AN ABSTRACT OF THE THESIS OF

EDWARD SAMUEL WALTON for the MASTER OF SCIENCE
(Name of student) (Degree)
in Chemistry (Organic) presented on March 1973
(Major) (Date)

Title: Part I THE SILOXY-COPE REARRANGEMENT OF 1, 2-
DIVINY-1-TRIMETHYLSILOXYCYCLOHEXANE
AND RELATED SYSTEMS

Part II THE ACID-CATALYZED REARRANGEMENT OF
BICYCLO [5. 1. 0] OCTYL-8-METHANOL

Abstract approved: Redacted for Privacy
Dr. Richard W. Thies

Part I

The pyrolysis of cis- and trans- 1, 2-divinyl-1-trimethylsiloxycyclohexane, II- and III-TMS, under the same conditions as the pyrolysis of cis-1-vinyl-1-trimethylsiloxycyclooct-3-ene, 1-TMS, confirms that a sequence of concerted reactions for the rearrangement of II- and III-TMS to trans-1-trimethylsiloxycyclodec-3-ene, 4-TMS, is a viable pathway in the overall rearrangement of 1-TMS.

Part II

The solvolysis of exo-bicyclo [5. 1. 0] octyl-8-methanol in aqueous dioxane with perchloric acid catalysis leads to a 4:1 ratio of bicyclo [5. 2. 0] nonan-8-ol and 2-vinylcycloheptanol.
The Siloxy-Cope Rearrangement of 1, 2-divinyl-1-trimethyl-siloxycyclohexane and Related Systems

The Acid-Catalyzed Rearrangement of Bicyclo [5.1.0] octyl-8-methanol

by

Edward Samuel Walton

A THESIS

submitted to

Oregon State University

in partial fulfillment of the requirements for the degree of Master of Science

June 1973
APPROVED:

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Date thesis is presented 16 March 1973

Typed by Opal Grossnicklaus for Edward S. Walton
ACKNOWLEDGEMENTS

I wish to thank those who have made significant contributions to this work by their understanding, encouragement, and stimulating discussion. I especially thank Dr. R. W. Thies for his guidance and contributions. Dr. J. Billigmeier deserves mention for his suggestions and helpful hints. Of course, my sincere appreciation and love to my wife, Martha, for her hard work and understanding during this study.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Part I</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>15</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>26</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Part II</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>INTRODUCTION</td>
<td>36</td>
</tr>
<tr>
<td>RESULTS AND DISCUSSION</td>
<td>47</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>51</td>
</tr>
<tr>
<td>BIBLIOGRAPHY</td>
<td>52</td>
</tr>
</tbody>
</table>
## LIST OF SCHEMES

### Part I

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Diradical</td>
</tr>
<tr>
<td>II</td>
<td>Concerted</td>
</tr>
<tr>
<td>III</td>
<td>Synthesis of trans- and cis- 1, 2-divinyl-1-trimethylsiloxy-cyclohexane, II- and III-TMS</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

## Part I

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Pyrolysis of I-TMS and a mixture of II- and III-TMS at 230.5° for one hour.</td>
<td>18</td>
</tr>
<tr>
<td>2.</td>
<td>Pyrolysis of I-TMS in toluene and I-TMS with no toluene for 3 1/2 hours at 281 °C.</td>
<td>19</td>
</tr>
<tr>
<td>3.</td>
<td>Chromatography columns.</td>
<td>34</td>
</tr>
<tr>
<td>4.</td>
<td>GC retention times.</td>
<td>35</td>
</tr>
</tbody>
</table>
INTRODUCTION

Since its discovery by A. C. Cope in the early forties, the Cope reaction has gained much attention, much of which has been given to discerning the mechanism of this so called, "no mechanism" reaction. Cope's original example was the thermal rearrangement of 4-cyano-4-ethylcarboxylate-5-methyl-2, 6-heptadiene to ethyl-2-cyano-3, 4-dimethyl-2, 6-heptadienoate (1).

In the early work, it was not realized that just simple 1, 5-hexadiene systems will undergo the Cope reaction (2).

Because the product is identical to the reactant for R=H, this reaction is difficult to observe. With R being some other group, however, the transformation is easily detected.
According to Woodward and Hoffman "a sigmatropic change of order \([i, j]\) is the migration of a sigma bond, flanked by one or more \(\pi\) electron systems, to a new position whose termini are \(i-1\) and \(j-1\) atoms removed from the original bonded loci, in an uncatalyzed intramolecular process" (3). In other words, it is the shift of a sigma bond accompanied by a shift of the \(\pi\) electron system to form a new species which has the sigma bond located \(i-1\) and \(j-1\) atoms away from the original atoms joined by the sigma bond. A few examples will help illustrate (4).

\[
\begin{align*}
\text{i=1} & \\
\text{j = 1 2 3 4 5} & \quad \text{1 2 3} & \quad \text{1 2 3 4 5} \\
\text{\[1, 3\] shift} & \quad \text{[1, 5] shift}
\end{align*}
\]

\[
\begin{align*}
\text{i} & = 1 2 3 4 5 \\
\text{C=C-C=C-C} & \quad \text{C=C-C} & \quad \text{C=C-C} \\
\text{\[3, 3\] shift} & \quad \text{[3, 5] shift}
\end{align*}
\]

Formally then, the Cope rearrangement is a \([1, 3]\) or a \([3, 3]\) sigmatropic shift. Many examples of the \([3, 3]\) shift are well known. There are few examples of the \([1, 3]\) shift (5).
One of the most important experiments for determining the transition state of this reaction was done by Von E. Doering and W. R. Roth (6). They proposed that the transition state would be either a six center roof (boat or book)-like one or a four center chair-like one.

To determine which is preferred, they studied the rearrangement of racemic and meso-2,3-dimethyl-1,5-hexadiene. From their experiments, they concluded that the four center chair-like transition state was preferred by about 5.7 kcal/mole in $\Delta\Delta G^\ddagger$. More recently, M. J. Goldstein has conducted an elegant labeling study to calculate $\Delta\Delta G^\ddagger_{523} = 5.8$ kcal/mole (7). His value, $\Delta\Delta H^\ddagger = 11.2$ kcal/mole, is about double that predicted by Von Doering and Roth.
By a series of complex calculations, involving transition state geometries and rates of reaction calculations, Goldstein arrives at the conclusion that there are transition states in addition to the chair and boat-like ones that Von Doering and Roth's experiments (and Goldstein's own experiments) would not distinguish (8).

It was discovered early that part of the driving force of the Cope reaction is the formation of conjugation of R with one of the \( \pi \) systems (9). It was found that for \( R=CN, CO_2Et, C_3H_5 \) (10), and later \( OH \) (9) and \( OSi(CH_3)_3 \) (11) that the reaction was facilitated. As these various R groups were added, several nomenclatures have developed to distinguish the various types of the Cope rearrangement.

\[
\begin{array}{ccc}
R' & R & \text{Name} \\
H & H & \text{degenerate Cope} \\
H & OH & \text{oxy-Cope (enolic Cope)} \\
H & OSi(CH_3)_3 & \text{trimethylsiloxyl-Cope} \\
OH & OH & \text{bisenolic-Cope} \\
\end{array}
\]

In the middle sixties, A. Viola and coworkers investigated the "enologenic Cope rearrangement" of 3-hydroxy-1, 5-hexadiene (2, 12). They found strong evidence (i.e. no radical coupling products) for a
concerted mechanism instead of a radical mechanism involving a pair of radicals. They felt that it is not reasonable to expect the radical fragments to remain close enough together to rejoin without the cyclic constraints of an external cyclic skeleton.

In addition to the Cope rearrangement, 3-hydroxy-1,5-hexadiene systems may rearrange by other routes. All of these rearrangements are permitted by Woodward-Hoffman rules (13).
The synthetic usefulness of the oxy-Cope rearrangement to make ketone compounds has been noticed since the mid-sixties. J. A. Berson showed that the oxy-Cope rearrangement of syn-7-vinyl-anti-7-hydroxynorbornene as one of the easiest methods to produce the bicyclo[3.2.2]noneneone system (14).

In studying the mechanism of 3-hydroxy-1,5-hexadiene system rearrangements, J. A. Berson suggested two alternatives in addition to the diradical or concerted type of mechanism (15). One, the oxy-radical mechanism, involved the initial formation of an oxy-radical followed by β fragmentation and hydrogen abstraction (which
continues the chain) to give the products.

This mechanism was ruled out with the results of reactions with optically active compounds.

The second mechanism was a series of concerted steps: a Diels-Alder retrogression-recombination mechanism. A control study using cyclohexadiene and 2-methoxy-1,3-butadiene failed to give any of the bicyclo[4.4.0] system.

By noting that the rate of reaction for syn- and anti-7-vinyl-7-hydroxy- norbornenes were the same, Berson proposed that the mechanism is a diradical one (16). J. A. Berson and E. J. Walsh
have estimated the allylic resonance energy effect on the strength of adjacent carbon-carbon bonds (17). From the thermolysis of exo- and endo-2-vinylbicyclooct-5-enes, they determined the energy available to lower the bond dissociation at 14 kcal/allyl group. This would be a strong factor in favor of a diradical process.

A useful synthesis of medium sized rings (8-11) was discovered by Marvell and Whalley (18). They found that when trans-1, 2-divinyl-cyclohexanol was heated as a 10% solution for three hours at 220°, they obtained trans-cyclodec-5-ene-1-one in 90% yield.
When cis-1, 2-divinylcyclohexanol was heated for two hours at 220° in a 10% solution, a mixture of cis- and trans-cyclodec-5-ene-1-ones was obtained in a 50% yield.

R. W. Thies found that the pyrolysis of 1-vinylcyclonon-3-en-1-ol, IX, results in only 23% of ring expanded material, X, XI (11).

<table>
<thead>
<tr>
<th>R</th>
<th>IX</th>
<th>X</th>
<th>XI</th>
<th>XII</th>
<th>XIII</th>
<th>olefin</th>
<th>yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>13</td>
<td>49</td>
<td>10</td>
<td>5</td>
<td>10</td>
<td>13</td>
<td>23%</td>
</tr>
<tr>
<td>Si(CH₃)₃</td>
<td>6</td>
<td>53</td>
<td>29</td>
<td>10</td>
<td>-</td>
<td>2</td>
<td>76%</td>
</tr>
</tbody>
</table>
Roughly 60% is polymer produced from polymerization of the product obtained from β hydroxy-olefin cleavage, XIII. The yield of ring expanded material is increased to 76% by the use of the trimethylsilyl (TMS) derivative. The TMS derivative is made quantitatively from the alcohol and after pyrolysis can be easily hydrolyzed back to give the corresponding enol forms which then tautomerize to the ketone forms.

In studying the mechanism of the rearrangement of IX-TMS, R. Thies found that the activation parameters \( (E_a=47.7 \text{ kcal/mole} \) and \( \log A=14.75 \)), loss of stereochemistry, and rates of reaction would suggest a biradical mechanism (13). The diradical, XIV, could lead to the products observed. From the ratio of X-TMS to XI-TMS, the barrier to reclosure of XIV-TMS would have to be
3 kcal/mole lower than the barrier to rotation of the allyl radical (reclosure is the preferred course). The barrier to rotation of the allyl radical has been estimated at 7 to 13 kcal/mole (19). The barrier to reclosure must then be 4 to 10 kcal/mole. Attempts to trap the diradical in toluene were unsuccessful. This would indicate that the barrier to reclosure is small (20).

R. Thies and coworkers have also investigated the siloxy-Cope and oxy-Cope rearrangements of cis-1-vinylcyclooct-3-ene-1-ol (21). Pyrolysis of I-TMS followed by hydrolysis gives a mixture of five components plus starting material. One difference between the pyrolysis of the nine membered ring case (IX-TMS) and the eight membered ring case (I-TMS) is the formation of two ring contracted products, II and III. These arise formally from a [1, 3] shift of the type not usually observed for the 3-oxy-1, 5-hexadiene system. A [1, 3] Cope type shift formally accounts for IV and V while VI formally
arises from a \([3, 3]\) shift. The activation energy obtained by rate determinations at various temperatures is 53.89 kcal/mole and the log of the preexponential term is 15.88. These parameters would suggest that a diradical mechanism is operative. (See Scheme I.)

The formation of II and III might indicate that a series of concerted steps could also account for the formation of all the products. The formation of IV-TMS could arise from a series of concerted steps (eg. \(I-TMS \rightarrow II-TMS \rightarrow IV-TMS\). See Scheme II).

The fact that the ring contracted products are seen in the eight membered case and not the nine is probably due to ring strain effects. In the nine membered case, IX, the force driving the reaction toward the ring expanded products is the formation of enolates—roughly 5 kcal/mole in favor of the enolate. The ring contraction is not favored by any release of strain in going to the seven membered ring from the nine. The eight membered ring loses about 6 kcal/mole of strain energy in going to the six membered products (II and III). The enolate formation (5 kcal) favors the ring expanded products (V and VI).

The interconversion of products was studied in order to elucidate more information concerning the mechanism of this reaction. Since IV-TMS could not arise by a one step concerted process, but through a series of concerted steps or a diradical process, it was of special interest. Preliminary studies indicated that the concerted path might be ruled out. When I-TMS was heated for
Scheme I Diradical

I-TMS → VII

OTMS

→ V-TMS

II-, III-, VI-TMS

Scheme II Concerted

II-TMS

O-TMS

[3, 3]

III-TMS

O-TMS

[3, 3]

II-TMS

O-TMS

[1, 3]

III-TMS

O-TMS

[1, 3]

V-TMS

[1, 3]

OTMS

[3, 3]

VI-TMS

[1, 3]

IV-TMS

[1, 3]
.08 hours at 316°, it underwent 4% conversion. IV-TMS made up 16% of this 4% conversion. When II-TMS was heated for one hour at 285°, it underwent 4% conversion. This would indicate that the series of concerted steps leading to IV-TMS through II- and III-TMS was much slower than the process (a diradical) leading to IV-TMS through VII-TMS. The data was somewhat uncertain due to the two temperatures used and the fact that different analytical methods were used in the two measurements.

The product interconversion study also revealed that the equilibrium of this system is very complex. Samples of I-TMS that were gc impure gave essentially the same products upon thermolysis, but the ratios of products were much different. Ring expanded products were favored. Some steps of the equilibrium are much faster than others, but essentially the same ratio of components may be observed by starting with I-TMS, a mixture of II- and III-TMS, or a mixture of IV-, V-, and VI-TMS. These product interconversion difficulties led to the need for an experiment which would compare I-TMS and II- and III-TMS more carefully.
RESULTS AND DISCUSSION

Results

In order to elucidate more about the mechanism of the interconversion of products in the thermolysis of I-TMS, we undertook the preparation and thermolysis of trans- and cis- 1, 2-divinyl-1-trimethylsiloxycyclohexane, II- and III-TMS. Two general schemes of synthesis of these compounds were used (see Scheme III). A key intermediate in both schemes is 2-vinylcyclohexanol. This compound was oxidized with Collins reagent (CrO$_3$·2 pyridine in methylene chloride) in very poor yields: the best yield was 30% of crude ketone. The crude ketone was reacted with vinyl magnesium bromide in a standard Grignard reaction and the resulting alcohol purified by preparative gas chromatography. The alcohol was converted to the trimethylsiloxy derivative and purified by preparative gc just prior to thermolysis. One has to be especially careful to remove all alcohol and the ampuls must be scrupulously dry. Any trace of moisture will hydrolyze the TMS derivative and lead to polymer formation upon thermolysis.

The key intermediate, 2-vinylcyclohexanol, was made in two methods starting with cyclohexene. One method involved epoxidation followed by ring opening with vinyl magnesium bromide. The other
Scheme III Synthesis of trans- and cis- 1,2-divinyl-1-trimethyl-siloxycyclohexane, II- and III- TMS.

1) $\text{C}_2\text{H}_5\text{O}_2\text{CCHN}_2$
2) LAH

$\xrightarrow{\text{CH}_3\text{CO}_3\text{H}}$

$\text{CH}_2\text{OH}$

$\xrightarrow{\text{H}_3\text{O}^+}$

$\text{OH}$

$\text{OH}$

$\xrightarrow{\text{CrO}_3}$

$\text{pyr, CH}_2\text{Cl}_2$

$\xrightarrow{\text{1) CH}_2=\text{CH MgBr}}$

$\xrightarrow{\text{2) H}_2\text{O}}$

$\text{OH}$

$\xrightarrow{\text{1) CH}_2=\text{CH MgBr}}$

$\xrightarrow{\text{2) H}_2\text{O}}$

$\text{OTMS}$

TriSil

II- TMS and III- TMS 65:35
method involved the preparation of ethyl bicyclo[4.1.0]heptyl-7-carboxylate from cyclohexene and ethyldiazoacetate. This was then reduced to the alcohol with lithium aluminum hydride. The bicyclo[4.1.0]heptyl-7-methanol was solvolyzed to yield 2-vinylcyclohexanol quantitatively. Both methods had their advantages and drawbacks. The epoxidation route, however, seemed to work better than the other. The yield, based on cyclohexene, is also better considering the huge excess of cyclohexene one employs in the ethyl diazoacetate cyclization reaction. The oxidation of 2-vinylcyclohexanol was the most disappointing reaction of all. Jones reagent could not be used because of the sensitivity of 2-vinylcyclohexanone to acid (25). Yields were increased slightly by filtration of the reaction mixture through SilicAR CC7 100-200 mesh instead of filtration through celite.

The analysis of the thermolysis products was carried out by analytical gc. These compounds had been previously identified. In the analysis, the retention times of IV-, V-, and VI-TMS all
overlapped badly. In order to determine their ratio, the mixture was hydrolyzed to the enols which tautomerized to the ketones. This mixture of ketones was then analyzed by gc. The hydrolysis of the TMS derivatives was done in pyridine/HCl solution to minimize any acid catalyzed reactions. Samples of II- and III-TMS and samples of I-TMS, supplied by L. E. Schick, were pyrolyzed under the same conditions of temperature and time (280.5°C and one hour). The results in Table 1 were obtained.

**Table 1.** Pyrolysis of I-TMS and a mixture of II- and III-TMS at 280.5°C for one hour.

<table>
<thead>
<tr>
<th></th>
<th>I-TMS</th>
<th>II-TMS</th>
<th>III-TMS</th>
<th>IV-TMS</th>
<th>V-TMS</th>
<th>VI-TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-TMS</td>
<td>96.0</td>
<td>1.73</td>
<td>1.99</td>
<td>.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>II- and III-TMS</td>
<td>70.0</td>
<td>18.0</td>
<td></td>
<td>11.20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**HYDROLYSIS DATA**

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-TMS</td>
<td>96.9</td>
<td>0.21</td>
<td>0.41</td>
<td>0.14</td>
<td>0.26</td>
<td>0.09</td>
</tr>
<tr>
<td>II- and III-TMS</td>
<td>33.23</td>
<td>21.60</td>
<td>23.40</td>
<td>22.40</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

Pyrolysis of I-TMS leads to 4% conversion, 3.7% of which is II- and III-TMS, while 0.14% is IV-TMS. When II- and III-TMS were pyrolyzed, it showed that II- and III-TMS had undergone 11.2% conversion and 5.7% of this was IV-TMS. The limiting amount of IV-TMS which could be produced from the pyrolysis of I-TMS would be 5.7% of 4% (.057 x 4 = .23%). Since less is formed (0.14%) this would suggest that the series of concerted steps leading from I-TMS
to II- and III-TMS to IV-TMS is viable.

Pyrolysis of I-TMS in toluene for three and one half hours at 281°C leads to the results in Table 2 (22). The same products are formed as in the pyrolysis of I-TMS without toluene. The ratio of products is somewhat changed. Ring expanded products IV-, V-, VI-TMS are favored relative to ring contracted products, II- and III-TMS.

Table 2. Pyrolysis of I-TMS in toluene and I-TMS with no toluene for 3 1/2 hours at 281°C.

<table>
<thead>
<tr>
<th></th>
<th>I-TMS</th>
<th>II-TMS</th>
<th>III-TMS</th>
<th>IV-TMS</th>
<th>V-TMS</th>
<th>VI-TMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>86.7</td>
<td>2.4</td>
<td>3.8</td>
<td></td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>no Toluene</td>
<td>84.3</td>
<td>8.0</td>
<td>6.3</td>
<td></td>
<td>1.1</td>
<td></td>
</tr>
</tbody>
</table>

HYDROLYSIS DATA

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>83.7</td>
<td>4.6</td>
<td>8.1</td>
<td>1.5</td>
<td>2.0</td>
<td>--</td>
</tr>
<tr>
<td>no Toluene</td>
<td>90.7</td>
<td>1.8</td>
<td>2.4</td>
<td>1.0</td>
<td>2.5</td>
<td>1.4</td>
</tr>
</tbody>
</table>

To provide some additional information on this mechanism, cis- and trans-1-phenyl-1-trimethylsiloxycyclodec-3-ene was prepared by reaction of phenyl magnesium bromide with the ketone. The ketone was prepared by Jones reagent oxidation of a mixture of trans- and cis-cyclodec-3-ene-1-ol, which was supplied by J. E. Billigmeier. The rate for interconversion of the trans to cis compound was determined to be about $2.26 \times 10^{-5}$ sec$^{-1}$. The simple
interconversion of trans to cis was complicated by formation of an unidentified compound which is probably the [1, 3] shift product.

![Diagram of interconversion](image)

**Discussion**

The diradical formed from I-TMS would be the same as the diradical formed from II- or III-TMS (see diradical scheme in the introduction section). Since II- and III-TMS are thermodynamically more stable than I-TMS (ca. 6 kcal/mole (13)), we would expect formation of this diradical to be much slower from II- and III-TMS than from I-TMS and, hence, the interconversion of II- and III-TMS would be slower than the rearrangement of I-TMS. This is not observed. The interconversion of II- and III-TMS is at least forty times as fast as the rate of rearrangement of I-TMS (21). One problem involved in the study of product interconversion is that samples which are
loaded with three or more times the standard amount of sample lead to the same products, but in different ratios. Ring expanded material is enhanced relative to ring contracted material. These results could conceivably be due to surface catalyzed interconversion of the ring expanded isomers which could allow a more rapid attainment of the final equilibrium. (The final equilibrium favors the ring expanded products.) To test this idea, samples were run as toluene solutions with enough volume of solution to insure a liquid phase in the ampuls. The results in toluene solution do not support the surface catalysis hypothesis since, under these conditions, ring expanded products are enhanced. The choice of toluene as a solvent was based on: gc properties, no overlap with any products; low volatility; and high temperature stability. In addition, toluene was used as a radical trap. We observe no products characteristic of a trapped diradical.

C. G. Overberger has recently generated the diradical XVI, which undergoes hydrogen abstraction to yield a mixture of cis- and trans-1,6-diphenyl-1-hexenes, and a mixture of 1,2-diphenylcyclohexanes which arise from reclosure of the diradical (23). We observe no hydrogen abstraction products in the thermolysis of I-TMS.
The activation parameters for the thermolysis of I-TMS (Ea=53.89 and log A=15.88) would be strong evidence for a diradical process except for some recent findings by J. A. Berson (24). Berson suggests that symmetry "forbidden" reactions may have activation parameters approaching those of diradicals. By means of simple molecular orbital theory, Berson shows that the order of preference for the three processes is: allowed concerted > forbidden concerted > diradical. His evidence is not entirely theoretical. In the thermal rearrangement of \textit{exo}-5-methyl bicyclo[3.2.0]hept-2-ene-endo-7-acetate to \textit{exo}-3-methyl bicyclo[2.2.1]hept-5-ene-2-acetate, the activation parameters are: \( E_a = 47.1 \text{ kcal/mole} \) and \( \log A = 14.2 \). The magnitudes of these numbers would indicate a diradical, but the stereochemical integrity of the system is not characteristic of a diradical mechanism. The 10:1 ratio of inversion to retention would indicate that, if the reaction is concerted, the "allowed" pathway is only a few kcal/mole favored over the "forbidden" pathway.
Although the conversion of I-TMS to IV-TMS can be accounted for by a series of concerted "allowed" steps, it seems unlikely that all reactions are indeed "allowed." The concerted symmetry "allowed" process for the conversion of I-TMS to II- or III-TMS would be difficult, if not impossible, to occur. During this process, the anti-symmetric use of the p orbital of the carbon bearing the vinyl and the OTMS groups and the symmetric use of the allyl moiety would result in the rotation of the OTMS or vinyl group through the allyl moiety.

The concerted symmetry "forbidden" process would relieve much of this steric interaction by a symmetric use of the allylic moiety and
a symmetric use of the \( p \) orbital. This puts the vinyl and OTMS groups over the allyl moiety and not through it.

More information about this mechanism might be obtained by the thermolysis of the optically active \textit{cis}-1-trimethylsiloxy-1-phenylcyclooct-3-ene. The phenyl group would block reaction to

![Diagram](attachment:image.png)

ring expanded and [3, 3] shift products, while still allowing observance of the [1, 3] shift products. The "allowed" process would

![Diagram](attachment:image.png)

require an inversion of configuration at \( C_1 \), while the "forbidden" process would require a retention. A pure diradical would be
expected to give a 50:50 mixture of retention to inversion.

In conclusion, the mechanism may be accounted for by either a diradical or concerted mechanism, although the high activation parameters would have been sufficient criteria in the past to label this a diradical process.
EXPERIMENTAL

General

All gas chromatography analyses were done on a Varian Aerograph Series 1200 Analytical Gas Chromatograph, fitted with a flame ionization detector, using the columns indicated in Table 3 of the Experimental section. All pyrolysis samples were purified by preparative scale gas chromatography on an Aerograph Gas Chromatograph Model A-90-P using the columns listed in Table 3. Infrared spectra were run on a Beckman IR 8 Infrared Spectrophotometer as films unless otherwise indicated. Nuclear Magnetic Resonance spectra were run on a Varian HA-100 Nuclear Magnetic Resonance Spectrometer. These were run at room temperature as CCl₄ solutions with 1% TMS standard unless otherwise stated.

Preparation of Ethyldiazoacetate (C₂H₅OOCHN₂)

Sodium acetate (0.4 g, 0.005 mole) was dissolved in 75 ml of water and cooled to 0°C. Sodium nitrite (53 g, 0.77 mole) was also dissolved in 75 ml of water and cooled to 0°C. A solution of 70 g (0.5 mole) glycine ethyl ester hydrochloride (C₂H₅OOCH₂NH₂HCl) in 50 ml of anhydrous ethyl ether was added to a three neck 500 ml round bottom flask fitted with a reflux condenser, mechanical stirrer and addition funnel. The sodium acetate and sodium nitrite solutions
were added. The reaction pot was cooled on an ice bath and stirred as 10 ml of 10% sulfuric acid was added slowly (1 ml/min). The mixture was stirred for an additional fifteen minutes after the addition of the sulfuric acid. The ether layer was separated from the aqueous layer and the aqueous layer was collected. The procedure was repeated twice, combining the ether layers each time. The ether layers were washed before combining with 20 ml of 10% sodium bicarbonate. The ether layers were concentrated to give a yellow-green liquid in 70% yield; ir (neat) 3.18, 3.31, 4.70 (azo), 5.95 (ester carbonyl), and 13.48 μ.

**Preparation of Bicyclo [5.1.0] octyl-8-methanol, XX**

To a three neck round bottom flask, fitted with a magnetic stirrer, nitrogen inlet, addition funnel, and condenser was added 140 g (1.45 mole) cycloheptene. Copper (II) sulfate (3 g, 0.02 mole) was added in increments with stirring. After the addition was complete, the reaction pot was heated in an oil bath to 70°C. Ethyl diazoacetate (21.3 g, 0.21 mole) was added slowly with stirring. After stirring overnight, the solution was filtered to remove CuSO₄. The crude ester was added dropwise to a solution of excess lithium aluminum hydride (LAH) in 100 ml dry ether. The excess LAH was quenched with Rochelle salt solution. The ether was dried over MgSO₄, concentrated and distilled to yield 20 g (70%) of XX.
The infrared spectrum of the crude ester showed the strong carbonyl band at 5.8 µ in addition to bands at 3.40, 6.90, 8.6, and 14.6 µ. Upon attempted epimerization of the ester with sodium ethoxide in ethanol, using cis-decalin as a standard, the exo isomer was apparently destroyed leaving the endo isomer. The infrared spectrum of alcohol XX showed major absorptions at 3.05 (OH), 3.45, 9.15, 9.80, and 10.15 µ. The nmr of the alcohol (exo- and endo-) showed absorptions at 0.64-2.50 δ (m, 13 H) and 3.2-3.70 (m, 3 H). Both the ir and nmr of the alcohols were consistent with reported spectra (27). GC analysis on column A showed an 85:15 ratio of exo- to endo- alcohols. The alcohols were purified by preparative gas chromatography on column F before solvolysis. Pure exo (98%) could be obtained, but pure endo (75%) was difficult to obtain because of tailing of exo.

**Rearrangement of Bicyclo [5.1.0] octyl-8-methanol XX**

Typically, 0.5 g of alcohol was placed in a 25 ml round bottom flask, fitted with a reflux condenser and a magnetic stirrer. Ten ml of dioxane and 2 or 3 ml of 0.23 M HClO₄ was added and the mixture heated at reflux (85-90°C) overnight or until the reaction was complete by gc analysis. A small amount of ether was added and the acid neutralized by washing until neutral with several ml of saturated sodium bicarbonate. Excess solvent was removed by rotary
evaporation.

**Preparation of Trimethylsilyl (TMS) derivatives of alcohols**

To one part of alcohol in three parts DMSO was added two parts Tri-Sil (a commercial trimethylsilylating reagent). This mixture was shaken for ten to fifteen minutes and allowed to stand for thirty minutes. The top layer is the TMS derivative and was pipetted off. The remaining DMSO layer was washed once with five parts of pentane. The combined pentane and TMS layer was washed once with an equal volume of water and dried over MgSO₄.

**Preparation of epoxycyclohexane**

To an ice bath cooled, mechanically stirred mixture of 5.74 g (0.07 mole) cyclohexene and 30 g (0.3 mole) sodium carbonate in 75 ml methylene chloride was added, dropwise, 13.3 g (0.07 mole) 40% peracetic acid which had been "pretreated" with 1 g (0.012 mole) sodium acetate. (1 g sodium acetate was dissolved in the peracetic acid.) The mixture was stirred at room temperature until a negative test was obtained with starch-iodide paper. The solid salts were removed by filtration and washed well with additional solvent. Excess solvent was removed with a rotary evaporator to give 6.25 g (91%) of a clear liquid; ir (neat) 3.4, 6.9, 10.9, 11.9, 12.5, and 14.0 μ.
The liquid gave a positive periodate test for epoxides and gave cyclo-
hexanol when reduced with LAH.

**Preparation of 2-vinylcyclohexanol**

To a 1 l. three neck flask, fitted with a dry ice reflux condenser, addition funnel, mechanical stirrer, and nitrogen inlet, was added 2.88 g (0.12 mole) magnesium metal turnings and 70 ml freshly dried tetrahydrofuran (THF). A crystal of iodine and several drops of ethylene bromide were added as 12 ml (almost 0.12 mole) vinylbromide was added. Heat was applied to initiate the reaction. The mixture was allowed to stir to dissolve all the magnesium. The reaction pot was cooled to 0°C and 3.92 g (0.04 mole) expoxycyclohexane was added dropwise as a solution in 100 ml dry THF. The reaction was allowed to stir overnight at room temperature. The excess vinyl magnesium bromide was quenched with 20 ml saturated ammonium chloride solution. The organic and aqueous layers were separated and the organic layer was washed once with an equal volume of water and once with an equal volume of salt solution and dried over MgSO₄: yield 3.78 g (70%); ir (neat) 2.95 (OH), 3.40, 3.49, 6.9, 8.5, 9.35, 10.5, and 14.5 μ (gem methylene); nmr (CCl₄) δ 0.95-2.10 (m, 9 H), 2.95-3.3 (b m, 2 H), 4.90-5.2 (m, 2 H), 5.5-6.00 (m, 1 H).
Preparation of 2-vinylcyclohexanone

To a 1 l. three neck flask, fitted with mechanical stirrer and addition funnel, was added 500 ml methylene chloride and 3.2 g (0.04 mole) pyridine. Chromium trioxide (2 g, 0.02 mole) was added in small increments with stirring. After all was added, an ice bath was used to cool the reaction pot to room temperature. The mixture was stirred for forty minutes and then 3.72 g (0.03 mole) 2-vinylcyclohexanol was added quickly. The reaction stirred for an additional fifteen minutes after the last of the alcohol was added. The reaction mixture was filtered through SilicAR CC7 100-200 mesh. The methylene chloride solution was washed for one hour with an equal volume of 5% sodium bicarbonate. The organic and aqueous layers were separated and the organic layer was washed once with an equal volume of water and once with an equal volume of 0.6 N hydrochloric acid, then dried over calcium chloride. The yield was 30% of crude ketone; ir (neat) 3.4, 3.5, 5.90 (carbonyl), 7.0, 10.9, 12.5, 13.4, and 14.2 μ.

Preparation of 1,2-divinylcyclohexanol II and III

To a 1 l. three neck flask, fitted with dry ice reflux condenser, mechanical stirrer, addition funnel, and nitrogen inlet, was added 2.16 g (0.09 mole) magnesium metal turnings and 70 ml freshly
dried THF. This was stirred at room temperature as 10 ml vinyl bromide in several ml dry THF was added along with a crystal of iodine and several drops of ethylene bromide. The reaction mixture was stirred until all the magnesium was dissolved. The reaction pot was cooled to 0°C and 3.72 g (0.03 mole) crude 2-vinylcyclohexanone was added dropwise with stirring. The reaction was allowed to stir overnight. The excess vinyl magnesium bromide was quenched with several ml of saturated ammonium chloride solution. The organic layer was combined with 100 ml dry THF and washed once with an equal volume of water and dried over magnesium sulfate. The alcohol was purified on columns A and C. The nmr and infrared spectra were consistent with those reported for the compound (18); ir (neat) 3.45 (OH), 3.40, 6.9, 10.1, 11.0, and 14.3 μ: nmr (CCl₄) δ6.2-4.7 (m, 6 H), 2.3-1.3 (m, 10 H).

Pyrolysis of 1,2-divinyl-1-trimethylsiloxy cyclohexane II-and III-TMS

Typically one or two drops (10-20 mg) of the freshly preparative gas chromatographed TMS derivative was placed in a 10 ml pyrex ampul (roughly 100 mm long by 12 mm i.d.) and sealed under vacuum. The ampul had been rinsed with distilled water, acetone, and ammonium hydroxide and dried overnight in a drying oven. The sealed ampul was placed in a fused salt (potassium nitrate- sodium nitrite) bath at the desired temperature (280-300°C). The bath was
maintained to within 0.5°C by a Bailey Model 124 Temperature Controller. At the end of a run, the ampuls were removed and cooled in the combined draft of a hood and a blower. The ampuls were scratched with a file and opened. The organic material was recovered by rinsing with ether.
<table>
<thead>
<tr>
<th>Column</th>
<th>Liquid Phase</th>
<th>Support</th>
<th>Length, Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.5% KOH</td>
<td>80-100</td>
<td>2 meters x 1/8 in., copper</td>
</tr>
<tr>
<td></td>
<td>2.5% Carbowax 4000</td>
<td>Chromosorb W</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>Apiazon N</td>
<td></td>
<td>100 feet, stainless steel capillary</td>
</tr>
<tr>
<td>C</td>
<td>CW 1000</td>
<td>4 ml of a solution of 1 g CW in 8 g of CH₂Cl₂ flushed through at 5 lbs/m² pressure, Baked 12 hrs @ 110°, overnight @ 125°</td>
<td>100 feet, stainless steel capillary</td>
</tr>
<tr>
<td>D</td>
<td>UCON</td>
<td></td>
<td>75 feet, stainless steel capillary</td>
</tr>
<tr>
<td>E</td>
<td>UCON</td>
<td></td>
<td>125 feet, stainless steel capillary</td>
</tr>
<tr>
<td>F</td>
<td>5% KOH</td>
<td>80-100</td>
<td>10 feet x 1/4 in., copper</td>
</tr>
<tr>
<td></td>
<td>5% CW 4000</td>
<td>Chromosorb W</td>
<td></td>
</tr>
<tr>
<td>G</td>
<td>Carbowax 4000</td>
<td>110-120</td>
<td>8 feet x 1/4 in., copper</td>
</tr>
<tr>
<td></td>
<td>Anachrome</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>20% SF 96</td>
<td>60-80</td>
<td>4 feet x 1/4 in., copper</td>
</tr>
</tbody>
</table>

Columns A-E are analytical columns. Columns F-H are preparative columns.
Table 4. GC retention times.

<table>
<thead>
<tr>
<th>Column</th>
<th>Conditions</th>
<th>Compound</th>
<th>Time, minutes</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>100°C, flow-</td>
<td>I-TMS</td>
<td>5.5</td>
</tr>
<tr>
<td></td>
<td>meter 15/7.5</td>
<td>II-TMS</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>III-TMS</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV-TMS</td>
<td>8.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V-TMS</td>
<td>8.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VI-TMS</td>
<td>8.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>I-OH</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>II-OH</td>
<td>9.9</td>
</tr>
<tr>
<td></td>
<td></td>
<td>III-OH</td>
<td>11.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>IV-OH</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>V-OH</td>
<td>23.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>VI-OH</td>
<td>26.0</td>
</tr>
<tr>
<td>E</td>
<td>130°C, 15/7.5</td>
<td>ethyl bicyclo[5.1.0]octyl-8-</td>
<td>endo 9.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>carboxylate</td>
<td>exo 12.0</td>
</tr>
<tr>
<td>A</td>
<td>110°C, 2.7</td>
<td>XX</td>
<td>exo 4.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>endo 5.0</td>
</tr>
</tbody>
</table>
THE ACID-CATALYZED REARRANGEMENT OF BICYCLO[5.1.0]OCTYL-8-METHANOL

INTRODUCTION

The solvolysis of bicyclo[n.1.0] systems capable of cyclopropyl-carbinyl-cyclopropylcarbinyl rearrangement leads primarily to ring expanded or ring opened products. K. Wiberg and G. Szemies studied the solvolysis and acetolysis of exo- and endo-bicyclo[2.1.0]pentyl-5-methyl tosylate (26). They found that solvolysis of the endo compound gives primarily ring expanded products, while solvolysis of the exo compound gives no rearranged products.

In the acetolysis of the same compound, they found that the endo compound again leads to ring expanded products and the exo compound leads to ring opened products.
K. Wiberg and A. Ashe have studied the acetolysis of bicyclo[3.1.0] hexane-6-methyl tosylate (27). They found that the \textit{exo} isomer gives predominantly ring opened products.
The \textit{endo} tosylate gives a complex mixture of products with ring expanded products predominating. From rate and product studies of the acetolysis of cycloheptene-3-yl tosylate, the authors felt that this molecule was a reactive intermediate formed from II. To test
this idea the solvolysis was carried out in aqueous ethanol, a
more nucleophilic solvent which limits ion pair return. The endo
isomer gives little ring expanded products under these conditions
which shows that the ring expanded products formed during acetolysis
arise from reaction of cycloheptene-3-yl tosylate. The exo isomer
gives approximately the same proportion of products in either solvent.

These workers also investigated the solvolysis of exo- and endo-
bicyclo[3.2.0]heptane-6-yl tosylates, III and IV.
The similarity in products between I and III would indicate a common intermediate for the solvolysis of I and III. **Trans-2-vinylcyclopentyl tosylate**, found in the solvolysis of I but not in the solvolysis of III, was found to be more reactive than III, so its absence from the solvolysis mixture of III is not surprising.

T. L. Bond and coworkers found that when **exo-bicyclo[4.1.0]heptyl-7-methanol** was solvolyzed in 10% HCl, ring opened products were formed (28).

**Similar results were obtained for the acetolysis of the tosylates** (27, 28). J. A. Moschino reports the formation of a small amount of
ring expanded material for the acetolysis (29).

\[
\begin{align*}
\text{H} & \quad \text{HOAc} \quad \text{H} \\
\text{CH}_2\text{OTs} & \quad \text{HOAc} \\
\end{align*}
\]

The solvolysis of bicyclo[5.1.0] octane-8-methyl tosylate leads predominantly to ring expanded products (30).

The solvolysis of bicyclo[5.2.0] nonyl tosylate gives the same products in roughly the same ratio.
Solvolysis of bicyclo[6.1.0] nonyl-2-orthodinitrobenzoate also gives the same products. These results would indicate that these solvolyses have a common intermediate.

Wiberg and coworkers feel that two possible pathways would account for these results (26). One path involves backside use of the \( C_2-C_3 \) bond with no rotation of methylene to give cation VI.
The other path would involve a cyclobutyl cation or related activated complex which could lead to VI.

For exo compounds these pathways would lead to trans fused rings and that would only be possible for the larger systems. For example:

C. D. Poulter and S. Weinstein have studied the perchloric acid catalyzed rearrangement of syn- and anti-bicyclo [7.1.0] decan-2-ol systems in aqueous dioxane (31). Treatment of the syn isomer leads to 82% conversion to cis-cyclodec-3-ene-1-ol.
The fact that there are no crossover products (i.e. both systems are stereospecific) would indicate that each isomer leads to a specific noninterconverting homoallylic cation. The authors suggest the structures below.
It has been shown that this stereospecificity does not hold for the lower bicyclo homologs (31, 32, 34). Putting a trans double bond into the smaller ring systems is not energetically favorable.

R. Thies and J. E. Billigmeier found that the acid catalyzed rearrangement of exo-bicyclo [6.1.0] nonane-9-methanol leads to formation of trans-cyclodec-3-ene-1-ol (5, 33).
The endo isomer gives a mixture of cis and trans-cyclodec-3-ene-1-ols. They suggested that the loss of stereochemistry for the endo isomer could be due to formation of a classical cyclobutyl cation or to a secondary 2-vinylcyclooctyl cation. The endo isomer could not engage in a cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement because of the steric interactions. In the reaction of the exo isomer, a cyclopropylcarbinyl-cyclopropylcarbinyl rearrangement is favored and this could account for the high degree of stereospecificity.

The thesis work sought to determine whether the acid catalyzed rearrangement of bicyclo [5.1.0] octyl-8-methanol would lead to a good yield of 2-vinylcycloheptanol, which was the key intermediate in the synthesis of 1,2-divinylcycloheptanol. Rearrangement of lower homologs produce good yields of ring opened material, while rearrangements of higher homologs lead to stereospecific ring expansion.
RESULTS AND DISCUSSION

Results

The preparation of exo- and endo-ethyl bicyclo[5.1.0]octyl-8-carboxylate from the reaction of ethyl diazoacetate and cycloheptene proceeds smoothly in reasonable yield to give an 85:15 ratio of exo to endo ester. Reduction of the ester with excess lithium aluminum hydride in anhydrous ethyl ether leads to a quantitative yield of bicyclo[5.1.0]octyl-8-methanol, XX. Rearrangement of the exo alcohol in aqueous dioxane with perchloric acid catalysis leads to the formation of two products.

The minor component was found to be 2-vinylcycloheptanol. Its identity was verified by gc retention time with an authentic sample prepared by epoxidation of cycloheptene followed by ring opening with vinyl magnesium bromide. The nmr and ir of the minor component were consistent with the reported spectra as well as with the authentic sample (18).

The major component was found to be bicyclo[5.2.0]nonan-8-ol. It went unnoticed for several runs because it overlaps badly with starting material on the gc. When the reaction mixture was studied as the trimethylsilyl derivatives, the bicyclo[5.2.0]nonan-8-ol separates well from the starting material. It was identified by its
nmr which is consistent with that reported for the compound, and the fact that, when oxidized to the ketone with Collins reagent, the ketone band shows at 5.6 μ which is characteristic of a four membered ring ketone.

**Discussion**

The rearrangement of exo-bicyclo [5.1.0] octyl-8-methanol (exo-XX) leads to both ring expanded and ring opened products.

Solvolysis of the exo-tosylate (XX-OTs) leads to somewhat different results (30).
These results may be explained by the formation of the trans-fused cyclopropyl cation, XXV, which is apparently a common step to rearrangement of both the alcohol and the tosylate.

In the tosylate solvolysis, the kinetically controlled conditions may allow this cation to be "trapped" out which leads to formation of the major product for that solvolysis. We would expect to see very little of this product because, under the acid conditions, this product would be quite unstable. XXV may react further to give the cis-fused cyclobutyl cation, XXVI. Capture by water would lead to the major product of our rearrangement. The path for the occurrence of XXII
is not entirely clear. It is also not clear why none of this ring opened product was observed in the solvolysis of XX-OTs. Perhaps the small concentration (ca. 2.25% of the products) accounted for its omission in the analysis.
EXPERIMENTAL

General

See Part I.

Preparation of Bicyclo [5.1.0] octyl-8-methanol

See Part I.

Solvolysis of Bicyclo [5.1.0] octyl-8-methanol

See Part I.

2-Vinylcycloheptanol

The spectra are as follows: nmr (CCl₄) δ 0.9-2.1 (m, 11 H), 2.9-3.2 (m, 2H) and 4.8-6.1 (m, 3H); ir (neat) 2.95, 3.22, 6.10, 9.5, 10.1 and 11.0 μ.

Bicyclo [5.2.0] nonan-8-ol

The spectra are as follows: nmr (CCl₄) δ 0.95-2.55 (m, 14 H), 3.70-4.16 (m, 1H) and 2.85 (s, 1H disappears in D₂O); ir (neat) 3.0 (OH), 3.45, 6.9, 8.0, 8.7, 9.2, 10.95, 11.95, 13.4 μ.
BIBLIOGRAPHY


15. J. A. Berson, E. J. Walsh, Jr., ibid., 90, 4730 (1968).


17. J. A. Berson, E. J. Walsh, Jr., ibid., 90, 4730 (1968).


22. The results in Table 2 are actual values for one run. Additional runs show similar results.


