

To my father

THE PHOTOCHEMISTRY OF TRIFLUOROMETHYLALKENES

**THE PHOTOCHEMISTRY OF 2-TRIFLUOROMETHYLNORBORNENE
AND 7-TRIFLUOROMETHYLBICYCLO[4.2.0]OCT-7-ENE.**

**DEFINITION OF π,π^* AND $\pi,R(3S)$ REACTIVITY IN THE
PHOTOCHEMISTRY OF SUBSTITUTED NORBORNENES AND
ALKYLCYCLOBUTENES.**

By

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7-trifluoromethylbicyclo[4.2.0]oct-7-ene. Definition of π, π^* and $\pi, R(3s)$
reactivity in the photochemistry of substituted norbornenes and alkylcyclobutenes.

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ABSTRACT

2-Trifluoromethylnorbornene has been synthesized from norbornene. The UV photoelectron spectra and optical UV absorption spectra of norbornene, 2-methylnorbornene and 2-trifluoromethylnorbornene have been studied, and indicate that the π,π^* state is the lowest excited singlet state. Direct photolysis of 2-trifluoromethylnorbornene with 193 nm light yields 1-trifluoromethyl-2-norcarene (in 90% yield) by formal [1,3]-sigmatropic rearrangement. Chlorobenzene-sensitized photolysis affords the photoreduction products, exo- and endo-2-trifluoromethylnorbornane, decane isomers, and several products of higher molecular weight.

By comparing the photochemistry of 2-trifluoromethylnorbornene to those previously reported for norbornene and 2-cyanonorbornene as well as on the basis of spectroscopic evidence, it is proposed that the π,π^* state is the lowest energy excited singlet state in 2-trifluoromethylnorbornene. Trifluoromethyl substitution has the effect of significantly raising the energy of the $\pi,R(3s)$ Rydberg state in simple alkenes without altering the high energy or the localized character of the π,π^* state.

7-Trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**) was synthesized from bicyclo[4.2.0]oct-7-ene (**84**). By comparing the UV photoelectron spectroscopy and optical spectra of **86**, **84**, **97**, it is concluded that the π,π^* state is the lowest excited singlet state in **86**. Direct photolysis with 193 nm light yields three diene isomers derived from formal electrocyclic π,π^* ring opening, and cyclohexene

derived from fragmentation. Comparison of spectroscopic and photochemical results for this compound to those of bicyclo[4.2.0]oct-7-ene (**84**) and 7-methylbicyclo[4.2.0]oct-7-ene (**97**) indicate that ring-opening is non stereospecific and arises largely from the π,π^* singlet state. Fragmentation arises largely from the Rydberg excited state.

CHAPTER I

INTRODUCTION

1. Spectroscopy of alkenes and conjugated alkenes

The photochemistry of simple alkenes in solution is often complex. Direct irradiation of aliphatic olefins in solution results in photolysis products which are consistent with the involvement of two singlet excited states: the π,π^* (valence) state and the $\pi,R(3s)$ Rydberg state. Gas phase UV absorption spectra verify that these two states are of similar energy in simple alkenes¹; the gas phase spectrum of most simple alkenes shows two overlapping bands. The more intense band at shorter wavelengths corresponds to the π,π^* state. The less intense band at longer wavelengths corresponds to the $\pi,R(3s)$ state (Figure 1).² The π,π^* state has a λ_{\max} in the region of 170 nm -190 nm and an extinction coefficient of approximately 10,000. The $\pi,R(3s)$ Rydberg state has an extinction coefficient of 500-1000. M. B. Robin¹ has summarized the spectroscopy of ethylene and methylethylenes. Increasing methyl substitution at the C=C bond in alkylethylenes results in decreases in the energy of the $\pi,R(3s)$ Rydberg state which parallel those in the π -ionization potentials. Moreover, as ethylene is increasingly alkylated, the $\pi,R(3s)$ term value (the difference between the spectral band maximum and the lowest vertical π -ionization potential) decreases from 27410 cm^{-1} and will approach 21000 cm^{-1} while the π,π^* term value decreases from 23050 cm^{-1} to 14440 cm^{-1} .³ Thus, the decrease of the π,π^* term value is larger than that of the $\pi,R(3s)$.

Weak fluorescence has been observed from several simple alkenes upon excitation at 184.9 nm in the vapor and liquid phases.⁴ Fluorescence quantum

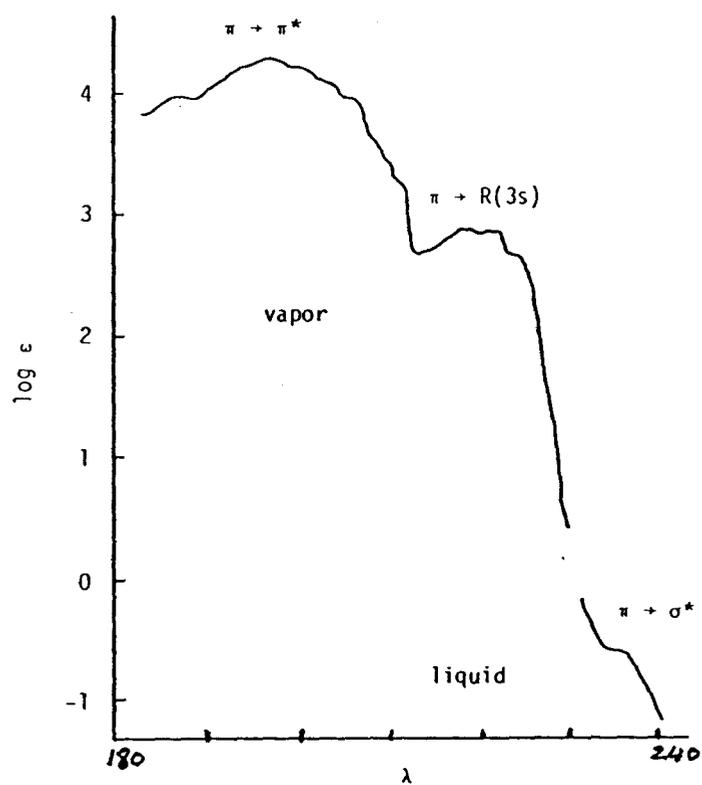


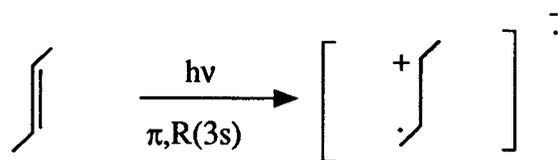
Figure1 Generalized alkene absorption spectrum²

yields ϕ_f and wavelength maxima λ_f of the fluorescence spectral distributions have been determined for these compounds by Hirayama and Lipsky. The result is that an increase in ϕ_f can be correlated with an increasing number of alkyl substituents on the carbons of the double bond. With the substitution of a fourth alkyl group to form tetramethylethylene, an even more remarkable increase of fluorescence intensity was observed.⁴ These results indicate that alkene fluorescence originates from the $\pi, R(3s)$ Rydberg state. The spectral position of Rydberg state absorption (λ_R) shifts smoothly to the red with increasing number of alkyl substituents, whereas that of the π, π^* state (λ_V) correlates less well in this regard.⁴ Therefore, the π, π^* state energy is altered only slightly (though in the same way). The fluorescence excitation spectra of di-, tri-, and tetraalkylethylenes support the assignment of the emissive state as the $\pi, R(3s)$ excited state.⁵

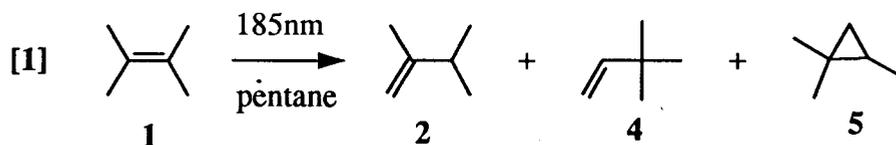
In contrast to the situation with simple alkenes, conjugated alkenes such as 1,3-butadiene have the π, π^* state as the lowest excited singlet state. This is clearly shown by the crystal spectra of butadiene.⁴ The energy of the π, π^* state in dienes depends on conformation. In a s-cis diene, the π MO-energies differ from those of the s-trans conformer due to interactions between C_1 and C_4 , possible nonplanarity, and ring-strain effects.⁴ S-cis cyclic dienes have π, π^* absorption bands at lower frequencies than s-trans cyclic dienes.⁶

2. Photochemistry of the $\pi, R(3s)$ Rydberg state

Excitation to the Rydberg state involves promotion of an electron from the valence π -molecular orbital to the 3s orbital. Because the 3s orbital is quite diffuse and is approximately of molecular size for small alkenes such as tetramethylethylene, the Rydberg state can be considered to have radical cation character at the C=C double bond.⁷ An electron has been removed from the core



but is not completely separated from the influence of the core. The correlation between $\pi, R(3s)$ state energy and π -ionization potential is apparent from this simple model. The $\pi, R(3s)$ Rydberg state is thought to lead to the products of carbene intermediates derived from [1,2]-hydrogen or [1,2]-alkyl migration, and in alcohol solvents to the products of nucleophilic addition to the C=C bond.² Products attributable to [1,3]-hydrogen or [1,3]-alkyl migration are also observed in alkene photochemistry.^{1-2,9-10} These products may be formed from either

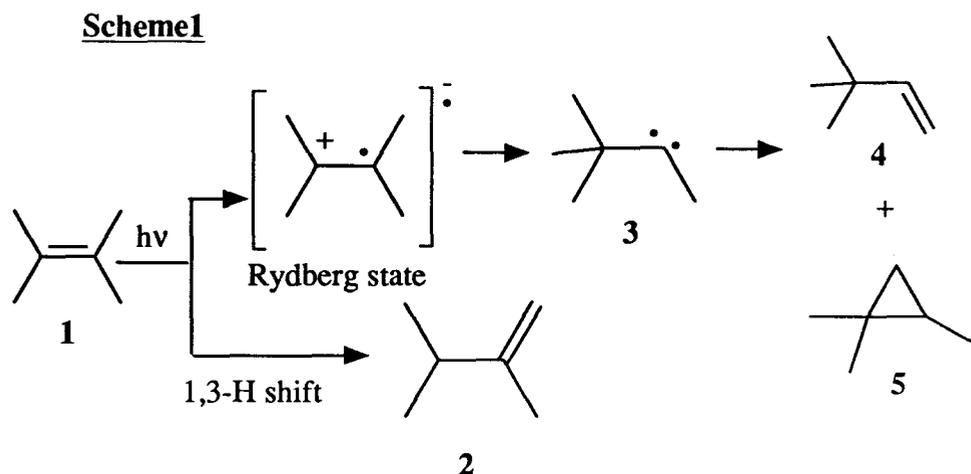


concerted or stepwise pathways involving carbene intermediates, and arise from either the π, π^* or $\pi, R(3s)$ state. As a specific example, the photochemistry of 2,3-dimethyl-2-butene is illustrated in Equation 1.

2.1 Carbene intermediates

2.1.1 Acyclic alkenes

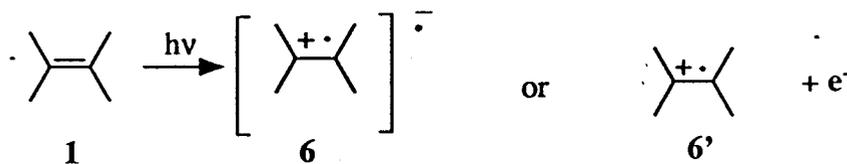
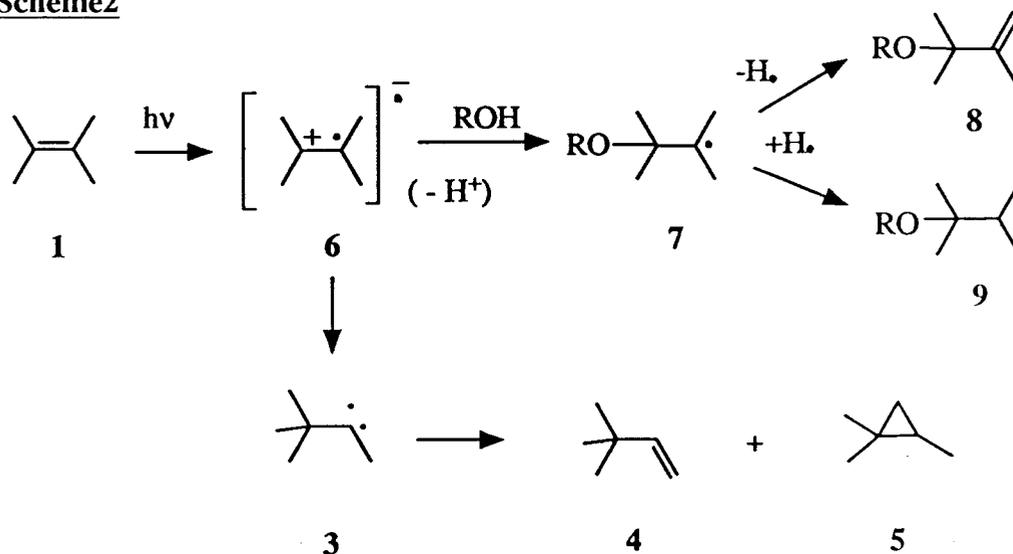
Y. Inoue and co-workers have studied the photochemistry of 2,3-dimethyl-2-butene (**1**) in solution at 185 nm, 214 nm, and 229 nm (Eqn.1).⁵ The mechanisms proposed for formation of the three observed products are shown in Scheme 1. The combined yield of products **4** and **5**, which are thought to derive from carbene **3**, increases with increasing excitation wavelength. In addition, the relative fluorescence quantum yield correlates well with the relative product ratio $(4+5)/2$. This coincidence reinforces the reaction mechanism



proposed by Kropp¹² and Inoue¹³ that the carbene **3** arises from the $\pi, R(3s)$ Rydberg state.

Kropp has reported that direct irradiation of 2,3-dimethyl-2-butene in hydroxylic media leads to the formation of a mixture of saturated and unsaturated ethers.¹²⁻¹³ By contrast, in nonhydroxylic solvents such as ether, octane, or pentane, rearrangement to a 1.03:1 mixture of the 1-butene(**4**) and the cyclopropane (**5**) occurs. The isomer 2,3-dimethyl-1-butene is formed in both hydroxylic and nonhydroxylic media. Moreover, in alcoholic solvents of low nucleophilicity substantial amounts of **4** and **5** are formed in competition with the ethers as shown in Scheme 2. The ratio $(7+8+9):(4+5)$ decreases in the order methanol > ethanol > 1-propanol > 1-butanol. The formation of ethers has been interpreted in term of nucleophilic trapping of the $\pi, R(3s)$ Rydberg excited state. Hydrogen atoms could be formed by the reaction of the ejected electron and the solvent as shown in Scheme 3. Nucleophilic trapping of the first Rydberg excited state, represented by **6**, followed by loss of the excited electron to the solvent would afford the same radical intermediate **7** as obtained by nucleophilic trapping of the radical cation **6'**.¹³ However, a radical cation intermediate is not

Scheme 2

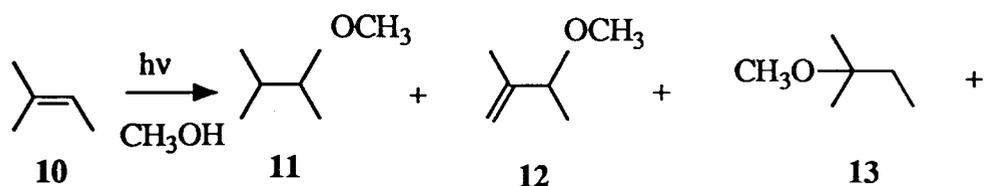
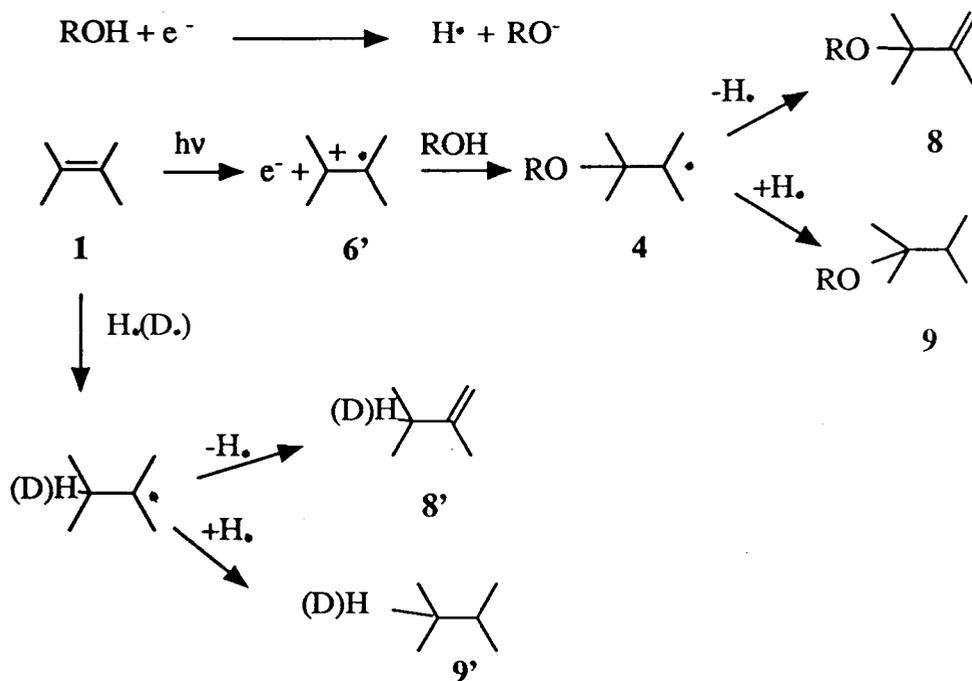


consistent with the observation of reaction at 253.7 nm. Appropriate control studies showed that none of the photoproducts **2**, **4** and **5** serves as a precursor to the ethers **8** and **9** in methanol ($R = \text{CH}_3$) as shown in Equation 1.

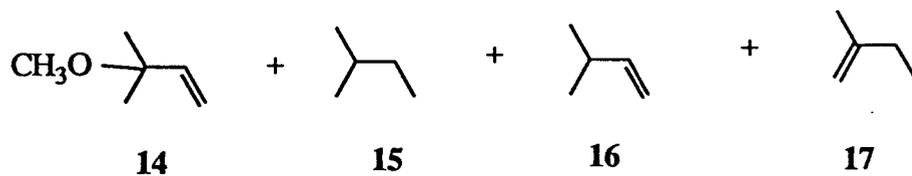
Upon direct irradiation in methanol, tri-alkyl substituted alkene **10** undergoes much less efficient reaction than tetra-alkyl substituted alkene **1** does under similar conditions (Equation 2). Further support for the intermediacy of carbenes has been provided by Kropp, who compared the product mixtures from photolysis of **1** and **10** with those obtained when the postulated carbenes were generated independently from the corresponding tosylhydrazones.

2.1.2 Cyclic alkenes

Carbene or carbene-like intermediates have also been proposed to be

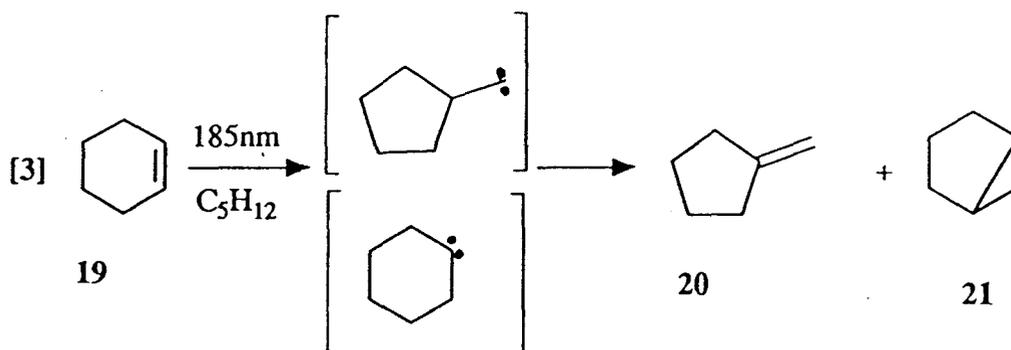
Scheme3

[2]

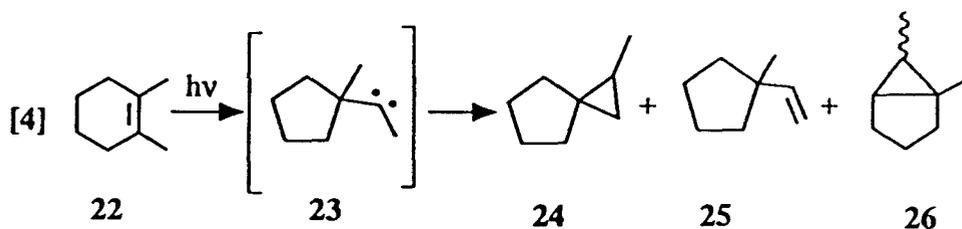


involved in the photochemistry of cyclohexene.^{14,15} Irradiation of cyclohexene

(19) in pentane at 185nm leads to methylenecyclopentane (20) and bicyclo [3.1.0]

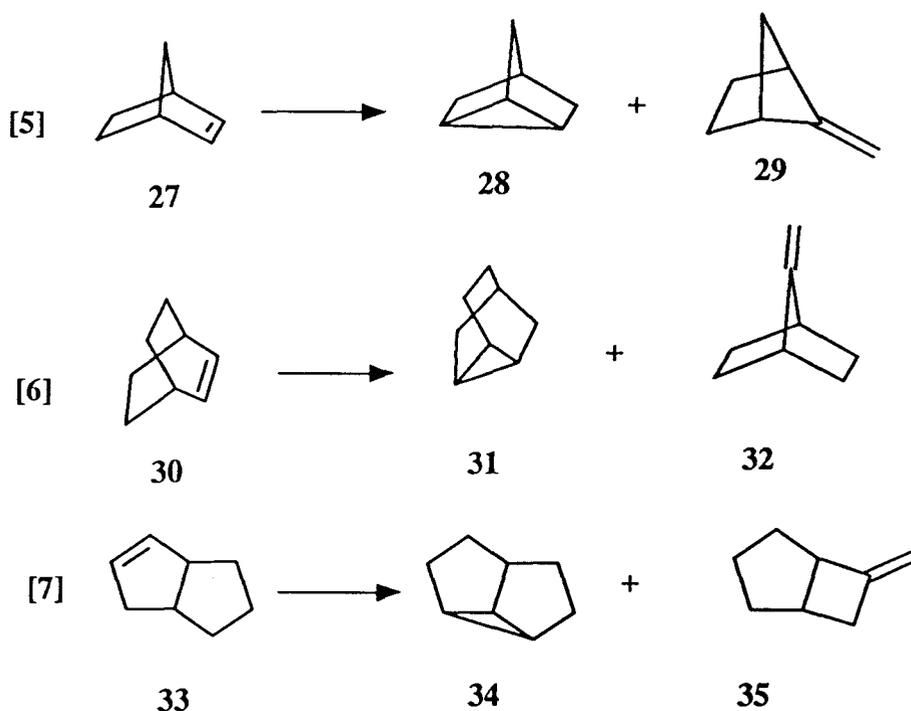


hexane (21). These products suggest the formation of cyclopentylmethylene and cyclohexanylidene, which derive from 19 via [1,2]-alkyl and [1,2]-hydrogen migration respectively (Eqn.3). From deuterium labelling studies of 3,3,6,6-tetradeuterocyclohexene (19-d₄) at 185 nm in pentane solution, Srinivasan and Brown showed that the ratio of cyclopentylmethylene and cyclohexanylidene was 5:1. The photochemistry of 1,2-dimethylcyclohexene (22; Eqn.4) is slightly different from that of 19 since the formation of a



methylene cyclopentane is blocked in the corresponding exocyclic carbene 23.

The direct photolysis of bicyclic olefins 27, 30, and 33 at 185nm gave the products shown in Equations 5-7. It was proposed that the saturated products 28, 31 and 34 are produced from a carbene which is formed by initial migration of a C-H bond, while the unsaturated products 29, 32 and 35 are produced from a carbene which is formed by initial migration of a C-C bond as shown in scheme



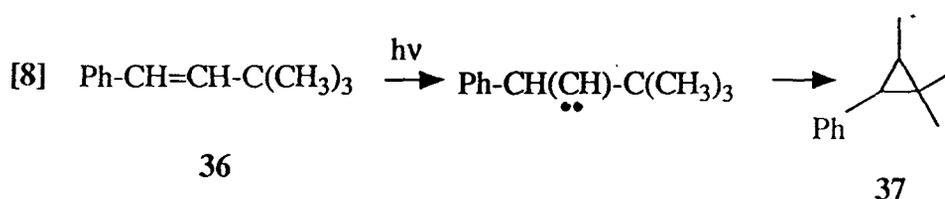
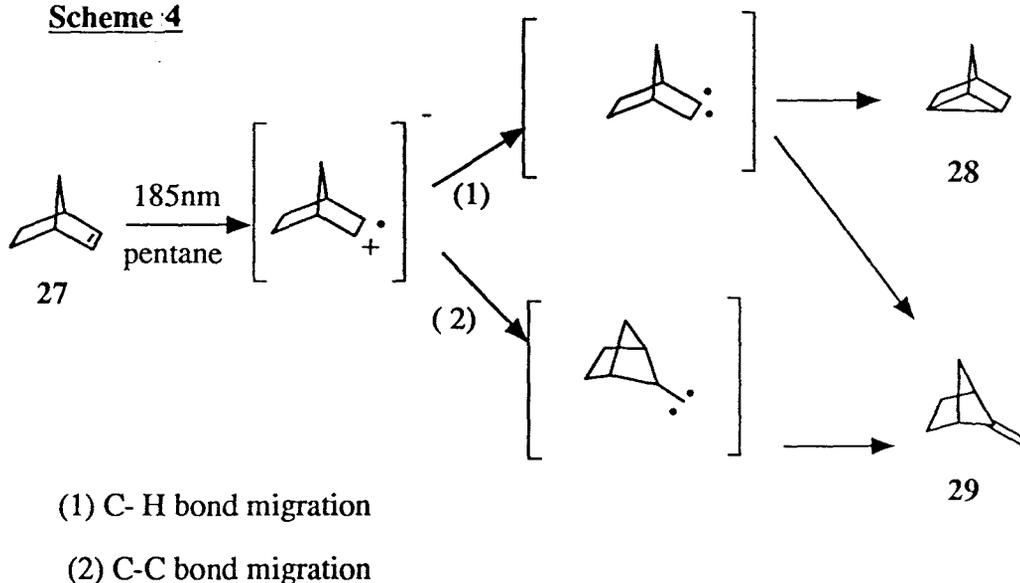
Gas phase UV absorption^{12,1} and fluorescence emission spectroscopies show that the $\pi, R(3s)$ Rydberg state, which leads to carbene-derived products in simple alkenes, is lower in energy than the π, π^* state in each of these cases. It is interesting that [1,2]-alkyl migration leading to ring contraction predominates over migration of other alkyl substituents in the photochemistry of cyclic olefins.^{2,17}

2.2 Reaction involving hydrogen and alkyl migration

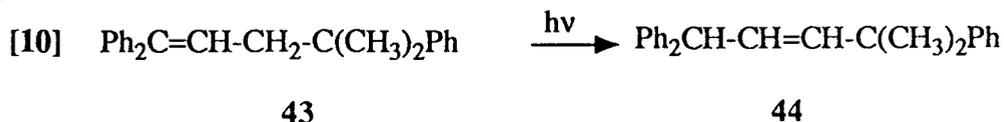
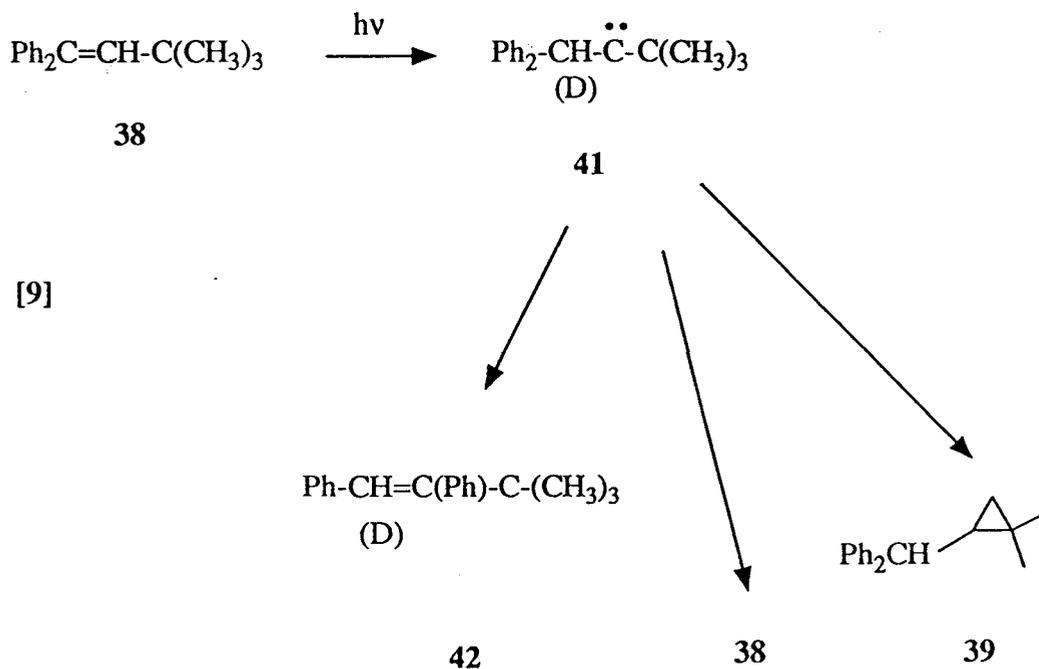
The products of carbene intermediates, obtained from direct photolysis of tetra-substituted olefins in solution, are thought to arise from the $\pi, R(3s)$ Rydberg state. It is known that tetra-substituted olefins as well as some tri- and di-substituted olefins also undergo [1,2]-hydrogen, [1,2]-alkyl, [1,3]-hydrogen, and [1,3]-alkyl migrations.

In addition to the carbene-derived products **5** and **4** which arise from photolysis of **1** (Eqn.1), substantial amounts of product **2** are also formed.

Scheme 4



Presumably, 2 arises from [1,3]-hydrogen migration in the π, π^* state. Direct photolysis of β -alkylstyrene derivatives also affords products consistent with the intermediacy of carbenes formed by [1,2]-migrations, in addition to products of [1,3]-migration and cis-trans isomerization. These compounds have lowest π, π^* excited singlet states. Specific examples are shown in Equations 8-10. While carbene intermediates have been proposed in these cases, it should be noted that these are all extremely inefficient reactions. The formation of carbene-derived products from photolysis of alkylethylenes is generally much more efficient. The formation of 37 from photolysis of 36 has been proposed to arise from 1,2-migration of a γ -substituent to form a carbene intermediate as shown in



Equation 8. The excited singlet state of 38 undergoes a [1,2]-shift of its vinyl hydrogen to form carbene 41; 41 is then trapped by insertion into one of the γ -C-H bonds of CH_3 groups to form 39. 42 is formed by phenyl migration as shown in Equation 9. Non-conjugated olefin 44 is the product of [1,3]-hydrogen migration in 43 (Eqn.10).

3. Chemistry of the π,π^* state

The π,π^* state is biradical-like or zwitterionic and is thought to lead to cis,trans-isomerization in acyclic and larger ring cyclic ($\geq \text{C}_6$) alkenes, unimolecular dehydrogenation¹⁸, and possibly hydrogen abstraction reactions.

3.1 Cis,trans-isomerization

Cis,trans-isomerization is the principal photoreaction of acyclic alkenes, large-ring cyclic alkenes and exocyclic alkenes. The reaction occurs in both direct and triplet-sensitized irradiations. For large-ring cyclic alkenes, the reactivity depends on ring size. When ring size is greater than C₇, the orthogonal singlet or triplet excited state is relatively unstrained and decay to either the cis or trans isomer is facile.¹⁹ For example, direct irradiation of cis-cyclooctene is a convenient method for preparation of the trans isomer. Highly constrained alkenes cannot undergo cis,trans-isomerization.

3.2 Hydrogen atom abstraction

Photoreduction products are commonly formed in minor amounts in the photolyses of alkenes in solution. It is not clear which excited state effects the hydrogen abstraction, but the more likely candidate is the π,π^* state.²⁰

4. Investigation of pure π,π^* reactivity in simple alkenes

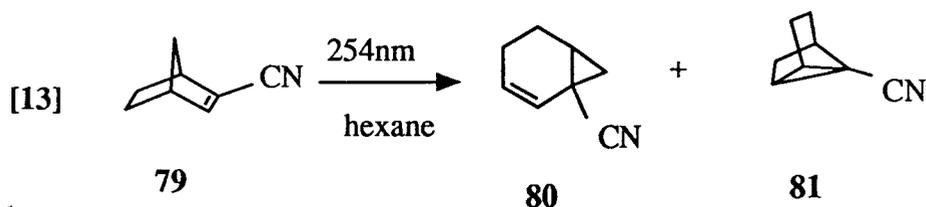
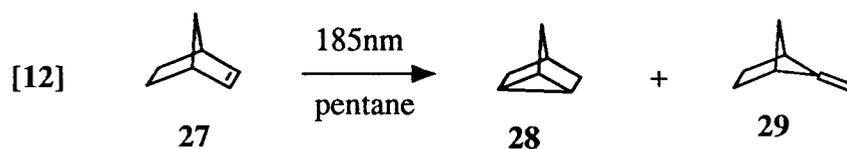
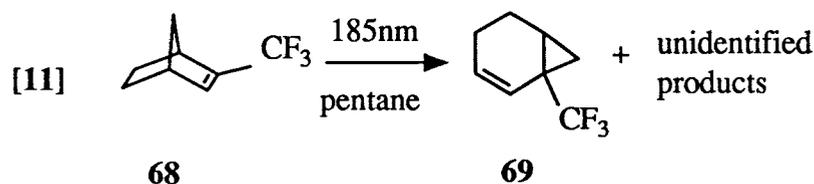
From the above reports, it is clear that the photochemistry of simple alkenes in solution is often complex. The complicated photobehaviour has been attributed to the involvement of two states of comparable energies: the π,π^* state and $\pi,R(3s)$ state.² In order to gain further information on the intrinsic reactivity of these two excited states in simple alkenes, one needs to separate the states by using substituents.

In tri- and tetra-alkyl substituted alkenes, the Rydberg state is lower in energy than the π,π^* singlet state in the gas phase as well as in solution.² The energy of the Rydberg state is more sensitive to alkyl substitution than the π,π^* state. Increasing the degree of alkyl substitution at the C=C bond causes a lowering in the energy of the Rydberg state at the expense of that of the π,π^* state. The evidence discussed above shows that the $\pi,R(3s)$ is most likely responsible for the formation of carbene-derived products in alkene

photochemistry. However, even with alkenes in which the Rydberg state is substantially lower in energy than the π,π^* state, a variety of other photoproducts are often formed. In order to define more precisely the behaviour of the valence and Rydberg states in the photochemistry of simple alkenes, it would be useful to alter the natural ordering of the two states.

While conjugating substituents can be used to lower the energy of the π,π^* state at the expense of the Rydberg state, they also change the basic character of the chromophore by producing a lower energy, delocalized π,π^* state.

The purpose of our study was to attempt to raise the energy of the $\pi,R(3s)$ Rydberg state in a simple alkene so that the π,π^* state would be rendered the lower in energy, but still maintain the high energy and localized character of that in the basic system. From the simple radical-cation model of the $\pi,R(3s)$ state discussed earlier, we reasoned that a strong inductive electron-withdrawing group might raise its energy. The energy and localized nature of the ethylenic π,π^* singlet state should be unaffected if the substituent is non-conjugative. 2-Trifluoromethylnorbornene was chosen as the best candidate for our initial study, since its synthesis has been reported and is straightforward (Eqn.11).²¹ In addition, the photochemistry of norbornene and 2-cyanonorbornene have been reported and are thus available for comparison with that of 2-trifluoromethylnorbornene. The photochemistry of these two compounds is very different. Direct photolysis of norbornene in solution leads predominantly to carbene-derived products via [1,2]-alkyl and [1,2]-hydrogen migrations (presumably via the $\pi,R(3s)$ Rydberg state,(Eqn.12)), while direct photolysis of 2-cyanonorbornene in solution yields only products consistent with π,π^* state excitation (Eqn.13).²² The major photoproduct of 2-cyanonorbornene is derived from (supra,supra)[1,3]-migration of the bridgehead carbon from C₄ to C₇. The



minor photoproduct has been suggested to derive from a ($\sigma_{2a} + \pi_{2a}$)[1,2]-migration pathway similar to those postulated in β -alkylstyrene derivatives. Finally, it is a constrained olefin, so that cis, trans isomerization is not possible. Preliminary studies have shown that direct photolysis (185 nm) of 2-trifluoromethylnorbornene in hydrocarbon solution leads to one major product in ca. 85% yield (Eqn.11). This product was tentatively identified as **69** on the basis of spectral evidence. These preliminary studies imply that trifluoromethyl substitution **does** result in reversal of the π, π^* and $\pi, R(3s)$ ordering in alkenes.

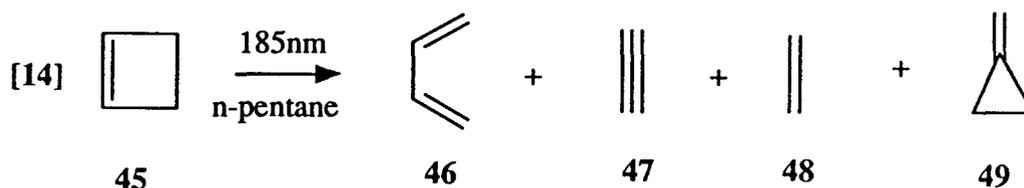
The first part of this thesis describes a study of the electronic excited states of 2-trifluoromethylnorbornene, norbornene, and 2-methylnorbornene by gas- and solution-phase UV absorption spectroscopy, and a complete characterization of the photochemistry of 2-trifluoromethylnorbornene upon direct and triplet-sensitized photolysis.

The second part of this thesis describes an application of the "trifluoromethyl effect" in defining the role of the π,π^* and $\pi,R(3s)$ states in the photochemistry of alkylcyclobutenes.

5. Application - Rydberg vs. valence state reactivity in cyclobutene photochemistry

5.1 General

As do simpler alkenes, alkylcyclobutenes have low-lying π,π^* and $\pi,R(3s)$ singlet excited states which are of similar energies and accessibility upon direct photolysis in solution.²² The photochemistry of alkylcyclobutenes in solution is characterized by competing ring-opening to the corresponding conjugated dienes and fragmentation to an alkene and an alkyne, in addition to formation of other minor rearrangement products. Direct irradiation of cyclobutene itself in pentane at 185 nm leads to the products shown in Equation 14.³¹ The stereochemistry



and mechanisms of the two main photoprocesses have been studied by various workers and are reviewed below.

5.2 Electrocyclic ring opening

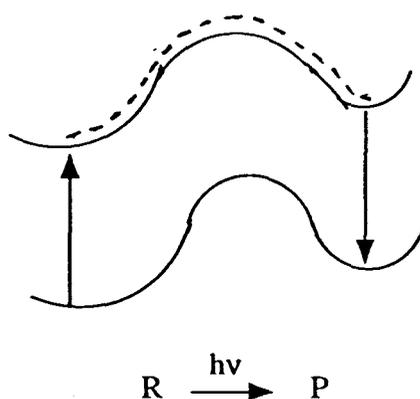
Orbital symmetry selection rules predict that singlet excited state ring-opening of cyclobutene should proceed by the disrotatory pathway, while thermal ring opening should proceed with the opposite (i.e. conrotatory) stereochemistry (Scheme 5). A large number of examples demonstrate that the thermal ring-opening does proceed by the symmetry-allowed, conrotatory

pathways are relatively high energy processes in the excited state of this compound. In a reinvestigation of the photochemistry of these compounds, Leigh and Zheng have found that both *cis*- and *t*-50 yield 51 upon photolysis with monochromatic 193 nm, 214 nm or broadband excitation.

Several other recent studies have provided examples which indicate that in general, the photochemical ring-opening of alkylcyclobutene derivatives proceeds non-stereospecifically to yield a distribution of all possible, stable isomers of the corresponding conjugated dienes. These results, which conflict with the widely accepted view that the photochemical electrocyclic ring-opening of cyclobutene is governed by orbital symmetry selection rules,³⁰ are summarized in Eqns. 17-24. There are at least four mechanistic possibilities for the non-stereospecificity of the reaction²⁸.

1/ Adiabatic, disrotatory π,π^* -state ring opening to yield diene in the first excited singlet state.

Adiabatic photoreaction

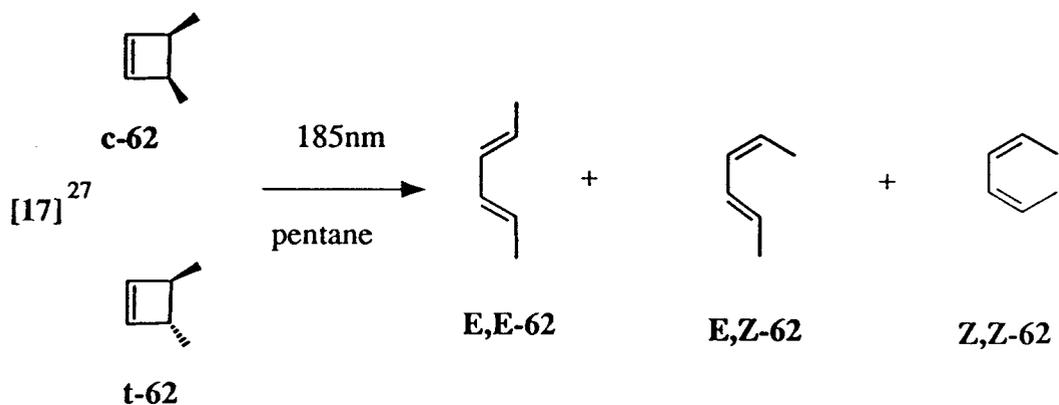


2/ Competitive ring-opening from two or more excited states (e.g. the π,π^* and Rydberg states).

3/ Competitive ring-opening from both excited (disrotatory) and

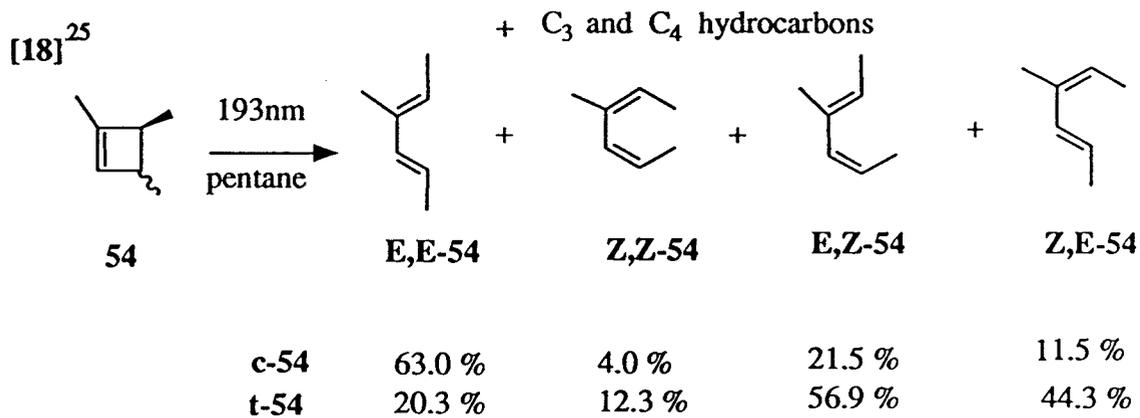
vibrationally-excited ground state (conrotatory) surfaces.

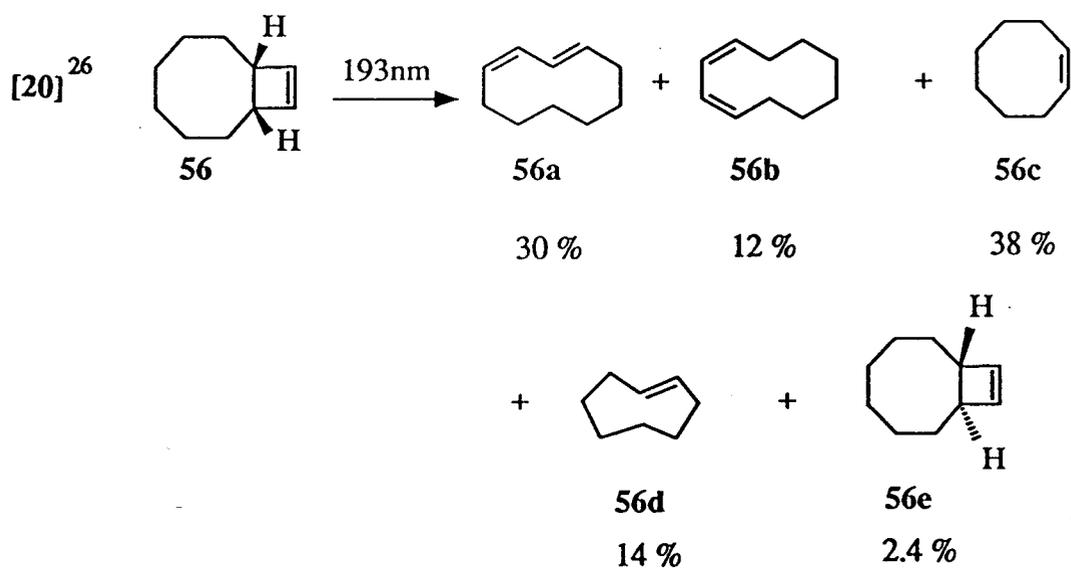
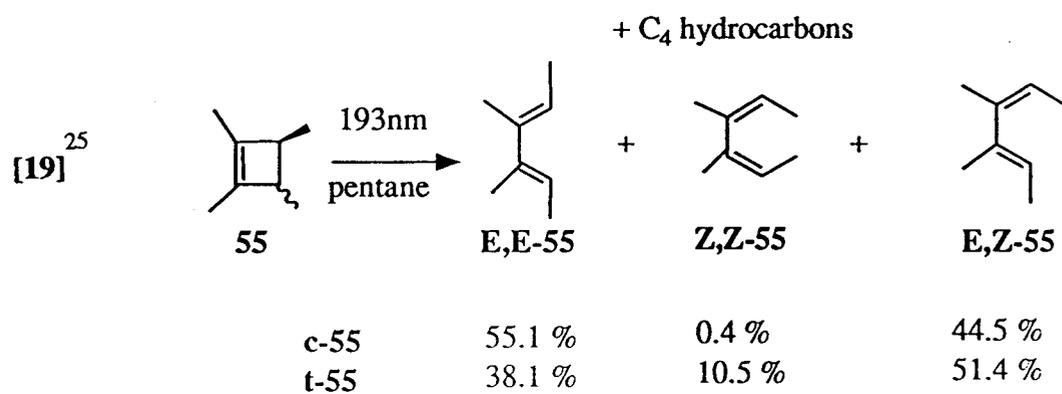
4/ Excited state ring-opening by a "non-concerted" pathway.

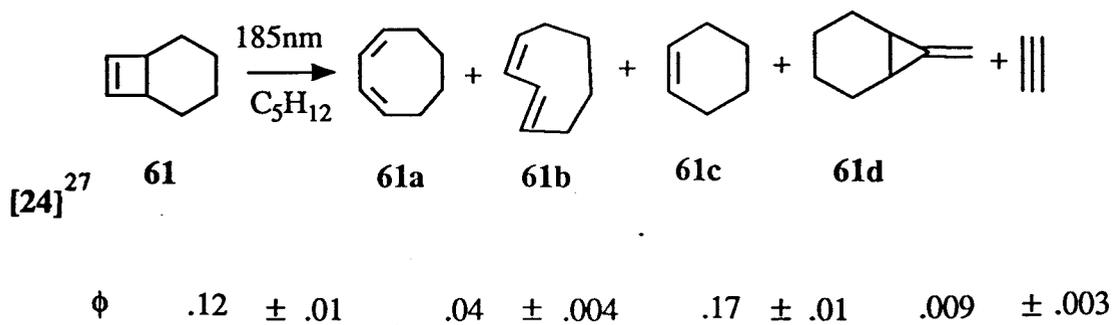
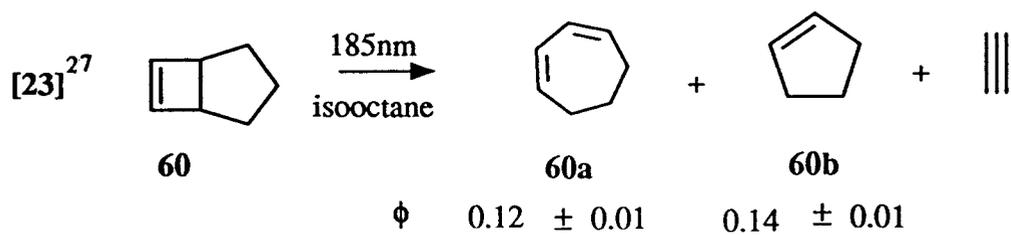


Relative yield:

c-62	3.5:6:1
t-62	2.8:2.6:1

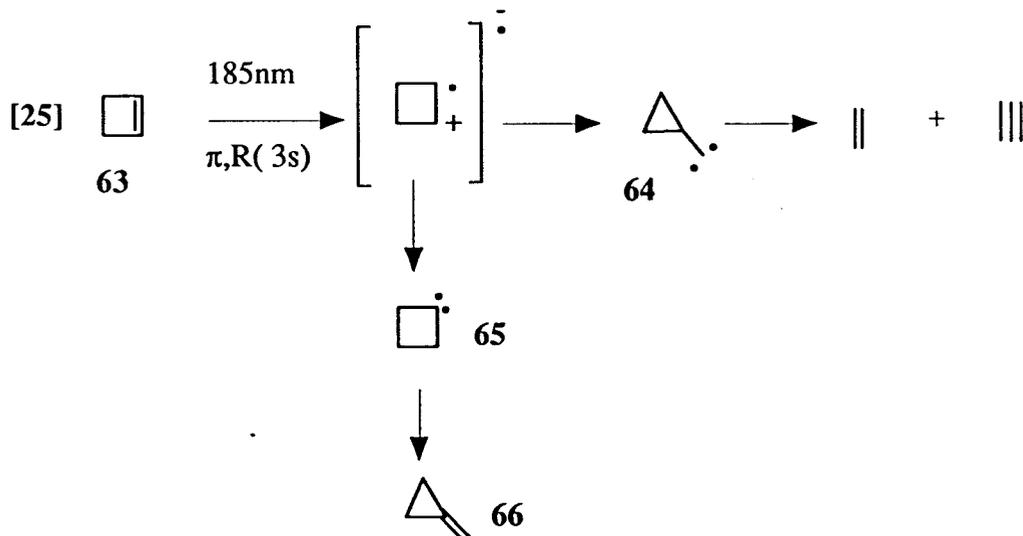






5.3 Molecular fragmentation

The other main products from direct photolysis of alkylcyclobutenes in solution are the alkene and alkyne derived from fragmentation of the C₁-C₄ and C₂-C₃ bond in cyclobutene. Numerous examples have shown that the alkene is



formed stereospecifically, with the same stereochemistry as that defined in the cyclobutene precursor. Two possible mechanisms could account for these results.

* Symmetry allowed ($\sigma_{2s} + \sigma_{2s}$) cycloreversion

This mechanism was postulated to explain the stereospecific formation of enynes which were formed from photolysis of **c-50** and **t-50**.⁴⁰

* Rydberg-derived non-concerted cycloreversion

The formation of ethene, acetylene, and methylene cyclopropane (**66**) could result from the initial formation of cyclopropylmethylene (**64**) and cyclobutylidene (**65**) by [1,2]-alkyl or hydrogen migration due to $\pi, R(3s)$ Rydberg excitation^{31,32} as shown in Equation 25. The intermediacy of cyclobutylidene has been proposed to explain the high yield of

methylenecyclopropane.

Studies of the photochemistry of 1,3,4,4- and 1,3,3,4-tetramethylcyclobutene³² have demonstrated that cyclopropyl carbenes involved are probably formed in the photolysis of alkylcyclobutenes.

Cyclopropylmethylenes which are generated by thermolysis or photolysis of the appropriate diazo compound or tosylhydrazone salt are well known to undergo stereospecific fragmentation to the corresponding alkene and alkyne in addition to ring-expansion to the corresponding cyclobutene derivative.³³

While many of the reported studies of alkylcyclobutene photochemistry have addressed the possibility of competing involvement of the π,π^* and $\pi,R(3s)$ states, none have successfully defined the role of the two excited states in accounting for the various products formed. The study of the photochemistry of *c*-, *t*-**62**, **54** and **55**, in which the $\pi,R(3s)$ state is systematically lowered in energy compared to the π,π^* state, failed to reveal any consistent trends that could define the role of the $\pi,R(3s)$ state. The problem cannot be studied by lowering the energy of the π,π^* state with conjugative substituents: phenylcyclobutenes do not undergo ring-opening upon direct photolysis in solution.⁸ We have therefore synthesized the series of *cis*-fused bicyclic cyclobutene derivatives (**84**, **86** and **97**) and studied their photochemistry in solution, in an attempt to define the role of the Rydberg and valence excited states in the photochemistry of cyclobutene. This thesis describes our studies of **86**. In order to define the π,π^* and $\pi,R(3s)$ reactivity in the photochemistry of alkylcyclobutenes and to know the mechanistic details of the ring opening and fragmentation reactions, the 7-trifluoromethylbicyclo[4.2.0]oct-7-ene was chosen for study. The photochemistry as well as the UV spectroscopy of this compound are also compared to those of bicyclo[4.2.0]oct-7-ene and

7-methylbicyclo[4.2.0]oct-7-ene.

CHAPTER II

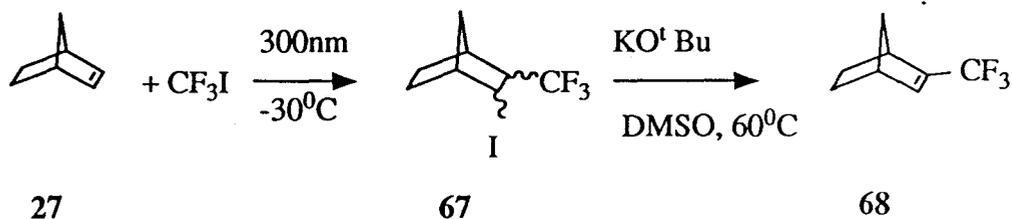
RESULTS

Synthesis and photochemistry of 1-trifluoromethylnorbornene (68)

1. Synthesis of 68

2-Trifluoromethylnorbornene (**68**) was synthesized from norbornene (**27**) according to the synthetic Scheme 6.

Scheme 6



1.1 Conversion of norbornene (27) to 2-iodo-3-trifluoromethyl bicyclo [2.2.1]heptane (67)

Photochemical addition of trifluoromethyl iodide to norbornene (free radical addition) at -30°C resulted in the formation of 2-iodo-3-trifluoromethylbicyclo[2.2.1]heptane (**67**) as a major product. The intermediate (**67**) was not fully characterized, but exhibited spectral characteristics consistent with its proposed general structure. The ^1H nmr (90 MHz) of (**67**) is similar to that reported for 2-iodo-3-heptafluoropropylbicyclo[2.2.1]heptane.³⁴

1.2 Dehydroiodination of 2-iodo-3-trifluoromethylbicyclo[2.2.1]heptane (67)

Compound **67** was dehydroiodinated by treatment with potassium tert-butoxide in dimethylsulfoxide at 60°C to yield 2-trifluoromethylnorbornene (**68**). Compound **68** was purified by bulb-to-bulb distillation under vacuum and by semi-preparative vpc. It was identified by ¹H nmr, ¹³C nmr, ¹⁹F nmr, IR, UV absorption and mass spectroscopy.

2. Characterization of excited states of substituted norbornenes

The excited states of norbornene (**27**), 2-methylnorbornene (**75**) and 2-trifluoromethyl norbornene (**68**) were characterized by UV photoelectron spectroscopy and by gas and solution phase UV absorption spectroscopy.

2.1 UV photoelectron spectroscopy

The HeI photoelectron spectra (PES) of **68**, **27** and **75** are shown in figure 2.³⁵ The lowest vertical π -ionization potentials of **68**, **27** and **75** are -9.6 eV, -9.2 eV and -8.5 eV, respectively. Thus, methyl substitution decreases the π -ionization potential (0.7 eV) while trifluoromethyl substitution increases the π -ionization potential (0.4 eV). The ionization energies (PES) and computed (AM1) eigenvalues of **68**, **27**, **75** are summarized in table 1a.

2.2 Optical spectra

The gas phase UV absorption spectra of **68**, **27**, and **75** were recorded on a conventional UV spectrometer with sample pressures in the 1.5-2 Torr range and are shown in figure 3. The spectra of **68**, **27** and **75** in deoxygenated n-pentane solution with the same system and under identical conditions are shown in figure 4. The energies, term values, and possible assignments for features in the gas-phase UV absorption spectra of **68**, **27**, **75** are collected in table 1b.

2.3 Discussion

The Rydberg transitions in the optical spectra are sharp and well defined compared to the valence π, π^* transition. The gas phase spectrum of norbornene

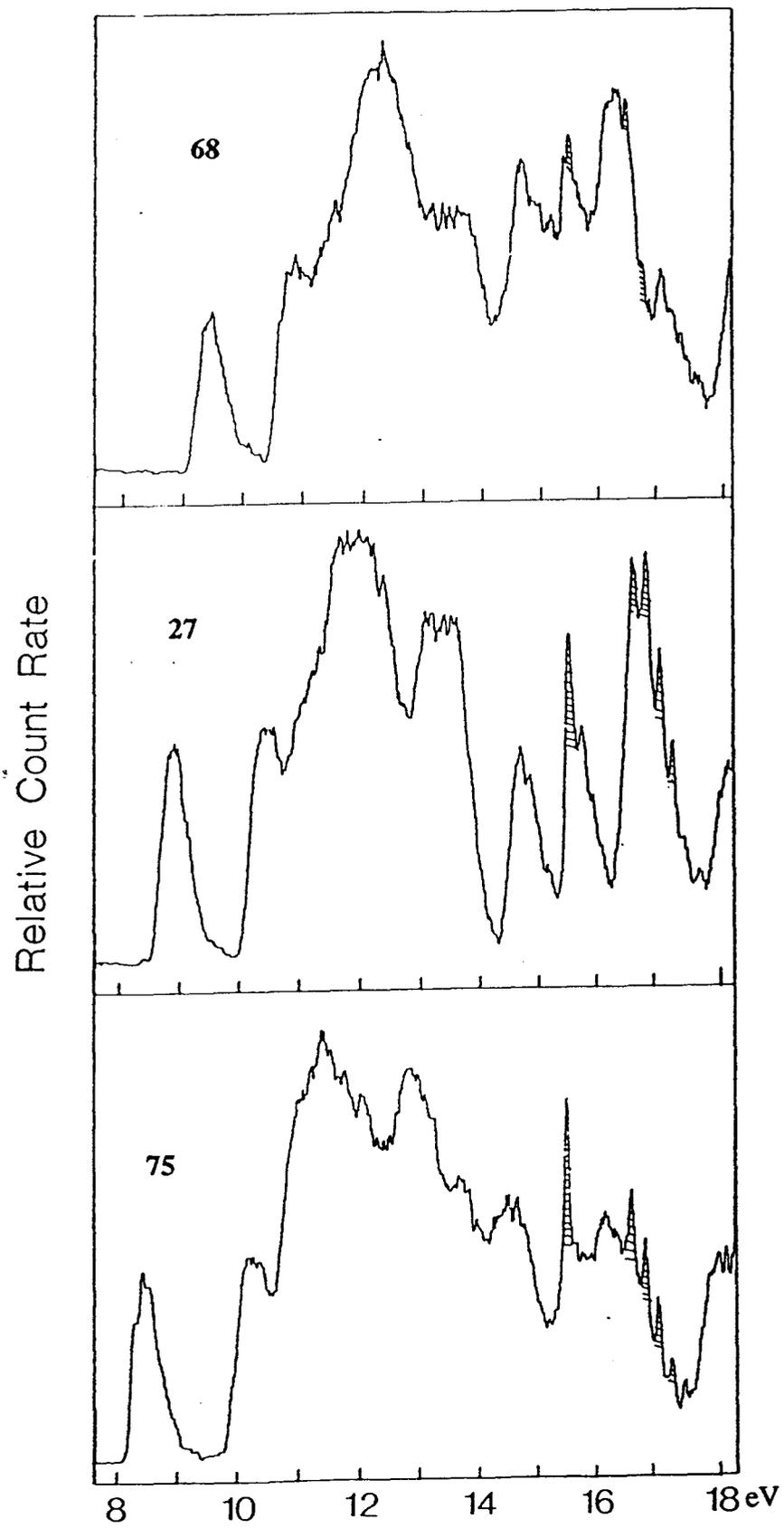


Figure 2 HeI UV photoelectron spectra of 68, 27, 75

Table 1a

Compound	Ionization energy (eV) ^a		ϵ^b	
	π	σ	π	σ
68	-9.6	-11.1	-10.4	-11.5
27	-9.2	-10.6	-9.6	-10.9
75	-8.5	-10.3	-9.2	-10.9

a. Error estimated at ± 0.1 eV

b. Computed using AM1

27 is similar to that previously reported. The bands centered at 6.02 and 6.30 eV have been assigned to $\pi, R(3s)$ and π, π^* excitations respectively. The 6.02 eV band is absent in the solution phase spectrum, which is consistent with the Rydberg assignment. The term values (the difference between absorption maxima and the vertical ionization potential) of the 6.02 and the 6.30 eV band are 3.2 and 2.9 eV respectively. The gas phase optical spectrum of 2-methylnorbornene (75) shows three absorption bands centered at 5.62, 6.16 and 6.43 eV. The 5.62 and 6.46 eV bands are absent in the solution phase spectrum, while the most intense band at 6.16 is unaffected. The latter is thus assigned to π, π^* excitation. It should be noted that the term value associated with this band is increased significantly from that of the π, π^* excitation in norbornene. The 5.62 and 6.46 eV bands are assigned to $\pi, R(3s)$ and $\pi, R(3p)$ absorptions. The term value of the 5.62 eV band (2.9 eV) is very similar to that in norbornene, which is also consistent with this assignment. The gas phase spectrum of 2-trifluoromethylnorbornene (68) shows a single, symmetrical absorption band centered at 6.44 eV that can be assigned to the π, π^* transition and a sharp

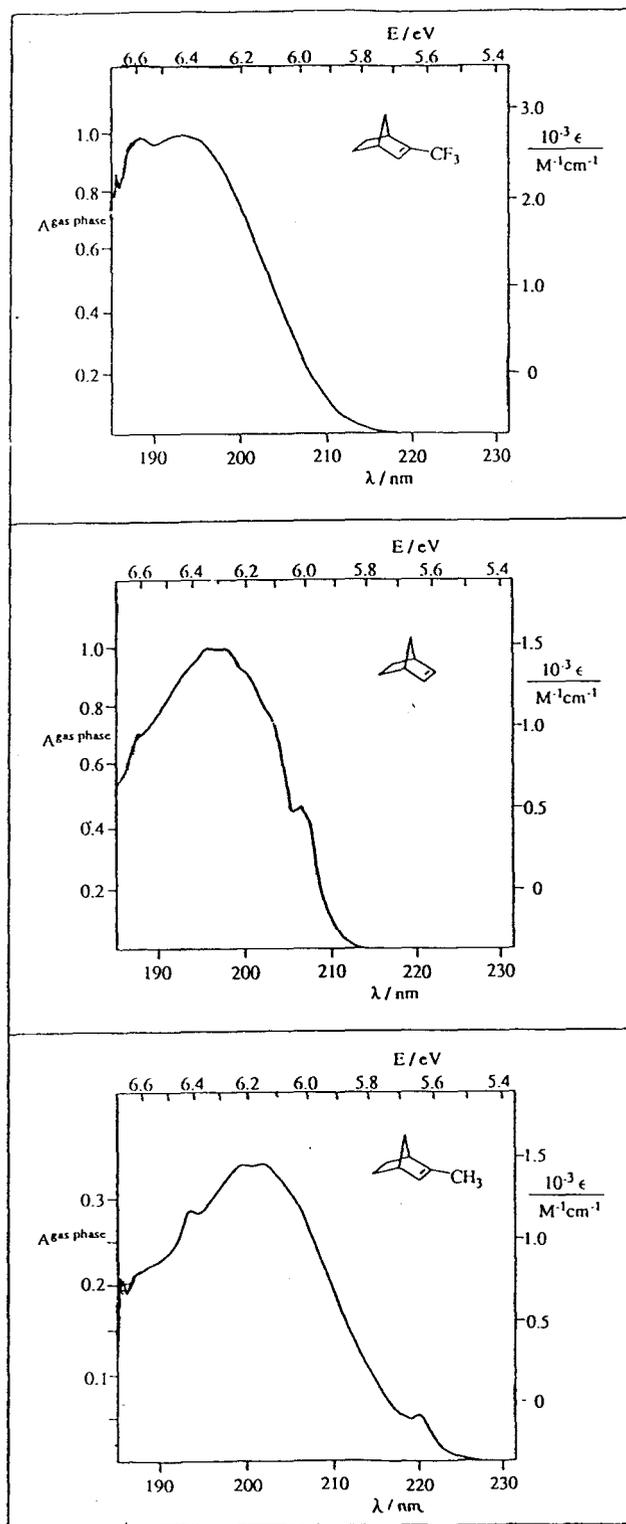


Figure 3 The gas phase UV absorption spectra of 68, 27, 75.

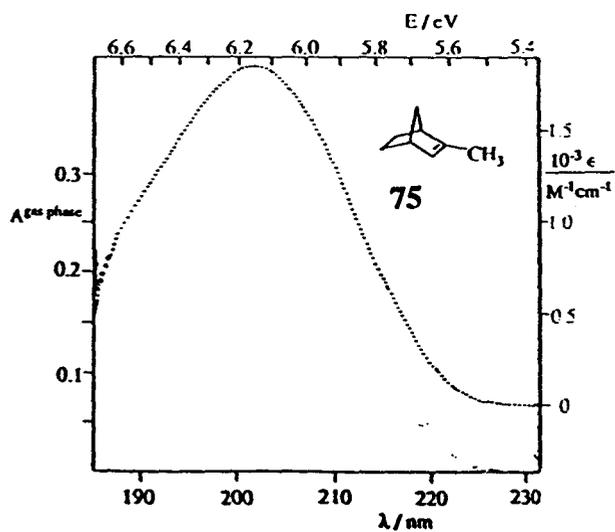
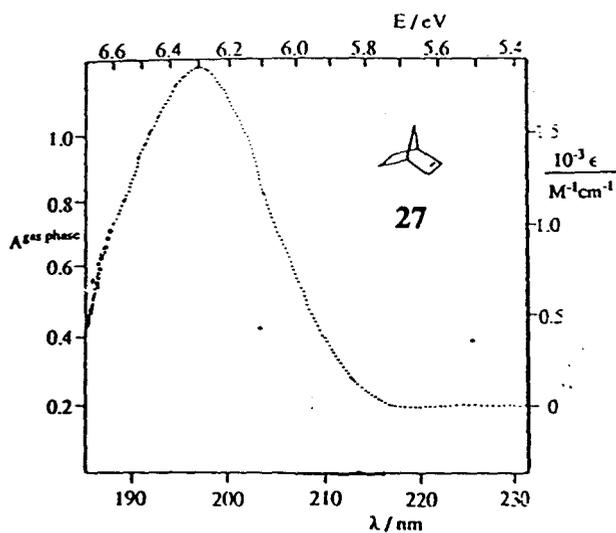
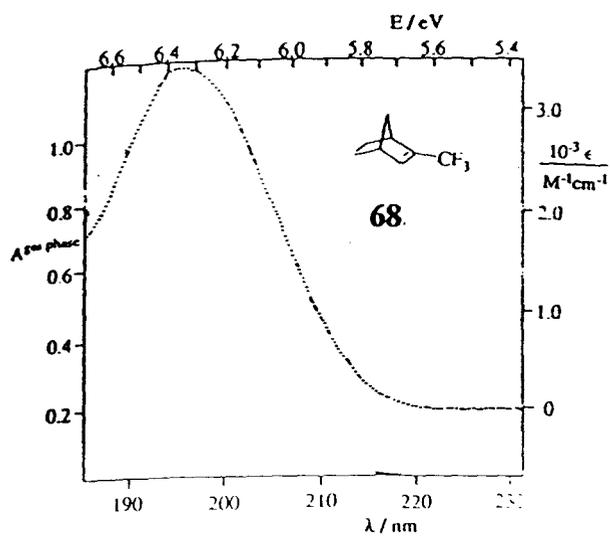


Figure 4 The solution phase UV absorption spectra of **68**, **27**, **75**.

Table1b

Feature	68 E/eV(T/eV)	27 E/eV(T/eV)	75 E/eV(T/eV)	Assignment
1		6.02(3.2)	5.62(2.9)	$\pi, R(3s)$
2	6.46(3.1)	6.30(2.9)	6.16(2.3)	π, π^*
3			6.43(2.1)	$\pi, R(3p)$

absorption band at 6.59 eV that can be assigned to the $\pi, R(3s)$ transition. The slight shift of the absorption maximum in the solution phase spectrum of **68** may be due to background absorption by the solvent.

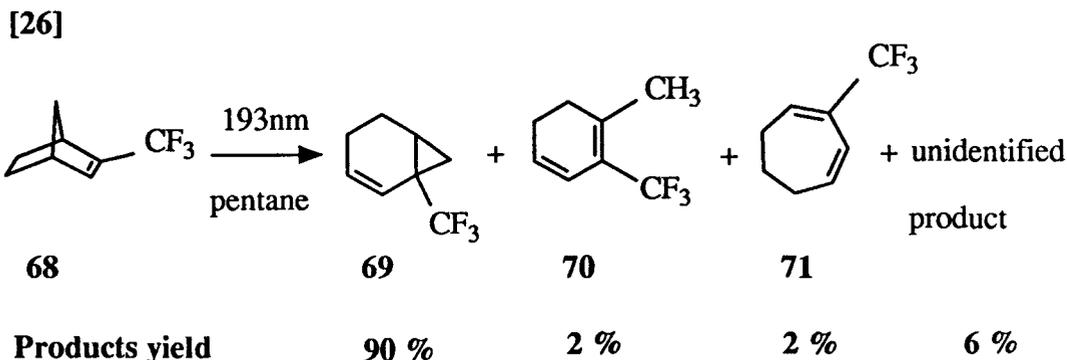
The Rydberg excitation can be viewed as involving "partial" ionization of the molecule. The larger and more diffuse the Rydberg orbital, the better the correlation should be between transition energy and ionization potential. Therefore, methyl substitution, which decreases the π -ionization potential energy, should also decrease the $\pi, R(3s)$ Rydberg excited state energy, and trifluoromethyl substitution, which increases the π -ionization potential energy, should increase the $\pi, R(3s)$ Rydberg excited state energy. In other words, the π, π^* state is the lowest singlet excited state in 2-trifluoromethylnorbornene (**68**) and the $\pi, R(3s)$ state is the lowest singlet excited state in norbornene (**27**) and 2-methylnorbornene (**75**). Furthermore, gas- and solution-phase UV spectroscopic studies of norbornene (**27**), 2-trifluoromethylnorbornene (**68**) and 2-methylnorbornene (**75**) are consistent with the assignment of a π, π^* lowest singlet excited state in 2-trifluoromethylnorbornene (**68**). The spectroscopic data show that the lowest vertical $\pi, R(3s)$ Rydberg state in **68** is at least 0.3 eV higher in energy than the π, π^* state.³⁶

In conclusion, trifluoromethyl substitution raises the energies of the Rydberg state without altering the energy or localized character of the π, π^* state.

3. The photochemistry of 2-trifluoromethylnorbornene (68)

3.1 The direct photolysis of 2-trifluoromethylnorbornene (68)

Direct photolysis of a deoxygenated, 0.02 M pentane solution of **68** with the pulses (193 nm, ca. 80 mJ) from an Ar/F₂ excimer laser produced the product



mixture shown in Equation 26.

Products **69**, **70** and **71** were isolated by preparative vpc from semi-preparative runs (ca. 300 mg scale) carried to ca. 40% conversion, and were identified by their ¹H nmr, ¹³C nmr, ¹⁹F nmr, IR, UV absorption, and mass spectra. ¹H nmr and ¹³C nmr spectra of the major product **69** are very similar to those reported³⁷ for the analogous cyano-substituted derivative, which is the major product from direct photolysis of 2-cyanonorbornene in solution. The structure of bicyclo[4.1.0]hept-2-ene-1-carbonitrile (**78**) was proven by the determination of the crystal structure of its p-bromobenzenesulfonate derivative.

The product yields shown in Eqn.26 were obtained from the slopes of plots of product concentration vs. excitation dose constructed from small scale runs that were monitored between 0.3% and 4% conversion. Typical plots of this type are shown in figure 5. The material balance is estimated to be at least 98% at 4% conversion.

A deoxygenated pentane solution of **69** (0.02M) was photolysed at 193 nm

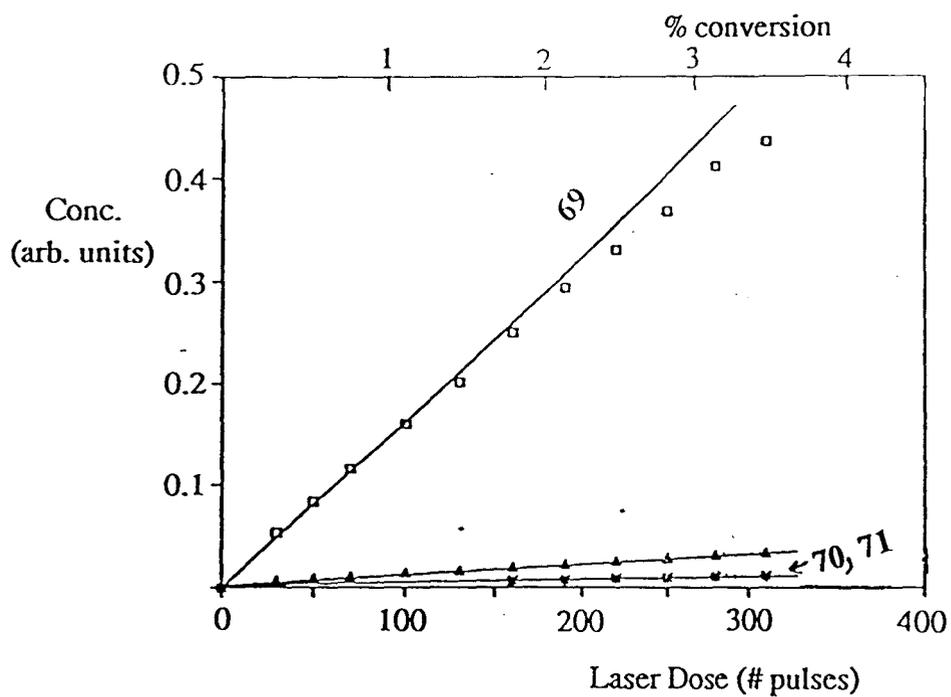


Figure 5 plots of product concentration vs. excitation dose for 193 nm photolysis of deoxygenated 0.02 M pentane solution of 68

under similar conditions to those used for the photolysis of **68**. Products **70** and **71** are formed from photolysis of **69**, but only as minor products. The major products in this photolysis were not identified but could not be detected as products from the photolysis of **68** at low conversions, within the accuracy limits of our analytical method. Therefore, the two minor products **70** and **71** are primary products from photolysis of **68** and do not arise from secondary photolysis of **69**. One other minor product (ca. 6%) from the photolysis of **68** could not be identified because quantities adequate for its identification could not be obtained.

3.2 Identification of the products from irradiation of 2-trifluoromethylnorbornene

3.2.1 Identification of the major product (69)

The major photoproduct **69** from irradiation of 2-trifluoromethylnorbornene (**68**) has a parent ion in its mass spectrum at $m/e = 162$ indicating that it arises by rearrangement of **68**. The calculated mass for $C_8H_9F_3$ is 162.0656. The exact found mass is 162.0664. Therefore, **69** has the molecular formula $C_8H_9F_3$. The proton NMR spectrum contained two olefinic hydrogen resonances: a doublet of doublets at δ 6.02 ($J_{H_2-H_3} = 7.3$ Hz) and a doublet of triplets centered at δ 5.64 ($J_{H_3-H_2} = 7.7$ Hz, $J_{H_3-H_4} = 1.6$ Hz). The other seven hydrogens in the molecule appear from δ 0.92 to δ 2.03. The 1H nmr spectrum of 1-trifluoromethylbicyclo[4.1.0]hept-2-ene (**69**) is very similar to that of bicyclo[4.1.0]hept-2-ene-1-carbonitrile (**80**) which was reported by McCullough and co-workers.²² The ^{13}C nmr and spin sort ^{13}C nmr spectra of **69** showed only seven resonances instead of the eight expected resonances. The missing resonance is the quaternary carbon. Two resonances at 122.7 and 125.7 indicate two vinyl carbons C_3 and C_2 respectively. The resonance at 127.7 (quartet) is due

to the trifluoromethyl carbon and is split into a quartet by the three fluorine atoms. A long relaxation time could account for the absence of the quaternary carbon. The four other resonances are in the aliphatic carbon region (14.7, 17.1, 18.1, 20.0). These results are very similar to that of **80**, which shows resonances at 125.3, 123.7, 24.3, 20.2, 19.4, 17.0. The ^{19}F nmr spectrum shows a sharp singlet at -65.3. All evidences for the major product **69** correlate quite well with that for **80**. Thus, we can conclude that both framework structures are similar. The UV absorption spectrum of **69** has λ_{max} at 200 nm, similar to that of 2-norcarene ($\lambda_{\text{max}} = 200$ nm). The IR spectrum of **69** is similar to that of 2-norcarene also.

3.2.2 Identification of the minor product

1-methyl-2-trifluoromethyl-1,3-cyclohexadiene (70)

The minor product (**70**) from irradiation of 2-trifluoromethylnorbornene (**68**) has a parent ion in its mass spectrum at $m/e = 162$ indicating that it arises by rearrangement of **68**. The calculated mass for $\text{C}_8\text{H}_9\text{F}_3$ is 162.0656. The exact found mass is 162.0662. Therefore, **70** has the molecular formula $\text{C}_8\text{H}_9\text{F}_3$. The ^{19}F nmr shows a sharp singlet at -60.3. The proton NMR spectrum contains two olefinic hydrogen resonances: a doublet of triplets at δ 5.78 and a doublet at δ 6.00. The proton at C_4 is split into a triplet by two protons at C_5 ($J_{\text{H}_4\text{-H}_5} = 4.2$ Hz) and a doublet by proton at C_3 ($J_{\text{H}_3\text{-H}_4} = 9.8$ Hz). The proton at C_3 is split into the doublet by the proton at C_4 ($J_{\text{H}_3\text{-H}_4} = 9.8$ Hz) and is broadened by weak coupling of fluorine. The three hydrogens of the methyl group appear at δ 1.95 as a broad singlet. The other four hydrogens in the molecule appear at δ 2.14 and δ 2.21 as multiplets. The ^{13}C nmr spectrum of **70** shows only five resonances instead of the eight expected resonances, indicating three quaternary centres. The two resonances at 120.7 ppm and 124.9 ppm indicate two vinyl carbons. The three

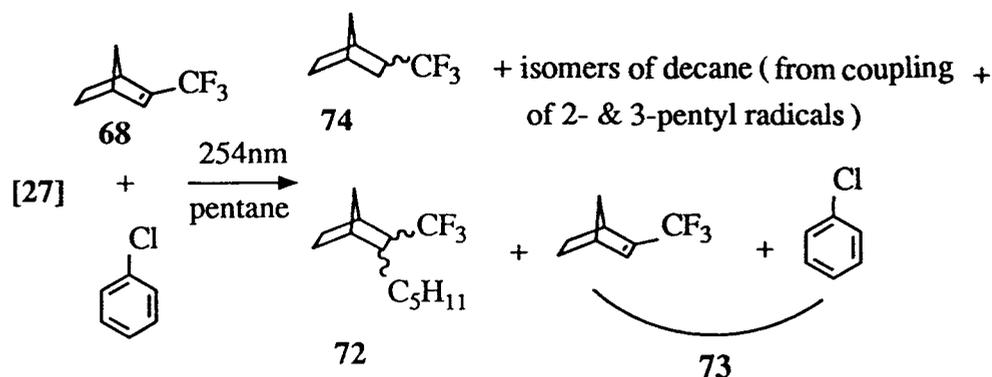
other resonances are in the aliphatic carbon region (20.3 ppm, 21.6 ppm, 30.7 ppm). The UV absorption spectrum has λ_{\max} at 263 correlating quite well with that of 1,3-cyclohexadiene ($\lambda_{\max} = 257.5$).

3.2.3 Identification of the minor product 2-trifluoromethyl-1,3-cycloheptadiene (71)

The minor product **71** from photolysis of 2-trifluoromethylnorbornene **68** has a parent ion in its mass spectrum at $m/e = 162$ indicating that it arises by rearrangement of **68**. The calculated mass for $C_8H_9F_3$ is 162.0656. The exact found mass is 162.0651. Therefore, **71** has the molecular formula $C_8H_9F_3$. The ^{19}F nmr spectrum shows a sharp singlet at -68.0. The proton NMR spectrum contains three olefinic hydrogen resonances: a broadened doublet at $\delta 5.84$ (proton at C_3 , $J_{H3-H4} = 12.1$ Hz), a doublet of triplets at $\delta 6.04$ (proton at C_4 , $J_{H3-H4} = 12.0$ Hz, $J_{H4-H5} = 5.1$ Hz) and a triplet at $\delta 6.46$ (proton at C_1). The other six hydrogens in the molecule appear at $\delta 1.86$ (2H) and $\delta 2.37$ (4H) as multiplets. The ^{13}C nmr spectrum of **71** shows only six resonances instead of the eight expected resonances. The three olefinic carbon resonances were present at 119.9, 134.9, and 136.9 ppm. The three other resonances were present in the aliphatic carbon region (25.1, 29.9, 31.5 ppm). The two resonances missing are the quaternary carbon and the trifluoromethyl carbon. A long relaxation time could account for the absence of the former. The UV absorption spectrum has λ_{\max} at 243 nm correlating quite well with that of cycloheptadiene ($\lambda_{\max} = 246$ nm).

3.3 Triplet sensitized photolysis of 2-trifluoromethylnorbornene (68)

Irradiation of a deoxygenated solution of 2-trifluoromethylnorbornene (0.01M) in pentane at 254 nm, with chlorobenzene or toluene as the sensitizer (0.002M), afforded complex mixtures of products. The products from the chlorobenzene-sensitized photolysis are shown in Equation 27. The major products of both photolyses are exo- and endo-2-trifluoromethylnorbornane (**74**).

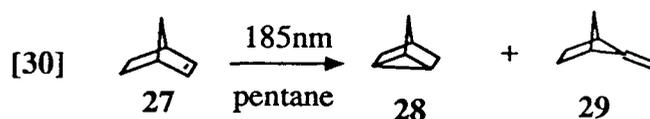


These products are volatile and formed in roughly equal yields. Exo- and endo-2-trifluoromethylnorbornane (**74**) were isolated from the crude photolysate by semi-preparative vpc and were identified by ^1H nmr³⁸, ^{13}C nmr, IR and mass spectra. The ^1H nmr spectrum (90 MHz) of exo-**74** is similar to that of exo-2-bromonorbornane.¹⁶ Endo-**74** exhibits $J_{2,3}$ (endo, exo)=4.5 Hz and $J_{2,3}$ (exo, exo)=2.95 Hz. Exo-**74** exhibits $J_{2,3}$ (endo, exo)=3.8 Hz and $J_{2,3}$ (endo, endo)=10.4 Hz. Three products which have parent ions of 234 amu, corresponding to addition products of **68** with the solvent, were also indicated by GC/MS. One other minor product of parent ion mass 274 amu (**73**) was formed and is presumably a cycloaddition product between **68** and the sensitizer chlorobenzene.

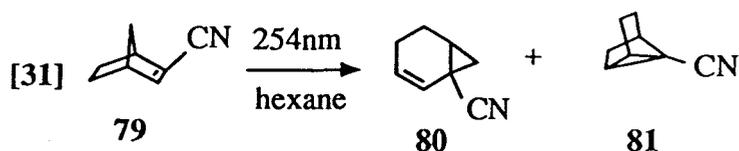
3.4 Discussion

None of the products formed in the direct photolysis of 2-trifluoromethylnorbornene **68** was detected in the sensitized photolysis. Therefore, these products are formed via the singlet excited state.

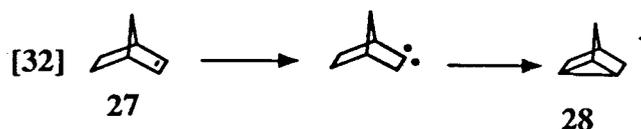
The triplet sensitized photolysis of 2-trifluoromethylnorbornene (**68**) is to be compared to that previously reported for 2-methyl-2-norbornene.⁴¹ Irradiation of 2-methyl-2-norbornene (**75**) in xylene-methanol afforded a mixture of the



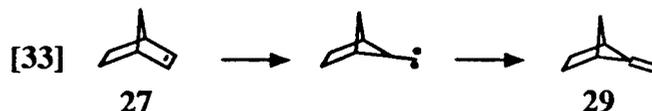
5-methylenebicyclo[2.1.1]hexane (**29**) which are thought to derive from carbenes. Some minor products such as norbornane, norbornyl dimers, solvent-addition products, and solvent-derived dimers which are thought to arise from hydrogen abstraction from the solvent were also produced. Hydrogen abstraction upon



direct photolyses of norbornene (**27**) has been tentatively attributed to the π,π^* excited singlet state.¹⁴ Product **28** from photolysis of **27** is thought to derive from



norbornanylidene, formed by [1,2]-hydrogen migration in the $\pi,\text{R}(3\text{s})$ Rydberg state as shown in Equation 32. Product **29** from photolysis of **27** is thought to

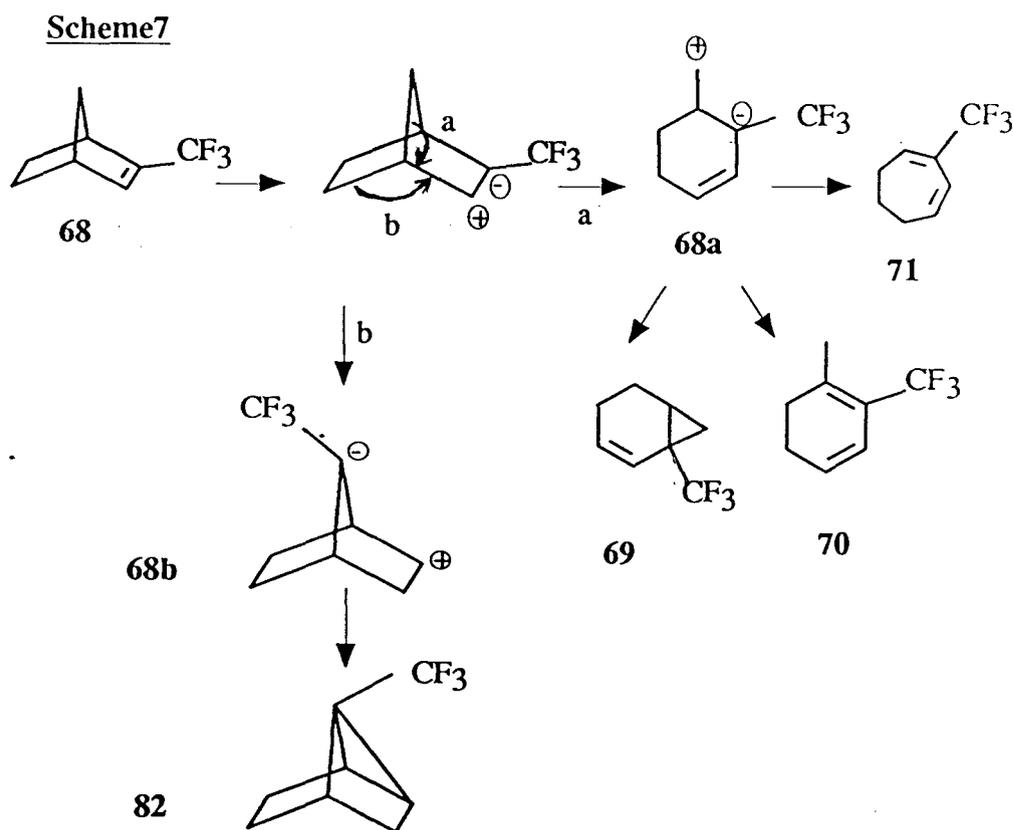


derive from the carbene formed via [1,2]-alkyl migration in the $\pi,\text{R}(3\text{s})$ Rydberg state as shown in Equation 33.

While the $\pi,\text{R}(3\text{s})$ Rydberg state is the lowest energy singlet excited state of norbornene in the gas-phase, its energy in solution is unknown. The oscillator strengths of Rydberg transitions drop dramatically in the condensed phase and the band is slightly blue-shifted. The most likely mechanism for Rydberg state

population in solution probably involves internal conversion from the initially populated π,π^* state.

Direct irradiation of 2-cyanonorbornene (**79**) in hexane produced bicyclo[4.1.0]hept-2-ene-1-carbonitrile (**80**) as a major product and tricyclo[4.1.0.0^{3,7}]heptane-7-carbonitrile (**81**) as a minor product in a 20:1 ratio.



The lowest energy singlet excited state in **79** is the π,π^* state because of the conjugative effect of the $-\text{CN}$ substituent. Moreover, on the basis of the correlation between Rydberg state energies and the π -ionization potential of the alkenes¹, the CN substituent is predicted to raise the energies of the alkene Rydberg states compared to the situation in **27**. Thus the photochemistry of 2-cyanonorbornene (**79**) is remarkably different from that of norbornene (**27**).

McCullough and co-workers reported that the major product (**80**) derived from formal (supra, supra) [1,3]-migration of the bridgehead carbon from C₄ to C₇ in 2-cyanonorbornene (**79**) and the minor product **81** proceeded from **79** via a ($\sigma_{2a} + \pi_{2a}$) [1,2]-migration pathway similar to that postulated in β -alkylstyrene derivatives.^{42,43}

Direct irradiation at 193 nm in pentane of 2-trifluoromethyl norbornene (**68**) leads to the formation of one major product and three minor products in 45:1:1:3 ratio. The formation of all three identified products can be rationalized as arising from a mechanistic pathway which involves initial heterolytic cleavage of the C₄-C₇ bond in **68** to form the intermediate **68a** which can then collapse to form 1-trifluoromethylbicyclo[4.1.0]hept-2-ene (**69**), undergo [1,2]-hydrogen migration to form 1-methyl-2-trifluoromethyl-1,3-cyclohexadiene (**70**) or [1,2]-alkyl migration (ring expansion) to form 2-trifluoromethyl-1,3-cycloheptadiene (**71**). Comparing with the minor product tricyclo[4.1.0.0^{3,7}]heptane-7-carbonitrile (**81**) which was produced from photolysis of 2-cyanonorbornene, the unidentified product from photolysis of 2-trifluoromethylnorbornene could be 7-trifluoromethyl-tricyclo[4.1.0.0^{3,7}]heptane (**82**). This product can be rationalized as arising from a mechanistic pathway which involves initial heterolytic cleavage of the C₄-C₅ bond in **68** to form the intermediate **68b** which can then collapse to form **82** as shown in Scheme 7. However, the major product is formally the product of a 1,3-sigmatropic rearrangement of type $\sigma_{2s} + \pi_{2s}$ which is a symmetry-allowed photochemical process, according to the Woodward-Hoffmann rules of orbital symmetry (figure 6). Naturally, it is not possible to define whether **69** is formed by one or both of these two possible routes. The main product from photolysis of 2-trifluoromethylnorbornene (**68**) is

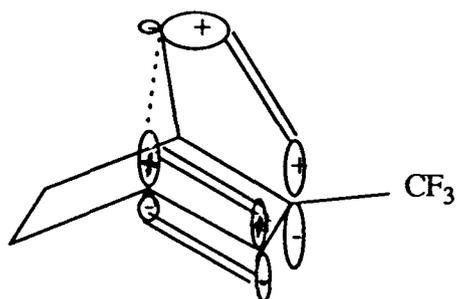


Figure 6: orbitals involved in 1,3-sigmatropic rearrangement in 2-trifluoromethylnorbornene

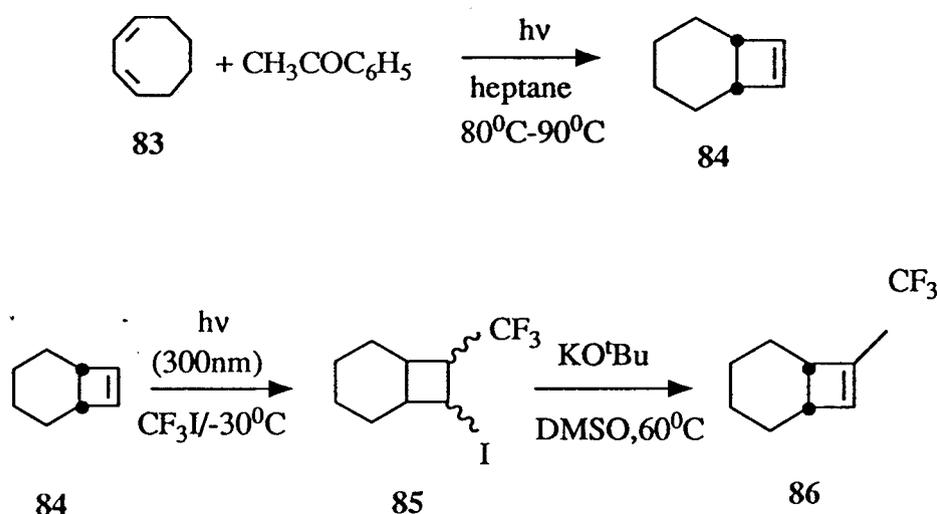
the 1,3-migration product similar to that obtained from photolysis of 2-cyanonorbornene (79). This indicates that the configuration and reactivity of the lowest excited singlet states in these two compounds are the same. In other words, the π, π^* state is the lowest singlet excited state in 68.

Synthesis and photochemistry of 86

4. Synthesis of 86

7-Trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**) was synthesized from *cis,cis*-1,3-cyclooctadiene (COD) (**83**) according to synthetic Scheme 8

Scheme 8



4.1 Conversion of *cis,cis*-1,3-COD (**83**) to bicyclo[4.2.0]oct-7-ene (**84**)

The procedure followed was that of Liu.⁴⁴ A solution of *cis,cis*-1,3-cyclooctadiene (**83**) in heptane when irradiated with acetophenone sensitizer, resulted in the formation of bicyclo[4.2.0]oct-7-ene (**84**) (97% yield) (literature⁴⁴ : 98%). **84** has an IR spectrum identical in all essential respects to that previously reported by Evans and co-workers.⁴⁵

4.2 Conversion of **84** to 7-iodo-8-trifluoromethylbicyclo[4.2.0]octane (**85**)

Photochemical addition of trifluoromethyl iodide to **84** (300 nm, -30°C) resulted in the formation of 7-iodo-8-trifluoromethylbicyclo[4.2.0]octane (**85**) as

the major product. The mechanism is free radical addition. The intermediate **85** was not fully characterized but exhibited spectral characteristics consistent with its proposed general structure.

4.3 Dehydroiodination of 7-iodo-8-trifluoromethylbicyclo[4.2.0]octane (**85**)

85 was dehydroiodinated by treatment with potassium *tert*-butoxide in dimethylsulfoxide at 60°C to yield 7-trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**). Compound **86** was purified by bulb-to-bulb distillation under vacuum and by semi-preparative vpc. **86** was then identified on the basis of its ¹H nmr, ¹³C nmr, IR (neat), UV absorption, and mass spectra and by comparison to the spectra of **84** and **97**

5. Characterization of excited states of cis-fused bicyclic cyclobutene derivatives

Bicyclo[4.2.0]oct-7-ene (**84**), 7-trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**) and 7-methylbicyclo[4.2.0]oct-7-ene (**97**)⁴⁷ were characterized by UV photoelectron spectroscopy and by gas and solution phase UV absorption spectroscopy.

5.1 UV photoelectron spectroscopy⁴⁶

The results of HeI photoelectron spectra (PES) of **97**, **84**, **86** are summarized in Table 2. The lowest vertical π -ionization potentials of **97**, **84**, **86** are -8.5 eV, -9.0 eV and -9.7 eV respectively. Thus, methyl-substitution decreases the π -ionization potential (0.5 eV) while trifluoromethyl-substitution increases the π -ionization potential (0.7 eV) relative to its value in the unsubstituted compound. The UV photoelectron spectra of **97**, **84**, and **86** are shown in figure 7.

5.2 Optical spectra

The gas phase UV absorption spectra of **97**⁴⁷, **84** and **86** were recorded on a conventional UV spectrometer with sample pressures in the 1.5-2 Torr range.

Table 2 Gas-phase spectroscopic properties of substituted bicyclo[4.2.0]oct-7-enes.

Compound	π -IP ^a	$E_{\pi,R(3s)}/\text{eV}^b$
97	8.5 ± 0.1	5.91
84	9.0 ± 0.1	6.37
86	9.7 ± 0.2	>6.7

a. Lowest vertical ionization potential from photoelectron spectrum.

b. Band maximum of $\pi,R(3s)$ absorption in gas-phase UV absorption spectrum.

The spectrum of **84** exhibits a weak shoulder absorption centered at 6.37 eV, which is shifted to 5.91 eV in the spectrum of **97**. The absorption is not evident in the spectrum of **86** and the minimum value of 6.7 eV is speculative. The variation in the position of this band with substituent is similar to that in the lowest vertical π -IP from the PES. Furthermore, it is not observed in the solution phase spectra of **84** and **97**. This absorption band is thus assigned to the $\pi,R(3s)$ transition. The gas and solution phase UV absorption spectra of **97**, **84** and **86** are shown in figure 8.

5.3 Conclusion

The parallel effects of methyl- and trifluoromethyl-substitution on the π -IP and position of $\pi,R(3s)$ transitions in **84**, as well as the lack of an effect on the π,π^* transition energy are similar to those reported previously for norbornene (**27**). It may be concluded that trifluoromethyl-substitution raises the energies of

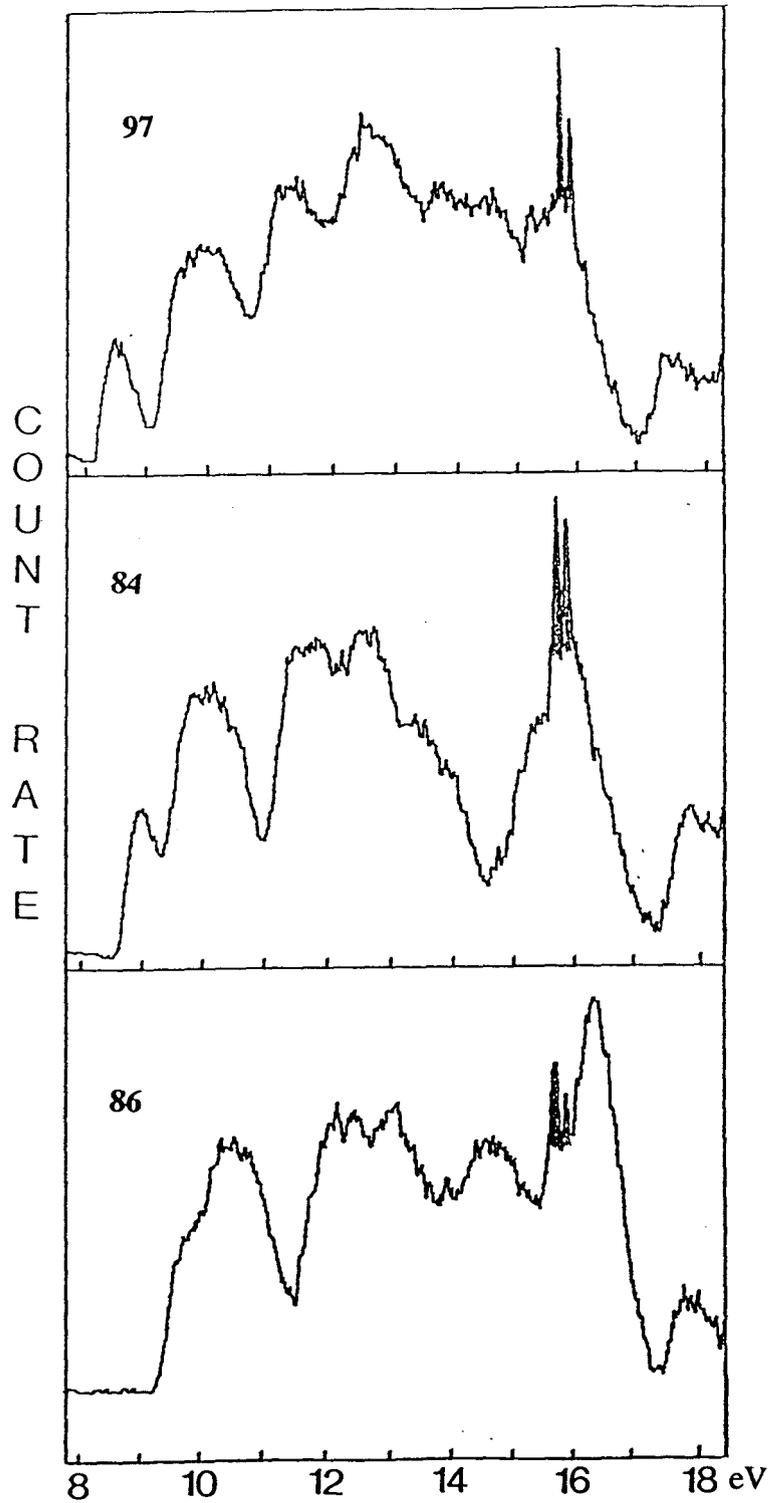


Figure7 The UV photoelectron spectra of 97, 84, 86

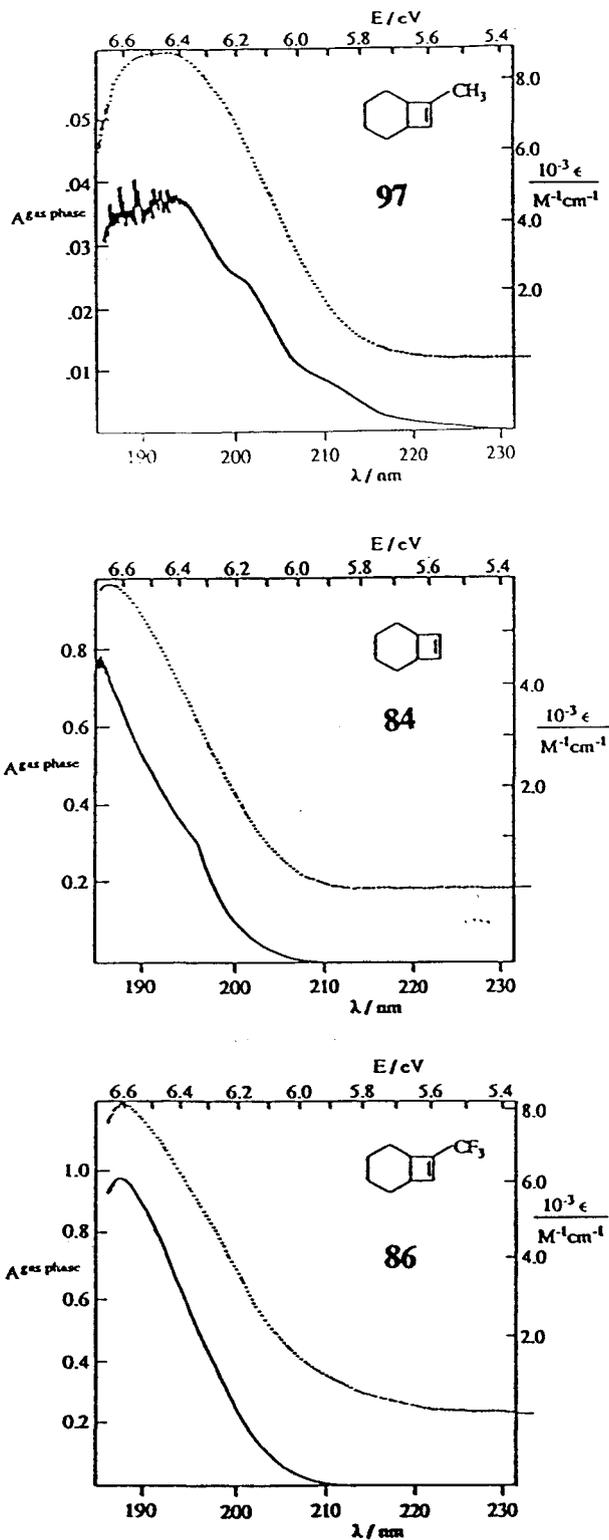


Figure 8 UV absorption spectra of 97, 84, 86 in the gas phase (—) and in deoxygenated pentane solution (...)

slopes of plots of product concentration vs. excitation dose constructed from small scale runs that were monitored between 0.3% and 3% conversion of starting material. Product yields are 56%, 34%, 3%, and 7% for **87**, **88 + 89**, **90** and **91** respectively. Typical plots of this type are shown in figure 9. These plots were linear over the conversion range investigated. The material balance is estimated to be at least 99% at 3% conversion.

6.2 Identification of the products from irradiation of 86

The photoproducts **87**, **88**, and **89** are identified on the basis of their ^1H nmr, ^{13}C nmr, IR, UV absorption, and mass spectra, and by comparison to the UV spectra and the ^1H nmr coupling constants $J_{\text{H3-H4}}$ of cis,cis-, cis,trans-1,3-cyclooctadiene, as well as cis,cis-, cis,trans-, trans,cis-2-methyl-1,3-cyclooctadiene. These data are collected in table 3.

6.2.1 Identification of the major product 87

The major product **87** from irradiation of 7-trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**) has a parent ion in its mass spectrum at $m/e = 176$ indicating that it arises by rearrangement of **86**. The exact mass is 176.0815; therefore, **87** has the molecular formula $\text{C}_8\text{H}_9\text{F}_3$. The proton NMR spectrum contains three olefinic hydrogen resonances: a triplet of quartets, a doublet of triplets and a broad doublet. A triplet of quartets centered at $\delta 6.27$ indicates that the proton at C_1 is split into a quartet by three fluorine atoms and a triplet by two protons at C_8 ($J_{\text{H1-F}} = 1.5$ Hz, $J_{\text{H1-H8}} = 7.9$ Hz). A doublet of triplets centered at $\delta 5.95$ is due to the proton at C_4 which is split by two protons at C_5 and one proton at C_3 ($J_{\text{H3-H4}} = 11.3$ Hz, $J_{\text{H4-H5}} = 7.1$ Hz). A broad doublet at $\delta 5.86$ is due to the proton H_3 which is split into a doublet by the proton at C_4 ($J_{\text{H3-H4}} = 11.3$ Hz) and is broadened by the weak coupling of fluorine. The other eight protons at C_6 , C_7 , C_5 and C_8 in the molecule appear at $\delta 1.48$, 1.51,

Figure 9 Plots of product concentration vs. excitation dose from 193 nm photolysis of **86** (0.02 M).

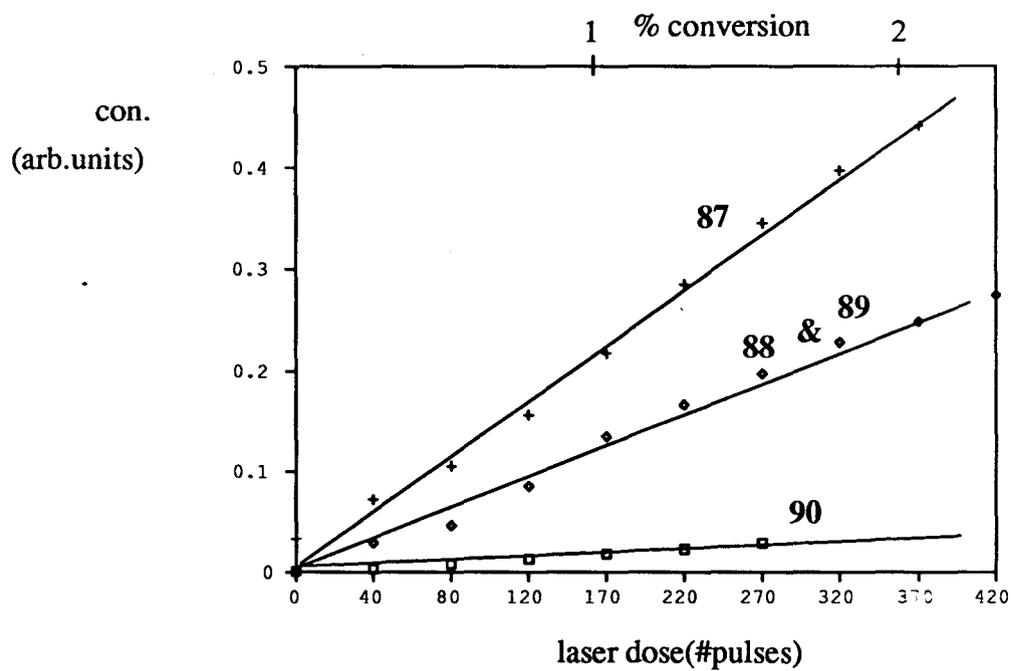


Table 3

	 (a)	 (a)	 (b)	 (b)	 (b)
UV λ_{\max} (nm)	228	230.5	~ 225	230	235
$J_{\text{H3-H4}}$ (Hz)	10.5	15.8	11.3	11.4	9.4

(a) reference 51

(b) reference 47

2.15, and 2.22 respectively. In addition, **87** is the most stable isomer of the three cyclooctadienes. It exhibits $J_{\text{H3-H4}} \approx 11.3$ Hz, similar to the vinylic coupling constant in *cis,cis*-2-methyl-1,3-cyclooctadiene ($J_{\text{H3-H4}} = 11.3$ Hz) and in the parent *cis,cis*-1,3-cyclooctadiene ($J_{\text{H3-H4}} = 10.5$ Hz).

The ^{13}C nmr spectrum of **87** showed nine resonances. The three resonances at 119.6, 133.5, 136.6 indicate three vinyl carbons. The resonance centered at 128.5 (quartet) is due to the quaternary carbon with $J_{\text{CF}} = 32$ Hz. The resonance centered at 124 (from 121 to 126) is due to the trifluoromethyl carbon which is split into quartet by three fluorine atoms with $J_{\text{CF}} = 274$ Hz. The four other resonances are in the aliphatic carbon region (21.9, 22.6, 27.2, 28.3). The UV absorption spectrum has λ_{\max} at 222.2 nm.

6.2.2 Identification of the minor products *cis,trans*-**89** and *trans,cis*-**88**

Cis,trans-**89** and *trans,cis*-**88** have mass spectral parent ions at $m/e = 176$ indicating that they arise by rearrangement of **86**. These two isomers undergo

facile thermal ring-closure to **86** at temperatures greater than 120⁰C in the vpc detector. The vinylic region in the ¹H nmr spectra of the two isomers **cis,trans-89** and **trans,cis-88** consist of three multiplets due to the protons at C₁, C₃, and C₄. The stereochemical assignment for **cis,trans-89** and **trans,cis-88** were made by comparisons of the vicinal vinylic coupling constants to those for the corresponding isomers of **97**. **89** has a broad doublet centered at $\delta 5.97$ from the proton at C₁ ($J_{H_1-H_8} = 6.5$ Hz), a multiplet centered at $\delta 5.69$ due to the proton at C₃, a multiplet centered at $\delta 5.62$ due to proton at C₄. The other eight protons at C₇, C₅, C₆, C₈ appear from $\delta 1.8$ to 2.55. The chemical shifts of the H₃- and H₄-protons in **89** are almost identical in deuteriochloroform solution. Addition of deuterobenzene (20%) splits the two signals apart enough to allow extraction of the vicinal coupling constant, $J_{H_3-H_4} = 15.8$ Hz), which verifies its identity as **cis,trans-89**. The ¹³C nmr spectrum of **89** showed only seven resonances instead of the nine expected resonances. The two resonances missing are the quaternary carbon and the trifluoromethyl carbon. The three resonances at 121.47, 140.91, 146.35 are due to the vinyl carbon atoms. The four other resonances are in the aliphatic carbon region (26.96, 32.34, 32.96, 33.95). The ¹⁹F nmr spectrum shows a sharp singlet at -67.50. The UV absorption spectrum has λ_{max} at 234 nm, correlating quite well with those of **cis,trans-1,3-cyclooctadiene** ($\lambda_{max} = 230.5$ nm) and **cis,trans-2-methyl-1,3-cyclooctadiene** ($\lambda_{max} = 230$ nm).

The proton nmr spectrum of **trans,cis-88** contains three olefinic hydrogen resonances: a triplet of doublets, a doublet of triplets, and a doublet of multiplets. A triplet doublet centered at $\delta 5.87$ is due to the proton at C₄ which is split into a triplet by two protons at C₅ ($J_{H_4-H_5} = 8.3$ Hz) and a doublet by the proton at C₃ ($J_{H_3-H_4} = 9.3$ Hz). A doublet triplet centered at $\delta 6.01$ is due to the proton at C₁

which is split into a triplet by the two protons at C₈ ($J_{H1-H8} = 14.4$ Hz). A doublet multiplet centered at $\delta 6.12$ is due to the proton at C₃ ($J_{H3-H4} = 9.3$ Hz). The other eight protons appear at $\delta 2.35$ (C₅), 2.55 (C₅), 1.65 (C₆), 2.25 (C₆), 1.79 (C₇), 1.45 (C₇), 2.45 (C₈), 2.11 (C₈). The ¹⁹F nmr spectrum shows a sharp singlet at -61.3. The UV absorption spectrum of **trans,cis-88** has λ_{max} at 236 nm, correlating quite well with those of **trans,cis-2-methyl-1,3-cyclooctadiene** ($\lambda_{max} = 235$ nm).

6.3 Control photolysis experiments

To ensure that the formation of **cis,trans-** and **trans,cis-2-trifluoromethyl-1,3-cyclooctadienes** were not due to secondary photolysis of the **cis,cis-isomer**, the following control experiment was carried out. A deoxygenated pentane solution containing **86** (0.03M) and a mixture of **Z,Z-** and **E,Z-3-ethylidenecyclohexene (7:3) (92)** (3.10^{-4} M) was irradiated with the Ar/F₂ excimer laser for 320 pulses (1 pulse per second). **92** was also used as internal vpc standard. After about 5% conversion, the photoproducts of **86** could be detected by vpc analysis of the photolysate and were similar to those obtained in the absence of **92**. The relative amounts of **Z,Z-** and **E,Z-92** changed by less than 3%. In other words, photoisomerization of **Z,Z-** and **E,Z-92** did not occur to a significant extent during the photolysis. This experiment shows that the two isomers **cis,trans-** and **trans,cis-2-trifluoromethyl-1,3-cyclooctadiene** are the primary photolysis products of **86** and do not arise from secondary photolysis of **cis,cis-2-trifluoromethyl-1,3-cyclooctadiene (87)**.

In order to obtain a semi-quantitative measure of relative product quantum yields from direct photolysis of **86** and **84**, the following experiment was carried out. A deoxygenated pentane solution containing **86** (0.02 M) and isooctane (10^{-3} M) was irradiated with the Ar/F₂ excimer laser in a small scale run that was monitored between 0.3% and 2% conversion. A deoxygenated pentane solution

$$[35] \frac{\left[\begin{array}{c} \text{Slope} \\ \text{Cyclohexene} \end{array} \right]_{\text{CF}_3}}{\left[\begin{array}{c} \text{Slope} \\ \text{Cyclohexene} \end{array} \right]_{\text{H}}} = \frac{\phi_{\text{CF}_3}}{\phi_{\text{H}}} = 0.22$$

containing **84** (0.02 M) and isooctane (10^{-3} M) was irradiated concurrently under identical conditions. The relative quantum yields for cyclohexene which was produced from the photolysis of **86** and **84** were calculated as the ratio of slopes from plots of the yield of cyclohexene (relative to internal standard) vs. dose for the two compounds using Equation 35. The quantum yields for product

Table 4

Diene distributions and fragmentation quantum yields from direct photolysis of substituted bicyclo[4.2.0]oct-7-enes

R	$\frac{\text{cc}}{\text{ct+tc}}$	$\phi_{\text{c,c-diene}}^{(a)}$	$\phi_{\text{c,t+l,c-dienes}}^{(a)}$	$\phi_{\text{cyclohexene}}$
CF ₃	1.6	0.186	0.106	0.02
H	1.4	0.100	0.075	0.11
CH ₃	1.4	0.049	0.038	0.10

(a) from ref.²⁸

formation from **86** were then calculated using a value of $\phi = 0.14$ for the quantum yield of cyclohexene from photolysis of **84** at 193 nm.²⁷ These results are collected in Table 4.

6.4 Calibration of GC detector

To ensure that 2-trifluoromethyl-cis,cis-1,3-octadiene is a major product and cyclohexene is a minor product, the following calibration experiment was performed. Solutions of isooctane A (10^{-4}M), **86** (10^{-4}M), **90** (10^{-4}M), **87** (10^{-4}M) in pentane were prepared. Various mixtures were then prepared and analysed by vpc. The slopes of plots of products' area over internal standard's area which were constructed by vpc analysis of these solutions vs. moles of products over moles of internal standard are shown in Figure 10. The relative slopes of these plots describe the relative response of the detector towards the various products. The quantum yields shown in Table 4 have been corrected taking this into account.

6.5 Triplet sensitized isomerization of **87**

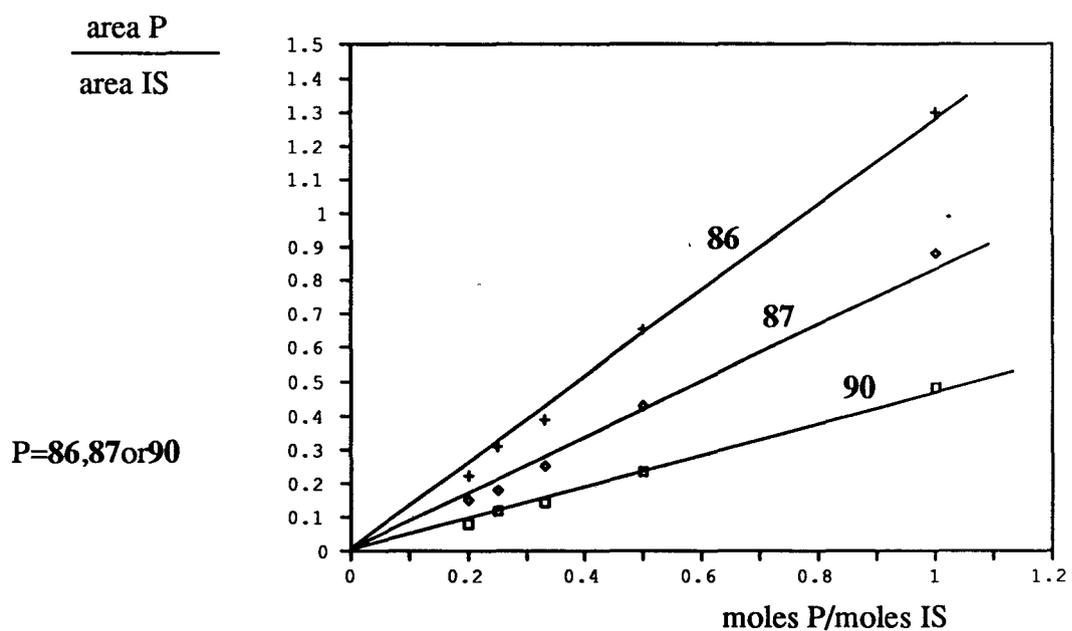
A mixture of 4-methoxyacetophenone (0.002 M) and **87** (0.01 M) in pentane was deoxygenated and irradiated at 300 nm for ca. two minutes. Two major products were formed. Coinjection of this solution with a solution of **86** in pentane that had been photolysed at 193 nm to 3% conversion showed that the two products are identical to the two minor products of photolysis of **86**. This shows that these two products are geometrical isomers of cis,cis-2-trifluoromethyl-1,3-cyclooctadiene.

7. Discussion

It is well known that cyclobutenes have two low-lying singlet excited states in the gas-phase and in solution: the π,π^* and the $\pi,R(3s)$ Rydberg states. This is verified by the UV absorption spectra of **84** and **97**. Both states are similar in energy and could be responsible for the major products of photolysis of alkylcyclobutenes. Excitation of the π,π^* state could lead to both ring-opening and cycloreversion by pericyclic mechanisms. Leigh and co-workers²⁷ have

Figure10

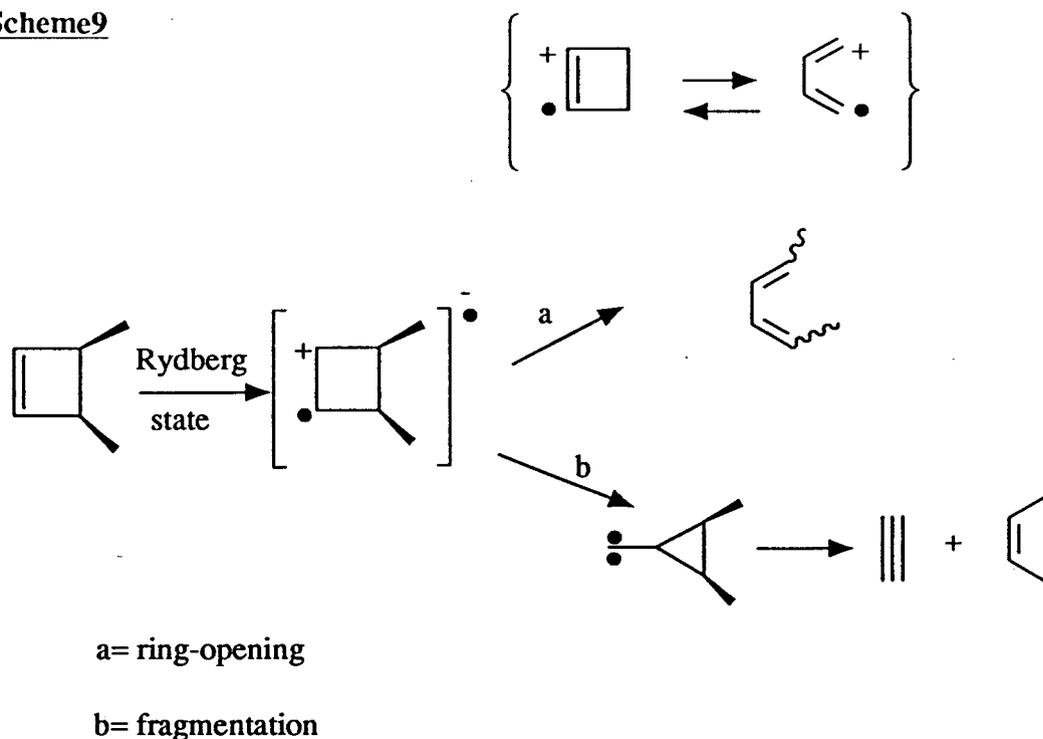
Plots of area products / area IS vs.
moles products / moles IS



shown that ring-opening is non-stereospecific and suggested that the reaction is largely non-concerted.

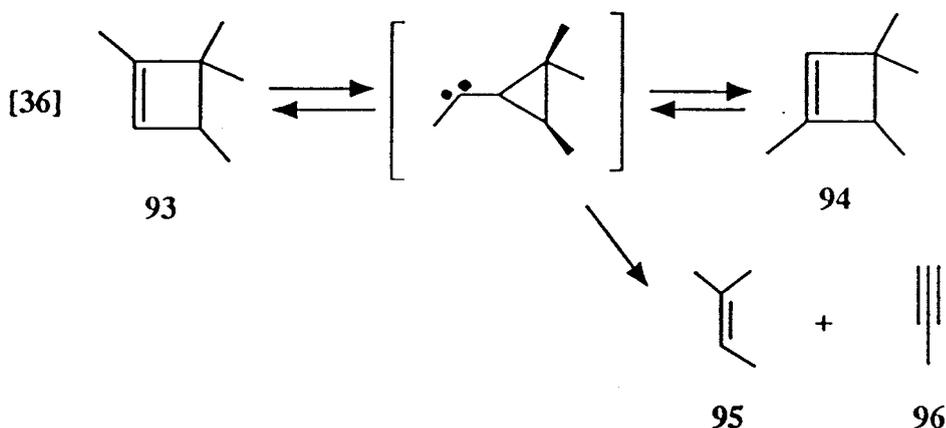
It has been suggested that the $\pi, R(3s)$ Rydberg state could also lead to both ring-opening and formal cycloreversion or fragmentation. The simple model of Mulliken for alkene Rydberg states views the Rydberg state as a semi-ionized species which has radical-cation character at the C=C bond as shown in Scheme 9. Cyclobutene radical-cations are known to yield butadiene radical-cations in

Scheme 9



the gas phase⁴⁸ and, in special cases, in solution.⁴⁹ Therefore, it is possible that ring-opening occurs from the $\pi, R(3s)$ state. Stereospecific fragmentation could proceed from cyclopropyl carbenes formed by [1,2]-alkyl migration (ring contraction^{50,40,27,32}). This photoreaction is characteristic of $\pi, R(3s)$ Rydberg state excitation. Indirect evidence for the involvement of cyclopropyl carbenes in cyclobutene photolysis was provided by Clark and Leigh,³² through the

observation of the photoisomerization of 1,3,4,4-tetramethylcyclobutene (**93**) and 1,3,3,4-tetramethylcyclobutene (**94**) in low quantum yield (ca. 0.02). The most



reasonable pathway for this interconversion is shown in Eqn.36. However, a photochemically allowed $\sigma_{2s} + \sigma_{2s}$ cycloreversion pathway would also lead to the same products **95** and **96**. Therefore, although this study provided good evidence for the formation of cyclopropyl carbenes in the photolyses of alkylcyclobutenes, it did not allow evaluation of what proportion of the fragmentation process proceeds via the carbene pathway. A study of the photochemistry of cis-, trans-1,3,4-trimethylcyclobutene and cis-, trans-1,2,3,4-tetramethylcyclobutene was carried out to attempt to deal with the question of π, π^* and $\pi, R(3s)$ involvement. The results suggested that at least two excited states contribute to ring-opening in these compounds, and that orbital symmetry factors do not play a consistent role in controlling the stereochemistry of the reaction. However, comparison of product distributions throughout the series cis-, trans-3,4-dimethylcyclobutene, cis-, trans-1,3,4-trimethylcyclobutene, cis-, trans-1,2,3,4-tetramethylcyclobutene did not reveal any trends from which an assignment could be made.

From the study of the photochemistry of norbornene, we have shown that

trifluoromethyl-substitution (at the C=C bond) raises the Rydberg state energies in norbornene without altering the energy or localized character of the π,π^* state. The photochemistry of 2-trifluoromethylnorbornene can be assigned to reaction only from the π,π^* singlet state and is much cleaner than the photochemistry of norbornene. Therefore, trifluoromethyl-substitution is a good candidate to use to investigate pure π,π^* photochemistry in simple cyclobutenes, without complications from Rydberg state excitation. Spectroscopic results for 7-trifluoromethylbicyclo[4.2.0]oct-7-ene (**86**), bicyclo[4.2.0]oct-7-ene (**84**) and 7-methylbicyclo [4.2.0]oct-7-ene (**97**), reveal the same trends as those observed in the analogous norbornene derivatives. They show that while the $\pi,R(3s)$ state is lower in energy than the π,π^* in **84** and **97**, the ordering is reversed in **86**. The results of direct photolysis of **97**, **84** and **86** listing the ratios of formally-allowed to formally-forbidden dienes and the relative fragmentation quantum yields for the series are collected in Table 4. The quantum yield for ring-opening increases in the order **97** < **84** < **86**. Thus, ring-opening products are predominantly derived from the π,π^* state. Moreover, since the distribution of isomeric dienes from photochemical ring-opening of **97**, **84** and **86** do not change markedly throughout the series, the π,π^* state is also responsible for the non-stereospecificity observed. The non-stereospecificity associated with the photochemical ring-opening of alkylcyclobutenes cannot be assigned to some constituent of the reaction that arises from Rydberg state excitation as suggested previously.

On the other hand, the quantum yield of cyclohexene from the 7-methyl derivative is approximately equal to that from the parent cyclobutene, and is much higher than that from the 7-trifluoromethyl derivative. This is a good indication that the formal cycloreversion reaction is derived largely from the $\pi,R(3s)$ singlet state, presumably by the cyclopropyl carbene pathway discussed

earlier. The small "residual" yield of cyclohexene formed from **86** may be due to a minor (π, π^*) component of the reaction that proceeds by the $\sigma_{2s} + \sigma_{2s}$ mechanism.

CHAPTER III

SUMMARY AND CONCLUSIONS

The photochemistry of simple alkenes as well as simple cyclobutenes is often complex due to the involvement of two singlet excited states of comparable energies: the π, π^* valence and the $\pi, R(3s)$ Rydberg states. The far-UV solution phase photochemistry of 2-trifluoromethylnorbornene (**68**) shows significant differences compared to that reported previously for norbornene (**27**) under similar conditions. The photochemical results for **68**, compared to those for **27**, are consistent with an inversion of the ordering of the π, π^* and the $\pi, R(3s)$ singlet states in these two compounds: **68** has the π, π^* state as the lowest singlet state while **27** has the $\pi, R(3s)$ state as the lowest singlet state. The gas-phase UV absorption, electron energy loss, and HeI photoelectron spectra of **68** and **27** are all consistent with these conclusions. It is proposed that trifluoromethyl-substitution raises the energies of Rydberg states due to the strong inductive electron-withdrawing CF_3 group, without altering the energy or localized character of the π, π^* state. The photoreactivity of 2-trifluoromethylnorbornene (**68**) is typical of π, π^* state excitation. The $\pi, R(3s)$ Rydberg state does not contribute to the photochemistry of **68**. In the photolysis of cyclobutenes, both π, π^* and $\pi, R(3s)$ Rydberg states are responsible for the major products obtained. Trifluoromethyl substitution was used to investigate pure π, π^* photochemistry in simple cyclobutenes, without complication from the Rydberg States. The gas-phase UV absorption and the HeI

photoelectron spectroscopy of bicyclo[4.2.0]oct-7-ene (**84**), 7-trifluoromethyl bicyclo[4.2.0]oct-7-ene (**86**) and 7-methylbicyclo[4.2.0]oct-7-ene (**97**) indicate that the $\pi, R(3s)$ Rydberg state is the lowest energy state in **84** and **97** and the π, π^* state is the lowest energy state in **86**. Direct photolysis of **84**, **86**, and **97** in pentane with monochromatic far-UV (193 nm) light leads to competitive ring-opening to the corresponding cis,cis- and cis,trans-1,3-cyclooctadiene derivatives, as well as fragmentation to cyclohexene and alkyne. The quantum yield for fragmentation from **97** is approximately equal to that from **84** and is much greater than that from **86**. These results suggest that fragmentation arises largely from the Rydberg state, presumably via cyclopropyl carbenes formed by [1,2]-alkyl migration. The quantum yields and distribution of isomeric dienes of **84**, **86**, and **97** have been measured. The results indicate that ring-opening is non-stereospecific and arises almost exclusively from the π, π^* state.

CHAPTER IV

Experimental

1. General

^1H nmr spectra were recorded on Varian EM390 (90 MHz) or Bruker AM500 (500 MHz) spectrometers in deuteriochloroform solution. ^{13}C nmr and ^{19}F nmr spectra were recorded at 125.6 and 235.4 MHz, respectively, on the Bruker AM500. All spectra are reported in parts per million (δ) downfield from tetramethylsilane (CFCl_3 for the ^{19}F spectra). Mass spectra were recorded on a VG 7070 mass spectrometer interfaced with a Varian 3700 gas chromatograph, equipped with DB-1 or DB-1701 (30 m x 0.25 mm; Chromatographic Specialties, Inc.) fused silica capillary columns. Exact masses were determined on a VGH ZABE mass spectrometer, and employed a mass of 12.000000 for carbon. Ultraviolet absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrometer equipped with a Model 3600 Data Station. The spectrometer sample compartment was continuously flushed with dry nitrogen. Samples were contained in 1 cm. Suprasil UV cells (Hellma) which were fitted with a glass stopcock for gas-phase spectra. Gas-phase samples were prepared by introducing the compound into the cell from a cold-finger on a vacuum line whose pressure was measured by a Varian 801 vacuum gauge. A background spectrum, recorded under identical conditions with the empty cell (evacuated to 30 mtorr), was electronically subtracted from the sample spectra. Reference and sample solutions for the solution-phase spectra were deoxygenated with a stream of

argon for 10 minutes prior to recording the spectrum. Infrared spectra were recorded on a Perkin-Elmer 283 spectrometer in carbon tetrachloride solution or as the neat liquids (where noted); spectra are reported in wavenumbers, calibrated using the 1601.9 cm^{-1} polystyrene absorption.

UV photoelectron spectra were recorded in conventional mode using a spectrometer which has been described in detail elsewhere³⁹, and are averages of 50-100 scans. The spectra were calibrated relative to the peak at 15.67 eV corresponding to the ionization of argon.

Analytical vpc separations were carried out with a Hewlett-Packard 5890 gas chromatograph (injector temperature = 120°C) equipped with a flame ionization detector, a borosilicate megabore capillary column (30mx0.75mm SPB-1; Supelco, Inc.), and a Hewlett-Packard 3396 recording integrator.

Semi-preparative vpc separations employed a Hewlett-Packard 5750B gas chromatograph equipped with a thermal conductivity detector (detector temperature = 120°C) and one of the following stainless steel columns (Supelco, Inc.): (a) 3% OV-17 on 80/100 Chromosorb WAW (6' x 0.25"); (b) 15% Carbowax 20M on 60/80 Chromosorb W (5' x 0.25"); (c) 3.8% UCW 982 on 80/100 Supelcoport (24' x 0.25"); (d) 20% 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb 80/100 PNAW (12' x 0.25"); (e) 1,2,3-tris(2-cyanoethoxy)propane (TCEP) on Chromosorb 80/100 PNAW (5' x 0.25"). The hydrocarbon solvents used in the photolyses and UV absorption studies, n-pentane, 2,2,4-trimethylpentane (isooctane), were Baker Photrex grade and used as received from the suppliers. Dimethylsulfoxide (Fisher Reagent) was distilled from calcium hydride. Chlorobenzene and toluene were used as received from Fisher Chemical Co. Cyclohexene, cis,cis-1,3-cyclooctadiene, acetophenone, 4-methoxyacetophenone, and potassium *tert*-butoxide were all

used as received from Aldrich Chemical Co. Trifluoromethyl iodide was used as received from Columbia Organics. E,E- and E,Z-3-ethylidenecyclohexene (92) were synthesized as a mixture according to the published procedure,⁵² and enriched in one of the isomers by semi-preparative vpc (column c). Norbornene (Aldrich) was vacuum distilled before use. 2-Methylnorbornene was available from an earlier study⁵³ and was purified by vacuum distillation, followed by semi-preparative vpc (column a).

Synthetic photolyses employed a Hanovia 450 watt medium pressure mercury lamp with quartz or Pyrex immersion wells (Ace Glass, Inc.), or a Rayonet photochemical reactor fitted with 2 to 12 lamps (253.7 or 300 nm) and a merry-go-round apparatus.

2. Preparation and purification of 2-trifluoromethylnorbornene

2-Trifluoromethylnorbornene (68) was prepared using the following typical procedure.^{54,55} Norbornene (10 g, 0.106 mol) was placed in a thick-walled Pyrex tube (6" x 1" o.d.) fitted at one end with a Rotaflo stopcock. The tube was attached to a vacuum line via a rubber hose, and degassed twice by the freeze-pump-thaw method. It was then placed on a balance in a dewar containing liquid nitrogen, and trifluoromethyl iodide (40.0 g, 0.2 mol) was introduced through a separate stopcock on the vacuum line. The stopcock was closed, and the tube was removed from the vacuum line. After allowing the contents to melt and the norbornene to dissolve, the tube was placed in a quartz dewar containing dry ice and isopropanol at about -30°C in a Rayonet reactor. The solution was then irradiated with twelve 300 nm Rayonet lamps until it turned yellow (about six hours), periodically adding dry ice to the dewar to maintain a temperature of about -30°C. The tube was reattached to the vacuum line and the excess trifluoromethyl iodide was separated from the product by distillation into another

sealable Pyrex tube (cooled with liquid nitrogen). The slightly yellow liquid that remained (30.5 g), was used without further purification in the following step.

On the basis of its 90 MHz ^1H nmr spectrum (Varian EM390; CDCl_3 ; $\delta = 1.27$ (t, 2H), 1.4-1.9 (m, 4H), 2.1-2.5 (m, 3H), 4.14 (m, 1H), the major component of the liquid was identified as 2-iodo-3-trifluoromethylbicyclo[2.2.1]heptane.⁵⁴

A portion of the product from the above reaction (2.0 g, 6.8 mmol), was placed in a large Pyrex tube containing deoxygenated dimethyl sulfoxide (25 ml) and potassium *tert*-butoxide (1.5 g), affording a deep yellow solution. The tube was placed in a dry ice/isopropanol bath, evacuated and sealed, and then heated at 60°C for 12 hours. The tube was opened and the deep red reaction mixture was placed in a separatory funnel. Water (25 ml) was added and the resulting mixture was extracted with *n*-pentane (4 x 15 ml). The combined extracts were washed thrice with water, dried over anhydrous sodium sulfate and filtered. Careful removal of the solvent by distillation afforded a yellow liquid which was bulb-to-bulb distilled under vacuum to yield a colourless liquid that was shown to consist of 2-trifluoromethylnorbornene **68** (0.44 g, 2.7 mmol, 40%) contaminated with a small amount (< 5%) of residual *n*-pentane and dimethyl sulfoxide (by vpc analysis). Compound **68** was purified by semi-preparative vpc, using one pass through column (a) to remove residual DMSO followed by two passes through column (b), after which it was >99.8% pure by vpc. Compound **68** has the following spectral properties: ^1H nmr: $\delta = 1.07$ (m, 1H), 1.19 (m, 2H), 1.53 (m, 1H), 1.73 (m, 2H), 2.98 (br s, 1H), 3.08 (br s, 1H), 6.46 (br s, 1H); ^{13}C nmr: $\delta = 24.4, 24.7, 41.3, 42.5, 49.1, 124.2, 137.8, 138.7$; ^{19}F nmr: $\delta = -65.3$; IR (neat): 3010 (sh, w), 2982 (s), 2881 (m), 1626 (m), 1450 (w), 1356 (s), 1299 (s), 1269 (m), 1233 (m), 1150 (s), 1101 (s), 1037 (s), 876 (m), 843 (m), 831 (w), 730 (w), 688 (m); MS (m/e (I)): 162 (6), 134 (93), 135 (7), 127 (8), 115(9), 114 (10), 93

(4), 91 (4), 84 (6), 65 (6); Mass: Calcd. for $C_8H_9F_3$: 162.0656. Found: 162.0664; UV (λ_{max} (ϵ)): 194 (3190).

3. Preparation and purification of bicyclo[4.2.0]oct-7-ene

Bicyclo[4.2.0]oct-7-ene (**84**) was prepared and purified according to the published method,⁴⁴ and exhibited 1H nmr, IR, and mass spectral characteristics identical in all essential respects to those previously published.⁴⁵

Cis,cis-1,3-cyclooctadiene (200 g previously bulb-to-bulb distilled under vacuum (ca. 0.02 mm Hg)), n-heptane (400 mL), and acetophenone (6.66 g) were placed in a large Pyrex tube and deoxygenated with a stream of dry nitrogen. The tube was placed in a dry ice/isopropanol bath, evacuated and sealed, and then heated at 80°C (using oil bath). The solution was irradiated with a 450 Watt Hanovia medium pressure mercury lamp. A complete conversion was reached after 10 days. At the end of the irradiation period, a small amount of polymeric material began to coat the well. The irradiated solution that is a mixture of bicyclo[4.2.0]oct-7-ene, cis,cis-1,3-cyclooctadiene, cis,trans-1,3-octadiene, and n-heptane, was filtered and then was carefully distilled through a long Vigreux column. The fraction boiling at 90-95°C is bicyclo[4.2.0]oct-7-ene (about 97% pure).

4. Preparation and purification of 7-trifluoromethylbicyclo[4.2.0]oct-7-ene

(86)

86 was prepared using the same typical procedure for 2-trifluoromethylnorbornene (**68**). **84** (7.3 g, 0.068 mol) was placed in a thick-walled Pyrex tube (6" x 1" o.d.) fitted at one end with a Rotaflo stopcock. The tube was attached to a vacuum line, degassed with two freeze-pump-thaw cycles, and then placed on a balance in a dewar containing liquid nitrogen. Trifluoromethyl iodide (10.0 g, 0.05 mol) was condensed into the tube through a

separate stopcock on the vacuum line. The stopcock was closed, and the tube was removed from the vacuum line. After allowing the contents to melt and mix, the tube was placed in a quartz dewar containing dry ice/isopropanol at about -30°C in a Rayonet reactor. The solution was then irradiated with twelve 300 nm Rayonet lamps until it turned yellow (about fourteen hours), periodically adding dry ice to the dewar to maintain a temperature about -30°C . After photolysis, the tube was reattached to the vacuum line and the excess trifluoromethyl iodide was separated from the product by distillation into another sealable Pyrex tube (cooled with liquid nitrogen). The slightly yellow liquid that remained (16.1 g), was used without further purification in the following step but was identified as consisting largely of 7-iodo-8-trifluoromethylbicyclo[4.2.0]octane on the basis of its 90 MHz ^1H nmr spectrum (Varian EM390; CDCl_3 ; $\delta = 1.5$ (cplx m, 8H), 2.9 (cplx m, 2H), 4.5 (m, 1H), 6.2 (m, 1H).

A portion of the product from the above reaction (11.8 g, 0.039 mol) was placed in a large Pyrex tube containing deoxygenated dimethyl sulfoxide (110 ml) and potassium *tert*-butoxide (6.6 g), affording a deep yellow solution. The tube was placed in a dry ice/isopropanol bath, evacuated, sealed and then heated at 60°C for 12 hours. The tube was opened and the deep red reaction mixture was placed in a separatory funnel. Water (125 ml) was added and the resulting mixture was extracted with *n*-pentane (5 x 25 ml). The combined extracts were washed thrice with water, dried over anhydrous sodium sulfate and filtered. Careful removal of the solvent by distillation afforded a yellow liquid which was bulb-to-bulb distilled under vacuum to yield a colourless liquid that was shown to consist of 7-trifluoromethylbicyclo[4.2.0]oct-7-ene **86** (3.5 g, ca. 30% yield from **84**) contaminated with a small amount (< 7%) of residual *n*-pentane and dimethyl sulfoxide (by vpc analysis). Compound **86** was purified by semi-preparative vpc,

using one pass through column (e) to remove residual DMSO followed by two passes through column (c), after which it was >99.8% pure by vpc. Compound **86** has the following spectral properties: ^1H nmr: δ = 1.43 (cplx m, 2H), 1.57 (cplx m, 3H), 1.68 (cplx m, 1H), 1.74 (cplx m, 2H), 2.82 (m, 1H), 3.06 (m, 1H), 6.49 (m, 1H); ^{13}C nmr (C_7 not detected), δ (CDCl_3) = 17.85, 18.40, 23.44, 38.46, 39.77, 119.71 (q, J = 269 Hz), 142.20; ^{19}F nmr, δ (CDCl_3) = -67.5; IR (neat), 3060 (w), 2940 (s), 2871 (m), 1650 (s), 1450 (m), 1360 (w), 1330 (s), 1300 (m), 1270 (m), 1250 (w), 1220 (m), 1150 (s), 1125 (s), 1050 (m), 1010 (m), 940 (m), 920 (w), 870 (m), 820 (m); MS, $m/e(I)$ =176(4), 161(26), 148(27), 147(27), 146(12), 141(27), 134(26), 127(42), 115(31), 107(56), 91(21), 80(23), 79(100), 77(23), 67(26), 54(21); Mass: Calcd. for $\text{C}_9\text{H}_{11}\text{F}_3$: 176.0825; Found: 176.082

5. Synthesis of photoproducts

5.1 The photolysis products of 2-trifluoromethylnorbornene (68)

Analytical and preparative-scale photolysis experiments employed the pulses (193 nm, ca. 15 ns, ca. 40 mJ; 0.5 Hz repetition rate) from a Lumonics TE-861M excimer laser filled with an argon/fluorine/helium mixture. Analytical photolyses were carried out at ambient temperature (ca. 22°C) in rectangular cells constructed from 10 x 20 mm rectangular Suprasil tubing (Vitro Dynamics), using a 0.5-1 Hz laser pulse repetition rate. Solutions of **68** and isooctane (as internal standard) in n-pentane were deoxygenated with argon prior to irradiation, and the sample was agitated during photolysis with a magnetic stirrer. The course of photolysis was monitored between 0.2 and 4% conversion, with aliquots being removed periodically for vpc analysis. Relative product yields were determined from the slopes of concentration vs. laser dose constructed for all components of the mixture relative to the internal standard. Preparative scale (ca. 300 mg) photolyses were carried out in 2" x 2" cylindrical cells with Suprasil

windows (ca. 50 mL volume), using a 6 Hz laser pulse repetition rate. The deoxygenated solutions were vigorously stirred during photolysis which was monitored by vpc to ca. 40% conversion. After photolysis, the pentane was carefully distilled from the mixture through a long Vigreux column. The residue from the distillation was bulb-to-bulb distilled under vacuum, and the products were separated by preparative vpc using column (d). One product (ca. 6% yield) could not be isolated in pure form since it eluted just slightly before **66** on all three vpc columns employed in this work. The photolysis products, listed in order of increasing vpc retention time on this column, had the following spectral characteristics:

1-Trifluoromethylbicyclo[4.1.0]hept-2-ene (69)

¹H nmr: δ = 0.92 (t, 1H), 1.21 (m, 1H), 1.57 (m, 1H), 1.74 (m, 2H), 1.93 (m, 1H), 2.03 (m, 1H), 5.64 (m, 1H), 6.02 (dd, 1H).

¹³C nmr: 14.7, 17.1, 18.1, 20.0, 122.7, 125.7, 127.7 (q).

¹⁹F nmr: -65.3.

IR: 3050 (w), 2940 (m), 2870 (w), 1442 (w), 1412 (m), 1394 (m), 1354 (s), 1334 (s), 1318 (s), 1181 (m), 1162 (s), 1147 (s), 1134 (s), 1067 (m), 927 (w), 689 (m).

MS: (m/e(I)): 162 (36), 147 (22), 141 (7), 127 (64), 114 (6), 115 (5), 93 (100), 83 (6), 77 (54), 65 (23).

Mass: Calcd. for C₈H₉F₃: 162.0656. Found: 162.0665.

UV: λ_{max} = 200 (ϵ = 830).

1-Methyl-2-trifluoromethyl-1,3-cyclohexadiene (70)

¹H nmr: δ = 1.95 (br s, 3H), 2.14 (m, 2H), 2.21 (m, 2H), 5.78 (dt, 1H), 6.00 (tt, 1H).

¹³C nmr: 20.3, 21.6, 30.7, 120.7, 124.9 (quaternary carbons not detected).

¹⁹F nmr: -60.3.

IR: 2940 (s), 2880 (w), 2840 (w), 2340 (w), 1650 (w), 1600 (w), 1420 (w), 1410 (w), 1360 (s), 1305 (s), 1160 (s), 1120 (s), 1030 (s), 887 (w), 704 (w), 636 (m).

MS: (m/e(I)): 162 (24), 147 (17), 141 (4), 134 (10), 127 (60), 93 (100), 91 (40), 77 (50), 69 (8), 65 (16).

Mass: Calcd. for C₈H₉F₃: 162.0656. Found: 162.0662.

UV: λ_{\max} = 263 (ϵ unknown).

2-trifluoromethyl-1,3-cycloheptadiene (71)

¹H nmr: δ = 1.86 (m, 2H), 2.37 (m, 4H), 5.84 (d, 1H), 6.04 (dt, 1H), 6.46 (t, 1H).

¹³C nmr: 25.1, 29.9, 31.5, 119.9, 134.9, 137.0 (quaternary carbons not detected).

¹⁹F nmr: -68.0.

IR: 2940 (m), 1360 (w), 1305 (s), 1180 (s), 1120 (s).

MS: (m/e(I)): 162 (65), 147 (43), 134 (22), 127 (47), 101(8), 93 (100), 91 (31), 77 (35), 69 (8), 65 (17).

Mass: Calcd. for C₈H₉F₃: 162.0656. Found: 162.0651.

UV: λ_{\max} = 243 (ϵ unknown).

Chlorobenzene-sensitized photolysis of a deoxygenated pentane solution (70 mL) containing **68** (0.01 M), chlorobenzene (0.02 M), and isooctane (0.001 M) was carried out in a quartz tube with a Rayonet reactor fitted with twelve 253.7 nm lamps. The photolysis was continued until ca. 60% conversion of **68**, with periodic monitoring by vpc, and final analysis by gc/ms. These analyses showed that the photolysate consisted of four main volatile (C₁₀ or less) products, in addition to several products that eluted only at relatively high column temperatures. Gc/ms analysis of the volatile components showed that two of the products had molecular weights of 164 amu, while the other two had molecular weights of 142 amu and were tentatively identified as decane isomers on the basis of their fragmentation patterns. The major higher molecular weight products

had parent ions of 234 amu, corresponding to the free radical addition product of pentane to **68** (3 isomers). A relatively small peak with parent ion mass of 274 eluted at even longer time. This is the correct mass for a cycloaddition product of **68** with chlorobenzene. The first two volatile products were isolated from the photolysate by semi-preparative vpc (column c and d), after removal of the solvent and bulb-to-bulb distillation of the residue under vacuum. The structures of the two products, listed below in order of their elution from the SPB-1 megabore capillary column, were identified primarily on the basis of their ^1H nmr spectra.³⁸ They exhibit the following spectral characteristics:

Exo-2-trifluoromethylnorbornane (exo-74)

^1H nmr: $\delta = 1.17$ (m, 2H), 1.22 (m, 1H), 1.50 (m, 2H), 1.55 (m, 3H), 2.07 (m, 1H), 2.30 (br s, 1H), 2.43 (br s, 1H).

IR (CDCl_3): 2960 (s), 2880 (w), 1315 (w), 1275 (s), 1265 (w), 1220 (w), 1110 (s), 1040 (w).

MS: (m/e(I)): 164 (11), 149 (30), 136 (40), 122 (13), 103 (8), 95 (50), 77 (21), 68 (96), 67 (100), 55 (19), 44 (77)

Endo-2-trifluoromethylnorbornane (endo-74)

^1H nmr: $\delta = 1.27$ (m, 2H), 1.34 (br s, 2H), 1.37 (m, 1H), 1.57 (m, 1H), 1.73 (m, 2H), 2.30 (br s, 1H), 2.44 (br s, 1H) 2.47 (m, 1H).

IR (CDCl_3): 2960 (s), 2920 (w), 2880 (w), 1380 (br, w), 1320 (m), 1275 (s), 1260 (w), 1220 (w), 1180 (w), 1160 (s), 1130 (m), 1100 (br, w), 1050 (w).

MS: (m/e(I)): 164 (26), 149 (42), 136 (34), 122 (18), 103 (6), 95 (73), 85 (6), 77 (23), 68 (90), 67 (86), 55 (23), 44 (100).

5.2 The photolysis products of 7-trifluoromethylbicyclo[4.2.0]oct-7-ene (86)

Analytical and preparative-scale photolysis experiments employed pulses (193 nm, ca. 15 ns, ca. 40 mJ; 0.5 Hz repetition rate) from a Lumonics TE-861M

excimer laser filled with an argon/fluorine/helium mixture. Analytical photolyses were carried out at ambient temperature (ca. 22°C) in rectangular cells constructed from 10 x 20 mm rectangular Suprasil tubing (Vitro Dynamics), using a 0.5-1 Hz laser pulse repetition rate. Solutions of **84** and isooctane (as internal standard) in n-pentane were deoxygenated with argon prior to irradiation, and the sample was agitated with a magnetic stirrer during photolysis. The course of photolysis was monitored between 0.3 and 5% conversion, with aliquots being removed periodically for vpc analysis. Relative product yields were determined from the slopes of concentration vs. laser dose constructed for all components of the mixture relative to the internal standard. The concentration vs. time plots were linear up to at least 3% conversion. The response of the vpc detector toward **86**, **87**, and **90** was calibrated relative to the internal standard with standard solutions.

Preparative scale (ca. 300 mg) photolyses of **86** were carried out in 2" x 2" cylindrical cells with Suprasil windows (ca. 50 mL volume), using a 6 Hz laser pulse repetition rate and vigorous stirring of the deoxygenated solutions during photolysis to ca. 40% conversion (monitoring by vpc). After photolysis, the pentane was carefully distilled from the mixture on a rotary evaporator. The residue from the distillation was bulb-to-bulb distilled under vacuum, and the products were separated by preparative vpc using columns (d) and (e). Photolysis of **86** affords the four products shown in Eqn.34 in addition to one other (ca. 5%) which was not isolated. The trans,cis-2-trifluoromethyl-1,3-cyclooctadiene (**88**) and the cis,trans-2-trifluoromethyl-1,3-cyclooctadiene (**89**) were also prepared in more easily-isolable quantities by 4-methoxyacetophenone-sensitized or direct cis,trans-photoisomerization of the corresponding cis,cis-isomers in deoxygenated pentane solution (254 nm). These isomers are extremely sensitive

to the presence of acidic impurities. Detector temperatures of semi-preparative vpc separations higher than 120°C resulted in isomerization of **88** and **89** (especially) to the corresponding bicyclo[4.2.0]oct-7-ene derivative **86**. The injector and column operating temperatures of analytical vpc separations were kept low enough (120°C and 80-100°C, respectively) to avoid thermal isomerization of the products of photolysis of **86**. The trans,cis-isomer undergoes thermal cyclization at lower temperatures than the cis,trans-isomer does because of its greater degree of ring strain. The photolysis products, listed in order of increasing vpc retention time on vpc columns (d) and (e), had the following spectral characteristics:

Cis,cis-2-trifluoromethyl-1,3-cyclooctadiene (87)

¹H nmr: δ (CDCl₃) = 1.49 (m, 4H), 2.15 (m, 2H), 2.22 (m, 2H), 5.86 (d, J = 11.3 Hz, 1H), 5.95 (dt, J = 11.3, 7.1 Hz, 1H), 6.27 (tq, J=7.9, 1.5 Hz, 1H).

¹³C nmr: δ = 21.99, 22.66, 27.17, 28.32, 119.64, 123.8 (q, J = 274 Hz), 128.4 (q, J = 32 Hz), 133.49, 136.65.

¹⁹F nmr: δ (CDCl₃) = -67.4.

IR (neat): 3030 (w), 2940 (s), 2865 (m), 1660 (m), 1640 (w), 1460 (s), 1422 (m), 1360 (m), 1315 (s), 1270 (m), 1180 (s), 1160 (s), 1120 (s), 1080 (w), 1050 (s), 960 (m), 930 (m), 840 (m), 770 (m), 740 (s).

MS: (m/e(I)) = 176 (20), 161 (8), 148 (10), 147 (11), 127 (12), 121(18), 119 (22), 107 (18), 88 (100), 86 (41), 82 (21), 79 (34), 67 (9).

Mass: Calcd. for C₈H₁₁F₃: 176.0825; Found: 176.0815.

UV: λ_{max} = 222 nm (ϵ unknown).

Cis,trans-2-trifluoromethyl-1,3-cyclooctadiene (89)

¹H nmr: δ (CDCl₃) = 1.42 (m, 1H), 1.65 (m, 1H), 1.78 (dd, 1H), 2.13 (cplx d, 1H), 2.09 (cplx d, 1H), 2.24 (dt, 1H), 2.45 (cplx m, 1H), 2.54 (dt, 1H), 5.87 (dd,

$J=9.3, 8.3$ Hz, 1H), 6.00 (cplx d, $J=14.4$ Hz, 1H), 6.12 (d, $J=9.3$ Hz, 1H).

^{19}F nmr: δ (CDCl_3) = -61.3

IR (CDCl_3): 3015 (w), 2930 (s), 2858 (m), 1637 (w), 1596 (m), 1438 (w), 1392 (w), 1365 (w), 1295 (w), 1270 (s), 1220 (m), 1168 (s), 1139 (s), 1115 (s), 1098 (s), 1006 (w).

MS: (m/e(I)) = 176 (7), 147 (10), 141 (59), 134 (10), 127 (100), 115 (40), 114 (11), 109 (11), 107 (30), 95 (13), 91 (27), 80 (11), 79 (99), 77 (46), 69 (10), 65 (11), 51 (20), 41 (9), 39 (28).

Mass: Calcd. for $\text{C}_8\text{H}_{11}\text{F}_3$: 176.0825.

UV: $\lambda_{\text{max}} = 236$ nm (ϵ unknown).

Trans,cis-2-trifluoromethyl-1,3-cyclooctadiene (88)

^1H nmr: δ (CDCl_3) = 1.41 (m, 1H), 1.63 (m, 1H), 1.82 (m, 1H), 2.10 (cplx m, 2H), 2.25 (m, 1H), 2.42 (m, 1H), 2.55 (m, 1H), 5.91 (m, 2H), 6.22 (m, 1H), addition of 20% C_6D_6 to the solution caused the 5.91 multiplet to split into two complex doublets with splitting $J = 15.8$ Hz, the spectrum also contained signals at 1.41 (m, ca. 1H), 1.63 (m, ca. 2H), 2.08 (m, ca. 2H), 2.43 (m, ca. 2H), which COSY experiments demonstrated were not related to the others listed above.

^{13}C nmr: δ (CDCl_3) = 26.96, 32.34, 32.96, 33.95, 121.47, 140.91, 146.35, quaternary and CF_3 carbons not detected;

^{19}F nmr: δ (CDCl_3) = -67.5.

IR (CDCl_3): 3005 (w), 2935 (s), 2851 (m), 1637 (m), 1597 (m), 1437 (m), 1419 (w), 1374 (w), 1327 (w), 1301 (s), 1275 (s), 1167 (s), 1117 (s), 1040 (s), 977 (m), 962 (m), 824 (m), 809 (m).

MS: (m/e(I))=176 (8), 148 (9), 141 (49), 127 (93), 115 (34), 114 (9), 109 (11), 107 (28), 95 (10), 91 (23), 80 (22), 79 (100), 78 (10), 77 (41), 69 (10), 51 (16), 41 (8), 39 (24).

UV: $\lambda_{\text{max}} = 234 \text{ nm}$ (ϵ unknown).

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