2-CYCLOHEXENONE PHOTOADDITIONS

MECHANISTIC STUDIES
ON THE PHOTOADDITION REACTIONS OF SOME 2-CYCLOHEXENONES WITH NORBORNADIENE AND CYCLOPENTENE

By

PAUL W. RASMUSSEN, M.Sc.

A Thesis
Submitted to the Faculty of Graduate Studies
in Partial Fulfilment of the Requirements
for the Degree
Doctor of Philosophy

McMaster University
(October) 1969

DOCTOR OF PHILOSOPHY (1969)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario

TITLE: Mechanistic Studies on the Photoaddition Reactions of Some 2-Cyclohexenones with Norbornadiene and Cyclopentene

AUTHOR: Paul W. Rasmussen, B.Sc. (Acadia University)
M.Sc. (Acadia University)

SUPERVISOR: Dr. J. J. McCullough

NUMBER OF PAGES: vii, 123

SCOPE AND CONTENTS:

In order to gain mechanistic information of photoaddition reactions of 2-cyclohexenones, the additions of 2- and 3-methyl-2-cyclohexenone and 2-cyclohexenone to bicyclo[2.2.1]hepta-2,5-diene have been studied. Substituted 2-cyclohexenone products are obtained in addition to cyclobutane derivatives, and it is proposed that the former adducts arise from diradical intermediates and intramolecular hydrogen shifts. The photorearrangement of 4,4-dimethyl-2-cyclohexenone, and its photocycloaddition to cyclopentene, was studied in order to identify the enone excited state responsible for cycloaddition. These results, and naphthalene quenching experiments, indicate that all of the additions studied proceed *via* triplet excited states.

ACKNOWLEDGMENTS

It is a pleasure to thank Dr. J. J. McCullough for his interest and expert guidance during the course of this work. I would also like to thank Dr. R. A. Bell, Mr. B. Sayers, and Mr. J. Saunders for obtaining the 100 Mc nmr spectra, and Dr. J. Warkentin for kindly providing an authentic sample of 7-norbornane carboxylic acid.

Special thanks are due to Dr. C. W. Huang and Mr. F. F. Snyder for discussions which were both stimulating and enjoyable, and to Miss Edie Tingle, who maintained her aplomb while typing this thesis.

Financial assistance from the Chemistry Department, McMaster University, and the Ontario Department of University Affairs is gratefully acknowledged.

TABLE OF CONTENTS

INTRODUCTION

PART ONE: GENERAL

Organic chemistry, originally the study of the building material of living matter, is now more generally defined as the study of compounds of carbon. Similarly, organic photochemistry is the study of the effect of light on carbon compounds. Although the general field of organic chemistry has enjoyed a century of rapid growth, it was not until quantum mechanics provided a workable theory that photochemistry became a clearly defined area of research. Early observations, such as the bleaching of linen by light, and the ability of green plants to utilize sunlight, could then be correlated under the one theory. However, due to the fact that many organic photoreactions yield intricately structured products, or complicated mixtures, extensive study of the effects of light on organic compounds became possible only with the advent of modern instrumental methods for identification and separation, such as nuclear magnetic resonance spectroscopy and vapour phase chromatography. Since these methods became generally available, the wealth of data produced makes it a prime task of the organic photochemist to attempt to correlate research results into hypotheses which may be generally applicable.

In the absence of light (or in general, electromagnetic radiation) an organic molecule will normally occupy the lowest electronic state available to it. This "ground state" molecule[*] can then undergo various reactions, depending on the influence to which it is submitted, such as heat, acid, or other reagents. These reactions then constitute what is known as organic chemistry. However, in addition to the ground state, every organic molecule has available to it several other electronic states. These are known as "excited states", since they are of higher energy (and hence generally more reactive) than the ground state. Excited states are formed from the ground state by the absorption of ultraviolet or visible light, and organic photochemistry is concerned with the properties and reactions of these excited states.

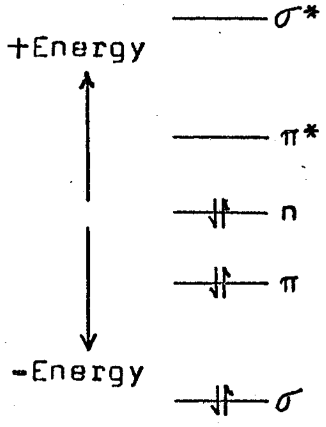
A large number of organic excited state reactions are now known[1], and consequently no attempt will be made here to discuss, or even enumerate, them. However, a discussion of photoadditions and photorearrangements of α,β-unsaturated ketones is pertinent to this thesis and will be presented in some detail. First of all, a short summary of the basic theory used in describing excited states will be given; the principles will be illustrated by reference to carbonyl compounds.

---

[*] Photochemical terminology used but not defined in this thesis may be found in J. N. Pitts, Jr., F. Wilkinson, and G. S. Hammond, Advan. Photochem., 1, 1 (1963).

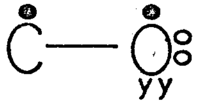
PART TWO: EXCITED STATE THEORY

All organic molecules can contain electrons which occupy three types of orbitals. These types are σ (sigma) and π (pi), both bonding in character, and n, or non-bonding, orbitals[2]. These are the orbitals which are normally populated in the ground state. Orbitals of higher energy are called anti-bonding, designated by an asterisk, and are not usually populated in the ground state. Hence, the molecular orbitals of a carbonyl (C=O) group may be represented by the energy level diagram:



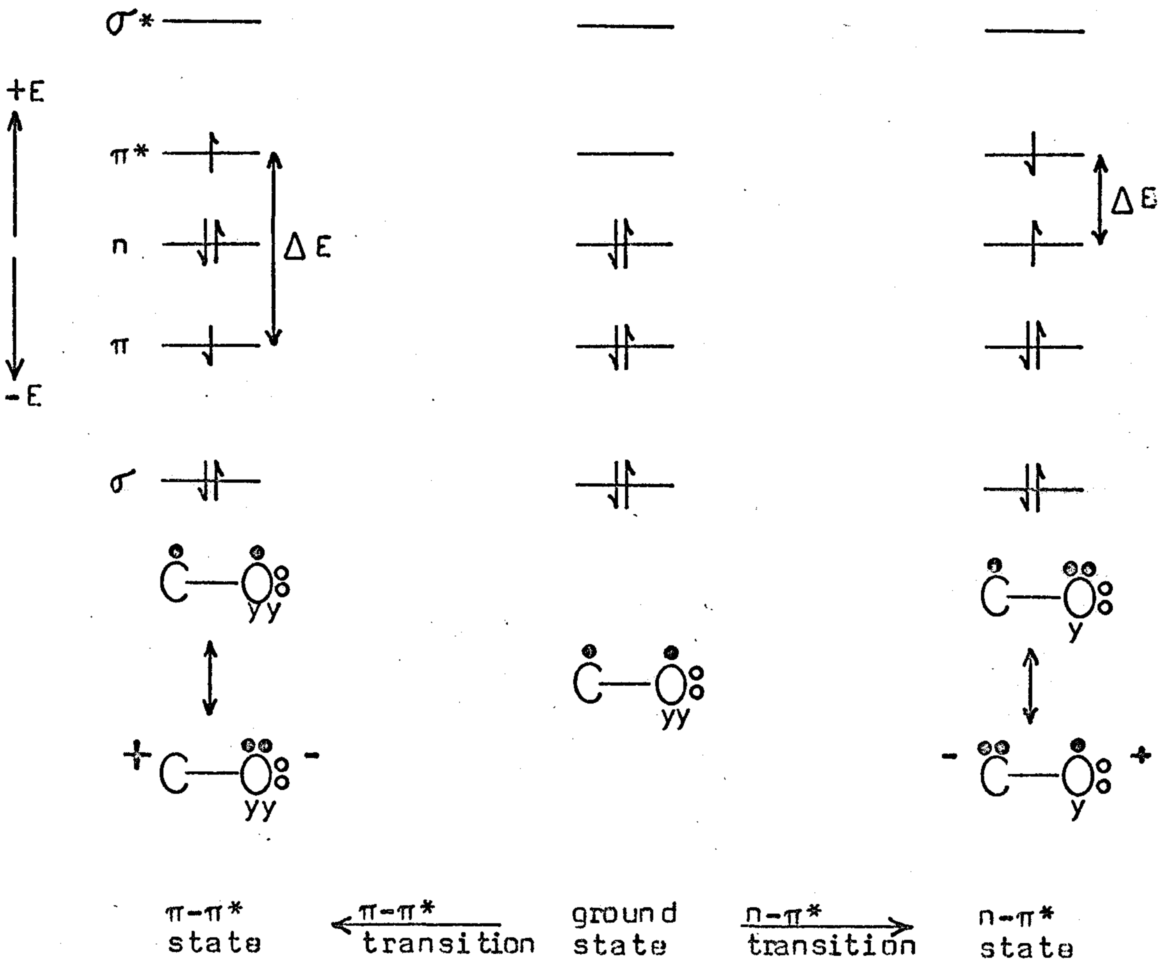
In accordance with the Pauli Exclusion Principle, each orbital may contain no more than two electrons, and so the six electrons of the carbonyl group (four forming the double bond, and two non-bonding localized on oxygen) can be placed in the three orbitals of lowest energy. When two electrons occupy the same orbital, they must have opposed spins, as indicated by the arrows pointing in opposite directions. This then represents the ground state configuration, since the electrons cannot be rearranged to produce a molecule of lower energy.

It is often desirable to be able to show an electronic state schematically. Several methods of accomplishing this have been proposed[3]; here we choose to use that of Zimmerman[3b], which may be illustrated by the carbonyl ground state under discussion:



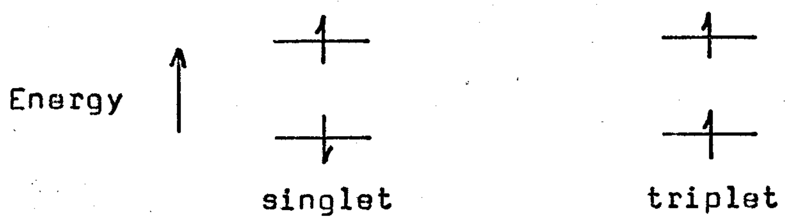
The σ-electrons are represented by the line joining the carbon and oxygen, the π-electrons by the solid circles, and the n-electrons by the Y's. The open circles are additional non-bonding electrons localized on oxygen; however, they are of such low energy that they do not take part in photochemical transformations, and hence are not pictured in the energy level diagram.

Now when the molecule absorbs ultraviolet light, excitation may occur in several different ways. Excitation of a σ electron to either the π^* or σ^* orbital involves a large amount of energy, and normally does not occur in the range of wavelengths of light (250 to 400 mμ) transmitted by quartz. Similarly, excitation from either π or n to σ* is a high-energy jump, obtainable only at wavelengths less than 250 mμ. Thus, the carbonyl group is generally electronically excited by promotion of either a π or a n electron to the π* orbital. These are designated as π-π* and n-π* transitions, respectively, and the excited states which are formed are called π-π* and n-π* states. The energy level diagrams and schematic representations are as follows:



It may be seen that the π-π* process requires more energy than the n-π*, since the two levels are spaced farther apart.

Furthermore, since in both cases we now have two singly-occupied orbitals, the two electrons need no longer be opposed in spin. They may be opposed, this arrangement giving rise to a singlet state, or parallel, resulting in a triplet state.



In the ground state, the electrons must be opposed in spin (Pauli Principle), and hence the ground state is a singlet state. Since electronic excitation to an upper triplet state is forbidden in a first approximation, the excited state first formed must also be a singlet state. However, if the singlet excited state is sufficiently long-lived (reaction with a ground state molecule, or deactivation by transferring energy to the surrounding medium, is slow) it may subsequently cross to a triplet state. It has been found[4-9] that cyclic α,β-unsaturated ketones usually undergo triplet reactions; that is, the singlet originally formed by absorption of light decays to a triplet before undergoing reaction.

Since the energy delivered to a molecule by light depends on the wavelength of the light, a given transition (n-π^* for example) in a given molecule can only be accomplished if light of the proper wavelength is used. The energy to wavelength correspondence is given by:

$$E = \frac{2.86 \times 10^4}{\lambda}$$

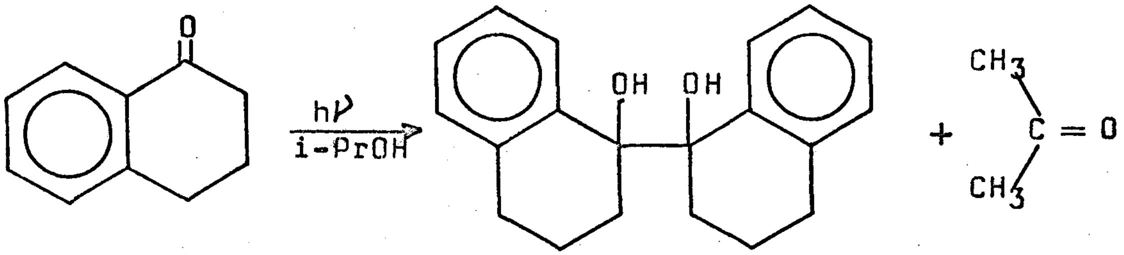
where E is energy in Kcal/mole, and λ is wavelength in millimicrons ($1 m\mu = 10^{-7}$ cm). Hence, if a molecule has its n and π^* levels separated by 95 Kcal/mole, the n-π^* transition can be effected with light of wavelength 300 mμ.

In general, the π-π^* transitions of ketones correspond to wavelengths about 190 mμ, and the n-π^* transitions require about wavelengths of 290 mμ. The introduction of an α,β-double bond shifts these wavelengths to approximately 230 and 330 mμ, respectively. In this work we are interested in exciting cyclic α,β-unsaturated ketones (enones) only to their n-π^* state. This is accomplished most easily by filtering the light from the lamp through pyrex glass, which removes ultraviolet light of wavelength less than 290 mμ.

PART THREE: CYCLIC ENONE PHOTOCHEMISTRY

Cyclic conjugated enones have been observed to undergo various types of reactions on photolysis. These include reduction, bond dissociation, oxetane formation, dimerization, rearrangement, and addition.

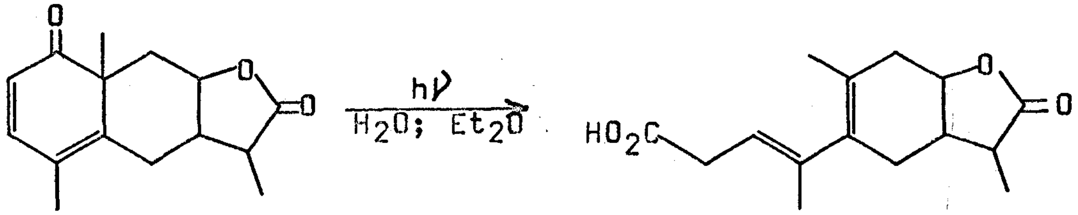
Photoreduction, a common reaction of saturated ketones when photolysed in protic solvents, is also encountered when the ketone is conjugated with one or more double bonds[10]. An example is the photoreduction of 1 in isopropanol[11]:



1

In the absence of proton donors, this reaction is not observed.

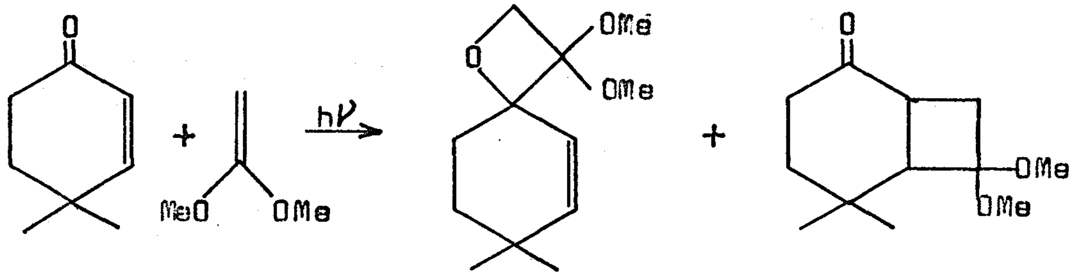
Photodissociation, an example of which is the photolysis of 2[12], is a common reaction[13], but is not relevant



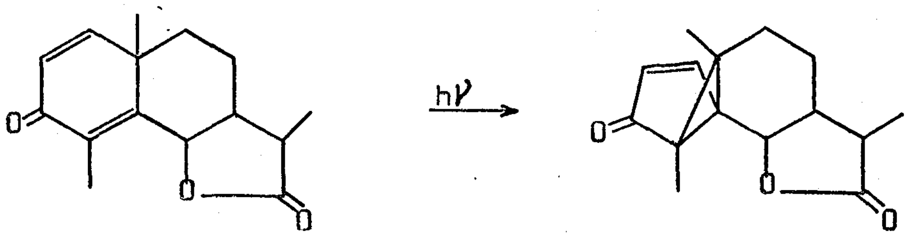
2

to the work in this thesis.

Oxetane formation, generally known as the Paterno-Buchi reaction[14], competes well with other possible reaction pathways of saturated ketones. However, the presence of a conjugated double bond in the ketone generally suppresses the Paterno-Buchi reaction in favor of the formation of cyclobutane products. There exist instances, nevertheless, in which oxetane formation is not completely suppressed. One such case is the reaction studied by Chapman[9], to which we will have occasion to refer later:

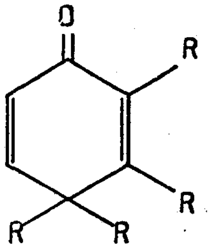


Photorearrangement, the rearrangement of an electronically excited molecule, accompanied or followed by loss of the excitation energy to form a new molecule, was one of the earliest photochemical reactions to be observed. Hence,

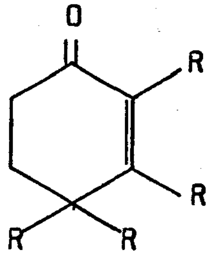


3

as early as 1830[15,16] it was noted in the literature that α-santonin (3) undergoes a light-induced rearrangement, although it was not until recent times[16] that the structure of the product was elucidated. Not only has it been found that almost all compounds containing the cyclohexadienone structure (4) undergo this reaction, but cyclohexenones (5), lacking one double bond, also give formally analogous

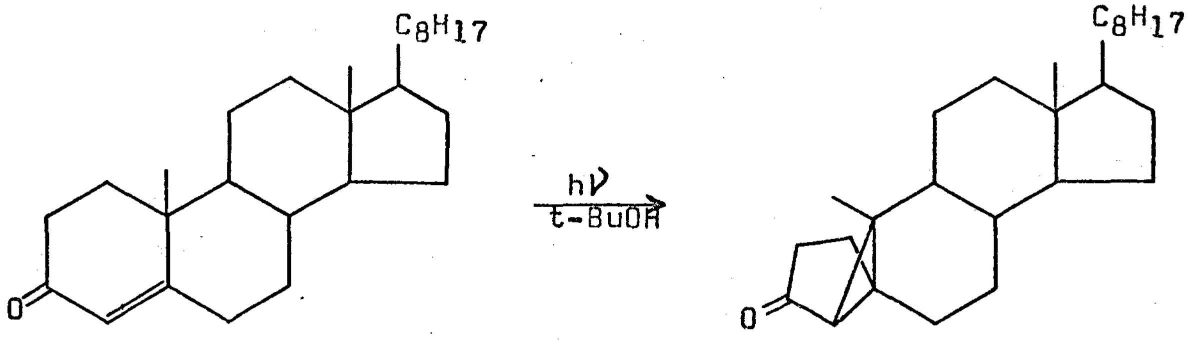


4



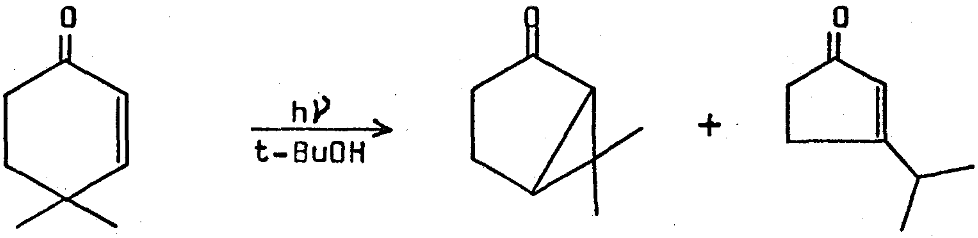
5

photorearrangement products. Thus, cholest-4-en-3-one (6) yields the cyclopropane product 7 on irradiation in *tert*-butyl alcohol[17].



6 7

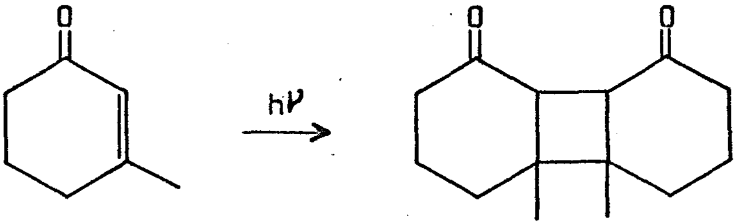
A simpler example is the one on which part of the work in this thesis is based; that is, the 4,4-dimethyl-2-cyclohexenone (8) rearrangement[18,19]. These enone rearrangements



8 9 10

are generally quite inefficient[‡]; however, they have been sufficiently well characterized to permit the study of other reactions which can be performed in competition with the rearrangement (see Discussion).

Photodimerization of cyclic conjugated enones has long been known, and is a very general reaction[20]. One of the earliest examples to be studied was 3-methyl-2-cyclohexenone (11), which was found to yield a dimer (12) when alcoholic solutions were exposed to sunlight[21].

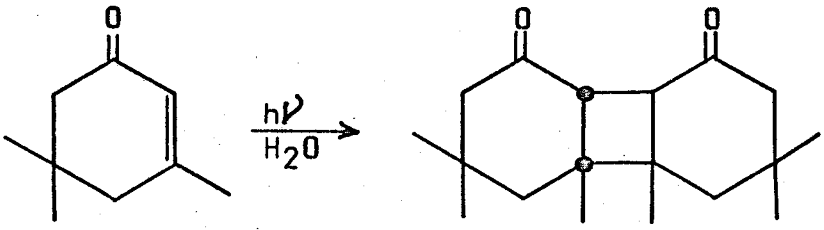


11 12

[‡] The efficiency of a photochemical reaction is generally given in terms of its quantum yield (ϕ) which is defined as:

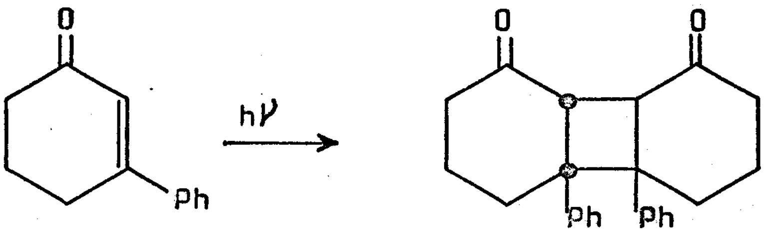
$$\phi = \frac{\text{Moles of enone undergoing reaction}}{\text{Moles of light absorbed by enone}}$$

In some cases the orientation of the monomer moieties within the dimer has not been well established. However, it has been suggested that the photodimer of isophorone (13) has the head-to-head *cis-anti-cis* structure (14)[22]:

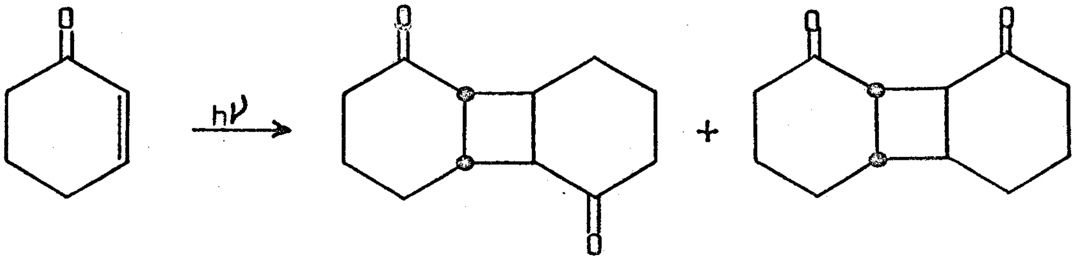


13 14

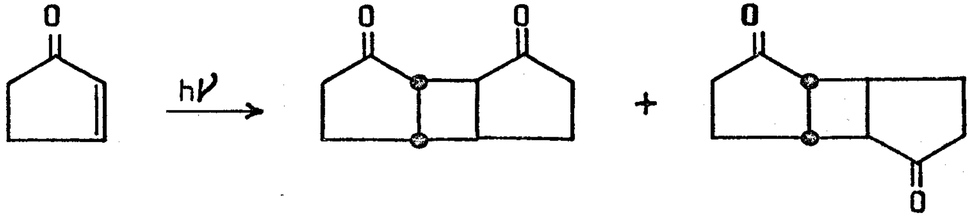
This same configuration has been shown[23] to be present in the dimer of 3-phenyl-2-cyclohexenone:



Cyclohexenone itself, however, yields two photodimers, both having the *cis-anti-cis* configuration[5]:

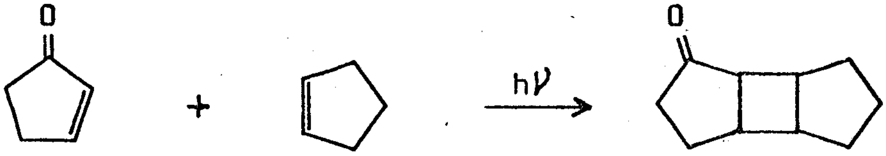


The same difficulty in identifying the various isomeric dimers is encountered with 2-cyclopentenone. This enone (15) yields approximately equal amounts of the head-to-head and head-to-tail dimers, 16 and 17, both of which were shown to be cis-anti-cis[24].

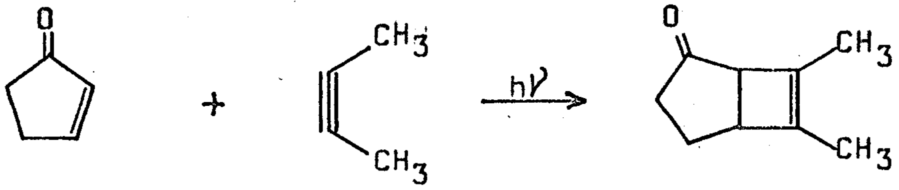


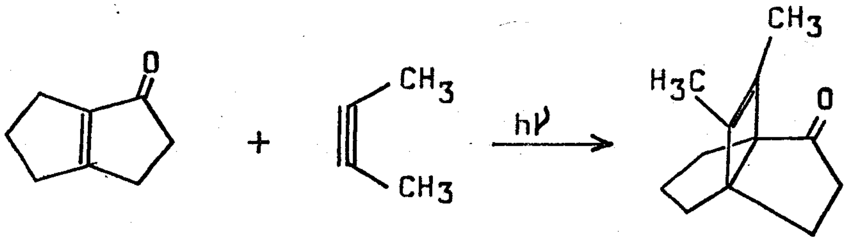
15 16 17

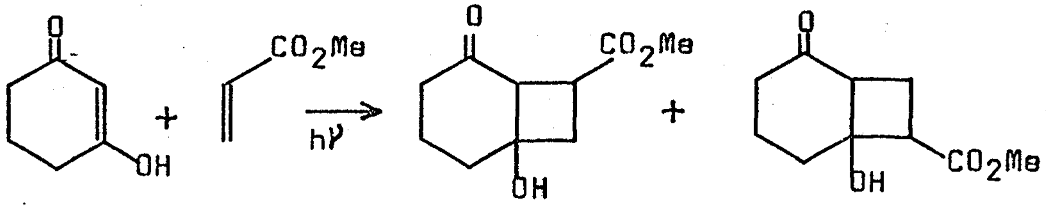
Mixed addition, a quite general reaction of cyclic α,β-unsaturated ketones, can compete favorably with dimerization. Hence the presence of a large excess of cyclopentene suppresses the formation of cyclopentenone dimers[24]:



A few general examples of mixed additions[25-27] are:




O
CH3
CH3
hν
CH3
H3C
O

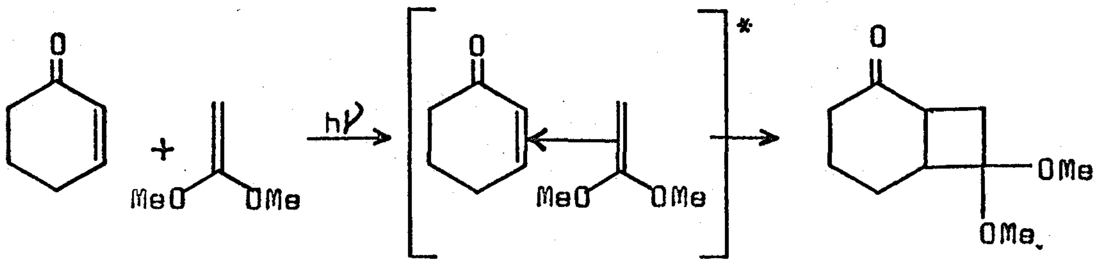

O
OH
CO2Me
hν
O
CO2Me
OH
O
OH
CO2Me

PART FOUR: MECHANISTIC ASPECTS

In presenting the known photoaddition chemistry of cyclic enones, it is necessary to discuss in some detail several recent publications. Eaton's work on the dimerization of cyclopentenone[6,24] led him to expect that mixed additions of this enone might be as facile as dimerization. This he found to be the case[24]. However, the broad scope of this addition reaction was first demonstrated by Corey and coworkers[28], using 2-cyclohexenones (18) and a variety of ethylene derivatives. The tentative conclusions that Corey drew from his results are discussed below:

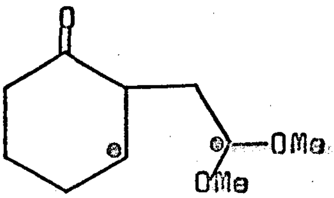
a) Definitive experiments to determine the multiplicity (singlet or triplet) of the excited state were not performed. However, since initial excitation was to the n-π* singlet, and since it is well known that intersystem crossing of this species to the triplet is facile, Corey favored the n-π* triplet as the reactive excited state.

b) To explain the orientational specificity of the products obtained, i.e. from cyclohexenone (18) and 1,1-dimethoxyethylene (19), Corey proposed initial formation of a charge-transfer complex between the excited state of the enone and the ground state of the olefin (20):

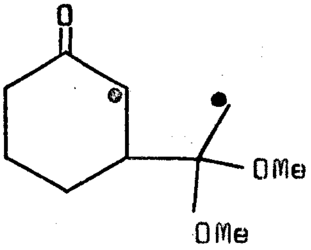


18 19 20

c) The excited state complex subsequently collapses to a diradical species which then yields the observed products. This diradical may be written as either <u>21</u> or <u>22</u>, <u>21</u> being the more stable of the two, and hence probably a more realistic representation:

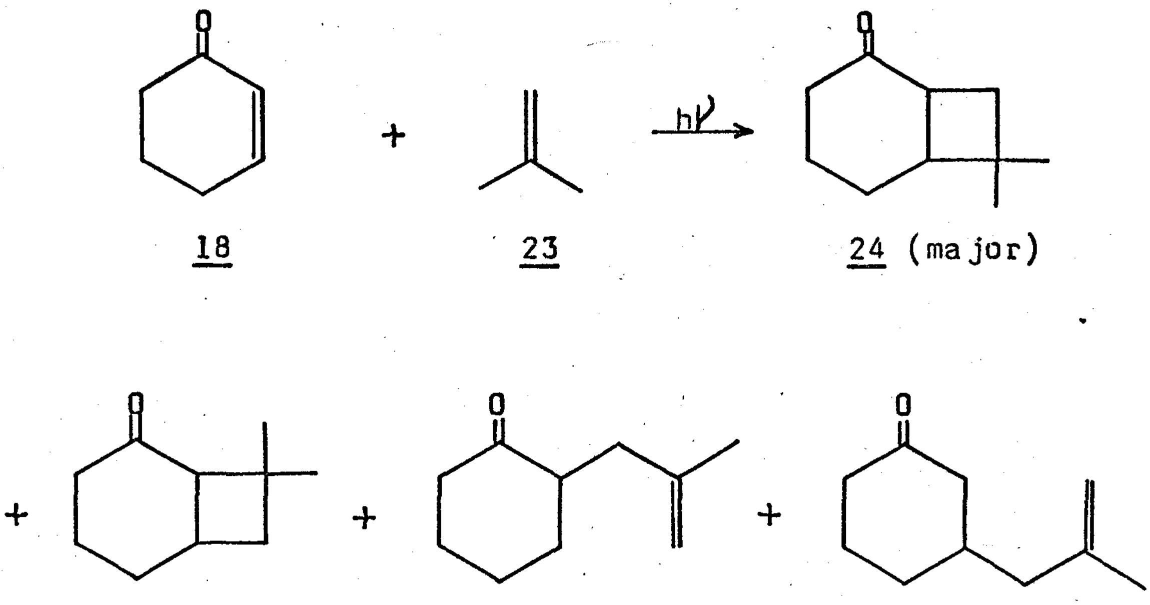


21



22

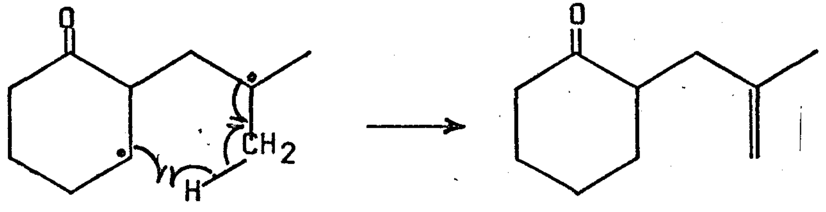
This diradical intermediate was suggested to explain the result that both <u>cis</u>- and <u>trans</u>-2-butene give the same products on addition to cyclohexenone. Furthermore, the presence of isobutenyl-substituted cyclohexanones (<u>25</u>, <u>26</u>) in the reaction product of isobutylene (<u>23</u>) with cyclohexenone can be easily rationalized by postulating a



18 23 24 (major)

(minor) 25 26

1,5-hydrogen transfer in the diradical intermediate:

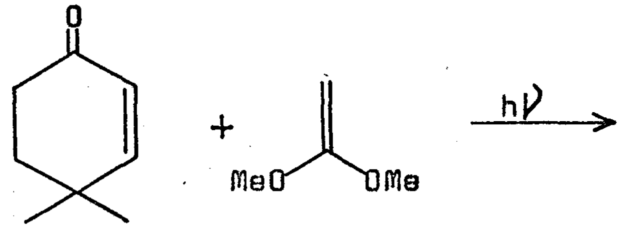


21 25

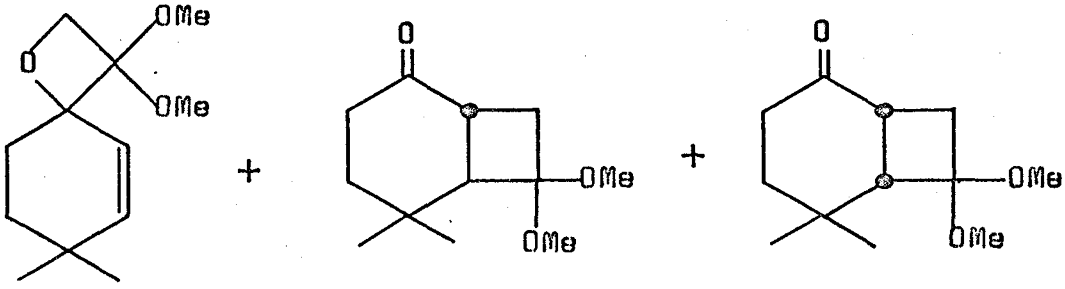
d) *Trans*-fused cyclobutanes are formed in all of the cyclohexenone cycloaddition reactions studied by Corey[28], often in greater amounts than the corresponding *cis*-isomers. Hence, the major product in the above reaction (24) is a mixture of *cis*- and *trans*-fused cyclobutanes in the ratio of approximately 1:4. An explanation of this was not given.

Recently, considerable controversy has arisen concerning the enone excited state (or states) that is responsible for cycloadditions with olefins. In the photodimerization of 2-cyclopentenone[24], it was originally suggested that the reaction was via the triplet[6], and this is now quite definite[7b]. Similar tentative conclusions were made in the case of 2-cyclohexenone dimerization[5]. However, it has recently been reported that the 2-cyclopentenone excited species involved in cycloadditions with cyclohexene is not the lowest lying triplet (T_1), but rather a triplet of higher energy (T_2) [8].

In the reaction of 4,4-dimethyl-2-cyclohexenone (8) with 1,1-dimethoxyethylene (19), Chapman and coworkers[9] have postulated that the three products observed (27-29) arise from two distinct triplet species. Oxetane formation (27)



8 19



27 28 29

is quenched by di-tert-butyl nitroxide (a known triplet quencher) at approximately the same rate as that of the trans-fused cyclobutane (28), while formation of the cis-fused adduct (29) is quenched at a faster rate.

In summary, three major questions about enone photoadditions remain unanswered. These are:

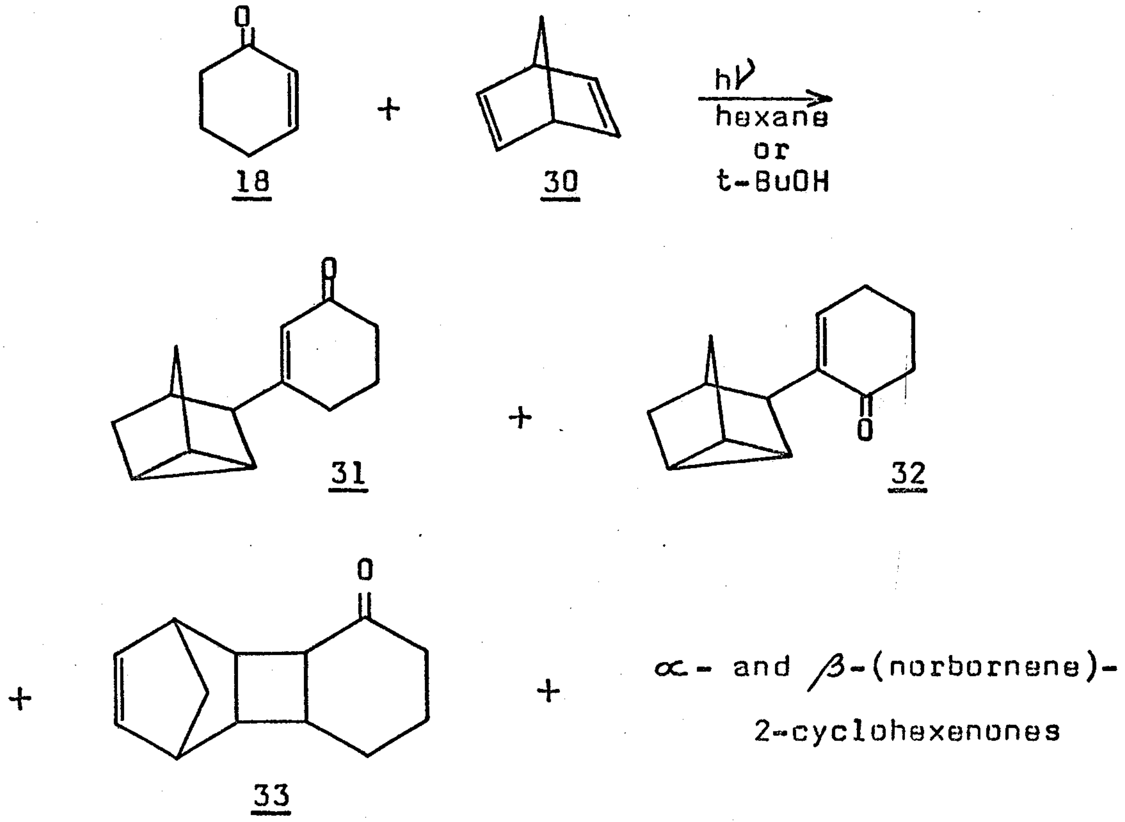
a) What is the origin of the trans-fused cyclobutanes?

b) What is the multiplicity of the excited species, and is more than one excited state involved in these reactions?
(When this work was begun, no answers were available for these questions).

c) Are the diradicals proposed by Corey[28] a general feature of these reactions?

The work presented in this thesis attempts to answer these questions. A study of the photoadditions of 4,4-dimethyl-2-cyclohexenone (8) and cyclopentene, in competition with the rearrangement of the enone, was undertaken with two goals in mind. First, since the rearrangement is known to proceed via the triplet state, quenching experiments should reveal the nature of the excited species leading to adduct formation. Second, quenching experiments similar to those performed by Chapman[9] may allow further data to be gathered on the formation of trans-fused cyclobutanes. It was thought that these strained products arise as a result of the geometry of the reacting enone excited state, but data on excited state geometries is not available in the literature. The results of recent calculations by Santry and Ohorodnyk[29] in this department, which provide the first information on this problem, will be given in the Discussion.

In attempting to clarify the matter of diradical intermediates, McCullough and Kelly[30] began a study of the 2-cyclohexenone-norbornadiene system. They found the following products:



An extensive study of this reaction, including the effects of methyl substituents at the α- and β-positions of the enone, is presented in this thesis.

RESULTS

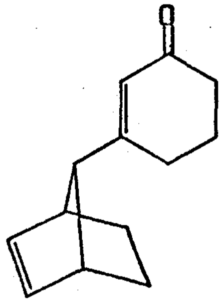
PART ONE: ISOLATION AND IDENTIFICATION OF PRODUCTS

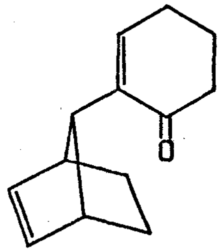
As noted in the introduction, the photoaddition of 2-cyclohexenone and norbornadiene had been investigated by McCullough and Kelly[30]. The structures of some of the products had been assigned (see page 21); however, the structures of the α- and β-(norbornenyl)-cyclohexenones were not known with certainty. It was believed that these were 5-substituted norbornene derivatives, and further studies were undertaken to confirm this, and to allow an assignment of the stereochemistry of the cyclohexenone moiety.

Since the cyclohexenone-substituted adducts are formed by a hydrogen shift[30], the effect of substituting a blocking methyl group for hydrogen in the enone reactant was of great interest. Therefore the author's work began with investigations of the reactions of 2-cyclohexenone and 2-methyl- and 3-methyl-2-cyclohexenone with norbornadiene. The products from these will be described first.

The 2-cyclohexenone-norbornadiene system

The structures of the norbornenyl cyclohexenones were investigated first. Isolation of the β-norbornenyl cyclohexenone was achieved by preparative vapour phase chromatography (vpc) [30]. The 100 Mc nuclear magnetic resonance (nmr) spectrum of this compound, shown in Figure 1, is consistent with a 7-substituted norbornene. Thus, the exo- and endo-proton resonances appear as two multiplets (two hydrogens each) of an AA'XX' system, the endo-proton resonance being at higher field[31]. Decoupling irradiation of the multiplet at 2.9 ppm (assigned to the bridgehead protons) causes the multiplet at 1.6 ppm to simplify to a quartet, thus identifying the latter resonance as that of the exo-protons[32]. Furthermore, irradiation of the multiplet at 2.2 ppm, which includes the resonance of the allylic proton, H_7, causes the endo-multiplet to collapse to a quartet. This shows that H_7 is coupled to the endo-protons, thereby establishing that the cyclohexenone moiety is anti to the norbornene double bond[32,33]. On the basis of this nmr data, and the results reported earlier[30], the structure 3-(7-anti-norborn-2-enyl)-2-cyclohexenone (34) is assigned to this adduct.


34


35

The other cyclohexenone adduct[30] is assigned the structure 2-(7-anti-norborn-2-enyl)-2-cyclohexenone (35) by comparison with the α-substituted cyclohexenone adducts

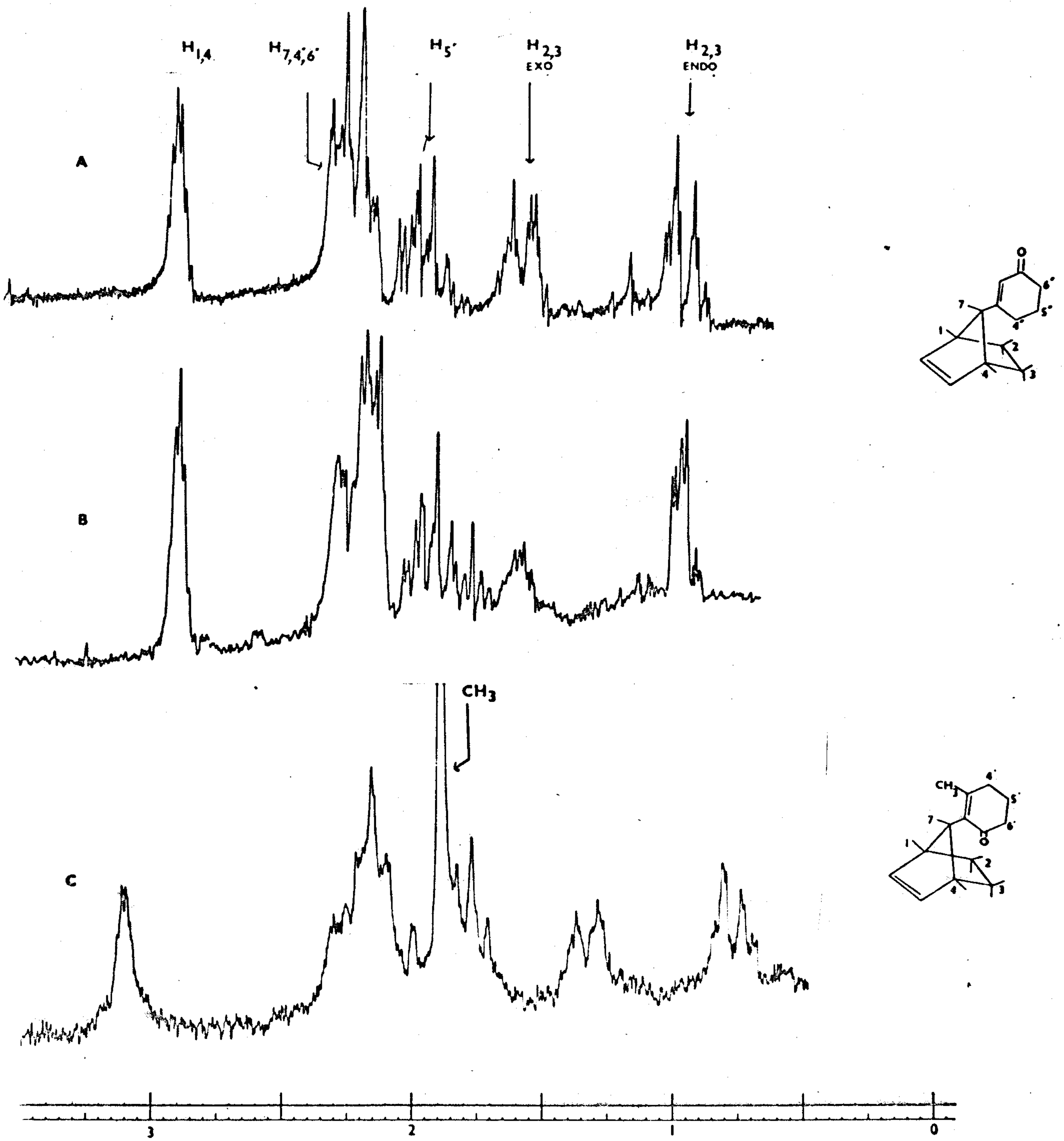
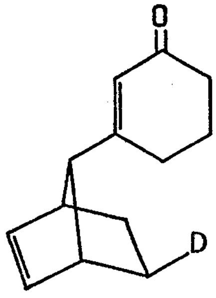


FIGURE 1. 100 MHZ NMR SPECTRA. A, spectrum of 34. B, spectrum of 36, showing one deuterium in the exo-position. C, spectrum of 37.

obtained from the photoaddition of 3-methyl-2-cyclohexenone (see later results).

The photolysis of 3-deutero-2-cyclohexenone[34] and norbornadiene was carried out as described in the Experimental section. The product mixture obtained was identical to that from the 2-cyclohexenone photoaddition[30]. The product corresponding to the adduct 34 was isolated and characterized by spectroscopic means. Its mass spectrum (parent ion at m/e 189) and elemental analysis were consistent with incorporation of one deuterium ($C_{13}H_{15}DO$), and its infrared spectrum was identical to that of the undeuterated adduct (34).

The nmr of this monodeuterated adduct is shown in Figure 1. It is seen that the deuterium is located in an *exo*-position of the norbornene moiety, since the relative area of the multiplet at 1.6 ppm is decreased to one-half its value in the non-deuterated adduct. In all respects, the nmr is consistent with the 7-substituted structure 36.



36

The stereochemical implications of this result with 3-deutero-2-cyclohexenone will be given in the Discussion section.

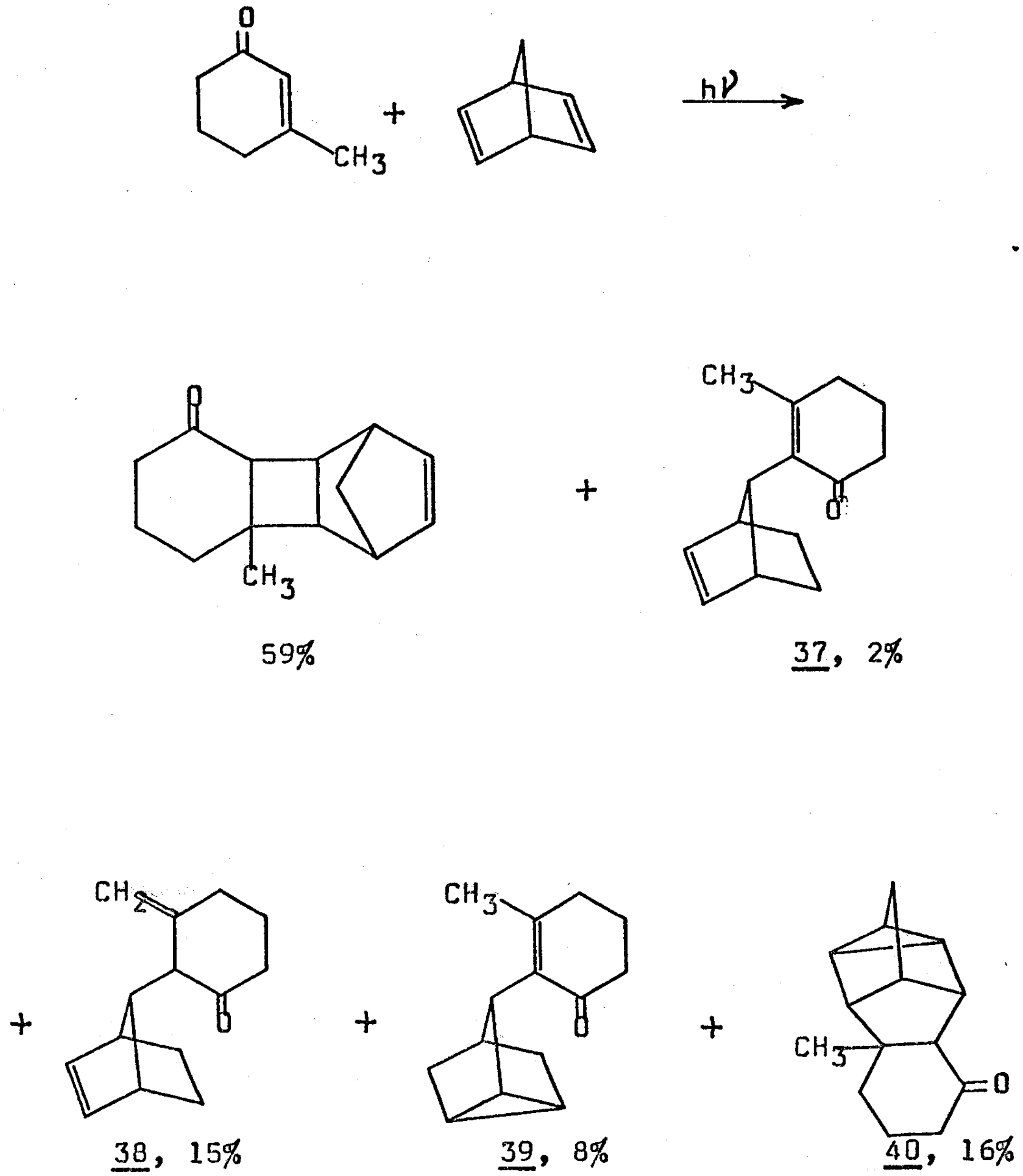
The 3-methyl-2-cyclohexenone-norbornadiene system

Irradiation of 3-methyl-2-cyclohexenone and norbornadiene, as outlined in the Experimental section, gave rise to four 1:1 adducts (mass spectrum parent m/e 202) other than the expected cyclobutane derivatives. These products are shown in Scheme 1.

The cyclobutane products were not extensively examined; however, cis- and trans-fused isomers were present, as indicated by infrared bands at 5.90 and 5.81μ,[28] respectively. The trans-fused isomers could not be isolated, as they were unstable to vpc and alumina. They survived column chromatography on silica gel, but could not be obtained free of the cis-fused cyclobutanes by this method.

Two of the cis-fused cyclobutanes were isolated; one gave an infrared spectrum with strong bands at 5.90 and 14.20μ (the latter is typical of norbornenes[35]), the other showed these bands at 5.91 and 14.12μ.

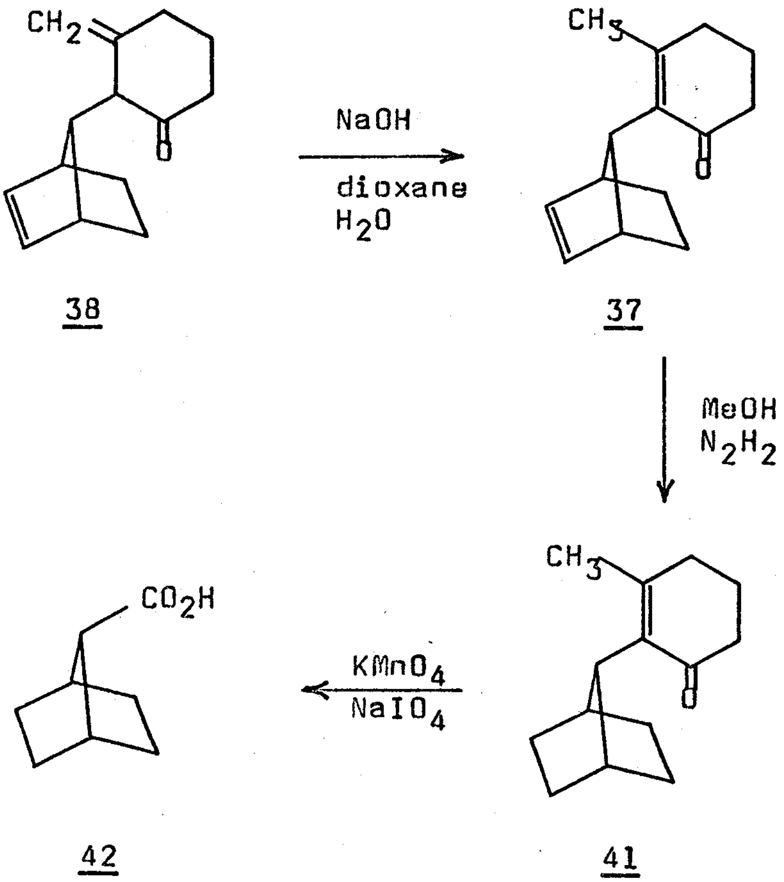
The structures assigned to the two norbornene enones (37 and 38) were based on spectroscopic evidence and a chemical degradation. In the infrared spectra, both compounds had bands at 14.2μ (norbornene double bond[35]), while the carbonyl band for 37 was at 5.99μ, and that for 38 at 5.83μ. The latter compound also showed a strong band at 11.2μ which is assignable to the exocyclic methylene group. These two enones were shown to be tautomers, since mild treatment of 38 with base caused clean isomerization to 37.



SCHEME 1

PHOTOADDITION OF 3-METHYL-2-CYCLOHEXENONE AND NORBORNADIENE

Diimide reduction[36] of 37 gave the corresponding norbornane (41, see Scheme 2) in quantitative yield. Oxidation of the latter with aqueous permangante-periodate[37] gave 7-norbornane carboxylic acid (42), mp 74-75°C (Lit.[38] 75-76.5°C), identified by comparison with an authentic sample.



SCHEME 2

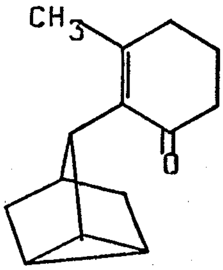
DEGRADATION OF EXOCYCLIC METHYLENE ADDUCT

The nmr of the conjugated enone 37 is shown in Figure 1, and is seen to be similar to those of the two 7-substituted norbornene derivatives discussed previously (also shown in Figure 1). Decoupling irradiation at the multiplet centred at 2.2 ppm, which includes the vinylic 7-proton resonance, causes the endo-multiplet[31] at 0.8 ppm to simplify[33]. This evidence, coupled with the results of the unambiguous degradation, confirms that both enones 37 and 38 are 7-substituted derivatives.

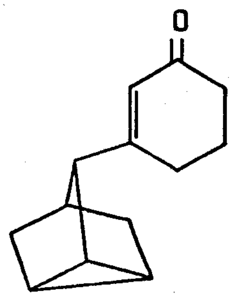
The nmr of the unconjugated enone (38) is quite different in appearance from those shown in Figure 1. Resonances appear at 4.60 and 4.70 ppm, which are attributed to the exocyclic methylene protons, and a triplet at 6.11 ppm is due to the norbornene vinyl protons. The endo-protons give rise to a multiplet (two hydrogens) centred at 0.9 ppm[31]; the remaining proton resonances are all included in a multiplet bounded by 1.5 and 2.6 ppm.

This unique nmr may be explained from an inspection of a space-filling model[39] of the enone 38. This reveals that there is severe steric hindrance to rotation of the methylenecyclohexanone substituent, and this would create an anisotropic environment for the exo- and the bridgehead-protons, thus resulting in an anomalous nmr. If the barrier to rotation is fairly low, it should be possible to overcome it by raising the temperature. This was attempted using hexadeutero-dimethylsulphoxide as solvent, but no change in the nmr was apparent at temperatures up to 150°C.

The nortricyclic enone adduct (39, Scheme 1) was assigned this structure from spectroscopic data (infrared bands at 5.99μ and 12.37μ, the latter being typical of the nortricyclene system^{40}) and by comparison with the nortricyclic enone adduct isolated from the 2-cyclohexenone addition (31)^{30}. The two adducts were found to yield similar nmr spectra, except, of course, for the presence of a



39



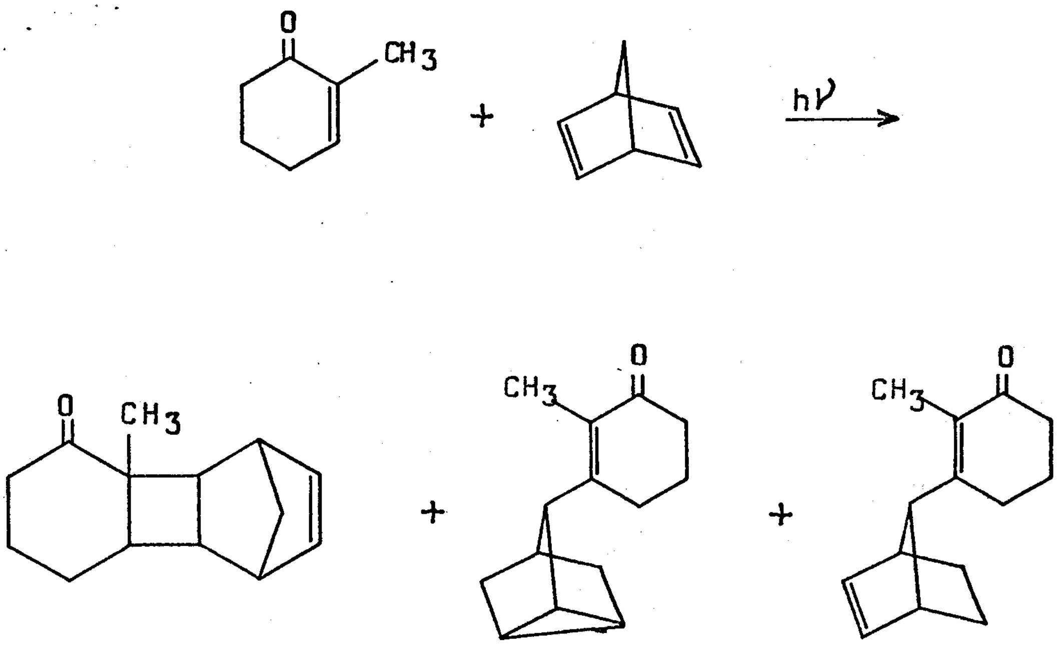
31

methyl singlet in the nmr of the former compound (39).

The product which was assigned the five-membered ring structure (40) in Scheme 1 was very difficult to obtain free of the other reaction products. Since all of the other adducts contain at least one double bond, they were removed from 40 by oxidation with aqueous permanganate-periodate^{37}. The pure product 40 had infrared bands at 5.90 and 12.37μ (doublet, nortricyclene). The nmr showed no signals in the vinyl proton region, but had a methyl resonance at 1.02 ppm. The mass spectrum showed the parent ion at m/e 202, which was also the base peak, the rest of the spectrum being comparatively featureless (see Appendix). The structure was thus assigned on its stabliity in the mass spectrometer, its resistance to oxidation, and the above spectroscopic results.

The 2-methyl-2-cyclohexenone-norbornadiene system

Photolysis of 2-methyl-2-cyclohexenone and norbornadiene yielded two substituted cyclohexenone 1:1 adducts (mass spectra of all products have the parent ion at m/e 202) in addition to cyclobutane products, as outlined in Scheme 3.



76% 43, 14% 44, 10%

SCHEME 3

PHOTOADDITION OF 2-METHYL-2-CYCLOHEXENONE AND NORBORNADIENE

The cyclobutane adducts included both cis- and trans-fused bicyclo[4.2.0]octan-2-ones as shown by the infrared spectrum of the mixture, which had carbonyl bands at 5.90 and 5.80μ. It is evident that the presence of the 2-methyl substituent will block the enolization which leads to isomerization of a trans-fused cyclobutane. Hence, it was possible to isolate a trans-fused cyclobutane from this photolysis product via preparative vpc.

The two substituted cyclohexenone products 43 and 44 both gave an infrared carbonyl frequency of 5.98μ (α,β-unsaturated). The nortricyclic derivative showed the band typical of these systems at 12.37μ, while the norbornenyl isomer gave the norbornene double bond band at 14.2μ.

The nortricyclic product (43) gave an nmr that is consistent with the proposed structure. Thus, its nmr showed narrow peaks at 1.15 and 1.25 ppm which are attributable to the nortricyclene system (similar peaks are present in the nmr spectra of all such systems studied here), and a singlet at 1.65 ppm due to the allylic methyl protons. This product was synthesized by an independent route, as outlined in Scheme 4.

The structure of the norbornenyl product (44) was assigned from the infrared data discussed above, and its nmr, shown in Figure 2. This nmr has the following features: a multiplet at 0.97 ppm due to the pair of endo-protons; a broad peak at 2.52 ppm assigned to the C_7 proton of the

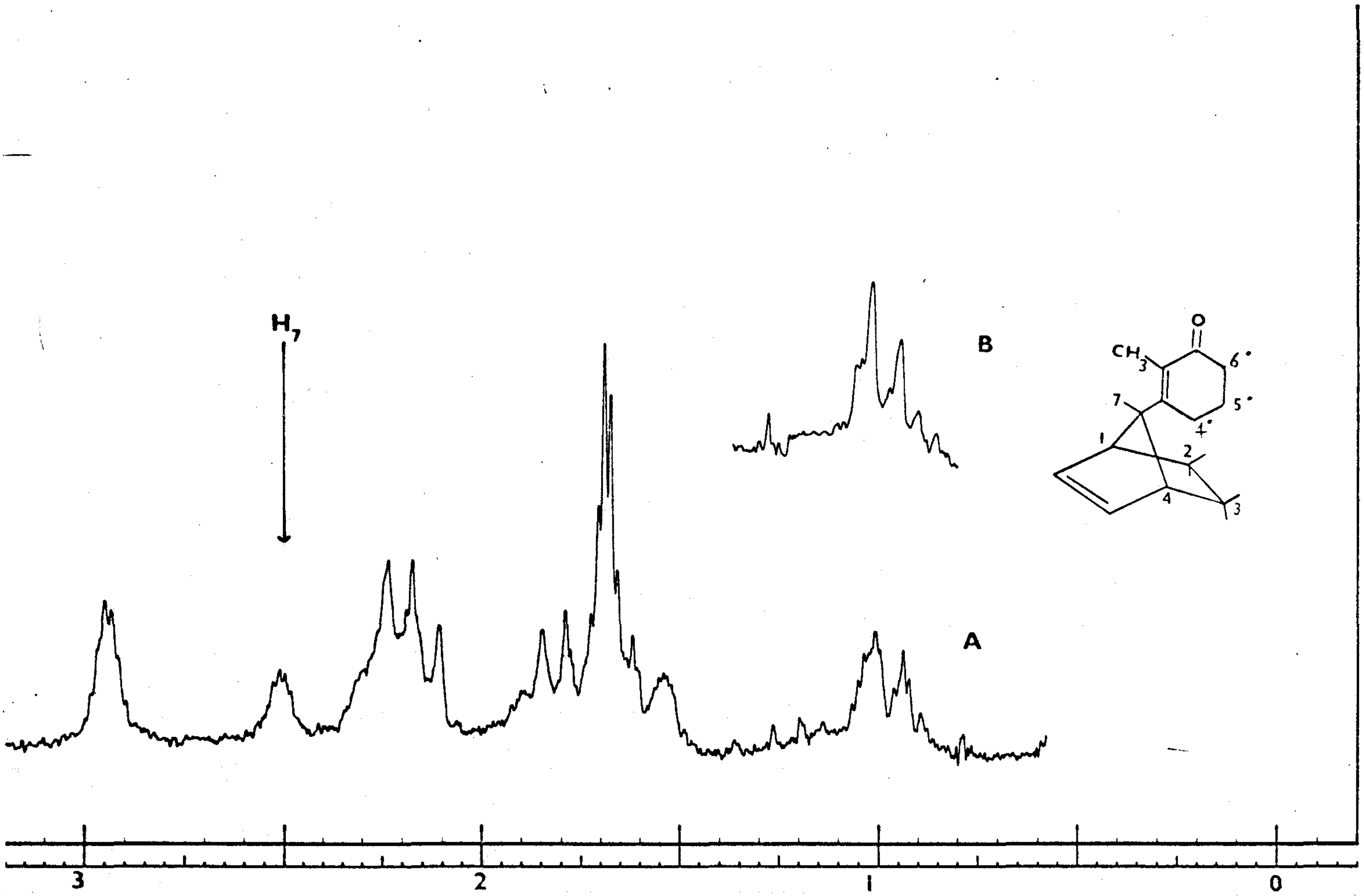
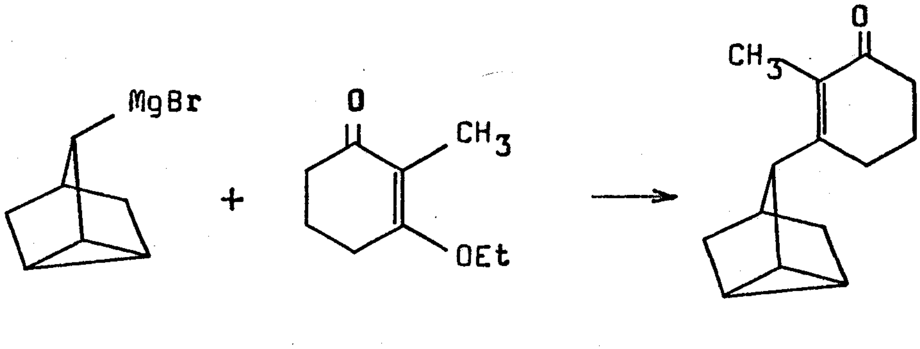


FIGURE 2. NMR SPECTRUM OF 2-METHYL-3-(7-ANTI-NORBORNENYL)-2-CYCLOHEXENONE (44)

A, normal spectrum; B, endo-proton multiplet when H_7 peak is irradiated.



43

SCHEME 4

SYNTHESIS OF

2-METHYL-3-(TRICYCLO[2.2.1.$0^{2.6}$]HEPTYL)-2-CYCLOHEXENONE

norbornene; a multiplet at 2.95 ppm (bridgehead protons); and a sharp triplet at 6.11 ppm (norbornene vinyl protons). The remaining protons gave resonances which were contained in two complex multiplets centred at 1.70 ppm (7 H) and 2.20 ppm (4 H); the former included the finely split methyl proton resonance.

Decoupling irradiation of the H_7 resonance at 2.52 ppm resulted in the simplification of the endo-proton multiplet at 0.97 ppm (see Figure 2), thus indicating that the cyclohexenone substituent is anti to the norbornene double bond[32,33].

In all three of these additions to norbornadiene, quadricyclene was formed, and the amount of this product varied with the structure of the cyclohexenone used (see below, Table 5).

The above structural work on the cyclohexenone-norbornadiene addition represented a major part of the research described in this thesis. The mechanistic aspects of this reaction, particularly the origin of cyclohexenone derivatives, and the relevance of the results to enone additions, will be dealt with in the Discussion.

The remainder of the Results will report work on additions to cyclopentene, followed by the results of experiments designed to gain mechanistic information on all of these reactions.

The 4,4-dimethyl-2-cyclohexenone-cyclopentene system

Irradiation of 4,4-dimethyl-2-cyclohexenone[41] with an excess of cyclopentene gives rise to three products (Scheme 5), as shown by nmr (see below). These three products are 1:1 adducts (mass spectra parent ions at m/e 192) having no vinyl proton resonances in the nmr, and hence are assigned cyclobutane structures.

Attempted preparative vpc on the photolysis mixture afforded only two adducts; one isomer apparently does not survive the relatively high temperature. One of the cyclobutanes isolated contains a *cis*-fused 6-4 ring junction (carbonyl band at 5.91μ in the infrared) and is assigned the $1\alpha,2\beta,6\beta,7\alpha$ configuration (45)[‡]. This assignment

---

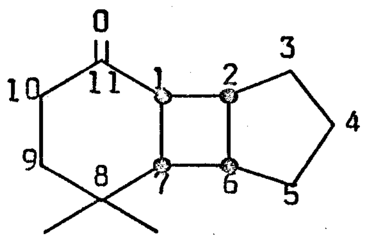
[‡] The configuration about the cyclobutane ring in these adducts is specified as in steroid nomenclature. Hence

is based on the fact that only one cis-fused isomer is formed in the photolysis, and hence most probably is the less sterically hindered isomer (45) (see Discussion).

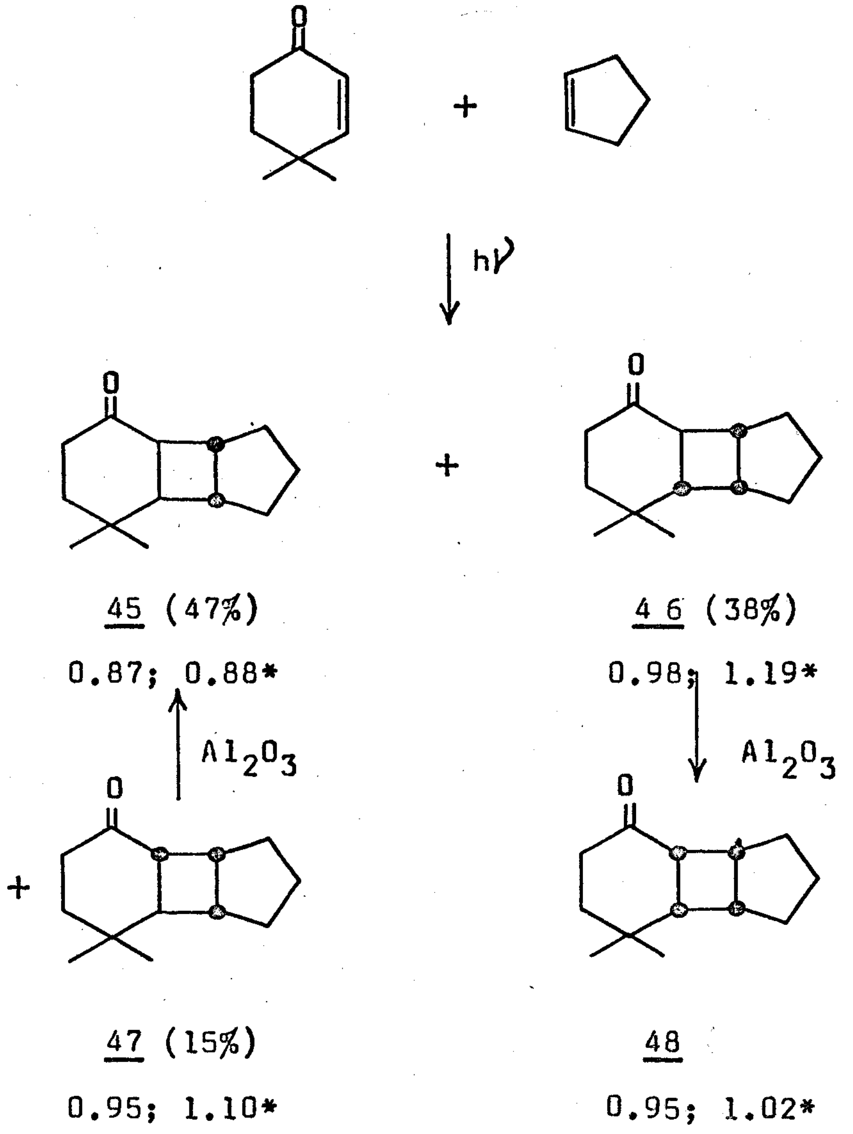
The other cyclobutane isolated is trans-fused (carbonyl band at 5.83μ) and is found to isomerize cleanly and rapidly to a cis-fused cyclobutane (carbonyl band at 5.91μ) on treatment with basic alumina. This new cis-fused isomer is different from the cis-fused adduct formed in the photolysis (as shown by nmr--see below) and hence is assigned the $1\beta,2\beta,6\beta,7\beta$ configuration (48). The trans-fused adduct isolated must therefore be the $1\alpha,2\beta,6\beta,7\beta$ compound (46).

Analysis by vpc of the above mixture of adducts was found to be impossible, since the four adducts share two retention times on both FFAP and FS1265 vpc columns. Fortunately, nmr provides a method of analysis, because each adduct shows a characteristic pair of methyl proton resonances.

$1\beta,2\beta,6\beta,7\beta$ indicates that the hydrogens at carbons 1, 2, 6, and 7 are above the plane of the paper, as shown



in the accompanying formula. Hydrogens below the plane of the paper are designated by α.



*Numbers indicate the chemical shifts (in ppm) of the methyl proton resonances.

SCHEME 5

PHOTOADDITION OF

4,4-DIMETHYL-2-CYCLOHEXENONE AND CYCLOPENTENE

The second trans-fused cyclobutane (47) can also be detected. Thus, nmr of the photolysis products showed the pairs of methyl resonances due to 45 (0.87, 0.88 ppm) and 46 (0.98, 1.19 ppm), and a third pair (0.95, 1.10 ppm) which did not correspond to that of the cis-fused adduct, 48 (0.95, 1.02 ppm). When the mixture was stirred in ether with basic alumina this third pair disappeared, as did the pair due to 46. The nmr of the equilibrated product indicated the presence of only the two cis-fused isomers 45 and 48. Hence the third adduct present in minor amount in the photolysis product was assigned the $1\beta,2\beta,6\beta,7\alpha$ configuration (47). The characteristic methyl proton resonances of each of these isomers are given in Scheme 5 in ppm downfield from tetramethylsilane, along with their relative percentages, as measured by nmr.

PART TWO: MECHANISTIC ASPECTS

Quenching of 2-cyclohexenone-norbornadiene adduct formation

In order to elucidate the multiplicity of the enone excited state which gives rise to the products of these enone-norbornadiene reactions, quenching experiments with naphthalene were carried out.

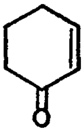
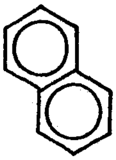
Naphthalene is known to be an efficient quencher of 2-cyclohexenone triplets[4]. Furthermore, photocycloadditions (formation of cyclobutanes) of 2-cyclohexenones have been shown to generally involve the triplet excited state[5-9]. Thus, addition of naphthalene to the 2-cyclohexenone-norbornadiene photolysis should retard the overall rate of the reaction, without altering the adduct ratio, provided that the substituted cyclohexenone products arise from the same excited state(s) as do the cyclobutanes. The results of quenching this photoaddition with 0.050 M naphthalene are given in Table 1.

Quenching of 4,4-dimethyl-2-cyclohexenone-cyclopentene adduct formation

In the presence of naphthalene (0.0500 M), the photoaddition of 4,4-dimethyl-2-cyclohexenone to cyclopentene is slowed by a factor of approximately three. The effect of this quenching on the product ratio (as measured by nmr

TABLE 1

QUENCHING OF 2-CYCLOHEXENONE-NORBORNADIENE ADDUCT FORMATION

Solvent	Molar Concentrations			Relative Percentages[a]		
				cyclo-butanes	α-sub. enones	β-sub. enones
[b]7% MeOH in t-BuOH	0.0247	0.280	0.0500[c]	51±4	16±1	34±2
t-BuOH	0.0240	0.262	0.0500[c]	46±4	17±1	37±2
[d]t-BuOH	0.0241	0.262	-	53±4	16±1	31±2
[d]Hexane	0.0250	0.250	-	54±4	14±1	31±2

a. Analyses by vpc on column B.

b. Light filtered by a copper-bismuth solution[4a], equilibrated at 35°C. Pyrex glass filter used in the other runs.

c. Quenched runs required three times as much irradiation time; measurements made at about 70% conversion of starting enone.

d. Ref. 30b. These percentages represent averages of measurements made at about 25, 45 and 70% conversion of starting enone.

TABLE 2

QUENCHING OF 4.4-DIMETHYL-2-CYCLOHEXENONE-CYCLOPENTENE ADDUCT FORMATION

Molar Concentration[a]		Irrad. time (hr.)	Percent of Product[b]			
cyclopentene	naphthalene		45	46	47	48[c]
0.797	-	3[d]	47	38	15	-
0.570	-	3[e]	47	37	16	-
0.570	0.0500	9[e]	44	30	11	15
0.570	0.0500	9[e]	43	28	14	15

a. Methanol as solvent. Enone concentration, 0.0143 M.

b. As measured by integration of the methyl proton resonances, estimated maximum error: ±8%.

c. Numbers refer to products, Scheme 5.

d. About 10% starting enone remaining (by vpc).

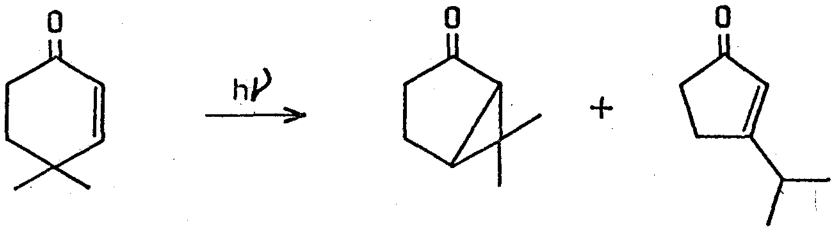
e. About 2% starting enone remaining (by vpc).

integration of the methyl proton resonances, and independently checked by vpc analysis) is outlined in Table 2.

In addition, the two unquenched reactions were performed with different concentrations of cyclopentene--no effect on the product ratio is apparent from the results in Table 2.

Competition of unimolecular rearrangement and bimolecular photoaddition of 4,4-dimethyl-2-cyclohexenone

If cyclopentene is used in excess in the photoaddition of 4,4-dimethyl-2-cyclohexenone, only 1:1 adducts are obtained. However, if the concentration of cyclopentene is reduced to about 0.1 M, the well-known[18,19] rearrangement of 4,4-dimethyl-2-cyclohexenone (shown in Scheme 6) can compete with adduct formation. Since this rearrangement has been shown[42,4a] to proceed *via* a triplet excited state, it was of interest to determine if added naphthalene--which does quench the rearrangement reaction[4a]--would have any effect on the rearrangement/adduct ratio. The results of this quenching experiment are recorded in Table 3.



8 9 10

SCHEME 6

PHOTOREARRANGEMENT OF 4,4-DIMETHYL-2-CYCLOHEXENONE[18,19]

TABLE 3

COMPETITION OF UNIMOLECULAR REARRANGEMENT AND BIMOLECULAR PHOTOADDITION OF 4,4-DIMETHYL-2-CYCLOHEXENONE

Naphthalene	Percent Conversion of Starting Enone	Product Composition (Mole Percent)[a, d]		
		Rearrangement Product		Addition Products
		9[b]	10[b]	
-	72.5	10.6	8.4 [d]	81.0
-	83.0	10.3	5.8	83.9
-	76.4	10.0	6.9	83.2
0.050 M[c]	80.4	10.4	11.0	78.6
0.050 M	73.8	10.5	11.0	78.5
0.050 M	82.7	10.7	11.1	78.2

a. Analysis by vpc on column 8, 175°.

b. Numbers refer to products, Scheme 6.

c. Methanol as solvent. Molar concentrations were 0.0143 and 0.0858 (1:6) for starting enone and cyclopentene respectively.

d. Estimated maximum error: ±4%. The greater variation in the percentage of 10 is probably due to decomposition on the vpc.

Quenching of quadricyclene formation in the 2-cyclohexenone-norbornadiene photoaddition

Quadricyclene was found in the reactions of 2- and 3-methyl-2-cyclohexenone, and 2-cyclohexenone, with norbornadiene (see Experimental section). To determine the excited species giving rise to the quadricyclene, the effect of naphthalene quenching on the quadricyclene/adduct ratio was measured for the 2-cyclohexenone-norbornadiene reaction. These results are shown in Table 4.

TABLE 4

QUENCHING OF QUADRICYCLENE FORMATION IN THE 2-CYCLOHEXENONE-NORBORNADIENE PHOTOADDITION

Molar Concentrations			Mole Percentages[b]		Percent
Cyclohexenone	Norbornadiene	Naphthalene	Quadricyclene	Total Adducts	Enone Conversion
0.0462[c]	1.11	-	79±4	21±1	44
0.0460[c]	1.11	-	81±4	19±1	42
0.0462[d]	1.11	0.0500	83±4	17±1	58

a. Hexane as solvent.

b. Calculated from actual weight of product formed, as measured by vpc with an internal standard.

c. Irradiation time: 1 hr.

d. Irradiation time: 3 hr.

Quantum yields

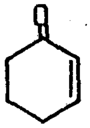
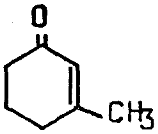
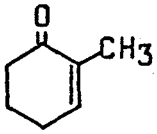
The details of these measurements are given in the Experimental section. The quantum yields of product formation in the photoadditions of 2-cyclohexenone and its 2- and 3-methyl derivatives to norbornadiene were measured, and these are given in Table 5.

The method of analysis used for these measurements is as follows: In the 3-methyl-2-cyclohexenone reaction, the total amount of 1:1 adduct formed was measured by vpc (column B) by cutting out and weighing the adduct peaks, and comparing the weight of these with the weight of the peak due to a known amount of internal standard (di-n-butyl phthalate), added after the photolysis was terminated. In the cases of the 2-cyclohexenone and its 2-methyl derivative, it was deemed more accurate to measure the weight ratio of the internal standard peak and that of the 3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone adduct (31 or 43). Then, on the assumption that the response of the flame-ionization detector is the same for isomeric compounds, the quantum yield for total adduct formation could be calculated from the known percentage of nortricyclic enone (31 or 43) in the product. A calibration curve was obtained for the vpc using 3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (31), purified by preparative vpc.

The amount of quadricyclene formed in each reaction was measured against an internal standard (toluene) by the

TABLE 5[‡]

QUANTUM YIELDS

Enone	Light Absorbed (millieinsteins)	Amount of Adduct		Amount of Quadricyclene		Quantum Yields	
		mg	mmoles	mg	mmoles	Adducts	Quadricyclene
	11.5	154	0.822	783	8.51	0.072	0.74
	11.4	152	0.812	771	8.38	0.071	0.74
	31.3	351	1.74	729	7.93	0.064	0.25
	34.2	440	2.18	787	8.55	0.056	0.25
	107	316	1.56	324	3.52	0.015	0.033
	105	226	1.12	302	3.28	0.011	0.031

[‡] Molar concentrations in hexane were: starting enone: 0.0192; norbornadiene: 0.525. Estimated maximum error of quantum yields: ±8%.

same method (cutting out and weighing of vpc peaks). This assay was performed separately from the adduct measurements, since quadricyclene requires much lower temperatures to ensure its stability on the vpc.

DISCUSSION

PART ONE: NORBORNADIENE AS SUBSTRATE

A large part of the Results section described the photoadditions of 2-cyclohexenone derivatives and norbornadiene, and some of the adducts formed were shown to have novel structures which would not have been predicted. Consequently, the first part of the Discussion will deal with the way in which these structures arise, and a fairly definitive mechanism will be proposed. Discussion of this mechanism will be divided into three parts:

a) The excitation process, and the nature of the reacting excited state.

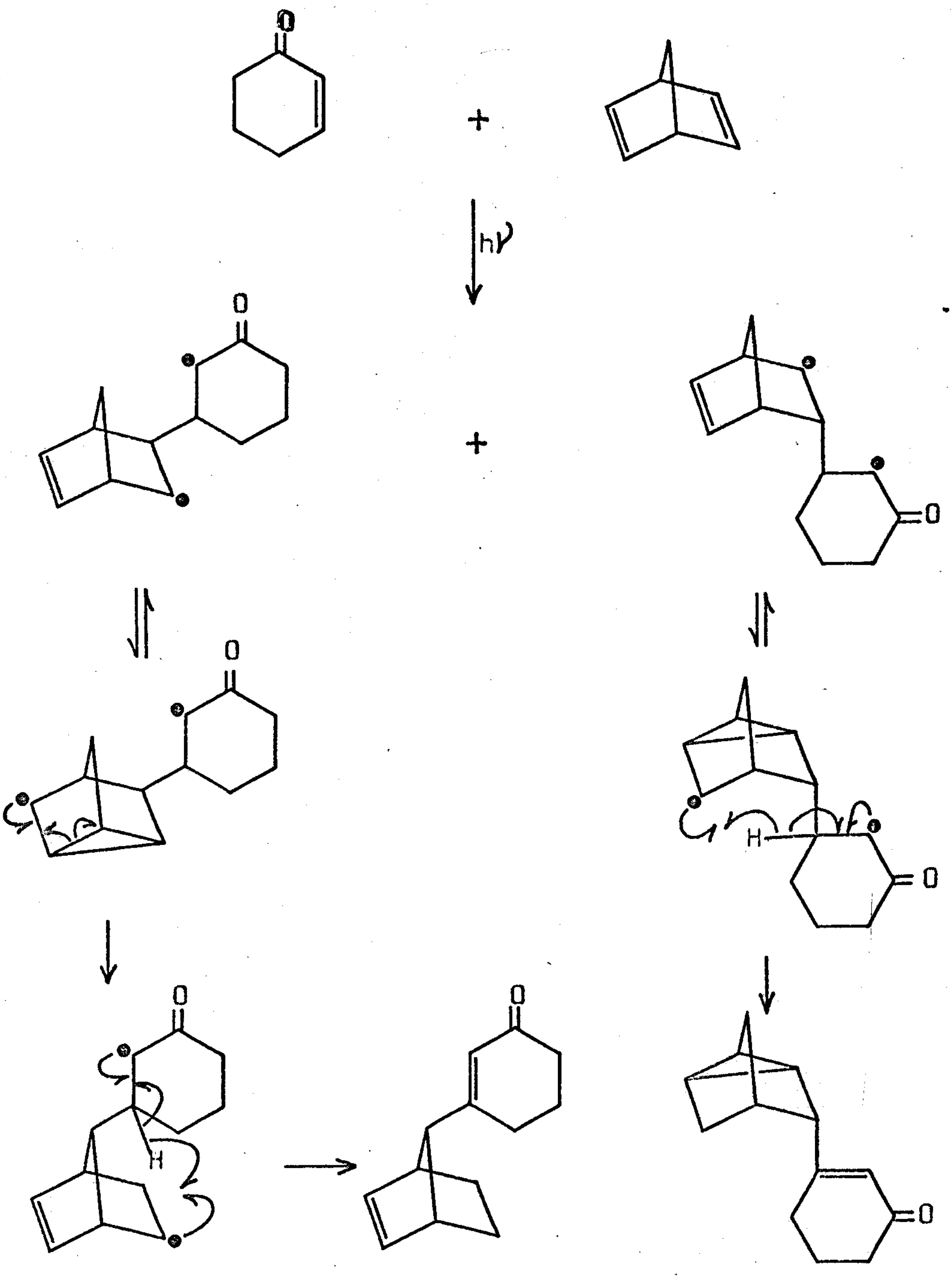
b) The reaction of the excited state with ground state substrate.

c) Subsequent migrations and/or rearrangements which lead to the adducts.

As an aid in the following discussion, Scheme 7 outlines the mechanism proposed for formation of two of the observed adducts.

The Excitation step

As mentioned in the Introduction (p 8), α,β-unsaturated ketones (*i.e.* 2-cyclohexenones) show absorption maxima in the ultraviolet at *ca.* 230 and 330 mμ, the latter band being due to the n-π^* transition. In all the work



34 31

SCHEME 7

FORMATION OF SUBSTITUTED CYCLOHEXENONE ADDUCTS reported here, pyrex glass was used to filter the light from the photolysis lamp, thereby ensuring that light of wavelength less than 290 mμ was not admitted to the photolysis solution. Thus, the first step of the photoaddition must be excitation of the cyclohexenone to its $n-\pi^*$ singlet state (norbornadiene does not absorb light above 290 mμ).

It is known that photochemical reactions of cyclic enones, including rearrangements[4] and cycloadditions[5-9], generally proceed *via* triplet excited states. Furthermore, if many photoreactions of cyclohexenones are carried out in the presence of naphthalene, the latter acts as an efficient quencher of the cyclohexenone triplets[4]. Thus, if the reaction of 2-cyclohexenone and norbornadiene, leading to substituted cyclohexenones, arises from the same triplet species that leads to the cyclobutanes (see p 21), the addition of naphthalene should retard the reaction without altering the product distribution.

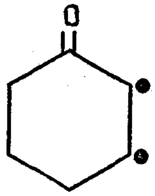
It was found that, in the reaction of 2-cyclohexenone and norbornadiene, the presence of 0.05 M naphthalene caused a threefold retardation in rate without changing the product ratio, as measured by vpc (Table 1, Results section). Therefore, all the products must arise from the same triplet excited state, or two triplets may be involved which transfer energy to naphthalene at similar rates.

It should be pointed out that, although the product distribution, as measured by vpc, did not change, infrared spectra of the photolysis mixture showed that the fraction of *cis*-fused cyclobutanes was considerably smaller in the quenched runs. This finds parallel in the results of Chapman *et al.*[9]. The apparent discrepancy between the vpc and infrared data may be due to both proposed [9] enone triplets being involved in the formation of cyclohexenone derivatives, or the change in the *cis*-/*trans*-fused cyclobutane ratio may not be large enough to cause appreciable change in the vpc. It is also possible that both vpc analyses (quenched and unquenched) are measuring only *cis*-fused cyclobutanes, since it is known that the *trans*-fused isomers do not survive preparative vpc[30].

The electronic configuration of the reacting triplet(s) is not known at present, since the n-π* singlet may decay to either the n-π* or π-π* triplet, or both. Although calculations[43] show that, for ground state geometry, the cyclohexenone n-π* triplet should be lowest in energy, confirmation of the proposed[8,9] two-triplet mechanism would obviate this arguement. (See the later discussion on the 4,4-dimethyl-2-cyclohexenone work).

Bimolecular reaction of the excited state

The second step in the photoaddition must be attack of the cyclohexenone triplet(s) on the norbornadiene to form one new single bond. This is probably best described by picturing the cyclohexenone triplet as a biradical, *i.e.*:



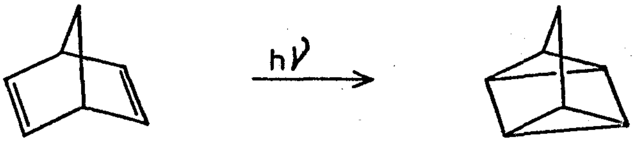
This representation is accurate in that it accounts for the formation of α- and β-substituted cyclohexenones, such as <u>31</u> and <u>32</u> (p 21). These are certainly a result of respective reactions of the diene at the α- and β-positions of the enone.

Whether the α- or the β-carbon of the excited enone is the major site of attack is a difficult problem; the factors which determine the ratio of α- to β-attack are not clear. Hückel-type calculations for acrolein-like systems indicate that the higher electron density should be at the β-position for both the n-π* and π-π* triplet[44]; consequently, if reaction occurs faster at higher odd-electron density, β-attack should be the major pathway. This would seem to be borne out by the α-/β-substituted cyclohexenone product ratio in the reaction of 2-cyclohexenone, which has hydrogen substituents at both positions. This ratio is 4:9[30]. However, it is unsafe to attach great significance to this ratio because the relative amounts of cyclobutanes which arise from initial α- and β-bonding to the enone triplet are not known (and cannot be determined at the present time).

Corey has suggested[28] that α-attack is the major pathway in the photoadditions of 2-cyclohexenones. He based this on the observation that an α-methyl substituent considerably retarded the rate of reaction while a β-methyl did not appear to have an appreciable effect. In this work it was shown (Table 5, Results section) that an α-methyl substituent decreases the quantum yield for formation of adducts by a factor of 5.5, relative to the unsubstituted enone. This indicates that α-attack is an important mode of reaction, since a methyl group should not significantly change the electronic configuration of the enone excited state. This finding is therefore in agreement with that of Corey[28].

It would appear, however, that such a straightforward explanation may not be applicable. A β-methyl substituent should be far enough removed so that it would not hinder α-attack; in spite of this, β-methyl substitution on the reacting enone is found to decrease the quantum yield for formation of adducts by a factor of 1.2 (Table 5, Results section). Also, as noted above, in the cyclohexenone-norbornadiene reaction, β-substituted cyclohexenones are the major enone products, a result not consistent with α-attack being the preferred mode of reaction.

It is important to consider the possibility that cyclohexenone derivatives arise in the norbornadiene photoadditions _via_ energy transfer from the enone to norbornadiene, followed by attack of the excited norbornadiene on the enone. An energy-transfer mechanism such as this appears to be unlikely since intramolecular cycloaddition of excited norbornadiene to form quadricyclene (49) is fast enough



49

to exclude dimerization. Thus, in the direct[45] or sensitized[46] irradiation of norbornadiene, no dimer is detected. Therefore, it is unlikely that excited norbornadiene is sufficiently long-lived to permit addition to cyclohexenone, which is present in low concentration (0.0192 M, see Table 5, Results section).

The detection of large amounts of quadricyclene (49) in these photoadditions to norbornadiene (see later Discussion) suggests another possible mechanistic pathway to the observed adducts; that is, energy transfer from the enone to norbornadiene to form quadricyclene (a process observed with sensitizers such as acetone and acetophenone[46]), followed by attack of excited enone on the quadricyclene. This was easily eliminated by irradiation of 2-cyclohexenone and quadricyclene; no adducts were formed (see Experimental section).

Thus, the most probable mode of initial attack in the cyclohexenone-norbornadiene photoadditions is single bond formation from ground state norbornadiene to the α- or β-carbon of the cyclohexenone. The intermediate formed is most probably a diradical. Zwitterionic intermediates seem unlikely since the product ratios in these photoadditions are identical in _n_-hexane and _tert_-butyl alcohol[30] (see also Table 1, Results section). It has also been shown[47] that the β-carbon of an excited cyclohexenone is not electron deficient, making Zwitterions less likely than diradicals. Such a diradical species has been proposed previously[28,48] as the species which cyclizes to a four-membered ring, and yields products of a hydrogen transfer[28].

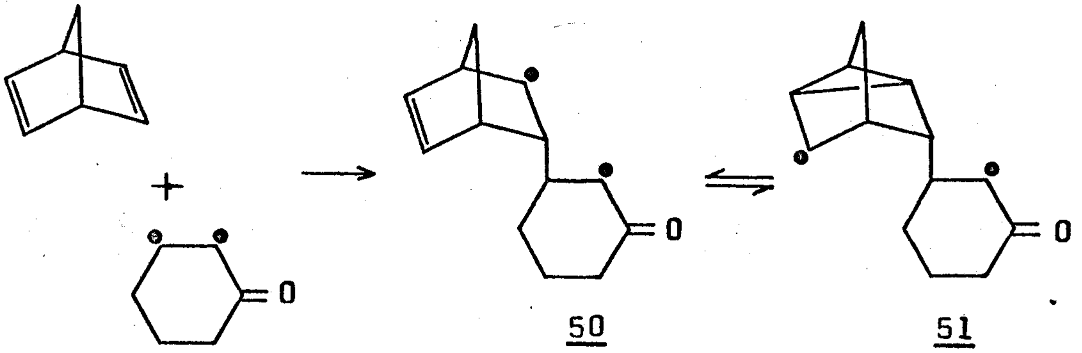
The derivation of the observed products from diradical intermediates will be outlined in the next section.

The Formation of the adducts

Consideration of the geometry of the substituted cyclohexenone products obtained leads to the conclusion that two distinct diradical intermediates are formed in these photoaddition reactions--one arising from _endo_-attack of the excited cyclohexenone, the other from _exo_-attack. We will consider these two separately.

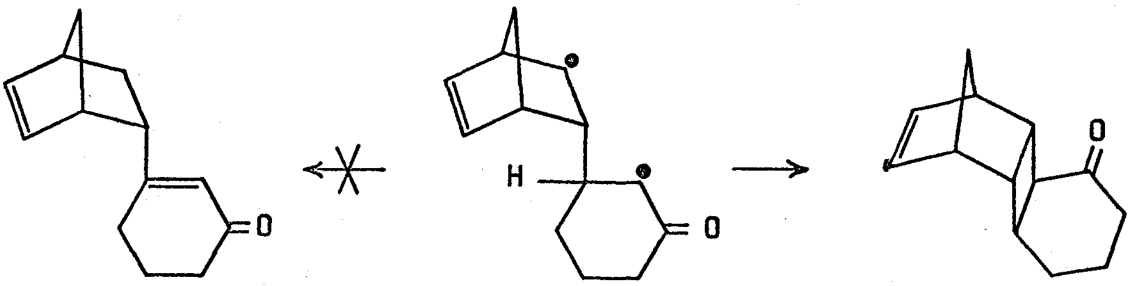
Endo-attack leads to a diradical intermediate which may exist in two forms, _50_ and _51_. Only β-attack is shown; attack by the α-position of the enone would lead to diradicals and α-substituted products in an analogous manner.

Disregarding the possibility of decay to starting materials (to be discussed later), two possible reaction pathways are open to _50_ and _51_: closure of the diradical, and hydrogen transfer to form the stable enone system.



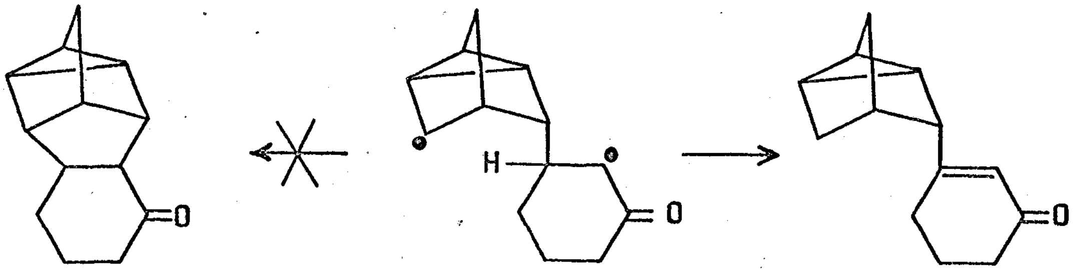
50 51

Radical combination in 50 leads to the well-known cyclobutane formation, while the 1,3-hydrogen shift necessary for formation of an enone product does not occur, since no 5-substituted norbornenes (52) are observed. This is not a surprising result, since 1,3-hydrogen shifts do not occur readily in radical systems[49].



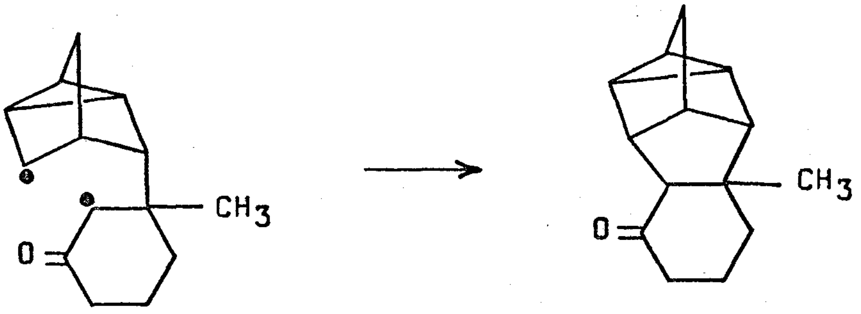
52 50

The tautomer 51, on the other hand, yields a product which must be a result of a 1,4-hydrogen shift (31), while



51 31

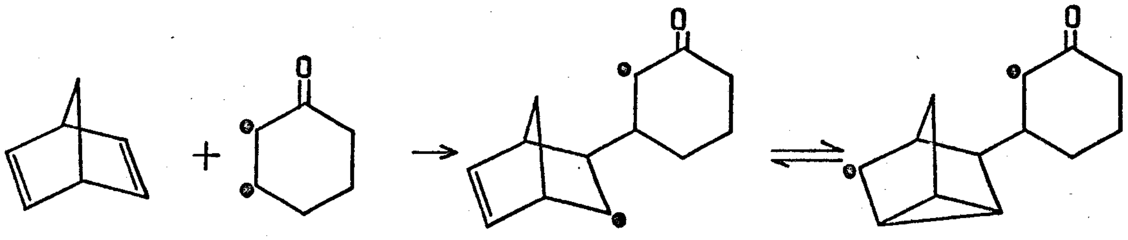
simple closure to a five-membered ring is not observed (unless a β-methyl substituent is present, see below). Although the 1,4-hydrogen shift postulated is known in radical reactions[50], it is difficult to see why the ring closure reaction is not competitive. Models indicate that the strain opposing such a closure should be small. Thus, the 1,4-shift must be quite fast. This is borne out by the fact that closure does occur when the 1,4-hydrogen shift is blocked by a methyl substituent:



40

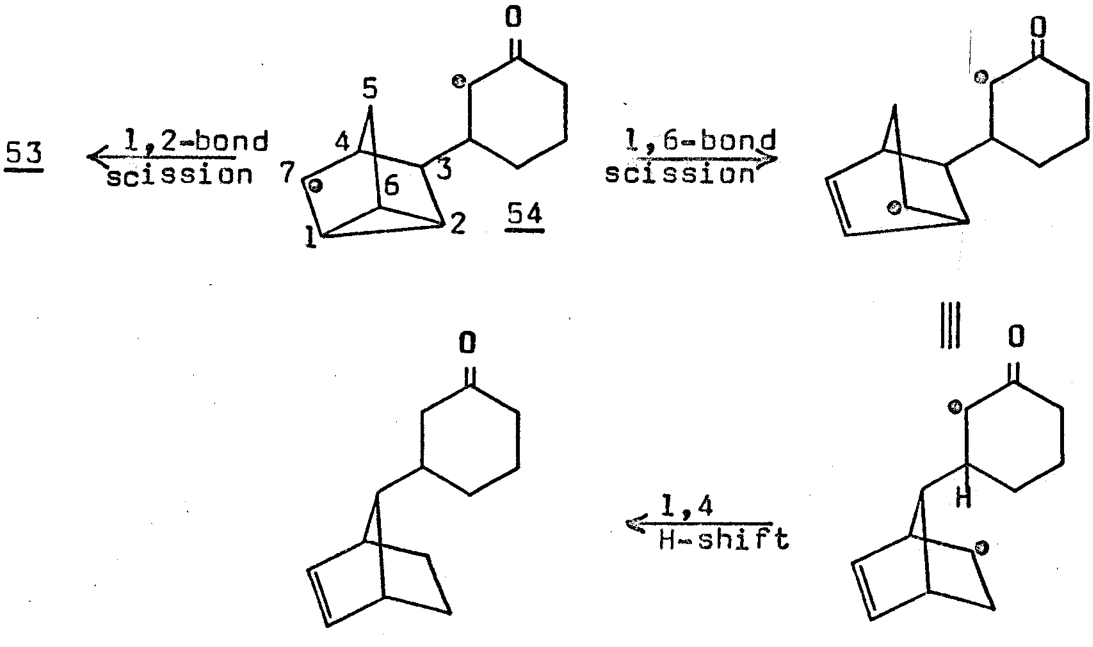
It is seen that endo-attack of the excited enone, acting as a diradical, gives rise to the nortricyclene products detected in these photoadditions (and also, in one case, the five-membered ring adduct, 40). Therefore, to account for the products, at least 26% of enone attack must be from the endo-side in the cyclohexenone-norbornadiene reaction[30]. In the 2-methyl-2-cyclohexenone reaction, this figure becomes 14% (Scheme 3), for 3-methyl-2-cyclohexenone, 24% (Scheme 1). These results can be reconciled with ground state free radical additions to norbornadiene--there have been at least two reports of 20% of a free-radical addition proceeding via endo-attack[51].

Exo-attack of the excited cyclohexenone must be postulated to explain the formation of 7-substituted norbornene products. Again, we can envisage two tautomeric diradicals (53 and 54) being formed via exo-attack. The tautomer 53 can only undergo closure to form cyclobutanes; the alternate pathway of 1,3-hydrogen transfer is not observed. The



53 54

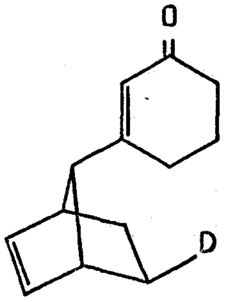
tautomer 54 does not have a geometry that is favorable for either closure or 1,4-hydrogen transfer. Thus, there are two pathways that this intermediate may follow. Scission of



34 55

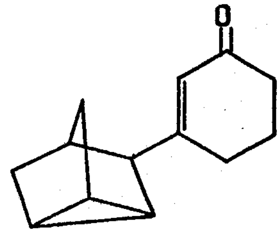
the 1,2-bond merely results in regeneration of tautomer 53. However, the near-symmetry of 54 demands that opening of the 1,6-bond be as likely as 1,2-bond scission. The former would result in the formation of diradical 55, which has a suitable geometry to allow a facile 1,4-hydrogen shift, to form an observed product (34).

If the above mechanism for the formation of 7-substituted norbornenes is correct, it should be possible to demonstrate that the 1,4-hydrogen shift is intramolecular. This was accomplished by irradiating 3-deutero-2-cyclohexenone in the presence of excess norbornadiene. The product mixture obtained was identical by vpc to that of the undeuterated enone-norbornadiene photolysis[30]. The product 36 was isolated and it was found by mass spectrum to contain one deuterium atom/molecule. The nmr showed that the deuterium was situated wholly in the *exo*-position, as indicated in the structure 36 (see Results section).



36

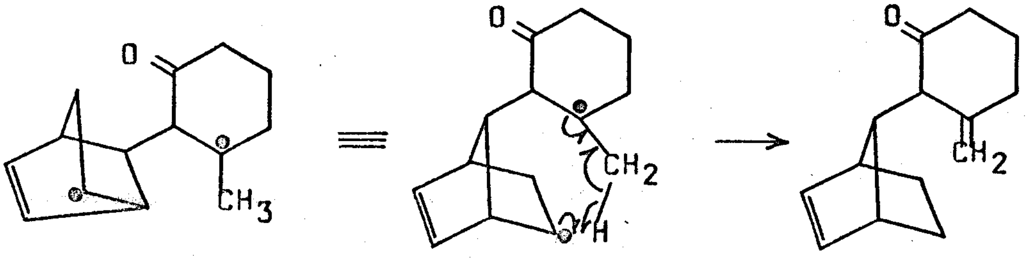
The deuterium-containing analog of 31 was also isolated from the reaction, and shown to be the result of intramolecular deuterium transfer (see Experimental section),



31

providing further evidence in support of the above diradical mechanism.

The unique exocyclic methylene product (38) isolated from the reaction of 3-methyl-2-cyclohexenone and norbornadiene can be envisaged as arising from an intermediate (56) which is analogous to the diradical intermediate 55.

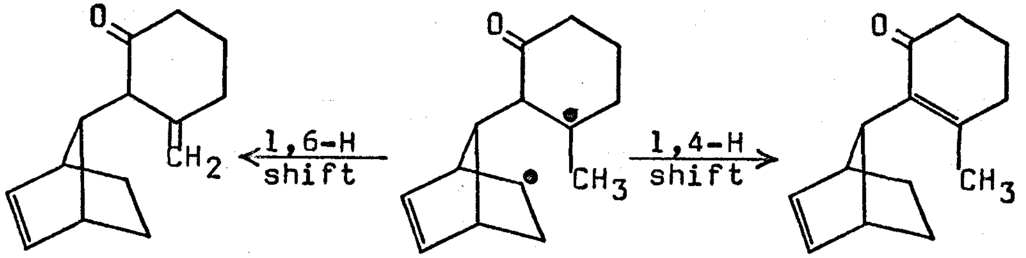


56

38

Thus, attack by the α-carbon of the enone, followed by bridging and bond scission, leads to the diradical 56. A 1,6-hydrogen shift then yields the observed product.

A 1,6-hydrogen shift in radical systems has not apparently been reported in the literature, but this may be due to lack of systems with the appropriate geometry. It seems that such a geometry is present in this system. Thus the exocyclic methylene compound (38) probably arises from the same intermediate as the conjugated photoproduct (37).



38 56 37

It is surprising that the 1,6-shift is apparently favored over the 1,4-process (approximately 7:1, see Results section). A control experiment was performed, showing that 37 is quite stable to photolysis, and certainly is not the precursor of 38 in the reaction.

The Question of complex formation

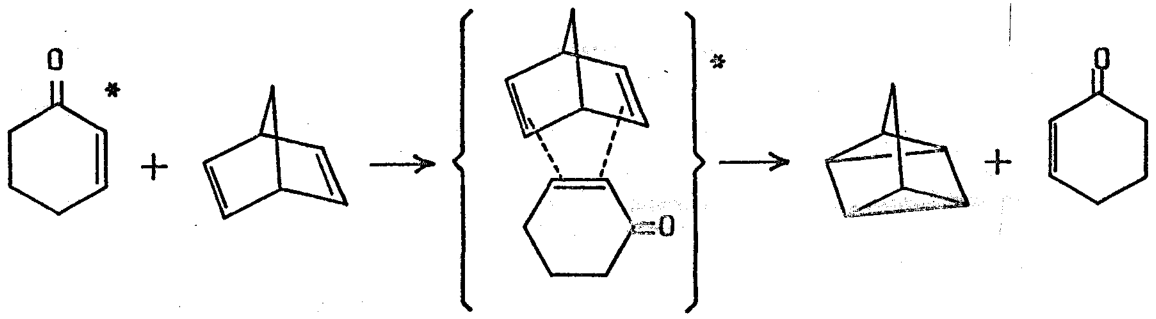
As mentioned earlier, an energy transfer mechanism leading to excited norbornadiene is an unlikely mechanistic pathway to the observed 1:1 adducts. It remains then to explore the possibility that the quadricyclene formed in all of these photoadditions to norbornadiene (see Table 5, p 47) arises through such a mechanism.

It is well known that the conversion of norbornadiene to quadricyclene is easily accomplished *via* photosensitization with low energy triplet sensitizers such as benzil ($E_T \approx 54$ kcal/mole) and 2-naphthaldehyde ($E_T \approx 60$ kcal/mole)[46]. Since 2-cyclohexenone has been shown to have a triplet energy of 61 kcal/mole[5], it would seem that energy transfer from this enone to norbornadiene could occur. However, methyl substituents on 2-cyclohexenone should not appreciably alter its π system, and the triplet excited state energy of 2-cyclohexenone should be similar to that of its methyl derivatives. All three enones should therefore transfer energy to norbornadiene at the same rate (if at all), since triplet-triplet energy transfer depends mainly on the donor and acceptor energy levels[52]. This is found not to be the case (see Table 5, p 47). A β-methyl substituent on the enone decreases the quantum yield of quadricyclene formation by a factor of three; an α-methyl by a factor of 23. Clearly, the quadricyclene cannot arise from simple triplet energy transfer.

It is possible that the observed effect of a methyl group on the quantum yields is due to a difference in triplet lifetimes of the enones. That is, if the presence of a methyl substituent on the cyclohexenone decreases the enone lifetime (*i.e.*, increases the rate of triplet processes, such as radiationless decay to ground state, which do not lead to products), it would necessarily decrease the quantum yield of product formation. No data is as yet available on lifetimes; however, the possibility of a lifetime effect is deemed unlikely for two reasons. First, because of its (probable) negligible effect on the electronic structure of the enone, a methyl group should not greatly change the lifetime. Any small change that does occur should be similar for both α- and β-methyl substitution, and this is contrary to experimental findings (Table 5). Second, a lifetime effect would probably be of the same order in both adduct and quadricyclene formation. Experimentally, an α-methyl substituent has an effect four times greater on quadricyclene formation than on adduct formation.

It remains then to propose a mode of attack of the excited enone on norbornadiene which is consistent with the data available. If quadricyclene is not formed *via* energy transfer, it must arise from a reversibility of the initial attack of the enone. This can be envisaged as reversible formation of a complex, or as an initially formed diradical which can decompose to starting enone plus quadricyclene. We shall consider both of these possibilities.

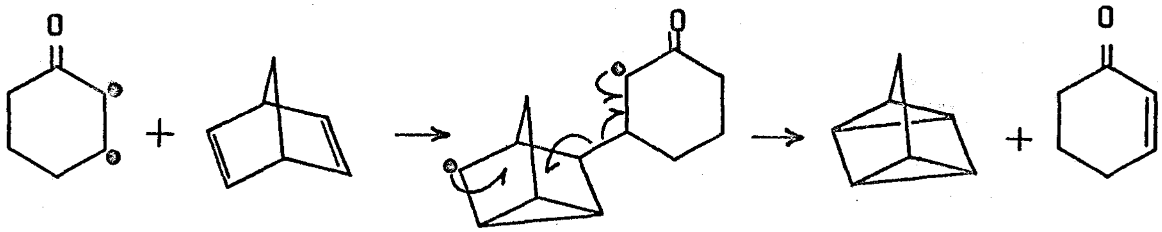
An initially formed complex similar to that proposed by Corey^{28} may be formulated as 57:



57

Calculations have shown that the excited triplet of norbornadiene has appreciable bonding character between the two non-conjugated double bonds^{53}. Hence, a complex formed between excited enone and norbornadiene could well have such a bonding interaction, and decay to ground state enone and quadricyclene is possible if the complex is sufficiently long-lived (that is, if collapse to a diradical is sufficiently slow). Endo-complexes (in the ground state) of norbornadiene are well known[54], but if the enone products arise from collapse of a complex to diradicals, invocation of an exo-complex is necessary to explain the 7-substituted norbornene products (see above). Such a complex has not been observed experimentally; however, if excited 2-cyclohexenone can form a complex with simple olefins (as suggested by Corey[28] to explain orientational specificity), complex formation from the exo-side of norbornadiene cannot be ruled out.

Little attention has been devoted to a possible reversible σ-bond formation step[55] as an alternative to complex formation, although in most cases it is difficult (if not impossible) to differentiate between the two possibilities. Thus, the quadricyclene formed can arise from a complex, as shown above, or from reversible diradical formation:



The ambiguity is illustrated by recent work on the photocycloaddition[56] and photodimerization[57] of cyclopentenone. The data suggests a reversible addition step, but the nature of this step (formation of an actual bond or a complex) is not clear. Clarification of this problem must await further experimental results.

PART TWO: CYCLOPENTENE AS SUBSTRATE

Quenching studies

It was shown in an earlier part of this Discussion that, in the addition of 2-cyclohexenone and norbornadiene, the nortricyclyl and norbornenyl products arise from the same triplet state or states as do the cyclobutane adducts (p 52). At the time this work was begun, it was not known whether mixed photoadditions of cyclic enones and alkenes proceeded entirely or partially by way of a triplet state. It was fairly certain, however, that triplets were involved to some extent, in view of their intermediacy in many other photoreactions[4a,6,7].

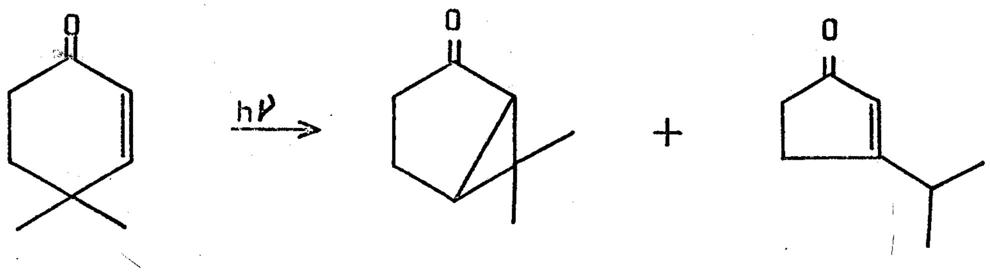
The reaction chosen to examine this problem was the photoaddition of 4,4-dimethyl-2-cyclohexenone and cyclopentene; this choice was made because it is known that the "type A" enone rearrangement (Scheme 6, Results section), which 4,4-dimethyl-2-cyclohexenone undergoes[18], is a triplet state reaction[4a]. In view of the relatively slow rate of this reaction[4a], it seemed that interception of the triplet was possible with a suitable concentration of alkene. Cyclopentene was used as the alkene in the competing addition reaction since the number of isomeric adducts possible was small.

It was found that, on photolysis of 4,4-dimethyl-2-cyclohexenone in the presence of 0.0858 M cyclopentene, 1:1

mixed addition products were formed, and so also was a measurable amount of "type A" rearrangement product (9, Scheme 6). The adducts were isolated and characterized, and were of the cyclobutane type. Speculation on the origin of these adducts, with particular reference to their stereochemistry, is reserved for later discussion.

To establish the intermediacy of triplet states in the addition reaction, the photolysis was performed in the presence of naphthalene (known to quench the "type A" rearrangement[4a]), and the adduct/type A product ratio was measured. The results are given in Table 3, p 44. It was found that the overall reaction is slowed down by a factor of three by 0.050 M naphthalene (the same as in the quenching of the 2-cyclohexenone-norbornadiene reaction, Table 1, p 41) while the product ratio did not change significantly. The adducts must therefore arise from the same excited triplet state(s) as the type A rearrangement product (9).

The comparison of the quenched to unquenched product ratio is most consistent if only the rearrangement product 9



8 9 10

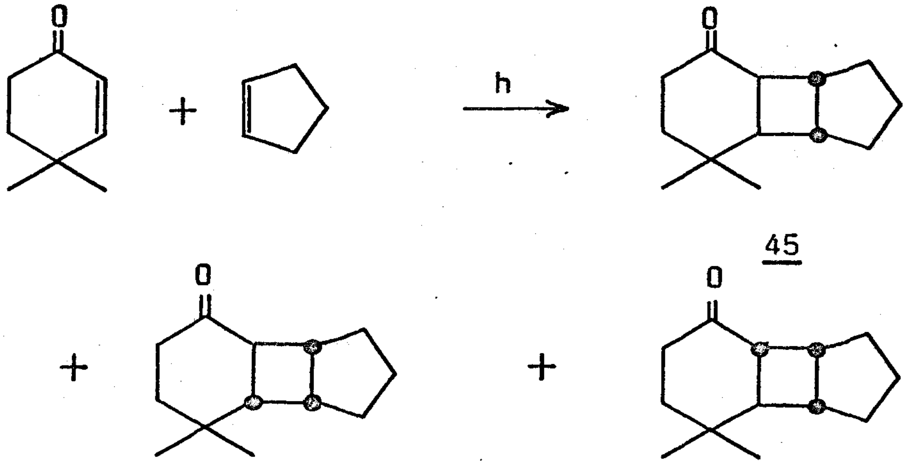
is considered. However, the minor product 10 has been shown to be a primary photoproduct[58] (formed *via* initial absorption of light by 8), and is formed in considerable amounts under the conditions used here. It was found that the 9/10 product ratio was approximately two in the absence of naphthalene, but this figure decreased to about unity in the quenched runs. It is difficult to speculate on the meaning of this variation in the absence of further data.

The cyclobutane adducts formed in this reaction were isolated and characterized (see Results and Experimental). Three adducts were formed, two of which contained *trans*-fused ring junctions. Although analysis of the mixture of cyclobutanes was difficult by vpc, each isomer exhibited a characteristic pair of methyl singlets in the nmr, thus providing a convenient method of analysis. Consequently, quenching studies were performed in order to determine the effect of naphthalene on the adduct isomer ratio. Excess cyclopentene was used to suppress the rearrangement reaction and avoid extraneous peaks in the nmr.

The results (Table 2, p 42) show that the overall *cis*-/*trans*-fused cyclobutane ratio is not appreciably changed on quenching with 0.050 M naphthalene. Furthermore, the highly strained *cis*-fused isomer (48) which is not observed in the absence of naphthalene, seems to be formed in significant amounts on quenching. No explanation can be offered at present for this observation.

The Origin of *cis*- and *trans*-fused cyclobutanes

In order to discuss the origin of the *cis*- and *trans*-fused cyclobutanes in the 4,4-dimethyl-2-cyclohexenone-cyclopentene addition, it is first necessary to outline the method by which the isomeric structures were assigned. Since only one *cis*-fused cyclobutane is formed (45), it was assigned the *cis*-*anti*-*cis* configuration on the basis of published results on analogous reactions.



45

46

47

Thus, cyclopentenone forms two dimers[24] and a cross-addition adduct with cyclopentene[24], all of which were shown to be *cis*-*anti*-*cis*. Similarly, the major 2-cyclohexenone-cyclohexene adduct[59] and the dimer of 3-phenyl-2-cyclohexenone[23] have been assigned this configuration. Corey and Nozoe[60] have found that the major adduct of the photoaddition of 3-methyl-2-cyclohexenone and 4,4-dimethylcyclopentene can be converted to α-caryophyllene alcohol (the structure of which is well known[61]), thus unambiguously specifying the configuration of the former as being cis-anti-cis.

Therefore, the major adduct in the photoaddition of 4,4-dimethyl-2-cyclohexenone and cyclopentene (the only cis-fused adduct) is almost certain to have the cis-anti-cis structure, 45. The configurations of the other two photoadducts then can be easily assigned, as outlined in the Results section, p 37.

It does not seem possible at this time to postulate a general hypothesis on the origin of cis- and trans-fused cyclobutane adducts. Although the suggestion of Corey[28] that a diradical can cyclize to afford both types of ring junction may be correct, there remains the question of why the more strained trans-fused system often predominates in the mixtures formed.

The possibility that two distinct triplets may be involved in some photoaddition reactions has been recognized by some workers. Both Chapman[62] and Yang[14b] considered two triplet states in an attempt to explain some photochemistry of 9-nitroanthracene. In the photoaddition of 9-anthraldehyde to trimethylethylene, Yang[14b] advanced a two-triplet hypothesis, and later showed[63] that two reactive excited states were indeed involved. Related to these results is the later observation that the phosphorescence of 1-indanone involves two triplets of differing lifetimes[64].

It has been reported by de Mayo that 2-cyclopentenone yields two photochemically reactive triplet states on photolysis[8]. An upper triplet (T_2), which cannot be sensitized by benzophenone, gives rise to mixed cycloadditions, while a lower triplet (T_1) is unreactive towards olefins. It was shown that 2-cyclopentenone quenches the photoreduction of benzophenone by isopropanol, a reaction known to proceed *via* benzophenone triplets[65]. Thus benzophenone is capable of transferring triplet energy to 2-cyclopentenone, but the excited enone triplet thereby formed does not undergo the cycloaddition reaction.

Chapman was led to postulate two reactive triplets in the photodimerization of isophorone[66], and he later extended this postulate to the photoadditions of isophorone and 4,4-dimethyl-2-cyclohexenone with 1,1-dimethoxyethylene[9]. Stern-Volner plots obtained by quenching the two mixed photoadditions showed that formation of the *cis*-fused cyclobutane adduct was quenched faster than that of the *trans*-fused product.

The intervention of two triplets, which lead to adducts of different geometries, is an intriguing possibility, and if this is indeed the case, then the *trans*-fused adducts should be formed from a non-planar triplet. Recent calculations in this department[29] indicate that the lowest triplet state of acrolein (a model for the enone system) is $n-\pi^*$ in character and planar in its equilibrium conformation.

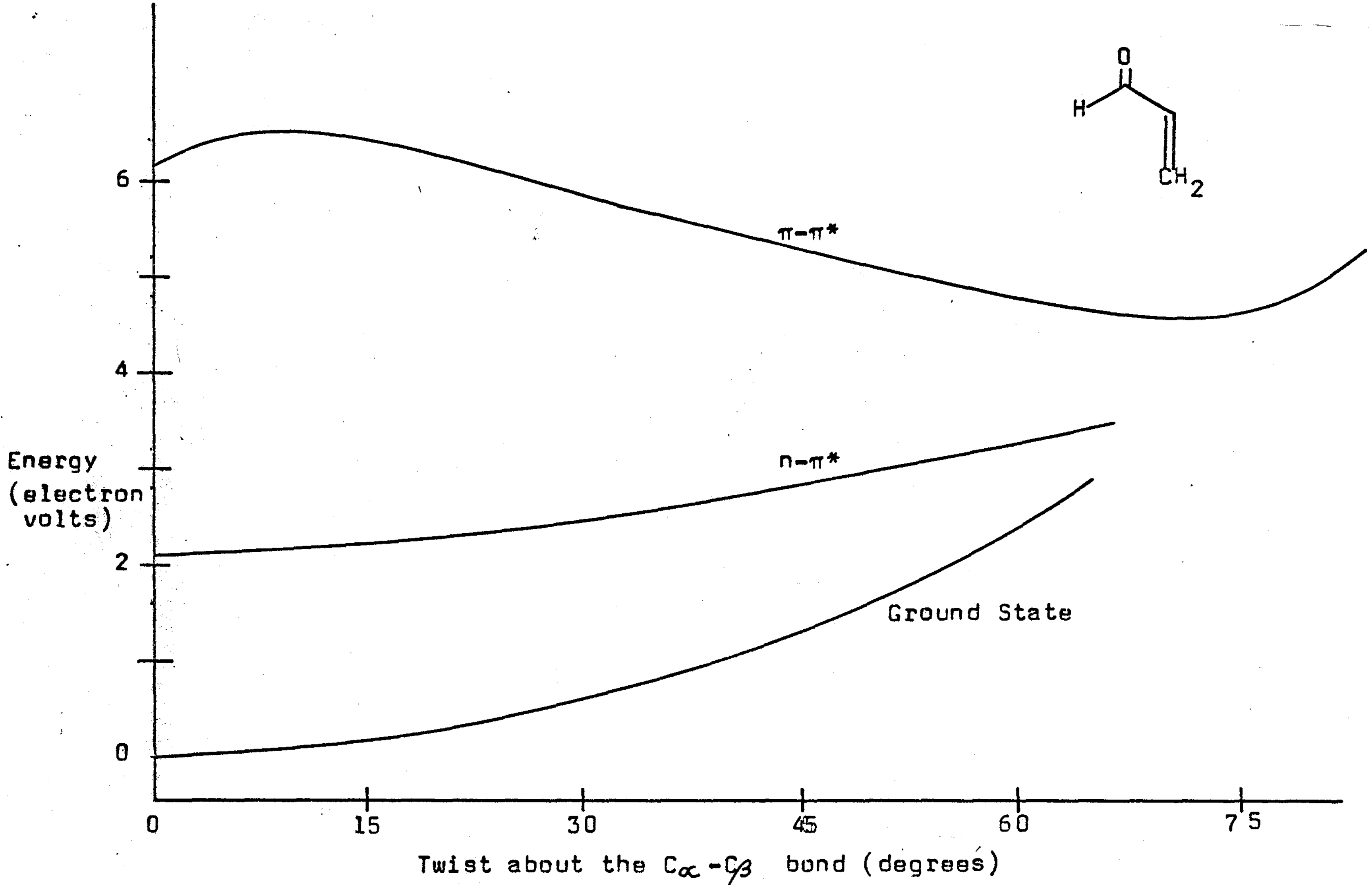


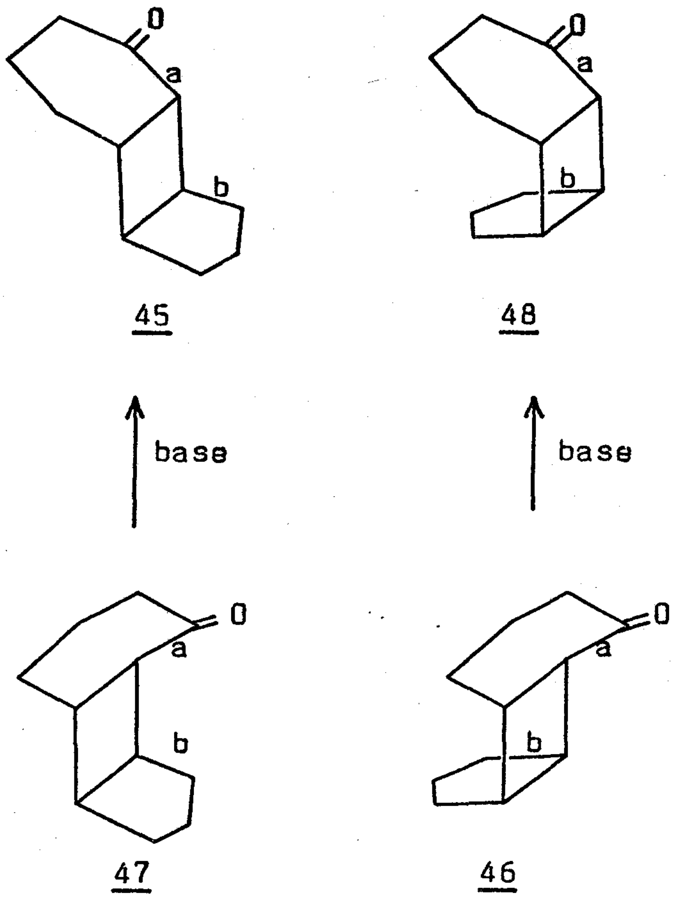
FIGURE 3: CALCULATIONS BY SANTRY AND OHORODNYK[29]

However, the triplet of next highest energy (π-π^*) is non-planar with respect to the CH_2 twisting coordinate. The equilibrium angle of rotation of the CH_2 group was calculated to be approximately 72°. The potential curves calculated for the ground state and two lowest triplets of acrolein are shown in Figure 3 (p 74).

It is obvious from these calculations that the non-planar π-π^* triplet of enones may well be the reactive species from which the _trans_-fused cyclobutane products are derived.

In the photoaddition of 4,4-dimethyl-2-cyclohexenone and cyclopentene, only one _cis_-fused cyclobutane (the _cis-anti-cis_ isomer _45_) is formed. This is not surprising since the _cis-syn-cis_ isomer (_48_) is highly strained. It remains, however, to account for the formation of two _trans_-fused adducts (_46_ and _47_), and more particularly, why one of them (_46_) predominates in the product mixture. Examination of models reveals that the amount of strain should be about the same in both isomers.

Assuming that original attack on the cyclopentene is by the α-carbon of the excited enone, the two major products of the reaction (_45_ and _46_) have one feature in common (see diagram). That is, the bond formed by C_α of the enone is formed in such a way as to put the carbonyl and methylene groups _trans_ to one another, _i.e._, bonds a and b are _trans_ in the two major adducts (_45_ and _46_). This is reasonable, since this mode of attack presents the least amount of steric



45 48 47 46

hindrance. Thus, it is postulated that this first step determines the course of the reaction (*cf.* review by Eaton[67]); subsequent steps can yield only 45 (as a *cis*-fused adduct) or 46 (*trans*-fused) by diradical closure. Reaction in the opposite sense (the initial bond having a *cis*-configuration) is sterically hindered, so much so that the *cis*-fused adduct 48 cannot be detected in the photolysis product. The presence of the *trans*-fused isomer 47 in the product may be due to the twisted excited enone presenting less steric hindrance to initial *cis*-bond formation, or it may arise from attack of

C_β of the enone.

It is possible that an argument such as the above may be valid as a first approximation, but, as pointed out previously in connection with photoadditions to norbornadiene, simple α-attack by an excited enone probably is an oversimplification.

PART THREE: CONCLUSIONS

It should be noted that the results reported here demand that hydrogen transfer (to form the substituted cyclohexenone products with norbornadiene) takes place intramolecularly after the initial bond formation step. Although Corey postulated such a sequence in his work[28], he was not able to eliminate the possibility of hydrogen abstraction being the initial step in formation of non-cyclobutane adducts.

The formation of large amounts of quadricyclene in the reactions with norbornadiene is also of interest, since it is unlikely that this highly strained hydrocarbon arises *via* simple energy transfer. Whether this isomerization proceeds by reversible σ-bond formation or not is a problem which deserves attention in the future.

Finally, although much is now known about enone photocycloadditions (cyclobutane formation), much remains to be done. This is amply illustrated by the uncertainty that exists regarding the origin of *trans*-fused cyclobutanes, and by the growing conviction that not only the lowest triplet of an excited state is capable of undergoing reaction in solution.

EXPERIMENTAL

Materials

All solvents and reagents for photoaddition reactions were distilled before use. The cyclohexenones used had the following boiling points: 2-cyclohexenone (Aldrich reagent), bp 61-62°C/16 mm; 3-methyl-2-cyclohexenone (Aldrich reagent), bp 58°C/10 mm; 2-methyl-2-cyclohexenone[68], bp 60-66°C/20 mm; 4,4-dimethyl-2-cyclohexenone[41], bp 53-55°C/2.5 mm.

Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, Aldrich reagent) was distilled at atmospheric pressure, bp 89-90°C, and was used immediately, as it polymerized on standing. Cyclopentene was Aldrich reagent, bp 44°C.

Hexane (Eastman practical grade) was purified by successive shaking with concentrated sulphuric acid, aqueous potassium permanganate, and water. It was dried (Drierite), filtered through silica gel, and distilled (bp 66.5-67.5°C). The solvent thus purified had negligible absorption above 250 mμ. Cyclohexane (bp 80-80.5°C) and cyclopentane (bp 55.0-56.0°C) were purified in the same manner. Tert-butyl alcohol was Baker Analysed reagent, bp 82°C. Methanol was B&A Reagent, and had bp 64.5-65°C. Naphthalene (Fisher purified) was recrystallized from benzene, mp 80°C.

Photolyses

All photolyses were run under nitrogen, Canadian Liquid Air certified grade, further purified by successive passage through vanadous sulphate solution[69], concentrated sulphuric acid, and over potassium hydroxide pellets. The lamp used was a Hanovia Type L450W, fitted with a pyrex sleeve in a water-cooled quartz immersion apparatus.

Chromatography

Column chromatography was on silica gel, Grace, grade 923 (100-200 mesh). Analytical vapour phase chromatography (vpc) was performed on a Varian-Aerograph Model 204-B dual column instrument with flame ionization detectors. The following columns were used with a flow rate (helium carrier gas) of 27 ml/min: Column A, 5' x 1/8" 10% FFAP on 60/80 Chromosorb W; Column B, 10' x 1/8" 12% FS1265 on 60/80 Chromosorb W; Column C, 5' x 1/8" 10% UCON 300X on 60/70 Chromosorb W. Preparative vpc was conducted on a Varian-Aerograph Model 200 dual column instrument with thermal conductivity detectors. A helium flow rate of approximately 60 ml/min was used with the following columns: Column D, 9' x 3/8" 20% FS1265 on 60/80 Chromosorb W; Column E, 3' x 3/8" 25% FFAP on 45/60 Chromosorb W; Column F, 15' x 3/8" 30% FFAP on 60/80 Chromosorb W.

Spectra

Nuclear magnetic resonance (nmr) spectra were routinely run on a Varian A-60 instrument ; carbon disulphide was the usual solvent, with tetramethylsilane as internal standard. Chemical shifts are given in parts per million (ppm) downfield from this standard. Spectra in which spin-decoupling was required were run at 100 Mc on a Varian HA-100 instrument.

Infrared spectra were recorded with a Beckman IR-5 or a Perkin-Elmer Model 337 instrument. Precise measurements were obtained from a Perkin-Elmer 521 spectrometer. Usually spectral grade carbon disulphide was the solvent.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer; usually Fisher "spectroanalysed n-hexane" was the solvent.

Mass spectra were obtained using a Hitachi Perkin-Elmer MRU6 instrument.

Elemental analyses were by the Spang Microanalytical Laboratory, Ann Arbor, Michigan.

Photoaddition of 3-methyl-2-cyclohexenone and norbornadiene

Irradiation of 3-methyl-2-cyclohexenone (4.583 g; 0.0416 mole) and norbornadiene (50.0 g; 0.543 mole) in *tert*-butyl alcohol (350 ml) and methanol (20 ml) for 3 hr, resulted in reaction of about 60% of the 3-methyl-2-cyclohexenone, estimated by infrared and vpc (column B, 231°C) monitoring. After solvent distillation, the liquid residue (5.960 g) was chromatographed on a 36 x 4 cm column of silica gel, slurry-packed in 3% ethyl acetate-benzene. The column was eluted with 5 litres of 3%, 6 litres of 5%, and 10 litres of 15% ethyl acetate-benzene, and 200 ml fractions were collected. The fractions were monitored by infrared and nmr spectra, and by vpc on column C (195°C), on which all the products of interest had different retention times.

Fractions 10-12 (688 mg) contained a single product, 3-methylene-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-cyclohexanone (38), retention time 12.4 min; fractions 13-15 (1.045 g) contained five products: 38, retention time 12.4 min; a cis-fused cyclobutane adduct of norbornadiene and 3-methyl-2-cyclohexenone, 18.0 min; 9-methyl-pentacyclo-$[7.4.0^{1,9}.0^{2,7}.0^{3,5}.0^{4,8}]$tridecan-13-one (40), 19.6 min; 3-methyl-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (37), 21.4 min; and 3-methyl-2-(3-tricyclo$[2.2.1.0^{3,6}]$heptyl)-2-cyclohexenone (39), 24.4 min.

Fractions 16 and 17 (474 mg) contained cis- and trans-fused cyclobutane adducts of 3-methyl-2-cyclohexenone and norbornadiene, but showed only one vpc peak (retention time 19.0 min). Fractions 18-60 contained a mixture of cis- and trans-fused cyclobutanes (1.090 g) which were not investigated in detail. 3-Methyl-2-cyclohexenone (1.619 g) was eluted in the later fractions. Recovery from the column was 4.916 g (84%). From the vpc analyses of the chromatography fractions, an estimate of the various product yields could be made. These yields are given below for each component along with its isolation and characterization.

3-Methylene-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-cyclohexanone (38)

The yield of this product was 15%, also measured by vpc of the original reaction mixture on column B at 230°C.

Preparative vpc (column E, 245°C) of fractions 10-12 afforded pure 38, retention time 11 min. The spectral data showed that this compound was a cyclohexanone, and contained a vinyl methylene group and a norbornene double bond. The ultraviolet spectrum showed enhanced n-π* absorption, λ_{max}^{hexane} 300 mμ, ε 103, suggesting a β,γ-unsaturated ketone. The mass spectrum had a parent ion of m/e 202.

Anal. Calculated for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found; C, 83.22; H, 8.86.

Cis-fused cyclobutane adducts

Two such adducts were isolated from the photolysis mixture.

Fraction 13 from the column was subjected to preparative vpc, column E at 245°C (retention time 17 min). The infrared spectrum had strong bands at 5.90 and 14.20μ, consistent with a cis-fused cyclobutane structure.

Fractions 16 and 17 showed a peak of retention time 18 min (column E, 235°C) which contained both cis- and trans-fused cyclobutanes (infrared bands at 5.86 and 5.91μ). The latter part of this peak was collected (column E, 235°C) to yield a 1:1 adduct (mass spectrum parent ion at m/e 202) which showed infrared absorption at 5.91 and 14.12μ. The adduct was thus identified as a *cis*-fused cyclobutane.

Anal. Calculated for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.19; H, 8.95.

9-Methyl-pentacyclo$[7.4.0^{1,9}.0^{2,7}.0^{3,5}.0^{4,8}]$*tridecan-13-one* (*40*)

The infrared and nmr spectra of fractions 14 and 15 suggested the presence of a nortricyclic adduct having a cyclohexanone carbonyl (infrared band at 5.90μ). Since it could not be isolated by preparative vpc, the following oxidation procedure[37] was employed to remove unsaturated compounds from the mixture.

A mixture (640 mg) containing 57% (by vpc on column C) of the five-membered ring compound (*40*), in 30 ml of *tert*-butyl alcohol-water azeotrope, was added to K_2CO_3 (278 mg) in water (70 ml) with stirring. This was followed by the addition of 5 ml of a solution of sodium metaperiodate (2.0 g) in water (25 ml) and 2.0 ml of 0.8% aqueous potassium permanganate. A further 10 ml of periodate solution was added over 10 min, followed by 7.0 ml over 20 min. Further additions of permanganate solution were made--one ml after 2 min, then six 0.5 ml portions added at 5 min intervals.

Stirring was continued for 3 hr, excess bisulphite solution was added, and the solution concentrated to half volume *in vacuo*; it was cooled in ice, neutralized with cold

50% H_2SO_4, and extracted with ether. The extracts were washed with water and dried over calcium sulphate.

Evaporation of the ether gave pure 40 (160 mg), retention time 21 min (column C, 195°C). The infrared spectrum had peaks at 5.90μ (cyclohexanone carbonyl) and 12.35μ (nortricyclene doublet). The nmr showed a methyl signal at 1.02 ppm, and no absorption downfield of 2.5 ppm. The mass spectrum had a molecular ion of m/e 202, which was also the base peak. The yield of 40 from the photolysis is estimated at 16%. An analytical sample was obtained by preparative vpc (column E, 227°C).

Anal. Calculated for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.10; H, 8.87.

3-Methyl-2-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (39)

Fraction 13 from chromatography of the photolysis mixture was subjected to preparative vpc (column E, 235°C). A peak of retention time 18 min was collected and afforded pure 39, which had a methyl peak at 2.07 ppm in the nmr, and no vinylic proton resonances. The infrared bands were at 6.00 and 12.37μ. This product was formed in 8% yield in the photolysis.

3-Methyl-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (37): Base catalysed isomerization of 38 to 37

The exocyclic methylene ketone (38) (0.786 g; 0.00388 mole) was stirred with sodium hydroxide (0.494 g;

0.0124 mole) in dioxane (150 ml) and water (60 ml) under nitrogen for 52 hr at 25°C. The solution was ether extracted (4 x 50 ml), the extracts washed with water (8 x 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave 0.50 g (64%) of a 2-cyclohexenone (infrared band at 5.99μ), identified with component 37 of the photolysis by vpc on columns A, B and C (on column C at 200°C the retention time was 19.6 min). This compound (37) was not isolated from the photolysis, since it was only formed in 2% yield. The spectral data (see Results) were obtained on material from this isomerization.

Anal. Calculated for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 82.99; H, 8.97.

Diimide reduction[36] of 3-methyl-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (37)

Compound 37 (0.50 g; 0.00247 mole) and dipotassium salt of azodicarboxylic acid (0.800 g; 0.00412 mole) in methanol (30 ml) were stirred under nitrogen while glacial acetic acid was added dropwise until all of the solid salt had dissolved. Saturated $NaHCO_3$ solution (40 ml) was added, the solution was extracted with ether (3 x 25 ml) and the extracts were dried ($MgSO_4$). Evaporation of the ether afforded 0.450 g (90%) of liquid which gave one peak on vpc (column B, 228°C). This compound was a cyclohexenone (infrared band at 5.99μ) and showed no vinylic proton resonances in the nmr. The mass spectrum had a molecular ion, m/e 204, consistent with the structure 3-methyl-2-(7-bicyclo[2.2.1] heptyl)-2-cyclohexenone (41).

Oxidative degradation[37] of 3-methyl-2-(7-bicyclo[2.2.1] heptyl)-2-cyclohexenone (41).

To a mixture of the 7-norbornyl cyclohexenone (41) from the diimide reduction (0.450 g; 0.00221 mole) and potassium carbonate (0.452 g; 0.00328 mole) dissolved in 13 ml of water and 48 ml of *tert*-butyl alcohol-water azeotrope, 8 ml of a solution of sodium metaperiodate (3.23 g in 40 ml of water) and 8 ml of 0.8% aqueous potassium permanganate were added. A further 33 ml of the above periodate solution was added at the rate of 1.8 ml/min for 10 min, then 0.5 ml/min for 30 min. A further 8 ml of the permanganate solution was added 5 min after the beginning of the reaction.

When the addition of the periodate was complete, sodium bisulphite solution was added until the solution turned from red to brown, then a slight excess. The solution was concentrated under reduced pressure to about 30 ml, cooled to 4°C, acidified with ice-cold 50% H_2SO_4 (40 ml), and extracted with ether (4 x 25 ml). The extracts were washed with sodium bisulphite, then with water, dried ($MgSO_4$), and the ether removed. The oily residue was subjected to liquid-liquid partition chromatography[70] on a 3 x 55 cm column slurry packed in pentane with 83.3 g of silicic acid (Mallinckrodt) and 16.7 g of Eagle-Picher Celatom, which had been coated with a mixture of 8.5 ml water, 40 ml methanol, 7.5 drops of 1N ammonia, and 5 ml of bromocresol green solution (0.200 g/25 ml methanol). Pentane was used as eluent and 125 ml fractions were collected. Fractions 3 and 4 contained an acid, mp 56-64°C, which was sublimed twice at atmospheric pressure to afford waxy white crystals, mp 74.0-75.0°C, identical to an authentic sample of 7-norbornane carboxylic acid (Lit.[38] mp 75-76.5°C) by infrared, nmr, and mixture melting point.

Photostability of 3-methyl-2-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (37)

The conjugated enone (37) (141 mg) from isomerization of the exocyclic methylene compound (38), in hexane (54 ml), was irradiated with the Hanovia 450W lamp for 5.5 hr. Gas chromatography (column C, 195°C) did not show any peaks other than that due to 37, retention time 23 min. Evaporation of the hexane afforded a quantitative recovery of 37, characterized by infrared and nmr spectroscopy.

Photoaddition of 2-methyl-2-cyclohexenone and norbornadiene

2-Methyl-2-cyclohexenone (2.327 g; 0.0211 mole) and norbornadiene (19.854 g; 0.2155 mole) in *tert*-butyl alcohol (375 ml) and methanol (20 ml) were photolysed for 8 hr under the usual conditions. Monitoring by vpc (column B, 245°C) showed peaks of retention times 2.8 min, 6.9 min (<u>44</u>), and 7.9 min (<u>43</u>). Also observed were several peaks of retention times between 3.8 and 4.6 min; these were shown to be *cis*-fused cyclobutanes (see below) and were not investigated in detail. The vpc analysis also showed that approximately 75% of the starting enone had reacted. The infrared spectra of aliquots had carbonyl bands at 5.80, 5.90 and 5.99μ.

The mixture remaining after solvent removal was chromatographed on a 36 x 4.0 cm column of silica gel, slurry packed in 2% ethyl acetate-benzene. The column was eluted with 6 litres of 2%, 1.5 litres of 3%, 2.5 litres of 4%, and 2 litres of 15% ethyl acetate-benzene, 200 ml fractions being collected.

Fractions 12-17 (1.145 g) contained the components with retention times 3.8-4.6 min, and these had infrared absorption at 5.90 and 14.13μ (*cis*-fused cyclobutanes). Fraction 12 showed an additional band at 5.80μ and was shown by vpc to contain mainly the compound of 2.8 min retention time. Fractions 18-60 (688 mg) contained compounds <u>43</u> and <u>44</u>. Recovery from the column was 1.833 g.

Trans-fused cyclobutane adduct

The peak of 2.8 min retention time in fraction 12 was collected by preparative vpc (column E, 245°C) The pure compound had infrared carbonyl absorption at 5.80 and 14.2μ, typical of *trans*-fused cyclobutane adducts of 2-cyclohexenones and norbornadiene. This product was formed in approximately 5% yield in the photolysis.

2-Methyl-3-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (44)

Fractions 20-28 were resolved by preparative vpc (column E, 245°C). The component of retention time 36 min was collected and showed infrared bands at 5.99 (conjugated carbonyl) and 14.20μ (norbornene double bond). The nmr is discussed in the results section, and is consistent with the structure 44. This compound constituted 10% of the photolysis product.

2-Methyl-3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (43)

Fractions 36-44 contained the compound 43, which was purified by preparative vpc (column E, 245°C), retention time 40 min. The infrared spectrum showed unsaturated carbonyl absorption at 5.99μ and a nortricyclene band at 12.37μ. The nmr was similar to those of other nortricyclene derivatives which have been characterized in this laboratory. This compound (43) constituted 14% of the photolysis product, and its structure was confirmed by independent synthesis.

2-Methyl-3-ethoxy-2-cyclohexenone

This was prepared by a modification of the method of Gannon and House[71]. A mixture of 2-methyl-1,3-cyclohexanedione (Aldrich, 24.82 g; 0.197 mole), p-toluenesulphonic acid monohydrate (1.035 g; 0.00544 mole), absolute ethanol (115 ml) and benzene (400 ml) were heated for 10 hours so that sufficient benzene-water-ethanol azeotrope distilled during this time to reduce the volume to half. The mixture was extracted as described for 3-ethoxy-2-cyclohexenone[71]. The dried ether solution was evaporated, and the following crystallization procedure was conducted in a dry-box, under dry nitrogen.

To the solid residue from the ether evaporation was added 300 ml of dry hexane, and the solid was dissolved by warming. The solution deposited white crystals on cooling, which were filtered, mp 58.5-59.5°C, 11.75 g. A second and third crop (total 6.85 g) of yellow crystals were obtained from the filtrate; these had mp 56-59°C. Total yield was 18.60 g (61%). The infrared showed two peaks in the carbonyl region, at 6.05 and 6.18μ, which are also shown by 3-ethoxy-2-cyclohexenone. The nmr was consistent with the structure 2-methyl-3-ethoxy-2-cyclohexenone.

Anal. Calculated for $C_8H_{12}O_2$: C, 70.10; H, 9.15. Found: C, 70.26; H, 9.25.

The crystals were very hygroscopic, and liquified rapidly in the air of the laboratory.

Synthesis of 2-methyl-3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone (43)

The Grignard reagent from 3-nortricyclyl bromide

(Aldrich, 8.572 g; 0.0495 mole) and magnesium (1.227 g; 0.0505 mole) in ether (30 ml) was prepared by the procedure of Woods *et al.*[72]. The reaction was run in a dry-box under dry nitrogen. To the Grignard reagent, cooled to 0°C, was added, with stirring, 2-methyl-3-ethoxy-2-cyclohexenone (7.735 g; 0.0502 mole) in ether (45 ml); the addition required 15 min. Stirring was continued for a further 30 min, and the solution was allowed to reach ambient temperature. After decomposition with 5% H_2SO_4, the ether solution was separated, washed with water, and dried ($CaSO_4$). The ether was evaporated to yield 7.62 g of oil, which was chromatographed on a 44 x 3 cm column of silica gel, slurry packed in 6% ethyl acetate-benzene, and eluted with this solvent. Collection was by 200 ml fractions. Fractions 3-7 contained 1.10 g (11% yield) of compound, judged pure by vpc (column C, 195°C), and identical with the photolysis product (**43**) by infrared and nmr.

Anal. Calculated for $C_{14}H_{18}O$: C, 83.12; H, 8.97. Found: C, 83.21; H, 8.90.

Isolation of quadricyclene from the 2-methyl-2-cyclohexenone-norbornadiene photolysis

2-Methyl-2-cyclohexenone (3.300 g; 0.0300 mole) and norbornadiene (42.7 g; 0.465 mole) in hexane (350 ml) were irradiated, as described previously, for 10 hours. The solvent-quadricyclene-norbornadiene mixture was distilled under reduced pressure, and the distillate subjected to slow distillation at atmospheric pressure through a 30 cm Vigreaux column. Distillation was discontinued when the head temperature reached 90°C, and the residue was analysed by vpc (column E, 78°C). Besides hexane, with a retention time of 4 min, the vpc showed only two peaks, with retention times of 14 min and 28 min, the former corresponding to norbornadiene and being in large excess. This excess diene was then removed <u>via</u> its silver ion complex[53] as follows:

The 20 ml of residue from the distillation was poured into aqueous silver nitrate (40 g in 50 ml water), the mixture shaken, and the curdy white precipitate (which rapidly darkened) was filtered and washed with water. The combined filtrate and washings were extracted three times, and the precipitate once, with ether. The ether extracts were combined, washed with water and saturated NaCl, and dried ($CaSO_4$). Removal of most of the ether, and vpc analysis of the residue as above showed the two components, with retention times of 14 and 28 min, to be in the approximate ratio of 2:1. Preparative vpc under the same conditions resulted in the isolation of pure norbornadiene (14 min) and quadricyclene (28 min). The latter was identical to authentic quadricyclene by infrared, nmr, and vpc analysis (columns B and E).

Preparation of quadricyclene[46]

Norbornadiene (68.2 g; 0.741 mole) and acetophenone (3.074 g; 0.0256 mole), dissolved in ether (1000 ml), were irradiated for 29 hr with the Hanovia 450W lamp under the usual conditions. Analysis by vpc (column B, 33°C) showed 96% conversion of norbornadiene (retention time 5.5 min) to a new compound of retention time 9.8 min. Removal of the ether, and distillation of the residue at atmospheric pressure yielded 30.9 g (45.4%) of quadricyclene, bp 108-109°C, containing 2% norbornadiene, as shown by vpc (column B, 33°C) and nmr. Redistillation and collection of the fraction boiling at 108.5-109°C yielded 99% pure quadricyclene, which gave infrared and nmr spectra identical to those reported[45, 73].

Photolysis of 2-cyclohexenone and quadricyclene

2-Cyclohexenone (0.888 g; 0.00925 mole) was dissolved in 200 ml of hexane and the solution divided into two equal portions. Norbornadiene (10.198 g; 0.111 mole) was added to one portion, and quadricyclene (10.203 g; 0.111 mole) to the other. The two solutions were then irradiated simultaneously in identical pyrex tubes for one hour. Analysis (vpc on column B at 215 °C) of the two solutions showed approximately 50% conversion of the starting enone in the norbornadiene case, and less than 0.2% as much reaction in the case of quadricyclene.

Photoaddition of 3-deutero-2-cyclohexenone and norbornadiene

3-Deutero-2-cyclohexenone[34] (4.955 g; 0.0510 mole), judged 99% deuterated at the β-position by nmr, and norbornadiene (36.72 g; 0.399 mole) in hexane (380 ml) were photolysed for 5 hr in the usual way. The photolysate (8.623 g) obtained on solvent evaporation was analysed by vpc (column A, 228°C) and showed the same product distribution as the photoaddition of 2-cyclohexenone and norbornadiene[30].

5-Deutero-3-(7-anti-bicyclo[2.2.1]hept-2-enyl)-2-cyclohexenone (36) and monodeutero-3-(3-tricyclo[2.2.1.$0^{2,6}$]heptyl)-2-cyclohexenone were isolated in the same manner as the corresponding undeuterated adducts (34 and 31, respectively)[30].

The adduct 36 gave a mass spectrum with parent ion m/e 189, an infrared spectrum with bands at 5.99 and 14.20μ, and an nmr which is treated in detail in the Results section.

Anal. Calculated for $C_{13}H_{15}DO$: C, 82.50; H+D, 9.05. Found: C, 82.53; H, 9.11.

The deuterated nortricyclic derivative gave a mass spectrum with parent ion m/e 189, an infrared spectrum identical to that of the undeuterated adduct (31)[30], and an nmr differing only in relative peak areas from that of 31.

Naphthalene quenching of the 2-cyclohexenone-norbornadiene photoaddition

2-Cyclohexenone (0.947 g; 0.00987 mole), norbornadiene (10.329 g; 0.112 mole), and naphthalene (2.560 g; 0.0200 mole) were dissolved in 30 ml of methanol, diluted to 400 ml with *tert*-butyl alcohol, and photolysed for 6 hours in the usual way. The products were then analysed by vpc (see Table 1, Results section) before removal of the solvent. The solvent was removed, and an infrared spectrum taken on the residue. The carbonyl region showed only two distinct bands, at 5.82 and 5.98μ, as opposed to the unquenched product, which shows an additional, equally intense, band at 5.89μ[30].

Ultraviolet spectra were run on the photolysis solution (for which hexane was the solvent) before and after irradiation, and the two were found to be essentially the same.

Quenching of quadricyclene formation in the 2-cyclohexenone-norbornadiene photolysis

2-Cyclohexenone (0.886 g; 0.0922 mole) and norbornadiene (20.406 g; 0.222 mole) were dissolved in hexane to make 200 ml of solution. This solution was divided exactly in half, and naphthalene (0.640 g; 0.00500 mole) was dissolved in one portion. The two solutions were placed in identical pyrex tubes, mounted directly to the lamp well, surrounded with cooling water, and irradiated with the Hanovia 450W lamp. The tube containing no naphthalene was removed after one hour, the other after a total of three hours irradiation.

The two solutions were analysed immediately by vpc on column B. The total amount of 1:1 adduct formed was measured at an oven temperature of 205°C, using di-n-butyl phthalate (Fisher CP, bp 142-146°C/0.9 mm) as an internal standard. Measurement of the amount of quadricyclene formed was accomplished at an oven temperature of 30°C, using toluene (Mallinckrodt Reagent, bp 109°C) as the internal standard. In analysing for quadricyclene, it was necessary to use injector temperatures of less than 120° to insure its stability. At the conditions used (injector: 110°C; detector: 110°C; oven: 30°C), an injection of pure quadricyclene showed only one peak (detection of extraneous peaks possible to less than 0.1%). The results of this experiment are given in Table 4, Results section.

Photoaddition of 3-methyl-2-cyclohexenone and norbornene

3-Methyl-2-cyclohexenone (0.957 g; 0.00870 mole) and resublimed norbornene (10.43 g; 0.111 mole), in hexane (400 ml), were irradiated for 4 hours in the usual manner. The solvent was removed, and analysis by vpc (column D, 245°C) showed three product peaks of retention times 11.8, 12.9, and 14.5 min in the approximate ratio of 1:3:1, and more than 90% conversion of starting enone. An infrared spectrum of the product mixture showed no nortricyclic absorption (12-12.5μ), and no carbonyl band above 5.91μ (at least two bands are present between 5.80 and 5.91μ). The nmr showed no resonances below 3 ppm.

Quantum yield determinations on the photoadditions to norbornadiene

The light source used was a Philips 500W high pressure mercury arc lamp giving directed radiation, placed at the focus (12 cm) of a lens 11 cm in diameter.

Filter solutions were used to provide the appropriate wavelength band; these were contained in a cell made up of three compartments, each 11.7 cm in diameter with 5 cm path length, and each cooled internally with a cooling coil. The compartments were separated, and the ends covered, with gasketed quartz disks. The filter solutions used in this work were: compartment one (nearest lamp), distilled water; compartment two, 1.6 g of stannous chloride dihydrate per litre of 15% hydrochloric acid; compartment three, 160 g of cobalt sulphate heptahydrate and 60 g of nickelous sulphate hexahydrate per litre of 3N H_2SO_4[4a]. This combination of solutions had maximum transmission of 45% at 330 mμ, and 0% at 298 and 375 mμ. A small amount of light (ca. 0.5% T) was transmitted at 430 mμ.

It was found that the transmission properties of the cobalt-nickel solution did not change significantly during prolonged irradiation; however, the stannous chloride solution was freshly prepared immediately preceeding each quantum yield determination.

For quantum yield measurements, a cell with quartz windows, 11.7 cm in diameter by 10 cm path length, was used to contain the solution of the enone and norbornadiene. Behind this, a similar cell with 5 cm path length contained 0.006 M potassium ferrioxalate and was used to measure the light output of the lamp[74].

Each determination required three irradiations: the first with only the actinometer (ferrioxalate) present, the second with both actinometer and photolysis solution; the third was a repeat of the first. When only actinometer was present, it was placed in the position occupied by the photolysis solution in the second irradiation. The first and third irradiations, which generally differed by less than 2%, were then used to calculate the light output during the second irradiation, corrected for the change in the actinometer during the latter run. This calculation assumed the quantum efficiency of conversion of ferrioxalate to be 1.23 at the band of wavelengths used[74]. Fresh actinometer solutions were used for each irradiation. Cooling of all the cells with tap water, circulated through the cooling coils, maintained the temperature at 6-8°C.

Duplicate quantum yields were measured on 2-cyclohexenone and its 2- and 3-methyl derivatives. In each case the photolysis was performed on 1200 ml of hexane, 0.0200 M in the enone, and 0.524 M in norbornadiene. The solution was purged of oxygen with argon (Canadian Liquid Air) before and during irradiation. Both the photolysis and the actinometer solutions were stirred mechanically.

In a typical run, 3-methyl-2-cyclohexenone was irradiated for 200 minutes, leading to the absorption by the enone of 3.42×10^{-2} Einsteins of light. Analysis by vpc showed the formation of 440 mg (2.18×10^{-3} moles) of 1:1 adduct, and 787 mg (8.55×10^{-3} moles)of quadricyclene, thus leading to quantum yields of 0.064 and 0.25 for adduct and quadricyclene formation, respectively. The quantum yield results are given in Table 5, Results section.

Photoaddition of 4,4-dimethyl-2-cyclohexenone and cyclopentene

4,4-Dimethyl-2-cyclohexenone (2.009 g; 0.0162 mole) and cyclopentene (22.1 g; 0.324 mole), in methanol (400 ml), were irradiated under the usual conditions for 2 hours, resulting in reaction of about 70% of the starting enone, as estimated by infrared and vpc (column D, 225°C) monitoring. The vpc analysis showed two products of retention times of 16 and 19 min, in the ratio of approximately 7:3. These two adducts were isolated by preparative vpc (column D, 225°C). The major product, retention time 16 min, showed carbonyl absorption at 5.91μ in the infrared, and two sharp singlets in the nmr at 0.87 and 0.88 ppm. Its mass spectrum had a parent ion at m/e 192, and it was assigned (see Results section) the structure 1α,2β,6β,7α-8,8-dimethyltricyclo-$[5.4.0.0^{2,6}]$undecan-11-one (<u>45</u>).

<u>Anal</u>. Calculated for $C_{13}H_{20}O$: C, 81.25; H, 10.42. Found: C, 81.02; H, 10.40.

The minor component (retention time 19 min) had a carbonyl band at 5.83μ in the infrared, and sharp methyl singlets at 0.98 and 1.19 ppm in the nmr. The mass spectrum showed the parent ion at m/e 192. It was assigned (see Results) the structure 1α,2β,6β,7β-8,8-dimethyltricyclo-$[5.4.0.0^{2,6}]$undecan-11-one (<u>46</u>).

<u>Equilibration of the 4,4-dimethyl-2-cyclohexenone-cyclopentene photolysis product</u>

The nmr of the above photolysis showed the following methyl singlets, given with their relative peak areas and assignment: 0.87 and 0.88 ppm, 41% (<u>45</u>); 0.98 and 1.19 ppm, 19% (<u>46</u>); 1.17 ppm, 28%, starting enone; 0.95 and 1.10 ppm, 12%, assigned to the <u>trans</u>-fused adduct (<u>47</u>), see below.

The photolysis mixture (0.75 g) was stirred in ether (50 ml) with basic alumina (Fisher, 13 g) for one hour, after which time monitoring by vpc (column B, 245°C) showed complete disappearance of the slower moving component. An infrared spectrum of the product showed only one carbonyl band, at 5.91μ, and analysis by vpc (column E, 218°C) gave two peaks in the approximate ratio of 6:4. Equilibration caused the methyl singlets at 0.98 and 1.19 ppm (**46**) in the nmr, as well as those at 0.95 and 1.10 ppm, to disappear, with the appearance of two new singlets at 0.95 and 1.02 ppm. Since the peaks at 0.98 and 1.19 ppm are assigned to the *trans*-fused isomer (**46**), which is known to give the *cis*-fused isomer (**48**) on equilibration (see below), the two singlets at 0.95 and 1.10 ppm are assigned to the other *trans*-fused adduct (**47**, the $1\beta,2\beta,6\beta,7\alpha$ isomer). Hence, on equilibration of the photolysis mixture, the *trans*-fused compound (**47**) is converted to the major *cis*-fused isomer (**45**). These results are shown in Scheme 5, Results section.

Preparative vpc (column E, 218°C) was carried out on the equilibrated product, resulting in isolation of the $1\alpha,2\beta,6\beta,7\alpha$ isomer (**45**), retention time 13 min (identical by vpc, nmr and infrared spectrum to that isolated from the photolysis product), and a new compound, retention time 15 min. This new isomer was assigned the structure $1\beta,2\beta,6\beta,7\beta$-8,8-dimethyltricyclo$[5.4.0.0^{2,6}]$undecan-11-one (**48**, see Results section). It showed a carbonyl band at 5.91μ in the infrared, and two methyl singlets in the nmr at 0.95 and 1.02 ppm.

Equilibration of $1\alpha,2\beta,6\beta,7\beta$-8,8-dimethyltricyclo$[5.4.0.0^{2,6}]$undecan-11-one (46)

The *trans*-fused cyclobutane adduct (**46**, *ca.* 50 mg) isolated from the photolysis product was stirred with basic alumina (10 g), in ether (50 ml) solution, until the infrared spectrum showed complete disappearance of the carbonyl band at 5.83μ, with appearance of a new band at 5.91μ. The alumina was filtered and the ether evaporated to yield a compound (*ca*. 50 mg) identical by vpc, nmr, and infrared spectra to the $1\beta,2\beta,6\beta,7\beta$ isomer (**48**) isolated from the equilibrated photolysis product.

Photorearrangement of 4,4-dimethyl-2-cyclohexenone[18]

4,4-Dimethyl-2-cyclohexenone (3,586 g; 0.0289 mole) was dissolved in *tert*-butyl alcohol (370 ml) and methanol (30 ml) and irradiated in the usual way for 60 hours. The solution was concentrated to about 6 ml under reduced pressure; analysis by vpc (column B, 180°C) showed more than 95% conversion of the starting enone.

Four major products were detected by vpc (column F, 215°C); their retention times (in min) and relative percentages are: 22 (20%), 30 (55%), 36 (6%), and 45 (19%). Preparative vpc was carried out under these conditions, isolating in greater than 95% purity the products of retention times 30 and 45 min. The other two products were not characterized, as they are most probably products of secondary photochemical reactions.

The major product (retention time 30 min) showed a singlet in the nmr at 1.10 ppm, equal in area to a complex multiplet centred at 1.8 ppm. Its infrared spectrum showed a carbonyl band at 5.82μ. From this evidence, which is consistent with that reported in the literature[18a,42], the major product is assigned the structure 6,6-dimethyl-bicyclo[3.1.0]-hexan-2-one (9).

The minor product (retention time 45 min) showed two singlets at 1.13 and 1.23 ppm in the nmr (total: 6 hydrogens), a complex multiplet centred at 2.3 ppm (5 hydrogens), and a quartet at 5.73 ppm (one hydrogen). The infrared spectrum had a carbonyl band at 5.84μ. Thus this product is 3-isopropyl-2-cyclopentenone (10)[18a,42].

The 4,4-dimethyl-2-cyclohexenone-cyclopentene system: measurement of product ratios

4,4-Dimethyl-2-cyclohexenone (0.0143 M in methanol) was divided equally between four identical pyrex tubes. Cyclopentene was added to each tube to make three solutions 0.570 M in cyclopentene, the other 0.797 M. Naphthalene (0.050 M) was added to two of the tubes which were 0.570 M in cyclopentene. All tubes were then purged of oxygen by three freeze-pump-thaw cycles, sealed under nitrogen, and irradiated simultaneously. The unquenched solutions were removed after 3 hr, the solutions containing naphthalene after a total of 9 hours. The ratio of the adduct products was then measured by nmr, without removal of the solvent. These results are given in Table 2, Results section.

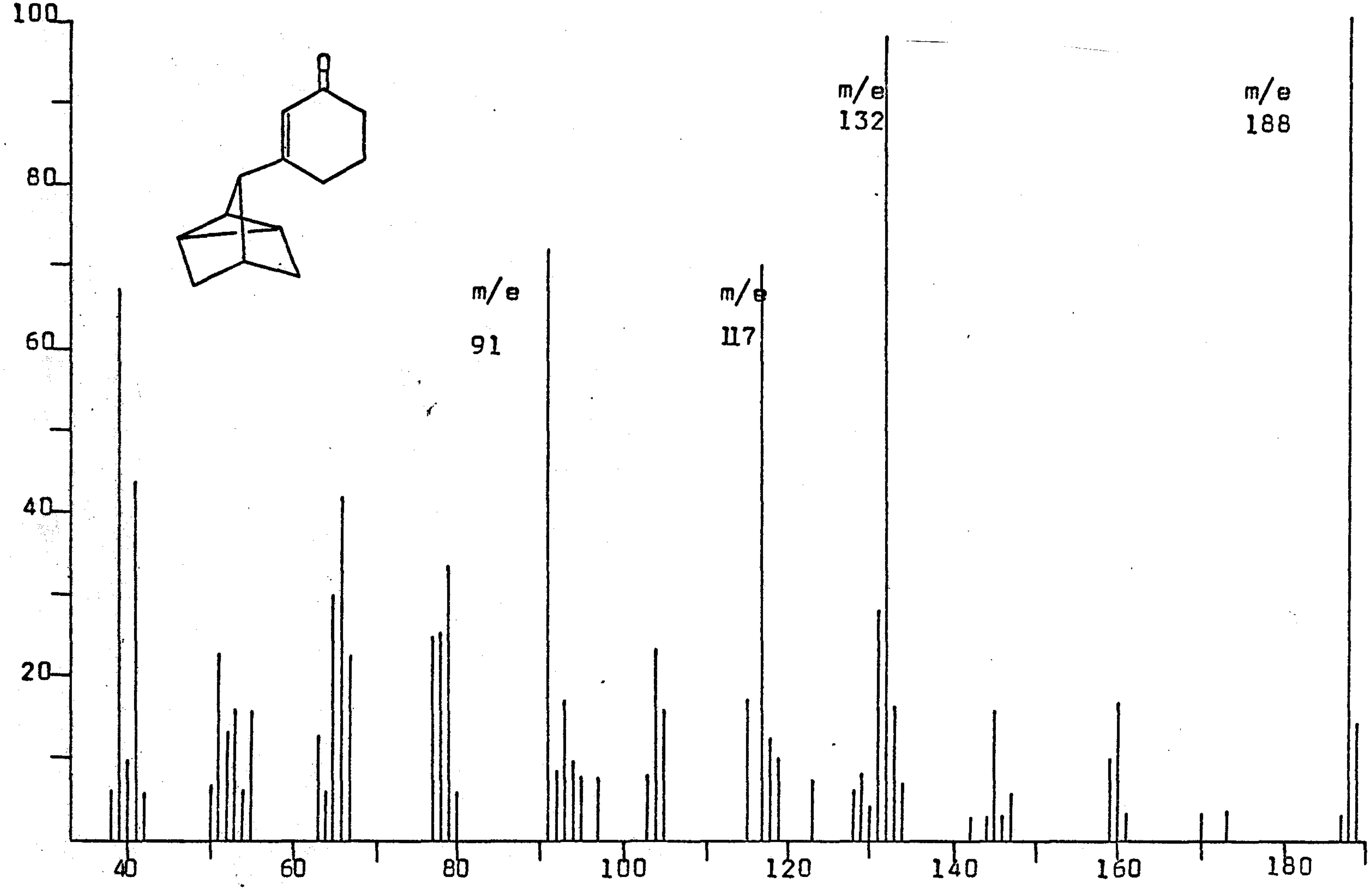
Six methanolic solutions (0.0143 M in 4,4-dimethyl-2-cyclohexenone and 0.0858 M in cyclopentene), three of which were made 0.050 M in naphthalene, were cooled in dry ice-acetone, flushed with purified nitrogen for ½ hour, and irradiated. The unquenched solutions were photolysed for 190 min, those containing naphthalene for 570 min. The products (rearrangement and 1:1 adduct products) were analysed by vpc (column B, 175°C) without removal of the solvent. The product ratios obtained are given in Table 3, Results section. The vpc was calibrated for this work with prepared mixtures of purified adduct and rearrangement product.

Low temperature photolysis of 4,4-dimethyl-2-cyclohexenone and cyclopentene

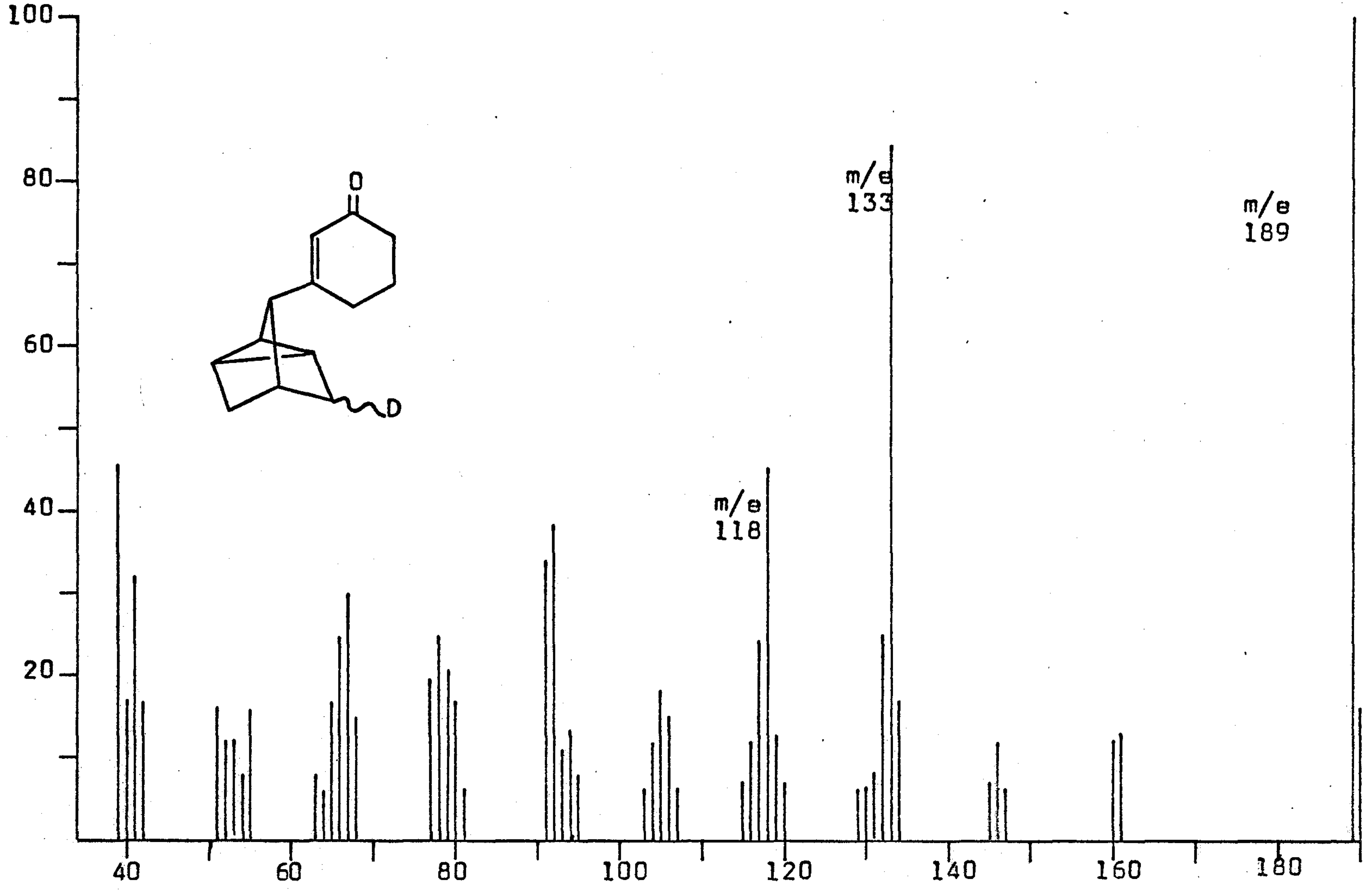
4,4-Dimethyl-2-cyclohexenone (0.105 g; 0.000847 mole) and cyclopentene (3.9 g; 0.057 mole), in cyclopentane (50 ml) were deoxygenated by three cycles of the freeze-pump-thaw method and sealed under nitrogen in a pyrex tube. It was then irradiated with a 275W Hanovia medium pressure mercury arc lamp for 5 hours (surrounded by methylene chloride for cooling), and analysed by vpc (column B, 204°C). The analysis showed three components other than solvent: starting enone (retention time 2.3 min, relative percent 88), and two adducts (7.6 and 8.5 min, combined relative percent 12) with the peak area ratio of 66:34.

An identical experiment was carried out, this time cooling the solution to -78°C with a dry ice-methylene chloride bath during irradiation. The vpc analysis (column B, 204°C) showed the product consisted of 95% starting enone, plus three products with retention times of 7.0, 7.6 and 8.5 min, in the ratio of 13:46:41. Meaningful analysis of the above products by nmr or infrared spectroscopy was made impossible by the large amount of starting enone present.

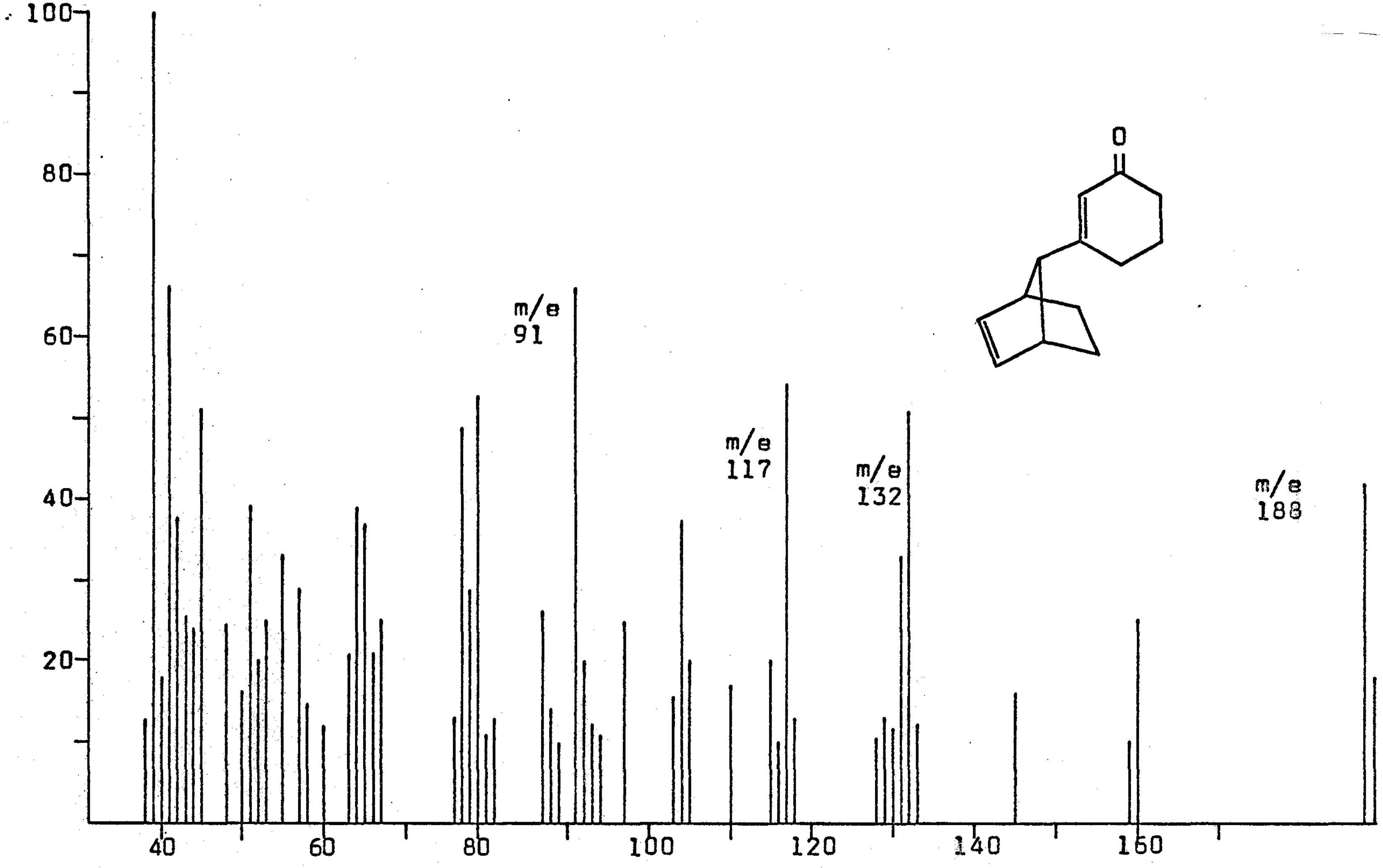
APPENDIX



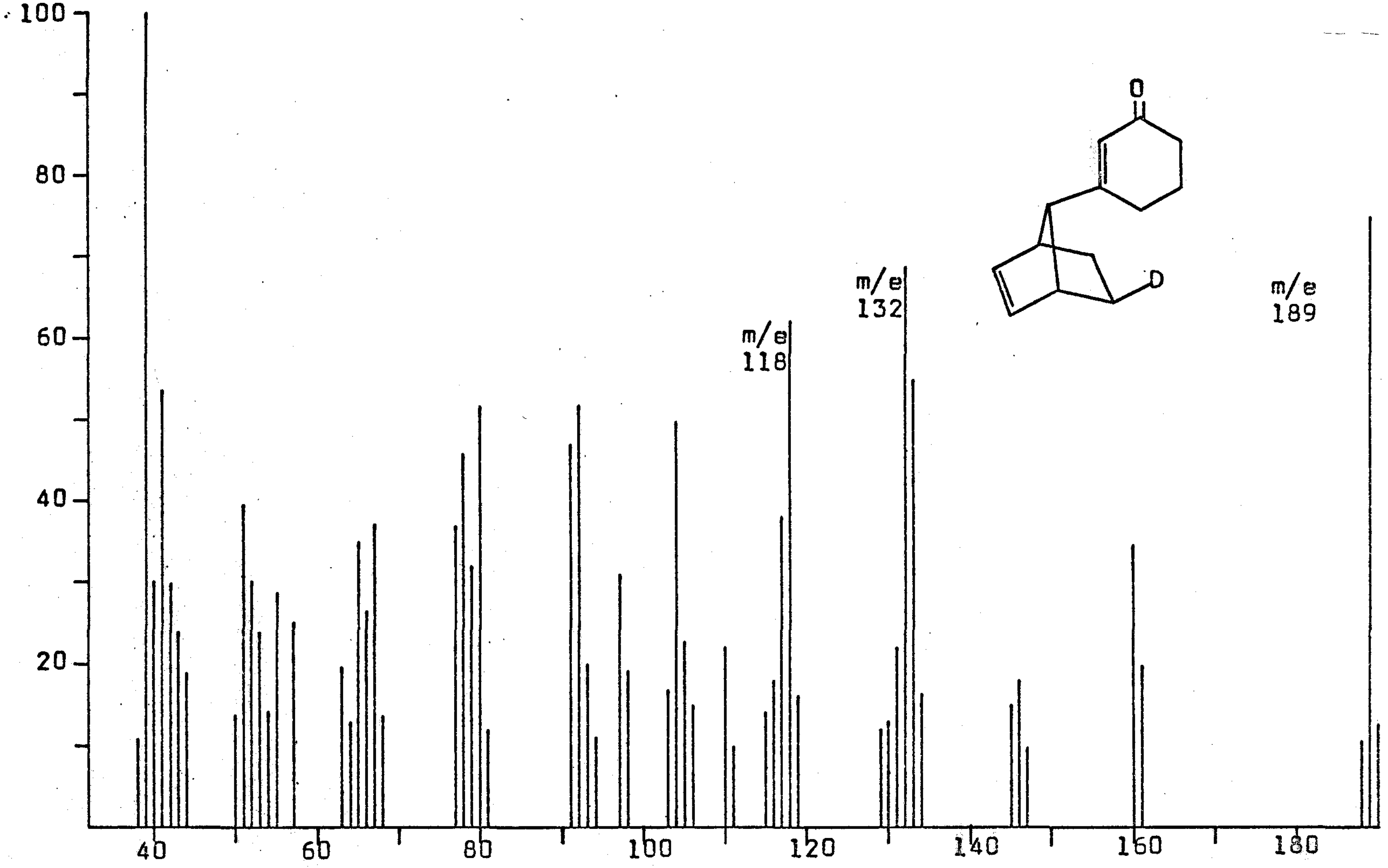
MASS SPECTRUM OF 3-(3-TRICYCLO[2.2.1.0^{2,6}]HEPTYL)-2-CYCLOHEXENONE (<u>31</u>)^{30}



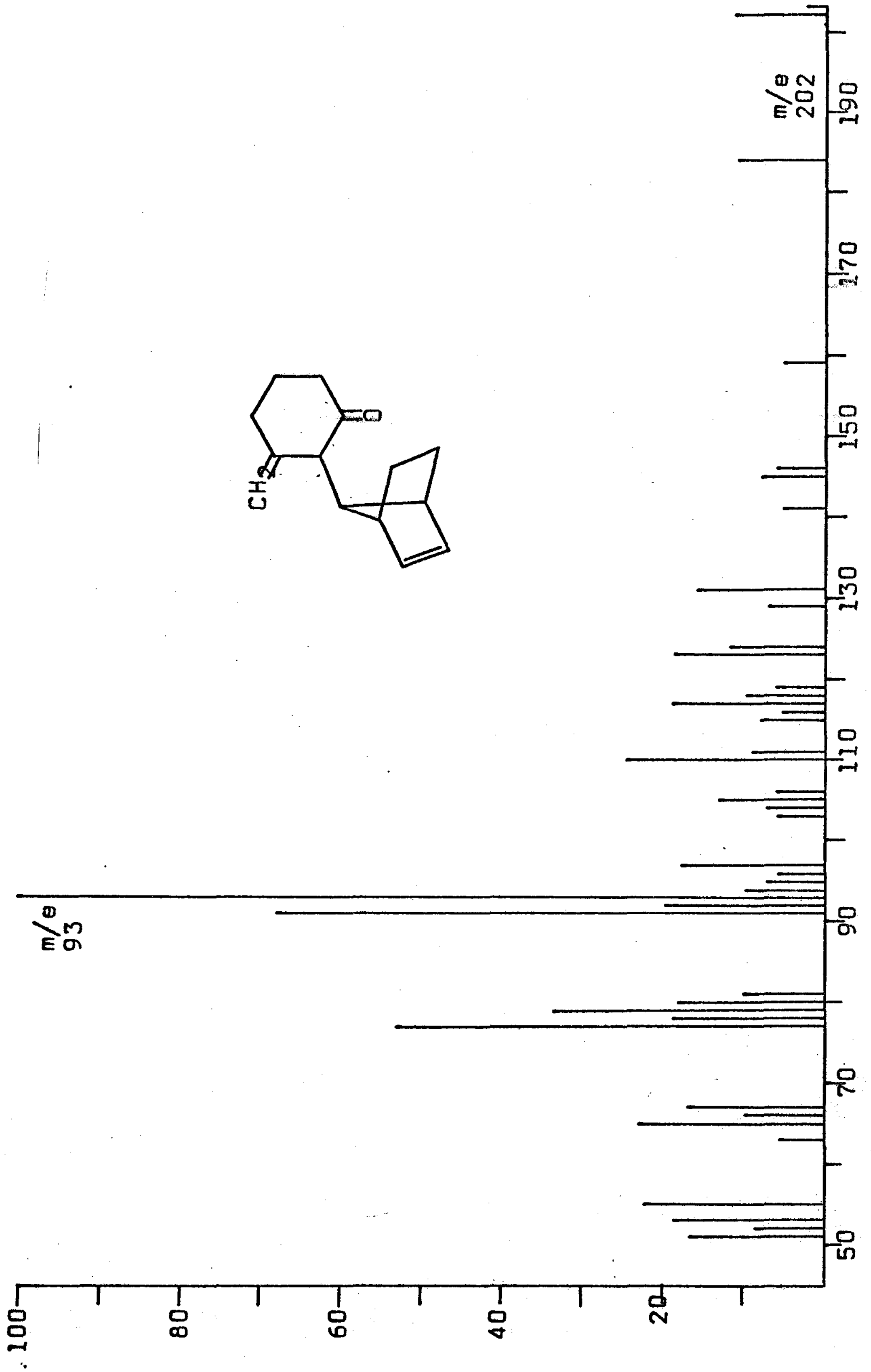
MASS SPECTRUM OF MONODEUTERO-3-(3-TRICYCLO[2.2.1.0^{2,6}]HEPTYL)-2-CYCLOHEXENONE



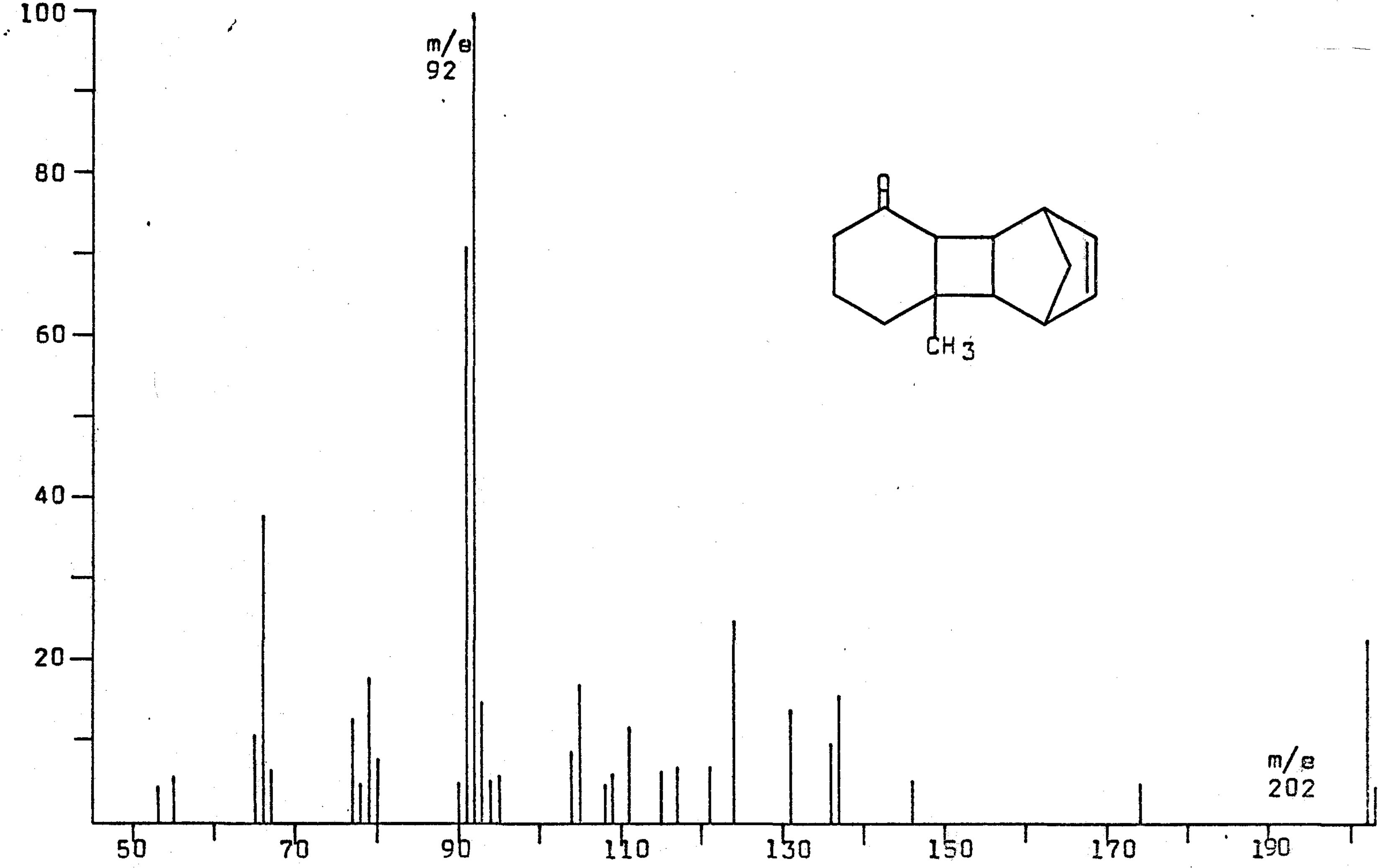
MASS SPECTRUM OF 3-(7-ANTI-BICYCLO[2.2.1]HEPTYL-2-ENYL)-2-CYCLOHEXENONE (<u>34</u>)^{30}



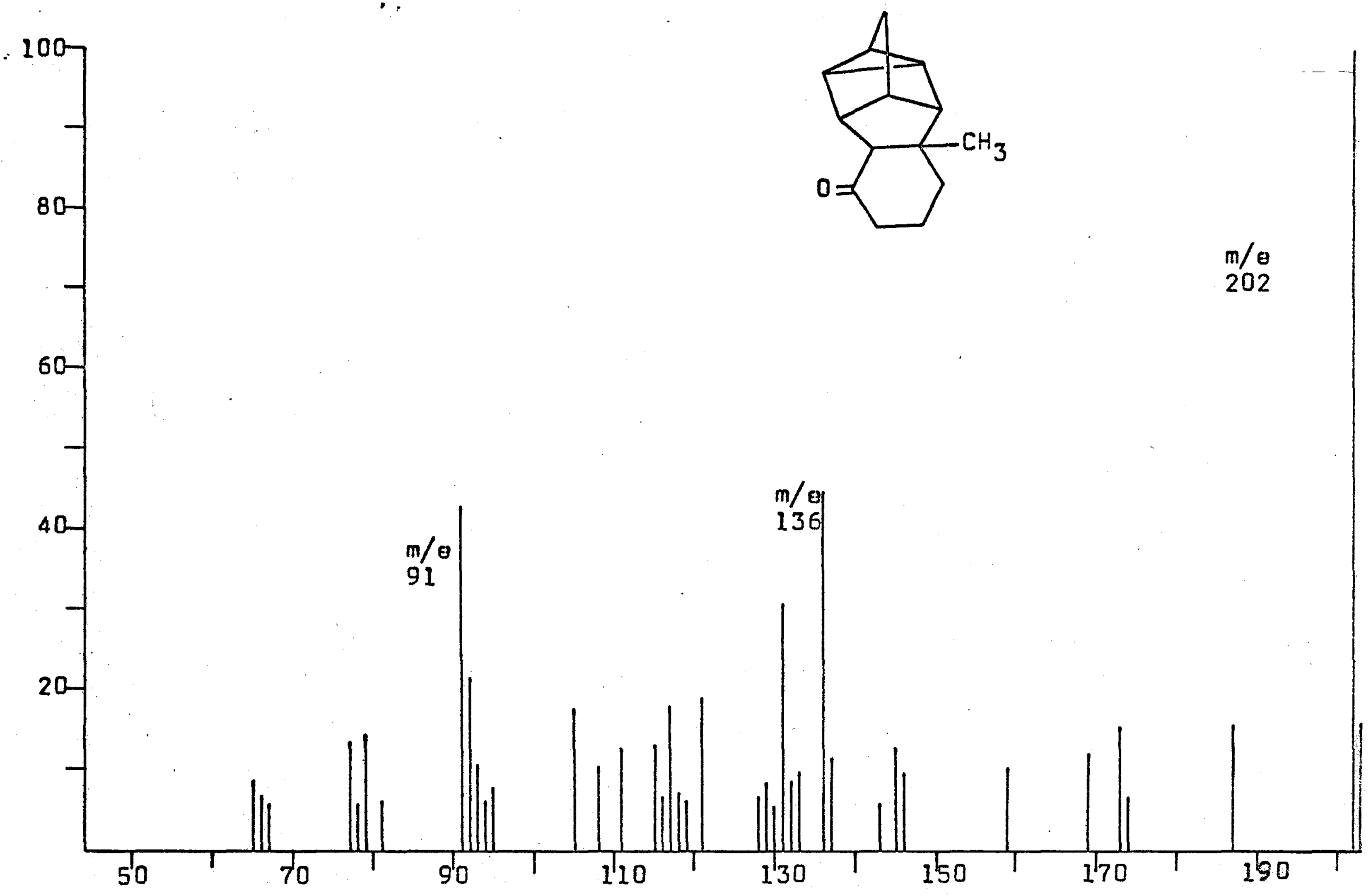
MASS SPECTRUM OF 5-EXO-DEUTERO-3-(7-ANTI-BICYCLO[2.2.1]HEPT-2-ENYL)-2-CYCLOHEXENONE



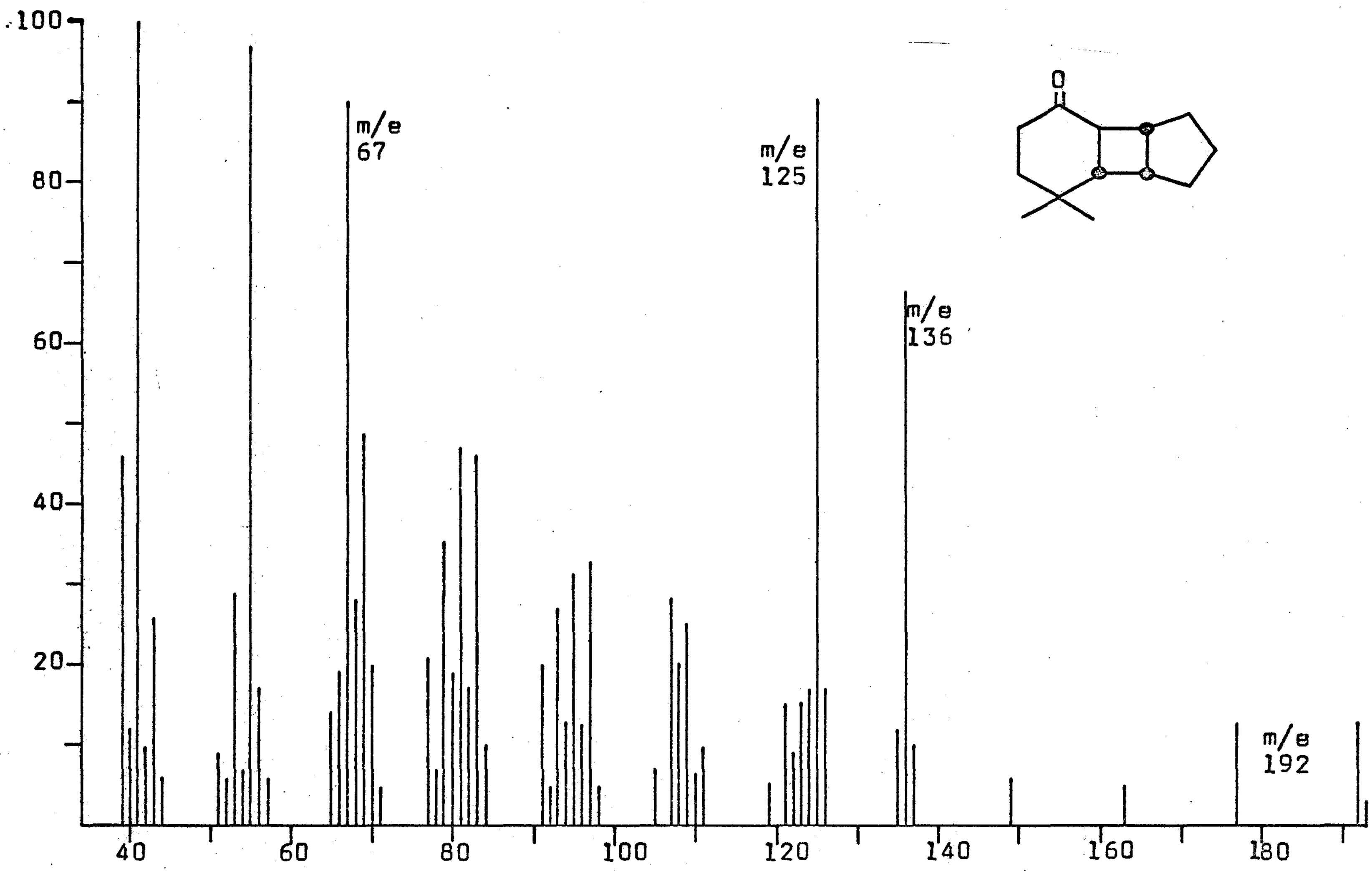
MASS SPECTRUM OF 3-METHYLENE-2-(7-<u>ANTI</u>-BICYCLO[2.2.1]HEPT-2-ENYL)CYCLOHEXANONE (<u>38</u>)



MASS SPECTRUM OF A CYCLOBUTANE ADDUCT OF 3-METHYL-2-CYCLOHEXENONE AND NORBORNADIENE



MASS SPECTRUM OF 9-METHYL-PENTACYCLO$[7.4.0^{1,9}.0^{2,7}.0^{3,5}.0^{4,8}]$TRIDECAN-13-ONE (<u>40</u>)



MASS SPECTRUM OF A TRANS-FUSED CYCLOBUTANE ADDUCT OF
4,4-DIMETHYL-2-CYCLOHEXENONE AND CYCLOPENTENE (46)

REFERENCES

1. Kan, R. O. "Organic Photochemistry". McGraw-Hill, New York, 1966.

2. Reference 1, p 4.

3. a) Chapman, O. L. Adv. Photochem., 1, 323 (1963).

   b) Zimmerman, H. E. ibid., 1, 183 (1963).

   c) Tezuka, T. Tett. Lett., 5677 (1968).

4. a) Zimmerman, H. E., Lewis, R. G., McCullough, J. J., Padwa, A., Staley, S. W., and Semmelhack, M. J. Am. Chem. Soc., 88, 1965 (1966).

   b) Zimmerman, H. E., and Hancock, K. G. ibid., 90, 3749 (1968).

5. Lam, E. Y. Y., Valentine, D., and Hammond, G. S. ibid., 89, 3482 (1967).

6. Eaton, P. E., and Hurt, W. S. ibid., 88, 5038 (1966).

7. a) Ruhlen, J. L., and Leermakers, P. A. ibid., 88, 5671 (1966).

   b) Ruhlen, J. L., and Leermakers, P. A. ibid., 89, 4944 (1967).

8. a) de Mayo, P., Pete, J.-P., and Tchir, M. ibid., 89, 5712 (1967).

   b) de Mayo, P., Pete, J.-P., and Tchir, M. Can. J. Chem., 46, 2535 (1968).

9. Chapman, O. L., Koch, J. H., Klein, F., Nelson, P. J., and Brown, E. L. J. Am. Chem. Soc., 90, 1657 (1968).

10. Schonberg, A., and Mustafa, A. Chem. Revs., 40, 181 (1947).

11. Bergman, F., and Hirshberg, Y. J. Am. Chem. Soc., 65, 1429 (1943).

12. Dauben, W. G., Lightner, D. A., and Hayes, W. K. J. Org. Chem., 27, 1897 (1962).

13. Quinkert, G. Angew. Chem. Intl. Ed., 4, 211 (1965).

14. a) Yang, N. C., Nussim, M., Jorgenson, M. J., and Murov, S. Tett. Lett., 3657 (1964).

b) Yang, N. C. Pure Appl. Chem., 9, 591 (1964).

15. Kahler. Arch. Pharm., 34, 318 (1830).

16. Kropp, P. J. "Organic Photochemistry", Vol. I. (O. L. Chapman, ed.) Marcel Dekker, New York, 1967. p 2.

17. a) Kwie, W. W., Shoulders, B. A., and Gardner, P. D. J. Am. Chem. Soc., 84, 2268 (1962).

b) Shoulders, B. A., Kwie, W. W., Klyne, W., and Gardner, P. D. Tetrahedron, 21, 2973 (1965).

18. a) Chapman, O. L., Rettig, T. A., Griswold, A. A., Dutton, A. I., and Fitton, P. Tett. Lett., 2049 (1963).

b) Dauben, W. G., and Cargill, R. L. Tetrahedron, 12, 186 (1961).

19. Chapman, O. L., and Lenz, G. "Organic Photochemistry", Vol. I. (O. L. Chapman, ed.) Marcel Dekker, New York, 1967. p 303.

20. Mustafa, A. Chem. Revs., 51, 1 (1952).

21. Treibs, W. J. Prakt. Chem., 138, 299 (1933).

22. Jennings, P. W. Diss. Abs., 26, 698 (1965).

23. Yates, P., Eğe, S. N., Buchi, G., and Knutsen, D. Can. J. Chem., 45, 2927 (1967).

24. Eaton, P. E. J. Am. Chem. Soc., 84, 2344, 2454 (1962).

25. Criegee, R., and Furrer, H. Ber., 97, 2949 (1964).

26. Cargill, R. L., Dorn, J., and Siebert, A. E. Abstract of Papers, Am. Chem. Soc., Chicago, August, 1964, 25S.

27. Hikino, H., and de Mayo, P. J. Am. Chem. Soc., 86, 3582 (1964).

28. Corey, E. J., Bass, J. D., Le Mahieu, R., and Mitra, R. B. ibid., 86, 5570 (1964).

29. McCullough, J. J., Ohorodnyk, H., and Santry, D. P. *Chem. Comm.*, in press.

30. a) McCullough, J. J., and Kelly, J. M. *J. Am. Chem. Soc.*, *88*, 5935 (1966).

    b) Kelly, J. M. M.Sc. Thesis, McMaster University, Hamilton, Ontario, 1967.

31. a) Fraser, R. R. *Can. J. Chem.*, *40*, 78 (1962).

    b) Foster, R. G., and McIvor, M. C. *Chem. Comm.*, 280 (1967).

32. Marchand, A. P., and Rose, J. E. *J. Am. Chem. Soc.*, *90*, 3724 (1968) and references cited therein.

33. Meinwald, J., and Meinwald, Y. C. *ibid.*, *85*, 2514 (1963).

34. Gannon, W. F., and House, H. O. *Org. Syn.*, *40*, 148 (1960).

35. a) Bellamy, L. J. "The Infrared Spectra of Complex Molecules", 2nd ed. John Wiley and Sons, New York, 1958. p 48.

    b) Kaplan, L, Kwart, H., and Schleyer, P. von R. *J. Am. Chem. Soc.*, *82*, 2341 (1960).

36. Baird, W. C., Franzus, B., and Surridge, J. H. *ibid.*, *89*, 410 (1967).

37. Edward, J. T., Holder, D., Lunn, W. H., and Puskas, I. *Can. J. Chem.*, *39*, 599 (1961).

38. Yates, P., and Crawford, R. J. *J. Am. Chem. Soc.*, *88*, 1562 (1966).

39. Courtauld's atomic models, available from Griffin and George, Ltd., Wembley, Middlesex, England.

40. Pollard, G. E. *Spectrochim. Acta*, *18*, 837 (1962).

41. Bordwell, F. G., and Wellman, K. M. *J. Org. Chem.*, *28*, 1347 (1963).

42. Rettig, T. A. *Diss. Abs.*, *B27*, 114 (1966).

43. Zimmerman, H. E., Binkley, R. W., McCullough, J. J., and Zimmerman, G. A. *J. Am. Chem. Soc.*, *89*, 6589 (1967).

44. Coulson, C. A., and Streitwieser, A. "Dictionary of π-Electron Calculations". W. H. Freeman and Co., San Francisco, 1965. p 227.

45. Dauben, W. G., and Cargill, R. L. Tetrahedron, 15, 197 (1961).

46. a) Hammond, G. S., Turro, N. J., and Fischer, A. J. Am. Chem. Soc., 83, 4674 (1961).

 b) Hammond, G. S., Wyatt, P., De Boer, C. D., and Turro, N. J. ibid., 86, 2532 (1964).

47. Zimmerman, H. E., Rieke, R. D., and Scheffer, J. R. ibid., 89, 2033 (1967).

48. Schneider, R. A., and Meinwald, J. ibid., 89, 2023 (1967).

49. a) Freidlina, R. Kh. Advan. Free Radical Chem., 1, 211 (1965).

 b) Walling, C. "Molecular Rearrangements", Vol. I. (P. de Mayo, ed.) Interscience, New York, 1963. p 407.

50. Gordon, H. A. S., and McNesby, J. R. J. Chem. Phys., 31, 853 (1959).

51. a) Van Auken, T. V., and Rick, E. A. Tett. Lett., 2709 (1968).

 b) Kwart, H., and Nyce, J. L. J. Am. Chem. Soc., 86, 2601 (1964).

52. Sandros, K., and Backstrom, H. L. J. Acta Chem. Scand., 16, 958 (1962).

53. Wilcox, C. F., Winstein, S., and McMillan, W. G. J. Am. Chem. Soc., 82, 5450 (1950).

54. Huisgen, R., Grashey, R., and Sauer, J. "The Chemistry of Alkenes" (S. Patai, ed.) Interscience, London, 1964. p 927.

55. a) Sivertz, C. J. Phys. Chem., 63, 34 (1959).

 b) Yang, N. C., Cohen, J. I., and Shani, A. J. Am. Chem. Soc., 90, 3264 (1968).

56. de Mayo, P., Nicholson, A. A., and Tchir, M. F. Can. J. Chem., 47, 711 (1969).

57. Wagner, P. J., and Bucheck, D. J. ibid., 47, 713 (1969).

58. Chapman, O. L. Program of the 20th National Organic Chemistry Symposium of the A. C. S., Burlington, Vermont, June 18-22, 1967. pp 127-139.

59. Valentine, D., Turro, N. J., Jr., and Hammond, G. S. *J. Am. Chem. Soc.*, *86*, 5202 (1964).

60. Corey, E. J., and Nozoe, S. *ibid.*, *86*, 1652 (1964).

61. a) Gemmell, K. W., Parker, W., Roberts, J. S., and Sim, G. A. *ibid.*, *86*, 1438 (1964).

    b) Nickon, A., McGuire, F. J., Mahajan, J. R., Umezawa, B., and Narang, S. A. *ibid.*, *86*, 1437 (1964).

62. a) Chapman, O. L., Griswold, A. A., Hoganson, E., Lenz, G., and Reasoner, J. W. *Pure Appl. Chem.*, *9*, 585 (1964).

    b) Chapman, O. L., Heckert, D. C., and Reasoner, J. W. *J. Am. Chem. Soc.*, *88*, 5550 (1966).

63. Yang, N. C., Loeschen, R., and Mitchell, D. *ibid.*, *89*, 5465 (1967).

64. Yang, N. C., and Murov, S. *J. Chem. Phys.*, *45*, 4358 (1966).

65. a) Moore, W. M., Hammond, G. S., and Foss, R. P. *J. Am. Chem. Soc.*, *83*, 2789 (1961).

    b) Hammond, G. S., Baker, W. P., and Moore, W. M. *ibid.*, *83*, 2795 (1961).

    c) Beckett, A., and Porter, G. *Trans. Faraday Soc.*, *59*, 2039, 2051 (1963).

    d) Porter, G., and Wilkinson, G. *ibid.*, *57*, 1686 (1961).

    e) Pitts, J. N., Johnson, H. W., and Kuwana, T. *J. Phys. Chem.*, *66*, 2456, 2471 (1962).

66. Chapman, O. L., Nelson, P. J., King, R. W., Trecker, D. J., and Griswold, A. A. *Record Chem. Progr.*, *28*, 167 (1967).

67. Eaton, P. E. *Acc. Chem. Research*, *1*, 50 (1968).

68. Warnhoff, E. W., Martin, D. G., and Johnson, W. S. *Org. Syn.*, Coll. Vol. *4*, 162 (1963).

69. Meites, L, and Meites, T. Anal. Chem., 20, 984 (1948).

70. Neville, W. A., Frank, D. S., and Trepka, R. D. J. Org. Chem., 27, 422 (1962).

71. Cannon, W. F., and House, H. O. Org. Syn., 40, 41 (1960).

72. Woods, G. F., Griswald, P. H., Jr., Armbrecht, B. H., Blumenthal, D. I., and Plapinger, R. J. Am. Chem. Soc., 71, 2028 (1949).

73. Tori, K., Hata, Y., Muneyuki, R., Takano, Y., Tsuji, T., and Tanida, H. Can. J. Chem., 42, 926 (1964).

74. Hatchard, C. G., and Parker, C. A. Proc. Roy. Soc., 235, 518 (1956).