1971

Mechanism of the photoconversion of 5, 5-dimethylbicyclo-[4.1.0] hept-3-en-2-one to 2,3,5-trimethylphenol and 3,4,5-trimethylphenol

Terence Lee McDowell

Iowa State University

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McDowell, Terence Lee, 1943-
MECHANISM OF THE PHOTOCONVERSION OF 5,5-
DIMETHYLBICYCLO[4.1.0]HEPT-3-EN-2-ONE TO
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TRIMETHYLPHENOL.

Iowa State University, Ph.D., 1971
Chemistry, organic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

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by

Terence Lee McDowell

A Dissertation Submitted to the Graduate Faculty in Partial Fulfillment of The Requirements for the Degree of DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

Signature was redacted for privacy.

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State University
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The photorearrangement of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one to 2,3,5-trimethylphenol and 3,4,5-trimethylphenol in polar solvents is actually a series of three separate photochemical reactions. The first reaction appears to be a photochemical cleavage of the 1,7-bond of the cyclopropane ring followed by a hydrogen shift to form 3,4,4-trimethylcyclohexa-2,5-dienone. The cyclopropane ring opening is a known photoreaction of bicyclo[4.1.0]heptan-2-ones and the hydrogen shift is supported by mass spectral evidence. The intermediates can't be detected because each subsequent reaction is much faster than the initial reaction.

The intermediate dienone was synthesized and irradiated under a variety of conditions and always formed 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one as the primary photoproduct. The bicyclic enone can photochemically rearrange to the two phenols in polar solvents at room temperature. However, in nonpolar solvents such as cyclohexane the major product is 3,6,6-trimethylcyclohexa-2,4-dienone. This reaction is not very clean and many byproducts are formed.
The low temperature photochemistry of the bicyclic enone follows two main reaction paths. In one path a ketene is formed which is the precursor of the linearly conjugated 2,4-cyclohexadienone. The ketene can also be trapped by methanol at -78° or lower. The second path involves isomerization to a cyclopropanone which is unstable at room temperature and thermally rearranges to form the phenols. The cyclopropanone can be trapped by methanol or furan at -78°.

The photochemistry of 4,4-dimethylcyclohexa-2,5-dienone was studied under the same conditions as the 3,4,4-trimethylcyclohexa-2,5-dienone. The results of the two systems were very similar with minor variations in reactivity and temperature effects.

The photochemistry of the two dienones and two bicyclic enones agreed well with the literature results at room temperature. The additional low temperature results involving ketenes strengthen what was suspected in many earlier reports on similar systems.
TABLE OF CONTENTS

INTRODUCTION 1

HISTORICAL

- Photochemistry of 4,4-Disubstituted 2-Cyclohexenones 3
- Photochemistry of 4,4-Disubstituted Cyclohexa-2,5-dienones 9
- Photochemistry of Bicyclo[3.1.0]hex-3n-2-one 19
- Photochemistry of some Conjugated Cyclopropyl Ketones 24

RESULTS

- Photochemistry of 5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one 28
- Photochemistry of 3,4,4-Trimethylcyclohexa-2,5-dienone and 4,6,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one 42
- Photochemistry of 4,4-Dimethylcyclohexa-2,5-dienone and 6,6-Dimethylbicyclo[3.1.0]hex-3-en-2-one 59
- Photochemistry of 6,6-Dimethyltricyclo[5.1.0.0^3,5]octan-2-one 69
- Photochemistry of 5,5-Dimethylbicyclo[4.1.0]heptan-2-one 69
- Photochemistry of 5-Methylbicyclo[3.2.0]hept-3-en-2-one (117) 70
- Photochemistry of 1,2-Dimethyltricyclo[4.3.0.0^2,6]non-4-en-3-one (119) 71
- Photochemistry of 4,4-Dimethyl-5(4H)-indenone (120) 72

DISCUSSION 73

EXPERIMENTAL 94
<table>
<thead>
<tr>
<th>Instruments and Methods</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental for the Photolysis of 5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one</td>
<td>94</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 3,4,4-Trimethylcyclohexa-2,5-dienone</td>
<td>95</td>
</tr>
<tr>
<td>Experimental for the Irradiation 4,6,6-Trimethylbicyclo[3.1.0]hex-3-en-2-one</td>
<td>105</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 4,4-Dimethylcyclohexa-2,5-dienone</td>
<td></td>
</tr>
<tr>
<td>Experimental for the Photolysis of 6,6-Dimethyltricyclo[5.1.0.0,3,5]octane-2-one</td>
<td>118</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 5,5-Dimethylbicyclo[4.1.0]heptan-2-one</td>
<td>119</td>
</tr>
<tr>
<td>Experimental for the Phosphorescence Spectra</td>
<td>124</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 5-Methylbicyclo[3.2.0.]hept-3-en-2-one (117)</td>
<td>127</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 1,2-Dimethyltricyclo[4.3.0.0,2,6]non-4-en-3-one (119)</td>
<td>128</td>
</tr>
<tr>
<td>Experimental for the Photolysis of 4,4-Dimethyl-5(4H)-indanone (120)</td>
<td>129</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>130</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>131</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>132</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Figure 1.</td>
<td>Polar state mechanism for enone rearrangement</td>
</tr>
<tr>
<td>Figure 2.</td>
<td>Radical mechanism for rearrangement of enone</td>
</tr>
<tr>
<td>Figure 3.</td>
<td>Summary of reactions of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone</td>
</tr>
<tr>
<td>Figure 4.</td>
<td>Mechanism for zwitterion rearrangement</td>
</tr>
<tr>
<td>Figure 5.</td>
<td>Zimmerman electronic mechanism for dienone rearrangement</td>
</tr>
<tr>
<td>Figure 6.</td>
<td>Polar and diradical mechanisms for rearrangement of lumisantonin</td>
</tr>
<tr>
<td>Figure 7.</td>
<td>Diagram of cyclopropane-carbonyl interaction</td>
</tr>
<tr>
<td>Figure 8.</td>
<td>Nuclear magnetic spectra</td>
</tr>
<tr>
<td>Figure 9.</td>
<td>Infrared spectra</td>
</tr>
<tr>
<td>Figure 10.</td>
<td>Nuclear magnetic spectra</td>
</tr>
<tr>
<td>Figure 11.</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>Figure 12.</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>Figure 13.</td>
<td>Infrared spectra</td>
</tr>
<tr>
<td>Figure 14.</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>Figure 15.</td>
<td>Infrared spectra</td>
</tr>
<tr>
<td>Figure 16.</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>Figure 17.</td>
<td>Low temperature ir spectra</td>
</tr>
<tr>
<td>Figure 18.</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>Figure 19.</td>
<td>X-ray structure of 11-oxa-7,7-dimethyl-tricyclo[4.3.1.12,5]undeca-3,8-dien-10-one</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
</tr>
<tr>
<td>20</td>
<td>Low temperature ir spectra for 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one</td>
</tr>
<tr>
<td>21</td>
<td>Mechanism for photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in cyclohexane</td>
</tr>
<tr>
<td>22</td>
<td>Mechanism for the photorearrangement of 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one</td>
</tr>
<tr>
<td>23</td>
<td>Approach of furan to the cyclopropanone</td>
</tr>
<tr>
<td>24</td>
<td>Low temperature photochemistry of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one</td>
</tr>
<tr>
<td>25</td>
<td>Summary of photochemistry of 4,4-dimethylcyclohexa-2,5-dienone</td>
</tr>
<tr>
<td>26</td>
<td>Mechanism proposed for formation of methyl-trans-4-methyl-2-cyclohexene carboxylate from 5-methylbicyclo[3.2.0]hept-3-en-2-one</td>
</tr>
<tr>
<td>27</td>
<td>Proposed mechanism for the photorearrangement of 119, 120 and 136</td>
</tr>
<tr>
<td>28</td>
<td>Infrared spectra</td>
</tr>
<tr>
<td>29</td>
<td>Nuclear magnetic resonance spectra</td>
</tr>
<tr>
<td>30</td>
<td>Infrared spectra</td>
</tr>
</tbody>
</table>
vi

LIST OF TABLES

Table 1. Substituent effect on rearrangement of 4-n-propylcyclohexa-2,5-dienone  

Table 2. Solvent effect on the irradiation of 1
INTRODUCTION

The photochemistry of cross-conjugated cyclohexadienones has been studied in some detail and they have been found to undergo a facile rearrangement to give bicyclo[3.1.0]hex-3-en-2-one derivatives. The photolysis of the bicyclo[3.1.0]hex-3-en-2-one derivatives gave further products including phenols, cyclopropanones, ketenes, acids, and substituted 2,4-cyclohexadienones. However, no system has been reported to give all of these products.

The observation that 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (1) photochemically rearranged in polar solvents to 2,3,5-trimethylphenol (2) and 3,4,5-trimethylphenol (3) led us to study this reaction in greater detail. It seemed probable that several intermediates would occur in this reaction, some of which should be thermally stable. The possibility of chemically trapping other short-lived intermediates or detecting them spectroscopically using low temperature techniques was also considered.

This thesis describes the photochemistry of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one including solvent effects and deuterium labeling.
studies. The photochemistry of 3,4,4-trimethylcyclohexa-2,5-dienone at several temperatures and in different solvents is also reported in detail. The previously studied 4,4-dimethylcyclohexa-2,5-dienone is investigated at low temperature and compared to 3,4,4-trimethylcyclohexa-2,5-dienone. An attempt is made to fit all of the various reactions into one overall scheme.
Photochemistry of 4,4-Disubstituted 2-Cyclohexenones

The photochemistry of 4,4-dimethyl-2-cyclohexenones (4) has been studied in detail and undergoes a number of reactions. It adds to olefins to form oxetanes (5) and cyclobutanes (6) (1). In t-butyl alcohol (2) 4,4-dimethyl-2-cyclohexenone (4) photochemically rearranges to give 6,6-dimethylbicyclo[3.1.0]hexan-2-one (7) and 3-isopropyl-2-cyclopentenone (8). In acetic acid solution (2) two additional products
(9, 10) are obtained. Photoreduction of 4,4-dimethyl-2-cyclohexenone occurs in isopropyl alcohol (3).

The mechanism of the rearrangement of 4,4-dimethyl-2-cyclohexenone was rationalized in terms of the polar state hypothesis (Figure 1). The

![Figure 1. Polar state mechanism for enone rearrangement](image)

photochemical rearrangement did not proceed smoothly in aprotic solvent, thus suggesting that proton donation by the solvent was important at some stage of the reaction (2).

In the cases of 4,4-diphenylsubstituted 2-cyclohexenones, phenyl migration occurs preferentially over skeletal rearrangement. Zimmerman and Wilson (4) have found that 4,4-diphenyl-2-cyclohexenone (13) rearranges to cis- and trans-5,6-diphenylbicyclo[3.1.0.] hexan-2-one (14 and 15) when photolyzed in dioxane.

Zimmerman et al., (5) favor a mechanism in which the β-carbon of
the enone has mainly radical character instead of being electron deficient or electron rich. This mechanism is supported by the migratory aptitudes of substituted phenyls. Both p-methoxyphenyl and p-cyanophenyl groups migrate preferentially to phenyl. Sensitization experiments indicated that these rearrangements were proceeding via the triplet excited state.

The photorearrangement of 4,4-disubstituted 2-cyclohexenones has
been reported in many other cases. Zimmerman et al., (6) found that 4a-methyl-4,4a,9-tetrahydro-2(3H) phenanthrone (25) and $\Delta^{1,9}$-10-methyl-2-octalone (26) rearrange to (27) and (28), respectively. They suggested the mechanism shown in Figure 2 for the rearrangement of (25).

* = y if n-\(n^*\) or \(\Pi-\Pi^*\)

Figure 2. Radical mechanism for rearrangement of enone 25
to (27). The complete fission of the 1-10 bond would destroy any opti-
cal activity at C-10.

However, Chapman et al., (7) have shown that the photolysis of
optically active (25) produces (27) with a minimum of 95% retention of
optical activity. This clearly excludes any mechanism in which complete
fission of the 1-10 bond occurs resulting in a plane of symmetry.

In 1962 Gardner et al., (8) reported the photorearrangement of $\Delta^4$
cholesten-3-one (28) to lumicholestenone (29). Irradiation of testos-

terone acetate (30) in t-butyl alcohol gives (31) and (32) in a similar

Dauben et al., (10) have investigated the scope of the photochemical
rearrangement in alkyl-substituted 2-cyclohexenones and found that the rearrangement occurred only if the C-4 position was fully alkylated. If this requirement was not met, photodimers were the major products. The substituent requirement was necessary but not sufficient to insure rearrangement as other substituents either retarded or inhibited the reaction. For example, methyl substitution at the C-2 or C-3 position completely prevented photorearrangement, although dimer formation still occurred. If the C-3 substituent was part of a 5 or 6 member ring photorearrangement still occurred in most cases.

\[ \text{Compound} \xrightarrow{h\nu} \text{Compound} + \text{Dimers} \]

\[ \text{Compound} \xrightarrow{h\nu} \text{Compound} + \text{Dimers} \]

\[ \text{Compound} \xrightarrow{h\nu} \text{Dimer (trace)} \]

\[ \text{Compound} \xrightarrow{h\nu} \text{Dimer (trace)} \]
Photochemistry of 4,4-Disubstituted Cyclohexa-2,5-dienones

The photoconversion of santonin (33) to lumisantonin (34) was first reported in 1957 by Barton et al. (11) and Buchi et al. (12). Fisch and Richards (13) studied the mechanism of the rearrangement and found that 33 was sensitized by benzophenone and quenched by piperylene. Based on these results they concluded that the photochemistry of santonin involved the triplet state as the species which underwent rearrangement.
The same photorearrangement occurred in similar compounds that didn't have a C-4 methyl group. For example, compound \(35\) produced \(36\) upon irradiation in acidic media, or more conveniently, in hexane (14).

Steroidal systems also undergo the santonin to lumisantonin type rearrangement with the C-4 methyl group present. Photolysis of 1-dehydro-4-methyltestosterone (37) in aqueous dioxane gave the lumiproduct (38) (15).

The substituent effect of a methyl group at C-2 and C-4 was also studied in the octalone system (16, 17). Dienone \(38\) which has a C-2
methyl gave a bicyclic enone (39) in methanol or dioxane which reacted further to eventually produce (41). However, compound 42 gave only a small amount of phenol (43) which was thought to come from enone 44.

Other examples involving substitution at the α-positions are shown below (18).

a) R = R' = H
b) R = CH₃, R' = H
c) R = H, R' = CH₃
Also 3β-acetoxylanosta-5,8-dien-7-one (45) photorearranges to 46 (19).

Hart and Lankin (20) have reported the photochemical rearrangement of 47 to 48 in methanol.

Schuster and Patel (21) have studied the photochemistry of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone (49) in great detail. This system was chosen in order to study the nature of the intermediates. Schuster and Patel have postulated that diradical intermediates (50, 51) precede the ionic intermediates (52) since in the case of appropriately substituted dienones an alternate radical reaction path competes effectively with the ionic reactions. The reactions are summarized in Figure 3 (22, 23).
Figure 3. Summary of reactions of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone
The formation of 2-methoxy-6-methyl-6-trichloromethylbicyclo[3.1.0]hexan-3-one (53) was the first reported case of trapping a zwitterionic intermediate in the dienone system (24). The reaction was carried out in a methanol-hydrochloric acid solution at room temperature.

The rearrangement of 4-methyl-4-trichloromethylcyclohexa-2,5-dienone (49) to 6-methyl-6-trichloromethylbicyclo[3.1.0.]hex-3-en-2-one (54) is stereoselective with the trichloromethyl group being endo (25). Schuster and Patel have suggested that the formation of only one isomer was due to preferential formation of isomer 51a during 3,5-bonding in order to minimize nonbonded and dipolar interactions with the trichloromethyl group. The product (54) could then be formed by pivoting around the 5-6 bond after electronic demotion to the zwitterion (52).

Rodgers and Hart (26) have studied the substituent effect on the photolysis of 4-methyl-4-n-propylcyclohexa-2,5-dienone (55) by varying the groups at C-3 and C-5. They found that the ratio of 56 to 57 increased as the substituent at C-3 and C-5 was changed from hydrogen to methyl. The results are summarized in Table 1. The results are explained by the zwitterionic intermediate (58) which forms so that the larger group
Table 1. Substituent effect on rearrangement of 4-n-propylcyclohexa-2,5-dienone

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Products (Yield)</th>
<th>Substituents</th>
</tr>
</thead>
<tbody>
<tr>
<td>55a</td>
<td>56a (44%) 57a (56%)</td>
<td>a, R₄=R₅=H</td>
</tr>
<tr>
<td>55b</td>
<td>56b (68%) 57b (32%)</td>
<td>b, R₄=CH₃, R₅=H</td>
</tr>
<tr>
<td>55c</td>
<td>56c (91%) 57c (9%)</td>
<td>c, R₄=R₅=CH₃</td>
</tr>
</tbody>
</table>

is endo if A and B are large enough to cause steric hindrance. The bond migration then occurs with retention of configuration at C-4.
Schuster and Curran (27) reported another dienone rearrangement where both bicyclic isomers were formed. In this case an unsymmetrical spirodienone (59) photorearranged to the bicyclic enones 60 and 61. The ratio of 60/61 was solvent dependent, varying from 2.50 in methanol to 0.79 in cyclohexane.

Zimmerman and Crumrine (28) and Brennan and Hill (29) have generated zwitterions similar to 58 by chemical methods and found that they rearrange with retention of configuration Figure 4. This seems to

Figure 4. Mechanism for zwitterion rearrangement
support the explanation proposed by Rogers and Hart (26).

Srinivasan et al., (30) have studied 4,4-dimethylcyclohexa-2,5-
dienone (62) which due to its simple structure gives a clearer picture
of the overall photochemical processes of 4,4-dialkylsubstituted 2,5-
cyclohexadienones. Photolysis of 62 in cyclohexane gave 6,6-dimethyl-
bicyclo[3.1.0.] hex-3-en-3-one (63) and 6,6-dimethylcyclohexa-2,4-
dienone (64). It was also shown that 63 rearranged to 64 photo-
chemically under the reaction conditions. In aqueous dioxane 62 formed
63 and two phenols which were identified as 2,3- and 3,4-dimethylphenol
(65 and 66). The gas phase photolysis of 62 gave 63 and 64 as in

cyclohexane. Based on these results the authors concluded that
zwitterionic intermediates aren't necessary for the formation of ketones
63 and 64. Since the phenols 65 and 66 are formed only in polar solvents
and not in the gas phase, they must come from ionic intermediates.
The photochemistry of 4,4-diphenylcyclohexa-2,5-dienone (67) has been investigated extensively by Zimmerman and Schuster (31). In aqueous dioxane 67 rearranged to 6,6-diphenylbicyclo [3.1.0.] hex-3-en-2-one (68) which reacted further to form 2,3-diphenylphenol (69) and an acid (70). A detailed study was made of the electric factors involved which led to the mechanism shown in Figure 5 (32, 33).

![Figure 5. Zimmerman electronic mechanism for dienone rearrangement](image-url)
The photochemistry of several bicyclo [3.1.0] hex-3-en-2-ones has been studied in recent years beginning with umbellulone. In 1959 Wheeler and Eastman (34) reported that photolysis of umbellulone (71) produced thymol (72) in quantitative yield.

\[
\text{hv} \quad \text{20 hours, quartz}
\]

In 1967 Chapman et al., (35) reported the low temperature photochemistry of umbellulone and found that two mechanistic pathways were operable. Photolysis of umbellulone (71) at \(-190^\circ\) produced a ketene (73) and another ketone identified as 3-methyl-6-isopropylcyclohexa-2,4-dienone (74). During warmup, ketone 74 went rapidly to thymol (72) at about \(-90^\circ\) and the ketene (73) went to thymol at \(-70^\circ\). The ketene (73) could also be trapped as a methyl ester (75) if umbellulone was irradiated at \(-190^\circ\) in an ether-methanol (4:1) glass. A ketene-carbene which was initially suggested by van Tamelen et al., (36) might be an intermediate between 71 and 73.

A more detailed study (37, 38) of the photochemistry of lumisantonin led to the discovery of a new ketone intermediate in the conversion to photosantonic acid. Photolysis of lumisantonin (34) in anhydrous ether formed mazdasantonin (76), which could in turn be
converted to photosantonic acid (77) by photolysis in water. In benzene

another minor product (78) was observed in 10% yield (39).

The polar state concept (37) was originally used to rationalize the conversion of 34 to 76 as shown in Figure 6 (Path A). Fisch and
Richards (39) postulated an initial diradical (79) which could come from breaking bond "a" in the n-π* triplet state (Path B). The diradical could be demoted to give the zwitterion (80) as shown in Figure 6.

Photolysis of lumisantonin (34) at -190° gave a ketene (81) as a primary photoprodut (35). At room temperature the ketene (81) cyclized to mazdasantonin (76). If lumisantonin was irradiated in an EPA glass at -190° and then warmed above -160°, the ketene absorption (2113 cm⁻¹) disappeared and a band at 1738 cm⁻¹ appeared which was assigned to the ester 82.

Kropp and Erman (40) photolyzed 83 in aqueous acid and recovered phenol 84. They suggested a spiro intermediate (85) which could ring expand to give the phenol.
Chapman et al., (41) have reported the low temperature photochemistry of 83. Photolysis at -190° produced a photoproduct (86) with an intense absorption at 1812 cm\(^{-1}\) and a weaker absorption at 1840 cm\(^{-1}\). Continued photolysis converted the initial photoproduct (86) to carbon monoxide and diene 87. If the initial photoproduct was warmed in the presence of furan, the adduct 88 was formed. This evidence clearly identified 86.
as a cyclopropanone.

The bicyclo[3.1.0.] hex-3-en-2-one photochemistry has also been studied with phenyl substitution. Zimmerman et al., (42) have reported the conversion of 6,6-diphenylbicyclo[3.1.0.] hex-3-en-2-one (68) to 2,3- and 3,4-diphenylphenol (69 and 89) and acid 70a in aqueous dioxane.

With shorter wavelength light and prolonged irradiation, some acid 70b (trans) was obtained. The ratio of 69/89 was about 4:1 in aqueous dioxane, but in acidic solution the ratio was pH dependent varying from...
The migratory aptitude of p-cyanophenyl versus phenyl was also studied by Zimmerman and Grunewald (43). Based on the preferential migration of the phenyl group of 90 to form 91, he concluded that the ground state zwitterion 92 was rearranging and not the electronically excited intermediate 93.

Photochemistry of some Conjugated Cyclopropyl Ketones

The photochemistry of conjugated cyclopropyl ketones has been studied by several groups. In 1954 Pitts and Norman (44) photolyzed methylcyclopropylketone to methylpropenylketone. There have also been studies on the photochemical cis-trans isomerization 2-benzoyl cyclopropanecarboxylic acid (45). The photoconversion of 94 to 95 was reported by two groups recently (46, 47).

Dauben and Shaffer (48) have studied the substituent effects in the
photochemistry of the bicyclo[4.1.0]heptan-2-one system. A few of the pertinent reactions are shown below. The results showed that cyclopropyl
ring opening as a primary process could compete with \( \alpha \)-cleavage of the
C\(_2\)-C\(_3\) bond only when C-3 was unsubstituted or when C-7 was substituted.
Only the cyclopropyl bond which conjugated best with the carbonyl group will open.

Dauben and Berezin (49) offer the following theory about which
cyclopropane bond in the bicyclo[4.1.0]heptan-2-one system has the best
overlap with the carbonyl group (Figure 7).

**Figure 7. Diagram of cyclopropane-carbonyl interaction**

The 1-6 bond is practically in the same plane (0-5° variance) as the
atoms of the carbonyl group. The 1-7 bond overlaps best having a
dihedral angle of 25-30° between the plane of the \( \pi \)-orbitals and the 1-7
bond. Since in the \( \pi-\pi^* \) excited state, the \( \alpha, \beta \)-unsaturated system is
polarized to make the oxygen more negative than the \( \beta \)-carbon and since the
cyclopropane ring acts as an electron donor in such a system, it
would be expected that substituents at C-7 which are electron donating would bring about a maximal bathochromic shift. Also, a substituent at C-1 would be expected to have a larger effect than a similar substituent on C-6, and this effect has been found.

The photolysis of (+)-cis-caran-5-one (96) in ether (50) affords principally (-)-cis-m-menth-8-en-5-one (97), (-)-cis-m-methan-5-one (98) and (-)-m-menth-3-en-5-one (99). The results agree with Dauben and Shaffer's results above (48).
RESULTS

Photochemistry of 5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one

5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one (1) was irradiated in a $\epsilon$-butanol solution ($3.90 \times 10^{-2}$ M) and monitored by vapor phase chromatography (VPC). Two products appeared with much longer retention times than 1. The product mixture was chromatographed on silica gel and partial separation of the two products occurred. Pure samples were obtained by preparative VPC (Column B).

The major product (shortest retention time by VPC and first off the silica gel column) was identified as 2,3,5-trimethylphenol (2) on the basis of spectral comparison (IR, UV, NMR and mass spectra) with an authentic sample (Aldrich Chemical Co.). The NMR spectrum (CDCl$_3$) (Figure 8) had singlets at $\delta$ 2.10 (3H), 2.20 (6H), 6.39 (1H), 6.57 (1H) and a broad peak at 4.55 (1H) which exchanged in deuterium oxide. The UV spectrum (50% EtOH) had maxima at 201 nm ($\epsilon$, 42,900) and 282 nm ($\epsilon$, 1,230). The mass spectrum had a molecular ion at 136 m/e (82%), which was correct for C$_9$H$_{12}$O, and fragment ions at 121 (100%) and 91 (21%). The mp was 87-90°, Lit 95-96° (51), Aldrich sample 94-96°. The IR spectrum (Figure 9) (KBr) had bands at 839, 968, 1025, 1138, 1300, 1455, 1585, 1625, 2925 and 3330 cm$^{-1}$.

The minor product was identified as 3,4,5-trimethylphenol (3) by spectral comparison with an authentic sample (Aldrich Chemical Co.): mass spectrum, m/e (relative intensity), 136 (parent ion, 66), 135 (29), 121 (100), 91 (16); UV max (50% EtOH), 198 nm ($\epsilon$, 52,000) and 282 nm.
nmr (CDCl₃), singlets at δ 2.05 (3H), 2.16 (6H), 6.48 (2H) and a broad peak at 5.50 (1H) which exchanged in deuterium oxide (Figure 8); mp 105-107°, Lit 109.3-109.6° (52), Aldrich 108-109°; ir (KBr) (Figure 9) 700, 845, 855, 1025, 1140, 1305, 1475, 1600, 2920 and 3250 cm⁻¹.

The irradiation of 1 was repeated in isopropyl alcohol and in methanol to see if a solvent effect occurred. The disappearance of 1 was faster in both solvents compared to t-butanol. The yield of the phenols was also much greater in both solvents, although the order was reversed. Isopropyl alcohol gave the fastest reaction, but methanol gave the best yield. There was a significant change in the ratio of 2 to 3 varying from 3.0 in t-butanol to 0.88 in methanol. The results are summarized in Table 2.

Table 2. Solvent effect on the irradiation of 1

<table>
<thead>
<tr>
<th>Solvent</th>
<th>2 / 3</th>
<th>% reactionᵃ</th>
<th>irrad. time</th>
<th>efficiencyᵇ</th>
<th>yieldᶜ</th>
</tr>
</thead>
<tbody>
<tr>
<td>t-butanol</td>
<td>3.0</td>
<td>50</td>
<td>48 hr</td>
<td>25%</td>
<td>13%</td>
</tr>
<tr>
<td>isopropanol</td>
<td>1.5</td>
<td>86</td>
<td>52 hr</td>
<td>31%</td>
<td>26%</td>
</tr>
<tr>
<td>methanol</td>
<td>0.88</td>
<td>66</td>
<td>50 hr</td>
<td>57%</td>
<td>38%</td>
</tr>
</tbody>
</table>

ᵃ % reaction based on amount of 1 consumed.
ᵇ % reacted 1 converted to phenols.
ᶜ Net yield of phenols after 50 hours irradiation.

A solution of 1 in cyclohexane (4.67 X 10⁻² M) was irradiated and monitored by vpc. After 52 hours only 33% 1 remained. The product mixture was chromatographed on silica gel and the three main products isolated. The first fraction (100 ml benzene / fraction) contained a
Figure 8. Nuclear magnetic spectra

Top: 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one

Middle: 2,3,5-trimethylphenol

Bottom: 3,4,5-trimethylphenol
Figure 9. Infrared spectra

Top: 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one

Middle: 2,3,5-trimethylphenol

Bottom: 3,4,5-trimethylphenol
compound (60 mg) with a molecular ion at m/e 166 (53%) and fragment ions at 83 (53%), 82 (100%), 65 (49%) and 53 (58%). The nmr had two broad peaks at δ 1.05 and 1.70 and nothing further downfield. Based on this data the material was tentatively identified as bicyclohexyl (100).

The second product (80 mg, fr. 3-5) had a molecular ion at m/e 202 (40%) which was correct for C_{15}H_{22} (C_{9}H_{12}O + C_{6}H_{12} - H_{2}O). Fragment ions were also present at 187 (32%), 119 (60%), 105 (100%) and 91 (58%). The ir spectrum had no strong bands in the carbonyl region and nothing in the hydroxyl stretching region indicating that the oxygen has been lost. The nmr spectrum was not helpful since the region below δ 5.50 may not have been scanned, and the sample was very dilute. One possible structure that fits the available data is 2-(cyclohexylidene)-5,5-dimethylbicyclo [4.1.0] hept-3-ene (101).

The third product (100 mg, fr. 6-8) had a molecular ion at m/e 220 (28%) which was correct for C_{15}H_{24}O (C_{9}H_{12}O + C_{6}H_{12}). Fragment ions were present at 137 (100%), 110 (26%), 109 (25%), 95 (77%), 67 (29%), and 55 (60%). The ir spectrum had a carbonyl band at 1692 cm^{-1} (CCl_{4}) which was almost the same as 5,5-dimethylbicyclo [4.1.0] heptan-2-one, 1685 cm^{-1} (CCl_{4}). The compound contained no vinyl protons since the nmr spectrum had nothing below δ 2.20 ppm. The proposed structure for the product is 4-cyclohexyl-5,5-dimethylbicyclo [4.1.0] heptan-2-one (102).

Three deuterium labeled isomers of 1 were synthesized (1a-1c) and irradiated to help determine the mechanism of the rearrangement. The deuterated phenols were isolated from the reaction mixture by silica gel chromatography. The nmr spectra were run and the peak areas determined
by integration. The ortho (2,6), meta (3,5) and para (4) methyl groups all have different chemical shifts as do the ortho (2,6) and para (4) ring protons. In all cases the position of the deuterium atoms could be determined unambiguously as either ortho (2,6) or para (4) for the ring deuterons and ortho (2,6), meta (3,5) or para (4) for the deuterated methyl groups.

Irradiation of 1a (Figure 10) in methanol produced 2 with no deuterium present (Figure 10) and 3a with deuterium at one of the ortho positions (Figure 10). The loss of deuterium in 2 indicated that the C-2 methyl group was attached to the same carbon as the deuterium was in 1a.

The irradiation of 1b (Figure 11) under the same conditions produced 2a with deuterium at the ortho position as seen in the nmr (Figure 11). The 3a formed in this reaction had the same nmr (Figure 11) as the the 3a formed from 1a i.e., the deuterium was at one of the equivalent ortho positions (2 or 6).

The irradiation of 1c (Figure 12) showed that the methylene in the cyclopropane ring became a methyl group in the phenols. The nmr integral (Figure 12) of 2b or 2c showed a ratio of 4:3 for the hydrogens
Figure 10. Nuclear magnetic spectra

Top: 3-deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one

Middle: 2,3,5-trimethylphenol

Bottom: 2-deuterio-3,4,5-trimethylphenol
Figure 11. Nuclear magnetic resonance spectra

Top: 1-deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one

Middle: 6-deuterio-2,3,5-trimethylphenol

Bottom: 2-deuterio-3,4,5-trimethylphenol
Figure 12. Nuclear magnetic resonance spectra

Top: 7,7-dideuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one

Middle: 2,3-dimethyl-5-dideuteriomethylphenol
or 2,5-dimethyl-3-dideuteriomethylphenol

Bottom: 3,4-dimethyl-5-dideuteriomethylphenol
on the meta (3 and 5) and ortho (2) methyl groups respectively. The nmr of 3b (Figure 12) showed a ratio of 4:3 for the hydrogens on the meta (3 and 5) and para (4) methyl groups. In both cases the deuterium was incorporated on one of the meta (3 or 5) methyl groups.

\[
\begin{align*}
1a & \xrightarrow{h\nu} 2 + 3a \\
1b & \xrightarrow{h\nu} 2a + 3a \\
1c & \xrightarrow{h\nu} 2b \text{ or } 2c + 3b
\end{align*}
\]

Photochemistry of 3,4,4-Trimethylcyclohexa-2,5-dienone and 4,6,6-
Trimethylbicyclo [3.1.0] hex-3-en-2-one

The anticipated stable intermediate 3,4,4-trimethylcyclohexa-
2,5-dienone (103) was synthesized and its photochemistry studied. Pho-
tolysis of 103 in methanol (ca. 40°) gave a new product which rapidly
built up to a maximum concentration in 50 min and then began to
decrease. This product was isolated by silica gel chromatography and identified as 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one (104): uv max (95% EtOH), 228 nm (ε, 4,770), 253 nm (ε, 3,790), 315 nm (ε, 241); ir (neat) (Figure 13) 753, 862, 1290, 1345, 1375, 1439, 1606, 1687 and 2960 cm⁻¹; nmr (CCI₄) (Figure 14) δ 0.98-1.20 (m, 1H), 1.15 (s, 3H), 1.23 (s, 3H), 1.7-2.0 (m, 1H), 2.05 (d, 3H), 5.50 (m, 1H).

Continued irradiation caused the initial product (104) to disappear along with the starting material (103). Shortly after the beginning of the reaction two other products appeared and increased throughout the reaction. They were isolated and identified as the same phenols 2 and 3 which were formed by photolysis of 1.

The irradiation of 103 in cyclohexane (0.033 M) produced 104 initially and after a time it began to decrease as in the methanol irradiation. The major product after most of 103 and 104 had reacted was 3,6,6-trimethylcyclohexa-2,4-dienone (105) which was identified by its spectra: ir (CCI₄) (Figure 13) 867, 1185, 1220, 1252, 1296, 1320, 1381, 1445, 1470, 1576, 1646, 1662 and 2975 cm⁻¹; nmr (CCI₄) (Figure 14) δ 1.12 (s, 6H), 2.04 (d, 3H), 5.77 (m, 1H), 5.92 (q, 1H), 6.23 (d, 1H); mass spectrum, m/e (relative intensity), 136 (parent, 93), 121 (33),
Figure 13. Infrared spectra

Top: 3,4,4-trimethylcyclohexa-2,5-dienone

Middle: 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one

Bottom: 3,6,6-trimethylcyclohexa-2,4-dienone
Figure 14. Nuclear magnetic resonance spectra

Top: 3,4,4-trimethylcyclohexa-2,5-dienone

Middle: 4,6,6-trimethylbicyclo [3.1.0] hex-3-en-2-one

Bottom: 3,6,6-trimethylcyclohexa-2,4-dienone
Irradiation of a 10% solution of 103 in carbon tetrachloride produced new bands in the ir spectrum at 1693, 1349 and 866 cm$^{-1}$ which matched the ir spectrum of 104. This reaction allowed the conversion of 103 to 104 to be monitored by spectroscopy in order to see if any intermediates were formed which may have been destroyed by vpc or silica gel chromatography. However, none were observed at room temperature.

A ketene and a cyclopropanone were considered as possible intermediates formed by the photolysis of 104. Attempts were made to chemically trap these intermediates at lower temperatures where the thermal reactions would be slower. Irradiation of 103 in methanol-ether (1:2) at -78° produced three methanol adducts which were isolated and identified as methyl 3,6-dimethylhepta-3,5-dienoate (106), 2-methoxy-3,5,5-trimethylcyclohex-3-enone (107) and 2-methoxy-3,5,5-trimethylcyclohex-2-enone (108). The spectral data is given in the EXPERIMENTAL section. Adduct 108 appeared to be a rearrangement product of adduct
since the ratio of 108 to 107 varied but the total yield of the two remained about the same.

Irradiation of dienone 103 in ether-furan (4:1) at -78° produced a crystalline solid (mp 68-70°) which on the basis of its spectra was identified as 11-oxa-7,7,9-trimethyltricyclo[4.3.1.1^2,5]undeca-3,8-dien-10-one (109): uv max (95% EtOH) 284 nm (ε, 128) and end absorption (ε, 1,800 at 200 nm); ir (CCl4) (Figure 15) 871, 970, 1162, 1181, 1317, 1362, 1444, 1555, 1720, 1737 and 2970 cm⁻¹; nmr (CCl4) (Figure 16, 60 mHz) δ 0.98 (s, 3H), 1.24 (s, 3H), 1.74 (d, 3H), 1.96 (m, 1H), 2.43 (t, 1H), 4.61 (q, 1H) 4.83 (q, 1H), 5.26 (t, 1H), 6.25 (distorted AB, 2H); mass spectrum m/e (relative intensity) 204 (parent, 100), 198 (55), 161 (43), 136 (35) and 121 (43). The 100 mHz nmr was spin decoupled (the decoupling work was performed by Dr. Hal Wright) with the following results:
Figure 15. Infrared spectra

Top: 11-oxa-7,7,9-trimethyltricyclo[4.3.1.1^2,5]undeca-3,8-dien-10-one

Middle: methyl 6-methylhepta-3,5-dienoate

Bottom: 11-oxa-7,7-dimethyltricyclo[4.3.1.1^2,5]undeca-3,8-dien-10-one
Figure 16. Nuclear magnetic resonance spectra

Top: methyl 3,6-dimethylhepta-3,5-dienoate

Middle: 11-oxa-7,7,9-trimethyltricyclo[4.3.1.1^2,5]undeca-3,8-dien-10-one

Bottom: 11-oxa-7,7-dimethyltricyclo[4.3.1.1^2,5]undeca-3,8-dien-10-one
The C9-methyl group (δ1.74) was split by the vinyl proton H-8 (5.28, J=1.5 Hz). In addition H-8 was coupled to H-6 (1.96, J=1.5 Hz). H-6 had additional couplings with H-5 (4.82, J=2.5 Hz) and H-1 (2.43, J=1.0-1.5 Hz). Also H-1 was coupled to H-2 (4.62, J=2.5 Hz). H-3 (6.26) and H-4 (6.18) formed an AB pattern (J=6.0 Hz) with each half being split identically by H-2 and H-5 respectively (J=1.5 Hz). The gem dimethyl groups were at δ0.98 and 1.24.

The photolysis of the bicyclic enone 104 in ether-furan was also carried out and the same furan adduct (109) was formed as shown by its nmr.

The photochemistry of the bicyclic enone 104 at -190° was more complex than at other temperatures. Irradiation between salt plates in the low temperature cell produced three primary products with bands at 2107 (110), 1810 (111) and 1801 cm⁻¹. The low temperature ir spectra are shown in Figure 17. The cyclopropanone (111) at 1810 cm⁻¹ increased rapidly and by the second minute has already started to decrease. At the end of 8 minutes it was almost completely gone. The trace of carbon monoxide detected probably came from decarbonylation of the cyclopropanone (41). The ketene (110) at 2107 cm⁻¹ increased rapidly the first 4 minutes and had decreased slightly at the 8 minute mark. Both the cyclopropanone and the ketene were thermally unstable. The band at 1801 cm⁻¹ band grew very slowly and was not visible until after the cyclopropanone band at 1810 cm⁻¹ had decreased greatly. The band at 1801 cm⁻¹ was thermally stable.

A dry sample of dienone 103 was irradiated between salt plates at -190° and the only primary photoproduct was a ketene at 2108 cm⁻¹. The
Figure 17. Low temperature ir spectra

Top: $4,6,6$-trimethylbicyclo[3.1.0]hept-3-en-2-one

Middle and Bottom: $4,4$-dimethylcyclohexa-2,5-dienone
ketene band grew throughout the 3 hour irradiation and a weak band at 1715 cm\(^{-1}\) appeared at the 1 hour mark. This band could have been a photoproduct of the ketene. A trace of carbon monoxide was first observed at the 4 minute mark. Both ketene and carbon monoxide disappeared during warmup while the product at 1715 cm\(^{-1}\) was stable.

Irradiation of a 10% solution of dienone 103 in methanol at -190° produced a product with a carbonyl band shifted by solvent effects from its normal 1693 cm\(^{-1}\) in CCl\(_4\) and 1683 cm\(^{-1}\) neat. A small amount of ketene (2110 cm\(^{-1}\)) and carbon monoxide (2140 cm\(^{-1}\)) were detected also.
The reaction was so slow at \(-190^\circ\) that large scale reactions in methanol were not practical.

\[
\begin{align*}
\text{hv} & \quad \text{MeOH} \\
103 & \quad 1702 \text{ cm}^{-1} + 2110 \text{ cm}^{-1} + \text{CO}
\end{align*}
\]

A similar irradiation of a 10% solution of dienone 103 in carbon tetrachloride at \(-190^\circ\) gave a ketene (2112 cm\(^{-1}\)) and carbon monoxide (2136 cm\(^{-1}\)) as main products. The first new band was at 1810 cm\(^{-1}\), but it remained very small throughout the reaction.

\[
\begin{align*}
\text{hv} & \quad \text{CCl}_4 \\
103 & \quad 2112 \text{ cm}^{-1} + \text{CO} + 1810 \text{ cm}^{-1} \text{ (trace)}
\end{align*}
\]
Photochemistry of 4,4-Dimethylcyclohexa-2,5-dienone and 6,6-Dimethylbicyclo[3.1.0]hex-3-en-2-one

The photochemistry of 4,4-dimethylcyclohexa-2,5-dienone (62) was studied and compared to the photochemistry of 3,4,4-trimethylcyclohexa-2,5-dienone (103). In a repeat of the work by Srinivasan et al., (30) 62 was irradiated in cyclohexane and monitored by vpc. The first product formed was 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) which was identified by its spectral data (see EXPERIMENTAL section). A second product began to appear shortly after the appearance of 63. The second product accumulated throughout the reaction while 63 began to decrease after a time. The new product was 6,6-dimethylcyclohexa-2,4-dienone (64) based on the results of Srinivasan et al., (30). The compound was not characterized since it has been reported as being very unstable even for short periods of time (53). The ir spectrum appeared to be a mixture of dimer and monomer.

The photolysis of 62 in methanol was also performed and again 63 was the initial product. The reaction was continued until most of 62 and 63 were gone, leaving four final products. Two of the products were 2,3-dimethylphenol (65) and 3,4-dimethylphenol (66) which Srinivasan
et al., (30) found during irradiation in aqueous dioxane. Another product was identified as methyl 6-methylhepta-3,5-dienoate (112) by comparison of its nmr to that of another sample (see next paragraph). The fourth product was not identified.

A solution of dienone 62 in methanol-ether (1:2) was irradiated at -78° and only one product besides bicyclic enone 63 was isolated. On the basis of its spectra it was identified as methyl 6-methylhepta-3,5-dienoate (112): ir (neat) (Figure 15) 763, 789, 960, 987, 1017, 1163, 1197, 1250, 1320, 1331, 1380, 1437, 1660, 1745, 2920 and 2960 cm\(^{-1}\); uv max (95% EtOH) 238 nm (\(\varepsilon\), 20,700), Lit 238 nm (\(\varepsilon\), 22,300) (54); nmr (CCl\(_4\)) (Figure 18) 6 1.75 and 1.81 (broad singlets, 6H), 3.10 (d, 2H), 3.60 (s, 3H), 5.15-6.45 (m, 3H); mass spectrum, m/e (relative intensity), 154 (parent, 33), 95 (100), 93 (26), 80 (18), 78 (19), 68 (27), 56 (27). This ketene adduct was analogous to the adduct formed from irradiation of bicyclic enone 104, but no corresponding cyclopropanone adducts with methanol were found. Ester 112 was unstable and isomerized slowly which
Figure 18. Nuclear magnetic resonance spectra

Top: 4,4-dimethylcyclohexa-2,5-dienone

Middle: methyl 6-methylhepta-3,5-dienoate

Bottom: 2,2-dimethyl-5-methoxybicyclo[4.1.0]heptane
probably accounts for the low ε value in the uv spectrum and the triplet at δ 3.10 in some of the nmr spectra.

Irradiation of dienone 62 in methanol-furan (4:1) at -78° produced a furan adduct plus a small amount of bicyclic enone 63. The adduct was identified as 11-oxa-7,7-dimethyltricyclo[4.3.1.12,5]undeca-3,8-dien-10-one (113): mp 113-115°; ir (CCl₄) (Figure 15) 864, 883, 968, 979, 993, 1044, 1123, 1194, 1319, 1364, 1692 (w), 1734 (s) and 2970 cm⁻¹; uv max (95% EtOH) 275 nm (ε, 113) and end absorption at 200 nm (ε, 7,050); mass spectrum, m/e (relative intensity), 190 (parent, 100), 175 (34), 147 (58), 122 (66), 107 (62), 79 (52), 77 (39), 68 (36); nmr CCl₄ (Figure 16) δ 1.05 (s, 3H), 1.30 (s, 3H), 2.17 (m, 1H), 2.80 (m, 1H), 4.68 (q, 1H), 4.99 (q, 1H), 5.64 (q, 1H), 5.69 (s, 1H) and 6.30 (distorted AB, 2H).

The molecular structure of photoproduct 113 was determined by an X-ray diffraction experiment. Crystals of C₁₂H₁₄O₂ belong to the monoclinic space group P2₁/c (C₅ 2h) with cell constants a = 15.240 (3), b = 6.473 (5), c = 11.148 (4) Å and β = 111.15 (7)°. There are four molecules per unit cell. Full-matrix least squares refinements on the 1130
independent, non-zero, diffractometer measured intensities reduced the discrepancy index to 10.2%. There are no unusual bond lengths or angles (Figure 19). X-ray structure was determined by Dr.'s Jon Clardy and Hal Wright, Iowa State University.

Neat dienone \(^\text{62}\) was irradiated between salt plates at -190° (Figure 17) and new bands appeared at 1692 cm\(^{-1}\) after 1 min and at 2107 and 1815 cm\(^{-1}\) after 3 min. New bands also appeared at 1714 and 1801 cm\(^{-1}\) after 6 min. After 30 min irradiation the band at 1691 cm\(^{-1}\) began to decrease, but the bands at 2107, 1801 and 1714 cm\(^{-1}\) were still increasing after 3 hr. The band at 1815 cm\(^{-1}\) was lost under the 1801 cm\(^{-1}\) band. The cell was warmed to room temperature and only the band 2107 cm\(^{-1}\) disappeared. The sample was irradiated for another 3 hr and the bands at 2107, 1801 and 1714 cm\(^{-1}\) continued to grow. The bands at 1801 and 1714 cm\(^{-1}\) again persisted during warmup with only the ketene disappearing. The band at 1801 cm\(^{-1}\) was not affected by treatment with methanol even after 6 hr. This stability toward methanol and heat is contrary to the behavior expected of a cyclopropanone intermediate. A large scale irradiation of dienone \(^\text{62}\) in a quartz test tube at -190° did not produce enough product after 8 hr to be detected by nmr.

A thin film of bicyclic enone \(^\text{63}\) was irradiated at -190° (Figure 20) and after 1 min new carbonyl bands were observed at 1801 (w), 1815 (s), 1885 (w), 2109 (s) and 2134 cm\(^{-1}\) (w). After 2 min the 2 bands at 1815 (cyclopropanone) and 1885 cm\(^{-1}\) had started to decrease while the bands at 2109 and 2134 cm\(^{-1}\) continued to increase. The ketene band (2109 cm\(^{-1}\)) began to decrease after 4 min irradiation and the carbon monoxide (2134 cm\(^{-1}\)) increased throughout the 15 min irradiation. A
Figure 19. X-ray structure of 11-oxa-7,7-dimethyltricyclo[4.3.1.1\(^2,5\)]undeca-3,8-dien-10-one
Figure 20. Low temperature IR spectra for 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one
a new band appeared at the 8 min mark at 1715 cm$^{-1}$ and was still increasing at the end of the reaction. It was also thermally stable as was the band at 1801 cm$^{-1}$ which grew slowly during the reaction. The bands at 1815, 1885, 2109 and 2134 cm$^{-1}$ all disappeared during warmup to room temperature and no new bands were observed.

Photochemistry of 6,6-Dimethyltricyclo[5.1.0.0$^3,5$]octan-2-one

A solution of 6,6-dimethyltricyclo[5.1.0.0$^3,5$]octan-2-one (114) in methanol was irradiated and the reaction followed by vpc. Although the starting material slowly disappeared, no products could be detected by vpc or separated by silica gel chromatography.

![Diagram of 114 with chemical structure]

Photochemistry of 5,5-Dimethylbicyclo[4.1.0]heptan-2-one

A solution of 5,5-dimethylbicyclo[4.1.0]heptan-2-one (115) was irradiated in methanol and 1 major and several minor products were detected by vpc. The major component was isolated by silica gel chromatography and spectral data collected: ir (neat) 765, 789, 934, 1058, 1084, 1110, 1132, 1193, 1263, 1367, 1457, 2835 and 2960 cm$^{-1}$; mass spectrum, m/e (relative intensity), 154 (parent, 25) 152 (7), 139 (14), 137 (12), 98 (53), 85 (45), 84 (100), 83 (84), 70 (24), 69 (16), 55 (39),
43 (78), 41 (39), 39 (86); nmr (CCl₄) (Figure 17) δ 0.76 (s, 3H), 0.90 (s, 3H), 0.70-1.90 (m, 8H), 3.05 (s, 1H), 3.09 (s, 3H). 2,2-dimethyl-5-methoxybicyclo[4.1.0]heptane (116, mixture of stereoisomers) appears to fit the spectral data best.

Photochemistry of 5-Methylbicyclo[3.2.0]hep-3-en-2-one (117)

A thin film of 117 was irradiated between salt plates at -190° and after 1 min new infrared bands had appeared at 1775 and 1755 cm⁻¹. The 1775 cm⁻¹ band grew rapidly throughout the reaction (60 min) and became very strong. The 1755 cm⁻¹ band was weak and soon became lost under the 1775 cm⁻¹ band. After 2 min a shoulder appeared at 1725 cm⁻¹ on the side of the 1700 cm⁻¹ band (117). The shoulder grew rapidly into a separate band and after 60 min it was nearly as large as the 1700 cm⁻¹ band. There didn't appear to be any change during warmup. A weak band also appeared at 2135 cm⁻¹ but never became very prominent. The bands at 1700, 1775 and 1725 cm⁻¹ are all 15 cm⁻¹ lower than the values reported by Cargill (private communication from R. L Cargill to O. L. Chapman) for 117, 2-methylbicyclo[2.2.1]hept-2-en-7-one (118) and dimer(s). Dimer(s) and 118 were reported by Cargill et al.
(55) as the room temperature products of 117 in pentane or methylene chloride.

\[
\begin{array}{c}
\text{117} \\
\text{hv} \\
pentane or \text{CH}_2\text{Cl}_2 \\
\text{118} \\
\text{+ dimer(s)}
\end{array}
\]

Photochemistry of 1,2-Dimethyltricyclo[4.3.0.0^{2,6}]non-4-en-3-one (119)

A neat sample of 119 was irradiated between salt plates at -190° and 2 new infrared bands appeared immediately at 2106 and 1801 cm\(^{-1}\). The band at 1801 cm\(^{-1}\) grew throughout the reaction (4.5 hr) and did not disappear during warmup. The 2106 cm\(^{-1}\) band reached a maximum after 30 min and decreased slowly during the rest of the irradiation. The rest of the band disappeared during warmup. A new band appeared at 2135 cm\(^{-1}\) (carbon monoxide) after 4 min reaction and another at 2340 cm\(^{-1}\) (carbon dioxide) after 1 hr reaction. A band also appeared after 10 min at 1730 cm\(^{-1}\) and gradually increased and shifted to 1712 cm\(^{-1}\) after 4.5 hr. This band was also thermally stable.
A 10% solution of 119 in tetrahydrofuran was irradiated at -78° and new bands appeared at 1802 and 1772 cm\(^{-1}\) initially. No ketene band was observed. After 4 min a new peak appeared at 1715 cm\(^{-1}\) and grew until about 13 min irradiation. After 20 min irradiation all the bands had started to decrease because of a leak in the solution cell.

**Photochemistry of 4,4-Dimethyl-5(4H)-indanone (120)**

A neat sample of 120 was irradiated between salt plates at -190° and the only primary product was a ketene with a very strong absorption at 2109 cm\(^{-1}\). This band reached nearly 100% absorption after 8 min. The reaction was run for a total of 60 min which decreased the starting material by about 25%. The ketene disappeared during warmup and no new bands were observed. The bands for the starting material appeared to be the same although this would be impossible to measure exactly due to changes in the baseline during warmup. There was also a small band at 1727 cm\(^{-1}\) which was probably some type of dimer.
DISCUSSION

The formation of 2,3,5-trimethylphenol and 3,4,5-trimethylphenol from the irradiation of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one was unexpected and prompted further study of the system in order to determine the mechanism. A tentative mechanism was proposed which involved three separate photochemical steps. The first step was a photochemical opening of the cyclopropyl ring of 1 to form a cross conjugated dienone (103). The dienone could then rearrange photochemically to a bicyclic enone (104) followed by a third photochemical step involving a methyl shift to form the phenols 2 and 3.

There are examples of all three reactions in the literature which are reviewed in the HISTORICAL section. The intervention of bicyclic enone 104 in the sequence was particularly desirable since it allowed both phenols to be formed from the same intermediate with only a single methyl shift. Other mechanisms without a bicyclic intermediate would require either multiple methyl shifts or unknown skeletal rearrangements and would not provide a common precursor to both phenols. The phenols
2 and 3 do not interconvert photochemically.

The first attempt at testing the proposed mechanism involved deuterium labeling. Compounds 1a–1c were synthesized and irradiated. If the mechanism involved cyclopropyl ring ring opening followed by a dienone type rearrangement the position of the deuterium in the phenols 2 and 3 would correspond to the following labeled isomers:

The nmr data was consistent with the predicted structures, although in 2b both meta methyl groups have the same chemical shift but aren't chemically equivalent since the molecule is unsymmetrical.

Compound 1 labeled at the C-6 position would be useful in determining if a hydrogen shift occurred from C-6 (bicyclic numbering) to the C-5 methyl group (phenol numbering). However, the synthesis would involve
C-1 labeled isobutyraldehyde which is difficult to synthesize.

There was no direct evidence for the first proposed photochemical step involving breakage of the cyclopropyl bond to form a cross conjugated dienone. However, bicyclo[4.1.0]heptan-2-ones were known to undergo two types of photoreaction. Dauben and Shaffer (48) have shown that the competition between \( \alpha \)-cleavage to form an aldehyde (121) and cyclopropyl ring opening to form a 3-methylcyclohex-2-enone (122) depends on the substituents at the C-3 and C-7 positions. Methyl substitution at C-3 favors \( \alpha \)-cleavage and methyl substitution at C-7 favors cyclopropyl ring opening. Methyl substitution at C-6 prevents cyclopropyl ring opening and in fact very little reaction occurs at all (56).

This lack of reactivity could be caused by the lack of a C-6 hydrogen to migrate to the C-7 methylene to form the 3-methylcyclohex-2-enone.
Dauben et al., (57) have some mass spectral data to support this mechanism. He has found that bicyclo[4.1.0]heptan-2-ones which rearrange photochemically to 3-methylcyclohex-2-enones also have fragmentation patterns similar to the corresponding 3-methylcyclohex-2-enones. The major fragmentation peak for 3-methylcyclohex-2-enones (123) is loss of C-5 and C-6 in a retro Diels Alder process. The same pattern appears in bicyclo[4.1.0]heptan-2-ones (124) which lose C-3 and C-4 presumably after opening to the 3-methylcyclohex-2-enone isomer.

6-Methylbicyclo[4.1.0]hept-2-one does not lose C_2H_4 in the mass spectrometer indicating that it doesn't go through a 3-methylcyclohex-2-enone intermediate. This is also consistent with the photochemical results.

The closest model for 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one was
reported by Ourisson et al., (58) who irradiated 5,5,7,7-tetramethylbicyclo[4.1.0]hept-3-en-2-one (125). They isolated a diene (126) from irradiation in benzene and a hemiketal (127) in methanol. Both products could be derived from an intermediate cyclopropanone (128). However, the endo C-7 methyl is essential for the formation of the cyclopropanone (128) since it donates a hydrogen to the C-4 position. The C-7 methyl is absent in 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one making this mechanism unlikely.

The most reasonable initial step in the photochemistry of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (1) is the breakage of the 1-7 bond of the cyclopropane ring followed by a hydrogen shift to give 3,4,4-trimethylcyclohexa-2,5-dienone (103). The dienone (103) has never
been detected in the product mixture, but this is probably due to the much greater photochemical reactivity of dienones in general.

The cyclopropyl ring opening was solvent dependent. Irradiation of 1 in t-butanol, isopropanol or methanol gave phenols 2 and 3. But in nonpolar cyclohexane radical type addition products were formed with the cyclopropane ring remaining intact. The stability of the cyclopropane ring to cleavage in cyclohexane may be due to a more rapid hydrogen abstraction process (Figure 21). Irradiation of 1 in a nonpolar solvent that isn't a good hydrogen donor might give the same results as the polar solvents for the initial reaction. The need for a polar solvent in what appears to be a radical type reaction is not obvious, although the theory of Dauben and Berezin (49) seems to offer the best explanation.

The second proposed photochemical step was studied by irradiating 3,4,4-trimethylcyclohexa-2,5-dienone (103) under several sets of conditions. The only primary product identified was 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one (104) which formed in cyclohexane, methanol and carbon tetrachloride at room temperature. The bicyclic enone (104) appeared to be the initial product in reactions at -78° using methanol-

Figure 21. Mechanism for photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in cyclohexane
ether or furan-ether as the solvent. The products isolated in these reactions were solvent adducts derived from a ketene (110) and a cyclopropanone (111) which are known to form during irradiation of the bicyclic enone (104). It seems very unlikely that the adducts (106, 107, 108, 109) could be formed directly from the dienone (103).

The results of irradiating dienone 103 at -190° are not completely clear. Neat dienone slowly formed a ketene (2108 cm⁻¹) as the only primary photoproduct. However, this ketene could not be the same ketene produced by irradiation of bicyclic enone 104, since 104 would have to be an intermediate and was not observed. After an hour a band started to grow at 1715 cm⁻¹ which might have been a secondary product derived from the ketene.

Irradiation of a 10% solution of dienone 103 in carbon tetrachloride produced a primary product with a band at 1810 cm⁻¹ which remained very small throughout the reaction. The main products were a ketene (2112 cm⁻¹) and carbon monoxide. The carbon monoxide was probably produced by decarbonylation of the product at 1801 cm⁻¹. The identity of the 1801 cm⁻¹ band is not known since it is hard to imagine a cyclopropanone being formed directly from the dienone (103).

Irradiation of a 10% methanol solution produced a band at 1702 cm⁻¹
which could have been bicyclic enone 104. However 104 would be expected to react further instead of building up. A trace of ketene and carbon monoxide were also observed in methanol.

Several attempts were made to repeat the low temperature reactions of dienone 103 on a larger scale and all failed. The difficulty might have been due to temperature differences in the two methods or, more likely, to the large differences in thickness and volume of the sample.

The rearrangement of 3,4,4-trimethylcyclohexa-2,5-dienone to 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one was probably regioselective, although none of the other possible isomer (5,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one) was detected. Several systems have been studied where the substitutents at C-4 were different. Rogers and Hart (26) studied the substituent effect at C-3 and C-5 on the endo to exo ratio for 4-methyl-4-n-propylcyclohexa-2,5-dienone (55) and found that increased steric hindrance at C-3 and C-5 increased the endo to exo ratio. The stereochemistry was determined during 3-5 bonding to form zwitterion 58. The endo form was favored because the bulky n-propyl group has to move past A and B if they are large enough to cause steric hindrance.

When only the C-3 or the C-5 position was substituted, migration
occurred exclusively away from the substituent. The bond migration
then occurred with retention of configuration at C-4.

Zimmerman and Crumrine (28) and Brennan and Hill (29) have generated
zwitterions similar to 58 and have found that they always rearrange with
retention of configuration. Molecular orbital considerations would also
predict retention of stereochemistry by 4-6 bonding at the back side of
the C-6 orbital which grows as the 1-6 bond is broken (Figure 4). The
pivot mechanism (28) which involves rotation about the 5-6 bond would
not give a favorable orbital overlap or correct stereochemistry.

The third photochemical step of the proposed mechanism turned out to
be much more complex than expected. Irradiation of the bicyclic enone
(104) in methanol produced phenols 2 and 3 as expected. However,
irradiation of 104 in cyclohexane produced 3,6,6-trimethylcyclohexa-2,4-
dienone (105) and some phenol 2. These results suggested that two dif-
ferent mechanisms were in competition.

The possibility of thermally unstable intermediates was tested by
irradiating the bicyclic enone (104) in methanol-ether at -78°. Three
methanol adducts were isolated and identified. The ester (106) appeared to be a ketene adduct, and the two methoxy enones (107 and 108) appeared to be cyclopropanone adducts. The nonconjugated methoxy enone (107) appeared to be the primary product which could isomerize to form the conjugated methoxy enone (108).

Irradiation of 104 in ether-furan at -78° produced a furan adduct (109) derived from a cyclopropanone. These adducts are very good evidence for the intermediacy of ketene 110 and cyclopropanone 111.

More direct evidence for a ketene and a cyclopropanone was provided
by the low temperature results. Irradiation of neat bicyclic enone (104) between salt plates at -190° produced intense bands at 2107 cm⁻¹ and 1810 cm⁻¹ which are characteristic bonds for ketenes (35) and cyclopropanones (41), respectively.

The competition between ketene and cyclopropanone formation is both temperature and solvent dependent. At room temperature irradiation in cyclohexane favors ketene formation, and irradiation in polar solvents favors phenol formation. The phenols could come from the cyclopropanone or its zwitterion. Irradiation at -78° give about equal amounts of ketene and cyclopropanone products in polar solvents (ether, methanol and furan). During neat irradiation at -190°, both ketene and cyclopropanone bands become quite strong.

The formation of the ketene (110) appears to be a concerted photochemical reaction since it occurs in nonpolar solvents which wouldn't favor zwitterionic intermediates such as 131a-131c. The opening of bicyclic enone 104 to a ketene is formally the reverse of the closure of a hexatriene to a bicyclo[3.1.0]hex-2-ene which has been reported many times (59 and references therein). The photochemical closure of 1,2,6-triphenyl-(E,Z,E)-hexa-1,3,5-triene (129) to exo,exo-3,4,6-triphenylbicyclo[3.1.0]hex-2-ene (130) was reported by Padwa and Clough (59) to proceed by \( \pi^4s + \pi^2a \) route. The reaction was also allowed
allowed by a \( \pi^2 \alpha + \pi^2 \beta \) route (60) but no corresponding product was observed. The formation of 130 photochemically is allowed by a concerted process, but the concertedness hasn’t been demonstrated.

The closure of the ketene (110) to the dienone (105) is allowed thermally (disrotatory) and photochemically (conrotatory). However, there is no evidence of any 105 being formed during the low temperature irradiation. The ketene (110) does disappear rapidly during warmup and presumably the product is dienone 105. A product absorbing at 1715 cm\(^{-1}\) does form during irradiation and could be due to some type of photoproduct of the ketene (110). Other bicyclo[3.1.0]hex-3-en-2-one systems have been reported to give ketene derivatives (35, 42).

The formation of the cyclopropanone (111) from the bicyclic enone (104) is formally an allylic shift. The Woodward-Hoffmann rules (60) would predict a concerted reaction since superficial 1,3-sigmatropic shifts are allowed photochemically. The reaction has been observed in a similar case (41). The cyclopropanone is not thermally stable and is probably in thermal equilibrium with the zwitterion which has three resonance forms (131a-131c). The zwitterion appears to be the reactive species in all cases (Figure 22).

Zwitterions 131a and 131b can form phenols 2 and 3 by undergoing a 1,2-methyl shift and enolizing. The third zwitterion cannot undergo a 1,2-methyl shift and is not important at room temperature, where the methyl shifts occur very rapidly. As the temperature is lowered the zwitterion lifetime becomes longer and other reaction can occur.

Zwitterion 131c can add methanol to form adduct 107. Methanol adducts of 131a and 131b are not observed, however. This could be due
Figure 22. Mechanism for the photorearrangement of 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one to a steric hindrance to the approach of methanol by the \textit{gem}-dimethyl group. The possibility of the methoxy enone (107) being formed from the cyclopropanone (111) instead of the zwitterion (131c) was considered. However, cyclopropanones are known to react with methanol to form hemiketals (61, 62, 63).

Zwitterions 131a and 131c can react with furan in a concerted manner to form adduct 111. The reaction is classified as a 3 + 4 7 (6) addition (64). Similar cases have been reported by Turro and Hammond (61, 63) and Chapman et al. (41).
The appearance of a cyclopropanone in the low temperature ir spectrum can be explained by a temperature dependent equilibrium between the zwitterions 131a and 131c and the cyclopropanone (111). At -190° the cyclopropanone (111) is more stable and predominates. During warmup 111 is converted to the zwitterion which can rearrange to form the phenols 2 and 3.

The observed solvent effect on the ratio of 2 to 3 may be due to differences in the stability of zwitterions 131a and 131b. 131a should be slightly more stable since the conjugated system is linear while 131b has a branched system. The less polar t-butanol provides less solvation and causes the more stable 131a to predominate in the reaction and results in a high ratio of 2 to 3. The more polar methanol can solvate both 131a and 131b about equally resulting in about equal amounts of 2 and 3.

A second mechanism for the conversion of 104 to 2 and 3 differs from the first only in the role of the cyclopropanone (111). 111 might come from the zwitterions (131a-131c) and not be the initial photoproduct. There is no evidence of zwitterions in the low temperature spectra, however.

The photochemistry of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) paralleled bicyclic enone 104 closely at room temperature and at -78°. The only exception was the irradiation of 63 in methanol at -78° where 63 didn't form a cyclopropanone adduct corresponding to methoxy enone 107. The reason was probably a difference in reactivity of the two cyclopropanones. The whole series of reactions starting from
4,4-dimethylcyclohexa-2,5-dienone (62) are faster than the corresponding reactions in the 3,4,4-trimethylcyclohexa-2,5-dienone (103) series. The furan adduct 113 had a sharp and fairly high melting point (113-115°) and formed crystals suitable for x-ray crystallography. The results show that the oxygens are on opposite sides of the molecule. The furan approaches the cyclopropanone zwitterion so that the large rings are farthest apart or exo (Figure 23). The endo approach would be hindered by the gem dimethyl group. There is even some distortion of the bridge oxygen by the gem dimethyl group in the exo model.

The irradiation of neat 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) for 1 min at -190° produced strong bands at 1815 (cyclopropanone) and 2109 cm⁻¹ (ketene) as expected. After 1 min weaker bands had also appeared at 2134 (carbon monoxide), 1885 and 1801 cm⁻¹. The carbon monoxide came from decarbonylation of the cyclopropanone (132) as in the previous case with bicyclic enone 104. The growth and disappearance of the weak 1885 cm⁻¹ band was the same as the 1815 cm⁻¹ band. The 1801 cm⁻¹ band grew throughout the reaction and was thermally stable. Its identity is still a mystery. It has been observed in other cases. A new
band appeared after 8 min at 1715 cm$^{-1}$ and was probably a photoproduct of the ketene (133). In all cases where a strong ketene band was present a band has formed at 1715 cm$^{-1}$ if the reaction was carried far enough. The proposed sequence is shown in Figure 24.

Figure 24. Low temperature photochemistry of 6,6-dimethylbicyclo-[3.1.0]hex-3-en-2-one

The irradiation of neat 4,4-dimethylcyclohexa-2,5-dienone (62) at -190° for 1 min produced a new carbonyl band at 1692 cm$^{-1}$ which is the same as that of 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) which was the expected product. The rest of the results were similar to the irradiation of neat 63 shown in Figure 22. The new bands that appeared after 3 min at 2107 and 1815 cm$^{-1}$ correspond to the ketene (133) and the cyclopropanone (132), respectively. Both bands came from 63 and not 62 since they weren't present after 1 min of irradiation.

The band at 1714 cm$^{-1}$ appeared to be a photoproduct of the ketene
(133) and not 62 or 63. The band at 1801 cm\(^{-1}\) was not identified, and its source was not obvious. It wasn't observed at the 3 min mark when the band at 1815 and 1714 cm\(^{-1}\) were first seen, but it quickly became much more intense and broader than the band at 1815 cm\(^{-1}\). If 1801 cm\(^{-1}\) came from 63, as suspected, it must have had a short induction period before it started forming. The ketene (133) was thermally unstable as expected and the bands at 1714 and 1801 cm\(^{-1}\) were thermally stable and insensitive to alcohol.

Figure 25 is a summary of the known reactions of 62 and 63 and their products. The reaction conditions have been included in many of the reactions, although some may have more than one possibility.

The irradiation of neat 5-methylbicyclo[3.2.0]hept-3-en-2-one (117) at -190\(^{\circ}\) produced two major products with bands at 1775 and 1725 cm\(^{-1}\) and a minor product at 1755 cm\(^{-1}\). The major products correspond to 2-methylbicyclo[2.2.1]hept-2-en-7-one (118) and dimer(s) reported by Cargill et al., (55) at room temperature in pentane or methylene chloride.

Cargill and Sears (65) reported an additional product when 117 was irradiated in methanol. It was identified as methyl trans-4-methyl-2-cyclohexenecarboxylate (134) and was present in about a 15% yield. The reaction sequence proposed by Cargill and Sears is shown in Figure 26. Low temperature irradiation of 117 gave no evidence for formation of the proposed cyclopropanone intermediate (135). There was also no evidence for a ketene intermediate. The absence of a cyclopropanone during irradiation of a neat sample of 117 doesn't completely rule out the possibility of a cyclopropanone intermediate during a room temperature
Figure 25. Summary of photochemistry of 4,4-dimethylcyclohexa-2,5-dienone
Figure 26. Mechanism proposed for formation of methyl-trans-4-methyl-2-cyclohexene-carboxylate from 5-methylbicyclo[3.2.0]hept-3-en-2-one

irradiation in methanol.

Drury Caine (private communication with O. L Chapman) has reported that the irradiation of 1,2-dimethyltricyclo[4.3.0.0^{2.6}]non-4-en-3-one (119) for 90 min in dioxane produced 4,4-dimethyl-5(4H)-indanone (120) in 85% yield. A small amount of 1a, 4-dimethyl-5(1aH)-indanone (136) was also present. Irradiation of 119 for 30 min under the same conditions produced a mixture of 119, 120 and 136 in a ca. 2:2:1 ratio.
Low temperature irradiation of neat 119 produced a ketene (2106 cm\(^{-1}\)) (137) and an unknown product with a carbonyl band at 1801 cm\(^{-1}\). Corresponding bands were also observed during irradiation of 63. The ketene was expected, but the 1801 cm\(^{-1}\) band wasn't and its identity is still a mystery.

The low temperature irradiation of 120 gave a ketene (2109 cm\(^{-1}\)) (137) as the only primary product. This ketene was expected since many linearly conjugated cyclohexadienones have been reported to give ketenes or ketene derivative (37, 38, 66). A mechanism which explains the low temperature results and Caine's results and is consistent with results of similar systems is shown in Figure 27.

![Figure 27. Proposed mechanism for the photorearrangement of 119, 120 and 136](image)

The conversion of 119 to the ketene (137) is similar to the conversion of lumisantonin (34) and umbellulone (71) to ketenes in that a 1,2-shift (methyl or hydrogen) has to occur in addition to ring opening
(35). Again, the possibility exists of a ketene-carbene intermediate (138) as a precursor to the ketene (137). A 1,2-methyl shift would then give the ketene.
EXPERIMENTAL

Instruments and Methods

The uv spectra were obtained in 95% ethanol on a Cary Model 14 spectrophotometer. The ir spectra were recorded on a Beckman Model IR-9 spectrometer unless noted otherwise. The nmr spectra were obtained on either a Varian Associates Model A-60 spectrometer or a Varian Associates Model HA-100 spectrometer. The spectra were run in deuteriochloroform or carbon tetrachloride using tetramethylsilane as an internal standard. Chemical shifts are reported as ppm on the δ scale. Mass spectra were obtained on an Atlas Model CH-4 mass spectrometer. The elemental analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, New York and samples were purified by vpc. All melting points were taken on a Kofler hot stage. Melting and boiling points are uncorrected.

An Aerograph Model 1520 gas chromatograph was used for all analytical and preparative gas-liquid chromatography. The analytical work was performed on an 8 ft. by 0.25 in. column packed with 10% polyethylene glycol (Carbowax 20 m) and 90% 60/80 mesh Chromosorb W (acid washed, dimethyldichlorosilane treated) (Column A). Preparative work was performed on either an 11 ft. by 0.375 in. column packed with 20% polyethylene glycol (Carbowax 20 m) and 80% Chromosorb W (Column B) or an 11.5 ft. by 0.375 in. column packed with 10% ethylene glycol succinate (LAC 728) and 90% Chromosorb W (60/80 mesh, acid washed) (Column C).

Photolyses were performed with the following three types of
lamps: 1. Hanovia 450 watt medium pressure mercury arc lamp; 2. Westinghouse 800 watt high pressure mercury arc lamp (1 cm arc length); 3. Rayonet Photochemical Reactor Lamp (3000 A or 2537 A). Phosphorescence spectra were obtained from an Aminco-Bowman Spectrophotofluorometer (Model 4-8202, American Instrument Co., Inc., Silver Spring, Md.) using 2-methyltetrahydrofuran as solvent.

Experimental for the Photolysis of 5,5-Dimethylbicyclo-\[4.1.0\]hept-3-en-2-one

4,4-Dimethylcyclohex-2-enone

The isobutyraldehyde piperidine enamine was prepared by adding distilled isobutyraldehyde (300 g, 4.16 moles) and distilled piperidine (722 g, 8.50 moles) to benzene (1150 ml) in a 3 l flask. The solution was refluxed for 6 hr with 73 ml of water being formed and removed in a Dean-Stock trap. Distillation at ambient pressure removed most of the benzene (80° to 100°). The remaining benzene and piperidine were removed at reduced pressure (24 mm) with fractions boiling below 60° containing mixtures. The fractions boiling between 60° and 75° contained only enamine. The total yield was 448 g (77.5%); \textit{ir} (CCl\textsubscript{4}) 2920, 2780, 1680, 1450, 1383, 1340, 1177, 1133, 1110 and 1035 cm\textsuperscript{-1}; \textit{Lit.} (67) bp 60°/8 mm.

The isobutyraldehyde piperidine enamine (448 g, 3.22 moles) was placed in a 5 l flask equipped with a magnetic stirrer, a 500 ml addition funnel and a nitrogen inlet tube. The flask was placed in an
ice bath and the contents kept at 0 -5° during dropwise addition of
freshly distilled methyl vinyl ketone (232.5 g, 3.32 moles). The solution
was stirred rapidly and a nitrogen atmosphere maintained throughout the
reaction. The ice bath was removed at the end of the addition and
stirring was continued for 37 hr.

A hydrochloric acid solution (3.6 l, 15%) was added and the re-
action mixture stirred for 54 hr. at room temperature. The reaction
mixture was maintained at 90° for an additional 24 hr. After cooling
the mixture was extracted 4 times with 600 ml of ether. The ether
extracts were combined and washed 4 times with 5% sodium bicarbonate.
The solution was dried over anhydrous magnesium sulfate and the ether
removed in vacuo. Distillation gave 216 g (54% based on enamine) of
very pure 4,4-dimethylcyclohex-2-enone: bp 70° (20 mm), Lit. (67)
76° (21 mm); nmr and ir are identical to Lit. (67); nmr (CCl4)δ1.17
(s, 6H), 1.84 (t, 2H), 2.35 (t, 2H), 5.69 (d, 1H), 6.57 (d, 1H); ir
(neat) 802, 1120, 1202, 1234, 1325, 1376, 1420, 1470, 1680 2970 cm⁻¹.

5,5-Dimethylbicyclo[4.1.0]heptan-2-one

Using the method of Corey and Chaykovsky (68), trimethyloxosulfonium
iodide (25.37 g, 0.115 mole) and sodium hydride (5.54 g, 0.115 mole)
were placed in a 250 ml three-necked flask equipped with a mechanical
stirrer, dropping funnel, nitrogen inlet tube and glycerine bubbler.
The system was flushed with nitrogen and dimethylsulfoxide (125 ml;
distilled from calcium hydride) was added slowly with evolution of
hydrogen. Then 4,4-dimethylcyclohex-2-enone (13.0 g, 0.105 mole) dis-
solved in dimethylsulfoxide (25 ml) was added slowly with some cooling
in an ice bath. The solution was stirred at room temperature for 2 hr. and at 50° for an additional 2 hr.

The solution was added to water (400 ml) and extracted 3 times with ether (200 ml). The combined ether extracts were washed 2 times with water (200 ml) and then dried over anhydrous magnesium sulfate. The ether was removed in vacuo and the oil vacuum distilled using a short path distillation apparatus. Two fractions of 5,5-dimethylbicyclo-[4.1.0]heptan-2-one were collected weighing a total of 10.18 g (77%); bp 45° (1.2 mm); ir (CCl₄) 804, 833, 883, 906, 943, 1015, 1225, 1348, 1475, 1685 and 2925 cm⁻¹; nmr (CCl₄) δ 1.12 (s, 6H), 0.87-2.25 (m, 8H); uv max (95% EtOH) 272 nm (ε, 31) and end absorption at 210 nm (ε, 2,980); mass spectrum, m/e (relative intensity) 138 (parent, 16), 123 (17), 109 (14), 97 (19), 96 (45), 95 (59), 83 (31), 82 (26), 81 (50), 70 (18), 69 (20), 68 (28), 67 (52), 55 (100), 53 (21), 41 (60), 39 (53).

Found: C, 78.08; H, 10.14.

5,5-Dimethylbicyclo[4.1.0]hept-2-enyl acetate

A 250 ml flask was charged with 5,5-dimethylbicyclo[4.1.0]heptan-2-one (21.3 g, 0.154 mole), isopropenyl acetate (115 ml) and p-toluenesulfonic acid (1.5 g). The mixture was refluxed for 8 hr. using a glass helices-packed Vigreux column (69). The acetone and excess isopropenyl acetate was removed in vacuo and the dark oil was added to benzene (300 ml). The benzene solution was extracted with 10% sodium bicarbonate (175 ml) and washed 2 times with water. After drying over anhydrous magnesium sulfate, the benzene was removed in vacuo, and the
black oil vacuum distilled to give 24.0 g (87%) of pure 5,5-dimethylbicyclo[4.1.0]hept-2-enyl acetate: bp 42° (0.03 mm); ir (neat) 906, 1040, 1102, 1133, 1183, 1225, 1367, 1462, 1683, 1760, 2873 and 2964 cm⁻¹; nmr (CCl₄) δ 0.55-1.30 (m, 4H), 1.05 (s, 3H), 1.10 (s, 3H), 1.70 (d, 2H), 2.06 (s, 3H), 4.88 (m, 1H); uv max (95% EtOH) end absorption, ε = 6,610 at 210 nm; mass spectrum, 180 (8), 138 (89), 123 (65), 95 (97), 43 (100).

Anal. Calcd. for C₁₁H₁₆O₂: C, 73.30; H, 8.95. Found: C, 72.97; H, 9.06

3-Bromo-5,5-dimethylbicyclo[4.1.0]heptan-2-one

The 5,5-dimethylbicyclo[4.1.0]hept-2-enyl acetate (24.0 g, 0.134 mole) was dissolved in carbon tetrachloride (125 ml) in a 1 liter three-neck flask equipped with a condenser and addition funnel. Then bromine (21.4 g, 0.134 mole) dissolved in carbon tetrachloride (280 ml) was added dropwise with stirring and cooling in an ice bath. The excess carbon tetrachloride and acetyl bromide were removed in vacuo giving 29.0 g (100%) of 3-bromo-5,5-dimethylbicyclo[4.1.0]heptan-2-one: ir (CCl₄) 887, 1220, 1372, 1473, 1702 and 2970 cm⁻¹; nmr (CCl₄) δ 0.85-1.55 (m, 4H), 1.17 (s, 3H), 1.20 (s, 3H), 1.75-2.40 (m, 3H). The bromo-ketone was not stable enough to distill or purify by vpc.

5,5-Dimethylbicyclo[4.1.0]hept-3-en-2-one

The 3-bromo-5,5-dimethylbicyclo[4.1.0]heptan-2-one (29.0 g, 0.134 mole) was added to a mixture of lithium bromide (29.0 g, 0.334 mole) and lithium carbonate (24.7 g, 0.334 mole) in N,N-dimethylformamide (300 ml) and refluxed for 15 hr. under nitrogen (70).
The cooled mixture was added to benzene (600 ml) and water (150 ml) and separated after settling was complete. The benzene layer was washed 6 times with water (150 ml) and then dried over anhydrous magnesium sulfate. After removing the benzene, the dark oil was vacuum distilled to give 10.9 g (60% based on enol acetate) of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one: ir (CCl₄) 888, 1062, 1378, 1470, 1666 and 2950 cm⁻¹ (Figure 9, page 33); nmr (CCl₄) δ 1.20 (s, 3H, methyl), 1.28 (s, 3H, methyl), 0.8 (m, 1H, cyclopropyl), 1.1-1.4 (m, 1H, cyclopropyl), 1.4-1.8 (m, 2H, cyclopropyl), 5.51 (q, 1H, α-vinyl), 6.16 (q, 1H, β-vinyl) (Figure 8, page 31); uv max (95% ethanol) 220 nm (ε, 9,700); mass spectrum m/e (relative intensity), 136 (molecular ion, 21), 121 (42), 108 (28) 93 (100), 91 (47), 80 (28) 77 (57).


Photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in t-butyl alcohol

A solution of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (1.39 g, 0.010 mole) in 265 ml t-butyl alcohol (0.038 M) was irradiated for 25.5 hr. in a quartz immersion well with a Hanovia 550 watt lamp. The solvent was removed and the product mixture was chromatographed on silica gel (Baker) using benzene as the eluent. Eleven fractions of 200 ml were collected and analyzed by vpc. The first two fractions contained two unknown solid compounds, and fractions 3-11 contained mostly starting material (1). The two solids were purified by vpc (column B),
and identified as 2,3,5-trimethylphenol (300 mg) and 3,4,5-trimethylphenol (100 mg) by spectral comparison with authentic samples (Aldrich Chemical Co.). 2,3,5-Trimethylphenol had the following data: ir (KBr pellet) (Figure 9, page 33) 839, 968, 1025, 1138, 1300, 1455, 1585, 1625, 2925 and 3330 cm⁻¹; nmr (CDCl₃) (Figure 8, page 31) δ 2.10 (s, 3H), 2.20 (s, 6H), 6.39 (s, 1H), 6.57 (s, 1H) and a broad peak at 4.55 (1H) which exchanged in deuterium oxide; mass spectrum, m/e (relative intensity), 136 (parent, 82), 121 (100) and 91 (21); uv max (50% EtOH) 201 nm (ε, 42,900) and 282 nm (ε, 1,230); mp 87-90°, Lit. (51) 95-96°, Aldrich sample 94-96°. 3,4,5-Trimethylphenol was characterized by the following data: ir (KBr pellet) (Figure 9, page 33) 700, 845, 1025, 1140, 1305, 1475, 1600, 2920 and 3250 cm⁻¹; nmr (CDCl₃) (Figure 8, page 31) δ 2.05 (s, 3H), 2.16 (s, 6H), 6.48 (s, 2H) and a broad peak at 5.50 (1H) which exchanged in deuterium oxide; mass spectrum, m/e (relative intensity), 136 (parent, 66), 135 (29), 121 (100), 91 (16); uv max (50% EtOH) 198 nm (ε, 52,000) and 282 nm (ε, 1,550); mp 105-107°, Lit. (52) 109.3-109.6°, Aldrich 108-109°.

**Photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in isopropyl alcohol**

A solution of the bicyclic enone (1.00 g, 7.35 X 10⁻³ mole) in 100 ml dry isopropyl alcohol (7.35 X 10⁻² M) in a quartz tube was irradiated for 52 hr. in a Rayonet reactor with 2537 A lamps. The solvent was removed and the product mixture chromatographed on Silicar (Mallinckrodt). The column was eluted with benzene and the fractions
were analyzed by vpc. The fractions contained 160 mg of 2,3,5-tri-
methylphenol and 105 mg of 3,4,5-trimethylphenol. Elution with
chloroform gave other material which was not characterized.

**Photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in methanol**

A solution of the bicyclic enone (0.85 g, 6.25 x 10^-3 mole) in
100 ml methanol was irradiated for 49.5 hr. in a quartz tube with a
Rayonet reactor equipped with 2537 A lamps. The methanol was evaporated
and the product mixture chromatographed on Silicar (Mallinckrodt). The
fractions were analyzed by vpc and 150 mg of 2,3,5-trimethylphenol and
170 mg of 3,4,5-trimethylphenol were found in the first two fractions.
Also, elution with chloroform gave material which was not characterized.

**Photolysis of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one in cyclohexane**

A solution of the bicyclic enone (0.635 g, 4.67 x 10^-3 mole) in
100 ml cyclohexane in a quartz tube was irradiated for 52 hr. in a
Rayonet reactor with 2537 A lamps. The excess cyclohexane was evaporated
and the yellow oil was chromatographed on Silicar (Mallinckrodt). The
column was eluted with benzene and 19 fractions of 100 ml were collected.
Many new peaks were present when the fractions were analyzed by vpc,
but only three were present in large enough quantity to isolate and
characterize. Fraction 1 contained 60 mg of an oil with a molecular
ion at m/e 166 (53%) and fragment ions at 83 (53%), 82 (100%), 65 (49%)
and 53 (58%). The nmr spectrum had two broad peaks at 81.05 and 1.70
and nothing further downfield. The compound was tentatively identified
as bicyclohexyl (100).
Fractions 3-5 contained 80 mg of an oil which had a molecular ion at m/e 202 (40%) which was correct for C\textsubscript{15}H\textsubscript{22}. Fragment ions were also present at 187 (32%), 119 (60%), 105 (100%) and 91 (58%). The ir spectrum had no strong bands in the carbonyl region and nothing in the hydroxyl stretching region. The nmr spectrum was very weak and the region below 5.50 may not have been scanned for presence of vinyl protons. One possible structure that fits the meager data is 2-(cyclohexylidene)-5,5-dimethylbicyclo[4.1.0]hept-3-ene (101).

The third product (100 mg, fr. 6-8) had a molecular ion at m/e 220 (28%) which was correct for C\textsubscript{15}H\textsubscript{24}O. Fragment ions were present at 137 (100%), 110 (26%), 109 (25%), 95 (77%), 67 (29%) and 55 (60%). The ir spectrum had a carbonyl band at 1692 cm\textsuperscript{-1} (CCl\textsubscript{4}) which was almost the same as 5,5-dimethylbicyclo[4.1.0]heptan-2-one, 1685 cm\textsuperscript{-1} (CCl\textsubscript{4}). There were no peaks below 2.20 in the nmr spectrum. The tentative structure for the compound is 4-cyclohexyl-5,5-dimethylbicyclo[4.1.0]heptan-2-one (102).

**3-Deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one**

A solution of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (2.50 g, 0.020 mole) and sodium methoxide (5.0 g) in deuterium oxide (30 ml) and deuteriomethanol (30 ml) was refluxed for 5 hr. The mixture was filtered, extracted 3 times with carbon tetrachloride and dried over anhydrous magnesium sulfate. The solvent was removed in vacuo and oil vacuum distilled to give 3-deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (1.94 g, 77%). The quartet at 5.51 ppm disappeared completely in the
nmr (Figure 10, page 37) and the mass spectrum had a molecular ion at 
m/e 137 (10.3% D₀, 80.5% D₁, 8.2% D₂).

**Photolysis of 3-deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one**

in methanol

A solution of the deuterated enone (1.12 g, 8.18 X 10⁻³ mole) in
100 ml methanol (8.18 X 10⁻² M) was irradiated through quartz for 52.5
hr. in a Rayonet reactor with 2537 A lamps. The solvent was evaporated
and the residue chromatographed on a Silicar (Mallinckrodt) column with
benzene. The fractions were analyzed by vpc and fractions 4 and 6 con­
tained 2,3,5-trimethylphenol and 1-deuterio-3,4,5-trimethylphenol
respectively. Nmr spectra are in Figure 10, page 37.

**1-Deuterio-5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one**

A solution of 4,4-dimethylcyclohex-2-enone (5.03 g, 0.040 mole)
and sodium bicarbonate (4.25 g) in deuterium oxide (50 ml) was refluxed
for 12 hr. and stirred an additional 16 hr. at room temperature. The
solution was extracted 3 times with carbon tetrachloride and the combined
extracts were dried over anhydrous magnesium sulfate. Evaporation of
the solvent gave 2,6,6-trideuterio-4,4-dimethylcyclohex-2-enone (4.21 g,
84%). The rest of the synthesis was the same as for the undeuterated
isomer. The mass spectrum showed 22.4% D₀, 52.2% D₁, 19.0% D₂ and 5.0%
D₃ in the final product.
Photolysis of 1-deuterio-5,5-dimethylbicyclo 4.1.0 hept-3-en-2-one in methanol

A solution of the deuterated enone (0.30 g, 2.19 X 10^-3 mole) in 100 ml methanol (2.19 X 10^-2 M) was irradiated through quartz for 66 hr in a Rayonet reactor with 2537 Å lamps. The methanol was evaporated and the products chromatographed on Silicar (Mallinckrodt). The fractions were analyzed by vpc and fractions 4 and 6 contained 6-deuterio-2,3,5-trimethylphenol and 1-deuterio-3,4,5-trimethylphenol respectively. Nmr spectra are in Figure 11, page 39.

7,7-dideuterio-5,5-dimethylbicyclo[4,1.0]hept-3-en-2-one

The synthesis of the deuterated isomer was identical to the synthesis of the parent compound except for the first step. The cyclopropyl ring is formed using trimethyloxosulfonium iodide-D9 (71). The mass spectrum indicated 10.0% D0, 18.1% D1, 57.2% D2, 8.8% D3 and 5.0% D4 in the final product. The nmr is shown in Figure 12, page 41.

Photolysis of 7,7-dideuterio-5,5-dimethylbicyclo[4,1.0]hept-en-2-one in methanol

A solution of the deuterated enone (0.493 g, 3.57 X 10^-3 mole) in 100 ml methanol (3.57 X 10^-2 M) was irradiated through quartz for 45 hr in a Rayonet reactor with 2536 Å lamps. The solvent was evaporated and the product mixture chromatographed on Silicar (Mallinckrodt). The fractions were analyzed by vpc and fractions 4 and 6 were identified as 2,3-dimethyl-5-dideuteriophenol or 2,5-dimethyl-3-dideuteriophenol respectively and 3,4-dimethyl-5-dideuteriophenol (see Figure 12, page 41).
Experimental for the Photolysis of 3,4,4-Trimethylcyclohexa-2,5-dienone

**3,4,4-trimethylcyclohexanone**

Using the technique of House et al. (72), methyllithium (256 ml, 0.40 mole) was added to dry ether (400 ml) in a 2 l three-necked flask in a nitrogen glove bag. Then dry cuprous iodide (73) (38.0 g, 0.20 mole) was added slowly so that the reaction didn't become too exothermic. The flask was stoppered and transferred from the glove bag to the hood. After equipping the flask with a condenser, addition funnel and nitrogen inlet, 4,4-dimethylcyclohex-2-enone (12.4 g, 0.10 mole) in dry ether (500 ml) was added dropwise and with stirring over a 2 hr. period.

After stirring an additional 30 minutes, the solution was added to 5% ammonium chloride (1200 ml, pH8). The ether layer was separated and combined with the 2 ether washes of the aqueous phase. The solution was dried over anhydrous magnesium sulfate and the ether evaporated in vacuo. The yellow oil was vacuum distilled to give 3,4,4-trimethylcyclohexanone (11.33 g, 81%): nmr (CDCl₃) 0.90 (d, 3H), 1.00 (s, 3H), 1.03 (s, 3H), 1.4-1.9 (m, 3H), 2.0-2.4 (m, 4H); ir (neat) 1015, 1149, 1248, 1286, 1350, 1371, 1380, 1395, 1423, 1456, 1475, 1720 and 2975 cm⁻¹, Lit (74) 1724 cm⁻¹.

**2,6-Dibromo-3,4,4-trimethylcyclohexanone**

A solution of 3,4,4-trimethylcyclohexanone (11.33 g, 0.0808 mole) was added to glacial acetic acid (35 ml) in a 500 ml flask equipped with a dropping funnel and reflux condenser. Then bromine (25.9 g, 0.162 mole) in a glacial acetic acid (35 ml) was added dropwise over a
2 hr. period with stirring at room temperature (75). The solution was added to water (1000 ml) and extracted 2 times with ether (500 ml). The ether was washed with water and dried over anhydrous magnesium sulfate. Evaporation of the ether gave the dibromoketone (24.1 g) which was used without further purification: \textit{ir} (neat) 1300, 1712 and 2975 cm\(^{-1}\).

\textbf{3,4,4-trimethylcyclohexa-2,5-dienone}

The 2,6-dibromo-3,4,4-trimethylcyclohexanone (24.1 g, 0.0808 mole) was added to a mixture of lithium bromide (20.5 g, 0.239 mole) and lithium carbonate (17.7 g, 0.239 mole) in N,N-dimethylformamide (240 ml) and refluxed for 18 hr. The cooled solution was added to benzene (250 ml) and water (100 ml) and separated after about 15 minutes. The benzene solution was washed 5 times with water (75 ml) and then dried over anhydrous magnesium sulfate. The benzene was removed \textit{in vacuo} and the oil vacuum distilled to give the dienone (4.29 g, 39%) from the dibromoketone: \textit{ir} (neat) (Figure 13, page 45) 881, 1115, 1295, 1380, 1467, 1606, 1625, 1667 and 2980 cm\(^{-1}\), Lit (74) 1661 cm\(^{-1}\); \textit{uv max} (95% EtOH) 237 nm (\(\epsilon\), 13,600), 308 nm (\(\epsilon\), 52); \textit{nmr} (\(\text{CDCl}_3\)) (Figure 14, page 47) \(\delta\) 1.25 (s, 6H), 1.99 (d, 3H), 6.02 (q, 2H), 6.78 (d, 1H); mass spectrum \(\text{m/e}\) (relative intensity), 136 (parent, 73), 121 (59), 108 (45), 93 (100), 91 (56), 79 (59), 77 (58).

\textit{Anal.} Calcd. for C\textsubscript{9}H\textsubscript{12}O: C, 79.37; H, 8.88.

Found: C, 79.11; H, 8.89.
Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol

A solution of the dienone (0.275 g, 2.03 \times 10^{-3} \text{ mole}) in 60 ml methanol (3.38 \times 10^{-2} \text{ M}) in a quartz tube was irradiated for 2.0 hr in a Rayonet reactor with 2537 A lamps. The reaction was monitored by vpc with samples taken at 0, 16, 32, 50, 80 and 120 minutes (Column temp = 200\degree). The starting enone (3.5 min) disappeared rapidly and a new peak with a slightly shorter retention time (2.3 min) appeared. This peak reached a maximum at 50 minutes and decreased steadily after that. Two other new peaks also appeared which grew throughout the reaction (7.0 min and 10.5 min). The reaction mixture was chromatographed on silica gel (Baker) and the two isolated products were identified as 2,3,5-trimethylphenol and 3,4,5-trimethylphenol by comparing their nmr's to known samples (Aldrich Chemical Co.).

Another solution of the enone (0.290 g, 2.13 \times 10^{-3} \text{ moles}) in 60 ml methanol (3.55 \times 10^{-2} \text{ M}) was irradiated for 52 min under the same conditions as above. Silica gel (Baker) chromatography of the product mixture using benzene (1 1) and 50% benzene/chloroform (400 ml) as eluent gave 0.085 g (29\%) of 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one: ir (neat) (Figure 13, page 45) 753, 862, 1290, 1345, 1439, 1606, 1687 and 2960 cm^{-1}; nmr (CCl\textsubscript{4}) (Figure 14, page 47) \delta 0.98-1.20 (m, 1H), 1.15 (s, 3H), 1.23 (s, 3H), 1.7-2.0 (m, 1H), 2.05 (d, 3H), 5.50 (m, 1H); uv max (95\% EtOH), 228 nm (\epsilon, 4,770), 253 nm (\epsilon, 3,790), 315 nm (\epsilon, 241).

Anal. Calcd. for C\textsubscript{9}H\textsubscript{12}O: C, 79.37; H, 8.88.
Found: C, 79.32; H, 8.89.
Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in cyclohexane

A solution of the dienone (0.450 g, 3.31 X 10^{-3} mole) in 100 ml cyclohexane (3.31 X 10^{-2} M) in a vycor tube was irradiated for 3.0 hr in a Rayonet reactor with 2537 A lamps. The reaction was monitored by vpc and 3 peaks with shorter retention times (2.8, 3.5 and 5.1 min) than the starting enone (8.2 min) were observed (Column temp = 175°). The peak at 5.1 min began to decrease after 1 hr and was identified as 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one (104) by its nr spectrum. The other peaks continued to grow. The mixture was chromatographed on silica gel (Baker) and the material with a retention time of 2.8 min was in fraction 7. However, it was not identified. Fraction 11 and 12 contained the material with the 3.5 min retention time. Spectral analysis identified it as 3,6,6-trimethylcyclohexa-2,4-dienone (105): ir (CCl₄) (Figure 13, page 45) 867, 1185, 1220, 1252, 1296, 1320, 1381, 1445, 1470, 1576, 1646, 1662 and 2975 cm⁻¹; nr (CCl₄) (Figure 14, page 47) δ 1.12 (s, 6H), 2.04 (d, 3H), 5.77 (m, 1H), 5.92 (q, 1H), 6.23 (d, 1H); mass spectrum m/e (relative intensity), 136 (parent, 93), 121 (33), 108 (18), 93 (100), 91 (45), 77 (44), 65 (15).


Found: C, 79.47; H, 9.01.

Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in carbon tetrachloride

A 10% solution of the dienone in carbon tetrachloride was irradiated in a low temperature ir cell at room temperature. An 800 watt
Westinghouse lamp was used with 2 quartz lenses and a Corning CS-052 filter (% T < 0.5% at 334 nm and > 60% at 365 nm). The reaction was monitored by IR with spectra being taken at 0, 2, 5, 10, 20 and 60 min. The starting dienone slowly disappeared and new bands began to grow at 1693, 1349 and 866 cm\(^{-1}\) which matched the strongest bands of bicyclic enone 104 in CCl\(_4\). No other new bands appeared during the reaction.

**Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol-ether at -78°**

A solution of the dienone (0.50 g, 3.68 \(\times\) 10\(^{-3}\) mole) in 30 ml methanol-ether (1:2) was irradiated in a quartz tube for 160 min using a Hanovia 450 watt lamp. The solution was cooled to -78° in an unsilvered quartz Dewar using a Dry Ice-acetone mixture.

Column chromatography on silica gel (Baker) gave 3 unknown compounds labeled A, B and C in order of their elution with benzene. Compound A (88 mg) was identified as methyl 3,6-dimethylhepta-3(Z),5-dienoate (106) by its spectra: IR (neat) (Figure 28, page 111) 758, 847, 1010, 1175, 1263, 1440, 1622, 1742, 2925, 2980 and 3025 cm\(^{-1}\); NMR (CCl\(_4\)) (Figure 15, page 51) \(\delta\) 1.73 (s, 3H), 1.82 (m, 6H), 3.06 (s, 2H), 3.62 (s, 3H), 5.97 (m, 2H); Mass spectrum, m/e (relative intensity), 168 (parent, 53), 109 (100), 93 (45), 91 (36), 67 (76); UV max (95% EtOH) 244 nm (\(\epsilon\), 21,500).

**Anal.** Calcd. for C\(_{10}\)H\(_{16}\)O\(_2\): C, 71.39; H, 9.59.

**Found:** C, 71.25; H, 9.37.
Figure 28. Infrared spectra

Top: methyl 3,6-dimethylhepta-3(Z),5-dienoate

Middle: 2-methoxy-3,5,5-trimethylcyclohex-3-enone

Bottom: 2-methoxy-3,5,5-trimethylcyclohex-2-enone
Compound B (85 mg) was identified tentatively as 2-methoxy-3,5,5-trimethylcyclohex-3-enone (107) on the basis of the following spectral data: ir (neat) (Figure 28, page 111) 790, 1072, 1120, 1198, 1367, 1450, 1678, 1732 and 2967 cm\(^{-1}\); nmr (CCI\(_4\)) (Figure 29, page 114) \(\delta 1.02\) (s, 3H), 1.08 (s, 3H), 1.75 (d, 3H), 2.19 and 2.47 (AB quartet, \(J=12\), 2H); mass spectrum, \(m/e\) (relative intensity), 168 (parent, 35), 153 (12), 136 (67), 121 (100), 112 (54).

Compound C (165 mg) was identified as 2-methoxy-3,5,5-trimethylcyclohex-2-enone (108) by the following spectral data: ir (neat) (Figure 28, page 111) 1005, 1040, 1120, 1133, 1157, 1210, 1318, 1380, 1640, 1680 and 2970 cm\(^{-1}\); nmr (CCI\(_4\)) (Figure 29, page 114) \(\delta 1.03\) (s, 6H), 1.82 (d, 3H), 2.19 (s, 4H), 3.60 (s, 3H); nmr (benzene) (Figure 29, page 114) \(\delta 0.72\) (s, 6H), 1.62 (d, 3H), 1.69 (m, 2H), 2.07 (s, 2H), 3.65 (s, 3H); mass spectrum \(m/e\) (relative intensity), 168 (parent, 66), 153 (19), 112 (41), 84 (44), 82 (23), 69 (100); uv max (95% EtOH) 247 nm (\(\epsilon\), 9,620).

**Anal. Calcd. for C\(_{10}\)H\(_{16}\)O\(_2\): C, 71.39; H, 9.59.**

Found: C, 71.13; H, 9.63.

**Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in ether-furan at -78°**

A solution of the dienone (0.260 g, 1.91 \(\times\) 10\(^{-3}\) mole) in 60 ml of ether-furan (4:1) was irradiated for 95 min in a Pyrex tube with a 450 watt Hanovia lamp in a quartz immersion well. The solution was cooled to -78° during the reaction using a Dry Ice-acetone mixture in an unsilvered quartz Dewar. Evaporation of the solvent gave 0.410 g of
Figure 29. Nuclear magnetic resonance spectra

Top: 2-methoxy-3,5,5-trimethylcyclohex-3-enone

Middle: 2-methoxy-3,5,5-trimethylcyclohex-2-enone (CCl₄)

Bottom: 2-methoxy-3,5,5-trimethylcyclohex-2-enone (Benzene)
material which was chromatographed on silica gel (Baker). Fractions 6-10 (200 ml benzene / fraction) contained 130 mg of pure 11-oxa-7,7,9-trimethyltricyclo[4.3.1.1^{2,5}]undeca-3,8-dien-10-one (109): ir (CCl₄) (Figure 15, page 51) 871, 970, 1162, 1181, 1317, 1362, 1444, 1555, 1720, 1737 and 2970 cm⁻¹; nmr (CCl₄) (Figure 16, page 53) δ 0.98 (s, 3H), 1.24 (s, 3H), 1.74 (d, 3H), 1.96 (m, 1H), 2.43 (t, 1H), 4.61 (q, 1H), 5.26 (t, 1H), 6.25 (distorted AB, 2H); mass spectrum, m/e (relative intensity), 204 (parent, 100), 189 (55), 161 (43), 136 (35) and 121 (43); uv max (95% EtOH) 284 nm (ε, 128) and end absorption at 200 nm (ε, 1,800).

Anal. Calcd. for C₁₃H₁₆O₂: C, 76.44; H, 7.90.
Found: C, 76.28; H, 7.78.

**Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone at -190°**

A sample of the dienone (neat) was irradiated between salt plates in the low temperature cell at -190° with an 800 watt lamp (2 lenses). The reaction was monitored by ir spectroscopy, and spectra were recorded at 0, 1, 2, 4, 10, 30, 60 and 180 min and during the warmup period. New carbonyl bands were observed at 2135, 2108 and 1715 cm⁻¹. The band at 2108 cm⁻¹ grew throughout the 3 hour irradiation. A trace of carbon monoxide (2135 cm⁻¹) was first observed at the 4 min mark, but it remained at a low level during the reaction. A band at 1715 cm⁻¹ appeared at the 1 hour mark and continued to grow. It was also thermally stable. Both the 2135 and 2108 cm⁻¹ disappeared during warmup.
Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol at -190°

A 10% solution of the dienone in methanol was irradiated in the low temperature solution cell at -190° with an 800 watt lamp (2 lenses). The reaction was monitored by taking ir spectra after 1, 10, 20, 30, 40 and 60 min and during warmup. The major product had a carbonyl band at 1702 cm⁻¹ that grew during the entire reaction. A trace of a ketene (2110 cm⁻¹) and carbon monoxide (2140 cm⁻¹) were detected also. The band at 1702 cm⁻¹ was the only thermally stable product.

Photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in carbon tetrachloride at -190°

A 10% solution of the dienone in carbon tetrachloride was irradiated with an 800 watt lamp (2 lenses) in the low temperature solution cell at -190°. Ir spectra were taken after 2, 5, 10, 20, 40, 60, 80 and 120 min irradiation and during warmup. After 2 min a weak band was visible at 1810 cm⁻¹, but it remained very weak throughout the irradiation. The major products were a ketene (2112 cm⁻¹) and carbon monoxide (2136 cm⁻¹) which first appeared at the 5 min mark and increased steadily during the rest of the reaction. None of the new bands remained after warmup.

Attempted preparative photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol/2-methyltetrahydrofuran at -190°

A solution of the dienone (100 mg, 7.35 X 10⁻⁴ mole) in 10 ml of a methanol-2-methyltetrahydrofuran (2-MeTHF) glass (7:3) at -190° was irradiated for 2.25 hr in a quartz tube with an 800 watt lamp (1 lens).
The glass was formed in liquid nitrogen in an unsilvered quartz Dewar. No reaction was detectable by nmr.

**Attempted preparative photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in ether-isopentane at -190°**

A sample of the dienone (100 mg, $7.35 \times 10^{-4}$ mole) in 7 ml ether-isopentane (2:1) was irradiated with a 450 watt Hanovia lamp in an all quartz system at -190°. The nmr spectrum showed no reaction after 9 hr.

**Attempted preparative photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol-ether at -190°**

A glass (-190°) containing dienone (100 mg), ether (500 mg) and methanol (200 mg) was irradiated in a quartz nmr tube with an 800 watt lamp (1 lens). The nmr spectrum showed no change after 8 hr.

**Preparative photolysis of 3,4,4-trimethylcyclohexa-2,5-dienone in methanol at -120°**

A solution of the dienone (115 mg) in methanol was irradiated in a quartz nmr tube at -120° (ethanol-liquid nitrogen slurry) with an 800 watt lamp (1 lens). The nmr spectrum showed a mixture of products, two of which were isolated by vpc. They were identified by their mass spectra and ir spectra as the previously reported 2-methoxy-3,5,5-trimethylcyclohex-3-enone (107) and 2-methoxy-3,5,5-trimethylcyclohex-2-enone (108).
Experimental for the Irradiation $4,6,6$-Trimethylbicyclo-$[3.1.0]$hex-3-en-2-one

Photolysis of $4,6,6$-trimethylbicyclo$[3.1.0]$hex-3-en-2-one in ether-furan at $-78^\circ$C

A solution of the bicyclic enone (38 mg, $2.79 \times 10^{-4}$ mole) in 10 ml of ether-furan (4:1) was irradiated in a Pyrex tube for 4 hr at $-78^\circ$ with a 450 watt Hanovia lamp. The solvent was evaporated leaving 56 mg product whose nmr spectrum (HA-100) was identical to that of furan adduct 109, which was obtained from the photolysis of $3,4,4$-trimethylcyclohexa-2,5-dienone in furan-ether (Figure 16, page 53).

Photolysis of $4,6,6$-trimethylbicyclo$[3.1.0]$hex-3-en-2-one at $-190^\circ$C

Neat bicyclic enone was irradiated between sodium chloride plates at $-190^\circ$ with an 800 watt lamp (1 lens). The reaction was monitored by ir and spectra were recorded after 0, 1, 2, 4 and 8 min and during warmup (Figure 17, page 56). Three primary products were formed with carbonyl bands at 2107, 1810 and 1801 cm$^{-1}$. The 1810 band increased very quickly and had started to decrease by the second minute. At the end of 8 min it was almost completely gone. The band at 2107 cm$^{-1}$ also grew rapidly the first 4 min and decreased slightly at the 8 min mark. The band at 1801 cm$^{-1}$ grew slowly and wasn't visible until the 4 min mark, after the 1810 cm$^{-1}$ band had decreased greatly. The bands at 2107 and 1810 cm$^{-1}$ were thermally unstable, while the band at 1801 cm$^{-1}$ remained during warmup.
Experimental for the Photolysis of 4,4-Dimethylcyclohexa-2,5-dienone

4,4-Dimethylcyclohexa-1,5-dienyl acetate

A mixture of 4,4-dimethylcyclohexa-2-enone (12.4 g, 0.10 mole), isopropenyl acetate (75 ml, 0.75 mole) and p-toluenesulfonic acid (1.0 g) was refluxed for 10 hr in a 250 ml flask equipped with a glass helices-packed Vigreaux column. At the end of 10 hr the solution was distilled for a short time to remove the acetone and other low boiling materials. The remaining isopropenyl acetate was removed in vacuo and the dark oil added to benzene (200 ml). The benzene solution was extracted 2 times with 10% sodium bicarbonate (100 ml) and washed 2 times with water (100 ml). The solution was dried over anhydrous magnesium sulfate, and the benzene evaporated in vacuo. Vacuum distillation of the black oil gave 13.1 g (79%) 4,4-dimethylcyclohexa-1,5-dienyl acetate: ir (neat) 743, 914, 935, 1012, 1042, 1146, 1164, 1189, 1225, 1374, 1471, 1668, 1763, 2878 and 2970 cm⁻¹; nmr (CCl₄) δ 1.03 (s, 6H), 2.03 (s, 3H), 2.18 (d, 2H), 5.20 (m, 1H), 5.50 (d, 2H); mass spectrum, m/e (relative intensity), 166 (parent, 9), 125 (28), 109 (100), 43 (37); uv max (95% EtOH) 257 nm (ε, 3,230).

Anal. Calcd. for C₁₀H₁₄O: C, 72.26; H, 8.49.

Found: C, 72.14; H, 8.35.

6-Bromo-4,4-dimethylcyclohex-2-enone

The dienyl acetate (13.1 g, 0.079 mole) was dissolved in carbon tetrachloride (150 ml). Then bromine (12.65 g, 0.079 mole) in carbon
tetrahydrofuran (60 ml) was added dropwise with stirring and cooling in an ice bath. The solvent and acetyl bromide were evaporated in vacuo to give 6-bromo-4,4-dimethylcyclohex-2-enone (16.05 g, 100%): ir (CCl₄) 1688 cm⁻¹, Lit. (76) 1690 cm⁻¹. The bromoketone was used immediately without any further characterization due to its instability.

4,4-Dimethylcyclohexa-2,5-dienone

The bromoketone (138) (16.05 g, 0.079 mole) was added to a mixture of lithium carbonate (14.0 g, 0.19 mole), lithium bromide (16.5 g, 0.19 mole) and N,N-dimethylformamide (200 ml) and refluxed for 16 hr. After cooling, the mixture was added to benzene (400 ml) and water (150 ml) and allowed to settle for 15 min. The aqueous layer was drained off and the dark benzene solution washed 5 times with water (100 ml). The solution was dried over anhydrous magnesium sulfate and the benzene removed in vacuo. The black oil was vacuum distilled to give 4,4-dimethylcyclohexa-2,5-dienone (3.92 g, 40.7% from the dienyl acetate): ir (neat) (Figure 30, page 126) 856, 959, 1100, 1251, 1398, 1468, 1629, 1662 and 2965 cm⁻¹, Lit. (77) 859, 962, 1104, 1254, 1402, 1471, 1635, 1668, 2960; uv max (95% EtOH) 235 nm (ε, 14,200), 307 nm (ε, 40); nmr (CCl₄) (Figure 18, page 62) δ 1.25 (s, 6H), 6.03 (d, 2H), 6.78 (d, 2H), Lit (76) δ 1.35 (s, 6H), 6.02 (d, 2H), 6.82 (d, 2H).

Photolysis of 4,4-dimethylcyclohexa-2,5-dienone in cyclohexane

A solution of the dienone (0.30 g, 2.46 X 10⁻³ mole) in ml cyclohexane (2.46 X 10⁻² M) was irradiated in a quartz tube for 8 hr.
in a Rayonet reactor with 2537 A lamps. The reaction was followed by
vpc which showed 2 new peaks. One began to decrease after 2 hr and at
the end of 8 hr very little remained. This compound was identified
by ir as 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) which was
reported by Srinivasan et al., (30) under the same conditions: ir
(CCl₄) 1700 cm⁻¹, Lit (30) 1710 cm⁻¹. The final product was 6,6-
dimethylcyclohexa-2,4-dienone (64) which was thermally unstable.
The ir spectrum of the sample collected by vpc had a weak carbonyl band
at 1669 cm⁻¹ which may have been from the monomer (77) 1670 cm⁻¹, (78)
1665 cm⁻¹ and strong bands at 1691 and 1726 cm⁻¹ which may have been
from a dimer.

Photolysis of 4,4-dimethylcyclohexa-2,5-dienone in methanol

A solution of the dienone (0.30 g, 2.46 X 10⁻³ mole) in 100 ml
methanol (2.46 X 10⁻² M) was irradiated for 160 min in a vycor tube
in a Rayonet reactor with 2537 A lamps. The reaction was followed by
vpc and 6,6-dimethylbicyclo[3.1.0]hex-3-en-2-one (63) was an initial
product, but decreased after continued irradiation. Four final products
were indicated by vpc. The reaction mixture was chromatographed on
silica gel (Baker) with benzene. The first compound off the column was
methyl 6-methylhepta-3,5-dienoate (112) which was identified by comparing
its nmr spectrum with that of a pure sample (see next paragraph). The
second product was 2,3-dimethylphenol (65) which was identified by its
nmr spectrum: (CCl₄) δ 2.10 (s, 3H), 2.25 (s, 3H), 5.33 (broad, 1H),
6.35-7.00 (m, 3H). The third compound was 3,4-dimethylphenol (66) which
was also identified by nmr: (CCl₄) δ 2.10 (s, 6H), 6.23 (broad, 1H),
6.33-6.97 (m, 3H). The last product was not identified.

**Photolysis of 4,4-dimethylcyclohexa-2,5-dienone in methanol-ether at -78°**

A solution of the dienone (0.30 g, 2.46 x 10^{-3} mole) in 10 ml methanol-ether (1:2) was irradiated in a quartz tube for 9 hr. at -78° with an 800 watt lamp (2 lenses). The reaction was monitored by vpc and only one product besides 6,6-dimethylbicyclo[3.1.0]hexa-3-en-2-one (63) was seen. It was identified as methyl 6-methylhepta-3,5-dienoate (112) on the basis of its spectra: ir (neat) Figure 15, page 51) 763, 789, 960, 987, 1017, 1163, 1197, 1250, 1320, 1331, 1380, 1437, 1660, 1745, 2920 and 2960 cm^{-1}; nmr (CCl₄) (Figure 18, page 62) 1.75 and 1.81 (broad singlets, 6H), 3.10 (d, 2H), 3.60 (s, 3H), 5.15-6.45 (m, 3H); mass spectrum, m/e (relative intensity), 154 (parent, 33), 95 (100), 93 (26), 80 (18), 78 (19), 68 (27) and 56 (27); uv max (95% EtOH) 238 nm (ε, 20,700), Lit. (54) 238 nm (ε, 22,300).

**Photolysis of 4,4-dimethylcyclohexa-2,5-dienone in methanol-furan at -78°**

A solution of the dienone (0.25 g, 2.05 x 10^{-3} mole) in 60 ml methanol-furan (4:1) was irradiated in a quartz tube at -78° with a 450 watt Hanovia lamp. The 345 mg of product was chromatographed on silica gel (Baker) and the fractions were analyzed by vpc. Fractions 5-11 (200 ml benzene/fraction) contained a furan adduct (113) plus some impurities. The impure adduct was sublimed (50°/0.03 mm) to give white crystals of 11-oxa-7,7-dimethyltricyclo[4.3.1.1^{2,5}]undeca-3,8-dien-10-one (113): mp 113-115; ir (CCl₄) (Figure 15, page 51) 864, 883, 968, 979, 993, 1044, 1123, 1194, 1319, 1364, 1692 (w), 1734 (s) and 2970 cm^{-1};
nmr (CCl₄) (Figure 16, page 53) 1.05 (s, 3H), 1.30 (s, 3H), 2.17 (m, 1H), 2.80 (m 1H), 4.68 (q, 1H), 4.99 (q, 1H), 5.64 (q, 1H), 5.69 (s, 1H), 6.30 (distorted AB, 2H); mass spectrum, m/e (relative intensity), 190 (parent, 100), 175 (34), 147 (58), 122 (66), 107 (62), 79 (52), 77 (39) and 68 (36); uv max (95% EtOH) 275 nm (ε, 113) and end absorption 200 nm (ε, 7,050).

Found: C, 75.71; H, 7.33.

Photolysis of 4,4-dimethylcyclohexa-2,5-dienone at -190°

Neat dienone was irradiated between salt plates in the low temperature ir cell at -190° with an 800 watt lamp (2 lenses). The reaction was monitored by ir with spectra being recorded after 0, 1, 3, 15, 30, 60, 180, 240 and 360 min and during warmup (Figure 17, page 56). New bands appeared at 1692 cm⁻¹ after 1 min, at 2107 and 1815 cm⁻¹ after 3 min and at 1714 and 1801 cm⁻¹ after 6 min. After 30 min irradiation the band at 1692 cm⁻¹ began to decrease, but the bands at 2107, 1801 and 1714 cm⁻¹ were still increasing after 3 hr. The band at 1815 cm⁻¹ was lost under the 1801 cm⁻¹ band. The cell was warmed to room temperature and only the band at 2107 cm⁻¹ disappeared. The sample was irradiated for another 3 hr and the bands at 2107, 1801 and 1714 cm⁻¹ continued to grow. The bands at 1801 and 1714 cm⁻¹ again were thermally stable with only the 2107 cm⁻¹ disappearing. The band at 1801 cm⁻¹ was not affected by treatment with methanol even after 6 hr.

A 300 mg sample of the dienone was irradiated in a quartz tube under the same conditions as above, but after 8 hr there was no detectable difference in the nmr.
Experimental for the Photolysis of 6,6-Dimethyltricyclo-[5.1.0.0^3,5] octane-2-one

6,6-Dimethyltricyclo[5.1.0.0^3,5]octan-2-one

A 250 ml three-necked flask equipped with an addition funnel, mechanical stirrer and condenser was charged with sodium hydride (1.05 g, 0.022 mole) and trimethyloxosulfonium iodide (4.88 g, 0.022 mole). Then dry dimethylsulfoxide (25 ml; distilled from calcium hydride) was added slowly under nitrogen with stirring and cooling. After warming to room temperature, 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one (1) (2.72 g, 0.020 mole) in dry dimethylsulfoxide (10 ml) was added dropwise. The solution was stirred for 4.5 hr. at 65° and then cooled. The solution was added to water (80 ml) and extracted 3 times with ether (60 ml). The combined ether extracts were washed twice with water (40 ml) and dried over anhydrous magnesium sulfate. The ether was evaporated and the crude solid recrystallized from cyclohexane to give 6,6-dimethyltricyclo-[5.1.0.0^3,5]octan-2-one (114) (0.85 g, 28.3%): ir (CCl₄) (Figure 30) 905, 973, 1048, 1257, 1358, 1669 (S), 1694 (w) and 2970 cm⁻¹; uv max (95% EtOH) 271 nm (ε, 38) end absorption at 200 nm (ε, 10,000); nmr (CCl₄) (Figure 30) δ 1.32 (s, 6H), 0.7 to 1.9 (Complex multiplet, 8H); mass spectrum, m/e (relative intensity) 150 (parent, 29), 136 (19), 108 (20), 96 (100), 95 (24), 94 (23), 92 (28), 80 (42), 68 (48), 56 (87).

Found: C, 80.21; H, 9.39.
Figure 30. Infrared spectra

Top: 4,4-dimethylcyclohexa-2,5-dienone

Middle: 6,6-dimethyltricyclo[5.1.0.0^{3,5}]octan-2-one

Nuclear magnetic resonance spectrum

Bottom: 6,6-dimethyltricyclo[5.1.0.0^{3,5}]octan-2-one
Photolysis of 6,6-dimethyltricyclo[5.1.0.0^3,5]octan-2-one

A solution of the ketone (110 mg, 7.33 X 10^-4 mole) in 100 ml methanol (7.33 X 10^-3 M) was irradiated in a quartz tube for 11 hr with a 450 watt Hanovia lamp. The reaction was monitored by vpc and no major products were formed as the starting material disappeared. The material was chromatographed on silica gel (Baker) and still no products were isolated.

Experimental for the Photolysis of 5,5-Dimethylbicyclo-[4.1.0]heptan-2-one

A solution of the ketone (515 mg, 3.73 X 10^-3 mole) in 100 ml menthol (3.73 X 10^-2 M) was irradiated for 26 hr. in a quartz tube in a Rayonet reactor with 2537 A lamps. The reaction was monitored by vpc and one major and several minor products were observed. The solution was evaporated and the residue chromatographed on silica gel (Baker) using benzene as solvent. The fractions were analyzed by vpc, and fractions 3-6 contained the major product plus some impurities. The yield of the major product was estimated at 120 mg (21%) by estimating the purity of fractions 3-6 from the vpc data. The major product was purified by vpc on column C and the following spectral data was obtained:

- ir (neat) 765, 789, 934, 1058, 1084, 1110, 1132, 1193, 1263, 1367, 1457, 2835 and 2960 cm^-1;
- nmr (CCl₄) (Figure 18, page 62) δ 0.76 (s, 3H), 0.90 (s, 3H), 0.70-1.90 (m, 8H), 3.05 (s, 1H), 3.09 (s, 3H); mass spectrum, m/e (relative intensity) 154 (parent, 25), 152 (7), 139 (14), 137 (12),
128

98 (53), 85 (45), 84 (100), 83 (84), 70 (24), 69 (16), 55 (39),
43 (78), 41 (39), 39 (86).

High resolution mass spectrum, in lieu of microanalysis
Theoretical for C_{10}H_{18}O: 154.1358 (M^+). Found: 154.1344 (M^+)

Experimental for the Phosphorescence Spectra

Phosphorescence spectra were run at -195° on 10^{-3}M samples of
4,4-dimethylcyclohexa-2,5-dienone (62), 3,4,4-trimethylecyclohexa-2,5-
dienone (103), 5,5-dimethylbicyclo[4.1.0]hept-3 en-2-one (1) and
6,6-dimethyltricyclo[5.1.0.0^{3,5}]octan-2-one (114). In every case the
only phosphorescence was due to an impurity in the solvent (2-methyl-
tetrahydrofuran).

Experimental for the Photolysis of 5-Methylbicyclo-
[3.2.0]hept-3-en-2-one (117)

A sample of 117 was furnished by R. L. Cargill, University of South
Carolina, Columbia, S.C. Neat 117 was irradiated between salt plates
in the low temperature infrared cell at -190° with an 800 Watt lamp
(2 lenses). The reaction was monitored by infrared spectroscopy with
spectra being recorded at 0.5, 1, 2, 4, 10, 20 and 60 minutes and after
warmup. New bands appeared at 1775 and 1775 cm^{-1} after 1 minute and
at 1725 after 2 minutes. The 1775 cm^{-1} band grew rapidly throughout the
reaction and became very strong. The 1755 cm^{-1} band was weak and soon
became lost under the 1775 cm^{-1} band. The 1725 cm^{-1} band grew rapidly
and after 60 minutes it was nearly as large as the 1700 cm^{-1} band of
starting enone (117). A weak band appeared at 2135 cm\(^{-1}\), but it never became very prominent. There was no change in any of the bands during warmup.

Experimental for the Photolysis of 1,2-Dimethyltricyclo-[4.3.0.0\(^{2,6}\)]non-4-en-3-one (119)

A sample of 119 was furnished by D. S. Caine, Georgia Institute of Technology, Atlanta, Georgia. Neat 119 was irradiated between salt plates in the low temperature infrared cell at -190\(^\circ\) with an 800 watt lamp (2 lenses). The reaction was monitored by infrared spectroscopy with spectra being recorded at 1, 2, 4, 10, 30, 60, 150 and 270 minutes after warmup. After 1 minute new bands had appeared at 2106 and 1801 cm\(^{-1}\). The band at 1801 cm\(^{-1}\) grew throughout the reaction and did not disappear during warmup. The 2106 cm\(^{-1}\) band reached a maximum after 30 minutes and decreased slowly during the rest of the irradiation. The remainder of the 2106 cm\(^{-1}\) disappeared during warmup. A thermally stable band also appeared at 1730 cm\(^{-1}\) after 10 minutes reaction. The band gradually increased and shifted to 1712 cm\(^{-1}\) after 4.5 hours.

A 10% solution of 119 in tetrahydrofuran was irradiated at -78\(^\circ\) in the low temperature solution cell. Ir spectra were recorded at 2, 4, 6, 8, 13 and 20 minutes. New bands appeared at 1802 and 1772 cm\(^{-1}\) after 2 minutes and grew throughout the reaction. After 4 minutes a new band was observed at 1715 cm\(^{-1}\). After 20 minutes all the bands started to decrease due to a leak in the solution cell.
Experimental for the Photolysis of 4,4-Dimethyl-5(4H)-indanone (120)

A sample of 120 was furnished by D. S. Caine, Georgia Institute of Technology, Atlanta, Georgia. Neat 120 was irradiated between salt plates in the low temperature infrared cell at -190° with an 800 watt lamp (2 lenses). The reaction was monitored by infrared spectroscopy with spectra being recorded at 0, 1, 2, 4, 8, 16, 30 and 60 minutes and during warmup. A very intense band at 2109 cm\(^{-1}\) grew throughout the reaction and reached nearly 100% absorption after only 8 minutes. After 60 minutes the starting dienone (120) had decreased by 25%. The sample was warmed to room temperature and the ketene disappeared without any new bands being observed. The intensity of the carbonyl band of the dienone (120) did not change noticeably either. A weak band was also observed at 1727 cm\(^{-1}\) during the irradiation.
SUMMARY

The photorearrangement of 5,5-dimethylbicyclo[4.1.0]hept-3-en-2-one to 2,3,5-trimethylphenol and 3,4,5-trimethylphenol in polar solvent is actually a series of three separate photochemical reactions. The first reaction appears to be a photochemical cleavage of the 1,7-bond of the cyclopropane ring followed by a hydrogen shift to form 3,4,4-trimethylcyclohexa-2,5-dienone. The cyclopropane ring opening is a known photoreaction of bicyclo[4.1.0]heptan-2-ones (48) and the hydrogen shift is supported by mass spectral evidence (57). The intermediates can't be detected because each subsequent reaction is much faster than the initial reaction.

The intermediate dienone was synthesized and irradiated under a variety of conditions and always formed 4,6,6-trimethylbicyclo[3.1.0]hex-3-en-2-one as the primary photoprodut. The bicyclic enone can photochemically rearrange to the two phenols in polar solvents at room temperature. However, in nonpolar solvents such as cyclohexane the major product is 3,6,6-trimethylcyclohexa-2,4-dienone. This reaction is not very clean and many byproducts are formed.

The low temperature photochemistry of the bicyclic enone follows two main reaction paths. In one path a ketene is formed which is the precursor of the linearly conjugated 2,4-cyclohexadienone. The ketene can also be trapped by methanol at $-78^\circ$ or lower. The second path involves isomerization to a cyclopropanone which is unstable at room temperature and thermally rearranges to form the phenols. The cyclopropanone can be trapped by methanol or furan at $-78^\circ$. 
The photochemistry of 4,4-dimethylcyclohexa-2,5-dienone (30) was studied under the same conditions as the 3,4,4-trimethylcyclohexa-2,5-dienone. The results of the two systems were very similar with minor variations in reactivity and temperature effects.

The photochemistry of the two dienones and two bicyclic enones agreed well with the literature results at room temperature. The additional low temperature results involving ketenes strengthen what was suspected in many earlier reports on similar systems. The observance of cyclopropanones may also explain some other observations or may revise them drastically.
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137

ACKNOWLEDGMENTS

The author wishes to thank his parents for their encouragement and support during his many years of college.

The author is grateful to Dr. Harry Morrison for his advice and support during the undergraduate years.

The author expresses his gratitude and appreciation to Professor O. L. Chapman for the advice, guidance and encouragement given him during the course of this work and his graduate study. Special thanks are also due to members of the Chapman group for their friendship, counsel and experimental assistance.