THE ADDITION OF TRIMETHLYTIN HYDRIDE AND TRIMETHYLGERMANIUM HYDRIDE TO DIENES

RICHARD HERBERT FISH

Follow this and additional works at: https://scholars.unh.edu/dissertation

Recommended Citation
https://scholars.unh.edu/dissertation/813

This Dissertation is brought to you for free and open access by the Student Scholarship at University of New Hampshire Scholars' Repository. It has been accepted for inclusion in Doctoral Dissertations by an authorized administrator of University of New Hampshire Scholars' Repository. For more information, please contact Scholarly.Communication@unh.edu.
FISH, Richard Herbert, 1939—
THE ADDITION OF TRIMETHYLTIN HYDRIIDE
AND TRIMETHYLGERMANIUM HYDRIIDE TO
DIENES.

University of New Hampshire, Ph.D., 1965
Chemistry, organic

University Microfilms, Inc., Ann Arbor, Michigan
THE ADDITION OF TRIMETHYLTIN HYDRIDE AND
TRIMETHYLGERMANIUM HYDRIDE TO DIENES

BY

RICHARD HERBERT FISH
B. S., University of Rhode Island, 1961

A THESIS
Submitted to the University of New Hampshire
In Partial Fulfillment of
The Requirements for the Degree of
Doctor of Philosophy

Graduate School
Department of Chemistry
This thesis has been examined and approved.

Gloria S. Lyer

James B. Hamilton

Kenneth K. Anderson

January 27, 1965

Date

Director of Thesis Research

Director of Thesis Research
ACKNOWLEDGEMENTS

The author would like to express his appreciation to Dr. Henry G. Kuivila for his enthusiasm and patience as well as his constant guidance throughout this research program.

For financial support, the author is grateful to the National Science Foundation.
The author would like to dedicate this thesis to Ann J. Fish whose love and understanding has been a constant inspiration.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. ADDITION OF TRIMETHYLTIN HYDRIDE TO DIENES</td>
<td>3</td>
</tr>
<tr>
<td>A. 1,3-DIENES</td>
<td>3</td>
</tr>
<tr>
<td>1. Background</td>
<td>3</td>
</tr>
<tr>
<td>2. Results</td>
<td>8</td>
</tr>
<tr>
<td>3. Discussion</td>
<td>23</td>
</tr>
<tr>
<td>B. 1,2-DIENES</td>
<td>31</td>
</tr>
<tr>
<td>1. Background</td>
<td>31</td>
</tr>
<tr>
<td>2. Results</td>
<td>32</td>
</tr>
<tr>
<td>3. Discussion</td>
<td>44</td>
</tr>
<tr>
<td>III. ADDITION OF TRIMETHYLGERMANIUM HYDRIDE TO DIENES</td>
<td>54</td>
</tr>
<tr>
<td>1. Background</td>
<td>54</td>
</tr>
<tr>
<td>2. Results</td>
<td>56</td>
</tr>
<tr>
<td>3. Discussion</td>
<td>74</td>
</tr>
<tr>
<td>IV. EXPERIMENTARY</td>
<td>83</td>
</tr>
<tr>
<td>1. Materials</td>
<td>83</td>
</tr>
<tr>
<td>2. Preparation of Trimethyltin Hydride</td>
<td>84</td>
</tr>
<tr>
<td>3. Trimethyltin Hydride-1,3-Butadiene Reaction</td>
<td>84</td>
</tr>
<tr>
<td>4. Determination of the Purity of trans-Crotyltrimethyltin</td>
<td>85</td>
</tr>
<tr>
<td>5. Reaction of 1,3-Butadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid</td>
<td>85</td>
</tr>
<tr>
<td>6. Preparation of Allylcarbinyl Bromide</td>
<td>86</td>
</tr>
<tr>
<td>7. Preparation of Allylcarbinyltrimethyltin</td>
<td>87</td>
</tr>
<tr>
<td>8. Reaction of 2-Methyl-1,3-butadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid</td>
<td>87</td>
</tr>
<tr>
<td>9. Reaction of the Cyclopentadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid</td>
<td>88</td>
</tr>
<tr>
<td>10. Preparation of 4-Bromocyclopentene-1</td>
<td>89</td>
</tr>
<tr>
<td>11. Preparation of Cyclopent-3-en-1-ytrimethyltin</td>
<td>89</td>
</tr>
<tr>
<td>Chapter</td>
<td>Title</td>
</tr>
<tr>
<td>---------</td>
<td>----------------------------------------------------------------------</td>
</tr>
<tr>
<td>12</td>
<td>Attempted Isomerization of Cyclopent-3-en-1-yltrimethyltin</td>
</tr>
<tr>
<td>13</td>
<td>Reaction of the 1,3-Cyclohexadiene-Trimethyltin Hydride Adducts with Tri-fluoroacetic Acid</td>
</tr>
<tr>
<td>14</td>
<td>Preparation of 4-Bromocyclohexene-1</td>
</tr>
<tr>
<td>15</td>
<td>Preparation of Cyclohex-3-en-1-yltrimethyltin</td>
</tr>
<tr>
<td>16</td>
<td>Trimethyltin Hydride-Allene Reaction</td>
</tr>
<tr>
<td>17</td>
<td>Trimethyltin Hydride-Methylacetylene Reaction</td>
</tr>
<tr>
<td>18</td>
<td>Reaction of cis-But-2-en-2-yltrimethyltin and Trifluoroacetic Acid</td>
</tr>
<tr>
<td>19</td>
<td>Reaction of Trimethyltin Hydride and 1,5-Hexadiene</td>
</tr>
<tr>
<td>20</td>
<td>Preparation of Trichlorophenylgermanium</td>
</tr>
<tr>
<td>21</td>
<td>Preparation of Trimethylphenylgermanium</td>
</tr>
<tr>
<td>22</td>
<td>Preparation of Trimethylgermanium Bromide</td>
</tr>
<tr>
<td>23</td>
<td>Preparation of Trimethylgermanium Hydride</td>
</tr>
<tr>
<td>24</td>
<td>Reaction of Trimethylgermanium Hydride with Bicyclo-(2•2 *1)-heptadiene-2,5</td>
</tr>
<tr>
<td>25</td>
<td>Attempted Reaction of 4-Ethyl(2'-trimethylgermyl)cyclohexene-1 with Tri-fluoroacetic Acid</td>
</tr>
<tr>
<td>26</td>
<td>Reaction of cis- and trans-Crotyltrimethylgermanium with Trifluoroacetic Acid</td>
</tr>
<tr>
<td>27</td>
<td>Reaction of Cyclooct-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid</td>
</tr>
<tr>
<td>28</td>
<td>Reaction of Cyclohex-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid</td>
</tr>
<tr>
<td>29</td>
<td>Reaction of Cyclopentadiene-Trimethylgermanium Hydride Adducts with Trifluoroacetic Acid</td>
</tr>
<tr>
<td>30</td>
<td>Hydrogenation of the Trimethylgermanium Hydride-Bicyclo-(2•2 *1)-heptadiene-2,5 Adducts</td>
</tr>
<tr>
<td>31</td>
<td>Ultraviolet Spectra</td>
</tr>
</tbody>
</table>

V. SUMMARY ........................................... 110

VI. BIBLIOGRAPHY AND ACKNOWLEDGEMENTS .......... 111
### LIST OF TABLES

<table>
<thead>
<tr>
<th>Number</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.</td>
<td>The Addition of Organotin Hydrides to 1,3-Dienes</td>
<td>4</td>
</tr>
<tr>
<td>II.</td>
<td>The Addition of Trimethyltin Hydride to 1,3-Dienes</td>
<td>9</td>
</tr>
<tr>
<td>III.</td>
<td>Infrared Spectra of Trimethyltin Hydride-1,3-Diene Adducts</td>
<td>18</td>
</tr>
<tr>
<td>IV.</td>
<td>Nuclear Magnetic Resonance Spectra of Trimethyltin Hydride-1,3-Diene Adducts</td>
<td>20</td>
</tr>
<tr>
<td>V.</td>
<td>Proton Designations for Trimethyltin Hydride-1,3-Diene Adducts</td>
<td>21</td>
</tr>
<tr>
<td>VI.</td>
<td>Data on Trimethyltin Hydride Addition to 1,2-Dienes at 100°</td>
<td>34</td>
</tr>
<tr>
<td>VII.</td>
<td>Nuclear Magnetic Resonance Spectral Data on Trimethyltin Hydride-1,2-Diene Adducts</td>
<td>40</td>
</tr>
<tr>
<td>VIII.</td>
<td>Proton Designations for Trimethyltin Hydride-1,2-Diene Adducts</td>
<td>41</td>
</tr>
<tr>
<td>IX.</td>
<td>Infrared Spectra of Trimethyltin Hydride-1,2-Diene Adducts</td>
<td>42</td>
</tr>
<tr>
<td>X.</td>
<td>Proportions of Central and Terminal Attack in the Trimethyltin Hydride-1,2-Diene Reaction</td>
<td>46</td>
</tr>
<tr>
<td>XI.</td>
<td>Hydrogen Abstraction at the Primary, Secondary and Tertiary Radical Positions Resulting from Central Attack on the Allenic Systems by Trimethyltin Radicals</td>
<td>46</td>
</tr>
<tr>
<td>XII.</td>
<td>Cis and Trans Isomers in the Trimethyltin Hydride-1,2-Diene Adducts</td>
<td>51</td>
</tr>
<tr>
<td>XIII.</td>
<td>Pertinent Data on the Trimethylgermanium Hydride-Diene Reactions</td>
<td>59</td>
</tr>
<tr>
<td>XIV.</td>
<td>Isomerization of 1,5-Cyclooctadiene to 1,3-Cyclooctadiene</td>
<td>65</td>
</tr>
<tr>
<td>XV.</td>
<td>Chemical Shifts of the Trimethylgermanium Group in the Saturated and Unsaturated Bicyclic Compounds</td>
<td>69</td>
</tr>
<tr>
<td>XVI.</td>
<td>Infrared Spectral Data for the Trimethylgermanium Hydride-Diene Adducts</td>
<td>70</td>
</tr>
<tr>
<td>Number</td>
<td>Title</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>----------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>XVII.</td>
<td>Nuclear Magnetic Resonance Spectral Data for the Trimethylgermanium Hydride-Diene Adducts</td>
<td>72</td>
</tr>
<tr>
<td>XVIII.</td>
<td>Proton Designations for Trimethylgermanium Hydride-Diene Adducts</td>
<td>73</td>
</tr>
<tr>
<td>XIX.</td>
<td>Data on the Addition of Trimethyltin Hydride to Dienes</td>
<td>93</td>
</tr>
<tr>
<td>XX.</td>
<td>Physical and Analytical Data on Trimethyltin Hydride-Diene Adducts</td>
<td>95</td>
</tr>
<tr>
<td>XXI.</td>
<td>Data on the Addition of Trimethylgermanium Hydride to Dienes</td>
<td>102</td>
</tr>
<tr>
<td>XXII.</td>
<td>Physical and Analytical Data on Trimethylgermanium Hydride-Diene Adducts</td>
<td>103</td>
</tr>
<tr>
<td>XXIII.</td>
<td>The Ultraviolet Spectra of Several Allylic Germanium and Tin Compounds</td>
<td>109</td>
</tr>
<tr>
<td>Number</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.</td>
<td>Intermediates for Trimethyltin Hydride-1,3-Butadiene Reactions</td>
<td>25</td>
</tr>
<tr>
<td>2.</td>
<td>Initial Radical Attack on the Allenic System</td>
<td>45</td>
</tr>
<tr>
<td>3.</td>
<td>The Isomerization of 1,5-Cyclooctadiene to 1,3-Cyclooctadiene via a Germanium-Platinum-Hydride Complex</td>
<td>77</td>
</tr>
</tbody>
</table>
PART I

INTRODUCTION

The addition of organotin hydrides to olefins has been found to be a very useful method for the preparation of functionally substituted organotin compounds. Van der Kerk and his co-workers\(^1,2,3,4\) found that organotin hydrides added to activated olefins without catalysis. Van der Kerk postulated an ionic mechanism for the addition reaction, Eq. (1).

\[
R_3\text{Sn-H} + \underset{-C}{\overset{C}{\bigtriangledown}} \rightarrow R_3\text{Sn-}{\overset{\bigtriangledown}{\underset{-C}{\bigtriangleup}}} \quad (1)
\]

 Recently, Neumann and co-workers\(^5,6,7\) have shown that the addition of organotin hydrides to olefins is, in fact, a free radical reaction and not an ionic reaction, Eq. (2,3). The following chain mechanism has been proposed.\(^7,8\)

\[
R_3\text{Sn.} + \underset{C}{\overset{-C}{\bigtriangledown}} \rightarrow R_3\text{Sn-}{\overset{\bigtriangledown}{\underset{-C}{\bigtriangleup}}} \quad (2)
\]

\[
R_3\text{Sn-}{\overset{\bigtriangledown}{\underset{-C}{\bigtriangleup}}} + R_3\text{Sn-H} \rightarrow R_3\text{Sn-}{\overset{\bigtriangledown}{\underset{-C}{\bigtriangleup}}}H + R_3\text{Sn.} \quad (3)
\]

Kuivila has reviewed the work done on the addition of organotin hydrides to olefins.\(^8\) In view of this, the author will cite only the more recent literature on the addition of organotin hydrides to dienes.

When this work was started, the only conjugated diene to which addition of organotin hydride had been reported was cyclopentadiene.\(^9\) While this work was in progress, Neumann and co-workers\(^10\) communicated on the addition of organotin hydrides to a variety of conjugated dienes. These results will be discussed below in connection with those obtained in this work.
The purpose of this work was to obtain a better understanding of the course and mechanism of the addition of organotin hydrides to dienes. Five 1,2-dienes and five 1,3-dienes were studied. The results will be presented in Part II of this dissertation.

The addition of organogermanium hydrides to olefins has also produced a variety of functionally substituted organogermanium compounds. This work has been carried out largely by Lesbre and co-workers.\textsuperscript{11-14} The reactions of organogermanium hydrides with dienes have not been reported in the literature. Thus, a variety of dienes was allowed to react with trimethylgermanium hydride in order to ascertain the course of these addition reactions. These results, as well as previous work on olefin-organogermanium hydride additions, will be discussed in detail in Part III of this dissertation.
PART II

ADDITION OF TRIMETHYLTIN HYDRIDE TO DIENES

A. 1,3-DIENES

Background

The addition of organotin hydrides to nonconjugated dienes was studied by Neumann and co-workers.° The double bonds of these dienes react independently, Eq. (4).

\[ R_3\text{SnH} + \text{C}=(\text{CH}_2)_{x+1}\text{C}=(\text{CH}_2)_x\rightarrow R_3\text{Sn} \bigg\{ \begin{array}{c} \text{C}=(\text{CH}_2)_{x+1} \\ \text{C}=(\text{CH}_2)_x \end{array} \bigg\} \]

\[ x = 1 \text{ and } 3 \]

The reactions of conjugated dienes, on the other hand, might be expected to involve both double bonds of the diene, and it was this type of diene-tin hydride reaction that was of considerable interest, Eq. (5).

\[ R_3\text{SnH} + \text{C}=(\text{CH}_2)_{x+1}\text{C}=(\text{CH}_2)_x \rightarrow R_3\text{SnCH}_2\text{CH}=(\text{CH}_2)_{x+1}\text{CH}=(\text{CH}_2)_x + \]

\[ R_3\text{SnCH}_2\text{CH}=(\text{CH}_2)_{x+1}\text{CH}=(\text{CH}_2)_x \]

When this work was started, the only conjugated diene which had been studied was cyclopentadiene.° Van der Kerk and co-workers, however, did not assign a structure for their 1:1 adduct. While this work was in progress, Neumann and co-workers°° communicated on the addition of organotin hydrides to conjugated dienes. F. H. Pollard and co-workers°°° also communicated on the addition of trimethyltin hydride to 1-methyl-1,3-butadiene. Their results, however, are not con-
sistent with those obtained by Neumann$^{10}$ nor the work presented in this dissertation.

Neumann and co-workers obtained the results shown in Table I.

Table I

The Addition of Organotin Hydrides to 1,3-Dienes

<table>
<thead>
<tr>
<th>Diene</th>
<th>Organotin hydride</th>
<th>$^1,4$-adduct$^a$</th>
<th>$^1,2$-adduct$^b$</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C-C-C</td>
<td>Et$_3$SnH</td>
<td>80</td>
<td>20</td>
<td>70-75°C with AIBN catalysis</td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>C=C-C=C</td>
<td>Et$_3$SnH</td>
<td>81$^c$</td>
<td>19</td>
</tr>
<tr>
<td>C=C-C=C</td>
<td>CH$_3$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 2 3 4</td>
<td>C=C-C=C-CH$_3$</td>
<td>Et$_3$SnH</td>
<td>66</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>CH$_3$ CH$_3$</td>
<td>Bu$_3$SnH</td>
<td>72</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\phi$$_3$SnH</td>
<td>95</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Et$_3$SnH</td>
<td>87$^d$</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\phi$$_3$SnH</td>
<td>94</td>
<td>6</td>
</tr>
<tr>
<td>4 3 2 1</td>
<td>$\phi$-C=C-C-C</td>
<td>$\phi$$_3$SnH</td>
<td>64</td>
<td>36</td>
</tr>
</tbody>
</table>

$^a$Sn adding to C$^1$ and H to C$^4$

$^b$Sn adding to C$^1$ and H to C$^2$

$^c$contains very little of the 4,1 adduct

$^d$dicyclopentadiene-tin hydride adduct is by-product
These results indicate that different organotin hydrides give different results. This can be explained on the basis of electronic and steric factors both in the diene and the organotin hydride. This will be discussed when the mechanism is elucidated.

F. H. Pollard and co-workers\textsuperscript{15} investigated the following reaction, Eq. (6).

\[
\begin{align*}
\text{CH}_3\text{C}==\text{C}==\text{CH}_2 + \text{Me}_3\text{SnH} & \quad \xrightarrow{100^\circ} \quad \text{Me}_3\text{SnCH}_2\text{CH}_2\text{C}==\text{C}==\text{CH}_3 + \\
\text{Me}_3\text{SnCH}_2\text{CH}_2\text{C}==\text{C}==\text{CH}_3 & \quad + \quad \text{CH}_3\text{C}==\text{C}==\text{CHCH}_3
\end{align*}
\] (6)

They failed to report any evidence, either spectral or chemical, for their structure assignment. They failed to point up that a 1,4-addition could take place.

**Free Radical Additions to 1,3 Dienes**

The free radical addition of several reagents to conjugated dienes has been studied by a number of workers. Those that have been studied are reactions initiated by attack on the diene by electrophilic radicals, i.e., halogen\textsuperscript{16,17} atoms, thyl\textsuperscript{18-23} and halogenated methyl radicals.\textsuperscript{24-28} They have provided products resulting mainly from 1,4-addition. Consideration of steric and polar factors has given some insight into the mechanism of these radical reactions.

Kharasch and co-workers\textsuperscript{24-26} studied the addition of bromotrichloromethane to butadiene, cyclopentadiene and cyclohexadiene, while Chen and co-workers\textsuperscript{27,28} studied its addition to butadiene, isoprene and 2,3-dimethyl-butadiene, Eq. (7-11).
\[
\begin{align*}
\text{H}_2\text{C} &=\text{C} -\text{C} -\text{CH}_2 \quad + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{CCH}_2\text{C} &=\text{C} -\text{CH}_2\text{Br} \quad + \quad \text{Trace 1,2} \quad (7) \\
&\text{H} \quad \text{H} \\
\text{H}_2\text{C} &=\text{C} -\text{C} -\text{CH}_2 \quad + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{CCH}_2\text{C} &=\text{C} -\text{CH}_2\text{Br} \\
&\text{CH}_3 \quad \text{H} \\
&\text{H} \quad \text{H} \\
&\text{H} \quad 95\% \quad \text{Product} \\
&\text{H} \quad \text{H} \\
\text{H}_2\text{C} &=\text{C} -\text{C} -\text{CH}_2 \quad + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{CCH}_2 -\text{C} &=\text{C} -\text{CH}_2\text{Br} \\
&\text{CH}_3 \quad \text{CH}_3 \\
&\text{CH}_3 \quad \text{H} \\
&\text{CH}_3 \quad \text{CH}_3 \\
&\text{H} \quad 72\% \quad \text{CH}_3 \\
&\text{H} \quad \text{H} \\
&\text{Cl}_3\text{CCH}_2 -\text{C} &=\text{C} -\text{CH}_2\text{Br} \quad (8) \\
&\text{H} \quad 26\% \\
&\text{Trace 4, 3- and 1,2 Product} \\
&\text{H} \quad \text{H} \\
\text{H}_2\text{C} &=\text{C} -\text{C} -\text{CH}_2 \quad + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{CCH}_2 -\text{C} &=\text{C} -\text{CH}_2\text{Br} \\
&\text{CH}_3 \quad \text{CH}_3 \\
&\text{CH}_3 \quad \text{CH}_3 \\
&\text{CH}_3 \quad \text{CH}_3 \\
&\text{H} \quad 100\% \\
&\text{H} \quad \text{H} \\
\text{norbornadiene} + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{C} &=\text{Br} \\
&\text{100\%} \\
&\text{H} \quad \text{H} \\
\text{bicyclo[2.2.2]octatriene} + \quad \text{BrCCl}_3 \quad \rightarrow \quad \text{Cl}_3\text{CCl}_3 &-\text{Br} \quad \text{Br} \\
&68\% \quad 32\% \quad \text{(11)}
\end{align*}
\]
Oswald and co-workers\textsuperscript{18-23} have studied the reaction of a variety of conjugated dienes with aromatic and aliphatic thyl radicals, as well as carrying out autoxidation reactions, Eq. (12-15).

\[
\begin{align*}
H_2C=CHCH_2 & \stackrel{RS-H}{\longrightarrow} \text{RS-CH}_2\text{C}^\bigcap\text{C}|-\text{CH}_3 + 5\% \text{ 1,2 addition (12)} \\
\text{H}_2\text{C}-\text{C}-\text{CH}_2 & \stackrel{RS-H}{\longrightarrow} \text{RS-CH}_2\text{C}^\bigcap\text{C}-\text{CH}_3 + \text{RS-CH}_2\text{C}^\bigcap\text{C}-\text{CH}_3 \\
\text{H}_2\text{C}-\text{C}-\text{CH}_2 & \stackrel{RS-H}{\longrightarrow} \text{RS-CH}_2\text{C}^\bigcap\text{C}-\text{CH}_3 + \text{Trace 1,2 product (14)} \\
\text{CH}_3\text{C}-\text{C}-\text{C}^{-}\text{CH}_3 & \stackrel{\text{1)} RSH}{\longrightarrow} \text{RS-(CH}_3)_2\text{C}^\bigcap\text{C}|-\text{CH}_3 \stackrel{\text{2)} 0_2}{\longrightarrow} \text{RS-(CH}_3)_2\text{C}^\bigcap\text{C}|-\text{O}_2H \\
\text{CH}_3 & \stackrel{\text{H}}{\longrightarrow} \text{CH}_3 \\
\end{align*}
\]

The electrophilic radicals preferentially attack the site of highest electron density and give the product which results from 1,4-addition. The free radical addition reactions to conjugated dienes studied thus far produce the thermodynamically more stable product from abstraction at the sterically more favorable position. This is true if the second step has an appreciable activation energy. The second steps in autoxidation reactions (Eq. 15) are of low activation energies and they produce the thermodynamically less stable products.
Results

Trimethyltin hydride was used in these addition reactions for the following reasons: (1) addition products were readily distillable liquids; (2) gas liquid chromatography could be used to separate the isomers; (3) the nuclear magnetic resonance (n.m.r.) signal of the trimethyltin group is a sharp singlet, and does not contribute complexity to the spectrum.

The reactions of trimethyltin hydride with dienes, catalyzed with azobisisobutyronitrile (AIBN), were carried out in sealed glass ampoules, heated in a bomb at the desired temperatures. The products were separated by gas-liquid chromatography (g.l.c.) and the structures elucidated by a combination of elemental analyses, infrared (I.R.) and nuclear magnetic resonance (n.m.r.) spectroscopy, as well as independent synthesis, in some cases. The results are summarized in Table II and discussed in detail below.

1,3-Butadiene. - The addition of trimethyltin hydride to 1,3-butadiene gave three products, Eq. (16).

\[
\text{Me}_3\text{SnH} + \text{CH}_2\text{C} - \text{CH} = \text{CH}_2 \rightarrow \text{Me}_3\text{SnCH}_2\text{C} = \text{C} - \text{CH}_3 + \text{Me}_3\text{SnCH}_2\text{H} \quad (55.4\%)
\]

\[
\text{Me}_3\text{SnCH}_2\text{H} \quad (37.5\%) + \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH} = \text{CH}_2 \quad (7.1\%)
\]
Table II

Addition of Trimethyltin Hydride to 1,3-Dienes

<table>
<thead>
<tr>
<th>Diene</th>
<th>% Yield</th>
<th>% 1,4 Product&lt;sup&gt;a&lt;/sup&gt;</th>
<th>% 1,2 Product&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Condition&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Time, hrs.</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C=C—C=C</td>
<td>60</td>
<td>92.9</td>
<td>7.1</td>
<td>13</td>
<td>100°</td>
<td></td>
</tr>
<tr>
<td>C=C—C=C</td>
<td>65</td>
<td>89.1&lt;sup&gt;d&lt;/sup&gt;</td>
<td>10.9&lt;sup&gt;e&lt;/sup&gt;</td>
<td>11</td>
<td>100°</td>
<td></td>
</tr>
<tr>
<td>CH₃</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C=C—C=C</td>
<td>66</td>
<td>77</td>
<td>23</td>
<td>11</td>
<td>100°</td>
<td></td>
</tr>
<tr>
<td>CH₃ CH₃</td>
<td>67</td>
<td>57</td>
<td>43</td>
<td>8</td>
<td>100°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>57.5</td>
<td>≥89</td>
<td>≤11</td>
<td>5-7</td>
<td>175°</td>
<td></td>
</tr>
<tr>
<td></td>
<td>54.5</td>
<td>66</td>
<td>34</td>
<td>11</td>
<td>110°</td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup> Me₃Sn adds to C₁ and H to C₄

<sup>b</sup> Me₃Sn adds to C₁ and H to C₂

<sup>c</sup> All reactions run at 100-110° were catalyzed with 2 mole percent azobisisobutyronitrile.

<sup>d</sup> This includes 45.5% of the reverse 4,1-adduct.

<sup>e</sup> This includes 5.5% of the reverse 4,3-adduct.
Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) was used to separate the cis- and trans-crotyltrimethyltins, 1 and 2, and the peak areas were used to calculate the relative amounts of the isomers. The trans isomer, which was contaminated with allylcarbinyltrimethyltin, 3, had the shortest retention time. The I.R. spectrum of 1 was superimposable on the compound characterized by Verdone as cis-crotyltrimethyltin. Compound 2 had all the characteristic I.R. bands of trans-crotyltrimethyltin with the exception of bands at 910 cm$^{-1}$ and 3075 cm$^{-1}$; these are characteristic of a terminal vinyl group, indicating the presence of some 1,2-addition product, 3. Since the extinction coefficient for pure trans-crotyltrimethyltin at 225 m$\mu$ was known, the purity of 2 could be determined. Compound 2 was found to be 84% pure trans, contaminated with 16% of 3.

Compound 3 was isolated by destroying 1 and 2 with trifluoroacetic acid, Eq. (17).

$$
\text{Me}_3\text{SnCH}_2\text{CH-CHCH}_3 + \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH=CH}_2 \xrightarrow{\text{CF}_3\text{COOH}} \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH=CH}_2 \\
+ \text{CH}_2=\text{CH-CH}_2\text{CH}_3 + \text{Me}_3\text{SnO-CCF}_3
$$

(17)

The extremely high reactivity of allylic organometallic compounds in the presence of electrophiles is well documented. Compound 3, whose I.R. spectrum was superimposable on that of the compound recovered from the reaction of Eq. (17), was also prepared by an independent synthesis, Eq. (18).

$$
\text{CH}_2=\text{CHCH}_2\text{CH}_2\text{Br} + \text{Me}_3\text{SnCl} \xrightarrow{\text{Mg, Et}_2\text{O}} \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH-CH}_2
$$

(18)
2-Methyl-1,3-butadiene.- The addition of trimethyltin hydride to 2-methyl-1,3-butadiene gave four products, Eq. (19).

\[ \text{Me}_3\text{SnH} + \text{CH}_2=\text{C} - \text{CH} = \text{CH}_2 \rightarrow \text{Me}_3\text{SnCH}_2\text{CH} - \text{CH} = \text{CH}_2 \quad (5.4\%) + \]

\[ \text{Me}_3\text{SnCH}_2\text{CH}_2\text{CH} - \text{CH} = \text{CH}_2 \quad (5.5\%) + \text{Me}_3\text{SnCH}_2\text{CH} _2\text{C} - \text{CH}_3 \quad (45.5\%) + \]

\[ \text{Me}_3\text{SnCH}_2\text{C} - \text{CH}_3 \quad (43.6\%) \quad (19) \]

Structure Assignment.- G.l.c. (20 ft. 20% silicone nitrile column) could be used to separate 4 cleanly. The peak for 5 was partially hidden under that for 6, and 5 and 6 were not completely separated from 7. The retention times increased in the order \(4 < 6 < 5 < 7\). The I.R. spectrum of 4 showed bands at 3075 cm.\(^{-1}\), 990 cm.\(^{-1}\), and 910 cm.\(^{-1}\), characteristic of a terminal vinyl group.\(^3\) The I.R. spectrum of 6 showed a weak band at 3015 cm.\(^{-1}\) and a band at 845 cm.\(^{-1}\), characteristic of a trisubstituted double bond.\(^3\) A weak band at 885 cm.\(^{-1}\) was evident, this being characteristic of a terminal methylene group\(^3\), due to the presence of 5. The I.R. spec-
trum of 7 showed bands at 3015 cm.\(^{-1}\) and 820 cm.\(^{-1}\), characteristic of a trisubstituted double bond. The n.m.r. spectrum\(^{38}\) of 6 showed a vinyl proton, \(\tau\) 4.68, as a triplet (J = 9.0 c.p.s.), due to coupling with the methylene protons, as expected for a 4,1-addition product. It also contained a multiplet at \(\tau\) 5.30 which was attributed to the terminal methylene group of the 4,3-addition product. Compound 7 showed a vinyl proton quartet at \(\tau\) 5.07 (J = 6.5 c.p.s.) due to a coupling with methyl group, as expected for a 1,4-addition product. In order to substantiate the structures of 6 and 7, assigned on the basis of I.R. and n.m.r. data, a trifluoroacetic acid cleavage was carried out on the mixture of products. If we assume an SE\(^2\) Mechanism\(^{37}\), the 4,1 product, 6, would cleave to give 3-methyl-1-butene, Eq. (20), while the 1,4 product, 7, would give 2-methyl-1-butene, Eq. (21).

\[
\begin{align*}
\text{Me}_3\text{SnCH}_2\text{CH}_2\text{C} & \overset{\text{CF}_3\text{COOH}}{\longrightarrow} \text{Me}_3\text{SnOCF}_3 + \text{CH}_2\text{CH}_2\text{CHCH}_3 \\
\text{Me}_3\text{SnCH}_2\text{C} & \overset{\text{CF}_3\text{COOH}}{\longrightarrow} \text{Me}_3\text{SnOCF}_3 + \text{CH}_2\text{CCH}_2\text{CH}_3
\end{align*}
\]

(20) (21)

The results of the cleavage reaction were not as quantitative as desired, since 2-methyl-1-butene was found to react with trifluoroacetic acid. Both 3-methyl-1-butene (94.5%) and 2-methyl-1-butene (5.4%) were identified by comparison of their retention times (g.l.c. on a 20 ft. 20% silicone nitrile column) with authentic samples and by infrared spectroscopy, which was consistent with 3-methyl-1-butene, the predominant product. This confirms that our structural assignments for 6 and 7 were correct. Since the allylic isomers 6 and 7 could be preferen-
tially destroyed, leaving 4 and 5 intact, we used this method to determine the percentage of 5. After the addition of the trifluoroacetic acid, the remaining material was analyzed by g.l.c. (4 ft. 17% silicone nitrile column), revealing the presence of 4 and 5. From previous g.l.c. analysis, the percentage of 4 was found to be 5.4%; thus, the peak area of 4 was equal to 5.4% and the peak area of 5 was calculated to be 5.5%. The percentage of 6 was now determined by subtracting 5.5% from that calculated for 5 and 6.

2,3-Dimethyl-1,3-butadiene.- The addition of tri-methyltin hydride to 2,3-dimethyl-1,3-butadiene gave two products, Eq. (22).

\[ \text{Me}_3\text{SnH} + \text{CH}_2 \overset{\text{C-C}}{\text{CH}_2} \rightarrow \text{Me}_3\text{SnCH}_2\text{C-CH}_2 \text{CH}_3 \text{CH}_3 \quad (23\%) + \]

\[ \text{Me}_3\text{SnCH}_2\text{C-CH} \overset{\text{CH}_3}{\text{CH}_3} \quad (77\%) \quad (22) \]

Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) was used to separate 8 and 9, 8 having the shorter retention time. The peak areas were used to calculate percentages. The I.R. spectrum of 8 showed bands at 3065 cm.\(^{-1}\) and 890 cm.\(^{-1}\), characteristic of a terminal methylene group. Compound 9 showed the very weak C-C stretch at 1650 cm.\(^{-1}\), as well as the absence of a vinyl hydrogen stretch. The n.m.r. spectrum of 8 showed multiplets at \(\tau\) 5.42 and \(\tau\) 5.47 (J=1.0 c.p.s.), integrating for two protons. A methyl doublet \(\tau\) 8.95 and methylene doublet \(\tau\) 8.99 were
coupled with a tertiary proton $\tau$ 7.61 with a multiplicity of 6 ($J = 7.0$ c.p.s.) in the ratio of 3:2:1. The trimethyltin group was a singlet at $\tau$ 9.95 integrating for nine protons. The n.m.r. spectrum of 9 showed singlets at $\tau$ 8.42 (six protons), $\tau$ 8.35 (three protons), and $\tau$ 8.28 (two protons), as well as a singlet at $\tau$ 9.93 (nine protons). The n.m.r. spectra for 8 and 9 are thus consistent with the assigned structures.

**Cyclopentadiene.**- The addition of trimethyltin hydride to cyclopentadiene gave two products, 10 and 11, which are formed in different ratios, depending on the reaction conditions, Eq. (23).

$$\text{Me}_3\text{SnH}$$

$$\begin{array}{c}
\text{H} \\
\text{SnMe}_3
\end{array}$$

$$\begin{array}{c}
\text{Cyclopentadiene} \\
\text{SnMe}_3
\end{array}$$

$$\begin{align*}
\text{Me}_3\text{SnH} + \text{Cyclopentadiene} &\xrightarrow{100^\circ} \text{Me}_3\text{SnCyclopentadiene}^\text{(57%) + Me}_3\text{SnCyclopentadiene}^\text{(43%)} \\
&\xrightarrow{175^\circ} \text{Me}_3\text{SnCyclopentadiene}^\text{(89%) + Me}_3\text{SnCyclopentadiene}^\text{(11%)}
\end{align*}$$

(23)

If the mixture of 57% 10 and 43% 11 was heated to 175° for six hours, only a small change in its composition was evident, i.e., to 62% 10 and 38% 11. In another experiment a pure sample of 11 was heated at 175° for eight hours in the presence of a catalytic amount of trimethyltin hydride, and no change (g.l.c.) was evident in its composition. We can say for sure that no isomerization of 11 to 10 was taking place at 175°; however, we cannot explain why at higher temperature 10 seems to form in preference to 11.
Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) was used to separate 10 and 11, 11 having the shorter retention time. The peak areas were used to calculate their percentages. The I.R. spectrum of 10 had a C=C stretching frequency at 1590 cm.\(^{-1}\) contrasted to 11 whose C=C stretching frequency was at 1610 cm.\(^{-1}\). This may be due in part to some sort of d\(\pi\) p\(\pi\) interaction in the allylic compound, 10, with the tin d-orbitals and the \(\pi\)-orbitals of the double bond which lowers the wave length. Other spectral differences are evident; for example, compound 10 has a strong band at 900 cm.\(^{-1}\) absent in 11 and 11 has a strong band at 670 cm.\(^{-1}\) absent in 10. The chemical reactivity of the allylic product 10 was conveniently used to isolate the 1,2-addition product, 11. In an experiment to completely substantiate the assignment of each isomer, 10 was destroyed by reaction with trifluoroacetic acid, Eq. (24).

\[
\begin{align*}
\text{SnMe}_3 + \text{SnMe}_3 & \xrightarrow{\text{CF}_3\text{COOH}} \text{Me}_3\text{SnOCF}_3 + \text{SnMe}_3 \\
\end{align*}
\]
Compound 11 was also prepared via an independent synthesis, Eq. (25), and had an I.R. spectrum which was superimposable on that compound recovered from the trifluoroacetic acid cleavage reaction (Eq. 24).

\[
\begin{align*}
\text{Br} & \quad + \quad \text{Me}_3\text{SnCl} & \quad \xrightarrow{\text{Mg, Et}_2\text{O}} & \quad \text{SnMe}_3
\end{align*}
\]

\text{(25)}

1,3-Cyclohexadiene.- The addition of trimethyltin hydride to 1,3-cyclohexadiene gave two products, Eq. (26)

\[
\begin{align*}
\text{Me}_3\text{SnH} & \quad + \quad \text{C}_2\text{H}_4 & \quad \rightarrow & \quad \text{SnMe}_3 & \quad (66\%) \\
& & & \quad (34\%) \\
\end{align*}
\]

\text{(26)}

Structural Assignments.- G.l.c. failed to separate 12 and 13; the n.m.r. spectrum, however, indicated two trimethyltin singlets, at \( \tau \) 9.91 and \( \tau \) 9.96, with areas in the ratio 66\% to 34\%. An experiment was performed in which 12 and 13 were subjected to trifluoroacetic acid cleavage, then analyzed by n.m.r. spectroscopy, Eq. (27).

\[
\begin{align*}
\text{SnMe}_3 & \quad + \quad \text{SnMe}_3 & \quad \xrightarrow{\text{CF}_3\text{COOH}} & \quad \text{SnMe}_3 + \quad \text{Me}_3\text{SnOCCF}_3 + \quad \text{SnMe}_3
\end{align*}
\]

\text{(27)}
The trimethyltin singlet at 7 9.91 (66%) disappeared, and this was assigned to 12. Compound 13 was collected by preparative g.l.c. (20 ft. 20% silicone nitrile column) and had I.R. and n.m.r. spectra that were identical to the known 13 prepared by independent synthesis, Eq. (28).

\[
\text{Br} + \text{Me}_3\text{SnCl} \xrightarrow{\text{Mg, Et}_2\text{O}} \text{SnMe}_3
\]  

(28)

Characteristic bands in the I.R. spectra of the several adducts are given in Table III. N.m.r. spectral data are to be found in Table IV and assignments in Table V.
Table III

Infrared Spectra of Trimethyltin Hydride - 1,3-Diene Adducts

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 3012 (m)</td>
<td>1648 (s)</td>
<td>1190 (s)</td>
<td>725 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 3010 (m)</td>
<td>1650 (m)</td>
<td>1190 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 3075 (m)</td>
<td>1649 (m)</td>
<td>1185 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 3075 (m)</td>
<td>1638 (m)</td>
<td>1185 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 3015 (w)</td>
<td>1650 (w)</td>
<td>1190 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 3015 (w)</td>
<td>1655 (m)</td>
<td>1185 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 3065 (m)</td>
<td>1645 (m)</td>
<td>1188 (m)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>1650 (w)</td>
<td>1185 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10 3050 (m)</td>
<td>1590 (m)</td>
<td>1190 (s)</td>
<td>710 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 3040 (m)</td>
<td>1610 (m)</td>
<td>1185 (m)</td>
<td>700 (w)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 3017 (m)</td>
<td>1655 (m)</td>
<td>1185 (s)</td>
<td>700 (w)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*a bands in cm⁻¹; liquid smears.

b out of plane deformation.
<table>
<thead>
<tr>
<th></th>
<th>=CH$_2$ o.o.p. def.</th>
<th>Vinyl C-H o.o.p. def.</th>
<th>CH$_3$Sn Rocking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td></td>
<td>770 (s)</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td>770 (s)</td>
</tr>
<tr>
<td>3</td>
<td>910 (s)</td>
<td></td>
<td>765 (s)</td>
</tr>
<tr>
<td>4</td>
<td>910 (s)</td>
<td></td>
<td>765 (s)</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>845 (m)</td>
<td>765 (s)</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>820 (w)</td>
<td>760 (s)</td>
</tr>
<tr>
<td>8</td>
<td>890 (s)</td>
<td></td>
<td>765 (s)</td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>760 (s)</td>
</tr>
<tr>
<td>10</td>
<td></td>
<td></td>
<td>760 (s)</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td></td>
<td>765 (s)</td>
</tr>
<tr>
<td>13</td>
<td></td>
<td></td>
<td>765 (s)</td>
</tr>
</tbody>
</table>
Table IV

Nuclear Magnetic Resonance Spectra of Trimethyltin Hydride-1,3-Diene Adducts$^a,b$

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Conc. in CC$_4$</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>(f)</th>
<th>(g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>neat</td>
<td>5.10 (m)</td>
<td>5.14 (m)</td>
<td>4.3 (m)</td>
<td>7.80 (4)</td>
<td>9.12 (3)</td>
<td>9.50 (1)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ja-b 1.5, Ja-c 6.0, Jc-b 10.5, Jc-d 7.5, Je-d 7.5</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6$^c$</td>
<td>neat</td>
<td>4.68 (3)</td>
<td>8.31 (m)</td>
<td>8.31 (m)</td>
<td>3.31 (m)</td>
<td>9.90 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ja-d 9.0,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>50%</td>
<td>5.07 (4)</td>
<td>8.42 (m)</td>
<td>8.42 (m)</td>
<td>8.42 (m)</td>
<td>9.90 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ja-b 6.5,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>30%</td>
<td>5.48 (m)</td>
<td>5.47 (m)</td>
<td>8.31 (2)</td>
<td>7.61 (6)</td>
<td>8.95 (2)</td>
<td>8.99 (2)</td>
<td>9.95 (1)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Ja-b 1.0, Ja-c and Jb-c 0.5, Jd-e and Jd-f 7.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>50%</td>
<td>8.42 (1)</td>
<td>8.35 (1)</td>
<td>8.28 (1)</td>
<td>9.93 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10$^d$</td>
<td>neat</td>
<td>4.35 (m)</td>
<td>7.80 (m)</td>
<td>9.95 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11$^d$</td>
<td>neat</td>
<td>4.35 (m)</td>
<td>7.75 (m)</td>
<td>9.97 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13$^d$</td>
<td>35%</td>
<td>4.47 (m)</td>
<td>7.95 (m)</td>
<td>8.10 (m)</td>
<td>9.99 (1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$ See Table V for structure and proton designation.

$^b$ Values reported in $\gamma$ units and measured at the center of each multiplet. $^c$ Contaminated with compound 5.

$^d$ Coupling constants not calculated; spectrum too complicated.

$^e$ $^d$
Table V

Proton Designation for Trimethyltin Hydride-1,3-Diene Adducts

<table>
<thead>
<tr>
<th>Proton Designation (Area)</th>
<th>3 Me₃SnCH₂CH₂C-C₂H₃</th>
<th>6 Me₃SnCH₂CH₂C=C-C₂H₃</th>
<th>7 Me₃SnCH₂CH₂C=C-C₂H₃</th>
<th>8 Me₃SnCH₂CH₂C=C-C₂H₃</th>
<th>9 Me₃SnCH₂CH₂C=C-C₂H₃</th>
<th>10 Me₃SnCH₂CH₂C=C-C₂H₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>a,b(2), c(1), d(2), e(2), f(9)</td>
<td>a(1), b,c,d(8), e(9)</td>
<td>a(1), b,c,d(8), e(9)</td>
<td>a(1), b,c,d(8), e(9)</td>
<td>a(1), b,c,d(8), e(9)</td>
<td>a(1), b,c,d(8), e(9)</td>
<td>a(2), b(5), c(9)</td>
</tr>
</tbody>
</table>
Table V cont.

Proton Designation (Area)

11

\[ \begin{array}{c}
\text{a(2), b(5), c(9)} \\
\end{array} \]

13

\[ \begin{array}{c}
\text{a(2), b(4), c(3), d(9)} \\
\end{array} \]
Discussion

Free Radical Mechanism.- The mechanism of the addition of organotin hydrides to olefins has been investigated by Neumann and co-workers.\textsuperscript{5,6,7} They have shown, without a doubt, that the organotin hydride adds to olefins via a free radical mechanism; they have inhibited the addition reaction by introducing radical scavengers such as hydroquinone and galvinoxyl. Their studies have also pointed out that the tin radical itself is an outstanding radical trap. The mechanism presented for the addition of trimethyltin hydride to 1,3-dienes will be explained by invoking a radical process.

Catalyzed and Uncatalyzed Addition Reactions.- The addition of trimethyltin hydride to 1,3-dienes proceeded smoothly with or without azobisisobutyronitrile (AIBN) catalysis. The catalyzed and uncatalyzed reactions, i.e., 1,3-butadiene gave the same products, and their ratios were identical. In contrast to the 1,3-diene reactivity, a nonconjugated diene failed to react with trimethyltin hydride under thermal conditions. For example, 1,5-hexadiene gave only a trace of addition product when heated with trimethyltin hydride at 100° for nine hours. When two mole per cent of AIBN was added, an addition product was obtained in 59\% yield, Eq. (29).

\[
\text{Me}_3\text{SnH} + \text{CH}_2\text{CH(CH}_2\text{)}_2\text{CH}^\cdot \text{CH}_2 \xrightarrow{2 \text{ mole } \% \text{ AIBN}} \text{Me}_3\text{Sn(CH}_2\text{)}_4\text{C}^\cdot \text{CH}_2\text{H}
\]

(29)

The contrasted reactivity of 1,3-dienes and the unconjugated diene, 1,5-hexadiene, can be attributed to a special driving force provided by the formation of an intermediate allylic radical in the reaction of the 1,3-diene with trimethyltin hydride.
Allylic Radical Intermediates. - The added driving force for the addition of trimethyltin hydrides to 1,3-dienes can be explained by invoking an allylic radical intermediate, Eq. (30).

\[ \text{Me}_3\text{Sn} \cdot + \text{CH}_2\cdot \text{CH} = \text{CH} \cdot \text{CH}_2 \rightarrow \text{Me}_3\text{SnCH}_2\text{CH} = \text{CH} \cdot \text{H} \quad (30) \]

The first step of the mechanism is the attack of an organotin radical on a carbon-carbon double bond. This step is estimated to be endothermic since it involves breaking a carbon-carbon double bond (ca. 60 kcal.) and making a tin-carbon bond (ca. 50 kcal.), Eq. (31).

\[ \text{R}_3\text{Sn} \cdot + \text{C} = \text{C} \rightarrow \text{R}_3\text{Sn} \cdot \text{C} = \text{C} \quad (31) \]

or \( \Delta H = +10 \text{ kcal.} \)

The second step, or displacement step, is exothermic since it involves breaking a tin-hydrogen bond (\(<50 \text{ kcal.}\)) making a carbon-hydrogen bond (ca. 98 kcal.), Eq. (32).

\[ \text{R}_3\text{Sn} \cdot \text{C} = \text{C} \cdot + \text{R}_3\text{Sn} \cdot \text{H} \rightarrow \text{R}_3\text{Sn} \cdot + \text{R}_3\text{Sn} \cdot \text{C} = \text{C} \cdot \text{H} \quad (32) \]

or \( \Delta H = -48 \text{ kcal.} \)

When an allylic radical is formed, the activation energy for the first step (Eq. 31) is considerably lower, since a stable intermediate is being formed, while the second step, even though still exothermic, may have an appreciable activation energy. Incidentally, the first step in the addition reaction (Eq. 31) has not been shown experimentally to be reversible. This work has not given an answer to that question; it has shown, however, that the overall reaction is not reversible, the proof being the stability of the cyclopentadiene-tri-
methyltin hydride adducts when heated to 175°C.

The addition of trimethyltin hydride to 1,3-butadiene has given a rather interesting result; the addition reaction produced 55.4% cis- and 37.5% trans-crotyltrimethyltin. The following scheme is proposed to account for this result, Figure 1.
Intermediate $I_{\text{trans}}$ forms when a trimethyltin radical attacks the transoid form of 1,3-butadiene, and Intermediate $II_{\text{cis}}$ forms when a trimethyltin radical attacks the cisoid form. Intermediate $II_{\text{cis}}$ would have added stabilization due to participation by the tin atom. This predominance of $\text{cis}$ is unusual in that the few cases of additions to dienes have produced predominance of the $\text{trans}$ isomer, although the stereochemistry has not been studied extensively.\textsuperscript{18-23} The energy differences between $\text{cis}$ and $\text{trans}$ isomers is probably not significant, and the predominance of one form over the other is more likely for relief of steric strain. An example of this has been observed by Walling and Thaler.\textsuperscript{40} They have reacted $\text{cis}$-2-butene and $\text{trans}$-2-butene with $t$-butyl hypochlorite, Eq. (33), and found that $\text{cis}$-2-butene reacted faster, since it is more strained than $\text{trans}$-2-butene.

\[
\begin{align*}
\text{CH}_3\text{C} & \cdot \text{CH}_3 & t-\text{BuO} & \rightarrow & \text{CH}_2\cdot\text{C} & \text{CH}_3 & t-\text{BuOCl} & \rightarrow & \text{ClCH}_2\text{C} & \cdot \text{CH}_3 \\
\text{H} & & & & \text{CH}_3 & & & & \text{H} & & \text{H}
\end{align*}
\]

(33)

This relief of steric strain in formation of the intermediate radical provides the driving force for the difference in reactivity. The cisoid conformation of 1,3-butadiene reacts faster with a trimethyltin radical because it is the less stable, energy-rich conformer of 1,3-butadiene. This, coupled with formation of the bridged Radical II, is apparently responsible for the formation of an excess of $\text{cis}$ over $\text{trans}$-crotyltrimethyltin in the ratio 1.48 to 1. The cyclic dienes that were studied proved interesting. The cyclopentadiene reaction was studied at two different temperatures, $100^\circ$ and $175^\circ$. The results show that at $175^\circ > 89\%$ of the 1,4
addition product, 10, is formed; while at 100° the amount was 57%. This result cannot be explained with the information available on organotin hydride addition reactions. The difficulty lies in the fact that energy factors cannot be discussed unless more is known about each step in the addition reaction. The first step (attack of an organotin radical on the olefin, Eq. (31)) has not been shown to be reversible or irreversible, while the overall reaction has been shown in this research (no isomerization of cyclopent-3-en-1-yltrimethyltin to cyclopent-2-en-1-yltrimethyltin at 175° in the presence of trimethyltin hydride), to be irreversible under these conditions. The second step is probably not reversible since it would be endothermic by ca. 70 kcal. However, a detailed study of both steps needs to be undertaken to clarify the results obtained.

**Polar Factors in the Trimethyltin Hydride Additions to 1,3-Dienes.** The contributions of polar effects in radical addition reactions has given considerable information regarding the mechanisms of such reactions. Walling has described these phenomena in detail. The trimethyltin radical can act as the donor radical and the 1,3-diene, the acceptor. Thus the energy of a transition state may be sufficiently lowered if electron transfer from the radical to the olefin has occurred.

\[
\text{Me}_3\text{Sn} \cdot \quad \text{C=CH}_2 \quad \leftrightarrow \quad \text{Me}_3\text{Sn} | \cdot \quad \text{C=CH}_2
\]

Thus electron withdrawing groups in the olefins and electron donating groups on the tin atom would facilitate the addition reaction. Experimentally it has been shown that electron withdrawing groups, i.e., -OAc, -CH₂CN, on the olefin facili-
tate organotin hydride additions. However, no relative rate studies have been made in which electron withdrawing and donating groups on the olefins and on the tin atom were used. Polar effects are evident in 1,3-diene-trimethyltin hydride reactions. For example, 2-methyl-1,3-butadiene produced 51% of the products from attack of the trimethyltin radical on the double bond without the methyl group, Eq. (34).

\[
\text{Me}_3\text{Sn}^* + \text{H}_2\text{C} \equiv \text{C} \equiv \text{CH}_2 \rightarrow \text{Me}_3\text{SnCH} \equiv \text{C} \equiv \text{CH}_2
\]  

(34)

This would be expected since the electron donating trimethyltin radical initially attacks the site of lowest electron density. In contrast, electrophilic radicals, such as aromatic thiyl radicals, produce products exclusively from attack at carbon 1, Eq. (35).

\[
\text{RS}^* + \text{H}_2\text{C} \equiv \text{C} \equiv \text{CH}_2 \rightarrow \text{RS}-\text{CH} \equiv \text{C} \equiv \text{CH}_2
\]  

(35)

Not only does the trimethyltin radical show preference in its attack on an olefin, but the second step, Eq. (36), also reveals the operation of polar effects. It has been shown that primary radical sites are more reactive than secondary and tertiary radicals in displacement steps. Thus, in an allyl radical, abstraction at the primary site would be favored sterically, and would also produce the thermodynamically-
cally more stable product. Significant abstraction, however, has been observed at the most sterically hindered position of the allylic radical to give the thermodynamically less stable product. This is pronounced in the reaction of 2,3-dimethyl-1,3-butadiene with trimethyltin hydride, where 23% of the product comes from abstraction at the tertiary radical site of the allylic system, Eq. (37).

\[ \text{Me}_3\text{SnCH}_2\text{C}==\text{C}==\text{CH}_2 + \text{Me}_3\text{SnH} \rightarrow \text{Me}_3\text{SnCH}_2\text{C}==\text{C}==\text{CH}_2 \]  

(37)

This can be accounted for on the basis of the following contributing polar structure.

\[
\begin{align*}
\text{Me}_3\text{Sn} & \quad \text{CH}_3 \quad \text{H} \\
\text{Me}_3\text{Sn} & \quad \text{CH}_2 \quad \text{H} \\
\text{Me}_3\text{Sn} & \\
\end{align*}
\]

This explanation may also be evident with the cyclic dienes, where significant 1,2-addition product is produced (43% at 100°).

\[
\begin{align*}
\text{Me}_3\text{Sn} & \quad \text{Me}_3\text{Sn} \\
\text{Me}_3\text{Sn} & \\
\end{align*}
\]

It is also evident in the 1,3-cyclohexadiene reaction where 34% 1,2-product is produced.

In the case of triethyltin hydride we see a significant amount of abstraction at the sterically less favored secondary and tertiary allylic radical positions, giving the
thermodynamically less stable product (see p.4). The ethyl group, being a better electron donor, makes the hydride hydrogen more electron-rich; hence its greater reactivity at the secondary (1,3-butadiene) and tertiary (2-methyl- and 2,3-dimethyl-1,3-butadiene) allylic radical positions. The decrease in abstraction at these positions when using tributyltin hydride may be due to steric factors in this bulkier organotin hydride.

The abstraction step is influenced by two factors. The first, the polar factor, which we have discussed, produced the thermodynamically less stable isomer from abstraction at the sterically less favorable position. The second, the electron distribution factor, puts higher odd electron density at the primary site, giving the thermodynamically more stable product from abstraction at the sterically more favorable position. This can be rationalized by visualizing the methyl and trimethyltin groups (see intermediate allylic radical in Eq. 37), perturbing the electron distribution in such a way that the higher odd electron density is on the carbon atom at the end away from the methyl and trimethyltin groups. The polar effect from trimethyltin to triethyltin hydride becomes more important since more of the thermodynamically less stable product is produced with triethyltin hydride.
B. 1,2-DIENES

Background

The variety of reagents that have been added to allenes (1,2-dienes) under radical conditions has been limited. Haszeldine and co-workers\textsuperscript{43} added trifluoromethyl iodide to allene under the influence of ultraviolet light to give the product of terminal attack by the trifluoromethyl radical, Eq. (38).

\[
\text{CF}_3^\cdot + \text{CH}_2\text{CCH}_2 \xrightarrow{hv} \text{CF}_3\text{CH}_2\cdot\text{CH}_2
\]

\[
\text{CF}_3\text{CH}_2\cdot\text{CH}_2 + \text{CF}_3\text{I} \rightarrow \text{CF}_3\text{CH}_2\cdot\text{CH}_2
\]

The addition of hydrogen bromide to allene was shown to occur with attack by bromine at the central carbon atom\textsuperscript{44,45,46}, Eq. (39).

\[
\text{Br}^\cdot + \text{H}_2\text{C}^\cdot\text{CCH}_2 \rightarrow \cdot\text{CH}_2\cdot\text{CH}_2
\]

\[
\cdot\text{CH}_2\cdot\text{CH}_2 + \text{HBr} \rightarrow \text{CH}_3\cdot\text{CH}_2
\]

Thiyl radicals have also been added to a variety of allenes\textsuperscript{47,48,49}, and the results show that, as the allenic system is substituted with methyl groups, central attack increases. Szwarc and Rajbenbach\textsuperscript{50,51} studied the attack of methyl radicals on a variety of allenes; they failed, however, to identify any of their products. They concluded, from methyl affinity studies, that the central carbon atom was the
chief site of attack. The fact that considerable differences are noted in the results obtained, in regard to the orientation of radicals on the allene system, led us to investigate the additions of trimethylin hydride to a variety of substituted allen-es.

**Results**

**Allene.**—The addition of trimethylin hydride to allene gave two products, Eq. (40).

\[
\text{Me}_3\text{SnH} + \text{CH}_2=\text{C}=\text{CH}_2 \rightarrow \text{CH}_3\begin{array}{c}
\text{C} \\
\text{Me}_3\text{Sn}
\end{array} \text{CH}_2 \ (45.2\%) +
\]

\[
\text{Me}_3\text{SnCH}_2\begin{array}{c}
\text{C} \\
\text{H}
\end{array} \text{CH}_2 \ (54.8\%) \quad \text{(40)}
\]

**Structural Assignments.**—G.l.c. (20 ft. 20% silicone nitrile column) was used to separate 14 and 15, and peak areas were used to calculate the percentage of each isomer. Compound 14 had the shortest retention time. The I.R. spectrum of 14 had bands at 3040 cm\(^{-1}\), 1600 cm\(^{-1}\) and 910 cm\(^{-1}\), characteristic of a terminal methylene group; the I.R. spectrum of 15 had bands at 3080 cm\(^{-1}\), 1630 cm\(^{-1}\), 985 cm\(^{-1}\), and 880 cm\(^{-1}\), characteristic of a terminal vinyl group.\(^3\) The n.m.r. spectrum of 14 had multiplets at \(\tau\) 4.37 and \(\tau\) 4.90 (J=1.5-1.6 c.p.s.), integrating for two protons, a triplet at \(\tau\) 8.08 (J=1.5-1.6 c.p.s.), three protons, and a singlet at \(\tau\) 9.9, nine protons. The multiplet at \(\tau\) 4.90 was assigned to the hydrogen cis to the trimethylin group. The effect of
a trimethyltin group, as will be seen in other cases, is to shield a cis vinyl hydrogen.

\[
\begin{align*}
\text{R} & \text{C=CR} \\
\text{H} & \text{SnMe}_3
\end{align*}
\]

All the physical constants for \textit{14} were in accord with those reported by Seyferth and Vaughan, and those for \textit{15} in accord with an authentic sample prepared by Verdone. See Table VI for data on trimethyltin hydride-1,2-diene reactions.

\textbf{1,2-Butadiene.}- The addition of trimethyltin hydride to 1,2-butadiene gave five products, Eq.(41).

\[
\text{Me}_3\text{SnH} + \text{CH}_3\text{C} \equiv \text{C} \text{CH}_2 \rightarrow \begin{array}{c}
\text{Me}_3\text{Sn} \\
\text{H}
\end{array} \text{CH}_3\text{C} \equiv \text{C} \text{CH}_2 \text{H} (31.5\%) + \\
\text{CH}_3\text{C} \equiv \text{CCH}_3 \text{Me}_3\text{Sn} (38.6\%) + \\
\text{Me}_3\text{Sn} \text{CH}_2\text{CH}_{2}\text{SnMe}_3 (10.0\%) + \\
\text{Me}_3\text{Sn} \text{CH}_2\text{SnMe}_3 (10.0\%) + \\
\text{Me}_3\text{Sn} \text{CH}_2\text{SnMe}_3 (3.5\%) (41)
\]

\textbf{Structural Assignments.}- G.l.c. (20 ft. 20\% silicone nitrile column) was used to separate all five products. Compound \textit{16} had the shortest, and \textit{20} the longest, retention time. The I.R. spectrum of \textit{16} showed bands at 3055 cm.$^{-1}$, 1600 cm.$^{-1}$, and 915 cm.$^{-1}$, characteristic of a terminal
Table VI
Data on Trimethyltin Hydride Addition to 1,2-Dienes at 100°

<table>
<thead>
<tr>
<th>1,2-Diene</th>
<th>Time, hrs.</th>
<th>Total Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃C=CH₂</td>
<td>9</td>
<td>67</td>
</tr>
<tr>
<td>CH₃C=C=CH₂</td>
<td>10.5</td>
<td>72.6</td>
</tr>
<tr>
<td>CH₃C=CH₂</td>
<td>11</td>
<td>72</td>
</tr>
<tr>
<td>CH₃C=C(CH₃)CH₃</td>
<td>8.5</td>
<td>65</td>
</tr>
<tr>
<td>CH₃C=C(CH₃)H</td>
<td>10</td>
<td>82.5</td>
</tr>
</tbody>
</table>
methylene group. Compound 17 had bands at 3000 cm$^{-1}$, 1615 cm$^{-1}$, and 18, 3000 cm$^{-1}$, 1626 cm$^{-1}$, and 820 cm$^{-1}$; both 17 and 18 had I.R. spectra characteristic of trisubstituted ethylenes. Compounds 19 and 20 had I.R. spectra superimposable on authentic trans- and cis-crotyltrimethyltin, respectively. The n.m.r. spectrum of 16 had multiplets at $\gamma$ 4.33 and $\gamma$ 4.88 (J=1.3 c.p.s.); a methylene quartet at $\gamma$ 7.65 coupled to a methyl triplet $\tau$ 8.95 (J=7.0 c.p.s.). The trimethyltin singlet appeared at $\gamma$ 9.82. The integrated ratios were 1:1:2:3:9. The n.m.r. spectrum of 17 had a sixteen peak vinyl signal at $\gamma$ 4.36, coupled with methyl protons at $\tau$ 8.33 (J=7.0 c.p.s.) and $\tau$ 8.17 (J=2.0 c.p.s.). The methyl protons were also coupled with each other (J=1.0 c.p.s.). The trimethyltin singlet appeared at $\gamma$ 9.95. Integrated area ratios were 1:3:3:9. The n.m.r. spectrum of 18 was essentially the same as 17, except for chemical shifts and coupling constants. The vinyl proton (16 lines) $\gamma$ 3.96 coupled with methyl protons $\gamma$ 8.30 (J=6.6 c.p.s.) and at $\gamma$ 8.15 (J=1.8 c.p.s.). The trimethyltin singlet appeared at $\gamma$ 9.84; the integrated area ratios were 1:3:3:9. Compound 17 was assigned the cis configuration, since its vinyl hydrogen was shielded to higher field due to the trimethyltin group. In order to substantiate this assigned stereochemistry, a relatively pure sample of 17 was cleaved with trifluoroacetic acid. The stereochemistry of electrophilic substitution reactions of organometallic compounds at an olefinic carbon atom has been shown to occur with retention of configuration. The cis-but-2-en-2-ytrimethyltin gave 94% cis-2-butene and 6% trans-2-butene when reacted with trifluoroacetic acid, Eq. (42).

$$\text{CH}_3\text{C} = \text{C}\text{CH}_3 \text{Me}_3\text{Sn} \xrightarrow{\text{CF}_3\text{COOH}} \text{CH}_3\text{C} = \text{C}\text{CH}_3 (94\%) + \text{CH}_3\text{C} = \text{C}\text{CH}_3 (6\%)$$

(cis) (trans)
The 6% trans-2-butene resulted from the trans isomer, 18.

3-Methyl-1,2-butadiene.- The addition of trimethyltin hydride to 3-methyl-1,2-butadiene gave two products, Eq. (43).

\[
\text{Me}_3\text{SnH} + \text{CH}_3\text{C} = \text{C-CH}_2 \rightarrow \text{CH}_3\text{CH} = \text{C-CH}_2 \text{Me}_3\text{Sn} \quad (26.8\%) +
\]

\[
\text{CH}_3\text{C} = \text{C-CH}_2 \quad (73.2\%)
\]

(43)

21

22

Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) was used to separate 21 and 22, with 21 having the shortest retention time. The I.R. spectrum of 21 showed bands at 3030 cm.\(^{-1}\), 1590 cm.\(^{-1}\), and 916 cm.\(^{-1}\), characteristic of a terminal methylene group. Compound 22 had a C-C stretching frequency at 1630 cm.\(^{-1}\), as well as the absence of a vinyl hydrogen stretching frequency. The n.m.r. spectrum of 21 had multiplets at \(\tau\) 4.33 and \(\tau\) 4.82 (J=2.0 c.p.s.) and a tertiary proton multiplet at \(\tau\) 7.58, coupled with six methyl protons \(\tau\) 9.0(2) (J=6.5 c.p.s.). The trimethyltin singlet appeared at \(\tau\) 9.86. The integrated area ratios were 1:1:1:6:9. The n.m.r. spectrum of 22 had methyl singlets at \(\tau\) 8.28, \(\tau\) 8.35, and a trimethyltin singlet at \(\tau\) 9.25. The integrated area ratios were 6:3:9, as expected for 22.
2,3-Pentadiene.- The addition of trimethyltin hydride to 2,3-pentadiene gave two products, Eq. (44)

\[ \text{Me}_3\text{SnH} + \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array} \text{C}=\text{C} \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array} \rightarrow \begin{array}{c} \text{CH}_3 \text{CH}_2 \\ \text{Me}_3\text{Sn} \end{array} \text{C}=\text{C} \begin{array}{c} \text{CH}_3 \\ \text{H} \end{array} \] (46.1%)

\[ \begin{array}{c} \text{CH}_3 \text{CH}_2 \\ \text{Me}_3\text{Sn} \end{array} \text{C}=\text{C} \begin{array}{c} \text{H} \\ \text{CH}_3 \end{array} \] (53.9%)

Structural Assignments.- All attempts to separate 23 and 24 by g.l.c. failed; however, the n.m.r. spectrum indicated the presence of two trimethyltin singlets and the areas of these singlets were used to calculate the percentage of each isomer. The I.R. spectra of 23 and 24 had bands at 3005 cm.\(^{-1}\), 1626 cm.\(^{-1}\), and 825 cm.\(^{-1}\), characteristic of trisubstituted ethylenes. The n.m.r. spectrum of 23 and 24 had two vinyl proton quartets at \( \tau \) 3.96 and \( \tau \) 4.35 coupled with their respective methyl groups, which, interestingly, had the same chemical shifts \( \tau \) 8.45(2) (J=6.5 c.p.s.). The ethyl protons in both 23 and 24 also had the same chemical shifts; the methylene quartets, \( \tau \) 7.85, were coupled to methyl triplets, \( \tau \) 9.1 (J=7.2-7.5 c.p.s.). The cis compound, 23, was assigned the trimethyltin singlet at \( \tau \) 9.93 from our previous observations. The trimethyltin singlet at \( \tau \) 9.86 was assigned to the trans isomer, 24.
2-Methyl-2,3-pentadiene.- The addition of trimethyltin hydride to 2-methyl-2,3-pentadiene gave three products, Eq. (45).

\[
\text{Me}_3\text{SnH} + \text{CH}_3\text{C} = \text{C} - \text{CH}_3 \rightarrow \text{CH}_3\text{C} = \text{C} - \text{C}\text{H} \quad (42.2\%) +
\]

\[
\text{CH}_3\text{C} = \text{CHCH}_3 \quad (12.3\%) + \text{CH}_3\text{C} = \text{CCH}_2\text{CH}_3 \quad (45.5\%) \quad (45)
\]

Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) gave a separation of 27 from 25 and 26. Compounds 25 and 26 could not be separated by g.l.c.; however, the n.m.r. spectrum indicated two trimethyltin singlets. The peak areas in the g.l.c. and n.m.r. spectrum were used to calculate the percentages of each isomer. The I.R. spectrum of 25 and 26 had bands at 3005 cm\(^{-1}\), 1620 cm\(^{-1}\), and 835 cm\(^{-1}\) characteristic of trisubstituted ethylenes. The I.R. spectrum of 27 had a C\(_2\)C stretching frequency at 1620 cm\(^{-1}\) and showed the absence of a vinyl hydrogen stretching frequency. The n.m.r. spectrum of 25 and 26 indicated two vinyl proton quartets at \(\tau\) 3.96 and \(\tau\) 4.46 coupled with their respective vicinal methyl protons, which had the same chemical shift at \(\tau\) 8.31(2) (J=7.0 c.p.s.). The isopropyl groups for both 25 and 26 also had the same chemical shift with a tertiary proton multiplet \(\tau\) 7.61 coupled with the six methyl protons at \(\tau\) 9.05(2) (J=7.0 c.p.s.). The trimethyltin singlet at \(\tau\) 9.90 was assigned to the cis isomer, 25, and the trimethyltin singlet at \(\tau\) 9.82 to the trans isomer, 26. Compound 27 had
methyl singlets at $\tau$ 8.27 and $\tau$ 8.20 and a methylene quartet $\tau$ 7.80 coupled to a methyl triplet $\tau$ 9.12 ($J=7.5$ c.p.s.). The trimethyltin singlet appeared at $\tau$ 9.85. The integrated area ratios were 3:3:2:3:9.

**Methylacetylene.** - In order to determine whether allene was being isomerized to the corresponding acetylene isomer, a control experiment was carried out. The addition of trimethyltin hydride to methylacetylene gave three products, Eq. (46).

$$\text{Me}_3\text{SnH} + \text{CH}_3\text{C}≡\text{CH} \rightarrow \text{Me}_3\text{Sn}-\text{CH}≡\text{CH}_3 \quad (70.4\%) \quad +$$

$$\begin{align*}
\text{Me}_3\text{Sn}-\text{C}≡\text{C}_3 &\quad (29\%) \\
\text{Me}_3\text{Sn}-\text{C}≡\text{CH}_3 &\quad (\text{ca. 0.6\%})
\end{align*}$$

This same reaction was carried out by Seyferth and Vaughan. They obtained 68% of 28, 28% of 29, and 4% of 14: the results indicate that no allene was being isomerized to acetylene under the conditions used. The excess allene gas from the reaction of allene and trimethyltin hydride was also shown by g.l.c. and I.R. spectroscopy to contain no methylacetylene. The n.m.r. spectral data for several adducts are found in Table VII and the proton designations in Table VIII. The infrared spectral data are found in Table IX.
Table VII

Nuclear Magnetic Resonance Spectral Data on
Trimethyltin Hydride-1,2-Diene Adducts\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Conc. in CCl\textsubscript{4}</th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
<th>(d)</th>
<th>(e)</th>
<th>Ja-b(1.5-1.6)</th>
<th>Ja-c(1.5-1.6)</th>
<th>Jb-c(1.5-1.6)</th>
<th>Jc-d(1.5-1.6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>50%</td>
<td>4.37(m)</td>
<td>4.90(m)</td>
<td>8.08(3)</td>
<td>9.9(1)</td>
<td></td>
<td>1.5-1.6</td>
<td>1.5-1.6</td>
<td>1.5-1.6</td>
<td>1.5-1.6</td>
</tr>
<tr>
<td>16</td>
<td>50%</td>
<td>4.33(m)</td>
<td>4.88(m)</td>
<td>7.65(4)</td>
<td>8.95(3)</td>
<td>9.82(1)</td>
<td>1.3</td>
<td>1.3</td>
<td>1.3</td>
<td>7.5</td>
</tr>
<tr>
<td>17</td>
<td>50%</td>
<td>4.36(16)8.33(2)</td>
<td>8.17(m)</td>
<td>9.95(1)</td>
<td></td>
<td></td>
<td>7.0</td>
<td>2.0</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>35%</td>
<td>3.96(16)8.30(2)</td>
<td>8.15(m)</td>
<td>9.84(1)</td>
<td></td>
<td></td>
<td>6.6</td>
<td>1.8</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>50%</td>
<td>4.33(m)</td>
<td>4.82(m)</td>
<td>7.58(m)</td>
<td>9.0(2)</td>
<td>9.86(1)</td>
<td>2.0</td>
<td>1.0</td>
<td>1.0</td>
<td>6.5</td>
</tr>
<tr>
<td>22</td>
<td>neat</td>
<td>8.28(1)</td>
<td>8.35(1)</td>
<td>9.25(1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>neat</td>
<td>4.35(4)c8.45(2)</td>
<td>7.85(4)</td>
<td>9.1(3)</td>
<td>9.93(1)c</td>
<td>6.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td>7.2-7.5</td>
</tr>
<tr>
<td>24</td>
<td>neat</td>
<td>3.95(4)c8.45(2)</td>
<td>7.85(4)</td>
<td>9.1(3)</td>
<td>9.86(1)c</td>
<td>6.5</td>
<td>1.0</td>
<td></td>
<td></td>
<td>7.2-7.5</td>
</tr>
<tr>
<td>25</td>
<td>50%</td>
<td>4.46(4)</td>
<td>8.31(2)</td>
<td>7.61(m)</td>
<td>9.05(2)</td>
<td>9.90(1)</td>
<td>7.0</td>
<td>1.1</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>26</td>
<td>50%</td>
<td>3.96(4)</td>
<td>8.31(2)</td>
<td>7.61(m)</td>
<td>9.05(2)</td>
<td>9.82(1)</td>
<td>7.0</td>
<td>1.1</td>
<td></td>
<td>7.0</td>
</tr>
<tr>
<td>27</td>
<td>50%</td>
<td>8.27(1)</td>
<td>8.20(1)</td>
<td>7.80(4)</td>
<td>9.12(3)</td>
<td>9.85(1)</td>
<td></td>
<td></td>
<td></td>
<td>7.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a} See Table VIII for structure and proton designation.

\textsuperscript{b} Values reported in T units and measured at the center of each multiplet. J values in c.p.s.

\textsuperscript{c} Je-a 1.2 c.p.s.
Table VIII
Proton Designations for
Trimethyltin Hydride-1,2-Diene Adducts

<table>
<thead>
<tr>
<th></th>
<th>Proton Designations</th>
<th></th>
</tr>
</thead>
</table>
| 14 | \( c CH_3 \quad C \quad H \quad a \)  \
|   | \( d \text{Me}_3\text{Sn} \quad C \quad H \quad b \)  \
| 15 | \( \text{Me}_3\text{Sn} \quad \text{CH}_2 \quad C \quad \text{CH}_2 \)  \
|   | \( d \text{CH}_3 \quad \text{C} \quad \text{H} \quad a \)  \
|   | \( e \text{Me}_3\text{Sn} \quad \text{C} \quad \text{H} \quad b \)  \
| 16 | \( \text{cCH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{b} \)  \
|   | \( d \text{Me}_3\text{Sn} \quad \text{C} \quad \text{H} \quad a \)  \
| 17 | \( \text{cCH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{b} \)  \
|   | \( d \text{Me}_3\text{Sn} \quad \text{C} \quad \text{H} \quad a \)  \
| 18 | \( \text{cCH}_3 \quad \text{C} \quad \text{CH}_3 \quad \text{a} \)  \
|   | \( d \text{Me}_3\text{Sn} \quad \text{C} \quad \text{CH}_3 \quad \text{b} \)  \
| 19 | \( \text{CH}_3 \quad \text{C} \quad \text{CH}_2\text{SnMe}_3 \)  \
| 20 | \( \text{CH}_3 \quad \text{C} \quad \text{CH}_2\text{SnMe}_3 \)  \
|   | \( \text{H} \quad \text{H} \)  \
| 21 | \( \text{dCH}_3 \quad \text{C} \quad \text{C} \quad \text{H} \quad \text{a} \)  \
|   | \( \text{eMe}_3\text{Sn} \quad \text{C} \quad \text{H} \quad \text{b} \)
### Table IX

**Infrared Spectra of Trimethyltin Hydride-1,2-Diene Adducts**

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>3040 (m)</td>
<td>1600 (w)</td>
<td>1190 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>3080 (m)</td>
<td>630 (s)</td>
<td>1190 (s)</td>
<td>985 (m)</td>
<td>880 (s)</td>
</tr>
<tr>
<td>16</td>
<td>3055 (m)</td>
<td>1600 (w)</td>
<td>1190 (s)</td>
<td></td>
<td>915 (s)</td>
</tr>
<tr>
<td>17</td>
<td>3000 (vw)</td>
<td>1615 (m)</td>
<td>1190 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>3000 (vw)</td>
<td>1625 (m)</td>
<td>1190 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>3010 (m)</td>
<td>1650 (m)</td>
<td>1185 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3012 (m)</td>
<td>1648 (s)</td>
<td>1190 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>3030 (m)</td>
<td>1590 (w)</td>
<td>1190 (s)</td>
<td></td>
<td>916 (s)</td>
</tr>
<tr>
<td>22</td>
<td></td>
<td>1630 (s)</td>
<td>1190 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23 + 24</td>
<td>3005 (w)</td>
<td>1625 (m)</td>
<td>1190 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 + 26</td>
<td>3005 (w)</td>
<td>1620 (m)</td>
<td>1189 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td>1620 (m)</td>
<td>1188 (m)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*^a^ band in cm.$^{-1}$; liquid smears.

*^b^ out of plane deformation.*
<table>
<thead>
<tr>
<th>Comp.</th>
<th>C-H o.o.p. def. Trans d'ble bond</th>
<th>Vinyl C-H o.o.p. def.\textsuperscript{b} Trisub. ethylene</th>
<th>CH\textsubscript{3}–Sn Rocking</th>
<th>C-H o.o.p. def.\textsuperscript{b} Cis d'ble bond</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>18</td>
<td></td>
<td>820 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>960 (s)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20</td>
<td></td>
<td></td>
<td>770 (s)</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td></td>
<td></td>
<td>770 (s)</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td></td>
<td></td>
<td>770 (s)</td>
<td></td>
</tr>
<tr>
<td>23 + 24</td>
<td></td>
<td>835 (m)</td>
<td>770 (s)</td>
<td></td>
</tr>
<tr>
<td>25 + 26</td>
<td></td>
<td>835 (m)</td>
<td>770 (s)</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td></td>
<td></td>
<td>760 (s)</td>
<td></td>
</tr>
</tbody>
</table>
Discussion

Free Radical Mechanism. - The addition of organotin hydride to olefins, as previously stated, has been shown to be a free radical process.\(^5,6,7\) The addition of trimethyltin hydride to allenes was catalyzed by azobisisobutyronitrile; consequently, a radical process will be invoked to explain the results obtained.

Allylic Radical Intermediate. - The course of a free radical reaction is determined largely by the intermediate radicals which may be formed. As we have seen, the driving force for the reaction of 1,3-dienes with trimethyltin radicals is the formation of an intermediate allylic radical. The allene system is complex because attack of a free radical on the central carbon atom initially would give a primary radical, since the double bond is out of the plane of the developing radical, if rotation about the breaking double bond did not accompany the attack. The attack of a free radical on the terminal carbon atom would lead to a vinylic radical. This initial attack at the central carbon atom may have a higher activation energy than attack at the terminal carbon atom\(^47,48\), Fig. 2.
In spite of the fact that the initial attack on the central carbon atom of allene gives a primary radical, there seems to be little reason why an allylic radical might not form directly. This would only involve a 90° rotation about the bond being attacked, as shown below.
The results obtained show that an allylic radical is probably formed as the intermediate, Tables X and XI.

### Table X

**Proportions of Central Attack and Terminal Attack in the Trimethyltin Hydride-1,2-Diene Reaction**

<table>
<thead>
<tr>
<th>1,2-Diene</th>
<th>Central Attack</th>
<th>Terminal Attack</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allene</td>
<td>45.2</td>
<td>54.8</td>
</tr>
<tr>
<td>1,2-Butadiene</td>
<td>86.5</td>
<td>13.6</td>
</tr>
<tr>
<td>3-Methyl-1,2-butadiene</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2,3-Pentadiene</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-2,3-pentadiene</td>
<td>100</td>
<td>-</td>
</tr>
</tbody>
</table>

### Table XI

**Abstraction at the Primary, Secondary, and Tertiary Radical Positions, Resulting from Central Attack on the Allenic Systems by Trimethyltin Radicals**

<table>
<thead>
<tr>
<th>1,2-Diene</th>
<th>% Primary</th>
<th>% Secondary</th>
<th>% Tertiary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allene</td>
<td>45.2</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,2-Butadiene</td>
<td>54.9</td>
<td>31.5</td>
<td>-</td>
</tr>
<tr>
<td>3-Methyl-1,2-butadiene</td>
<td>73.2</td>
<td>-</td>
<td>26.8</td>
</tr>
<tr>
<td>1,2-Pentadiene</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>2-Methyl-1,2-pentadiene</td>
<td>-</td>
<td>45.5</td>
<td>54.5</td>
</tr>
</tbody>
</table>
The results obtained by Jacobs and Illingworth\textsuperscript{48} lend some support to this conclusion. They added ethane-thiyl radicals to allene, 1,2-butadiene, and 3-methyl-1,2-butadiene. Their results show increasing attack at the central carbon atom—allene 12.8%, 1,2-butadiene 48.2%, and 3-methyl-1,2-butadiene 100%. They explained this increase in central carbon attack with increasing methyl substitution as being due to formation of a more stable secondary or tertiary radical. Moreover, the only product they obtained from the reaction of 3-methyl-1,2-butadiene with thiophenol or ethylmercaptan was the product of abstraction at the terminal carbon atom, Eq. (47).

\[
\text{RSH} + \begin{array}{c} \text{CH}_3 \text{C} - \text{C} \text{CH}_2 \\ \text{CH}_3 \end{array} \rightarrow \begin{array}{c} \text{CH}_3 \text{C} - \text{C} \text{CH}_3 \\ \text{RS} \end{array} \quad (47)
\]

If the thiyl radical attacks the central carbon atom to form the tertiary radical, then abstraction at the terminal position would more logically arise from an allylic radical intermediate since the only product found was the tetrasubstituted ethylene (Eq. 47). The increase in attack at the central atom would be a result of decreasing reactivity of the methyl-substituted terminal carbon atom of the allenic triad due to steric effects and increasing stability of the allylic radicals due to hyperconjugation with the methyl groups.

\textbf{Polar Contributions to Free Radical Additions to Allenes.}—Pullman\textsuperscript{58} has done some molecular orbital calculations of radical localization energies for allene and 1,2-butadiene. The results are given below in $\beta$-units.
These calculations predict that radicals would attack, preferentially, the terminal position, then the central carbon atom in the allene case. This has been shown experimentally\(^{47,48}\) in the addition of thiyl radicals (87% terminal attack) and trifluoromethyl radicals (100% terminal attack). The trimethyltin radical gave 54.8% terminal attack. The addition of hydrogen bromide to allene\(^{44,45,46}\), on the other hand, gave results opposite to those expected. This can be attributed to a bridged radical intermediate, which opens to the more stable allylic radical, or is attacked at the sterically more favorable terminal position, Eq. (48).

\[
\begin{align*}
\text{BrCH}_2\text{CCH}_2 & \xrightarrow{\text{HBr}} \text{BrCH}_2\text{CCH}_2 \\
\text{H}_2\text{C} \text{CCH}_3 & \xrightarrow{\text{HBr}} \text{H}_2\text{C} \text{CCH}_3 \\
\text{CH}_2\text{C} \text{CCH}_2 & \xrightarrow{\text{HBr}} \text{CH}_2\text{C} \text{CCH}_2
\end{align*}
\]

\(\text{trace} \quad 95\%
\)

The 1,2-butadiene results predict attack of radicals at the 3-position. The thiyl radical\(^{48}\), however, attacks the 1-position (45%), the 2-position (48.2%), and the 3-position (6.3%).
The trimethyltin radical gave 86.5% attack at the central carbon atom and 13.6% at the terminal carbon atom; both radicals produce the result opposite of that predicted. It is evident that whether the initial attack is by a thiyl radical, which is electrophilic, or the trimethyltin radical, which is nucleophilic, the product of overall addition is that formed from increasing radical attack at the central carbon atom of the allenic system. It is clear, then, that polar factors are not of great importance in determining the direction of addition to allenes; it is suggestive, rather, of increasing tendency toward the formation of an allylic radical intermediate with increasing methyl substitution. We would also like to make clear that the first step (attack of the trimethyltin radical on the allenic system) may be reversible. Any statement as to whether the products formed are the result of kinetic control in the formation of intermediate radicals, or whether the first step is reversible and competes with, or is faster than, the second step (abstraction of a hydrogen from a trimethyltin hydride molecule by the intermediate radical) cannot be made unless more is known about the nature of the first step.

The contribution of polar factors in the abstraction step may be more difficult to assess since the trimethyltin group is on the middle carbon of the allylic triad.
More experimentation is needed to fully understand these polar factors; possibly, using substituted phenyl groups in an allylic system could shed more light on the subject.

**Stereochemistry of the Trimethyltin Hydride-1,2-Diene Adducts.** - The addition of trimethyltin hydride to 1,2-diienes has given some interesting stereochemical results as shown in Table XII.

The allylic radical intermediate in the 1,2-buta-diene reaction may have configuration I or II.

![Configuration I](image1)

![Configuration II](image2)

Configuration I gives **cis-but-2-en-2-yltinmethy1tin** and II **trans-but-2-en-2-yltrimethyltin** when abstraction occurs at C₁. Since the **cis** isomer, 17, predominates over the **trans**, 18, by a ratio of 38.6:16.3, configuration I seems to be the more stable. The trimethyltin group probably has the steric bulk of a methyl group. This is due to the fact that the C-Sn has a length of 2.14 Å compared to a C-C bond length of 1.54 Å, making its steric contribution considerably smaller. If we compare configurations I and II, the trimethyltin group **trans** to the methyl (I) is more favorable. However, the methyl on C₃ and the hydrogen on C₁ present some nonbonded interactions. This nonbonded interaction of the 1,3-groups becomes evident when the C₁ has a methyl group, as in the case of the allylic radical intermediate in the 2,3-penta-diene reaction, configurations III and IV.
Table XII

Cis and Trans Isomers in the
Trimethyltin Hydride-1,2-Diene Adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>% Cis</th>
<th>% Trans</th>
<th>Cis/Trans</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{C} = \text{C} \text{CH}_3]</td>
<td>38.6</td>
<td></td>
<td>2.37</td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{C} = \text{C} \text{CH}_3]</td>
<td>16.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{CH}_2\text{C} = \text{C} \text{CH}_3]</td>
<td>46.1</td>
<td></td>
<td>.86</td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{CH}_2\text{C} = \text{C} \text{CH}_3]</td>
<td>53.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{C} = \text{C} \text{CH}_3]</td>
<td>12.3</td>
<td></td>
<td>.29</td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{CH}_3\text{C} = \text{C} \text{CH}_3]</td>
<td>42.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[\text{Me}_3\text{Sn} \text{CH}_3\text{H}]</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The interaction of cis-1,3-methyl groups (IV) might be compared with that found in diaxial 1,3-dimethylcyclohexane which has an interaction energy of 5.4 kcal. This unfavorable interaction in configuration IV would favor configuration III. Both cis and trans isomers could arise from III where abstraction at C$_3$ gives the trans isomer, or at C$_1$ gives the cis isomer. There is a slight preference for the trans isomer, 53.9:46.1.

The 2-methyl-2,3-pentadiene reaction leads to configuration V and VI.

The fact that the trans isomer predominates 42:12 definitely shows that VI is the more favorable configuration. Space-filling models show considerable steric interaction between the methyl groups at C$_1$ and C$_3$ when the allylic radical is formed from the tertiary radical of configuration V. This might imply that the cis product arises from the tertiary radical prior to allylic radical formation, or that twisting occurs after allylic radical formation to relieve steric strain.
The twisting relieves steric strain producing considerable tertiary radical character. Then abstraction at the tertiary radical center occurs preferentially. The overall reaction produces 54.5% of the trisubstituted ethylene products and 45.5% of the tetrasubstituted products. Configuration VI could produce 87.7% of the products. Abstraction at $C_3$ gives the trans isomer and at $C_1$ gives the tetrasubstituted isomer. The trimethyltin hydride addition to allenes is determined by a combination of the relative rates of attack at the terminal and central carbon atom of the allenic triad, the relative rates of reversal, and the relative rates of reaction of the intermediate radical with the trimethyltin hydride. The net effect is to minimize polar effects and to make intermediate radical stability increasingly important as the allenic system becomes substituted with methyl groups.
PART III

ADDITION OF
TRIMETHYLGERMANIUM HYDRIDE TO DIENES

Background

The addition of organogermanium hydrides to olefins has been investigated by a number of workers. The most comprehensive work has been carried out by Lesbre and co-workers. They have studied the addition of organogermanium hydrides to a variety of substituted olefins, catalyzed by chloroplatinic acid or platinum on asbestos. Free radical catalysis does not seem to be as efficient as the platinum catalysis. The following types of olefins were used, Eq. (49,50).

\[
R_3\text{Ge-H} + CH_2=CH-X \rightarrow R_3\text{GeCH}_2-CH_2-X + R_3\text{GeCH-CH}_3 \quad \text{(49)}
\]

\[
Y = H, \emptyset, CH_2\text{OH}, -(CH_3)_3\text{CH}_3, -\text{C-(CH}_3)_2 OH
\]

Gilman and Fuchs added triphenylgermanium hydride to 1-octene, cyclohexene, and 1,1-diphenylethene under free
radical conditions, Eq. (51-53).

\[ \phi_3\text{GeH} + \text{CH}_2\text{-CH(\text{CH}_2)}_5\text{CH}_3 \xrightarrow{\text{or}} \phi_3\text{GeCH}_2(\text{CH}_2)_6\text{CH}_3 \quad (51) \]

\[ \phi_3\text{GeH} + \text{peroxide} \quad (52) \]

\[ \phi_3\text{GeH} + \text{C=CH}_2 \xrightarrow{\text{peroxide} \quad \text{or}} \phi_3\text{Ge} + \text{H} \quad (53) \]

Lesbre and co-workers reacted organogermanium halohydrides with substituted olefins in the absence of catalyst, Eq. (54).

\[ \text{R}_2\text{GeH} + \text{CH}_2\text{-CH-Z} \rightarrow \text{R}_2\text{GeCH}_2\text{-CH}_2\text{-Z} \quad (54) \]

\[ \text{Z} = \text{CH}_2\text{OH}, \text{OCH}_3, \text{CH}_2\text{CN} \]

Petrov and co-workers allowed triethylgermanium hydride to react with several olefins, Eq. (55).

\[ \text{Et}_3\text{Ge-H} + (\text{CH}_3)_2\text{C=CH-CH}_2 \rightarrow (\text{CH}_3)_2\text{C=CHCHCHCH}_2 \quad (55) \]

The only example of addition of germanium hydrides to dienes was the work of Mironov and co-workers. They added trichlorogermanium hydride to 1,3-butadiene, 2-methyl-1,3-butadiene, 1-methyl-1,3-butadiene, and cyclopentadiene, Eq. (56-59).
Cl₃GeH + CH₂=CH-CH=CH₂ \rightarrow \text{addition} \rightarrow \begin{array}{c}
\text{Me₃GeCH}_2-\text{CH-CHCH}_3
\end{array}

Cl₃GeH + CH₂-\text{C}-(CH=CH₂ \rightarrow \text{addition} \rightarrow \begin{array}{c}
\text{Me₃GeCH}_2-\text{C}-\text{CHCH}_3
\end{array}

Cl₃GeH + CH₃CH·CH=CH₂ \rightarrow \text{addition} \rightarrow \begin{array}{c}
\text{CH₃CH₂CH-CHCH₂GeMe₃} \\
\text{CH₃CH=CH-CHCH₃}
\end{array}

Cl₃GeH + \text{Cyclopentene} \rightarrow \text{addition} \rightarrow \begin{array}{c}
\text{GeMe₃}
\end{array}

There had been no work done on the addition of organogerma­

niun hydride to dienes. Thus, a study of the addition of tri­
methylgermanium hydride to a variety of dienes was carried
out in order to ascertain the course of these reactions.

Results

The addition of trimethylgermanium hydride to a
variety of dienes was carried out in sealed ampoules at
various temperatures in the presence of chloroplatinic
acid. The products were analyzed by gas-liquid chroma­
tography (g.l.c.), and the structures elucidated by a com­
bination of infrared (I.R.) and nuclear magnetic resonance
(n.m.r.) spectroscopy, as well as by chemical degradation and elemental analyses.

**Allene.** - The addition of trimethylgermanium hydride to allene gave two products, Eq. (60).

\[ \text{Me}_3\text{GeH} + \text{CH}_2\text{C} = \text{CH}_2 \rightarrow \text{Me}_3\text{GeCH}_2\text{CH} = \text{CH}_2 \ (60.5\%) + \]

\[ \text{Me}_3\text{GeC} = \text{CH}_2 \ (39.5\%) \ (60) \]

A higher boiling compound, which was not identified, was formed also; however, it is postulated to be a low molecular weight polymer of isopropenyltrimethylgermane.

**Structure Assignment.** - G.l.c. (20ft 20% silicone nitrile column) led to separation of 30 and 31, with 31 having the shorter retention time. Peak areas were used to calculate the percentages of each isomer. The I.R. spectrum of 30 had bands at 3065 cm.\(^{-1}\), 1630 cm.\(^{-1}\), 987 cm.\(^{-1}\), and 890 cm.\(^{-1}\), characteristic of an allylic germanium compound. The I.R. spectrum of 31 had bands at 3045 cm.\(^{-1}\), 1605 cm.\(^{-1}\), and 915 cm.\(^{-1}\), characteristic of vinyl germanium compounds. The n.m.r. spectrum of 30 had a vinyl proton multiplet at \( \gamma 4.35 \) (J=15 c.p.s., 11 c.p.s., and 8 c.p.s.). The terminal methylene protons had multiplets at \( \gamma 5.23 \) and \( \gamma 5.48 \) (J=1.0 c.p.s.) and the methylene group a doublet at \( \gamma 8.43 \) (J=8.0 c.p.s.). The trimethylgermanium singlet appeared at \( \gamma 9.88 \). The integrated area ratios were 1:2:2:9. The n.m.r. spectrum of 31 had multiplets at \( \gamma 4.67 \) and \( \gamma 5.04 \) (J=1.2 c.p.s.) and the methyl protons as a partially resolved triplet at \( \gamma 8.2 \) (J=1.4 c.p.s.). The trimethylgermanium singlet appeared at \( \gamma 9.80 \). The integrated area ratios were 1:1:3:9.
Compound 30 had a refractive index in good agreement with the known compound. See Table XIII for pertinent data on the trimethylgermanium hydride-diene reactions.

1,3-Butadiene.- The addition of trimethylgermanium hydride to 1,3-butadiene gave two products, Eq. (61).

\[
\text{Me}_3\text{GeH} + \text{CH} = \text{CH} - \text{CH} = \text{CH}_2 \rightarrow \text{Me}_3\text{GeCH} - \text{C} - \text{C} \quad (40\%) + \\
\text{Me}_3\text{GeCH}_2\text{C} - \text{C} \quad (60\%) 
\]

Structural Assignments.- G.l.c. (20 ft. 20% silicone nitrile column) was used to separate 32 and 33, with 32 having the shorter retention time. The I.R. spectrum of 32 exhibited bands at 3013 cm.\(^{-1}\), 1650 cm.\(^{-1}\), and 960 cm.\(^{-1}\), characteristic of a trans disubstituted olefin. Compound 33 had bands at 3012 cm.\(^{-1}\), 1645 cm.\(^{-1}\), and 720 cm.\(^{-1}\), characteristic of a cis disubstituted olefin. N.m.r. spectroscopy has been a very useful method in determining cis and trans structures. However, due to the effect of the trimethylgermanium groups, the coupling constant for the cis and trans vinyl protons in 32 and 33 were approximately equal. Thus, n.m.r. spectroscopy could not be used to substantiate the assigned stereochemistry for 32 and 33. Allylic germanium compounds are quite reactive towards electrophiles; thus, 32 and 33 were reacted with trifluoroacetic acid. This exothermic reaction produced 1-butene, characterized by its retention time (g.l.c. on a 15 ft. dimethylsulfolane column) compared with a known sample, Eq. (62).
**Table XIII**

Pertinent Data on the Trimethylgermanium Hydride-Diene Reactions

<table>
<thead>
<tr>
<th>Diene</th>
<th>Products</th>
<th>Total Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conditions&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=C-CH$_2$</td>
<td>30,31</td>
<td>47.5&lt;sup&gt;c&lt;/sup&gt;</td>
<td>115° 8.5</td>
</tr>
<tr>
<td>CH$_2$=CHCH-CH$_2$</td>
<td>32,33</td>
<td>65</td>
<td>140° 10</td>
</tr>
<tr>
<td></td>
<td>34,35</td>
<td>25</td>
<td>175° 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>13</td>
<td>100° 9</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>60</td>
<td>140° 10</td>
</tr>
<tr>
<td></td>
<td>36</td>
<td>49</td>
<td>140° 10</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>30&lt;sup&gt;d&lt;/sup&gt;</td>
<td>160° 10</td>
</tr>
<tr>
<td></td>
<td>37</td>
<td>42</td>
<td>150° 10</td>
</tr>
</tbody>
</table>
Table XIII cont.-

<table>
<thead>
<tr>
<th>Diene</th>
<th>Products</th>
<th>Total Yield&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Conditions&lt;sup&gt;b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="Diene 1" /></td>
<td>38</td>
<td>46.7%</td>
<td>150° 8</td>
</tr>
<tr>
<td><img src="image" alt="Diene 2" /></td>
<td>39,40,41</td>
<td>80%</td>
<td>140° 8</td>
</tr>
</tbody>
</table>

<sup>a</sup> Total yield based on trimethylgermane

<sup>b</sup> Reactions catalyzed with 0.2 to 0.5 cc of ca 0.1N chloroplatinic acid solution in absolute ethanol

<sup>c</sup> 19.1% of an unidentified higher boiling compound was also formed.

<sup>d</sup> Some of the compound was spilled on transfer and yield not accurately determined.
The formation of 1-butene can be rationalized by invoking an SE2' mechanism, Eq. (63).

Mironov and Gar characterized crotyltrimethylgermane formed from the addition of trichlorogermainium hydride to 1,3-butadiene followed by methylation; they failed, however, to determine the stereochemistry of the product.

**Cyclopentadiene.** The addition of trimethylgermanium hydride to cyclopentadiene gave two products, Eq. (64).

**Structural Assignments.** G.l.c. (20 ft. 20% silicone nitrile column) gave separation of 34 and 35, with 34 having the shorter retention time. The peak areas were used to calculate the ratios of both isomers. The I.R. spectrum of 34 had bands at 3020 cm.\(^{-1}\) and 1595 cm.\(^{-1}\), and that of 35 had bands at 3050 cm.\(^{-1}\), 1595 cm.\(^{-1}\), and 715 cm.\(^{-1}\). The
n.m.r. spectrum of 34 had a vinyl proton multiplet at $\tau$ 4.31 (J=2.1 c.p.s.) and multiplets at $\tau$ 7.75 and $\tau$ 8.20. The trimethylgermanium singlet appeared at $\tau$ 9.84. The integrated area ratios were 1:4:2:9, consistent with the proposed structure for 34. The n.m.r. spectrum for 35 had a vinyl proton multiplet at $\tau$ 4.45, a multiplet at $\tau$ 7.90 and a trimethylgermanium singlet at $\tau$ 9.90. The integrated area ratios were 2:5:9. The 62.7:37.3 mixture of 34 and 35 was treated with trifluoroacetic acid, after which analysis by g.l.c. (20 ft. 20% silicone nitrile column) indicated that 35 was completely destroyed. The chemical reactivity of 35 substantiates its assigned structure as an allylic germanium compound. The formation of 34 will be discussed when the mechanism is elucidated. Mironov and Gar prepared cyclopentenyltrimethylgermane by addition of trichlorogermanium hydride to cyclopentadiene followed by methylation; however, they made no attempt to elucidate the structure of the adduct. The refractive index of 35 was in good agreement with that reported by Mironov and Gar for their adduct.

1,3-Cyclohexadiene.- The addition of trimethylgermane to 1,3-cyclohexadiene gave one product, Eq. (65).

$$\text{Me}_3\text{GeH} + \text{C} \rightarrow \text{C} \quad (100\%)$$  (65)

Structural Assignment.- G.l.c. (4 ft. Apiezon L Column) indicated one component. The I.R. spectrum of 36 showed bands at 3013 cm.\(^{-1}\), 1630 cm.\(^{-1}\), and 715 cm.\(^{-1}\). The n.m.r. spectrum was quite definitive for assigning the structure of 36. The vinyl protons appeared as a multiplet $\tau$ 4.40,
while the methylene protons alpha to the double bond were at \( \tau \) 8.06, deshielded, due to the magnetic anisotropic effect of the double bond.\(^7\) The remaining protons were a multiplet at \( \tau \) 8.30 and a trimethylgermanium singlet at \( \tau \) 9.87. The integrated area ratios were 2:2:5:9. Compound 36 reacted exothermally with trifluoroacetic acid to give cyclohexene and trimethylgermanium trifluoroacetate, presumably by an SE\(^2\) mechanism\(^6\), Eq. (66).

\[
\begin{array}{c}
\text{CF}_3\text{COOH} \\
\text{GeMe}_3
\end{array} \xrightarrow{\text{}^{\circ}\text{C}} \begin{array}{c}
\text{Me}_3\text{GeOCCF}_3 \\
\text{C}
\end{array} + \begin{array}{c}
\text{Cyclohexene}
\end{array}
\]

(66)

Cyclohexene was characterized by comparison of its I.R. spectrum and retention time (g.l.c. on a 20 ft. 20% silicone nitrile column) with an authentic sample. The trimethylgermanium trifluoroacetate was identified by its I.R. spectrum.

**1,4-Cyclohexadiene.** The reaction of 1,4-cyclohexadiene with trimethylgermane gave one product, Eq. (67).

\[
\begin{array}{c}
\text{Me}_3\text{GeH}
\end{array} \xrightarrow{\text{Me}_3\text{GeH}} \begin{array}{c}
\text{Cyclohexadiene}
\end{array} \xrightarrow{\text{100\%}} \begin{array}{c}
\text{GeMe}_3
\end{array}
\]

(67)

The compound was identical in its infrared and n.m.r. spectra to the product from the reaction of 1,3-cyclohexadiene and trimethylgermanium hydride. A careful look at the starting material (g.l.c.) showed that 1,3-cyclohexadiene was present along with 1,4-cyclohexadiene. This means that the 1,4-cyclohexadiene is isomerized to the 1,3-cyclohexadiene which then reacts to form 36. This is also evident in the reaction of 1,3- and 1,5-cyclooctadiene which will be discussed next.
1,3-Cyclooctadiene.- The reaction of 1,3-cyclooctadiene and trimethylgermanium hydride gave one product, Eq. (68).

\[
\text{Me}_3\text{GeH} + \text{C}_8\text{H}_{16} \rightarrow \text{Me}_3\text{Ge}(\text{C}_8\text{H}_{16}) (100\%)
\]

Structural Assignment.- G.L.c. (4 ft. Apiezon L column) indicated one pure component. The I.R. spectrum of 37 had bands at 3022 cm.\(^{-1}\), 1650 cm.\(^{-1}\), and 700 cm.\(^{-1}\). The n.m.r. spectrum was quite definitive in elucidating the structure of 37. The vinyl protons were a multiplet at \(\delta 4.35\); a multiplet at \(\delta 7.85\) was assigned to the methylene group alpha to the double bond, deshielded due to the magnetic anisotropic effect of the double bond.\(^{70}\) The remaining protons were a multiplet at \(\delta 8.45\) and the trimethylgermanium singlet at \(\delta 9.90\). The integrated area ratios were 2:2:9:9. Compound 37 reacted exothermally with trifluoroacetic acid producing cyclooctene and trimethylgermanium trifluoroacetate, Eq. (69).

\[
\text{C}_8\text{H}_{16} + \text{CF}_3\text{COOH} \rightarrow \text{C}_8\text{H}_{16} + \text{Me}_3\text{GeOCCF}_3
\]

The cyclooctene was identified by comparing its I.R. spectrum and retention time (g.l.c. 4 ft. Carbowax 20 M column) with an authentic sample. The trimethylgermanium trifluoroacetate was isolated (g.l.c. 4 ft. Carbowax 20 M column) and characterized by its I.R. spectrum and elemental analyses.
1,5-Cyclooctadiene.- The reaction of 1,5-cyclooctadiene with trimethylgermanium hydride gave one product, Eq. (70).

\[
\text{Me}_3\text{GeH} + \text{1,5-Cyclooctadiene} \rightarrow \text{GeMe}_3\text{GeH} \quad (100\%)
\]

The infrared and n.m.r. spectra, as well as its retention time in the g.l.c., were identical with the compound from the reaction of 1,3-cyclooctadiene and trimethylgermanium hydride. In order to substantiate that 1,5-cyclooctadiene was being isomerized to 1,3-cyclooctadiene before addition took place, three experiments were carried out, Table XIV.

Table XIV

<table>
<thead>
<tr>
<th>Sealed tube</th>
<th>Contents</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,5-Cyclooctadiene</td>
<td>No change</td>
</tr>
<tr>
<td>2</td>
<td>1,5-Cyclooctadiene and a catalytic amount of chloroplatinic acid</td>
<td>No change</td>
</tr>
<tr>
<td>3</td>
<td>1,5-Cyclooctadiene and a catalytic amount of trimethylgermanium hydride and chloroplatinic acid</td>
<td>A mixture of 1,3- and 1,5-cyclooctadiene was present.</td>
</tr>
</tbody>
</table>

\[ \text{a} \]
The compounds were heated at 160° for nine hours.

\[ \text{b} \]
Analyzed by g.l.c. on an 11 ft. 17% silicone nitrile on Chromosorb P column. 1,3-Cyclooctadiene was collected and identified by comparison of its I.R. spectrum with an authentic sample.
The starting material from the addition reaction was analyzed by g.l.c. and I.R. and found to contain only 1,3-cyclooctadiene. This further confirms the suggestion that the 1,5-cyclooctadiene is being isomerized to 1,3-cyclooctadiene. A plausible route to 1,3-cyclooctadiene will be discussed when the mechanism is elucidated.

4-Vinyl Cyclohexene-1.- The addition of trimethylgermanium hydride to 4-vinyl cyclohexene-1 gave one product, Eq. (71).

\[ \text{Me}_3\text{GeH} + \begin{array}{c}
\text{38}
\end{array} \rightarrow \begin{array}{c}
\text{GeMe}_3
\end{array} \quad (100\%) \quad (71) \]

Structural Assignment.- G.l.c. (4 ft. Apiezon L column) indicated one pure component. The I.R. spectrum of 38 had bands at 3020 cm.\(^{-1}\) and 1650 cm.\(^{-1}\). The absence of bands in the region 880-920 cm.\(^{-1}\) and 980 cm.\(^{-1}\) indicated that the trimethylgermanium hydride added to the exocyclic vinyl group. The n.m.r. spectrum of 38 had a vinyl proton multiplet \(\tau\) 4.45; a multiplet at \(\tau\) 8.0 assigned to the two methylene groups alpha to the double bond. A multiplet at \(\tau\) 9.25 was assigned to the methylene protons on the carbon bearing the trimethylgermanium group. The remaining protons were a multiplet at \(\tau\) 8.67 and the trimethylgermanium singlet at \(\tau\) 9.88. The integrated area ratios were 2:4:2:5:9.

Compound 38 was unreactive towards trifluoroacetic acid even after heating a mixture of compound 38 and trifluoroacetic acid in tetrahydrofuran at 100° overnight. This is added proof that germanium compounds with isolated double bonds (non-allylic) do not undergo acid cleavage reactions except under drastic conditions.
Bicyclo-(2.2.1)-heptadiene-2,5. - The reaction of trimethylgermanium hydride with bicyclo-(2.2.1)-heptadiene-2,5 gave three products, Eq. (72).

\[
\text{Me}_3\text{GeH} + \text{GeMe}_3 \rightarrow \text{Me}_3\text{Ge} + \text{GeMe}_3 \quad (75\%)
\]

40 41  (10%)

Structural Assignments.- The I.R. spectrum of the mixture of 39, 40 and 41 had bands at 3040 cm.\(^{-1}\), 1570 cm.\(^{-1}\), 1335 cm.\(^{-1}\), and 720 cm.\(^{-1}\), characteristic of bicyclo-(2.2.1)-heptene-2 compounds.\(^{71}\) Since the g.l.c. failed to separate 39, 40 and 41, the n.m.r. was used exclusively to determine the ratios of the products. The following method has been applied to the corresponding silicon compounds by Kuivila and Warner.\(^{71}\) The magnetically anisotropic double bond of the norbornene system shields protons or proton substituents on the endo 5-position (A) and deshields on the exo 5-position (B).\(^{72}\)
Thus, the protons of the endo-trimethylgermanium group (A) appear as a singlet at $\tau$ 9.96 and those of the exo-trimethylgermanium group (B) appears as a singlet at $\tau$ 9.88. The ratio of endo to exo was obtained by measuring the area of the trimethylgermanium peaks; the ratio was 75:25. In order to determine the amount of nortricyclene, 41, the mixture of 39, 40, and 41 was hydrogenated. The norbornenes, 39 and 40, were thus converted to their saturated analogs, while the nortricyclene product, 41, did not react, Eq. (73).

\[
\begin{align*}
\text{GeMe}_3 & + \text{GeMe}_3 + \text{GeMe}_3 \\
39 & + 40 + 41 \\
\text{GeMe}_3 & + \text{GeMe}_3 + \text{GeMe}_3 \\
42 & + 43 + 41
\end{align*}
\]
This eliminated the magnetic anisotropic effect of the double bond, and the endo and exo were now shifted to their "proper" positions. The endo trimethylgermanium group in the saturated analog, 42, shows a singlet at $\tau$ 9.89, while that of 43 appears at $\tau$ 9.94. The ratio of areas was 85:15. Thus the nortricyclene product, 41, amounts to 10% since the apparent ratio of endo to exo goes from 75:25 to 85:15, upon hydrogenation. Compounds 40 and 41, therefore, show the singlet at $\tau$ 9.88, and 41 and 42 show the singlet at $\tau$ 9.89, Table XV.

Table XV

Chemical Shifts of the Trimethylgermanium Group in the Saturated and Unsaturated Bicyclic Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chemical Shift ((\tau))</th>
</tr>
</thead>
<tbody>
<tr>
<td>39</td>
<td>9.96</td>
</tr>
<tr>
<td>40</td>
<td>9.88</td>
</tr>
<tr>
<td>41</td>
<td>9.88</td>
</tr>
<tr>
<td>42</td>
<td>9.89</td>
</tr>
<tr>
<td>43</td>
<td>9.94</td>
</tr>
</tbody>
</table>

In addition to the trimethylgermanium singlets at $\tau$ 9.96 and $\tau$ 9.88, the n.m.r. spectra of 39, 40, and 41 each had vinyl proton triplet at $\tau$ 4.13 (J 1.5 c.p.s.) consistent with the predominating endo isomer (75%). The bridgehead protons appeared at $\tau$ 7.12 and the remaining protons as a multiplet at $\tau$ 8.5. The integrated area ratios were 2:2:5. The I.R. spectral data for the adducts are found in Table XVI. The n.m.r. spectral data are found in Table XVII and the proton designations in Table XVIII.
Table XVI

Infrared Spectral Data for the Trimethylgermanium Hydride-Diene Adducts\textsuperscript{a,b}

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>3065 (m)</td>
<td>1630 (s)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>31</td>
<td>3045</td>
<td>1605 (vw)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>32</td>
<td>3013 (m)</td>
<td>1650 (w)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>33</td>
<td>3012 (m)</td>
<td>1645 (m)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>34</td>
<td>3020 (m)</td>
<td>1595 (m)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>35</td>
<td>3050 (m)</td>
<td>1595 (m)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>36</td>
<td>3013 (s)</td>
<td>1630 (m)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>37</td>
<td>3022 (m)</td>
<td>1550 (w)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>38</td>
<td>3020 (m)</td>
<td>1650 (w)</td>
<td></td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
<tr>
<td>39-41</td>
<td>3040 (m)</td>
<td>1570 (w)</td>
<td>1335 (m)</td>
<td></td>
<td></td>
<td>1235 (s)</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Liquid smear

\textsuperscript{b} Bands in cm\textsuperscript{-1}
Table XVI cont.

<table>
<thead>
<tr>
<th>Adduct</th>
<th>=C&lt;sub&gt;H&lt;/sub&gt; o.o.p. def.</th>
<th>Trans C=C o.o.p.def.</th>
<th>cis C=C o.o.p.def.</th>
<th>CH&lt;sub&gt;3&lt;/sub&gt;-Ge Rocking</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>890 (s)</td>
<td></td>
<td></td>
<td>825 (s)</td>
</tr>
<tr>
<td>31</td>
<td>915 (s)</td>
<td></td>
<td></td>
<td>825 (s)</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td>960 (s)</td>
<td></td>
<td>825 (s)</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td></td>
<td>720 (m)</td>
<td>825 (s)</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td></td>
<td></td>
<td>825</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td></td>
<td>715 (m)</td>
<td>825</td>
</tr>
<tr>
<td>36</td>
<td></td>
<td></td>
<td>715 (m)</td>
<td>825</td>
</tr>
<tr>
<td>37</td>
<td></td>
<td></td>
<td>700 (m)</td>
<td>825</td>
</tr>
<tr>
<td>38</td>
<td></td>
<td></td>
<td>710 (m)</td>
<td>825</td>
</tr>
<tr>
<td>39-41</td>
<td></td>
<td></td>
<td>720 (s)</td>
<td>825 (s)</td>
</tr>
</tbody>
</table>
Table XVII

Nuclear Magnetic Resonance Spectral Date for the Trimethylgermanium Hydride-Diene Adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Conc. in CCl₄</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>e</th>
<th>Ja-b</th>
<th>Ja-c</th>
<th>Jb-c</th>
<th>Jc-d</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>Neat</td>
<td>5.48 (m)</td>
<td>5.23 (m)</td>
<td>4.35 (6)</td>
<td>8.43 (2)</td>
<td>9.88 (1)</td>
<td>1.0</td>
<td>15</td>
<td>11</td>
<td>8.0</td>
</tr>
<tr>
<td>31</td>
<td>25%</td>
<td>4.67 (m)</td>
<td>5.04 (m)</td>
<td>8.2 (3)</td>
<td>9.80 (1)</td>
<td></td>
<td>1.2</td>
<td>1.4</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>25%</td>
<td>4.70 (m)</td>
<td>8.41 (m)</td>
<td>9.90 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>25%</td>
<td>4.75 (m)</td>
<td>8.46 (m)</td>
<td>9.87 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>35%</td>
<td>4.31 (m)</td>
<td>7.75 (m)</td>
<td>8.2 (m)</td>
<td>9.84 (1)</td>
<td></td>
<td>2.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>40%</td>
<td>4.45 (m)</td>
<td>7.90 (m)</td>
<td>9.90 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Neat</td>
<td>4.40 (m)</td>
<td>8.06 (m)</td>
<td>8.3 (m)</td>
<td>9.87 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>20%</td>
<td>4.35 (m)</td>
<td>7.85 (m)</td>
<td>8.45 (s)</td>
<td>9.90 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>Neat</td>
<td>4.45 (2)</td>
<td>8.0 (m)</td>
<td>8.67 (m)</td>
<td>9.25 (m)</td>
<td>9.88 (1)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>39-41</td>
<td>Neat</td>
<td>4.13 (3)</td>
<td>7.12 (m)</td>
<td>8.5 (m)</td>
<td>9.88 (1)</td>
<td>9.96 (1)</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a See Table XVIII for structure and proton designations.

b Values reported in T units and measured at the center of each multiplet; J values in c.p.s.

c See Ref. 71 for explanation of coupling constants.
Table XVIII
Proton Designations for Trimethylgermanium Hydride-Diene Adducts

30  \[
\begin{array}{c}
\text{Me}_3\text{GeCH}_2\text{C} \quad \text{C} \\
\text{H} \quad \text{H} \quad \text{a} \\
\text{H} \quad \text{c} \quad \text{H} \\
\text{b} \quad \text{d} \\
\end{array}
\]

31  \[
\begin{array}{c}
\text{Me}_3\text{Ge} \quad \text{C} \\
\text{H} \quad \text{a} \\
\text{c} \\
\text{b} \\
\text{d} \\
\end{array}
\]

32  \[
\begin{array}{c}
\text{Me}_3\text{GeCH}_2\text{C} \\
\text{c} \\
\text{d} \\
\text{b} \\
\text{H} \quad \text{a} \\
\text{H} \quad \text{c} \\
\text{H} \\
\text{d} \\
\text{H} \\
\text{a} \\
\text{H} \\
\text{b} \\
\text{H} \\
\end{array}
\]

33  \[
\begin{array}{c}
\text{Me}_3\text{GeCH}_2\text{C} \quad \text{C} \\
\text{H} \quad \text{b} \\
\text{c} \\
\text{b} \\
\text{H} \quad \text{a} \\
\text{H} \quad \text{a} \\
\text{H} \\
\end{array}
\]

34  \[
\begin{array}{c}
\text{Me}_3\text{Ge} \\
\text{b} \\
\text{a} \\
\text{H} \\
\text{H} \\
\text{H} \\
\text{b} \\
\text{H} \\
\text{d} \\
\end{array}
\]

35  \[
\begin{array}{c}
\text{Me}_3\text{Ge} \\
\text{c} \\
\text{b} \\
\text{H} \\
\text{b} \\
\text{a} \\
\text{H} \\
\text{b} \\
\text{H} \\
\end{array}
\]

36  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{d} \quad \text{Me}_3\text{Ge} \\
\text{b} \quad \text{H} \\
\text{H} \\
\text{H} \\
\text{c} \quad \text{H} \\
\end{array}
\]

37  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{H} \\
\text{c} \quad \text{Me}_3\text{Ge} \\
\text{d} \quad \text{H} \\
\text{d} \quad \text{H} \\
\text{c} \quad \text{H} \\
\end{array}
\]

38  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{H} \\
\text{c} \quad \text{H} \\
\text{d} \quad \text{H} \\
\text{e} \quad \text{Me}_3\text{Ge} \\
\text{c} \quad \text{H} \\
\end{array}
\]

39-41  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{Me}_3\text{Ge} \\
\text{c} \quad \text{Me}_3\text{Ge} \\
\text{d} \quad \text{Me}_3\text{Ge} \\
\end{array}
\]

40  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{H} \\
\text{c} \quad \text{H} \\
\text{d} \quad \text{Me}_3\text{Ge} \\
\text{c} \quad \text{H} \\
\end{array}
\]

41  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{H} \\
\text{c} \quad \text{Me}_3\text{Ge} \\
\text{d} \quad \text{H} \\
\text{e} \quad \text{H} \\
\text{c} \quad \text{H} \\
\end{array}
\]

42  \[
\begin{array}{c}
\text{a} \quad \text{H} \\
\text{b} \quad \text{Me}_3\text{Ge} \\
\text{c} \quad \text{H} \\
\text{d} \quad \text{Me}_3\text{Ge} \\
\text{e} \quad \text{H} \\
\end{array}
\]
Discussion

**Mechanism.**— The use of platinum catalysts in silicon hydride addition reactions has been studied by Spier, Benkeser, and West. Their work indicates that a complex mechanism seems in operation. Lesbre and Satge have carried out chloroplatinic acid catalyzed reactions with organogermanium hydrides in the presence of radical inhibitors and have shown that the reaction is not retarded.

**Active Catalysts.**— The mechanism of the addition of silanes to olefins in the presence of chloroplatinic acid was studied in detail by Spier and co-workers; they have shown that internal olefins, i.e., 2-pentene, give the products of terminal addition, Eq. (74).

\[
\text{Cl}_3\text{SiH} + \text{CH}_3\text{CH} = \text{CHCH}_2\text{-CH}_3 \xrightarrow{\text{H}_2\text{PtCl}_6} \text{Cl}_3\text{SiCH}_2(\text{CH}_2)_3\text{CH}_3 \quad (74)
\]

The chloroplatinic acid and silane have been shown to isomerize starting olefins during the addition reaction. In a very elegant study, Spier and Ryan have shown that during the addition of trichlorosilane-d (Cl\(_3\)SiD) in the presence of chloroplatinic acid, extensive exchange occurs between the Si-D and C-H of the olefin. They postulated the following type of mechanism to rationalize their results.
\[
\text{Cl}_3\text{SiD} + \text{Pt} \rightleftharpoons \text{SiPtD} \quad (A) \quad \frac{\text{Cl}_3\text{SiD}}{-\text{Cl}_3\text{SiD}} \quad (\text{Cl}_3\text{Si})_2\text{PtD}_2 \quad (B)
\]

\[
\text{CH}_2^+\text{CHCH}(\text{CH}_3)_2
\]

\[
\begin{align*}
\text{CH}_2\text{D} & \quad + (\text{C}) \\
(\text{Cl}_3\text{Si})_2\text{PtDCHCH(}\text{CH}_3)_2 & \quad \rightarrow \quad + (\text{Cl}_3\text{Si})_2\text{PtDCH}_2\text{CHDCH(}\text{CH}_3)_2 \\
- (\text{Cl}_3\text{Si})_2\text{PtDH} & \quad \downarrow \quad \downarrow \quad \downarrow
\end{align*}
\]

\[
\text{Cl}_3\text{SiPtD} + \text{Cl}_3\text{SiCH}_2\text{CHD-CH(}\text{CH}_3)_2
\]

\[
\text{CHD-CHCH(}\text{CH}_3)_2 + \text{CH}_2^+\text{D-CHC(}\text{CH}_3)_2
\]

\[
\begin{align*}
\text{B} & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
\text{Etc.}
\end{align*}
\]

The olefin is thought to engage in a series of reversible reactions in which it adds the catalyst and eliminates it, by which process it becomes isomerized and deuterated. The extent of exchange seems to be inversely proportional to the ease of making alkylsilanes. In order of increasing extent of exchange, olefins may be arranged as follows:

\[
\text{RCH} = \text{CH}_2 < \text{CH}_3^+\text{C-CH}_2 < \text{CH}_3\text{-C-CHCH}_3 < \text{[cyclic structure]} < \text{[cyclic structure]}
\]

The same principle can be applied to the addition of trimethylgermanium hydride to dienes catalyzed by chloroplatinic acid. The complex formed in the silane reactions appears to be homogeneous.
Spier and Ryan \(^{76}\) did not observe any precipitates. In contrast to this observation, all the addition reactions that were carried out with trimethylgermanium hydride and catalyzed by chloroplatinic acid had black precipitates, after the reaction was complete, which demonstrate the presence of platinum metal.

An alternate explanation may depend on the fact that trimethylgermanium hydride is a better reducing agent than the trichlorosilane; hence, it reduces the chloroplatinic acid or the active catalyst to platinum metal. Anderson\(^{79a}\) has shown that triethylgermanium hydride reduces potassium hexachloroplatinate toatinum metal and more recently Chalk and Harrod\(^{79b}\) have observed dark colored reaction mixtures during the addition of trialkylsilicon hydrides to olefins in the presence of platinum catalysts. The catalyst responsible for the reaction may possibly be a lower valence form of platinum made by reduction of chloroplatinic acid by trimethylgermanium hydride. This platinum can react with trimethylgermanium hydride to form a germanium-platinum complex, Eq. (75).

\[
\begin{align*}
\text{Pt} + \text{Me}_3\text{GeH} & \rightleftharpoons \text{Me}_3\text{GePtH} \rightleftharpoons \text{Me}_3\text{GeH} \\
& \quad \text{(A)} \quad \text{(B)}
\end{align*}
\] (75)

The complex (A) or (B) may be thought of as the active catalyst during the addition reaction.

**Isomerization of Nonconjugated Dienes.** - The complex can add to a nonconjugated diene by a process which is rapid and reversible. A diene, such as 1,4-cyclohexadiene or 1,5-cyclooctadiene can be isomerized to its 1,3 analog by the following scheme, Fig. 3.
Figure 3

The Isomerization of 1,5-Cyclooctadiene to 1,3-Cyclooctadiene via a Germanium-Platinum-Hydride Complex

\[ \text{Me}_3\text{GeH} + \text{Pt} \rightleftharpoons \text{Me}_3\text{GePtH} \quad (A) \quad \text{Me}_3\text{GeH} \quad \rightarrow \quad (\text{Me}_3\text{Ge})_2\text{PtH}_2 \quad (B) \]

\[ \begin{array}{c}
\text{Me}_3\text{GeH} + \text{Pt} \\
\text{Me}_3\text{GePtH} \quad (A) \\
(\text{Me}_3\text{Ge})_2\text{PtH} \\
\end{array} \]
**Coordination Control.**—The fact that 1,3-dienes are more reactive in the addition reactions, as evidenced by the isomerization of the nonconjugated diene, leads us to postulate a mechanism in which "coordination control" plays a major role. Kuivila and Warner\textsuperscript{71} invoked "coordination control" to explain the predominance of endo addition in the reaction of silicon hydrides and bicycloheptadiene in the presence of platinum catalysts. The complex can sit in the center of the conjugated system, facilitating coordination of the \( \pi \)-electrons of the diene with vacant d-orbitals of the metal atoms.

\[
\text{(Me}_3\text{Ge)}_2\text{PtH}_2
\]

This can explain the predominance of 1,4 addition observed in these addition reactions with 1,3-dienes and can also account for the predominance of endo addition (75\%) in the reaction of bicycloheptadiene with trimethylgermanium hydride. The endo side of bicycloheptadiene has been shown to be more favorable for coordination with metals.\textsuperscript{71,80}

\[
\text{(Me}_3\text{Ge)}_2\text{PtH}_2
\]
The addition of trimethylgermanium hydride to 1,3-butadiene produced 60% cis-crotyltrimethylgermanium and 40% trans-crotyltrimethylgermanium. The cis product can be explained by visualizing the cisoid form of 1,3-butadiene coordinating with the trimethylgermanium platinum hydride complex followed by 1,4-addition.

The trans form of 1,3-butadiene, however, would not be in the proper conformation for coordination with the metal-hydride complex. Ryan and Spier\textsuperscript{76} have proposed that the secondary and tertiary alkyl platinum intermediates form rapidly and reversibly with substituted olefins. The possibility that a dimetal-hydride complex is formed, followed by the trans elimination of the secondary complex, could explain the formation of trans-crotyltrimethylgermanium, Eq. (76).

\[
\begin{align*}
\text{(Me}_3\text{Ge})_2\text{PtCH}_2\text{CH} \cdot \text{CHCH}_3 & \quad \xrightarrow{\text{(Me}_3\text{Ge})_2\text{PtH}_2} \quad \text{(Me}_3\text{Ge})_2\text{PtCH}_2\text{CH} \cdot \text{CHCH}_3 \cdot \text{Pt}(\text{GeMe}_3)_2 \\
\text{(Me}_3\text{Ge})_2\text{PtH}_2 & \quad \xrightarrow{\text{(Me}_3\text{Ge})_2\text{PtH}_2} \quad \text{(Me}_3\text{Ge})_2\text{PtH}_2 \\
\text{Me}_3\text{GeCH}_2 & \quad \xrightarrow{-\text{Me}_3\text{GePtH}} \quad \text{(Me}_3\text{Ge})_2\text{PtCH}_2 \cdot \text{CHCH}_3 \quad (76)
\end{align*}
\]
Smith and Burwell\textsuperscript{81} propose a similar mechanism to explain the formation of trans-2-butene during the hydrogenation of 1-butene over a platinum catalyst. The formation of 34 can also be substantiated by invoking a mechanism where a di-metal hydride complex is formed followed by rapid elimination of one complex, Eq. (77).

\[
\begin{align*}
\text{(Me}_3\text{Ge})_2\text{PtH}_2 & \rightarrow \text{(Me}_3\text{Ge})_2\text{Pt}^2\text{PtH}_2 \\
\text{(Me}_3\text{Ge})_2\text{Pt}^2\text{PtH}_2 & \rightarrow \text{(Me}_3\text{Ge})_2\text{PtH}_2
\end{align*}
\]

\text{(77)}

Terminal Addition vs. Isomerization.- 4-Vinyl-cyclo-hexene-1 did not isomerize to a 1,3-diene system during the addition reaction. Ryan and Spier\textsuperscript{76} have observed that olefins which form primary alkyl silanes with great ease seldom engage in exchange processes. They proposed that in the formation of the alkyl platinum intermediates, the primary intermediates decompose rapidly and irreversibly to product and catalyst. This same process can be applied to the 4-vinyl-cyclohexene-1 system where a primary alkyl platinum intermediate forms rapidly and irreversibly, precluding isomerization.

Ionic Additions to Allene.- Ionic additions to allene have occurred generally according to Markovnikov's rule\textsuperscript{82-86}, Eq. (78).
The addition of trimethylgermanium hydride to allene gave a 47% yield, comprising 60% allyl and 40% isopropenyl trimethylgermane, and 19% of a higher boiling compound, which is postulated to be a low molecular weight polymer of isopropenyl trimethylgermane (n.m.r. and I.R.). Both the terminal and central atoms were attacked equally by the trimethylgermanium-platinum-hydride complex. Markovnikov addition gives the allyl isomer, while anti-Markovnikov gives the isopropenyl isomer, Eq. (79,80).

\[
\text{Me}_3\text{GePtH} + \text{Me}_3\text{GeCH}_2\text{CH}_2\text{CH}_2
\]

\[
\text{Me}_3\text{GePtH} + \text{Me}_3\text{GeCH}_2\text{CH}_2\text{CH}_2
\]

The presence of considerable attack on the central carbon atom may imply formation of an allylic intermediate; however, more experimentation with a series of substituted allenes is needed before this question is answered.

The additions of trimethylgermanium hydride to dienes, catalyzed with chloroplatinic acid, have established "coordin-
nation control" as an important contributor to reactions
where metal atoms can coordinate with unsaturated systems.
This is substantiated by isomerization of nonconjugated di-
enes to conjugated dienes and by the predominance of endo
addition in the bicycloheptadiene reaction. Isomerization
is absent, however, when a terminal olefinic site is avail-
able, i.e., 4-vinyl-cyclohexene-1.
PART IV

EXPERIMENTAL

Boiling points are uncorrected. Elemental analyses were carried out by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer (sodium chloride optics). The nuclear magnetic resonance spectra were recorded on a Varian A-60 instrument with tetramethyldisilane as a standard. The gas-liquid chromatographic (g.l.c.) analyses were carried out with an Aerograph A 700 and an F & M Model 300 instrument.

Materials.- 1,3-Butadiene (Matheson Co.) was used directly from the cylinder. 2-Methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, and 1,5-hexadiene (Matheson, Coleman and Bell) were distilled before use. 1,3-Cyclohexadiene (Aldrich Chemical Co.) was checked (g.l.c.) on a 4 ft., 17% silicone nitrile column and used without further purification. 4-Vinyl cyclohexene, 1,3-cyclooctadiene and 1,5-cyclooctadiene were used without further purification; bicycloheptadiene was distilled before use. Dicyclopentadiene (Eastman Chemical Co.) was cracked to give cyclopentadiene. 1,4-Cyclohexadiene was prepared by the method of Bothner-By. Allene (Matheson Co.) was 98.5% pure with 1.5% propylene as the only impurity noted (g.l.c. on a 15 ft., 1/4 in., dimethylsulfolane column on firebrick at room temperature). 1,2-Butadiene (K & K Laboratories) was 75% pure with 17% 1-butene and 8% 2-butene (g.l.c. on a 15 ft. dimethylsulfolane column at room temperature). The 3-methyl-1,2-butadiene, 2,3-pentadiene, and 2-methyl-2,3-pentadiene were prepared by Dr. W.
Rahman according to the previously described method. \(^{91,92}\) 2,2-Azobisisobutyronitrile (AIBN), m.p. 102-104°(dec.) was supplied by Matheson, Coleman and Bell. The chloroplatinic acid was supplied by Fisher Co.

**Preparation of Trimethyltin Hydride.** In a three-necked flask equipped with a dropping funnel, stirrer, and distilling head was placed 10.5 g. (0.282 mole) lithium aluminum hydride suspended in 300 ml. of bis(2-ethoxyethyl)-ether. To this solution was added, over a two hour period, 112.3 g. (0.565 mole) trimethyltin chloride \(^{93}\) dissolved in 100 ml. of bis(2-ethoxyethyl)ether. The flask was heated with an oil bath such that distillation of trimethyltin hydride was simultaneous with addition of trimethyltin chloride. The trimethyltin hydride obtained was redistilled, giving 80.32 g., 87%, b. p. 60°/760 mm and stored in glass ampoules under nitrogen.

**Trimethyltin Hydride-1,3-butadiene Reaction.** To 8.2 g. (0.050 mole) trimethyltin hydride was added 5.4 g. (0.10 mole) 1,3-butadiene along with 0.18 g. (1 x 10^{-3} mole) AIBN in a glass ampoule. The ampoule was sealed at -78° and then heated in a bomb at 100° for 13 hours. The crude mixture was analyzed by g.l.c. on a 20 ft. x 3/8 in., 20% silicone nitrile (G.E. XF 1150) on Chromosorb P (60-80 mesh), isothermally at 125°, flow rate 200 cc./min., revealing the presence of cis-crotyltrimethyltin (55.4%) and trans-crotyltrimethyltin (44.6%) which was found to contain 7.1% allylcarbinyltrimethyltin. Distillation gave 6.56 g. of product, b.p. 69-72°/25 mm. (60% yield based on trimethyltin hydride).
Determination of the Purity of trans-Crotyltrimethyltin.- The infrared spectrum and the nuclear magnetic resonance spectrum of trans-crotyltrimethyltin indicated that it was contaminated with allylcarbinyltrimethyltin. The extinction coefficient was known for pure trans-crotyltrimethyltin at a wave length of 225 m\(\mu\). An \(8.17 \times 10^{-5}\) molar solution in methanol of the contaminated trans-crotyltrimethyltin compound, formed in the addition of trimethyltin hydride to 1,3-butadiene was prepared; the optical density (O.D.) at 225 m\(\mu\) was obtained on a Beckman DU spectrophotometer.

\[
\text{O.D.} = 0.468 \quad \varepsilon = \frac{0.468}{8.17 \times 10^{-5}} = 5728 \text{ mole}^{-1}
\]

\(\text{trans-crotyltrimethyltin} \quad \varepsilon = 6830 \text{ at } 225 \text{ m}\(\mu\)\)

\[
\begin{align*}
6830 &= 5728 \\
x &= \frac{8.17 \times 10^{-5}}{9.74 \times 10^{-5}} \\
&= 84\% \text{ trans-crotyltrimethyltin}
\end{align*}
\]

Since 44.6% of the addition product was the trans isomer and the allylcarbinyltrimethyltin, the ratios are 37.5% trans-crotyltrimethyltin and 7.1% allylcarbinyltrimethyltin.

Reaction of 1,3-Butadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid.- In a flask equipped with a side-arm containing a septum and a magnetic stirrer was placed 1.78 g. \((8.15 \times 10^{-3} \text{ mole})\) of the mixture of products, 55.4\% cis-crotyltrimethyltin, 37.5\% trans-crotyltrimethyltin and 7.1\% allylcarbinyltrimethyltin dissolved in 2 ml. of pentane. To this stirring solution was added dropwise from a
syringe 0.872 g. (7.65 x 10^{-3} mole) trifluoroacetic acid. The reaction produced the immediate precipitation of trimethyltin trifluoroacetate. The addition took ca. five minutes, after which water was added dissolving the trimethyltin trifluoroacetate. The pentane layer was separated and dried over magnesium sulfate, then distilled to give 0.35 g. of a clear liquid. The liquid was analyzed by g.l.c. (4 ft. x 1/4 in., 17% silicone nitrile column isothermally at 100\degree), showing the presence of pentane and one predominant peak. This peak was collected, and an infrared spectrum showed the absence of the cis and trans o.o.p. deformation bands and the presence of strong bands at 910 \text{cm}^{-1} and 990 \text{cm}^{-1} indicative of a terminal vinyl group. The infrared spectrum was superimposable on that of an authentic sample prepared by independent synthesis.

Preparation of Allylcarbinyl Bromide.\textsuperscript{91} - In a flask equipped with dropping funnel, stirrer, and drying tube was placed 16.87 g. (0.234 mole) of allylcarbinyl dissolved in 25 ml. of pentane. To this solution cooled in an ice bath (0\degree) was added over a 1.5 hour period 32.4 g. (0.117 mole) phosphorus tribromide dissolved in 25 ml. of pentane. After addition was complete, the mixture was stirred at room temperature for eight hours. The excess phosphorus tribromide was hydrolyzed with cold water; the pentane layer was separated and washed twice with water and twice with 5% sodium carbonate. The pentane layer was dried over magnesium sulfate. The pentane was distilled and 5.34 g. of product, 17%, b.p. 98-100\degree/760 mm. was obtained. The infrared spectrum of the bromide was identical to that published by Roberts.\textsuperscript{94}
Preparation of Allylcarbinyltrimethyltin (3).- In a 100 ml. flask equipped with condenser, dropping funnel, and stirrer was added 50 ml. of ether and 0.96 g. (0.0396 mole) magnesium turnings. To this was added 5.35 g. (0.0396 mole) allylcarbinyl bromide. The reaction proceeded smoothly and addition was complete in 30 minutes. To the Grignard was added 10 g. (0.05 mole) trimethyltin chloride in 25 ml. of ether. The addition was complete in 15 minutes, and the mixture was stirred overnight with gentle reflux. The mixture was hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated and washed thrice with water, then dried over magnesium sulfate. Distillation gave 3.0 g. of product, 35%, b.p. 48-50°/15 mm. G.l.c. on a 4 ft., 17% silicone nitrile column, isothermally at 100° gave one peak having the same retention time as the mixture of 2 and 3.

Reaction of 2-Methyl-1,3-butadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid.- In a flask equipped with a serum cap and gas outlet connected to a trap immersed in dry ice-acetone was placed 1.33 g. (5.72 x 10^{-3} mole) of 2-methyl-1,3-butadiene-trimethyltin hydride adducts (compounds 4,5,6,7). The flask was cooled in an ice bath and 0.65 g. (5.5 x 10^{-3} mole) of trifluoroacetic acid was added via a syringe. The flask was heated to 60° and the product collected in the trap. G.l.c. analysis (20 ft. x 3/8 in., 20% silicone nitrile on Chromosorb P at room temperature, flow rate 40 cc./min.) of the contents in the trap showed two products, 3-methyl-1-butene (94.5%) and 2-methyl-1-butene (5.5%). The 2-methyl-1-butene was found to react with trifluoroacetic acid, and this reduced its percentage. This was substantiated by reacting a known sample of 2-methyl-1-butene with trifluoro-
acetic acid. The 3-methyl-1-butene and 2-methyl-1-butene were identified by comparing retention times in the g.l.c. with known samples and by infrared spectrum which was superimposable on a spectrum of 3-methyl-1-butene, the predominant product.

In another experiment, 2.9 g. (0.0125 mole) of adduct, dissolved in pentane, was reacted with 1.36 g. (0.0119 mole) trifluoroacetic acid. After water was added to dissolve the trimethyltin trifluoroacetate, the pentane layer was separated and analyzed by g.l.c. (4 ft., 17% silicone nitrile column, isothermally at 100°, flow rate 30 cc./min.) showing two peaks; the first peak was the 1,2-addition product, 4, (5.4%) and the second peak was postulated to be the 4,3-addition product, 5, (5.5%), shown to be present in the n.m.r. spectra of 6.

Reaction of the Cyclopentadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid.- In a 25 ml. flask equipped with a side-arm containing a septum, magnetic stirring bar, and a drying tube was placed 0.74 g. (3.2 x 10⁻³ mole) of a mixture of 10 (57%) and 11 (43%) dissolved in 2 ml. of pentane. To this solution was added dropwise with a syringe 0.218 g. (1.9 x 10⁻³ mole) of trifluoroacetic acid. The addition took five minutes and then water was added to dissolve the trimethyltin trifluoroacetate. The pentane layer was separated and dried over magnesium sulfate. The pentane was distilled and the remaining liquid was analyzed by g.l.c (20 ft x 3/8 in., 20% silicone nitrile column, isothermally at 140°, flow rate 200 cc./min.) showing one peak. This product was collected and had an I.R. spectrum which was superimposable on the compound identified as cyclopent-3-en-1-yltrimethyltin.
Preparation of 4-Bromocyclopentene-1. In a 500 ml. three-necked flask equipped with a dropping funnel, stirrer, and drying tube was placed 39.8 g. (0.6 mole) of cyclopentadiene, dissolved in 100 ml. of petroleum ether. The flask was cooled to -40° and 96 g. (0.6 mole) of bromine dissolved in 200 ml. petroleum ether was added over 1.5 hours keeping the temperature below -30°. The mixture was poured into a 500 ml. Erlenmeyer flask cooled to -78°; then the solvent was decanted. The residue was dissolved in 200 ml. of anhydrous ether and reduced immediately with lithium aluminum hydride.

To a solution of 11.4 g. (0.3 mole) lithium aluminum hydride suspended in 300 ml. of ether was added, with cooling, the ethereal solution of 3,5-dibromocyclopentene. The addition was complete in 1.5 hours, and then the mixture was stirred for five hours and refluxed for 30 hours. The mixture was filtered through glass wool and the filtrate poured over crushed ice. The ether layer was separated, washed with water, and then dried over magnesium sulfate. The ether was distilled at atmospheric pressure and the residue distilled to give 5.88 g., 6.7% of product, b.p. 67-68°/40 mm., \( n_D^{25} 1.4993 \) (lit. \( n_D^{25} 1.4992 \)). The infrared had all the bands reported by Bartlett and Rice.

Preparation of Cyclopent-3-en-1-yltrimethyltin. - To 0.98 g. (0.0406 mole) magnesium metal in 50 ml. of anhydrous ether was added with stirring 5.68 g. (0.039 mole) 4-bromocyclopentene dissolved in 25 ml. of ether. The addition was complete in 45 minutes. To the Grignard was added 8.15 g. (0.041 mole) of trimethyltin chloride dissolved in 25 ml. of ether over a 25 minute period. The mixture was refluxed eight hours and then hydrolyzed with a saturated ammonium
The ethereal layer was separated and washed five times with water and then dried over magnesium sulfate. Distillation gave 2.53 g., 27.8%, b.p. 35-37°/1.2 mm. of product. G.l.c. analysis on a 4 ft., 17% silicone nitrile column, isothermally at 100°, flow rate 30 cc./min. indicated one peak. The I.R. and n.m.r. spectra were identical to those of 11.

**Attempted Isomerization of Cyclopent-3-en-l-yltrimethyltin.**

<table>
<thead>
<tr>
<th>Sealed Tube</th>
<th>Contents</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>cyclopent-3-en-l-yl trimethyltin</td>
<td>no change</td>
</tr>
<tr>
<td>II</td>
<td>cyclopent-3-en-l-yl trimethyltin and catalytic amount of trimethyltin hydride</td>
<td>no change</td>
</tr>
</tbody>
</table>

The sealed tubes were heated for eight hours at 175° in a bomb. G.l.c. analysis on a 20 ft. x 3/8 in., 20% silicone nitrile column, isothermally at 140°, showed no change in the starting compound. A mixture of 57% compound 10 and 43%, 11 was also heated in a sealed tube at 175° for 6 hrs. G.l.c. analysis indicated no appreciable change in composition, 62% to 38%.

**Reaction of the 1,3-Cyclohexadiene-Trimethyltin Hydride Adducts with Trifluoroacetic Acid.** In a 25 ml. flask with a side-arm containing a septum and a magnetic stirrer was added 0.54 g. (2.2 x 10⁻³ mole) of a mixture containing 66% 12 and 34% 13 in 2 ml. of carbon tetrachloride. To this stirring mixture was added by a syringe 0.171 g. (1.54 x 10⁻³
mole) of trifluoroacetic acid. After the addition of all the acid was complete, water was added and the carbon tetra-chloride layer separated and dried over magnesium sulfate. Preparative g.l.c. (20 ft. x 3/8 in., 20% silicone nitrile on Chromosorb P, 60-80 mesh; isothermally at 150°, flow rate 200 cc./min.) was used to collect the remaining product. The I.R. and n.m.r. spectra were superimposable on that of an authentic sample prepared by an independent synthesis.

Preparation of 4-Bromocyclohexene-1.- To 9.74 g. (0.091 mole) of vinyl bromide was added 4.8 g. (0.089 mole) 1,3-butadiene in a glass ampoule, cooled to -78°, along with 2 mole per cent 2,6-di-tert-butyl cresol as an inhibitor. The ampoule was heated at 145° for 9.5 hours in a bomb. Distillation gave 3 g., 21%, b.p. 45-46°/15 mm., of product; \( n^\circD 1.5146 \) (lit. \( n^\circD 1.5168 \)).

Preparation of Cyclohex-3-en-1-yltrimethyltin.- To 0.43 g. (0.017 mole) magnesium turnings in 50 ml. anhydrous ether was added, dropwise, over a period of five minutes, 2.8 g. (0.017 mole) 4-bromocyclohexene-1 dissolved in 10 ml. of ether. The solution was stirred for 0.5 hours, and then 3.4 g. (0.017 mole) of trimethyltin chloride was added over a ten minute period. The mixture was refluxed for eight hours and then hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated, washed five times with water, and dried over magnesium sulfate. The ether was removed on a Rinco rotary evaporator and the product purified by preparative g.l.c. (20 ft. x 3/8 in., 20% silicone nitrile on Chromosorb P, 60-80 mesh, isothermally at 150°, flow rate 200 cc./min.) to give 1.0 g., 24%, product.
Trimethyltin Hydride-Allene Reaction.- To 4.41 g. (0.027 mole) trimethyltin hydride was added 2.08 g. (0.052 mole) allene along with 0.09 g. (5.4 x 10^-4 mole) AIBN in a glass ampoule. The ampoule was sealed at -78° and then heated in a bomb at 100° for nine hours. The crude mixture was analyzed by g.l.c. (20 ft. x 3/8 in., 20% silicone nitrile column on Chromosorb P, 60-80 mesh, isothermally at 90°, flow rate 200 cc./min.) revealing the presence of allytrimethyltin (54.8%) and isopropenyltrimethyltin (45.2%). Distillation gave 3.14 g. of product, b.p. 123.5-124.5/760 mm. and 0.53 g., b.p. 38°/25 mm. The total was 3.67 g. (67% yield based on trimethyltin hydride). The excess allene gas which was collected in a dry ice-acetone trap, during distillation, showed no methylacetylene (g.l.c. and I.R. spectrum). See Tables XIX and XX for pertinent data on the trimethyltin hydride-diene adducts.

Trimethyltin Hydride-Methylacetylene Reaction.- To 5.88 g. (0.035 mole) trimethyltin hydride was added 3.0 g. (0.075 mole) methylacetylene in a glass ampoule, along with 0.1 g. (7 x 10^-4 mole) AIBN. The sealed ampoule was heated in a bomb at 100° for nine hours. The crude mixture was subjected to g.l.c. analysis (20 ft. x 3/8 in., 20% silicone nitrile column, isothermally at 90°, flow rate 200 cc./min.) and showed the presence of trans-propenyltrimethyltin (70.4%), cis-propenyltrimethyltin (29.0%), and isopropenyltrimethyltin (ca. 0.6%). The contents of the ampoule were distilled giving 3.0 g., 43%, b.p. 125-126°/760 mm.
<table>
<thead>
<tr>
<th>Diene</th>
<th>Moles Diene</th>
<th>Moles trimethyltin hydride</th>
<th>B.p. °/mm.</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Butadiene</td>
<td>0.10</td>
<td>0.050</td>
<td>69-72/25</td>
<td>60</td>
</tr>
<tr>
<td>1,3-Butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.04</td>
<td>0.021</td>
<td>26/1.6</td>
<td>47</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene</td>
<td>0.087</td>
<td>0.044</td>
<td>36-37.5/2</td>
<td>66</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.112</td>
<td>0.056</td>
<td>46-49/3.2</td>
<td>55</td>
</tr>
<tr>
<td>2,3-Dimethyl-1,3-butadiene</td>
<td>0.051</td>
<td>0.102</td>
<td>46-48.5/1.2</td>
<td>66</td>
</tr>
<tr>
<td>2,3-Dimethyl-1,3-butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.035</td>
<td>0.027</td>
<td>24-25/0.2</td>
<td>41</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>0.030</td>
<td>0.0138</td>
<td>30/0.3</td>
<td>67</td>
</tr>
<tr>
<td>Cyclopentadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.041</td>
<td>0.034</td>
<td>36-38/1.2</td>
<td>58</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>0.032</td>
<td>0.032</td>
<td>34-37/0.75</td>
<td>55</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>0.031</td>
<td>0.031</td>
<td>30-30.5/0.08</td>
<td>55</td>
</tr>
<tr>
<td>1,5-Hexadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.087</td>
<td>0.044</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>1,5-Hexadiene</td>
<td>0.074</td>
<td>0.037</td>
<td>37.5-39/0.3</td>
<td>59</td>
</tr>
<tr>
<td>Allene</td>
<td>0.052</td>
<td>0.027</td>
<td>123.5-124.5/760</td>
<td>67</td>
</tr>
<tr>
<td>1,2-Butadiene</td>
<td>0.076</td>
<td>0.052</td>
<td>55-57/25</td>
<td>73</td>
</tr>
<tr>
<td>3-Methyl-1,2-butadiene</td>
<td>0.051</td>
<td>0.045</td>
<td>37.5-39/2.5</td>
<td>72</td>
</tr>
<tr>
<td>2,3-Pentadiene</td>
<td>0.016</td>
<td>0.015</td>
<td>39-41/1.4</td>
<td>65</td>
</tr>
<tr>
<td>2-Methyl-2,3-pintadiene</td>
<td>0.035</td>
<td>0.032</td>
<td>39.5-40/1.2</td>
<td>83</td>
</tr>
</tbody>
</table>

<sup>a</sup> Reaction not catalyzed; all other catalyzed with 2 mole % AIBN.
<table>
<thead>
<tr>
<th>Diene</th>
<th>Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hrs.</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>13</td>
</tr>
<tr>
<td>1,3-Butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>10</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene</td>
<td>11</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>11</td>
</tr>
<tr>
<td>2,3-Dimethyl-1,3-butadiene</td>
<td>11</td>
</tr>
<tr>
<td>2,3-Dimethyl-1,3-butadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8.5</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>8</td>
</tr>
<tr>
<td>Cyclopentadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>7</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>6</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>11</td>
</tr>
<tr>
<td>1,5-Hexadiene&lt;sup&gt;a&lt;/sup&gt;</td>
<td>8</td>
</tr>
<tr>
<td>1,5-Hexadiene</td>
<td>9</td>
</tr>
<tr>
<td>Allene</td>
<td>9</td>
</tr>
<tr>
<td>1,2-Butadiene</td>
<td>10.5</td>
</tr>
<tr>
<td>3-Methyl-1,2-butadiene</td>
<td>11</td>
</tr>
<tr>
<td>2,3-Pentadiene</td>
<td>8.5</td>
</tr>
<tr>
<td>2-Methyl-2,3-pentadiene</td>
<td>10</td>
</tr>
</tbody>
</table>

<sup>a</sup> Indicates a specific condition or note related to the diene.
Table XX

Physical and Analytical Data on Trimethyltin Hydride-Diene Adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
<th>$^{25}$D</th>
<th>C (Calcd)</th>
<th>H (Calcd)</th>
<th>C (Found)</th>
<th>H (Found)</th>
<th>Infrared Bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>C$<em>7$H$</em>{16}$Sn</td>
<td>1.4686</td>
<td>38.39</td>
<td>7.31</td>
<td>38.28</td>
<td>7.36</td>
<td>3075(m), 2975(s), 2925(s), 1649(s), 1450(m), 1420(m), 1185(s), 990(s), 910(s), 765(s)</td>
</tr>
<tr>
<td>4</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>-</td>
<td>41.25</td>
<td>7.73</td>
<td>41.45</td>
<td>7.93</td>
<td>3075(m), 2950(s), 2920(s), 1638(m), 1450(m), 1360(m), 1185(m), 990(s), 910(s), 765(s)</td>
</tr>
<tr>
<td>6</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>1.4766</td>
<td>41.25</td>
<td>7.73</td>
<td>41.53</td>
<td>7.61</td>
<td>3015(w), 2960(s), 2910(s), 1655(m), 1335(m), 1370(m), 1185(m), 960(m), 820(w), 760(s)</td>
</tr>
<tr>
<td>7</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>1.4823</td>
<td>41.25</td>
<td>7.73</td>
<td>41.54</td>
<td>7.82</td>
<td>3015(w), 2960(s), 2915(s), 1655(m), 1450(m), 1375(m), 1190(m), 845(m), 755(s)</td>
</tr>
<tr>
<td>8</td>
<td>C$<em>9$H$</em>{20}$Sn</td>
<td>1.4748</td>
<td>43.77</td>
<td>8.10</td>
<td>44.06</td>
<td>8.43</td>
<td>3065(m), 2950(s), 2910(s), 1645(m), 1450(m), 1370(m), 1185(m), 890(s), 765(s)</td>
</tr>
</tbody>
</table>
### Table XX continued-

#### Elemental Analyses

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
<th>( n_D )</th>
<th>Calcd.</th>
<th>Found</th>
<th>Infrared Bands (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>( \text{C}<em>9\text{H}</em>{20}\text{Sn} )</td>
<td>1.4850</td>
<td>43.77</td>
<td>8.10</td>
<td>43.92 8.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>( \text{C}<em>8\text{H}</em>{16}\text{Sn} )</td>
<td>1.5031</td>
<td>41.61</td>
<td>6.94</td>
<td>41.85 7.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>( \text{C}<em>8\text{H}</em>{16}\text{Sn} )</td>
<td>1.4935</td>
<td>41.61</td>
<td>6.94</td>
<td>41.42 7.06</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 &amp; 13</td>
<td>( \text{C}<em>9\text{H}</em>{18}\text{Sn} )</td>
<td>1.5092</td>
<td>44.11</td>
<td>7.35</td>
<td>44.30 7.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>( \text{C}<em>9\text{H}</em>{18}\text{Sn} )</td>
<td>1.5032</td>
<td>44.11</td>
<td>7.35</td>
<td>43.90 7.20</td>
</tr>
</tbody>
</table>
## Table XX continued -

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
<th>( n_D )</th>
<th>( ^{25} \text{C} )</th>
<th>( \text{H} )</th>
<th>( ^{25} \text{C} )</th>
<th>( \text{H} )</th>
<th>Infrared Bands (( \text{cm}^{-1} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>14</td>
<td>( \text{C}<em>6\text{H}</em>{14}\text{Sn} )</td>
<td>1.4608</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3040 (m), 2975 (s), 2935 (s), 1600 (w), 1440 (s), 1190 (s), 995 (w), 930 (w), 910 (s), 765 (s), 710 (m)</td>
</tr>
<tr>
<td>15</td>
<td>( \text{C}<em>6\text{H}</em>{14}\text{Sn} )</td>
<td>1.4740</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>3080 (m), 2985 (s), 2915 (s), 1630 (s), 1190 (s), 1090 (m), 1020 (m), 985 (m), 930 (m), 880 (s), 765 (s)</td>
</tr>
<tr>
<td>16</td>
<td>( \text{C}<em>7\text{H}</em>{16}\text{Sn} )</td>
<td>1.4656</td>
<td>38.41</td>
<td>7.32</td>
<td>38.67</td>
<td>7.49</td>
<td>3035 (m), 2960 (s), 2930 (s), 1600 (w), 1460 (s), 1375 (w), 1310 (w), 1190 (s), 1070 (m), 1000 (w), 915 (s), 765 (s)</td>
</tr>
<tr>
<td>17</td>
<td>( \text{C}<em>7\text{H}</em>{16}\text{Sn} )</td>
<td>1.4738</td>
<td>38.41</td>
<td>7.32</td>
<td>38.31</td>
<td>7.49</td>
<td>3000 (vw), 2975 (s), 2910 (s), 2850 (m), 1615 (m), 1440 (m), 1190 (s), 1050 (w), 990 (w), 765 (s), 705 (m)</td>
</tr>
<tr>
<td>18</td>
<td>( \text{C}<em>7\text{H}</em>{16}\text{Sn} )</td>
<td>1.4753</td>
<td>38.41</td>
<td>7.32</td>
<td>38.28</td>
<td>7.21</td>
<td>3000 (vw), 2965 (s), 2920 (s), 1450 (m), 1190 (m), 1055 (w), 1025 (w), 820 (m), 770 (s), 710 (m)</td>
</tr>
<tr>
<td>Adduct</td>
<td>Formula</td>
<td>$n_D$</td>
<td>Calcd.</td>
<td>Found</td>
<td>Infrared Bands (cm$^{-1}$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>---------</td>
<td>-------</td>
<td>--------</td>
<td>--------</td>
<td>---------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>1.4678</td>
<td>41.23</td>
<td>7.73</td>
<td>41.40</td>
<td>7.90</td>
<td>3030(m), 2950(s), 2850(m), 1590(w), 1450(m), 1375(m), 1350(m), 1190(s), 916(s), 770(s), 710(m)</td>
</tr>
<tr>
<td>22</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>1.4847</td>
<td>41.23</td>
<td>7.73</td>
<td>41.41</td>
<td>7.95</td>
<td>2975(s), 2910(s), 1630(s), 1450(s), 1375(m), 1190(s), 1115(m), 770(s), 705(m)</td>
</tr>
<tr>
<td>23 &amp; 24</td>
<td>C$<em>8$H$</em>{18}$Sn</td>
<td>1.4750</td>
<td>41.23</td>
<td>7.73</td>
<td>41.42</td>
<td>7.81</td>
<td>3005(w), 2960(s), 2910(s), 1625(m), 1450(m), 1375(w), 1190(m), 835(m), 770(s), 705(m)</td>
</tr>
<tr>
<td>25 &amp; 26</td>
<td>C$<em>9$H$</em>{20}$Sn</td>
<td>1.4779</td>
<td>43.76</td>
<td>8.10</td>
<td>43.56</td>
<td>8.02</td>
<td>3005(vw), 2960(s), 2910(s), 2860(m), 1460(m), 1380(m), 1360(m), 1189(m), 835(m), 770(s), 710(m)</td>
</tr>
<tr>
<td>27</td>
<td>C$<em>9$H$</em>{20}$Sn</td>
<td>1.4837</td>
<td>43.76</td>
<td>8.10</td>
<td>43.47</td>
<td>7.87</td>
<td>2950(s), 2900(s), 2860(s), 1620(m), 1440(m), 1360(m), 1300(w), 1188(m), 1050(w), 760(s), 705(m)</td>
</tr>
</tbody>
</table>
Reaction of cis-But-2-en-2-yltrimethyltin and Tri-fluoroacetic Acid.- To 0.1337 g. (6.1 x 10^{-4} mole) cis-but-2-en-2-yltrimethyltin in a flask equipped with a serum cap and a gas outlet connected to a trap immersed in dry ice-acetone was added, with a syringe, 0.06 g. (6.1 x 10^{-4} mole) trifluoroacetic acid. The reaction was very exothermic; trimethyltin trifluoroacetate precipitated immediately. The gas was analyzed by g.l.c. (15 ft., 28% dimethylsulfolane on C-22 Firebrick, 40-60 mesh, at room temp.) giving 94% of a component with the same retention time as cis-2-butene and 6% with the same retention time as trans-2-butene. The trimethyltin trifluoroacetate had m.p. 122-124° dec., undepressed when admixed with an authentic sample.

Reaction of Trimethyltin Hydride and 1,5-Hexadiene.- The addition of trimethyltin hydride to 1,5-hexadiene was successful only when catalyzed with AIBN.

To 6.07 g. (0.037 mole) trimethyltin hydride was added 6.1 g. (0.074 mole) 1,5-hexadiene in a glass ampoule along with 0.12 g. (7.4 x 10^{-4} mole) AIBN. The glass ampoule was heated in a bomb for nine hours at 100°. Distillation gave 5.36 g., 59%, b.p. 37.5-39°/0.3 mm. of product; n_D^25 1.4689; I.R. spectrum v_max (film) 3075 (m), 1640 (s), 1440 (m), 1190 (m), 995 (s), 910 (s) and 768 (s) cm.^{-1}. N.m.r. spectrum (neat): \( \tau \) 4.2 (m) (J 16.5, 11.5, 6.5 c.p.s.); \( \tau \) 5.05 (m) (J 2.0 c.p.s.); \( \tau \) 7.94 (4) (J 6.5 c.p.s.); \( \tau \) 8.45 (m); \( \tau \) 9.15 (3) (J 7.0 c.p.s.); \( \tau \) 9.95 (1) integrated area ratios 1:2:2:4:2:9.

Anal. calcd. for C_9H_20Sn: C, 43.77; H, 8.10; Sn, 48.13. Found: C, 43.54; H, 8.31; Sn, 47.63.
Preparation of Trichlorophenylgermanium. 98 - To 15.3 g. (0.071 mole) germanium tetrachloride 99 was added 6.8 g. (0.0178 mole) tetraphenylgermanium 100 in a sealed tube. The sealed tube was heated in a bomb at 300° for 36 hours. Distillation gave 13.74 g., 77%, b.p. 84-86°/1.8 mm. of product.

Preparation of Trimethylphenylgermanium. - To 0.372 mole methylmagnesium bromide in 500 ml. anhydrous diethyl ether was added, with cooling, 15.88 g. (0.062 mole) trichlorophenylgermanium dissolved in 100 ml. anhydrous diethyl ether. Addition was complete in two hours, and the mixture was stirred overnight. The excess Grignard was hydrolyzed with a saturated ammonium chloride solution. The ether layer was separated and washed thrice with cold water, then dried over magnesium sulfate. Distillation gave 7.6 g., 67%, b.p. 82-85°/20 mm. of product. By not cooling the Grignard upon addition of the trichlorophenylgermanium and refluxing the mixture for nine hours, yields were increased to 80%.

Preparation of Trimethylgermanium Bromide.- To 7.6 g. (0.039 mole) trimethylphenylgermanium dissolved in 15 ml. of ethyl bromide was added dropwise over a one-hour period 6.25 g. (0.039 mole) bromine dissolved in 15 ml. of ethyl bromide. Distillation gave 7.63 g., 98%, b.p. 113-115°/760 mm., \( n_D^{101} 1.4688, \) (Lit. b.p. 113-114°/760 mm., \( n_D^{20} 1.4713 \)) of product.

Preparation of Trimethylgermanium Hydride.- In a flask equipped with a stirrer, dropping funnel, and distilling head was placed 0.735 g. (0.0193 mole) lithium aluminum hydride suspended in 25 ml. of 1,2-dimethoxyethane. To this solution was added 7.63 g. (0.0386 mole) trimethylgermanium bromide dissolved in 15 ml. of 1,2-dimethoxyethane. After addition was complete, the flask was heated to 70° with a wax bath; the
product was distilled to give 3.51 g., 77%, b.p. 26°/760 mm.

Reaction of Trimethylgermanium Hydride with Bicyclo-(2.2.1)-heptadiene-2,5.- To 3.51 g. (0.029 mole) trimethylgermanium hydride was added 2.9 g. (0.0315 mole) bicyclo-(2.2.1)-heptadiene-2,5 in a glass ampoule along with 0.3 cc. of a 0.1N chloroplatinic acid solution (ethanol). The ampoule was sealed at -78° and then heated in a bomb at 140° for eight hours. Distillation gave 4.89 g., 80%, b.p. 82-84°/1.7 mm. of product. G.l.c. (4 ft. x 1/4 in., 20% Apiezon L on Chromosorb P, 60-80 mesh) indicated one component; n.m.r. spectroscopy, however, showed the presence of three components: 39, 75%; 40, 15%; 41, 10% (Table XV). See Tables XXI and XXII for pertinent data on the trimethylgermanium hydride-diene adducts.

Attempted Reaction of 4-Ethyl(2'-trimethylgermyl)cyclohexene-1 (38) with Trifluoroacetic Acid.- To 0.4453 g. (1.97 x 10⁻³ mole) 4-ethyl(2'-trimethyl-germanyl)cyclohexene-1 was added 0.225 g. (1.97 x 10⁻³ mole) trifluoroacetic acid. Upon mixing the two components only a color change was evident, but no reaction had taken place. G.l.c. analysis (4 ft. x 1/4 in., 20% Apiezon L on Chromosorb P, 60-80 mesh) indicated that only starting materials were present. A few drops of tetrahydrofuran were added and a homogeneous solution resulted. This solution was heated on a steam bath overnight; g.l.c., however, indicated that no reaction had taken place.

Reaction of cis- and trans-Crotyltrimethylgermanium with Trifluoroacetic Acid.- In a flask equipped with a septum and a gas outlet to a dry ice-acetone trap was placed 0.141 g. (8.2 x 10⁻⁴ mole) cis- and trans-crotyltrimethylgermanium (60% cis; 40% trans). To this was added with a syringe 0.01 g. (8.2 x 10⁻⁴ mole) trifluoroacetic acid. The reaction was very exothermic, liberating a gas which was
Table XXI

Data on the Addition of Trimethylgermanium Hydride to Dienes\textsuperscript{a,b}

<table>
<thead>
<tr>
<th>Diene</th>
<th>Moles Diene</th>
<th>Moles Trimethyl-germanium hydride</th>
<th>B.p. °/mm.</th>
<th>% Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Allene</td>
<td>0.560</td>
<td>0.0284</td>
<td>97-98/760</td>
<td>47.5</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>0.045</td>
<td>0.025</td>
<td>125-127/760</td>
<td>65</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>0.028</td>
<td>0.028</td>
<td>52-54/15</td>
<td>25</td>
</tr>
<tr>
<td>Cyclopentadiene</td>
<td>0.019</td>
<td>0.019</td>
<td>55-57/25</td>
<td>13</td>
</tr>
<tr>
<td>1,3-Cyclohexadiene</td>
<td>0.038</td>
<td>0.0242</td>
<td>38-39/1.5</td>
<td>60</td>
</tr>
<tr>
<td>1,4-Cyclohexadiene</td>
<td>0.039</td>
<td>0.0274</td>
<td>34/1.0</td>
<td>49</td>
</tr>
<tr>
<td>1,3-Cyclooctadiene</td>
<td>0.038</td>
<td>0.034</td>
<td>78-78.5/0.75</td>
<td>30</td>
</tr>
<tr>
<td>1,5-Cyclooctadiene</td>
<td>0.031</td>
<td>0.028</td>
<td>93-95/1.5</td>
<td>40</td>
</tr>
<tr>
<td>1,5-Cyclooctadiene</td>
<td>0.015</td>
<td>0.013</td>
<td>47.5/0.2</td>
<td>42</td>
</tr>
<tr>
<td>4-Vinyl-cyclohexene-1</td>
<td>0.039</td>
<td>0.036</td>
<td>93-94/0.3</td>
<td>47</td>
</tr>
<tr>
<td>Bicyclo-(2·2·1)-heptadiene-2,5</td>
<td>0.032</td>
<td>0.029</td>
<td>82-84/1.7</td>
<td>80</td>
</tr>
</tbody>
</table>

\textsuperscript{a} All reactions were catalyzed with 0.3-0.6 cc. of a 0.1N chloroplatinic acid solution in absolute ethanol.

\textsuperscript{b} Reaction conditions are given in Table XIII.
Table XXII

Physical and Analytical Data of Trimethylgermanium Hydride-Diene Adducts

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
<th>$n_D$</th>
<th>Calcd.</th>
<th>Found</th>
<th>Infrared Bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>$C_6H_{14}Ge$</td>
<td>1.4278</td>
<td>45.40</td>
<td>8.83</td>
<td>45.65  9.00</td>
</tr>
<tr>
<td>31</td>
<td>$C_6H_{14}Ge$</td>
<td>1.4260</td>
<td>45.40</td>
<td>8.83</td>
<td>45.60  8.92</td>
</tr>
<tr>
<td>32</td>
<td>$C_7H_{16}Ge$</td>
<td>1.4375</td>
<td>48.67</td>
<td>9.27</td>
<td>48.49  9.32</td>
</tr>
<tr>
<td>33</td>
<td>$C_7H_{16}Ge$</td>
<td>1.4430</td>
<td>48.67</td>
<td>9.27</td>
<td>48.83  9.48</td>
</tr>
</tbody>
</table>
Table XXII continued-

<table>
<thead>
<tr>
<th>Adduct</th>
<th>Formula</th>
<th>$n_D$</th>
<th>Calcd.</th>
<th>Found</th>
<th>Infrared Bands (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>C$<em>8$H$</em>{16}$Ge</td>
<td>1.4657</td>
<td>52.00</td>
<td>8.67</td>
<td>52.10</td>
</tr>
<tr>
<td>35</td>
<td>C$<em>8$H$</em>{16}$Ge</td>
<td>1.4662</td>
<td>52.00</td>
<td>8.67</td>
<td>52.10</td>
</tr>
<tr>
<td>36</td>
<td>C$<em>9$H$</em>{18}$Ge</td>
<td>1.4795</td>
<td>54.38</td>
<td>9.06</td>
<td>54.36</td>
</tr>
<tr>
<td>37</td>
<td>C$<em>{11}$H$</em>{22}$Ge</td>
<td>1.4869</td>
<td>58.25</td>
<td>9.70</td>
<td>58.40</td>
</tr>
<tr>
<td>Adduct</td>
<td>Formula</td>
<td>$n_D$</td>
<td>Calcd.</td>
<td>Found</td>
<td>Infrared Bands (cm$^{-1}$)</td>
</tr>
<tr>
<td>--------</td>
<td>-----------</td>
<td>-------</td>
<td>---------</td>
<td>--------</td>
<td>---------------------------</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
<td>C</td>
</tr>
<tr>
<td>38</td>
<td>C$<em>{11}$H$</em>{22}$Ge</td>
<td>1.4756</td>
<td>58.25</td>
<td>9.70</td>
<td>58.46</td>
</tr>
<tr>
<td>39-41</td>
<td>C$<em>{10}$H$</em>{18}$Ge</td>
<td>1.4834</td>
<td>56.98</td>
<td>8.54</td>
<td>56.82</td>
</tr>
</tbody>
</table>
collected in the trap. G.l.c. analysis (15 ft. 28% dimethylsulfolane on C-22 Firebrick, 40-60 mesh, at room temp.) indicated the presence of 1-butene, whose retention time was identical with an authentic sample. Water and pentane were added to the remaining liquid and the pentane layer was analyzed by g.l.c. (4 ft. x 1/4 in., 17% silicone nitrile on Chromosorb P, 60-80 mesh, isothermally at 90°, flow rate 30 cc./min.). The g.l.c. analysis indicated a small amount of trans isomer present and a trace of cis isomer. The relative reactivity indicates cis faster than trans, which is in good agreement with the corresponding tin analogs.

**Reaction of Cyclooct-2-en-1-yltrimethylgermanium with Trifluoroacetic Acid.** - In a flask equipped with a serum cap was placed 0.716 g. (3.16 x 10⁻³ mole) cyclooct-2-en-1-yltrimethylgermanium. To this was added 0.36 (3.16 x 10⁻³ mole) trifluoroacetic acid with a syringe. The reaction was very exothermic and was over in less than one minute. Water and pentane were added; the pentane layer was separated, dried, and analyzed by g.l.c. (4 ft., 20% Carbowax 20 M on Chromosorb P, 40-60 mesh, isothermally at 75°, flow rate 20 cc./min.). The g.l.c. indicated that all the starting material was gone and that two products were present. The products were collected (g.l.c.); the first peak was trimethylgermanium trifluoroacetate; the second, cyclooctene. The cyclooctene had an I.R. spectrum which was superimposable on that of an authentic sample. Trimethylgermanium trifluoroacetate, n_D²⁰ 1.3820, provided the following I.R. spectral data: v_max (film) 2985 (m), 2900 (m), 1750 (s), 1400 (s), 1245 (m), 1210 (s), 1170 (s), 835 (s) cm⁻¹.

Reaction of Cyclohex-2-en-l-yltrimethylgermanium with Trifluoroacetic Acid.- To 0.2901 g. (1.46 x 10^{-3} mole) cyclohex-2-en-l-yltrimethylgermanium was added with a syringe 0.168 g. (1.4 x 10^{-3} mole) trifluoroacetic acid. An exothermic reaction commenced and was over in less than one minute. Water and pentane were added, and the pentane layer separated and dried over magnesium sulfate. G.l.c. analysis (4 ft., 20% Apiezon L on Chromosorb P, 60-80 mesh, 100-220°, program 13°/min.) indicated the presence of two peaks. The first peak was trimethylgermanium trifluoroacetate identified by I.R. spectrum. The second was cyclohexene, identified by comparison of its retention time and I.R. spectrum with an authentic sample. The starting material had completely reacted (g.l.c.).

Reaction of Cyclopentadiene-Trimethylgermanium Hydride Adducts with Trifluoroacetic Acid.- To 0.1 g. (6.7 x 10^{-4} mole) cyclopentadiene-trimethylgermanium hydride adducts (62.7%, 34; 37.3%, 35) was added 0.07 g. (6.7 x 10^{-4} mole) trifluoroacetic acid dropwise from a syringe. The reaction mixture was analyzed by g.l.c. (20 ft. x 3/8 in. 20% silicone nitrile on Chromosorb P, 60-80 mesh, isothermally at 135°, flow rate 200 cc./min.), showing that 35 reacted preferentially with the trifluoroacetic acid. The cyclopentene which was formed had a retention time (g.l.c.) which was identical to an authentic sample.

Hydrogenation of the Trimethylgermanium Hydride-Bicyclo-(2·2·1)-heptadiene-2,5 Adducts.- To 0.70 g. of the trimethylgermanium hydride-bicyclo-(2·2·1)-heptadiene-2,5 adducts (39,40,41) dissolved in 5 ml. of ethyl acetate was added 0.1 g. of Adams catalyst. The mixture was hydrogenated at 25 p.s.i. in a Parr hydrogenator for 15 hours. The ethyl
acetate was removed and the I.R. spectrum indicated the absence of unsaturation. The n.m.r. spectrum had trimethylgermanium singlets at $\tau$ 9.89 and $\tau$ 9.94 in the ratio 85:15 (Table XIV) $n_D^{25}$ 1.4813; I.R. spectrum: $\nu_{max}$ 2960 (s), 1460 (m), 1250 (s), 1175 (w), 920 (w), 875 (w), 840 (s); n.m.r. spectrum: (neat) $\tau$ 7.7 (m), $\tau$ 8.7 (m), $\tau$ 9.89 (1), $\tau$ 9.94 (1).


**Ultraviolet Spectra.** - The ultraviolet spectra of several allylic germanium and tin compounds showed extinction coefficients which seemed quite high for isolated double bonds, Table XXIII. Verdone has suggested that compounds of this type might exist in a conformation such that overlap between the $\pi$ electrons and the vacant d-orbitals of the metal atom gives rise to increased absorption in the ultraviolet. Verdone, however, stated that there is no proof for such an interaction.
Table XXIII

The Ultraviolet Spectra of Several Allylic Germanium and Tin Compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max}}^a$</th>
<th>$\varepsilon$</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>211</td>
<td>10,750</td>
</tr>
<tr>
<td>10</td>
<td>220</td>
<td>7,600</td>
</tr>
<tr>
<td>30</td>
<td>210</td>
<td>4,582</td>
</tr>
<tr>
<td>32</td>
<td>210</td>
<td>4,579</td>
</tr>
<tr>
<td>33</td>
<td>209</td>
<td>5,540</td>
</tr>
<tr>
<td>36</td>
<td>207</td>
<td>6,950</td>
</tr>
<tr>
<td>37</td>
<td>205</td>
<td>7,150</td>
</tr>
</tbody>
</table>

$^a$ Measured on a Beckman DU spectrophotometer in methanol (concentration $10^{-4}$ to $10^{-5}$ molar).
SUMMARY

Trimethyltin hydride has been added to a variety of 1,3- and 1,2-dienes under free radical conditions. The products were separated by gas-liquid chromatography, and the structures and configurations were assigned on the basis of infrared and nuclear magnetic resonance spectroscopy, as well as elemental analysis and independent synthesis. The driving force for most of these addition reactions is the formation of an allylic radical intermediate. The results of these addition reactions have been discussed in terms of electronic and steric factors.

Trimethylgermanium hydride was added to a variety of dienes, catalyzed by chloroplatinic acid. The structures were assigned on the basis of infrared and nuclear magnetic resonance spectroscopy, as well as elemental analysis and chemical reactivity. The active catalyst was proposed to be a trimethylgermanium-platinum-hydride complex which can add to the diene rapidly and reversibly. This type of complex can be helpful in explaining the isomerization of nonconjugated dienes to conjugated dienes and in showing how "coordination control" can play a major role during the addition reaction.
BIBLIOGRAPHY AND ACKNOWLEDGEMENTS


42. Both the polar and electron distribution factors give opposite results, since we are dealing with a nucleophilic hydrogen radical.


46. Dr. Paul I. Abell, private communication.


78. T. G. Selin and R. West, ibid., 84, 1863 (1962).


87. The purchase of which was made possible by a grant from the National Science Foundation.
88. A gift from Cities Service research and development.
89. A gift from Shell Development Co.
93. A gift from M & T Chemicals, Inc.
98. R. Schwarz and E. Schmaisser, Ber., 69, 579 (1936).
99. Purchased from the Eagle-Picher Co.
100. A gift from Dr. G. J. M. van der Kerk, Institute for Organic Chemistry T.N.O., Utrecht, Holland.