PHOTO-ADDITIONS

THE PHOTO-ADDITION
OF 2-CYCLOHEXENONE AND
NORBORNADIENE

by

John Moffat Kelly, B.Sc.

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AUTHOR: John Moffat Kelly, B.Sc. (Manchester)

SUPERVISOR: Dr. J. J. McCullough

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SCOPE AND CONTENTS:

The photo-addition of 2-cyclohexenone to norbornadiene has been investigated. A substantial proportion of the products formed were α,β unsaturated ketones. The structure of these has been assigned and a rationale is presented to explain the formation of these products

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CHAPTER I

INTRODUCTORY AND HISTORICAL

Part I

General Introduction

The aim of our study is to collect and correlate the legacy of knowledge left by earlier workers not only in organic chemistry, but in related fields of scientific endeavour. The theories thus formulated should enable us to predict the course of new reactions and the properties of novel compounds.

Organic photochemistry is certainly not a new field of study, the action of light as a source of energy for initiation of chemical reactions having been long recognised. Thus every elementary text in organic chemistry gives examples of reactions "carried out in sunlight", and many interesting and useful reactions were performed in Italy and other sunny countries during the early years of this century. In most most of this work, however, no mechanism was proposed to rationalise the products formed.

A physical approach to photochemistry was extensively developed by workers such as Noyes and Norrish, although their work was commonly restricted to the study of small molecules where the reaction could be more closely defined. The combination of the physical and organic aspects of our study is, however, a development of the last decade.

The scope of organic photochemistry is extensive, the only requirement being that the system under investigation absorb light. Reactions may be carried out at any desired temperature in the gas, liquid or solid phase, or in solution. A degree of selectivity may sometimes be obtained, if special filters are used, whereby only one species is energised, a course not possible under conditions of thermal activation.

As we shall see later, the course of reaction may sometimes be markedly affected by variation in phase, solvent, concentration, or wavelength of the radiation used. The use of triplet sensitizers of various energies has also contributed to the scope and selectivity of some reactions.

Our aim as organic chemists must be to extend the range and to increase the selectivity of known reactions. This is achieved not by haphazard experimentation but by a planned study based on our knowledge of analagous systems and on an appreciation of probable mechanistic pathways.

Photochemical reactions are of interest as the products so obtained are often different from those of ground state reactions. This is not surprising since the structure and electronic properties of the excited molecule are very different from those of the ground state species. Indeed it is not immediately clear why a photoexcited molecule should react in any specific manner. As Zimmerman (1) has pointed out, it is a great assumption that a photo-excited molecule, which has typically absorbed 100 Kcals. of energy, will not break bonds indiscriminately; however it is an assumption which appears to be valid for many substances in solution, as their excited states usually react through reasonable pathways.

In proposing a mechanism we are interested in three features:-

(i) The nature of the excited state
(ii) The nature of the primary reaction
(iii) The nature of the secondary reaction.

Of these the first is perhaps the most difficult to determine.

Although spectroscopic and kinetic measurements may yield information on the configuration and multiplicity of the state, an electronic model is still lacking for most compounds, but we may expect that in the future advanced quantum mechanical calculations will replace much of the present speculation on this matter.

Photoadditions have already been shown to be of synthetic use, both in the preparation of natural products, e.g. the synthesis of caryophyllene (2), and in the preparation of novel compounds, previously considered to be mere chemical fantasy, such as cubane (3).

In the author's opinion we may expect photochemistry to become increasingly important as a synthetic tool, as advance in our mechanistic understanding will allow a consequent improvement in reaction control.

Part II

Photoaddition Reactions of α,β Unsaturated Carbonyl Compounds

(1) Physical Aspects

The ultra-violet spectra of α,β unsaturated compounds have two principal bands. The first is of short wavelength and high extinction coefficient ($\varepsilon = 10^4$ approx.) and the other of longer wavelength and low extinction coefficient ($\varepsilon = 10 - 100$). These are respectively the $\pi - \pi^*$ and $n - \pi^*$ bands, and the low extinction coefficient of the latter illustrates the strictly symmetry forbidden nature of this transition. Although in esters and amides the $n - \pi^*$ band is only poorly resolved from the intense $\pi - \pi^*$, this is not the case with α,β unsaturated aldehydes and ketones where the two bands are distinctly separated. (4)

Thus it is possible to selectively energise a molecule to the $n - \pi^*$ singlet by use of a suitable filter. In early work where photolyses were carried out in glass tubes exposed to sunlight, this was usually the case.

Having absorbed light, the molecule is present as a vibrationally and electronically excited singlet state. However in solution vibrational energy is rapidly transferred to the solvent and the molecule deactivates to the zero vibrational level of the state. This singlet may further lose energy in several ways:-

(i) It may react photochemically by either unimolecular or bimolecular processes.

(ii) It may return to ground state either with emission of radiation (fluorescence) or non radiatively (internal conversion).

(iii) It may undergo intersystem crossing to produce the triplet state.

For many carbonyl compounds in solution mechanism (iii) is of unit efficiency, even though it is strictly multiplicity forbidden (5). This presumably is because the intersystem crossing involves:-

$n - \pi^*$ singlet $\rightarrow$ $\pi - \pi^*$ triplet $\rightarrow$ $n - \pi^*$ triplet.

S - T processes in which transitions are between states of the same configuration are forbidden since spin-orbit coupling is not possible (6).

The triplet may have either a $\pi - \pi^*$ or $n - \pi^*$ configuration. In most cases studied it is $n - \pi^*$ (7)(8), but this is not always so, especially when the conjugated system is extensive (9) (10).

The triplet state may react further:-

(i) By photochemical reaction of either unimolecular or bimolecular pathway.

(ii) By return to ground state with emission of radiation (phosphorescence). This process is seldom observed for carbonyl compounds in solution, although phosphorescence spectra may be obtained at 77°K in rigid media .

(iii) By returning to ground state without emission of radiation (intersystem crossing).

Since processes (ii) and (iii) are strictly forbidden the lifetime of the triplet state is often long and the possibility of chemical reaction is high. Triplet lifetimes of carbonyl compounds in solution are commonly of the order of 10^{-5} sec..

(2) Chemical Aspects

Examples of photoadditions of this type have been known since 1900. Thus Ciamician (11) found that carvone was changed into carvone-camphor on exposure to Italian sunlight for one year. An early-recognised example of an intermolecular cycloaddition was the dimerisation of coumarin, although in this as in most cases the complete structural elucidation was achieved only in recent years (12, 13, 14).

A large number of intramolecular cycloadditions involving unsaturated carbonyl compounds are now known (15). Examples include α,β unsaturated ketones, esters, quinones and pyrones.

However of more immediate interest is the galaxy of intermolecular cycloadditions which have been investigated. The two species interacting may be distinguished as the α,β unsaturated compound and the olefin moiety. Extensive variation is possible in these substrates. For example the α,β unsaturated compound may be an α,β unsaturated ketone (8, 16, 17), ester (18), lactone (14), acid (19), anhydride (22, 23, 24); a diketone (20) or nitro compound (21). The olefinic moiety may be an α,β unsaturated ketone (8), lactone (14), or acid (19); a diene (22); aromatic such as benzene (23) or anthracene (25); substituted or unsubstituted olefin (16, 17, 26); acetylene (16); or cumulene such as allene (16, 17).

The work of E. J. Corey and coworkers (17) on the cycloaddition of 2-cyclohexenone to substituted olefins is of particular interest and a detailed study of this will serve as a guide to several aspects of the general reaction.

The products formed on irradiation of 2-cyclohexenone in presence of a fifteen-fold excess of isobutylene are shown in Chart I.

Several points are notable.

(i) Formation of a compound with trans 6,4 ring junction even though this is approximately 10 Kcals. less stable than the cis compound.

(ii) Orientational specificity is shown by the high yield of the 7,7 dimethyl compound. In the reaction with 1,1 dimethoxy ethylene only the 7,7 substituted compounds are formed.

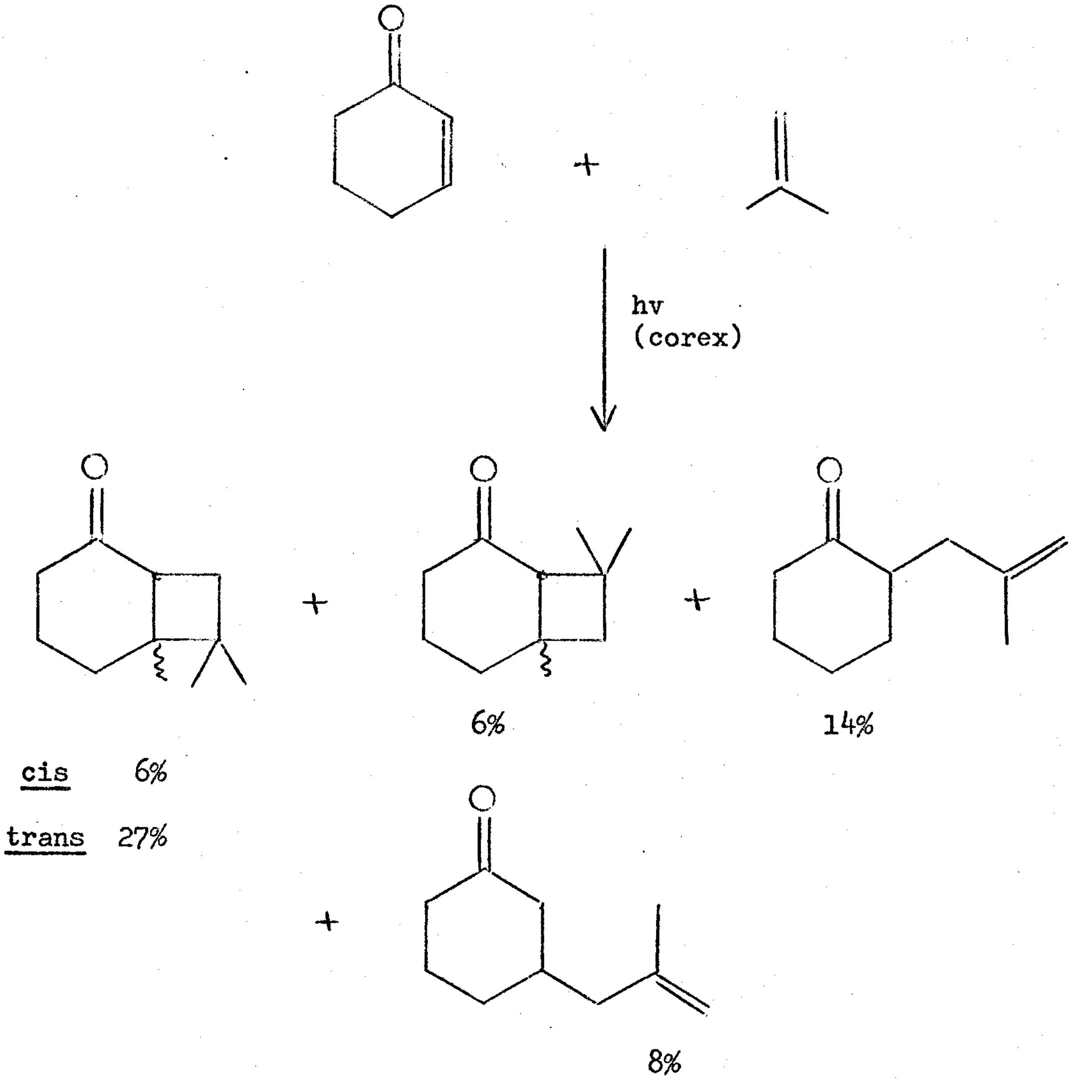
(iii) Reaction of 2 cyclohexenone with cis 2-butene gives same product distribution as reaction with trans 2-butene.

(iv) Reaction of the 2-methyl 2-cyclohexenone is much slower than that of 3-methyl 2-cyclohexenone.

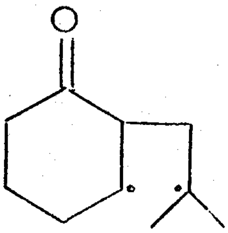
(v) Competition experiments indicate that 2-cyclohexenone is a moderately electrophilic species in its reaction with olefins.

To explain these facts Corey proposed the formation of a charge transfer complex between the excited state enone and ground state olefin. It was postulated that this complex has a definite geometry as a result of the dipole of the excited ketone. The complex collapses to give diradical species as shown in Figure I. This hot diradical may then cyclise or undergo intramolecular hydrogen atom transfer to yield the observed products. Initial bond formation appears to be principally to the 2 position, a postulate supported by the low reactivity of the

Products from 2-cyclohexenone and isobutylene photolysis (17)



Diradical species possible intermediates in above reaction


A

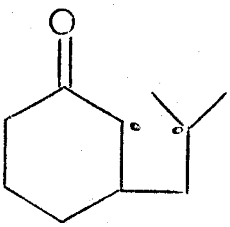

B

Chart I

2-substituted enones. This gives the diradical A, which in ground state reactions would be less stable than B. Thus this cycloaddition differs from others where the diradical intermediate is always the most stable one possible (27).

Concerted addition, although allowed by the rules of Woodward and Hoffmann (28), is not consistent with the addition to the cis and trans 2-butenes.

However as Corey (17) remarks, it is dangerous to consider that only one mechanism will be applicable to all systems of the above general type and significant differences have already been observed.

One observation of mechanistic importance is the formation of ground state complexes between the reactants. Thus although these cannot be observed in the ultra-violet spectra of enones in olefins, (17), they are certainly formed by cyclohexene and methyl fumarate (18), and by benzene and maleic anhydride (23). Clearly such a complex will form products of a preferred configuration.

Another significant aspect of these reactions is the question of the multiplicity of the reacting excited species. The use of such tools as triplet quenching (e.g. with piperylene or naphthalene) and sensitization with triplet sensitizers (e.g. benzophenone) is now standard (29). In several reactions the reactive species is known. De Mayo (18) has shown that both singlet and triplet excited states are involved in the reaction of cyclohexene and dimethyl fumarate or maleate. In the study of the dimerisation of coumarin, (14), Hammond has shown that the singlet is the reactive species in ethanolic solution. In the latter case it has been shown that the triplet species gives different products than the singlet, an observation which may be of more general applicability.

The configuration of the excited state is also most important as it has been shown that $n-\pi^*$ and $\pi-\pi^*$ triplets can show markedly differing reactivities. This effect is particularly marked in the photoreduction of para-substituted benzophenones (9) (10).

In the cycloaddition reactions of cyclic enones with olefins neither the configuration nor the multiplicity of the reactive species has been determined. Corey (17) has reasonably assumed this to be the $n-\pi^*$ triplet, although attempts to obtain phosphorescence spectra were unsuccessful. However in other photochemical reactions of cyclohexenones the reactive species is known. Eaton (8) has shown that the dimerisation of cyclopentenone proceeds through the triplet state; and in the type A rearrangement of Δ^{1-9} 10-methyl 2-octalone, Zimmerman (7) has shown that the reaction is strongly inhibited by triplet quenchers.

A further aspect of bimolecular photochemical reactions which is not yet completely understood is the effect of solvent. Many reactions which proceed smoothly in one solvent will not proceed in another (e.g. the photolyses of 4,4-dimethyl 2-cyclohexenone in tertiary butanol is clean but in aprotic solvents this is not so(30)). Hammond in his study of coumarin dimerisation (14) has shown that a marked solvent effect allows singlet self quenching to compete with dimer formation in non-polar solvents. Also the variation in product distribution in the dimerisation of cyclopentenone (8) has been attributed to a solvent effect, the nature of which is not defined. However solvent effects have not been remarked in the cyclic enone-olefin system although a variety of solvents have been used.

Thus before a complete mechanism can be proposed consideration of the above-mentioned facets of the reaction system is necessary and it is to be expected that a single mechanism for all reactions of this general type is improbable.

Part III

The Addition Reactions of Norbornadiene

(Bicyclo (2,2,1) hepta (2,5) diene)

These additions may be classified as follows:-

(i) Attack by electrophilic species

(ii) Attack by free radical species

(iii) Concerted addition reactions.

(i) Attack by electrophilic species

This type of reaction has stimulated great interest because the intermediate carbonium ion formed may interact with the remaining double bond in the ring system to produce a system which may be described as "non-classical".

Typical electrophilic reagents are bromine, acetic acid and hydrogen halides. These react with norbornadiene to give variable yields of nortricyclyl and dehydronorbornyl derivatives.

Thus treatment with bromine at -10° gives 80% nortricyclyl dibromides and 20% dehydronorbornyl dibromides as shown in Chart II. (31), but attack by hydrogen bromide yields 30% nortricyclyl compounds, the remainder being dehydronorbornyl derivatives (31). As may be readily seen the reactions usually involve Wagner-Meerwein rearrangements to some extent.

These products have been rationalised either in terms of a non-classical carbonium ion or as a series of rapidly equilibrating classical carbonium ions (31, 32).

(ii) Attack by Free Radical Species

As ketone and enone excited states have been shown to exhibit

The reaction of norbornadiene and bromine.

Products and proposed pathways (31)

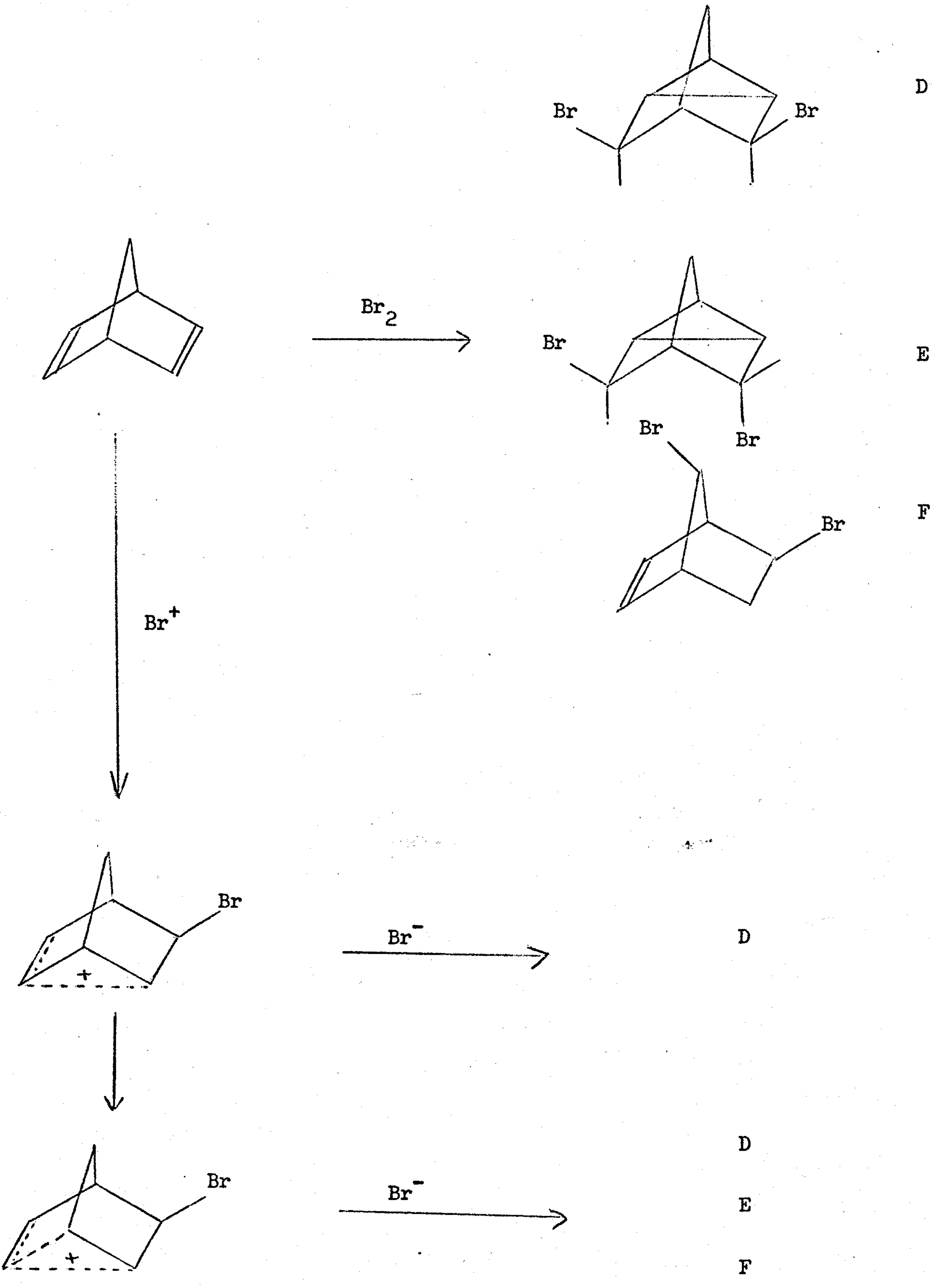


Chart II

radical type character, it is important that we examine carefully the nature of free radical additions to norbornadiene. A multiplicity of reagents has been used and a few of these are:- Thiols (34), Aldehydes (35), Polyhalogenomethanes (35, 36), Iodoperfluoropropane (36) and aromatic sulphonyl halides (37). Products isolated are the nortricyclyl and dehydronorbornyl compounds.

As the reaction is formally analagous to the cationic reaction, Cristol (34) performed experiments to test whether the norbornenyl radical exhibits "non-classical" behaviour. His kinetic study of the reaction with aryl thiols showed that this was not the case, as variation of the thiol concentration produced a variation in the ratio of norbornenyl to nortricyclyl products. Clearly then this test is useful in those cases where the chain transfer step of the reaction is faster than the equilibration process.

This is not always the case however. Thus with iodoperfluoropropane (36), norbornadiene yields entirely the nortricyclyl products, presumably indicating that the equilibrium lies far over in favour of the nortricyclyl compound and that the chain transfer step is slow with rexpect to this.

Further evidence for the classical behaviour of the dehydronorbornyl radical system is presented by Trecker and Henry (35). They showed that the ratio of addition rate of carbon tetrachloride to norbornadiene and norbornene was 2.06:1, indicating negligible anchimeric assistance. Work by Martin and de Jongh (38) with the decomposition of norbornenyl peresters also showed that no anchimeric assistance is present in this radical system.

The actual position of the equilibrium in the nortricyclyl-dehydronorbornyl radical system is still uncertain. Davies, Done and Hey (39) have found that radicals produced by the action of cobaltous chloride on the Grignard reagent of both exo-dehydronorbornyl bromide and nortricyclyl bromide give an equilibrium distribution of 70:30 in favour of the nortricyclyl component. However radicals produced by decarbonylation of the corresponding carboxyaldehydes are in the ratio of 55:45 (40).

Clearly then in the case of substituted radicals, product distribution will be more variable as the steric effect of the substituent will be significant and the probable distribution, therefore, will be impossible to predict.

Stereochemistry of free radical attack.

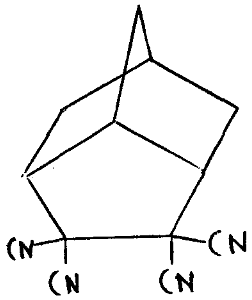
This has been stated by Trecker and Henry (35) to be exclusively exo, and to the knowledge of the author this appears to be true at present, as all cases of initial endo attack appear to involve preliminary formation of a complex or are formed from a concerted multi-centre transition state (vide infra).

(iii) Concerted Addition Reactions

Several examples of the homo Diels Alder reaction of norbornadiene are now known (41).

The first of these, reported by Ullman in 1958 (42) was the addition of maleic anhydride to norbornadiene in low yield. However yields of 78% have recently been reported for this reaction (43).

In 1959 Blomquist and Meinwald (44) observed the addition of tetra cyano-ethylene, "the record dienophile" in 66% yield. The structure is as shown below:-



Further examples are the addition of acrylonitrile (13%) (45), hexafluoro 2-butyne (78%) (46) and dimethyl azodicarboxylate (10%) (47) to give the corresponding homo Diels-Alder derivatives.

The addition is thermally induced and the concerted addition is allowed by the rules of Woodward and Hoffmann (28) as an example of a 2,2,2, addition. The photochemical addition to this system cannot be concerted if the above rules are obyed.

Virtually all Diels-Alder reactions may be interpreted in terms of a multicentre concerted transition state which arises from a charge transfer complex (48). The formation of a complex is suggested by the parallelism between acceptor strength in charge transfer complexes and dienophilic reactivity. Clearly the complex will form in the region of highest electron density. Since the homo Diels Alder reaction is strictly analagous we may therefore expect the cyclisation product to result from a collapse of an initially formed complex in the region of highest electron density (that is in the endo position)

Reactions which also have been shown to proceed through a concerted transition state yield substantial quantities of the endo substituted product.

Thus treatment of norbornadiene with diborane followed by hydrogen peroxide yields 88% exo and 12% endo dehydronorbornyl alcohols (49).

Similarly Simmons-Smith methylene addition, using zinc-copper couple and di-iodo methane yields 15% endo and 85% exo cyclopropane compounds (50). These reactions proceed through a four and three membered transition state respectively.

Part IV

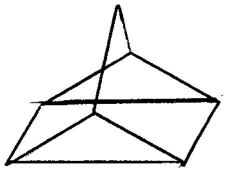
Photochemistry of Norbornadiene

The ultra-violet spectrum of norbornadiene shows long wavelength absorption (51, 52) and this has been attributed to the interaction of the π orbitals, as the absorption observed in unconjugated olefins is usually of much lower wavelength.

Molecular orbital calculations by Wilcox, Winstein and McMillan (51) indicate that although no 2-6 or 3-5 bonding is expected in the ground state, the excited state is calculated to have a 2-6 bond order of 0.12 if a refined Pariser and Parr or Longuet-Higgins model is used.

Irradiation of bicycloheptadiene with 2537 Å light at pressures of 4 to 31 mm. gives acetylene and cyclopentadiene (52). Toluene was formed as a minor product. As the excited singlet state remains vibrationally excited for relatively long periods in the gas phase at low pressures, it is probable that this is the reactive species here.

Irradiation in ether solution at 2537 Å gives the valence tautomer quadricyclene in good yield (53).



Quadricyclene reconverts to norbornadiene on thermolysis. In the presence of triplet sensitisers (acetone, acetophenone, benzophenone) norbornadiene is converted to quadricyclene (54, 55). However of more theoretical interest is the observation that quadricyclene isomerises to norbornadiene if triplet sensitisers of low energy (e.g. Fluorenone : 54 Kcals) are used (55). A photostationary state is formed with approximately 70% norbornadiene. It should be noted that the triplet energy of these sensitisers is below that of norbornadiene and quadricyclene. To explain these phenomena, non - vertical excitation to a relaxed triplet was postulated. (Note high energy sensitisers favour formation of quadricyclene.)

A photochemical reaction of interest is the photosensitised dimerisation of norbornene to yield the exo trans endo isomer (88%) and the exo trans exo (12%) (56). This product distribution is probably due to the configuration of the triplet norbornene. If the photolysis is carried out in the presence of cuprous bromide the exo trans exo compound is formed predominantly (97%) (56, 57), presumably because of the geometry of the metal complex.

Part V

The 2-Cyclohexenone-Norbornadiene System

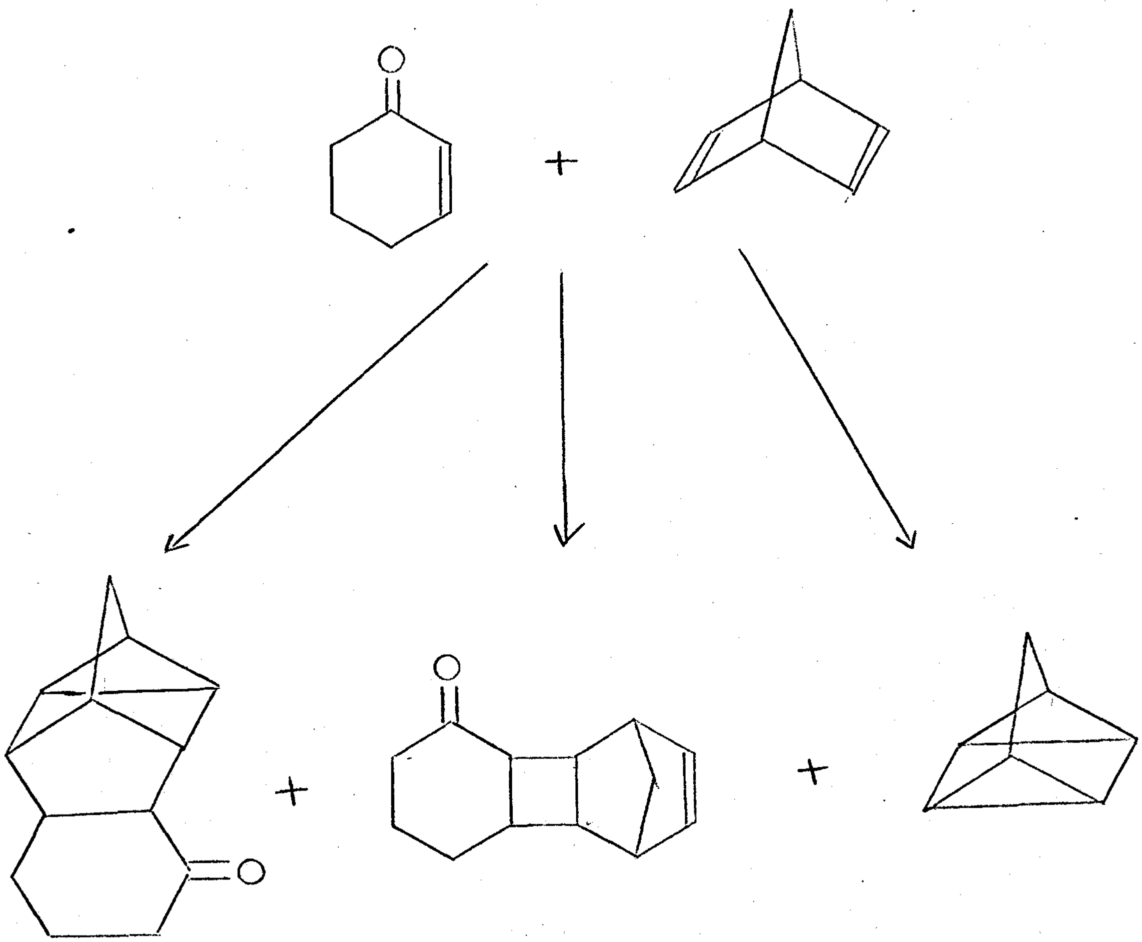
As was noted in Part II, the reaction of 2-cyclohexenone and a variety of olefinic compounds has been investigated and a mechanistic pathway proposed to rationalise the formation of the observed products. This mechanism however did not explain all facets of the reaction course. For example, the reaction of 3-methyl 2-cyclohexenone and isobutylene to yield predominantly the 6,8,8 -trimethyl bicyclo (4,2,0) octan-2-one; and the formation of a trans 6,4 ring junction from a diradical species was interesting as this species is approximately ten Kcals less stable than the cis 6,4 ring junction.

The 2-cyclohexenone-norbornadiene system was of interest for several reasons.

(i) If a complex was formed this might be expected to take place in the endo position, giving rise to endo substituted products (41), whereas attack by a free radical type species would be expected to yield almost entirely exo substituted compounds (35). Free radical character has been shown for enone excited states in other reactions (33).

(ii) A diradical species, analagous to that proposed by Corey and coworkers, might be expected to give rise to a product (G) as shown in Chart III. Although this product is similar to those derived by homo Diels-Alder reaction, it cannot be formed by a concerted mechanism if the Woodward-Hoffmann (28) rules are applicable. This is an example of a 2+2+2 system which is thermally allowed but photochemically forbidden to proceed by a concerted pathway.

Predicted Products from reaction of 2-cyclohexenone and norbornadiene



G H J

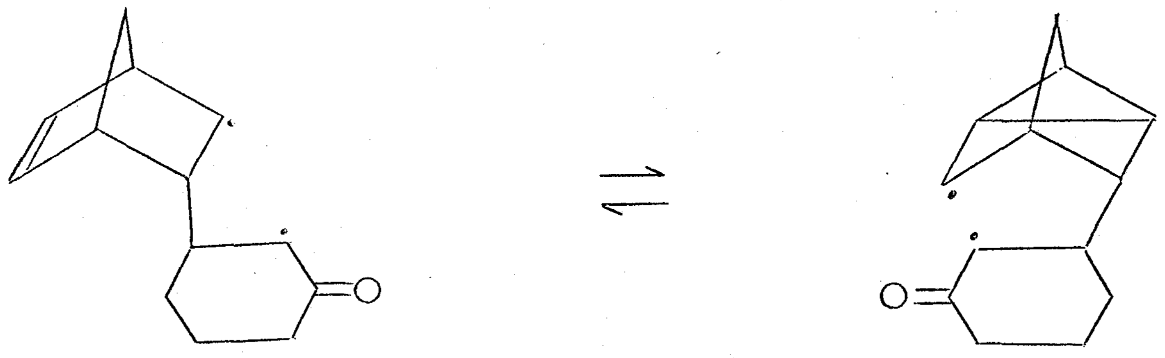
Chart III

(iii) The radical species (K-N) might be trapped by thiols (60), if these diradicals have a sufficiently long lifetime. In ground state cycloadditions where diradicals are known intermediates the lifetime of the species is only 10^{-10} sec. However if the diradical is derived from the attack of triplet cyclohexenone on norbornadiene, then the initially formed diradical would have to spin invert before ring closure, perhaps allowing radical trapping to occur. The use of thiols is suggested as Cohen and coworkers (60) have shown these to specific radical trappers and not to quench triplet ketonic species (e.g. benzophenone). This radical trapping (if successful) would allow an estimation of the extent of reaction proceeding by diradical species and the ratio of intermediates K+L to M+N in the reaction to be determined.

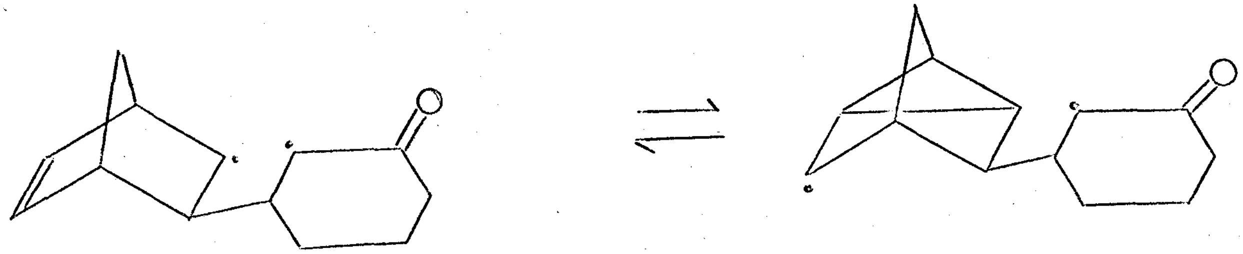
(iv) As noted in Part IV, the valence tautomerism of norbornadiene to quadricyclene is sensitised by the triplets of acetophenone (74 Kcals) and benzophenone (68.5 Kcals). As the triplet energy of 2-cyclohexenone has been estimated to be 70 Kcals., (17), we might expect competition between photosensitisation and photoaddition in this system. This might allow a rough estimate of the rate of cycloaddition if the ratio of quadricyclene to addition products is determined.

The following chapters will deal with the results of the photolysis of 2-cyclohexenone and norbornadiene, and a rationaleis suggested for the results observed.

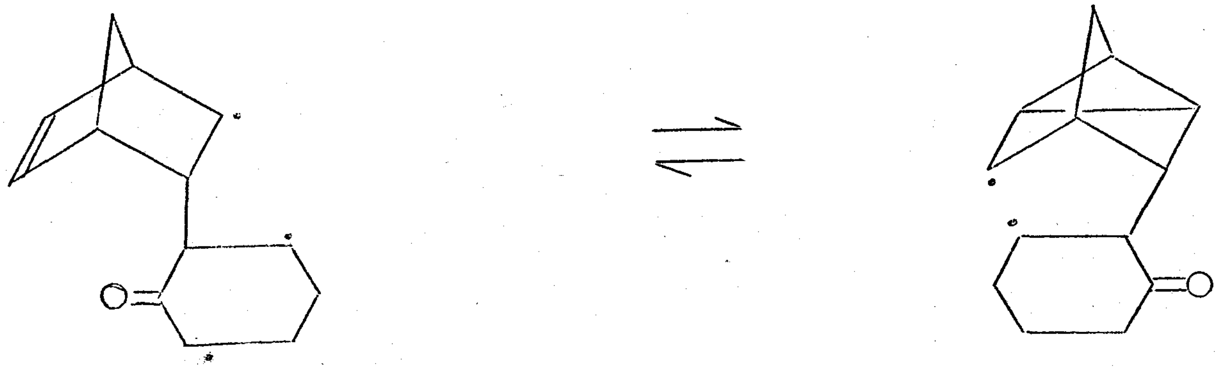
Radical Species from Photoaddition of 2-Cyclohexenone to Norbornadiene



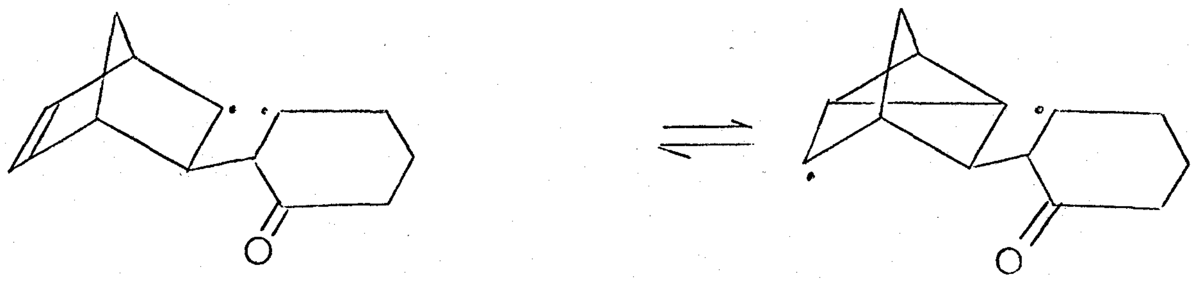
(K)



(L)



(M)



(N)

Chart IV

CHAPTER II

EXPERIMENTAL RESULTS

The photochemical reactions described were carried out with a high pressure mercury arc lamp (Hanovia Type L, 450 w.) in a water-cooled quartz immersion well. Light was filtered in all cases with a pyrex glass sleeve, 1 mm. thick, (0% transmission at 280 mμ; 90% at 320 mμ), thus ensuring that only the $n-\pi^*$ band of the 2-cyclohexenone absorbed radiation.

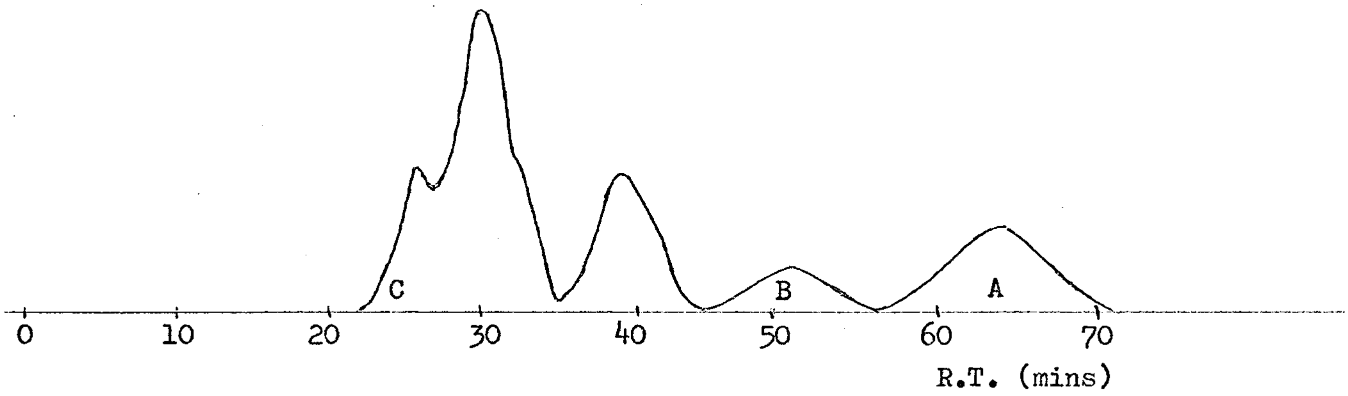
In a typical experiment a solution of freshly distilled 2-cyclohexenone (0.025 M) and freshly distilled norbornadiene (bicyclo (2,2,1) hepta (2,5) diene) (0.25 M) in purified hexane was photolysed for 1 hour under the above conditions. The reaction was followed by taking aliquots at 15 minute intervals, and analysing by ultra-violet and infra-red spectroscopy and by vapour phase chromatography (v.p.c.). After one hour 70% of the 2-cyclohexenone had disappeared as determined by a quantitative analysis method using acetophenone as an external standard.

The mixture was examined on several vapour phase chromatography columns. Good separation was obtained with columns A and B. (For description of columns see experimental section). Typical traces are shown in Figure I.

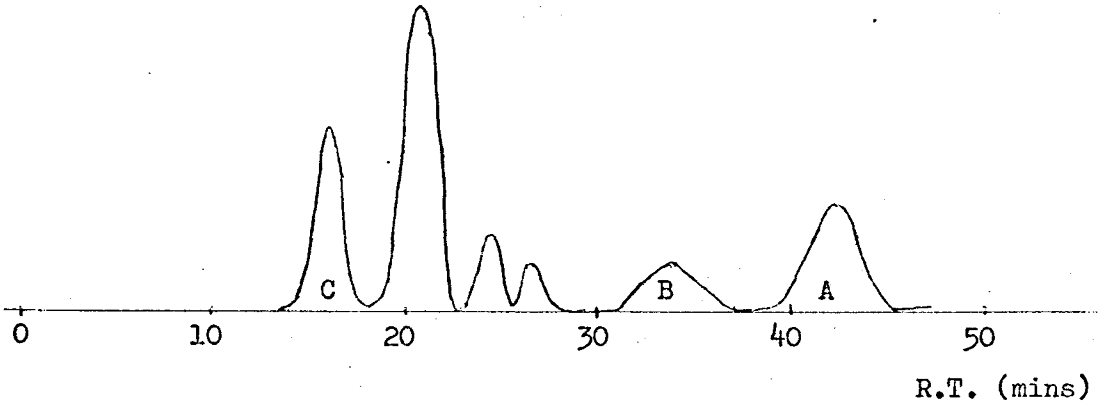
The ultra-violet spectra still showed absorption above 300 mμ, although the fine structure had changed, suggesting that α,β unsaturated carbonyl compounds had been formed.

After removal of solvent and much of the 2-cyclohexenone, the infra-red spectrum was examined. The carbonyl region from 5.75 μ - 6.10 μ was quite complex; the sharp absorption of the 2-cyclohexenone at 5.92 μ having been replaced by a complex band as shown below with

V.p.c. Traces of Photolysis Reaction Mixture



(a) Column A 177° Flow Rate = 60 mls./min He



(b) Column B 184° Flow Rate = 60 mls./min He

Figure I

peaks at 5.82, 5.88 and 5.97 μ.

I.R. Carbonyl Region of crude reaction mixture

The absorption at 5.97 μ was of particular interest since it suggested that α,β unsaturated ketones might be present. Absorptions characteristic of the nortricyclyl and norbornenyl systems were observed at 12.30 - 12.45 μ and at 14.00 - 14.25 μ respectively (59, 62).

To examine whether a change in solvent polarity would affect the product distribution, the reaction was run in a t-butanol solution and the reaction was followed by taking aliquots frequently. The infra-red spectrum of the reaction mixture after irradiation was identical to that from the photolysis in hexane; and the v.p.c. traces on column B were very similar as is shown in Table I.

Product Distribution in Photolysis Mixtures

(a) Photolysis in Hexane

Conversion	22%	43%	70%	Average
R.T. (mins.)				
16.4	13.3	13.4	15.9	14.2
19.9	43.7	40.9	39.6	41.4
24.7	6.6	7.7	8.0	7.4
26.6	5.2	5.9	6.0	5.7
33.7	8.9	9.7	10.0	9.5
40.4	22.8	22.2	20.8	21.9

Analysis on Column B at 181°. Flow rate = 66 mls./min He

(b) Photolysis in t-Butanol

Conversion	26%	49%	70%	Average
R.T. (mins.)				
17.0	15.4	15.7	16.3	15.8
20.8	39.0	40.8	40.3	40.0
25.3	5.3	4.5	4.3	4.7
27.2	6.3	6.1	6.0	6.1
34.3	8.9	9.0	9.8	9.2
42.2	23.2	22.0	21.6	22.3

Analysis on Column B at 183°. Flow rate = 60 mls./min He

Table I

Isolation of the α,β unsaturated ketones from reaction mixture

Separation of the mixture was attempted using v.p.c. column D. This allowed collection of five fractions, corresponding to the peaks in Figure I(a).

Ret. time (as on Figure I(a))	Fraction	Peak (as in Figure I)
26 - 28.5	1	C
28.5 - 35	2	
35 - 45	3	
45 - 55	4	B
55 - 70	5	A

Fractions 1, 4 and 5 showed unsaturated carbonyl absorption in the I.R. at wavelengths greater than $5.97\ \mu$.

Substantial quantities of fractions 1 and 5 were obtained and these were further purified by a second pass through column D. It was more difficult to obtain large quantities of pure B, free of A.

Thin layer chromatography on silica gel using 5% ethyl acetate-benzene solution gave several spots. This suggested the use of liquid-solid chromatography using silica gel as packing and ethyl acetate-benzene solution as liquid phase. After some experimentation useful separation was achieved by gradually increasing concentration of the ethyl acetate in benzene from 2% to 5%.

C was eluted in the early fractions and could be obtained fairly pure by this method. A v.p.c. chromatogram with column E on this fraction indicated that two compounds were present, although the resolution was only partial. (Typical retention times were 113 and 123 mins.).

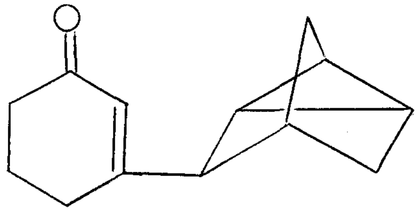
The middle fractions from the silica gel column contained saturated ketonic compounds with I.R. absorption between 5.82 μ and 5.88 μ. The later fractions, however, contain B and A; B being eluted earlier than A, although not completely resolved from it. However fractions containing 50% of B were obtained and these enriched samples were then separated by preparative v.p.c. on Col E to give both A and B of greater than 97.5% purity.

Identification of α,β unsaturated ketones in photolysis mixture

Enones A, B and C (see Figure I(a)) were examined by I.R., u.v., N.M.R. and mass spectrometric methods.

(1) Enone A

This compound was assigned the structure



i.e. 3-(3-tricyclo $(2,2,1,0^{2,6})$ heptyl) 2-cyclohexenone.

From the infra red spectrum (Table II), the following features of structural importance were observed:-

(i) Absorption at 6.00 µ and 6.16 µ. This is in agreement with values for other 3-substituted cyclohexenones (59, 61). The relatively intense band at 6.16 µ (approximately a third the intensity of peak at 6.00 µ) is indicative of a 3-substituted cyclohexenone (72).

(ii) Doublet at 12.42 µ and 12.35 µ is characteristic of mono-substituted nortricyclene compounds (58, 62, 63). The absorption at approximately 14.20 µ is very weak indicating the absence of a norbornenyl group (59, 69).

The ultra-violet spectrum in hexane showed a π-π^* band at 229 mµ (log E = 4.18) and n-π^* maxima and shoulders at 327 mµ (1.53), 338 mµ (1.53), 352 mµ (1.34) and 368 mµ (0.95). The π-π^* band wavelength is characteristic of that for α,β unsaturated ketones. The

Infra-Red Spectrum of Enone A

	$\lambda (\mu)$	E cm^{-1}
C-H Region	3.27	3060
	3.35	2988
	3.40	2940
	3.49	2869
=C-C=O Region	6.00	1665
	6.16	1623
Nortricyclene Region	12.35	811
	12.42	804
Other intense peaks	7.54	1323
	7.70	1299
	8.01	1244
	8.40	1190
	8.83	1130
	10.31	968
	11.14	898

Table II

$\pi-\pi^*$ band position is consistent with the value predicted by the Woodward rules (65) (i.e. 228 mμ) for a 3-alkylated cyclohexenone.

The n.m.r. spectrum provided further useful information:-

(i) No absorption greater than $\delta = 6.00$ p.p.m. was found indicating that no vinyl protons of a norbornenyl system were present (64, 71).

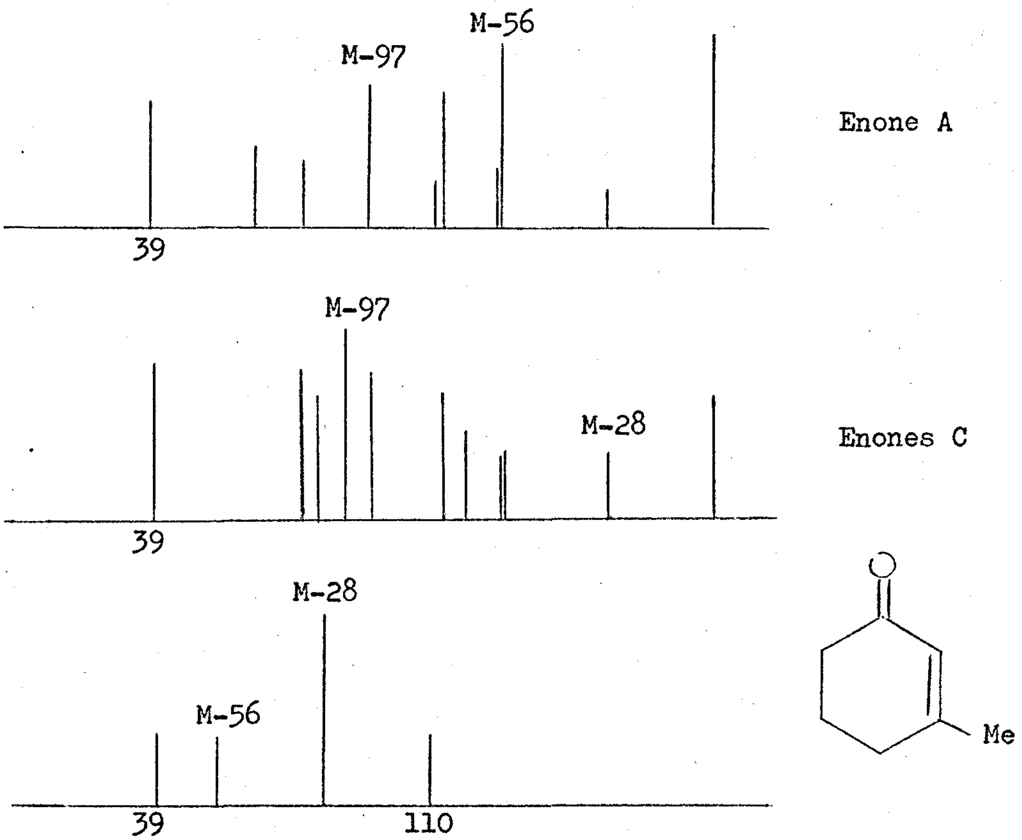
(ii) Absorption characteristic of a proton in the 2-position of a 3-alkylated cyclohexenone was observed at $\delta = 5.81$ p.p.m. (1 proton) (61, 68). A proton in the 3-position of a cyclohexenone absorbs with $\delta = 6.5$ p.p.m. (68). Of significance here is the spectrum of 2-cyclohexenone which has peaks at $\delta = 5.87$ (doublet) and $\delta = 6.92$ (multiplet) in carbon tetrachloride.

(iii) Complex absorption between $\delta = 1.80$ and $\delta = 2.30$ is presumably due to the remaining protons of the 2-cyclohexenone moiety (61).

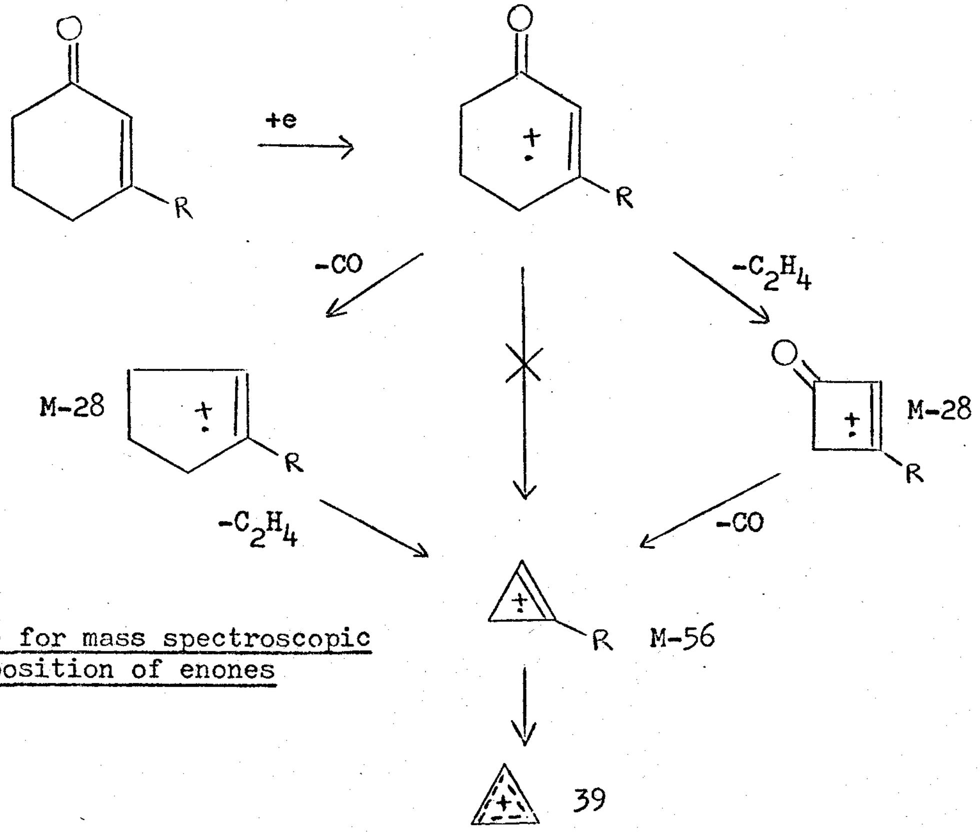
(iv) Two broad singlets at $\delta = 1.16$ and $\delta = 1.43$ (5 and 2 protons respectively) are difficult to assign but similar features are found in the spectra of other nortricyclyl compounds (47, 75).

The mass spectra of the compound is shown in Figure II. The molecular weight of the compound is indicated by the parent peak with $^M/e = 188$ and a possible scheme for the decomposition is described. This is supported by the mass spectra of 3-methyl 2-cyclohexenone. After the completion of this work, Bowie (66) published a paper on the mass spectra of certain enones and his scheme is in agreement with that suggested here.

As further evidence for the proposed structure for Enone A, a simple synthesis was devised using a method similar to that of Woods and coworkers (67).

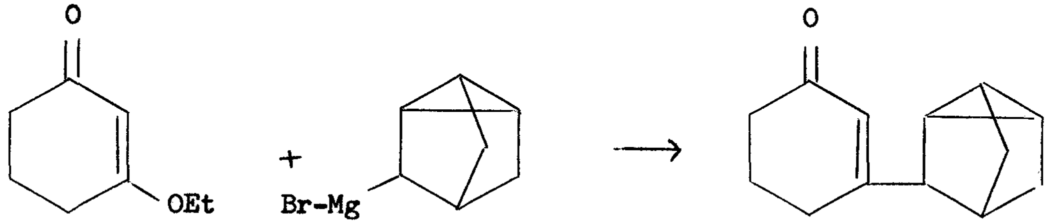


Mass Spectra of Enone A, Enones C and 3-methyl 2-cyclohexenone



Scheme for mass spectroscopic decomposition of enones

Figure II

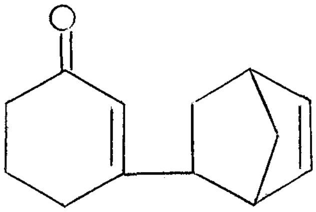


From this synthesis a product was obtained with identical v.p.c. retention time, I.R and N.M.R. spectra. No compounds with v.p.c. retention times corresponding to other photolysis products were obtained.

Thus we may confidently assign the structure of Enone A as 3-(3-nortricyclyl) 2-cyclohexenone.

(2) Enone B

This compound was assigned the structure



i.e. 3-(5-bicyclo (2,2,1) hept-2-enyl) 2-cyclohexenone.

The I.R spectrum was remarkably similar to that of Enone A (Table III), but the absorption between 12.30 - 12.50 µ was very weak while a strong absorption was present at 14.22 µ. The latter is characteristic of 5-substituted norbornenyl compounds (59, 69). The absorption at 5.99 µ and 6.16 µ is again consistent with a 3-substituted 2-cyclohexenone structure (61, 72).

Infra-Red Spectrum of Enone B

	(u)	E (cm^{-1})
C-H Region	3.26	3060
	3.38	2962
	3.40	2935
	3.49	2862
=C-C=O Region	5.99	1670
	6.18	1618
Norbornenyl Region	14.22	701
Other Intense Peaks	7.56	1322
	7.72	1293
	8.03	1246
	8.43	1188
	11.12	900

Table III

The u-v spectrum had a band at 227 mμ (log E = 4.10) and a series of maxima or shoulders at 327 mμ (1.51), 339 mμ (1.48), 354 mμ (1.32) and 369 mμ (0.85), closely similar to those for Enone A.

Although a complete assignment has not been made for the N.M.R. spectrum, the following details are significant.

(i) Absorption at $\delta = 6.11$ p.p.m. (triplet:coupling of 2 c.p.s.). This is the value expected for the vinyl system of a norbornenyl system. (64, 71).

(ii) Absorption at $\delta = 5.70$ p.p.m. (1 proton) indicates a proton in the 2-position of the cyclohexenone structure (68).

(iii) The protons at $\delta = 2.97$ p.p.m. may be assigned to the allylic, bridgehead protons of the norbornenyl entity.

(iv) The complex absorption between $\delta = 2.30$ and 1.80 is similar to that in Enone A and in 2-cyclohexenone.

(v) The absorption between $\delta = 0.91$ and $\delta = 1.70$ p.p.m. is produced by the protons in the 6 and 7 positions of the norbornenyl moiety.

The mass spectrum showed a parent peak at $^{M}/e = 188$ in agreement with the molecular formula of $C_{13}H_{16}O$.

An attempt to synthesise Enone B from norbornenyl magnesium bromide and 3-ethoxy 2-cyclohexenone, in a method analagous to that for Enone A, was unsuccessful. Only Enone A was isolated apparently because the norbornenyl Grignard reagent isomerises to the nortricyclyl compound, as has been passingly referred to in the literature (62).

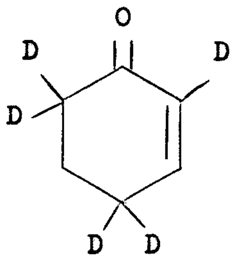
The stereochemistry (exo or endo)of Enone B at the 5-position of the norbornene system was not determined. In the N.M.R. spectrum the

5-proton was buried in the absorption due to the cyclohexenone moiety and no assignment of its position was thus possible. The position of this proton has been used in other cases to determine the sterochemistry of isomeric norbornene derivatives (64, 71). Also of interest is the work of Dinwiddie and McManus (70) who used the multiplicity of the vinyl protons of the norbornene system to distinguish the stereochemistry of endo. and exo. norbornene derivatives. Thus exo-substituted compounds show these vinyl protons as a triplet, whereas endo-substituted compounds have a multiplet. On this evidence our compound would be assigned the exo configuration although the evidence is indeed slim. An experiment to convert Enone B, at least partially, to its geometric isomer by base catalysis was unsuccessful (70). Possible experiments to show the stereochemistry of the compound might be:-

(i) Synthesis of the compound by the reaction of 3-vinyl 2-cyclohexenone and cyclopentadiene.

(ii) Use of a deuterated 2-cyclohexenone (as shown) in photolysis with norbornadiene.

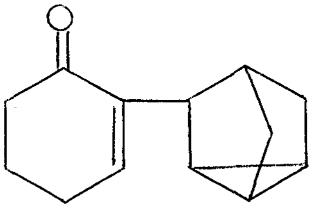
This would simplify N.M.R. and allow assignment of 5-proton in norbornenyl system.

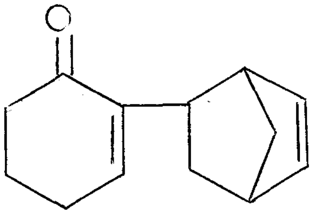


Deuterated 2-cyclohexenone for experiment (ii) above

(3) Enones C

Two compounds are present in this fraction in approximately equal quantities.





The infra-red spectrum of the unresolved mixture (Table IV), showed absorption at 6.00 μ with no side band between 6.10 μ and 6.20 μ visible. This is consistent with a 2-substituted cyclohexenone (59, 72). The doublet at 12.32 μ and 12.41 μ is characteristic of the nortricyclyl system (58, 62, 65) and the doublet at 14.02 μ and 14.20 μ with the 5-substituted norbornenes (59, 69). The partial resolution obtained using v.p.c. column E allowed collection of the earlier fraction which contains nortricyclyl compound.

The ultra-violet spectrum of the mixture has a $\pi-\pi^*$ band at 229 mμ (log E = 3.86), and $n-\pi^*$ absorption at 325 - 340 mμ (1.53), 355 mμ (1.30) and 372 mμ (0.85). Of interest is the relatively low extinction coefficient of the $\pi-\pi^*$ band (c.f Enone A) an effect which has been observed in analagous cases (73, 74).

The N.M.R. data has the following interesting aspects:-

(i) Multiplet at δ = 6.61 p.p.m. - consistent with a proton in the 3-position of a 2-cyclohexenone (68).

Infra-Red Spectrum of Enones C

	$\lambda(\mu)$	E (cm^{-1})
C-H Region	3.28	3050
	3.40	2937
	3.49	2862
=C-C=O Region	6.00	1668
Nortricyclyl Region	12.32	812
	12.41	806
Norbornenyl Region	14.02	713
	14.20	704
Other Intense Peaks	7.27	1376
	7.56	1323
	7.99	1252
	8.52	1174
	9.04	1106
	11.03	907

Table IV

(ii) The absorption at $\delta = 6.10$ p.p.m. (triplet) is similar to that for Enone B - vinyl protons of norbornene.

(iii) The absorption at $\delta = 3.00$ p.p.m. may be assigned to the allylic, bridgehead protons of the norbornene system.

(iv) The two spikes at $\delta = 1.05$ and $\delta = 0.95$ are indicative of the nortricyclyl system (47, 75).

(v) The ratio of intensity of absorption at $\delta = 6.61$ to that at $= 6.10$ is 24:26 corresponding to a ratio of 1:1.2 for nortricyclyl compound to norbornenyl derivative, a value in close agreement to that obtained by estimation from the v.p.c. chromatogram.

The mass spectra is shown in figure II, the parent peak having an $^{M}/e$ ratio of 188.

A synthesis of Enone C by reaction of nortricyclyl lithium and 1,2 cyclohexandione yielded a compound with an identical v.p.c. retention time to Enone C.

Thus Enone C has two components: 2-(3-nortricyclyl) 2-cyclohexenone (45%) and 2(5-norbornenyl) 2-cyclohexenone (55%).

Identity of saturated-carbonyl compounds

These products have not been thoroughly examined, however the following generalisations may be made:-

(i) Compounds both with a trans 6,4 ring junction and a cis 6,4 ring junction are probably formed. The former have an I.R. absorption at 5.80 - 5.83 μ, the latter between 5.85 μ and 5.88 μ. These values are similar to those found by Corey and coworkers for these systems (17). The trans compounds are stable to silica gel chromatography but do not survive passage through v.p.c. column D. The trans compounds may compose

30% of the saturated-carbonyl compounds.

(ii) No compound with I.R. absorption between 5.85 μ and 5.88 μ and between 12.30 μ and 12.50 μ could be detected in the fractions from v.p.c. and silica gel chromatography. Thus no compound formally derived by homo-Diels Alder addition (i.e. compound G of chart III) is present to an extent greater than 2%.

Photolysis of Enone A (3-(3-nortricyclyl) 2-cyclohexenone)

As the alkylated cyclohexenones absorb light during the reaction, it was decided to photolyse Enone A under reaction conditions to determine whether it was transformed to other photolysis products of the original reaction. Thus a cyclohexane solution of synthesised Enone A (0.006 M) was irradiated and the reaction course followed by v.p.c., I.R. and U.V. spectroscopy. Although the I.R. was basically unchanged after 14 hours, the absorption at 340 mμ in the U.V. showed a slight decrease. However no peaks corresponding to photolysis products appeared on the v.p.c. trace. Thus we may conclude that under the reaction conditions, Enone A is converted neither to the cyclobutane derivatives nor to the other enone compounds of the first photolysis.

Investigation of charge-transfer complexes between 2-cyclohexenone and norbornadiene

As has been indicated in Chapter I, charge transfer complexes are formed in several systems related to ours (18, 23), and such a ground state complex might be expected to influence the stereochemistry of the products formed.

If such a complex is formed, we might expect both the position and intensity of the $n-\pi^*$ band to be markedly affected. However solutions of cyclohexenone in norbornadiene and in norbornadiene/hexane mixtures gave u.v. spectra where the position and intensity of the $n-\pi^*$ band were closely similar to those of cyclohexenone in hexane. Thus no charge-transfer complex appears to be formed in our reaction system.

Summary

When irradiated with u.v. light ($\lambda >$ 2900 mμ) 2-cyclohexenone in the presence of a ten-fold excess of norbornadiene yields 46% unsaturated ketones as well as saturated ketonic cyclobutane derivatives. The reaction is essentially identical in polar and non-polar solvents, and does not appear to proceed via an initially-formed ground state complex.

The reaction course is shown in Chart V.

Product Distribution in Photolysis of 2-Cyclohexenone & Norbornadiene

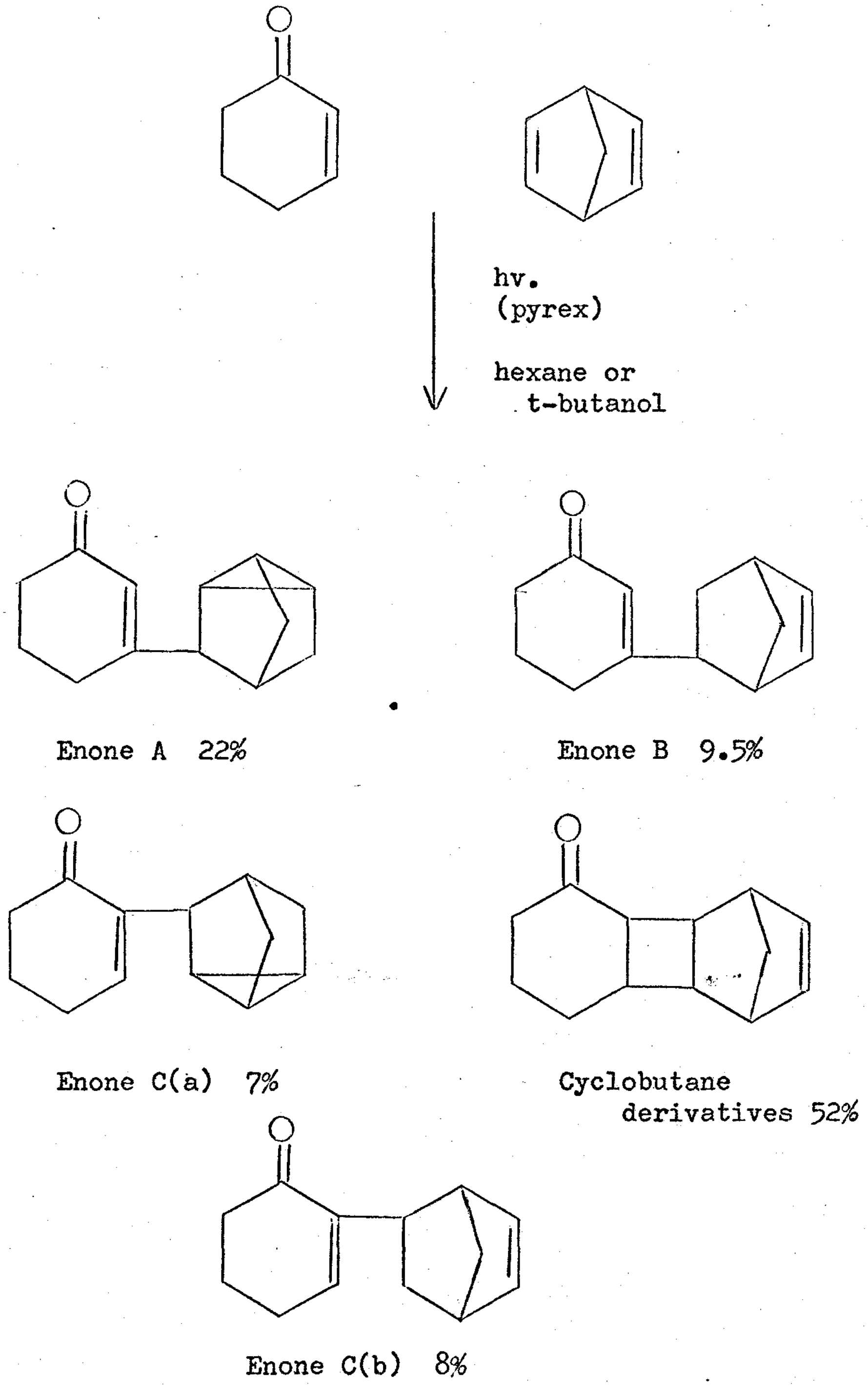


Chart V

CHAPTER III

DISCUSSION OF RESULTS

The formation of α, β unsaturated ketones in the photoaddition reaction of cyclic enones to olefins appears to be unprecedented, and in this discussion we shall be concerned with the mechanism of their formation. Clearly our work is not yet sufficiently comprehensive to allow us to propose a detailed scheme, but the rationale given below may involve points of more general application. This scheme is shown in Chart VI.

Several aspects of this are of further interest:-

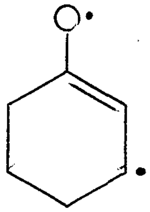
(a) The nature of the excited species of 2-cyclohexenone

(b) The possibility of complex formation between the excited ketone and ground state olefin

(c) The nature of the diradical species and their rearrangement to give the observed products.

(a) <u>Nature of the excited species</u>

As we have previously remarked the absorption of filtered u.v. light by the 2-cyclohexenone will give initially the $n-\pi^*$ singlet state. This may undergo intersystem crossing to yield the $n-\pi^*$ triplet, which is probably the state responsible for reaction as has been found in other reactions of excited enones and dienones (7, 8). This species has been shown to act in some cases as a type of biradical (as shown).



Simple M.O. theory illustrates that such a $n-\pi^*$ state might be expected to have free valence character at the 3-position. Further work to determine the nature of the reactive excited species is however required. (See end of this chapter).

(b) Complex formation

The formation of a complex between norbornadiene and the excited 2-cyclohexenone is suggested by the formation of products derived from initial endo attack on the norbornadiene. As we shall see later, enones A and C(a) arise from diradicals formed by such an attack, and constitute 29% of the reaction mixture.

As we indicated in Chapter I, most cases of endo-attack on norbornadiene involve formation of an initial complex or a concerted transition state, and this is also probably true here. This complex might be similar to that suggested by Corey et al. (17), who postulated a complex between excited 2-cyclohexenone and ground state olefin to explain the orientation of the products in their reactions.

As we indicated above the $n-\pi^*$ triplet might be expected to react as a free radical reagent. However Trecker and Henry (35) have pointed out that free radical attack on norbornadiene is exclusively exo; thus all products here should be derived from initial exo attack if the above model is valid.

Thus complex formation appears to be necessary for at least part of the reaction path. This complex might then collapse to yield the diradical species shown which further yield the observed enone products.

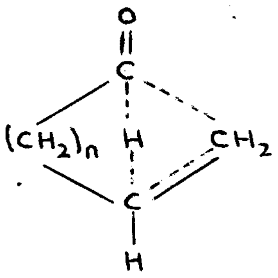
(c) The diradical species

The diradicals shown in Chart IV (p. 24) may be used to rationalise the formation of enones A, B, C(a) and C(b).

It should be noted that enones A and C(a) can only be formed from endo-substituted diradicals, if the mechanism is as illustrated, as the molecular conformations necessary for 1,4 hydrogen atom shifts are not possible from the exo-substituted intermediates.

1,4 shifts are quite familiar in radical systems and examples which may be quoted are the isomerisation of n-alkyl radicals (76, 77) and the photolysis of cyclopentanone (78). These shifts require a 5-membered transition state which does not involve too much Baeyer strain.

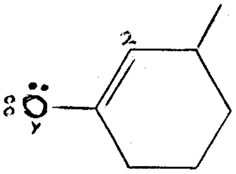
The formation of enones B and C(b) requires a 1,3 hydrogen atom shift as illustrated in Chart VI. Here the radical species may be in either the exo or endo configuration and so these enones may or may not be formed from the same species as enones A and C(a). The 1,3 hydrogen atom shift requires a 4-membered ring transition state which would certainly be quite strained, and this might account for the lesser quantities of enone B formed. These shifts are not so common as the 1,4 shifts though they have been postulated for the photoelimination of methanol from 4-methyl 4-methoxy 2-pentanone (79), and Srinivasan (80) has postulated that the photodecomposition of cyclic ketones involves a transition state where the hydrogen atom is transferred as shown.

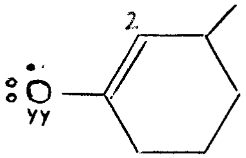


Of great interest is the absence of products formally derived by homo-Diels-Alder addition of 2-cyclohexenone to norbornadiene (e.g. product G in Chart III). The formation of this compound by concerted cycloaddition reaction is forbidden by the rules of Woodward and Hoffmann (28). However examination of diagrams and models for this molecule indicates that it should be stable and certainly the collapse of a ground state diradical, such as K or M of Chart IV, to this system would seem probable, as the necessary activation energy should be small. (Combination of radicals is normally of zero activation energy, and the strain of a 5-membered ring is slight.) However the hydrogen atom transfer reaction appears to be more favoured in our case.

Our error here might well lie in assuming that the postulated intermediate is a conventional diradical. Clearly if the excited state enone has interacted with the olefin, we might expect the resultant species to be electronically excited. These species might then demote $(\pi^* \rightarrow n)$ or undergo chemical reaction before demotion.

Let us consider the electronic configurations of (i) the excited species and (ii) the non-excited species of the above intermediate.





We may perform a simplified M.O. calculation on these systems. Suitable values for the Coulomb integral of the oxygen atom (α_o) and for the resonance integral of the C–O bond (β_{c-o}) must be chosen.

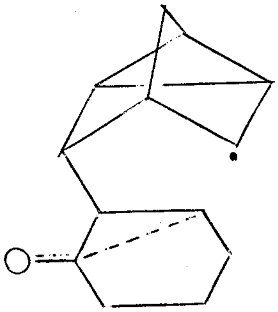
$$\alpha_o = \alpha_c + h\beta$$

$${}_{c-o} = k\,\beta_{c-c}$$

Following Streitwieser (81) we may use $h_o = 1$ and $k_{c-o} = k_{c=o} = 1$. These yield free valence for atom 2 of (i) 0.86 : (ii) 1.10. The value of h_o should be 2. This would give a value for (ii) of 0.98. This means that we have appreciably more free valence character in the unexcited species and that this species would be expected to behave more like a radical. On the other hand the excited state will have more olefinic character. These calculations are of course very qualitative but I believe they indicate the trend to be expected in the reactivity of these species.

If the intermediate is indeed an excited species of the type described, there is competition between hydrogen abstraction by a radical to yield a stabilised excited enone system and radical addition to a double bond to yield the saturated carbonyl species. Now addition of the trichloromethyl radical to cyclohexene and hydrogen atom abstraction from its allylic position by the radical proceed at similar rates. Further in our case hydrogen abstraction will yield an excited 2-cyclohexenone species whereas radical attack gives the cyclohexanone product in its excited state. The former product is of lower energy (c.f. the $n-\pi^*$ singlet for cyclohexenone is approximately 10 Kcals lower than that for cyclohexanone.), a factor which will undoubtedly favour the former process.

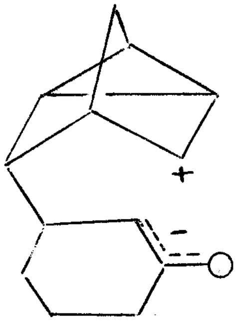
In the case of the 2-substituted diradical



a similar explanation is only possible if we assume there to be bonding between the 1 and 3 positions of the structure as shown. Such bonding is not possible in the n - π * excited state of the 2-cyclohexenone but might be found in the excited species shown, particularly if this had suitable geometry.

A factor which has not so far been considered is the multiplicity of the excited "diradical" species. As was stated earlier, the triplet species of 2-cyclohexenone is probably involved in the reaction, so the diradical species will initially have triplet character. Although spin inversion processes are probably rapid for such a species (82), this triplet nature might prevent ring closure to give a triplet cyclohexanone species while favouring hydrogen atom abstraction to yield the 2-cyclohexenone triplet.

Demotion of the excited intermediate would give a ground state diradical but might also possibly yield a switterionic species such as:-



from the excited state encompassing the enone system and the 5-position of the nortricyclyl system. This zwitterionic species may be regarded as a nortricyclyl cation and an enolate system. Formation of enone A would then require a 1,4 hydride ion shift, a step which seems quite reasonable geometrically but is apparently without precedent. However occurrence of such an intermediate would presumably produce different product distributions for reaction in solvents of different polarity, and our work shows little change in this for reactions in hexane and t-butanol. Recent work in our group has shown that the reaction in acetic acid under identical conditions does give different reaction products, an observation which may be of mechanistic significance (83).

No new evidence for the mechanism of the formation of the cyclobutane derivatives has been presented here, and as illustrated in Chart VI these may arise by either a concerted pathway (allowed by the Woodward and Hoffmann rules (28)) or via "diradical" intermediates or perhaps by both pathways.

As I have stated earlier this discussion presents a possible rationale for the formation of the α,β unsaturated ketones but does not give an explanation for the absence of such products in reactions such as those of Eaton (16) and Corey et al. (17).

<u>Suggestions for further work in connection with this system</u>

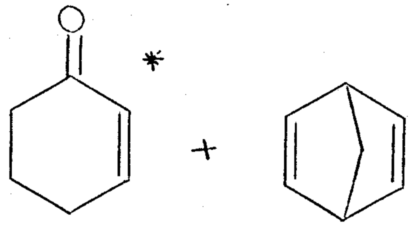
As well as the experiments mentioned in part 5 of Chapter I, the following would now seem worthwhile.

(i) Photolysis of 3-deutero 2-cyclohexenone and norbornadiene. This should give products analagous to enones A and B, and would be useful in showing that a 1,4 or 1,3 hydrogen atom shift is indeed involved in their formation.

(ii) The nature of the excited state involved in the photoadditions of cyclic enones to olefins might be determined by studying the competition between photoinduced rearrangement of 4,4-dimethyl cyclohexenone and its photoaddition to cyclopentene. As the rearrangement is known to proceed through the triplet state of the enone, a study of the variation of reaction products with and without the presence of triplet quenchers should show whether the n, π * triplet is the reactive species in the cycloaddition.

A study of the photodimerisation of cyclopentenone and its photoaddition to cyclopentene should yield similar results.

Mechanism for product formation in 2-cyclohexenone/norbornadiene photolyses



↓

Complex

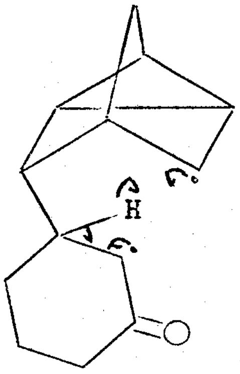
concerted (?) ↙ cyclobutane derivatives

↘ diradical species (as in Chart IV)

↓

Enones A, B, C(a), C(b) and cyclobutanes derivatives

Enone A Formation



Enone B Formation

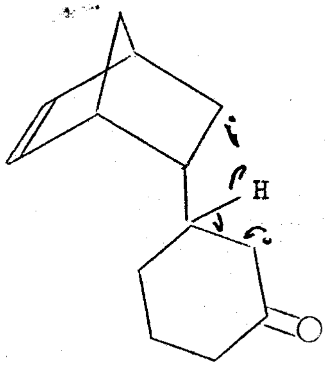


Chart VI

CHAPTER IV

EXPERIMENTAL SECTION

General Procedure for Photochemical Reactions

The apparatus consisted of an irradiation vessel fitted with a quartz water-cooled immersion well, a magnetic stirrer, a capillary inlet for nitrogen gas and an adapter to allow nitrogen escape and to allow entry for capillary polyethylene tubing for aliquot removal. The flask normally used was of 400 ml capacity.

The lamp used was a Hanovia Type L 450w high pressure mercury arc lamp. The light in all reactions was filtered with a pyrex sleeve, 1 mm. thick. This cut off radiation with wavelength lower than 280 mμ.

Before irradiation solutions were flushed free of oxygen by passing purified nitrogen through the solution for at least one hour and commonly overnight. The nitrogen used was of certified quality (less than 20 p.p.m. oxygen). This was purified by successive passage through an oxygen-purging vanadous ion solution (84) and concentrated sulphuric acid, and over potassium hydroxide pellets.

The lamp was cooled with tap water for photolyses in hexane: temperature of the solution was approximately 13° C. For photolyses in t-butanol, this system could not be used as the t-butanol solution froze and an external pump was used to circulate the water in a closed system: temperature of irradiated solution was approximately 39°C.

Purification of Materials

2-cyclohexenone. Aldrich reagent was distilled at atmospheric pressure or at reduced pressure. B.p. = 61-2°/16 mm. Judged pure by v.p.c.

Norbornadiene. Aldrich reagent was distilled at atmospheric pressure B.p. = 89-90°/760 mm. The compound was used immediately as the material polymerised on standing even at room temperature.

Hexane. In a standard purification, 1 litre of Eastman practical grade hexane was treated successively with 2 x 100 cc. of concentrated sulphuric acid, 2 x 100 cc. of water, 1 x 100 cc. of concentrated sulphuric acid, 1 x 100 cc. of potassium permanganate solution and finally washed with 2 x 100 cc. of water. It was then dried over calcium chloride, passed through a 34 cm. silica gel column and distilled. B.pt. = 66.5 - 67.5°. The ultra-violet absorption was negligible except at 2500 mμ (log $^{I}/I_o$ = 0.05).

t-Butanol. This was purified by distillation B.p. = 81 - 81.5°/749 mm.

Techniques for Separation of Mixture/Vapour Phase Chromatography (v.p.c.).

The instrument used was an Aerograph "Moduline" 200, dual column chromatograph with a thermal conductivity detector and manual programmer; the carrier gas was helium.

Columns used were as follows:

Col. A	15% FFAP	5' x 1/4"	60/80	Chromosorb W
Col. B	15% FS 1265	15' x 1/4"	60/80	Chromosorb W
Col. C	20% SE 30	5' x 1/4"	60/80	Chromosorb W
Col. D	30% FFAP	10' x 3/8"	60/80	Chromosorb W
Col. E	30% SE 30	10' x 3/8"	60/80	Chromosorb W

All were steel columns.

Thin layer chromatography

Two sets of conditions were used.

(i) Eastman kit silica gel K301R and 3% ethyl acetate in benzene.

(ii) Silica gel G - acc. to Stahl - Merck A.G. and 5% ethyl acetate in benzene.

Liquid - Solid Chromatography

Materials used were silica gel (Grace - grade 923: mesh size 100-200), benzene (reagent grade) and ethyl acetate (reagent grade).

In a typical separation of the photolysis reaction mixture a column of length 64 cm. and diameter 4 cm. was used. The solvent was successively 1250 ml. of 3% Et.OAc. / benzene, 1250 ml. of 4% Et.OAc. / benzene, 1500 ml. of 5% Et.OAc. / benzene, 200 ml. of 6-7% Et.OAc. / benzene and then eluted with 15% solvent.

Between 1250 and 2500 ml. the eluent contained Enone C only. Between 2500 ml. and 4500 ml. saturated carbonyl derivatives were eluted. Enone B was eluted between 4500 ml. and 6000 ml.; Enone A between 4500 ml. and completion (7000 ml.). The fraction between 4500 ml. and 4750 ml. contained 52% Enone B and 16% Enone A. The fraction between 4750 ml. and 5000 ml. contained 47% Enone B and 44% Enone A. Later fractions contained 80% Enone A. Total recovery from the column was approximately 88%.

Spectroscopic Analysis

(i) Infrared

Routine analyses were taken on a Beckmann I.R.5 instrument and precise measurements on a Perkin Elmer 521 Recording Spectrophotometer.

Spectra were usually taken in 0.1 mm. solution cells with sodium chloride windows. The solvents used were spectral grade carbon disulphide and carbon tetrachloride.

(ii) Nuclear Magnetic Resonance (n.m.r.) spectra

These were recorded on a Varian Associates A-60 instrument. An internal standard, hexa-methyl siloxane (δ = 0.06 p.p.m.) was used. All spectra were taken on approximately 20% carbon tetrachloride solutions.

(iii) Ultra-Violet Spectra

These were recorded on a Carey 14 spectrophotometer. Most spectra were taken in Fisher spectranalysed n-hexane.

(iv) Mass Spectra

These were obtained using a Hitachi Perkin Elmer MRU6 mass spectrometer.

Carbon-Hydrogen analysis of enone A

This was carried out by Spang Microanalytical Laboratory, on material isolated from photolysis by v.p.c.

Found C = 82.80%: H = 8.72%.

$C_{13}H_{16}O$ requires C = 82.93%: H = 8.57%

Synthesis of enone A

3-ethoxy 2-cyclohexenone was prepared by the method of Gannon and House (85).

The Grignard reagent of nortricyclyl bromide was prepared from magnesium (0.742g: 0.031 mole) and nortricyclyl bromide (5.26 g: 0.030 mole) in 20 ml. ether. Initiation with iodine was sometimes required. 3-ethoxy

2-cyclohexenone (4.17 g: 0.029 mole) in ether (10 ml.) was added to the Grignard reagent over a period of 10 minutes at 0°C. Reaction mixture (an avocaat-yellow) was stirred for 20 minutes, then decomposed with 5% sulphuric acid. The mixture was extracted with ether, dried over calcium chloride and the solvent removed. This product gave a v.p.c. peak with identical retention time as that for a photolytic sample of enone A. The enone A was separated from 3-ethoxy cyclohexenone by silica gel chromatography (6% EtOAc /Benzene 34 cm. x 3 cm. diameter). Total yield was 1270 mg. (23%). Undoubtedly this yield can be improved to at least 30%.

I.R. and N.M.R. spectra were identical to those for enone A isolated from photolysis mixture.

Attempted synthesis of enone B

5-norbornenyl bromide was prepared by the method of Roberts et al. (62). Although a glass tube was used for the reaction the mixture contained 30% nortricyclyl bromide as well as 70% 5-norbornenyl bromide.

The Grignard reagent was prepared by an analagous method to that for nortricyclyl bromide (vide supra) and the reaction with 3-ethoxy 2-cyclohexenone attempted as above. The reaction mixture was decomposed with water, the mixture ether extracted and dried over calcium chloride. A v.p.c. trace of this showed a peak analagous to that for enone A. Silica gel chromatography yielded pure enone A in 30% yield.

It was therefore assumed that norbornenyl Grignard reagent isomerises to the nortricyclyl isomer.

Attempted isomerisation of enone B

Enone B (4 mg.) was dissolved in 95% ethanol (0.4 ml.) and a 2% aqueous solution of sodium hydroxide (0.5 ml.) was added. Samples were taken after 20 minutes, 1 hour and 20 hours, ether extracted and analysed by v.p.c. on column B. Only 1 peak was found with a retention time corresponding to enone B. The reaction was performed at room temperature.

Synthesis of enone C(a)

Nortricyclyl lithium compound was prepared by dissolving nortricyclyl bromide (5.19 g: 0.030 mole) in anhydrous ether (15 ml.) and adding prepared lithium metal sheet (0.521 g: 0.074 mole). The mixture was heated to reflux and refluxed for 3 hours.

n-Butyl lithium (6.6 ml. : 0.0106 mole)was added to recrystallised 1,2 cyclohexandione (1.36 g: 0.0122 mole) in ether (30 ml.). The mixed solution was then added to the nortricyclyl lithium and the mixture refluxed for 7 hours. After evaporation of the ether, the mixture was ether-extracted and dried. Distillation under reduced pressure (1 mm.) yielded a product (b.pt. 110-160°). The v.p.c. of this sample indicated a peak corresponding to enone C. Attempts to isolate this component by v.p.c. or silica gel chromatography were unsuccessful.

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The following abbreviations are used below:-

Ang. Chem. Int.	Angewandte Chemie International
Aus. J. C.	Australian Journal of Chemistry
Ber.	Chemische Berichte
Can. J. Chem.	Canadian Journal of Chemistry
Chem. Comm.	Chemical Communications (London)
Chem. & Ind.	Chemistry & Industry (London)
Chem. Rev.	Chemical Reviews
I.U.P.A.C.	International Union of Pure and Applied Chemistry
J.A.C.S.	Journal of the American Chemical Society
J.C.S.	Journal of the Chemical Society
J.C.P.	Journal of Chemical Physics
J. Org. Chem.	Journal of Organic Chemistry
J.P.C.	Journal of Physical Chemistry
P.A.C.	Pure & Applied Chemistry
P.C.S.	Proceedings of the Chemical Society
T.F.S.	Transactions of the Faraday Society
Tetr.	Tetrahedron
Tet. Let.	Tetrahedron Letters

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