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WITH THALLIC ACETATE.

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OXIDATIVE CLEAVAGE OF CYCLOPROPANES

WITH THALLIC ACETATE

DISSertation

Presented in Partial Fulfillment of the Requirements for
the Degree Doctor of Philosophy in the Graduate
School of The Ohio State University

By

Aubrey South, Jr., B.S.

* * * * * *

The Ohio State University
1967

Approved by

Robert J. Carlinette
Adviser
Department of Chemistry
DEDICATION

To Peggy for her understanding and encouragement throughout the course of the study
I wish to thank Professor Robert J. Ouellette for suggesting this problem and to acknowledge his educational instruction throughout the course of this study.
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Studies in Inorganic Chemistry. Professor Sheldon Shore
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INTRODUCTION

Oxidations with lead tetraacetate\(^1\) and mercuric acetate\(^2-4\) have been studied extensively on a variety of substrates. Thallic acetate was first reported by Meyer\(^5\) in 1903, but it has been used only in recent years on a relatively limited scale. The oxidation potential of the thallic oxidation state is between those of mercuric and plumbic,\(^6\) and thallium appears immediately between mercury and lead in the periodic table.

\[
Pb^{+4} + 2e^- \rightarrow Pb^{+2} \quad E_o = ca. 1.7
\]

\[
Tl^{+3} + 2e^- \rightarrow Tl^+ \quad E_o = 1.25
\]

\[
Hg^{+2} + 2e^- \rightarrow Hg^0 \quad E_o = 0.854
\]

It is surprising that thallic oxidations have not been investigated more extensively. Oxidation by thallic salts would be expected to be more selective and less drastic than plumbic salts, yet more drastic than mercuric salts. Thallic acetate or other carboxylate salts have been used for the oxidation of phenols,\(^7\) thallation of aromatic compounds,\(^8\) and reactions with olefins\(^9-15\) and organomercury compounds.\(^16,17\) Kabbe\(^9\) reported in a comparative study that, in fact, the properties of thallic acetate are between those of lead tetraacetate and mercuric acetate.

In oxymercuration of olefins, the mercuric acetate addition adduct can easily be isolated,\(^2\) but only two adducts have been isolated and characterized with thallic acetate.\(^9,13\) The lead tetraacetate adduct with double bonds has yet to be isolated and characterized, although an adduct has been postulated to explain kinetic
data for the reaction with anethole.\textsuperscript{18} Weinstein\textsuperscript{13} isolated a very unstable solid, presumably the adduct, from the reaction of lead tetraacetate with norbornadiene, but was not able to characterize it.

The products from the reactions of olefins with these heavy metal acetates are explained best as proceeding through an addition adduct which is either isolated or decomposed, through a carbonium ion, to organic products and lower valent metal acetates or free mercury. The order of stability of the adducts are in agreement with the respective oxidation potentials of the metal ions.

\[
\begin{align*}
\text{C} = \text{C} & + M(\text{OAc})_x \rightarrow \text{C} - \text{C} \rightarrow \text{Products} + M(\text{OAc})_{x-2}
\end{align*}
\]

\[\text{AcO} \quad M(\text{OAc})_{x-1}\]

The stereochemistry of oxymetallation has been of interest to workers in heavy metal acetates oxidations. Oxymercuration is \textit{trans} with typical olefins, such as cyclohexene.\textsuperscript{19} However, oxymercuration of norbornene is \textit{cis-exo} with no rearrangement.\textsuperscript{19-21} The isolated oxythallated product from norbornadiene was shown to be \textit{cis-exo} by nmr analysis.\textsuperscript{22} Winston\textsuperscript{11} postulated that in the thallic acetate oxidation of cyclohexene and cyclopentene, the \textit{trans-1,2-diacetoxy-cycloalkane} was obtained by \textit{trans}-addition of thallic acetate. This \textit{trans}-adduct then decomposed with stabilization of the incipient positive charge by anchiomeric assistance of the neighboring acetate function. Neutralization of this charged intermediate by acetic acid or acetate ion resulted in producing \textit{trans}-diacetate.
Just prior to the introduction of thalic acetate into the literature, early workers in reactions of cyclopropanes were generating great interest in this strained reactive cycloalkane. Most electrophilic reagents commonly employed with olefins also attack cyclopropane bonds to give products resulting from ring cleavage. Many such reactions are summarized in Lukina's\textsuperscript{23} review on the structure and reactivity of cyclopropanes.

Physical and theoretical chemists became interested in cyclopropanes and suggested models to explain their reactivity.\textsuperscript{23} Coulson and Moffitt\textsuperscript{24} revised previous theories by considering that the hybridization of the carbon-carbon bonds is different than that of the carbon-hydrogen bonds, and that neither is sp\textsuperscript{2} nor sp\textsuperscript{3}. They postulated that the internal carbon-carbon bonds are bent, termed "banana" bonds. Using this model Ingraham\textsuperscript{25} calculated that the bent endo-ring orbitals are sp\textsuperscript{4.12} as exo-ring orbitals, sp\textsuperscript{2.28}. Ingraham suggested that these p-weighted internal cyclopropyl bonds are well placed for conjugation with unsaturated groups. Conjugation between cyclopropane rings and unsaturated substituents was first observed by Kizhner\textsuperscript{26} in 1913 and later by Robinson\textsuperscript{27} in 1916. The review by Lukina\textsuperscript{23} presents several examples of cyclopropyl conjugation effects.

Other physical evidence was presented showing that cyclopropanes are more similar to olefins than alkanes. Linnett\textsuperscript{28} found the force
constant for carbon-hydrogen stretching in cyclopropane is $5.0 \times 10^5$ dynes/cm. as compared to those of methane and ethylene being $4.79 \times 10^5$ and $5.1 \times 10^5$ dynes/cm., respectively. Muller\textsuperscript{30} found a coupling constant of 161 ops for cyclopropane, which is to be compared to 125 and 156 ops for methane and ethylene, respectively. An elementary molecular orbital treatment of cyclopropane by Handler\textsuperscript{32} also suggests that the internal bonds are close to $sp^2$ hybridization. The strain of the small ring is the ultimate reason for all the above anomalies relative to most cycloalkanes. Based on strain free cyclohexane, Seubold\textsuperscript{33} found the strain energy to be 27.4 kcal./mole.

The direction of cyclopropane ring opening by electrophilic reagents is of interest in substituted cyclopropanes. The ring cleavage can be considered to involve initial electrophilic attack to give an intermediate carbonium ion. Therefore, the stability of the generated charge affects the bond which is attacked and the direction of opening.\textsuperscript{23}

Cyclopropane reactions pertinent to this study are those involving oxidative cleavage with heavy metal acetates. Although this study is the only one known in thallic acetate cleavage, lead tetraacetate and mercuric acetate have been used. Monosubstituted cyclopropanes have been cleaved with lead tetraacetate and products examined.\textsuperscript{34} The products were explained as proceeding through an oxyplumbate adduct. Ring opening occurred at the bond which would lead to the most stable carbonium ion. Several mono- and poly-substituted cyclopropanes were cleaved with

$$R\overset{<}{\text{+ Pb(OAc)}_4 \rightarrow R\text{OAc}\overset{\text{Pb(OAc)}_3 \rightarrow \text{Products + Pb(OAc)}_2}$$
mercuric acetate to give the isolated oxymercuration adduct.\textsuperscript{35-38} Again the opening was in the direction so as to give the most stable intermediate carbonium ion.

\[
R \quad + \quad \text{Hg(0Ac)}_2 \xrightarrow{R'OH} \quad R' \quad \text{Hg0Ac}
\]

\[ R' = H \text{ or Me} \]

Ouellette,\textsuperscript{39} Criegee,\textsuperscript{40} and Moon\textsuperscript{41} have shown that bicyclo(n.1.0)-alkanes, when n is 2, 3, or 4, are cleaved with lead tetraacetate. Levina\textsuperscript{42} has cleaved them with mercuric acetate. In these bicyclic systems, there are two different cyclopropane bonds, internal bond, a, and two external bonds, b. Cleavage of either bond a or b would result in a secondary carbonium ion. However, the amount of internal bond cleavage increased with increasing strain of the system. The same result was observed with acid catalyzed ring opening of the same bicyclics by LaLonde.\textsuperscript{43}

The results from the preceding introduction prompted this study of thallic acetate oxidative cleavages of cyclopropanes. The compounds to be considered are bicyclo(n.1.0)alkanes, tricyclo(2.2.1.0\textsuperscript{2,6})heptane, tricyclo(3.2.1.0\textsuperscript{2,4})octane, and substituted phenylcyclopropanes will be discussed. An investigation of conditions for thallic acetate preparation and its kinetic decomposition will be presented.
CLEAVAGE OF BICYCLO(n.1.0)ALKANES

Bicyclo(n.1.0)alkanes, where n is 2, 3, and 4, react with thallic acetate in anhydrous acetic acid to give a mixture of diacetates and olefinic monoacetates. The thallic acetate was prepared in situ at 75° by the reaction of thallic oxide with anhydrous acetic acid and enough acetic anhydride to remove the water formed. To the thallic solution, a 50% excess of the bicyclic compound was added. After the reaction was complete, the acetic acid was removed, and the mixture of acetate esters was analyzed by gas chromatography. The products were identified with known prepared acetates. Bicyclo(4.1.0)heptane and bicyclo(3.1.0)hexane were cleaved at 75°, and bicyclo(2.1.0)pentane was reacted at 25°. The products and percentages are listed in Tables 2, 3, and 4 for n of 2, 3, and 4, respectively. The products from lead tetra-acetate reactions with these bicyclic compounds are also listed in the corresponding table for comparison.

In bicyclo(n.1.0)alkane systems there are two different cyclopropane bonds, two equivalent external bonds and the internal bond. External bond cleavage might be expected to predominate over internal cleavage because of less steric hindrance and a statistical factor of two. However, another important consideration is the relief of strain. Oxidation of bicyclo(2.1.0)pentane resulted only in internal bond cleavage products. The per cent internal bond cleavage increases with decreasing ring size, increasing strain, with thallic and plumbic acetates. Lalonde obtained similar results in the acid catalyzed
ring opening of the same bicyclics in acetic acid. A comparison of external to internal bond cleavage ratios for proton, thallic acetate, and lead tetraacetate is shown in Table 1. Levina has isolated products of oxymercuration from the reaction of these bicyclic systems with mercuric acetate in water. The products were not quantitatively investigated and only the isolated solid alkylmercuric acetates were reported. Products of oxymercuration were, where n is 2, 80% yield of 3-hydroxycyclopentylmercuric acetate, for n of 3, 2-hydroxycyclopentylmethylmercuric acetate, isolated as the mercuric bromide in 60% overall yield, and n of 4, 2-hydroxycyclohexylmethylmercuric acetate in 86% yield. A bond cleavage ratio can not be obtained from Levina's work with mercuric acetate. Solvolysis of alkylmercurials are known to be sensitive to changes in structure. Secondary alkylmercury compounds solvolyze $10^5$ times faster than primary alkylmercurials. Therefore, oxymercuration products from internal bond cleavage could solvolyze to organic acetates. If this were the case, then the yields which were unaccounted for could be, for the most part, from internal cleavage. The external

<table>
<thead>
<tr>
<th>n</th>
<th>$\text{Tl(OAc)}_3$</th>
<th>$\text{Pb(OAc)}_4$</th>
<th>Proton</th>
</tr>
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<tr>
<td>4</td>
<td>10.1</td>
<td>2.1</td>
<td>1.1</td>
</tr>
<tr>
<td>3</td>
<td>0.9</td>
<td>0.3</td>
<td>4.4</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>0</td>
<td>0</td>
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TABLE 1
EXTERNAL TO INTERNAL BOND CLEAVAGE RATIOS FOR ELECTROPHILIC ATTACK ON BICYCLO(n.1.0)ALKANES
to internal bond cleavage ratio could be approximated as 0, 1.5, and 6 for bicyclopentane, hexane and heptane, respectively. The values are at least minimum values which is in fair agreement with data in Table 1. The order of decreasing selectivity is proton > thallic acetate > lead tetraacetate. As an approximation the selectivity of mercuric acetate is about the same as that of thallic acetate. Qualitatively, this is to be expected.

The stereochemistry of the products of thallic acetate cleavage can be rationalized as initial trans-oxythallation of both external and internal bonds. However, the mode of decomposition of the adduct is also of considerable importance in determining the stereochemistry of the ultimate product.

Products from thallic acetate oxidation of bicyclo(2.1.0)pentane are a result of internal bond cleavage only (Table 2). The intermediate (I) from trans-oxythallation decomposes to give a carbonium ion (II). This ion can eliminate a proton from either of the two adjacent positions to yield the two observed olefinic acetates, (III) and (IV). Alternatively, the intermediate can decompose to give diacetates, however, this decomposition is stereospecific to give only
### TABLE 2

**CLEAVAGE PRODUCTS OF BICYCLO(2.1.0)PENTANE**

<table>
<thead>
<tr>
<th>Product</th>
<th>References</th>
<th>Tl(OAc)$_3$ Yield, %</th>
<th>Pb(OAc)$_4$ Yield, %</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>22.5</td>
<td>24.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>27.5</td>
<td>35.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>50.0</td>
<td>39.5</td>
</tr>
</tbody>
</table>

$^\text{a}$The author wishes to thank Dr. P. G. Gassman and Mr. K. Mansfield for the bicyclo(2.1.0)pentane used in this study.

trans-1,3-diacetoxy cyclopentane (V). This can be rationalized by an acetoxonium ion (IIa), which retains the stereochemistry of initial oxythallation.
Winstein\textsuperscript{11} postulated that oxythallation of cyclohexene was trans, followed by 1,2-acetate participation in decomposition to give trans-1,2-diacetoxycyclohexane. Dolby\textsuperscript{49} has reported 1,3-acetate participation in solvolysis of trans-2-acetoxymethylcyclohexyl brosylate to give cis-2-acetoxymethylcyclohexyl acetate stereospecifically. No 1,2-diacetoxycyclopentane was observed; if present, it was a small per cent of the total reaction mixture. Lalonde\textsuperscript{50} found that trans-1,2-dihalocyclopentanes were the major products from the reaction of bromine and chlorine with bicyclo(2.1.0)pentane. This was explained as attack on the internal bond by $\mathbf{X}^+$ to form a 1,3-bridged intermediate carbonium ion (IIb). This 1,3-bridged ion rearranges to the 1,2-bridged ion (IIc) by a 1,2-hydride shift. Attack of $\mathbf{X}^-$ on the less strained ion (IIc) yields

\begin{equation}
\text{cyclohexene} + \mathbf{X}^+ \rightarrow \text{trans-dihalocyclopentane}
\end{equation}

the trans-dihalocyclopentane. Oxymercuration of norbornene is known to occur without rearrangement.\textsuperscript{19-21} Oxythallation of norbornadiene also proceeds without rearrangement, but the adduct does rearrange during decomposition.\textsuperscript{13} Therefore, rearrangement of (I) to yield 1,2-diacetates would presumably occur through decomposition. An acetate would be a better 1,3-bridging group in (IIa) than halogen in (IIb) because of less strain, accounting for the absence of the 1,2-isomeric diacetate.

Products from bicyclo(3.1.0)hexane result from both internal and external bond cleavage (Table 3). The only observed product from
<table>
<thead>
<tr>
<th>Product</th>
<th>References</th>
<th>Tl(OAc)$_3$ Yield, %</th>
<th>Pb(OAc)$_4$ Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Product 1" /></td>
<td>45,51</td>
<td>19.6</td>
<td>24.0</td>
</tr>
<tr>
<td><img src="image2" alt="Product 2" /></td>
<td>45,52</td>
<td>24.9</td>
<td>27.0</td>
</tr>
<tr>
<td><img src="image3" alt="Product 3" /></td>
<td>39,45</td>
<td>46.5</td>
<td>24.5</td>
</tr>
<tr>
<td><img src="image4" alt="Product 4" /></td>
<td>45,53</td>
<td>3.4 Trace</td>
<td></td>
</tr>
<tr>
<td><img src="image5" alt="Product 5" /></td>
<td>45,53</td>
<td>5.6</td>
<td>24.5</td>
</tr>
</tbody>
</table>
external bond breaking is trans-2-acetoxymethylcyclopentyl acetate (VII).

\[
\begin{align*}
\text{[Diagram showing chemical structures]} \\
\text{This product is probably formed by stereospecific trans-addition to give} \\
\text{the organothallium intermediate (VI), which then decomposes in a manner} \\
\text{so as to preserve the trans-stereochemistry. The intermediate (VI) is the} \\
\text{result of ring opening in a direction to give the most stable carbonium} \\
\text{ion. The organothallium intermediate (VIII) derived from internal bond} \\
\text{cleavage decomposes to yield four products, (IX), (X), (XI), and (XII).}
\end{align*}
\]

The presence of \( \Delta^2 \) - and \( \Delta^3 \) -cyclohexenyl acetates (IX) and (X) are the expected products from loss of a proton during decomposition. The presence of both trans- and cis-1,2-diacetoxycyclohexane (XI) and (XII) is difficult to rationalize on the basis of available data. Lead tetra-acetate oxidation gave only cis-diacetate (XII) as reported independently by both Ouellette\(^{39} \) and Moon.\(^{41} \) The percentages of the cis- and trans-diacetates and olefinic acetates could be a function of the population of conformers (VIIIa) and (VIIIb) if the rates of decomposition are comparable to the rate of interconversion. However, it is more likely
that the activation energies for decomposition are greater than the energy required for interconversion of the conformers. Therefore, the Curtin-Hammett principle\(^{54}\) should apply and the product ratios are only a reflection of the activation energies for product formation and does not depend upon the population of the conformers. Jensen\(^{54}\) found that the bromomercuric group has no conformation preference, however, it is linear.

![Diagram](https://via.placeholder.com/150)

The conformational preference of the diacetoxythallium group is not known. Only in conformation (VIIIa), the acetate being axial, can 1,3-acetate participation be effective in directing the stereochemistry of the end product. A similar result has been noted with cycloolefins.

![Diagram](https://via.placeholder.com/150)
Thallic acetate oxidation of cyclopentene\textsuperscript{11} gives only \textit{trans}-1,2-diacetate whereas with cyclohexene\textsuperscript{11,15} both \textit{trans} and \textit{cis} are observed.

Cleavage of the external bond of bicyclo(4.1.0)heptane with thallium triacetate (Table 4), yields \textit{trans}-2-acetoxymethylcyclohexyl acetate (XIV) probably via the \textit{trans}-intermediate (XIII). The intermediate (XV) from \textit{trans} internal bond addition decomposed to give only

\[ \text{Cyclopentene} + \text{Ti(OAc)}_3 \rightarrow \text{trans-2-acetoxymethylcyclohexyl acetate (XIV)} \]

\[ \text{trans-2-acetoxymethylcyclohexyl acetate (XIV) - 91%} \]

\[ \Delta^3\text{-cycloheptenyl acetate (XVI)} \text{ and } \text{trans-1,3-diacetoxycycloheptane (XVII)} \]

The absence of the \(\Delta^2\)-olefinic acetate might be a reflection of the mode of decomposition of the intermediate (XV). Only \textit{trans}-1,3-diacetate (XVII) was observed which again could be the result of 1,3-acetate participation in a favorable conformational form.

There are other possible considerations which can affect the stereochemistry of the products. Stereochemistry of the organothallium intermediate could be maintained by internal return of an acetate from the diacetoxythallium group by a S\textsubscript{N}1 type substitution. Internal bond
<table>
<thead>
<tr>
<th>Product(^a)</th>
<th>References</th>
<th>Tl(OAc)(_3) Yield, %</th>
<th>Pb(OAc)(_4) (^*) Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image" alt="cyclooctene" /></td>
<td>45,56</td>
<td>Trace</td>
<td>8.9</td>
</tr>
<tr>
<td><img src="image" alt="cyclooctane" /></td>
<td>45,57</td>
<td>3.9</td>
<td>11.5</td>
</tr>
<tr>
<td><img src="image" alt="cyclooctane with acetate" /></td>
<td>45,58</td>
<td>91.0</td>
<td>69.2</td>
</tr>
<tr>
<td><img src="image" alt="cyclooctane with acetate" /></td>
<td>45,59</td>
<td>6.0</td>
<td>7.5</td>
</tr>
</tbody>
</table>

\(^a\)The author is indebted to Dr. L. J. Dolby for authentic samples of \(\text{cis-}\) and \(\text{trans-2-acetoxyethylcyclohexyl acetate}\).
cleavage could occur by cis-addition, followed by either $S_{n2}$ substitution or $S_{n1}$ solvolysis with 1,3-acetate participation to give trans-diacetate in both cases. If cis-addition occurred, an $S_{n1}$ mechanism would explain the cis-1,3-diacetoxycyclohexane. cis-Oxythallation of the external bond followed by acetate participation in the decomposition could result in trans-diacetate. This would necessitate attack of acetate ion or acetic acid solvent on the more stable secondary carbonium ion site. However

some acetoxyethylcycloalkenes would be expected, but were not observed. Levina reported that the oxymercuration product of bicyclo(4.1.0)heptane in water gave trans-2-(acetoxymercuration)-cyclohexanol. If the stereochemistry of oxythallation is analogous to oxymercuration, external bond addition is trans. However, trans-addition easily explains products from these thallic oxidations.
CLEAVAGE OF TRICYCLO(2.2.1.0^2,6)HEPTANE
AND TRICYCLO(3.2.1.0^2,4)OCTANE

Tricyclo(2.2.1.0^2,6)heptane, which shall be referred to as nortricyclene, was reacted with thallic acetate, prepared in situ, in anhydrous acetic acid at 75°. Only two products were observed by gas chromatography and each was collected by vpc. On the basis of the nmr spectrum of each compound, the products were assigned the structures endo-exo-bicyclo(2.2.1)heptane-2,6-diol diacetate (XVIII) and di-exo-bicyclo(2.2.1)heptane-2,6-diol diacetate (XIX). By vpc analysis the percent composition was found to be 62.5% of the endo-exo-diacetate (XVIII) and 37.5% of the di-exo-diacetate (XIX). The structural assignments were made on the basis of the field positions of the acetate methyl group in the nmr spectrum. The acetate methyl absorptions of the products were compared to those of 2-exo and 2-endo-norbornyl acetates and endo-exo- and di-exo-bicyclo(2.2.1)heptane-2,5-diol diacetates (Table 5). The exo-acetates exhibit resonances at higher field, ca. 117 cps down field from tetramethylsilane in carbon tetrachloride, than the endo-acetates,
### TABLE 5
NMR ACETATE METHYL POSITIONS OF BICYCLO(2.2.1)HEPTYL ACETATES

<table>
<thead>
<tr>
<th>Compound&lt;sup&gt;a&lt;/sup&gt;</th>
<th>exo-AcO-</th>
<th>endo-AcO-</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ppm from TMS in CCl&lt;sub&gt;4&lt;/sub&gt;</td>
<td></td>
</tr>
<tr>
<td><img src="image1.png" alt="Diagram" /></td>
<td>116</td>
<td>--</td>
</tr>
<tr>
<td><img src="image2.png" alt="Diagram" /></td>
<td>--</td>
<td>119</td>
</tr>
<tr>
<td><img src="image3.png" alt="Diagram" /></td>
<td>116.5</td>
<td>--</td>
</tr>
<tr>
<td><img src="image4.png" alt="Diagram" /></td>
<td>117.5</td>
<td>118.8</td>
</tr>
<tr>
<td><img src="image5.png" alt="Diagram" /></td>
<td>117</td>
<td>--</td>
</tr>
<tr>
<td><img src="image6.png" alt="Diagram" /></td>
<td>117</td>
<td>121.5</td>
</tr>
</tbody>
</table>

<sup>a</sup>The author wishes to express gratitude to Dr. J. Meinwald for the samples of endo-exo- and di-exo-bicyclo(2.2.1)heptane-2,5-diols.
ca. 119 cps. The product of greater yield showed two different acetates located at 117 and 121.5 cps. Therefore, it was assigned as endo-exo-bicyclo(2,2,1)heptane-2,6-diol diacetate (XVIII). The endo-acetate appears at lower field than any of the model compounds, which might be the result of the proximity of the exo-acetate. The product of lesser yield showed only one acetate methyl absorption at 117 cps and it was assigned di-exo-bicyclo(2,2,1)heptane-2,6-diol diacetate.

The products could be formed via trans- or cis- addition to one of the three equivalent cyclopropane bonds of nortricyclene. Two adducts can be obtained by trans-oxythallation (XXa) and (XXb) and two by cis-oxythallation (XXIa) and (XXIb). However, the di-endo-adduct (XXIb)

![Di-endo-adduct](image)

probably is the least likely adduct. The products can be formed from the adducts by three possible mechanisms, $S_n$, $S_{n-1}$ or $S_{n-1}$. 
$S_n^2$ acetylation of the eno-diacetoxythallium group inverts the stereochemistry at that position. $S_n^2$ acetylation of the exo-carbon-thallium bond is not considered likely because of steric requirements and has not ever been experimentally detected. However, di-exo-diacetate can be formed from the trans-adduct (XXa) via $S_n^1$ internal return of an acetate from the diacetoxythallium group. The endo-exo-diacetate (XVIII) can be formed by this mechanism from both trans-adducts (XXa) and (XXb). Internal return in the cis-adduct (XXIa) would give the di-exo-diacetate (XXI).
Adduct from both \textit{cis-} and \textit{trans-} addition can lead to a classical (XXIIa) or (XXIIb) or nonclassical carbonium (XXIII) ion by a $S_{n1}$ mechanism. Attack of acetate ion or acetic acid solvent at C-1 would give the endo-exo-diacetate (XVIII) and attack at C-2 would give the di-exo-diacetate (XIX). A fifty-fifty mixture of the diacetates might be expected if the acetate does not exhibit an influence upon which carbonium ion, (XXIIa) or (XXIIb), is attacked by acetic acid. There appears to be a preferential attack on ion (XXIIb), which can possibly be rationalized by a acetoxonium ion (XXIV). If the rates of product
formation from both classical ions are approximately the same, then there is a greater population of the ion (XXIIb), possibly as a result of increased stabilization of the charge by acetate participation. Initial study of lead tetraacetate oxidation of nortricyclopane has shown that the same two products are obtained in approximately the same percentages. In all other comparative studies between lead tetraacetate and thallic acetate, the product ratios have been considerably different. Therefore, this is suggestive that oxidation products of nortricyclopane by both metal acetates are derived from a common intermediate.

Other products could be formed by 3,2- or 6,2-hydride shifts. However, only 2,6-disubstituted norbornanes have been reported in reactions of electrophiles with nortricyclopane. The only product reported from the reaction of nortricyclopane with the acyl chloride-aluminum chloride complex was 2-acyl-bicyclo(2.2.1)heptane-6-chloride. The acyl group was postulated to be exo from chemical evidence, but no stereochemical assignment was suggested for the chloride. Deuteron catalyzed opening of nortricyclopane in deuteracetic acid gave an equal mixture of endo- and exo-6-deutero-bicyclo(2.2.1)heptane-2-exo-acetate. There was some evidence for a small amount of 6,2-hydride shift.

In the thallic acetate oxidation of nortricyclopane the endo-exo-bicyclo(2.2.1)heptane-2,5-diol diacetate was shown not to be present both by nmr (Table 5) and vpc. However, the di-exo-2,5 and 2,6-diacetates could not be separated by vpc and the acetate methyl nmr positions are very similar (Table 5). It was difficult to differentiate between the two di-exo-diacetates on the basis of the entire nmr spectra. Only a small amount of the di-exo-2,5-diacetate was available and the nmr
spectrum had to be run at a high amplitude. Therefore, the fine structure could not be seen readily.

*ex*-Tricyclo(3.2.12.4)octane was reacted with thallic acetate in anhydrous acetic acid at 75°. Analysis of the reaction mixture by vpc showed only two major peaks. Each peak had at least one smaller component as shown by the presence of a small shoulder near the base of the peaks. The first peak contained more of its minor component than did the second peak. Each major peak was collected by vpc and each was shown to have sharp acetate methyl absorptions at $\gamma'8$, complex absorptions between $\gamma'6.5$ and $\gamma'9$, and complex pattern at $\gamma'5.3$. In addition to these absorptions, the compound of shorter retention time showed a doublet at $\gamma'5.85$ with a coupling constant of 8 cps. This absorption results from coupling of the two acetoxyethylene hydrogens with an adjacent methine hydrogen. On the basis of the nmr spectrum, the lower retention time peak was assigned as being an acetoxyethyl-bicyclo(2.2.1)hepyl acetate. Two general structures, (XXV) and (XXVI), are reasonable possibilities

\[
\text{XXV} \quad \text{XXVI}
\]

which would fit this data. The data from the compound of longer retention time would fit several diacetates of bicyclo(3.2.1)octane or bicyclo-2,2,2)octane.
By vpc analysis the per cent composition was found to be 35% and 65% for the compounds of shorter and longer retention time respectively. By nmr analysis the per cent composition was approximated to be 31% and 69%. From vpc and nmr analysis it appears that di-endo-bicyclo(3.2.1)-octane-2,4-diol diacetate might be a small component of the longer retention time product. This assignment was made by both retention time and field position of the acetate methyl at ca. γ' 8.05. It is difficult to ascertain whether endo-exo-bicyclo(3.2.1)octane-2,4-diol diacetate is a component of the longer retention time product, but if it is, it does not appear to be a major component.

Acid catalyzed cleavage of tricyclo(3.2.1.0²,₄)octane in acetic acid has been reported to give a mixture of olefins and acetates. The five acetates which were 80% of the reaction mixture, were reduced to the alcohols. Only two of the five alcohols were identified, which were exo-bicyclo(3.2.1)octane-2-ol and bicyclo(2.2.2)octane-2-ol as 44 and 28%, respectively, of the total yield of alcohols.
CLEAVAGE OF PHENYLCYCLOPROPANES

Substituted phenylcyclopropanes were cleaved both with thallic acetate and lead tetraacetate in anhydrous acetic acid at 75°. The products were analyzed by gas chromatography and nuclear magnetic resonance. The reactions were carried out using 50% excess cyclopropane. In addition to the parent phenylcyclopropane, the following substituted compounds were studied: meta- and para-chloro-, meta- and para-methyl, and para-methoxy-. Only two products were observed in each reaction, cinnamyl acetates and 1-aryl-1,3-propanediol diacetates. The percent composition for the products of each reaction (Tables 6 and 7) were analyzed by both vpc and nmr. Products were identified with authentic prepared samples by vpc analysis. Analysis by nmr consisted of expanding the allyl methylene doublet of the cinnamyl acetates, \( \delta \approx 5.4 \), and the benzal hydrogen triplet of the diacetates, \( \delta \approx 4.2 \). Areas of the peaks from several spectra of each reaction mixture were averaged and corrected to area per hydrogen. Because of inherent experimental limitations, such as noise level and incomplete splitting of peaks, the vpc analysis is to be considered more reliable. The nmr analysis was a check as to whether the products were cracking or polymerizing under chromatographic conditions. The results showed that no or very little decomposition occurred.

Thallic acetate was prepared and used in situ as described in the discussion of results of bicyclo(n.1.0)alkanes. The method of thallic acetate preparation results in some decomposition to thallous acetate,
TABLE 6
SUBSTITUTED PHENYLCYCLOPROPYL CLEAVAGE
PRODUCTS FROM THALLIC ACETATE

<table>
<thead>
<tr>
<th>X</th>
<th>Cinnamyl acetate&lt;sup&gt;a&lt;/sup&gt;</th>
<th>1-Aryl-1,3-diacetoxy-propane&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield, %</td>
<td>Yield, %</td>
</tr>
<tr>
<td></td>
<td>vpc</td>
<td>nmr</td>
</tr>
<tr>
<td>p-MeO-</td>
<td>7</td>
<td>5</td>
</tr>
<tr>
<td>p-Me-</td>
<td>7.5</td>
<td>6</td>
</tr>
<tr>
<td>m-Me</td>
<td>9</td>
<td>7</td>
</tr>
<tr>
<td>H-</td>
<td>10</td>
<td>9</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>8</td>
<td>7</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

<sup>a</sup>The author wishes to express gratitude to Mr. D. L. Shaw for the preparation of para-chlorocinnamyl acetate and meta-chlorophenyl and phenyl-1,3-diacetoxypropanes.

which is discussed later in the section concerning thallic acetate. The thallous acetate reacts with thallic acetate in a one to one ratio to produce a thallous-thallic acetate double salt in equilibrium with the two salts. The evidence for this is presented in the kinetic section. The products from phenylcyclopropane were examined using pure thallic acetate to see if the double salt changed the course of the reaction. An overall yield was found, from this reaction, to be at least 68% by vpc analysis using an internal standard. The per cents of cinnamyl acetate and α,γ-diacetoxypropylbenzene were found to be 9% and 91%, respectively, with pure thallic acetate, and 10% and 90% with that prepared in situ. Therefore, it does not appear that the double salt alters the course of
TABLE 7
SUBSTITUTED PHENYL CYCLOPROPANE CLEAVAGE
PRODUCTS FROM LEAD TETRAACETATE

<table>
<thead>
<tr>
<th>X</th>
<th>Cinnamyl acetate</th>
<th>1-Aryl-1,3-diacetoxycyclopropane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Yield, %</td>
<td>Yield, %</td>
</tr>
<tr>
<td>vpc</td>
<td>nmr</td>
<td>vpc</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td>-----</td>
</tr>
<tr>
<td>p-MeO-</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>p-Me-</td>
<td>22</td>
<td>78</td>
</tr>
<tr>
<td>m-Me-</td>
<td>27</td>
<td>73</td>
</tr>
<tr>
<td>H-</td>
<td>29</td>
<td>71</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>26</td>
<td>74</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>21</td>
<td>79</td>
</tr>
</tbody>
</table>

The reaction. The low yield of 68% is probably because of decomposition of thallic acetate before the reaction was complete at 75°C. The total recovery of phenylcyclopropane and products was 83%. The phenylcyclopropane is sufficiently volatile to result in the 17% loss in total recovery during the work up procedure.

In monosubstituted cyclopropanes, there exist two different cyclopropyl carbon-carbon bonds, two equivalent α- bonds and one β. Direction of ring opening by electrophilic attack is such that the most stable carbonium ion is produced. Oxidation of phenylcyclopropanes
with thallic and plumbic acetates results only in $\sigma$-bond cleavage (Tables 6 and 7).

The reaction can be rationalized as proceeding via either an intermediate carbonium ion (XXVII), which upon neutralization of the charge with solvent gives the oxymetallated intermediate (XXVIII). Compounds similar to (XXVIII) have been isolated as relatively stable salts from oxymercuration of phenylcyclopropanes.\(^{35,36,64}\)

Several possibilities exist for the formation of the cinnamyl acetates (XXIX). The most probable is by loss of a proton from a benzylic carbonium ion. This could occur through the intermediate carbonium ion (XXVII) obtained from initial attack of the metal acetate before neutralization of charge by solvent, followed by acetolysis of the labile allylic carbon-metal bond. Alternatively, decomposition of the
adduct (XXVIII) with 1,3-acetate migration would result in a benzylic carbonium ion (XXVIIa) which upon loss of a proton would give the olefinic acetate.

\[
\begin{align*}
\text{Mc} & \quad \xrightarrow{\text{X}} \quad \text{XVIIa} & \quad \xrightarrow{\text{XXIX}} \\
& \quad \text{X} & \quad \text{X} \\
& \quad \text{X} & \quad \text{X}
\end{align*}
\]

Other less likely mechanisms exist. Direct elimination of a proton during the decomposition of the intermediate (XXVIII), without an acetate shift, would give an \(\alpha\)-arylallyl acetate (XXX). Under the

\[
\begin{align*}
\xrightarrow{\text{XXVIII}} & \quad \xrightarrow{\text{XXX}} & \quad \xrightarrow{\text{XXIX}} \\
& \quad \text{X} & \quad \text{X} & \quad \text{X}
\end{align*}
\]

reaction conditions, \(\alpha\)-arylallylacetates, except for the chlorophenyl compounds, were shown to rearrange to the thermodynamically more stable cinnamyl acetate quantitatively. The chloro-compounds did rearrange but they were slower, the \(\text{meta}\)-chloro being much slower than \(\text{para}\)-chloro, as would be expected. This rearrangement has been reported for \(\alpha\)-phenylallyl acetate.\(^{65}\) The formation of \(\alpha\)-arylallyl acetates seems unlikely with regard to the results from oxidative cleavage of bicyclo-(n.1.0)alkanes, in which postulated primary alkylmetal acetates gave only
products resulting from substitution. The 1-phenyl-1,3-propanediol diacetate, has been shown to be stable in acetic acid at 100°, and therefore is not a source of cinnamyl acetate.

The 1-aryl-1,3-propanediol diacetates (XXXI) are a result of acetylation of the carbon-metal bond of intermediate (XXVIII). Cinnamyl acetate was shown not to produce the diacetate under these reaction conditions. However, considerable cinnamyl acetate is lost under the reaction conditions but over a 40% longer period of time. The control reaction was run using ca. 0.11 M cinnamyl acetate in acetic acid at 75°. Using values from per cent conversion of thallic oxide to thallic acetate at 75°, to be discussed later, and the per cent recovery for the reaction of phenylcyclopropane with thallic acetate, the maximum concentration of cinnamyl acetate produced in the reaction would be ca. 0.015 M. The concentration is probably only ca. 0.006-0.005 M or less. The reaction was also monitored by vpc for the first several hours and the product ratio remained constant within experimental error and did not differ significantly from the final ratio after complete reaction.

Cleavage of the 1-bond of phenylcyclopropanes would give 2-aryl-1,3-propanediol diacetates (XXXIII) via adduct (XXXII). These symmetrical diacetates were shown to be absent by vpc analysis.
Oxidation of phenylcyclopropanes with thallic acetate is much cleaner than with lead tetraacetate. Thallic acetate gave 90–95% diacetate (Table 6) and lead tetraacetate 71–80% (Table 7), the remainder being cinnamyl acetates. Decomposition of 3-phenyl-3-acetoxypropylmercuric acetate in acetic acid results in formation of only cinnamyl acetate.\(^6^5\) The per cent of cinnamyl acetate increases in the order of metal acetates, thallic < plumbic < mercuric. Similar results have been reported in oxidation of cyclohexene with thallic acetate,\(^1^1\) lead tetraacetate\(^9,^6^6\) and mercuric acetate.\(^6^7\) The per cent of 3-acetoxy-cyclohexene was 3-11, 37, and 100 with thallic, plumbic, and mercuric acetates, respectively, however the reaction conditions were different. Cyclohexenylacetate from the reaction of cyclohexene with lead tetraacetate has been postulated to be the result of a radical substitution at the allylic position,\(^1\) but could also be an addition-elimination reaction. Mercuric acetate is thermally more stable than lead tetraacetate, yet only the olefinic acetate was observed. Therefore, the mode of decomposition of the intermediate oxymetallation adduct is significant in determining ultimate products.

A trend exists in the per cent of products obtained from thallic and plumbic oxidations of phenylcyclopropane. The per cent diacetate is maximum at the extremes of the scale for the activated and deactivated
cyclopropanes, i.e. para-methoxy and meta-chloro and minimum at the unsubstituted phenylcyclopropane. A continuous increase or decrease might be expected. This is either fortuitous or a result of the instability to reaction conditions of products containing electron donating substituents. However, within the series of cyclopropanes, cleavage by either metal acetate does not exhibit a significant substituent effect in the product ratios. This could be a reflection of the mode of decomposition of the adducts from oxymetallation.
KINETICS OF THE REACTION OF THALLIC ACETATE
WITH PHENYLCYCLOPROPANES

The reaction of thallic acetate with substituted phenylcyclo-
propanes in anhydrous acetic acid was studied kinetically in an attempt
to obtain more information about thallic acetate oxidations. Initially
attempts were made to follow the disappearance of cyclopropane relative
to an internal standard by gas chromatography. Following the decrease of
cyclopropane concentration was chosen as potentially the simplest
experimental method as monitoring of thallic acetate by reducing agents
could be complicated by the reactivity of the intermediate 3-aryl-3-
acetoxypropylthallium (III) diacetate toward reducing agents. If the
adduct accumulates and is reduced then any determination of thallic
acetate by titrations involving reducing agents would give meaningless
results. However, gas chromatography was found to be unsatisfactory.
The kinetic aliquots has to be freed from the acetic acid in order to
facilitate analysis by vpc. This was done by dispersing the aliquot in
an ice-water mixture, extracting with ether, and washing the ethereal
solution with ice water. The ethereal solution was then dried, concen-
trated to a small volume, and the resulting concentrate was analyzed. In
general, the results were not reproducible because of the volatility of
the cyclopropanes. Second order kinetic plots for equal molar concen-
trations of the two reactants produced curves. Initially the reaction
proceeded rapidly for approximately 30% reaction but then the rate was
drastically retarded (Figure 1).
Fig. 1.--Typical curve from a second order plot at 50.1° for the phenylcyclopropane concentration obtained by vpc

\[
\begin{align*}
[O]_0 &= 0.0257 \text{M} \\
[TI(OAc)_3]_0 &= 0.0257 \text{M} \\
[n-C_{10}H_{22}]_0 &= 0.0254 \text{M}
\end{align*}
\]
Consideration was given to the possibility of monitoring the disappearance of the aryl cyclopropane by ultraviolet spectroscopy. However, the low extinction coefficients of the cyclopropane compound in the region where products do not absorb precluded the use of this technique.

Finally the reduction of thallic acetate with excess standard ferrous solution followed by back titration of the excess ferrous ion with standard dichromate was examined, but the method was found not to be applicable. Solid thallic acetate in one normal sulfuric acid can be reduced readily by ferrous solution, but the presence of acetic acid drastically inhibits the rate of reduction. Removal of acetic acid from the aliquots by a vacuum transfer technique and analysis of the resulting solid dissolved in dilute sulfuric acid would limit experimentally the use of this method for the study of fast reactions. However, analysis of acetic acid solutions of thallic acetate can be accomplished by the addition of excess aqueous potassium iodide which results in the formation of thallous triiodide. The stability of thallic halides decrease in the order of fluoride > chloride > bromide > iodide. Thallic iodide does not exist as such because the thallic ion oxidizes the iodide to iodine forming thallous triiodide. The triiodide is then titrated with standard sodium thiosulfate solution using a starch indicator. The addition of

\[
\text{Tl(OAc)}_3 + x \text{c.I}^- \rightarrow \text{Tl}^+ \text{I}_3^-
\]

\[
\text{I}_3^- + 2 \text{S}_2 \text{O}_3^{-2} \rightarrow \text{S}_4 \text{O}_6^{-2} + 3 \text{I}^-
\]

thallic acetate to aqueous potassium iodide results in a heterogeneous yellow mixture. The dark mixture obtained after addition of the starch
indicator is titrated with thiosulfate to a pure yellow heterogeneous mixture of thallous iodide.

Either of two conditions must be met if titration of thallic acetate by the above described method is to allow kinetic analysis. The organothallic diacetate intermediate (XXXIV) must not accumulate in the course of the reaction, or if it does accumulate, it must not react so as to change the concentration of iodine obtained from the reduction of thallic acetate. The initial rate of disappearance of phenylcyclopropane as monitored by vpc and thallic acetate by iodimetry was shown to be the same for 0.015 M solutions at 50.1° (Figures 2 and 3). Therefore, these conditions appear to be met.

Second order plots for equal molar solutions showed an initial rapid loss of oxidizing power of the solution (thallium III in whatever form it may be present) followed by a drastic slowing of the rate (Figure 4). The same result was noted when the disappearance of cyclopropane was monitored by vpc. Hence the rate of disappearance of cyclopropane corresponds to the change in oxidizing power of the solution. It is known that thallic salts form double salts with other metal salts. The ammonium-thallic acetate and thallous-thallic bromide double salts are known. If the intermediate adduct (XXXIV) decomposes rapidly to give thallous acetate, then the thallous acetate could form a double salt with thallic acetate. Thallic acetate could possibly
Fig. 2.—Initial rate of disappearance of phenylecyclopropane at 50.1°
Fig. 3.—Initial rate of disappearance of thallic acetate at 50.1°
Fig. 4.—Typical curve from a second order plot at 50.1° from the thallie acetate concentration

\[
[Ti(\text{OAc})_3]_0 = 0.0150 \text{ M} \\
[\text{thallie}]_0 = 0.0150 \text{ M}
\]
facilitate decomposition of the organothallium intermediate, as in the
decomposition of alkylmercuric acetates which is accelerated by the
presence of mercuric acetate. Instead of free mercury being
produced, mercurous acetate is formed. The thallous-thallic acetate
double salt might then cleave the cyclopropane ring at a decreased rate
relative to the free thallic acetate. Alternatively, the double salt
could be in equilibrium with thallous acetate and thallic acetate. If
the equilibrium was in the direction of the double salt and if only free
thallic acetate cleaves cyclopropanes, then this would slow the rate of
reaction. The analytical method employed yields only the total concen-
tration of thallium III species. Thus the change in the oxidizing power
of the solution is not equivalent to the change in the concentration of
free thallium triacetate.

In order to derive a rate expression, the assumptions made are
that the equilibrium constant is very large in the direction of the
double salt and that only thallic acetate reacts with the cyclopropane.

\[
\text{TlOAc + Tl(OAc)}_3 \xrightarrow{\text{ reaction }} \text{Tl}^+\text{Tl(OAc)}_4^- \\
\]

In addition, it is assumed that thallous acetate is produced rapidly
after cleavage of the cyclopropyl ring, such that for every mole of
thallic acetate which is reduced another becomes essentially inactive by
double salt formation. The change in oxidizing power of the solution is
equal to the amount of cyclopropane cleaved products which is designated
as \(x\). The cyclopropane remaining is \([B_0-x]\), where \([B_0]\) is the initial
concentration of cyclopropane. The total thallium III species must be
separated into free thallium triacetate and thallous-thallic acetate
double salt. Assuming that the equilibrium lies to the right (K is large), then free thallic acetate is equal to \([A_0-2x]\), where \([A_0]\) is the initial concentration of thallic acetate. The following rate law and integrated expressions are derived. Plots using these expressions

\[
\text{Rate} = k[Tl(0Ac)_2][\varphi<\phi ]
\]

\[
dx/dt = k[A_0-2x][B_0-x]
\]

\[
\log \frac{[B_0-x]}{[A_0-2x]} = \frac{[2B_0-A_0]k_t}{2.303}
\]

where \([A_0] \neq [B_0]\) and \([A_0] \neq 2[B_0]\)

\[
\log \frac{[A_0-x]}{[A_0-2x]} = \frac{[A_0]k}{2.303}t
\]

where \([A_0] = [B_0]\)

produce straight lines (Figure 5). Accordingly the stoichiometry of the reaction shall be as indicated in the following equation.

\[
\varphi<\phi + Tl(0Ac)_2 \rightarrow 1/2 \varphi<\phi + 1/2 Tl^+Tl(0Ac)_4^- + \text{Products}
\]

Thus the oxidizing power of the medium (thallium III) should approach one-half that of the initial titer. The reaction does proceed very slowly beyond 50\% (Figure 4) indicating that either the double salt cleaves cyclopropanes or the equilibrium constant is not as large as it was assumed. If it is the latter, a two-fold excess of thallic acetate would shift the equilibrium toward the double salt. In addition the excess also allows the reaction to be followed to a greater per cent completion with respect to the phenylcyclopropane. The general integrated rate expression which was derived above for unequal molar concentrations is
Fig. 5.—Typical equal molar plot at 50.1°, assuming double salt formation.

\[ \log \frac{[A_0 - X]}{[A_0 - 2X]} \]

\[ [\text{Tl(OAc)}_2]_0 = 0.0149 \text{ M} \]

\[ [\text{[ }]_0 = 0.0149 \text{ M} \]
not applicable for this situation. A new expression must be derived from the assumed general rate law.

\[
\text{when } [A_0] = 2[B_0] \\
\frac{dx}{dt} = k[A_0 - 2x][A_0/2 - x] \\
x/dt = (k/2[A_0 - 2x])^2 \\
1/[A_0 - 2x] = kt
\]

When a two-fold excess of thallic acetate was used, straight line plots are obtained generally over two half-lives from plotting \(1/[A_0-2x]\) versus time (Figure 6). The observed rate constants from this treatment are concentration dependent. The kinetic data, summarized in Table 8, shows that as the concentration of thallic acetate decreases the rate constant increases. At low concentration the per cent dissociation of the double salt will increase, thus the actual free thallic acetate concentration is larger than predicted by the assumption of a large equilibrium constant for double salt formation. Therefore, the rate constants from runs in which highest thallic acetate concentration, approximately 0.03 M, was used, are closer to true rate constants. The observed rate constants were obtained from the best visual fit of the plotted points. The rate for para- methoxyphenylcyclopropane is too fast to be obtained directly and will be discussed later.

The existence of a thallous-thallic acetate double salt was shown by dissolving equal molar amounts of thallic acetate and thallous acetate in acetic acid. The acetic acid was removed under vacuum. The remaining white solid decomposed sharply at 178-180° with no prior observed discoloration or decomposition. Thallous acetate melts at
Fig. 6.—Typical plot at 50.1° for a 2:1 ratio of thallie acetate to phenylecyclopropane.
<table>
<thead>
<tr>
<th>$X$</th>
<th>$X$-φ-Å</th>
<th>$\text{Tl(OAc)}_3$</th>
<th>Temp.</th>
<th>$k \times 10^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-Me-</td>
<td>0.00347</td>
<td>0.00698</td>
<td>50.1</td>
<td>295</td>
</tr>
<tr>
<td>p-Me-</td>
<td>0.01492</td>
<td>0.02985</td>
<td>50.1</td>
<td>133</td>
</tr>
<tr>
<td>p-Me-</td>
<td>0.01492</td>
<td>0.02986</td>
<td>50.1</td>
<td>146</td>
</tr>
<tr>
<td>m-Me-</td>
<td>0.005038</td>
<td>0.01013</td>
<td>50.1</td>
<td>18.1</td>
</tr>
<tr>
<td>m-Me-</td>
<td>0.005584</td>
<td>0.01117</td>
<td>50.1</td>
<td>18.4</td>
</tr>
<tr>
<td>m-Me-</td>
<td>0.01538</td>
<td>0.03076</td>
<td>50.1</td>
<td>15.7</td>
</tr>
<tr>
<td>m-Me-</td>
<td>0.01583</td>
<td>0.03170</td>
<td>50.1</td>
<td>16.4</td>
</tr>
<tr>
<td>H-</td>
<td>0.009701</td>
<td>0.01952</td>
<td>29.6</td>
<td>1.34</td>
</tr>
<tr>
<td>H-</td>
<td>0.01002</td>
<td>0.02007</td>
<td>29.6</td>
<td>1.42</td>
</tr>
<tr>
<td>H-</td>
<td>0.01543</td>
<td>0.03186</td>
<td>29.6</td>
<td>1.64</td>
</tr>
<tr>
<td>H-</td>
<td>0.01606</td>
<td>0.03222</td>
<td>29.6</td>
<td>1.72</td>
</tr>
<tr>
<td>H-</td>
<td>0.005297</td>
<td>0.01063</td>
<td>50.1</td>
<td>8.15</td>
</tr>
<tr>
<td>H-</td>
<td>0.0149</td>
<td>0.0149</td>
<td>50.1</td>
<td>7.30b</td>
</tr>
<tr>
<td>H-</td>
<td>0.01508</td>
<td>0.03021</td>
<td>50.1</td>
<td>6.51</td>
</tr>
<tr>
<td>H-</td>
<td>0.01601</td>
<td>0.03202</td>
<td>50.1</td>
<td>6.42</td>
</tr>
<tr>
<td>X</td>
<td>X-φ&lt;4</td>
<td>Tl(OAc)$_3$</td>
<td>Temp.</td>
<td>k x 10</td>
</tr>
<tr>
<td>-----</td>
<td>-------</td>
<td>-------------</td>
<td>-------</td>
<td>--------</td>
</tr>
<tr>
<td></td>
<td>m/l</td>
<td>m/l</td>
<td>°C</td>
<td>l/m/min</td>
</tr>
<tr>
<td>H-</td>
<td>0.01547</td>
<td>0.03093</td>
<td>76.2</td>
<td>29.6</td>
</tr>
<tr>
<td>H-</td>
<td>0.01576</td>
<td>0.03155</td>
<td>76.2</td>
<td>30.3</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>0.007775</td>
<td>0.01554</td>
<td>50.1</td>
<td>1.57</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>0.01125</td>
<td>0.01828</td>
<td>50.1</td>
<td>1.71</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>0.01492</td>
<td>0.02988</td>
<td>50.1</td>
<td>1.88</td>
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<tr>
<td>p-Cl-</td>
<td>0.01505</td>
<td>0.03016</td>
<td>50.1</td>
<td>1.87</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>0.00911</td>
<td>0.01987</td>
<td>50.1</td>
<td>0.126</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>0.01013</td>
<td>0.02027</td>
<td>50.1</td>
<td>0.139</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>0.01517</td>
<td>0.03035</td>
<td>50.1</td>
<td>0.116</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>0.01540</td>
<td>0.03055</td>
<td>50.1</td>
<td>0.110</td>
</tr>
</tbody>
</table>

$^a$Rate constants were obtained from $\frac{1}{[A_o-2x]} = k_t$.

$^b$Rate constant was obtained from $\log\frac{[A_o-x]}{[A_o-2x]} = \frac{[A]k_t}{2.303}$.

$^c$Rate constant was obtained from $\log\frac{[B_o-x]}{[A_o-2x]} = \frac{[2B_o-A_o]k_t}{2.303}$. 
127-8° and turns darker with increasing temperature. Thallic acetate exhibits no sharp melting or sharp decomposition up to 200°.

To find a value of the equilibrium constant of the double salt, thallous-thallic acetate mixtures were used in kinetic studies of the cleavage of cyclopropanes. Using the previous outlined assumptions, the following expression is derived, where \([S_0]\) and \([I_0]\) are the initial concentrations of thallous-thallic acetate double salt and excess thallous acetate, respectively. Again, \([B_0]\) is the initial concentration of phenylcyclopropane. The integrated rate expression is as follows:

\[
[I_0]\log\left(\frac{B_0-x}{S_0-x}\right) + [B_0]\log[B_0-x] - [S_0]\log[S_0-x] = \frac{[B_0-S_0]}{2.303} \frac{k}{K} t
\]

where \([S_0] \neq [B_0]\)

Since only the thallium in the +3 oxidation state is measured, it is approximately \([S_0-x]\) because the equilibrium constant is assumed to be
very large. When the concentrations of phenylcyclopropane and the
double salt are equal, the expression is as follows:

\[
\frac{dx}{dt} = \frac{k}{K} \frac{[S_0-x]^2}{[I_0+x]}
\]

\[
\frac{[I_0+S_0]}{2.303} \frac{1}{[S_0-x]} + \log[S_0-x] = \frac{1}{2.303} \frac{kt}{K}
\]

where \([S_0] = [B_0]\)

Increasing the ratio of thallous acetate to thallic acetate
decreases the rate of loss of the thallium III concentration. This
trend is shown in Table 9 in terms of times necessary for 25% reaction as
a function of the thallous to thallic acetate ratio. Similar results
were obtained by using lithium acetate in place of thallous acetate.
Plots of the appropriate expression versus time gave straight lines
(Figure 7) and \(k/K\) values were calculated. If the equilibrium constant
is very large, constant \(k/K\) values would be observed for all ratios of
thallic acetates, or at least for the largest ratios. The equilibrium
constant could then be obtained knowing the rate constant. The observed
\(k/K\) ratios with thallous acetate (Table 10) and with lithium acetate
(Table 11) are not constant. The observed \(k/K\) values increase as the
ratio of monovalent metal acetate to thallic acetate increases. A salt
effect was ruled out because the observed \(k/K\) value remained constant
when doubling the concentration of the reactants but still maintaining a
ratio of one (Table 10). The observed \(k/K\) values varied linearly with
the initial ratios of thallic acetate to thallous acetate for ratios of
0.994 to 0.100 with a slope of \(-6.09 \times 10^{-4}\). This again verifies the
TABLE 9
TIME FOR 25% REACTION AS A FUNCTION OF INITIAL THALLIOUS TO THALLIC ACETATE RATIOS$^a$ AT 50.1$^\circ$C

<table>
<thead>
<tr>
<th>T1OAc/T1(0Ac)$_3$</th>
<th>$t_{25%}$ rx</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/l/m/l</td>
<td>min.</td>
</tr>
<tr>
<td>0</td>
<td>50</td>
</tr>
<tr>
<td>1.00</td>
<td>225</td>
</tr>
<tr>
<td>1.29</td>
<td>420</td>
</tr>
<tr>
<td>1.50</td>
<td>460</td>
</tr>
<tr>
<td>2.00</td>
<td>585</td>
</tr>
<tr>
<td>3.00</td>
<td>1055</td>
</tr>
<tr>
<td>10.01</td>
<td>3600</td>
</tr>
</tbody>
</table>

$^a$Initial concentrations are given in Tables 8 and 10.

previously observed fact that the equilibrium constant is not as large as assumed or that it is large and the double salt is the reacting specie. Therefore, the rate constants in Table 8 are only apparent rate constants.

The addition of lithium acetate in the reaction of mercuric acetate$^{64}$ or lead tetraacetate$^{72}$ with phenylcyclopropane has no effect on the rate. It is not surprising that the rate of cleavage with lead tetraacetate does not differ in the presence of lithium acetate. In order for the lead (IV) compound to form a double salt it would have to expand its valence shell. On the other hand, thallic acetate has a vacant p-orbital which can complex with an acetate anion. Mercuric acetate has two vacant p-orbitals and complex mercuric salts are known, but these complex salts are generally formed only with strong ligands.$^{73}$
Fig. 7.—Typical plot for obtaining $k/K$ at 50.1°.
### TABLE 10

OBSERVED k/K RATIOS FOR THE REACTION OF PHENYLCYCLOPROPANE WITH VARYING INITIAL THALLOUS-THALLIC ACETATE RATIOS AT 50.1°

<table>
<thead>
<tr>
<th>( \phi &lt;-1 )</th>
<th>( \text{Tl(OAc)}_3 ) m/l</th>
<th>( \text{TlOAc} ) m/l</th>
<th>( \frac{\text{TlOAc}}{\text{Tl(OAc)}_3} ) m/l/m/l</th>
<th>( k/K \times 10^4 ) min(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01574</td>
<td>0.01573</td>
<td>0.01574</td>
<td>1.00</td>
<td>2.70</td>
</tr>
<tr>
<td>0.02936</td>
<td>0.02936</td>
<td>0.02937</td>
<td>1.00</td>
<td>2.85</td>
</tr>
<tr>
<td>0.0154</td>
<td>0.0131</td>
<td>0.0169</td>
<td>1.29</td>
<td>4.08</td>
</tr>
<tr>
<td>0.01487</td>
<td>0.01491</td>
<td>0.02230</td>
<td>1.50</td>
<td>4.71</td>
</tr>
<tr>
<td>0.01501</td>
<td>0.01502</td>
<td>0.03010</td>
<td>2.00</td>
<td>5.84</td>
</tr>
<tr>
<td>0.01821</td>
<td>0.01823</td>
<td>0.05463</td>
<td>3.00</td>
<td>6.71</td>
</tr>
<tr>
<td>0.02284</td>
<td>0.02284</td>
<td>0.2287</td>
<td>10.01</td>
<td>9.53</td>
</tr>
</tbody>
</table>

### TABLE 11

OBSERVED k/K RATIOS FOR THE REACTION OF PHENYLCYCLOPROPANE WITH VARYING INITIAL LITHIUM-THALLIC ACETATE RATIOS AT 50.1°

<table>
<thead>
<tr>
<th>( \phi &lt;-1 )</th>
<th>( \text{Tl(OAc)}_3 ) m/l</th>
<th>( \text{LiOAc} ) m/l</th>
<th>( \frac{\text{LiOAc}}{\text{Tl(OAc)}_3} ) m/l/m/l</th>
<th>( k/K \times 10^4 ) min(^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02223</td>
<td>0.02223</td>
<td>0.04449</td>
<td>2.00</td>
<td>6.31</td>
</tr>
<tr>
<td>0.02339</td>
<td>0.02339</td>
<td>0.2352</td>
<td>10.06</td>
<td>16.4</td>
</tr>
</tbody>
</table>
The equilibrium constant was approximated from the kinetic data obtained with thallic-thallous acetate mixtures. From plots of \(1/[\text{Tl}^{+3}]\) versus time for each run, the initial rates for the first 10% reaction was calculated. The concentrations of thallic and thallous acetates and phenylcyclopropane were calculated at 5% reaction. From rearrangement of the previously derived rate law, the following logarithmic expression was obtained. Calculated values from each run were used in the expression and

\[
\log \left( \frac{dx}{dt} \right)[\text{Tl}^{+3}]^{-1}[\phi-\text{Ac}]^{-1} = \log \frac{k}{K} - \log[\text{Tl}0\text{Ac}]
\]

the \(\log \left( \frac{dx}{dt} \right)[\text{Tl}^{+3}]^{-1}[\phi-\text{Ac}]^{-1}\) value was plotted versus the corresponding \(\log[\text{Tl}0\text{Ac}]\) value. A curve was obtained (Figure 8). However, points from runs in which the initial thallous to thallic acetate ratios were 10, 3, and 2 gave a line of slope of -0.99. These higher acetate ratios might be expected to be near the equilibrium condition which was assumed. The slope of this line therefore verifies the order of thallous acetate as minus one. The intercept of this line is \(\log(k/K)\) and was found to be -3.07 or \(k/K\) is \(8.51 \times 10^{-4}\). For a rate constant of 0.651 l/m/min (Table 8), the equilibrium constant is 765. This equilibrium constant is not as large as assumed, therefore, the rate constants are observed not true rate constants. The value of 765 is a maximum value for \(K\).

Using the kinetic run at 50.1°C with a rate constant of 0.651 l/m/min from initial phenylcyclopropane concentration of 0.01509 M (Table 8), the concentrations of phenylcyclopropane were calculated from the thallic concentrations and plotted versus time to give the expected curve. Points were selected at random along the curve, and \(dx\) and \(dt\) found at 5% of the concentration of phenylcyclopropane at each point.
Fig. 8.--Plot to obtain kinetic order of thallous acetate and a true $k/K$ at 50.1°C
At each point the concentration of phenylcyclopropane and amounts of thallium in the +1 and +3 oxidation states were calculated. Using the law of mass action expression for an equilibrium constant of 765, the concentration of the double salt at each point was calculated, from which the concentration of free thallic acetate could be obtained. A plot of dx/dt versus the product of the concentrations of phenylcyclopropane and free thallic acetate gave a line from which a new rate constant was obtained. Using this rate a new equilibrium constant was calculated from $k/K = 8.51 \times 10^{-4}$. This process was repeated until the values converged (Table 12). Changing the equilibrium constant 27% from the values.

### TABLE 12

<table>
<thead>
<tr>
<th>K</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1/l_m</td>
<td>1/l_m/min</td>
</tr>
<tr>
<td>765</td>
<td>0.47</td>
</tr>
<tr>
<td>555</td>
<td>0.50</td>
</tr>
<tr>
<td>583</td>
<td>--</td>
</tr>
<tr>
<td>570</td>
<td>0.50</td>
</tr>
</tbody>
</table>

*Values were obtained by using data which gave an apparent rate constant of 0.65 l/m/min from an initial phenylcyclopropane concentration of 0.01508 M (Table 8).*

765 to 555 produced a change of only 6% in the rate constant from 0.47 to 0.50 l/m/min. Therefore, the process was not repeated for the value of 583, but a mean value of 570 was chosen for the equilibrium constant.
The rate constant was calculated using a $K$ of 570 for several kinetic runs in which the starting concentrations of reactants were different.

From the values obtained (Table 13) a true rate constant for the reaction of phenylcyclopropane with thallic acetate at 50.1° is in the order of magnitude of $0.50 \pm 0.09$ l/m/min. Henry\textsuperscript{12} calculated an equilibrium rate constant of 209 for the equilibrium of thallic acetate reacting with acetate ion forming the thallium (III) tetraacetate anion. However, the solvent system was mineral acid in aqueous acetic acid. In his system he postulated $\text{Tl(II)}^{+}$ was the most important reacting specie. He found an equilibrium constant of 362 for the equilibrium of $\text{Tl(II)}^{+}$ with acetate ion forming thallic acetate. Considering the inherent errors in this computation and the variety of starting concentrations, even when thallous acetate was added initially, reasonable results were obtained.

\begin{table}[h]
\centering
\caption{True Rate Constant for the Reaction of Phenylcyclopropane with Thallic Acetate at 50.1° from a Double Salt Equilibrium Constant of 570}
\begin{tabular}{c c c c}
\hline
$\phi$ & $\text{Tl(OAc)}_{3}$ & $\text{TlOAc}$ & $k$ \\
m/l & m/l & m/l & 1/m/min \\
\hline
0.01508 & 0.03021 & 0 & 0.50 \\
0.01513 & 0.01525 & 0 & 0.54 \\
0.00475 & 0.00954 & 0 & 0.56 \\
0.01487 & 0.01491 & 0.02230 & 0.43 \\
\hline
\end{tabular}
\end{table}

$k = 0.50 \pm 0.07$ l/m/min
Since the equilibrium constant is not as large as it was assumed, the initial rates of equal molar concentrations should be an approximation of the true rate constants (Figure 3). A value of \(0.50 \pm 0.05 \text{ l/m/min}\) was obtained from typical second order plots for approximately 25\% reaction of phenylcyclopropane with thallic acetate at 50.1° (Table 14). This is very good agreement with value obtained using the equilibrium constant. This is a good indication that the variance of the rate constants with concentration is from an equilibrium involving double salt formation and not oxidation by the double salt.

The rate constant for the thallic acetate oxidation of para-methoxyphenylcyclopropane is so large that it could not be found directly. The double salt method was employed to slow the reaction to a measurable rate. The same expression involving \(k/K\) derived earlier was used. The

<table>
<thead>
<tr>
<th>(\phi-4)</th>
<th>(\text{Tl(OAc)}_3)</th>
<th>(k)</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/l</td>
<td>m/l</td>
<td>l/m/min</td>
</tr>
<tr>
<td>0.0149</td>
<td>0.0149</td>
<td>0.55</td>
</tr>
<tr>
<td>0.0149</td>
<td>0.0149</td>
<td>0.53</td>
</tr>
<tr>
<td>0.0150</td>
<td>0.0150</td>
<td>0.46</td>
</tr>
<tr>
<td>0.0174</td>
<td>0.0174</td>
<td>0.50</td>
</tr>
<tr>
<td>0.0178</td>
<td>0.0178</td>
<td>0.46</td>
</tr>
</tbody>
</table>

\(k = 0.50 \pm 0.05 \text{ l/m/min}\)
same trends, which were discussed with respect to phenylcyclopropane were also observed with the para-methoxy-compound. The observed k/K values (Table 15) increased linearly with decreasing initial thallic to thallous

\[ \text{TABLE 15} \]

**OBSERVED k/K RATIOS FOR THE REACTION OF PARA-METHOXYPHENYLCYCLOPROPAINE WITH VARYING INITIAL THALLOUS-THALLIC ACETATE RATIOS AT 50.1°**

<table>
<thead>
<tr>
<th>p-MeO—</th>
<th>Tl(OAc)₃</th>
<th>TlOAc</th>
<th>TlOAc/Tl(OAc)₃</th>
<th>k/K</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/l</td>
<td>m/l</td>
<td>m/l</td>
<td>m/l/m/l</td>
<td>min⁻¹</td>
</tr>
<tr>
<td>0.01443</td>
<td>0.01442</td>
<td>0.02164</td>
<td>1.50</td>
<td>0.191</td>
</tr>
<tr>
<td>0.01586</td>
<td>0.01586</td>
<td>0.03172</td>
<td>2.00</td>
<td>0.205</td>
</tr>
<tr>
<td>0.01561</td>
<td>0.01561</td>
<td>0.04682</td>
<td>3.00</td>
<td>0.224</td>
</tr>
</tbody>
</table>

acetate ratio with a slope of \(-1.01 \times 10⁻¹\) for ratios of 0.666, 0.500, and 0.333. The value of k/K for a ratio of 1 was obtained by extrapolation. From this value of 0.156 a rate constant was approximated by comparison of the k/K value for phenylcyclopropane at a ratio of 1. If the k/K values are proportional to the rate constants, then the rate constant for the para-methoxy-compound is approximately 400 l/m/min. This is a minimum value and was obtained by using 0.651 l/m/min for the rate constant of phenylcyclopropane.

Activation parameters were obtained for phenylcyclopropane from kinetic runs in which the concentrations of 0.015 M and 0.030 M, respectively, at 29.6°, 50.1°, and 76.2°. The values for \(\Delta H^\ddagger\) and \(\Delta S^\ddagger\) are 12.35 ± 1.19 kcal/mole and -29.2 e.u., respectively (Table 16). These values are dependent upon the thermal sensitivity of the equilibrium
### TABLE 16

PARAMETERS FROM REACTIONS OF HEAVY METAL ACETATES WITH SUBSTITUTED PHENYL CYCLOPROPANES AND STYRENES IN ANHYDROUS ACETIC ACID

\[ X-\phi-R + M(OAc)_x \]

<table>
<thead>
<tr>
<th>R</th>
<th>M</th>
<th>( \Delta H^# )</th>
<th>( \Delta S^# )</th>
<th>( \rho )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>kcal/mole</td>
<td>e.u.</td>
<td></td>
</tr>
<tr>
<td>✿</td>
<td>Tl</td>
<td>12.35 ±1.19</td>
<td>-29.2</td>
<td>-4.41&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>✿</td>
<td>Hg&lt;sup&gt;64&lt;/sup&gt;</td>
<td>19.1</td>
<td>-9.6</td>
<td>-3.3</td>
</tr>
<tr>
<td>✿</td>
<td>Pb&lt;sup&gt;b,72&lt;/sup&gt;</td>
<td>20.0</td>
<td>-13.0</td>
<td>-1.8</td>
</tr>
<tr>
<td>✿</td>
<td>Tl&lt;sup&gt;c,74&lt;/sup&gt;</td>
<td>7.89</td>
<td>-40.6</td>
<td>-2.2</td>
</tr>
</tbody>
</table>

<sup>a</sup>This value is not inclusive of the approximated rate constant for para-methoxyphenylcyclopropane. The \( \rho \) is -3.87 when the para-methoxy-compound is included.

<sup>b</sup>Activation parameters are for para-methoxyphenylcyclopropane.

<sup>c</sup>Activation parameters are for styrene.

constant for the double salt. If the equilibrium constant changes substantially over this temperature range, the activation parameters will change. If the equilibrium constant decreases as the temperature increases, then \( \Delta H^\# \) will increase and \( \Delta S^\# \) will decrease. It has already been seen that a change of 27% in the equilibrium constant results in a change of only 6% in the rate constant. Activation parameters from other heavy metal acetate reactions are listed in Table 16 for comparison. Thallic acetate oxidation of substituted styrenes<sup>74</sup> also has a high negative entropy of activation which could be a reflection of the complexing ability of thallic acetate which gives a very tightly bound and highly
ordered complex in the transition state. The double bond, having more ν-electron density than cyclopropane, could possibly form a tighter complex with thallic acetate. The ΔS° for mercuric\textsuperscript{64} and plumbic\textsuperscript{72} acetates oxidations of phenylcyclopropane are only -9.6 and -13.0 e.u., respectively. The ΔH° value of thallic oxidation of styrene is only 7.89 kcal./mole as compared with 12.35 for phenylcyclopropane. While the ΔH° 's for mercuric and plumbic acetates are 19.1 and 20.0, respectively.

A rigorous explanation for the variances of these activation parameters is impossible. The oxidizing agents differ considerably. Many variables, such as species in solution, attacking species, and differences in solvation and symmetry of the reactants and transition states, would have to be considered. This information is not available at the present.

Using a Hammett equation for σ⁺ a plot of log k versus σ⁺ (Figure 9) for the rate constants from kinetic runs, in which the concentrations of the reactants were approximately 0.015 and 0.030 M, gave a ρ of -3.87 with a correlation coefficient of 0.995. This includes the approximated rate for the para-methoxy-compound. Without para-methoxy-phenylcyclopropane, the ρ is -4.41 with a correlation coefficient of 0.999. The values used for σ⁺ are those obtained by Brown\textsuperscript{75,76} for the solvolysis of substituted 2-phenyl-2-propyl chlorides in 90% acetone. The rate constant obtained for para-methoxyphenylcyclopropane is considerably smaller than that expected from a Hammett equation. This equation predicts a rate constant of approximately 1000 1/m/min from the rate constants for the other substituents. The value of 400 was obtained indirectly and the assumptions which were made in order to arrive at it
Fig. 9.—Hammett $\sigma^+$ plot at 50.1°
may not be valid. In acetic acid the oxygen of the methoxy-group may be hydrogen bonded to a different degree than in 90% acetone, which was used to obtain the value for $\sigma^{-\dagger}$. This might diminish the resonance effect of the methoxy-group and as a result, the reaction rate would be slower than expected.

Oxidation of substituted phenylcyclopropanes is more sensitive to substituent effects than oxidations with mercuric or plumbic acetates (Table 16). The sensitivity increases as plumbic $< $ mercuric $< $ thallic acetates. The same trend is observed for the rates of oxidation of a given phenylcyclopropane. Qualitatively, this is reasonable. It might be expected that the fastest rate would be with lead tetraacetate because it has the largest oxidation potential. However, mercuric and thallic acetates have vacant p-orbitals and their rates of oxidation are in the same order as their respective oxidation potentials and their ability to complex. Lead tetraacetate has no available p-orbitals and the reaction must proceed by another mechanism, such as initial ionization or expansion of its valence shell. In the thallic oxidations of the cyclopropanes, the high negative $\rho$ indicates a large amount of carbonium ion character of the benzylic position and also that bond breaking is more important than bond formation. The $\rho$ for the oxidations of styrenes with thallic acetate (Table 16) is between those of mercuric and plumbic acetate oxidations of phenylcyclopropanes and it is approximately half that for thallic acetate oxidation of these cyclopropanes. This could possibly be because of the strain of the cyclopropyl ring.
PREPARATION AND DECOMPOSITION OF THALLIC ACETATE

Two general methods have been used to prepare thallic acetate. The first is that of Meyer,\textsuperscript{5} reported in 1903, in which thallic oxide is reacted with acetic acid at reflux. The mixture upon cooling yields the white crystalline thallic acetate. The second method is that of Grinstead\textsuperscript{10} which is a multi-step process. This method involves chlorination of thallous chloride to give thallic chloride followed by addition of sodium hydroxide which precipitates thallic hydroxide. The thallic hydroxide is then reacted with acetic acid to produce thallic acetate.

Initial attempts to obtain pure thallic acetate by Meyer's method were unsuccessful. Since thallic acetate is hydrolyzed to thallic oxide, acetic anhydride was used to remove the water formed in the conversion of the oxide to the acetate. After most of the thallic oxide

\[ \text{Tl}_2\text{O}_3 + 6\text{AcOH} \rightarrow 2 \text{Tl(0Ac)}_3 + 3\text{H}_2\text{O} \]

had reacted, the mixture was filtered, but upon cooling no crystallization occurred. The acetic acid was vacuum transferred and attempts to recrystallize the remaining white solid from a minimum amount of acetic acid generally were not successful. The solid as analyzed by the ferrous-dichromate method described in the previous section was not pure. The thallic oxide, dissolved in one normal sulfuric acid, was found to be at least 97\% pure. Therefore, decomposition occurs under the reaction conditions.
The per cent purity of thallic acetate was measured as a function of the temperature of preparation. The reactions were run using 0.05 g. thallic oxide in 10 ml. of 0.18 M acetic anhydride in acetic acid. After complete reaction, the solvent was vacuum transferred and the remaining solid was analyzed. As the temperature of preparation increases, the time necessary for complete reaction and the per cent thallic acetate decreases (Table 17). Preparation of thallic acetate at a low temperature would not be practical, since the time for reaction of 0.05 g. of thallic oxide is approximately 60 hours at 50°.

TABLE 17

<table>
<thead>
<tr>
<th>Reaction Time (hr.)</th>
<th>Temp. (°C)</th>
<th>Tl(OAc)₃ Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>50</td>
<td>90</td>
</tr>
<tr>
<td>23</td>
<td>60</td>
<td>80</td>
</tr>
<tr>
<td>6</td>
<td>75</td>
<td>68</td>
</tr>
<tr>
<td>0.75</td>
<td>100</td>
<td>60</td>
</tr>
<tr>
<td>0.17</td>
<td>ca. 118 (reflux)</td>
<td>36</td>
</tr>
</tbody>
</table>

In Grinstead's method of preparation thallic hydroxide is reacted with acetic acid. Since oxides react with water to produce their corresponding acid or base, another series of controls were examined. Instead of removing the water formed in the reaction, water was added. Using 0.05 g. of thallic oxide in 10 ml. acetic acid at 60°, the per cent thallic acetate was analyzed as a function of per cent aqueous
acetic acid. The analytical procedure was the same as that described above. As the per cent water increases, the reaction time decreases, but the thallic acetate purity remains approximately 95% (Table 18). The

**TABLE 18**

**PER CENT THALLIC ACETATE AS A FUNCTION OF PER CENT WATER AT 60°**

<table>
<thead>
<tr>
<th>Reaction Time (hr.)</th>
<th>H₂O % Added</th>
<th>Tl(0Ac)₃ Yield, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.5</td>
<td>2</td>
<td>95</td>
</tr>
<tr>
<td>4</td>
<td>4</td>
<td>95</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>95</td>
</tr>
<tr>
<td>1.7</td>
<td>10</td>
<td>95</td>
</tr>
</tbody>
</table>

values in Tables 17 and 18 are an average of two independent reactions and do not vary more than ±1.5%. A series of equilibria are apparently present in a mixture of thallic oxide in aqueous acetic acid which ultimately results in the formation of thallic acetate. When Meyer

\[
\begin{align*}
\text{Tl}_2\text{O}_3 & \rightleftharpoons \text{Tl}(0\text{Ac})_3 \\
\text{Tl}(\text{OH})_3 & \rightleftharpoons \text{Tl}(0\text{Ac})_3
\end{align*}
\]

first prepared thallic acetate in 1903 the acetic acid which was used most probably contained a sufficient quantity of water to facilitate thallic acetate formation.

Thallic acetate was readily obtained by using aqueous acetic acid. A mixture of 10 g. thallic oxide in 100 ml. of acetic acid and 25 ml. water stirred for 4 hours at 50° gave a 73.7% yield of thallic
acetate which was 98% pure. In another preparation a 65% yield of the acetate, 99% pure, was obtained by stirring a mixture of 15 g. thalllic oxide in 100 ml. acetic acid and 15 ml. water for 21 hours at 55°.

The kinetics of decomposition of thalllic acetate in anhydrous acetic acid was studied at 75.3° and 99.3°. The thalllic concentration was followed by the iodide-thiosulfate method, which was described in the previous kinetic section. The decomposition of thalllic acetate might be expected to follow first order kinetics. However, first order plots gave reasonable straight lines only for the first half-life, after which the apparent rate of decomposition of thalllic acetate increased considerably (Figure 10). The initial observed first order rate constants are inversely related to the initial thalllic acetate concentration (Table 19). Therefore, either the decomposition is not a first order process or it is first order and there are secondary reactions taking place. The addition of thallous acetate produced only a slight decrease in the apparent first order rate constant at 99.3° (Table 20). The mixed salt runs gave the same curve when plotted by a first order expression as that which was obtained in the absence of initial added thallous acetate. Therefore, double salt formation between thallous and thalllic acetate is not a significant secondary process at 99.3°. However, reactions of thalllic acetate with the organic decomposition products might explain the observed kinetic results, but the organic decomposition products are not known. Therefore, the effect of added organic products could not be examined.

Since the decomposition of thalllic acetate does not obey first order kinetics, other kinetic orders were considered. Probable simple
Fig. 10.—Typical first order kinetic plot for the decomposition of thallic acetate at 99.4°C.
<table>
<thead>
<tr>
<th>$\text{Tl(OAc)}_3$ m/l</th>
<th>Temp. °C</th>
<th>$k \times 10^3$ min$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03006</td>
<td>75.3</td>
<td>0.321</td>
</tr>
<tr>
<td>0.02996</td>
<td>75.3</td>
<td>0.315</td>
</tr>
<tr>
<td>0.03088</td>
<td>99.3</td>
<td>4.22</td>
</tr>
<tr>
<td>0.03051</td>
<td>99.3</td>
<td>4.39</td>
</tr>
<tr>
<td>0.02105</td>
<td>99.3</td>
<td>5.89</td>
</tr>
<tr>
<td>0.02094</td>
<td>99.3</td>
<td>5.98</td>
</tr>
<tr>
<td>0.01560</td>
<td>99.4</td>
<td>7.44</td>
</tr>
<tr>
<td>0.01557</td>
<td>99.4</td>
<td>7.68</td>
</tr>
<tr>
<td>0.01074</td>
<td>99.3</td>
<td>11.3</td>
</tr>
<tr>
<td>0.01065</td>
<td>99.3</td>
<td>11.2</td>
</tr>
</tbody>
</table>
kinetic orders which might apply are one-half order and pseudo-zero order. Although straight lines were obtained from both one-half and pseudo-zero order plots, the apparent rate constants are still concentration dependent. For one-half order kinetics the observed rate constants are inversely related to the initial concentration, but apparent pseudo-first order rate constants are directly related to the initial concentration.

**TABLE 20**
INITIAL APPARENT FIRST ORDER RATE CONSTANTS FROM THE DECOMPOSITION OF THALLIC ACETATE WITH INITIAL ADDED THALLOUS ACETATE AT 99.3°

<table>
<thead>
<tr>
<th>Tl(0Ac)₃ m/l</th>
<th>Tl0Ac m/l</th>
<th>Tl0Ac/Tl(0Ac)₃ m/l</th>
<th>k x 10³ min⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.02094</td>
<td>0</td>
<td>0</td>
<td>5.98 a</td>
</tr>
<tr>
<td>0.02006</td>
<td>0.04038</td>
<td>2.01</td>
<td>5.59</td>
</tr>
<tr>
<td>0.02014</td>
<td>0.08050</td>
<td>4.00</td>
<td>5.12</td>
</tr>
</tbody>
</table>

a This value is taken from Table 19.

The simplest expressions, with which the data from the decomposition of thallic acetate can be interpreted, are one-third and one-fourth order rate laws. Results from plotting [Tl⁺³]²/₃ or [Tl⁺³]³/₄ versus time gave more consistent rate constants (Table 21) and the reaction can be described over a greater per cent reaction (Figures 11 and 12). It is difficult kinetically to distinguish between one-third order and one-fourth order processes. This fractional kinetic order does not appear to be an artifact. Using one-half order kinetic plots obtained from data for kinetic runs initially approximately 0.03 M and 0.01 M in
TABLE 21

APPEARANT RATE CONSTANTS FROM ONE-THIRD AND ONE-FOURTH ORDER
PLOTS FOR THE DECOMPOSITION OF THAL LIC ACETATE

<table>
<thead>
<tr>
<th>Tl(0Ac)₃</th>
<th>Temp. °C</th>
<th>$k \times 10^4$ (m/l)$^{2/3}$/min</th>
<th>$k \times 10^4$ (m/l)$^{3/4}$/min</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.03088</td>
<td>99.3</td>
<td>3.58</td>
<td>2.53</td>
</tr>
<tr>
<td>0.03051</td>
<td>99.3</td>
<td>3.86</td>
<td>2.67</td>
</tr>
<tr>
<td>0.02105</td>
<td>99.3</td>
<td>3.55</td>
<td>2.47</td>
</tr>
<tr>
<td>0.02094</td>
<td>99.3</td>
<td>3.60</td>
<td>2.44</td>
</tr>
<tr>
<td>0.01560</td>
<td>99.4</td>
<td>3.64</td>
<td>2.56</td>
</tr>
<tr>
<td>0.01557</td>
<td>99.4</td>
<td>3.58</td>
<td>2.52</td>
</tr>
<tr>
<td>0.01074</td>
<td>99.3</td>
<td>3.81</td>
<td>2.45</td>
</tr>
<tr>
<td>0.01065</td>
<td>99.3</td>
<td>4.34</td>
<td>2.71</td>
</tr>
</tbody>
</table>

thallic acetate, initial instantaneous rates, $dx/dt$, were calculated. From the equation below, where $\left(\frac{dx}{dt}\right)_1$ and $\left(\frac{dx}{dt}\right)_2$ are the instantaneous

$$\frac{\left(\frac{dx}{dt}\right)_1}{\left(\frac{dx}{dt}\right)_2} = \frac{c_1^n}{c_2^n}$$

rates at concentrations $c_1$ and $c_2$ for runs of different initial concentrations, the kinetic order $n$ can be found. The initial kinetic order was found to be in the order of magnitude of 0.25. This is only an approximation because of inherent errors in the calculation. However, it does show that even initially the decomposition of thallic acetate is a fractional kinetic order. A much more complex expression is not ruled out, but present data does not allow a rigorous treatment.
Fig. 11.—One-third order plot for the decomposition of thallic acetate at 99.4°.
Fig. 12.—One-fourth order plot for the decomposition of thallic acetate at 99.4°
An inverse relationship between the initial concentration and the rate of reaction has been observed in the decomposition of acetyl peroxide in acetic acid\textsuperscript{77} and the decomposition of cumene hydroperoxide in benzyl alcohol.\textsuperscript{78} This inverse relationship was also observed in the decomposition of lead tetraacetate in acetic acid containing sodium acetate.\textsuperscript{79} Sodium acetate was found to increase the rate of decomposition of plumbic acetate. A complex rate law was used to describe the data and it was suggested that the concentration dependence was a result of plumbic acetate forming a relatively stable complex with a "retarder," a reaction product.

This kinetic study shows that the rate of decomposition of thallic acetate is sufficiently slow, so as not to interfere with the kinetics of cleavage of phenylocyclopropanes by thallium triacetate.
EXPERIMENTAL

All elemental analyses were performed at the Alfred Bernhardt Microanalytical Laboratory. Nuclear magnetic resonance spectra were run of a Varian A-60 instrument and infrared spectra were run on Perkin-Elmer 137 Spectrophotometer. Melting points are uncorrected and were obtained using a Thomas capillary melting point apparatus. Boiling points were obtained using an immersion thermometer and are uncorrected.

Cleavage of bicyclo(4.1.0)heptane with thallic acetate

A mixture of 0.25 g. (0.000547 mole) of thallic oxide, 0.167 g. (0.00164 mole) of acetic anhydride, and 10 ml. of anhydrous acetic acid was stirred at 75° for 19 hr. To the thallic acetate solution was added 0.15 g. (0.0015 mole) of bicyclo(4.1.0)heptane and the solution was stirred at 75° for 82 hr. The reaction mixture was allowed to cool to room temperature and then dissolved in ether. The ethereal solution was washed several times with water and finally with saturated sodium bicarbonate solution. The ether layer was dried over anhydrous magnesium sulfate, filtered, and carefully concentrated by distilling the ether through a 15-cm. Vigreux column. The concentrate was analyzed by vpc on a 10 ft. x 1/8 in. 20% Carbowax 20M on 60/80 Chromosorb W column at 180°. The olefinic acetate was analyzed at 115°. The products were identified from retention times of authentic samples and the yield percents are listed in Table 4.
Cleavage of bicyclo(3.1.0)hexane with thallic acetate

Bicyclo(3.1.0)hexane was cleaved by thallic acetate as in the above procedure using 0.56 g. (0.0012 mole) of thallic oxide, 0.39 g. (0.0038 mole) of acetic anhydride, 10 ml. of anhydrous acetic acid, and 0.31 g. (0.0038 mole) of bicyclo(3.1.0)hexane. After the addition of the bicyclic hexane, the solution was stirred for 62 hr. at 75°. The mixture of acetates was analyzed under the same conditions as that obtained from the bicycloheptane. The products and yield per cent are listed in Table 3.

Cleavage of bicyclo(2.1.0)pentane with thallic acetate

Bicyclo(2.1.0)pentane was cleaved with thallic acetate as described in the cleavage of bicycloheptane using 0.68 g. (0.0015 mole) of thallic oxide, 0.51 g. (0.005 mole) of acetic anhydride, 10 ml. of anhydrous acetic acid, and 0.2 g. (0.0029 mole) of bicyclo(2.1.0)pentane. After addition of the bicyclopentane, the solution was stirred for 60 hr. at 25°. The mixture of acetate was analyzed on a 10 ft. x 1/4 in. 20% Dgs on 60/80 Chromosorb W vpc column at 170° and the olefinic acetates were resolved on a 10 ft. x 1/8 in. 20% Carbowax 20M on 60/80 Chromosorb W column at 95°. The analysis of products is summarized in Table 2.

Preparation of bicyclo(3.1.0)hexane

A mixture of 21 g. (0.32 mole) of powdered zinc-copper couple, 80.5 g. (0.30 mole) of methylene iodide, 20.8 g. (0.30 mole) of cyclopentane, 35 ml. of dry glyme, and 95 ml. of anhydrous ether was stirred
mechanically under reflux. After 24 and 48 hr. 40 g. (0.15 mole) of methylene iodide, 11 g. (0.16 mole) of powdered zinc-copper couple, and 20 ml. of dry glyme were added. Anhydrous ether was added as needed to facilitate efficient mixing. After 72 hr. total reaction time 100 ml. of ether was added and the mixture was carefully suction-filtered and the solid was washed with ether. The filtrate was washed once with saturated ammonium chloride solution, once with saturated sodium bicarbonate solution, and several times with water. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and the ether was carefully and slowly distilled through a 30-cm. Vigreux column. The concentrate was distilled through a 15-cm. Vigreux column at atmospheric pressure. A 63% yield of 15.8 g. (0.19 mole) of bicyclo(3.1.0)hexane was obtained with a bp of 75-7°, reported bp 78°.

Preparation of bicyclo(4.1.0)heptane

A mixture of 12.3 g. (0.15 mole) of cyclohexene, 26.1 g. (0.15 mole) of methylene bromide, 13.1 g. (0.20 mole) of powdered zinc-copper couple, 18 g. (0.20 mole) of dry glyme, and 50 ml. of anhydrous ether was stirred mechanically under reflux. After 24 and 48 hr. 26.1 g. (0.15 mole) of methylene bromide, 13.1 g. (0.20 mole) of powdered zinc-copper couple, and 18 g. (0.20 mole) of dry glyme were added. Ether was added as needed to facilitate efficient mixing. After 78 hr. total reaction time 150 ml. of ether was added and the mixture was carefully suction-filtered. The solid was washed several times with ether. The filtrate was washed once with saturated ammonium chloride solution, once with saturated sodium bicarbonate solution, and several times with water. The
ethereal layer was dried over anhydrous magnesium sulfate, filtered, and concentrated by carefully distilling the ether through a 30-cm Vigreux column. The concentrate was distilled through a 15-cm Vigreux column at atmospheric pressure. A 35% yield of 5.0 g. (0.052 mole) of bicyclo-(4.1.0)heptane was obtained with a bp of 111-5°, reported bp 116-7°.

Preparation of powdered zinc-copper couple

To an 125 ml. Erlenmeyer flask containing a large magnetic stirring bar was introduced 12.3 g. (0.19 mole) of zinc dust. The zinc was washed for 1 min. each with vigorous stirring with the following order of reagents; 4 times with 10 ml. of 3% hydrochloric acid, 5 times with 25 ml. of distilled water, 2 times with 19 ml. of 2% cupric sulfate, 5 times with 25 ml. of distilled water, 4 times with 25 ml. of absolute alcohol, and 5 times with 25 ml. of anhydrous ether. After each washing the solution was decanted, and the ethanol and ether washings were decanted onto a fritted glass funnel. At the conclusion of the washings, the powdered zinc-copper couple was suction-filtered onto the fritted glass funnel and the couple was washed with additional anhydrous ether. The couple was covered tightly with a rubber dam, suctioned dry until it warmed to room temperature, and then dried overnight over phosphorus pentoxide, in a vacuum desiccator.

Cleavage of tricyclo(2.2.1.02,6)heptane with thallic acetate

A mixture of 0.50 g. (0.0022 mole) of thallic oxide, 0.70 g. (0.0069 mole) of acetic anhydride, and 10 ml. of anhydrous acetic acid was stirred at 75° for 21 hr. To the thallic acetate solution was then added 0.18 g. (0.0019 mole) of tricyclo(2.2.1.02,6)heptane and 2 ml. of
The solution was stirred at 75° for 94.5 hr. and then allowed to cool to room temperature. The solution was added to ether and then washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The concentrate was analyzed on a vpc 5 ft. x 1/4 in. 20% Dega's on 60/80 Chromosorb W column at 160°. Only two well resolved symmetrical peaks were obtained, the shorter retention time peak was 62.5% and the longer was 37.5%. Assuming norbornyl diacetates were the products, analysis by nmr showed the reaction mixture to be approximately 67 and 33% on the basis of the areas of the acetate methyls. The endo-acetate methyls come at lower field position than the exo-acetate methyls. Each of the two cleavage products were collected by vpc and then each was analyzed by nmr. The shorter retention time product showed two acetate methyl absorptions at 117 and 121.5 cps down field from tetramethyilsilane in carbon tetrachloride and it was assigned as endo-exo-bicyclo(2.2.1)heptane-2,6-diol diacetate. The longer retention time product showed only one acetate methyl absorption at 117 cps and was assigned as di-exo-bicyclo(2.2.1)heptane-2,6-diol diacetate. A more detailed discussion can be found in the section of the cleavage of tricyclo(2.2.1.0^2.6)heptane.

Preparation of di-exo-bicyclo(2,2,1)-heptane-2,5-diol diacetate

To a solution of 5 drops of pyridine, ca. 1 mg. of di-exo-bicyclo(2.2.1)heptane-2,5-diol, and 4 ml. of anhydrous ether was added 4 drops of acetyl chloride. The mixture was stirred magnetically for 60 hr. at room temperature. The mixture was transferred to a 25-ml.
pears-shaped flask with rinsing of the reaction flask with small amounts of ether and then water. The ether solution was washed several times with water and finally with saturated sodium bicarbonate solution. The lower aqueous layers were removed by means of a disposable pipette. The remaining ethereal solution was dried over a small amount of anhydrous magnesium sulfate and carefully separated from the solid by the use of a disposable pipette. The ether solution was carefully concentrated on a rotary evaporator and when most of the ether was removed, carbon tetrachloride was added and the solution was concentrated further. The remaining carbon tetrachloride solution, after addition of tetramethylsilane, showed only one acetate methyl at 116.5 cps down field from TMS.

**Preparation of endo-exo-bicyclo(2,2,1)-heptane-2,5-diol diacetate**

To a solution of ca. 2.5 mg. of endo-exo-bicyclo(2,2,1)heptane-2,5-diol, 5 drops of pyridine and 4 ml. of anhydrous ether was added 4 drops of acetyl chloride. The mixture was stirred magnetically at room temperature for 60 hr. The same work-up procedure was used as described above in the preparation of the di-exo-2,5-diacetate. By nmr analysis, two acetate methyl absorptions were seen at 117 and 121.5 cps down field from TMS in carbon tetrachloride.

**Cleavage of exo-tricyclo(3.2.1.0²⁴)octane with thallic acetate**

A solution of 0.68 g. (0.0063 mole) of exo-tricyclo(3.2.1.0²⁴)-octane, 1.7 g. (0.0045 mole) of thallic acetate, and 25 ml. of anhydrous acetic acid was allowed to stand at 75° for 120 hr. The solution was then allowed to cool to room temperature and then added to ether. The ethereal solution was washed several times with water and finally with
saturated sodium bicarbonate solution. The ether layer was dried over anhydrous magnesium sulfate, filtered, and concentrated. The concentrate was analyzed on a 5 ft. x 1/4 in. 20% Degas on 60/80 Chromosorb W vpc column at 165°. Two main peaks were observed, but both contained at least one smaller component as observed by small shoulders near the base of the peaks. On the basis of vpc analysis, the shorter retention time products are 35% of the two main peaks, and the longer retention time products are 65%. Each main product was collected by vpc and analyzed by nmr. Each collected product showed sharp acetate methyl absorptions at ca. γ8, complex absorptions between ca. γ6.5 and γ9, and a complex pattern at ca. γ5.3. In addition, the shorter retention time product showed a doublet (J = 8 cps) at γ5.85. The lower retention time product was assigned as an acetoxymethylnorbornyl acetate. The longer retention time peak was assigned as bicyclo(3.2.1) and/or bicyclo(2.2.2)-octyl diacetates. From nmr analysis of the original reaction mixture, the per cents were approximated to be 31 and 69% of the acetoxymethylenebiciclic acetate and bicyclooctyl diacetates on the basis areas of the doublet at γ5.85 and complex multiplet at ca. γ5.3. From both vpc retention time and nmr field position of an acetate methyl at γ8.05, di-endo-bicyclo(3.2.1)octane-2,4-diol diacetate could be a small component of the longer retention time product. The presence of endo-exo-bicyclo(3.2.1)octane-2,4-diol diacetate is difficult to ascertain. A more thorough discussion of this cleavage has already been discussed in the text.
Preparation of bicyclo(3,2,1)octane-2-ol

A mixture of 50 g. (0.40 mole) of 5-hydroxymethylnorbornene, 50 ml. of 95% ethanol, and 1 g. of palladium on carbon was hydrogenated on a Parr hydrogenation apparatus. After complete hydrogenation the mixture was suction-filtered through celite and the filtrate concentrated under reduced pressure to remove the aqueous ethanol.

Upon mixing the 2-hydroxymethylnorbornane reaction product from the above hydrogenation with 125 ml. of pyridine and 85 g. (0.45 mole) of p-toluenesulfonyl chloride, the mixture warmed to reflux from the heat of reaction. After the mixture was stirred at room temperature for 16 hr. and then poured over 250 g. of ice, 200 ml. of ether was added, and concentrated hydrochloric acid was added with vigorous stirring until a pH of 3-4 was obtained. The layers were separated and the ethereal layer was washed with water until the pH of the washings was \( \geq 5 \), dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

A mixture of the above tosylate with 1 g. of p-toluenesulfonic acid in 120 ml. of acetic acid and 550 ml. of water was refluxed with stirring for 23 hr. The mixture was allowed to cool and 300 g. of 40% aqueous sodium hydroxide was added slowly with stirring. The mixture was refluxed with stirring for 3.5 hr. and then the solid bicyclo(3,2,1)-octane-2-ol was steam distilled. The distillate contained a heterogeneous mixture of the solid alcohol and the aqueous layer. The distillate was saturated with sodium chloride and extracted three times with ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated by distilling the ether through a 15-cm.
Vigreux column at atmospheric pressure and finally under reduced pressure at 12 mm. A 81.5% yield of 41.1 g. (0.033 mole) of bicyclo(3.2.1)-octane-2-ol was obtained with a mp range of 145-165°, reported at 140-166°.

Preparation of bicyclo(3.2.1)octane-2-one

To a solution of 41 g. (0.033 mole) of bicyclo(3.2.1)octane-2-ol in 40 ml. of acetic acid was added dropwise over a 1 hr. period with stirring a solution of 35 g. (0.35 mole) of chromic oxide in 20 ml. of water and 40 ml. of acetic acid. An ice bath was used to maintain the reaction temperature at 25°. After the dropwise addition the solution was stirred for 24 hr. at room temperature, then diluted with 1 l. of water and extracted several times with benzene. The combined benzene extracts were dried over anhydrous magnesium sulfate filtered, and concentrated under reduced pressure. A slush remained which would not completely crystallize. The reaction mixture showed a strong carbonyl absorption in the infrared at ca. 1730 cm⁻¹ and only one major product by vpc analysis on a 18 in. x 1/4 in. 20% Carbowax 20M on 60/80 Chromosorb W column at 100°. A 78.5% yield of 31.8 g. (0.26 mole) of bicyclo(3.2.1)-octane-2-one was obtained, reported mp at 127-9° from purification via its semicarbazone. No further attempt was made to purify the product, but it was used in the next step.

Preparation of bicyclo(3.2.1)-3-octane-2-one

To 31.8 g. (0.26 mole) of bicyclo(3.2.1)octane-2-one dissolved in 150 ml. of absolute ethanol was added 97 g. (0.26 mole) of ca. 85% pure pyridine hydrobromide perbromide in small portions with stirring at
room temperature. The mixture was concentrated under reduced pressure. To the remaining heterogeneous mixture anhydrous ether was added and the white solid was suction-filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

The above 3-bromo-bicyclo(3.2.1)octane-2-one was dissolved in 200 ml of dry dimethylformamide which had been freshly distilled at atmospheric pressure. To the bromide solution was added 60 g. of lithium bromide, which had been dried in a vacuum oven at 190° and stored in a vacuum desiccator, and 60 g. of lithium carbonate. Upon mixing of the reactants, an exothermic reaction occurred. The mixture was stirred under reflux for 5.5 hr. and then allowed to stand overnight at room temperature. Ether was added to the thick, dark brown reaction mixture and stirred with a glass rod. The ether was decanted and the process repeated twice. Water was added to the brown reaction mixture and an attempt to extract with ether resulted in the formation of an emulsion. The emulsion was suction-filtered and the layers separated. The aqueous layer was extracted several times with ether. The ether extractions were combined with the previous ether washings, and dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The concentrate was vacuum distilled through a 15-cm. Vigreux column. A yield of 32.5% of 10.1 g. (0.083 mole) of bicyclo(3.2.1)-3-octene-2-one was obtained with a bp 62-4°, reported bp 86°.

Preparation of bicyclo(3.2.1)-3-octene-2-one oxide

To a solution of 15 ml. of water in 25 ml. of methanol was added dropwise with stirring a solution of 2.44 g. (0.020 mole) of
bicyclo(3,2,1)-3-octene-2-one in 12 ml. of 30% hydrogen peroxide at such a rate that the reaction temperature was maintained at 25-30°. During the dropwise addition the pH of the reaction solution was maintained at ca. 9 by the addition of 1 N aqueous sodium hydroxide. After the 20-min. dropwise addition, the reaction mixture was stirred for 15 min. The solution was saturated with sodium chloride and extracted several times with ether. The combined ether extractions were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining slush was heated with low-boiling petroleum ether and then cooled in a dry ice-isopropyl alcohol bath. The solid was collected and dried under reduced pressure. A yield of 75% of 2.1 g. (0.015 mole) of the amorphous solid bicyclo(3,2,1)-3-octene-2-one oxide was obtained with a mp of 88-102°, reported at 90-108°.

Preparation of endo-exo-bicyclo(3,2,1)-octane-2,4-diol

To a slurry of 1 g. (0.027 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added dropwise with stirring a solution of 2.1 g. (0.015 mole) of bicyclo(3,2,1)-3-octene-2-one oxide in 10 ml. of anhydrous ether. The mixture was then refluxed with stirring for 3 hr. After cooling to room temperature, the reaction mixture was hydrolyzed with water and suction-filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. A white solid remained which showed essentially one product by vpc analysis on a 5 ft. x 1/4 in. 18% Cyanosilicone XF-1150 on 60/80 Chromosorb W column at 170°. A yield of 50% of 1.9 g. (0.013 mole) of endo-exo-bicyclo-(3,2,1)octane-2,4-diol was obtained with a mp of 250-49°, reported at 252-4°.
**Preparation of endo-exo-bicyclo(3,2,1)-octane-2,4-diol diacetate**

To a solution of 1 g. (0.007 mole) of endo-exo-bicyclo(3,2,1)-octa-2,4-diol and 3 ml. of pyridine in 100 ml. of anhydrous ether was added dropwise with stirring 2 ml. of acetyl chloride in 5 ml. of anhydrous ether. The mixture was stirred at room temperature for 50 hr. To the mixture was added 25 ml. of water and the layers were separated. The ether layer was washed several times with water and finally with saturated sodium bicarbonate solution. The ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid showed essentially one product on a vpc 5 ft. x 3/8 in. 20% Carbowax 20M on 60/80 Chromosorb W column at 180°. The main product of a portion of the liquid was collected by vpc. The collected product showed two acetate methyls by nmr analysis at 88.0 and 88.05 in carbon tetrachloride.

**Preparation of bicyclo(3,2,1)octane-2,4-dione**

A mixture of 35 g. (0.32 mole) of norcamphor and 35 g. (0.32 mole) of selenium dioxide in 90 ml. of xylene was stirred vigorously at 140-150° for 4 hr. The mixture was allowed to cool to room temperature and was suction-filtered through celite. The xylene was removed under reduced pressure. An attempt to fractionally distill the norcamphor quinone through a 15-cm. Vigreux column under reduced pressure resulted in the yellow quinone solidifying in the column. The solid was washed from the column with ether and the ether solution was concentrated under reduced pressure. A yield of 14% of 7 g. (0.056 mole) of the crude
norcamphor quinone was obtained. The solid was not characterized further, but it was used immediately.

A solution of diazomethane was prepared by adding 20 g. of powdered nitrosomethylurea in small amounts to a mixture of 200 ml. of ether at 5° and 60 ml. of 40% aqueous potassium hydroxide. The yellow ethereal diazomethane solution was decanted into a flask containing several potassium hydroxide pellets. The cold dry ethereal diazomethane solution was added slowly in small portions to a solution at 5° of the above prepared 7 g. (0.056 mole) of the crude norcamphor quinone in 100 ml. of anhydrous ether. The solution was allowed to stand overnight at room temperature, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid of bicyclo-(3.2.1)octane-2,4-dione enolmethyl ether was not purified further.

A mixture of the impure bicyclo(3.2.1)octane-2,4-dione enolmethyl ether in 25 ml. of ether and 25 ml. of 15% aqueous hydrochloric acid was stirred at room temperature for 12 hr. The aqueous phase was saturated with sodium chloride and continuously extracted with ether for 56 hr. The dark brown ether solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining dark brown viscous liquid was vacuum distilled through a short path distillation and a colorless viscous liquid was collected, bp\textsubscript{0.25} 117-121°. Addition of a small amount of ether to the distillate yielded a white solid upon scratching the sides of the test tube with a glass rod. The solid was collected and dried under reduced pressure. A yield of 13% of 1 g. (0.0073 mole) of bicyclo(3.2.1)octane-2,4-dione was obtained with a mp of 127-8°, reported \textsuperscript{85} mp 128-9°.
Preparation of di-endo-bicyclo(3,2,1)-octane-2,4-diol

To a solution of 0.68 g. (0.005 mole) of bicyclo(3,2,1)octane-2,4-dione in 30 ml. of absolute ethanol under a nitrogen atmosphere was added with stirring at room temperature 1.6 g. (0.078 mole) of small pieces of freshly cut sodium. The sodium was added over a period of 45 min. and the mixture was stirred under a nitrogen atmosphere at room temperature for 3.5 hr. To the reaction mixture was carefully added 50 ml. of 50% aqueous ethanol. Most of the ethanol was removed by distillation through a 15-cm. Vigreux column under reduced pressure. The remaining aqueous solution was saturated with sodium chloride and continuously extracted with ether for 52 hr. The ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. A white solid of 0.15 g. was obtained with a mp of 214-222°, reported mp at 225-26° after purification on a Woelm alumina column. The solid di-endo-bicyclo(3,2,1)octane-2,4-diol in methanol was shown to contain ca. 20% of the axial-equatorial isomer by analysis on a 10 ft. x 1/8 in. 10% FFAP on 70/80 DMCS (AW-W) vpc column at 190°.

Neutralization of the basic aqueous solution from the continuous ether extraction, followed by continuous ether extraction for 50 hr. yielded 0.25 g. of a white solid, mp 127-8°, which was identified as unreacted bicyclo(3,2,1)octane-2,4-dione.

Preparation of di-endo-bicyclo(3,2,1)-octane-2,4-diol diacetate

To a solution of 0.228 g. (0.0016 mole) of the crude di-endo-bicyclo(3,2,1)octane-2,4-diol, prepared above, and 1 ml. of pyridine in 15 ml. of anhydrous ether was added dropwise with stirring 1 ml. of
acetyl chloride. The mixture was stirred at room temperature for 48 hr.
Water was added and the layers were separated. The ether layer was
washed several times with water and finally with saturated sodium
bicarbonate solution. The ether was dried over anhydrous magnesium
sulfate, filtered, and concentrated under reduced pressure. The remaining
liquid was shown to contain two products in the ratio of ca. 1:4 by
analysis on a 10 ft. x 3/8 in. 20% SF-96 on 60/80 Chromosorb W vpc column
at 175°. The shorter and smaller retention time product was shown to the
exo-endo isomer. The longer and larger retention time product of
di-endo-bicyclo(3.2.1)octane-2,4-diol diacetate was collected by vpc and
showed an acetate methyl absorption at 7.85 in carbon tetrachloride.

Cleavage of phenylcyclopropane with
thallic acetate

A mixture of 0.25 g. (0.000547 mole) of thallic oxide and 0.167 g.
(0.00164 mole) of acetic anhydride in 10 ml. of anhydrous acetic acid was
stirred at 75° for 19 hr. To the thallic acetate solution was added
0.177 g. (0.0015 mole) of phenylcyclopropane and the solution was stirred
for 120 hr. at 75°. The reaction mixture was dissolved in ether and the
ethereal solution was washed several times with water and finally with
saturated sodium bicarbonate solution. The ethereal layer was dried over
anhydrous magnesium sulfate, filtered, and concentrated. The concentrate
was analyzed on a 5 ft. x 1/4 in. 20% Carbowax 20M on 60/80 Chromosorb W
vpc column at 185° and found to contain, in addition to phenylcyclo-
propane, 10% cinnamyl acetate and 90% 1-phenyl-1,3-propanediol diacetate.
The products were identified by retention times of authentic samples.
Analysis of the reaction mixture by nmr showed an allyl methylene doublet
of cinnamyl acetate at $\gamma'5.4$ and the benza hydrogen triplet of the diacetate at $\gamma'4.2$ in carbon tetrachloride. The absorptions were expanded and areas of the peaks from several spectra were averaged and corrected to area per hydrogen. On the basis of nmr analysis, the reaction mixture was found to be 9% cinnamyl acetate and 91% diacetate.

**Per cent reaction of phenylcyclopropane with thallic acetate**

A solution of 0.138 g. (0.00117 mole) of phenylcyclopropane and 0.385 g. (0.00101 mole) of thallic acetate in 10 ml. of anhydrous acetic acid was allowed to stand at 75° for 91.5 hr. in a sealed tube. The same procedure and vpc analysis was followed which was previously described. After removal of the ether, 0.112 g. (0.000660 mole) of diphenyl ether was added to the reaction mixture as an internal vpc standard. The acetate products were found to be 91% 1-phenyl-1,3-propanediol diacetate and 9% cinnamyl acetate in an over-all yield of 68%. The total recovery of products and phenylcyclopropane was 83%.

**Cleavage of substituted phenylcyclopropanes with thallic acetate**

Substituted phenylcyclopropanes were cleaved with thallic acetate, as previously described, by dissolution at 75° of 0.25 g. (0.000547 mole) of thallic oxide in 10 ml. of anhydrous acetic acid containing 0.167 g. (0.0164 mole) of acetic anhydride. To the prepared thallic acetate solution was added 0.0015 mole of the substituted phenylcyclopropane and stirred at 75° for 120 hr. The reaction mixture was analyzed as described previously and the results are listed in Table 6.
Cleavage of phenylcyclopropane with lead tetraacetate

A solution of 0.486 g. (0.00110 mole) of lead tetraacetate at 0.212 g. (0.00179 mole) of phenylcyclopropane in 10 ml. of anhydrous acetic acid was allowed to stand at 75° for 121.5 hr. The same procedure and analysis was followed as previously described. The reaction mixture was shown by vpc to be 29% cinnamyl acetate and 71% 1-phenyl-1,3-propanediol diacetate.

Cleavage of substituted phenylcyclopropanes with lead tetraacetate

Substituted phenylcyclopropanes were cleaved by lead tetraacetate as described above using 0.485 (0.00109 mole) of lead tetraacetate and 0.0015 mole of the substituted phenylcyclopropane in 10 ml. of anhydrous acetic acid. The solution was allowed to stand at 75° for 120 hr. The results are listed in Table 7.

Preparation of α-phenylallyl alcohol

Phenylmagnesium bromide was prepared by adding 3 ml. of a solution of 31.4 g. (0.20 mole) of bromobenzene in 25 ml. of anhydrous ether to a mixture of 100 ml. anhydrous ether and 5 g. (0.21 mole) of magnesium turnings, which were freshly polished in a mortar and pestle. The reaction was started by the addition of several drops of ethylene bromide and stirring. The remaining ethereal bromide solution was added dropwise with stirring. After the dropwise addition, the mixture was stirred an additional 30 min. To this mixture was added dropwise with stirring, a solution of 14 ml. (11.8 g. 0.21 mole) of acrolein in 15 ml. of anhydrous ether. After the dropwise addition the mixture was poured into 100 ml. of 15% aqueous ammonium chloride and ice with stirring. The mixture was
suction-filtered through a glass wool pad. The layers of the filtrate were separated and the aqueous layer extracted with 50 ml. of ether. The combined extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The concentrate was vacuum distilled through a 15-cm. Vigreux column. A 60% yield of 15.7 g. (0.12 mole) of α-phenylallyl alcohol was obtained, bp\(_{18}\) 76-7\(^\circ\) reported\(^\text{89}\) bp\(_{0.15}\) 53-4\(^\circ\). Analysis by nmr showed complex multiplets at γ\(^4\) 4.6-5.1 (3H) and γ\(^3\) 3.7-4.35 (1H) in carbon tetrachloride.

**Preparation of α-(substituted-phenyl)-allyl alcohols**

The α-(substituted-phenyl)-allyl alcohols were prepared as in the above procedure. The per cent yields and boiling points are listed in Table 22, and the elemental analyses are listed in Table 23. All of the alcohols show nmr absorptions which were listed for α-phenylallyl alcohol.

<table>
<thead>
<tr>
<th>X</th>
<th>Yield</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO-</td>
<td>46</td>
<td>100-3(^\circ) (0.35-.45 mm.)</td>
</tr>
<tr>
<td>p-Me-</td>
<td>66</td>
<td>72-3(^\circ) (0.35 mm.)</td>
</tr>
<tr>
<td>m-Me-</td>
<td>56</td>
<td>72-5(^\circ) (0.40-.42 mm.)</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>66</td>
<td>80-1(^\circ) (0.18 mm.)</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>45</td>
<td>82-4(^\circ) (0.65-.70 mm.)</td>
</tr>
</tbody>
</table>
TABLE 23

ELEMENTAL ANALYSIS OF α-(SUBSTITUTED-PHENYL)-ALLYL ALCOHOLS

<table>
<thead>
<tr>
<th>X</th>
<th>C %</th>
<th>H %</th>
<th>Cl %</th>
<th>C %</th>
<th>H %</th>
<th>Cl %</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO-</td>
<td>73.15</td>
<td>7.37</td>
<td>--</td>
<td>73.27</td>
<td>7.31</td>
<td>--</td>
</tr>
<tr>
<td>p-Me-</td>
<td>81.04</td>
<td>8.16</td>
<td>--</td>
<td>81.29</td>
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<tr>
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<td>81.04</td>
<td>8.16</td>
<td>--</td>
<td>81.04</td>
<td>8.10</td>
<td>--</td>
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<tr>
<td>p-Cl-</td>
<td>64.11</td>
<td>5.38</td>
<td>21.03</td>
<td>64.03</td>
<td>5.42</td>
<td>20.69</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>64.11</td>
<td>5.38</td>
<td>21.03</td>
<td>63.93</td>
<td>5.33</td>
<td>20.72</td>
</tr>
</tbody>
</table>

Preparation of 1,3-dibromo-1-phenylpropane

Method A—A mixture of 29.8 g. (0.15 mole) of 1-phenyl-3-bromopropane, 26.6 g. (0.15 mole) of N-bromosuccinimide, and a trace of benzoyl peroxide in 250 ml. of carbon tetrachloride was stirred under reflux with irradiation by a 250 watt red sun lamp. After the reaction was complete, as indicated by the conversion of the crystalline N-bromosuccinimide to the white fluffy succinimide, the mixture was cooled in an ice bath. The solid succinimide was suction-filtered and the filtrate concentrated. The concentrate was dissolved in ether and washed twice with water to remove the remaining succinimide. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The concentrate was vacuum distilled through a 15-cm. Vigreux column. A 80% yield of 33.6 g. (0.12 mole) of 1,3-dibromo-1-phenylpropane was obtained, bp\textsubscript{0.7} 94-5\textdegree, reported\textsuperscript{90} bp\textsubscript{10} 142-3\textdegree. Analysis by nmr showed a quartet \(\gamma\) 4.9 (1H), and multiplets at \(\gamma\) 7.45 (2H) and \(\gamma\) 6.65 (2H) in carbon tetrachloride.
Method B—Hydrogen bromide was bubbled through a solution of 6.5 g. (0.04 mole) of α-phenylallyl alcohol in 20 ml. of ether at 10\degree with stirring for 30 min. After 30 min. 0.1 g. of antimony tribromide was added and the hydrogen bromide addition was continued for 2 hr. The mixture was poured over ice and then extracted with ether. The ethereal solution was washed with cold water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. A concentrate was vacuum distilled through a 10-cm. Vigreux column. A 65% yield of 8.84 g. (0.032 mole) of 1,3-dibromo-1-phenylpropane was obtained, bp\textsubscript{0.75} 93-95\degree, reported\textsuperscript{90} bp\textsubscript{10} 142-3\degree.

Preparation of 1,3-dibromo-1-(substituted-phenyl)-propanes

The 1,3-dibromo-1-(substituted-phenyl)-propanes were prepared as in the above procedure by method B. Time required for complete reaction was a function of the substituent, the p-methoxy and p-methyl compounds reacted rapidly without addition of antimony tribromide. The reaction of the m-chloro compound was slower and could be followed by disappearance of the methylene doublet, absorption, ca. \textgamma 6, of meta-chlorocinnamyl bromide by nmr. The per cent yields and boiling points are listed in Table 24, and the elemental analyses are listed in Table 25. The p-methoxy and p-methyl bromides were too unstable to isolate. By nmr analysis all the dibromides showed a quartet at \textgamma 4.9 (1H) and multiplets at \textgamma 7.45 (2H) and 6.65 (2H) in carbon tetrachloride.

Preparation of phenylcyclopropane

To a mixture of 14 g. (0.21 mole) of granular zinc-copper couple and 700 ml. of anhydrous ether was added 33.6 g. (0.12 mole) of
TABLE 24

YIELDS AND BOILING POINTS OF 1,3-DIBROMO-1-(SUBSTITUTED-PHENYL)-PROPANES

<table>
<thead>
<tr>
<th>X</th>
<th>Yield</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>m-Me-</td>
<td>84</td>
<td>108-10⁰ (0.65-.60 mm.)</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>82</td>
<td>102-5⁰ (0.20 mm.)</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>70</td>
<td>105-6⁰ (0.2 mm.)</td>
</tr>
</tbody>
</table>

TABLE 25

ELEMENTAL ANALYSES OF 1,3-DIBROMO-1-(SUBSTITUTED-PHENYL)-PROPANES

<table>
<thead>
<tr>
<th>X</th>
<th>% Calculated</th>
<th>% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>m-Me-</td>
<td>41.13</td>
<td>4.14</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>34.60</td>
<td>2.90</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>34.60</td>
<td>2.90</td>
</tr>
</tbody>
</table>

1,3-dibromo-1-phenylpropane in one portion. Upon addition of the dibromide the ether immediately began to reflux. The mixture was stirred under reflux for 24 hr. and the ethereal solution was decanted from the excess zinc and washed once with saturated ammonium chloride, once with saturated sodium bicarbonate, and finally with water. The ether was dried over anhydrous magnesium sulfate, filtered, and concentrated. The remaining liquid was vacuum distilled through a 15-cm. Vigreux column. A 35% yield of 4.9 g. (0.042 mole) of phenylcyclopropane was obtained,
bp$_2$ 69-70°, reported$^{91}$, bp 172-4°. Analysis by nmr showed complex multiplets at $\gamma'8.25$ (1H) and $\gamma'9.25$ (4H).

Preparation of substituted phenylcyclopropanes

Substituted phenylcyclopropanes were prepared as described in the above method. The reaction mixtures from the preparation of the p-methoxy- and p-methyl- dibromides were reacted with zinc-copper couple. These dibromides are too unstable to isolate. By nmr analysis all the phenylcyclopropanes showed complex multiplets at $\gamma'8.25$ (1H) and $\gamma'9.25$ (4H) in carbon tetrachloride. The yields and boiling points are listed in Table 26.

### TABLE 26

<table>
<thead>
<tr>
<th>X</th>
<th>% Yield</th>
<th>Boiling Point</th>
<th>Reported Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO-</td>
<td>16$^a$</td>
<td>103-4° (34-6 mm.)</td>
<td>223.5-4° (745 mm.)$^{92}$</td>
</tr>
<tr>
<td>p-Me-</td>
<td>22$^a$</td>
<td>79-80° (14 mm.)</td>
<td>194.5° (745 mm.)$^{92}$</td>
</tr>
<tr>
<td>m-Me-</td>
<td>44</td>
<td>100-103° (34-6 mm.)</td>
<td>194° (742 mm.)$^{93}$</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>51</td>
<td>107-9° (24-5 mm.)</td>
<td>76-7° (7 mm.)$^{94}$</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>49</td>
<td>113-5° (35 mm.)</td>
<td>--</td>
</tr>
</tbody>
</table>

$^a$Yield was based on the starting phenylallyl alcohol.

$^b$Elemental analysis; calculated for C$_{9}$H$_{7}$Cl: C, 70.82; H, 5.94; Cl, 23.30; found: C, 70.76; H, 6.09; Cl, 23.41.
Preparation of para-methoxyphenyl-cyclopropane

To a stirred slurry of 9.6 g. (0.24 mole) of lithium aluminum hydride in 300 ml. of dry glyme, a glyme solution of 48.6 g. (0.24 mole) of ethyl p-methoxycinnamate was added dropwise. The mixture was stirred under reflux for 16 days. The mixture was cooled to room temperature and 250 ml. of ether was added and the hydride hydrolyzed with water. The solid was suction-filtered and washed with ether. The filtrate was washed several times with water and the ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The residue was vacuum distilled through a 15-cm. Vigreux column. A 50% yield of 18.2 g. (0.12 mole) of para-methoxyphenylcyclopropane was obtained, bp\textsubscript{8} 77-80°, reported\textsuperscript{92} bp\textsubscript{745} 223.5-4°.

Preparation of para-methylphenyl-cyclopropane

Using above procedure with 51.8 g. (0.27 mole) of ethyl para-methylcinnamate and 10.8 g. (0.27 mole) of lithium aluminum hydride in 300 ml. of dry glyme for 16 days at reflux, a 58% yield of 20.6 g. (0.16 mole) of para-methylphenylcyclopropane was obtained, bp\textsubscript{8} 67-8°, reported\textsuperscript{92} bp\textsubscript{745} 194-194.5°.

Preparation of granular zinc-copper couple

To a 250 ml. Erlenmeyer flask with a large magnetic stirring bar was introduced 1 g. of cupric acetate monohydrate and 100 ml. of glacial acetic acid. The mixture was heated with stirring. After dissolution of the cupric acetate, 70 g. of granular (20 mesh) zinc was added and the
mixture was vigorously stirred while hot for 3 min. The acetic acid was
decanted and the zinc-copper couple was washed with 100 ml. of hot
glacial acetic acid and decanted. After the couple cooled, it was
washed three times with 100 ml. portions of anhydrous ether for 1 min.
each. The couple was dried under a nitrogen stream.

Preparation of \( \alpha \)-phenylallyl acetate

To a solution of 6.7 g. (0.05 mole) of \( \alpha \)-phenylallyl alcohol
and 8 ml. (7.8 g., 0.1 mole) of pyridine in 75 ml. of anhydrous ether was
added dropwise with stirring a solution of 6 ml. (6.6 g., 0.085 mole) of
acetyl chloride in 15 ml. of anhydrous ether. The mixture was stirred
at room temperature for 30 hr. Water was added and the layers were
separated. The ethereal layer was washed several times with water and
finally with saturated sodium bicarbonate. The ether layer was dried
over anhydrous magnesium sulfate, filtered, and concentrated under
reduced pressure. The remaining slightly yellow liquid was dissolved in
anhydrous ether, shaken with activated charcoal, filtered through celite,
and concentrated under reduced pressure. A colorless liquid remained
which by nmr analysis showed the same complex absorptions as the
starting alcohol at \( \gamma \) 3.7-4.35 (1H) and \( \gamma \) 4.6-5.05 (3H), and also an
acetate methyl at \( \gamma \) 8.0 (3H) in carbon tetrachloride. A yield of 84% of
7.4 g. (0.042 mole) of \( \alpha \)-phenylallyl acetate was obtained.

Preparation of \( \alpha \)-(substituted-phenyl)-
allyl acetates

The \( \alpha \)-(substituted-phenyl)-allyl acetates were prepared as
described above. All of the allyl acetates exhibit complex absorptions
at \( \gamma \) 3.7-4.35 (1H) and \( \gamma \) 4.6-5.05 (3H) and also an acetate methyl at
8.0 (3H) in carbon tetrachloride. The elemental analyses of the undistilled $\alpha$-(substituted-phenyl)-allyl acetates are listed in Table 27.

**TABLE 27**

**ELEMENTAL ANALYSES OF $\alpha$-(SUBSTITUTED-PHENYL)-ALLYL ACETATES**

<table>
<thead>
<tr>
<th>$X$</th>
<th>C</th>
<th>H</th>
<th>Cl</th>
<th>% Calculated</th>
<th>C</th>
<th>H</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO-</td>
<td>69.88</td>
<td>6.84</td>
<td>--</td>
<td>69.62</td>
<td>6.80</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>p-Me-</td>
<td>75.76</td>
<td>7.42</td>
<td>--</td>
<td>75.71</td>
<td>7.30</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>m-Me-</td>
<td>75.76</td>
<td>7.42</td>
<td>--</td>
<td>75.86</td>
<td>7.43</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>p-Cl-</td>
<td>62.72</td>
<td>5.26</td>
<td>16.84</td>
<td>62.49</td>
<td>5.27</td>
<td>16.78</td>
<td></td>
</tr>
<tr>
<td>m-Cl-</td>
<td>62.72</td>
<td>5.26</td>
<td>16.84</td>
<td>62.51</td>
<td>5.26</td>
<td>16.75</td>
<td></td>
</tr>
</tbody>
</table>

Rearrangement of $\alpha$-phenylallyl acetate

A solution of 0.1 g. (0.00057 mole) of $\alpha$-phenylallyl acetate in 5 ml. of anhydrous acetic acid in a sealed tube was allowed to stand at $75^\circ$ for 120 hr. The reaction mixture was dissolved in ether and washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. Analysis of the remaining liquid by nmr in carbon tetrachloride showed a doublet at $\gamma 5.4$ (2H), multiplet at $\gamma 3.2-4.1$ (2H), singlet at $\gamma 2.7$ (5H), and acetate methyl at $\gamma 8.0$ (3H). This spectrum is identical to cinnamyl...
acetate. The complex pattern at $\gamma^4.6-5.05$ (3H) in the starting $\alpha$-phenylallyl acetate was absent.

**Rearrangement of $\alpha$-(substituted-phenyl)-allyl acetates**

The m- and p-chloro-, m- and p-methyl-, and p-methoxyphenylallyl acetates also rearranged to the corresponding cinnamyl acetates under the conditions described above. The rearrangements were quantitative except for meta-chlorophenylallyl acetate on the basis of nmr analysis. All of the reaction mixtures showed a doublet at $\gamma^5.4$, multiplet at $\gamma^3.2-4.1$, and acetate methyl at $\gamma^8.0$. The meta-chloro-compound also showed the complex absorptions at $\gamma^4.6-5.05$ from the meta-chlorophenylallyl acetate.

**Preparation of cinnamyl acetate**

To a solution of 13.4 g. (0.01 mole) of cinnamyl alcohol and 15 ml. (14.7 g., 0.19 mole) of pyridine in 125 ml. of anhydrous ether was added dropwise with stirring a solution of 10 ml. (11 g., 0.16 mole) of acetyl chloride in 10 ml. of anhydrous ether. The mixture was stirred at room temperature for 24 hr. Water was added and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was distilled through a 15-cm. Vigreux column. A yield of 82% of 14.5 g. (0.082 mole) of cinnamyl acetate was obtained, $bp_{11}$ 133°, reported $bp_{2.5}$ 115°. Analysis by nmr in carbon tetrachloride showed a doublet at $\gamma^5.4$ (2H), multiplet at $\gamma^3.2-4.1$ (2H), singlet $\gamma^2.7$ (5H), and singlet $\gamma^8.0$ (3H).
Preparation of meta-methylcinnamyl acetate

A solution of \( \alpha-(\text{meta-tolyl})\)-allyl acetate, prepared as previously described from 4.44 g. (0.03 mole) of \( \alpha-(\text{meta-tolyl})\)-allyl alcohol, in 100 ml. of anhydrous acetic acid at 75° for 126 hr. gave a 63\% yield of 3.43 g. (0.019 mole) of meta-methylcinnamyl acetate, bp\(0.3\) 89°, reported\(^8\) bp\(13\) 145°.

Preparation of meta-chlorocinnamyl acetate

meta-Chlorocinnamyl acetate was prepared, as above, from 5.06 g. (0.03 mole) of \( \alpha-(\text{meta-chlorophenyl})\)-allyl alcohol. The corresponding allyl acetate in 100 ml. of anhydrous acetic acid at 75° for 12 days and 100° for 8 days gave a 70\% yield of 4.45 g. (0.021 mole) of meta-chlorocinnamyl acetate, bp\(0.3\) 113-5°. Analysis by nmr in carbon tetrachloride showed a singlet at \( \gamma 7.95 \) (3H), doublet at \( \gamma 5.3 \) (2H), multiplet \( \gamma 3.2-4.0 \), and aromatic absorptions at \( \gamma 2.85 \) (4H).

Preparation of para-methoxycinnamyl acetate

para-Methoxycinnamyl acetate was prepared, as above, from 5.73 g. (0.035 mole) of \( \alpha-(\text{para-anisyl})\)-allyl alcohol. The corresponding allyl acetate in 10 ml. of anhydrous acetic acid at 75° for 15 hr. gave a 18\% yield of 1.3 g. (0.0063 mole) of para-methoxycinnamyl acetate, bp\(0.25\) 110-112°. Analysis by nmr showed singlets at \( \gamma 8.0 \) (3H) and \( \gamma 6.3 \) (3H), a doublet at \( \gamma 5.45 \) (2H), a multiplet (2H) \( \gamma 4.1 \) extending under the aromatic \( A_2B_2 \) pattern at \( \gamma 3.05 \) (4H).
Preparation of para-methylocinna myl acetate

To a slurry of 1.9 g. (0.05 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added dropwise a slurry of 8.1 g. (0.05 mole) para-methylocinnamic acid in 100 ml. of anhydrous ether. The mixture was stirred under reflux for 24 hr. The reaction mixture was hydrolyzed and suction-filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

A solution of the remaining para-methylocinna myl alcohol and 7 ml. (6.9, 0.087 mole) of pyridine in 125 ml. of anhydrous ether was acetylated, as described previously, with 5 ml. (5.5 g., 0.07 mole) of acetyl chloride in 20 ml. of anhydrous ether. The ester was vacuum-distilled through 10-cm. Vigreux column. A yield of 5.70 g. of impure para-methylocinna myl acetate was obtained, bp\textsuperscript{10} 132-9\degree, reported\textsuperscript{99} bp\textsuperscript{10} 140\degree. Analysis by vpc of a 5 ft. x 1/4 in. 20\% Carbowax 20M on 60/80 Chromosorb W column at 180\degree showed two products. Analysis by nmr showed, in addition to the typical cinnamyl acetate absorptions, other absorptions from hydrocinnamyl acetate.\textsuperscript{95}

Preparation of ethyl 3-hydroxy-3-(para-tolyl)-propionate

To 8 g. (0.12 mole) of powdered zinc was added dropwise with stirring a solution of 12 g. (0.1 mole) of para-tolualdehyde and 12 ml. (18.2 g., 0.11 mole) of ethyl bromoacetate in 16 ml. of dry benzene and 4 ml. of anhydrous ether. The mixture was stirred under reflux in a nitrogen atmosphere for 6 hr. and then cooled in an ice bath. To the mixture was added 40 ml. of cold 10\% sulfuric acid with vigorous stirring. The layers were separated, and the organic layer was washed twice with
3 ml. portions of cold 5% sulfuric acid, once with saturated sodium bicarbonate solution, and finally with water. The washings were combined and extracted twice with ether. The ether extracts were combined with the organic layer, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm. Vigreux column. A yield of 69% of 14.3 g. (0.069 mole) of ethyl 3-hydroxy-3-(para-tolyl)-propionate was obtained, bp<sub>0.35</sub> 111-2°. Analysis by nmr showed a triplet at γ5.1 and a doublet at γ7.5 and the ethyl triplet and quartet at γ8.85 and 6.0, respectively.

Preparation of ethyl 3-hydroxy-3-(substituted-phenyl)-propionates

The ethyl 3-hydroxy-3-(substituted-phenyl)-propionates were prepared as in the above described procedure. The same nmr absorptions as listed in the preceding procedure are present in spectra of the other substituted compounds. The para-methoxy compound was not distilled. The meta-methyl compound was prepared in 52% yield, bp<sub>0.2</sub> 103-5° and the para-chloro compound in 42% yield, bp<sub>0.3-4</sub> 134-6°. None of the ethyl 3-hydroxy-3-phenyl-propionates were purified sufficiently for analytical samples.

Preparation of 1-(para-tolyl)-1,3-propanediol diacetate

To a slurry of 2 g. (0.052 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added dropwise a solution of 10.4 g. (0.05 mole) of ethyl 3-hydroxy-3-(para-tolyl)-propionate in 10 ml. of anhydrous ether. The mixture was stirred under reflux for 24 hr., hydrolyzed with water, and suction-filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated.
A solution of the 1-(para-tolyl)-1,3-propanediol and 13 ml. (12.8 g., 0.16 mole) of pyridine in 125 ml. of anhydrous ether was acetylated with 12 ml. (11.9 g., 0.15 mole) of acetyl chloride. The mixture was stirred at room temperature for 36 hr., water was added, and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The ethereal solution was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm. Vigreux column. A yield of 74% of 9.32 g. (0.037 mole) of 1-(para-tolyl)-1,3-propanediol diacetate was obtained, bp 0.4 124°. Analysis by nmr showed a triplet at \( \gamma \) 4.3 (1H), a multiplet at \( \gamma \) 6.0 (2H) and two acetate methyl groups at \( \gamma \) 8.03 and 8.07. Another multiplet appears under the acetate methyls.

**Preparation of 1-(substituted-phenyl)-1,3-propanediol diacetates**

The 1-(substituted-phenyl)-1,3-propanediol diacetates were prepared as described in the above procedure. All of the 1-phenyl-1,3-propanediol diacetates exhibit absorptions in their nmr spectra as listed in the preceding procedure. The para-methoxy diacetate was obtained in 29% yield (based upon para-anisaldehyde), bp 0.25 144-150. The meta-methyl diacetate was collected on a vpc 5 ft. x 1/4 in. 20% Carbowax 20M on 60/80 Chromosorb W column at 185°, 58% yield, analysis; calculated for \( \text{C}_{14}\text{H}_{18}\text{O}_4 \): C, 67.18; H, 7.25; found, C, 66.88; H, 6.84. The para-chloro diacetate was obtained in 70% yield, bp 0.25 136-8°, analysis; calculated for \( \text{C}_{13}\text{H}_{16}\text{O}_4\text{Cl} \): C, 57.68; H, 5.58; Cl, 13.10; found, C, 57.43; H, 5.53; Cl, 13.30.
Preparation of ethyl phenylacetate

A solution of 15.6 g. (0.1 mole) of phenylacetic acid in 125 ml. of absolute ethanol containing 1 ml. concentrate sulfuric acid was refluxed for 18.5 hr. The solution was poured over 300 ml. of ice and water and the aqueous mixture was extracted with ether. The combined extracts were washed with water, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining ester was vacuum distilled through a 15-cm. Vigreux column. A 90% yield of 14.7 g. (0.09 mole) of ethyl phenylacetate was obtained, bp \(_{14-15}\) 105-9°, reported \(^{100}\) bp\(_{32}\) 132-8°.

Preparation of ethyl para-anisyl- and meta-tolylacetates

Ethyl para-anisyl- and meta-tolylacetates were prepared as described in the preceding method. Ethyl para-anisylacetate was obtained in 91% yield, bp \(_{11}\) 136-7°, reported \(^{101}\) bp\(_{1}\) 100-2°. Ethyl meta-tolylacetate was prepared in 76% yield, bp \(_{11-12}\) 105-8°, reported \(^{102}\) 237-8°.

Preparation of ethyl para-tolylacetate

A solution of 35.2 g. (0.25 mole) of para-tolylacetonitrile in 100 ml. of 95% ethanol and 25 ml. of concentrated sulfuric acid was refluxed for 7 hr. The mixture was allowed to cool and was poured over 300 g. of ice and water. The aqueous mixture was extracted three times with ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was vacuum distilled through a 15-cm. Vigreux column. A 68% yield of 30.2 g. (0.17 mole) of ethyl para-tolylacetate was obtained, bp \(_{13-14}\) 111-3°, reported \(^{103}\) bp\(_{0.9}\) 72-4°.
Preparation of ethyl para- and meta-chlorophenylacetates

Ethyl para- and meta-chlorophenylacetates were prepared as in the above procedure. A 75% yield of ethyl para-chlorophenylacetate was obtained, bp 107-8°, reported \cite{104} bp 260°. The meta-chlorophenylacetate was not distilled.

Preparation of diethyl phenylmalonate

To 25 ml. of absolute ethanol (distilled from sodium) was added 1.15 g. (0.05 mole) of freshly cut sodium. After dissolution of the sodium, 7.31 g. (0.05 mole) of diethyl oxalate was added in one portion immediately followed by the addition of 8.2 g. (0.05 mole) of ethyl phenylacetate in one portion. The mixture was stirred until the solid enolate salt formed (10 min.), suction-filtered and the salt washed with anhydrous ether. The salt was shaken with 2 ml. of concentrated sulfuric acid in 25 ml. of water and the mixture was extracted with ether. The ether extracts were combined, dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The remaining liquid was heated at 175° at 15 mm. for 5 hr. and then vacuum distilled through a 10-cm. Vigreux column. A 37% yield of 4.36 g. (0.19 mole) of diethyl phenylmalonate was obtained, bp \textit{0.07} 94-6°, reported \cite{105} bp \textit{10} 158-62°.

Preparation of diethyl substituted-phenylmalonates

Diethyl substituted-phenylmalonates were prepared as described in the preceding method. The per cent yields and boiling points are listed in Table 28. The \textit{meta}-chlorophenylmalonate was not distilled because of the small quantity available.
TABLE 28
PER CENT YIELDS AND BOILING POINTS OF DIETHYL SUBSTITUTED-PHENYLALONATES

<table>
<thead>
<tr>
<th>X</th>
<th>% Yield</th>
<th>Boiling Point</th>
<th>Reported Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-MeO-</td>
<td>32</td>
<td>118-21° (0.05-.08 mm.)</td>
<td>152-3° (2.5 mm.)^106</td>
</tr>
<tr>
<td>p-Me-</td>
<td>16</td>
<td>133-5° (1.25 mm.)</td>
<td>124-5° (1-2 mm.)^107</td>
</tr>
<tr>
<td>m-Me-</td>
<td>56</td>
<td>110-1° (0.25 mm.)</td>
<td>125-32° (2 mm.)^108</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>52</td>
<td>124-6° (0.7-.6 mm.)</td>
<td>178-80° (15 mm.)^109</td>
</tr>
</tbody>
</table>

Preparation of 2-phenyl-1,3-propanediol diacetate

To a slurry of 4.5 g. (0.11 mole) of lithium aluminum hydride in 200 ml. of anhydrous ether was added dropwise a solution of 23.6 g. (0.1 mole) of diethyl phenylmalonate in 50 ml. of anhydrous ether. The mixture was stirred under reflux for 25 hr., hydrolyzed with water, and suction-filtered. The filtrate was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure.

To a solution of the 2-phenyl-1,3-propanediol and 20 ml. (19.6 g., 0.26 mole) of pyridine in 150 ml. of anhydrous ether was added dropwise a solution of 18 ml. (19.8 g., 0.25 mole) of acetyl chloride in 20 ml. of anhydrous ether. The mixture was stirred at room temperature for 24 hr., water was added, and the layers were separated. The ethereal layer was washed several times with water and finally with saturated sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate, filtered, and concentrated under reduced pressure. The ester was vacuum distilled through a 15-cm. Vigreux column. A 57% yield of 13.4 g. (0.057 mole) of 2-phenyl-1,3-propanediol diacetate was
obtained, bp \text{3.35} 110-3^\circ \text{C}, reported \text{162-4^\circ C}. Analysis by nmr showed a quintet at \text{\gamma} 6.75 (1H), doublet at \text{\gamma} 5.75 (4H), and acetate methyl groups at \text{\gamma} 8.05 (6H).

Preparation of 2-(substituted-phenyl)-1,3-propanediol diacetates

The 2-(substituted-phenyl)-1,3-propanediol diacetates were prepared as described in the above procedure. Analysis by nmr showed the 2-phenyl-1,3-propyl diacetates to exhibit a quintet at \text{\gamma} 6.75 (1H), doublet \text{\gamma} 5.75 (4H), and acetate methyl at \text{\gamma} 8.05. The yields and boiling points are listed in Table 29 and the elemental analyses are listed in Table 30. The 2-(meta-chlorophenyl)-1,3-propanediol diacetate was collected by vpc on a 5 ft. x 1/4 in. 20\% Carbowax 20M on 60/80 Chromosorb W column.

\begin{table}[h]
\centering
\caption{PERCENT YIELDS AND BOILING POINTS OF 2-(SUBSTITUTED-PHENYL)-1,3-PROPANEDIOL DIACETATES}
\begin{tabular}{lcc}
\hline
X & \% Yield & Boiling Point \\
\hline
p-MeO- & 50 & 152-3^\circ \text{C} (0.65 mm.) \\
p-Me- & 37 & 132^\circ \text{C} (0.75 mm.) \\
m-Me- & 38 & 156^\circ \text{C} (2.6 mm.) \\
p-Cl- & 53 & 118-21^\circ \text{C} (0.8 mm.) \\
\hline
\end{tabular}
\end{table}
TABLE 30

ELEMENTAL ANALYSIS OF 2-(SUBSTITUTED-PHENYL)-1,3-PROPANEDIOL DIACETATES

<table>
<thead>
<tr>
<th>X</th>
<th>% Calculated</th>
<th>% Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>p-MeO-</td>
<td>63.15</td>
<td>6.81</td>
</tr>
<tr>
<td>p-Me-</td>
<td>67.18</td>
<td>7.25</td>
</tr>
<tr>
<td>m-Me-</td>
<td>67.18</td>
<td>7.25</td>
</tr>
<tr>
<td>p-Cl-</td>
<td>57.68</td>
<td>5.58</td>
</tr>
<tr>
<td>m-Cl-</td>
<td>57.68</td>
<td>5.58</td>
</tr>
</tbody>
</table>

Kinetics of cleavage of
phenylcyclopropanes

The solutions for kinetic analysis were prepared by weighing an amount of the cyclopropane into a volumetrically measured amount of anhydrous acetic acid. From the weight of the cyclopropane, the desired amount of thallic acetate was calculated, weighed out, and added to the solution.

The methods of sampling were dependent upon the rate of cleavage. For extremely fast reactions partition flasks were used. Aliquots of each reactant were pipetted into opposite sides of the partition flask, allowed to equilibrate at the bath temperature, and the solutions mixed by shaking so as to allow passage over the partition barrier. When the rate of cleavage was moderate and the temperature such that evaporation was not a complication, aliquots were pipetted from the reaction flask. For slow reactions and high temperatures, in which evaporation would be a complication, aliquots were sealed in test tubes.
The method of analysis consisted of quenching the aliquot in excess 5% aqueous potassium iodide. To the resulting yellow heterogeneous mixture was added a starch-iodine indicator. The dark mixture was titrated to a pure yellow mixture with standard sodium thiosulfate solution.

Monitoring the reaction by vpc with an internal standard was carried out by quenching aliquots in an ice-water mixture. The ice-water mixture was extracted with ether and the ether extraction was washed several times with ice-water and finally with cold saturated sodium bicarbonate solution. The ethereal layer was dried over anhydrous magnesium sulfate, filtered, and carefully concentrated to a volume such that a 50 µl. sample of the ether solution could be analyzed on a 10 ft. x 1/4 in. 20% Apiezon J on 60/80 Chromosorb W vpc column. The decrease of the area of the cyclopropane peak was measured relative to the internal standard. The method of sampling was the same as described above. Preparation of the kinetic solutions were the same as described above except decane or dodecane, as internal standards, was weighed into the acetic acid solution of the cyclopropane.

**Purification of acetic acid**

The anhydrous acetic acid which was used as the solvent for the kinetics and cleavage of cyclopropanes was obtained by refluxing 1.5 l. of glacial acetic acid containing 50 ml. of acetic anhydride and 3 g. of para-toluenesulfonic acid for 24 hr. The acetic acid was then distilled through a 60-cm. glass-helice packed column. The fraction, bp 117.5-118°, was collected.
Per cent thallic acetate as a function of temperature

Time and per cent thallic acetate obtained by the dissolution of ca. 0.05 g. of thallic oxide in 10 ml. of 0.18 M acetic anhydride in acetic acid were measured as a function of temperature. After complete reaction, the acetic acid was vacuum transferred and the remaining solid was dissolved in 25 ml. of 1 N sulfuric acid. To the solution was pipetted 10 ml. of 0.0889 N ferrous ammonium sulfate and the solution was allowed to stand under a nitrogen atmosphere for 2 hr. After addition of 10 drops of 86% phosphoric acid and 10 drops of 0.005 M diphenylamine sodium sulfonate and the solution was titrated with 0.100 N potassium dichromate to the purple end point. The results are listed in Table 17 and each value is an average of two independent reactions which do not vary more than ±1.5%.

Per cent thallic acetate as a function of per cent water

Time and per cent thallic acetate obtained by the dissolution of ca. 0.05 g. of thallic oxide in varying per cent aqueous acetic acid at 60° were determined. The same analytical procedure as described above was used and the results are listed in Table 18. Each value is an average of two independent reactions which do not vary more than ±1.5%.

Preparation of thallic acetate

A mixture of 10 g. (0.022 mole) of thallic oxide in 100 ml. of acetic acid and 25 ml. of water was stirred at 50° for 4 hr. The residual solid was removed by suction-filtration. Most of the acetic acid was removed under reduced pressure. The solid was dissolved in a
minimum amount of acetic acid at 75° and the thallic acetate crystallized upon cooling. The solid was suction-filtered and dried under a continuous vacuum. A 73.7% yield of 12.3 g. (0.032 mole) of thallic acetate was obtained and the dry solid stored in a desiccator. The thallic acetate was found to be 98% pure by the previously described iodide-thiosulfate analytical procedure.

In another preparation a mixture of 15 g. (0.033 mole) of thallic oxide in 100 ml. of acetic acid and 15 ml. of water was stirred for 21 hr. at 55°. A yield of 65% of 99% pure thallic acetate was obtained.

Thallic acetate exhibits no sharp decomposition or melting point to 200° but it does begin slow decomposition at ca. 75-80°.

**Preparation of thallous-thallic acetate double salt**

A solution of 0.527 g. (0.0020 mole) of thallous acetate and 0.763 g. (0.0020 mole) of thallic acetate in 15 ml. of anhydrous acetic acid was concentrated under reduced pressure. The remaining white solid exhibits a sharp decomposition at 178-180° with no prior discoloration or melting.

**Kinetics of decomposition of thallic acetate**

Solutions for kinetic analysis were prepared by dissolving the desired amount of thallic acetate in a volumetrically measured quantity of anhydrous acetic acid. Aliquots were sealed in test tubes and the iodide-thiosulfate procedure was used to analyze the aliquots.
Appendix

Results of a typical kinetic run at 50.1°

\[ [A_0] = [\text{Tl(0Ac)}_3]_0 = 0.03021 \text{ M} \]

\[ [B_0] = [\text{\phi-d}]_0 = 0.01508 \text{ M} \]

Two milliliter aliquots were quenched in 10 ml. of 5% aqueous potassium iodide solution. After addition of a starch-iodine indicator, the dark mixture was titrated with 0.02534 N sodium thiosulfate solution to a pure yellow mixture.

<table>
<thead>
<tr>
<th>Aliquot</th>
<th>ml. S\text{2O}_3^-</th>
<th>[A_0-x]</th>
<th>[A_0-2x]</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>--</td>
<td>0.03021</td>
<td></td>
<td>33.1</td>
</tr>
<tr>
<td>1</td>
<td>4.420</td>
<td>0.02800</td>
<td>38.0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>4.030</td>
<td>0.02553</td>
<td>48.0</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>3.842</td>
<td>0.02434</td>
<td>54.1</td>
<td>30</td>
</tr>
<tr>
<td>4</td>
<td>3.690</td>
<td>0.02338</td>
<td>60.5</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>3.568</td>
<td>0.02260</td>
<td>66.7</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>3.468</td>
<td>0.02197</td>
<td>72.8</td>
<td>60</td>
</tr>
<tr>
<td>7</td>
<td>3.359</td>
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<tr>
<td>8</td>
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<tr>
<td>9</td>
<td>3.218</td>
<td>0.02039</td>
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<td>90</td>
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<tr>
<td>10</td>
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<td>104.3</td>
<td>100</td>
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<tr>
<td>11</td>
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<td>0.01978</td>
<td>106.9</td>
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</table>

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REFERENCES CITED


5. R. J. Meyer and E. Goldschmidt, Ber., 36, 238 (1903).


60. R. J. Ouellette, unpublished data.
64. R. J. Ouellette and R. D. Robins, unpublished work.


72. R. J. Ouellette and D. S. Miller, unpublished results.


78. V. Stannett and R. B. Mesrobian, ibid., 72, 4125 (1950).


84. C. Djerassi and C. R. Scholz, ibid., 70, 417 (1948).


88. F. Arndt, ibid., p. 461.


98. H. Burton, ibid., 1650 (1928).


102. M. Senkowski, Monatshefte für Chemie, 2, 855 (1888).


104. Walther and Wetzlich, J. Prak. Chem. [2], 61, 196 (via Beilstein, 2, 448).


