PHOTOCHEMISTRY OF TRIPHENYL METHYL CYCLOPENTADIENE
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OF
TRIPHENYLMETHYLCYCLOPENTADIENE

By
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The products and mechanism of the photolytic rearrangement of the equilibrium mixture of triphenylmethylcyclopentadienes have been studied. Direct irradiation of the equilibrium mixture of triphenylmethylcyclopentadienes yields 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene. Photolysis with a triplet sensitizer yields dimeric products in addition to 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene. Thermolytic isomerization of 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene is reported. The predominant isomer in the equilibrium mixture of triphenylmethylcyclopentadiene has been established as 2-triphenylmethylcyclopentadiene.
ACKNOWLEDGEMENTS

It is a pleasure to express my gratitude for the contribution made to this thesis by the following people:

Dr. J. Warkentin for his guidance and advice throughout the course of this investigation. I also wish to thank him for his warm hospitality.

Mr. B. Sayer for obtaining many of the n.m.r. spectra and for his valuable discussions.

My wife, Irene, for her understanding over the years.
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CHAPTER 1

INTRODUCTION
Cyclopentadiene is a simple hydrocarbon containing two conjugated double bonds in the planar five membered carbocycle.

As early as 1936, it was recognized by Alder and Holzrichter that alkylcyclopentadienes are comprised not only of 5-alkylcyclopentadienes but mainly of a mixture of 1- and 2-alkylcyclopentadienes. An attempt to unravel the precise mechanism for this intricate product formation was not undertaken until recent years.

Miranov observed that 5-deuterocyclopentadiene was the initial product of the substitution reaction, and during the establishment of equilibrium changed first into 1-deuterocyclopentadiene, then into a mixture of 2, 3, and 2-deuterocyclopentadiene, in the proportion of 1:1:1.

Alkylcyclopentadienes, on the other hand, are mainly mixtures of 1- and 2-isomers. Hydrogen migration in methylcyclopentadiene, the
simplest derivative of cyclopentadiene, has been most extensively studied by McLean et al. (4). At ambient temperature vinylic isomers 6 and 7 predominate with their ratio being 0.82:1 respectively; 5 constitutes 1% or less of the equilibrium mixture. Formation of adducts of each diene with N-phenylmaleimide served to corroborate the structural assignments made for the separated components. They concluded that the equilibrium between the double bond isomers is established via an intramolecular 1,2-hydrogen shift. In terms of orbital symmetry rules of Woodward and Hoffmann, (5) the thermally induced hydrogen migration can be regarded as an example of {1,5} sigmatropic rearrangement.

Phenyl substituted methylcyclopentadienes, such as triphenylmethylcyclopentadiene, have been little investigated. In the isomeric mixture of triphenylmethylcyclopentadiene, the predominance of 1- and 2-triphenylmethylcyclopentadiene, 8 and 9 respectively, was substantiated by R. Riemschneider and co-workers. (6) H. Werner confirmed the composition of the isomeric mixture and established an isomer ratio of 3.8:1 on the basis of spectroscopic evidence. An assertion as to whether 8 or 9 is the predominant isomer could not be made due to the exceptionally
complex character of the vinylic $^1$H n.m.r. signals.

(ii) **Photochemical Reactions**

Photosensitized cycloaddition of conjugated dienes has been extensively studied in recent years. Principal developments in this area have resulted from the investigation of Hammond and his co-workers.\(^{(8-12)}\)

The photosensitized cycloaddition of cyclic 1,3-dienes has also been examined.\(^{(9,13)}\) Cyclopentadiene,\(^1\), in the presence of a number of organic sensitizers, gives rise to a mixture of 3 dimers: two stereoisomers of the Diels-Alder type, \(10\) and \(11\), in a ratio quite different from that resulting from thermal dimerization, and one cyclobutane derivative \(\text{trans-}(3.0.3.0)\text{tricyclo}-2,8\)-decadiene,\(^{12}\). The three products are produced in approximately equal amounts. Hammond and Turro\(^{(9)}\) postulated that this type of cycloaddition proceeds via a biradical intermediate whose spins are unpaired at the moment of formation, but must become paired in order that ring closure to the cycloadduct may occur. Kramer and Bartlett\(^{(14)}\) have carried out the photosensitized addition of cyclopentadiene to \(\text{cis-}\) and \(\text{trans-}\)but-2-ene. The cyclo-
addition yielded mixtures of three stereoisomeric 5,6-dimethylnorbornenes and four stereoisomeric 6,7-dimethylbicyclo[3.2.0]heptenes (scheme 1).

Scheme 1

The mixture of threo and erythro products from cis- and trans-but-2-ene were identical; only the relative amounts of erythro and threo differed. Evidence for the formation of a triplet biradical is the total loss of the original olefin configuration during cycloaddition. The stereochemical randomization must mean that the intermediate exists as a biradical during a number of cycles of intramolecular rotation.

There is no evidence for photosensitized valence isomerization
with these dienes. In contrast, direct excitation of cyclopentadiene

\[
\begin{align*}
\text{1} \quad & \xRightarrow{\text{hv}} \quad \text{15} \\
\text{15} & \xRightarrow{\text{hv sens.}} \quad \text{1}
\end{align*}
\]

results in bicyclo(2.1.0)pent-2-ene, \textit{15}. \textit{(15)}

(iii) \textbf{Di-\textpi-methane Rearrangement}

The photochemical rearrangement of arylpropenes to cyclopropanes in solution was first reported by Griffin in 1965. \textit{(16,17)} These contain a phenyl and a \textit{vinyl} moiety bonded to a single \textit{sp}\textsuperscript{3}-hybridized carbon atom in an acyclic arrangement. The transformation, effected by direct irradiation, involved phenyl migration to yield cyclopropane products \textit{17} and \textit{19}.  

\[
\begin{align*}
\text{16} & \xrightarrow{\text{hv}} \quad \text{17} \\
\text{18} & \xrightarrow{\text{hv}} \quad \text{19}
\end{align*}
\]
The rearrangement has been termed the di-\( \pi \)-methane rearrangement by Zimmerman who first noted its generality in the photochemical conversion of barrelene,\(^{20}\), to semibullvalene,\(^{21}\), using acetone sensitization.\(^{18}\) In an attempt to understand the mechanistic pathway,\(^{19}\) barrelene,\(^{22}\), was labelled at all vinyl positions with deuterium, leaving only the bridgehead positions still bearing hydrogen. A product

distribution of nearly 1:1 ratio of hexadeuteriosemibullvalene labelled
as in 23 and 24 was found. This experimental evidence, in conjunction with theoretical calculations, led to the conclusion that the conversion of barrelene, 20, to semibullvalene, 21, proceeds via a bicyclic allylic, triplet biradical having a finite lifetime. Direct irradiation of 20 afforded the singlet which proceeds instead to cyclooctatetraene.

The structure-multiplicity relationship was first observed by Zimmerman and Mariano (20). They proposed that in systems where free rotation about unconstrained π-bonds can bring about efficient deactivation from their triplet excited states, the di-π-methane rearrangement proceeds via the singlet state. This aspect was clearly demonstrated in the photochemistry of cis- and trans-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene, 25 and 26 respectively (21). Rearrangement of the cis and trans isomer occurred only upon direct irradiation and then with extreme regiospecificity.
In dramatic contrast to the direct irradiation of dienes 25 and 26, triplet-sensitized photolysis led only to efficient cis-trans isomerization, interconverting 25 and 26. Another example substantiating the structure-multiplicity relationship is found in the transformation of 1-methylene-4,4-diphenyl-2-cyclohexene 29, via phenyl migration, in the singlet manifold only. Of the cis and trans bicyclic olefins 30 and 31, the trans diastereomer 30 is the predominant product. (22)

In the absence of any exocyclic π-bonds the triplet di-π-methane reactivity is restored. In accord with this view is the transformation
Scheme 2  Pathways for Di-π-Methane Excited State Deactivation (24)
of the endo-cyclic diene $32$ upon sensitized photolysis, to its corresponding $\pi$-substituted cyclopropane products $33$ and $34$. Direct excitation of $32$ afforded 1,1-diphenyl-1,3,5-hexatriene $35$.

Various exceptions to the behaviour pattern, summarized in Scheme 2, have been recorded. Hähn and Rothman$^{(25)}$ reported the facile conversion of benzo(6,7)bicyclo[3.2.1]octa-2,6-diene,$36$, to benzo(3,4) tricyclo[3.2.1.$0^2,7$]octene,$37$, upon direct or sensitized irradiation. The facility of the unsensitized photochemical transformation of $36$ to $37$ is in marked contrast to the reported failure of benzobarrelene$^{(26)}$ to undergo such rearrangement on direct irradiation. It is possible that the excited singlet state of $36$ directly initiates a di-$\pi$-methane rearrangement, or on the other hand, intersystem crossing and triplet rearrangement could predominate in the absence of an efficient competitive singlet process.

Zimmerman and Pratt$^{(21)}$ first recognized that the controlling factor, for the extreme regiospecificity of the di-$\pi$-methane rearrangement, is maintenance of maximum odd electron stabilization. The photochemistry of cis- and trans-1,1-diphenyl-3,3-dimethyl-1,4-hexadiene,
25 and 26 respectively, not only demonstrated quite explicitly the structure-multiplicity relationship but also the migratory preference. In each case the sole product isolated resulted from a pathway involving migration of the less conjugated $\pi$-moiety to the more conjugated $\pi$ chromophore. One plausible view of the pathway is a concerted transformation formally depicted by orbital representation (Scheme 3). This pathway involves cleavage of bond 3-4 and formation of bonds 1-3 and 2-4 with inversion of configuration at C-3. The transition state for this rearrangement consists of a monocyclic array of six orbitals with one sign inversion and thus is Mebius like. (20) While a Mebius system in a ground state is antiaromatic with six electrons it is aromatic and stable in the excited state. Although bond cleavage and bond formation proceeds in a concerted manner the last overlap (i.e. formation of bond 1-3) lags behind the other bond changes.

Studies by Hixson (27) on migratory aptitudes for an aryl-vinyl

![Scheme 3]

Table 1 Relative rates of rearrangements of substituted 1,3-diphenyl-
propenes

<table>
<thead>
<tr>
<th>Substituents</th>
<th>Relative rate of rearrangement</th>
</tr>
</thead>
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<tr>
<td>X = CN; Y = H</td>
<td>38</td>
</tr>
<tr>
<td>X = H; Y = OCH$_3$</td>
<td>39</td>
</tr>
<tr>
<td>X = H; Y = CN</td>
<td>40</td>
</tr>
<tr>
<td>X = Y = H</td>
<td>41</td>
</tr>
<tr>
<td>X = OCH$_3$; Y = H</td>
<td>42</td>
</tr>
</tbody>
</table>
Scheme 3 Basis Orbital Array

- Old bonds
- Bonds forming
- Bond forming late in reaction
systems showed that those having p-methoxyphenyl and p-cyanophenyl groups have excited singlets which rearrange more rapidly than that of the parent compound. This is consistent with a rearrangement in which the migrating group moves to an odd electron center. The relative rates of migration are shown in Table 1. To rationalize the directionality of this transformation qualitative resonance reasoning has been successfully employed, but it has to be recognized that the biradical species are only useful in depicting odd electron disposition along the reaction coordinate.

Triplet di-π-methane rearrangements also show regiospecificity, but the factors which control migratory preferences appear more complex than those of the singlet reorganization reactions. The migratory aptitude in many cases can be explained in terms of energy minimization by interaction between the π-moieties. Other factors such as odd electron stabilization and stabilization of intermediate diradicals are also capable of controlling the regiospecificity in π-migration.

An important aspect of the di-π-methane rearrangement is its stereochemistry and its relationship to the mechanism of this excited state process. Zimmerman and co-workers have noted that the major pathway in the singlet excited-state chemistry of 29 involves inversion at C-3 and requires anti-disrotatory three-ring formation. Further investigations by Zimmerman and Mariano indicated that the configurational integrity about the π-bond in the migrating moiety is maintained and cyclopropane ring formation between C-3 and C-5 during rearrangement must occur exclusively with disrotatory overlap of the
orbitals involved, anti to the migrating group. All these examples support the concerted mechanism for the singlet di-π-methane processes.

Although the stereochemistry of the triplet di-π-methane rearrangement has not been extensively investigated, it seems from the few examples at hand that the process in the triplet manifold proceeds also with stereospecificity in C-3, C-5 ring closure. (23)

(iv) Vinylcyclopropane Rearrangement

Vinylcyclopropane isomerization in general and bicyclo(3.1.0) hex-2-ene rearrangements specifically are of current interest to both thermal kineticists and photochemists. (33, 34)

The first recorded example of the thermal vinylcyclopropane rearrangement is the skeletal rearrangement of 1,1-dichloro-2-vinylcyclopropane to a mixture of chlorocyclopentadienes. (35) Subsequently Vogel et al (36) and Overberger and Borchert (37) independently reported several examples of the prototypical rearrangement of vinylcyclopropane to cyclopentene. The thermal reaction, of the vinylcyclopropane moiety incorporated into a six membered ring was first reported by Doering and Lambert. (38) They demonstrated that the pyrolysis of 8-thujene, 43, leads
in about equal parts to two isomeric substances 44 and 45 of which structure 44 would have been expected of the thermal reorganization of \( \beta \)-thujene in the manner of the vinylcyclopropane-cyclopentene rearrangement.

Studies have shown that experimental conditions employed in the thermal rearrangement of bicyclo(3.1.0)hex-2-ene are of utmost importance in determining the course of isomerization. At \( 255^\circ C \) rapid, reversible conversion of 46 into 47 (using deuterium labelling to follow the reaction) was observed by Doering and Roth.\(^{(39)}\) In the range 314-347\( ^\circ C \), 46, yielded three hydrocarbon products, cyclohex-1,3-diene, cyclohex-1,4-diene, and benzene; 48, 49, and 50 respectively.

\[
\begin{align*}
\text{46} & \xrightarrow{255^\circ} \text{47} \\
\text{46} & \xrightarrow{314^\circ-347^\circ} \text{48} + \text{49} + \text{50} + \text{H}_2
\end{align*}
\]

Since the elucidation of the vinylcyclopropane rearrangement in \( \beta \)-thujene by Doering and Lambert\(^{(38)}\) the thermal isomerization of bicyclo(3.1.0)hex-2-ene systems has been subjected to mechanistic scrutiny. In the limited number of bicyclo(3.1.0)hex-2-ene systems where the isomerization reaction has been studied, the results have generally been interpreted in terms of a biradical formalism where the intermediates arise from the cleavage of the internal cyclopropane bond.\(^{(38,40,41,42)}\)
Experimental studies by Cooke and Andrews,\(^{(34)}\) of the degenerate rearrangement, using deuterium as positional marker, have demonstrated that the mechanism of the automerization is consistent either with a biradical formalism requiring disrotatory ring opening and closing pathways or with the competition of at least three concerted pathways. The biradical intermediate involved possesses either \(C_2\nu\) or \(C_8\) symmetry.

Ellis and Frey\(^{(40)}\) discussed the non-degenerate transformation of bicyclo\{3.1.0\}hex-2-ene,\(^{51}\) to 1,3-cyclohexadiene,\(^{53}\), and 1,4-cyclohexadiene,\(^{54}\), in terms of a mechanism involving a biradical intermediate \(^{52}\), arising from cleavage of the internal cyclopropane bond, in which an intermediate possessing \(C_2\nu\) symmetry undergoes rate-determining 1,2-hydrogen migration. Later studies by Cooke and Andrews\(^{(43)}\) disclosed
that the orbital symmetry allowed mechanism ($\sigma^2s + \sigma 2\alpha$) which involves synchronous cleavage of the cyclopropane ring and hydrogen migration is also consistent with experimental results.

Recent work by Swenton and Wexler\textsuperscript{(41)} has suggested that hindered rotation of the proposed biradical intermediate influences the ratio of distinguishable products formed in the thermolyses of bicyclo\{3.1.0\}hex-2-ene systems bearing stereochemical markers. Thermolysis of trans-5,6-diphenylbicyclo\{3.1.0\}hex-2-ene,\textsuperscript{55}, in cyclohexane at either 130°C or 170°C yielded a nearly temperature invariant mixture of 60% \textsuperscript{55} and 40% trans-4,5-diphenylbicyclo\{3.1.0\}hex-2-ene,\textsuperscript{57}. Less than 2% of the corresponding \emph{cis}-isomers, \emph{cis}-5,6-,\textsuperscript{58}, and \emph{cis}-4,5-diphenylbicyclo\{3.1.0\}hex-2-ene,\textsuperscript{60}, was detected in the time necessary for the \textsuperscript{55:57} equilibrium to be established.
CHAPTER 2

RESULTS AND DISCUSSION
(i) **Analysis of the Mixture of Isomeric Triphenylmethylcyclopentadienes**

Although n.m.r. is a very powerful diagnostic tool, substantiating the predominant isomer in the mixture by this method would have been at best only suggestive. Separation and isolation of individual isomers is a rather difficult task as they must be performed at temperatures low enough to prevent prototropic rearrangement. Thus verification of the principal component in the mixture of isomers was attained by adduct formation.

The reaction of an equilibrium mixture of triphenylmethylcyclopentadienes with tetracyanoethylene (TCNE) gave only the 2-triphenylcyclopentadiene adduct. \(^ {61} \). A \(^1\)H n.m.r. spectrum of the crude, immediately after reaction, showed the complete absence of resonance peaks attributable to the major isomer, but the peaks associated with the minor isomer were still fully present. Another \(^1\)H n.m.r. spectrum of the same crude after four days depicted only resonance peaks typical of \(^ {61} \).

This result indicates that only the sterically less hindered isomer, 2-triphenylmethylcyclopentadiene, reacts with TCNE. Also, at room temperature 1-triphenylmethylcyclopentadiene rearranges slowly to 2-triphenylmethylcyclopentadiene which in turn immediately reacts to form the TCNE adduct \(^ {61} \).

Spectral and chemical data for the adduct \(^ {61} \) are given on the following page.
Anal. Calc. for $\text{C}_{30}\text{H}_{20}\text{N}_{4}$: C, 82.54; H, 4.62; N, 12.84

Found: C, 82.23; H, 4.85; N, 12.99

Table 2 $^{13}\text{C}$ n.m.r. (CDCl$_3$) Chemical Shifts for 61

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Chemical Shift$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^b\text{C}_1$</td>
<td>58.78</td>
</tr>
<tr>
<td>$^b\text{C}_2$</td>
<td>-----</td>
</tr>
<tr>
<td>$^b\text{C}_3$</td>
<td>-----</td>
</tr>
<tr>
<td>$^b\text{C}_4$</td>
<td>55.88</td>
</tr>
<tr>
<td>$^b\text{C}_5$</td>
<td>46.85</td>
</tr>
<tr>
<td>$^b\text{C}_6$</td>
<td>47.98</td>
</tr>
<tr>
<td>$\text{C}_7$</td>
<td>48.89</td>
</tr>
<tr>
<td>$\text{C}^\text{N}$</td>
<td>109.82; 111.47; 112.06; 112.22</td>
</tr>
<tr>
<td>$\phi_3\text{C}$</td>
<td>63.39</td>
</tr>
</tbody>
</table>

$^a$ The chemical shifts are in ppm on the $\delta$-scale from TMS reference.

$^b$ Assignments of $\text{C}_1$ and $\text{C}_4$, and of $\text{C}_5$ and $\text{C}_6$ could be reversed.

$^c$ Resonance peaks of $\text{C}_2$ and $\text{C}_3$ were completely obscured by a complex pattern of phenyl carbon resonances.
Figure 1 The $^1$H n.m.r. spectrum of triphenylmethylcyclopentadienes recorded in CDCl$_3$ solution at 60 MHz.

Figure 2 The $^1$H n.m.r. spectrum of triphenylmethylcyclopentadienes and tetracyanoethylenes, after 30 minutes reaction time, recorded in CDCl$_3$. 
Figure 3  The $^1$H n.m.r. spectrum of 2-triphenylmethyl-5,5,6,6-tetracyano[bicyclo(2.2.1)hept-2-ene recorded in CDCl$_3$ solution at 60 MHz.
Table 3  
$^1$H n.m.r. (CDCl$_3$) Data for 61

<table>
<thead>
<tr>
<th>Proton(s)</th>
<th>Chemical Shift$^a,d$</th>
<th>Coupling Constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_1$</td>
<td>4.44 (m)</td>
<td></td>
</tr>
<tr>
<td>H$_3$</td>
<td>6.13 (d,d)</td>
<td></td>
</tr>
<tr>
<td>H$_4$</td>
<td>3.95 (m)</td>
<td></td>
</tr>
<tr>
<td>H$_7n$</td>
<td>2.38 (AB quartet)</td>
<td>$J_{AB} = 11.4$</td>
</tr>
<tr>
<td>H$_7x$</td>
<td>$\delta A 2.27$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\delta B 2.50$</td>
<td></td>
</tr>
</tbody>
</table>

In the mass spectrum there was an intense peak at m/e = 308 and a much less intense peak at m/e = 436. A weak parent peak and a very intense peak at m/e = 308 indicates that a retro Diels-Alder reaction occurs. The assignments of the bridgehead, bridge, and olefinic hydrogens in the $^1$H n.m.r. spectrum of 61 (Table 3) were verified by comparison with the $^1$H n.m.r. spectrum of the cyclopentadiene-TCNE adduct. The $^{13}$C n.m.r. spectrum of the triphenylmethylcyclopentadiene-TCNE adduct (Table 2) which showed at high field three quaternary, two tertiary, and one secondary carbon, again was consistent with structure 61.

Methylcyclopentadiene is the simplest and most extensively studied organic derivative of cyclopentadiene and similarly exists as a mixture of isomers. The qualitative analysis of the proton spectra of all three isomers has been performed by MCLean and Haynes.$^4$ $^{13}$C n.m.r. spectra (proton noise decoupled) of vinylic isomers have also been

---

$^a$ The chemical shifts are in ppm on the $\delta$-scale from TMS reference.

$^d$ d,d (doublet of doublets), and m (multiplet).
Table 4  \(^1\)H n.m.r. (CDCl\(_3\)) Chemical Shifts\(^a\) and Coupling Constants\(^b\) of Cyclopentadienes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(H_1)</th>
<th>(H_2)</th>
<th>(H_3)</th>
<th>(H_4)</th>
<th>(H_5)</th>
<th>Phenyls</th>
<th>(J_{1,3})</th>
<th>(J_{1,4})</th>
<th>(J_{3,4})</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>6.05-6.4</td>
<td>6.05-6.4</td>
<td>6.05-6.4</td>
<td>2.89</td>
<td>7.15</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>6.00</td>
<td>6.25</td>
<td>6.07</td>
<td>2.70</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.4</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>6.08</td>
<td>6.20</td>
<td>6.33</td>
<td>3.03</td>
<td>7.15</td>
<td>1.4</td>
<td>2.1</td>
<td>5.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>5.83</td>
<td>6.23</td>
<td>6.23</td>
<td>2.79</td>
<td>—</td>
<td>1.4</td>
<td>1.8</td>
<td>5.4</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>6.28</td>
<td>6.43</td>
<td>6.43</td>
<td>2.80</td>
<td>—</td>
<td>1.09</td>
<td>1.94</td>
<td>5.06</td>
<td>46, 47(^a)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5  \(^13\)C n.m.r. (CDCl\(_3\)) Chemical Shifts\(^a\) of Cyclopentadienes

<table>
<thead>
<tr>
<th>Compound</th>
<th>(C_1)</th>
<th>(C_2)</th>
<th>(C_3)</th>
<th>(C_4)</th>
<th>(C_5)</th>
<th>Exo cyc.</th>
<th>(C)</th>
<th>Phenyl carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>154.2</td>
<td>128.3</td>
<td>132.7</td>
<td>131.3</td>
<td>44.5</td>
<td>62.2</td>
<td>147.0</td>
<td>130.6 127.6 126.1</td>
</tr>
<tr>
<td>6</td>
<td>144.6</td>
<td>128.4</td>
<td>134.1</td>
<td>130.7</td>
<td>45.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>130.1</td>
<td>152.4</td>
<td>136.9</td>
<td>131.9</td>
<td>40.6</td>
<td>60.9</td>
<td>146.1</td>
<td>130.6 127.6 126.1</td>
</tr>
<tr>
<td>7</td>
<td>127.3</td>
<td>142.6</td>
<td>136.5</td>
<td>133.4</td>
<td>40.7</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1</td>
<td>133.0</td>
<td>133.4</td>
<td>133.4</td>
<td>133.0</td>
<td>42.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(^a\) The chemical shifts are in ppm on the \(\delta\)-scale from TMS reference.

\(^b\) The coupling constants are in Hz.
analysed. The n.m.r. data of methylcyclopentadienes were useful for analysis and assignment of the n.m.r. spectra of triphenylmethylcyclopentadiene.

From spectral data (Table 4) of methylcyclopentadiene and of cyclopentadiene, it was observed that $H_1$ in those systems resonates upfield relative to other vinylic protons. Thus, considering the $^1H$ n.m.r. spectrum of the isomeric triphenylmethylcyclopentadiene mixture, it seemed quite in order to assign the multiplet at 6.08 ppm to $H_1$ in 2-triphenylmethylcyclopentadiene. That this peak does indeed belong to 2-triphenylmethylcyclopentadiene was shown initially by integration and later by proton decoupling experiments. Irradiation of the methylene group at 3.01 ppm not only removed the complexity in the vinylic region but also revealed an $AB$ spectral pattern (Figure 4). From this pattern

$$J_{34} = 5.5 \text{ Hz}$$

$$J_{14} = 2.1 \text{ Hz}$$

$$J_{13} = 1.4 \text{ Hz}$$

Figure 4 Decoupled $^1H$ n.m.r. spectrum of triphenylmethylcyclopentadienes the chemical shifts for $H_3$ and $H_4$ plus the coupling constants for the
interacting groups were evaluated. The long-range coupling constants between the vinyl protons of 2-triphenylmethylcyclopentadiene show great similarity in magnitudes to those of cyclopentadiene and 2-methylcyclopentadiene. Assuming the smaller coupling constant value can again be assigned to the allylic 1-3 coupling, then the higher field resonance can be assigned to $H_3$ and the lower field resonance to $H_4$.

The imbalance in isomer ratio, on the one hand, eased the evaluation of $^1H$ n.m.r. data of the predominant isomer, but on the other hand, it completely negated a proper study of the low field region of the minor component. However, data obtained from the $^{13}C$ n.m.r. spectrum did allow a tentative assignment of carbon chemical shifts for 1-triphenylmethylcyclopentadiene.

Comparison of the chemical shifts between triphenylmethylcyclopentadiene and methylcyclopentadiene shows that the protons for the trityl substituted cyclopentadiene resonate at lower field. This effect can be attributed to the deshielding ability by the phenyl groups of the substituent.

The isomer ratio of 2-triphenylmethylcyclopentadiene to 1-triphenylmethylcyclopentadiene was obtained from the area of the ring methylene signals in the $^1H$ n.m.r. spectrum of the mixture. The protons appear as quartets and are separated by 0.14 ppm. H. Werner and co-workers(7) reported the isomer ratio as 3.8 : 1. Triphenylmethylcyclopentadiene, synthesized on three separate occasions, crystallized from benzene with isomer ratios of 9.1 : 1; 4.5 : 1; and 3.7 : 1. No
plausible rationale for this phenomenon can at this stage be advanced although such factors as the statistical advantage of the major isomer in the nucleation process, rate of crystallization, and equilibration during crystallization cannot be excluded.

(ii) Photochemical Rearrangement of Triphenylmethylcyclopentadiene

Direct irradiation of triphenylmethylcyclopentadiene in benzene (11 RPR 3000 Å lamps) or cyclohexane (Hanovia L450 W lamps) gave 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene (d,2), 62 in 45% conversion. No side products were detected. Mass spectroscopy (m/e = 308) and microanalysis confirmed the molecular formula C_{24}H_{20}. The photolysis product, 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, 62, was a colourless crystalline solid with a melting point of 108-109°C.

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

\[
\begin{align*}
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

Acetophenone sensitized irradiation of triphenylmethylcyclopentadiene in benzene (11 RPR 3500 Å lamps or Hanovia L450 W with pyrex filter), however, gave in addition to 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, 62, dimeric photoproducts.
Osmometric molecular weight determination showed that the other photoproducts consisted largely of a mixture of dimers. The recrystallized mixture showed, under microscopic magnification, the presence of two different crystalline solids melting at 199°C and 234°C. The two dimeric photoproducts were produced in approximately equal amounts. Theoretically a possibility for the formation of at least fourteen stereoisomeric products existed but only two were actually observed. However, the major interest was not in the dimerization but in rearrangement of triphenylmethyl cyclopentadiene, hence further structural investigations were not pursued.

When triphenylmethylcyclopentadiene is subjected to photochemical excitation, two rearrangements, an electrocyclic reaction leading to the bicyclo[2.1.0]pentene skeleton and hydrogen migration by a \( \{1,3\} \) sigmatropic reaction, are allowed by the Woodward-Hoffmann rules.\(^{(5)}\)

The photochemical conversion of the equilibrium mixture of methylcyclopentadienes to a product which contained methylbicyclo[2.1.0]-pentene has been observed previously by McLean and Findlay.\(^{(47b)}\) They observed and isolated only 2-methylbicyclo[2.1.0]pentene in a relatively pure state. Failure to obtain any observable electrocyclic rearrangement product in the direct irradiation of the equilibrium mixture of triphenylmethylcyclopentadiene, is probably caused by the trityl group in
the compound. Under the reaction conditions employed, the substituent must either inhibit the bond forming process leading to the bicyclopentene or increase the rate of retrograde thermal reaction to such an extent that the product does not last long enough to be isolated.

In addition to 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, two other isomers 63 and 64, both of which may formally be derived from triphenylmethylcyclopentadiene 8 and 9 by reasonable mechanistic pathways, had to be initially considered.

\[ \text{Ph} \quad \text{Ph} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{Ph} \quad \text{Ph} \]

H. E. Zimmerman and co-workers\textsuperscript{(48)} in 1968 synthesized 6,6-diphenylbicyclo[3.1.0]hex-2-ene, 65. The U.V. spectrum of this compound closely resembled the spectrum of the photoproduct from 8. Both displayed absorption maxima at identical wavelength, only the magnitude of the molar extinction coefficient was different. Also the i.r. spectrum of photoproduct 62 was in accord with model compound 65.

The occurrence of bands at 3.25μ and 9.80μ in the i.r. spectrum serves as evidence for the presence of a cyclopropane ring system. Derfer, Pickett, and Boord\textsuperscript{(49)} found that in three hundred hydrocarbon spectra the 9.80μ band was not present more often than it would be expected to occur by chance. They, therefore, regarded this band as
Table 6  
$^1$H n.m.r. spectrum of 5,6,6-Triphenylbicyclo(3.1.0)hex-2-ene

<table>
<thead>
<tr>
<th>Proton</th>
<th>Chemical Shift$^a$ (p.p.m.)</th>
<th>Coupling Constants (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>3.21 (q)</td>
<td>$J_{1,2}=2.0$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>5.91 (m)</td>
<td>$J_{1,3}=0$</td>
</tr>
<tr>
<td>$H_3$</td>
<td>5.19 (m)</td>
<td>$J_{1,4}=J_{1,5}=1.5$</td>
</tr>
<tr>
<td>$H_4$</td>
<td>2.83 (q)</td>
<td>$J_{2,3}=5.5$</td>
</tr>
<tr>
<td>$H_5$</td>
<td>2.83 (q)</td>
<td>$J_{2,4}=J_{3,5}=2.0$</td>
</tr>
<tr>
<td>Phenyl</td>
<td>6.75-7.30 (m)</td>
<td>$J_{2,5}=J_{3,4}=2.0$</td>
</tr>
</tbody>
</table>

$q$=quartet, $m$=multiplet.

$^a$ Run in CCl$_4$.

Table 7  
$^{13}$C n.m.r. spectrum of 5,6,6-Triphenylbicyclo(3.1.0)hex-2-ene

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Chemical Shift$^a$ δ</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$</td>
<td>40.54</td>
</tr>
<tr>
<td>$C_4$</td>
<td>42.06</td>
</tr>
<tr>
<td>$C_5$</td>
<td>44.31</td>
</tr>
<tr>
<td>$C_6$</td>
<td>48.18</td>
</tr>
</tbody>
</table>

$^a$ Run in chloroform-$d_4$ with TMS as internal standard.
Table 8  
I.R. spectrum of 5,6,6-Triphenylbicyclo{3.1.0}hex-2-ene

<table>
<thead>
<tr>
<th>Wavelength ((\mu))</th>
<th>3.24 m</th>
<th>3.27 s</th>
<th>3.30 s</th>
<th>3.44 m</th>
<th>3.53 w</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>6.28 m</td>
<td>6.74 m</td>
<td>6.94 m</td>
<td>7.04 w</td>
<td>7.30 w</td>
</tr>
<tr>
<td></td>
<td>7.48 w</td>
<td>7.58 w</td>
<td>7.67 w</td>
<td>7.87 w</td>
<td>8.62 w</td>
</tr>
<tr>
<td></td>
<td>8.78 w</td>
<td>9.38 m</td>
<td>9.80 m</td>
<td>9.94 w</td>
<td>10.72 w</td>
</tr>
<tr>
<td></td>
<td>10.87 w</td>
<td>10.99 w</td>
<td>11.11 w</td>
<td>12.69 w</td>
<td>12.85 w</td>
</tr>
<tr>
<td></td>
<td>13.21 s</td>
<td>13.61 s</td>
<td>13.87 s</td>
<td>14.34 s</td>
<td>14.53 s</td>
</tr>
</tbody>
</table>

Solvent: carbon tetrachloride and carbon disulphide.
Intensity: w=weak, m=medium, s=strong.

Table 9  
U.V. spectrum of 5,6,6-Triphenylbicyclo{3.1.0}hex-2-ene

<table>
<thead>
<tr>
<th>(\lambda_{max}) (nm)</th>
<th>(\epsilon_{max})</th>
</tr>
</thead>
<tbody>
<tr>
<td>227 (p)</td>
<td>20,153</td>
</tr>
<tr>
<td>260 (p)</td>
<td>1,205</td>
</tr>
<tr>
<td>267 (p)</td>
<td>850</td>
</tr>
<tr>
<td>275</td>
<td>350</td>
</tr>
</tbody>
</table>

\(p=\) plateau
being typical of the cyclopropane structure and suggested that it arises from a ring deformation mode.

Particularly significant in the structure elucidation was the $^1$H n.m.r. spectrum. The quartet at 2.83 ppm can be fitted to the methylene protons and the quartet at 3.21 ppm to the bridgehead proton in structure 62. It is most unlikely that the C-6 endo and the C-6 exo protons in structure 64 should experience the same anisotropic shielding by the π electrons, or that the peak at 2.83 ppm is comprised of a C-6 and a bridgehead proton.

The chemical shifts of the ring protons in substituted cyclic systems are generally abnormal. Such protons exhibit a special dependence of chemical shifts on substitution, because these always occupy well defined positions in space, and because of the possibility of transmission of electron withdrawal. Further, if more than one substituent is present, they interact both electronically and sterically thus making the substituent effect non-additive. It is the presence of those limitations that prompted the correlation of coupling constants rather than chemical shifts to key models.

On the basis of the Karplus equation, $J = J^0 \cos^2 \theta - C$ where $J^0 = 8.5$Hz, $\theta = 55^\circ$ and $C = -0.3$Hz, the vicinal coupling constant, for an unperturbed H-C-C-H fragment, should have a minimum value of 3.1Hz. Factors other than the dihedral angle are known to influence the magnitude of the vicinal coupling constants, however, in model bicyclo(3.1.0)hex-2-ene systems the vicinal coupling constants are in the
Figure 5 The $^1$H n.m.r. spectrum of 5,6,6-triphenylbicyclo(3.1.0)hex-2-ene recorded in CCl$_4$ solution at 100MHz.
Figure 6 Decoupled $^1$H n.m.r. spectrum of 5,6,6-triphenylbicyclo(3.1.0)hex-2-ene
Figure 7  Decoupled $^1$H n.m.r. spectrum of 5,6,6-triphenylbicyclo(3.1.0)hex-2-ene
range of 7 to 8Hz.\textsuperscript{(51,52)} Double irradiation experiments have shown conclusively that each methylene proton, \(H_4\) and \(H_5\), is coupled to the cyclopropyl proton with a coupling constant of only 1.5Hz; implying long range rather than vicinal coupling.\textsuperscript{(53)} These results indicate that the structure and stereochemistry of the photoproduct are as shown in 62.

The \(^1\text{H}\) n.m.r. spectrum of starting material recovered after photochemical reaction indicated that it consisted almost entirely of 2-triphenylmethylcyclopentadiene. This result suggests that rapid photoisomerization of 1-triphenylmethylcyclopentadiene, 8, to 5,6,6-triphenylbicyclo\{3.1.0\}hex-2-ene, 62, depletes the starting mixture of 1-triphenylmethylcyclopentadiene. Owing to slow interconversion of isomers the rate of product formation should thereafter be limited by the rate of formation of 1-triphenylmethylcyclopentadiene, 8, from 2-triphenylmethylcyclopentadiene, 9. The experimental observation that 8 is depleted faster than 9 is consistent with the formation of photoproduct 62 (See scheme 4).

Extensive investigations of the photochemistry of phenyl substituted propenes\textsuperscript{(17,54)} have indicated that the transformation to vinylcyclopropanes can be accounted for on the basis of the di-\(\pi\)-methane rearrangement.
Triphenylmethylcyclopentadiene similarly contains the di-π-methane system comprising phenyl and vinyl moieties in an acyclic arrangement. The mechanism for formation of 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene will thus be considered in terms of the di-π-methane rearrangement.

The multiplicity of the triphenylmethylcyclopentadiene excited state undergoing reaction has not been unambiguously established. For this molecule either singlet and triplet give the same product, or intersystem crossing is facilitated by the aromatic rings, and both direct and sensitized reaction yield the triplet reactant. However, direct irradiation of triphenylmethylcyclopentadiene in benzene or cyclohexane gave 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, 62, as the sole product whereas sensitized irradiation of triphenylmethylcyclopentadiene also formed dimeric compounds. It thus appears reasonable to attribute the direct irradiation to a singlet and the sensitized irradiation to a triplet di-π-methane process.

An aspect of interest, requiring consideration, is the selective formation of only one of the two a priori possible vinylcyclopropane skeletons. This selectivity is explicable on the basis of maximum electron delocalization during the product formation and is expressed in scheme 2 in qualitative resonance terms. In the molecular reorganization leading to 62 allylic delocalization extensively stabilizes the odd electron center while in the formation of 63 such stabilization is completely absent.

Zimmerman and co-workers\(^{(20,22)}\) suggested that the singlet di-π-methane rearrangement is concerted. While electron delocalization in species 66 accounts for the preferential product formation, it is certain that 66...
Scheme 4  Qualitative Valence Bond Representation of the Di-π-Methane Rearrangement
cannot represent a long lived intermediate. Hence the biradical-like entities in scheme 4 may just be points on an excited state reaction potential energy surface and not represent energy minima.

An alternative but equivalent representation of the reaction is given by following the change in basis orbitals as the reaction proceeds (see scheme 5). This pathway would structurally involve nearly simultaneous cleavage of bond 3-4 and formation of bonds 1-3 and 2-4 with inversion of configuration at C-4. Although bond cleavage and bond formation proceeds in a concerted manner attention has to be focussed on the fact that bonding between orbitals 1 and 3 is minimal early along the reaction coordinate. The transition state 69 for this transformation consists of a monocyclic array of six orbitals with one sign inversion. With six delocalized electrons, a Möbius array affords a ground state forbidden but excited state allowed transition state.

An interesting facet in the rearrangement via triplet manifold is the formation of dimers in addition to 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, 62. The mechanistic rationalization for this observation is in terms of a non-concerted two-step reaction mechanism via an intermediate cyclopropyldicarbinyldiradical (triplet analogue of 66 in scheme 4). The preference for formation of 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, 62, rather than 1,5,5-triphenylbicyclo[2.1.1]hex-2-ene, 64, in the collapse of the intermediate diradical might be due to good initial overlap between the back lobe at C-3 with the anti-lobe at C-1.
Scheme 5  Basis Orbital Array

old bonds

bonds forming

bond forming late in reaction
(iii) Thermolysis of 5,6,6-Triphenylbicyclo{3.1.0}hex-2-ene, 62

It has been noted from previous studies (see introduction) that the thermolysis of bicyclo{3.1.0}hex-2-enes results in either a cyclohexadiene carbon framework or rearranged bicyclo{3.1.0}hex-2-ene(s).

Another example of the facile thermal interconversion of a bicyclo{3.1.0}hex-2-ene system is the thermolysis of 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene, 62. Compound 62, in cyclohexane at 210°C, underwent structural rearrangement, but contrary to previous observations neither a cyclohexadiene nor a bicyclo{3.1.0}hex-2-ene structure was obtained. Chemical and spectral data for the thermolysis product are given below:

Analysis
Calc. for C_{24}H_{20} : C, 93.46; H, 6.54

Found : C, 93.53; H, 6.67

Table 10
\textbf{1H n.m.r. Spectrum (CDCl₃) of Thermolysis Product}

<table>
<thead>
<tr>
<th>Chemical Shift \textsuperscript{a}</th>
<th>Multiplicity \textsuperscript{b}</th>
<th>Number of Protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.26</td>
<td>m</td>
<td>1</td>
</tr>
<tr>
<td>2.09</td>
<td>m</td>
<td>2</td>
</tr>
<tr>
<td>2.55</td>
<td>d,t</td>
<td>1</td>
</tr>
<tr>
<td>2.67</td>
<td>m</td>
<td>1</td>
</tr>
<tr>
<td>3.01</td>
<td>d</td>
<td>1</td>
</tr>
<tr>
<td>6.69</td>
<td>d,d</td>
<td>1</td>
</tr>
<tr>
<td>6.92</td>
<td>d,d</td>
<td>1</td>
</tr>
<tr>
<td>7.05</td>
<td>m</td>
<td>2</td>
</tr>
<tr>
<td>7.36</td>
<td>m</td>
<td>10</td>
</tr>
</tbody>
</table>

\textsuperscript{a} The chemical shifts are in ppm on the \( \delta \)-scale from TMS reference.

\textsuperscript{b} d(doublet); d,d(doublet of doublets); d,t(doublet of triplet); and m(multiplet).
Table 11 $\text{^{13}C n.m.r. spectrum (CDCl}_3\text{) of Thermolysis Product}$

<table>
<thead>
<tr>
<th>Chemical Shift $^a$</th>
<th>Type of Carbon</th>
<th>Intensity</th>
<th>Number of Carbons</th>
</tr>
</thead>
<tbody>
<tr>
<td>23.47</td>
<td>$sp^3$ secondary</td>
<td>477</td>
<td>1</td>
</tr>
<tr>
<td>35.01</td>
<td>$sp^3$ tertiary</td>
<td>531</td>
<td>1</td>
</tr>
<tr>
<td>47.53</td>
<td>$sp^3$ secondary</td>
<td>462</td>
<td>1</td>
</tr>
<tr>
<td>47.98</td>
<td>$sp^3$ quaternary</td>
<td>239</td>
<td>1</td>
</tr>
<tr>
<td>52.63</td>
<td>$sp^3$ tertiary</td>
<td>517</td>
<td>1</td>
</tr>
<tr>
<td>62.87</td>
<td>$sp^3$ quaternary</td>
<td>270</td>
<td>1</td>
</tr>
<tr>
<td>122.76</td>
<td>$sp^2$ secondary</td>
<td>471</td>
<td>1</td>
</tr>
<tr>
<td>123.89</td>
<td>$sp^2$ secondary</td>
<td>534</td>
<td>1</td>
</tr>
<tr>
<td>126.20</td>
<td>$sp^2$ secondary</td>
<td>668</td>
<td>1</td>
</tr>
<tr>
<td>126.30</td>
<td>$sp^2$ secondary</td>
<td>671</td>
<td>1</td>
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<td>126.66</td>
<td>$sp^2$ secondary</td>
<td>650</td>
<td>1</td>
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<td>126.75</td>
<td>$sp^2$ secondary</td>
<td>592</td>
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<td>127.73</td>
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<td>2</td>
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<td>128.31</td>
<td>$sp^2$ secondary</td>
<td>1201</td>
<td>2</td>
</tr>
<tr>
<td>128.51</td>
<td>$sp^2$ secondary</td>
<td>1183</td>
<td>2</td>
</tr>
<tr>
<td>129.94</td>
<td>$sp^2$ secondary</td>
<td>1027</td>
<td>2</td>
</tr>
<tr>
<td>141.51</td>
<td>$sp^2$ tertiary</td>
<td>196</td>
<td>1</td>
</tr>
<tr>
<td>144.70</td>
<td>$sp^2$ tertiary</td>
<td>195</td>
<td>1</td>
</tr>
<tr>
<td>145.15</td>
<td>$sp^2$ tertiary</td>
<td>232</td>
<td>1</td>
</tr>
<tr>
<td>151.40</td>
<td>$sp^2$ tertiary</td>
<td>208</td>
<td>1</td>
</tr>
</tbody>
</table>

$^a$ The chemical shifts are in ppm on the $\delta$-scale from TMS reference.
Table 12  I.R. Spectrum of Thermolysis Product

Solvents: carbon tetrachloride, carbon disulphide.

Intensity: w = weak, m = medium, s = strong.

<table>
<thead>
<tr>
<th>Wavelength (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.24 m</td>
</tr>
<tr>
<td>3.27 s</td>
</tr>
<tr>
<td>3.30 s</td>
</tr>
<tr>
<td>3.40 s</td>
</tr>
<tr>
<td>3.42 s</td>
</tr>
<tr>
<td>3.45 m</td>
</tr>
<tr>
<td>3.49 m</td>
</tr>
<tr>
<td>3.51 m</td>
</tr>
<tr>
<td>3.89 m</td>
</tr>
<tr>
<td>9.36 w</td>
</tr>
<tr>
<td>10.89 w</td>
</tr>
<tr>
<td>13.40 s</td>
</tr>
<tr>
<td>11.04 w</td>
</tr>
<tr>
<td>13.87 m</td>
</tr>
<tr>
<td>11.74 m</td>
</tr>
<tr>
<td>14.81 m</td>
</tr>
<tr>
<td>12.33 w</td>
</tr>
<tr>
<td>14.99 w</td>
</tr>
<tr>
<td>12.85 m</td>
</tr>
<tr>
<td>15.55 w</td>
</tr>
<tr>
<td>13.02 w</td>
</tr>
<tr>
<td>16.05 w</td>
</tr>
</tbody>
</table>

Table 13  U.V. Spectrum of Thermolysis Product

<table>
<thead>
<tr>
<th>λ_{cyclohexane}^{max} (nm)</th>
<th>ε_{max}</th>
</tr>
</thead>
<tbody>
<tr>
<td>230 p</td>
<td>19,574</td>
</tr>
<tr>
<td>259</td>
<td>999</td>
</tr>
<tr>
<td>262</td>
<td>1,026</td>
</tr>
<tr>
<td>264</td>
<td>1,026</td>
</tr>
<tr>
<td>269</td>
<td>943</td>
</tr>
<tr>
<td>280</td>
<td>741</td>
</tr>
</tbody>
</table>

p = plateau

Mass spectrum  m/e = 308 (parent peak)
Scheme 6
The thermolysis of 62 might best be understood by reference to a diradical mechanism as outlined in scheme 4. As the \textit{endo} cyclic cyclopropane bond is cleaved in a disrotatory fashion, the ring approaches the diradical structure 70. In proceeding from 62 to the diradical intermediate 70, molecular models suggest no pronounced changes in steric interaction. To produce 71, phenyl migration is a prerequisite. In the course of phenyl migration steric interaction between the phenyl groups is substantially increased. This is especially acute since the phenyl moiety must remain coplanar with the radical center at C-5 for maximum benzylic stabilization. Closure of 70 by overlap of the top lobe of the p-orbital at C-5 with the allylic center at C-1(C_{1,5} bonding) regenerates 62, while closure at C-3(C_{3,5} bonding) yields 74. Maximum orbital overlap can be also achieved, with reasonable ease, between the π-orbital of the C-6 \textit{endo} phenyl moiety and either C_{1} or C_{3} of the allylic center, forming either benzo(3.4)-1,2-diphenyltricyclo[3.2.1.0^{2,7}]octene, 75, or benzo(7.8)-1,2-diphenyltricyclo[4.2.0.0^{2,7}]octene, 76.

The lack of vinylic protons in the $^1$H n.m.r. spectrum excludes the cyclohexadiene structures 71, 72, 73, and the bicyclo[3.1.0]hex-2-ene system 74 as the possible thermolysis product. This observation again is in complete agreement with the $^{13}$C n.m.r. proton noise decoupled spectrum, where a total of eighteen low field unsaturated (sp$^2$) and six high field saturated (sp$^3$) carbons can be counted, suggesting a tricyclic system with benzo[6]fusion as a viable structure.

Two benzo[6]fused tricyclic structures obtained by reasonable mechanistic pathways (scheme 6) are 75 and 76. But, from spectral properties, 75 seems the most likely carbon framework of the thermolysis
product. The $^1$H n.m.r. spectrum does not display the typical high field cyclopropyl proton resonance peaks$^{(55,56)}$ nor are the chemical shifts in $^{13}$C n.m.r. indicative of a cyclopropyl methylene moiety.$^{(57)}$ Contrary to expectation, comparison of the $^1$H n.m.r. chemical shifts to those of model compound benzo[3,4]tricyclo[3.2.1.0$^{2,7}$]octene$^{(25),37}$, did not help to corroborate the molecular structure. It is clear that the nature of the

![Chemical Structure Diagram]

$^{37}$

Table 14 $^1$H n.m.r. Data for $^{37}$

<table>
<thead>
<tr>
<th>Proton</th>
<th>Chemical Shift$^a$</th>
<th>Multiplicity$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_1$</td>
<td>1.62</td>
<td>d</td>
</tr>
<tr>
<td>$H_2$</td>
<td>2.10</td>
<td>t</td>
</tr>
<tr>
<td>$H_5$</td>
<td>3.00</td>
<td>t</td>
</tr>
<tr>
<td>$H_{6n}$</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>$H_{6x}$</td>
<td>1.78</td>
<td>q</td>
</tr>
<tr>
<td>$H_7$</td>
<td>1.62</td>
<td>d</td>
</tr>
<tr>
<td>$H_{8n}$</td>
<td>0.95</td>
<td></td>
</tr>
<tr>
<td>$H_{8x}$</td>
<td>1.78</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ The chemical shifts are in ppm on the $\delta$-scale from TMS reference.
$^b$ d(doublet), t(triplet), and q(quartet).
substituents and their configurational requirement, have a profound influence on the proton and carbon chemical shifts. Thus, unless the spectral data are compared to a reasonable model no absolute structural proof can be advanced. At this stage of the experimental investigation it can therefore only be postulated that 75 is the structure of the thermolysis product.
CHAPTER 3

CONCLUSIÓN
Conclusion

This study has demonstrated that: a) The major isomer in the equilibrium mixture of triphenylmethylcyclopentadiene is 2-triphenylmethylcyclopentadiene: b) Direct or sensitized irradiation of the equilibrium mixture of triphenylmethylcyclopentadiene forms 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene. The sensitized irradiation produced, in addition to 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene, dimeric products via the photochemically allowed 2 + 2 cycloaddition. The most reasonable representation of the photochemical transformation involves 1-triphenylmethylcyclopentadiene as the reactive isomer which presumably rearranges by the di-π-methane mechanism to form 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene: c) The facility of the thermal transformation of 5,6,6-triphenylbicyclo{3.1.0}hex-2-ene is in complete accord with the vinylcyclopropane rearrangement. But in contrast to previous studies of this mode of rearrangement, no cyclohexadiene structure or rearranged bicyclo{3.1.0}-hex-2-ene system is observed. Presumably, the formation of a benzofused tricyclic compound reflects the system's inability to adopt the most favourable configuration for C3,5 bond formation due to steric interference from the C6 endo phenyl group.
CHAPTER 4

EXPERIMENTAL SECTION
(i) Materials

Petroleum ether and benzene were distilled before use. Benzene, for reactions conducted under anhydrous conditions, was refluxed for 24 hours over phosphorous pentoxide and the fraction boiling at 80°C was collected. The petroleum ether used was Mallinckrodt Analytical Reagent and had boiling range 30-60°C. Ether used as solvent for reactions refers to Mallinckrodt anhydrous ethyl ether. Cyclohexane, the solvent for direct irradiation, was spectroquality grade from Matheson, Coleman, and Bell. The remaining solvents used were all of analytical reagent grade and were not purified.

Reagents distilled prior to usage were: acetophenone (Fisher Certified Reagent), b.p. 196-198°C; acetyl chloride (Baker Analyzed Reagent) b.p. 49.0-55.0°C.

Cyclopentadiene was obtained by thermally cracking its dimer (Eastman Organic Chemicals).

Other reagents used were all reagent grade chemicals and were used as supplied.

(ii) Photochemical Reaction Conditions and Analytical Methods

For the monomer-dimer product ratio study eleven RPR 3000A lamps were utilized in a Srinivasan-Griffith Photochemical Reactor (Rayonet)
manufactured by the Southern New England Ultraviolet Company.

Column chromatography was done on neutral alumina (Fisher Scientific, 80-200 mesh), and on Silica Gel (M. Woelm, Activity grade 1). Thin layer chromatography (t.l.c.) on Silica Gel (Baker flex 1B2-F) and alumina (Polygram Aluminum oxide N/UV) was used in many cases to determine the number of components in the reaction mixture, and the purity of column chromatographed fractions.

The major means of analysis was n.m.r. spectroscopy. The n.m.r. spectra were recorded on Varian T-60, Varian HA-100, Varian HR 220, and Bruker WH-90 (Fourier transform) spectrometers with carbon tetrachloride or chloroform-d as solvent. Chemical shifts are reported as p.p.m. downfield from internal tetramethylsilane. Where n.m.r. was used to determine the abundance of one or more materials, the average of several integrations was used. The estimated maximum analytical error was 5%.

Ultraviolet spectra were recorded on a Cary 14 Spectrophotometer with spectroquality cyclohexane (Matheson, Coleman, and Bell) as solvent. The infra-red spectra of compounds were recorded on a Perkin-Elmer 521 instrument employing carbon tetrachloride or carbon disulphide solution. Mass spectra were recorded on a C.E.C. 21-110B mass spectrometer. Melting points were taken on a Kofler hot stage and are uncorrected.

Elemental analysis were performed by Schwarzkopf Microanalytical Laboratory, Inc., Woodside, New York.
I Preparation of Triphenylmethylcyclopentadiene

(i) Synthesis of Triphenylmethanol

The method used for synthesizing triphenylmethanol was similar to that described by W. E. Bachmann.\(^{(59)}\)

The triphenylmethanol synthesis was carried out in a 1-L three-necked flask equipped with a separatory funnel, a reflux condenser fitted with a CaCl\(_2\) tube, gas inlet tube, and a mechanical stirrer.

Magnesium turnings (13.5g, 0.55g atom) were placed in the warm, dry, three-necked flask, the dry equipment assembled, flushed with \(N_2\) and cooled to room temperature. A solution of bromobenzene (91.0g, 0.575 mol) and 100 ml of anhydrous ether was slowly added to the magnesium turnings. As soon as the reaction was initiated an additional 125 ml of anhydrous ether was added to the bromobenzene. After the complete addition of bromobenzene-ether solution, the stirring and refluxing was continued for 20 more minutes.

To the Grignard solution 91.0g (0.5 moles) of benzophenone in 200 ml of dry benzene was added at such a rate that the mixture refluxed gently. The flask was cooled in a pan of cold water during the addition. After the addition was complete, the mixture was refluxed for an hour. The reaction mixture was cooled in an ice-salt bath and then poured slowly, with constant stirring, into a mixture of 1.5kg of cracked ice and 50 ml of concentrated sulfuric acid. Ammonium chloride (50g) and benzene (500 ml) were added and the mixture stirred until all the solid
that separated at the benzene-water interface had dissolved. The benzene layer was separated and washed, successively, with 200 ml of water, 200 ml of a 5% NaHCO₃ solution, and 200 ml of water. The solvents were removed as completely as possible by distillation on a steam bath and the remaining solid mass was steam-distilled to remove biphenyl and unchanged bromobenzene. The product was filtered, washed with water and dried. Recrystallization of crude triphenylmethanol from CCl₄ yielded 98g (76%) of colourless crystals: m.p. 161-162°C. Lit. m.p. 161-162°C.

(ii) Synthesis of Triphenylchloromethane

The procedure described is that used by W. E. Bachmann.(60)

The reaction was carried out in a 500 ml round bottom flask equipped with a reflux condenser fitted with a CaCl₂ tube, a magnetic stirrer, and a heating mantle.

Pure triphenylmethanol (100.0g 0.38 mole) was combined with 32 ml of dry benzene and heated. When it was hot, 20.0 ml (0.28 mole) of freshly distilled acetyl chloride was added through the top of the condenser. Heating was continued while the mixture was stirred vigorously. In about 5 minutes all the solid triphenylcarbinol disappeared and a clear yellow solution resulted. In the course of 10 minutes, an additional 40.0 ml (0.56 mole) of acetyl chloride was added in 4 ml portions. The solution was refluxed for 30 minutes before it was cooled with water. During the cooling process 80 ml of petroleum ether (30-60°C) was added through the top of the condenser. The mixture
was cooled further in an ice-bath for 2 hours during which time the triphenylchloromethane separated in sugar-like crystals. The product was filtered and washed with 60 ml of petroleum ether. Filtration was performed rapidly to prevent hydrolysis of product by moisture in the air. The solid, after drying in the desiccator over P₂O₅, weighed 85g (79%). The final product, which was recrystallized by dissolving it in 30 ml of hot benzene and cooling the solution after diluting it with 60 ml of petroleum ether, had m.p. 112-113°C. Lit. m.p. 111-112°C.

(iii) Synthesis of Triphenylmethylcyclopentadiene

The synthesis, described by Riemschneider(6) was carried out in a 500 ml three-necked flask equipped with a pressure-equalizing separatory funnel, a reflux condenser, gas inlet tube, and a mercury-sealed mechanical stirrer.

To a stirred solution of ethylmagnesium bromide prepared from magnesium (4.0g, 0.16g atom) and ethylbromide (20.0g, 0.18 mol) in 60 ml of anhydrous ether was added freshly distilled cyclopentadiene (10.0g, 0.15 mol). Addition was completed in one hour and stirring at reflux temperature for 8 hours resulted in the precipitation of colourless crystals from the solution. A solution of triphenylchloromethane (26.0g, 0.095 mol) dissolved in 75 ml anhydrous ethyl ether and 25 ml dry benzene was then added dropwise over a one hour period. Occasional cooling was required to maintain the reaction mixture near room temperature. Since triphenylmethylcyclopentadiene is only sparingly soluble in ethyl ether, it coprecipitated with magnesium bromide from the solution. The entire
mass was then poured into an aqueous ammonium chloride solution with which it was thoroughly agitated before the ethereal phase was filtered. The yield, after washing, drying, and recrystallization from benzene, was 11.5g (40%), m.p. 197-199°C. The n.m.r. spectrum had peaks at δ 2.89(q), 3.03(q), 6.08(m), 6.10-6.39(m), and 7.15(s). Lit. m.p. 197-199°C.

II  Preparation of Triphenylmethylcyclopentadiene (alternate route)

(i)  Synthesis of Triphenylmethylcyclopentadiene from Diphenylfulvene and Phenyllithium

The synthesis was carried out in a 100 ml three-necked flask equipped with a gas inlet tube, a pressure-equalizing dropping funnel, a magnetic stirrer, and a reflux condenser fitted with a CaCl₂ drying tube. A slow stream of purified nitrogen was passed through the system prior and during the course of the reaction.

Phenyllithium (15 ml, 0.03 mol) was added dropwise to a stirred solution of 6,6-diphenylfulvene (5.0022g, 0.022 mol) dissolved in 40 ml of anhydrous ethyl ether. After the addition of phenyllithium, the mixture was refluxed gently over a 2.5 hour period. A saturated, aqueous ammonium chloride solution (14 ml) was then added to the reaction mixture, upon which the solution turned to a pale yellow colour. The ether-benzene phase was separated, washed twice with 30 ml portions of water, dried over anhydrous MgSO₄ and concentrated. The concentrated reaction mixture was again redissolved in approximately 20 ml cyclohexane to which absolute ethanol was then slowly added. A pale yellow solid which precipitated
from solution was filtered and recrystallized from absolute ethanol.

Thin layer chromatography revealed three components of which the minor product had the same R_f value as the previously prepared triphenylmethylcyclopentadiene. The identity of that component was confirmed by separating it and comparing its spectra and m.p. with those of triphenylmethylcyclopentadiene. The yield from the phenyllithium-fulvene route was only 7%.

III Analysis of the Mixture of Isomeric Triphenylmethylcyclopentadienes

(i) Reaction of Tetracyanoethylene with Triphenylmethylcyclopentadiene

Triphenylmethylcyclopentadiene (0.5003g, 1.62 X 10^{-3} mol), in dry benzene (8.0 ml) was added dropwise over a period of 10 minutes to a stirred solution of tetracyanoethylene (0.2090g, 1.63 X 10^{-3} mol) in dry benzene (7 ml). The reaction mixture was stirred at room temperature for four days. After 30 minutes, next to the adduct, only 1-triphenylmethylcyclopentadiene was observed in the reaction mixture. The solvent was then evaporated at reduced pressure and the residue was recrystallized from benzene-petroleum ether solvent mixture to yield colourless crystals (0.576g, 81.7%). The adduct, 2-triphenylmethyl-5,5,6,6-tetracyanobicyclo{2.2.1}hept-2-ene, decomposed at 206^\circ C and had n.m.r. (CDC1_3) \delta 2.38(AB quartet, J_{AB}=5.7 Hz, 2H), 3.95(m, 1H), 4.44(m, 1H), 6.13(doublet of doublets, 1H), 7.05-7.40(m, 15H).

Anal. Calc'd for C_{30}H_{20}N_4: C, 82.54; H, 4.62; N, 12.84
Found: C, 82.23; H, 4.85; N, 12.99
IV  Photochemical Reactions

(i)  Acetophenone Sensitized Irradiation of Triphenylmethylcyclopentadiene

The lamp used in the photochemical irradiation was a Hanovia type L 450 W in a water-cooled immersion apparatus. The sensitized photolysis was performed with a pyrex sleeve placed around the lamp. A magnetic stirrer was provided along with a capillary inlet and outlet for argon. Argon was passed through the solution during and for 30 minutes prior to the photolysis.

A solution of triphenylmethylcyclopentadiene (10.0003g, 0.0292 mol) and freshly distilled acetophenone (5.0270g, 0.0418 mol) in 500 ml benzene was irradiated for 12 hours. The solvent was removed by distillation under vacuum.

Thin layer chromatography of the reaction mixture revealed 4 components, one of which was unreacted starting material, the other acetophenone.

The solid phase chosen for all column chromatographic separations was neutral Alumina 80-200 mesh (Fisher A-90 Brockman Activity 1). During each separation procedure 50 ml fractions were collected. Thin layer chromatography checks on fractions were performed on Polygram 0.2 mm Aluminum oxide N/UV plates with solvent mixture of 50% n-hexane-50% cyclohexane.

The 4 compounds were separated on a 4.0 cm. dia. X 63.0 cm column.
For removal of starting material, the solvent mixture used for elution
was 50% n-hexane-50% cyclohexane. After removal of starting material the
solvent mixture was gradually changed to 10% benzene-90% n-hexane. A
major part of the second component was eluted in a relatively pure state
with this solvent mixture before a mixture of second and third components
followed. As soon as the second component was nearly removed the
composition of solvent mixture was gradually changed to 20% benzene-80%
n-hexane. All pure fractions of the same material were combined and the
solvent was removed by distillation under vacuum. The mixture of the
second and third components was again passed through a 2.2 cm X 55.0 cm
column. Six liters of 50% n-hexane-50% cyclohexane were run through the
column before the solvent mixture was gradually changed to 10% benzene-
90% n-hexane. All pure fractions of a given component were combined, the
solvent was removed by distillation under vacuum, and each component was
recrystallized from benzene.

Recrystallization of the second component resulted in prism
shaped colourless crystals; m.p. 108-109°C; i.r. (CCl₄, CS₂) strong 3.27,
3.30, 13.21, 13.61, 13.87, 14.34, 14.53 μ, medium 3.24, 3.44, 6.28, 6.74,
6.94, 9.38, 9.80 μ, weak 3.53, 7.04, 7.30, 7.48, 7.58, 7.67, 7.87, 8.62,
8.78, 9.94, 10.72, 10.87, 10.99, 11.11, 12.69, and 12.85 μ; n.m.r. spectrum
(CC1₄) δ 2.83(q, 2H, ring methylene), 3.21(q, 1H, bridgehead), 5.19(m, 1H,
viny), 5.91(m, 1H, viny), 6.75-7.30(m, 15H, phenyl); U.V. (cyclohexane)
λ max 275(350), plateau, 267(850), 260(1205), and plateau, 227nm" (20,153):
The mass spectrum had a parent peak at m/e=308.

Anal. Calc'd for C₂₄H₂₀: C, 93.46; H, 6.54
Found: C, 93.18; H, 6.50
Recrystallization of the third component gave granular shaped crystals: m.p. 199-234°C; n.m.r. (CCl₄), 0.85(t), 1.28(broad singlet), 1.68-2.80(m), 5.50-5.60(m), 6.90(m).

The third component seems to consist of a heterogeneous mixture of two crystals. Under microscopic magnification on the Kofler hot stage, two different types of crystals, having sharp melting points at 199°C and 234°C, were observed.

Agreement of the osmometric molecular weight (616) with the mass spectrometric molecular weight (616) suggests that the components are isomers.

(i1) Study of the Variation of Monomer-dimer Product Ratio with Change in Reactant Concentration

Five 1.7 X 14.0cm quartz tubes were irradiated in a Rayonet reactor equipped with a bank of 11 RPR 3000A lamps and a turntable.

Each tube contained 25 ml of solution, 0.083M in acetophenone, and different concentrations (0.016, 0.065, 0.065, 0.114, and 0.162M) of triphenylmethylcyclopentadiene. The solutions were degassed 3 times by the freeze-pump-thaw cycle and sealed under vacuum. All tubes, except one of the two tubes containing 0.065M solution, were irradiated for 18 hours. The remaining tube was irradiated for 48 hours. Each orange coloured reaction mixture was then concentrated, the solvent was completely removed under vacuum, and the residue was redissolved in a known amount of CDCl₃. Two hundred microliters from each solution was
syringed into separate n.m.r. tubes.

Analysis of the spectra indicated in each case the presence of only triphenylmethylcyclopentadiene and 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene but none of the expected dimeric product. The amount of photoproduct (5,6,6-triphenylbicyclo[3.1.0]hex-2-ene) in the 0.065M solution, irradiated for 48 hours, was 0.501g (41%) as determined by n.m.r.

(iii) Acetophenone Sensitized Irradiation of 5,6,6-Triphenylbicyclo[3.1.0]hex-2-ene

The lamp used in the photochemical irradiation was a Hanovia type 125W in an air cooled pyrex immersion apparatus. A magnetic stirrer was provided along with a capillary inlet and outlet for argon. Argon was passed through the solution during, and for 30 minutes prior to the photolysis.

A solution of 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene (0.0719g, 2.33 x 10^-4 mole) and acetophenone (0.0816g, 6.80 x 10^-4 mole) in 125 ml of benzene was photolyzed for 14.3 hours. For about 3 hours the irradiation mixture reached a temperature of approximately 65°C. The solvent was removed by distillation under vacuum. The n.m.r. spectrum displayed peaks at δ 1.27(s), 2.48(s), 2.83(q), 3.21(q), 5.19(m), 5.91(m), and 6.75-7.80(m). Analysis of these peaks showed the presence of 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene, acetophenone, and dissolved polyethylene from capillary inlet. The maximum temperature reached during photolysis was adequate to dissolve some of the polyethylene capillary inlet.
(iv) **Irradiation of Triphenylmethylcyclopentadiene**

The lamp used in the unsensitized photochemical irradiation was a Hanovia type L450W in a water-cooled immersion apparatus. A magnetic stirrer was provided along with a capillary inlet and outlet for argon. Argon was passed through the solution during, and for one hour prior to, the photolysis.

Thin layer chromatography checks on fractions were performed on Baker-flex silica gel 1B2-F with CC\textsubscript{14} used as solvent.

A solution of triphenylmethylcyclopentadiene (2.0535g, 0.0067 mole) in 400 ml of spectroquality cyclohexane (Matheson, Coleman, and Bell) was irradiated through quartz for 12 hours. The solvent was removed by distillation under vacuum. The orange coloured residue was partially separated on a 2.2 cm X 33.0 cm column using CC\textsubscript{14} as eluant. The solid phase chosen for column chromatography was silica gel (M. Woelm activity grade 1). During each separation procedure 250 ml fractions were collected. A considerable overlap between reactant and product of interest occurred. For final separation, on preparative thin layer chromatography, only fractions that contained a minor amount of other components were used. The component of interest was then removed from silica gel with a solvent mixture of 50\% ether and 50\% benzene. The n.m.r. spectrum and \( R_f \) value from thin layer chromatography were identical to those of the second component obtained from the sensitized irradiation of triphenylcyclopentadiene. N.m.r. spectrum consisted of \( \delta \) 2.83(q), 3.21(q), 5.19(m), 5.91(m), 6.75-7.30(m) with CC\textsubscript{14} as solvent. Trace
V Thermal Rearrangement of a Vinylcyclopropane Moiety.

(i) Thermolysis of 5,6,6-Triphenylbicyclo[3.1.0]hex-2-ene

A solution of 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene (0.1402g, 4.55 x 10^-4 mole) m.p. 108-109°C in 13.0 ml spectroquality cyclohexane was vacuum sealed in a thick walled glass tube which was placed in a high pressure bomb. The high pressure bomb was heated to 210°C for 46 hours. The vapour pressure of the resulting solution was reduced by freezing the glass tube with liquid nitrogen before breaking off the seal. The excess cyclohexane was removed by evaporation under reduced pressure at room temperature. Crystallization from benzene gave colourless crystals, m.p. 170°C. For ¹H n.m.r., ¹³C n.m.r., i.r., and U.V., data see Tables 10, 11, 12, and 13, respectively. Osmometric molecular weight was 307. During the thermolysis, the 5,6,6-triphenylbicyclo[3.1.0]hex-2-ene was completely converted.
REFERENCES


(60) Dr. J. Warkentin, *Unpublished results*.