PART ONE HE HYDROSTANNATION OF SOME CYCLIC DIENES WITH TRIMETHYLTIN HYDRIDE PART TWO THE DIPOLE MOMENT OF GLYOXAL SULFATE

IRENE JOSEPHINE TYMINSKI

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PART ONE HE HYDROSTANNATION OF SOME CYCLIC DIENES WITH TRIMETHYLTIN HYDRIDE PART TWO THE DIPOLE MOMENT OF GLYOXAL SULFATE

Keywords
Chemistry, Organic

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PART ONE
THE HYDROSTANNATION OF SOME CYCLIC DIENES
WITH TRIMETHYL Tin HYDRIDE

PART TWO
THE DIPOLE MOMENT OF GLYOXAL SULFATE

BY
IRENE JOSEPHINE TYMINSKI
B. S., University of Massachusetts, 1962

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
April, 1967

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This thesis has been examined and approved.

Advisor Part One

Advisor Part Two

Date April 5, 1969
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This thesis is dedicated to my parents, Josephine and Thomas.

[Signature]

Dene J. Tyminski
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PART ONE

THE HYDROSTANNATION OF SOME CYCLIC DIENES

WITH TRIMETHYLTIN HYDRIDE
I. SUMMARY

The free radical addition of trimethyltin hydride across one of the carbon-carbon double bonds in 4-vinylcyclohexene, 1,3-cyclopentadiene, 1,5-cyclopentadiene, and bicyclo(2.2.1)hepta-2,5-diene was accomplished thermally and photochemically. However, it was not possible to add trimethyltin hydride to cyclopentene under similar conditions.

The mechanism of the addition to the dienes was similar to that to simple olefins. However, because of the presence of a second olefinic linkage and the geometry of the dienes, a second higher energy path was available for reaction of these dienes. This path yielded saturated products by interaction of the second olefinic linkage with the intermediate radical formed during the addition reaction.

The thermal reactions of 4-vinylcyclohexene, 1,3-cyclopentadiene, and 1,5-cyclopentadiene were carried out by heating at 70-90° with periodic addition of 2 mole % of 2,2'-azobisisobutyronitrile (AIBN) until the hydride was consumed. The thermal addition to bicyclo(2.2.1)hepta-2,5-diene was accomplished without a catalyst. The photochemical reactions were run in Pyrex tubes at 25-36° utilizing a 400 watt high pressure mercury vapor lamp.

The products obtained in the photochemical reactions were the same as in the thermal reactions. With the exception of the 1,5-cyclopentadiene product mixture, the ratio of components in product mixtures was also similar. In general the products were thermally stable, but air sensitive, and had to be stored under an inert atmosphere.
Only one product, 2-(cyclohex-3-en-1-yl)ethyltrimethyltin (1), was obtained in the reaction of 4-vinylcyclohexene. The reaction with 1,3-cyclooctadiene yielded two unsaturated products, cyclooct-2-en-1-yltrimethyltin (2) and cyclooct-3-en-1-yltrimethyltin (3). Both saturated and unsaturated products were obtained from the addition of one mole of trimethyltin hydride to 1,5-cyclooctadiene and bicyclo(2.2.1)hepta-2,5-diene. A mixture of exo- and endo-

bicyclo(2.2.1)hept-2-en-5-yltrimethyltin (4 and 5) and tricyclo(2.2.1.0²,6)hept-3-yltrimethyltin (6) was obtained from the reaction of bicyclo(2.2.1)hepta-2,5-diene. The reaction with 1,5-cyclooctadiene yielded a mixture of cyclooct-4-en-
1-yltrimethyltin (7), bicyclo(3.3.0)oct-2-yltrimethyltin (8), and bicyclo(4.2.0)oct-2-yltrimethyltin (9). The ratio of saturated to unsaturated products formed in the latter reaction was shown to be a function of the kinetic energy of the reacting molecules.

One mole of trifluoroacetic acid reacted readily with 1, 7, and 8, to produce methane and the corresponding dimethylnit tin trifluoroacetate. Reaction of 2 with one mole of the acid yielded cyclooctene, presumably by an SE' reaction.
II. INTRODUCTION

The addition of organotin hydrides to unsaturated linkages, hydrostannation, was first reported by van der Kerk in 1956. Since then, the hydrostannation of a variety of unsaturated linkages has been reported: olefins, allenes, acetylenes, ketones, azomethines, isocyanates, and isothiocyanates. The course of the reaction, in some cases was found to be influenced by free radical initiators and scavengers. In others these had negligible effect and solvent polarity was important. Moreover, some reactions were found to be catalyzed by ultraviolet light, and others by zinc chloride, or aluminum alkyls. No systematic investigation of the mechanisms of hydrostannation has, however, been completed.

The hydrostannation of olefinic linkages with monohydrides has been reported to occur thermally and to be catalyzed by aluminum alkyls, 2,2'-azobisisobutyronitrile (AIBN), and ultraviolet radiation. The thermal reactions of simple olefinic linkages are believed to be free radical reactions. Galvinoxyl and hydroquinone methyl ether were shown to retard the hydrostannation of styrene with triethyltin hydride and triphenyltin hydride, respectively. The acceleration of the reaction with triethyltin hydride by AIBN was also demonstrated. In general, thermal additions to activated olefinic linkages gave good yields, and triaryltin hydrides were found to be more reactive than trialkyl analogs. In the additions to simple olefins, poor yields were obtained unless catalysts were employed. Furthermore, the thermal
decomposition of triphenyltin hydride in octane, benzene, or ethyl alcohol at 80-120° has been shown to proceed by a free radical mechanism. Hexaphenylditin, tetraphenylditin, plus a trace of polymer were among the products of decomposition.

In the photochemical decomposition of dimethyltin dihydride at 130°, trimethyltin hydride was among the products obtained after six hours of irradiation. (After irradiation at 25° for forty hours, 92% of the starting material remained.) After forty hours of irradiation at 130°, tetramethyltin, hexamethylditin, metallic tin, and hydrogen were obtained. A free radical mechanism for the photochemical decomposition of dimethyltin dihydride was suggested by the products. It would appear that these results also suggest a free radical mechanism for the photochemical decomposition of trimethyltin hydride. Moreover, the photochemical decomposition of triphenyltin hydride in n-octane was also shown to yield products that resulted from free radical intermediates.

The hydrostannations which were reported to proceed by a polar mechanism involved isocyanates, isothiocyanates, electrophilic acetylenes, and acrylonitrile. In particular, it was shown for acrylonitrile that both a polar and a free radical mechanism were operative in the thermal hydrostannation. However, only the product of a free radical reaction was obtained from the thermal hydrostannation of methyl acrylate under the same conditions. In view of these results the thermal hydrostannation of even polarized olefins would be expected to react only to a small extent, if at all, by a polar mechanism. In addition, in the presence of AIBN, the hydrostannation of acrylonitrile yielded only the product of a free radical process.
The hydrostannation of olefinic linkages has also been reported to occur with di- and tritin hydrides. In general the reactions were stepwise and accelerated by free radical catalysts.

The following addition reaction chain has been suggested to explain the results of free radical hydrostannations of olefins:

\[
\text{R'}_3\text{-Sn} \cdot + \text{RCH}=\text{CH}_2 \rightarrow \text{RCH}-\text{CH}_2\text{SnR'}_3
\]

\[
\text{RCH}-\text{CH}_2\text{SnR'}_3 + \text{R'}_3\text{-SnH} \rightarrow \text{RCH}_2-\text{CH}_2\text{SnR'}_3 + \text{R'}_3\text{Sn}.
\]

In view of the energetics of the reaction, it was suggested that reaction 2 would be very fast. For reaction 1, the heat of the reaction is given by equation:

\[
-\Delta H = (-R_a - R_o + R_p) - D_{C=C} + D_{C-Sn}
\]

the resonance stabilization energy of the attacking radical, \(R_a\), that of the olefin, and \(R_p\) that of the radical produced; \(D_{C=C}\) and \(D_{C-Sn}\) are the corresponding bond energies. Since the heat of a reaction determines its minimum activation energy, the ease of hydrostannation of olefins should reflect the exothermicity of the reaction. If the general values of 60 and 50 kcal. per mole are taken for respectively \(D_{C=C}\) and \(D_{C-Sn}\), then the resonance stabilization terms become important in determining the exothermicity of the reaction. Although \(R_o\) and \(R_p\) oppose each other, the effect of \(R_p\) is expected to predominate, since it is known that the stabilization of an olefin by a given substituent is less effective than that of the corresponding radical.
In this situation the heat of the reaction will be determined by the stability of the intermediate radical, which should then reflect the ease of reaction. In this regard the literature revealed that the hydrostannation of conjugated olefins occurred more readily than that of simple olefins. In particular, the AIBN-catalyzed hydrostannation of methyl acrylate had been accomplished in 5 hours at 40° (93% yield), whereas that of n-octene required 45 hours at 90-100° (79% yield). These reactions required periodic initiation of the chain, indicating a short chain, which in view of the energetics of the reaction would seem to indicate that reaction 1 was endothermic.

In addition, steric, electronic, and resonance factors, particular to each reaction would influence the general bond dissociation energies indicated above and thus affect the heat of the reaction. In the present work the monohydrostannations of 4-vinylcyclohexene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, and bicyclo(2.2.1)hepta-2,5-diene with trimethyltin hydride were effected thermally and photochemically.
III. RESULTS AND DISCUSSION

A. GENERAL

In the monohydrostannation of 4-vinylcyclohexene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene repeated initiation of the reaction was necessary. This fact indicated short reaction chains, and consequently that reaction 1 for these dienes was endothermic. The endothermicity of the reaction with 4-vinylcyclohexene would be expected to compare with that of a terminal olefin (n-octene cited on page 7), because $R_p$ for the two intermediates should be similar. The reactions with the cyclooctadienes would be expected to be more endothermic than with a terminal olefin due mainly to a larger energy requirement for conversion of a double bond to a single bond, $D_{C=C}$, in this system. The latter would result because the steric strain in this system increases with increasing saturation.

The failure of cyclooctene to undergo hydrostannation could be explained by a large positive heat of reaction for reaction 1. It seems likely that the significant factor contributing to $\Delta H$ would be $D_{C=C}$ and evidence indicates that $D_{C=C}$ would be larger for cyclooctene than for the dienes.

In contrast to these reactions, the hydrostannation of bicyclo(2.2.1)hepta-2,5-diene required no catalyst. Since conversion of this diene to a more saturated system results in relief of strain, $D_{C=C}$ would be less than for a terminal olefin. Consequently, reaction 1 would be more exothermic for this strained diene than the terminal olefin.
The results of the thermal hydrostannations, excluding that of bicyclo(2.2.1)hepta-2,5-diene and cyclooctene, are summarized in Table I. Of the two sources of AIBN used, the newer one appeared to be more efficient. To the extent that it was possible, an inert atmosphere was maintained over the reaction mixture during the periodic testing for hydride and the additions of AIBN. However, since these manipulations and the initial measuring of reactants were not carried out in an inert atmosphere box, varying times of exposure to air of the reactants resulted. This may be significant since traces of oxygen are known to catalyze free radical reactions, and oxygen has often been used as a scavenger for radicals. In addition it has been shown that on exposure to air triphenyltin hydride forms a compound capable of catalyzing its addition to olefins. It appears possible, therefore, that the yields and times indicated in Table I reflected to some extent the circumstances of the reactions, as indicated above.

The photochemical hydrostannations, as indicated in the experimental section, were not conducted under optimum conditions. Nevertheless the yields of products in these reactions (see Table II) compared well with those in the thermal reactions. The products obtained were the same as in the thermal reactions, and, with the exception of the 1,5-cyclooctadiene product mixture, the ratio of components in product mixtures was also similar. No products of valence tautomers were obtained. Since the dienes were transparent to the radiation (> 3000 Å) employed, isomerization of starting material was not expected.
TABLE I

The AIBN Catalyzed Hydrostannations

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Total Yield</th>
<th>Total Heating</th>
<th>Total AIBN Added</th>
<th>Temp.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td>C&lt;sub&gt;8&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td>Time</td>
<td>mole %</td>
</tr>
<tr>
<td>A. 4-vinylcyclohexene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>38</td>
<td>1.4/1</td>
<td>52</td>
<td>18</td>
</tr>
<tr>
<td>9</td>
<td>40</td>
<td>2.1/1</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>B. 1,3-cyclooctadiene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>28&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.0/1</td>
<td>33</td>
<td>18</td>
</tr>
<tr>
<td>10</td>
<td>26</td>
<td>1.4/1</td>
<td>30</td>
<td>22</td>
</tr>
<tr>
<td>12</td>
<td>30&lt;sup&gt;c&lt;/sup&gt;</td>
<td>1.4/1</td>
<td>57</td>
<td>17</td>
</tr>
<tr>
<td>C. 1,5-cyclooctadiene</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>21</td>
<td>4.7/1</td>
<td>44</td>
<td>4</td>
</tr>
<tr>
<td>3</td>
<td>36</td>
<td>2.7/1</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>21</td>
<td>3.0/1</td>
<td>46</td>
<td>25</td>
</tr>
<tr>
<td>6</td>
<td>19</td>
<td>1.1/1</td>
<td>63</td>
<td>50</td>
</tr>
<tr>
<td>13</td>
<td>58&lt;sup&gt;c&lt;/sup&gt;</td>
<td>2.4/1</td>
<td>26</td>
<td>11</td>
</tr>
</tbody>
</table>

a. Old source of AIBN used for reactions 2-4 and 6-10; new source of AIBN used for reactions 12 and 13.

b. No separation of isomeric products.

c. Crude yield after excess solvent and solid by-products removed.

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TABLE II

The Photochemical Hydrostannations

<table>
<thead>
<tr>
<th>Reactant</th>
<th>Yielda</th>
<th>Reaction Time</th>
<th>%</th>
<th>hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-vinylcyclohexene</td>
<td>68</td>
<td></td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>1,3-cyclooctadiene</td>
<td>26</td>
<td></td>
<td>42b</td>
<td></td>
</tr>
<tr>
<td>1,5-cyclooctadiene</td>
<td>50</td>
<td></td>
<td>42b</td>
<td></td>
</tr>
<tr>
<td>cyclooctene</td>
<td>0</td>
<td></td>
<td>42b</td>
<td></td>
</tr>
<tr>
<td>bicyclo(2.2.1)hept-2,5-diene</td>
<td>67 (70)c</td>
<td></td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>

a. No separation of isomeric products.
b. The presence of trimethyltin hydride indicated by a positive hydride test.
c. Yield in thermal hydrostannation.
The free radical hydrostannation of these dienes would be expected to proceed in a manner similar to that of olefins, reaction 1 and 2. Initially, the stannyl radical would react with one of the olefinic linkages to produce an intermediate radical, reaction 4. The resulting radical could then, as in the reaction of olefins, abstract a hydrogen atom from a molecule of tin hydride, reaction 5.

However, the geometric conformations of the dienes (4-vinyl-cyclohexene*, cyclooctadienes, and bicyclo(2.2.1)-hepta-2,5-diene) is such that the proximity of the second double bond to the reaction site can influence the course of reaction. Interaction of the second olefinic linkage with the intermediate radical to yield a bicyclic radical, reaction 6 (or in the case of bicyclo(2.2.1)hepta-2,5-diene a tricyclic radical) is therefore an alter-

* In one of its conformations models indicate the vinyl group could approach the internal double bond closely, i.e., \( \angle = \alpha \).
native course. Abstraction of a hydrogen atom from a molecule of tin hydride by the new intermediate would yield saturated products, reaction 7. The two competing reactions

\[
\begin{align*}
\text{CH} = \text{CH} & \quad \rightarrow \quad \text{CH} - \text{CH} \\
\text{CH} - \text{CH} & \quad \rightarrow \quad \text{CH} - \text{CH} \\
\text{R}_3\text{Sn} & \quad \rightarrow \quad \text{R}_3\text{Sn} \\
\end{align*}
\]

involve cleavage of a tin-hydrogen bond with formation of a carbon-hydrogen bond (reaction 5), and conversion of a carbon-carbon double bond to a single bond plus the formation of a transannular carbon-carbon bond (reaction 6). The energy requirement for the cleavage of a tin-hydrogen bond is less than that for the conversion of a carbon-carbon double to a single bond. Moreover, the energy liberated in the formation of a carbon-hydrogen bond is generally slightly greater than that liberated in the formation of a carbon-carbon bond. Therefore for the two competing reactions we have: \((D_{C-H} - D_{\text{Sn-H}}) > (D_{C-C} - D_{C=C})\), and consequently, the products of path 5 would be expected to predominate.

A preliminary investigation of the reactions of trifluoroacetic acid with the isomeric unsaturated octyltrimethyltins was conducted. For tetraalkyltin cleavage reactions with halogens, two first order rate series had been reported: the series for polar solvents was \(\text{CH}_3 > \text{C}_2\text{H}_5 > \text{n-C}_3\text{H}_7 > \text{i-C}_3\text{H}_7\), and for non polar solvents \(\text{CH}_3 < \text{C}_2\text{H}_5 < \text{n-C}_3\text{H}_7 < \text{i-C}_3\text{H}_7\). In the present work the cleavages were run neat. Since the dielectric constant of the acid was 8.42 (20°), the polar rate series should obtain. However, because of the presence of unsaturation in these compounds, their geometry, and the low nucleo-
philicity of the trifluoroacetic acid, an alternative course to the simple cleavage of a methyl-tin bond seemed reasonable. Protonation of the unsaturated center, reaction 8, would yield a cationic center, which might react with carbon 1 in an electrophilic displacement of the trimethyltin group, reaction 9.

\[
\begin{array}{cccc}
\text{CH} = \text{CH} & \xrightarrow{(8)} & \text{CH}_2 - \text{CH} & \xrightarrow{(9)} \text{CH}_2 - \text{CH} \\
\text{CH} - \text{CH} & & \text{CH} - \text{CH}_2 & + \text{Me}_3\text{SnOOCCF}_3 \\
\text{Me}_3\text{Sn} & & \text{Me}_3\text{Sn} & \\
\end{array}
\]

For all compounds, except cyclodct-2-en-l-yltrimethyltin (2), reaction with one mole of trifluoroacetic acid resulted in the cleavage of a methyl-tin bond to yield methane and the corresponding dimethyltin trifluoroacetate. The allylic nature of 2 was indicated in its reaction with one mole of the acid to yield cyclooctene. The cleavage of allyltin compounds has been shown to proceed by an SE' mechanism.\textsuperscript{44,45}

B. THE DIENES

1. 4-Vinylcyclohexene. 4-Vinylcyclohexene contained two reaction sites for hydrostannation. Because of its greater reactivity\textsuperscript{46}, the reaction would be expected to occur at the external double bond. Furthermore, the hydrostannation of terminal olefins has been shown to yield the product that results from terminal addition of the stannyl radical.\textsuperscript{3} Consequently, 10 would be the predicted intermediate radical in the monohydrostannation of 4-vinylcyclohexene. This intermediate could then react by abstract-
ing a hydrogen atom from a molecule of tin hydride (reaction 5) to give 1, 2-(cyclohex-3-en-1-yl)ethyltrimethyltin, or by addition to the internal double bond (reaction 6) to yield bicyclic radicals, 11 and 12, which would then yield the corresponding saturated compounds by hydrogen abstraction (reaction 7).

2-(Cyclohex-3-en-1-yl)ethyltrimethyltin was the sole product obtained in both the thermal-AIBN catalyzed and the photochemical reactions. The product analysis was consistent with the formation of 1:1 adduct. Infrared and n.m.r. analyses indicated that terminal addition of the stannyl radical had occurred. In particular the infrared spectrum of the adduct as compared to that of the reactant indicated disappearance of the absorptions (in units of cm.$^{-1}$) at 3087 (CH stretch of CH$_2$=) and 995 (CH out of plane deformation of CHR=CH$_2$), decrease in intensity of absorptions at 915 (CH$_2$ out-of-plane deformation of CH$_2$=CHR) and 1650 (C=C), presence of absorption at 652 (CH out-of-plane deformations of cis-CHR=CHR') and 1185 and 1130 (symmetrical CH$_3$ deformations of CH$_3$-Sn)$^{47-49}$, 762 and 712 (CH$_3$ rocking of CH$_3$-Sn). The n.m.r. spectrum indicated the presence of the trimethyltin group, the absence of any other methyl protons (indicating terminal addition), and the ratio of 1:10 for olefinic protons to all other.
Two cases of terminal hydrostannation of 4-vinylcyclohexene have recently been reported. 2-(Cyclohex-3-en-1-yl)ethyltriethyltin has been obtained in 53% yield from a corresponding reaction with triethyltin hydride catalyzed by AIBN, and also from a reaction catalyzed by triethyl aluminum (80%).

In regard to photochemical additions to 4-vinylcyclohexene, benzenethiol has been reported to add photochemically to yield the product that resulted from terminal addition.

Treatment of \( \text{I} \) with one mole of trifluoroacetic acid yielded a gas and a white solid (95%). From its infrared spectrum the gas was identified as methane, indicating that cleavage of a methyl-tin bond had occurred. Presumably, therefore, the solid was 2-(cyclohex-3-en-1-yl)ethyltrimethyltin trifluoroacetate. An infrared spectrum (mull) of the solid showed the presence of the internal double bond with absorptions (in units of cm\(^{-1}\)) at 3025 (m), 1450 (s) and 652 (s) and the presence of the trifluoroacetate group by absorptions at 1650 (v.s), 1200 (broad,v.s), and 1155 (v.s,sh). In addition five strong absorptions appeared at 854, 796, 755 (sh), 726 and 600 cm\(^{-1}\). These five absorptions were also present in the infrared spectrum (mull) of some authentic trimethyltintrifluoroacetate. This latter compound showed absorptions of the trifluoroacetate group at 1657 (v.s), 1200 (broad,v.s), and 1160 (v.s,sh) cm\(^{-1}\).

2. 1,3-Cyclooctadiene. The monohydrostannation of conjugated diene systems has led to products resulting from 1,2- or 1,4- addition or both. If the reaction of 1,3-cyclooctadiene followed a similar path, the intermediate radical \( \text{I} \) would yield cyclooct-3-en-1-yltrimethyltin, \( \text{III} \), by
1,2-addition and cyclooct-2-en-1-yltrimethyltin, 2, by 1,4-addition. However, since the two unsaturated linkages in 1,3-cyclooctadiene are not coplanar, reaction by this path may not occur readily. In fact, intermediate 13 would be expected to resemble a vinylic radical more than an allylic, since models indicate that interactions of trans-annular atoms might prevent formation of a typical allylic radical. In view of this, products 3 and 2 might be formed more readily by 1,2- and 2,1- addition, where the intermediate radicals are respectively 13 and 14. In addition, reaction of these intermediate radicals by path 6-7 would yield compounds 15 and 16.

The products obtained in both the photochemical and thermal-AIBN catalyzed reactions were 2 and 3, in a ratio of 7:1. The separation of these two components was achieved by g.l.c., see experimental section. Their infrared spectra were very similar and indicated the presence of methyl-tin...
groups and of unsaturation. N.m.r. analysis indicated unsaturation in both compounds.

Some authentic cyclooct-2-en-1-yltrimethyltin, 2, was obtained from the reaction of 3-bromocyclooctene with trimethyltin chloride in the presence of amalgamated magnesium. The infrared spectrum of the authentic sample was found to be identical with that of the major component of the reaction mixture.

Compound 2 was very sensitive to air decomposition, and after a short period of exposure to air deposited white crystals. It could, however, be stored refrigerated under an inert atmosphere.

The minor component was assigned structure 3, since its infrared spectrum indicated the presence of unsaturation, was similar to that of cyclooct-2-en-1-yltrimethyltin and different from that of cyclooct-4-en-1-yltrimethyltin.

Addition of a deficiency of trifluoroacetic acid to the product mixture, 2 plus 3, resulted in a selective reaction with 2. G.l.c. analysis (Nitrile Silicone Fluid) of the reaction mixture indicated the presence of cyclooctene plus starting material. This would be the expected product from an SE' reaction (reaction 10). The cleavages of allyltrialkyltin compounds have been shown to proceed by an SE' mechanism. 44,45

\[
\text{Me}_3\text{Sn} + \text{HOOCCF}_3 \xrightarrow{(10)} \text{Me}_3\text{SnOOCCF}_3 + \text{Cyclooctene}
\]
Thus far, no free radical additions to 1,3-cyclooctadiene have been reported. An attempt to add 2-cyano-2-propyl radicals to the diene was unsuccessful. Moreover, cis, cis-1,3-cyclooctadiene has been reported to undergo no thermal cyclization reactions.

3. 1,5-Cyclooctadiene. The monohydrostannation of 1,5-cyclooctadiene might yield both saturated and unsaturated products. Initially, the stannyl radical would be expected to react with one of the olefinic linkages to give radical 17. Reaction of this radical by the usual path, abstraction of a hydrogen atom from another molecule of trimethyltin hydride (reaction 5) would yield cyclooct-4-en-1-yltrimethyltin (7).

Alternatively, two bicyclic radicals, 18 and 19, could be produced by reaction of the intermediate radical with the remaining double bond (reaction 6). The respective bicyclic compounds, 8 and 9, would then result by abstraction of hydrogen from a molecule of tin hydride.

The thermal-AIBN catalyzed hydrostannation yielded a mixture (5:1:11) of three components which were assigned the structure bicyclo(3.3.0)oct-2-yltrimethyltin (8), bicyclo(4.2.0)oct-2-yltrimethyltin (9), and cyclooct-4-en-1-yltrimethyltin (7). Three products were also obtained in the photochemical hydrostannation, but these conditions gave nearly a quantitative yield of the unsaturated product.
and only a trace of the saturated products. Infrared analysis indicated the unsaturated product in the thermal and photochemical reactions to be identical. An indication that the minor components in both reactions were similar was obtained by g.l.c. analysis of combinations of the two mixtures. It was also found that no isomerization of reaction products took place under the photolytic conditions.

The difference in the amount of saturated products obtained in the thermal-AIBN catalyzed reaction (80°) and the photochemical reaction (25-36°) is reasonable in view of the energetics of the two paths, reactions 5 and 6, available to intermediate 17. As indicated previously for hydrostannations in general, path 5 would be favored as the lower energy path. Furthermore, during formation of the bicyclic radicals, steric strain would be expected to increase. This effect would tend to increase the energy necessary to convert a carbon-carbon double bond to a single bond, and decrease the energy gained by the formation of the carbon-carbon single bond. Both these effects favor the path of abstraction of a hydrogen atom over the formation of bicyclic intermediates as the lower energy path. Consequently, the formation of only 3% of saturated products in the photochemical reaction (25-36°) and of 35% in the thermal-AIBN catalyzed reaction (80°), appeared to indicate that at 25-36° the molecules did not possess enough kinetic energy to react to any degree by path 6. The difference in energy of the two paths, therefore, appears to be significant.

To increase the yield of saturated products, the kinetic energy of the molecules was increased by carrying out the hydrostannation at 175°. The amount of saturated products increased to 56%.
Components of the product mixture were obtained pure by g.l.c. separation as indicated in the experimental section. The collection of sizable quantities by g.l.c. was difficult because one or two reinjections were necessary to obtain pure material, and because condensation of the components from the effluent gas was difficult.

The unsaturated component was assumed to be cyclo-
öct-4-en-l-yltrimethyltin (7), since it was expected to arise from addition of the hydride to one of the double bonds. The chemical analysis of this compound was consistent with the formation of a 1:1 adduct. The presence of methyl-
tin groups and of unsaturation were indicated by its infrared spectrum. Furthermore, n.m.r. analysis of this compound indicated the presence of the trimethyltin moiety at 710.00 (taken as the reference point) and the olefinic protons at 74.39 as a pentuplet. Two broad singlets at 78.40 and 7.86 were assigned to the methylene protons and the allylic protons, respectively. These chemical shifts are in agree­ment with those reported for cycloöctenes (see Table III).

As indicated previously, the saturated components could have either the bicyclo(3.3.0)octane or the bicyclo-
(4.2.0)octane structure. The predominant saturated compound gave an elemental analysis corresponding to a 1:1 diene-
hydride adduct. On the basis of its n.m.r. spectrum it was assigned the bicyclo(3.3.0)oct-2-yltrimethyltin structure, 8. The n.m.r. spectrum of the product indicated with respect to the trimethyltin singlet assigned 710.00 (nine protons), methylene resonance as a broad singlet centered at 78.53 (ten protons), a small sharp signal which might be due to the carbon-2 proton at 77.95 (one proton), and the bridge-
head protons as an extended singlet at 77.65 (two protons).
### TABLE III

Reported N.M.R. Spectra of Cyclooctenes  
(chemical shifts with respect to TMS in \( \tau \) values)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( =\text{C-H} )</th>
<th>HCR-C- ( \text{R=H or R'} )</th>
<th>C-( \text{CH}_2-\text{C} )</th>
<th>Ph</th>
<th>Me</th>
</tr>
</thead>
<tbody>
<tr>
<td>55</td>
<td>4.44 triplet</td>
<td>7.89 broad</td>
<td>8.50</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>56</td>
<td>4.43 multiplet</td>
<td>6.35(1H) broad; 7.86 (2H)</td>
<td>8.36 2.87</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>( \text{R'} = \text{Ph} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>4.3; 4.5 pair of doublets</td>
<td>7.1 multiplet</td>
<td>8.26</td>
<td>--</td>
<td>8.62</td>
</tr>
<tr>
<td>( \text{R'} = \text{Me}_2\text{C(CN)} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>4.33 triplet</td>
<td>8.0-7.2 multiplet (5H)(also ( C_2-\text{CHPh} ))</td>
<td>8.7-8.0 2.88</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>( \text{Ph} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>4.32</td>
<td>Two triplets overlapping</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{OH} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>4.35</td>
<td>Two triplets coincident</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SAc} )</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>4.34</td>
<td>(4.36)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \text{SPh} )</td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>
The preceding assignments were substantiated by the n.m.r. spectrum of bicyclo(3.3.0)octane and N-t-butyl-exo-cis-bicyclo(3.3.0)octane-2-carboxamide. For these compounds the methylene signal appeared at, respectively, \( \tau 8.25-9.37 \) and \( 8.21-8.49 \) and the bridgehead protons at, respectively, \( \tau 7.83 \) and \( \tau 7.47 \). In cycloalkanes the chemical shift of the protons with respect to TMS was reported for the 4-, 5-, 6-, and 8-membered ring as a singlet at respectively, \( \tau 8.04 \), \( \tau 8.49 \), \( \tau 8.56 \), and \( \tau 8.46 \). The chemical shift of the trimethyltin group in the product should approximate well the chemical shift of TMS, so some comparison can be made between reported and observed chemical shifts. The chemical shift of the methylene protons appeared in the region reported for five and six-membered cycloalkanes; however, the presence of only one type of methylene group indicated the bicyclo(3.3.0)octane structure. Furthermore, a report on the n.m.r. spectrum of cis-bicyclo(3.3.0)octane indicated that a low intensity signal attributed to the bridgehead protons appeared at 40 cps (at 40 mc.) downfield from the main absorption. At 60 mc., this difference in chemical shifts becomes 60 cps or 1 ppm. In the spectrum of the product this difference is 0.88 ppm., a good correlation.

Only a small pure sample of the other saturated component was obtained, and as a result the only data obtained on this compound was an infrared spectrum, which indicated the presence of methyl-tin groups and the absence of unsaturation. The spectra of the two saturated components, as would be expected for \( 8 \) and \( 9 \), were similar in the 4000-1400 cm.\(^{-1} \) region, but very different in the fingerprint region.
The attempted synthesis of bicyclo(4.2.0)oct-2-yl-trimethyltin, \( \text{9} \), was unsuccessful. The limited amount of bromide obtained in this reaction sequence was a critical factor.

The stereochemistry of the saturated products was not determined. However, 2-bicyclo(3.3.0)octanes produced in free radical additions to 1,5-cyclooctadiene have been shown to have cis ring fusion and the substituent exo. \( \text{59,62,63} \) These exo-cis-2-bicyclo(3.3.0)octanes were the exclusive products in thermal additions of a variety of carbon radicals to the diene. Furthermore, the photochemical addition of carbon tetrachloride to the diene was reported to yield the same product. \( \text{59} \) It is assumed, therefore, that the products from the hydrostannation were also exo-cis. There remains the possibility, however, that the minor component is endo-cis \( \text{8} \) rather than exo-cis \( \text{9} \).

Also, it appeared that for the addition of carbon radicals to the diene, reaction \( \text{6} \) became the lower energy path. On the other hand, however, reaction \( \text{5} \) appeared as the lower energy path in the photoaddition of formamide \( \text{64} \) and p-quinones \( \text{65,66} \) to the diene, as indicated by the exclusive formation of cyclooct-4-enyl adducts. These have also been reported as the exclusive products in additions of thiols to the diene. \( \text{57} \)

Treatment of \( \text{7} \) with one mole of trifluoroacetic acid yielded a gas and a white waxy solid. The gas was identified as methane from its infrared spectrum. The cleavage of a methyl-tin bond to produce methane would yield cyclooct-4-en-1-yldimethyltin trifluoroacetate as the product. An infrared spectrum (mull) of the solid had absorptions (in units of \( \text{cm}^{-1} \)) indicating the presence of the internal
double bond at 3020 (m), 1445 (s), and 650 (m), and of the trifluoroacetate group at 1660 (v.s), 1200 (broad, v.s), and 1150 (v.s, sh). In addition, five strong absorptions that appeared to be indicative of the tin trifluoroacetate group (see page 16) were present at 850, 795, 770 (sh), 723, and 605 cm⁻¹.

Treatment of 7 with an excess of trifluoroacetic acid either neat or in pentane, yielded bicyclo(3.3.0)-octane, an ester, and unidentified products of incomplete cleavage. The bicyclo(3.3.0)octane was identified by comparison of its infrared spectrum with that of the authentic hydrocarbon. The infrared spectrum of the ester was identical with that of one prepared by the addition of trifluoroacetic acid to cyclooctene, under the conditions of the cleavage reaction. It appears, therefore, that cyclooctene may have been a product in the cleavage reaction, but reacted under the conditions to yield the ester. The addition of trifluoroacetic acid to cyclooctene has been reported to yield cyclooctyl trifluoroacetate. Furthermore, the n.m.r. spectrum of the ester prepared by the addition of the acid to the olefin was consistent with this assignment. It had two broad overlapping singlets at 9.20 and 9.09, and a broad singlet at 7.42. The signal at 7.42 corresponded to one proton and was assigned to the methine proton. The overlapping singlets corresponded to 14 protons and were ascribed to the methylene protons.

Treatment of 8 with one mole of trifluoroacetic acid yielded a gas and a white solid. Infrared analysis indicated the gas to be methane. The solid was not isolated, but cleavage of a methyl-tin bond was taken to indicate the formation of bicyclo(3.3.0)oct-2-yldimethyltin trifluoro-
acetate. The solid was treated with three additional moles of the acid, in an attempt to obtain complete cleavage of the four carbon tin bonds. Identification of the hydrocarbon obtained from this cleavage, would have served as proof of the ring system. However, the reaction was incomplete, and only products of incomplete cleavage resulted. The small amount of the pure compound available, limited the attempts in this area.

4. **Cyclooctene.** Both the thermal and the photochemical hydrostannations of cyclooctene were unsuccessful. The reaction mixture consisted of only cyclooctene, trimethyltin hydride, and decomposition products of the tin hydride. It appeared, therefore, that for cyclooctene, step 1 is substantially endothermic. This is evident from a simple consideration of bond energies.

Carbon tetrachloride, bromotrichloromethane, and trichloromethanesulfonyl chloride have added to cyclooctene in free radical reactions. The larger energy gain in the formation of a carbon-carbon bond as compared to a carbon-tin bond in step 1, may serve as the explanation for the successful addition of carbon radicals to cyclooctene as opposed to tin radicals.

5. **Bicyclo(2.2.1)hepta-2,5-diene.** The monohydrostannation of bicyclo(2.2.1)hepta-2,5-diene would be expected to yield both bicyclo(2.2.1)hept-2-en-5-yl, which will be referred to as norbornenyl, and tricyclo(2.2.1.0²,⁶)hept-3-yl, which will be referred to as nortricyclyl, products. In this reaction as in the case of the previous dienes, the intermediate radical (20), could react by two paths, 11 or 12.
Norbornenyl products would arise from this intermediate by abstraction of a hydrogen atom from another molecule of tin hydride (reaction 11). Alternatively, reaction of the intermediate radical with the remaining double bond, reaction 12, would produce a tricyclic radical, 22, which by hydrogen abstraction would give the corresponding nortricyclyl compound, 6.

The thermal monohydrostannation of bicyclo(2.2.1)-hept-2,5-diene with trimethyltin hydride has been observed to occur readily without catalyst. The product mixture was believed to consist of exo- and endo-bicyclo(2.2.1)hepta-2-en-5-yltrimethyltin (4 and 5) plus ca. 10% tricyclo(2.2.1.02,6)-hept-3-yltrimethyltin (6).

The thermal and photochemical hydrostannations of bicyclo(2.2.1)hepta-2,5-diene yielded the same product mixture (which will be designated A), as indicated by g.l.c., n.m.r., and infrared analyses. Indications that the product mixture (A) consisted of 4, 5, and 6 have been obtained.
The n.m.r. spectrum of this product mixture (A) indicated the presence of at least three components. Two major signals for trimethyltin groups at $\tau_{10.03}$ and $\tau_{9.94}$ appeared along with a minor signal at $\tau_{9.95}$ (total of ten protons). In addition the spectrum had a complex multiplet (seven protons), which had its strongest signals at $\tau_{8.95}$, $\tau_{8.88}$, $\tau_{8.78}$ and $\tau_{8.61}$, from $\tau_{9.38}$ to $\tau_{7.96}$; two broad overlapping singlets (two protons) at $\tau_{7.13}$ and $\tau_{6.97}$; and a multiplet (two protons), which was attributed to olefinic protons, at $\tau_{4.05}$. The reported n.m.r. spectrum of norbornene indicated the olefinic protons as an unsymmetrical multiplet at $\tau_{4.12}$, the bridgehead protons as a broad unresolved multiplet at $\tau_{7.20}$, and a complex absorption at $\tau_{8.30-9.04}$. The n.m.r. spectrum reported for nortricyclene indicated bridgehead protons at $\tau_{8.09}$ and the carbon-3 protons at $\tau_{8.78}$. On this basis it was assumed that the protons of 6 would have appeared in the region of the complex multiplet. If this were the case, then the relative areas of the signals in the n.m.r. spectrum of the product mixture (A), could be accounted for by a 1:1 mixture of norbornenyl to nortricyclyl products. The indication of ten trimethyltin protons might be accounted for by the presence of ca. 10% hexamethylditin.

The infrared spectrum of the product mixture (A) had absorptions (in units of cm.$^{-1}$) indicating the presence of norbornenes at 1565 (w) (C=C stretch), 1330 (s) (CH in plane deformation), and 705 (m) (CH out of plane deformation). The presence of methyl-tin groups was indicated by absorptions at 1185 (m) and 762 (s) cm.$^{-1}$. The presence of a 3-nortricyclene was indicated by absorption at 805 (m).
By preparative g.l.c. the product mixture (A) was separated into fractions B and C. Because of the small amount of fraction C, only its infrared spectrum was obtained. It showed the presence of methyl-tin groups with absorptions at 1185 (s) and 762 (s) cm\(^{-1}\). The presence of absorption near 3070 cm\(^{-1}\) could be attributed to the carbon-hydrogen stretch of either the olefinic protons of a norbornene or the cyclopropyl protons of a nortricyclene. Since 3-nortricyclenes have a strong doublet at 818-800 cm\(^{-1}\), lack of strong absorption in this region ruled out compound 6 as a possibility. Although there was no strong absorption in the carbon-carbon double bond stretching region, strong bands appeared at 1330 and 704 cm\(^{-1}\), characteristic of cis-olefinic in-plane and out-of-plane deformations, respectively. The spectrum of C supports a norbornenyltrimethyltin structure. However, this compound was air sensitive*, and its purity could not be determined.

Elemental analysis of fraction (B) was consistent with the formation of a 1:1 diene-hydride adduct. The presence of methyl-tin groups was indicated in the infrared spectrum by absorptions at 1185 (s) and 762 (s) cm\(^{-1}\). Absorption appeared in the 3070 cm\(^{-1}\) region. A strong doublet at 800 cm\(^{-1}\), distinct but overlapping with the 762 cm\(^{-1}\) absorption was present and strongly suggested the presence of a 3-nortricyclcyl product. Furthermore, the presence of a norbornenyl product was indicated by absorptions at 1565 (m), 1330 (s), and 705 (s) cm\(^{-1}\).

* The spectrum had been run on the liquid as a film. After the spectrum had been obtained, the liquid sample turned crystalline when the infrared salt plates were opened; this was taken as an indication that the compound was sensitive to air decomposition.
The n.m.r. spectrum of (B)* was similar to the product mixture (A). Removal of fraction C resulted in a decrease in intensity of the signal at $\tau 6.97$. This was the principal difference in the two spectra, although in addition, the appearance of the olefinic multiplet changed, and there was a subtle change in the appearance of the $\tau 9.38$-$9.30$ region. The presence of three different types of trimethyltin groups was still indicated.

The signal at $\tau 6.97$ had been ascribed to the resonance of the bridgehead protons in a norbornenyl system. The change in this region in addition to the change in the olefinic pattern was a further indication of the norbornenyl nature of fraction C. Furthermore, these changes in the spectrum could not have been accounted for by removal of a nortricyclyl compound, since the lowest signal of nortricyclene was reported at $\tau 8.09$, and of tricyclo(2.2.0$^{2,6}$)-hept-3-yltrimethylsilane at $\tau 8.06$.

The hydrostannation of product mixture (A) resulted in the selective addition of the second mole of trimethyltin hydride to a component of fraction B. Removal of this component from fraction B in this way, left fraction F. The infrared spectrum of fraction F was different from that of B. It contained no absorption in the 1560 cm.$^{-1}$ region and lacked the strong 1330 cm.$^{-1}$ band. It had a strong doublet, characteristic of 3-nortricycloenes, at 800 cm.$^{-1}$ and also had absorption at 3060 (m) cm.$^{-1}$. The presence of methyltin groups was indicated by bands at 1185 (m) and 760 (s) cm.$^{-1}$. G.l.c. analysis of the infrared sample indicated that it was slightly impure.

* Since fraction B was a mixture (see experimental section), it is possible that the ratio of the components in B was changed from their ratio in A during removal of fraction C.
An alternate synthesis of 6 was attempted and a liquid whose infrared spectrum showed a strong doublet at 800 cm.\(^{-1}\), lacked absorption at 1560 cm.\(^{-1}\), and had no strong 1330 cm.\(^{-1}\) band was obtained. The spectrum was identical with that of F, except for the presence of some absorption at 1110 cm.\(^{-1}\) in F. The small amount of material obtained did not allow any further analyses to be conducted. The infrared spectrum was consistent with a structure such as 6, but can not in the absence of other analyses, be considered conclusive.

It appeared, therefore, that fraction B consisted of norbornenyl and nortricyclen products and that reaction of B with a second mole of trimethyltin hydride removed the norbornenyl product and left the nortricyclen 6 as F. Fraction C was also assigned a norbornenyltrimethyltin structure on the basis of its infrared spectrum, but the geometry of the norbornenyl products was not determined.

Although 4, 5, and 6 have not been synthesized by unequivocal routes, the preceding observations were a good indication of their presence as the principal components in the product mixture from the monohydrostannation of bicyclo-(2.2.1)hepta-2,5-diene.

The products indicated that the reaction was taking place by both path 11 and 12. It appeared from the n.m.r. spectrum of the product mixture (A) that nearly a 1:1 mixture of norbornenyl to nortricyclen products was obtained. In comparison to this, the free radical additions of carbon tetrachloride, chloroform, butanal, and heptal have been reported to yield exclusively the corresponding nortricyclen compounds.\(^{71}\) With thiophenol as addend, a mixture of nortri-
cyclyl (72%) and norbornenyl (19%) products was obtained. Furthermore, the AIBN-catalyzed addition of trichlorosilane yielded 53% nortricycl, 28% exo-norbornenyl, and 7% endo-norbornenyl products.
IV. EXPERIMENTAL

A. GENERAL CONSIDERATIONS

1. Gas-liquid Chromatographic (g.l.c.) Analysis. An F & M Model 300 Programmed Temperature Gas Chromatograph (F & M Scientific Corporation), and an Aerograph Model A-700 Automatic Preparation Gas Chromatograph (Wilkens Instrument & Research, Inc.), both utilizing thermal conductivity detectors, were employed for the g.l.c. analyses. Helium was used as the carrier gas at a flow rate of 30 ml. and 150 ml. per minute, respectively, for the F & M and the Aerograph. The reaction mixtures and the organotin compounds were examined on the F & M using a 4 ft. x 1/4 in. column of Nitrile Silicone Fluid (17%) on Chromosorb P (60-80), Carbowax 20M (20%) on Chromosorb P (42-60), or Silicone Oil 200 (5%) on Haloport F, and on the Aerograph using a 20 ft. x 3/8 in. column of Nitrile Silicone Fluid XF 1150 (20%) on Chromosorb P (60-80). In the experimental section the F & M column employed in the analysis was indicated in parenthesis. Where the use of the Aerograph was indicated, only the column indicated above was employed.

2. Infrared Absorption Analysis. The infrared absorption spectra were recorded on a Perkin-Elmer Model 337 Grating Spectrophotometer or a Perkin-Elmer Model 21 Infrared Spectrophotometer equipped with sodium chloride optics. The spectra of liquids were determined as films, and those of solids as mulls. Halocarbon Oil and Nujol were used to prepare mulls for the 4000-1330 cm.\(^{-1}\) region and the 1300-650 cm.\(^{-1}\) region, respectively. The absorption bands were indicated as strong (s), medium (m), and weak (w) intensity.
A shoulder was indicated by (sh), and (v) was used to indicate very.

3. **Ultraviolet Absorption Analysis.** A Beckman D.U. Spectrophotometer Model 2400 was employed to obtain the ultraviolet absorption data. Fisher Analytical Grade Methanol (0.01% water) was used as solvent. Prior to analysis all compounds were purified by g.l.c. (Aerograph).

4. **Nuclear Magnetic Resonance (n.m.r.) Analysis.** The n.m.r. spectra were recorded on a Varian A-60 Analytical N.M.R. Spectrometer (Varian Associates).

5. **Refractive Index Determination.** A Bausch and Lomb Abbe Refractometer was used to determine the refractive indices. The compounds were purified by g.l.c. (Aerograph) prior to the measurement.

6. **Analytical Data.** The microanalyses were done by Galbraith Laboratories, Inc. (Knoxville, Tennessee).

**B. THE HYDROSTANNATIONS**

1. **The Dienes.** 4-Vinylcyclohexene, cis-cyclo\text{octetene}, cis,cis-1,3-cyclo\text{octadiene}, and cis,cis-1,5-cyclo\text{octadiene} were gifts of Cities Service Research & Development Company. Bicyclo(2.2.1)hepta-2,5-diene was obtained as a gift from the Shell Chemical Corporation.

2. **Preparation of Trimethyltin Hydride.** A dispersion of lithium aluminum hydride (1.9 g., 0.050 mole) in bis(2-ethoxyethyl)ether (50 ml.) was prepared in a flask equipped with a mechanical stirrer and pressure equalizing dropping funnel. The reaction vessel was then fitted with a Claisen head with condenser and receiving flask. An inert atmosphere was introduced into the system, and the dispersion
was heated. When the bath temperature reached 80°, a solution of trimethyltin chloride (10.0 g., 0.050 mole) in solvent (20 ml.) was added slowly. As soon as the solvent was saturated, the hydride distilled and was collected in a receiver immersed in a cold bath. During the distillation the temperature of the heating bath was allowed to increase, so that by the time the bath had reached 125°, the distillation of the hydride was complete.* A 70% yield of trimethyltin hydride (5.8 g., 0.035 mole), b.p. 57-60° was obtained.

3. General Procedure for the AIBN-Catalyzed Hydrostannation. This procedure was used for the hydrostannation of 4-vinylcyclohexene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene (see Table I).

The dienes were distilled using a 12 cm. column containing a spiraled wire, and the fractions boiling at 125-126°, 140-141°, and 149-150°, respectively, for 4-vinylcyclohexene, 1,3-cyclooctadiene, and 1,5-cyclooctadiene, were used.

Trimethyltin hydride, the diene, and AIBN were heated in an inert atmosphere in a flask fitted with a reflux condenser. The best results were obtained by heating the reaction mixture at 80-90° with two mole percent AIBN for a period of 2 1/2 - 3 hours, cooling the reaction mixture, adding two percent more AIBN, and continuing in this manner until the tin-hydrogen infrared absorption band at 1838 cm.⁻¹

* Caution! Thermal decomposition of lithium aluminum hydride occurs at 125-150° (A. E. Finholt et al., J. Am. Chem. Soc., 69, 1199 (1947). In one case where the dispersion had been held at 125-130° for nearly one half hour, thermal decomposition of the dispersion was noted. The decomposition was halted only after considerable cooling.
disappeared, or until an acid test\(^*\) indicated the absence of hydride. The AIBN was added as a solid to the reaction mixture, in which it was insoluble.

When all the hydride had been consumed, the reaction mixture was cooled and filtered to remove the solid by-products. Excess diene was removed by vacuum distillation at ca. 30 mm., and the adducts were distilled from the residue at ca. 0.5 mm. The boiling points for the adducts of the three dienes were: for 4-vinylcyclohexene, 70° (0.85 mm.); for 1,3-cyclooctadiene, 65° (0.50 mm.); for 1,5-cyclooctadiene, 51° (0.25 mm.). No separation of isomers was achieved in this distillation. The results of the reactions are summarized in Table I.

4. Thermal Hydrostannation of 1,5-Cyclooctadiene.\(^{81}\) A mixture of undistilled 1,5-cyclooctadiene (7.3 g., 0.067 mole) and trimethyltin hydride (6.4 g., 0.039 mole), sealed in a glass ampoule, was heated for twelve hours under pressure with periodic agitation. The reaction vessel was initially heated to 225°, then allowed to cool to 175°, and maintained there for twelve hours.

After this time, grey particles of metallic tin were present in the ampoule. Distillation of the reaction mixture yielded 19% (1.2 g., 0.0070 mole) of unreacted trimethyltin hydride, b.p. 69-70°. The excess diene was distilled off, and the residue was examined by g.l.c. (Aerograph). In addition to the three adducts, two components of shorter

\(^*\) A 2/1 mixture of ether/38% hydrochloric acid was used as the acid mixture. A positive test for the hydride was indicated by the evolution of gas when a drop of the reaction mixture was added to the acid-ether solution.
Retention time were present. (These were most likely hexamethylditin plus unremoved 1,5-cyclooctadiene.) Using a planimeter, the area under the adduct peaks was compared with that under the sum of all the peaks, to give an approximate yield of 38% for the adduct mixture.

5. Thermal Hydrostannation of Cyclooctene (Attempted). An excess of undistilled cyclooctene was heated with trimethyltin hydride and a trace of AIBN in a sealed glass ampoule under pressure at 100° for nine hours. After this time grey particles of metallic tin were present in the ampoule. Distillation of the reaction mixture yielded only unreacted trimethyltin hydride and cyclooctene.

6. Thermal Hydrostannation of Bicyclo(2.2.1)hepta-2,5-diene. The reaction was carried out under an inert atmosphere. Trimethyltin hydride (82 g., 0.50 mole) was added dropwise to undistilled bicyclo(2.2.1)hepta-2,5-diene (52 g., 0.57 mole). The reaction mixture was then heated to reflux. In all the mixture was heated for five hours at 80°, 4 1/2 at 85-95°, and 2 at 110°. The excess diene was removed by distillation, and the adduct was collected as a clear liquid, b.p. 41° (0.50 mm.) - 42° (0.55 mm.), in 70% yield.

7. General Procedure for the Photochemical Hydrostannation. The photolysis apparatus used was the one used by P. Maxfield. This procedure was used for 4-vinylcyclohexene, 1,3-cyclooctadiene, 1,5-cyclooctadiene, bicyclo(2.2.1)hepta-2,5-diene, and cyclooctene. The dienes and cyclooctene were used as received. Each reactant was placed in a Pyrex tube (I.D. 7 mm.) and deoxygenated by bubbling Matheson argon (99.998% pure) into it for several minutes. The hydride was then added, care being taken to maintain an argon atmosphere
over the liquid surface. A very fine copper wire was used to fasten a balloon, which had been flushed with argon to the top of the Pyrex tube. The samples were positioned in a circle around a 400 watt high pressure mercury vapor lamp (General Electric) which was cooled by a water bath. The samples irradiated were also in a water bath, which might have reached a maximum temperature of 36°.

The samples were irradiated for 34 hours and 15 minutes. At this time each tube contained a white precipitate and a few bits of grey material. The reactions were tested for completion by testing for the presence of the hydride with an acid-ether solution, and also by checking for the presence of the tin-hydrogen absorption in the infrared region. The reaction mixtures that gave a positive test for hydride after 34 1/2 hours included: 1,3-cyclooctadiene, 1,5-cyclooctadiene, and cyclooctene. The reaction mixtures in which the hydride was still present were irradiated for another eight hours. (White precipitate along the sides of the tubes may have blocked the radiation from the samples and in so doing be responsible for the long reaction time.) The reaction mixtures which gave a negative hydride test were refrigerated until work up.

The tubes which were irradiated for an additional eight hours still gave a positive hydride test. Because a heavy white precipitate covered the sides of the tubes, the irradiation was not continued.

Before photolysis all balloons were slightly inflated. Deflation of the balloons after irradiation indicated a decrease in volume in all reactions. Since no pressure was built up in this reaction, it is recommended that the tubes be sealed more effectively to prevent diffusion of reactants out of the tube.
The yields in the photochemical hydrostannations were: for 4-vinylcyclohexene, 68%; for 1,3-cyclooctadiene, 26%; for 1,5-cyclooctadiene, 50%; for cyclooctene, 0%; for bicyclo(2.2.1)hepta-2,5-diene, 67%.

C. THE HYDROSTANNATION PRODUCTS

1. 4-Vinylcyclohexene. The AIBN-catalyzed hydrostannation of 4-vinylcyclohexene, according to the general procedure, yielded a clear liquid, b.p. 70° (0.85 mm.), which g.l.c. analysis (Carbowax 20 M and Nitrile Silicone Fluid) indicated contained one component. The infrared spectrum of the product obtained by the photochemical hydrostannation, was identical with that obtained by the AIBN-catalyzed reaction.

2-(Cyclohex-3-en-1-yl)ethyltrimethyltin (1). Infrared and n.m.r. analyses indicated that terminal hydrostannation had occurred. \( v \max. \) in cm.\(^{-1} \) units: 3050 (sh,w), 3013 (s), 3000 (s), 2970 (m), 2830 (s), 1650 (w), 1450 (m), 1430 (m), 1185 (m), 1130 (w), 1040 (w), 915 (w), 868 (w), 853 (w), 800 (sh,m), 762 (s), 712 (s), 652 (s). N.m.r. (neat) in \( \tau \) units: singlet (nine protons), 10.00 (Me\(_3\)Sn\(^{118}\)); extended multiplet (eleven protons), 9.38-7.88; singlet (two protons), 4.46 (CHR=CHR). \( n_D \) (23.0°) 1.5000.

Found: C, 48.12; H, 7.93.

2. 1,3-Cyclooctadiene. The AIBN-catalyzed hydrostannation of 1,3-cyclooctadiene, according to the general procedure, yielded a clear liquid, b.p. 65° (0.50 mm.). G.l.c. analysis (Carbowax 20 M) indicated the liquid to be a mixture (1:7) of two components. The photochemical hydrostannation yielded a similar mixture. The two components were first
enriched and then purified by preparative g.l.c. (Aerograph).

**Cyclo\(\text{oct}-2\)-en-1-yltrimethyltin (2).** The infrared spectrum of the principal component was identical with that of cyclo\(\text{oct}-2\)-en-1-yltrimethyltin prepared from 3-bromocyclo-
\text{octene}. For \(\nu\) max. and \(n_D\) see alternate synthesis. N.m.r.
(25% in CCl\(_4\); TMS, ref.) in \(\tau\) units: singlet (nine protons),
9.97 (Me\(_3\)Sn\(_{118}\)); broad singlets (eleven protons), 9.21
(CCH\(_2\)C), 9.10 (SnCHC=), and 8.91 (CH\(_2\)C=); extended multiplet
(two protons), 7.23 (=CHC). \(\lambda\) 210 (e 6631); \(\lambda\) 216 (e 7261):
\(\lambda\) max. 216 \(\mu\)m. (e 7287).

**Anal.** Calcd. for C\(_{11}\)H\(_{22}\)Sn: C, 48.36; H, 8.12.
Found: C, 48.28; H, 8.30.

**The Minor Component.** The infrared spectrum of the
minor component indicated the presence of methyl-tin groups
and of unsaturation; it was similar, but not identical, to
that of cyclo\(\text{oct}-2\)-en-1-yltrimethyltin, and different from
that of cyclo\(\text{oct}-4\)-en-1-yltrimethyltin; on the basis of this
it was assigned the cyclo\(\text{oct}-3\)-en-1-yltrimethyltin structure
(3). \(\nu\) max. in cm.\(^{-1}\) units: 3050 (sh,w), 3005 (m), 2970 (m),
2915 (s), 2850 (s), 1700-1625 (w), 1460 (m), 1450 (m), 1220
(w), 1185 (m), 1140 (w), 1130 (w), 1080 (w), 1065 (w), 1045
(w), 910 (w), 890 (w), 872 (w), 808 (sh,m), 760 (s), 708 (m).
N.m.r. (20% in CCl\(_4\); TMS, ref.) in \(\tau\) units: singlet (nine
protons), 9.97(Me\(_3\)Sn\(_{118}\)); broad singlet and extended multi-
plet (eleven protons) respectively, 9.24 (CCH\(_2\)C, SnCHC\(_2\)) and
8.91 (=CHC\(_2\)); symmetrical multiplet (two protons), 7.12 (=CHC).
\(\lambda\) 210 (e 7206); \(\lambda\) 217 (e 4594); \(\lambda\) 216 (e 4984). \(n_D\) (25.0\(^{\circ}\))
1.5125.

**Anal.** Calcd. for C\(_{11}\)H\(_{22}\)Sn: C, 48.36; H, 8.12.
Found: C, 48.38; H, 8.28.
3. 1,5-Cyclooctadiene. The AIBN-catalyzed hydrostannation of 1,5-cyclooctadiene, according to the general procedure, yielded a clear liquid, b.p. 50° (0.25 mm.). G.l.c. analysis (Carbowax 20 M) indicated the liquid to be a mixture (5:1:11) of three components. The infrared spectra of the two major components, obtained by g.l.c. separation, indicated that both contained methyl-tin groups and that only the predominant one was unsaturated.

The product obtained from the thermal (175°) hydrostannation was examined by g.l.c. (Aerograph) and found to be a mixture (4:1:4) of three components. Infrared analysis indicated that the two major products of this reaction were identical with those obtained in the previous one.

Photochemical hydrostannation, as indicated by g.l.c. analysis (Nitrile Silicone Fluid), yielded the unsaturated component and the other two products in a ratio of 30:1. A portion of the thermal reaction mixture was enriched, using preparative g.l.c. (Aerograph), in the minor products and then photolyzed, in order to determine whether isomerization might occur under photolytic conditions. After seventy-seven hours of irradiation, no significant isomerization had occurred. In addition, a sample to which a trace of trimethyltin hydride had been added was irradiated for fifty-five hours. No significant isomerization was observed.

Preparative g.l.c. (Aerograph) was used to obtain enriched fractions of the components. The pure component was obtained by further purification (Aerograph) of these fractions.
Unsaturated Component. The unsaturated component was expected to arise from addition of the hydride to one unsaturated linkage and was therefore assumed to be cyclo-oct-4-en-1-yltrimethyltin (7). \( \nu \max. \) in cm\(^{-1}\) units: 3010 (m), 2970 (m), 2905 (s), 2845 (s), 1680 (w), 1640 (w), 1460 (m), 1440 (m), 1350 (w), 1195 (sh,w), 1185 (m), 1120 (w), 1095 (w), 1070 (w), 1015 (w), 995 (w), 982 (w), 920 (w), 900 (w), 880 (m), 762 (s), 720 (s), 700 (m). N.m.r. (30% in CCl\(_4\)) in \( \tau \) units: singlet (nine protons), 10.00 (Me\(_3\)Sn); broad singlets (eleven protons), 8.40 (CCH\(_2\)C) and 7.86 (CH\(_2\)C=); pentuplet, ca. 1:1:2:1:1 (two protons), 4.39 (=CH). \( \lambda \) 210 (e 4567). \( n_D \) (24.5°) 1.5127.

Found: C, 48.17; H, 7.96.

Saturated Component. On the basis of its n.m.r. spectrum, the saturated component was assigned the bicyclo-(3.3.0)oct-2-yltrimethyltin structure (8). \( \nu \max. \) in cm\(^{-1}\) units: 3100-3000 (w), 2974 (sh,m), 2936 (s), 2858 (s), 1700 (v.w), 1440 (m), 1410 (sh,w), 1205-1190 (w), 1185 (m), 1095 (w), 1075 (w), 1030 (w), 1020 (w), 920 (w), 830 (sh,w), 805 (sh,m), 760 (s), 700 (m). N.m.r. (50% in CCl\(_4\)) in \( \tau \) units: singlet (nine protons), 10.00 (Me\(_3\)Sn); singlets (thirteen protons), 8.53 (CCH\(_2\)C), 7.95 (C\(_2\)HSn), and 7.65 (C\(_2\)CHC). \( n_D \) (26.0°) 1.5028.

Found: C, 48.48; H, 8.07.

Minor Component. G.l.c. analysis (Nitrile Silicone Fluid) of an enriched sample of the minor reaction component, indicated it to be a mixture. An infrared spectrum was obtained of the pure principal component. It indicated it to be saturated, and the bicyclo(4.2.0)oct-2-yltrimethyltin
structure (9) was assigned to it. $v_{\text{max}}$ in cm$^{-1}$ units: 3100-3000 (w), 2974 (sh,m), 2936 (s), 2858 (s), 1700 (v.w), 1440 (m), 1410 (sh,w), 1208 (w), 1190 (w), 1185 (m), 1150 (v.w), 1085 (w), 1050 (w), 1000 (w), 965 (w), 910 (w), 850 (w), 762 (s), 705 (m).

4. Cyclooctene. Both the thermal and the photochemical reactions resulted in no hydrostannation. Some cyclooctyltrimethyltin was, however, obtained by the hydrogenation of cyclooct-4-en-1-yltrimethyltin.

5. Bicyclo(2.2.1)hepta-2,5-diene. The thermal hydrostannation of bicyclo(2.2.1)hepta-2,5-diene yielded a clear liquid, b.p. 41° (0.50 mm.)-42° (0.55 mm.). G.l.c. analysis (Nitrile Silicone Fluid) indicated the liquid, which will be designated as product mixture (A), to consist of a major component (B) and a minor component (C) (ca. 10%). Further analysis of the product mixture (A) by g.l.c. (Aerograph) indicated that at least three components were present. The major component (B) indicated by previous g.l.c. analysis (Nitrile Silicone Fluid) appeared as two major overlapping peaks. The ratio of the two major peaks (B) to the minor (C) was 10:1.

The photochemical hydrostannation, as indicated by g.l.c., n.m.r., and infrared analyses, yielded the same product mixture.

**Product Mixture (A).** N.m.r. (neat, TMS ref.) in $\tau$ units: singlets (total of ten protons), 10.03 (strong signal) ($\text{Me}_3\text{Sn}^{118}$), 9.95 (weak signal) ($\text{Me}_3\text{Sn}^{118}$), and 9.94 (strong signal) ($\text{Me}_3\text{Sn}^{118}$); complex multiplet (seven protons), 9.38-7.96 with strongest signals at 8.95, 8.88, 8.78, and 8.61; two broad overlapping singlets (two protons), 7.13 and 6.97; multiplet (two protons), 4.05 (CH=CH).
By preparative g.l.c. (Aerograph), the minor product (C) was separated from B. Examination of this fraction of B by g.l.c. (Aerograph) indicated it to be a mixture of 1:2.5.

Major Products (B). \( \nu \) max. in cm.\(^{-1} \) units: 3125 (sh,w), 3055 (sh,m), 2965 (s), 2930 (sh,s), 2900 (sh,s) 2865 (s), 1700 (w), 1625 (w), 1565 (m), 1460 (m), 1450 (s), 1330 (s), 1275 (doublet, m), 1185 (s), 1120 (m), 1087 (m), 870 (doublet, s), 822 (sh,m), 805 (sh,s), 795 (s), 762 (s), 717 (s), 705 (sh,s), 675 (w). N.m.r. (neat, TMS ref.) in \( \tau \) units: singlet, 10.03 (Me\(_3\)Sn\(^{119}\)); singlet, 9.95 (Me\(_3\)Sn\(^{118}\)); singlet, 9.94 (Me\(_3\)Sn\(^{118}\)); complex multiplet 9.38-7.96; broad unsymmetrical singlet 7.05; multiplet, 4.05 (CH=CH). \( n_D \) (24.8°) 1.5135.

Anal. Calcd. for C\(_{10}\)H\(_{18}\)Sn: C, 46.75; H, 7.06. Found: C, 46.9; H, 6.89.

Minor Component (C). \( \nu \) max. in cm.\(^{-1} \) units: 3120 (v.w), 3050 (sh,m), 2960 (s), 2910 (sh,s), 2865 (s), 1700 (w), 1620 (v.w), 1565 (v.w), 1540 (v.w), 1450 (doublet, w), 1330 (s), 1265 (doublet, w), 1185 (s), 1107 (m), 1082 (m), 963 (m), 910 (doublet, m), 870 (s), 824 (sh,m), 785 (sh,s), 762 (s), 735 (sh,s), 704 (s), and 635 (w). The purity of this component could not be determined since after the spectrum had been obtained, the liquid sample turned crystalline when the infrared salt plates were opened; this was taken as an indication that the compound was sensitive to air decomposition.

Hydrostannation of the Product Mixture (A). The photolysis of either the product mixture (A) or the product mixture (A) plus a trace amount of trimethyltin hydride for 34 hours, according to the general procedure for the photochemical hydrostannations, resulted in no significant change in the ratio of minor (C) to major (B) components (g.l.c.)
analysis, Nitrile Silicone Fluid).

The product mixture (A) (1.5 g., 0.0060 mole) plus trimethyltin hydride (1.1 g., 0.0070 mole) were photolyzed, according to the general procedure for the photochemical hydrostannation, for 42 hours. After photolysis the reaction mixture gave a positive test for the hydride, and examination of the reaction mixture by g.l.c. (Nitrile Silicone Fluid) indicated in addition to unreacted starting material (D), the presence of a substance, presumably the product of dihydros tannation, with longer retention time than the starting material. Furthermore, this analysis indicated that the ratio of major to minor components in the unreacted starting material, designated D, decreased.

The unreacted starting material (D) was separated into minor (E) and major (F) fractions by preparative g.l.c. (Aerograph). Because of the small amount of material obtained, only infrared spectra of the two fractions were obtained. The infrared spectrum of the minor fraction (E) was identical with that of the minor product (C), and this material was also air sensitive. The infrared spectrum of the major fraction (F) was different from that of B. Except for the presence of some absorption at 1110 cm.\(^{-1}\), it was identical with that of 6 prepared by an alternate synthesis. G.l.c. analysis (Nitrile Silicone Fluid) of the infrared sample indicated that it was slightly impure.

6. By-Products. Infrared analysis indicated that most of the by-products contained methyl-tin groups\(^{47-49}\): 1200-1180 cm.\(^{-1}\) (m-s), symmetrical methyl deformation vibrations of methyl-tin groups; 700-900 cm.\(^{-1}\) (s), methyl rocking vibrations of methyl-tin groups.
In general the solid filtered from the thermal reaction mixture consisted of some white material, some yellow needles, and grey particles of metallic tin. An infrared spectrum of the white material, purified by sublimation, had absorption in cm.\(^{-1}\) units at: 2990 (m), 2910 (m), 1540 (s), 1525 (sh,s), 1200 (sh,m), 1190 (sh,m), 1180 (m), 1068 (s), 837 (s), 780 (s), 740 (sh,s), and 705 (sh,s). Some of this material, as indicated by a comparison of infrared spectra, usually sublimed into the condenser during the removal of excess diene. It was soluble in acetone, but when taken to 300° in a capillary tube, did not melt or sublime.

A portion of a solid by-product mixture was left exposed to the air to dry. During this time the white material disappeared. An infrared spectrum of the remainder, purified by sublimation, indicated nitrile absorption and methyl-tin absorption: 3000 (m), 2910 (m), 2155 (w), 1400 (w), 1205 (m), 1190 (m), 780 (s) cm.\(^{-1}\). The formation of trimethyltin cyanide was reasonable, and Neumann et al.\(^{30,83}\) has reported triethyltin cyanide as a reaction product in hydrostannation with triethyltin hydride catalyzed by AIBN.

In a case where excess diene was distilled from the unfiltered reaction mixture, some crystals sublimed into the condenser. An infrared spectrum indicated these to be trimethyltin hydroxide\(^{84}\): 3620 (s) (OH stretching vibration), 2990 (m), 2910 (m), 1375 (w), 1190 (m), 920 (s) (Sn-OH deformation vibration), 765 (s). This hydroxide undoubtedly resulted from exposure of the hydride to oxygen.

Hexamethylditin was also a by-product in these reactions. A trace of it usually distilled just prior to the product. Its infrared spectrum was identical to that of some, b.p. 82° (26 mm.), reported 85-88° (45 mm.), prepared by the thermal decomposition of trimethyltin hydride (120°
for 1 hr.): 2985 (s), 2920 (s), 1685 (w), 1450 (w), 1375 (w), 1187 (m), 760 (s), 695 (sh,m).

The small amount of heavy, brown-yellow oil remaining after distillation of the adducts from the reaction mixture was not examined.

In the photochemical hydrostannations traces of metallic tin were noted. In addition a white material formed along the sides of the tubes adjacent to the light source. The white material formed in the attempted hydrostannation of cyclooctene had the following infrared absorption bands: 2980 (m), 2920 (m), 1490 (w), 1375 (w), 1195 (m), 1180 (sh,m), 760 (s), 725 (sh,m). This spectrum resembled one of dimethyltin oxide.85

D. THE HYDROGENATION OF CYCLOOCT-4-EN-1-YLTRIMETHYLTIN

Cyclooct-4-en-1-yltrimethyltin* (1.0 g.) dissolved in twelve ml. of ethyl acetate was hydrogenated in the presence of platinum oxide (0.10 g.) in a standard Parr Hydrogenation apparatus. The reaction was run at room temperature (31-32°). After twenty-four hours the pressure was constant. The liquid that remained after the catalyst was filtered off, and after the solvent was evaporated, was examined by g.l.c. (Nitrile Silicone Fluid). The chromatogram indicated the presence of two trace components (see footnote), which were present in the starting material, and one major component. The major component was collected and its infrared and n.m.r. spectra were consistent with the

* The adduct of the photochemical hydrostannation of 1,5-cyclooctadiene, which consisted essentially of cyclooct-4-en-1-yltrimethyltin (3% saturated products).
cyclooctyltrimethyltin structure. $\nu$ max. in cm.$^{-1}$ units:
2975 (sh, m), 2910 (s), 2850 (s), 1475 (m), 1450 (m), 1350 (w), 1220 (w), 1185 (m), 1140 (w), 1040 (w), 760 (s), 700 (s). N.m.r. (30% in CCl$_4$) in $\tau$ units: singlet (nine protons), 10.00 (Me$_3$Sn$^{118}$); singlet (fifteen protons), 9.22 (CCH$_2$C, C$_2$CHSn). $\lambda 210$ (e 3090).

E. ALTERNATE SYNTHESSES

1. Cyclooct-2-en-1-yltrimethyltin. The bromide was prepared (50% yield) by the method of A. C. Cope and L. L. Ester, Jr.\textsuperscript{86}

Amalgamated magnesium was prepared by allowing magnesium (3.0 g., 0.13 g. at.) and mercuric chloride (1.3 g., 0.0050 mole) in dry diethyl ether (25 ml.) to stir overnight protected from moisture.

A round bottom flask equipped with dropping funnel, reflux condenser, and mechanical stirrer served as the reaction vessel. The usual precautions were taken to exclude moisture, and an argon atmosphere was maintained in the reaction vessel.

The amalgamated magnesium was washed with several portions of dry ether, by shaking with the ether, to remove the white precipitate of magnesium chloride that had formed during the chemical amalgamation. In as little ether as possible (100-150 ml.) it was transferred to the reaction vessel. A solution of 3-bromocyclooctene (5.0 g., 0.025 mole), trimethyltin chloride (10.0 g., 0.050 mole), and dry diethyl ether (10 ml.) was added to the dropping funnel. The reaction was initiated by the addition of ethylene bromide (1 ml.); then the solution of the two halides was added slowly. The reaction was exothermic, but could be controlled well by the rate of addition of the halides.
After the addition was completed (1 1/2 hours), the reaction mixture was refluxed (1 hour) on a steam bath. The reaction mixture was then filtered, and the residue washed well with dry ether. To remove excess trimethyltin chloride, the ether solution was washed with a saturated potassium fluoride-water solution, followed by water. The organic layer was dried, concentrated, and distilled to give hexamethylditin (1.5 g., 0.0040 mole) and cyclooct-2-en-1-yltrimethyltin (2.2 g., 0.0080 mole) 32%, b.p. 63.5° (0.25 mm.) - 68.5° (0.25 mm.). ν max. in cm.\(^{-1}\) units: 3034 (sh, w), 3000 (s), 2970 (m), 2922 (s), 2850 (s), 1700 (w), 1630 (m), 1475 (w), 1450 (m), 1260 (w), 1185 (m), 1140-995 (series of ca. 13 bands, w), 835 (sh, w), 810 (sh, w), 780 (sh, s), 765 (s), 705 (m). \(n_D\) (24.8°) 1.51725. λ 210 (e 7910); λ max. 216 μm (ε 8664); λ 217 (ε 8644).

Anal. Since the infrared spectrum was identical with that of 2, only one compound was analyzed; see p. 40.

2. Bicyclo(4.2.0)oct-2-yltrimethyltin (Attempted).

Cycloocta-2,4-dien-1-yl Acetate. The 5-bromocycloocta-1,3-diene was prepared according to the procedure of Cope et al. 87

With cooling and stirring, 5-bromo-cycloocta-1,3-diene (25 g., 0.13 mole) dissolved in acetic acid (50 ml.) was slowly (1 hour) added to a solution of silver acetate (29 g., 0.17 mole) in acetic acid (80 ml.). The mixture was stirred (2 1/2 hours), filtered, and the silver bromide precipitate washed well with acetic acid. The acetic acid was removed under reduced pressure, and the residue distilled to give the acetate (79%), b.p. 55.5° (0.50 mm.).
Bicyclo(4.2.0)oct-7-en-2-yl Acetate. The bicyclic acetate was prepared by the photochemical isomerization of cycloocta-2,4-dien-1-yl acetate.

The radiation source was a 400 watt high pressure mercury arc lamp (General Electric) inserted into a quartz water-cooled jacket which was inserted into the center neck of a five liter three-necked flask that served as the reaction vessel. The flask was equipped with a reflux condenser. The cycloocta-2,4-dien-1-yl acetate (16 g., 0.010 mole) dissolved in dry diethyl ether (2 l.) was added, the reaction vessel was shielded with aluminum foil, and the irradiation begun.

During irradiation the solution was magnetically stirred, and a nitrogen atmosphere was maintained over the surface of the reactants. After forty hours of irradiation, the reaction mixture was concentrated. Distillation yielded 6.3 g. of liquid, b.p. 64° (2 mm.) plus polymer. A comparison of the extinction coefficient of this liquid at 222 mp with that of the starting acetate, indicated that the reaction was not more than half completed.

During the irradiation, a yellow polymeric film formed on the water jacket of the source and on the walls of the reaction vessel. This was removed by carefully washing with a 10% hydrofluoric acid solution. The product mixture plus some additional acetate (1.6 g.) was then irradiated for 47 hours.

G.l.c. analysis (Nitrile Silicone Fluid) of the reaction mixture indicated the absence of starting material and the presence of two products (the exo- and the endo-bicyclic acetates, presumably) plus polymeric material.
The ether was removed under reduced pressure, and the product (2.1 g., 0.013 mole) was collected at 0.10 mm. in a receiver cooled in a dry ice bath. The major product, however, was a heavy yellow-brown polymer.

**Bicyclo(4.2.0)oct-2-yl Acetate.** Bicyclo(4.2.0)-oct-2-yl acetate (1.9 g., crude) was obtained from the hydrogenation of bicyclo(4.2.0)oct-7-en-2-yl acetate (2.1 g., crude) in ethyl acetate (150-200 ml.) with platinum oxide (0.10 g.) as catalyst.

The hydrogenation was carried out with constant magnetic stirring in a filter flask; the flask was fitted with a balloon on the side arm and with a two holed rubber stopper containing a dropping funnel and a stopcock. After the catalyst and solvent were added to the flask, hydrogen was admitted through the stopcock until the balloon was filled. The catalyst was allowed to stir under hydrogen for a few minutes; the flask was then flushed with nitrogen, the sample added in solvent through the funnel, and the balloon filled with hydrogen. During the course of the reaction the balloon was refilled as needed.

**Bicyclo(4.2.0)octan-2-ol.** The lithium aluminum hydride reduction of bicyclo(4.2.0)oct-2-yl acetate (1.9 g., crude) yielded bicyclo(4.2.0)octan-2-ol (0.81 g., crude, the infrared spectrum indicated the presence of some acetate).

**Bromination of Bicyclo(4.2.0)octan-2-ol.** The foregoing crude alcohol (0.81 g.) was brominated in pentane using phosphorous tribromide (100% excess). The reaction was carried out at 0°, the reaction mixture was stirred at room temperature (8 hours), and then refluxed (3 hours). Hydrolysis was carried out with cold water. The mixture was extracted with methylene chloride, washed, neutralized, dried, and

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concentrated to yield bicyclo(4.2.0)oct-2-yl bromide (0.66 g., crude, the infrared spectrum indicated the presence of some acetate).

**Bicyclo(4.2.0)oct-2-yltrimethyltin (Attempted).** The amalgamated magnesium, prepared from magnesium (0.40 g., 0.016 g. at.), mercuric chloride (0.17 g.) and dry diethyl ether (5 ml.), was washed free of magnesium chloride with several portions of dry diethyl ether, and then transferred to a round bottom flask equipped with a dropping funnel and reflux condenser. The usual precautions were taken to exclude moisture.

A solution of the bromide (0.66 g., 0.0035 mole, crude), trimethyltin chloride (1.4 g., 0.0070 mole), and dry diethyl ether (6 ml.) was added to the dropping funnel. Ethylene bromide was used to initiate the reaction, and then the solution of the halides was added slowly. During the reaction, the reaction mixture was stirred magnetically, and a nitrogen atmosphere was maintained in the reaction vessel.

After addition of the halides was completed, the reaction mixture was refluxed for two hours. The mixture was then filtered from excess magnesium, and the residue washed well with dry ether. To aid in the removal of excess trimethyltin chloride, as the less soluble fluoride, the etheral solution was washed with a saturated potassium fluoride solution and then with water. The ether layer was dried, concentrated, and examined by g.l.c.

G.l.c. analysis (Nitrile Silicone Fluid) revealed the presence of six components. Infrared spectra of four of the components were obtained. However, the spectra all lacked the characteristic methyl-tin bands.
The residual magnesium and salts were hydrolyzed with hydrochloric acid. The solution was extracted with diethyl ether. The ether layer was washed with saturated potassium fluoride solution and then water; the ether layer was dried and concentrated to yield only a trace of liquid. The infrared spectrum of this liquid was identical to that of the mixture obtained above, except for the presence of a strong absorption band at 723 cm\(^{-1}\).

3. **Tricyclo(2.2.1.0\(^{2,6}\))hept-3-yltrimethyltin.** The halide for the reaction had been prepared by the sealed tube reaction of cyclopentadienyl dimer and vinyl bromide. Examination of this reaction mixture by g.l.c. (Nitrile Silicone Fluid) indicated the presence of two components, presumably tricyclo(2.2.1.0\(^{2,6}\))hept-3-yl bromide and bicyclo-(2.2.1)hept-2-en-5-yl bromide. The infrared spectra of the collected components indicated the unsaturated one to predominate. The mixture of the halides was used in the reaction, since both halides gave the 3-nortricyclyl Grignard reagent.

Amalgamated magnesium was prepared by allowing magnesium (1.5 g., 0.060 g. at.) and mercuric chloride (0.61 g., 0.42 mole) to stir overnight protected from moisture in 13 ml. of dry diethyl ether. Before being transferred to the reaction flask, the amalgamated magnesium was washed with several portions of dry ether, by shaking with ether to remove the white precipitate of magnesium chloride that had formed during the chemical amalgamation. The usual precautions were taken to maintain a dry atmosphere during the reaction. The reaction was initiated with a few drops of ethylene bromide, and then a solution of the distilled bromide mixture (4.0 g., 0.023 mole) and trimethyltin chloride
(5.0 g., 0.025 mole) in dry ether (8 ml.) was slowly added. After the addition was completed the reaction mixture was refluxed on a steam cone (1-1 1/2 hours). The reaction mixture was then filtered and the residue washed well with dry ether. The ether was removed and an inert atmosphere kept over the resulting liquid. Examination of the liquid by g.l.c. (Nitrile Silicone Fluid) revealed the presence of four components; after exposure to air five components were present. The first component was air sensitive, and its retention time in the chromatogram corresponded to that of minor component (C) in the product mixture from the bicyclo-(2.2.1)hept-2,5-diene reaction. It was possible to obtain infrared spectra of the other three components. One component had a spectrum that strongly suggested the coupled product as this component. The characteristic feature of another component was a very broad methyl-tin band at 780 cm.$^{-1}$, which indicated that perhaps the main component was hexamethylditin. A third component had an infrared spectrum that would correspond to tricyclo(2.2.1.0$^{2,6}$)hept-3-yltri-methyltin; vmax. in cm.$^{-1}$ units: 3125 (v.w), 3060 (m), 2970 (s), 2935 (s), 2905 (sh,s), 2865 (s), 1700 (v.w), 1450 (doublet, w), 1327 (w), 1305 (w), 1294 (m), 1209 (w), 1185 (m), 1132 (w), 1000 (v.w), 952 (v.w), 800 (doublet, s; 802 and 794), 760 (s), 718 (s). The limited amount of the fractions available did not allow any other analyses to be carried out. Therefore, although the infrared spectrum of the third component was a good indication of $\delta$, the results were not conclusive.
F. REACTIONS WITH TRIFLUOROACETIC ACID (PROCEDURE)

Trifluoroacetic acid was added slowly to the neat compound (or if indicated in the discussion, to a pentane solution of the organotin compound) cooled in an ice-water bath. To collect the evolving gas, a syringe needle topped with a balloon was inserted into the syringe cap stoppering the reaction vessel. The reaction mixture was allowed to warm to room temperature, and except in the case of cyclo-oct-2-en-1-yltrimethyltin, in which case the reaction was instantaneous, was allowed to stand at room temperature.

In the work up of the cleavages of the 1,5-cyclo-octadiene adducts with excess acid, the reaction mixture was extracted with pentane. The pentane layer was washed to neutralize it, dried, and then examined by g.l.c. (Nitrile Silicone Fluid and Silicone Oil).

The details of these reactions are indicated in the discussion.
BIBLIOGRAPHY AND ACKNOWLEDGEMENTS


34. Ref. 33, p. 121.
35. Ref. 33, p. 52.
41. Ref. 33, p. 50.


58. Infrared and n.m.r. spectra supplied by L. Friedman.
69. H. G. Kuivila and O. R. Khan, unpublished observations.


80. A generous gift of trimethyltin chloride from M & T Chemicals, Inc., is gratefully acknowledged.

81. Technical assistance by R. Fish is gratefully acknowledged.


85. Ref. 48, spectrum 6.8 no. 3.


89. The reaction was carried out by C. Warner and R. Fish.
PART TWO

THE DIPOLE MOMENT OF GLYOXAL SULFATE
I. SUMMARY

The dipole moments of diethyl sulfate (1), ethylene sulfate (1,3,2-dioxathiolane 2,2-dioxide) (2), and glyoxal sulfate (dihydro-1,3,2-dioxathiolo(1,3,2)dioxathiole 2,2,5,5-tetraoxide) (3) were determined as 4.43, 5.64, and 5.35 D., respectively, from dielectric constant and density measurements at 24.9° in dioxane. The induced polarization of the molecules was assumed equal to their molar refraction measured at the sodium D-line, and the molar refractions were calculated from standard bond refractions. The dipole moments were calculated by computer using a program based on the method of Halverstadt and Kumler.

The dipole moment of glyoxal sulfate formed from the reaction of 1,1,2,2-tetrachloroethane with fuming sulfuric acid was consistent with the cis-isomer.
II. INTRODUCTION

The reaction of 1,1,2,2-tetrachloroethane with fuming sulfuric acid to yield glyoxal sulfate was first reported by Ott in 1922.\(^1\)

\[
\text{CHCl}_2\text{CHCl}_2 + 4\text{SO}_3 + 2\text{H}_2\text{SO}_4 \xrightarrow{\text{H}_2\text{SO}_4, 60^\circ} 4\text{ClSO}_3\text{H} + (\text{CHO}_2\text{SO}_2)_2
\]

The dicyclic sulfate formed in this reaction was initially formulated as 4, the product of two geminal cyclizations. Subsequently, proof that methylene sulfate (5) was dimeric\(^2,3\), suggested the instability of the four-membered ring system in 4 and led Baker and Field to propose 3 as the more probable structure for glyoxal sulfate. This revision was supported by similarities in the physical properties of 3 and 5.

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Additional indications that the four-membered ring system in structure 4 would be considerably less stable than the product isolated were available today. Sulfur trioxide existed in several modifications. Although the monomer, a six-membered ring trimer (6), and two polymers, one linear and one cross-linked, were known, no cyclic dimer had been reported. In addition, sultones (7), the cyclic esters of hydroxysulfonic acids, were reported to be a very reactive class of compounds exhibiting a decrease in stability as \( n \) decreased. The only 2-hydroxy-1-ethanesulfonic acid sultones (7, \( n = 0 \)) isolated have been the 2-phenyl-\(^7\) and some halofluoro-compounds. Furthermore, 2-hydroxy-1-ethanesulfonic acid sultone (8) appeared to be unstable; attempts to prepare it have yielded carbyl sulfate (9).\(^9\)

In contrast to the predicted instability of 4 was the reported preparation of stable fused five-membered ring systems containing a 1,3,2-dioxathiolane ring. Compounds 10, 11, and 12 have been prepared as the cis-isomers and compound 13 as the trans.\(^{10-12}\)

\[
\begin{align*}
\text{10} & \quad \text{0} \quad \text{SO} \\
\text{11} & \quad \text{0} \quad \text{SO} \\
\text{12} & \quad \text{0} \quad \text{SO} \\
\text{13} & \quad \text{0} \quad \text{SO}
\end{align*}
\]

\[
\begin{align*}
\left(\text{CHO}_2\text{SO}_2\right)_2 + & \quad \text{HO} \quad \text{HO} \quad \text{(2)} \quad \text{HO} \\
\text{14} & \quad \text{0} \quad \text{0} \quad \text{0} \quad \text{0} \\
\text{15} & \quad \text{0} \quad \text{0}
\end{align*}
\]
The reported reaction (2) of glyoxal sulfate with ethylene glycol\(^\ddagger\) has not helped to clarify the chemical structure of the sulfate. The formation of a mixture of trans-1,4,5,8-naphthiodioxane (14) and 2,2'-bis 1,3-dioxolane (15) might indicate that the sulfate consisted of a mixture of 4 and 3, or that both possible cyclizations were taking place from one isomer. Moreover, the reaction of 1,1,2,2-tetramethoxyethane with ethylene glyxol under similar conditions was reported to yield the same product mixture.\(^\ddagger\) The latter reaction indicated that for the open tetraacetal both cyclizations took place. It appeared, therefore, that glyoxal sulfate was reacting in a manner similar to the open tetraacetal, and therefore, no information concerning its chemical structure could be deduced from the reaction.

The reaction of glyoxal sulfate with two moles of phenylmagnesium bromide was reported to yield \(\text{dl-hydrobenzoin}\). If the mechanisms for the ring opening and hydrolysis in this reaction were assumed to be identical with those for ethylene sulfate (2) under comparable conditions, \(\text{dl-hydrobenzoin}\) would be obtained from the cis-isomer of 3. Under both acidic and basic conditions the ethylene sulfate ring was opened by C-0 cleavage with inversion to give the monoester. Hydrolysis of the monoester occurred at sulfur with retention in acidic solution and at carbon with inversion in basic solution. Assuming this mechanism to be operative in reactions of glyoxal sulfate, two ring openings (under acidic or basic conditions) to give an inversion at each carbon would yield a di-monoester of the same stereochemistry as the starting sulfate. Hydrolysis of the di-monoester under acidic conditions with two S-0 cleavages would yield product with the same stereochemistry as the starting sulfate. Basic hydrolysis
of this di-monoester would occur with an inversion at each carbon yielding, again, the product with the same stereochemistry as the starting material. Although not confirmed, it appears therefore that glyoxal sulfate prepared by this method was the \textit{cis}-isomer.

In the present work, the dipole moment of glyoxal sulfate was determined in order to ascertain its stereochemistry. No moment was expected for the \textit{trans}-isomer, which contained a center of inversion, and ethylene sulfate was used as a model to predict the magnitude of the moment for the \textit{cis}-isomer.
III. RESULTS AND DISCUSSION

A. GENERAL

A convenient method for preparing small quantities of ethylene sulfate was the reaction of silver sulfate with 1,2-dibromoethane (yield 10%).\textsuperscript{2,10} Unfortunately, as others have reported\textsuperscript{17}, only a trace of product was obtained by this method. The permanganate oxidation of ethylene sulfite in acetone (yield 25%)\textsuperscript{17} or in acetic acid (yield 14%)\textsuperscript{18} with barium or sodium permanganate, respectively, appeared to be a satisfactory procedure. However, utilizing the materials on hand a sufficient quantity of ethylene sulfate was obtained from a reaction of sulfuryl chloride with ethylene glycol (yield 3%).\textsuperscript{19} No attempt was made to optimize the yield since several different preparations have already been reported.\textsuperscript{20}

Glyoxal sulfate has always been prepared from fuming sulfuric acid and 1,1,2,2-tetrachloroethane.\textsuperscript{1,13,21-26} The reported melting point of 176-177° appeared to be the melting point of the product after just washing and drying. It was not surprising, therefore, that recrystallization from ethyl ether increased the melting point to 183°. The infrared spectra of the sample before recrystallization (m.p. 177° dec.) and after recrystallization (m.p. 183° dec.) were identical.

The infrared spectrum of glyoxal sulfate (mull) showed a sharp, medium CH (stretching vibration) absorption band at 3074 cm.\textsuperscript{-1}, and a sharp, strong CH (deformation vibration) band at 1344 cm.\textsuperscript{-1}. In hydrocarbons these CH bands have been reported to be of weak intensity and to
appear at 2900-2890 cm.\(^{-1}\) and 1350-1315 cm.\(^{-1}\), respectively.\(^{27,28}\) The strong intensity of these bands in the spectrum of glyoxal sulfate could be accounted for by the presence of the adjacent oxygen atoms.\(^{27,28}\) An increase in the CH stretching vibration as compared to hydrocarbons would be expected since, an increase occurred for triethoxymethane (> 3000 cm.\(^{-1}\)),\(^{29}\) cyclic acetal (3012-2967 cm.\(^{-1}\))\(^{30}\), and ethylene sulfate (3062, 2991 cm.\(^{-1}\)).\(^{31}\) The CH deformation vibration occurred in the region (1350-1325 cm.\(^{-1}\)) reported for the OCH\(_2\)O group.\(^{32}\)

The SO\(_2\) absorption bands of glyoxal sulfate appeared as broad, strong bands at 1440, 1430 (asymmetrical stretch) and 1240, 1216 cm.\(^{-1}\) (symmetrical stretch).\(^{33-35}\) These appeared at higher frequency than for ethylene sulfate (1373 and 1196 cm.\(^{-1}\)).\(^{31}\) As in the case of carbonyl frequencies, this change might result from ring fusion.\(^{36}\)

The n.m.r. spectrum of glyoxal sulfate in deuterioacetone showed a sharp singlet at \(\tau\) 2.32. A combination of factors might be responsible for this low field signal. Protons on electronegatively substituted carbon atoms generally appeared deshielded with respect to the corresponding hydrocarbon.\(^{37}\) In particular, the chemical shifts of methylene protons alpha to the sulfate group have been reported as \(\tau\) 5.74 (diethyl sulfate)\(^{38}\), 5.74 (\(\beta,\beta\)-dimethyl trimethylene sulfate)\(^{39}\), 5.32 (ethylene sulfate)\(^{40}\), and 5.27 (trimethylene sulfate).\(^{41}\) The change in chemical shift of these sulfates with respect to the corresponding hydrocarbons is indicated in Table IV. It has an average value of 3.2 ppm.

If the chemical shift of ethylene sulfate were used to predict that of glyoxal sulfate, assuming that substitution of a second sulfate group would have the same deshielding
TABLE IV

Deshielding of Methylene Protons by the Sulfate Group

<table>
<thead>
<tr>
<th>Hydrocarbon</th>
<th>Chemical Shift in $\tau$ Units</th>
<th>Sulfate</th>
<th>Change in Chemical Shift in ppm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{CH}_3(\text{CH}_2)_n\text{CH}_3$</td>
<td>8.75</td>
<td>$\text{Et}_2\text{SO}_4$</td>
<td>5.74</td>
</tr>
<tr>
<td>$\text{C}<em>6\text{H}</em>{12}$</td>
<td>8.56</td>
<td></td>
<td>5.27</td>
</tr>
<tr>
<td>$\text{C}_5\text{H}_8$</td>
<td>8.49</td>
<td></td>
<td>5.32</td>
</tr>
</tbody>
</table>

3.2 Average
effect as the first, the resonance signal would occur near $\tau$ 2.1. However, the deshielding effect of electronegative substituents on the chemical shift of alpha protons has not been generally additive.\textsuperscript{42} Consequently, the deshielding effect of the second sulfate group would be expected to be less than 3.2 ppm. Additional deshielding might be expected to arise from ring fusion.* In addition a small solvent effect might contribute to the deshielding since the resonance signal of ethylene sulfate was observed at $\tau$ 5.08 in deuterioacetone.\textsuperscript{31} In view of the uncertainty involved in approximating the effects indicated, the observed chemical shift for glyoxal sulfate appeared reasonable.

B. DIPOLE MOMENT STUDY

The dipole moments for glyoxal sulfate, ethylene sulfate, and diethyl sulfate were determined as 5.35, 5.64, and 4.43 D., respectively, in dioxane at 24.9°. The moments were calculated by the method of Halverstadt and Kumler from dielectric constant and density data\textsuperscript{44}, and the computer program of Allinger\textsuperscript{45} was employed for the actual calculations (see Experimental Section).

The induced polarization of the molecules was assumed equal to the molar refraction for the sodium D-line. Neglecting atomic polarization should not affect the conclusion, since the moments were large and the relative moments were involved.

*The resonance signal of the bridgehead proton in bicyclo-(3.3.0)octane occurs at $\tau$ 7.8 (see p. 23) as compared with $\tau$8.5 for either cyclopentane or the methinyl proton of isobutane (ref. 43).
The dipole moment data were consistent with the formation of the cis-isomer of 3 from the reaction of 1,1,2,2-tetrachloroethane with fuming sulfuric acid. The trans-isomer (16) would be expected to possess a resultant moment of zero, since it had a center of inversion. The moment expected for the cis-isomer (17) was calculated using the determined moment of ethylene sulfate to approximate the dipole moment of the 1,3,2-dioxathiolane rings in 17. Taking the angle between the two 1,3,2-dioxathiolane rings as 120°, the expected angle between the planes assuming tetrahedrally hybridized carbons, the calculated moment was 5.64 D. The calculated moment was in agreement with the determined value. Furthermore, using the moments determined for ethylene sulfate and glyoxal sulfate, the angle between the two 1,3,2-dioxathiolane rings in 17, would have a value of 123 ± 2° (the uncertainty being based on an uncertainty of ± 0.1 D. in the dipole moment).

The dipole moment of diethyl sulfate was less than that of ethylene sulfate. This would be expected since the reported moments of cyclic esters have been found to be more than the open forms.46
IV. EXPERIMENTAL

A. GENERAL CONSIDERATIONS

1. Melting Point Determination. A Thomas Hoover Capillary Melting Point Apparatus (A. H. Thomas Company, Pennsylvania) was used to determine the melting points of solids; they are reported as corrected.

2. Infrared Absorption Analysis. The infrared absorption spectra were recorded on a Perkin-Elmer Model 337 Grating Spectrophotometer. The spectra of solids were determined as mulls. Halocarbon Oil and Nujol were used to prepare mulls for the 4000-1330 cm$^{-1}$ region and the 1300-650 cm$^{-1}$ region, respectively. The absorption bands were indicated as strong (s), medium (m), and weak (w) intensity; a shoulder was indicated by (sh).

3. Refractive Index Determination. A Bausch and Lomb Abbe Refractometer was used to determine the refractive indices of liquids.

4. Nuclear Magnetic Resonance (n.m.r.) Analysis. The n.m.r. spectra were recorded on a Varian A-60 Analytical N.M.R. Spectrometer (Varian Associates). The spectra were obtained immediately after the solutions were prepared.

5. Analytical Data. The microanalyses were done by Galbraith Laboratories, Inc. (Knoxville, Tennessee).

B. MATERIALS

1. Dioxane. Some dry dioxane with only a trace of peroxides was available. The peroxides were removed by shaking the dioxane with alumina (redried at 300° for 24 hours).
Immediately, sodium was added to the filtered solvent, and the solvent brought to reflux. The solvent was allowed to reflux over sodium 3-4 days before being used, and was kept refluxing while in use. A fraction distilled off had $n_D^{(24.9^\circ)} 1.42000$ (lit. $n_D^{(25^\circ)} 1.4199^{48}$ and $1.42032^{49}$).

2. **Diethyl Sulfate** (1). Purification of the commercial liquid was effected by washing with ice water followed by a sodium bicarbonate solution, and then distilling under reduced pressure. A clear fraction, b.p. 83° (6mm.), was collected, dried over molecular sieves (type 4A, redried at 300° for 24 hrs.), and redistilled. The fraction used for the dipole moment determination had b.p. 85° (7 mm.) and $n_D^{(24.9^\circ)} 1.39850$ (lit. b.p. 93.0-93.2° (13 mm.) and $n_D^{(20^\circ)} 1.40010$).

3. **Ethylene Sulfate** (1,3,2-Dioxathiolane 2,2-dioxide) (2). Ethylene glycol (20.8 g. 0.335 mole) was added to a round bottom flask equipped with magnetic stirrer, thermometer, and a dropping funnel vented through a drying tube. The sulfuryl chloride, Eastman practical, (47.9 g., 0.355 mole) was introduced into the dropping funnel and added dropwise to the reaction vessel which had been heated to 40-50°. The addition was accompanied by a slight evolution of gas and the temperature increased to 55-65°. The rate of addition was adjusted to maintain this range. The addition of the last half of the sulfuryl chloride was accompanied by a copious evolution of gas.

The reaction mixture, a clear solution, was then degassed by bubbling in nitrogen gas for a few minutes and left overnight at room temperature.

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Any unreacted sulfuryl chloride was removed under reduced pressure using a water aspirator. Then, while under vacuum, the reaction mixture was heated slowly to 150° during 2 1/2 hours and held at 150° for 15 minutes. During this time the reaction mixture slowly darkened, some unidentified liquid distilled over, and some crystals of ethylene sulfate sublimed into the condenser.

The reaction mixture, now a heavy brown-black liquid, was sublimed using an apparatus with a cylindrical* condensing surface. The sublimation was effected at 80° (0.1 mm.) with magnetic stirring of the reaction mixture. In addition, to the product, some liquid condensed onto the condensing surface. This mixture was melted in the presence of a few drops of benzene, allowed to solidify, and filtered to give 1.62 g. (3.9%) of waxy white needles. Recrystallization of this material from benzene yielded 0.99 g. (2.4%) of white needles, m.p. 95-96.5° and 0.31 g. of a second crop, m.p. 88-91°.

From a similar reaction of a larger scale, ethylene sulfate was obtained, after two recrystallizations from benzene and drying in a vacuum desiccator over calcium chloride, in 2.6% yield (m.p. 96.5-97.5°).

The sample melting 96.5-97.5° was sublimed at 60° (0.1 mm.) and used for the microanalyses and the dipole moment determination. It had m.p. 96.5-97.5° (lit. 17 97-98°) after sublimation. νmax in cm.-1 units: 3062 (w), 2991 (w), 2919 (w), 1467 (sharp, m), 1373 (broad, s, doublet), 1196 (broad, s) 1115 (w), 1004 (broad, s), 972 (sh, m), 904 (broad, s), 874 (sh, s), 787 (broad, s), 722 (m), and 650

*Because some liquid condensed in addition to the product, removal of the product when employing a flattened cold finger as the condensing surface was difficult.

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N.m.r. (in CD$_3$COCD$_3$; TMS, ref.) in $\tau$ units: singlet, 5.08 (lit. 40 in CCl$_4$-CHCl$_3$, singlet, 5.32).


4. Glyoxal Sulfate (Dihydro-1,3,2-dioxathiolo(1,3,2)-dioxathiole) (3). $^{21}$ 1,1,2,2-Tetrachloroethane (200 g., 1.13 mole), b.p. 71.5° (53 mm.), and mercuric sulfate (4.0 g., 0.013 mole) were added to a flask equipped with a mechanical stirrer, condenser, and dropping funnel. Fuming sulfuric acid, 65%, (480 g.) was introduced into the dropping funnel, and the reaction vessel immersed in an oil bath heated to 50°. The addition of the acid was carried out with mechanical stirring during the period of one hour. During this time, the bath was maintained at 53-57°. After the addition was completed, the reaction mixture was allowed to stir for an additional hour, during which time the temperature of the oil bath dropped to 43°. The temperature of the bath was then brought slowly to 58°, and the reaction mixture allowed to cool to room temperature with stirring.

The dark brown reaction mixture was cooled and the precipitated beige needles were filtered from the reaction mixture using suction. After drying the needles as well as possible with suction they were placed into a desiccator. This first crop of glyoxal sulfate (78.7 g., 0.360 mole) melted at 162° with decomposition and an evolution of a gas.*

---

*The melting points of all glyoxal sulfate samples were determined by placing the capillaries into a preheated bath (160°). A sample that melted at 183° dec., had m.p. 181° dec. when determined from a cold bath (25°).
Overnight the mother liquor deposited a second crop of beige needles. These were collected, dried as well as possible with suction, and then washed with cold dry carbon tetrachloride by stirring the needles with the cold dry solvent, filtering off the solvent, and repeating twice more. This washing removed some of the color of the needles. The needles were next washed by stirring with an ice-cold sodium bicarbonate-water mixture. The formation of foam during this washing indicated an evolution of gas, and thus that some neutralization had occurred. The crystals were collected and the washing repeated twice more. Finally, the crystals were washed with ice water in the same manner, three or four times, dried as well as possible with suction, and placed into a vacuum desiccator. This second crop (11.0 g., 0.050 mole) had m.p. 177° dec. The total yield of glyoxal sulfate was 89.7 g., 35%.

Although glyoxal sulfate was only slightly soluble in diethyl ether, it was found to be a better solvent for recrystallization than ethyl acetate or benzene. A satisfactory procedure for recrystallization consisted of extracting the sulfate with several portions of boiling ether, filtering the hot extracts from insoluble material, and concentrating the volume of the combined filtrates. All crystals were dried in a vacuum desiccator over calcium chloride.

One recrystallization of the second crop yielded colorless needles with m.p. 183° dec. (lit.² 176-177°). Two recrystallizations of the first crop yielded colorless needles with m.p. 183° dec., and an additional recrystallization did not increase the melting point.
The sample recrystallized to constant melting point was used in the dipole moment determination. $\nu$ max. in cm.$^{-1}$ units: 3074 (m), 1440, 1430 (broad, s, doublet), 1344 (sharp, s), 1303 (w), 1240 (broad, s), 1216 (s, sh), 1091 (broad, s), 1001 (very broad, s), 905 (s), 882 (s), 802 (s), 765 (s), and 664 (sharp, s). N.m.r. (in CD$_3$COCD$_3$; TMS, ref.) in $\tau$ units: singlet, 2.32.

Anal. Calcd. for C$_2$H$_2$O$_8$S$_2$: C, 11.01; H, 0.92; S, 29.40. Found: C, 11.10; H, 0.92; S, 29.60.

C. DIPOLE MOMENT DETERMINATIONS

1. Apparatus and Procedure. A WTW Dipolemeter Type DM 01 (Wissenschaftlich-Technische Werkstätten, GmbH, Weilheim, Germany)* with a measuring frequency of two megacycles was employed for measuring the dielectric constants. The instrument utilized the heterodyne-beat principle with a cathode-ray tube as the indicator. The cell (DFL 2) was provided with a thermostatic jacket and a recirculating water bath was used to maintain the temperature at 24.90 $\pm$ 0.02°. The base of the cell was closed with a Teflon stopcock, and the ground glass opening at the top of the cell was provided with a ground joint connected to a drying tube. Except during the filling of the cell, the ground joint and drying tube were always in place. The cell was cleaned by rinsing with purified redistilled acetone$^{52}$, and drying with stream of prepurified nitrogen led through a Drierite drying tower, to the drying tube on the cell opening, and out the base. The consistency of the cell was checked by determining the capacitance reading for nitrogen after each cleaning. Before filling, the cell was always rinsed with the sample solution

*Distributed by Kahl Scientific Instrument Corp., San Diego, California.
to remove any moisture film present. All capacitance readings were determined after allowing fifteen minutes for the cell contents to reach thermal equilibrium. The average value of three measurements (not differing from each other by more than ± 0.1 scale division) on the cell contents was taken as the capacitance reading. A small correction had to be applied to this reading from a scale diagram supplied with the instrument to obtain the corrected scale value.

Calibration of the measuring condenser (M1 range) was carried out using cyclohexane (spectranalyzed), benzene (99 mole per cent pure, thiophene free), and prepurified nitrogen (passed through a Drierite drying tower). The values for the dielectric constants of cyclohexane and benzene at 24.9° were computed from the information given in the N.B.S. Circular 514 and were respectively, 2.0152 and 2.2742. The dielectric constant of nitrogen at one atmosphere pressure and 24.9° was computed as 1.0005 from information from N.B.S. Circular 537. The solvents for the calibration were dried by passing them through a column (1.5 cm. x 45 cm.) which was packed half with alumina and half with silica gel, both of which had been redried at 300° for 24 hours. The base of the column was closed with a Teflon stopcock and the top with a drying tube. Using Teflon fittings, a 10 ml. syringe with the plunger removed was fitted to the column tip so that solvent released from the column would fill the syringe body. The syringe tip was fitted with 7 cm. of tapered Teflon tubing which, when inserted into the ground glass opening of the cell allowed the cell to be filled directly from the column.
The difference in the dielectric constants of the standard solvent \( e_{STD} \) and of nitrogen \( e_N \) compared with the respective scale value differences \( S_{STD} \) and \( S_N \) was used to calibrate the measuring condenser:

\[
\frac{e_{STD} - e_N}{S_{STD} - S_N} = \frac{\Delta e}{\Delta S}
\]

For benzene the \( \Delta e/\Delta S \) value was \( 6.7170_{1} \times 10^{-4} \) and for cyclohexane \( 6.7170_{6} \times 10^{-4} \). The negative reciprocal of equation 3 was used to define \( K(CELL) \) in the computer program.

The sample solutions (15-20 ml.) were made up in glass stoppered flasks the day of the determination, and stored in a desiccator until used. A 10 ml syringe fitted with an extended length of flexible Teflon tubing (ca. 1 mm. diameter) was used to fill the cell with the sample solutions. The densities of the samples were determined using a pycnometer (ca. 5 ml.) with capillary side arms, which had been calibrated with water.

2. Calculations. The calculations were carried out by computer (IBM 1620) using the program of Allinger (see Appendix) which was based on the method of Halverstadt and Kumler. Initially the program instructed the computer to calculate the mole fraction of solute \( N_2 \) and the density and dielectric constant for each solution \( d_{12} \) and \( e_{12} \). A least squares treatment of this data was then used to plot \( N_2 \) vs \( d_{12} \) and \( e_{12} \) vs \( N_2 \). The allowed deviations (of \( N_2 \) vs \( d_{12} \) in mole fraction and of \( e_{12} \) vs \( N_2 \) in dielectric constant) for the experimental points from the least squares lines were part of the data. These two plots yielded values for the density and dielectric constant of solvent \( d_1 \) and \( e_1 \) and for \( \alpha \) and \( \beta \) according to:
\[ e_{12} = e_1 + \alpha N_2 \]  
(4)  
\[ d_{12} = d_1 + \beta N_2 \]  
(5)

Then the molar polarization of the solute at infinite dilution \((P_{2\infty})\) was calculated from the equation:

\[
P_{2\infty} = \left[ \frac{e_1 - 1}{e_1 + 2} \right] \left[ \frac{1}{d_1} \right] \left[ \frac{M_2 - M_1 \beta/d_1}{d_1} \right] + \left[ \frac{3M_1 \alpha/(e_1 + 2)^2 d_1}{d_1} \right]
\]  
(6)

where \(M_1\) and \(M_2\) were the molecular weight of solvent and solute respectively. In the calculation of the dipole moment \((\mu)\), the induced polarization was assumed equal to the molar refraction measured at the sodium D-line \((R_D)\)\(^{56}\), and \(\mu\) was calculated according to:

\[
\mu = 0.012181 \times 10^{-18} \left[ (P_{2\infty} - R_D)T \right]^{1/2}
\]  
(7)

where \(T\) was the absolute temperature of the measurement. Molar refractions were calculated as the sum of standard bond refractions\(^{57}\) and were part of the data.

3. Correction Calculation. The program defined \(e_{12}\) according to equation 8, where \(S_N\) and \(S_{12}\) referred to the scale value for nitrogen and the solution, respectively, \(K(\text{CELL})\) was the negative reciprocal of equation 3, and \(1\) was the dielectric constant of nitrogen.

\[
e_{12} = \frac{S_N - S_{12}}{K(\text{CELL})} + 1
\]  
(8)

Since the value of the dielectric constant used for nitrogen should have been 1.0005 (see p. 79), a correction of + 0.0005 had to be applied to \(e_{12}\) as calculated by
the program. In the $e_{12}$ vs $N_2$ plot, the correction resulted in the addition of a constant to all points of the abscissa, and therefore increased the value of $e_1$ by +0.0005 but had no effect on $\alpha$, the slope. Consequently, 0.0005 was added to the values of $e_1$ typed out by the computer and the dipole moments were recalculated from equations 6 and 7. Values for $\alpha, \beta$ and $d_1$ were obtained from the computer calculations, since these were unaffected by the correction. The corrected values for $e_1, P_{2\infty}$, and $\mu$ are listed in the tables.

4. Dipole Moment Data for Diethyl Sulfate. The data from six determinations were read into the computer. One determination was discarded from the $N_2$ vs $d_{12}$ plot and one from the $e_{12}$ vs $N_2$ plot. Preliminary graphs had indicated the discarded points to be outside the experimental error. Both $d_1$ and $e_1$ were calculated on the basis of five determinations. In the calculation of $\mu$, $T$ had the value 298.07 and the molar refractivity at the sodium D-line, 31.752 cc. The data are listed in Table V.

5. Dipole Moment Data for Ethylene Sulfate. The data from five determinations were read into the computer. No determinations were discarded from the $N_2$ vs $d_{12}$ plot, but one was discarded from the $e_{12}$ vs $N_2$ plot. In the calculation of the dipole moment, $T$ had the value 298.05, and the molar refractivity at the sodium D-line, 20.400 cc. The data are listed in Table VI.

6. Dipole Moment Data for Glyoxal Sulfate. The data from six determinations were read into the computer. All the data was used for the $N_2$ vs $d_{12}$ plot, but one determination was discarded from the $e_{12}$ vs $N_2$ plot. Preliminary graphs had indicated the discarded point to be outside experimental error. In the calculation of the dipole
moment, T had the value 298.05, and the molar refractivity at the sodium D-line, 29.448 cc. The data are listed in Table VII.
TABLE V
Dipole Moment Data for Diethyl Sulfate at 24.9°
(dioxane solvent)

<table>
<thead>
<tr>
<th>$N_2$</th>
<th>$d_{12}$</th>
<th>$e_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000</td>
<td>1.02840</td>
<td>2.2066</td>
</tr>
<tr>
<td>0.001026</td>
<td>1.02983</td>
<td>2.2387</td>
</tr>
<tr>
<td>0.002082</td>
<td>1.02857</td>
<td>2.2377</td>
</tr>
<tr>
<td>0.003824</td>
<td>1.02891</td>
<td>2.3082</td>
</tr>
<tr>
<td>0.004363</td>
<td>1.02909</td>
<td>2.3314</td>
</tr>
<tr>
<td>0.005612</td>
<td>1.02935</td>
<td>2.3593</td>
</tr>
</tbody>
</table>

$\alpha = 27.1439$  $\beta = 0.1730$  $e_1 = 2.2084$

$d_1 = 1.02832$  $P_{2\alpha} = 432.87 \, \text{cc.}$  $\mu = 4.43 \, \text{D.}$
TABLE VI

Dipole Moment Data for Ethylene Sulfate at 24.9°
(dioxane solvent)

<table>
<thead>
<tr>
<th>( N_2 )</th>
<th>( d_{12} )</th>
<th>( e_{12} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000</td>
<td>1.02834</td>
<td>2.2043</td>
</tr>
<tr>
<td>0.000748</td>
<td>1.02848</td>
<td>2.2195</td>
</tr>
<tr>
<td>0.001624</td>
<td>1.02888</td>
<td>2.2711</td>
</tr>
<tr>
<td>0.002269</td>
<td>1.02942</td>
<td>2.2995</td>
</tr>
<tr>
<td>0.003660</td>
<td>1.02977</td>
<td>2.3671</td>
</tr>
</tbody>
</table>

\( \alpha = 44.3857 \quad \beta = 0.4432 \quad e_1 = 2.2017 \)

\( d_1 = 1.02822 \quad p_{2\infty} = 670.28 \text{ cc.} \quad \mu = 5.64 \text{ D.} \)
**TABLE VII**

Dipole Moment Data for Glyoxal Sulfate at 24.9°
(dioxane solvent)

<table>
<thead>
<tr>
<th>$N_2$</th>
<th>$d_{12}$</th>
<th>$e_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.000000</td>
<td>1.02824</td>
<td>2.2054</td>
</tr>
<tr>
<td>0.000523</td>
<td>1.02894</td>
<td>2.2284</td>
</tr>
<tr>
<td>0.000780</td>
<td>1.02928</td>
<td>2.2292</td>
</tr>
<tr>
<td>0.001711</td>
<td>1.03042</td>
<td>2.2732</td>
</tr>
<tr>
<td>0.002886</td>
<td>1.03199</td>
<td>2.3190</td>
</tr>
<tr>
<td>0.004991</td>
<td>1.03460</td>
<td>2.4074</td>
</tr>
</tbody>
</table>

$\alpha = 40.1470$  
$\beta = 1.2742$  
$e_1 = 2.2055$

$d_1 = 1.02826$  
$P_{2\infty} = 613.86$ cc.  
$\mu = 5.35$ D.
BIBLIOGRAPHY AND ACKNOWLEDGEMENTS


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20. For a recent review see ref. 6, pp. 367-371.
29. Ref. 28, p. 370.
31. Experimental Section, pp. 75, 76.
32. Ref. 28, p. 276.
34. Ref. 27, p. 350.
42. Ref. 37, p. 59.
43. Ref. 37, p. 52.

47. Technical assistance by R. J. Panicci is gratefully acknowledged.


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APPENDIX I

The Fortran II Program Used in The Calculation of the Dipole Moments
**TABLE VIII**

Input Data for Calculation of Dipole Moments

<table>
<thead>
<tr>
<th>Card Space</th>
<th>Card 1</th>
<th>Card 2--Card N+1</th>
<th>Card N+2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1--10</td>
<td>N</td>
<td>weight of flask</td>
<td>D</td>
</tr>
<tr>
<td>11--20</td>
<td>M₁</td>
<td>weight of flask</td>
<td>E</td>
</tr>
<tr>
<td></td>
<td></td>
<td>plus sample</td>
<td></td>
</tr>
<tr>
<td>21--30</td>
<td>M₂</td>
<td>weight of flask</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>plus sample plus solvent</td>
<td></td>
</tr>
<tr>
<td>31--40</td>
<td>M(R)</td>
<td>weight of full</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pycnometer</td>
<td></td>
</tr>
<tr>
<td>41--50</td>
<td>T</td>
<td>weight of empty</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pycnometer</td>
<td></td>
</tr>
<tr>
<td>51--60</td>
<td>KC</td>
<td>volume of</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pycnometer</td>
<td></td>
</tr>
<tr>
<td>61--70</td>
<td>K(CELL)</td>
<td>scale value for</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>nitrogen</td>
<td></td>
</tr>
<tr>
<td>71--80</td>
<td>BL</td>
<td>scale value for</td>
<td>BL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sample solution</td>
<td></td>
</tr>
</tbody>
</table>

N = number of solutions plus one (for solvent).
M₁, M₂ = molecular weight of solvent and sample, respectively.
M(R) = molar refraction
T = absolute temperature
KC = condenser correction which was not necessary with the instrument employed and was left blank.
K(CELL) = cell constant.
BL = blank.
D = allowed deviation from the least squares line of $N_2$ vs $d_{12}$ in mole fraction.
E = allowed deviation from the least squares line of $e_{12}$ vs $N_2$ in dielectric constant.
C  DIPOLE MOMENT PROGRAM
DIMENSIONC(37),Y(131),XN2(10),D(10),EP(10)
1  PRINT 201
201  FORMAT(15H1 DIPOLE MOMENT,/)  
2  READ 101, C1, C2, C3, C4, C5, C6, C7, C8
101  FORMAT(8F10.5)
   IC=C1
   IC=8*IC
3  READ 101, (Y(IQ),IQ=1,IC)
250  FORMAT(1HK,10X,2HN=,F4.0,5X,3HM1=,F10.5,5X,3HM2=,F10.5,5X,5HM(R)=,F10.5)
   PRINT 250,C5,C6,C7
251  FORMAT(1HK,10X,2HT=,F7.2,8X,3HKC=,F10.5,5X,8HK(CELL)=,F10.3)
   NCTR=C1
   DO 260 I=1,NCTR
   K=I*8-7
   J=I*8
   L=I*8-4
   M=I*8-3
   PRINT 261,1,(Y(IQ),IQ=K,L)
261  FORMAT(1HK,5X,6HP1N0T,12,4F13.5)
260  PRINT 262,(Y(KQ),KQ=M,J)
262  FORMAT(1HK,13X,4F13.5)
4  READ 102,Y(120),Y(121)
102  FORMAT(8F10.9)
99  N=C1
   PRINT 265,Y(120),Y(121)
265  FORMAT(1HK,10X,2HD=,F11.9,5X,2HE=,F11.9)
   IB=C1
   DO 8 I=1,N
   Y81=(Y(8*I-6)-Y(8*I-7))/C3
   C(3*I+5)=Y81/(Y81+((Y(8*I-5)-Y(8*I-6))/C2))
   XN2(I)=C(3*I+5)
   C(3*I+6)=(Y(8*I-4)-Y(8*I-3))/Y(8*I-2)
   D(I)=C(3*I+6)
   C(3*I+7)=(Y(8*I-1)-Y(8*I)+C6+C7)/C7
   EP(I)=C(3*I+7)
   PRINT 202,1*XN2(I),D(I),EP(I)
8  PRINT 203,1*XN2(I),D(I),EP(I)
202  FORMAT(1HK,5X,2H1=,12,5X,3HN2=,F12.9,5X,2HD=,F10.7,5X,2HE=,F10.5)
203  FORMAT(5X,2H1=,12,5X,3HN2=,F12.9,5X,2HD=,F10.7,5X,2HE=,F10.5,17X,1
   5HPUNCH)
   DO 10 I=1,N
   Y(I+89)=C(3*I+5)
10  Y(I+99)=C(3*I+6)
11  Y110=C1
12  I4=0
13  D2=0
64  I5=Y110
73  J=Y110
   DO 65 I=1,J
65  Y(I+121)=Y(I+99)
14  Y82=0
   Y83=0
   Y84=0
   Y85=0
18  K=Y110
   DO 22 I=1,K
   Y82=Y82+Y(I+89)

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Y83 = Y83 + Y(I+99)
Y84 = Y84 + (Y(I+99) * Y(I+89))
22 Y85 = Y85 + (Y(I+89) * Y(I+89))
Y86 = Y82 * 2
24 Y87 = (Y110 * Y84) - (Y82 * Y83) / (Y110 * Y85) - Y86
25 Y88 = (Y83 / Y110) - (Y87 * Y82) / Y110
26 I = 0
27 I = 0
28 I = I + 1
29 Y89 = (Y88 + (Y87 * (Y(I+89))) - Y(I+99))
Y(I) = Y89
IF (I <= 1) 161, 17, 17
17 D(I) = Y89
61 ERROR = Y89
ERROR = ERROR + CB
PRINT 204, I, ERROR
PRINT 205, I, ERROR
204 FORMAT(1HJ, 10X, 2HI = , 12, 5X, 6HErrOr = , F12.9)
205 FORMAT(10X, 2HI = , 12, 5X, 6HErrOr = , F12.9, 43X, 5HPUNCH)
62 Y = ABSF(Y89)
Y111 = Y(I+120) - Y
30 IF (Y111) 31, 31, 36
31 I = I + 1
IF (I <= 1) 32, 15, 15
15 I8 = I8 - 12
X2(I) = 0
32 PRINT 207, 14, 12, Y(I+89), Y(I+99)
19 PRINT 208, 14, 12, Y(I+89), Y(I+99)
207 FORMAT(1HI, 10X, 3HI = , 12, 5X, 3H12 = , 12, 5X, 3HN2 = , F12.9, 5X, 2HX = , F10.7)
208 FORMAT(10X, 3HI = , 12, 5X, 3H12 = , 12, 5X, 3HN2 = , F12.9, 5X, 2HX = , F10.7, 18X, 5HPUNCH)
33 I1 = Y110
IF (I1 <= 1) 34, 34, 38
34 I6 = 2 * I12
35 IF (N <= 16) 5, 5, 40
5 Y(I+120) = 2 * Y(I+120)
74 GO TO 99
36 I3 = I3 + 1
37 Y(I3+89) = Y(I+89)
38 Y(I+99) = Y(I+99)
39 GO TO 33
40 M = Y110
IF (I3 - M) 41, 42, 41
41 Y110 = I3
63 I5 = Y110
69 GO TO 14
42 IF (I4 <= 1) 44, 43, 43
43 GO TO 53
44 Y112 = Y88
45 Y113 = Y87
46 DO 48 I = 1, N
47 Y(I+89) = C(I3+15)
48 Y(I+99) = C(I3+7)
49 I4 = 1
50 I2 = 0
51 Y110 = C1
52 GO TO 14
53 Y114 = (Y88 - 1) / ((Y88+2) * Y112)
54 Y115 = C2 / Y112
55 Y116 = (I3 * C2) / ((Y88+2) * (Y88+2) * Y112)

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56 \ Y117=\(Y114*(C3-(Y115*Y113))\)+Y116*Y87
57 \ Y117=Y117-C4
58 \ IF (Y117) 77,77,57
59 \ Y118=0.*
60 \ C40=0.*
61 \ GO TO 59
62 \ Y118=Y117*C5
63 \ Y118=Y118*0.5
64 \ Y118=0.*01281*Y118
65 \ Y117=Y117+C4
66 \ PRINT 209,Y87,Y88,Y112,Y113
67 \ PRINT 210,Y87,Y88,Y112,Y113
68 \ FORMAT(1HJ,5X,2HA=,F10.4,5X,3HE1=,F10.5,5X,3HD1=,F10.6,5X,2HB=,F10.4)
69 \ FORMAT(5X,2HA=,F10.4,5X,3HE1=,F10.5,5X,3HD1=,F10.6,5X,2HB=,F10.4,
70 \ 10X,5HPUNCH)
71 \ C38=0.*
72 \ C39=0.*
73 \ C40=0.*
74 \ I9=N
75 \ D0 75 I=1,18
76 \ C38=C38+D(I)*D(I)
77 \ D0 76 I=1,19
78 \ C39=C39+XN2(I)*XN2(I)
79 \ C40=C40+XN2(I)
80 \ C40=C40*C40
81 \ C40=C38/(C39*C41-C40)
82 \ C40=(C41/(C41-2.*))*C40
83 \ C40 = SQRTF(C40)
84 \ C40=0.*0046*C40/Y118
85 \ C40=C40*C2
86 \ PRINT 211,Y117,Y118,C40
87 \ PRINT 212,Y117,Y118,C40
88 \ FORMAT(1HJ,5X,6HP2INF=,F10.2,5X,7HMOMENT=,F7.4,5X,6HERROR=.F6.4)
89 \ FORMAT(5X,6HP2INF=,F10.2,5X,7HMOMENT=,F7.4,5X,6HERROR=.F6.4,23X,1 5HPUNCH)
90 \ GO TO 1
91 \ END
APPENDIX II

Output Data From The Calculation of The Dipole Moment of Diethyl Sulfate
**Dipole Moment**

<table>
<thead>
<tr>
<th>( N )</th>
<th>( M_1 )</th>
<th>( M_2 )</th>
<th>( M(R) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>88.10720</td>
<td>154.18590</td>
<td>31.58200</td>
</tr>
</tbody>
</table>

\( T = 298.07 \), \( K = 0.00000 \), \( K(CELL) = -1488.760 \)

| POINT, 1 | 18.84590 | 4.84346 | 774.59000 | 2570.11000 |
| POINT, 2 | 23.94910 | 23.98630 | 44.68670 | 23.78840 |
| POINT, 3 | 24.02340 | 24.26210 | 46.26180 | 23.82040 |
| POINT, 4 | 18.84590 | 4.83386 | 774.59000 | 2756.00000 |
| POINT, 5 | 23.68070 | 23.75660 | 44.54260 | 23.83710 |
| POINT, 6 | 18.84590 | 4.83117 | 774.56000 | 2716.45000 |

\( D = .00000000 \), \( E = .01000000 \)

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<th>( N_2 )</th>
<th>( D )</th>
<th>( E )</th>
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</thead>
<tbody>
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<td>1.0293512</td>
<td>2.35884</td>
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\( I = 3 \) \( \text{ERROR} = .00040610 \)

\( I = 4 \) \( \text{ERROR} = .00040610 \)

\( I = 5 \) \( \text{ERROR} = .00040610 \)

\( I = 6 \) \( \text{ERROR} = .00040610 \)

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<th>I =</th>
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\[
\begin{align*}
I &= \frac{1}{2} \\
N &= \frac{1}{2} \\
X &= 2.2371973
\end{align*}
\]

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<tr>
<th>A</th>
<th>E1</th>
<th>D1</th>
<th>R</th>
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<td>27.1439</td>
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<tr>
<td>27.1439</td>
<td>2.20787</td>
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\[
P2_{\text{INF}} = 432.95 \quad \text{MOMENT} = 4.4307 \quad \text{ERROR} = 0.0778
\]
APPENDIX III

Output Data From The Calculation of
The Dipole Moment of Ethylene Sulfate
### Dipole Moment

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<thead>
<tr>
<th>N</th>
<th>M1</th>
<th>M2</th>
<th>M(R)</th>
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<tbody>
<tr>
<td>5</td>
<td>88.10720</td>
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**Point 1**

<table>
<thead>
<tr>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>KC</th>
<th>M(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.84530</td>
<td>4.83040</td>
<td>774.59000</td>
<td>2566.75000</td>
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**Point 2**

<table>
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<tr>
<th>X</th>
<th>Y</th>
<th>Z</th>
<th>KC</th>
<th>M(C)</th>
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</thead>
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<tr>
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<td>20.41970</td>
<td>774.59000</td>
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**Point 3**

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<th>Z</th>
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<tbody>
<tr>
<td>19.68440</td>
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**Point 4**

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</thead>
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<tr>
<td>23.23660</td>
<td>23.28740</td>
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**Point 5**

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<th>Z</th>
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<th>M(C)</th>
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<tr>
<td>23.07910</td>
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**Error Calculation**

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**Additional Data**

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<th>B</th>
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APPENDIX IV

Output Data From The Calculation of
The Dipole Moment of Glyoxal Sulfate
**Dipole Moment**

<table>
<thead>
<tr>
<th>N</th>
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<th>M2</th>
<th>M(M)</th>
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<tbody>
<tr>
<td>6</td>
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<table>
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<td>4.83040</td>
<td>774.59000</td>
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<tr>
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<td>40.09890</td>
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<td>D = 1.0282378</td>
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<tr>
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</tr>
<tr>
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<td>D = 1.0319874</td>
</tr>
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<table>
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<td>E = 2.40686</td>
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| I = 5 ERROR = -.00005010 | I = 5 ERROR = -.00005010 |
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| I4 = 1 I2 = 1 N2 = .00079992 | X = 2.2287474 |

| I = 4 ERROR = -.0042830 | I = 4 ERROR = -.0042830 |
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