THE FAR ULTRAVIOLET PHOTOCHEMISTRY OF ALKYL-SUBSTITUTED CYCLOBUTENES

by

KENNETH BRADY CLARK, B.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
In Partial Fulfillment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
December, 1987

DOCTOR OF PHILOSOPHY (1987)
(CHEMISTRY)

McMaster University
Hamilton, Ontario

TITLE: The Far Ultraviolet Photochemistry of Alkyl-Substituted Cyclobutenes

AUTHOR: KENNETH BRADY CLARK, B.Sc. (McMaster University)

SUPERVISOR: Dr. William J. Leigh

NUMBER OF PAGES: xii, 176

ABSTRACT

Electrocyclic reactions of ground and excited state hydrocarbons are well known. These transformations have helped to form a basis on which modern organic chemistry has been built. For a variety of reasons, the photochemical transformations of one of the simplest systems, the cyclobutene system, are not well understood. This thesis attempts to provide the first thorough and systematic study of the excited state behaviour of cyclobutene in solution. The direct photochemistry of some simple, alkyl-substituted derivatives of cyclobutene is the main concern of the following chapters; the prime concern of the thesis is on the stereochemistry of the photochemical electrocyclic ring opening process.

Ten cyclobutene systems were synthesized with a view to delineating the path of formal electrocyclic ring opening, formal $[\sigma 2_s + \sigma 2_s]$ cycloreversion, and the possible rôle of intermediates in the photochemistry of these systems. These studies have revealed that, in general, photochemical ring opening of cyclobutenes with monochromatic far ultraviolet (185, 193, and 214nm) light sources in solution proceeds non-stereospecifically to yield mixtures of all the corresponding diene geometric isomers. These results appear to contradict orbital symmetry selection rules.

Ultraviolet absorption spectra and the dependence of the photochemistry on excitation wavelength have been studied in hydrocarbon solution in order to investigate the possible involvement of two or more excited states in the direct photochemistry of these compounds. The

direct photochemistry of these cyclobutene derivatives shows varying degrees of wavelength dependence throughout the series. In addition, far UV irradiations have been carried out in a hydrocarbon liquid at low temperatures, in order to study the dynamics of the formal electrocyclic ring opening process. These studies have shown that a slight barrier exists for the formally forbidden conrotatory process relative to the formally allowed disrotatory process.

It is not possible to correlate these results within the framework of the most recently calculated (ab initio) state correlation diagrams for the ground and excited state interconversions of butadiene and cyclobutene. The results of this thesis contradict the most recent ab initio calculations, which predict that the process should proceed stereospecifically in a disrotatory fashion for the π,π^* excited state of cyclobutene, indicating possibly that the theoretical work does not adequately describe the excited state character of cyclobutene or at least that theoretical results for cyclobutene itself cannot be extrapolated to substituted systems.

ACKNOWLEDGEMENTS

I would like to thank Willie Leigh for his direction over the last four years. As my supervisor, I benefitted greatly from Willie's unparalleled interest and enthusiasm for chemistry, for in the face of fire, flood, and the occasional threat of terrorism, Willie has taught me how to get the job done. As a friend, I thank him for taking my moods in stride and listening to my concerns.

To my labmates, Brian and Scott, I thank you for your friendship and for the support you have shown me. Thanks also to my lab neighbour George Timmins for his assistance in things ranging from the periodic loan of equipment, to lessons in the fine art of column packing. The best of luck guys and may the good Lord take a liking to you!

I thank Dr. Werstiuk for obtaining the UV photoelectron spectra of some of the compounds studied within this thesis and for giving freely of his time to explain the ways of PES.

To my good friends Howard and Julie, whom I appreciate for sharing in the trials and tribulations of the last few years, thanks for being there.

I thank my brother-in-law Michael Frendo, who gave up many hours to help print this thing out.

And special thanks to Debbie, my patient and loving wife who has gracefully put up with an often preoccupied and self-centred husband. I have been surely blessed.

TABLE OF CONTENTS

CHAPTER I: Introduction 1

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

Introduction

1.1 General

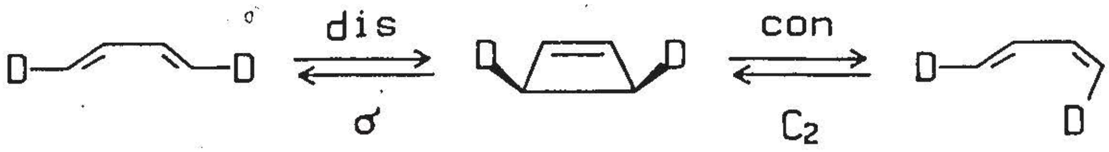
The interconversions of cyclobutene and 1,3-butadiene occupy a position of prominence in the theory of orbital symmetry and electrocyclic reactions. Indeed, this system is one of the principal examples furnished in the famous papers by Woodward and Hoffmann on the stereochemistry of electrocyclic reactions[1-3] and is the prime example put forth in Abrahamson and Longuet-Higgins' paper on electrocyclic reactions.[4] Since that time the thermal chemistry of this system has been studied exhaustively. Marvel has written an extensive review covering the experimental and theoretical results that have been reported on the thermal character of this system.[5] The vast collection of data has established an excellent understanding of the chemistry occurring in the ground state manifold.

The symmetry-allowed disrotatory photochemical electrocyclic closure of 1,3-butadiene to cyclobutene generally appears to be experimentally[6-13] and theoretically[14-18] well understood. The reverse process, the symmetry-allowed disrotatory ring opening of simple cyclobutenes however, is poorly documented. In spite of the intense activity of organic photochemistry over the last twenty years there is little documentation on the direct photochemistry of simple cyclobutenes.[19-21] In considering the central nature of this strategic molecule to the development of the theory of conservation of orbital symmetry and that theory's role in our understanding of pericyclic reactions,[3] it is surprising that the photochemistry of cyclobutene and its simple derivatives has been, for the most part, ignored.

1.2 The Theory of the Conservation of Orbital Symmetry

The development of a general theory of electrocyclic reactions (the theory actually encompasses all pericyclic reactions) has been attained primarily through the efforts of Woodward and Hoffmann. In their work the most simple but fundamental ideas of molecular orbital theory were used to rationalize and predict the stereochemical course of virtually any concerted organic reaction, including the interconversion of cyclobutene and 1,3-butadiene. These concepts include symmetry, overlap, interaction, bonding and the nodal structure of wave functions. Woodward and Hoffmann recognized that phase relations among p-orbitals in conjugated systems such as butadiene resulted in orbital interaction via cyclic transition states under favourable conditions. An energetically favourable transition to bonding orbitals in the product would result only via certain rotational operations and these orbital conversions could be mapped using simple symmetry operations and orbital correlation diagrams.

In order to illustrate the method at work consider the example put forth first by Woodward and Hoffmann.[1] The two possible modes of converting cyclobutene to 1,3-butadiene are conrotatory and disrotatory motions (Scheme 1.1). Woodward and Hoffmann emphasized that the stereochemical course of an electrocyclic reaction is determined by the symmetry of the highest occupied molecular orbital (HOMO) of the



SCHEME 1.1 Con- and disrotatory motions of the butadiene-cyclobutene interconversions.

reactant. In their original procedure, extended Huckel Theory was used to show that the symmetry of the highest occupied molecular orbital determines the course of a reaction. When symmetry of the proper kind is present, as in the cyclobutene molecule, orbital correlation diagrams may be constructed in order to qualitatively predict reaction pathways (this method was actually first implemented for the cyclobutene-butadiene system by Abrahamson and Longuet-Higgins[4]). The procedure consists of constructing orbital correlation diagrams for the molecular orbitals of the reactant as well as product and classifying the levels with respect to the symmetry properties of the transition state (Fig. 1.1). In the electrocyclic process the four molecular orbitals of cyclobutene undergo change as they pass adiabatically into those of the product. The symmetry elements present in the reactant and the product must be defined. How the orbitals of the two species are correlated depends on the mode of isomerization, i.e. conrotatory or disrotatory motion. The participating orbitals in reactant and product are then classified as symmetric (S) or antisymmetric (A) with respect to the previously defined symmetry element. The correlation diagram is then constructed and each orbital is then connected with "conservation of symmetry", into an

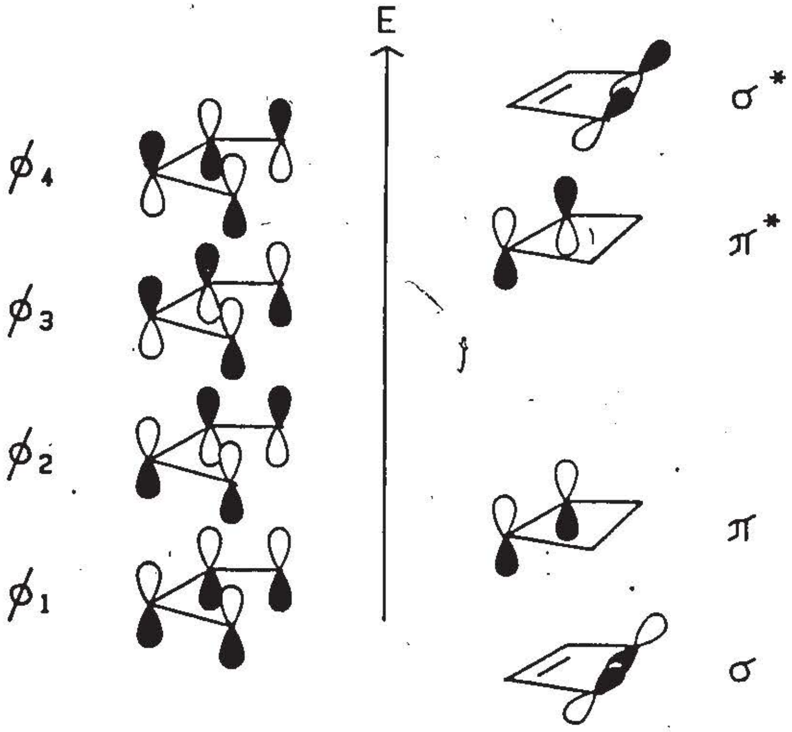


FIGURE 1.1 Molecular orbitals and their approximate relative energies for the butadiene-cyclobutene interconversions.

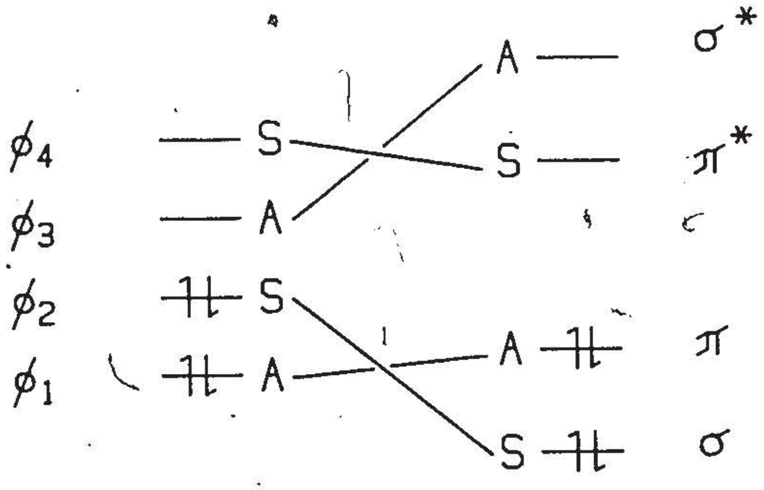


FIGURE 1.2 Correlation diagram for the thermally-allowed interconversion of butadiene and cyclobutene.

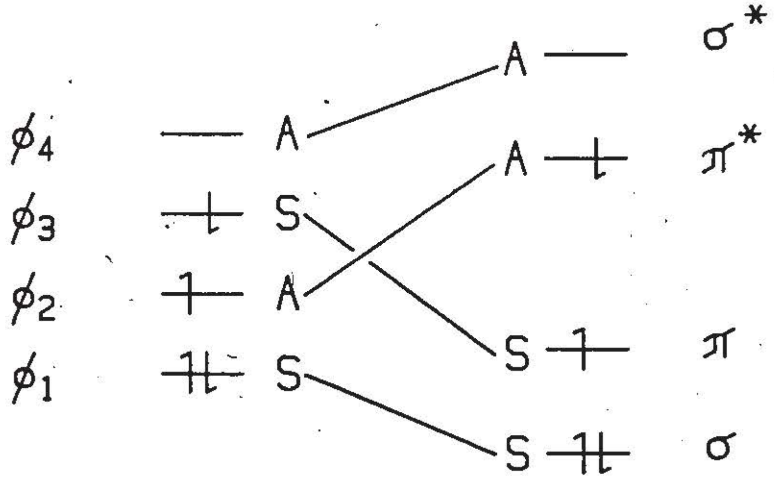


FIGURE 1.3 Correlation diagram for the allowed photochemical interconversion of butadiene and cyclobutene.

orbital of the product as in Figures 1.2 and 1.3 for con- and disrotatory interconversions, respectively. The orbital correlation diagrams reveal that the ground state of butadiene, $\phi_1{}^2\phi_2{}^2$, correlates directly with the ground state of cyclobutene, $\sigma^2\pi^2$, only for the conrotatory intercon-version pathway (C_2 symmetry maintained). This pathway is thus thermally allowed, in contrast to the symmetry forbidden disrotatory path which correlates $\phi_1{}^2\phi_2{}^2$ with a doubly excited state, $\sigma^2\pi^{*2}$, of cyclobutene.

Photolysis results in π,π^* excitation, one π electron has been promoted to the next highest orbital, the π^* orbital. In undergoing disrotatory motion the system maintains a plane of symmetry (contrary to conrotation which maintains a C_2 axis of symmetry). As shown in Figure 1.3, the first excited state of butadiene correlates with that of cyclobutene and the photochemical disrotatory interconversion is therefore regarded as symmetry-allowed. The correlation diagram of Figure 1.2 reveals that photochemical interconversion via conrotatory motion correlates the first excited state of butadiene, $\phi_1{}^2\phi_2{}^1\phi_3{}^1$, with an upper excited state of the product, $\sigma\pi^2\sigma^*$, and is hence symmetry-forbidden.

From these examples it becomes obvious that it is the effect on the π orbital, the HOMO of cyclobutene, which determines whether the reaction is symmetry-allowed or symmetry-forbidden. The HOMO is usually thought of as containing the most easily perturbed electrons in the molecule during reaction; in light of this, the conclusion above is not surprising. Longuet-Higgins and Abrahamson supplemented this theory by pointing out that the reaction was also controlled by the product HOMO as shown above.

Marvel has provided a summary of early theoretical approaches to

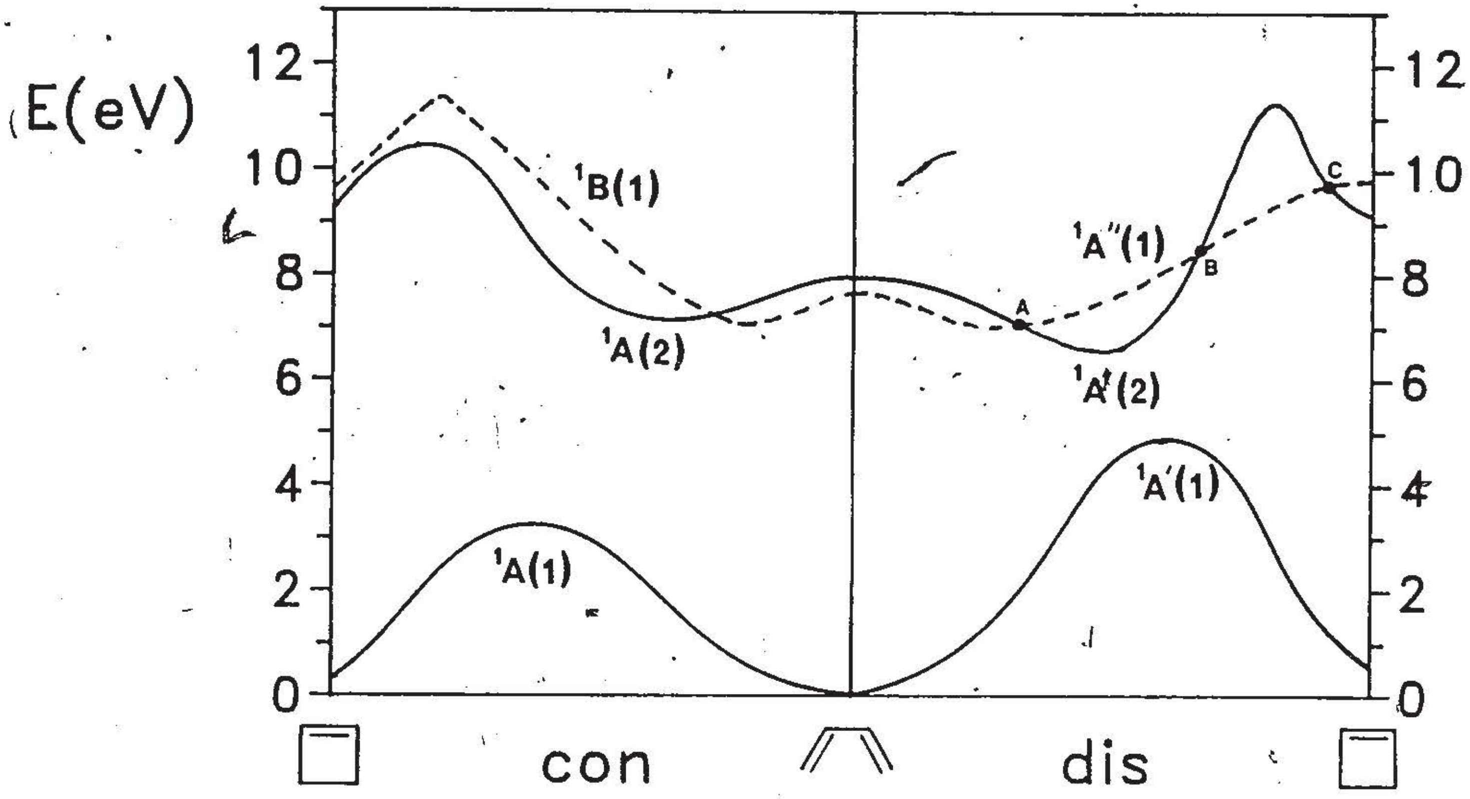
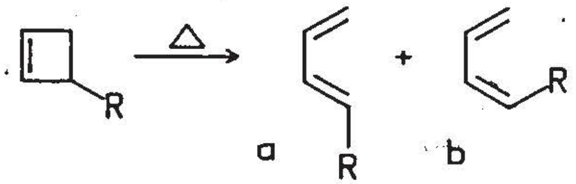


FIGURE 1.4 Calculated potential energy curves for the ground and excited state con– and disrotatory interconversions of cyclobutene and 1,3–butadiene.

the electrocyclic processes of the cyclobutene/butadiene interconversion.[5] More recent ab initio calculations for the ground and excited state interconversions[18] afford the same predictions as the qualitative correlation diagrams do (Fig 1.4). These calculations show the transition state for the thermally forbidden disrotatory opening/closure to be ca. 15 kcal/mol higher in energy than that for the conrotatory process. Thermally, therefore, conrotatory opening/closure is an energetically more favourable path.

Houk and coworkers[22-24] have recently developed a theory to explain the tendency for (a) outward versus (b) inward conrotation of a substituent (**R**) as a function of its electron-donating character (Eqn 1.1).

1.1)

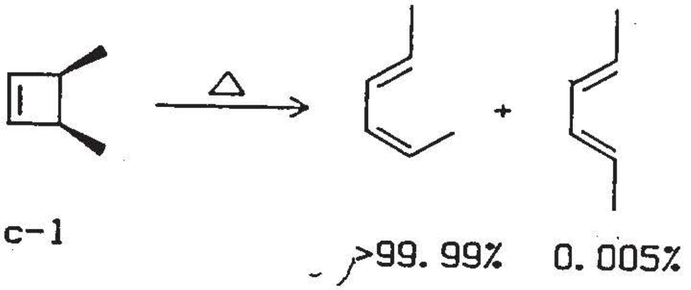


1.3 Thermal Electrocyclic Reactions

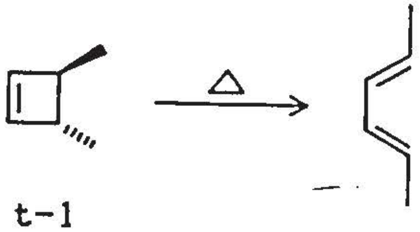
Marvel, in his excellent review of thermal electrocyclic reactions, has devoted an entire chapter to thermal cyclobutene-butadiene interconversions.[5]

As the simple theory predicts, the thermal ring opening of cyclobutenes to 1,3-butadienes is stereospecific, and proceeds in a conrotatory fashion as reported in the majority of cases studied. Generally, the ring opening is reported to go smoothly to completion in solution or in the gas phase at temperatures ranging from approximately 120°C to 200°C. Brauman and Archie have shown that the thermal ring opening of cis-3,4-dimethyl-cyclobutene, **c-1**, in the gas phase at 280°C proceeds with greater than 99.99% stereospecificity and yields only

1.2

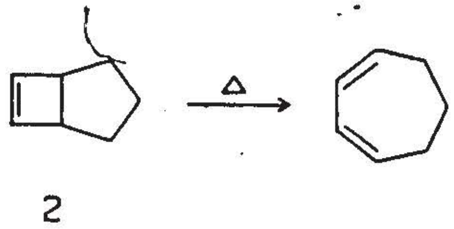


1.3

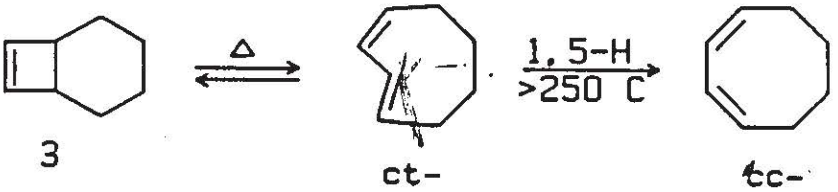


ca. 0.005% of the symmetry-forbidden product, trans,trans-2,4-hexadiene (Eqn 1.2).[25] From this result it was inferred that the transition state for conrotatory opening experiences ≥15 kcal/mol added electronic stabilization compared to the transition state for disrotatory opening. This result agrees well with the recent theoretical calculations discussed earlier. Winter reported that the pyrolysis of trans-3,4-dimethylcyclobutene, **t-1**, leads to just one product, the symmetry-allowed trans,trans-2,4-hexadiene (Eqn 1.3).[26] The other formally allowed diene isomer, cis,cis-2,4-hexadiene was not observed, indicating that this pathway is subject to a substantially higher activation barrier, presumably a result of the un-favourable effects of methyl group interaction as ring opening proceeds.

1.4



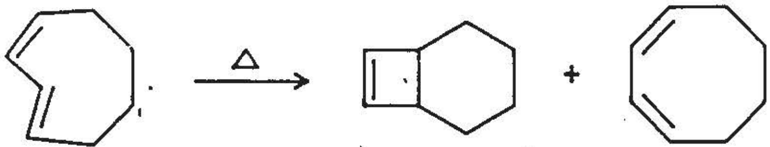
1.5



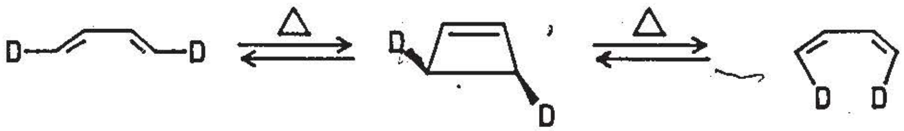
Unlike the monocyclic systems, fused cyclobutenes 2 and 3 are thermally stable. Bicyclo[3.2.0]hept-6-ene (2) does not isomerize below ca. 380°C.[27] At 380°C 2 undergoes electrocyclic opening to afford the formally forbidden cis,cis-1,3-cycloheptadiene (Eqn 1.4), while bicyclo[4.2.0]oct-7-ene (3) undergoes isomerization to formally forbidden cis,cis-cyclooctadiene at ca. 250°C.[28] Symmetry-allowed conrotatory ring opening requires the formation of highly strained cis,trans-dienes. The annelated cyclobutenes are postulated to undergo ring opening via the symmetry-forbidden pathway, with high activation energies to yield cis,cis-diene isomers because the allowed one is rendered inaccessible by ring constraint. More careful studies of 3 have resulted in the observation of the cis,trans-diene.[29,30] A mechanism involving symmetry-controlled ring opening to cis,trans-diene followed by a 1,5-H shift, as shown in Eqn 1.5, has been postulated to account for the observation of only symmetry-forbidden cis,cis-diene at 250°C or greater.[30] RRKM calculations have indicated that this pathway may be available to **2** at 380°C, which would account for the apparent stereochemistry of its thermal ring opening.[27] Cis-fused bicyclo[5.2.0]non-7-ene (c-**4**) undergoes stereospecific conrotatory ring opening to afford an equilibrium mixture of the cyclobutene and trans-1,3-cyclononadiene at 200°C.[31]

There are very few examples of the reverse process which, considering the heats of formation of cyclobutene (ΔH_f = 37.5 kcal/mol) and 1,3-butadiene (ΔH_f = 26.3 kcal/mol), is not surprising. Most known examples involve highly strained cyclic dienes where the diene ground state energy has increased due to ring strain. For instance, cis,trans-1,3-cyclooctadiene undergoes stereospecific conrotatory cyclization to cis-bicyclo[4.2.0]oct-7-ene, at 80°C (Eqn 1.6). The cis,cis-diene isomer, on the other hand, cannot be made to undergo closure to cyclobutene at comparable temperatures.

1.6



1.7



Stereospecifically formed and opened cyclobutene has been suggested as an intermediate in a thermal reaction. The thermal cis,trans-isomerization of 1,3-butadienes at very high temperatures by vacuum flash pyrolysis at >900K (Eqn 1.7) has been suggested to proceed by a mechanism involving stereospecific interconversions with cyclobutene intermediates.[32]

Marvel has described the use of thermal electrocyclic ring opening of cyclobutene systems in synthesis. For example, a procedure has been developed for the synthesis of a variety of alkaloids, steroids, and intermediates for terpene synthesis.[5]

1.4 Photochemical Electrocyclic Reactions

According to the correlation diagrams discussed above, electrocyclic reactions initiated by ultraviolet light are expected to be stereospecific, but in the sense opposite to the thermal processes for the cyclobutene/1,3-butadiene interconversions. In the first excited state the LUMO, which has symmetry opposite to that of the HOMO, is populated and therefore, orbital symmetry considerations predict that excitation will alter the stereochemistry of ring opening or closure. The ring opening/closure process is predicted to occur disrotatory. A recent *ab initio* study[18] (summarized in Figure 1.4) predicts the same result, but a problem arises with the simple model.

1,3-diene -> cyclobutene: The photochemical butadiene -> cyclobutene closure has been shown to occur disrotatory in substituted systems.[6-11,13] A problem arises in the simple model when one considers that the spectroscopic singlet excited state of cyclobutene, S_1, is ca.

50 kcal/mol above that of 1,3-butadiene rendering the adiabatic ring-closure impossible. The <u>ab initio</u> studies, while agreeing with the conclusion made by the correlation diagrams, have provided a reasonable mechanism for disrotatory closure of 1,3-butadiene which is more complicated than simple theory suggests. The most recent calculated state correlation diagram for the ground and excited state con- and disrotatory interconversions of cyclobutene and 1,3-butadiene is shown in Figure 1.4.[18] The photochemically initiated disrotatory process involves an allowed adiabatic crossing from S_1 ($^1A''(1)$) to the S_2 ($^1A'(2)$) potential energy surface (due to overlapping nuclear vibrations) which is decreasing in energy at the point of crossing. As Figure 1.4 reveals, S_2 ($^1A'(2)$) decreases in energy and passes through a minimum before rising steeply in energy. The S_2 ($^1A'(2)$) energy minimum closely corresponds to a geometry near the maximum on the ground state disrotatory surface, S_0 ($^1A'(1)$). At this point, funneling to S_0 ($^1A'(1)$) allows disrotatory closure to proceed to completion providing cyclobutene in the ground state. Simple theory predicts adiabatic formation of cyclobutene, but forcing the process to occur entirely within the singlet excited state is not possible since, as already stated, the cyclobutene singlet excited state is ca. 50 kcal/mol higher in energy than that of the diene.

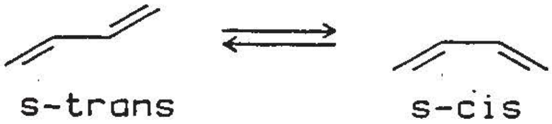
The conrotatory path allows no comparable opportunity for funneling from the excited state surface and, as well, there is a substantial barrier to conrotation on the S_1 ($^1A''(1)$) surface, hence a disrotatory pathway is followed for closure. The result remains as simple theory predicts but <u>ab initio</u> studies reveal that cyclobutene may be formed non-adiabatically in the ground state. This generally appears to be the "rule" in photochemistry (i.e. photochemical reaction begins on the excited state surface but the product is formed in the ground state) and is one of the main reasons why photochemical reactions generally follow orbital symmetry rules.[33]

Experimentally, 1,3-dienes have been found to be converted to cyclobutenes stereospecifically via a disrotatory process. It is important to note that s-cis dienes are required for closure to cyclobutenes to occur. The effect of diene conformation on the direct photolysis of dienes may be observed by studying the process in various substituted acyclic and cyclic dienes.

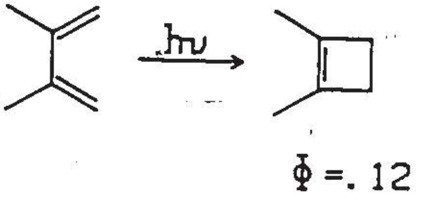
Cyclic dienes are the most instructive examples of the closure process as they are constrained to be s-cis, although there is variation in the dihedral angle from system to system, and they form fused cyclobutenes. Photolysis of cis,cis-1,3-cycloheptadiene cleanly and efficiently gives bicyclo[3.2.0]hept-6-ene <u>2</u>.[7] Some portion of the cyclobutene is known to be formed by a two step process involving initial cis,trans photoisomerization to cis,trans-1,3-cycloheptadiene, followed by thermal conrotatory closure to product.[34] The photochemical cyclization of cis,cis-1,3-cyclooctadiene is relatively inefficient but does give cis fused bicyclo[4.2.0]oct-7-ene <u>3</u>.[35] The cyclization process is a direct one at room temperature, as cis,trans-1,3-cyclooctadiene is stable up to 80°C.[36] The inefficiency of ring closure in this case is probably due to conformational constraints on the 1,3-diene portion of the molecule.[37,38] The double bonds, constrained to be almost perpendicular to one another in the most stable ground state conformation, are in an exceedingly poor geometry for ring-closure.[38]

Acyclic 1,3-dienes, are conformationally-labile about the C2,C3 bond, which results in an equilibrium mixture of s-cis and s-trans dienes (Eqn. 1.8).[39] Disrotatory closure of 1,3-dienes has been shown to proceed only when there is a significant proportion of s-cis diene conformers present in solution.[11,13] This requirement is demonstrated by the results of the direct photolysis of substituted butadienes. Substituents at C2 and C3 of butadiene shift the equilibrium toward s-cis conformers, whereas C1 and/or C4 substituents shift the equilibrium toward s-trans conformers. Accordingly, 2,3-dimethyl-1,3-butadiene (7) closes to 1,2-dimethylcyclobutene (Eqn 1.9) with a relatively high quantum yield (ca. 0.12).[40,41] In contrast, trans,trans-2,4-hexadiene (8) yields cis-3,4-dimethylcyclobutene in solution inefficiently (ϕ=0.02), as shown in Eqn 1.10, while ring closure of the cis,trans- and cis,cis-isomers, which are not expected to form s-cis conformers easily, is negligible.[11]

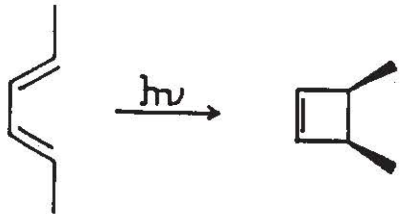
1.8



1.9



1.10



$\Phi = .02$

Quantum yields for ring closure to cyclobutenes are generally low in acyclic 1,3-dienes because cis,trans-isomerization is the major pathway for decay of the singlet excited state.[42,43]

Cyclobutene -> 1,3-dienes: The simple theory predicts that cyclobutene undergoes disrotatory opening during direct photolysis. On close examination of the ab initio state correlation diagram, disrotatory opening is also predicted. While substantial calculated energy barriers to ring opening exist for both the con- and disrotatory pathways along the S1 ($^{1}A'(2)$) surface, a second allowed crossing to the S2 ($^{1}A''(1)$) surface is available to the disrotatory path which is not present on the conrotatory path. Crossing at point C in **Figure 1.4** followed by another allowed crossing at point B provides a relatively low energy pathway to the minimum on the S1 ($^{1}A'(2)$) cyclobutene surface. At this point, funnelling to S0 ($^{1}A'(1)$) allows ring-opening to proceed to completion affording butadiene in the ground state. These calculations predict that a non-adiabatic process leads to stereospecific, disrotatory ring-opening.

1.5 Photochemistry of Cyclobutenes

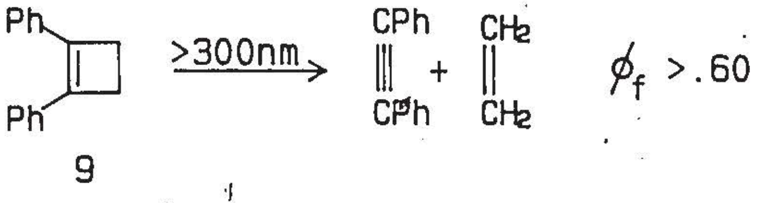
There are few reported examples that illustrate the photochemical electrocyclic ring opening process in simple, alkyl-substituted cyclobutenes[19-21] which may largely be due to practical experimental problems. Conventional photochemical techniques in solution require substrates that absorb at wavelengths greater than or equal to 230nm. Typically, simple, alkyl-substituted cyclobutenes absorb at wavelengths less than 210nm. Photochemistry at wavelengths less than this is plagued by a variety of problems. The choice of readily available, cheap light sources is limited to the low pressure mercury lamp which emits chiefly at 253.7nm with a line at 184.9nm comprising only 8-10% of the total output. Experimental problems arise with the transmission of the solvent and the reaction vessel material as well as absorption by air and water at 185nm. The use of Suprasil apparatus and UV-transparent hydrocarbon solvents such as n-pentane, 2,2,4-trimethylpentane, and cyclopentane allow far UV study of simple cyclobutene systems in solution.

Classically, cyclobutenes have been studied in the readily accessible regions (≥254nm) by substitution of chromophores at the double bond. These chromophores interact conjugatively with the double bond, thereby lowering the energy of the excited state and drastically altering its electronic character. The result appears to be a complete modification in the spectroscopic and photochemical behaviour of the chromophore.

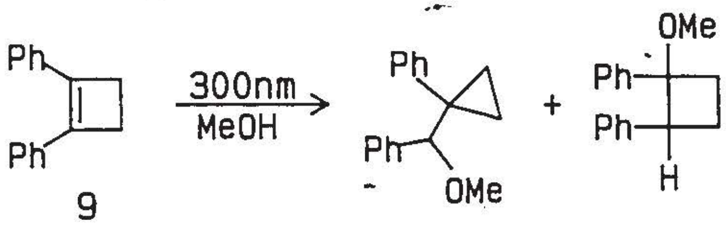
A case in point is the photochemistry of 1,2-diphenylcyclobutene (<u>9</u>).[44-46] While more highly substituted isomers of <u>9</u> undergo stereospecific thermal conrotatory ring opening in solution,[47] DeBoer and

Schlessinger[44] reported that the singlet excited state of **9** is efficiently deactivated by fluorescence ($\phi_f \simeq 1$). Dimers were the only observed products ($\phi = 0.001$) resulting from 313 or 335nm photolysis. As part of a larger study this system was reinvestigated by Kaupp[45] who reported the fluorescence quantum yield to be ca. 0.6. Product studies revealed that fragmentation (formally a $[\sigma 2_s + \sigma 2_s]$ cycloreversion) of **9** (Eqn 1.11) effectively competes with fluorescence, affording diphenylacetylene and ethylene ($\phi \simeq 0.2$).

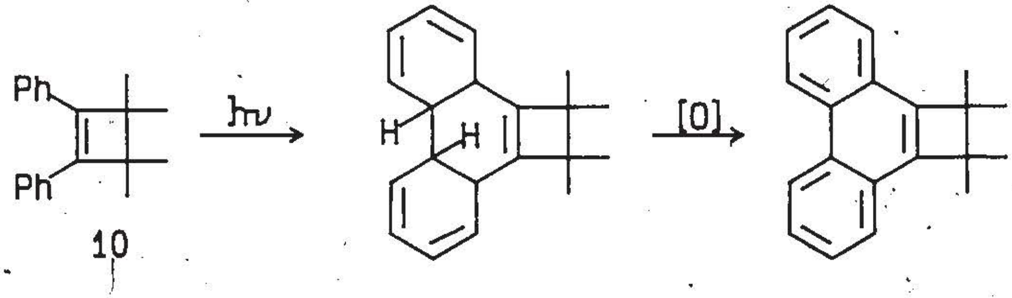
1.11



1.12

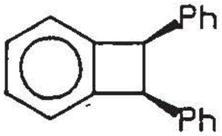


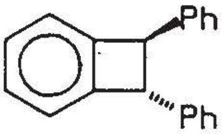
1.13

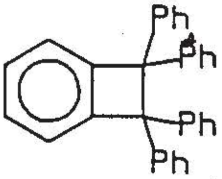


Irradiation of **9** at 330nm in nucleophilic solvents such as methanol and acetic acid leads to photosolvolysis products as shown in Eqn 1.12.[46] The photochemical ionic addition to **9** is thought to involve rearrangement of a cyclobutyl cation to a cyclopropylmethyl cation after protonation of the excited cyclobutene. The addition reaction occurs exclusively from the singlet excited state since fluorescence of 9 is substantially quenched by methanol.

In contrast to 9, 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (10) does not undergo any of these reactions when irradiated, but instead 10 cyclizes inefficiently to ultimately yield a cyclobutaphenanthrene derivative in solution (Eqn 1.13).[48]


c-11

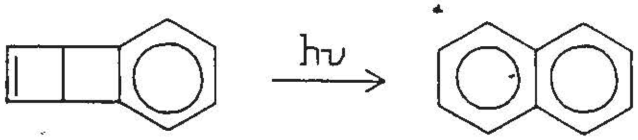

t-11


12

Benzocyclobutenes (11) reportedly do not undergo stereospecific photochemical ring opening[49] although the thermal ring opening process has been shown to obey the rules of symmetry.[50] Reaction from both the singlet and triplet excited states of cis- and trans-11 have been put forward. Triplet upper-excited states have been postulated to lead to vibrationally hot cyclobutenes to explain the non-stereospecific nature of the photoreaction. Triplet reactivity has been shown to play a role in the ring opening of the tetra-substituted cyclobutene (12).[51]

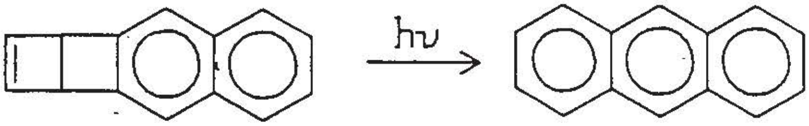
Photoexcited 1,4-dewarnaphthalene[52] and anthracene,[53] ((13) and (14), respectively) undergo ring-opening stereospecifically with high efficiency (Eqn 1.14 and 1.15). The ring opening process occurs adiabatically in both the singlet and triplet manifold, as evidenced by the characteristic naphthalene and anthracene excited state emissions

1.14



13

1.15



14

that result from excitation of their dewar isomers.

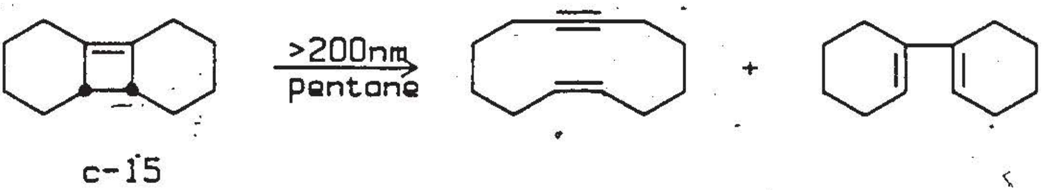
The phenyl substituents in these cases drastically alter the electronic character of the singlet excited states of these cyclobutenes. Singlet excited states, which do not normally intersystem cross to triplets in alkyl substituted systems, are perturbed by the phenyl-substituents to such an extent in these examples that reaction entirely within the singlet state manifolds appears impossible. Triplet reactivity in cyclobutenes has been explored and found not only to be possible but quite complex as well.[54,55] Srinivasan[55] has studied the mercury sensitized photolysis of c-1 in the gas phase and observed non-stereospecific ring opening. The formation of symmetry-forbidden cis,trans-2,4-hexadiene was postulated to arise from a vibrationally "hot" ground state of c-1.

It is apparent that the only systems from which stereochemical information on the direct photochemical ring opening process may be obtained are those with non-conjugating substituents; these are the systems which require far-uv techniques for their investigation.

1.6 The Far-Ultraviolet Photochemistry of Simple Cyclobutenes

There is only one published report[19] that offers conclusive stereochemical information on the photochemical electrocyclic ring-opening of cyclobutene. Saltiel and Ng Lim[19] reported the photochemistry of the tricyclic cyclobutene derivatives c- and t-<u>15</u> (Eqn 1.16 and 1.17) providing results which strongly suggest that photochemical ring opening prefers the symmetry-allowed disrotatory pathway. Direct photolysis of c-<u>15</u> results in ring opening to yield 1,1'-bicyclohexenyl as well as

1.16

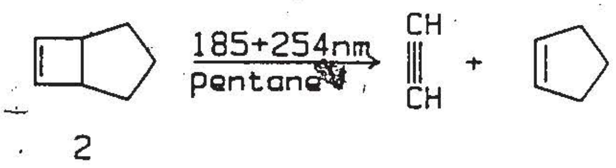


1.17

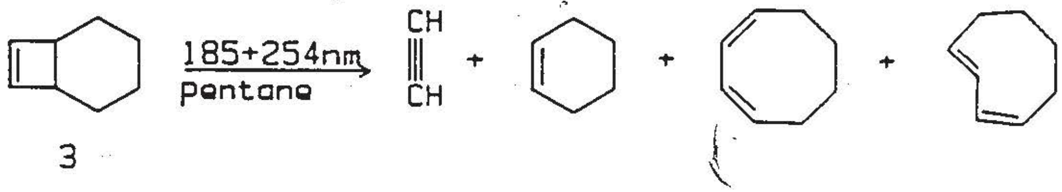
concerted fragmentation (formally a [$\sigma2_s + \sigma2_s$] cycloreversion) to afford the cis-en-yne. Trans-<u>15</u> however, undergoes stereospecific fragmentation only, giving the trans-en-yne as the sole product. In the case of t-<u>15</u>, disrotatory opening, had it occurred, would yield the highly strained cis,trans-isomer of 1,1'-bicyclohexenyl. This relatively high energy (though formally allowed) process does not occur upon photolysis of **t-15** since it is now known that the formation of the cis,trans-isomer, even as a transient intermediate, would have been detected as the apparent isomerization of **t-15** to **c-15**.[56] The major implication of the photochemical behaviour of **15** is that ring opening to cyclobutene is stereospecific and disrotatory for the cis-isomer while the geometrically easier but formally forbidden conrotatory pathway does not occur to any detectable extent in the case of the trans isomer.

A more recent study by Inoue and co-workers concerned the 185nm photochemistry of the annelated systems bicyclo[3.2.0]hept-6-ene (**2**) and bicyclo[4.2.0]oct-7-ene (**3**).[20] The results (Eqn 1.16 and 1.17) suggest that photochemical, electrocyclic ring opening, in the case of **2**, does not occur and ring opening of **3** is non-stereospecific. Although Inoue was able to show that the molecular fragmentation process occurs with high efficiency the study afforded no reliable information on the

1.18



1.19



stereochemistry of ring opening or its competition with fragmentation. Our perception of these results is that they are artifacts of the experimental conditions employed. Since the light source was unfiltered (185 + 254nm), products formed upon 185nm excitation were then vulnerable to secondary irradiation from the more intense 254nm line of the lamp. As a result, build-up of cis,cis-1,3-cycloheptadiene was precluded in the case of <u>2</u> since, as mentioned previously, it undergoes very efficient electrocyclic closure at 254nm.[7] For example, Leigh and Srinivasan[57] concluded that the presence of <u>2</u> in the photolysis of 2-norcarene (<u>16</u>), was due to secondary photolysis of 1,3-cycloheptadiene when an unfiltered mercury lamp was employed. The cyclobutene continued to be observed even when a band pass filter was used with the mercury lamp. The transmittance of this filter is ca. 4.5% at 254nm. Cyclobutene <u>2</u> was not observed in the photolysate when monochromatic light scurces such as an argon fluoride excimer laser (193nm) was used.

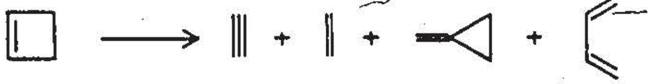
In the case of <u>3</u> any cis,cis-1,3-cyclooctadiene formed is subject to secondary cis,trans-photoisomerization when the 254nm line is present. It follows then that the results of Inoue, therefore cannot be considered reliable.

Inoue and co-workers did, however, make one interesting proposal concerning the mechanism of molecular fragmentation. While diene formation was attributed to the π,π^* excited state of cyclobutene, the fragmentation process (yielding acetylene and the corresponding cycloalkene) was suggested to result from cyclopropylmethylene carbene intermediates formed via the molecular π,R(3s) excited state. The carbene was proposed to result from a [1,2]-alkyl shift after π,R(3s) or

Rydberg excitation, a process that has been proposed previously[58] to explain analogous rearrangements in simple alkenes upon direct irradiation.

The solution phase photochemistry of cyclobutene itself (**17**) has been reported recently by Adam and co-workers.[21] In addition to the ring opening and molecular fragmentation products, a high yield of methylenecyclopropane was observed as exhibited in Eqn 1.20. 1,3-Butadiene was thought to occur via electrocyclic ring opening from the π,π^* excited state. The remaining photoproducts were rationalized in terms of the intermediacy of carbenes formed by [1,2]-alkyl and hydrogen shifts after π,R(3s) excitation.

1.20



17

1.7 Mechanistic Concepts in Far UV Photochemistry

Inoue[20] and Adam[21] have suggested involvement of two excited states in the direct photochemistry of cyclobutenes. It has been generally accepted that simple alkenes contain two low lying electronic excited states of comparable energies.[58-62] From gas-phase UV absorption spectra of alkenes it is apparent that the singlet manifold contains two excited states; the π,π^* or valence excited state and the π,R(3s) or

Rydberg excited state.[59,60] The direct, 185nm photoreactivity of alkenes in solution is often quite complex due to the presence of the two singlet excited states of similar energies. In spite of the similar energies of these excited singlet states, a distinct photoreactivity is perceived to result from each upon excitation. The π,π^* state energy is less affected by the presence of alkyl substituents than the π,R(3s) state is, and therefore, as alkyl substitution at the double bond increases, the Rydberg excited state becomes the lowest one in energy, in the condensed as well as the gas phase.[60]

As Figure 1.5 shows, a typical gas phase UV absorption spectrum[60] of an alkene exhibits two extensively overlapped bands. The more intense band, at shorter wavelengths, has a maximum between 160-190nm. This band, having an extinction coefficient of approximately 4000-10,000 is accepted as that corresponding to the $\pi \rightarrow \pi^*$ or valence transition. The valence excited state is perceived as being biradicaloid or zwitterionic in nature. Reactions characteristic of the π,π^* excited state have been identified as cis,trans isomerization, [1,3]-alkyl and hydrogen migrations and possibly hydrogen atom abstraction. Cyclobutene, because of its geometry, represents a special case as it is unable to undergo cis,trans isomerization. Instead, it may undergo formal $[\sigma 2_s + \sigma 2_s]$ cycloreversion and disrotatory electrocyclic ring opening; two pathways that are unavailable to larger cycloalkenes.

A less intense band (ϵ = 500-1000) in the gas phase UV absorption spectrum of Fig. 1.5 appears at longer wavelengths relative to the π,π^* band and was originally assigned as due to the π,R(3s) state excitation on the basis of pressure studies on the vacuum-UV spectra of alkenes.[63]

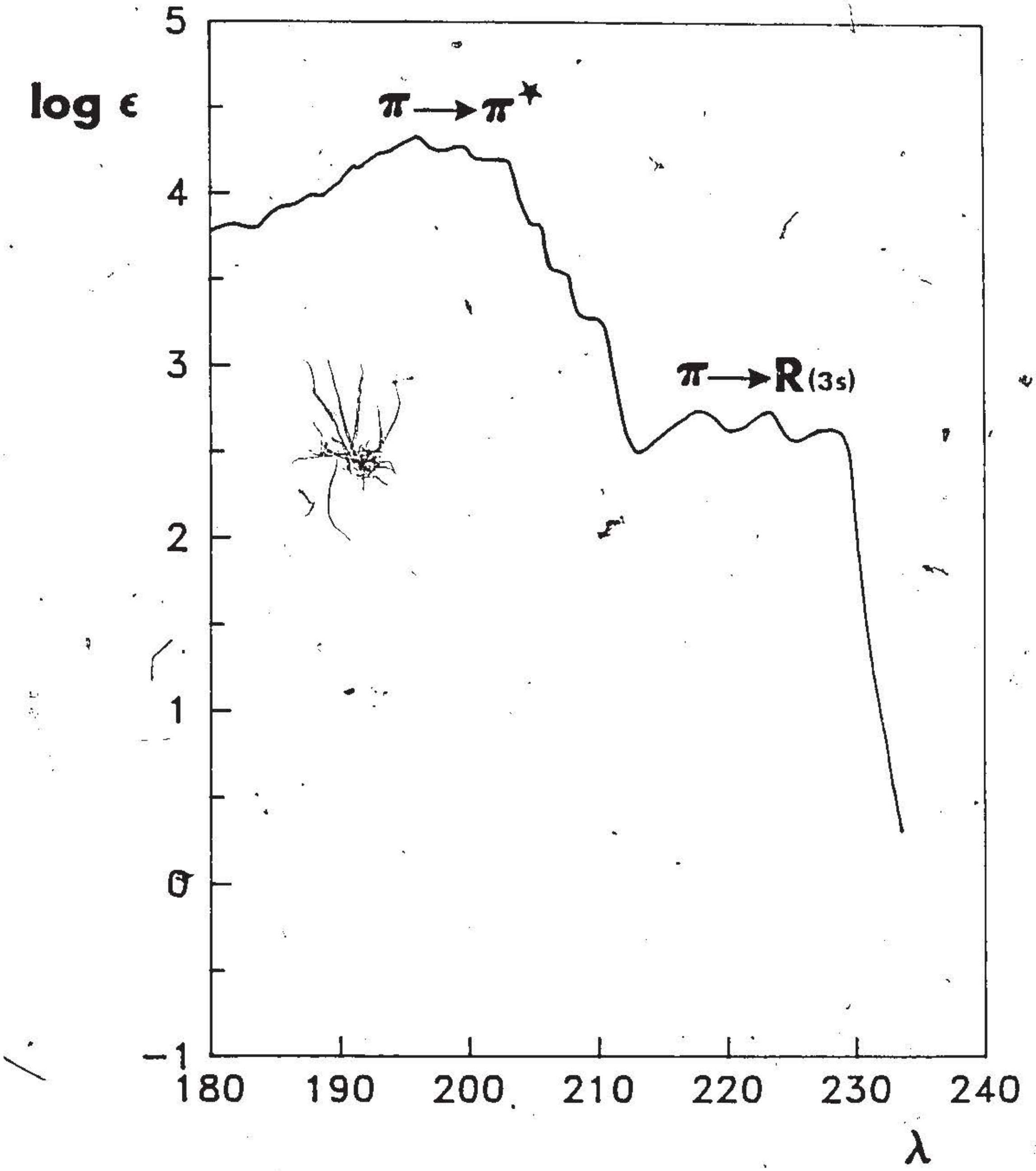


FIGURE 1.5 Typical gas phase ultraviolet absorption spectrum of a simple alkene.[60]

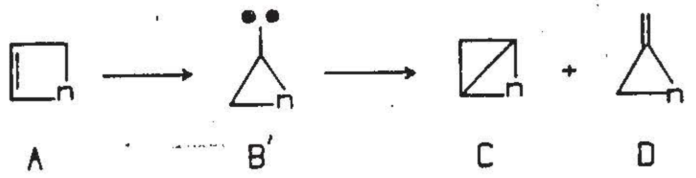
Further evidence comes from studies of the effect of substituents on the absorption[59,60] and fluorescence[61,62] spectra of simple alkenes. Gas phase absorption spectra reveal that the 0,0 band of the π,R(3s) absorption moves much more rapidly to the red than that of the π,π^* band with increasing numbers of substituents on ethylene.[60] The result is that the Rydberg bands that superpose the valence bands in ethylene stand out clearly as alkyl substitution is increased. This is generally believed to result from a greater ability of the electron donating substituents to stabilize the "semi-ionized" π,R(3s) state compared to the π,π^* excited state. In keeping with the excited state assignment described above, the far UV photochemistry of 2,3-dimethyl-2-butene (<u>18</u>) shows a dramatic dependence on excitation wavelength between 185nm and 229nm.[65] The relative yields of Rydberg derived products increase with increasing excitation wavelength compared to π,π^* products. The quantum yield for fluorescence from simple alkenes reportedly increases with additional substitution and the maximum shifts to longer wavelengths.[62] This trend has led to the proposal that alkene fluorescence originates from the π,R(3s) state. Curiously, moving from the gas to the condensed phase has only a minor effect on the fluorescence[62] of alkenes contrasting absorption[60] which is weaker and shifted to shorter wavelengths in solution.

Generation of the π,R(3s) excited state involves promotion of a π electron from the HOMO to a molecular orbital (3s orbital) that is larger than the molecular core, thereby creating an electron deficiency at the core. The π,R(3s) excited state of a molecule may suitably be described as a semi-ionized radical-cation; the radius of the excited electron is sufficiently small that the electron is still influenced by the core. Evidence consistent with the description of the π,R(3s) excited state as one in which an electron is ejected to a rather large, diffuse molecular orbital has been obtained using sulfur hexafluoride as an electron trap in alkenes.[66]

The Rydberg state of simple alkenes can thus be pictured as radical-cation like since Rydberg excitation involves a semi-ionized molecular core, and its associated reactivity is analogous to that of carbenium ions. The products of direct photolysis of simple alkenes have been rationalized in terms of carbene intermediates formed via [1,2]-alkyl or hydrogen shifts after Rydberg excitation.[58] Scheme 1.2 shows the products of photolysis of norbornene (**19**) at 185nm where carbenes were suggested as the precursors to both products.[67] The formation of products consistent with the intermediacy of carbenes appears now to be a general feature of the photochemistry of simple alkenes in solution. A number of recent reviews of far-ultraviolet photochemistry contain numerous references to these types of processes in alkenes.[58,69-71] Evidence for these carbenes comes from comparison of the behaviour of thermally generated carbenes with those resulting from the 185nm irradiation of alkenes. Generally the distribution of carbene derived product mixtures obtained from alkene photolysis differ from those obtained when the carbenes are independently generated either thermally or photochemically from the corresponding diazo compound or tosylhydrazone salt. It is well known that carbene reactivity can vary markedly depending on the procedure of generation.[110] The similarities in product distributions of the cyclic analogs in Table 1.1, however,

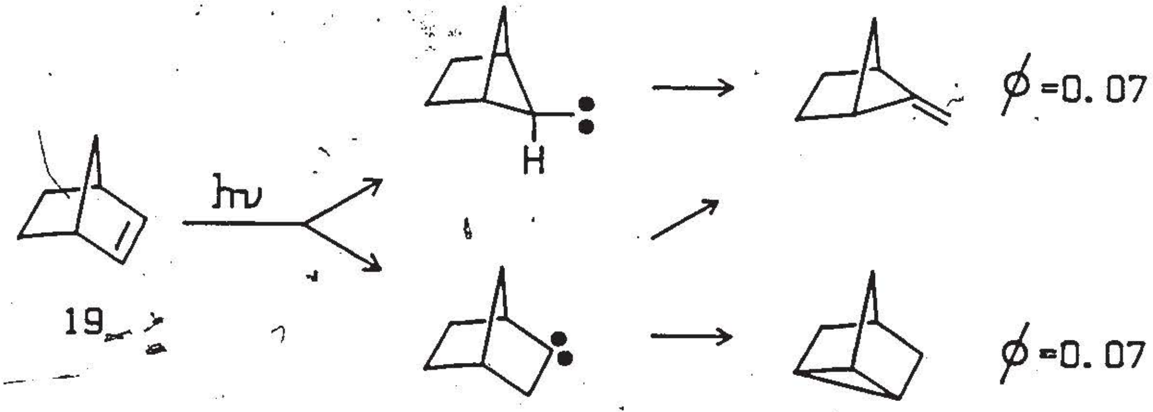
TABLE 1.1[a]

Comparison of Product Ratios from the 185nm Photolysis of Homologous Cycloalkenes with those from the Thermolysis of the Corresponding Tosylhydrazone Salts.



	Quantum Yields		Product Ratios, D/C	
n	C[b]	D[b]	185nm	Thermolysis[c]
5	0.008	0.007	0.9	-
4	0.02	0.10	5.0	11.5
3	0.07	0.05	0.7	0.4
2	0.03	0.04	1.3	1.4
1	[d]	0.12	-	-

[a] Adapted from reference 69. [b] ϕ=quantum yield of product formation. [c] The cyclopropylmethylenes **B** were generated via base-catalysed decomposition of the corresponding tosylhydrazones. The basic decomposition of cyclopropyl carbaldehyde tosylhydrazone did not lead to bicyclo[1.1.0]butane **C**, n=1. [d] Not formed.



SCHEME 1.2 185nm photochemistry of norbornene (19).

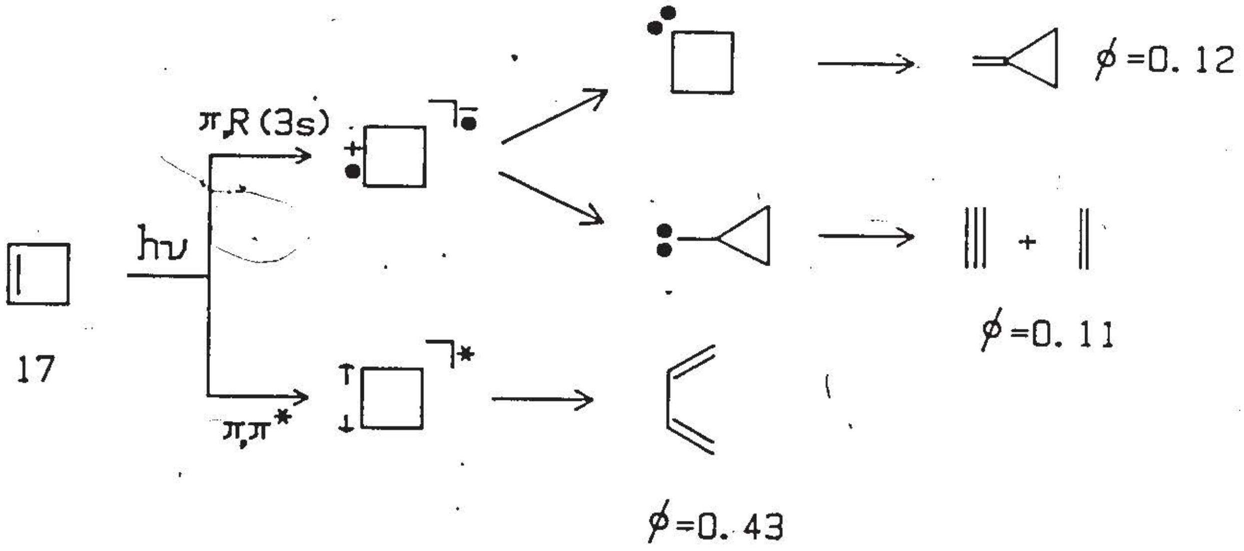
provide rather convincing evidence for the role of carbenes as intermediates in the former process.

Further support for carbene intermediates has been provided by deuterium labelling studies.[67,68] Photosolvolysis of alkenes in nucleophilic media have also been attributed to the involvement of Rydberg state-derived carbenes.[58]

Carbene intermediates arising from π,R(3s) excitation may also be involved in the 185nm photochemistry of simple cyclobutenes as mentioned in an earlier section. The results of 185nm photolysis of the annelated cyclobutenes <u>2</u> and <u>3</u> have been rationalized in terms of an analogous mechanism to that depicted in Scheme 1.3 in which π,π^* excitation results in ring-opening to dienes while the π,R(3s) state rearranges to the cyclopropylmethylene carbene which subsequently fragments to yield acetylene and a cycloalkene.[20] Although the latter possibility has been offered as an alternative to concerted $[\sigma 2_s + \sigma 2_s]$ cycloreversion, no firm evidence has been presented to support it.

The 185nm photochemistry of cyclobutene (<u>17</u>) has been rationalized in terms of carbene intermediates.[21] Acetylene and ethylene were attributed to cyclopropylmethylene, while methylenecyclopropane was attributed to cyclobutylidene;[21] these products were suggested to arise via [1,2]-alkyl and -hydrogen shifts, respectively. Butadiene was thought to arise via electrocyclic ring opening from the π,π^* excited state (Scheme 1.3).

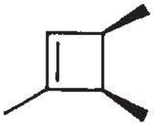
Support for carbene involvement comes primarily from comparisons of their behaviour when generated independently from diazo and tosylhydrazone[107,115] precursors with the results from 185nm irradiation of cyclobutenes. Cyclopropylmethyl carbenes are known[107] to undergo fragmentation to alkyne and alkene as well as ring expansion to cyclobutenes. For example, cyclopropylmethylene affords acetylene/ethylene and cyclobutene in yields of 22% and 65%, respectively. Cyclobutylidenes are known to undergo [1,2]-hydrogen shifts yielding cyclobutenes, but ring contraction affording methylenecyclopropane derivatives is the major decay path for this carbene when generated thermally.[115] Thus, this could indeed account for the presence of methylenecyclopropane in the photolysis of cyclobutene.



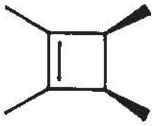
SCHEME 1-3. 185nm photochemistry of cyclobutene **17**.

1.8 Statement of the Problem

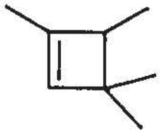
Ten alkyl-substituted cyclobutenes (1-6, 20 and 21) were prepared with a view to delineating the photochemical behaviour of the singlet excited state of cyclobutene by direct irradiation using far ultraviolet



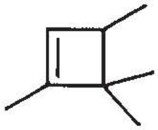
5



6



20



21

photochemical techniques. In particular, the study was to be concerned with the investigation of: (1) the excited state(s) involved in formation of the various products from direct photolysis, (2) the stereochemistry of the photochemical electrocyclic ring opening process, (3) formal $[\sigma 2_s + \sigma 2_s]$ cycloreversion; and (4) the possible participation of carbene intermediates in these systems. Our goal was to provide a clear and conclusive understanding of the photochemical behaviour of the parent system, cyclobutene, which has been thoroughly investigated theoretically. It was imperative that Inoue's original study of 2 and 3 be repeated correctly. The monocyclic systems are unconstrained relative to systems previously studied;[19,20] and therefore it was our hope that structural effects would not prejudice the ring opening reaction. System 1 represents the most simple alkyl-substituted cyclobutene capable of providing stereochemical information on the electrocyclic ring opening and cycloreversion processes, and therefore represents the parent system of this study. Cyclobutenes 5 and 6 were chosen in order to study the effect of methyl substituents on the excited state manifold and photochemical behaviour of the system. The bicyclic systems, although probably more strained, provide systems that are easier to study since only two conjugated diene isomers are possible from electrocyclic opening.

It was hoped that some insight into the dynamics of the potential energy surface(s) for the ring opening and molecular fragmentation processes could be gained through appropriate wavelength and temperature dependence studies.

The possible involvement of carbene intermediates has been studied with <u>**20**</u> and <u>**21**</u>. In these cases, since 1,2-migrations should afford common carbene intermediates from <u>**20**</u> and <u>**21**</u>, the occurence of the process should be revealed by the interconversion of the two isomers.

CHAPTER II

The Direct Photochemistry of Mono- and Bicyclic Cyclobutene Derivatives

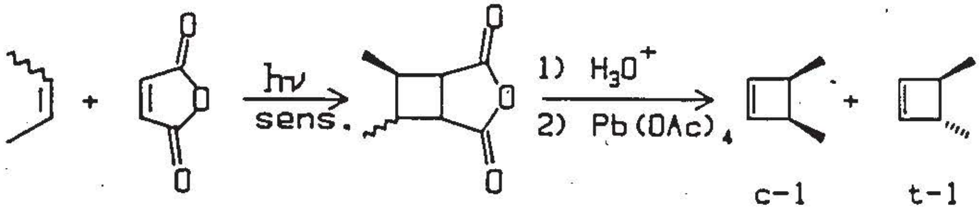
A. Results

2.1 Preparation of Compounds

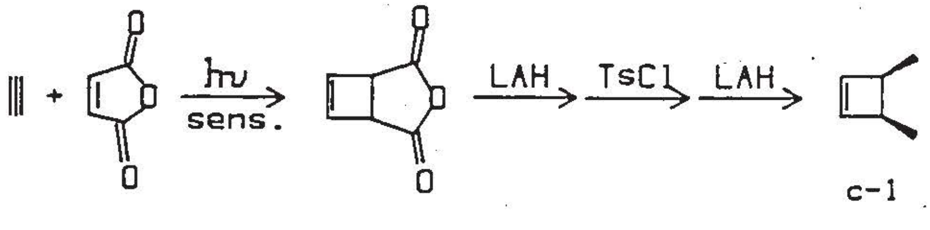
3,4-Dimethylcyclobutene (1)

Cis- and trans-3,4-dimethylcyclobutene (**c-1** and **t-1** respectively) were synthesized as a mixture of isomers by the route shown in Equation 2.1.[74] Compounds **c-** and **t-1** were separated and purified by preparative gas chromatography (vpc) and their structures were assigned on the basis of their IR, mass, and 90 MHz ^{1}H NMR spectra. The assignments were confirmed by an independent synthesis of **c-1** using the route shown in Equation 2.2.[25]

2.1



2.2

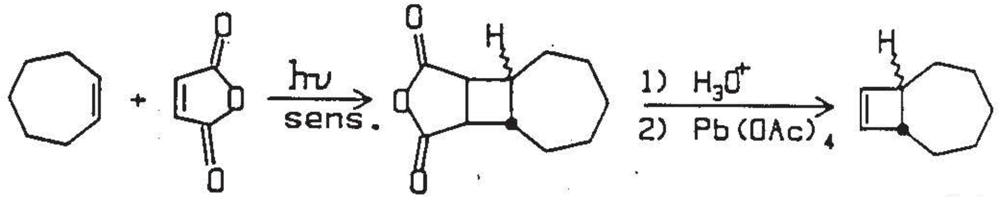


Bicyclo[3.2.0]hept-6-ene (2) and Bicyclo[4.2.0]oct-7-ene (3)

Bicyclo[3.2.0]hept-6-ene, 2, was prepared by photochemical electrocyclic ring-closure of cis,cis-1,3-cycloheptadiene.[7] Bicyclo[4.2.0]oct-7-ene, 3, was prepared in a manner similar to that of 2 from cis,cis-1,3-cyclooctadiene[35].

Bicyclo[5.2.0]non-8-ene (4)

Cis- and trans-bicyclo[5.2.0]non-8-ene 4 were prepared as a mixture of isomers by the route shown in Equation 2.3.[74] Compounds **c-** and **t-4** were separated and purified by semi-preparative vpc and their structures were assigned on the basis of IR, mass, and 500MHz ^{1}H NMR spectra and comparisons to literature spectra.[9,31] The isomers can be distinguished by the chemical shifts of the vinyl hydrogens, which are at 6.05 and 6.14ppm for **c-** and **t-4**, respectively, and those of the protons at C1 and C7, which appeared at 2.89 (d) and 2.53 (dd) for **c-** and **t-4**, respectively.[9,31] These features were also compared to those reported for cis- and trans-bicyclo[6.2.0]dec-9-ene derivatives and the chemical

2.3 

c- and t-4

shifts were found to be similar.[75] These features are also similar to those exhibited by cis-and trans-1 for the chemical shifts of the hydrogens at C3 and C4 in 1. The cyclobutene isomers were further distinguished by pyrolysis of **c-4**. After 1h at 200°C, 33% of **c-4** had been converted to cis,trans-1,3-cyclononadiene.

Cis-1,3,4-trimethylcyclobutene (5) and cis-1,2,3,4-tetramethylcyclobutene (6).

Compounds 5 and 6 were synthesized independently by a procedure similar to the synthesis of cis-3,4-dimethylcyclobutene, **c-1**, (Eqn. 2.2) and were identified on the basis of their ^{1}H NMR, IR, mass, and UV absorption spectra.

2.2 Ultraviolet Absorption Spectra of 1 - 6.

Ultraviolet absorption spectra of 1 to 6 were recorded in deoxygenated cyclohexane solution and are summarized in Table 2.1.

TABLE 2.1

Solution UV Absorption Data[a,b,c]

Cyclobutene	λ_{max} (nm)	E_{max} (kcal/mol)[d]	ϵ_{max}
cis-1	186.5	153	5,900
trans-1	188.2	152	5,100
cis-5	189.4	151	6,900
cis-6	190.3	150	11,100
2	186.5	153	4,200
3	186.6	153	6,200
cis-4	186.5	153	4,900
trans-4	186.6	153	5,600

[a] ca. 0.002M solutions in cyclohexane; 23°C. [b] solutions deoxygenated with argon. [c] 0.1 cm path length. [d] energy at λ_{max}.

2.3 Direct Photolysis of 1 - 6 in Hydrocarbon Solution.

Light Sources

Irradiations were performed using 185nm, 193nm, and (occasionally) 214nm light sources.

The 185nm light source consists of a 10W low pressure mercury lamp, the output of which consists predominantly of two lines at 184.9nm and 253.7nm. Typically, only about 10% of the total output intensity is due to the 184.9nm line while ca. 78% is due to the line at 253.7nm. A ^{60}Co-irradiated LiF crystal[76,77] was used in conjunction with the lamp to eliminate the 253.7nm line of the low pressure mercury lamp. An ultraviolet absorption spectrum of a filter is exhibited in the Appendix section.

The monochromatic 193nm light source was provided by the pulses (193nm, 10ns, 20-100 mJ, 0.5 Hz repetition rate) from an excimer laser filled with an Ar/F_2/He mixture. The unfocussed laser beam was directed at the sample cell containing a magnetic stirrer, and placed ca. 8ft from the source.

The 214nm light source was provided by a 16W zinc resonance lamp set up in a manner identical to the 185nm light source, but without the ^{60}Co-irradiated LiF filter.

For more detail on the far ultraviolet light sources see the experimental section in Chapter V.

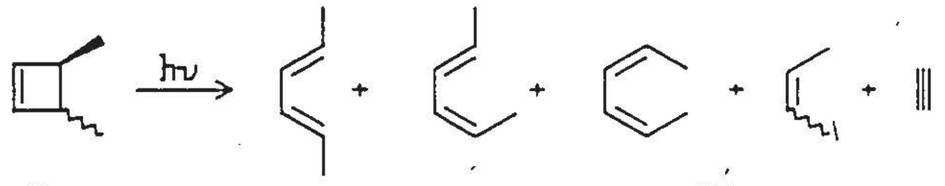
Quantum Yield Determinations

Quantum yields were calculated using the cis -> trans-cyclooctene actinometer.[78,79] Quantum yields were determined after calculating the light flux from the concentration vs. time plot for the formation of trans-cyclooctene from the cis-isomer, whose photolysis was conducted concurrently with the substrate of interest. A value of 0.32 ±.02 was used for the actinometric quantum yield.[79] Back reaction, involving the conversion of trans -> cis-cyclooctene, was assumed to be negligible in these studies, since they were all carried out to low (<5%) conversions. Quantum yields were determined for 185nm excitation and occasionally for 193nm as well. For more detail on the procedure see the experimental section in Chapter V.

Photolysis of Cis- and Trans-3,4-dimethylcyclobutene, (c- and t-1)

Photolysis of deoxygenated, 0.02M isooctane or pentane solutions of cis- and trans-1 with the 185nm light source produced the product mixture shown in Equation 2.4. Photolysis of either isomer yielded tt-, ct-, and cc-2,4-hexadiene 22 in the relative yields shown in Table 2.2. Product yields were determined from the slopes of concentration vs. time plots constructed for the isomeric dienes 22 (Fig 2.1). These plots were linear over the conversion range investigated (0.2-3.0%; based on the amount of 1 consumed at the end of the experiment). The formation of

2.4



1 tt- ct- cc-22

cis- and/or trans-2-butene and acetylene was also evident in the runs carried out in isooctane (their presence in the photolysate was confirmed by coinjection of authentic samples), but their yields were not monitored in either case. Apart from one additional unidentified minor product in the photolysis of 1, no other products could be detected in >10% yield from the photolysis of either isomer of 1 in either solvent. The three isomeric dienes were identified by coinjection of authentic samples on a number of vpc columns. Relative diene yields are given for 185 and 193nm irradiations in Table 2.2.

TABLE 2.2

Relative Diene Yields from Photolysis of cis- and trans-1 in isooctane solution (23 C) at 185 and 193nm.[a,b]

Cyclobutene	Wavelength (nm)	tt-22	ct-22	cc-22
cis-1	185	3.5 ± .4	6.0 ± .5	1.0 ± .1
	193	3.2 ± .2	4.9 ± .3	1.0 ± .1
trans-1	185	2.8 ± .5	2.6 ± .4	1.0 ± .1
	193	2.5 ± .2	3.2 ± .2	1.0 ± .1

[a] Product yields and errors were calculated from concentration vs. time plots for the 185nm photolyses, and from single point determinations (average of at least two experiments for the 193nm photolyses). [b] Acetylene was identified as a product in the photolyses but its yield was not determined. The formation of 2-butene was followed but its yield is omitted from the table since its response factor relative to 2,4-hexadiene has only been crudely determined.

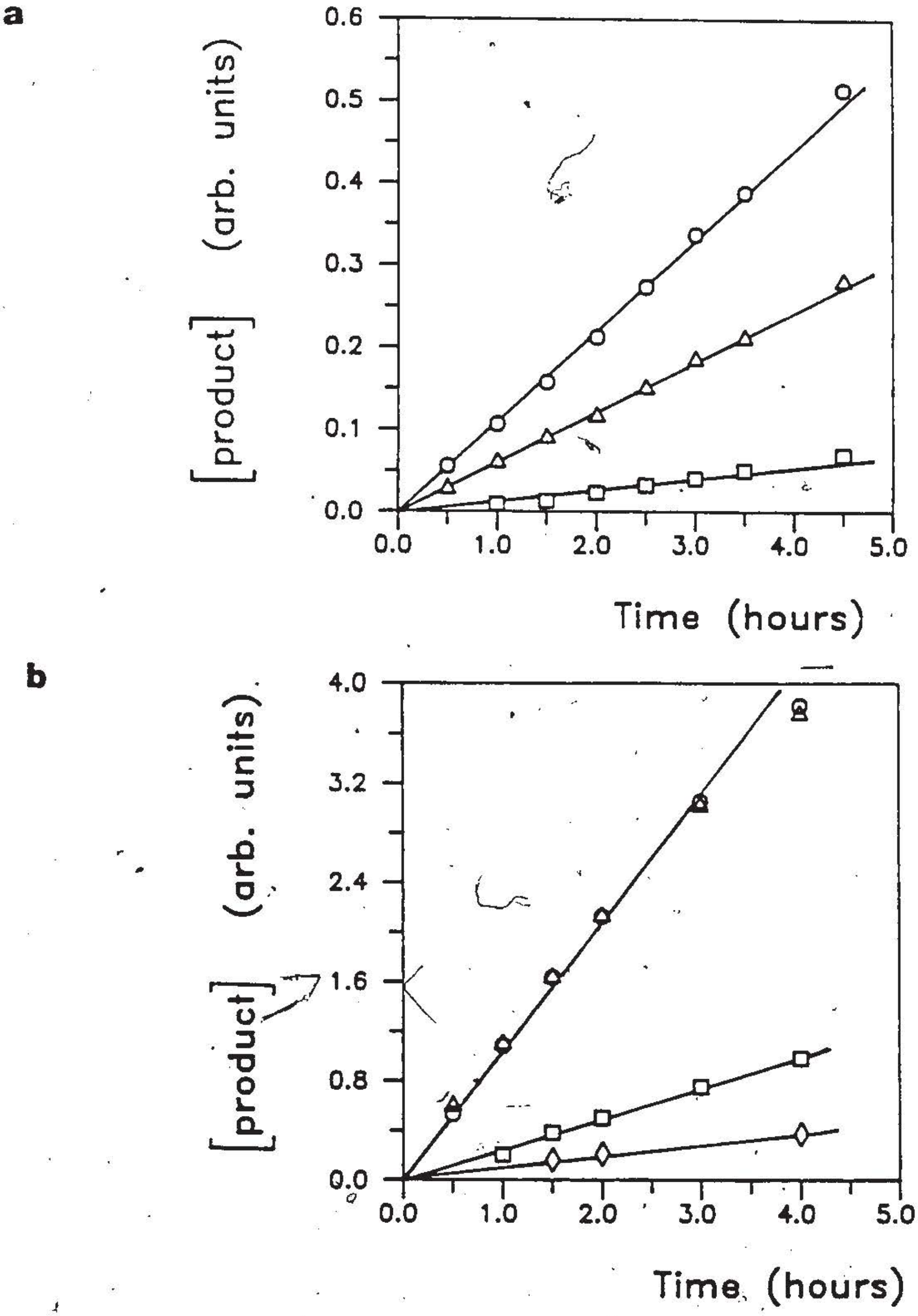
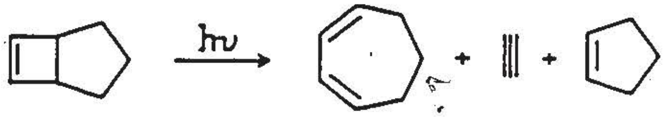


FIGURE 2.1 (a) and (b) Concentration vs. irradiation time for the formation of tt- (△), ct- (○), and cc-22 (□), and an unidentified product (◇) from the 185nm photolysis of (a) c-1 and (b) t-1 in isooctane.

Photolysis of Bicyclo[3.2.0]hept-6-ene, 2

Irradiation of 2 as a deoxygenated, 0.018M solution in isooctane at 185 and 193nm produced the product mixture shown in Equation 2-5. Product yields were determined from the slopes of concentration vs. time plots constructed for 23 and 24; as shown for the 185nm photolysis (Figure 2.2), these plots were linear over the conversion range investigated (0.1 - 2.0%) at both wavelengths. The relative yields of 23 and 24 differed slightly at the two wavelengths studied. The identity of 23 and 24 as photoproducts was verified by coinjection of authentic samples on three vpc columns. The yield of acetylene was not determined, but its presence in the photolysate was confirmed in a similar manner. No other products in addition to those reported in Equation 2.5 were observed in greater than ca. 10% yield; this represents the limits of detection for this experiment. Product quantum yields were determined for both 185nm and 193nm excitation and are collected in Table 2.3.

2.5



2 23 24

TABLE 2.3

Quantum Yields for Formation of 23 and 24 from Photolysis of Bicyclo[3.2.0]hept-6-ene (2) in isooctane solution (23°C).[a,b]

Wavelength (nm)	23	24
185	0.12 ± .01	0.14 ± .01
193	0.09 ± .01	0.09 ± .01

[a] By cyclooctene actinometry using a value of ϕ = 0.32[79] for the quantum yield of the trans-cyclooctene at 185 and 193nm. Product yields and errors were calculated from concentration vs. time plots. [b] Acetylene was identified as a product in the reaction but its yield was not determined.

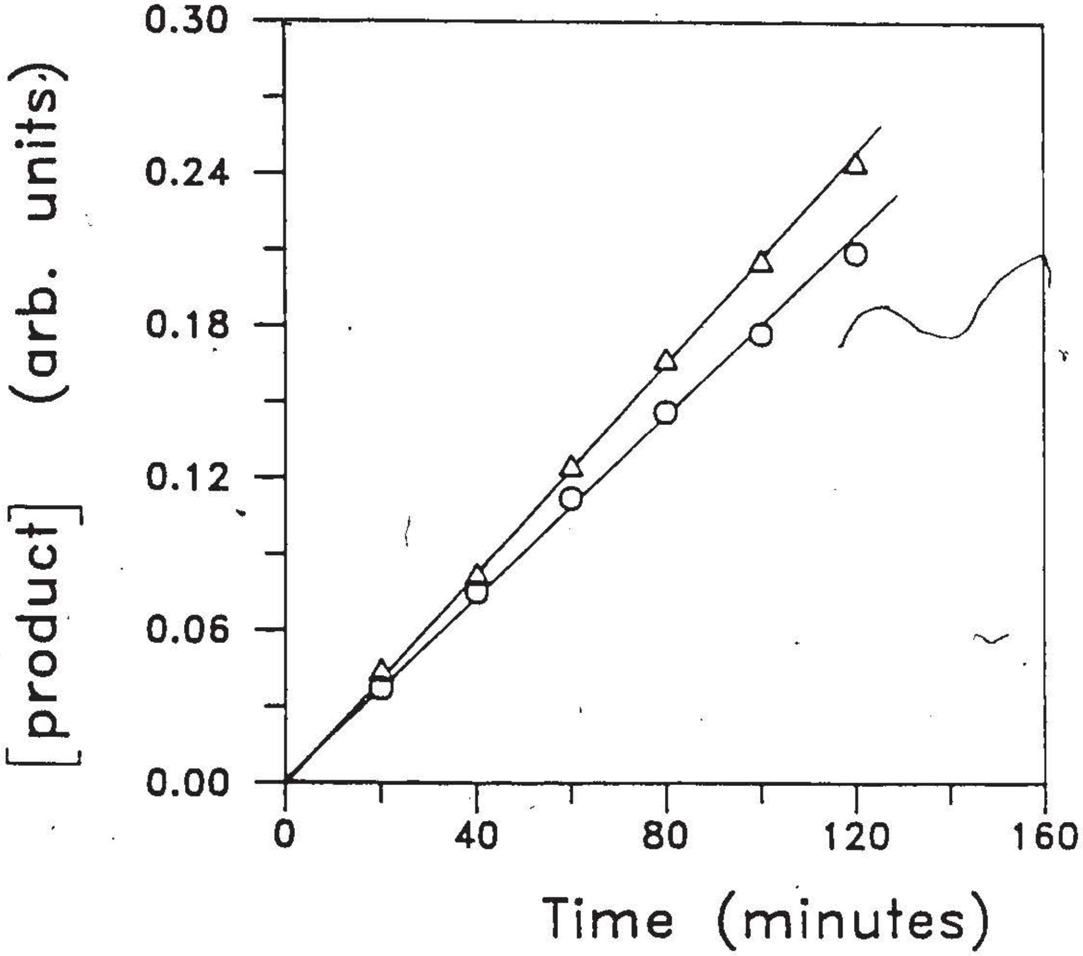
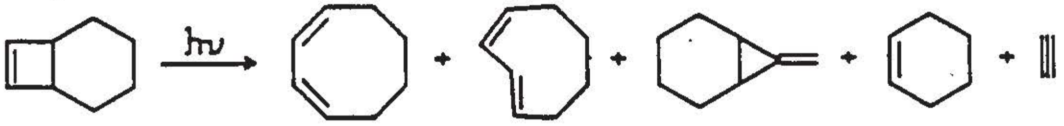


FIGURE 2.2 Concentration vs. time plot for the formation of cyclopentene (△) and 1,3-cycloheptadiene (○) from the 185nm photolysis of **2** in isooctane.

Photolysis of Bicyclo[4.2.0]oct-7-ene, 3

Photolysis of 0.017M deoxygenated solutions of 3 in pentane solution with 185 and 193nm light afforded the product mixture shown in Equation 2-6. Product identification was carried out by coinjection of authentic samples on several vpc columns. One other product, formed with a quantum yield twice that of 27 ,was not identified. The relative yields of cis,cis- (cc-) and cis,trans- (ct-) 25 showed marked wavelength dependence. Figure 2.3 shows concentration vs. time plots for cc- and ct-25, constructed from data in the 0.1 - 2.5% conversion range in the case of the 185nm photolysis. Similarly, the 193nm plot was constructed from data taken at low conversions. Quantum yields were determined at both wavelengths and are collected in Table 2.4.

2.6 

3 cc-25 ct-25 27 26

TABLE 2.4

Quantum Yields for the Formation of Products from the Photolysis of Bicyclo[4.2.0]oct-7-ene (3) in deoxygenated pentane solution (23 C).[a,b]

Wavelength (nm)	cc-25	ct-25	26	27
185	0.12 ± .01	0.040 ± .004	0.17 ± .01	0.009 ± .003
193	0.08 ± .01	0.055 ± .008	0.11 ± .01	[c]

[a] By cyclooctene actinometry, using a value of $\phi = 0.32$[79] for the quantum yield of the trans-cyclooctene at 185 and 193nm. Product yields and errors were calculated from concentration vs. time plots. [b] Acetylene was identified as a product in the reaction but its yield was not determined. [c] not determined.

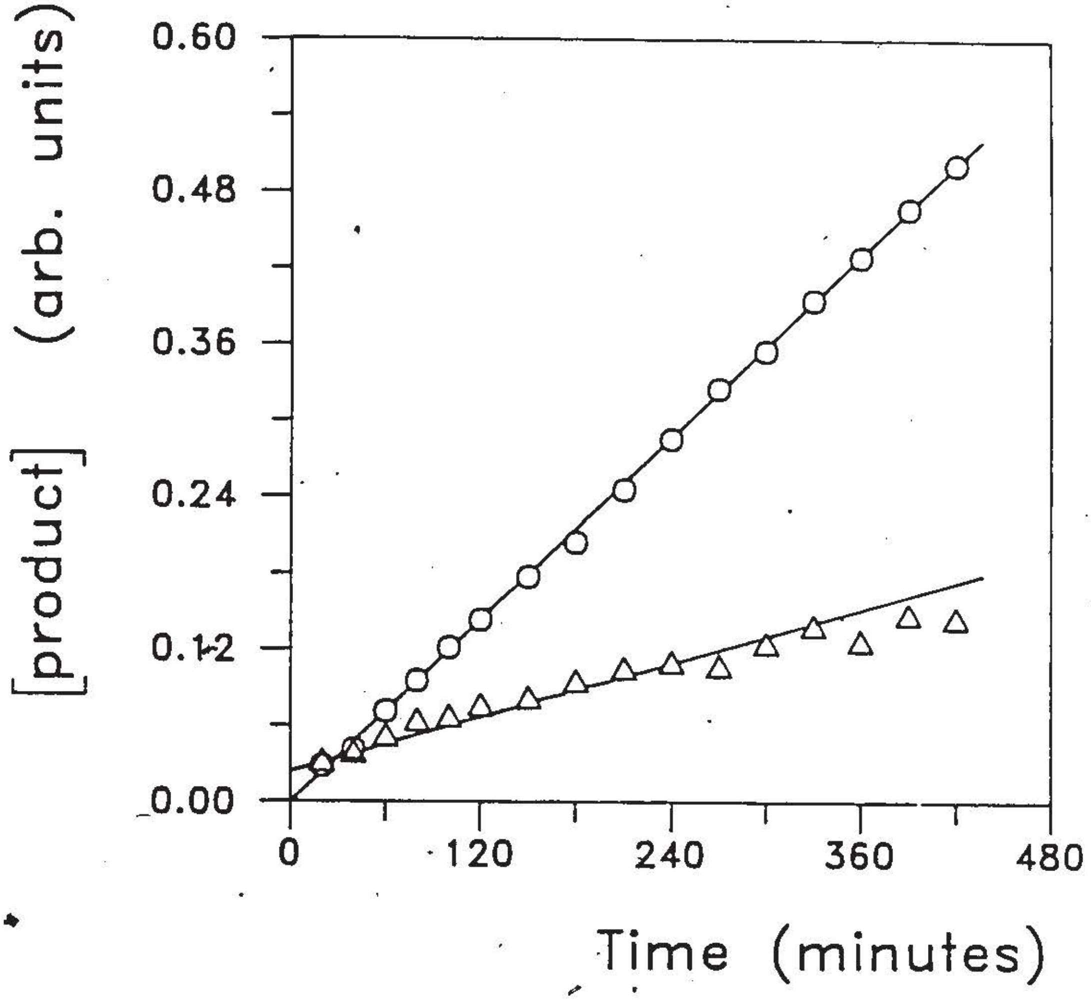


FIGURE 2.3 Concentration vs. time plot for the formation of cc-<u>25</u> (○) and ct-<u>25</u> (△) from the 185nm photolysis of <u>3</u> in isooctane.

Photolysis of Cis-bicyclo[5.2.0]non-8-ene (c-**4**)

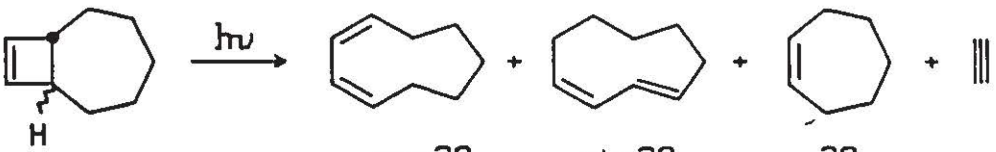
Irradiation of deoxygenated 0.02M solutions of c-**4** in pentane at 185nm and 193nm yielded the product mixture shown in Equation 2-7. Products were identified by comparison of the mass and 90 MHz ^{1}H NMR spectra of authentic samples to those (**28**, cc-**29**, and ct-**29**) isolated from a preparative scale 193nm photolysis. As well, coinjection of authentic samples on a vpc capillary column with the photolysis mixtures aided in product identification. Figure 2.4 shows a concentration vs. time plot for the fragmentation and ring opening products at 185nm.

At least four other minor primary products were observed in addition to those shown in Eqn 2.7, but their identification was not possible.

Trans-bicyclo[5.2.0]non-8-ene (t-**4**)

Compound t-**4** was irradiated as a deoxygenated, 0.011M solution in pentane at 185 and 193nm. The identities of the products in this case were verified to be identical to those obtained from c-**4** by coinjection of authentic samples. The resulting product mixture, as in the case of c-**4**, is shown in Eqn 2.7. Figure 2.5 shows concentration vs. time plots for formation of the fragmentation and ring opening products from the 185nm photolysis. Five other products were formed in addition to those identified in Eqn 2.7, one of these having a quantum yield ($\phi = 0.05$) higher than that of the minor diene, cc-**29** ($\phi = 0.04$). Two of these additional products were also observed in the photolysate from c-**4**. The identities of these isomers were not determined. The yield of acetylene was not monitored, nor was any attempt made to confirm its presence in the photolysate.

2.7



4 cc-29 ct-29 28

TABLE 2.5

Relative Yields of the Products formed in the Photolyses of Cis- and Trans-bicyclo[5.2.0]non-8-ene (c- and t-4) in pentane (23°C).[a,b]

Compound	λ (nm)	Yield (ϕ)		
		28	ct-**29**	cc-**29**
cis-**4**	185	4.3 ±.05 (0.26 ±.07)	2.7 ±.05 (0.16 ±.04)	1.0 ±.06 (0.06 ±.02)
	193	3.8 ±.06	2.1 ±.14	1.0 ±.08
trans-**4**	185	1.2 ±.03 (0.05 ±.01)	3.2 ±.02 (0.13 ±.03)	1.0 ±.06 (0.04 ±.01)
	193	2.1 ±.09	3.1 ±.09	1.0±.04

[a] Acetylene was identified as a product in the reaction but its yield was not determined. [b] By cyclooctene actinometry, using a value of $\phi = 0.32$[79] for the quantum yield of the trans-cyclooctene at 185nm. Product yields and errors were calculated from concentration vs. time plots.

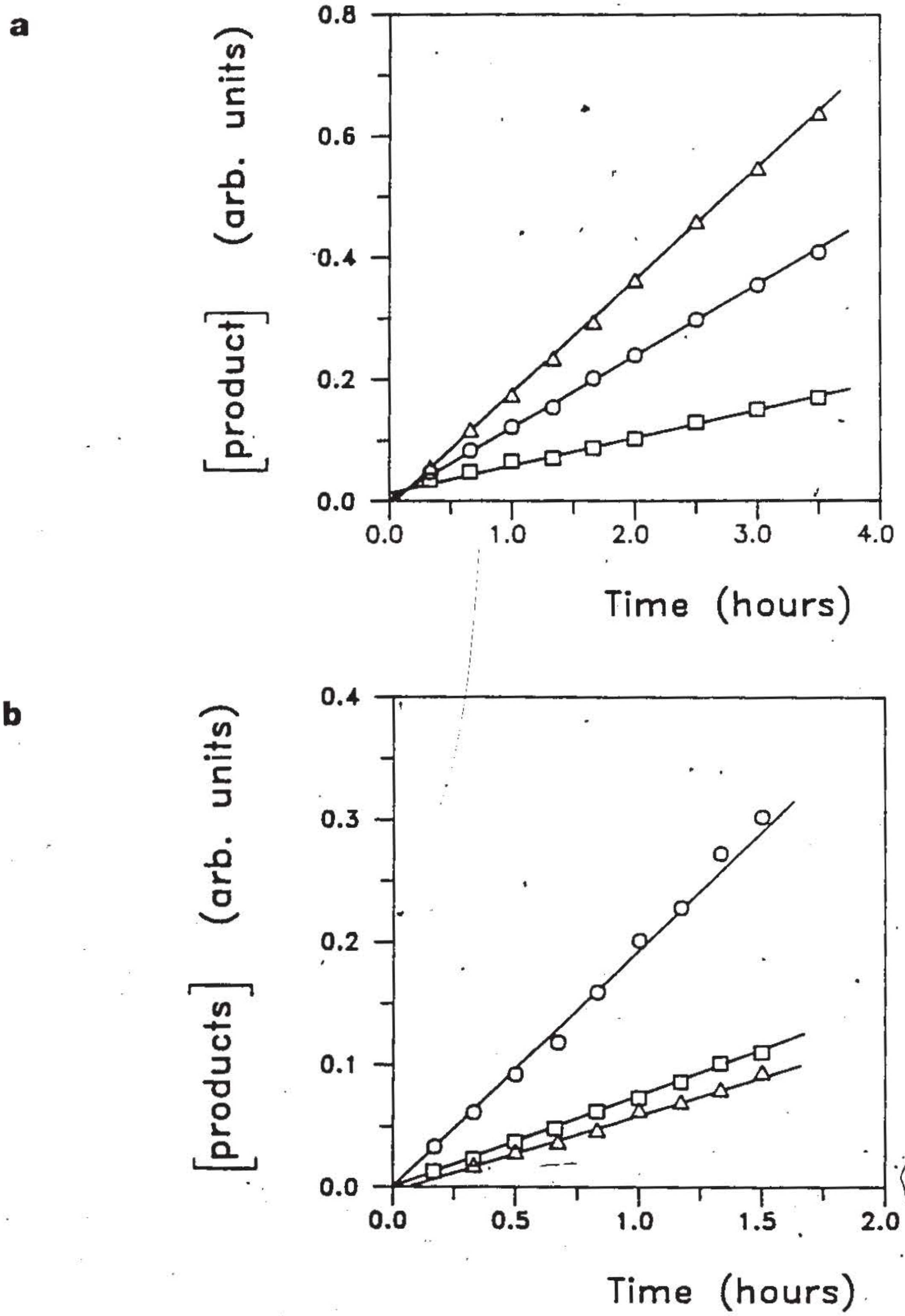


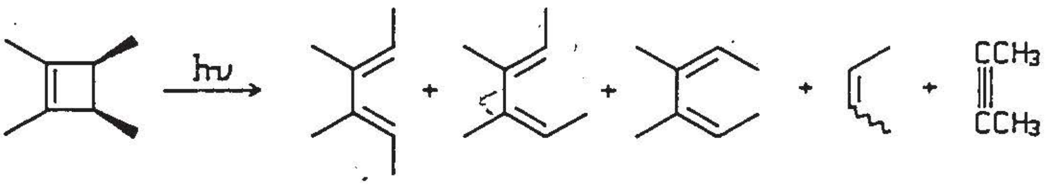
FIGURE 2.4 (a and b) Concentration vs. time plot for the formation of **28** (△), **cc-29** (□) and **ct-29** (○) from the 185nm photolysis of (a) **c-4** and (b) **t-4** in isooctane.

Photolysis of Cis-1,2,3,4-tetramethylcyclobutene, 6

Cis-1,2,3,4-tetramethylcyclobutene, (6), was irradiated as 0.02 and 0.06M pentane solutions at 193 and 214nm, respectively. Both photolyses afforded mixtures of all three geometric isomers of 3,4-dimethyl-2,4-hexadiene, 30, as shown in Eqn. 2.8. Figure 2.5 shows the concentration vs. time plot for the formation of the diene isomers (**Z,Z-** **E,Z-**, and **EE**-30) at 193nm. The products were identified by coinjection of authentic samples on a vpc capillary column. The formation of ethylene was observed although the observation of butyne was obscured by the solvent on the vpc capillary column and therefore the course of their formation was not followed.

At least four other minor products were observed in addition to the ones shown in Eqn. 2-8 during the 193nm photolysis (3% conversion) but their identification was not attempted. One of these products was also observed in minor yields in the 214nm photolysis. The combined yields of the minor unidentified products from the 193nm photolysis is estimated to be ca. 10%.

2.8



6 E, E- E, Z- Z, Z-30

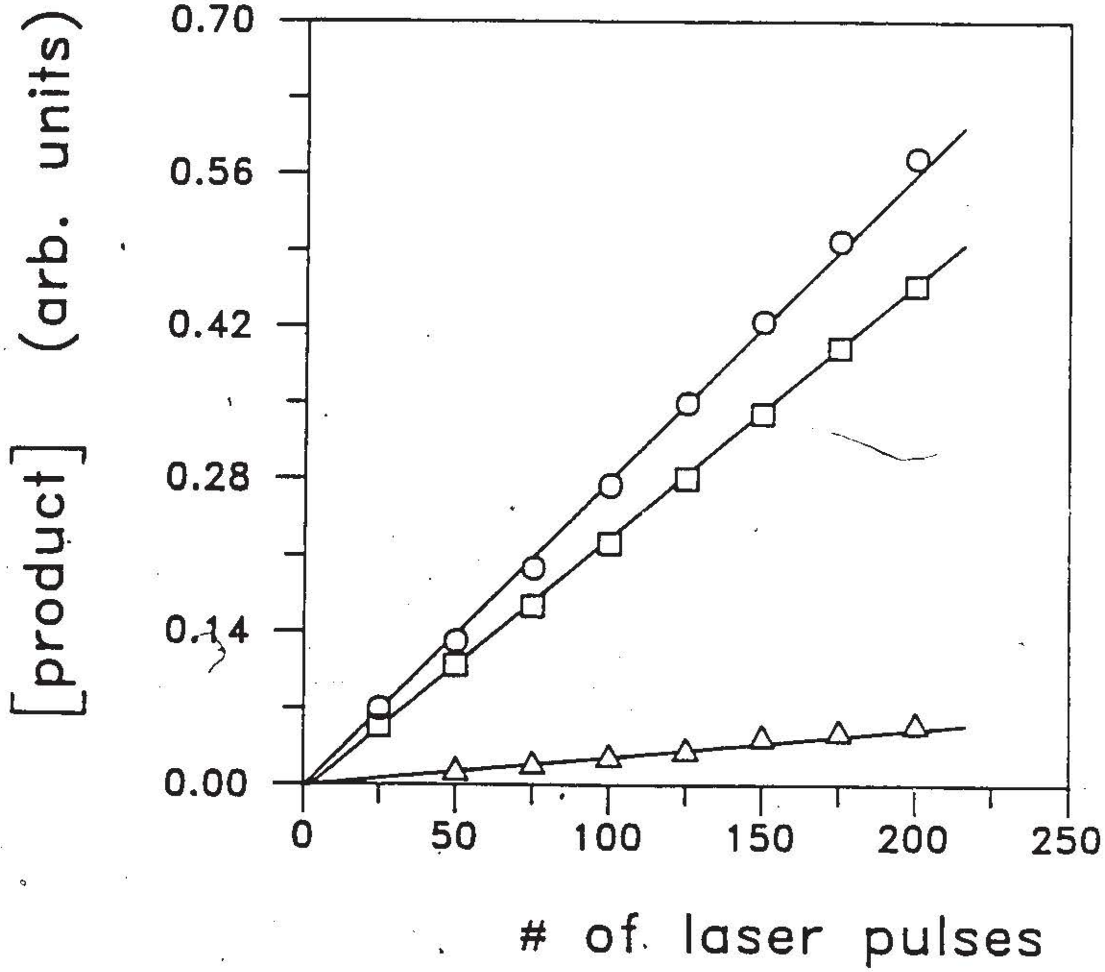


Figure 2.5 (a and b) Concentration vs. time plot for the formation of Z,Z-<u>30</u> (△), E,Z-<u>30</u> (□), and E,E-<u>30</u> (○) from the 193nm photolysis of <u>6</u> in pentane.

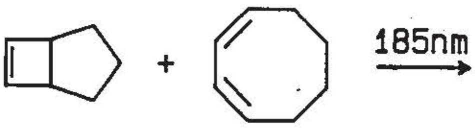
2.4 Control Photolysis Experiments

Secondary product photolysis due to the 254nm line of the low pressure mercury lamp has posed serious problems for those investigating photoreactivity at 185nm where products are formed that are photolabile at the longer wavelengths. Simple cyclobutene systems perhaps illustrate this problem best, in that the dienes formed in the initial photoprocess absorb strongly at 254nm. The resulting secondary events with 254nm photons have been known to seriously obscure experimental results[20]. We have utilized the LiF crystal as a 254nm filter[76] in order to alleviate the problem of secondary photolysis. Colour centres are produced in LiF crystals upon irradiation with gamma or X-rays; these colour centres exhibit a broad absorption band centred around ca. 245nm.[77] There is also some absorbance at 185nm but it is only marginal in most crystals. The ^{60}Co-irradiated LiF crystals that were used as filters for the 185nm photolyses of the cyclobutenes were always maintained with an optical density (O.D.) of between 3 and 5 absorbance units at 254nm and thus appeared quite reliable. But, the absence of secondary processes in these experiments had to be exemplified by suitable control experiments. It should be noted that some of the LiF crystals, although commercially made to identical specifications in all cases, were not suitable as filters after ^{60}Co-irradiation, since they could not sustain their colour centres long enough for a photochemical study. These crystals were not used in any of the 185nm irradiations.

185nm Photolysis of c-1 and 2 in the Presence of a Diene

To ensure that the formation of the formally forbidden diene isomer(s) in the photolyses of the cyclobutenes was not due to direct secondary photolysis or sensitization by spurious impurity triplets of the symmetry allowed isomers, the following control experiments were performed.

Control 1: A deoxygenated pentane solution containing 2 (0.02M) and **cc-25** (0.0002M) was irradiated with the filtered 185nm source under conditions equivalent to those described above. After ca. 3% conversion, only 2, its photolysis products and **cc-25** could be detected by vpc analysis of the photolysate as shown in Equation 2.9. The presence of **ct-25** could not be detected within the limits of vpc detection and the relative yields of the photoproducts were indistinguishable from those obtained from the photolysis of 3 alone. After four hours of 185nm irradiation (ca. 6% conversion of 2), the presence of **ct-25** was detected, but at a concentration <10% of the symmetry-allowed isomer.

2.9 

Products from the photolysis of 2 and unisomerized cc-25. (low conversions)

2 (0.02M)

cc-25 (0.0002M)

Control 2: A deoxygenated isooctane solution of cis-1 (0.017M) and trans-1,3-pentadiene (0.00017M) was irradiated with the filtered 185nm source under conditions similar to those employed above. The photolysis was carried out to ca. 3% conversion of cis-1, at which point negligible isomerization of the trans-1,3-pentadiene had occurred.

Effects of Laser Intensity on Product Yields from Photolysis of 3 at 193nm.

The excimer laser is an extremely convenient tool for the photochemist as it is capable of providing intense, monochromatic lines at several regions in the near and far ultraviolet, including the line at 193nm. Due to the nature of the laser beam, precautions must be undertaken to ensure against two photon absorption.[80] We have tried to rule against the possibility of sequential, two photon excitation by performing the photolysis of 3 at different laser fluxes through the use of neutral density filters. It was found that varying the flux of the laser beam with conventional neutral density filters as well as a chemical filter consisting of spectroscopic grade n-pentane (1cm, O.D. is 1 at 193nm) did not cause a variation in relative product yields within experimental error as shown in Table 2.6.

TABLE 2.6

Filtered 193nm Laser Photolysis of Bicyclo[4.2.0]oct-7-ene (3) in pentane solution at 23°C.

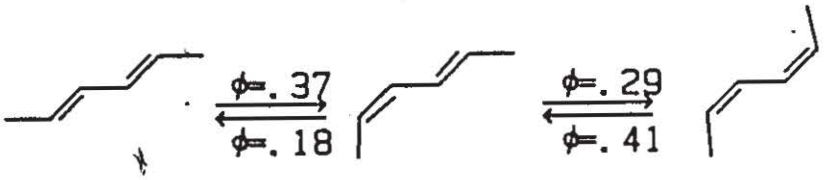
Intensity	cc-25/ct-25	R.O./M.F.[a,b]
10%[c]	1.38 ±.08	1.52 ±.09
100%[d]	1.42 ±.08	1.50 ±.09

[a] Ratio of combined ring opening to molecular fragmentation products. [b] Rate of molecular fragmentation determined by following rate of cyclohexene formation. [c] Filter = n-pentane (optical density ca. 1 at 193nm). [d] Air.

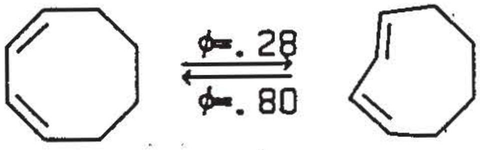
2.5 Photostationary States and Relative Quantum Yields for Direct Photoisomerization of cc- and ct-29.

Photostationary states and relative quantum yields for the direct cis,trans-photoisomerization of dienes obtained from the photolysis of 2-4 provide information on their excited state decay characteristics. Such information is available for the 2,4-hexadienes[13] and the 1,3-cyclooctadienes[35] but not for cis,cis- and cis,trans-1,3-cyclononadiene, even though the direct photolysis (254nm) of both isomers has been reported.[9]

2.10



2.11



Direct irradiation of the 2,4-hexadienes in hydrocarbon solution at 254nm leads to a photostationary state comprised of 40.6% tt-, 26.4% ct-, and 33.0% cc-isomer.[13] The quantum yields for the direct photoisomerization are given in Equation 2.10.

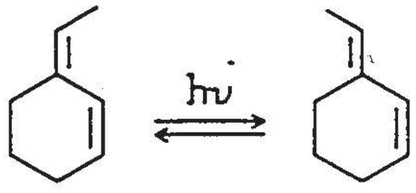
Quantum yields for the direct photoisomerization have also been reported for the 1,3-cyclooctadiene system (Equation 2.11). $\phi_{cc->ct}$ was tentatively assigned at 0.28 while $\phi_{ct->cc}$ was determined to be 0.80.[35]

Determination of the Relative Quantum Yields for the Direct cis,trans Photoisomerization of ct- and cc-29

The direct photolyses of ct- and cc-29 were studied in pentane solution (0.011 and 0.012M respectively) at room temperature. The samples were irradiated in parallel using a merry-go-round apparatus inside a Rayonet type RS reactor equipped with 254nm lamps. After an irradiation period of 2.4 minutes the ct- and cc- isomers had experienced ca. 9% and 5% conversion to the other isomer, respectively. Concentration vs. time plots for isomerization up to these conversions were linear in each case (Figure 2.6), and the ratio of their slopes affords an estimate of $\phi_{ct\to cc}/\phi_{cc\to ct} = 4.7 \pm .1$.

Ethylidenecyclohexene

The photoisomerizations of Z,Z- and E,Z-ethylidene-cyclohexene[81] (Z,Z- and E,Z-31, respectively, 0.05M) were studied qualitatively in pentane solution. The samples were irradiated (254nm) in parallel under conditions similar to those above. Both dienes were observed to rapidly (within 3 min.) achieve photostationary state mixtures that were comprised of ca. 90% of the diene tentatively identified as the Z,Z-isomer.



Z,Z-31 E,Z-31

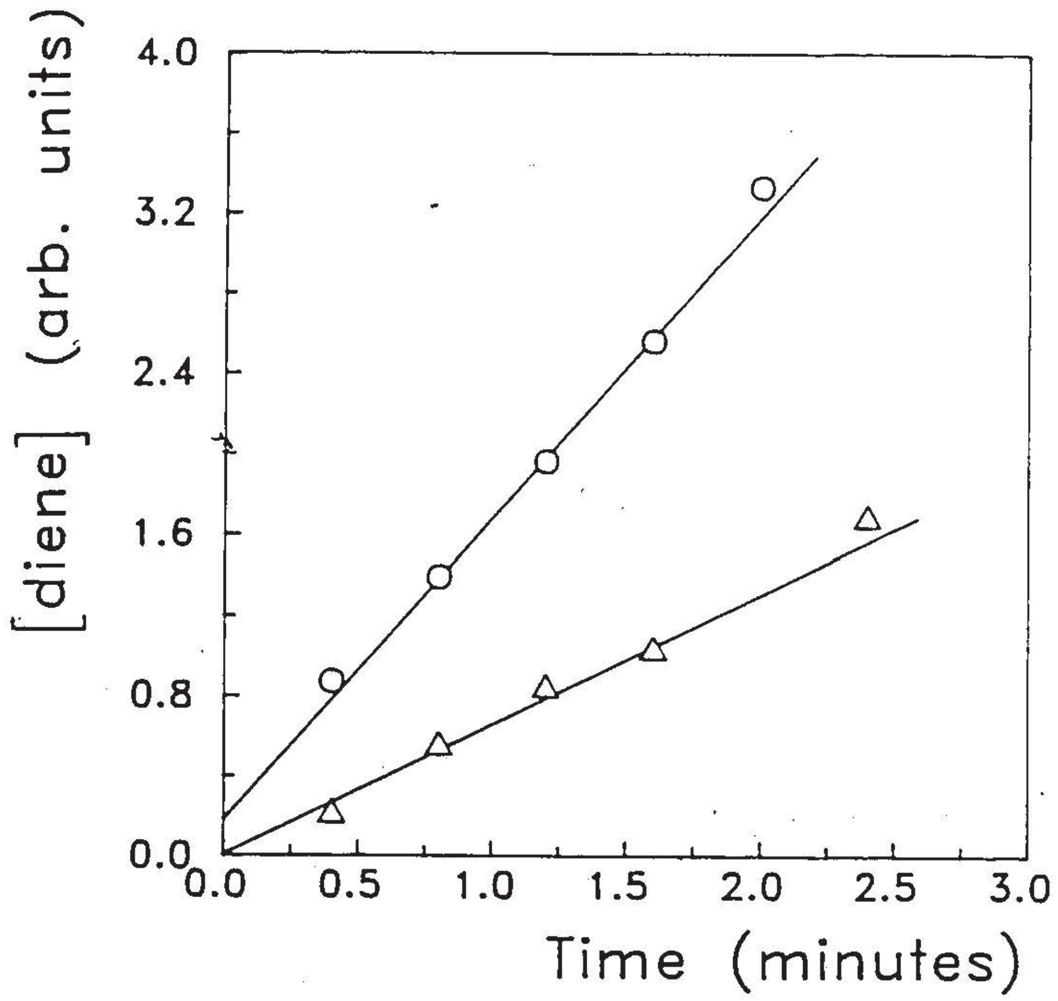


FIGURE 2.6 Concentration [illegible] plot for the formation of **cc-29** (○) and **ct-29** (△) fro[illegible]nm photolysis of **ct-29** and **cc-29**, respectively, in pen[illegible]

2.6 193nm Photolysis of 1, 2, and 3 at 77K.

Low temperature studies were performed at liquid nitrogen temperature (77K) using the 193nm line of the excimer laser with a custom made Suprasil quartz dewar and cuvettes. The photolyses were undertaken in 4:1 isopentane:cyclopentane to ensure that the solvent remained fluid during the low temperature studies. The experiments consisted of performing the photochemistry at 77K using the special apparatus described above. The photolysis was then repeated using the same apparatus but at room temperature. Similar conversions (ca. 3-5%) of starting material were maintained at both temperatures. Product yields were determined by averaging two or three experiments at room temperature and at 77K. Each sample was analyzed in triplicate by vpc on a capillary column. The single-point determinations were verified to be accurate within 10% to determinations made by slow irradiation and concentration vs. excitation dose plots (**cc-25/ct-25** from the photolysis of 3 equals 1.40 ±.08 vs. 1.45 ±.13 from the single point determination and the concentration vs. excitation dose, respectively).

TABLE 2.7

Relative Yields of Dienes from 193nm Photolysis of cis-and trans-1 at 296K and 77K.[a,b]

Isomer	Temp.(K)	tt-22	ct-22	cc-22
t-1	296	2.5 ±.2	3.2 ±.2	1.0 ±.1
	77	1.9 ±.2	2.8 ±.2	1.0 ±.1
c-1	296	3.2 ±.2	4.9 ±.3	1.0 ±.1
	77	2.5 ±.2	3.4 ±.2	1.0 ±.1

[a] Yields and errors determined from the average of at least three single point determinations at each temperature. [b] In 4:1 methylbutane/cyclopentane.

TABLE 2.8

Relative Yields of Products from 193nm Photolysis of Bicyclo[4.2.0]oct-7-ene (3) at 77K.[a,b]

Temperature (K)[c]	25	cc-26	ct-26
296	1.6 ± 0.1	1.4 ± 0.1	1.0 ± 0.1
77	2.0 ± 0.1	3.3 ± 0.2	1.0 ± 0.1

[a] Yields and errors determined from the average of at least three single-point determinations at each temperature. [b] In 4:1 methylbutane/cyclopentane. [c] Relative yields uncorrected for vpc response.

TABLE 2.9

Molecular Fragmentation Vs. Ring Opening at 77K and Room Temperature for <u>2</u> and <u>3</u>.[a,b]

Cyclobutene	Temperature	M.F./R.O.
<u>2</u>	296 K	1.9 ± 0.2
	77 K	2.2 ± 0.2
<u>3</u>	296 K	1.5 ± 0.2
	77 K	2.2 ± 0.2

[a] Yields and errors determined from the average of at least three single-point determinations at each temperature. [b] In 4:1 methylcyclobutane/cyclopentane. [c] Relative yields uncorrected for vpc response.

B. Discussion

The preceding assembly of photochemical data on compounds 1 through 4 leads one to the rather surprising conclusion that the photochemically initiated electrocyclic ring opening of simple alkyl-substituted cyclobutenes is clearly non-stereospecific. In addition, molecular fragmentation resulting from formal $[\sigma 2_S+\sigma 2_S]$ cycloreversion is a competing reaction pathway, as has been well established in previous studies.[19-21] The observation of non-stereospecific ring opening for simple cyclobutenes appears to be the first under conditions in which the vinylic portion of the ring itself is the chromophore and secondary photolysis is clearly not a factor.[20] Indeed, this is apparently the first systematic study of the photochemistry of simple, alkyl-substituted systems to be performed.

2.7 Electrocyclic Ring Opening

Bicyclo[3.2.0]hept-6-ene (2) undergoes ring opening with relatively high efficiency to yield cis,cis-1,3-cycloheptadiene (24) competing effectively with molecular fragmentation to yield acetylene and cyclopentene. This result contrasts the results of Inoue and coworkers[20] for the same compound. These workers reported that 2 did not undergo ring opening to give 24 but afforded only acetylene and cyclopentene via molecular fragmentation. Inoue and co-workers failed to observe any 24 due to the light source utilized (an unfiltered low pressure mercury lamp), the output of which is comprised primarily of the 185nm and 254nm mercury lines in an approximate intensity ratio of 1:6.[82] The more intense 254nm mercury line precludes the build-up of photolabile compounds that absorb strongly at this wavelength such as 1,3-dienes. It is well known that **24** undergoes very efficient ring closure to yield **2**, as discussed in Chapter I.[57] It is therefore clear that any 1,3-cycloheptadiene formed in the unfiltered photolysis (185 + 254nm) might be completely converted back to starting material due to secondary processes stimulated by 254nm excitation. The use of monochromatic light sources in the present study circumvents problems of this type and the control experiments that were performed indicate conclusively that secondary diene photolysis has been rigorously avoided.

Although our results for **2** have provided new information on its excited state behaviour and corrected previous work in the literature, this example does not provide stereochemical information on the electrocyclic ring opening, since under the conditions of our experiments, any **ct-24** formed by ring opening of **2** would be rapidly converted back to starting material or to the cis,cis-isomer.[35] Observation of **ct-24** would be possible only under conditions where the diene isomer is stable (<-78°C)[35] or perhaps by transient spectroscopic methods. This is the subject of future work. Cis,trans-1,3-cycloheptadiene has been successfully trapped,[34] affording 3-methoxycycloheptene, when the cis,cis-isomer was irradiated in acidic methanol. However the cis,trans- diene isomer was not trapped in neutral methanol under the same conditions.[34] We have carried out a 193nm photolysis of **2** in neutral methanol but have not observed any methanol addition products. A photolysis of **2** in acidic methanol has yet to be carried out.

Irradiation of bicyclo[4.2.0]oct-7-ene (**3**) at 185 or 193nm leads to the efficient formation of both **cc-** and **ct-25**. Since these results are clearly not artifacts of secondary diene photolysis, the formally symmetry forbidden ct-diene isomer is considered to be a primary photoproduct. Unlike **ct-24**, **ct-25** is reportedly stable up to 80°C where it undergoes rapid (conrotatory) thermal closure to **3**.[35] Therefore, **ct-25** can be detected under the experimental conditions established. In fact, injection of a pure sample of **ct-25** into the gas chromatograph results in no observable isomerization under our vpc conditions.

As in the case of **3**, far ultraviolet photolysis of the cyclobutene isomers of **1** and **4** results in nonstereospecific ring opening to yield mixtures of all the possible geometric diene isomers. Several mechanistic possibilities may exist for the apparent nonstereospecificity of the ring opening. In general, three basic mechanistic processes may occur in the photochemistry of a molecule[83]: (A) the electronically excited reactant molecule may pass directly to the electronically excited state of the product followed by crossing to the ground state, (B) the electronically excited reactant undergoes continuous, non-adiabatic reorganization, passing to the ground state of the product(s), or (C) the electronically excited reactant molecule crosses directly to a vibrationally excited or "hot" ground state of the reactant which then undergoes a thermal reaction to give ground state products. Before considering other alternative explanations for the observed nonstereospecificity, it is worthwhile to examine our results in the context of currently accepted theory; i.e. that ring-opening proceeds purely by the disrotatory pathway, and the forbidden isomers arise as a result of secondary events involving isomerization of the initially formed diene isomers. Only one mechanistic possibility is consistent with a formally allowed ring opening pathway in the case of **1**, **3** and **4** which leads to mixtures of all possible geometric isomers; this is pathway (A) which involves adiabatic, disrotatory opening to yield excited dienes that in turn yield all the geometric isomers as a result of their subsequent decay. Combined pathways (A) and (B) or (B) and (C) could possibly lead diene mixtures as well. Adiabatic ring opening has been observed upon excitation of **13** and **14**, part of a rather specialized family of cyclobutenes as already discussed in chapter one.[52,53]

The process may be visualized effectively using the most recent calculated (*ab initio*) state correlation diagrams[18] for the ground and excited state con- and disrotatory interconversions of cyclobutene and butadiene shown in Figure 2.7. Although these potential energy surfaces have been calculated for the unsubstituted parent system, the calcula-

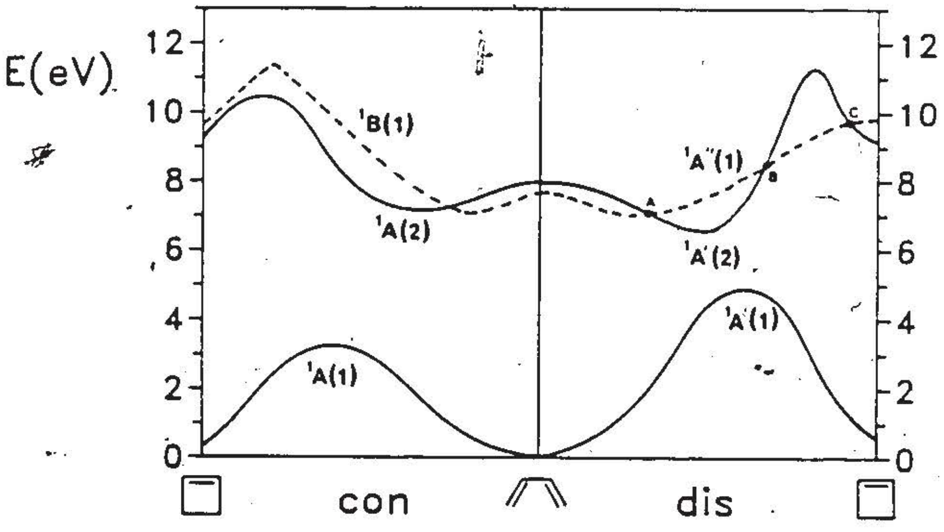
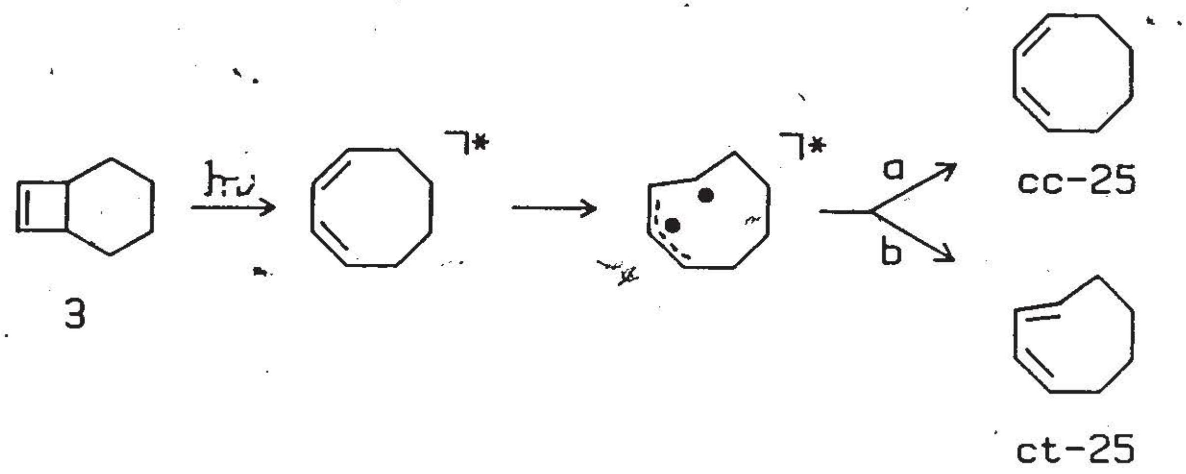


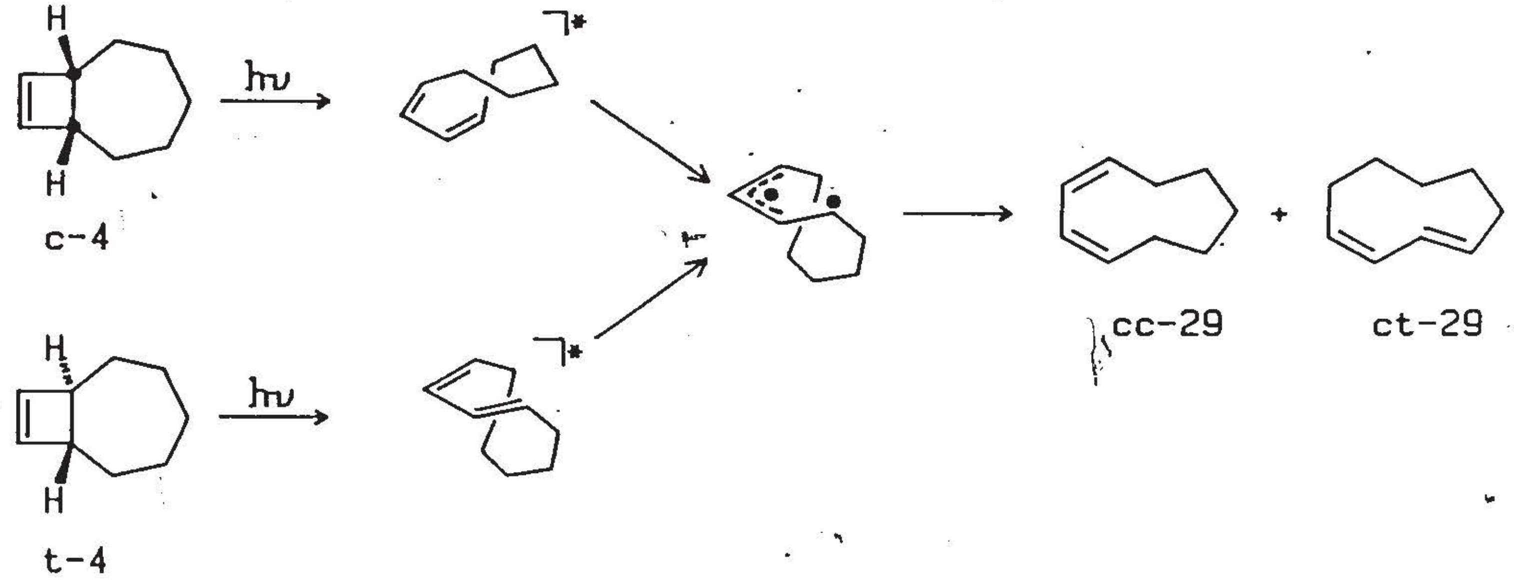
FIGURE 2.7 Calculated potential energy curves for the ground and excited state con- and disrotatory interconversions of cyclobutene and butadiene.

the calculations are, in general, consistent with experimental examples involving the thermal and photochemical interconversions of these compounds. The process begins with excitation of the cyclobutene to the S_1 ($^1A'(2)$) surface where disrotatory ring opening commences. Two crossings, from S_1 ($^1A'(2)$) to S_2 ($^1A''(1)$) at C and then back to S_1 ($^1A'(2)$) at B, provide an energetically accessible path to the minimum on the cyclobutene S_1 ($^1A'(2)$) potential energy surface. A third crossing at A would provide a path to the fully open diene in the first excited singlet state, this pathway is 5-8 kcal/mole endothermic relative to the S_1 ($^1A'(2)$) minimum.[18] Once obtained, the singlet excited diene is expected to decay by cis,trans isomerization or disrotatory closure to regenerate the precursor.[42,43] The mixture of dienes obtained should be governed by the decay characteristics of the singlet excited diene. This process would have to compete effectively with internal conversion to the ground state disrotatory surface at the partially open geometry in order to account for our results. This would require an over-estimation in the calculated barrier of 5-8 kcal/mol or that the excited molecule contain enough vibrational energy to overcome the barrier.

Mechanistically, the apparent non-stereospecificity with which **1**, **3**, and **4** undergo photochemical ring opening may be explained in terms of such an adiabatic process, where concerted disrotatory ring opening proceeds to yield fully open diene in the first excited state, which in turn decays by torsional relaxation to a distorted excited state intermediate. Scheme 2.1 serves to exemplify this process for **3** which, according to this mechanism would open via disrotation to excited cc-**25**. Scheme 2.2 shows the mechanistic path for c- and t-**4**.



SCHEME 2.1. Adiabatic disrotatory electrocyclic ring opening mechanism for 3 affording both cc- and ct-25.



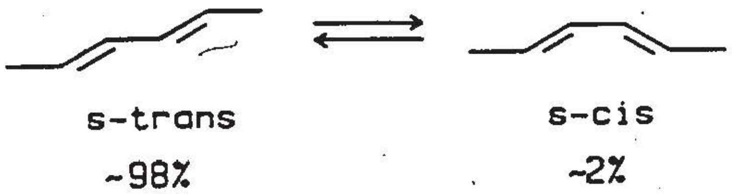
SCHEME 2.2 Adiabatic mechanism for the non-stereospecific ring opening of **4**.

As shown in Scheme 2.1 for 3 and in Scheme 2.2 for c- and t-4, their photolysis can result in just two diene isomers which are linked by a common twisted intermediate. As a first approximation, we assume that the decay characteristics of the excited dienes produced from cyclobutene ring-opening are similar to those that determine the quantum yields for direct cis,trans-photoisomerization of the dienes themselves. This being the case, we can use the latter values, or ratios, to calculate the expected distribution of diene isomers obtained in the limit of purely disrotatory, purely adiabatic ring opening. The direct photoisomerization of cc- and ct-25 has been studied by Nebe and Fonken, who reported values for $\phi_{ct->cc}$ (0.80) and $\phi_{cc->ct}$ (0.28).[35] The sum of these quantum yields is sufficiently close to unity to suggest that both isomers decay predominantly via torsional relaxation to yield a common twisted excited state. Comparison of the isomeric diene ratio (cc/ct = 3.0 ± 0.5) obtained from the photolysis of 3 with the quantum yield ratio for the direct photoisomerization of the dienes as obtained by Nebe and Fonken (cc/ct = 2.9 ±.5), reveals that they are equivalent within experimental error. While these results are thus compatible with the adiabatic mechanism for photochemical ring-opening, photolysis at 193 and 214nm afford dramatically different isomeric distributions (cc/ct = 1.5 at 193nm) which may indicate that the perfect fit of 3 to the purely adiabatic mechanism is coincidental.

The next highest system in the homologous series of annelated cyclobutenes, the cis- and trans-fused bicyclo[5.2.0]-8-enes (c- and t-4 respectively) provides a good system to study the adiabatic mechanism, since according to the proposed mechanism each isomer of 4 should pass adiabatically through the same twisted excited state and therefore lead to equivalent isomeric diene mixtures (Scheme 2.2). Although cis- and trans-**4** yield similar isomeric diene mixtures (Equation 2.7), suggesting the involvement of a common intermediate, the results do not fit with the purely disrotatory, adiabatic ring opening mechanism. The ratio of the quantum yields for direct diene cis,trans-photoisomerization, $\phi_{ct\to cc}/\phi_{cc\to ct}$, is 2.2 ±0.1, indicating that the twisted excited state relaxes preferentially to afford the cis,cis-isomer. In contrast, cis,trans-1,3-cyclononadiene is the major diene isomer formed in the photolyses of both c- and t-**4**.

Far ultraviolet irradiation of the simplest alkyl-substituted cyclobutenes, cis- and trans-3,4-dimethylcyclobutene, (c- and t-1) yields mixtures of the three possible geometric isomers of 2,4-hexadiene (22) in each case, as shown in Equation 2.4. The diene mixtures obtained from both cyclobutenes are weighted toward the isomer(s) resulting from the formally forbidden conrotatory ring opening pathway. Since three diene isomers exist for 2,4-hexadiene, determination of the expected relative yields of these dienes from c- and t-1, according to an adiabatic mechanism, is less straightforward than in the cases above where only two isomers were possible. Assuming that adiabatic ring opening does occur in this case, a simple calculation has been made in order to estimate the expected relative diene yields using the quantum yields for their direct photoisomerization which are displayed in Eqn 2.10.[13] The numbers calculated from the diene ratios are clearly very different from the values obtained experimentally. The discrepancy in the numbers may be due to a dissimilarity in the intermediates that have been postulated for the direct diene isomerization[13] and the intermediate(s) hypothetically formed upon adiabatic disrotatory ring opening of cyclobutene. An important feature of polyene photochemistry is reactivity control due to excitation of individual ground state conformers, whose excited states do not interconvert during their lifetimes. The facile rotation about the bond between the conjugated double bonds in 1,3-dienes results in the existence of more than one diene conformer in solution.[73] This rotation results in an equilibrium mixture of s-cis and s-trans diene conformers as shown for **tt-22** in Equation 2.12. Butadienes substituted at C1 and/or C4, such as 2,4-hexadiene, have equilibria shifted almost entirely to the s-trans conformer at room temperature in solution. Thus, measured quantum yields for direct photoisomerization of dienes of this type essentially reflect the decay characteristics of s-trans diene singlets.[39] On the other hand, cyclobutene ring opening presumably yields dienes initially in the s-cis conformations. There is good reason to expect the decay characteristics of s-cis diene singlets to differ from those of the s-trans conformers[42,43] and therefore the relatively simple calculation performed using the decay characteristics inferred from the direct photoisomerization of 2,4-hexadiene should not necessarily be expected to fit. The observations made on the direct photochemistry of cyclobutene should therefore be considered more

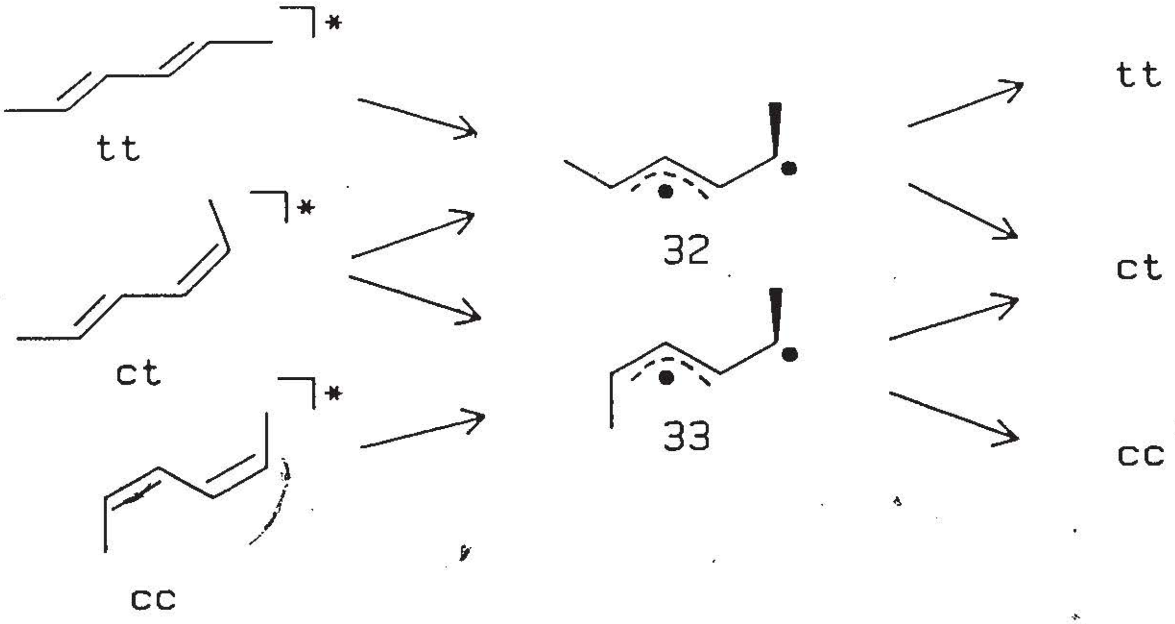
2.12



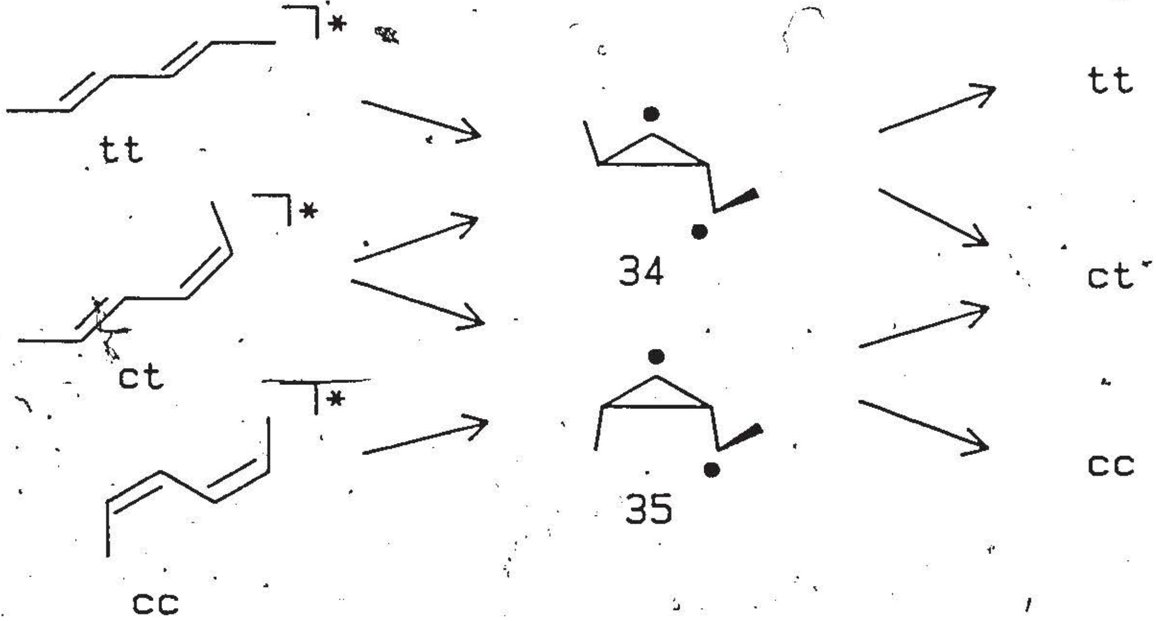
carefully within the realm of postulated mechanisms for direct cis,trans photoisomerization of acyclic 1,3-dienes.[12,13,42,43]

Saltiel and co-workers have studied the direct photoisomerization of the three geometric isomers of 2,4-hexadiene and have determined the quantum yields for their interconversions.[13,42] The results reveal that diene excited singlet states isomerize about only one bond in contrast to the triplet state which leads to two-bond isomerization. This conclusion is evident in the quantum yields for tt -> cc and cc -> tt isomerization, which are both indistinguishable from zero.[13,42] These two results show that the lowest singlet excited states undergo torsional relaxation about only one double bond and therefore an intermediate such as an excited 1,4-biradical singlet is excluded as a possibility.[42,43]

One bond isomerization in singlet excited 2,4-hexadiene is nicely accounted for in terms of the allylmethylene mechanism.[13,42,43,84,85] In order to explain the results shown in Equation 2.10 a minimum of two distinct twisted intermediates, each leading to isomerization about one bond, is required. This mechanism explains the isomerization by involving torsional relaxation of initially planar singlet excited dienes about only one double bond through relaxed, noninterconverting, diradicaloid excited states. This mechanism is not able to account for the observation that more than 50% of the excited dienes decay without undergoing cis,trans isomerization as revealed by the quantum efficiencies (all <.50) exhibited in Equation 2.10. Thus some component of excited state decay that proceeds directly to the starting isomer in its ground state without torsional relaxation is required. The above considerations disregard excitation of 1,3-dienes that are in s-cis conformations.



SCHEME 2.3a Allylmethylene mechanism for the photoisomerization of 2,4-hexadienes, <u>22</u>.

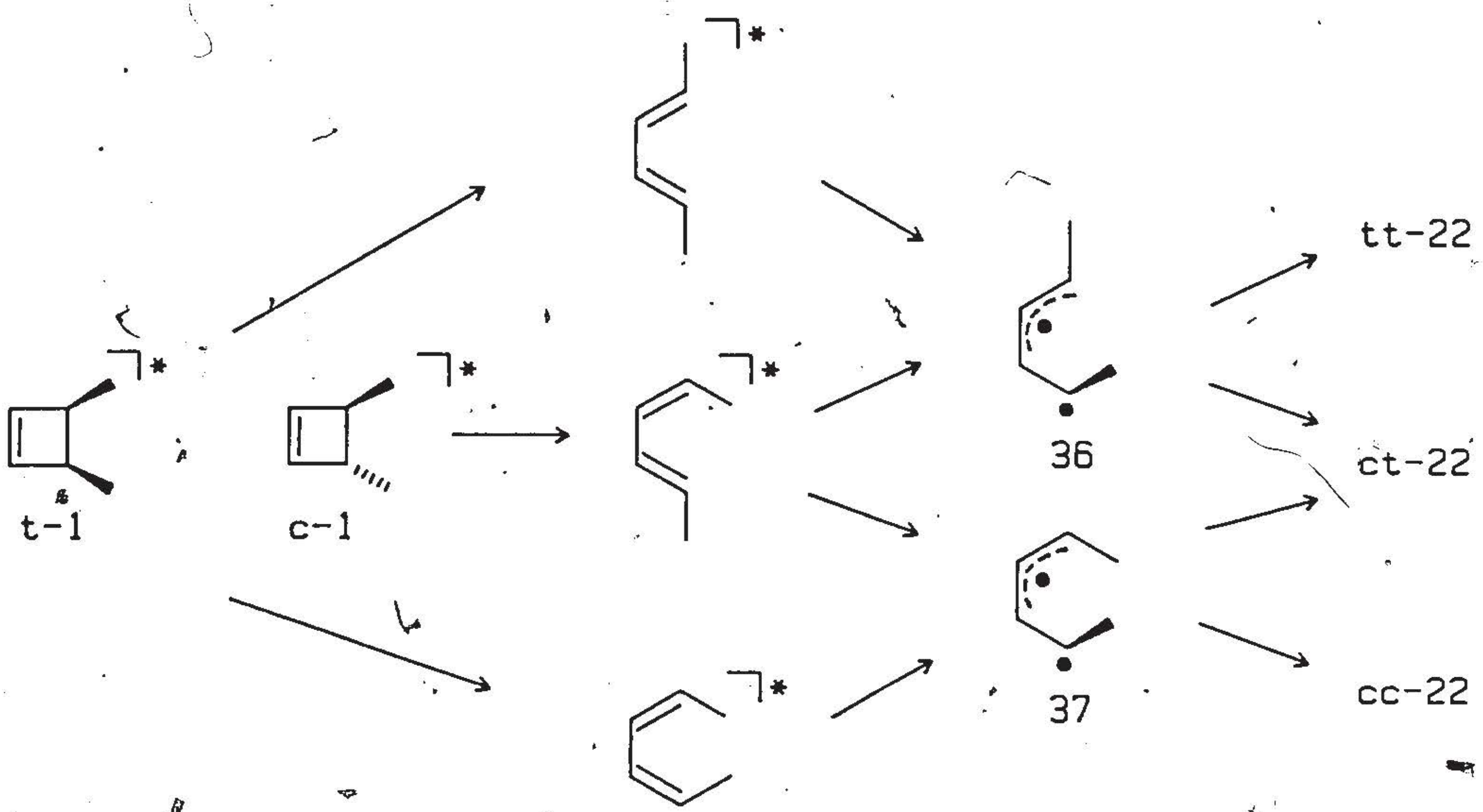


SCHEME 2.3b Cyclopropylcarbinyl diradical mechanism for the photoisomerization of 2,4-hexadienes, <u>22</u>.

As Scheme 2.3a shows, twisted allylmethylene singlets can account for the one-bond isomerization, provided that s-trans/s-cis conformational equilibration is slow and unable to compete with torsional relaxation of the planar s-trans singlets that lead to intermediates 32 and 33.

A second mechanistic possibility involves cyclopropylcarbinyl diradical intermediates, first proposed by Srinivasan,[86] and involves 1,3-bonding in the excited diene to yield cyclopropylmethylene type biradicals, 34 and 35 (Scheme 2.3b).[13] To account for one-bond isomerization of singlet excited dienes, stereospecific formation and ring opening of two biradical intermediates, 34 and 35, is required.

We have considered the adiabatic ring opening of cyclobutenes c- and t-1 within the framework of these diradical mechanisms described above for the direct photoisomerization of 1,3-dienes. The analogous process gives s-cis dienes formed by adiabatic, disrotatory ring opening of the singlet excited cyclobutenes. As in the case of direct photoisomerization of dienes, we assume that s-trans/s-cis conformational equilibration is slow compared to torsional relaxation of the s-cis planar diene singlets. As shown in Scheme 2.4, the proposed mechanism can give all the geometric isomers of 2,4-hexadiene through allylmethylene intermediates 36 and 37, which are assumed to be distinct and non-interconverting. If one assumes that ring opening occurs only by the purely adiabatic, disrotatory pathway, then this mechanism cannot account for the observation that c- and t-1 each yield diene mixtures weighted in favour of the formally forbidden isomer(s). This can be shown by solving the set of four simultaneous equations involving the four unknown partition coefficients in Scheme 2.4 using the four independent product



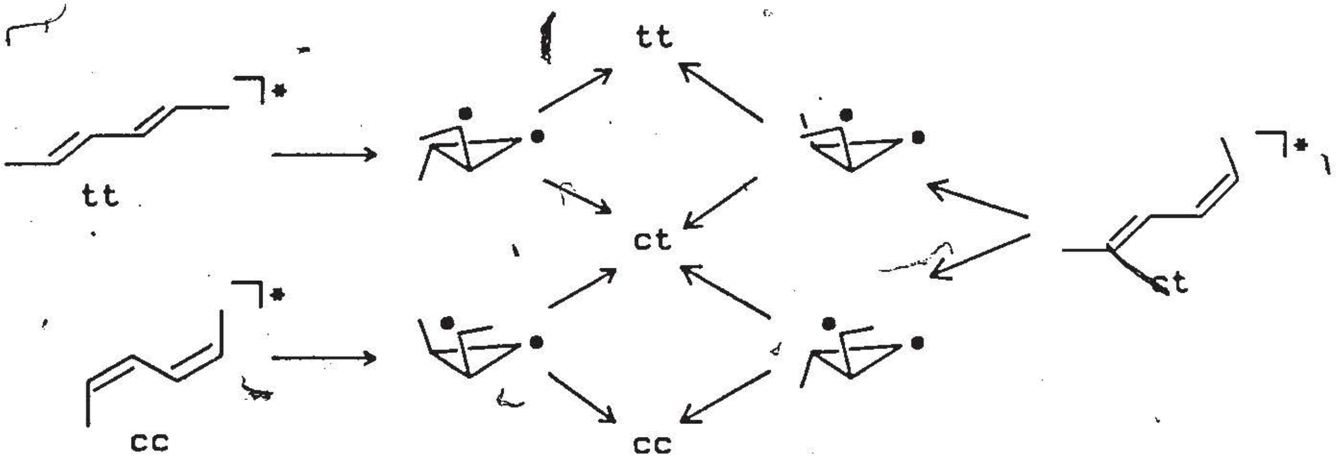
SCHEME 2.4 Non-stereospecific ring opening of 1 via allylmethylene biradical intermediates.

ratios obtained from Table 2.2. The values obtained in this manner for the partition coefficients have no physical meaning as some are greater than one or less than zero. Physically meaningful values do not result even if the relative product yields are allowed to vary by as much as 15% from the experimental values, which is well outside our limits of experimental error.

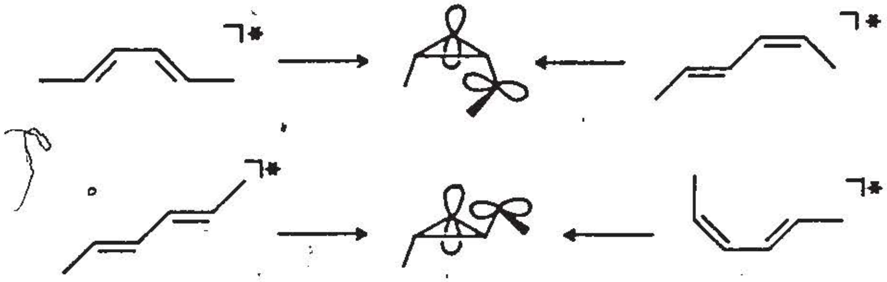
The cyclopropylcarbinyl diradical mechanism[13] shown in Scheme 2.3b is operationally equivalent to the allylmethylene mechanism and similarly incapable of accounting for our experimental results.

Scheme 2.5 shows a modified version of the cyclopropylcarbinyl mechanism for diene photoisomerization. This mechanism differs from that of Figure 2.3b in that all four possible cyclopropylcarbinyl diradicals, formed by concerted closure of the three isomeric 2,4-hexadienes are represented as distinct, non-interconverting species. Conformational s-trans/s-cis equilibration of the planar diene singlets must be slow relative to relaxation to the diradicaloid species. Rotation about the exocyclic bond must necessarily be slow compared to re-opening of the diradical which generates the diene via another concerted ring opening. Diene isomerization therefore results from the mode of concerted ring opening processes (it does not matter whether the process is dis- or conrotatory as long as the mode of closing/opening is consistent) and not torsional relaxation about the exocyclic double bond.

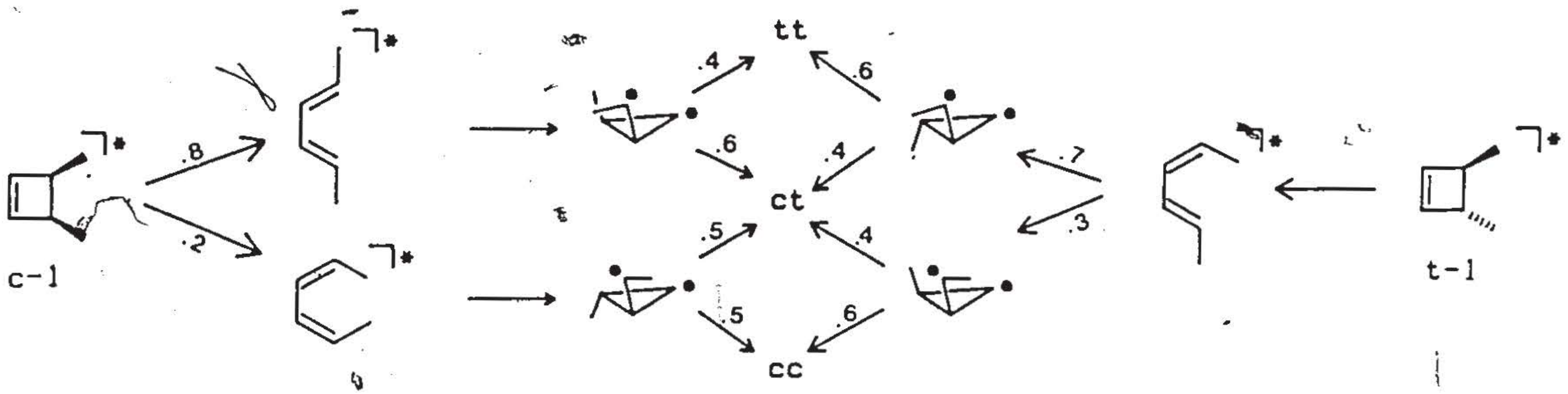
The purely disrotatory, adiabatic ring-opening can be represented using this mechanism. Cyclobutenes c- and t-1 each generate two distinct intermediates, and their mechanisms for ring opening (Scheme 2.6) are thus not coupled as in the previous examples. In this case, though, the



SCHEME 2.5a Modified cyclopropylcarbinyl diradical mechanism for the photoisomerization of 2,4-hexadiene.



SCHEME 2.5b Interconversion of s-cis and s-trans geometric isomers via modified cyclopropylcarbinyl diradical intermediates.



SCHEME 2.6 Modified cyclopropylcarbinyl diradical mechanism for the nonstereospecific ring opening of 1.

intermediates arising from the s-cis singlets from cyclobutene are identical to those involved in the direct isomerization of s-trans-1,3-dienes (Scheme 2.5b). Since in this case the diene mixtures formed by cyclobutene ring-opening and direct diene excitation are linked by the same intermediates, calculation of the entire set of partition coefficients given in Scheme 2.6 is possible using the product ratios from photolysis of 1 and using the quantum yields from the 2,4-hexadiene photolysis.[42] In this case the values obtained for the partition coefficients are physically meaningful (please consult appendix A for the calculation details). Although reasonable values for the various partition constants are obtained from the calculations, the mechanism is probably unrealistic. Intermediates of this type would be expected to experience some degree of bonding between the radical centres if rotation about the exocyclic C-C bond must be slow. This should be reflected in the product mixtures from the direct photolysis of 1,3-dienes where one would expect to observe rather higher yields of bicyclobutanes than is normally the case; they are in fact minor products.[12,13] Bicyclobutanes, as far as we are aware, have not been observed in the direct photolysis of cyclobutenes, although they may be minor products.[19-21] Finally, our study of the photoisomerization of Z,Z- and E,Z-ethylidene-cyclohexene provides evidence that disputes this mechanism for diene cis,trans photoisomerization. The requirement of this mechanism is that: (i) s-cis and s-trans diene conformers be linked by common cyclopropyl-carbinyl diradicals (figure 2.5b) the result of which is one-bond isomerization of an s-trans or s-cis diene conformer via the diradical intermediate affording a geometric isomer in the other conformation or (ii) the

(ii) the diradical simply re-opens in the direction of initial ring closure resulting in no apparent isomerization. Thus, the mechanism implies that cis,trans isomerization of conformationally constrained dienes such as **Z,Z-** and **Z,E-31** should be inefficient. Ring opening of the bicyclic cyclopropylcarbinyl diradical to the other diene isomer may be precluded due to constraint imposed by the fused rings. Instead it may only open in the direction of the initial ring closure resulting in no apparent isomerization. In fact, we have observed the isomers of **31** to be very rapidly isomerized upon direct irradiation of 254nm light to a photostationary state that consists mainly (90%) of the diene tentatively identified as the Z,Z-isomer of ethylidenecyclohexene.

Thus, the bulk of the experimental evidence obtained is inconsistent with a mechanism for non-stereospecific diene formation that involves purely disrotatory, adiabatic ring opening, unless excited dienes formed by adiabatic cyclobutene ring-opening do not isomerize by the same mechanism that leads to diene isomerization upon direct excitation in solution. Perhaps the non-stereospecificity exhibited by the cyclobutenes above is due partly to an adiabatic component of disrotatory opening, but other processes for the formation of the formally-forbidden diene isomers exist that compete with the excited diene singlets that have been assumed to isomerize via the simple twisting mechanism of Scheme 2.5. Torsional momentum effects[87] could account for the observed diene mixtures from **1** and **c-4** within the adiabatic, disrotatory ring opening mechanism, for example. The possibility of torsional momentum effects in the photoisomerizations of alkenes and dienes has been derived theoretically,[87] and the concept is incompatible with the theories of equilibrated common intermediates that have been described above. Experimentally the effect of torsional momentum would be signalled by quantum yields for isomeric diene photoisomerization that are equal to or greater than 0.5 in both directions of diene photoisomerization. No experimental evidence has been reported that supports torsional momentum effects in the photoisomerizations of neutral systems, although there are systems (charged[88] as well as complexed[89] systems) that do support the idea. This and the fact that the photochemistry of <u>3</u> and t-<u>4</u> does not appear to involve torsional momentum effects of the excited singlets, render this possibility quite unattractive.

Other Mechanistic Possibilities.

The excellent fit of <u>3</u> to a purely adiabatic, disrotatory ring-opening mechanism is almost certainly coincidental considering the results obtained for <u>1</u> and <u>4</u> and from the 193nm photolysis of <u>3</u>. Therefore other mechanistic possibilities for non-stereospecific ring opening mechanisms must be considered.

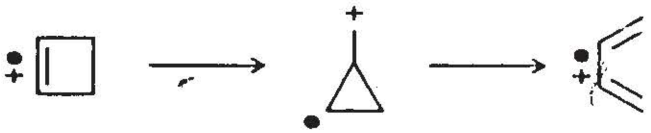
One possibility is that ring opening of the cyclobutenes occurs from the excited singlet state (adiabatically or non-adiabatically) in competition with radiationless decay to vibrationally "hot" cyclobutene ground states that subsequently undergo conrotatory ring opening. High vibrational overtone photochemistry of cyclobutene using direct single-photon (infrared) excitation of high CH stretching overtone transitions has been observed to induce isomerization to 1,3-butadiene.[90] In addition, Srinivasan proposed vibrationally "hot" cyclobutenes to explain the formation of formally forbidden diene isomers in the triplet sensitized photochemistry of c-**1**.[54] A similar mechanism has been suggested in the photochemistry of **9**.[49]

A distinction between a reaction involving an electronic excited state vs. vibrationally excited ground states may be difficult to ascertain. The involvement of highly vibrationally excited ground states is rather common in photolyses of alkenes conducted in the gas phase. The pressure effect, which has been utilized in the case of far UV gas phase photochemistry of some simple alkenes, may possibly provide a useful test for the vibrationally "hot" ground state cyclobutene concept in the gas phase. For example, it has been proposed that the yield of photoproducts from highly excited vibrational ground states of alkenes that result from rapid internal conversion, is suppressed by addition of foreign gases. Thus, the participation of "hot" cyclobutene ground states may be signalled by quenching of formally forbidden diene isomers as the pressure of inert gas is increased in a gas phase study.[91] It is difficult to imagine that such secondary effects would lead to the large variation in product yields observed here in solution where deactivation of "hot" cyclobutenes by the solvent should be highly efficient, thereby quenching the process. Laser flash photolysis may prove useful in determining the extent of "hot" cyclobutenes in the photochemistry of these systems in solution. The fluorescent excited states of simple alkenes have decay rates in the ~~order of~~ 10^{11} s^{-1}.[61] It follows then that primary processes involving the singlet excited state will react at comparable rates. Secondary processes involving vibrationally excited ground states may react more slowly and these processes might be observable by flash photolysis techniques. The laser flash photolysis experiment has precedence in the study of the photochemistry (193nm) of 2,3,3-trimethyl-1-butene and 2,3-dimethyl-2-pentene.[92]

Isomerization of hot diene ground states formed after disrotatory ring opening cannot account for the observed product mixtures. RRKM theory[93] predicts that isomerization of a photochemically generated hot ground state is statistical in nature (ie. the energy remaining after rapid internal conversion is randomized among the ground state vibrational modes before reaction) and therefore reactivity should not differ from thermally generated dienes.

Compound **15** is the only cyclobutene derivative that has been observed to undergo stereospecific ring opening.[19] Interestingly, only the cis-fused isomer undergoes electrocyclic ring opening at all. The most obvious difference between this system and the ones studied here is the degree as well as the type of substitution of the cyclobutene chromophore.

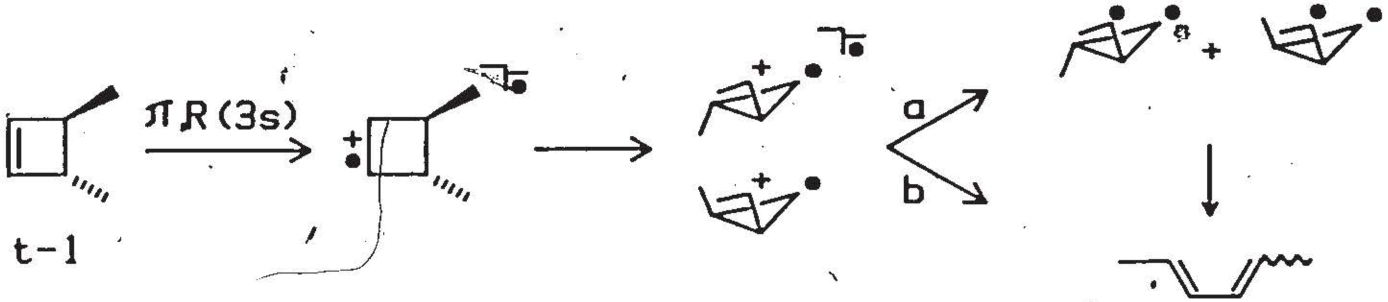
In view of the effect of substituents on the relative energies of excited states in alkenes one may consider the possible role of the Rydberg excited state in these ring opening reactions. The effect of increasing alkyl-substitution in simple alkenes has been shown to stabilize the π,R(3s) excited state to a much greater extent than the π,π^* excited state.[59,60] In light of this trend, the Rydberg excited state, possibly the lower in energy of the two in the case of **15**, may be responsible for stereospecific disrotatory ring opening. As mentioned in the introduction, the Rydberg excited state of simple alkenes may be referred to as a semi-ionized radical-cation, and therefore, it may be instructive to use cyclobutene radical-cations as models for the Rydberg state of cyclobutene. Cyclobutene radical-cations, studied both theoretically[94] and experimentally in the gas phase,[95-97] have been shown to open expediently to the analogous 1,3-diene radical-cations. Various workers have attempted to consider the reactions of the open-shell systems within the context of orbital symmetry rules even though it is apparently not clear what effect the removal of an electron has on these orbital symmetry considerations.[98,99] The only conclusion that appears clear in the studies that have been carried out is that cyclobutene radical-cations undergo thermal ring opening more easily than their neutral counterparts.[94-97] Gross and Russell, who have used the technique of ion cyclotron resonance spectrometry to generate alkyl[95,96] and aryl[97] substituted cyclobutene radical-cations, have estimated that the maximum activation energy for this process is ca. 7-14 kcal/mol. Bauld and co-workers,[94] who have studied the problem theoretically via several models, found the concerted mechanism to involve a preferred <u>conrotatory</u> motion which has an MNDO/3 and MNDO activation energy of 34 and 31 kcal/mol, respectively. The interesting conclusion to arise from Bauld's work was the establishment of a second pathway leading to diene radical-cations having an MNDO/3 activation energy for the opening of 21 kcal/mol. This pathway involves ring contraction to a cyclopropylcarbinyl radical-cation which cleaves to give a diene, as shown in Scheme 2.7. The theoretical viability of the asynchronous pathway was confirmed using extended basis set optimized <u>ab initio</u> SCF MO calculations, which yielded an activation energy of 20 kcal/mol for the ring opening process. Interestingly, this mechanism bears a close resemblance to the



SCHEME 2.7 Ring opening mechanism for cyclobutene radical-cation.

cyclopropylcarbinyl diradical mechanism for diene photoisomerization (Scheme 2.6).

If the π,R(3s) excited state of cyclobutene behaves analogously to its radical-cation, then the results of Bauld and co-workers have two major implications with respect to the role of Rydberg excitation in determining the stereochemistry of the ring opening of cyclobutene derivatives. First, electrocyclic ring opening may occur conrotatory as Bauld has determined theoretically.[94] The second implication is that the electrocyclic pathway in fact may not be the lowest energy path to ring opening, but a non-synchronous, unsymmetrical pathway may be the one responsible for diene formation. Scheme 2.8 illustrates the process explicitly for trans-3,4-dimethylcyclobutene, t-1. The ring contraction process has been depicted to occur adiabatically in order to clarify the course of rearrangement, but this is not meant to imply that ring contraction proceeds as such. Electron demotion as the rearrangement proceeds could afford the ground state cyclopropylcarbinyl diradical directly. If the stereochemistry of ring contraction is governed only by steric effects, then a mixture of all diene isomers should result, and the two isomers of 1 might be expected to afford different mixtures of dienes. On the basis of these considerations one concludes that the



SCHEME 2.8 Hypothetical reaction mechanism for the Rydberg excited state of t-1 within the framework of Bauld's mechanism for cyclobutene radical-cations.

π,R(3s) state may not give stereospecific ring-opening if it reacts in a manner similar to cyclobutene radical-cations.

However, the behaviour of **c-** and **t-<u>15</u>** appears inconsistent with the above hypothesis, since these compounds are expected to have low-lying Rydberg excited states. The failure of **t-<u>15</u>** to undergo ring-opening to any extent indicates that the cyclobutene Rydberg state does not undergo conrotatory opening as theory has predicted for the radical-cation, and also renders the asynchronous pathway unlikely.

Recently, cis-3,4-diphenylcyclobutene (<u>38</u>) radical-cations have been shown to undergo stereospecific conrotatory electrocycloreversion to cis,trans-1,4-diaryl-1,3-butadiene in solution when generated by the photoexcitation of the electron donor-acceptor (EDA) complexes of the cyclobutene and tetracyanoethylene or under photoinduced electron-transfer conditions.[100] A stepwise mechanism involving the intervention of a cyclopropylcarbinyl radical-cation intermediate similar to the one described above, is not supported by the observed stereospecific nature of this reaction. In addition, the radical cation of 1,2-diphenyl-3,3,4,4-tetramethylcyclobutene (<u>39</u>), generated similarly in solution, has been shown to undergo ring-opening to the corresponding diene rather inefficiently.[48] Of course, the latter example offers no stereochemical information on the process but does imply that cyclobutene radical-cations undergo ring opening rather reluctantly.

The Rydberg excited state has been described as radical-cationic in character.[57] This description does not however necessitate that it will behave as a pure radical-cationic species. In fact, the r_{max} (the maximum distance of the excited electron from the core) of the excited electron is sufficiently small that the core should be distinctly affected by its presence.[58] If the Rydberg excited state is involved in ring opening, then the behaviour of **c-** and **t-15**[19] indicate that the disrotatory pathway is the preferred one.

In order to ascertain the possible role of structure in the photochemistry of 15 we have studied the photochemistry of cis-1,2,3,4-tetramethylcyclobutene (**c-6**) at 193 and 214nm. The UV absorption spectrum of **c-6** in solution (Appendix) reveals that the Rydberg state, whose absorption extends out to ca. 230nm, is indeed lower in energy than the π,π^* excited state. Compound **c-6** opens non-stereospecifically when irradiated at 193nm, yielding all three geometric isomers of 3,4-dimethyl-2,4-hexadiene (**ZZ-**, **EZ-**, and **EE-30**). Irradiation at 214nm also results in non-stereospecific isomeric diene mixtures, but the yield of formally forbidden diene isomer is increased. The UV absorption spectrum of **c-6** reveals considerable overlap of the π,π^* and π,R(3s) states at 214nm and therefore the photochemistry arising from irradiation at this wavelength is almost certainly not due entirely to Rydberg excitation alone. While it is thus not clear from the results of the 214nm photolysis to what extent product formation results from excitation of the long wavelength absorption band, the formation of formally forbidden diene isomers does appear to correlate with excitation of the lower energy excited state in this compound. Irradiation at 229nm using a cadmium resonance lamp will be the subject of future work on **c-6** in order to clarify the contribution of the lower energy excited state to the photochemistry of **c-6**.

From the observations for **c-6** it follows that **15** represents a unique system relative to the cyclobutenes studied here, and it is implied that configurational constraints may play an important role in the photochemistry of **c-** and **t-15**. The possibility that the photochemistry of **15** is highly influenced by structural constraint is supported by the results of the photolysis of **c-6** at 193 and 214nm. As far as we are aware, **t-15** represents the only example of a relatively simple alkyl-substituted cyclobutene that does not undergo electrocyclic ring opening to 1,3-dienes to any observable extent. Complete consideration of our results for mono- and bicyclic systems and those for **c-** and **t-15** may indicate that ring opening is initiated by disrotatory motions in the cyclobutene excited state(s), but the stereochemical sense of the process is "forgotten" at some later stage on the reaction coordinate, perhaps as a result of intermediates that ultimately afford mixtures of the isomeric dienes. In the case of **t-15**, which does not undergo electrocyclic ring opening, the ring opening process may begin disrotatory but at some point along the reaction coordinate structural constraint prevents completion of the process.

Wavelength and Low Temperature Studies

At least three singlet excited states may be participating in the photochemistry of the cyclobutene system. These are the S_1 (π,π^*), S_2 (π,σ^*), and π,R(3s) Rydberg states. Ab initio studies indicate that the S_1 as well as S_2 potential energy surfaces play an important role in the electrocyclic ring-opening of the parent cyclobutene.[18] There is some experimental evidence supporting Rydberg excited state involvement in the photochemistry of cyclobutene,[21] but as far as we are aware no one has suggested electrocyclic ring opening via this excited state. Wavelength dependence studies with 2,3-dimethyl-2-butene have provided rather convincing evidence concerning the relative extent of π,π^* and π,R(3s) excited state participation in simple alkenes and their respective reaction pathways.[65]

Absorption spectra for cyclobutenes 1 - 6 have been recorded (see Appendix). In general, the spectra consist of single absorption bands which extend out to ca. 210-215nm for compounds unsubstituted at the double bond. The absorption maxima in both cis- and trans-substituted compounds remain well defined at 186.5nm in all cases but t-1 which has a maximum shifted to 188nm. Curiously, the absorption bands of trans-substituted cyclobutenes appear slightly more diffuse, tailing out an additional 5-8nm. In contrast, the absorption bands of the substituted cyclobutenes 5 and 6 are more diffuse than in the unsubstituted cases. Within the series of cis-substituted derivatives 1, 5, and 6 the absorption maximum shifts to progressively longer wavelengths (185.5 to 190.2nm) with increasing substitution at the double bond. While the spectra of 1 and 5 show featureless single bands at 186 and 189nm, respectively, 6 exhibits a band at 190nm (ϵ = 11,700) and another at 215nm (ϵ = 1000).

The narrow absorption bands of the cyclobutenes studied here may be comprised of two or more overlapping electronic transitions, as the UV absorption spectrum of 6 reveals that at least two excited states are accessible in the cyclobutene derivatives. Within the rather narrow absorption band, studies at 185, 193, and 214nm reveal a dependence of the photochemistry of these cyclobutenes on excitation wavelength.

Moving from 185 to 193nm appears to have a rather anomalous effect on the photochemistry of these cyclobutenes, however. The results vary from an increase in the amount of symmetry-allowed diene(s) in **c-1**, **t-1** and **c-4**, through no apparent effect on the diene ratio in the case of **t-4**, to an increase in the yield of the formally forbidden diene isomer in the case of **3**, as excitation wavelength is increased. Wavelength effects may conceivably arise from various origins: (a) involvement of two or more excited states that are uncoupled, so that internal conversion to the lowest state does not compete with reaction from the upper one, (b) the independent excitation of structural or conformational isomers, (c) the excitation of ground state complexes, or (d) the secondary reaction of primary photo-products.[101] Possibility (b) may be ruled out in the case of the monocyclic derivatives, and (c) in all cases. Furthermore, we have shown that secondary photolysis effects are not a problem here. The source of these apparently anomalous effects is not obvious to us at this time. Involvement of two or more excited states would seem consistent with these results in light of the wavelength dependence of the photochemistry of **c-6** which clearly has two absorption bands in its ultraviolet spectrum. In the case of **c-6**, the ratio of the formally allowed over the formally forbidden pathway decreases from 1.4 at 193nm to 0.7 at 214nm. At 214nm, it is almost certain that both the π,π^* and the π,R(3s) transitions are being stimulated. It follows then that perhaps the increase in the amount of the formally forbidden diene is due to Rydberg excitation as described previously. In the case of the parent system, disrotatory opening would appear to be the preferred path only because of the S_2 involvement. If it were not for the allowed crossings along S_1 and S_2 one would predict that conrotatory opening would be the preferred mode of ring opening on the basis of the ab initio calculations. The barrier to disrotatory opening in the parent system is, in fact, larger than that of the conrotatory path by ca. 15 kcal/mol according to these calculations. As well, the ab initio calculations exclude the participation of the π,R(3s) state, which may play a prominent role in the photochemistry of cyclobutene. In our study, the energy gap between the π,π^* and π,R(3s) excited states is not expected to vary significantly among the cyclobutenes studied, that are unsubstituted at the double bond. However, cyclobutene **6**, the only compound substituted at the double bond (and therefore the only compound to exhibit two absorption bands in the UV spectra) shows a marked dependence on wavelength proceeding from 193 to 214nm.

Low temperature studies (193nm) performed on **1** and **3** indicate that the barrier to formal conrotatory opening is slightly higher than that for the disrotatory process at 77K. In the case of the monocyclics the difference appears to be small, but for **3** a seemingly larger barrier to conrotation exists as the cc/ct ratio increases from 1.4 at room temperature to 3.3 at 77K. This change in the degree of stereospecificity corresponds to a calculated difference in the energetics at 296 and 77K of ca. 0.7 kcal/mol. These results may indicate that electrocyclic ring-opening occurs both dis- and conrotatory, since dienes pertaining to both symmetry-allowed and forbidden paths are observed at 77K. The reduced amount of formally forbidden diene isomer at 77K may also result from an increased propensity of the vibrationally "hot" ground state cyclobutenes to lose their excess energy to the surroundings, and therefore undergo no apparent reaction.

The overall picture for the wavelength and temperature dependence is undoubtedly more complicated than this and quite possibly involves mutual conversions amongst at least two and possibly three excited states. Completely independent excitation of the possible states does not seem probable in light of the narrow absorption band for the cyclobutenes studied, except possibly for higher substituted systems such as **6**, where photolysis at 229nm would hit the tail of the long wavelength absorbance postulated to be due to the π,R(3s) transition.

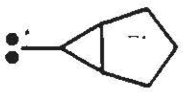
The results appear to underline the failure of the *ab initio* calculations to represent the potential energy surfaces of these substituted cyclobutenes, assuming the photoreactivity observed here results from π,π^* excitation.

2.8 Molecular Fragmentation

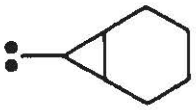
Molecular fragmentation, formally a $[\sigma2_S + \sigma2_S]$ cycloreversion, has been observed for each cyclobutene system in the present study. The process, which affords an alkyne and an alkene, the latter stereospecifically, has been observed in earlier studies.[19-21] Two mechanistic paths have been forwarded to explain the reaction. The first (and most commonly accepted) mechanism is the symmetry allowed $[\sigma2_S + \sigma2_S]$ cycloreversion, postulated to explain the stereospecific formation of en-ynes resulting from photolysis of **c-** and **t-15**.[19] More recently, a route involving cyclopropylmethylene carbenes, presumably formed as a result of Rydberg excitation, has been suggested as an alternative to the concerted cycloreversion mechanism.[21]

A clear trend exists in the quantum yields for the retrocycloaddition of the four annelated cyclobutenes studied herein. As the size of the saturated ring is increased for the cis-fused systems the efficiency of molecular fragmentation also increases. One might initially assume that fragmentation would be more efficient as the total amount of ring strain in the bicyclic system increases and therefore the opposite trend would have been predicted. The fact that only **t-4** experiences a marked decline in the fragmentation process, in which the strained trans-cycloheptene is formed, may indicate that the efficiency of the process is reduced when highly strained products must result.

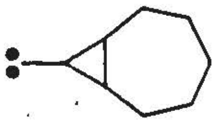
The stepwise mechanism involving ring contraction from the π,R(3s) state would presumably occur via cyclopropylmethylenes **40** - **42** for **2**, **3**, and **4** respectively. The thermal chemistry of these carbenes, generated by thermal decomposition of the appropriate tosylhydrazone, has been studied by Kirmse and coworkers.[102] Each carbene reacted with ca. 70% rearrangement and 30% fragmentation, indicating an apparent insensitivity to ring strain due to annelation. Assuming carbenes **40** - **42** formed from Rydberg excitation are responsible in whole or in part for fragmentation and that they behave similarly to the thermally generated ones, their relative reactivities would remain constant through the cis-fused series. It follows then, that such carbenes may not be responsible for the variation in the efficiency of this process in these systems assuming that the efficiency of their formation does not vary from **40** - **42**. It therefore follows that perhaps the trends observed in molecular fragmentation originate in the π,π^* excited state, although it is possible that the efficiency of carbene formation increases as the size of ring annelation increases since the extent of minor products increases in the series **40** - **42**. Until the identities of some of the minor products are confirmed, it is difficult to say, with any certainty, where this effect may originate.



40



41



42

A mild wavelength dependence is observed for the fragmentation process in all the annelated cyclobutene systems studied when varying the excitation wavelength from 185nm to 193nm. All cis-fused systems experience a decrease in fragmentation efficiency moving to the longer wavelength. In contrast, the trans-fused compound, t-4, undergoes the process more efficiently at longer wavelengths. Low temperature studies on the fragmentation process were completed for 2 and 3. The amount of molecular fragmentation was observed to decrease at 77K relative to ring opening.

2.9 Other Processes

All photolyses produced relatively clean product mixtures. Nevertheless, some minor products were observed in each case except that of 2. One unidentified product was observed in the photolysis of c-1.

The additional product may be a methylenecyclopropane derivative similar to that found in the photolysis of cyclobutene by Adam.[21]

Two additional C_8H_{12} isomers were present in the photolysate of 3 one of which was identified as 7-methylenebicyclo[4.2.0]heptane by coinjection of the authentic sample. Adam has suggested that methylenecyclopropane, a major product in the 185nm photolysis of cyclobutene, occurs from cyclobutylidene carbene resulting from Rydberg excitation.[21] Contrary to that report we observe only minor amounts of the derivative formed in the photolysis of 3.

The higher annelated cyclobutenes (c- and t-4) yield more complex photolysis mixtures containing 5-6 minor products, none of which have been identified at this time.

CHAPTER III

Carbene Intermediates in the Direct Photochemistry of Cyclobutenes

A. Results

3.1 Preparation of Cyclobutenes

Unsymmetrically Substituted Tetramethylcyclobutenes

1,3,4,4- and 1,3,3,4-tetramethylcyclobutene (20 and 21, respectively) were prepared as a (ca. 1:1) mixture of isomers by the synthetic scheme shown in Equation 3.1.[74] The separation and purification of 20 and 21 were carried out by preparative vapour phase chromatography (vpc). The structures were assigned on the basis of their IR, mass, ^{13}C, and, in particular, the ^1H NMR spectra. The isomeric cyclobutenes were differentiated by the coupling between the two ring protons in the ^1H NMR spectra. In the case of isomer 20 no coupling was observed between the two protons; in contrast, the coupling was observed to be 0.9 Hz for 21. The ^1H NMR data for these compounds are summarized in Table 3.1.

3.1

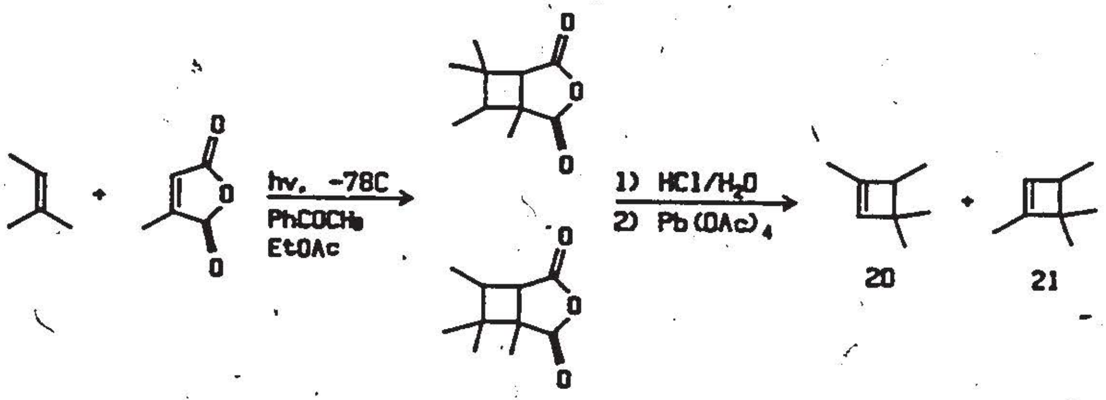


TABLE 3.1

500 MHz ^{1}H NMR Data for Cyclobutenes 20 and 21.[a]

Compound	δ (ppm)	Integr.	Pattern	J (Hz)	Proton
20	0.94	3	d	7.2	$=CCH_3$
	0.96	3	s	-	$-C(CH_3)_2$
	1.08	3	s	-	$-C(CH_3)_2$
	1.57	3	dd	1.6, 1.2	$-CHCH_3$
	2.23	1	qq	7.2, 1.2	$-CHCH_3$
	5.66	1	q	1.6	$=C-H$
21	0.93	3	s	-	$-C(CH_3)_2$
	0.96	3	d	7.1	$=CCH_3$
	1.06	3	s	-	$-C(CH_3)_2$
	1.53	3	m	1.5	$-CHCH_3$
	2.30	1	qd	7.1, 0.9	$-CHCH_3$
	5.58	1	dq	0.9, 1.5	$=C-H$

[a] Recorded in deuterochloroform solution.

3.2 UV Absorption Spectra

The UV absorption spectra of 20 and 21 were obtained as deoxygenated cyclohexane solutions (0.00127 and 0.00191M, respectively) and are summarized in Table 3.2 (see also Appendix). Each cyclobutene displayed a rather broad absorption, devoid of any fine structure, which extended out to ca. 220nm.

TABLE 3.2

Solution Phase UV Absorption Data for Cyclobutenes 20 and 21 in Cyclohexane (23 C).[a,b]

Cyclobutene	λ_{max} (nm)	Energy (kcal)	ϵ_{max}
20	191.9	149.0	4,950
21	192.7	148.3	6,700

[a] Solutions deoxygenated with stream of argon. [b] Path length = 0.1 cm.

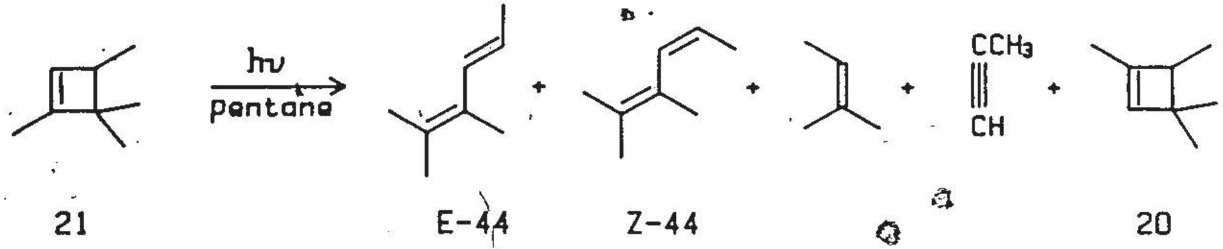
3.3 Photolysis of Cyclobutenes 20 and 21

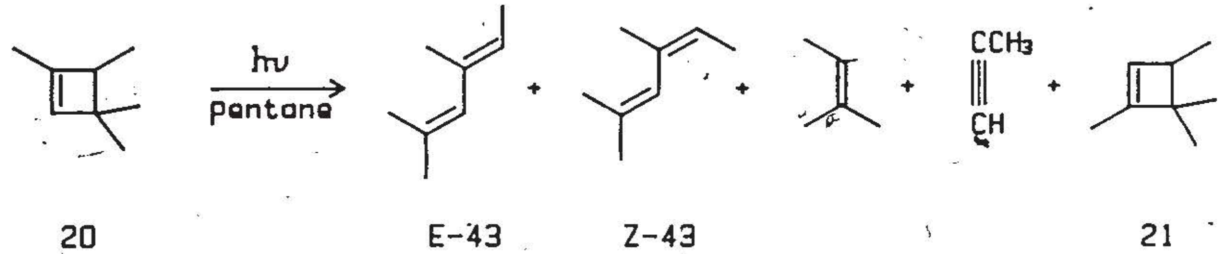
Photolysis in Hydrocarbon Solution: Photolyses of cyclobutenes 20 and 21 were undertaken in deoxygenated pentane or 2-methylbutane (isopentane) solutions with three different light sources; the filtered low pressure mercury lamp (185nm), the pulses of an argon fluoride excimer laser (193nm), or an unfiltered zinc resonance lamp (214nm). Photolyses employing any one of these light sources produced the product mixtures shown in Equation 3.2 and 3.3 for 20 and 21, respectively. Propyne and methyl-2-butene were identified by GC/MS and by coinjection on two vpc columns. The fragmentation product, methyl-2-butene, and the dienes 43 and 44 were isolated by preparative vpc from the photolyses of 20 and 21, respectively. A few other minor products were also observed in the photolyses of 20 and 21 but they were not identified. The results of the 185nm photolysis (quantum yields) are exhibited in Table 3.3 . The preparative scale photolyses, using 0.025M solutions in pentane, were carried out at 193nm to ca. 40% conversion. The dienes were isolated after distillation of the solvent and identified on the basis of their ^{13}C and 500 MHz ^{1}H NMR, IR, mass spectra, and by comparison to the spectra of independently

TABLE 3.3

Product quantum yields of product formation from 185nm photolysis of 20 and 21 in deoxygenated pentane (23 C).

Cmpd.	E-diene	Z-diene	2-MB	Cyclobutene
20	0.09 ±.01	0.036 ±.002	0.21 ±.02	0.015 ±.002
21	0.096 ±.010	0.030 ±.020	0.092 ±.016	0.010 ±.003

3.3 
hν
pentane
CCH3
CH
21
E-44
Z-44
20

3.2 
hν
pentane
CCH3
CH
20
E-43
Z-43
21

synthesized authentic samples (see Experimental). The ^{1}H NMR data for the dienes are presented in Table 3.4. The dienes resulting from the direct photolysis provide further support for the structural assignments of **20** and **21**.

The E- and Z-isomers of dienes **43** and **44** were identified on the basis of their ^{1}H NMR and UV spectra, as well as their UV photoelectron spectra (PES) in conjunction with AM1/AMPAC[103] calculations of their geometries and molecular orbital energies.

The E- and Z-isomers of **44** were differentiated primarily on the basis of the vicinal coupling between the two protons at the disubstituted double bond; these were 15.3 and 11.1 Hz for E- and Z-**44**, respectively. The UV and NMR spectra of E- and Z-**44** compared favourably with those published.[104]

NMR identification of the E- and Z-isomers of **43** is more difficult because allylic coupling, the only kind present in the isomers of **43**, is not a good indicator of stereochemistry in systems of this type.[105] Tentative identification of the two isomers was made on the basis of comparisons with the methyl proton chemical shifts of the previously assigned isomers of 3,4-dimethyl-2,4-hexadiene.[106] Consistent changes in the chemical shifts of the terminal methyl group protons occur, moving through the series from Z,Z- to E,E-3,4-dimethyl-2,4-hexadiene. The chemical shift of the protons of the terminal methyl groups moves upfield from 1.70 ppm when constrained in the E-geometry to 1.47 ppm when constrained in the Z-geometry. Dienes **43** and **44** both display the same systematic trend. In the case of **44**, the change is from 1.76 ppm to 1.52 ppm for the E- and Z-isomers, respectively. The chemical shift of the protons on the terminal methyl group at C-5 moves from 1.65ppm for the isomer assigned as **E-43** to 1.48 for that assigned as **Z-43**.

TABLE 3.4

500 MHz ^{1}H NMR Data for Dienes 43 and 44.

Compound	δ (ppm)	Integration	Pattern	J (Hz)
E-**44**[a]	1.69	3	s	-
	1.74	3	s	-
	1.77	6	m	-
	5.47	1	dq	15.3, 6.8
	6.38	1	d	15.8
Z-**44**[a]	1.52	3	dd	11.8, 6.9
	1.58	3	s	-
	1.67	3	s	-
	1.69	3	s	-
	5.35	1	dq	11.1, 6.9
	5.80	1	d	11.1
E-**43**[b]	1.65	3	d	6.9
	1.69	3	s	-
	1.73	3	s	-
	1.74	3	s	-
	5.29	1	q	6.9
	5.61	1	br s	-
Z-**43**[b]	1.48	3	d	6.8
	1.56	3	s	-
	1.70	3	br s	-
	1.76	3	s	-
	5.26	1	q	6.8
	5.54	1	br s	-

[a] Recorded in carbon tetrachloride solution. [b] Recorded in deuterochloroform solution.

Further structural information on the E- and Z- isomers of **43** and **44** were obtained by UV photoelectron spectroscopy (PES) in collaboration with Dr. N.H. Werstiuk.[107] It has been shown that the π_-, π_+ MO-energy splittings observed in the PES of an extensive series of cyclic and acyclic dienes correlate very closely with calculated (AM1) values and with the calculated dihedral angle about the central single bond in the diene unit.[107] The magnitude of the π_-, π_+ splitting decreases as the dihedral angle varies from 0° (planar s-cis diene) through 90° and increases from 90° to 180° (planar s-trans diene). Low π_-, π_+ energy splittings such as 0.8eV for Z-**43** reveal that the diene exists primarily in twisted conformations. The experimentally determined π_-, π_+ energy splittings have been compared with the values calculated using AM1 of AMPAC. The heat of formation for each diene isomer is calculated as a function of dihedral angle using AM1; this information establishes the extent to which the diene exists as an s-cis or s-trans conformer. From this information, the most stable conformer Z-**43** is neither s-cis nor s-trans, but its lowest energy conformations exist with dihedral angles between 60° and 120°. AM1 predicts a π_-,π_+ splitting of about 0.8eV (average value) for these dihedral angles, which agrees nicely with the splitting determined by PES. Table 3.5 summarizes the predictions of the AM1 calculations and the results of the PES studies of **43** and **44**. The UV absorption spectra of E- and Z-**43** corroborate these assignments (Table 3.8) as the maximum (as in the case of 3,4-dimethyl-2,4-hexadiene[106]) experiences a bathochromic shift proceeding from the E-isomer of the diene (λ_{max} = 232nm, ϵ=10,700) to the Z-isomer (λ_{max} = 217nm, ϵ=6,800). The E- and Z-isomers of **44** show similar behavior (Table 3.8).

Product yields were determined from the slopes of concentration vs. time plots, constructed for all products except propyne. Product formation was monitored by vpc analyses of runs carried to ca. 3-4% conversion. The relative yields for the formation of identified products (except propyne) are displayed in Table 3.6. Figures 3.1 and 3.2 exhibit plots of the formation of products for the 193nm photolyses of **20** and **21**.

TABLE 3.5

PES and MNDO Data for the E- and Z- isomers of 43 and 44.

Diene Conformer	AM1		PES
	Dihedral Angle[a]	π_-,π_+ Splitting[b]	π_-,π_+ Splitting
E-**43**	30-75	1.2 eV	1.3 eV
Z-**43**	60-120	0.8 eV	0.8 eV
E-**44**	180	2.2 eV	2.1 eV
Z-**44**	75-120	0.9 eV	1.2 eV

[a] Angle(s) of the lowest energy conformation calculated by AM1. Angles <90 are the s-cis conformers while those >90 are the s-trans. [b] Average value of the π_-,π_+ splitting determined by taking the average of at least three points in the low energy trough of the AM1 calculated heats of formation for dihedral angles 0 -> 180 . .

TABLE 3.6

Relative rates of product formation from 185, 193, and 214nm photolysis of 20 and 21 in hydrocarbon solution (23°C).[a]

Cmpd.,	λ (nm)	Diene		2-methyl-butene (fragmentation)	Cyclobutene Isomer (interconversion)
		E	Z		
20	185[b]	5.4 ±.5	2.76 ±.12	12.0 ±1.2	0.92 ±.12
	193[c]	5.4 ±.3	1.44 ±.04	7.2 ±.5	0.58 ±.02
	214[c]	4.9 ±.4	1.49 ±.03	5.7 ±1.0	0.55 ±.03
21	185[b]	6.3 ±.5	2.0 ±.1	6.5 ±.8	0.64 ±.1
	193[c]	6.4 ±.1	1.86 ±.03	7.2 ±1.3	0.3 ±.1
	214[b]	5.2 ±.4	2.6 ±.2	10.0 ±2.2	0.6 ±.2[d]

[a] Relative rates were calculated from the slopes of concentration vs. time plots for formation of products from **20** and **21**. [b] In n-pentane. [c] In isopentane. [d] Single-point determination at ca. 4% conversion only.

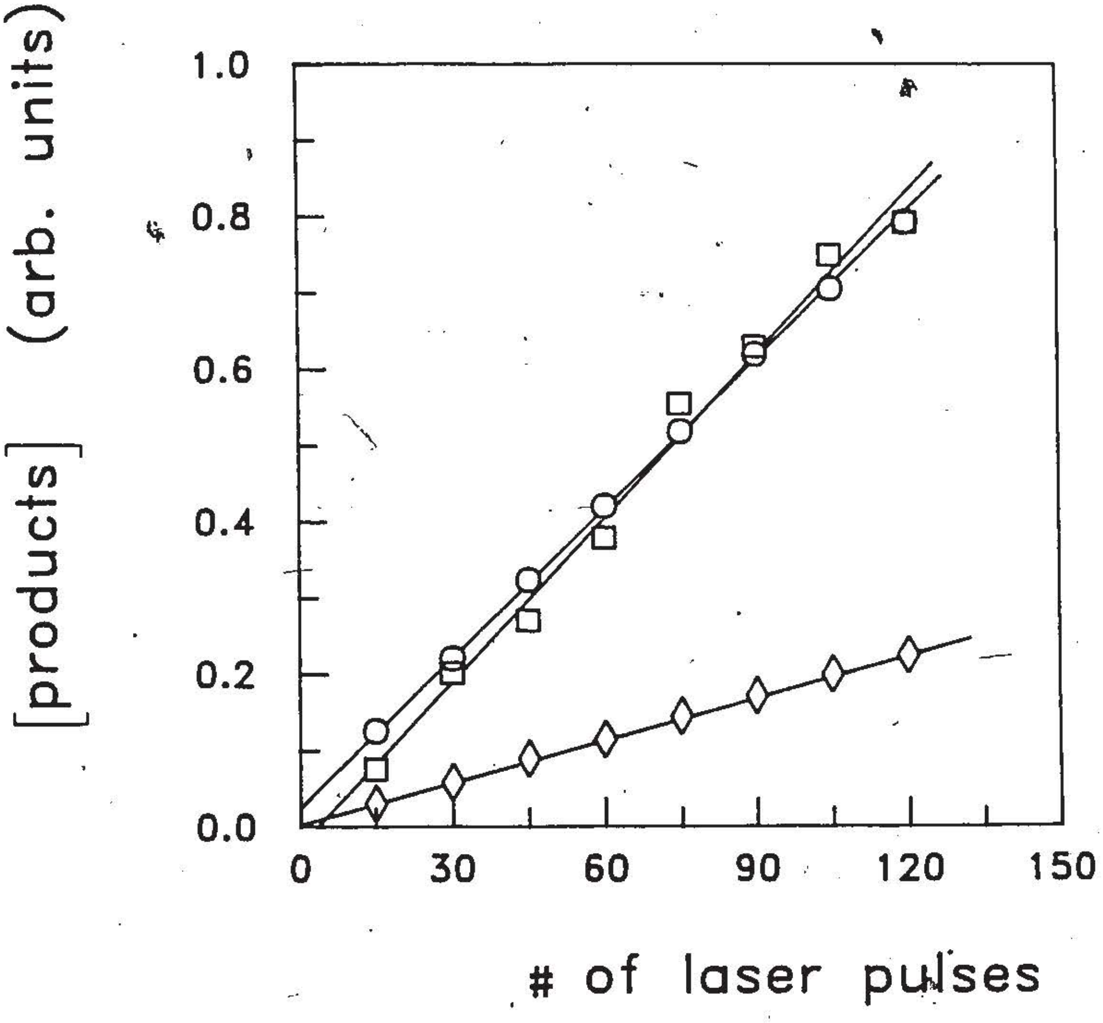


FIGURE 3.1 Concentration vs. excitation dose (# of laser pulses) for the formation of **E-43** (○), **Z-43** (◇), and methyl-2-butene (□) from the 193nm photolysis of **20** in deoxygenated isopentane solution at 23°C.

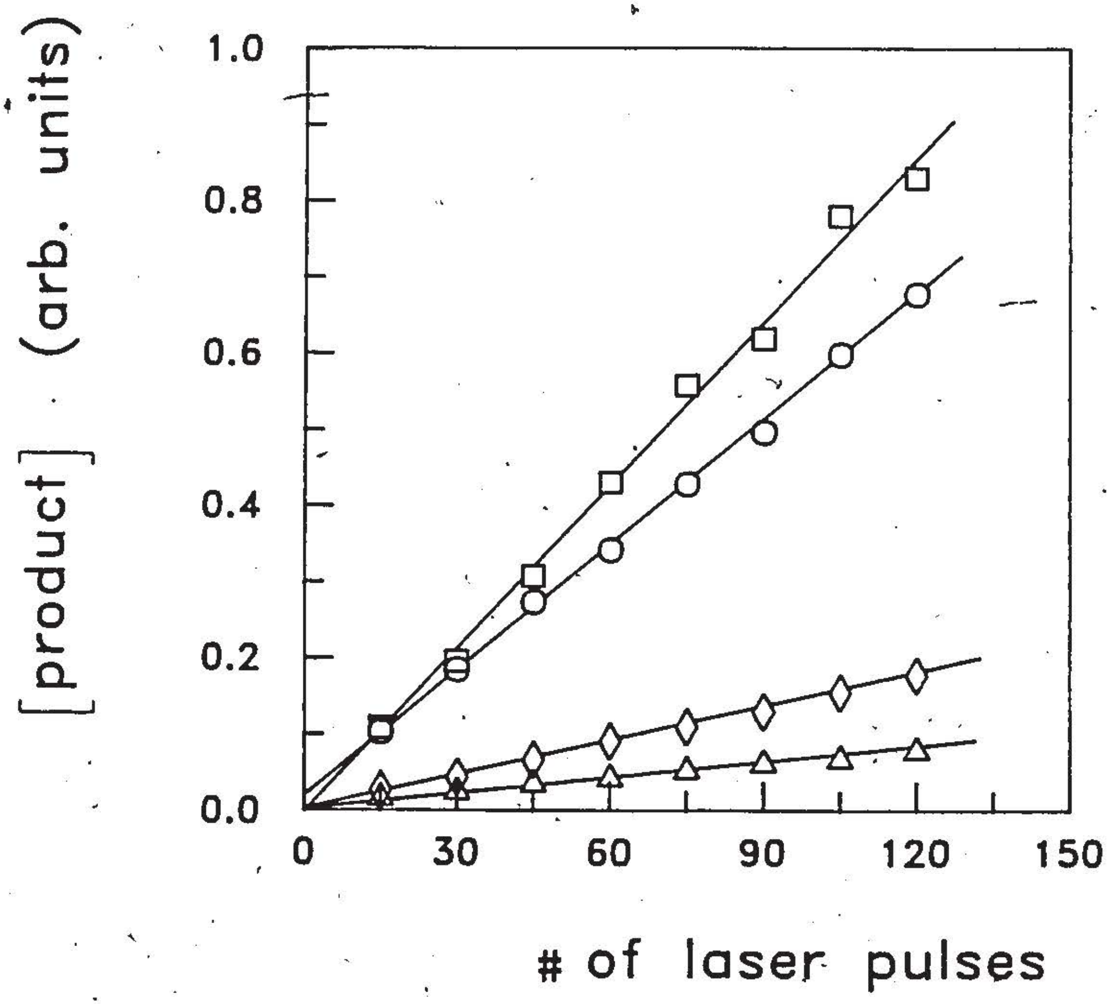


FIGURE 3.2 Concentration vs. excitation dose (# of laser pulses) for the formation of 20 (△), **E-44** (○), **Z-44** (◇), and methyl-2-butene (□) from the 193nm photolysis of 21 in deoxygenated n-pentane solution at 23°C.

Photolysis in Methanol: Photolyses of 20 and 21 were undertaken in dry, deoxygenated methanol solution (0.014M and 0.011M for 20 and 21, respectively) at room temperature using the zinc resonance lamp (214nm). No products in addition to those observed in the pentane photolyses (Eqns 3.2 and 3.3) were found in either case. Relative product yields are summarized in Table 3.7 along with the relative yields for 214nm photolyses carried out in hydrocarbon solution. The formation of 2-methyl-2-butene and propyne could not be monitored in the methanol runs, since solvent co-elution made their detection impossible on bonded phase capillary columns. A study using other available columns was not possible due to the incompatible nature of the solvent with their liquid phases.

TABLE 3.7

Relative Product Yields for the Irradiation of 20 and 21 in Methanol and Hydrocarbon Solution at 214nm.

		Products			
Cmpd.	Solvent	E-Diene	Z-Diene	Cyclobutene	E/Z
20	MeOH	1.7 ±.1	0.8 ±.1	a	2.1 ±.2
	i-C_5H_{12} [b]	5.7 ±.4	2.6 ±.2	0.60 ±.2	2.2 ±.2
21	MeOH	7.8 ±.5	2.2 ±.1	0.35 ±.17	3.5 ±.4
	C_5H_{12} [c]	4.9 ±.2	1.5 ±.03	0.55 ±.27	3.3 ±.2

[a] Not determined [b] Isopentane; 23°C. [c] n-pentane; 23°C.

3.4 Ultraviolet Absorption Spectra of Dienes 43 and 44.

The UV absorption spectra of dienes **43** and **44** were recorded in cyclohexane solution in order to determine the extinction coefficients at 254nm for use in relative quantum yield determinations for direct diene cis,trans-photoisomerization. The results of these studies are summarized in Table 3.8.

TABLE 3.8

Ultraviolet Absorption Spectra of Dienes 43 and 44 in cyclohexane solution (23C).[a]

Diene	λ_{max} (nm)	ϵ_{max}	ϵ_{254}
E-**43**	232	10,700	2,700
Z-**43**	217	6,800	800
E-**44**	241	21,250	10,100
Z-**44**	223	3,500	1,100

[a] Solutions deoxygenated with argon stream.

3.5 Photostationary States and Relative Quantum Yields for Direct Photoisomerization of 43 and 44.

The photoisomerizations of E- and Z-**43** and **44** (ca. 0.003M) were studied in pentane solution at room temperature. The samples were irradiated using a merry-go-round apparatus inside a Rayonet type RS reactor equipped with 254nm lamps. Each sample was photolysed to the photostationary state (PSS) which was determined from concentration vs. time plots as shown in Figures 3.3 and 3.4. The relative quantum yields for the isomers of **43** and **44** were calculated using Eqn 3.4, and are collected in Table 3.9. Other products were formed in the photolyses but they were not identified.

Equation 3.4

$$\frac{\phi_{Z \to E}}{\phi_{E \to Z}} = \frac{(E / Z)_{PSS}}{\varepsilon_Z / \varepsilon_E}$$

TABLE 3.9

Relative Quantum Yields for the Direct Photoisomerization of 43 and 44 calculated using Eqn. 3.4

2,4-dimethyl-2,4-hexadiene <u>43</u>:	$\phi_{Z\to E} / \phi_{E\to Z} = 1.2 \pm .1^{a}$
	$E/Z = 0.36 \pm .03^{b}$
2,3-dimethyl-2,4-hexadiene <u>44</u>:	$\phi_{Z\to E} / \phi_{E\to Z} = 2.3 \pm .1^{a}$
	$E/Z = 0.25 \pm .01^{b}$

[a] Calculated from the E/Z ratios and the 254nm extinction coefficient ratios from the UV absorption spectra of the pure isomers in cyclohexane at 23 ° C. [b] from the assymptotes of the concentration vs. time plots (E/Z vs. time) for the photolysis (254nm) of each isomer. The photostationary states were approached from both diene geometric isomers in each case.

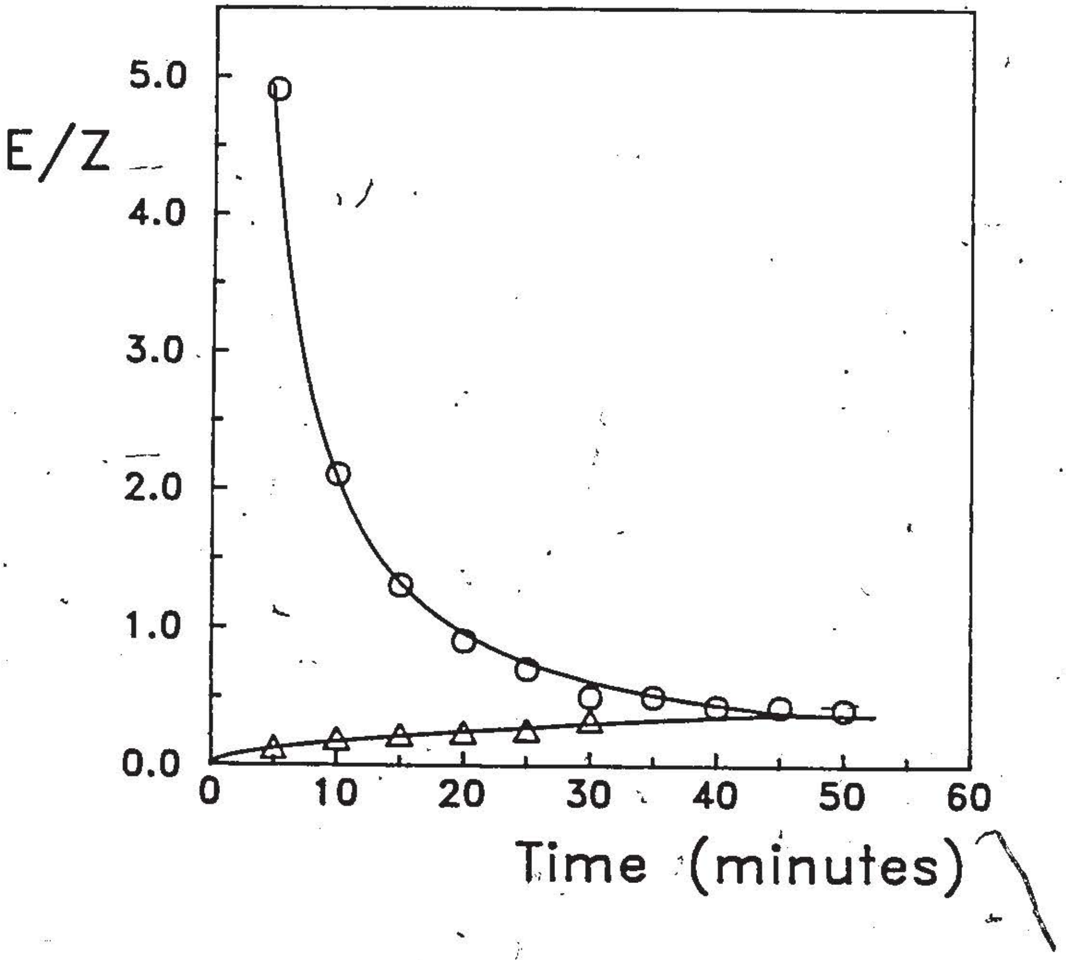


FIGURE 3.3. Photolysis of 2,4-dimethyl-2,4-hexadiene (**E-43**) at 254nm. (○) E/Z starting with **E-43**, (△) E/Z starting with **Z-43**.

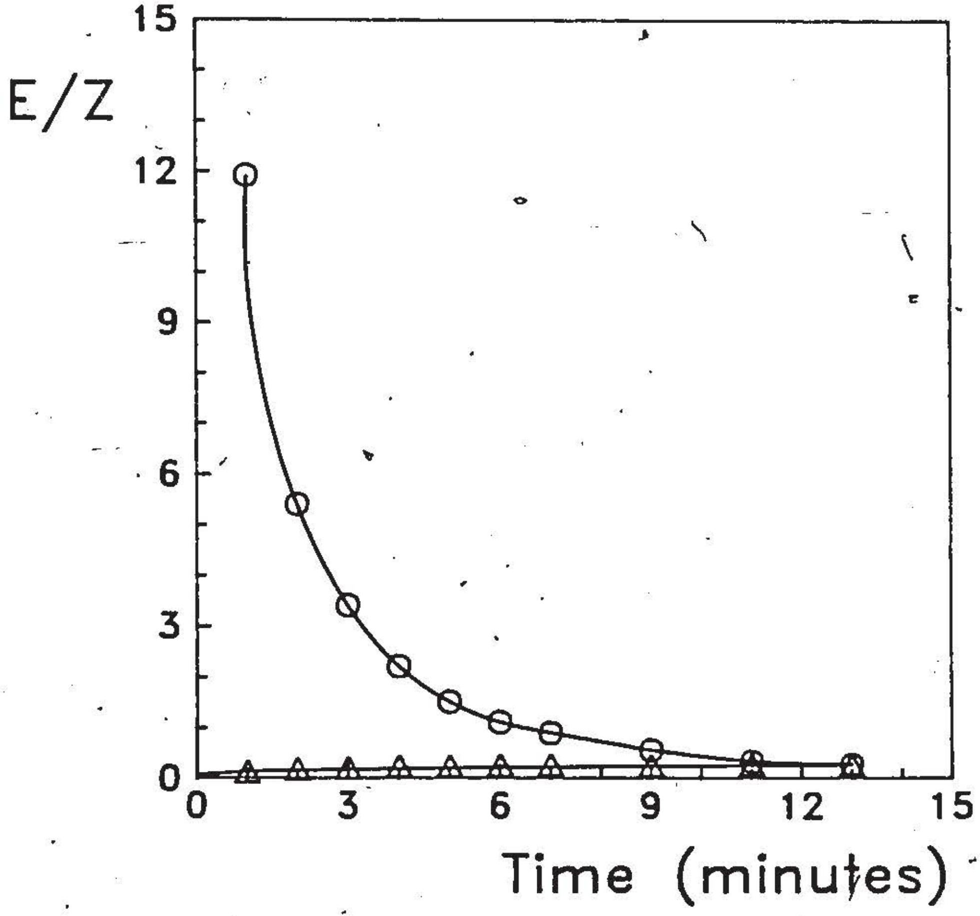


FIGURE 3.4. Photolysis of 2,3-dimethyl-2,4-hexadiene (E-**44**) at 254nm. (○) E/Z starting with E-**44**, (△) E/Z starting with Z-**44**.

B. Discussion

Clearly, 20 and 21 undergo photochemistry that has been well established in the previous section of this thesis and in studies by others[19-21] when irradiated with monochromatic far ultraviolet light. It is not surprising then, that 20 and 21 undergo molecular fragmentation to give propyne and methyl-2-butene as well as formal electrocyclic ring opening to afford two geometric diene isomers as the two major processes during photolysis. Especially pertinent to this study is the observation of the interconversion of the two cyclobutene derivatives, albeit in relatively low efficiency. The participation of carbene intermediates can account for the process. The formation of products consistent with the intermediacy of carbenes appears to be well established as a general feature of the photochemistry of simple alkenes in the condensed phase.[58] This generality was suggested to extend to cyclobutene by Adam, who reported evidence for cyclobutylidene involvement in the photochemistry of cyclobutene itself.[21] In chapter II we established the possible involvement of cyclobutylidene derivatives in the photochemistry of 3 as evidenced by the formation of methylene bicyclo[4.1.0]heptane (27) in low yields. The far ultraviolet photochemistry of cyclobutenes 20 and 21 provide the only direct evidence to date for the involvement of cyclopropylmethylenes in the photochemistry of simple alkyl-substituted cyclobutenes.

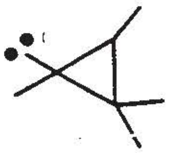
3.6 Molecular Fragmentation and Interconversion

Both cyclobutene isomers 20 and 21 undergo molecular fragmentation, formally a $[\sigma 2_s + \sigma 2_s]$ cycloreversion, to give propyne and methyl-

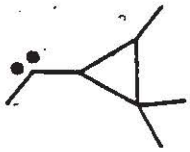
2-butene. Interestingly, **21** undergoes the process with an efficiency greater than twice that of **20** ($\phi = 0.09$ vs. 0.21 for **20** and **21**, respectively). As well, the cyclobutenes are interconverted, albeit in minor amounts, upon direct irradiation with far ultraviolet light.

As has been pointed out,[20] two pathways are possible for the formation of fragmentation products. A symmetry-allowed $[\sigma 2_S + \sigma 2_S]$ cycloreversion leading to the stereospecific formation of enynes after π,π^* excitation of tricyclic compounds c- and t-**15** explains the result within the framework of orbital symmetry selection rules (Eqn 1.16 and 1.17).[19] The second mechanistic possibility involves secondary reactions of carbene intermediates formed from the π,R(3s) state.[21] In the case of cyclobutene itself, cyclobutylidene (**45**) has been suggested as the precursor to methylenecyclopropane while cyclopropylmethylene (**46**) can account for overall fragmentation to acetylene and ethylene.

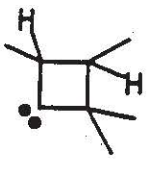
On the basis of the known chemistry of thermally generated cyclopropyl carbenes, involvement of these species in the photochemistry of **20** and **21** should be signalled by the interconversion of the two isomers, as has indeed been observed. In principle, the possibility exists for the involvement of four carbene intermediates, **47**-**50**, in the photochemistry of these two compounds. The cyclopropylmethylenes, **47** and **48**, would result from 1,2-alkyl migration while the cyclobutylidenes, **49**



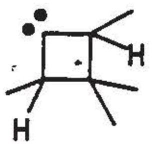
47



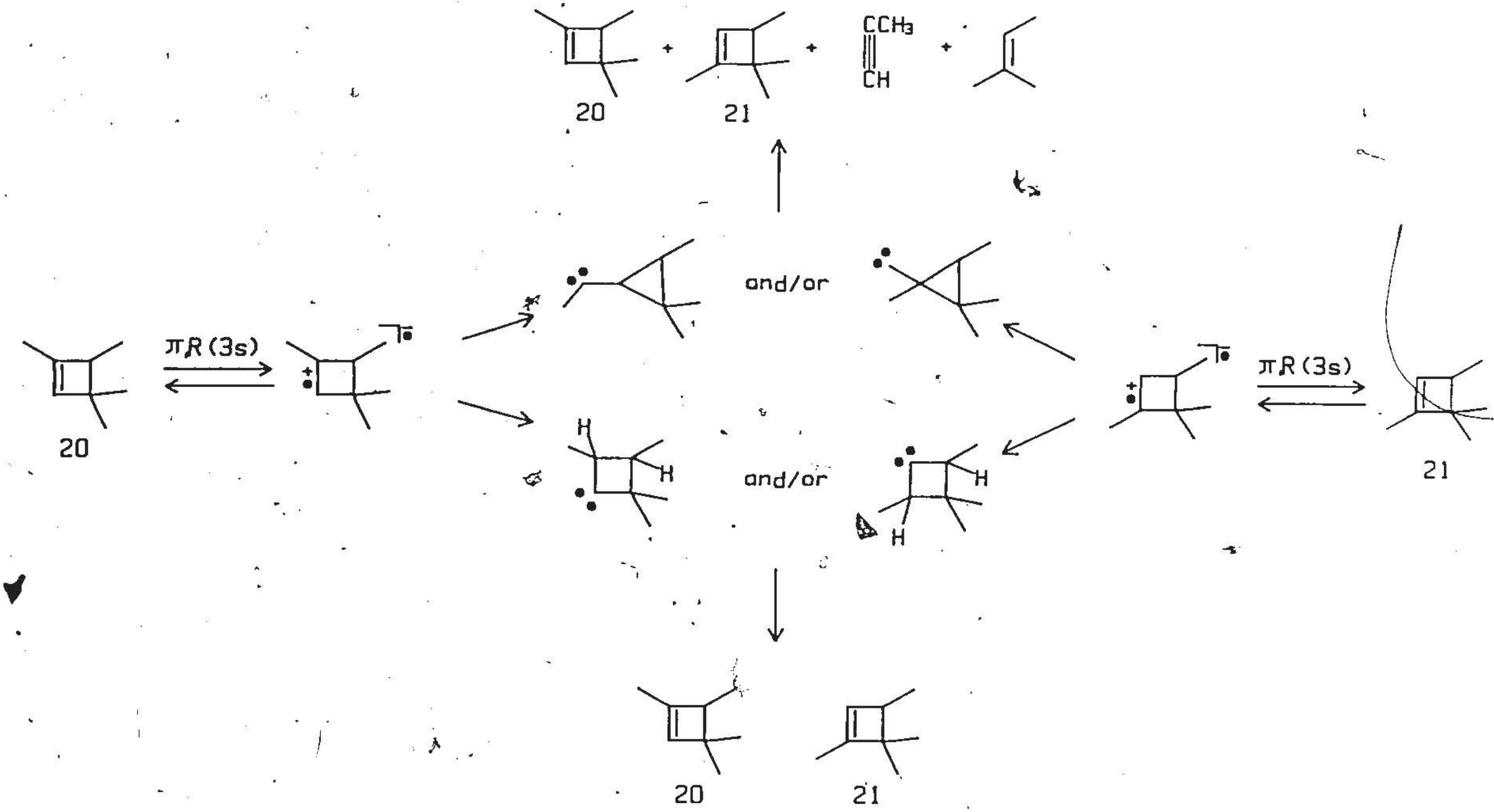
48



49



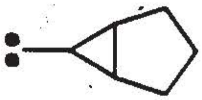
50



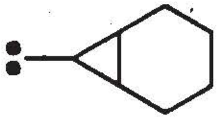
SCHEME 3.1 The far ultraviolet photochemistry of 20 and 21. Mechanism for the photochemical interconversion of 20 and 21 via the Rydberg state.

and **50**, would arise via 1,2-hydrogen and -methyl migration, respectively. Both cyclobutene precursors are assumed to be capable of providing carbenes **47**-**50**. The extent to which 1,2-H, 1,2-Me and 1,2-alkyl migrations compete in the photochemistry of alkenes is not well known. Such information would be very useful in determining the relative importance of **47** - **50** and would probably comprise a sizeable study.

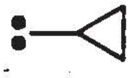
Scheme 3.1 illustrates the mechanism for interconversion of **20** and **21** involving cyclopropylmethylene intermediates. The intermediates may also account for the formation of propyne and methyl-2-butene in the case of **20** and **21**, as originally proposed in studies of other cyclobutene systems.[20,21] As stated in Chapter I, evidence for carbene intermediates in the photochemistry of simple alkenes comes from comparison of the behaviour of the thermally generated carbenes (i.e. Table 1.1). Cyclopropylmethylenes were previously postulated as intermediates in the photochemistry of **2**, **3**, and cyclobutene itself, on the basis of studies of the decay of thermally generated carbenes such as **40**,[102] **41**,[102] and **45**[108] which have been shown to undergo ring expansion to cyclobutenes as well as fragmentation affording acetylene and the corresponding alkene. Many other examples exist that show similar reactivity.[109-112,114,115] Larger homologs of the bicyclic cyclopropylmethylenes do not undergo ring expansion when generated via their tosylhydrazone salts, but they do



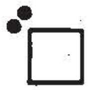
40



41



45



46

experience fragmentation to alkene and acetylenic derivatives.[113] There is an obvious danger in predicting that carbenes generated via a photochemically excited state decay similarly to those generated thermally or photochemically from independent sources. Several methods exist for the generation of carbenes (eg. by thermolysis or photolysis of tosylhydrazone salts, diazo compounds, diazirines, and geminal dihalides).[111,112] It is well established that for a given multiplicity, carbene reactivity varies considerably with the conditions of generation,[111,112] and therefore one should not expect the behaviour of carbenes generated by these methods to strictly parallel those generated from excitation of alkenes.

In unsymmetrically substituted cyclopropylmethyl carbenes such as 51 - 53 (Figure 3.5), it is the less substituted (and therefore stronger) bond that migrates in the ring expansion.[114,115] Carbene 54.

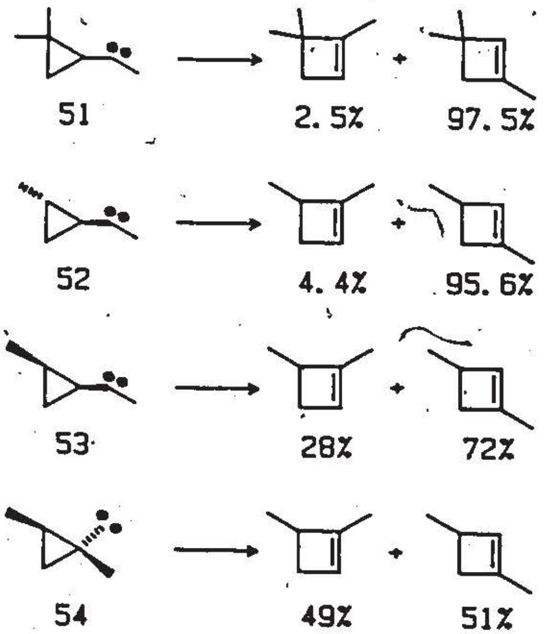
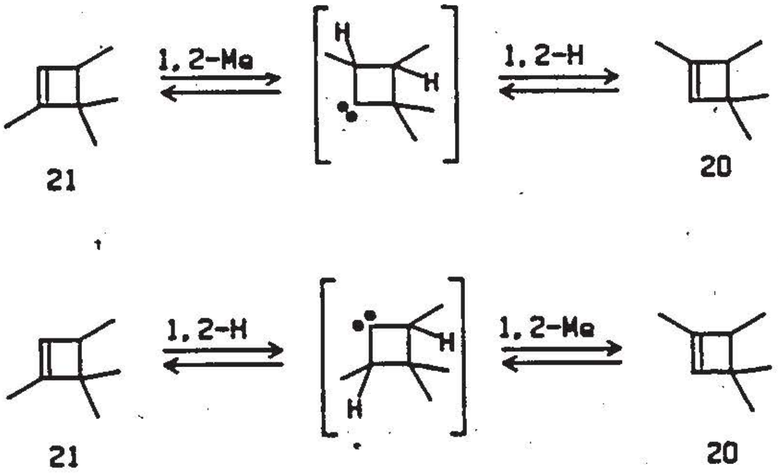


FIGURE 3.5 Rearrangement of Unsymmetrically substitited cyclopropylmethylenes.

shows no selectivity in rearrangements to cyclobutene derivatives. It thus appears difficult to predict how **47** and **48** will partition in their ring expansion to 20 and 21, or even to what extent ring expansion might compete with fragmentation to propyne and methyl-2-butene.

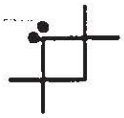
As already stated the interconversion of 20 and 21 may also occur via carbenes **49** and 50. Such carbenes are known to rearrange yielding the isomeric methylenecyclopropane derivative and minor amounts of the cyclobutene when generated independently from thermolysis of cyclobutanone tosylhydrazone[116] or geminal dihalocyclobutane[117] precursors. However, interconversion of 20 and 21 by this pathway requires sequential [1,2]-Me/[1,2]-H or [1,2]-H/[1,2]-Me migrations (Scheme 3.2) which can be expected to be highly inefficient. [1,2]-Hydrogen migrations are common in both alkene[58] and carbene chemistry and usually dominate over [1,2]-Me migrations when both are available.[111,112] Di- and tri-substituted alkenes have revealed an inherent inefficiency in their photobehaviour which has been interpreted as being due to the formation of carbene intermediates derived via [1,2]-hydrogen shifts



SCHEME 3.2 Interconversion of 20 and 21 via [1,2]-H and -Me shifts.

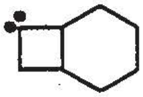
which can, in turn, regenerate the starting alkene via the reverse reaction.[58] If cyclobutenes **20** and **21** follow suit, then the intermediacy of **49** and **50** may be largely undetectable.

While [1,2]-hydrogen shifts are thus known to be facile in both alkene and carbene chemistry, [1,2]-methyl shifts are exceedingly inefficient. In alkene photochemistry [1,2]-methyl migrations are generally less efficient than both [1,2]-hydrogen and -alkyl (skeletal) shifts.[58] In the case of branched alkylcarbenes, [1,2]-hydrogen shifts occur ca. ten times faster than [1,2]-methyl insertions.[112] Cyclobutylidene (**45**) primarily undergoes ring contraction to give methylenecyclopropane (ca. 80%) but also undergoes a 1,2-H shift yielding cyclobutene (ca. 20%). [1,2]-Me shifts do not appear to play important roles in the methyl-substituted cyclobutylidene derivatives; for example, methylenecyclopropane derivatives are still the major products as in the case of **55**.[119] More extensively substituted cyclobutylidenes have been observed to undergo carbon-hydrogen insertion and no ring contraction or 1,2-H migrations as in the case of carbene **56**.[120] [1,2]-Methyl migrations are reportedly only significant in cases involving ethereal substituents.[121,122] The presence of 1,2,3,4-tetramethylcyclobutene which would occur from carbene **49** via a 1,2-Me shift did not appear to be present to any extent in the photolysate.



55

56



57

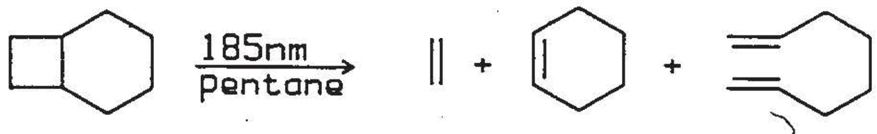
It follows then, that cyclobutylidenes **49** and **50** would not appear to provide an efficient path for **20**/**21** interconversion. The intermediacy of cyclobutylidenes in the photochemistry of **20** and **21** should be signalled by the formation of methylenecyclopropane derivatives. In the case of **21** at least, we have not observed the formation of any products in addition to those shown in Equation 3.3. The photolysis of **20** however, was not as clean; in this case five additional minor products totalling ca. 10% of the reaction mixture were observed. Identification of these products was not possible and therefore a product of this type may be present, but in minor amounts. As revealed ~~in Chapter II~~, we have observed the formation of 7-methylene-bicyclo-[4.1.0]octane, **27**, in the photolysis of **3** (Eqn 2.6), which is consistent with the formation of cyclobutylidene. Cyclobutylidene **57**, generated from the pyrolysis of the bicyclic tosylhydrazone cyclobutanone, is known to afford **21**.[118] We are, however, skeptical about the importance of cyclobutylidene derivatives in the photochemistry of any of the cyclobutenes comprising our study, since we have observed rather insignificant amounts of ring contracted products compared to the amounts reported by Adam and coworkers in the case of cyclobutene itself.[21]

It follows then, that cyclopropylmethylenes **47** and **48** may undergo rearrangement to cyclobutenes more efficiently than cyclobutylidenes **49** and **50** and, in addition, may also account to some extent for the formation of propyne and methyl-2-butene.

1,3-H and 1,3-Me migrations, both possible from π,π^* excitation,[58,69-71] cannot interconvert **20** and **21** but may lead to the formation of other cyclobutene isomers such as 1,2,3,4-tetramethylcyclobutene or 3,3,4,4-tetramethylcyclobutene. We can rigorously rule out the former as one of the minor products in the photolyses of 20 and 21.

Curiously, fragmentation of 21 (to afford propyne and 2-butene) occurs with greater than twice the efficiency of that of 20 for 185nm excitation. The reason for this may be steric in nature. In the case of photochemical $[\sigma 2_s + \sigma 2_s]$ cycloreversions of cyclobutanes, various examples illustrate that the relief of steric interaction in the ground state determines the regioselectivity of the fragmentation reaction.[123] For example, photochemical cleavage of bicyclo[4.2.0]octane (58) occurs relatively efficiently at 185nm in pentane solution, affording 1,7-octadiene, cyclohexene, and ethylene as shown in Eqn 3.4, where formation of 1,7-octadiene is much more efficient than is the formation of cyclohexene and ethylene.[124] The cleavage reaction is postulated to occur via a radical-cation formed after σ,R(3s)-Rydberg excitation at 185nm. This proposal is consistent with the observation of efficient cyclobutane cleavage in electron-transfer photolyses with quinones as

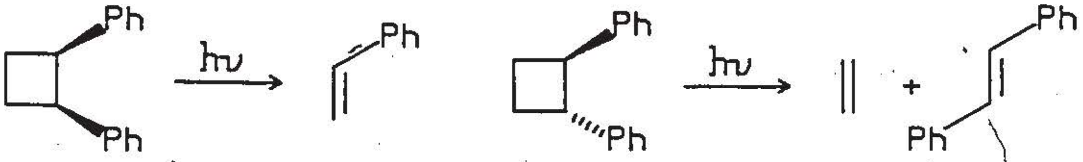
3.4



58

ϕ= 0.03 0.10

3.5



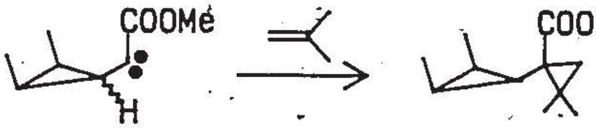
c-59 t-59

sensitizers.[125] The behaviour of cis- and trans-59 upon direct photolysis is clearly different (Eqn 3.5), lending additional support to the role of steric factors in photo-fragmentation reactions of cyclobutanes.[126] It has been proposed that vicinal substitution in cyclobutanes controls the regioselectivity of ring cleavage due to steric interactions. In cyclobutene 21, three methyl groups (at positions 1 and 4) are vicinal. It may well be that relief of steric interactions due to the increased vicinal interactions results in more efficient formal $[\sigma 2_S + \sigma 2_S]$ cycloreversion for 21 relative to 20.

A further point on the difference in the molecular fragmentation process for these cyclobutenes involves the proposed cyclopropylmethylenes. If one assumes that the Rydberg excited state of cyclobutenes 20 and 21 yields the same carbene intermediates then the difference in the fragmentation quantum yields implies that this pathway cannot alone be responsible for fragmentation products. The relative yields of interconversion products from 20 and 21 are the same within experimental error, while a dramatic difference exists for the fragmentation process. If the proposed carbenes were alone responsible for fragmentation then one would also expect proportionately similar differences in the quantum yields for interconversion of the two isomers. Interestingly, unsymmetrically substituted cyclopropylmethylenes that have been generated from thermal decomposition of tosylhydrazones have been found to undergo negligible amounts of fragmentation to alkyne and alkene.[114,115]

3.7 Nucleophilic Trapping Studies

Irradiation of alkenes in methanolic solution frequently results in the formation of ethers, which result from nucleophilic trapping of reactive intermediates such as highly strained cyclic olefins or carbenes.[58] There appear to be no reported attempts to trap cyclopropylcarbenes or cyclobutylidene derivatives in such media, however. Our own attempts to trap the proposed carbene intermediates as the methanol insertion products failed to provide any conclusive evidence for their existence. This result does not necessarily reflect an absence of such intermediates, but may be due to exceedingly fast rates for intramolecular reaction. Jones and Gallucci have reported the failure of singlet dimethylcyclopropylcarbomethoxycarbene to form an adduct with cis-2-butene.[127] Only the carbene rearrangement products cis-3,4-dimethyl-1-carbomethoxycyclobutene along with the fragmentation products methyl propiolate and 2-butene were observed. Under similar conditions,

3.6 

minor product

the singlet carbene formed extremely small amounts of the addition product with isobutylene as shown in Eqn 3.6 (ca. 4% relative to the cyclobutene derivative). Larger amounts of addition adduct were formed with triplet carbenes but these were still only ca. 20% relative to the amount of rearrangement to the cyclobutene.[127] Singlet diphenyl carbenes, which do not undergo intramolecular reaction, have been shown to insert into the O-H bond of methanol at a rate that is close to the diffusion controlled limit, while reaction with alkenes is about a magnitude slower.[128]

Unfortunately, the relative yield of the fragmentation products, methyl-2-butene and propyne, was unobtainable in the case of either cyclobutene (**20** and **21**) photolysis in methanol. A value for the relative yield of the interconversion product for **20** could not be determined either. No products in addition to those observed in the 214nm photolysis in hydrocarbon solution were observed in the methanolic photolysis.

3.8 Electrocyclic Ring Opening

Electrocyclic ring opening in cyclobutenes **20** and **21** leads to the two possible geometric isomers of 2,4-dimethyl-2,4-hexadiene and 2,3-dimethyl-2,4-hexadiene, respectively. The efficiency of the process appears to be similar for the two isomers at 185nm, and closely parallels the efficiencies of the same process in the unsubstituted mono-and bicyclic- cyclobutenes discussed in chapter II. Due to the nature of the ring substituents, stereochemical information is not possible to extract from this set of cyclobutenes, therefore it is impossible to elaborate on the origin(s) of the dienes. It is clear, however, that the proportion of diene isomers favours the E- over the Z-diene in the photolysis of both **20** and **21**. The decay characteristics $(\phi_{Z \rightarrow E}/\phi_{E \rightarrow Z})$ of these dienes when irradiated at 254nm reveal only a slight tendency towards favouring the E-isomer in the case of 2,4-dimethyl-2,4-hexadiene, but in the case of 2,3-dimethyl-2,4-hexadiene, the E-isomer is favoured to a greater extent. Examination of the isomeric diene ratios obtained from far ultraviolet irradiation of 20 and 21 (see Table 3.6) and comparison of these with the E/Z diene quantum yield ratios for the direct photoisomerization at 254nm reveals that the relative isomeric diene yields obtained from cyclobutene photolysis do not appear related to the decay characteristics of the diene singlet excited state, given by $\phi_{Z \rightarrow E}/\phi_{E \rightarrow Z}$. However, this comparison ignores the probable difference in s-cis/s-trans compositions of the dienes in solution.

3.9 Excitation Wavelength Studies

The photochemical behaviour of 20 and 21 shows no marked wavelength dependence in either case. Although the ultraviolet absorption spectra of these compounds show only a single broad, featureless absorption band, the maxima are red-shifted ca. 5nm in comparison to cis-3,4-dimethylcyclobutene, **c-1**, which is unsubstituted at the double bond. As well, the spectra for 20 and 21 are much broader and tail out to 220nm, contrasting that of **c-1** which has no absorption beyond 210nm. From this observation, combined with the wavelength dependence and UV absorption studies in the previous chapter, it follows that the single absorption bands of 20 and 21 are likely to be comprised of at least two overlapping transitions. The insensitivity to excitation wavelength in the photochemistry of 20 and 21 may be the result of the various excited states in this region being approximately isoenergetic.

Changes in the E/Z diene ratio for 20 occur as the excitation the diene ratios for the 214nm photolysis. Cyclobutene absorption at 214nm is weak while that for the dienes is rather strong at the same wavelength; therefore secondary diene photolysis may contribute to the observed ratios from 214nm photolysis when using relatively dilute solutions (<0.015M). Secondary diene photolysis may not be evident in the concentration vs. time plots under these conditions. However, we note that the E/Z ratio from the 214nm photolysis of **21** is identical to the ratio obtained from the shorter wavelength photolysis, within experimental error.

CHAPTER IV

Summary and Conclusions

4.1 Contributions of the Study

The theory of conservation of orbital symmetry is one of the great developments in modern organic chemistry. This work has consisted of the first systematic study of one of the central examples of the selection rules pertaining to photochemical reactivity. Prior to this study, only a few examples existed that illustrate the photochemistry of simple cyclobutene derivatives. Only one of these studies offered reliable information concerning the stereochemistry of formal electrocyclic ring opening.

Direct photolysis of alkylcyclobutenes in solution results in fragmentation to yield an alkene and an alkyne and ring-opening to yield all possible geometric isomers of the corresponding dienes. The fragmentation reaction has been shown previously to occur stereospecifically, and may occur via $[\sigma 2_S + \sigma 2_S]$ cycloreversion or a stepwise route involving cyclopropyl carbene intermediates. This study has provided direct experimental evidence for the formation of cyclopropyl carbenes in the photochemistry of cyclobutene derivatives, indicating that the latter pathway presumably does account for some portion of the fragmentation products. The extent to which the concerted pathway contributes to the formation of these products is still unknown however, since experiments designed to determine this by quenching the proposed intermediate with methanol were unsuccessful.

The non-stereospecific nature of photochemical cyclobutene-ring opening has been demonstrated with several mono- and bicyclic derivatives, and thus appears to be quite general. An adiabatic mechanism for this process, involving purely disrotatory ring opening to yield dienes in the first singlet excited state, has been ruled out. While several alternative mechanisms have been suggested, the present data do not allow definitive mechanistic conclusions to be derived. One possibility is that excited state decay to "hot" cyclobutene ground states, which subsequently undergo conrotatory ring-opening, competes with adiabatic or non-adiabatic disrotatory excited state ring-opening. A second possibility that has been actively investigated in this study is that two (or more) excited states are accessible in the 185 - 214nm region and lead to ring opening with different stereochemistries.

A considerable amount of evidence supports the presence of at least two cyclobutene excited states in this region, analogous to the situation with simple alkenes. The ultraviolet absorption spectra of derivatives with varying degrees of methyl substitution at the cyclobutene double bond provide clear evidence for this; one excited state is stabilized considerably by alkyl substitution, while the other is largely unaffected. By analogy with simple alkenes, these are assigned as the $\pi,R(3s)$ and π,π^* states, respectively. No systematic variations exist in the degree of stereospecificity observed as a function of substitution for photolysis at a given wavelength however, so the two states are presumably strongly coupled. Increasing the excitation wavelength for photolysis of individual derivatives results in consistent increases in the yield of formally forbidden dienes, indicating that the Rydberg state may be largely responsible for the non-stereospecificity observed. This may be due to stereorandom ring opening or preferred conrotatory opening from this excited state; some evidence for the latter possibility has been presented using the cyclobutene radical-cation as a model for the Rydberg state.

Our study has revealed that the cyclobutene systems undergo efficient reaction photochemically. Generally, electrocyclic ring opening occurs with an efficiency of ca. 0.15 - 0.20 at 185nm. Formal $[\sigma 2_S + \sigma 2_S]$ cycloreversion generally occurs with efficiencies ranging from ca. 0.15 - 0.25. Other minor processes occur with much lower efficiencies; combined these processes reach values of ca. 0.03 to ca. 0.10.

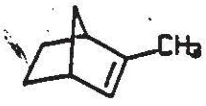
Low temperature photolyses at 193nm have revealed that a small barrier to conrotation relative to disrotatory ring opening exists. Given the complexity of the excited state manifold and our uncertainties regarding the origins or extent of the non-stereospecific component of excited state ring opening, it is not clear with what this small relative barrier is associated. Taking our results together with the previously reported results for constrained tricyclic derivatives indicates that ring opening by the overall non-stereospecific pathway may involve disrotatory motions in the initial stages of the process; structural constraints then result in stereospecific disrotatory electrocyclic ring opening for the cis-isomer and a complete abscence of this process in the trans-isomer.

We have attempted, where possible, to explain the results within the framework of the most recent ab initio calculations for the parent system. It is clear, that the photochemistry of substituted cyclobutene systems in general, cannot be entirely rationalized within this framework. We have presented evidence that the Rydberg excited state (as well as π,π^*) may be involved in the photochemistry of some of these systems, but we cannot say anything definite about its involvement in the formal electrocyclic processes. To this point, more activity in this area by theoreticians would be very advantageous in order to calculate the potential energy surfaces of simple substituted cyclobutenes, especially in determining the excited state potential energy surfaces for the π,R(3s) excited states. It should be pointed out that in fact, it has yet to be ascertained whether the most recent ab initio calculations actually represent the true potential energy surfaces of the parent cyclobutene as, to date, the stereospecificity of the formal electrocyclic ring opening process in the excited state has not been studied. A study of the photochemistry of 3,4-dideuteriocyclobutene would therefore seem particularly appropriate along with other simply substituted cyclobutenes.

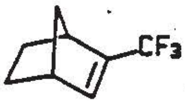
4.2 Future Work

Further work in this area should concentrate on defining the competition between Rydberg and Valence excitation on the photochemistry of cyclobutenes. Continuing studies on the wavelength and temperature dependence of these systems is in progress. In order to achieve any understanding into the intrinsic behaviour of these excited states in the photo-behaviour of cyclobutenes it is necessary to selectively excite individually. This is clearly difficult with alkyl-substituted systems. The photochemistry reported for c-6 in this thesis is part of a larger study on the substituent effects on the photochemistry of cyclobutenes, which is already in progress for the c- and t- isomers of 1, 5 and 6. As the solution UV absorption spectra of these compounds reveal, methyl group substitution at the double bond stabilizes π,R(3s) to a greater extent than π,π^*. We hope to study 6 using excitation at 229nm in the ~~hope of~~ observing the result of ,R(3s) excitation without observing any reaction due to accompanying π,π^* excitation as in the cases with irradiations at 214nm and shorter wavelengths.

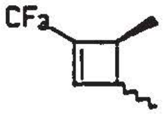
The other alternative is to develop a method that destabilizes π,R(3s) excitation relative to π,π^* excitation. We are in the process of completing a study of -CF$_3$ substituent effects on the photochemistry of the simple alkene norbornene. The photochemistry of norbornene itself has been studied previously and is thought to involve Rydberg excitation when irradiated in the far ultraviolet. Our preliminary results on the far UV photochemistry of trifluoromethylnorbornene (60) and methylnorbornene (61) have indicated that the excited singlets of these compounds decay by very different pathways, providing direct evidence for participation of discretely different excited states in each case.



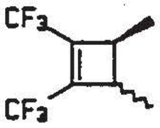
60



61



62



63

On the basis of the studies made for **60** and **61** we hope to observe the photochemistry of cyclobutenes reacting purely from the π,π^* excited state by irradiating $-CF_3$ substituted cyclobutenes such as **62** or **63** at wavelengths from 185 to 229nm. The singlet excited states of cyclobutene must be discretely stimulated in order to ascertain specifically the roles of the π,π^* and π,R(3s) excited states in the photochemistry of cyclobutene.

CHAPTER V

Experimental

5.1 General

^{1}H NMR spectra were recorded on Varian 390 (90 MHz) or Bruker AM500 (500 MHz) spectrometers in deuteriochloroform (or carbon tetrachloride where noted) and ^{13}C NMR spectra were recorded at 125.6 MHz on the Bruker AM500; all are reported in parts per million downfield from tetramethylsilane. Mass spectra were recorded on a VG7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph equipped with a 30m x 0.25mm DB-1 (Chromatographic Specialties, Inc.) fused silica capillary column. Exact masses were determined on a VGH ZABE mass spectrometer by direct probe injection. A mass of 12.000000 was employed for carbon. Ultraviolet absorption spectra were obtained in cyclohexane (or pentane where noted) solution using a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 Data Station. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer as the neat liquids (or in chloroform or carbon tetrachloride solution where noted) and are reported in wavenumbers calibrated against the 1601.9 cm^{-1} absorption of a polystyrene reference.

Analytical vpc separations were carried out using a Varian 3700 gas chromatograph (injector temp. = 80°C) equipped with a flame ionization detector (detector temp. = 200°C) and a Varian CDS101 or Hewlett-Packard HP-3393a integrator. The following vpc columns were utilized during this study: (a) 1.0 μm SPB-1 wide-bore fused silica capillary column (30m x 0.75mm ID borosilicate) and (b) 3.8% UC W982 on

80/100 Supelcort (24ft x 1/8in, stainless steel) (c) 20% β,β-ODPN on 80/100 chromosorb PNAW (14ft x 1/8in stainless steel) (d) 20% tris-(cyanoethoxy)propane (TCEP) on 80/100 Chromosorb PNAW (12ft x 1/4in (0.2cm i.d.) glass) (e) 0.25 μm HPOV-1 wide-bore capillary (25m x 0.31mm i.d. fused silica). The detector response was calibrated for each photoproduct relative to an internal standard (n-pentane, methylcyclohexane, n-octane, 2,2,4-trimethylpentane, or n-nonane) by construction of working curves from a number of standard solutions.

Semi-preparative vpc separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector (TC detector temp. = 160°C) and the following vpc columns: (f) 3.8% UC W982 on 80/100 Supelcort (24ft x 1/4in, stainless steel) and (g) 20% TCEP on chromosorb 80/100 PNAW (12ft x 1/4in, stainless steel) (h) 20% β,β-oxybis(dipropionitrile (ODPN) on 80/100 Chromosorb PNAW (20ft x 1/4in, stainless steel) (i) 5% QF-1 on 100/120 Supelcoport (14ft x 1/4in, stainless steel) (j) 3% OV-17 on 80/100 Chromosorb WAW (6ft x 1/4in, stainless steel).

5.2 Solvents

The hydrocarbon solvents used in the photolyses and UV absorption studies, pentane (Baker Photrex), 2,2,4-trimethylpentane (isooctane,Baker Photrex), cyclohexane (Burdick and Jackson), 2-methylbutane (Aldrich spectrophotometric) and cyclopentane (Aldrich Gold Label) were all used as received from the suppliers. Methanol (HPLC Grade, Caledon Labs) was purified by distillation from magnesium methoxide before use. The internal standards n-octane and n-nonane (Quant Grade, Polyscience

Corp.), pentane and 2,2,4-trimethylpentane (Baker Photrex) were used as received. Methylcyclohexane (Aldrich) was purified by vpc using column (f) before use as an internal standard.

5.3 Preparation and Purification of Cyclobutenes

Cis- and trans-3,4-dimethylcyclobutene (c-1 and t-1).[74] Acetophenone (8.0g, 0.067 mol) and maleic anhydride (47g, 0.48 mol) were dissolved in ethyl acetate (400mL). The solution was placed in a Pyrex immersion well apparatus equipped with a magnetic stirrer and the solution was deoxygenated with N_2 gas at room temperature. The solution was cooled to ca. $-78^{o}C$ with an external dry ice/acetone bath, saturated with cis-2-butene (C.L.A), and irradiated at $-78^{o}C$ with a medium pressure mercury lamp. After 24h irradiation, ^{1}H NMR analysis of the photolysate revealed the disappearance of the maleic anhydride to be >90% complete. The solution was allowed to warm to room temperature and the solvent was removed on a rotary evaporator to yield a yellow oil, from which acetophenone and unreacted maleic anhydride were removed by further distillation (ca. 0.2mm Hg). Portions (10g) of the brown oil (45g) which remained were stirred in 10% aqueous hydrochloric acid (HCl, 50mL) for 12h at room temperature, and then extracted with ether (3 x 50mL). The extracts were washed with water (50mL), saturated brine (50mL), dried over anhydrous sodium sulfate, and the solvent was distilled to yield a yellow oil (9g). The ^{1}H NMR spectrum of this material showed resonances that were consistent with 3,4-dimethylcyclobutane-1,2-dicarboxylic acid anhydride obtained as a mixture of isomers.

^{1}H NMR (90MHz): δ = 1.10 (m, 6H), 2.80 (m, 2H), 3.68 (d, 2H), 9.07 (s, 2H).

The oil was dissolved in dry pyridine (50mL, distilled from barium oxide), placed in a 100mL, two-necked, round-bottomed flask fitted with a gas inlet and a reflux condenser connected to three sequential dry ice/acetone traps, and then saturated with oxygen at room temperature. Lead tetraacetate (15g, 0.034 mol) was added, a slight positive pressure of dry N_2 was applied, and the mixture was placed in a 70°C oil bath where vigorous CO_2 evolution occurred within 2-3 minutes. The mixture was left stirring for a further 24h. The colourless liquid (ca. 2mL) which had collected in the traps was dissolved in an equivalent amount of pentane, washed with 5% aqueous HCl and water, dried over anhydrous sodium sulfate, filtered, and then purified by vpc. Vpc analysis of the product mixture (column f) revealed the presence of three components. The two major products (ca. 1:1 ratio) were collected by semi-preparative vpc (column f, injector temp. = 120°C, detector temp. = 120°C, oven temp. = 40°C). Compounds **c-** and **t-1** were obtained in >99% purity by further semi-preparative vpc purification on columns f and h.

t-1: **^{1}H NMR:** δ = 1.08 (d, 6H), 2.30 (q, 2H), 6.03 (s, 2H);
IR (neat, cm^{-1}): 3133(m), 3053(s), 2963(s), 2928(s), 2903(s), 2868(s), 2713(w), 1678(m), 1615(m), 1567(m), 1452(s), 1371(s), 1335(s), 1311(s), 1281(m), 1205(m), 1068(s), 1043(s), 975(s), 884(w), 862(w), 765(s), 701(s);
MS: M/e(I) = 82(14), 70(40), 67(84), 55(43), 43(82), 42(100), 41(70);
UV (cyclohexane): λ_{max} = 188.2nm (ε = 5050).

c-1: **^{1}H NMR:** δ = 0.96 (d, 6H), 2.90 (m, 6H), 6.03 (s, 2H);
IR (neat, cm^{-1}): 3134(m), 3043(s), 2963(s), 2908(s), 2713(w), 2638(w), 2608(w), 1665(m), 1635(m), 1568(m), 1460(s), 1377(s), 1323(s), 1287(s), 1216(w), 1186(w), 1154(m), 1131(w), 1078(s), 1042(s), 983(m), 886(w), 862(w), 768(s), 746(s), 716(s);

MS: M/e(I) = 82(20), 67(100), 53(38), 41(100), 39(93);
UV (cyclohexane): λ_{max} = 186.5nm (ϵ = 5900).

Compound **c-1** was also synthesized stereospecifically by the method of Brauman and Archie[25] in order to conclusively assign the cis- and trans- identities of the cyclobutene isomers.

Cis-3,4-dimethylcyclobutene (c-1). Acetophenone (13mL, 13.4g, 0.112mol) and maleic anhydride (41.3g, 0.421mol) were dissolved in ethyl acetate (1.9L). The solution was placed in a Pyrex reaction kettle equipped with magnetic stirrer and gas inlet and the solution was cautiously saturated with acetylene at -78°C. The solution was then degassed with a stream of dry nitrogen for 15min and then irradiated with a medium pressure mercury lamp (450W, Hanovia) for 40h at a temperature maintained close to -78°C. The irradiation was terminated when >80% of the maleic anhydride had been consumed as determined by ^{1}H NMR. The reaction mixture was allowed to warm to ca. OC ridding the mixture of excess acetylene, and the solvent was evaporated on the rotary evaporator. The brown oil that remained was distilled in vacuo (ca. 1.0mm Hg) to remove acetophenone and any remaining maleic anhydride. The dark brown solid residue (27.5g, 0.22mol, yield 52%) that remained exhibited a ^{1}H NMR spectrum consistent with cyclobutene-3,4-dicarboxylic acid anhydride.

^{1}H NMR (90 MHz): δ = 2.84 (s, 2H), 5.43 (s, 2H).

The anhydride (6g, 0.048mol) was dissolved in dry ether (15 mL) and added dropwise to a suspension of lithium aluminum hydride (4.9g, 0.125mol) in dry ether (250 mL) in a 500mL three-necked, round-bottomed flask equipped with reflux condenser, addition funnel, and magnetic stirrer. The mixture was refluxed for 72h and then cooled and quenched slowly with ice (100g).

The ethereal portion of the mixture was separated from the remaining lithium and aluminum salts by filtration. The salts were extracted (3 x 50mL) with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was distilled to afford a clear yellow oil (2.6g, 0.023mol, yield 48%) whose ^{1}H NMR spectrum was consistent with cis-3,4-di(hydroxymethyl)cyclobutene.

^{1}**H NMR** (90 MHz): δ = 3.26 (m, 2H), 3.77 (m, 4H), 4.82 (br s, 2H), 6.05 (s, 2H)

The diol (2.6g, 0.023mol) was added dropwise, as a neat solution, to pyridine (130 mL, dried over KOH) in a 250 mL round bottomed flask. p-Toluenesulfonylchloride (24.3g, 0.057mol) was added to the mixture at 0°C, stoppered, and left at 0°C for 72h. The mixture was poured into 250g of ice, vigorously stirred for 20min, then cooled at 0°C for 1-2h. The solid precipitate was collected by filtration, washed in methanol, and dried in vacuo (ca. 10mm Hg) to afford a light brown solid (3.8g, 0.009mol, yield 39%) whose ^{1}H NMR spectrum was consistent with cis-3,4-di(hydroxymethyl)cyclobutene ditosylate.

^{1}**H NMR** (90 MHz): δ = 2.40 (s, 6H), 3.17 (m, 2H), 4.02 (d, 4H) 5.93 (s, 2H), 7.55 (dd, 8H).

The ditosylate from above (3.8g, 0.009mol) was added slowly, as a solid, to a suspension of lithium aluminum hydride (2.0g, 0.051mol) in dry diglyme (50 mL, stored over calcium hydride and distilled from lithium aluminum hydride) in a 100mL two-necked, round-bottomed flask equipped with an 8in Vigreux column and short path distillation unit connected to three sequential dry ice/acetone traps, solid addition funnel, nitrogen inlet and magnetic stirrer. One hour after addition of the ditosylate, the mixture was heated to ca. 80°C and a slow stream of nitrogen swept the volatile product from the reaction mixture to the traps over a period of 8h. The combined contents of the traps were bulb-to-bulb distilled in vacuo (ca. 0.02mm Hg) to afford a clear colourless liquid (ca. 0.5 mL). The spectra of the cyclobutene prepared in this manner were identical to **c-1** prepared by the method above.

Bicyclo[3.2.0]hept-6-ene (2) was synthesized by photolysis of a deoxygenated pentane (100mL) solution of 1,3-cycloheptadiene (1.0g, 0.011 mol) with a low pressure mercury lamp through a Vycor filter for 4h. Concentration of the photolysate by distillation left a slightly yellow liquid which was bulb-to-bulb distilled under vacuum (ca. 0.02mm Hg) to yield a clear colourless liquid, from which 2 was isolated by semi-preparative vpc (column f). Three further vpc purifications (alternating between columns f and h) afforded 2 in >99.5% purity. The material exhibited spectral features similar to those previously reported.[7]

2: **^{1}H NMR** (90 MHz): δ = 0.9-2.1 (m, 6H), 3.16 (d, 2H), 5.88 (s, 2H);

IR (neat, cm^{-1}): 3128(m), 3041(s), 2933(s), 2872(s), 2856(s), 1664(m), 1626(w), 1565(m), 1460(m), 1444(s), 1323(s), 1298(s), 1258(s), 1206(w), 1144(m), 1102(m), 1084(m), 1051(m), 932(m), 890(m), 839(s), 804(m), 730(s), 568(w);

MS: M/e(I) = 94(9), 93(17), 91(15), 79(100), 77(40), 66(29), 65(13), 53(11), 51(9), 39(32), 32(30);

UV (cyclohexane): λ_{max} = 186.5nm (ε = 4200).

Bicyclo[4.2.0]oct-7-ene (3) was synthesized by photolysis of a pentane solution of 1,3-cyclooctadiene (2g, 0.018 mol, 0.6M) in a Rayonet reactor fitted with 254nm lamps. Irradiation of the 0.6M solution for 9 days yielded a mixture of 3 and cis,cis- and cis,trans-1,3-cyclooctadiene. Compound 3 was separated from the other compounds by semi-preparative vpc (column f) following concentration of the photolysate by distillation. A sample of 3 in >99.5% purity was obtained by three further purifications by semi-preparative chromatography on column f. The material obtained exhibited spectral features similar to those previously reported.[129]

3: **^{1}H NMR** (90 MHz): δ = 1.54 (m, 8H), 2.88 (s broad, 2H), 6.15 (s, 2H);
IR (neat, cm^{-1}): 3122(m), 3044(s), 2933(s), 2866(s), 2671(w), 1704(w), 1631(w), 1557(m), 1462(s), 1446(s), 1356Z(s), 1309(s), 1296(s), 1196(w), 1170(w), 1136(m), 1110(w), 1057(m), 986(m), 932(w), 873(w), 857(w), 786(s), 770(s), 742(m), 716(s), 700(s);
MS: M/e(I) = 108(2), 107(3), 93(51), 91(24), 81(5), 80(53), 79(100), 78(15), 77(36), 67(49), 66(18), 65(17), 54(17), 53(12), 51(17), 50(9), 41(35);
UV (cyclohexane): λ_{max} = 186.6nm (ε = 6200).

Cis- and trans-bicyclo[5.2.0]non-8-ene (c-4 and t-4).

Cycloheptene (10g, 0.104mol), maleic anhydride (11.4g, 0.116mol) and acetophenone (5.0g, 0.042mol) were dissolved in ethyl acetate (350mL) in a Pyrex immersion well equipped with a magnetic stirrer. The mixture was deoxygenated by bubbling dry N_2 through the solution for ca. 20 min., during which time the mixture was cooled at ca. 0°C in an ice-water bath. The solution was then irradiated with a medium pressure mercury lamp (450W, Hanovia), agitating constantly with the magnetic stirrer as well as with a slow stream of dry nitrogen. After 15h irradiation, ^{1}H NMR analysis of the crude photolysate revealed the disappearance of maleic anhydride to be >95% complete. Evaporation of solvent with a rotary evaporator afforded an orange-yellow oil which was further distilled in vacuo (ca. 0.5mm Hg) to remove acetophenone and unreacted anhydride.

The orange, viscous oil that remained (20g, 0.103mol) was added to 8% aqueous HCl (50mL) and tetrahydrofuran (10mL), and stirred for ca. 12h at room temperature. The H_2O/THF phase was decanted from the solid residue that remained and extracted with ether (3 x 50mL). The ether extracts were combined with the solid residue, benzene (25 mL) was added in order to azeotrope any remaining water, and the solvent was evaporated on the rotary evaporator. The remaining solid was taken up in anhydrous ether (50 mL), dried over anhydrous sodium sulfate, and then distilled to afford a light brown solid residue (21.0g, 0.099mol, 96%).

The residue (4.9g, 0.023mol) was added to pyridine (60mL, distilled from barium oxide), and the resulting solution was placed in a 100mL two-necked, round-bottomed flask with a condenser connected to three sequential dry ice/acetone traps. The mixture was saturated with oxygen, lead tetraacetate (15g, 0.034mol) was added, a slight positive N_2 pressure applied, and the mixture was placed in a 70°C oil bath where vigorous evolution of CO_2 occurred within 2-3min. CO_2 evolution was complete within 8 min and the reaction was left for a further 1h at 70°C. The reaction mixture was cooled to room temperature and the pyridine was carefully distilled in vacuo (ca. 1mm Hg), with three dry ice/acetone traps placed between the first trap and the pump. After the mixture had been distilled to dryness, the distillate collected in the traps was combined and ca. 25mL ether were added. The mixture was then washed with

5% aqueous HCl (5 x 100mL) to eliminate pyridine. The organic fraction remaining was washed with water (5 x 10mL) until neutral to litmus, saturated brine (10mL), dried over anhydrous sodium sulfate, filtered, and then concentrated by distillation. Vpc analysis (column a) of the clear, colourless liquid revealed two major products (ca. 4:1 ratio). The components were initially separated from any remaining solvent and low molecular weight by-products by semi-preparative vpc (column j). The two components were separated from each other by several runs on column g. After a final run with column f the two isomers were obtained in >99% purity. The ^{1}H NMR spectra of the 2 components were consistent with that for cis- and trans-bicyclo[5.2.0]non-8-ene.

cis-4: **^{1}H NMR** (500MHz): δ = 1.17 (m, 2H), 1.37 (m, 2H), 1.75 (m, 6H), 2.89 (d, J = 12.6Hz, 2H), 6.05 (s, 2H);
IR (neat, cm^{-1}): 3126(w), 3041(m), 2923(s), 2852(s), 2693(w), 2676(w), 1566(w), 1463(m), 1454(m), 1441(m), 1350(w), 1319(w), 1289(m), 1208(w), 1146(w), 1048(w), 924(m), 848(m), 773(m), 753(s), 688(m);
MS: M/e(I) = 122(4), 121(5), 107(19), 94(32), 93(64), 91(16), 81(59), 80(85), 79(100), 77(33), 68(21), 67(36), 66(18), 65(14), 55(15), 54(19), 53(15), 51(12), 41(29);
UV (cyclohexane): λ_{max} = 186.5nm (ϵ = 4900).

trans-4: **^{1}H NMR** (500MHz): δ = 1.33 (m, 2H), 1.56 (m, 4H), 1.73 (m, 4H), 2.53 (dd, J = 12.2, 3.1Hz, 2H), 6.14 (s, 2H);
IR (neat, cm^{-1}): 3102(w), 3039(m), 2924(s), 2856(s), 2659(w), 1551(w), 1447(m), 1369(w), 1349(w), 1284(w), 1253(w), 1223(w), 1215(w), 1149(w), 1097(w), 949(w), 887(w), 851(w), 805(m), 763(m), 729(m), 683(s);
MS: M/e(I) = 122(1), 121(2), 107(14), 94(20), 93(34), 91(19), 81(37), 80(40), 79(100), 77(34), 68(16), 67(32), 66(16), 65(16), 55(13), 54(14), 53(27), 51(16), 41(36);

UV (cyclohexane): λ_{max} = 186.6nm (ε = 5600).

cis-1,3,4-Trimethylcyclobutene (5). Maleic anhydride (40.0g, 0.41mol) and acetophenone (15mL, 15.3g, 0.127mol) were added to ethyl acetate (2L) in a Pyrex reaction kettle equipped with magnetic stirrer and gas inlet and the solution was saturated with propyne at -78°C. The solution was degassed with a stream of dry nitrogen for 20min and then irradiated with a medium pressure mercury lamp (450W, Hanovia) for 29h at temperatures maintained between -55 to -70°C. The irradiation was terminated when >90% of the maleic anhydride had been consumed as determined by ^{1}H NMR, and the solvent was evaporated on the rotary evaporator. The dark brown oil that remained was distilled in vacuo (ca. 0.5mm Hg) to remove acetophenone and traces of maleic anhydride, affording a dark brown solid residue (59.3g) whose ^{1}H NMR spectrum was consistent with 1-methylcyclobutene-3,4-dicarboxylic acid anhydride.

^{1}H NMR (90 MHz): δ = 1.90 (s broad, 3H), 3.87 (s, 2H), 6.11 (m, 1H).

The material from above (11.5g, 0.083mol) was dissolved in dry ether (30 mL) and added dropwise to a suspension of lithium aluminum hydride (7.3g, 0.103mol) and dry ether (500mL) in a 1L three-necked, round-bottomed flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. The mixture was refluxed for 12h, then cooled and quenched slowly with ice water (250g). The ethereal portion of the mixture was separated and the remaining lithium and aluminum salts were extracted with ether (5 x 30mL). The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was distilled to afford a clear, yellow oil (9.1g, 0.058mol, 70%), the ^{1}H NMR of which was consistent with 1-methyl-cis-3,4-di-(hydroxymethyl)-cyclobutene.

^{1}H NMR (90MHz): δ = 1.63 (s, 3H), 3.00 (m, 2H), 3.73 (m, 4H), 4.36 (s broad, 2H), 5.63 (s, 1H).

The diol from above (10g, 0.064mol) was dissolved in pyridine (ca. 20 mL) and added dropwise to toluenesulfonyl chloride (31g, 0.163moL) dissolved in 100mL dry pyridine in a 250mL round bottomed flask at 0°C, stoppered, and left at 0°C for 48h. The mixture was poured into 200g of ice, vigorously stirred for 15min, then cooled at 0°C for 1h. The solid precipitate was collected by filtration, washed in methanol, and dried in vacuo (ca. 10mm Hg) to afford a light brown solid (21.0g, 0.048mol, 75%) whose ^{1}H NMR spectrum was consistent with 1-methyl-cis-3,4-di(hydroxymethyl)-cyclobutene ditosylate.

^{1}H NMR (90MHz): δ = 1.63 (s, 3H), 2.48 (s, 6H), 3.05 (m, 2H), 4.07 (t, 4H), 5.65 (s, 1H), 7.62 (dd, 8H).

The ditosylate (19.5g, 0.045mol) was added slowly to a suspension of lithium aluminum hydride (7.0g, 0.184mol) in dry diglyme (300mL) in a 500mL three-necked, round-bottomed flask equipped with an 8 in vigreux column and short path distillation unit, solid addition funnel, nitrogen inlet, and magnetic stirrer. The mixture was slowly heated to 105°C. The volatile product was collected in a series of two dry-ice/acetone traps, the contents of which were bulb-to-bulb distilled under vacuum (ca. 0.02mm Hg) to afford a clear, colourless liquid with a ^{1}H NMR spectrum consistent with cis-1,3,4-trimethylcyclobutene, <u>**5**</u>. Cyclobutene <u>**5**</u> was obtained in >99% purity by semi-preparative vpc (column f, injector temp. = 100°C, oven temp. = 45°C, detector temp. = 120°C).

<u>5</u>: **^{1}H NMR** (90MHz): δ = 0.90 (d, 6H), 1.55 (d, 3H), 2.66 (m, 2H), 5.64 (d, 1H);
IR (neat, cm^{-1}): 3038(s), 2956(s), 2933(s), 2886(s), 2716(w), 2631(w), 1641(s), 1616(w), 1466(m), 1442(s), 1376(s), 1329(m), 1316(m), 1273(m), 1193(w), 1091(m), 1039(m), 806(s), 631(w), 601(m);
MS: M/e(I) = 96(27), 95(4), 81(100), 79(18), 77(7), 67(16), 56(10), 57(18), 53(26), 41(38), 39(23);
UV (cyclohexane): λ_{max} = 189nm (ε = 6900).

cis-1,2,3,4-tetramethylcyclobutene (<u>6</u>).[130] Butyne (75mL, 50.3g, 0.93mol), maleic anhydride (35.5g, 0.36mol), and acetophenone (15mL, 15.3g, 0.127mol) were added to 1.9L of ethyl acetate in a Pyrex reaction kettle equipped with magnetic stirrer and gas inlet. The solution was degassed at ca. -40°C with a stream of dry nitrogen for 20 min and then irradiated with a medium pressure mercury lamp (450W, Hanovia) for 43h while the temperature was maintained between -30 to -40°C. The irradiation was terminated when >90% of the maleic anhydride had been consumed as determined by ^{1}H NMR, and the solvent was evaporated on the rotary evaporator. The dark yellow oil that remained was distilled in vacuo (ca. 0.5mm Hg) to remove acetophenone and traces of maleic anhydride, affording a dark yellow solid which exhibited a ^{1}H NMR spectrum consistent with 1,2-dimethylcyclobutene-3,4-dicarboxylic acid anhydride.[130]

^{1}H NMR (90 MHz): δ = 1.80 (s, 6H), 3.75 (s, 2H).

The solid from above (15g, $\leq$0.099mol) was dissolved in 30mL dry ether and added dropwise to a suspension of lithium aluminum hydride (7.3g, 0.203mol) in dry ether (300mL) in a 500mL three-necked, round-bottomed flask equipped with a reflux condenser, addition funnel, and magnetic stirrer. The mixture was refluxed for 5h, cooled, and quenched carefully with ice water (250g). The ethereal portion of the mixture was separated from the solid salts and the solvent was distilled with the rotary evaporator. The aluminum and lithium salts were further extracted with ether using a soxhlet extractor and ether, but no additional diol was obtained. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and the solvent was distilled on the rotary evaporator to yield a clear yellow oil (6.9g, 0.049mol, 50%) where the ^{1}H NMR spectrum was consistent with 1,2-dimethyl-cis-3,4-di(hydroxymethyl)-cyclobutene[130].

^{1}H NMR (90MHz): δ = 1.53 (s, 6H), 2.87 (m, 2H), 3.33-3.96 (m, 4H), 4.30 (s broad, 2H).

The material from above (5g, 0.035mol) was added dropwise to toluenesulfonyl chloride (15g, 0.079mol) dissolved in dry pyridine (50mL) in a 100mL round-bottomed flask at 0°C, stoppered, and left at 0°C for 48h. The mixture was poured into 200g of ice, vigorously stirred for 15min, and then allowed to stand at 0°C for 30min. The solid precipitate was collected by filtration, washed with 2% aqueous HCl (25mL), water (25mL), filtered, dried in vacuo (ca. 10mm Hg), and recrystallized from methanol to afford a light brown solid (8.3g, 0.018mol, 53%). The ^{1}H NMR spectrum of the compound was consistent with 1,2-dimethyl-cis-3,4-di(hydroxymethyl)cyclobutene ditosylate[125].

^{1}H NMR (90MHz): δ = 1.50 (s, 6H), 2.45 (s, 6H), 2.93 (m, 2H), 4.07 (d, 4H), 7.58 (dd, 8H).

The ditosylate (10g, 0.022mol) was added slowly to a suspension of lithium aluminum hydride (5.0g, 0.133mol) in dry ether (150 mL) in a

250mL three-necked, round-bottomed flask equipped with a solid addition funnel, reflux condenser, nitrogen inlet, and magnetic stirrer. The mixture was refluxed for 12h, cooled, and then quenched by cautious addition of 2% aqueous NaOH. The ethereal portion of the mixture was separated and the solid salts were extracted further with ether. The combined ether extracts were dried over anhydrous sodium sulfate, filtered, and the solvent removed by slow distillation. The product was bulb-to-bulb distilled under vacuum (ca. 0.02mm Hg) to afford a clear, colourless liquid with a ^{1}H NMR spectrum consistent with cis-1,2,3,4-tetramethylcyclobutene, <u>**6**</u>[130] after separation from two minor products by vpc. Cyclobutene <u>6</u> was obtained in >99% purity by semi-preparative vpc (column f, injector temp. = 100°C, oven temp. = 60°C, detector temp. = 120°C).

<u>6</u>: **^{1}H NMR** (90MHz): δ = 0.90 (d, 6H), 1.48 (s, 6H), 2.58 (m, 2H);
IR (neat, cm^{-1}): 2953(s), 2929(s), 2906(s), 2866(s), 2716(w), 2621(w), 1688(w), 1461(m), 1435(s), 1374(s), 1326(w), 1316(m), 1289(m), 1211(w), 1133(m), 1096(m), 1024(m), 996(m), 976(w), 658(m), 628(m);
MS: M/e(I) = 110(37), 109(3), 95(100), 91(5), 81(14), 79(9), 77(7), 67(48), 56(14), 55(37), 53(18), 51(7), 41(29), 39(20);
UV (cyclohexane): λ_{max} = 190nm (ε = 11,100).

1,3,3,4- and 1,3,4,4-tetramethylcyclobutene (<u>20</u>) and (<u>21</u>).

Citraconic anhydride (15g, 0.134 mole), 2-methyl-2-butene (20g, 0.286 mole) and acetophenone (5.15g, 0.043 mole) were dissolved in ethylacetate (500mL) in a Pyrex immersion well equipped with a magnetic stirrer. The reaction mixture was cooled to ca. 5°C with an external ice-water bath and deoxygenated by bubbling dry nitrogen through the solution for approximately 30 minutes. The solution was then irradiated with a medium pressure mercury lamp (450W, Hanovia), agitating constantly throughout the irradiation period with the magnetic stirrer as well as with a slow stream of dry nitrogen. After 11h irradiation, ^{1}H NMR analysis of the photolysate revealed the disappearance of citraconic anhydride to be >95% complete. The solvent was removed with a rotary evaporator to yield an orange-yellow oil which was then distilled in vacuo (ca. 0.2 mm Hg) to remove acetophenone and a small amount of citraconic anhydride.

A portion (12 g) of the clear, orange and viscous oil that remained (17 g) was stirred in 12% aqueous HCl (75 mL) for ca. 10 h at room temperature and then extracted with ether (3 x 50mL). The extracts were washed with water (50 mL), saturated brine (50mL), dried over sodium sulphate and then distilled to afford a light brown solid (11g).

A portion (4g, 0.019 mole) of the solid was added to pyridine (60mL, distilled from barium oxide) and the solution was placed in a 100mL, two-necked, round-bottomed flask fitted with a gas inlet tube and a Vigreux column connected to three sequential dry ice/acetone traps. The solution was saturated with oxygen at room temperature, lead tetraacetate (10g, 0.023 mole) was added, a slight positive pressure of dry nitrogen was applied, and the mixture was placed in an oil bath (70°C) where CO_2 evolution occurred within 2-3 min. When gas evolution had subsided, the temperature of the oil bath was increased to 90°C and nitrogen was slowly bubbled through the reaction mixture for 24h. The colourless liquid which had collected in the traps was dissolved in pentane (5-10mL), washed with 5% aqueous HCl (4 x 5mL), water (3 x 5mL), dried over anhydrous sodium sulphate, filtered, and concentrated by slow distillation. Vpc analysis (column f) of the product revealed the presence of two major products in ca. 1:1 ratio. These were separated by semi-preparative vpc (column f, injector temp. = 120°C, detector temp. = 150°C, oven temp. = 70°C). Compounds **20** and **21** were obtained in >99% purity by further purification using semi-preparative vpc on column (h).

20: ^{1}**H NMR** (500 MHz): δ = 5.66 (q, 1H, J = 1.6 Hz), 2.23 (qq, 1H, J = 7.2, 1.2 Hz), 1.57 (dd, 3H, J = 1.6, 1.2 Hz), 1.08 (s, 3H), 0.96 (s, 3H), 0.94 (d, 3H, J = 7.2 Hz);
^{13}**C NMR** (125.6 MHz): δ = 13.04, 13.89, 21.87, 27.27, 42.22, 48.70, 135.78, 146.71;
IR (neat, cm^{-1}): 3026(s), 2950(s), 2910(s), 2866(s), 1626(m), 1436(s), 1363(s), 1326(m), 1282(m), 1211(m), 1121(w), 1091(m), 1051(m), 1022(m), 810(s);
MS: M/e(I) = 110 (34), 95 (100), 91 (3), 81 (11), 79 (9), 77 (7), 67 (45), 65 (5), 55 (44), 53 (17), 41 (28), 39 (16), 27 (11);
Exact mass: Calculated for C_8H_{14}, 110.1116, found 110.1100.
UV (cyclohexane): λ_{max} = 192nm (ε = 4950).

21: ^{1}**H NMR** (500 MHz): δ = 5.58 (qd, 1H, J = 1.5, 0.9Hz), 2.30 (qd, 1H, J = 7.1, 0.9 Hz), 1.53 (m, 3H, J = 1.5Hz), 1.06 (s, 3H), 0.96 (d, 3H, J = 7.1 Hz), 0.93 (s, 3H);
^{13}**C NMR**: (125.6 MHz): δ = 11.36, 14.72, 20.08, 25.13, 44.47, 45.59, 128.74, 153.03;
IR (neat, cm^{-1}): 3036(s), 2951(s), 2866(s), 1641(m), 1436(s), 1361(s), 1328(m), 1284(m), 1214(m), 1140(w), 1071(w), 1027(s), 1000(s), 974(m), 871(w), 808(s);
MS: M/e(I) = 110 (55), 95 (100), 93 (9), 91 (3), 81 (13), 79 (13), 77 (6), 69 (15), 67 (85), 65 (7), 55 (79), 53 (31), 41 (69), 29 (16), 27 (10);
Exact mass: Calculated for C_8H_{14}, 110.1116, found 110.1100;
UV (cyclohexane): λ_{max} = 193nm (ε = 6700).

5.4 Synthesis of Photoproducts

2,4-Hexadiene isomers (<u>22</u>). Cis,trans-2,4-hexadiene, **ct-<u>22</u>**, (0.3g, ca. 0.004 mol; Aldrich) was placed with 30mL pentane into a quartz tube and degassed for 15min. at 0°C with dry N_2. The solution was placed in a Rayonet equipped with ten 254nm lamps and irradiated to a photostationary state within three hours, at which time vpc analysis (column a) revealed the mixture to contain **ct-<u>22</u>** and two other major components. The solvent was evaporated by slow distillation, leaving ca. 0.5mL of a clear colourless liquid. The residue was bulb-to-bulb distilled in vacuo (ca. 0.02mm Hg) and the three major components were separated by semi-preparative vpc (column h). The ^{1}H NMR spectra of these compounds allowed identification as **tt-**, **ct-**, and **tt-<u>22</u>** by comparison to published spectra.[131]

tt-<u>22</u>: ^{1}**H NMR** (90 MHz): δ = 1.75 (d, 6H), 5.54 (m, 2H), 6.12 (m, 2H).
ct-<u>22</u>: ^{1}**H NMR** (90 MHz): δ = 1.76 (m, 6H), 5.20-6.66 (m, 4H).
cc-<u>22</u>: ^{1}**H NMR** (90 MHz): δ = 1.72 (d, 6H), 5.55 (m, 2H), 6.33 (m, 2H).

Cis,trans-1,3-cyclooctadiene (ct-<u>25</u>) was synthesized according to the published methods.[35,132] Acetophenone (2g, 0.017mol) and cis,cis-1,3-cyclooctadiene (21g, 0.194mol, previously bulb-to-bulb distilled under vacuum (ca. 0.02mm Hg) was added to ethyl acetate (350 mL) and placed in a Pyrex immersion well apparatus equipped with a magnetic stirrer and gas inlet. The mixture was degassed with dry nitrogen for 20 min and then irradiated with a medium pressure mercury lamp (450W, Hanovia) at ca. 0°C until a photostationary state (c,c/c,t $\approx$ 2.2) was reached (ca. 4h). Aqueous silver nitrate (20%, 15g in 75mL water) was added at 0°C turning the mixture brown and the contents were stored (periodically stirred vigorously) at 3°C for ca. 8h. The crystals which had formed were separated from solution by vacuum filtration, washed with pentane (50 mL), methanol (50 mL), and then pentane (50 mL). The white needle-like crystals were dried in vacuo (ca. 5mm Hg) to afford the cis,trans-1,3-cyclooctadiene/$AgNO_3$ complex (10g, 40% yield based on amount of starting cis,cis-isomer, m.p. = 133.5 - 134.5°C). The cis,trans-1,3-cyclooctadiene was liberated by the dropwise addition of concentrated ammonia (20 mL) to a stirred suspension of the silver nitrate complex (5g) in pentane (20mL). The mixture was poured into water (30mL) and the pentane layer separated. The aqueous phase was extracted with pentane (3 x 10mL). The combined pentane extracts were dried over anhydrous sodium sulphate, filtered, and the solvent evaporated on a rotary evaporator to yield a clear colourless liquid. Vpc analysis (column a) of the liquid dissolved in pentane revealed one major component (ca. 98% purity). The IR[132] and ^{1}H NMR[133] spectra agreed with that previously published for cis,trans-1,3-cyclooctadiene.

ct-25: **^{1}H NMR** (90 MHz): δ = 6.16 (d, 1H), 5.52-6.00 (m, 3H), 2.25 (m, 4H), 1.10-2.33 (m, 4H);
0.90 (m, 2H), 1.27 (m, 2H), 1.4-2.0 (m, 4H), 5.47-6.30 (m, 4H);
IR (neat, cm^{-1}): 3000(s), 2920(s), 2840(s), 1720(w), 1630(s), 1605(m), 1435(s), 1275(m), 1255(m), 1185(m), 1085(m), 1055(m), 985(s), 960(s), 945(s), 915(m), 872(m), 825(s), 800(s), 740(s), 690(m), 655(s), 550(m), 477(m);
MS: M/e(I) = 108(15), 107(4), 93(50), 91(22), 80(49), 79(100), 77(34), 67(52), 66(17), 54(12), 41(20), 39(25).

7-methylenebicyclo[4.2.0]heptane (27) was synthesized according to the procedure of Arora and Binger[134] and purified by semi-preparative vpc using column f.

27: ^{1}**H NMR** (90 MHz): δ = 1.24 (m, 4H), 1.57 (m, 2H), 1.70 (m, 4H), 5.33 (s, 2H);
IR: (in CCl4, cm^{-1}): 3060(m), 2980(s), 2920(s), 2855(s), 2670(w), 1770(w), 1743(m), 1442(s), 1345(m), 1325(m), 1296(w), 1132(m), 970(w), 918(w), 875(s) 534(m);
MS: M/e(I) = 108(3), 107(8), 93(100), 91(23), 80(30), 79(90), 77(41), 67(27), 53(16), 41(37), 39(35).

cis,cis-1,3-cyclononadiene (cc-29). Cis,cis-1,3-cyclononadiene was prepared via 1,2-cyclononadiene. 1,2-Cyclononadiene was prepared from cyclooctene according to the Doering-Moore-Skattebol route.[135] Cyclooctene (20g, 0.18 mol) and potassium t-butoxide (25g, 0.23 mol) were added with 150 mL dry pentane to a 250mL two-necked, round-bottomed flask. Bromoform (46g, 0.18mol) was added dropwise and the mixture was stirred for ca. 12h. It was then poured into water (100 mL) and separated. The pentane fraction was washed with water (50 mL), dried over anhydrous sodium sulfate, filtered, and then distilled on a rotary evaporator. Distillation in vacuo (ca. 0.02mm Hg) afforded 28g (53% yield) of a golden oily residue whose spectra were consistent with 9,9-dibromo-bicyclo[6.1.0]nonane.

^{1}**H NMR** (90MHz): δ = 1.48 (m, 12) 2.06 (d, 2H);
IR (neat, cm^{-1}): 3020(s), 2925(s), 2860(s), 2690(w), 1465(s), 1448(s), 1363(m), 1143(s), 1163(s), 1060(m), 1020(w), 930(w), 890(w), 855(m), 812(m), 760(s), 745(s), 705(s), 650(s).

Lithium metal (1.75g, 0.25mol) was added in small pieces to a solution of methyl iodide (17.8g, 0.125 mol) in anhydrous ether (100 mL) in a 250mL two-necked, round-bottomed flask fitted with a reflux condenser, magnetic stirrer, and gas inlet under an argon atmosphere at room temperature.

The mixture was stirred for an additional 30min after the lithium had completely dissolved. The reaction mixture was then placed in a dry ice/acetone bath and allowed to cool to ca. -78°C. The dibromide (28g, 0.100 mol) in ca. 50mL ether was then added dropwise. The reaction mixture was allowed to stir for 1h after addition was complete. The temperature was increased to ca. 10°C and saturated aqueous ammonium chloride (50 mL) was added. The ethereal layer was separated, washed with water (50 mL), saturated brine (50 mL), dried over anhydrous sodium sulfate, and filtered. The ether was evaporated on the rotary evaporator to afford a clear yellow liquid whose ^{1}H NMR spectrum was consistent with 1,2-cyclononadiene contaminated with a small amount of starting material. The liquid was distilled in vacuo (ca. 0.02mm Hg) to afford a clear colourless liquid (12g, yield >95%) whose ^{1}H NMR spectrum was consistent with 1,2-cyclononadiene.

^{1}H NMR (90 MHz): δ = 5.22 (m, 2H), 2.15 (m, 2H), 1-1.9 (m, 10H); **MS:** M/e(I) = 122(4), 107(7), 94(22), 93(48), 91(16), 81(49), 80(55), 79(100), 77(30), 68(7), 67(32), 66(13), 65(16), 55(14), 53(23), 41(40), 39(52).

1,2-Cyclononadiene (5g, 0.041mol) was added dropwise to a solution of potassium t-butoxide (4.3g, 0.038mol, 0.77M) in dry DMSO (50 mL) in a 100mL two-necked, round-bottomed flask at ca. 72°C under a dry nitrogen atmosphere. The reaction was left to stir at this temperature for 100min after addition of the diene was complete. The reaction mixture was then cooled to room temperature, quenched by the addition of ca. 50mL water, and the product was extracted with ether (3 x 50mL). The ether extracts were washed with water (50 mL), saturated brine (50 mL), dried over anhydrous sodium sulfate, and filtered. Evaporation of the solvent afforded a clear, colourless liquid which consisted of two major compounds (ca. 4:1 ratio by vpc). The major portion was separated by preparative vpc and afforded a ^{1}H NMR spectrum consistent with cis,cis-1,3-cyclononadiene.[136]

cc-**29**: **^{1}H NMR** (90 MHz): δ = 1.53 (m, 6H), 2.13 (m, 4H), 5.44-6.00 (m, 4H);
IR (neat, cm^{-1}): 3054(s), 3003(s), 2920(s), 2856(s), 2688(w), 1745(w), 1708(w), 1636(m), 1478(m), 1458(s), 1443(s), 1354(w), 1280(w), 1089(m), 1051(m), 978(m), 878(m), 843(m), 815(m), 768(s), 733(s), 707(m), 661(s), 607(w), 584(w);
MS: M/e(I) = 122(28), 107(17), 93(51), 81(71), 80(68), 79(100), 67(47), 53(27), 41(39), 39(50).

Cis,trans-1,3-cyclononadiene (ct-29) was prepared by the pyrolysis of cis-bicyclo[5.2.0]non-8-ene, **c-4**. **Cis-4** (0.2g, 0.0016mol) was sealed in a 1/4in o.d. glass tube following a degassing procedure of three freeze/pump/thaw cycles, and placed in an oil bath (198°C) for 1h. Vpc analysis (column a) revealed the presence of two components in the pyrolysis mixture, one of which was unreacted **c-4** (66%). The other component was isolated by semi-preparative vpc (column g, injector temp. = 120°C, detector temp. = 150°C, oven temp. = 90°C) and identified as cis,trans-1,3-cyclononadiene (**ct-29**) on the basis of its ^{1}H NMR and mass spectra.

ct-29: **^{1}H NMR** (90 MHz): δ = 1.56 (br s, 6H), 2.27 (br s, 4H), 5.58-6.00 (m, 2H), 6.17 (d, 2H);
MS: M/e(I) = 122(14), 107(13), 94(18), 93(42), 91(16), 81(54), 80(60), 79(100), 77(30), 67(49), 53(20), 41(29), 39(35).

E- and Z-2,4-dimethyl-2,4-hexadiene (E- and Z-43). Triphenylphosphine (11g, 0.042 mol) and ethyl bromide (6g, 0.047 mol), were dissolved in dry benzene (25 mL) in a 50mL round-bottomed flask equipped with an efficient reflux condenser and magnetic stirrer. The mixture was refluxed for 24h, cooled, filtered, and dried in vacuo to afford a white solid that was identified as ethyltriphenylphosphonium bromide on the basis of its ^{1}H NMR spectrum (11.2g, 0.029 mol, yield 69%).

^{1}H NMR (90MHz): δ = 7.77 (s broad, 15H), 3.83 (m, 2H), 1.41 (dt, 3H). Sodium hydride (0.8g, 0.033mol) and dry dimethylsulfoxide (10 mL, distilled from barium oxide) were placed in a 100mL, two-necked, round-bottomed flask equipped with a reflux condenser, magnetic stirrer, gas inlet, and addition funnel. The mixture was heated under a nitrogen atmosphere at 85°C until gas evolution ceased (ca. 45min) and then cooled to room temperature. Ethyltriphenylphosphonium bromide (9g, 0.023 mol) was dissolved in warm DMSO (30 mL) and added dropwise over 20min. The orange-coloured reaction mixture was stirred for 1h at room temperature and heat mesityl oxide (2.3g, 0.024 mol) was added dropwise over 20min., affording a milky white mixture which was stirred overnight at room temperature. The resulting mixture was filtered through Celite, poured into water (50 mL), and extracted with pentane (5 x 25mL). The extracts were washed with DMSO/water (1:1 ratio), water (50 mL), saturated brine (50 mL), and dried over anhydrous sodium sulfate. The filtered extracts were slowly distilled to remove the solvent. Bulb-to-bulb distillation (ca. 0.2mm Hg) of the residue afforded a mixture of **E-** and **Z-43** isomers as clear, colourless liquids. Dienes **E-** and **Z-43** (0.47g, 0.0043mol, yield 18%) were isolated as a mixture by semi-preparative vpc on column f.

Separation and further purification under the same conditions (injector temp. = 120°C, detector temp. = 160°C) afforded each isomer in >99% purity.

E-<u>43</u>: **^{1}H NMR** (500MHz) in $\mathrm{CDCl_3}$: δ = 5.61 (br s, 1H), 5.29 (q, J = 6.9 Hz, 1H), 1.74 (s, 3H), 1.73 (s, 3H), 1.69 (s, 3H) 1.65 (d, J = 6.9 Hz, 3H);
IR (neat, cm^{-1}): 3020(s), 2967(s), 2922(s), 2862(s), 1656(w), 1445(s), 1374(m), 1182(w), 1052(w), 857(s), 772(w), 511(w);
MS: M/e(I) = 110 (36), 95 (100), 81 (17), 77 (13), 67 (64), 55 (59), 53 (32), 41 (53), 39 (50), 27 (34).
Exact mass: Calculated for C_8H_{14}, 110.1116; found 110.1088;
UV (cyclohexane): λ_{max} = 232nm (ε= 10,700).

Z-<u>43</u>: **^{1}H NMR** (500MHz) in $\mathrm{CDCl_3}$: δ = 5.54 (br s, 1H), 5.26 (q, J = 6.8 Hz, 1H), 1.76 (s, 3H), 1.70 (br s, 3H), 1.56 (s, 3H), 1.48 (d, J = 6.8 Hz, 3H);
IR (neat, cm^{-1}): 3020(s), 2966(s), 2922(s), 2863(s), 2661(w), 1625(w), 1446(s), 1385(m), 1206(w), 1185(w), 1035(m), 824(m), 783(m), 554(w);
MS: M/e(I) = 110 (57), 95 (100), 81 (20), 77 (21), 67 (61), 55 (43), 53 (23), 41 (35), 39 (32), 27 (19);
Exact mass: Calculated for C_8H_{14}, 110.1116; found 110.1087;
UV (cyclohexane): λ_{max} = 217nm (ε= 6800).

E-2,3-dimethyl-2,4-hexadiene (E-<u>44</u>). Propyne (ca.5mL, 0.083 mole) was condensed into a dry ice/acetone trap and transferred into 70mL anhydrous ether in a 250mL two-necked, round-bottomed flask equipped with magnetic stirrer, dry ice condenser, thermometer and gas inlet at -78°C. n-Butyllithium (36mL of a 2M hexane solution) was added dropwise with stirring under an argon atmosphere, at a rate slow enough to ensure that the temperature of the reaction mixture did not rise above -50°C. The reaction mixture was stirred at -78°C for 1h, and then 3-methyl-2-butanone (6g, 0.071mol) was added dropwise with stirring. The reaction mixture was allowed to warm to room temperature and then stirred for several hours. The mixture was then poured into a saturated aqueous ammonium chloride solution (30 mL) and extracted with ether (3 x 25mL). The extracts were washed with water (10 mL), saturated brine (10 mL) and finally dried over anhydrous sodium sulphate. The filtered extracts were distilled to remove the solvent and then bulb-to-bulb distilled under vacuum (ca. 0.2mm Hg) to yield a clear, colourless liquid (5g, 0.04mol, 56%) identified as 4,5-dimethylhex-2-yn-4-ol on the basis of its ^{1}H NMR, IR, and mass spectra.

> **^{1}H NMR** (90MHz): δ = 1.8 (m, 4H), 1.35 (s, 3H), 0.95 (dd,6H);
> **IR** (cm^{-1}): 3440(s broad), 2970(s), 2920(s), 2880(s), 2250(w), 1460(m), 1445(m), 1365(s);
> **MS**: M/e(I) = 126(1), 125(1), 111(34), 93(9), 91(8), 84(45), 83(100), 81(24), 77(12), 69(19), 67(27), 65(14), 55(21), 53(15).

The alkynol (2.7g, 0.021 mol), Lindiar catalyst (0.08g) and anhydrous ether (25 mL) were placed into a 100mL two-necked, round-bottomed flask equipped with magnetic stirrer and hydrogenated at 1 atm for 7h. The reaction mixture was filtered through Celite and the solvent was distilled to afford a clear, colourless liquid that was identified as Z-4,5-dimethylhex-2-en-4-ol (2.3g, 0.0185mol, yield 87%) on the basis of its ^{1}H NMR spectrum.

> **^{1}H NMR** (90 MHz): δ = 5.45 (m, 2H), 1.86 (d, 3H), 1.75 (m, 1H), 1.30 (s, 3H), 0.90 (d, 6H).

The alkenol (1[illegible]0075mol), propionic anhydride (5 mL), and a grain of iodine were [illegible] a 10mL round bottom flask equipped with a reflux condenser and magnetic stirrer. The mixture was stirred at ca. 120°C for

1h. The flask was then cooled to room temperature and the contents were poured into ether (15 mL). The solution was washed with saturated aqueous bicarbonate (3 x 25mL), water (20 mL), dried over anhydrous sodium sulfate, and filtered. The solution was slowly distilled to remove the solvent and then bulb-to-bulb distilled under vacuum (0.2mm Hg) to yield a clear, colourless liquid. Vpc analysis of the liquid (column a) showed it to contain one major product, which was isolated by semi-preparative vpc (column f, injector temp. = 120°C, detector temp. = 170°C, oven temp. = 90°C). Diene E-**44** was obtained in >99% purity by further vpc purification on column f (0.63g, 70% yield from the alkenol). The diene exhibited spectral features similar to those previously reported.[104]

E-44: **^{1}H NMR** (500 MHz): δ = 6.38 (d, J = 15.8Hz, 1H), 5.47 (dq, J = 15.3, 6.8 Hz, 1H), 1.77 (m, 6H), 1.74 (s, 3H), 1.69 (s, 3H);
IR (neat, cm^{-1}): 3040(s), 2919(s), 2862(s), 1446(m), 1375(m), 1142(w), 1051(w), 1005(w), 956(s), 781(w); **MS**: M/e(I) = 110 (58), 95 (100), 81 (13), 77 (10), 67 (49), 55 (34), 53 (16), 41 (37), 39 (28), 27 (14);
Exact mass: Calculated for C_8H_{14}, 110.1116; found 110.1087;
UV (cyclohexane): λ_{max} = 241nm (ε = 21,250).

Z-2,3-dimethyl-2,4-hexadiene (Z-44). was synthesized by photolysis of a deoxygenated pentane (30mL) solution of E-**44** (0.4g, 0.0036mol) in a Rayonet reactor fitted with ten 254nm lamps. Irradiation of the 0.12M solution for 5h yielded a mixture of E-**44** and Z-**44** along with one other minor product. The pentane was removed by slow distillation and the concentrated photolysate was bulb-to-bulb distilled under vacuum (ca. 0.2mm Hg). Diene Z-**44** was separated cleanly from the other compounds by semi-preparative vpc using column (c) and finally obtained in >99% purity after further vpc purification with the same column. The diene exhibited spectral features similar to those previously reported.[104]

Z-<u>44</u>: **^{1}H NMR** (500MHz): δ = 5.80 (br d, J = 11.1Hz, 1H), 5.35 (dq, J = 11.1, 6.9Hz, 1H), 1.69 (s, 3H), 1.67 (s, 3H), 1.58 (s, 3H), 1.52 (dd, J = 11.8, 6.9Hz, 3H);
IR (neat, cm^{-1}): 3004(s), 2920(s), 2863(s), 1444(m), 1405(w), 1372(m), 1156(w), 1124(w), 930(m), 735(m), 713(m);
MS: M/e(I) = 110 (75), 95 (100), 81 (14), 77 (11), 67 (55), 55 (38), 53 (20), 41 (40), 39 (28), 27 (16);
Exact mass: Calculated for C_8H_{14}, 110.1116; found 110.1090;
UV (cyclohexane): λ_{max} = 223nm (ε = 8,500).

E,E- and E,Z-ethylidenecyclohexene (E,E- and E,Z-<u>31</u>).[81] Vinylcyclohexane (10g, 0.093 mol) and potassium t-butoxide (5.6g, 0.050 mol) were added to dry dimethylsulfoxide (30 mL, distilled from barium oxide) in a 100mL two-necked, round-bottomed flask equipped with a reflux condenser, magnetic stirrer, gas inlet tube and thermometer. The mixture was stirred for 20h at 85°C under a dry nitrogen atmosphere, then poured into water (50 mL) and extracted with ether (3 x 50mL). The extracts were washed with water (2 x 50mL), dried over magnesium sulfate, and filtered. The solvent was evaporated on the rotary evaporator and the remaining clear, colourless liquid was distilled under a N_2 atmosphere to rid the mixture of low boiling impurities. The remaining material gave a complex ^{1}H NMR spectrum; vpc analysis of the liquid (column a) revealed the presence of two major products (ca. 40:60 ratio). The ^{1}H NMR spectrum was consistent with the previously reported spectrum of the two unseparated isomers.[81]

^{1}H NMR (90 MHz): 1.6 (d) and 1.75–2.45 (m) (9H combined), 5.2 (q, 1H), 5.53–5.95 (m, 1H), 6.07 (d, 1H), 6.47 (d, 1H).

The doublets at 6.07 and 6.47ppm were tentatively assigned to the resonances of the proton at C2 on the ring for **E,Z-** and **Z,Z-31** respectively. The isomers were separated by semi-preparative vpc using columns f and g (injector temp. = 120°C, detector temp. = 170°C, oven temp. = 80°C) and obtained in >90% isomeric purity.

5.5 Solution UV Absorption Studies

All spectra were recorded in deoxygenated (bubbling Ar, 23°C) cyclohexane (Burdick & Jackson) solution using Suprasil optical cells (0.1 cm path length) at room temperature. The spectra were corrected for solvent absorption in each case by placing an optically matched cell containing the solvent in the reference beam.

5.6 Photolysis of Cyclobutenes

Photochemical experiments employed a 10W Osram HNS 10W/U OZ low pressure mercury lamp (185 + 254nm), a 16W Philips 93106E Zn resonance lamp (214nm), or the pulses (193nm, ca. 10ns, 20-100mJ, 0.5 - 1 Hz repetition rate) from a Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture. The low pressure mercury and zinc resonance lamps were given a 20 min warmup period before each experiment and cooled with a stream of nitrogen. The low pressure mercury and zinc resonance lamps were surrounded by a metal case which incorporated a 1" port to contain the sample cell (and in the case of the low pressure mercury lamp, a filter). The filter consisted of a 25 x 3mm LiF disc (Harshaw VUV grade) which had been irradiated with ca. 1.7 Mrad of irradiation from a ^{60}Co source. The transmittance spectrum of the filter was monitored closely during photolysis experiments as the transmittance at 254nm tends to increase slowly after prolonged exposure to the light from a low pressure mercury lamp. A freshly prepared filter typically has an optical density of ca. 0.5 at 185nm and ca. 5 at 254nm.

All irradiations at room temperature were carried out in 0.01-0.05M solutions of the cyclobutene in either pentane, cyclohexane, or 2,2,4-trimethylpentane. Solutions were deoxygenated before use by bubbling dry nitrogen or argon through cooled (ca. 0C) solutions for 15 min. In all runs, the sample was agitated during photolysis with a small magnetic stirrer.

Photolyses were carried out at ambient temperature (ca. 23C) in 10 x 25mm cylindrical Supracil quartz UV cells (Hellma). Preparative photolyses were carried out in rectangular cells (10 mL volume) constructed from 10 x 20mm rectangular Suprasil quartz tubing (Vitro Dynamics) at ca. 23C using the 193nm output of the excimer laser.

Photolyses were generally carried to 1-3% conversion with aliquots being withdrawn at suitable time intervals for vpc analysis. Relative product yields were determined from the slopes of concentration versus time plots constructed for all components of the mixture relative to an internal standard. Relative detector responses were calibrated for all identified products using a few standard solutions made up from authentic samples. All concentration versus time plots were linear.

5.7 Low Temperature Photolyses

Photolyses at 77K were carried out in degassed (bubbling Ar, 15 min) 2-methylbutane/cyclopentane (4:1 ratio) solutions contained in Suprasil quartz cuvettes (0.3 x 0.7 cm) in a Suprasil quartz dewar. Liquid nitrogen was used as the coolant. The 0.02M cyclobutene solutions were irradiated using the pulses of the argon fluoride excimer laser (193nm). The relative yields of products were determined by vpc from single-point determinations after 3-5% conversion. The results represent the average of two or three experiments, each of which was analyzed at least twice.

5.8 Irradiation of Dienes

The photostationary states for direct cis,trans-photoisomerization of **29**, **31**, **43**, and **44** were determined at 254nm using 1-4 RPR 254 nm lamps in a Srinivasan-Griffin Photochemical Reactor (Rayonet) model RPR 100. The irradiations were carried out in pentane (0.02-0.05M in diene) solutions contained in 7mm quartz tubes and were previously deoxygenated (bubbling N_2 or Ar, 0°C). The Rayonet reactor was used in conjunction with a merry-go-round apparatus in order to irradiate all samples equally and simultaneously. The formation of products was monitored by analytical vpc and recorded as concentration vs. time plots in order to determine the photostationary state (in the case of dienes **43** and **44**) or relative quantum yields for isomerization (as determined in the case of dienes **29** and **31**). The photostationary states were approached from both directions.

5.9 Quantum Yield Determinations at 185nm

Quantum yields were determined using the cis -> trans-cyclooctene actinometer[78,79] at 185nm, and in the case of **2** and **3**, also at 193nm. The quantum yields of products were determined after calculating the light flux from a concentration vs. time plot for the formation of trans-cyclooctene from the cis-isomer. Photolyses were conducted concurrently with the substrate of interest, using approximately matched cells and alternately irradiating the substrate and actinometer solutions for identical, short periods of time. The actinometer solutions were constantly agitated during the irradiation periods by a small magnetic stirrer. Generally the concentration of the actinometer was made identical to that of the substrate and was considered optically dense (optical density >>2.0 abs.units). The progress of cis -> trans isomerization of cyclooctene was monitored by analytical vpc using column d (injector temp. = 100C, oven temp. = 80C, detector temp. = 200C). The response of the flame ionization detector was calibrated for trans-cyclooctene using cis-cyclooctene which has a retention time on the column quite close to the trans-isomer. A value of 0.32 ± 0.02 was employed for the actinometric quantum yield.[79]

APPENDIX A

Calculation of the partitioning constants for the decay of c-, t-1, s-cis and s-trans ct-22 and cyclopropylcarbinyl diradicaloid intermediates.

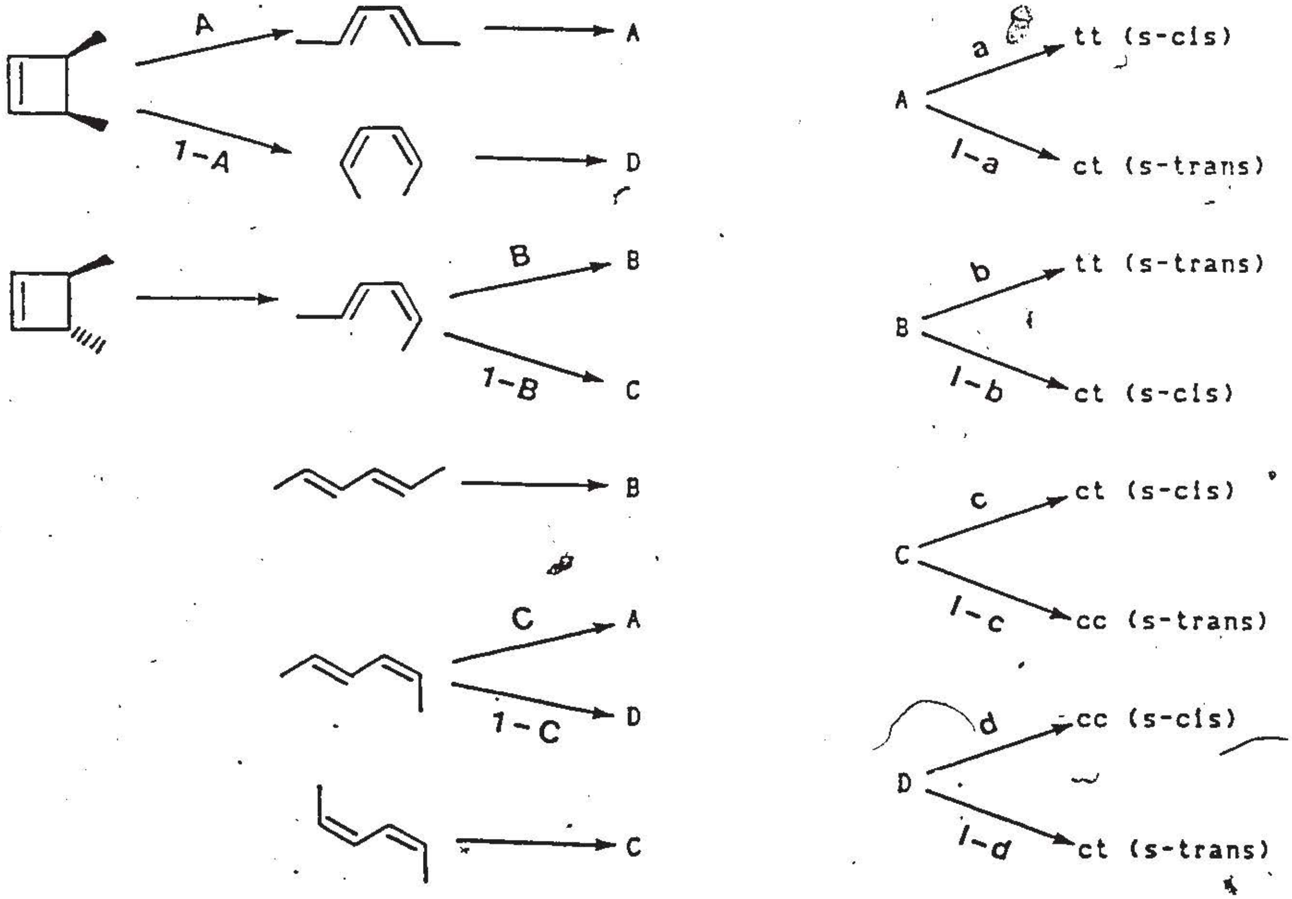

A


B


C


D

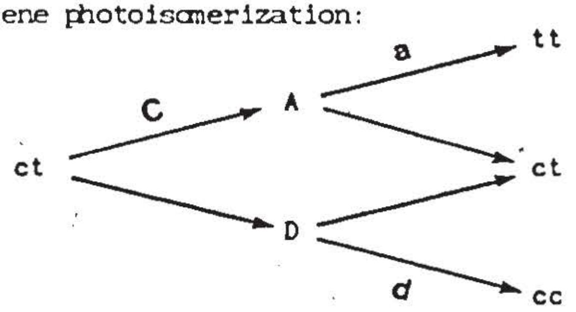
Reaction Schemes involved:



Calculations:

Calculation of partitioning constants for A and D using: (1) the results of the direct diene photoisomerization and (2) the results of the direct photoisomerization of **c-** and **t-1**.

(1) from direct diene photoisomerization:

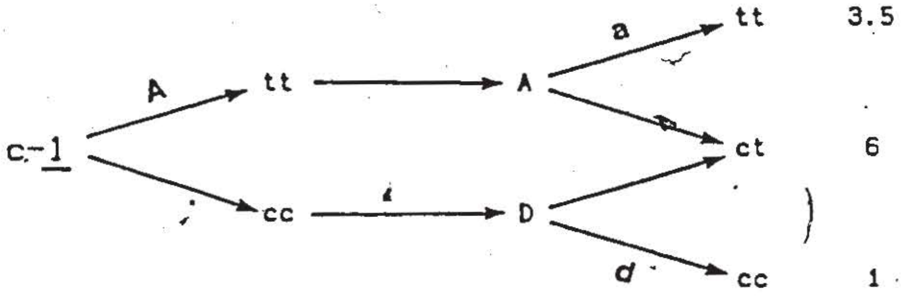


$$\phi_{ct \rightarrow tt} = 0.18 = C\,a \qquad C = 0.18/a \qquad (1)$$

$$\phi_{ct \rightarrow cc} = 0.29 = (1-C)\,d \qquad C = (d-0.29)/d \qquad (2)$$

$$a = \frac{0.18\;d}{d - 0.29} \qquad (3)$$

(2) from direct photolysis of **c-1**:



$$\frac{A\;a}{d\;(1-A)} = 3.5 \qquad (4)$$

$$\frac{A\;(1-a) + (1-A)\;(1-d)}{d\;(1-A)} = 6.0 \qquad (5)$$

$$a = \frac{3.5\;d}{(10.5\;d - 1)} \qquad (6)$$

Equations (3) and (6) are combined:

$$a = \frac{0.18\ d}{[illegible] - 0.29} = \frac{3.5\ d}{10.5\ d - 1} \qquad (7)$$

-solving for d in turn leads to the solutions for a, A, and C:

$d = 0.52$

$a = 0.41$

$A = 0.82$

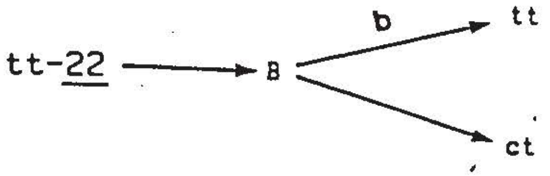
$C = 0.44$

-from the direct photochemistry diene **22**:

$\phi_{tt \to ct} = 0.37$

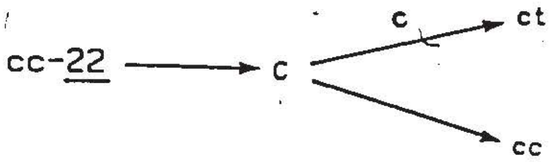
$1-b = 0.37$

$b = 0.63$

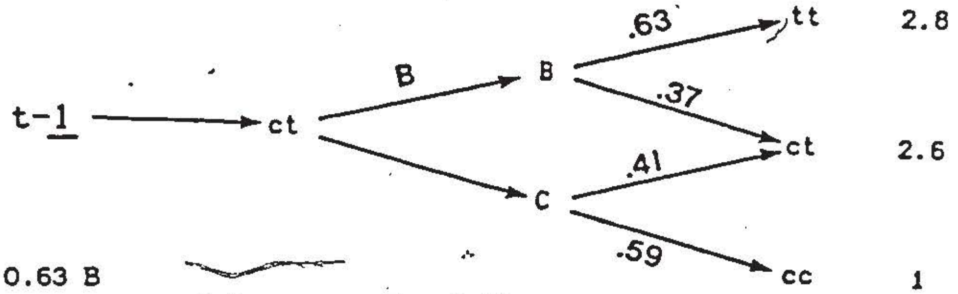


$\phi_{cc \to ct} = 0.41$

$c = 0.41$



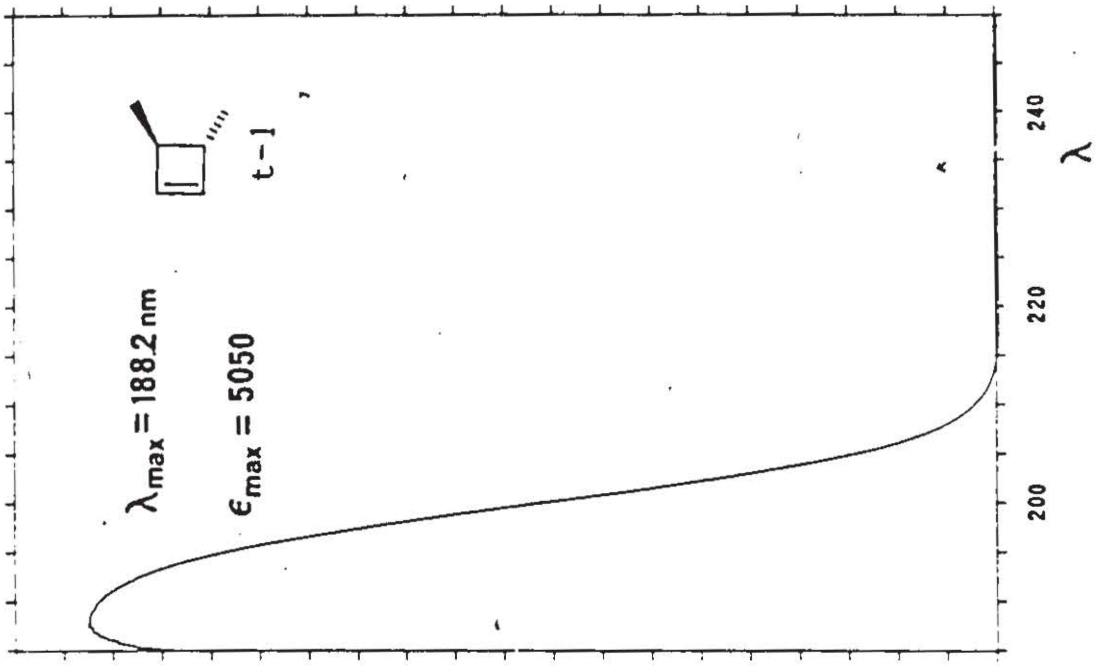
-from the photolysis of t-1:

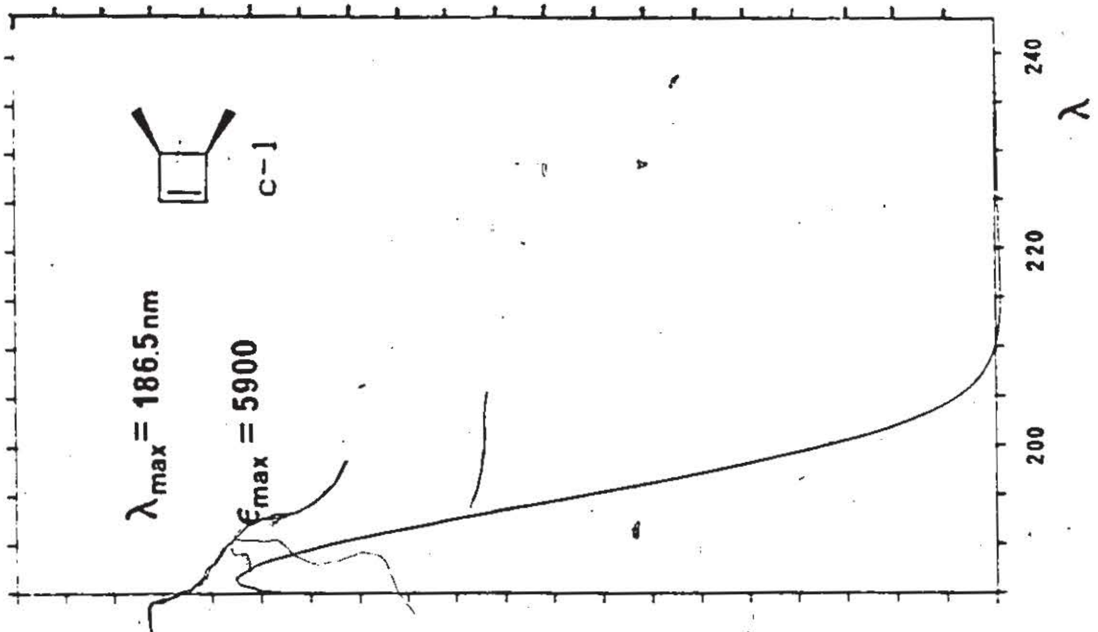


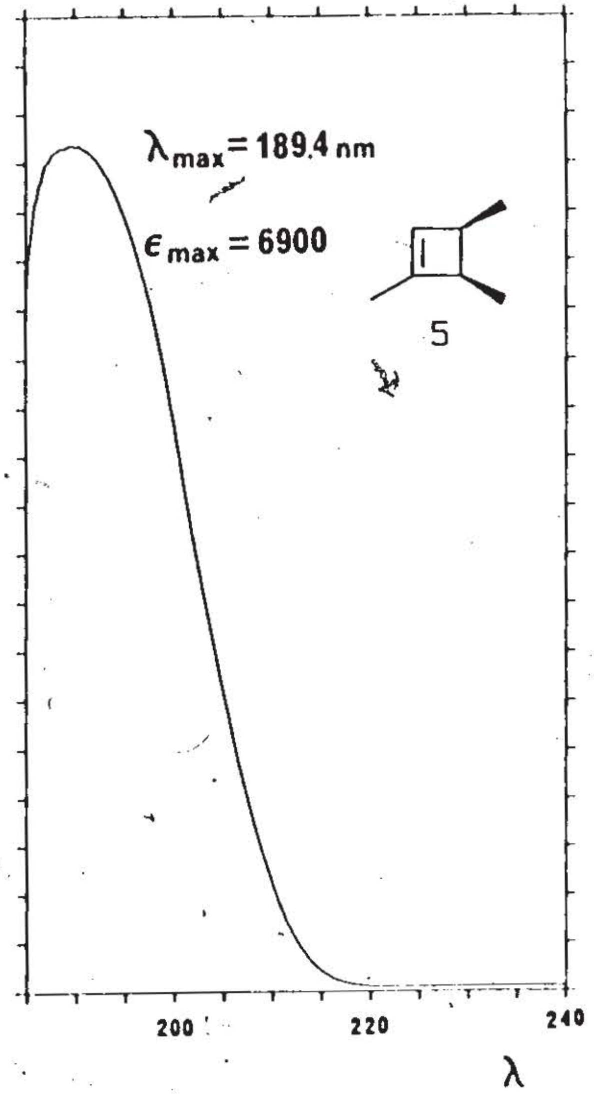
$$\frac{0.63\ B}{0.59\ (1 - B)} = 2.8 \qquad B = 0.72$$

APPENDIX B

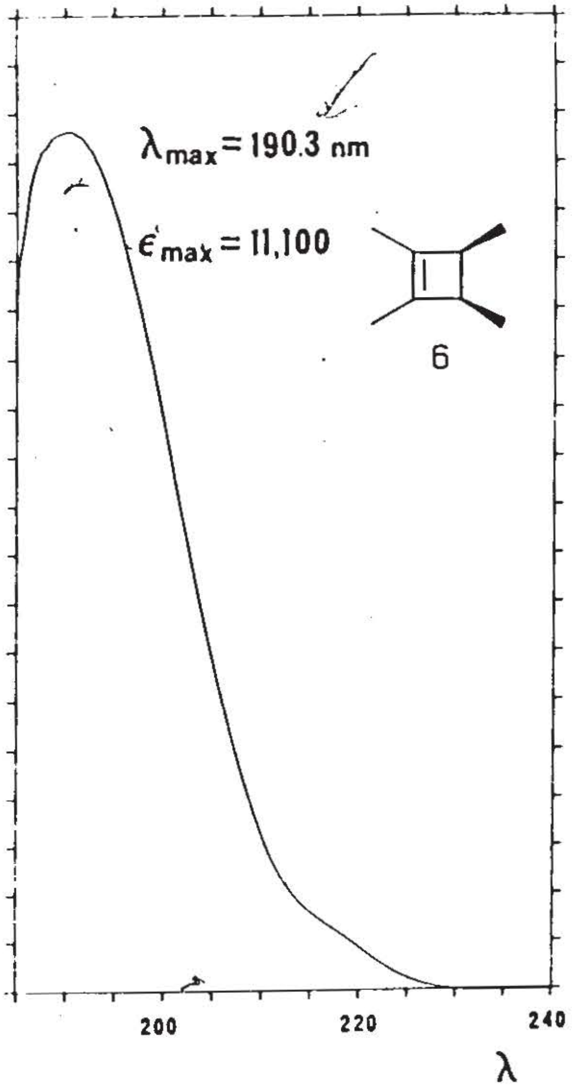
Ultraviolet Absorption Spectra of Cyclobutenes 1 - 6, 20, and 21.



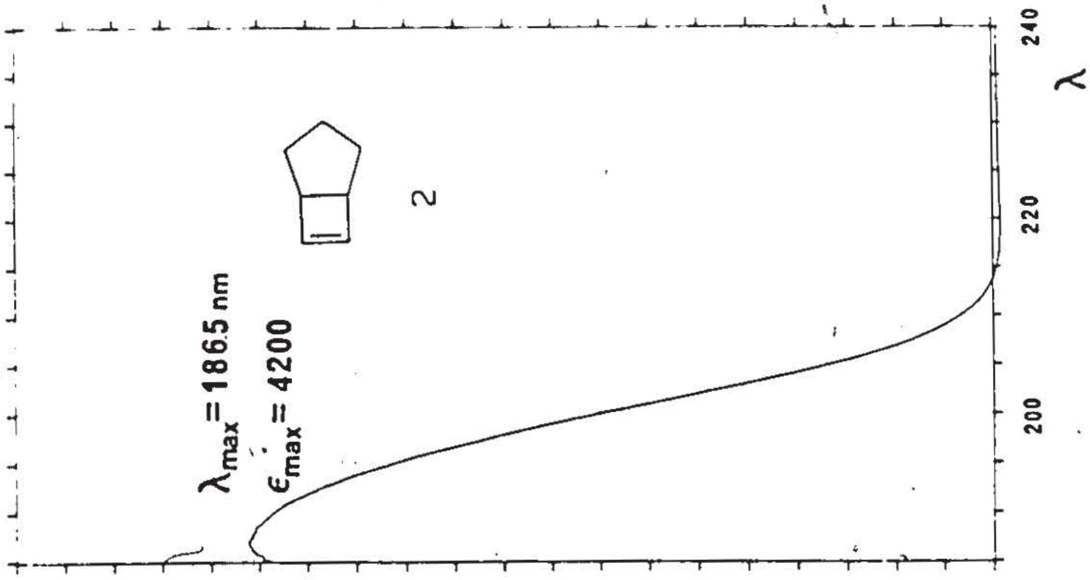


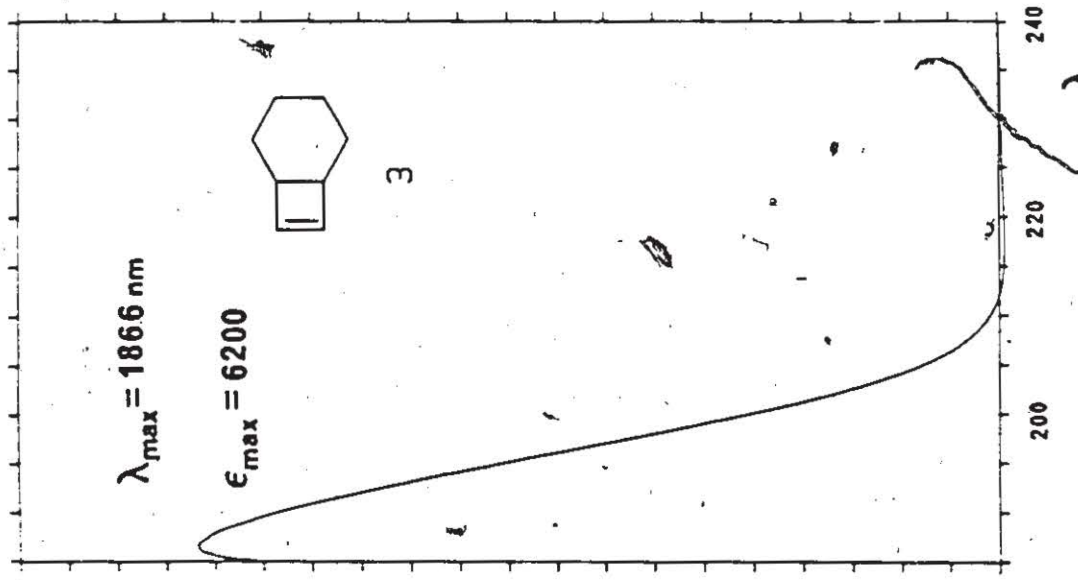


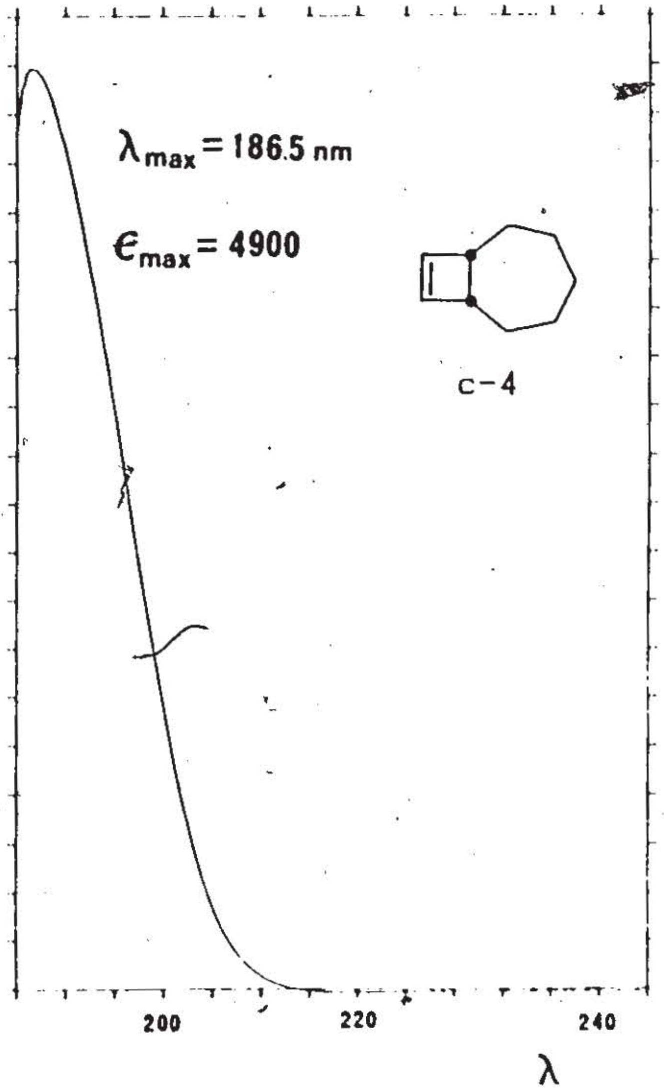
$\lambda_{max} = 189.4$ nm
$\epsilon_{max} = 6900$
5
200
220
240
λ

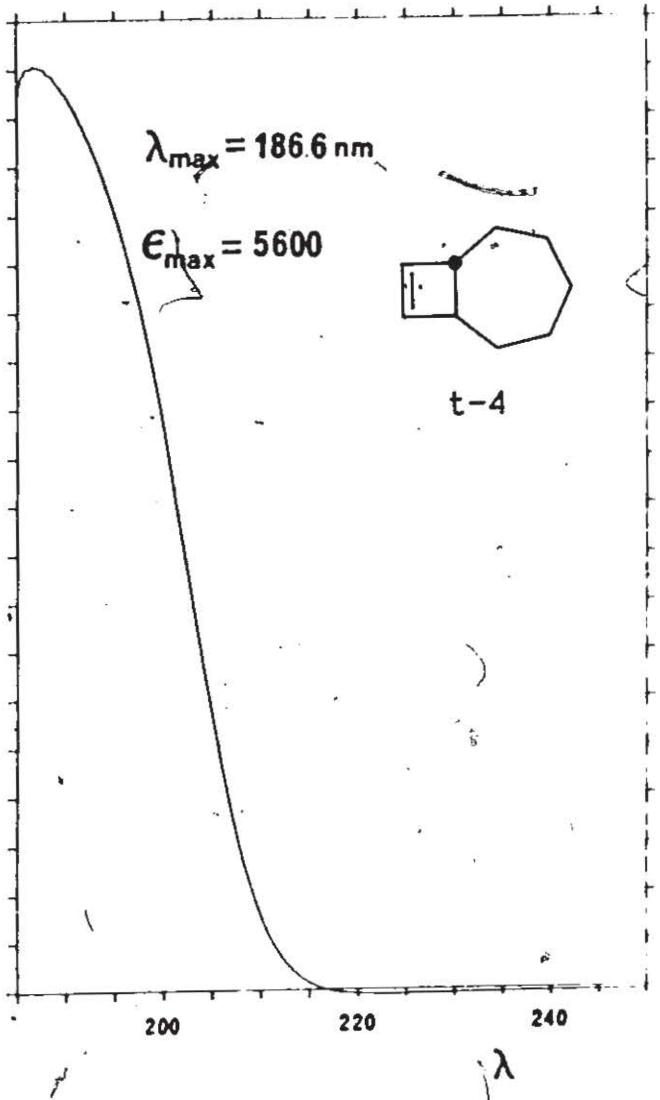


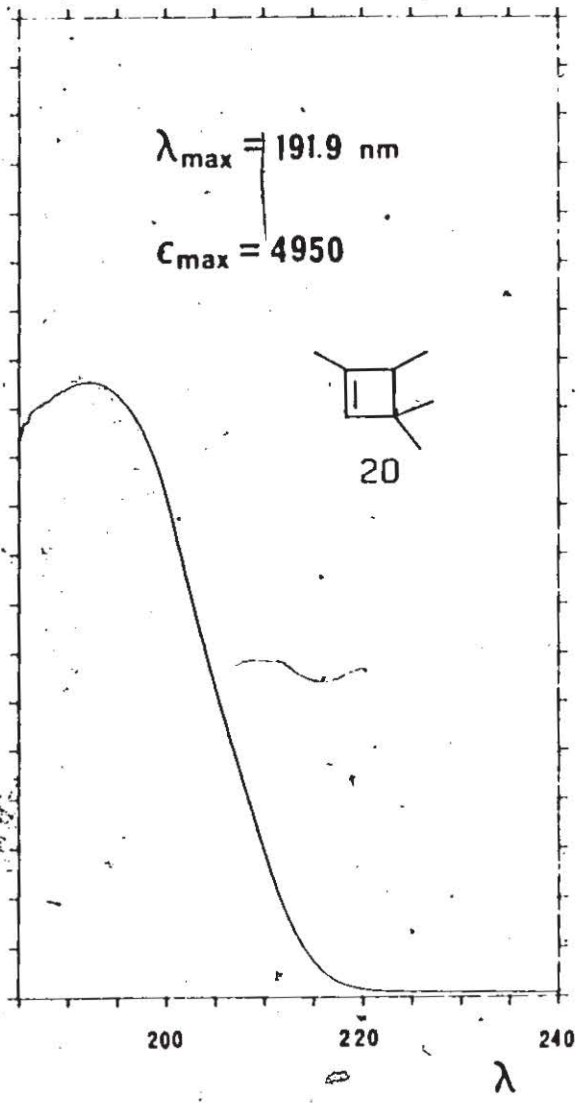
$\lambda_{max} = 190.3$ nm
$\epsilon_{max} = 11,100$
6
200
220
240
λ

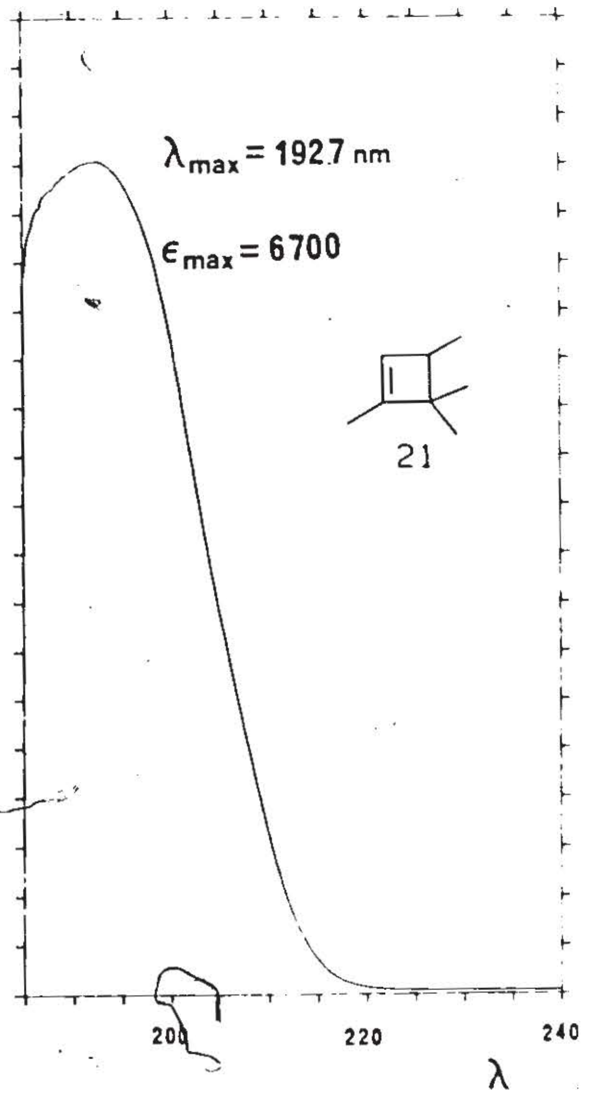

λ_{max} = 186.5 nm
ϵ_{max} = 4200
2
λ
200
220
240


λ_{max} = 186.6 nm
ϵ_{max} = 6200
3
λ
200
220
240

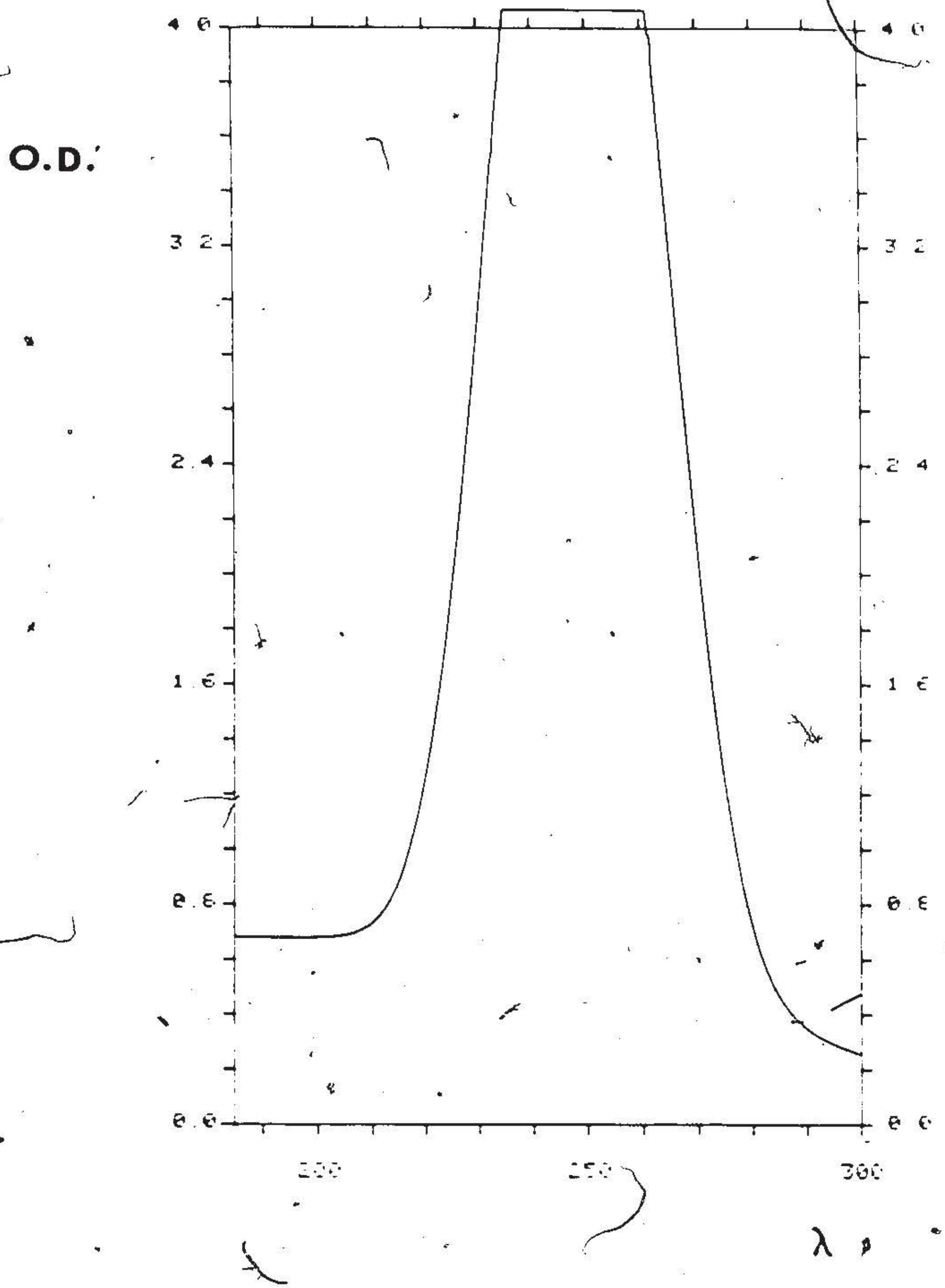

$\lambda_{max} = 186.5$ nm
$\epsilon_{max} = 4900$
c-4
200
220
240
λ


$\lambda_{max} = 186.6$ nm
$\epsilon_{max} = 5600$
t-4
200
220
240
λ


$\lambda_{max} = 191.9$ nm
$\epsilon_{max} = 4950$
20
200
220
240
λ


$\lambda_{max} = 192.7$ nm
$\epsilon_{max} = 6700$
21
200
220
240
λ

Ultraviolet Absorption Spectrum of LiF crystal (3 mm thickness) after exposure to ^{60}Co (1.7 Mrad).



REFERENCES

1. R.B.Woodward and R.Hoffmann, **J. Am. Chem. Soc.**, 87, 395, (1965).
2. R.B.Woodward and R.Hoffmann, **Acc. Chem. Res.**, 1, 17 (1968).
3. R.B. Woodward and R. Hoffmann, **Angew. Chem., Int. Ed. Engl.**, 8, 781 (1969).
4. H.C.Longuet-Higgins and G.W.Abrahamson, **J. Am. Chem. Soc.**, 87, 2045 (1965).
5. Elliot N. Marvel, "**Thermal Electrocyclic Reactions**", Academic Press, New York, 1980, Chapt.5, pp.124-213 and references cited therein.
6. W.G. Dauben and G.J. Fonken, **J. Am. Chem. Soc.**, 81, 4060, (1959).
7. O.L. Chapman, D.J. Pasto, G.W. Borden, A.A.J. Griswold, **J. Am. Chem. Soc.**, 84, 1220, (1962).
8. W.G. Dauben and A.A.J. Griswold, **J. Org. Chem.**, 27, 1910, (1962).
9. K.M. Schumate and G.J. Fonken, **J. Am. Chem. Soc.**, 88, 1073, (1966).
10. W.G. Dauben, R.G. Cargill, R.M. Coates, J. Saltiel, **J. Am. Chem. Soc.**, 88, 2742, (1966).
11. R. Srinivasan, **J. Am. Chem. Soc.**, 90, 4498, (1968).
12. S. Boue and R. Srinivasan, **J. Am. Chem. Soc.**, 92, 3226, (1970).
13. J. Saltiel, L. Metts, M. Wrighton, **J. Am. Chem. Soc.**, 92, 3227, (1970).
14. W.Th.A.M. Van der Lugt and L.J. Oosterhoff, **J. Am. Chem. Soc.**, 91, 6042, (1969).
15. D. Grimbert, G. Segal, A. Devaquet, **J. Am. Chem. Soc.**, 97, 6629, (1975).

16. T.L. Welsher, W.A. Seitz, B. Yurke, R.A. Gonzales, F.A. Matsen, **J. Am. Chem. Soc.**, <u>**99**</u>, 8389, (1977).

17. K. Morihashi, O. Kikuchi, K. Suzuki, **Chem. Phys. Lett.**, <u>**90**</u>, 346, (1982).

18. D. Morihashi and O. Kikuchi, **Theor. Chim. Acta.**, <u>**67**</u>, 293, (1985).

19. J. Saltiel and L.-S. Ng Lim, **J. Am. Chem. Soc.**, <u>**91**</u>, 5404, (1969).

20. Y. Inoue, M. Sakae, T. Hakushi, **Chem. Lett.**, 1495, (1983).

21. W. Adam, T. Oppenlander, G. Zang, **J. Am. Chem. Soc.**, <u>**107**</u>, 3921, (1985).

22. W. Kirmse, N.G. Rondan, K.N. Houk, **J. Am. Chem. Soc.**, <u>**106**</u>, 7989, (1984).

23. N.G. Rondan and K.N. Houk, **J. Am. Chem. Soc.**, <u>**107**</u>, 2099, (1985).

24. K. Rudolf, D.C. Spellmeyer, K.N. Houk, **J. Org. Chem.**, <u>**52**</u>, 3708, (1987).

25. J.I. Brauman and W.C. Archie, **J. Am. Chem. Soc.**, (1972), <u>**94**</u>, 4262.

26. R.E.K. Winter, **Tetrahedron Lett.**, 1207, (1965).

27. O.L. Chapman and D.J. Pasto, **J. Am. Chem. Soc.**, <u>**82**</u>, 3642, (1960).

28. R. Criegee, D. Seeback, R.E. Winter, B. Borretzen, H.-A. Brune, **Chem. Ber.**, <u>**98**</u>, 2339, (1965).

29. J.S. McConaghy, Jr. and J.J. Bloomfield, **Tetrahedron Lett.**, 3433, (1969).

30. J.J. Bloomfield, J.S. McConaghy, Jr., A.G. Hartmann, **Tetrahedron Lett.**, 2723, (1969).

31. K.M. Shumate, P.N. Neuman, G.J. Fonken, **J. Am. Chem. Soc.**, <u>**87**</u>, 3996, (1965).

32. L.M. Stephenson, Jr. and J.I. Brauman, **Accts. Chem. Res.**, 7, 65, (1974).

33. N.J. Turro, "**Modern Molecular Photochemistry**", Benjamin/Cummings Publishing Co., Menlo Park, Cal., 1978.

34. Y. Inoue, S. Hagiwara, Y. Daino, T. Hakushi, **J. Chem. Soc., Chem. Commun.**, 1307, (1985).

35. W.J. Nebe and C.J. Fonken, **J. Am. Chem. Soc.**, 91, 1249, (1969).

36. R.S.H. Liu, **J. Am. Chem. Soc.**, 89, 112, (1967).

37. W.G. Dauben, R.G. Williams, R.D. McKelvey, **J. Am. Chem. Soc.**, 95, 3932, (1973).

38. **MM2** calculations reveal a dihedral angle of 71 about the C2-C3 bond in cis,cis-1,3-cyclooctadiene.

39. M.E. Squillacote, R.S. Sheridan, O.L. Chapman, F.A.L. Anet, **J. Am. Chem. Soc.**, 101, 3657, (1979).

40. R. Srinivasan, **J. Am. Chem. Soc.**, 84, 4141, (1962).

41. D.H. Aue and R.N. Reynolds, **J. Am. Chem. Soc.**, 95, 2027, (1973).

42. J. Saltiel, J. D'Agostino, E.D. Megarity, L. Metts, K.R. Neuberger, M. Wrighton, O.C. Zafiriou, **Org. Photochem.**, 3, 1, (1973) and references cited therein.

43. J. Saltiel and J.L. Charlton in "**Rearrangements in Ground and Excited States**", Vol. 3, P. de Mayo, Ed., Academic Press, New York, 1980, p.25 and references cited therein.

44. C.D. de Boer and R.H. Schlessinger, **J. Am. Chem. Soc.**, 90, 803, (1968).

45. G. Kaup and M. Stark, **Chem. Ber.**, 111, 3608, (1978).

46. M. Sakuragi and M. Hasegawa, **Chem. Lett.**, 29, (1974).

47. G.A. Doorakian, H.H. Freedman, **J. Am. Chem. Soc.**, (1968), **90**, 5310.

48. Y. Kawamura, M. Thurnauer, G.B. Schuster, **Tetrahedron**, **42**, 6195, (1986).

49. G. Quinkert, M. Finke, J. Palmowski, **Mol. Photochem.**, **1**, 433, (1969).

50. G. Quinkert, K. Opitz, W.-W. Wiersdorff, **Justus Liebigs. Ann. Chem.**, **693**, 44, (1966).

51. G. Quinkert, W.-W.Wiersdorff, M. Finke, K. Opitz, F.-G. von der Haar, **Chem. Ber.**, **101**, 2302, (1968).

52. R.V. Carr, B. Kim, J.K. McVey, N.C. Yang, W. Gerhartz, J. Michl, **Chem. Phys. Lett.**, **39**, 57, (1976).

53. N.C. Yang, R.V. Carr, E. Li, J.K. McVey, S.A. Rice, **J. Am. Chem. Soc.**, **96**, 2297, (1974).

54. R. Srinivasan and K.A. Hill, **J. Am. Chem. Soc.**, **88**, 3765, (1966).

55. R. Srinivasan, **J. Am. Chem. Soc.**, **91**, 7557, (1969).

56. J. Saltiel, G.R. Marchand, R. Bonneau, **J. Photochem.**, **28**, 367, (1985).

57. W.J. Leigh and R. Srinivasan, **J. Am. Chem. Soc.**, **105**, 514, (1983).

58. P.J. Kropp, **Org. Photochem.**, **4**, 1, (1979) and references cited therein.

59. W.J. Potts, Jr., **J. Chem. Phys.**, **23**, 65, (1955) and references cited therein.

60. A.J. Merer and R.S. Mulliken, **Chem. Rev.**, **69**, 639, (1969).

61. S. Lipsky et al in "**Chemical Spectroscopy and Photochemistry in the Vacuum-Ultraviolet**", C. Sandorfy, P.J. Ausloos, M.B. Robin, eds., Reidel, Boston, 1974.

62. F. Hirayama and S. Lipsky, **J. Chem. Phys.**, **62**, 576, (1975).

63. M.B. Robin and N.A. Kuebler, **J. Mol. Spectrosc.**, 33, 274, (1970).

64. M.B. Robin, "**Higher Excited States of Polyatomic Molecules**", Academic Press, New York, 1975; Vol. 2, Chapt. 4.

65. Y. Inoue, T. Mukai, T. Hakushi, **Chem. Lett.**, 1665, (1983).

66. H.G. Fravel, Jr. and P.J. Kropp, **J. Org. Chem.**, 40, 2434, (1975).

67. R. Srinivasan and K.H. Brown, **J. Am. Chem. Soc.**, 100, 4602, (1978).

68. Y. Inoue, T. Mukai, T. Hakushi, **Chem. Lett.**, 1045, (1982).

69. W. Adam and T. Oppenlander, **Angew. Chem. Int. Ed. Engl.**, 25, 661, (1986) and references cited therein.

70. W.J. Leigh and R. Srinivasan, **Accts. Chem. Res.**, 20, 107, (1987) and references cited therein.

71. M.G. Steinmetz, **Org. Photochem.**, 8, 67, (1987) and references cited therein.

72. W. Adam and T. Oppenlander, **J. Am. Chem. Soc.**, 107, 3924, (1985).

73. W.G. Dauben, E.L. McInnis, D.M. Michno in "**Rearrangements in Ground and Excited States**", Paul de Mayo, ed., Academic Press, New York, 1980, Essay 15.

74. A general procedure for the oxidative bis-decarboxylation of diacids may be found by R.A. Sheldon and J.K. Kochi, **Organic Reactions**, 19, 279, (1972).

75. P. Radlick, R. Klem, S. Spurlock, J.J. Sims, E.E. van Tamelen, T. Whitesides, **Tet. Lett.**, 5117 (1968).

76. J.L. Weeks, S. Gordon, G.M.A.C. Meaburn, **Nature**, 191, 1186,(1961).

77. R.A. Holroyd and T.E. Pierce, **J. Phys. Chem.**, 68, 1392, (1964).

78. R. Srinivasan and K.H. Brown, **J. Am. Chem. Soc.**, 100, 2589,(1978).

79. H.-P. Schuchmann, C. von Sonntag, R. Srinivasan, **J. Photochem.**, 15, 159, (1981).

80. J.C. Scaiano and P.J. Wagner, **J. Am. Chem. Soc.**, 106, 4626, (1984).

81. S. Bank, C.A. Rowe, Jr., A. Schriesheim, L.A. Naslund, **J. Org. Chem.**, 33, 221, (1968).

82. Osram Corporation Technical Bulletin for HNS 10W/U oz low pressure mercury lamp. Osram Corp., Jeanne Dr., PO Box 7062, Newburgh, New York, 12550.

83. E.F. Ullman, **Acc. Chem. Res.**, 1, 353, (1968).

84. J. Saltiel, L. Metts, M. Wrighton, **J. Am. Chem. Soc.**, 91, 5684, (1969).

85. H.L. Hyndman, B.M. Monroe, G.S. Hammond, **J. Am. Chem. Soc.**, 91, 2852, (1969).

86. R. Srinivasan, **J. Am. Chem. Soc.**, 90, 4498, (1968).

87. R.M. Weiss and A. Warshel, **J. Am. Chem. Soc.**, 101, 6131, (1979).

88. A.G. Doukas, M.R. Junnarkar, R.R. Alfano, R.H. Callender, T. Kakitani, B. Honig, **Proc. Natl. Acad. Sci. USA**, 81, 4790, (1984).

89. F.D. Lewis, D.K. Howard, S.V. Barancyk, J.D. Oxman, **J. Am. Chem. Soc.**, 108, 3016, (1986).

90. J.M. Jasinski, J.K. Frisoli, C.B. Moore, **J. Chem. Phys.**, 79, 1312, (1983).

91. J.P. Cheswick, **J. Chem. Phys.**, 45, 3934, (1966).

92. N. Nakashima, N. Shimo, N. Ikeda, K. Yoshihara, **J. Chem. Phys.**, 81, 3738, (1984).

93. P.J. Robinson and K.A. Holbrook in "**Unimolecular Reactions**", Wiley-Interscience, London, 1972.

94. N.L. Bauld, D.J. Bellville, R. Pabon, R. Chelsky, G. Green, **J. Am. Chem. Soc.**, 105, 2378, (1983).

95. M.L. Gross and D.H. Russell, **J. Am. Chem. Soc.**, 101, 2082, (1979).

96. C. Dass, T.M. Sack, M.L. Gross, **J. Am. Chem. Soc.**, 106, 5780, (1984).

97. C. Dass and M.L. Gross, **J. Am. Chem. Soc.**, 105, 5724, (1983).

98. R.A.W. Johnstone and S.D. Ward, **J. Chem. Soc. C**, 1805, (1968).

99. M.J. Bishop and I. Fleming, **J. Chem. Soc. C**, 1712, (1969).

100. T. Miyashi, K. Wakamatsu, T. Akiya, K. Kikuchi, T. Makai, **J. Am. Chem. Soc.**, 109, 5270, (1987).

101. N.J. Turro, V. Ramamurthy, W. Cherry, W. Farneth, **Chem. Rev.**, 78, 125, (1978).

102. W. Kirmse and K.-H. Pook, **Chem. Ber.**, 98, 4022, (1965).

103. AMPAC, Austin Method 1 Package (QCPE 506). Dewar Research Group and J.P. Stewart. QCPE Bull. 6, 2, (1986).

104. P.G. Gassman, T.J. Atkins and F.J. Williams, **J. Am. Chem. Soc.**, 93, 1821 (1971).

105. D.J. Pasto and C.R. Johnson, **Laboratory Text for Organic Chemistry**, Prentice Hall, Inc., New Jersey, 1979, pp. 205-206.

106. W. Reeve and D.M. Reichel, **J. Org. Chem.**, 37, 68, (1972).

107. N.H. Werstiuk and G. Timmins, **Can. J. Chem.**, submitted for publication.

108. J.A. Smith, H. Shechter, J. Bayless and L. Friedman, **J. Am. Chem. Soc.**, 87, 658, (1965).

109. W. Kirmse and G.Wachtershauser, **Tetrahedron**, 22, 63, (1966).

110. A. Guarino and A.P. Wolf, **Tetrahedron Lett.**, 655, (1969).

110. A. Guarino and A.P. Wolf, **Tetrahedron Lett.**, 655, (1969).

111. W. Kirmse, "**Carbene Chemistry**", Academic Press, New York, 1971, pp. 473-475 and references cited therein.

112. W.J. Hendrick, M. Jones Jr., R.H. Levin and M.B. Sohn in "**Carbenes**", Vol.1, M. Jones Jr. and R.A. Moss, eds., Wiley, New York, 1973. pp. 37-43 and references cited therein..

113. S.S. Olin and R.M. Venable, **J. Chem. Soc., Chem. Commun.**, 104, 273, (1974).

114. C.L. Bird, H.M. Frey and I.D.R. Stevens, **J. Chem. Soc., Chem. Commun.**, 707, (1967).

115. I.D.R. Stevens, H.M. Frey, and C.L. Bird, **Angew. Chem. Int. Ed. Engl.**, 7, 646, (1968).

116. L. Friedman and H. Shechter, **J. Am. Chem. Soc.**, 82, 1002, (1960).

117. U.H. Brinker and G. Schenker, **J. Chem. Soc., Chem. Commun.**, 679, (1982).

118. A.S. Kende and E.E.Riecke, **J. Chem. Soc., Chem. Commun.**, 383, (1974).

119. J. Meinwald, J.W. Wheeler, A.A. Nimetz and J.S. Liu, **J. Org. Chem.**, 30, 1038, 1965.

120. K.B. Wiberg, G.J. Burgmaier and P. Warner, **J. Am. Chem. Soc.**, 93, 246, (1971).

121. J.R. Chapman, **Tetrahedron Lett.**, 113, (1969).

122. B. Singh, **J. Org. Chem.**, 31, 181, (1966).

123. E. Schaumann and R. Ketcham, **Angew. Chem. Int. Ed. Engl.**, 21, 225, (1982).

124. W. Adam and T. Oppenlander, **Angew. Chem. Int. Ed. Engl.**, **23**, 641, (1984).

125. H.D. Roth and A.A. Lamola, **J. Am. Chem. Soc.**, **94**, 1013, (1972).

126. G. Kaup and M. Stark, **Chem. Ber.**, **110**, 3084, (1977).

127. R.R. Gallucci and M. Jones Jr., **J. Am. Chem. Soc.**, **98**, 7704 (1976).

128. D. Griller, A.S. Nazran, J.C. Scaiano, **Tetrahedron**, **41**, 1525, (1985).

129. M.V. Evans and R.C.J. Lord, **J. Am. Chem. Soc.**, **83**, 3411, (1961).

130. R. Criegee, U. Zirngibl, H. Furrer, D. Seebach, G. Freund, **Chem. Ber.**, **97**, 2942, (1964).

131. **The Aldrich Library of NMR Spectra, 1ST Edition**, C.J. Pouchert and J.R. Campbell Eds., Aldrich Chemical Co., Inc., Milwaukee, Wis., 1974, p27.

132. A.C. Cope and C.L. Baumgardner, **J. Am. Chem. Soc.**, **78**, 2812, (1956).

133. R. Isaksson, J. Roschester, J. Sandstrom, L.-G. Wistrand, **J. Am. Chem. Soc.**, **107**, 4074, (1985).

134. S. Arora and P. Binger, **Synthesis**, 801, (1974).

135. L. Skattebol and S. Solomon, **Org. Synth.**, **49**, 35, (1969).

136. T.J. Stierman and R.P. Johnson, **J. Am. Chem. Soc.**, **107**, 3971, (1985).