

PHOTOCHEMISTRY OF SUBSTITUTED 2-CYCLOHEXENONES

THE PHOTOCHEMISTRY OF SOME SUBSTITUTED
2-CYCLOHEXENONES
AND THE EXCITED STATES INVOLVED

By

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A Thesis

Submitted to the Faculty of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Master of Science

McMaster University

October 1969

To MOM and DAD
on Your 25th Anniversary

MASTER OF SCIENCE (1969)
(Chemistry)

McMASTER UNIVERSITY
Hamilton, Ontario.

TITLE: The Photochemistry of some Substituted 2-Cyclohexenones
and the Excited States Involved

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NUMBER OF PAGES: viii, 87

SCOPE AND CONTENTS:

The photoadditions of 3-phenyl-2-cyclohexenone to bicyclo [2.2.1] - hepta-2,5-diene, bicyclo [2.2.1] hept-2-ene and cyclopentene have been studied. In all cases cis fused cyclobutane products were obtained. Quenching and sensitization experiments indicated a singlet excited state to be active in photocycloaddition. Phosphorescence and fluorescence emission were observed from 3-phenyl-2-cyclohexenone. Energy transfer to the lowest triplet of 3-phenyl-2-cyclohexenone was evident from the quenching of Michler's ketone phosphorescence. Two norbornene dimers were detected in the photolysis of 3-phenyl-2-cyclohexenone and norbornene giving evidence for a higher triplet excited state of the enone. The photoaddition of 3-methyl-2-cyclohexenone to cyclopentene was studied for comparison and both cis and trans fused adducts were obtained. In photolyses with bicyclo [2.2.1] hepta-2,5-diene or cyclopentene, 2-phenyl-2-cyclohexenone was unreactive.

ACKNOWLEDGEMENTS

It is a pleasure to express my gratitude to Dr. J. J. McCullough for his guidance and encouragement throughout this work. I also thank Dr. C. W. Huang and Dr. P. W. Rasmussen for enlightening discussions and their jovial company.

An Ontario Graduate Fellowship from the Province of Ontario and financial assistance from the Department of Chemistry, McMaster University, are gratefully acknowledged.

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I N T R O D U C T I O N

A. GENERAL INTRODUCTION

Long before being recognized or appreciated, photochemical reactions have been operative. Light induced reactions have an integral role in maintaining the balance in transformations between plants, bacteria and animals in our environment.

Several examples catch ones attention which illustrate the fundamental nature of light induced reactions. Experiments simulating primitive earth conditions have shown that short ultra-violet irradiation of mixtures of methane, ammonia and water, produces amino acids¹, the molecular building blocks of living matter. More remarkable is the example of photosynthesis in plants. In converting carbon dioxide and water to oxygen and carbohydrates, plants use sunlight for the production of food and power. With the availability of sunlight, perhaps energy storing photochemical reactions can be developed, not requiring plants and fertile soil.

Other examples are related to our sense of vision. In the retina of the eye are light sensitive pigments, one of which is rhodopsin², vital to our vision mechanism. The application of the sensitivity of silver salts to light has been the basis of the photographic process. Investigators such as Schultz (1727), Beccarius (1757) and Scheele (1777) began photochemical studies of silver salts as early as the eighteenth century³.

It is, however, the last decade which has produced an awesome volume of knowledge in the field of photochemistry. Several factors have made this advancement possible. A difficult practical

problem in the early days was the barrier of isomeric or complex product mixtures often obtained in photochemical reactions. This problem is now successfully being handled by a variety of chromatographic techniques. Of paramount impact was the development of quantum theory. Once the theoretical foundation of quantum mechanics was laid, coupled with its application in electronic spectroscopy, the mechanism of photochemical processes began to be unravelled.

B. THEORY AND BEHAVIOUR OF THE EXCITED STATE

Organic photochemistry encompasses the reactions of carbon based compounds having absorbed visible or ultraviolet light. Molecules absorbing light have their normal electronic configuration (ground state) promoted to an electronically excited state. The magnitude of the excitation energy is given by the equation:

$$E_2 - E_1 = h\tilde{\nu}c = \frac{2.86 \times 10^5}{\lambda}$$

where $E_2 - E_1$ is the energy difference between the excited and ground states (expressed in kilocalories per mole), h is Planck's constant, c is the velocity of light, $\tilde{\nu}$ the wave number and λ the wavelength (in angstroms) of the absorption⁴.

Absorption of light by organic molecules having singlet ground states S_0 (paired electron spin), as required by the Pauli principle, results in singlet to singlet electronic excitation since transitions involving a change in multiplicity are forbidden. Conversion from higher to the lowest excited singlet S_1 is rapid. Fluorescence is the emission of the short lived excited singlet returning to ground state, S_1 to S_0 , the lifetime of S_1 being about 10^{-8} seconds. Intersystem crossing from an excited singlet state can lead to the triplet state (unpaired electron spins). At lower frequencies or longer wavelength than fluorescence, the relatively long lived phosphorescence emission (10^{-3} seconds or greater) is observed from the triplet returning to ground state, in the forbidden T_1 to S_0 transition. Reactions in solution generally proceed from

either the S_1 or T_1 states but often the triplet has a better chance of reacting because of its longer lifetime.

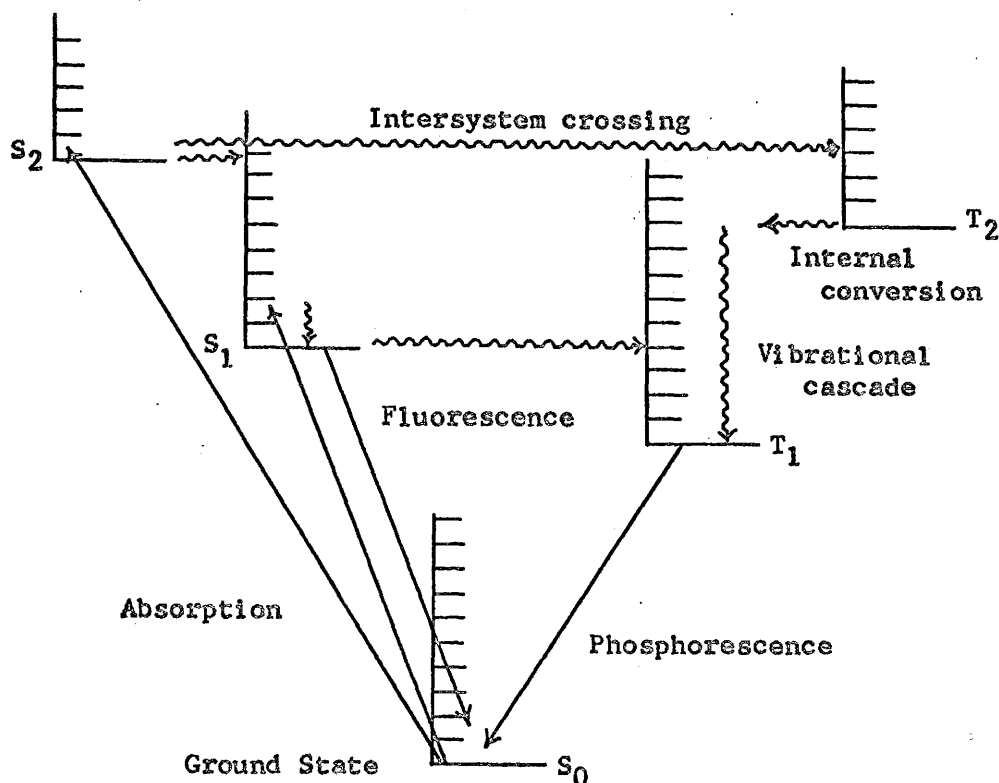


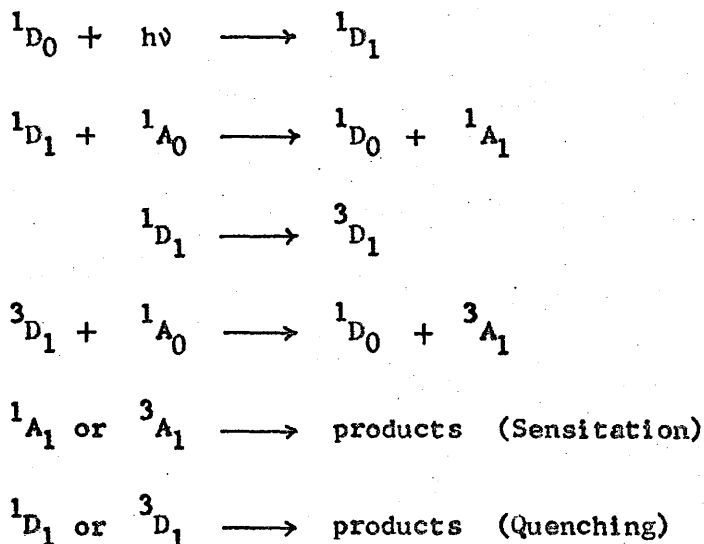
DIAGRAM 1: TYPICAL ENERGY LEVEL DIAGRAM

Two types of electronic excitation are described by molecular orbital theory and are easily illustrated with the carbonyl group. The lowest excitation is of a non-bonding n oxygen electron to an antibonding π^* orbital which is the lowest unoccupied orbital. This is the $n-\pi^*$ transition which is forbidden on the basis of orbital

symmetry, hence absorption bands are of low intensity. The second type of excitation is of an electron in the bonding carbon-oxygen π orbital to the antibonding π^* orbital, a π - π^* transition allowed by symmetry rules.

Organic photochemistry is therefore concerned with singlet and triplet n - π^* states and the singlet and triplet π - π^* states. This study deals with α,β -unsaturated ketones and their transitions are generally analogous to those of the carbonyl group, differing only insofar as excitation is into a delocalized four centre antibonding π^* orbital.

The processes of bimolecular energy transfer are important in understanding the mechanism of photochemical reactions. When two molecules are present in solution, one of which absorbs light (D), the other being transparent (A), it is often possible for an excited state molecule D_1 to transfer energy to ground state A_0 , provided the process is thermodynamically favorable. If the excited state singlet A_1^1 or triplet A_1^3 of the nonabsorbing molecule is reactive, then the reaction is being sensitized by the acceptance of energy from the excited donor molecule. If the singlet D_1^1 or triplet D_1^3 species of the light absorbing molecule are reactive, then A_0 will quench the reaction by dissipating energy via nonreactive pathways. The mechanism of energy transfer may be outlined in the following manner.



D = DONOR

A = ACCEPTOR

It is known that the quenching of donor triplets occurs at a diffusion controlled rate if the acceptor triplet level is lower in energy⁵. In practical experiments the appropriate choice of sensitizer or quencher provides information regarding the multiplicity and energy level of the reactive excited state. Control over the reactive excited state can also be of synthetic utility⁶.

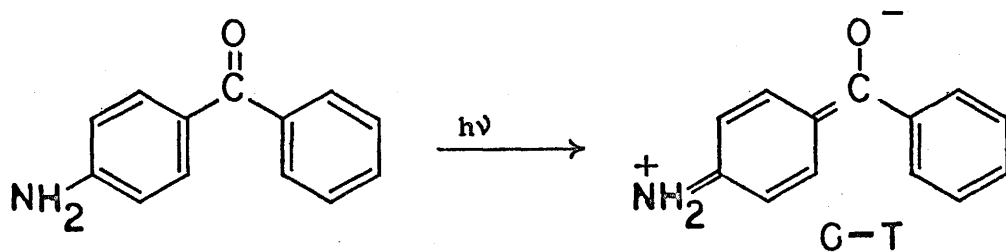
The geometrical structure of an electronically excited molecule may differ appreciably from the ground state. Bond lengths generally become longer and valence angles change. These basic changes should alter the reactivity of the excited molecule and each excited state is potentially unique. While experimental measurement of the size, shape and charge distribution of an excited molecule remain very difficult, correlation between theoretical calculations

of the excited state and the stereochemistry of photoadducts is imminent.

As Corey noted in 1964, little information was available concerning the equilibrium geometries of the excited states of α,β -unsaturated carbonyl compounds^{7,8}. Recently, calculations on acrolein and cinnamaldehyde have been performed in this department and will be presented with the discussion of results.

reduction will be favored by an $n-\pi^*$ excited state. Porter has shown that the quantum yield of pinacolization is unity for benzophenone in isopropanol solvent^{9,10}.

In the case of 4-aminobenzophenone a charge transfer state, C-T, in which electrons are donated from the amine group is proposed.



The charge transfer state is stabilized in the polar solvent isopropanol, strongly inhibiting photoreduction. If, however, cyclohexane is used as solvent, the $n-\pi^*$ state remains lowest in energy and photoreduction occurs. In the case of 4-hydroxybenzophenone, the excited state apparently loses the hydroxyl proton, leaving negatively charged oxygen, again a strongly electron donating substituent.

When the carbonyl group is conjugated with a naphthalene nucleus, normal photoreduction reactions do not occur. The low reactivity, relative to benzophenone, of 1-naphthaldehyde and 2-acetonaphthone has been attributed to their lowest triplet state having the $\pi-\pi^*$ configuration¹². By conjugating the carbonyl group with the naphthalene nucleus, the $\pi-\pi^*$ state is lowered to a larger extent than the $n-\pi^*$ state. One example from the benzophenone series, p-phenylbenzophenone, also having a $\pi-\pi^*$ lowest triplet¹³, has the reduced quantum yield of 0.1 for pinacolization⁹.

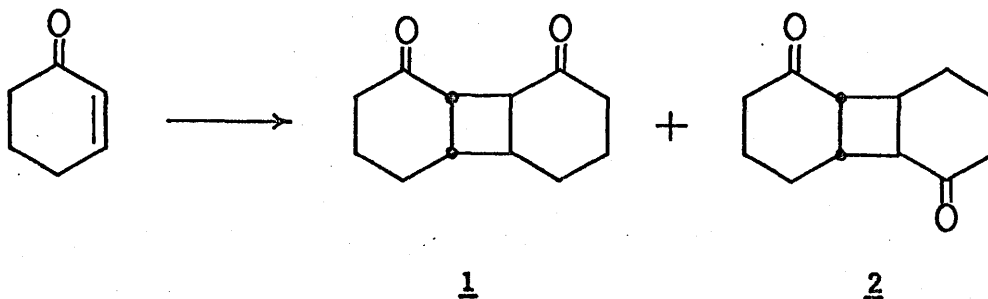
The following conclusions can be drawn from these studies.

When the lowest triplet level is $n-\pi^*$, the quantum yield of pinacolization is near unity, whereas if the lowest triplet level is C-T, the quantum yield is zero. In cases where the $\pi-\pi^*$ triplet state is lowest in energy, photoreduction does not readily occur. Thus the surrounding molecular structure and effect of substituents on the carbonyl group are shown to determine the reactive excited state, thereby altering the reactivity in the photoreduction reaction.

D. PHOTOADDITION OF α,β -UNSATURATED KETONES

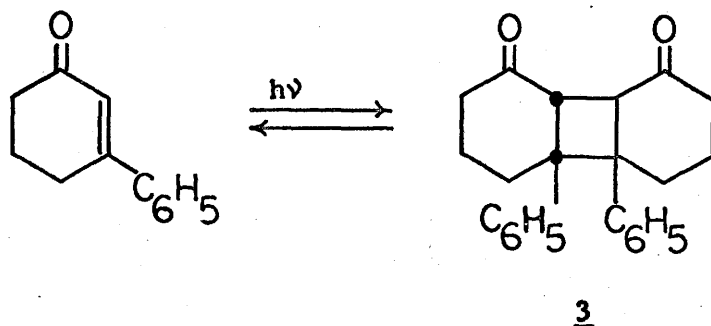
Irradiation of an α,β -unsaturated ketone commonly gives a cyclobutane photodimer, or irradiation in the presence of a high olefin concentration gives cross-photoaddition products. Due to the variety of enone and olefin reactants possible, their photoaddition is a very general reaction. Significant application of this photocycloaddition reaction has been made in syntheses such as that of α -caryophyllene alcohol¹⁴, caryophyllene^{15,16}, and other bicyclic and polycyclic molecules^{17,18}. The exact stereochemistry of photodimers is often difficult to determine, but those which have been studied make comparison worthwhile.

The dimerization of cyclopentenone leads to approximately equal amounts of head-to-head and head-to-tail products in several solvents¹⁹. Each have the cis-anti-cis configuration about the cyclobutane ring. Evidence for a reactive triplet species was obtained from quenching and sensitization experiments. Similarly, Hammond²⁰ has shown that cyclohexenone gives predominantly two dimers, 1 and 2, whose ratio varies with solvent.



A triplet mechanism is supported for the dimerization since the reaction is quenched by piperylene²⁰.

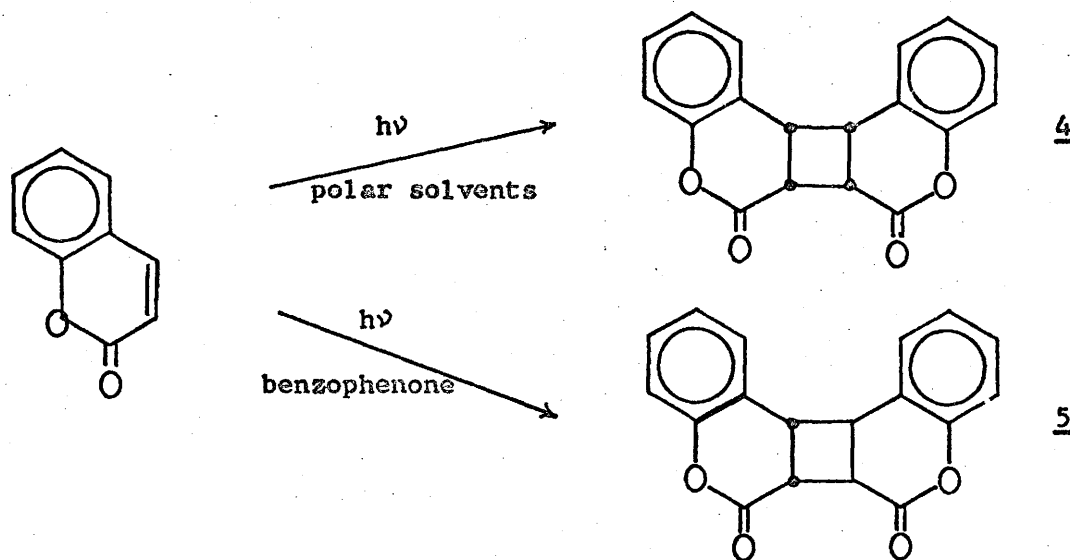
In contrast to the two previous examples, 3-phenyl-2-cyclohexenone gives one dimer having the head-to-head and cis-anti-cis configuration²¹.



Variation in solvent polarity does not affect the dimer formation. The dimerization is also found to be a reversible photolytic process which apparently is not the case with cyclopentenone¹⁹. A p-methoxy or a p-nitro group on the phenyl ring of 3-phenyl-2-cyclohexenone did not alter the mode of dimerization, giving in each case a single dimer corresponding in structure to 3²². While no information regarding the multiplicity of the reaction was advanced, the formation of a sole head-to-head dimer suggests the possibility of a stepwise biradical mechanism proceeding through the more stable benzyl radical. A similar explanation is offered for the photodimerization of indenes^{23,24}.

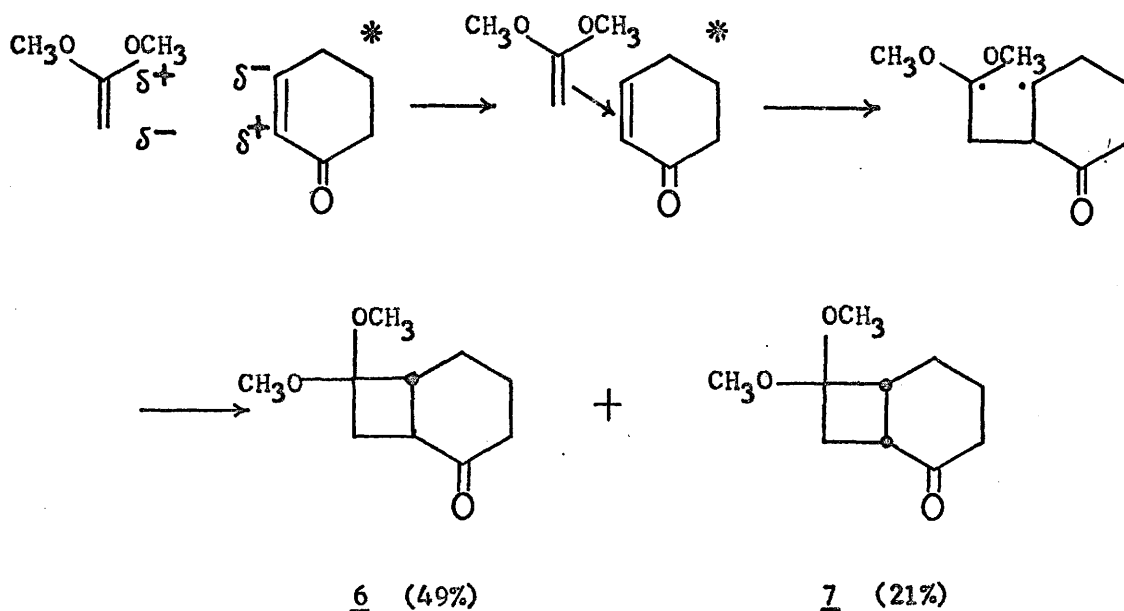
The photodimerization of coumarin gives different products from direct and sensitized irradiation. Direct irradiation of coumarin in polar solvents leads to almost exclusive formation of the syn dimer (4) in low yield^{25,26}. An excited state bimolecular

complex derived from the excited state singlet of coumarin is proposed as the reactive species²⁶. The anti dimer (5) is formed when coumarin is irradiated in the presence of a triplet sensitizer such as benzophenone. In this latter case, the reaction may be quenched by piperylene giving further evidence that the dimer 5 is formed via monomeric triplet species. Thus, a change in the multiplicity of the reactive excited state is shown to result in the formation of a different photodimer of coumarin.



Corey was the first to systematically study the photoaddition of 2-cyclohexenones with substituted olefins⁷. Several important trends are apparent in his results. Electron donating substituents at the double bond of the olefin promote high reactivity, thus the relative rate in decreasing order of photoaddition is 1,1-dimethoxyethylene, methoxyethylene and cyclopentene. A degree of orientational specificity was observed in the products as shown in the case of 1,1-dimethoxyethylene, where the major products 6 and 7 have 7,7-dimethoxy substitution...

The orientation is such that the α -carbon of 2-cyclohexenone apparently becomes attached to the most nucleophilic carbon of the double bond. The formation of trans fused bicyclo [4.2.0] octanone adducts is quite general and the major product (6) has a trans fused ring juncture.



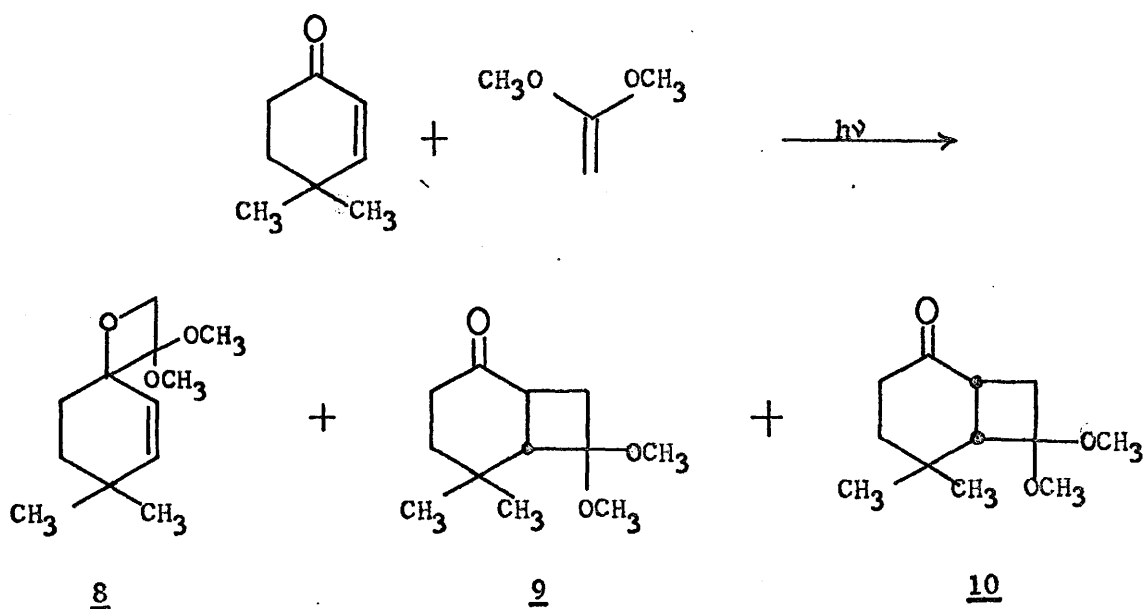
The photoaddition of both cis- and trans-2-butene to 2-cyclohexenone gave the same products⁷. To account for these products a π complex of the $n-\pi^*$ excited state of 2-cyclohexenone and ground state olefin was postulated. The complex would itself have stereospecific orientation arising from the dipole interaction of olefin and excited enone. With bond formation a diradical may form which subsequently leads to the observed products.

It is also of interest to note that a 2-methyl-substituent

on cyclohexenone greatly diminishes the rate of photoaddition as compared to a 3-methyl-substituent which in turn is nearly as reactive as 2-cyclohexenone⁷.

The multiplicity of the reactive excited state was not established by Corey, but recent studies by de Mayo and Chapman have been devoted to this question. In the case of the observed trans products, a diradical intermediate may be a reasonable postulate but different excited forms or states of the enone are viable alternates.

Irradiation of 4,4-dimethyl-2-cyclohexenone and 1,1-dimethoxyethylene gave products 8, 9, and 10²⁷.



Chapman and co-workers²⁷ reported the interesting result that the ratio of cis to trans fused adducts, 9 and 10, varies considerably with solvent and all three adducts can be formed by sensitization with triphenylamine, indicating triplet excited states are involved. Quenching experiments with di-*t*-butylnitroxide lead to differential quenching of the adducts,

the formation of the cis adduct (10) being quenched faster than the trans adduct (9). Chapman concluded that two distinct triplets gave rise to the cis and trans adducts respectively. This interpretation itself encompasses alternatives. Is a single triplet electronic configuration reactive having variable structure or geometry, or are two distinct triplet states involved?

Evidence for a reactive higher triplet state has been reported by de Mayo in the photoaddition of cyclopentenone to cyclohexene^{28,29}. Benzophenone (triplet energy, 69 kcal/mole) is unable to sensitize the photoaddition although triplet energy is transferred to the cyclopentenone. Energy transfer was demonstrated by cyclopentenone quenching both the photoreduction reaction and phosphorescence of benzophenone. Cycloaddition can be sensitized, however, with high energy sensitizers such as acetophenone (triplet energy, 74 kcal/mole) giving evidence for a higher triplet T_2 of cyclopentenone, which is reactive.

In the preceding examples, results indicate that with cyclohexenones, differing stereochemical products have been associated with different excited species. This is illustrated in the two modes of coumarin dimerization and the analysis of cis and trans fused photoadducts from 4,4-dimethyl-2-cyclohexenone (isophorone was demonstrated to be similar²⁷). Cyclopentenone apparently has two distinct triplets, only the higher being active in photocycloaddition with cyclohexene. With regard to higher triplet states, Liu also reports reactions from a higher triplet state of anthracenes, sensitizing the rearrangement of rigid and nonrigid molecules^{30,31,32}.

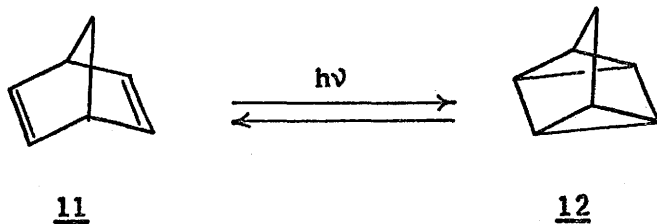
E. PERTINENT OLEFIN PHOTOCHEMISTRY

A resume of the photochemistry of the olefin reactants used in this work will serve as a basis for later discussion. In the photoaddition reactions studied, the following olefins were used: bicyclo [2.2.1]hepta-2,5-diene, (norbornadiene); bicyclo [2.2.1]hept-2-ene, (norbornene); and cyclopentene.

Norbornadiene

The photoaddition reaction with norbornadiene has shown to be more than a potentially interesting reaction. Reactions involving rearrangement from 2,6-nortricycle bridging or cycloaddition giving the homo Diels-Alder products are possibilities. The photoaddition of 2-cyclohexenone, 3-methyl- and 2-methyl-2-cyclohexenone has been studied in this laboratory by McCullough, Kelly and Rasmussen^{33,34}. The unusual α and β substituted cyclohexenone products were obtained in the photoaddition along with the normal cyclobutane adducts.

Norbornadiene irradiated in the presence of benzophenone, acetophenone or acetone undergoes efficient internal addition to afford quadricyclene (12)^{35,36}.

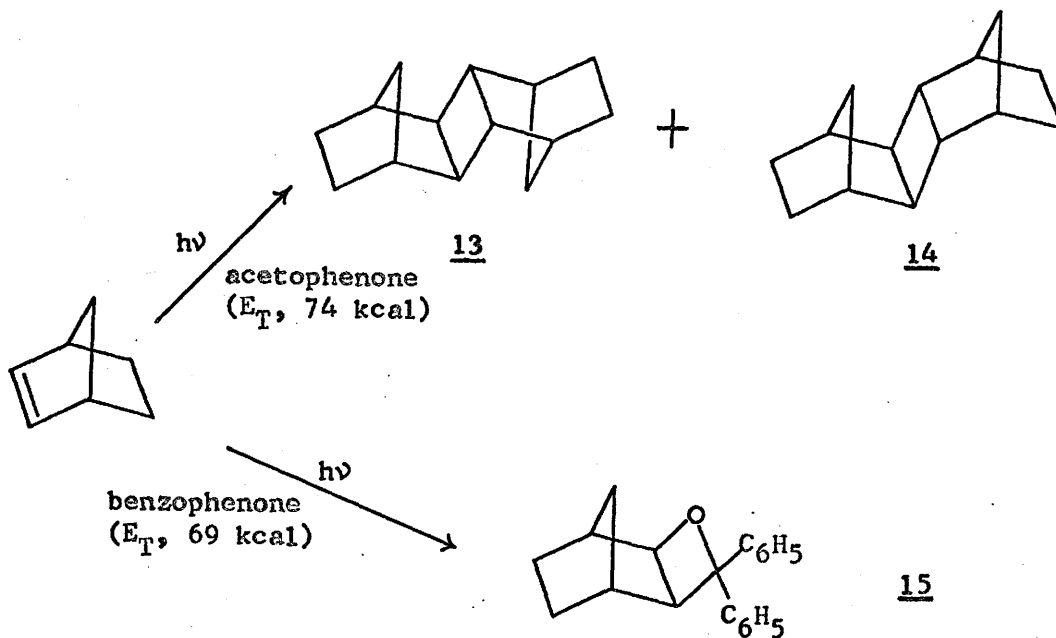


Molecular orbital calculations of the excited state of this diene

indicate an appreciable 2-6 bond order³⁷, a consequence of the spatial relationship of the double bonds. The reaction is reversible and irradiation of quadricyclene with low energy sensitizers such as fluorenone (triplet energy 54 kcal/mole) gives a photostationary state containing 11 and 12³⁶.

Norbornene

Few examples of the photosensitized dimerization of simple alkenes are known. The photosensitized dimerization of norbornene gives the exo-trans-exo (13) and endo-trans-exo (14) isomers in the ratio 12:88³⁸. The ratio of 14 to 15 is independent of the sensitizer used provided its triplet energy is sufficiently high to transfer energy to the norbornene. When benzophenone is used as sensitizer (triplet energy 69 kcal/mole), addition occurs giving the oxetane (15)³⁹.



A rather precise estimate of the triplet energy level of norbornene is available from the following data. Triplet-triplet energy transfer of an excited carbonyl to norbornene causes dimerization. The formation of oxetanes, however, has been shown to be quite general with ketones whose $n-\pi^*$ triplet energy levels lie below that of the olefin substrate⁴⁰. Arnold^{41,42} has shown that a difference in triplet energy of only about 0.5 kilocalories is determining in the photolysis of norbornene.

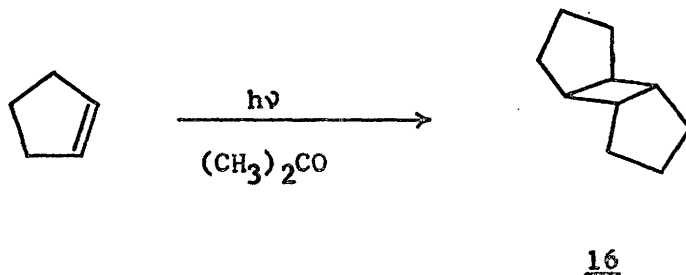
Irradiation of norbornene with 4-chloroacetophenone as sensitizer (triplet energy 72.1 kcal/mole) gave almost exclusively the two dimers, whereas 3-trifluoromethylacetophenone (triplet energy 71.6 kcal/mole) gave the oxetane to the extent of 92%. Thus the dimerization of norbornene requires a sensitizer having a minimum triplet energy level very close to 72.0 kilocalories per mole. This figure should be of value in establishing the energy level of a sensitizer whose triplet energy is unknown or difficult to measure.

Irradiation of the cuprous chloride complex and norbornene showed high stereoselectivity in the products giving 13 to the extent of 97%³⁸.

Norbornene also readily undergoes mixed photoaddition reactions forming cyclobutane adducts. For example, the photoaddition of dimethyl maleate to norbornene gave two exo substituted cyclobutane adducts^{43,44}, indicating the strong preference of norbornene to undergo exo attack rather than endo attack. The preferential addition is thought to arise from the steric shielding of the endo hydrogens on the opposing ethylene bridge⁴⁵.

Cyclopentene

Cyclopentene is also known to dimerize giving 16 in 55% yield along with cyclopentyl cyclopentenenes when irradiated with acetone as sensitizer⁴⁶.



Several cross-addition reactions with cyclopentene are known, notably that with cyclopentenone giving predominantly a single isomer having the cis-anti-cis configuration about the cyclobutane ring⁴⁷.

RESULTS

A. PHOTOADDITION REACTIONS AND PRODUCT IDENTIFICATION

Photoaddition of 3-phenyl-2-cyclohexenone and norbornadiene

The photolysis of 3-phenyl-2-cyclohexenone and norbornadiene gave three major adducts as shown by gas chromatography (vpc) and infrared monitoring. Products were separated by silica gel column and vpc as described in the Experimental section. The two major products have been assigned the structures shown in Diagram 2, which are cis-anti-exo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridec-4,5-en-9-one (17) and cis-syn-endo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridec-4,5-en-9-one (19). While tert-butyl alcohol was normally used as solvent, the same products were obtained using benzene or glacial acetic acid.

Structural identification was based upon spectroscopic data and a comparison of the hydrogenated derivatives 20 and 21 with the photoadducts of 3-phenyl-2-cyclohexenone and norbornene.

Isomer 17, melting point (mp) 75 - 83°C, was obtained from preparative vpc. Infrared absorption at 5.88 μ indicated a cis fused cyclohexenone⁷ and bands at 13.20 μ and 14.24 μ a monosubstituted phenyl group⁴⁸.

The nuclear magnetic resonance (nmr) spectrum showed aromatic resonance centered at 7.12 ppm (5 hydrogen, multiplet) and vinyl protons at 5.92 ppm (2H, triplet) characteristic of the remaining norbornene double bond. Resonance at 0.98 ppm (2H) was attributed to endocyclic cyclobutane ring protons in an exo fused norbornene. Norbornene has endocyclic protons at 0.95 ppm⁴⁹ and the exo-trans-endo norbornadiene dimer has endo protons at 1.13 ppm³⁸. The vinylic triplet at 5.92 ppm

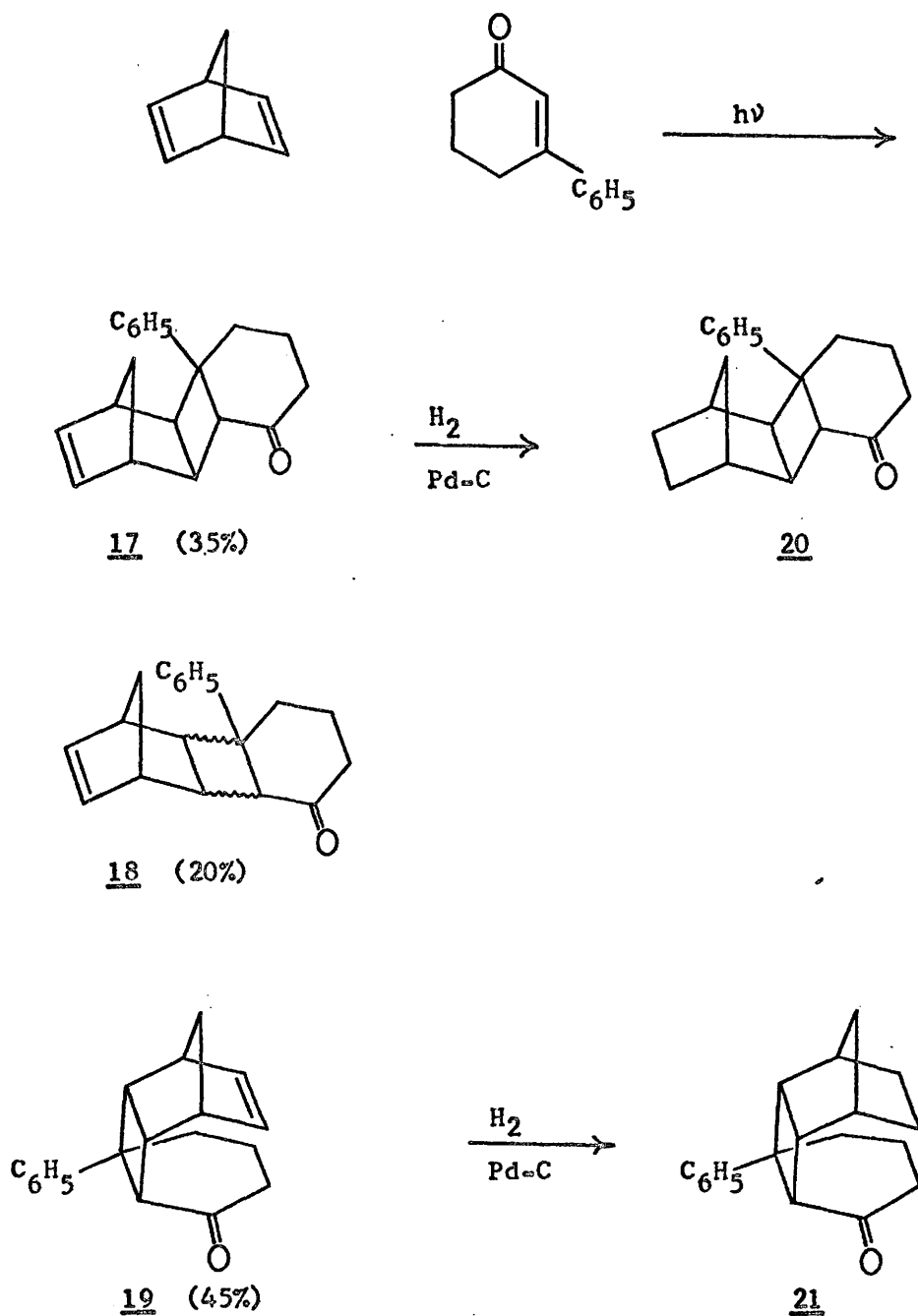


DIAGRAM 2

PHOTOADDUCTS OF 3-PHENYL-2-CYCLOHEXENONE AND NORBORNADIENE

was consistent with exo substitution since norbornene vinyl protons remain at higher field with an exocyclic juncture (5.82 - 5.97 ppm) than with an endocyclic juncture³⁸. A multiplet extending from 1.6 ppm to 2.9 ppm bounded the remaining protons.

Catalytic reduction of the norbornene double bond in 17 gave 20, mp 86 - 88°C. Infrared absorption at 5.88 μ , 13.66 μ and 14.25 μ were analogous to the precursor 17. Compound 20 had coincident retention time on vpc and the same nmr and infrared spectra as the major product of the photoaddition of 3-phenyl-2-cyclohexenone and norbornene (see below). A mixed melting point of the reduced isomer and the major photolytic product of the latter reaction gave mp 85 - 88°C, indicating that they were the same isomer. Coupling constants of a cyclobutane ring proton in isomer 20 (presented later) suggested anti ring systems about the cyclobutane, thus defining the structure for 17 as cis-anti-exo.

The minor photolytic product (18) was inseparable from 17 and 19, both on silica gel column and preparative vpc. Product 18 is tentatively assigned as a cyclobutane adduct on the basis of spectra of fractions containing 18. These spectra showed infrared absorption at 5.88 μ (cis fused system⁷), vinylic proton resonance at 6.0 ppm (2 hydrogens) and aromatic resonance centered at 7.2 ppm (5 hydrogens).

The major adduct (19), mp 104.5 - 106.5°C, had carbonyl absorption at 5.85 μ , near the lower limit for a cis fused cyclohexanone⁷. Equilibration on basic alumina produced no change in the infrared or nmr spectra giving support for the cis structure.

The nmr spectrum of 19 (Figure 1) showed sharp aromatic resonance

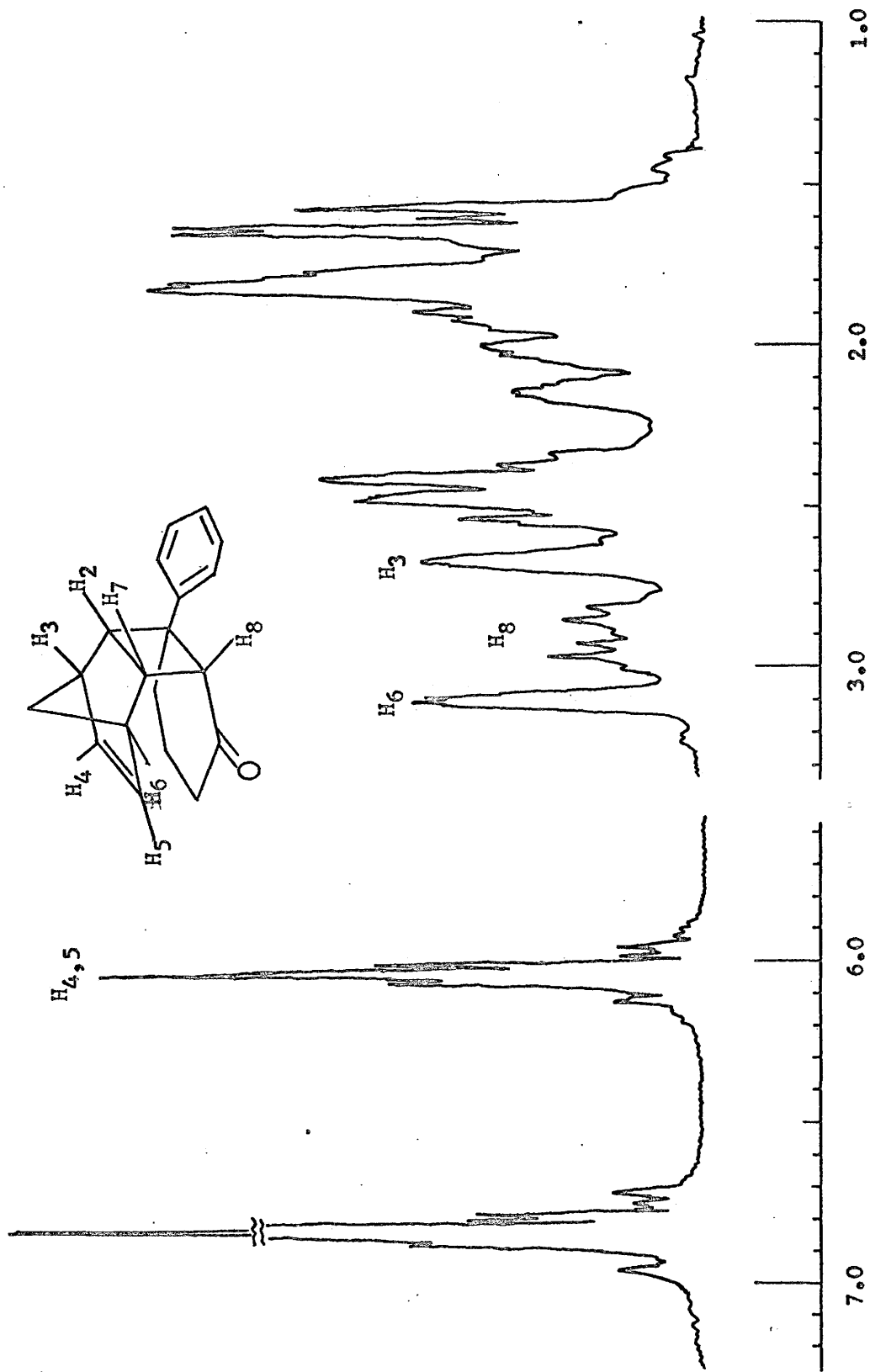


FIGURE 1 100 Mcps NMR SPECTRUM OF 19

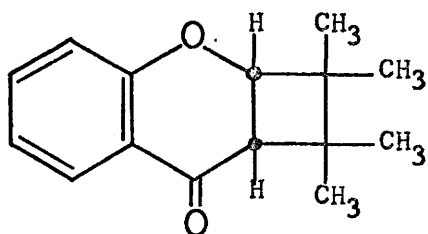
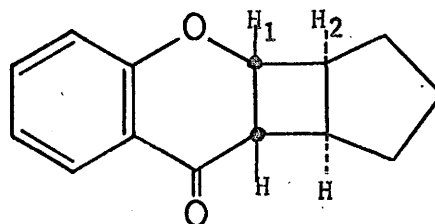
at 6.87 ppm (5H) and a vinyl multiplet centered at 6.16 ppm (2H). The lack of proton resonance above 1.65 ppm suggests the absence of endocyclic hydrogens. Since an endocyclic juncture shifts vinyl protons to lower field³⁸ (isomer 17 has vinylic resonance at 5.92 ppm) the vinyl multiplet at 6.16 ppm is consistent with endo substitution. The vinyl protons of 19 are not a simple triplet as in the case of 17 and this difference has also been suggested as a means of distinguishing endo- and exo-norbornene substitution^{50,51}. The above spectral data is compelling evidence for an endo substituted norbornene structure.

Irradiation of the vinyl multiplet at 6.16 ppm caused the peak at 3.20 ppm to sharpen. This shows the peak at 3.20 ppm to be resonance from a bridgehead proton (H_6). In endo-norbornadiene dimers the bridgehead protons have been assigned at 2.72 or 2.82 ppm³⁸. Thus the single proton peak at 2.79 ppm was assigned to the other bridgehead proton (H_3).

A doublet of triplets centered at 3.01 ppm (1H, $J=11.0$ cps) was assigned to the cyclobutane ring proton (H_8) adjacent to the carbonyl group and the carbon bearing the phenyl group. This is reasonable since this proton appears at 3.53 ppm in the dimer of 3-phenyl-2-cyclohexenone (lit. 3.60 ppm²¹).

The magnitude of vicinal cis hydrogen coupling constants is known in many cases to be greater than that for trans hydrogens in the cyclobutane system. In substituted chromones the cis coupling constants are 9 cps and 8 cps for 22 and 23 respectively⁵². Schenck⁵³ also provides examples of cis couplings between vicinal hydrogens on the cyclobutane ring ranging from 7 - 11.5 cps. The trans coupling

constant in 23 was much smaller ($J_{12}=3.5$ cps)⁵². The observed coupling constant of 11.0 cps for H_8 is therefore attributed to a vicinal cis hydrogen establishing a syn orientation of ring junctures about the cyclobutane ring in 19. The complete stereochemistry of the adduct is now defined by the preceding arguments.

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The syn structure also provides a rationale for one bridgehead being shifted downfield. Molecular models show the carbonyl group to lie under the bridgehead proton H_6 . Examples of the deshielding effect of the carbonyl group, are of the order of 0.3 ppm and 0.73 ppm⁵⁴. Thus the observed difference of 0.4 ppm between bridgehead protons H_3 and H_6 is plausible.

Hydrogenation of crystalline 19 gave 21, mp 86-89.5°C with a molecular ion of m/e 266 as the base peak. The nmr showed aromatic protons at 6.97 ppm (5 hydrogens) and the absence of vinyl protons. A multiplet extending from 1.0 ppm to 3.0 ppm contained the remaining protons.

Analysis of the photolysis of 3-phenyl-2-cyclohexenone and norbornadiene by vpc, qualitatively showed that quadricyclene was formed during the irradiation.

Photolysis of 3-phenyl-2-cyclohexenone and norbornene

Irradiation of 3-phenyl-2-cyclohexenone and norbornene in tert-butyl alcohol gave two major cross-addition products, which are assigned as cis-anti-exo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] - tridecan-9-one (20) and cis-anti-endo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] - tridecan-9-one (24), shown in Diagram 3. Two norbornene dimers (13 and 14) were also found in the photolysis.

Chromatography on a silica gel column gave the norbornene dimers in the initial fractions. The major adduct could be obtained from the photolysis mixture by crystallization. The minor adduct was obtained by preparative vpc.

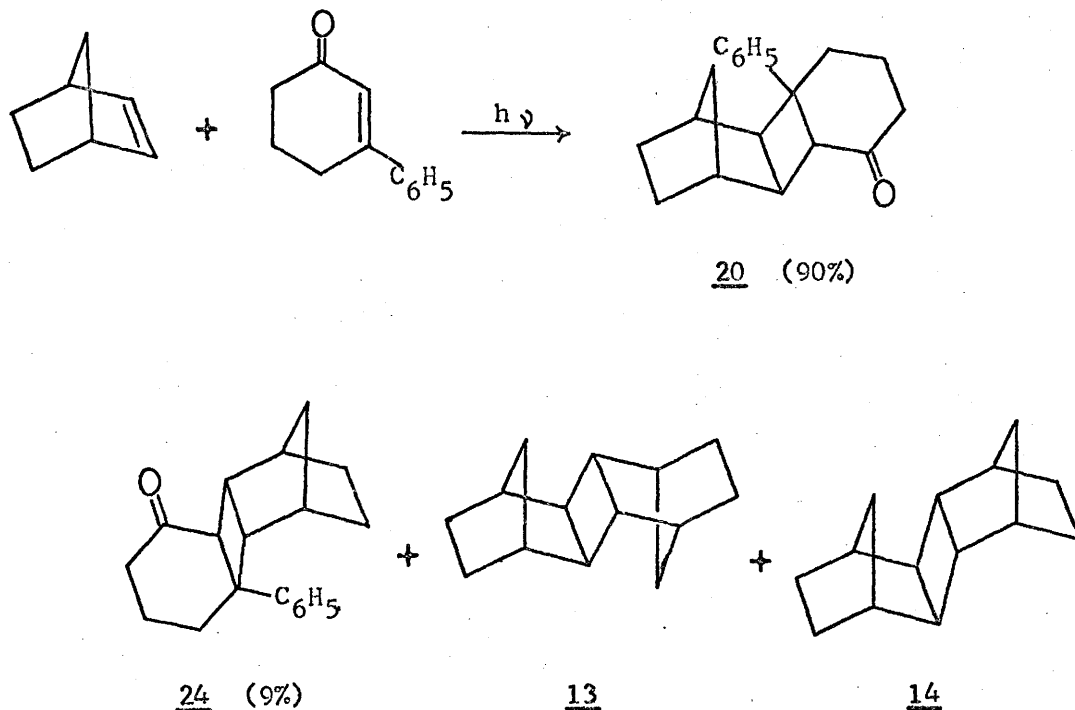


DIAGRAM 3

PHOTOLYSIS OF 3-PHENYL-2-CYCLOHEXENONE AND NORBORNENE

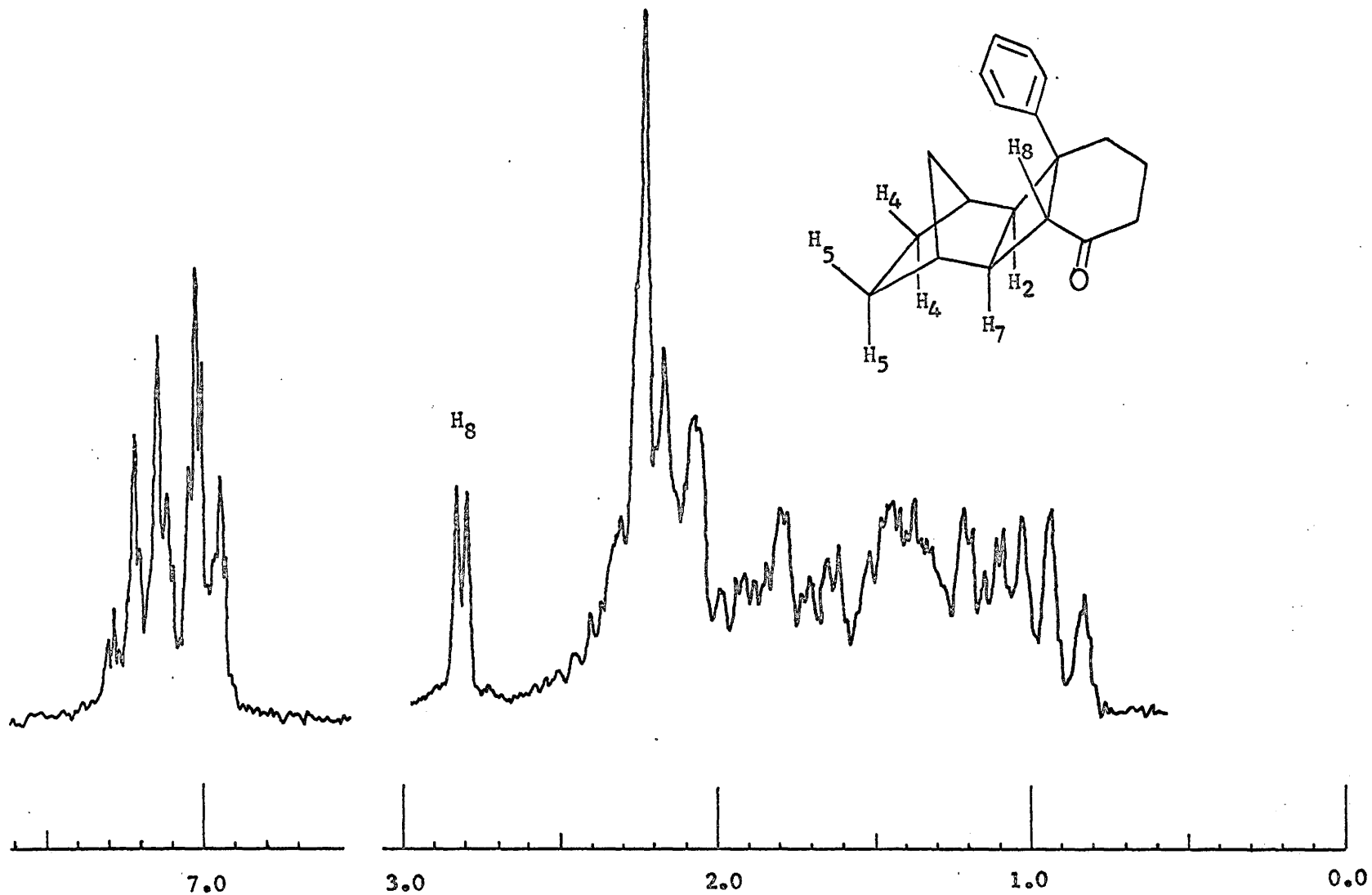


FIGURE 2

100 Mcps NMR SPECTRUM OF 20

The major adduct (20), mp 87 - 88.5°C, has been shown to have the same spectroscopic properties as a reduced derivative of product 17. The nmr of 17 pointed to an exo fused norbornene fragment. An exo structure for the major adduct, 20 is also in accordance with the known preference of norbornene to undergo exo addition in ground state^{45,55} and photochemical reactions^{39,43,44}.

Adduct 20 has carbonyl absorption at 5.88 μ indicating a cyclohexanone which is cis fused⁷. The mass spectrum showed a molecular ion of m/e 266 and base peak m/e 173, the latter corresponding to cleavage of the cyclobutane ring.

The nmr spectrum of 20 is shown in Figure 2 and the single proton peak at 2.84 ppm (doublet, J=3.6 ppm) was assigned to the cyclobutane proton (H_g) adjacent to the phenyl substituted carbon and carbonyl group. A coupling constant of 3.6 cps is consistent with trans coupling of vicinal hydrogens as in 23, where $J_{12} = 3.5$ cps⁵². Thus the norbornene and cyclohexanone rings are assigned the anti configuration about the cyclobutane ring.

The minor adduct (24) was also a cis fused cyclohexanone having carbonyl absorption at 5.88 μ . Resonance centered at 7.17 ppm (5H, multiplet) from aromatic protons and a peak at 2.87 ppm (1H) characterized the nmr spectrum. The signal at 2.87 ppm, assigned the cyclobutane proton (H_g), was distinguishable as a doublet (J=3 cps) which again is characteristic of anti ring junctures. Thus isomer 24 is assigned the cis-anti-endo structure.

Column chromatography separated the norbornene dimers from the other components and vpc showed that dimers 13 and 14 were formed in

the ratio 10:90. The major component (14) was obtained pure by preparative vpc and its mass spectrum had a molecular ion m/e 188 as required for a norbornene dimer. Its nmr spectrum was identical to that published for the endo-trans-exo dimer³⁸. Both the nmr and infrared spectra were identical to those of an authentic sample of the endo-trans-exo dimer prepared by using acetophenone as sensitizer.

Acetophenone is known to sensitize the dimerization of norbornene³⁸ and this reaction gave the exo-trans-exo (13) and endo-trans-exo (14) dimers in the ratio 10:90 (lit. 12:88³⁸). From analytical vpc, both retention times and ratio of 13 and 14 in the photolysis of 3-phenyl-2-cyclohexenone and norbornene were the same as the products of the acetophenone sensitized dimerization of norbornene.

Photolysis of 3-phenyl-2-cyclohexenone and cyclopentene

Irradiation of 3-phenyl-2-cyclohexenone and cyclopentene gave two mixed addition products in the ratio 90:7, which are $1\beta, 2\alpha, 6\alpha, 7\beta$ -1-phenyltricyclo [5.4.0.0^{2,6}] undecan-8-one, 25 (77%); and $1\beta, 2\beta, 6\beta, 7\beta$ -1-phenyltricyclo [5.4.0.0^{2,6}] undecan-8-one, 26 (6%). The photo-dimer (3) was also isolated and these products are shown in Diagram 4.

The photo-dimer of 3-phenyl-2-cyclohexenone (13) was isolated in 12% yield, mp 195 - 199°C (lit. 204 - 205°C)²¹. Its mass spectrum had a weak molecular ion at m/e 344, showing that it was a dimer of 3-phenyl-2-cyclohexenone, and a base peak at m/e 172. Infrared absorption at 5.86μ indicated a cis fused cyclohexanone ring⁷ and bands at 13.87μ and 14.34μ are in accord with monosubstituted phenyl groups⁴⁸.

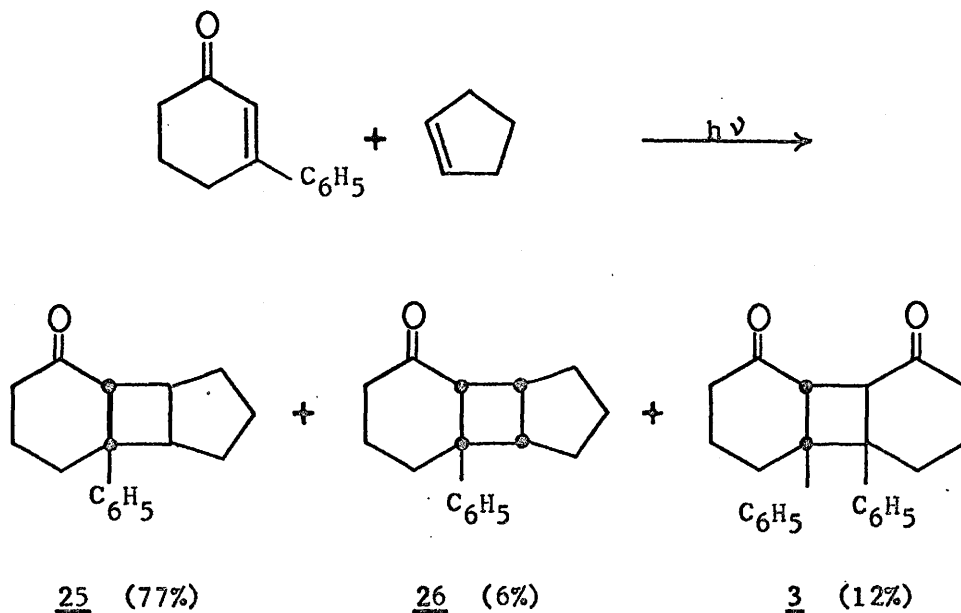


DIAGRAM 4

PHOTOLYSIS OF 3-PHENYL-2-CYCLOHEXENONE AND CYCLOPENTENE

The NMR spectrum was the same as that given by Yates and co-workers²¹ showing a singlet at 3.53 ppm (2H) for the cyclobutane protons, aromatic protons at 7.36 ppm (10H) and multiplets centered at 2.4 ppm (4H) and 1.7 ppm (8H). Yates²¹ has established the structure of the photo dimer as the cis-anti-cis head-to-head cyclobutane derivative (3).

The major cross-addition product (25), mp 59.5 - 61°C, had carbonyl absorption at 5.91 μ for the six membered ring fused cis to the four membered ring. The mass spectrum showed that 25 was a cross-addition product having a parent peak at m/e 240 and base peak at m/e 173.

The nmr spectrum of 25 had the following signals in the high field region: a multiplet at 2.79 ppm (3H) including the cyclobutane ring protons; a multiplet at 2.3 ppm (2H) assigned to the geminal protons adjacent to the carbonyl; multiplets centered at 1.9 ppm (4H) and 1.4 ppm (6H) contained the remaining protons. Aromatic proton resonance extended from 6.9 - 7.4 ppm (5H).

Since 25 was unchanged by equilibration on basic alumina a cis 4-6 ring fusion is indicated and supported by the carbonyl absorption. Presumably the geometry at the 4 - 5 ring fusion is also cis, as implied by the fact that only two isomers were formed in the photolysis.

On the basis that the preferred stereochemistry for ring junctures is anti to one another, as established in the photodimer (3), the major adduct has been assigned the cis-anti-cis configuration.

The minor adduct (26), obtained as an oil, was shown to be a one to one adduct having a molecular ion at m/e 240 and base peak of m/e 173. Infrared absorption of 26, which was unchanged on equilibration, showed a band at 5.85μ for cis 4 - 6 ring fusion. Having assigned the major adduct, this component was assigned the cis-syn-cis structure. The carbonyl absorption at 5.85μ is identical with the absorption of the syn structures assigned photoproducts 19 and 21.

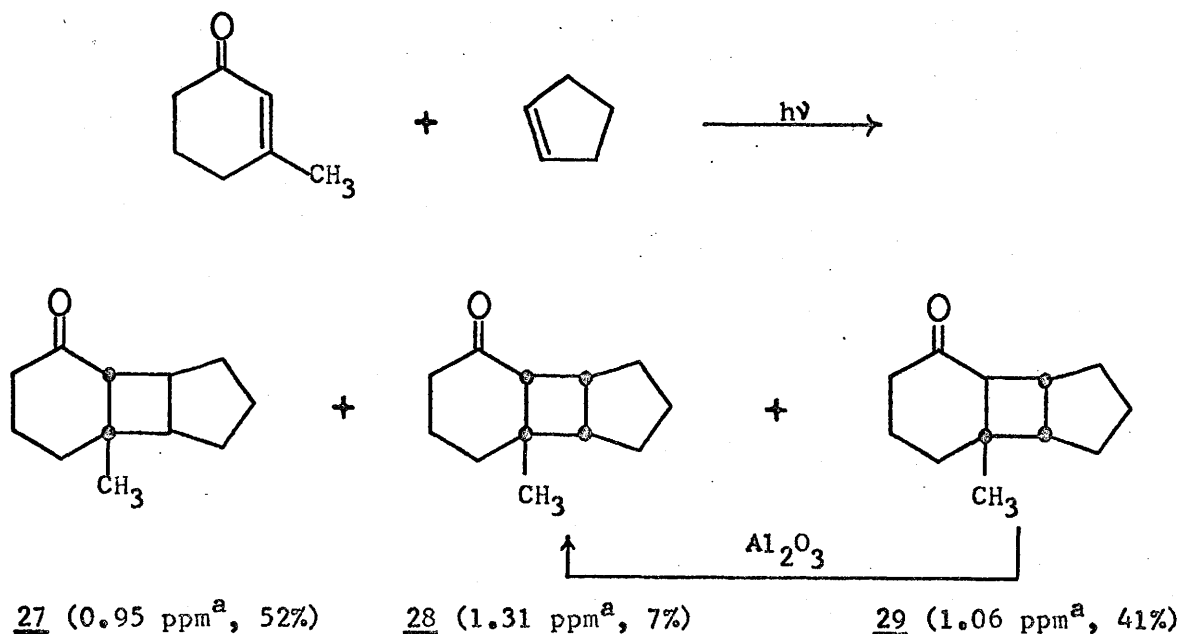
Photoaddition of 3-methyl-2-cyclohexenone and cyclopentene

The photoaddition of 3-methyl-2-cyclohexenone and cyclopentene in tert-butyl alcohol gave three products to which the structures shown in Diagram 5 have been assigned. These structures are

$1\beta, 2\alpha, 6\alpha, 7\beta$ -1-methyltricyclo $[5.4.0.0^{2,6}]$ undecan-8-one, 27 (52%);

$1\beta, 2\beta, 6\beta, 7\beta$ -1-methyltricyclo $[5.4.0.0^{2,6}]$ undecan-8-one, 28 (7%);

and $1\beta, 2\beta, 6\beta, 7\alpha$ -1-methyltricyclo [5.4.0.0^{2,6}] undecan-8-one, 29 (41%).



^a Chemical Shift of Methyl Singlet in the NMR.

DIAGRAM 5

PHOTOADDUCTS OF 3-METHYL-2-CYCLOHEXENONE AND CYCLOPENTENE

Analysis of the photolysis mixture by vpc indicated the formation of three adducts. Two bands of near equal intensity at 5.82μ and 5.91μ in the infrared suggested products having trans and cis 4-6 ring fusion. Product ratios were established by nmr since three unsplit methyl peaks were visible, each corresponding to a photoadduct. The relative percentage of each adduct are given following the chemical shift of the methyl protons: 0.95 ppm, 52% (27); 1.31 ppm, 7% (28); 1.06 ppm, 41% (29). All three adducts were separated by preparative vpc and were obtained as

colorless oils.

Equilibration of the photolysis mixture (27, 28 and 29) with basic alumina caused the methyl signal at 1.06 ppm to disappear. An infrared spectrum after equilibration showed only one carbonyl band at 5.91μ , while the nmr showed two remaining methyl resonances at 0.95 ppm (52%) and 1.31 ppm (48%). Analysis by vpc also showed two peaks in the ratio 52:48.

The major adduct (27) had carbonyl absorption at 5.91μ for cis 4-6 ring fusion⁷ and methyl resonance at 0.95 ppm (3H) as a singlet. Other resonance was confined to a multiplet extending from 1.4 - 2.8 ppm. The mass spectrum had a molecular ion of m/e 178 and base peak at m/e 112 confirming 27 to be a cyclobutane adduct of 3-methyl-2-cyclohexenone and cyclopentene.

This component is assigned cis-anti-cis ring systems on the basis that it is the major isomer and should prefer the orientation of minimal steric interaction. A similar photoadduct of known stereochemistry supports this conclusion. The major product in the photoaddition of 3-methyl-2-cyclohexenone and 4,4-dimethylcyclopentene is a cis-anti-cis adduct as required in Corey's synthesis of α -caryophyllene alcohol¹⁴. The structure of α -caryophyllene alcohol has been assigned on the basis of x-ray diffraction⁵⁶ and chemical studies⁵⁷.

The minor adduct (28) also had carbonyl absorption at 5.91μ indicating cis 4-6 ring fusion. A methyl singlet at 1.31 ppm (3H) was characteristic of this isomer and there was no proton resonance below 2.5 ppm. Its mass spectrum was the same as that of 27. Having assigned the major adduct the cis-anti-cis structure, this isomer must be a cis-syn-cis adduct.

Isomer 29 had infrared absorption at 5.82μ characteristic of trans 4-6 ring fusion⁷. The nmr spectrum had a methyl singlet at 1.06 ppm (3H). Equilibration of pure 29 on basic alumina gave a product having infrared absorption at 5.91μ and a methyl singlet resonance at 1.30 ppm as in isomer 28. Other features of the nmr were also identical to those of 28. Thus isomerization of 29 to 28 showed that these ketones differ only in configuration at the methine carbon adjacent to the carbonyl group; isomer 29 has a trans 4-6 ring fusion and 28 a cis 4-6 fusion.

Photolyses with 2-phenyl-2-cyclohexenone

The synthesis of 2-phenyl-2-cyclohexenone as described in the Experimental section, appears to be an improvement over other methods which have been reported^{58,59}.

Irradiation of 2-phenyl-2-cyclohexenone and an excess of cyclopentene gave no significant reaction in 45 hours. Similarly the photolysis of 2-phenyl-2-cyclohexenone and norbornadiene for 46 hours resulted in no appreciable product formation as indicated by vpc analysis.

B. EXAMINATION OF THE EXCITED STATES OF 3-PHENYL-2-CYCLOHEXENONE

To determine the multiplicity of the excited state of 3-phenyl-2-cyclohexenone which gives rise to photoadducts, the effect of several triplet energy acceptors and donors was examined. A standard photolysis solution without quencher or sensitizer present was simultaneously irradiated for comparison in each case. In all runs tert-butyl alcohol containing 5% methanol was used as solvent. The ratio of products to starting enone was measured by vpc (column A) giving the extent of reaction. Interpretation of the following results will be presented in the Discussion.

The photolysis of 3-phenyl-2-cyclohexenone with cyclopentene and norbornene respectively was conducted in the presence of naphthalene. The results for various concentrations of reactants are given in Table 1. A similar experiment was conducted using biacetyl as quencher and the results are given in Table 2. No retardation in the rate of reaction was observed with naphthalene or biacetyl present in the photolysis solution.

TABLE 1 INVESTIGATION OF NAPHTHALENE QUENCHING

REACTANTS (Molar Concentration)						
	3-phenyl-2-cyclohexenone	cyclopentene	norbornene	naphthalene	Hours Irradiated	Extent of Reaction
1	0.025	0.50		-	11.0	96%
2	0.025	0.50		0.050	11.0	98%
3	0.025		1.00	-	2.0	96%
4	0.025		1.00	0.050	2.0	98%
5	0.020		0.80	-	3.5	98%
6	0.020		0.80	0.06	3.5	98%

TABLE 2 INVESTIGATION OF BIACETYL QUENCHING

REACTANTS (Molar Concentration)					
	3-phenyl-2-cyclohexenone	cyclopentene	biacetyl	Hours Irradiated	Extent of Reaction
1	0.025	0.507	-	1.5	93%
2	0.025	0.507	0.050	1.5	98%

In a subsequent photolysis of 3-phenyl-2-cyclohexenone and cyclopentene, the concentration of naphthalene was increased such that naphthalene absorbed a fraction of the incident light. The rate of reaction was increased with naphthalene present as shown in Table 3.

TABLE 3 INVESTIGATION OF NAPHTHALENE SENSITIZATION

REACTANTS (Molar Concentration)					
	3-phenyl-2-cyclohexenone	cyclopentene	naphthalene	Extent of Reaction	Hours Irradiated
1	0.025	0.50	-	87%	1.75
2	0.025	0.50	0.126	86%	1.25

Sensitization experiments using p,p-dimethylaminobenzophenone (Michler's ketone) and 1-naphthaldehyde as energy donors were performed for the photolysis of 3-phenyl-2-cyclohexenone with cyclopentene and with norbornene. The results given in Table 4 indicate that the photoaddition reaction was not sensitized, but rather, diminished in proportion to the amount of light absorbed by the sensitizer.

In the case of the photoaddition of 3-phenyl-2-cyclohexenone and norbornene, the mixture was analyzed for the norbornene dimers. This was achieved by chromatography of the mixture on a silica gel column followed by analysis of the initial fraction by vpc. The norbornene dimers were shown to be present in the standard irradiation (Run 3, Table 4) but absent in the photolysis containing Michler's ketone (Run 4, Table 4).

TABLE 4 SENSITIZATION EXPERIMENTS

A. Michler's ketone as energy donor

REACTANTS (Molar Concentration)						
	3-phenyl-2-cyclohexenone	cyclopentene	norbornene	Michler's ketone	Hours Irradiated	Extent of Reaction
1	0.0145	0.475		-	1.5	96%
2	0.0145	0.475		0.0056	2.0	26%
3	0.020		0.80	-	3.5	99%
4	0.020		0.80	0.0158	3.5	3%

B. 1-Naphthaldehyde as energy donor

REACTANTS (Molar Concentration)					
	3-phenyl-2-cyclohexenone	cyclopentene	1-naphthaldehyde	Hours Irradiated	Extent of Reaction
1	0.025	0.50	-	1.75	87%
2	0.025	0.50	0.125	1.75	2%

The quantum yield of the photoaddition of 3-phenyl-2-cyclohexenone and cyclopentene was measured by the method described in the Experimental section. In two determinations corresponding to 8.5% and 5.3% conversion of starting enone, only adduct 25 was formed as indicated by vpc. The quantum yield was calculated from the ratio of the moles of cyclobutane adduct (25) formed to the light absorbed by 3-phenyl-2-cyclohexenone as given in Table 5. The results for a quantum yield determination having Michler's ketone in solution are also given.

TABLE 5 QUANTUM YIELD OF 3-PHENYL-2-CYCLOHEXENONE AND
CYCLOPENTENE PHOTOADDITION

	MOLAR CONCENTRATION		Moles of <u>25</u> formed	Light absorbed by Enone ^a	Quantum Yield
	Enone	Cyclopentene			
1	0.0110	0.48	9.32×10^{-4}	3.66×10^{-2} E	0.025
2	0.0107	0.48	5.66×10^{-4}	2.30×10^{-2} E	0.025
3 ^b	0.00485	0.24	2.28×10^{-4}	5.42×10^{-2} E	0.004

a Light absorbed is given in Einsteins.

b Quantum yield determination with 0.0112 M Michler's ketone in solution

Phosphorescence spectra were measured in ethanol-ether 2:1, at 77°K. The solutions were not degassed. The emission band maximum for 3-phenyl-2-cyclohexenone was observed at 5310 Å corresponding to a triplet energy of 53.8 kcal/mole. The emission maximum for 2-phenyl-2-cyclohexenone was observed at 4720 Å corresponding to a triplet energy of 60.6 kcal/mole.

The phosphorescence spectrum of Michler's ketone was measured in the presence of 3-phenyl-2-cyclohexenone. Phosphorescence emission from a 0.0231 M solution of Michler's ketone, measured at 4970 Å, was used as the emission intensity reference (I_0). Excitation by 3700 Å ($\log \epsilon = 4.69$ for Michler's ketone) ensured that all incident light was being absorbed by Michler's ketone. The phosphorescence intensity (I) of solutions with increasing concentration of 3-phenyl-2-cyclohexenone was measured (see Table 6). A plot of I_0/I versus the concentration of 3-phenyl-2-cyclohexenone is given in Figure 3.

The fluorescence spectrum of 3-phenyl-2-cyclohexenone was measured at 25°C in ethanol giving a maximum at 5120 Å. The solution was not degassed.

The effect of cyclopentene on the fluorescence emission of 3-phenyl-2-cyclohexenone was studied at the concentrations given in Table 7. The solutions were not degassed for these determinations. A plot of I_0/I versus the square of the cyclopentene concentration is given in Figure 4.

TABLE 6 QUENCHING OF MICHLER'S KETONE PHOSPHORESCENCE^a
BY 3-PHENYL-2-CYCLOHEXENONE

3-phenyl-2-cyclohexenone	I_0/I
-	1.000
0.0058 M	1.062
0.0097 M	1.108
0.0194 M	1.354
0.0291 M	1.443
0.0466 M	1.595
0.0583 M	1.785

a All solutions were 0.0231 M Michler's ketone

TABLE 7 FLUORESCENCE OF 3-PHENYL-2-CYCLOHEXENONE^a IN THE
PRESENCE OF CYCLOPENTENE

MOLAR CONCENTRATION cyclopentene	$[\text{cyclopentene}]^2$	I_0/I
-	-	1.000
1.025	1.050	1.020
1.882	3.541	1.059
2.605	6.786	1.084
3.50	12.25	1.148
4.23	17.89	1.213
4.83	23.33	1.264

a All solutions were 0.136 M 3-phenyl-2-cyclohexenone

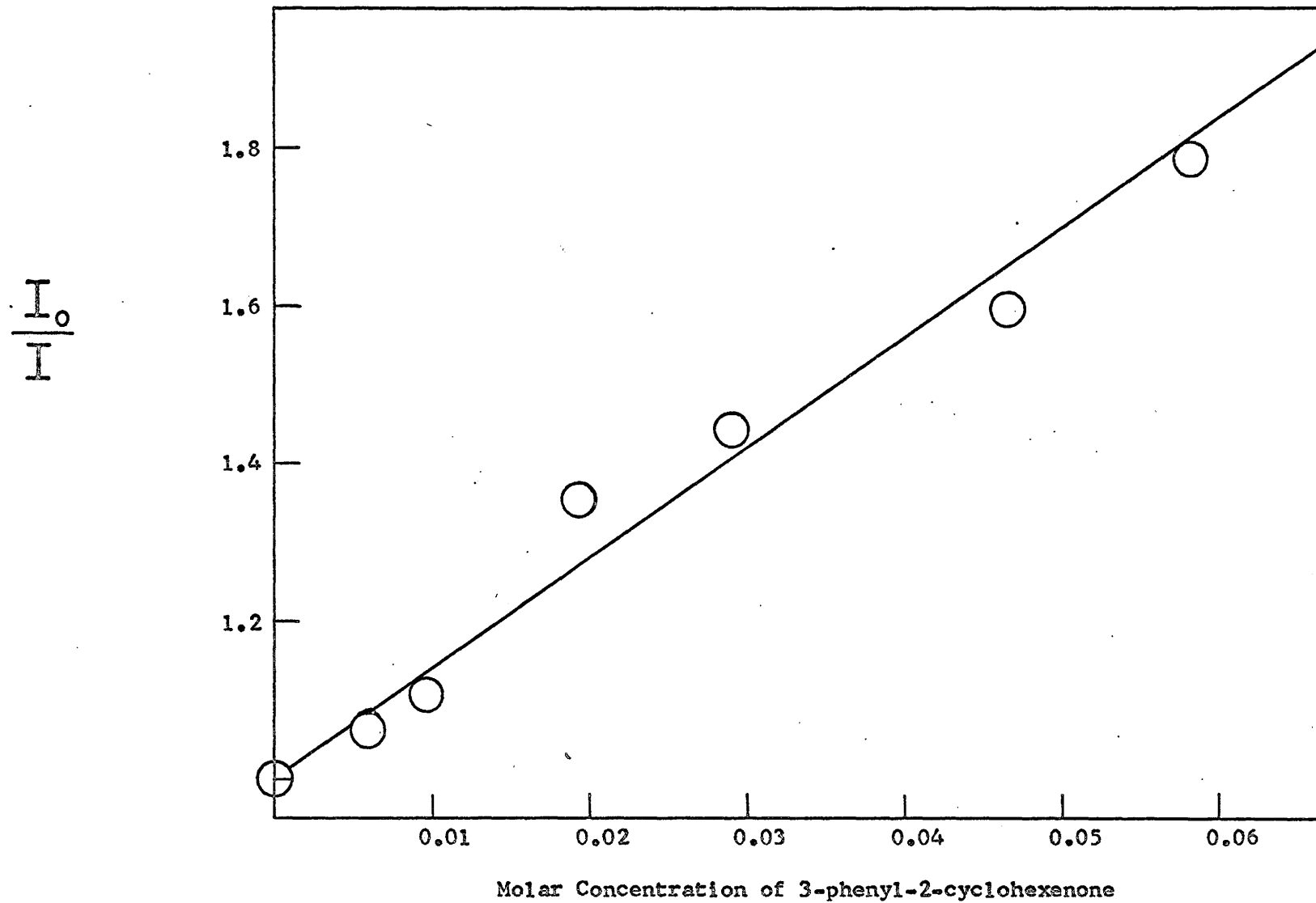


FIGURE 3 QUENCHING OF MICHLER'S KETONE PHOSPHORESCENCE BY 3-PHENYL-2-CYCLOHEXENONE AT 77°K

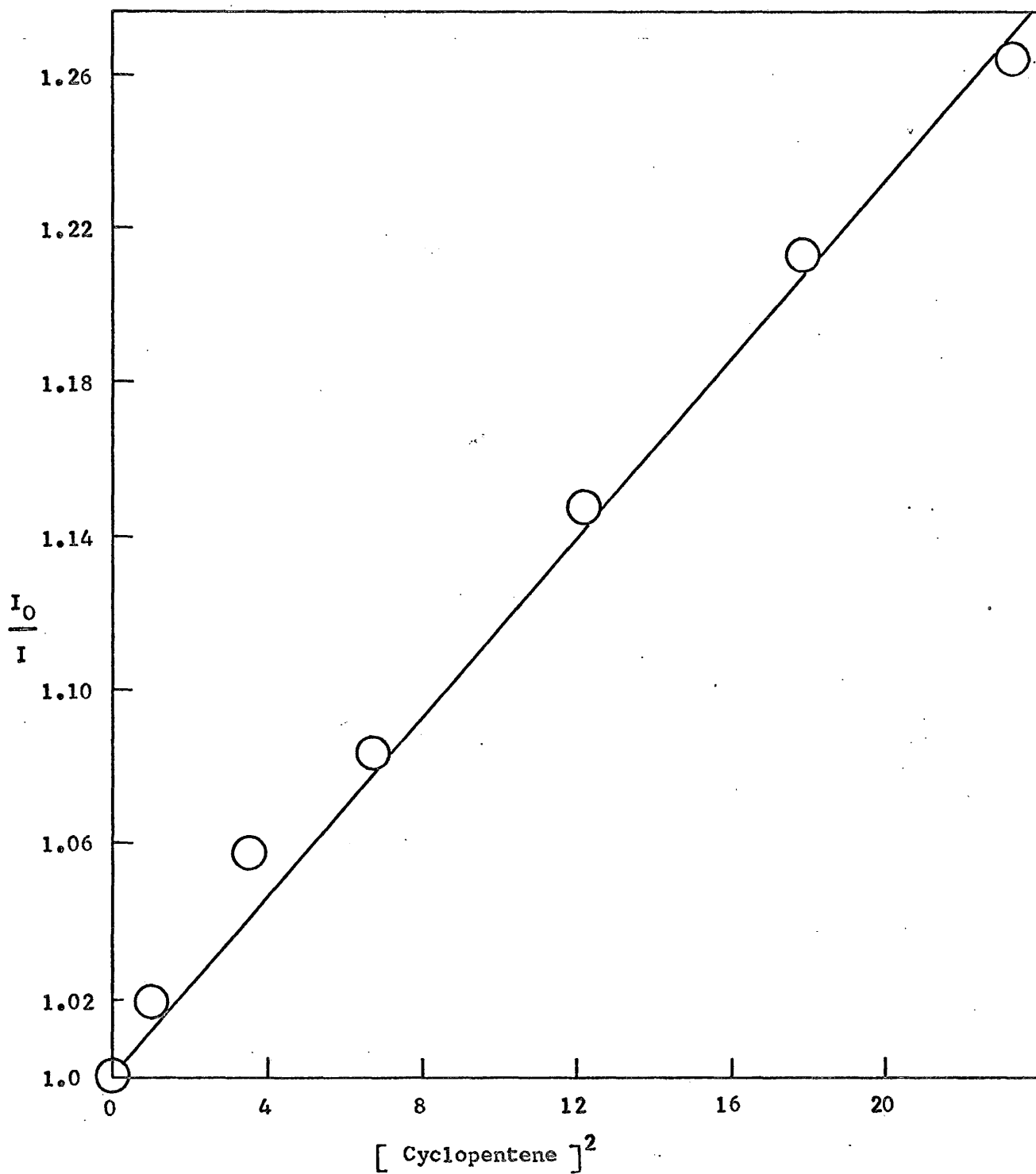


FIGURE 4 PLOT OF RELATIVE FLUORESCENCE INTENSITY OF 3-PHENYL-
2-CYCLOHEXENONE AGAINST THE SQUARE OF THE CYCLOPENTENE
CONCENTRATION (MOLES PER LITER)

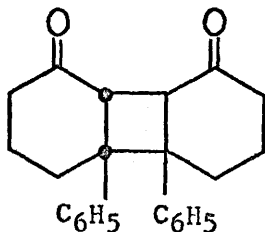
DISCUSSION

A. MECHANISTIC IMPLICATIONS OF THE STRUCTURE OF PHOTOADDUCTS

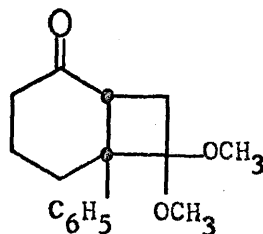
Photoadditions of 3-phenyl-2-cyclohexenone

The photoaddition products of 3-phenyl-2-cyclohexenone are shown in Diagrams 1, 2 and 3. All photoadducts are cyclobutane derivatives of the enone and have cis 4-6 ring fusion. In the photolysis with norbornene and also that with cyclopentene, a single adduct corresponded to 90% of the cross-addition products. The major product with norbornadiene is derived from endo addition (19, 45%) and the other isolated product from exo addition (17, 35%).

The head-to-head structure of the photodimer (3) and the single addition product reported⁶⁰ with 1,1-dimethoxyethylene (30) suggests the following mechanistic pathways. Addition may occur through an oriented π complex of the excited enone and ground state olefin⁷. The complex may subsequently undergo concerted addition to products or alternately collapse to a diradical intermediate which gives rise to products. Cycloaddition by way of the stable benzyl radical appears possible if the α -carbon of the enone is initially involved in bond formation.

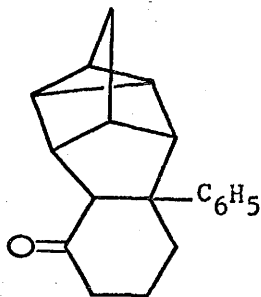
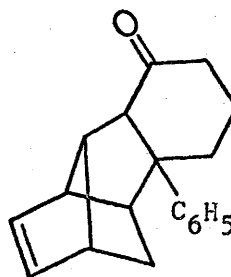


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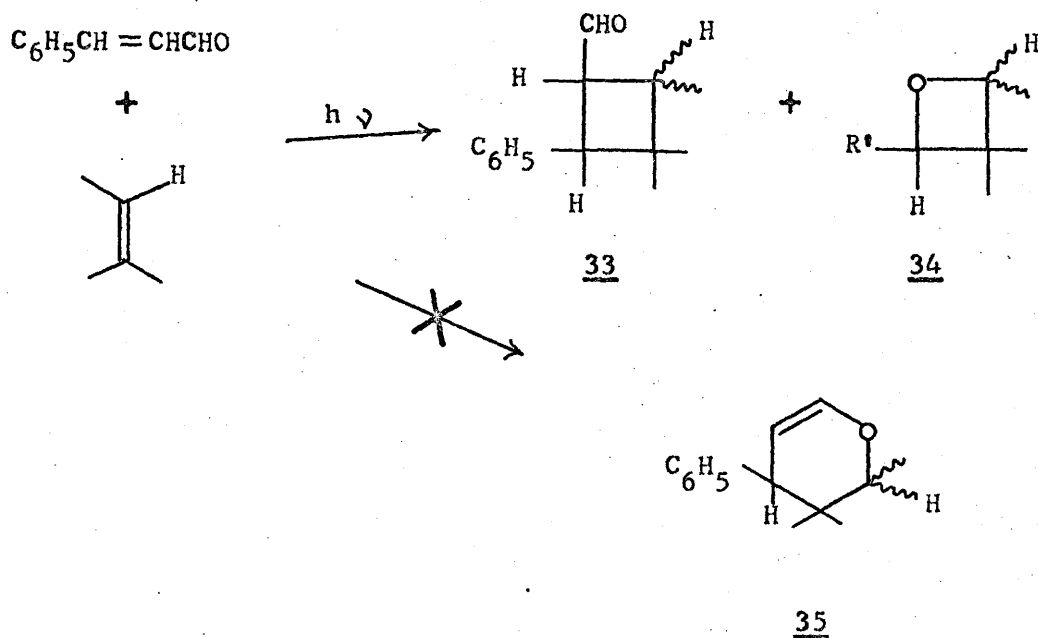


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The photoaddition with norbornadiene provides some information on this point. Products resulting from the rearrangement of an intermediate (probably biradical) species have been reported in the 2-cyclohexenone and norbornadiene photoaddition^{33,34}. Neither of the two major products in the photolysis of 3-phenyl-2-cyclohexenone and norbornadiene appear to be rearrangement products. Two such structures, 31 and 32, for which one can write a biradical mechanism, were considered in assigning the structure of the major adducts, but have been ruled out on the basis of the nmr spectra of isolated adducts (see Results).

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In the photoaddition of cinnamaldehyde and 2-methyl-2-butene, oxetane (34) and cyclobutane aldehyde (33) products were obtained⁶¹. Dihydropyrans (35) were not detected and Yang suggests that these results indicate free radical intermediates are unlikely in the formation of 34.



If the photoaddition of 3-phenyl-2-cyclohexenone is the allowed concerted cycloaddition⁶², then one must invoke the argument of an oriented π complex to account for the exclusive formation of products 3 and 30.

The exclusive formation of cis fused photoadducts may be attributed to a preference of the phenyl group to remain in the same plane as the enone system. It has also been suggested that a coplanar phenyl group would not be expected to exert a large blocking effect in the addition reaction⁶⁰.

There is no apparent solvent effect in the photoadditions of 3-phenyl-2-cyclohexenone. This is indicated in the results of this work where photolyses in tert-butyl alcohol, benzene or glacial acetic acid gave the same products. A single photodimer is obtained in ethanol, benzene or cyclohexane²¹. Other mixed photoadditions have been performed in ethyl ether⁶⁰.

Reactivity of 2-phenyl-2-cyclohexenone

The lack of reactivity of 2-phenyl-2-cyclohexenone with cyclopentene or norbornadiene is not readily apparent. A comparison of the effect of a 2-methyl-substituent on cyclohexenone photochemistry is available. In photoadditions to norbornadiene, Rasmussen has found that 2-cyclohexenone reacts about 6 times as efficiently as 2-methyl-2-cyclohexenone⁶³. Corey also observed the retardation in the rate of addition of 2-methyl-2-cyclohexenone⁷. If the phenyl group is not coplanar with the enone system, perhaps a significantly larger steric effect is operative.

The appropriate choice of olefin may facilitate photoaddition. Relative to cyclopentene, acrylonitrile reportedly adds 8 times faster to 3-methyl-2-cyclohexenone and 1,1-dimethoxyethylene is more reactive than cyclopentene by a factor of 18 in adding to 3-phenyl-2-cyclohexenone⁶⁰. It would therefore be of interest to examine the photolysis of 2-phenyl-2-cyclohexenone with acrylonitrile, which can act as an acceptor in an excited complex, and also with 1,1-dimethoxyethylene, a donor.

Origin of the 3-methyl-2-cyclohexenone and cyclopentene adducts

Three cyclobutane adducts were isolated from the photolysis of 3-methyl-2-cyclohexenone and cyclopentene as shown in Diagram 6. A trans fused adduct comprised a very significant percentage of the adducts. The trans fused isomer (29) could be isomerized to the minor photolytic cis isomer (28) showing that they differ only in configuration at the methine carbon adjacent to the carbonyl. Thus a comparison of the photoaddition to cyclopentene of 3-phenyl-2-cyclohexenone, giving only two cis fused adducts, and that of 3-methyl-2-cyclohexenone,

giving a trans fused adduct in 41%, shows remarkable differences.

The photolysis of 3-methyl-2-cyclohexenone and cyclopentene has now been reported by other workers⁶⁰. Their results differ in some respects from those reported in this study. Notably, the isomer which they have identified as having trans ring fusion, reportedly has infrared absorption at 5.89μ for the carbonyl. Equilibration of the pure trans isomer was not reported. In contrast, the infrared bands of products in this work correspond to those reported by Corey for fused cyclohexenones⁷, namely 5.82μ for the trans fused isomer (29) and 5.91μ for the cis isomers, 27 and 28.

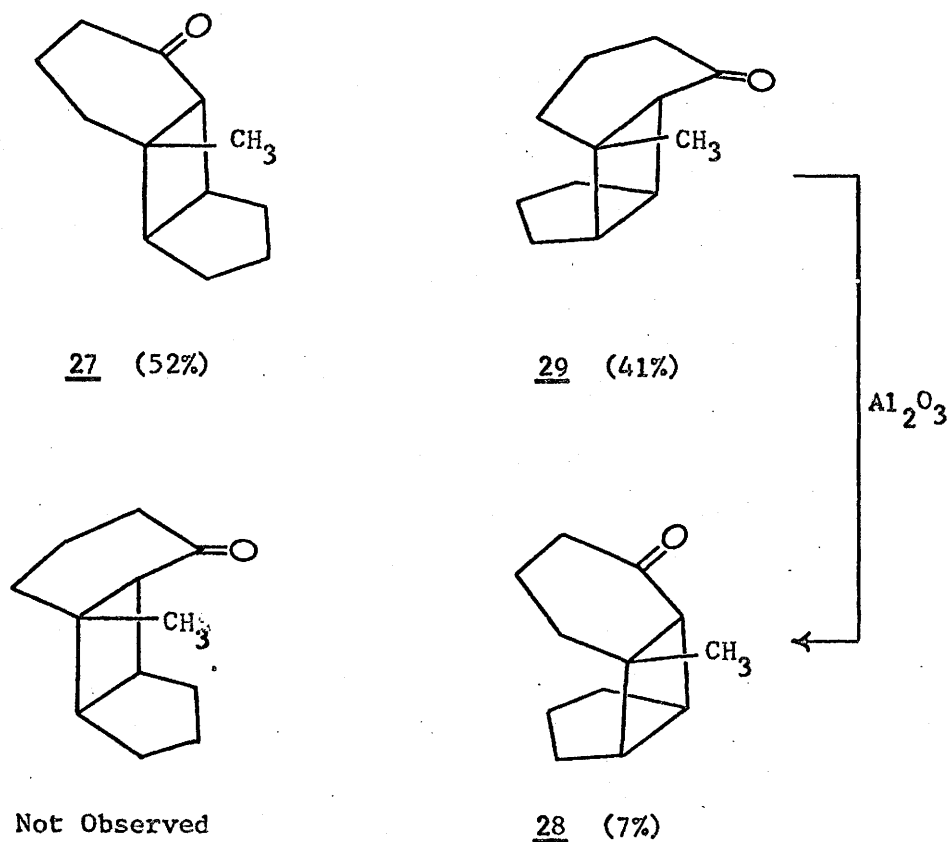


DIAGRAM 6 3-METHYL-2-CYCLOHEXENONE - CYCLOPENTENE ADDUCTS

The origin of trans fused cyclohexanone photoadducts has generated considerable interest. Corey has suggested that diradical intermediates are sufficiently energetic to produce the trans system⁷. Chapman has advanced the alternative explanation, which Corey also recognized, that two triplets may be involved in the formation of the cis and trans adducts. He reached this conclusion from the differential quenching of the cis and trans products observed in the addition of 1,1-dimethoxyethylene to isophorone and 4,4-dimethyl-2-cyclohexenone²⁷. The nature of the active triplets remained an open question.

Information concerning the equilibrium geometry of the lowest triplet excited states of acrolein, a model for α,β -unsaturated ketones, has been provided by Santry and Ohorodnyk⁶⁴. The equilibrium geometry of the $n-\pi^*$ triplet state of acrolein was found to be planar. Of great interest was the result indicating the energy minimum for the $\pi-\pi^*$ triplet occurs at approximately 72° twist about the $C\alpha-C\beta$ bond as shown in Figure 5. It is reasonable then to suggest that the origin of the trans fused adduct may be a twisted $\pi-\pi^*$ triplet excited state.

Another question is raised by the observation that the trans fused product (29), formed in the photolysis, isomerizes to the minor cis isomer (28), while the trans isomer which would equilibrate to the major cis isomer (27) was not formed in the photolysis. The formation of a single trans fused isomer which isomerizes to the minor photolytic cis adduct was also observed by Corey and Nozoe¹⁴ in the photoadducts of 3-methyl-2-cyclohexenone and 4,4-dimethylcyclopentene.

If one assumes that the α -carbon of the excited enone is

initially involved in bond formation, examination of 27 and 29 shows that the cyclohexenone and cyclopentene moieties have the anti orientation about this bond. Although this initial mode of bond formation may be common, the two differing products would result from subsequent cyclobutane ring closure. Unfortunately it is difficult to envisage experiments which may qualify these ideas.

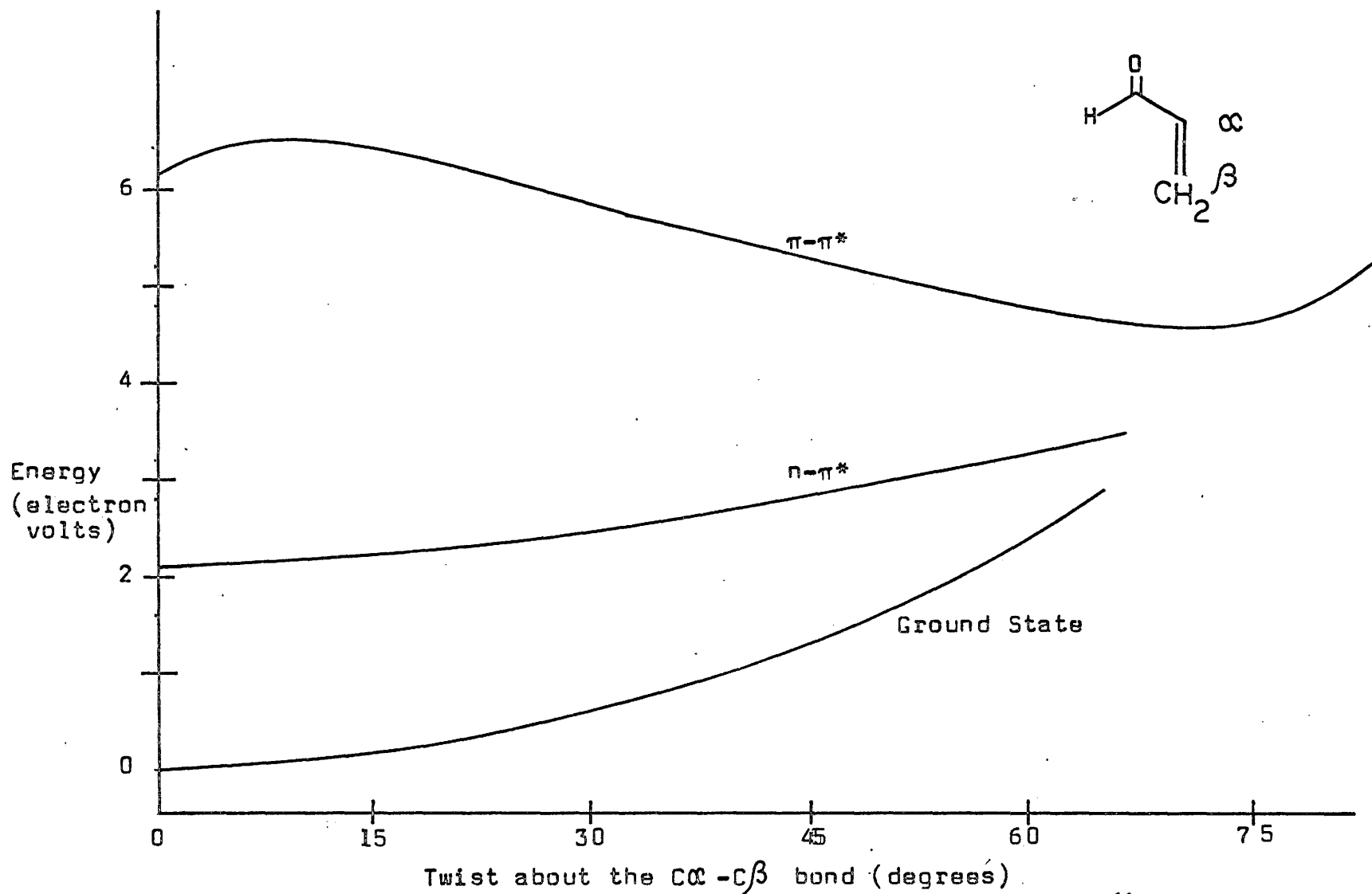


FIGURE 5 : CALCULATIONS BY SANTRY AND OHORODNYK⁶⁴
OF TRIPLET STATE GEOMETRIES

B. THE NATURE OF THE EXCITED STATES OF 3-PHENYL-2-CYCLOHEXENONE

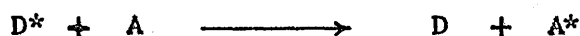
A very interesting description of the excited states of 3-phenyl-2-cyclohexenone can now be extracted from the study of the photoaddition reactions and emission spectra. This discussion will serve to interpret the experimental results, leading to an energy level diagram for the aromatic enone.

Phosphorescence emission from 3-phenyl-2-cyclohexenone provides an estimate of the lowest triplet energy level. The shortest wavelength emission maximum at $5310 \overset{\circ}{\text{A}}$ corresponds to a triplet energy of about 54 kcal/mole. The extended π system apparently lowers the triplet energy relative to that of 2-cyclohexenone. Although phosphorescence from 2-cyclohexenone is seemingly unobserved, the lowest triplet energy level has been estimated at 61 kcal/mole by non-spectroscopic methods^{7,20}. The cross conjugated π system of 2-phenyl-2-cyclohexenone does not appreciably alter the lowest triplet state as the observed emission maximum at $4720 \overset{\circ}{\text{A}}$ corresponds to a triplet energy level of about 60.6 kcal/mole.

The photoaddition of 3-phenyl-2-cyclohexenone with cyclopentene and that with norbornene could not be sensitized. Both Michler's ketone (E_T , 61 kcal/mole) and 1-naphthaldehyde (E_T , 56 kcal/mole) failed to sensitize the addition reaction, even though the triplet energy level of these donors is greater than the lowest triplet energy level of 3-phenyl-2-cyclohexenone. It has been shown when the triplet energy level of the donor is equal or greater than that of acceptor,

energy transfer can occur at a diffusion controlled rate^{65,66}. Thus the lack of reactivity in the presence of Michler's ketone and 1-naphth-aldehyde suggests the lower triplet of 3-phenyl-2-cyclohexenone is unreactive in cycloaddition.

The quenching of Michler's ketone phosphorescence by the enone demonstrated that triplet energy was in fact being transferred to 3-phenyl-2-cyclohexenone. If the quenching effect may be represented by the following equation:



where D represents Michler's ketone and A 3-phenyl-2-cyclohexenone, then the effect of added quencher is given by the usual Stern-Volmer expression.

$$I_0/I = 1 + Kq\tau [A]$$

I_0 and I are the phosphorescence emission intensity of Michler's ketone in the absence and presence of acceptor, Kq is the bimolecular quenching constant for deactivation of the donor by energy transfer, τ is the measured lifetime of the donor excited state ($\tau = 0.27$ seconds for Michler's ketone¹¹) and A is the concentration of acceptor (enone). From the slope of the plot in Figure 3 (13.9 litre/mole), the quenching constant (Kq) was calculated to be 52 litre/mole-sec. Ermolaev and Terenin¹³ report similar rate coefficients for the sensitization of naphthalene phosphorescence by benzophenone (160 sec^{-1}) and diphenylamine (0.54 sec^{-1}) at 78°K. Thus although Michler's ketone is shown to transfer triplet energy to 3-phenyl-2-cyclohexenone, this lowest triplet state (T_1) does not undergo cycloaddition.

Further attempts were made to quench the photoaddition reaction with triplet energy acceptors because cyclohexenones have been shown to react via triplet states^{20,27,34,67,68}. In experiments with naphthalene (E_T , 61 kcal/mole) or biacetyl (E_T , 55 kcal/mole) in solution no retardation in the rate of reaction was observed. Naphthalene is known to accept triplet energy^{13,67,68} so the results indicate that triplets of the enone higher in energy than naphthalene or biacetyl are not involved in the addition reactions studied.

After the completion of the work presented in this thesis, it was suggested by other workers that xanthone (E_T , 74 kcal/mole) is capable of sensitizing the photoaddition of 3-phenyl-2-cyclohexenone and cyclopentene⁶⁰. They found the extent of conversion of photoadducts after irradiation as compared to the conversion in the absence of sensitizer to be 0.38. Equimolar ratios of xanthone and 3-phenyl-2-cyclohexenone were irradiated, the light being filtered by pyrex. A comparison of the absorption spectra of 3-phenyl-2-cyclohexenone with that of xanthone and the transmittance of pyrex indicates about 35% of the light may be absorbed by 3-phenyl-2-cyclohexenone, thus accounting for the observed extent of reaction. A definitive experiment would be helpful using an increased molar concentration of xanthone relative to enone such that 3-phenyl-2-cyclohexenone could not absorb a significant fraction of the light. It seems unlikely that this is a triplet reaction for the reason that no quenching effect was observed with naphthalene.

In an irradiation where naphthalene absorbed a fraction of the incident light (see Table 3), the rate of reaction was increased. This effect was presumed not to be due to triplet energy transfer since

Michler's ketone, having the same triplet energy level as naphthalene, is shown to be ineffective in sensitizing the photoaddition. Naphthalene fluorescence has been quenched by cyclohexenones⁶⁹ which suggests singlet-singlet energy transfer from naphthalene to 3-phenyl-2-cyclohexenone may account for the increased rate. Naphthalene has a sufficiently high singlet energy level (91 kcal/mole)⁷⁰ to accomplish such energy transfer.

The absorption spectrum of 3-phenyl-2-cyclohexenone extends to about 3950 Å and the onset of fluorescence emission occurs in the same region giving an approximate lowest singlet energy level of 72 kcal/mole. This apparently is the first case of fluorescence being observed from a cyclohexenone, the lack of fluorescence from 2-cyclohexenone being attributed to rapid intersystem crossing from singlet to triplet states⁷. The effect of cyclopentene on the fluorescence intensity of 3-phenyl-2-cyclohexenone is indicated by the plot in Figure 4.

Direct energy transfer to cyclopentene from the enone would be a very unfavorable endothermic process because the lowest excited singlet of cyclopentene is certain to be significantly higher in energy than that of 3-phenyl-2-cyclohexenone. The quenching is most readily rationalized on the basis of an excited state complex³⁶ of excited 3-phenyl-2-cyclohexenone and cyclopentene, two molecules of the latter perhaps being involved. The magnitude of the observed quenching was small and therefore difficult to measure experimentally; further interpretation of this result is perhaps not warranted. Nevertheless, the sum of the evidence obtained points to a singlet state of 3-phenyl-2-cyclohexenone being active in photoaddition.

The presence of the norbornene dimers (13 and 14) in the photolysis of 3-phenyl-2-cyclohexenone and norbornene was a surprising result. Consequently a higher triplet (T_2) of 3-phenyl-2-cyclohexenone is proposed which must be of sufficient excitation energy for triplet energy transfer to norbornene. As already indicated, the dimerization of norbornene requires a sensitizer having a minimum triplet energy level very close to 72 kcal/mole^{38,41,42}. It appears that the lowest triplet of 3-phenyl-2-cyclohexenone (T_1 , 54 kcal/mole) should be unable to sensitize the dimerization of norbornene. Verification of the inability of the lowest triplet to sensitize the dimerization was obtained by selectively exciting T_1 of the enone with Michler's ketone. No norbornene dimers were obtained in this photolysis.

De Mayo has reported a higher triplet state (T_2) of cyclopentenone which is active in photoaddition. The lower triplet of cyclopentenone is apparently unreactive^{28,29}.

A low energy pathway of excitation involving twisting of the double bond (non-vertical excitation) is not available with a rigid molecule such as norbornene. Liu has studied the photosensitized rearrangement of the rigid molecules, benzonorbornene and norbornadiene^{30,32}. In his studies, triplet-triplet energy transfer from the second triplet states of anthracenes has been found.

The dimerization of norbornene in the presence of 3-phenyl-2-cyclohexenone was shown to give two dimers in the same ratio as those formed when using acetophenone (E_T , 74 kcal/mole) as sensitizer. The specific ratio of exo-trans-exo to exo-trans-endo dimers (about 10:90)

is apparently independent of the triplet sensitizer used (for example acetophenone, benzene, acetone, dicyclopropyl ketone and cyclopropyl phenyl ketone³⁸). This specific dimer ratio adds further evidence to the postulate that triplet-triplet energy transfer from excited 3-phenyl-2-cyclohexenone to norbornene occurs.

The detection of quadricyclene in the photolysis with norbornadiene may also be attributed to energy transfer from the higher triplet of the enone. Both benzophenone (E_T , 69 kcal/mole) and acetophenone (E_T , 74 kcal/mole) have been shown to efficiently sensitize the isomerization of norbornadiene to quadricyclene³⁶.

From these studies a rather descriptive picture of the excited states of 3-phenyl-2-cyclohexenone has been obtained. Calculations in this department have shown that the $\pi-\pi^*$ state is lower in energy than the $n-\pi^*$ state for a planar geometry of cinnamaldehyde⁷¹. If these energetics are applied to the cyclic enone, 3-phenyl-2-cyclohexenone, they suggest that T_1 (54 kcal/mole) is a $\pi-\pi^*$ triplet state and T_2 (about 72 kcal/mole) is a $n-\pi^*$ state. The $\pi-\pi^*$ state is also thought to be the lowest triplet for other ketones conjugated with aromatic systems. Recall that the lowest triplet states of 1-naphthaldehyde and 2-acetonaphthone, shown to be unreactive in photoreduction are thought to be $\pi-\pi^*$ states¹². Spectroscopic evidence also points to a $\pi-\pi^*$ lowest triplet state for 2-naphthaldehyde, 4-methoxy- and 4-hydroxy-acetophenone⁷².

TABLE 8 LOCATION OF THE LOWEST $n-\pi^*$ AND $\pi-\pi^*$ TRIPLET STATES⁷²

COMPOUND	OBSERVED GROUND STATE-TRIPLET STATE PHOSPHORESCENCE TRANSITIONS (ANGSTROMS)		BAND ^a
	$n-\pi^*$	$\pi-\pi^*$	
2-naphthaldehyde	3820	4780	4900
acetophenone	3780	-	3850
4-methoxyacetophenone	3650	3940	4050
4-hydroxyacetophenone	3610	3950	4000

a Position of the 0-0 band

It appears that 2-naphthaldehyde, 4-methoxy- and 4-hydroxy-acetophenone may have suitable energy states to sensitize the dimerization of norbornene from their T_2 excited states (see Table 8). This would be an interesting experiment particularly in the case of 2-naphthaldehyde where the observed triplet level splitting is comparable to that proposed for 3-phenyl-2-cyclohexenone.

In summary, two triplet excited states of 3-phenyl-2-cyclohexenone are apparent, the lower being assigned from the phosphorescence spectrum and the higher being active in sensitizing the dimerization of norbornene. From quenching and sensitization experiments, it appears that a triplet excited state is not involved in the photoaddition reaction. Fluorescence has been observed from 3-phenyl-2-cyclohexenone and a singlet excited state active in photoaddition accounts for the results of this study. Other ketones in which adduct formation results from an excited singlet are coumarin²⁶ and fluorenone⁷³. An energy state diagram for 3-phenyl-2-cyclohexenone is given in Diagram 7.

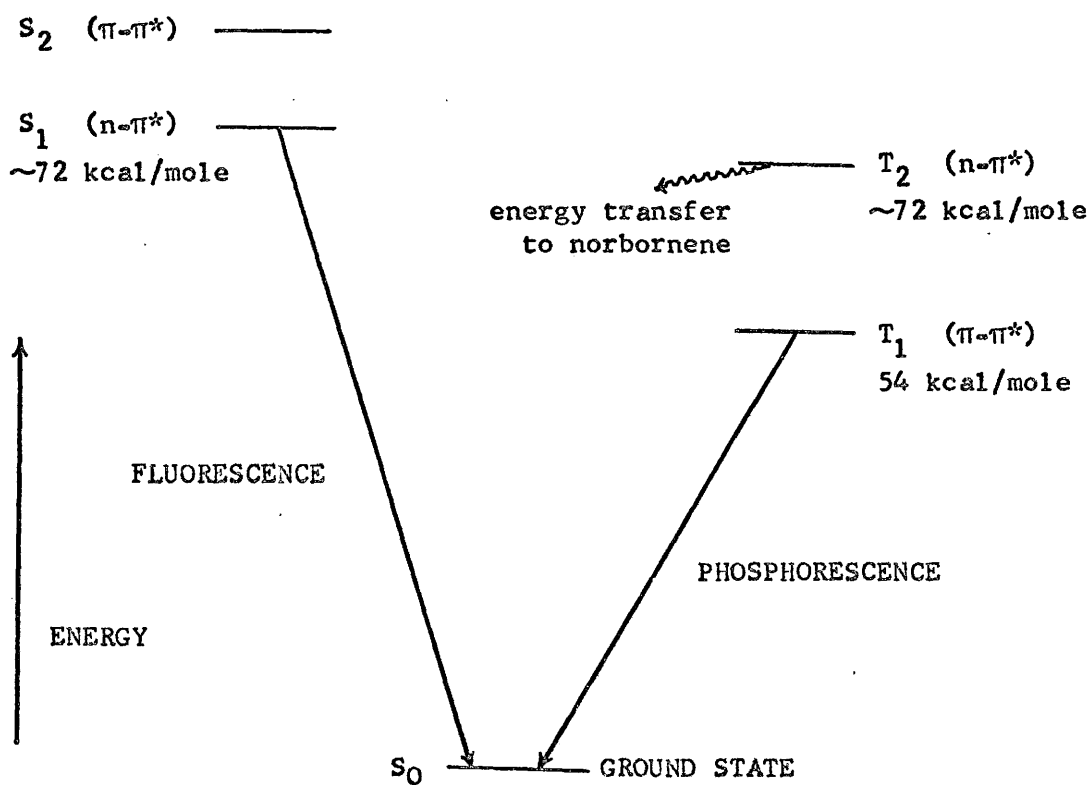


DIAGRAM 7

ENERGY LEVELS OF 3-PHENYL-2-CYCLOHEXENONE

EXPERIMENTAL

Materials

All solvents and reagents for photoaddition reactions were distilled prior to use.

Bicyclo [2.2.1] hepta-2,5-diene (Aldrich reagent) was distilled at atmospheric pressure, bp 89-90°C, and used immediately since it polymerizes on standing. Bicyclo [2.2.1] hept-2-ene (Aldrich reagent) had mp 45-47°C. Cyclopentene (Aldrich reagent) was distilled at atmospheric pressure, bp 44°C.

Tert-butyl alcohol was Baker Analyzed reagent, bp 82°C. Methanol was Mallinckrodt Analytical Reagent, bp 64.5-65°C. Benzene for column chromatography was Mallinckrodt Analytical Reagent.

Naphthalene, mp 80°C (Fischer purified), benzophenone, mp 47.5-48°C (Eastern Chemical Corp.), and Michler's ketone, mp 173.5-174°C (Matheson, Coleman and Bell) were recrystallized from ethanol.

Aldrich reagent 3-methyl-2-cyclohexenone had bp 58°C/10 mm. The method of Gannon and House⁷⁴ was used in preparing 3-ethoxy-2-cyclohexenone, bp 110-113°C/3 mm. From this 3-phenyl-2-cyclohexenone was prepared by the method of Woods and Tucker⁷⁵, Allen and Converse⁷⁶, and had mp 63.5-64°C (lit 64-65°C²¹). The ultraviolet spectrum of 3-phenyl-2-cyclohexenone has λ_{\max} (EtOH) 222 m μ ($\epsilon=14,200$) and 284 m μ ($\epsilon=17,200$)²¹.

Synthesis of 2-phenyl-2-cyclohexenone

A modification of the method of Warnhoff, Martin and Johnson⁷⁷ was used in the synthesis of 2-phenyl-2-cyclohexenone. To 15.50 g (0.089 mole) of 2-phenylcyclohexanone, mp 50-52°C (Aldrich), in dry carbon tetrachloride (100 ml), with one drop of concentrated HCl, was added during 90 min, sulfuryl chloride (12.03 g, 0.0891 mole) in dry CCl₄ (15 ml). The reaction was stirred for an additional 3 hours and maintained at 25°C throughout. After successive washings with 2×25 ml distilled water, 2×20 ml saturated NaHCO₃ solution and 25 ml saturated sodium chloride solution, the solution was dried over anhydrous magnesium sulphate. A clear pale yellow solution remained after solvent removal.

To this residue, N,N-dimethylformamide (25 ml) and lithium chloride (2.34 g) was added. After flushing with nitrogen, the reaction flask was heated to 100°C for 40 min with stirring. The mixture was then cooled, ether (100 ml) and 3% H₂SO₄ (100 ml) added, and stirred for 4 hours. The aqueous layer was separated and extracted with 2×50 ml portions of ether. The combined ether fractions were washed with 40 ml saturated NaCl solution, 40 ml saturated NaHCO₃ solution, and dried over anhydrous magnesium sulphate. The product solidified upon removal of the ether. Recrystallization from hexane gave 2-phenyl-2-cyclohexenone (6.78 g, 44% yield) as pale yellow needles, mp 91-94°C (lit 94-94.5°C⁵⁸).

Photolyses

All photolyses were run under nitrogen, Canadian Liquid Air certified grade, further purified by successive passage through vanadous sulphate solution⁷⁸, concentrated sulphuric acid and over potassium hydroxide pellets. The lamp was a Hanovia Type L 450W, 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 control instrument, having flame ionization detectors. The following columns were used with helium carrier gas at 30 ml/min:

Column A: 3'x1/8" 10% FFAP on 60-70 Chromosorb W

Column B: 10'x1/8" 12% FS1265 on 60-70 Chromosorb W

Column C: 10'x1/8" 10% Carbowax on 60-70 Chromosorb W

Preparative vpc was conducted on a Varian-Aerograph dual column instrument with thermal conductivity detectors. The following columns were used with a helium flow rate of 60-80 ml/min:

Column D: 10'x3/8" 20% FS1265 on 45-60 Chromosorb W

Column E: 5'x3/8" 20% FS1265 on 45-60 Chromosorb W

Column F: 4'x3/8" 20% FFAP on 45-60 Chromosorb W

Melting points were taken on a Reichert hot stage and are reported uncorrected.

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

Spectra

Nuclear Magnetic Resonance (nmr) spectra were run on a Varian A-60, T-60 or HA-100 instrument, in spectral grade CCl_4 , using tetramethylsilane as internal standard and chemical shifts are given in parts per million (ppm) downfield from this standard.

Infrared spectra were recorded with a Beckman IR 5 or a Perkin-Elmer Model 337 instrument, using CS_2 (Fischer spectroanalyzed) as solvent.

Ultraviolet spectra were recorded on a Cary 14 spectrophotometer using ethanol as solvent.

Mass spectra were obtained using an Hitachi Perkin-Elmer RMU 6A instrument.

Phosphorescence and fluorescence spectra were recorded from an Aminco-Bowman Spectrophotofluorometer.

Photoaddition of 3-phenyl-2-cyclohexenone and norbornadiene

Irradiation of 3-phenyl-2-cyclohexenone (2.279 g, 0.0132 mole) and norbornadiene (26.86 g, 0.292 mole) in tert-butyl alcohol (375 ml) and methanol (20 ml) for 10 hours resulted in reaction of 98% of 3-phenyl-2-cyclohexenone, as determined by vpc (Column A, 245°C). The vpc analysis showed that three major products were formed, with retention times: 6.5 min, 17; 9.0 min, 18; 11.5 min, 19. They were in the ratio; 34:20:46.

After solvent distillation, 1.848 g of the residue was chromatographed on a 4x83 cm column of silica gel, slurry packed in benzene, and 200 ml fractions were collected. The column was eluted by successively increasing the percentage of ethyl acetate in benzene: 3.6 litres of 1%,

3.0 litres of 1.5%, 1.8 litres of 2%, 1.0 litre of 6%, 0.6 litre of 10%, and 1.2 litres of 20%. Fractions were monitored by infrared and vpc. Fraction 22 contained mainly 19 (526 mg), fractions 27-42 contained mainly 17 (248 mg) and no fraction contained 18 as the major component. Recovery from the column was 1.655 g (90%).

Identification of 17,

cis-anti-exo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridec-4,5-en-9-one

This component was separated by vpc on column E (245°C), having a retention time of 21 min. Crystallization from ether - light petroleum, bp 30-60°C, gave mp 75-83°C. The infrared showed bands at 3.41 μ , 5.88 μ (cis fused 6-4 ring system⁷), 13.20 μ , and 14.24 μ (monosubstituted benzene⁴⁸). Also nmr resonance at 7.12 ppm (5H, aromatic protons), 5.92 ppm (2H, vinylic proton triplet) and 0.98 ppm (2H, endocyclic protons) indicated a cyclobutane adduct.

This product was formed in approximately 34% yield, as indicated by vpc and column chromatography.

Analysis Calculated for C₁₉H₂₀O : C, 86.30; H, 7.63.

Found : C, 86.36; H, 7.74.

Identification of 19,

cis-syn-endo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridec-4,5-en-9-one

Fraction 22 from chromatography was dissolved in ether - light petroleum, bp 30-60°C, from which crystalline 19 (180 mg) was obtained, mp 104.5-106.5°C. The infrared showed absorption at 3.41 μ , 5.85 μ (carbonyl), 13.31 μ and 14.15 μ (monosubstituted benzene⁴⁸). In the nmr spectrum, resonance at 6.87 ppm (5H, aromatic protons), 6.16 ppm (2H, vinylic protons) were observed and from decoupling experiments

(see Results) further proton assignment was made. The mass spectrum had a molecular ion, m/e 264 (73); base peak, m/e 143 (100); and intense peak, m/e 121 (53).

The infrared and nmr spectra of compound 19 were shown to be unchanged after attempted equilibration. A solution of the adduct (35.0 mg) in 20 ml ether, was stirred with basic alumina (2.0 g) for 8 hours. This indicated that 19 has a cis fused cyclohexenone ring.

This component was formed in approximately 45% yield.

Analysis Calculated for $C_{19}H_{20}O$: C, 86.30; H, 7.63.

Found : C, 86.40; H, 7.63.

Hydrogenation of the photolysis products

The photolysis mixture (880 mg) was dissolved in 95% ethanol (150 ml), to which 92 mg of 5% palladium on charcoal (Englehard Industries Inc.) was added, and agitated for 18.5 hours under a hydrogen atmosphere (55 psi). Complete reduction was indicated by the absence of vinyl proton resonance in the nmr. Analysis by vpc (column A 245°C) showed both retention times and proportion of 17, 18 and 19 remained unchanged after hydrogenation. Preparative vpc of the hydrogenated mixture on column E at 245°C gave isomers 20 and 21.

Identification of 20

This isomer is the product of reducing the norbornene double bond in compound 17, having the same retention time on vpc (6.5 min). The fraction of 22 min retention time from preparative vpc, gave 20, mp 72-79°C, having mp 86-88°C from ether - light petroleum, bp 30-60°C. Infrared absorption at 3.41 μ , 5.88 μ , 13.16 μ and 14.25 μ (monosubstituted benzene) were analogous to the precursor 17. The infrared and nmr

spectra were identical to that of the major product of the photoaddition of 3-phenyl-2-cyclohexenone and norbornene (see below). A mixed melting point with the major photoadduct, 85-88°C, further demonstrated that the reduced and photolytic compounds were in fact the same isomer.

Analysis Calculated for $C_{19}H_{22}O$: C, 85.65; H, 8.32.

Found : C, 85.45; H, 8.39.

Identification of 21

Reduction of the norbornene double bond in 19 gave isomer 21, both having the same retention time on vpc, 11.5 min. From a fraction collected at 30 min on preparative vpc or reduction of pure 19, was obtained 21, mp 86-89.5°C, crystallized from ether - light petroleum, bp 30-60°C. The nmr showed resonance at 6.97 ppm (5H, aromatic protons) and the absence of vinyl protons. Infrared bands were at 3.41 μ , 5.85 μ (carbonyl), 12.74 μ , 13.34 μ and 14.30 μ (phenyl group). The mass spectrum had a molecular ion, m/e 266 (100) and intense peak, m/e 141 (66).

Analysis Calculated for $C_{19}H_{22}O$: C, 85.65; H, 8.32.

Found : C, 85.50; H, 8.46.

Quadricyclene detection in 3-phenyl-2-cyclohexenone and norbornadiene photolysis

Pure samples of norbornadiene and quadricyclene had retention times of 6.0 min and 10.8 min on column C at 48°C (injector, 116°C; detector, 112°C). Analysis of the solution to be photolyzed showed no peak corresponding to quadricyclene. After a standard irradiation to 95% reaction of 3-phenyl-2-cyclohexenone, a peak at 10.8 min, the same retention time as quadricyclene, was detected in the photolysis solution.

Photolysis of 3-phenyl-2-cyclohexenone and norbornene

Irradiation (in a pyrex tube) of 3-phenyl-2-cyclohexenone (0.301g, 0.00175 mole) and norbornene (6.578 g, 0.070 mole) in tert-butyl alcohol (65 ml) and methanol (5 ml) for 2 hours resulted in 96% reaction of 3-phenyl-2-cyclohexenone, as determined by vpc analysis on column A (245°C). The vpc indicated three products, whose retention time and ratio were: 4.3 min, 1%; 5.0 min, 90% (20); and 7.5 min, 9% (24). After distillation of the solvent, chromatography of the photolysis mixture (580 mg) on a 3x27 cm column of silica gel slurry packed in benzene, yielded a mixture of two norbornene dimers in the first 2x100 ml fractions, eluting with benzene. Following two additional 100 ml fractions using benzene, the column was eluted with 400 ml ether giving quantitative recovery. Fractions were monitored for the dimers by vpc on Column C (185°C). From the fractions eluted with ether, the major adduct 20 crystallized.

Identification of 20

cis-anti-exo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridecan-9-one

This adduct was obtained by crystallization from the photolysis mixture. Recrystallization from ether - light petroleum gave colorless plates, mp 87-88.5°C. The infrared had absorption at 3.40 μ , 5.88 μ (cis fused cyclohexenone), 13.18 μ and 14.24 μ (monosubstituted benzene). The nmr showed a single proton resonance at 2.84 ppm (doublet) and complex aromatic resonance at 7.10 ppm (see Results). A molecular ion of m/e 266 (46), base peak m/e 173 (100), and strong peak m/e 144 (67), were exhibited in the mass spectrum.

This adduct was formed in 90% yield.

Analysis Calculated for $C_{19}H_{22}O$: C, 85.65; H, 8.32.

Found : C, 85.58; H, 8.39.

Identification of 24

cis-anti-endo-1-phenyltetracyclo [6.4.0.0^{2,7}.1^{3,6}] tridecan-9-one

From preparative vpc of the photolysis mixture on column E (245°C), compound 24 was obtained (retention time, 29 min). The infrared showed absorption at 3.41μ , 5.88μ (cis fused cyclohexenone)⁷, 13.29μ (d) and 14.25μ (monosubstituted benzene). Complex aromatic (5H) resonance at 7.17 ppm, single proton at 2.87 ppm and two proton peak at 1.00 ppm characterized the nmr spectrum.

Compound 24 was formed in 9% yield.

Analysis Calculated for $C_{19}H_{22}O$: C, 85.65; H, 8.32.

Found : C, 85.57; H, 8.40.

Isolation and Identification of the exo-trans-exo and endo-trans-exo norbornene dimers

From the first two fractions of chromatography, a mixture of the photodimers of norbornene (about 100 mg) was obtained. The retention time and ratio (column C, 185°C) of the exo-trans-exo and endo-trans-exo dimers were: 6.8 min, 10%; 8.5 min, 90%. Preparative vpc of the mixture on column F (180°C) gave pure endo-trans-exo dimer (retention time, 12 min). Its nmr and infrared spectra were identical to those published³⁸ and the mass spectrum had a molecular ion at m/e 188, and mp 35-36.5°C (lit 38-39°C³⁸).

Synthesis of the exo-trans-exo and endo-trans-exo dimers of norbornene³⁸

A pyrex tube containing norbornene (28.24 g, 0.30 mole) and acetophenone (3.617 g, 0.031 mole) in benzene (40 ml) was irradiated for 22 hours. Solvent and unreacted norbornene were removed by distillation

and the remaining mixture was chromatographed on a 3X28 cm column of silica gel slurry packed in benzene. The first 2X100 ml fractions, eluted with benzene, contained the dimers (5.661 g). Analysis of these fractions by vpc (column C, 185°C), indicated two peaks with retention time and ratio: 6.8 min, 10%; 8.5 min, 90%.

Separation of these was afforded on column D (167°C). The peak at 16 min was not readily obtained, but had mp 51-57°C (lit 63.5-64°C³⁸) corresponding to the minor exo-trans-exo dimer. The major fraction collected at 21 min had mp 37.5-38.5°C (lit 38-39°C³⁸) and nmr identical to that published for the endo-trans-exo norbornene dimer.

Photoaddition of 3-phenyl-2-cyclohexenone and cyclopentene

Irradiation of 3-phenyl-2-cyclohexenone (1.663 g, 0.0097 mole) and cyclopentene (11.06 g, 0.163 mole) in tert-butyl alcohol (375 ml) and methanol (20 ml) for 7 hours, resulted in reaction of 97% of 3-phenyl-2-cyclohexenone, determined by vpc analysis (column A, 245°C). The vpc analysis showed that two products were formed having retention times: 7.4 min (25) and 12.3 min (26), in the ratio 90:7 as measured from vpc peak areas. After removing the solvent by distillation, the residue (1.873 g) was chromatographed on a 3X28 cm column of silica gel slurry packed in benzene, collecting 200 ml fractions. Fractions 1 to 5 were eluted with benzene, 6-10 with 0.5% ethyl acetate - benzene, 11-20 with 1%, 21-25 with 2%, 26 and 27 with 4%, 28 with 8% and fractions 29-30 with 15% ethyl acetate - benzene. Fractions 14-16 contained the major photoadduct (25), 959 mg, and fractions 29-30 contained the photo-dimer of 3-phenyl-2-cyclohexenone. Recovery from the column was essentially quantitative.

Identification of 25

1 β ,2 α ,6 α ,7 β -1-phenyltricyclo [5.4.0.0^{2,6}] undecan-8-one

Fractions 14-16 were combined and by successive crystallization from pentane and aqueous ethanol were obtained colorless prisms, mp 59.5-61°C. The infrared absorption bands were at 3.41 μ , 5.91 μ (cis fused cyclohexenone⁷), 13.19 μ and 14.27 μ (monosubstituted benzene) and the nmr showed the aromatic proton's resonance as a broad multiplet centered at 7.15 ppm. The mass spectrum had a weak molecular ion, m/e 240; a base peak, m/e 173 (100); and additional strong peaks of m/e 144 (66), m/e 115 (23). This product was formed in 77% yield in the photolysis.

Attempted equilibration of 25 (20 mg) on basic alumina (2.8 g) in 15 ml ether with stirring for six hours, produced no change in the infrared and nmr spectra, thus confirming the cis 4-6 ring fusion assignment.

Analysis Calculated for C₁₇H₂₀O : C, 84.95; H, 8.39.

Found : C, 84.99; H, 8.30.

Identification of 26

1 β ,2 β ,6 β ,7 β -1-phenyltricyclo [5.4.0.0^{2,6}] undecan-8-one

Preparative vpc of the photolysis mixture separated the photo-adducts 25 and 26, having retention times of 14 and 19 min on column E (242°C). A 25 mg quantity of 26 collected from vpc, had infrared absorption bands at 3.41 μ , 5.85 μ (cis fused 4-6 rings⁷), 13.25 μ and 14.23 μ (monosubstituted benzene). The nmr showed the aromatic protons at 7.05 ppm. The mass spectrum had a molecular ion peak at m/e 240, a base peak at m/e 173 (100) and additional intense peaks at m/e 144 (55),

m/e 141 (49), and m/e 115 (33). This adduct was formed in 6% yield.

Isolation of the photodimer of 3-phenyl-2-cyclohexenone

Fractions 29 and 30 of the chromatography (223 mg, mp 188-197°C) were recrystallized from ether - light petroleum, bp 30-60°C, raising the melting point to 195-199°C (lit 204-205°C)²¹. The infrared and nmr spectra were identical to that of the head-to-head, cis-anti-cis dimer of 3-phenyl-2-cyclohexenone²¹. The mass spectrum had a weak molecular ion, m/e 344, base peak, m/e 172 (100) and additional intense peaks m/e 144 (94) and m/e 115 (30). Yield of the dimer based on its isolation by chromatography was 12%.

Photoaddition of 3-methyl-2-cyclohexenone and cyclopentene

Irradiation of 3-methyl-2-cyclohexenone (2.374 g, 0.0133mole) and cyclopentene (24.52 g, 0.360 mole) in tert-butyl alcohol (375 ml) and methanol (20 ml) for 5.5 hours resulted in reaction of about 99% of the enone. The solvent was distilled in vacuo at 30°C, into a receiver at -78°C. Infrared bands at 5.82 μ (trans 6-4 ring fusion⁷) and 5.91 μ (cis 6-4 ring fusion⁷) indicated a near equimolar ratio of cis and trans 6-4 fused rings. Analysis of the photolysis mixture by vpc on column B (194°C) showed three products of retention times: 8.3 min, 9.5 min, and 10.5 min, but distortion of the peaks was symptomatic of isomerization on the column.

The nmr of the photolysis mixture showed the disappearance of the methyl signal at 1.97 ppm, from 3-methyl-2-cyclohexenone, and the appearance of three methyl singlets. By measuring the area of the methyl peaks, product ratios were established and are given following the chemical shift: 0.95 ppm, 51.6% (27); 1.06 ppm, 41.3% (29);

1.31 ppm, 7.1% (28). The isomers were separated by preparative vpc on column D at 183°C.

Equilibration of the adducts of 3-methyl-2-cyclohexenone and cyclopentene

The photolysis mixture (1.80 g) was dissolved in 150 ml ether to which 35.0 g basic alumina were added, stirred for 9 hours, filtered and the ether evaporated. Infrared showed only one carbonyl band at 5.91 μ , while nmr showed two of the methyl peaks remained at 1.31 ppm (48.4%) and 0.95 ppm (51.6%), with the peak at 1.06 ppm absent. Analysis by vpc showed the component of 10.5 min retention time was gone, while peaks at 8.3 and 9.5 min were in the ratio of 48:52.

Identification of 27,

1 β ,2 α ,6 α ,7 β -1-methyltricyclo [5.4.0.0^{2,6}] undecan-8-one

This isomer was isolated by vpc on column D, having a retention time of 38 min, as a colorless liquid. Infrared absorption was at 3.41 μ and 5.91 μ (cis fused cyclohexenone). The nmr showed a methyl singlet at 0.95 ppm. The mass spectrum had a weak molecular ion m/e 178 and a base peak m/e 112. The yield was 51.6%.

Analysis Calculated for C₁₂H₁₈O : C, 80.84; H, 10.18.

Found : C, 80.84; H, 10.14.

Identification of 29,

1 β ,2 β ,6 β ,7 α -1-methyltricyclo [5.4.0.0^{2,6}] undecan-8-one

The peak of retention time 42 min was collected and showed infrared absorption at 3.41 μ and 5.82 μ (trans 4-6 ring fusion⁷). The nmr had a methyl singlet at 1.06 ppm. Product 29 was formed in 41.3% yield.

Analysis Calculated for C₁₂H₁₈O : C, 80.84; H, 10.18.

Found : C, 80.64; H, 10.11.

Equilibration of 29

The photoadduct 29 (30 mg) was dissolved in 30 ml ether, basic alumina (2.0 g) added, and stirred for 3.5 hours. After filtration and evaporating the ether, the infrared showed bands at 3.41μ and 5.91μ and the nmr had a methyl singlet at 1.30 ppm, characteristic of isomer 28 (see below). Analysis on column B (194°C) showed the disappearance of 29 (retention time, 10.5 min) and the appearance of a peak at 8.3 min corresponding to 28.

Identification of 28,

$1\beta, 2\beta, 6\beta, 7\beta$ -1-methyltricyclo [5.4.0.0^{2,6}] undecan-8-one

A fraction of retention time 33 min was collected from column D. Absorption at 3.41μ and 5.91μ (cis 4-6 ring fusion) and methyl proton resonance at 1.31 ppm were measured. The mass spectrum had a weak molecular ion m/e 178 and a base peak at m/e 112. Isomer 28 was formed in 7.1% yield.

Analysis Calculated for $C_{12}H_{18}O$: C, 80.84; H, 10.18.

Found : C, 80.97; H, 10.20.

Photolyses with 2-phenyl-2-cyclohexenone

Irradiation of 2-phenyl-2-cyclohexenone (1.779 g, 0.0103 mole) and cyclopentene (16.87 g, 0.248 mole) for 45 hours in tert-butyl alcohol (380 ml) and methanol (20 ml) gave less than 5% cross-addition products as indicated by vpc and recovery of starting enone. Similarly, irradiation of 2-phenyl-2-cyclohexenone (1.569 g, 0.0091 mole) and norbornadiene (24.15 g, 0.262 mole) for 46 hours gave no significant amount of addition products.

Investigation of naphthalene quenching the addition reactions
of 3-phenyl-2-cyclohexenone

A solution of 3-phenyl-2-cyclohexenone (0.6031 g, 0.025 M) and cyclopentene (4.769 g, 0.50 M) in tert-butyl alcohol (130 ml) and methanol (10 ml) was divided in two equal portions and placed in pyrex tubes. To one tube, naphthalene (0.4483 g, 0.050 M) was added. The solutions were degassed by repeating three cycles of successively freezing in liquid nitrogen, evacuating, admitting nitrogen and thawing. The tubes were irradiated simultaneously for 11 hours and analyzed by vpc on column A (218°C).

A similar experiment was conducted with biacetyl in the photolysis solution.

A solution of 3-phenyl-2-cyclohexenone (0.6011 g, 0.025 M) and norbornene (13.156 g, 1.00 M) in tert-butyl alcohol (130 ml) and methanol (10 ml) was equally divided in two pyrex tubes. Naphthalene (0.4482 g, 0.050 M) was added to one tube. The tubes were simultaneously irradiated for 2 hours with continuous nitrogen ebullition and analyzed by vpc on column A (220°C). The procedure was repeated using different concentrations (see Results).

Naphthalene sensitized photoaddition of 3-phenyl-2-cyclohexenone
and cyclopentene

Two pyrex tubes containing 3-phenyl-2-cyclohexenone (0.2875 g, 0.025 M) and cyclopentene (4.122 g, 0.50 M), were irradiated simultaneously. One tube contained naphthalene (0.9723 g, 0.126 M). The products were analyzed by vpc on column A at 222°C.

Sensitization experiments with Michler's ketone and 1-naphthaldehyde

Irradiation of 3-phenyl-2-cyclohexenone with cyclopentene and with norbornene respectively, was conducted using Michler's ketone and 1-naphthaldehyde as sensitizers. A standard photolysis without sensitizer present was irradiated at the same time for comparison. Analyses were by vpc on column A for the photoaddition products. In the case of norbornene as olefin, the reaction was analyzed for norbornene dimers also. Details are given in the Results section.

Phosphorescence Spectra

All phosphorescence spectra were measured in ethanol - ether (2:1) at 77°K. The solvents were redistilled 95% ethanol and ether (analytical reagent) distilled from sodium metal just prior to use. The data obtained from the following experiments is reported in the Results section.

The phosphorescence emission of 3-phenyl-2-cyclohexenone (excitation 350 m μ) and 2-phenyl-2-cyclohexenone were measured.

The quenching of Michler's ketone phosphorescence by 3-phenyl-2-cyclohexenone was measured at various concentrations of enone.

Fluorescence spectra

The fluorescence spectrum of 3-phenyl-2-cyclohexenone (excitation 395 m μ) was measured in ethanol at room temperature. The effect of cyclopentene on the fluorescence emission from 3-phenyl-2-cyclohexenone was also studied (see Results).

Quantum yield determination

The light source was a Philips SP500W high pressure mercury arc lamp, placed at the focal length (12 cm) of a quartz lens (11cm in diameter) giving directed irradiation. Filter solutions provided the appropriate emission band and were contained in a three cell unit. Each cell had a diameter of 11.7 cm, path length of 5 cm, and an internal cooling coil. Cell partitions and ends were gasketed quartz disks. The filter solutions used were : cell one (nearest lamp), 160 g of cobalt sulphate hepta-hydrate and 60 g of nickelous sulphate hexa-hydrate per litre of 3 N H_2SO_4 ⁶⁷; cell two, 1.6 g of stannous chloride dihydrate per litre of 15% hydrochloric acid; cell three, distilled water. This filter combination had a maximum transmission of 45% at 330 $\text{m}\mu$, and 0% at 299 and 375 $\text{m}\mu$. A small amount of light (0.5%) was transmitted at 430 $\text{m}\mu$.

It was found that the transmission properties of the cobalt - nickel mixture did not change significantly during irradiation. The stannous chloride solution was freshly prepared for each quantum yield determination.

For quantum yield determinations a cell with quartz windows, 11.7 cm in diameter by 5.0 cm path length contained the solution of enone and cyclopentene. Behind this, a duplicate cell contained 0.006 M potassium ferrioxalate and was used to measure the light output of the lamp. Each determination required three irradiations: the first with only the ferrioxalate actinometer present, the second with photolysis and actinometer solutions in place, and the third, as initially, with only the actinometer. The first and third irradiations, which differed

by less than 5%, were used to calculate the light output during the second irradiation and corrected for change in actinometer during that run. This calculation assumed the quantum efficiency of conversion of ferrioxalate to be 1.23 at $330 \text{ m}\mu^{79}$. Fresh actinometer solutions were used for each irradiation. All cells were cooled with tap water maintaining the temperature at $9 \pm 1^\circ\text{C}$.

Duplicate quantum yields were measured on the photolysis of 3-phenyl-2-cyclohexenone and cyclopentene. The photolysis of 3-phenyl-2-cyclohexenone (0.0107 M) and cyclopentene (0.48 M) in tert-butyl alcohol (525 ml) and methanol (50 ml) was performed with continuous argon (Canadian Liquid Air) ebullition. In a typical run, 3-phenyl-2-cyclohexenone was irradiated for 180 min during which the enone absorbed 2.30×10^{-2} Einsteins of light. Analysis by vpc (using benzophenone as an internal standard) showed the formation of 135.8 mg (5.66×10^{-4} mole) of adduct 25, thus giving the quantum yield of 0.025 for adduct formation.

The quantum yield was also measured using Michler's ketone as sensitizer (see Results).

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