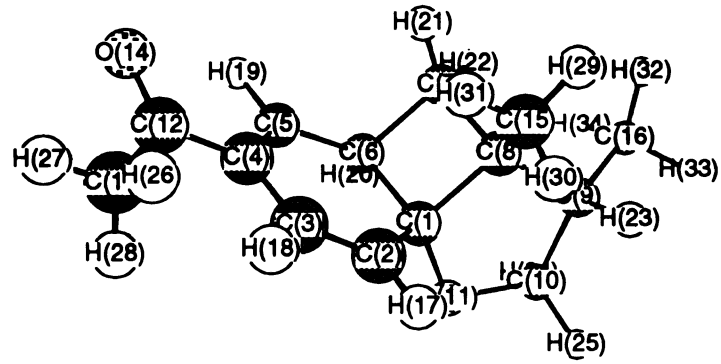


Table 24 Coupling Constants of **p-M_2M_3CH**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(17)-C(2)-C(3)-H(18)	0.633	b	10.2
H(19)-C(5)-C(6)-H(20)	-54.526	3.0	5.5
H(20)-C(6)-C(7)-H(21)	-131.334	3.8	6.9
H(20)-C(6)-C(7)-H(22)	5.289	8.1	10.9
H(23)-C(9)-C(10)-H(24)	-136.910	4.8	7.0
H(23)-C(9)-C(10)-H(25)	-13.567	7.7	10.9
H(23)-C(9)-C(16)-H(32)	-71.754	c	6.8

H(23)-C(9)-C(16)-H(33)	47.826	c	6.8
H(23)-C(9)-C(16)-H(34)	167.572	c	6.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 27. Best geometry of **p-M_3M_4CH**

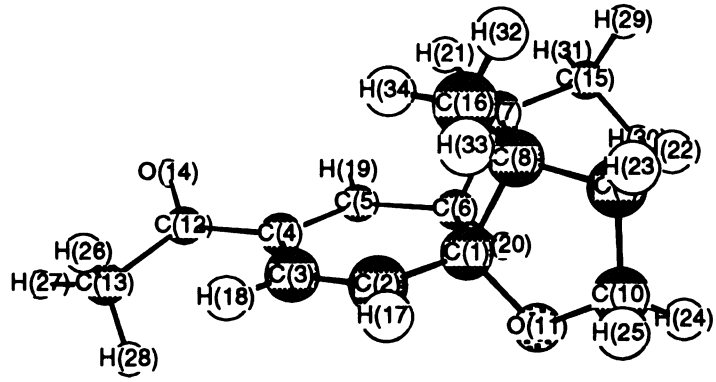


Table 25 Coupling Constants of **p-M_3M_4CH**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(17)-C(2)-C(3)-H(18)	0.448	b	9.7
H(19)-C(5)-C(6)-H(20)	-53.638	3.2	5.8
H(20)-C(6)-C(7)-H(21)	136.128	4.6	10.7
H(21)-C(7)-C(15)-H(29)	66.827	c	7.5
H(21)-C(7)-C(15)-H(30)	-172.424	c	7.5
H(21)-C(7)-C(15)-H(31)	-52.549	c	7.5
H(22)-C(9)-C(10)-H(24)	7.919	8.0	9.2
H(22)-C(9)-C(10)-H(25)	131.627	3.9	6.2

H(23)-C(9)-C(10)-H(24)	-110.920	0.9	3.6
H(23)-C(9)-C(10)-H(25)	12.785	7.7	7.5

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 28. Best geometry of **p-$M_1M_3M_4$CH**

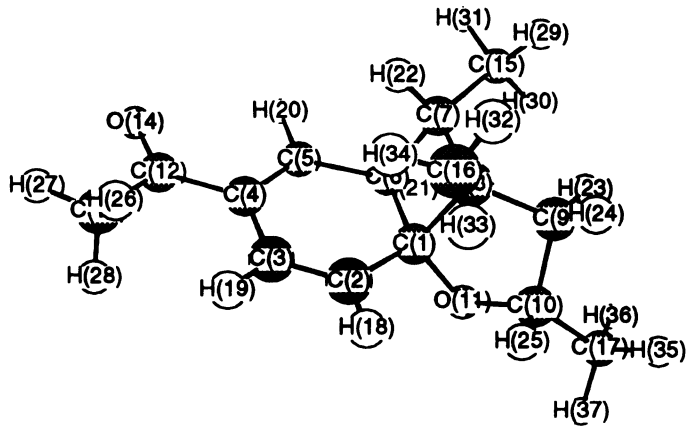


Table 26 Coupling Constants of **p-$M_1M_3M_4$CH**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(2)-C(3)-H(19)	0.316	b	10.2
H(20)-C(5)-C(6)-H(21)	-51.447	3.2	6.3
H(21)-C(6)-C(7)-H(22)	139.936	5.3	10.0
H(22)-C(7)-C(15)-H(29)	68.885	c	7.5
H(22)-C(7)-C(15)-H(30)	-169.181	c	7.5
H(22)-C(7)-C(15)-H(31)	-50.130	c	7.5
H(23)-C(9)-C(10)-H(25)	163.008	8.3	10.8
H(24)-C(9)-C(10)-H(25)	43.654	4.1	4.8
H(25)-C(10)-C(17)-H(35)	-63.834	c	5.9

H(25)-C(10)-C(17)-H(36)	175.923	c	5.9
H(25)-C(10)-C(17)-H(37)	55.920	c	5.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 29. Best geometry of **p-M_0COT**

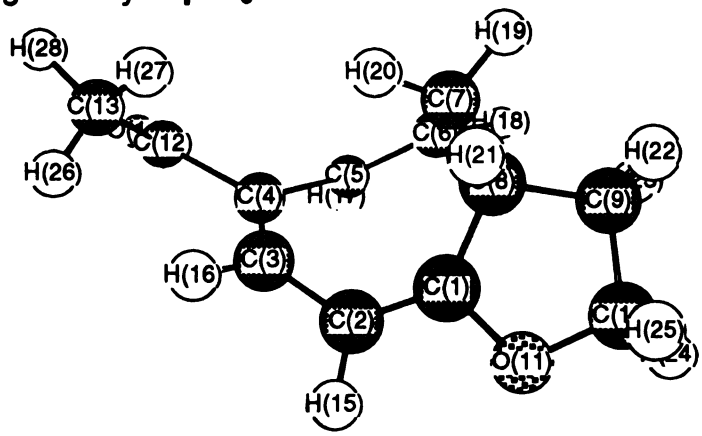


Table 27 Coupling Constants of **p-M_0COT**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(15)-C(2)-C(3)-H(16)	50.074	b	8.1
H(17)-C(5)-C(6)-H(18)	-3.380	b	11.3
H(18)-C(6)-C(7)-H(19)	30.673	5.9	4.0
H(18)-C(6)-C(7)-H(20)	147.850	6.4	7.9
H(19)-C(7)-C(8)-H(21)	75.292	0.3	3.5
H(20)-C(7)-C(8)-H(21)	-40.683	4.5	8.2
H(21)-C(8)-C(9)-H(22)	-26.845	6.5	7.7
H(21)-C(8)-C(9)-H(23)	-147.137	6.4	6.0
H(22)-C(9)-C(10)-H(24)	-108.937	3.8	5.4

H(22)-C(9)-C(10)-H(25)	16.420	7.5	8.8
H(23)-C(9)-C(10)-H(24)	11.663	7.8	9.2
H(23)-C(9)-C(10)-H(25)	137.018	4.8	4.9

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 30. Best geometry of **p-M$_1$COT**

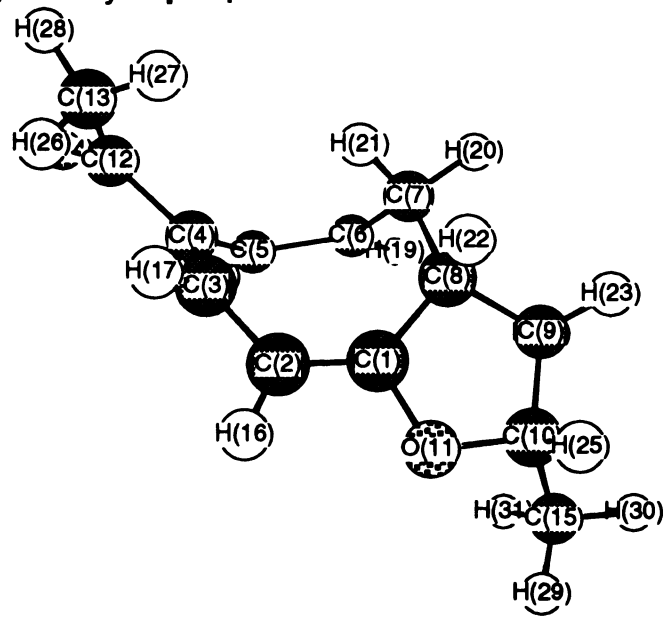


Table 28 Coupling Constants of **p-M$_1$COT**

Atoms	ϕ dihedral angle	J $_{calc}$ (Hz)	J $_{expl}$ (Hz) [a]
H(16)-C(2)-C(3)-H(17)	50.207	b	8.0
H(18)-C(5)-C(6)-H(19)	-2.900	b	11.3
H(19)-C(6)-C(7)-H(20)	29.899	6.1	7.9
H(19)-C(6)-C(7)-H(21)	147.654	6.4	7.9
H(20)-C(7)-C(8)-H(22)	75.360	0.3	3.0

H(21)-C(7)-C(8)-H(22)	-40.991	4.4	10.5
H(22)-C(8)-C(9)-H(23)	-28.625	6.3	5.4
H(22)-C(8)-C(9)-H(24)	-148.969	6.5	11.9
H(23)-C(9)-C(10)-H(25)	20.739	7.1	9.9
H(24)-C(9)-C(10)-H(25)	141.200	5.4	6.0
H(25)-C(10)-C(15)-H(29)	57.233	c	6.2
H(25)-C(10)-C(15)-H(30)	62.707	c	6.2
H(25)-C(10)-C(15)-H(31)	177.031	c	6.2

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 31. Best geometry of **p-M_1M_3COT**

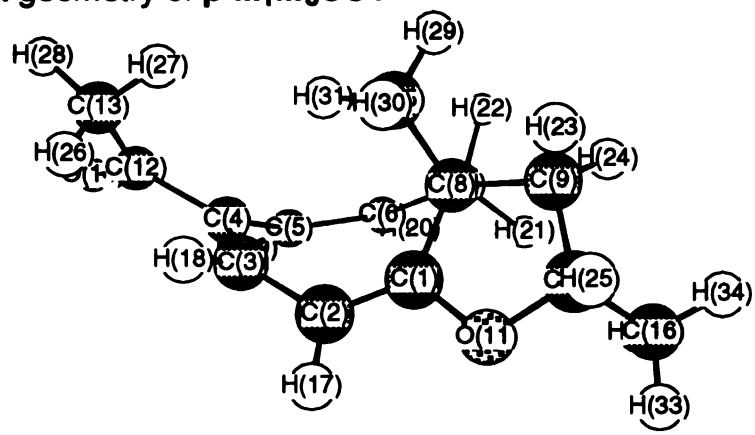


Table 29 Coupling Constants of **p-M_1M_3COT**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(17)-C(2)-C(3)-H(18)	52.277	b	6.6
H(19)-C(5)-C(6)-H(20)	-2.215	b	10.8
H(20)-C(6)-C(7)-H(21)	-41.375	4.5	9.1

H(20)-C(6)-C(7)-H(22)	72.791	1.4	7.1
H(23)-C(9)-C(10)-H(25)	-2.451	8.2	10.2
H(24)-C(9)-C(10)-H(25)	116.700	1.6	4.9
H(25)-C(10)-C(16)-H(32)	-180.000	c	6.1
H(25)-C(10)-C(16)-H(33)	60.625	c	6.1
H(25)-C(10)-C(16)-H(34)	-59.291	c	6.1

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 32. Best geometry of **p-I_1M_3COT**

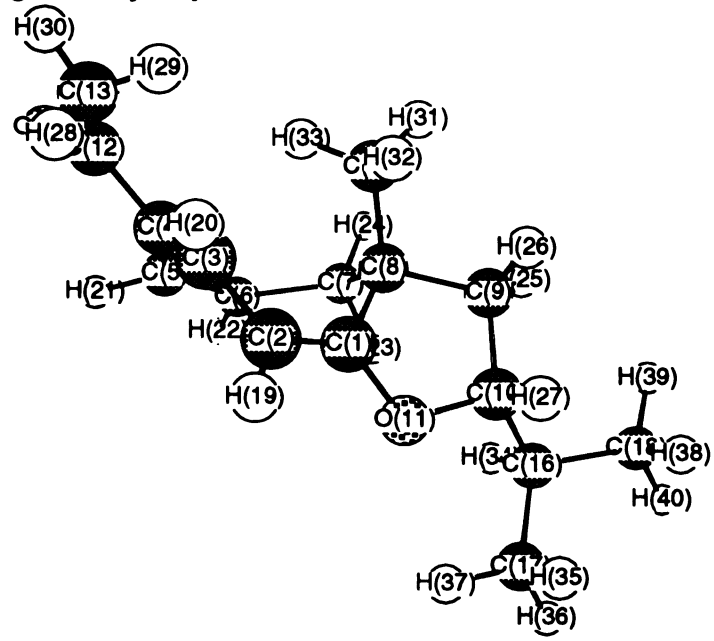


Table 30 Coupling Constants of **p-I_1M_3COT**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz) [a]
H(19)-C(2)-C(3)-H(20)	58.366	b	6.6
H(21)-C(5)-C(6)-H(22)	-0.448	b	10.6

H(22)-C(6)-C(7)-H(23)	-39.393	4.8	9.4
H(22)-C(6)-C(7)-H(24)	73.457	1.2	7.2
H(25)-C(9)-C(10)-H(27)	114.500	1.3	5.2
H(26)-C(9)-C(10)-H(27)	-3.182	8.2	11.4
H(27)-C(10)-C(16)-H(34)	-172.123	8.9	7.6
H(34)-C(16)-C(17)-H(35)	-179.051	c	6.7
H(34)-C(16)-C(17)-H(36)	60.920	c	6.7
H(34)-C(16)-C(17)-H(37)	-58.403	c	6.7
H(34)-C(16)-C(18)-H(38)	180.000	c	6.7
H(34)-C(16)-C(18)-H(39)	59.216	c	6.7
H(34)-C(16)-C(18)-H(40)	-60.333	c	6.7

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 33. Best geometry of **o-I$_1$COT**

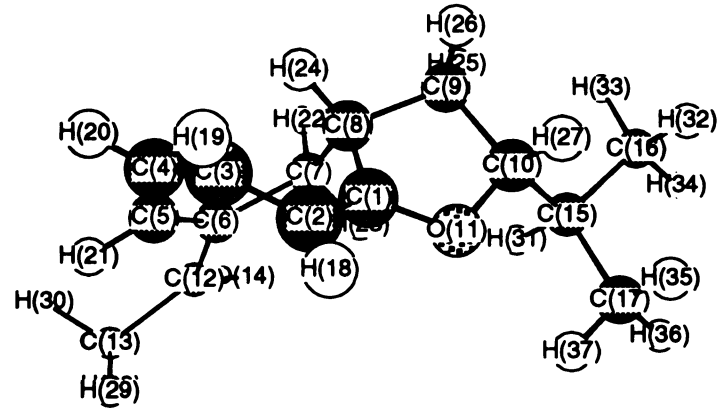


Table 31 Coupling Constants of **o-I_1COT**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(18)-C(2)-C(3)-H(19)	53.675	b	9.4
H(19)-C(3)-C(4)-H(20)	-2.645	b	13.2
H(20)-C(4)-C(5)-H(21)	-43.729	b	6.1
H(22)-C(7)-C(8)-H(24)	61.793	1.6	1.8
H(23)-C(7)-C(8)-H(24)	177.390	9.1	7.4
H(24)-C(8)-C(9)-H(25)	-92.258	0.0	5.4
H(24)-C(8)-C(9)-H(26)	25.868	6.5	8.8
H(25)-C(9)-C(10)-H(27)	110.348	0.8	4.7
H(26)-C(9)-C(10)-H(27)	-9.232	8.0	10.9
H(27)-C(10)-C(15)-H(31)	-178.483	9.2	7.5
H(31)-C(15)-C(16)-H(32)	179.294	c	6.8
H(31)-C(15)-C(16)-H(33)	58.530	c	6.8
H(31)-C(15)-C(16)-H(34)	-60.868	c	6.8
H(31)-C(15)-C(17)-H(35)	-179.453	c	6.8
H(31)-C(15)-C(17)-H(36)	60.786	c	6.8
H(31)-C(15)-C(17)-H(37)	-58.619	c	6.8

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

Figure 34. Best geometry of **o-I_1M_3COT**

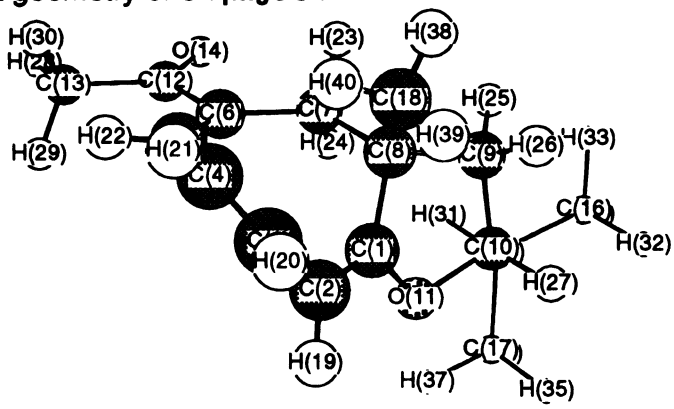


Table 32 Coupling Constants of **o-I_1M_3COT**

Atoms	ϕ dihedral angle	J_{calc} (Hz)	J_{expl} (Hz)[a]
H(19)-C(2)-C(3)-H(20)	54.928	b	8.2
H(20)-C(3)-C(4)-H(21)	-4.509	b	12.9
H(21)-C(4)-C(5)-H(22)	-40.491	b	5.9
H(25)-C(9)-C(10)-H(27)	116.195	1.5	5.2
H(26)-C(9)-C(10)-H(27)	-1.002	8.2	11.0
H(27)-C(10)-C(15)-H(31)	-177.878	9.1	7.3
H(31)-C(15)-C(16)-H(32)	179.051	c	6.7
H(31)-C(15)-C(16)-H(33)	58.427	c	6.7
H(31)-C(15)-C(16)-H(34)	-61.076	c	6.7
H(31)-C(15)-C(17)-H(35)	-178.775	c	6.7
H(31)-C(15)-C(17)-H(36)	61.198	c	6.7
H(31)-C(15)-C(17)-H(37)	-58.186	c	6.7

a. 300 MHz ^{1}H-NMR

b. Olefinic protons

c. Free rotation protons

The following table 12 is given to demonstrate the *cis* olefinic coupling constants[69] in comparison with the cyclobutenes, cycloheptenes, cyclohexenes and cyclononenes obtained in this dissertation.

Table 33 *Cis* Olefinic Coupling Constants in Cyclic Systems

Ring size	$J_{H-C=C-H}$ (Hz)
3	0.5 - 1.5
4	2.5 - 3.7
5	5.1 - 7.0
6	8.8 - 11.0
7	9.0 - 12.5 [a]
8	10.0 - 13.0
cis -Cyclononene	10.7 [b]
cis -Cyclodecene	10.8

a: J_{trans} = 15.0 - 17.2 Hz

b: J_{trans} = 15.5 - 16.5 Hz

DISCUSSION

I. Diastereoselectivity

Diastereoselectivity in organic reactions relates to the control of relative stereochemistry. Stereoselective reactions are those which involve preferential formation of one stereoisomer when more than one is possible.

The diastereoselectivity with which *o*- and *p*-butenoxy acetophenones undergo intramolecular [2+2] photocycloadditions were measured in this work. Twelve *para* - and two *ortho*- substituted acetophenones with alkyl substitution on the tether or phenyl ring were examined in terms of the diastereomeric excess of their photocycloaddition products.[70] The basic reaction creates six new stereocenters, two of which (the 6/4 bridge) are lost when the initial cyclohexadiene (**CH**) photoproduct opens to cycloöctatriene (**COT**). However, two more stereocenters are created at the new 6/4 bridge when this cycloöctatriene photocyclizes to cyclobutene (**CB**). Substituents on C-1, C-2 and C-4 of tether produce stereocenters that persist throughout the reaction. Each can exist in two geometrical relationships relative to stereocenter created by photolysis.

The diastereoselectivity in intramolecular [2+2] *ortho* cycloaddition of double bonds to triplet benzenes is extremely high. This photocycloaddition is able to produce a cycloadduct with two new rings and up to six new stereocenters in one steps. These six new stereocenters include four reactive centers and two inducible centers (on the tether). Theoretically, there are at most thirty two possible diastereoisomers of cycloadducts. However, there is exclusively one major diastereomer obtained in most cases and the diastereoselectivity is impressive.

The stereochemistry of substituents on the tether is established when the first bond is formed, to produce an intermediate 1,4-biradical. Alkyl groups on the tether or the double bond show high *trans* stereoselectivity with regard to configuration of the bridgehead stereocenters. Within the error limits of ^{1}H-NMR integration, identical diastereoselectivities were obtained in both photostable **CB** and thermally stable **CH** or **COT**. This is understandable since no bonds are broken adjacent to the stereocenters during interconversion.

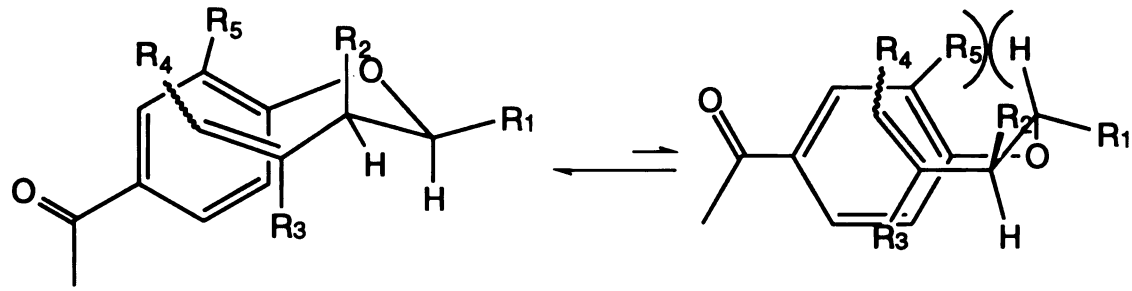
Since the first bond formation in these intramolecular [2+2] photocycloadditions generates a five-membered ring, the observed diastereoselectivity is related to the energies of transition state conformations leading to the five-membered ring. There are two possible low-energy conformations for a simple five-membered ring model, cyclopentane, and both of which have analogous in the cyclohexane series. One is chair-like (half chair) and the other is boat-like (envelope).[71] Both of them are flexible forms which are easily interconvertible by pseudorotations. There is no energy maxima or minima on the cyclopentane profile. It seems that conformational analysis is more difficult for cyclopentane than cyclohexane.

This degeneracy can, however, be changed by suitable substitution. In our system, replacement of a methylene group by an oxygen atom would induce a preference for chair-like conformation because two pairs of H-H eclipsing interaction (torsional strain) have been removed. The severe non-bonded interaction between R_1 and phenyl hydrogen (or R_5) *ortho* to the tether also favors the chair-like conformation (if R_1 is in a favored pseudoequatorial position in Sch. 19). Therefore, the chair-like conformation is more favored and will be employed as the transition state model.

The most stable chair-like conformation requires the substituents to occupy pseudoequatorial position. Since the degree of diastereoselectivity is

representative of the conformational preference of the substituent, it should be most pronounced with bulky groups.

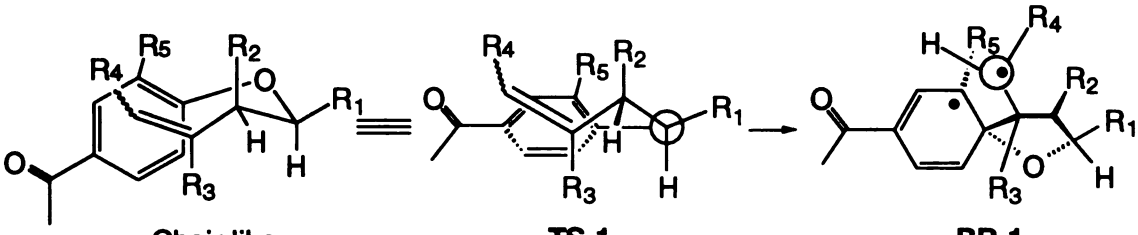
Scheme 19



Chair-like Boat-like

In all cases the major product has R_1 or R_2 *trans* to R_3. Biradical formation sets the R_1 / R_3 or R_2 / R_3 relationship shown in Scheme 20. When R_1 = methyl and R_3 = H in **p-M$_1$K**, diastereoselectivity is only modest (de = 41% for **CB** and de = 56% for **COT**). Diastereoselectivity is improved (67% for **CB** and 61% for **COT**) for R_1 = isopropyl and R_3 = H in **p-I$_1$K** due to increased steric bulk of an isopropyl compared to a methyl substituent.

Scheme 20

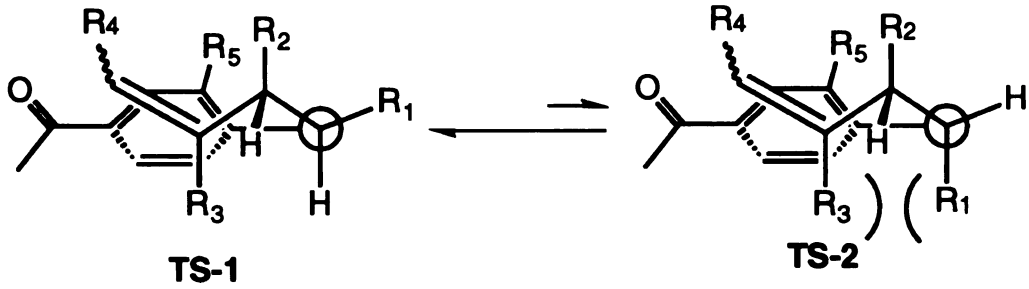


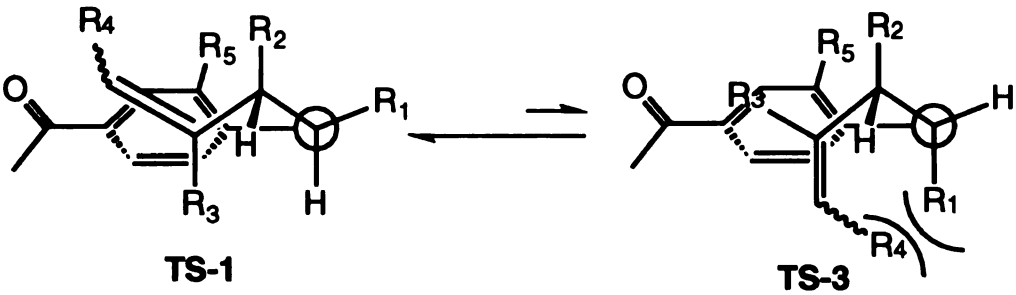
Chair-like **TS-1** **BR-1**

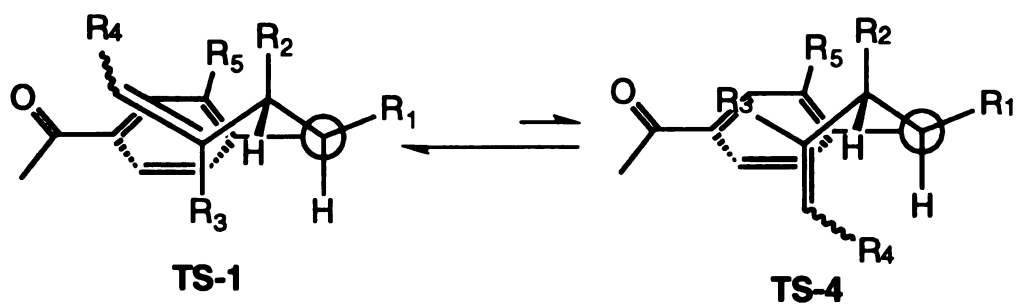
"A" values (conformational free energy difference) for equatorial preference in cyclohexane systems indicate that $A_{isopropyl}$ (2.28) is larger than A_{methyl} (1.74).[72] This means that the isopropyl group is more sterically demanding than a methyl group. Isopropyl group still favors a pseudo-equatorial position in **TS-1** , although "A" values are considered to be smaller in cylcopentane than in cyclohexane.[73]

When R_1 = methyl and R_3 = methyl in **p-M_1M_3K**, diastereoselectivity increases to 80% in both **CB** and **COT**. Diastereoselectivity become total (> 95%) when R_1 = isopropyl and R_3 = methyl in **p-I_1M_3K**. Scheme 21 depicts Newman projections viewing down the tether C–O bond. The two approaches of the double bond to the benzene ring that produce diastereomeric products with different degrees of pseudo-1,3-diaxial nonbonded interaction are shown by **TS-1** , **TS-2** and **TS-3**. In **TS-1**, R_1 group favors to occupy at pseudo-equatorial position, which is also away from the phenyl ring. In both **TS-2** and **TS-3**, R_1 group occupies an unfavored pseudo-axial position and also suffers from a severe pseudo-1,3-diaxial nonbonded interaction either from R_3 or from R_4.

Scheme 21







The difference between **TS-1** and **TS-4** is in vinyl bond orientation which is achieved by a bond rotation. Regardless of bulk of R_3, the double bond prefers to occupy a pseudo-equatorial position. **TS-1** seems to suffer from a pseudo-1,3-diaxial nonbonded interaction between R_3 and hydrogen at C-1 when R_3 is methyl group. However, the secondary orbital electronic effect plays an important role in this model and leads the double bond to remain at pseudo-equatorial position.[74,75] When the double bond approaches the phenyl group for bond formation, the π^* orbital of double bond is stabilized by the phenyl π orbital to produce a secondary attractive interaction in chair-like transition state. There is no such an effect in **TS-4**. The double bond occupies at pseudo-axial position in **TS-4** and the π^* orbital of double bond is away from the phenyl ring, especially after the first bond formation.

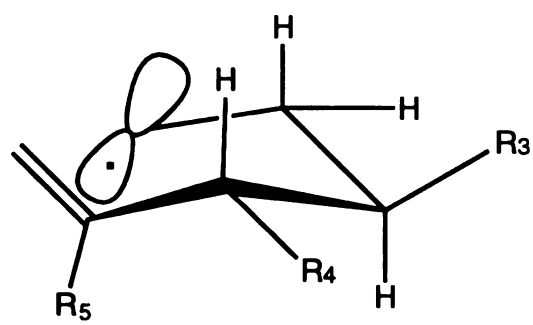
Pre-existing torsional effects between R_2 = Me and R_3 = Me favor R_3 being *trans* to R_2 in **p-M_2M_3K**. The *trans*ition-state model (**TS-4**) emphasizes the importance of minimization of eclipsing interaction[76] of R_2 and R_3 instead of 1,3-allylic strain.[77,78] Interaction between the methyl group and vinyl group is small when R_4 is hydrogen.

For *ortho*-ketones, diastereoselectivity of R_1 and R_3 is similar to the *para*. case. Diastereoselectivity of **CB** and **COT** is 60% in **o-I_1K** and 80% in **o-I_1M_3K**. Selectivity decreases slightly for **CB** formation in **o-I_1M_3K** compared to **p-I_1M_3K** (> 95%). This is probably due to the increased steric strain found in the angular ring system compared to the linear.

The above diastereoselectivity reveals that there is a delicate balance among nonbonded interaction, torsional strain, allylic strain and secondary orbital electronic effect. The minor products may be generated from either **TS-2**, **TS-3**, **TS-4** or boat-like transition state mentioned previously.

Beckwith has proposed general guidelines to predict the stereochemical outcome of intramolecular free-radical cyclization reactions of simple substituted hex-5-enyl radicals.[79-81] Cyclization of 1- and 3-substituted hex-5-enyl radicals leads mostly to *cis*-disubstituted cyclopentyl products, whereas 2- and 4-substituted hex-5-enyl radicals give predominantly *trans* products. Observed stereochemical results were rationalized by invoking a theoretically derived "chair-like" *trans*ition state (Scheme 22) which has a long incipient bond (ca. 2.3 Å), in accordance with an early *trans*ition state predicted for these reactions.[82]

Scheme 22



The major product is formed via a conformation where the substituents occupy a pseudo-equatorial position. The diastereomeric excess formed in 3-methyl-hex-5-enyl radical cyclization was 46% of *cis*-methyl- cyclopentyl product. This is similar to the results of **p-M_1K** (41%). The only difference is a replacement of the methylene group in position 2 by an oxygen atom in our system.

Diastereoselectivity of ring closure for each radical is due primarily to differences in activation energy between conformations leading to the two diastereomers. For modest diastereoselectivity (46%) obtained above, 0.63 kcal/mol of difference in activation energy is required.[80] This difference was

calculated to be 0.36 kcal/mol by Houk with the inclusion of a boat-like exo *trans*ition structure in addition to Beckwith's chair-like *trans*ition structure.[83] The difference in activation energy of two diastereomers in our system should also be relatively small and close to 0.6 kcal/mol.

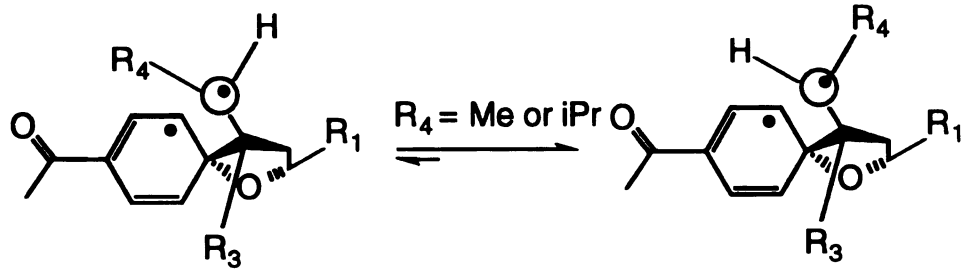
In 4-methyl hex-5-enyl radical cyclization, the *trans*-dimethyl cyclopentyl product was obtained with 64% diastereomeric excess.[80] In our system using **p-M_2M_3K** the opposite selectivity was observed. The reaction appeared to proceed *via* formation of the *cis*-dimethyl-oxy-cyclopentyl radical with R_2 being *trans* to R_3. This is attributed to the torsional interaction between R_2 and R_3 as mentioned previously.

Biradical closure sets the R_3 / R_4 relationship. This intermediate itself shows strong conformational preferences during its cyclization, which results from steric effects of substituents on the tether. In **p-M_3M_4K**, only one diastereomer is observed (> 95%) for R_3 = R_4 = methyl. As shown in Scheme 23, the best conformation of the biradical **BR-1** has R_4 pointed away from the six-membered ring and placed it anti to R_3.

The diastereomeric excess of 80% observed in **p-$M_1M_3M_4K$** example is similar to that measured from irradiation of **p-M_1M_3K** and **p-M_3M_4K**; R_1 and R_3 have 80% diastereomeric preference to be *trans* to each other and R_3 and R_4 have > 95% diastereomeric excess *trans* to each other.

Diastereoselectivity (80%) observed when R_3 = H and R_4 = methyl in **p-M_4K** progresses to > 95% when an isopropyl group (R_4) is placed in **p-I_4K**. The *trans* preference between R_3 and R_4 exists regardless if R_3 is H or a methyl group in above cases.

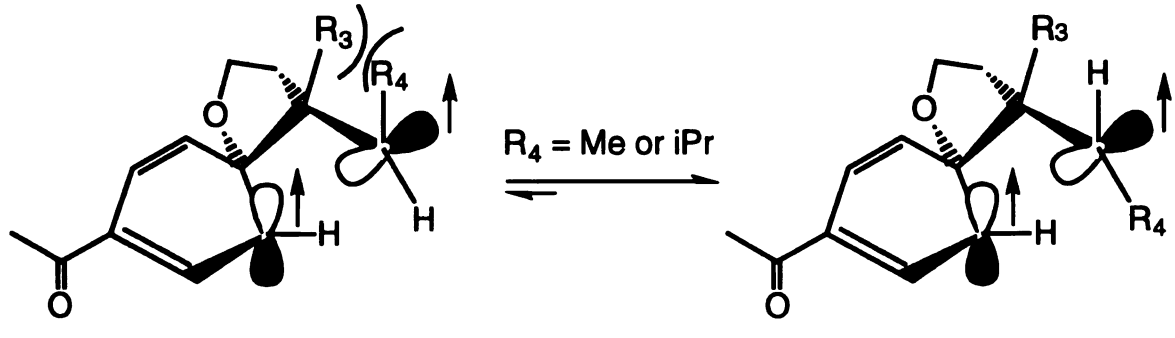
Scheme 23



BR-2 **BR-1**

Becker and coworkers investigated the diastereoselectivity induced by substituents at the end of olefins in [2+2] intramolecular photocycloaddition of cycloenones. In contrast to our phenyl ketone systems, lower selectivity was obtained.[40,41] Their explanation for the selectivity by the relative stability using molecular mechanics (MM2) was inconclusive since the calculations gave similar steric energies for both stereoisomers. An alternative explanation can be based on a model proposed for oxetanes by Griesbeck.[84] This assumed that for effective triplet to singlet spin inversion the p orbitals of a 1,4-biradical intermediate have to be perpendicular to each other. It seems reasonable that the methyl or bulky isopropyl group will orient itself to the least crowded environment, which is away from the ring skeleton. (Scheme 24)

Scheme 24

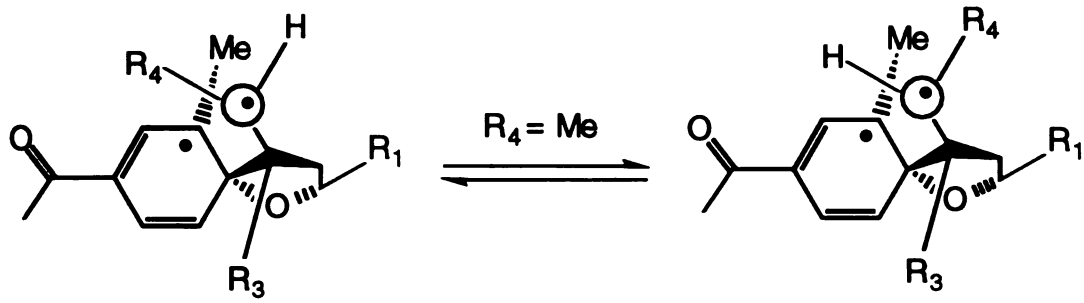


BR-2 **BR-1**

The ring methyl in **p-M_4M_5K**, **p-$M_3M_4M_5K$** and **p-$M_1M_3M_4M_5K$** promotes complete regioselectivity.[6] This means that the double bond approach toward the methyl group on the benzene ring is not hindered by R_4, however the diastereoselectivity of R_3 and R_4 is reduced. Scheme 25 portrays the high selectivity of R_3 / R_4 which decreases when there is a methyl group on the benzene ring. Steric interactions between R_4 and R_5 (= Me) cause the 1,4-biradical to have no rotational preference as shown in **BR-3** and **BR-4**.

^{1}H-NMR analysis of cyclobutene geometry indicated that there is only one proton $H_{4\alpha}$ having allylic coupling with vinyl proton H_2. The other, $H_{4\beta}$, doesn't show allylic coupling in most cases. From AM1 calculations, the dihedral angle of C2-C3-C4-$H_{4\alpha}$ is normally about 145° and the dihedral angle of C2-C3-C4-$H_{4\beta}$ about 90°. However, $H_{4\beta}$ has allylic coupling with vinyl proton H_2 in **p-M_4CB** (1.9 Hz) and **p-I_4CB** (1.7 Hz) and their dihedral angle of C2-C3-C4-$H_{4\beta}$ are 131° and 147°, respectively. This means that the substituents change the geometry of cyclobutene remarkably and the allylic coupling constants are sensitive to geometry variation as observed in vicinal coupling constants (see Results).

Scheme 25



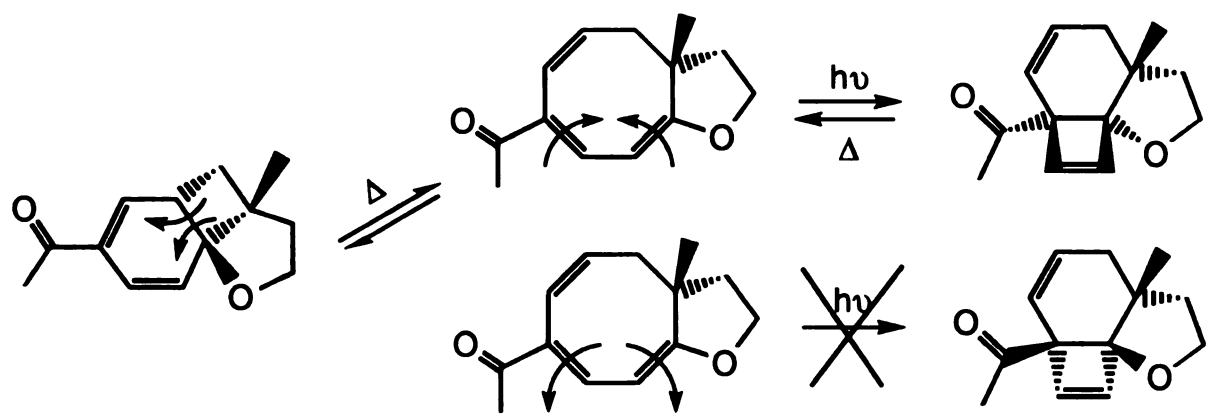
BR-3 **BR-4**

R_3 and the cyclobutene ring are always *cis* to each other in all bicycloöcta-2,10-diene (**CB**) compounds as Scheme 26 indicates. The initial cycloaddition to

the benzene ring must be *cis*, disrotatory thermal opening furnishes a boat-shaped all-*cis* cycloöctatriene. The regiospecific photoclosure of a diene is also disrotatory and forms a *cis* 4/6 ring fusion, but proceeds only in the direction that also produces a *cis* 5/6 ring fusion, such that the five-membered ring is *trans* to the cyclobutene ring. Presumably the more conjugated diene unit with the strong oxygen-to-carbonyl donor-acceptor property[2,4,70] flattens out when excited and the fused five-membered ring then allows the eight-membered ring to pucker only in one direction.

In compounds formed from *p*-tethered ketones, this selectivity probably represents a simple steric effect. There is no obvious steric hindrance; yet stereoselectivity is complete. Compounds generated from *o*-tethered ketones also show high stereoselectivity. The minimum energies of both *cis* and *trans* conformers of linear cyclobutenes were calculated using PC MODEL (MMX) after optimization. The minimum energies of *cis* isomers were much lower than *trans*.[85]

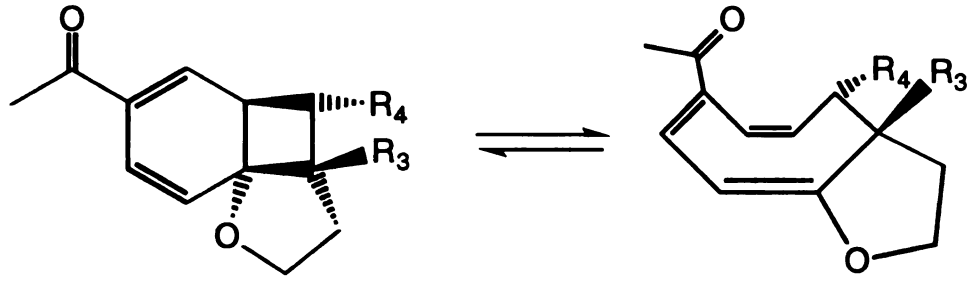
Scheme 26



Valence tautomerism between bicyclo[4,2,0]octa-2,4-diene and cycloöcta-1,3,5-triene is affected by the additional bulky groups on the methylene carbons. Without bulky groups, equilibrium of basic skeleton favors cycloöctatriene. The

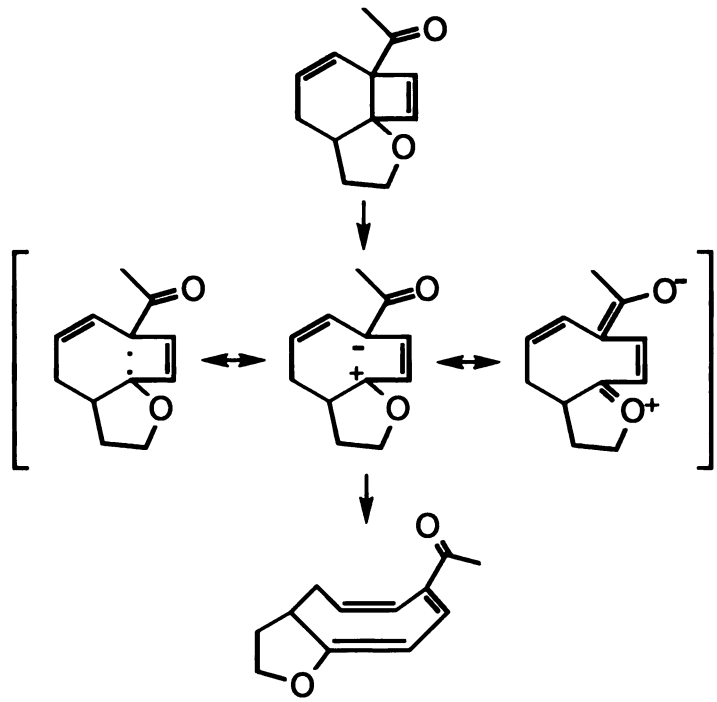
equilibrium is reversed to cyclohexadiene with 95% preference when both methylene carbons are methyl-substituted.[86] It is particularly noteworthy that most of the examples in our system favor the cycloöctatriene in the equilibrium mixture (Scheme 27). However, equilibrium is reversed when R_4 is changed from H to an alkyl group. This indicates that the alkyl substituents have a remarkable effect on the equilibrium between cycloöctatriene and cyclohexadiene. The variations in the equilibrium constant for this reaction is estimated to be at least two orders of magnitude at room temperature.

Scheme 27



Thermal conversion of the cyclobutenes (**CB**) back to cycloöctatriene is much more facile than originally thought. Thermal opening of **CB** has been found to be greatly accelerated in methanol. Since this cyclobutene ring opening is disrotatory rather than the orbital symmetry allowed conrotatory, it is thought to involve an zwitterionic intermediate with donor-acceptor property (Scheme 28).[4] Catalysis by a trace of acid in methanol provides further support for a charge separated intermediate in this thermal *trans*formation. The enhancement of ring opening rate catalyzed by a trace of acid in benzene is also observed by other co-workers in the similar photoreaction.[5,6]

Scheme 28



Ab initio quantum mechanical calculations on model of the *trans*ition state structures of disrotatory electrocyclizations of butadienes indicated the substituent effects. The electron-withdrawing groups at the bridgehead have larger effects than electron-donating groups on reducing the activation energy for this orbital symmetry forbidden process. Electron-donating groups have smaller effects.[87] This can explain why an acetyl group at the bridgehead in our reaction enhances ring opening.

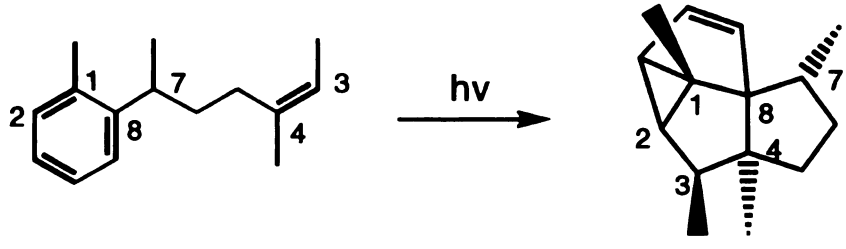
Steric effect plays an important role in diastereoselectivity of photocycloaddition. The nonbonded interactions and torsional strain are supposed to be minimized in the biradical closure. Steric interaction results in a conformational preference during biradical coupling. In summary, the bridgehead methyl group (R_3) induces homoallylic (R_1), allylic (R_2) and terminal (R_4) centers *trans* to itself during cycloaddition.

A promising discovery was made by Wender group in total synthesis of natural products by using photocycloaddition. *Meta*-photocycloaddition was used

as a key step in synthesis of several angular (e.g., Cedrene,[35] Isocomene,[88] Subergorgic Acid[36]) and linear triquinane compounds, (e.g., Hirsutene,[89] Coriolin.[90]) The mechanism is proposed via singlet excited state and concerted pathway different from that proposed for our triplet cycloaddition. High stereoselectivity in *meta*-photocycloaddition was also observed.

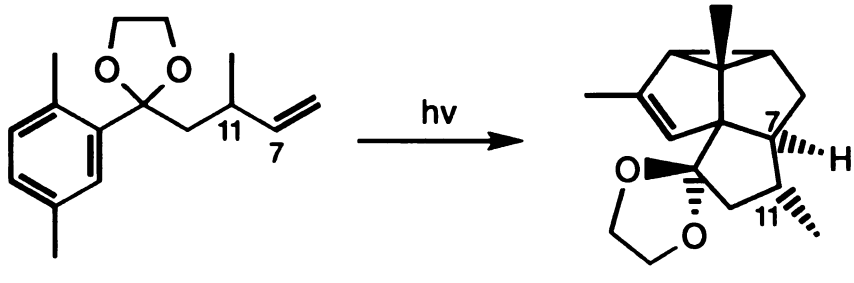
In synthesis of Isocomene, the cycloadduct has two methyl groups (on C-3 and C-4) on the double bond *trans* to each other. This is similar to our results except ithat it involves concerted singlet reaction. The methyl group (on C-4) also induces benzylic methyl (on C-7) to be*cis* to itself. (Scheme 29)

Scheme 29



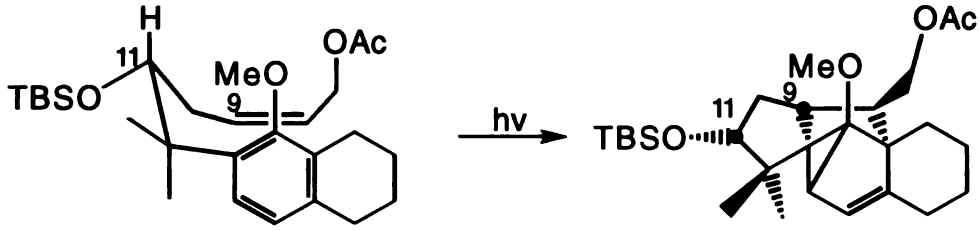
The synthesis of Subergorgic Acid reflects on the developing relative stereochemistry between hydrogen (on C-7) of the double bond and allylic methyl group (on C-11) *trans* to each other. (Scheme 30)

Scheme 30



The examination of stereoinduction by a homo-allylic stereogenic center was performed in synthesis of Grayanotoxin II. The bridgehead hydrogen on C-9 of cycloadduct is *trans* to the large protecting TBSO group on homo-allylic stereogenic center C-11. (Scheme 31) Stereoselectivities shown below are attributed to the steric effect involved in transition states.

Scheme 31



From a synthetic viewpoint, our *ortho*-photocycloaddition offers access to 4-5-6-membered rings and eight-membered rings instead of poly-five-membered rings obtained in *meta*-photocycloaddition. High stereo- as well as regio-selectivity was observed in both cases. Therefore, our triplet *ortho*-photocycloaddition shows a remarkable potential to become the key step in a total synthesis.

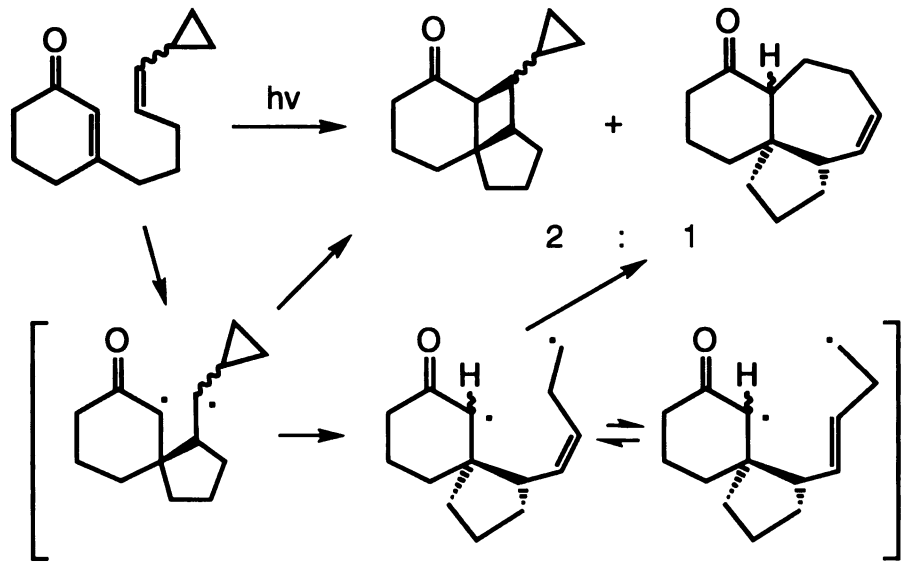
II. Biradical Intermediacy

Efficient *cis* -> *trans* isomerization of the double bond of *p*-(*cis*-3-hexenoxy)-phenyl ketone occurs during photolysis with a quantum yield Φ = 0.27.[1] This reveals that the cycloaddition mechanism does not proceed via a concerted process. It has been thought to represent the cleavage of 1,4-biradical intermediates that are characteristic of other triplet [2+2] photocycloadditions[91,92] and of Norrish type II reactions.[93] The previous chapter about diastereoselectivity was concentrated on conformational preferences during biradical formation and closure. Incorporation of a cyclopropylcarbinyl radical clock in this reaction, the intermediacy of a 1,4-biradical was confirmed. Results show that cyclization is very slow.[94]

Rapid opening of cyclopropylcarbinyl radicals to allylcarbinyl radicals is well known in free radical chemistry and has been widely used both as a kinetic clock[57,95] and as a mechanistic probe[96] for radical and biradical intermediates. Such isomerization has been observed in the [2+2] photocycloadditions of enones[92,97,98] and ketones[99] to double bonds, as well as in a host of other photogenerated biradicals.[100]

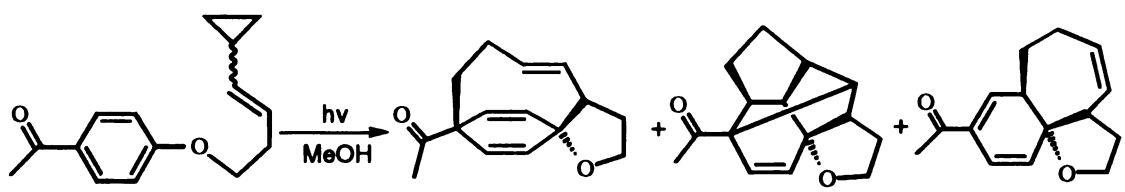
Becker and co-workers generated a biradical from the dienone with a cyclopropyl substituent on the double bond in the side chain.[42] The isolated rearrangement product as well as normal [2+2] cycloadduct showed in a ratio of 1:2. This indicated that the ring-opening of biradical occurred on roughly same order of rate as ring closure. (Scheme 32)

Scheme 32



Irradiation of **p-C_4K** resulted in formation of three products. NMR analysis showed no trace of residual cyclopropyl resonances. These products were assigned the following structures: **1,4-adduct**, **polycyclic ketone** and a **1,2-adduct** (Scheme 33). They are produced in the proportion of 5 : 3 : 1, respectively, as determined by NMR integration. The **polycyclic ketone**; and the **1,2-adduct** were the only isolated products. The **1,4-adduct** was unstable thermally and could not be isolated by chromatography.

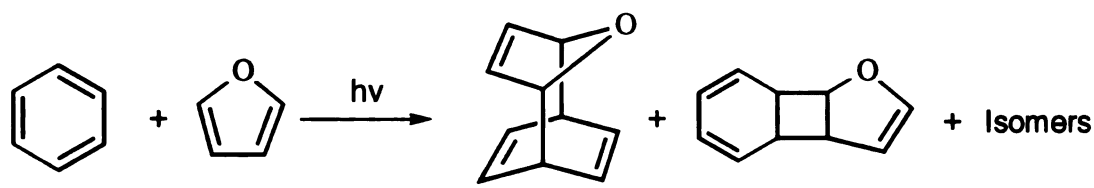
Scheme 33



p-C_4K

Existence of a **1,4-adduct** and a **1,2-adduct** in product mixtures was also observed in the photochemical reactions of benzene with furans.[101,102] The major **1,4-adduct**, minor **1,2-adduct** and other minor products were obtained. Product ratios were affected by changes in relative concentration of reactants or irradiation condition. In most cases, the major **1,4-adduct** product was too thermally labile at room temperature, which is similar to our results. (Scheme 34)

Scheme 34



5 : 1

The mechanism presented in Scheme 35 shows three products might be formed by ring-opening of the suspected initial 1,4-biradical **BR-5** to a *cis/trans* mixture of the 1,7(9)-biradical **BR-6** and **BR-7**. The major product is formed by *para* closure of **BR-6** as a 1,9- biradical. Such a *para* addition is similar to the photoaddition of a diene to benzene.[39,103]

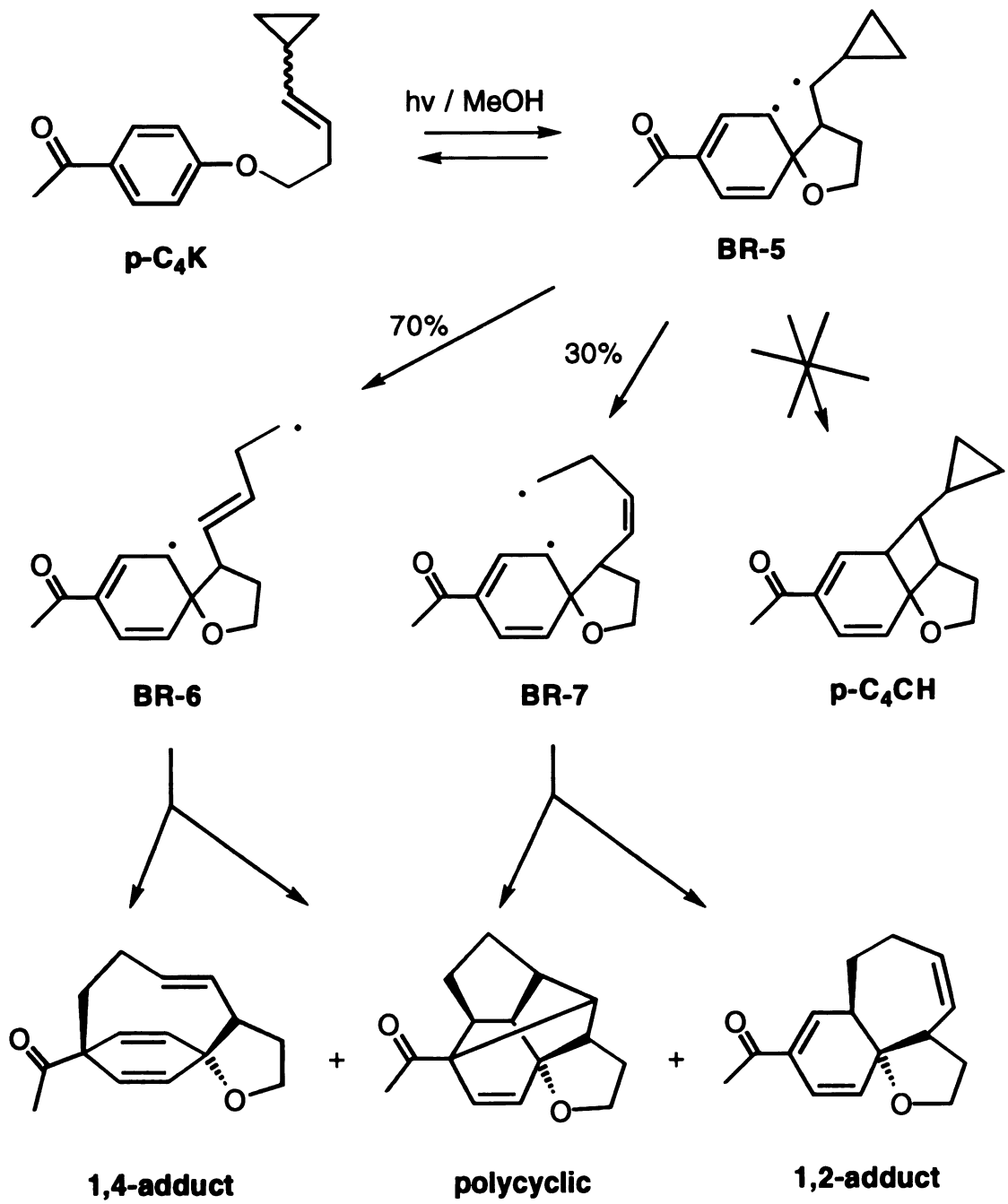
Minor product **1,2-adduct** is formed by *ortho* coupling of **BR-7** as a 1,7-biradical. While it seems reasonable that **BR-6** can cyclize only to a 9-membered ring, due to steric strain in a *trans*-**1,4-adduct**; it is not so evident why **BR-7** cyclizes to the 7-membered ring. The instability of **1,4-adduct** suggests that *para*-coupling introduces sufficient ring strain that **BR-6** so couples only instead of doing nothing. As a bicyclo[4.5.0]undecadiene, **1,2-adduct** is less strained than the bicyclo[4.2.0]octadienes normally formed by cyclization of biradicals like **BR-5**; so it does not undergo the further electrocyclic rearrangements observed

for the initial [2+2] photoadduct of most *o*- and *p*-alkenoxyacetophenones.[1] It is considered to be unlikely that any of the observed products arise by secondary rearrangements of **p-C_4CH**, since the cyclopropyl group is not on a double bond in any such rearrangement products.

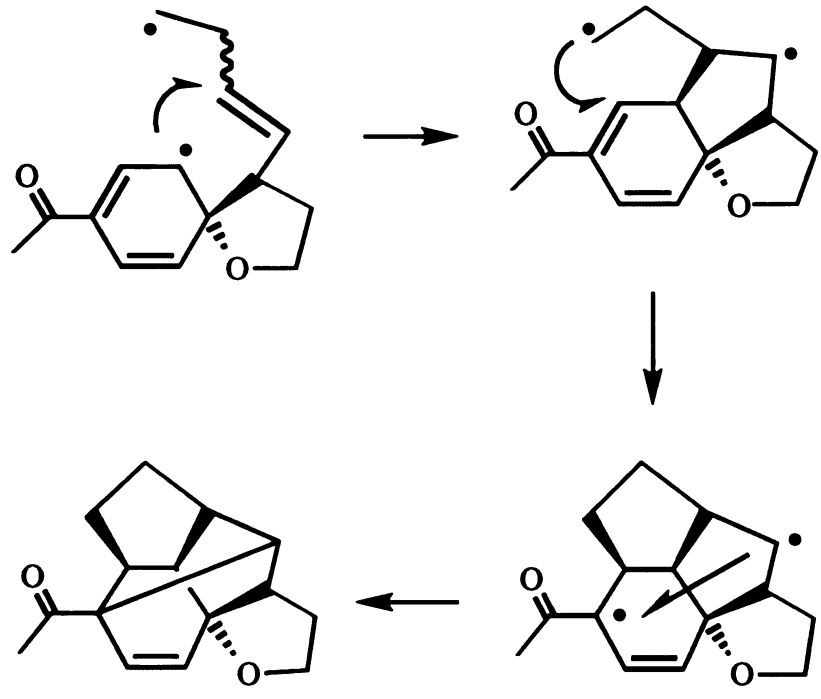
The formation of **polycyclic ketone** can be explained by a tandem *biradical* cyclization process obeying the "rule of five", comparable to a tandem radical cyclization,[104-106] as shown in Scheme 36. The first step is a normally disfavored endo-cyclization, here facilitated by the two frozen bonds of the spiro structure. If we assume that **polycyclic ketone** is formed equally from *trans* and *cis* allylcarbinyl biradicals, the ratios of **BR-6** and **BR-7** can be estimated as 2.4/1, the same as the 2.3/1 *trans/cis* 2-penten-5-yl radical ratio measured for the opening of 1-cyclopropylethyl radical.[107]

The total quantum yield for formation of isolated compounds was measured, Φ = 0.21-0.15, by irradiating samples of **p-C_4K** in parallel with a valerophenone actinometer. The total quantum yield for reaction thus is 0.47-0.34. It agrees with our earlier measurement that almost half of the 1,4- biradicals **BR-5** undergo rearrangement and the rest revert to starting ketone.[1] Since the rate constant for opening of the model 1-cyclopropylethyl radical to the allylcarbinyl radical is known to be 7×10^7 s^{-1},[108] the rate constant of cleavage of biradical **BR-5** can be concluded to be 8×10^7 s^{-1}, whereas coupling is relatively slow , $k \leq 3 \times 10^6$ s^{-1}.

Scheme 35


hv / MeOH
p-C4K
BR-5
70%
30%
BR-6
BR-7
p-C4CH
1,4-adduct
polycyclic
1,2-adduct

Scheme 36



Low cyclization / cleavage ratio for **BR-5** is similar to that deduced for several of the 1,4-biradicals that intervene in enone cycloadditions,[109] given that both processes require the same biradical conformation. However, the reasons remain unknown. This 1,4-biradical intermediate with one highly conjugated radical site is shorter-lived than most other 1,4-biradicals, which have lifetimes from 24 to 2200 ns as determined by laser flash photolysis[110,111] or photoacoustic calorimetry.[112]

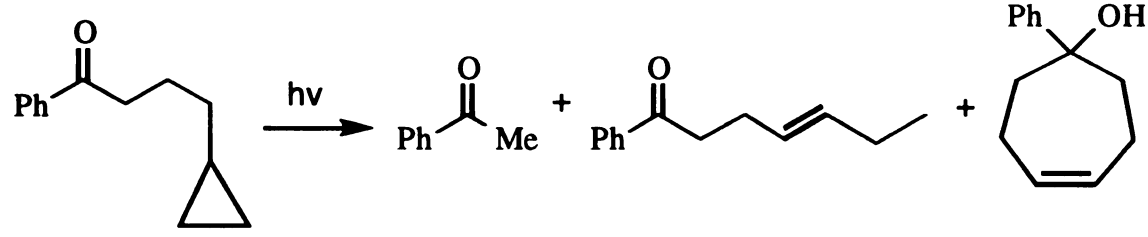
In contrast, the 1,7(9)-biradicals **BR-6** and **BR-7** are much longer lived, since one third of the time they undergo a relatively slow 5-hexenyl radical cyclization.[113] The slow coupling is normal for 1,4-biradicals;[114] the cleavage is unusually fast and may be aided by rearomatization.

The main issues that this work addresses are the presence of a biradical intermediate involved in the triplet *ortho*-photocycloaddition reaction and the estimation of the triplet 1,4-biradical **BR-5** closure rate using a appropriate

cyclopropylcarbinyl radical clock. From above results, the 1,4-biradical **BR-5** seems to behave like a monoradical in undergoing rearrangement and tandem cyclization.[105,115]

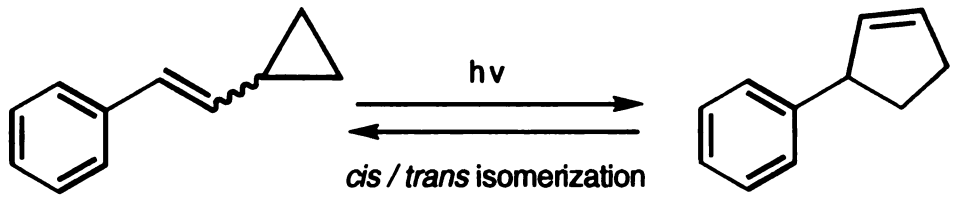
In fact, a similar estimation of 1,4-biradical's lifetime was first presented in Norrish type II photoreactions by Wagner.[96] The photochemistry of γ-cyclopropylbutyrophenone shows that the 1,4-biradical generated by triplet-state hydrogen γ-abstraction undergo typical radical rearrangement in competition with its normal type II reaction. (Scheme 37) The rearrangement percentages and biradical lifetime could be properly predicted if the biradicals rearrange with the same rate constants characteristic of monoradicals.

Scheme 37



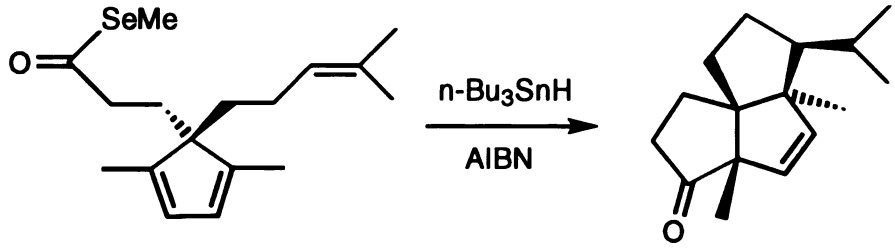
Recently, there is another example using cyclopropylcarbinyl clock to study the perpendicular alkene triplets. Caldwell and Zhou reported that the triplet states of β-cyclopropylstyrene can be described as 1,2-biradicals.[116] The reactivities of the triplets in reactions for which the termini act independently are similar to corresponding reactivities for cyclopropylcarbinyl free radical opening. (Scheme 38)

Scheme 38



In terms of possible synthetic potential, the tandem radical cyclization illustrates an efficient approach to construct multiple five-membered rings. Curran and co-workers have reported several studies of total syntheses by employing a tandem radical cyclization strategy.[105] Tandem cyclization initiated by the tin hydride has appeared to be a powerful key step in synthesizing the complicated compounds, such as triquinane Hirsutene[117] and tetraquinane Crinipellin A[118]. (Scheme 39)

Scheme 39



The basic component of tandem radical cyclization is to allow intermediate radicals to live long enough to cyclize. This means that all cyclization must be faster than radical-radical or radical-solvent reactions. The tandem cyclization has both the advantage and disadvantage of biradical vs. free radical cyclizations. The intramolecular biradical cyclization, which is very clean, competes better with the various internal cyclizations than does the bimolecular trapping employed in traditional tin,[104] oxidative manganese-based[119] or reductive SmI_2[120] methods. The control of initiator concentration is the main problem of the above intermolecular-initiated radical cyclizations. However, there is no such problem associated with intramolecular biradical cyclization. The biradical cyclization is easily conducted (only by light) and is compatible with a wide variety of functional groups. The only issue which needs to be addressed is how to delay the biradical coupling to achieve tandem cyclization.

Since there is only one stereoisomer of **polycyclic ketone** obtained after photolysis, our tandem biradical cyclization has proven to have high stereoselectivity and chemical yield. Formation of four bonds and four rings in one step has an important synthetic potential. The bowl-shaped **polycyclic ketone** also seems to be a good host candidate in host-guest chemistry.

III. Overall Mechanism

From the photocycloaddition of alkoxyacetophenone **p-M_0K**, the cyclobutene and a small amount of cycloöctatriene were observed in the time-resolved ^{1}H-NMR spectrum. After extended irradiation only cyclobutene is obtained. Cycloöctatrienes were claimed never to be detected during irradiation in ^{1}H-NMR spectrum before.[59] Similar results were obtained for other compounds. Cyclobutene with its thermodynamically preferred cycloöctatriene in **p-M_1K** and cyclobutene with its thermodynamically favored cyclohexadiene in **p-M_3M_4K** were identified at low conversion by ^{1}H-NMR spectroscopy. This follows the proposal of *first* formation of cyclohexadiene, which is in thermal equilibrium with cycloöctatriene, followed by photoelectrocyclization to cyclobutene.

The mechanism of [2+2] *ortho* photocycloaddition for formation of cyclohexadiene was verified to be stepwise and revertible. Initial kinetic studies showed *p*-alkoxyphenyl ketone, an acceptor, undergoes intramolecular charge transfer with the remote donor double bond to generate an exciplex followed by 1,4-biradical formation[1] The *ortho* addition mode and a charge transfer process might be predicted by the Bryce-Smith ionization potential difference rule;[17] Δ I.P. is larger than 0.5 eV between *p*-alkoxyphenyl ketone (8.7 eV) and multi-substituted alkenes (ca. 9.3 eV).[121]

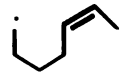
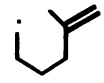
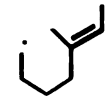
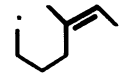
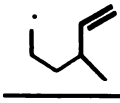
Exciplex formation is supported by the regioselectivity from electronic *inductive* substituents on the benzene observed in the triplet decay kinetics.[5,6] However, both electron-withdrawing ($CONH_2$) and electron-donating (CH_3) groups showed similar regioselectivity. This indicated that there is another controlling *steric* factor of regioselectivity.

1,4-Biradical intermediacy was confirmed by the diastereoselectivity and utility of "radical clock" in **p-C_4K** mentioned previously in this thesis. The former

was explained by the conformational preferences in both biradical formation and closure processes. The latter showed an efficient biradical rearrangement.

A wide range of quantum yields $\Phi = 0.07$ to 0.25 (Table 7) for formation of either cyclohexadienes or cycloöctatrienes were measured. All of the quantum yields were measured at low conversion (< 15%) to prevent secondary photoreactions. *Ortho* compounds have higher quantum yields than *para* which is similar to early reports,[2] and non-substituted compounds have higher quantum efficiencies than substituted ones. It is believed that these retarding effects of the alkyl substitution on the tether would result if the rate-determining step is radical formation, with cyclization of the 5-hexenyl radical as the model.[122] The alkyl-substituted 5-hexenyl radicals have lower rate constants for cyclization than the unsubstituted ones. (Table 34)

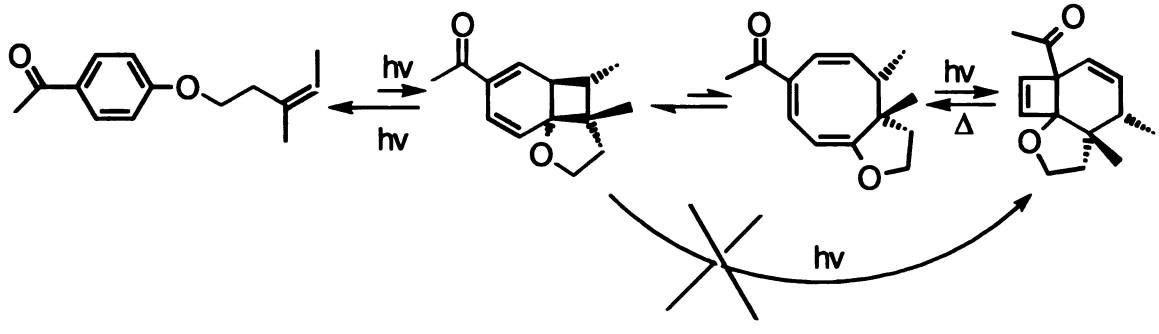
Table 34 Rate Constants for Cyclizations of Substituted 5-Hexenyl Radicals at 25°C

Radical	$k_{1,5\ exo}$
	2.3×10^5
	2.2×10^5
	1.4×10^4
	2.5×10^4
	3.5×10^4
	7.5×10^4

The efficient photoreversion of the thermally stable cyclohexadiene **p-M_3M_4CH** to phenyl ketone **p-M_3M_4K** (Φ = 0.70 - 0.78) explains the lowest quantum yield (Φ = 0.07) for conversion of **p-M_3M_4K** to **p-M_3M_4CH**. No **p-M_3M_4CB** could be detected *at low conversion* during irradiation of **p-M_3M_4CH**. Extended irradiation may generate some **p-M_3M_4COT**, which could photo-convert to **p-M_3M_4CB** (Scheme 40). Similar behavior has been observed for *meta*-methoxy *p*- butenoxyacetophenone and its analog in which the anchoring oxygen is replaced with a methylene group.[6,7]

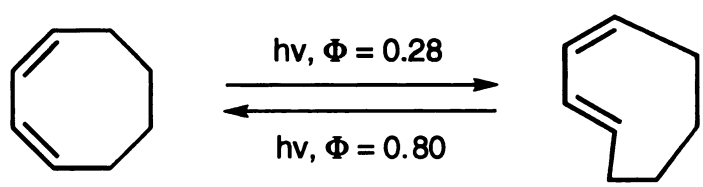
It is well-known that the photoreversions of biradicals in cycloaddition of triplet enones to double bonds are efficient.[123] From analysis of kinetic data for the addition of cyclohexene to cyclopentenone, de Mayo concluded that over half of the biradicals formed reverted to alkene and ground-state ketone.[114] In general, reversion of the biradical is a major source of inefficiency in the cycloaddition reaction. Agosta and coworkers determined that the quantum yields for reversion are much higher than for product formation in intramolecular [2+2] photocycloadditions of dienones.[124] The similar situation has been observed in our reaction with the increasing cleavage of the cyclobutane ring to form 1,4-biradical and thus, the enhancement of reversion to phenyl ketone.

Scheme 40



Quantum yields of formation of cyclobutenes in secondary photochemical electrocyclizations are 0.05-0.21 (Table 8). Alkyl substitutions seem to have no significant influence on the quantum yields. The possibility of involving a triplet sensitized reaction by the original phenyl ketones in photochemical electrocyclization has been ruled out. There was no enhancement of quantum yields for cyclobutenes formation from parallel experiments using 4-methoxy-acetophenone. The moderate quantum yields may be attributed to *cis/trans* photoisomerization of cycloöctatrienes since an intensely efficient photoisomerization between *cis,cis* and *cis,trans* cycloöcta-1,3-diene was observed (Scheme 41).[125]

Scheme 41



AM1 calculations showed that the heat formation is -34.5 Kcal/mole for *cis,cis*-acetyl-11-oxabicyclo[6.3.0]undeca-1,3-5-triene and -14.5 Kcal/mole for *cis,trans*-acetyl-11-oxabicyclo[6.3.0]undeca-1,3-5-triene.[68] The *cis,cis* isomer is 20 Kcal//mole more stable than *cis,trans* one in ground state. However, both of them can undergo *cis/trans* isomerization photochemically.

V. Conclusion

High diastereoselectivities of cyclohexadienes, cycloöctatrienes and photostable cyclobutenes are observed in the intramolecular *ortho* cycloaddition of double bonds to triplet benzenes. The observed diastereoselectivities are explained by the chair-like transition states involved in biradical-generated and biradical-coupled processes. The steric effects containing non-bonded interaction, eclipsing and allylic strains, and secondary orbital effect are the factors that determine high diastereoselectivity.

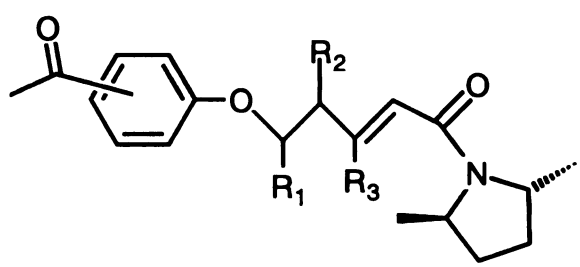
A free radical clock (cyclopropylcarbinyl radical-allylcarbinyl radical rearrangement) provided evidence to confirm presence of a biradical intermediate in this reaction. The lifetime of biradical could also be estimated by this radical clock.

A rare tandem biradical cyclization process is observed. Generation of four five-membered rings with high yield and stereoselectivity in one step may offer a particularly attractive route to synthesize some congested natural products.

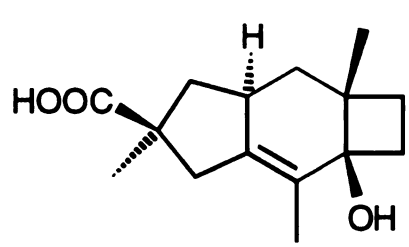
V. Suggestions of Further Research

Previous work has demonstrated the directing effect of a carbonyl substituent *ortho* to a butenoxy tether; *ortho* [2+2] photoaddition of the double bond to the benzene ring is regiospecific. The high diastereoselectivity of this reaction was studied in this work. This has prompted an investigation into the feasibility of promoting enantioselectivity.

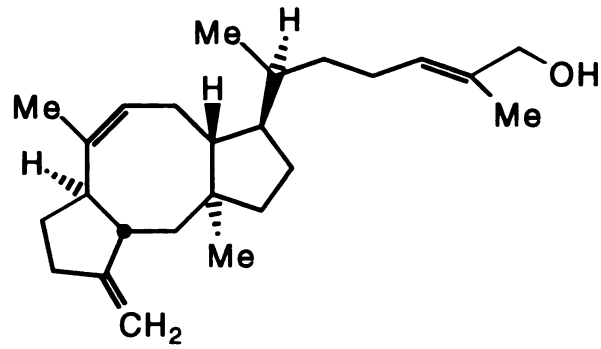
Recently, high enantioselectivity was induced using either *trans*-(-)-(2R,5R)-2,5-dimethylpyrrolidine or (7R)-(+)-camphorsultam chiral auxiliary reagents located *ortho* to a tether.[126] A second approach might be to include the chiral auxiliary groups directly on the tether itself.



Both methods may help to reach the goal of establishing a feasible route to the asymmetric photochemical synthesis of a series of natural products, e. g. the sesquiterpene class.[127]



The isolated cyclooctatrienes consist of a skeleton of bicyclic eight-five-membered rings. This means that our [2+2] *ortho* photocycloaddition may provide considerable impetus for the development of new synthetic methodology of medium ring compounds, such as Ceroplastol I.[128]



Preliminary studies using tethers containing triple bonds were unsuccessful. However, the reaction may become successful by the assistance of the electronic substituents on either benzene or the alkyne. This may prove to be another method to provide the derivatives of cycloöctatetraene.

EXPERIMENTAL

I. General Procedures

All ^{1}H NMR and ^{13}C NMR spectra were obtained on a 300 MHz Varian Gemini, a 300 MHz Varian VXR-300 or a 500 MHz Varian-500 instrument. All the IR spectra were recorded by using a solution in CCl_4 or a solid in KBr on a Nicolet 2R/42 Fourier *Trans*form IR spectrometer with a Hewlett Packard color pro recorder and 0.025 mm Z12308-0 Aldrich IR cell. UV spectra were recorded on a Shimadzu UV-160 spectrometer. Low resolution Mass spectra were obtained on a Hewlett Packard 5890 GC/MS trio-1 and high resolution Mass spectra were obtained on a Joel JMS-HX110 Mass spectrometer in the MSU Mass spectroscopic facility. The electron impact (EI) and direct probe method were used. The range of molecular weight detected was between 45 and 750.

Gas chromatographic analyses were performed on Varian 1400 or 3400 machines with flame ionization detectors. The GC was connected to either a Hewlett-Packard 3395A, 3393A, or 3392A integrating recorder. Three types of columns were used for GC analysis; Magabore DB-1, Magabore DB210 and Magabore DBWAX. HPLC analyses were performed on a Beckman 332 gradient system equipped with a Perkin Elmer LC-75 UV detector, on a silica column. The HPLC system was connected to a Hewlett-Packard 6080 integrating recorder. Preparative collections were done on a Rainin Dynamax HPLC system. For the preparative TLC, Analtech Uniplate silica gel plates of 20 x 20 cm, 1000 microm were used.

II. Purification of Chemicals

A. Solvents

Benzene- The mixture of 0.5 L conc. sulfuric acid and 3.5 L of reagent grade benzene were stirred for a couple of days at room temperature. The benzene layer was separated and extracted with 200 mL portions of conc. sulfuric acid several times until the sulfuric acid layer didn't turn yellow. The benzene was washed with distilled water and then extracted with saturated aqueous sodium bicarbonate solution till pH = 7. The benzene was separated, dried over magnesium sulfate and filtered into a 5 L round bottomed flask. Phosphorous pentoxide (100 g) was added and the solution was refluxed overnight. The benzene was distilled through a one meter column packed with stainless steel helices. The first and last 10 % portions were discarded.

Methanol- 500 mL reagent grade absolute methanol was refluxed over 5 g magnesium turnings with several pieces of iodine for 6 hours then distilled through a half meter column packed with glass helices. The first and last 10 % portions were discarded.[129]

B. Internal Standards

Methyl benzoate- Methyl benzoate was purified by fractional distillation by Boli Zhou.

n-Penty benzoate- n-Pentyl benzoate was purified by fractional distillation by Boli Zhou.

n-Heptyl benzoate- n-Heptyl benzoate was purified by fractional distillation by Boli Zhou.

n-Octyl benzoate- n-Octyl benzoate was purified by fractional distillation by Boli Zhou.

meta-Dibutyl phthalate- meta-Dibutyl phthalate was purified by fractional distillation.

Ethyl phenyl acetate- Ethyl phenyl acetate was purified by fractional distillation by Kung-Lung Cheng.

Dodecane(C12)- Dodecane was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Pentadecane(C15)- Pentadecane was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Hexadecane(C16)- Hexadecane was washed with sulfuric acid and distilled by Dr. Peter J. Wagner.

Valerophenone- Valerophenone was prepared from the acylation of benzene with valeryl chloride by Bong Ser Park.

C. Column Chromatography

All columns were run flash style with 200-425 mesh silica gel or 60-325 mesh neutral alumina. The column diameter was selected according to the amount of material to be loaded: for up to one gram the diameter was 0.5", for one to three grams the diameter was 1", and for three to ten grams the diameter was 2". The column was packed using cotton balls at the stopcock. Silica gel, after being stirred with solvent completely, was poured to fill about 60% of the total column length. The solvent was poured onto the column carefully so as not to disturb the silica gel and about one volume was allowed to elute by gravity. A layer of sand was placed on the top of the column to insure that the silica gel would not be disturbed during loading. The material was loaded carefully by pipet. Amount of solvent were added behind the loaded material as it eluted into

the silica gel. Once the material was completely eluted onto the silica gel, a full volume of solvent was added and an eluting pressure to produce two drops/second was applied.[130]

III. Equipment and Procedures

A. Photochemical Glassware

All photolysis glassware including pipets, volumetric flasks, syringes and Pyrex test tubes for irradiations were rinsed with acetone, then with distilled water, and boiled in a solution of Alconox laboratory detergent in distilled water for 24 h. The glassware was rinsed with distilled water, and boiled in distilled water for a couple of days, with the water being changed every 24 h. After final rinse with distilled water, the glassware was dried in an oven at 140 °C overnight and then cooled to room temperature.

Ampoules used for irradiation were made by heating 13 X 100 mm Pyrex culture tubes (previously cleaned by the procedure mentioned above) approximately 2 cm from the top with an oxygen-natural gas torch and drawing them out to an uniform 15 cm length.

B. Sample Preparations

All solutions were prepared either by directly weighing the starting material into volumetric flasks or by dilution of a stock solution. Equal volume (2.8 mL) of sample were placed via syringes into each ampoule.

C. Degassing Procedures

Filled irradiation tubes were attached to a vacuum line with a diffusion pump. These tubes were arranged on a circular manifold equipped with twelve

vacuum stopcocks which fitted with size 00 one hole rubber stoppers. The sample tubes were frozen to liquid nitrogen temperature and evacuated for 5- 10 min. The vacuum was removed and the tubes were allowed to thaw to the room temperature in distilled water. This freeze-pump-thaw cycle was repeated three times. The tubes were then sealed with an oxygen-natural gas torch while still under vacuum.

D. Irradiation Procedures

All samples for quantum yield measurements were irradiated in parallel with actinometer solutions in a merry-go-round apparatus immersed in a water bath at approximately 25 °C. A water cooled Hanovia medium pressure mercury lamp was used as the irradiation source. An alkaline potassium chromate solution (0.002 M K_2CrO_4 in 1 % aqueous potassium carbonate) was used to isolate the 313 nm emission band. A Corning CS 7-37 Filter was used for 366 nm emission band.

For chemical yield and diastereoselectivity measurement using NMR, the NMR tubes containing samples with internal standard (Methyl Benzoate) were fixed into 13 X 100 mm Pyrex culture tubes with rubber septum and bubbled with argon through a nine inches needle and then irradiated. Both the yield and selectivity were determined by the integration of well-separated and high-resolution ^1H NMR spectra.

Preparative scale irradiation was done in two different method. A large test tube (100 mL) with sample solution was fitted with a 24/40 rubber septum and the sample was degassed by bubbling argon through for 20 min. or throughout the irradiation. The test tube was attached to an immersion well by wire and irradiated. For the larger scale reaction, photolysis was done in an immersion well equipped with a quartz cooling jacket, a water cooling condenser.

Hanovia 450 W medium pressure lamp with a Pyrex filter tube was used as the light source and argon was bubbled during the irradiation.

E. Calculation of Quantum Yields

Quantum yields were calculated with the following equation,

$$\Phi = [\ p\ ] / I \qquad (5)$$

where [p] is the concentration of photoproducts and I is the intensity of light absorbed by samples.

The intensity of light, I, was determined by either valerophenone actinometer for 313 nm or benzophenone actinometer for 366 nm depending upon the efficiency of the photoreaction. A degassed 0.10 M valerophenone or 0.01 M benzophenone and 0.10 M benzhydrol solution in benzene was irradiated in parallel with the samples to be analyzed. After irradiation was stopped at the period of conversion (less than 10 % of GC determination, 10-15 % of HPLC determination and 30-60 % of UV determination), the valerophenone sample was analyzed by GC for acetophenone using the following equation.

$$[\ AP\ ] = R_f \times [\ Std\ ] \times A_{AP} / A_{Std} \qquad (6)$$

where [AP] is the concentration of acetophenone, R_f is the instrument response factor of acetophenone, [Std] is the concentration of the added internal standard, A_{AP} is the integrated area of acetophenone, and A_{Std} is the integrated area of the internal standard.

The intensity of light can be calculated using the acetophenone concentration based on Φ_{AP} = 0.33[62] or Φ = 0.78 for disappearance of benzophenone by UV spectrometer.[63]

$$I = [\,AP\,] / 0.33 \quad \text{or} \quad I = \Delta [\,BP\,] / 0.78 \tag{7}$$

The concentration of the photoproduct, [P], can be calculated using the following equation.

$$[\,P\,] = R_{f(P)} \times [\,Std\,] \times A_p / A_{Std} \tag{8}$$

where $R_{f(P)}$ is the response factor of photoproduct and A_p is the integrated area for the photoproduct.

The instrumental response factors for photoproducts were obtained from the following relationship.

$$R_{f(P)} = ([\,P\,] / [\,Std\,]) \times (A_{Std} / A_p) \tag{9}$$

If photoproducts are difficult to isolate or too unstable to analyze accurately, the following equation was used to calculate the response factors. This method is known to give pretty reasonable value for GC response factor.

$$\text{R. F.} = \frac{\{\#\text{ of Carbons} + 1/2\ (\#\text{ of C}-\text{O bonds})\}_{std}}{\{\#\text{ of Carbons} + 1/2\ (\#\text{ of C}-\text{O bonds})\}_{Photo}} \tag{10}$$

IV. Preparation of Starting Ketones

All ketones were assured to be > 99% pure on gas chromatography or no extra peak to interfere the interpretation in ^{1}H-NMR spectra before irradiation.

4'-(1-Methyl-3-buten-1-oxy)acetophenone (p-M_1K):

2-Tosyl-4-pentene:

A solution of 4-penten-2-ol (4.98 g, 0.057 mol) and pyridine (24.5 g, 0.31 mol, purified by distillation from barium oxide) was placed in a 100 mL three necked round bottom flask with condenser and drying tube and treated with recrystallized p-toluenesulfonyl chloride (11g, 0.057 mol) by portions at 0 °C for 3 h.[131] The reaction mixture was poured into 20 % sulfuric acid aqueous solution (60 mL) and then extracted with ether (3 x 100 mL). The organic layer was washed with 2N NaOH (150 mL), saturated $NaHCO_3$ (150 mL), brine (150 mL) and dried over $MgSO_4$. After solvent was evaporated, the residue was purified by chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.38) and a slightly yellowish oil (10.3 g, 75 %) was obtained.

^{1}H-NMR ($CDCl_3$) : δ 1.23 (d, J = 6.2 Hz, Me) 2.34 (m, 2H) 2.42 (s, Me) 4.62 (sext, J = 6.2 Hz, 1H) 5.02 (m, 2H) 5.56 (m, 1H) 7.31 (d, J = 8.4 Hz, 2H) 7.77 (d, J = 8.4 Hz, 2H).

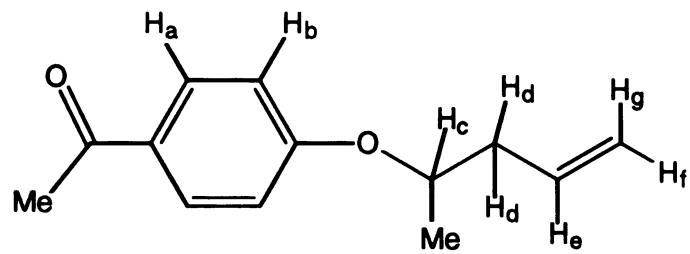
^{13}C-NMR ($CDCl_3$) : δ 20.0, 21.4, 40.6, 79.3, 118.8, 127.9, 129.9, 132.3, 134.6, 144.7.

IR(CCl_4) : 3080, 2980, 1654, 1601, 1507, 1250, 1216, 1169, 920 cm^{-1}.

p-M_1K:

A solution of 2-tosyl-4-pentene (1.0 g, 4 mmol), 4-hydroxyacetophenone (0.68 g, 5 mmol) and anhydrous potassium carbonate (0.69 g, 5 mmol) in

acetone (25 mL) was placed in a 100 mL three necked round bottom flask with condenser and refluxed for 42 h under an argon atmosphere. The potassium salt was removed by filtration and acetone was evaporated under vacuum. The mixture was dissolved in ether (50 mL) and washed with 2N NaOH (2 x 50 mL), saturated $NaHCO_3$ (50 mL), brine (50 mL) and dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.32) and the product was colorless and obtained as an oil (0.2 g, 25 %).



^{1}H-NMR ($CDCl_3$) : δ 1.31 (d, J = 6.1 Hz, Me) 2.35 (ddddd, J = 12.7, 7.0, 6.1, 1.6, 1.3 Hz, Hd) 2.48 (ddddd, J = 12.7, 7.0, 6.1, 1.6, 1.3 Hz, Hd) 2.52 (s, COMe) 4.50 (sext, J = 6.1 Hz, Hc) 5.07 (ddt, J = 10.2, 1.6. 1.3 Hz, Hf) 5.13 (dq, J = 17.1, 1.6 Hz, Hg) 5.82 (ddt, J = 17.1, 10.2, 7.0 Hz, He) 6.89 (d, J = 6.9 Hz, 2Hb) 7.89 (d, J = 6.9 Hz, 2Ha).

^{13}C-NMR ($CDCl_3$) : δ 18.9, 25.9, 40.1, 73.1, 115.1, 117.8, 130.1, 130.6, 133.7, 162.1, 196.9 (C=O).

IR(CCl_4) : 2981, 1683 (C=O), 1601, 1507, 1253, 1171 cm^{-1}.

UV(MeOH) : λ_{max} = 271 nm (16210), 313 nm (1140).

MS (m/e) : 204 (M^+), 189, 163, 136, 121, 69, 68 (base), 68, 65, 53, 43, 41.

Hi-Res MS : $C_{13}H_{16}O_2$, Calculated : 204.1150, Found : 204.1141.

4'-(1-Isopropyl-3-buten-1-oxy)acetophenone (p-I_1K):

2-Methyl-5-hexen-3-ol:

A solution of isobutyraldehyde (10 g, 0.13 mol) in 100 mL anhydrous ether was added dropwise to stirred solution of allyl magnesium bromide (prepared from 7.5 g of magnesium turnings and 35 g of allyl bromide in a 200 mL anhydrous ether) under an argon atmosphere at room temperature. The resulting mixture was refluxed under argon for 6 h. The mixture was cooled down to room temperature and was poured into saturated NH_4Cl aqueous solution (400 mL). After the precipitation was filtered, two layers were separated and the aqueous layer was extracted with ether (3 x 100 mL). The combined organic layers were washed with distilled water, saturated sodium bicarbonate solution and saturated NaCl solution. After drying over $MgSO_4$, the solvent was evaporated to give a yellow oil. The oil was purified by vacuum distillation to give a colorless liquid (9.1 g, 62 %) with boiling point = 75 °C (5.0 Torr).

^{1}H-NMR ($CDCl_3$) : δ 0.91 (d, J = 6.8 Hz, Me) 0.92 (d, J = 6.8 Hz, Me) 1.56 (s, O-H) 1.67 (septd, J = 6.8, 5.6 Hz, 1H) 2.09 (dddt, J = 14.0, 9.0, 8.0, 1.0 Hz, 1H) 2.29 (dddt, J = 14.0, 6.3, 3.6, 1.4 Hz, 1H) 3.37 (ddd, J = 9.0, 5.6, 3.6 Hz, 1H) 5.12(m, 2H) 5.82 (dddd, J = 14.3, 10.0, 8.0, 6.3 Hz, 1H).

^{13}C-NMR ($CDCl_3$) : δ 17.2, 18.5, 32.8, 38.6, 117.3, 135.4.

IR(CCl_4) : 3492 (O-H), 3079, 2963, 1640, 1496, 1367, 992, 917 cm^{-1}.

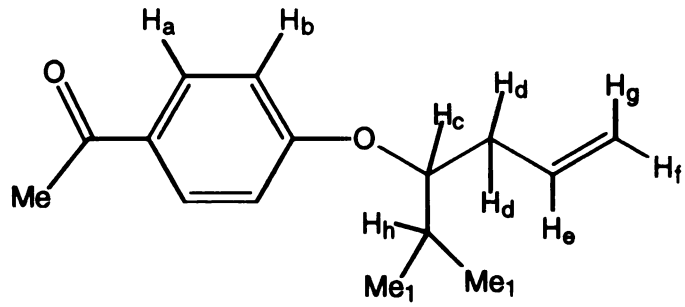
2-Methyl-3-tosyl-5-hexene:

The same procedure used to make 2-tosyl-4-pentene was used. The 2-methyl-5-hexen-3-ol (13 g, 0.13 mol) and p-toluenesulfonyl chloride (22 g, 0.13 mol) in pyridine (45 mL) produced 2-methyl-3-tosyl-5-hexene (27.2 g, 78 %) with boiling point = 105 °C (0.5 Torr).

^{1}H-NMR ($CDCl_3$) : δ 0.82 (d, J = 6.9 Hz, Me) 0.84 (d, J = 6.9 Hz, Me) 1.90 (septd, J = 6.9, 5.4 Hz, 1H) 2.33 (m, 2H) 2.41 (s, Me) 4.41 (dd, J = 7.1, 5.4 Hz, 1H) 4.97 (m, 2H) 5.59 (m, 1H) 7.30 (d, J = 8.1 Hz, 2H) 7.76 (d, J = 8.1 Hz, 2H).

p-H_1K:

A solution of 2-methyl-3-tosyl-5-hexene (10 g, 0.037 mol), 4-hydroxyacetophenone (6.4 g, 0.047 mol) and anhydrous potassium carbonate (15 g, 0.11 mol) in DMF (100 mL) was placed in a 250 mL three necked round bottom flask with condenser and refluxed for 10 h under an argon atmosphere.[132] The mixture was poured into water (200 mL) and extracted with ether (3 x 150 mL). The ether layer was washed with 2N NaOH (2 x 200 mL), saturated $NaHCO_3$ (200 mL), brine (200 mL) and dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 9/1, R_f = 0.60) to give a colorless oil (3.0 g, 35 %).



^{1}H-NMR (CD_3OD) : δ 0.96 (d, J = 6.8 Hz, Me_1) 1.00 (d, J = 6.8 Hz, Me_1) 2.01 (septd, J = 6.8, 5.3 Hz, H_h) 2.41 (ddd, J = 6.0, 5.8, 1.2 Hz, $2H_d$) 2.54 (s, COMe) 4.32 (td, J = 5.8, 5.3 Hz, H_c) 5.02 (ddt, J = 10.1, 2.1, 1.2 Hz, H_f) 5.08 (dt, J = 17.1, 2.1 Hz, H_g) 5.83 (ddt, J = 17.1, 10.1, 6.0 Hz, H_e) 6.98 (d, J = 9.0 Hz, $2H_b$) 7.94 (d, J = 9.0 Hz, $2H_a$).

^{13}C-NMR ($CDCl_3$) : δ 18.2, 26.2, 30.9, 34.9, 82.1, 114.1, 115.2, 117.4, 130.6, 134.0, 162.9, 196.6 (C=O).

IR(CCl_4) : 2965, 2876, 1682 (C=O), 1600, 1576, 1506, 1357, 1270, 1252, 1169, 986 cm^{-1}.

UV(MeOH) : λ_{max} = 277 nm (18470), 313 nm (1540).

MS (m/e) : 232 (M^+), 191, 136, 121, 96, 81 (base), 77, 65, 43, 41.

Hi-Res MS : $C_{15}H_{20}O_2$, Calculated : 232.1463, Found : 232.1468.

4'-(1,3-Dimethyl-3-buten-1-oxy)acetophenone (p-M_1M_3K):

4-Methyl-4-penten-2-ol:

A solution of acetaldehyde (0.88 g, 0.02 mol) and 3-chloro-2-methylpropene (2.72 g, 0.03 mol) in 30 mL anhydrous ether was added dropwise to a stirred ether solution (5 mL) of magnesium turnings (0.84 g, 0.035 mol) under an argon atmosphere with heating provided by a heating gun.[133] The duration of adding process lasted more than 1h. Then the resulting mixture was gently refluxed under argon for 6 h. The mixture was cooled down to room temperature and poured into a saturated NH_4Cl aqueous solution (50 mL). After the precipitate was filtered, two layers were separated and the aqueous layer was extracted with ether (3 x 50 mL). The combined organic layers were washed with distilled water, saturated sodium bicarbonate solution and saturated NaCl solution. After it was dried over $MgSO_4$, solvent was evaporated to give a yellowish oil. The oil was purified by vacuum distillation to give a colorless liquid (1.2 g, 60 %) with boiling point = 78 °C (5.5 Torr).

^{1}H-NMR ($CDCl_3$) : δ 1.19 (d, J = 6.1 Hz, Me) 1.73 (s, Me) 2.11 (d, J = 7.6 Hz, 2H) 2.13 (s, O-H) 3.91 (tq, J = 7.6, 6.1 Hz, 1H) 4.77 (s, 1H) 4.86 (s, 1H).

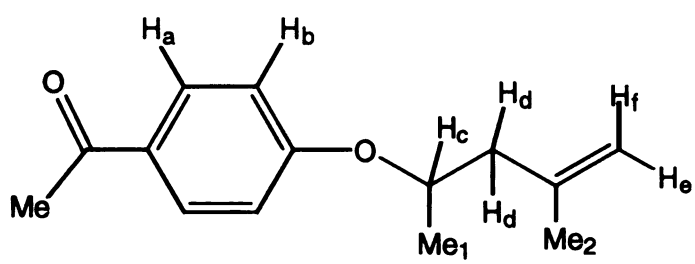
4-Methyl-2-tosyl-4-pentene:

4-Methyl-4-penten-2-ol (0.5 g, 5 mmol) and p-toluenesulfonyl chloride (1.6 g, 7.5 mmol) in pyridine (4 mL) produced 4-methyl-2-tosyl-4-pentene (1.07 g, 84 %, hexane/ethyl acetate = 4/1, R_f = 0.54), by the same procedure as used for 2-tosyl-4-pentene.

^{1}H-NMR ($CDCl_3$) : δ 1.25 (d, J = 6.2 Hz, Me) 1.56 (s, Me) 2.15 (dd, J = 14.0, 6.6 Hz, 1H) 2.33 (dd, J = 14.0, 6.4 Hz, 1H) 2.42 (s, Me) 4.66 (s, 1H) 4.71 (ddq, J = 6.6, 6.4, 6.2 Hz, 1H) 4.73 (s, 1H) 7.30 (d, J = 8.4 Hz, 2H) 7.77 (d, J = 8.4 Hz, 2H).

p-M_1M_3K:

The same procedure was used as for 4'-(1-isopropyl-3-buten-1-oxy)acetophenone . A solution of 4-methyl-2-tosyl-4-pentene (0.45 g, 1.8 mmol), 4-hydroxyacetophenone (0.27 g, 2 mmol) and anhydrous potassium carbonate (0.9 g, 6 mmol) in DMF (50 mL) produced 4'-(1,3-dimethyl-3-buten-1-oxy)acetophenone which was purified by silica gel column chromatography (0.13 g, 34 %, methylene chloride/hexane = 19/1, R_f = 0.70) and obtained a colorless oil.



^{1}H-NMR ($CDCl_3$) : δ 1.31 (d, J = 6.1 Hz, Me_1) 1.75 (s, Me_2) 2.25 (dd, J = 14.2, 6.4 Hz, H_d) 2.49 (dd, J = 14.2, 6.3 Hz, H_d) 2.52 (s, COMe) 4.61 (ddq, J = 6.4, 6.3, 6.1 Hz, H_c) 4.76 (d, J = 1.5 Hz, H_e) 4.81 (d, J = 1.5 Hz, H_f) 6.89 (d, J = 9.0 Hz, 2H_b) 7.90 (d, J = 9.0 Hz, 2H_a).

^{13}C-NMR ($CDCl_3$) : δ 19.4, 22.9, 26.3, 44.3, 72.3, 113.2, 114.9, 130.0, 130.6, 141.7, 162.0, 196.7 (C=O).

IR(CCl_4) : 2977, 2936, 1682 (C=O), 1601, 1507, 1357, 1253, 1170 cm^{-1}.

UV(MeOH) : λ_{max} = 274 nm (16360), 313 nm (1080).

MS (m/e) : 218 (M^+), 163, 137, 121, 82, 67, 55 (base), 41.

Hi-Res MS : $C_{14}H_{18}O_2$, Calculated : 218.1307, Found : .218.1303.

4'-(1-Isopropyl-3-methyl-3-buten-1-oxy)acetophenone (p-I_1M_3K):

2,5-Dimethyl-5-hexen-3-ol:

The same procedure employed for the synthesis of 4-methyl-4-penten-2-ol was used. The isobutyraldehyde (1.44 g, 0.02 mol) and 3-chloro-2-methylpropene (2.72 g, 0.03 mol) in a 35 mL anhydrous ether generated 2,5-dimethyl-5-hexen-3-ol (2.05 g, 80 %, b.p. = 82°C at 4.5 Torr).

^{1}H-NMR ($CDCl_3$) : δ 0.92 (d, J = 6.8 Hz, Me) 0.94 (d, J = 6.8 Hz, Me) 1.70 (m, 1H) 1.75 (s, Me) 1.83 (s, O-H) 2.04 (dd, J = 12.0, 5.5 Hz, 1H) 2.20 (dd, J = 12.0, 9.7 Hz, 1H) 3.47 (m, 1H) 4.80 (s, 1H) 4.87 (s, 1H).

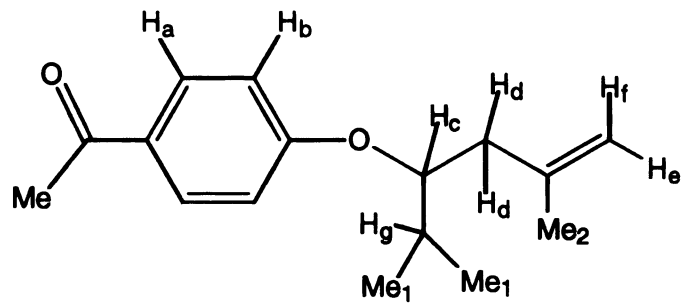
2,5-Dimethyl-3-tosyl-5-hexene:

The same procedure as used to make 2-tosyl-4-pentene was employed. 2,5-Dimethyl-5-hexen-3-ol (2.1 g, 0.016 mol) and p-toluenesulfonyl chloride (3.2 g, 0.017 mol) in pyridine (7.1 mL) produced 2,5-dimethyl-3-tosyl-5-hexene (3.7 g, 82 %, b.p. = 102°C at 0.5 Torr).

^{1}H-NMR ($CDCl_3$) : δ 0.84 (d, J = 6.9 Hz, Me) 0.86 (d, J = 6.9 Hz, Me) 1.60 (s, Me) 1.94 (septd, J = 6.9, 3.8 Hz, 1H) 2.26 (d, J = 6.6 Hz, 2H) 2.41 (s, Me) 4.58 (td, J = 6.6, 3.8 Hz, 1H) 4.65 (d, J = 1.5 Hz, 1H) 4.68 (d, J = 1.5 Hz, 1H) 7.28 (d, J = 8.0 Hz, 2H) 7.75 (d, J = 8.0 Hz, 2H).

p-H_1M_3K:

The coupling procedure as for the synthesis of 4'-(1-isopropyl-3-buten-1-oxy)acetophenone was followed. A solution of 2,5-dimethyl-3-tosyl-5-hexene (21 g, 0.07 mol), 4-hydroxyacetophenone (12.8 g, 0.09 mol) and anhydrous potassium carbonate (30 g, 0.22 mol) in DMF (250 mL) produced 4'-(1-isopropyl-3-methyl-3-buten-1-oxy)acetophenone which was purified by silica gel column chromatography (4.3 g, 25 %, hexane/ethyl acetate = 4/1, R_f = 0.53).



^{1}H-NMR ($CDCl_3$) : δ 0.95 (d, J = 6.9 Hz, Me_1) 0.98 (d, J = 6.9 Hz, Me_1) 1.74 (s, Me_2) 2.01 (septd, J = 6.9, 4.4 Hz, H_g) 2.29 (dd, J = 14.5, 5.2 Hz, H_d) 2.36 (dd, J = 14.5, 7.0 Hz, H_d) 2.53 (s, COMe) 4.34 (ddd, J = 7.0, 5.2, 4.4 Hz, H_c) 4.75 (d, J = 1.5 Hz, H_e) 4.78 (d, J = 1.5 Hz, H_f) 6.89 (d, J = 8.9 Hz, 2H_b) 7.88 (d, J = 8.9 Hz, 2H_a).

^{13}C-NMR ($CDCl_3$): δ 17.4, 18.1, 23.0, 26.3, 30.8, 38.5, 81.0, 113.1, 115.1, 129.9, 130.6, 142.2, 162.9, 196.7 (C=O).

IR(CCl_4) : 2966, 1682 (C=O), 1600, 1575, 1506,1357, 1252, 1169, 895 cm^{-1}.

UV(MeOH) : λ_{max} = 279 nm (16040), 313 nm (1310).

MS (m/e) : 246 (M^+), 191, 137, 121, 110, 95, 69 (base), 55, 43.

Hi-Res MS : $C_{16}H_{22}O_2$, Calculated : 246.1620, Found : 246.1617.

4'-(2,3-Dimethyl-3-buten-1-oxy)acetophenone (p-M_2M_3K):

3-Methyl-5-oxa-7-thia-2-octanone:

A solution of 1-hydroxy-2-methyl-3-butanone (9.8 g, 0.09 mol) and DMSO (280 mL) was added dropwise to a mixture of acetic anhydride (196 mL) and acetic acid (35 mL) over 30 min under argon atmosphere.[134] The resulting solution was stirred for 24 hours at room temperature. The mixture was then poured into water (500 mL) and extracted with ether (400 mL x 3). The ether layer was washed with saturated $NaHSO_4$ (500 mL x 2) and 2N NaOH (500 mL), and then dried over $MgSO_4$. Solvent and excess DMSO could be removed by distillation and the product was further purified by silica gel column chromatography (7.3 g, 75 %, hexane/ethyl acetate = 4/1, R_f = 0.51).

^{1}H-NMR ($CDCl_3$) : δ 1.06 (d, J = 8.0 Hz, Me) 2.07(s, Me) 2.14 (s, Me) 3.10 (qdd, J = 8.0, 7.5, 5.2 Hz, 1H) 3.53 (dd, J = 9.3, 5.2 Hz, 1H) 3.63 (dd, J = 9.3, 7.5 Hz, 1H) 4.55 (s, 2H).

2,3-Dimethyl-5-oxa-7-thia-1-octene:

A solution of methyl triphenylphosphonium bromide (36 g, 0.1 mol) in dry THF (250 mL) was cooled to -78°C using a dry ice-acetone bath. After 20 min, n-BuLi (2M, 55 mL) was added by syringe to the solution; the color changed from white to dark yellow.[135] The solution was allowed to warm to room temperature for 1 h. The solution was again cooled by dry ice-acetone bath, and a solution of 3-methyl-5-oxa-7-thia-2-octanone (8.1 g, 0.05 mol) in THF (70 mL) was added dropwise. The solution was then stirred vigorously at room temperature for 3 h. The mixture was quenched by water (500 mL) and extracted with ether (300 mL x 3). The ether layer was washed with 3 % H_2O_2 aqueous solution (500 mL), saturated $NaHSO_4$ (500 mL x 2) and saturated brine (500 mL), and then dried over $MgSO_4$. After the solvent was evaporated, the residue was purified by

column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.92) and a slightly yellowish oil (4.4 g, 58 %) was obtained.

^{1}H-NMR ($CDCl_3$) : δ 1.03 (d, J = 7.0 Hz, Me) 1.71 (d, J = 1.2 Hz, Me) 2.12 (s, Me) 2.43 (dqdd, J = 7.1, 7.0, 6.6, 1.5 Hz, 1H) 3.39 (dd, J = 9.2, 6.6 Hz, 1H) 3.51 (dd, J = 9.2, 7.1 Hz, 1H) 4.62 (s, 2H) 4.75 (dq, J = 1.7, 1.2 Hz, 1H) 4.76 (dd, J = 1.7, 1.5 Hz, 1H).

2,3-Dimethyl-3-buten-1-ol:

A solution of 2,3-dimethyl-5-oxa-7-thia-1-octene (3.0 g, 19 mmol) and mercury chloride (8.0 g, 29 mmol) in a 80 % acetonitrile aqueous solution (200 mL) was stirred at 25°C for 24 h.[136] The acetonitrile was carefully removed by low temperature evaporation and the resulting solution was filtered through celite and repeatedly eluted by ether (250 mL). The filtration was added with 1N NH_4OAc aqueous solution (250 mL) and extracted. The aqueous layer was extracted by another portion of ether (250 mL) and the combined ether layers were washed with saturated brine and dried over K_2CO_3. After the solvent was evaporated, the product was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.26) and a colorless oil (1.3 g, 65 %) was obtained.

^{1}H-NMR ($CDCl_3$) : δ 1.01 (d, J = 7.0 Hz, Me) 1.69 (d, J = 1.0 Hz, Me) 2.19 (s, O-H) 2.36 (qtd, J = 7.0, 6.7, 1.5 Hz, 1H) 3.49 (d, J = 6.7 Hz, 2H) 4.79 (dq, J = 1.9, 1.0 Hz) 4.86 (dd, J = 1.9, 1.5 Hz, 1H).

2,3-Dimethyl-1-tosyl-3-butene:

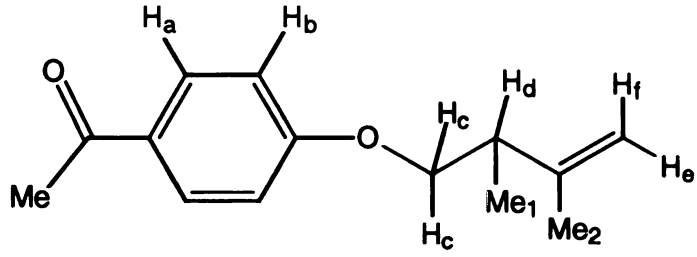
The same procedure as used to make 2-tosyl-4-pentene was employed. 2,3-Dimethyl-3-buten-1-ol (1.1 g, 0.011 mol) and p-toluenesulfonyl chloride (3.2

g, 0.017 mol) in pyridine (7.1 mL) produced 2,3-dimethyl-1-tosyl-3-butene (1.6 g, 57 %, b.p. = 111°C in 0.6 Torr).

^{1}H-NMR ($CDCl_3$) : δ 0.99 (d, J = 7.0 Hz, Me) 1.60 (s, Me) 2.42 (s, Me) 2.46 (dqd, J = 7.2, 7.0, 6.6 Hz, 1H) 3.84 (dd, J = 9.5, 7.2 Hz, 1H) 3.97 (dd, J = 9.5, 6.6 Hz, 1H) 4.67 (d, J = 1.5 Hz, 1H) 4.76 (d, J = 1.5 Hz, 1H) 7.32 (d, J = 8.3 Hz, 2H) 7.76 (d, J = 8.3 Hz, 1H).

p-M_2M_3K:

The coupling procedures of the title compound was that used to make 4'-(1-isopropyl-3-buten-1-oxy)acetophenone. A solution of 2,3-dimethyl-1-tosyl-3-butene (1.2 g, 4.7 mmol), 4-hydroxyacetophenone (0.8 g, 6 mmol) and anhydrous potassium carbonate (3 g, 0.022 mol) in DMF (50 mL) produced a colorless oil of 4'-(2,3-dimethyl-3-buten-1-oxy)acetophenone after purified by silica gel column chromatography (0.2 g, 25 %, hexane/ethyl acetate = 4/1, R_f = 0.55).



^{1}H-NMR ($CDCl_3$) : δ 1.15 (d, J = 6.9 Hz, Me_1) 1.75 (s, Me_2) 2.53 (s, COMe) 2.64 (dqd, J = 7.1, 6.9, 6.3 Hz, H_d) 3.84 (dd, J = 9.1, 7.1 Hz, H_c) 4.00 (dd, J = 9.1, 6.3 Hz, H_c) 4.80 (d, J = 1.5 Hz, H_e) 4.83 (d, J = 1.5 Hz, H_f) 6.90 (d, J = 8.9 Hz, $2H_b$) 7.90 (d, J = 8.9 Hz, $2H_a$).

^{13}C-NMR($CDCl_3$) : δ 16.3, 20.4, 26.2, 40.3, 71.7, 111.1, 114.2, 130.1, 130.5, 146.5, 162.9, 196.7 (C=O).

IR(CCl_4) : 2970, 1683 (C=O), 1602, 1577, 1509, 1358, 1253, 1170 cm^{-1}.

UV(MeOH) : λ_{max} = 270 nm (16070), 313 nm (840).

MS (m/e) : 218 (M^+), 189, 161, 149, 136, 121 (base), 97, 85, 69, 55, 43.

Hi-Res MS : $C_{14}H_{18}O_2$, Calculated : 218.1307, Found : 218.1269.

4'-(3-Methyl-3-penten-1-oxy)acetophenone (p-M_3M_4K):

3-Methyl-3-penten-1-ol:[137,138]

Magnesium turnings (6.0 g, 0.25 mol) in anhydrous THF (25 mL) with a few pieces of iodine were added dropwise with 2-bromo-2-butene (28 mL, 0.27 mol, *cis/trans* mixture in a ratio of 1/5 obtained from Aldrich) in anhydrous THF (75 mL) and then with gently reflux under argon atmosphere. The Grignard solution was cooled down using dry ice /acetonitrile mixture (-40°C) for 20 min. The dropping funnel was removed and CuI (4.3 g, 0.023 mol) was added directly into the Grignard solution, with strong stirring. A gas condensing dropping funnel was fitted to the flask. After 10 min, ethylene oxide (ca. 13 mL) was gently added by gas condensed dropping funnel containing a mixture of dry ice/acetone. The solution was allowed to warm to room temperature. After 2 h, acetic acid (20 mL) in ice (100 g) was added. The green salt was filtered using celite and the THF/water solution was extracted with ether (150 mL x 2). The combined THF/ether solution was washed with saturated $NaHSO_4$ (200 mL x 2), saturated brine (200 mL) and dried over $MgSO_4$. The resulting alcohol in a *cis/trans* mixture 1/5.5 (determined by the integration of methyl groups at δ 1.67 and 1.69 in ^{1}H-NMR) was a colorless oil, purified by vacuum distillation (b.p. = 80-84°C at 4.5 Torr, 22 g, 88%). Since the starting material 2-bromo-2-butene was obtained in a *cis/trans* mixture 1/5 from Aldrich, we assumed that the major product is *trans*.

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.58 (d, J = 6.6 Hz, Me) 1.69 (s, Me) 1.72 (s, O-H) 2.31 (t, J = 6.7 Hz, 2H) 3.66 (t, J = 6.7 Hz, 2H) 5.39 (q, J = 6.6 Hz, 1H); (*cis*) δ

1.60 (d, J = 6.3 Hz, Me) 1.67 (s, Me) 1.75 (s, O-H) 2.22 (t, J = 6.1 Hz, 2H) 3.64 (t, J = 6.1 Hz, 2H) 5.29 (q, J = 6.3 Hz, 1H).

3-Methyl-1-tosyl-3-pentene:

The same procedure to make 2-tosyl-4-pentene was used. 3-Methyl-3-penten-1-ol (11 g, 0.11 mol) and p-toluenesulfonyl chloride (32 g, 0.17 mol) in pyridine (70 mL) produced 3-methyl-1-tosyl-3-pentene (14 g, 53%, b.p. = 105-108 °C in 0.6 Torr) with *cis/trans* = 1/6.2, determined by the integration of vinyl protons at δ 5.19 and 5.29 in ^{1}H-NMR. (Fig. 35)

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.48 (d, J = 6.8 Hz, Me) 1.58 (s, Me) 2.35 (t, J = 7.3 Hz, 2H) 2.43 (s, Me) 4.02 (t, J = 7.3 Hz, 2H) 5.29 (q, J = 6.8 Hz, 1H) 7.32 (d, J = 8.3 Hz, 2H) 7.77 (d, J = 8.3 Hz, 2H); (*cis*) δ 1.53 (d, J = 6.6 Hz, Me) 1.59 (s, Me) 2.28 (t, J = 6.7 Hz, 2H) 2.47 (s, Me) 4.03 (t, J = 6.7 Hz, 2H) 5.19 (q, J = 6.6 Hz, 1H) 7.35 (d, J = 8.0 Hz, 2H) 7.75 (d, J = 8.0 Hz, 2H).

p-M_3M_4K:

The coupling procedure used to make 4'-(1-isopropyl-3-buten-1-oxy)acetophenone was followed. A solution of 3-methyl-1-tosyl-3-pentene (3.0 g, 12 mmol), 4-hydroxyacetophenone (2.5 g, 18 mmol) and anhydrous potassium carbonate (10 g, 72 mmol) in DMF (70 mL) produced the colorless 4'-(3-methyl-3-penten-1-oxy)acetophenone, which was purified by silica gel column chromatography (0.73 g, 28 %, hexane/ethyl acetate = 4/1, R_f = 0.55), in a *cis/trans* .= 1/5.2 mixture determined by the integration of Me_1 at δ = 1.64 and 1.74 in ^{1}H-NMR. (Fig. 36)

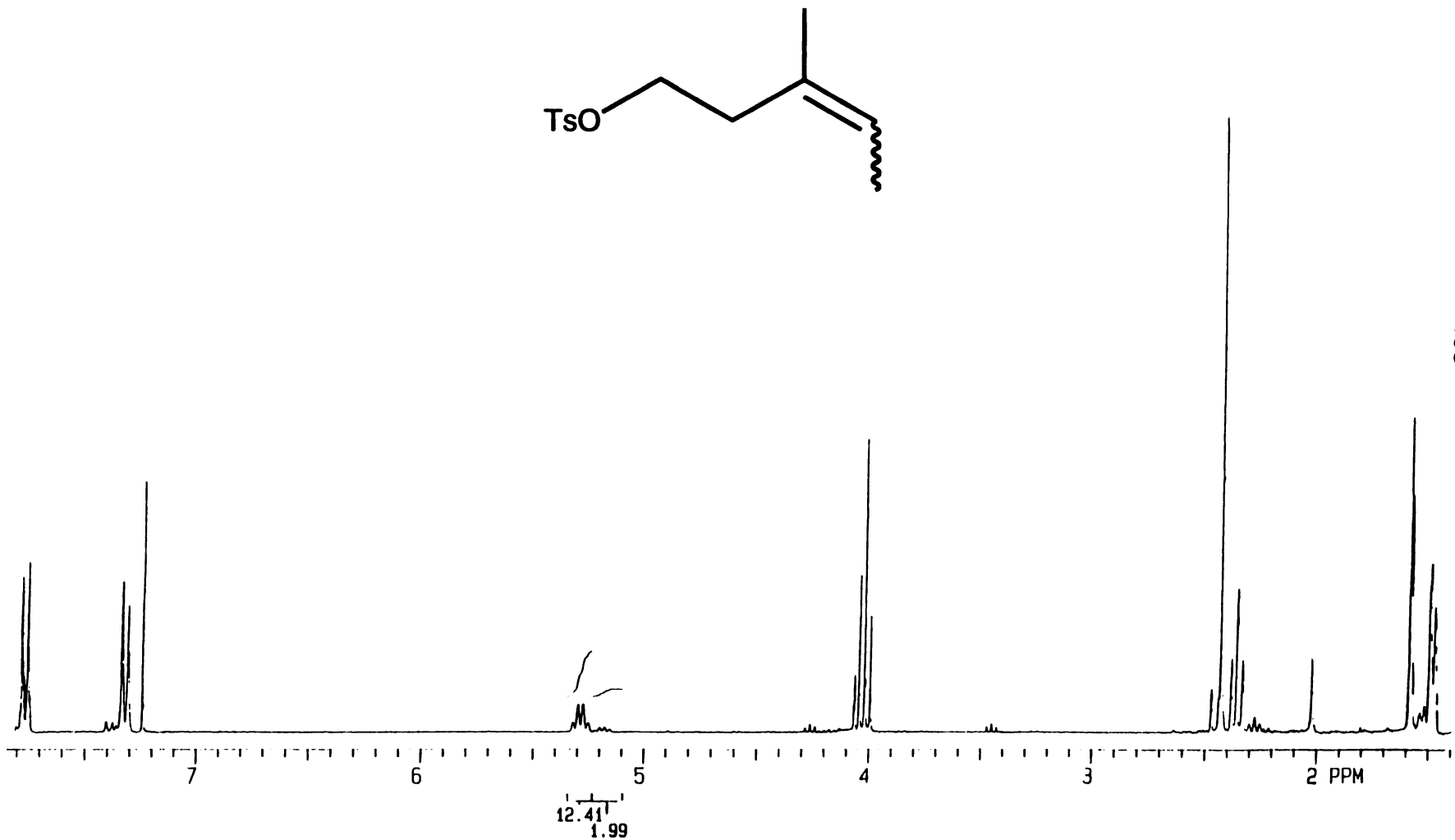


Figure 35. ^{1}H-NMR spectrum of *cis/trans* 3-methyl-1-tosyl-3-pentene in $CDCl_3$.

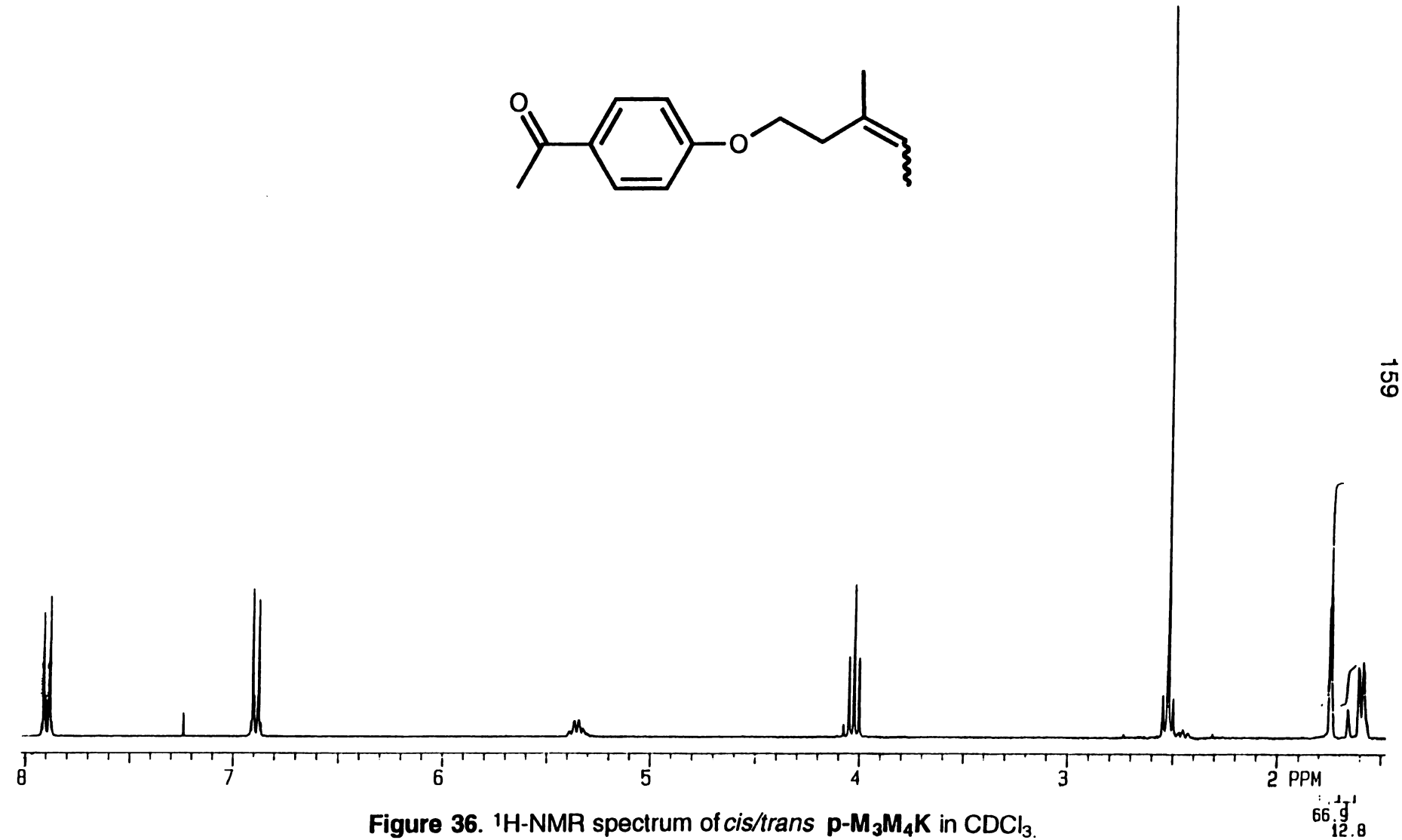
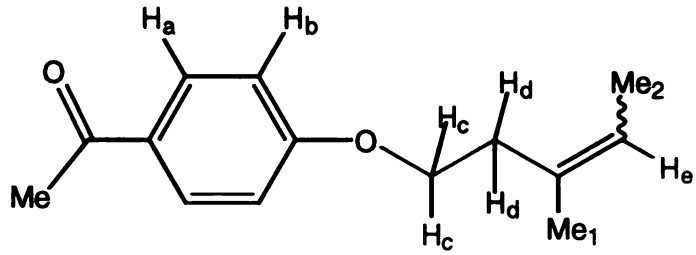


Figure 36. ^{1}H-NMR spectrum of *cis/trans* **p-M$_3$M$_4$K** in $CDCl_3$.



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.59 (d, J = 6.8 Hz, Me_2) 1.74 (s, Me_1) 2.50 (s, COMe) 2.52 (t, J = 7.2 Hz, $2H_d$) 4.03 (t, J = 7.2 Hz, $2H_c$) 5.36 (q, J = 6.8 Hz, H_e) 6.89 (d, J = 8.9 Hz, $2H_b$) 7.90 (d, J = 8.9 Hz, $2H_a$); (*cis*) δ 1.57 (d, J = 6.4 Hz, Me_2) 1.66 (s, Me_1) 2.45 (t, J = 7.0 Hz, $2H_d$) 2.51 (s, COMe) 4.05 (t, J = 7.0 Hz, $2H_c$) 5.34 (q, J = 6.4 Hz, H_e) 6.89 (d, J = 8.9 Hz, $2H_b$) 7.90 (d, J = 8.9 Hz, $2H_a$).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 13.1, 23.5, 25.9, 30.9, 66.1, 113.9, 121.7, 129.9, 130.1, 131.4, 162.6, 196.1; (*cis*) δ 13.2, 15.7, 26.0, 38.6, 66.9, 113.8, 120.9, 130.0, 130.3, 131.2, 162.7, 196.2 (C=O).

IR(CCl_4) : (mixture) 2972, 1683 (C=O), 1603, 1506, 1469, 1455, 1357, 1255, 955 cm^{-1}.

UV(MeOH) : (mixture) 216 nm (12500), λ_{max} = 270 nm (16285), 290 nm (10465), 313 nm (1255).

MS (m/e) : 218 (M^+), 176, 136, 121 (base), 91, 82, 67, 55, 43.

Hi-Res MS : $C_{14}H_{18}O_2$, Calculated : 218.1307, Found : 218.1319.

4'-(1,3-Dimethyl-3-penten-1-oxy)acetophenone (p-$M_1M_3M_4$K):

4-Methyl-4-hexen-2-ol:

A solution of vinyl magnesium bromide-prepared from magnesium turnings (3.8 g, 0.16 mol) and 2-bromo-2-butene (18.3 mL, 0.18 mol, *cis/trans* mixture in a ratio of 1/5, obtained from Aldrich), CuI (2.85 g, 0.015 mol) and propylene oxide (5.8 g, 0.1 mol) in THF (150 mL) produced the colorless 4-methyl-4-hexen-2-ol

(11.0 g, 95 %) which was purified by vacuum distillation (b.p. = 83-86°C at 4.5 Torr).

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.19 (d, J = 6.3 Hz, Me) 1.59 (d, J = 6.6 Hz, Me) 1.69 (d, J = 1.5 Hz, Me) 1.71 (s, O-H) 2.02 (dd, J = 13.3, 4.4 Hz, 1H) 2.32 (dd, J = 13.3, 8.6 Hz, 1H) 3.92 (dqd, J = 8.6, 6.3, 4.4 Hz, 1H) 5.40 (qq, J = 6.6, 1.5 Hz, 1H); (*cis*) δ 1.15 (d, J = 6.2 Hz, Me) 2.13 (dd, J = 13.3, 3.8 Hz, 1H) 2.23 (dd, J = 13.3, 7.8 Hz, 1H) 3.85 (m, 1H) 5.30 (q, J = 5.9 Hz, 1H).

IR(CCl_4) : (mixture) 3339 (O-H), 2975, 1445, 1380, 1037 cm^{-1}.

4-Methyl-2-tosyl-4-hexene:

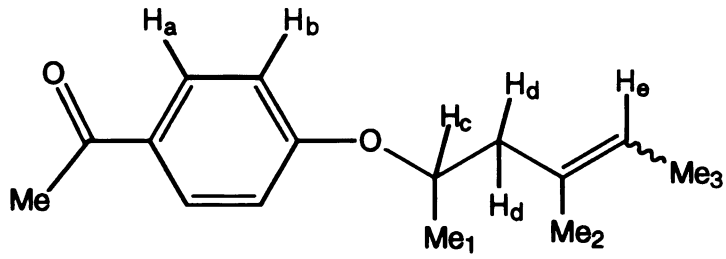
The tosylation procedure used to make 2-tosyl-4-pentene was followed. The 4-methyl-4-hexen-2-ol (11.4 g, 0.1 mol) and p-toluenesulfonyl chloride (22.8 g, 0.12 mol) in pyridine (47 mL) produced 4-methyl-2-tosyl-4-hexene (16 g, 60%, b.p. = 102-106°C at 0.5 Torr).

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.25 (d, J = 6.2 Hz, Me) 1.46 (d, J = 6.7 Hz, Me) 1.51 (d, J = 1.5 Hz, Me) 2.17 (dd, J = 13.7, 7.1 Hz, 1H) 2.35 (dd, J = 13.7, 6.6 Hz, 1H) 2.42 (s, Me) 4.66 (ddq, J = 7.1, 6.6, 6.2 Hz, 1H) 5.21 (qq, J = 6.7, 1.5 Hz, 1H) 7.30 (d, J = 8.3 Hz, 2H) 7.76 (d, J = 8.3 Hz, 2H); (*cis*) δ 1.23 (d, J = 6.3 Hz, Me) 1.45 (d, J = 6.3 Hz, Me) 2.08 (dd, J = 14.0, 6.7 Hz, 1H) 2.27 (dd, J = 14.0, 6.9 Hz, 1H) 2.43 (s, Me) 4.67 (ddq, J = 6.9, 6.7, 6.3 Hz, 1H) 5.20 (m, 1H) 7.74 (d, J = 8.3 Hz, 2H).

p-$M_1M_3M_4K$:

The previous coupling procedure to make 4'-(1-isopropyl-3-buten-1-oxy)acetophenone was used. A solution of 4-methyl-2-tosyl-4-hexene (10 g, 37 mmol), 4-hydroxyacetophenone (5.5 g, 40 mmol) and anhydrous potassium carbonate (16.5 g, 80 mmol) in DMF (70 mL) produced 4'-(1,3-dimethyl-3-penten-

1-oxy)acetophenone *cis/trans* in a ratio of 1/5.5 measured from Me_2 groups at δ 1.74 (*cis*) and 1.79 (*trans*) in ^{1}H-NMR, which was purified by silica gel column chromatography (3.3 g, 38 %, hexane/ethyl acetate = 4/1, R_f = 0.59) and colorless.



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.31 (d, J = 6.1 Hz, Me_1) 1.61 (d, J = 6.9 Hz, Me_3) 1.74 (d, J = 1.5 Hz, Me_2) 2.35 (dd, J = 13.6, 6.1 Hz, H_d) 2.50 (dd, J = 13.6, 6.9 Hz, H_d) 2.53 (s, COMe) 4.72 (tq, J = 6.9, 6.1 Hz, H_c) 5.34 (qq, J = 6.9, 1.5 Hz, H_e) 6.97 (d, J = 9.0 Hz, 2H_b) 7.92 (d, J = 9.0 Hz, 2H_a); (*cis*) δ 1.29 (d, J = 6.0 Hz, Me_1) 1.64 (d, J = 6.9 Hz, Me_3) 1.79 (d, J = 1.6 Hz, Me_2) 2.30 (dd, J = 13.4, 6.0 Hz, H_d) 2.50 (dd, J = 13.4, 6.9 Hz, H_d) 2.55 (s, COMe) 4.75 (tq, J = 6.9, 6.1 Hz, H_c) 5.31 (qq, J = 6.9, 1.6 Hz, H_e) 6.97 (d, J = 9.0 Hz, 2H_b) 7.92 (d, J = 9.0 Hz, 2H_a).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 13.6, 19.5, 24.1, 26.2, 38.0, 72.9, 114.9, 122.2, 129.9, 130.5, 131.7, 162.1, 196.6 (C=O); (*cis*) δ 13.4, 19.8, 25.1, 27.2, 40.0, 72.8, 114.7, 123.1, 128.9, 131.1, 131.9, 162.5, 196.2 (C=O).

IR(CCl_4) : (mixture) 2966, 1682 (C=O), 1600, 1506, 1479, 1450, 1357, 1252, 1169, 955 cm^{-1}.

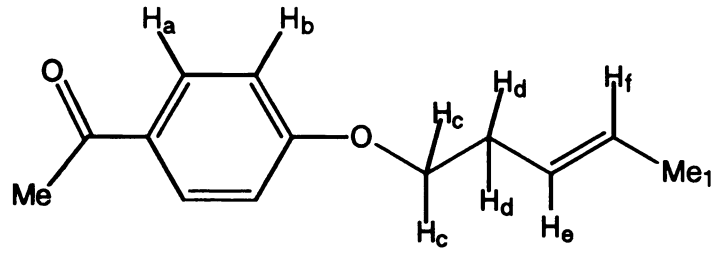
UV(MeOH) : (mixture) λ_{max} = 271 nm (16500) 313 nm (1350).

MS (m/e) : 232 (M^+), 189, 163, 136, 121 (base), 113, 111, 95, 43.

Hi-Res MS : $C_{15}H_{20}O_2$, Calculated : 232.1463, Found : 232.1441.

4'-(*trans*-3-Penten-1-oxy)acetophenone (p-M_4K):

A solution of 1-bromo-3-pentene (2.5 g, 17 mmol, > 95% *trans*- isomer, purchased from K&K Chemical Company and checked by ^{1}H-NMR), 4-hydroxyacetophenone (2.5 g, 18 mmol) and anhydrous potassium carbonate (7.5 g, 50 mmol) in DMF (30 mL) produced colorless *trans* 4'-(3-penten-1-oxy)acetophenone which was purified by silica gel column chromatography (1.1 g, 33 %, hexane/ethyl acetate = 19/1, R_f = 0.35).



^{1}H-NMR ($CDCl_3$) : δ 1.65 (dd, J = 6.3, 1.2 Hz, Me_1) 2.45 (qd, J = 6.8, 1.2 Hz, $2H_d$) 2.51 (s, COMe) 3.98 (t, J = 6.8 Hz, $2H_c$) 5.46 (dtq, J = 15.3, 6.8, 1.2 Hz, H_e) 5.56 (dqt, J = 15.3, 6.3, 1.2 Hz, H_f) 6.88 (d, J = 9.0 Hz, $2H_b$) 7.88 (d, J = 9.0 Hz, $2H_a$). (see Table 33)

^{13}C-NMR ($CDCl_3$) : δ 17.9, 26.2, 32.2, 67.9, 114.0, 126.1, 127.9, 130.1, 130.5, 162.8, 196.6 (C=O).

IR(CCl_4) : 1682 (C=O), 1602, 1577,1509, 1357, 1254, 1170 cm^{-1}.

UV(MeOH) : 215 nm (12000), λ_{max} = 270 nm (16085), 290 nm (10265), 313 nm (1210).

MS (m/e) : 204 (M^+), 163, 136, 121, 91, 77, 69 (base), 43, 41.

Hi-Res MS : $C_{13}H_{16}O_2$, Calculated : 204.1150, Found : 204.1149.

3'-Methyl-4'-(3-methyl-3-penten-1-oxy)acetophenone (p-$M_3M_4M_5$K):

3'-Methyl-4'-(1,3-dimethyl-3-penten-1-oxy)acetophenone (p-$M_1M_3M_4M_5$K):

3'-Methyl-4'-(*trans*-3-penten-1-oxy)acetophenone (p-M_4M_5K):

o-Acetoxytoluene:

A solution of *o*-cresol (22g, 0.2 mol) in benzene (100 mL) was added to pyridine (32.3 g, 0.4 mol) in 0°C under argon atmosphere. After 30 min, acetyl chloride (24 g, 0.3 mol) was added dropwise to the benzene solution. The ice bath was removed and the solution was stirred vigorously at room temperature for 24 h. Aqueous HCl (5%, 50 mL) was added and the mixture was extracted with benzene (100 mL x 2). The combined benzene layer was washed with 2N NaOH (100 mL x 2), saturated $NaHSO_4$ (200 mL), saturated brine (200 mL) and dried over $MgSO_4$. Evaporation of benzene and the colorless o-acetoxytoluene was isolated (31.8 g, 99 %, hexane/ethyl acetate = 4/1, R_f = 0.66).

^{1}H-NMR ($CDCl_3$) : δ 2.17 (s, Me) 2.30 (s, Me) 6.97 (d, J = 7.7 Hz, 1H) 7.13 (dd, J = 9.1, 7.3 Hz, 1H) 7.19 (dd, J = 7.7, 7.3 Hz, 1H) 7.23 (d, J = 9.1 Hz, 1H).

4-Hydroxy-3-methylacetophenone:

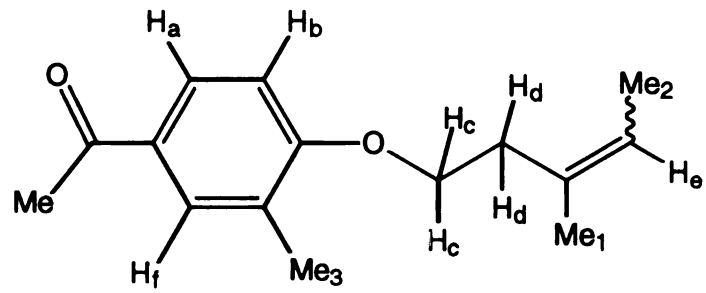
o-Acetoxytoluene (31.8 g, 0.21 mol) was added dropwise at 0°C to a solution of alumina chloride (68 g, 0.5 mol) in nitrobenzene (500 mL). After addition, the solution was stirred strongly at room temperature for 90 h. Aqueous HCl solution (5%, 125 mL) and ether (400 mL) were added and the organic layer was separated. The nitrobenzene and ether organic layer was extracted with 2N NaOH (aq). The aqueous layer was acidified to pH 2 with HCl, and then extracted with ether (2 x 500 mL). The combined ether layers were washed with saturated $NaHSO_4$ (500 mL), saturated brine (500 mL) and dried over $MgSO_4$. The ether was evaporated to give 4-hydroxy-3-methylacetophenone (15.7 g, 50 %, hexane/ethyl acetate = 4/1, R_f = 0.20).

^{1}H-NMR ($CDCl_3$) : δ 2.29 (s, Me) 2.57 (s, COMe) 6.88 (d, J = 9.0 Hz, 1H) 7.31 (s, O-H) 7.72 (dd, J = 9.0, 1.5 Hz, 1H) 7.79 (d, J = 1.5 Hz, 1H).

^{13}C-NMR ($CDCl_3$) : δ 15.9, 26.2, 114.8, 124.4, 128.7, 129.6, 132.0, 159.4, 198.5 (C=O).

p-$M_3M_4M_5K$:

A solution of 3-methyl-1-tosyl-3-pentene (4 g, 16 mmol, *cis/trans* mixture in a ratio of 1/6.2, see above), 4-hydroxy-3-methylacetophenone (2.4 g, 16 mmol) and anhydrous potassium carbonate (10 g, 72 mmol) in DMF (50 mL) produced the colorless 3'-methyl-4'-(3-methyl-3-penten-1-oxy)acetophenone (*cis/trans* mixture in a ratio of 1/5.6 measured by the integration of Me_2 groups in ^{1}H-NMR) after purification by silica gel column chromatography (32 %, hexane/ethyl acetate = 4/1, R_f = 0.40).



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.61 (d, J = 6.8 Hz, Me_2) 1.76 (s, Me_1) 2.22 (s, Me_3) 2.52 (s, COMe) 2.55 (t, J = 6.9 Hz, 2H_d) 4.05 (t, J = 6.9 Hz, 2H_c) 5.36 (q, J = 6.8 Hz, H_e) 6.81 (d, J = 8.3 Hz, H_b) 7.75 (s, H_f) 7.78 (d, J = 8.3 Hz, H_a); (*cis*) δ 1.59 (d, Me_2) 1.68 (s, Me_1) 1.75 (s, Me_3) 2.52 (s, COMe, overlap with *trans*) 2.47 (t, J = 6.6 Hz, 2H) 4.07 (t, J = 6.6 Hz, 2H) 5.35 (m) 7.79 (d).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 13.3, 16.3, 23.7, 26.2, 31.2, 66.3, 109.7, 121.7, 126.7, 128.3, 129.6, 130.8, 131.7, 161.1, 196.9 (C=O); (*cis*) δ 12.4, 15.9, 22.7, 27.1, 33.2, 66.4, 109.9, 122.7, 124.3, 127.8, 128.6, 130.2, 133.5, 164.1, 196.4 (C=O).

IR(CCl_4) : (mixture) 2924, 1681 (C=O),1603, 1502, 1357, 1261, 1252, 1143 cm^{-1}.

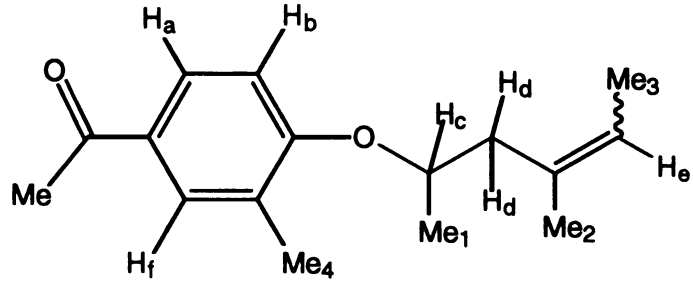
UV(MeOH) : (mixture) 221 nm (12950), λ_{max} = 273 nm (14170), 313 nm (1420).

MS (m/e) : 232 (M^+), 190, 161, 151, 150, 136 (base), 83, 77, 67, 55, 43.

Hi-Res MS : $C_{15}H_{20}O_2$, Calculated : 232.1463, Found : 232.1461.

p-$M_1M_3M_4M_5K$:

A solution of 4-methyl-2-tosyl-4-hexene (2.7 g, 10 mmol, *cis/trans* mixture, see above), 4-hydroxy-3-methylacetophenone (1.5 g, 10 mmol) and anhydrous potassium carbonate (4.5 g, 30 mmol) in DMF (50 mL) produced 3'-methyl-4'-(1,3-dimethyl-3-penten-1-oxy)acetophenone, which was colorless after purified by silica gel column chromatography (35 %, hexane/ethyl acetate = 4/1, R_f = 0.40, cis/*trans* mixture in a ratio of 1/4.8, determined by the integration of Me_3 groups in ^{1}H-NMR).



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 1.31 (d, J = 6.1 Hz, Me_1) 1.61 (d, J = 6.8 Hz, Me_3) 1.72 (s, Me_2) 2.20 (s, Me_4) 2.32 (dd, J = 13.7, 6.1 Hz, H_d) 2.51 (s, COMe) 2.53 (dd, J = 13.7, 6.6 Hz, H_d) 4.61 (d quint, J = 6.6, 6.1 Hz, H_c) 5.32 (q, J = 6.8 Hz, H_e) 6.82 (d, J = 9.0 Hz, H_b) 7.75 (s, H_f) 7.78 (d, J = 9.0 Hz, H_a); (*cis*) δ 1.30 (d, Me) 1.55 (d, J = 6.7 Hz, Me_3) 2.19 (s, Me_4) 2.43 (m) 2.45 (m) 4.59 (m) 5.31 (m) 7.79 (d, 1H).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 16.5, 19.6, 24.1, 26.2, 38.1, 46.3, 72.9, 110.7, 122.0, 127.4,128.2, 129.3, 131.1, 131.9, 160.3, 196.9 (C=O); ; (*cis*) δ 12.7, 17.8, 25.5, 26.8, 32.3, 45.2, 67.3, 109.6, 125.3, 126.5, 126.6, 128.1, 129.4, 130.5, 160.8, 196.6 (C=O).

IR(CCl_4) : (mixture) 2978, 1680 (C=O), 1602, 1498, 1357, 1261, 1142 cm^{-1}.

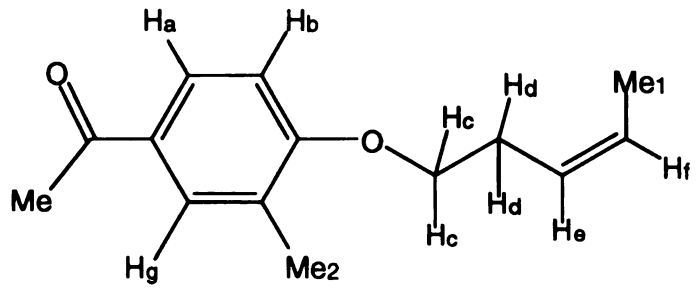
UV(MeOH) : (mixture) 223 nm (13200), λ_{max} = 277 nm (13560), 313 nm (2000).

MS (m/e) : 246 (M^+), 203, 190, 177 (base), 113, 97, 81, 69, 55, 43.

Hi-Res MS : $C_{16}H_{22}O_2$, Calculated : 246.1620, Found : 246.1622.

p-M_4M_5K:

A solution of *trans* 1-bromo-3-pentene (1.08 g, 7.5 mmol, obtained from Aldrich), 4-hydroxy-3-methylacetophenone (1.34 g, 8.9 mmol) and anhydrous potassium carbonate (4.5 g, 30 mmol) in DMF (25 mL) produced *trans* 3'-methyl-4'-(3-penten-1-oxy)acetophenone after 6 h gentle refluxed. The ketone was colorless after purified by silica gel column chromatography (39 %, hexane/ethyl acetate = 4/1, R_f = 0.48).



^{1}H-NMR ($CDCl_3$) : δ 1.67 (dd, J = 5.9, 1.0 Hz, Me_1) 2.22 (s, Me_2) 2.48 (q, J = 6.7 Hz, $2H_d$) 2.53 (s, COMe) 4.00 (t, J = 6.7 Hz, $2H_c$) 5.52 (dq, J = 15.9, 5.9 Hz, H_f) 5.57 (dtq, J = 15.9, 6.7, 1.0 Hz, H_e) 6.79 (d, J = 8.2 Hz, H_b) 7.76 (s, H_g) 7.77 (d, J = 8.2 Hz, H_a).

^{13}C-NMR ($CDCl_3$) : δ 16.0, 17.8, 26.0, 32.2, 67.7, 109.7, 126.2, 126.5, 127.7, 128.2, 129.4, 130.6, 160.9, 196.7 (C=O).

IR(CCl_4) : 2922, 1680 (C=O), 1603, 1581, 1503, 1260 cm^{-1}.

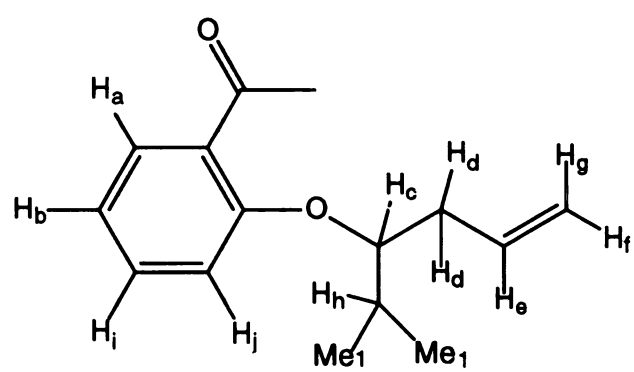
UV(MeOH) : 221 nm (12850), λ_{max} = 273 nm (13870), 313 nm (1420).

MS (m/e) : 218 (M^+), 150, 135, 121, 107, 77, 69 (base), 53, 43.

Hi-Res MS : $C_{14}H_{18}O_2$, Calculated : 218.1307, Found : 218.1321.

2'-(1-Isopropyl-3-buten-1-oxy)acetophenone (o-I_1K):

A solution of 2-methyl-3-tosyl-5-hexene (15 g, 0.06 mol, see above), 2-hydroxyacetophenone (9.6 g, 0.07 mol) and anhydrous potassium carbonate (22.5 g, 0.16 mol) in DMF (100 mL) in 250 mL three-necked round bottom flask was refluxed at 100°C for 7h. The solution was added by water (150 mL) and extracted by diethyl ether (3 x 100 mL). After the ether was removed, the colorless ketone was obtained after purified by silica gel column chromatography (3.2 g, 23 %, hexane/ethyl acetate = 17/1, R_f = 0.70).



^{1}H-NMR ($CDCl_3$) : δ 0.97 (d, J = 6.9 Hz, Me_1) 1.01 (d, J = 6.9 Hz, Me_1) 2.08 (septd, J = 6.9, 4.9 Hz, H_h) 2.43 (ddt, J = 7.0, 4.9, 1.2 Hz, $2H_d$) 2.61 (s, COMe) 4.30 (q, J = 4.9 Hz, H_c) 5.02 (ddt, J = 10.1, 2.1, 1.2 Hz, H_f) 5.08 (ddt, J = 17.1, 2.1, 1.2 Hz, H_g) 5.78 (ddt, J = 17.1, 10.1, 7.0 Hz, H_e) 6.91 (d, J = 7.2 Hz, H_j) 6.93

(dd, J = 8.2, 8.0 Hz, H_b) 7.39 (ddd, J = 8.2, 7.2, 1.9 Hz, H_i) 7.68 (dd, J = 8.0, 1.9 Hz, H_a).

^{13}C-NMR ($CDCl_3$) : δ 17.9, 18.2, 30.4, 32.2, 34.6, 81.9, 113.0, 117.6, 120.1, 129.1, 130.6, 133.3, 133.9, 157.6, 200.3 (C=O).

IR(CCl_4) : 3077, 2965, 1681 (C=O), 1597, 1479, 1450, 1357, 1237, 985 cm^{-1}.

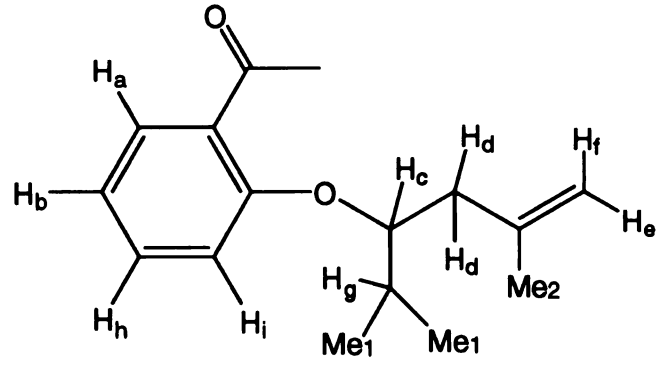
UV(MeOH) : λ_{max} = 247 nm (7700), 306 nm (4050) 313 nm (3850).

MS (m/e) : 232 (M^+), 191, 136, 121 (base), 97, 81, 77, 65, 55, 43.

Hi-Res MS : $C_{15}H_{20}O_2$, Calculated : 232.1463, Found : 232.1473.

2'-(1-Isopropyl-3-methyl-3-buten-1-oxy)acetophenone (o-I_1M_3K):

A solution of 2,5-dimethyl-3-tosyl-5-hexene (5.0 g, 0.018 mol, see above), 4-hydroxyacetophenone (2.5 g, 0.019 mol) and anhydrous potassium carbonate (7.5 g, 0.05 mol) in DMF (70 mL) was refluxed at 110°C for 6h. The solution was added by water (100 mL) and extracted by diethyl ether (2 x 100 mL). The ether layer was washed by $NaHSO_4$ (100 mL) and NaCl (100 mL) aqueous solution. After the ether was removed, the colorless 2'-(1-isopropyl-3-methyl-3-buten-1-oxy)acetophenone was obtained after purified by silica gel column chromatography (0.9 g, 21 %, hexane/ethyl acetate = 4/1, R_f = 0.67).



^{1}H-NMR ($CDCl_3$) : δ 1.01 (d, J = 6.9 Hz, Me_1) 1.04 (d, J = 6.9 Hz, Me_1) 1.73 (t, J = 1.2 Hz, Me_2) 2.09 (septd, J = 6.9, 4.0 Hz, H_g) 2.37 (dd, J = 14.5, 5.1 Hz, H_d)

2.46 (dd, J = 14.5, 7.7 Hz, H_d) 2.60 (s, COMe) 4.46 (ddd, J = 7.7, 5.1, 4.0 Hz, H_c) 4.76 (dq, J = 1.6, 1.2 Hz, H_e) 4.88 (dq, J = 1.6, 1.2 Hz, H_f) 6.93 (ddd, J = 7.7, 6.6, 1.0 Hz, H_i) 7.11 (dd, J = 8.5, 1.0 Hz, H_b) 7.45 (ddd, J = 8.5, 6.6, 1.9 Hz, H_h) 7.59 (dd, J = 7.7, 1.9 Hz, H_a).

^{13}C-NMR ($CDCl_3$) : δ 17.5, 18.1, 22.7, 30.3, 32.2, 38.3, 80.4, 112.8, 113.1, 120.0, 129.2, 130.5, 133.3, 141.9, 157.7, 200.4 (C=O).

IR(CCl_4) : 2965, 1680 (C=O), 1597, 1479, 1450, 1357, 1290, 1236, 986 cm^{-1}.

UV(MeOH) : λ_{max} = 245 nm (6360), 306 nm (3470) 313 nm (3280).

MS (m/e) : 246 (M^+), 191, 149. 136, 121 (base), 95, 77, 69, 55, 43.

Hi-Res MS : $C_{16}H_{22}O_2$, Calculated : 246.1260, Found : 246.1260.

4'-(4-Cyclopropyl-3-buten-1-oxy)acetophenone (p-C_4K):

3-Hydroxypropyltriphenylphosphonium chloride:

A solution of triphenylphosphine (75 g, 0.29 mol) and 3-chloropropanol (27 g, 0.29 mol) in benzene (250 mL) was refluxed for 4 days. A white solid was filtered, dried and identified as 3-hydroxypropyltriphenylphosphonium chloride salt (20 g, 20%, m.p. = 222°C).

^{1}H-NMR (CD_3OD) : δ 1.85 (tt, J = 8.3, 5.8 Hz, 2H) 3.46 (dt, J_{P-H} = 16.5 Hz, J = 8.3 Hz, 2H) 3.70 (t, J = 5.8 Hz, 2H) 5.80 (s, O-H) 7.83 (m, 15 Ar-H).

4-Cyclopropyl-3-buten-1-ol:

A solution of 3-hydroxypropyltriphenylphosphonium chloride (1.44 g, 4 mmol) in dry THF (25 mL) was cooled to -78°C. After 30 min, n-BuLi (2N, 2.2 mL) was added by syringe. The color changed from white to dark yellow. The solution was allowed to warm to room temperature over 1 h. The solution was cooled again to -78°C, and a solution of cyclopropane-carboxaldehyde (0.14 g, 2 mmol) in THF (10 mL) was added dropwise. The resulting solution was stirred strongly

at room temperature for 3 h.[139,140] The mixture was quenched by water (100 mL) and extracted with ether (30 mL x 3). The organic layers were washed with 3 % H_2O_2 aqueous solution (100 mL), saturated $NaHSO_4$ (100 mL x 2) and saturated brine (100 mL) and then dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.25) to give the product as a mixture of *trans* /*cis* (=1.6/1, determined by the integration of vinyl protons at δ = 5.39 for *trans* and 5.22 for *cis* in ^{1}H-NMR, Fig. 37) isomers(0.12 g, 48%).

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.25 (dt, J = 6.6, 4.2 Hz, 2H) 0.58 (ddd, J = 8.2, 6.6, 4.2 Hz, 2H) 1.28 (dtt, J = 8.7, 8.2, 4.2 Hz, 1H) 2.17 (qd, J = 6.5, 1.2 Hz, 2H) 2.56 (s, O-H) 3.52 (t, J = 6.5 Hz, 2H) 4.97 (ddt, J = 15.2, 8.7, 1.2 Hz, 1H) 5.39 (dt, J = 15.2, 6.5 Hz, 1H); (*cis*) δ 0.25 (dt, J = 6.5, 4.3 Hz, 2H) 0.66 (ddd, J = 8.0, 6.5, 4.3 Hz, 2H) 1.49 (dtt, J = 9.4, 8.0, 4.3 Hz, 1H) 2.37 (qd, J = 6.6, 1.4 Hz, 2H) 2.56 (s, O-H) 3.58 (t, J = 6.6 Hz, 2H) 4.81 (ddt, J = 10.7, 9.4, 1.4 Hz, 1H) 5.22 (dt, J = 10.7, 6.6 Hz, 1H)

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 6.3, 13.5, 35.7, 61.9, 123.4, 136.8; (*cis*) δ 6.7, 9.50, 30.9, 62.1, 123.2, 137.0.

4-Cyclopropyl-1-tosyl-3-butene:

The standard tosylation procedure was used. 4-Cyclopropyl-3-buten-1-ol (*trans*/*cis* = 1.7/1 mixture, 0.11 g, 1 mmol) and p-toluenesulfonyl chloride (0.3 g, 1.5 mmol) in pyridine (0.6 mL) were stirred at 0°C for 12 h. After ether / dilute HCl aqueous solution work-up, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.62, 78 %) and a slightly yellowish oil with the *trans* / *cis* = 1.7/1 ratio (determined by the integration of vinyl protons at δ = 5.29 for *trans* and 5.12 for *cis* in ^{1}H-NMR) was obtained.

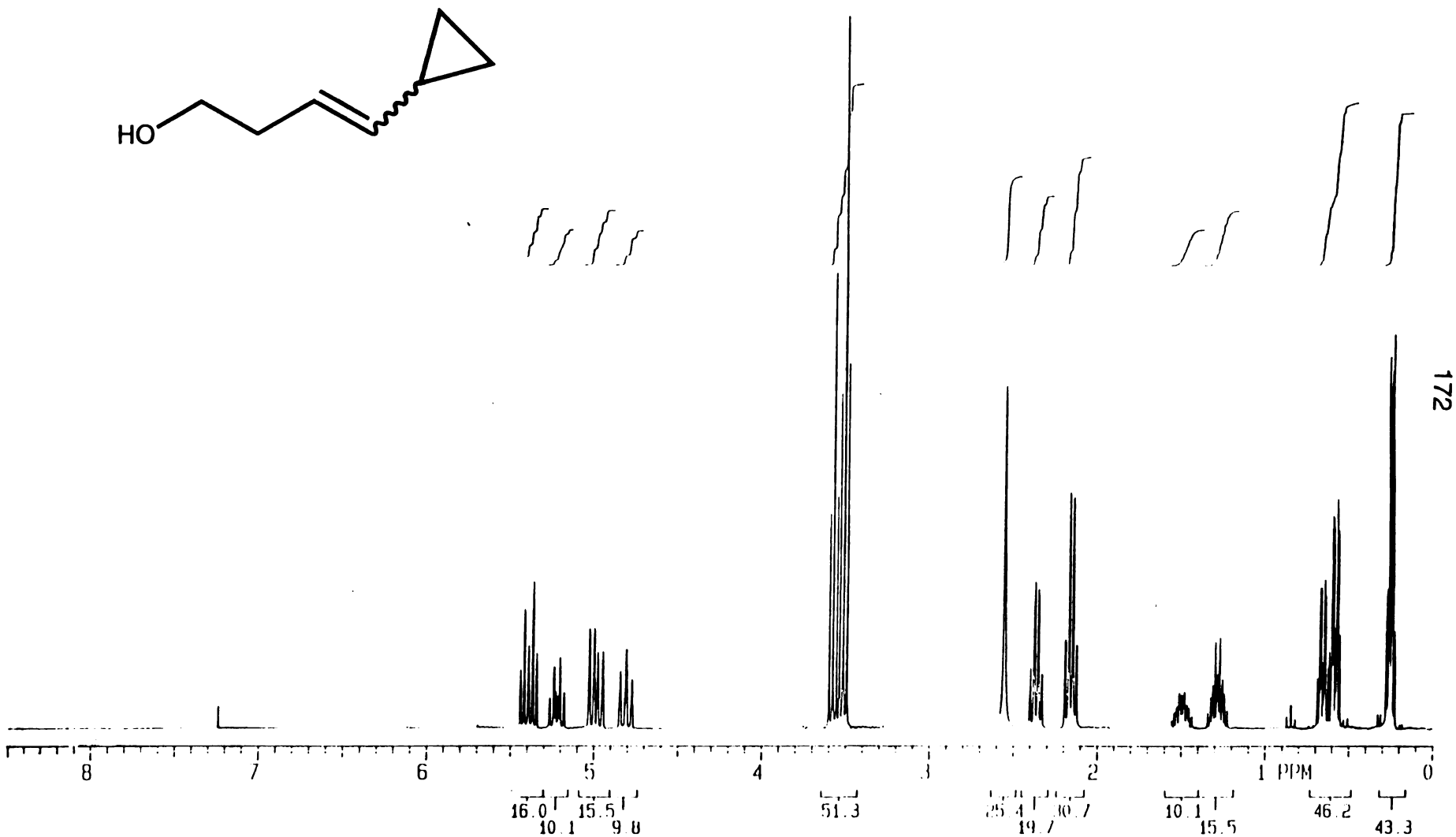
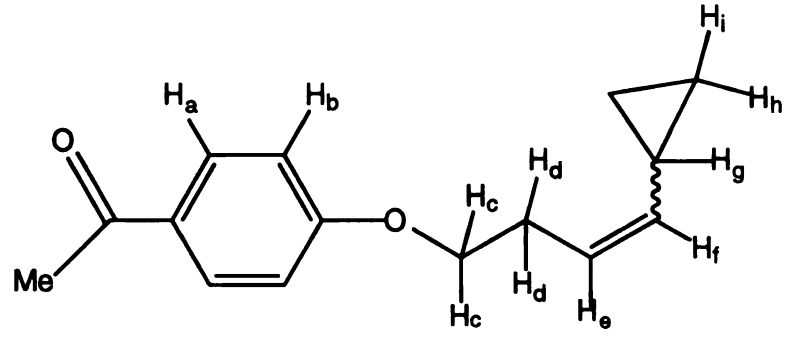


Figure 37. ^{1}H-NMR spectrum of *cis/trans* 4-cyclopropyl-3-buten-1-ol in $CDCl_3$.

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.26 (dt, J = 6.1, 4.1 Hz, 2H) 0.63 (ddd, J = 8.1, 6.1, 4.1 Hz, 2H) 1.27 (dtt, J = 8.6, 8.1, 4.1 Hz, 1H) 2.29 (qd, J = 6.9, 1.3 Hz, 2H) 2.43 (s, Me) 3.98 (t, J = 6.9 Hz, 2H) 4.96 (ddt, J = 15.3, 8.6, 1.3 Hz, 1H) 5.29 (dt, J = 15.3, 6.9 Hz, 1H) 7.32 (d, J = 8.4 Hz, 2H) 7.76 (d, J = 8.4 Hz, 2H); (*cis*) δ 0.28 (dt, J = 6.4, 4.4 Hz, 2H) 0.69 (ddd, J = 8.1, 6.4, 4.4 Hz, 2H) 1.40 (dtt, J = 8.6, 8.1, 4.1 Hz, 1H) 2.43 (s, Me) 2.50 (qd, J = 7.1, 1.4 Hz, 2H) 4.03 (t, J = 7.1 Hz, 2H) 4.81 (ddt, J = 10.5, 8.6, 1.4 Hz, 1H) 5.12 (dt, J = 10.5, 7.1 Hz, 1H) 7.32 (d, J = 8.4 Hz, 2H) 7.78 (d, J = 8.4 Hz, 2H).

p-C_4K:

A solution of 4-cyclopropyl-1-tosyl-3-butene (1.50 g, 5.6 mmol), 4-hydroxyacetophenone (1.25 g, 8 mmol) and anhydrous potassium carbonate (5.02 g, 32 mmol) in DMF (50 mL) produced 4'-(4-cyclopropyl-3-buten-1-oxy)acetophenone with the *trans* / *cis* = 1.7/1 ratio, determined by the integration of H_e protons at δ = 5.55 for *trans* and 5.36 for *cis* in ^{1}H-NMR. This compound was purified by silica gel column chromatography (0.44 g, 34 %, hexane/ethyl acetate = 4/1, R_f = 0.43) and colorless.



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.32 (dt, J = 6.1, 4.0 Hz, 2H_i) 0.67 (ddd, J = 8.1, 6.1, 4.0 Hz, 2H_h) 1.36 (dtt, J = 8.7, 8.1, 6.0 Hz, H_g) 2.47 (qd, J = 6.9, 1.3 Hz, 2H_d) 2.53 (s, COMe) 4.00 (t, J = 6.9 Hz, 2H_c) 5.09 (ddt, J = 15.3, 8.7, 1.3 Hz, H_f) 5.55

(dt, J = 15.3, 6.9 Hz, H_e) 6.89 (d, J = 8.9 Hz, 2H_b) 7.90 (d, J = 8.9 Hz, 2H_a); (*cis*) δ 0.34 (dt, J = 6.3, 4.4 Hz, 2H_i) 0.74 (ddd, J = 8.0, 6.3, 4.4 Hz, 2H_h) 1.55 (dtt, J = 8.5, 8.0, 4.4 Hz, H_g) 2.53 (s, COMe) 2.67 (qd, J = 7.1, 1.4 Hz, 2H_d) 4.05 (t, J = 7.1 Hz, 2H_c) 4.89 (ddt, J = 10.4, 8.5, 1.4 Hz, H_f) 5.36 (dt, J = 10.4, 7.1 Hz, H_e) 6.92 (d, J = 8.9 Hz, 2H_b) 7.91 (d, J = 8.9 Hz, 2H_a).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 6.2, 13.4, 27.4, 31.9, 67.7, 114.3, 122.1, 130.0, 130.1, 136.8, 162.2, 196.3 (C=O); (*cis*) δ 6.7, 9.5, 25.9, 31.9, 67.5, 113.8, 122.4, 129.8, 130.3, 136.6, 162.2, 196.1 (C=O).

IR(CCl_4) : (mixture) 3008, 1683 (C=O), 1602, 1509, 1357, 1254, 1171 cm^{-1}.

UV(MeOH) : (mixture) λ_{max} = 270 nm (17530), 313 nm (975).

MS (m/e) : 230 (M^+), 187, 121 (base), 95, 81, 77, 67, 53, 43.

Hi-Res MS : $C_{15}H_{18}O_2$, Calculated : 230.1307, Found : 230.1327.

4'-(4-Isopropyl-3-buten-1-oxy)acetophenone (p-I_4K):

5-Methyl-3-hexen-1-ol:

The same Wittig reaction procedures were followed as for 4-cyclopropyl-3-buten-1-ol. A solution of 3-hydroxypropyltriphenylphosphonium chloride (1.44 g, 4 mmol) in dry THF (25 mL) was cooled to -78°C. After 30 min, n-BuLi (2N, 2.2 mL) was added by syringe. The color changed from white to dark yellow. The solution was allowed to warm to room temperature over 1 h. The solution was cooled again to -78°C, and a solution of isobutyraldehyde (0.15 g, 2 mmol) in THF (10 mL) was added dropwise. The resulting solution was stirred strongly at room temperature for 3 h. The mixture was quenched by water (100 mL) and extracted with ether (30 mL x 3). The organic layers were washed with 3 % H_2O_2 aqueous solution (100 mL), saturated $NaHSO_4$ (100 mL x 2) and saturated brine (100 mL) and then dried over $MgSO_4$. After solvent was evaporated, the residue was purified by column chromatography (SiO_2, hexane/ethyl acetate = 4/1, R_f = 0.29)

to give the product as a mixture of *trans* / *cis* (=2.1/1 from vinyl proton integration at δ 5.33 for *trans* and 5.21 for *cis* in ^{1}H-NMR) isomers (0.10 g, 43%).

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.96 (d, J = 6.9 Hz, 2Me) 1.50 (s, O-H) 2.23 (q, J = 6.3 Hz, 2H) 2.60 (septd, J = 6.9, 6.5 Hz, 1H) 3.60 (t, J = 6.3 Hz, 2H) 5.33 (dt, J = 15.4, 6.3 Hz, 1H) 5.52 (dd, J = 15.4, 6.5 Hz, 1H); (*cis*) δ 0.90 (d, J = 6.9 Hz, 2Me) 1.90 (s, O-H) 2.31 (q, J = 6.5 Hz, 2H) 2.40 (septd, J = 6.9, 5.7 Hz, 1H) 3.62 (t, J = 6.5 Hz, 2H) 5.21 (dt, J = 10.9, 6.5 Hz, 1H) 5.52 (dd, J = 10.9, 5.7 Hz, 1H).

5-Methyl-1-tosyl-3-hexene:

The same tosylation procedures were followed as for 4-cyclopropyl-1-tosyl-3-butene.

^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.90 (d, J = 6.8 Hz, 2Me) 2.17 (septdd, J = 6.8, 6.5, 1.2 Hz, 1H) 2.29 (qd, J = 6.7, 1.3 Hz, 2H) 2.42 (s, Me) 3.99 (t, J = 6.7 Hz, 2H) 5.17 (dtd, J = 15.5, 6.7, 1.2 Hz, 1H) 5.42 (ddt, J = 15.5, 6.5, 1.3 Hz, 1H) 7.32 (d, J = 8.2 Hz, 2H) 7.76 (d, J = 8.2 Hz, 2H); (*cis*) δ .0.88 (d, J = 6.7 Hz, 2Me) 2.37 (qd, J = 7.1, 1.4 Hz, 2H) 2.42 (s, Me) 2.47 (dseptd, J = 9.5, 6.7, 0.9 Hz, 1H) 3.97 (t, J = 7.1 Hz, 2H) 5.06 (dtd, J = 10.8, 7.1, 0.9 Hz, 1H) 5.28 (ddt, J = 10.8, 9.5, 1.4 Hz, 1H) 7.32 (d, J = 8.2 Hz, 2H) 7.76 (d, J = 8.2 Hz, 2H).

p-I_4K:

The standard coupling method was used. A solution of 5-methyl-1-tosyl-3-hexene (3.10 g, 11 mmol), 4-hydroxyacetophenone (2,35 g, 15 mmol) and anhydrous potassium carbonate (10.02 g, 64 mmol) in DMF (100 mL) was refluxed at 90°C for 6h and produced *cis/trans* products in a ratio of 2.2/1, measured by the integration of vinyl protons in ^{1}H-NMR.(Fig. 38) Ketone was colorless after purified by silica gel column chromatography (1,12 g, 44 %, hexane/ethyl acetate = 4/1, R_f = 0.46).

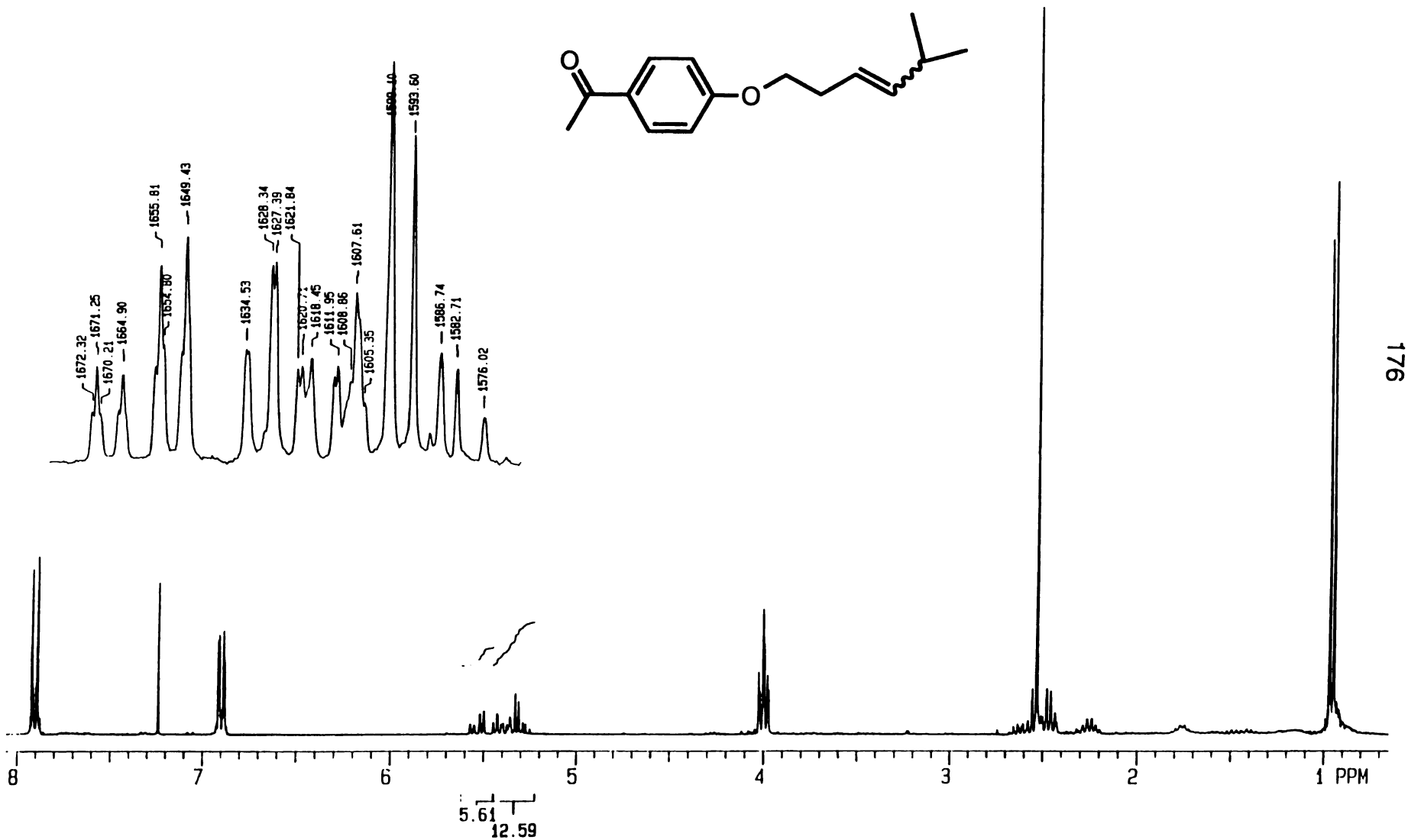
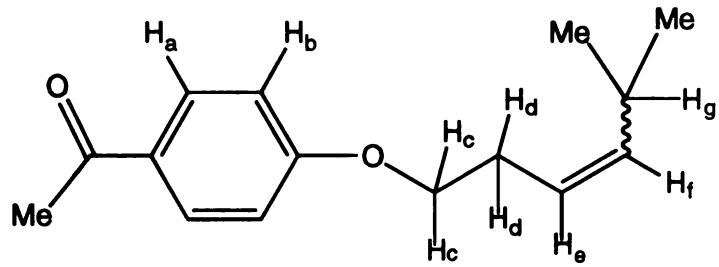


Figure 38. ^{1}H-NMR spectrum of *cis/trans* **p-I$_4$K** in $CDCl_3$.



^{1}H-NMR ($CDCl_3$) : (*trans*) δ 0.96 (d, J = 6.8 Hz, 2Me) 2.25 (septdd, J = 6.8, 6.4, 1.0 Hz, Hg) 2.46 (qd, J = 6.9, 1.1 Hz, 2Hd) 2.53 (s, COMe) 4.00 (t, J = 6.9 Hz, 2Hc) 5.40 (dtd, J = 15.5, 6.9, 1.0 Hz, He) 5.53 (ddt, J = 15.5, 6.4, 1.1 Hz, Hf) 6.90 (d, J = 8.9 Hz, 2Hb) 7.90 (d, J = 8.9 Hz, 2Ha); (*cis*) δ .0.96 (d, J = 6.8 Hz, 2Me) 2.53 (s, COMe) 2.55 (qd, J = 6.9, 1.2 Hz, 2Hd) 2.62 (dseptd, J = 8.7, 6.8, 2.0 Hz, Hg) 3.99 (t, J = 6.9 Hz, 2Hc) 5.30 (m, 2H) 6.89 (d, J = 8.8 Hz, 2Hb) 7.90 (d, J = 8.8 Hz, 2Ha).

^{13}C-NMR ($CDCl_3$) : (*trans*) δ 22.3, 26.1, 26.5, 32.2, 67.9, 114.0, 121.6, 130.0, 130.4, 140.6, 162.8, 195.5 (C=O); (*cis*) 22.9, 26.4, 27.2, 30.9, 67.6, 113.9, 121.7, 130.1, 130.2, 140.3, 162.7, 196.4 (C=O).

IR(CCl_4) : (mixture) 2998, 1679 (C=O), 1601, 1510, 1255 cm^{-1}.

UV(MeOH) : (mixture) λ_{max} = 273 nm (18630), 313 nm (1400).

MS (m/e) : 232 (M^+), 192, 137, 121, 96, 81, 69, 55 (base), 43.

Hi-Res MS : $C_{15}H_{20}O_2$, Calculated : 232.1463, Found : 232.1465.

4'-(4-Trimethylsilyl-3-butyn-1-oxy)acetophenone:

1-Tosyl-3-butyne:

3-Butyn-1-ol (0.1 mol, 7 g, Aldrich) was converted into its tosylate in the presence of pyridine (50 mL) and p-toluenesulfonyl chloride (20 g, Aldrich) at 0°C.

^{1}H-NMR ($CDCl_3$) : δ 1.96 (t, J = 2.7 Hz, 1H) 2.44 (s, Me) 2.53 (td, J = 7.0, 2.7 Hz, 2H) 4.19 (t, J = 7.0 Hz, 2H) 7.32 (d, J = 8.2 Hz, 2H) 7.78 (d, J = 8.2 Hz, 2H).

4'-(3-Butyn-1-oxy)acetophenone:

The tosylate was coupled with 4-hydroxyacetophenone by the standard coupling method. Ketone was purified by silica gel column chromatography (hexane/ethyl acetate = 4/1, R_f = 0.56).

^{1}H-NMR ($CDCl_3$) : δ 2.16 (t, J = 2.7 Hz, 1H) 2.56 (s, COMe) 2.71 (td, J = 7.0, 2.7 Hz, 2H) 4.27 (t, J = 7.0 Hz, 2H) 6.94 (d, J = 8.9 Hz, 2H) 7.92 (d, J = 8.9 Hz, 2H).

^{13}C-NMR ($CDCl_3$) : δ 25.9, 27.6, 62.2, 66.7, 76.6, 111.6, 126.7, 131.5, 163.4, 196.6 (C=O).

IR(CCl_4) : 2254, 1683 (C=O), 1609, 1545, 1451, 1216 cm^{-1}.

MS (m/e) : 188 (M^+), 173, 121(base), 65, 53, 43.

Acetal of 4'-(3-butyn-1-oxy)acetophenone:

The 4'-(3-butyn-1-oxy)acetophenone (8.4 g, 0.045 mol) and excess ethylene glycol (6.2 g, 0.1 mol) were refluxed in a catalytic amount p-toluenylsulfonic acid in benzene (100 mL) for 24 h. After the solvent was removed, the acetal (10.2 g, 95%) was obtained.

^{1}H-NMR ($CDCl_3$) : δ 1.64 (s, Me) 2.11 (t, J = 2.7 Hz, 1H) 2.68 (td, J = 7.0, 2.7 Hz, 2H) 3.76 (ddd, J = 7.4, 6.3, 3.6 Hz, 2H) 4.00 (ddd, J = 7.4, 6.3, 3.6 Hz, 2H) 4.09 (t, J = 7.0 Hz, 2H) 6.87 (d, J = 8.9 Hz, 2H) 7.39 (d, J = 8.9 Hz, 2H).

Acetal of 4'-(4-trimethylsilyl-3-butyn-1-oxy)acetophenone:

A solution containing acetal of 4'-(3-butyn-1-oxy)acetophenone (10.2 g, 0.09 mol) and THF (100 mL) was cooled to -78°C. n-BuLi (2M, 55 mL) was added by syringe and the temperature was kept at -78°C over 1 h. Trimethylsilyl

chloride (10.5 g, 0.1 mol) in THF (30 mL) was added dropwise. After ether extraction, the product was recrystallized from hexane.

^{1}H-NMR ($CDCl_3$) : δ 0.14 (s, 3Me) 1.62 (s, Me) 2.70 (t, J = 7.4 Hz, 2H) 3.77 (ddd, J = 7.4, 6.3, 3.6 Hz, 2H) 4.01 (ddd, J = 7.4, 6.3, 3.6 Hz, 2H) 4.07 (t, J = 7.4 Hz, 2H) 6.85 (d, J = 8.9 Hz, 2H) 7.36 (d, J = 8.9 Hz, 2H).

4'-(4-Trimethylsilyl-3-butyn-1-oxy)acetophenone:

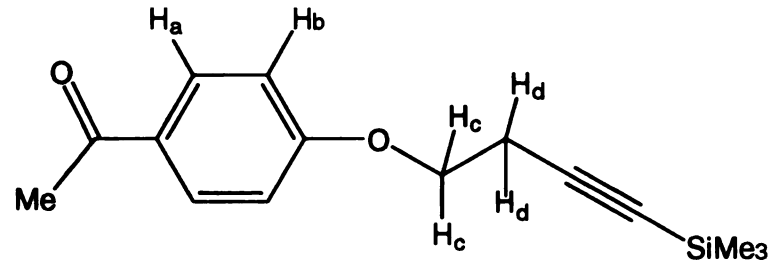
The above acetal of 4'-(4-trimethylsilyl-3-butyn-1-oxy)acetophenone was dissolved in THF (50 mL) and 10 % HCl aqueous solution (25 mL) was added dropwise. After 3 h, the resulting solution was extracted with ether and then the ether was removed. Ketone was failed to recrystallize from hexane at 0°C and then purified by silica gel column chromatography (hexane/ethyl acetate = 4/1, R_f = 0.65) to obtain a colorless oil.

^{1}H-NMR ($CDCl_3$) : δ 0.15 (s, 3Me) 2.52 (s, COMe) 2.72 (t, J = 7.2 Hz, 2H_d) 4.13 (t, J = 7.2 Hz, 2H_c) 6.92 (d, J = 8.9 Hz, 2H_b) 7.91 (d, J = 8.9 Hz, 2H_a).

^{13}C-NMR ($CDCl_3$) : δ 0.0, 20.9, 27.6, 63.7, 66.2, 77.0, 111.2, 126.5, 130.4, 162.4, 196.7 (C=O).

IR(CCl_4) : 2254, 1683 (C=O), 1604, 1559, 1450, 1216, 983 cm^{-1}.

MS (m/e) : 260 (M^+), 245, 219, 173, 121, 73, 71(base), 43.

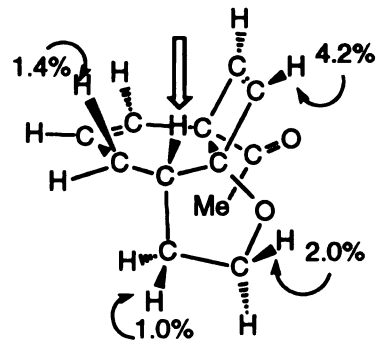


V. Identification of Photoproducts:

Reactant : **p-M_0K**

The ketone **p-M_0K** (obtained from Nahm) was dissolved in 0.7 mL CD_3OD in an NMR tube (2.0 X 10^{-2} M). The solution was irradiated by mercury arc (Pyrex filtered) for 1 h. The colorless photoproduct was identified as 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene by the following spectroscopic properties. The same CD_3OD solution, left on the bench at room temperature for two days, converted to yellowish 4-acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene, identified by the ^{1}H-NMR spectroscopy.

Low temperature (-30°C) nOe results (see appendix for details) indicated that 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene had enhancements of H_{10} (4.2 %), $H_{4\beta}$ (1.4 %), $H_{6\beta}$ (1.0 %) and $H_{7\beta}$ (2.0 %) when bridgehead proton H_5 was irradiated.



1-Acetyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : δ 1.78 (dddd, J = 12.6, 11.5, 10.4, 7.0 Hz, $H_{6\alpha}$) 1.85 (dddd, J = 11.3, 10.4, 9.0, 5.1 Hz, $H_{6\beta}$) 2.18 (s, COMe) 2.20 (dddd, J = 17.0, 6.0, 3.0, 2.2 Hz, $H_{4\alpha}$) 2.26 (ddd, J = 17.0, 7.6, 4.5 Hz, $H_{4\beta}$) 2.39 (dddd, J = 12.6, 9.0, 7.6, 6.0 Hz, $H_{5\beta}$) 3.78 (ddd, J = 13.5, 11.5, 5.1 Hz, $H_{7\beta}$) 3.82 (ddd, J = 13.5, 11.3, 7.0 Hz, $H_{7\alpha}$) 5.75 (dd, J = 10.2, 3.0 Hz, H_2) 5.85 (ddd, J = 10.2, 4.5, 2.2 Hz, H_3) 6.27, 6.37 (AB q, J = 2.8 Hz, H_{10}, H_{11}).

4-Acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

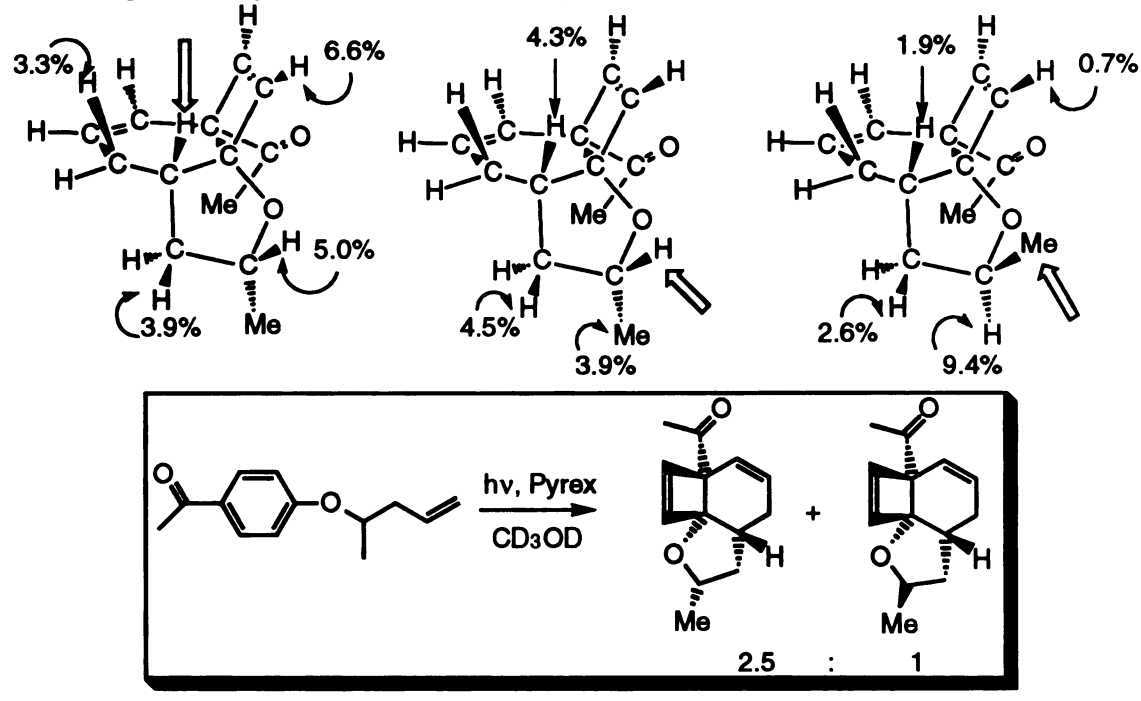
^{1}H-NMR (CD_3OD) : δ 1.96 (dddd, J = 11.7, 9.2, 7.7, 4.9 Hz, $H_{9\alpha}$) 2.13 (dddd, J = 11.7, 8.8, 6.0, 5.4 Hz, $H_{9\beta}$) 2.31 (s, COMe) 2.35 (dddd, J = 13.2, 8.2, 7.9, 2.1 Hz, $H_{7\alpha}$) 2.50 (dddd, J = 13.2, 4.0, 3.5, 2.1 Hz, $H_{7\beta}$) 3.10 (dddd, J = 8.2, 7.7, 6.0, 3.5 Hz, $H_{8\beta}$) 4.20 (ddd, J = 12.2, 9.2, 5.4 Hz, $H_{10\beta}$) 4.28 (ddd, J = 12.2, 8.8, 4.9 Hz, $H_{10\alpha}$) 5.41 (d, J = 8.1 Hz, H_2) 5.95 (ddd, J = 11.3, 7.9, 4.0 Hz, H_6) 6.26 (dt, J = 11.3, 2.1 Hz, H_5) 7.12 (d, J = 8.1 Hz, H_3).

Reactant : **p-M_1K**

In an NMR tube, 4.8 mg **p-M_1K** was dissolved in 0.7 mL CD_3OD (3.4×10^{-2} M) with internal standard methyl benzoate 3.3 mg and bubbled with argon for 20 min. Irradiations were performed with a mercury arc filtered only by Pyrex or by alkaline K_2CrO_4 filter solution (313 nm). Both of them provided identical results. ^{1}H-NMR spectra were obtained (every 15 min) during the irradiation until 100 % conversion. A pair of photoproducts was identified as the diastereomers of 1-acetyl-7-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene in a ratio of 70 :30, as determined by integration of ^{1}H-NMR spectra. The major photoproduct has bridgehead proton H_5 and Me_7 *trans* to each other. The minor photoproduct has bridgehead proton H_5 and Me_7 *cis* to each other according to the following nOe results.

In nOe experiments, which were performed at -20°C to prevent further thermal rearrangement, the major product had enhancements of H_{10} (6.6 %), $H_{4\beta}$ (3.3 %), $H_{6\beta}$ (3.9 %) and $H_{7\beta}$ (5.0 %) when bridgehead proton H_5 was irradiated. Similarly, there was an enhancement of H_5 (4.3 %), $H_{6\beta}$ (4.5 %) and 7-Me (3.9 %) when H_7 was irradiated. The minor product had enhancements of H_{10} (0.7 %), $H_{5\beta}$ (1.9 %), $H_{6\beta}$ (2.6 %) and $H_{7\alpha}$ (9.4 %) when 7-Me was irradiated.

The notations of α- and β- used in this dissertation are defined as the stereochemistry of substituents below the plane of the ring and above the plane of the ring in the cyclic form, respectively.



rac-(1S,5R,7S,9R)-1-Acetyl-7-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 1.05 (d, J = 6.0 Hz, 7-Me) 1.48 (ddd, J = 12.8, 11.3, 10.5 Hz, $H_{6\alpha}$) 1.83 (ddd, J = 10.5, 6.0, 5.1 Hz, $H_{6\beta}$) 2.14 (dddd, J = 17.1, 8.0, 3.1, 2.3 Hz, $H_{4\alpha}$) 2.185 (s, COMe) 2.26 (ddd, J = 17.1, 6.6, 2.1 Hz, $H_{4\beta}$) 2.51 (dddd, J = 12.8, 8.0, 6.0, 2.1 Hz, $H_{5\beta}$) 4.06 (dqd, J = 11.3, 6.0, 5.1 Hz, $H_{7\beta}$) 5.74 (dd, J = 10.1, 3.1 Hz, H_2) 5.81 (ddd, J = 10.1, 6.6, 2.3 Hz, H_3) 6.29, 6.42 (AB q, J = 2.8 Hz, H_{10}, H_{11}).

^{13}C-NMR (CD_3OD) : (major) δ 21.4, 25.0, 30.1, 36.6, 42.8, 76.6, 92.7, 106.8, 126.8, 126.9, 140.2, 140.6, 215.0 (C=O).

rac-(1S,5R,7R,8R)-1-Acetyl-7-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

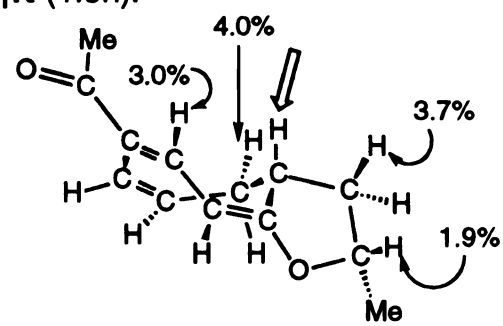
^{1}H-NMR (CD_3OD) : (minor) δ 1.14 (d, J = 6.3 Hz, 7-Me) 1.56 (ddd, J= 12.1, 7.9, 3.8 Hz, $H_{6\alpha}$) 1.83 (m, $H_{6\beta}$) 2.07 (m, $H_{4\alpha}$) 2.183 (s, COMe) 2.22 (m, $H_{4\beta}$) 2.46 (m,

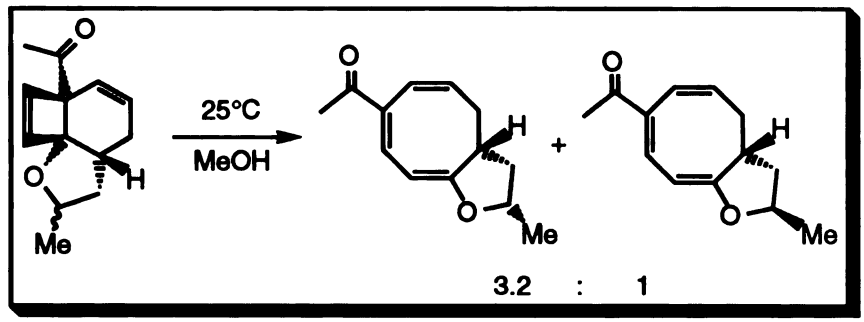
H_5) 4.09 (m, $H_{7\beta}$) 5.71 (dd, J = 10.1, 2.1 Hz, H_2) 5.84 (ddd, J = 10.1, 6.0, 3.0 Hz, H_3) 6.28, 6.34 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

Ketone **p-M_1K** 0.12 g was dissolved in 75 mL dry MeOH (8 x 10^{-3} M) and bubbled with argon for 20 min. During the irradiation (Pyrex filter), reaction was monitored by TLC or GC (received the sample by the syringe) until 100 % conversion. Solvent was evaporated and the residue was purified by column chromatography (SiO_2, R_f = 0.33 with hexane/ethyl acetate = 9/1) and a yellowish oil was obtained (0.075 g, 63 %). The diastereomers of cycloöctatriene were separated by neutral alumina chromatography with gradient hexane/ethyl acetate ratio from 99/1 to 95/5 (volume/volume). The chemical shifts and coupling constants obtained from the NMR spectra of isolated cycloöctatrienes are identical to the NMR spectra of mixture.

The major cycloöctatriene has bridgehead proton H_8 and Me_{10} *trans* with each other. In nOe experiments, the major product had enhancements of H_3 (3.0 %), $H_{7\beta}$ (4.0 %), $H_{9\beta}$ (3.7 %) and $H_{10\beta}$ (1.9 %) when bridgehead proton H_8 was irradiated.

The 3.2:1 ratio of cycloöctatriene diastereomers (3.0 mg) was dissolved in CD_3OD (0.75 mL) in NMR tube, bubbled with argon for 10 minute, and then irradiated (Pyrex filter) to obtained the same ratio of cyclobutene diastereomers. However, the irradiation time of this experiment (0.5h) was shorter than the previous one from **p-M_1K** (1.5h).





rac-(8R,10S)-4-Acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (major) δ 1.33 (d, J = 6.2 Hz, 10-Me).1.51 (td, J = 11.9, 9.9 Hz, $H_{9\alpha}$) 2.19 (ddd, J = 11.9, 6.0, 5.4 Hz, $H_{9\beta}$) 2.25 (ddd, J = 13.7, 10.5, 7.9 Hz, $H_{7\alpha}$) 2.31 (s, COMe) 2.56 (ddd, J = 13.7, 7.9, 3.0 Hz, $H_{7\beta}$) 3.07 (dddd, J = 11.9, 10.5, 5.4, 3.0 Hz, $H_{8\beta}$) 4.41 (tq, J = 9.9, 6.0 Hz, $H_{10\beta}$) 5.36 (dd, J = 8.0, 2.2 Hz, H_2) 6.02 (dt, J = 11.3, 7.9 Hz, H_6) 6.36 (d, J = 11.3 Hz, H_5) 6.89 (d, J = 8.0 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : (major) δ 20.4, 26.2, 28.8, 39.5, 43.5, 77.3, 95.8, 127.2, 133.3, 133.7, 137.4, 170.7, 199.7 (C=O).

rac-(8R,10R)-4-Acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (minor) δ 1.34 (d, J = 6.1 Hz, 10-Me) 1.77 (dt, J = 12.2, 8.0 Hz, $H_{9\alpha}$) 1.90 (ddd, J = 12.2, 6.0, 3.3 Hz, $H_{9\beta}$) 2.32 (m, 1H) 2.35 (s, COMe) 2.42 (m, 1H) 3.20 (m, 1H) 4.71 (tq, J = 8.0, 6.1 Hz, H_{10}) 5.41 (d, J = 6.3 Hz, H_2) 5.89 (dt, J = 13.1, 5.0 Hz, H_6) 6.25 (dt, J = 13.1, 1.6 Hz, H_5) 7.04 (d, J = 6.3 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : (minor) δ 21.0, 26.1, 29.8, 33.5, 40.7, 78.8, 96.8, 125.0, 132.3, 133.9, 138.4, 171.3, 199.2 (C=O).

IR(CCl_4) : (mixture) 2929, 1682 (C=O), 1600, 1507, 1358, 1253, 1170 cm^{-1}.

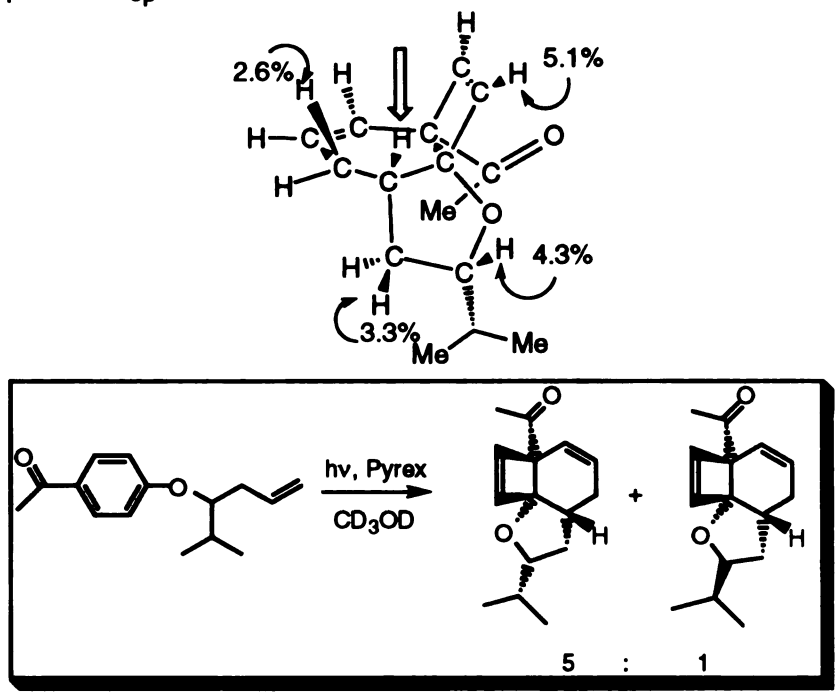
UV(MeOH) : 313 nm (6900), λ_{max} = 344 nm (10800).

MS (m/e) : (mixture) 204 (M^+), 161, 121, 105, 91, 69, 55, 43 (base).

Reactant : **p-I_1K**

A mixture of 2.0 mg of **p-I_1K** in CD_3OD (0.6 mL, 0.015 M) with 4.3 mg internal standard methyl benzoate was irradiated by mercury arc with a Pyrex filter. ^{1}H-NMR showed photoproducts as a pair of diastereomers of 1-acetyl-7-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene like the previous 1-acetyl-7-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene compound. Chemical yield (90 %) and diastereomeric excess (67 %) were measured by integration of two H_{10} groups in ^{1}H-NMR spectra.

In nOe experiments, performed at -20°C, the major product had enhancements of H_{10} (5.1 %), $H_{4\beta}$ (2.6 %), $H_{6\beta}$ (3.3 %) and $H_{7\beta}$ (4.3 %) when bridgehead proton $H_{5\beta}$ was irradiated.



rac-(1S,5R,7S,9R)-1-Acetyl-7-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 0.74 (d, J = 6.6 Hz, Me) 0.88 (d, J = 6.6 Hz, Me) 1.27 (ddd, J = 12.0, 11.4, 10.3 Hz, $H_{6\alpha}$) 1.48 (ddd, J = 12.0, 6.8, 5.2 Hz, $H_{6\beta}$) 1.85 (dsept, J = 9.3, 6.6 Hz, 1H) 2.09 (dddd, J = 13.3, 6.5, 3.2, 2.1 Hz, $H_{4\alpha}$) 2.20

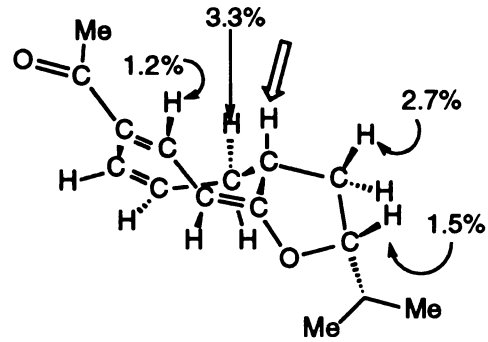
(s, COMe) 2.22 (dddd, J = 11.4, 6.8, 6.5, 2.2 Hz, $H_{5\beta}$) 2.44 (ddd, J = 13.3, 8.7, 2.2 Hz, $H_{4\beta}$) 3.46 (ddd, J = 10.3, 9.3, 5.2 Hz, $H_{7\beta}$) 5.75 (dd, J = 10.1, 3.2 Hz, H_2) 5.81 (ddd, J = 10.1, 8.7, 2.1 Hz, H_3) 6.25 (d, J = 2.8 Hz, H_{11}) 6.45 (dd, J = 2.8, 0.7 Hz, H_{10}).

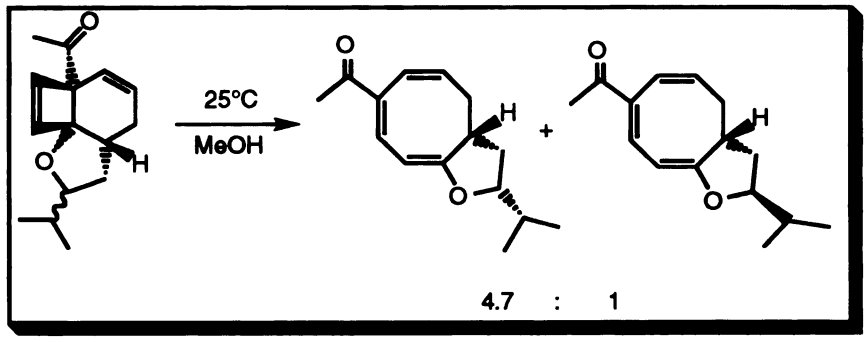
rac-(1S,5R,7R,9R)-1-Acetyl-7-isopropyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 0.83 (d, J = 6.8 Hz, Me) 0.90 (d, J = 6.8 Hz, Me) 1.31 (ddd, J = 9.4, 5.7, 2.5 Hz, $H_{6\alpha}$) 1.58 (ddd, J = 9.4, 7.9, 1.6 Hz, $H_{6\beta}$) 1.72 (m, 1H) 2.11 (m, 1H) 2.16 (m, 1H) 2.17 (s, COMe) 2.48 (m, 1H) 3.63 (ddd, J = 7.9, 7.0, 5.7 Hz, $H_{7\beta}$) 5.85 (m, 2H) 6.27, 6.35 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

A solution of 0.20 g **p-I_1K** in a 60 mL dry MeOH, bubbled with argon for 20 min, was irradiated through Pyrex filter and monitored by TLC or GC until 100 % conversion. After solvent was evaporated, the residue was purified by silica gel column chromatography (R_f = 0.43 with hexane/ethyl acetate = 4/1) to give a mixture of diastereomers in 68% (0.136 g). Attempts to separate the diastereomers by TLC, HPLC, silica gel or alumina column chromatography were unsuccessful.

The major product had enhancements of H_3 (1.2 %), $H_{7\beta}$ (3.3 %), $H_{9\beta}$ (2.7 %) and $H_{10\beta}$ (1.5 %) when bridgehead proton $H_{8\beta}$ was irradiated in nOe experiments.





rac-(8R,10S)-4-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR (CD_3OD) : (major) δ 0.90 (d, J = 6.7 Hz, Me) 1.00 (d, J = 6.7 Hz, Me) 1.56 (ddd, J = 12.4, 11.5, 10.2 Hz, $H_{9\alpha}$) 1.72 (dsept, J = 7.5, 6.7 Hz, 1H) 2.20 (ddd, J = 12.4, 7.5, 5.4 Hz, $H_{9\beta}$) 2.26 (ddd, J = 13.0, 10.5, 8.1 Hz, $H_{7\alpha}$) 2.31 (s, COMe) 2.59 (ddd, J = 13.0, 8.1, 3.1 Hz, $H_{7\beta}$) 3.09 (dddd, J = 11.5, 10.5, 5.4, 3.1 Hz, $H_{8\beta}$) 4.00 (ddd, J = 10.2, 7.5, 4.9 Hz, $H_{10\beta}$) 5.37 (dd, J = 8.4, 2.2 Hz, H_2) 6.05 (dt, J = 10.8, 8.1 Hz, H_6) 6.32 (d, J = 10.8 Hz, H_5) 7.09 (d, J = 8.4 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : (major) δ 17.7, 18.8, 26.4, 28.7, 32.9, 34.3, 39.2, 86.1, 95.6, 123.7, 130.2, 133.6, 138.5, 171.0, 199.5 (C=O).

rac-(8R,10R)-4-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR (CD_3OD) : (minor) δ 0.89 (d, J = 6.7 Hz, Me) 0.99 (d, J = 6.7 Hz, Me) 1.73 (m, 1H) 1.87 (ddd, J = 11.75, 8.8, 1.6 Hz, H_9) 2.08 (m, 1H) 2.27 (m, 1H) 2.34 (s, COMe) 2.43 (m, $H_{7\beta}$) 3.18 (m, $H_{8\beta}$) 4.30 (ddd, J = 8.8, 7.4, 6.6 Hz, H_{10}) 5.40 (d, J = 6.3 Hz, H_2) 5.86 (dt, J = 13.2, 4.3 Hz, H_6) 6.20 (dt, J = 13.2, 2.2 Hz, H_5) 7.17 (d, J = 6.3 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : (minor) δ 17.8, 18.9, 26.5, 32.8, 33.4, 35.4, 43.4, 86.8, 95.7, 127.0, 132.1, 132.9, 137.1, 170.5, 199.1 (C=O).

IR(CCl_4) :(mixture) 2963, 2930, 1682 (C=O), 1600, 1507, 1357, 1253, 1171 cm^{-1}.

UV(MeOH) : 313 nm (7350), λ_{max} = 346 nm (11800).

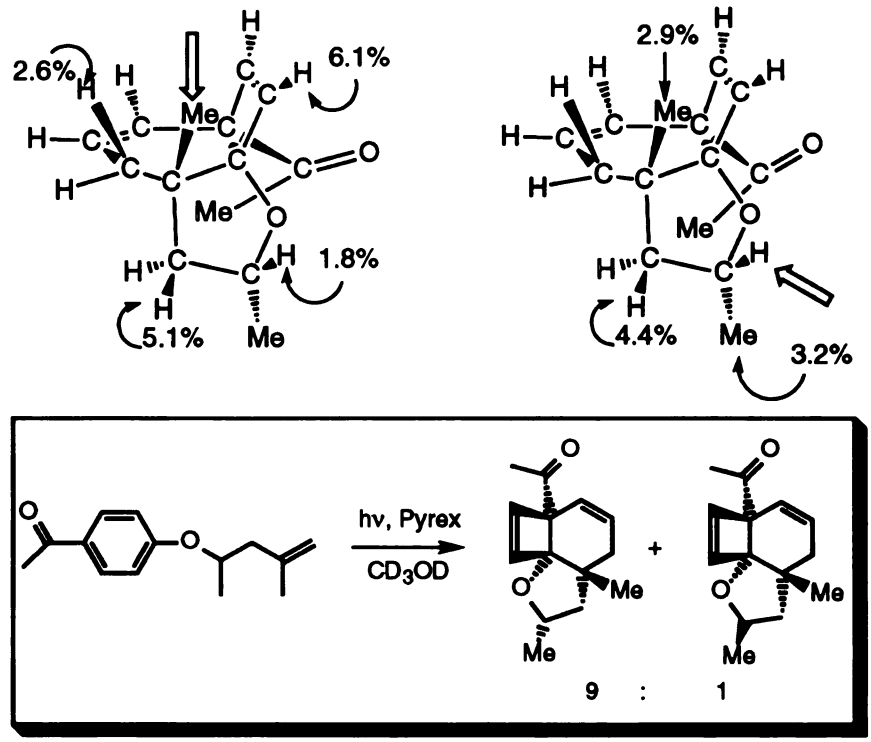
MS (m/e) : (mixture) 232 (M^+), 189, 137, 133, 121, 105, 91, 81, 69, 55, 43 (base).

Hi-Res MS : Calculated : 232.1464, Found : 232.1490.

Reactant : **p-M_1M_3K**

A mixture of 4.0 mg **p-M_1M_3K** and 2.8 mg methyl benzoate in a 0.75 mL CD_3OD (0.024 M) was placed in a NMR tube and irradiated through Pyrex filter after bubbled with argon. The reaction was followed by ^1H-NMR and was finished in 3 h. The products were characterized as two diastereomers of 1-acetyl-5,7-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene which has 78 % chemical yield and a 9:1 diastereomeric ratio, determined by the integration of two H_7 protons.

The nOe experiments performed on the major product at -20°C indicated an enhancement of H_{10} (6.1 %), $H_{4\beta}$ (2.6 %), $H_{6\beta}$ (1.8 %) and $H_{7\beta}$ (5.1 %) when 5-Me was irradiated and of 5-Me (2.9 %), $H_{6\beta}$ (4.4 %) and 7-Me (3.2 %) when H_7 was irradiated.



rac-(1S,5R,7S,9R)-1-Acetyl-5,7-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene:

^1H-NMR (CD_3OD) : (major) δ 1.02 (d, J = 6.2 Hz, 7-Me) 1.08 (s, 5-Me) 1.52 (dd, J = 12.0, 5.7 Hz, $H_{6\beta}$) 1.67 (dd, J = 12.0, 10.4 Hz, $H_{6\alpha}$) 1.91 (ddd, J = 13.2, 6.1, 2.9

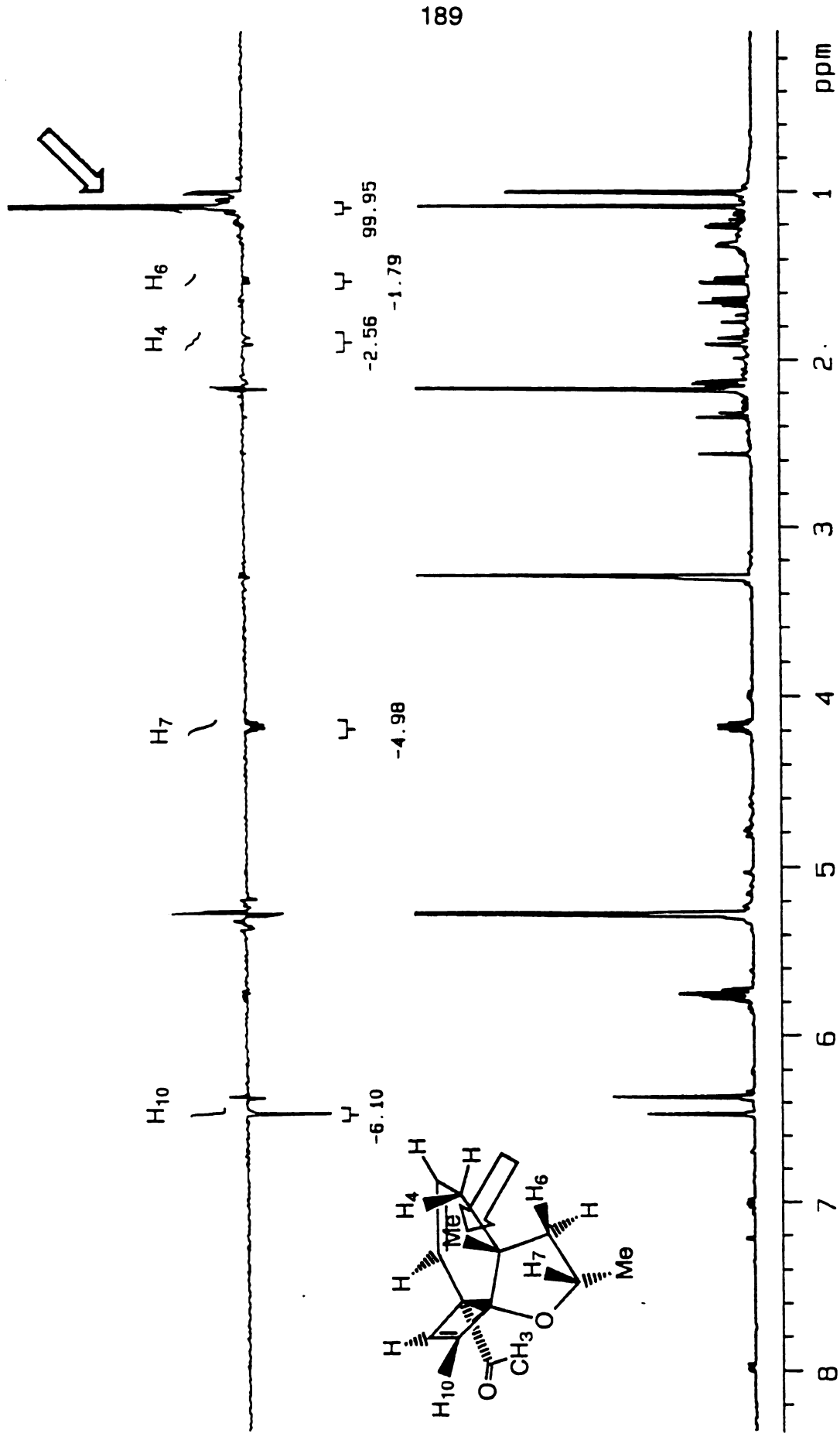


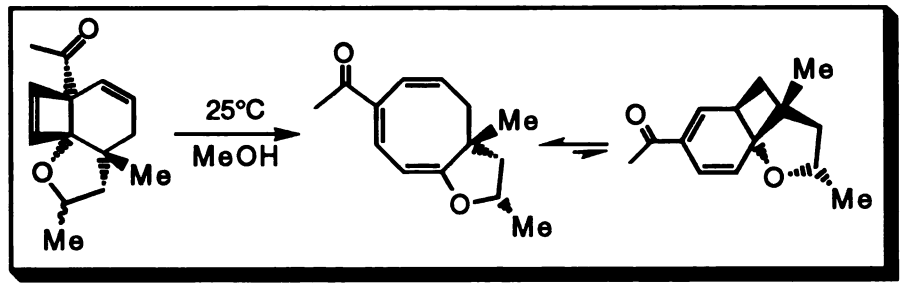
Figure 39. NOE experiments of rac-(1S,5R,7S,9R)-1-acetyl-5,7-dimethyl-8-oxatricyclo- [7.2.0.0^{5,9}]undeca-2,10-diene (**p-M$_1$M$_3$CB**) in CD_3OD

Hz, $H_{4\alpha}$) 2.15 (dd, J = 13.2, 1.7 Hz, $H_{4\beta}$) 2.17 (s, COMe) 4.18 (dqd, J = 10.4, 6.2, 5.7 Hz, $H_{7\beta}$) 5.75 (dd, J = 10.0, 2.9 Hz, H_2) 5.77 (ddd, J = 10.0, 6.1, 1.7 Hz, H_3) 6.35, 6.45 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

rac-(1S,5R,7R,9R)-1-Acetyl-5,7-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.075 (s, 5-Me) 1.19 (d, J = 6.3 Hz, 7-Me) 4.02 (dqd, $H_{7\alpha}$).

A methanol solution of **p-M_1M_3K** 0.01 M was irradiated at > 290 nm and completed in 12 h. The solution was heated in 30°C warm water for 24 h until its color changed to yellow. The solvent was removed. After silica gel column chromatography (hexane / ethyl acetate = 19 / 1, R_f = 0.52), the product was identified as the equilibrium mixture of 4-acetyl-8,10-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene and 4-acetyl-8,10-dimethyl-11-oxatricyclo[6.3.0.0]undeca-2,4-diene in a ratio of 3 : 1, determined by two acetyl groups. A tiny amount of the other cyclohexadiene diastereomer could be detected by ^{1}H-NMR. The overall isolated yield was 48 %.



rac-(8R,10S)-4-Acetyl-8,10-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene

^{1}H-NMR ($CDCl_3$) : δ 1.20 (s, 8-Me) 1.30 (d, J = 6.1 Hz, 10-Me) 1.95 (dd, J = 12.7, 10.2 Hz, H_9) 2.09 (dd, J = 13.4, 7.1 Hz, H_7) 2.17 (dd, J = 12.7, 4.9 Hz, H_9) 2.32 (s, COMe) 2.36 (dd, J = 13.4, 9.1 Hz, H_7) 4.58 (dqd, J = 10.2, 6.1, 4.9 Hz, H_{10})

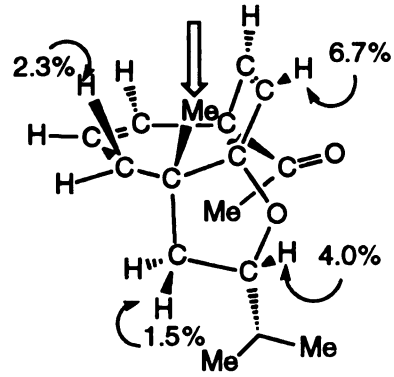
5.17 (d, J = 6.6 Hz, H_2) 6.19 (ddd, J = 10.8, 9.1, 7.1 Hz, H_6) 6.36 (d, J = 10.8 Hz, H_5) 7.17 (d, J= 6.6 Hz, H_3).

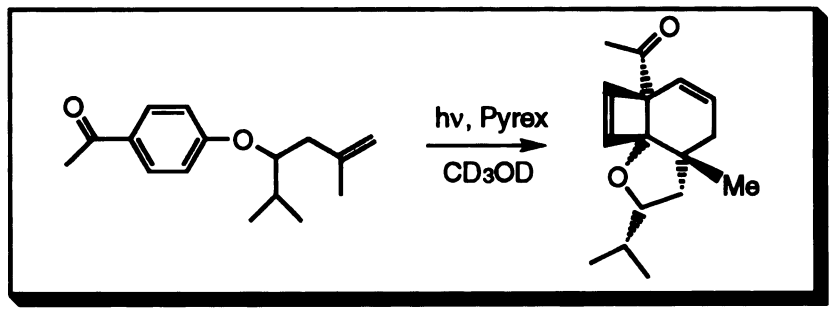
rac-(8R,10S)-4-acetyl -8,10-dimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene : **^{1}H-NMR ($CDCl_3$)** : δ 1.16 (s, 8-Me) 1.32 (d, J = 6.0 Hz, 10-Me) 1.42 (dd, J = 11.8, 6.5 Hz, H_7) 1.81 (dd, J = 11.8, 10.4 Hz, H_7) 1.98 (dd, J = 12.4, 9.6 Hz, H_9) 2.25 (dd, J = 12.4, 4.8 Hz, H_9) 2.30 (s, COMe) 3.14 (dt, J = 10.4, 6.5, Hz, H_6) 4.29 (dqd, J = 9.6, 6.0, 4.8 Hz, H_{10}) 5.59 (d, J = 10.2 Hz, H_2) 6.68 (dd, J = 10.2, 1.6 Hz, H_3) 7.01 (dd, J = 6.5, 1.6 Hz, H_5); (another minor diastereomer) δ 1.18 (s) 1.70 (m) 5.47 (d) 6.58 (dd) 6.98 (dd).

Reactant : **p-I_1M_3K**

A CD_3OD solution (0.6 mL) of **p-I_1M_3K** (2.4 mg) and methyl benzoate (3.1 mg) was irradiated through Pyrex filter for 1 h. It provided only one product which was identified by ^{1}H-NMR spectroscopy as *trans*-1-acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene. The chemical yield was 75 %. ^{13}C-NMR spectroscopy was obtained at -20°C to prevent thermal rearrangement.

The nOe experiment, also carried out at -20°C, had an enhancement shown below when the bridgehead methyl group 5-Me was irradiated; H_{10} (6.7 %), $H_{4\beta}$ (2.3 %), $H_{6\beta}$ (1.5 %) and $H_{7\beta}$ (4.0 %). This indicated that 5-Me is *trans* to 7-iPr but *cis* to the cyclobutene ring.





rac-(1S,5R,7S,9R)-1-Acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

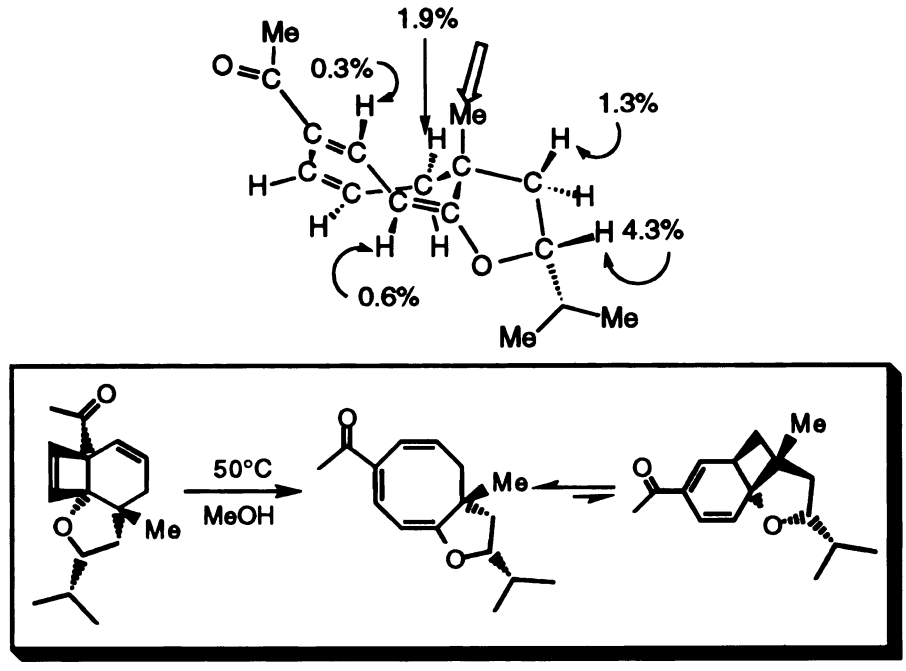
^{1}H-NMR (CD_3OD) : δ 0.71 (d, J = 6.6 Hz, iPr) 0.88 (d, J = 6.6 Hz, iPr) 1.08 (s, 5-Me) 1.24 (septd, J = 6.6, 5.7 Hz, 1H) 1.53 (dd, J = 11.9, 5.7 Hz, $H_{6\beta}$) 1.68 (dd, J = 11.9, 10.4 Hz, $H_{6\alpha}$) 1.90 (dd, J = 16.5, 1.6 Hz, $H_{4\alpha}$) 2.12 (dd, J = 16.5, 5.8 Hz, $H_{4\beta}$) 2.20 (s, COMe) 3.51 (dt, J = 10.4, 5.7 Hz, $H_{7\beta}$) 5.72 (ddd, J = 10.2, 5.8, 1.6 Hz, H_3) 5.78 (d, J = 10.2 Hz, H_2) 6.34, 6.47 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

^{13}C-NMR (CD_3OD) : δ 19.6, 21.8, 24.2, 31.0, 34.6, 36.6, 40.8, 46.8, 70.7, 86.2, 95.7, 127.0, 127.5, 139.7, 140.9, 214.9 (C=O).

UV(MeOH) : λ_{max} = 275 nm (750).

The photoproduct from **p-H_1M_3K** was heated at 50°C overnight and purified by silica gel column chromatography (R_f = 0.50 with hexane / ethyl acetate = 85 / 15). ^{1}H-NMR spectra showed an equilibrium between cycloöctatriene and cyclohexadiene with a 3 : 1 ratio by the integration of two acetyl groups at room temperature. The overall isolated yield was 46 %.

The nOe experiment on cycloöctatriene provided enhancements of H_2 (0.6 %), H_3 (0.3 %), $H_{7\beta}$ (1.9 %), $H_{9\beta}$ (1.3 %) and $H_{10\beta}$ (4.3 %) when the bridgehead methyl group 8-Me was irradiated.



rac-(8R,10S)-4-Acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : δ 0.88 (d, J = 6.7 Hz, iPr) 0.99 (d, J = 6.7 Hz, iPr) 1.14 (s, 8-Me) 1.77 (dsept, J = 7.6, 6.7 Hz, 1H) 1.88 (dd, J = 11.4, 10.7 Hz, $H_{9\beta}$) 2.03 (dd, J = 10.7, 5.2 Hz, $H_{9\alpha}$) 2.08 (dd, J = 13.5, 7.2 Hz, $H_{7\alpha}$) 2.34 (s, COMe) 2.40 (br. dd, J = 13.5, 9.4 Hz, $H_{7\beta}$) 4.07 (ddd, J = 11.4, 7.6, 5.2 Hz, H_{10}) 5.23 (d, J = 6.6 Hz, H_2) 6.18 (ddd, J = 10.6, 9.4, 7.2 Hz, H_6) 6.41 (d, J = 10.6 Hz, H_5) 7.08 (d, J= 6.6 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : (major) δ 18.3, 19.4, 20.8, 28.2, 33.1, 36.8, 42.3, 47.2, 84.6, 94.2, 129.2, 131.4, 135.3, 138.6,172.2, 198.6 (C=O).

rac-(8R,10S)-4-Acetyl-10-isopropyl-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene:

^{1}H-NMR ($CDCl_3$) : δ 0.92 (d, J = 6.7 Hz, iPr) 0.94 (d, J = 6.7 Hz, iPr) 1.13 (s, 8-Me) 1.45 (dd, J = 11.3, 9.2 Hz, H_7) 1.74 (dd, J = 11.3, 4.4 Hz, H_7) 1.76 (dsept, J = 6.9, 6.7 Hz, 1H) 2.00 (dd, J = 11.2, 4.2 Hz, H_9) 2.17 (dd, J = 11.2, 9.7 Hz, H_9)

2.28 (s, COMe) 3.08 (ddd, J = 9.2, 6.2, 4.4 Hz, H_6) 3.86 (ddd, J = 9.7, 6.9, 4.2 Hz, H_{10}) 5.61 (d, J = 10.3 Hz, H_2) 6.74 (dd, J = 10.3, 1.6 Hz, H_3) 6.80 (dd, J = 6.2, 1.6 Hz, H_5).

^{13}C-NMR ($CDCl_3$) : (minor) δ 17.6, 19.0, 25.1, 26.4, 33.2, 35.9, 39.1, 46.1, 56.2, 81.9, 88.0, 122.4, 125.5, 132.9, 138.6, 196.7 (C=O).

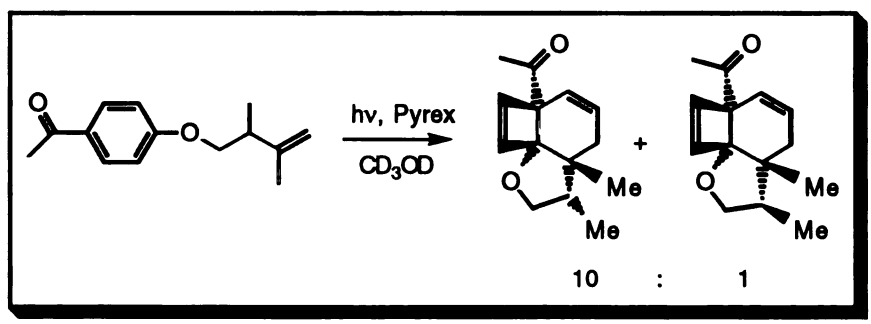
IR(CCl_4) : (mixture) 2936, 2929, 1676 (C=O), 1647 (C=O), 1361, 1253, 1166, 1097, 1044 cm^{-1}.

UV(MeOH) : (mixture) 313 nm (5600), λ_{max} = 334 nm (7060).

MS (m/e) : (mixture) 246 (M^+), 147, 137, 121, 110, 95, 91, 77, 69, 55, 43 (base).

Reactant : **p-M_2M_3K**

An NMR scale irradiation of a CD_3OD solution of **p-M_2M_3K** with a 0.9 mg methyl benzoate at > 290 nm for 12 h provided a pair of diastereomers of 1-acetyl-5,6-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene in a 10:1 ratio (measured by the integration of 5-Me groups) and 76 % chemical yield.



rac-(1S,5R,6S,9R)-1-Acetyl-5,6-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

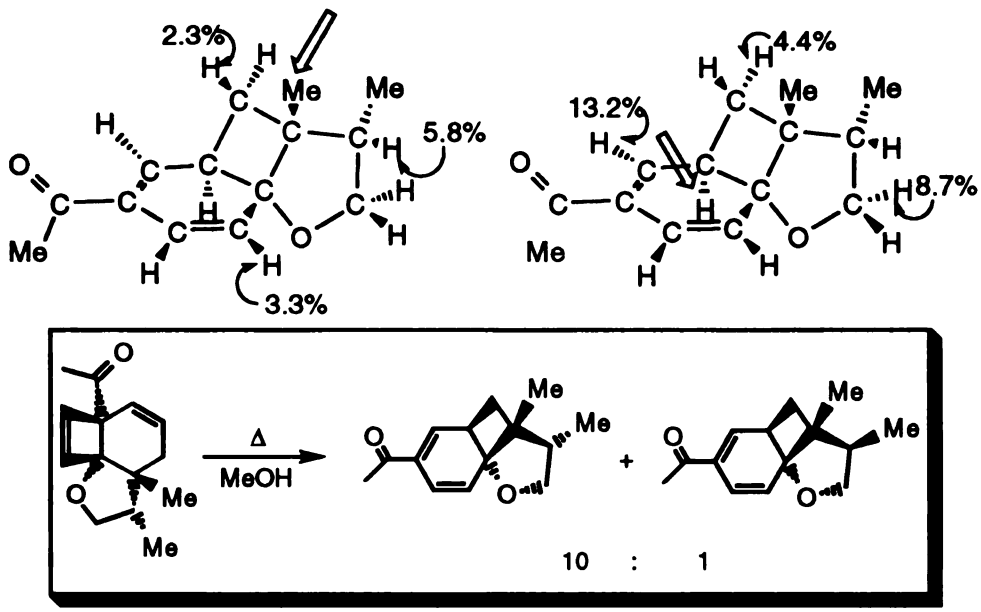
^{1}H-NMR (CD_3OD) : (major) δ 0.97 (s, 5-Me) 1.02 (d, J = 6.9 Hz, 6-Me) 1.42 (dqd, J = 10.8, 6.9, 4.0 Hz, $H_{6\beta}$) 1.89 (dd, J = 15.9, 6.8 Hz, $H_{4\beta}$) 2.06 (s, COMe) 2.15 (ddd, J = 15.9, 2.9, 2.6 Hz, $H_{4\alpha}$) 3.54 (dd, J = 10.8, 8.1 Hz, $H_{7\alpha}$) 3.95 (dd, J = 8.1,

4.0 Hz, $H_{7\beta}$) 5.70 (dd, J = 9.8, 2.9 Hz, H_2) 6.01 (ddd, J = 9.8, 6.8, 2.6 Hz, H_3) 6.21, 6.33 (AB q, J = 3.0 Hz, H_{10}, H_{11}).

rac-(1S,5R,6R,9R)-1-Acetyl-5,6-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene: **^{1}H-NMR (CD_3OD)** : (minor) δ 1.11 (s) 1.07 (d) 2.20 (m) 3.79 (m).

Large scale photolysis (0.2 g) in a test tube of **p-M_2M_3K** was undertaken similar to NMR scale experiments. Photoproducts were allowed to stay at room temperature for a couple of days and then purified by silica gel column chromatography in 58 % isolated yield (hexane/ethyl acetate = 4/1, R_f = 0.45). The diastereomeric ratio was determined by the integration of 8-Me groups in ^{1}H-NMR.

The nOe experiment indicated there was an enhancement of H_2 (3.3 %), $H_{7\beta}$ (2.3 %), $H_{9\beta}$ (5.8 %) when bridgehead 8-Me was irradiated and H_5 (13.2 %), $H_{7\alpha}$ (4.4 %), $H_{10\alpha}$ (8.7 %) when 6-H was irradiated



rac-(8R,9S)-4-Acetyl-8,9-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene: **^{1}H-NMR ($CDCl_3$)** : (major) δ 0.84 (d, J = 6.8 Hz, 9-Me) 1.08 (s, 8-Me) 1.38 (dd, J = 12.4, 6.9 Hz, $H_{7\beta}$) 1.86 (ddq, J = 10.9, 7.0, 6.8 Hz, $H_{9\beta}$) 2.27 (s, COMe) 2.36

(dd, J = 12.4, 10.9 Hz, $H_{7\alpha}$) 2.94 (ddd, J = 10.9, 6.9, 5.5 Hz, H_6) 3.68 (dd, J = 10.9, 9.2 Hz, $H_{10\alpha}$) 4.08 (dd, J = 9.2, 7.0 Hz, $H_{10\beta}$) 5.46 (dd, J = 10.2, 1.0 Hz, H_2) 6.59 (dd, J = 10.2, 1.6 Hz, H_3) 6.74 (dd, J = 5.5, 1.0 Hz, H_5).

rac-(8R,9R)-4-Acetyl-8,9-dimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene:

^{1}H-NMR ($CDCl_3$) : (minor) δ 0.91 (d, J = 6.7 Hz, 9-Me) 0.95 (s, 8-Me) 1.54 (dd, J = 11.7, 7.2 Hz, H_7) 1.84 (tq, J = 8.1, 6.7 Hz, H_9) 2.26 (s, COMe) 2.29 (m, H_7) 3.05 (ddd, J = 10.2, 7.2. 4.5 Hz, H_6) 3.95 (t, J = 8.1 Hz, $H_{10\alpha}$) 4.22 (t, J = 8.1 Hz, $H_{10\beta}$) 5.20 (dd, J = 8.2, 1.1 Hz, H_2) 6.60 (dd, J = 8.2, 1.5 Hz, H_3) 6.75 (dd, J = 4.5, 1.1 Hz, H_5).

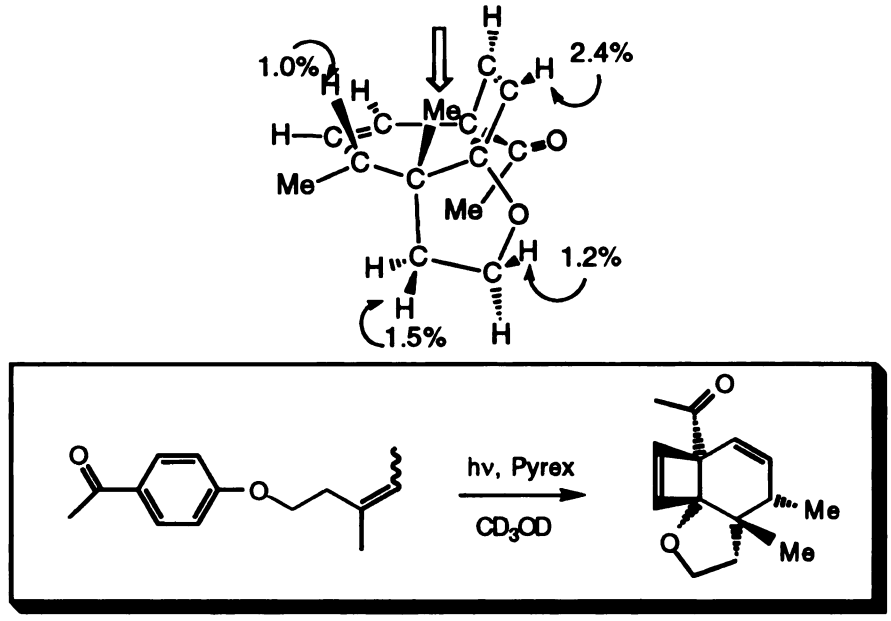
^{1}H-NMR ($CDCl_3$) : (small amount of cycloöctatriene) δ 5.20 (dd, J = 6.5, 1.1 Hz, 1H) 5.95-6.10 (m) 7.02 (d, J = 6.5 Hz, 1H).

Reactant : **p-M_3M_4K**

An NMR tube containing 3.0 mg **p-M_3M_4K** and 4.4 mg methyl benzoate was dissolved in CD_3OD and irradiated at > 290 nm for 1.5 h. Only one photoproduct was identified by ^{1}H-NMR spectroscopy in 45 % chemical yield.

Since this cyclobutene was stable compared with others, large scale isolation could be undertaken. A solution 0.2 g of **p-M_3M_4K** in 70 mL methanol was photolyzed at > 290 nm for 90 h. Solvent was removed at room temperature and the residue was purified by silica gel column chromatography with 1 % triethyl amine (hexane/ethyl acetate = 3/1, R_f = 0.43). The first fractions collected from the column contained a cyclobutene which the remained fractions contained mixtures of cyclobutene and cyclohexadiene.

There is an enhancement of H_{10} (2.4 %), $H_{4\beta}$ (1.0 %), $H_{6\beta}$ (1.5 %) and $H_{7\beta}$ (1.2 %) from nOe experiment when 5-Me was irradiated.



rac-(1S,4R,5R,9R)-1-Acetyl-4,5-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene:

^{1}H-NMR ($CDCl_3$) : δ 0.93 (s, 5-Me) 1.04 (d, J = 7.4 Hz, 4-Me) 1.61 (ddd, J = 13.7, 7.7, 5.9 Hz, $H_{6\beta}$) 2.14 (s, COMe) 2.16 (ddd, J = 13.7, 8.3, 6.9 Hz, $H_{6\alpha}$) 2.33 (qdd, J = 7.4, 4.1, 1.6 Hz, $H_{4\beta}$) 3.75 (ddd, J = 14.2, 8.3, 5.9 Hz, $H_{7\alpha}$) 3.82 (ddd, J = 14.2, 7.7, 6.9 Hz, $H_{7\beta}$) 5.64 (dd, J = 10.0, 1.6 Hz, H_2) 5.77 (dd, J = 10.0, 4.1 Hz, H_3) 6.33 ,6.44 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

^{1}H-NMR (CD_3OD) : δ 0.96 (s, 5-Me) 1.04 (d, J = 7.4 Hz, 4-Me) 1.71 (ddd, J = 13.7, 7.7, 5.9 Hz, $H_{6\beta}$) 1.86 (ddd, J = 13.7, 8.3, 6.9 Hz, $H_{6\alpha}$) 2.15 (s, COMe) 2.27 (qdd, J = 7.4, 4.1, 1.6 Hz, $H_{4\beta}$) 4.10 (ddd, J = 14.2, 8.3, 5.9 Hz, $H_{7\alpha}$) 4.17 (ddd, J = 14.2, 7.7, 6.9 Hz, $H_{7\beta}$) 5.64 (dd, J = 10.0, 1.6 Hz, H_2) 5.79 (dd, J = 10.0, 4.1 Hz, H_3) 6.46 ,6.50 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

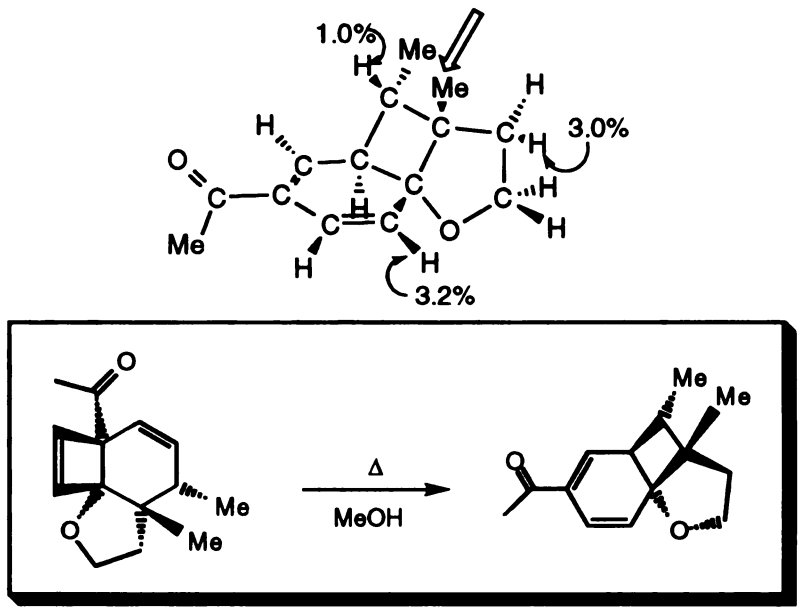
^{13}C-NMR ($CDCl_3$) : δ 15.2, 18.7, 28.4, 35.6, 36.8, 45.2, 50.5, 64.7, 92.6, 124.9, 134.5, 139.5, 141.0, 209.8 (C=O).

IR(CCl_4) : 2968, 1703 (C=O), 1300, 1250, 1022 cm^{-1}.

UV(MeOH) : λ_{max} = 280 nm (875), 290 nm (550) .

MS (m/e) : 218 (M^+), 203, 175, 147, 91, 86, 84 (base), 77, 55, 43.

All fractions containing a mixture of cyclobutene and cyclohexadiene from the previous experiment were combined. The photoproducts then heated in methanol at 40°C for 24 h to ensure the cyclobutene totally converted into cyclohexadiene. The cyclohexadiene was then isolated by silica gel column chromatography (hexane/ethyl acetate = 3/1, R_f = 0.30, 45 %). The enhancements of H_2 (3.2 %), $H_{7\beta}$ (1.0 %) and $H_{9\beta}$ (3.0 %) were recorded when 8-Me group was irradiated. This confirmed two methyl groups *trans* to each other.



rac-(7R,8R)-4-Acetyl-7,8-dimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene:

^{1}H-NMR ($CDCl_3$) : δ 0.95 (d, J = 7.5 Hz, 7-Me) 1.03 (s, 8-Me) 1.76 (ddd, J = 12.4, 9.2, 7.5 Hz, H_9) 1.85 (ddd, J = 12.4, 6.2, 3.6 Hz, H_9) 2.30 (s, COMe) 2.54 (dq, J = 10.7, 7.5 Hz, $H_{7\beta}$) 3.35 (dd, J = 10.7, 5.8 Hz, $H_{6\alpha}$) 4.07 (ddd, J = 12.2, 7.5, 3.6 Hz, H_{10}) 4.15 (ddd, J = 12.2, 9.2, 6.2 Hz, H_{10}) 5.45 (d, J = 9.7 Hz, H_2) 6.59 (d, J = 9.7 Hz, H_3) 6.61 (d, J = 5.8 Hz, H_5).

^{13}C-NMR ($CDCl_3$) : δ 11.4, 15.9, 25.2, 39.5, 41.7, 42.6, 56.3, 67.0, 82.5, 122.1, 125.7, 135.2, 137.5, 196.3 (C=O).

UV(MeOH) : 290 nm (2160), λ_{max} = 295 nm (2200), 313 nm (1635).

MS (m/e) : 218 (M^+), 203, 176, 137, 121, 83, 55, 43 (base).

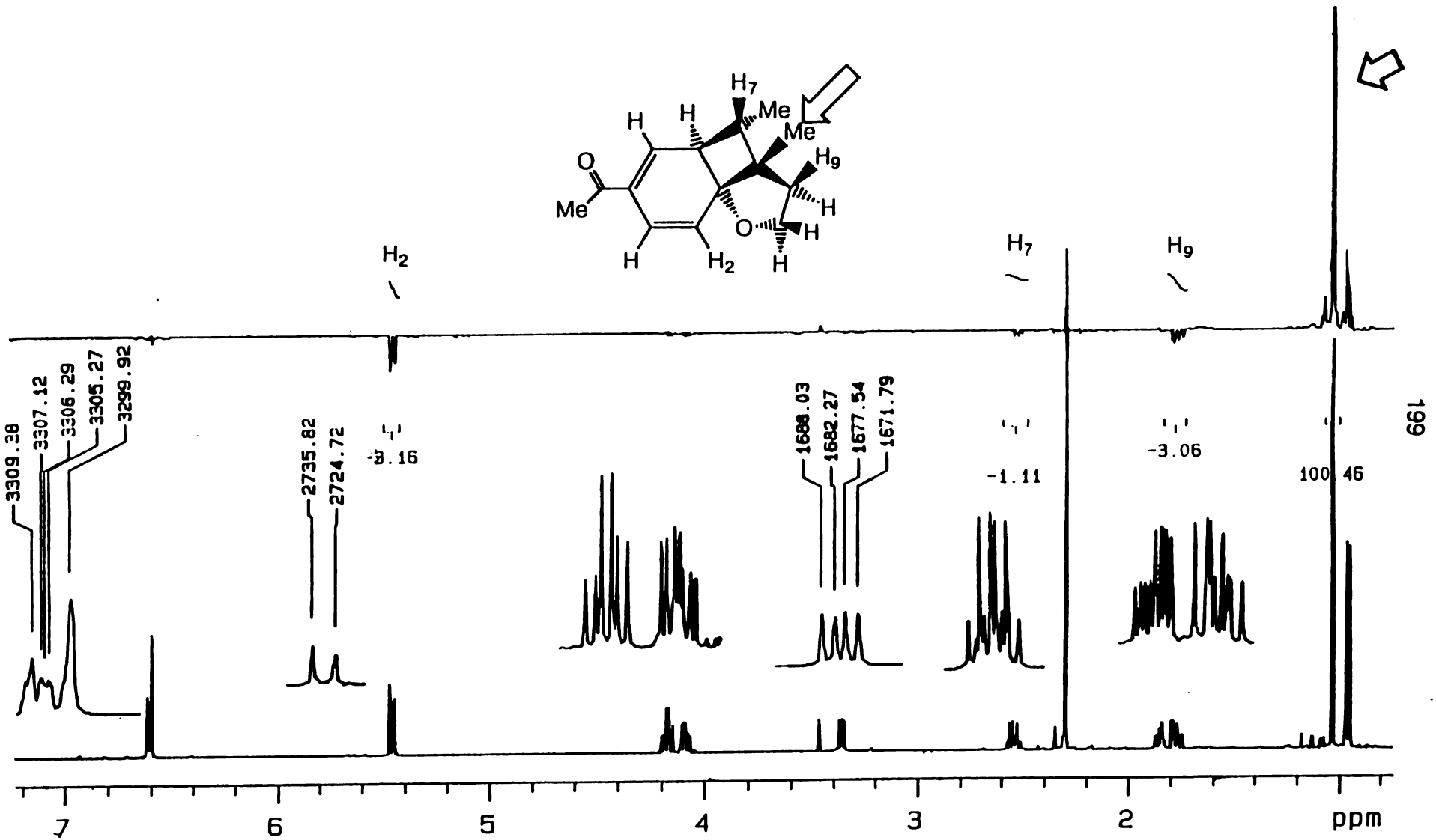
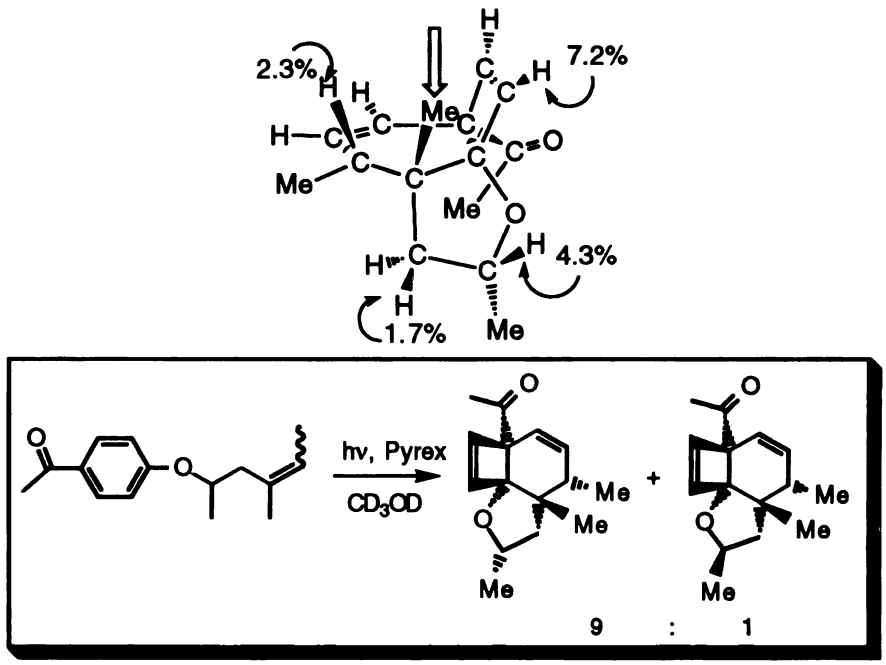


Figure 40. NOE experiments of rac-(7R,8R)-4-acetyl-7,8-dimethyl-11-oxatricyclo-[6.3.0.0^{1,6}]undeca-2,4-diene (**p-M_3M_4CH**) in $CDCl_3$.

Reactant : **p-$M_1M_3M_4K$**

An NMR scale photolysis of **p-$M_1M_3M_4K$** (3.0 mg) and methyl benzoate (3.7 mg) in CD_3OD (0.6 mL) was undertaken at > 290 nm for 18 h under oxygen-free condition. Diastereomeric ratio was formed to be 9:1 from two acetyl groups and chemical yield was 49 %, measured from ^{1}H-NMR spectroscopy. The nOe experiment verified that the major diastereomer has bridgehead 5-Me group *cis* to cyclobutene ring but *trans* to 4-Me and 7-Me since there was an enhancement of H_{10} (7.2 %), $H_{4\beta}$ (2.3 %), $H_{6\beta}$ (1.7 %) and $H_{7\beta}$ (4.3 %) when 5-Me was irradiated.



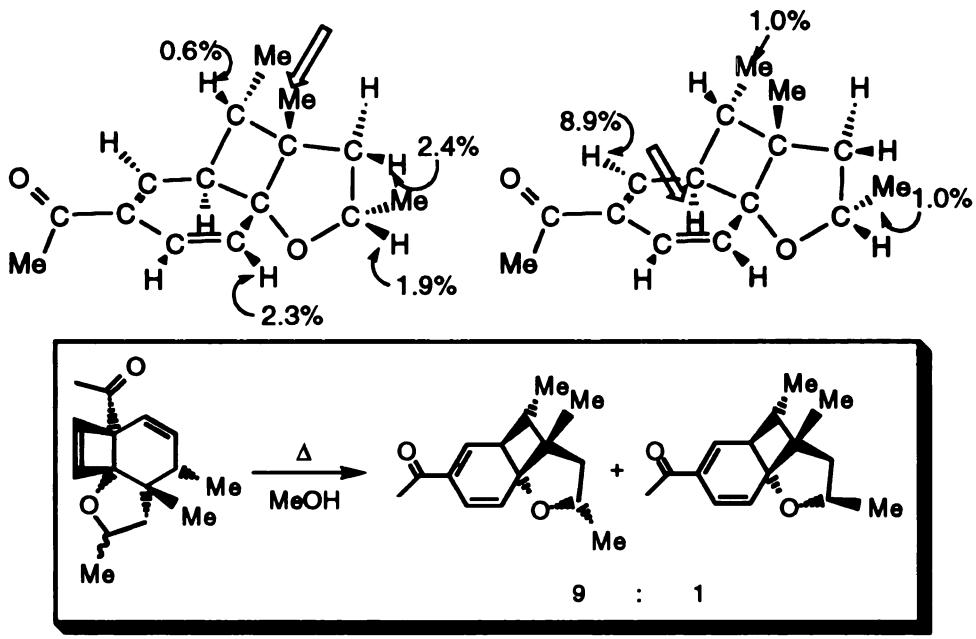
rac-(1S,4R,5R,7S,9R)-1-Acetyl-4,5,7-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 0.98 (s, 5-Me) 1.05 (d, J = 7.4 Hz, 4-Me) 1.11 (d, J = 6.1 Hz, 7-Me) 1.71, 1.74 (AB q, J = 7.3 Hz, $2H_6$) 2.13 (s, COMe) 2.29 (qdd, J = 7.4, 4.3, 1.6 Hz, $H_{4\beta}$) 4.12 (ddq, J = 9.0, 7.3, 6.1 Hz, $H_{7\beta}$) 5.68 (dd, J = 10.0, 1.6 Hz, H_2) 5.80 (dd, J = 10.0, 4.3 Hz, H_3) 6.47, 6.50 (AB q, J = 3.0 Hz, H_{10}, H_{11}).

rac-(1S,4R,5R,7R,9R)-1-Acetyl-4,5,7-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 0.86 (s), 1.12 (d) 1.20 (d) 2.0-2.2 (m) 2.13 (s) 2.50 (m) 4.22 (m) 5.69 (dd) 5.80 (dd) 6.25, 6.36 (AB q).

A 120 mL methanol solution of **p-$M_1M_3M_4K$** (0.014 M) was irradiated through Pyrex filter for 45 h. The solution was heated and the residue was purified on silica gel column chromatography (hexane/ethyl acetate = 4/1, R_f = 0.47) in 50 % isolated yield and 80% de from the integration of H_2 protons. The stereochemistry of this compound, confirmed by nOe experiments, has bridgehead 8-Me group *trans* to 7-Me and 10-Me. An enhancement was observed for H_2 (2.3 %), $H_{7\beta}$ (0.6 %), $H_{9\beta}$ (2.4 %) and $H_{10\beta}$ (1.9 %) when 8-Me was irradiated or for H_5 (8.9 %), 7-Me (1.0 %) and 10-Me (1.0 %) when 6-H was irradiated.



rac-(7R,8R,10S)-4-Acetyl-7,8,10-trimethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : (major) δ.0.89 (d, J = 7.5 Hz, 7-Me) 1.04 (s, 8-Me) 1.32 (d, J = 5.9 Hz, 10-Me) 1.96 (dd, J = 12.3, 10.8 Hz, $H_{9\alpha}$) 2.19 (dd, J = 12.3, 4.8 Hz, $H_{9\beta}$) 2.31 (s, COMe) 2.52 (dq, J = 10.0, 7.5 Hz, $H_{7\beta}$) 3.42 (dd, J = 10.0, 6.3 Hz, $H_{6\alpha}$)

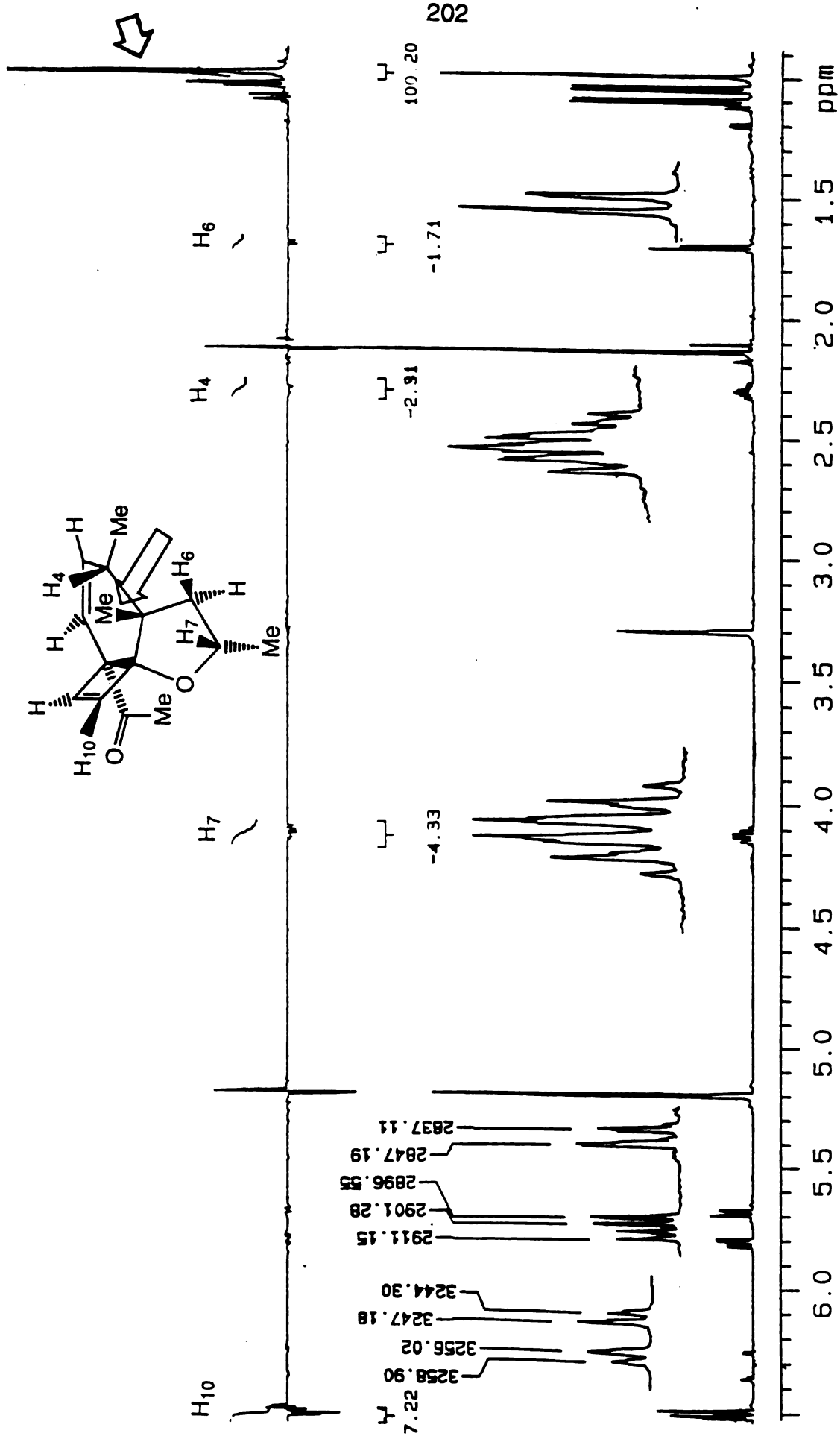


Figure 41. NOE experiments of rac-(1S,4R,5R,7S,9R)-1-acetyl-4,5,7-trimethyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene (**p-M$_1$M$_3$M$_4$CB**) in CD_3OD.

4.27 (dqd, J = 10.8, 5.9, 4.8 Hz, $H_{10\beta}$) 5.62 (d, J = 10.2 Hz, H_2) 6.61 (dd, J = 10.2, 1.5 Hz, H_3) 6.83 (dd, J = 6.3, 1.5 Hz, H_5).

^{13}C-NMR ($CDCl_3$) : (major) δ 12.1, 15.2, 21.2, 25.3, 40.3, 44.9, 54.6, 56.9, 79.7, 83.0, 123.2, 127.9, 136.4, 139.0, 198.7 (C=O).

rac-(7S,8R,10S)-4-Acetyl-7,8,10-trimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.09 (d) 2.33 (s) 4.60 (m) 5.41 (d) 6.48 (d) 7.03 (d).

Reactant : **p-M_4K**

A solution of 3.5 mg pure *trans* **p-M_4K** and 2.2 mg methyl benzoate in 0.75 mL CD_3OD was irradiated through Pyrex filter under oxygen-free condition. The 100% pure *trans* **p-M_4K** was purified from *trans* (> 95%) and *cis* mixtures by silica gel column chromatography (hexane/ethyl acetate = 99/1) and detected by HPLC to assure only *trans* isomer. At low conversion (7 % in 50 min), the signal of *cis* **p-M_4K** could be detected by either ^{1}H-NMR spectrum or HPLC. The retention time of *trans* **p-M_4K** is 13.0 min and *cis* **p-M_4K** is 13.6 min in HPLC with hexane/ethyl acetate = 95/5 elute solvent system. After high conversion (> 95 % in 18 h), a diastereomeric mixture of **CB**'s in a ratio of 11 : 1 by the integration of acetyl groups was isolated in 41 % chemical yield.

The nOe experiment verified that the major diastereomer has bridgehead group $H_{5\beta}$ *cis* to cyclobutene ring but *trans* to 4-Me since there was an enhancement of H_3 (1.9 %), $H_{4\beta}$ (3.6 %), and $H_{6\alpha}$ (0.7 %) when 4-Me was irradiated and H_{10} (4.2 %), $H_{4\beta}$ (1.3 %), $H_{6\beta}$ (1.7 %) and $H_{7\beta}$ (3.3 %) when 5-H was irradiated.

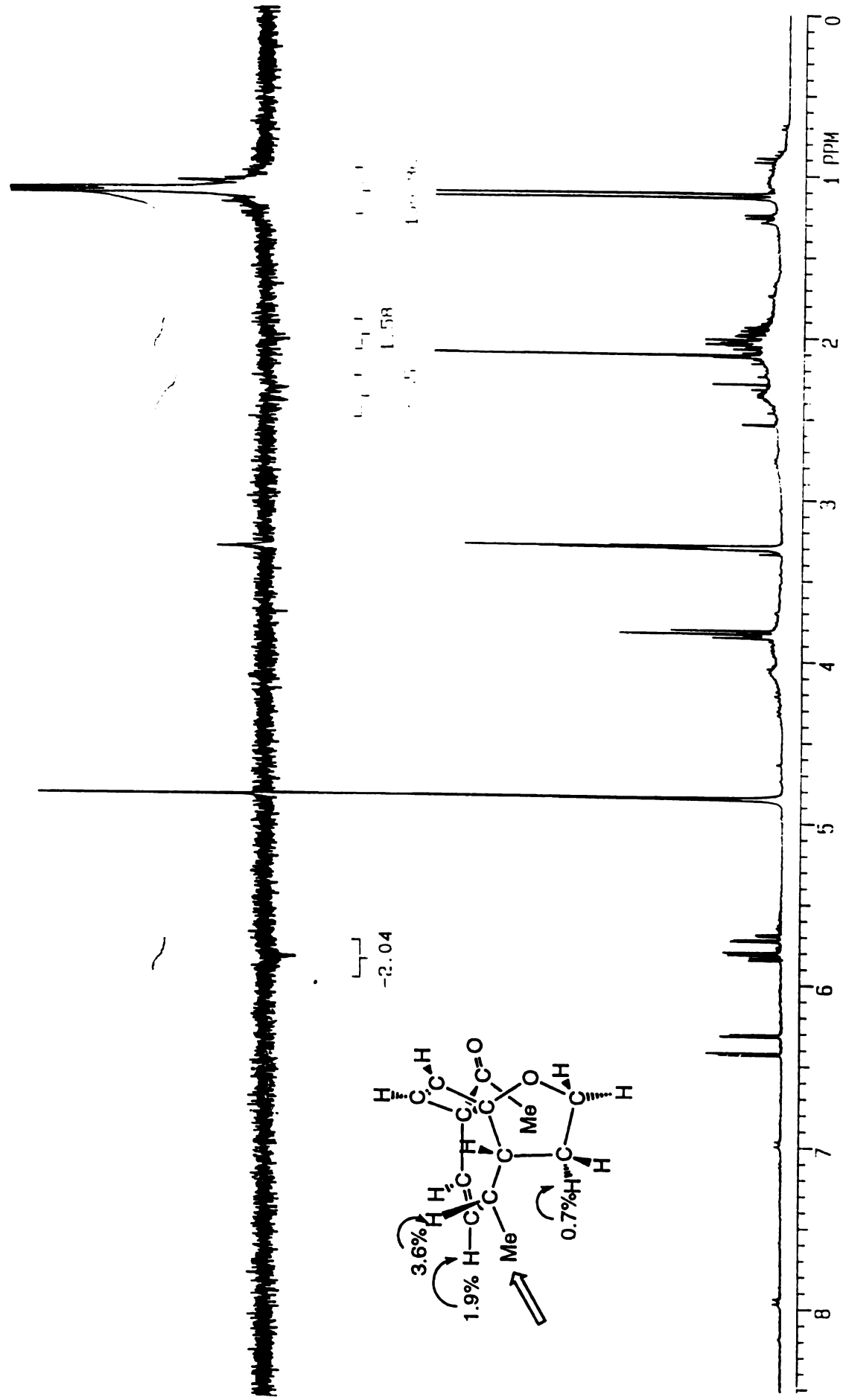
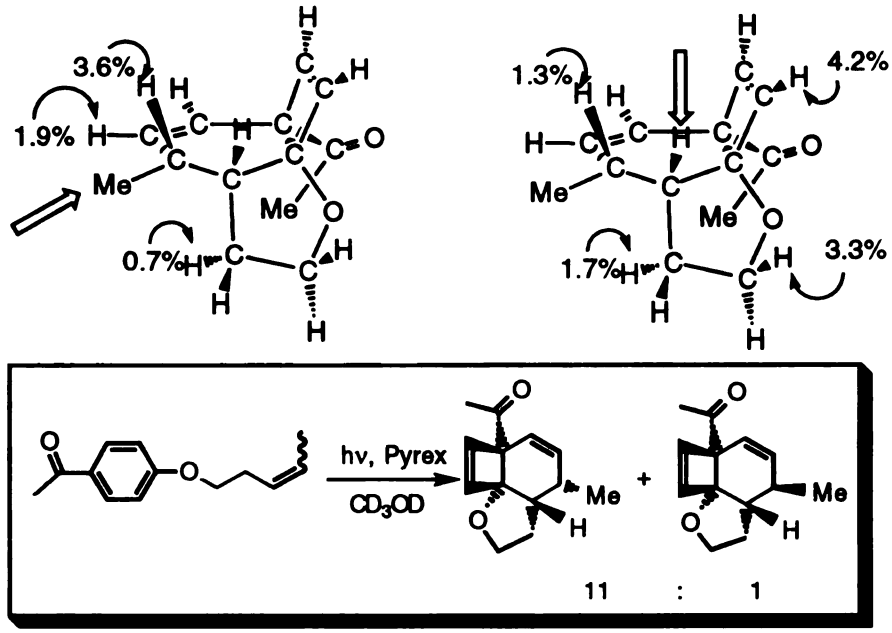


Figure 42. NOE experiments of rac-(1S,4R,5R,9R)-1-acetyl-4-methyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene (**p-M$_4$CB**) in CD_3OD.



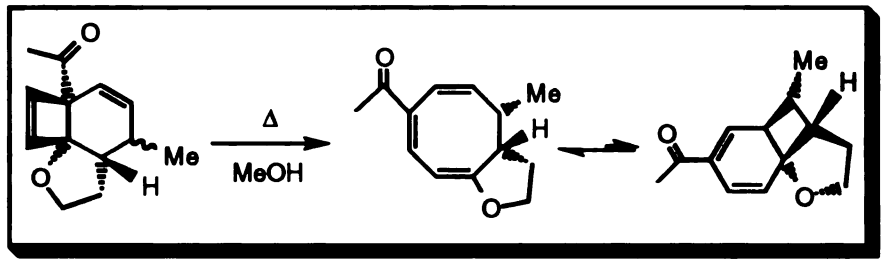
rac-(1S,4R,5R,9R)-1-Acetyl-4-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 1.13 (d, J = 7.2 Hz, 4-Me) 1.87 (ddd, J = 13.4, 7.5, 5.2 Hz, $H_{6\beta}$) 1.89 (ddd, J = 13.4, 9.3, 7.5 Hz, $H_{6\alpha}$) 2.02 (qddd, J = 7.2, 5.2, 3.7, 1.9 Hz, $H_{4\beta}$) 2.12 (s, COMe) 2.37 (ddd, J = 9.3, 7.2, 5.2 Hz, $H_{5\beta}$) 3.81, 3.83 (AB q, J = 6.7 Hz, $2H_7$) 5.71 (dd, J = 10.1, 1.9 Hz, H_2) 5.82 (dd, J = 10.1, 3.7 Hz, H_3) 6.31, 6.43 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

rac-(1S,4R,5S,9R)-1-Acetyl-4-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 2.16 (s, COMe) 3.84 (AB q, $2H_7$) 5.60-5.70 (m) 6.22, 6.37 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

Large scale (0.2 g) of **p-M_4K** was irradiated at > 290 nm in dry MeOH for 16 h. After a few days in a refrigerator, the original colorless solution has turned yellow. The mixture was purified by silica gel column chromatography. Products were identified as a 5:1 diastereomeric mixture of 4-acetyl-7-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene and to a small amount (< 15 %) of 4-acetyl-7-methyl-11-oxatricyclo[6.3.0.0^{1,6}]-undeca-2,4-diene. The overall ratio is 15 (major COT) :2 (minor COT) :2 (major CH) :1 (minor CH), determined by the integration of H_3 groups in NMR.



rac-(7R,8R)-4-Acetyl-7-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (major) δ 1.08 (d, J = 6.8 Hz, 7-Me) 1.85 (ddd, J = 12.4, 12.0, 3.2 Hz, $H_{9\alpha}$) 2.06 (ddd, J = 12.4, 6.8, 3.4 Hz, $H_{9\beta}$) 2.32 (s, COMe) 2.46 (dqd, J = 8.8, 6.8, 1.4 Hz, $H_{7\beta}$) 3.05 (ddd, J = 12.0, 3.4, 1.4 Hz, $H_{8\beta}$) 4.15, 4.17 (AB q, $2H_{10}$) 5.45 (d, J = 7.4 Hz, H_2) 5.63 (dd, J = 12.3, 8.8 Hz, H_6) 6.17 (d, J = 12.3 Hz, H_5) 6.98 (d, J = 7.4 Hz, H_3).

^{13}C-NMR ($CDCl_3$) : δ 20.1, 26.2, 32.8, 39.5, 41.5, 72.2, 91.8, 127.2, 134.3, 135.7, 137.2, 170.1, 199.2 (C=O).

rac-(7S,8R)-4-Acetyl-7-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (minor) δ 1.02 (d, J = 6.7 Hz, 7-Me) 1.95-2.20 (m) 2.31 (s, COMe) 4.25 (m) 5.32 (d, J = 6.1 Hz, H_2) 5.65 (m, H_6) 6.26 (d, J = 11.0 Hz, H_5) 7.00 (d, J = 6.1 Hz, H_3).

rac-(7R,8R)-4-Acetyl-7-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene:

^{1}H-NMR ($CDCl_3$) : (major) δ 1.06 (d, J = 7.4 Hz, 7-Me) 2.29 (s, COMe) 2.80 (m, H_6) 3.92 (ddd, J = 14.5, 8.5, 6.0 Hz, H_{10}) 4.05 (ddd, J = 14.5, 8.7, 6.0 Hz, H_{10}) 5.91 (d, J = 10.5 Hz, H_3) 6.52 (d, J = 10.5 Hz, H_2) 6.81 (d, J = 6.1 Hz, H_5).

rac-(7S,8R)-4-Acetyl-7-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene:

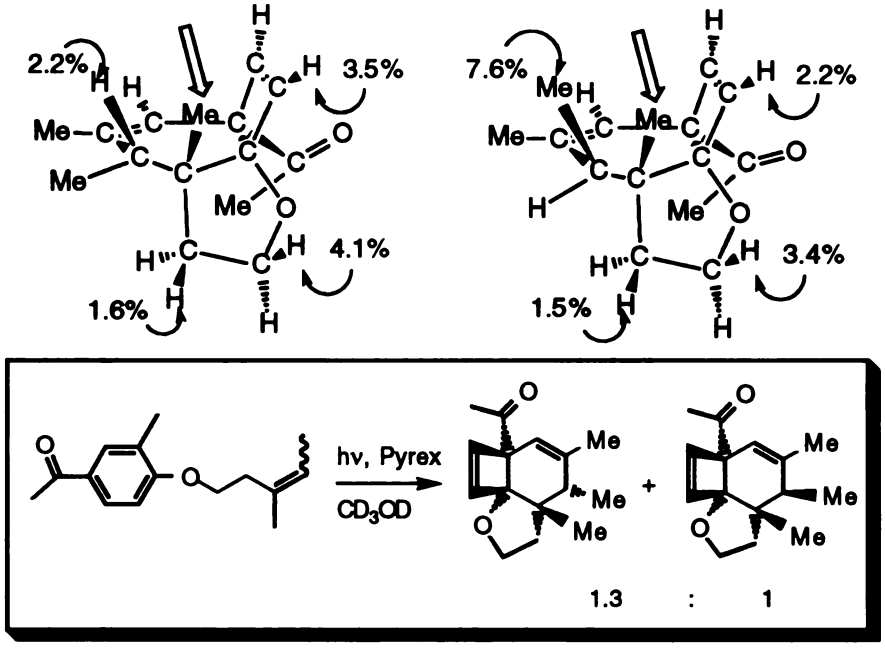
^{1}H-NMR ($CDCl_3$) : (minor) δ 5.90 (d) 6.62 (m).

UV(MeOH) : (mixture) 313 nm (8500), λ_{max} = 337 nm (10400).

Reactant : **p-$M_3M_4M_5K$**

A 0.015 M methanol solution of *cis/trans* mixture of **p-$M_3M_4M_5K$** in a NMR tube was photolyzed at > 290 nm for 6 h. The diastereomeric excess (13 %, measured by acetyl groups) and chemical yield (45 %) were directly obtained from the ^{1}H-NMR spectrum.

The nOe experiment at room temperature indicated the major diastereomer has bridgehead group 5-Me *cis* to cyclobutene ring but *trans* to 4-Me since there was an enhancement of $H_{4\beta}$ (2.2 %), $H_{6\beta}$ (1.6 %), $H_{7\beta}$ (4.1 %) and H_{10} (3.5 %) when 5-Me was irradiated. The minor diastereomer has bridgehead group 5-Me *cis* to cyclobutene ring and 4-Me due to an enhancement of 4-Me (7.6 %), $H_{6\beta}$ (1.5 %), $H_{7\beta}$ (3.4 %) and H_{10} (2.2 %) when 5-Me was irradiated.



rac-(1S,4R,5R,9R)-1-Acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 1.06 (s, 5-Me) 1.08 (d, J = 7.2 Hz, 4-Me) 1.63 (ddd, J = 12.1, 7.4, 3.9 Hz, $H_{6\beta}$) 1.73 (ddd, J = 12.1, 7.6, 6.5 Hz, $H_{6\alpha}$) 1.79 (d, J = 1.4 Hz, 3-Me) 2.05 (q, J = 7.2 Hz, $H_{4\beta}$) 2.15 (s, COMe) 4.05 (ddd, J = 11.5, 7.6, 3.9

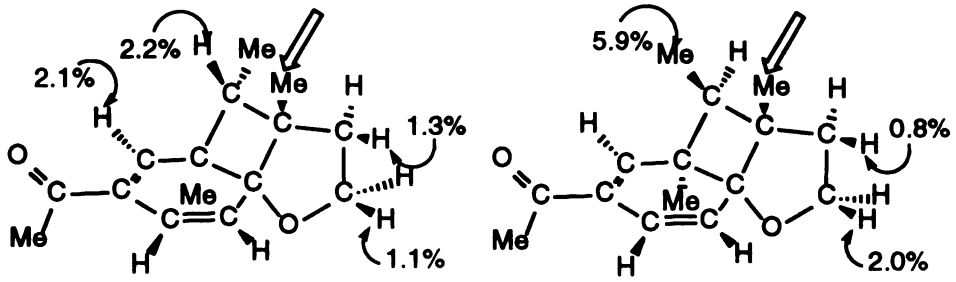
Hz, $H_{7\alpha}$) 4.15 (ddd, J = 11.5, 7.4, 6.5 Hz, $H_{7\beta}$) 5.37 (q, J = 1.4 Hz, H_2) 6.39, 6.44 (AB q, J = 3.0 Hz, H_{10}, H_{11}).

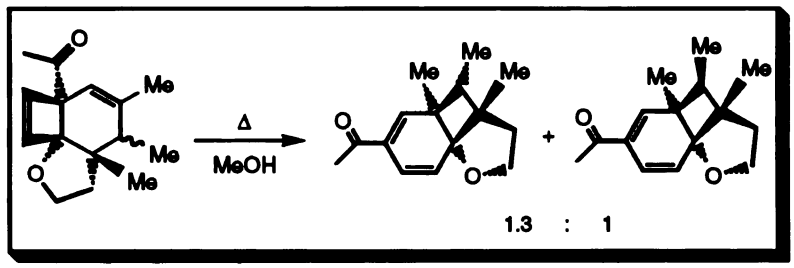
rac-(1S,4S,5R,9R)-1-Acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.03 (s, 5-Me) 1.13 (d, J = 7.3 Hz, 4-Me) 1.51(m, $2H_6$) 1.76 (d, J = 1.4 Hz, 3-Me) 2.15 (s, COMe) 2.25 (qd J = 7.3, 1.4 Hz, $H_{4\alpha}$) 3.78 (m, $2H_7$) 5.45 (quintet, J = 1.4 Hz, H_2) 6.31, 6.33 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

A MeOH solution of diastereomeric mixture of 1-acetyl-3,4,5-trimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene obtained from the above experiment was heated at 40°C for 24 h and ^{1}H-NMR was recorded.

The nOe experiments at room temperature showed that the major diastereomer has bridgehead group 8-Me *trans* to 5-Me and 6-Me because there was an enhancement of H_5 (2.1%), $H_{7\beta}$ (2.2 %), $H_{9\beta}$ (1.3 %) and $H_{10\beta}$ (1.1 %) when 8-Me was irradiated. The minor diastereomer has bridgehead group 8-Me *cis* to 7-Me but *trans* to 6-Me since there was an enhancement of 7-Me (5.9 %), $H_{9\beta}$ (0.8 %) and $H_{10\beta}$ (2.0 %) when 8-Me was irradiated.





rac-(6R,7R,8R)-4-Acetyl-6,7,8-trimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : (major) δ 1.03 (s, 8-Me) 1.06 (d, J = 7.3 Hz, 7-Me) 1.09 (s, 6-Me) 1.60 (m, $2H_9$) 2.20 (q, J = 7.3 Hz, $H_{7\beta}$) 2.32 (s, COMe) 4.15 (m, $2H_{10}$) 5.28 (d, J = 10.1 Hz, H_2) 6.41 (dd, J = 10.1, 1.6 Hz, H_3) 6.70 (s, H_5).

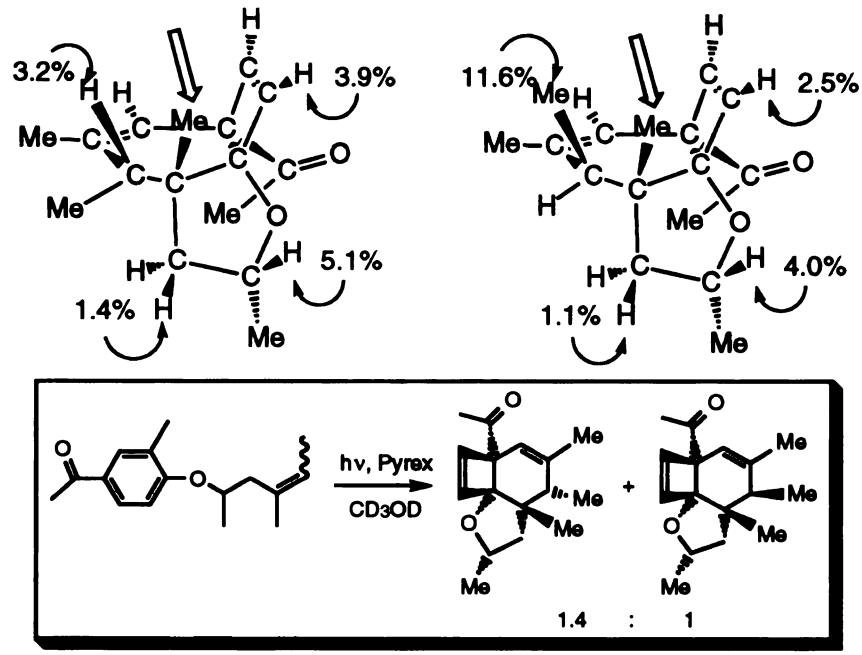
rac-(6R,7S,8R)-4-Acetyl-6,7,8-trimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.09 (s, 8-Me) 1.11 (d, J = 7.4 Hz, 7-Me) 1.13 (s, 6-Me) 1.70 (m, $2H_9$) 2.21 (q, J = 7.4 Hz, $H_{7\alpha}$) 2.30 (s, COMe) 4.10 (m, $2H_{10}$) 5.44 (d, J = 10.1 Hz, H_2) 6.55 (dd, J = 10.1, 1.7 Hz, H_3) 6.76 (s, H_5).

Reactant : **p-$M_1M_3M_4M_5K$**

A 0.021 M methanol solution of a *cis/trans* mixture of **p-$M_1M_3M_4M_5K$** in a NMR tube was photolyzed at > 290 nm for 8 h. The diastereomeric excess (19 %) and chemical yield (55 %) were directly obtained from the ^{1}H-NMR spectrum.

The nOe experiment showed that the major diastereomer has bridgehead group 5-Me *cis* to cyclobutene ring but *trans* to 4-Me and 7-Me since there was an enhancement of $H_{4\beta}$ (3.2 %), $H_{6\beta}$ (1.4 %), $H_{7\beta}$ (5.1 %) and H_{10} (3.9 %) when 5-Me was irradiated. The minor diastereomer has bridgehead group 5-Me *cis* to cyclobutene ring and 4-Me but *trans* to 7-Me since there was an enhancement of 4-Me (11.6 %), $H_{6\beta}$ (1.1 %), $H_{7\beta}$ (4.0 %) and H_{10} (2.5 %) when 5-Me was irradiated.



rac-(1S,4R,5R,7S,9R)-1-Acetyl-3,4,5,7-tetramethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 1.00 (d, J = 6.2 Hz, 7-Me) 1.03 (d, J = 7.4 Hz, 4-Me) 1.11 (s, 5-Me) 1.55 (dd, J = 12.1, 5.8 Hz, $H_{6\beta}$) 1.66 (dd, J = 12.1, 10.2 Hz, $H_{6\alpha}$) 1.78 (d, J = 1.5 Hz, 3-Me) 2.08 (q, J = 7.4 Hz, $H_{4\beta}$) 2.15 (s, COMe) 4.15 (dqd, J = 10.2, 6.2, 5.8 Hz, $H_{7\beta}$) 5.43 (q, J = 1.5 Hz, H_2) 6.43, 6.50 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

rac-(1S,4S,5R,7S,9R)-1-Acetyl-3,4,5,7-tetramethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.01 (d, J = 6.2 Hz, 7-Me) 1.07 (d, J = 7.4 Hz, 4-Me) 1.12 (s, 5-Me) 1.42 (dd, J = 11.2, 10.5 Hz, $H_{6\alpha}$) 1.54 (dd, J = 11.2, 5.6 Hz, $H_{6\beta}$) 1.75 (d, J = 1.4 Hz, 3-Me) 2.16 (s, COMe) 2.22 (qd, J = 7.4, 1.4 Hz, $H_{4\alpha}$) 4.11 (dqd, J = 10.5, 6.2, 5.6 Hz, $H_{7\beta}$) 5.47 (quintet, J = 1.4 Hz, H_2) 6.31, 6.41 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

A mixture of 1-acetyl-3,4,5,7-tetramethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene diastereomers from the above experiment was heated in MeOH at

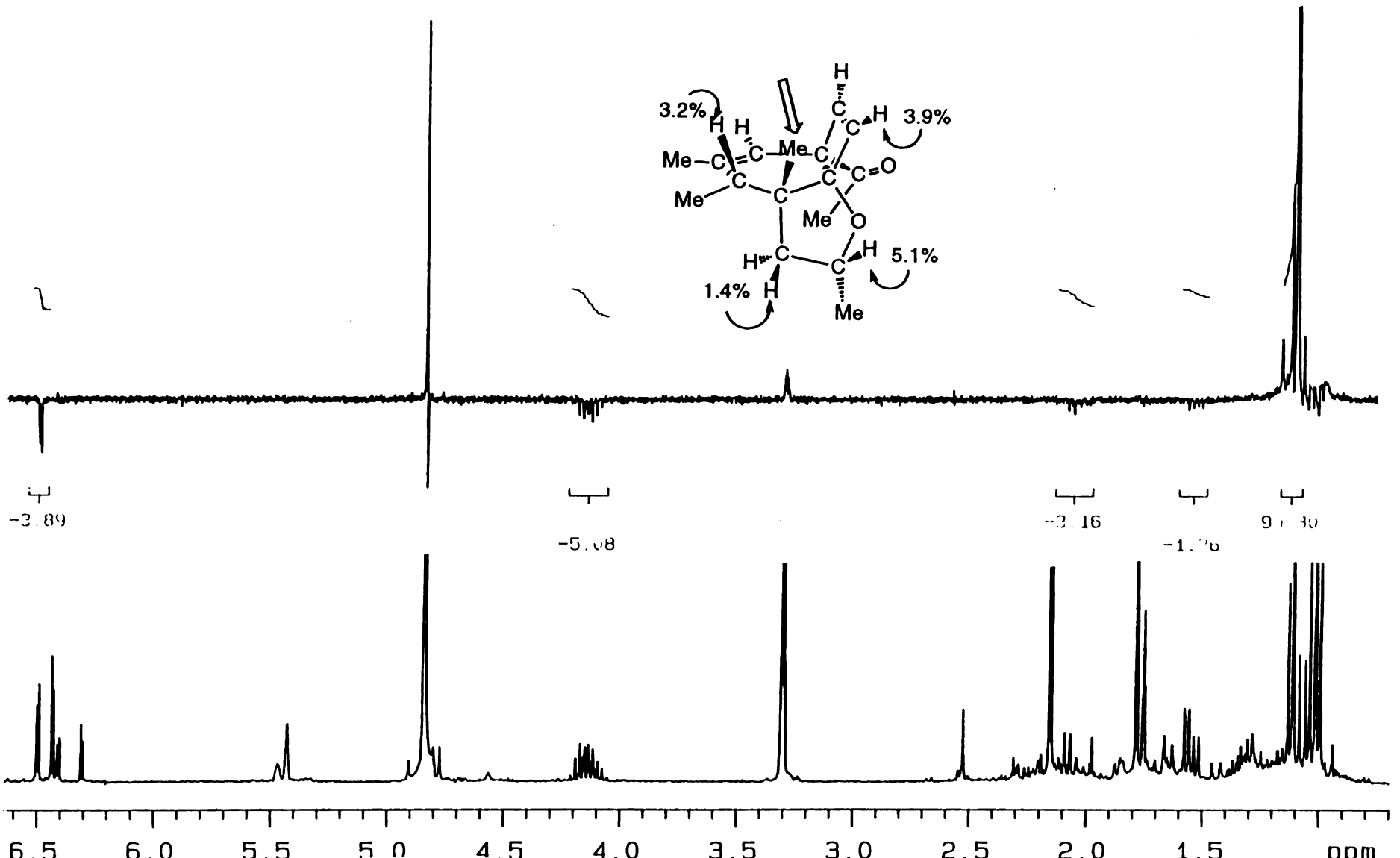
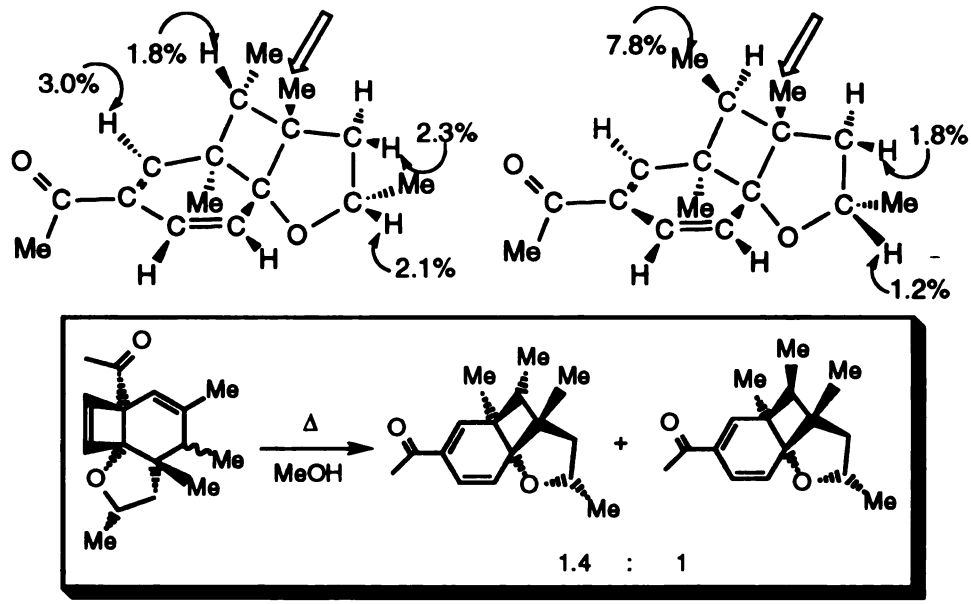


Figure 43. NOE experiments of rac-(1S,4R,5R,7S,9R)-1-acetyl-3,4,5,7-tetramethyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene (**p-$M_1M_3M_4M_5$CB**) in CD_3OD.

40°C for 46 h. An identical diastereoselectivity was obtained for the photoproducts.

The nOe results indicated that the major diastereomer has bridgehead group 8-Me *trans* to 5-Me, 6-Me and 10-Me since there was an enhancement of H_5 (3.0%), $H_{7\beta}$ (1.8 %), $H_{9\beta}$ (2.3 %) and $H_{10\beta}$ (2.1 %) when 8-Me was irradiated. The minor diastereomer has bridgehead group 8-Me *cis* to 7-Me but *trans* to 6-Me and 10-Me since there was an enhancement of 7-Me (7.8 %), $H_{9\beta}$ (1.8 %) and $H_{10\beta}$ (1.2 %) when 8-Me was irradiated.



rac-(6R,7R,8R,10S)-4-Acetyl-6,7,8,10-tetramethyl-11-oxatricyclo[6.3.0.0]undeca-2,4-diene:

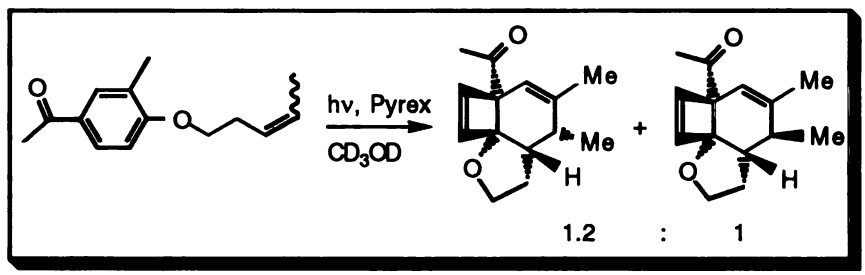
^{1}H-NMR (CD_3OD) : (major) δ 1.00 (s, 8-Me) 1.04 (d, J = 7.4 Hz, 10-Me) 1.11 (s, 6-Me) 1.17 (d, J = 6.0 Hz, 7-Me) 1.83 (m, $2H_9$) 2.01 (q, J = 6.0 Hz, $H_{7\beta}$) 2.33 (s, COMe) 4.50 (m, $H_{10\beta}$) 5.30 (d, J = 10.1 Hz, H_2) 6.41 (d, J = 10.1 Hz, H_3) 6.69 (s, H_5).

rac-(6R,7S,8R,10S)-4-Acetyl-6,7,8,10-tetramethyl-11-oxatricyclo[6.3.0.0]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.01 (s, 8-Me) 1.03 (d, J = 7.4 Hz, 10-Me) 1.13 (s, 6-Me) 1.21 (d, J = 5.5 Hz, 7-Me) 1.78 (m, $2H_9$) 2.10 (q, J = 5.5 Hz, $H_{7\alpha}$) 2.31 (s, COMe) 4.23 (m, $H_{10\beta}$) 5.56 (d, J = 10.1 Hz, H_2) 6.58 (d, J = 10.1 Hz, H_3) 6.75 (s, H_5).

Reactant : **p-M_4M_5K**

A 0.017 M methanol solution of **p-M_4M_5K** in an NMR tube was photolyzed at > 290 nm for 6 h. The diastereomeric excess (10 %, measured by acetyl groups) and chemical yield (61 %) were directly obtained from the ^{1}H-NMR spectrum.



rac-(1S,4R,5R,9R)-1-Acetyl-3,4-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

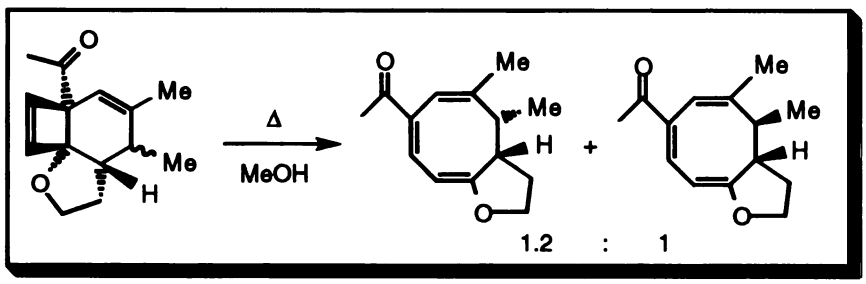
^{1}H-NMR (CD_3OD) : (major) δ 1.12 (d, J = 6.4 Hz, 4-Me) 1.68 (dddd, J = 12.5, 10.2, 7.2, 4.1 Hz, $H_{6\beta}$) 1.74 (dddd, J = 12.5, 7.7, 6.9, 6.0 Hz, $H_{6\alpha}$) 1.80 (d, J = 1.5 Hz, 3-Me) 2.13 (s, COMe) 2.23 (qd, J = 6.4, 2.6 Hz, $H_{4\beta}$) 2.42 (ddd, J = 10.2, 7.7, 2.6 Hz, H_5) 3.95 (ddd, J = 11.9, 6.9, 4.1 Hz, $H_{7\alpha}$) 4.12 (ddd, J = 11.9, 7.2, 6.0 Hz, $H_{7\beta}$) 5.42 (q, J = 1.5 Hz, H_2) 6.33, 6.35 (AB q, J = 2.8 Hz, H_{10}, H_{11}).

rac-(1S,4S,5R,9R)-1-Acetyl-3,4-dimethyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.16 (d, J = 7.2 Hz, 4-Me) 1.77 (d, J = 1.5 Hz, 3-Me) 1.82-1.89 (m, $2H_6$) 2.14 (s, COMe) 2.30 (qdd, J = 7.2, 2.0, 1.5 Hz, $H_{4\alpha}$) 2.39

(m, H_5) 3.71-3.75 (m, $2H_7$) 5.40 (quint, J = 1.5 Hz, H_2) 6.29, 6.33 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

A mixture of 1-acetyl-3,4-dimethyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene diastereomers obtained from the above experiment was heated at 40°C in MeOH for 40 h to give the same diastereoselectivity (10 %, measured by acetyl groups) from NMR spectra.



rac-(7R,8R)-4-Acetyl-6,7-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR (CD_3OD) : (major) δ 1.07 (d, J = 7.0 Hz, 7-Me) 1.93 (d, J = 1.5 Hz, 6-Me) 2.20 (m, $2H_9$) 2.30 (s, COMe) 2.45 (qdd, J = 7.0, 6.5, 2.1 Hz, $H_{7\beta}$) 3.13 (ddd, J = 7.8, 6.5, 4.4 Hz, $H_{8\beta}$) 3.98 (ddd, J = 13.7, 8.5, 6.4 Hz, H_{10}) 4.12 (ddd, J = 13.7, 8.7, 6.0 Hz, H_{10}) 5.34 (d, J = 6.9 Hz, H_2) 6.08 (q, J = 1.5 Hz, H_5) 7.10 (dd, J = 6.9, 1.2 Hz, H_3).

rac-(7S,8R)-4-Acetyl-6,7-dimethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR (CD_3OD) : (minor) δ 1.09 (d, J = 6.9 Hz, 7-Me) 1.82 (d, J = 1.5 Hz, 6-Me) 2.00 (m, $2H_9$) 2.32 (s, COMe) 2.75 (qdd, $H_{7\alpha}$) 3.12 (ddd, $H_{8\beta}$) 4.23 (m, $2H_{10}$) 5.44 (dd, J = 8.2, 2.0 Hz, H_2) 6.01 (q, J = 1.5 Hz, H_5) 7.08 (d, J = 8.2 Hz, H_3).

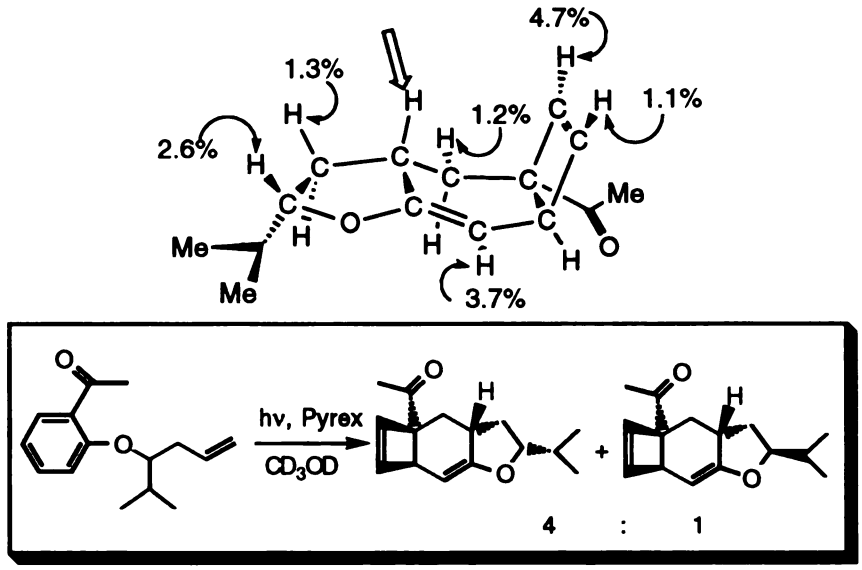
UV(MeOH) : (mixture) 313 nm (8500), λ_{max} = 337 nm (10500).

Reactant : **o-I_1K**

In an NMR tube, a solution of **o-I_1K** (1.8 mg) and 1.6 mg methyl benzoate was irradiated in CD_3OD (0.6 mL) at > 290 nm (Pyrex) for 1 h. The

photoproducts were identified as a pair of diastereomers of 9-acetyl-5-isopropyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene in a ratio of 4 : 1 by the integration of two H_{10} protons and in 71 % chemical yield in NMR spectra.

The nOe experiments performed at -20°C indicated that there was an enhancement of major product of H_{10} (4.7 %), H_{11} (1.1 %), H_2 (3.7 %), $H_{5\beta}$ (2.6 %), $H_{6\beta}$ (1.3 %) and $H_{8\beta}$ (1.2 %) when H_7 was irradiated.



rac-(1S,5S,7R,9R)-9-Acetyl-5-isopropyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 0.89 (d, J = 6.7 Hz, iPr) 0.99 (d, J = 6.7 Hz, iPr) 1.40 (ddd, J = 13.5, 12.4, 9.8 Hz, $H_{6\alpha}$) 1.45 (ddd, J = 13.5, 4.9, 3.8 Hz, $H_{6\beta}$) 1.71 (octet, J = 6.7 Hz, 1H) 2.12 (dd, J = 12.9, 5.2 Hz, $H_{8\beta}$) 2.17 (s, COMe) 2.24 (dd, J = 12.9, 8.7 Hz, $H_{8\alpha}$) 2.56 (dddd, J = 9.8, 8.7, 5.2, 3.8 Hz, $H_{7\beta}$) 3.42 (dd, J = 6.6, 1.7 Hz, $H_{1\alpha}$) 3.87 (ddd, J = 12.4, 6.7, 4.9 Hz, $H_{5\beta}$) 4.72 (dd, J = 6.6, 2.5 Hz, H_2) 6.11, 6.15 (AB q, J = 2.8 Hz, H_{10}, H_{11}).

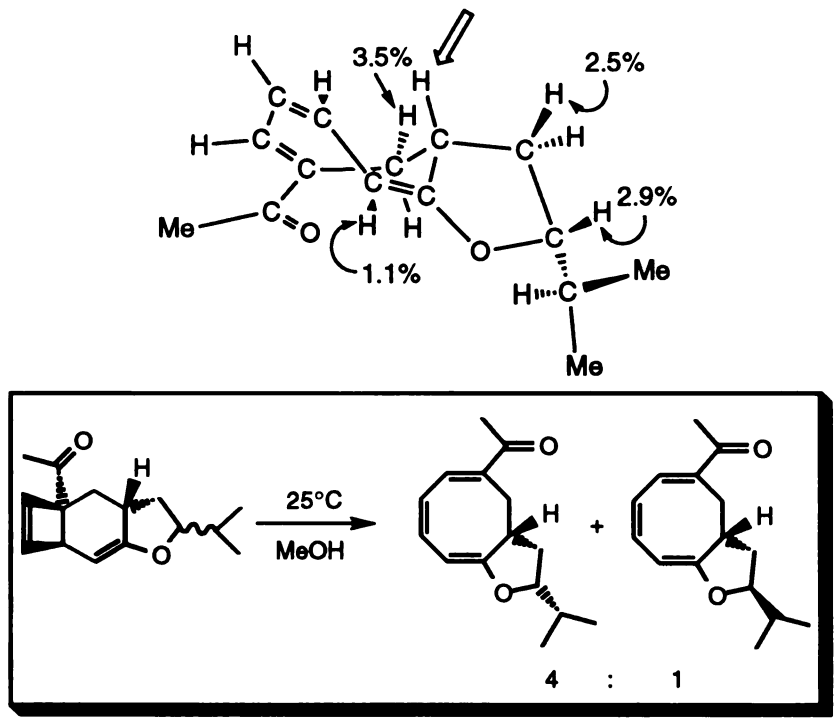
rac-(1S,5R,7R,9R)-9-Acetyl-5-isopropyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 0.88 (d, J = 6.8 Hz, iPr) 0.93 (d, J = 6.8 Hz, iPr) 1.58 (m, $2H_6$) 1.80 (m, 1H) 2.07 (m, 1H) 2.16 (s, COMe) 2.27 (m, 1H) 2.67 (m,

1H) 3.41 (m, 1H) 3.85 (m, 1H) 5.61 (dd, J = 5.4, 0.8 Hz, H_2) 5.89, 5.91 (AB q, J = 2.5 Hz, H_{10}, H_{11}).

A solution of 0.2 g **o-I_1K** in 60 mL dry methanol was irradiated at > 290 nm for 5 h. The residue was purified by silica gel column chromatography (R_f = 0.53 with hexane/ethyl acetate = 4/1) with the isolated yield = 52 %. The diastereoselectivity was 60 %, measured from the integration of two H_5 in ^{1}H-NMR. Separation of diastereomers was unsuccessful.

In nOe experiments, the major product had enhancements of H_3 (1.1 %), $H_{7\beta}$ (3.5 %), $H_{9\beta}$ (2.5 %) and $H_{10\beta}$ (2.9 %) when bridgehead proton $H_{8\beta}$ was irradiated.



rac-(8R,10S)-6-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (major) δ 0.85 (d, J = 6.8 Hz, iPr) 0.93 (d, J = 6.8 Hz, iPr) 1.51 (ddd, J = 12.4, 10.9, 8.8 Hz, $H_{9\alpha}$) 1.51 (ddd, J = 12.4, 5.4, 4.7 Hz, $H_{9\beta}$) 1.70 (septd, J = 6.8, 7.5 Hz, 1H) 2.16 (dd, J = 12.7, 7.4 Hz, $H_{7\alpha}$) 2.33 (s, COMe) 2.70

(dddd, J = 8.8, 7.4, 5.4, 1.8 Hz, $H_{8\beta}$) 3.06 (dd, J = 12.7, 1.8 Hz, $H_{7\beta}$) 3.92 (ddd, J = 10.9, 7.5, 4.7 Hz, $H_{10\beta}$) 5.33 (dd, J = 9.4, 2.5 Hz, H_2) 5.73 (dd, J = 13.2, 6.1 Hz, H_4) 6.01 (dd, J = 13.2, 9.4 Hz, H_3) 7.05 (d, J = 6.1 Hz, H_5).

^{13}C-NMR ($CDCl_3$) : (major) δ 17.6, 25.4, 27.0, 31.3, 36.2, 44.4, 85.3, 95.7, 118.7, 130.5, 138.8, 141.5, 169.6, 198.0 (C=O).

rac-(8R,10R)-6-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR ($CDCl_3$) : (minor) δ 0.85 (d, J = 6.6 Hz, iPr) 0.91 (d, J = 6.6 Hz, iPr) 1.89 (m, 1H) 2.05 (ddd, J = 12.4, 5.8, 1.3 Hz, 1H) 2.25(m, 2H) 2.32 (s, COMe) 2.89 (m, 1H) 2.91 (dd, J = 13.5, 2.2 Hz, 1H) 4.07 (m, H_{10}) 5.31 (m, H_2) 5.75 (dd, J = 12.6, 7.1 Hz, H_4) 6.04 (dd, J = 12.6, 8.0 Hz, H_3) 7.03 (d, J = 7.1 Hz, H_5).

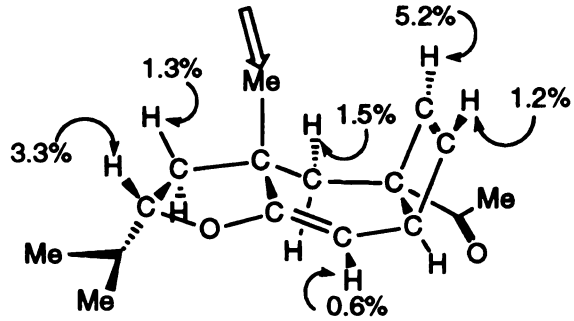
^{13}C-NMR ($CDCl_3$) : (minor) δ 18.9, 25.0, 25.5, 32.5, 34.7, 40.2, 85.7, 95.3, 118.4, 131.9, 137.3, 140.3, 169.3, 199.2 (C=O).

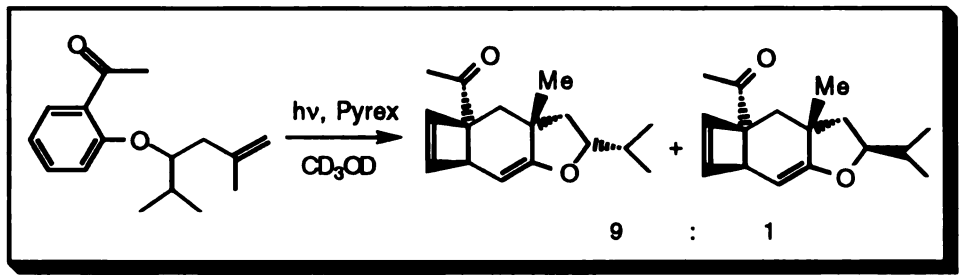
UV(MeOH) : (mixture) 313 nm (1525), λ_{max} = 377 nm (4500).

Reactant : **o-I_1M_3K**

The same irradiation procedure for **o-I_1K** was used. After half an hour irradiation (>290 nm), a solution of 3.0 mg **o-I_1M_3K** with internal standard in CD_3OD provided one major product which was characterized as *trans*-9-acetyl-5-isopropyl-7-methyl-4-oxatricyclo[7.2.0.$0^{3,7}$]undeca-2,10-diene with a small amount of the *cis*-isomer in a ratio of 9 : 1 by the H_2 integration in NMR. Chemical yield was 67 %.

The major product's stereochemistry was determined by nOe experiments at -20°C, shown below. There was an enhancement when the bridgehead methyl group 7-Me was irradiated; H_2 (0.6 %), H_{10} (5.2 %), H_{11} (1.2 %), $H_{8\beta}$ (1.5 %), $H_{6\beta}$ (1.3 %) and $H_{5\beta}$ (3.3 %). This indicated that the product has methyl group bridgehead, 7-Me, *cis* to the cyclobutene group but *trans* to the 5-iPr.





rac-(1S,5S,7R,9R)-9-Acetyl-5-isopropyl-7-methyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (major) δ 0.86 (d, J = 6.8 Hz, iPr) 0.98 (d, J = 6.8 Hz, iPr) 1.28 (s, 7-Me) 1.46 (br t, J = 11.5 Hz, $H_{6\alpha}$) 1.65 (oct, J = 6.9 Hz, 1H) 1.82 (d, J = 13.8 Hz, $H_{8\alpha}$) 1.93 (dd, J = 11.5, 5.0 Hz, $H_{6\beta}$) 2.11 (d, J = 13.8 Hz, $H_{8\beta}$) 2.19 (s, COMe) 3.49 (dd, J = 6.6, 0.9 Hz, $H_{1\alpha}$) 4.07 (ddd, J = 11.0, 7.5, 5.0 Hz, $H_{5\beta}$) 4.76 (d, J = 6.6 Hz, H_2) 6.24 (d, J = 2.8 Hz, H_{10}) 6.36 (dd, J = 2.8, 0.9 Hz, H_{11}).

^{13}C-NMR (CD_3OD) : (major) δ 18.3, 19.8, 25.0, 26.1, 34.8, 41.0, 41.9, 64.5, 79.7, 85.9, 90.8, 130.9, 140.6, 145.8, 165.0, 212.7 (C=O).

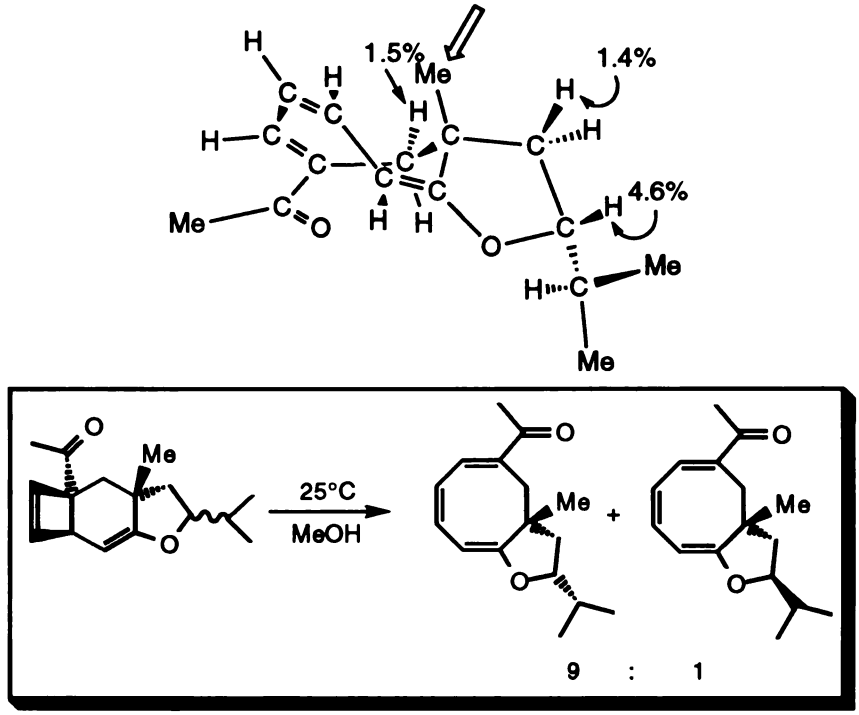
rac-(1S,5R,7R,9R)-1-9-Acetyl-5-isopropyl-7-methyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : (minor) δ 4.83 (d) 6.23 (d) 6.31 (d).

Large scale (0.2 g) photolysis in a test tube was performed and the residue was purified by silica gel chromatography (R_f = 0.53 with hexane/ethyl acetate = 5/1). The product was dark yellow in 60 % isolated yield with a

diastereomeric excess 80 %, measured by the integration of acetyl groups in ^{1}H-NMR spectroscopy.

The nOe results indicated that the major cycloöctatriene has 10-iPr group *trans* to 8-Me group. There was an enhancement of $H_{7\beta}$ (1.5 %), $H_{9\beta}$ (1.4 %) and $H_{10\beta}$ (4.6 %) when the 8-Me was irradiated.



rac-(8R,10S)-6-Acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

^{1}H-NMR (CD_3OD) : (major) δ 0.86 (d, J = 6.7 Hz, iPr) 0.96 (d, J = 6.7 Hz, iPr) 1.03 (s, 8-Me) 1.64 (dsept, J = 7.3, 6.7 Hz, 1H) 1.74 (dd, J = 12.2, 11.0 Hz, $H_{9\alpha}$) 1.89 (dd, J = 12.2, 5.2 Hz, $H_{9\beta}$) 2.39 (s, COMe) 2.89, 2.93 (AB q, J = 12.2 Hz, $2H_7$) 4.04 (ddd, J = 11.0, 7.3, 5.2 Hz, $H_{10\beta}$) 5.13 (d, J = 8.2 Hz, H_2) 5.88 (dd, J = 12.9, 5.9 Hz, H_4) 6.15 (dd, J = 12.9, 8.2 Hz, H_3) 7.29 (d, J = 5.9 Hz, H_5).

^{13}C-NMR (CD_3OD) : (major) δ 18.0, 19.2, 25.5, 26.4, 34.3, 35.1, 44.4, 85.2, 95.5, 108.9, 122.2, 132.6, 140.7, 143.3, 173.2, 201.7 (C=O).

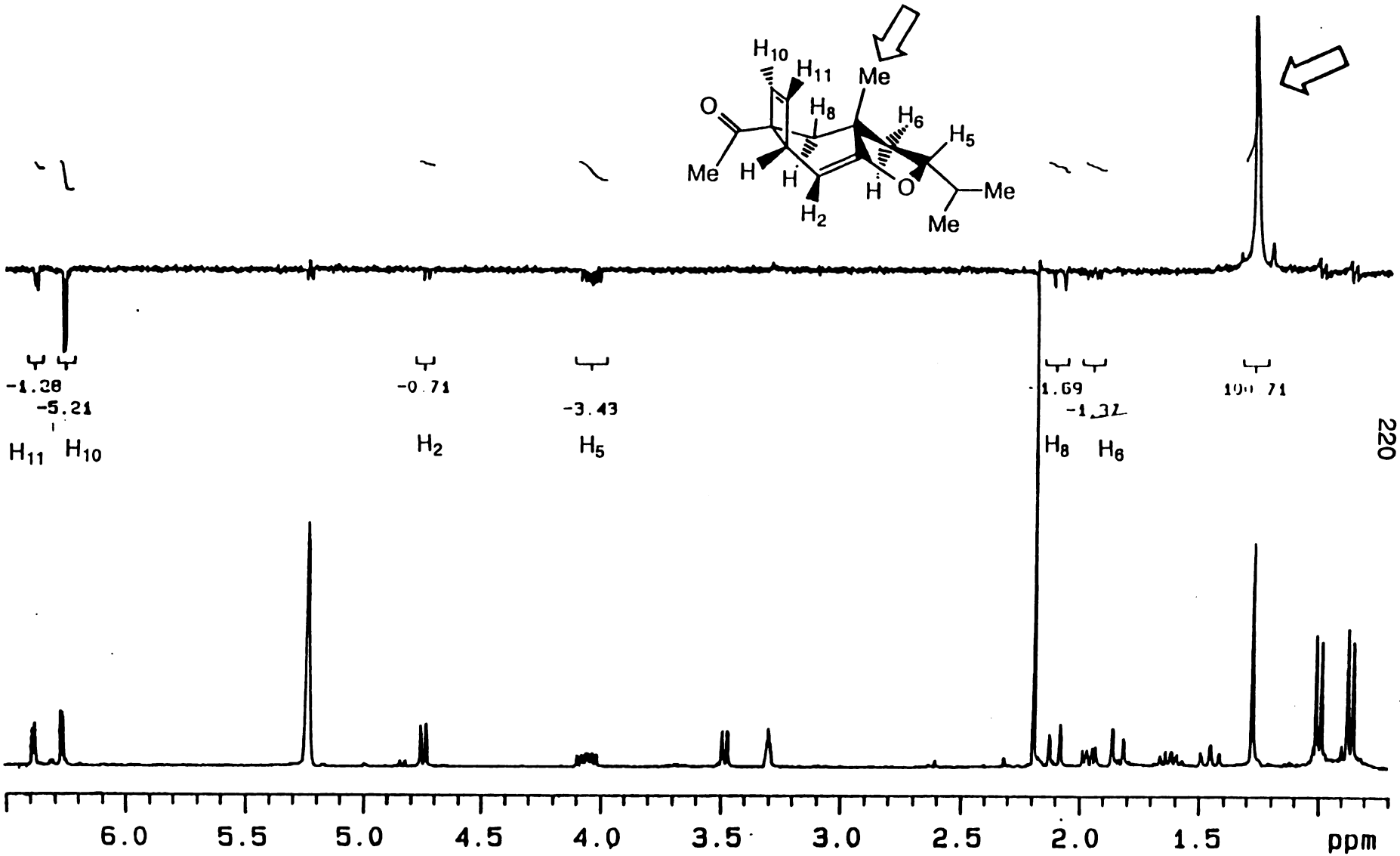


Figure 44. NOE experiments of rac-(1S,5S,7R,9R)-9-acetyl-5-isopropyl-7-methyl-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-diene (**o-I$_1$M$_3$CB**) in CD_3OD.

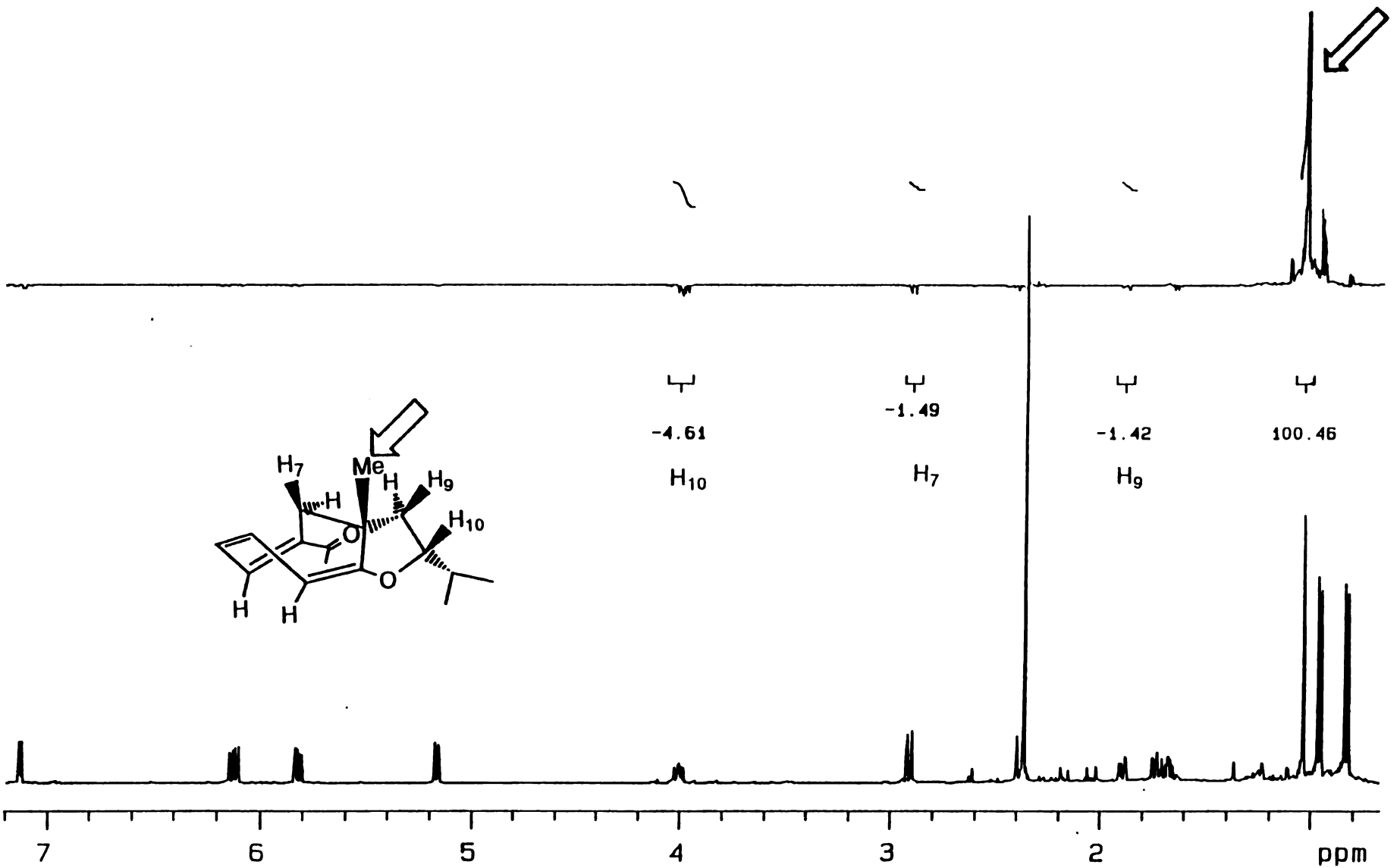


Figure 45. NOE experiments of rac-(8R,10S)-6-acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (**o-I$_1$M$_3$COT**) in $CDCl_3$.

rac-(8R,10R)-6-Acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene:

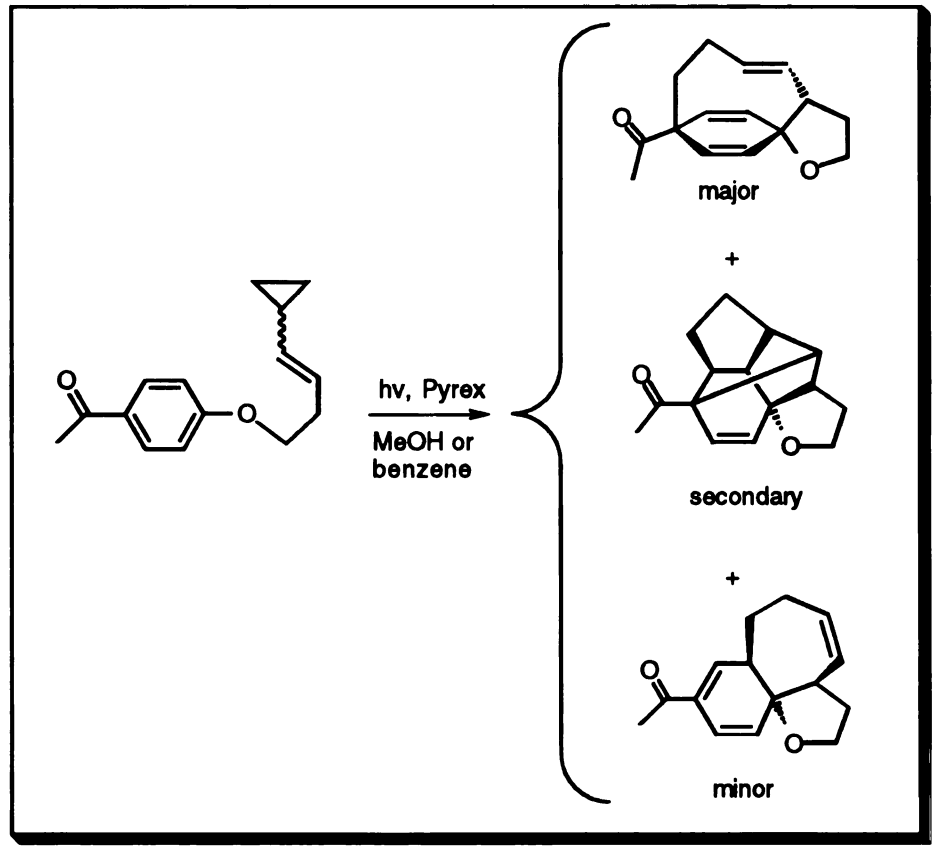
^{1}H-NMR (CD_3OD) : (minor) δ 2.40 (s, Me) 4.05 (m) 5.23 (d) 7.25 (d).

UV(MeOH) : (mixture) 313 nm (410), λ_{max} = 388 nm (4400).

Reactant : **p-C_4K**

A NMR scale solution of **p-C_4K** (1.7/1 = *trans*/*cis* mixture, 3.0 mg) and methyl benzoate (1.7 mg) in CD_3OD was photolyzed at >290 nm for 1h. The reactions were carried out repeatedly in different photolysis resource (313 nm) or solvent (C_6D_6) but results were identical except the product ratio (5:3:1 or 5:2:1). At complete conversion, there were three photoproducts: the 1,4-adduct (major); the polycyclic ketone (secondary) and the 1,2-adduct (minor), detected directly from ^{1}H-NMR spectra with 80 % overall chemical yield. The ratio is approximately 5 : 3 : 1 even though there is slightly change of ratio in the different runs .

A large scale photolysis (0.24 g ketone in 60 mL) was also carried out through Pyrex filter during 20 h. The secondary polycyclic ketone (R_f = 0.38 with hexane/ethyl acetate = 4/1) and 1,2-adduct (R_f = 0.35 with hexane/ethyl acetate = 4/1) could be isolated by silica gel column chromatography. The secondary polycyclic ketone could be further recrystallized from hexane/ethyl acetate mixture in refrigerator. However, the major 1,4-adduct wasn't stable on silica gel and generated a non-identified rearranged product after column chromatography (R_f = 0.20 with hexane/ethyl acetate = 4/1).



^{1}H NMR (CD_3OD) : (major) δ 1.87 (m, 2H) 2.03 (s, COMe) 2.07 (m, 2H) 2.20 (m, 2H) 2.31 (m, 1H) 3.94 (ddd, J = 15.4, 10.8, 9.1 Hz, 1H) 4.03 (ddd, J = 15.4, 8.5, 6.8 Hz, 1H) 5.03 (dd, J = 16.0, 9.3 Hz, 1H) 5.51 (dddd, J = 16.0, 11.5, 9.3, 2.8 Hz, 1H) 5.69 (dd, J = 11.1, 2.1 Hz, 1H) 5.74 (dd, J = 11.1, 2.4 Hz, 1H) 5.85 (dd, J = 10.2, 2.1 Hz, 1H) 5.94 (dd, J = 10.2, 2.4 Hz, 1H).

^{1}H NMR ($CDCl_3$) : (secondary) δ 1.49 (dddd, J = 12.6, 9.2, 6.2, 3.0 Hz, 1H) 1.59 (ddd, J = 12.3, 9.1, 3.0 Hz, 1H) 1.71 (ddd, J = 12.6, 9.1, 7.1 Hz, 1H) 2.02 (ddd, J = 9.7, 6.5, 1.9 Hz, 1H) 2.04 (dd, J = 1.6, 0.9 Hz, 1H) 2.07 (ddd, J = 12.3, 9.2, 7.1 Hz, 1H) 2.10 (dd, J = 6.2, 1.0 Hz, 1H) 2.16 (s, COMe) 2.19 (dd, J = 7.1, 6.5 Hz, 1H) 2.44 (ddt, J = 9.7, 9.1, 6.7 Hz, 1H) 2.55 (dd, J = 6.5, 1.0 Hz, 1H) 2.77 (ddd, J = 9.7, 1.9, 1.6 Hz, 1H) 3.95 (ddd, J = 11.7, 6.7, 6.5 Hz, 1H) 3.97 (dd, J = 11.7, 6.7 Hz, 1H) 5.52 (dd, J = 9.9, 1.6 Hz, 1H) 5.86 (dd, J = 9.9, 0.9 Hz, 1H).

^{13}C NMR ($CDCl_3$, DEPT) : δ 24.5 (2°), 26.7 (2°), 27.8 (1°), 38.4 (2°), 44.4 (3°), 46.7 (3°), 47.0 (3°), 47.6 (3°), 54.9 (3°), 59.1 (4°), 60.8 (2°), 84.8 (4°), 128.2 (3°), 134.0 (3°), 210.2 (4°, C=O).

IR(KBr) : 2958, 2920, 1693 (C=O), 1359, 1277, 1101, 757 cm^{-1}.

MS (m/e) : 230 (M^+), 215, 202, 187, 107, 81 (base), 43.

^{1}H NMR ($CDCl_3$) : (minor) δ 1.59 (m, 2H) 1.72 (dddd, J = 14.8, 7.2, 5.0, 3.6 Hz, 1H) 1.83 (dddd, J = 14.8, 8.6, 6.6, 2.2 Hz, 1H) 2.02 (m, 2H) 2.09 (s, COMe) 2.28 (ddd, J = 6.6, 6.4, 3.6 Hz, 1H) 2.87 (ddq, J = 8.0, 2.2, 1.5 Hz, 1H) 3.90 (ddd, J = 13.7, 8.6, 5.0 Hz, 1H) 4.11 (ddd, J = 13.7, 7.2, 2.2 Hz, 1H) 5.16 (dd, J = 10.5, 6.4 Hz, 1H) 5.52 (dd, J = 10.3, 1.5 Hz, 1H) 5.63 (ddd, J = 10.5, 6.1, 2.0 Hz, 1H) 5.70 (d, J = 8.0 Hz, 1H) 6.26 (dd, J = 10.3, 1.5 Hz, 1H).

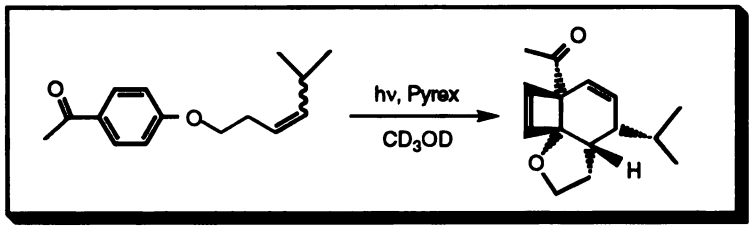
^{13}C NMR ($CDCl_3$) : δ 25.4, 26.7, 30.9, 34.8, 46.7, 52.7, 68.0, 84.6, 124.7, 127.6, 133.4, 133.7, 133.9, 136.8, 199.0 (C=O).

IR(CCl_4) : 3155, 2984, 1709 (C=O), 1669, 1382, 1096 cm^{-1}.

MS (m/e) : 230 (M^+), 187, 145, 107 (base), 81, 79, 43.

Reactant : **p-I_4K**

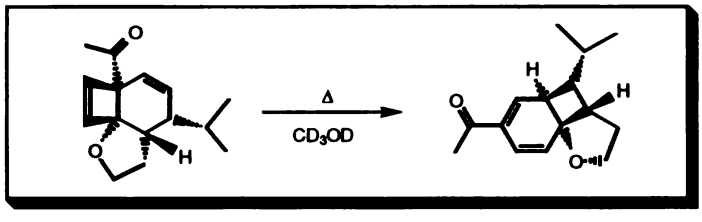
A 0.020 M CD_3OD solution of **p-I_4K** (1.7/1 = *trans/cis* mixture, determined by NMR, see above) was photolyzed in a NMR tube at >290 nm. The photoreaction was inefficient and couldn't be completed; product found decomposed gradually during the irradiation. The best condition was 10 h irradiation with barely 38 % chemical yield at 50 % conversion compared the integration of acetyl groups of **p-I_4K** and **p-I_4CB** to methoxy group of methyl benzoate in ^{1}H-NMR.



rac-(1S,4R,5R,9R)-1-Acetyl-4-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene:

^{1}H-NMR (CD_3OD) : δ 0.87 (d, J = 6.7 Hz, iPr) 1.01 (d, J = 6.7 Hz, iPr) 1.87 (ddd, J = 13.5, 10.5, 7.5 Hz, $H_{6\beta}$) 1.90 (ddd, J = 13.5, 7.5, 5.0 Hz, $H_{6\alpha}$) 1.93 (septd, J = 6.7, 6.3 Hz, 1H) 1.98 (dddd, J = 7.3, 6.3, 4.4, 1.7 Hz, $H_{4\beta}$) 2.12 (s, COMe) 2.35 (ddd, J = 10.5, 7.3, 5.0 Hz, $H_{5\beta}$) 3.79, 3.81 (AB q, J = 7.5 Hz, $2H_7$) 5.78 (dd, J = 10.3, 1.7 Hz, H_2) 5.94 (dd, J = 10.3, 4.4 Hz, H_3) 6.33, 6.43 (AB q, J = 2.9 Hz, H_{10}, H_{11}).

The above product was heated at 40°C for 48 h. The baseline of NMR had lots of noises and only portion of the peaks could be identified by ^{1}H-NMR spectroscopy.



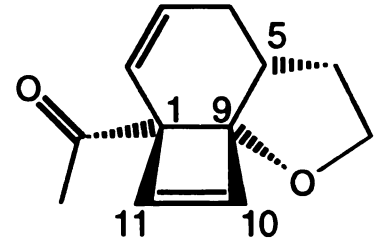
rac-(7R,8R)-4-Acetyl-7-isopropyl-11-oxatricyclo[6.3.0.0]undeca-2,4-diene:

^{1}H-NMR (CD_3OD) : δ 0.88 (d, J = 6.6 Hz, iPr) 0.99 (d, J = 6.6 Hz, iPr) 1.64 (m, 1H) 1.75 (m, $2H_9$) 2.00 (m, $H_{7\beta}$) 2.27 (m, H_8) 2.33 (s, COMe) 3.17 (ddd, J = 7.7, 5.5, 2.2 Hz, H_6) 4.12 (m, $2H_{10}$) 6.26 (d, J = 10.1 Hz, H_2) 6.45 (d, J = 10.1 Hz, H_3) 6.70 (d, J = 7.7 Hz, H_5).

Photolysis of Triplet bond Derivatives:

Photolyses in NMR tube scale of 4'-(4-trimethylsilyl-3-butyn-1-oxy)acetophenone and 4'-(3-butyn-1-oxy)acetophenone were undertaken at > 290 nm in d-methanol, d-acetonitrile, d-hexane or d-benzene (concentration 0.015 M), but only starting materials were recovered after more than 48 h irradiation. Irradiation of 4'-(3-butyn-1-oxy)acetophenone in 100 mL test tube (concentration 0.005 M in methanol) for 36 h was failed to react but decompose some ketone by checking with GC. Even sensitized photolysis of acetyl derivative of 4'-(4-trimethylsilyl-3-butyn-1-oxy)acetophenone in acetone (0.001 M) through quartz showed no cycloaddition.

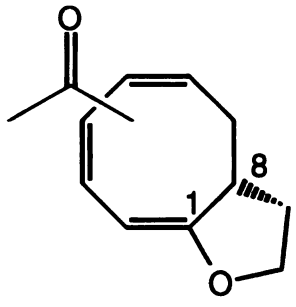
Table 35 Nuclear Overhauser Effect (nOe) on the Major Product of Various 1-Acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-dienes (**CB**)



Cyclobutene(**CB**)	Irradiated	H_{10}	$H_{4\beta}$	$H_{6\beta}$	$H_{7\beta}$
M_0-CB[a]	5-H_β	4.2 %	1.4 %	1.0 %	2.0 %
M_7-CB	5-H_β	6.6 %	3.3 %	3.9 %	5.0 %
I_7-CB	5-H_β	5.1 %	2.6 %	3.3 %	4.3 %
M_5M_7-CB	5-Me_β	6.1 %	2.6 %	1.8 %	5.0 %
M_5I_7-CB	5-Me_β	6.7 %	2.3 %	1.5 %	4.0 %
M_4M_5-CB	5-Me_β	2.4 %	1.0 %	1.5 %	1.2 %
$M_4M_5M_7$-CB	5-Me_β	7.2 %	2.3 %	1.7 %	4.3 %
$M_3M_4M_5M_7$-CB	5-Me_β	3.9 %	3.2 %	1.4 %	5.1 %

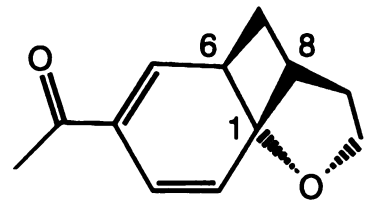
a: non-substituted 1-acetyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-dienes

Table 36 Nuclear Overhauser Effect (nOe) on the Major Product of Various 4- or 6-Acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-trienes (**COT**)



Cycloöctatriene (**COT**)	Irradiated	3-H	7-Hβ	9-Hβ	10-Hβ	2-H
original **4-COT**	8-Hβ	4.1 %	4.8 %	5.4 %	1.8 %	
4-M$_{10}$COT	8-Hβ	3.0 %	4.0 %	3.7 %	1.9 %	
4-H$_{10}$COT	8-Hβ	1.2 %	3.3 %	2.7 %	1.5 %	
4-M$_8$H$_{10}$COT	8-Meβ	0.3 %	1.9 %	1.3 %	4.3 %	0.6 %
6-H$_{10}$COT	8-Hβ		1.0 %	0.9 %	3.5 %	
6-M$_8$H$_{10}$COT	8-Meβ		1.5 %	1.4 %	4.6 %	

Table 37 Nuclear Overhauser Effect (nOe) on the Major Product of Various 4-Acetyl-11-oxatricyclo[6.3.0.0^{1,6}] undeca-2,4-dienes (**CH**)



Cyclohexadiene (**CH**)	Irradiated	2-H	7-H$_\beta$	9-H$_\beta$	10-H$_\beta$
M$_8$M$_9$-CH	8-Me$_\beta$	3.3 %	2.3 %	5.8 %	
M$_7$M$_8$-CH	8-Me$_\beta$	3.2 %	1.0 %	3.0 %	
M$_7$M$_8$M$_{10}$CH	8-Me$_\beta$	2.3 %	0.6 %	2.4 %	1.9 %

Cyclohexadiene (**CH**)	Irradiated	5-H	7-	10-
M$_8$M$_9$-CH	6-H$_\alpha$	13.2 %	4.4 % (7-H$_\alpha$)	8.7 % (10-H$_\alpha$)
M$_7$M$_8$M$_{10}$-CH	6-H$_\alpha$	8.9 %	1.0 % (7-Me)	1.0 % (10-Me)

Table 38 GC Response Factors of Various Acetophenones (**K**) and Cycloöctatrienes (**COT**)

Isolated product / Internal standard	Exp'l	Calc'd
Acetophenone (**Ap**) / C_{12}	1.92	1.72
Ap / C_{15}	2.18	2.15
Ap / C_{16}	2.24	2.28
Ap / Ethyl phenyl acetate	1.10	1.28
p-M$_0$K / $C_{18}OH$	1.44	1.64
p-M$_0$COT / $C_{18}OH$	1.83	1.64
p-M$_1$K / n-Heptyl benzoate	1.18	1.09
p-M$_1$COT / n-Heptyl benzoate	1.33	1.09
p-I$_1$K / n-Octyl benzoate	0.96	1.00
p-I$_1$COT / n-Octyl benzoate	1.12	1.00
p-I$_1$M$_3$K / m-Dibutyl pathalate	1.17	0.93
p-I$_1$M$_3$COT / m-Dibutyl pathalate	0.86	0.93
o-I$_1$K / n-Pentyl benzoate	0.62	0.78
o-I$_1$COT / n-Pentyl benzoate	0.71	0.78
o-I$_1$M$_3$K / n-Pentyl benzoate	0.89	0.73
o-I$_1$M$_3$COT / n-Pentyl benzoate	0.88	0.73
p-C$_4$K / m-Dibutyl phthalate	0.93	1.00
polycyclic-K / m-Dibutyl phthalate	0.90	1.00
p-C$_4$K / n-Octyl benzoate	0.95	1.00
polycyclic-K / n-Octyl benzoate	0.99	1.00
p-I$_4$CH / n-Heptyl benzoate	0,89	0.93

Table 39 HPLC Response Factors of Acetophenones (**K**) and Cyclohexadienes (**CH**)

Isolated product / Internal standard	R_f value
p-M_3M_4K	0.017
p-M_3M_4CH	0.014

Nuclear Overhauser Enhancement (NOE)

The following parameters have been used for all NOE experiments

d1 = 15-18, the length of first delay and approximately five times of T1

bs = 2 or 4, the block size in order to store the data periodically

il = 'y', in order to run the arrayed experiments

gain = 25, receiver gain

temp = 25, to set the temperature of sample in the probe

dpwr = 6-10, the decoupler power

nt = 64, 96, 128 or 160, the number of transients to be acquired

time, how much time does the experiment take

dof, to set the frequencies of the protons which are irradiated

sd, to obtain the frequencies of the protons which are irradiated

da, to assure the corrected frequencies of the irradiated protons

dssa, to display the overall spectra consecutively

clradd, to delete the original spectrum in experiment 5

spadd, to generate the new space in experiment 5

addi, to display both original and irradiated spectra

sub, to substrate the original and irradiated spectra

The procedure of calculation was shown below. A structure was drawn in a new file in CAChe program by the help of three dimension stereotype glasses. This structure was minimized by molecular mechanics (MM2) to obtain the rough geometry and stabilization energy.

Reopen the CAChe file to confirm the structure followed the valence bond rule. The rough geometry was then optimized at the semi-empirical level (AM1) by using unrestricted Hartree-Fock (UHF) treatment to obtain the better geometry. This procedure was repeated a few times by little variation of bond length and angle to acquire the best geometry and heat of formation. The best geometry was translated to Chem3D file. The structure in cylindrical bond type and dihedral angle were obtained and saved in ChemDraw file for conformational analysis. The structure in ball and stick type was saved for the display of nOe experimental data.

APPENDIX

Table 40 Quantum Yield Determination of Formation of 1-Acetyl-8-oxatricyclo-[7.2.0.$0^{5,9}$]undeca-2,10-diene at 313 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 2.50 x 10^{-4} M in methanol, λ = 343 nm

Actinometers: [VP] = 1.05 x 10^{-2} M, [Ethyl phenyl acetate] = 1.20 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.25	1.50	0.75	7.39 x 10^{-5}	0.14
2.25	1.45	0.80	7.95 x 10^{-5}	0.15
2.25	1.49	0.76	7.48 x 10^{-5}	0.14

A(AP)/A(std.) = 0.137

Actinometers: [AP] = 1.81 x 10^{-4} M, I_0 = 5.43 x 10^{-4} M

3. Irradiation time: 20 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 90°C, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.14

Table 41 Quantum Yield Determination of Formation of 4-Acetyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 1.05×10^{-2} M, [$C_{18}OH$] = 1.00×10^{-3} M in methanol

Actinometers: [VP] = 1.05×10^{-2} M, [Ethyl phenyl acetate] = 1.20×10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.230	0.421	4.22×10^{-4}	0.20
0.235	0.430	4.31×10^{-4}	0.21
0.226	0.414	4.09×10^{-4}	0.19

A(AP)/A(std.) = 0.534

Actinometers: [AP] = 7.05×10^{-4} M, $I_0 = 2.10 \times 10^{-3}$ M

3. Irradiation time: 45 min

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 150°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 89°C, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.20

Table 42 Quantum Yield Determination of Formation of 1-Acetyl-7-methyl-8-oxatricyclo-[7.2.0.0^{5,9}]undeca-2,10-diene at 313 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 2.04 x 10^{-4} M in methanol, λ = 344 nm

Actinometers: [VP] = 1.99 x 10^{-1} M, [C_{12}] = 4.40 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.20	1.20	1.00	9.98 x 10^{-5}	0.05
2.20	1.16	1.04	1.03 x 10^{-4}	0.05
2.20	1.31	0.89	8.87 x 10^{-5}	0.04

A(AP)/A(std.) = 0.076

Actinometers: [AP] = 6.39 x 10^{-4} M, I_0 = 1.94 x 10^{-3} M

3. Irradiation time: 25 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.05

Table 43 Quantum Yield Determination of Formation of 4-Acetyl-10-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 1.00×10^{-2} M, [n-Heptyl benzoate] = 2.10×10^{-3} M in methanol

Actinometers: [VP] = 1.99×10^{-1} M, [C_{12}] = 4.40×10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.231	0.307	5.72×10^{-4}	0.10
0.254	0.338	6.29×10^{-4}	0.11
0.231	0.307	5.72×10^{-4}	0.10

A(AP)/A(std.) = 0.234

Actinometers: [AP] = 1.98×10^{-3} M, $I_0 = 5.99 \times 10^{-3}$ M

3. Irradiation time: 1.5 h

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 145°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.10

Table 44 Quantum Yield Determination of Formation of 1-Acetyl-7-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene at 313 nm in Methanol (1, COT -> CB)

1. Before irradiation

Sample: [COT] = 2.07 x 10^{-4} M in methanol, λ = 346 nm

Actinometers: [VP] = 9.96 x 10^{-2} M, [C_{15}] = 1.90 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.44	1.43	1.01	8.41 x 10^{-5}	0.08
2.44	1.42	1.02	8.50 x 10^{-5}	0.09
2.44	1.44	1.00	8.33 x 10^{-5}	0.08

A(AP)/A(std.) = 0.092

Actinometers: [AP] = 3.80 x 10^{-4} M, I_0 = 1.15 x 10^{-3} M

3. Irradiation time: 25 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.08

Table 45 Quantum Yield Determination of Formation of 1-Acetyl-7-isopropyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene at 313 nm in Methanol (2, COT -> CB)

1. Before irradiation

Sample: [COT] = 2.00 x 10^{-4} M in methanol, λ = 346 nm

Actinometers: [VP] = 9.96 x 10^{-2} M, [C_{12}] = 2.20 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.36	1.32	1.04	8.82 x 10^{-5}	0.11
2.36	1.22	1.14	9.60 x 10^{-5}	0.12
2.36	1.60	0.76	6.41 x 10^{-5}	0.08

A(AP)/A(std.) = 0.065

Actinometers: [AP] = 2.67 x 10^{-4} M, I_0 = 8.28 x 10^{-4} M

3. Irradiation time: 30 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.10

6. No significant change on COT concentration by adding 4-methoxy-acetophenone

Table 46 Quantum Yield Determination of Formation of 4-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 1.01×10^{-2} M, [n-Octyl benzoate] = 2.00×10^{-3} M in methanol

Actinometers: [VP] = 9.96×10^{-2} M, [C_{15}] = 1.90×10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	A(product)/A(std.)	Concentration	Φ
0.256	0.287	5.72×10^{-4}	0.10
0.298	0.334	6.68×10^{-4}	0.12
0.410	0.459	9.19×10^{-4}	0.17
0.343	0.384	7.66×10^{-4}	0.14

A(AP)/A(std.) = 0.430

Actinometers: [AP] = 1.78×10^{-3} M, $I_0 = 5.41 \times 10^{-3}$ M

3. Irradiation time: 2 h

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 160°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.12

Table 47 Quantum Yield Determination of Formation of 1-Acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene at 313 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 3.31 x 10^{-4} M in methanol, λ = 334 nm

Actinometers: [VP] = 1.05 x 10^{-2} M, [Ethyl phenyl acetate] = 1.20 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.33	1.78	0.55	7.79 x 10^{-5}	0.24
2.33	2.08	0.25	3.56 x 10^{-5}	0.11
2.33	2.10	0.23	3.25 x 10^{-5}	0.10

A(AP)/A(std.) = 0.079

Actinometers: [AP] = 1.04 x 10^{-4} M, I_0 = 3.13 x 10^{-4} M

3. Irradiation time: 15 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 90°C, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.11

Table 48 Quantum Yield Determination of Formation of 1-Acetyl-7-isopropyl-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene at 366 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 2.81 x 10^{-4} M, λ = 334 nm

Actinometers: [Benzophenone] = 1.00 x 10^{-2} M, [Benzhydrol] = 1.00 x 10^{-1} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
1.98	0.80	1.18	1.70 x 10^{-4}	0.11
1.98	0.80	1.18	1.70 x 10^{-4}	0.11
1.98	1.22	0.76	1.11 x 10^{-4}	0.07

Actinometers: Δ [B.P.] = 1.27 x 10^{-3} M*, I_0 = 1.59 x 10^{-3} M

3. Irradiation time: 13 min

4. UV conditions

Actinometers: average of 6 tubes

5. Quantum yield Φ = 0.11

* : Average of two tubes.

Table 49 Quantum Yield Determination of Formation of 4-Acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 1.07 x 10^{-2} M, [meta Dibutyl phthalate] = 8.99 x 10^{-4} M in methanol

Actinometers: [VP] = 1.05 x 10^{-2} M, [Ethyl phenyl acetate] = 1.20 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/A(s)	Concentration	Φ
0.549	0.472	5.70 x 10^{-4}	0.36
0.289	0.248	3.01 x 10^{-4}	0.19
0.290	0.249	3.09 x 10^{-4}	0.19

A(AP)/A(std.) = 0.409

Actinometers: [AP] = 5.40 x 10^{-4} M, I_0 = 1.62 x 10^{-3} M

3. Irradiation time: 50 min

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 160°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 90°C, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.19

Table 50 Quantum Yield Determination of Formation of 9-Acetyl-5-isopropyl-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene at 313 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 2.37 x 10^{-4} M in methanol, λ = 377 nm

Actinometers: [VP] = 1.05 x 10^{-1} M, [C_{12}] = 5.10 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
1.07	0.48	0.59	1.40 x 10^{-4}	0.10
1.07	0.47	0.60	1.47 x 10^{-4}	0.10
1.07	0.47	0.60	1.47 x 10^{-4}	0.10

A(AP)/A(std.) = 0.022

Actinometers: [AP] = 5.06 x 10^{-4} M, I_0 = 1.53 x 10^{-3} M

3. Irradiation time: 15 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.10

Table 51 Quantum Yield Determination of Formation of 6-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 1.06×10^{-2} M, [n-Pentyl benzoate] = 1.30×10^{-3} M in methanol

Actinometers: [VP] = 1.02×10^{-1} M, [C_{12}] = 2.40×10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.877	0.623	8.10×10^{-4}	0.25
0.758	0.538	7.01×10^{-4}	0.23
0.974	0.692	9.00×10^{-4}	0.27

A(AP)/A(std.) = 0.237

Actinometers: [AP] = 1.09×10^{-3} M, $I_0 = 3.29 \times 10^{-3}$ M

3. Irradiation time: 80 min

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 145°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.25

Table 52 Quantum Yield Determination of Formation of 9-Acetyl-5-isopropyl-7-methyl-4-oxatricyclo-[7.2.0.0^{3,7}]undeca-2,10-diene at 313 nm in Methanol (COT -> CB)

1. Before irradiation

Sample: [COT] = 5.75 x 10^{-4} M in methanol, λ = 388 nm

Actinometers: [VP] = 9.84 x 10^{-2} M, [C_{12}] = 3.60 x 10^{-3} M in benzene

2. After irradiation at 25°C

Before OD	After OD	Δ[Absorption]	ΔConcentration	Φ
2.50	1.55	0.95	2.10 x 10^{-4}	0.21
2.50	1.60	0.90	1.99 x 10^{-4}	0.20
2.50	1.60	0.96	2.13 x 10^{-4}	0.21

A(AP)/A(std.) = 0.044

Actinometers: [AP] = 3.04 x 10^{-4} M, I_0 = 9.22 x 10^{-4} M

3. Irradiation time: 10 min

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.21

Table 53 Quantum Yield Φ Determination of Formation of 6-Acetyl-10-isopropyl-8-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol (K -> COT)

1. Before irradiation

Sample: [K] = 9.3 x 10^{-3} M, [n-Pentyl benzoate] = 3.00 x 10^{-3} M in methanol

Actinometers: [VP] = 9.84 x 10^{-2} M, [C_{12}] = 3.60 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.177	0.156	4.67 x 10^{-4}	0.15
0.189	0.167	4.93 x 10^{-4}	0.16
0.180	0.158	4.75 x 10^{-4}	0.15

A(AP)/A(std.) = 0.152

Actinometers: [AP] = 1.05 x 10^{-3} M, I_0 = 3.18 x 10^{-3} M

3. Irradiation time: 45 min

4. GC conditions

Sample: 15 meter DB1 Megabore Column, Varian 1400, He = 25 mL/min, column = 130°C, injector = 240°C, detector = 230°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.15

Table 54 Quantum Yield Determination of Formation of Polycyclic Ketone and 1,2-Adduct from 4'-(4-Cyclopropyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol (1)

1. Before irradiation

Sample: [K] = 1.02 x 10^{-2} M, [meta Dibutyl phthalate] = 1.00 x 10^{-3} M in methanol

Actinometers: [VP] = 1.05 x 10^{-2} M, [Ethyl phenyl acetate] = 1.20 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.370	0.333	3.33 x 10^{-4}	0.20
0.351	0.316	3.16 x 10^{-4}	0.19
0.443	0.399	3.99 x 10^{-4}	0.24

A(AP)/A(std.) = 0.421

Actinometers: [AP] = 5.56 x 10^{-4} M, I_0 = 1.67 x 10^{-3} M

3. Irradiation time: 1 h

4. GC conditions

Sample: 30 meter DBWAX Megabore Column, Varian Aerograph 1400, He = 30 mL/min, column = 180°C, injector = 150°C, detector = 230°C.

Actinometers: 30 meter DBWAX Megabore Column, Varian Aerograph 1400, He = 30 mL/min, column = 90°C, injector = 150°C, detector = 230°C.

5. Quantum yield Φ = 0.21

Table 55 Quantum Yield Determination of Formation of Polycyclic Ketone and 1,2-Adduct from 4'-(4-Cyclopropyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol (2)

1. Before irradiation

Sample: [K] = 1.05 x 10^{-2} M, [n-Octyl benzoate] = 2.00 x 10^{-3} M in methanol

Actinometers: [VP] = 9.92 x 10^{-2} M, [C_{16}] = 4.10 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.227	0.225	4.50 x 10^{-4}	0.15
0.229	0.227	4.55 x 10^{-4}	0.15
0.243	0.241	4.82 x 10^{-4}	0.16

A(AP)/A(std.) = 0.109

Actinometers: [AP] = 9.99 x 10^{-4} M, I_0 = 3.03 x 10^{-3} M

3. Irradiation time: 1 h

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 165°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 90C, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.15

Table 56 Quantum Yield Determination of Formation of Polycyclic Ketone and 1,2-Adduct from 4'-(4-Cyclopropyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol (3)

1. Before irradiation

Sample: [K] = 1.05×10^{-2} M, [n-Octyl benzoate] = 2.00×10^{-3} M in methanol

Actinometers: [VP] = 1.05×10^{-1} M, [C_{12}] = 5.10×10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.376	0.372	7.46×10^{-4}	0.15
0.427	0.423	8.45×10^{-4}	0.17

A(AP)/A(std.) = 0.169

Actinometers: [AP] = 1.66×10^{-3} M, $I_0 = 4.98 \times 10^{-3}$ M

3. Irradiation time: 1.5 h

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 165°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.16

Table 57 Quantum Yield Determination of Formation of 4-Acetyl-7,8-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene at 313 nm in Methanol (K -> CH)

1. Before irradiation

Sample: [K] = 1.22 x 10^{-2} M, [Methyl benzoate] = 3.96 x 10^{-2} M in methanol

Actinometers: [VP] = 1.03 x 10^{-1} M, [C_{12}] = 3.60 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
1.659	0.023	9.20 x 10^{-4}	0.07
2.133	0.030	1.18 x 10^{-3}	0.09
1.180	0.017	6.57 x 10^{-4}	0.05

A(AP)/A(std.) = 0.620

Actinometers: [AP] = 4.29 x 10^{-3} M, I_0 = 1.29 x 10^{-2} M

3. Irradiation time: 5 h

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. HPLC condition

Sample: 4.6 x 250 mm, Dyn Microsorb Silica Column, Flow Rate 1.0 mL/ min, 80 % Hexane / 20 % Ethyl acetate, 290 nm.

6. Quantum yield Φ = 0.07

Table 58 Quantum Yield Determination of Formation of 4'-(3,4-Dimethyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol (CH -> K) and Quenching Study by 2,5-Dimethyl-2.4-hexadiene

1. Before irradiation

Sample: [CH] = 5.01 x 10^{-3} M, [Methyl benzoate] = 8.09 x 10^{-2} M in methanol

Actinometers: [VP] = 1.01 x 10^{-1} M, [C_{12}] = 3.70 x 10^{-3} M in benzene

2. After irradiation at 25°C

$[Q]^*$, M	$A_{(photo)} / A_{(std)}$	Φ_0 / Φ
0.000	0.650	1.00
0.089	0.448	1.45
0.871	0.119	5.39

Actinometers: [AP] = 3.77 x 10^{-4} M, I_0 = 1.14 x 10^{-3} M

3. Irradiation time: 1 h

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. HPLC conditions

Sample: 4.6 x 250 mm, Dyn Microsorb Silica Column, Flow Rate 1.0 mL/min, 80 % Hexane / 20 % Ethyl acetate, 290 nm.

6. Quantum yield Φ = 0.78, $k_q\tau$ = 5.0

* : Quencher = 2,5-dimethyl-2.4-hexadiene

Table 59 Quantum Yield Determination of Formation of 4'-(3,4-Dimethyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol (CH -> K) and Quenching Study by Sorbic Acid

1. Before irradiation

Sample: [CH] = 4.98 x 10^{-3} M, [Methyl benzoate] = 8.36 x 10^{-2} M in methanol

Actinometers: [VP] = 1.01 x 10^{-1} M, [C_{12}] = 3.70 x 10^{-3} M in benzene

2. After irradiation at 25°C

$[Q]^*$, M	$A_{(photo)} / A_{(std)}$	Φ_0 / Φ
0.000	0.591	1.00
0.121	0.400	1.49
1.379	0.090	6.58

Actinometers: [AP] = 3.98 x 10^{-4} M, I_0 = 1.21 x 10^{-3} M

3. Irradiation time: 1 h

4. GC conditions

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. HPLC conditions

Sample: 4.6 x 250 mm, Dyn Microsorb Silica Column, Flow Rate 1.0 mL/min, 80 % Hexane / 20 % Ethyl acetate, 290 nm.

6. Quantum yield Φ = 0.70, $k_q\tau$ = 4.1

* : Quencher = sorbic acid

Table 60 Quantum Yield Determination of Formation of 4-Acetyl-7-isopropyl-11-oxabicyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene at 313 nm in Methanol (K -> CH)

1. Before irradiation

Sample: [K] = 1.23 x 10^{-2} M, [n-Heptyl benzoate] = 1.55 x 10^{-3} M in methanol

Actinometers: [VP] = 1.02 x 10^{-1} M, [C_{12}] = 2.40 x 10^{-3} M in benzene

2. After irradiation at 25°C

A(product)/A(std.)	Mol(p)/Mol(s)	Concentration	Φ
0.515	0.458	7.11 x 10^{-4}	0.08
0.773	0.688	1.08 x 10^{-3}	0.12
0.515	0.458	7.11 x 10^{-4}	0.08

A(AP)/A(std.) = 0.642

Actinometers: [AP] = 2.96 x 10^{-3} M, I_0 = 8.88 x 10^{-3} M

3. Irradiation time: 5 h

4. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 150°C, injector = 200°C, detector = 220°C.

Actinometers: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 50°C for 5 min, 50-100°C 10°C/min, 100°C for 1.5 min, 100-185°C 15°C/min, 185°C for 10 min, injector = 200°C, detector = 220°C.

5. Quantum yield Φ = 0.08

Table 61 Chemical Yield Determination of 4-Acetyl-10-isopropyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene at 313 nm in Methanol

1. Before irradiation

Sample: [K] = 1.01 x 10^{-2} M, [n-Octyl benzoate] = 2.00 x 10^{-3} M in methanol

2. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 160°C, injector = 200°C, detector = 220°C.

3. Chemical yield = 95.0% (120 min.)

Irradiation Time (min.)	A(Ketone)/A(std.)	Concentration of Reacted Ketone	A(P)/A(s)
0	5.260	0	-----
30	5.168	1.77 x 10^{-4}	0.078
60	5.074	3.57 x 10^{-4}	0.159
120	4.893	7.06 x 10^{-4}	0.298

Table 62 Chemical Yield Determination of Polycyclic Ketone and 1,2-Adduct from 4'-(4-Cyclopropyl-3-buten-1-oxy)acetophenone at 313 nm in Methanol

1. Before irradiation

Sample: [K] = 1.05 x 10^{-2} M, [n-Octyl benzoate] = 2.00 x 10^{-3} M in methanol

2. GC conditions

Sample: 15 meter DB210 Megabore Column, Varian 3400, He = 25 mL/min, column = 160°C, injector = 200°C, detector = 220°C.

3. Chemical yield = 45.0% (60 min.)

Irradiation Time (min.)	A(Ketone)/A(std.)	Concentration of Reacted Ketone	A(P/A(s)
0	5.526	0	-----
20	5.347	3.40 x 10^{-4}	0.099
40	5.149	7.17 x 10^{-4}	0.180
60	4.995	1.01 x 10^{-3}	0.228

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