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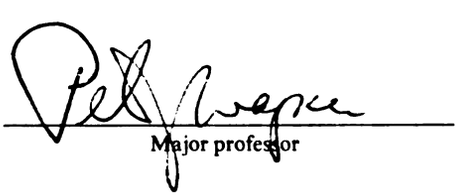
Nuances In Intramolecular Cycloadditions
Of Double Bonds To Triplet Benzene Rings

presented by

Robert Paul Smart

has been accepted towards fulfillment
of the requirements for

Ph.D. degree in Chemistry



Major professor

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NUANCES IN INTRAMOLECULAR CYCLOADDITIONS OF DOUBLE BONDS TO TRIPLET BENZENE RINGS

By

Robert Paul Smart

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ABSTRACT

NUANCES IN INTRAMOLECULAR CYCLOADDITIONS OF DOUBLE BONDS TO TRIPLET BENZENE RINGS

By

Robert Paul Smart

The regioselectivity with which *ortho*-substituted *p*-butenoxyacetophenones undergo intramolecular triplet [2+2] photocycloaddition to tricycloundeca-2,10-dienes was investigated. Both electron donating and withdrawing groups produce the same absolute selectivity: addition of the remote double bond exclusively toward the *ortho* ring substituent. It is likely that the observed regioselectivity is associated with differentiating effects on both the initial triplet-state cycloaddition and the subsequent electrocyclic reactions. Steric interactions between *meta*-ring substituents and the approaching double bond can effectively alter the regiochemical course of the reaction. Conformational restrictions imposed by the tether connecting the arene and alkene attenuate the directing influence exerted by the *ortho* substituents. The regioselectivity associated with the *ortho* [2+2] photocycloaddition process involving an *ortho* alkyl group may be due solely (or in part) to the formation of a triplet dienol. Independent studies have shown that the triplet biradical of the photoenol lives for microseconds. There should be sufficient spin density at the *para* carbon to produce some hexenyl radical cyclization prior to decay to the ground state enol. Such a process would occur exclusively from the syn biradical, effectively bypassing the direct interaction of the triplet benzene and the double bond.

Photosensitization techniques have been performed on cyano and carboxy analogs of *p*-butenoxyacetophenones that do not absorb in the near UV range or do not efficiently form excited triplet states. Triplet-triplet energy transfer from the solvent acetone results in efficient [2+2] photocycloadditon to form cyano and ester substituted tricycloundeca-2,10-dienes and tricyclododeca-2,11-dienes in 50-75% isolated yields. In most but not all cases, the same products were formed by direct irradiation at 254 nm.

Although the main thrust of this project has been mechanistic, the ultimate goal is to incorporate the findings in the synthesis of natural products. Many natural products have 8/5 fused and 4/5/6 ring systems as their skeletal framework; one such class is the ophiobolins. The knowledge of the factors which control regioselectivity of [2+2] cycloaddition and efficiency of triplet sensitization of non-keto aromatics provides a firm foundation toward use of this reaction for the synthesis of natural products.

Acknowledgments

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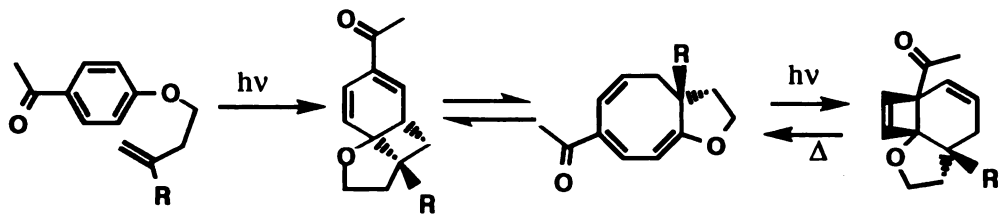
INTRODUCTION

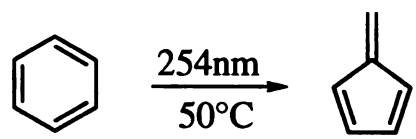
Research Objective

The overall goal of this research was to gain a clearer understanding of the mechanism and synthetic potential of photochemical cycloadditions of excited triplet aromatic substrates to olefins. This study focused on two separate but related aspects: 1) to determine the regioselectivity of the initial [2+2] *ortho* addition onto more highly substituted benzene rings and 2) to examine the effects of triplet sensitization techniques on related aromatic substrates that do not absorb in the near UV range or do not efficiently form excited triplet states when irradiated. The results presented, in conjunction with previous work, will hopefully allow this reaction to be exploited in the synthesis of natural products.



Background

The onset of modern arene photochemistry arose from a landmark discovery of the photoisomerization of benzene to fulvene (**1**).[1]



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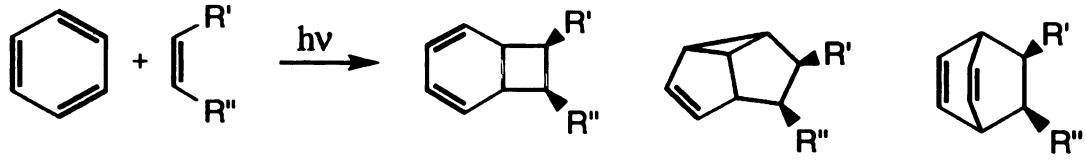
This finding undermined the established belief that benzene was photochemically inert. Much of the subsequent arene photochemical research has been centered around the interactions of benzene with alkenes.

During the past few decades, arene-alkene photocycloaddition has profoundly affected organic synthesis as demonstrated by the many successful synthetic approaches that currently utilize this reaction as a key step.[2, 3, 4, 5] Use of mild photochemical activation in construction of complex polycyclic molecules allows for control of the chemo-, regio-, and stereoselectivity that is not fully accessible by more traditional synthetic procedures.

Irradiation of benzene at 254 nm in the presence of an alkene can lead to formation of 1,2-(*ortho*), 1,3-(*meta*), and 1,4-(*para*) cycloadducts depending on the substitution pattern of the arene and olefin. For example, intermolecular photoaddition of benzene to 1,2-disubstituted ethylene leads to bicyclo[4.2.0]octa-2,4-diene **2**, tricyclo[3.3.0.$0^{4,6}$]oct-2-enes **3**, or bicyclo[2.2.2] octa-2,5-dienes **4** depending upon the electronic nature of the ethylene substituents. For all modes of cycloaddition, the stereochemistry of the alkene is preserved in the products.[6] Generally, *para* cycloaddition is very inefficient and rarely observed. In contrast, both *ortho* and *meta* photocycloadditions are facile and occur with a wide variety of substituted double bonds and aromatic rings.



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Mechanistic Considerations

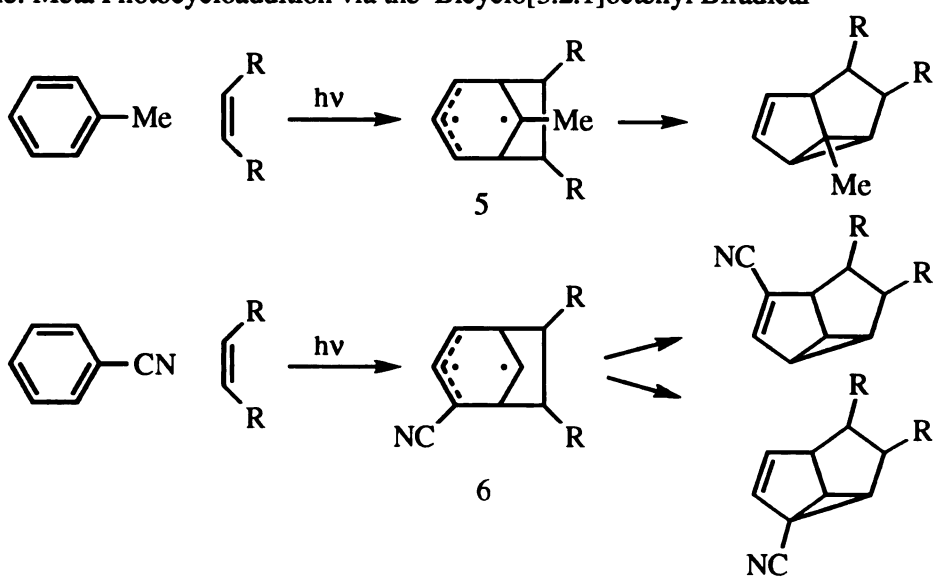
Since the initial discovery of photocycloaddition of excited benzenes to alkenes,[7] the factors which influence the mode of addition have been investigated. Several groups have focused intensely on the mechanism behind this synthetically useful reaction.[5, 8] The reaction is believed to occur from the singlet manifold of the arene. Morrison and co-workers studied sensitization of the photocycloaddition of 6-phenylhex-2-ene.[9, 10] Benzene-sensitization of the cis-isomer produced both cis-trans isomerization and cyclization at approximately equal rates. Alternatively, triplet sensitization using

benzophenone or acetone produced no cycloaddition products. Quenching studies using cis-piperylene provided additional information. Cis-piperylene was ineffective at quenching both cycloaddition and cis-trans isomerization of 6-phenylhex-2-ene.

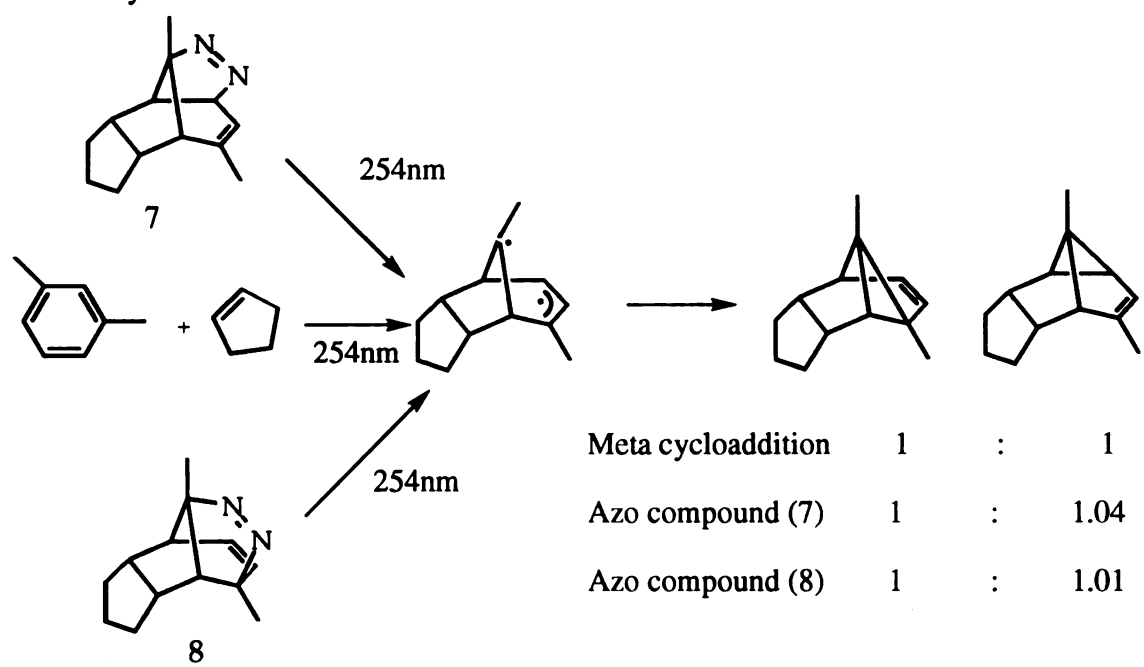
Mattay[11] provided additional evidence for singlet state cycloaddition. The quantum yields for *ortho*, *meta*, or *para* cycloaddition of benzene to 1,3-dioxoles were reduced up to 70% when irradiated in the presence of xenon compared to argon purged samples; xenon is known to accelerate singlet-triplet intersystem crossing. Thus, Mattay concluded that the photocycloaddition of 1,3-dioxoles and benzene involve exclusively the singlet excited state.

Bryce-Smith[12],Gilbert[13, 14] and Sheridan[15, 16] have suggested the possible presence of a biradical intermediary with the bicyclo[3.2.1] octenyl skeletons, **5** and **6**, in the *meta* photocycloaddition process. Based on the high degree of regioselectivity associated with this reaction, it is believed that biradical formation must be superseded by an interaction of the excited benzene and alkene. The excited complex is highly polarized due to the differing behavior of electron donating and electron withdrawing substituents on the arene ring.

Scheme: Meta Photocycloaddition via the Bicyclo[3.2.1]octenyl Biradical



Reedich and Sheridan[16] generated the proposed bicyclo[3.2.1] octenyl biradical by photochemical explusion of nitrogen. The chemistry of this biradical mirrors that involved in the *meta* cycloaddition process. These radicals couple to form a cyclopropyl ring and, more importantly, if asymmetrically substituted molecules are used from which two different *meta* cycloadducts are formed, these products are produced in the same ratio as in the *meta* cycloaddition case.



Meta cycloaddition	1	:	1
Azo compound (7)	1	:	1.04
Azo compound (8)	1	:	1.01

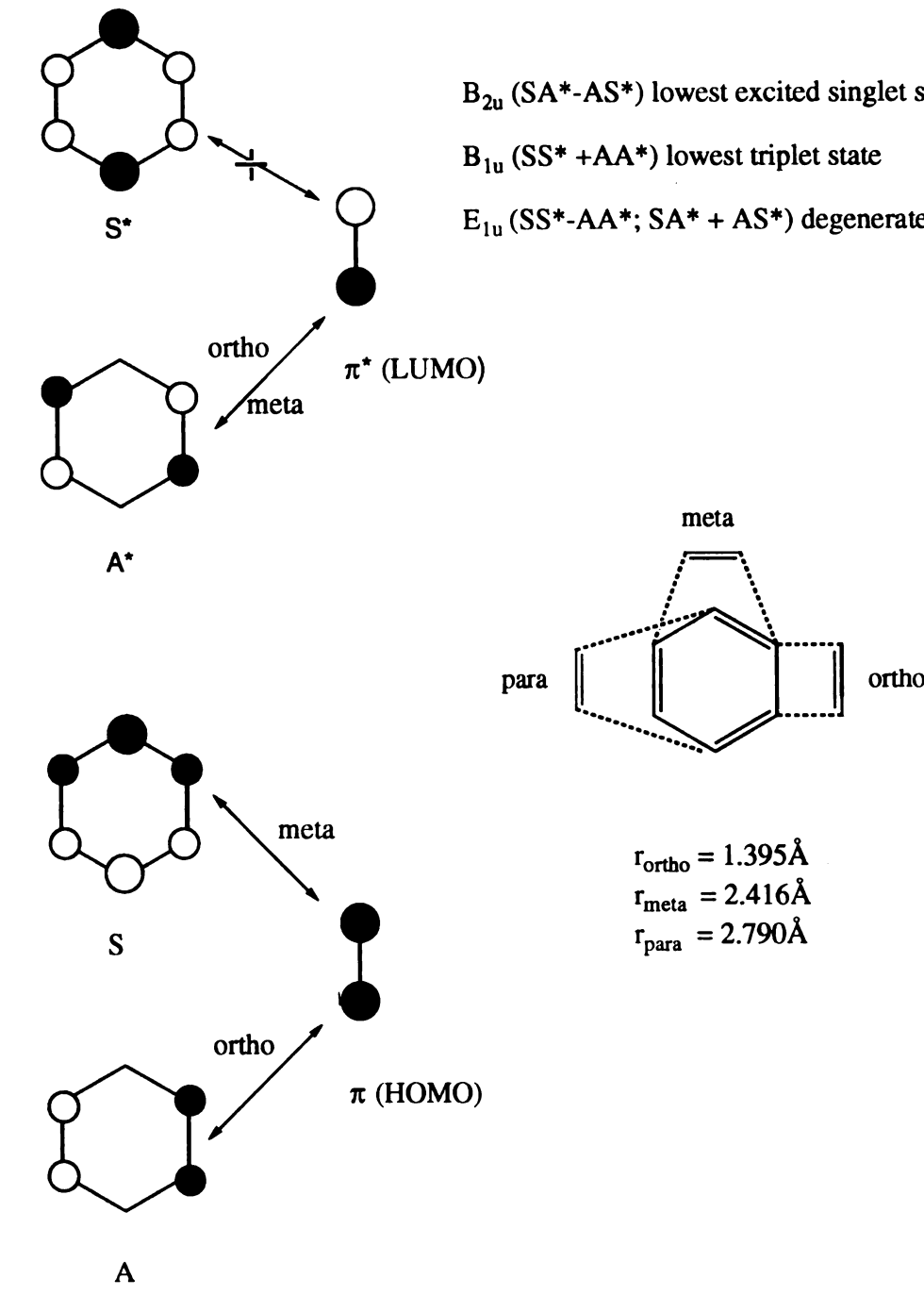
Exciplex formation was first proposed as an intermediate in *meta* photocycloaddition by Morrison and Ferree in their paper on intramolecular reactions of 6-phenylhex-2-ene.[10] No experimental evidence corraborating its involvement was presented.

Mattay, Scharf and Leismann[17, 18] provided the first direct evidence for an exciplex intermediate in 1977. They observed an emmision (ca. 400 nm) during photocycloaddition of benzene to substituted 1,3-dioxoles and 1,4-dioxenes in acetonitrile, but not in cyclohexane. They also found that triethylamine effectively quenches exciplex

emmision with a rate constant of k_{SV}=11.6±0.4 L mol^{-1}. This is nearly identical to that for quenching of *meta* cycloaddition (k_{SV}=11.7±1.5 L mol^{-1}).

Houk[19] provided a qualititative picture based on frontier orbital theory to rationalize regioselectivity associated with cycloaddition of benzene to alkenes. The HOMO's and LUMO's of benzene are labelled S, A, S*, and A* according to their symmetries with respect to a plane perpendicular to the benzene ring and passing through the position of attachment. Actual frontier orbitals of benzene are combinations of lowest excited singlet B_{2u} (SA*-AS*) and lowest triplet B_{1u} (SS*+AA*). In an *ortho* approach, stabilization can be achieved by mixing of the alkene's HOMO (π) with the benzene A orbital. In a *meta* approach, stabilization is afforded by interaction of the alkene's HOMO with the S orbital of benzene. These interactions are depicted below. Slight stabilization for both *meta* and *ortho* addition can be accomplished through interactions of the π^* orbital of the alkene and the A* orbital of benzene. *Para*-approach is only weakly stabilized by an interaction of benzene S and alkene π orbitals. Thus, it is predicted that *meta* complexation is stabilized by the S-A* transition, whereas, *ortho* complexation is stabilized by the A-S* transition.

Frontier Orbital Theory accurately describes partitioning between modes of cyclization when substituents are placed on the arene ring or ethylene unit. Addition of a substituent, whether it be electron donating or withdrawing, effectively removes the degeneracy of the HOMO and LUMO molecular orbitals. Interaction of ethylene with donor substituted benzene promotes *meta* addition at positions 2 and 6. This selectivity is due to preferential stabilization of the S-A* transition. Alternatively, benzene rings bearing an electron withdrawing substituent promote *ortho* cycloaddition due to increased charge transfer interactions.



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

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

E_{1u} (SS*-AA*; SA* + AS*) degenerate states

r_{ortho} = 1.395Å
r_{meta} = 2.416Å
r_{para} = 2.790Å

Figure 1: Stabilization of the Singlet Excited State by Benzene-Ethylene Orbital Interactions

Predicting The Mode Of Photocycloaddition

Several investigators have attempted to formulate factors which affect the regioselectivity of arene-olefin photocycloaddition. Bryce-Smith postulated that the mode of cyclization can be predicted based on differences in ionization potentials (ΔIP) between the benzene ring and the alkene.[20] Reactions of benzene (IP=9.24eV) with alkenes having IP's ranging from 9.6 eV to 8.65 eV proceed along a *meta* pathway. *Ortho* cycloaddition is preferred with strong donor and acceptor alkenes (9.6eV < IP < 8.65eV). Generally, this rule provides temendous predictive value.

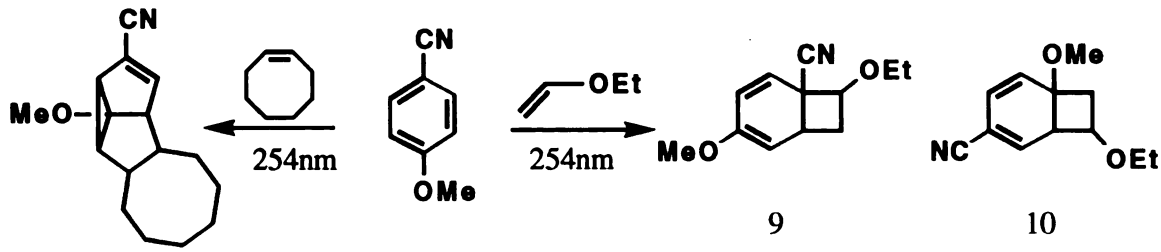
Mattay[21, 22] has also derived a general rule for predicting the mode of photocycloaddition of benzene to alkenes, based on the Rehm-Weller theory of electron transfer . According to this equation, the Gibbs free energy (ΔG) of electron transfer can be accurately calculated from redox potentials of starting materials and excitation energy of the excited species. This rule allows correlations to be made for a wide variety of substituted arenes and alkenes. In general:

1. The mode of cycloadditon changes from *meta* to *ortho* when ΔG< 1.4-1.6 eV indicating an increasing degree of charge transfer developing in the excited state complex.
2. Electron transfer predominates when $\Delta G \leq 0$.

Arene-Alkene Ortho Photocycloaddition

Ortho photocycloaddition is greatly favored and in many cases is the sole pathway in bichromophoric pairs which have a strong electron donor-acceptor relationship. Gilbert demonstrated this principle in photoreactions of arenes having both electron donor and electron acceptor substituents. Irradiation of 4-methoxybenzonitrile with electron rich ethyl vinyl ether produces a 2:1 mixture of *ortho* cycloaddition products, 1-cyano-8-ethoxy-4-

methoxy[4.2.0^{1,6}] octa -2,4-diene (**9**) and 4-cyano-7-ethoxy-1-methoxy[4.2.0^{1,6}] octa -2,4-diene (**10**) respectively. Alternatively, irradiation of 4-methoxybenzonitrile and cis-cyclooctene produces the endo *meta* cycloadduct, **11**, in 65% isolated yield.[23]



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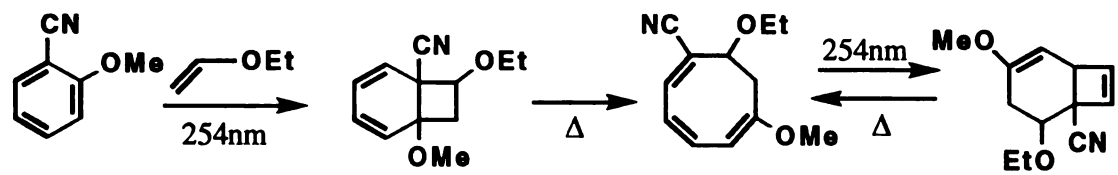
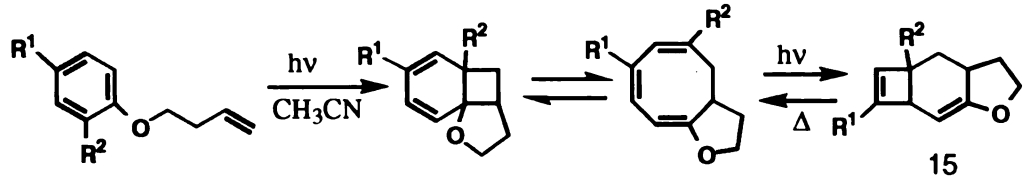
Gilbert also reported that direct photocycloaddition of electron rich alkenes to 2-methoxybenzonitriles proceeds in high yields.[24] Initially formed 1-cyano-8-ethoxy-6-methoxy[4.2.0^{1,6}] octa -2,4-diene (**12**) rapidly opens to 1-cyano-8-ethoxy-methoxycycloocta-1,3,5-triene (**13**). The resulting cyclooctatriene undergoes photochemical diene to cyclobutene ring closure to form 1-cyano-8-ethoxy-6-methoxybicyclo[4.2.0] octa-2,5-diene (**14**). Similar reactions were observed with methyl-2-methoxybenzoate and 2-methoxyacetophenone, however, the yields were appreciably lower.



12 13 14

Intramolecular variants of this reaction have also been investigated. Cyano and methoxycarbonyl substituted 4-phenoxybut-1-enes undergo efficient intramolecular cycloaddition to give good yields of 4-oxatricyclo[7.2.0.0^{3,7}] undeca-2,10-dienes

(**15**).[25, 26] The formation of intermediate cyclooctatriene was efficiently quenched by 1,3-dienes, but its rapid photochemical ring closure was uneffected by triplet quenchers.

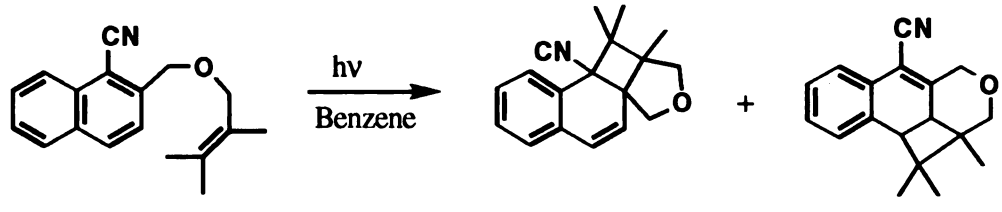


15

R^1= CN, COOMe ; R^2= H

R^1= H ; R^2= CN, COOMe

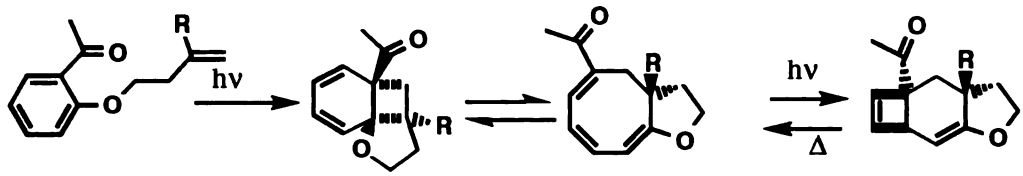
McCullough[27] observed similar results for naphthonitrile systems. For example, irradiation of 2,3-dimethyl-2-butenyl(1-cyano-2-naphthyl) methyl ether in benzene provided a 20:1 mixture of two *ortho* cycloaddition products, **16** and **17**, respectively. Prolonged irradiation produced only one cycloadduct, **17** (initially the minor isomer). Ring opening to cyclooctatriene was not observed.



16 17

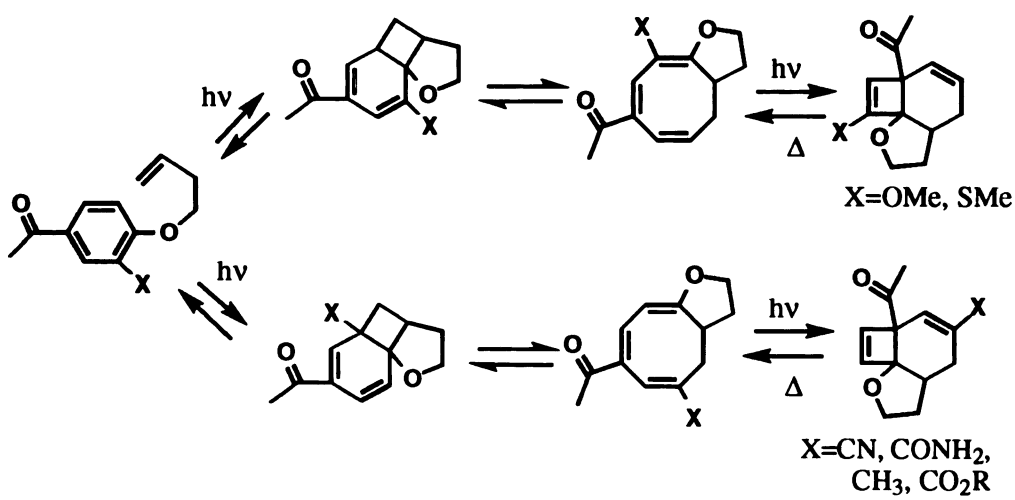
In an attempt to measure the degree of intramolecular quenching of π,π* triplets of ketones substituted with unsaturated tethers, Wagner and Nahm discovered the first reported 1,2-photocyclization of a triplet benzene to a remote olefin.[28, 29] Upon irradiation, the remote double bond underwent an intramolecular [2+2] cycloaddition with the benzene ring of the *o*-alkoxyphenyl alkyl ketone. The resulting intermediate, bicyclo[4.2.0] octa-2,4-diene **18**, was thermally converted to cyclooctatriene **19**. Additional irradiation of the cyclooctatriene effected a photochemical diene-to-cyclobutene interconversion to give bicyclo[4.2.0] octa-2,7-diene **20**. The stereochemistry of

photostable bicyclo[4.2.0] octa-2,7-dienes was determined by nOe studies. In all cases, disrotatory photoclosure of the cyclooctatriene resulted in formation of a cis 4/6 ring fusion. In fact, closure occurred only in one direction to form a cis 5/6 ring fusion.



18 19 20

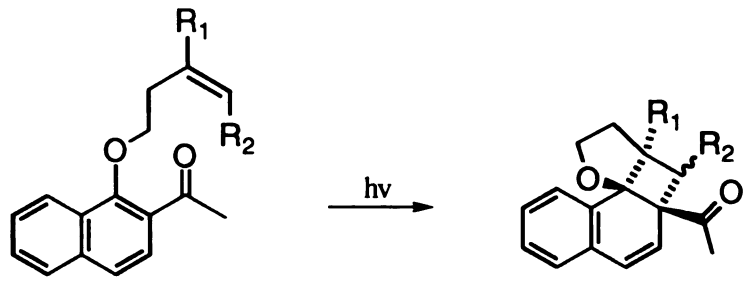
Recently, it has been demonstrated that this reaction proceeds with a high degree of regioselectivity.[30, 31] Electron withdrawing groups and alkyl groups *ortho* to the olefin tether direct cyclization toward the substituent, while strong electron donating groups drive the remote double bond away. Selectivity appears to reflect inductive effects both on the nature of initial triplet state cycloaddition and the competing thermal and photochemical electrocyclization reactions of the resultant photoproducts.



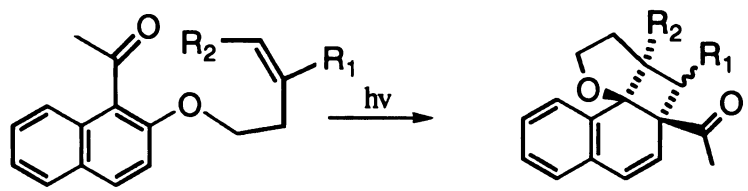
X=OMe, SMe

X=CN, $CONH_2$, CH_3, CO_2R

Triplet napthalenes have also been also shown to undergo *ortho* photocycloaddition with simple alkenes.[30] Irradiation of 1-butenoxy-2-acetonaphthones and 2-butenoxy-1-acetonaphthones in benzene results in formation of *ortho* [2+2] cycloadducts in high chemical yield. The quantum yields for 1-butenoxy-2-acetonapthones were substanially higher than for 2-butenoxy-1-acetonapthones. Presumably this difference is due to 1-butenoxy-2-acetonapthone's ability to stabilize the radical character in the rate determining step.

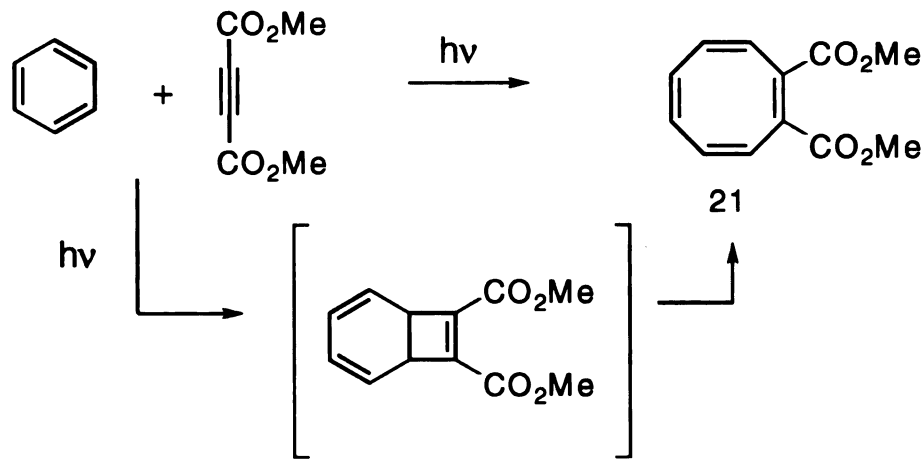


R_1=R_2=H Φ=0.23
R_1=Me, R_2=H Φ=0.17
R_1=H, R_2=Et Φ=0.31

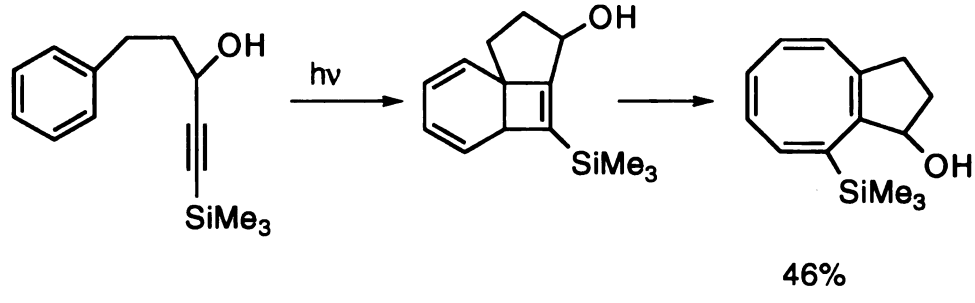


R_1=R_2=H Φ=0.01
R_1=Me, R_2=H Φ=0.04
R_1=H, R_2=Et .....

Ortho photocycloaddition occurs readily in systems involving alkynes. In nearly all cases, the initially formed cyclobutene adduct opens to the all cis cyclooctatetraene. Wender and Fisher have shown that when benzene and dimethyl acetylenedicarboxylate are irradiated, cyclooctatetrene **21** is obtained in good yield.[32]

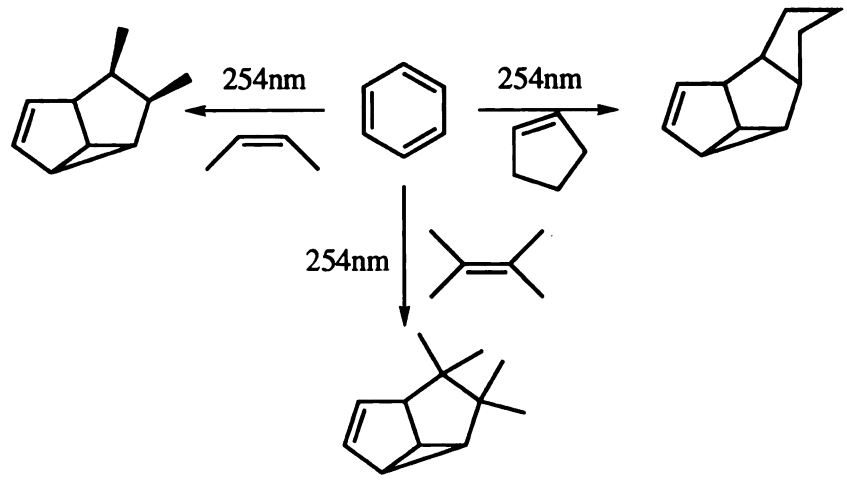


While intermolecular cycloaddition between an alkyne and benzene is facile, the intramolecular variant of this reaction is inefficient.[33] Pirrung has overcome this problem by incorporating a trialkylsilyl group on the alkyne.[34]

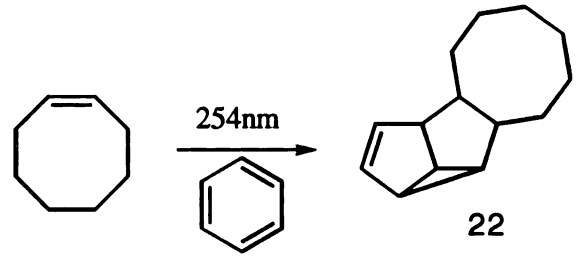


Arene-Alkene Meta Photocycloaddition

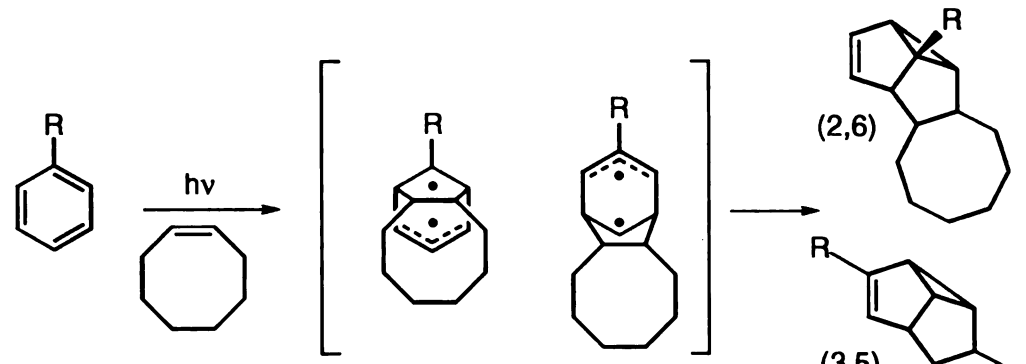
Intermolecular *meta* photocycloaddition was discovered simultanously by two independent reseach groups in 1966. Wilzbach and Kaplan reported the formation of 1:1 adducts upon irradation (254 nm) of 10% solutions of cyclopentene, cis-2-butene and 2,3-dimethylbut-2-ene in benzene.



Bryce-Smith, Gilbert and Orger reported addition of cis-cyclooctene to benzene to form a 1:1 adduct in 85% isolated yield. On the basis of spectroscopic and chemical evidence the adduct was identified as tetracyclo[6.6.0.$0^{2,4}$.$0^{3,7}$]tetradec-5-ene **22**.



Regioselectivity of *meta* cycloaddition is influenced considerably by steric interactions.[35, 36] As depicted above, intermolecular *meta* photocycloaddition generally proceeds with the double bond moiety adding to the 2- and 6- positions of the arene, relative to the electron donor group. As the steric bulk of donor groups increases, regioselectivity migrates to the 3- and 5-position relative to the ring substituent.



R	2,6 : 3,5
methyl	only 2,6
iso-propyl	2:1
t-butyl	1:1.5

Substituents on the arene ring profoundly effect the regioselectivity of intermolecular *meta* photocycloaddition.[37, 38, 39, 40] Donor ring substituents orient preferently to position 3, while acceptor ring substitutents prefer positions 4 and 6.

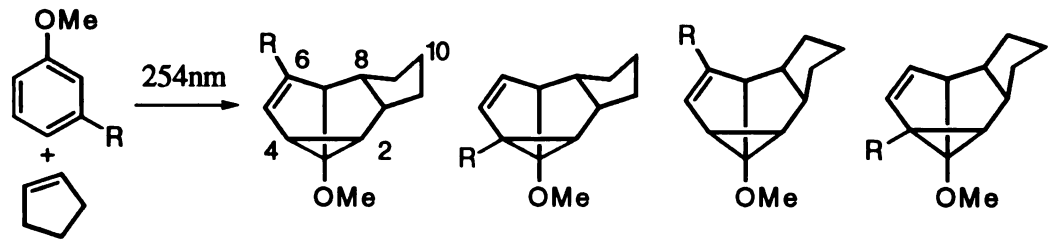
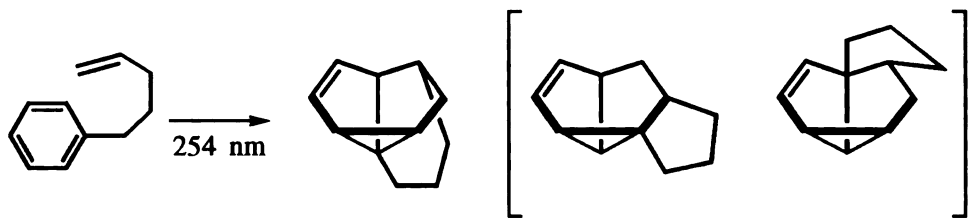


Table 1: Relative Ratios For The Possible *Meta* Photoproducts

CN	13	7	13	67
CF_3	5	16	36	43
F	0	0	51	49
Me	0	0	43	57
H	13		87	

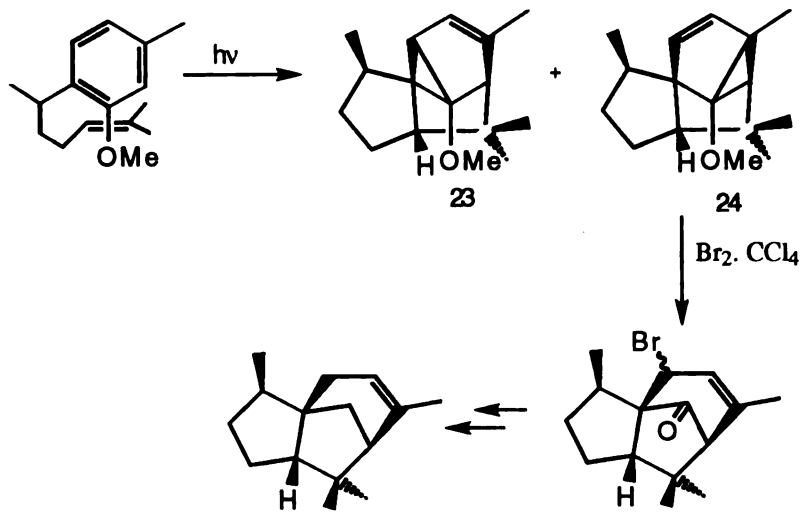
Regioselectivity is also observed in intramolecular photocycloaddition. There are two principal modes of cycloaddition available to 5-phenylpent-1-ene and its derivatives: 1,3-addition and 2,6-addition. Gilbert and Taylor[41] reported that 5-phenylpent-1-ene undergoes 2,6 as well as 1,3 addition in a ratio of 72:28.



2,6-addition 1,3-addition

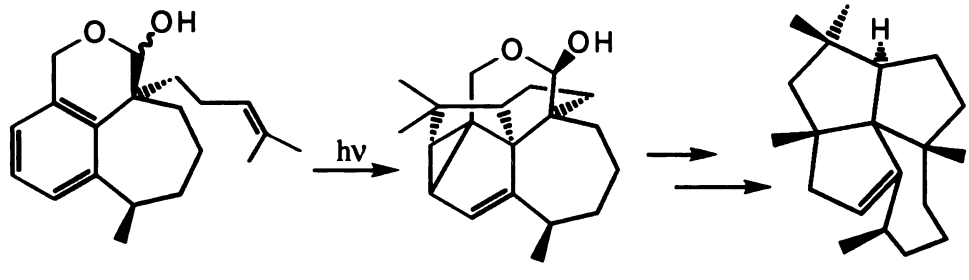
72 : 28

The usefulness of *meta* arene-alkene cycloaddition in polycyclopentanoid synthesis is exemplified by the total synthesis of the sesquiterpene (±)-cedrene.[42] The key photochemical reaction is photolysis of the anisole, yielding cycloadducts **23** and **24** in 65% isolated yield. Rapid increase in molecular complexity due to *meta* photocycloaddition dramatically shortens the total synthesis of (±)-cedrene to four steps. The observed regioselectivity is dictated by the presence of the *ortho* methoxy group.



(±)-cedrene

Recently, Wender reported the stereocontrolled synthesis of (±)-laurenene, a naturally occurring fenestrane.[3] The synthesis was based on the most complex example of an arene-olefin *meta* photoaddition to date, and provided a novel strategy for the preparation of other rosettane analogs. The successful cycloaddition of the lactol indicates that the key cycloaddition step can be extended to more highly congested substrates.



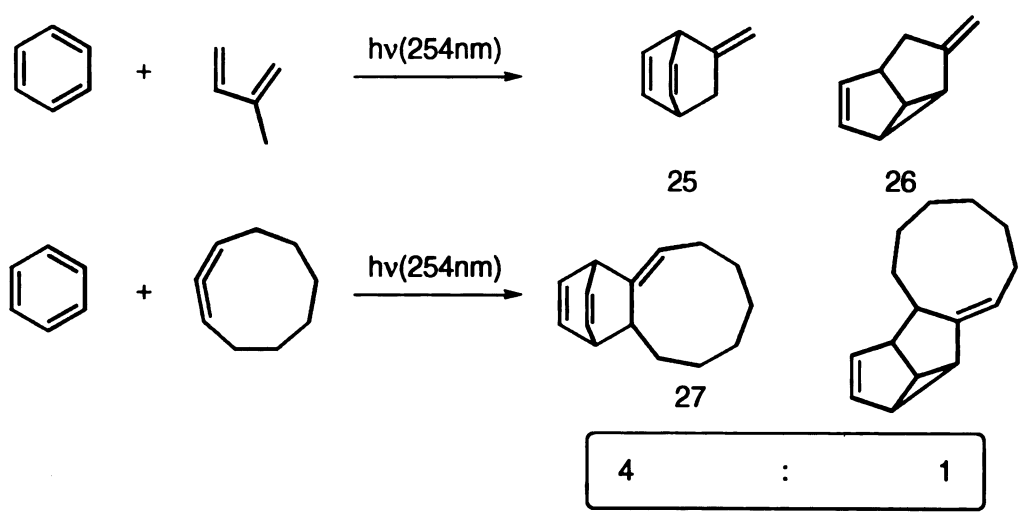
(±)-laurenene

Arene-Alkene Para Photocycloaddition

While *ortho* and *meta* photocycloadditions have been throughly investigated, little effort has been spent to determine the factors which control *para* cycloaddition. As

previously mentioned, *para* cycloadditon is very inefficient and is the major mode of addition in only a few isolated cases: addition of dienes and allenes to benzene.[43]

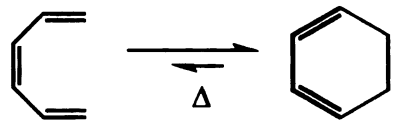
When benzene was irradiated in the presence of isoprene, the *para* cycloadduct **25** was isolated as the major product by prepative glc, along with a minor amount of the 1,3-adduct **26**. Similarly, photolysis of cyclonona-1,2-diene afforded the 1,4-adduct **27** as the major product. The aforementioned reactions were the first reported examples in which hydrocarbon olefins underwent unsensitized 1,4-cycloaddition to benzene as the major process.[44, 45]



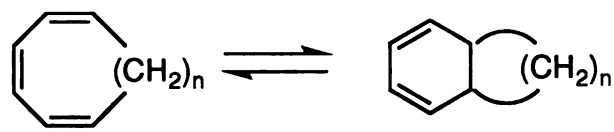
Thermal Rearrangements

Equilbrium between Cyclooctatriene and Cyclohexadiene

Cope first observed the near unity thermal equilibrium between cycloocta-1,3,5-triene **29** and its valence isomer bicyclo[4.2.0] octa-2,4-diene **28**.[46] This interconversion is an orbital topology-allowed, six electron, disrotatory process.



In the case of hexatriene, the electrocyclic equilibrium favors its tautomer, cyclohexadiene, due to the energetically favored formation of a σ-bond relative to a π-bond. Incorporating the hexatriene system in a ring dramatically alters this equilibrium.[47] For large rings, greater than eight carbons, the equilibrium lies in favor of bicyclohexadienes. In contrast, equilibrium greatly favors cyclohepta-1,3,5-triene, where the ends of the triene are linked by one methylene unit. This is due to the severe ring strain in norcaradiene.



n=1 $K_{eq}<<1$

n=2 $K_{eq}\approx 1$

n≥3 $K_{eq}>>1$

Kinetic parameters for electrocyclic equilibrium between several substituted cyclooctatrienes and their tautomers, bicyclo[4.2.0] octa-2,4-dienes, were reported by Huisgen.[48]

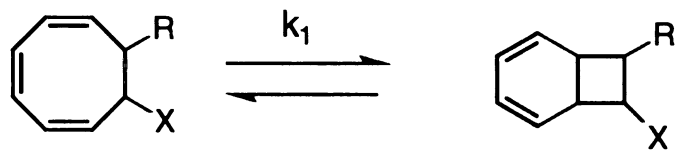
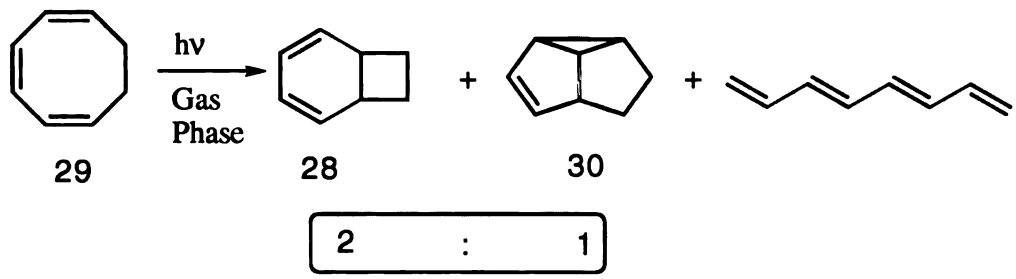


Table 2: Kinetic parameters for Electrocyclic Equilbrium between Several Substituted Cyclooctatrienes and Bicyclo[4.2.0] octa-2,4-dienes

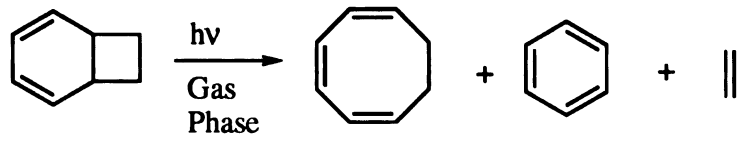
R, X	K_{eq} (100°C)	$10^7 k_1$, sec^{-1}	$\Delta H^{\neq}$(kcal/mol)	$\Delta S^{\neq}$(eu)
H, H	0.12	53	26.6	-1
Br, H	0.54	60	22.2	-7
OAc, H	1.13	81	24.6	+2
Me, Me	4.25	33	24.7	+1

Since the free energies of 1,3,5-cyclooctatriene and bicyclo[4.2.0] octa-2,4-diene differ only slightly, electronic and steric effects will ultimately alter the equilibrium between valence isomers. Substitution in the 7- or 8- positions stabilizes the bicyclo [4.2.0] octa-2,4-diene skelton relative to the unsubstituted cyclooctatriene.

Roth and Peltzer reported the independent gas phase photochemistry of 1,3,5-cyclooctatriene **29** and its valence tautomer **28** in 1965.[49] Irradiation of **29** produced two major products, **28** and **30**, in a ratio of 2:1. A minor amount of "unzipped" product, octa-1,3,5,7-tetrene, was also present.

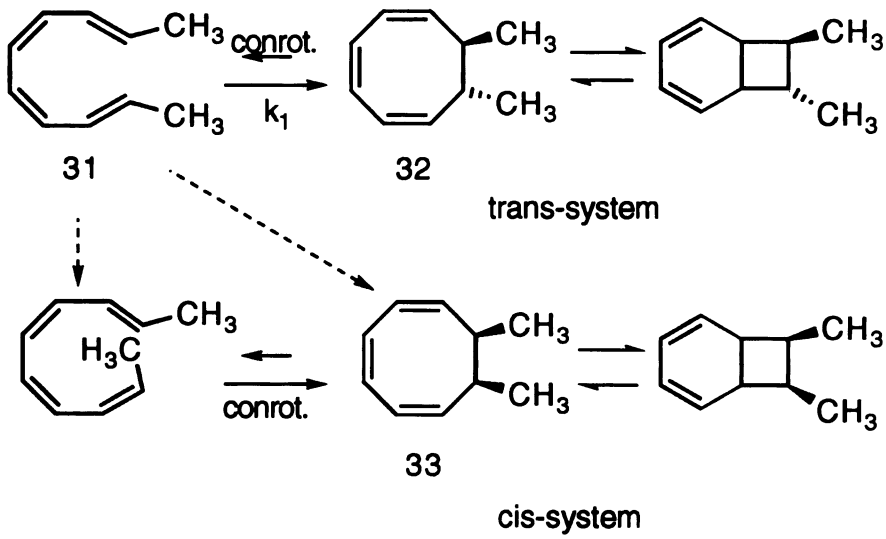


Irradiation of bicyclo[4.2.0] octa-2,4-diene **28** produces its isomer **29**, along with benzene and ethylene.[49, 50] Photofragmentation has been seen in other fused ring systems.



28 29

Huisgen and Dahmen[51] reported the presence of two 1,3,5-cyclooctatriene isomers, **32** and **33**, arising from the thermolysis (171°C) of trans, cis, cis, trans-decatetra-2,4,6,8-ene (**31**). trans-7,8-Dimethyl-1,3,5-cyclooctatriene (**32**) comprised 99.68% of the products. The amount of cis-7,8-dimethyl-1,3,5-cyclooctatriene (**33**) increased to 0.71% of products when the temperature of reaction was increased to 205°C. In both cases, cyclooctatrienes were in thermal equilibrium with their corresponding bicyclo [4.2.0] octa-2,4-dienes. The equilibrium constant favored the bicyclic isomer for both the trans-system (K_{eq}=4.25) and cis-system (K_{eq}=15.7).[48]



Triplet Sensitization Techniques [52]

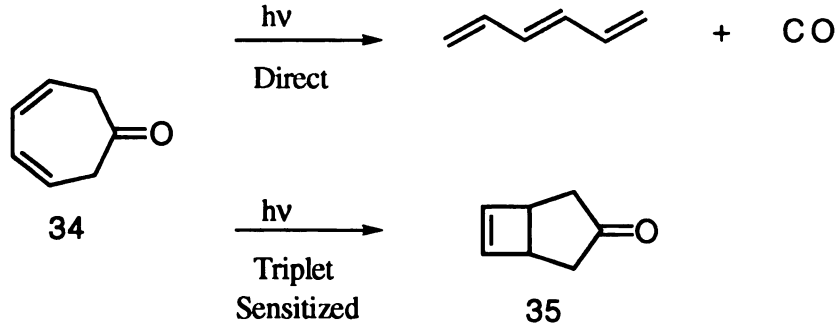
Energy transfer permits population of electronic states of a molecule in a different manner than by absorption of light. The chemistry arising from sensitization often differs

dramatically from the direct process. The most common types of energy transfer are triplet-triplet and singlet-singlet, both allowed by spin conservation.[53]

The efficiency of triplet-triplet energy transfer is dependent on a number of factors.[54] First and foremost, the acceptor's S_0-T_1 energy gap must be smaller than, or equivalent to, the donor's S_0-T_1 energy gap for energy transfer to take place. Next, the sensitizer (donor) must be chemically inert and absorb wavelengths that are not absorbed or weakly absorbed by the acceptor molecule. Finally, the rate of intersystem crossing of sensitizer must be high.

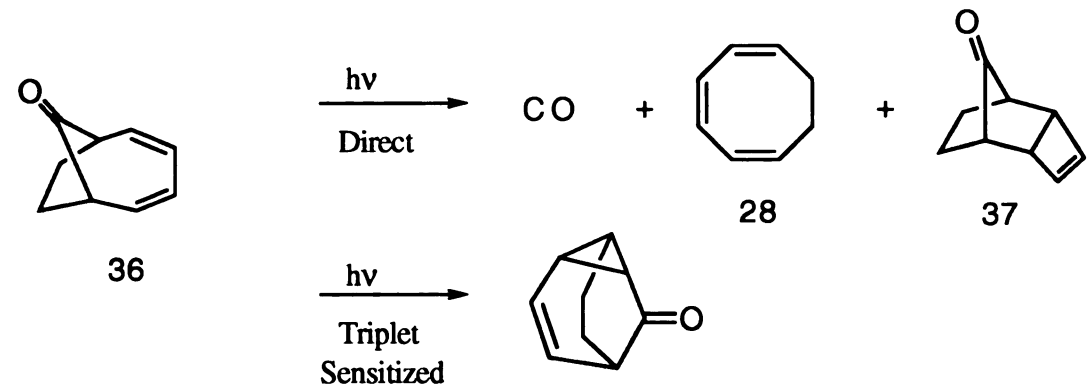
Triplet Sensitization---Representative Examples

Direct photolysis of 3,5-cycloheptadienone, **34**, led to efficient formation of carbon monoxide and 1,3,5-hexatriene through photofragmentation.[55] This reaction could not be quenched by either piperylene or napthalene. Schuster later found that triplet sensitization of **34** produced another reaction, leading to the valence tautomer bicyclo[3.2.0] hept-6-en-3-onediene (**35**) *via* a diene to cyclobutene ring closure.[56] These observations indicated that photodecarbonylation occurs *via* the singlet manifold and prevents intersystem crossing to the triplet state.

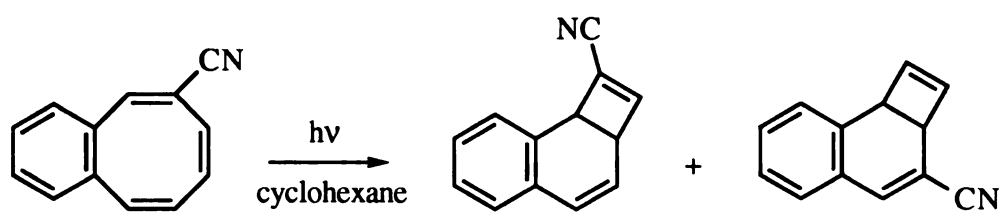


Similar results were found in the direct and sensitized photochemistry of bicyclo[4.2.1] nona-2,4-dien-9-one (**36**). Schuster found that direct photoylsis of **36** in diethyl ether or cyclohexane produced 1,3,5-cyclooctatriene (**28**) by decarboxylation and

endo-tricyclo[4.2.1.$0^{2,5}$] non-3-en-9-one (**37**) in a ratio of 5:1.[57] Alternatively, irradiation of **36** in the presence of a triplet sensitizer (acetone, Michler's ketone, benzophenone, or triphenylene) gave dihydrobarbaralone (**38**) as the major product in all cases. Small amounts of products **28** and **37** were also present when acetone was used as a sensitizer.

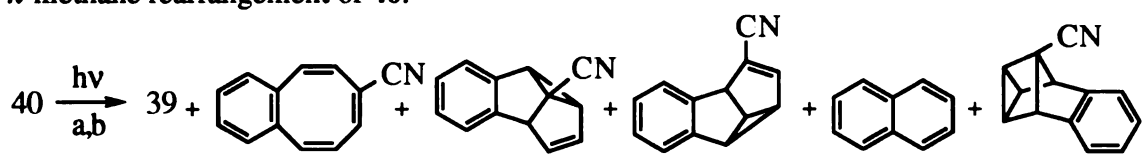


Direct irradiation of 6-cyanobenzocyclooctatetrene, **39**, in cyclohexane afforded 5- and 8-cyano-2,3-benzobicyclo[4.2.0] octa-2,4,7-triene, **41** and **40**, in 21 and 63% yields respectively.[58]



Triplet-sensitized irradiation of **40** using Michler's ketone provided 1- and 6-cyanobenzosemibullvalenes, (**43**) and (**44**) (Φ=0.88 and 0.006 respectively) and naphthalene (**45**) (Φ=0.012). Direct irradiation of **40** in cyclohexane led to formation of

five products, the major being **44**. The cyclooctatetrenes **39** and **42** were observed only by direct irradiation. Deuterium labeling studies suggested that **39** and **42** were not formed by electrocyclic ring opening of **40**. The major product by both methods arose from a di-π-methane rearrangement of **40**.



42 43 44 45 46

Table 3: Chemical and Quantum Yields for Products Arising from Photolysis of 40

Conditions	**39**	**42**	**43**	**44**	**45**	**46**
Direct(a) >290nm	8%(.007)	8%(.007)	----	55%(.05)	15%(.015)	5%(.004)
Sensit.(b) 334nm	----	----	7%(.006)	78%(.088)	11%(.012)	----

Quantum Yield Determination

The quantum yield of formation of a given species is given by the ratio of molecules formed to the number of photons absorbed (equation 1).

$$\text{Quantum Yield} = \frac{\text{moles of product formed}}{\text{moles of photons of irradation absorbed}} \qquad (1)$$

Knowledge of the amount of light absorbed by the reacting species is determined independently by chemical actinometry. Most actinometry, however, only determines the amount of incident light upon the sample. Fortunately, Beer's Law relates the amount of incident light to the amount of light absorbed by the reacting species (equation 2).

$$I_a = I_o(1-10^{-\varepsilon cl}) \qquad (2)$$

where: I_a = light absorbed
I_o = incident light
ε = molar extinction coefficient
l = path length
c = concentration of actinometer(absorbing species)

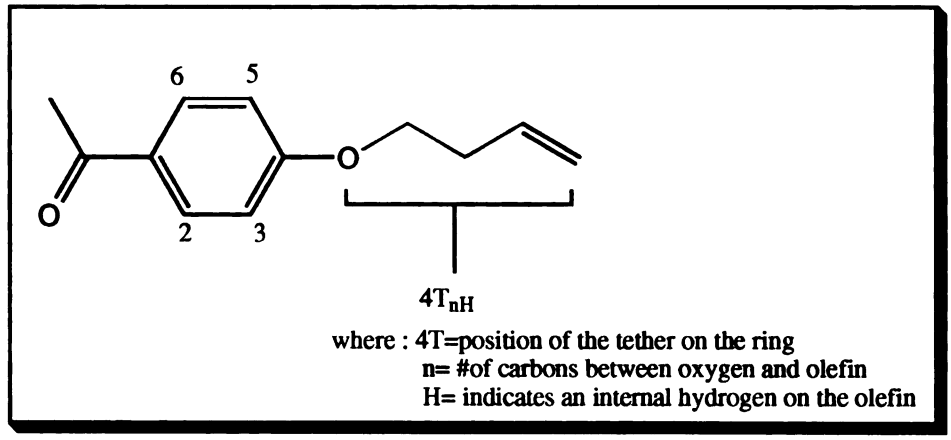
According to this equation, the amount of absorbed light will equal the amount of incident light when the optical density of the absorbing species is ≥ 2.

RESULTS

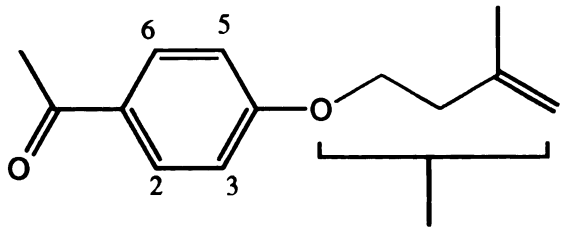
Ring Substitution

Several *ortho* substituents have been prepared to examine regioselectivity in the photocycloaddition of *p*-butenoxyacetophenones. Their structures and corresponding thesis notations are listed below.

para-Alkenoxyacetophenones and derivatives



Ring Substituents	Thesis Notation
R_2,R_3, R_5, & R_6=H; n=3	4T$_{3H}$-K
R_2,R_3, R_5, & R_6=H; n=2	4T$_{2H}$-K
R_2=Me; R_3, R_5, & R_6=H; n=2	2Me-4T$_{2H}$-K
R_2=Me; R_5=Me; R_3 & R_6=H; n=2	2,5Me-4T$_{2H}$-K
R_2=Me; R_5=isopropyl; R_3 & R_6=H; n=2	2Me-4T$_{2H}$-5I-K



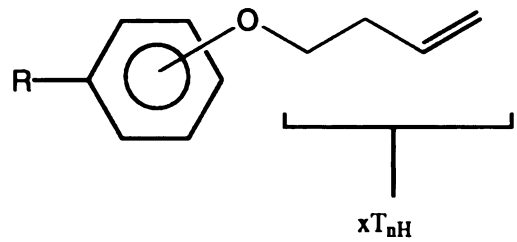
$4T_{2Me}$

where : 4T=position of the tether on the ring
2= #of carbons between oxygen and olefin
Me= indicates an internal methyl substituent

Ring Substituents	**Thesis Notation**
R_2=Me; R_3,R_5, & R_6=H	2Me-$4T_{2Me}$-K
R_2=OMe; R_3,R_5, & R_6=H	2OMe-$4T_{2Me}$-K
R_2=F; R_3,R_5, & R_6=H	2F-$4T_{2Me}$-K
R_2=CF_3; R_3,R_5, & R_6=H	2CF_3-$4T_{2Me}$-K
R_2=isopropyl; R_3,R_5, & R_6=H	2I-$4T_{2Me}$-K
R_2=CN; R_3,R_5, & R_6=H	2CN-$4T_{2Me}$-K
R_2=CD_3; R_3,R_5, & R_6=H	2CD_3-$4T_{2Me}$-K
R_2=Me; R_6=Me; R_3 & R_5=H	2,6Me-$4T_{2Me}$-K
R_2=Me; R_5=Me; R_3 & R_6=H	2,5Me-$4T_{2Me}$-K
R_2=Me; R_5=isopropyl; R_3 & R_6=H	2Me-$4T_{2Me}$-5I-K
R_1-R_2=3-methylcyclopent-1-one	Indanone-3Me-$5T_{2Me}$-K

Several *o*- or *p*-butenoxybenzonitriles and benzoate esters were prepared which do not absorb strongly in the near UV (>300 nm). They are listed below. Comparisons will be made between their direct and triplet sensitized photoreactivity. Triplet-triplet energy transfer from acetone was used to produce 100% triplet reaction.

Non-ketone Reactants

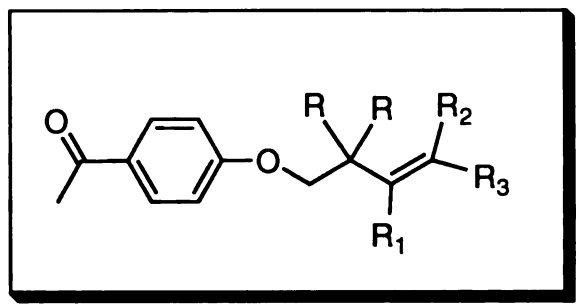


where : xT =position of the tether on the ring
n = #of carbons between oxygen and olefin (2 or 3)
H = indicates an internal hydrogen on the olefin

Ring Substituents	**Thesis Notation**
R=CN; n=3; x=4	1CN-4T3H
R=CN; n=2; x=4	1CN-4T2H
R=COOEt; n=3; x=4	1EC-4T3H
R=COOEt; n=2; x=4	1EC-4T2H
R=COOEt; n=3; x=2	1EC-2T3H
R=CN; n=3; x=2	1CN-2T3H
R=CN; n=2; x=2	1CN-2T2H

Several *p*-butenoxyacetophenones were prepared which have substitution along the tether. Their structures and corresponding thesis notations are listed below.

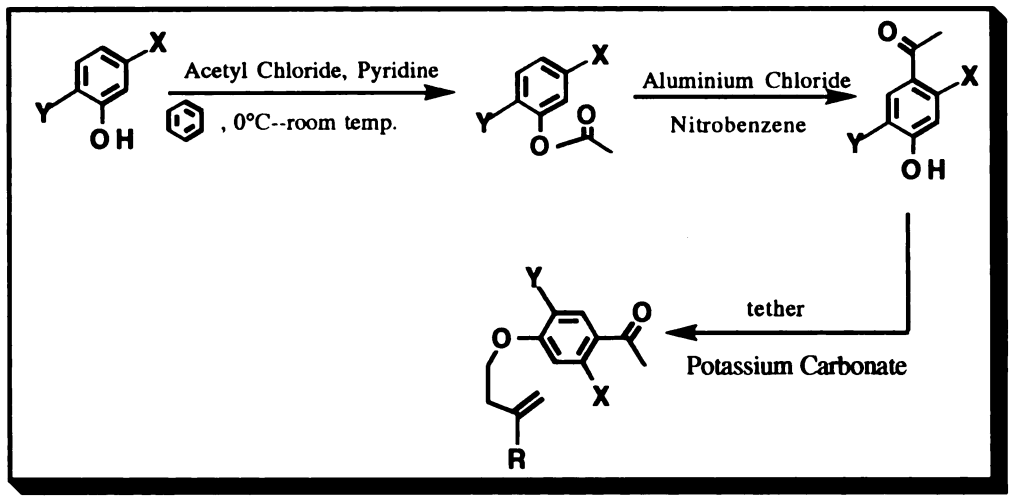
Tether Substitution



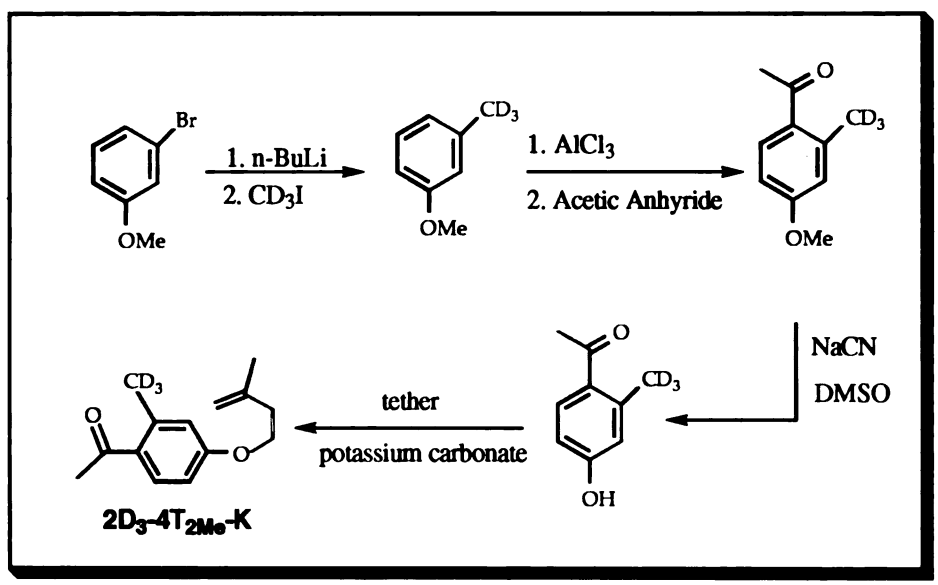
Tether Substituents	Thesis Notation
R=Me; R_1, R_2=H; R_3=CN	$4T_{2N}$(CN)-K
R,R_1, R_3=H; R_2=Et	$4T_{2N}$(Et)-K
R=H;R_1, R_2, R_3=F	$4T_{2N}$(F)-K

Preparation of Reactants

The majority of *para*-alkenoxyacetophenone derivatives were prepared by Fries rearrangement of their corresponding acetates in nitrobenzene at, or below, room temperature, followed by etherification in acetone or DMF. **2Me-$4T_{2Me}$-K**, **2Me-$4T_{2H}$-K**, **2OMe-$4T_{2Me}$-K**, **2F-$4T_{2Me}$-K**, **2,5Me-$4T_{2Me}$-K**, **2,5Me-$4T_{2H}$-K**, **2Me-$4T_{2Me}$-5I-K** and **2Me-$4T_{2H}$-5I-K** were synthesized as shown below.

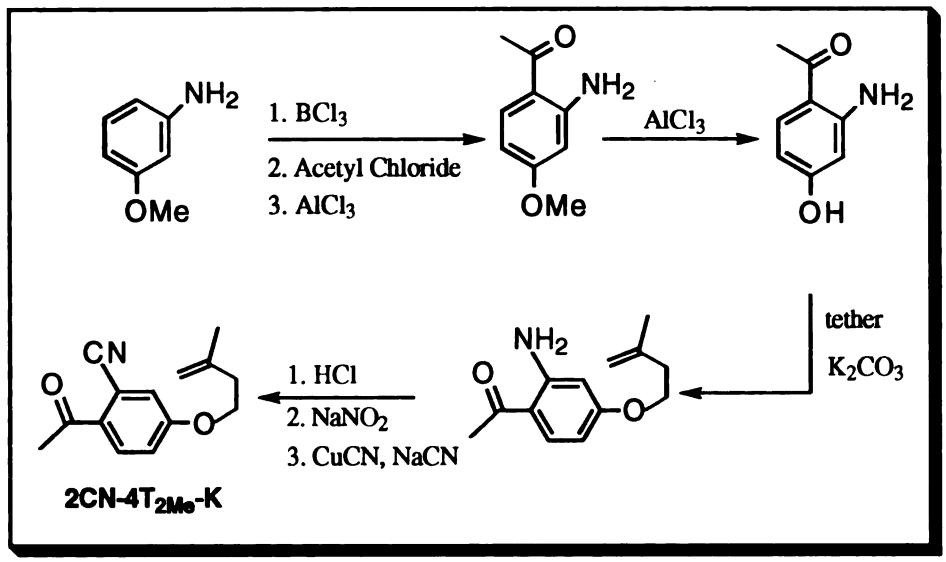


2CD3-4T2Me-K was prepared by alkylation of 3-bromoanisole using n-butyllithium and iodomethane-d3. The resulting anisole was acylated using a Friedel-Craft reaction followed by deprotection using sodium cyanide in DMSO. 2-Methyl(d3)-4-hydroxyacetophenone was finally converted into **2CD3-4T2Me-K** by etherification.

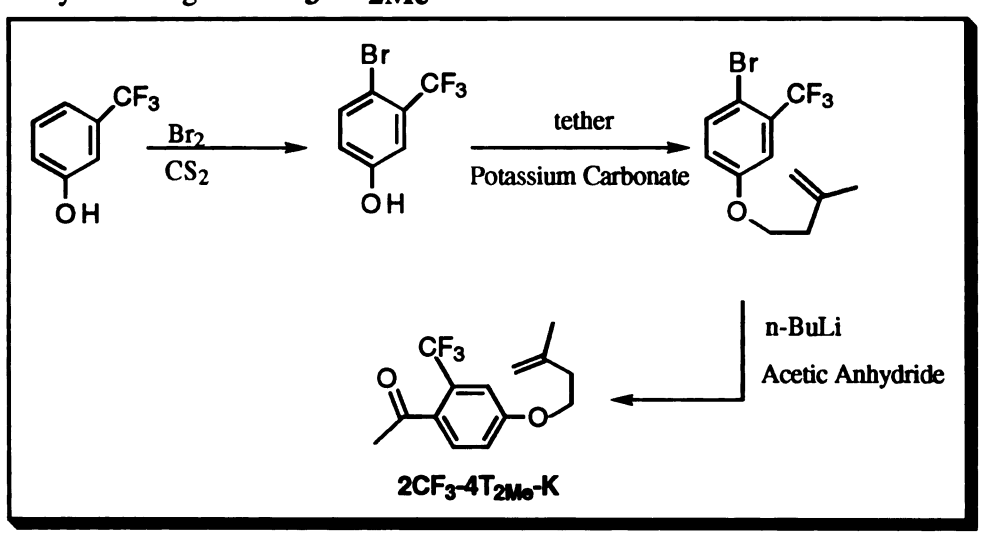


2CN-4T2Me-K was prepared by acylating *m*-anisidine using boron trichloride and acetyl cloride, followed by deprotection of the hydroxy group using aluminium chloride. The resulting 2-amino-4-hydroxyacetophenone was then converted to 2-amino-4-

(3'-methyl-3'-buten-1'-oxy)acetophenone by an etherification. Finally, the amino group was transformed to a nitrile by a Sandmeyer reaction.

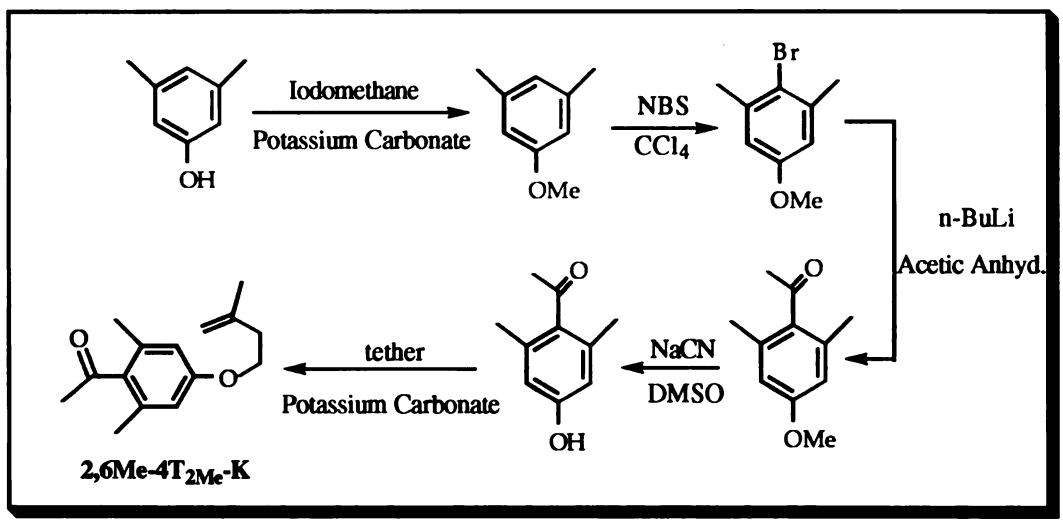


2CF3-4T2Me-K was prepared by bromination of 3-trifluoromethylphenol in carbon disulfide at 0°C, followed by etherification. The resulting compound, 1-bromo-2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)benzene was lithiated and quenched with acetic anhydride to give **2CF3-4T2Me-K**.

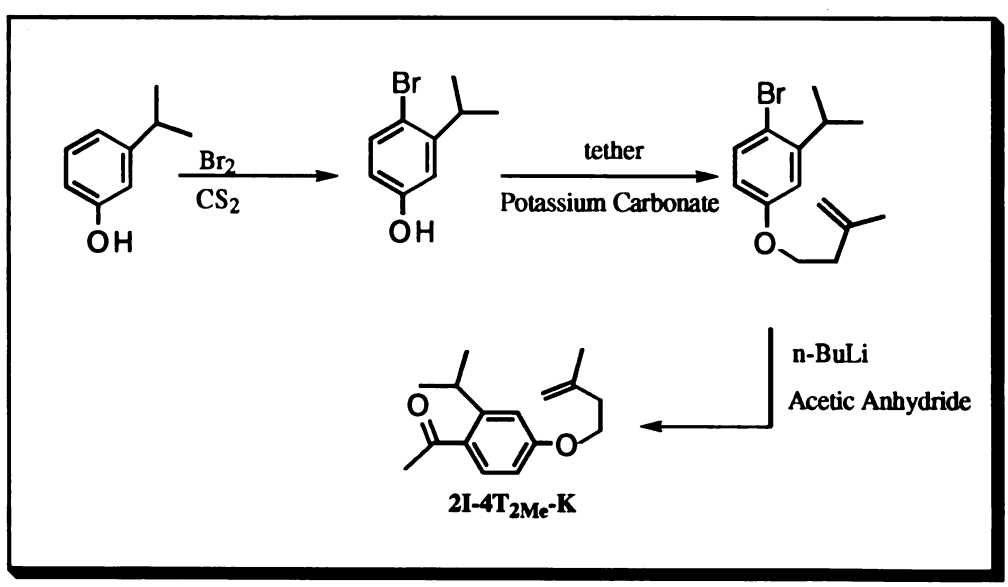


2,6Me-4T2Me-K was prepared by several steps as shown below. 3,5-dimethylphenol was protected and then brominated *para* to the methoxy group by NBS.

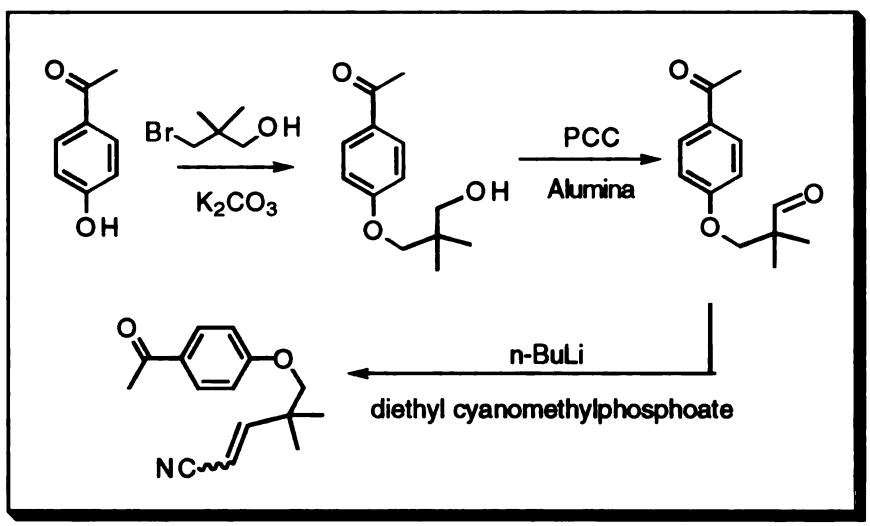
The resulting compound was converted to 2,6-dimethyl-4-hydroxyacetophenone by lithium-halogen exchange, nucleophilic substitution, and deprotection. Finally, coupling of the phenol with 4-tosyl-2-methyl-1-butene provided **2,6Me-4T2Me-K**.



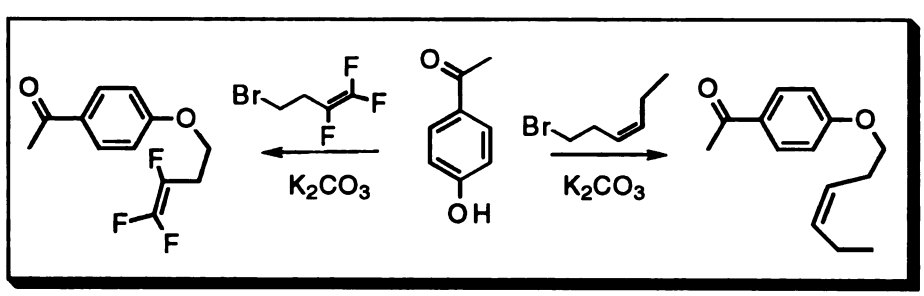
2I-4T2Me-K was prepared in the same manner as **2CF3-4T2Me-K**. This is accomplished by bromination, etherification, and acylation by way of a lithium-halogen exchange.



4T2N(CN)-K was prepared in several steps as shown below. Etherification of 4-hydroxyacetophenone with 3-bromo-2,2-dimethylpropan-1-ol provided 3-(4'-acetylphenoxy)-2,2-dimethylpropan-1-ol, which was then oxidized to an aldehyde using PCC. The resulting compound, 3-(4'-acetylphenoxy)-2,2-dimethylpropanal was ultimately converted to **4T2N(CN)-K** *via* a modified Wittig reaction.



4T2N(Et)-K and **4T2N(F)-K** were prepared by coupling 4-hydroxyacetophenone with cis-6-bromo-3-hexene and 4-bromo-1,1,2-trifluoro-1-butene respectively. Potassium carbonate was used as a base in both cases to deprotonate the phenol.



Characterization of Products

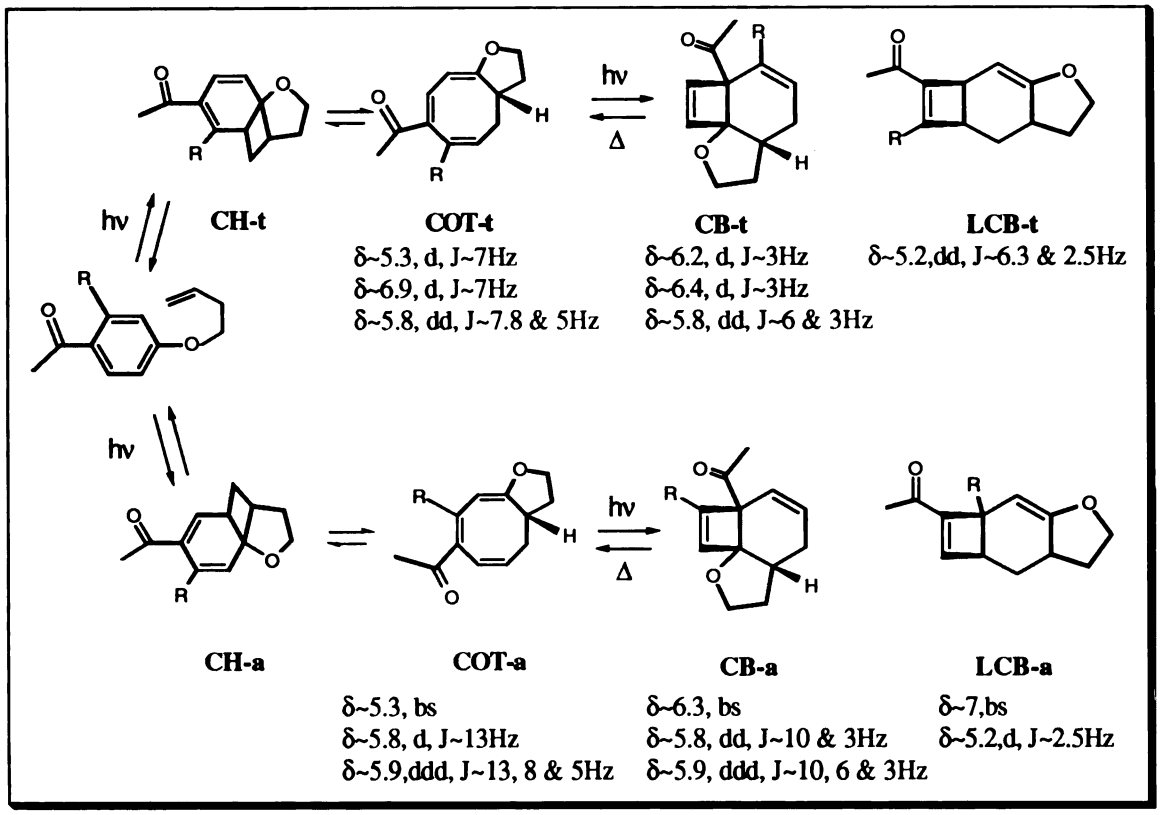
Derivatives of *para*-alkenoxyacetophenones (0.01-0.02 M solutions in deuterated methanol or benzene) were irradiated in NMR tubes with a medium pressure mercury arc filtered through Pyrex. Generally, the majority of the starting ketone disappeared after five hours of irradiation, and analogs of 1-acetyl-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene were formed. Products arising from γ-hydrogen abstraction were also observed with reactants bearing an *ortho* alkyl group.[59, 60]

Large scale irradiations were performed using 0.2-0.3 g of ketone in argon-bubbled methanol or benzene. The photoproducts were isolated by column chromatography or preparative TLC using hexane/ethyl acetate as the eluent. All reactants and photoproducts were characterized by ^{1}H NMR (300MHz), ^{13}C NMR (75MHz), FTIR, mass spectrometry and UV-visible spectroscopy depending upon their thermal stability.

The regioselectivity of addition was determined by the relative ratios of the cyclobutene photoproducts or the relative ratios of the corresponding thermal products. There are four cyclobutene structures possible from this two photon process. Each cyclobutene has an unique vinyl resonance--having distinct coupling constants and chemical shifts. Predicted chemical shifts and coupling constants for each possible product are shown in the scheme below.

Cyclobutenes **CB-t** and **LCB-t** arise from cyclization of the double bond toward the *ortho* substituent. **CB-t** has three vinyl protons: two doublets at ~6.2 and ~6.4 ppm and a doublet of doublets at ~5.8 ppm. The two doublets are weakly coupled to one another (3 Hz), which is characteristic of vinyl coupling in cyclobutene.[61] Alternatively, **LCB-t** has only one vinyl proton which is shifted upfield due to its enol-ether character. It has two allylic couplings of ~6.3 and ~2.5 Hz. Thermal ring opening of either **LCB-t** and **CB-t** results in the formation of the cyclooctatriene isomer, **COT-t**. **COT-t** has three vinyl protons: a downfield doublet at ~6.9 ppm , a doublet of doublets at ~5.8 ppm and an

upfield doublet at ~5.3 ppm. Two of the vinyl protons are coupled to one another with a ~7 Hz coupling constant.



CB-a and **LCB-a** arise from cyclization of the remote olefin away from the *ortho* ring substituent. **CB-a** has three vinyl protons: a broad singlet at ~6.3 ppm, a doublet of doublets of doublets at 5.9 ppm and a doublet of doublets at ~5.8 ppm. The two multiplets are coupled to one another with roughly a 10 Hz coupling, characteristic of vinyl coupling in a cyclohexene ring.[61] **LCB-a** has two vinyl protons positioned at opposite ends of the olefin region: a downfield singlet (~7 ppm) due to its conjugation with the acetyl group and an upfield doublet at ~5.2 ppm. This vinyl proton is coupled allylically to the six-five bridge-head proton. Thermal ring opening of **CB-a** and **LCB-a** produces its valence tautomer, **COT-a**. **COT-a** has three vinyl protons similar to **COT-t**, however, their chemical shifts and couplings are dramatically different. The three vinyl protons in **COT-a** are grouped closely together between 6.0 and 5.0 ppm. The two multiplets, the doublet at

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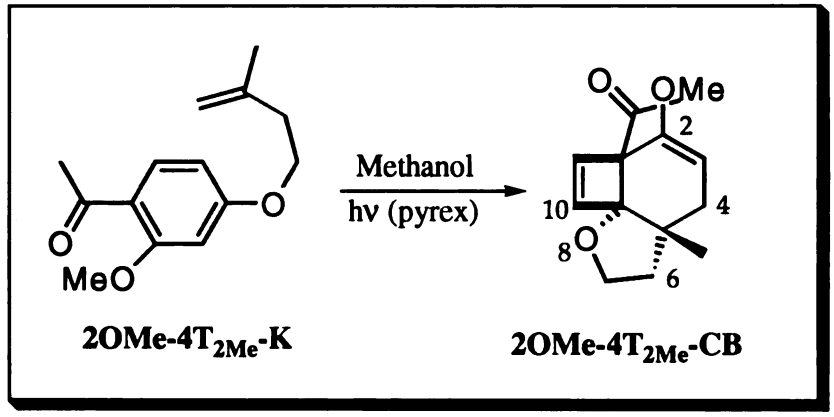
~5.8 ppm and the doublet of a doublet of doublets at ~5.9 ppm are coupled together with a large 13 Hz coupling constant. This coupling is characteristic of vinyl coupling in cis-cyclooctatriene.[61]

The stereochemistry of the photostable tricyclo[7.2.0.0^{5,9}] octa-2,10-diene was determined by nOe studies. In all cases, disrotatory photoclosure of the cyclooctatriene resulted in formation of a cis 4/6 ring fusion. In fact, closure occurred in only one direction to form a cis 5/6 ring fusion. In some instances, rapid thermal ring opening of the cyclobutenes prevented stereochemical elucidation by nOe. The stereochemistry of these compounds was determined by comparing their chemical shifts and coupling constants to cyclobutenes previously characterized by nOe.

Photochemistry of **2OMe-4T$_{2Me}$-K** in methanol



2OMe-4T$_{2Me}$-K **2OMe-4T$_{2Me}$-CB**

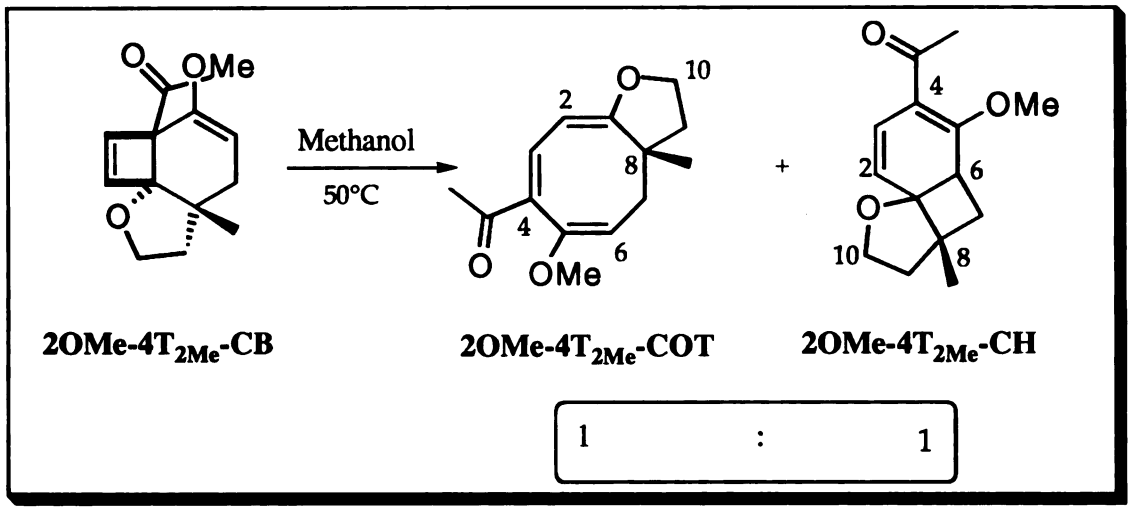
A solution of **2OMe-4T$_{2Me}$-K** (2.6 mg in 1 mL solvent) in methanol-d4 was purged with argon and irradiated with a medium pressure mercury arc filtered through Pyrex. A single photoproduct was observed by ^{1}H NMR after eight hours of irradiation at room temperature. The product was characterized as 1-acetyl-5-methyl-2-methoxy-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene, **2OMe-4T$_{2Me}$-CB**. Preparatory scale photolysis (850 mg in 300 mL solvent) was carried out through Pyrex to isolate **2OMe-4T$_{2Me}$-CB**. After 28 hours of irradiation, the reaction mixture was concentrated under

reduced pressure. ^{1}H NMR showed the presence of the starting ketone and its photoproduct, **2OMe-4T2Me-CB**. Purification of the reaction mixture by silica gel chromatography afforded a mixture of products arising from the decomposition of **2OMe-4T2Me-CB**. The decomposition products were determined to be **2OMe-4T2Me-CH** and **2OMe-4T2Me-COT**.

Photoproduct **2OMe-4T2Me-CB** was identified by its characteristic ^{1}H NMR. It showed signals corresponding to three vinyl protons: a doublet at 6.35 ppm(H-10), a doublet at 6.23 ppm(H-11) and a doublet of doublets at 4.75 ppm(H-3). Peaks at 6.35 and 6.23 ppm are coupled to one another with a 3 Hz coupling constant. This AB quartet pattern uniquely identifies angular cyclobutenes arising from cyclization toward the ring substitutent. The signal at 4.75 ppm is assigned to a proton on an enol ether based on its upfield shift. Homonuclear decoupling experiments indicate that proton (H-3) is coupled to vicinal protons H-4α and H-4β with 6.1 and 3.2 Hz coupling constants. Due to the thermal instability of **2OMe-4T2Me-CB**, nOe studies could not be proformed. The stereochemistry of **2OMe-4T2Me-CB** was determined by comparison of chemical shifts and coupling constants to those obtained through nOe characterizations of other cyclobutenes.

Thermal Chemistry of **2OMe-4T2Me-CB**

The crude photolysis mixture of **2OMe-4T2Me-K** and **2OMe-4T2Me-CB** was dissolved in methanol, purged with argon and heated at 50°C in a constant temperature bath. After complete disappearance of **2OMe-4T2Me-CB** as determined by TLC, the reaction mixture was purified by column chromatography. Two products were isolated as an equilibrium mixture; a 1:1 ratio was determined by integration of the vinyl protons in the ^{1}H NMR spectra. The thermal products were identified as 4-acetyl-5-methoxy-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene, **2OMe-4T2Me-CH** and 4-acetyl-5-methoxy-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **2OMe-4T2Me-COT**.



Their structures were identified based on characteristic chemical shifts and couplings in their ^1H NMR spectra. The fact that the cyclohexadiene and cyclooctatriene are in a 1:1 equilibrium made proton assignment difficult especially for the methylenes in the five membered ring. ^1H NMR of the equilibrium mixture showed five signals corresponding to vinyl protons: a doublet at 7.2 ppm(H-3_{COT}), a doublet at 6.7 ppm (H-3_{CH}), a doublet of doublets at 5.24 ppm(H-2_{CH}), a doublet of doublets at 5.24 ppm (H-6_{COT}) and a doublet at 5.1 ppm(H-2_{COT}). Homonuclear decoupling experiments indicate that the peak frequencies at 6.7 ppm(H-3_{CH}) and 5.24 ppm(H-2_{CH}) are coupled to each other (10 Hz). This coupling uniquely identifies a cyclohexadiene arising from thermal ring opening of cyclobutene (**CB-t**). The two vinyl protons at opposite ends of the vinyl region, H-3_{COT} and H-2_{COT}, are coupled to one another (5.3 Hz). The large upfield shift of proton H-2_{COT} is indicative of an enol ether proton. The other remaining signal for vinyl proton H-6_{COT} is coupled to two vicinal allylic protons H-7α and H-7β with 9.3 and 7.1Hz coupling constants.

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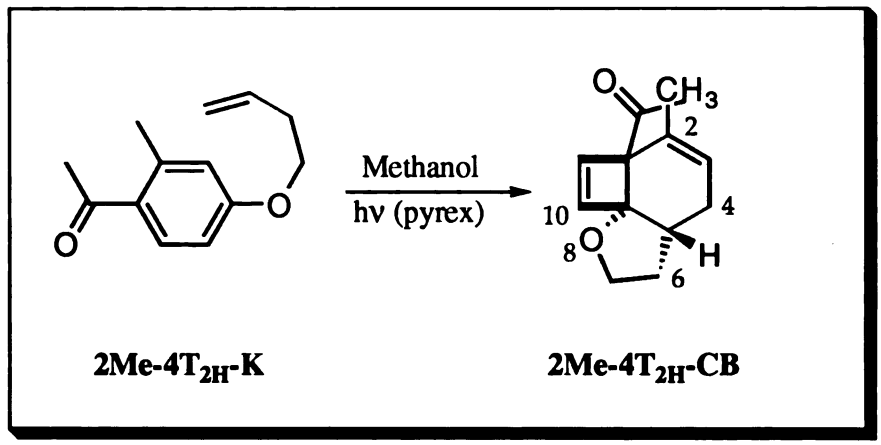
Photochemistry of **2Me-4T2H-K**

Irradiation of **2Me-4T2H-K** (~0.01 M) in argon-purged methanol through a Pyrex filter provided a single photoproduct after three hours (50% completion). This was identified as 1-acetyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T2H-CB**, based on its ^{1}H NMR spectrum. Large scale photolysis (0.5 g per 300 mL solvent) of **2Me-4T2H-K** in argon-purged methanol was carried out to isolate **2Me-4T2H-CB**. The reaction was monitored by gas chromatography. At near depletion of the starting material, the reaction mixture was concentrated *in vacuo*. ^{1}H NMR analysis of the reaction mixture showed the presence of **2Me-4T2H-K** and its photoproduct, **2Me-4T2H-CB**. **2Me-4T2H-CB** was converted to its thermal product, **2Me-4T2H-COT**, before isolation (see below).



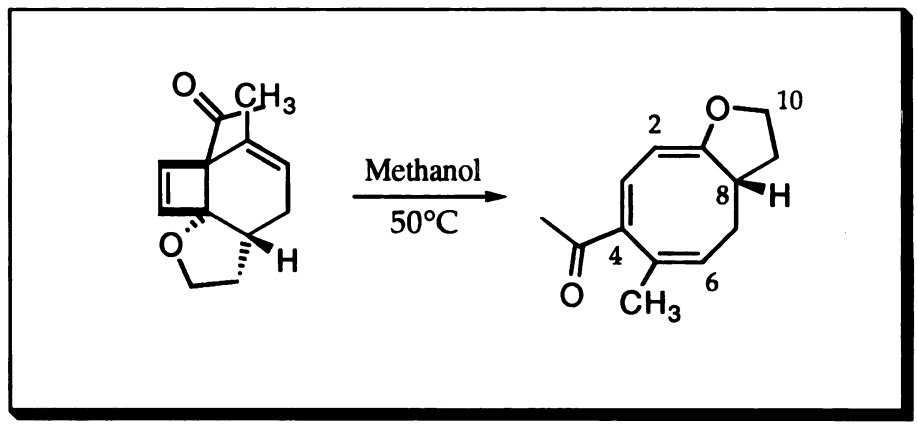
2Me-4T2H-K **2Me-4T2H-CB**

The photoproduct, **2Me-4T2H-CB** was identified based on its ^{1}H NMR spectrum. It showed signals corresponding to three vinyl protons: a doublet at 6.5 ppm(H-10), a doublet at 6.3 ppm(H-11), and a quartet of doublets of doublets at 5.6 ppm (H-3). Frequencies at 6.5 and 6.3 ppm are coupled to one another (3 Hz). This AB quartet pattern was seen in **2OMe-4T2H-CB** and uniquely identifies angular cyclobutene arising from cycloaddition toward the *ortho* substituent. Homonuclear decoupling experiments on the peak frequency at 5.62 ppm indicate that this proton is coupled to two adjacent vicinal protons (H-4α and H-4β) with J=4.4 and 4.4 Hz respectively. It is also coupled allylically

to protons of the vinylic methyl (J=1.6 Hz). This vinyl pattern was also seen in **2Me-4T2Me-CB**, **2,5Me-4T2H-CB**, and **2Me-4T2H-5I-CB-t**.

Thermal Chemistry of **2Me-4T2H-CB**

A crude photolysis mixture of **2Me-4T2H-CB** and **2Me-4T2H-K** was dissolved in methanol (300 mL), purged with argon, and heated in a constant temperature bath at 50°C. The reaction progress was monitored by thin layer chromatography. After complete conversion of **2Me-4T2H-CB** (4 hours), the reaction mixture was purified by column chromatography (hexanes: ethyl acetate, 85:15). A single product was identified as 4-acetyl-5-methyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene, **2Me-4T2H-COT** (134 mg, 27% yield based on starting ketone).

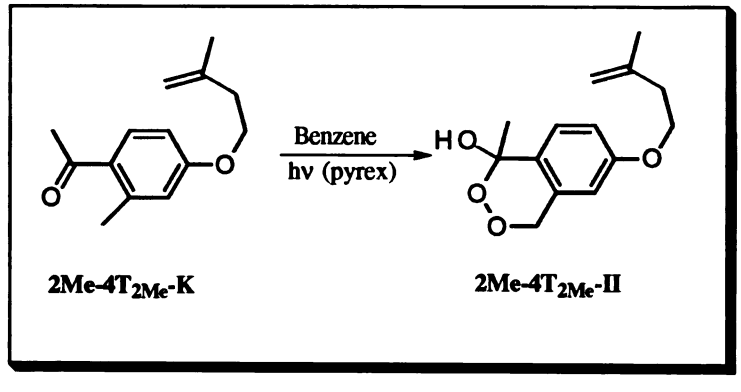


The product was characterized by MS, UV-Vis and by NMR spectroscopy. **2Me-4T2H-COT** has the same molecular ion peak as the starting ketone, **2Me-4T2H-K**. Six signals were observed in the vinyl region (165.7, 138.7, 137.7, 136.7, 127.3, and 94.7 ppm) in the ^{13}C NMR spectrum. A peak frequency corresponding to the acetyl group at 198.5 ppm was also observed. ^{1}H NMR of **2Me-4T2H-COT** showed the presence of three signals corresponding to vinyl protons: a doublet of doublets at 6.94 ppm (H-3), a quartet of doublets of doublets at 5.94 ppm (H-6) and a doublet of doublets at 5.25 ppm

(H-2). The downfield shift of proton H-3 is indicative of a proton that is conjugated to an electron withdrawing group. Homonuclear decoupling experiments indicate that the vinylic hydrogen H-6 is coupled to both vicinal protons H-7α and H-7β with a 9.3 and 6.6 Hz couplings. It is further coupled allylically to the protons of the vinylic methyl group with a 1.5 Hz coupling. The upfield shift of H-2 is indicative of a proton of an enol ether. It is coupled to the upfield proton H-3 (5.6 Hz) and allylically to the eight/five bridgehead proton H-9 (2.1Hz). The UV-Vis spectrum showed a λ_{max} at 320 nm (ε~1760) indicative of a highly conjugated system. The excitition coefficient was low in comparison to other cyclooctatrienes isolated in this study. This is due to decomposition of the cyclooctatriene.

Photochemistry of **2Me-4T$_{2Me}$-K** in Benzene

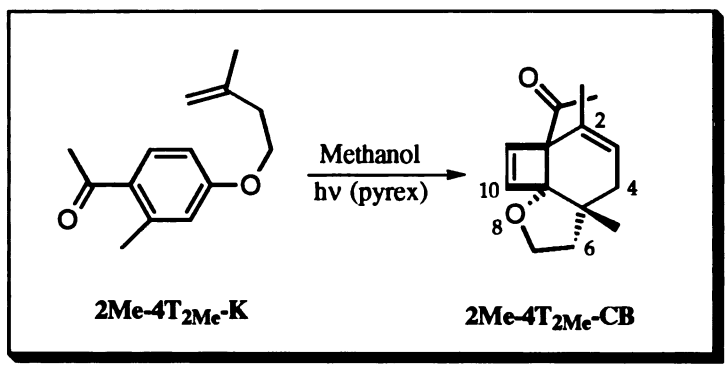
NMR scale irradiation of **2Me-4T$_{2Me}$-K** (2.1 mg in 1 mL solvent) was carried out in argon-purged benzene-d_6 through a Pyrex filter. After three hours of irradiation, **2Me-4T$_{2Me}$-K** was partially converted(~60%) into a single photoproduct. The newly formed product was believed to be 1,2,3,4-tetrahydro-1-methyl-6-(3'-methyl-3'-buten-1'-oxy)-2,3-dioxa-1-naphthol, **2Me-4T$_{2Me}$-II**, arising from hydrogen atom abstraction from the *ortho* methyl group. Purification of **2Me-4T$_{2Me}$-II** by column chromatography was unsuccessful. No observable 2+2 photocycloaddition products where formed under these conditions.



2Me-4T$_{2Me}$-K **2Me-4T$_{2Me}$-II**

Identification of **2Me-4T2Me-II** was accomplished by analysis of the ^{1}H NMR spectrum. Structural comparisions were made with the starting ketone, **2Me-4T2Me-K** and previously reported benzocyclobutenols.[6, 62] The ^{1}H NMR spectrum of **2Me-4T2Me-II** showed several diagnostic protons: a downfield AB quartet at 5.1 and 4.3 ppm (J_{AB}=15.5 Hz) and a methyl singlet at 1.57 ppm. The aromatic protons in **2Me-4T2Me-II** are shifted upfield compared to **2Me-4T2Me-K**. The aromatic protons appear at 6.68(d), 6.67(dd), and 6.2 ppm(d). All other peak resonances in **2Me-4T2Me-II** mirrored the starting ketone having nearly identical chemical shifts for the protons on the tether. Typically, the chemical shifts of methylene protons in benzocyclobuteneols are 2.9 and 3.1 ppm.[61, 62] The dramatic downfield chemical shift of the methylene protons in **2Me-4T2Me-II** is due to the proximity of a heteroatom.

Photochemistry of **2Me-4T2Me-K** in methanol

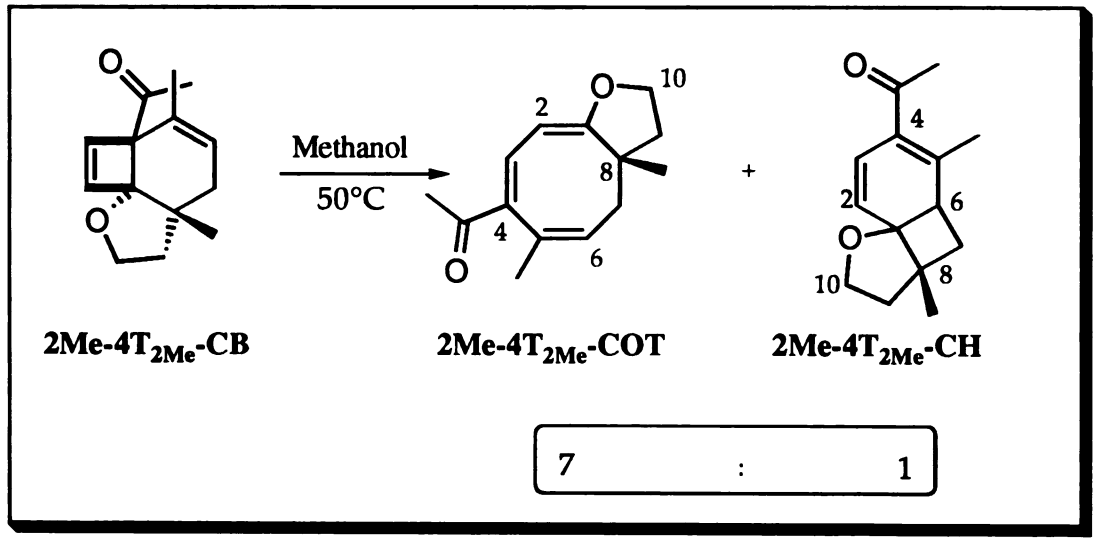


Irradiation of a 0.01 M solution of **2Me-4T2Me-K** in argon-purged methanol resulted in the formation of a single photoproduct after three hours. The product was determined as 1-acetyl-2,5-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T2Me-CB**. Deuterium incorporation was also observed by the rapid depletion of the peak frequency corresponding to the *ortho* methyl group at 2.5 ppm. Prolonged irradiation caused decomposition of **2Me-4T2Me-K** and **2Me-4T2Me-CB**.

The photoproduct, **2Me-4T2Me-CB** was identified based on its ^{1}H NMR spectrum. It showed signals corresponding to three vinyl protons: a doublet at 6.5 ppm, a doublet at 6.3 ppm, and a broad triplet at 5.54 ppm. Frequencies at 6.5 and 6.3 ppm are coupled to one another (3 Hz). This AB quartet pattern has been seen in previous cases and is characteristic of cyclobutenes arising from cyclization toward the substituent.[61] Homonuclear decoupling experiments on the peak frequency at 5.54 ppm indicate that this proton is coupled to two adjacent vicinal protons (H-4α and H-4β) with J=4.6 and 4.5 Hz respectively. It is also coupled allylically to protons of the vinylic methyl (J=1.5 Hz).

Thermal Chemistry of **2Me-4T2Me-CB**

Preparatory scale photolysis (245 mg per 75 mL) in purged methanol was carried out to isolate **2Me-4T2Me-CB**. At 50% conversion the photolysis was stopped and the solvent removed. ^{1}H NMR analysis of the reaction mixture showed the presence of **2Me-4T2Me-CB**. The photolysis mixture was redissolved in methanol(~0.01 M) and heated at 50°C for two hours. Purification of the mixture by silica gel chromatography provided an equilibrium mixture of 4-acetyl-5,8-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene, **2Me-4T2Me-CH** and 4-acetyl-5,8-dimethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **2Me-4T2Me-COT** in 1:7 ratio as determined by integration of the vinyl protons.

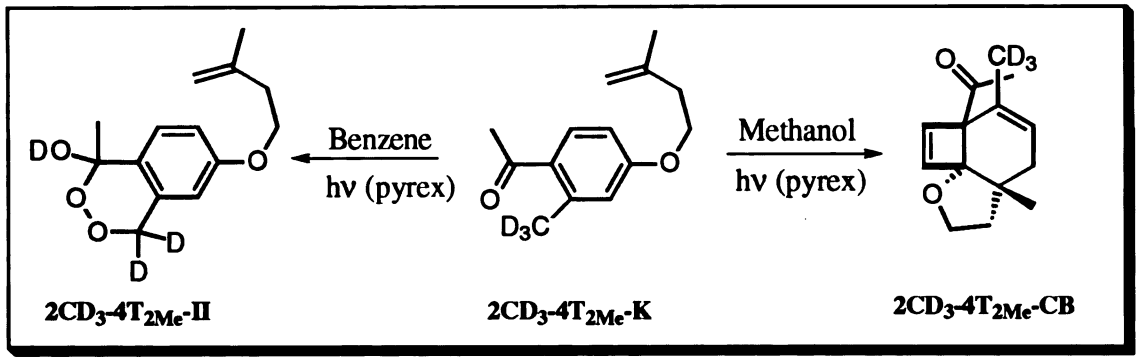


The thermal product, **2Me-4T2Me-COT**, was fully characterized by ^{1}H NMR, ^{13}C NMR, IR, MS and UV-Vis spectroscopy. **2Me-4T2Me-COT** has the same molecular ion peak as **2Me-4T2Me-K**. ^{1}H NMR showed the presence of three vinyl protons: a doublet at 6.95 ppm (H-3), a quartet of doublets of doublets at 5.9 ppm (H-6), and a doublet at 5.1 ppm (H-2). Homonuclear decoupling experiments show that protons H-3 and H-2 are coupled (5.1 Hz). Again, chemical shifts of these two protons are diagnostic. The large downfield shift of proton H-3 indicates conjugation with the acetyl group. Likewise, the upfield shift of the vinyl proton H-2 is indicative of a proton of a enol ether. The chemical shifts and couplings of these two protons uniquely identifies cyclooctatrienes arising from cyclization toward the ring substituents. The signal corresponding to proton H-6 (5.9 ppm) is coupled to two vicinal protons H-7α and H-7β (J=9.5 and 6.3 Hz). Weak allylic coupling (1.6 Hz) afforded by the adjacent methyl is also observed for proton H-6. ^{13}C NMR further confirmed the structural assignment. Six peak signals were observed in the vinylic region, one of which is shifted considerable upfield (93 ppm). A peak corresponding to the acetyl group (198 ppm) was also observed. UV-Visible spectroscopy showed a λ_{max} at 321 nm (ε~5300) and the IR showed a carbonyl stretch at 1672cm^{-1} both of which are indicative of a highly conjugated system.

The structure of the minor thermal product, **2Me-4T2Me-CH**, was assigned, based on it ^{1}H NMR. The spectrum showed two signals corresponding to vinyl protons: a doublet at 6.3 Hz (H-3) and a doublet at 5.3 Hz (H-2). The two protons are coupled to one another (10 Hz), characteristic of vinyl protons in a cis cyclohexene.[61]

Photochemistry of **2CD3-4T2Me-K**

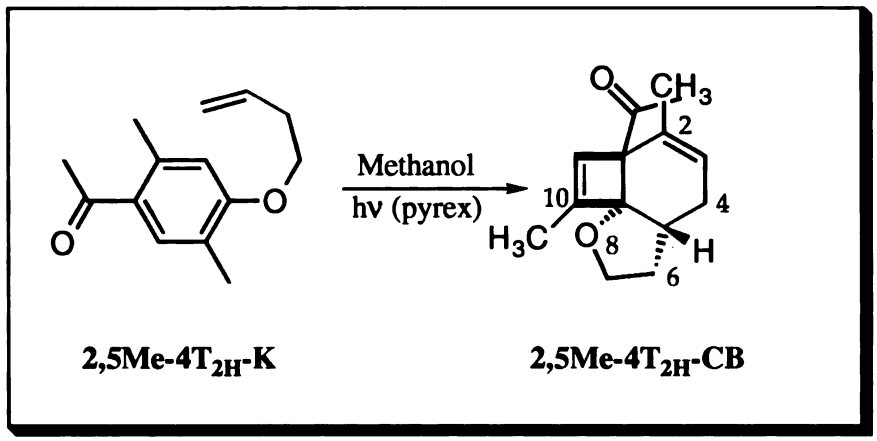
Similiar photochemistry was observed for **2CD3-4T2Me-K** as for **2Me-4T2Me-K**. Irradiation of **2CD3-4T2Me-K** (0.015 M) in benzene through a Pyrex filter resulted in the partial formation (~40%) of **2CD3-4T2Me-II** after three hours. Products arising from *ortho* 2+2 cycloaddition were not observed.



Irradiation of **2CD3-4T2Me-K** (~0.01 M) in argon purged methanol provided a single photoproduct in the same fashion as **2Me-4T2Me-K** . The product was indentified as **2CD3-4T2Me-CB** based on comparison to the ^{1}H NMR spectrum of **2Me-4T2Me-CB**. The chemical shifts and couplings observed in the ^{1}H NMR of **2CD3-4T2Me-CB** and **2Me-4T2Me-CB** are similar.

Photochemistry of **2,5Me-4T2H-K** in methanol

Compound **2,5Me-4T2H-K** provided a model compound to determine the relative effects of alkyl substituents at the *ortho* and *meta* positions. Photolysis of **2,5Me-4T2H-K** (0.0098 M) in argon-purged methanol through a Pyrex filter provided a single photoproduct after eight hours. This was identified as 1-acetyl-2,10-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2,5Me-4T2H-CB**. Thus, a methyl group *ortho* to the acetyl suppressed the selectivity associated with a methyl *ortho* to the tether.[31] Large scale photolysis (1 g per 500 mL solvent) of **2,5Me-4T2H-K** in argon-purged methanol afforded **2,5Me-4T2H-CB** (365 mg, 37%) after purification by dry column flash chromatography (hexanes:ethyl acetate, 80:20) .



Characterization of **2,5Me-4T2H-CB** was accomplished by ^{1}H NMR and ^{13}C NMR. A structural comparison can be made between **2Me-4T2H-5I-CB-t** and **2,5Me-4T2H-CB**. ^{1}H NMR showed signals corresponding to two vinyl protons: a quartet at 6.1 ppm (H-11) and a quartet of doublets of doublets at 5.6 ppm (H-3). Homonuclear decoupling experiments on the peak frequency at 5.6 ppm(H-3) indicate that it is coupled to two adjacent vicinal protons (H-4α and H-4β) with a 5.8 (2.2 ppm) and 4.0 Hz (1.9 ppm). It is also coupled allylically to protons of the vinylic methyl (1.6 ppm). A similar coupling pattern was observed in the spectra for **2Me-4T2H-CB** and **2Me-4T2H-5I-CB-t**. Proton (H-11) is found to be coupled allyically to the vinylic methyl group. Five signals were observed in the vinyl region (151, 137, 131, 124, and 123 ppm) in the ^{13}C NMR spectrum. A peak frequency corresponding to the acetyl group at 212 ppm was also observed.

The stereochemistry of **2,5Me-4T2H-CB** was determined by nOe experiments. Irradiation of the methyl group on C-10 afforded enhancements at H-11(1.75%), H-7 (1.36%), and the bridgehead proton H-5 (2.85%). Thus indicating that the cyclobutene ring is cis to bridgehead proton H-5.

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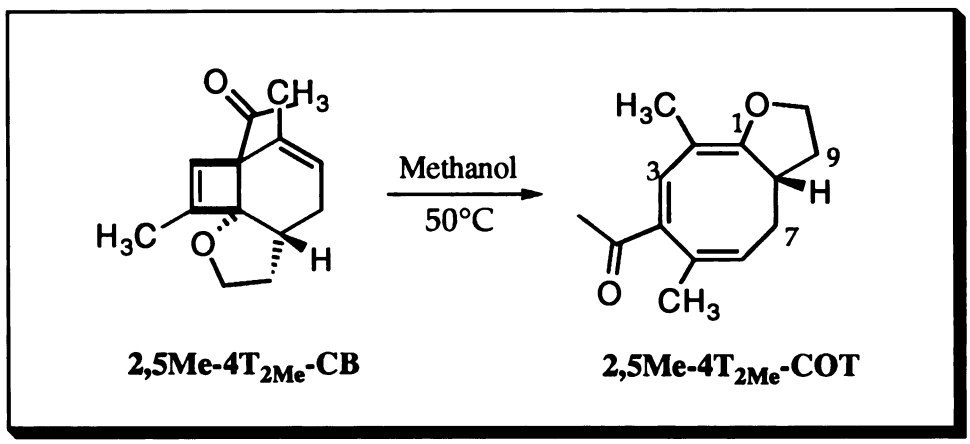
Thermal Chemistry of **2,5Me-4T2H-CB**

A solution of **2,5Me-4T2H-CB** (30 mg per 50 mL solvent) in argon-purged methanol was heated at 50°C for 48 hours. ^{1}H NMR analysis showed little thermal ring opening. Addition of a catalytic amount of *para*- toluenesulfonic acid caused rapid conversion of **2,5Me-4T2H-CB** to **2,5Me-4T2H-COT**. Purification of the reaction mixture by thin layer chromatography provided **2,5Me-4T2H-COT** (26 mg, 88%).

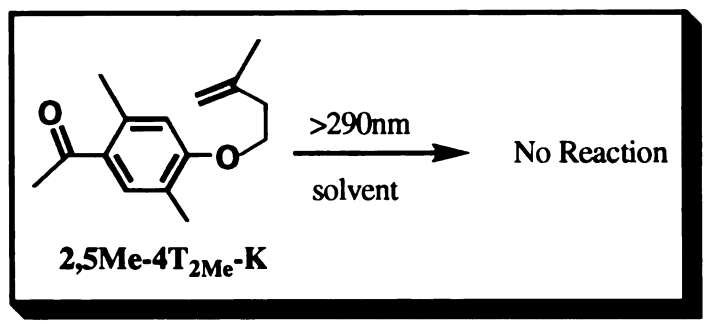


2,5Me-4T$_{2Me}$-CB **2,5Me-4T$_{2Me}$-COT**

The structure was characterized by MS, IR, UV-Vis and by NMR spectroscopy. **2,5Me-4T2H-COT** has the same molecular ion peak as the starting ketone, **2,5Me-4T2H-K** in the mass spectrum. The ^{1}H NMR of **2,5Me-4T2H-COT** showed signals corresponding to two vinyl protons: a broad singlet at 6.9 ppm (H-3) and a quartet of doublets of doublets at 5.9 ppm (H-6). The downfield shift of proton H-3 is indicative of a proton that is conjugated to an electron withdrawing group. Homonuclear decoupling experiments indicate that the vinylic proton H-6 is coupled to both vicinal protons (H-7α and H-7β) with a 9.3 and 6.7 Hz coupling. It is further coupled allylically to the vinylic methyl group. Six signals were observed in the vinyl region (158, 142, 139, 137, 126, and 102 ppm) in the ^{13}C NMR spectrum. A frequency corresponding to the acetyl group at 199 ppm was also observed. UV-Vis spectroscopy showed a λ_{max} at 329 nm (ε~5400) indicative of a highly conjugated system. The presence of an acetyl group was further confirmed by a carbonyl stretch at 1660 cm^{-1} by IR.

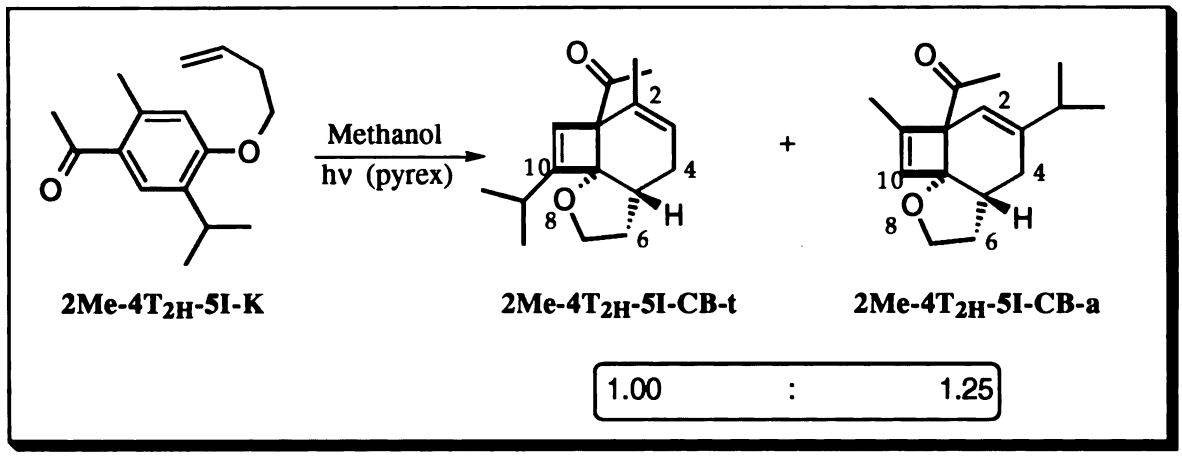
Photochemistry of **2,5Me-4T$_{2Me}$-K**

Photolysis of **2,5Me-4T$_{2Me}$-K** (~0.01 M) in argon-purged benzene or methanol resulted in no observable photoproducts by ^{1}H NMR at extended periods (>20 hours). The methyl group on the double bond of **2,5Me-4T$_{2Me}$-K** appears to suppress the photocycloaddition process. Similar results have been seen elsewhere in an analogous system.[31]



Photochemistry of **2Me-4T$_{2H}$-5I-K** in methanol

A solution of **2Me-4T$_{2H}$-5I-K** (2.6mg per 1mL solvent) in CD_3OD was degassed with argon and irradiated through Pyrex. Reaction progress was monitored by time resolved ^{1}H NMR. ^{1}H NMR analysis showed the presence of two photoproducts in a ratio of 1.25:1 after four hours of irradiation. The cyclobutene photoproducts were identified as 1-acetyl-3-isopropyl-11-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T$_{2H}$-5I-CB-a** and 1-acetyl-10-isopropyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T$_{2H}$-5I-CB-t** respectively. In this case, there is a slight preference for cyclization away from the *ortho* substituent. Preparatory scale photoylsis (1.2g per 500mL) in argon-purged methanol afforded **2Me-4T$_{2H}$-5I-CB-t** (0.218g) and **2Me-4T$_{2H}$-5I-CB-a** (0.273g) in 41% yield overall after purification by silca gel chromatography.

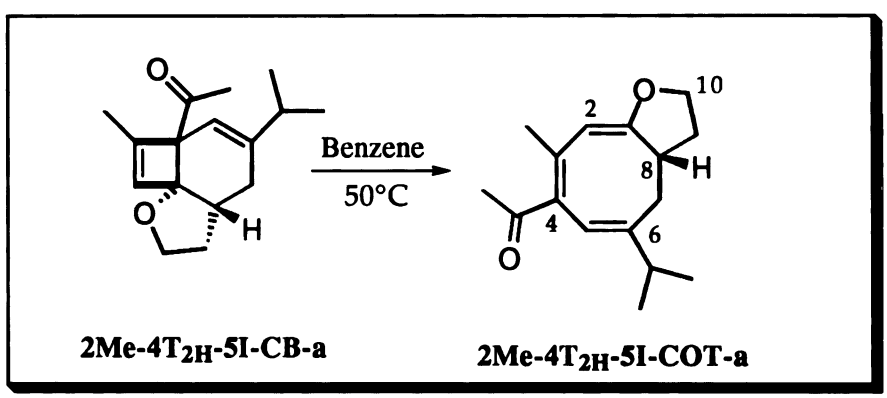


Characterization of **2Me-4T$_{2H}$-5I-CB-t** was accomplished by ^{1}H NMR, IR and Mass spectroscopy. A structural comparison can be made between **2Me-4T$_{2H}$-5I-CB-t** and **2,5Me-4T$_{2H}$-CB**. The IR spectrum had a strong absorbance at 1700cm^{-1} indicative of a nonconjugated carbonyl compound. An identical molecular ion peak to the starting ketone was found in the mass spectrum. ^{1}H NMR showed signals corresponding to two vinyl protons: a doublet at 6 ppm (H-11) and a quartet of doublets of doublets at 5.3 ppm (H-3). Homonuclear decoupling experiments on the peak frequency at 5.3 ppm(H-3) indicate that it is coupled to two adjacent vicinal protons (H-4α and H-4β) with a 4.2 (1.8 ppm) and 4.0 Hz (1.6 ppm). It is also coupled allylically to protons of the vinylic methyl (1.6 ppm). A similar coupling pattern was observed in the spectra for **2,5Me-4T$_{2H}$-CB** and **2Me-4T$_{2H}$-CB**. Proton (H-11) is found to be coupled allyically to the methine proton of the adjacent isopropyl group.

The ^{1}H NMR of **1AP-2Me-4T$_{2H}$-5IPr-CB-a** showed signals corresponding to two vinyl protons: a doublet of a quartet at 5.8 ppm (H-10) and a broad singlet at 5.6 ppm (H-2). Homonuclear decoupling experiments suggest that proton H-3 is coupled allylically to the five/six bridgehead proton (H-5), and to the vinylic methyl at 1.5 ppm. **2Me-4T$_{2H}$-5I-CB-a** has the same molecular ion peak as the starting ketone, **2Me-4T$_{2H}$-5I-K**.

Thermal Chemistry of **2Me-4T$_{2H}$-5I-CB-a**

A solution of **2Me-4T$_{2H}$-5I-CB-a** (270mg per 100mL solvent) in argon-purged benzene was heated 50°C in a constant temperature water bath. After 48 hours, NMR analysis showed little thermal ring opening. Addition of a catalytic amount of *para*-toluenesulfonic acid caused the rapid conversion of **2Me-4T$_{2H}$-5I-CB-a** to **2Me-4T$_{2H}$-5I-COT-a**. Purification of the reaction mixture by thin layer chromatography provided **2Me-4T$_{2H}$-5I-COT-a** (170.6mg, 63%).

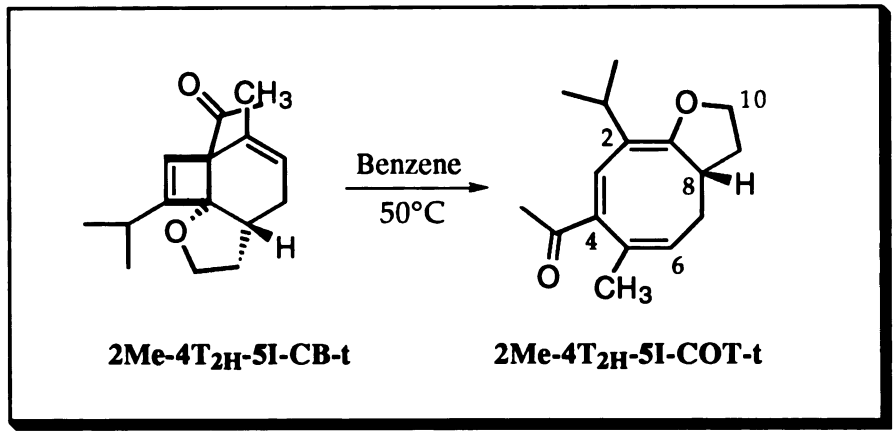


2Me-4T$_{2H}$-5I-CB-a **2Me-4T$_{2H}$-5I-COT-a**

The structure was identified based on its MS, UV-Vis, and ^{1}H NMR spectra. **2Me-4T$_{2H}$-5I-COT-a** has the same molecular ion peak as the starting ketone,**2Me-4T$_{2H}$-5I-K** and **2Me-4T$_{2H}$-5I-CB-a** by mass spectroscopy. The UV-Vis spectrum showed a λ_{max} at 313.5 nm (ε~4810) indicative of a highly conjugated system. The ^{1}H NMR of **2Me-4T$_{2H}$-5I-COT-a** showed signals corresponding to two vinyl protons: a broad singlet at 6 ppm (H-5) and a singlet at 5.4 ppm (H-2). The upfield chemical shift of H-2 is indicative of an enol ether proton. Proton H-5 is weakly coupled to allylic protons H-7α and H-7β. There are distinct differences in the spectra for **2Me-4T$_{2H}$-5I-COT-a** and its regioisomer **2Me-4T$_{2H}$-5I-COT-t** discribed below.

Thermal Chemistry of **2Me-4T2H-5I-CB-t**

The thermal ring opening of **2Me-4T2H-5I-CB-t** to **2Me-4T2H-5I-COT-t** was sluggish at 50°C in benzene. After 24 hours of heating only a small amount (<25%) of **2Me-4T2H-5I-COT-t** was present by ^{1}H NMR analysis. However, addition of a catalytic amount of *para*-toluenesulfonic acid caused rapid ring opening to **2Me-4T2H-5I-COT-t**. Purification of the reaction by silica gel column chromatography gave **2Me-4T2H-5I-COT-t** in 79% yield.



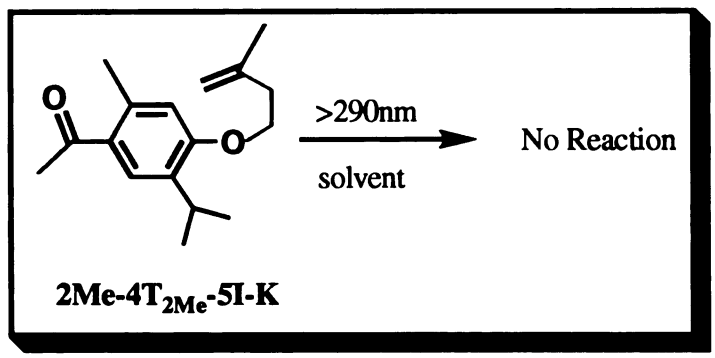
2Me-4T2H-5I-CB-t **2Me-4T2H-5I-COT-t**

The structure was characterized by MS, IR, UV-Vis and by NMR spectroscopy. A direct structural comparison can be made with **2,5Me-4T2H-COT**. **2Me-4T2H-5I-COT-t** has the same molecular ion peak as the starting ketone, **2Me-4T2H-5I-K**. Six signals were observed in the vinyl region (156.2, 141.2, 139.2, 136.3, 126.1, and 112.6 ppm) in the ^{13}C NMR spectrum. A signal corresponding to the acetyl group at 199 ppm was also observed. ^{1}H NMR of **2Me-4T2H-5I-COT-t** showed signals corresponding to two vinyl protons: a broad singlet at 7 ppm (H-3) and a quartet of doublets of doublets at 5.7 ppm (H-6). The downfield shift of proton H-3 is indicative of a proton that is conjugated to an electron withdrawing group. Homonuclear decoupling experiments suggest that the vinylic hydrogen H-6 is coupled to both vicinal protons H-7α (6.3 Hz) and H-7β (5.1 Hz). It is further coupled allylically to the protons of the vinylic methyl group with a 1.6 Hz coupling. The UV-Vis spectrum showed a λ_{max} at 330.5 nm (ε~5750)

indicative of a highly conjugated system. An acetyl group was further confirmed by a carbonyl stretch at 1670cm^{-1}.

Photochemistry of **2Me-4T$_{2Me}$-5I-K**

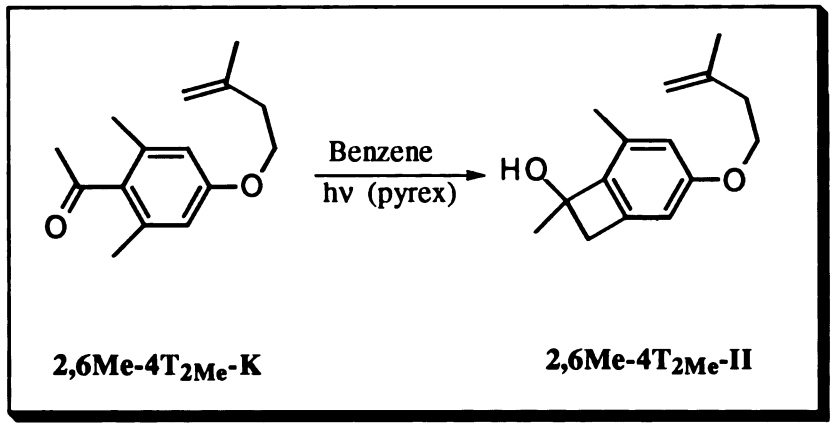
Photolysis of **2Me-4T$_{2Me}$-5I-K** (~0.015M) in argon-purged benzene or methanol resulted in no observable photoproducts by ^{1}H NMR at extended periods (>20 hours). The methyl group on the double bond of **2Me-4T$_{2Me}$-5I-K** appears to suppress the photocycloaddition process, as seen previously seen for **2,5Me-4T$_{2Me}$-K**.



Photochemistry of **2,6Me-4T$_{2Me}$-K**

Irradiation of a 0.01M solution of **2,6Me-4T$_{2Me}$-K** in argon-purged benzene resulted in the formation of a single photoproduct after five hours. A single product was determined to be 2'-methyl-4'-(3'-methyl-3'-buten-1'-oxy)-1-methylbenzocyclobutenol, **2,6Me-4T$_{2Me}$-II**, arising from hydrogen abstraction from an *ortho* methyl group. No observable 2+2 photocycloaddition products where formed under these conditions.

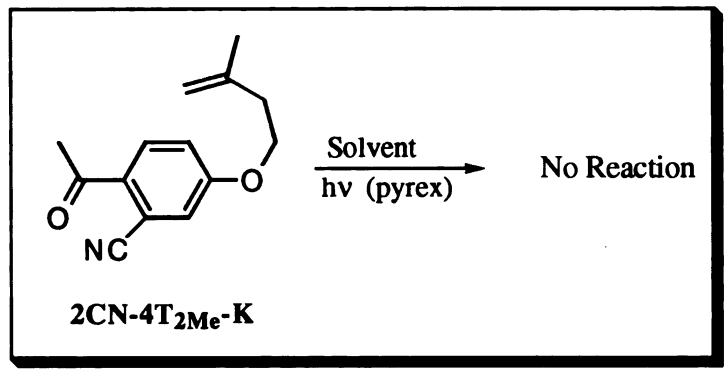
Similarly, NMR scale photolysis of **2,6Me-4T$_{2Me}$-K** (2.1mg in 1mL solvent) was carried out in argon-purged methanol-d4 through a Pyrex filter. Deuterium incorporation was observed by the depletion of the peak resonance corresponding to the *ortho* methyl group. No photoproducts arising from *ortho* 2+2 cyloaddition were observed by ^{1}H NMR after ten hours.



Photoproduct **2,6Me-4T2Me-II** was identified by its characteristic ^{1}H NMR. A direct structural comparison can be made with 2'-methyl-4'-methoxy-1-methylbenzocyclobutenol, obtained from photolysis of 2,6-dimethyl-4-methoxyacetophenone.[62] The ^{1}H NMR of **2,6Me-4T2Me-II** showed several diagnostic protons: an AB quartet of 13.8 Hz at 3.0 and 2.9 ppm and a methyl singlet at 1.56 ppm. All other peak resonances in **2,6Me-4T2Me-II** mirrored the starting ketone. Typically, the chemical shifts for the methylene protons in benzocyclobutenols are 2.9 and 3.1 ppm.[61, 62]

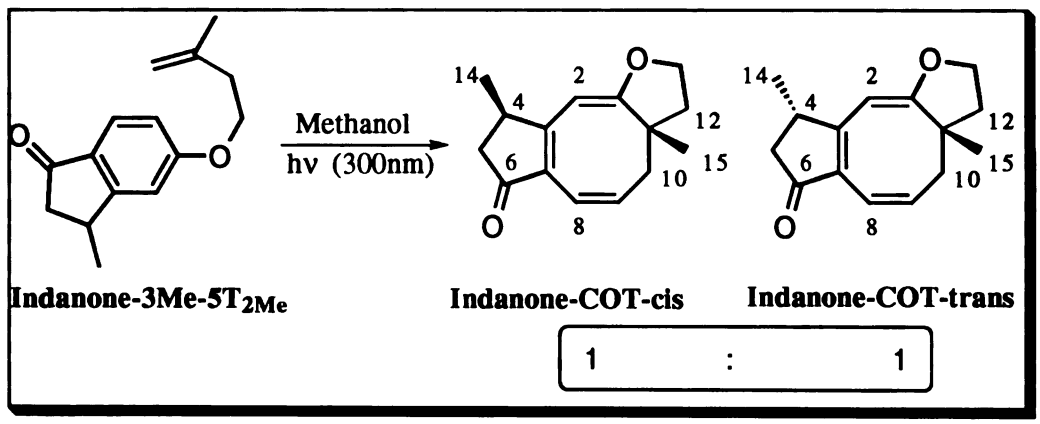
Photochemistry of **2CN-4T2Me-K**

NMR scale photolysis of **2CN-4T2Me-K** (2mg ketone per 0.75mL solvent) was carried out in argon-purged methanol or benzene at 313 nm or through Pyrex. The progress of the reactions was monitored by ^{1}H NMR. At either of the four reaction conditions, no photocycloaddition was observed. **2CN-4T2Me-K** remained photostable after long periods of irradiation (>20 hours).



Photochemistry of **Indanone-3Me-5T2Me**

A solution of **Indanone-3Me-5T2Me** (1.9mg per 0.75mL solvent) in CD_3OD was degassed with argon and irradiated at 300 nm in a Rayonet. The reaction was monitored by time resolved ^1H NMR. Analysis showed the presence of two photproducts in ratio of 1:1 after sixteen hours. The cyclooctatriene photoproducts were identified as trans-4,11-dimethyl-14-oxatricyclo[9.3.0.$0^{3,7}$]tetradecatri-1,3,8-ene-6-one, **Indanone-COT-trans**, and cis-4,11-dimethyl-14-oxatricyclo [9.3.0.$0^{3,7}$] tetradecatri-1,3,8-ene-6-one, **Indanone-COT-cis**. Attempts to separate the diastereomers were unsuccessful by either alumina or silica gel column chromatography.

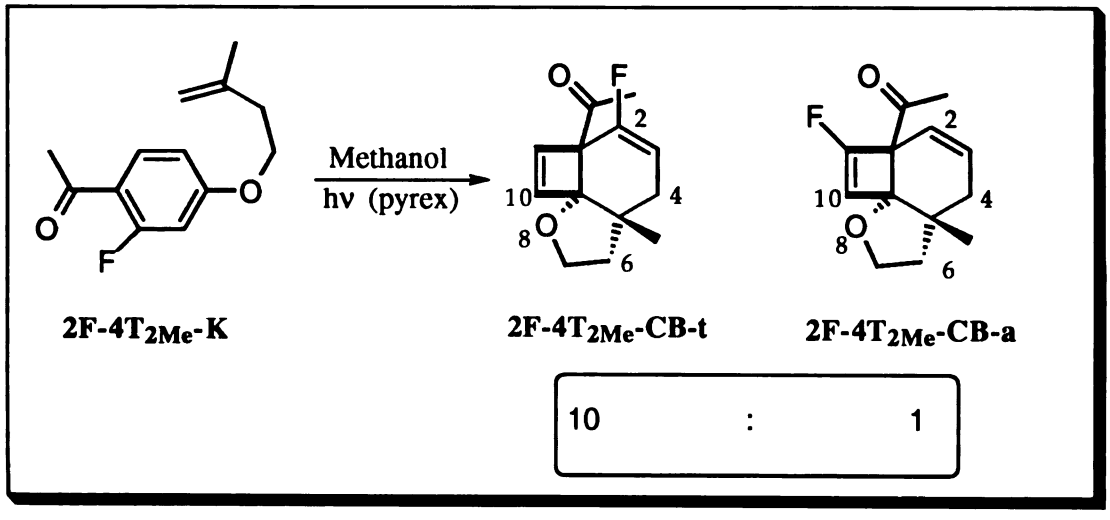


The ^1H NMR of the diastereomeric mixture shows distinct vinyl signal pairs: two doublets of triplets at 6.4 and 6.2 ppm (H-8_{cis} and H-8_{trans}), two overlapping doublet of

doublets of doublets at 5.9 ppm (H-9_{cis} and H-9_{trans}) and two singlets at 5.6 and 5.5 ppm (H-2_{cis} and H-2_{trans}). The chemical shifts of the two singlet protons are diagnostic. The upfield shift of these protons are indicative of vinyl protons of enol ethers. Homonuclear decoupling of the vinyl pairs indicates that H-8 and H-9 are strongly coupled to each other with a coupling of 12 Hz. This coupling constant is characteristic of vinyl protons of cis-cyclooctene and uniquely identifies cyclooctatriene arising from cyclization away from the *ortho* substituent. The adjacent methylene protons, H-10α and H-10β, are coupled allylically to H-8 and vinylically to H-9. The methyl protons for cis- and trans-cyclooctatriene also have distinct signals. The signals for the eight/five bridgehead methyls are at 1.20 and 1.17 ppm. The cyclopentanone methyls in cis- and trans-**Indanone-COT** appear as doublets (7 Hz coupling) at 1.21 and 1.23 ppm.

Photochemistry of **2F-4T2Me-K**

Irradiation of a solution of **2F-4T2Me-K** (2.2mg) in argon-purged methanol (1mL) provided two products in a ratio of 10:1 after three hours. The products were identified as 1-acetyl-2-fluoro-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene , **2F-4T2Me-CB-t**, and its regioisomer 1-acetyl-11-fluoro-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene, **2F-4T2Me-CB-a** respectively.

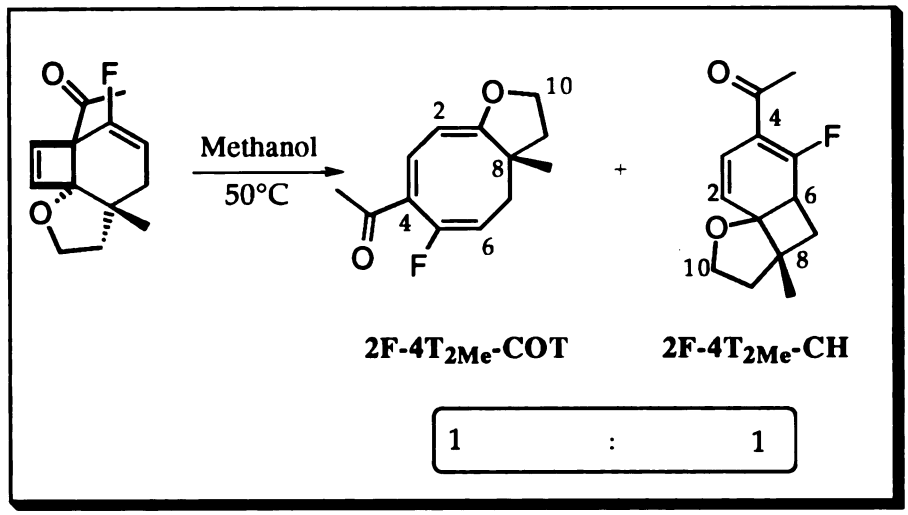


2F-4T2Me-K **2F-4T2Me-CB-t** **2F-4T2Me-CB-a**

Difficultly arose in characterizing the minor cyclobutene regioisomer, **2F-4T$_{2Me}$-CB-a**, due to extensive overlap of the peak frequencies in the ^{1}H NMR's aliphatic region by the major isomer. The two regioisomers can be distinguished based on the couplings of the vinyl protons. The major isomer, **2F-4T$_{2Me}$-CB-t**, has three signals in the vinyl region: an AB quartet at 6.5 (H-10) and 6.35 ppm (H-11) with a 2.9 Hz coupling and a doublet of doublets of doublets at 5.3 ppm. The AB quartet coupling is characteristic of vinyl protons of a cyclobutene ring. The multiplet at 5.3 ppm (H-2) is coupled to the vicinal protons, H-4α and H-4β with a 6.5 and 2.8 Hz coupling. A strong fluorine coupling of 15.6 Hz is also observed in H-3. The minor regioisomer, **2F-4T$_{2Me}$-CB-a**, has a characteristic coupling between two vinyl protons (H-2 and H-3) of 10 Hz. This coupling is indicative of vinyl protons in a *cis*-cyclohexene ring.[61] Proton H-2 (5.65 ppm) is coupled allyically to only one of the methylene protons at C-4. Proton H-3 is coupled to both vicinal protons H-4α and H-4β (6.7 and 2.4 Hz). The coupling between H-10 and fluorine was not determined.

Thermal Chemistry of **2F-4T$_{2Me}$-CB-t**

A dry methanol solution of **2F-4T$_{2Me}$-K** (700mg per 300mL solvent) was bubbled with argon and irradiated through a Pyrex filter until ~90% conversion (by GC). ^{1}H NMR analysis of the reation showed the presence of the starting ketone and **2F-4T$_{2Me}$-CB-t**. The reaction mixture was then heated at 50°C in argon-purged methanol (200mL) for five hours. Purification of the crude reaction mixture by dry column flash chromatography (ethyl acetate:hexanes, 5:95) gave a 1:1 ratio of 4-acetyl-5-fluoro-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene, **2F-4T$_{2Me}$-CH** and 4-acetyl-5-fluoro-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **2F-4T$_{2Me}$-COT** in 36% yield (254mg).

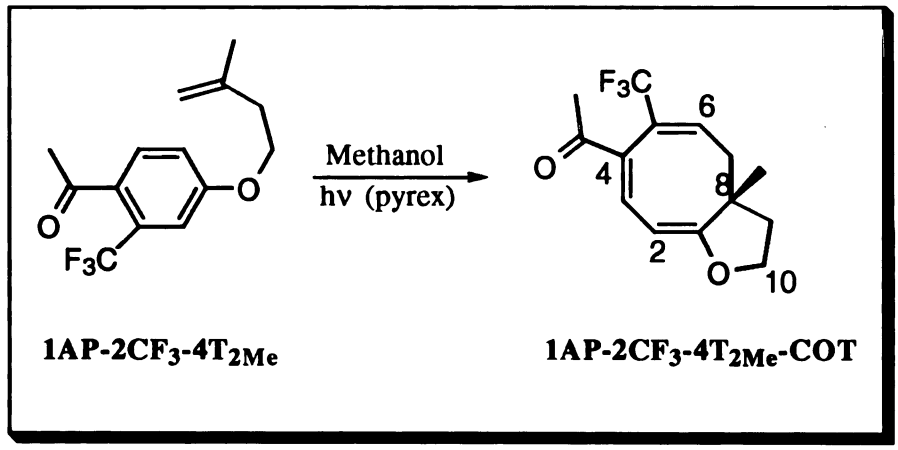


The thermal products **2F-4T2Me-COT** and **2F-4T2Me-CH** were identified based on their characteristic chemical shifts and couplings in the ^{1}H NMR. The fact that the cyclohexadiene and cyclooctatriene are in a 1:1 equilibrium made proton assignment difficult especially for the methylenes in the five membered ring. ^{1}H NMR of the equilibrium mixture showed the presence of five vinyl protons: a doublet of doublets at 7.3 ppm(H-3$_{COT}$), a doublet of doublets at 6.5 ppm(H-3$_{CH}$), a doublet of doublets of doublets at 5.85 ppm (H-6$_{COT}$), a doublet of doublets at 5.3 ppm(H-2$_{CH}$), and a doublet of doublets of doublets at 5.1 ppm(H-2$_{COT}$). Homonuclear decoupling experiments suggest that frequencies at 6.5 ppm(H-3$_{CH}$) and 5.3 ppm(H-2$_{CH}$) are strongly coupled to each other with a coupling of 10 Hz. This coupling is characteristic of vinyl protons on *cis*-cyclohexene. The two vinyl protons at opposite ends of the vinyl region, H-3$_{COT}$ and H-2$_{COT}$ are coupled to one another (6 Hz). The large upfield shift of proton H-2$_{COT}$ is indicative of a proton of an enol ether. The other remaining vinyl proton, H-6$_{COT}$ is coupled to two vicinal protons H-7α_{COT} and H-7β_{COT} with a 9.6 and 7.5 Hz coupling. Flourine coupling is observed for all vinyl protons in both **2F-4T2Me-COT** and **2F-4T2Me-CH**. A large flourine vinyl coupling of 17 Hz is observed in H-6$_{COT}$. The ^{13}C NMR provided additional information. Two singlets were observed in the carbonyl region

196 (doublet, 3 Hz) and 193 ppm (doublet, 3 Hz). Two C=O stretches were observed in the IR at 1682 and 1678cm^{-1}.

Photochemistry of **2CF3-4T2Me-K**

A solution of **2CF3-4T2Me-K** (1.7mg per 0.75mL solvent) in methanol-d4 was purged with argon and irradiated through a Pyrex filter. A single photoproduct was observed by ^{1}H NMR after twenty-three hours of irradiation at room temperature. The product was characterized as 4-acetyl-5-trifluoromethyl-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **2CF3-4T2Me-COT**. Preparatory scale photolysis (180mg per 60mL solvent) was carried out to isolate **2CF3-4T2Me-COT**. Purification of the photolysis mixture by silica gel column chromatography caused decomposition of **2CF3-4T2Me-COT**. The structure of **2CF3-4T2Me-COT** was determined from the ^{1}H NMR of the photolysis mixture.



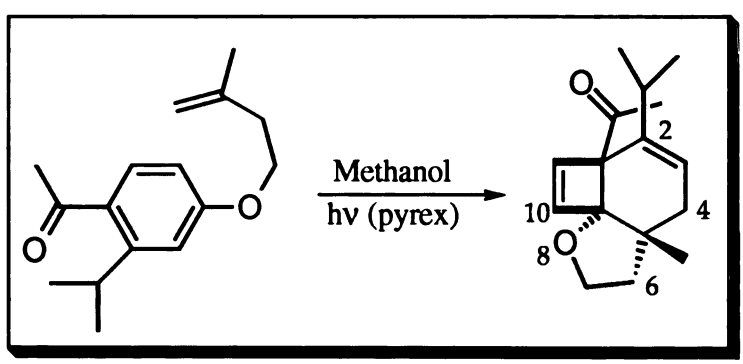
1AP-2CF3-4T2Me **1AP-2CF3-4T2Me-COT**

Photoproduct **2CF3-4T2Me-COT** was identified based on its characteristic ^{1}H NMR. It showed signals corresponding to three vinyl protons: a doublet at 7.2 ppm(H-3), a quartet of doublets of doublets at 6.8 ppm(H-6) and a doublet at 6.23 ppm(H-2). Peak resonances at 7.2 and 5.2 are coupled to one another with a 4.8 Hz coupling constant . This AB quartet pattern uniquely identifies cyclooctatrienes arising from cyclization toward

the *ortho* ring substituents. Proton (H-2) is assigned as a proton on an enol ether based on its upfield shift. The downfield shift of proton (H-3) is indicative of a proton that is conjugated to an electron withdrawing group. Homonuclear decoupling experiments indicate that proton (H-6) is coupled to both vicinal protons H-7α and H-7β with 9.2 and 6.5 Hz coupling constants.

Photochemistry of **2I-4T2Me-K**

A solution of **2I-4T2Me-K** (2.6mg per 0.75mL solvent) in CD_3OD was degassed with argon for fifteen minutes and irradiated using a medium pressure mercury lamp fitted with a Pyrex filter. ^1H NMR analysis of the reaction mixture showed only minimal product formation (~10% conversion) after nine hours of irradiation. The major product was identified as 1-acetyl-2-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2I-4T2Me-CB**.

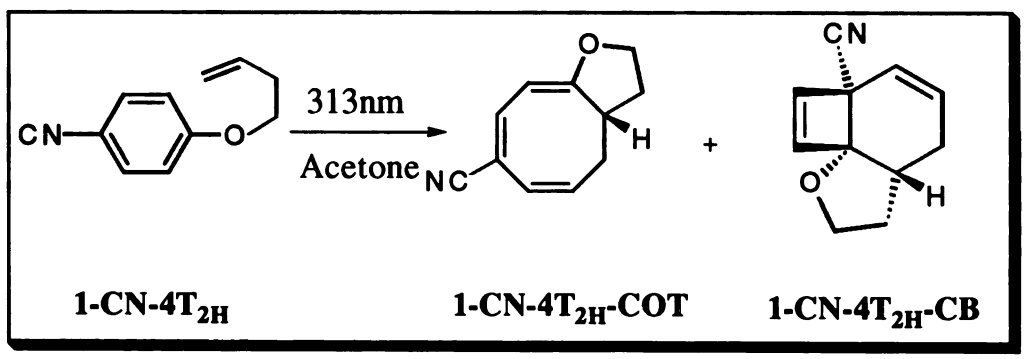


The structure was identified based on its characteristic chemical shifts and coupling constants in the ^1H NMR spectrum. The fact that the reaction was so inefficient made proton assignment difficult especially for the methylenes in the five membered ring. ^1H NMR showed signals corresponding to three vinyl protons: a doublet at 6.49 ppm(H-10), a doublet at 6.24 ppm(H-11), and a doublet of doublets of doublets at 5.65 ppm(H-3). Peaks at 6.40 and 6.24 ppm are coupled to one another with a 3 Hz coupling constant.

This AB quartet pattern uniquely identifies angular cyclobutenes arising from cyclization toward the ring substituent.

Photochemistry of **1CN-4T$_{2H}$** in Acetone

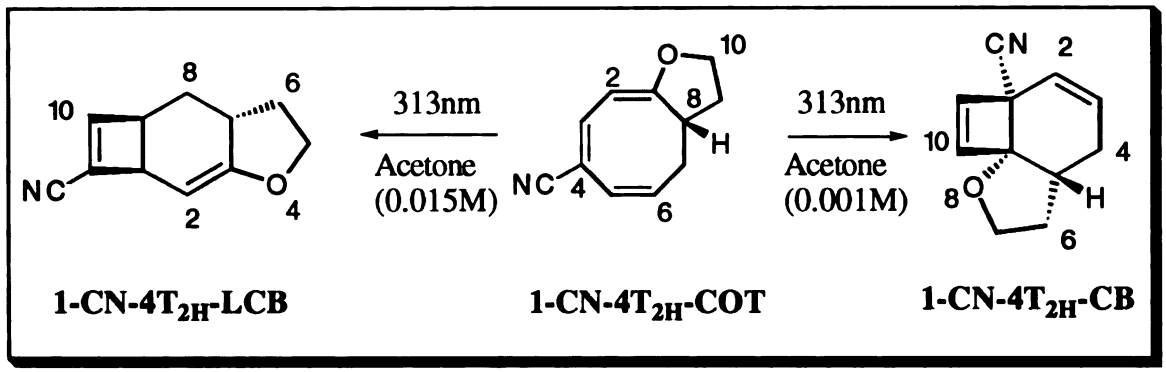
NMR scale photolysis of **1CN-4T$_{2H}$** (2mg benzonitrile per 0.75mL solvent) was carried out in argon-purged acetone-d_6 at 313 nm. The reaction progress was monitored by ^{1}H NMR. Analysis showed the presence of two products. The ratio of these products were time dependent. At 20% conversion, the ratio of products was approximately 1:1. Upon prolonged irradiation only one product was present. Attempts were made to isolate both products. Large scale irradiation of **1CN-4T$_{2H}$** (420mg per 160mL solvent) in acetone at 313 nm led to the formation of two products at 25% depletion of the benzonitrile by GC analysis. The reaction mixture was stopped at this point, concentrated, and separated by silica gel colunm chromatography Two products, 1-cyano-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene, **1CN-4T$_{2H}$-CB** and 4-cyano-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **1CN-4T$_{2H}$-COT**, were isolated along with the starting benzonitrile. **1CN-4T$_{2H}$-CB** was isolated in 51.5 % when **1CN-4T$_{2H}$** is irradiated to near completion.



1-CN-4T$_{2H}$ **1-CN-4T$_{2H}$-COT** **1-CN-4T$_{2H}$-CB**

Photochemistry of **CN-4T2H-COT**

The fate of **CN-4T2H-COT** was determined by irradiating pure samples in acetone-d6. At low concentrations of **1CN-4T2H-COT** (~0.001M), a condition where nearly all incidental light is absorbed by the solvent, **1CN-4T2H-COT** underwent diene to cyclobutene ring closure to form **1CN-4T2H-CB** at 313 nm irradiation. However, at higher concentrations of **1CN-4T2H-COT** (~0.015M), **1CN-4T2H-COT** formed **1CN-4T2H-LCB**.



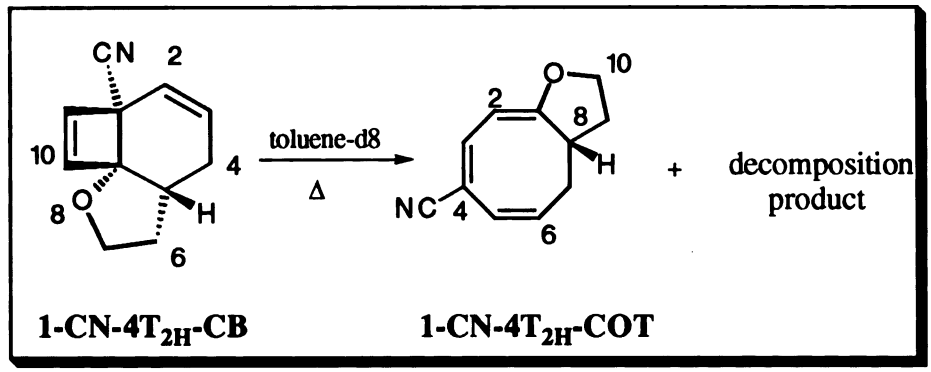
Photoproducts **1CN-4T2H-CB** and **1CN-4T2H-COT** were characterized using mass spectroscopy and ^{1}H NMR. **1CN-4T2H-CB** has the same molecular ion peak as both **1CN-4T2H-COT** and **1CN-4T2H**. ^{1}H NMR of **1CN-4T2H-CB** showed the presence of four signals corresponding to vinyl protons: a doublet at 6.26 ppm(H-10), a doublet at 6.11 ppm(H-11), a doublet of doublets of doublets at 5.8 ppm(H-3), and a doublet of doublets at 5.75 ppm(H-2). The signals at 6.26 and 6.11 are coupled to one another (2.8 Hz) and characteristic of vinyl protons in a cyclobutene. Likewise, frequencies at 5.8 and 5.75 ppm are coupled (10 Hz). This value is in accord with vinyl coupling in cyclohexene. These two coupling constants uniquely identifes the angular cyclobutene photoproduct. It is interesting to note that H-4α is coupled to the allylic (H-2) in this tricyclic system, whereas H-4β is not.

The stereochemistry of **1CN-4T2H-CB** was elucidated by nOe experiments Irradiation at the resonance corresponding to the six/five bridgehead proton, H-5, produces enhancements at H-4α(0.46%), H-6(2.17%), and the vinyl proton of cyclobutene, H-11(1.07%). These results indicate that the cyclobutene ring is cis to the bridgehead proton H-5, which further suggests that the six/five ring juncture is cis-fused.

The ^{1}H NMR of **1CN-4T2H-COT** showed the presence of four vinyl protons: a doublet at 6.6 ppm (H-3), a doublet of doublets of doublets at 5.9 ppm (H-6), a doublet at 5.85 ppm (H-5) and a doublet at 5.3 ppm (H-2). Homonuclear decoupling of these protons indicate that H-6 and H-5 are coupled to each other (12.7 Hz). The magnitude of this coupling is characteristic of vinyl protons of cis-cyclooctene.[61] Protons H-3 and H-2 are also shown to be coupled (6.9 Hz). The proton H-2 appears to be a proton of an enol ether based on its chemical shift. The upfield shift of proton H-3 indicates a high degree of deshielding offered by an adjacent electron-withdrawing group. ^{13}C NMR further confirmed this structural assignment. Six singlets were observed in the vinylic region, two of which were shifted considerable upfield (104.34 and 95.72 ppm). A frequency corresponding to the cyano(~121 ppm) was also observed. The UV-Visible spectrum showed a λ_{max} at 326 nm (ε~7500) indicative of a highly conjugated system. Characterization of **1CN-4T2H-LCB** is presented below.

Thermal Chemistry of **1CN-4T2H-CB**

Heating **1CN-4T2H-CB** in toluene-d8 (2.0mg in 1mL solvent) provided a minor amount of **1CN-4T2H-COT** as well as a considerable amount of an unidentified decomposition product. This result is surprising since cyclobutene ring opening to cyclooctatriene has been reported by Wagner to readily occur in substituted 1-acetyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-dienes.[28]

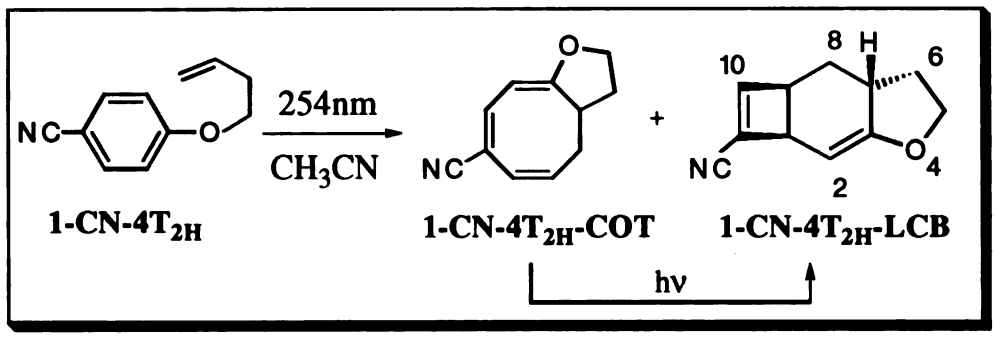


Photolysis of **1CN-4T2H** at 254 nm in Acetonitrile

Irradiation of **1CN-4T2H** in argon-purged acetonitrile at 254 nm in a quartz vessel (126mg reactant in 45mL solvent) gave two products in a 1:1 ratio after complete disappearance of starting material (2 hours). Purification of the reaction mixture by silica gel column chromatography gave 11-cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene, **1CN-4T2H-LCB** and 4-cyano-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **1CN-4T2H-COT**. The ratio of these two photoproducts was time dependent. Prolonged irradiation produced only **1CN-4T2H-LCB**. The fate of **1CN-4T2H-COT** was determined by independent irradiation. Photolysis of **1CN-4T2H-COT** in argon-purged acetonitrile-d3 gave **1CN-4T2H-LCB** as the only observable photoproduct at 254 nm. Gilbert has reported similiar results.[25]

Thermal Chemistry of **1CN-4T2H-LCB**

Heating a solution of **1CN-4T2H-LCB** in argon-purged toluene-d8 gave no observable thermal rearranged products after 12 hours. **1CN-4T2H-LCB** decomposed upon heating at 100°C for extended periods.



1-CN-4T$_{2H}$ **1-CN-4T$_{2H}$-COT** **1-CN-4T$_{2H}$-LCB**

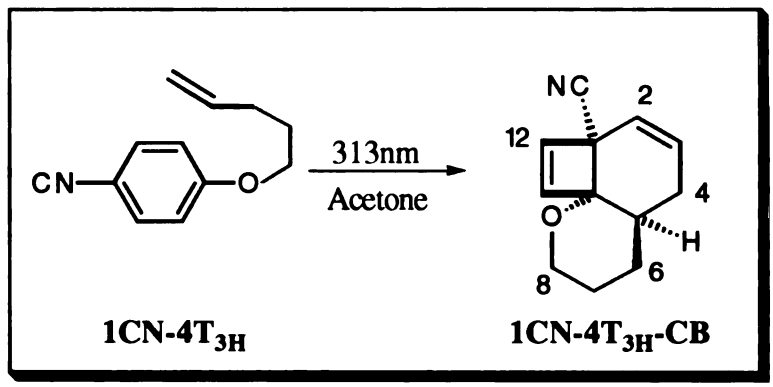
Photoproduct **1CN-4T2H-LCB** showed the same molecular ion peak as the starting benzonitrile, **1CN-4T2H**, by mass spectroscopy. ^{1}H NMR showed signals coresponding to two vinyl protons: a broad singlet at 5.9 ppm (H-10) and a doublet of doublets at 4.9 ppm(H-2). Homonuclear decoupling experiments indicate that the vinyl proton (H-2) is coupled to the four-six bridgehead proton, H-1(6.3 Hz) and allylically to the six-five bridgehead proton, H-7(2.4 Hz). The vinylic proton (H-10) is coupled to the four-six bridgehead proton, H-9, which is further coupled to the methylene group, H-8α,β (5.9 and 1.5 Hz) and H-1 (4.3 Hz).

The stereochemistry of **1CN-4T2H-LCB** was determined by nOe analysis. Irradiation of the peak frequency corresponding to the cyclobutene proton, H-10, afforded enhancements at H-9 (2%), H-8(1%) and the five-six bridge-head, H-7(1%).

Structural elucidatation for **1CN-4T2H-LCB** was assisted by its reported crystal structure and ^{1}H NMR. Proton coupling and chemical shift comparisions were made between Gilbert's published ^{1}H NMR data and those reported in this work. The stereochemistry of **1CN-4T2H-LCB**, determined by nOe, was in accord with the published crystal structure.[25]

Photochemistry of **1CN-4T3H**

The photochemistry of **1EC-4T3H** is nearly identical to that of **1CN-4T3H.** A solution of **1CN-4T3H** (2mg per 1mL) in acetone-d_6 was degassed and irradiated through a 313 nm filter solution. The reaction was monitored by time resolved ^{1}H NMR. Product formation was slow (>15hours). A single photoproduct was indentified as 1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene,**1CN-4T3H-CB** by ^{1}H NMR. An attempt was made to isolate this by large scale photolysis (450mg per 160ml) in argon-purged acetone. This afforded 263mg (58.4%) of **1CN-4T3H-CB** after purification by silica gel column chromatography. The expected intermediate, **1CN-4T3H-COT** could not be isolated, however its possible presence was detected by UV-Visible spectroscopy; A λ_{max} at ~300 nm was observed during photolysis, indicative of a highly conjugated system.



Photoproduct **1CN-4T3H-CB** was characterized using mass spectroscopy, IR, ^{13}C and ^{1}H NMR. **1CN-4T3H-CB** has the same molecular ion peak as **1CN-4T3H.** ^{1}H NMR of **1CN-4T2H-CB** showed signals corresponding to four vinyl protons: a doublet at 6.75 ppm(H-11), a doublet at 6.19 ppm(H-12), a doublet of doublets of doublets at 5.95 ppm(H-3), and a doublet of doublets at 5.75 ppm(H-2). The peak frequencies at 6.75 and 6.19 ppm are characteristic of vinyl protons in cyclobutene. Likewise, peak frequencies at 5.8 and 5.75 ppm are coupled to one another (10 Hz). This

vinyl pattern uniquely identifies the angular cyclobutene photoproduct. Homonuclear decoupling experiments confirmed all proton interactions. The ^{13}C NMR provided additional information. Four singlets were observed in the vinyl region (137.5, 136.3, 131.1, and 119.0 ppm). The presence of a cyano group was confirmed by a carbon-nitrogen stretch of 2240cm^{-1} in the IR, and a singlet at 123 ppm in the ^{13}C NMR spectrum.

The stereochemistry of **1CN-4T3H-CB** was elucidated by nOe experiments. Irradiation of the cyclobutene proton H-11 afforded enhancements at H-6(2.52%), H-8 (2.8%), and H-12(3.66%). The bridgehead proton H_5 was uneffected by irradiation at H-11. X-ray crystallography provided clear evidence of the stereochemistry of **1CN-4T3H-CB**. The cyclobutene ring of **1CN-4T3H-CB** is trans to the bridgehead proton H-5.

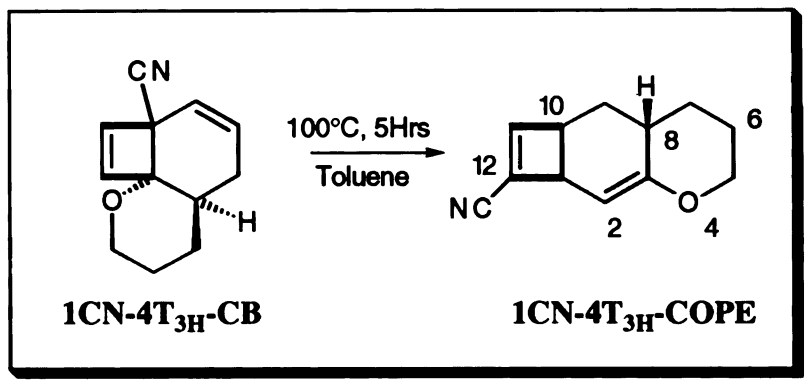
Photolysis of **1CN-4T3H** in acetonitrile at 254 nm

Irradiation of **1CN-4T3H** in aceonitrile at 254 nm provided similar results as that carried out in acetone at 313 nm. A quartz test tube containing **1CN-4T3H**(126mg) in argon-purged acetonitrile (45mL) was irradiated at 254 nm in an ice bath. The solution rapidly turned yellow and the reaction was complete after three hours as determined by GC analysis. A single photoproduct was isolated by column chromatography and recrystallized in ethyl aceate and hexane. The product was determined to be **1CN-4T3H-CB** based on its identical melting point.

Thermal Chemistry of **1CN-4T3H-CB**

Time resolved ^1H NMR was used to investigate the thermal ring opening of **1CN-4T3H-CB**. In a NMR tube, a solution of **1CN-4T3H-CB** in toluene-d8(0.015M) was heated at 100°C. After five hours analysis showed quantative conversion of **1CN-4T3H-CB** to 12-cyano-4-oxatricyclo[8.2.0.0^{3,8}]dodeca-2,11-diene, **1CN-4T3H-COPE**, via a

Cope rearrangement. Ring opening to the cyclooctatriene did not occur even with the addition of a catalytic amount of *para* toulenesulfonic acid to **1CN-4T3H-CB** in toluene.



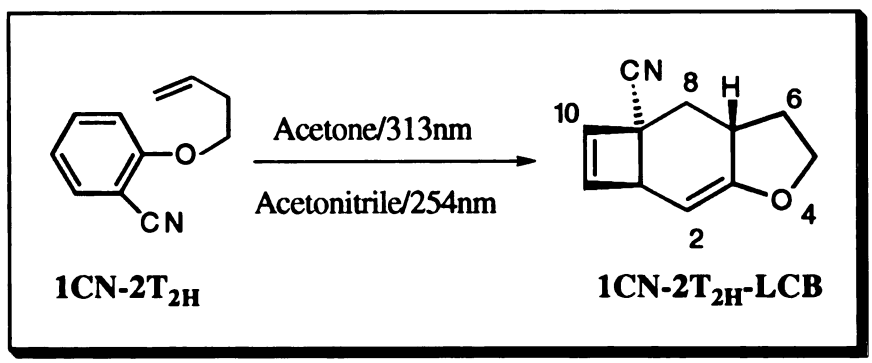
1CN-4T$_{3H}$-CB **1CN-4T$_{3H}$-COPE**

Thermal product **1CN-4T3H-COPE** was characterized ^{1}H NMR. It showed signals corresponding to two vinyl protons: a broad singlet at 5.93 ppm(H-11) and a doublet of doublets at 5.05 ppm(H-2). Homonuclear decoupling experiments were used to confirmed all proton connections. Proton H-2 is adjacent to an enol ether based on its upfield chemical shift. It is coupled allyically to bridgehead proton H-8 (2.5 Hz). Further coupling (5.9 Hz) to the adjacent four-six bridgehead (H-1) was also observed. Vinylic proton (H-11) is coupled to the four-six bridge-head proton, H-10, which in turn is coupled to the methylene, group H-9α,β (6.0 and 4.3 Hz). A structural comparision can be made to **1CN-2T2H-LCB**.

A similiar thermal rearrangement was observed in the chemistry of 1-trifluoroacetyl-7-oxa[7.2.0^{1,9}.0^{5,9}]undeca-2,10-diene, structural analog to **1CN-4T3H-CB**.[63] The stereochemistry is opposite to that found for **1CN-4T3H-CB**. The six-six bridgehead proton H-8 is cis to the cis-fused cyclobutene ring.

Photochemistry of **1CN-2T2H**

Irradiation of **1CN-2T2H** (0.01M) in argon-purged acetone through a 313 nm filter solution produced a single product after four hours. At roughly 70% conversion, the photochemistry was stopped and the yellow reaction mixture was concentrated. Purification of the mixture by silica gel chromatography gave **1CN-2T2H-LCB** in 74% isolated yield based on consumed starting material. A similar result was obtained for the photochemistry of **1CN-2T2H** in acetonitrile at 254 nm in a quartz reaction vessel. However, the conversion of **1CN-2T2H** to **1CN-2T2H-LCB** was more rapid (< 2 hours in an ice bath) under these conditions.



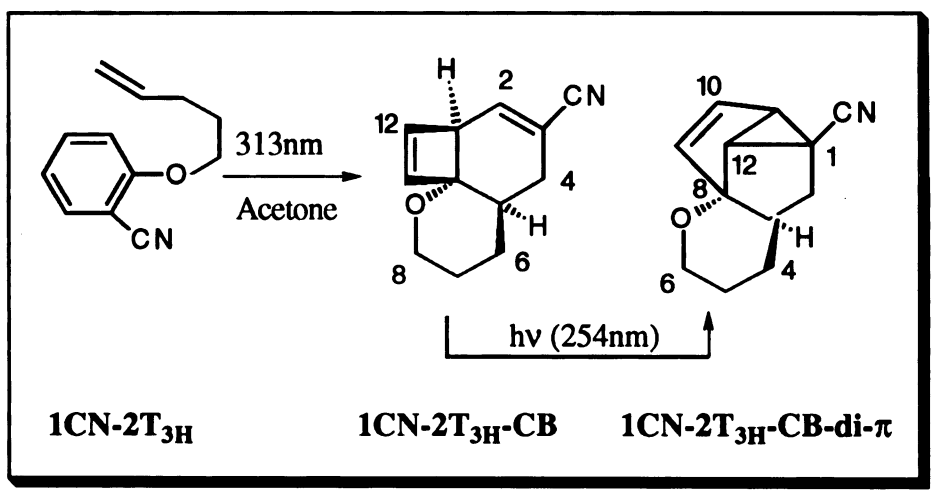
1CN-2T2H **1CN-2T2H-LCB**

Photoproduct **1CN-2T2H-LCB** was characterized by MS, ^{1}H NMR and ^{13}C NMR. **1CN-2T2H-LCB** showed the same molecular ion peak as the starting benzonitrile, **1CN-4T2H**, by mass spectroscopy. ^{1}H NMR showed signals corresponding to three vinyl protons: a doublet of doublets at 6.1 ppm (H-11) a doublet at 6 ppm (H-10), and a doublet of doublets at 4.8 ppm (H-2). The AB quartet at 6.1 and 6 ppm represents the protons on a cyclobutene ring. Homonuclear decoupling experiments suggest that the cyclobutene proton (H-11) is further coupled allylically to the four-six bridgehead proton,H-1(1 Hz). The upfield chemical shift of H-2 at 4.8 ppm is indicative of a enol ether proton. Proton (H-2) is coupled to the four-six bridgehead, H-1 (6.5 Hz) and allylically to the six-five bridgehead H-7. ^{13}C NMR provides additional structural

evidence. Four peak frequencies were observed in the vinyl region (160.6, 142.2, 131.9 and 88.6). A peak frequency corresponding to a cyano group was also observed at 122 ppm.

Photochemistry of **1CN-2T3H** in acetone

A 0.015M argon-purged acetone-d_6 solution of 5-(2'-cyanophenoxy)pent-1-ene was photolyzed in a NMR tube through a 313 nm monochromic solution. The reaction was monitored by ^{1}H NMR. Reaction was 50% complete after eight hours. A single photoproduct was indentified as 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1CN-2T3H-CB**. Preparatory scale photolysis (950mg per 400mL acetone) was carried out to isolate the single photoproduct, **1CN-2T3H-CB**, which was isolated by silica gel column chromatography as a pale yellow liquid in 49% yield.



Photochemistry of **1CN-2T3H** in acetonitrile at 254 nm

Similar results were obtained when **1CN-2T3H** was irradiated in acetonitrile at 254 nm. Photolysis of **1CN-2T3H** in argon-purged acetonitrile at 254 nm in a quartz vessel (126mg reactant in 45mL solvent) gave two products in a 2:1 ratio after complete depletion of the starting material. The products were determined to be **1CN-2T3H-CB**

and a di-π-methane rearranged isomer, 1-cyano-7-oxatetracyclo[7.4.1.0.$0^{8,3}$] dodeca-9-ene respectively, **1CN-2T$_{3H}$-CB-di-π**. Prolonged irradiation of **1CN-2T$_{3H}$-CB** at 254 nm resulted in complete conversion to **1CN-2T$_{3H}$-CB-di-π**.

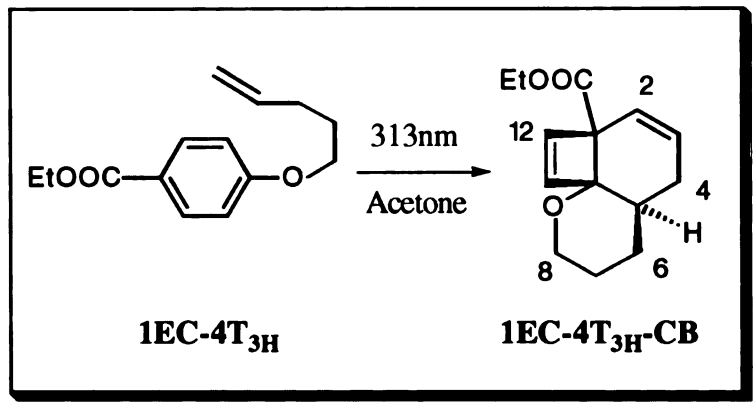
Photoproduct **1CN-2T$_{3H}$-CB** was characterized by MS and ^{1}H NMR. **1CN-2T$_{3H}$-CB** showed the same molecular ion peak as the starting benzonitrile, **1CN-2T$_{3H}$**, by mass spectroscopy. ^{1}H NMR showed signals corresponding to three vinyl protons: a doublet of doublets at 6.7 ppm (H-2), a doublet at 6.6 ppm (H-11), and a doublet of doublets at 6.2 ppm (H-12). An AB quartet at 6.6 and 6.2 ppm represents the protons on the cyclobutene with a characteristic coupling of 3 Hz. Homonuclear decoupling experiments indicate that the cyclobutene proton (H-12) is further coupled to the four/six bridgehead proton, H-1(0.8 Hz). H-1 is further coupled to the adjacent vinyl proton (H-2) with a 5.5 Hz coupling. H-2 is allylically coupled only to H-4α (3 Hz) as seen previously for **1CN-4T$_{2H}$-CB**.

The stereochemistry of **1CN-2T$_{3H}$-CB** was elucidated by nOe experiments. Irradiation of the cyclobutene proton H-11 afforded enhancements at H-8 (2.8%), and H-12(1.5%). Bridgehead proton H$_5$ was uneffected by irradiation at H-11. The cyclobutene ring of **1CN-4T$_{3H}$-CB** is therefore trans to the bridgehead proton H-5.

The di-π-methane rearranged photoproduct, **1CN-2T$_{3H}$-CB-di-π** was fully characterized spectroscopically. **1CN-2T$_{3H}$-CB-di-π** showed the same molecular ion peak as **1CN-2T$_{3H}$-CB** by mass spectroscopy. Several diagnostic protons are observed in the ^{1}H NMR spectrum. It showed signals coresponding to two vinyl protons: a doublet at 6.1 ppm (H-9) and a doublet of doublets at 5.9 ppm (H-10). These protons are coupled to each another (6 Hz) and are characteristic of vinyl protons in a cyclopentene ring.[61] Homonuclear decoupling experiments indicate that the cyclopentene proton (H-10) is further coupled to a tertiary cyclopropyl proton, H-11 (2.4 Hz). H-11 is further coupled to the other tertiary cyclopropyl proton H-12 at 3.1 ppm (6.6 Hz). Substantial downfield shifts of protons H-11 and H-12 have been reported previously by Cornellisse. ^{13}C NMR

provides additional structural evidence. Two singlets were observed in the vinyl region (129.5 and 127.9 ppm). A peak frequency corresponding to a cyano group was also observed at 121.6 ppm. Cyclopropyl carbons are shifted downfield >20 ppm in **1CN-2T3H-CB-di-π**. This uncharacteristic chemical shift for cyclopropyl carbons have been observed in other strained fused ring systems. The presence of a cyano group was further confirmed by a carbon-nitrogen stretch at 2231cm^{-1} by IR.

Photochemistry of **1EC-4T3H** in acetone



In a NMR tube, **1EC-4T3H** (0.0154M) in acetone-d_6 was degassed with argon and irradiated by a mercury arc lamp through a 313 nm monochromic filter. Time resolved NMR analysis of the photolysis mixture showed the reaction 50% complete after four hours. A single photoproduct was identified as 1-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1EC-4T3H-CB**. Large scale photolysis (500mg per 160mL acetone) was carried out to isolate the single photoproduct. **1EC-4T3H-CB** was isolated by silica gel column chromatography as a pale yellow liquid in 51.2% yield.

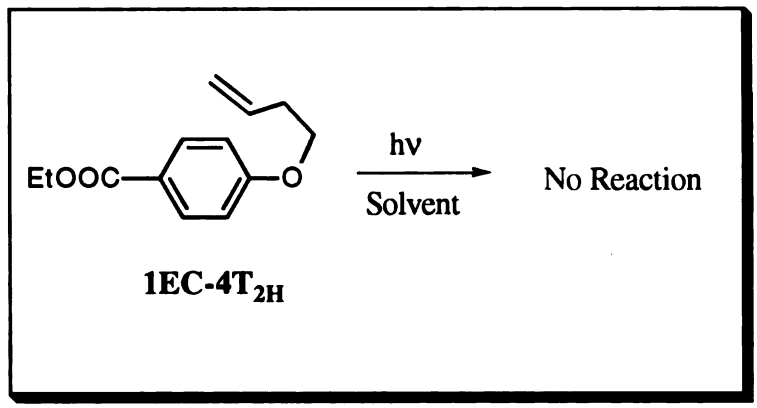
Photochemistry of **1EC-4T3H** in acetonitrile at 254 nm

Irradiation of **1EC-4T3H** in aceonitrile at 254 nm provided a similar result as that in acetone at 313 nm. A quartz test tube containing **1EC-4T3H** (140mg) in argon-purged acetonitrile (50mL) was irradiated at 254 nm in an ice bath. The solution rapidly turned yellow. GC analysis showed formation of two products in a 6:1 ratio after 2.5 hours. These were determined to be 1-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene and its C-5 epimer.

Photoproduct **1EC-4T3H-CB** was characterized by ^{1}H NMR . A direct structural comparison can be made with **1CN-4T3H-CB** spectrum. ^{1}H NMR spectroscopy showed four vinyl protons: a doublet at 6.7 ppm (H-11), a doublet at 6.3 ppm (H-12), a doublet of doublets of doublets at 5.9(H-3), and a doublet of doublets at 5.7 ppm (H-2). The AB quartet at 6.7 and 6.3 ppm (3 Hz), as well as the 10 Hz coupling observed between H-2 and H-3, uniquely identifies the angular cyclobutene photoproduct. Homonuclear decoupling experiments confirmed all proton interactions.

Photochemistry of **1EC-4T2H**

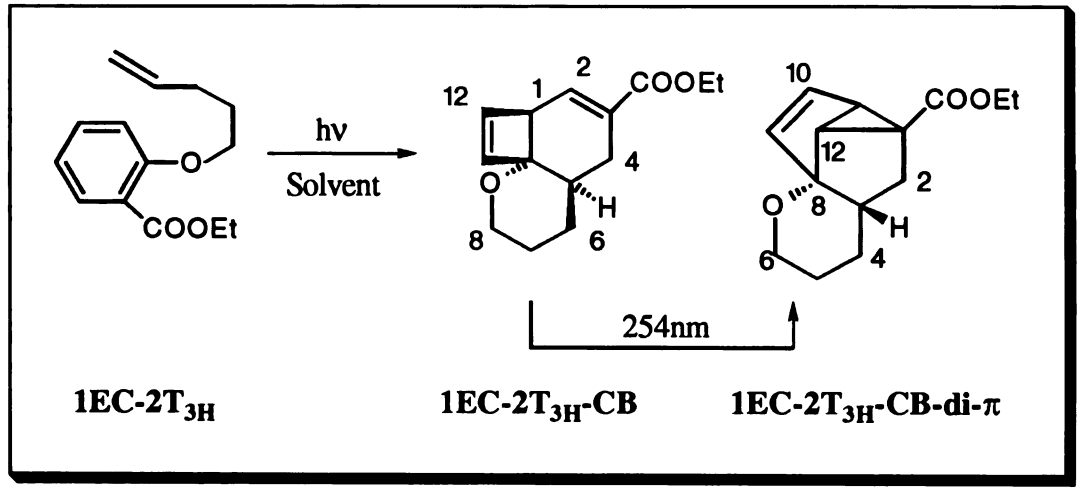
Photolysis (254nm or 313nm) of **1EC-4T2H** (~0.015M) in argon-purged acetonitrile or acetone resulted in no observable photoproducts by ^{1}H NMR at extended periods (>10 hours). Instead, **1EC-4T2H** was rapidly converted to polymeric material. Gilbert reported similar results for the methyl benzoate derivative when irradiated at 254nm in acetonitrile.[25]



1EC-4T$_{2H}$

Photochemistry of **1EC-2T$_{3H}$**

The photochemistry arising from **1EC-2T$_{3H}$** is similar to that of **1CN-2T$_{3H}$**. A 0.014M argon-purged acetone-d$_6$ solution of **1EC-2T$_{3H}$** was photolyzed in a NMR tube through a 313 nm monochromic solution. Two products was observed by time resolved NMR. The major was characterized as 3-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1EC-2T$_{3H}$-CB**, which undergoes secondary photolysis to **1EC-2T$_{3H}$-CB-di-π**. Preparatory scale photolysis (500mg **1EC-2T$_{3H}$** per 160mL acetone) was carried out to isolate **1EC-2T$_{3H}$-CB**. Upon completion, the crude reaction mixture was purified by silica gel chromatography. **1EC-2T$_{3H}$-CB** was obtained in 43% yield.



1EC-2T$_{3H}$ **1EC-2T$_{3H}$-CB** **1EC-2T$_{3H}$-CB-di-π**

Photolysis of **1EC-2T3H** in acetonitrile at 254 nm

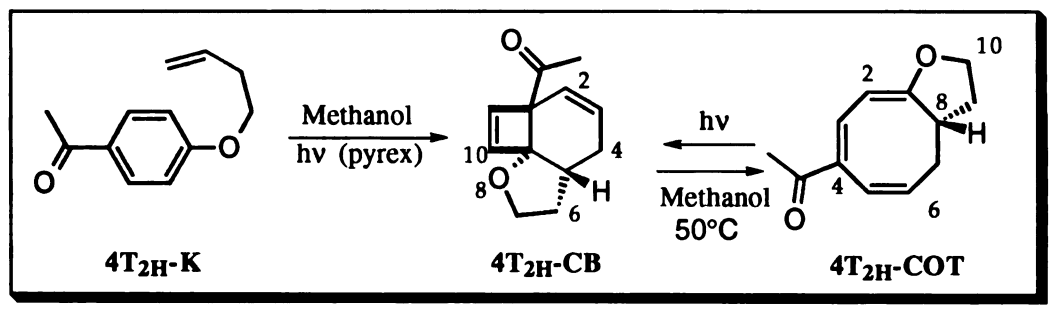
Irradiation of **1EC-2T3H** in argon-purged acetonitrile at 254 nm in a quartz reaction vessel resulted in the formation of two products in a 8:1 ratio after 3.25 hours. The two products were determined to be **1EC-2T3H-CB** and 1-ethoxycarbonyl-7-oxatetracyclo[7.4.1.0.$0^{8,3}$] dodeca-9-ene, **1EC-2T3H-CB-di-π**, a di-π-methane rearranged product. Irradiation of **1EC-2T3H-CB** (0.015M) in acetonitrile at 254 nm resulted in formation of **1EC-2T3H-CB-di-π**.

Photoproduct **1EC-2T3H-CB** was characterized by MS and ^{1}H NMR. **1EC-2T3H-CB** showed the same molecular ion peak as the starting ethyl ester, **1EC-2T3H**, by mass spectroscopy. ^{1}H NMR showed signals corresponding to three vinyl protons: a doublet of doublets at 7 ppm (H-2), a doublet at 6.6 ppm (H-11), and a doublet of doublets at 6.15 ppm (H-12). The two upfield protons (H-11 and H-12) are coupled to each other (3 Hz), characteristic of vinyl protons of a cyclobutene ring. Homonuclear decoupling experiments indicate that the downfield vinyl proton (H-2) is coupled to the four-six bridgehead (H-1) with a 5.5 Hz coupling. The bridgehead proton (H-1) is futher coupled to the vinyllic proton (H-12) (1 Hz).

The secondary photoproduct, **1EC-2T3H-CB-di-π** was characterized using MS, IR and ^{1}H NMR spectroscopy. A direct structural comparison can be made with **1CN-2T3H-CB-di-π**. **1EC-2T3H-CB-di-π** showed the same molecular ion peak as **1EC-2T3H-CB**, by mass spectroscopy. The ester group was confirmed by a carbonyl stretch at 1711cm^{-1} by IR. ^{1}H NMR showed signals corresponding to two vinyl protons: a doublet at 6.1 ppm (H-9) and a doublet of doublets at 5.9 ppm (H-10). The two vinyl protons are coupled to each other (5.8 Hz), characteristic of vinyl protons of a *cis* -cyclopentene.[61] Proton (H-10) is further coupled to a tertiary cyclopropyl proton, H-11 (2.4 Hz); this in turn is further coupled to the other tertiary cyclopropyl proton H-12 at 2.6 ppm (6.8 Hz).

Photochemistry of 4-(3'-buten-1'-oxy)acetophenone (**4T2H-K**)- Nahm's Compound

A solution of **4T2H-K** (2.1 mg in 0.75 mL solvent) in methanol-d4 was purged with argon and irradiated with a medium pressure mercury arc filtered through Pyrex. A single photoproduct was observed by ^{1}H NMR after 1.5 hours of irradiation at room temperature. The product was characterized as 1-acetyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **4T2H-CB**. Preparatory scale photolysis (300 mg **4T2H-K** in 200 mL solvent) was carried out through Pyrex to isolate **4T2H-CB**. The reaction progress was monitored by thin layer chromatography. After complete disappearance of the starting ketone (13 hours), the reaction mixture was heated at 50°C for six hours. During this time the reaction solution turned bright yellow. Purification of the reaction mixture by silica gel column chromatography (hexanes:ethyl acetate, 90:10) provided 4-acetyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene as a yellow solid, **4T2H-COT** (0.198 g, 66%). Irradiation of **4T2H-COT** (~0.012M) in argon-purged methanol provided complete reversion to **4T2H-CB**.



Photoproduct **4T2H-CB** was identified by its characteristic ^{1}H NMR. It showed signals corresponding to four vinyl protons: a doublet of doublets at 6.34 ppm(H-10), a doublet at 6.27 ppm(H-11), a doublet of doublets of doublets at 5.84 ppm(H-3) and a doublet of doublets at 5.72 ppm(H-2). Homonuclear decoupling experiments indicate that

the peaks at 6.34 and 6.27 ppm are coupled to one another with a 3 Hz coupling constant. The vinyl proton signal at 5.72 ppm is coupled strongly (10 Hz) to the vinyl proton at 5.84 ppm and allyically to the proton resonance at 2.2 ppm(H-4).

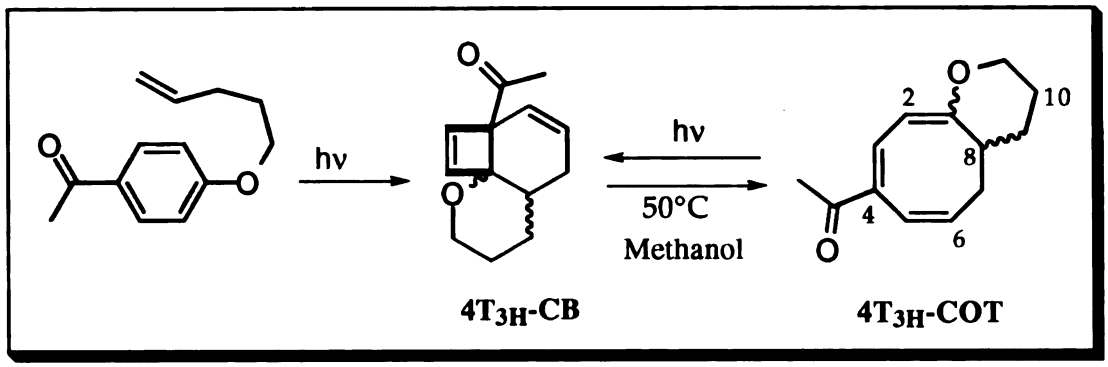
The stereochemistry of the photostable tricyclo[7.2.0.0.^{5,9}]octa-2,10-diene, **4T$_{2H}$-CB**, was determined by nOe studies.[64] Irradiation of the 5/6 bridgehead proton, H_5 (2.38 ppm), afforded an enhancement at the cyclobutene proton H-10.

The thermal product, **4T$_{2H}$-COT**, was identified based on its characteristic chemical shifts and coupling constants in the ^{1}H NMR spectrum. It showed signals corresponding to four vinyl protons: a doublet at 7.03 ppm (H-3), a triplet of doublets at 6.31 ppm (H-5), a doublet of doublets of doublets at 5.95 ppm (H-6), and a doublet at 5.42 ppm (H-2). Homonuclear decoupling of the vinyl pairs indicates that H-5 and H-6 are strongly coupled to each other with a coupling of 12.3 Hz. This coupling constant is characteristic of vinyl protons of cis-cyclooctene. The chemical shifts of the two doublet protons are also diagnostic. The upfield shift of H-2 is indicative of a vinyl proton of an enol ether and the downfield shift of H-3 is indicative of a proton that is conjugated to an electron withdrawing group.

Photochemistry of 4-(4'-penten-1'-oxy)acetophenone (**4T$_{3H}$-K**)

In a NMR tube, **4T$_{3H}$-K** was dissloved in argon-purged deuterated benzene (2.3 mg per 0.75 mL solvent) and irradiated through a Pyrex filter sleeve. Reaction progress was monitored by time resolved ^{1}H NMR. After 16 hours of irradiation, **4T$_{3H}$-K** was only partially converted (<30%) into a single photoproduct, 1-acetyl-9-oxatricyclo[8.2.0.0^{10,5}] undeca-2,11-diene, **4T$_{3H}$-CB**. Preparatory scale photolysis (400 mg per 250 mL benzene) was carried out to isolate **4T$_{3H}$-CB**. After 68 hours of irradiation through Pyrex, the reaction was ceased and concentrated *in vacuo*. The reaction mixture was redissolved in 60 mL of methanol and heated for five hours at 50°C.

Purification of the reaction mixture by silica gel column chromatography (hexanes:ethyl acetate, 90:10) provided 4-acetyl-12-oxabicyclo[6.4.0] undeca-1,3,5-triene as a yellow oil.

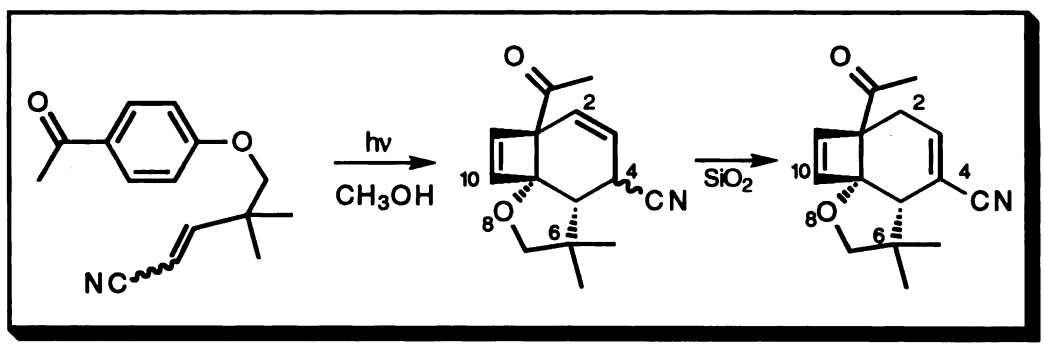


The thermal product, **4T3H-COT**, was identified based on its characteristic chemical shifts and coupling constants in the ^{1}H NMR spectrum. A structural comparsion can be made with **4T2H-COT**. The ^{1}H NMR spectra showed signals corresponding to four vinyl protons: a doublet at 6.9 ppm (H-3), a triplet of doublets at 6.35 ppm (H-5), a doublet of doublets of doublets at 6.1 ppm (H-6), and a doublet at 5.95 ppm (H-2). Homonuclear decoupling of the vinyl pairs indicates that H-5 and H-6 are strongly coupled to each other with a coupling of 11.4 Hz. This coupling constant is characteristic of vinyl protons of cis-cyclooctene. The chemical shifts of the two doublet protons are also diagnostic. The upfield shift of H-2 is indicative of a vinyl proton of an enol ether and the downfield shift of H-3 is indicative of a proton that is conjugated to an electron withdrawing group. It is interesting to note that the downfield chemical shift of proton H-2 is less pronounce in **4T3H-COT** than in **4T2H-COT**. This would suggest that the triene unit of the 8-6 fused system is less conjugated with the oxygen than in the 8-5 fused ring system.

Photochemistry of **4T2N(CN)-K**

Irradiation of a 1:9 cis/trans mixture of 5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile (2.1mg) in argon-purged methanol (0.75mL) provided rapid isomerization of the double bond (1:2.5 cis/trans) after 15 minutes as determined by integration of the vinyl

protons. Prolonged irradiation of the reaction mixture produced two products in a 1:1.3 ratio as determined by integration of peak resonances corresponding to the acetyl groups at ~2.1 ppm. The photoproducts were determined to be (4-endo)-1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene and (4-exo)-1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene. Preparatory scale photolysis was carried out to isolated the photoproducts. cis-and trans-5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile (0.06g) was dissolved in freshly distilled methanol (25mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by thin layer chromatography. Purification of the crude reaction mixture by thin layer chromatography (hexanes:ethyl acetate, 80:20) gave 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene and its thermal rearranged isomer 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-3,10-diene. The exact stereochemistry of the latter could not be determined due to its thermal instability.



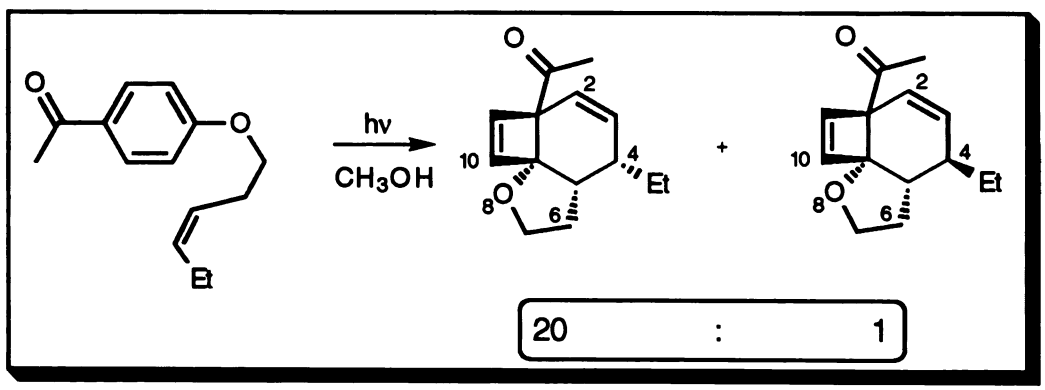
Characterization of 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene was accomplished by ^{1}H NMR. It showed the presence of four vinyl protons: a doublet at 6.6 ppm (H-10), a doublet at 6.5 ppm(H-11), a doublet of doublets at 6.1 ppm(H-2), and a doublet of doublets at 5.8 ppm (H-3). The AB quartet pattern at 6.6 and 6.5ppm (3 Hz), as well as the 10.2 Hz coupling observed between H-2 and H-3, uniquely identifies the angular cyclobutene photoproduct. Homonuclear decoupling

experiments on the peak frequencies at 5.8 ppm(H-3) and 6.1 ppm(H-2) indicate that they are further coupled to the peak resonace at 3.5 ppm (4.8 and 1.5 Hz respectively).

The thermal product, 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.$0^{9,5}$] undeca-3,10-diene, was characterized by ^{1}H NMR. It showed signals corresponding to three vinyl protons: a broad doublet of doublets at 6.85 ppm(H-3), a doublet at 6.3 ppm (H-10), and a doublet at 6.2 ppm (H-11). The AB quartet pattern at 6.3 and 6.2 ppm (3 Hz) is characteristic of vinyl protons in cyclobutene.[61] The downfield shift of proton H-3 is indicative of a proton that is conjugated to an electron withdrawing group. Homonuclear decoupling of proton (H-3) indicates that it is coupled to two vicinal protons at 3.12 ppm and 2.05 ppm (2.7 and 6.3 Hz respectively).

Photochemistry of **cis-4T$_{2N}$(Et)-K**

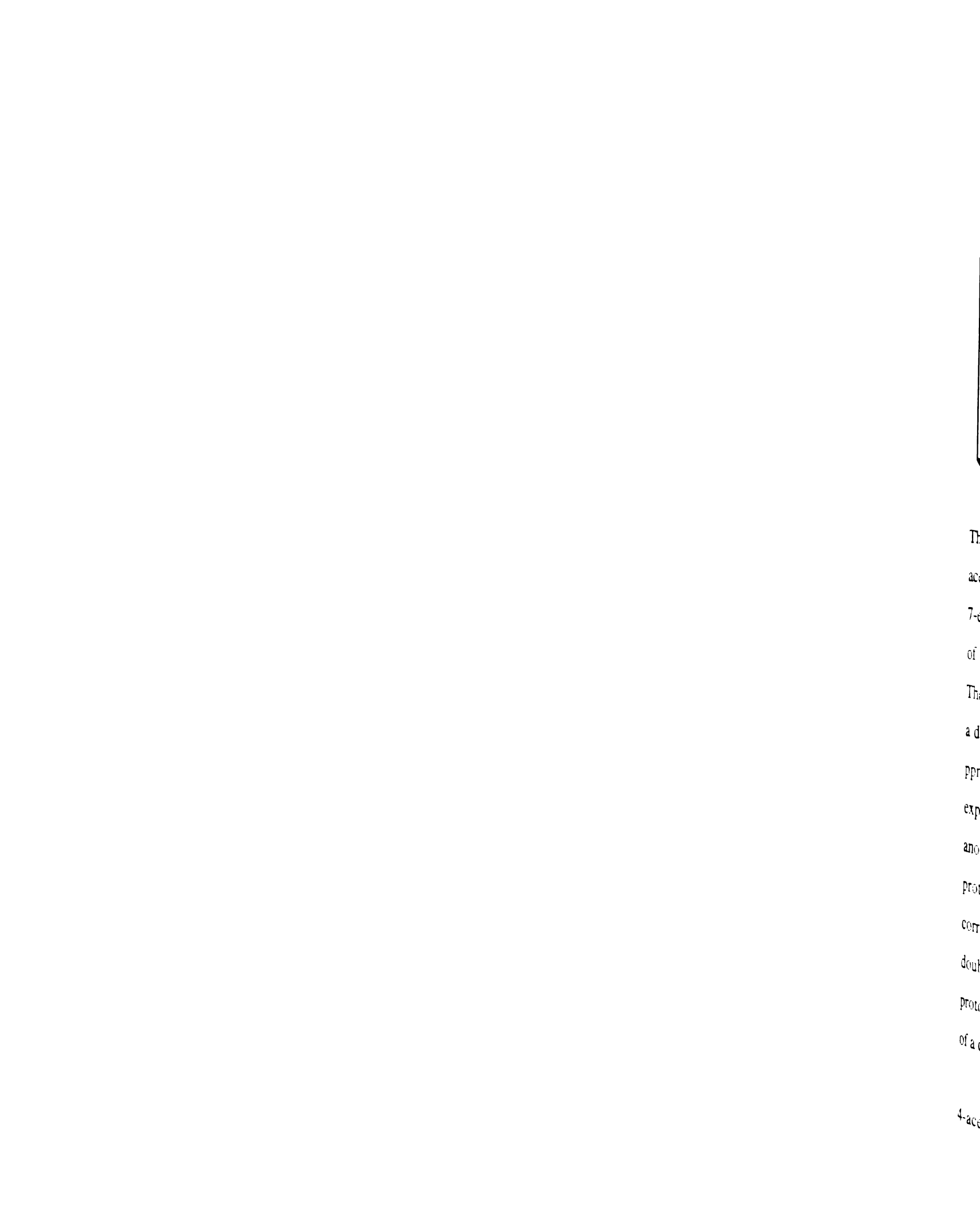
Irradiation of a solution of cis-6-(4'-acetylphenoxy)-3-hexene (3.2 mg) in argon-purged methanol (0.8 mL) provided two products in a 20:1 ratio as determined by integration of peak resonances corresponding to the cyclobutene proton (H-11) at 6.3 and 6.2 ppm. The two photoproducts were determined to be (4-endo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.$0^{9,5}$]undeca-2,-10-diene, **(4-endo)-Et-CB**, and (4-exo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.$0^{9,5}$] undeca-2,-10-diene, **(4-exo)-Et-CB**, respectively. Cis/trans isomerization of the double bond was also observed during the photoreaction as determined by the observation new double bond resonances (J=16Hz).

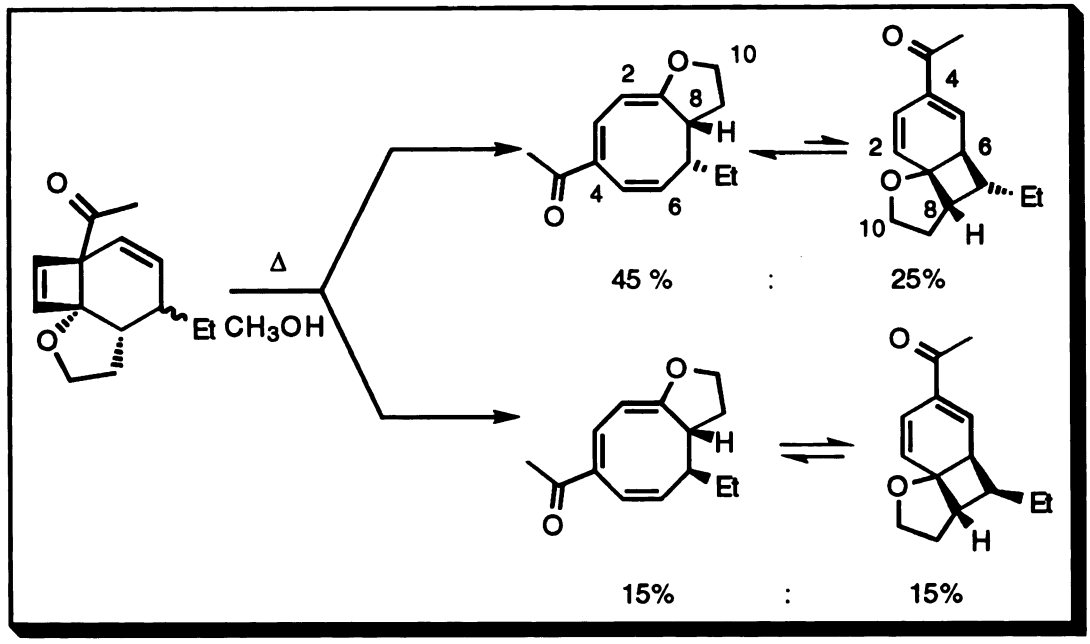


Characterization of (4-endo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,-10-diene was accomplished by ^{1}H NMR. It showed the presence of four vinyl protons: a doublet at 6.4 ppm (H-10), a doublet at 6.3 ppm (H-11), a doublet of doublets at 5.9 ppm (H-2), and a doublet of doublets at 5.7 ppm (H-3). The AB quartet pattern at 6.4 and 6.3ppm (3 Hz), as well as the 10.2 Hz coupling observed between H-2 and H-3, uniquely identifies the angular cyclobutene photoproduct. Nearly identical chemical shifts and coupling constants were observed for (4-exo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,-10-diene. The stereochemistries of these compounds were determined by comparing their chemical shifts and coupling constants to (4-endo)-1-acetyl-4-methyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,-10-diene previously characterized by nOe.[64]

Thermal Ring Opening of **endo and exo-4T$_{2N}$(Et)-CB**

cis-6-(4'-Acetylphenoxy)-3-hexene (0.2 g) was dissolved in freshly distilled methanol (250mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by thin layer chromatography. After complete disappearance of the starting ketone (28 hours), the reaction mixture was heated at 50°C for six hours. The reaction mixture turned yellow during this time. Attempts to separate the crude reaction mixture were unsuccessful by thin layer chromatography (hexanes:ethyl acetate, 80:20). NMR analysis of the photoproducts showed a diastereomeric mixture of (endo and exo)-4-acetyl-7-ethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene and (endo and exo)-4-acetyl-7-ethyl-11-oxatricyclo[6.3.0.0.^{1,6}]undeca-2,4-diene. The overall ratio of products was 3 **(7-endo)-Et-COT** : 1.5 **(7-endo)-Et-CH** : 1 **(7-exo)-Et-COT** : 1 **(7-exo)-Et-CH** as determined by integration of their vinyl protons.





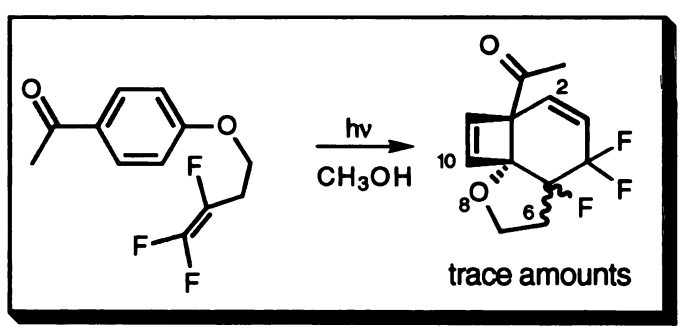
Thermal ring opening of **(4-endo)-Et-CB** provided a 2:1 equilibrium mixture of 4-acetyl-7-ethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene, **(7-endo)-Et-COT** and 4-acetyl-7-ethyl-11-oxatricyclo[6.3.0.0.^{1,6}] undeca-2,4-diene, **(7-endo)-Et-CH**. The structures of these compounds were determined by their characteristic vinyl regions in the ^{1}H NMR. The ^{1}H NMR of **(7-endo)-Et-COT** showed signals corresponding to four vinyl protons: a doublet at 6.96 ppm (H-3), a doublet at 6.29 ppm (H-5), a doublet of doublets at 5.65 ppm (H-6), and a doublet of doublets at 5.54 ppm (H-2). Homonuclear decoupling experiments indicate that the peak frequencies at 5.65 and 6.29 ppm are coupled to one another with a coupling constant of 12.1 Hz. This coupling is characteristic of vinyl protons in cis cyclooctene.[61] The ^{1}H NMR of **(7-endo)-Et-HX** showed signals corresponding to three vinyl protons: a broad doublet at 6.78 ppm (H-5), a doublet of doublets at 6.52 ppm (H-2), and a doublet of doublets at 5.72 ppm (H-3). The two upfield protons (H-2 and H-3) are coupled to each other (10.1 Hz), characteristic of vinyl protons of a cyclohexene ring.[61]

Thermal ring opening of **(4-exo)-Et-CB** provided a 1:1 equilibrium mixture of 4-acetyl-7-ethyl-11-oxabicyclo[6.3.0]undeca-1,3,5-triene, **(7-exo)-Et-COT** and 4-

acetyl-7-ethyl-11-oxatricyclo[6.3.0.0.^{1,6}] undeca-2,4-diene, **(7-exo)-Et-CH**, as determined by integration of the vinyl protons. The structures of these compounds were determined by their characteristic vinyl regions in the ^{1}H NMR. Nearly identical chemical shifts and coupling constants were observed between the diastereomers.

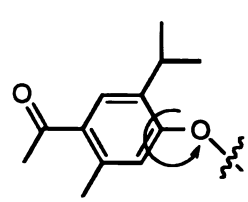
Photochemistry of **4T2N(F)-K**

A solution of 4-(3',4',4'-trifluoro-3'-buten-1'-oxy)acetophenone (3 mg per 1 mL solvent) in CD_3OD was degassed with argon and irradiated through Pyrex. Reaction progress was monitored by time resolved ^{1}H NMR. After 30 minutes of irradiation, much of the starting ketone disappeared and only a trace amount of photoproduct was observed. The photoproduct was determined to be 1-acetyl-4,4,5-trifluoro-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,-10-diene based on its characteristic vinyl region in ^{1}H NMR.



Computational Studies

Semi-empirical studies of the excited and ground state were carried to provide additional insight into the factors which control the regio- and stereoselectivity associated with ortho [2+2] photocycloaddition.



- Rotational Barriers in **2Me-4T2H-5I**

5-Isopropyl-4-methoxy-2-methylacetophenone was used as the model compound to determine the energies of rotation around the methoxy bond. Nonbonded interactions between the protons of the homoallylic carbon and the isopropyl group on the benzene ring result in a calculated ~7kcal/mol preference in exciplex formation toward the isopropyl group rather than away from it (see Appendix)

- Optimized Geometries for **1CN-2T$_{2H}$-COT**, **1CN-2T$_{3H}$-COT**, **1AP-4T$_{2H}$-COT***, and **1CN-4T$_{2H}$-COT***

Semi-empirical calculations of the ground state minima of **1CN-2T$_{2H}$-COT** and **1CN-2T$_{3H}$-COT** were carried out to determine the degree of triene conjugation in the fused cyclooctatrienes. Calculations indicated that the triene unit in the 8-5 fused ring system was nearly planar in the ground state. However, in the case of the 8-6 fused ring system, one of the double bonds is nearly orthogonal to the adjacent diene in the cyclooctatriene. Ring closure will occur exclusively from this highly conjugated diene unit.

AM1 calculations on the excited singlet of **1AP-4T$_{2H}$-COT** and **1CN-4T$_{2H}$-COT** were carried out to determine electric charge distribution in the excited cyclooctatriene unit. The partitioning of charge in the excited state shows definite cationic (C1-C3) and anionic regions (C4-C6). The results suggest that ring closure to cyclobutene should occur from either diene unit (see Discussion).

Table 4: Isolated Yields of Various Cyclobutenes Arising From Tiplet Sensitization

Cyclobutene	Isolated yield[a]
1CN-4T$_{3H}$-CB	58%
1CN-4T$_{2H}$-CB	52%
1EC-4T$_{3H}$-CB	51%
1CN-2T$_{2H}$-CB	74%
1EC-2T$_{3H}$-CB	43%

a: irradiation in acetone

Table 5: Isolated Yields of Various *Ortho* Substituted Cyclobutenes and Cyclooctatrienes

Products	Isolated yield
2,5Me-4T$_{2H}$-CB-t	37%[a]
2Me-4T$_{2H}$-5I-CB-t	18%[a]
2Me-4T$_{2H}$-5I-CB-a	23%[a]
4T$_{2H}$-COT	66%[a]
2Me-4T$_{2H}$-COT	27%[a]
2Me-4T$_{2H}$-5I-COT-t	79%[b]
2Me-4T$_{2H}$-5I-COT-a	63%[b]

a: from starting ketone
b: from cyclobutene

V. Quantum Yields

Quantum yields for cyclobutene formation were measured at moderate conversion (30-60 %) by the means of UV-Vis spectroscopy. Methanol solutions of cyclooctatrienes(10^{-5} M), which could be detected by UV-Vis, were degassed by the freeze-and-thaw method and irradiated at 313 nm in parallel with valerophenone actinometer ($\Phi_{AP} = 0.33$) in a merry-go-round apparatus at room temperature.

Quantum yields of 2+2 cycloadduct formation were analyzed at low conversion (5-15 %) by the means of gas chromatography. Methanol solutions of starting ketones (0.01M) were degassed by the freeze-and-thaw method and irradiated at 313 nm in parallel with valerophenone actinometer ($\Phi_{AP} = 0.33$) in a merry-go-round apparatus at room temperature.

Table 6: Quantum Yields of Various Cyclooctatrienes or Cyclobutenes

Reactant	Product	Quantum yield Φ
2,5Me-4T2H-COT	**2,5Me-4T2H-CB**	0.038[a]
2Me-4T2Me-COT	**2Me-4T2Me-CB**	0.028[a]
2Me-4T2H-5I-COT-t	**2Me-4T2H-5I-CB-t**	0.015[a]
2Me-4T2H-5I-COT-a	**2Me-4T2H-5I-CB-a**	0.097[a]
2,5Me-4T2H-K	**2,5Me-4T2H-COT**	0.039[b]
2Me-4T2H-5I-K	**2Me-4T2H-5I-COT-t**	0.043[b]
2F-4T2Me-K	**2F-4T2Me-COT**	0.0025[b]

a: **CB** determined by UV-Vis

b: **COT** determined by GC

Quantum Yields for cyclobutene formation were measured at low conversion (<10%) by gas chromatography. Acetone solutions of the starting nitrile or ester (~0.01M) were degassed by the freeze-thaw method and irradiated at 313 nm in parallel with valerophenone actinometer. The quantum yield for cyclooctatriene ring closure to cyclobutene was determined in the same fashion as *ortho* substituted cyclooctatrienes for comparison purposes.

Table 7: Quantum Yields of Cyclobutene Formation

Reactants	Quantum yield Φ
1CN-4T3H	0.019[a]
1CN-2T2H	0.016[a]
1CN-2T3H	0.009[a]
1EC-2T3H	0.011[a]
1CN-4T2H-COT	0.055[b]

a: in acetone

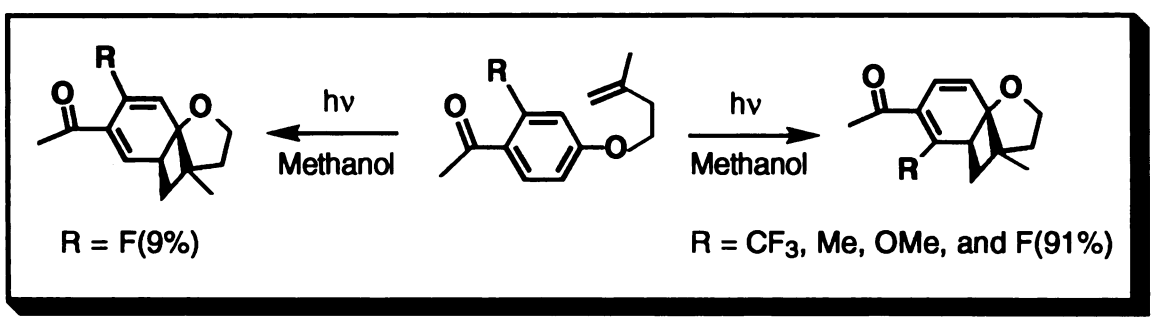
b: in methanol

DISCUSSION

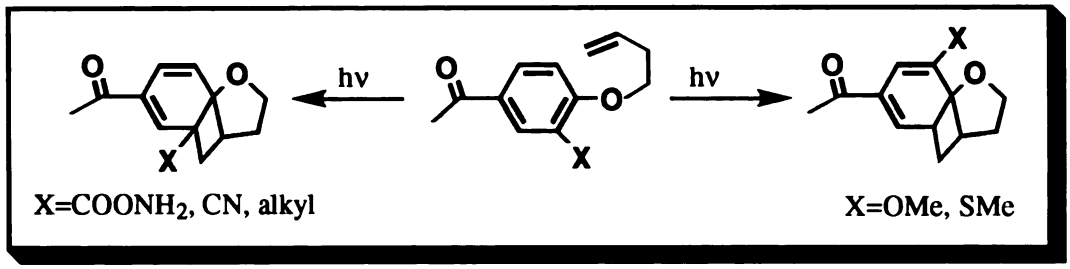
The results presented, in conjunction with previous studies, have provided numerous clues into this unique photocycloaddition reaction. At the same time, these results spur a myriad of new questions that will be addressed in future studies.

Regioselectivity

The high degree of regioselectivity observed in photocycloaddition of *ortho* substituted *p*-butenoxyacetophenones is quite remarkable. In nearly all cases studied, the initial [2+2] *ortho* cycloaddition of the remote double bond is directed exclusively toward the *ortho* ring substituent.



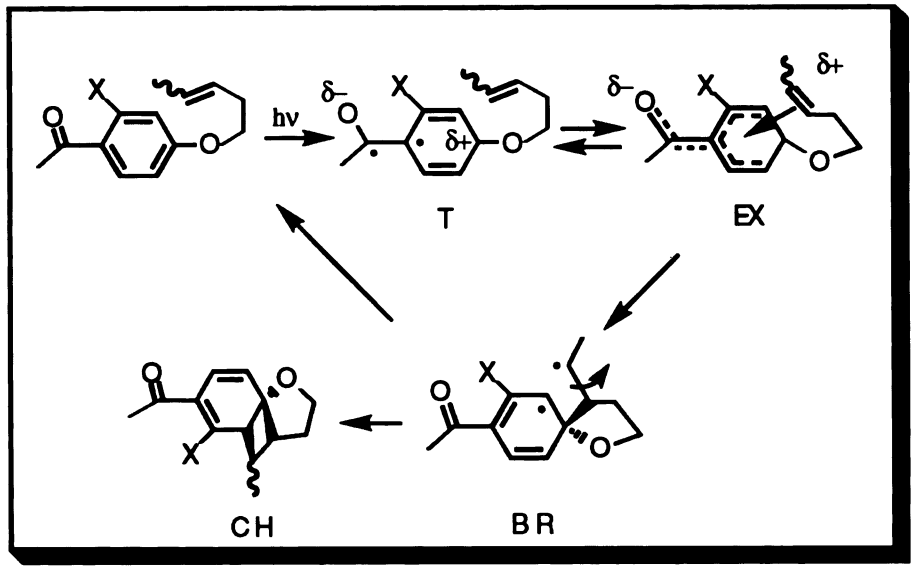
Similar strong regioselectivity was observed with substituents *meta* to the acetyl group.[31] This selectivity was attributed in large part to inductive effects of the *meta* ring substituents on the nature of initial triplet state cycloaddition reaction. Alkyl and electron withdrawing groups *ortho* to the olefin tether (*meta* to the acetyl) direct cyclization toward themselves, while only strong electron donating groups drive the remote double bond away.



The major question that must be answered is why the observed regioselectivty is nearly absolute. Clearly, this reaction is subject to very powerful differentiating effects. The fact that both electron withdrawing and electron donating groups foster the same absolute regioselectivity suggests that the inductive effect of the *ortho* substituent is not solely responsible for the majority of the observed selectivity as was shown for *meta* substituents. It is believed that the observed *ortho* substituent regioselectivity is associated with differentiating effects on both the initial triplet-state cycloaddition and the subsequent electrocyclic reactions.

Overall Mechanism

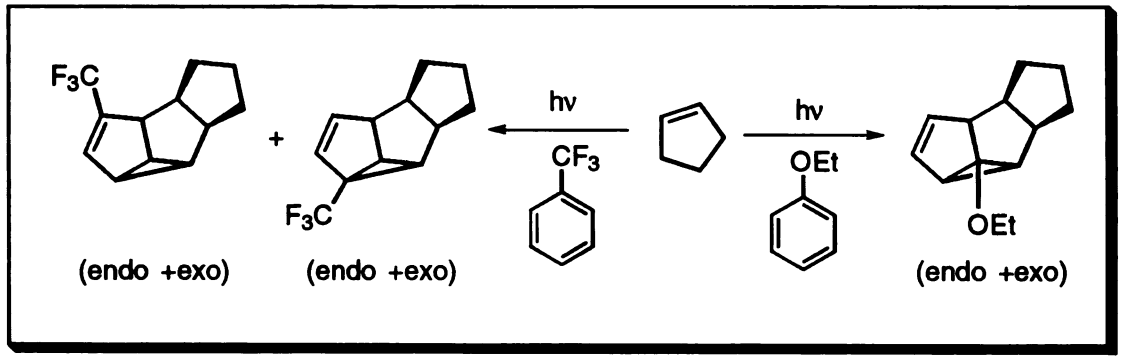
The mechanism of this reaction is assumed to be analogous to that for addition of olefins to cyclohexenones.[65, 66] Irradiation of *p*-butenoxyacetophenone derivatives generates a charge transfer complex (exciplex) that subsequently collapses to a biradical **BR**, which can either revert back to starting material or couple to form cyclohexadiene **CH** as shown below.



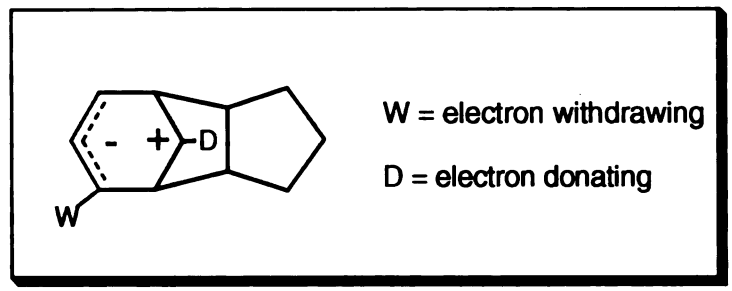
Subtle differences in electronics or sterics at any stage during this triplet-state cycloaddition reaction could potentially have profound effects on the observed regioselectivity. The significance of these factors on each step of the reaction scheme will be discussed.

Exciplex Formation

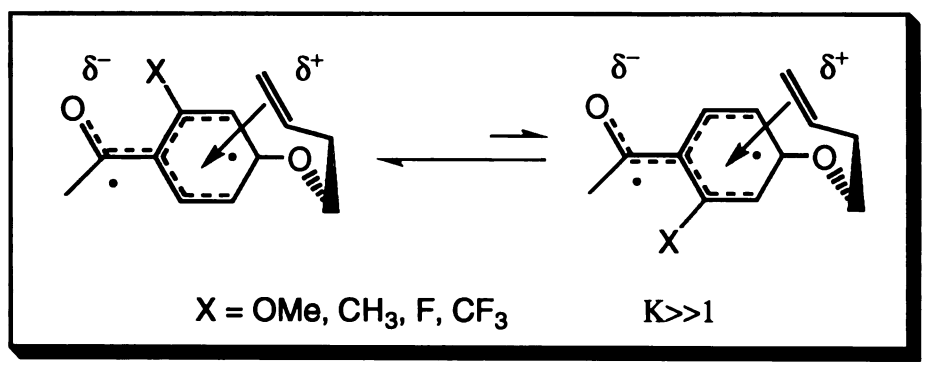
Exciplex orientation has been shown to greatly effect regioselectivity in *meta* photocycloaddition.[8, 21, 22, 67] Olefins preferentially add 2,6- to electron rich benzenes, placing the donor at position 3, whereas electron deficient benzenes direct addition 2,4- as shown in the scheme below.



This selectivity has been rationalized by the substituent's ability to stabilize the developing charge upon addition of the olefin.



Inductive and resonance effects of *ortho* substituents also may play a critical role in establishing the regiochemistry of the initially formed cycloadduct. The approach and reactivity of the donor double bond is affected by the degree of electron density present at carbon centers *ortho* to the tether. Charge transfer interactions will be strongest with the more positive adjacent center. Donor ring substituents (OMe, F, and Me) supply electron density to positions *ortho* and *para* by resonance. More electron density is afforded to the *para* position than the *ortho* positions. No resonance stabilizing effect is possible for the electron withdrawing substituent CF_3. Inductively, all *ortho* ring substituents deplete electron density to varying degree at adjacent carbon centers. Inductive effects diminish the further the substituent is from the charge center.

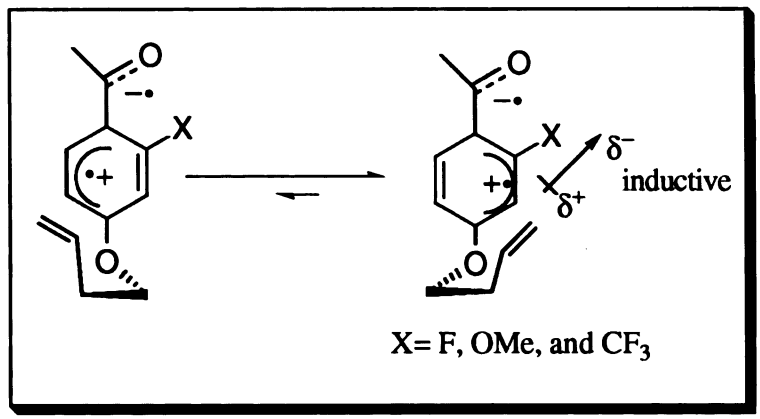


The σ_R and σ_I values for the *ortho* ring substituents are presented below and used in this study to describe both the resonance and inductive effects of the substituents in relative terms.

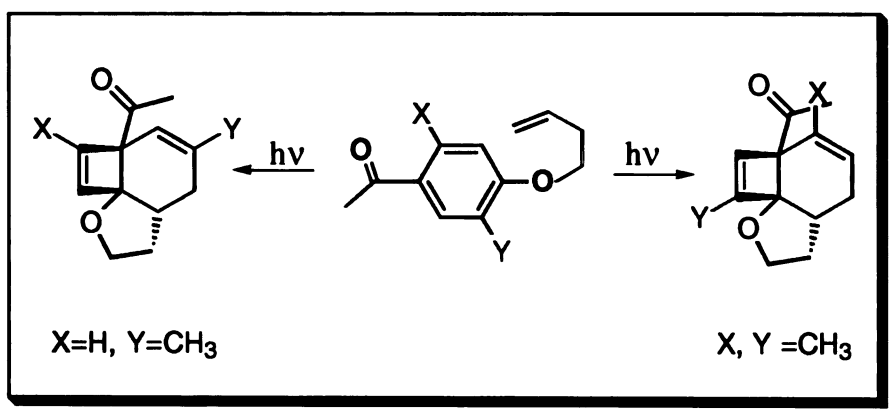
Table 8: σ_R and σ_I values[68] for *Ortho* Substituents in 4-Butenoxyacetophenone

Ortho Substituent	σ_R (*para*)	σ_I (*para*)
OMe	-0.42	0.27
F	-0.31	0.50
CF_3	0.08	0.42
Me	-0.13	-0.04

In **2CF3-4T2Me-K**, exciplex formation occurs in the direction of the *ortho* substituent due to induction (σ_I=0.42). The *ortho* trifluoromethyl group removes the electron density from the adjacent carbon center making the interaction between the donor double bond and the acceptor benzene ring strong. Similarly, the *ortho* substituents in **2OMe-4T2Me-K** and **2F-4T2Me-K** will orientate the exciplex toward themselves. Both fluorine (σ_I=0.5) and methoxy (σ_I=0.27) inductively create positive charge at the carbon next to the one it is attached. These substituents also generate electron density on *para* and *ortho* carbon atoms through resonance. Thus, the carbon atom *ortho* to both the tether and substituents will be the more positive carbon center. Exciplex formation will be orientated toward this center as shown below.

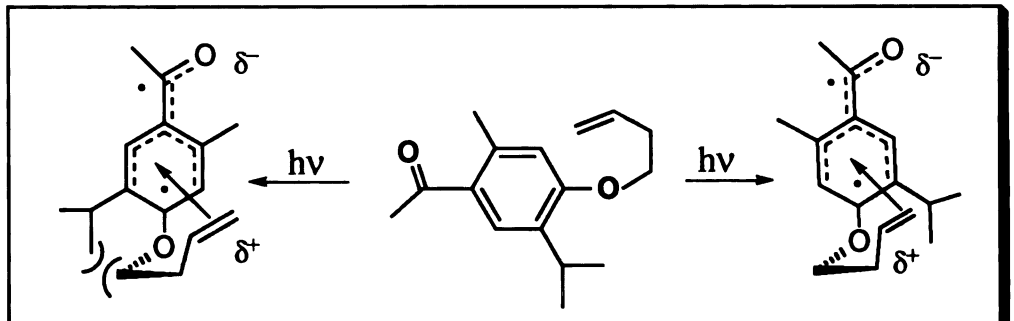


The directing ability of the *ortho* substituents was pitted against those of *meta* substituents in order to determine which factors effect regioselectivity. Compound **2,5Me-4T2H-K** provided a model compound to determine the relative effects of alkyl substituents at the *ortho* and *meta* positions. Irradiation of **2,5Me-4T2H-K** in methanol provided a single photoproduct, **2,5Me-4T2H-CB-t**, resulting from cyclization toward the *ortho* alkyl group. The *ortho* substituent completely surpresses the directing prowess of the *meta* alkyl substituent.[31] The regioselectivity associated with *ortho* alkyl substituents will be discussed later, but in short, is due to the formation of a triplet dienol via hydrogen abstraction by the acetophenone group.



Steric interactions between ring substituents and the approaching double bond can effectively alter the regiochemical course of the reaction. The constraint of the tether

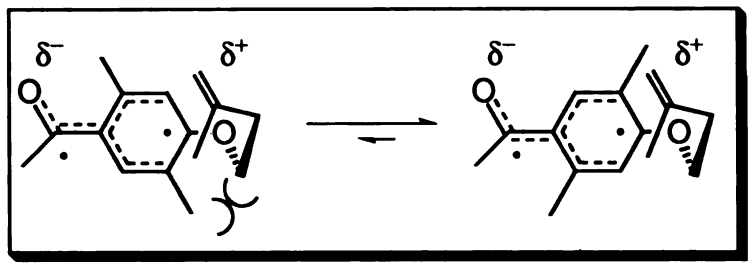
connecting the arene and alkene limits the possibilities for substituents on the arene ring to exert their directing influenece. This effect is seen in the photochemistry of **2Me-4T$_{2H}$-5I-K**. In all cases studied, addition of the double bond is toward the *ortho* ring substituent. The introduction of an isopropyl group *ortho* to the tether causes reversal of regioselectivity, favoring addition away from the *ortho* substituent in a ratio of 1:1.25. During exciplex formation, the tether will orientate the double bond over the benzene ring. The homoallyic carbon-oxygen bond will twist away from the side of the ring in which complexation will occur. This is illustrated in the scheme below.



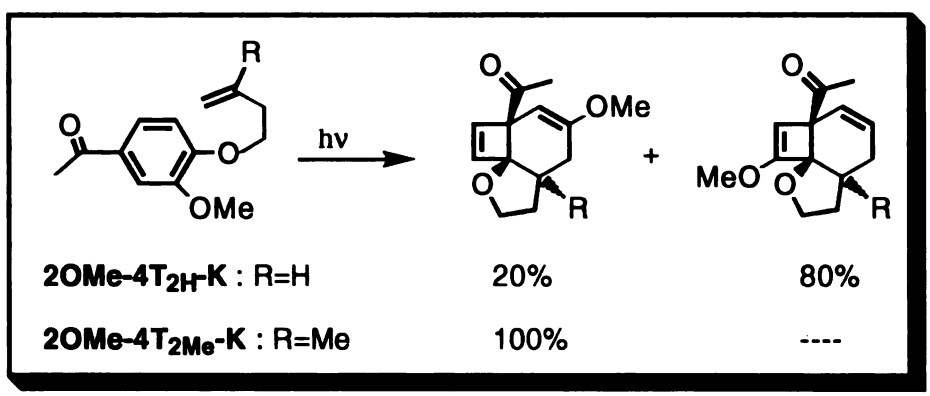
2Me-4T$_{2H}$-5I-K

Semi-empirical (AM1) calculations on the rotational barrier of the tether provided insights into the observed selectivity. 5-Isopropyl-4-methoxy-2-methylacetophenone was used as the model compound. Nonbonded interactions between the protons of the homoallylic carbon and the isopropyl group on the ring result in a calculated ~7kcal/mol preference in exciplex formation toward the isopropyl group rather than away from it (see Appendix).

Similarly, steric interactions can surpress the otherwise preferred syn addition of **2,5Me-4T$_{2H}$-K**. The lack of reactivity of **2,5Me-4T$_{2Me}$-K** results from nonbonded interactions between the *meta* methyl on the ring and the methyl on the double bond during exciplex formation, which are enhanced during biradical formation.



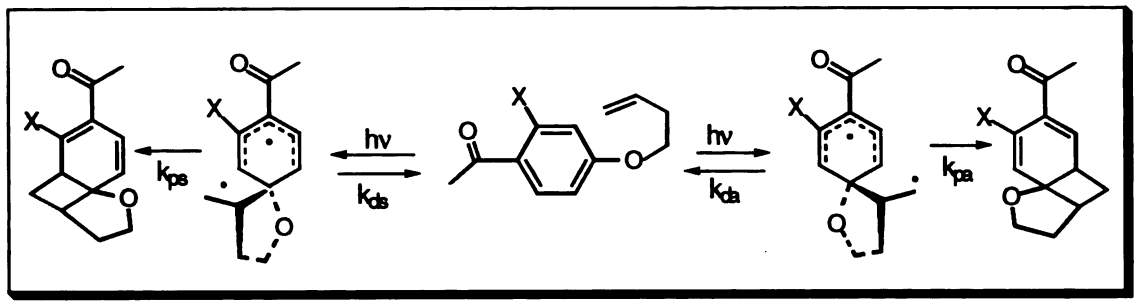
Identical observations have been reported before in the photochemistry of 4-(3'-buten-1'-oxy)-3-methoxyacetophenone, **3OMe-4T2H-K**.[31] Irradiation of **3OMe-4T2H-K** in benzene through Pyrex produces a 4:1 ratio of cyclobutene photoproducts, **3OMe-4T2H-CB-a** and **3OMe-4T2H-CB-t** respectively. However the regioselectivity is completely reversed by a methyl group on the double bond as in **3OMe-4T2Me-K**.



2OMe-4T2H-K : R=H	20%	80%
2OMe-4T2Me-K : R=Me	100%	----

Possibilities Arising From Biradical Formation

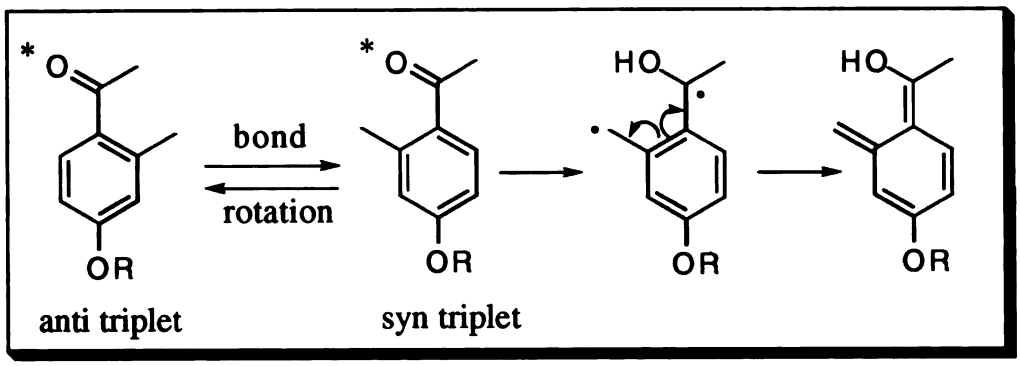
Addition of a ring substitutent in 4-(3-buten-1-oxy)acetophenone allows for the formation of two separate noninterconverting biradicals due to the spirocyclic bonding in the intially formed cyclohexadiene. These biradicals can subsequently couple to form either syn or anti products or decay to ground state acetophenone.



It is possible that $k_{ps} \neq k_{pa}$; but for the observed selectivity of *ortho* substituent to be derived solely from differential biradical partitioning, $k_{ps} >> k_{pa}$ must hold since there can be little difference in biradical decay to the ground state ($k_{ds}=k_{da}$). The two biradicals must have essentially the same stability relative to the ground state acetophenone, since the ring substituent should not accelerate cyclopentyl ring opening in either biradical. The ring substituent X, however, will cause a slight puckering in the ring at the *ortho* carbon which might enhance coupling between these two radical centers. It is unlikely that is the sole reason for the absolute regioselectivity observed in these reactions.

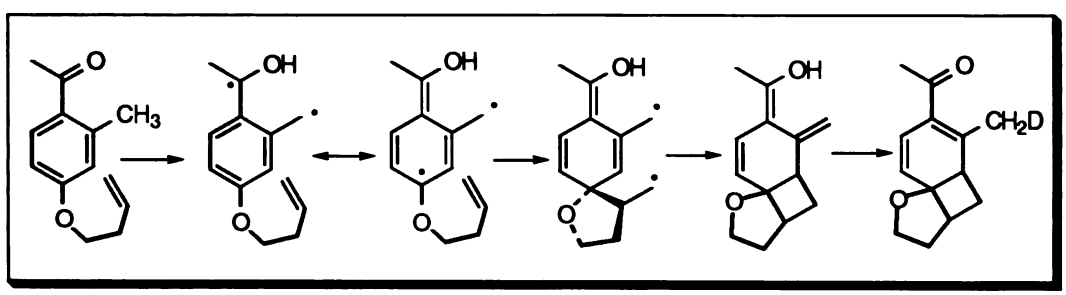
Photoenolization of o-alkylphenyl ketones

Phenyl ketones containing an *ortho* alkyl group are known to have two different conformers, anti and syn, which interconvert via a bond rotation about the C-C bond connecting the carbonyl to the aromatic ring. The geometries of both conformers were described by Wagner and Chen[60] as rotational minima in which the carbonyl oxygen and *ortho* alkyl group are on the same or opposite side of the plane perpendicular to the benzene ring bisecting the *para* carbon and carbonyl carbon.

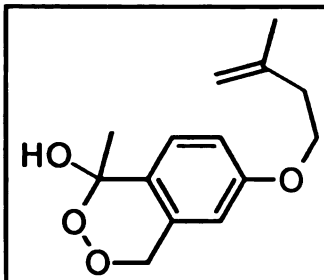
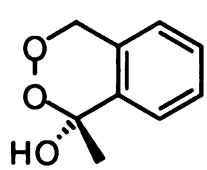
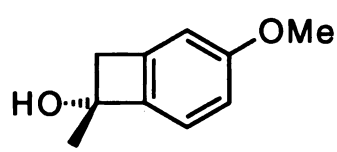


Photokinetic studies have shown that photoenolization of o-alkyl phenyl ketones effeciently competes with other photochemical processes common to these compounds. Wagner and Chen reported the substantial decrease(by a factor of 20) in quantum yield for Norrish type II cleavage of valerophenone when the parent compound is altered by an *ortho*-methyl group.[60] The rate of hydrogen abstraction from a syn *ortho* alkyl group was determined to be on the order of $5x10^9 s^{-1}$ by measuring the triplet lifetime of 8-methyl-1-tetralone.[60]

The regioselectivity associated in the [2+2] photocycloaddition of *ortho* alkyl substituted *p*-butenoxyacetophenones may be due solely (or in part) to the formation of a triplet dienol. Studies have shown that the triplet biradical of the photoenol lives for microseconds.[69, 70] There should be sufficient spin density at the *para* carbon to produce some hexenyl radical cyclization before decay to the ground state enol occurs. Such a process would occur exclusively from the syn biradical effectively bypassing the direct interaction of the triplet benzene and the double bond.

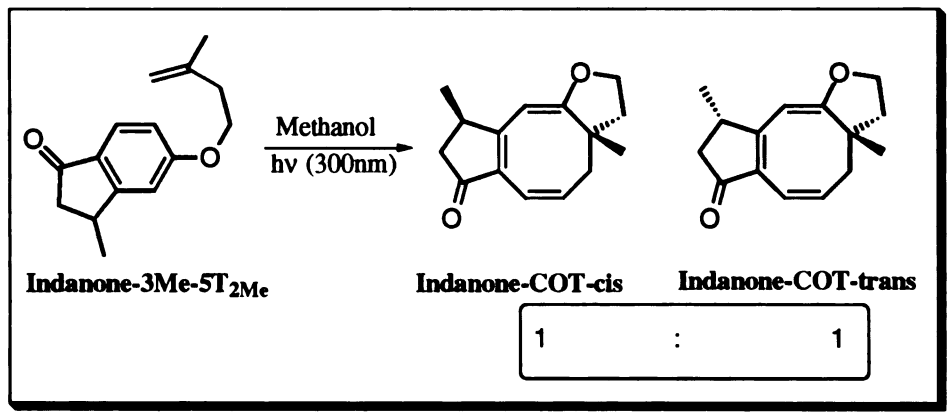


Evidence for the existence of a triplet dienol was determined experimentally. Irradiation of **2Me-4T$_{2Me}$-K** in deuterated methanol (0.015M) resulted in the rapid depletion of the resonance corresponding to the *ortho* methyl group (2.50 ppm) in the starting material. Deuterium incorporation was also observed in the photoproduct, **2Me-4T$_{2Me}$-CB**. It is quite possible that the trace amount of acid present in methanol[71] quenches the enol and that both efficient benzylic H-D exchange and cycloaddition are faster than cyclobutenol formation under this condition. Photolysis of **2Me-4T$_{2Me}$-K** in deuterated benzene results in the formation of cyclobutenol. Based on the chemical shift of the benzylic protons in the cyclobutenol photoproduct and comparison with previously reported adducts,[62, 72] it is believed that the triplet enol was trapped by oxygen. Similar results were seen in the photochemistry of **2CD$_3$-4T$_{2Me}$-K**.

 **2Me-4T$_{2Me}$-II**		
5.1 & 4.3 AB Quartet, 15.5Hz	5.07 & 4.3 AB Quartet, 14Hz, reference[62]	3.05 & 2.9 AB Quartet, 14Hz, reference[62]

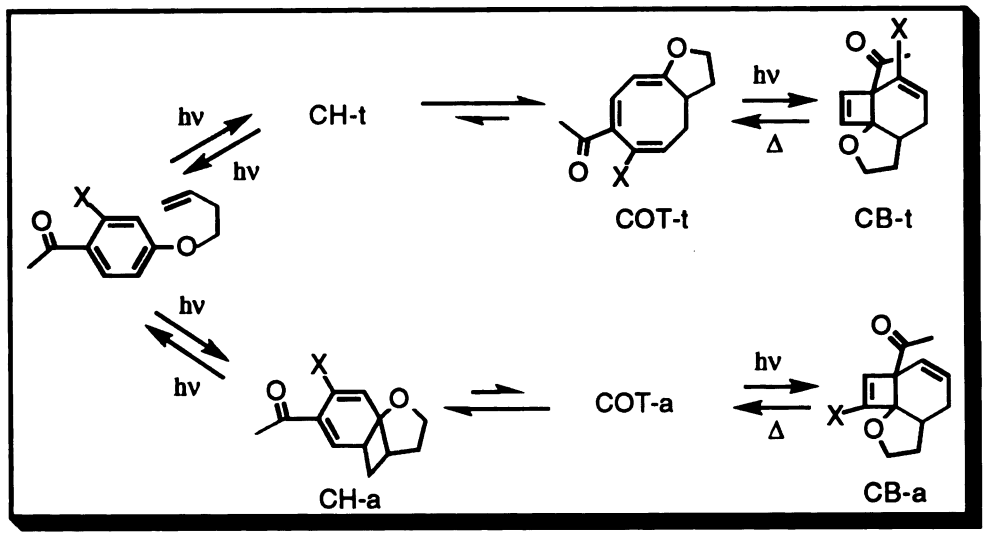
3Me-5T$_{2Me}$-Indanone was synthesized to determine the importance of a triplet dienol in the regioselectivity of *ortho* alkyl substituents. A structural analogy can be made between the indanone and *ortho* methyl acetopheneone in the anti conformation. The fused system prevents bond rotation of the ketone to form the perferred syn conformer.

Irradiation of **3Me-5T2Me-Indanone** in methanol provides a 1:1 ratio of cyclooctatriene diastereomers, **Indanone-COT-trans** and **Indanone-COT-cis**. The two cyclooctatrienes arise from ortho [2+2] cycloaddition away from the alkyl portion of the cyclopentanone ring. Thus, **3Me-5T2Me-Indanone** provides the opposite regioselectivity from that shown for other alkyl substituents. No photoproducts were observed when **3Me-5T2Me-Indanone** was irradiated in benzene or acetonitrile.



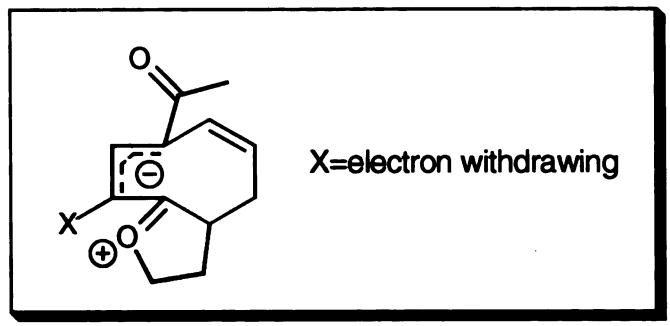
Differential Rates of Electrocyclizations

The thermal equilibrium between the initially formed cyclohexadiene (**CH**) and its valance tautomer cyclooctatriene (**COT**) may be crucial in determining the overall regioselectivity of this reaction due to the differing photochemistries of these two isomers.



It has been shown experimentally that cyclobutene (**CB**) formation occurs from disrotatory ring closure of cyclooctatriene. The quantum efficiency of this process is low (5-10%). In contrast, cyclohexadiene rapidly reverts photochemically to starting ketone with a quantum efficiency of ~70%.[73] Thus, the direction in which the thermal equilibrium lies could potentially determine the observed photoproduct. Perhaps only the cyclohexadiene that opens quickest to cyclooctatriene produces the photostable cyclobutene as shown in the scheme above.

The rates of thermal ring opening of the regioisomeric cyclobutenes may also be a major factor in the observed regioselectivity of this reaction. Quite possibly, the minor cyclobutene (**CB-a**), obtained from cyclization away from the ortho substituent, opens faster to a equilibrium mixture of cyclooctatriene and cyclohexadiene than the major cyclobutene, **CB-t**. The position and chemical nature of the substituent will alter ring opening of cyclobutene. In **CB-t**, the substituents are at a node in the π system and will not offer any stabilization of the zwiterionic intermediate believed to be involved ring opening process.[28] In contrast, substituents in **CB-a** are conjugated with the acceptor π system and should facilitate ring opening if the substituent is electron withdrawing.



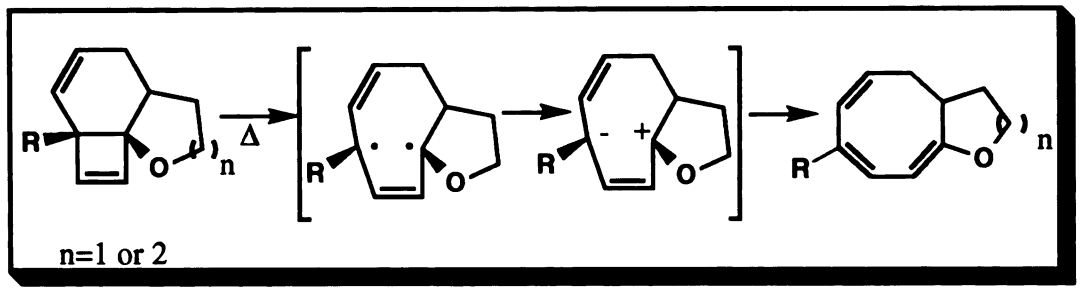
Quantum Yields

Quantum yields for the initial 2+2 photocycloaddition of *ortho* substituted phenyl ketones to cyclohexadienes (cyclooctatrienes) are roughly a factor of 10 lower than for phenyl ketones without *ortho* substitution.[64] This substantial difference may be due in part to low population of the π,π^* triplet state of the phenyl ketone upon excitation. Steric bulk of the *ortho* substituent prevents complete conjugation of the acetyl with the benzene ring which is necessary for π,π^* state population. Population of other energetically similar states (i.e. n,π^*) can then occur. This is seen in the photochemistry of **2Me-4T$_{2Me}$-K**, **2Me-4T$_{2Me}$-K**, and **2,6Me-4T$_{2Me}$-K**.

Quantum yield studies indicate that photoreversion of cyclohexadiene to starting ketone proceeds efficiently (70%).[64] This would account in part for the low quantum and chemical yields observed for the overall process from starting ketone to cyclobutene. In general, reversion of the biradical is a major source of inefficiency in the cycloaddition reaction. Agosta has determined that the quantum yields for reversion are much higher than for product formation in intramolecular 2+2 photocycloadditions of carbonyl-substituted 1,5-hexadienes.[74, 75] Photoreversions of biradicals have also been shown to be highly efficient in cycloadditions of triplet enones to double bonds.[76, 77, 78]

Differences in the Thermal Chemistry Between Acetyl and Cyano Substituted Cyclobutenes

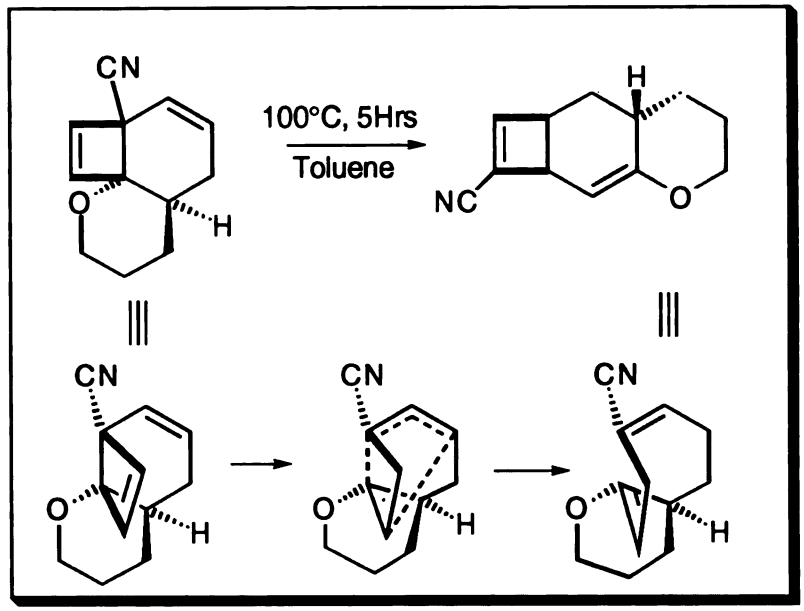
Heating derivatives of 4-Acetyltricyclo[7.2.0.0^{5,9}]undeca-2,10-dienes in methanol at 50°C rapidly causes ring opening of cyclobutenes to all-cis cyclooctatrienes. This transformation presumably involves the formation of a biradical followed by an electron transfer to form an intermediate with a high degree of zwiterionic character.[28]



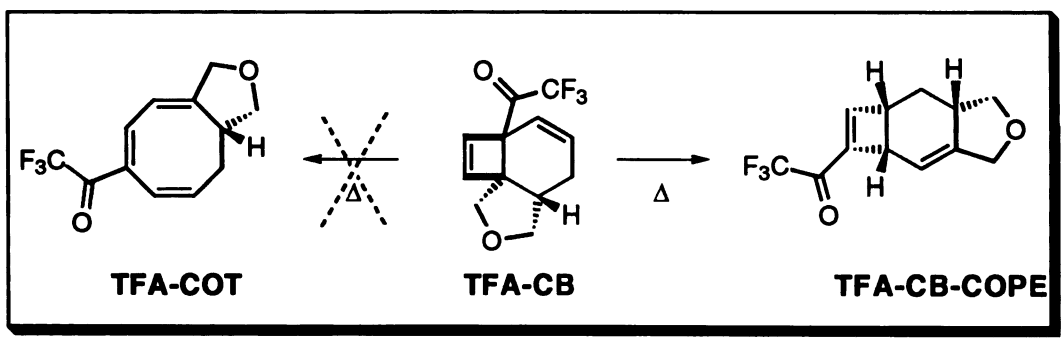
In contrast, cyano and ethoxycarbonyl substituted 9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-dienes and 8-oxatricyclo [7.2.0.0^{5,9}] undeca-2,10-dienes do not thermally open to cyclooctatrienes. The differences in thermal chemistry hinges on the ability of the acetyl or cyano substituent to stabilize the developing zwiterionic character in the ring opening transition state. A good judge of their stabilizing prowess can be obtained from their pKa's. The difference in pKa's between acetone and acetonitrile (20 and 25 respectively) suggests that acetyl substituted cyclobutene is ~7 kcals/mol more likely to open to the all cis cyclooctatriene than its cyano substituted counterpart. It must be stressed that this is only a relative number since the zwiterionic intermediate is a developing dipole, not a solvated ion as in the pKa measurements.

The sluggish ring opening of 1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene to cyclooctatriene allows for Cope rearrangement to compete. Thermal transformation through Cope rearrangement is symmetry allowed. The transition state for

this rearrangement resembles a chair configuration. The stereochemistry at the six-six ring junction is reversed in the Cope product.

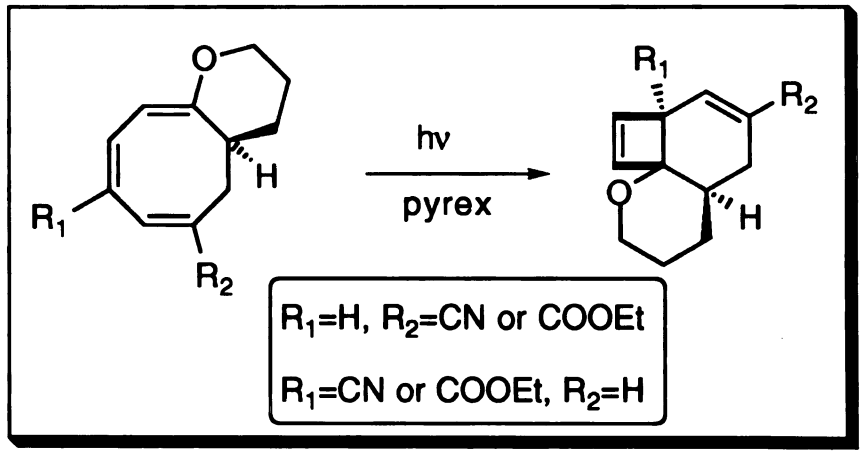


Similiar results were observed in the thermal chemistry of 1-trifluoroacetyl-7-oxa[7.2.0^{1,9}.0^{5,9}]undeca-2,10-diene,**TFA-CB**. Warming a solution of **TFA-CB** in toluene at 100°C resulted in the formation of **TFA-CB-COPE** via a Cope rearrangement.[63] Ring opening to cis-cyclooctatriene, **TFA-COT** was not observed. The formation of the eight membered ring is favored when there is an electron donating or withdrawing group conjugated with the bridge-bond of cyclobutene. Stabilization of the developing zwitterionic intermediate is necessary for cyclooctatriene formation.

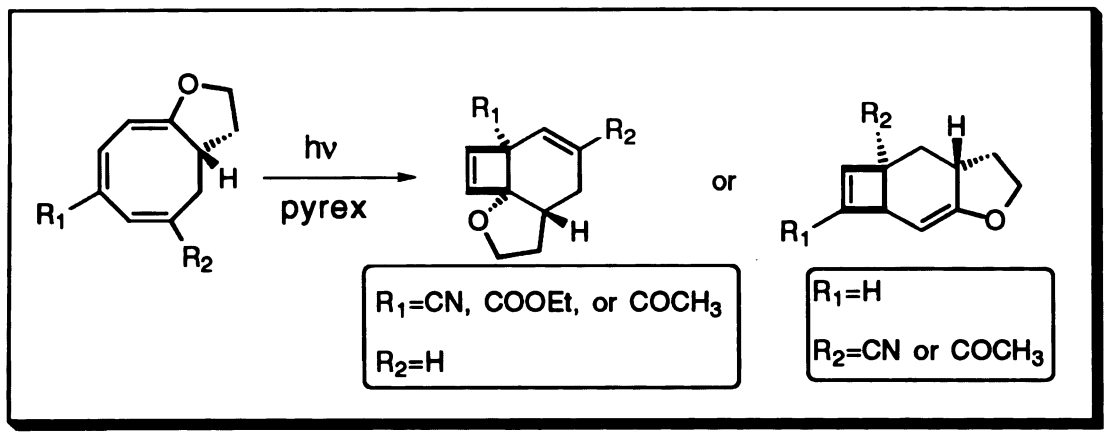


Photolysis of 4- and 6-substituted-12-oxabicyclo[6.4.0]dodeca-1,3,5-trienes

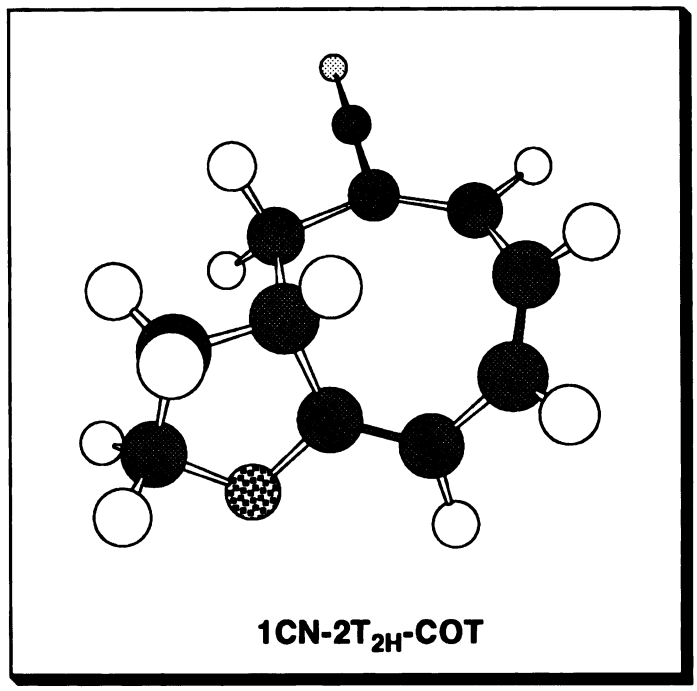
Ring closure of cyclooctatriene to cyclobutene is highly regioselective. This selectivity appears to be dependent on the size of the accompanying ring. Iradiation of 4- or 6-cyano-12-oxabicyclo[6.4.0] dodeca-1,3,5-triene at 313 nm results in the formation of 1- or 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene respectively. Photochemical ring closure produced only the angular cyclobutene irrespective of the cyclooctatriene isomer.



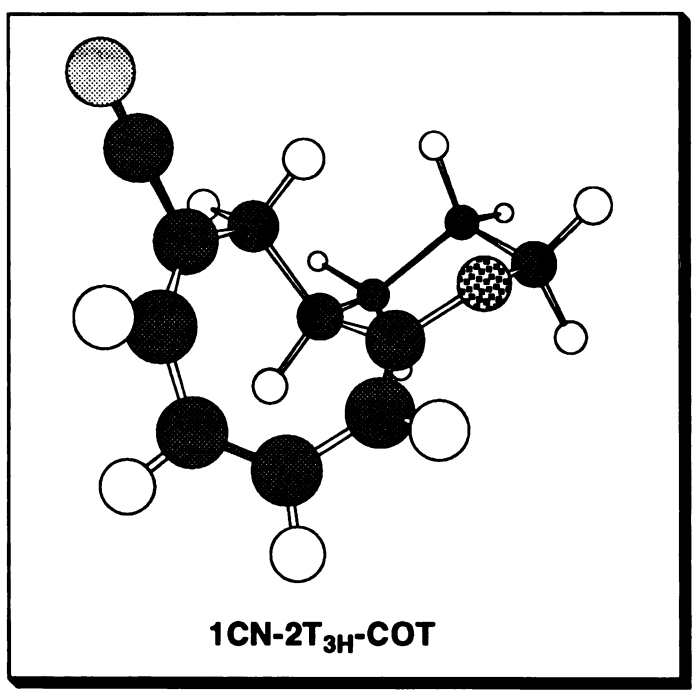
In contrast, irradiation of the corresponding fused eight-five ring system produced different cyclobutene regioisomers. Photolysis of 4-R-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (where R=acetyl, cyano, ethoxycarbonyl) at 313 nm gave 1-R-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene. Irradiation of 6-R-11-oxabicyclo[6.3.0]undeca-1,3,5-triene (where R=acetyl, cyano) at 313 nm produced the linear cyclobutene, 9-R-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene.



Semi-empirical calculations(AM1) of the ground state minima of 6-cyano-11-oxabicyclo[6.3.0]undeca-1,3,5-triene **1CN-2T2H-COT** and 6-cyano-12-oxabicyclo[6.4.0]dodeca-1,3,5-triene **1CN-2T3H-COT** are presented below. The triene unit in the 8-5 fused ring system was nearly planar in the ground state. Both diene units are thus able to close to form either the angular or linear cyclobutene. However, in the case of the 8-6 fused ring system, one of the double bonds is nearly orthogonal to the adjacent diene in the cyclooctatriene. Ring closure will occur exclusively from this highly conjugated diene unit. The lack of triene conjugation for the 8-6 fused ring system was noted in the ultraviolet-visible spectroscopy of these compounds. A λ_{max} of 305 nm was recorded for 6-cyano-12-oxabicyclo[6.4.0]dodeca-1,3,5-triene compared to a λ_{max} of 335 nm for 6-cyano-11-oxabicyclo[6.3.0]undeca-1,3,5-triene.



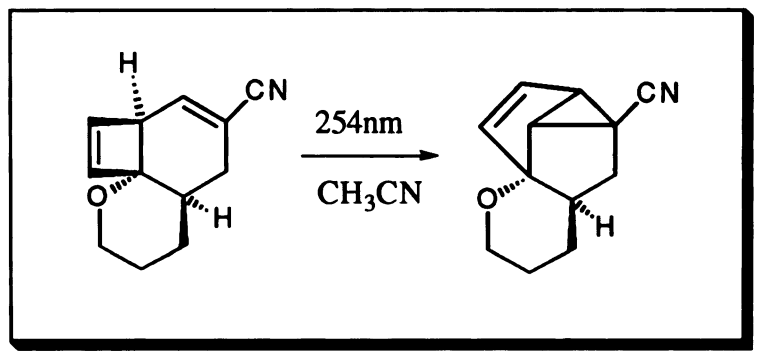
1CN-2T$_{2H}$-COT



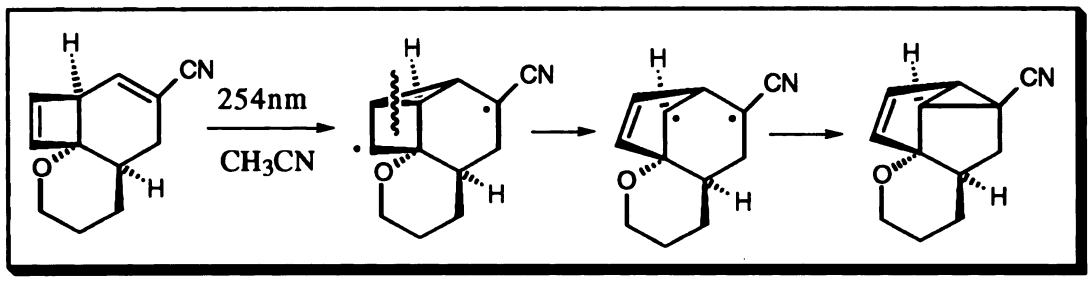
1CN-2T$_{3H}$-COT

Photolysis of 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene

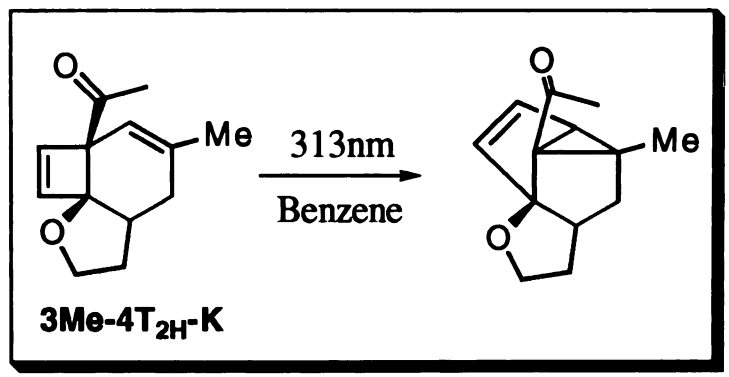
Direct irradiation of 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1CN-2T3H-CB** in acetonitrile produced 1-cyano-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene via a di-π-methane rearrangement. Photosensitized irradiation of **1CN-2T3H-CB** in acetone gave only a minor amount of di-π-methane product, indicating that the reactive state in this system is most likely S_1.



The mechanism for this photochemical transformation is presumably stepwise in nature due to the rigid framework of **1CN-2T3H-CB**. The overall process can formally be considered as a 1,2-shift of one π unit to the other π unit with concomitant ring closure to form the cyclopropane ring between the methylene group and the other end of the nonmigrating π moiety.[79] The observed regioselectivity can be rationalized by considering the stabilities of the developing biradicals produced on cleavage of the first formed cyclopropane ring as shown in the scheme below. The product arises exclusively from cleavage of the three-four bridge bond to give the biradical stabilized by nitrile delocalization. The alternative biradical formed from cleavage of the three-six bridged bond has only minor stabilization afforded by a secondary carbon center and would revert to **1CN-2T3H-CB** via a 1,2-alkyl shift followed by recombination of the biradical.

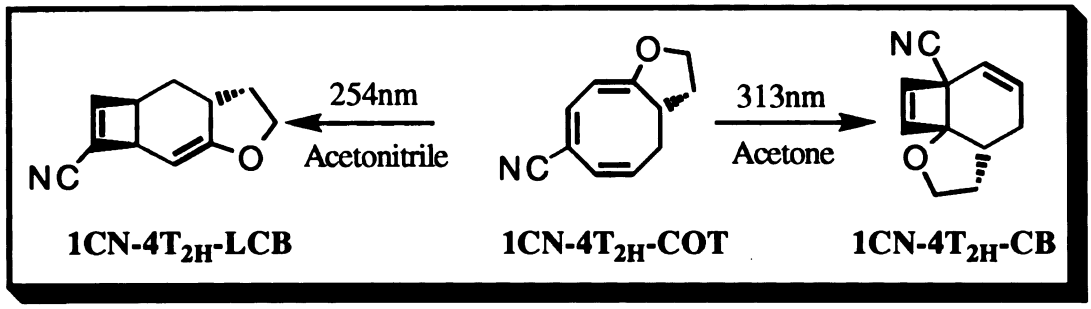


Similar results have been obtained in the photochemistry of 4-(3'-buten-1'-oxy)-3-methylacetophenone, **3Me-4T2H-K** at 313 nm in benzene-d6.[31] Irradiation of **3Me-4T2H-K** produced mainly **3Me-4T2H-CB** plus a minor amount of a di-π–methane rearrangement product. Irradiation at >334 nm produced only **3Me-4T2H-CB**, thus indicating that the di-π–methane rearrangement arose from **3Me-4T2H-CB**.



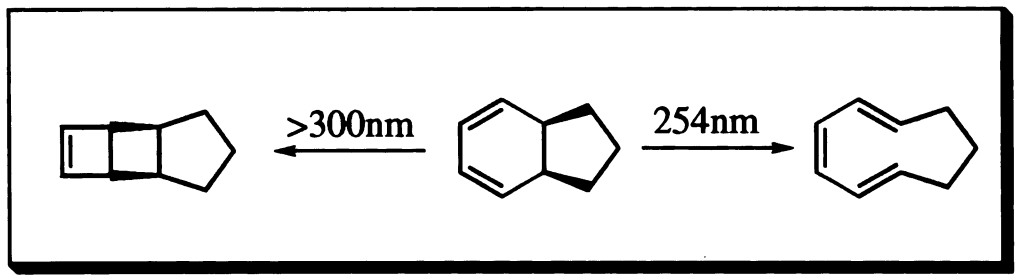
Photochemistry of **1CN-4T2H-COT**

Possibly the most intriguing finding to stem from the photosensitization of benzonitriles is the observation that different cyclobutene photoproducts arise when irradiation conditions are changed in the case of **1CN-4T2H-COT**.



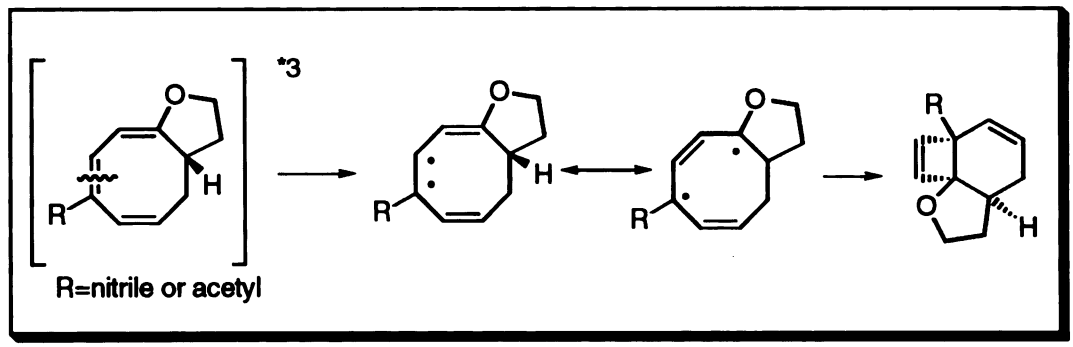
These observations are open to a number of possible explanations. One such explanation suggests that chemistry arising from the singlet and triplet electronic states of **1CN-4T2H-COT** are remarkably different and thus different photoproducts are obtained. Gilbert has shown that 1,3-dienes (0.50 M^{-1}) quenched the formation of **1CN-4T2H-COT** by approximately 50% in cyclohexane solution.[25] The photocyclization of **1CN-4T2H-COT** (at 320 nm) was uneffected by the presence of the 1,3-dienes. Thus it is concluded that the latter process results from the singlet state.

Another plausible explanation suggests a strong wavelength dependency of the photoproduct distribution in the photochemistry of **1CN-4T2H-COT**. Numerous investigations have shown that product distributions are affected by slight changes in the source of excitation. For example, Dauben has shown wavelength dependency in the photochemistry of cis-bicyclo [4.3.0] nona-2,4-diene.[80] Irradiation of cis-bicyclo [4.3.0] nona-2,4-diene with >300 nm light generates cis-tricyclo [$4.4.0^{1,6}.0^{7,10}$] deca-8-ene, the π^4 product. Alternatively, irradiation at shorter wavelengths(254 nm) produces nona-1,3,5-triene via a π^6 process. Dauben has suggested that conformational factors may dictate these wavelength dependent reactions.

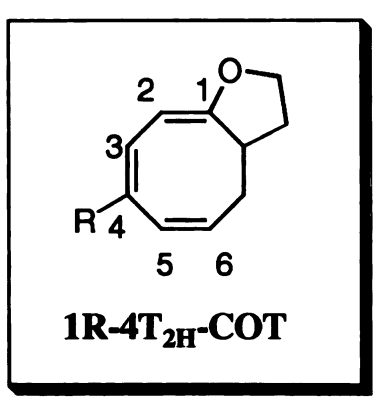


Experiments were performed to distinguish between the two possible explanations. Irradiation of **1CN-4T2H-COT** in acetonitrile at either 313 nm or 254 nm provided only the linear cyclobutene adduct. This indicates that its photochemistry is not wavelength dependent. **1CN-4T2H-LCB** must be arising from the excited singlet of **1CN-4T2H-COT**. Further evidence in favor of state dependency was obtained by irradiation of **1CN-4T2H-COT** in acetone at longer wavelengths(313 nm). At low concentrations of **1CN-4T2H-COT**, a condition present in the photochemistry of **1CN-4T2H**, all the light is absorbed by acetone. Triplet-triplet energy transfer from acetone to **1CN-4T2H-COT** will occur. This process should be highly exothermic due to the large triplet energy of acetone (E_T~ 78 kcal/mole[79]). However, at higher concentrations (0.015M in acetone), **1CN-4T2H-COT** will compete with acetone for the light due to the substantial absorption of the cyclooctatriene (ε~7500 at 325 nm). Thus ample amounts of **1CN-4T2H-LCB** should be formed by 313 nm irradiation. This has been confirmed by experiment.

Regioselective triplet ring closure of cyclooctatriene to cyclobutene can be rationalized in terms of biradical stability. Excitation of **1CN-4T2H-COT** in acetone will afford its excited triplet via triplet-triplet energy transfer from the solvent. Twisting of the double bond of acrylonitrile will generate a 1,2 diradical. Both radicals are effectively allylic and stabilized through resonance as shown in the scheme below.



In all cases previously studied, *para*-substituted 1-(3'-buten-1'-oxy)benzene efficiently cyclized to form the photostable angular cyclobutene via a two photon process. AM1 calculations on the excited singlet of **1CN-4T2H-COT** and **1AP-4T2H-COT** were carried out to determine the plausible explanation for diene ring closure of **1CN-4T2H-COT** to **1CN-4T2H-LCB**. Electric charge distribution (presented below) indicates that cyclooctatriene ring closure to cyclobutene is likely to occur at either diene unit to give both the angular or linear cyclobutene. The partitioning of charge in the excited state shows definite cationic (C1-C3) and anionic regions (C4-C6). The minimized geometry of the excited singlet of **1CN-4T2H-COT** showed that both diene units are slightly twisted but neither more than the other.



1R-4T2H-COT

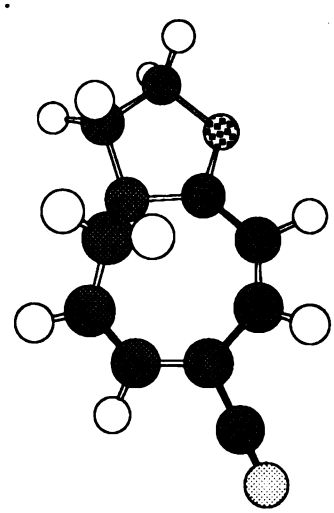
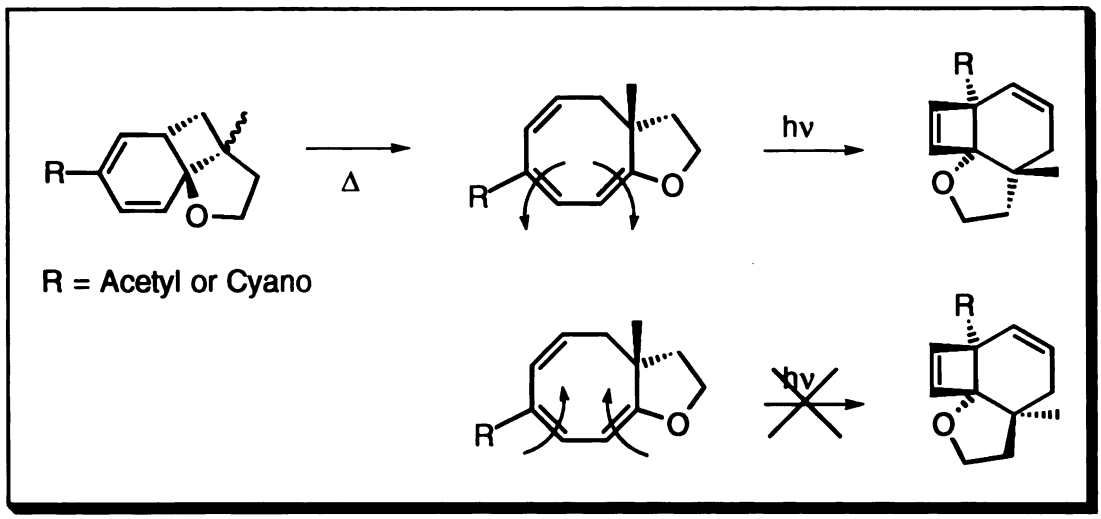


Table 9: Electronic Charge Distributions for the excited singlet of 1R-4T2H-COT		
Carbon Number	R=Acetyl	R=Cyano
C-1	0.33	0.22
C-2	-0.15	-0.11
C-3	0.32	0
C-4	-0.61	-0.18
C-5	-0.10	-0.10
C-6	-0.36	-0.35

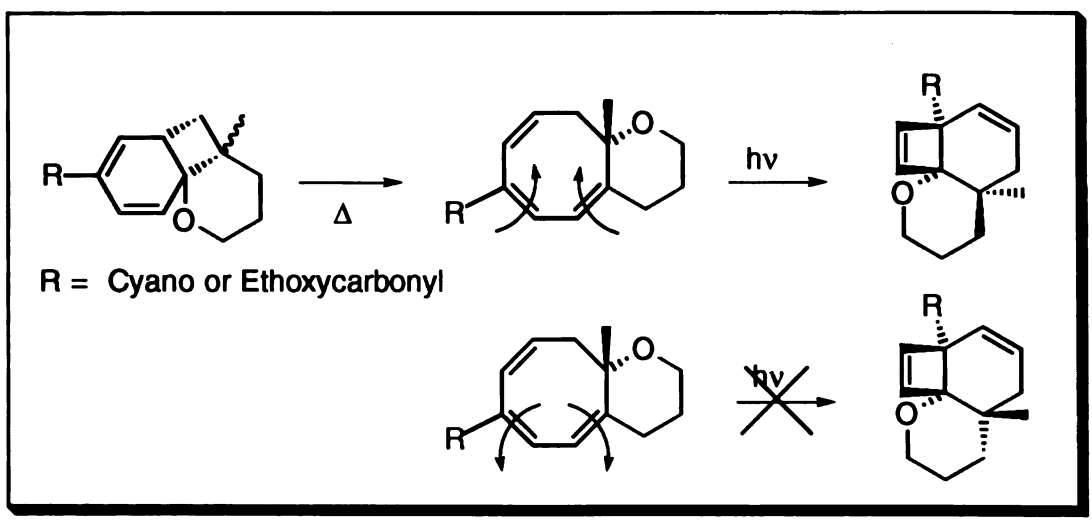
The regioselective cyclooctatriene ring closure of **1CN-4T2H-COT** to **1CN-4T2H-LCB** is perplexing. AM1 calculations suggest that either diene unit can close to form a mixture of cyclobutenes. Possibly, steric interactions between the acetyl group and the diene protons during ring closure may prevent formation of the linear cyclobutene. The linearity of the nitrile will preclude this interaction. Further research on the regioselectivity of cyclooctatriene ring closure should be carried out.

Stereoselectivty

The exact stereochemistry of the tricyclic photoproducts has been established by nOe and in the case of **1CN-4T3H-CB** by x-ray crystallography (see appendix). Clear stereochemical trends are present. Photoproducts with a four-five-six skeletal framework have the bridgehead substitutent (H or CH_3) cis to the cyclobutene ring. Presumably, the stereochemistry arises from disrotatory photochemical ring closure of the all-cis cyclooctatriene in only one direction to produce a cis 5/6 and a cis 4/6 ring fusion. The five membered ring must constrain the eight membered ring in a particular puckered geometry.



Surprisingly, the stereochemistry of the four-six-six skeletal framework is opposite that of the four-five-six framework. In the former case the bridgehead proton is trans to the cyclobutene ring. Woodward-Hoffman rules dictate photochemical diene ring closure to occur in a disrotatory fashion to produce a cis fused cyclobutene ring. Quite possibly the six membered ring may pucker the cyclooctatriene in a opposite manner to that of the five membered ring.



AM1 calculations on the ground states of **1CN-4T2H-COT** and **1CN-4T3H-COT** were performed. The minimized structures are presented. The cyclic ether is puckered in the opposite manner for the 8/5 ring system than in the 8/6 ring system. Disrotatory ring

closure of the cyclooctatriene will provide cyclobutenes with opposite stereochemistries at the bridgehead.

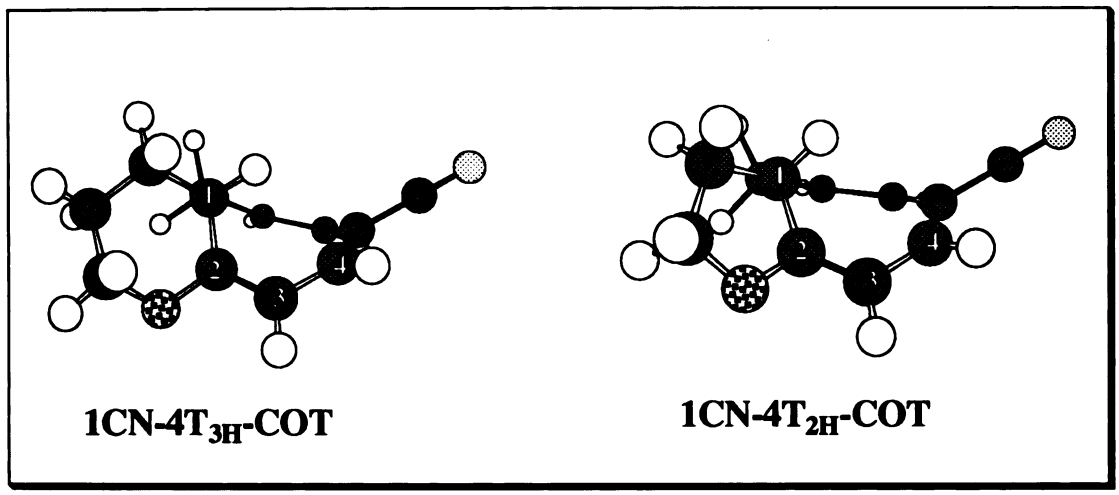


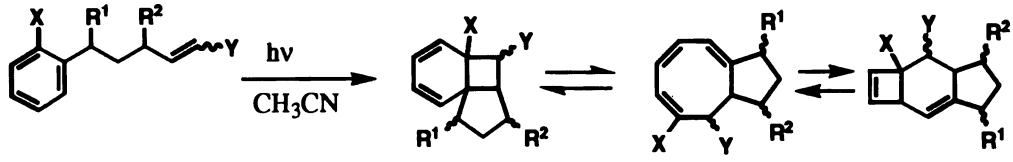
Table 10: Selected Dihedral Angles for **1CN-4T2H-COT** and **1CN-4T3H-COT**		
Atom Connections	**1CN-4T2H-COT**(°)	**1CN-4T3H-COT**(°)
C1-C2-C3-C4	3.305	-4.016
0-C2-C3-C4	-170.763	175.788

Future Work

Stereoselectivity

It would be instructive to determine the stereoselectivity of singlet state *ortho* cyclization as a function of substitution along the tether. Wagner and Cheng[81] have shown a high degree selectivity associated with the corresponding triplet *ortho* cyclization of substituted phenyl ketones. In theory, singlet state cyclization should be substantially more selective than the triplet due in large part to differences in their electronic nature. A variety

of mono-, di-, and trisubstituted tethers will be synthesized to determine the stereo- and diastereoselectivity of this reaction.



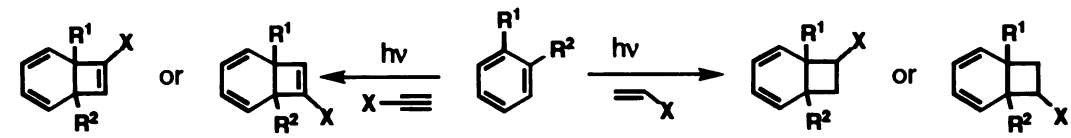
X=OMe, $SiMe_3$, SMe; Y=CN, COOMe, CF_3

X=CN, COOMe, CF_3; X=OMe, $SiMe_3$, Me

Regioselectivity

The determination of which carbons of a polysubstituted benzene are attacked by an alkene is of fundamental importance both mechanistically and synthetically. We have demonstrated that the corresponding triplet intramolecular *ortho* cyclization proceeds with a high degree of regioselectivity when electron donating or withdrawing groups are *ortho* or *meta* to the alkene tether.[30, 31] The regioselectivity is partially suppressed in the intramolecular process due to the propensity of the tether to form a five membered ring system.

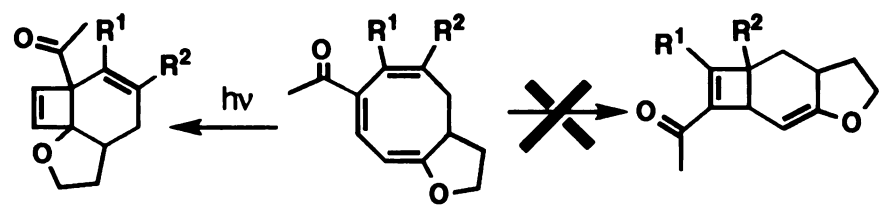
The bimolecular variant should provide a clearer understanding of the initial *ortho* 2+2 cycloaddition reaction. It is anticipated that electron donor and electron acceptor substituents on the benzene ring will have opposite directing natures depending on the electronic character of the reacting alkene or alkyne. An analogy can be drawn with the intermolecular cyclization of substituted alkenes to cyclohexenones.[66, 82] A representative group of olefins with either electron donating or withdrawing substituents, symmetrically or unsymmetrically disposed will be used to test the relative reactivity as a function of electron richness and regioselectivity as a function of inductive effects of the substituents. A variety of substituted alkynes will also be used since they are known to add *ortho* to singlet benzenes.



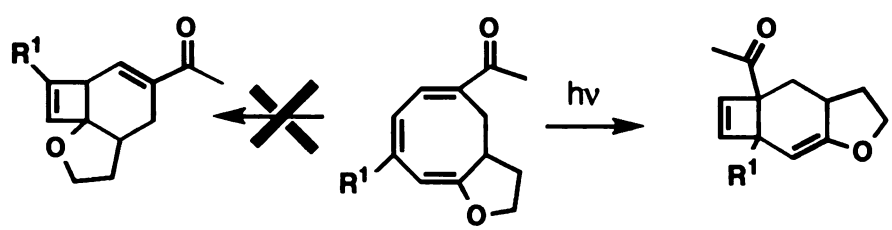
R^1 = CN, COOMe, COMe, COOH

R^2 = OMe, Me

Another important structural question that must be addressed is the regiochemistry of the cyclooctatriene-bicyclo[4.2.0] octa-2,7-diene closure. In all cases studied,[8,10-12] ring closure of the cyclooctatrienes was regioselective, involving only one of the two diene subunits. This tendency must be due to a subtle mixture of steric and electronic effects.



R^1, R^2= COOMe, CF_3, CH_3, OMe, and H

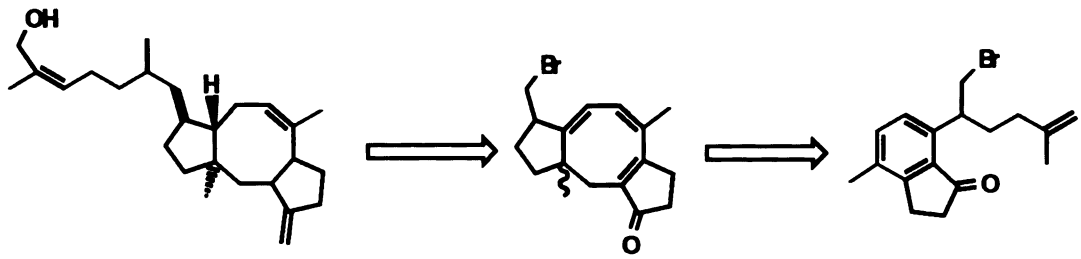


R^1= CN, F, OMe, and H

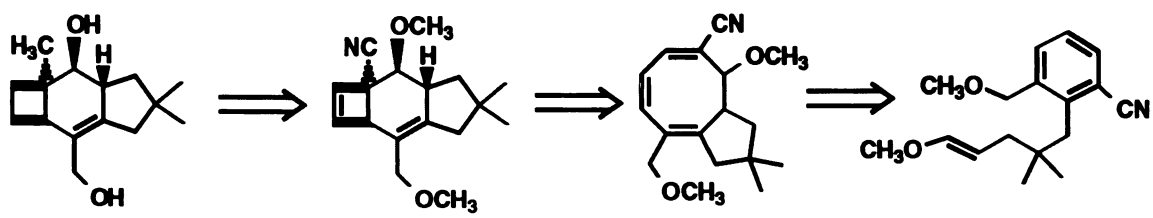
Natural Product Synthesis

Although the main thrust of this project to date is mechanistic, the ultimate goal would be to incorporate the findings into natural product synthesis. Many natural products have 8/5 fused ring systems as their skeletal framework; one such class is the ophiobolins.

Recently, Dauben reported the stereocontrolled route to the ceroplastin nucleus via a McMurry coupling of a dicyclopentane system.[83] Alternatively, one could incorporate *ortho* photocycloaddition as the key step in formation of this natural product. This is illustrated in the retrosynthetic scheme below.



Ortho photocyclization provides an unprecedented opportunity for the construction of a variety of fused 5/6/4 tricyclic systems. Abell and Leech have recently isolated and characterized the sterpurene *meta*bolite, 7,12-Dihydroxysterpurene, from the fungus Stereum purpureum.[84] A plausible synthesis to this sterpurene is presented below. All bicyclo [4.2.0] octa-2,7-dienes so far isolated by Gilbert and Wagner have the 6/5 bridgehead proton cis to the cyclobutene ring. Reduction of the cyclobutene is generally preferred over cyclohexene reduction due to ring strain.



7,12-Dihyrdoxysterpurene

EXPERIMENTAL

I. Instrumentation

This section describes the instrumentation used to characterize all substrates presented in this work.

^{1}H and ^{13}C NMR:	Varian Gemini 300, Varian VXR-300, and Varian VXR-500
FTIR:	Nicolet 42/Infrared Spectrophotometer with a 0.025mm Z12308-0 Aldrich IR cell
UV:	Shimadzu UV-160 Recording UV-VIS
GC:	Varian 1400 and 3400 Gas Chromatographs with Hewlett Packard HP3393A, HP3392A, and HP3395 Integrators
HPLC:	Rainin Dynamax HPLC interfaced with a dual wavelength programmable detector and fraction collector
MS:	Joel JMS-HX110 Mass Spectrometer and VG Trio-1 Benchtop GC-MS with a Hewlett Packard 5890 Gas Chromatogrph
Melting Points:	Thomas Hoover Capillary Melting Point Apparatus. Melting points are not corrected.

II. Chemicals

This section describes the preparation, purification, and identification of all chemicals used in this work. All substrates used in the preparation of the photoprecursors were the highest purity commerially available. The purity of such compounds was checked by gas chromatography or ^{1}H NMR prior to use.

A. Solvents

Benzene[85]

Reagent-grade benzene (3.5L) was stirred over conc. H_2SO_4 (0.5L) until the acid washing remained colorless (usually three portions of 0.5L of conc. H_2SO_4). The benzene layer was subsequently separated, washed with distilled water (3 x150mL), saturated $NaHCO_3$ (3 x200mL), saturated NaCl (2x100mL), and then dried over $MgSO_4$. The filtered benzene was then refluxed for 24 hours over P_2O_5(150 g). After the stated period, the benzene was distilled through a meter column packed with stainless steel helices. The first and last 10% were discarded. The middle fraction distilled between at 78-80°C.

Methanol[86]

Reagent-grade absolute methanol was refluxed over Mg *metal* (2.5 g/1200 mL) overnight, then distilled through a half meter column packed with glass helices. The middle fraction (80%) which distilled between 64-65°C was saved.

Acetone[85]

Capillary GC/GC-MS grade acetone (2L) was treated successively with small amounts of $KMnO_4$ (0.5 gram portions) until a violet color persists. Anhydrous K_2CO_3 (8 g) was added and the mixture was refluxed for 12 hours. The solvent was then fractionally distilled through a one foot column packed with glass helices. The middle fraction (90%) which distilled between at 56-57°C was saved and stored over type 4Å Linde molecular sieves.

Acetonitrile[85]

Reagent-grade acetonitrile (2L) was refluxed over P_2O_5 (2 g) for four hours, then distilled through a one foot column packed with glass helices. The solvent was then refluxed over CaH_2 for 24 hours and then fractionally distilled through a half meter column

packed with glass helices. The middle fraction (80%) which boiled at 81-82°C was saved and stored over type 4Å Linde molecular sieves.

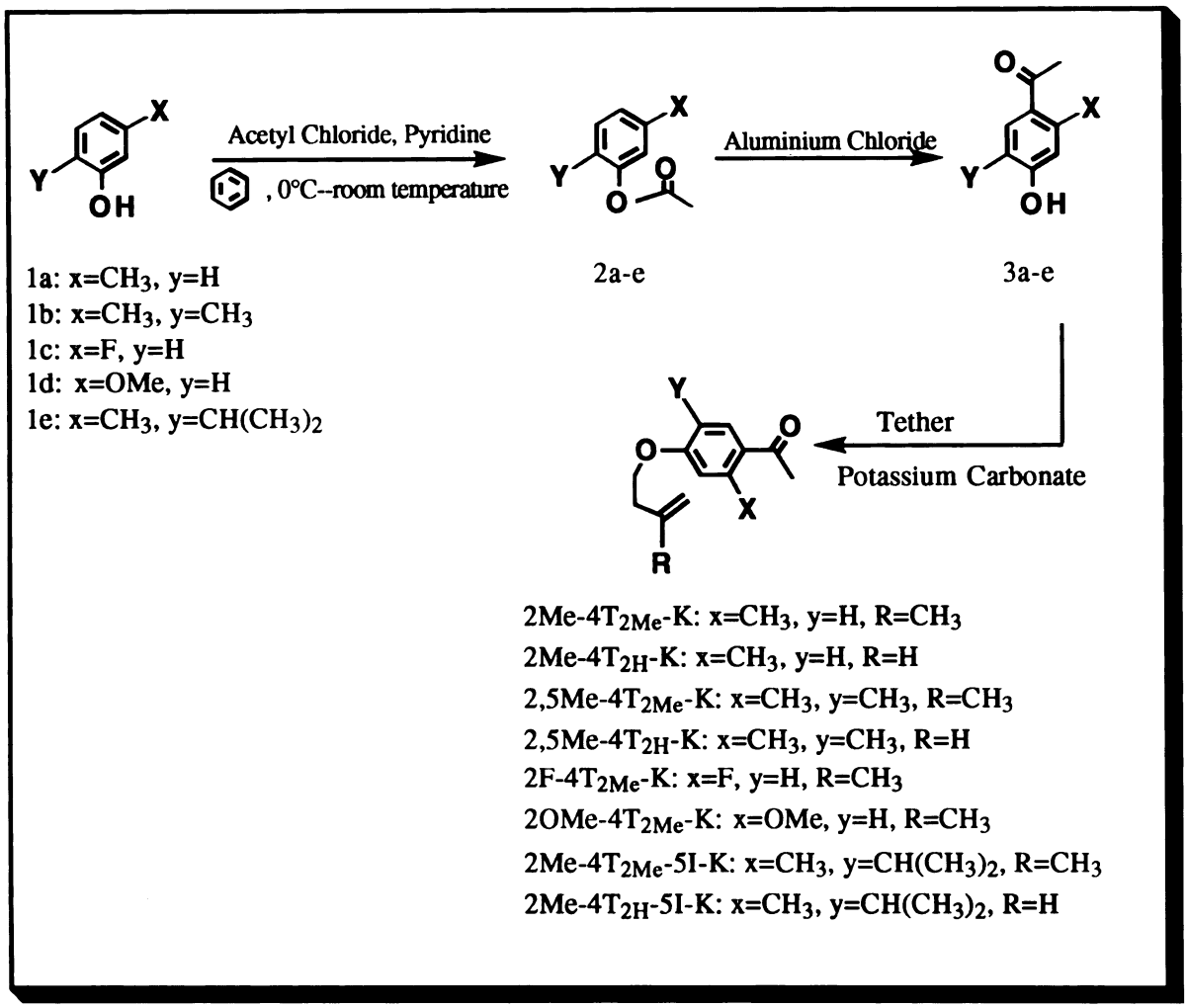
B. Chromatography Material

The majority of the photoprecursors and photoproducts were purified by silica gel chromatography. Preparative thin layer chromatography (Analtech Uniplate silica gel plates of 20x20cm, 1000 microm) was utilized for samples up to 150millig. Flash chromatography (Aldrich [cat#22,719-6] Silica gel, Merck, grade 60, 230-400 mesh, 60A.) was used for larger samples up to five g. The column diameter was selected according to the size of the sample. "Dry column flash chromatography" (Aldrich [cat. #28,850-0] TLC standard grade silica gel without binder) was utilized for samples larger than five g and for samples that decompose on silica gel while being eluted.

C. Internal Standards

Ethyl phenyl acetate:	Ethyl phenyl acetate was purified by fractional distillation.
Dodecane(C12):	Dodecane 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 Dr. Bong-Ser Park.
Methyl benzoate:	Methyl benzoate was purified by fractional distillation.
n-Pentyl benzoate:	n-Pentyl benzoate was purified by fractional distillation.
n-Heptyl benzoate:	n-Heptyl benzoate was purified by fractional distillation.
n-Octyl benzoate:	n-Octyl benzoate was purified by fractional distillation.

D. Preparations



3-Methylphenyl acetate (2a)

Acetyl chloride (21.78 g, 0.2775 mol) was added in a dropwise manner to a solution of m-cresol **1a** (20.0 g, 0.185 mol) and pyridine (29.26 g, 0.3699 mol) in 75mL of dry benzene at 0°C. The mixture was stirred under argon at room temperature for 24 hours. The reaction mixture was hydrolyzed with 5% HCl (25 mL) and separated. The organic layer was extracted four times with 30 mL portions of 2N NaOH and dried over magnesium sulfate. The extract was concentrated *in vacuo* to give a crude yellow oil.

Purification of the crude product by vacuum distillation gave 3-methylphenyl acetate **2a** as a colorless liquid (27.1 g, 98%).

^{1}H NMR (300MHz; $CDCl_3$) : δ 2.27(s, 3H), 2.34(s, 3H), 6.86(m, 2H), 7.02(broad d, J=7.8 Hz, 1H), 7.24(dd, J=8.4 Hz and 7.2 Hz, 1H).

^{13}C NMR(75MHz; $CDCl_3$) : 21.05, 21.22, 118.44, 122.10, 126.57, 129.07, 139.53, 150.56 and 169.54.

IR(CCl_4) : 1208, 1370, 1489, 1590, 1615, 1769, 2924 and 3036 cm^{-1}.

2,5-Dimethylphenyl acetate (2b)

The acetate was prepared in the same manner as 3-methylphenyl acetate **2a** by reacting 2,5-dimethylphenol **1b** (25.0 g, 0.2046 mol), pyridine (32.37 g, 0.4092 mol) and acetyl chloride (24.09 g, 0.3069 mol) in benzene at 0°C. The product was obtained as a colorless liquid in 93% yield [Chem. Abstracts Registry # 877-48-5].

^{1}H NMR (300MHz; $CDCl_3$) : δ 2.13(s, 3H), 2.30(s, 3H), 2.31(s, 3H), 6.82(s, 1H), 6.94(broad d, J=7.83 Hz, 1H), 7.10(d, J=7.71 Hz, 1H).

^{13}C NMR(75MHz; $CDCl_3$) : 15.63, 20.72, 20.79, 122.29, 126.70, 126.77, 130.75, 136.81, 149.07 and 169.29.

IR(CCl_4) : 1208, 1441, 1458, 1510, 1580, 1773, 2867 and 2955 cm^{-1}.

3-Fluorophenyl acetate (2c)

The acetate was prepared in the same manner as 3-methylphenyl acetate **2a** by reacting 3-fluorophenol **1c** (10.0 g, 0.089 mol), pyridine (14.08 g, 0.178 mol) and acetyl chloride (10.50 g, 0.1340 mol) in benzene at 0°C. The reaction was completed in 24 hours at room temperature. Purification by vacuum distillation gave 3-fluorophenyl acetate **2c** (11.20 g, 82%) as a colorless liquid [Chem. Abstracts Registry # 701-83-7].

^{1}H NMR (300MHz; $CDCl_3$) : δ 2.28(s, 3H), 6.82(dd, J=2.5 & 2.3 Hz, 1H), 6.92(ddd, J=8.5, 2.5 & 0.9 Hz, 1H), 7.25(m, 2H).

3-Methoxyphenyl acetate (2d)

The acetate was prepared in the same manner as 3-methylphenyl acetate **2a** by reacting 3-methoxyphenol **1d** (15.0 g, 0.121 mol), pyridine (19.14 g, 0.242 mol) and acetyl chloride (14.23 g, 0.1815 mol) in benzene at 0°C. The reaction was completed in 24 hours at room temperature. Purification by vacuum distillation gave 3-methoxyphenyl acetate **2d** (19.09 g, 95%) as a pale yellow liquid [Chem. Abstracts Registry # 5451-83-2].

^{1}H NMR (300MHz; $CDCl_3$) : δ 2.27(s, 3H), 3.77(s, 3H), 6.63(dd, J=2.31 Hz and 2.28 Hz, 2H), 6.67(ddd, J=8.01 Hz, 2.19 Hz and 0.87 Hz, 1H), 6.76(ddd, J=8.4 Hz. 2.49 Hz and 0.81 Hz, 1H), 7.26(dd, J=8.16 Hz and 8.13 Hz, 1H).

^{13}C NMR(300MHz; $CDCl_3$) : 21.04, 55.29, 107.54, 111.56, 113.70, 129.74, 151.55 160.40 and 169.31.

IR(CCl_4) : 1468, 1491, 1609, 1789, 2838, 2959 and 3005 cm^{-1}.

2-Isopropyl-5-methylphenyl acetate (2e)

The acetate was prepared in the same manner as 3-methylphenyl acetate **2a** by reacting thymol **1e** (15.0 g, 0.1 mol), pyridine (15.8 g, 0.2 mol) and acetyl chloride (11.75 g, 0.15 mol) in benzene at 0°C. The reaction was completed in 24 hours at room temperature. Purification by vacuum distillation gave 2-isopropyl-5-methylphenyl acetate **2e** (17.1 g, 89%) as a colorless liquid [Chem. Abstracts Registry # 6380-28-5].

4-Hydroxy-2-methylacetophenone (3a)

A solution of 3-methylphenyl acetate **2a** (15.0 g, 0.1 mol) in nitrobenzene (50 mL) was added dropwise to a solution of aluminum chloride (26.67 g, 0.2 mol) in nitrobenzene

(200 mL) at 0°C under argon. The reaction mixture was warmed to room temperature and stirred for 96 hours. After the stated period, the mixture was hydrolyzed with 5% HCl (200 mL). The nitrobenzene layer was diluted with ether (200 mL) and extracted with 50 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to a pH of 3-5 and extracted with ether (6 x 100 mL). The organic extracts were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Purification by vacuum distillation gave 4-hydroxy-2-methylacetophenone **3a** as a white solid (7.5 g, 50%), m.p(129-131°C).

^{1}H NMR (300MHz; CDCl$_3$) : δ 2.53(s, 6H), 6.67(broad s, 1H), 6.70(d, J=2.55 Hz, 1H) and 7.69(d, J=8.64 Hz, 1H).

^{13}C NMR(75MHz; CDCl$_3$) : 22.54, 29.05, 112.38, 118.96, 133.05, 148.21, 158.77, and 200.16.

4-Hydroxy-2,5-dimethylacetophenone (3b)

2,5-Dimethylphenyl acetate **2b** was converted to the ketone by Fries rearrangement in the same manner as 3-methylphenyl acetate. A solution of 2,5-dimethylphenyl acetate **2b** (20.0 g, 0.122 mol) in nitrobenzene was added to a solution of aluminum chloride (40.65 g, 0.3049 mol) in nitrobenzene at 0°C. The reaction was completed in 96 hours at room temperature with a 49.1% yield. The product was recrystallzed twice from hexane:ether (40:60) [Chem. Abstracts Registry # 26216-10-4].

^{1}H NMR (300MHz; CDCl$_3$) : δ 2.13(s, 3H), 2.51(s, 3H), 2.52(s, 3H), 6.6(s, 1H), 6.65(s, 1H) and 7.5(s, 1H).

2-Fluoro-4-hydroxyacetophenone (3c)

3-Fluorophenyl acetate **2c** (11.20 g, 0.0727 mol) was added dropwise to a cooled solution (5°C) of aluminium chloride (14.54 g, 0.10905 mol) dissolved in dichloroethane (30mL). Upon complete addition of the acetate, the ice bath was removed and the reaction mixture was refluxed for four days under an argon atmosphere. The reaction mixture was

then poured over 200 g of ice and extracted with ether (5x50mL). The combined extracts were washed twice with 25mL portions of brime, dried over magnesium sulfate and concentrated *in vacuo*. Purification of the crude product by dry column flash chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 2.4 g of 2-fluoro-4-hydroxyacetophenone and 4.8 g of 4-fluoro-2-hydroxyacetophenone.

4-fluoro-2-hydroxyacetophenone [Chem. Abstracts Registry # 98619-07-9]

^{1}H NMR (300MHz; CDCl$_3$) : δ 2.58(d, J=5.2 Hz,3H), 6.02(s, 1H), 6.58(dd, J=12.6 & 2.4 Hz, 1H), 6.72(dd, J=8.8 & 2.5 Hz, 1H), 7.845(t, J=8.7 Hz, 1H).

4-Hydroxy-2-methoxyacetophenone (3d)

3-Methoxyphenyl acetate **2d** was converted to the ketone by a Fries rearrangement in the same manner as 3-methylphenyl acetate **2a.** To a solution of aluminum chloride (19.27 g, 0.1445 mol) in nitrobenzene was added a solution of 3-methoxyphenyl acetate **2d** (12.0 g, 0.073 mol) in nitrobenzene in a dropwise manner at 0°C under argon. The reaction was completed in 96 hours at room temperature with a 40% yield. The product was recrystallized from ethanol:water(50:50) (mp 138-139°C, lit.[87] 138°C).

^{1}H NMR (300MHz; CDCl$_3$) : δ 2.7(s, 3H), 3.9(s, 3H), 6.45(m, 2H), and 7.75(d, J=8.8 Hz, 1H).

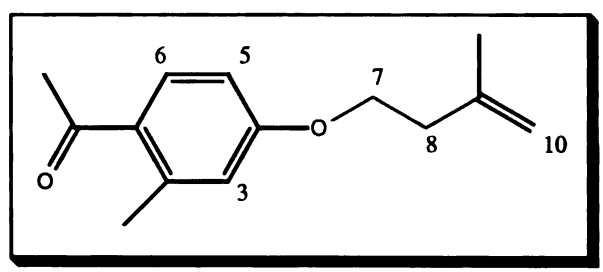
4-Hydroxy-5-isopropyl-2-methylacetophenone (3e)

2-Isopropyl-5-methylphenyl acetate **2e** was converted to the ketone in the same manner as 3-fluorophenyl acetate **2c**, using a 1.2 molar excess of aluminum chloride in respect to the acetate 2e. Purification of the crude reaction mixture by dry column flash chromatography, followed by recrystallization in wet ethanol gave 4-hydroxy-5-isopropyl-2-methylacetophenone as a off-white powder in 81% yield (mp 123-125°C) [Chem. Abstracts Registry # 37847-35-1].

^{1}H NMR (300MHz; $CDCl_3$) : δ 1.25(d, J=6.9 Hz, 6H), 2.17(s, 3H),2.54(s,3H), 3.17(sept., J=6.9 Hz, 1H), 5.21(br s, 1H), 6.57(s, 1H), 7.60(s, 1H).

4-(3'-Methyl-3'-buten-1'-oxy)-2-methylacetophenone (2Me-4T_{2Me}-K)

4-Hydroxy-2-methylacetophenone **3a** (4.0 g, 0.0266 mol), 4-tosyl-2-methyl-1-butene (4.60 g, 0.019 mol) and anhydrous potassium carbonate (11.03 g, 0.078 mol) in dry acetone (50 mL) were refluxed under argon for 40 hours. The cooled mixture was gravity filtered to remove the salt formed during the reaction and concentrated *in vacuo*. The resulting yellow oil was diluted with ether (50 mL) and extracted with 2N NaOH (4x25mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated *in vacuo* to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone **2Me-4T_{2Me}-K** in 68% yield.



^{1}H NMR (300MHz; $CDCl_3$) : δ 1.78(3, 3H), 2.48(t, J=6.87 Hz, $2H_8$), 2.52(s, 3H), 2.53(s, 3H), 4.09(t, J=6.87 Hz, $2H_7$), 4.78(br s[allylic coupling], $1H_{10}$), 4.83(br s[allylic coupling], $1H_{10}$), 6.73(m, $2H_{3,5}$) and 7.72(m[second order],$1H_6$).

^{13}C NMR(75MHz; $CDCl_3$) : 22.6, 22.7, 29.0, 37.0, 66.4, 111.0, 112.2, 118.03, 129.8, 132.5, 141.8, 142.1, 161.2 and199.3.

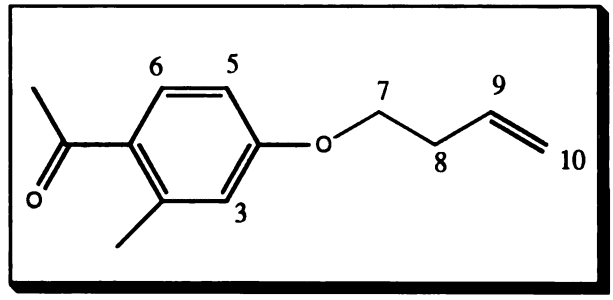
IR(CCl_4) : 1138.2, 1240.4, 1317.6, 1566.4, 1603.0, 1680.2, 2930.2, 2972.7, and 3080.7 cm^{-1}.

MS(m/z):41.1, 43.1, 69.1, 135.1(Base), 150.1, 218.1 and 219.2(M+1).

HRMS: calculated 218.1307 **and found** 218.1300

4-(3'-Buten-1'-oxy)-2-methylacetophenone (2Me-4$_{2H}$-K)

4-Hydroxy-2-methylacetophenone **3a** (5.40 g, 0.036 mol), 4-bromo-1-butene (7.28 g, 0.054 mol) and anhydrous potassium carbonate (14.93 g, 0.108 mol) in 50 mL of dry acetone were refluxed under an argon atmosphere for 90 hours. The cooled mixture was gravity filtered to remove potassium bromide formed during the reaction and concentrated *in vacuo*. The resulting yellow oil was diluted with ether (50mL) and extracted with 2N NaOH (4x25mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated *in vacuo* to give a crude yellow liquid. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-(3'-buten-1'-oxy)-2-methylacetophenone **2Me-4$_{2H}$-K** in 57.9% yield.



^{1}H NMR (300MHz; CDCl$_3$) : δ 2.52(s, 3H), 2.57-2.50(m, 2H$_8$), 4.04(t, J=6.72 Hz, 2H$_7$), 5.20-5.08(m, 2H$_{10}$), 5.88(ddt, J= 17.1 Hz, 10.23 Hz, and 6.69 Hz, 1H$_9$), 6.73(m, 2H$_{3,5}$) and 7.72(d, J=9.39 Hz, 2H$_6$).

^{13}C NMR(75MHz; CDCl$_3$) : 22.54, 28.99, 33.39, 67.09, 110.93, 117.20, 117.96, 129.80, 132.46, 134.00, 142.10, 161.21 and 199.30.

IR(CCl$_4$) : 1138.15, 1240.39, 1317.55, 1566.40, 1603.05, 1680.21, 2928.32, and 3082.64 cm^{-1}.

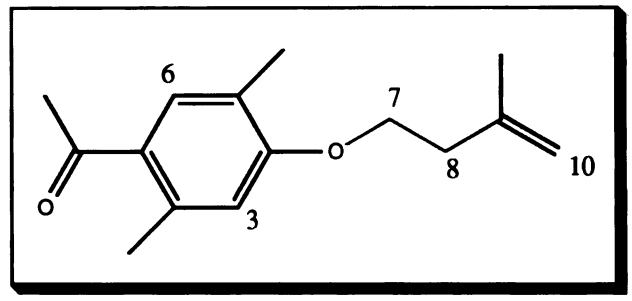
MS(m/z):43, 55.1, 77.1, 135.(Base), 189.1, 204.1 and 205.1(M+1).

HRMS: calculated 204.1151 **and found** 204.1138

4-(3'-Methyl-3'-buten-1'-oxy)-2,5-dimethylacetophenone

(1AP-2Me-4T$_{2Me}$-5Me)

The ketone was prepared from 4-hydroxy-2,5-dimethylacetophenone **3b** (3.0 g, 0.0183 mol), 4-tosyl-2-methyl-1-butene (6.58 g, 0.0274 mol) and potassium carbonate (7.59 g, 0.0549 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3'-methyl-3'-buten-1'-oxy)-2,5-dimethylacetophenone **1AP-2Me-4T$_{2Me}$-5Me** in 71% yield.



^{1}H NMR (300MHz; CDCl$_3$) : δ 1.80(s,3H), 2.18(s, 3H), 2.51(t, J=6.5 Hz, 2H$_8$), 2.52(s, 3H), 2.53(s,3H), 4.10(t, J=6.6 Hz, 2H$_7$), 4.79(d, J=0.93 Hz, 1H$_{10}$), 4.83(d, 1.53 Hz, 1H$_{10}$), 6.62(s, 1H$_3$) and 7.54(s, 1H$_6$).

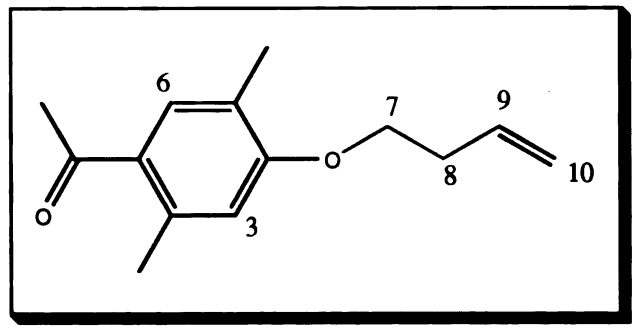
^{13}C NMR(75MHz; CDCl$_3$) : 15.6, 22.3, 22.6, 29.0, 37.1, 66.4, 112.1, 113.9, 123.5, 128.9, 132.9, 141.9, 159.3, and 199.4.

IR(CCl$_4$) : 11059.0, 1142, 1257.8, 1321.4, 1562.5, 1678.3, 2928.3 and 2972.7 cm^{-1}.

4-(3'-Buten-1'-oxy)-2,5-dimethylacetophenone (2,5Me-4T$_{2H}$-K)

The ketone was prepared from 4-hydroxy-2,5-dimethylacetophenone (3.0 g, 0.0183 mol), 4-bromo-1-butene (3.71 g, 0.0274 mol) and potassium carbonate (7.59 g, 0.0549 mol) in the same fashion as that of 4-(3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl

acetate, 93:7) gave 4-(3'-buten-1'-oxy)-2,5-dimethylacetophenone, **2,5Me-4T$_{2H}$-K** in 62% yield.



^{1}H NMR (300MHz; CDCl$_3$) : δ 2.17(s, 3H), 2.49(d, J=0.72 Hz, 3H), 2.52(s, 3H), 2.54(br t, J=6.57 Hz, 2H$_8$), 4.01(t, J=6.57 Hz, 2H$_7$), 5.10-5.06(br d, J=10.26 Hz, 1H$_{10}$), 5.17-5.11(br d, J=17.22, 1H$_{10}$), 5.95-5.81(ddt, 17.1, 10.32 & 6.7 Hz, 1H$_9$), 6.59(s, 1H$_3$) and 7.52(s, 1H$_6$).

^{13}C NMR(75MHz; CDCl$_3$) : 15.55, 22.30, 28.92, 33.49, 67.06, 114.02, 116.98, 123.47, 128.99, 132.88, 134.15, 139.37, 159.25 and 199.39.

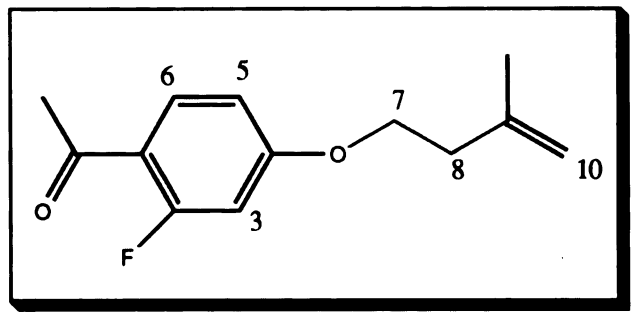
IR(CCl$_4$) : 2928.3, 1678.3, 1610.8, 1564.5, 1356.1, 1321.4, 1257.8, 1142.0, 804.4

MS(m/z): 41.1, 43.1, 69.1, 135.1(Base), 150.2, 218.2 and 219.2(M+1).

HRMS: calculated 218.1307 **and found** 218.1301

4-(3'-Methyl-3'-buten-1'-oxy)-2-fluoroacetophenone (2F-4T$_{2Me}$-K)

The ketone was prepared from 4-hydroxy-2-fluoroacetophenone **3c** (2.40 g, 0.0156 mol), 4-tosyl-2-methyl-1-butene (4.49 g, 0.0187 mol) and potassium carbonate (6.468 g, 0.0468 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3'-methyl-3'-buten-1'-oxy)-2-fluoroacetophenone **2F-4T$_{2Me}$-K** in 71.5% yield.



^{1}H NMR (300MHz; CDCl$_3$) : δ 1.78(s, 3H), 2.50(t, J=6.84 Hz, 2H$_8$), 2.57(d, J=5.22 Hz, 3H), 4.10(t, J=6.81 Hz, 2H$_7$), 4.77(br s, 1H$_{10}$), 4.84(br s, 1H$_{10}$), 6.58(dd, J=13.14 & 2.4 Hz, 1H$_3$), 6.72(dd, J=8.79 & 2.49 Hz, 1H$_5$), 7.85(t, J=8.79 Hz, 1H$_6$).

^{13}C NMR(75MHz; CDCl$_3$) : 22.7, 31.2, 36.8, 67.0, 102.0(d), 111.0(d), 112.4, 118.0(d), 132.0(d), 141.4, 164.1(d), 165.5 and 194.4.

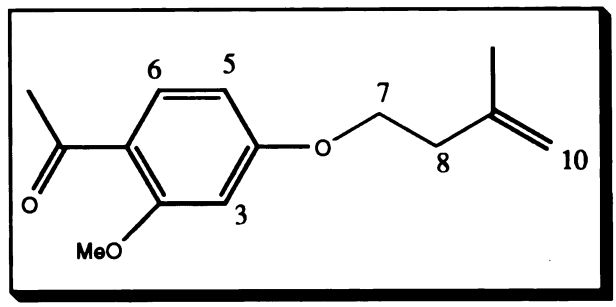
IR(CCl$_4$) : 1116.9, 11128.5, 1265.5, 1361.9, 1616.6, 1684.1, 2938 and 3080.7 cm^{-1}.

MS(m/z):41.1(Base), 43.1, 69.1, 139.1, 155.1, 222.2 and 223.2.

HRMS: calculated 222.1056 **and found** 222.1021

4-(3'-Methyl-3'-buten-1'-oxy)-2-methoxyacetophenone (2OMe-4T$_{2Me}$-K)

The ketone was prepared from 4-hydroxy-2-methoxyacetophenone **3d** (2.25 g, 0.0136 mol), 4-tosyl-2-methyl-1-butene (4.878 g, 0.0203 mol) and potassium carbonate (5.64 g, 0.041 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(3'-methyl-3'-buten-1'-oxy)-2-methoxyacetophenone **2OMe-4T$_{2Me}$-K**.



^{1}H NMR (300MHz; $CDCl_3$) : δ 1.79(s, 3H), 2.49(t, J=6.8 Hz, $2H_8$), 2.55(s, 3H), 3.87(s, 3H), 4.11(t, J=6.8, $2H_7$), 4.78(br s, $1H_{10}$), 4.84(br s, $1H_{10}$), 6.44(d, J=2.2 Hz, $1H_3$), 6.50(dd, J=8.73 & 2.3 Hz, $1H_5$) and 7.79(d, J=8.7 Hz, $1H_6$).

^{13}C NMR(75MHz; $CDCl_3$) : 22.6, 31.7, 36.9, 55.4, 66.5, 98.7, 105.4, 112.2, 120.9, 132.5, 141.6, 160.9, 163.8 and 197.5..

IR(CCl_4) : 1035.9, 1140.1, 1167.1, 1203.8, 1265.5, 1358.1, 1603.1, 1672.5 and 2939.9 cm^{-1}.

MS(m/z): 39, 41, 43, 69, 151(base), 166, 219, 234 and 235(M+1)

HRMS: calculated 234.1256 **and found** 234.1250.

5-Isopropyl-4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone (2Me-4T_{2Me}-5I-K)

The ketone was prepared from 4-hydroxy-5-isopropyl-2-methylacetophenone **3e** (2.25 g, 0.0136 mol), 4-tosyl-2-methyl-1-butene (4.878 g, 0.0203 mol) and potassium carbonate (5.64 g, 0.041 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 5-isopropyl-4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone, **2Me-4T_{2Me}-5I-K** in 75% yield.

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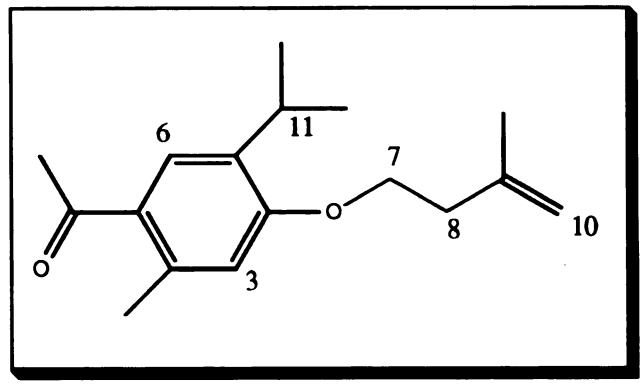
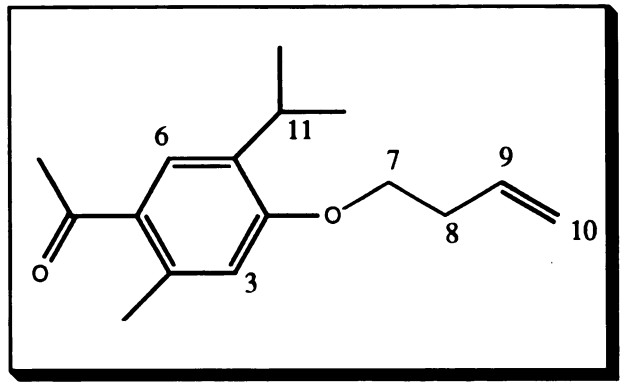


^{1}H NMR (300MHz; $CDCl_3$) : δ 1.20(d, J=6.93 Hz, 6H), 1.79(s, 3H), 2.52(br t, J=6.57 Hz, $2H_8$), 2.53(s, 3H), 2.54(s, 3H), 3.25(septet, J=6.9 Hz, $1H_{11}$), 4.11(t, J=6.6 Hz, $2H_7$), 4.80(m, $2H_{10}$), 6.64(s, $1H_3$) and 7.59(s, $1H_6$).

^{13}C NMR(75MHz; $CDCl_3$) : 22.36, 22.45, 22.63, 26.82, 29.19, 37.27, 66.36, 112.282, 114.35, 128.68, 129.47, 133.97, 139.20, 141.96, 158.58 and 199.96.

5-Isopropyl-4-(3'-buten-1'-oxy)-2-methylacetophenone (2Me-4T$_{2H}$-5I-K)

The ketone was prepared from 4-hydroxy-5-isopropyl-2-methylacetophenone **3e** (2.25 g, 0.0136 mol), 4-bromo-1-butene (4.878 g, 0.0203 mol) and potassium carbonate (5.64 g, 0.041 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 5-isopropyl-4-(3'-buten-1'-oxy)-2-methylacetophenone, **2Me-4T$_{2H}$-5I-K** in 61% yield.



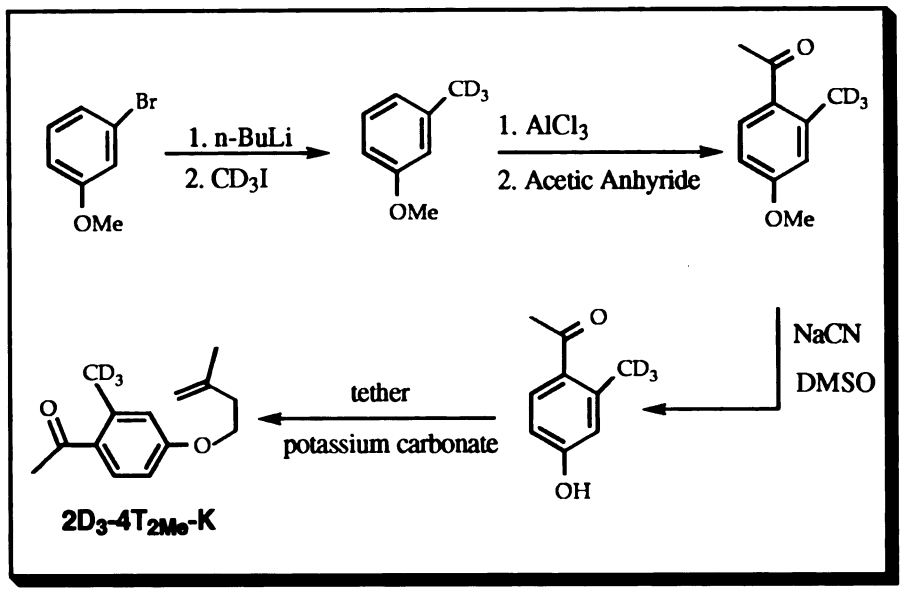
^{1}H NMR (300MHz; $CDCl_3$) : δ 1.21(d, J=6.9 Hz, 6H), 2.53(s, 3H), 2.54(s,3H), 2.56(dddt, J=6.54, 6.54, 1.32 & 1.29 Hz, $2H_8$), 3.26(septet, J=6.87 Hz, $1H_{11}$), 4.05(t, J=6.5 Hz, $2H_7$), 5.10(ddt, J=10.23, 1.83 & 1.17 Hz, $1H_{10}$), 5.16(ddt, J=17.19, 1.67 & 1.59 Hz, $1H_{10}$), 5.90(ddt, J=17.07, 10.26 & 6.78 Hz, $1H_9$), 6.63(s, $1H_3$) and 7.59(s, $1H_6$).

^{13}C NMR(75MHz; $CDCl_3$) : 22.31, 22.38, 26.83, 29.11, 33.62, 67.13, 114.32, 117.10, 128.62, 129.40, 133.83, 134.32, 139.14, 158.49 and 199.80.

IR(CCl_4) : 1055.2, 1072.6, 1165.1, 1240.1, 1356.1, 1558.7, 1608.8, 1678.3 and 2964.9cm^{-1}.

MS(m/z): 55, 91, 149, 177(base), 189, 231, 246 and 247(M+1).

HRMS: calculated 246.1620 **and found** 246.1624 .



3-Methyl(d3)anisole

A solution of 3-bromoanisole (2.0 g, 0.0107 mol) in tetrahydrofuran (25mL) was cooled to -78°C. n-BuLi (5.88 mL, 2.0M) in hexanes was added dropwise to the stirred mixture. The mixture was stirred at -78°C for 1.5 hours and then transferred via a double-ended needle (using argon pressure) to a -78°C solution of iodomethane-d3 (1.55 g, 0.0107 mol) in tetrahydrofuran (15 mL). The mixture was stirred at -78°C for thirty minutes and was slowly warmed to 0°C. The mixture was quenched with saturated NH_4Cl solution (20mL) at 0°C. The mixture was tranferred to a separatory funnel with ether (100mL) and the organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by dry column chromatography on silica gel (hexane:ethyl acetate=95:5) gave 3-methyl(d3)anisole (1.10 g, 82%) [Chem. Abstracts Registry # 20369-34-0].

4-Methoxy-2-methyl(d3)acetophenone

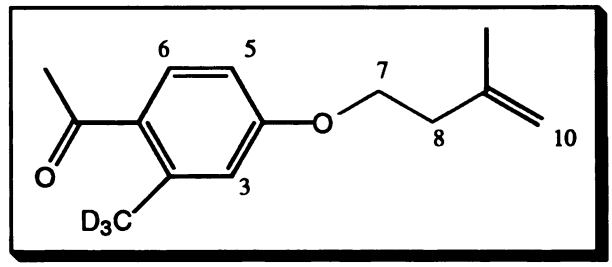
A solution of 3-methyl(d3)anisole (1.10 g, 0.0088 mol) in dry carbon disulphide (25 mL) was cooled to 5°C. Finely powdered anhydrous aluminium chloride (2.58 g, 0.01936 mol) was added to the stirred mixture. Freshly distilled acetic anhydride (0.0898 g, 0.0088 mol) was then slowly added via a syringe over a 10 minute period. The mixture was allowed to warm to room temperature and refluxed for 24 hours. The mixture was cooled to room temperature and poured over ice (50 g). The mixture was transferred to a separatory funnel with ether (100mL) and the organic phase was washed with 50 mL portions of 10% HCl, water, and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered, and concentrated at reduced pressure. Purification of the crude product by dry column flash chromatography on silica gel (hexane:ethyl acetate=90:10) gave 4-methoxy-2-methyl(d3)acetophenone in 66% yield.

4-Hydroxy-2-methyl(d3)acetophenone

4-Methoxy-2-methyl(d3)acetophenone (1.0 g, 0.006 mol) and sodium cyanide (1.47 g, 0.03 mol) were suspended in DMSO (30 mL) and heated at 165°C (bath temperature) under argon. After 16 hours, the reaction mixture was poured over ice and acidified with 6N HCl (caution : HCN evolution). The mixture was tranferred to a separatory funnel with ether (100 mL) and extracted with 25 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to a pH of 3-5 and extracted with ether(3x100 mL). The organic extracts were dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by silica gel column chromatography (hexane:ethyl acetate=90:10) gave 4-hydroxy-2-methyl(d3)acetophenone in 33% yield.

2-Methyl(d3)-4-(3'-methyl-3'-buten-1'-oxy)acetophenone (2D3-4T2Me-K)

The ketone was prepared from 4-hydroxy-2-methyl(d3)acetophenone (0.03 g, 0.00196 mol), 4-tosyl-2-methyl-1-butene (0.471 g, 0.00294 mol) and potassium carbonate (0.948 g, 0.0069 mol) in the same fashion as that used for 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 2-methyl(d3)-4-(3'-methyl-3'-buten-1'-oxy)acetophenone **2D3-4T2Me-K** in 74% yield.

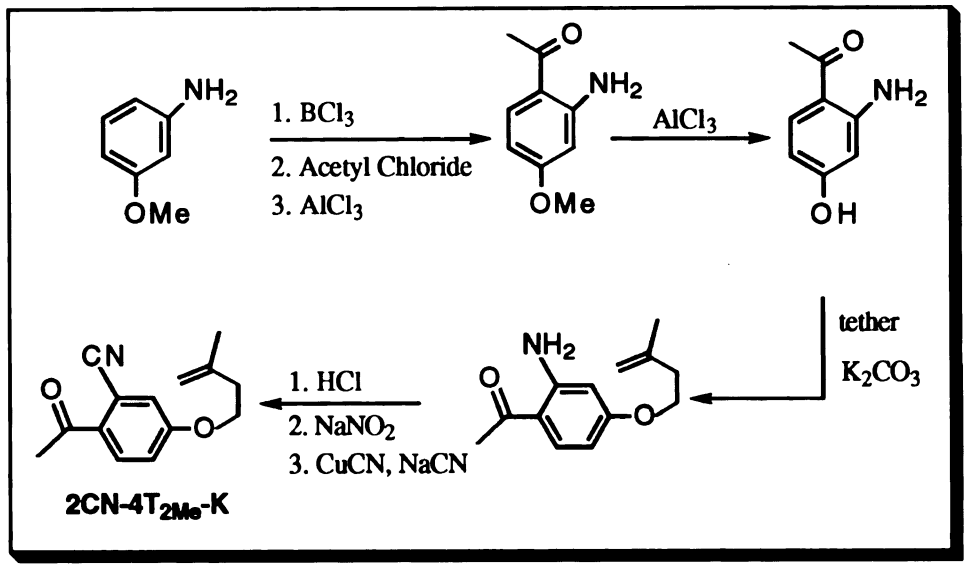


1H NMR (300MHz; CDCl3) : δ 1.79(br s, 3H), 2.49(t, J=6.84 Hz, 2H8), 2.53(s, 3H), 4.10(t, J=6.81 Hz, 2H7), 4.78(m, 1H10), 4.83(m, 1H10), 6.72(d, J=2.7 Hz, 1H3), 6.73(dd, J=6.81 & 2.64 Hz, 1H5) and 7.74(m[second order], 1H6).

13C NMR(75MHz; CDCl3) : 22.75, 29.01, 36.98, 66.37, 110.99, 112.19, 118.0, 129.84, 132.51, 141.81, 142.07, 161.27 and 199.39.

MS(m/z):41.2, 43.1, 69.1, 137.2, 138.2(Base), 153.2, 221.2 and 222.3(M+1).

HRMS: calculated 221.1496 **and found** 221.1511



2-Amino-4-methoxyacetophenone

A solution of m-anisidine (6.4 g, 0.052 mol) in CH_2Cl_2 (30mL) maintained at -50°C was slowly treated with a solution of BCl_3 in CH_2Cl_2 (50 mL, 1M, 0.05 mol) to give a slurry, which was stirred for 30 minutes at -50°C. Freshly distilled acetyl chloride (3.925 g, 0.05 mol) and aluminium chloride (6.67 g, 0.05 mol) were added sequentially. The mixture was stirred at -50°C for one hour , at ambient temperature for 18 hours, and at 40°C for three hours. The mixture was cooled to room temperature and then poured over ice (100 g). The aqueous mixture was made alkaline with 10% NaOH, transferred to a separatory funnel with ethyl acetate (200 mL) and extracted with ethyl acetate (4x100mL). The combined organic phases were washed with 100 mL of saturated NaCl, dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product (black oil) by column chromatography (diethyl ether:methylene chloride, 20:80) gave 2-amino-4-methoxyacetophenone (2.64 g, 32%) [Chem. Abstracts Registry # 42465-53-2].

2-Amino-4-hydroxyacetophenone

A solution of 2-amino-4-methoxyacetophenone (1.5 g, 0.0091 mol) in CH_2Cl_2 (25 mL) was treated with aluminium chloride (2.44 g, 0.0182 mol) in five portions. The mixture was stirred for 18 hours, then additional aluminium chloride (1.22 g, 0.0091 mol) was added. The mixture was stirred vigorously for four hours, poured over ice (100 g) and extracted with ethyl acetate (3x100 mL). The combined organic phases were extracted with 25 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to a pH of 3-5 and extracted with ethyl acetate (3x100 mL). The organic extracts were dried over magnesium sulfate, filtered, and concentrated at reduced pressure to give 2-amino-4-hydroxyacetophenone as a pale yellow solid (80% yield, mp163-165°C) [Chem. Abstracts Registry # 90033-64-0].

2-Amino-4-(3'-methyl-3'-buten-1'-oxy)acetophenone

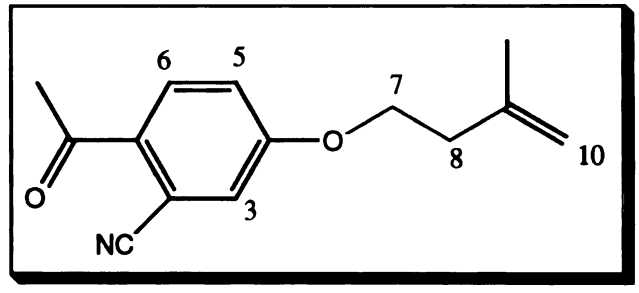
The ketone was prepared from 2-amino-4-hydroxyacetophenone (1.10 g, 0.0073 mol), 4-tosyl-2-methyl-1-butene (1.92 g, 0.008 mol), and potassium carbonate (3.027 g, 0.0219 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 2-amino-4-(3'-methyl-3'-buten-1'-oxy)acetophenone in 77.5% yield.

^{1}H NMR (300MHz; $CDCl_3$) : δ 1.78(s, 3H), 2.47(t, J=6.84 Hz, 2H), 2.49(s, 3H), 4.05(t, J=6.94 Hz, 2H), 4.77(br s, 1H), 4.83(br s, 1H), 6.09(d, J=2.42 Hz, 1H), 6.23(dd, J=9.0 & 2.46 Hz, 1H), 6.5(br s, 2H) and 7.61(d, J=9.0 Hz, 1H).

5-(3'-Methyl-3'-buten-1'-oxy)-2-acetylbenzonitrile (2CN-4T$_{2Me}$-K)

A solution of 2-amino-4-(3'-methyl-3'-buten-1'-oxy)acetophenone (0.4 g, 0.00183 mol) in water (3 mL) maintained at 5°C was slowly treated with 1.5 mL of concentrated HCl to give the amino salt. The salt solution was subsequently treated with a cooled solution (5°C) of sodium nitrite (0.152 g, 0.002196 mol) in water (2 mL). The diazonium

salt was immediately added to a cooled solution (5°C) of sodium cyanide (0.269 g, 0.055 mol) and cuprous cyanide (0.197 g, 0.0027 mol) in water (25 mL). The reaction mixture was stirred for six hours at room temperature. The mixture was filtered through a cotton plug and transferred to a separatory funnel with ether (100 mL). The organic phase was washed with 50 mL portions of water, saturated sodium chloride solution, dried over magnesium sulfate, filtered, and concentrated at reduced pressure. Purification of the crude product by silica gel column chromatography (hexane:ethyl acetate, 95:5) gave 5-(3'-methyl-3'-buten-1'-oxy)-2-acetylbenzonitrile, **2CN-4T$_{2Me}$-K** in 38.5% yield (mp 71-72°C).



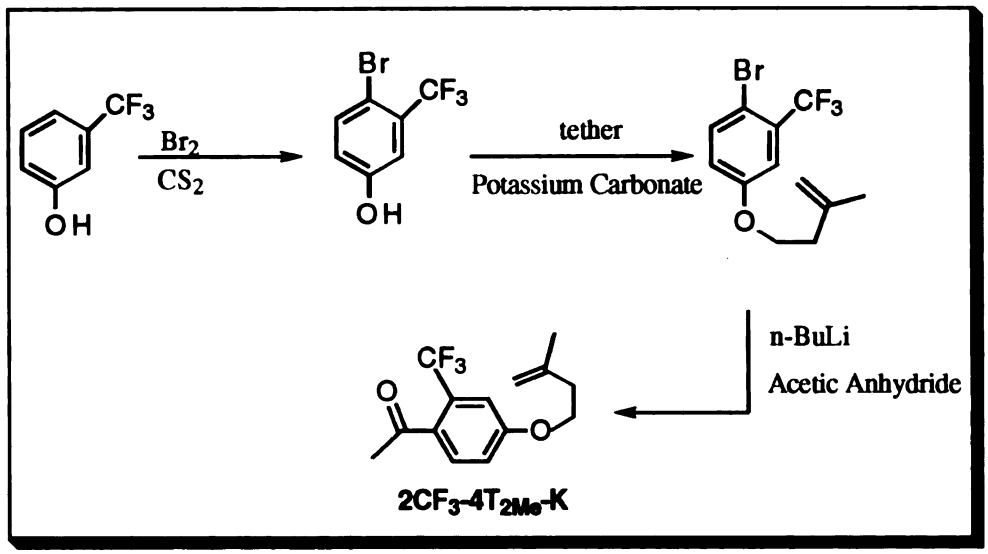
^{1}H NMR (300MHz; CDCl$_3$) : δ 1.79(s, 3H), 2.52(t, J=6.75 Hz, 2H$_8$), 2.63(s, 3H), 4.14(t, J=6.75 Hz, 2H$_7$), 4.78(br s, 1H$_{10}$), 4.86(br s, 1H$_{10}$), 7.11(dd, J=8.79 & 2.6 Hz, 1H$_5$), 7.26(d, J=2.6 Hz, 1H$_3$) and 7.87(d, J=8.79 Hz, 1H$_6$).

^{13}C NMR(75MHz; CDCl$_3$) : 22.64, 27.38, 36.66, 67.20, 112.60, 112.78, 118.02, 121.18, 131.92, 132.22, 141.13, 161.69 and 194.58.

IR(CCl$_4$) : 737, 909, 1260, 1319, 1360, 1597, 1688, 1742, 2180 and 2940 cm^{-1}.

MS(m/z):39, 41, 69(Base), 146, 229 and 230(M+1).

HRMS: calculated 229.1103 **and found** 229.1107.



4-Bromo-3-trifluoromethylphenol

A solution of 3-trifluoromethylphenol (5.0 g, 0.03086 mol) in carbon disulfide (10 mL) maintained at 0°C was slowly treated with a solution of bromine (5.0 g, 0.0313 mol) in carbon disulfide (10 mL) over a 10 minute period. The mixture was stirred at 0°C for one hour, follwed by three hours at room temperature. The resulting reaction mixture was added to water (25 mL) and then subjected to repeated extraction with methylene chloride (150 mL). The methylene chloride layer was washed with aqueous sodium bicarbonate, water, and saturated sodium chloride. The organic layer was dried over sodium sulfide, gravity filtered and concentrated at reduced pressure. Purification of the crude product by dry column flash chromatography on silica gel (hexane:ethyl acetate, 90:10) gave 4-bromo-3-trifluoromethylphenol (3.1 g, 42%).

^{1}H NMR (300MHz; CDCl3) : δ 5.65(s, 1H), 6.84(dd, J=8.6 & 2.9 Hz, 1H), 7.15(d, J=2.9 Hz, 1H) and 7.51(d, J=8.6 Hz, 1H).

1-Bromo-2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)benzene

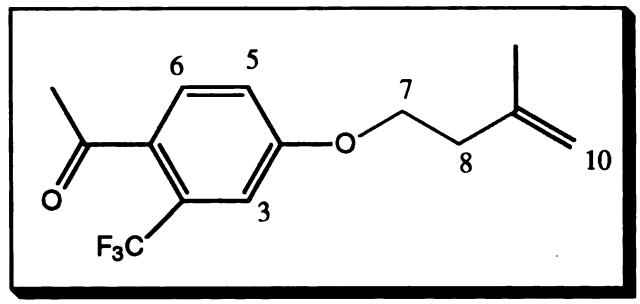
The bromobenzene was prepared from 4-bromo-3-trifluoromethylphenol (2.0 g, 0.0083 mol) , 4-tosyl-2-methyl-1-butene (2.39g, 0.00996 mol) and potassium carbonate

(3.44 g, 0.0249 mol) in the same fashion as that for 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 1-bromo-2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)benzene in 64% yield.

^{1}H NMR (300MHz; $CDCl_3$) : δ 1.78(s, 3H), 2.49(t, J=6.7 Hz, 2H), 4.06(t, J=6.7 Hz, 2H), 4.78(br s, 1H), 4.84(br s, 1H), 6.89(dd, J=8.8 & 3.0 Hz, 1H), 7.20(d, J=3.0 Hz, 1H) and 7.55(d, J=8.8 Hz, 1H).

2-Trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone ($2CF_3$-$4T_{2Me}$-K)

A solution of 1-bromo-2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)benzene (0.5 g, 0.0016 mol) in tetrahyrofuran (10mL) was cooled to -78°C. n-BuLi (1.0 mL of 2.0M) in hexanes was added dropwise to the stirred mixture. The mixture was stirred at -78°C for 1.5 hours and then transferred via a double-ended needle (using argon pressure) to a -78°C solution of acetic anhydride (0.408 g,0.004 mol) in tetrahydrofuran (15 mL). The mixture was stirred at -78°C for thirty minutes and was slowly warmed to 0°C. The mixture was stirred for 2 hours at 0°C and then quenched with saturated NH_4Cl solution (20mL). The mixture was tranferred to a separatory funnel with ether (100mL) and the organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate=95:5) gave 2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone **1AP-$2CF_3$-$4T_{2Me}$** in 32% yield.



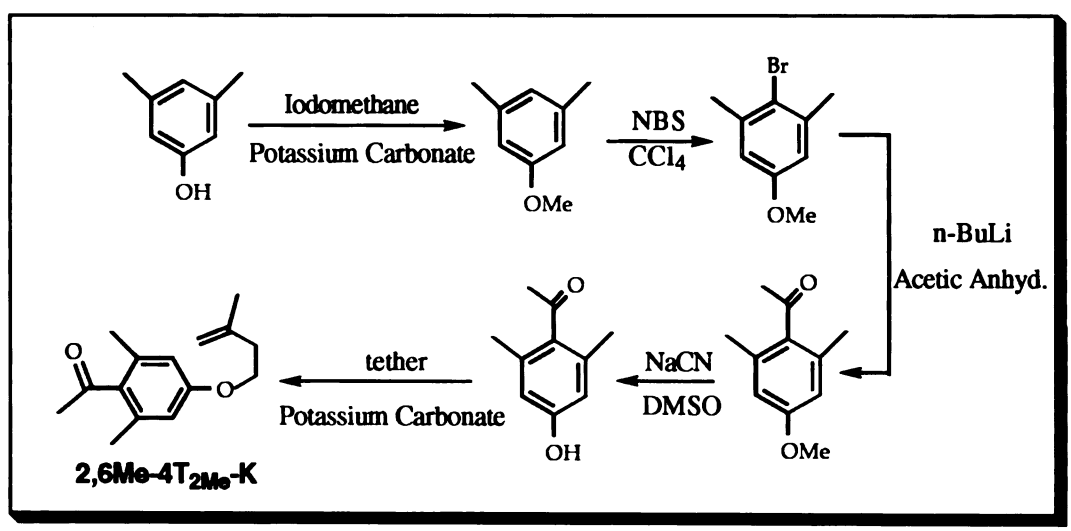
^{1}H NMR (300MHz; CDCl3) : δ 1.79(s, 3H), 2.50(br t, J=6.7 Hz, $2H_8$), 2.54(s, 3H), 4.12(t, J=6.72 Hz, $2H_7$), 4.78(br s, $1H_{10}$), 4.85(br s,$1H_{10}$), 7.03(dd, J=8.60 & 2.50,$1H_5$), 7.2(d, J=2.49 Hz, $1H_3$) and 7.50(d, J=8.7 Hz, $1H_6$).

^{13}C NMR(75MHz; CDCl3) : 22.71, 30.8, 36.85, 66.93, 112.49, 113.69(q, J=5.6 Hz), 116.50, 123.29(q, J=272 Hz), 130.31, 141.48, 160.36, and 200.11.

IR(CCl_4) : cm^{-1}.

MS(m/z):41.1, 43.1, 69.1(base), 189.0, 205.1, 272.2 and 273.2(M+1).

HRMS: calculated 272.1024 **and found** 272.1013.



3,5-Dimethylanisole

3,5-Dimethylphenol (20 g, 0.164 mol), iodomethane (27.9 g, 0.196 mol) and anhydrous potassium carbonate (45.3 g, 0.328 mol) in dry acetone (200 mL) were refluxed for 24 hours under argon. The cooled mixture was filtered and concentrated at reduced pressure. The resulting oil was diluted with ether (100mL) and extracted with 2N NaOH (4x25mL). The ether layer was dried over magnesium sulfate, gravity filtered and concentrated. Purification of the crude product by fractional distillation gave 3,5-dimethylanisole (bp 193-195°C) in 72% yield.

^{1}H NMR(300MHz;CDCl$_3$) : δ6.59(s, 1H), 6.53(s, 2H), 3.76(s, 3H) and 2.28(s, 6H).

4-Bromo-3,5-dimethylanisole

To a solution of 3,5-dimethylanisole (5.0 g, 0.0373 mol) in carbon tetrachloride (80 mL) were added N-bromosuccinimide (7.96 g, 0.0447 mol) and Merck 60 silica gel (20 grmas). The mixture was vigorously stirred at room temperature for 22 hours. The insoluble material was removed by filteration. The organic layer was then washed with aqueous sodium thiosulfate and dried over magnesium sulfate. The solution was gravity filtered and concentrated at reduced pressure. Purification of the crude product by kugelrohr distillation gave 7.33 g (92%) of 4-bromo-3,5-dimethylanisole.

^{1}H NMR(300MHz;CDCl$_3$) : δ6.63(s, 2H), 3.75(s, 3H) and 2.34(s, 6H).

MS(M/Z): 39, 40, 51, 65, 77, 91, 92, 105, 135, 171, 173, 214 and 216(Base and M+1).

2,6-Dimethyl-4-methoxyacetophenone

A solution of 4-bromo-3,5-dimethylanisole (3.0 g, 0.0141 mol) in dry ether (25mL) was cooled to -78°C and 14 mL of 2.0M n-BuLi in hexanes was added dropwise to the stirred mixture. The mixture was stirred at -78°C for one hour and then transferred via

a double-ended needle (using argon pressure) to a -78°C solution of acetic anhydride (5.75 g, 0.0564 mol) in ether (20 mL). The mixture was stirred at -78°C for one hour and was slowly warmed to room temperature. The mixture was quenched with saturated NH_4Cl solution (25mL). The mixture was tranferred to a separatory funnel with ether (100mL) and the organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by dry column flash chromatography on silica gel (hexane:ethyl acetate=90:10) gave 2,6-dimethyl-4-methoxyacetophenone (0.44 g, 18%) [Chem. Abstracts Registry # 104174-28-9].

^1H NMR(300MHz;$CDCl_3$) : δ6.53(s, 2H), 3.76(s, 3H), 2.43 (s, 3H) and 2.22(s, 6H).

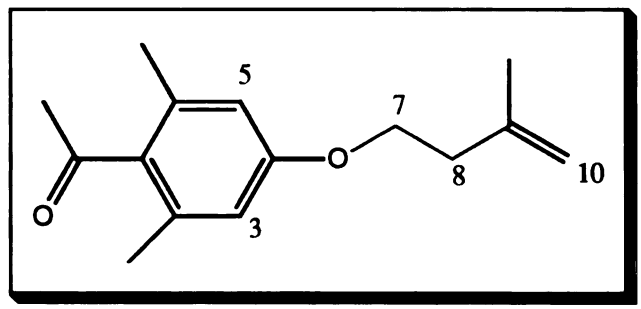
2,6-Dimethyl-4-hydroxyacetophenone

2,6-Dimethyl-4-methoxyacetophenone (0.44 g, 0.00247 mol) and sodium cyanide (0.605 g, 0.01235 mol) were suspended in DMSO (15 mL) and heated at 145°C (bath temperature) under argon. After 20 hours, the reaction mixture was poured over ice and acidified with 6N HCl (caution : HCN evolution). The mixture was tranferred to a separatory funnel with ether (50 mL) and extracted with 25 mL portions of 2N NaOH. The combined aqueous washings were acidified with HCl to a pH of 3-5 and extracted with ether (3x50 mL). The organic extracts were dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by silica gel column chromatography (hexane:ethyl acetate, 90:10) gave 2,6-dimethyl-4-hydroxyacetophenone (0.0759 g) [Chem. Abstracts Registry # 91060-92-3].

2,6-Dimethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone

(2,6Me-4T$_{2Me}$-K)

The ketone was prepared from 2,6-dimethyl-4-hydroxyacetophenone (0.0759 g, 0.0046 mol), 4-tosyl-2-methyl-1-butene (0.1333 g, 0.0056 mol) and potassium carbonate (0.3174 g, 0.0023 mol) in dry acetone in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 2,6-dimethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone.

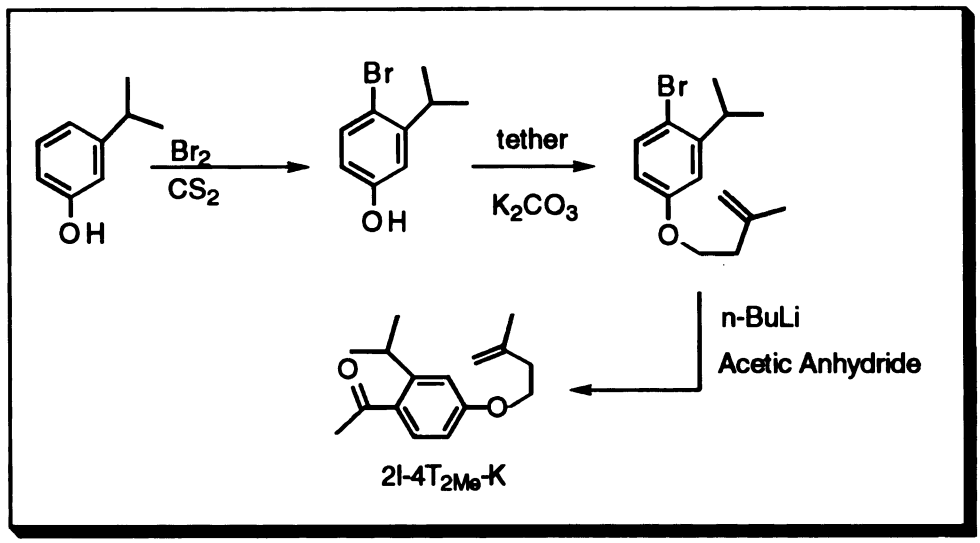


^{1}H NMR (300MHz; CDCl$_3$) : δ 1.78(br s, 3H), 2.21(s, 6H), 2.43(s, 3H), 2.46(t, J=6.87 Hz, 2H$_8$), 4.03(t, J=6.81 Hz, 2H$_7$) and 6.54(s, 2H$_{3,5}$).

^{13}C NMR(75MHz; CDCl$_3$) : 19.61, 22.77, 32.41, 37.12, 66.27, 111.99, 113.76, 134.45, 135.44, 142.10, 158.72 and 208.01.

MS(m/z): 69, 77, 91, 121, 149(base), 164, 217, 232, and 233(M+1).

HRMS: calculated 232.1464 **and found** 232.1462.



4-Bromo-3-isopropylphenol

Bromination of 3-isopropylphenol was carried out in the same manner as 4-bromo-3-trifluorophenol. A solution of 3-isoproylphenol (5.0 g, 0.0367 mol) in carbon disulfide was slowly treated with a solution of bromine (7.33 g, 0.0459 mol) in carbon disulfide at 0°C. The reaction was completed in three hours at room temperature. Purification of the crude product by dry flash column chromatography (hexane:ethyl acetate, 90:10) gave 4-bromo-3-isopropylphenol (2.90 g, 37%).

^{1}H NMR (300MHz; CDCl3) : δ 1.20(d, J=6.84 Hz, 6H0, 3.27(sept., J=6.87 Hz, 1H), 5.03(br s, 1H), 6.53(dd, J=8.6 & 3.0 Hz, 1H), 6.75(d, J=3.0 Hz, 1H) and 7.35(d, J=8.6 Hz, 1H).

4-Bromo-1-(3'-methyl-3'-buten-1'-oxy)-3-isopropylbenzene

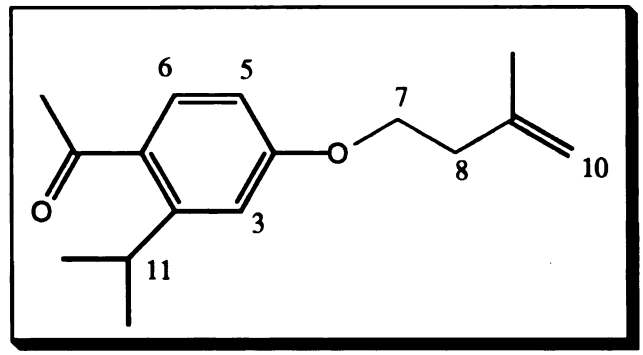
The coupled product was prepared in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone by reacting 4-bromo-3-isopropylphenol (2.90 g, 0.0135 mol), 4-tosyl-2-methyl-butene (3.89 g, 0.0162 mol) and potassium carbonate (5.60 g, 0.0405 mol) in acetone. Purification of the crude product by silica gel column

chromatography (hexane:ethyl acetate, 90:10) gave 4-bromo-1-(3'-methyl-3'-buten-1'-oxy)-3-isopropylbenzene (2.6 g, 68%).

^{1}H NMR (300MHz; $CDCl_3$) : δ 1.20(d, J=6.87 Hz, 6H), 1.79(s, 3H), 2.47(br t, J=6.86 Hz, 2H), 3.29(sept., J=6.87 Hz, 1H), 4.02(t, J=6.87 Hz, 2H), 4.78(m, 1H), 4.83(m, 1H), 6.59(dd, J=8.73 & 3.03 Hz, 1H), 6.81(d, J=3.03 Hz, 1H) and 7.37(d, J=8.73 Hz, 1H).

2-Isopropyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone (2I-4T$_{2Me}$-K)

A solution of 4-bromo-1-(3'-methyl-3'-buten-1'-oxy)-3-isopropylbenzene (1.5 g, 0.0053 mol) in dry tetrahydrofuran (25mL) was cooled to -78°C and 4 mL of 2.0M n-BuLi in hexanes was added dropwise to the stirred mixture. The mixture was stirred at -78°C for two hours and then transferred via a double-ended needle (using argon pressure) to a -78°C solution of freshly distilled acetic anhydride (2.16 g, 0.0212 mol) in tetrahydrofuran (20 mL). The mixture was stirred at -78°C for one hour and was slowly warmed to room temperature, followed by refluxing for four hours. The mixture was quenched with saturated NH_4Cl solution (25mL). The mixture was tranferred to a separatory funnel with 100mL ether and the organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by dry flash column chromatography on silica gel (hexane:ethyl acetate, 95:05) gave 2-isopropyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone **2I-4T$_{2Me}$-K** (0.40 g, 31%).



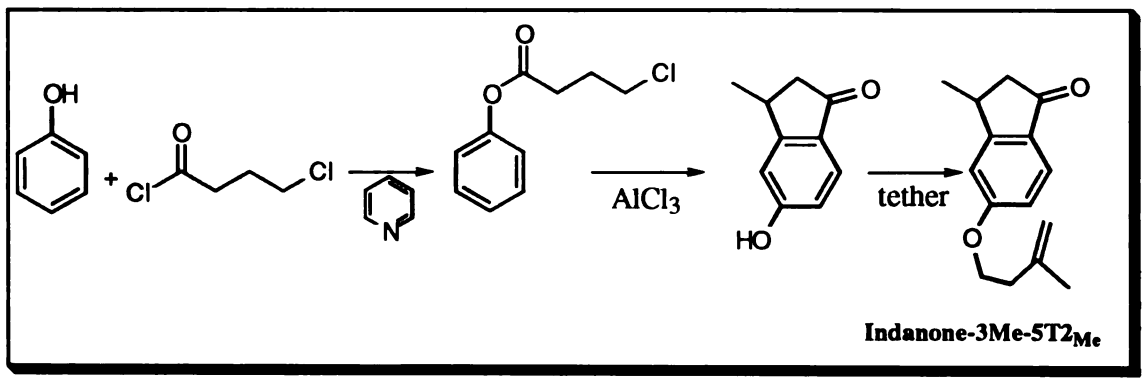
^{1}H NMR (300MHz; $CDCl_3$) : δ 1.20(d, J=6.81 Hz, 6H), 1.80(s, 3H), 2.50(t, J=6.87 Hz, $2H_8$), 2.53(s, 3H), 3.73(sept. J=6.85 Hz, $1H_{11}$), 4.10(t, J=6.86 Hz, $2H_7$), 4.80(m, $2H_{10}$), 6.70(dd, J=8.61 & 2.61,$1H_5$), 6.91(d, J=2.64 Hz, $1H_3$) and 7.58(d, J=8.61 Hz, $1H_6$).

^{13}C NMR(75MHz; $CDCl_3$) : 22.80, 23.96, 29.02, 30.03, 37.08, 66.40, 110.25, 112.23, 130.48, 131.48, 141.88, 152.03, 161.38 and 201.03.

IR(CCl_4) : 1055.2, 1190.2, 1232.7, 1249.1, 1307.9, 1354.2, 1566.4, 1603.1, 1680.2 and 2968.8 cm^{-1}.

MS(m/z): 69, 91, 45, 163(base), 246 and 247(M+1).

HRMS: calculated 246.1620 **and found** 246.1594.



Phenyl 4-chlorobutyroate

The ester was prepared in the same manner as 3-methylphenyl acetate **2a** by reacting phenol (6.0 g, 0.064 mol), pyridine (15.1 g, 0.191 mol) and 4-chlorobutyryl

chloride (13.5 g, 0.096 mol) in benzene at 0°C. The reaction was completed in 24 hours at room temperature. Purification by fractional vacuum distillation gave Phenyl 4-chlorobutyroate (11.32 g, 89%, bp 107°C at 1.2 torr) as a pale yellow liquid.

^{1}H NMR (300MHz; $CDCl_3$) : δ 2.22(tt, J=7.2 & 6.24hz, 2H), 2.79(t, J=7.2 Hz, 2H), 3.69(t, J=6.24 Hz, 2H), 7.1(m, 2H), 7.24(m, 1H), and 7.39(m, 2H).

5-Hydroxy-3-methyl-1-indanone

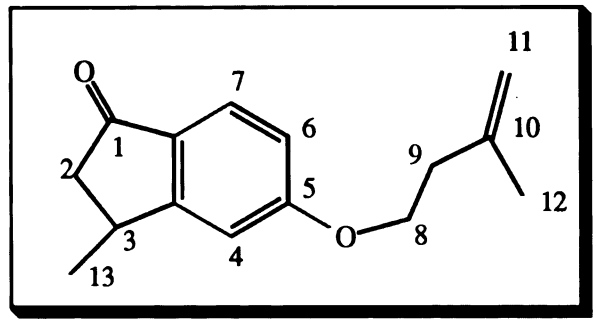
In a argon-purged 100mL round bottom flask, aluminum chloride (8.46 g, 0.063mol) was slowly added via a solid addition funnel to neat Phenyl 4-chlorobutyroate (5.6 g, 0.028mol). The addition was highly exothermic. Upon complete addition of $AlCl_3$, the reaction mixture was heated to 150°C for five hours. The reaction mixture was allowed to cool to 50°C and quenched with 10% HCl and ice. The mixture was taken up into ether (100mL) and extracted with 2N NaOH (6x30mL). The base washings were combined and acidified to a pH~3 with concentrated HCl. The resulting solution was extracted with ether (4x40mL). The organic extracts were dried over magnesium sulfate, filtered, and concentrated *in vacuo*. Recrystalization from 15% ethanol/water gave 5-hydroxy-3-methyl-1-indanone (0.4g, 9%, mp 145-146°C).

^{1}H NMR (300MHz; $CDCl_3$) : δ 7.65(d, J=8.3 Hz, 1H), 6.88(br s, 1H), 6.85(dd, J=8.2 & 1.6 Hz, 1H), 3.5(ddq, J=3.5, 7.5 & 7.14 Hz, 1H), 2.9(dd, J=18.9 & 7.5 Hz, 1H), 2.25(dd, J=18.9 & 3.5 Hz, 1H) and 1.35(d, J=7.14 Hz, 3H).

3-Methyl-5-(3'-methyl-3'-buten-1'-oxy)indan-1-one

The indanone was prepared from 5-hydroxy-3-methyl-1-indanone (0.4 g, 0.0025 mol), 4-tosyl-2-methyl-1-butene (0.889 g, 0.0037 mol) and potassium carbonate (1.025 g, 0.0074 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on

silica gel (hexane:ethyl acetate, 90:10) gave 3-methyl-5-(3'-methyl-3'-buten-1'-oxy)indan-1-one in 76% yield.



^{1}H NMR (300MHz; CDCl$_3$) : δ 7.63(d, J=9.3 Hz, 1H$_7$), 6.89(br s, 1H$_4$), 6.86(dd, J=9.3 & 2.1 Hz, 1H$_6$), 4.85(br s, 1H$_{11}$), 4.79(br s, 1H$_{11}$), 4.14(t, J=6.8 Hz, 2H$_8$), 3.35(ddq, J=3.5, 7.6, & 7.1 Hz, 1H$_3$), 2.89(dd, J=18.9 & 7.6 Hz, 1H$_2$), 2.52(br t, J=6.8 Hz, 2H$_9$), 2.24(dd, J=18.9 & 3.5 Hz, 1H$_2$), 1.80(s, 3H$_{12}$) and 1.36(d, J=7.1 Hz, 3H$_{13}$).

^{13}C NMR(75MHz; CDCl$_3$) : 204.6, 164.7, 162.9, 141.7, 129.7, 125.2, 115.4, 112.3, 109.2, 66.8, 45.5, 37.0, 32.7, 22.8 and 21.3.

IR(CCl$_4$) : 2965, 1711, 1601, 1296 and 1254.

MS(m/z): 41, 69, 147(base), 162, 163, 230 and 231(M+1).

HRMS: calculated 230.1307 **and found** 230.1280.

5-bromo-1-pentene

A three-necked flask equipped with a stillhead/condenser, dropping funnel and a magnetic stir bar was charged with 1,5-dibromopentane (100g, 0.435mol). The 1,5-dibromopentane was heated to 195-200°C on an oil bath. HMPA (70.62g, 0.394mol) was then added dropwise at a rate of 1-2 drops/second. Distillation of the crude 5-bromo-1-pentene began upon the addition of HMPA. Purification by fractional distillation gave 5-bromo-1-pentene(bp 125-127°C) as a clear liquid (41.6g, 71%yield.).

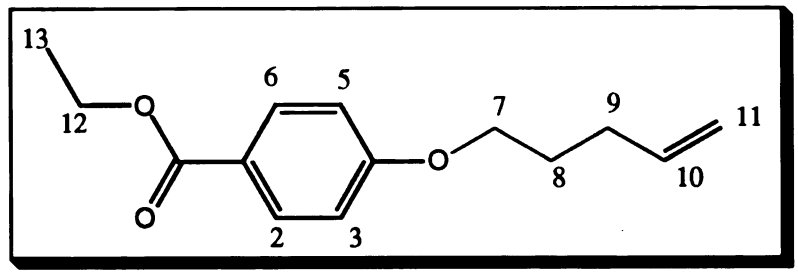
^{1}H NMR (300MHz; $CDCl_3$) : δ 1,93(q, J=6.93 Hz, 2H), 2.16-2.23(dt, J=6.81and 6.84 Hz, 2H), 3.40(t, J=6.78 Hz, 2H), 4.9-5.0(dq, J=10.69 and 1.35 Hz, 1H), 5.0-5.1(dq, J=17.22 and 1.65 Hz, 1H), 5.75(ddt, J=17.07, 10.23 and 6.75 Hz, 1H).

^{13}C NMR(75MHz; $CDCl_3$) : 31.73, 32.01, 33.11, 115.87, and 136.71.

5-(4'-Ethoxycarbonylphenoxy)pent-1-ene

4-Hydroxybenzoic acid was converted into ethyl 4-hydroxybenzoate by Fischer esterification. In a 100mL round bottom flask equipped with a reflux condenser, 4-hydroxybenzoic acid (10 g, 0.0725 mol) was dissolved in ethyl alcohol (50mL, approx. 20 fold excess). The reaction was acid catalyzed by the addition of 2 mL of H_2SO_4 to the solution. The reaction was refluxed until complete conversion (24 hours). The reaction mixture was neutralized with aqueous sodium bicarbonate, tranferred to a separatory funnel with ether (100mL). The organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Ethyl 4-hydroxybenzoate was obtained in 88% yield as a white powder.

Ethyl 4-hydroxybenzoate (4.0 g, 0.024 mol), 5-bromo-1-butene (4.3 g, 0.0288 mol) and anhydrous potassium carbonate (8.4 g, 0.0608mol) was suspended in dry acetone (50mL). The stirred reaction mixture was refluxed under argon until thin layer chromatography showed the disappearance of starting material. Upon completion, the mixture was gravity filtered to remove potassium bromide, formed during the reaction, and concentrated. The resulting oil was diluted with diethyl ether (50mL) and extracted with 2N NaOH (4x20mL). The ether solution was dried over magnesium sulfate, gravity filtered and concentrated. Purification of the crude product by silica gel chromatography (32 cm x 2.0 cm)(hexane: ethyl acetate, 90:10) gave 5-(4'-Ethoxycarbonylphenoxy) pent-1-ene as a colorless liquid in 53% yield.



5-(4'-Ethoxycarbonylphenoxy) pent-1-ene (1EC-4T3H)

^{1}H NMR(300MHz;CDCl3) : δ7.96(d, J=8.7 Hz, $2H_{2,6}$), 6.88(d, J=8.7 Hz, $2H_{3,5}$), 5.82(ddt, J=16.9, 10.2 & 6.6 Hz, $1H_{10}$), 5.05(dq, J=17.1 & 1.8 Hz, $1H_{11}$), 4.99(dq, J=10.2 & 1.8 Hz, $1H_{11}$), 4.32(q, J=7.2 Hz, $2H_{12}$), 4.0(t, J=6.45 Hz, $2H_7$), 2.22(dt, J=6.9 &6.6 Hz, $2H_9$), 1.89(tt, J=6.4 & 6.9 Hz, $2H_8$) and 1.36(t, J=7.1 Hz, $3H_{13}$).

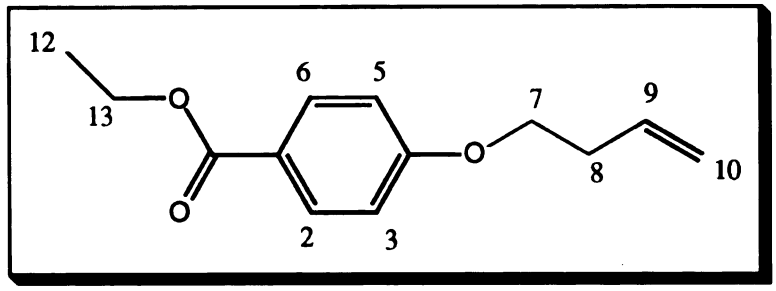
^{13}C NMR(75MHz; CDCl3) : 14.40, 28.27, 30.03, 60.61, 67.32, 114.02, 115.39, 122.79, 131.52, 137.59, 162.78 and 166.44.

MS(m/z): 39, 41(Base) 68, 69, 121, 138 and 235(M+1)

HRMS: calculated 234.1256 **and found** 234.1250

4-(4'-Ethoxycarbonylphenoxy)but-1-ene

The ester was prepared from ethyl 4-hydroxybenzoate (4.0g, 0.024mol), 4-bromo-1-butene (3.9g, 0.0288mol) and anhydrous potassium carbonate (8.4g, 0.0608mol) in the same fashion as **1EC-4T3H**. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 95:5) gave 4-(4'-ethoxycarbonylphenoxy) but-1-ene in 61% yield.



4-(4'-Ethoxycarbonylphenoxy) but-1-ene (1EC-4T$_{2H}$)

^{1}H NMR(300MHz;CDCl$_3$) : δ 7.96(d, J=8.7 Hz, 2H$_{2,6}$), 6.89(d, J=8.7 Hz, 2H$_{3,5}$), 5.89(ddt, J=17.1, 10.4 & 6.9 Hz, 1H$_9$), 5.15(dq, J=17.1 & 1.6 Hz, 1H$_{10}$), 5.11(dq, J=10.3 & 1.2 Hz, 1H$_{10}$), 4.32(q, J=7.2 Hz, 2H$_{13}$), 4.04(t, J=6.8 Hz, 2H$_7$) 2.55 (qt, J=6.9 & 1.5 Hz, 2H$_8$), and 1.36(t, J=7.2 Hz, 3H$_{12}$).

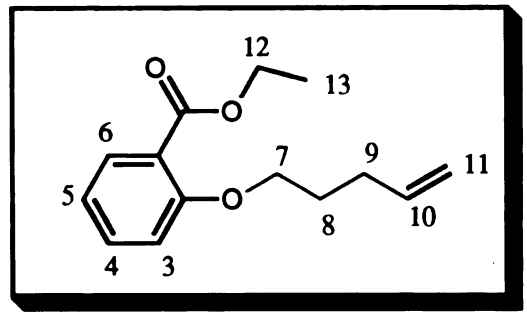
^{13}C NMR(75MHz; CDCl$_3$) : 14.35, 33.44, 60.57, 67.28, 114.01, 117.27, 122.87, 131.48, 134.03, 162.57, and 166.36.

MS(m/z): 39, 53, 54, 55(Base), 65, 93, 103, 121, 138, 192, 220 and 221(M+1).

HRMS: calculated and found

5-(2'-Ethoxycarbonylphenoxy)pent-1-ene

The *ortho* ester was prepared by acid catalyzed Fischer esterification in the same fashion as **1EC-4T$_{3H}$** by reacting 2-hydroxybenzoic acid (10 g, 0.725 mol) in ethyl alcohol (50 mL). After work-up, ethyl 2-hydroxybenzoate was obtained asa white solid (9.8 g, 81.7%). Williamson etherification of ethyl 2-hydroxybenzoate (4.0 g, 0.024 mol) with 5-bromo-1-butene (4.3g, 0.0288 mol) and anhydrous potassium carbonate (8.4 g, 0.0608 mol) gave 5-(2'-ethoxycarbonylphenoxy) pent-1-ene (2.75 g, 49%) as a colorless liquid.



5-(2'-Ethoxycarbonylphenoxy) pent-1-ene (1EC-2T3H)

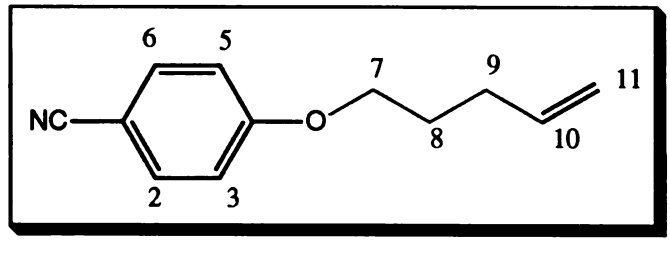
^{1}H NMR(300MHz;CDCl3) : δ7.74(dd, J=7.5 & 1.9 Hz, 1H6), 7.4(ddd, J=8.4, 7.5 & 1.9 Hz, 1H4), 6.94(m, 2H3,5), 5.83(ddt, J=17.0, 10.20 & 6.70 Hz, 1H10), 5.08-5.0(dq, J=17.10 & 1.7 Hz, 1H11), 5.0-4.95(dm, J=10.2 Hz, 1H11), 4.33(q, J=7.2 Hz, 2H12), 4.02(t, J=6.3 Hz, 2H7), 2.26(br dt, J=6.9 & 6.6 Hz, 2H9), 1.90(tt, J=6.9 & 6.36 Hz, 2H8) and 1.36 (t, J=7.13 Hz, 3H13).

^{13}C NMR(75MHz; CDCl3) : 14.27, 28.31, 29.98, 60.69, 67.92, 113.06, 115.13, 119.99, 120.88, 131.43, 133.07, 137.73, 158.34 and 166.63.

HRMS: calculated 234.1256 **and found** 234.1255.

5-(4'-Cyanophenoxy)pent-1-ene

The benzonitrile was prepared by coupling 4-cyanophenol (4.15 g, 0.035 mol), 5-bromo-1-butene (4.3 g, 0.0288 mol) and anhydrous potassium carbonate (14.5 g, 0.105 mol) in the same fashion as **1EC-4T3H**. Purification of the crude reaction mixture using dry column flash chromatography (hexane:ethyl acetate, 90:10) gave 5-(4'-cyanophenoxy)pent-1-ene (3.3 g).



5-(4'-Cyanophenoxy)pent-1-ene (1CN-4T3H)

^{1}H NMR(300MHz;CDCl3) : δ7.55(d, J=8.91 Hz, $2H_{2,6}$), 6.92(d, J=8.91 Hz, $2H_{3,5}$), 5.88-5.75(ddt, J=17.07, 10.35 & 6.66 Hz, $1H_{10}$), 5.08-5.01(dq, J=17.07 & 1.67 Hz, $1H_{11}$), 5.02-4.97(dq, J=10.3 & 1.42 Hz, $1H_{11}$), 3.99(t, J=6.41 Hz, $2H_7$) 2.24-2.18(dt, J=6.66 & 6.87 Hz, $2H_9$) and 1.93-1.84 (tt, J=6.45 & 6.81 Hz, $2H_8$).

^{13}C NMR(75MHz; CDCl3) : 28.02, 29.85, 67.45, 103.66, 115.11, 115.48, 119.23, 133.88, 137.29 and 162.29.

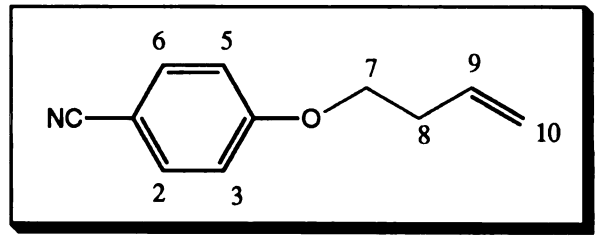
IR(CCl_4) : 1170.9, 1257.8, 1510.5, 1608.8, 2228.1, 2947.6 and 3082.6 cm^{-1}.

MS(m/z): 39, 41(base), 67, 68, 69, 187 and 189(M+2).

HRMS: calculated 187.0997 **and found** 187.1001.

4-(4'-Cyanophenoxy)but-1-ene

The benzonitrile was prepared by refluxing 4-cyanophenol (3 g, 0.025 mol), 4-bromo-1-butene (3 g, 0.022 mol), and potassium carbonate (10.4 g, 0.075 mol) in acetone for 48 hours in the same fashion as **1EC-4T2H**. Purification of the crude reaction mixture by dry column flash chromatography, followed by distillation under reduced pressure gave 4-(4'-cyanophenoxy)but-1-ene as a colorless liquid (1.6 g, 42%).



4-(4'-cyanophenoxy)but-1-ene (1CN-4T2H)

^{1}H NMR(300MHz;CDCl3) : δ7.55(d, J=9 Hz, $2H_{2,6}$), 6.92(d, J=8.97 Hz, $2H_{3,5}$), 5.93-5.79(ddt, J=17.16, 10.38 & 6.69 Hz, $1H_9$), 5.20-5.13(dq, J=17.2 & 1.58 Hz,

$1H_{10}$), 5.15-5.09(dq, J=10.9 & 1.36 Hz, $1H_{10}$), 4.04(t, J=6.69 Hz, $2H_7$) and 2.58-2.51 (dddt, J=6.66, 6.63, 1.34 & 1.34 Hz, $2H_8$).

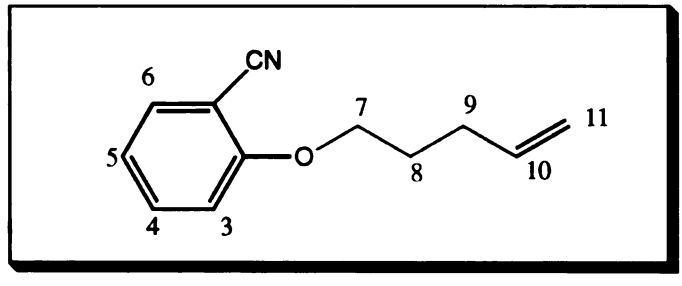
^{13}C NMR(75MHz; $CDCl_3$) : 33.25, 67.48, 103.83, 115.17, 117.50, 119.20, 133.69, 133.91 and 162.14.

IR(CCl_4) : 835.3, 1172.9, 1255.8 1508.6, 1608.8, 2230.0, 2934.1 and 3084.6 cm^{-1}.

HRMS: calculated 173.0841 **and found** 173.0840

5-(2'-Cyanophenoxy)pent-1-ene

The *ortho* alkenoxybenzonitrile was synthesized in the same manner as **1EC-2T3H** by refluxing 2-cyanophenol (5g, 0.042mol), 5-bromo-1-pentene (5.4g, 0.036mol) and potassium carbonate (16.5g, 0.12mol) in acetone. Dry column flash chromatography gave 5-(2'-cyanophenoxy) pent-1-ene as a colorless liquid.



5-(2'-Cyanophenoxy)pent-1-ene (1CN-2T3H)

^1H NMR(300MHz;$CDCl_3$) : δ7.50(ddd, J=8.0, 7.6 &1.7 Hz, $1H_4$), 7.4(dd, J=7.56 &1.7 Hz, $1H_6$), 6.96(ddd, J=7.56, 7.6 & 0.87 Hz, $1H_5$), 6.92(br d, J=8.1 Hz, $1H_3$),5.9-5.75(ddt, J=17.0, 10.2,& 6.69 Hz, $1H_{10}$), 5.09-5.01(dq, J=17.1 & 1.65 Hz, $1H_{11}$), 5.02-4.97(dm, J=10.17 Hz, $1H_{11}$), 4.06(t, J=6.36 Hz, $2H_7$), 2.27(dt, J=6.93 &6.7 Hz, $2H_9$) and 1.93-1.84 (tt, J=6.93 & 6.36 Hz, $2H_8$).

^{13}C NMR(75MHz; $CDCl_3$) : 27.97, 29.84, 68.07, 112.19, 115.53, 116.45, 120.59, 133.75, 134.22, 137.38 and 160.70.

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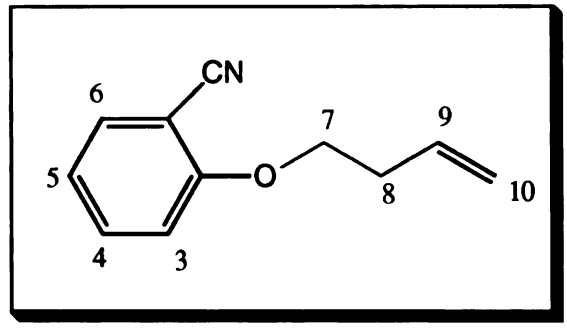
IR(CCl_4) : 918.2, 1111.1, 1261.6, 1288.6, 1495.0, 1601.1, 2231.9, 2945.7 and 3082.6 cm^{-1}.

HRMS: calculated 187.0997 **and found** 187.0997.

4-(2'-Cyanophenoxy)but-1-ene

4-(2'-Cyanophenoxy)but-1-ene was prepared by coupling 2-cyanophenol (5.0 g,0.042 mol) and 4-bromo-1-butene (5.7 g, 0.42 mol) using potassium carbonate (14.5 g, 0.105 mol) as the base. Work-up and purification was similar to **1EC-4T3H**. 4-(2'-cyanophenoxy)but-1-ene was isolated in 51% (3.7 g).



4-(2'-Cyanophenoxy)but-1-ene (1CN-2T2H)

^1H NMR(300MHz;$CDCl_3$) : δ7.5(ddd, J=7.5, 7.2 &1.7 Hz, $1H_4$), 7.4(dd, J=7.6 & 1.7 Hz, $1H_6$),6.96(ddd, J=7.5, 7.3 & 0.96 Hz, $1H_5$), 6.94(br d, J=7.7 Hz, $1H_3$), 5.97-5.84(ddt, J=17.13, 10.30 & 6.75 Hz, $1H_9$), 5.21-5.15(dq, J=17.13 & 1.57 Hz, $1H_{10}$), 5.13-5.10(dm, J=10.9 Hz, $1H_{10}$), 4.09(t, J=6.66 Hz, $2H_7$) and 2.58-2.51 (dddt, J=6.72, 6.69, 1.30 & 1.30 Hz, $2H_8$).

^{13}C NMR(75MHz; $CDCl_3$) : 33.27, 68.24, 102.14, 112.23, 116.36, 117.69, 120.71, 133.55, 133.77, 134.22,and 160.53.

IR(CCl_4) : 742.7, 1111.1, 1261.6, 1288.6, 1495.0, 1601.1 and 2231.9 cm^{-1}.

HRMS: calculated 173.0841 **and found** 173.0836.

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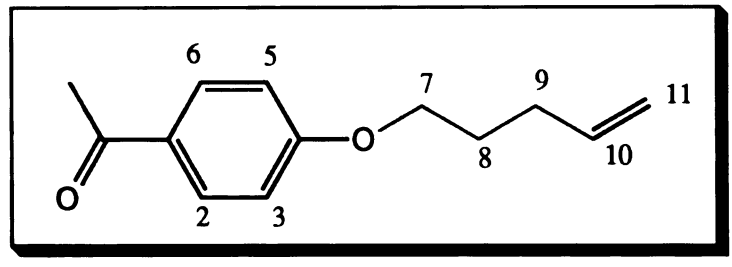
5-(4'-Acetylphenoxy) pent-1-ene

The ketone was prepared from 4-hydroxyacetophenone (2.0 g, 0.015 mol), 5-bromo-1-pentene (2.25 g, 0.015 mol) and potassium carbonate (7.6 g, 0.055 mol) in the same fashion as that of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane/ethyl acetate 95:5) gave 5-(4'-acetylphenoxy) pent-1-ene **(1AP-4T3H)** in 68% yield.



5-(4'-Acetylphenoxy) pent-1-ene (1AP-4T3H)

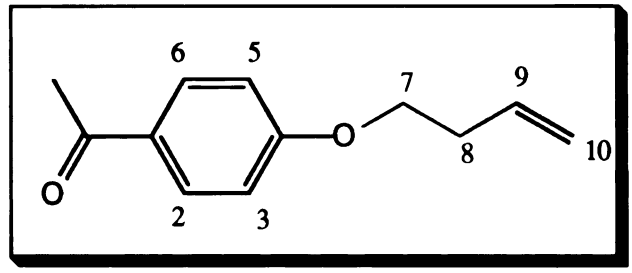
^{1}H NMR(300MHz;CDCl3) : δ7.90(d, J=8.94 Hz, $2H_{2,6}$), 6.89(d, J=8.97 Hz, $2H_{3,5}$), 5.89-5.76(ddt, J=17.0, 10.2 & 6.7 Hz, $1H_{10}$), 5.04(dq, J=17.0 & 1.62 Hz, $1H_{11}$), 4.98(dm, J=10.2 Hz, $1H_{11}$), 4.01(t, J=6.40 Hz, $2H_7$), 2.53(s, 3H), 2.23(br dt, J=6.9 & 6.6 Hz, $2H_9$) and 1.88 (tt, J=6.5 & 6.9 Hz, $2H_8$).

^{13}C NMR(75MHz; CDCl3) : 26.22, 28.12, 29.9, 67.28, 114.05, 115.32, 130.6, 130.5, 137.42, 162.94 and 196.77.

IR(CCl_4) : 2947.6, 1682.1, 1603.0, 1255.8, 1170.9, 800.6, and 711.6.

4-(4'-Acetylphenoxy) but-1-ene

4-(4'-Acetylphenoxy) but-1-ene was prepared by Nahm. The sample was purified by silica column chromatography using a mixture of hexanes and ethyl acetate (90:10) as the eludent.

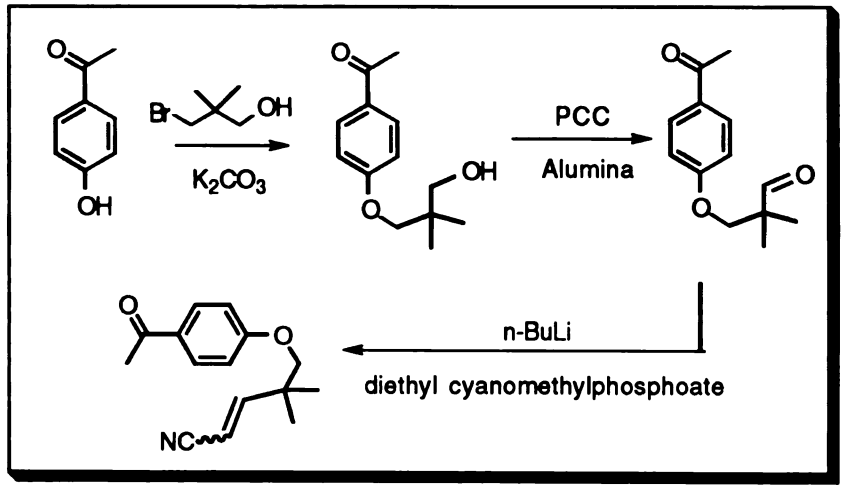


4-(4'-Acetylphenoxy) but-1-ene (1AP-4T$_{2H}$)

^{1}H NMR(300MHz;CDCl$_3$) : δ7.90(d, J=8.9 Hz, 2H$_{2,6}$), 6.90(d, J=8.9 Hz, 2H$_{3,5}$), 5.87(ddt, J=17.10, 10.20 & 6.7 Hz, 1H$_9$), 5.16(dq, J=17.2 & 1.65 Hz, 1H$_{10}$), 5.10(dq, J=10.2 & 1.14 Hz, 1H$_{10}$), 4.06(t, J=6.7 Hz, 2H$_7$) and 2.58-2.51 (tdt, J=1.23, 6.7 & 6.7 Hz, 2H$_8$), 2.53(s, 3H).

^{13}C NMR(75MHz; CDCl$_3$) : 26.28, 33.40, 67.34, 114.13, 117.32, 130.25, 130.53, 133.94, 162.79 and 196.71.

IR(CCl$_4$) : 2930.2, 1682.1, 1603.0, 1253.9, 1170.9, 800.6, 771.6.



3-(4'-Acetylphenoxy)-2,2-dimethylpropan-1-ol

4-Hydroxyacetophenone (3 g, 0.022 mol), 3-bromo-2,2-dimethylpropanol (3.68 g, 0.022 mol) and anhydrous potassium carbonate (9.12 g, 0.066 mol) in 50 mL of dry acetone were refluxed under an argon atmosphere for 72 hours. The cooled mixture was gravity filtered to remove potassium bromide formed during the reaction and concentrated *in vacuo*. The resulting yellow oil was diluted with ether (50mL) and extracted with 2N NaOH (3x25mL). The organic layer was dried over magnesium sulfate, gravity filtered and concentrated *in vacuo* to give a crude yellow liquid. Unreacted 3-bromo-2,2-dimethylpropanol was removed from the raction mixture by fractional distillation (bp 185°C). Purification of the crude product by recrystallization (ethanol:water) gave 3-(4'-Acetylphenoxy)-2,2-dimethylpropan-1-ol as a white solid in 44% yield (mp 31-33°C).

^{1}H NMR (300MHz; $CDCl_3$) : δ 7.9(d, J=9 Hz, 1H), 6.92(d, J=9 Hz, 1H), 3.9(s, 2H), 3.5(s, 2H), 2.5(s, 3H), 0.92(s, 6H).

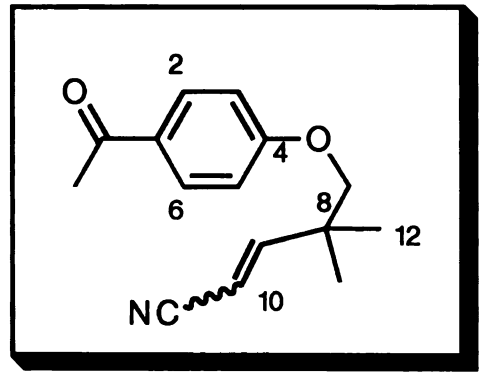
3-(4'-Acetylphenoxy)-2,2-dimethylpropanal

Oxidation of 3-(4'-Acetylphenoxy)-2,2-dimethylpropan-1-ol to the aldehyde was accomplished by treatment with PCC. A suspension of 3-(4'-Acetylphenoxy)-2,2-dimethylpropan-1-ol (4 g, 0.018 mol), PCC (8 g , 0.036) and basic alumina (50 grams) in dichloromethane (75mL) was stirred under argon at room temperature. The reaction progress was monitored by thin layer chromatography. After complete conversion of the alcohol (20 hours), the mixture was gravity filtered. The organic filtrate was concentrated *in vacuo*. The resulting brown oil was purfied by column chromatography (hexane:ethyl acetate, 80:20) to give 3-(4'-Acetylphenoxy)-2,2-dimethylpropanal, which was used immediately.

^{1}H NMR(300MHz;CDCl$_3$) : δ 9.9(s, 1H), 7.9(d, J=9 Hz, 2H), 6.89(d, J=9 Hz, 2H), 3.8(s, 2H), 2.54(s, 3H), 1.2(s,6H).

5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile

A solution of diethyl cyanomethylphosphonate (2.25 g, 0.0127 mol) in dry THF (50mL) was cooled to -23°C and 8 mL of 1.6M n-BuLi in hexanes was added dropwise to the stirred mixture. The mixture was stirred at -23°C for one hour and 3-(4'-acetylphenoxy)-2,2-dimethylpropanal (3.5 g, 0.16 mol) in THF (10mL) was added via a gas-tight syringe. The mixture was stirred at -23°C for one hour and was slowly warmed to room temperature. The mixture was quenched with saturated NH_4Cl solution (25mL). The mixture was tranferred to a separatory funnel with ether (90mL) and the organic phase was washed with 50 mL portions of water and saturated NaCl solution. The organic phase was dried over magnesium sulfate, filtered and concentrated at reduced pressure. Purification of the crude product by dry column flash chromatography on silica gel (hexane:ethyl acetate=95:5) gave trans- and cis-5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile (~9:1) in 23% yield as a white solid(mp. 60-61°C).



^{1}H NMR(300MHz;CDCl$_3$) : δ7.93(d, J=9 Hz, 2H$_{2,6}$), 6.89(d, J=9 Hz, 2H$_{3,5}$), 6.80(d, J=16.7, 1H$_{9trans}$), 6.48(d, J=12.4, 1H$_{9cis}$), 5.38(d, J=16.7, 1H$_{10trans}$), 5.38(d, J=12.4, 1H$_{10cis}$), 3.89(s, 2H$_{7cis}$), 3.78(s, 2H$_{7trans}$), 2.54(s, 3H$_{trans}$),

2.53(s,3H_{cis}), 1.54(s, 3$H_{11trans}$), 1.39(s, 3H_{11cis}), 1.2(s, 3$H_{12trans}$), and 1.2(s, 3H_{12cis}).

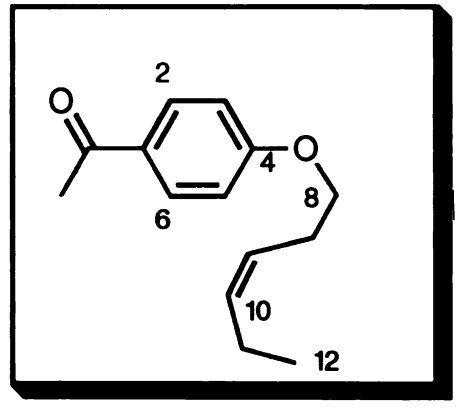
^{13}C NMR(75MHz; $CDCl_3$) : 196.7, 162.4, 160.7, 130.8, 117.5, 114.1 98.7, 75.1, 39.0, 26.3, and 23.3.

IR(CCl_4) : 2255, 1675, 1601, 1173, 920, and 750cm^{-1}.

MS(m/z): 43(32%), 65(16%), 81(16%), 107(22%), 119(18%), 121(90%), 149(base), 243(24%), and 244(M+1).

cis-5-(4'-Acetylphenoxy)-3-pentene

The ketone was prepared from 4-hydroxyacetophenone (3 g, 0.022 mol), cis-1-bromo-3-hexene (3.6 g, 0.022 mol) and potassium carbonate (9.1 g, 0.066 mol) in the same fashion as that used for 4-(3'-buten-1'-oxy)-2-methylacetophenone. Purification of the crude product by column chromatography on silica gel (hexane:ethyl acetate, 90:10) gave cis-5-(4'-Acetylphenoxy)-3-pentene in 77% yield.



^{13}C NMR(75MHz; $CDCl_3$) : 196.5, 162.8, 134.5, 130.4, 130.0, 123.5, 114.0, 67.6, 27.0, 26.15, 20.5, and 14.1.

IR(CCl_4) : 2966, 1682, 1603, 1254, 1171 and 750cm^{-1}.

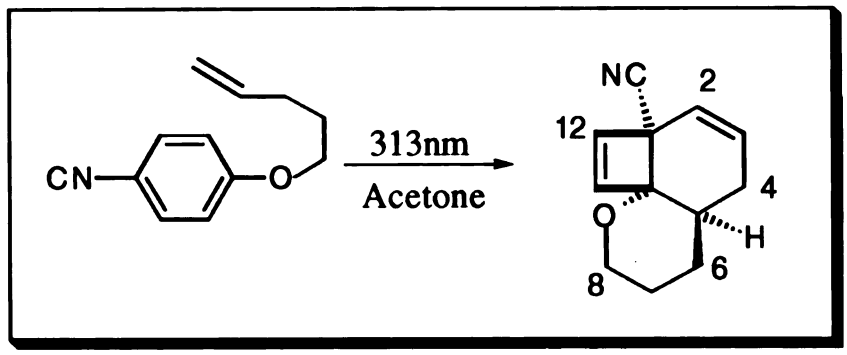
MS(m/z): 39(16%), 41(62%), 43(42%), 55(base), 67(46%), 82(57%), 83(77%), 121(99%), 136(23%), 137(26%), 218(36%), and 219(M+1).

III. Identification of Photoproducts

Photolysis of 5-(4'-cyanophenoxy)pent-1-ene **(1CN-4T3H)**

In a NMR tube, 5-(4'-cyanophenoxy)pent-1-ene (2.0mg) was dissloved in deuterated acetone (0.75mL, 1.5 x 10^{-2}M). The sample was purged with argon for 15 minutes and then irradiated through a 313 nm filter solution. The reaction was monitored by time resolved NMR. Product formation was slow (>15 hours). It is believed that an impurity in the deuterated acetone was impeding the photoreaction. A single photoproduct was indentified as 1-cyano-9-oxatricyclo[8.2.0.$0^{5,10}$]dodeca-2,11-diene. Large scale photolysis was carried out to isolated the photoproduct. 5-(4'-Cyanophenoxy)pent-1-ene (450mg) was dissolved in freshly distilled acetone (160mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. The reaction mixture was concentrated at reduced pressure and separated using silica gel chromatography (hexanes:ethyl acetate, 85:15). 1-Cyano-9-oxatricyclo[8.2.0.$0^{5,10}$] dodeca-2,11-diene.was obtained as clear needles in 58% yield (263mg).

Similar results were obtained when **(1CN-4T3H)** was irradiated in acetonitrile at 254 nm. In a quartz test tube, 5-(4'-cyanophenoxy)pent-1-ene (126mg) was dissloved in acetonitrile (45mL), purged with argon for twenty minutes and irradiated at 254 nm using a Rayonet The reaction progress was monitored by gas chromatography. The reaction solution rapidly turned yellow and by GC analysis showed the formation of one major product after three hours of irradiation. Purification of the crude product by silica gel column chromatography (ethyl acetate/hexanes 10:90) gave 1-cyano-9-oxatricyclo[8.2.0.$0^{5,10}$]dodeca-2,11-diene. The melting points of the products obtained from direct and sensitized irradiation were identical (mp.70-71°C).



1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene

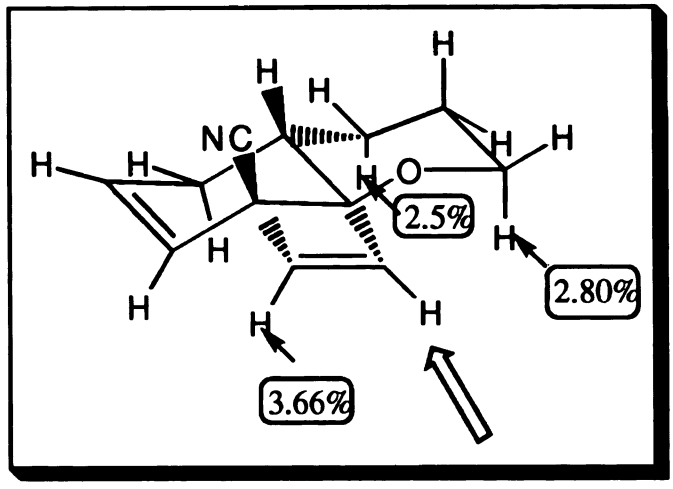
^{1}H NMR(300MHz;CDCl$_3$) : δ6.75(d, J=2.94 Hz, 1H$_{11}$), 6.19(d, J=2.97 Hz, 1H$_{12}$), 5.95(ddd, J=9.9, 7.4 & 2.0 Hz, 1H$_3$), 5.75(dd, J=9.9 & 2.9 Hz, 1H$_2$), 4.04(dddd, J=11.8, 4.8, 1.65 & 1.35 Hz, 1H$_8$), 3.61(ddd, J=14.6, 11.8 & 2.7 Hz, 1H$_8$), 2.03(ddd, J=15.6, 7.4 & 2.8 Hz, 1H$_4$), 1.2-1.74(m, 2H$_{7,6}$), 1.6-1.5(m, 3H$_{7,6,5}$), and 1.5(dddd, J=15.6, 2.9 &2.0 Hz, 1H$_4$)

^{13}C NMR(75MHz; CDCl$_3$) : 137.53, 136.29, 131.31, 123.71, 119.03, 84.74, 65.38, 47.29,38.62, 28.27, 26.24, and 26.09.

IR(CCl$_4$) : 2936.0, 2856.6, 2239.6, 1286.7, 1091.9, 947.2, 706.0cm^{-1}.

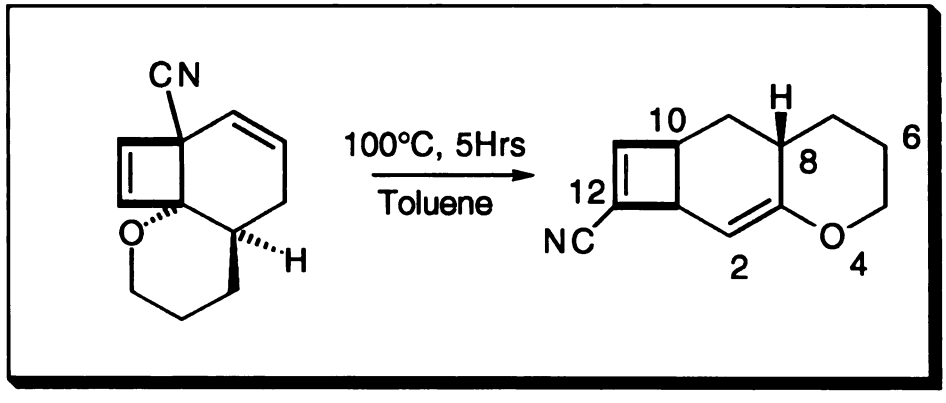
MS(m/z) : 39(90%), 41(94%), 51(56%), 55(97%), 69(51%), 77(100%), 91(82%), 103(54%), 104(82%), 130.1(61%), 160.1(54%), 161.1(73%), 187.1, 188.1(M+1)

Nuclear Overhauser Enhancement (nOe) experiments were carried out on the photoproduct to determine the stereochemistry. Irradiation of the cyclobutene proton H$_{11}$ afforded enhancements at H$_6$(2.52%),H$_8$ (2.80%), and H$_{12}$(3.66%). The bridgehead proton H$_5$ was uneffected by irradiation at H$_{11}$.



Thermal Rearrangement of 1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene.

In a NMR tube, 1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene (25mg) was dissolved in toluene-d8 (0.75mL). The reaction mixture was purged with argon and heated for five hours at 100°C. NMR analysis of the reaction mixture showed quantitative conversion of 1-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene to 12-cyano-4-oxatricyclo[8.2.0.0^{3,8}]dodeca-2,11-diene, via a cope rearrangement in which C-8 is inverted.



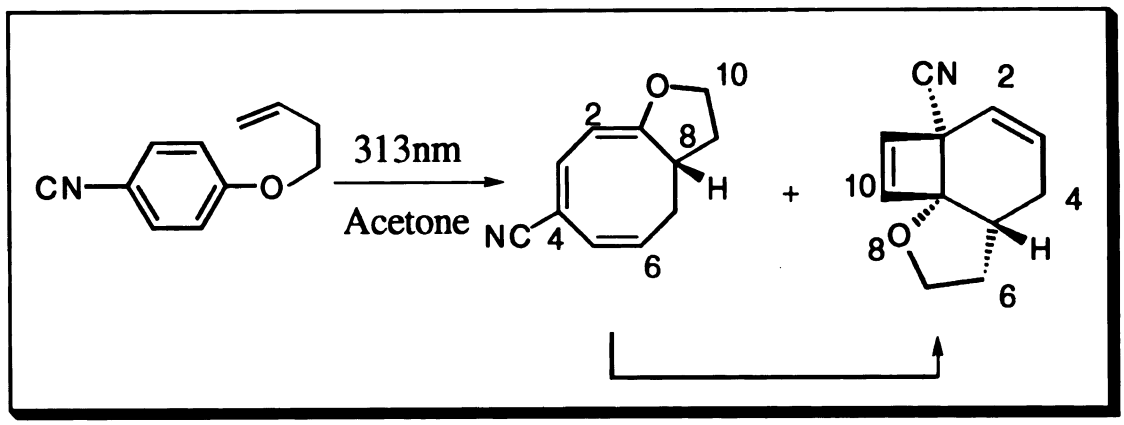
12-cyano-4-oxatricyclo[8.2.0.0^{3,8}]dodeca-2,11-diene

^{1}H NMR(300MHz;Toluene-d8) : δ 5.93(br s, 1H$_{10}$), 5.05(dd, J=5.85 & 2.55 Hz, 1H$_2$), 3.70(dddd, J=10.8, 4.1, 2.3 & 2.3 Hz, 1H$_5$), 3.22(ddd, J=11.8, 10.8 & 2.8 Hz,

$1H_5$), 3.08(ddd, J=5.8, 4.2 & 1.4 Hz, $1H_1$)2.47(dddd, J=6.0, 4.3, 1.8 & 1.38 Hz, $1H_{10}$), 1.60(m, $1H_8$), 1.50-1.30(m, 3H), 1.26(ddd, J=13.35, 4.45 & 1.95 Hz, $1H_9$), 0.85(ddd, J=13.4, 11.5 & 5.9 Hz, $1H_9$) and 0.75(ddd, J=12.7, 11.8 & 3.9 Hz, 1H).

Photolysis of 4-(4'-cyanophenoxy)but-1-ene **(1CN-4T$_{2H}$)**

In a NMR tube, 1.95mg of 4-(4'-cyanophenoxy)but-1-ene was dissloved in acetone-d_6 (0.75mL), purged with argon for ten minutes, and irradiated using a medium pressure mercury arc filtered with a solution consisting of 0.002M K_2CrO_4 in 1% aqueous K_2CO_3 (313 nm). The reaction solution rapidly turned yellow and NMR analysis showed the formation of two isomers. The ratio of the product isomers were time dependent. At low conversion of **1CN-4T$_{2H}$** (<20%), two products were present in a 1:1 ratio, but upon high conversion of the starting material only one product was present. Preparatory scale photolysis allowed for the isolation of the two photoproducts. 4-(4'-Cyanophenoxy)but-1-ene (420mg) was dissolved in freshly distilled acetone (160mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. The photolysis was stopped after 25% conversion. Purification of the crude mixture by silica gel chromatography (ethyl acetate/hexane, 15:85) afforded pure samples of two photoproducts, 1-cyano-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene, **1-CN-4T$_{2H}$-CB** and 4-cyano-11-oxabicyclo[6.3.0] undeca-1,3,5-triene,**1-CN-4T$_{2H}$-COT**. Prolonged irradiation produced only 1-cyano-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene (51.5%). 1-Cyano-8-oxatricyclo [7.2.0.$0^{5,9}$]undeca-2,10-diene decomposed upon heating in toluene at 100°C for an extended period of time; only a minor amount of ring opening to cyclooctatriene,**1-CN-4T$_{2H}$-COT**, was present. There was no evidence of any cope-rearranged product.



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

^{1}H NMR(300MHz;CDCl3) : δ6.6(d, J=6.9 Hz, 1H3), 5.9(ddd, J=12.6, 7.7 & 5.1 Hz, 1H6), 5.85(d, J=12.9 Hz, 1H5), 5.3(d, J=6.6 Hz, 1H2), 4.3(ddd, J=8.7, 6.9 & 6.9 Hz, 1H10), 4.2(ddd, J=8.7, 7.8 & 4.8 Hz, 1H10), 3.15(m, 1H8), 2.47(m, 2H9), 2.2(ddd, J=15.6, 12.6 & 7.8 Hz, 1H7) and 1.8(ddd, 12.3, 6.6 & 5.1 Hz, 1H7)

^{13}C NMR(75MHz;CDCl3) : δ171.74, 141.01, 133.89, 123.21, 121.69, 104.34, 95.72, 69.63, 39.74, 32.28, and 31.24.

UV-Vis (Methanol) : λ_{max} (326 nm) 7425, (313 nm) 6579.

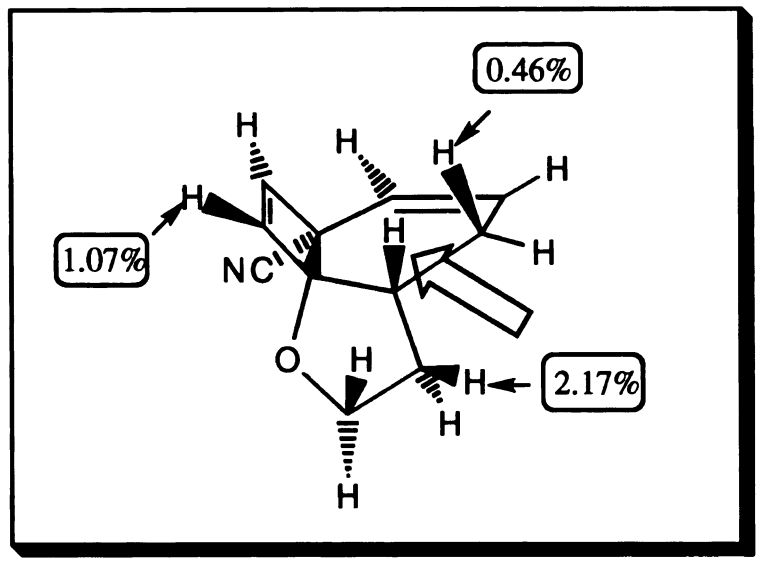
MS(m/z): 39(25%), 55(Base), 77(28%), 104(24%), 117(27%), 145(25%), 173(55%) and 174(M+1).

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

^{1}H NMR(300MHz;CDCl3) : δ6.26(d, J=2.8 Hz, 1H), 6.11(d, J=2.8 Hz, 1H), 5.83(ddd, J=9.9, 6.0 & 2.2 Hz, 1H), 5.75(dd, J=10.0 & 2.7 Hz, 1H), 4.11(ddd, J=8.3, 8.3 & 4.65 Hz, 1H), 3.93(ddd, J=9.15, 8.3 & 7.6 Hz, 1H), 2.45 (dddd, J=13, 8.3, 5.9 & 2.4 Hz, 1H), 2.31(ddd, J=17.5, 6.1 & 2.4 Hz, 1H), 2.18(dddd, J=17.4, 5.9, 2.6 & 2.3 Hz, 1H) and 1.96(m, 2H).

MS(m/z) : 39(100%), 41(40%), 51(37%), 55(99%), 63(27%), 77(41%), 91(27%), 104(26%), 117(28%), 173(23%) and 174(M+1).

The stereochemistry of 1-cyano-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene was determined by nOe experiments. Irradiation of the six-five bridgehead proton H_5 afforded enhancements at H_4(0.46%), H_6 (2.17%), and the cyclobutene proton, H_{11}(1.07%).



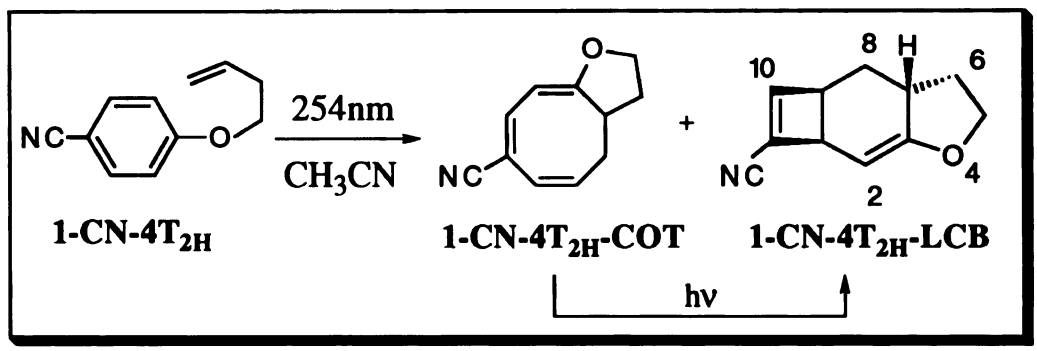
In a quartz vessel, 4-(4'-cyanophenoxy)but-1-ene (119mg) was dissloved in acetonitrile(45mL), purged with argon for twenty minutes and irradiated at 254 nm using a Rayonet in an ice bath. The reaction progress was monitored by gas chromatography. The reaction solution rapidly turned yellow. GC analysis showed the formation of two products after two hours of irradiation. Purification of the crude product by preparative thin layer chromatography (ethyl acetate/hexanes 5:95) gave 11-cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene, **1-CN-4T2H-LCB** and 4-cyano-11-oxabicyclo[6.3.0] undeca-1,3,5-triene, **1-CN-4T2H-COT** in a 1:1 ratio. Irradiation of **1-CN-4T2H-COT** in acetonitrile-d3 (2.4mg in 1mL solvent) at 254 nm gave **1-CN-4T2H-LCB**. Nearly identical results were obtained by Gilbert.

In a NMR tube, **1-CN-4T2H-COT** (2.9mg) was dissolved in deuterated acetonitrile (0.8 mL), flushed with argon for 10 minutes to remove oxygen and irradiated at

313 nm. The reaction progress was monitored by ^{1}H NMR analysis. After one hour, **1-CN-4T2H-COT** was completely converted to **1-CN-4T2H-LCB**.

Thermal Chemistry of **1-CN-4T2H-LCB**

Heating a sample of **1-CN-4T2H-LCB** in an argon-purged toluene-d8 gave no observable thermal rearranged products by ^{1}H NMR analysis. **1-CN-4T2H-LCB** readily decomposed upon heating at 100°C. Gilbert reported a high degree of polymerization with a minor amount of **1-CN-4T2H-COT** upon heating.

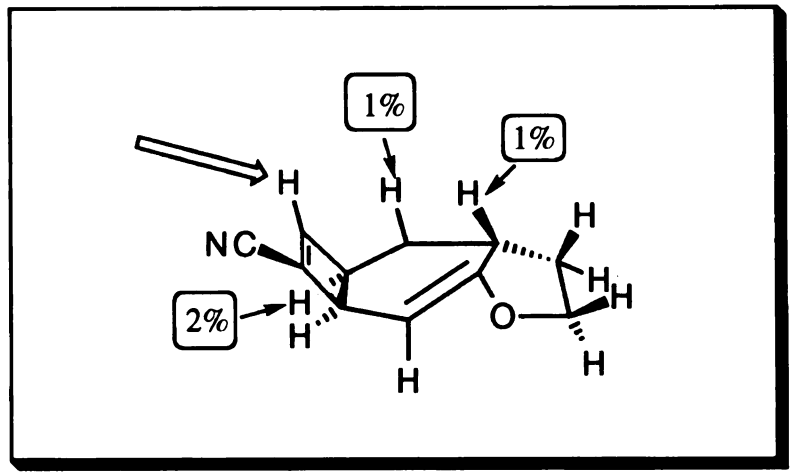


11-cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene

^{1}H NMR(300MHz;C6D6) : δ5.87(br s, 1H10), 4.89(dd, J=6.3 & 2.4 Hz, 1H2), 3.70(dd, J=8.3 & 8.5 Hz, 1H5), 3.45(ddd, J=11.8, 8.5& 5.5 Hz, 1H5), 3.12(ddd, J=6.3, 4.35 & 0.87 Hz, 1H1), 2.46(dddd, J=5.9, 4.3, 1.5 & 1.5 Hz, 1H9), 1.65(m, 1H7), 1.43(ddd, J=13.2, 5.2 & 1.6 Hz, 1H8), 1.34(m, 1H6), 1.0(m, J=11.6 & 8.5 Hz, 1H6) and 0.59(dddd, J=13.2, 11.8 & 5.9 Hz, 1H8)

MS(m/z) : 39(100%), 51(45%), 53(24%), 55(70%), 63(26%), 66(26%), 77.1(33.7%), 117(24%), 121(23%), 122(37%), 173(17%) and 174(M+1).

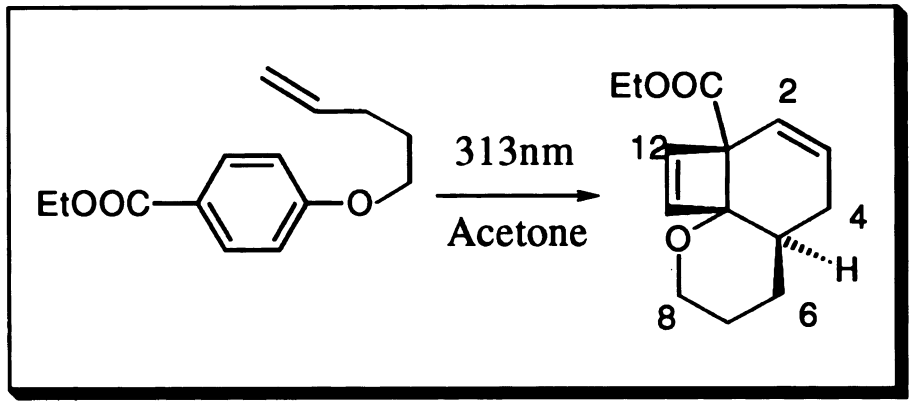
The stereochemistry of 11-cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene was determined by nOe experiments. Irradiation of the cyclobutene proton H10 afforded enhancements at H9(2%), H8 (1%), and the six-five bridgehead proton, H7(1%).



Photolysis of 5-(4'-Ethoxycarbonylphenoxy) pent-1-ene **(1EC-4T3H)**

In a NMR tube, 5-(4'-Ethoxycarbonylphenoxy) pent-1-ene (2.7mg) was dissloved in 0.75mL acetone-d6 (1.54 x 10^{-2}M). The sample was purged with argon for 20 minutes and irradiated through a 313 nm filter solution. NMR analysis of the reaction mixture showed that reaction was 50% complete after four hours. The single photoproduct was identified as 1-ethoxycarbonyl-9-oxatricyclo[8.2.0.$0^{5,10}$]dodeca-2,11-diene. Preparatory scale photolysis was carried out to isolate the photoproduct. 5-(4'-Ethyoxycarbonylphenoxy)pent-1-ene (500mg) was dissolved in freshly distilled acetone (160mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. Purification of the crude reaction mixture by silica gel column chromatography (ehtyl acetate:hexanes, 10:90) gave 1-ethoxycarbonyl-9-oxatricyclo[8.2.0.$0^{5,10}$]dodeca-2,11-diene in 51% (256mg) as a pale yellow liquid.

Similar photolysis was carried out at 254 nm. In a quartz vessel, 5-(4'-ethyoxycarbonylphenoxy)pent-1-ene (140mg) was dissloved in acetonitrile(50mL), purged with argon, and irradiated in a Rayonet reaction chamber at 254 nm. The reaction was completed after 2.5 hours. Two products were identified as 1-ethoxycarbonyl-9-oxatricyclo[8.2.0.$0^{5,10}$]dodeca-2,11-diene and its C-5 epimer in a 6:1 ratio.

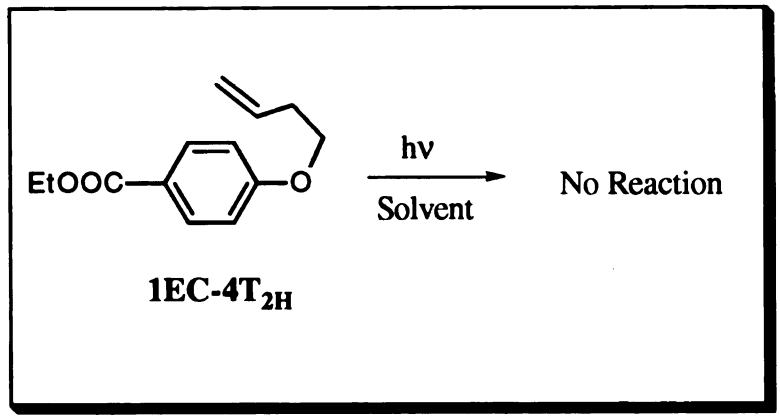


1-Ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene

^{1}H NMR(300MHz;CDCl3) : δ6.74(d, J=3.06 Hz, 1H$_{11}$), 6.27(d, J=3.06 Hz, 1H$_{12}$), 5.90(ddd, J=9.9, 7.3 & 2.0 Hz, 1H$_3$), 5.71(dd, J=9.9 & 2.85 Hz, 1H$_2$), 4.20(bq, J=7.0 Hz, 2H), 3.85(dddd, J=11.7, 4.65, 1.65 & 1.4 Hz, 1H$_8$), 3.59(ddd, J=12.8, 11.8 & 2.6 Hz, 1H$_8$), 2.01(ddd, J=15.2, 7.3 & 2.6 Hz, 1H$_4$), 1.8(m, 2H$_{7,6}$),1.6(m, 3H$_{7,6,5}$), 1.5(dddd, 15.2, 2.85 & 2.0 Hz, 1H$_4$), and 1.26(t, J=7.0 Hz, 3H).

Photochemistry of **1EC-4T2H**

Photolysis (254nm or 313nm) of **1EC-4T2H** (~0.015M) in argon-purged acetonitrile or acetone resulted in no observable photoproducts by ^{1}H NMR at extended periods (>10 hours). Instead, **1EC-4T2H** was rapidly converted to polymeric material. Gilbert reported similar results for the methyl benzoate derivative when irradiated at 254nm in acetonitrile.[25]



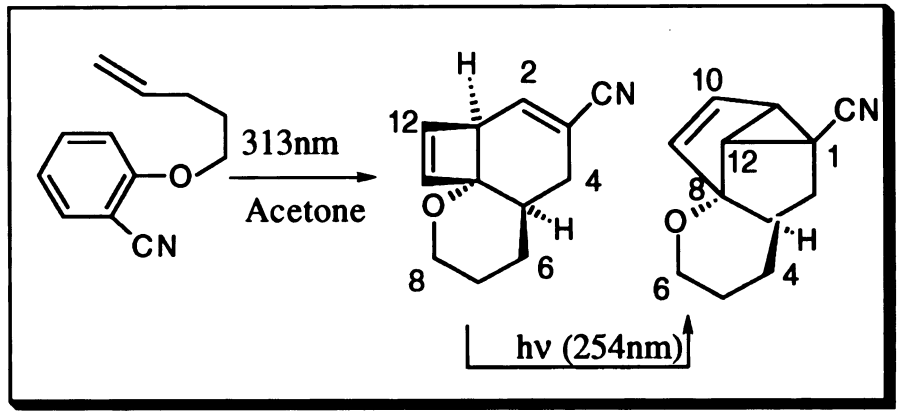
1EC-4T$_{2H}$

Photolysis of 5-(2'-cyanophenoxy) pent-1-ene **(1CN-2T3H)**

In a NMR tube, 5-(2'-cyanophenoxy)pent-1-ene (2.1mg) was dissolved in 0.75mL deuterated acetone (1.5 x 10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a 313 nm filter solution (0.002M K_2CrO_4 in 1% aqueous K_2CO_3). The reaction was monitored by time resolved NMR. The reaction was 50% complete after eight hours. A single photoproduct was indentified as 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene. Large scale photolysis was carried out to isolate the photoproduct. 5-(2'-Cyanophenoxy)pent-1-ene (950mg) was dissolved in freshly distilled acetone (400mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. The reaction mixture was concentrated at reduced pressure and separated using silica gel chromatography (ethyl acetate/hexane 5:95). 3-Cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene was obtained as a pale yellow liquid

Similar results were obtained when **1CN-2T3H** was irradiated in acetonitrile at 254 nm. In a quartz vessel, 5-(2'-cyanophenoxy)pent-1-ene (141mg) was dissloved in acetonitrile (50mL), purged with argon to remove oxygen, and irradiated in a Rayonet reaction chamber at 254 nm. The reaction was complete in 2.0 hours of irradiation. Two products, 3-cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1CN-2T3H-CB** and its di-π-methane rearranged isomer, 1-cyano-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene,

were obtained in a 2:1 ratio. Prolonged irradiation of **1CN-2T3H-CB** resulted in complete conversion to 1-cyano-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene.



3-Cyano-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene

^{1}H NMR(300MHz;CDCl3) : δ 6.66(dd, J=5.5 & 3.0 Hz, 1H$_2$), 6.65(d, J=3.0 Hz, 1H$_{11}$), 6.16(dd, J=2.97 & 0.84 Hz, 1H$_{12}$), 3.88(tdd, J=1.7, 11.7 & 5.2 Hz, 1H$_8$), 3.56(ddd, J=12.1, 11.7 & 3.0 Hz, 1H$_8$), 3.19(dd, J=5.6 & 0.8 Hz, 1H$_1$), 2.18(dd, J=16.1 & 3.8 Hz, 1H$_4$), 1.80(dddd, J=16.1, 12.45, 3.0 & 1.6 Hz, 1H$_4$) 1.7-1.3(m, 5H).

MS(m/z) : 39(83%), 41(100%), 55(66%), 77(94%), 91(88%), 103(67%), 104(75%), 135(77%), 161(92%), 187(66%), and 188(M+1).

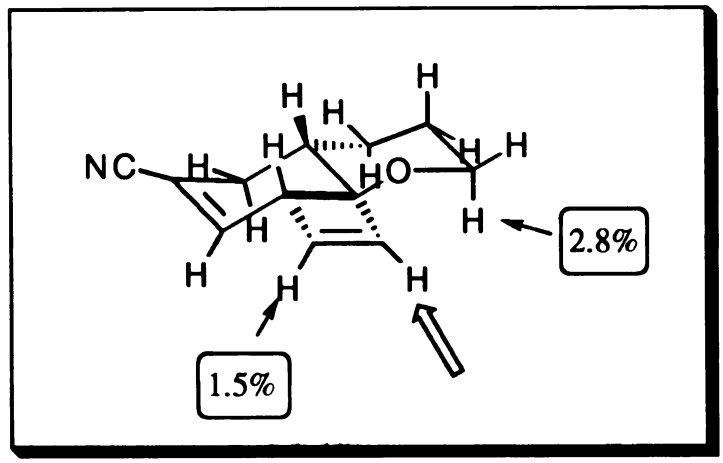
1-Cyano-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene:

^{1}H NMR(300MHz;CDCl3) : δ 6.11(d, J=6.0 Hz, 1H$_9$), 5.91(dd, J=6.0 & 2.4 Hz, 1H$_{10}$), 3.86(dddd, J=11.7, 5.2, 1.7 & 1.7 Hz, 1H$_6$), 3.71(ddd, J=12.1, 11.7 & 3.9 Hz, 1H$_6$), 3.12(d, J=6.6 Hz, 1H$_{12}$), 2.59(dd, J=6.6 & 2.4 Hz, 1H$_{11}$), 2.37(m, 1H$_3$), 2.05(dd, J=13.2 & 7.5 Hz, 1H$_2$), 1.8-1.5(m, 3H$_{4,5,5}$), 1.28(dd, J=13.2 & 12.4 Hz, 1H$_2$), and 1.26(dq, J=3.9 & 12.5, 1H$_4$).

^{13}C NMR(75MHz;$CDCl_3$) : δ129.5, 127.9, 121.6, 84.6, 64.3, 55.9, 48.0, 38.2, 28.6, 25.8, 25.7 and 24.1.

IR(CCl_4) : 2938.0, 2868.5, 2231.9, 1356.1, 1082.2, 908.6 and 733cm^{-1}.

MS(m/z): 39, 41, 51, 77, 116, 117, 130, 143.1(base), 187, and 188(M+1).

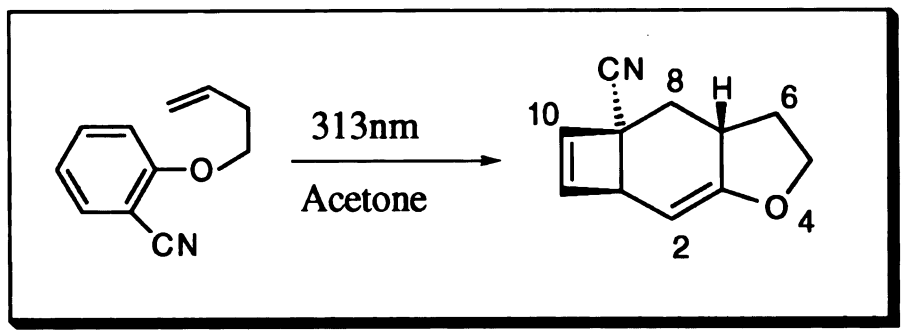


Nuclear Overhauser Enhancement (nOe) experiments were carried out on the photoproduct to determine the stereochemistry. Irradiation of the cyclobutene proton H_{11} afforded enhancements at H_8 (2.80%) and H_{12}(1.5%). The bridgehead proton H_5 was uneffected by irradiation at H_{11}.

Photolysis of 4-(2'-cyanophenoxy)but-1-ene **(1CN-2T_{2H})**

In a NMR tube, 4-(2'-cyanophenoxy)but-1-ene (2.1mg) was dissloved in acetone-d_6 (0.75mL), purged with argon for twenty minutes, and irradiated using a medium pressure mercury arc filtered with a 313 nm solution. The reaction solution rapidly turned yellow, and by NMR analysis showed the formation of one product after four hours of irradiation. Large scale photolysis allowed for the isolation of the photoproduct. 4-(2'-Cyanophenoxy)but-1-ene (900mg) was dissolved in freshly distilled acetone(400mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. At 70% conversion, the photolysis was stopped and the reaction mixture was concentrated at reduced pressure. Purification of the crude

mixture by silica gel chromatography (ethyl acetate/hexane 10:90) gave 9-cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene was a pale yellow liquid (460mg, 74%, based on 70% conversion of **1CN-2T$_{2H}$**.)



9-Cyano-4-oxatricyclo[7.2.0.0^{3,7}]undeca-2,10-diene

^{1}H NMR(300MHz;CDCl$_3$) : δ6.06(dd, J=2.7 & 0.9 Hz, 1H), 5.98(d, J=2.8 Hz, 1H), 4.84(dd, J=6.5 & 2.2 Hz, 1H), 4.21(ddd, J=8.6, 8.6 & 0.9 Hz, 1H), 3.94(ddd, J=11.8, 8.6 & 5.6 Hz, 1H), 3.72(br dd, J=6.5 & 0.8 Hz, 1H), 2.45(m, 2H), 2.21(m, J=5.6 & 0.9 Hz, 1H), 1.72(m, J=11.8 & 8.6 Hz, 1H) and 1.47(m, 1H).

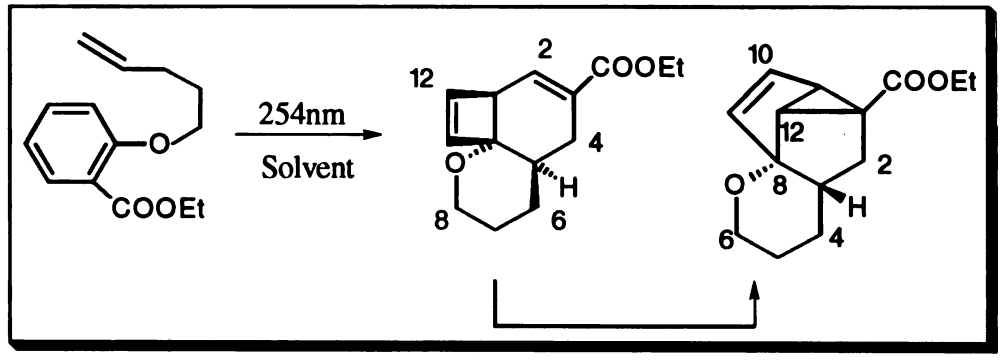
^{13}C NMR(75MHz;CDCl$_3$) : δ160.58, 142.17, 131.86, 122.08, 88.53, 69.59, 47.70, 42.09, 35.86, 32.83, and 30.61.

Photolysis of 5-(2'-Ethoxycarbonylphenoxy) pent-1-ene **(1EC-2T$_{3H}$)**

In a NMR tube, 5-(2'-Ethoxycarbonylphenoxy) pent-1-ene (2.5mg) was dissloved in 0.75mL acetone-d6 (1.42 x 10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a 313 nm filter solution. NMR analysis of the reaction mixture showed the presence of two photoproducts. The major photoproduct was identified as 3-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene. The minor photoproduct arose from secondary photolysis of 3-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene. Preparatory scale photolysis was carried out to isolated the major photoproduct. 5-(2'-Ethyoxycarbonylphenoxy)pent-1-ene (500mg)was dissolved in

freshly distilled acetone (160mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by gas chromatography. Purification of the crude reaction mixture by silica gel column chromatography gave 3-ethoxycarbonyl-9-oxatricyclo[8.2.0.0^{5,10}]dodeca-2,11-diene, **1EC-2T3H-CB**, in 42.6 % (213mg) as a pale yellow liquid.

Similar photolysis was carried out at 254 nm. In a quartz vessel, 5-(2'-ethyoxycarbonylphenoxy)pent-1-ene (150mg) was dissloved in acetonitrile (50mL), purged with argon to remove oxygen, and irradiated in a Rayonet reaction chamber at 254 nm. The reaction was complete in 3.25 hours of irradiation. Two products were obtained in a 8:1 ratio. The products was determined to be **1EC-2T3H-CB** and its di-π-methane rearranged isomer, 1-ethoxycarbonyl-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene. Prolonged irradiation of produced complete conversion to 1-ethoxycarbonyl-7-oxatetracyclo[7.4.1.0.0^{8,3}] dodeca-9-ene.



3-ethoxycarbonyl-9-oxatricyclo[8.2.0.0$^{5.10}$]dodeca-2,11-diene

^{1}H NMR(300MHz;CDCl3) : δ 6.96(dd, J=5.5 & 2.8 Hz, 1H$_2$), 6.64(d, J=3.0 Hz, 1H$_{11}$), 6.15(dd, J=3.0 & 0.9 Hz, 1H$_{12}$), 4.15(q, J=7.1 Hz, 2H), 3.89(dddd, J=11.6, 5.0, 1.6 & 1.6 Hz, 1H$_8$), 3.56(ddd, J=12.0, 11.7 & 2.9 Hz, 1H$_8$), 3.20(dd, J=5.6 & 0.9 Hz, 1H$_1$), 2.56(dd, J=16.0 & 3.1 Hz, 1H), 1.79-1.57(m, 4H), 1.5-1.4(m, 2H), and 1.26(t, J=7.1 Hz, 3H).

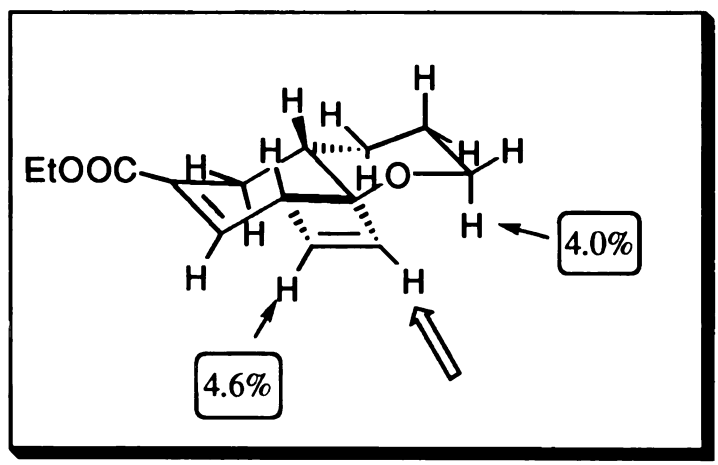
MS(m/z) : 39(59%), 41(59%), 51(43%), 55(54%), 65(36%), 77(63%), 91(52%), 135(44%), 159(32%), 161(100%), 208(40%), 234(3%), and 235(M+1).

1-ethoxycarbonyl-7-oxatetracyclo[7.4.1.0.$0^{8,3}$] dodeca-9-ene

^{1}H NMR(300MHz;CDCl$_3$) : δ 6.07(d, J=5.8 Hz, 1H$_9$), 5.93(dd, J=5.8 & 2.4 Hz, 1H$_{10}$), 4.08(q, J=7.1 Hz, 2H), 3.85(dddd, J=11.6, 4.8, 1.7 & 1.3 Hz, 1H$_6$), 3.73(ddd, J=11.8, 11.6 & 4.1 Hz, 1H$_6$), 3.01(d, J=6.8 Hz, 1H$_{12}$), 2.65(dd, J=6.8 & 2.4 Hz, 1H$_{11}$), 2.39(dd, 12.9 & 7.7 Hz, 1H$_2$), 2.25(m, 12.4, 7.7 & 3.3 Hz, 1H$_3$), 1.6-1.3(complex, 4H), 1.21(t, J=7.1 Hz, 3H) and 1.06(dd, J=12.9 & 12.4 Hz, 1H$_2$).

IR(CCl$_4$) : 2932.2, 1711.1, 1256.5 and 1076.4cm^{-1}.

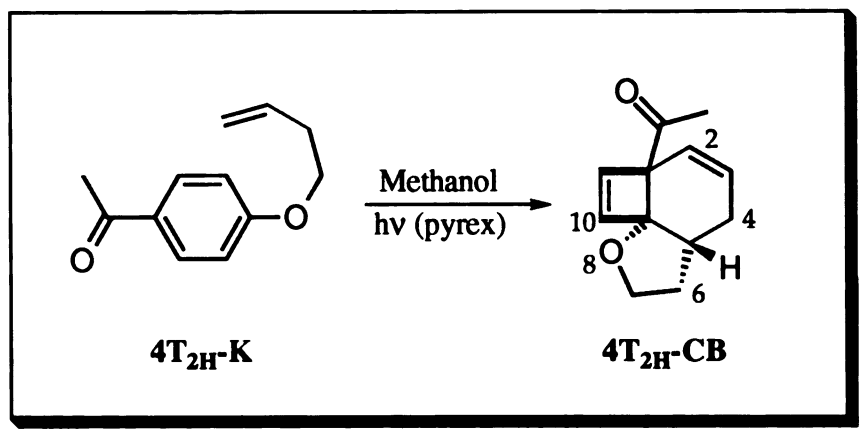
MS(m/z) : 39(35%), 41(66%), 77(33%), 91(47%), 121(34%), 138(32%), 161.1(base), 234(10%) and 235(M+1)



Nuclear Overhauser Enhancement (nOe) experiments were carried out on the photoproduct to determine the stereochemistry. Irradiation of the cyclobutene proton H$_{11}$ afforded enhancements at H$_8$ (4.0%) and H$_{12}$(4.6%). The bridgehead proton H$_5$ was uneffected by irradiation at H$_{11}$.

Photolysis of 4-(3'-buten-1'-oxy)acetophenone (**4T2H-K**)

In a NMR tube, **4T2H-K** was dissloved in argon-purged deuterated methanol (2.1 mg per 0.75 mL solvent) and irradiated through a Pyrex filter sleeve. Reaction progress was monitored by time resolved ^{1}H NMR. After 1.5 hours of irradiation, **4T2H-K** was converted into a single photoproduct, 1-acetyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **4T2H-CB**.



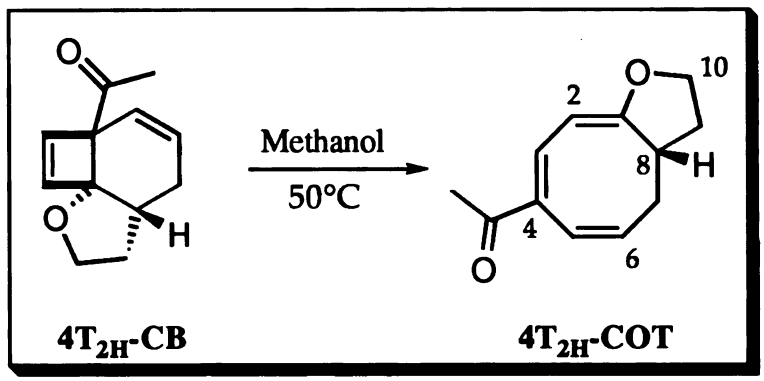
1-acetyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CD$_3$OD) : δ6.34(dd, J=3.03 & 0.6 Hz, 1H$_{10}$), 6.27(d, J=2.9 Hz, 1H$_{11}$), 5.84(ddd, J=10, 5.7, & 2.9 Hz, 1H$_3$), 5.72 (dd, J=10 & 2.3 Hz, 1H$_2$), 3.77(dd, J=8.6 & 5.6 Hz, 2H$_7$), 2.38 (m, 1H$_5$), 2.26(ddd, J=16.7, 5.8 & 4.6 Hz, 1H$_4$), 2.20(dddd, J=16.7, 6.1, 3.0, & 2.3 Hz, 1H$_4$), 2.16 (s, 3H$_{acetyl}$), and 2.0-1.8 (m, 2H$_6$).

Thermal Chemistry of **4T2H-CB**

4-(3'-buten-1'-oxy)acetophenone (0.3 g) was dissolved in freshly distilled methanol (200mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by thin layer chromatography. After complete disappearance of the starting ketone (13 hours), the reaction mixture was heated at 50°C for six hours.

During this time the reaction solution turned bright yellow. Purification of the reaction mixture by silica gel column chromatography (hexanes:ethyl acetate, 90:10) provided 4-acetyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene as a yellow solid (0.198 g, 66%).



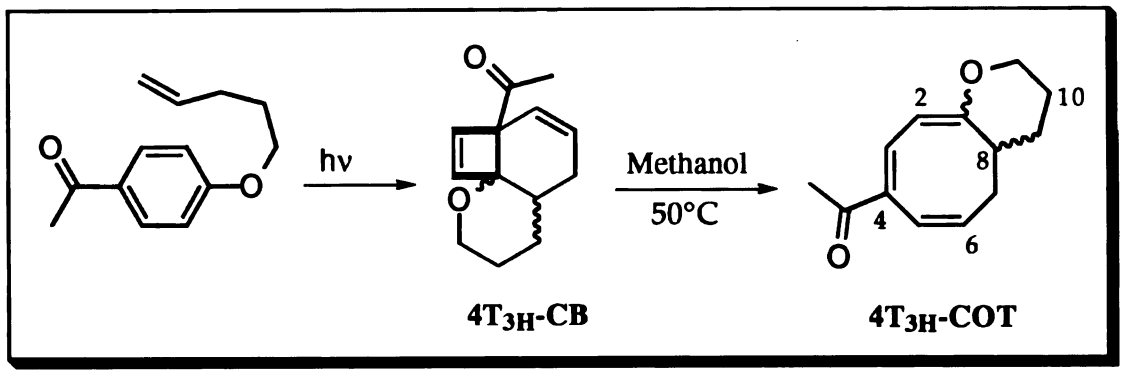
4-acetyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl3) : δ7.03(d, J=6.7 Hz, 1H3), 6.31(td, J=1.5 & 12.4 Hz, 1H5), 5.95(ddd, J=12.3, 6.3, & 5.8 Hz, 1H6), 5.42(d, J=6.8 Hz, 1H2), 4.28(ddd, J=8.7, 6.9 & 6.5 Hz, 1H10), 4.16(ddd, J=8.7, 7.5, & 6.0 Hz, 1H10), 3.1(m, 1H8), 2.5(dddd, J=16.0, 5.6, 3.7, & 1.6 Hz, 1H7), 2.35(dddd, J=16.0, 9.6, 6.0, & 1.5 Hz, 1H7), 2.34 (s, 3Hacetyl), 2.15(dddd, J=12.1, 7.4 &6.9Hz, 1H9) and 1.83 (dddd, J=12.9, 12.1, 6.5, & 6.0Hz, 1H9).

Photolysis of 4-(4'-penten-1'-oxy)acetophenone (**4T3H-K**)

In a NMR tube, **4T3H-K** was dissloved in argon-purged deuterated benzene (2.3 mg per 0.75 mL solvent) and irradiated through a Pyrex filter sleeve. Reaction progress was monitored by time resolved ^{1}H NMR. After 16 hours of irradiation, **4T3H-K** was only partially converted (<30%) into a single photoproduct, 1-acetyl-9-oxatricyclo[8.2.0.0^{10,5}] undeca-2,11-diene, **4T3H-CB**. Preparatory scale photolysis (400 mg per 250 mL benzene) was carried out to isolate **4T3H-CB**. After 68 hours of irradiation through Pyrex, the reaction was ceased and concentrated *in vacuo*. The reaction

mixture was redissolved in 60 mL of methanol and heated for five hours at 50°C. Purification of the reaction mixture by silica gel column chromatography (hexanes:ethyl acetate, 90:10) provided 4-acetyl-12-oxabicyclo[6.4.0] undeca-1,3,5-triene as a yellow oil.



4-acetyl-12-oxabicyclo[6.4.0] undeca-1,3,5-triene

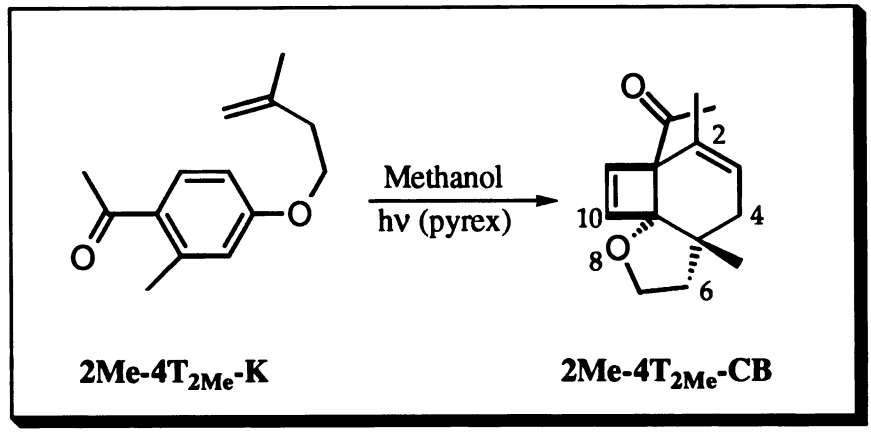
^{1}H NMR(300MHz;CDCl3) : δ6.9(d, J=7.2 Hz, 1H3), 6.35(td, J=1.2 & 11.4 Hz, 1H5), 6.1(ddd, J=11.4, 7.5, & 7.2 Hz, 1H6), 5.95(br d, J=7.2 Hz, 1H2), 4.09(ddd, J=8.4, 8.1 & 5.7 Hz, 1H11), 3.76(ddd, J=11.1, 8.1, & 3.9 Hz, 1H11), 2.72(m, 1H8), 2.4(dddd, J=13.8, 7.5, & 0.9 Hz, 1H7), 2.33(s, 3Hacetyl), 2.24(dddd, J=13.8, 7.5, 3.6, & 1.2 Hz, 1H7), 1.9-1.7(m, 2H) and 1.6-1.4 (m, 2H).

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone (**2Me-4T2Me-K**)

---In Methanol

In a NMR tube, 4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone (1.5mg) was dissolved in 0.75mL of deuterated methanol (0.0092M). The sample was purged with argon for fifteen minutes and irradiated using an medium pressure mercury arc lamp fitted with a Pyrex filter. The reaction progress was followed closely by time resolved NMR. After three hours of irradiation, the reaction was 50% complete and only one cycloadduct was observed by proton NMR. The product was determined to be 1-acetyl-2,5-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T2Me-CB**. Deuterium incorporation was also observed by ^{1}H NMR by the rapid depletion of the peak frequency

corresponding to the *ortho* methyl group. Prolonged irradiation produced polymerization of the reaction mixture.

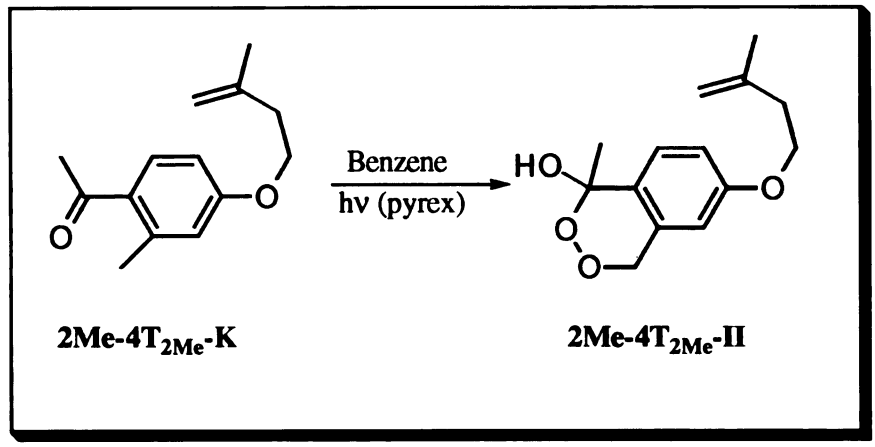


1-acetyl-2,5-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CD$_3$OD) : δ6.50(d, J=3.03 Hz, 1H$_{10}$), 6.28(d, J=3.03 Hz, 1H$_{11}$), 5.54(br t, J=4.4 Hz, 1H$_3$), 3.80(m, 2H$_7$), 2.28(dd, J=16.8 & 4.6 Hz, 1H$_4$), 2.14 (s, 3H$_{acetyl}$), 2.1 (m, 1H$_6$), 1.92(ddd, J=16.6, 4.5 & 2.0 Hz, 1H$_4$), 1.7(ddd, J=12.5, 6.9 & 5.3 Hz, 1H$_6$), 1.58(q, J=1.65 Hz, 3H) and 1.01(s, 3H).

---In Benzene

4-(3'-methyl-3'-buten-1'-oxy)-2-methylacetophenone was dissolved in benzene (2.1mg in 1mL solvent), purged with argon, and irradiated through a Pyrex filter. The reaction progress was monitored by ^{1}H NMR. After three hours of irradiation, the starting material was partially converted into a single photoproduct. The product was believed to be 1,2,3,4-tetrahydro-1-methyl-6-(3'-methyl-3'-buten-1'-oxy)-2,3-dioxa-1-naphthol. This type of oxygen trapped product has been observed by Matsuura[72] and Yates[88].



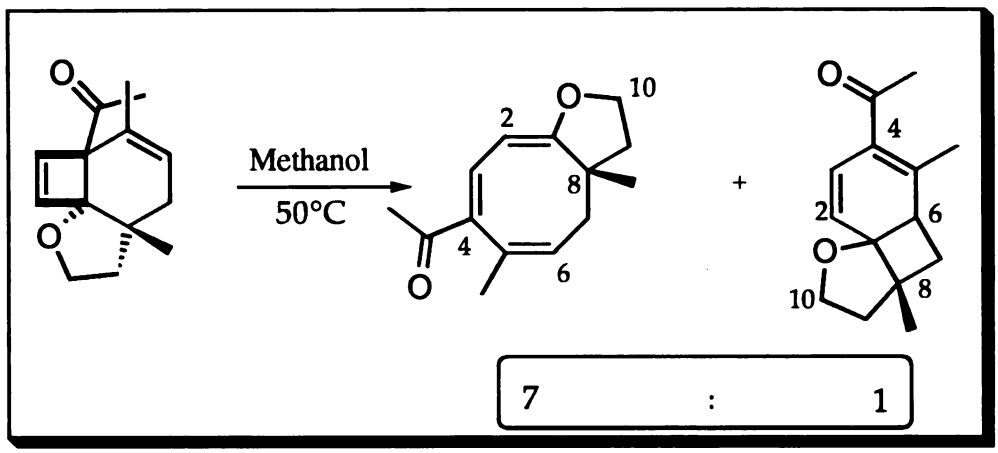
2Me-4T$_{2Me}$-K **2Me-4T$_{2Me}$-II**

1,2,3,4-tetrahydro-1-methyl-6-(3'-methyl-3'-buten-1'-oxy)-2,3-dioxa-1-naphthol

^{1}H NMR(300MHz;C$_6$D$_6$) : δ6.68(d, J=7.95 Hz, 1H), 6.67(dd, J=7.95 & 2.85 Hz, 1H), 6.20(d, J=2.6 Hz, 1H), 5.1 & 4.3(AB Quartet, J=15.5 Hz, 2H),4.85(br s, 1H), 4.81(br s, 1H), 3.70(dt, J=6.84 & 1.5 Hz, 2H), 2.3(br t, J=6.84 Hz, 2H), 1.62(br s, 3H), 1.57(s, 3H).

Thermal Chemistry of **2Me-4T$_{2Me}$-CB**

Warming an argon-purged sample of in methanol at 50°C results in the formation of two thermal products after two hours of heating. Purification of the reaction mixture by silica gel column chromatography (hexanes:ethyl acetate 95:5) gave a equilibrium mixture of 4-acetyl-5,8-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene and 4-acetyl-5,8-dimethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene in 1:7 ratio.



4-acetyl-5,8-dimethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl$_3$) : δ 6.95(d, J=5.1 Hz, 1H$_3$), 5.92(qdd, J=1.6, 9.5 & 6.3 Hz, 1H$_6$), 5.1(d, J=5.1 Hz, 1H$_2$), 4.15(br t, J=8.7 Hz, 1H$_{10}$), 4.07(ddd, J=11.6, 8.6 & 5.5 Hz, 1H$_{10}$), 2.31(s, 3H), 2.24(dd, J=13.7 & 9.4 Hz, 1H$_7$), 2.2(ddd, J=11.9, 11.6 and 8.9 Hz, 1H$_9$), 2.05(dd, J=13.7 & 6.3 Hz, 1H$_7$), 1.74(br s, 3H), 1.63(br dd, J=11.9 & 5.5 Hz, 1H$_9$), 1.12(s, 3H).

^{13}C NMR(75MHz; CDCl$_3$) : δ 198.5, 169.4, 141.0, 137.9, 137.6, 126.9, 93.3, 67.5, 46.9, 37.7, 37.0, 27.2, 26.5, and 22.1.

UV-Vis (Methanol) : λ_{max} (321 nm) 5311, (313 nm) 5074.

IR(CCl$_4$) : 2966.9, 1672.5, 1651.3, 1354.2, 1176.7, 1147.8, 1124.6, 1068.7 cm^{-1}.

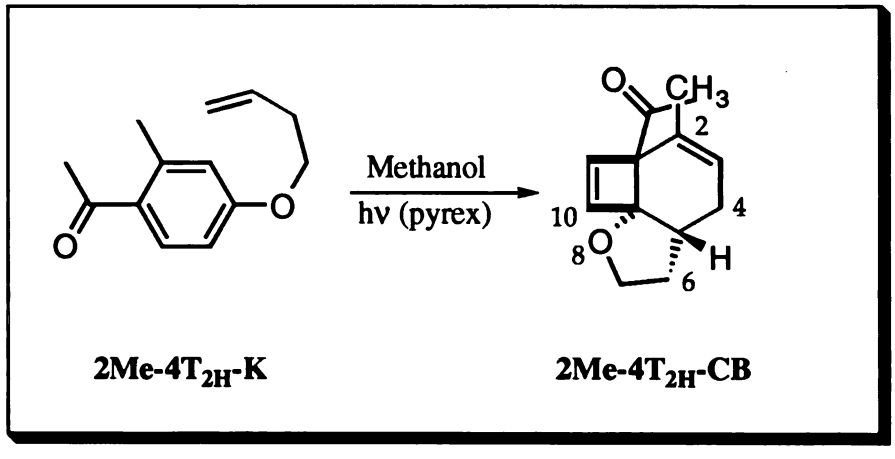
MS(m/z): 41(40.2%), 43(37.9%), 69(43%), 135(Base), 150(30.5%), 218(16.4%) and 219.2(M+1).

4-acetyl-5,8-dimethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene

^{1}H NMR(300MHz;CDCl$_3$) (partial) : δ6.27(d, J=10 Hz, 1H$_3$), 5.31(d, J=10 Hz, 1H$_2$), 4.2-4.0(m, 2H$_{10}$), 2.88(dd, J=10.5 & 7.7 Hz, 1H$_6$), 2.26(s, 3H) and 1.13(s, 3H)

Photolysis of 4-(3'-buten-1'-oxy)-2-methylacetophenone (**2Me-4T$_{2H}$-K**)

In a NMR tube, 4-(3'-buten-1'-oxy)-2-methylacetophenone (1.5mg) was dissolved in 0.75mL methanol-d4 (~0.01M). The sample was purged with argon for 15 minutes and then irradiated through a Pyrex filter. NMR analysis of the reaction mixture showed that the reaction was 50% complete after three hours of irradiation. A single photoproduct was identified as 1-acetyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2Me-4T$_{2H}$-CB**. Preparatory scale photolysis was carried out to isolated the photoproduct. **2Me-4T$_{2H}$-K** (0.5g) was dissolved in freshly distilled methanol (300mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by gas chromatography. At near depletion of the starting material, the reaction was stopped and then concentrated under reduced pressure at room temperature. A proton NMR was immediately taken and showed a mixture of starting ketone and its photoproduct, **2Me-4T$_{2H}$-CB**.



2Me-4T$_{2H}$-K **2Me-4T$_{2H}$-CB**

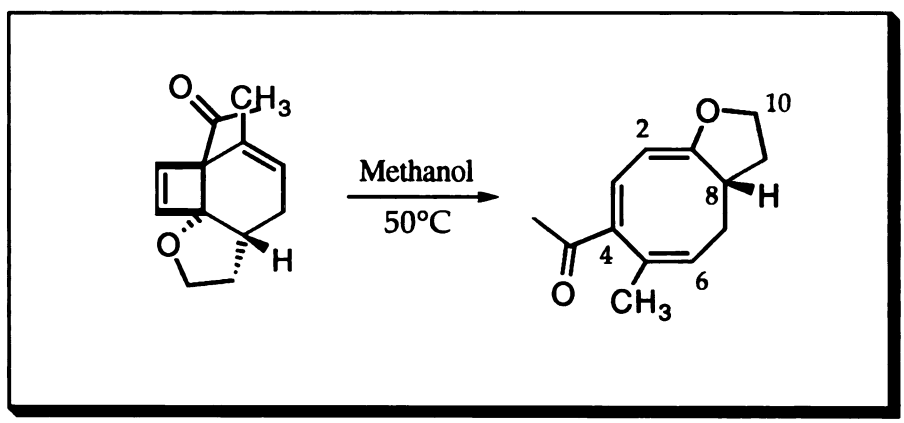
1-acetyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CD$_3$OD) : δ6.47(d, J=3 Hz, 1H$_{10}$), 6.29(d, J=3 Hz, 1H$_{11}$), 5.62(qdd, J=1.6,4.4, & 4.4 Hz, 1H$_3$), 3.86(ddd, J=8.1, 7.5 & 6.1 Hz, 1H$_7$), 3.72(ddd, J=8.1, 7.9 &5.3 Hz, 1H$_7$), 2.29(ddd, J=15.9, 5.1 & 4.4 Hz, 1H$_4$), 2.2(m, 1H$_5$),

2.09(s, 3H), 2.06(ddd, J=12, 7.5, & 6.4 Hz, $1H_6$), 1.92(m, $1H_4$), 1.84(ddd, J=12, 7.5, &5.3 Hz, $1H_6$), and 1.59(q, J=1.7 Hz, 3H)

Thermal Chemistry of **2Me-4T$_{2H}$-CB**

A crude photolysis mixture of **2Me-4T$_{2H}$-CB** and **2Me-4T$_{2H}$-K** was dissolved in methanol (300mL), purged with argon, and heated in a constant temperature bath at 50°C. The reaction progress was monitored by thin layer chromatography. After complete conversion of **2Me-4T$_{2H}$-CB** (4 hours), the reaction mixture was purified by column chromatography (hexanes: ethyl acetate, 85:15). A single product was identified as 4-acetyl-5-methyl-11-oxabicyclo [6.3.0] undeca-1,3,5-triene, **2Me-4T$_{2H}$-COT** (134mg, 27% yield based on starting ketone).



4-acetyl-5-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl3) : δ6.94(dd, J=5.6 & 1.6 Hz, $1H_3$), 5.94(qdd, J=1.5, 9.3 & 6.6 Hz, $1H_6$), 5.25(dd, J=5.6 & 2.1 Hz, $1H_2$), 4.19(ddd, J=8.85, 5.34 & 3.7 Hz, $1H_{10}$), 3.95(ddd, J=8.85, 8.55 & 6.6 Hz, $1H_{10}$), 3.03(m, $1H_8$), 2.5 (ddd, J=13.7, 9.25 & 4.43 Hz, $1H_7$), 2.30 (s, 3H), 2.29 (m,$1H_9$), 2.10(ddd, J=13.7, 6.5 & 3.03 Hz, $1H_7$), 1.98(dddd, 11.0, 8.6, 4.95, &3.7 Hz, $1H_9$) 1.58(q, J=1.65 Hz, 3H), and 1.7(br s, 3H).

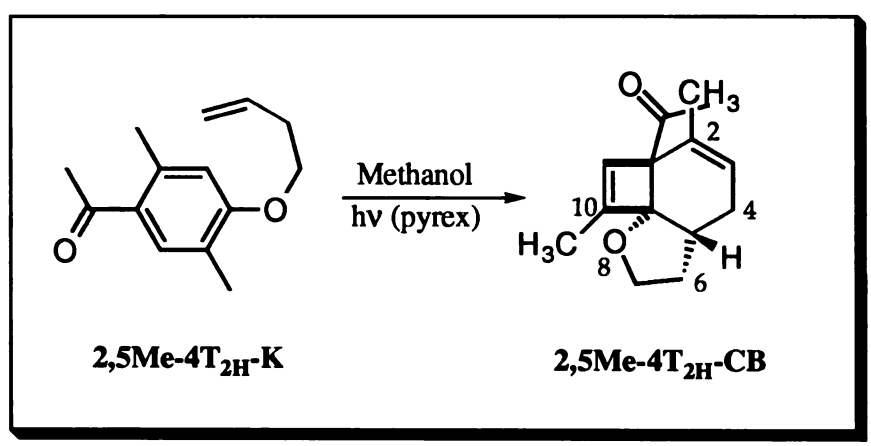
^{13}C NMR(75MHz; $CDCl_3$) : δ198.5, 165.7, 138.7, 137.7, 136.7, 127.3, 94.7, 68.8, 42.6, 31.6, 27.6, 25.6, and 22.3.

UV-Vis (Methanol) : λ_{max} (320 nm) 1760 **low value may be due to rapid decomposition of the cyclooctatriene.

MS(m/z): 43(75%), 55(base), 77(33%), 91(40%), 105(33%), 119(26%), 133(24.5%), 135(82%), 161(41%), 204(83%) and 205(11%).

Photolysis of 4-(3'-buten-1'-oxy)-2,5-dimethylacetophenone **(2,5Me-4T$_{2H}$-K)**

In a NMR tube, 4-(3'-buten-1'-oxy)-2,5-dimethylacetophenone (1.6mg) was dissolved in 0.75mL methanol-d_4 (9.8 x 10^{-3}M). The sample was purged with argon for 20 minutes and then irradiated through a Pyrex filter. NMR analysis of the reaction mixture showed that the reaction was 100% complete after eight hours of irradiation. A single photoproduct was identified as 1-acetyl-2,10-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene, **2,5Me-4T$_{2H}$-CB**. Preparatory scale photolysis was carried out to isolated the photoproduct. 4-(3'-Buten-1'-oxy)-2,5-dimethylacetophenone (1.0g) was dissolved in freshly distilled methanol (500mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by gas chromatography. Purification of the crude reaction mixture by dry column flash chromatography (hexanes:ethyl acetate, 80:20) gave **2,5Me-4T$_{2H}$-CB** (365mg, 37%).



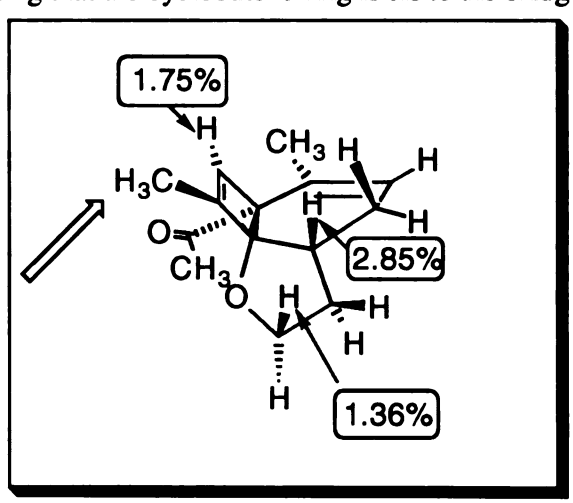
2,5Me-4T$_{2H}$-K **2,5Me-4T$_{2H}$-CB**

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

^{1}H NMR(300MHz;CD$_3$OD) : δ6.08(q, J=1.6 Hz, 1H$_{11}$), 5.59(qdd, J=1.6, 5.8 & 4.0 Hz, 1H$_3$), 3.91(dd, J=7.8 & 5.9 Hz, 2H$_7$), 2.18(ddd, J=15.9, 5.7, & 2.2 Hz, 1H$_4$), 2.1(m, 1H$_5$), 2.06(s, 3H$_{acetyl}$), 1.88(ddd, J=6, 10.1, & 12 Hz, 1H$_6$), 1.87(m, 1H$_4$), 1.76(ddd, J=12, 7.5, 4.7 Hz, 1H$_6$), 1.66(d, J=1.6 Hz, 3H), and 1.56(q, 1.6 Hz, 3H)

^{13}C NMR(75MHz, CD$_3$OD) : δ 212, 151, 137, 131, 124, 123, 92, 68, 40, 32, 28, 27, 19, and 11.

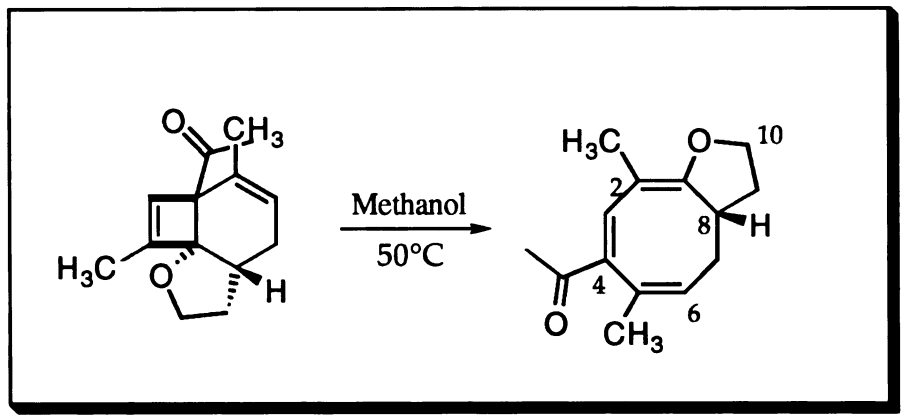
The stereochemistry of 1-acetyl-2,10-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene was determined by nOe experiments. Irradiation of the methyl group on c-10 afforded enhancements at H$_{11}$ (1.75%), H$_7$ (1.36%), and the bridgehead proton H$_5$ (2.85%). Thus indicating that the cyclobutene ring is cis to the bridgehead proton H$_5$.



Thermal Chemistry of **2,5Me-4T$_{2H}$-CB**

In a large Pyrex test tube, **2,5Me-4T$_{2H}$-CB** (30mg) was dissolved in methanol (50mL), purged with argon, and heated in a constant temperature water bath (50°C). The reaction progess was monitored by thin layer chromatography. After 48 hours of heating, *para*-toluenesulfonic acid (2mg) was added to the reaction solution to help facilitate

rearrangement. NMR analysis of the reaction mixture showed quantitative conversion of 1-acetyl-2,10-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene to its ring opened isomer, 4-acetyl-2,5-dimethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene. Purification of the crude reaction mixture was accomplished by preparative thin layer chromatography (ethyl acetate:hexanes, 5:95).



4-acetyl-2,5-dimethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene (26mg, 88%)

^{1}H NMR(300MHz;CDCl3) : δ6.88(br s, 1H3), 5.88(qdd, J=1.5, 9.3 & 6.7 Hz, 1H6), 4.22(ddd, J=8.9, 8.3 & 3.3 Hz, 1H10), 3.97(ddd, J=12.0, 8.9 & 6.7 Hz, 1H10), 3.03(m, 1H8), 2.45 (ddd, J=13.8, 9.3 & 4.0 Hz, 1H7), 2.43 (s, 3H$_{Acetyl}$), 2.09(ddd, J=13.8, 6.7 & 4.26 Hz, 1H7), 1.98(m, 2H9), 1.76(br s, 3H$_{Me}$) 1.70(d, J=1.60 Hz, 3H$_{Me}$).

^{13}C NMR(75MHz, CDCL3) : δ 198.74, 158.41, 142.28, 138.65, 136.23, 126.44, 101.75, 68.06, 41.58, 31.90, 29.07, 26.41, 23.04, and 15.89.

IR(CCl4) : 2974.6, 1657.6, 1354.2, 1167.1, 1151.7, 1109.21, 908.6 cm^{-1}.

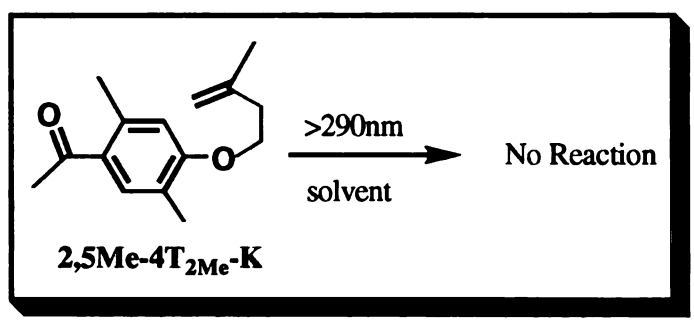
UV-Vis (Methanol) : λ_{max} (329 nm) 5420

MS : 39(25%), 41(27%), 43(87%), 53(22%), 55(base), 77(37%), 91(43%), 149(42%), 218(55%), and 219(M+1).

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-2,5-dimethylacetophenone

(2,5Me-4T$_{2Me}$-K)

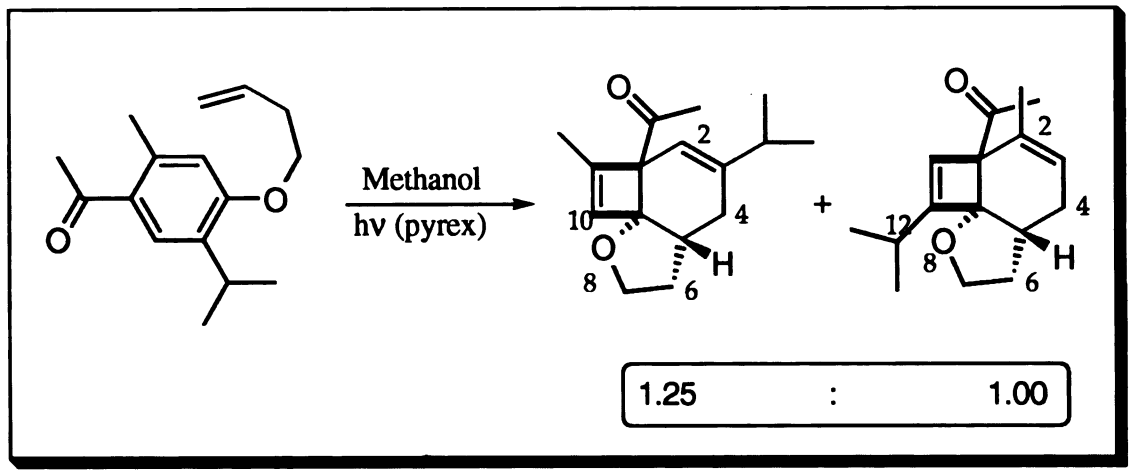
In a NMR tube, 4-(3'-methyl-3'-buten-1'-oxy)-2,5-dimethylacetophenone (1.8mg) was dissolved in 0.75mL methanol-d4 (1.0×10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a Pyrex filter. ^{1}H NMR analysis of the reaction mixture showed no observable photoproducts after 20 hours of irradiation. Similar results were obtained using benzene as the solvent. The methyl group on the double bond of **2,5Me-4T$_{2Me}$-K** appears to suppress the photocycloaddition process.



Photolysis of 5-isopropyl-4-(3'-buten-1'-oxy)-2-methylacetophenone(**2Me-4T$_{2H}$-5I-K**)

In a NMR tube, **2Me-4T$_{2H}$-5I-K** (2.6mg) was dissolved deuterated methanol (1mL), purged with argon, and irradiated through a Pyrex filter. The reaction progress was monitored proton NMR spectroscopy. The reaction was nearly complete after four hours of irradiation. **2Me-4T$_{2H}$-5I-K** was converted into two cyclobutene photoproducts, 1-acetyl-3-isopropyl-11-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene and 1-acetyl-3-isopropyl-11-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene in a 1.25:1 ratio respectively. Preparatory scale photolysis was carried out to isolate the cyclobutene photoproducts. **2Me-4T$_{2H}$-5I-K** (1.2g) was dissolved in methanol (500mL), purged with argon and irradiated in an immersion well through a Pyrex sleeve. The reaction progress was monitored by gas chromatography. Purification of the crude reaction mixture by silica gel column chromatography gave 1-acetyl-3-isopropyl-11-

methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene (0.273g) and 1-acetyl-10-isopropyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene (0.218g) (overall yield 41%).



1-acetyl-3-isopropyl-11-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;C_6D_6) : δ 5.83(dq, J=0.6 &1.5 Hz, 1H$_{10}$), 5.62(br s, 1H$_2$), 3.65(ddd, J=8.4, 7.9 &3.0 Hz, 1H$_7$), 3.57(ddd, J=9.3, 8.4 & 6.9 Hz, 1H$_7$), 2.18(s, 3Hacetyl), 2.14(br qq, J=6.9 & 6.9 Hz, 1H$_{IPr}$), 2.08(d, J=11.1 Hz, 1H$_4$), 1.96(dddd, J=12.0, 9.3, 7.9 & 6.3 Hz, 1H$_6$), 1.7(m, 2H$_{5,4}$), 1.49(d, J=1.5 Hz, 3H$_{Me}$), 1.4(dddd, J=12.0, 6.7, 4.3 & 3.0 Hz, 1H$_6$), 0.93-0.91(d, J=6.9 Hz, 3H$_{IPr}$) and 0.92-0.90(d, J=6.9 Hz, 3H$_{IPr}$).

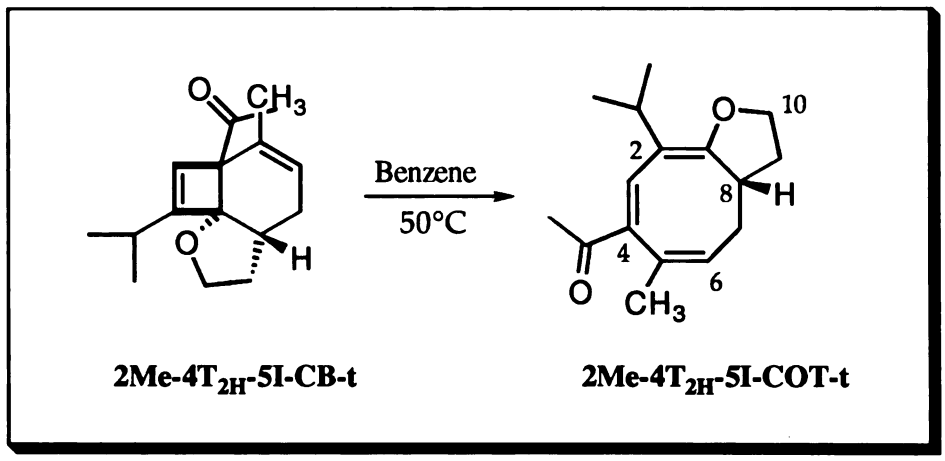
1-acetyl-10-isopropyl-2-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;C_6D_6) : δ5.97(d, J=1.5 Hz, 1H$_{11}$), 5.34(qdd, J=1.5, 4.2 & 4.0 Hz, 1H$_3$), 3.72(ddd, J=9.3, 8.2 & 6.5 Hz, 1H$_7$), 3.62(ddd, J=8.2, 7.0 & 5.8 Hz, 1H$_7$), 2.14(s, 3Hacetyl), 2.18(dqq, J=1.5, 6.9 & 6.9 Hz, 1H$_{IPr}$), 1.96(dddd, J=12.8, 9.4, 7.0 & 0.96 Hz, 1H$_6$), 1.8(m, 2H$_{4,5}$), 1.61(dddd, J=12.8, 6.5, 5.8 & 4.3 Hz,1H$_6$), 1.59(m, 1H$_4$), 1.58(d, J=1.5 Hz, 3H$_{Me}$), 1.03(d, J=6.9 Hz, 3H$_{IPr}$) and 0.96(d, J=6.9 Hz, 3H$_{IPr}$).

IR(CCl_4) : 2963.0, 2930.2, 1699.5, 1458.4, and 1250.0cm^{-1}.

Thermal Chemistry of **2Me-4T$_{2H}$-5I-CB-t**

In a large test tube, **2Me-4T$_{2H}$-5I-CB-t** (218mg) was dissolved in freshly distilled benzene (100mL), purged with argon, and heated in a constant temperature bath at 50°C. The reaction progress was monitored by thin layer chromatography. After 24 hours, a crystal of *para*-toluenesulfonic acid was added to the reaction mixture. **2Me-4T$_{2H}$-5I-CB-t** opened rapidly after the addition of acid. Purification of the crude reaction mixture by silica gel column chromatography (hexanes:ethyl acetate:dichloromethane, 80:5:15) gave **2Me-4T$_{2H}$-5I-COT-t** (173mg, ~79%).



2Me-4T$_{2H}$-5I-CB-t **2Me-4T$_{2H}$-5I-COT-t**

4-acetyl-2-isopropyl-5-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;C$_6$D$_6$) : δ6.98(d, J=1.5 Hz, 1H$_3$), 5.68(qdd, J=1.6, 6.3, & 5.1 Hz, 1H$_6$), 3.74(ddd, J=8.2, 6.9 & 4.2 Hz, 1H$_{10}$), 3.51(ddd, J=9.5, 8.2 & 6.6 Hz, 1H$_{10}$), 3.30(dqq, J=1.5,6.9 & 6.9 Hz, 1H), 2.66(m, 1H$_8$), 2.28 (ddd, J=14.5, 6.0 & 5.1 Hz, 1H$_7$), 2.09 (s, 3H$_{acetyl}$), 1.88(s, 3H$_{methyl}$), 1.71(ddd, J=14.5, 6.3 & 4.5 Hz, 1H$_7$), 1.38(overlapping dddd's, J=11.9, 9.5, 6.9, 6.6 & 4.2 Hz, 2H$_9$), 1.10(d, J=6.9 Hz, 3H$_{iso}$), and 0.92(d, J=6.9 Hz, 1H$_{iso}$).

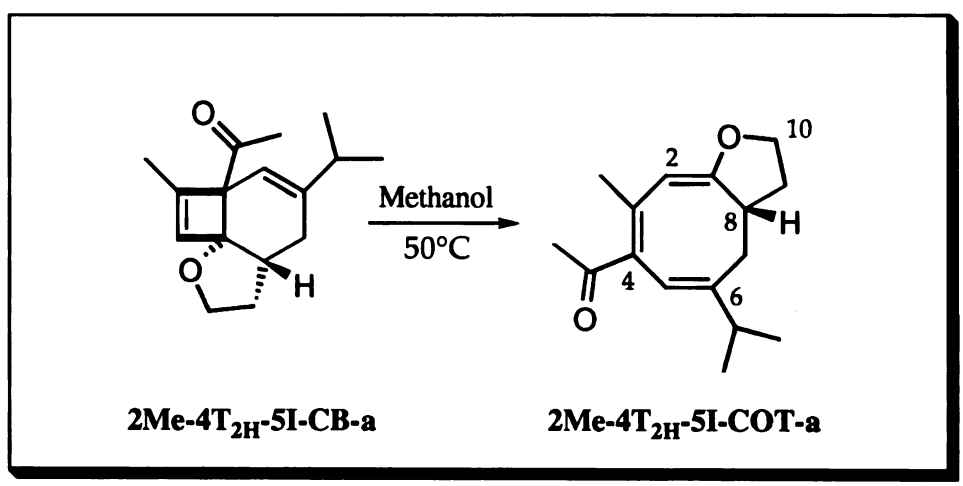
^{13}C NMR(75MHz, CDCL$_3$) : δ 198.63, 156.23, 141.16, 139.15, 136.30, 126.13, 112.59, 67.97, 41.13, 31.89, 29.55, 27.84, 26.57, 23.07, 22.03, and 20.58.

IR(CCl$_4$) : 2963.0, 1668.6, 1649.4, 1145.9, 1022.4 cm^{-1}.

UV-Vis (Methanol) : λ_{max} (330.5 nm) 5747

Thermal Chemistry of **2Me-4T$_{2H}$-5I-CB-a**

In a large Pyrex test tube, **2Me-4T$_{2H}$-5I-CB-a** (270mg) was dissolved in benzene (100mL), purged with argon, and heated in a water bath at 50°C. After 24 hours of heating, a crystal of *para*-toluenesulfonic acid was added to the reaction mixture to accelerate ring opening. ^{1}H NMR and thin layer chromatography showed the complete conversion of **2Me-4T$_{2H}$-5I-CB-a** to a single product. Purification of the reaction mixture by silica gel column chromatography gave **2Me-4T$_{2H}$-5I-COT-a** in 63% yield (170.6mg).



2Me-4T$_{2H}$-5I-CB-a **2Me-4T$_{2H}$-5I-COT-a**

4-acetyl-6-isopropyl-3-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;C$_6$D$_6$) : δ5.92(br s, 1H$_5$), 5.36(s, 1H$_2$), 3.68(dt, J=8.3 & 7.1 Hz, 1H$_{10}$), 3.52(ddd, J=8.3, 8.3 & 5.0 Hz, 1H$_{10}$), 2.81(dddd, J=9.0, 7.3, 5.6 & 1.7 Hz, 1H$_8$), 2.06(ddd, J=15.9, 5.5 & 1.9 Hz, 1H$_7$), 1.97(s, 3H$_{Acetyl}$), 1.97(s, 3H$_{Me}$), 1.96(m, 1H), 1.67(dd,J=15.9 & 9.0 Hz, 1H$_7$), 1.32(m, J=12.0 & 7.4 Hz, 1H$_9$), 1.09(m, J=12.0 & 5.1 Hz, 1H$_9$), 0.85(d, J=6.9 Hz, 3H$_{iso}$), and 0.83(d, J=6.9 Hz, 1H$_{iso}$).

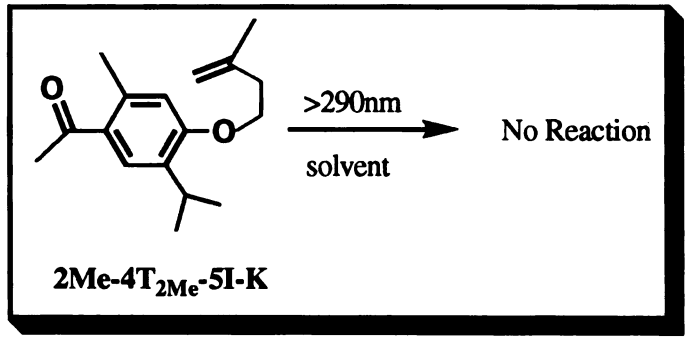
^{13}C NMR(75MHz;$CDCl_3$) : 205.8, 156.3, 141.3, 139.2, 136.4, 126.2, 112.7, 68.1, 41.2, 32.0, 29.7, 28.0, 23.2, 22.1, and 20.7.

UV-Vis (Methanol) : λ_{max} (313.5 nm) 4813.

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-5-isopropyl-2-methylacetophenone

(2Me-4T$_{2Me}$-5I-K)

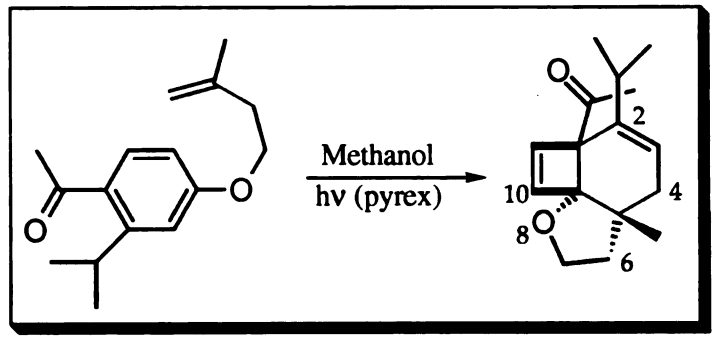
In a NMR tube, 4-(3'-methyl-3'-buten-1'-oxy)-5-isopropyl-2-methylacetophenone (2mg) was dissolved in 0.75mL methanol-d4 (1.0×10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a Pyrex filter. ^1H NMR analysis of the reaction mixture showed no observable photoproducts after 20 hours of irradiation. Similar results were obtained using benzene as the solvent. The methyl group on the double bond of **2Me-4T$_{2Me}$-5I-K** appears to suppress the photocycloaddition process, as seen previously seen for **2,5Me-4T$_{2Me}$-K**.



Photolysis of 2-isopropyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone(**2I-4T$_{2Me}$-K**)

A solution of **2I-4T$_{2Me}$-K** (2.6mg per 0.75mL solvent) in CD_3OD was degassed with argon for fifteen minutes and irradiated using a medium pressure mercury lamp fitted with a Pyrex filter. ^1H NMR analysis of the reaction mixture showed only minimal product formation (~10% conversion) after nine hours of irradiation. The major product

was identified as 1-acetyl-2-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene.

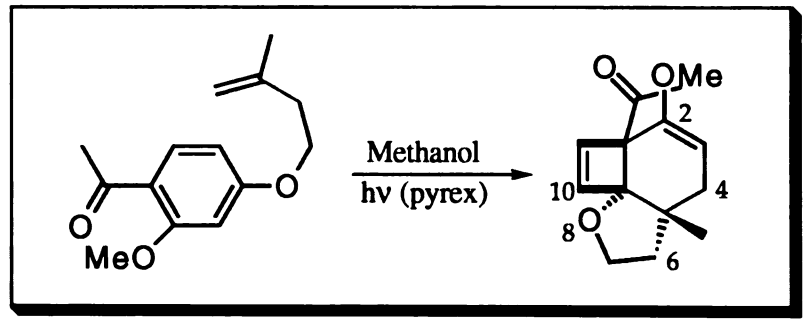


1-acetyl-2-isopropyl-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene

^{1}H NMR(300MHz;CD$_3$OD)(partial): δ6.49(d, J=3.1 Hz, 1H$_{10}$), 6.24(d, J=3.0 Hz, 1H$_{11}$), 5.65(ddd, J=5.0, 4.1 & 0.8 Hz, 1H$_3$), 3.8(m, 2H$_7$), 2.12 (s, 3H), 1.04(s, 3H), 1.0(d, J=7 Hz, 3H$_{iso}$) and 0.98(d, J=7Hz, 3H$_{iso}$)

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-2-methoxyacetophenone(**2OMe-4T$_{2Me}$-K**)

In a NMR tube, **2OMe-4T$_{2Me}$-K** was dissloved in argon-purged deuterated methanol (2.6mg per 1mL solvent) and irradiated through a Pyrex filter sleeve. Reaction progress was monitored by time resolved ^{1}H NMR. After eight hours of irradiation, **2OMe-4T$_{2Me}$-K** was converted into a single photoproduct, 1-acetyl-5-methyl-2-methoxy-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene, **2OMe-4T$_{2Me}$-CB**.



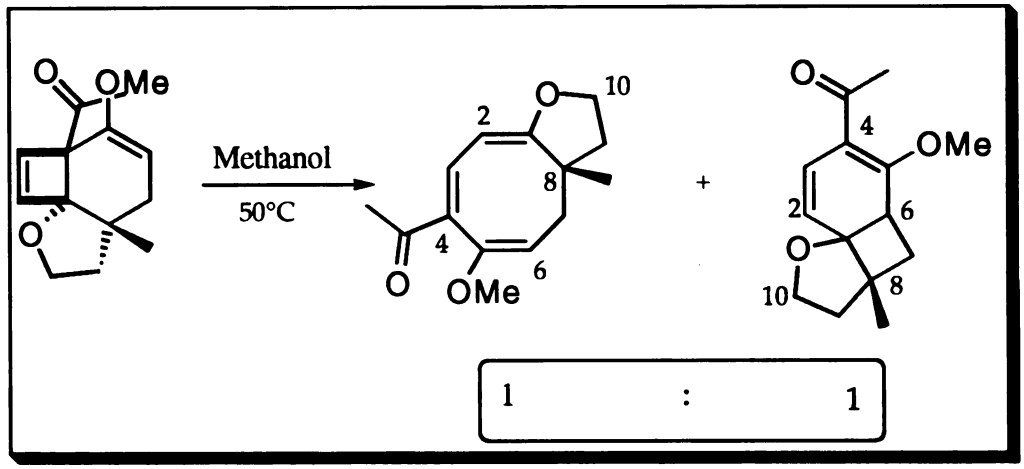
1-acetyl-5-methyl-2-methoxy-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene

^{1}H NMR(300MHz;CD$_3$OD) : δ6.35(d, J=2.97 Hz, 1H$_{10}$), 6.23(d, J=2.97 Hz, 1H$_{11}$), 4.75(dd, J=6.1 &3.2 Hz, 1H$_3$), 3.87(m, 2H$_7$), 3.49(s, 3H), 2.35(dd, J=16.4 & 6.09 Hz, 1H$_4$), 2.16(m, 1H$_6$), 2.09 (s, 3H), 2.04(dd, J=16.4 & 3.15 Hz, 1H$_4$), 1.65(ddd, J=12.3, 5.8 & 4.5 Hz, 1H$_6$) & 1.04(s, 3H).

Large scale photolysis was carried out to isolate **2OMe-4T$_{2Me}$-CB**. **2OMe-4T$_{2Me}$-K** (850mg) was dissloved in methanol (300mL), purged with argon and irradiated in an immersion well through Pyrex. The reaction was monitored by thin layer chromatography. At near depletion of the starting material, the reaction was stopped and then concentrated under reduced pressure at room temperature. A proton NMR was immediately taken and showed a mixture of starting ketone and its photoproduct, **2OMe-4T$_{2Me}$-CB**.

Thermal Chemistry of **2OMe-4T$_{2Me}$-CB**

A crude photolysis mixture of **2OMe-4T$_{2Me}$-CB** and **2OMe-4T$_{2Me}$-K** was dissolved in methanol (200mL), purged with argon, and heated in a constant temperature bath at 50°C. The reaction progress was monitored by thin layer chromatography. After complete conversion of **2OMe-4T$_{2Me}$-CB**, the reaction mixture was purified by column chromatography. Two products were isolated in equilibrium (1:1 ratio). They are determined to be the thermal products of **1AP-2OMe-4T$_{2Me}$-CB**, 4-acetyl-5-methoxy-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene and 4-acetyl-5-methoxy-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene.



4-acetyl-5-methoxy-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene

^{1}H NMR(300MHz;CDCl$_3$) : δ6.7(d, J=10.1 Hz, 1H$_3$), 5.1(d, J=10 Hz, 1H$_2$), 4.1-4.1(m, 2H$_{10}$), 3.58(s, 3H), 3.27(dd, J=10.1 & 7.95 Hz, 1H$_6$), 2.25(s, 3H), 2.26(dd, J=12 & 10.1 Hz, 1H$_7$), 1.89(ddd, J=12.6, 5.6 & 4.1 Hz, 1H$_9$), 1.81(dd, 12.5 & 7.9 Hz, 1H$_9$),1.78(ddd, J=11.9, 8.0 & 0.9 Hz, 1H$_7$) and 1.14(s, 3H).

4-acetyl-5-methoxy-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl$_3$) : δ7.19(d, J=5.34 Hz, 1H$_3$), 5.24(dd, J=9.3 & 7.1 Hz, 1H$_6$), 5.14(dd, J=5.34 & 0.5 Hz, 1H$_2$) 4.1-4.2(m, 2H$_{10}$), 3.69(s, 3H), 2.35(s, 3H), 2.27(dd, J=14.1 & 9.3 Hz, 1H$_7$), 2.10(dd, J=14.1 &7.2 Hz, 1H$_7$), 1.76(ddd, J=11.8, 8.0 & 0.9 Hz, 1H$_9$), 1.65(dd, J=11.7 & 5.6 Hz, 1H$_9$) and 1.59(s, 3H).

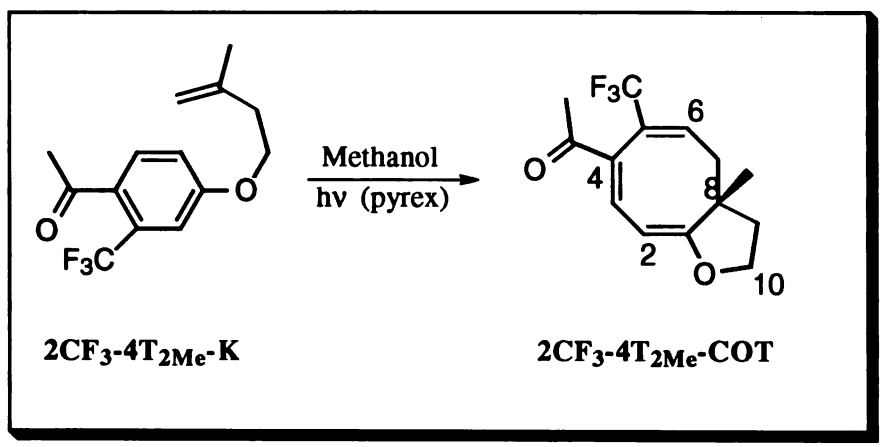
^{13}C NMR(75MHz;CDCl$_3$)(equilibrium-partial) : 200, 196, 160, 154, 139, 130, 127, 123, 114, 99, 93, 61, 57, 47, 44, 41,32 and 24.

Photolysis of 2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone

($2CF_3$-$4T_{2Me}$-K)

---In Methanol

In a NMR tube, 2-trifluoromethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone (1.7mg) was dissolved in 0.75mL of deuterated methanol (0.008M). The sample was purged with argon for fifteen minutes and irradiated using an medium pressure mercury arc lamp fitted with a Pyrex filter. The reaction progress was followed closely by time resolved ^1H NMR. After twenty-three hours of irradiation, the reaction was 50% complete and only one cycloadduct was observed by proton NMR. The product was determined to be **$2CF_3$-$4T_{2Me}$-COT**. Large scale photolysis of **$2CF_3$-$4T_{2Me}$-K** (180mg) in argon-purged methanol (60mL) provided **$2CF_3$-$4T_{2Me}$-COT**. Purification of the photolysis mixture by silica gel column chromatography caused decomposition of **$2CF_3$-$4T_{2Me}$-COT**. The structure of **$2CF_3$-$4T_{2Me}$-COT** was determined from the ^1H NMR of the photolysis mixture.



$2CF_3$-$4T_{2Me}$-K **$2CF_3$-$4T_{2Me}$-COT**

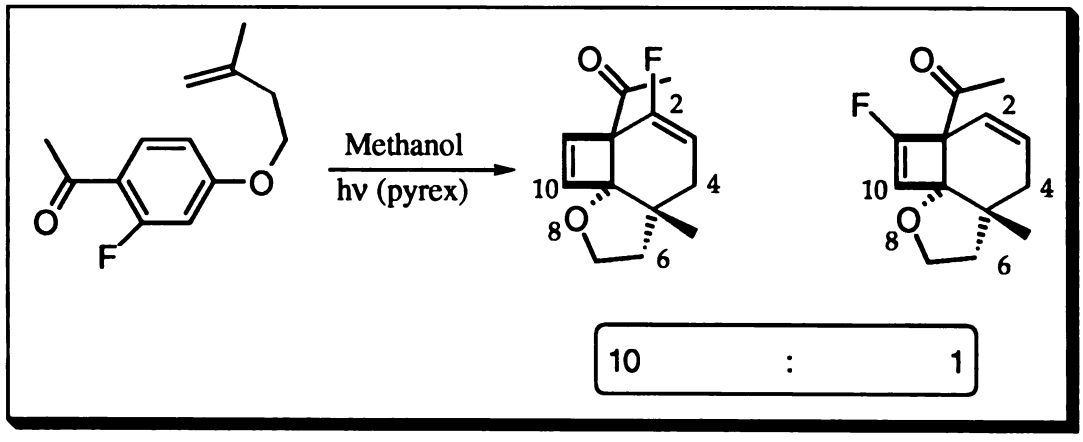
4-acetyl-5-trifluoromethyl-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^1H NMR(300MHz;CDCl3) : δ7.2(d, J=4.8 Hz, $1H_3$), 6.8(qdd, J=1.6, 9.2 & 6.5 Hz, $1H_6$), 5.2(d, J=4.8 Hz, $1H_2$), 4.2(br dd, J=9.0 & 8.7, $1H_{10}$), 4.12(ddd, J=11.4,

9.0 & 5.4 Hz, 1H10), 2.4(dd, J=12.4 & 9.2 Hz, 1H7), 2.3(s, 3H), 2.2(m, 1H9), 1.76(dd, J=12.4 & 6.3 Hz, 1H7), 1.6(m, 1H9), and 1.21(s, 3H).

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-2-fluoroacetophenone (**2F-4T2Me-K**)

In a NMR tube, 4-(3'-methyl-3'-buten-1'-oxy)-2-fluoroacetophenone (2.2mg) was dissloved in 1mL deuterated methanol (1 x 10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a Pyrex filter. The reaction was monitored by time resolved NMR. After three hours, the reaction was nearly complete. Two photoproducts were indentified by ^{1}H NMR in a ratio of ~10:1 as 1-acetyl-2-fluoro-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene, **2F-4T2Me-CB-t** and its regioisomer, 1-acetyl-11-fluoro-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene, **2F-4T2Me-CB-a** respectively. Indentification of the minor product was difficult due to extensive overlap of the structurely similar major photoproduct. A partial ^{1}H NMR for 1-acetyl-11-fluoro-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}]undeca-2,10-diene is presented, stressing the characteristic olefin region.



1-acetyl-2-fluoro-5-methyl-8-oxatricyclo[7.2.0.0^{5,9}] undeca-2,10-diene

^{1}H NMR(300MHz;CD3OD) : δ6.5(d, J=2.94 Hz, 1H10), 6.35(d, J=2.90 Hz, 1H11), 5.31(ddd, J=15.6, 6.5 & 2.8 Hz, 1H3), 3.85(ddd, J=9.6, 8.25 & 6.9 Hz, 1H7), 3.79(ddd, J=9.4, 8.25 & 2.9 Hz, 1H7), 2.32(ddd, J=16.9, 6.6 & 3.9 Hz, 1H4),

2.25(ddd, J=12.2, 9.6, & 9.4 Hz, 1H_6), 2.17(d, J=0.63 Hz, 3H_{Acetyl}), 2.02(ddd, J=16.9, 6.0 & 2.8 Hz, 1H_4), 1.64(ddd, J=12.2, 6.8 & 2.9 Hz, 1H_6) & 1.07(s, 3H).

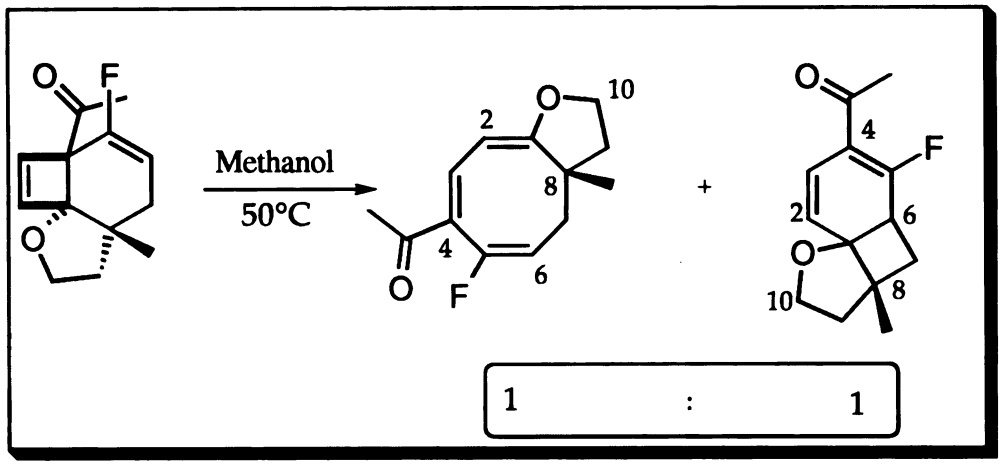
1-acetyl-11-fluoro-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$]undeca-2,10-diene

^{1}H NMR(300MHz;CD_3OD) : δ5.92(ddd, J=10.1, 6.7 & 2.4 Hz, 1H_3), and 5.65(dd, J=10.1 & 3.2 Hz, 1H_2).

Preparatory scale photolysis was carried out to isolate **2F-4T$_{2Me}$-CB**. **2F-4T$_{2Me}$-K** (700mg) was dissolved in freshly distilled methanol (300mL), purged with argon and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitiored by thin layer chromatography and stopped at near depletion of **2F-4T$_{2Me}$-K**. The reaction mixture was concentrated under reduced pressure and its ^{1}H NMR was taken. Purification of the reaction mixture by coloumn chromatography gave a mixture of three products, **2F-4T$_{2Me}$-CB** and two thermal rearranged isomers.

Thermal Chemistry of **2F-4T$_{2Me}$-CB**

In a large Pyrex test tube, crude **2F-4T$_{2Me}$-CB** (250mg) was dissolved in methanol (100mL), purged with argon, and heated in a constant temperature water bath (50°C). The reaction progess was monitored by thin layer chromatography. After 5 hours of heating, **2F-4T$_{2Me}$-CB** was completely converted. Purification of the crude reaction mixture by preparative thin layer chromatography (ethyl acetate:hexanes, 5:95) gave a 1:1 ratio of 4-acetyl-5-fluoro-8-methyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene and 4-acetyl-5-fluoro-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene.



4-acetyl-5-fluoro-8-methyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene

^{1}H NMR(300MHz;CDCl$_3$) : δ6.53(dd, J=10 & 7.6 Hz, 1H$_3$), 5.3(dd, J=10 & 2.34 Hz, 1H$_2$), 4.12(dd, J=8.6 & 4.5 Hz, 2H$_{10}$), 3.25(ddd, J=10, 9.8 & 7.4 Hz, 1H$_6$), 2.4(d, J=5.7 Hz, 3H), 2.23(dd, J=12.4 &10 Hz, 1H$_7$), 1.87(dd, J=12.4 & 7.4 Hz, 1H$_7$), 1.9-1.7(complex, 2H$_9$) and1.17(s, 3H).

4-acetyl-5-fluoro-8-methyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl$_3$) : δ7.3(dd, J=6.03 & 0.75 Hz, 1H$_3$), 5.85(ddd, J=17.1, 9.6 & 7.5 Hz, 1H$_6$), 5.23(ddd, J=6.03, 3.1, & 0.75 Hz, 1H$_2$) 4.25(br t, J=8.9 Hz,1H$_{10}$), 4.18(ddd, J=11.3, 8.7 & 5.7 Hz, 1H$_{10}$), 2.3(d, J=2.0 Hz, 3H), 2.25(ddd, J=14.3, 10, & 2.0 Hz, 1H$_7$), 2.12(ddd, J=14.3, 7.5, & 1.5 Hz, 1H$_7$), 1.9-1.7(complex, 2H$_9$), and 1.13(s, 3H).

^{13}C NMR(75MHz, CDCL$_3$) (equilibrium): δ 195.6(d, J=3 Hz, carbonyl) and 193(d, J=3 Hz, carbonyl), 172.8(d), 172.5, 168.7, 158.1, 154.8, 142.5(d), 129.1(d), 123.4, 120.8, 112.5(d), 108.6, 93.8, 87.5(d), 67.7, 67.1, 54.8, 47.4, 40.4, 37.7, 37.2, 36.9, 33.0(d), 31.3(d), 27.4, 27.0, and 21.9.

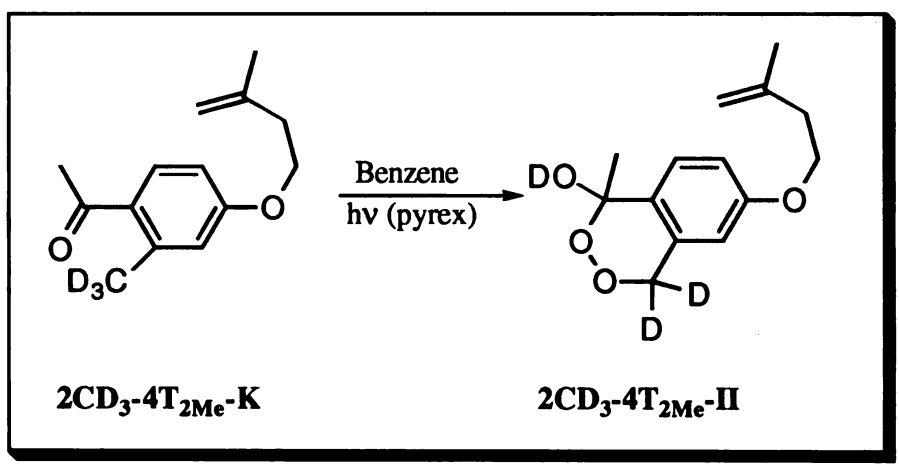
IR(CCl$_4$) (equilibrium) : 2965, 2667, 1682, 1678, 1377, 1069, and 908.6cm^{-1}.

Photolysis of 4-(3'-methyl-3'-buten-1'-oxy)-2-methyl(d3)acetophenone

(2CD3-4T2Me-K)

---In Benzene

4-(3'-methyl-3'-buten-1'-oxy)-2-methyl(d3)acetophenone was dissolved in benzene (2.0mg in 1mL solvent), purged with argon, and irradiated through a Pyrex filter. The reaction progress was monitored by ^{1}H NMR. After three hours of irradiation, the starting material was partially converted into a single photoproduct (~40%). Purification of **2CD3-4T2Me-II** by preparative thin layer chromatography (hexanes:ethyl acetate, 90:10) was unsuccessful. No observable 2+2 photocycloaddition products were formed under these conditions.



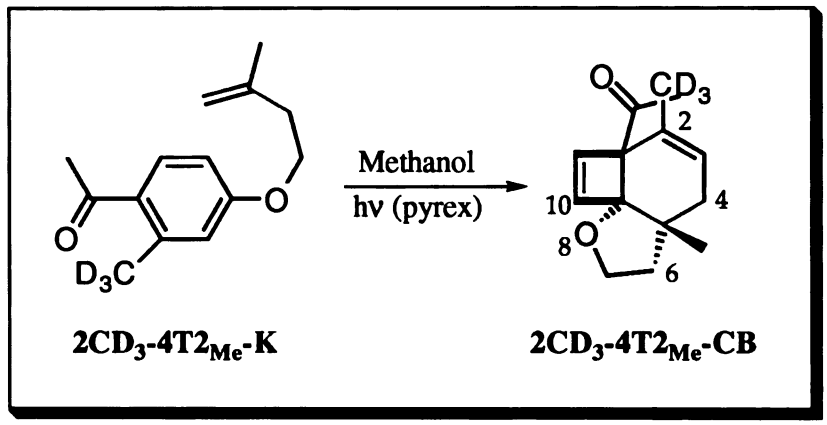
2CD3-4T2Me-II

^{1}H NMR(300MHz;C6D6) : δ6.94(dd, J=8.1 & 0.7 Hz, 1H), 6.76(dd, J=8.1 & 2.0 Hz, 1H), 6.65(dd, J=2.1 & 0.7 Hz, 1H), 4.85(br s, 1H), 4.79(br s, 1H), 3.78(t, J=6.84 Hz, 2H), 2.3(t, J=6.84 Hz, 2H), 1.59(br s, 3H), 1.54(s, 3H).

---In Methanol

In a NMR tube, 4-(3'-methyl-3'-buten-1'-oxy)-2-methyl(d3)acetophenone (1.5mg) was dissolved in 0.75mL of deuterated methanol (~0.01M). The sample was purged with

argon for fifteen minutes and irradiated using an medium pressure mercury arc lamp fitted with a Pyrex filter. The reaction progress was followed closely by time resolved NMR. After eleven hours of irradiation, **$2CD_3$-$4T_{2Me}$-K** was converted into a single photoproduct, 1-acetyl-2-methyl (d3)-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$] undeca-2,10-diene, **$2CD_3$-$4T_{2Me}$-CB**.



1-acetyl-2-methyl (d3)-5-methyl-8-oxatricyclo[7.2.0.$0^{5,9}$] undeca-2,10-diene

^{1}H NMR(300MHz;CD_3OD) : δ6.50(d, J=3.03 Hz, $1H_{10}$), 6.28(d, J=3.0 Hz, $1H_{11}$), 5.54(dd, J=4.8 &4.14 Hz, $1H_3$), 3.80(m, $2H_9$), 2.26(dd, 16.8 & 4.8 Hz, $1H_4$), 2.12 (s, 3H), 2.1 (m, $1H_6$), 1.94(dd, J=16.8 & 4.14 Hz, $1H_4$), 1.69(ddd, J=12.8, 7.23 & 5.61 Hz, $1H_6$), and 1.01(s, 3H).

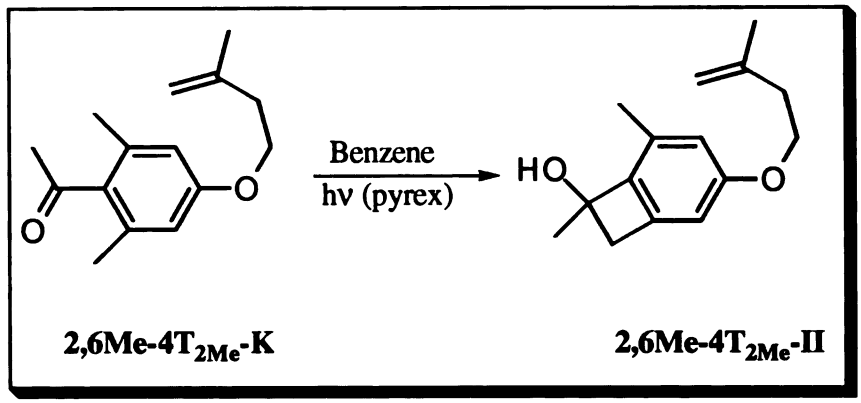
Photolysis of 2,6-dimethyl-4-(3'-methyl-3'-buten-1'-oxy)acetophenone

(2,6Me-$4T_{2Me}$-K) :

In a NMR tube, **2,6Me-$4T_{2Me}$-K** (1.7mg) was dissolved in 0.75mL of deuterated benzene (~0.01M). The sample was purged with argon for fifteen minutes and irradiated using an medium pressure mercury arc lamp fitted with a Pyrex filter. The reaction progress was followed closely by time resolved ^{1}H NMR. Five hours of irradiation resulted in the formation of a single photoproduct. The photoproduct was

determined to be 2'-methyl-4'-(3'-methyl-3'-buten-1'-oxy)-1-methylbenzocyclobutenol, **2,6Me-4T$_{2Me}$-II**, arising from hydrogen abstraction from an *ortho* methyl group.

Similarly, NMR scale photolysis of **2,6Me-4T$_{2Me}$-K** (2.1mg in 1mL solvent) was carried out in argon-purged methanol-d4 through a Pyrex filter. No photoproducts arising from *ortho* 2+2 cyloaddition were observed by ^{1}H NMR after ten hours.



2,6Me-4T$_{2Me}$-K **2,6Me-4T$_{2Me}$-II**

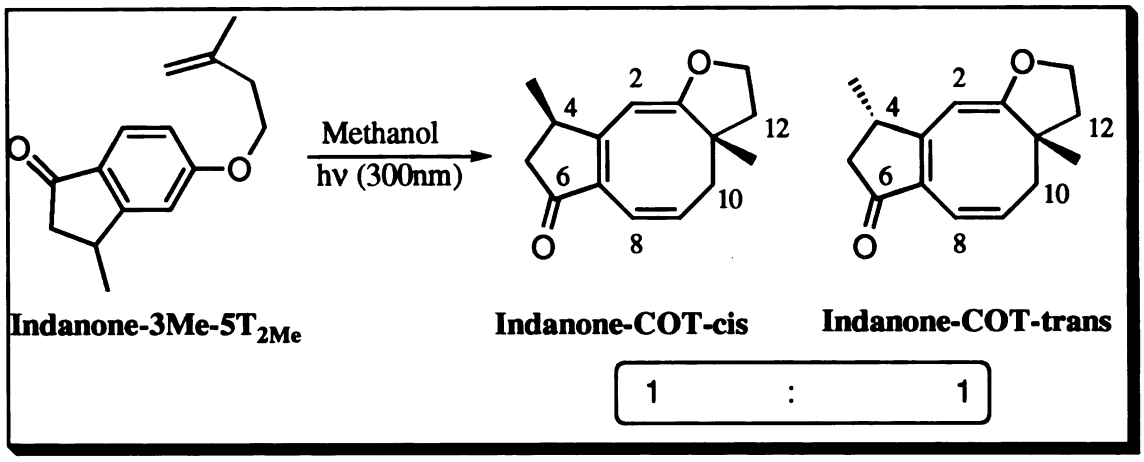
2'-methyl-4'-(3'-methyl-3'-buten-1'-oxy)-1-methylbenzocyclobutenol

^{1}H NMR(300MHz;C$_6$D$_6$) : δ6.63(br s, 1H), 6.53(br s, 1H), 4.82(m, 2H), 3.82(t, J=6.6 Hz, 2H), 3.02 & 2.88(AB Quartet, J=13.8 Hz, 2H), 2.34(t, J=6.6 Hz, 2H), 2.12(s, 3H), 1.62(br s, 3H) and 1.56(s, 3H).

Photolysis of 3-Methyl-5-(3'-methyl-3'-buten-1'-oxy)indan-1-one

(Indanone-3Me-5T$_{2Me}$)

A solution of **Indanone-3Me-5T$_{2Me}$** (1.9mg per 0.75mL solvent) in CD3OD was degassed with argon and irradiated at 300 nm in a Rayonet. The reaction was monitored by time resolved ^{1}H NMR. Analysis showed the presence of two photproducts in ratio of 1:1 after sixteen hours. The cyclobutene photoproducts were identified as trans-4,11-dimethyl-14-oxatricyclo[9.3.0.0^{3,7}]tetradecatri-1,3,8-ene-6-one, **Indanone-COT-trans**, and cis-4,11-dimethyl-14-oxatricyclo[9.3.0.0^{3,7}]tetradecatri-1,3,8-ene-6-one, **Indanone-COT-cis**. Attempts to separate the diastereomers were unsuccessful by either alumina or silica gel column chromatography.

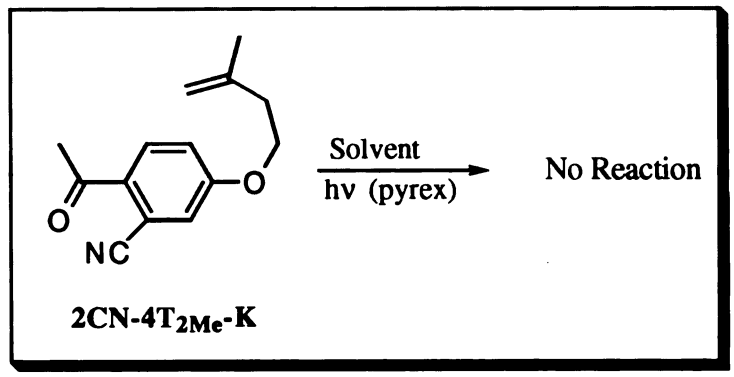


cis- and trans-4,11-dimethyl-14-oxatricyclo[9.3.0.0^{3,7}]tetradecatri-1,3,8-ene-6-one

^{1}H NMR(300MHz;CD$_3$OD) (mixture of diastereomers) : δ 6.36(dt, J=11.8 & 1.4 Hz, 1H$_8$), 6.23(br dt, 12.1, 1.35 Hz, 1H$_8$), 5.99(tdd, J=12.0, 8.5 & 7.5 Hz, 2H$_9$), 5.62(s, 1H$_2$), 5.47(s, 1H$_2$), 4.28(ddd, J=10.3, 9.0 & 6.0 Hz, 1H$_{13}$), 4.8-4.19(m, 3H$_{13}$), 2.88(bq, J=7.2 Hz, 2H$_4$), 2.69-2.62(dd, J=18.8 & 7.0 Hz, 1H$_5$), 2.69-2.62(dd, J=18.8 & 7.0 Hz, 1H$_5$), 2.46(dd, J=14.4 & 8.5 Hz, 2H$_{10}$), 2.04-1.98(dd, J=18.8 & 2.05 Hz, 2H$_5$), 1.23(d, J=7.1 Hz, 3H$_{Me}$), 1.21(d, J=7.1 Hz, 3H$_{Me}$), 1.20(s, 3H$_{Me}$), 1.17(s, 3H$_{Me}$).

Photolysis of 5-(3'-methyl-3'-buten-1'-oxy)-2-acetylbenzonitrile **(2CN-4T$_{2Me}$-K)**

NMR scale photolysis of **2CN-4T$_{2Me}$-K** (2mg ketone per 0.75mL solvent) was carried out in argon-purged methanol or benzene at 313 nm or through Pyrex. The progress of the reactions was monitored by 1H NMR. At either of the four reaction conditions, no photocycloaddition was observed. **2CN-4T$_{2Me}$-K** remained photostable after long periods of irradiation (>20 hours).

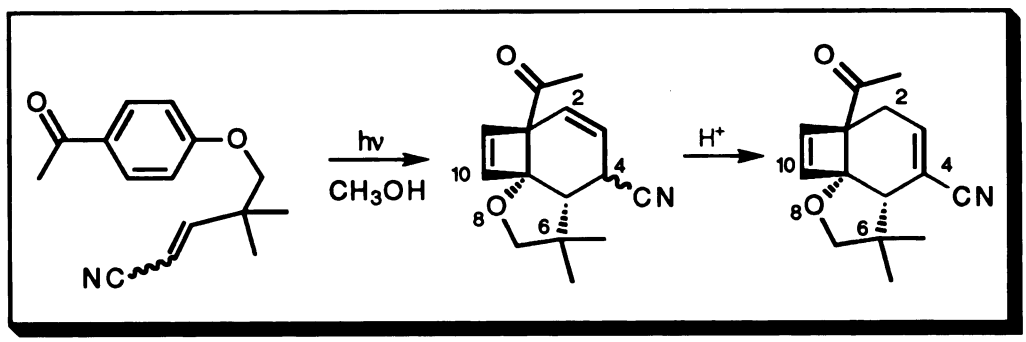


Photolysis of cis-and trans-5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile

(4T2N(CN)-K)

In a NMR tube, cis-and trans-5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile (2.1mg) was dissolved in 0.75mL methanol-d4 (1.15×10^{-2}M). The sample was purged with argon for 20 minutes and then irradiated through a Pyrex filter. NMR analysis of the reaction mixture showed rapid cis-trans isomerization of the double bond after 15 minutes (9:1 trans-cis to 2.5:1 trans-cis). Continued irration of the reaction mixture produced two products in a 1:1.3 ratio as determined by integration of peak resonances corresponding to the acetyl groups (~2.1 ppm). The photoproducts were determined to be (4R)-1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene and (4S)-1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene. Preparatory scale photolysis was carried out to isolated the photoproducts. cis-and trans-5-(4'-Acetylphenoxy)-4,4-dimethyl-2-pentenenitrile (0.06g) was dissolved in freshly distilled methanol (25mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by thin layer chromatography. Purification of the crude reaction mixture by thin layer chromatography (hexanes:ethyl acetate, 80:20) gave 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene and its thermal rearranged isomer 1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-3,10-diene. The exact stereochemistry of the isolated 1-acetyl-4-cyano-6,6-dimethyl-8-

oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene could not be determined due to its thermal instability.



1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CDCl$_3$) : δ 6.56(d, J=3 Hz, 1H$_{10}$), 6.47(d, J=3 Hz, 1H$_{11}$), 6.09(dd, J=10.2 & 1.5 Hz, 1H$_2$), 5.83(dd, J=10.2 & 4.8 Hz, 1H$_3$), 3.60(AB Quartet, J=8.7 Hz, 2H$_7$), 3.49(ddd, J=4.8, 4.2 & 1.5 Hz, 1H$_4$), 2.37(d, J=4.2 Hz, 1H$_5$), 2.21(s, 3H$_{acetyl}$) , 1.11(s, 3H), and 0.98(s, 3H).

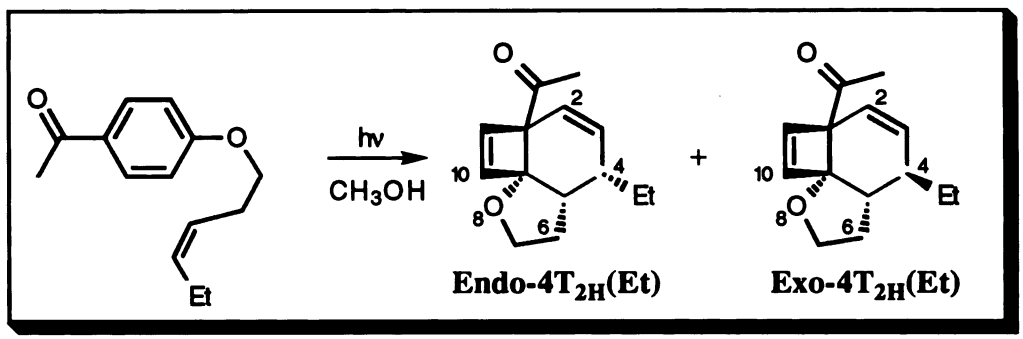
1-acetyl-4-cyano-6,6-dimethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-3,10-diene

^{1}H NMR(300MHz;CDCl$_3$) : δ 6.85(br dd, J=6.3 & 2.7 Hz, 1H$_3$), 6.33(d, J=3 Hz, 1H$_{10}$), 6.23(d, J=3 Hz, 1H$_{11}$), 3.64(AB Quartet, J=8.4 Hz, 2H$_7$), 3.12(ddd, J=19.5, 2.7, & 2.4 Hz, 1H$_2$), 2.6(br s, 1H$_5$), 2.24(s, 3H$_{acetyl}$) , 2.05(ddd, J=19.5, 6.3, & 1.5 Hz, 1H$_2$), 1.2(s, 3H), and 0.9(s, 3H).

Photochemistry of **4T2N(Et)-K**

Irradiation of a solution of cis-6-(4'-acetylphenoxy)-3-hexene (3.2 mg) in argon-purged methanol (0.8 mL) provided two products in a 20:1 ratio as determined by integration of peak resonances corresponding to the cyclobutene proton (H-11) at 6.3 and 6.2 ppm. The two photoproducts were determined to be (4-endo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}]undeca-2,-10-diene, **(4-endo)-Et-CB**, and (4-exo)-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,-10-diene, **(4-exo)-Et-CB**, respectively.

Cis/trans isomerization of the double bond was also observed during the photoreaction as determined by the observation new double bond resonances (J=16Hz).



endo-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CD3OD) : δ 6.43(d, J=2.9 Hz, 1H$_{10}$), 6.31(d, J=2.9 Hz, 1H$_{11}$), 5.92(dd, J=10.2 & 4.7 Hz, 1H$_3$), 5.73(dd, J=10.2 & 1.4 Hz, 1H$_2$), 3.81(dd, J=7.75 & 6.15 Hz, 2H$_7$), 2.2(m, 1H$_5$), 2.13(s, 3H$_{acetyl}$) , 2.0(dddt, J=4.7, 1.4, & 3.7Hz, 1H$_4$), 1.5(m, 2H$_6$), 1.0(dq, J=7.4 & 3.7Hz, 2H), and 0.97(t, J=7.4 Hz, 3H).

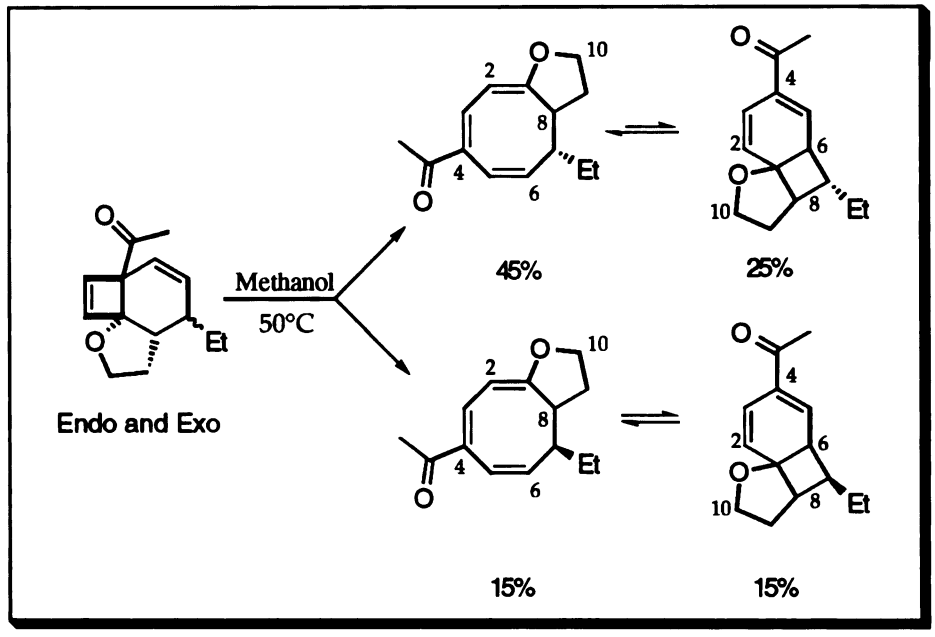
exo-1-acetyl-4-ethyl-8-oxatricyclo[7.2.0.0^{9,5}] undeca-2,10-diene

^{1}H NMR(300MHz;CD3OD) : δ 6.35(d, J=3 Hz, 1H$_{10}$), 6.22(d, J=3 Hz, 1H$_{11}$), 5.92(dd, J=10.2 & 4.7 Hz, 1H$_3$), 5.8-5.6(m, 2H$_{2,3}$), 3.7(AB Quartet, 2H$_7$), 2.14(s, 3H$_{acetyl}$).

Thermal Ring Opening of **endo and exo-4T2N(Et)-CB**

cis-6-(4'-Acetylphenoxy)-3-hexene (0.2 g) was dissolved in freshly distilled methanol (250mL) and irradiated in an immersion well through a Pyrex filter. The reaction progress was monitored by thin layer chromatography. After complete disappearance of the starting ketone (28 hours), the reaction mixture was heated at 50°C for six hours. Attempts to separate the crude reaction mixture were unsuccessful by thin layer chromatography (hexanes:ethyl acetate, 80:20). NMR analysis of the photoproducts showed a diastereomeric mixture of (endo and exo)-4-acetyl-7-ethyl-11-

oxabicyclo[6.3.0]undeca-1,3,5-triene and (endo and exo)-4-acetyl-7-ethyl-11-oxatricyclo[6.3.0.0.^{1,6}]undeca-2,4-diene. The overall product ratio was 3 **(7-endo)-Et-COT** : 1.5 **(7-endo)-Et-CH** : 1 **(7-exo)-Et-COT** : 1 **(7-exo)-Et-CH** as determined by integration of their vinyl protons.



endo-4-acetyl-7-ethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

^{1}H NMR(300MHz;CDCl3) : δ6.97(d, J=7.75 Hz, 1H3), 6.29(d, J=12.1 Hz, 1H5), 5.64(dd, J=12.1 & 7.14 Hz, 1H6), 5.44(dd, J=7.8 & 1.4 Hz, 1H2), 4.3-4.0(m, 2H10), 3.1(m, 1H8), 2.31(s, 3H), 0.9(t, J=7.4 Hz, 3H)

endo-4-acetyl-7-ethyl-11-oxatricyclo[6.3.0.0^{1,6}]undeca-2,4-diene

^{1}H NMR(300MHz;CDCl3) : δ6.78(br d, J=6.1 Hz, 1H5), 6.62(dd, J=10.1 & 1.5 Hz, 1H2), 5.72(dd, J=10.1 & 1.0 Hz, 1H3), 4.3-4.0(m, 2H10), 2.8(m, 1H6), 2.29(s, 3H), 0.9(t, J=7.4 Hz, 3H)

exo-4-acetyl-7-ethyl-11-oxabicyclo[6.3.0] undeca-1,3,5-triene

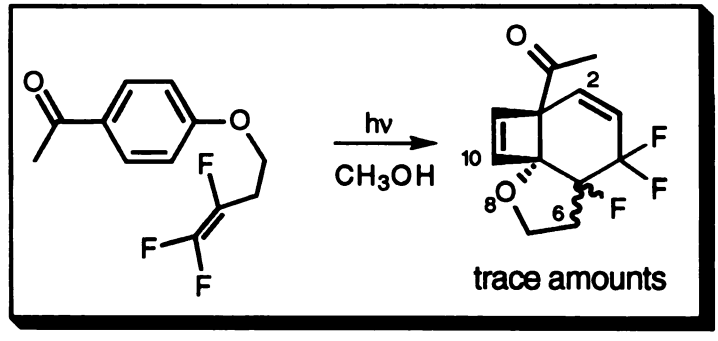
^{1}H NMR(300MHz;CDCl3) : δ7.03(dd, J=6.15 & 1.4 Hz, $1H_3$), 6.31(d, J=10.9 Hz, $1H_5$), 5.84(dd, J=10.9 & 6.75 Hz, $1H_6$), 5.31(dd, J=6.12 & 1.4 Hz, $1H_2$), 4.3-4.0(m, $2H_{10}$), 3.1(m, $1H_8$), 2.30(s, 3H), 0.9(t, J=7.4 Hz, 3H)

exo-4-acetyl-7-ethyl-11-oxatricyclo[6.3.0.$0^{1,6}$]undeca-2,4-diene

^{1}H NMR(300MHz;CDCl3) : δ6.67(td, J=1.2 & 5.94 Hz, $1H_5$), 6.51(dd, J=10 & 1.5 Hz, $1H_2$), 5.68(td, J=1.1 & 10 Hz, $1H_3$), 4.3-4.0(m, $2H_{10}$), 2.8(m, $1H_6$), 2.29(s, 3H), 0.9(t, J=7.4 Hz, 3H).

Photochemistry of **$4T_{2N}$(F)-K**

A solution of 4-(3',4',4'-trifluoro-3'-buten-1'-oxy)acetophenone (3 mg per 1 mL solvent) in CD_3OD was degassed with argon and irradiated through Pyrex. Reaction progress was monitored by time resolved ^{1}H NMR. After 30 minutes of irradiation, much of the starting ketone disappeared and only a trace amount of photoproduct was observed. The photoproduct was determined to be 1-acetyl-4,4,5-trifluoro-8-oxatricyclo[7.2.0.$0^{9,5}$] undeca-2,-10-diene based on its characteristic vinyl region in ^{1}H NMR.



IV. Photokinetic Data

A. Photochemical Glassware

The glassware used for quantum yield studies was class A volumetric except for the polyethylene syringes used to fill irradiation test tubes The glassware was cleaned in the following fashion: 1) rinsed with acetone, 2) boiled in a bath of distilled water/alconox at a boil for 24 hours, 3) rinsed five times with distilled water, 4) boiled in a bath of distilled water at a boil for 24 hours, 5) rinsed five times with distilled water, and finally 6) dried in an oven overnight at 180°C.

The irradiation ampoules were made by streching 13x100mm Pyrex culture tubes just below the telfon label to an uniform length of 15cm. It is essential that the tubes are uniform in both length and thickness so that an accurate measure of the quantum yield can be determined.

B. Sample Preparation

All weighings were done on a Mettler AE163 top loading digital analytical balance, which is accurate to within 0.00001 g. Equal volumes of sample (2.8mL) were placed via a Rainin Precision Microliter Pipette into each ampoule.

C. Degassing Procedure

The filled irradiation tubes were fitted onto a 12-port degassing cow with #00 one hole rubber stoppers. The samples were then frozen to liquid nitrogen temperature and evacuated with a diffusion pump for 15 minutes. The stopcocks were closed and the samples were allowed to warm to room temperature. This freeze-pump-thaw cycle was repeated four times. The samples were finally sealed *in vacuo* with an oxygen-natural gas torch.

D. Irradiation Chambers

All samples for kinetic studies were irradiated in parallel with actinometer solutions in a merry-go-round apparatus having 7mm slits. A Hanovia 450W medium pressure mercury lamp cooled in a quartz immersion well was used as the light source. The whole apparatus was immersed inside a 10 gallon crock filled with distilled water. The 313 nm chamber used a 1cm filter solution consisting of 0.002M K_2CrO_4 in 1% aqueous K_2CO_3. A Corning CS-7-37 filter was used to isolate the 365 nm emission band.

E.Calculation of Quantum Yields

Quantum yields were measured utilizing the following equation,

$$\Phi=[Prod]/I$$

where I is the intensity of light absorbed by the reactant and [P] is the concentration of the photoproduct measured by analytical techniques.

Light intensity absorbed was determined by irradiating the reactant in parallel with either valerophenone(VP) or 2-methylvalerophenone(2-MeVP) actinometer which have well defined quantum yields. The quantum yields of Norish-type II cleavage (Φ_{II}) for VP and 2-MeVP at 0.1M in benzene are 0.33[89] and 0.016[90] respectively.

$$I = [AP] / 0.33 \text{ or } I = [2\text{-MeVP}] / 0.16$$

The actinometers and photoproducts observed were analyzed using gas chromatographs equipped with flame ionization detectors. Retention times of the observed photoproducts and the internal standards were compared with authentic samples of each. Response factors for the various photoproducts and their corresponding internal standards are listed below.

Gas Chromatograph Response Factors for Various Photoproducts

Photoproduct / Internal standard	Exp'l	Calc'd
Ap / C_{12}	1.90	1.72
Ap / Ethyl phenyl acetate	1.125	1.28
1CN-4T$_{3H}$-CB/n-pentyl benzoate	1.42	1.08
1AP-2Me-4T$_{2H}$-5Me-COT/n-heptyl benzoate	1.38	1.00
1AP-2Me-4T$_{2H}$-5IP-COT-t/n-heptyl benzoate	1.41	1.09
1CN-2T$_{3H}$-CB/n-heptyl benzoate	1.315	1.15
1EC-2T$_{3H}$-CB/n-heptyl benzoate	1.42	0.942
1CN-2T$_{2H}$-LCB/n-pentyl benzoate	1.25	1.00
1AP-2F-4T$_{2Me}$/n-heptyl benzoate	1.30	
1AP-2Me-4T$_{2Me}$-COT/n-heptyl benzoate	1.334	

$$R_f(\text{product})_{exp} = ([\text{prod.}]/[\text{int.std.}]) \times (\text{Area}_{\text{int std}}/\text{Area}_{\text{prod.}})$$

$$R_f(\text{product})_{calc'd} = \frac{\{ \#\text{ of carbons} + 1/2\ (\#\text{ of C-O bonds})\}_{Std}}{\{ \#\text{ of carbons} + 1/2\ (\#\text{ of C-O bonds})\}_{Prod}}$$

The concentration of photoproducts and the products resulting from the Type II cleavage of the actinometer were determined using the following equations:

$$[prod] = R_f(prod) \times [int.\ std.] \times Area_{prod} / Area_{int.\ std.}$$

$$[AP] = R_f(AP) \times [int.\ std.] \times Area_{AP} / Area_{int.\ std.}$$

where, [prod] and [AP] are the concentration of the photoproduct and acetophenone respectively, R_f is the instrument response factor(see above), [int. std] is the concentration of the internal standard, and Area $_x$ is the integrated area for that particular compound.

Computational Parameters

Semi-empirical studies of the excited and ground state were carried to provide additional insight into the factors which control the regio- and stereoselectivity associated with ortho [2+2] photocycloaddition.

General Procedures for Calculations:

- The structure was constructed in the Editor Program in CAChe system
- The structure was then minimized using molecular mechanics (MM2)
    - MM2 Options
        1. Cut-off distances for Van der Waals interactions-- 9Å
        2. Optimization relaxation factors-- 1.00
        3. Convergence-- 0.001kcals/mol
- Finally, the MM2 output structure was further minimized using AM1[91]
- To distinguish between a local minima and the global minima, the MOPAC[92] output structure was altered by varying bond angles or distances and then resubmitted to MOPAC. If similar energies were obtained then it is assumed to be the global minima.

Specific Procedure for Calculations:

- Rotational Barriers in **2Me-4T$_{2H}$-5I**

5-Isopropyl-4-methoxy-2-methylacetophenone was used as the model compound to determine the energies of rotation around the methoxy bond. The compound was constructed and minimized as described above. The resulting compound was then submitted to MOPAC using the following parameters:

- Calculation Type: Optimized Search
- Search Type: Reaction Coordinate
- Multiplicity : Triplet using UHF
- Parameters: AM1
- Key Words: noanci

- Optimized Geometries for **1CN-2T$_{2H}$-COT**, **1CN-2T$_{3H}$-COT**, **1AP-4T$_{2H}$-COT***, and **1CN-4T$_{2H}$-COT***

These compounds were constructed and minimized as described above and then submitted to MOPAC using the following parameters:

- Calculation Type: Optimized Geometry
- Multiplicity: Singlet and Excited Singlet*
- Parameters: AM1
- Key Words: NONE

Electronic charge distributions calculated for **1AP-4T$_{2H}$-COT** and **1CN-4T$_{2H}$-COT** were obtained from the MOPAC output file, which can be opened in Microsoft Word.

APPENDIX

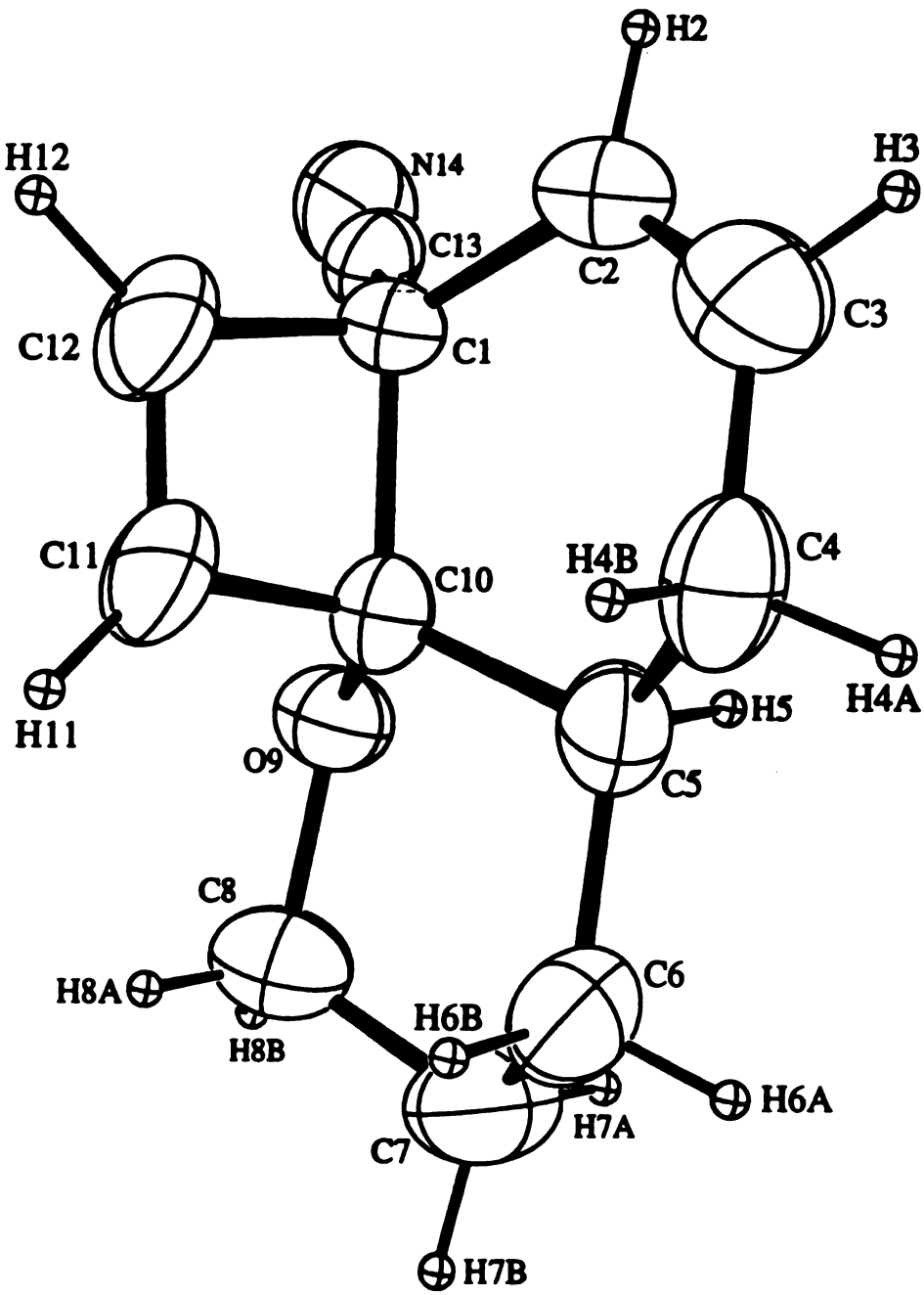


Figure 2: Crystal Structure of **1CN-4T3H-CB**[93]

Crystal Data For **1CN-4T3H-CB**

Empirical Formula	$C_{12}H_{13}ON$
Formula Weight	187.24
Crystal Color, Habit	colorless, plate
Crystal Dimensions (nm)	0.04 x 0.20 x 0.28
Crystal System	monoclinic
# of Reflections Used for Unit Cell Det.	5 (20.1-21.0°)
Omega Scan Peak Width at Half-height	0.34
Lattice Parameters	a = 6.442Å b = 10.653Å c = 14.974Å β = 95.18° V = 1023Å^3
Space Group	$P2_1/c$
z value	4
D_{calc}	1.215 g/cm^3
F_{000}	400
μ(MoKα)	0.72 cm^{-1}

Table 11: Bond Distances for **1CN-4T3H-CB**

atom	atom	distance
C1	C2	1.50
C1	C10	1.59
C1	C12	1.54
C1	C13	1.46
C2	C3	1.31
C2	H2	0.95
C3	C4	1.50
C3	H3	0.95
C4	C5	1.50
C4	H4A	0.95
C4	H4B	0.95
C5	C6	1.53
C5	C10	1.52
C6	H6A	0.95
C6	H6B	0.95
C7	C8	1.52
C7	H7A	0.95
C7	H7B	0.95
C8	O9	1.438
C8	H8A	0.95
C8	H8B	0.95
O9	C10	1.415
C10	C11	1.51
C11	C12	1.30
C11	H11	0.95
C12	H12	0.95
C13	N14	1.14

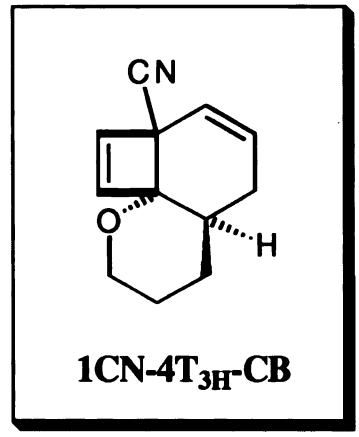
Table 12: Bond Angles for **1CN-4T3H-CB**

atom	atom	atom	angle(°)
C2	C1	C10	113.9
C2	C1	C12	111.8
C2	C1	C13	111.7
C10	C1	C12	82.7
C10	C1	C13	115.2
C12	C1	C13	118.8
C1	C2	C3	123.1
C1	C2	H2	118.46
C3	C2	H2	118.46
C2	C3	C4	123.5
C2	C3	H3	118.26
C4	C3	H3	118.26
C3	C4	C5	110.4
C3	C4	H4A	109.25
C3	C4	H4B	109.25
C5	C4	H4A	109.25
C5	C4	H4B	109.25
H4B	C4	H4B	109.46
C4	C5	C6	115.5
C4	C5	C10	112.3
C4	C5	H5	106.36
C6	C5	C10	109.4
C6	C5	H5	106.36
C5	C6	H6A	109.39

Table 12 (cont'd): Bond Angles for **1CN-4T3H-CB**

atom	atom	atom	angle(°)
C5	C6	H6B	109.39
C7	C6	H6A	109.39
C7	C6	H6B	109.39
H6A	C6	H6B	109.46
C6	C7	C8	111.2
C6	C7	H7A	109.04
C6	C7	H7B	109.04
C8	C7	H7A	109.05
C8	C7	H7B	109.05
H7A	C7	H7B	109.46
C7	C8	O9	111.1
C7	C8	H8A	109.07
C7	C8	H8B	109.07
O9	C8	H8A	109.07
O9	C8	H8B	109.07
H8A	C8	H8B	109.46
C8	O9	C10	111.2
C1	C10	C5	114.5
C1	C10	O9	110.9
C1	C10	C11	86.4
C5	C10	O9	110.2
C5	C10	C11	117.9
O9	C10	C11	114.9
C10	C11	C12	94.4
C10	C11	H11	132.8
C12	C11	H11	132.8
C1	C12	C11	96.3
C1	C12	H12	131.87
C11	C12	H12	131.86
C1	C13	N14	177

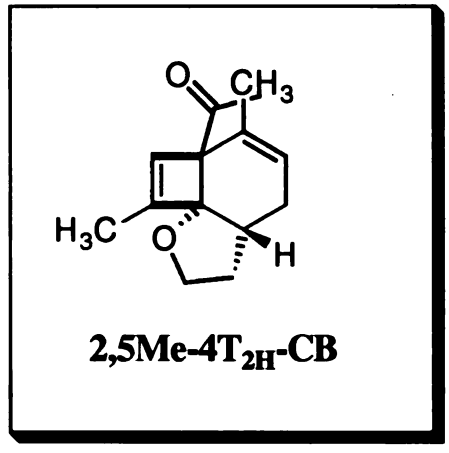
Table 13: Quantum Yield Determination of **1CN-4T$_{3H}$-CB** at 313 nm in acetone



1CN-4T$_{3H}$-CB

GC Conditions for **1CN-4T$_{3H}$-CB**	1400 Varian GC, He = 25 mL/min DB-1+ Megabore Column (15 meters) Column=135°C, Injector=230°C, Detector=230°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=100°C, Injector=200°C, Detector=220°C.
Before Irradiation	[**1CN-4T$_{3H}$**]=0.0102M in acetone [n-pentyl benzoate]=0.0008958M in acetone [Valerophenone]=0.09909M in benzene [Ethyl phenylacetate]=0.01044M in benzene
After Irradiation	[**1CN-4T$_{3H}$-CB**]=0.000652M [Acetophenone]=0.01145M; I=0.0347
Quantum Yield	0.019

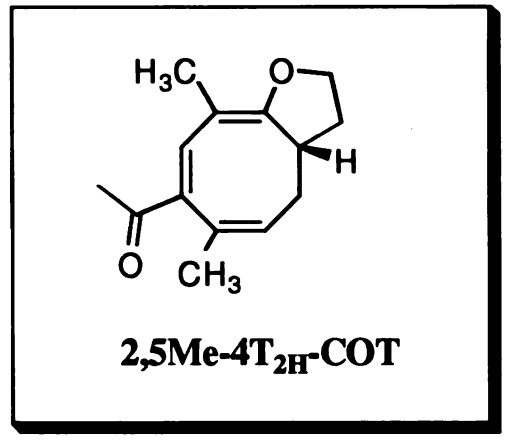
Table 14: Quantum Yield Determination of **2,5Me-4T$_{2H}$-CB** at 313 nm in methanol



2,5Me-4T$_{2H}$-CB

GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=95°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[2,5Me-4T$_{2H}$-COT]**=0.000312M [Valerophenone]=0.1021M in benzene [Ethyl phenylacetate]=0.00993M in benzene
After Irradiation	**[2,5Me-4T$_{2H}$-CB]**=0.0000927M *** [Acetophenone]=0.0008053M; I=0.00244
Quantum Yield	0.038
***	Determined by UV Spectroscopy by ΔOD

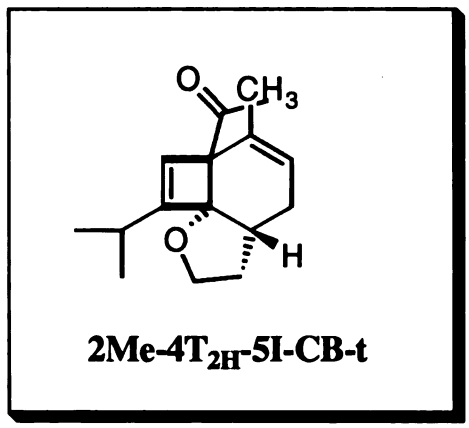
Table 15: Quantum Yield Determination of **2,5Me-4T$_{2H}$-COT** at 313 nm in methanol



2,5Me-4T$_{2H}$-COT

GC Conditions for Cyclooctatriene	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=145°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=100°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[2,5Me-4T$_{2H}$-K]**=0.0103M in methanol [n-heptyl benzoate]=0.00102M in methanol [Valerophenone]=0.0996M in benzene [Ethyl phenylacetate]=0.0108M in benzene
After Irradiation	**[2,5Me-4T$_{2H}$-COT]**=0.000708M [Acetophenone]=0.00593M; I=0.01796
Quantum Yield	0.039

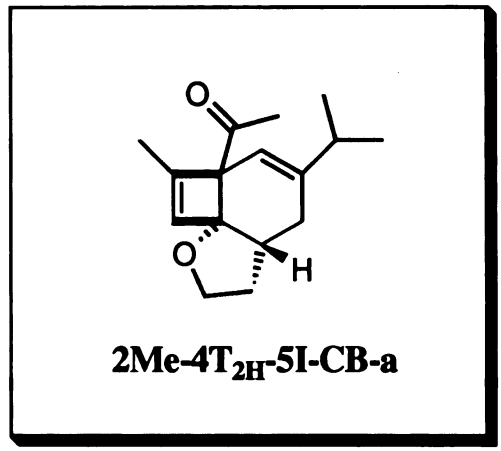
Table 16: Quantum Yield Determination of **2Me-4T$_{2H}$-5I-CB-t** at 313 nm in methanol



2Me-4T$_{2H}$-5I-CB-t

GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=95°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[2Me-4T$_{2H}$-5I-COT-t]**=0.00039M [Valerophenone]=0.1019M in benzene [Ethyl phenylacetate]=0.01105M in benzene
After Irradiation	**[2Me-4T$_{2H}$-5I-CB-t]**=0.0000718M *** [Acetophenone]=0.0015934M; I=0.00483
Quantum Yield	0.015
***	Determined by UV Spectroscopy by ΔOD

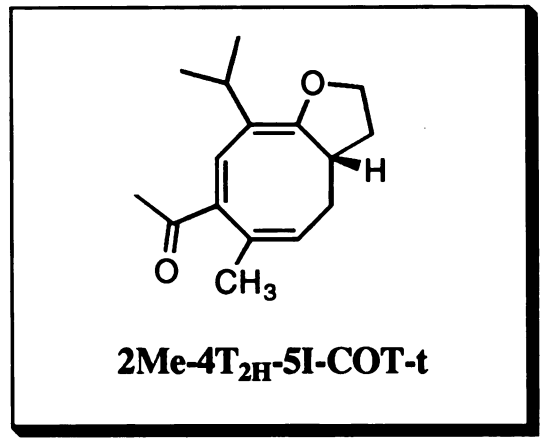
Table 17: Quantum Yield Determination of **2Me-4T$_{2H}$-5I-CB-a** at 313 nm in methanol



2Me-4T$_{2H}$-5I-CB-a

GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=95°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[2Me-4T$_{2H}$-5I-COT-a]**=0.000393M [Valerophenone]=0.0997M in benzene [Ethyl phenylacetate]=0.0095M in benzene
After Irradiation	**[2Me-4T$_{2H}$-5I-CB-a]**=0.000289M *** [Acetophenone]=0.000986M; I=0.00299
Quantum Yield	0.0967
***	Determined by UV Spectroscopy by ΔOD

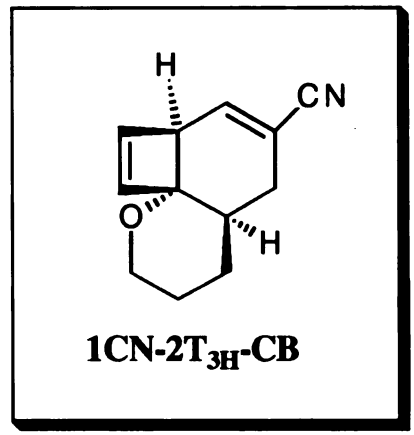
Table 18: Quantum Yield Determination of **2Me-4T$_{2H}$-5I-COT-t** at 313 nm in methanol



2Me-4T$_{2H}$-5I-COT-t

GC Conditions for Cyclooctatriene	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=135°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=95°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[2Me-4T$_{2H}$-5I-K]**=0.00993M in methanol [n-heptyl benzoate]=0.00104M in methanol [Valerophenone]=0.0991M in benzene [Ethyl phenylacetate]=0.00915M in benzene
After Irradiation	**[2Me-4T$_{2H}$-5I-COT-t]**=0.000218M [Acetophenone]=0.00168M; I=0.00509
Quantum Yield	0.0428

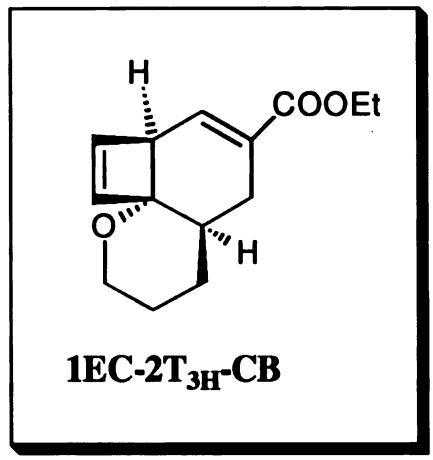
Table 19: Quantum Yield Determination of **1CN-2T$_{3H}$-CB** at 313 nm in acetone



1CN-2T$_{3H}$-CB

GC Conditions for **1CN-2T$_{3H}$-CB**	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=140°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=100°C, Injector=200°C, Detector=220°C.
Before Irradiation	[**1CN-2T$_{3H}$**]=0.01007M in acetone [n-heptyl benzoate]=0.001309M in acetone [Valerophenone]=0.1013M in benzene [Ethyl phenylacetate]=0.0108M in benzene
After Irradiation	[**1CN-2T$_{3H}$-CB**]=0.000528M [Acetophenone]=0.0204M; I=0.0618
Quantum Yield	0.00854

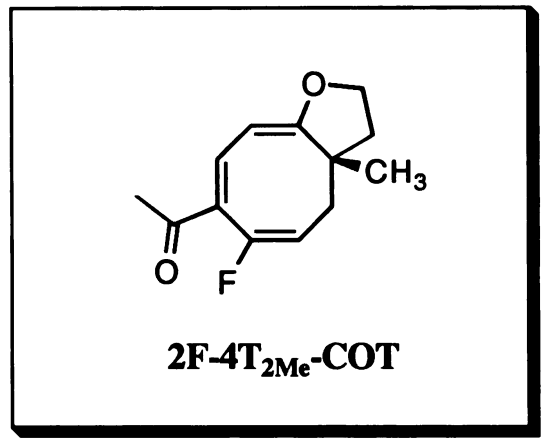
Table 20: Quantum Yield Determination of **1EC-2T$_{3H}$-CB** at 313 nm in acetone



1EC-2T$_{3H}$-CB

GC Conditions for **1EC-2T$_{3H}$-CB**	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=140°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=100°C, Injector=200°C, Detector=220°C.
Before Irradiation	**[1EC-2T$_{3H}$]**=0.0082M in acetone [n-heptyl benzoate]=0.00104M in acetone [Valerophenone]=0.1013M in benzene [Ethyl phenylacetate]=0.0108M in benzene
After Irradiation	**[1EC-2T$_{3H}$-CB]**=0.000696M [Acetophenone]=0.0204M; I=0.0618
Quantum Yield	0.0113

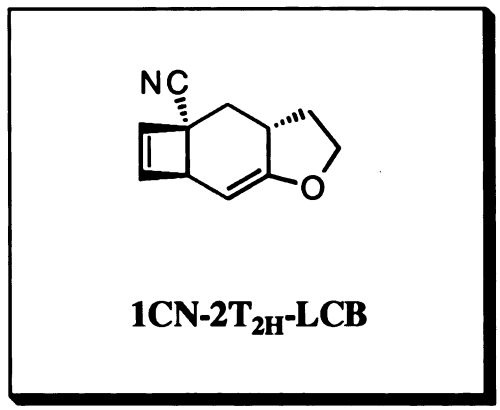
Table 21: Quantum Yield Determination of **2F-4T$_{2Me}$-COT** at 313 nm in methanol



2F-4T$_{2Me}$-COT

GC Conditions for Cyclooctatriene	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=140°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Injector=200°C, Detector=220°C,Column=ramped {70°C(9min)-140°C(10°C/min)-185°C}
Before Irradiation	[**2F-4T$_{2Me}$-K**]=0.0104M in methanol [n-heptyl benzoate]=0.001127M in methanol [Valerophenone]=0.10M in benzene [Dodecane]=0.0096M in benzene
After Irradiation	[**2F-4T$_{2Me}$-COT**]=0.0008372M [Acetophenone]=0.0109M; I=0.033
Quantum Yield	0.0025

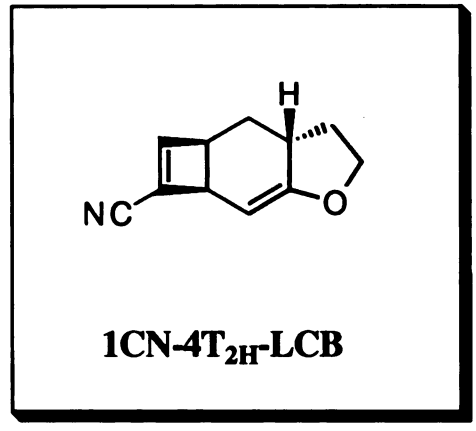
Table 22: Quantum Yield Determination of **1CN-2T$_{2H}$-LCB** at 313 nm in acetone



1CN-2T$_{2H}$-LCB

GC Conditions for **1CN-2T$_{2H}$-LCB**	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Column=135°C, Injector=200°C, Detector=220°C.
GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Injector=200°C, Detector=220°C,Column=ramped {70°C(5min)-100°C(10°C/min)-185°C}
Before Irradiation	[**1CN-2T$_{2H}$**]=0.01064M in acetone [n-pentyl benzoate]=0.001146M in acetone [Valerophenone]=0.09988M in benzene [Dodecane]=0.009624M in benzene
After Irradiation	[**1CN-2T$_{2H}$-LCB**]=0.0007934M [Acetophenone]=0.01644M; I=0.0498
Quantum Yield	0.0159

Table 23: Quantum Yield Determination of **1CN-4T$_{2H}$-LCB** at 313 nm in methanol

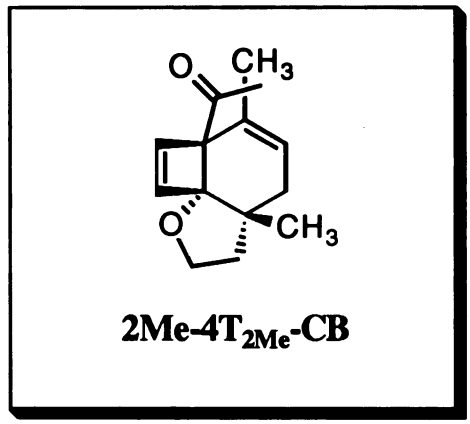


1CN-4T$_{2H}$-LCB

GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Injector=200°C, Detector=220°C,Column=ramped {70°C(5min)-100°C(10°C/min)-185°C}
Before Irradiation	**[1CN-4T$_{2H}$-COT]**=0.000267M [Valerophenone]=0.1008M in benzene [Dodecane]=0.00285M in benzene
After Irradiation	**[1CN-4T$_{2H}$-LCB]**=0.0000957M *** [Acetophenone]=0.000579M; I=0.001755
Quantum Yield	0.0545

*** Determined by UV Spectroscopy by ΔOD

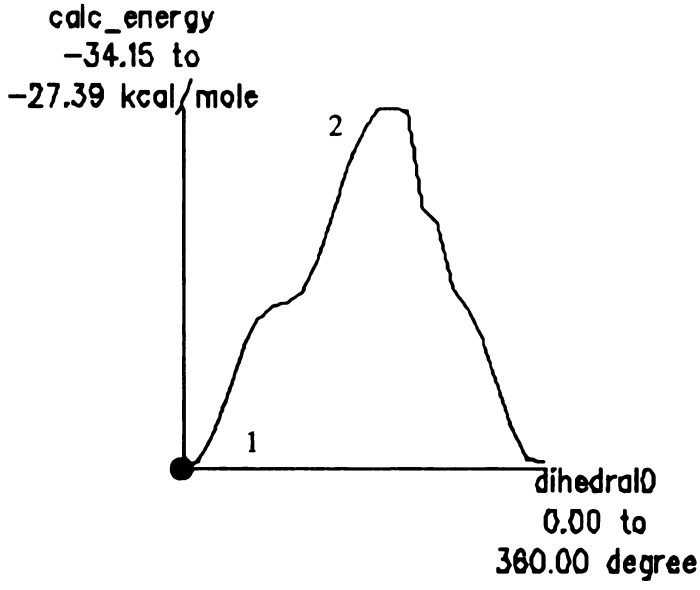
Table 24: Quantum Yield Determination of **2Me-4T$_{2Me}$-CB** at 313 nm in methanol

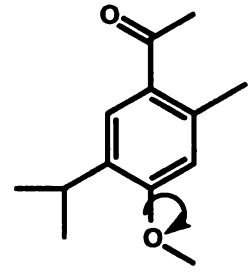


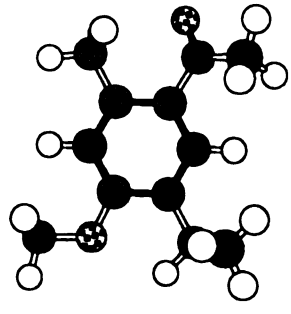
2Me-4T$_{2Me}$-CB

GC Conditions for Valerophenone Act.	3400 Varian GC, He = 25 mL/min DB-210 Megabore Column (15 meters) Injector=200°C, Detector=220°C,Column=ramped {70°C(5min)-100°C(10°C/min)-185°C}
Before Irradiation	**[2Me-4T$_{2Me}$-COT]**=0.000336M [Valerophenone]=0.0994M in benzene [Dodecane]=0.00939M in benzene
After Irradiation	**[2Me-4T$_{2Me}$-CB]**=0.0001044M *** [Acetophenone]=0.00124M; I=0.00377
Quantum Yield	0.0277
***	Determined by UV Spectroscopy by ΔOD

AM1 Calculation of the Rotational Barrier in 5-isopropyl-2-methyl-4-methoxyacetophenone

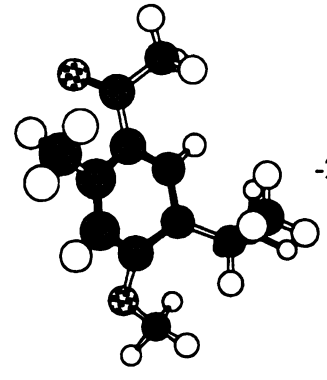






-34.15 Kcals/mol

1



-27.4 Kcals/mol

2

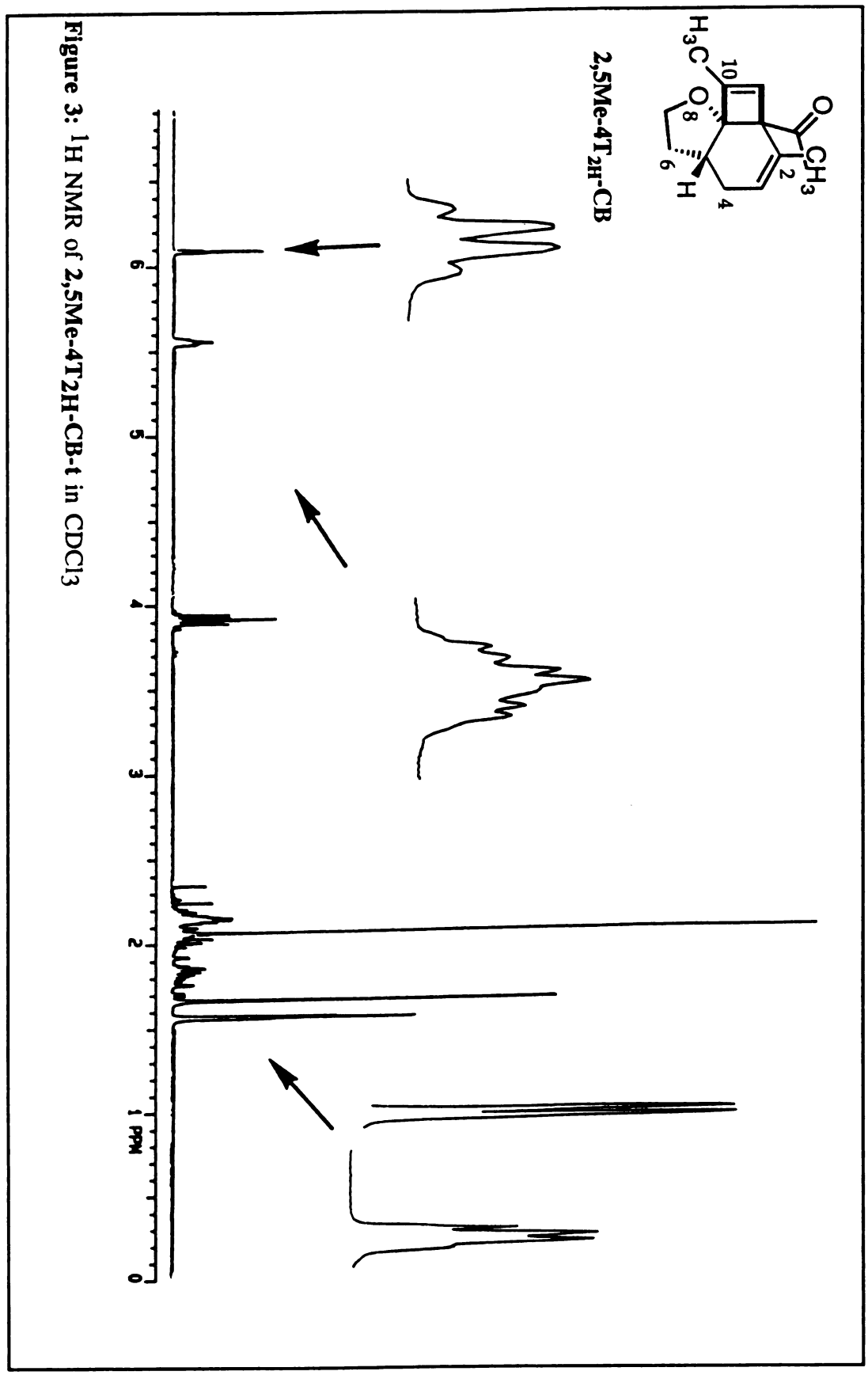


Figure 3: ^{1}H NMR of **2,5Me-4T2H-CB-t** in $CDCl_3$

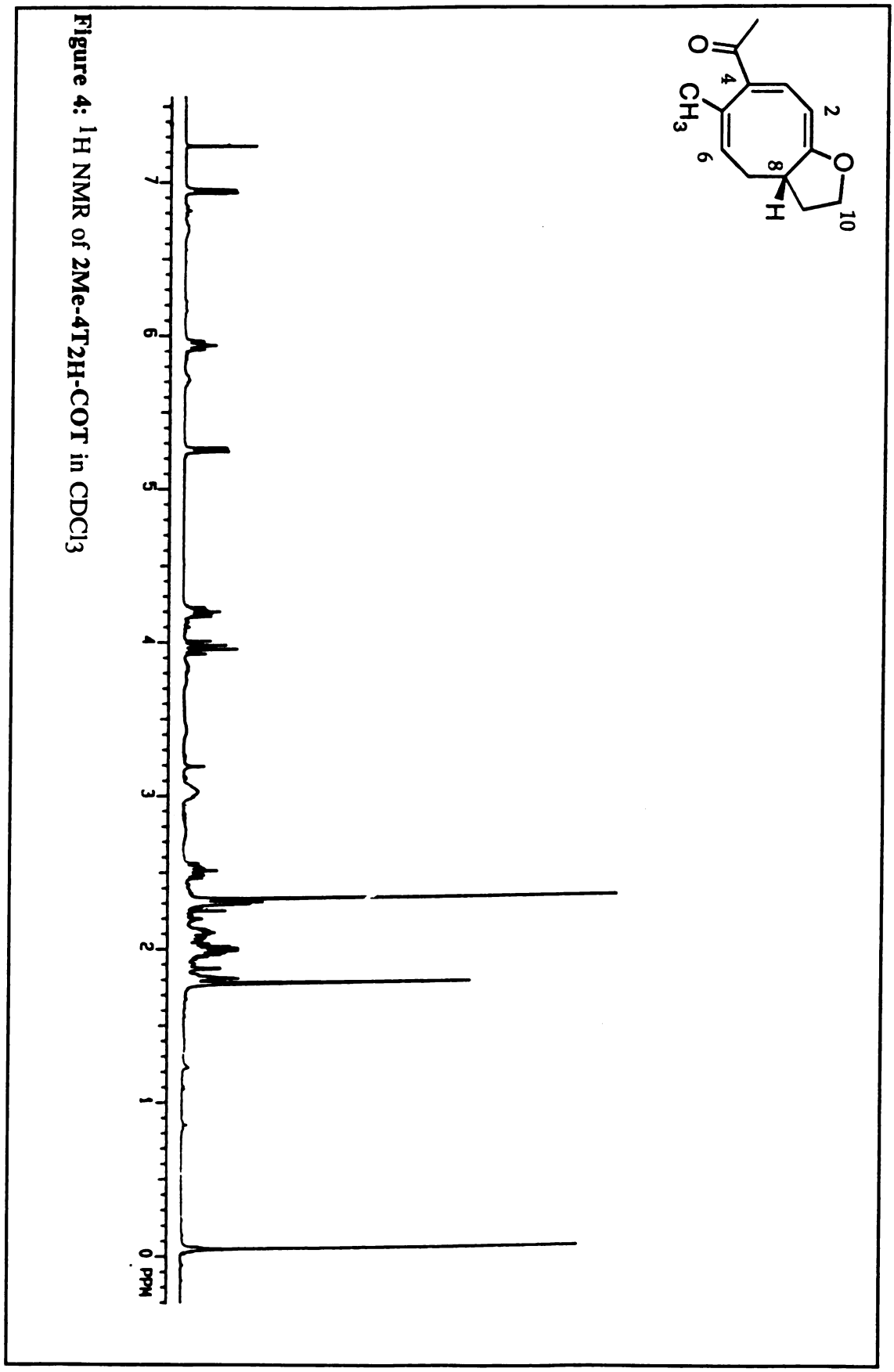


Figure 4: ^{1}H NMR of **2Me-4T2H-COT** in $CDCl_3$

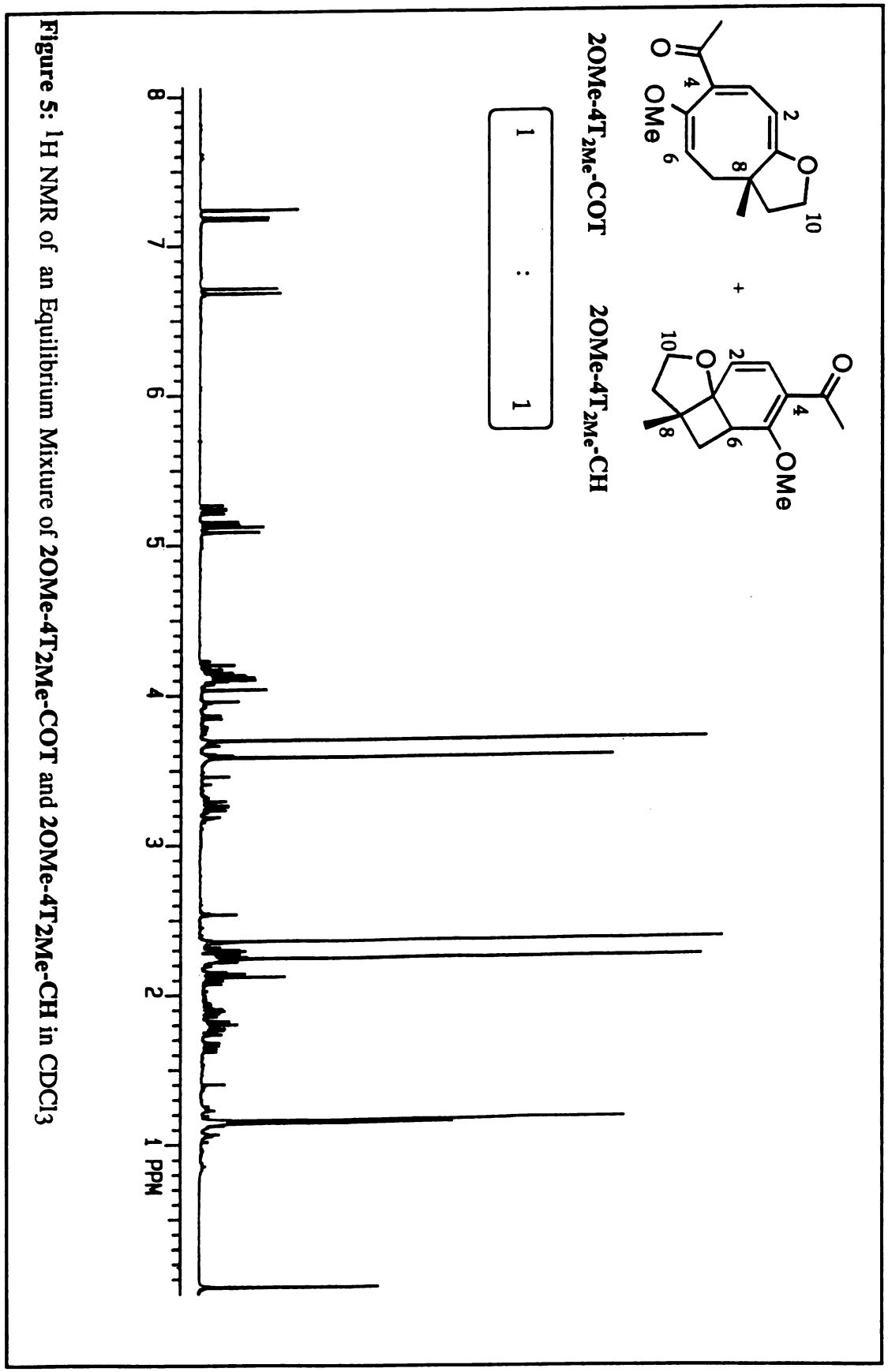


Figure 5: ^{1}H NMR of an Equilibrium Mixture of **2OMe-4T2Me-COT** and **2OMe-4T2Me-CH** in $CDCl_3$

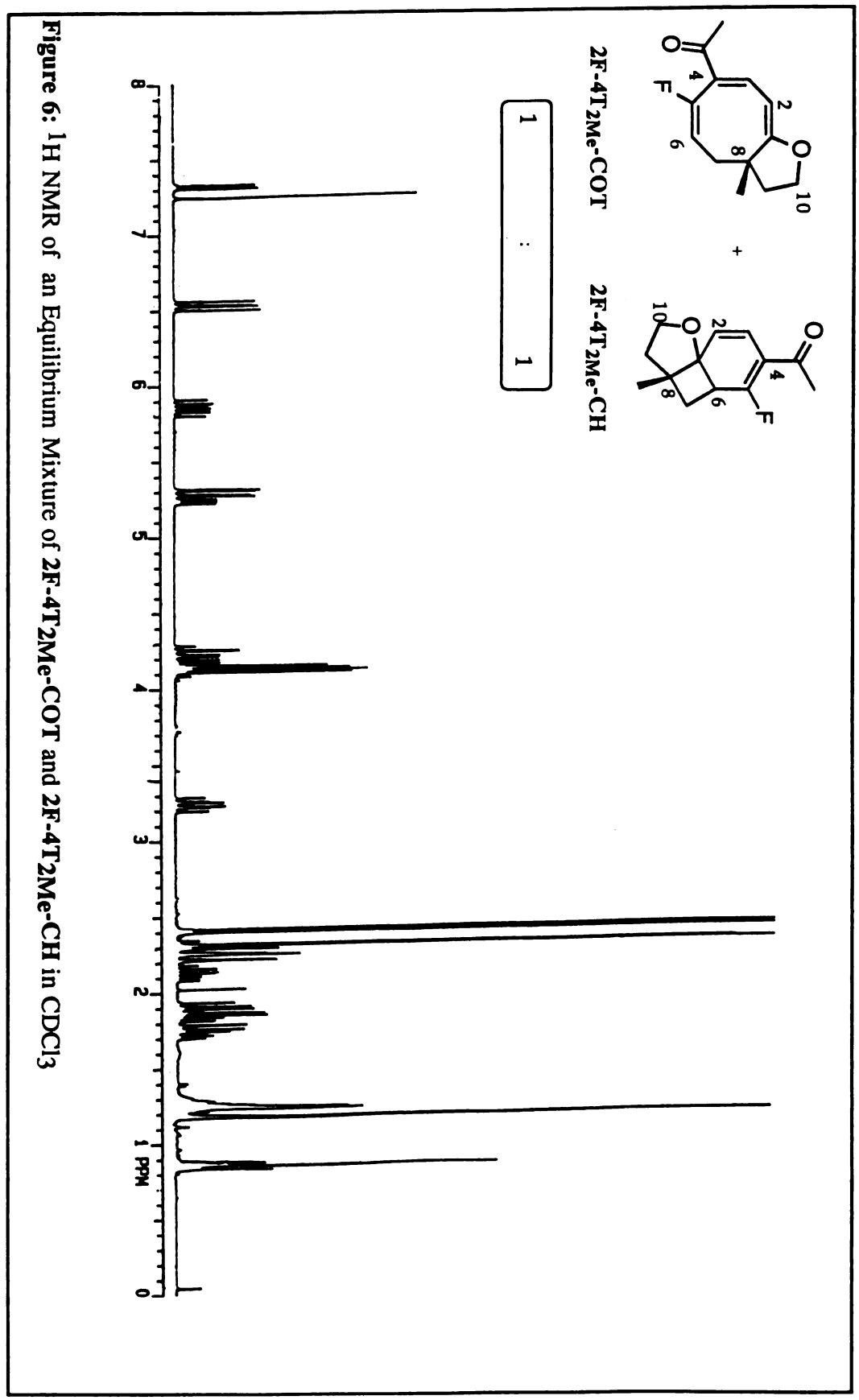


Figure 6: ^{1}H NMR of an Equilibrium Mixture of **2F-4T2Me-COT** and **2F-4T2Me-CH** in $CDCl_3$

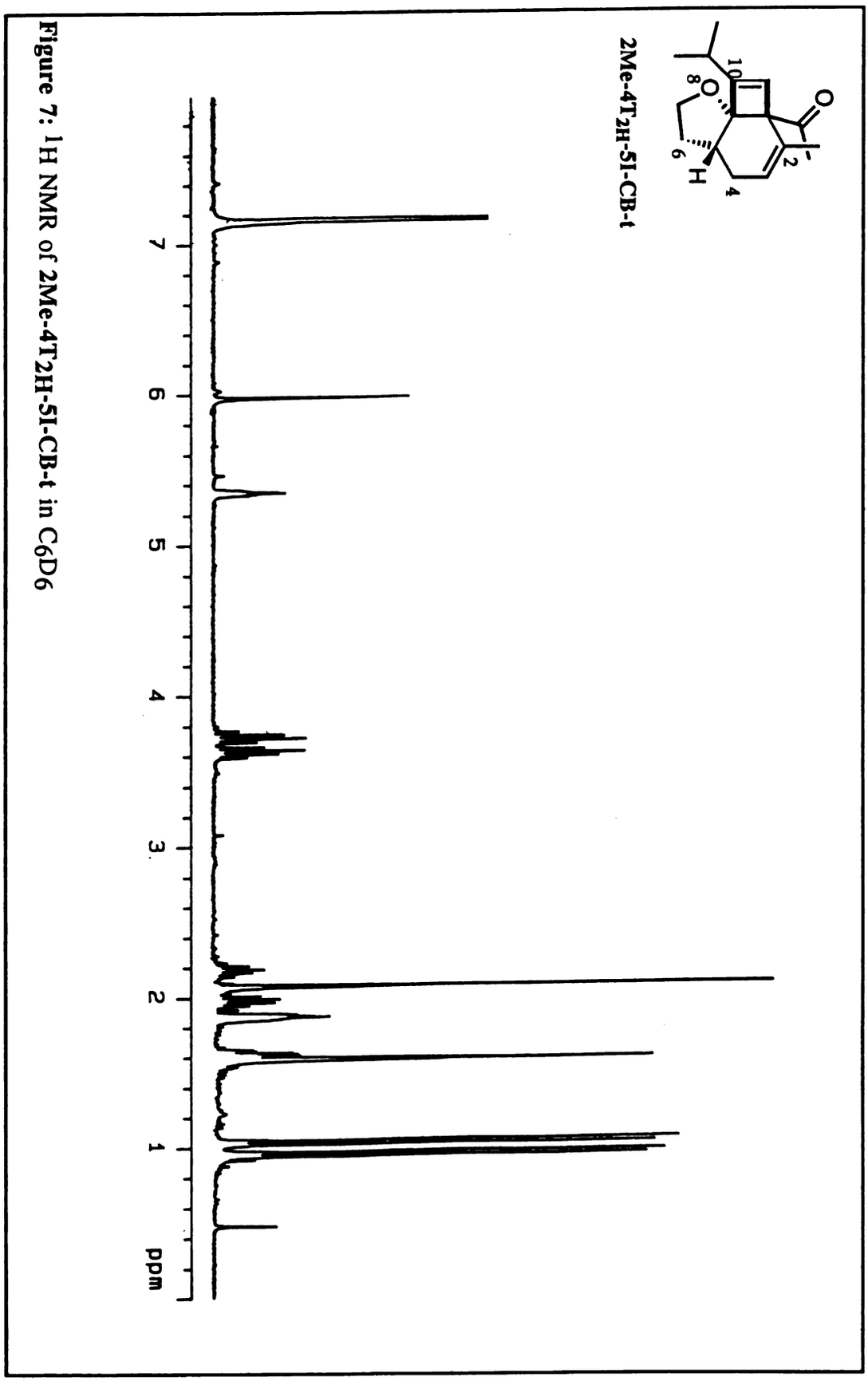


Figure 7: ^{1}H NMR of **2Me-4T2H-5I-CB-t** in C_6D_6

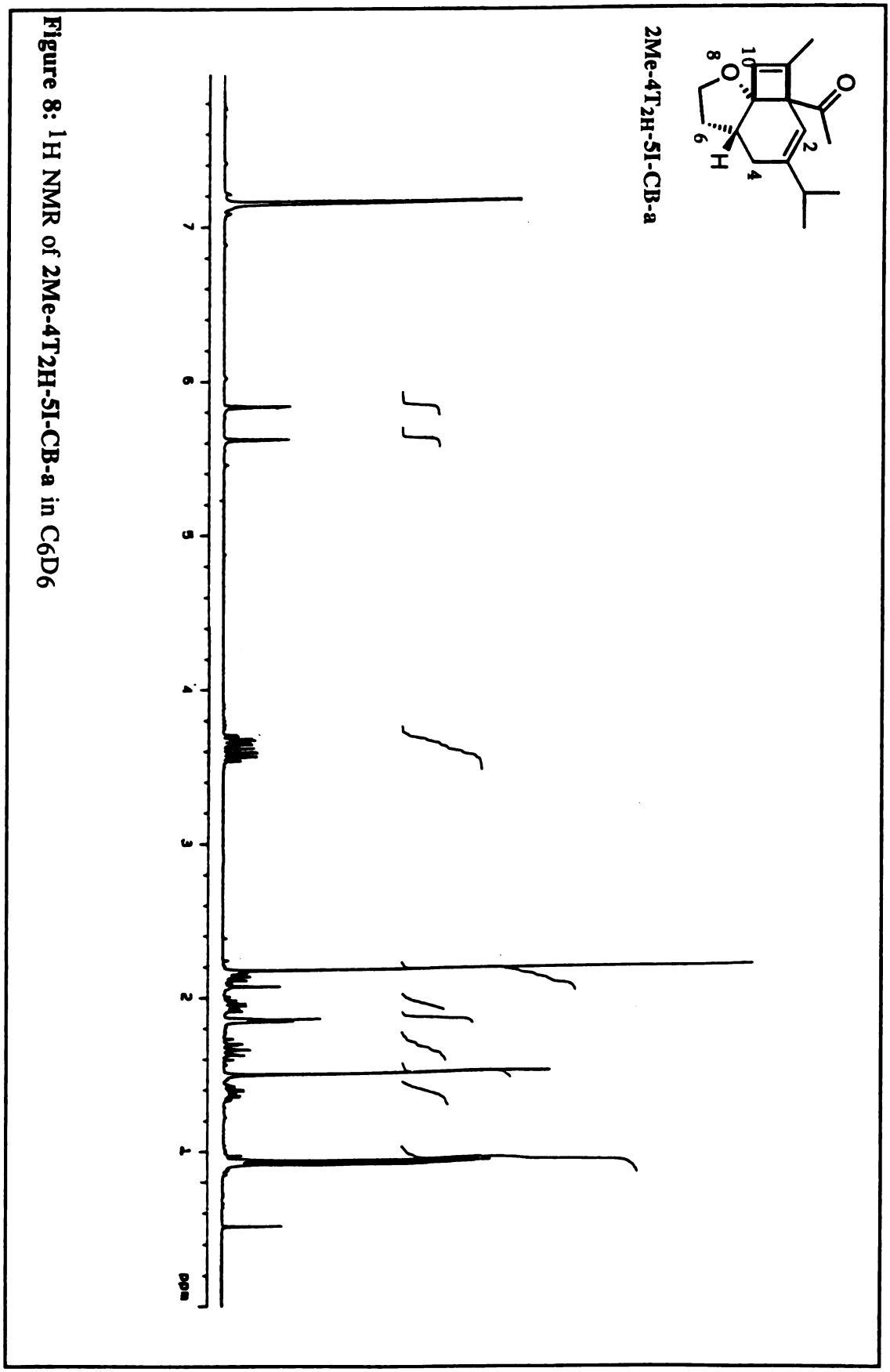


Figure 8: ^{1}H NMR of **2Me-4T2H-5I-CB-a** in C_6D_6

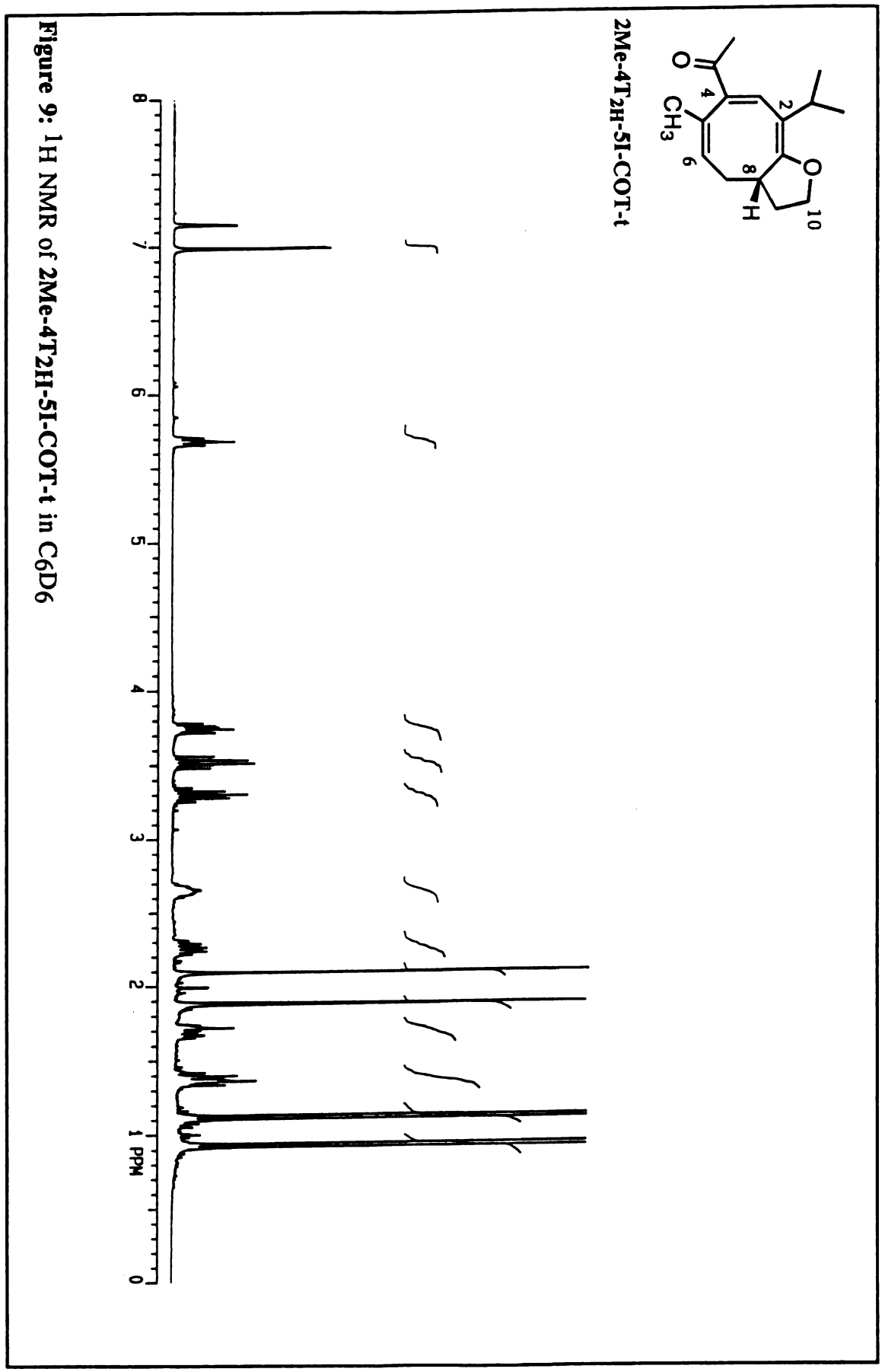


Figure 9: ^{1}H NMR of **2Me-4T2H-5I-COT-t** in C_6D_6

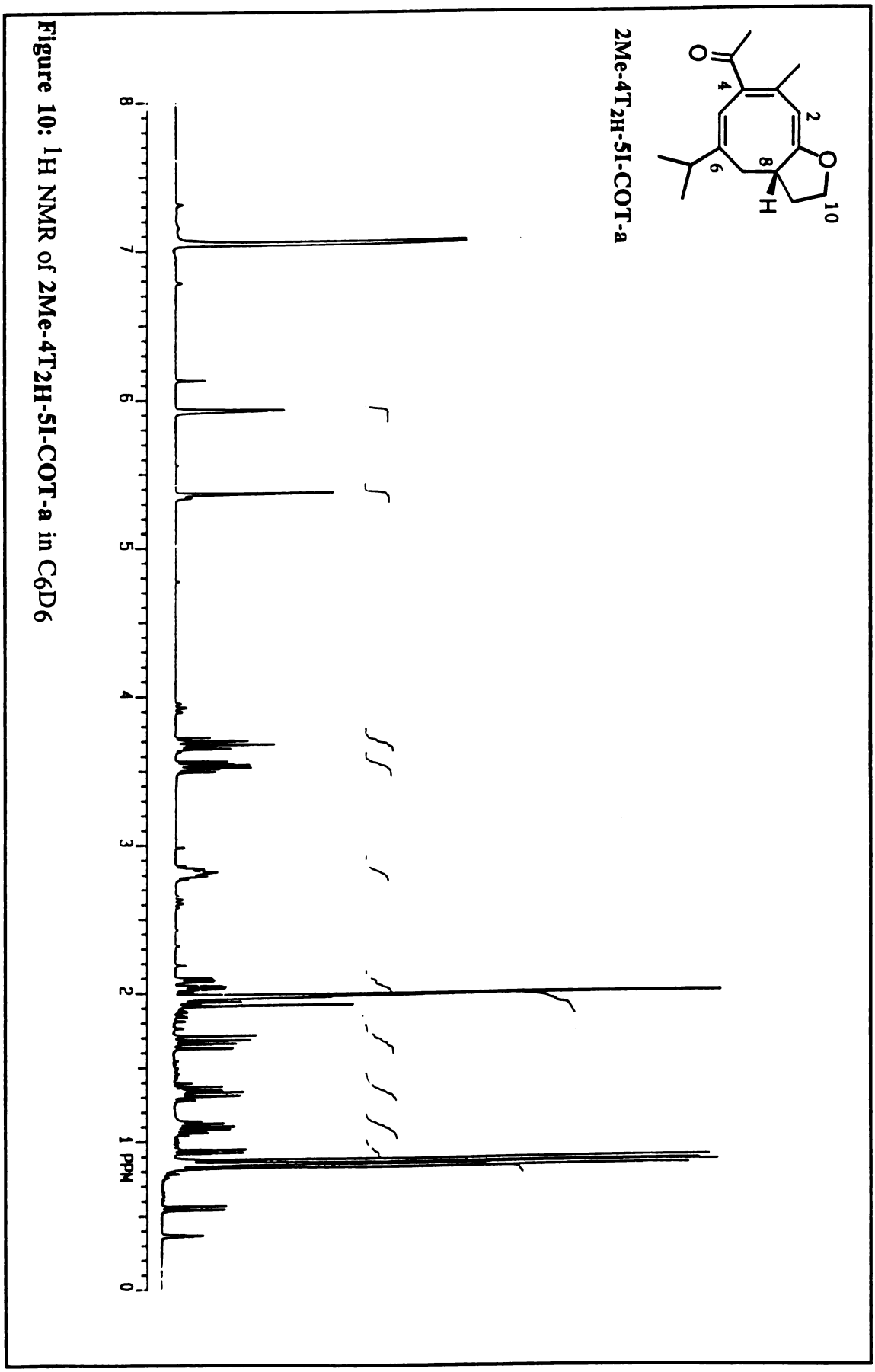
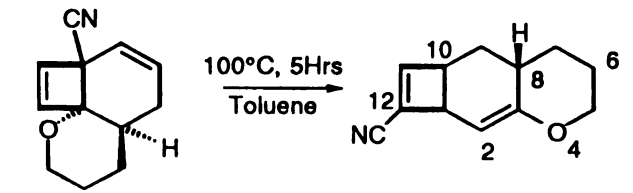


Figure 10: ^{1}H NMR of **2Me-4T2H-5I-COT-a** in C_6D_6



100°C, 5Hrs
Toluene

1CN-4T3H-CB

1CN-4T3H-COPE

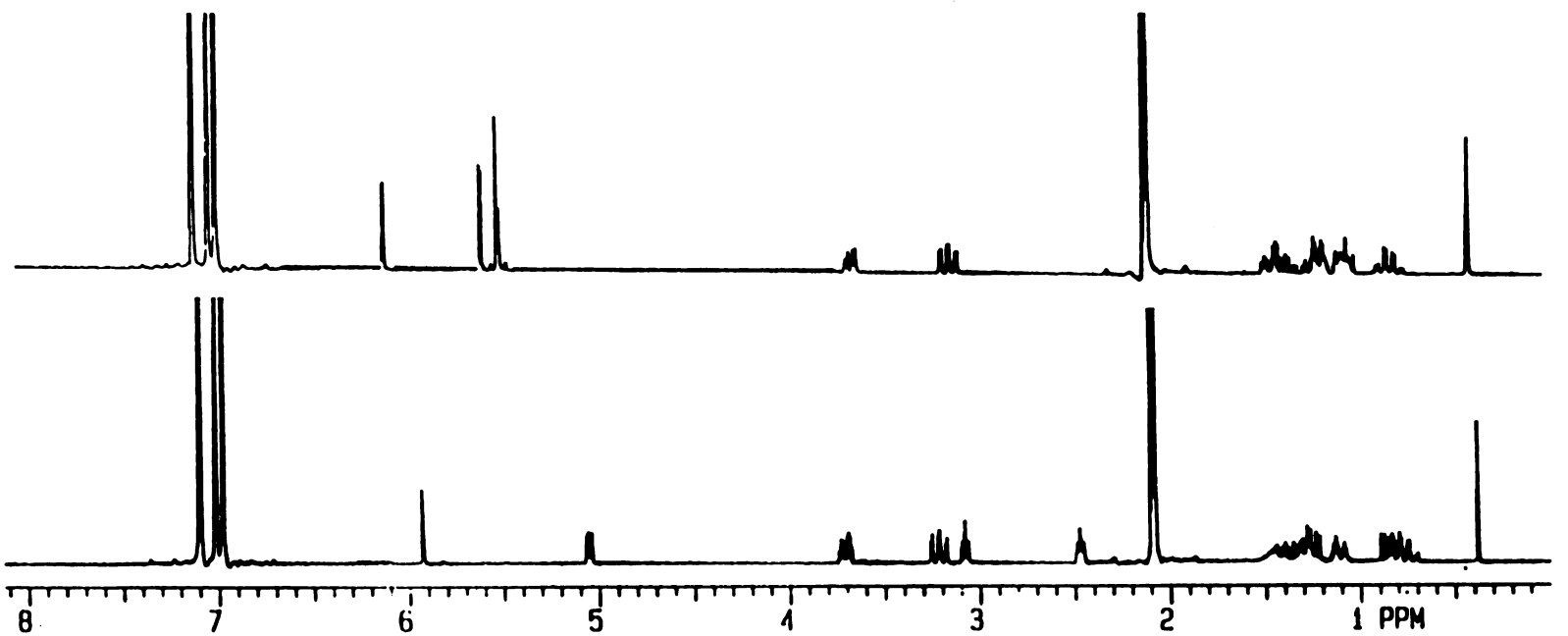


Figure 11: ^{1}H NMR of **1CN-4T3H-CB** (bottom) and **1CN-4T3H-COPE** (top) in toluene-d8

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