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THE PHOTOCHEMICAL AND THERMAL REACTIVITY
OF SELECTED MEDIUM-RING KETONES AND OLEFINS.

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THE PHOTOCHEMICAL AND THERMAL REACTIVITY
OF SELECTED MEDIUM-RING KETONES AND OLEFINS

DISSERTATION
Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By
Richard Frank Eizember, B.S., M.S.

* * * * *

The Ohio State University
1969

Approved by

[Signature]
Adviser
Department of Chemistry
DEDICATION

This thesis is dedicated to my wife, Toni, my daughter, Laura Ellen, and to my parents, Mr. and Mrs. Frank R. Eizember.
ACKNOWLEDGMENT

I would like to acknowledge the guidance of Dr. Leo A. Paquette, my adviser, during the past four years and the assistance of my wife, Toni, in the typing of this thesis.
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INTRODUCTION

Due to the diversity of the subject material, the contents of this dissertation have been organized into three general sections.

The first section, "The Photochemistry of 3-Cycloheptenones", deals with the photoreactivity of \( \beta,\gamma \)-unsaturated ketones.

In the second section, "The Photochemistry of Medium-Ring Cyclopropyl Ketones and Their Methylene Analogs", a large variety of cyclopropyl ketones were synthesized and their photochemical behavior was studied. Additionally, methylene analogs were synthesized and their photochemistry was studied.

"The Pyrolysis of Medium-Ring Cyclopropyl Ketones and Their Methylene Analogs", is the subject of the third section. A series of ketones and their methylene analogs were pyrolyzed in the vapor state and their resulting chemistry was studied.
PART I

PHOTOCHEMISTRY OF 3-CYCLOHEPTENONES

Introduction

Spectroscopic measurements of \( \beta, \gamma \)-unsaturated ketones have indicated an enhancement of the \( n - \pi^* \) absorption generally associated with the homoconjugated carbonyl chromophore.\(^1\) The extent of such interaction between the carbonyl function and the double bond appears to be dependent upon the orientation of the two groups, since varying degrees of \( \pi \)-overlap are geometrically possible. Thus, upon irradiation, one could expect to see characteristic photochemical reactions either of the double bond, the carbonyl group, or the composite of the homoconjugated carbonyl chromophore.

Before photochemical investigations into the reactivity of homoconjugated ketones began in this laboratory, several isolated reports concerning the light-induced rearrangements of \( \beta, \gamma \)-unsaturated ketones had appeared in the literature. One of the earlier published studies is due to Büchi and Burgess.\(^2\) These authors pos-
tulated cleavage of the allylic bond adjacent to the carbonyl function followed by rebonding at the alternate terminus of the allylic radical system to account for the product observed. Investigating an analogous case, Criegee and Furrer\textsuperscript{3} rationalized their product formation by reiterating the mechanism postulated by Büchi and Burgess.

The behavior of dehydronorcamphor was investigated by Schuster and coworkers.\textsuperscript{4} The initially produced bicyclic ketone

underwent further photolysis to yield cyclopentadiene and ketene as the photoreaction products. This fact was established simultaneously and independently by Schenck and Steinmetz.\textsuperscript{5}

An early study described the photochemical equilibration
of a $\beta$,Y-cycloalkenone to a $\gamma$,6-cycloalkenone. The decarbonylation of a homoconjugated ketone was reported by Starr and Eastman.

Two studies on acyclic $\beta$,Y-unsaturated ketones were completed recently. Yang and Thap investigated the photochemistry of isomesityl oxide and isolated about 60% of a cyclobutanol derivative (Norrish Type II product) and about 25% of products derivable from recombination of various radical fragments. Kiefer and Karlsson studied the photolysis of the closely related 2,3,3-trimethyl-1-penten-4-one molecule and observed analogous results, viz. 55% cy-
clobutanol formation and 32\% of products arising from initial \(\alpha\)-cleavage of the allylic bond adjacent to the carbonyl function.

To further continuing interest in the transannular phenomena

\[
\begin{align*}
\text{hv} & \quad \text{hv} + \text{CH} \rightarrow \text{CH}CHCH=CHCH\rightarrow \text{HO} \\
\text{vpc} & \quad \text{vpc} + \text{CH}_3 \text{OCH}_2 \text{CH}=\text{CHCH}=\text{CH}_2 \\
\end{align*}
\]

of medium-sized rings in this laboratory, a photochemical investigation of the reactivity of \(\beta,\gamma\)-unsaturated ketones began initially with the study of 3-cyclooctenones. The photolabile parent compound rearranged upon irradiation by way of an initial Norrish Type I cleavage followed by transannular rebonding with the formation of 2-vinyl-cyclohexanone and by hydrogen abstraction with the formation of 5,7-octadienal. The 7-oxa-analog of 3-cyclooctenone led to the formation of analogous products. The photochemical results with 3-cyclo-
octenone were confirmed independently by Crandall and coworkers.\textsuperscript{10}

The next logical step in a photochemical investigation of transannular phenomena in medium-sized ring ketones would be to study the 3-cycloheptenone series, which is the topic of the following discussion.

**Results**

Investigation of the photochemical reactivity of 3-cycloheptenones was initiated in anticipation of finding transannular interactions similar to those observed in the 3-cyclooctenone series. In an effort to enhance the reactivity of the homoconjugated 3-cycloheptenones and stabilize the initially formed Norrish Type I diradical, two specific molecules were synthesized and studied: 2,2-dimethyl-3-cycloheptenone (6) and 2,2,7,7-tetramethyl-3,5-cycloheptadienone (8b).

2,2-Dimethyl-3-cycloheptenone (6). The molecule first chosen to initiate investigation into the photo-induced reactivity of 3-cycloheptenones was 2,2-dimethyl-3-cycloheptenone (6). This mole-
cule was easily prepared by reacting one molar equivalent of 2-cyclo-
heptenone (5) with two molar equivalents of both potassium \( \mathbf{\varepsilon} \)-butoxide
and methyl iodide according to established procedures.\(^{10}\) Irradiation

\[
\begin{array}{c}
\text{6} \\
\text{hv} \\
\text{7}
\end{array}
\]

of a dilute ether solution of 6 with a 450-w water-cooled Hanovia
quartz immersion lamp equipped with a Corex filter was monitored
by removal of microliter aliquots at preselected intervals and ex-
amination of these by vapor phase chromatography (vpc). After ap-
proximately four hr, a photostationary state appeared to have been
reached with the appearance of a lone volatile photoproduct (7).
The ratio of 7:6 was slightly larger than 4:1. Preparative scale
vpc yielded pure 7 which was identified as 2-isobutenylcyclopenta-
none on the basis of elemental analysis and spectral data.

The ultraviolet spectral data of photoisomer 7 showed ab-
sorption maxima in isooctane at 295(80), 310(90), 325(70), and 335
nm (\( \varepsilon 25 \)), which are characteristic of the enhanced \( \pi - \pi^* \) absorp-
tion of \( \beta, \gamma \)-unsaturated ketones. The infrared spectrum in carbon
tetrachloride indicated a cyclopentanone carbonyl (1750 cm\(^{-1} \)) and
a nonconjugated olefin (1670 cm\(^{-1} \)). The most useful spectral data
was that derived from nmr: doublet of septuplets centered at 64.90
(lone vinyl proton); slightly broadened singlets at 61.76 and 1.68
(methyl groups attached to \( \text{sp}^2 \)-hybridized carbon on the basis of
their chemical shifts); broad multiplet at δ3.0 (allylic α-carbonyl proton); and a broad absorption at δ1.25-2.5 (six methylene protons).

From the spectral data and the fact that 7 exists in equilibrium with 6, it was clear that the 2-isobutenylcyclopentanone structure represented a unique fit. The observation of the equilibrium between 2 and 3 was substantiated by resubmission of pure 3 to the photoreaction conditions. The 4:1 equilibrium of 7:6 was rapidly reestablished.

At this point, it should be mentioned that the two methyl groups were originally introduced α to the carbonyl to assist in the stabilization of the 2-vinylcyclopentanone derivative if such a molecule were produced. In contrast to simple 2-vinylcyclohexanone and 2-vinylcyclooctanone derivatives which are rapidly isomerized into conjugation during attempted purification by vpc, 11,12 7 was found to be completely stable to such conditions indicating that such substitution had accomplished its intended purpose.

A study of the multiplicity of the photoreaction was essential to a better understanding of the mechanistic details, and thus, both quenching and sensitization studies were initiated. Irradiation of 6 in ether solution containing piperylene and in neat piperylene (mixture of cis and trans isomers) was studied (see Table 1). The ultraviolet spectra of both piperylene and 6 indicates that piperylene was absorbing only a minimal amount of incident irradiation. Corex optics (absolute cutoff is at 2580 Å) were utilized. The results as indicated in Table 1 show that the photolysis of 6 is not
TABLE 1

Representative Time and Percentage Composition Values

for the Photorearrangement of

2,2-Dimethyl-3-cycloheptenone (6)\(^a\)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, min</th>
<th>Photolysate compn, %(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>6</td>
</tr>
<tr>
<td>Ether</td>
<td>30</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>22</td>
</tr>
<tr>
<td>Ether (0.16 M in added benzophenone)</td>
<td>60</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>49</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>11</td>
</tr>
<tr>
<td>Acetone(^d)</td>
<td>60</td>
<td>82</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>14</td>
</tr>
<tr>
<td>Ether (containing 33% by volume of piperylene)</td>
<td>60</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>24</td>
</tr>
<tr>
<td>Piperylene</td>
<td>60</td>
<td>41</td>
</tr>
</tbody>
</table>

\(^a\) All runs were performed with a 450-w Hanovia immersion lamp fitted with a Corex (absolute cutoff point 2580 \(\AA\)) filter.

\(^b\) Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are free of all normalization.

\(^c\) The concentration of benzophenone was such that this ketone was absorbing approximately 85\% of the incident light.

\(^d\) Acetone was absorbing greater than 95\% of the incident radiation.
quenched by piperylene \( (E_{T}^{\text{trans}} = 59 \text{ kcal/mole, } E_{T}^{\text{cis}} = 57 \text{ kcal/mole}) \).  

Both acetone \( (E_{T} = 82 \text{ kcal/mole}) \) \(^{14,15}\) and benzophenone \( (E_{T} = 68.5 \text{ kcal/mole}) \) \(^{13,14}\) failed to sensitize the photorearrangement of 6 (see Table 1). Thus, irradiation through Corex of an ether solution of 6 containing sufficient benzophenone to absorb >85% of the incident light resulted in a substantial reduction in the rate of formation of 7. Irradiation of 6 in acetone under conditions where the concentration of acetone was sufficiently high to absorb greater than ~95% of the incident light likewise diminished the rate of formation of 7. In this latter experiment, however, significant quantities of 6 (and perhaps also 7) appeared to be slowly destroyed by polymer formation as the reaction time was continued.

\[ \text{2,2,7,7-Tetramethyl-3,5-cycloheptadienone.} \] The generality of valence-bond isomerization of 1,3-cycloheptadiene derivatives, whether carbocyclic\(^{16}\) or heterocyclic,\(^{17}\) when exposed to ultraviolet irradiation is well known. However, two 3,5-cycloheptadienones have proved to be exceptions to the above generality.\(^{18}\) When 8a and

\[
\begin{align*}
\text{8a, } R &= \text{H} \\
\text{8b, } R &= \text{CH}_3 \\
\text{9a, } R &= \text{H} \\
\text{9b, } R &= \text{CH}_3
\end{align*}
\]
$8_b$ were photolyzed in ether solution with a broad-spectrum lamp in Pyrex vessels, carbon monoxide and the isomeric trienes $9_a$ and $9_b$ were produced. This unconventional behavior (cyclic ketones do not usually undergo photodecarbonylation in solution\textsuperscript{19}) was attributed to the noncoplanarity of the diene moiety allowing the molecule to behave as an unconjugated diene.\textsuperscript{18} Mislow and Gordon\textsuperscript{20} contradicted by showing that the two double bonds of $8_a$ or $8_b$ are stereochemically and spectroscopically equivalent due to the axis which passes through the carbonyl group and is two-fold symmetric with respect to either the entire molecule or the dienone chromophore.

Schuster and coworkers\textsuperscript{21} studied the multiplicity of this reaction and found that the photodecarbonylation of $8_a$ results exclusively from reaction through the singlet excited state. In striking contrast, the sensitized photolysis of $8_a$, which necessarily proceeds through the triplet state, yields only the valence bond isomer $10$.

The photochemical study of 2,2,7,7-tetramethyl-3,5-cycloheptadienone ($14$) was initiated to elucidate further the details of these phenomena. The inherent $C_2$ symmetry, the structural similarity to $2$, and the secondary steric requirements of $14$, all lend additional parameters to the mechanistic pathway of the photoreaction.
The preparation of 14 was readily realized by treating 1 with a two molar ratio of bromine to form 2,7-dibromocycloheptanone ethylene ketal (11) which without purification was reacted directly with sodium hydroxide in methanol to yield 2,6-cycloheptadienone ethylene ketal (12). Hydrolysis of 12 was accomplished with dilute sulfuric acid to yield 2,6-cycloheptadienone (13), which was then reacted with greater than four molar equivalents of both potassium t-butoxide and methyl iodide.

A dilute solution of 14 in ether was irradiated with a 450-w Hanovia immersion lamp equipped with Vycor optics and one major photoproduct was detected by vpc. Isolation of the isomeric photoproduct (15) was accomplished by preparative vpc; spectral data and
vpc retention times proved the photoproduct to be identical in all respects to an authentic sample of pure 3-methyl-4-caren-2-one (15). Figure 1 illustrates a typical time concentration curve for the irradiation of \( \text{JL} \) and the photodecomposition of \( \text{J} \) in the later stages of the reaction is expected due to the known lability of ketone \( \text{J} \) upon irradiation.

The multiplicity of the photoconversion of \( \text{JL} \) was studied. No quenching was observed over a concentration range of three powers of ten using naphthalene \( (E_T = 61 \text{ kcal/mole}) \) and piperylene. The rate of disappearance of the starting ketone \( \text{JL} \) remained roughly constant in the various runs. Sensitization in the photoconversion of \( \text{JL} \) was dramatically accomplished using benzophenone in ether and acetone at concentrations where the sensitizers were absorbing \( > 85\% \) of the incident light (see Table 2 and 3). Substantial quantities of \( \text{J} \) were prepared directly by irradiating gram quantities of \( \text{JL} \) in acetone solution through Corex optics.

**Discussion**

In a recent publication from this laboratory, an initial Norrish Type I reaction from the \( n \rightarrow \pi^* \) excited state was proposed to account for the photoproducts observed during the irradiation of 3-cyclooctenones. Two pathways are open to the \( n \rightarrow \pi^* \) excited states due to the partially occupied, electron-deficient \( \pi_y \) orbitals: hydrogen abstraction and attack of \( \pi \) systems.

In the photoreaction of \( \text{J} \), there is found no evidence of hydro-
Figure 1. Concentrations of $^{14}$ and $^{15}$ vs time during the irradiation of $^{14}$ through Vycor optics (dilute ether solution, 450-w Hanovia lamp).
### TABLE 2

**Representative Time and Percentage Composition**

Values for the Photorearrangement of

2,2,7,7-Tetramethyl-3,5-cycloheptadienone (14) Using Pyrex Optics

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, min</th>
<th>14, %</th>
<th>15, %</th>
<th>Photolysate comp, %&lt;sup&gt;a&lt;/sup&gt;</th>
<th>A&lt;sup&gt;b&lt;/sup&gt;</th>
<th>B&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ether</td>
<td>60</td>
<td>94</td>
<td>0.6</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>85</td>
<td>1.0</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>79</td>
<td>1.4</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>66</td>
<td>1.5</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>61</td>
<td>1.5</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td>Ether (8 x 10&lt;sup&gt;-2&lt;/sup&gt; M in naphthalene)</td>
<td>60</td>
<td>92</td>
<td>2.1</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>81</td>
<td>11</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>70</td>
<td>16</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>48</td>
<td>17</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>41</td>
<td>19</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ether (0.3 M in naphthalene)</td>
<td>60</td>
<td>92</td>
<td>6.0</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>83</td>
<td>7.5</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>76</td>
<td>10</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td>240</td>
<td>65</td>
<td>18</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>61</td>
<td>21</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ether (2.7 x 10&lt;sup&gt;-2&lt;/sup&gt; M in piperylene)</td>
<td>60</td>
<td>92</td>
<td>8</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>73</td>
<td>12</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>t</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>70</td>
<td>17</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
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<td></td>
<td>240</td>
<td>53</td>
<td>21</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>48</td>
<td>22</td>
<td>t&lt;sup&gt;c&lt;/sup&gt;</td>
<td>3.2</td>
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<td>..</td>
<td>t</td>
</tr>
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<td></td>
<td>90</td>
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<td>35</td>
<td>..</td>
<td>t</td>
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<td>60</td>
<td>6</td>
<td>82</td>
<td>..</td>
<td>t</td>
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</table>

<sup>a</sup>Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are not normalized.

<sup>b</sup>Photoproducts A and B (not characterized) were shown in separate experiments to arise from 15.

<sup>c</sup>t = trace.

gen abstracition in the product distribution. Therefore, no transannular hydrogen abstraction utilizing a five-centered transition

![Chemical Structures](image)

state as shown in structure 17 appears to be operative. Yet, intra-
### TABLE 3
Representative Time and Percentage Composition

Values for the Photorearrangement of

2,2,7,7-Tetramethyl-3,5-cycloheptadienone (14) Using Corex Optics

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, min</th>
<th>Photolysate comp, %&lt;sup&gt;a&lt;/sup&gt;</th>
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<th>15</th>
<th>A&lt;sup&gt;b&lt;/sup&gt;</th>
<th>B&lt;sup&gt;b&lt;/sup&gt;</th>
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<td>2.6</td>
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<td>4.5</td>
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</tbody>
</table>

<sup>a</sup>Cyclooctane was added throughout at the beginning of each photolysis for the purpose of internal standardization (see Experimental Section). The percentage composition values reflect the true composition of the reaction mixture and are not normalized.

<sup>b</sup>Photoproducts A and B (not characterized) were shown in separate experiments to arise from 15.
molecular hydrogen abstraction (~10%) was detected in the photochemistry of 3-cyclooctene. Since the total mass recovery in the irradiation of 6 in ether is in the area of 80%, we must acknowledge that small amounts of the diene aldehyde could possibly have been produced but isolation was not possible due to the instability of the aldehyde to the photolysis conditions. Yet, it is not surprising that 18 is absent since transannular hydrogen abstraction would necessitate a slightly more strained five-membered ring transition state as compared to the six-membered transition state that the 3-cyclooctene utilizes.

The Norrish Type I cleavage to diradical 16 is still the mechanism of choice. It is noteworthy and interesting that the intermediate acyl radical prefers to react exclusively by bonding at the alternate terminus of the allylic radical moiety.

Concerning the multiplicity studies, it is not unusual that sensitization of the photoconversion of 6 - 7 was unsuccessful since the $E_T$ of benzophenone is accepted to be above that of $\alpha,\beta$-enones and below that of saturated ketones. The failure of piperylene to quench the rearrangement signifies either that the reaction proceeds via singlet species or that the rate of intramolecular rearrangement of a triplet intermediate is more rapid than diffusion control.

Attention can now be directed toward the sterically hindered case of 2,2,7,7-tetramethyl-3,5-cycloheptadiene (14) and its non-methylated and monomethylated congeners (8a and 8b respectively).
To rationalize the photodecarbonylation of 8a and 8b, a concerted\textsuperscript{26} \(\omega\)-symmetric\textsuperscript{27} expulsion of carbon monoxide from an excited singlet state such as pictured in structure 19 is suggested. As shown in 19, two modes of disrotation at the 2 and 7 positions are possible.

\[
\begin{align*}
\text{In the spin-paired singlet state, symmetry dictates concertedness; however, in the spin-unpaired triplet state (necessitated by sensitizers) the C}_2 \text{ symmetry axis is lost, and concerted fragmentation is nonallowed with the alternate pathway leading to 10 as the result.}
\end{align*}
\]

However, no carbon monoxide or products resulting from photodecarbonylation could be detected in the photolysis of 14. The only product isolated was 3-methyl-4-caren-2-one (15) which was quite interesting since 14 also possesses a two-fold symmetry axis. Because the only difference are the four additional methyl groups, the exceptional behavior of 14 can be attributed to secondary steric forces exerting product formation control during the attempted bond reorganization necessary for carbon monoxide expulsion.

If bond rotation of 19 in either direction is visualized, the steric interactions between the approaching and opposing methyl
groups are apparently sufficient to raise the energy of activation associated with the concerted fragmentation high enough to permit exclusive operation of the alternative rearrangement pathway which leads to 15. This type of secondary steric effects has been observed previously in directing the concerted disrotatory cyclization of 2,3-homotropone and its hydrocarbon analog. The above study supports the evidence for the concertedness of the formation of 9a from 8a and 9b from 8b since 14 cannot expel carbon monoxide from its excited singlet state, the presence of which is apparent from our inability to quench the photoisomerization with effect triplet quenchers.

Although the formation of conjugated cyclopropyl ketones from \( \beta,\gamma \)-unsaturated ketones with ultraviolet light is not unprecedented, the conversion of 14 \( \rightarrow \) 15 under conditions of sensitized irradiation does not parallel the behavior of 8a under similar circumstances. Schuster suggests that the valence isomerization of 8a to 10 occurs by conversion of the excited triplet state to the

\[
\text{cis, trans-3,5-cycloheptadienone } 20a, \quad R = \text{H} \\
\text{20b, } R = \text{CH}_3
\]

cis, trans-3,5-cycloheptadienone 20a followed by conrotatory thermal cyclization of this twisted ketone. On this basis, the rate of formation of 20b from 14 can be expected to be inhibited due to the
severe intracyclic nonbonded interactions.

From the multiplicity studies, it is clear that there is no quenching by piperylene or naphthalene and definite sensitization by both benzophenone and acetone in the photoisomerization of 2,2,7,7-tetramethyl-3,5-cycloheptadienone (14) to 3-methyl-4-caren-2-one (15). These data indicate that triplet 14 is capable of rearranging to 15, and that singlet 14 can also lead to 15 or that a triplet intermediate is again formed but is rapidly consumed by reaction prior to diffusion.

Another coworker in this laboratory has studied the photochemistry of 3,3-dimethylbicyclo[5.1.0]oct-4-en-2-one (21). The only product observed was the result of Norrish Type I cleavage followed by rebonding through the allylic moiety. This experiment indicates that allylic α cleavage competes effectively with cyclopropyl ring opening.

It now becomes possible to make the generalization that the principal photochemical transformation of medium-sized cyclic $\beta,g$-$\gamma$-unsaturated ketones involves 1,3-acyl rearrangement and migration of the allylic double bond presumably via the $\pi \rightarrow \pi^*$ singlet state.
Since the initiation of this research effort, several publications have appeared concerning the photochemistry of β,γ-unsaturated ketones. With this added information, the photochemistry of β,γ-unsaturated ketones now seems capable of correlation. Cyclic and acyclic homoconjugated ketones may undergo four general types of photo-transformation depending upon the structure of each particular molecule: carbon monoxide expulsion, Norrish Type I cleavage, often accompanied by allylic rearrangement, conjugated cyclopropyl ketone formation, and photoreduction.

A typical example of carbon monoxide expulsion was reported by Hess and Pitts who studied the photochemistry of 3-cyclopentenone (22). The authors postulate a biradical intermediate (22a)

\[
\text{22} \quad \rightarrow \quad [\text{22a}] \quad \rightarrow \quad \text{allyl} + \text{CO}
\]

but state that a concerted pathway circumventing the biradical can also be envisaged.

Paquette and Meehan of this laboratory suggest an initial \( n \rightarrow \pi^* \) excitation of the carbonyl group and cleavage of the allylic

\[
\text{23} \quad \overset{\text{hv}}{\rightarrow} \quad \text{24}
\]

α-carbonyl bond in the photochemical interconversion of the illus-
trated ketones. These authors postulate that migration of the acyl function to the alternate terminus of the allyl moiety can proceed in a concerted fashion and therefore may not involve discrete diradical intermediates. Additionally, Erman and Kretschmar suggest a similar cleavage to an intermediate biradical in the formation of cyclobutanone. Ipaktschi has shown that sensitization of 27 with acetone results in initial Norrish Type I cleavage and formation of a strained cyclopropyl ketone (28) instead of the usual cyclobutanone product. Cyclopropyl ketone formation has been the subject of several recent studies. Kojima, Sakai, and Tanabe have shown that irradiation in acetone of steroid forms cyclopropyl ketone.
Yet, irradiation of 31 in benzene affords only oxetane 32. The authors postulate initial Norrish Type I cleavage to an intermediate diradical 33 which can rearrange through the allylic radical moiety to form the cyclopropyl ketone or abstract a hydrogen (1,8 hydrogen abstraction) to form the diene aldehyde which undergoes further internal addition to the original (\(\Delta^5\)) or newly formed olefinic linkage (\(\text{CH} = \text{CH}_2\)).

A recent paper by Scheffer and Lungle reports that 34 rearranges to 35 without any evidence of a Norrish Type I cleavage.

Baggiolini and coworkers found that 3-acetyl-1,2,3-trimethylcyclopent-1-ene undergoes a sigmatropic 1,3-acetyl shift as the major unimolecular reaction in the excited singlet state and a (ther-
mally reversible) 1,2-acetyl shift with cyclopropane ring-closure as the predominant triplet state reaction. The singlet reaction proceeds with racemization while the triplet proceeds with retention of optical activity. The authors postulate a concerted \((\sigma^2 + \pi^2)^{39}\) addition to explain the product formation and optical activity results.
PART II
THE PHOTOCHEMISTRY OF MEDIUM-RING CYCLOPROPYL KETONES AND THEIR METHYLENE ANALOGS

Introduction

The photolability of conjugated cyclopropyl ketones was first investigated in 1954 by Pitts and Norman. These workers noted that photolysis of acetylcyclopropane led to 2-penten-4-one and that the normal α-cleavage of ketones (Norrish Type I) was almost entirely suppressed in favor of this isomerization. Since this study, a large number of reports have been published dealing with the photolysis of cyclopropyl ketones. These publications can be conveniently organized into two groups according to the primary reaction process upon photochemical excitation: cis-trans isomerization and isomerization to α,β-enediones.

The cis-trans photoisomerization of conjugated cyclopropyl ketones is well established. A recent example of this phenomenon was published by Brown and Neumer. These authors showed that optically active α,α'-benzoylcyclopropane carboxylic acid produces optically inactive trans-acid and postulated a diradi-
cal dissociative mechanism to account for their results. Zimmer-

\[ \text{HO}_2 \text{C} \xrightarrow{\text{hv}} \text{CO}_2 \text{H} \]

man and coworkers have shown that [3.1.0]bicyclic ketones iso-

\[ \text{Ph} \xrightarrow{\text{hv}} \text{Ph} \]

merize through a triplet mechanism involving cleavage of both in-
ternal and external cyclopropyl bonds.

The more significant rearrangement of cyclopropyl ketones
upon photolysis is to \( \alpha,\beta \)-enones which has been the subject of
several publications. Pitts and coworkers have studied the
photochemistry of cyclopropyl ketones in the vapor phase. These

\[ \xrightarrow{\text{hv}} \]

authors find the primary process in the photoreaction of cyclo-
propyl ketones is to form \( \alpha,\beta \)-unsaturated ketones and explain
this product formation process as proceeding either through an intermediate diradical or through a six-membered cyclic transition state generally ascribed to Norrish Type II processes.

Winter and Lindauer\textsuperscript{42h} have studied the mechanism of this rearrangement in the case of 1-acetylbicyclo[4.1.0]heptane. They postulated a diradical intermediate in the transformation to 1-acetylcyloheptene.

![Diagram of reaction]

A number of studies concerning the photochemistry of cyclopropyl ketones in solution have also been published. The most extensive report is that of Dauben and Shaffer\textsuperscript{44} who studied the photoisomerization of bicyclo[4.1.0]ketones. In bicyclo[n.1.0]-alkan-2-ones, the two cyclopropyl bonds overlap unsymmetrically with the carbonyl $\pi$-lobes. This is experimentally indicated by

![Diagram of reaction]

their uv spectra\textsuperscript{45} and should lead to specific or selective photocleavage of the better-overlapped bond. This specificity has al-
ready been observed in the lithium/ammonia opening of cyclopropyl ketones. For example, Dauben showed that 3-methylbicyclo[4.1.0]-heptan-2-one isomerizes to a dienealdehyde via an intermediate unsaturated cyclopropyl aldehyde as illustrated. Yet, 3,7,7-trimethylbicyclo[4.1.0]hepta-2-one yields products derived both from cyclopropyl ring opening and from α-cleavage.

Dauben and coworkers postulated the following generalizations regarding the photoisomerizations of bicyclo[4.1.0]heptan-2-ones:

1. cyclopropyl ring opening as a primary process can compete with α-cleavage of the C2-C3 bond only when C3 is unsubstituted or when C7 is substituted; 2. when cyclopropyl ring opening occurs as a primary process, only that bond which conjugates best with the carbonyl group will open; 3. when both cyclopropyl bonds can overlap equally with the carbonyl group, only that bond with the highest degree of terminal substitution will open; and, 4. in cyclopropyl conjugated carbonyl compounds, Type II reactions will predominate if γ-hydrogens are present, provided the geometry of the system is such that these can be abstracted by the carbonyl oxygen.

Few photochemical investigations have been published concerning vinylcyclopropanes or divinyl cyclopropanes. An example of the
photolysis of a cis-divinylcyclopropane has been studied by Zimmerman and Grunewald. These authors noted that photolysis of 'semi-bullvalene' produces cyclooctatetraene and suggested that the illustrated diradical may be a possible intermediate.

Other examples having the vinylcyclopropane moiety have been investigated. In these examples, the vinylcyclopropane moiety was always in conjugation with a carbonyl function as illustrated.

In these cases, the photorearrangement occurs only with the cyclopropyl ketone moiety with no detectable lability of the vinylcyclo-
propane chromophore. In fact, a survey of the recent photochemical literature gives evidence that the vinylcyclopropane moiety is actually a product of the photorearrangement of a wide variety of organic compounds.

Results
In this section, a series of cyclopropyl ketones (36, 37, 38, 40) and vinyl cyclopropanes (39, 41) have been subjected to ultraviolet irradiation and their photoreaction products have been isolated and identified. Preparative photolyses were accomplished utilizing dilute solutions (1-2%) of the desired compound in the solvent of choice and photolyzing by means of 450-w Hanovia immersion lamp fitted with the desired filters. Careful concentration
of the photolyzed solutions and preparative vpc was the usual method of product isolation. Analytical data were obtained by photolysis of 20-30 mg samples of the molecule in question dissolved in 3 ml of solvent in a quartz test tube held in contact with the immersion well. Rubber septa were utilized to permit removal of aliquots by micro-liter syringe and subsequent monitoring by vpc analysis. The relative peak areas were determined by careful cutting and weighing; all percentages are normalized to give true values.

* cis-Bicyclo[6.1.0]nonan-2-one (36).* The first molecule that was synthesized to help elucidate the photochemical reaction pathways of medium-ring cyclopropyl ketones was 36. The synthesis of 36 was achieved readily according to the following scheme.

Cyclo-octene was treated with mercuric acetate in acetic acid to form 3-cyclooctenyl acetate 42 which was reduced with lithium aluminum hydride to form 3-cyclooctenol (43). A Simmons-Smith reaction on 43 afforded the cyclopropyl alcohol 44 which was readily oxidized with Jones reagent to the desired *cis*-bicyclo[6.1.0]nonan-2-one (36).
Irradiation of \( \text{36} \) in dilute ether solution using a 450-w Hanovia lamp and Corex (absolute cutoff at 2580 Å) or Pyrex filters (absolute cutoff at 2800 Å) was followed by withdrawal of small aliquots at periodic intervals and quantitative analysis of these by vapor phase chromatography (vpc). After 2 hr with Corex optics, cyclononanone (45, 21%) and 3-methylcyclooctanone (46, 10%) were produced; the remainder consisted of unreacted \( \text{36} \) (41%) and residual polymer (28%) (see Table 4). The volatile products were isolated by preparative scale vpc and shown to be identical with authentic samples. Careful examination of the solvent fraction revealed the presence of 47, in agreement with the fact that 45 and 46 are reduction products of \( \text{36} \).

Evidence for the multiplicity of the rearranging species was sought in the following manner. A solution of \( \text{36} \) and benzophenone \( (E_T = 68.5 \text{ kcal/mole})^{13,14} \) in ether was prepared in which the concentration of the sensitizer was such that it absorbed >95% of the incident radiation. Exposure of this solution to the identical light source equipped with a Pyrex filter for 5 hours resulted in the dis-
appearance of only minor amounts of 36; no new volatile products were detected (see Table 4). A like result was obtained with acetone ($E_T \approx 80$ kcal/mole) as sensitizer. The photolysis of 36 was quenched by the addition of 1,3-pentadiene, but concentrations of 0.05 M or higher were required.

Interestingly, irradiation of 36 in dilute $t$-butyl alcohol solution takes an entirely different course to give three new products (Table 4). This mixture could be separated with difficulty by preparative vpc. The products were identified in their order of elution as 4,8-nonadienal (48), 2-(4-pentenyl)cyclopropane carboxaldehyde (49), and $\text{trans}$-bicyclo[6.1.0]nonan-2-one (37).

The elemental analysis of the first component (48) indicated that this substance was isomeric with 36. The colorless liquid exhibited pertinent infrared bands at 2710 (aldehyde C-H stretch), 1735 ($\delta$C=O), and 1645 cm$^{-1}$ ($\gamma$C=O); its ultraviolet spectrum was devoid of peaks, except for end absorption. Its nmr spectrum
TABLE 4

Percentage Composition Ratios for the Irradiation of

cis-Bicyclo[6.1.0]nonan-2-one (36)

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<th>Time, hr</th>
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<td></td>
<td></td>
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\[ ^a \text{Cyclooctane was employed as the internal standard.} \]
\[ ^b \text{t = trace} \]

revealed several important points; specifically, the presence of

(a) an aldehyde proton necessarily spin-coupled to two \( \alpha \)-hydrogens,

(b) a terminal vinyl group in addition to two other vinyl protons,
and (c) only $-\text{CH}_2\text{O}^+$ and allylic protons in the remainder of the structure (absence of absorption above 62.0) was clearly indicated. These spectral features were uniquely congruent with the 4,8-nona-dienal assignment (6). This conclusion was reinforced by catalytic hydrogenation of 48 over 5% Pd-C which proceeded with the uptake of two molar equiv of hydrogen to give nonanal.

The second photoproduct (49) was also an unsaturated aldehyde since it likewise exhibited characteristic infrared bands at 2830, 2720, 1710, and 1645 cm$^{-1}$. The nmr spectrum suggests that the cyclopropane ring was intact; additionally, the aldehyde proton appeared as a doublet indicating the presence of only one $\alpha$-hydrogen, whereas the three vinyl protons displayed the spin-spin pattern typical of a terminal vinyl group. Catalytic hydrogenation of this colorless liquid did not give nonanal, but rather a new aldehyde which was assigned the structure 3-methyloctanal (54) on the basis of infrared and nmr evidence (see Experimental Section). From these considerations, it seemed that this photoproduct was cyclopropyl aldehyde 49 and this structural assignment was confirmed in the manner outlined in the following scheme.

Careful catalytic reduction of 2-octynol (50) over 5% Pd-Ba$\text{SO}_4$ with one mole of hydrogen afforded cis-2-octenol (51) which, under Simmons-Smith conditions, was stereospecifically cyclopropanated to give alcohol 52. Mild oxidation of 52 with Jones reagent in the cold yielded cis-2-(n-pentyl)cyclopropane carboxaldehyde (53) which upon catalytic hydrogenation afforded a
product identical in all respects to that which resulted from reduction of 49. In order to establish that this substance was indeed 3-methyloctanal (54), 2-hepten-4-ol (55) was vinylated in the presence of ethyl vinyl ether and mercuric acetate and the resulting allyl vinyl ether (56) was subjected to Claisen rearrangement by pyrolysis at 190°. The 3-methyl-4-octenal (57) so produced was hydrogenated to give authentic 3-methyloctanal (54) which proved to be identical in all respects to the samples isolated earlier.

The formation of trans-bicyclo[6.1.0]nonan-2-one (37) was unexpected. However, structure proof was accomplished by independent synthesis and comparison of the authentic sample of 37 and the photoproduct (37) indicated the two samples to be identical in all respects.

As before, the photoreactions which take place in t-butyl alcohol could not be sensitized and quenching was achieved only with higher concentrations of 1,3-pentadiene. Finally, it should be mentioned that the photochemically-induced transformations of 36 are very sensitive to solvent. For example, irradiation of 36 in methanol or pentane results uniquely in polymer formation; no volatile products could be detected at any stage of the irradiations.

trans-Bicyclo[6.1.0]nonan-2-one (37). In an effort to compare the photoreactivity and possible product distribution between the two possible geometric forms of bicyclo[6.1.0]nonanones, the trans isomer was synthesized and photolyzed. The synthesis was accomplished by adding dibromocarbene to cycloheptene (58) to form the
TABLE 5
Percentage Composition Ratios for the Irradiation of
trans-Bicyclo[6.1.0]nonan-2-one (37)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, hr</th>
<th>Composition, %&lt;sup&gt;a&lt;/sup&gt;</th>
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</thead>
<tbody>
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<td>t-Butyl Alcohol (Corex)</td>
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<td>100</td>
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<tr>
<td></td>
<td>4</td>
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<tr>
<td></td>
<td>8</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>33</td>
</tr>
<tr>
<td>Acetone (Pyrex)</td>
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<td>100</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>94</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>90</td>
</tr>
<tr>
<td>Ether (Corex)</td>
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<td>100</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>62</td>
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<tr>
<td></td>
<td>10</td>
<td>31</td>
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<sup>a</sup>Cyclooctane was employed as the internal standard.
<sup>b</sup> trace

bicyclic dibromide which was then reduced to the exo-monobromide (60)
in a stereospecific manner. Ring opening of the cyclopropane 60
occurs upon hydrolysis to afford the trans olefinic alcohol (61).
A Simmons-Smith reaction on 61 affords the trans-cyclopropyl al-
cohols (62) which is readily oxidized by the Jones reagent to the
desired trans-bicyclo[6.1.0]nonan-2-one (37).
TABLE 6

Percentage Composition Ratios for the Irradiation of trans-Bicyclo-
[6.1.0]nonan-2-one (37) in t-Butyl Alcohol (Corex Optics)

<table>
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<th>0.01 M in 1,3-pentadiene</th>
<th>0.2 M in 1,3-pentadiene</th>
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<td>37</td>
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<td>--</td>
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<tr>
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<td>50</td>
<td>35</td>
<td>44</td>
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<sup>a</sup>Cyclooctane was employed as the internal standard.

Irradiation of 37 in t-butyl alcohol with ultraviolet light of wavelength above 260 nm proceeded with less facility than 36 but afforded a single product in 50% yield after 12 hr. The colorless liquid analyzed correctly for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>, thus indicating that a molecule of solvent had been incorporated. On the basis of its nmr spectrum which displayed simply a broad 15 proton multiplet at
60.6-1.5 and 9 proton singlet at 61.45, the photoproduct was tenta-

tively defined as the \( \varepsilon \)-butyl ester 63. To confirm this structural

assignment, and particularly to establish the trans nature of the

substitution on the cyclopropane ring, 1-heptene (64) was heated

\[
\begin{align*}
\text{37} & \xrightarrow{hv} \text{38} \\
\text{64} & \xrightarrow{\text{CH}_2\text{CO}_2\text{Et}} \text{65}
\end{align*}
\]

at 90° with ethyl diazoacetate in the presence of copper powder,

and the resulting mixture of esters (65) was simultaneously equil-

ibrated and hydrolyzed with sodium hydroxide in methanol. Exposure

of this carboxylic acid to isobutylene in the presence of a small

amount of sulfuric acid yielded \( \varepsilon \)-butyl trans-2-(n-pentyl)cyclopro-

pane carboxylate (63), identical in all respects with the photo-

product.

Again in this instance, the effect of 1,3-pentadiene as a

possible quencher was examined. In contrast to the results ob-

tained with 36, however, no quenching of the formation of 63 was

seen over a twentyfold concentration range (Table 6).  

The question of the origin of 63 was investigated by the
photolysis of \( {\text{37}} \) in \( \text{t-BuOD} \). The position of the deuterium incorporation was determined by nmr spectroscopy which indicated the product to be \( \text{66} \).

Irradiation of an ether solution of \( {\text{37}} \) in an entirely analogous manner resulted in gradual disappearance of \( {\text{37}} \) but only polymer was produced. Similar observations were made in methanol and pentane solutions.

**cis-Bicyclo[6.1.0]non-6-en-2-one (38).** In an attempt to observe a possible competitive photoreaction in a single molecule, **cis-bicyclo[6.1.0]non-6-en-2-one (38)** was synthesized and its photochemistry was studied. The preparation of \( {\text{38}} \) was accomplished by the following synthetic sequence. Cyclooctadiene (67) was brominated allylically
with N-bromosuccinimide to form 5-bromocycloocta-1,3-diene (68) and then treated with silver acetate in acetic acid to yield 2,4-cyclooctadienyl acetate (69). The acetate (69) was reduced with lithium aluminum hydride to form 2,4-cyclooctadienol (70) and oxidized with Jones reagent to yield 2,4-cyclooctadienone (71). This ketone was then reacted with dimethylsulfonium methylide to yield cis-bicyclo[6.1.0]non-6-en-2-one (38).

The photolysis of 38 was attempted utilizing a larger variety of solvents, optics and light sources. In acetone, 38 slowly polymerized under influence of the 200- or 450-w Hanovia lamp, equipped with either Pyrex or Corex optics. Vpc showed 38 as the only volatile compound isolated from the reaction mixtures. In ether Vycor optics and 450-w lamp, 38 disappeared moderately fast (10% remaining after 3 hrs) but no volatile products were isolated. A yellow solid polymer coated the sides of the quartz test tube. With the 450-w lamp and Vycor optics, 38 dissolved in methyl alcohol disappeared slowly (25% remaining after 7 hrs) with no volatile products isolated. However, in methyl alcohol and also in t-butyl alcohol trace (1-3%) amounts of what appeared to be solvent incorporated products were barely detected by vpc; however, their small amounts precluded their isolation and identification.

2-Methylene-cis-bicyclo[6.1.0]non-6-ene (39). In an effort to study the photochemistry of a medium-ring conjugated cyclopropane without the directive influence of a carbonyl group, 2-methylene-cis-bicyclo[6.1.0]non-6-ene (39) was synthesized and its photochemistry
was investigated. The preparation of 39 was readily accomplished by treating 38 with methylene triphenylphosphorane.53

The photochemistry of 39 was studied in a large series of solvents, (including pentane, methanol, ether, and acetone) and various optics, (Vycor, Corex, and Pyrex). Changes of optics from no filter through Pyrex only resulted in slowing of the photoreaction without any improvement in starting material recovery, product yield, or inhibition of polymer formation. In pentane, methanol, and ether, moderate loss of starting olefin and only very slow product formation was observed by vpc. In acetone, without any filter, the photoreaction appeared to proceed more readily and the lone photoproduct appeared in low to moderate yield (see Fig 2). Trace amounts (1-5%) of what appeared to be dimers and/or trimers also were detected at long vpc retention times. Isolation of the photoproduct proved to be difficult in that preparative vpc recovery was low (due to either thermal lability of photoproduct or loss of column efficiency from the existing long retention time products). Attempted
molecular distillation resulted in very poor recovery of both $39$ and its photoproduct.

However, enough of the photoproduct of $39$ was isolated to permit elemental analysis (isomeric with $39$), IR, and NMR. The IR data indicated only unsaturated hydrocarbon while the NMR data was more informative: $\nu_{\text{max}}$ neat 2875, 1580, 1445 and 890 cm$^{-1}$; $\delta$CDCl$_3$ 1.1-3.0 (broad complex absorption - 12H), and 5.7 (broad singlet - 2 H). Integration of the NMR peaks show only two vinyl protons with a chemical shift similar to that of the vinyl protons within the ring in $39$, indicating some type of tricyclic photoproduct. Additionally, careful ozonolysis of milligram quantities of the photoproduct resulted in aldehyde polymers and no volatile ketone products.
Figure 3: Possible intermediates and product structures in the photolysis of 39 in acetone (450-w Hanovia lamp-quartz optics).
If one lists the possible reaction intermediates (73, 74, 75) and of the resulting products, (see Fig 3) it can be noted that of these, 75 appears to be the most stabilized by diallylic resonance. Additionally, since the nmr spectrum suggests a tricyclic product with the double bond positioned endocyclic in the ring, 83 is the most probable photoproduct. However, hydrocarbons 78, 80 and 81, derivable from intermediates 73, 74, and 75, possess structural parameters which also are in agreement with the limited spectral data.

1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-one (40). The photochemical investigation into the lability of seven-membered cyclic cyclopropyl ketones was begun with synthesis and subsequent photolysis of 1,4,4-trimethylbicyclo[5.1.0]oct-5-en-2-one (40). The synthesis of 40 was accomplished by the rearrangement of carvone (84) and eucarvone (85) through addition of HBr and subsequent elimination and rearrangement. Eucarvone (85) was treated with dimethyl-oxosulfonium methylide to afford the desired cyclopropyl ketone 40.

Samples of 40 were irradiated in a series of solvents and various optics (see Table 7) to yield one major photoproduct (86) and two
minor photoproducts that were left unidentified due to their low

\[ \text{40} \xrightarrow{hv} \text{86} \]

yield (1-2%). In ether, 8% of 86 was formed after 5 hr while in acetone, the reaction proceeded cleaner with 10% of 86 being formed but with almost 60% of 40 remaining after 5 hr. Methanol appeared to force the photoreaction to go faster in that only 6% of 40 remained and 8% of 86 formed in only 3 hr. Yet in pentane no 86 could be detected although only 9% of 40 remained after 2 hr.

Preparative vpc was utilized to isolate 86 (semicarbazone; mp 202-204°) which was identified as 1,4,4-trimethylbicyclo[3.3.0]-oct-6-en-2-one (86) on the basis of its spectral properties, particularly its unequivocal nmr spectrum; 40₅, 1745 and 1680 cm⁻¹; C₁₀H₁₆N₂O (C₁₀H₁₆N₂O) 266 nm (ε 40); CDCl₃ 3 1.10 (singlet, 6H, overlapping CH₃ groups at C₂), 1.29 (singlet, 3H, CH₃ group at C₁), 2.12 (AB quartet, J_AB = 16 Hz, J_A = 19.5 Hz, 2H, -COCH₂⁻), 2.40 (multiplet, 2H, -CH₂⁻ at C₆), 2.72 (multiplet, 1H, allylic proton at C₅), and 5.68 (broadened singlet, 2H, vinyl protons).

The photorearrangement was found not to be quenchable with varying concentrations of piperylene (E_T^trans = 59 kcal/mole, E_T^cis = 57 kcal/mole) or naphthalene (E_T = 61 kcal/mole) in ether. Neither was the photoreaction subject to sensitization with benzo-
TABLE 7

Percentage Composition Ratios for the Irradiation
of 1,4,4-Trimethyl[5.1.0]oct-5-en-2-one (40)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, hr</th>
<th>Composition, %&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Methanol (Vycor)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>8</td>
</tr>
<tr>
<td>Pentane (Vycor)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9</td>
</tr>
<tr>
<td>Ether (Corex)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>27</td>
</tr>
<tr>
<td>Acetone (Corex)</td>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>74</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>70</td>
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<tr>
<td></td>
<td>4</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>58</td>
</tr>
<tr>
<td>Piperylene (0.1 M) in Ether (Corex)</td>
<td>100</td>
<td>68</td>
</tr>
<tr>
<td>Benzo[ghi]phenone (2.5 M) in Ether (Corex)</td>
<td>100</td>
<td>95</td>
</tr>
<tr>
<td></td>
<td>94</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>84</td>
<td>1</td>
</tr>
</tbody>
</table>

<sup>a</sup> No observable products.
TABLE 7 (Continued)
Percentage Composition Ratios for the Irradiation

of 1,4,4-Trimethyl[5.1.0]oct-5-en-2-one (40)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, hr</th>
<th>Composition, %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>100</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(0.1 M) in</td>
<td>70</td>
<td>13</td>
<td>t</td>
</tr>
<tr>
<td>Ether</td>
<td>49</td>
<td>15</td>
<td>2</td>
</tr>
<tr>
<td>Corex</td>
<td>32</td>
<td>7</td>
<td>t</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>5</td>
<td>t</td>
</tr>
</tbody>
</table>

*Cyclooctane is used as the internal standard.
*Trace = t

phenone ($E_x = 68.5$ kcal/mole) or acetone ($E_x = 82$ kcal/mole) under conditions where the sensitizer absorbed the major portion of the incident radiation.

2-Methylene-1,4,4-trimethylbicyclo[5.1.0]oct-5-ene (41). In an effort to correlate the photochemical behavior of molecules containing a conjugated cyclopropyl structure with the effects of the n - n* excited states of the carbonyl group, the photochemistry of 2-methylene-1,4,4-trimethylbicyclo[5.1.0]oct-5-ene has been examined. The synthetic scheme used to prepare 41 utilized the Wittig reaction on

\[
\text{40 with methylenetriphenyl phosphorane.}
\]
Samples of 41 were photolyzed in a series of solvents (see Table 8) and one lone isomeric photoproduct (87) was detected by vpc with a trace (0-3%) of an unidentified photoproduct. In acetone only traces of both 41 and 87 remained after irradiation through Vycor for 8 hr. But in pentane and methanol, 87 was detected in amounts of 24% and 56% respectively after irradiation through Vycor for 8 and 10 hr, respectively. Isolation of 87 was accomplished through preparative vpc and the resulting clear liquid was identified as 2-methylene-1,4,4-trimethylbicyclo[3.3.0]oct-6-ene (87) by means of its spectral data:

\[ \nu_{\text{max}}^{\text{neat}} \text{ cm}^{-1} \] 2895, 1660, 1545, 1470, 884 and 689 cm\(^{-1}\); \( \delta_{\text{CDCl}_3} \) 0.88, 0.96 and 1.25 (singlets, 3H each, methyl groups), 2.04 (multiplet, 2H, methylene group at C8), 2.30 (multiplet, 3H, methylene at C3 and...
### TABLE 8

Percentage Composition Ratios for the Irradiation of
2-Methylene-1,4,4-Trimethyl-cis-bicyclo[5.1.0]oct-5-ene (41)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time, hr</th>
<th>Composition, %&lt;sup&gt;a&lt;/sup&gt; 41</th>
<th>Composition, %&lt;sup&gt;a&lt;/sup&gt; 87</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetone</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(Vycor)</td>
<td>2</td>
<td>47</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>21</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>6</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Pentane</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(Vycor)</td>
<td>2</td>
<td>85</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>70</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>43</td>
<td>24</td>
</tr>
<tr>
<td>Methanol</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(Vycor)</td>
<td>2</td>
<td>75</td>
<td>19</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>41</td>
<td>35</td>
</tr>
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<td></td>
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<td>31</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>14</td>
<td>47</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>3</td>
<td>56</td>
</tr>
<tr>
<td>Acetone</td>
<td>0</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>(Pyrex)</td>
<td>2</td>
<td>82</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>60</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>41</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>33</td>
<td>2</td>
</tr>
</tbody>
</table>

<sup>a</sup>Cyclooctane is used as the internal standard.

Methine proton at C<sub>5</sub>). Corroborative evidence for this assignment was ultimately derived by selective hydrogenation of 87 over 5% rhodium on carbon and ozonization of the dihydro derivative 88 to neat the cyclopentanone (ν<sub>max</sub> 1745 cm<sup>-1</sup>). This product was identical in all respects to the product of hydrogenation of 86.
Multiplicity studies showed that production of the triplet species by photolysis of \( ^{86} \) in acetone or benzophenone resulted in large amounts of polymer formation (see Table 8). The efficiency of the triplet transfer was unequivocally established in a series of experiments by effective quenching of benzopinacol formation by \( ^{86} \) when benzhydrol was added. Since \( ^{87} \) was independently found to be stable under these photolysis conditions, the polymerization cannot be construed as arising from the excited triplet state of \( ^{87} \).

Discussion

The photochemistry of cyclopropyl ketones in acyclic \(^{40,41f}\) and 'normal' (5- and 6-membered) ring \(^{42,44}\) ketones has been extensively studied. Rearrangement to \( \alpha,\beta \)-enones \(^{42} \) generally, and cis-trans isomerization \(^{41} \) in specific acyclic cases, are the preferred reaction pathways observed. The purpose of this research effort was to study the photorearrangement of some medium-ring cyclopropyl ketones and to compare their reactivity with that of analogous conjugated cyclopropanes lacking the \( n \rightarrow \pi^* \) excited state capabilities of the carbonyl substituent.

Since previous published studies \(^{42-44} \) have indicated that the cyclopropyl bond which best overlaps with the carbonyl \( \pi \)-lobes undergoes homolytic cleavage, frequently in highly specific fashion, cis- and trans-bicyclo[6.1.0]nonan-2-one \((36 \text{ and } 37)\), the simplest known pair of geometrically isomeric bicyclo[\(n.1.0\)]alkan-2-ones were
synthesized\textsuperscript{51} and their photochemistry studied.\textsuperscript{52} Examination of molecular models of \textsuperscript{36} suggested that the cyclooctyl ring in this structure is conformationally mobile; however, evaluation of bond angle deformations and nonbonded steric interactions has led to the conclusion that conformations \textsuperscript{36a-c} are likely preferred. Similar structural considerations have shown that \textsuperscript{37} is appreciably strained\textsuperscript{55} and significantly more rigid. It is apparent from models of this ketone that the minimum in the potential functions for this molecule is best represented by conformer \textsuperscript{37}. In \textsuperscript{37}, the internal C\textsubscript{1}-C\textsubscript{8} cyclopropyl bond is most suitably aligned for overlap with the $\pi^*$ orbital of the carbonyl group. However, since the geometry of the reactive $n-\pi^*$-excited keto group deviates only slightly, if at all, from a planar arrangement\textsuperscript{56} and because the rigidly enforced internal angle of the C\textsubscript{1}-C\textsubscript{8} and C = O
bonds approaches 120°, maximization of the extent of overlap is not geometrically possible. In contrast, overlap between the carbonyl π* orbital and a vicinal cyclopropyl bond in 36 is maximizable, but is a function of the particular conformation (36a - 36c). For example, in 36a the internal C1-C8 cyclopropyl bond is ideally positioned for stereoelectronic involvement with the carbonyl system; on the other hand, in 36b and 36c the external C1-C9 bond is best situated for maximum overlap with the π* orbital.

Irradiation of 36 produced cyclononanone (45), 3-methylcyclo-octanone (46), the dimer of diethylether 47, and unreacted 36. No products resulting from cis-trans isomerization or α,β-enone formation were detected. The failure to sensitize the photoreaction with acetone and benzophenone suggests that either the triplet excitation energy of 36 is of the same order of magnitude as a normal aliphatic ketone (~80 kcal/mole) or the photorearrangement occurs via the singlet manifold of this ketone. Since measurement of the triplet energy of a typical conjugated cyclopropyl ketone has not yet been reported, the effect of such conjugation on the singlet and triplet levels of the n→π* carbonyl band can only be surmised. In view of their ultraviolet spectra, however, the expectancy is that lowering of the triplet level should obtain, as seen with α,β-unsaturated ketones. Nevertheless, this conclusion is highly tentative. The photolysis of 36 was quenched by the addition of 1,3-pentadiene, but concentrations of 0.5 M or higher were required. Unfortunately, at these concentrations there existed substantial...
competition by the diene for the incident light under the conditions employed. Thus, it is not clear from these experiments whether singlet or triplet 36 was being quenched, particularly since quenching by high concentrations of dienes can no longer be accepted as uniquely sufficient evidence for a triplet reaction. From the foregoing data the nature of the excited state species in this photo-reaction does not appear subject to ready elucidation, particularly since the "fingerprint method" of analysis is not applicable. Irrespective of this fact, the mechanism of the formation of 45-47 is thought to be as shown below. Thus both the internal and proximate external cyclopropyl bonds in 36 are cleaved, with the first pathway being preferred by a factor approximating 2:1.
In 2-butanol, however, irradiation of 36 produces 4,8-nonadienal (48), 2-(4-pentenyl)cyclopropane carboxaldehyde (49), and trans-bicyclo[6.1.0]nonan-2-one (37). The formation of 37 is theoretically interesting. Although cis-trans photoisomerization of acyclic cyclopropyl ketones has been noted previously,59 the conversion of 36 to 37 is the first example to be encountered in a bicyclo[n.1.0]alkan-2-one. The production of 37 is necessarily a consequence either of homolytic rupture of cyclopropyl bonds C₁-C₈ or C₁-C₉, or acyl cleavage in the C₁-C₂ direction, and subsequent re-bonding to produce the less stable isomer. That 37 can be isolated from this photolysis is a reflection of its slower rate of reaction under these conditions (see Tables 4 and 5).

The formation of 49 is viewed as arising from the well-known Type I reaction14 of cyclic ketones. Diene aldehyde 48 appears

\[ 36 \xrightarrow{hv} 49 \xrightarrow{hv} \]

to be the result of a Type II reaction14 involving 49, and finds analogy in the photoconversion of 3-methylbicyclo[4.1.0]heptan-2-one to 4,6-octadienal.44 In contrast to the smaller bicyclo[n.1.0]-alkan-2-ones, therefore, α-cleavage of the C₂-C₃ bond occurs in 37 even though C₃ is unsubstituted. Multiplicity experiments indicated that the reaction could not be sensitized by acetone or benzophenone
and that high concentrations of piperylene were necessary to quench the reaction.

Irradiation of 37 in t-butanol produced one lone photoproduct (63) identified as the cyclopropyl t-butyl ester. The use of other solvents only resulted in polymer formation and no volatile photoproducts were observed (see Table 5). Again in this instance, the effect of 1,3-pentadiene as a possible quencher was examined. In contrast to the results obtained with 36, no quenching of the formation of 63 was seen over a twentyfold concentration range (Table 6). This result, in conjunction with the observation that acetone sensitization experiments were unsuccessful, suggests that a singlet mechanism is operative.

The question of the origin of 63 was investigated by photolysis of 37 in t-BuOD. The formation of 63 obviously necessitates α-cleavage of the C₂-C₃ bond; however, t-butyl ester 63 could be produced by

\[
\begin{align*}
90 & \quad \xrightarrow{\text{hv t-BuOH}} 91 \\
91 & \quad \rightarrow 92 \\
93 & \quad \xrightarrow{\text{t-BuOD}} 94
\end{align*}
\]

two different reactions of the resulting diradical (90), one of which
involves the interesting cyclopropyl ketene 93. The question is whether the terminal methylene group abstracts a proton from solvent or from the remote (eight-membered transition state) α-carbonyl position. In t-BuOD, the two pathways would give 92 and 94, respectively. The position of deuterium incorporation was determined in this instance by nmr spectroscopy which indicated the product to be 94.

Therefore, diradical 90 is converted to 93 despite the medium-sized nature of the requisite transition state, presumably through the operation of a solvent cage effect.

Irradiation of an ether solution of 37 in an entirely analogous manner resulted in the gradual disappearance of 37, but only polymer was produced. Analogous observations were made in methanol and pentane solutions. Thus, the photochemical behavior of 37 is even more solvent dependent than that of 36.

To summarize, the photochemical behavior of bicyclo[6.1.0]nonan-2-one is highly dependent on the stereochemistry of the two ketones. Furthermore, both 36 and 37 are seen to react quite differently from smaller bicyclo[n.1.0]alkan-2-ones, all of which have the common structural feature of an α,β-cyclopropyl carbonyl moiety.

That the conversion of 37 to 63, an α-cleavage of the C2-C3 bond, proceeds to the exclusion of other possible photochemical pathways, is indicated by the fact that no 3-methylcyclooctanone (46), cyclononanone (45), cis-bicyclo[6.1.0]nonan-2-one (36), or lumiproducts of the latter ketone (i.e., 48 and 49) could be de-
tected conditions were <0.5% concentration levels could be readily observed. Therefore, 37 shows no tendency to proceed to a less strained cis-isomer (36) by a C_1-C_2, C_1-C_8, or C_1-C_9 bond rupture-recombination pathway. In contrast, cis-36 does produce significant amounts of trans-37 under the same conditions. Additionally, the formation of 48 and 49, but no t-butyl ester comparable to 63, reveals that 36 prefers a Type I cleavage of the C_2-C_3 bond over the C_1-C_2 bond. This widely differing reactivity may be the exclusive result of conformational consequences; however, the role of geometric effects must not be underestimated. Until more data is obtained on cis-trans pairs of this type, it is perhaps most reasonable to attribute these significant differences to the combined influence of both factors.

This line of reasoning suggests a more general point. Specifically, since it has been often demonstrated in conformationally rigid conjugated cyclopropyl ketones that \( \pi^* \)-assisted cyclopropane opening is ideally operative when a bent bond of the three-membered ring overlaps the \( \pi \)-system of the carbonyl group, can the product distribution derived from 36 in ether solution be employed as a probe of the excited state conformations of this ketone? Unfortunately, an evaluation of this relationship is presently impeded by the paucity of examples and by the absence of sufficient information on the singlet and triplet energy levels of the compounds involved, and the like. It is important to note, however, that such considerations might in fact provide a means by which examination of excited-
state conformations of medium-ring ketones could be made possible.

In contrast, to the photochemical behavior of 36 and 37, bicyclo[6.1.0]non-6-en-2-one (38) yielded no volatile photoproducts under a large variety of various optics, solvents, and light sources. It was thought that extending the conjugation of the cyclopropyl ketone moiety by an additional site of unsaturation would lead to interesting transannular phenomena. The inability to isolate any volatile photoproducts indicates that the excited state species either rearranges to photoproducts that are also very photolabile under the given conditions or that the principle reaction pathway is polymer formation. Additionally, acetone sensitization failed, indicating the presence of a singlet pathway.

The photochemical behavior of 2-methylenebicyclo[6.1.0]non-6-ene (39) is theoretically interesting in that the few examples of cis-trans-divinylcyclopropanes have been studied photochemically. Irradiation of 39 in acetone yields one major photoproduct (72) in low yield whose structure has not yet been unambiguously determined (see Results, this section). However, spectral data indicates that

![Diagram](image)

formation of a bicyclic photoproduct involving intramolecular rearrangement of the exocyclic methylene substituent and the cyclo-
propyl group is the primary photochemical process. This is indicated by the disappearance in the nmr of the absorptions of the cyclopropyl and exo-methylene substituents. If we examine one possible diradical intermediate (75), we can visualize electron motion to account for formation of a possible product (83). Additionally, a concerted bond switching process is also possible. More photochemical investigations on compound 39 and other analogous structures are necessary before mechanistic details can be advanced.

The photochemistry of 1,4,4-trimethyl-cis-bicyclo[5.1.0]oct-5-en-2-one (40) was studied in an effort to gain added information about the role of stereoelectronic and stereochemical factors in the photorearrangements of cis-bicyclo[5.1.0]cyclooctenones. Irradiation of 40 yielded one product in low yield (see Table 7) which was identified as 1,4,4-trimethylbicyclo[3.3.0]oct-6-en-2-one (86). Multiplicity studies indicate that the photoreaction of 40 was neither sensitized with acetone or benzophenone nor quenched with piperylene or naphthalene indicating that either n → n* singlet states are primarily involved or rates of intramolecular rearrangement of the corresponding triplet states are faster than diffusion control.

Mechanistically speaking, exclusive cleavage of the cyclopropyl bond internal to the seven-membered ring affords products ultimately
derived from rebonding via a five-centered transition state. The

\[
40 \overset{\text{hv}}{\rightarrow} \text{[Structure]} \rightarrow \text{[Structure]} \rightarrow 86
\]

ability for light-induced rearrangement of 40 is likely founded
1) in the capability of the internal bent bond of the cyclopropyl
ring to maintain continuous overlap with both the carbonyl group
and the double bond and 2) the possibility of rebonding by way of
a relatively strain-free cyclic pathway.

Meehan and Paquette have studied the photochemistry of another

\[
\overset{\text{hv}}{\text{[Structure]}} \rightarrow \text{[Structure]} \rightarrow \text{[Structure]}
\]

bicyclo[5.1.0]octenone system (95) and found similar multiplicity
results, except that the preformed triplet of 95 also rearranges
to product 96.

The synthesis and photochemical study of the methylene analog
(41) of 40 was undertaken in an effort to determine whether the pri-
mary reaction processes would differ dramatically if the n→π*
carbonyl excited state were absent. 2-Methylene-1,4,4-trimethyl-
bicyclo[5.1.0]oct-5-ene was photolyzed and found to yield one major
product in good yield (see Table 8) which was identified as 2-methyl-
ene-1,4,4-trimethylbicyclo[3.3.0]oct-6-ene (87). Multiplicity studies indicate that in the case of divinyl
cyclopropane 41, there is a marked reluctance of the hydrocarbon
triplet state to rearrange to 87. Since intersystem crossing of
$S_1-T_1$ is not generally observed in olefinic systems it appears
that, in the case of 41, the excited singlet species leads to form-
ation of 87 but the excited triplet species leads only to polymer
formation. This gross behavior parallels the photochemistry of
the structurally related ketone. In marked contrast, Meehan and Paquette found that 97 re-
arranges to 98 but that the bond reorganization is quite markedly

\[
\begin{align*}
97 & \xrightarrow{\text{hv}} 98 \\
\end{align*}
\]
sensitized. A possible explanation for this differing behavior may
be that the energy of the triplet $\pi \rightarrow \pi^*$ excitation of 97, heavily
concentrated in the conjugated diene moiety (absent in 41) is expec-
ted to facilitate migration of the stereoelectronically favored in-
ternal cyclopropyl bond.

Since the inception of this research effort, several publica-
tions have appeared concerning the photochemistry of cyclopropyl ke-
toness. Dauben and coworkers studied the photoreduction of cyclo-
propyl ketones and postulated the illustrated scheme to account for product formation. Another study from the same laboratory\textsuperscript{62b} indicates that when an intramolecular hydrogen abstraction (Norrish Type II) can occur, this process will prevail over other types of hydrogen migration. In a study of the photochemistry of spiro-

\[ \text{ketones, no breaking of the cyclopropyl bonds was detected; rather, } \alpha\text{-cleavage is the primary reaction pathway. Finally, Dauben and Schaffer}\textsuperscript{62d} studied the photochemistry of an acyclic } \]
vinylcyclopropane carbonyl chromophore and found that dihydrofurans

and epoxycyclobutanones were the products of irradiation.
Part III
PYROLYSIS OF MEDIUM-RING CYCLOPROPYL KETONES
AND THEIR METHYLENE ANALOGS

Introduction

The thermal rearrangement of cyclopropyl ketones has received little attention in the past. However, in the "abnormal Claissen rearrangement", the currently accepted mechanism postulates a cyclopropyl ketone intermediate which then rearranges thermally to products. Roberts and Landolt were the first to attempt to verify the existence of the cyclopropyl ketone intermediate and to generalize this type of reaction by studying the

\[
\begin{align*}
\text{H}_3\text{C} & \text{C} \rightleftharpoons \text{H} \text{CH}_3 \\
R = \text{H,CH}_3 & \Delta \rightarrow \text{R} \text{CH}_3 \text{CH} = \text{CH}
\end{align*}
\]

rearrangement of 1-acetyl-2,2-dimethylcyclopropane to (3-methylallyl)-acetone. These authors also showed in the rearrangement of 1-acetyl-2-methylcyclopropane that the cis-isomer rearranged readily while the trans-isomer was stable to the reaction conditions. The intramolecular mechanism proposed for these rearrangements necessitates a 3-hydrogen in a cis relationship between the carbonyl and alkyl group. Most recently, Ando reported that cyclopropyl esters rearrange thermally.
to the corresponding homoallyl esters as illustrated.

\[
\begin{align*}
\text{H}_3\text{C}2\text{C} & \quad \xrightarrow{\Delta} \quad \text{H}_3\text{C}2\text{C} \\
\text{H}_3\text{CO}_2\text{C} & \quad \text{H}_3\text{CO}_2\text{C} \\
\text{H}_3\text{CO}_2\text{C} & \quad \text{H}_3\text{CO}_2\text{C}
\end{align*}
\]

From the meager literature reports, we can tentatively state that the preferred pathway for thermal rearrangement of cyclopropyl ketones is to homoallyl ketones.

On the other hand, the thermal rearrangement of vinyl cyclopropane to cyclopentene is well documented. However, interpretation of the kinetic parameters for the formation of cyclopentene have, on the one hand, led to the conclusion that the rearrangement is concerted, and, on the other hand, that a discrete diradical intermediate is involved.

In the description of cyclopropane rearrangements, there are only but three possible sets of molecular motions: 1) a simultaneous epimerization at two of the three carbon atoms in the ring, 2) epimerization exclusively at one carbon atom in the ring, or 3) ran-
domination of the stereochemistry at two of the three carbon atoms in the ring at each observable event. Most cyclopropane rearrangements have been carried out using substrates with a symmetry such that two, or even all three, of these descriptions ambiguously fit the kinetic and stereochemical results, thereby forcing the differentiation of mechanism to be made by carefully chosen structural tests.

Recently, two publications by Wilcott and Cargle have appeared that lend support to conclusion that a discrete free-rotating diradical intermediate was indeed involved in the rearrangement of vinyl cyclopropane. These authors assert that the geometrical and structural isomerization of cyclopropane involves formation of the trimethylene diradical as an intermediate, a process with an activation energy of 63 kcal/mole. The addition of a vinyl group to the cyclopropyl ring should lower the activation energy for formation of a diradical by about 13 kcal/mole (the resonance energy of the allylic radical), thus leading to a pre-
dicted and observed activation energy for formation of an intermediate in the vinylcyclopropane isomerization of 50 kcal/mole. The kinetic and nmr results are consistent only with a mechanism in which stereochemistry is lost simultaneously at two centers (case 3). It is possible to identify this sharply defined result as evidence for the intervention of a diradical.

Results

All of the compounds that will be discussed in this section have been described in detail in Part II, and additionally they have been in each case subjected to ultraviolet irradiation. Since few studies have been reported on the thermal lability of cyclopropyl ketones, the following research effort contributes first to the total knowledge of the thermal stability of cyclopropyl ketones, and secondly provides some comparative thermal lability data on vinyl cyclopropanes, divinyl cyclopropanes and cyclopropyl ketones. Finally, a comparison between photolytic and thermal reactivity of these molecules is made possible.

The apparatus used to achieve the pyrolysis study was a 14" x 3/4" quartz tube filled with glass beads and heated to the desired temperature with an exterior furnace. During the actual pyrolysis, nitrogen was bled very slowly through the hot tube to provide a flow system in which a specific molecule would remain in contact with the heated glass beads for less than a few seconds. The apparatus was evacuated to about 10 mm while the sample was vaporized by means of localized heating with a heat gun and collect-
ed utilizing a Dry-Ice trap. Total mass yields were arrived at after molecular distillation at 50° (10 mm) and starting material: product-ratios were determined by vpc analysis.

**Bicyclo[6.1.0]non-6-en-2-one (38).** With the pyrolysis tube held at 600°, a quantity of 38 was pyrolyzed and the resulting viscous liquid when analyzed by vpc showed two peaks in a ratio of 9:1; these were starting material and thermolysis product, respectively. Total recovery upon molecular distillation was nearly quantitative. At 650°, vpc analysis showed 67% of 38 and 33% of 90. At 700°, vpc analysis showed 17% of 90 and 83% of 38 which suggests possible fragmentation of 90 after its formation. Additionally, several low yield (3-5%) products were detected.

The pyrolysis product was isolated by preparative vpc, and spectral data and structural analysis suggested its structure to be that of cis-bicyclo[4.3.0]non-7-en-2-one (90): ν\text{ neat} 1710, 1450, and 710 cm\(^{-1}\) and δ\text{CDCl}_3\text{, }\text{TMS} 1.2-3.4 (broad absorption, 10 H) and 5.7 (multiplet, 2 vinyl hydrogens). To confirm the initial structural assignment, the pyrolysis product (90) was hydrogenated over
palladium on carbon to yield cis-bicyclo[4.3.0]nonan-2-one (91) which was identical in all respects to an authentic sample: 

\[ \nu_{\text{max}}^{\text{neat}} \approx 1705, 1450, \text{and} 1130; \delta_{\text{CDCl}_3}^{\text{TMS}} \approx 1.1-2.8 \text{ (broad absorption)}. \]

2-Methylenebicyclo[6.1.0]non-6-ene (39). A sample of 39 was introduced into the pyrolysis apparatus held at 600°. Virtual quantitative (92%) recovery of a light yellow liquid was realized, and vpc analysis of which showed 98% of one pyrolysis product (92) with less than 2% starting olefin 39 remaining. Spectral data and structure analysis indicated the product to be 2-methylenebicyclo-

\[ \text{[4.3.0]non-7-ene (92); } \nu_{\text{max}}^{\text{neat}} \approx 1645, 1440, 884, 893, \text{and} 705 \text{ cm}^{-1}; \delta_{\text{CDCl}_3}^{\text{TMS}} \approx 1.0-3.1 \text{ (complex broad absorption - 4 methylene and 6 allylic hydrogens), 4.7 (broad singlet - 2 exocyclic methylene hydrogens) and 5.8 (unresolved multiplet - 2 vinyl hydrogens). Confirmation of the assigned structure was attained through chemical comparison of reaction products. For instance, 92 was hydrogenated with} \]

\[ \text{H}_2 \rightarrow \]

\[ \text{92} \rightarrow 93 \]
two moles of hydrogen to yield 2-methyl-cis-bicyclo[4.3.0]nonane (93).
This hydrocarbon (93) was synthesized independently by treating the
available ketone (91)\(^{72}\) with methylene triphenylphosphorane\(^{73}\) to
obtain 2-methyl-cis-bicyclo[4.3.0]nonane (94), followed by hydrogen-

\[
\begin{align*}
\text{91} & \quad \text{Ph}_2\text{CH}\_2 \\
\text{94} & \quad \text{H}_2
\end{align*}
\]

ation. The independently prepared hydrocarbon was identical in
all respects to 93.

1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-one (40). A weighed
sample of (40) was subjected to the pyrolysis apparatus held at
500, 550, and 600°. At 500°, total mass recovery was nearly quan-
titative (95%) and vpc analysis showed two peaks present in a ratio
of 3:1 [starting ketone (40) to pyrolysis product (86)]. At 550°,
the pyrolysis product was about 2% contaminated with starting ketone;
the total mass yield in this run was approximately 81%. At 600°,
the reaction mixture showed one peak by vpc with only a minute trace
(< 1%) of starting ketone (40). The yield was in the vicinity of
50%.

Isolation of the thermal product (86) was accomplished by pre-
parative vpc and spectral data and structure analysis indicated the
thermal product to be 1,4,4-trimethylbicyclo[3.3.0]oct-6-en-2-
one (86). Comparison of the spectral data and vpc retention times on two columns with the photoproduct of 40 showed both to be identical in all respects.

2-Methylene-1,4,4-trimethylbicyclo[5.1.0]oct-5-ene (41). A weighed sample of 41 was introduced into the pyrolysis apparatus at temperatures of 500° and 550°. At 500°, vpc of the clear pyrolysate showed two peaks in the ratio of 1:4 [starting material (41) to pyrolysis product (87)]. The total mass recovery was 85%. At 550°, vpc analysis of the reaction mixture showed the clear liquid to be homogeneous. The total mass recovery was 70%. Isolation of the pyrolysis product 87 was accomplished by vpc, and spectral data of 87 proved it to be identical in all respects with the photoproduct of 41 as discussed in Part II.

Additionally, four other molecules (36, 37, 95, and 96) were subjected to analogous pyrolysis conditions. Pyrolysis temperatures up to 650° were used in each case and vpc analysis of the resulting
liquids showed only the presence of the starting ketones with less than 1\% of any unidentified peaks. Additionally, the conditions utilized for the vpc analysis would easily detect less than 0.5\% of any impurity. The total mass yields after pyrolysis in the case of 36 and 37 were about 85-90\% while those of 95 and 96 were 60-70\%.

**Discussion**

If the experimental data contained in this section is summarized, it is obvious that there are some well-defined generalities that can be advanced concerning the reactivity of the illustrated structures. The first observation is that molecules containing only a conjugated cyclopropyl ketone moiety (e.g. 36 and 37) appear stable to the standard pyrolysis conditions utilized in this study. Additionally, both 95 and 96 are also stable but they contain another site of unsaturation in the form of a double bond. There is, however,
little if any overlap between the double bond and cyclopropyl group

\[
\begin{align*}
40 & \xrightarrow{\Delta} 86 \\
38 & \xrightarrow{\Delta} 90 \\
36 & \xrightarrow{\Delta} \\
95 & \xrightarrow{\Delta} \\
41 & \xrightarrow{\Delta} 87 \\
39 & \xrightarrow{\Delta} 92 \\
37 & \xrightarrow{\Delta} \\
96 & \xrightarrow{\Delta} 
\end{align*}
\]

in both cases; thus, the two moieties behave independently of each other. Both \(\alpha,\beta\) and \(\beta,\gamma\)-unsaturated ketones appear stable to pyrolysis conditions.

The unreactivity of the cyclopropyl ketone function to pyrolysis conditions is supported by the near total absence of literature reports concerning this subject. However, two very recent reports, one on cyclopropyl ketones\(^6\) and one on cyclopropyl esters,\(^6\) indicate that the cyclopropyl ketone moiety is indeed thermally la-
bile. In both of these cases, the parent compounds (97 and 98) are acyclic in conformation and have \( \gamma \)-hydrogens available \textit{cis} to the carbonyl group for an intramolecular rearrangement as illustrated.

In the specific cyclic cyclopropyl ketones that are the subject of this study, there also exists hydrogens \( \gamma \) to the carbonyl group. However, these hydrogens are constrained by a ring system which prevents the necessary molecular movement to achieve the conformation conducive to an intramolecular rearrangement (e.g. 101).
Another generality that appears evident is that the remaining four structures containing either a divinyl cyclopropane moiety (72, 76) or a vinyl cyclopropyl ketone chromophore (70, 74), prefer to react under pyrolysis conditions to yield products derived from the well-known vinyl cyclopropane to cyclopentene rearrangement. As discussed in the introduction to this section, a discrete diradical species is favored over a concerted pathway as a possible intermediate in the vinyl cyclopropane to cyclopentene rearrangement. If we visualize the suggested diradical species for both the divinyl cyclopropane and vinyl cyclopropyl ketone, it is clear that the possible intermediates are quite stabilized species having either two allylic radicals (102) or one allylic radical and one radical α to a carbonyl (104). Both allylic radicals 74 and radicals α to carbonyls 75 are quite stabilized species.

We can postulate, then, that the pyrolyses of structures 70, 72, 74, and 76 proceed by an initial formation of a diradical intermediate which then rearranges through the allylic center to form products. A review of the thermal products of aforementioned structures, indicates that products arising from other
resonance forms (109 + 110) of the initially proposed diradical inter-

\[
\begin{align*}
R^\circ, CH_2
\end{align*}
\]

termediates are not detected in the reaction mixture. In fact,

\[
\begin{align*}
R^\circ, CH_2
\end{align*}
\]

the products isolated result only from the proposed intermediate

\[
\begin{align*}
R^\circ, CH_2
\end{align*}
\]

which rearranges in the illustrated manner (111). This can be rationalized on the basis of minimization of ring strain in product formation relative to that of starting material.

One last factor to consider is why only the internal cyclo-
propyl bond ruptures in preference to the other two bent bonds.

If one looks at the resulting diradical intermediate species (106, 112, and 113) one sees that the diradical species formed by cleavage of the internal cyclopropyl bonds results in a more resonance stabilized diradical which allows for a lower energy reaction pathway.
EXPERIMENTAL

Cycloheptanone Ethylene Ketal (2). Into a 500-ml round-bottomed flask equipped with a reflux condenser and a Dean Stark phase-separating head was placed 250 ml of benzene, 56 g (0.5 mole) of cycloheptanone, 31 g (0.5 mole) of ethylene glycol, and 0.3 g of p-toluenesulfonic acid. The reaction mixture was refluxed for 12 hr while 9 g (0.5 mole) of water collected in the Dean Stark trap. After washing with two 50-ml portions of 10% sodium bicarbonate solution, the organic solution was dried over magnesium sulfate, concentrated in vacuo, and fractionated to yield 62.4 g (80%) of cycloheptanone ethylene ketal, bp 60-62° (3 mm) [lit. 76 bp 50-52° (1 mm)].

2-Bromocycloheptanone Ethylene Ketal (3). To a solution of 150 ml of ethylene glycol and 18 g (0.12 mole) of cycloheptanone ethylene ketal was added 19.2 g (0.12 mole) of bromine dropwise keeping the reaction mixture about 30° by utilizing an ice bath. The reaction mixture was stirred for an additional 15 min and then poured slowly into a stirred mixture of 200 ml of pentane and 50 g of anhydrous sodium bicarbonate. Water was added (250 ml) and the organic layer separated, washed with dilute sodium bicarbonate solution and dried over anhydrous sodium bicarbonate. The organic solution was concentrated in vacuo and fractionated
to yield 19.7 g (71%) of 3, bp 76-81° (0.4 mm) [lit: 77 bp 79-83° (0.5 mm)].

2-Cycloheptenone Ethylene Ketal (4). Crude 2-bromocycloheptanone ethylene ketal (37.6 g, 0.16 mole) was refluxed for 48 hrs with 100 ml of methanol and 25 g of sodium hydroxide. The reaction mixture was poured into 200 ml of water and extracted with three 150-ml portions of pentane. The organic extracts were combined, dried over anhydrous magnesium sulfate, and concentrated to yield 18.5 g (75%) of 4, bp 72-74° (3 mm) [lit: 77 bp 67° (2.4 mm)].

2-Cycloheptenone (5). To 25 ml of 3% sulfuric acid solution in a 100 ml separatory funnel was added 18.5 g (0.12 mole) of 2-cycloheptenone ethylene ketal. The reaction mixture was shaken for 5 min and extracted with three 50-ml portions of ether. The ethereal extracts were washed with dilute sodium bicarbonate solution and brine, dried over magnesium sulfate, concentrated in vacuo and fractionated to yield 11.8 g (90%) of 2-cycloheptenone, bp 82-83° (15 mm) [lit: 77 bp 52-53° (2.4 mm)].

2,2-Dimethyl-3-cycloheptenone (6). 2-Cycloheptenone (3.3 g, 0.03 mole) was added to a solution of 10 g (0.09 mole) of potassium t-butoxide in 250 ml of absolute t-butyl alcohol. To this solution was added 22 g (0.15 mole) of methyl iodide dropwise with ice-bath cooling. The reaction mixture was stirred overnight, poured into 200 ml of water, and extracted with three 75-ml por-
tions of ether. The combined organic layers were dried, filtered, and evaporated, and the resulting oil was distilled to give 2.9 g (69%) of 6, bp 85-90° (12 mm) of approximately 90% purity (vpc analysis - 6' x $\frac{1}{4}$" Al column packed with 5% SP-96 on 60/80 Chrom G). Purification by preparative scale gas chromatography (same column) afforded 2.5 g (60%) of pure 6 as a colorless liquid, bp 85-90° (12 mm) of approximately 90% purity (vpc analysis - 6' x $\frac{1}{4}$" Al column packed with 5% SP-96 on 60/80 Chrom G). Purification by preparative scale gas chromatography (same column) afforded 2.5 g (60%) of pure 6 as a colorless liquid, bp 85-90° (12 mm) of approximately 90% purity (vpc analysis - 6' x $\frac{1}{4}$" Al column packed with 5% SP-96 on 60/80 Chrom G).

Irradiation of 2,2-Dimethyl-3-cycloheptenone (6). To a solution of 1.0 g of 6 in 450 ml of anhydrous ether was added 0.5 g of cyclooctane as internal standard. The solution was placed under an atmosphere of nitrogen and was irradiated with a 450-w Hanovia mercury vapor lamp in a quartz immersion-well apparatus fitted with a vycor filter. The course of the reaction was followed by removing small aliquots at various intervals. After 4.5 hr, a photostationary state consisting of approximately 8% of 2,2-dimethyl-3-cycloheptenone and 92% of a lone photoproduct 7 was attained. The solvent was evaporated at 0°, and the photoproduct was isolated by preparative scale vpc. Molecular distillation at 50° (3 mm) served to provide an analytical sample...
which was assigned the structure of 2-isobutenylcyclopentanone;

\[ \nu_{\text{C=O}}^{\text{max}} 1750 \text{ (s, carbonyl group)} \text{ and } 1670 \text{ cm}^{-1} (w, \text{ C=C}) ; \]

\[ \lambda_{\text{max}} \text{ isoctane } 295 \text{ (80)}, 310 \text{ (90)}, 325 \text{ (70)}, \text{ and } 355 \text{ nm (e 25)}; \]

\[ \delta_{\text{TMS}} \text{ CDCl}_3 4.97 \text{ (doublet of septuplets, J = 9.0 and 1.5 Hz, 1H, vinyl proton), ca. 3.0 \text{ (broad multiplet, 1H, allylic C-carbonyl proton), 1.6-2.5 \text{ (broad absorption, 6H, methylene protons), and 1.76 and 1.68 (singlets, 3H each, methyl groups).} } \]

Anal. Calc'd for C_{9}H_{14}O: C, 78.21; H, 10.21. Found: C, 78.06; H, 9.97.

2,7-Dibromocycloheptanone Ethylene Ketal (11). To a solution of 15.6 g (0.1 mole) of cycloheptanone ethylene ketal in 150 ml of anhydrous ether was added 32 g (0.2 mole) of bromine at such a rate as to maintain a gentle reflux of ether. Extra bromine (several drops) was added until the bromine color persisted for several minutes. A solution of monosodium ethylene glycolate prepared from 5 g of sodium and 75 ml of ethylene glycol was added slowly and the resulting mixture was poured into water. The ether layer was separated, dried over anhydrous magnesium sulfate, and concentrated in vacuo to yield 30 g (97%) of crude yellow oil which was used in the next step without further purification.

Cyclohepta-2,6-dienone Ethylene Ketal (12). The crude dibromo ketal product (3 g, 0.1 mole) was added to a mixture of 22 g (0.9 mole) of sodium hydroxide and 100 ml of methanol. The reaction
mixture was refluxed for 48 hr, cooled, poured into 200 ml of water, and extracted with two 100-ml portions of pentane. The extracts were dried over magnesium sulfate, concentrated \textit{in vacuo} and fractionated to yield 9.3 g (60%) of 12, bp 68-69° (1 mm) \cite{lit:77} bp 58° (0.75 mm).

Cyclohepta-2,6-dienone (13). To 7.6 g (0.05 mole) of cyclohepta-2,6-dienone ethylene ketal in a 100 ml separatory funnel was added 10 ml of a 3% sulfuric acid solution. The reaction mixture was shaken for 10 minutes and extracted with three 50-ml portions of ether. The ethereal extracts were washed with dilute sodium bicarbonate solution and brine, dried over magnesium sulfate, concentrated \textit{in vacuo}, and fractionated to yield 4.3 g (80%) of 13, bp 55-57° (0.6 mm) \cite{lit:77} bp 58° (0.75 mm).

2,2,7,7-Tetramethylcyclohepta-3,5-dienone (14). A 2.16 g (0.02 mole) sample of 2,5-cycloheptadienone was dissolved in 50 ml of dry tert-butyl alcohol containing 9.0 g (0.08 mole) of potassium tert-butoxide. To the ice-cooled solution, there was added 14.2 g (0.10 mole) of methyl iodide over a period of 30 min. This solution was allowed to warm to room temperature overnight and then poured into 200 ml of water and extracted with two 100-ml portions of ether. The combined organic extracts were washed with brine, dried over anhydrous magnesium sulfate, concentrated \textit{in vacuo}, and fractionated to yield 2.3 g (70%) of 14, bp 48-51° (1.5 mm). An analytical sample of 14 was
obtained by preparative scale vpc (10% SE-30 on Chromosorb G, 150°C);

\[ \nu_{max}^{CCl_4} = 1700, 1660, \text{and} 1615 \text{ cm}^{-1}; \lambda_{max}^{isoctane} = 235 \text{ (5170)} \text{ and} 282 \text{ nm (e 730)}; \lambda_{max}^{CH_2OH} \approx 243 \text{ (4680)} \text{ and} 290 \text{ nm (e 710)}; \delta_{TMS}^{CDCl_3} A_{2}B_{2} \text{ pattern}

centered at 5.77 (J_{AB} = J_{AB} = 10 \text{ Hz}; J_{BB} = 1 \text{ Hz}; 4H, vinyl protons)

and a singlet at 1.27 (12H, methyl groups).

**Anal.** Calcd for C_{11}H_{16}O: C, 80.44; H, 9.83. Found: C, 80.00; H, 9.83.

**Irradiation of 2,2,7,7-Tetramethylcyclohepta-3,5-dienone (14).**

A solution of 1.0 g of 14 in 450 ml of acetone was irradiated as above through Corex optics. After 55 min, the reaction was virtually complete. The solvent was evaporated and the nonpolymeric residue (0.7 g, 70%) was subjected to preparative scale vpc. The lone photoproduct was obtained as a colorless oil; \( \nu_{max}^{\text{next}} = 1700 \text{ cm}^{-1} \);

the nmr spectrum (in CDCl_3) displayed singlets at \( \delta = 8.73, 8.85, 8.89, \text{ and} 8.99 \text{ (3H each, methyl groups)}, \text{ a multiplet at} \ 8.26 \text{ (2H, cyclopropyl protons)}, \text{ and a multiplet at ca.} 4.38 \text{ (2H, vinyl protons).}

The identity of these spectra with the infrared and nmr spectra of an authentic sample of 3-methyl-4-caren-2-one (15) \text{22b} was clearly indicated.

**Photolysis Runs.** Results of the irradiation of 6 and 14 under a variety of conditions are tabulated in Tables 1-3. All of these photolyses were performed in quartz test tubes held in a vertical position on the outer surface of the water-cooled quartz immersion well. In a typical experiment, 250 mg of 14 and 100 mg of cyclo-
octane (internal standard) were diluted to a specific volume with the solvent of choice (each solvent was purified by appropriate methods until it was homogeneous to vpc). The quartz test tubes were carefully flushed with nitrogen and tightly stoppered with serum caps which permitted withdrawal of aliquots with a microsyringe. An aliquot was removed at time zero and analyzed by vpc. (A 0.125" x 10' stainless steel column packed with 5% SE-30 on 60/80 Chromsorb W at 155° was employed in conjunction with an Aerograph Hi-Fy Model 600D gas chromatograph equipped with a flame ionization detector). The gas chromatographic unit was carefully calibrated by the procedure utilized in one of our earlier papers. The areas of the various gas chromatographic peaks were determined by cutting and weighing Xerox reproductions of the vpc curves (good quality paper).

In the attempted quenching studies, piperylene (Aldrich) was freshly fractionated prior to use. Naphthalene (reagent grade) was employed as received.

In the sensitized runs, acetone (analytical reagent) and benzo-phenone (reagent grade) were employed as received.

7-Bromocyclooctene. Into a one liter round-bottom flask equipped with a condenser was added 300 ml carbon tetrachloride, 22 g (0.2 mole) of cyclooctene, 35 g (0.2 mole) of N-bromosuccin-imide and 0.5 g of benzoyl peroxide. The reaction mixture was heated over a steam bath for 24 hr, cooled, filtered to remove the
floating succinimide, and concentrated in vacuo to yield approximately
38 g (~100%) of 3-bromocyclooctene as a viscous oil which was used
without purification.

_Cycloocten-2-yl acetate (42)._ To 26.7 g (0.14 mole) of crude
3-bromocyclooctene was added with cooling a slurry of 28.2 g (0.17
mole) of silver acetate in 50 ml of acetic acid. The reaction mix­
ture was stirred overnight, filtered, washed well with two 25-ml
portions of acetic acid and concentrated in vacuo. The residue
was again filtered and fractionated to yield 16 g (75%) of a
clear liquid, bp 80-82°, (5 mm) [lit: bp 56-58° (1 mm)].

A second method of synthesis was by placing 10 g (0.09 mole)
of cyclooctene, 29 g (0.09 mole) of mercuric acetate and 10 ml of
acid into a 25-ml three-necked round-bottom flask equipped with a
condenser. This slurry was heated at 140° for 4 hrs during which
time the slurry became homogeneous and mercury had precipitated.
The mixture was cooled, decanted from the mercury, and concentrated
in vacuo. The residue was distilled to yield 6.0 g (60%) of pure
cycloocten-2-yl acetate, bp 81-82° (5 mm).

_2-Cycloocten-1-ol (43)._ To 5.6 g (0.1 mole) of potassium
hydroxide in 7 ml of water and 15 ml of ethanol was added 7.7 g
(0.45 mole) of cycloocten-2-yl acetate (42). The reaction mix­
ture was stirred magnetically for 4 hrs, diluted with 25 ml of
water, and extracted with two 100-ml portions of ether. The
ethereal extracts were combined, dried over anhydrous magnesium sulfate, concentrated in vacuo and fractionated to yield 5.3 g (91%) of a clear liquid, bp 74° (2 mm) [lit: bp 66-68° (1 mm)].

A second method of synthesis was achieved by adding 2-bromo-cyclooctene (24 g, 0.13 mole) to a mixture of 240 ml of acetone, 160 ml of water, and 25 g of sodium bicarbonate. The solution was refluxed for 1 hr and then the acetone was removed in vacuo. The aqueous residue was extracted with two 100-ml portions of ether. The organic extracts were dried over anhydrous magnesium sulfate, concentrated in vacuo and fractionated to yield 11.7 g (73%) of 2-cyclooctenol, bp 90-93° (12 mm).

cis-Bicyclo[6.1.0]nonan-2-ol (44). A mixture of 13 g of methylene iodide (0.05 mole) of methylene iodide, 0.05 g of iodine, 5.0 g of freshly prepared zinc-copper couple, and 30 ml of anhydrous ether was heated under reflux for 30 min. External heating was discontinued and 3.8 g (0.03 mole) of 2-cyclooctenol (43) in 10 ml of dry ether was added at a rate sufficient to maintain reflux. After addition was complete, the mixture was refluxed for two days. The solution was cooled, filtered, and washed successively with 3% hydrochloric acid solution (100 ml), 10% sodium bicarbonate solution (50 ml), and saturated brine. After drying the solution over anhydrous magnesium sulfate, the solvent was removed in vacuo and the alcohol was distilled to yield 2.6 g (70%) of 44, bp 97-98° (4 mm) [lit: bp 98° (4 mm)].
cis-Bicyclo[6.1.0]nonan-2-one (36). A solution (10 ml) of Jones reagent (prepared from 26.7 g of chromium trioxide and 23 ml of sulfuric acid diluted to 100 ml with water; 2.67 mmol/ml) was added to 2.89 g (0.02 mole) of cis alcohol 44 dissolved in 100 ml of acetone and cooled in an ice bath. A permanent (75 min) color change from a turbid green to a reddish brown indicated an excess of oxidant. Methyl alcohol (5 ml) was added to remove the excess oxidant and the mixture was decanted, the solid triturated with acetone, and all organic solutions were combined and concentrated in vacuo. Ether (50 ml) was added and the organic solution was washed with sodium bicarbonate solution, dried over anhydrous magnesium sulfate, concentrated, and fractionated to yield 2.4 g (86%) of 36 bp 99-100° (5 mm) [lit : 84 bp 72-74° (2.5 mm)].

Irradiation of 36 in Ether. A solution of 2 g of 36 in 450 ml of anhydrous ether was irradiated with a 450-w Hanovia mercury-vapor lamp in an immersion-well apparatus fitted with a Corex filter. The progress of the reaction was followed by withdrawal of small aliquots at periodic intervals and analysis of these by vapor phase chromatography. For quantitative work as in Table 4, carefully weighed amounts of 36 and cyclooctane were dissolved in ether and this solution was partitioned into several quartz test tubes which were affixed in vertical array around the immersion well. Each tube was then tightly stoppered with a serum cap which permitted the withdrawal of aliquot samples with a microsyringe.
Upon termination of the irradiation (2 hr), the solution was carefully concentrated, and the residual oil was subjected to preparative scale VPC (6' x 0.25" Al column packed with 5% SF-96 on Chromosorb G). The second substance to be eluted proved to be cyclononanone (45) by comparison with physical and spectral data of an authentic sample.

The first component was identified as 3-methylcyclooctane (46). This ketone was synthesized independently by the addition of methylmagnesium bromide to 2-cyclooctenone in the presence of cuprous chloride.

When the solvent fraction was examined gas chromatographically, the presence of 5 was detected. A small amount of this volatile substance was isolated by preparative VPC; \(^{1}H NMR\) 3.15-3.72 (multiplet, 6H, CHO-protons) and 1.0-1.3 (multiplet, 12H, methyl groups).

3-Methylcyclononanone (46). To a solution of methyl magnesium iodide prepared from 0.24 g (0.01 mole) of magnesium turnings in 30 ml of dry ether and 1.4 g (0.01 mole) of methyl iodide in 20 ml of dry ether under nitrogen was added 45 mg of cuprous chloride. The solution was cooled to 5° and a solution of 1.3 g (0.01 mole) of 2-cycloocten-1-one in 15 ml of dry ether was added. Internal temperature was maintained at 5-8° during the addition, and stirring was continued overnight at room temperature. The mixture was poured into 30 g of ice and cold 30% sulfuric acid was added (just enough to dissolve the hydroxide). The ether layer was separated and the
aqueous layer was extracted twice with ether. The combined ether layers were washed with 10% sodium bicarbonate, dried over anhydrous magnesium sulfate, concentrated in vacuo, and fractionated to yield 1.0 g (79%) of 3-methylcyclooctanone, bp 93-94° (11 mm) [lit:85 bp 88° (13 mm)].

Irradiation of 36 in t-Butyl Alcohol. cis-Ketone 36 was irradiated (Corex optics) in t-butyl alcohol solution. After approximately 8 hr, the solvent was carefully removed by fractional distillation, and the residual liquid was subjected to preparative scale vpc separation as described for photolysis of 36 in ether.

The first photoproduct to be eluted was subsequently shown to be 4,8-nonadienal (48); \( \nu^\text{max} \) \( \text{C}_2\text{H}_5\text{OH} \) only end absorption; \( \delta^\text{CDCl}_3 \) 9.36 (triplet, \( J \approx 1 \) Hz, aldehyde proton), 4.8-5.65 (multiplet, 5H, vinyl protons), and 2.0-2.65 (two broad peaks, 10H, allylic and \( \alpha \)-carbonyl protons).

Anal. Calcd for \( C_9H_{14}O \): C, 78.21; H, 10.21. Found: C, 78.50; H, 10.44.

The second component was subsequently shown to be 2-(4-pentenyl)cyclopropane carboxaldehyde (49); \( \nu^\text{max} \) \( \text{C}_2\text{H}_5\text{OH} \) and 1645 cm\(^{-1}\); \( \delta^\text{CDCl}_3 \) 8.95 (doublet, \( J = 5.0 \) Hz, aldehyde proton), 4.8-6.18 (multiplet, 3H, terminal vinyl group), 86 and 1.0-1.55 (broad absorption, 11H, methylene, allyl, and cyclopropyl protons).

The 2,4-dinitrophenylhydrazone of 7 had mp 102-104°.

Anal. Calcd for \( C_{15}H_{20}N_4O_4 \): C, 56.24; H, 5.92. Found: C, 56.05; H, 5.92.
The third and major photoproduct proved to be identical in all respects to an authentic sample of trans-bicyclo[6.1.0]nonan-2-one (37).

cis-2-Octenol (51). A solution of 1.26 g (0.01 mole) of 2-octynol (50), in 25 ml of hexane containing 5% palladium on barium sulfate was hydrogenated at atmospheric pressure and room temperature. After the consumption of one equivalent of hydrogen (224 ml), the catalyst was removed by filtration, and the filtrate was concentrated to give 1.26 g of 51. A pure sample of 51 was obtained by preparative vpc (5' x 1/8" Al column packed with 5% SF-96 on 60/80 Chromosorb G); $\nu_{\text{max}}$ 3250 cm$^{-1}$; $\delta_{\text{CDCl}_3}$ TMS 0.8-2.3 (11 H), 2.7 (1 H, singlet, OH), 4.0-4.2 (2 H, multiplet, -CH$_2$OH), 5.4-5.7 (2 H, multiplet, vinyl hydrogens).

cis-1-Hydroxymethyl-2-n-pentylcyclopropane (52). To a stirred mixture of 5 g of zinc-copper couple (freshly prepared by the Shank-Shechter method), 0.02 g of iodine, and 100 ml of anhydrous ether was added 8.7 g (0.05 mole) of methylene iodide. The flask was heated in the absence of atmospheric moisture until a spontaneous reaction began as evidence by continued refluxing of the ether when the heat source was removed. Upon completion of the exothermic reaction, the mixture was refluxed for 30 min. The heat was removed and to this mixture there was added a solution of 5.43 g (0.04 mole) of 51 in 10 ml of anhydrous ether at
a rate sufficient to maintain constant reflux. When the addition was completed, the mixture was refluxed for 3 hr. The flask was cooled and the mixture was filtered; the filtrate was washed with cold dilute hydrochloric acid and saturated sodium bicarbonate solution, dried, and concentrated in vacuo to yield 4.2 g (75%) of crude oil. A pure sample of 52 was obtained by preparative vpc (5” × ½” A1 column packed with 5% SF-96 on 60/80 Chromosorb G); ν<sub>max</sub><sup>νeak</sup> 3275 cm<sup>-1</sup> (-OH); δ<sup>CDCl₃</sup><sub>TMS</sub> 0.7-1.7 (15 H), 2.6-2.9 (1 H, multiplet, OH), and 3.6 (2 H, doublet, CH₂OH).

 CIS-2(p-Pentyl)cyclopropane Carboxaldehyde (53). A solution of 256 mg (0.002 mole) of 52 in 20 ml of acetone was cooled to 0° in an ice-salt bath. To this stirred solution was added slowly 0.0022 mole of Jones reagent. Upon completion of the addition, one ml of methanol was added to remove excess oxidant and the solution was filtered and carefully concentrated; ether was added and this solution was washed with dilute sodium bicarbonate, dried, and concentrated in vacuo. Preparative vpc on a 6’ × ½” A1 column of 5% SF-96 on 60/80 Chromosorb G of the residue gave 100 mg (55%) of 53; ν<sub>max</sub><sup>νeak</sup> 1710 cm<sup>-1</sup>; δ<sup>CDCl₃</sup><sub>TMS</sub> 0.8-2.5.


 Vinylation of 2-Hepten-4-ol (56). A solution of 1.14 g (0.01 mole) of 2-hepten-4-ol (55) and 1.0 g of mercuric acetate in 60 ml of vinyl ether was heated at reflux under nitrogen for
16 hr. After cooling, the mixture was treated with 0.1 g of glacial acetic acid, stirred for 3 hr at room temperature, and diluted with an equal volume of pentane. This solution was washed with 5 ml of 5% sodium hydroxide solution, dried over anhydrous potassium carbonate, and evaporated in vacuo. The residual oil (1.20 g, 95%) was shown to be 95% homogeneous by vpc. A pure sample of 56 was obtained by preparative scale vpc (6' x ½" Al column packed with 5% Carbowax 200 M on 60/80 mesh Chromosorb G); \( \nu_{\text{max}} \) 1640 and 1190 cm\(^{-1}\); \( \delta_{\text{TMS}} \) 0.7-1.7 (7 H), 1.7 (doublet, 3 H, allylic methyl group), 3.9-4.4 (3 H, 2 vinyl and 1 vinyl hydrogen next to oxygen), 5.4-5.7 (2 H, methylene), and 6.1-6.5 (1 H, methylene next to oxygen).

**Anal.** Calcd for C\(_9\)H\(_{16}\)O: C, 77.09; H, 11.50. Found: C, 76.62; H, 11.82.

3-Methyloct-4-en-1-al (57). Into a thick-walled Pyrex glass tube was placed 200 mg (0.018 mole) of the crude 4-(hept-2-enyl)vinyl ether (56) and the tube was flushed with nitrogen and sealed. The sealed Pyrex tube was lowered into a steel tube, wrapped with nichrome wire and heated to 180°, and the reaction vessel held at 180° for 3 hrs. The resulting viscous brown liquid was obtained by preparative vpc (6' x ½" Al column in 5% SF-96 on 60/80 Chrom G) to yield 165 mg (82%) of unsaturated aldehyde 57; \( \nu_{\text{max}} \) 2950(s), 2720(m), 1750(s), 1495(s), 1470(m), and 972(s) cm\(^{-1}\); \( \delta_{\text{TMS}} \) 0.7-3.0 (13 H), 5.4 (2 H, multiplet) and 9.75 (triplet, 1 H, aldehyde proton).

**Anal.** Calcd for C\(_{9}\)H\(_{16}\)O: C, 77.09; H, 11.50. Found: C, 77.37; H, 11.74.
3-Methyl-1-octanal (54). Into an atmospheric hydrogenation flask was placed 20 mg of 5% Pd/C catalyst, 25 ml of reagent grade hexane, and 42 mg (0.0003 mole) of 3-methyl-4-en-1-ol. After 90 min, approximately 1 eq (7.0 ml) of hydrogen was absorbed and the catalyst was removed by filtration. The organic filtrate was concentrated in vacuo to yield 38 mg (90%) of 3-methyl-1-octanal which was shown to be homogeneous by vpc. Preparative vpc (6' x ½" in 5% Carbowax on 60/80 Chrom G) afforded an analytical sample; ν neat max 2900(s), 2710(m), 1750(s), 1460(s), and 1380(m), cm⁻¹; δ TMS CDCl₃ 0.8-2.5 (17 H) and 9.8 (triplet, 1 H, aldehyde proton).


8,8-Dibromobicyclo[5.1.0]octane (59). To a stirred mixture of 26.8 g (0.24 mole) of potassium tert-butoxide, 17.1 g (0.17 mole) of cycloheptene, and 175 ml of dry pentane, cooled in an ice bath, was added 43.8 g (0.17 g) of bromoform under nitrogen over a period of 3 hr. The reaction was stirred for 16 hr at room temperature after which 30 ml of water was added dropwise. The resulting mixture was extracted with three 100-ml portions of ether and the organic extracts were dried over anhydrous magnesium sulfate, concentrated in vacuo, and fractionated to yield 24 g (50%) of 59, bp 75-77° (0.5 mm) [lit: 87 bp 73-74° (0.4 mm)].

exo-8-Bromobicyclo[5.1.0]octane (60). A solution of dimethyl sodium was prepared by stirring a mixture of 2.13 g (0.11 mole)
of sodium hydride (previously washed three times with pentane to remove the mineral oil) in 75 ml of dry dimethyl sulfoxide under a nitrogen atmosphere at 75° for 45 min. The resulting gray mixture was cooled in an ice bath (making sure the dimethyl sulfoxide did not freeze) as 10 g (0.035 mole) of dibromide (59) was added rapidly over a period of 2 min. The ice bath was removed and the resulting dark brown mixture was stirred at room temperature under nitrogen for 6 hrs, diluted with 250 ml of water, and extracted with three 100-ml portions of chloroform. The combined organic layers were washed with brine, dried over anhydrous magnesium sulfate, concentrated in vacuo, and fractionated to yield 4.5 g (64%) of 60, bp 90-93° (30 mm) [lit: bp 90-93° (30 mm)].

**trans-2-Cyclooctenol (61).** A mixture of 4.5 g (0.035 mole) of exo-8-bromobicyclo[5.1.0]octane, 115 ml of reagent grade dioxane, 57 ml of water, and 2.0 g of sodium bicarbonate was refluxed for 25 hrs, cooled, and concentrated in vacuo. Water (50 ml) was added to the sludge and the mixture was extracted with three 25-ml portions of ether. The combined ethereal phases were dried over anhydrous magnesium sulfate, concentrated in vacuo, and fractionated to yield 1.6 g (53%) of 61, bp 72-75° (1 mm) [lit: bp 82-83° (3 mm)].

**trans-Bicyclo[6.1.0]nonan-2-ol (62).** A mixture of 13 g (0.01 mole) of methylene iodide, 0.05 g of iodine, 5.0 g of freshly prepared zinc-copper couple,81 and 30 ml of anhydrous ether was heated
under reflux for 30 min. External heating was discontinued and 3.8 g
(0.03 mole) of \textit{trans}-2-cyclooctenol (61) in 10 ml of dry ether was
added at a rate sufficient to maintain reflux. After addition was
complete, the mixture was refluxed for 2 days. The solution was
cooled, filtered, and washed successively with 3% hydrochloric acid
(11 ml), 10% sodium bicarbonate solution (50 ml), and saturated
brine. After drying over anhydrous magnesium sulfate, the solvent
was removed in \textit{vacuo} and the residue was fractionated to yield 2.8 g
(78%) of 62, bp 68-69° (4 mm) \[\textit{lit}^{84,89}\text{ bp 63-65° (0.3 mm)}\].

\textit{trans}-Bicyclo[6.1.0]nonan-2-one (37). A solution (10 ml) of
Jones reagent\textsuperscript{83} (prepared from 26.7 g of chromium trioxide and 73 ml
of sulfuric acid diluted to 100 ml with water; 2.67 mmole/ml) was
added to 2.9 g (0.02 mole) of \textit{trans} alcohol 62 dissolved in acetone
and cooled in an ice bath. A permanent (75 min) color change from
a turbid green to a reddish brown indicated an excess of oxidant.
Methyl alcohol (5 ml) was added to remove the excess oxidant and
the mixture was decanted, the solid triturated with acetone, and
all organic solutions were combined and concentrated in \textit{vacuo}.
Ether (50 ml) was added and the organic solution was washed with
sodium bicarbonate solution, dried over anhydrous magnesium sul-
fate, concentrated, and fractionated to yield 2.2 g (80%) of 37,
bp 99-100° (45 mm) \[\textit{lit}^{84,89}\text{ bp 74-76° (2.5 mm)}\].

Irradiation of 37 in \textit{t}-Butyl Alcohol. A solution of 1.38 g
(0.01 mole) of 37 in 450 ml of dry \textit{t}-butyl alcohol was irradiated
through Corex optics in the above manner. After 12 hr, the solution was carefully concentrated and the lone photoproduct (63) was isolated by preparative vpc (6' x 0.25" Al column packed with 5% Carbowax 2000 M on 60/80 mesh Chromosorb G); ν<sub>max</sub><sup>nec</sup> 1715 cm<sup>-1</sup>; δ<sub>TMS</sub> 1.45 (singlet, 9 H) and two broad multiplets centered at 1.32 and 0.88 (peak at 0.88 represents central band of methyl absorption).

**Anal.** Caled for C<sub>13</sub>H<sub>24</sub>O<sub>2</sub>: C, 73.53; H, 11.39. Found: C, 73.70; H, 11.31.

For the deuterium labelling studies, the following analytical procedure was employed. That the underlined protons appeared at lower field in the δ1.32 envelope was established by comparison with spectra of simple model compounds. The remaining protons appear in the upfield envelope (δ0.88). The ratio of the two sets of protons is 3:1, and this value is clearly revealed by the spectrum of the unlabeled material. Should a deuterium atom be acquired in the terminal methyl group, the absorption of that substituent at δ0.88 should be greatly altered and the proton ratio should increase to 3.6:1. This was not the case. Rather, the methyl absorption was not perceptibly changed in the deuterated isomer and the proton ratio dropped to 2.7:1, in excellent agreement with the theoretical value of 2.8:1 demanded by structure 63.
Ethyl trans-2(n-Pentyl)cyclopropane Carboxylate (65). Ethyl diazoacetate (11.4 g, 0.1 mole) prepared according to Organic Syntheses was added under nitrogen to a vigorously stirred slurry of n-heptene (64) (14.7 g, 0.15 mole) and powdered copper metal (1.0 g, 0.015 g-at) heated to 90°. When addition was complete (approximately 1.5 hr) the metallic copper was filtered and the organic residue was fractionated to yield 4.1 g of excess 1-heptene, bp 105-109° (20 mm). The high boiling fraction contained three ethyl esters by vpc analysis (6' x 3" in 5% Carbowax on 60/80 Chrom G); fractions one and two (~40%) exhibited C=C stretch in the infrared resulting from carbene insertion into a C-H bond; fraction three (~50%) was the desired cyclopropyl ethyl ester. An analytical sample was isolated by preparative vpc (6' x 3" Al column packed with 5% Carbowax 60/80 Chrom G); v:\text{neat}^{\text{max}} = 2860(s), 1730(s), 1410(m), 1160(s), and 862(m) cm\(^{-1}\); \delta:\text{LH}^1 0.8-1.9 (18 H) and 4.2-4.7 (quartet, 2 H).

Anal. Calcd for C\(_{11}\)H\(_{20}\)O: C, 71.69; H, 10.94. Found: C, 71.73; H, 11.15.

t-Butyl trans-2(n-Pentyl)cyclopropane Carboxylate (63). The crude mixture of ethyl esters (1.84 g, 0.1 mole) (65) was added dropwise to a solution of 4 g (0.1 mole) of sodium hydroxide dissolved in 25 ml of methanol. An immediate exothermic reaction resulted with a rapid color change to yellow. After stirring for 3 hrs at 40°, the reaction mixture was poured over ice-H\(_2\)SO\(_4\), ether extracted, and the organic extracts were dried over anhydrous mag-
nesium sulfate. The dried organic solution was placed in a pressure bottle with 1 ml of sulfuric acid and 11 ml (0.2 mole) of isobutylene (condensed in a test tube at Dry-Ice temperature), was stoppered, tightly wired shut and shaken for 12 hrs. The reaction mixture was poured onto an ice-NaOH mixture and extracted with ether. The combined organic layers were dried over magnesium sulfate and concentrated, and the residue was purified by preparative vpc (6' x $\frac{1}{4}$" Al column packed with 5% Carbowax on 60/80 Chrom G) to yield 3 major products (yield 25, 35, 20% respectively). Products 1 and 2 were unsaturated t-butyl esters while product 3, a saturated t-butyl ester was the desired product. An analytical sample was isolated by preparative vpc (6' x $\frac{1}{4}$" Al column packed with 5% Carbowax on 60/80 Chrom G): $v_{\text{max}}^{\text{neat}}$ 1850(s), 1715(s), 1485(m), 1355(m), 1210(m), 1145(s) and 850(m); $\delta_{\text{CDCl}_3}^{\text{TMS}}$ 0.6-1.5 (15 H), and 1.45 $\delta$ (9 H, t-butyl).

5-Bromocycloocta-1,3-diene (68). A mixture of 33 g (0.3 mole) of cis,cis-1,3-cyclooctadiene, 54 g (0.3 mole) of N-bromosuccinimide and 1.0 g of benzoyl peroxide in 300 ml of carbon tetrachloride was refluxed under nitrogen for 24 hrs. The succinimide was separated by filtration and the filtrate was concentrated in vacuo. The viscous, brown oil was fractionated to yield 15.3 g (31%) of a clear liquid, bp 52-54° (1 mm) [lit: 91 bp 60-62° (1.5 mm)].
2,4-Cyclooctadiene-1-yl Acetate (69). A slurry of 29 g (0.17 mole) of silver acetate in 50 ml of acetic acid was added with cooling to a mixture of 25 g (0.13 mole) of 5-bromo-1,3-cyclooctadiene (68) and 50 ml of acetic acid. The mixture was stirred at room temperature overnight. The silver bromide that formed was separated by filtration and the filtrate was concentrated under reduced pressure. The filtrate was fractionated to yield 15.0 g (70%) of 2,4-cyclooctadien-1-yl acetate, bp 59-61° (0.75 mm) [lit: bp 56-57° (0.6 mm)].

2,4-Cyclooctadien-1-ol (70). A solution of 13.2 g (0.8 mole) of 2,4-cyclooctadien-1-yl acetate in 150 ml of anhydrous ether was added dropwise to 3.0 g (0.8 mole) of lithium aluminum hydride in 50 ml of anhydrous ether. The solution was refluxed for 4 hrs and hydrolyzed by the dropwise addition of 3.0 g of water, 9.0 g of 30% sodium hydroxide solution, and 3.0 g of water. The ether solution was separated, dried over magnesium sulfate, and concentrated under reduced pressure. The residue was fractionated to yield 7.0 g (70%) of 2,4-cyclooctadien-1-ol, bp 57-59° (0.8 mm). [lit: bp 57-58° (0.7 mm)].

2,4-Cyclooctadien-1-one (71). Jones reagent was prepared by adding 26.7 g of chromium trioxide to 23 ml of concentrated sulfuric acid which was then diluted to 100 ml with water (2.67 mmole/ml).
To a solution of 500 mg (0.04 mole) of 2,4-cyclooctadien-1-ol in 10 ml of acetone was added 1.5 ml of the stock solution. The color of the reaction mixture passed from blue to green and finally to brown upon completion of the reaction. A small amount of methanol (5 ml) was added to remove any excess oxidant. The reaction mixture was filtered, concentrated to dryness and dissolved in 25 ml of ether. The ether solution was washed with water, sodium bicarbonate solution, brine, and dried over magnesium sulfate. After removal of ether in vacuo, the crude ketone (400 mg, 80%) was used as is in the following reactions. Purification could be effected through the 2,4-dinitrophenylhydrazone, mp 179-181° [lit:92 mp 179.5-181.0°].

Bicyclo[6.1.0]nonan-6-en-2-one (38). Trimethylsulfonium iodide was prepared by refluxing a solution of 96 g (1.23 moles) of dimethyl sulfoxide and 180 ml of methyl iodide under nitrogen for 3 days. The precipitated solid was washed well with chloroform, dried, and stored in a desiccator (145 g, 54%). Sodium hydride (0.03 mole, 0.75 g) was washed with petroleum ether to remove the mineral oil, evacuated in a 3-necked round bottom flask to remove the ether and blanketed with nitrogen. Trimethylsulfonium iodide (7.0 g, 0.03 mole) was added and 50 ml of dry dimethyl sulfoxide was added while the reaction mixture was blanketed with nitrogen and stirred for 30 min by magnetic stirrer. A solution of 3.6 g (0.03 mole) of freshly distilled 2,4-cycloheptadienone (71)
in 20 ml of dimethyl sulfoxide was added, and the reaction mixture was allowed to stir for 2 hrs. The solution was poured into 100 ml of water, extracted with ether and the combined organic extracts were washed with water, dried over anhydrous magnesium sulfate, concentrated in vacuo, and fractionated to yield 3.4 g (80%) of clear colorless cyclopropyl ketone (38), bp 85-86° (2 mm); νmax 5.70-5.95, 6.35, 6.9, 7.27, 7.36, 8.02; δCDCl3 1.0-2.7 (multiplet, 10 H) and 5.6 (multiplet, 2 H, vinyl protons). The semicarbazone melted at 165-166°.


2-Methylene-cis-bicyclo[6.1.0]non-6-ene (39). To a suspension of 3.6 g (0.11 mole) of methyltriphenylphosphonium bromide and 50 ml of anhydrous ether under nitrogen was added 4.3 ml (0.011 mole, 1.6 molar) of n-butyllithium dripwise. The reaction mixture was stirred for 3 hr. A solution of 1.34 g (0.01 mole) of cis-bicyclo[6.1.0]-non-6-en-2-one (38) in 10 ml of ether was added dropwise and the resulting suspension was refluxed for 12 hr. About 5 ml of water was added, the ether layer separated, and the aqueous layers were extracted with ether. The ethereal layers were combined, washed with brine, dried over anhydrous magnesium sulfate, and concentrated carefully in vacuo. Pentane (50 ml) was added and the suspension was filtered, concentrated in vacuo and fractionated to yield 1.1 g (82%) of colorless olefin, bp 76-78° (10 mm); νmax CDCl3 2900,
1650, 1455, 1260, 1070, 885 and 758 cm\(^{-1}\); \(^6\)\text{CDCl}_3 \text{TMS} 0.2-2.7 (complex broad multiplet, 10 H), 4.8 (singlet, 2H, methylene protons) and 5.5 (broad singlet, 2 H, vinyl protons).

**Analysis**. Calcd for C\(_{10}\)H\(_{14}\): C, 89.49; H, 10.51. Found: C, 89.28; H, 10.49.

**Photolysis of 39.** A solution of 2 g of 39 in 450 ml of reagent acetone was irradiated with a 450-w Hanovia mercury-vapor lamp utilizing quartz optics. At periodic intervals, aliquots were removed and analyzed by vpc (6' x 1/4 Al column packed with 5% Carbowax on 60/80 Chrom G). After 2 hr, vpc showed (uncorrected %) 36% of 39 to 18% of photoproduct (72). Isolation of 72 was accomplished in poor yield by preparative vpc (same column). Spectral data indicated 2 olefin protons; \(^{\text{CDCl}_2}\) \(^{\text{TMS}}\) 875, 1580, 1445 and 895 cm\(^{-1}\); \(^{\text{CDCl}_3}\) \(^{\text{TMS}}\) 0.9-3.0 (broad complex absorption, 12 H) and 5.7 (broad singlet, 2 H, vinyl protons).

**Analysis**. Calcd for C\(_{10}\)H\(_{14}\): C, 89.49; H, 10.51. Found: C, 89.80; H, 10.42.

2,6,6-Trimethylcyclohepta-2,4-dien-1-one (Eucarvone) (35). Freshly distilled carvone (20 g, 0.13 mole) was added to a solution of 29.6 g (0.3 mole) of hydrogen bromide in glacial acetic acid at 10\(^{\circ}\). After addition, the solution was allowed to stir for 30 min. The resulting dark mixture was poured into 200 ml of water and extracted with ether. The combined organic layers were washed with water, saturated sodium bicarbonate solution, brine, and dried over anhydrous magnesium sulfate. The ether was removed in vacuo.
and the resulting yellow oil was added to 14.5 g (0.26 mole) of potassium hydroxide dissolved in 60 ml of anhydrous methyl alcohol. The solution was refluxed for 1 hr and poured onto an ice-sulfuric acid mixture to precipitate the eucarvone. The yellow oil was separated and the aqueous layer was extracted with ether. The combined organic layers were washed with sodium bicarbonate solution and steam distilled (with 2 g of barium carbonate). After collecting about 500 ml of distillate, the condensate was saturated with sodium chloride solution and extracted with ether. The organic layers were dried, concentrated in vacuo, and fractionated to yield 14.5 g (70%) of a light yellow liquid (85), bp 82-84° (8 mm) [lit: 93 bp 82-84° (8 mm)].

1,4,4-Trimethylbicyclo[5.1.0]octa-5-en-2-one (40). Trimethyloxosulfonium iodide was prepared by refluxing a solution of 96 g (1.23 mole) of dimethyl sulfoxide and 180 ml of methyl iodide under nitrogen for 3 days. The precipitated solid was washed well with chloroform, dried, and stored in a desiccator (145 g, 54%). Sodium hydride (0.06 mole, 1.51 g) was washed with petroleum ether to remove the mineral oil, evacuated in a 3-necked round bottom flask to remove the ether and blanketed with nitrogen. Trimethyloxosulfonium iodide (0.06 mole, 13.9 g) was added and 75 ml of dry dimethyl sulfoxide was added while the reaction mixture was blanketed with nitrogen and stirred for 30 min by magnetic stirrer. A solution of 9.1 g (0.06 mole) of freshly distilled eucarvone (85).
in 20 ml of dimethyl sulfoxide was added, and the reaction mixture was allowed to stir for 2 hr. The solution was poured into 200 ml of water, extracted with ether, and the combined organic extracts were washed with water, dried over magnesium sulfate, concentrated in vacuo, and fractionated to yield 7.8 g (80%) of clear colorless cyclopropyl ketone (40), bp 89-90° (10 mm) [lit: bp 89-90° (10 mm)].

**Irradiation of 1,4,4-Trimethylbicyclo[5.1.0]oct-5-en-2-one (40).**

A solution of 2 g of 40 in 450 ml of reagent acetone was irradiated with a 450-w Hanovia mercury-vapor lamp in an immersion well apparatus fitted with a Corex filter. The progress of the reaction was followed by withdrawal of small aliquots at periodic intervals (see Table 7) and analysis of these by vpc (6' x $\frac{1}{4}$" Al column packed with 5% SP-96 on 60/80 Chrom G). After 5 hr, the solvent was carefully evaporated and the nonpolymeric residue (1.9 g) was submitted to preparative vpc (same column). The lone photoproduct, obtained as a colorless liquid in 10% yield, was identified as 1,4,4-trimethylbicyclo[3.3.0]oct-6-en-2-one (86): $\nu_{\text{max}}^{\text{neat}}$ 1745 and 1680 cm$^{-1}$; $\lambda_{\text{max}}^{\text{EtOH}}$ 286 nm (ε 40) $\delta^{13}$CDCl$3$ 1.10 (singlet, 6 H, overlapping $\text{CH}_3$ groups at $C_4$), 1.29 (singlet, 3 H, $\text{CH}_3$ group at $C_1$), 2.12 (multiplet, 1 H, allylic proton at $C_3$) and 5.68 (broadened singlet, 2 H, vinyl protons); semicarbazone 202-204°.

Anal. Calcd for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.50; H, 9.84.
For quantitative work as in Table 7 carefully weighed amounts of 40 and cyclooctane were dissolved in 3 ml of solvent of choice and placed in quartz test tubes which were affixed in vertical array around the immersion well. Each tube was then tightly stoppered with a serum cap which permitted the withdrawal of aliquot samples with a microsyringe and vpc analysis. Percentage compositions were calculated according to established procedures.28

2-Methylene-1,4,4-trimethylbicyclo[5.1.0]oct-5-ene (41). To a suspension of 3.6 g (0.011 mole) of methyltriphenylphosphonium bromide in 50 ml of anhydrous ether under nitrogen, was added dropwise 4.3 ml (0.011 mole) of 1.6 M n-butyl lithium. The reaction mixture was stirred for 3 hrs. A solution of 1.64 g (0.01 mole) of 1,4,4-trimethylbicyclo[5.1.0]octa-5-en-2-one in 10 ml of anhydrous ether was added dropwise and the resulting suspension was refluxed for 12 hrs. About 75 ml of water was added, the ether layer was separated, and the aqueous layers were extracted with ether. The combined ethereal layers were washed with brine, dried over magnesium sulfate, and carefully concentrated. The oily residue was taken up in pentane and the salts were removed by filtration. The organic solution was then carefully concentrated and distilled to yield 0.8 g (50%) of olefin 41, bp 72-75° (1 mm), νmax neat 1.4887, νmax neω 6.9-6.15, 6.8-6.9, 7.35, 11.1, 11.25, 11.4, 11.65, and 12.08, νmax EtOH 275(140), δTMS δCDCl3 singlets 0.93 (3 H), 0.95 (3 H), and 1.20 (3 H), and multiplets 2.17 (2 H - allylic), 0.9 (3 H -
cyclopropyl) and 5.20 (4 H - methylene and vinyl protons).


Photolysis of 2-Methylene-1,4,4-trimethylbicyclo[5.1.0]oct-5-ene (41). A solution of 2 g of 41 in 450 ml of anhydrous methanol was irradiated with a 450-w Hanovia mercury vapor lamp in an immersion-well apparatus fitted with a Vycor filter. The progress of the reaction was followed by withdrawal of small aliquots at periodic intervals and analysis of these by vpc ($6' \times \frac{1}{8}'$ Al column packed with 5% Carbowax on 60/80 Chrom G). After 10 hr irradiation, the solution was carefully concentrated, and the residual oil was subjected to preparative vpc (same column). The lone product produced in 56% yield (see Table 8) was isolated and identified as 2-methylene-1,4,4-trimethylbicyclo[3.3.0]oct-5-ene (87) by spectral data: $\nu_{\text{max}}^\text{neat}$ 2895, 1660, 1545, 1470, 884 and 689 cm$^{-1}$; $\delta_{\text{C}_{6}D_{6}}^\text{CHCl}_3$ 0.88, 0.96 and 1.25 (singlets, 3$H$ each, methyl groups), 2.04 (multiplet, 2$H$, methylene group at $C_9$), 2.30 (multiplet, 3$H$, methylene group at $C_3$ and methine proton at $C_5$).

Anal. Calcd for $C_{12}H_{18}O$: C, 87.73; H, 12.27. Found: C, 87.48; H, 12.68.

For quantitative work as in Table 8, carefully weighed amounts of 41 and cyclooctane were dissolved in 3 ml of the solvent of choice and placed in quartz test tubes which were affixed in vertical array around the immersion well. Each tube was then tightly stoppered with a serum cap which permitted the withdrawal of aliquot samples.
with a microsyringe and vpc analysis. Percentage compositions were calculated according to established procedures.  

Pyrolysis of Bicyclo[6.1.0]non-6-en-2-one (38). cis-Bicyclo-
[4.3.0]non-7-en-2-one (90). A sample (100 mg, 0.0007 mole) of
38 was pyrolyzed in a 14" x 3/4" quartz tube filled with glass
beads and heated to 650° by means of an external furnace. Ni-
trogen was bled slowly through the apparatus at 10 mm while the
sample was vaporized with a heat gun and collected in a Dry-Ice
trap. Total reaction time was 2-5 min with residual time in the
hot tube less than 3 sec. The collected reaction mixture was
molecularly distilled at 50° (10 mm) to yield 84 mg (84%) of a
clear liquid. Vpc analysis (61 x V A 1 column packed with 5%
SF-96 on 60/80 Chrom G) showed the presence of two components
in a ratio of 2:1 (starting material (38) to product (90)). The
product was isolated by preparative vpc (same column) and spec-
tral data and analysis of the pyrolysis product suggested this
material to be cis-bicyclo[4.3.0]non-7-en-2-one (90); ν_{\text{max}}^{-1}
1710, 1450, and 710 cm \(^{-1}\); \(\delta_{\text{CDCl}_3}\) 1.2-3.4 (broad absorption -
10 H) and 5.7 (multiplet - 2 vinyl H).


Hydrogenation of Bicyclo[4.3.0]non-7-en-2-one (90). cis-
Bicyclo[4.3.0]nonan-2-one (91). A solution of 25 mg (0.0002
mole) of 90 and 5 mg of 10% palladium on carbon in 25 ml of hex-
ane was hydrogenated at atmospheric pressure over a two hr period during which time 4 ml (0.0002 mole) of hydrogen was absorbed. The solution was filtered through Celite to remove the catalyst, concentrated in vacuo, and subjected to preparative vpc (6' x 1/2" Al column packed with 60/80 Chrom G) to yield 16 mg (60%) of 91 which was identical in all respects to an authentic sample of cis-bicyclo[4.3.0]nonan-2-one: \( \nu_{\text{max}}^{\text{neat}} \) 1705, 1450, and 1130 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 1.1-2.8 (broad absorption).

Pyrolysis of 2-Methylenebicyclo[6.1.0]non-6-ene (39). 2-Methylenecis-bicyclo[4.3.0]non-7-ene (92). A sample (100 mg, 0.0002 mole) of 39 was pyrolyzed at 600° and 10 mm in the manner described above. Molecular distillation at 50° (10 mm) yielded 92 mg (92%) of a clear liquid which showed less than 2% starting olefin (39) remaining and 98% product (92) by vpc (6' x 1/2" Al column packed with 5% SF-96 on 60/80 Chrom G). Preparative vpc (same column) yielded pure 92 which was identified as 2-methylene-cis-bicyclo[4.3.0]non-2-ene by analysis and spectral data: \( \nu_{\text{max}}^{\text{neat}} \) 1645, 1440, 884, 893, and 705 cm\(^{-1}\); \( \delta_{\text{TMS}}^{\text{CDCl}_3} \) 1.0-3.1 (complex broad absorption 4 methylene and 6 allylic H), 4.7 (broad singlet - 2 exocyclic vinyl H) and 5.8 (unresolved multiplet - 2 vinyl H).

Anal. Calcd for C\(_{10}\)H\(_{14}\): C, 89.49; H, 10.51. Found: C, 89.66; H, 10.45.

Hydrogenation of 2-Methylene-cis-bicyclo[4.3.0]non-7-ene (92).

2-Methyl-cis-bicyclo[4.3.0]nonan (93). To 67 mg (0.0005 mole) of
was added 25 ml of reagent hexane and 5 mg of 5% palladium on carbon catalyst. The reaction mixture was hydrogenated at atmospheric pressure for 60 min during which time 22 ml of H₂ (0.001 mole) was absorbed. Vpc analysis (6' x 1/4" Al column packed with 5% Carbowax 2000 M on 60/80 Chrom G) of the filtered reaction mixture showed the solution to be homogeneous. The solution was concentrated in vacuo and separated by preparative vpc (same column) to yield 57 mg (80%) of a clear hydrocarbon (93) which was identified as 2-methyl-cis-bicyclo[4.3.0]nonane by comparison of spectral data and vpc retention times to an authentic sample synthesized independently.

2-Methylene-cis-bicyclo[4.3.0]nonane (94). To a solution of 3.5 g (0.001 mole) of triphenylphosphonium methyl bromide in 50 ml of anhydrous ether was added 12 ml of 1.2 M (0.001 mole) n-butyl lithium dropwise over a 10 min period. The reaction mixture was stirred magnetically for one hr under nitrogen. A solution of 71 mg (0.0005 mole) of 91 in 10 ml of anhydrous ether was added slowly to the stirred reaction mixture. After 4 hr, the reaction mixture was quenched by slow addition of 50 ml of water. The organic phase was separated, dried over magnesium sulfate, concentrated in vacuo. Pentane (50 ml) was added to the residue. The organic solution was filtered, concentrated in vacuo, and subjected to preparative vpc (6' x 1/4" Al column packed with 5% Carbowax 2000 M on 60/80 Chrom G) to yield 64 mg (80%) of olefin 94:
11435, 1440, 1025, and 890 cm$^{-1}$; 5 0.9-2.7 (broad complex absorption - 14 H) and 4.7 (slightly broadened singlet - 2 H).

Anal. Calcd for: C, 88.16; H, 11.84. Found: C, 87.91 H, 11.97

2-Methyl-cis-bicyclo[4.3.0]nonane (93). To a solution of 25 ml of reagent hexane and 5 mg of 5% palladium on carbon was added 41 mg (0.0003 mole) of olefin (94). The solution was hydrogenated atmospherically for 60 min during which time 6.7 ml (0.0003 mole) of hydrogen was absorbed. The reaction mixture was filtered, concentrated in vacuo and subjected to preparative vpc (6' x 2" Al column packed with 5% Carbowax 2000 M on 60/80 Chrom G) to yield 32 mg (75%) of hydrocarbon 93: $\nu_{\text{max}}$ 1450, 1375, 1300 cm$^{-1}$; $\delta_{\text{TMS}}^{\text{CDCl}}$ 1.0-2.8 (broad complex absorption).


Pyrolysis of 1,4,4-trimethyl-cis-bicyclo[5.1.0]oct-6-en-2-one (40). 1,4,4-trimethylbicyclo[3.3.0]oct-6-en-2-one (86). A sample (82 mg, 0.0005 mole) of cyclopropyl ketone (40) was pyrolyzed at 550° and 10 mm in the usual manner. Molecular distillation (50°, 10 mm) afforded 65 mg (81%) of a clear liquid. Vpc analysis (6' x 2" Al column packed with 5% SF-96 on Chrom G) showed the liquid to be nearly homogeneous (less than 0.5% starting ketone remaining). Preparative vpc afforded a clear liquid which was unambiguously identified as 86 on the basis of its identity to the photoproduct (86) of 40.
Pyrolysis of 2-Methylene-1,4,4-trimethyl-cis-bicyclo[5.1.0]-oct-5-ene (41). 2-Methylene-1,4,4-trimethyl-cis-bicyclo[3.3.0]-oct-6-ene (87). A sample (81 mg, 0.0005 mole) of olefin (41) was pyrolyzed in the usual manner at 550° and 10 mm. Molecular distillation (50°, 10 mm) afforded 61 mg (70%) of a clear liquid (87) which was homogeneous to vpc (6' x 1/8 Al column packed with 5% SF-96 on Chrom G). Retention times showed the homogeneous liquid to be a pyrolysis product and not starting material. Spectral data identified the pyrolysis product to be 87 which was identical in all respects to an authentic sample of 87 previously prepared by the photolysis of 41.


22. a) A. J. Bellamy and G. H. Whitham, J. Chem. Soc., 4035 (1964); b) We wish to thank Professor Whitham for making available to us the various spectra of authentic 3-methyl-4-caren-one (15).

23. The slightly greater in the case of pipervlene are definitely out of the range of experimental error and probably are the result of discrete amounts of adduct formation.


43. a) See ref. 42b; b) See ref. 34j and references therein cited.


47. Hess and Pitts (see ref. 40b) observed during the vapor phase irradiation of bicyclo[3.1.0]hexane-2-one, trace amounts of products which are formed from the opening of the other two cyclopropyl bonds. This could be a consequence of the
slower vibrational relaxation of excited states in the vapor phase.


51. Our thanks to Professor Whitham for communicating experimental details.


55. K. B. Wiberg and A. deMeijere, Tetrahedron Letters, 59 (1969) have estimated that an enthalpy difference of 3.5 kcal/mole separates 36 from 37.


71. The conditions employed in the vpc analysis could easily detect quantities of 0.5%. For a complete description of arriving at true percentage values see ref. 28.

72. We wish to thank Dr. Donald Kuhla for providing us with an authentic sample of 91.

73. For a summary of the Wittig reaction and other leading references see: A. Maucker, Org. Reactions, 14, 270 (1965).


86. For representative spectra of compounds containing a terminal vinyl group, see Varian Associates, "NMR Spectra Catalog", spectra nos. 134 and 298.
92. See ref. 91.