EXPLORATORY ORGANIC PHOTOCHEMISTRY. INTERNAL EPOXY KETONES AND MEDIUM SIZED RING DIENES

BY

RUDOLF ERICH GAYLER
Dipl. Chem. ETH, Zurich, 1968

A THESIS SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE in the Department of CHEMISTRY

We accept this thesis as conforming to the required standard

THE UNIVERSITY OF BRITISH COLUMBIA

May, 1971
In presenting this thesis in partial fulfilment of the requirements for an advanced degree at the University of British Columbia, I agree that the Library shall make it freely available for reference and study. I further agree that permission for extensive copying of this thesis for scholarly purposes may be granted by the Head of my Department or by his representatives. It is understood that copying or publication of this thesis for financial gain shall not be allowed without my written permission.

Department of Chemistry

The University of British Columbia
Vancouver 8, Canada

Date 6-71
ABSTRACT

In Part I of this work octahydro-4a,8a-epoxy-1(2H)-naphthalenone, hexahydro-3a,6a-epoxy-1(2H)-pentalenone, and octahydro-3a,8a-epoxy-4(1H)-azulenone were photolyzed. The major course of these reactions was one of polymerization. Small amounts of monomeric products could however be obtained with difficulty and were tentatively assigned the structures which arise mechanistically via the same path as in the rearrangement of ordinary aliphatic α,β-epoxy ketones i.e., 1,3-diketone formation. In order to prove the structure of the photoproduct of the naphthalenone epoxide the synthesis of 2-cyclopentylidene-cyclopentanone oxide was attempted.

In Part II of this thesis the nature of the excited state in the photolysis of cis,cis-cyclodeca-3,8-diene-1,6-dione was investigated by quenching and sensitization experiments. These suggested that the reactive excited state involved was a highly reactive triplet state. Furthermore, the thermal reaction of cis,trans-cyclodeca-3,8-diene-1,6-dione was investigated and found to give rise to three new products in low yields whose structures are still under investigation. They probably arose from an ene-reaction. Thermolysis of cis,cis-cyclodeca-3,8-diene-1,6-dione afforded 3a,5,8,8a-tetrahydro-8a-hydroxy-4(1H)-azulenone.

A low temperature photolysis of cis,trans-cyclodeca-3,8-diene-1,6-dione was carried out at 77°K in order to trap the potential intermediate trans,trans-cyclodeca-3,8-diene-1,6-dione. However, besides a minor amount of cis,cis-isomer, the low temperature photolysis afforded the same product as that obtained by photolysis at ambient temperature.
Finally the centrosymmetric anti-configuration of the tricyclic photo-product from \textit{cis,cis}\-cyclodeca-3,8-diene-1,6-dione was further supported by a dipole measurement and by infrared and Raman spectroscopy.
# TABLE OF CONTENTS

## PART I

PHOTOCHEMISTRY OF INTERNAL $\alpha,\beta$-EPOXY KETONES

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>A. Background of Epoxy Ketone Photochemistry</td>
<td>2</td>
</tr>
<tr>
<td>B. Objectives of Present Research</td>
<td>9</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>12</td>
</tr>
<tr>
<td>A. Hexahydro-3a,6a-epoxy-1(2H)-pentalenone</td>
<td>12</td>
</tr>
<tr>
<td>B. Octahydro-4a,8a-epoxy-1(2H)-naphthalenone</td>
<td>15</td>
</tr>
<tr>
<td>C. 2-Cyclopentylidene-cyclopentanone Oxide</td>
<td>16</td>
</tr>
<tr>
<td>D. Octahydro-3a,8a-epoxy-4(1H)-azulenone</td>
<td>24</td>
</tr>
<tr>
<td>SUMMARY</td>
<td>27</td>
</tr>
</tbody>
</table>

## PART II

THERMAL AND PHOTOCHEMICAL PROPERTIES OF $\text{cis,cis}$-CYCLODECA-3,8-
DIENE-1,6-DIONE

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>28</td>
</tr>
<tr>
<td>A. Intramolecular Photochemical Cycloadditions of Non-conjugated Dienes</td>
<td>29</td>
</tr>
<tr>
<td>B. Earlier Results of the Photochemistry of 1,6-Cyclo-decadiene Systems</td>
<td>35</td>
</tr>
</tbody>
</table>
| C. Previous Results of the Photochemistry of $\text{cis,cis}$-Cyclo
deca-3,8-diene-1,6-dione                                      | 36   |
| D. Objectives of Present Research                                      | 39   |
| RESULTS AND DISCUSSION                                                 | 41   |
ACKNOWLEDGEMENTS

I would like to thank Dr. J.R. Scheffer for his continual advice and encouragement throughout this work. I am also grateful to my fellow graduate students for many helpful discussions and for their cordial spirit.

I am further indebted to the many staff members of this department for their contributions and to the University for a Teaching Assistantship.

Last but not least I would like to thank my wife Barbara for her help and support.
PART I

PHOTOCHEMISTRY OF INTERNAL $\alpha,\beta$-EPOXY KETONES
INTRODUCTION

A. Background of Epoxy Ketone Photochemistry

Aliphatic and alicyclic α,β-epoxy ketones rearrange to 1,3-diketones upon ultraviolet irradiation. As shown in eq 1, one of the β-substituents migrates to the α-position. The first reaction of this type was reported by Bedforss in 1918.\(^1\) He observed the light-induced rearrangement of benzalacetophenone epoxide (3) to the corresponding 1,3-diketone 4 (eq 2). The mechanism of this rearrangement was not investigated until 1963 when Zimmerman and Reusch independently published a series of experiments which led them to the same conclusions.\(^2,3\) Zimmerman found that in the photolysis of 5 only the methyl group migrated.
Markos and Reusch found the following order of migratory aptitudes for different substituents: benzyl > hydrogen > methylene > methyl >> phenyl. An ionic mechanism could be ruled out since this would favor the 1,2-shift of the phenyl and not of the methyl group. Thus the possibility of a radical mechanism was investigated. Free radicals show much less tendency to undergo rearrangement than do more electron deficient species. Nevertheless 1,2-phenyl shifts have been observed. However, 1,2-alkyl or hydrogen shifts of free radicals are very rare. Where there is a choice between phenyl and alkyl migration, phenyl migration takes place exclusively. This was confirmed by molecular orbital calculations by Zimmerman and Zweig. The energy differences found for 1,2-shifts of phenyl vs. methyl are shown in eq 4 and 5.

\[
\begin{align*}
\text{Ph-C} & \quad \text{Ph-C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
\[\Delta E = -0.45 \beta \] (4)

\[
\begin{align*}
\text{Ph-C} & \quad \text{Ph-C} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]
\[\Delta E = -0.85 \beta \] (5)

However, two radical reactions have been reported where methyl expulsion or migration is favored over phenyl expulsion or migration. The first one by Kharash and coworkers deals with the thermal decomposition of hydroperoxide which gives alkoxy radical. The latter ejects only
methyl radicals which pick up a hydrogen from the solvent to form methane. If a phenyl radical would have been ejected, the product formed would have been acetone which was not observed.

The second example was reported by Greene and coworkers. The thermal decomposition of peroxylactone showed a five-fold preference for the product where the methyl group had migrated.

\[
\begin{align*}
\text{PhC(CH}_3\text{)}_2\text{OOH} \xrightarrow{\Delta} & \text{PhC(CH}_3\text{)}_2\text{O} \xrightarrow{\text{7}} \text{PhCOCH}_3 + \cdot \text{CH}_3 \\
\text{CH}_3\text{COCH}_3 + \text{Ph} &
\end{align*}
\]

(6)
The postulated intermediate 13 is analogous to the intermediate 15 put forward by Zimmerman. However, intermediate 15 should have a very short lifetime since it has been shown that the carbon α to the carbonyl group retains its stereochemistry as in the photolysis of 17.

![Diagram of compounds 17 and 18](image)

The validity of comparing intermediates 13 and 15 obtained by a thermal and a photochemical reaction finds support by the fact that thermolysis of pulegone oxides 19a or 19b in the liquid phase gives rise to the same products 20a and 20b as does photolysis (eq 10).

![Diagram of compounds 19a, 19b, 20a, and 20b](image)

19a α-oxide
19b β-oxide
20a cis-methyl groups
20b trans-methyl groups
However, thermolysis of other epoxy ketones such as 21 and 22 does not result in this kind of behavior. Nevertheless the pulegone oxide chemistry opens the possibility that the photochemical reaction proceeds by way of a vibrationally excited species.

Another point of interest in the mechanism of the epoxy ketone rearrangement was the question whether the migration of the substituent was concerted or stepwise. The latter mechanism would involve a more or less free radical migrating to the neighbouring carbon radical site. As Reusch pointed out, the preferential migration of hydrogen over methyl speaks against a fragmentation process since hydrogen atoms are not normally formed in preference to methyl radicals.

Further evidence along the same line comes from an investigation by Schaffner and coworkers. They found that in steroidal epoxy ketones such as 23, the stereochemistry at C10 was preserved (eq 11). From this it was concluded that the rearrangement of 23 to 25 was either concerted or at least so fast that in the transition state 26, C10 would not have time to epimerize. Sterically, continuous overlap between breaking and forming bonds is possible. The photolysis of steroid 27
represents an interesting case where two products would be expected if the reaction would be non-concerted. However, only one product, 30 is observed. The formation of 30 can occur with continuous overlap whereas the path leading to 32 involves rotation about two single bonds, marked by arrows in 31, and would therefore interrupt the overlap. This is the argument put forward to account for the selectivity of the reaction.
In contrast to these examples favoring a concerted reaction stands the photolysis of 33. Here a substituent is migrating which can form a very stable radical. From the formed dibenzyl it has to be concluded that some of the migrating benzyl groups escape the solvent cage and combine to give dibenzyl. Thus, the degree of concertedness seems to depend on the stability of the radical of the migrating substituent.

The nature of the excited state involved in the photochemical rearrangement of epoxy ketones was found to be a singlet state on the basis of sensitization and quenching experiments carried out with four different epoxy ketones.

**B. Objectives of Present Research**

Up to the present time, the photochemistry of "internal" α,β-epoxy ketones such as 36, has not been reported. It seemed interesting to study their photochemistry, since, if they reacted as other epoxy ketones, they would give spiro compounds 37 or 38 or both of them. No preference for path (a) or (b) can be found on the basis of migratory aptitudes since in both cases a methylene group is migrating. Other
new reactions might also take place of course. The initial step might be carbon-carbon bond cleavage of the epoxy bond although it has been shown for steroidal epoxy ketones that this does not occur. Another possibility would be that the migrating group would join with the carbonyl oxygen to give cyclic vinyl ethers 39 and 40 as is shown in eq 15.

The photolysis of "internal" epoxy ketones in addition to being significant from a photochemical point of view might provide a convenient synthesis of spiroketones. Particularly spiroketones of the type 37 would be of interest since spiroconjugative effects could be studied with these ketones and derivatives therefrom.
RESULTS AND DISCUSSION

A. Hexahydro-3a,6a-epoxy-1(2H)-pentalenone (42)

The first internal epoxy ketone chosen for study was 42. It was synthesized from tetrahydropentalenone 41 (obtained as a gift from BASF) by alkaline epoxidation with hydrogen peroxide in 68% yield.

If 42 would undergo the usual photochemical rearrangement of \( \alpha,\beta \)-epoxy ketones, two products 43 and 44 would be expected.

\[
\text{41} \xrightarrow{\text{H}_2\text{O}_2, \text{OH}^- \text{CH}_3\text{OH}} \text{42} \quad (16)
\]

\[
\text{42} \xrightarrow{\text{a}} \text{43} \quad \xrightarrow{\text{b}} \text{44} \quad (17)
\]
Compound 42 was photolyzed in benzene using a Pyrex filter and a medium pressure mercury lamp. The reaction was followed by glpc. Four major products, A, B, C, and D, in order of increasing glpc retention time were formed. They were isolated by glpc in the following yields: A, 1%; B, 1%; C, 5%; D, 1.5%. Although the starting material had almost completely reacted no other significant products could be observed by glpc. Thin layer chromatography showed a longish spot at the bottom of the plate, the kind of spot usually observed if polymeric compounds are present.

The ir spectrum of the major product (C) shows two carbonyl bands of equal intensity at 5.57 and 5.75 μ. The latter band corresponds to a five-membered ring ketone and the 5.57 μ band is close to the usual position of the carbonyl band of four-membered ring ketones at 5.62 μ. Thus the ir spectrum points to structure 43 for C. The shift to shorter wavelengths of the 5.57 μ band compared to the usual 5.62 μ band for cyclobutanones may be caused by mutual interaction of the two carbonyl groups. This phenomenon has been observed in the spectrum of spirodiketone 45 which shows two carbonyl bands at 5.81 and 5.68 μ. Although the two π-orbitals are perpendicular to each
other they are close enough (see structure 46) for mutual interaction. This can be seen in the uv spectrum of 45 which shows an enhanced extinction coefficient of 100 at 310 nm. The extinction coefficient for the same spiro compound with only one carbonyl function is about three times smaller.\textsuperscript{15}

The nmr spectrum of C shows a multiplet at 7.36 $\tau$ integrating to six hydrogens and a multiplet from 7.7-8.3 $\tau$ integrating to four hydrogens. On the basis of the nmr data it is hard to distinguish between structures 43 and 44 for C. However, the symmetric structure 44 might have been expected to give a simpler looking spectrum.

A complete structure determination of C would require a more substantial amount of it which could then be degraded for example by means of an aqueous base. Spiro-1,3-diketones of the type 43 and 44 are very base labile. For example, the structure of 47 has been proven\textsuperscript{16} by base degradation to the keto acid 48. The high reactivity of these

\begin{align*}
\text{47} & \xrightarrow{\text{OH}^-} \text{48} \\
\text{51} & \xrightarrow{\text{H}^+} \text{51}
\end{align*}
compounds towards base might be the reason for the observed instability of C which, when allowed to stand for three days at 0° had been about 30% converted, according to glpc, into one other product.

B. Octahydro-4a,8a-epoxy-1(2H)-naphthalenone (49)

This epoxide was chosen in analogy to the tetrahydropentalenone epoxide 42. If 49 would undergo the usual photochemical rearrangement reaction, the formation of 46 and 50 are possible. In this case the possible products 46 and 50 are less strained than 43 and 44 and might therefore be formed in greater yields.

\[
\begin{align*}
\text{49} & \xrightarrow{\text{hv}} \text{46} + \text{50} \\
\end{align*}
\]

(19)

Compound 49 was synthesized from the known 3,4,5,6,7,8-hexahydro-1(2H)-naphthalenone using alkaline hydrogen peroxide.17

Irradiation of epoxide 49 in dioxane through a Corex filter gave one product (50) only which could be collected by glpc in about 15% yield. One of the possible products, 46 is a known compound.16 The ir spectrum of the isolated photoproduct has carbonyl bands at 5.73, 5.76 (shoulder), and 5.88 μ. Compound 46 has carbonyl bands at 5.81 and 5.90 μ. Assigning the 5.76 band of 50 to an impurity (a glpc analysis after the nmr had been run showed a new peak amounting to 10%
of the starting material), the two remaining carbonyl bands could correspond to structure 50. The nmr of 50 shows a complex multiplet from 7.3 to 8.6 \( \tau \). Compound 46 has been reported to have a triplet at 7.38 \( \tau \) and a multiplet from 7.65 to 8.60 \( \tau \).\(^{16}\) This again rules out structure 46 as the photoproduct. The mass spectrum of a sample that had not decomposed to any degree showed the correct parent peak. Hence, structure 50 is very likely the one that has to be attributed to the photoproduct of 49.

C. 2-Cyclopentylidene-cyclopentanone oxide (52)

This compound was chosen to add further proof to structure 50 of the photoproduct of 49. If 52 would react photochemically undergoing the usual 1,2-shift of one of the \( \beta \)-substituents, compound 50 would be the only product formed. This product was expected to be identical with the photoproduct obtained from 49 thereby confirming the latter's structure.

The synthetic pathway leading to 52 was chosen in analogy to the alkaline hydrogen peroxide epoxidation of 2-cyclohexylidene-cyclohexanone (53).\(^{18}\)
Compound 55 was synthesized by an aldol condensation of cyclopentanone in alkaline aqueous ethanol by the method of Huckel. When 55 was treated with alkaline hydrogen peroxide the product obtained showed a hydroxyl band in the ir spectrum and carbonyl bands at 5.79 and 5.90 μ. It was thought that the epoxide might have opened under the reaction conditions used. Since it is known that temperatures above 20° cause the yield of this type of reaction to drop considerably, the epoxidation was carried out at 12°. However, the same product containing an alcohol function was obtained. Using a large excess of hydrogen peroxide did not improve the yield; the alcoholic product was obtained in about 10% yield. When the pH of the reaction mixture was checked after completion of the reaction (when the peak corresponding to 55 had
disappeared in the uv spectrum) it turned out to be acidic. At first this was thought to be caused by reaction of the alkaline solution with atmospheric carbon dioxide since the reaction time for the epoxidation was long enough (about two days) to allow carbon dioxide to react with the base present in solution. However, when the reaction was carried out under nitrogen atmosphere, the same product containing a hydroxyl function was obtained in about 10% yield. The same product was isolated from another run where an excess of sodium hydroxide had been used. A new product was obtained in 60% yield from this reaction when the acidified (using acetic acid) reaction mixture was extracted. The ir spectrum of this product showed hydroxyl bands from 2.8 to 4.0 μ which are characteristic for carboxylic acids. It also showed a strong carbonyl band at 5.86 μ and a shoulder at 5.76 μ. This compound might have been 56, obtained by the mechanism shown in eq 23.

\[
\begin{align*}
\text{55} & \quad \xrightarrow{\text{HO}^-} \quad \text{H}_2O \\
\text{56} & \quad \xrightarrow{\text{HO}^-} \quad \text{H}_2O
\end{align*}
\]
It was somewhat surprising that $5_{5}$, the five-membered ring analogue of $5_{3}$ should not undergo epoxidation since the latter reacts so smoothly. However, it was found in the literature that systems of the type $5_{7}$ are anomalous in their reactions with alkaline hydrogen peroxide.$^{20}$

House tried to epoxidize ketone $5_{8}$ with alkaline hydrogen peroxide but all attempts failed.$^{21}$ With a closer look at the mechanism of the epoxidation an explanation for the failure of epoxidation of this kind of system could be found. By a nucleophilic attack of the hydrogen peroxide anion on $5_{9}$, having two exocyclic double bonds, intermediate $6_{0}$ is formed which has one endocyclic double bond. This first step is energetically unfavorable according to a rule reported by H.C. Brown.$^{22}$ This rule says that reactions will proceed in such a manner as to favor the formation or retention of an exo double bond in five-membered rings
and to avoid the formation or retention of exo double bonds in the six-membered ring systems. A few examples supporting this rule are the two 1,3-diketones 62 and 63 which are enolized to different degrees, and 64 and 65 which upon heating isomerize to the products 66 and 67 predicted by the rule.

The enol form 68 of 62, present only as 4.5% resembles the probably unfavorable intermediate 60 formed by nucleophilic attack of hydrogen peroxide anion on 59 with respect to the formation of an endocyclic double bond.
In a related study of the addition of amines to ketone 58 very low yields of product 70 have been observed, compared to good yields obtained in the case of the six-membered ring analogous compounds.

This was explained by the same argument used in the epoxy ketone case. The formation of intermediate 69 was unfavorable on the basis of Brown's rule. In this case a reverse reaction is possible which is favored in the five-membered ring case since the exocyclic resonance structure 71 contributes to a higher degree than does the unfavourable endo structure 72. Elimination is favored from structure 71 and therefore favored
in the five-membered ring case. Thus an unfavorable equilibrium or a slow attack of the amine account for the small yields observed. In the epoxide case, however, it has to be the slow attack of peroxide anion which accounts for the failure of reaction since no reverse reaction is possible.

In order to obtain the desired epoxide 52 another route was tried as depicted in eq 29. The preparation of 73 has been reported by

\[ \text{52} \xrightarrow{\text{LiAlH}_4} \text{73} \]

Le Guillanton who obtained best yields (65-70%) using potassium borohydride as the reducing agent. In this work lithium aluminum hydride was used. Le Guillanton obtained only a 45% yield of 73 using this reagent in a molar ratio of 2:1 to 1 part of ketone 55. In the work-up he used acid which was found in another case to cause isomerization of the allylic alcohol formed (eq 30). Using water only in the work-up increased the yield of unrearranged alcohol dramatically (eq 31).
In this work lithium aluminum hydride and work-up without acid gave a 90% yield of the crystalline alcohol 73 whose melting point agreed with that reported. 24

Epoxidation of 73 with m-chloroperbenzoic acid gave epoxide 74. The nmr spectrum shows a triplet at 6.2 $\tau$ for the proton on the carbon bearing the hydroxyl group. The hydroxyl proton appears at 7.2 $\tau$ as a sharp singlet and the rest of the protons are found in a multiplet from 7.8 to 8.6 $\tau$.

The stereochemistry of 74 has not been established. However, the hydroxyl group is probably cis to the epoxy group since it has been found that allylic alcohols are epoxidized stereoselectively as for example 78 giving 79. 26
The isolated epoxy alcohol 74 was found to be moderately unstable. After standing at 0° for fourteen days the IR showed a strong carbonyl band at 5.90 μ and GLPC showed that the compound had decomposed giving two major products. Because of this low stability, the mild Collins reagent was chosen for the oxidation of 74. The mixture resulting from oxidation was found by GLPC and TLC to consist of a large number of products; a crude infrared spectrum showed at least four distinct carbonyl absorptions. As a result, this synthesis was abandoned.

D. Octahydro-3a,8a-epoxy-4(1H)-azulenone (80)

This compound was chosen to prove the structure of the photoproduct of the naphthalenone epoxide 49. If 80 would undergo the usual epoxy ketone rearrangement upon photolysis, spiro diketone 50 would very likely be formed. This is the structure tentatively assigned to the photoproduct of 49. Compound 80 might also rearrange to give 81, but probably to a lesser degree since 81 is more strained than 50.
Epoxy ketone 80 was synthesized from 82 as shown in eq 35.\textsuperscript{28} Hydrogenation of 82 gave diketone 83 in quantitative yield. According to a known procedure, refluxing of 83 in aqueous methanol containing potassium carbonate gave rise to azulenone 84 in 66\% yield.\textsuperscript{29} Upon alkaline epoxidation of 84 with hydrogen peroxide, 80 was obtained in quantitative yield.
Epoxy ketone 80 was photolyzed in dioxane using a Corex filter cutting off the light below 260 nm. The major part of 80 polymerized. One product, 83, was formed according to glpc. It was collected by glpc in 3% yield as a colorless liquid having two carbonyl bands at 5.71 and 5.82 μ. These bands did not correspond to 50 which had strong bands at 5.73 and 5.88 μ. Structure 81 corresponding to the photoproduct remains a possibility although the 5.71 μ band seems to be of rather high frequency for a seven-membered 1,3-diketone.
SUMMARY

Generally, the photolysis of internal $\alpha,\beta$-epoxy ketones led mostly to products formed by polymerization. The low yield of monomeric photoproducts did not promise much synthetic use. Thus the entire project was abandoned.
PART II

THERMAL AND PHOTOCHEMICAL PROPERTIES OF

cis,cis-CYCLODECA-3,8-DIENE-1,6-DIONE
INTRODUCTION

A. Intramolecular Photochemical Cycloadditions of Non-conjugated Dienes

Double bonds are able to undergo intramolecular photochemical cycloaddition in a straight or crossed manner. The general types of products so obtained are depicted in eq 36 and 37. Since different

- acyclic systems

\[
\begin{array}{c}
\text{hv} \\
\text{straight} \\
\text{crossed}
\end{array}
\]

(36)

- cyclic systems

\[
\begin{array}{c}
\text{hv} \\
\text{straight} \\
\text{crossed}
\end{array}
\]

(37)
ratios of straight to crossed products were observed in many systems, it was of interest to study the factors determining the changing ratios.

In 1967 Srinivasan reported an empirical rule predicting the direction of cycloaddition reactions. Table 1 summarizes a few of the examples on which the rule was based. It can easily be seen that 1,4- and 1,6-dienes form preferentially straight products whereas 1,5-dienes add in a crossed way. Since these reactions usually occur via a triplet excited state they are very likely stepwise processes. The first step postulated by Srinivasan was the formation of a cyclic biradical intermediate. From the examples in Table 1 it can be seen that radical stabilities do not always account for the preferential reaction path. For compounds 87 to 89, radical stability would predict the straight product to be the major one which is contrary to what was observed. For example the most stable biradical intermediate formed from 88 would have structure 91. This biradical would close to give 92 which is the minor product observed.
Table 1. Mercury ($^3P_1$) Sensitized Photolyses of Non-conjugated Dienes in the Gas Phase.

<table>
<thead>
<tr>
<th>Starting Material</th>
<th>Straight Product</th>
<th>Crossed Product</th>
<th>Product ratio</th>
<th>Crossed / Straight</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,4 diene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,5 diene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,6 diene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$m = major product$
Srinivasan postulated the Rule of Five which says that the cycloaddition prefers to go through a five-membered cyclic biradical intermediate. This rule predicts nicely the preferential formation of straight products for the 1,4- and 1,6-dienes and the crossed products for the 1,5-dienes. A much more sophisticated explanation for this rule has not yet been found.\textsuperscript{30a}

Independent of Srinivasan's study Liu and Hammond reported some extensive work on the triplet photosensitized internal addition of a diene moiety to an isolated double bond.\textsuperscript{31} Their results are compiled in Table 2. It is interesting to note that 103a and 103b give the same ratio of products whether they are photolyzed separately or as a mixture. It follows that they possess a common intermediate 110 having biradical character. Ring closure of 110 to the bicyclo[2.1.1]-hexane system is thought to be slow compared to rotation about a single bond for two main reasons. Firstly, the formation of a strained ring system should have a retarding effect. Secondly, the biradical intermediate should inherit triplet character from its precursor. Prior to closure of the biradical, spin inversion to the singlet state has to occur which is usually slow.\textsuperscript{32}
Table 2. Photosensitized Internal Addition of Dienes to Olefins.

\[
\begin{align*}
\text{95} & \rightarrow \text{96} & \text{106} & \text{107} \\
\text{98} & \rightarrow \text{100} & \text{108} & \text{109} \\
\text{101} & \rightarrow \text{102} \\
\text{103a} \overset{hv}{\rightarrow} \text{104} + \text{105} & \text{5.8:1} \\
\text{103b} \overset{hv}{\rightarrow} \text{104} + \text{105} & \text{5.8:1}
\end{align*}
\]
According to Liu and Hammond the preference for formation of five-membered rings may merely reflect the fact that the carbon atoms that become bonded are, on the average, closer together than those that would have to interact to form a six-membered ring. This statistical argument was criticized because it would require a highly oriented ground state of the substrate to account for the observed specificity of products, a condition unlikely to be met with in the simple hydrocarbons used.\textsuperscript{33} White and Gupta suggested that the mode of the cycloaddition is determined by complex formation between the excited diene and the ground state olefin prior to formation of the cyclic biradical intermediate.\textsuperscript{33} This theory, however, does not predict the mode of cycloaddition.

It is interesting to note that in radical chemistry the Rule of Five is effective as well. Decomposition of 6-heptenoylperoxide gives rise to radical 111 which closes preferentially to the methylcyclopentane system.\textsuperscript{34}

\begin{equation}
\begin{align*}
\text{111} & \quad \rightarrow \quad \text{30} + \text{1} \\
(40)
\end{align*}
\end{equation}

The Rule of Five has been verified in quite a few open chain systems. Only a few cyclic systems have been investigated, and one of these was studied in this work.\textsuperscript{35}
B. Earlier Results of the Photochemistry of 1,6-Cyclodecadiene Systems.

Only a few investigations have been reported on the photochemistry of 1,6-cyclodecadiene systems. In 1968 a mixture of cyclodecadienones 113 and 114 was photolyzed (eq 41). However, the geometry of bonds 2,3 and 3,4 was not known. Compound 116 is formed following the Rule of Five, however, 115 is not.

\[
\text{113} + \text{114} \xrightarrow{\text{hv}} \text{116 (32%)}
\]

Another 1,6-cyclodecadiene was studied by Scheffer and Boire. Upon photolysis, diene 117 apparently obeys the Rule of Five. The

\[
\text{117} \xrightarrow{\text{hv}} \text{118 (50%)} + \text{119 (30%)}
\]
third reported cycloaddition of a 1,6-cyclooctadiene was that of germacrene D (120). Here again the rule of five predicts the major product, 121.

\[
\begin{align*}
&\text{120} \\
&\text{(-)-\beta-bourbonene (121)} \\
&\text{major}
\end{align*}
\]

\[\text{hv} \quad 2537 \text{ Å} \]

C. Previous Results of the Photochemistry of \textit{cis,cis}-Cycloocta-3,8-diene-1,6-dione (82)

The cyclic \textit{cis,cis}-diketone 82 was studied by Scheffer and Lungle. It was used as a model to study photochemical intramolecular cycloadditions in cyclic dienes where the double bond was in the $\beta,\gamma$-position of a carbonyl function. Photolysis of 82 gave the two products shown in eq 44. This was the first reported example of an intramolecular cycloaddition of a $\beta,\gamma$-unsaturated ketone. A $\pi^S_2 + \pi^S_2$ concerted cycloaddition of 112 giving 122 is photochemically not allowed. Photochemically allowed $\pi^S_2 + \pi^S_2$ cycloaddition of 82, existing in the two conformations 123 and 124, would result in the formation of the tricyclic diketone 125 having a \textit{syn} geometry which, however, was not observed. Since 112 was found to be the only precursor of 122 and since this conversion could not be concerted, a biradical intermediate
126, formed upon excitation of 82 was postulated. The observed initial 1,5-bonding in 126 is another example for the rule of five. Biradical 126 then closes stereoselectively to give the anti-isomer 122 and not 125, the syn-isomer. Closure of 126 without bond rotation would result in a trans ring junction. Rotation about the 6,7-bond relieves the non-bonded interaction between the hydrogens on C7 and C10, whereas an increased interaction between the hydrogens on C5 and C2 would result by rotation about the 5,6-bond. The former rotation being favored, closure leads to the formation of the anti-isomer 122.

An alternative pathway involving isomerization of 112 to the trans,trans-diketone and subsequent photochemically allowed $[^2 \pi^s + ^2 \pi^s]$ cycloaddition could not be ruled out. When the investigation of the photolysis of 82 was near its completion a study on the photolysis of the same compound was reported by Shani. However, the stereochemistry of the tricyclic ketone was claimed to be syn. This assignment was
based on a hydrazone dimer 127, allegedly formed from the tricyclic ketone 125. The structure of 127 was based on the parent peak in the mass spectrum and on the C=N band in the ir spectrum. This assignment was contradicted by a subsequent investigation by Stankorb and Conrow who demonstrated that the mass spectrum of the hydrazone derivative had peaks at greater m/e values than the dimer parent peak. These peaks were attributed to fragments of hydrazone polymers. Since both the anti- and the syn-diketone 122 and 125 are potentially able to form polymers with hydrazine, this cannot be used as a structure proof. It should be noted that Stankorb and Conrow had strong arguments in favor of the anti-configuration 122 on the basis of degradation experiments.

D. Objectives of Present Research

In order to shed more light on the mechanism of the photolysis of cis,cis-diketone 82, the nature of the excited states involved was investigated by quenching and sensitization experiments.

Another point of interest was the thermochemistry of cis,trans-cyclodeca-3,8-diene-1,6-dione (112). It seemed conceivable that it
would undergo a thermally allowed $[\pi^2_s + \pi^2_a]$ cycloaddition to form syn or anti ketone 125 or 122. Via this route the formation of the syn isomer 125 of this dione was a possibility. If 125 could be isolated, it would clarify the assignment of the anti geometry to the tricyclic diketone obtained by photolysis of cis,cis-diketone 82.

A further point investigated arose from the fact that gas chromatograms of even very pure samples of cis,cis-diketone 82 always turned out to have a shoulder. This was suspected to arise from a thermal product formed at the elevated temperature of the injection port (about 200°) of the gas chromatograph.

The possible intermediacy of the trans-trans-isomer of 112 was investigated by low temperature photolysis. It was thought that the rotation barrier of the closure of the biradical 126 might be high enough to channel the reaction through the trans,trans-isomer.

As a last goal some further evidence for the anti-configuration of the tricyclic ketone 122 was gathered firstly by the results of a dipole determination, and secondly by comparing the infrared and Raman spectra of 122. The latter method had been previously used to differentiate centrosymmetric from non-centrosymmetric molecules.
RESULTS AND DISCUSSION

A. The Nature of the Excited State in the Photolysis of cis,cis-Cyclodeca-3,8-diene-1,6-dione

(a) Quenching

Piperylene, a commonly used triplet quencher was chosen for this investigation. According to glpc the same intermediate and final product were formed in approximately the same ratio as in the photolysis with no quencher present. Increasing the quencher concentration from 1.0 M to 10.0 M and at the same time the ratio of quencher to ketone from 20 to about 600 slowed the reaction down by a factor of about 3. Thus, the quenching was not considered to be very effective. Since this indicated that the reaction went via a singlet excited state, triplet sensitization was expected to give a clear answer.

(b) Sensitization

Benzophenone was the sensitizer of choice because it absorbs at longer wavelengths than compound 82. Its triplet energy of 68.5 kcal/mole is high enough to sensitize ketones which normally have triplet energies in this energy range. Sensitized photolysis of 82 in benzene gave rise to the same two photoproducts as the direct photolysis. The two products had identical retention times in glpc and on tlc. However, the rate of formation of the two photoproducts was different. On glpc the peak attributed to the cis,trans intermediate
112 never amounted to more than about 5% of total reactants. This contrasted the direct photolysis where more intermediate (~50%) had been formed before it was eventually converted to the final product. This made it difficult to isolate the intermediate in the sensitized photolysis. By column chromatography the intermediate could only be obtained as a mixture with final product 122. The latter, however, could be isolated as a pure compound and its ir and nmr spectra as well as its melting point were identical with the data of the product obtained by direct photolysis.

The positive sensitization results suggest that the reaction goes via triplet excited states. The negative quenching results lead to the conclusion that the chemical reaction is so fast that quenching rates cannot compete with it, or much less probable, that the singlet excited state gives rise to the same products as does the triplet state. A third very unlikely way to explain the negative quenching would be to assume that compound 27 had a lower triplet energy than piperylene (E_T ~ 61 kcal) in which case the piperylene would not be able to accept energy from a lower energy donor.

B. Thermolysis of cis,trans-Cyclodeca-3,8-diene-1,6-dione (112)

As was pointed out before, it was conceivable that the cis,trans-intermediate 112 might thermally cyclize in an allowed concerted $[\pi^2 + \pi^2]$ addition to the same product (122) obtained by photolysis. Thermolysis of 112 in xylene for five days at 192° gave rise to three products 128, 129 and 130 isolated by glpc in yields of 9%, 5% and 1% respectively. From mass spectral data 128 and 129 were found to be
isomers of 112. The ir spectrum of 128 which was obtained as colorless crystals showed carbonyl bands at 5.72 and 5.95 μ. The former band points to a five-membered ring ketone and the 5.95 μ band might be attributed to an α,β-unsaturated ketone. The uv spectrum supports the latter assignment since it has a high extinction coefficient of 14,000 at 226 nm. In the nmr spectrum the olefinic proton on the carbon β to the carbonyl group appears as a doublet of doublets at 2.98 τ with coupling constants of 10 and 2 Hz. The olefinic α-proton shows up as a doublet of doublets at 4.00 τ and coupling constants of 10 and 3 Hz. The coupling constant of 10 Hz can be assigned to a cis double bond. The nmr further shows a complex multiplet of 9 protons from 7.0-8.3 τ and a doublet of three protons at 8.83 τ with a coupling constant of 6 Hz. The mass spectrum shows a parent peak at m/e 164 from which it follows that 128 is isomeric with starting material. However, a peak appeared at m/e 211 amounting to about 10% of the parent peak. A molecule incorporating a five-membered ring ketone and an α,β-unsaturated ketone might arise from an ene-reaction of 112. The principle of this thermal reaction is shown in eq 47. If 112 undergoes an ene-reaction

```
\begin{align*}
\text{H} & \quad \rightarrow \\
\text{H} & \\
\end{align*}
```

(eq 47)
one of the possible products would arise via the mechanism shown in eq 48. The spectral data would fit structure 131 except for the doublet at 8.83 \( \tau \) integrating to three protons. It is not clear how three protons of 128 would give rise to the simple doublet at fairly high field. Compound 129, a colorless liquid, had virtually identical carbonyl bands in the ir as did 128. However, the nmr was more complex. One vinyl proton appeared as a complex multiplet from 2.8 to 3.5 \( \tau \). At 4.0 \( \tau \) it had a doublet of triplets with coupling constants of 10 Hz for the doublet splitting and 3 Hz for the triplet splitting. As in 128, a multiplet extended from 7.0 to 8.3 \( \tau \). In the high field part of the spectrum two doublets could be seen at 8.75 and 8.82 \( \tau \). The latter signal corresponds to the doublet at 8.83 \( \tau \) found for 128. Although 129 did not contain more than 5% of 128 according to glpc, the spectrum of 129 looked like a mixture of approximately two parts of 128 to one part of a new compound. The latter might have been an isomer of 131 with another geometry at the ring junction. The mass spectrum of 129 showed a parent peak at m/e 164. However, an additional peak amounting to about 15% of the parent peak was located at m/e 181, corresponding to the addition of water to an isomer of 112. Compound 130 which was...
obtained in 1% yield only gave an nmr spectrum which was similar to the spectra of 128 and 129. However, none of the spectra of these three thermal products resembled a tricyclo[3.3.0.0\(^2,6\)]cyclodeca-4,9-dione structure. A thermally allowed cycloaddition of 112 to give 122 or 125 could not be detected and the alternative thermal pathways were not pertinent and promising enough to be further pursued.

C. Thermolysis of cis,cis-Cyclodeca-3,8-diene-1,6-dione (82)

Since even very pure samples of 82 gave rise to a shoulder or even a second peak on gas chromatograms, a thermal reaction of 82 was thought to occur in the injection port of the gas chromatograph. When 82 was thermolyzed in toluene at 145° for two days most of the starting material reacted to give besides probably polymeric compounds one product which was thought to have structure 132, in a yield of 23%.

The reaction leading to 132 is effectively an intramolecular Aldol condensation. Structure 132 is supported by the nmr spectrum which shows a complex multiplet for the four vinyl protons at 4.2 \(\tau\). The bridgehead proton 3a appears quite downfield at 6.2 \(\tau\) as a broad singlet.
The large downfield chemical shift of this proton might be caused by the combined factors of its being allylic, tertiary, and \( \alpha \) to a carbonyl position. The two protons at \( C_5 \) appear as a doublet (\( J = 4 \) Hz) at 6.8 \( \tau \) which corresponds to the chemical shift of the \( \alpha \) proton of a \( \beta,\gamma \)-unsaturated ketone (as in 82). The rest of the protons appear as a multiplet from 7.4 to 7.7 \( \tau \). A sharp peak within this multiplet can be shifted upfield upon dilution and is therefore attributed to the hydroxyl proton. The IR spectrum shows a hydroxyl band at 2.88 \( \mu \) and the carbonyl band at 5.88 \( \mu \), the latter being the same frequency as that measured for 82. The presence of \( \beta,\gamma \)-unsaturated ketone is further supported by the UV spectrum having a maximum at 290 nm with an \( \epsilon \) of 98. This enhanced extinction coefficient is quite characteristic of \( \beta,\gamma \)-unsaturated ketones. Saturated ketones have \( \epsilon \) values of about 20. The geometry of the ring junction could not be determined on the basis of the data obtained. The mass spectrum shows the correct parent peak at m/e 164.

Further evidence for the structure of 132 was obtained by chemical degradation. Hydrogenation of 132 gave ketoalcohol 134 (eq 50). The
nmr spectrum shows the 3a proton as a doublet of triplets ($J_d = 2\text{Hz}, J_t = 7\text{Hz}$) at $6.8\,\tau$. The protons α to the carbonyl function appear at $7.5\,\tau$. The rest of the protons are included in a multiplet from $7.8\,\text{to}\,8.6\,\tau$. The hydroxyl proton can be shifted upfield by dilution. The ir spectrum shows a strong hydroxyl band at 2.91 μ and a carbonyl band at 5.90 μ corresponding to a seven-membered ring ketone.

As a β-hydroxy ketone 134 should be dehydrated easily by base or acid catalysis. Since 83 was known to give 84 upon refluxing in aqueous methanol containing potassium carbonate, the same conditions were used to dehydrate 134. The isolated product was 84 which was independently synthesized via 83 according to known procedures in the first part of this thesis. The ir spectra of the products obtained by these two different ways were superimposable showing a carbonyl band at 6.03 μ. Unfortunately the stereochemistry of the ring junction is lost in the dehydration step. However, the readiness of the dehydration to occur with a relatively weak base like potassium carbonate might indicate a trans ring junction which allows easy trans elimination of water. However, both isomers of 134 have been reported to dehydrate readily in cyclohexane solution in sealed tubes at 212°.
D. Low Temperature Photolysis of cis, trans-Cyclodeca-3,8-diene-1,6-dione

As was pointed out previously, trans,trans-cyclodeca-3,8-diene-1,6-dione (135) is sterically arranged to undergo cycloaddition to give 122 (eq 52).

In order to be able to trap 135, pathway (a) has to be favored over pathway (b). Also, reaction (e) should not be much faster than (b). Step (d) requires a fair amount of thermal activation energy for ring closure of the vibrationally deactivated biradical 126. However, the back reaction (c) has probably a lower activation energy since $E_a$ for the tetramethylene biradical 136 is smaller than $E_b$. 50
It was therefore thought that at low temperatures biradical 126 which is analogous to 136 might not close to give 122 but rather revert to give starting material 112. The latter would then react via path (b) to give the trans,trans-diketone 135. Subsequently, 135 would cycloadd to give 122 in step (e) which would probably be concerted and not temperature dependent.

Photolysis of 112 at 77°K in EPA (ether, iso-pentane, and ethanol) which forms a clear glass, gave rise to the tricyclic ketone 122 as the major product. To a lesser degree 112 isomerized back to the cis,cis-diketone 82. The rate of reaction at 77°K was slowed down compared to the run under the same conditions at room temperature by a factor of about eight. The products formed were compared by co-injection of authentic compounds into the gas chromatograph and by comparison of R_f values on tlc.

It might be that the trans,trans isomer 135 would not be very stable because of π-electron repulsions. These were found to determine the stability of the isomers of 1,6-cyclodecadienes. Isomerization experiments on these compounds by means of photochemically produced benzenethiy radicals to give thermodynamic product distributions
showed 96% cis,cis-isomer, 3.8% cis,trans isomer and no trans,trans isomer. The cis,cis isomer can avoid $\pi$-electron repulsion by a chair like conformation whereas the trans,trans isomer cannot. The chair conformation 124 was also found to be more stable than the boat conformation 123 in the case of cis,cis-cyclodeca-3,8-diene-1,6-dione. 41

![Diagrams](54)

E. Configuration of Tricyclo[5.3.0.0\(^2\),6\]dec-4,9-dione

(a) Dipole Moment

A _syn_ structure 125 was assigned by Shani to the final product of the photolysis of cis,cis-cyclodeca-3,8-diene-1,6-dione (82). 42 However, Scheffer and Lungle and Stankorb and Conrow assigned the _anti_ structure 122 (cf. Introduction). 36,43 To add further proof to the configuration, a dipole measurement was carried out. 52 The _anti_ configuration having a centre of symmetry was expected to give rise to a very small dipole moment, whereas the _syn_ diketone 125 would probably have a large dipole moment.

The moment measured turned out to be 1.45 D. This relatively high dipole moment ($\mu$ cyclopentanone = 2.89 - 3.03) may be caused by conformational distortions in the molecule. 53 This is not very unusual
since centrosymmetric molecules like 137, 138 and 139 have dipole moments in the same range as 122.\textsuperscript{54,55,56} The large dipole moment of 1,4-cyclohexadione has been assigned to the importance of boat structure 140.

\begin{align*}
\text{137} & : \mu = 1.26 \text{ D} \\
\text{138} & : \mu = 1.19 \text{ D} \\
\text{139} & : \mu = 1.09 \text{ D} \\
\text{140} &
\end{align*}
The dipole moment of 122, 1.45 D, while somewhat higher than expected, does not rule out the centrosymmetric anti geometry of 122.

(b) **Vibrational Spectroscopy**

Vibrational spectroscopy provides a tool to distinguish centrosymmetric from non-centrosymmetric molecules. The Rule of Mutual Exclusion states that for centrosymmetric molecules a vibrationally active infrared transition cannot be active in the Raman and *vice versa* for active Raman transitions. Therefore no coincidences should be observed between the two spectra for centrosymmetric molecules. However, in large molecules the possibility for accidental coincidences increases because of the great number of vibrations and the occurrence of combinations and overtones. Nevertheless, it has been found that the difference in the number of coincidences in the spectra of centrosymmetric vs. non-centrosymmetric molecules is significant enough for not too complex molecules to allow the determination of their symmetry. In the case of photodimers 124 and 141 of cyclopentenone six coincidences were found for 124 and twenty-six for 141.

![Molecules](image)

Proceeding to larger molecules like 142 and 143 one finds ten coincidences for 142 and sixteen for 143. This difference is not sufficiently great to allow an unambiguous symmetry assignment.
The tricyclic diketone 122 should be small enough to allow a clear determination of its symmetry. Two bands were considered to be coinciding if they were lying within a range of five wavenumbers, since the accuracies of the ir and Raman spectrophotometer were 2-3 cm$^{-1}$ each. Out of twenty distinct bands in the Raman and twenty-six bands in the ir spectrum, seven coincidences were found. This compares well with the six coincidences found for the centrosymmetric cyclopentenone dimer 124. As a result of this, the anti configuration 122 is once more supported.
EXPERIMENTAL

General

Infrared (ir) spectra were recorded on Perkin-Elmer Model 137 and Model 700 spectrophotometers using sodium chloride cells. Nuclear magnetic resonance (nmr) spectra were recorded by Miss P. Watson and Mr. R. Burton of this department on the following spectrometers: Varian Model A-60, T-60, and HA-100, and Jeolco Model C-60H. TMS was used as an internal standard. Ultraviolet (uv) spectra were recorded on a Unicam Model SP 800 B spectrophotometer using methanol as solvent unless otherwise indicated. An AEI-MS-9 spectrometer was used for mass spectra, recorded by Mr. G.D. Gunn of this department. Micro-analyses were performed by Mr. P. Borda of this department. Melting points were determined on a Fisher-Johns melting point block and are all uncorrected. For gas liquid partition chromatography (glpc) Varian Aerograph Model 90 P and Varian Aerograph Autoprep Model A 700 were used. Both were connected to Honeywell Electronik 15 strip chart recorders. The flow rate of helium as the carrier gas was approximately 60 ml/min. The following analytical columns (5' x 1/4") were used: 20% SE-30 on 60/80 Chromosorb W A/W DMCS, (column A); 3% SE-30 100/120 Varaport 30,(column B); 5% QF-1 60/80 Chromosorb W, (column C); 20% DEGS 60/80 Chromosorb W, (column D). The column temperatures are given in parentheses after the column specifications. For column
Chromatography silica gel (<0.08 mm) from E. Merck AG, Darmstadt was used under 5-10 psi nitrogen pressure. Thin layer chromatography (tlc) plates were developed in iodine chambers and prepared with Silica Gel G for tlc acc. to Stahl (10-40 μ). Photolyses were performed by means of a 450 watt medium pressure Hanovia lamp placed in a water-cooled quartz immersion well. All solutions were degassed at least 15 min. prior to photolysis with L grade nitrogen or argon. Unless otherwise mentioned, all organic compounds used were reagent grade.

Epoxidation of 3,4,5,6-Tetrahydro-1(2H)-pentalenone (41)

The starting material was a gift from the "Badische Anilin und Soda Fabrik" (BASF) to which the author would like to express his gratitude. Pentalenone 41 was recrystallized from low boiling petroleum ether at approximately -30° under nitrogen. The initial impurities could be reduced to 1-2% (checked by glpc, column A, 149°). The ir spectrum of a purified sample was identical with the one reported by Cope. 58

For the epoxidation, the procedure of Wasson and House was used. 19 A solution of 1.493 g (12.2 mmol) of purified 41 and 3.8 ml (37 mmol) of 30% hydrogen peroxide in 12 ml methanol was cooled to 15° by means of an ice bath. To this solution 1 ml of 6 N sodium hydroxide was added dropwise with stirring over a period of three hours. During the addition the temperature of the reaction mixture was maintained at 15-20° with a bath of cold water. After the addition was complete, the temperature was kept at 20-25°. The reaction was monitored by uv. After 3.5 hr the band of the unsaturated ketone at 240 nm had disappeared. All the glassware used for the work-up was washed with alkaline water.
prior to use. The water used for washing the organic layers was also rendered alkaline by adding a drop of 6 N sodium hydroxide to it. After the reaction was complete the resulting mixture was poured into 15 ml of cold water and extracted with $2 \times 15$ ml of cold ether. The organic layers were washed with 20 ml of water and dried over magnesium sulfate at 0° and subsequently concentrated in vacuo. This extraction procedure was repeated with $2 \times 15$ ml of chloroform. The combined concentrated layers gave 1.135 g (8.24 mmol, 68%) of hexahydro-3a,6a-epoxy-1(2H)-pentalenone (42), a colorless liquid which crystallized at approximately 0°; ir (CHCl$_3$) 5.78 (C=O) μ; nmr (CDCl$_3$) $\tau$ 7.2-8.1 (m); uv max (ethanol) 300 nm; mass spectrum (70 eV) m/e parent 138.

Photolysis of Hexahydro-3a,6a-epoxy-1(2H)-pentalenone (42)

A solution of 1.007 g of 42 in 400 ml of benzene was degassed and photolyzed using a Pyrex filter. The reaction was followed by glpc (column A, 130°). After 30.5 hr most of the starting material had disappeared and four major products were formed (A, B, C, and D in the order of increasing retention time; the respective ratios were 2:2:10:3). Half of the reaction mixture was concentrated under vacuum and the product collected by glpc (column A, 130°). Compound A was obtained in the form of colorless needlelike crystals (6 mg, 1% by weight): ir (CHCl$_3$) 5.57 (s, C=O), 5.80 (sh, C=O), 5.85 (s, C=O) μ. Compound B (5 mg, 1% by weight), a colorless liquid, consisted of three different products when checked by reinjection into the gas chromatograph. Compound C was a colorless liquid (24 mg, 5% by weight); ir (CHCl$_3$) 5.57 (s, C=O), 5.75 (s, C=O) μ; nmr (CDCl$_3$) $\tau$ 7.36 (center
of m, 6), 7.7-8.3 (broad m, 4). Compound D was a colorless liquid (8 mg, 1.5% by weight); ir (CHCl₃) 5.80-5.93 (m, C=O), 6.15 (s) μ. Compound C partly decomposed on standing for three days at 0° to a compound having the same retention time (glpc) as A.

**Photolysis of Octahydro-4a,8a-epoxy-1(2H)-naphthalenone (49)**

The author expresses his gratitude to J. Balf of this department for a sample of 49.

A solution of 44 mg (0.26 mmol) of epoxy ketone 49 in 7 ml of dioxane (dried over molecule sieve 5A) was degassed and photolyzed using a Corex filter. The reaction was monitored by glpc (column B, 115°), and after 8.5 hr one product was formed and all starting material had disappeared. After concentration in vacuo and collection by glpc (column B, 115°), 7 mg of a colorless liquid (50) was obtained. No decomposition had occurred since reinjection of 50 gave the same single peak as obtained in the collection; ir (film) 5.73 (s, C=O), 5.76 (sh), 5.88 (s, C=O) μ; nmr (CDCl₃) τ 7.3-8.6 (m); mass spectrum (70 eV) m/e parent 166. The compound was checked after the nmr spectrum had been recorded and it was found that about 10% had decomposed to give a second peak on glpc (column B, 115°).

**Epoxidation of 2,3,5,6,7,8-Hexahydro-4(1H)-azulenone (84)**

For the synthesis of 84 from 1,6-cyclodecadione see Experimental of the second part of this thesis.

The same procedure was followed as in the epoxydation of 41 using 252 mg (1.68 mmol) of 84 in 6 ml of methanol, 90 mg (2.25 mmol) of
sodium hydroxide in 0.5 ml of water, 2 ml of methanol, and 2 ml of 30% hydrogen peroxide (19.5 mmol). The reaction was followed by uv and was complete after 6 hr. After work-up, 273 mg (1.64 mmol, 98%) of octahydro-3a,8a-epoxy-4(1H)-azulenone (80) was obtained as a colorless liquid; ir (film) 5.91 (s, C=O) μ; uv max (cyclohexane 303 nm (ε 20, n–π*). The gas chromatogram (column B, 101°) showed one peak only.

Photolysis of Octahydro-3a,8a-epoxy-4(1H)-azulenone (80)

A solution of 50 mg (0.30 mmol) of epoxy ketone 80 in 7 ml of dioxane (dried over molecular sieve 5A) was degassed and photolyzed using a Corex filter. The reaction was followed by glpc (column B, 101°) and was stopped after 78 hr. At this point glpc showed that starting material had been completely consumed and a small amount of a new product had been formed. Its peak on glpc was very broad. However, it could be sharpened by dissolving the concentrated photolysis mixture in low boiling petroleum ether. The soluble part was concentrated in vacuo and the product collected by glpc (column B, 101°) to give 1.5 mg of a colorless liquid; ir (film) 5.71 (s, C=O), 5.82 (s, C=O) μ. A reinjected and collected sample showed two minor peaks at very long retention times.

2-Cyclopentylidene-cyclopentanone (55)

The procedure of Huckel was followed. To 50 g (0.595 mole) of cyclopentanone dissolved in 100 ml of ethanol a solution of 3.6 g potassium hydroxide in 45 ml of water was added. The resulting mixture turned dark red during the four days it was allowed to stand at 0°.
After concentration under vacuum, the solution was extracted with ether and the organic layers dried over magnesium sulfate. Concentration in vacuo gave 43.0 g of a dark red liquid, 24 g of which were distilled under vacuum to give 14.4 g (0.096 mole, 58%) of 2-cyclopentylidene-cyclopentanone (bp 88-90°/0.3 mm); ir (film) 5.85 (s, C=O), 6.10 (s C=C) μ; nmr (CCl₄) τ 7.3-8.4 (m); mass spectrum (70 eV) m/e parent 150; oxime mp 125° (lit. 126.5°). Thin layer chromatography (20% ether/chloroform) showed one spot. Glpc (column D, 150°) showed one peak only. The compound had to be injected with solvent. Otherwise it seemed to decompose since it gave rise to numerous broad peaks.

2-Cyclopentylidene-cyclopentanol (73)

A procedure which was successful in the reduction of mesityl oxide was used. A solution of 511 mg (3.4 mmol) of 2-cyclopentylidene-cyclopentanone in 5 ml of dry ether was added to 67 mg (1.97 mmol) of lithium aluminum hydride in 5 ml of dry ether so as to maintain gentle reflux. After 5 min, excess lithium aluminum hydride was cautiously destroyed with ice water, and more water (20 ml) added. The aqueous slurry was washed with 3 x 7 ml of ether and the ether layers washed, dried over magnesium sulfate, and concentrated in vacuo to give 462 mg (3.04 mmol, 90%) of colorless crystalline 73, mp 53-55° (lit. 50°); ir (CCl₄) 2.78-3.02 (OH) μ; nmr (CCl₄) τ 5.61 (broad s, 1, HC(OH)CH=C=), 7.40 (s, 1, OH), 7.50-8.10 (m, 6, allylic methylene), and 8.10-8.50 (m, 8, methylene). Thin layer chromatography (50% chloroform/ether) showed one spot which turned green by developing in iodine.
2-Cyclopentylidene-cyclopentanol oxide (74)

A solution of 372 mg (2.45 mmol) of 2-cyclopentylidene-cyclopentanol in 3 ml of chloroform was cooled to 0° and 555 mg (3.21 mmol) of m-chloroperbenzoic acid in 10 ml of chloroform added in 1 ml aliquots every ten minutes with stirring. Ten minutes after the last addition the reaction mixture was washed with 10 ml of a saturated sodium bicarbonate solution and subsequently with 10 ml of water. After drying over magnesium sulfate and concentration in vacuo 407 mg (2.42 mmol, 99%) of 2-cyclopentylidene-cyclopentanol oxide, a slightly yellow liquid, was obtained. Thin layer chromatography (50% benzene/ethyl acetate) showed one major spot and a faint minor spot having a smaller R_f value; ir (film) 2.94 (OH, s); 5.90 (w, C=O) μ; nmr (CCl_4) δ 6.2 (t, 1, J = 5 Hz, HC(OH)<), 7.2 (s, 1, OH), 7.8-8.6 (m, 14). This compound partially decomposed after standing at 0° for 14 days. (The ir band at 5.90 μ had very much increased in intensity.) Glpc (column B, 101°) of the decomposed compound showed two major and 4 minor peaks.

Dipyridine-chromium(VI) oxide Complex

A total of 5 g of chromium(VI) oxide (dried over phosphorus pentoxide) was added in small portions to 40 ml of anhydrous pyridine with stirring at 15-20°. Caution: adding pyridine to chromium(VI) oxide results in inflammation. The stirring was continued until the initially yellow precipitate turned red (after a few hours). The complex was isolated by washing several times with low boiling petroleum ether, filtration, and drying at about 10 mm pressure (higher vacuum causes surface decomposition).
Oxidation of 2-Cyclopentylidene-cyclopentanol Oxide (74)

The oxidation procedure of Collins was applied.\textsuperscript{27} A solution of 100 mg (0.595 mmol) of 74 in 5 ml of methylene chloride was added to a slurry of 960 mg (3.72 mmol) of the complex in 20 ml of methylene chloride. The resulting mixture was stirred for one hour, excluding any moisture by means of an attached drying tube. After washing with water and sodium bicarbonate the mixture was treated with Norit, filtered, dried, and concentrated \textit{in vacuo} to give 60 mg of products. Thin layer chromatography (50% benzene/ethyl acetate) showed 2 spots, one of them being an impurity already present in the starting material. Glpc (column B, 101° and C,95°) showed one major (\textgapprox 40%) and several minor peaks; ir (CHCl\textsubscript{3}) 5.72 (m, C=O), 5.79 (m, C=O), 5.86 (sh, C=O), 5.90 (m, C=O) \textmu; structureless fingerprint region bands. Due to lack of starting material and to the difficulty encountered in this oxidation, this synthetic sequence was abandoned.

Photolysis of \textit{cis},\textit{cis}-Cyclodeca-3,8-diene-1,6-dione in the Presence of Piperylene as a Quencher

Three runs were done with different piperylene concentrations. The diketone 82 (synthesis see ref. 28) was dissolved in benzene, except in run 3, and piperylene (tech. grade, distilled under nitrogen) was added, the resulting mixture degassed for 15 min and photolyzed using a Pyrex filter and the external photolysis flask. The latter consisted of a test-tube like flask made of quartz glass. For the photolysis this flask was clamped close to the regular immersion well and both were surrounded by a water filled beaker which provided the
cooling of the external flask. The reaction was followed by glpc (column A, 150°). Authentic cis,trans-cycloocta-3,8-diene-1,6-dione and cis,anti,cis-tricyclo[5.3.0.0²,6]decane-4,9-dione had identical retention times as the products formed in the presence of piperylene. They were formed in approximately the same ratio as in the direct photolysis.

<table>
<thead>
<tr>
<th>weight of 82</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>50 mg</td>
<td>33 mg</td>
<td>8 mg</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>benzene</th>
<th>6 ml</th>
<th>16 ml</th>
<th>-</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>piperylene</th>
<th>400 mg (6 mmol)</th>
<th>2.70 g (40 mmol)</th>
<th>2.03 g (30 mmol)</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>molarity of 82</th>
<th>0.047</th>
<th>0.01</th>
<th>0.016</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>molarity of quencher</th>
<th>0.94</th>
<th>2.0</th>
<th>10.0</th>
</tr>
</thead>
</table>

<table>
<thead>
<tr>
<th>reaction time (until no 82 left)</th>
<th>~1.5 hr</th>
<th>~1 hr</th>
<th>~1.5 hr</th>
</tr>
</thead>
</table>

Photolysis of cis,cis-Cycloocta-3,8-diene-1,6-dione (82) in the Presence of Benzophenone as a Sensitizer

A solution of the diketone 82 225 mg (1.37 mmol) and 1.00 g (5.5 mmol) of benzophenone were dissolved in 15 ml of benzene in the external photolysis flask. Between the latter and the immersion well a Corning filter was introduced (C.S. Number 0-52, glass number 7380) absorbing all the light at λ < 340 nm. The diketone has no absorption at λ > 340 nm in benzene. The uv spectrum of benzophenone was measured in benzene uv max 344 nm (ε 240). The photolysis of the degassed solution was followed by glpc (column A, 150°) and tlc. The two products formed were identical according to glpc and tlc (70% ether/n-hexane) to the
ones formed by photolysis in benzene using a Pyrex filter and no sensitizer. After 22 hr of photolysis, when no starting material was left, the solvent was evaporated. Most of the benzophenone could be removed by extracting the crude reaction mixture with n-hexane. The insoluble part (268 mg) was separated on a chromatography column (60% ether/n-hexane). From this 50 mg of cis,anti,cis-tricyclo[5.3.0.0\(^2\),6]-decane-4,9-dione could be isolated. The ir and nmr spectra as well as the melting point of this material were identical with those of authentic material. The cis,trans intermediate 112 never exceeded 5% of total reactants during the photolysis. This made it difficult to isolate it. What was isolated after column chromatography was a mixture of the intermediate and the final product 122 according to tlc (60% ether/hexane). The ir spectrum of this mixture showed a carbonyl band at 5.88 \(\mu\) corresponding to the carbonyl band of cis,trans diketone 112. A shoulder at 5.78 \(\mu\) corresponded to the tricyclic diketone 122 present according to tlc. The fingerprint region was not superimposable with the spectrum of authentic cis,trans diketone 112. However, it showed the 14.1 \(\mu\) band, a strong band in the spectrum of cis,trans diketone 112.

In order to make sure that no reaction occurred without sensitizer, 35 mg of 82 were photolyzed in 10 ml of benzene under the same conditions as with the sensitizer present. Even after 6 hr photolysis no reaction had taken place according to glpc (column A, 151°).

**Thermolysis of cis,cis-Cyclodeca-3,8-diene-1,6-dione (82)**

A solution of 234 mg of 82 in 10 ml of toluene was kept at 145° for two days in a sealed Pyrex tube in a sublimation apparatus. The
resulting brown solution was treated with Norit and extracted with low boiling petroleum ether in order to separate polymeric materials formed in the reaction. Thin layer chromatography (50% ethyl acetate/chloroform) showed one product and a faint spot corresponding to starting material. The petroleum ether soluble portion was concentrated under vacuum. After column chromatography (50% ethyl acetate/chloroform) 53 mg (23%) of 3a,5,8,8a-tetrahydro-8a-hydroxy-4(1H)-azulenone (132) was obtained as a colorless liquid; ir (film) 2.88 (m, OH), 5.88 (s, C=O) μ; nmr (CDCl₃) τ 4.2 (m, 4, vinyl H), 6.2 (broad s, 1, C₃₈-CH), 6.8 (d, 2, J = 4 Hz, (C(5)-CH₂-), 7.4-7.7 (m, 5); uv max 290 nm (ε 98); mass spectrum (70 eV) m/e parent 164.

Hydrogenation of 3a,5,8,8a-Tetrahydro-8a-hydroxy-4(1H)-azulenone (132)

A solution of 53 mg (0.32 mmol) of 132 in 10 ml of ethyl acetate was hydrogenated using 4 mg of platinum oxide as a catalyst. After 3 hr, tlc (50% ethyl acetate/chloroform) showed that all the starting materials had been converted into one hydrogenated product with an Rf value slightly greater than the one of the starting material. After concentration in vacuo, 53 mg (0.32 mmol, >99%) of octahydro-8a-hydroxy-4(1H)-azulenone (134) was obtained as a colorless liquid, ir (film) 2.91 (s, OH), 5.90 (s, C=O) μ; nmr (neat) τ 6.8 (d of t, 1, J₉ = 2 Hz, J₉₈ = 7 Hz, -CO-C(3a)H, bridgehead), 7.5 (m, 2,-C(5)H₂-CO-), 7.8-8.6 (m, 13). The presence of a hydroxyl proton was verified by the dilution technique.
Dehydration of Octahydro-8a-hydroxy-4(1H)-azulenone (134)

A solution of 35 mg (0.21 mmol) of 134 in 5 ml of aqueous methanol containing about 10 mg of potassium carbonate was refluxed for 0.5 hr. Thin layer chromatography (50% ethyl acetate/chloroform) showed one dehydrated product with a greater R_f value than starting material. The reaction mixture was extracted with chloroform and after concentration of the organic layers in vacuo, 17 mg (0.11 mmol, 50%) of 2,3,5,6,7,8-hexahydro-4(1H)-azulenone (84) was isolated as a colorless liquid; ir (film) 6.03 (s, C=O), 6.07 (s), 6.14 (s) μ; nmr (CDCl₃) δ 7.4 (m, 8, -CH₂CO- and allylic -CH₂-), 8.2 (m, 6, -CH₂-); uv max 252 nm (calculated according to the Woodward rules 249 nm). This azulenone was prepared independently following a known procedure (see below) and the ir spectra of the two independently synthesized azulenones were superimposable.

Hydrogenation of cis,cis-Cyclodeca-3,8-diene-1,6-dione (82)

A solution of 227 mg (1.38 mmol) of cis,cis-diketone 82 in 20 ml of ethyl acetate was subjected to hydrogenation using 4 mg of platinum oxide as a catalyst. Hydrogen take-up was 60 ml corresponding to 97% of the theoretical amount. After filtration of the reaction mixture and concentration under vacuum 226 mg (1.36 mmol, 99%) of crude cyclo­deca-1,6-dione (83) was isolated. Recrystallization from ethanol gave 120 mg (53%) of 83 as colorless crystals. Thin layer chromatography (60% ether/hexane) showed one pure compound.
2,3,5,6,7,8-Hexahydro-4(1H)-azulenone (84)

The procedure of Cope was followed. A solution of 120 mg (0.71 mmol) of cyclodeca-1,6-dione (83) in aqueous methanol containing about 10 mg of potassium carbonate was refluxed for about 1 hr. The reaction mixture was extracted three times with chloroform and the combined organic layers were dried and concentrated to leave 70 mg (0.47 mmol, 66%) of a slightly yellow liquid 84. The ir spectrum was superimposable with that of the azulenone obtained by dehydration of 134 (see above).

Thermolysis of cis,trans-Cyclodeca-3,8-diene-1,6-dione (112)

A solution of 233 mg (1.42 mmol) of 112 in 10 ml of xylene (bp 138-139°) was sealed in a Pyrex tube under atmospheric pressure. It was thermolized in a sublimation apparatus for five days at 192°. The resulting dark brown solution was concentrated under vacuum and checked by glpc (column D, 170°). Most of the starting material had reacted and three products (128, 129 and 130 in the order of increasing retention time) had been formed in a ratio of approximately 6:3:1. They were collected by glpc (column D, 150°). Compound 128 gave 18 mg of colorless crystals; mp 125°; ir (CHCl₃) 5.72 (s, C=O), 5.95 (s, C=O) μ; nmr (CDCl₃) τ 2.98 (d of d, 1, J₁ = 10 Hz, J₂ = 2 Hz), 4.00 (d of d, 1, J₁ = 10 Hz, J₂ = 3Hz), 7.0-8.3 (complex m, 9), 8.83 (d, 3, J = 6 Hz); uv max 226 nm (ε 14,000); mass spectrum (70 eV) m/e 45(100), 81(79), parent 164(24), 211(2).

Anal. Calcd. for C₁₀H₁₂O₂: C, 73.14; H, 7.37. Found: C, 71.65; H, 7.22 (error for C: 2.04%, for H: 2.04%).
Compound 129 was obtained as a colorless liquid, 10 mg; ir (film) 5.74 (s, C=O), 5.97 (s, C=O) μ; nmr (CDCl₃) τ 2.8-3.5 (complex m, 1), 4.0 (d of t, 1, J₆ = 10 Hz, J₇ = 3 Hz), 7.0-8.3 (m, 7), 8.75 and 8.82 (2d, 3, J₁ = J₂ = 6 Hz); mass spectrum (70 eV) m/e 81(100), parent 164(49), 181(7).

Only 3 mg of 130 could be collected as a colorless liquid; nmr (CDCl₃) τ 3.9 (m, 1), 7.0-8.0 (m, 12), 8.8 (d, 3, J = 6 Hz).

Photolysis of cis,trans-Cyclodeca-3,8-diene-1,6-dione (112) at 77°K

The solvent chosen for this photolysis was EPA, a mixture of ether, isopentane, and ethanol in a ratio of 5:5:2 which freezes as a glass at the temperature of liquid nitrogen. Because of solubility problems less polar solvents could not be used. A mixture of isopentane/n-pentane (5:2, freezes as a glass) and pure Freon 12 (dichlorodifluoromethane) had been tried but the dissolved diketone 112 precipitated at 77°K in the pentane mixture and was hardly soluble in Freon 12 even close to the latter's boiling point at -33°. The solutions tried were 0.02 M in the case of Freon 12 and 0.0024 M in the pentane mixture.

A solution of 40 mg (0.24 mmol) of 112 in 100 ml of EPA was degassed for 15 min and photolyzed in a large Pyrex finger (used as a cool trap for vacuum pumps). The immersion well containing a Pyrex filter was equipped with the 200 ml photolysis flask and the whole set-up including the external Pyrex finger was immersed in liquid nitrogen. Gaseous nitrogen was flushed through the 200 ml flask attached to the immersion well in order to prevent water from the air to condense and freeze on the flask walls. Furthermore the gaseous nitrogen prevented
the cooling water from freezing.

The reaction was followed by glpc (column A, not acid washed, 135°) and tlc (chloroform/ether 1:1). After 8 hrs about 10% of the tricyclic ketone 122 and about 5% of cis,cis-diketone 82 were formed according to the retention time of the gas chromatogram, checked by coinjection of authentic 122 and 82. The thin layer chromatogram showed the two spots corresponding to 122 and 82.

Photolysis of 112 in EPA at Room Temperature

A solution of 17 mg (0.104 mmol) of 112 in 43 ml of EPA was degassed and photolyzed in the same set-up used for the photolysis at 77°K. After 1 hr about 10% of 112 had reacted to give the tricyclic diketone 122 according to glpc (same conditions as in the 77°K photolysis). No cis,cis diketone 82 could be observed by glpc.

Dipole Moment of cis,anti,cis-Tricyclo[5.3.0.02,6]decane-4,9-dione

This measurement was carried out in the laboratory of Professor N.L. Allinger of the University of Georgia.\(^{52}\)

\[ \mu = 1.45 \pm 0.3 \text{ (25°C; solvent: benzene).} \]

Raman and Infrared Spectra of cis,anti,cis-Tricyclo[5.3.0.02,6]decane-4,9-dione

The Raman spectrum of a crystal of the tricyclic diketone was obtained with a Cary Model 81 Raman spectrophotometer, using the 6328 Å exciting line of a helium neon laser.\(^{61}\) Accuracy: \( \pm 2-3 \text{ cm}^{-1} \).
The IR spectrum was recorded on a Perkin-Elmer Model 21 double Beam Infrared Spectrophotometer. (Accuracy: at 4000 cm$^{-1}$: ±20 cm$^{-1}$; at 650 cm$^{-1}$: ±1.5 cm$^{-1}$).

<table>
<thead>
<tr>
<th>Raman [cm$^{-1}$]</th>
<th>IR [cm$^{-1}$]</th>
<th>Raman [cm$^{-1}$]</th>
<th>IR [cm$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>287</td>
<td>1005</td>
<td>-</td>
<td>1002</td>
</tr>
<tr>
<td>339</td>
<td>1024</td>
<td>-</td>
<td>1028</td>
</tr>
<tr>
<td>429</td>
<td>1060</td>
<td>439</td>
<td>1076</td>
</tr>
<tr>
<td>457</td>
<td>1083</td>
<td>472</td>
<td>1116</td>
</tr>
<tr>
<td>480</td>
<td>1136</td>
<td>554</td>
<td>1142</td>
</tr>
<tr>
<td>620</td>
<td>1150</td>
<td>638</td>
<td>1166</td>
</tr>
<tr>
<td>683</td>
<td>1243</td>
<td>749</td>
<td>1240</td>
</tr>
<tr>
<td>-</td>
<td>748</td>
<td>790</td>
<td>1252</td>
</tr>
<tr>
<td>-</td>
<td>792</td>
<td>826</td>
<td>1268</td>
</tr>
<tr>
<td>-</td>
<td>825</td>
<td>850</td>
<td>1290</td>
</tr>
<tr>
<td>879</td>
<td>1329</td>
<td>-</td>
<td>1328</td>
</tr>
<tr>
<td>927</td>
<td>1354</td>
<td>950</td>
<td>1360</td>
</tr>
<tr>
<td>1402</td>
<td>1393</td>
<td>1729</td>
<td>1718</td>
</tr>
</tbody>
</table>
BIBLIOGRAPHY

17. The author gratefully acknowledges a gift of this compound by J. Balf of this department.
30. R. Srinivasan and K.H. Carlough, ibid., 89, 4932 (1967);


52. The author is indebted to Prof. N.L. Allinger for carrying out the dipole measurement.


61. The author is very much indebted to Dr. A. Bree of this department for the recording of a Raman spectrum.