3-PHENYLCYCLOHEX-2-ENONE PHOTOADDICTIONS
To GRANDMA and GRANDPA
MECHANISTIC STUDIES
ON THE PHOTOADDITION REACTIONS OF
3-PHENYLCYCLOHEX-2-ENONE WITH OLEFINS

By

BELAMPALLI R. RAMACHANDRAN, M. Sc.

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A detailed study of the photoaddition of 3-phenylcyclohex-2-enone and 2,3-dimethylbut-2-ene was undertaken in order to gain mechanistic information of the photochemistry of this enone. Photoadditions of this enone with cyclopentene, norbornene, and but-2-ene were also studied. Sensitization experiments showed that photoaddition with 2,3-dimethylbut-2-ene occurs when triplet sensitizers such as Michler's ketone or 2-acetonaphthone are used. The sensitized reactions are less efficient than the direct irradiation, except at infinite 2,3-dimethylbut-2-ene concentration, when the quantum yields for direct and sensitized processes are the same. This quantitative result may be explained by (a) inefficiency in the energy-transfer process
from the sensitizer to enone, or (b) two excited states of enone being involved in the direct and sensitized processes. There are evidences that the excited state involved in the direct irradiation could possibly be the second triplet of the enone. The presence of a higher enone triplet (T₂) was established by the observed dimerization of norbornene. Cis-trans isomerization of but-2-ene was observed during photoaddition, which could also be attributed to a higher triplet, or to a 1,4-diradical intermediate. Quenching studies provided an estimate of the lifetime of the reactive excited state in the direct irradiation. The energies of the electronic states of the enone were estimated from spectroscopic and chemical measurements. The formation of an enone-olefin 1,4-diradical has been proposed to explain the effect of olefin concentration on the photoaddition.
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INTRODUCTION
PART I : GENERAL

Chemical changes in compounds may be achieved by application of heat, treatment with chemicals such as acids, bases or other reagents, or by irradiation with light. It is the last process - the unique type of chemical reaction resulting from the 'bimolecular interaction' between a light quantum and a molecule, and the subsequent physical and chemical changes - that constitutes the realm of 'photochemistry'. Just as organic chemistry is broadly defined as the study of carbon compounds (organic compounds), organic photochemistry may be defined as the study of the effects of light on organic compounds. Although the importance of photochemical reactions for photosynthesis and related phenomena had long been recognized, it was not until the 1940s that organic photochemistry became a clearly defined area of research. Many examples of organic photochemical processes had appeared in the literature before that time, but the only systematic studies that had been undertaken dealt with gas phase reactions. However, due to the fact that many organic photochemical reactions yield complex mixtures, the task of resolving the products and studying their intricate structures became possible only with the advent of modern techniques and instrumental methods of separation and identification, such as vapor phase chromatography and nuclear magnetic resonance.
spectroscopy. Moreover, the progress in the field depended heavily on the weather, as the sun was the only source of radiation, before artificial sources of ultraviolet and visible light of suitable spectral characteristics became available. Since there are now a variety of light sources and analytical techniques available, the organic chemist is able to obtain a great deal of data, which he attempts to correlate into hypotheses that may be applied generally.

An organic molecule has different electronic states available to it. In the absence of light it occupies the lowest electronic state (the state of lowest energy). This 'ground state' molecule, when exposed to ultraviolet or visible light of suitable wavelength, is promoted to higher electronic states known as 'excited states', and it is the study of the physical and chemical properties of these excited states that defines the subject of photochemistry.

Many varieties of excited state reactions are now known, but only a discussion of the reactions of $\alpha\beta$-unsatu-

† Photochemical terminology used but not defined in this thesis may be found in reference 1.

‡ There have been examples in recent literature where an excited state is generated without irradiation. A discussion of this field, often known as 'photochemistry without light' is not appropriate to the subject of this thesis and will not be considered.
rated carbonyl compounds will be presented, since it is pertinent to this thesis. A brief summary of the basic theory used to describe the excited states will be given with reference to carbonyl compounds before delving into the subject proper.
PART II: EXCITED STATE THEORY

Three types of molecular orbitals are of importance in organic photochemistry – \( \sigma \) (sigma)-orbitals (formed by the overlap of two atomic \( s \)-orbitals or by the linear overlap of an \( s \)- and a \( p \)-orbital or of two \( p \)-orbitals), \( \pi \) (pi)-orbitals (formed by the parallel overlap of two atomic \( p \)-orbitals\(^\dagger\)), and \( n \)-orbitals (containing the lone pair of \( p \)-electrons localized on hetero atoms like nitrogen or oxygen).

When two atomic orbitals combine, two molecular orbitals, one of lower and one of higher energy, are formed – for instance, two \( s \)- or \( p \)-orbitals leading to two \( \sigma \)-orbitals, or two \( p \)-orbitals (parallel overlap as shown in the illustration) leading to two \( \pi \)-orbitals. Molecular orbitals

\[ \begin{align*}
\pi^\bullet & \text{(anti-bonding)} \\
\pi & \text{(bonding)}
\end{align*} \]

\(^\dagger\) Atomic \( d \)-orbitals can also form \( \pi \)-orbitals, but are rare in organic compounds, and hence will not be considered.
of lower energy are called 'bonding orbitals', and those of higher energy 'antibonding' (denoted by an asterisk), Electrons occupy the latter orbitals only in excited states. Each orbital can accommodate only two electrons having opposite spins\* (denoted by arrows). Thus the six electrons of the carbonyl group (four forming the double bond and the two non-bonding electrons on oxygen) occupy the lowest three orbitals in a ground state.

When the carbonyl group absorbs a quantum, excitation may occur in various ways. However, transitions such as a σ-electron being excited to π* or σ*-level (represented as σ-π* and σ-σ* respectively), or a π- or n-electron being promoted to a σ*-orbital (π-σ* and n-σ*) are not of great interest to organic photochemists since they are of very high energy and the electromagnetic radiation transmitted by the usual quartz can not provide sufficient energy. Moreover, even if the proper kind of radiation is employed these transitions would lead to dissociation of the molecules. The transitions that interest organic photochemists are promotion of an n- or a π-electron to the π*-orbitals, leading to n-π* or to π-π* states respectively.

* Electrons having similar spin can not occupy the same orbital, the rule being known as 'Pauli's Exclusion Principle'. 
It is convenient to represent these states schematically* as follows:

<table>
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<th>Excited state</th>
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<td><img src="image1.png" alt="Diagram" /></td>
<td><img src="image2.png" alt="Diagram" /></td>
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Here the two \( \sigma \)-electrons are represented by the line between the two atoms, \( \pi \)-electrons by the solid circles, and the \( n \)-electrons by Y's. The open circles represent the additional pair of non-bonding \( s \)-electrons on the oxygen; however, since they are of very low energy, do not participate in any photochemical process. These states can be illustrated in terms of their electronic configuration, as in figure 1.

Since both \( \pi-\pi^* \) and \( n-\pi^* \) states have two singly occu-

* Several authors\(^4\) have proposed various ways of representing the electronic states schematically; we choose that of Zimmerman\(^4b\) here.
pumped orbitals, these states can exist in two different multiplicities (electronic spin configurations) - singlets (when spins are opposed) and triplets (when spins are parallel). The ground state, having a closed shell electronic configuration (i.e. all spins are paired) exists as singlet. Since transitions between different multiplicities are forbidden, excitation of the ground state leads only to higher singlet states, which through internal conversion cascade down to
the lowest excited singlet state ($S_1$). Now, if the lifetime of $S_1$ state is sufficiently long, it can cross over to the triplet state that is lower in energy (intersystem crossing)\(^*\). It is known that for carbonyl compounds this process is very efficient, and thus often the photochemical processes undergone by this class of compounds occur through their triplet states\(^5\). There have been many cases in literature where the intermediacy of triplets has been established for $\alpha\beta$-unsaturated carbonyl compounds\(^6\) also.

It may be seen from the energy level diagram of the carbonyl group (figure 1) that the $n-\pi^*$ transition requires less energy than $\pi-\pi^*$ transition. The energy-wavelength relationship is given by

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

where $E$ is energy in kcal per mole, and $\lambda$ is wavelength in millimicrons ($m\mu = 10^{-7}$ cm). Thus for $\alpha\beta$-unsaturated ketones $\pi-\pi^*$ and $n-\pi^*$ transitions occur at 230 and 330 $m\mu$ respectively.

---

\(^*\) Owing to the exchange interactions that stabilize triplets, they are of lower energy than the singlets of the same configuration.
PART III : PHOTOCHEMISTRY OF αβ-UNSATURATED CARBONYL COMPOUNDS

Compounds containing the αβ-unsaturated carbonyl chromophore are known to undergo various kinds of reactions on irradiation, such as dimerization, cycloaddition to olefins, oxetane formation, rearrangement, reduction, and bond dissociation. The last three processes are not pertinent to this thesis, and hence deserve only a brief discussion.

Photocycloaddition of enones to double bonds to form cyclobutane derivatives is a process long known to chemists. The earliest work of this kind is perhaps of Silber\textsuperscript{7} and Stobbe\textsuperscript{8}, at the beginning of this century, dealing with the solid state photodimerization of cinnamic acid to form truxinic acid (1) and truxillic acid (2).

\[ \text{C}_{6}\text{H}_{5}\text{COOH} \rightarrow \text{C}_{6}\text{H}_{5}\text{COOH} \]

Ciamician and Silber\textsuperscript{9} observed the carvone-carvonecamphor (3 → 4) isomerization which was later verified by Buchi and Goldman\textsuperscript{10}. Benzalacetone (5) is known to give, in addition to \textit{cis}-isomer (6), a mixture of dimers 7 and 8, when irradiated in ether\textsuperscript{11,12}. 
Another early example of this process is the dimerization of 3-methylcyclohex-2-enone (9) to give 10 in alcoholic solutions in presence of sunlight\textsuperscript{13}.

Yates et al\textsuperscript{14} have studied the dimerization of 3-phenylcyclohex-2-enone (11) in detail, and have established the structure of the dimer to be of head-to-head \textit{cis-anti-cis} configuration (12).
Cyclohex-2-enone\textsuperscript{15} and cyclopent-2-enone\textsuperscript{16}, however, yield mixtures of dimers, all of which have \textit{cis-anti-cis} configuration.

1,4-quinones also are known to dimerize on irradiation\textsuperscript{17-19}; in some cases leading to intricate cage-structured compounds.
Mixed addition to olefins to form cyclobutane derivatives is also a general reaction of αβ-unsaturated carbonyl compounds. The earliest example of such a process, perhaps, is the addition of enolised acetylacetone (13) to olefins to yield 1,5-diketones²⁰.

Soon after, many reports on this process followed¹⁶ᵇ,²¹,²². Eaton¹⁶ᵇ published his work on cyclopent-2-enene - olefin photoaddition.
Corey\textsuperscript{21} reported the addition of cyclohex-2-enone to various olefins; he used the addition of isobutylene as the key-step in the synthesis of caryophyllene. Cantrell\textsuperscript{22} studied the addition of 3-substituted cyclohex-2-enones to olefins.

\begin{align*}
\text{Cyclohex-2-enone} + \text{Isobutylene} & \xrightarrow{\text{hv}} \text{Addition Product} \\
\text{Cyclohex-2-enone} + \text{Isobutylene} & \xrightarrow{\text{hv}} \text{Addition Product} \\
\text{Cyclohex-2-enone} + \text{Isobutylene} & \xrightarrow{\text{hv}} \text{Addition Product}
\end{align*}

Chapman\textsuperscript{23} investigated the addition reactions of 4,4-dimethylcyclohex-2-enone (14) and of isophorone (19).
Further examples of this process are given below:

\[
\text{19} \quad \text{hv} \quad \rightarrow \quad \text{trans-17} \quad \text{18}
\]

\[
\text{19} \quad \text{hv} \quad \rightarrow \quad \text{cis-20} \quad \text{trans-20}
\]

\[
\text{CH}_2\text{OH} \quad \text{hv} \quad \rightarrow \quad \text{(24)}
\]

\[
\text{(25)}
\]

\[
\text{(26)}
\]
Oxetane formation, known as Paterno-Buchi reaction, is general for ketones\textsuperscript{28}. However, conjugation of a double bond suppresses this reaction in favor of addition across the C=C bond. A few enones, nevertheless, do form oxetanes\textsuperscript{23}. (see reactions of 14, p.14,15). 1,4-quinones are also known to form oxetanes, in some cases, in addition to cyclobutane products\textsuperscript{29}.

Photorearrangement, the rearrangement of a molecule in its electronically excited state to form a new molecule, is also a process long known to chemists. The well-known $\alpha$-santonin rearrangement $(21 \rightarrow 22)$ had been observed as early
as 1830\superscript{30}, although the structures of the products were elucidated only recently\superscript{31}.

Not only the cyclohexadienones (23) but also many cyclohex-2-enones (24) are known to undergo photorearrangement.

A simple example is the rearrangement of 4,4-dimethylcyclohex-2-enone (14) to yield 25 and 26\superscript{32}.

A different kind of photorearrangement has been reported by Cargill and Sears\superscript{33}.
Cis-trans isomerization of the double bond has been observed for many acyclic enones (see the reaction of benzalacetone, 5,11,12 in p. 11), and cyclic enones with seven or more carbons in the ring34,35. Apparently this intramolecular process effectively competes with the intermolecular dimerization and mixed addition which are characteristic of enones.

Photoreduction has been observed for many ketones in which the carbonyl group is conjugated to one or more double bonds36, an example of which is the reduction of 29 in isopropanol37. Irradiation has to be performed in protic sol-
vents for this process to occur. Reduction of C=C bond has also been observed for some enones\textsuperscript{38,39}.

\begin{equation}
\begin{array}{c}
\text{hv} \quad \text{iso-PrOH} \\
\text{hv} \quad \text{sensitizer} \quad \text{iso-PrOH}
\end{array}
\end{equation}

Photodissociation is encountered for many enones\textsuperscript{40}, an example of which is the conversion of luminosantonin (30) into photosantoninic acid (31)\textsuperscript{41,42}.
PART IV: MECHANISTIC ASPECTS

The elucidation of the mechanism of photoannelation of enones poses two major questions. (i) What is the reactive excited state involved in this process? (ii) Which path-way does the reaction follow, once the excited state is formed? It will be attempted in this section, to discuss briefly answers to these questions with reference to several recent publications.

Multiplicity of the excited state

It is generally accepted, in many cases has been established, that the photochemical reactions of cyclic enones and substituted simple enones in solution, including rearrangements, photoreduction, and cycloaddition proceed via triplet states having energies in the 70 kcal/mole region. The species has a short lifetime (of the order of $10^{-8}$ sec). Relaxation by stretching and by rotation about the C$_2$-C$_3$ bond can deactivate these triplets. Unless the rotation is restricted, the photoaddition will not occur at all. Eaton has shown that more flexible systems such as cycloheptenone (27) and cyclooctenone (28) undergo cis-trans isomerization about the $\pi$-bond, and not cycloaddition with olefins.

Recently, considerable controversy has arisen concerning the nature of the enone excited state (states) that
is (are) responsible for the cycloaddition. De Mayo\textsuperscript{44} suggested that the addition reactions of cyclopent-2-ene and related enones with olefins involved a triplet of higher energy (T\textsubscript{2}) and not the lowest-lying triplet (T\textsubscript{1}). However, Wagner et al\textsuperscript{45} pointed out that there was an alternative explanation for these results\textsuperscript{44}. Chapman et al\textsuperscript{23a} postulated the intermediacy of two triplets in the addition reactions of 4,4-dimethylcyclohex-2-ene (14) and of isophorone (19) with olefins. Kearns et al\textsuperscript{46} observed emission from both T\textsubscript{1} and T\textsubscript{2} states in some steroidal systems containing cyclohex-2-ene chromophore.

**Reaction pathway**

It is generally accepted that a complex is formed between the triplet state and the olefin\textsuperscript{21}, which in turn is transformed into a substituted 1,4-diradical, the latter leading to the product by ring-closure. The formation and subsequent steps were suggested by Corey et al\textsuperscript{21} to rationalize the orientation of the adducts obtained from cyclohex-2-ene. More than one complex leading to different diradicals to form different products have been postulated in some cases\textsuperscript{47}.

It has been found, in the addition of cyclopentenone to cyclohexene and cyclopentene\textsuperscript{44} and in the dimerization of cyclohexenone and cyclopentenone\textsuperscript{45}, that only a part of the absorbed energy could be accounted for, even after allowing for all observable modes of energy dissipation extrapo-
related to infinite olefin concentration. The triplet product yield differed for various olefins at infinite olefin concentration, suggesting that there is an energy-wasting step that involves both the enone and the olefin. This was explained by postulating that the diradical goes to the product partly and collapses to ground state starting material partly. Thus the general mechanistic steps could be represented as in scheme 1.

\[
\begin{align*}
\text{Enone} & \\
\downarrow h_v & \\
\text{[Enone \text{ singlet}}} & \\
\downarrow \text{isc} & \\
\text{[Enone \text{ triplet}}} & \\
\downarrow \text{olefin} & \\
\text{[Enone-olefin \text{ exciplex}}} & \\
\downarrow & \\
\text{[Enone-olefin \text{ diradical}}} & \\
\text{Enone + olefin} \quad \text{Photoadduct} & \\
\end{align*}
\]

\text{SCHEME 1}

\textit{Mechanism of photoaddition of enones and olefins}
PART V: SIMPLE CYCLIC ENONES VERSUS 3-PHENYLCYCLOHEX-2-ENONE

At the time the work presented in this thesis was started, little was known on the mechanistic aspects of the photochemistry of enones that contain substituents which change the nature of the \( \pi \)-system. The introduction of an aromatic substituent should produce a significant change in the \( \pi \)-system. It is known that presence of a benzene ring in a conjugating position has enormous influence on photoreduction of ketones\(^48\). 3-phenylcyclohex-2-enone was, therefore, chosen as the model compound for our studies on the important cinnamate system.

Little was known about the multiplicity of the excited state involved in the photoaddition reactions of 3-phenylcyclohex-2-enone and similar compounds\(^*\), even though there

\[ \text{Arnold}^{49} \text{ had observed } 2+4 \text{ photoaddition between } 2\text{-acetonaphthone and methyl cinnamate. However, the process involves the } \pi-\pi^* \text{ triplet of acetonaphthone and the ground state of the ester.} \]

\[ \text{After the work presented in this thesis was completed} \]
was ample evidence that triplets are involved in the reactions of simple enones.

3-phenylcyclohex-2-enone differs from simple enones in the nature of products also. The formation of only cis-fused cyclobutane adducts has been observed for this enone\textsuperscript{14,22}; simple enones, on the other hand, form mixture of cis- and trans-fused cyclobutanes\textsuperscript{21-23}, and oxetanes in some cases\textsuperscript{23}. Simple enones are also known to form products arising from hydrogen transfer\textsuperscript{21,22,24,27}, while 3-phenylcyclohex-2-enone does not\textsuperscript{14,22}.

A detailed study of the photoaddition of 3-phenylcyclohex-2-enone with olefins was undertaken in order to

Chapman et al\textsuperscript{50} reported on the photoaddition of $\beta$-substituted styrenes (32 and 34) to olefins; the authors suggest that the excited singlet of styrene is involved in the addition.
find answers to these questions, and the results obtained and the information that could be derived are presented in the following sections of this thesis.
RESULTS
PART I: ISOLATION AND IDENTIFICATION OF PRODUCTS

3-phenylcyclohex-2-enone - 2,3-dimethylbut-2-ene addition

The irradiation of 3-phenylcyclohex-2-enone and tetramethylethylene in tert-butyl alcohol gave a single mixed addition product 36, and the known dimer 12 of the enone. The products are shown in scheme 2. The formation of the photodimer could be suppressed using high concentrations of tetramethylethylene. Thus, the yield of the dimer was about 50% when a ten-fold excess of the olefin was used, but was negligible when the olefin was in sixty-fold excess.

The photodimer 12, m.p. 200-201°C (lit14. 204-205°C) showed a weak molecular ion peak at m/e 344, and a base peak

* 2,3-dimethylbut-2-ene will be referred to as tetramethylethylene or TME henceforth in this thesis.
at m/e 172. It had infrared absorption at 5.86 μ, indicating the presence of a cis-fused cyclohexanone ring\textsuperscript{21}, and bands at 13.87 μ and 14.34 μ in accord with the monosubstituted benzene ring\textsuperscript{51}. The nuclear magnetic resonance spectrum was the same as that described by Yates et al\textsuperscript{14}. It had a singlet at 3.52 ppm (2H) for the cyclobutane protons, aromatic protons at 7.35 ppm (10H), and complex multiplets centering around 2.41 ppm (4H) and 1.7 ppm (8H). The dimer has been characterised to be 1β,2α-diphenyl-7α,8β-tricyclo[6.4.0.0\textsuperscript{2,7}]dodecane-6,9-dione\textsuperscript{*}. 

The mixed addition product 36, isolated by column chromatography and purified by distillation, was an oil (bath

* The stereochemistry at the cyclobutane rings in these adducts is specified as in steroid nomenclature\textsuperscript{52}. Substituents above the plane of the paper are denoted by β, and those below by α. The numerals before the Greek letters indicate the carbons to which the groups are attached. Thus 1β,2α,7α,8β means that the phenyl group and the hydrogen attached to carbons 1 and 8 respectively are above, and those at carbons 2 and 7 are below the plane of the cyclobutane (plane of the paper)
temp. 170-180°C at 0.3 mm/Hg) which solidified to a waxy solid (m.p. 57-60°C after sublimation). The mass spectrum showed the molecular ion peak at m/e 256, and a base peak at m/e 172. The material had infrared absorption at 5.91 μ for the cis-fused cyclohexanone ring, and at 13.4 μ and 14.22 μ for the monosubstituted phenyl group. The nuclear magnetic resonance spectrum (figure 2) showed a broad multiplet in the region 6.8-7.4 ppm (5H) for the aromatic protons, a sharp singlet at 3.07 ppm (1H) for the methyne proton, complex multiplets around 1.3-2.7 ppm (6H) for the methylene protons, and sharp singlets at 1.22, 1.04 and 0.63 ppm (6H, 3H and 3H) for the methyl groups. The adduct was unchanged on treatment with basic alumina, showing the presence of cis-ring fusion, which was also supported by the carbonyl absorption in the infrared. Based on these evidences the adduct 36 was assigned the structure 1β-phenyl-7,7,8,8-tetramethyl-6β-bicyclo[4.2.0]octa-5-one.

3-phenylcyclohex-2-enone - cyclopentene addition

As noted in the introduction, the photoaddition of 3-phenylcyclohex-2-enone and cyclopentene has been investigated by Cantrell et al 22, and by Bowman and McCullough 47. However, the stereochemistry of the adducts 37 and 38 had not been established with certainty. Synthesis of a suitable derivative of the adduct was to be undertaken.

Irradiation of the enone and cyclopentene in tert-
FIGURE 2: 60 MHz NMR SPECTRUM OF 36
butyl alcohol gave two mixed addition products 37 and 38 in the ratio 90:7 (77% and 6%), and the dimer 12 (12%) as shown in scheme 3. The mixed addition products are 1β-phenyl-2α,6α,7β-tricyclo[5.4.0.0^{2,6}]undecan-8-one, 37, and 1β-phenyl-2β,6β,7β-tricyclo[5.4.0.0^{2,6}]undecan-8-one, 38.

![Scheme 3](image)

**SCHEME 3**

**PHOTOADDITION OF 3-PHENYLCYCLOHEX-2-ENONE AND CYCLOPENTENE**

Treatment of the major adduct 37 with thiosemicarbazide hydrochloride in ethanol-water solution, gave a crystalline derivative 39 (m.p. 165-169°C). Determination of the unit cell dimensions by X-ray diffraction measurements suggested that the molecule has cis-anti-cis stereochemistry about the cyclobutane ring. Thus the minor adduct 38, which is also believed to be cis-fused (from its carbonyl absorp-
tion at 5.91 μ and by its stability towards basic alumina) was assigned the cis-syn-cis configuration.

Norbornene dimerization in 3-phenylcyclohex-2-enone - norbornene photoaddition

The photoaddition of 3-phenylcyclohex-2-enone and norbornene has been studied by McCullough and Snyder. It gave two major cycloadducts 40 and 41, which were assigned as cis-anti-exo 1-phenyltetracyclo[6.4.0.0^2.7.13.6]tridecan-9-one (40) and cis-anti-endo 1-phenyltetracyclo[6.4.0.0^2.7.13.6]tridecan-9-one (41), and the two norbornene dimers 42 and 43. The products are shown in scheme 4. However, we were mainly interested in the norbornene dimerization. The norbornene dimers were separated from the cycloadducts by column chromatography on silica gel. The major dimer 42 obtained by preparative vapor phase chromatography was a waxy solid, m.p. 36-38°C. Its mass spectrum showed the molecular ion peak at m/e 188. The nuclear magnetic resonance spectrum was identical to that described for the exo-trans-endo dimer. An authentic sample of the dimer was prepared by the irradiation of norbornene using acetone as the sensitizer. Vapor
phase chromatographic analysis showed identical retention times for the synthetic sample and for the dimers formed in the 3-phenylcyclohex-2-ene-norbornene photolysis. This reaction will be referred to again later in this section.

\[ \text{Scheme 4} \]

PHOTOADDITION OF 3-PHENYLCYCLOHEX-2-ENE-NORBORNENE
Cis-trans isomerization of but-2-enes in 3-phenylcyclohex-2-enone - but-2-ene photolysis

Cis-trans isomerization of cis-but-2-ene was observed when a solution of cis-but-2-ene and 3-phenylcyclohex-2-enone in methanol was irradiated at -12°C. Since we were mainly interested in the isomerization, the photoadducts were not isolated. Vapor phase chromatographic analysis showed the presence of about 9% trans-but-2-ene at about 2% conversion of the enone.
PART II: MECHANISTIC ASPECTS

In order to elucidate the mechanism of photoaddition of 3-phenylcyclohex-2-enone to olefins, and to identify the nature of the excited state (states) involved, a quantitative study was undertaken for the enone - tetramethylethylene system. Tetramethylethylene was chosen because its low volatility permitted work at room temperature, and since it gives rise to a single photoadduct with the enone. Cyclopentene, norbornene and butenes were used in a few cases. The quantum yields of addition, the effect of olefin concentration on the quantum yield, and the effect of various energy donors and acceptors, and the photoluminescence of the enone were studied. The results are described in the following pages of this section.
**Investigation of triplet sensitization**

The photoaddition of 3-phenylcyclohex-2-enone to cyclopentene and to tetramethylethylene was found to be sensitized by triplet energy donors such as 4,4’-bis(dimethylamino)benzophenone (Michler's ketone) and by 2-acetophenone. In all sensitized runs the concentrations were so chosen that all the light was absorbed by the sensitizers. Lamps radiating the 350 mμ region of mercury arc spectrum were used for irradiation. The photolyses were conducted in tert-butyl alcohol medium. A standard photolysis solution without the sensitizers was irradiated simultaneously for comparison. The extent of the reaction in each case is given in table 1.

The enone-tetramethylethylene adduct in these sensitizations was isolated by chromatography, and the nuclear magnetic resonance, infrared and mass spectra were compared with those of the adduct 36 formed in the unsensitized photolysis. The spectra and the retention times in the vapor phase chromatographic analysis were identical, establishing that the same adduct was formed in the unsensitized and sensitized processes.
### TABLE 1a

**TRIPLET SENSITIZATION OF ENONE-TETRAMETHYLETHYLENE ADDITION**

<table>
<thead>
<tr>
<th>Enone (M)</th>
<th>TME</th>
<th>2-acetox</th>
<th>Michler's naphtone</th>
<th>Michler's ketone</th>
<th>Time of irradtn. (hrs)</th>
<th>Extent of reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>0.33</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>76</td>
</tr>
<tr>
<td>0.005</td>
<td>0.33</td>
<td>-</td>
<td>0.0025</td>
<td></td>
<td>1</td>
<td>22</td>
</tr>
<tr>
<td>0.005</td>
<td>0.33</td>
<td>0.05</td>
<td>-</td>
<td></td>
<td>1</td>
<td>20</td>
</tr>
</tbody>
</table>

### TABLE 1b

**TRIPLET SENSITIZATION OF ENONE-CYCLOPENTENE ADDITION**

<table>
<thead>
<tr>
<th>Enone (M)</th>
<th>Cyclo</th>
<th>Michler's pentene</th>
<th>Michler's ketone</th>
<th>Time of irradtn. (hrs)</th>
<th>Extent of reaction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>3</td>
<td>95</td>
</tr>
<tr>
<td>0.015</td>
<td>0.5</td>
<td>0.005</td>
<td></td>
<td>3</td>
<td>20</td>
</tr>
</tbody>
</table>
Quantum yields

The details of measurement of quantum yields are discussed in the Experimental section. The quantum yields of the unsensitized photoaddition of the enone to tetramethylethylene and to cyclopentene were measured and the results are given in tables 2a and 2b. Quantum yields of enone-tetramethylethylene addition sensitized by various triplet energy donors were also measured, which are given in table 3a. The quantum yield of enone-cyclopentene photoaddition sensitized by biacetyl (butane-2,3-dione) is given in table 3b.

+ The efficiency of a photochemical process is generally expressed in terms of its quantum yield (\( \phi \)). It is defined as

\[
\phi = \frac{\text{Number of molecules undergoing the process}}{\text{Number of quanta absorbed}} = \frac{\text{Number of moles undergoing the process}}{\text{Number of einsteins absorbed}}
\]

\[(1 \text{ einstein} = 6.23 \times 10^{23} \text{ quanta})\]
TABLE 2a

QUANTUM YIELD OF PHOTOADDITION OF
3-PHENYL-CYCLOHEX-2-ENONE AND TETRAMETHYLETHYLENE

<table>
<thead>
<tr>
<th>Light absorbed by enone (m.einsteins)</th>
<th>Amount of adduct (mgs)</th>
<th>Quantum yield (m.moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.91</td>
<td>78.9</td>
<td>0.3084</td>
</tr>
<tr>
<td>14.96</td>
<td>83.3</td>
<td>0.3254</td>
</tr>
<tr>
<td>15.38</td>
<td>89.9</td>
<td>0.3515</td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M
Concentration of TME: 0.33 M
Solvent: tert-butyl alcohol
Temperature: 23±0.5°C

The estimated error in these determinations is 5%.
TABLE 2b

QUANTUM YIELD OF PHOTOADDICTION OF
3-PHENYLCYCLOHEX-2-ENONE AND CYCLOPENTENE

<table>
<thead>
<tr>
<th>Light absorbed by enone (m.einsteins)</th>
<th>Amount of adduct (37) (mgs)</th>
<th>Quantum yield (m.moles)</th>
<th>Quantum yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.5</td>
<td>102</td>
<td>0.425</td>
<td>0.027a</td>
</tr>
<tr>
<td>36.6</td>
<td>224</td>
<td>0.932</td>
<td>0.02554</td>
</tr>
</tbody>
</table>

a. Concentration of enone: 0.00585 M
Concentration of CPT: 0.835 M
Solvent: methanol
Temperature: 10±0.5°C

The estimated error in these determinations is 5%. 
# TABLE 3a

Quantum Yields of Sensitized Photoaddition of 3-Phenylcyclohex-2-enone and Tetramethylethylene

<table>
<thead>
<tr>
<th>Sensitizer</th>
<th>Conc. of Sensitizer</th>
<th>Light</th>
<th>Amount of 36</th>
<th>Q.Y.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>m.einstein</td>
<td>mgs</td>
<td>m.moles</td>
</tr>
<tr>
<td>MK</td>
<td>0.0024</td>
<td>30.56</td>
<td>49.0</td>
<td>0.193</td>
</tr>
<tr>
<td>&quot;</td>
<td>&quot;</td>
<td>30.40</td>
<td>46.4</td>
<td>0.181</td>
</tr>
<tr>
<td>AN</td>
<td>0.05</td>
<td>26.84</td>
<td>39.9</td>
<td>0.156</td>
</tr>
<tr>
<td>BA&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.10</td>
<td>66.00</td>
<td>traces</td>
<td></td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M  
Concentration of TME: 0.33 M  
Solvent: tert-butyl alcohol  
Temperature: 23±0.5°C  
MK = Michler's ketone; AN = 2-acetonaphthone;  
BA = biacetyl.

Filter solutions and concentrations were so chosen that more than 97% of light was absorbed by the sensitizer.  
a. Two additional products (probably BA-TME adducts) were formed in this irradiation.

The estimated error in these determinations is 5%.
TABLE 3b

QUANTUM YIELD OF BIACETYL SENSITIZED PHOTOADDICTION
OF 3-PHENYLCYCLOHEX-2-ENONE AND CYCLOPENTENE

Biacetyl concn. 0.174 M  Light absorbed: 56.64 m.eins.

Enone concn. 0.00575 M  Amount of 37: 196 mg; 0.82 mmoles

Cyclopentene concn. 0.835 M

Solvent  methanol  Quantum yield: 0.142

Biacetyl absorbed more than 99% of the incident light in
this irradiation.

Effect of tetramethylethylene concentration on the quantum
yield of photoaddition

The relative quantum yields of photoaddition of
3-phenylcyclohex-2-enone and tetramethylethylene for various
concentrations of the olefin were determined, the details
of which are described in the Experimental section. The
absolute quantum yields were then calculated, based on the
value 0.022 for 0.33M tetramethylethylene (see table 2a).
The results are given in table 4. A plot of reciprocal
quantum yield versus the reciprocal tetramethylethylene con-
centration gave a straight line (figure 3).

The quantum yields of photoaddition sensitized by
Michler's ketone for various concentrations of tetramethyl-
ethylene are given in table 5. The concentration plot was
linear, and is given in figure 4.
### TABLE 4

EFFECT OF TETRAMETHYLETHYLENE CONCENTRATION ON THE QUANTUM YIELD OF PHOTOADDITION

<table>
<thead>
<tr>
<th>[TME] M</th>
<th>[TME]$^{-1}$ M$^{-1}$</th>
<th>Amount of 36 mgs</th>
<th>Relative Q.Y$^a$</th>
<th>Absolute Q.Y x 10$^3$</th>
<th>[Q.Y]$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>20</td>
<td>6.60</td>
<td>0.244</td>
<td>5.42</td>
<td>184.50</td>
</tr>
<tr>
<td>0.10</td>
<td>10</td>
<td>11.61</td>
<td>0.430</td>
<td>9.55</td>
<td>104.70</td>
</tr>
<tr>
<td>0.20</td>
<td>5</td>
<td>18.41</td>
<td>0.672</td>
<td>14.92</td>
<td>67.00</td>
</tr>
<tr>
<td>0.33</td>
<td>3</td>
<td>26.95</td>
<td>1.000</td>
<td>22.20</td>
<td>45.05</td>
</tr>
<tr>
<td>0.33</td>
<td>3</td>
<td>16.24</td>
<td>1.000</td>
<td>22.20</td>
<td>45.05</td>
</tr>
<tr>
<td>0.50</td>
<td>2</td>
<td>19.84</td>
<td>1.220</td>
<td>27.08</td>
<td>36.55</td>
</tr>
<tr>
<td>1.00</td>
<td>1</td>
<td>27.33</td>
<td>1.682</td>
<td>37.34</td>
<td>26.78</td>
</tr>
<tr>
<td>2.00</td>
<td>0.5</td>
<td>27.33</td>
<td>1.685</td>
<td>37.41</td>
<td>26.74</td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M

Solvent: tert-butyl alcohol

The estimated error in these determinations is 5%.

a. The relative quantum yields are given with respect to that for 0.33 M tetramethylethylene.
Slope: $8.37 \pm 0.12$

Intercept: $20.75 \pm 0.76$

**Figure 3**: EFFECT OF TME CONCENTRATION ON THE QUANTUM YIELD OF PHOTOADDITION
TABLE 5

EFFECT OF TETRAMETHYLETHYLENE CONCENTRATION ON THE QUANTUM YIELD OF SENSITIZED PHOTOADDITION

<table>
<thead>
<tr>
<th>[TME]</th>
<th>[TME]$^{-1}$</th>
<th>Amount of 36 mgs</th>
<th>Relative ( Q.Y^a )</th>
<th>Absolute ( Q.Y^b )</th>
<th>[Q.Y]$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M$^{-1}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.15</td>
<td>6.67</td>
<td>5.41</td>
<td>0.502</td>
<td>3.01</td>
<td>332.2</td>
</tr>
<tr>
<td>0.20</td>
<td>5.00</td>
<td>7.28</td>
<td>0.675</td>
<td>4.05</td>
<td>246.9</td>
</tr>
<tr>
<td>0.25</td>
<td>4.00</td>
<td>8.87</td>
<td>0.823</td>
<td>4.94</td>
<td>202.4</td>
</tr>
<tr>
<td>0.33</td>
<td>3.00</td>
<td>10.78</td>
<td>1.000</td>
<td>6.00</td>
<td>166.7</td>
</tr>
<tr>
<td>0.33</td>
<td>3.00</td>
<td>4.20</td>
<td>1.000</td>
<td>6.00</td>
<td>166.7</td>
</tr>
<tr>
<td>0.50</td>
<td>2.00</td>
<td>5.84</td>
<td>1.390</td>
<td>8.35</td>
<td>119.7</td>
</tr>
<tr>
<td>1.00</td>
<td>1.00</td>
<td>12.05</td>
<td>2.870</td>
<td>17.22</td>
<td>58.1</td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M

Concentration of MK : 0.0024 M

The sensitizer (Michler's ketone, MK) absorbed more than 98% of the incident light.

a. The relative quantum yields are given with respect to that for 0.33M tetramethylethylene.

b. A value of \( 6.0 \times 10^{-3} \) for 0.33M tetramethylethylene was used for calculating the absolute quantum yields (see table 3a).
Slope : 46.78 ± 1.50
Intercept : 19.35 ± 2.92

**Figure 4: Effect of TME Concentration on the Quantum Yield of Sensitized Photoaddition**
Quenching studies

Our next purpose was to find the effect of singlet and triplet quenchers on the quantum yield of photoaddition. Amines are known to act as efficient quenchers of excited states. Triethylamine was chosen for this purpose. A decrease in the rate of cycloaddition was qualitatively observed in presence of the amine. Quantitative studies, however, could not be carried out since side products were observed in these runs.

Di-tert-butyl nitrooxide (DBN), which is known to quench many singlets and triplets at diffusion controlled rates was the next alternative. The quantum yields in presence of various quencher concentrations were measured as described in the Experimental section. The results are given in table 6. Stern-Volmer plot ($\phi_0/\phi$ versus quencher concentration) was linear, and is shown in figure 5.

The effect of tetramethylethylene concentration on the quantum yield of cycloaddition in presence of a known quencher concentration was studied next. The results are given in table 7, and the concentration plot ($\phi^{-1}$ versus [TME]$^{-1}$) is given in figure 6.

The quantum yield of photoaddition of the enone and tetramethylethylene in presence of naphthalene (a known quencher of triplets) was also measured, and the result is given in table 8.
### TABLE 6

**EFFECT OF QUENCHER ON THE QUANTUM YIELD OF PHOTOADDITION OF 3-PHENYLCYCLOHEX-2-ENONE AND TETRAMETHYLETHYLENE**

<table>
<thead>
<tr>
<th>[DBN] M</th>
<th>Amount of 36 g</th>
<th>Relative Q.Y\textsuperscript{a}</th>
<th>Absolute Q.Y x 10\textsuperscript{3}</th>
<th>(\phi_0/\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000</td>
<td>14.80</td>
<td>1.000</td>
<td>22.20</td>
<td>1.00</td>
</tr>
<tr>
<td>0.001</td>
<td>5.46</td>
<td>0.369</td>
<td>8.19</td>
<td>2.71</td>
</tr>
<tr>
<td>0.002</td>
<td>3.54</td>
<td>0.239</td>
<td>5.31</td>
<td>4.18</td>
</tr>
<tr>
<td>0.003</td>
<td>2.02</td>
<td>0.137</td>
<td>3.04</td>
<td>7.33</td>
</tr>
<tr>
<td>0.0034</td>
<td>2.16</td>
<td>0.146</td>
<td>3.24</td>
<td>6.85</td>
</tr>
<tr>
<td>0.004</td>
<td>1.87</td>
<td>0.126</td>
<td>2.80</td>
<td>7.91</td>
</tr>
<tr>
<td>0.0046</td>
<td>1.62</td>
<td>0.109</td>
<td>2.42</td>
<td>9.14</td>
</tr>
<tr>
<td>0.005</td>
<td>1.55</td>
<td>0.105</td>
<td>2.33</td>
<td>9.55</td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M  
Concentration of TME: 0.33 M  

The amount of light absorbed by even the highest concentration of di-\text{tert}-butyl nitroxide was only 6\%.  
\textsuperscript{a} The relative quantum yields are given with respect to that for the unquenched process (i.e. [DBN] = 0.000)
Figure 5: Stern-Volmer plot for enone-TME photoaddition

Slope: $1.75 \times 10^3$
TABLE 7

EFFECT OF TETRAMETHYLETHYLENE CONCENTRATION ON THE QUANTUM YIELD OF PHOTOADDITION IN PRESENCE OF THE QUENCHER

<table>
<thead>
<tr>
<th>[TME]</th>
<th>[TME]$^{-1}$</th>
<th>Amount of 36 g</th>
<th>Relative Q.Y$^a$</th>
<th>Absolute Q.Y x 10$^3$</th>
<th>[Q.Y]$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>M$^{-1}$</td>
<td>mgs</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.25</td>
<td>4</td>
<td>6.3</td>
<td>0.74</td>
<td>6.06</td>
<td>165.0</td>
</tr>
<tr>
<td>0.33</td>
<td>3</td>
<td>8.5</td>
<td>1.00</td>
<td>8.19</td>
<td>122.1</td>
</tr>
<tr>
<td>0.50</td>
<td>2</td>
<td>12.3</td>
<td>1.45</td>
<td>11.90</td>
<td>84.0</td>
</tr>
<tr>
<td>0.66</td>
<td>1.5</td>
<td>13.8</td>
<td>1.62</td>
<td>13.27</td>
<td>75.4</td>
</tr>
<tr>
<td>1.00</td>
<td>1</td>
<td>18.5</td>
<td>2.18</td>
<td>17.85</td>
<td>56.0</td>
</tr>
</tbody>
</table>

Concentration of enone: 0.005 M
Concentration of DBN: 0.001 M

a. The relative quantum yields are given with respect to that for 0.33M tetramethylethylene.
Slope : 35.22
Intercept : 19.06

FIGURE 6 : EFFECT OF TME CONCENTRATION ON THE QUANTUM YIELD
OF PHOTOCATION IN PRESENCE OF THE QUENCHER (0.001 M)
### TABLE 8

**QUANTUM YIELD OF PHOTOADDITION OF 3-PHENYLCYCLOHEX-2-ENONE AND TETRAMETHYLETHYLENE QUENCHED BY NAPHTHALENE**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Enone concn.</td>
<td>0.005 M</td>
</tr>
<tr>
<td>Light absorbed</td>
<td>20.2 m.eins.</td>
</tr>
<tr>
<td>TME concn.</td>
<td>0.33 M</td>
</tr>
<tr>
<td>Amount of 36</td>
<td>73 mgs; 0.285 m.moles</td>
</tr>
<tr>
<td>Naphthalene concn.</td>
<td>0.100 M</td>
</tr>
<tr>
<td>Solvent: tert-butyl alcohol</td>
<td>Quantum yield: 0.142</td>
</tr>
</tbody>
</table>

The amount of light absorbed by naphthalene was less than 10% in this irradiation.

**Sensitized dimerization of norbornene**

It is known that norbornene dimerizes when sensitized by sensitizers having triplet energies above 72 k.cal/mole\(^{59-61}\). It was mentioned earlier that the dimers were formed as side products in the enone-norbornene photolysis. In a controlled irradiation of norbornene with only the adduct 36 also the dimerization was observed. In order to know the path through which the norbornene dimers are formed - whether sensitized by the enone or by the enone-olefin adducts that are formed during irradiation - a solution of enone and norbornene was photolysed to only 50% conversion. Comparison of optical densities of the enone and the enone-olefin adducts at that conversion showed that all the incident light (more than 99.9%) was absorbed by the enone. We did observe the formation of the dimers in this photolysis.
TABLE 9

SENSITIZATION OF NORBORNENE DIMERIZATION

<table>
<thead>
<tr>
<th>Sensitizer (Eₜ)</th>
<th>Dimerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone (80)</td>
<td>observed</td>
</tr>
<tr>
<td>Acetophenone (74)</td>
<td>observed</td>
</tr>
<tr>
<td>Michler's ketone (61)</td>
<td>not observed</td>
</tr>
<tr>
<td>2-acetonaphthone (59.5)</td>
<td>not observed</td>
</tr>
<tr>
<td>3-phenylcyclohex-2-enone (54)</td>
<td>observed</td>
</tr>
<tr>
<td>(T₂ 72)</td>
<td>observed</td>
</tr>
</tbody>
</table>

Photoadduct (36)

3-phenylcyclohex-2-enone + Michler's ketone (when all the incident light was absorbed by the sensitizer) not observed

Absorption and emission spectra

3-phenylcyclohex-2-enone showed two long wavelength absorption bands in hexane, with maxima at 270 mμ (log ε = 4.3) and at 340 mμ (log ε = 2.0). In ethanol, there was only one band (λₘₕₙ = 285 mμ; log ε = 4.3), and the tail of the band extended to 375 mμ. The spectrum of 3-phenylcyclohex-2-enone oxime showed only one absorption band (λₘₕₙ = 277 mμ; log ε = 4.3) in hexane; in ethanol, there was no detectable difference between the spectra of the enone and the oxime.

The fluorescence emission of 3-phenylcyclohex-2-enone
was not detectable. 3-phenylcyclopent-2-enone showed a very weak emission in 375-600 m\(\mu\) region (\(\lambda_{\text{max}}=410\) m\(\mu\)).

The phosphorescence emission of 3-phenylcyclohex-2-enone was measured in 2:1 ethanol-ether at 77°K. The emission band had the maximum at 531 m\(\mu\), corresponding to a triplet energy of 53.8 kcal/mole. The phosphorescence excitation spectrum (phosphorescence intensity at 531 m\(\mu\) as a function of excitation wavelength) matched with the absorption spectrum reasonably well.

The presence of tetramethylethylene did not cause any significant change in the absorption spectrum of the enone, suggesting that there is no interaction between the enone and the olefin in the ground state that could be observed in the spectrum.

The emission of biacetyl\(^63\) was measured in 99% ethanol at 23°C in deoxygenated solutions. It showed fluorescence emission in 450-500 m\(\mu\) region (\(\lambda_{\text{max}}=470\) m\(\mu\)), and phosphorescence in 500-600 m\(\mu\) region (\(\lambda_{\text{max}}=510\) m\(\mu\)).

In order to know whether there is any singlet energy transfer to biacetyl from the enone, biacetyl emission was monitored in a solution of biacetyl and enone. No biacetyl emission could be detected when all the incident light was absorbed by the enone, thus proving that the enone does not transfer singlet energy to biacetyl at a significant rate.

The phosphorescence emission of naphthalene was observed in 450-600 m\(\mu\) region. Naphthalene sensitized the
phosphorescence of the enone. The reverse sensitization (triplet energy-transfer from the enone to naphthalene), however, could not be detected.

**Attempted C.I.D.N.P studies on the 3-phenylcyclohex-2-enone-tetramethylethylene system**

Recently Chemically Induced Dynamic Nuclear Polarization (C.I.D.N.P) studies have been performed on many processes occurring via the intermediacy of radicals. Since 1,4-diradicals have been postulated as the intermediates in photocycloaddition reactions of enones, we attempted to see the C.I.D.N.P of the enone-tetramethylethylene system; however, no polarization was observed.
DISCUSSION
A bimolecular photochemical reaction may be represented, in general terms, by the following steps.

i. absorption of light by one of the reactants, and the simultaneous excitation of the ground state to its excited singlet state (see, however, the foot-note in page 3).

ii. reactions of the singlet state, or transformation to a different reactive excited species.

iii. bimolecular reaction between the excited species and the ground-state substrate, to form an excited state intermediate.

iv. further processes such as rearrangement or dissociation of this intermediate, leading to products*.

Thus the elucidation of the mechanism of a photochemical process necessitates the understanding of each of these steps reasonably well; in addition, the mechanism should be capable of explaining other features such as orientation and stereochemistry of the products.

The data obtained from the qualitative and quantitative analysis of the reaction products can provide insights into the mechanism. However, the bimolecular reaction between the excited species and the ground-state substrate may lead directly to products, if it is a concerted process.

* The bimolecular reaction between the excited species and the ground-state substrate may lead directly to products, if it is a concerted process.
tive studies described in the Results and Experimental sections of this thesis, help to derive a reasonably good mechanism for the photoaddition of 3-phenylcyclohex-2-enone to olefins; the mechanism is discussed with respect to each step mentioned above, in the following pages.

**Excitation step**

It was mentioned in the Results, that 3-phenylcyclohex-2-enone shows two long wavelength absorption bands, with the maxima at \( \text{ca} 270 \text{ m\(\mu\)} \) (\( \log \varepsilon = 4.3 \)) and at \( \text{ca} 340 \text{ m\(\mu\)} \) (\( \log \varepsilon = 2.0 \)) in hexane. This is in contrast to the absorption properties of simple cyclic enones, which show absorption maxima at \( \text{ca} 230 \text{ m\(\mu\)} \) and at \( \text{ca} 330 \text{ m\(\mu\)} \). For all these compounds, the more intense shorter wavelength bands arise from the \( \pi-\pi^* \) transition; the long wavelength bands are ascribed to \( n-\pi^* \) excitation, which is forbidden spectroscopically and hence weak. It is conceivable that the extended conjugation due to the phenyl group stabilizes the \( \pi-\pi^* \) and \( n-\pi^* \) singlet states, thus displacing the absorption bands to longer wavelengths; the \( \pi-\pi^* \) band is red-shifted more than the \( n-\pi^* \) band. In ethanol, 3-phenylcyclohex-2-enone shows only one long wavelength band, with the maximum at \( \text{ca} 285 \text{ m\(\mu\)} \) (\( \log \varepsilon = 4.3 \)). It is known that the \( \pi-\pi^* \) transitions of carbonyl compounds show a red-shift and \( n-\pi^* \) excitations a blue-shift as the polarity of the solvent is increased\(^{65}\). For 3-phenylcyclohex-2-enone, apparently, the weak \( n-\pi^* \) absorption underlies the \( \pi-\pi^* \) band in ethanol.
That this band is due to $\pi-\pi^*$ excitation received experimental support from a comparison of the absorption spectra of 3-phenylcyclohex-2-enone and its oxime. If an absorption band is due to $n-\pi^*$ transition of a carbonyl group, it should be absent from the spectrum of the oxime derivative. In hexane, 3-phenylcyclohex-2-enone oxime shows only one long wavelength band, with the maximum at ca 277 m$\mu$ ($\log \varepsilon=4.3$). In ethanol, there is no detectable difference between its spectrum and that of the enone ($\lambda_{\text{max}}=285$ m$\mu$; $\log \varepsilon=4.3$). Kearns et al$^{62}$ have used this method to identify the absorption bands of many carbonyl compounds; two examples of their studies are given in figure 7 to illustrate this point.

![Figure 7](image-url)

**FIGURE 7**

**EFFECT OF OXIME FORMATION ON THE SPECTRA OF KETONES**

A. Benzophenone system; B. fluorenone system

--- spectra of the ketone; ---- spectra of the oxime
RPR 3500 Å lamps were used for irradiation in most of the work presented in this thesis; medium pressure Hg-arc lamp was used occasionally. In all cases, pyrex glass was used to filter the light from the lamp, thereby ensuring that wavelengths shorter than 295 mμ were not admitted to the photolysis solution, preventing excitation of 3-phenylcyclohex-2-enone through short wavelength transitions. Thus the enone was excited to its π-π* singlet state in the first step (less than one per cent of the incident light would have been absorbed in the n-π* band). Mention is to be made, at this point, that olefins such as tetramethylethylene, cyclopentene, norbornene and but-2-enes do not absorb the wavelengths used in these irradiations, and hence are in their ground-states during photoaddition.

**Reactive excited state involved in the photoaddition**

The fluorescence emission of 3-phenylcyclohex-2-enone in solution was not detectable under any conditions; this might perhaps be due to a very short lifetime of the singlet state as a result of a rapid intersystem crossing to the triplet state and a fast radiationless decay to ground state. It was believed that the radiationless decay should slow down with decrease in ring-size; and we did observe a very weak fluorescence emission (λ_max=410 mμ) from 3-phenylcyclopent-2-enone; this emission provides a singlet energy of ca 74 kcal/mole for this molecule. The energy of the S_1 state of 3-phenylcyclohex-2-enone could be estimated roughly from
its absorption spectrum. The tail of the 285 m\(_\mu\) absorption band ends at \text{ca} 390 m\(_\mu\), providing a singlet energy of \text{ca} 73.3 kcal/mole. Phosphorescence emission from the enone provides an estimate of the energy of the triplet state; the shortest wavelength emission band shows a maximum at \text{ca} 531 m\(_\mu\) corresponding to a triplet energy of 54 kcal/mole. The triplet energies of simple alicyclic enones have been estimated to be of the order of 61 kcal/mole using photostationary states obtained in the \text{cis-trans} isomerization of stilbenes with the enones as sensitizers\textsuperscript{15,45}; De Mayo et al\textsuperscript{66}, however, obtained values close to 70 kcal/mole for the triplets of a number of constrained enones using spectroscopic methods. The extended conjugation in the \(\pi\)-system of 3-phenylcyclohex-2-enone apparently stabilizes its triplet state.

It is generally accepted that triplet states are involved in the photochemical reactions of enones\textsuperscript{6,68}. Chapman\textsuperscript{67} suggested a singlet state mechanism for the photo-addition of 4,4-dimethylcyclohex-2-enone and 1,1-diphenyl-ethylene. Rasmussen\textsuperscript{68}, however, has proved the intermediacy of a triplet state of this enone in its addition to cyclopentene. Little is known about the excited states involved in the photoreactions of \(\alpha\beta\)-unsaturated carbonyl compounds with a conjugated aromatic ring (the cinnamyl system). It is appropriate, at this point, to consider some of the recent work on the mechanistic aspects of the photochemistry of the cinnamyl system.
Ullman et al. have reported that the cinnamate derivatives of the type 44 and 45 undergo photoreduction and cis-trans isomerization about the double bond depending on the wavelength of excitation. They suggested that while π-π* triplets are responsible for the cis-trans isomerization, the photoreduction involves the n-π* states.

\[ \text{44} \quad \text{C}_6\text{H}_5 \]

\[ \text{45} \quad \text{C}_6\text{H}_5 \]

It was mentioned earlier in the Introduction that irradiation of β-substituted styrenes and tetramethylethylene leads to photocycloaddition and photoene reactions. Chapman et al. observed that neither of these processes is observed from triplet sensitization which leads only to cis-trans isomerization of the double bond. The authors believe that the photoaddition and photoene reactions involve the excited singlet state \( S_1 \) of the styrene derivatives.

It was found that the unsensitized photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene (0.33M) was more efficient (φ=0.022 mole/einstein) than the process sensitized by triplet energy donors such as Michler's ketone \( (E_T=61-62 \text{ kcal/mole}) \) and 2-acetonaphthone \( (E_T=59.5 \text{ kcal/mole}) \) (φ=0.006 and 0.0057 respectively). Similar results were
obtained for the enone-cyclopentene addition ($\phi_{\text{unsen}}=0.027$; $\phi_{\text{sen}}=0.00454$). The triplet energies of these sensitizers have been estimated both in rigid glass matrix at 77°K$^{70a}$ and in solution at room temperature$^{70b}$. It can be shown that when the triplet energy of the donor (sensitizer) is three kcal/mole or more higher than the acceptor, the former transfers energy at diffusion-controlled rate. It is also known that the intersystem crossing yields of these sensitizers are very close to unity$^{71}$. Thus, it seemed unlikely that the inefficiency of the sensitized photoaddition could be the result of an inefficient triplet energy-transfer to the enone (see, however, later discussion). This suggests that a more efficient path leading to the photoadduct is operative in the unsensitized photoaddition.

A plot of reciprocal quantum yield as a function of reciprocal tetramethylethylene concentration was linear over the concentration range studied (slope: $8.37 \pm 0.12$; intercept: $20.75 \pm 0.76$). The plot should be non-linear if more than one excited state are involved in the photoaddition, 

\* If for example, two excited states are reactive in the photoaddition, the overall quantum yield ($\phi$) may be dissected into the two components ($\phi_1$ and $\phi_2$) as 

$$\phi = \phi_1 \cdot \phi_2$$ 

Therefore, 

$$\frac{1}{\phi} = \frac{1}{(\phi_1 \cdot \phi_2)} = 1 \left( \frac{1}{\frac{1}{\phi_1} + \frac{1}{\phi_2}} \right)$$ 

$1/\phi_1$ and $1/\phi_2$ would be linearly dependent on $1/[\text{TME}]$, and the
since the olefin would almost certainly react with different excited states with different efficiencies. A non-linear concentration plot, for instance, has been obtained for the photoaddition of fluorenone to dimethyl-N-(cyclohexyl) ketenimine, for which the intermediacy of both the singlet and triplet states has been proposed\textsuperscript{57b}. This suggests that only one excited state is involved in the unsensitized photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene, and, at first sight, it is not the same triplet state which is reactive in the sensitized process. This fact was further evidenced by a similar study of the effect of tetramethylethylene concentration over the quantum yield of sensitized addition. The plot was linear, but entirely different from that obtained for the unsensitized process (slope: 46.8 \pm 1.5; intercept: 19.35 \pm 2.92). It has to be pointed out, however, above expression may be written as

\[
\frac{1}{\phi} = \frac{1}{f(1/[TME])} + \frac{1}{f'(1/[TME])}
\]

where \(f(x)\) and \(f'(x)\) are linear functions in \(x\); thus

\[
\frac{1}{\phi} = \frac{f(1/[TME]) \times f'(1/[TME])}{f(1/[TME]) + f'(1/[TME])}
\]

This equation suggests that a plot of the reciprocal quantum yield of addition against the reciprocal tetramethylethylene concentration would be non-linear.
that the error in the determination of quantum yields was about five per cent, and so five percent of a second excited state in one of these concentration plots would not have caused any detectable non-linearity.

As was mentioned earlier, when norbornene was used as the substrate, photoaddition was accompanied by the formation of the \textit{exo-trans-endo} (42) and \textit{exo-trans-exo} (43) dimers of norbornene in the ratio 9:1. The dimerization of norbornene has been studied rather extensively \cite{55,59-61}, and a precise estimate of the triplet energy of the olefin is known. The process occurs both by direct irradiation, and on triplet sensitization provided the triplet energy of the sensitizer is at least 72 kcal/mole. The specific dimer ratio, 88:12, is independent of the energy of the sensitizer. Sensitizers with a triplet energy slightly lower than 72 kcal/mole fail to sensitize the dimerization. Arnold \cite{59,60} has shown that those of ketones whose \textit{n-π*} triplet levels lie below the olefin substrates lead to the formation of oxetanes, and that a difference of only about 0.5 kcal/mole is critical determining the dimerization of norbornene. Thus, 4-chloroacetophenone (\(E_T = 72.1\) kcal/mole) is capable of sensitizing the dimerization, whereas 3-trifluoromethylacetophenone (\(E_T = 71.6\) kcal/mole) leads to the formation of oxetane in 93 per cent yield.

This led us to postulate the presence of an enone triplet of an energy close to 72 kcal/mole, which can transfer triplet energy to norbornene. No norbornene dimers were detected in
the sensitized irradiation of the enone and norbornene with Michler's ketone, establishing that neither the sensitizer nor the lowest triplet of the enone is capable of sensitizing the dimerization.

It has been reported that quadricyclene (47) was formed as a side-product in the photoaddition of 3-phenylcyclohex-2-enone and norbornadiene; this result may also be attributed to triplet energy-transfer from the higher triplet of the enone. Isomerization of norbornadiene to quadricyclene has been shown to be efficiently sensitized by high energy sensitizers such as acetophenone.

We observed cis-trans isomerization of but-2-enes, as a side reaction to the photoaddition to 3-phenylcyclohex-2-enone. This may also arise from energy-transfer to butene from the $T_2$ of the enone. Much significance should not, however, be attached to this observation, since other processes such as non-vertical energy transfer to this non-rigid olefin, or the formation of an 1,4-diradical enone-olefin intermediate (discussed later) may also lead to this isomerization.

The next question is, whether the second triplet state of the enone, which transfers energy to olefins, is
also reactive in the photoaddition reactions. To give an answer to this question, an estimate of the lifetime of the reactive excited state was necessary.

A simple mechanistic scheme can be written for the photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene, without specifying the nature of the excited state that is reactive. (E*).

\[ E_0 \xrightarrow{h\nu} E^1 \xrightarrow{a} E^* \]
\[ E^* \xrightarrow{k_d} E_0 \]
\[ E^* + \text{TME} \xrightarrow{k_r} [E-\text{TME}]^* \]
\[ [E-\text{TME}]^* \xrightarrow{k_{cyc}} \text{Adduct} \]
\[ [E-\text{TME}]^* \xrightarrow{k_{cle}} E_0 + \text{TME} \]

Here 'a' is the quantum yield of formation of E*, k_d is the overall unimolecular decay constant of the excited state, k_r is the bimolecular rate constant for complex formation between E* and ground-state TME (discussed later), k_{cyc} is the rate constant of product formation, and k_{cle} is the rate constant of dissociation of the complex into ground-state enone and olefin. Steady-state treatment of such a mechanism yields the following expression for the quantum yield of photoaddition.

\[ \phi = a \cdot P \cdot \left[ \frac{k_r[\text{TME}]}{k_r[\text{TME}] + k_d} \right] \]

where \( P = \frac{k_{cyc}}{k_{cyc} + k_{cle}} \)
\[ \frac{1}{\phi} = \frac{1}{a} \cdot \frac{1}{P} \left[ 1 + \frac{k_d}{k_r} \frac{1}{[TME]} \right] \]

The term 'a' would be equal to unity, if \( E^* \) is the excited singlet state of the enone, since for every photon that is absorbed, one excited singlet species is generated. If \( E^* \) is a triplet of the enone, then 'a' represents the intersystem crossing efficiency. The intersystem crossing efficiencies of cyclohex-2-enones and cyclopent-2-enones have been measured to be close to unity. Thus our assumption is that, the inefficiency at infinite olefin concentration (large intercept in the concentration plot) is a result of the formation of an enone-olefin complex intermediate \([E-TME]^*\), hereon referred to as 'partition intermediate'. The slope to intercept ratio gives \( k_d/k_r \), which, from the plot is computed to be ca 0.42.

In order to estimate the values of \( k_d \) and \( k_r \), the effect of di-tert-butyl nitroxide, a known quencher of singlets and triplets was studied. This compound, for instance, is known to quench the singlets of fluorenone\(^5\), and the triplets of benzophenone\(^5\) and of \( \alpha\beta \)-unsaturated ketones at diffusion-controlled rate. The Stern-Volmer plot \( \left( \phi_0/\phi_q \right) \) versus \([DBN] \), where \( \phi_0 \) is the quantum yield of photoaddition in the absence of the quencher, and \( \phi_q \) that in the presence of the quencher) for 3-phenylcyclohex-2-enone - tetramethylethylene system was linear, with a slope of \( 1.753 \times 10^3 \) liter/mole for 0.33M tetramethylethylene.
Two possible modes of quenching may be envisaged:

(i) quenching of a pure excited state (E*) of the enone, and/or,
(ii) quenching of a possible enone-olefin excited state
complex, [E-TME]*, if it is sufficiently long-lived to undergo bimolecular processes. The linearity of the Stern-Volmer plot is indicative of the occurrence of only one of these two modes. However, it cannot differentiate between the two.

To understand the nature of quenching, the effect of tetramethylethylene concentration on the quantum yield of photoaddition in the presence of a known concentration of the quencher was studied. If a pure excited state is quenched (mode i), the partition factor (P) is not affected, and the concentration plot would show an intercept equal to 20. If, on the other hand, mode ii is operative, there should be a decrease in the partition factor, since the partition intermediate, in addition to its own decay to ground-state molecules, is also quenched; the plot would then show a larger intercept. The expected plots for both the modes were calculated, assuming diffusion-controlled quenching, for 0.005 M enone, and 0.001 M di-tert-butyl nitroxide; They were, slope: 34.6, and intercept: 20.0 for mode i; and, slope: 23.1, and intercept: 55.0 for mode ii. The experimental plot had a slope of 35.22, and intercept of 19.06, in excellent agreement with the plot calculated for quenching by mode i. The quantum yield, for 0.001 M quencher, is then given by the following expression:
\[
\phi = P \cdot \frac{k_r [\text{TME}]}{k_d + k_r [\text{TME}] + k_q [0.001]}
\]

And,
\[
\frac{1}{\phi} = \frac{1}{P} \left[ 1 + \frac{k_d + k_q [0.001]}{k_r [\text{TME}]} \right]
\]

Using the slopes of the two concentration plots, and assuming diffusion-controlled quenching (3 x 10^9 liter/mole.sec in tert-butyl alcohol at room temperature), \(k_d\) and \(k_r\) were calculated to be 0.94 \(x\) 10^6 sec\(^{-1}\) and 2.24 \(x\) 10^6 liter/mole.sec. The lifetime of \(E^*\), therefore, is 1.06 \(x\) 10\(^{-6}\) sec.

The values of these rate constants could be derived from the Stern-Volmer plot also. The expression is given by
\[
\frac{\phi_0}{\phi_q} = 1 + \frac{k_d [\text{DNB}]}{k_d + k_r [0.33]}
\]

and the values of \(k_d\) and \(k_r\) obtained were 0.96 \(x\) 10^6 sec\(^{-1}\) and 2.29 \(x\) 10^6 liter/mole.sec, in very good agreement with those calculated from the concentration plots. These rate constants compare favorably with the values obtained by Chapman et al\(^{73}\) for the dimerization of isophorone.

Case for a singlet mechanism

At this stage, we can start speculating about the nature of \(E^*\). If it is the \(S_1\) state of the enone, it is really intriguing why its fluorescence emission could not be detected in spite of a long lifetime of about 10\(^{-6}\) sec. Generally, fluorescence emission has not been observed from
conjugated ketones. Fluorenone is a known exception to this generalization; it emits from its $S_1$ state in solution at room temperature, with a lifetime of less than $10^{-7}$ sec$^6$. As was mentioned earlier, we did observe a very weak fluorescence emission from 3-phenylcyclopent-2-enone in ethanol at room temperature.

Another result that was not in favor of a singlet mechanism, was our failure to sensitize the fluorescence of biacetyl using the enone. The former emits both from its singlet and triplet excited states in solution at room temperature (emission maxima: 464 m$\mu$ and 510 m$\mu$)$^6^3$. We expected that if the $S_1$ state of the enone is reactive in the photoadditions, with a long lifetime of $10^{-6}$ sec, it should be capable of transferring singlet energy to biacetyl. A solution of 0.01 M enone and 0.3 M biacetyl in ethyl alcohol was used for this purpose. Biacetyl emission was not observed from this solution, when all the incident light was absorbed by the enone. Too much emphasis, however, should not be laid upon this evidence, since the bimolecular interaction between the excited enone ($E^*$) and the ground-state olefin in the photoaddition may not be through an energy-transfer mechanism.

**Question of reversible intersystem crossing**

De Mayo$^7$ has suggested that when the excited singlet and triplet states are very close in energy, intersystem crossing may be reversible, and the triplet state may act as a reservoir for the singlets which may be reactive in the
photochemical process. Since a second triplet state of the enone, close in energy to the excited singlet state is postulated, this hypothesis is also considered here. It does explain most of the results described in this thesis, such as obtention of a linear concentration plot, and an apparent long lifetime of the reactive excited state. However, if \( S_1 \) and \( T_2 \) states are in reversible equilibrium, one can expect that di-tert-butyl nitrooxide would quench both these states, and the Stern-Volmer plot, in this case would be non-linear. A steady-state treatment of such a scheme (see Appendices) yields a complex expression for the Stern-Volmer plot as follows.

\[
\frac{\phi_0}{\phi_q} = a [Q] + b + \frac{1}{c [Q] + d}
\]

The experimentally obtained linear Stern-Volmer plot thus rules out such a mechanism. It should, however, be borne in mind, that constants \( a, b, c \) and \( d \) may have values, such that the non-linearity given by the expression may not be observable experimentally.

The evidences, described so far, argue against \( S_1 \) as the excited state, reactive in the unsensitized addition. Can the second excited state of the enone, which is capable of entering into bimolecular processes (e.g. norbornene dimerization), then, be responsible for the photoaddition of the enone to olefins?
Case for the second triplet as the reactive state

The presence of naphthalene ($E_T = 61$ kcal/mole) reduced the quantum yield of photoaddition. Since the $S_1$ state of naphthalene ($E_S = 91$ kcal/mole$^{75}$) lies well above the $S_1$ state of the enone ($E_S = 73-74$ kcal/mole), the above quenching could not be the result of singlet-singlet energy-transfer from the enone. On the other hand, naphthalene can act as an efficient quencher of the $T_2$ state of the enone, and could, in turn, sensitize its $T_1$ state ($E_T = 54$ kcal/mole). This double energy-transfer might reduce the quantum yield, since the triplet sensitized photoaddition is apparently less efficient than the unsensitized process. Our efforts to sensitize naphthalene phosphorescence by the enone, however, were unsuccessful. A plausible reason would be the back energy-transfer from naphthalene to the lowest triplet of the enone.

The possibility that more than one excited state may be active in photophysical and photochemical processes has been considered and recognized by many workers. Kearns et al$^{46}$ have shown that for many substituted acetophenones, for 2-naphthaldehyde, and for some $\alpha\gamma$-unsaturated cyclic enones such as 4-substituted testosterone acetates (48), two triplets lie below the lowest singlet excited state. Phosphorescence emission has been observed from both the triplets for some of these compounds.
Michl and Kolc\textsuperscript{76} have reported that the ring opening of 49 to yield 50 at 77°K involved any of the states between \( T_7 \) and \( T_2 \), and not the lowest triplet.

De Mayo\textsuperscript{44} has reported that two triplets are reactive in the photochemistry of cyclopent-2-enone and related systems. The lowest triplet can be sensitized by benzophenone, and is capable of quenching the photoreduction of the
latter in iso-propyl alcohol, but is unreactive towards photoaddition to olefins. The higher triplet, which can be generated by direct irradiation or from sensitization using high-energy sensitizers, is reactive in photoaddition. Wagner\textsuperscript{45}, however, reported that these observations can be explained by a hydrogen-transfer mechanism, without invoking a higher triplet of the enone.

Yang\textsuperscript{77} proposed the intermediacy of two triplets in the photoaddition of 9-anthraldehyde to tetramethylethylene. Both Chapman\textsuperscript{78} and Yang\textsuperscript{77a} considered the possible intermediacy of two triplets in the photochemistry of 9-nitroanthracene. Chapman\textsuperscript{23a} observed that in the photoaddition of 4,4-dimethylcyclohex-2-ene and of isophorone to 1,1-dimethoxyethylene, the formation of cis-fused adducts was quenched by di-tert-butyl nitroxide, faster than the formation of trans-fused adducts and of oxetanes; the authors attributed this to the involvement of two triplet states of the enone, in an attempt to explain this differential quenching.

A very elegant piece of work on the intermediacy of higher excited states in photochemical processes has been reported by Liu et al\textsuperscript{79}, on the photochemistry of anthracenes. These compounds sensitize the triplet state rearrangement of rigid systems \textsuperscript{51 - 54}, whose triplets lie well-above the T\textsubscript{1}\textsuperscript{1} states of these sensitizers\textsuperscript{78a,b}. These sensitizations are attributed to triplet-triplet energy-transfer from the T\textsubscript{2}
states of anthracenes.

If $T_2$ state is indeed reactive in the photoaddition of 3-phenylcyclohex-2-enone to olefins, it is really baffling how its lifetime can be so long ($10^{-6}$ sec). Normally, rates of internal conversion (vibrational deactivation within the same multiplicity) are of the order of $10^{11}-10^{12}$ sec$^{-1}$. The process slows down as the energy-gap between the two electronic levels ($T_2 - T_1$) increases. Liu et al. have estimated the $T_2$ level of anthracenes to be ca. 72 - 75 kcal/mole, while the energy of $T_1$ is ca. 40 - 43 kcal/mole. They explained that this large $T_2 - T_1$ energy-gap makes the upper state sufficiently long-lived to enter into bimolecular energy-transfer processes; they estimated the lifetime of $T_2$ state to be ca. $2 \times 10^{-10}$ sec, for these systems.

For 3-phenylcyclohex-2-enone, our estimates indicate a $T_2 - T_1$ energy-gap of about 18 kcal. We believe that the $T_1$ state has $\pi-\pi^*$ configuration for two reasons. Firstly, the phosphorescence emission from the enone is structureless consistent with a $\pi-\pi^*$ emitting state. Secondly, in general, singlet-triplet splitting is larger for $\pi-\pi^*$ states than for
n-π* states, and we know that the π-π* and n-π* singlets are very close in energy. Theoretical calculations in this department have shown that the π-π* triplet does lie below the n-π* triplet for cinnamaldehyde, a rough model for our enone system.

Santry et al. have done calculations which suggest that the lowest triplet of acrolein (a model for the simple enone system) is n-π* in configuration and is planar in its equilibrium conformation. The next triplet, which is π-π* in character in non-planar. The angle of twist of the Cα-Cβ bond, for the most stable conformation of the π-π* triplet has been calculated to be approximately 72°. We believe that the T₂ (n-π*) and T₁ (π-π*) triplets of cinnamaldehyde (and 3-phenylcyclohex-2-enone) might also differ in their equilibrium geometries.

Thus it is possible that a fairly large energy-gap between the two triplet states, their difference in electronic configuration (n-π* and π-π*), and the difference in their equilibrium geometries make the relaxation from T₂ to T₁ state very slow, providing a long lifetime for T₂ state. It may be pointed out that Chapman et al. obtained similar lifetimes (k_d = 5.7 \times 10^6 \text{ sec}^{-1} and 4.9 \times 10^6 \text{ sec}^{-1}) for the two triplets they proposed for the photodimerization of isophorone. It is also possible that the two triplets of the enone may act like two different chromophores. More theoretical calculations on the shapes and electron densities
of these states are needed to understand this system properly. Too much speculation is not warranted!

**Question of reversible energy-transfer from Michler's ketone**

- **Case for $T_1$ as the reactive state**

  It has been, so far, tacitly assumed that the quantum yield of energy-transfer from Michler's ketone to the enone is unity, in the sensitized photoaddition; as was mentioned earlier, the triplet energy of these compounds, and the unit quantum yield of intersystem crossing of the former, strongly support this assumption. However, attention is drawn now to some of the recent work on the photochemistry of Michler's ketone as a sensitizer\(^{82,83}\).

  Hammond et al\(^{82}\) have reported about the formation of the adduct \(\text{55}\) between Michler's ketone and benzophenone, when the former absorbed all the light. Quenching of this reaction by 1,3-hexadiene, and the high triplet energy of benzophenone (about 7 kcal/mole higher than the Michler's ketone triplet) suggest that a triplet exciplex is formed between the two compounds, which leads to adduct \(\text{55}\).
A photochemical exchange reaction of Michler's ketone which leads to the destruction of its triplets has been reported by Koch and Jones. Chapman observed that the photoaddition of 4,4-dimethylcyclohex-2-ene to olefins was dependent on the concentration of the sensitizers, whenever the sensitizers were of π-π* type; the quantum yield of photoaddition decreased with increase in the concentration of the sensitizers. The authors proposed the formation of eximers of these sensitizers, and subsequent self-quenching of their triplets. It is to be noted that the lowest triplet of Michler's ketone is π-π* in configuration.

Such processes, if present in our system, would reduce the quantum yield of energy-transfer from Michler's ketone to 3-phenylcyclohex-2-ene, and as a result, the quantum yield of photoaddition of the enone to olefins in the sensitization experiments. A steady-state treatment, however, shows that such a mechanism requires a larger intercept for the concentration plot of the sensitized process than that for the unsensitized, since it will be equal to $\phi_{e\cdot T}^{-1} \times p^{-1}$ for the former. If by sheer coincidence, the quantum yield of intersystem crossing of the enone has a value close to the quantum yield of energy-transfer from Michler's ketone $[T_1(MK)^+ S_0(E) \rightarrow S_0(MK) + T_1(E)]$, then the intercepts in the concentration plots would be equal; but, this condition then requires the slopes to be equal too.
which is not observed experimentally. Moreover, it was found that the concentration of Michler's ketone did not change during sensitization. Thus, these photochemical processes of Michler's ketone seem very unlikely in our system.

Incidentally, these arguments rule out the suggestion of Harpp and Heitner\textsuperscript{85} that the results are consistent with a $T_1$ mechanism in both the unsensitized and sensitized processes, and that the difference in slopes of the concentration plots could be attributed to the different lifetimes of the triplets (of the enone and of the sensitizer) involved.

Another process which deserves consideration is the reverse energy-transfer from the enone triplet to Michler's ketone, shown by the following equation. This process, would certainly reduce the number of enone triplets generated in the sensitized reaction, thus reducing the quantum yield of photoaddition. Further, this reduction becomes insignificant at infinite olefin concentration, so that it does not affect the intercept of the concentration plot for the sensitized photoaddition. However, a steady-state treatment of a triplet mechanism including this processes (see Appendices) shows that

$$\phi = \frac{k_r k_t [O] [E]}{(k_d + k_r [O]) (k_d + k_t [E]) - k_t' k_{-t} [S]}$$
and, \[ \frac{1}{\phi} = \frac{1}{P} \left[ \left( 1 + \frac{k_d}{k_r [O]} \right) \left( 1 + \frac{k'_d}{k_t [E]} \right) + \frac{k'_d k_{-t} [S]}{k_r k_t [O] [E]} \right] \]

where, \( k'_d \) is the overall unimolecular decay constant of the sensitizer (S) triplet, and \( k_{-t} \) is the bimolecular rate constant for the reverse energy-transfer. The other parameters have their usual meaning. This mechanism requires \( k_{-t}/k_t = 1 - 10 \) in order to explain the observed concentration plots, which seems not very likely. In a classic study of back transfer, Sandros determined the forward and reverse energy-transfer rate constants for biacetyl with a number of compounds of varying triplet energies. His results indicated that the rate of back transfer can be expressed by the equation:

\[
\log k_{-t} = \log k_t - \frac{\Delta E_T}{2.303 RT}
\]

where \( \Delta E_T \) is the difference in triplet energies between the donor and acceptor, \( k_t \) and \( k_{-t} \) are forward and reverse energy-transfer constants, \( R \) the gas constant, and \( T \) the absolute temperature. This suggests that the reverse energy-transfer to Michler's ketone from the enone would be an insignificant process, unless the triplet energy of the former is lowered to a considerable extent in tert-butyl alcohol at room temperature.
Thus, with the results described in this thesis, a definite choice between the $T_2$ and $T_1$ states of the enone as the reactive species in the unsensitized photoadditions is not possible, though the former must at least be considered as a candidate.

**Bimolecular reaction of the excited state and subsequent processes leading to product formation**

As was mentioned in the beginning of this section, the next step after the formation of the reactive excited species, is the bimolecular attack on the substrate. This, if concerted, would lead to cycloadducts directly. However, there is strong evidence against a concerted process in the photoadditions of enones. Corey\(^{21}\) observed that the same set of products was produced from the photoaddition of cis- or trans- but-2-ene and cyclohex-2-enone. This result indicated that a common intermediate species was formed in both the reactions. We observed cis-trans isomerization of but-2-ene in its photoaddition to 3-phenylcyclohex-2-enone. These results are inconsistent with a concerted cycloaddition.

The formation of only the head-to-head dimer, 12, a single adduct with 1,1-dimethoxyethylene, 56, and the differences in reactivities of various olefins in photoaddition to the enone\(^{22}\) are consistent with the intermediacy of an oriented $\pi$-complex of the excited enone and the ground-state olefin, first proposed by Corey\(^{21}\).
For an \( n-\pi^* \) excited state, the \( \pi \)-complex can be represented as 57, which collapses to a 1,4-diradical intermediate, 58.

The formation of the complex depends on the reactivity of the substrate, and olefins with electron releasing groups complex more efficiently. Corey proposed a 1,4-diradical intermediate of the type 58, to explain the stereochemistry of the adducts; orientation is determined during the complex formation itself. One can see that the initial bond formation at the \( \alpha \)-carbon of the enone is more likely, since, in the \( n-\pi^* \) state, the \( \alpha \)-carbon is more electrophilic than the \( \beta \)-carbon. Moreover, the resulting diradical from the \( \alpha \)-bond formation is expected to be more stable than the one arising from
The diradical, 58, can, in the final step of the reaction, undergo ring-closure to yield the adduct, or disproportionate to the ground-state enone and olefin. The observed intercept of 20 in the concentration plot indicates that the ring-closure to adduct occurs only once for every twenty diradical species dissociating. This type of partition intermediates has been proposed in many cases in recent years; for instance, in the photoaddition of cyclopen-2-enone to olefins[^44b], of benzophenone to furan[^87], in the dimerization of pyrimidines[^88], and of enones[^45].

Another interesting feature of our results was that the intercepts of the concentration plots for the unsensitized and Michler's ketone sensitized photoaddition were the same within experimental error (see figures 3 and 4). A common 1,4-diradical in both these processes was proposed to explain this observation - two different intermediates having similar cyclization to cleavage ratios would be quite a coincidence!
It was mentioned earlier that 1,4-diradicals have been recognized as intermediates in photoaddition reactions. These species can undergo three major types of chemical processes - ring-closure, cleavage and hydrogen atom transfer. All these processes have been subject of study in recent years, with particular emphasis on the stereospecificity of these reactions. The striking feature of these studies is the dependence of the nature of the products on the multiplicity of the precursor of the diradical. A triplet diradical has to intersystem cross to singlet manifold, before it can lead to cyclization or cleavage; rotation of all three σ-bonds connecting the radical centers can occur if this spin-inversion is slow. A potential energy surface, as shown in figure 8, was considered by Stephenson and Brauman for a general 1,4-diradical intermediate. It may be seen from the diagram, that the diradical faces small activation barriers (ca. 5-8 kcal/mole) for ring-closure and for cleavage. The position of the shallow minimum depends on the distance between the radical centers in the equilibrium conformation of the species. The position of the triplet diradical is very close to the singlet manifold near the minimum, but in the regions above the minima, the triplet potential-energy surface is repulsive (dotted line).
We can consider a similar potential energy surface for 3-phenylcyclohex-2-enone - tetramethylethylene diradical intermediate (58) as in figure 9. A greater dip in the shallow minimum for the species is expected due to the stabilizing effects of the phenyl and methyl groups. Moreover, because of the presence of bulky groups, the radical centers are expected to be farther away than in the simple enone-olefin diradical intermediate; this would cause the shallow minimum of the former to lie closer towards the cleavage products.

† These curves are meant to qualitatively show the energy-surface, and by no means are quantitative.
POTENTIAL ENERGY SURFACES FOR 1,4-DIRADICALS FORMED IN THE PHOTOADDITIONS OF ENONES AND OLEFINS

for simple enones and olefins

for 58

Such a potential energy surface does explain why trans- fused adducts are not formed from 3-phenylcyclohex-2-enone, whereas they are the major products in the photoadditions of simple enones. Even if a 'transoid' diradical species is formed in the 3-phenylcyclohex-2-enone-olefin system, it can rearrange to its less-strained 'cisoid' rotomer, since the large activation barrier would make the ring-closure slow.

The position of the energy minimum (the most stable
conformation of the diradical) of $S_8$, would favor cleavage with respect to ring-closure, since the geometry of $S_8$ is closer to cleavage products. This explains, why the cyclization factor is very low (ca 0.05) for 3-phenylcyclohex-2-enone - tetramethylethylene system. This factor has been measured to be about 0.36 and 0.74 for the dimerization of cyclopent-2-enone$^{45}$ and of cyclohex-2-enone$^{45}$, and about 0.2 and 0.5 for the photoaddition of trans-hex-3-ene and cyclohexene to cyclopent-2-enone respectively$^{44b}$.

Thus the results described in this thesis provide a mechanistic scheme for the photoaddition of 3-phenylcyclohex-2-enone and olefins (Scheme 5). A descriptive picture of the electronic energy levels of the enone is also provided by this study (figure 10).
Unsensitized process

\[ E_0 \xrightarrow{h_\nu} E^1 \longrightarrow E^* \xrightarrow{k_d^*} [E-O]^* \longrightarrow [E-O]^* \]

\[ \xrightarrow{k_d} E_0 \]

\[ S^3 + E_0 \longrightarrow S_O + E^3 \xrightarrow{k_r^*} [E-O]^3 \longrightarrow [E-O]^3 \]

Triplet sensitized process

\[ E_0, S_O, 0 \quad \text{Ground states of enone, sensitizer and olefin} \]

\[ E^* \quad \text{Reactive state in the unsensitized process} \]

\[ S^3 \quad \text{Sensitizer triplet} \]

\[ E^3 \quad \text{Lowest triplet of enone (T\textsubscript{1})} \]

\[ [E-O]^* \quad \text{Enone - olefin excited state complex (superscript denotes multiplicity)} \]

\[ \cdot \cdot \cdot [E-O] \quad \text{1,4-diradical (superscript denotes multiplicity)} \]

\[ k_d \quad \text{Overall unimolecular decay constants of excited states (superscript denotes the state that decays)} \]

\[ k_r \quad \text{Bimolecular rate constant of complex formation} \]

\[ k_{\text{cyc}} \quad \text{Rate constant of cyclization of the 1,4-diradical} \]

\[ k_{\text{cle}} \quad \text{Rate constant of cleavage of the 1,4-diradical} \]

SCHEME 5

MECHANISM OF PHOTOADDITION OF 3-PHENYLCYCLOHEX-2-ENO\textsubscript{E}NE TO OLEFINS
$S_2, S_1$ \( (\pi-\pi^* \text{ and } n-\pi^*) \) 

\(~73-74 \text{ kcal/mole}~\) 

$T_2 \ (n-\pi^*)$ 

\(~72 \text{ kcal/mole}~\) 

$T_1 \ (\pi-\pi^*)$ 

\(54 \text{ kcal/mole}~\) 

**FIGURE 10**

ENERGY LEVELS OF 3-PHENYLCYCLOHEX-2-ENONE
PART II : CONCLUSIONS

The work described in this thesis is perhaps the first case of a detailed mechanistic study on the photochemistry of 3-phenylcyclohex-2-enone. It provides a fairly good picture of the mechanism of photoaddition of this enone to olefins, and a clear description of its excited electronic states.

Because of the low solubility of Michler's ketone in tert-butyl alcohol, a successful study of the effect of sensitizer concentration on the quantum yield of photoaddition could not be carried out. This type of study using a different sensitizer will answer the question whether the reverse energy-transfer from the enone to the sensitizer occurs or not.

Since only one adduct was formed in the enone-tetramethylethylene addition, a comparison of the product distribution in the unsensitized and sensitized processes was not possible. Such quantitative study using an olefin such as cis- or trans-hex-3-ene will be worthwhile to get a deeper insight into the nature of the 1,4-diradical that has been proposed.

Finally, although enormous amount of work has been done on the photochemistry of enones, there still remain factors unsolved and unexplained, baffling the chemist.
As remarked by one author \(^6b\), a pause cannot be called let alone a halt to enone additions, until sufficient is known to render these photochemical processes of tactical use in complex synthesis.
EXPERIMENTAL
Materials

All solvents and reagents for photoaddition reactions were distilled before use.

Cyclopentene (Aldrich Reagent) was distilled at atmospheric pressure under nitrogen, b. p. 44-45°C, and was used immediately. Bicyclo[2.2.1]hept-2-ene (norbornylene, Aldrich Reagent) was used without further purification. Tetramethylethylene (Columbia Organic Chemicals) was distilled through a 12" vigreux column under nitrogen, b. p. 72-73°C. It was redistilled through a 12" column packed with glass helices for quantitative studies. Cis- and trans- but-2-enes were obtained from Matheson, Coleman and Bell of Canada, Ltd.

4,4'-bis(dimethylamino)-benzophenone (Michler's ketone, Matheson, Coleman and Bell) crystallized twice from benzene was a pale yellow solid, m. p. 173-173.5°C. 2-acetonaphthone (Eastman Organic Chemicals) was crystallized from absolute ethyl alcohol, m. p. 53-53.5°C. Benzophenone, once crystallized from ethyl alcohol had m. p. 48-49°C. Biacetyl (Matheson, Coleman and Bell, chromatoquality reagent) distilled many times through a 6" vigreux column, b. p. 88-89°C was used immediately. Naphthalene (Baker Analyzed Reagent) was crystallized from ethyl alcohol, m. p. 80-81°C.

Tert-butyl alcohol was Baker Analyzed Reagent, b. p. 82.- 83°C. Methanol was Mallinckrodt Analytical Reagent,
b. p. 64.5-65°C. Benzene used for column chromatography was Mallinckrodt Analytical Reagent.

3-ethoxycyclohex-2-enone was prepared by the method of Cannon and House; the boiling point was 49-52°C at 0.075-0.1 mm/Hg (lit. 66-68.5°C at 0.4 mm/Hg). From this 3-phenylcyclohex-2-enone was prepared by the method of Woods and Tucker. Allen and Converse; the pale yellow solid was distilled (135-145°C at 1 mm/Hg), and the material was chromatographed on a silica gel column, and finally was crystallized from alcohol-petroleum ether (30-60°C). Tert-nitrobutane was prepared by the method of Kornblum et al., from which di-tert-butyl nitroxide was prepared by the method of Hoffman et al.; it was a deep red liquid, b. p. 52-54°C at 10 mm/Hg (lit. 60°C at 11 mm/Hg). Potassium ferrioxalate, K₃Fe(C₂O₄)₃, used in the actinometry, was prepared by the method of Parker et al.

Chromatography

Silica gel, Grace, Grade 923 (100-200 mesh) or MN-silica gel G (Macherey, Nagel and Co) was used for column chromatography. Thin layer chromatography was conducted using silica gel coated sheets with fluorescent indicator (Eastman Organic Chemicals) or MN-silica gel G with fluorescent indicator (Macherey, Nagel and Co) coated on glass plates. Analytical vapor phase chromatography (vpc) was performed on a Varian-Aerograph Model 204-B dual control
instrument, having flame ionization detectors. Peak areas were determined using Varian Model 476 Electronic Digital Integrator. The following columns were used using helium as the carrier gas at 30 ml/min:

- **Column A**: 5° x 1/8" 4% QF 1 on 60-70 Diatopert
- **Column B**: 3° x 1/8" 10% FFAP on 60-70 Chromosorb W

Preparative vpc was conducted on a Varian-Aerograph Model 200 dual control instrument with thermal conductivity detectors. The following columns were used with a helium flow of 60-70 ml/min.

- **Column C**: 10° x 1/4" 31% SE 550 on Firebrick
- **Column D**: 4° x 3/8" 20% FFAP on 45-60 Chromosorb W

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

Elemental analysis was by Spang Microanalytical Laboratory, Ann Arbor, Michigan.

**Spectra**

Nuclear magnetic resonance spectra were recorded with a Varian T-60, A-60 or HA-100 instrument; spectrograde carbon tetrachloride was the usual solvent with tetramethyasilane as the internal standard. Chemical shifts are given in parts per million (ppm) downfield from the standard.

Infrared spectra were run on a Beckman IR-5 or a Perkin-Elmer Model 337 instrument. Spectrograde carbon tetra-
chloride (Fisher "spectroanalyzed" grade) was the usual solvent.

Ultraviolet spectra were recorded with a Cary Model 14 spectrophotometer; 99% ethyl alcohol or methyl alcohol was the usual solvent, unless specified.

Mass spectra were run on a Hitachi-Perkin-Elmer MRU6A instrument.

Emission spectra were recorded with an Aminco-Bowman spectrofluorometer.

Optical density measurements for quantum yield determinations were performed using a Baush and Lomb precision spectrophotometer.

**Photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene**

A solution of 3-phenylcyclohex-2-enone (3.44 g; 0.02 mole) and tetramethylethylene (16.0 g; 0.19 mole) in tert-butyl alcohol (375 ml) and methanol (25 ml) was irradiated with a Hanovia Type L 450W medium pressure mercury arc lamp, fitted with a pyrex sleeve, placed in a water-cooled quartz immersion apparatus. The photolysis solution was deoxygenated by bubbling argon through the solution before photolysis; a slight positive pressure of argon was maintained during irradiation.

The reaction was about 95% complete in 5 hours as estimated by vpc analysis (column A, 185°C). The analysis showed the formation of a single product with a retention
time of 4 minutes. The solvent and the excess olefin were stripped off from the photolysis solution, when white granular crystals separated, in addition to a viscous oil. The residue was dissolved in ethyl alcohol, cooled in dry ice-acetone mixture, and the crystals were filtered and dried (1.75 g).

The filterate was concentrated and chromatographed through a 3 x 23 cms column packed with silica gel in benzene, and 200 ml fractions were collected. Fractions 1-5 were eluted with benzene; 6-10 with 0.5% ethyl acetate in benzene; 11-20 with 1.0%; 21-25 with 2.0%; 26- and 27 with 4.0%; and 28-30 with 8.0% ethyl acetate in benzene. Fractions 8-10 contained the photoadduct (36).

Photodimer of 3-phenylcyclohex-2-enone

1β,2α-diphenyl-7α,8β-tricyclo[6.4.0.0²⁷]dodeca-6,9-dione (12)

The white solid that separated (m. p. 190-197°C) was crystallized from ether-petroleum ether(30-60°). The crystals had the melting point of 200-201°C (lit14, 204-205°C). The spectroscopic results were consistent with the structure 12, the head-to-head cis-anti-cis dimer of the enone. Yield of the dimer based on the weight of the solid that separated was 50%.

1β-phenyl-7,7,8,8-tetramethyl-6β-bicyclo[4.2.0]oct-5-one (36)

Removal of solvent from the combined fractions 8-10 gave a yellow oil which was distilled through a short-path
distillation set-up (bath temp. 170-180°C at 0.3 mm/Hg). The colorless distillate solidified into a waxy solid when left in the freezer. After two sublimations under reduced pressure, the solid had a melting point, 57-60°C.

The vpc analysis (column A, 185°C) showed a single peak with retention time of 4 minutes. The infrared, nmr and mass spectra confirmed the structure of the adduct.

**Analysis:** Calculated for C\textsubscript{18}H\textsubscript{24}O: C, 84.38; H, 9.38. Found: C\textsubscript{o} 84.47; H, 9.50.

**Attempted equilibration of the adduct (36)**

The photoadduct (0.050 g; 0.0002 mole) was stirred with basic alumina (3.0 g) in ether (30 ml) for 40 hours at room temperature. The alumina was then removed by filtration, and the solution was concentrated to give an oil (0.050 g). The nmr, infrared, mass spectral and vpc analyses showed that there was no change in the compound after equilibration, confirming the cis- 4-6 ring fusion.

**Photostability of 36**

The photoadduct (0.1 g; 0.0004 mole) in tert-butyl alcohol (70 ml) and methanol (5 ml) was irradiated for 4 hours. The spectra of the material were identical to those of a non-irradiated sample of 36.

**Photoaddition of 3-phenylcyclohex-2-enone and cyclopentene**

Irradiation of 3-phenylcyclohex-2-enone (1.032 g; 0.006 mole) and cyclopentene (10.0 g; 0.15 mole) in tert-
butyl alcohol (375 ml) and methanol (25 ml) for 6 hours, resulted in the disappearance of about 95% of the enone, as estimated by vpc analysis (column B, 195°C). The analysis showed that two products of retention times 9.0 minutes (37) and 15.0 minutes (38) were formed in the ratio 90:7. The solvent was stripped off, and the residue (1.2 g) was chromatographed on a 3 x 39 cm column of silica gel slurry packed in benzene; 200 ml fractions were collected. Fractions 1-10 were eluted with benzene; 11-15 with 1% ethyl acetate in benzene; 16-20 with 2%; 21-25 with 4%. Fractions 16-19 contained the major photoadduct (37)

Identification of 37

Fractions were combined, concentrated, and the residue crystallized twice from 90% ethyl alcohol; m. p. 57-59.5°C (lit 47. 59.5-61°C). Snyder and McCullough 47 have assigned 37 as the cis-anti-cis 1:1 enone-cyclopentene adduct.

Thiosemicarbazone 39 of 37

Adduct 37 (0.350 g; 0.00146 mole), thiosemicarbazide (0.35 g; 0.00385 mole), sodium acetate (0.4 g), few drops of 15% hydrochloric acid were dissolved in ethanol:water (~25 ml). The solution was boiled, shaken vigorously at its boiling point, and let stand. White crystals separated on standing. The contents were cooled in an ice bath, the crystals filtered, and crystallized from 99% ethyl alcohol; m. p. 165.5-169°C.
Thin layer chromatography showed a single spot. The compound did not show any carbonyl absorption in the infrared. It showed a weak molecular ion peak at m/e 313. Determination of unit cell dimensions of a single crystal of 39 by X-ray diffraction measurements\(^5\)\(^3\) suggested cis-anti-cis configuration for 39, thereby confirming the same stereochemistry for the photoadduct 37.

Norbornene dimerization accompanying the photoaddition of 3-phenylcyclohex-2-enone and norbornene

A solution of 3-phenylcyclohex-2-enone (1.0 g; 0.0058 mole), and norbornene (18 g; 0.19 mole) in tert-butyl alcohol (55 ml) and methanol (5 ml) was irradiated in a Rayonet Photochemical Reactor containing sixteen RPR 3500 Å lamps. About 85% of the enone disappeared in 13 hours. The residue (~2 g) was chromatographed on a 3 x 15 cm column of silica gel slurry packed in benzene. Two 200 ml fractions were collected with benzene as the eluant. The norbornene dimers 42 and 43 (0.075 g) came off in these fractions. Vpc analysis (column B, 105°C) showed two peaks in the ratio 3:1. (retention times, 2.5 and 3.5 minutes). Endo-trans-exo dimer 42 was collected by preparative vpc (column D, 180°C). The dimer was a waxy solid with melting point 36-38°C (lit\(^5\)\(^5\), 38-39°C). The mass spectrum showed a molecular ion peak at m/e 188.
Norbornene dimerization sensitized by 36

A solution of 36 (0.2 g; 0.00078 mole), and norbornene (4 g; 0.043 mole) in tert-butyl alcohol (45 ml) and methanol (5 ml) was irradiated using 350 mλ lamps for 3 hours. Analysis by vpc (column B, 105°C) showed the formation of 42 and 43 in the ratio 9:1.

Low temperature photolysis of 3-phenylcyclohex-2-enone and cis-but-2-ene — Cis-trans isomerization of butene

A solution of 3-phenylcyclohex-2-enone (1.0 g; 0.0058 mole) in 99% ethyl alcohol (300 ml) in a photolysis vessel was degassed by bubbling argon for half an hour. The solution was cooled down to -15 to -12°C by surrounding the solution with freezing mixture. cis-but-2-ene (15 g; 0.27 mole) was then added to the solution and the mixture was irradiated for two and a half hours. About 10 ml of this photolysis solution was withdrawn and injected into an evacuated flask, and allowed to come to room temperature. The vapors in the flask were then drawn into a gas syringe, and analyzed by vpc (column C, 45°C), which showed the presence of about 9% of trans-but-2-ene. The reaction corresponded to about 21 conversion of enone, as estimated by vpc (column A, 190°C).

Triplet sensitized photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene

A solution of 3-phenylcyclohex-2-enone (0.129 g; 0.00075 mole) and tetramethylethylene (4.2 g; 0.05 mole) in
tert- butyl alcohol (total volume: 75 ml) was equally divided in three pyrex tubes. To one 25 ml of 0.005 M Michler's ketone in tert- butyl alcohol was added; to another was added 25 ml of 0.1 M 2-acetonaphthone. The volume in the third tube was made to 50 ml with tert- butyl alcohol. The solutions were deoxygenated with argon, mounted on a rotating turn-table, and irradiated with 350 m\(\mu\) lamps (sixteen) in a Rayonet Photochemical Reactor for one hour. The extent of conversion of the enone was determined by vpc (column A, 185°C).

**Isolation and identification of the product of the sensitized photoaddition**

A solution of 3-phenylcyclohex-2-enone (0.2 g; 0.00116 mole), tetramethylethylene (7.5 g; 0.089 mole), and Michler's ketone (0.075 g; 0.00028 mole) in tert- butyl alcohol (50 ml) was irradiated as described previously. The reaction was 85% complete in eight hours. The photolysis mixture was concentrated, and the residue was chromatographed as described in the direct irradiation. Vpc, nmr, infrared and mass spectroscopic analyses confirmed the product to be identical with 36.

A similar experiment was conducted with the enone (0.2 g; 0.00116 mole), tetramethylethylene (7.5 g; 0.089 mole) and 2-acetonaphthone (2.015 g; 0.0119 mole).
Sensitized photoaddition of 3-phenylcyclohex-2-enone and cyclopentene

A solution of 3-phenylcyclohex-2-enone (0.086 g; 0.0005 mole) and cyclopentene (3.3 g; 0.049 mole) in tert-butyl alcohol (total volume: 50 ml) was divided equally into two pyrex tubes. To one was added Michler's ketone (0.620 g; 0.0025 mole). The solutions were diluted to 50 ml with tert-butyl alcohol, and were irradiated as described previously, using 350 m\( \mu \) lamps for three hours. The extent of conversion was determined by vpc (column B; 195°C)

Determination of quantum yields of photoaddition of 3-phenylcyclohex-2-enone and olefins

The light source used was a Phillips 500 W high pressure mercury arc lamp giving directed radiation, placed at the focus (12 cm) of a quartz lens 11 cm in diameter. The lamp had provision for being cooled by circulating cold water. The appropriate wavelength band of the mercury arc spectrum was provided by using various combinations of filter solutions; these were contained in a cell divided into three compartments, each 11.7 cm in diameter and 5 cm in path-length (capacity 575 ml), and were cooled internally with a cooling coil. The compartments were separated, and the ends covered with quartz discs gasketed with neoprene rings. The filter solutions used were different for various quantum yield determinations, and hence the details will be discussed wherever necessary.
For quantum yield measurements, a cell with two compartments, separated and the ends gasketed by quartz discs were used. These compartments were also cooled internally with a cooling coil, and also had similar dimensions as the ones for filter solutions. In addition, the front compartment had provision for bubbling argon for deoxygenation purposes and for inserting a thermistor probe for controlling temperature of the contents.

The temperature of the photolysis solution was maintained at the required level using a Thermistemp Temperature Controller - Model 63. The system could be preset to any required temperature, and the photolysis solution could be maintained at that temperature by immersing the thermistor probe in it; hot and cold water were circulated alternately automatically so that the preset temperature was maintained.

The amount of the enone-olefin adducts was determined by vpc using appropriate internal standards. The calibration of the internal standard was done by using known ratios of the internal standard and the adduct, and measuring the areas of the vpc peaks.

Actinometry (measurement of the amount of light absorbed) was performed with potassium ferrioxalate system. The com-

Ferrioxalate actinometry is based on the autooxidation-reduction of ferrioxalate anion induced by light; the details are described by Hatchard and Parker. The com-

\[ \text{CO}_3^{2-} \xrightarrow{hv} \text{CO}_2 + \text{CO} + e^{-1} \quad \text{Fe}^{3+} + e^{-1} \rightarrow \text{Fe}^{2+} \]
centration of potassium ferrioxalate to be used depended on the wavelength, and hence would be given wherever required.

Each quantum yield determination required three irradiations: the first with only the actinometer present; the second with both the actinometer and photolysis solutions; and the third same as the first. In the first and the last irradiations, the actinometer solution was placed in the first compartment of the photolysis cell; and in the middle irradiation, the photolysis solution was placed in the first, and the actinometer solution in the second. The first and the third irradiations, which generally differed by less than 5% were used to calculate the light output of the lamp, which was used to determine the total amount of light incident on the photolysis solution. The amount of light transmitted by it was calculated from the change in the actinometer solution in the second compartment during the second irradiation. Fresh actinometer solutions were used for each irradiation. Both the photolysis and actinometer solutions were stirred mechanically during irradiation.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene

The filter combination used in these determinations is described in table 10. This combination had maximum transmittance of 35% at 330 mμ; and 0% at 285 mμ and 375 mμ. A small amount of light (ca. 0.3% T) was transmitted at 430 mμ.
It was found that the transmission property of the cobalt-nickel solution was unaffected by prolonged irradiation; the stannous chloride solution, however, had to be freshly prepared prior to each quantum yield determination.

**TABLE 10**

**FILTER SOLUTION FOR ISOLATION OF 330 m\(\mu\) REGION OF THE Hg ARC SPECTRUM**

<table>
<thead>
<tr>
<th>Compartment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Pyrex</strong></td>
<td>CoSO(_4).7 H(_2)O (160 g)</td>
<td>SnCl(_2).2 H(_2)O (1.6 g)</td>
<td>Distilled water</td>
</tr>
<tr>
<td><strong>Plate</strong></td>
<td>NiSO(_4).6 H(_2)O (60 g)</td>
<td>per liter of 15% HCl</td>
<td>per liter of 3N H(_2)SO(_4)</td>
</tr>
<tr>
<td><strong>Dimensions</strong></td>
<td>3 mm</td>
<td>5 cm</td>
<td>5 cm</td>
</tr>
</tbody>
</table>

Quantum yields were measured for 3-phenylcyclohex-2-enone (0.005 M) and tetramethylethylene (0.33 M) in tert-butyl alcohol. A value of 1.23 was assumed as the quantum efficiency of the decomposition of ferrioxalate\(^{96} \), in calculating the amount of light absorbed by the enone. Benzophenone was used as the internal standard for estimating the amount of adduct, \(36 \) \(\mu\) formed.

In a typical run, the photolysis solution was irradiated for 200 minutes, during which time the enone absorbed 13.9 m\(\)einstein of light, and 0.0789 g (0.3084 mm\(\)ole) of
36 was formed, thus leading to a quantum yield of 0.0222 mole/einstein. The results are given in table 2a.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and cyclopentene

The same filter combination as described in the previous experiment was used for this determination. The amount of 37 was estimated by vpc (column B, 195°C) using p-bromobenzophenone as the internal standard. A quantitative recovery of the adduct was also achieved by column chromatography, which was in agreement with the vpc analysis.

In a typical run, a solution of enone (0.580 g; 0.00337 mole) and cyclopentene (32.7 g; 0.495 mole) in methanol (total volume: 575 ml) was irradiated for 180 minutes leading to the absorption of 15.5 m.einsteins of light, and to the formation of 0.102 g (0.000425 mole) of 37. The quantum yield was 0.0274.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene sensitized by Michler's ketone

The filter combination used for this determination is described in table 11. The transmission spectrum showed a maximum at 350 mµ (26%), and zero transmittence at 325 mµ. It showed a weak transmission (ca 0.5%) from 390-425 mµ, beyond which no light was transmitted.
TABLE 11

FILTER SOLUTION FOR ISOLATION OF 350 m\(\mu\) REGION
OF THE Hg ARC SPECTRUM

<table>
<thead>
<tr>
<th>Compartment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
</table>
| pyrex plate | CoSO\(_4\).7\(\text{H}_2\text{O}\) (160 g) | SnCl\(_2\).2\(\text{H}_2\text{O}\) | Distilled
| NiCO\(_4\).6\(\text{H}_2\text{O}\) (12 g) | saturated | water |
| per liter of 0.1 N\(\text{H}_2\text{SO}_4\) in 15\% HCl | 3 mm | 5 cm | 5 cm |

For quantum yield measurements, a solution of 3-phenylcyclohex-2-enone (0.005 M), tetramethylethylene (0.33 M), and Michler's ketone (0.0024 M) in tert-butyl alcohol was photolyzed. The amount of light absorbed by the enone was calculated to be less than 2\%. In a typical run, 30.56 m.einsteins of light were absorbed during 315 minutes of irradiation; and 0.049 g (0.000193 mole) of 36 was formed. The quantum yield thus was 0.00625.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene sensitized by 2-acetonaphthone

The filter combination was the same as described for Michler's ketone sensitized photoaddition (table 11). The photolysis solution was 0.005 M in the enone and 0.33 M in tetramethylethylene, and 0.05 M in 2-acetonaphthone in tert-
butyl alcohol. The irradiation was conducted for 210 minutes.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene sensitized by biacetyl

Biacetyl has n-π* absorption in the 435 m\(\mu\) region, and the following filter combination (table 12) was used for biacetyl sensitized photoaddition of 3-phenylcyclohex-2-enone and olefins.

**TABLE 12**

FILTER SOLUTION FOR ISOLATION OF 430 m\(\mu\) REGION OF THE Hg ARC SPECTRUM

<table>
<thead>
<tr>
<th>Compartment</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyrex</td>
<td>CuSO(_4) 5 H(_2)O (8.8 g)</td>
<td>NaNO(_2) (150 g)</td>
<td>Distilled</td>
</tr>
<tr>
<td></td>
<td>plate per liter of 2.7 M</td>
<td>per liter of aq. NH(_3)</td>
<td>water H(_2)O</td>
</tr>
<tr>
<td>3 mm</td>
<td>5 cm</td>
<td>5 cm</td>
<td>5 cm</td>
</tr>
</tbody>
</table>

The filter combination had maximum transmittance at 430 m\(\mu\) (70%) and zero transmission at 405 m\(\mu\) and 505 m\(\mu\). A solution of 0.05 M potassium ferrioxalate was used for actinometry, and a value of 1.03 was assumed for the quantum efficiency of the photodecomposition of ferrioxalate. During 240 minutes of irradiation of a solution of biacetyl (0.1 M),
3-phenylcyclohex-2-enone (0.005 M) and tetramethylethylene (0.33 M) in tert-butyl alcohol, the sensitizer absorbed 66.0 m.einsteins of light. Vpc analysis (column A, 185°C) showed the formation of two products with retention times 2.0 and 2.3 minutes. Very little (ca. 0.5%) photoadduct was detected.

Quantum yield of photoaddition of 3-phenylcyclohex-2-enone and cyclopentene sensitized by biacetyl

The filter combination was the same as described for the previous experiment. The photolysis solution was 0.00575 M in enone, 0.835 M in cyclopentene, and 0.174 M in biacetyl. During 180 minutes of irradiation, biacetyl absorbed 56.64 m.einsteins of light, and 0.196 g (0.00082 mole) of 37 was formed, thus leading to a quantum yield of 0.0142.

Effect of the concentration of tetramethylethylene on the quantum yield of photoaddition

Relative quantum yields of photoaddition were measured using a Rayonet® Photochemical Reactor with sixteen RPR 3500 Å lamps, and a turn-table arrangement by which many photolysis tubes could be rotated during irradiation. 23 x 2.5 cm pyrex tubes were used for photolysis. Exactly 50 ml solutions were taken in those tubes, such that each solution was 0.005 M in enone, and different concentrations (0.05, 0.10, 0.20, 0.33, 1.00, and 2.00 M) in tetramethylethylene. The solutions were then deoxygenated by three
cycles of freeze-pump-thaw method, and the tubes were sealed under nitrogen. They were then mounted on the turn-table, and were rotated during irradiation. The time of irradiation was so chosen as to give a good range of conversion in those tubes. The amount of photoadduct (36) in each tube was determined by vpc, using benzophenone as the internal standard. Since all the tubes were of same dimensions and contained exactly same volume of solution, and the concentration of the enone was the same in all, it was assumed that the light absorbed in each tube was the same, so that the amount of product was proportional to the quantum yield.

The absolute quantum yields could be determined using the known value of 0.0222 for 0.005 M enone and 0.33 M tetramethylethylene.

**Effect of concentration of tetramethylethylene on the quantum yield of photoaddition sensitized by Michler's ketone**

The general procedure of measurements has been described for the previous experiment. All tubes contained exactly 50 ml of photolysis solutions, 0.005 M in enone, 0.0024 M in Michler's ketone, and various concentrations (0.15, 0.20, 0.25, 0.33, 0.50 and 1.00 M) in tetramethylethylene. A value of 0.006 for the quantum yield for 0.33 M tetramethylethylene and 0.005 M enone was used to calculate the absolute quantum yields for other olefin concentrations.
Quenching of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene by naphthalene

The filter combination has been described in table 10. A solution of 3-phenylcyclohex-2-enone (0.005 M), tetramethylethylene (0.33 M) and naphthalene (0.10 M) in tert-butyl alcohol (575 ml) was irradiated for 220 minutes. Actinometry indicated that 20.22 m.einsteins of light were absorbed, during which time 0.073 g (0.000285 mole) of 36 was formed. The quantum yield thus was calculated to be 0.0142.

Quenching of photoaddition of 3-phenylcyclohex-2-enone and tetramethylethylene by di-tert-butyl nitroxide - effect of quencher concentration on the quantum yield

The relative quantum yields for various concentrations of di-tert-butyl nitroxide (enone: 0.005 M, tetramethylethylene: 0.33 M) were measured. The concentrations of the quencher were 0.001, 0.002, 0.0034, 0.004, 0.0046 and 0.005 M. The absolute quantum yields were computed by irradiating simultaneously a sample without quencher. The quantum yields and the Stern-Volmer plot are given in the Results section.

Effect of concentration of tetramethylethylene on the quantum yield of photoaddition in presence of the quencher

The quantum yields for various concentrations of tetramethylethylene (0.25, 0.33, 0.50, 0.66 and 1.00 M) and 0.005 M 3-phenylcyclohex-2-enone, in presence of 0.001 M di-tert-butyl nitroxide, were measured. A value of 0.00819
for 0.33 M tetramethylethylene was used to calculate the absolute quantum yields.

**Phosphorescence spectra**

All phosphorescence spectra were measured in ethanol:ether (2:1) at 77°C. The data are reported in the Results section.

The phosphorescence excitation and emission spectra of 3-phenylcyclohex-2-enone and of naphthalene were measured. It was attempted to sensitize naphthalene phosphorescence by the enone. For this a solution of enone (1.2 mg per ml) and naphthalene (2.4 mg per ml) was used (excitation: 350 mμ). The reverse sensitization was also studied by irradiating naphthalene in the mixture (excitation: 310 mμ). The excitation spectrum was also measured.

Biacetyl emits both fluorescence and phosphorescence in solution at room temperature. The emission and excitation spectra were measured in deoxygenated methanol solutions.

**Fluorescence spectra**

All fluorescence spectra were measured in deoxygenated ethanol or methanol solutions at room temperature.

Our attempts to measure the fluorescence of 3-phenylcyclohex-2-enone were unsuccessful. A weak emission was detected from 3-phenylcyclopent-2-enone.

It was attempted to sensitize the emission of biacetyl using 3-phenylcyclohex-2-enone. For this a solution of
enone (0.01 M) and biacetyl (0.3 M) in methanol was used, and was not deoxygenated. The fluorescence excitation spectrum was also measured, monitoring the fluorescence maximum of biacetyl (464 m\(\mu\)).
APPENDICES
Reversible intersystem crossing - steady-state kinetic treatment

\[ E_0 \xrightarrow{h\nu} E^1 \xleftarrow{\kappa_{ic}} \xrightarrow{\kappa_{ic}} E^3 \xrightarrow{\kappa_d} E_0 \]

\[ E_0 \xrightarrow{\kappa_d} k_r[0] \xrightarrow{\kappa_{ic}} [E-O]^* \xrightarrow{\kappa_{cle}} [E-O] \xrightarrow{\kappa_{cyc}} Adduct \]

\[
\frac{d[\text{Adduct}]}{dt} = k_{cyc} [E-O] \tag{1}
\]

\[
\frac{d[E-O]}{dt} = \frac{d[E-O]^*}{dt} = k_r[0][E^1] - k_{cyc}[E-O] - k_{cle}[E-O] = 0
\]

\[
[E-O] = \frac{1}{k_{cyc} + k_{cle}} \cdot k_r[0][E^1] \tag{2}
\]

\[
\frac{d[E^1]}{dt} = 1 + k_{ic}[E^3] - k_{ic}[E^1] - k_d[E^1] - k_r[0][E^1] = 0
\]

\[
[E^1] = \frac{1}{k_{ic} + k_d + k_r[0]} \cdot k_{ic}[E^3] \tag{3}
\]

\[
\frac{d[E^3]}{dt} = k_{ic}[E^1] - k_{ic}[E^3] - k_d^2[E^3] = 0
\]

\[
[E^3] = \frac{k_{ic}[E^1]}{k_{ic} + k_d^2} \tag{4}
\]

Combining (3) and (4)

\[
[E^3] = \frac{1}{[k_{ic} + k_d^3]} \cdot \frac{k_{ic}[E^1]}{[(k_{ic} + k_d^3)(k_{ic} + k_d^3)] - k_{ic} k_{ic}} \tag{5}
\]
Combining (1), (2) and (5)

\[
\frac{d[\text{Adduct}]}{dt} = p \cdot \frac{I (k_{ic} + k_{dc}^3) k_r[0]}{[(k_{ic} + k_{dc}^1 + k_r[0])(k_{ic} + k_{dc}^3) - k_{ic} k_{ic}]} 
\]

where

\[ p = \frac{k_{cyc}}{k_{cl} + k_{cyc}} \]

\[
\phi_{\text{adduct}} = \frac{d[\text{Adduct}]}{dt} / I = \frac{(k_{ic} + k_{dc}^3) k_r[0]}{[(k_{ic} + k_{dc}^1 + k_r[0])(k_{ic} + k_{dc}^3) - k_{ic} k_{ic}]} 
\]

\[
\frac{1}{\phi} = \frac{1}{p} \left[ 1 + \left( \frac{k_{ic} + k_{dc}^1 - k_{ic} k_{ic}}{k_{ic} + k_{dc}^3} \right) \frac{1}{k_r[0]} \right] 
\]

The concentration plot (\(\phi^{-1}\) versus \([0]^{-1}\)) will be linear.

This can explain the experimentally obtained apparent long lifetime of the excited state of enone, as follows.

\[
\frac{\text{slope}}{\text{intercept}} = \frac{1}{k_r} \left( \frac{k_{ic} + k_{dc}^1 - k_{ic} k_{ic}}{k_{ic} + k_{dc}^3} \right) 
\]

\[
= \frac{1}{k_r} \left( \frac{k_{ic} k_{ic}}{\tau_{E1}^{-1} - \tau_{E3}^{-1}} \right) = \frac{\tau_{E1}(\text{app})}{k_r} 
\]

i.e.

\[
\tau_{E1}^{-1}(\text{real}) - \frac{k_{ic} k_{ic}}{\tau_{E3}^{-1}} = \tau_{E1}^{-1}(\text{app}) 
\]

In presence of a quencher \([Q]\), assuming both the \(E^1\) and \(E^3\) are quenched, the quantum yield is given by

\[
\phi = p_o \left[ \frac{(k_{ic} + k_{dc}^3 + k_{dc}(Q)) k_r[0]}{[(k_{ic} + k_{dc} + k_r[0] + k_{dc}(Q))(k_{ic} + k_{dc} + k_{dc}(Q)) - k_{ic} k_{ic}]} \right] 
\]
and, the Stern-Volmer expression is given by

\[
\frac{\phi_o}{\phi_q} = \left[ \left( \frac{1}{\tau_{E1}^3 + k_{r}[0]} + \frac{k_q^1}{\tau_{E3}^3 + k_q^3} \right) - \frac{k_{-ic}k_{ic}}{\tau_{E3}^3 - k_{-ic}k_{ic}} \right] \frac{1}{\tau_{E3}^3 + k_q^3}
\]

This expression is of the type, \( a + b[Q] + \frac{1}{C[Q] + d} \), and hence a plot of \( \phi_o/\phi \) versus \( [Q] \) will not be linear.
Reversible energy-transfer from the sensitizer - steady-state kinetic treatment

\[
S_0 \xrightarrow{hv} S^1 \xrightarrow{i} S^3 \xrightarrow{k_t[E]} E^3 \xrightarrow{k_r[0]} [E-O]^* \xrightarrow{k_{cyc}} [E-O] \xrightarrow{k_{cle}} \text{Adduct}
\]

\[
\frac{d[\text{Adduct}]}{dt} = k_{cyc}[E-O] \tag{1}
\]

\[
\frac{d[E-O]}{dt} = k_r[0][E^3] - k_{cyc}[E-O] - k_{cle}[E-O] = 0
\]

\[
[E-O] = \frac{1}{k_{cyc} + k_{cle}} \cdot k_r[0][E^3] \tag{2}
\]

\[
\frac{d[E^3]}{dt} = k_t[E][S^3] - k_{-t}[E^3][S] - k_d[E^3] - k_r[0][E^3] = 0
\]

\[
[E^3] = \frac{k_t[E][S^3]}{k_{-t}[S] + k_d + k_r[0]} \tag{3}
\]

\[
\frac{d[S^3]}{dt} = I - k_d[S^3] - k_t[E][S^3] + k_{-t}[S][E^3] = 0
\]

\[
[S^3] = \frac{I + k_{-t}[S][E^3]}{k_d + k_t[E]} \tag{4}
\]

Combining (3) and (4),

\[
[E^3] = \frac{k_t[E]I}{(k_{-t}[S] + k_d + k_r[0])(k_d + k_t[E]) - k_t k_{-t}[E][S]} \tag{5}
\]
Combining (1), (2), (5), and \( \phi = \frac{d[\text{Adduct}]}{dt} / I \)

\[
\phi = p \frac{k_1 k_t [0] [E]}{(k_d + k_1 [0])(k_d' + k_t [E]) - k_d k_t [S]}
\]

where \( p = \frac{k_{cyc}}{k_{cyc} + k_{cle}} \)

\[
\frac{1}{\phi} = \frac{1}{p} \left[ \left(1 + \frac{k_d}{k_f [0]} \right) \left(1 + \frac{k_d'}{k_t [E]} \right) + \frac{k_d' k_t [S]}{k_f k_t [0] [E]} \right]
\]

A plot of \( \phi^{-1} \) versus \([0]^{-1}\) for this mechanism will be linear as follows

\[
\text{slope} = \frac{1}{p} \left( \frac{k_d}{k_f} + \frac{k_d' k_t [S]}{k_f k_t [E]} \right), \text{ and \ Intercept} = \frac{1}{p}
\]

From the experimentally obtained values of slope and intercept,

\[
\frac{\text{slope}}{\text{intercept}} = \frac{k_d}{k_f} + \frac{k_d' k_t [S]}{k_f k_t [E]} \approx 2.4, \quad (6)
\]

This ratio for the unsensitized process is \( \frac{k_d}{k_f} \approx 0.42 \) \( (7) \)

(6) - (7), \( \frac{k_d' k_t [S]}{k_f k_t [E]} \approx 2 \) \( (8) \)

\[\text{Since the experimental intercepts for the unsensitized and sensitized processes were the same within experimental error, it is assumed that } 1 + k_d'/k_t [E] \text{ is close to unity.}\]
Substituting the values for [S], [E], \( k_r \) and \( k_d \):

\[
\frac{k_{-t}}{k_t} \sim 1 \text{ to } 10
\]

\[\phi\]

\([E] = 0.005 \text{ M}\]

\([S] = \text{[Michler's ketone]} = 0.0024 \text{ M}\]

\(k_r = 2.3 \times 10^6 \text{ liter/mole.sec.}\)

A value of \(10^6\) to \(10^7\) sec\(^{-1}\) is assumed for \(k_d\). (references 82 and 83).
Mass spectrum of the photodimer (12) of 3-phenylcyclohex-2-enone
Mass spectrum of 3-phenylcyclohex-2-enone - tetramethylethylene photoadduct (36)
Mass spectrum of the thiosemicarbazone (39) of 3-phenylcyclohex-2-enone - cyclopentene photoduct.
Mass spectrum of the exo-trans-endo dimer (42) of norbornene


43. See Table I, reference 6b.


53. C. Calvo, private communication.


b. See references 187-192 and 221-223 of 56a.


c. footnote 11 and reference 12 of 57b.

d. See, however, Caldwell's paper.


65. See reference 3b, p. 9.


74. See footnote 13, reference 6b.


c. See, for a recent review, reference 56a, p. 259.


