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BORON TRIFLUORIDE CATALYZED ESTERIFICATIONS
WITH OLEFINS

and

THE PREPARATION OF SOME STEREOCHEMICALLY
INTERESTING POLYCYCLIC COMPOUNDS

by

Wallace S. Hay

A THESIS
SUBMITTED TO THE FACULTY
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

Houston, Texas
May, 1950

Approved
Edward S. Lewis
THIS THESIS IS
DEDICATED TO MY
WIFE
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### PART II  
**THE PREPARATION OF SOME STEREOCHEMICALLY INTERESTING POLYCYCLIC COMPOUNDS**

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PART I
BORON TRIFLUORIDE CATALYZED ESTERIFICATIONS
WITH OLEFINS
INTRODUCTION
The production of esters by the catalytic esterification of olefins with organic acids has been of great interest to chemists in recent years. The reaction offers a means of converting refinery by-products to useful and worth while compounds. The esters prepared have firmly established used as solvents and plasticizers.

In the past, nearly all commercially produced esters were obtained by the conventional esterification reaction of an alcohol with an organic acid using a mineral acid as a catalyst. This reaction is reversible, and in order to obtain good yields of ester the water obtained as a by-product must be removed as it is formed. The direct esterification of olefins to yield organic esters has many advantages over the conventional method. From an economic point of view, the cheap olefin replaces the more expensive alcohol as one of the reactants. In many cases where the alcohol is derived from an olefin by hydration, a step in the process is eliminated. The direct esterification of olefins is also a more rapid reaction in many instances. Last but not least, the recovery and purification of the product is more easily accomplished in the esterification of olefins as the ester is obtained directly. However in spite of these advantages over conventional methods, the method of direct esterification of olefins has not been used extensively.

The addition of organic acids to olefins in the presence of strong acid catalysts has been known for many years.
The classical example of this reaction is the preparation of bornyl acetate or isobornyl acetate from the terpene hydrocarbons, pinene or camphene, and acetic acid in the presence of sulfuric acid (1,2,3) or boron trifluoride (4). Kondakov (5), as early as 1893, converted isobutylene to t-butyl acetate in about 20% yield by reacting isobutylene with acetic acid in the presence of zinc chloride.

In the period from 1900 to 1930, a lapse occurs before any further investigation of this problem appears in print. From 1930 until the present time however, numerous articles and patents have appeared in the literature, advocating several catalysts for the reaction.

Sulfuric acid has been one of the most popular catalysts mentioned. Woolcock (6) reported the reaction of propylene with acetic acid in the presence of a mixture of sulfuric and acetic acid to give isopropyl acetate in a 27% yield and isopropyl alcohol in a 53% yield. The synthesis of sec-butyl and sec-amyl acetates by the reaction of acetic acid with olefins in butylene-butane and pentene-pentane mixtures in the presence of sulfuric acid has been described in detail (7,8). The patent literature contains numerous references to the use of sulfuric acid in promoting the direct esterification of olefins (9,10,11,12,13,14,15). However the yields reported were low, and long reaction time or high reaction temperature is required.

In contrast to the many references to the catalytic esterification of olefins with organic acids under irrevers-
ible conditions, the literature contains only scattered references to the equilibrium which results if the addition is carried out under reversible conditions in an inert solvent.

Altschul (40) recently investigated the reversible esterification of carboxylic acids with isobutylene and trimethyl ethylene in the presence of sulfuric acid using dimethoxane as a solvent medium. Quantitative measurements by iodimetric and acidimetric technique were obtained in the case of the esterification of benzoic acid, p-nitrobenzoic acid, and acetic acid with both isobutylene and trimethyl ethylene. The equilibrium constants were determined at two temperatures, and an estimate of the heats of the reactions were given. The reaction mechanism of Cohen and Schneider (42) for the acid-catalyzed alcoholysis of t-butyl esters in anhydrous methanol was modified to allow for the absence of hydroxyl reagent, and found to check with the observed first order kinetics.

Gaseous boron trifluoride has also been reported by many investigators to promote the direct esterification of olefins by organic acids. The preparation of ethyl acetate in unstated yield by the reaction of acetic acid with ethylene in the presence of boron fluoride and hydrogen chloride at 250° has been reported (16). Nieuland, et al (17) described the reaction of propylene with acetic, mono, di, and trichloroacetic, and benzoic acids in the presence of boron fluoride. The yields in 12-16 hour reactions for the olefin esterification were lower than in the conventional
reaction with isopropyl alcohol with the exception of benzoic acid. He also reported the reaction of propylene with m- and p-hydroxybenzoic acids using boron trifluoride (18). Sowa and Wunderly (19) reported the condensation of cyclohexene with acetic acid in the presence of boron trifluoride to give 65% yield of cyclohexyl acetate in 50-220 hours. The patent literature also contains two references to the use of boron trifluoride to promote the esterification of olefins (20,21). As in the case with sulfuric acid as a catalyst, long reaction times are necessary for good yields using gaseous boron trifluoride.

Complexes of boron trifluoride have also been used to advantage as catalysts in this reaction. Nieuland and Sowa (22) reported the esterification of propylene, ethylene, butylene and pentene with acetic acid using the dihydrofluoboric acid-boron trifluoride complex as a catalyst. Loder (23) reported the use of the stable boron trifluoride dihydrate as a catalyst for the esterification with olefins. A mixture of boron trifluoride and hydrogen fluoride has been reported recently to give better results than boron trifluoride or hydrogen fluoride when used separately (24, 25). From propylene and acetic acid in the presence of this mixture, 72% of isopropyl acetate was obtained.

Still other catalysts mentioned as adaptable to this reaction are hydrogen fluoride (26), zinc chloride (27), titanium tetrafluoride (20), and silicon tetrafluoride (20). Hydrogen fluoride however must be reacted at 0° or lower,
and must be in excessive amount in order to give a good yield. Zinc chloride promotes too excessive an amount of polymerization to be practical (27).

Preparation of esters by reaction of olefins with organic acids in the vapor phase over various catalysts at elevated temperatures has not proven too successful in obtaining high conversion to the esters. (28,29,30,31,32,33,34).

In this research, an investigation of the value of boron trifluoride etherate in promoting the addition of organic acids to olefins was attempted. When this work was begun, it was thought that the literature contained no mention of the use of this complex for the direct esterification of olefins. However after several months work, it was found that a Russian chemist, Zavgorodnii (35) had used the etherate complex to advantage to esterify various organic acids with 2-butene and 2-pentene. In general, no yields or reaction conditions were given in the abstract. The information that isobutylene reacted with acetic acid at room temperature in the presence of the boron trifluoride etherate to give a 58% yield of 3° butyl acetate was given however. In a later paper Zavgorodnii (36) reported that cyclohexene reacted at 50° with trichloroacetic acid to give an 88% yield of cyclohexyl trichloroacetate using the same catalyst. He also pointed out in this article that acetic acid and cyclohexene heated at 96°-99° for 118 hours in a sealed tube gave 61% of theoretical yield of cyclohexyl acetate.
Thus although Zavgorodnii has investigated the use of the complex of boron trifluoride and ethyl ether to esterify organic acids with olefins, the information on the value of this compound as a catalyst is far from complete.

Our interest in the use of the etherate of boron trifluoride was prompted by the fact that the material became commercially available in research quantities in 1946. Since the etherate is a stable liquid boiling at 126°-127° (wherein one mole of ethyl ether combines with one mole of boron trifluoride) and is consequently convenient to use, it seemed an ideal catalyst. The assumption that the etherate as a catalyst would minimize the polymerization of the olefins seemed logical. It was known that olefins are polymerized rapidly by the action of free boron trifluoride, and that the use of this compound to promote the addition of organic acids to olefins necessitated the formation of the acid complex to prevent excessive polymerization (19).

The reaction of boron trifluoride with water, alcohols, acids, esters and ethers to form complexes had been reported in detail (37, 38, 39). Meerwein (38) had shown that the complex formation of boron trifluoride with acids increases their acidities in such a way that the complexes formed resemble a strong acid like sulfuric in their behavior. Thus weak acids like acetic are able to add to olefins in much the same manner as the well known reaction of sulfuric acid with olefins.
It was proposed in this research to study fully the reaction of olefins with various representative acids using boron trifluoride etherate as a catalyst, and to investigate the conditions necessary to minimize the polymerization side-reaction in order to obtain high yields of the esters. The kinetics of the reaction were to receive consideration also.

Liquid unsaturates were to be used in the investigation; as a reactor capable of handling gaseous olefins was not available.
DISCUSSION OF EXPERIMENTAL RESULTS
According to the Lewis concept of acids and bases, an acid is any substance which is capable of accepting a share in a pair of electrons donated by another substance to form a bond. By this definition, the halides of boron, aluminum, tin, iron and zinc are then acid catalysts. Their catalytic activity stems from their ability to affiliate themselves with the unshared electrons of another compound. Usually the bond formed utilizes an already existing pair of unshared electrons, but in the case of unsaturated compounds the double bond may be utilized leaving an electron deficient carbon and consequently a positively charge complex molecule. In the instances where the complex molecule is uncharged, an ionization then occurs.

\[ \text{RCH}_2\text{OH} + \text{BF}_3 \rightleftharpoons \text{RCH}_2\text{OH} \]

\[ \text{RCH}_2\text{OH} \rightleftharpoons [\text{RCH}_2]^+ + [\text{HO} \rightarrow \text{BF}_3]^- \]

With this idea in mind, a mechanism for the reaction of an olefin with an organic acid in the presence of boron trifluoride-etherate may be postulated.

**DISCUSSION OF THE MECHANISM OF THE REACTION:**

The reaction of an olefin with an organic acid to produce an ester in the presence of boron trifluoride-etherate is far from simple when one stops to consider the mechanism.

\[ \text{RCH} \rightarrow \text{CHR} + \text{R'}\text{COOH} \rightleftharpoons \text{RCH} \rightarrow \text{CH}_2\text{R} \]

\[ \begin{array}{c}
\text{BF}_3 \cdot \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \\
0 \\
\text{C} = 0 \\
\text{R'}
\end{array} \]
To say that the acid adds to the olefin in such a manner that a proton adds to one side of the double bond, and the acid anion that remains adds to the other side of the double bond due to the result dipole formed, is not sufficient. The all important question of how this takes place must be answered. From experiments with trichloroacetic acid and cyclohexene, it is known that without the presence of the catalyst no addition takes place (36). This follows from the fact that the acid would be practically unionized in the olefin, due to the olefin's low dielectric constant.

If one assumes the presence of a proton, the following mechanism is logical.

(1) \[ \text{R-CH=CH-R} + \text{H}^+ \rightleftharpoons \text{R-CH}_2\text{C}-\text{R} \]

(2) \[ \text{R-CH}_2\text{CHR} + \text{R'}\text{COOH} \rightleftharpoons \text{RCH}_2\text{CHO} \text{C}-\text{R'} \]

(3) \[ \text{RCH}_2\text{H} \text{C}-\text{O} + \text{R'}\text{H}^+ \rightleftharpoons \text{RCH}_2\text{H} \text{C}-\text{OC}-\text{R'} + \text{H}^+ \]

In order to reconcile this mechanism with the catalytic effect of the boron trifluoride-etherate, one may write

\[ \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_5\text{OC}_2\text{H}_5 + \text{BF}_3 \]

\[ \text{BF}_3 + \text{R'}\text{COOH} \rightleftharpoons \text{R'}\text{C}-\text{O}^+ \text{BF}_3 \]

such that the necessary proton is formed. This ionization of the acid-boron trifluoride is not required, however.
A mechanism may be written involving the reaction of the olefin with boron trifluoride to give the carbonium ion intermediate.

(1) \[ C_2H_5OC_2H_5 + BF_3 \rightleftharpoons C_2H_5OC_2H_5BF_3 \]

(2) \[ RCH = CHR + BF_3 \rightleftharpoons RCH + CHR + BF_3 \]

(3) \[ RCH + R'COOH + BF_3 \rightleftharpoons RCH_2 + C'HR + H^+ \rightleftharpoons RCH_2 + H^+ + C'HR + BF_3 \]

A second mechanism involves the complex formed between the acid and boron trifluoride, but does not involve ionization of the complex.

(1) \[ C_2H_5OC_2H_5 + BF_3 \rightleftharpoons C_2H_5OC_2H_5BF_3 \]

(2) \[ R'COOH + BF_3 \rightleftharpoons R'CO + BF_3 \]

(3) \[ RCH = CHR + R'COOH + BF_3 \rightleftharpoons RCH_2 + C'HR + R'CO + BF_3 \]

(4) \[ RCH_2 + R'COOH \rightleftharpoons RCH_2 + H^+ + C'HR + BF_3 \]

(5) \[ H^+ + R'C + BF_3 \rightleftharpoons R'COOH + BF_3 \]

It is seen that the concentration of the catalyst would have a linear effect on the reaction rate as in the previous mechanism involving the olefin-boron trifluoride complex.
The extent of the dissociation of the boron trifluoride-etherate is not critical in either mechanism, as the boron trifluoride is regenerated.

Both mechanisms suggest that the reaction to form the ester should be first order in respect to olefin, acid, and boron trifluoride. The decomposition of the ester to give acid and olefin is first order in respect to ester and boron trifluoride. As formulated, the boron trifluoride is a true catalyst. Therefore, a pseudo second order condensation in competition with a pseudo first order decomposition is represented.

It might be well to point out that the olefin polymerization in the presence of acid catalysts also takes place by way of the formation of the olefin carbonium ion (50). With this in mind, it is easy to understand why polymerization of the olefin is an important side-reaction.

In unreported initial runs using acetic acid and an excess of cyclohexene, it was discovered that the concentration of the catalyst was very critical. High concentrations of boron trifluoride-etherate led to very little of the cyclohexyl acetate, but high yields of polymer.

**THE CORRELATION OF THE YIELD OF ESTER WITH THE IONIZATION CONSTANT OF THE ACID:**

A comparison of the yields of the cyclohexyl ester from the reaction of acetic, benzoic, oxalic, chloroacetic and trichloroacetic with cyclohexene is given in Table I. In these reactions, a 2:1 excess of olefin to acid was used in order to overcome the low solubility of the solid acids in
TABLE I

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexene</td>
<td>Acetic 0.80 M</td>
<td>0.01</td>
<td>12.3%</td>
<td>6</td>
<td>0.57 M</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexene</td>
<td>Benzoic 0.80 M</td>
<td>0.01</td>
<td>13.5%</td>
<td>6</td>
<td>0.12 M&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>3</td>
<td>Cyclohexene</td>
<td>Oxalic 0.80 M</td>
<td>0.01</td>
<td>7.5%</td>
<td>6</td>
<td>0.39 M</td>
</tr>
<tr>
<td>4&lt;sup&gt;c&lt;/sup&gt;</td>
<td>Cyclohexene</td>
<td>Oxalic 1.60 M</td>
<td>0.02</td>
<td>15.0%</td>
<td>6</td>
<td>1.20 M</td>
</tr>
<tr>
<td>5&lt;sup&gt;d&lt;/sup&gt;</td>
<td>Cyclohexene</td>
<td>Chloroacetic 0.80 M</td>
<td>0.01</td>
<td>46.8%</td>
<td>6</td>
<td>0.46 M</td>
</tr>
<tr>
<td>6</td>
<td>Cyclohexene</td>
<td>Trichloroacetic 0.80 M</td>
<td>0.01</td>
<td>42.2%</td>
<td>6</td>
<td>0.28 M</td>
</tr>
<tr>
<td>26</td>
<td>Cyclohexene</td>
<td>Trichloroacetic 0.80 M</td>
<td>0.01</td>
<td>87.0%</td>
<td>6</td>
<td>0.35 M</td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

<sup>a</sup> Most of the olefin was lost on 5% KOH extraction of the acid.  
<sup>b</sup> The dicyclohexyl-ester was formed.  
<sup>c</sup> The amounts of reactants were changed to maintain the previous ratios.  
<sup>d</sup> 10% NaHCO<sub>3</sub> was used to extract the un-reacted acid.  
<sup>e</sup> The acid took on excessive moisture on weighing.  
<sup>f</sup> The sample to be used was weighed, dried, and added directly to the mixture.
the olefin. The small amount of catalyst added was 0.01 moles in every case. When it became known that with oxalic acid only the di-ester was formed, the amounts of cyclohexene and catalyst were doubled. This was done in order to maintain the 2:1 olefin to acid group ratio, and a catalyst concentration of 0.01 moles per 0.40 moles of reacting carboxyl group. This series of runs shows a correlation between the yield of ester for a given reaction time with the ionization constant of the acid.

**THE EFFECT OF CATALYST CONCENTRATION:**

Figure I shows graphically the results of runs using a 2:1 excess of cyclohexene to acetic acid with varying amounts of catalyst added, together with the results of a similar set of runs using a slight excess of acetic acid. The data is given in Tables II and III. In all runs, a constant reaction temperature and time were used in order to compare the results.

In the case of the series of runs using a 2:1 excess of cyclohexene, a sharp peak was obtained with a maximum at 0.04 moles of catalyst, corresponding to a yield of 64.4% of cyclohexyl acetate. Larger amounts of catalyst led to lower yields of ester and increasing yields of polymer. The curve for the series where a slight excess acetic acid was used shows a more gradual increase in yield of ester with increasing catalyst added. A maximum appears, corresponding to approximately 0.07 moles of catalyst, followed by a very gradual fall in yield with increasing catalyst.
Figure I

A - {Cyclohexene 0.80M, Acetic Acid 0.40M, Catalyst 0.01-0.16}

B - {Cyclohexene 0.80M, Acetic Acid 0.94M, Catalyst 0.01-0.16}

% Yield of Ester vs. Moles Catalyst/100


<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.01</td>
<td>12.3%</td>
<td>6</td>
<td>0.57 M</td>
</tr>
<tr>
<td>8</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.02</td>
<td>34.0%</td>
<td>6</td>
<td>0.52 M</td>
</tr>
<tr>
<td>9</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>64.4%</td>
<td>6</td>
<td>0.37 M</td>
</tr>
<tr>
<td>10</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.06</td>
<td>52.7%</td>
<td>6</td>
<td>0.37 M\textsuperscript{a}</td>
</tr>
<tr>
<td>11</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.08</td>
<td>22.8%</td>
<td>6</td>
<td>0.43 M\textsuperscript{b}</td>
</tr>
<tr>
<td>12</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.16</td>
<td>9.5%</td>
<td>6</td>
<td>0.23 M\textsuperscript{c}</td>
</tr>
<tr>
<td>51</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>76.5%</td>
<td>6\textsuperscript{d}</td>
<td>0.37 M</td>
</tr>
<tr>
<td>75</td>
<td>Cyclohexene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>12.3%</td>
<td>6</td>
<td>0.56 M</td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

\textsuperscript{a} In addition, 4.4 gms. of unsaturated product B.P. 70\textdegree-77\textdegree @ 3-4mm was obtained. \textsuperscript{b} 11.0 gms. of unsaturated product B.P. 78\textdegree-85\textdegree @ 4-5mm. \textsuperscript{c} 40.0 gms. of unsaturated product B.P. above 120\textdegree @ 6mm. \textsuperscript{d} This reaction was carried out in a sealed tube over which steam was passed. \textsuperscript{e} 0.4 cc. (0.022 M) of water was added to the reaction mixture.
## TABLE III

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.</td>
<td>Cyclohexene Acetic 0.80 M 0.94 M</td>
<td></td>
<td>0.01</td>
<td>2.2%</td>
<td>6</td>
<td>0.55 M</td>
</tr>
<tr>
<td>14.</td>
<td>Cyclohexene Acetic 0.80 M 0.94 M</td>
<td></td>
<td>0.04</td>
<td>34.7%</td>
<td>6</td>
<td>0.41 M</td>
</tr>
<tr>
<td>15.</td>
<td>Cyclohexene Acetic 0.80 M 0.94 M</td>
<td></td>
<td>0.08</td>
<td>61.1%</td>
<td>6</td>
<td>0.28 M</td>
</tr>
<tr>
<td>16.</td>
<td>Cyclohexene Acetic 0.80 M 0.94 M</td>
<td></td>
<td>0.16</td>
<td>57.2%</td>
<td>6</td>
<td>0.29 M</td>
</tr>
</tbody>
</table>

| 52.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 30.8%       | 5         | 0.65 M        |
| 53.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 43.5%       | 1         | 0.55 M        |
| 54.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 57.0%       | 2         | 0.47 M        |
| 55.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 63.8%       | 3         | 0.43 M        |
| 56.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 65.1%       | 4         | 0.43 M        |
| 57.     | Cyclohexene Acetic 0.80 M 0.40 M |                      | 0.04        | 65.8%       | 5         | 0.45 M        |

All reaction mixtures were heated on a steam bath.
Sowa and Wunderly (19), using gaseous boron trifluoride which they bubbled into acetic acid in order to form the acid-boron trifluoride complex, were able to get a 65% yield of cyclohexyl acetate. The reactions were run in a sealed bottle at 80° for 50-220 hours. Since the amount of acid used was not given, a comparison of results is impossible. Their plot of per cent yield of ester versus amount of catalyst had the same general shape as the curve obtained here for a slight excess of acid.

**THE EFFECT OF WATER ON THE YIELD OF ESTER:**

At this point, it might be well to mention the critical effect of a small amount of water on the yield of ester. In Run #75, identical with Run #9 where 64.4% of cyclohexyl acetate was formed, 0.4 cc. (0.022 moles) of water was added. The yield of ester fell to 12.3%. This is undoubtedly due to the formation of the hydrate of boron trifluoride which should be stable at the reflux temperature of the mixture (85°-90°). Thus, most of the catalyst would be inactivated, and the yield would be correspondingly low. In Run #36 (Table VII) however, very special care was taken to dry the reactants thoroughly immediately before their use; and the yield of ester was quite low in comparison to similar runs without these special precaution.

**THE EFFECT OF PRESSURE AND TEMPERATURE:**

In Table II, there is also given the results of Run #51 similar to that in which a 64.4% yield of cyclohexyl acetate was obtained with one exception. The reaction was run in a
sealed tube over which steam was passed. The yield of ester increased to 76.5%. This is to be expected, because of the temperature increase over the run at reflux conditions, and the increase in pressure which leads to a higher concentration of the olefin in the liquid phase.

Zavgorodnii (36) obtained a 61% yield of cyclohexyl acetate by heating an unstated amount of cyclohexene, acetic acid, and boron trifluoride-etherate in a sealed tube at 96°-97° for 118 hours.

THE EFFECT OF REACTION TIME:

In Table III, the results of a series of reactions between cyclohexene and acetic acid for various reaction times are given, wherein a 2:1 ratio of olefin to acid and a constant amount of catalyst (0.04 moles) was maintained. The plot of the results of this series is given in Figure II. The yield of ester reaches a maximum in the three hour reaction period, and then remains essentially constant. The flattening off of the curve is consistent with the view that there is an equilibrium between olefin and acid on the one hand and the ester on the other— the yield of ester being determined by the position of the equilibrium.

THE EFFECT OF ACID CONCENTRATION:

In still another series of runs with cyclohexene and acetic acid, the amount of cyclohexene and catalyst used was kept constant, but the amount of acid used was varied. Ratios of acid to olefin varying from 1:1 to 3:1 were used. The reaction time was six hours on a steam bath, as in all pre-
Figure II

- % Yield of Ester

<table>
<thead>
<tr>
<th>Time in Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

A - [Cyclohexene 0.8 M
Acetic Acid 0.4 M
Catalyst - 0.04 M]

B - [Cyclohexene 0.8 M
Benzoic Acid 0.4 M
Catalyst - 0.04 M]
vious runs. Table IV gives the results of these runs (#17, 
#18,#19). The yields show a gradual increase with increasing amount of acid. In Run #20, where the cyclohexene was added dropwise to the acetic acid-catalyst mixture over a one hour period before heating for five additional hours, a 64.1% yield of cyclohexyl acetate was obtained. This technique was tried in order to simulate the conditions of a large excess of acid to olefin. A 2:1 excess of acid gave 61.5% of the ester, whereas under the same conditions a 2:1 excess of olefin gave 64.4% previously. There was little difference in the amount of residue obtained with excess acid compared with previous runs with excess olefin, except in the cases where a large amount of catalyst was used with the olefin in excess.

THE EFFECT OF THE NATURE OF THE ACID:

In Table V, the results of a series of reactions of cyclohexene with chloroacetic, trichloroacetic, and oxalid acid are given.

Chloroacetic acid gave a yield of approximately 79.3% of ester with 0.03 moles of catalyst added, as compared to a similar reaction with acetic acid where 64.4% of the ester was obtained with 0.04 moles of catalyst. Trichloroacetic acid on the other hand was very difficult to handle, due to the rapidity with which the samples absorbed moisture on weighing. In the run where a weighed sample was dried, and used directly without reweighing, an 87.0% yield of cyclohexyl trichloroacetate was obtained under conditions comparable to
### TABLE IV

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recvd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>17.</td>
<td>Cyclohexene 0.40 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>52.7%</td>
<td>6</td>
<td>0.24 M</td>
</tr>
<tr>
<td>18.</td>
<td>Cyclohexene 0.40 M</td>
<td>Acetic 0.30 M</td>
<td>0.04</td>
<td>54.7%</td>
<td>6</td>
<td>0.25 M</td>
</tr>
<tr>
<td>19.</td>
<td>Cyclohexene 0.40 M</td>
<td>Acetic 1.20 M</td>
<td>0.04</td>
<td>61.5%</td>
<td>6</td>
<td>----</td>
</tr>
<tr>
<td>20.</td>
<td>Cyclohexene 0.40 M</td>
<td>Acetic 0.80 M</td>
<td>0.04</td>
<td>64.1%</td>
<td>6^a</td>
<td>----</td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

^a. The cyclohexene was added dropwise to the acetic acid-catalyst mixture for one hour of the six hour reaction.
### TABLE V

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.</td>
<td>Cyclohexene 0.80 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.01</td>
<td>46.8%</td>
<td>6</td>
<td>0.46 M</td>
</tr>
<tr>
<td>23.</td>
<td>Cyclohexene 0.80 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.03</td>
<td>79.3%</td>
<td>6</td>
<td>0.40 M</td>
</tr>
<tr>
<td>24.</td>
<td>Cyclohexene 0.80 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.04</td>
<td>80.0%</td>
<td>7</td>
<td>0.40 M</td>
</tr>
<tr>
<td>6.</td>
<td>Cyclohexene 0.80 M</td>
<td>Trichloroacetic&lt;sup&gt;a&lt;/sup&gt; 0.40 M</td>
<td>0.01</td>
<td>42.2%</td>
<td>6</td>
<td>0.28 M</td>
</tr>
<tr>
<td>7.</td>
<td>Cyclohexene 0.80 M</td>
<td>Trichloroacetic&lt;sup&gt;a&lt;/sup&gt; 0.40 M</td>
<td>0.04</td>
<td>49.0%</td>
<td>6</td>
<td>0.17 M&lt;sup&gt;b&lt;/sup&gt;</td>
</tr>
<tr>
<td>25.</td>
<td>Cyclohexene 0.76 M</td>
<td>Trichloroacetic&lt;sup&gt;a&lt;/sup&gt; 0.38 M</td>
<td>0.04</td>
<td>66.4%</td>
<td>4</td>
<td>0.38 M&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>26.</td>
<td>Cyclohexene 0.80 M</td>
<td>Trichloroacetic&lt;sup&gt;d&lt;/sup&gt; 0.40 M</td>
<td>0.01</td>
<td>87.0%</td>
<td>6</td>
<td>0.35 M</td>
</tr>
<tr>
<td>3.</td>
<td>Cyclohexene 0.80 M</td>
<td>Oxalic&lt;sup&gt;e&lt;/sup&gt; 0.40 M</td>
<td>0.01</td>
<td>7.5%&lt;sup&gt;f&lt;/sup&gt;</td>
<td>6</td>
<td>0.39 M</td>
</tr>
<tr>
<td>4.</td>
<td>Cyclohexene 1.60 M</td>
<td>Oxalic&lt;sup&gt;e&lt;/sup&gt; 0.40 M</td>
<td>0.02</td>
<td>15.0%</td>
<td>6</td>
<td>1.20 M</td>
</tr>
<tr>
<td>21.</td>
<td>Cyclohexene 1.60 M</td>
<td>Oxalic&lt;sup&gt;e&lt;/sup&gt; 0.40 M</td>
<td>0.04</td>
<td>15.1%</td>
<td>6</td>
<td>----</td>
</tr>
<tr>
<td>28.</td>
<td>Cyclohexene 1.60 M</td>
<td>Oxalic&lt;sup&gt;e&lt;/sup&gt; 0.40 M</td>
<td>0.08</td>
<td>14.9%</td>
<td>6</td>
<td>1.22 M&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

a. the acid took on moisture on weighing.  b. 25 gms. of unsaturated product B.P. above 120° @ 5mm.  c. No high boiling unsaturated product was found.  d. The sample to be used was weighed, dried, and added directly to the mixture.  e. In no case did all the acid dissolve.  f. The dicyclohexyl-ester was formed.  g. The amounts of reactants were changed to maintain the previous ratios.  h. 2.0 gms. cyclohexanol were also obtained.
the yields mentioned above, but with 0.01 moles of catalyst. With oxalic acid, the reaction gave low yields. With reference to the data given in Table V, it is seen that the yield of dicyclohexyl oxalate in reactions where there was a 2:1 excess of olefin to acid as in the runs with acetic, chloroacetic, and trichloroacetic acids, was approximately 15%. Also, an increase in the amount of catalyst had no effect on the yield. In Run #3 where the amount of cyclohexene was halved, the yield was only 7.5%. A comparison of this yield data, along with the fact that in none of these reactions was all the oxalic acid in solution, suggests the theory that the amount of ester formed is directly dependent on the solubility of the acid in cyclohexene.

Benzoic acid was then investigated more extensively. The results are summarized in Table VI. All runs were made with a 2:1 excess of cyclohexene to benzoic acid in order to employ the olefin as a solvent as well as a reactant. With the usual technique of adding the catalyst to the olefin-acid mixture at approximately room temperature, a 55.0% yield of cyclohexyl benzoate was obtained in six hours with a 2:1 excess of cyclohexene to benzoic acid, using 0.04 moles of boron trifluoride-etherate.

**THE EFFECT OF THE MODE OF ADDITION OF THE CATALYST:**

In a series of reactions involving cyclohexene and benzoic acid, the catalyst was added slowly through the top of the reflux condenser to the hot acid-olefin mixture. The temperature of the mixture was approximately five degrees
TABLE VI

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv’d Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Cyclohexene 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.01&lt;sup&gt;b&lt;/sup&gt;</td>
<td>13.5%</td>
<td>6</td>
<td>0.12 M&lt;sup&gt;a&lt;/sup&gt;</td>
</tr>
<tr>
<td>27.</td>
<td>Cyclohexene 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.04&lt;sup&gt;b&lt;/sup&gt;</td>
<td>55.0%</td>
<td>6</td>
<td>0.40 M</td>
</tr>
<tr>
<td>61.</td>
<td>Cyclohexene 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.02&lt;sup&gt;c&lt;/sup&gt;</td>
<td>57.0%</td>
<td>6</td>
<td>0.38 M</td>
</tr>
<tr>
<td>62.</td>
<td>Cyclohexene&lt;sup&gt;d&lt;/sup&gt; 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>67.0%</td>
<td>5</td>
<td>0.38 M</td>
</tr>
<tr>
<td>63.</td>
<td>Cyclohexene&lt;sup&gt;d&lt;/sup&gt; 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>74.0%</td>
<td>1</td>
<td>0.35 M</td>
</tr>
<tr>
<td>64.</td>
<td>Cyclohexene&lt;sup&gt;d&lt;/sup&gt; 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>75.7%</td>
<td>2</td>
<td>0.32 M</td>
</tr>
<tr>
<td>65.</td>
<td>Cyclohexene&lt;sup&gt;d&lt;/sup&gt; 0.80 M</td>
<td>Benzoic 0.40 M</td>
<td>0.04&lt;sup&gt;c&lt;/sup&gt;</td>
<td>76.3%</td>
<td>3</td>
<td>0.24 M</td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

a. Most of the olefin was lost on 5% KOH extraction of the acid.  
b. The catalyst was added to the olefin-acid mixture at room temperature.  
c. The catalyst was added to the olefin-acid mixture at a temperature just below the reflux temperature.  
d. An unsaturated product boiling 90°-92° @ 6mm was obtained in these runs in the following amounts: #62 - 4.0 gms., #63 - 5.0 gms., #64 - 6.5 gms., and #65 - 7.5 gms.
below the reflux temperature. The yield of cyclohexyl benzoate per unit time was greatly increased by this technique. The results are plotted in Figure II, showing that in a reaction time of one hour the reaction is practically complete. As in the comparable reactions of cyclohexene with acetic acid, the curve flattens out indicating an equilibrium has been reached. The equilibrium concentration corresponded to a 76% yield of the ester.

One disadvantage to the method of adding the catalyst to the hot reaction mixture was the production of a small amount of the dimer of cyclohexene (1-cyclohexyl cyclohexene). In the method whereby the catalyst is added to the reaction mixture at approximately room temperature, no distinguishable amount of the dimer ever appeared.

A satisfactory explanation for the increase in rate by adding the catalyst to the hot mixture can not be found.

**MIXED ESTERIFICATIONS:**

In order to further investigate the correlation of the ionization constant of the acid and the per cent yield of the ester, a series of runs were made in which two acids reacted simultaneously with cyclohexene (see Table VII). Chloroacetic acid was used in each run because of it's greater strength along with an equal amount of the weaker acetic, benzoic, and oxalic acids. The reactions were run in such a way that molar ratio of olefin to total acid was 2:1. The amounts of cyclohexene and catalyst added were adjusted, when using oxalic acid, to take into account that the acid is
dibasic. A tabular summary of comparable mixed esterification runs and normal runs is given below.

**Mixed Esterifications**

Mole Ratio of Olefin to Total Acid - 2:1
Reaction Time - 6 Hours on a steam bath

<table>
<thead>
<tr>
<th>Cat./.4M Moles/COOH</th>
<th>% Ester in Normal Reaction</th>
<th>Mixed Esterification with Chloroacetic % Ester</th>
<th>% Chloroacetate in Normal Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>% Chloroacetate</td>
<td></td>
</tr>
<tr>
<td>Acetic Acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>34.0</td>
<td>40.7</td>
<td>71.3</td>
</tr>
<tr>
<td>0.04</td>
<td>64.4</td>
<td>69.4</td>
<td>86.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Benzoic Acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>----</td>
<td>75.0</td>
<td>97.5</td>
</tr>
<tr>
<td>0.04</td>
<td>55.0a</td>
<td>76.7</td>
<td>97.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Oxalic Acid</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.02</td>
<td>15.1</td>
<td>42.4</td>
<td>80.7</td>
</tr>
<tr>
<td>0.04</td>
<td>14.9</td>
<td>31.0</td>
<td>75.0</td>
</tr>
</tbody>
</table>

a. The value given for the yield of cyclohexyl benzoate is that obtained by adding the catalyst to the reaction mixture at room temperature.

Both the yields of the ester of the weaker acid and of cyclohexyl chloroacetate increased over the yields obtained in normal runs, so that trans-esterification favoring the stronger acid did not occur. The relative increase in the yields of the esters of acetic, benzoic, and oxalic acids over the yields obtained in comparable normal runs appear to correlate inversely with the relative solubilities of these
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Reactants and Moles</th>
<th>Cat. / .4 M Ester</th>
<th>Time</th>
<th>Recv'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Moles/COOH</td>
<td>Yield</td>
<td>Hrs.</td>
</tr>
<tr>
<td>29.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.04</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>31.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.04</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Acetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzoic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>33.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.04</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Benzoic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>35.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxalic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>36.</td>
<td>Cyclohexene</td>
<td>2.40</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxalic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>37.</td>
<td>Cyclohexene</td>
<td>2.40</td>
<td>0.04</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxalic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>38.</td>
<td>Cyclohexene</td>
<td>1.60</td>
<td>0.02</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>Chloroacetic</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p-Nitrobenzoic (^{d})</td>
<td>0.40</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

All reaction mixtures were heated on a steam bath.

- a. 13.8 gms. of product B.P. 68°-72° @ 2-3mm. was obtained.  
- b. 8.0 gms. of cyclohexanol also obtained.  
- c. Special care was taken in drying all reactants immediately before being used.  
- d. The acid was very insoluble in the olefin.  
- e. 12 gms. of unsaturated residue was obtained.
acids in cyclohexene. The solubility of the acids in cyclo-
hexene increases from oxalic to acetic, whereas the relative in-
crease in the yields of ester in these so-called "mixed
esterification runs" is in the reverse order. This solubil-
ity effect may be explained by the increase in the over-all
volume of the olefin in these runs when compared to normal
reactions, even though the molar ratios of olefin to total
acid are the same.

THE EFFECT OF THE NATURE OF THE UNSATURATE:

The use of boron trifluoride-etherate to promote addi-
tion of acetic acid to \( \alpha \)-pinene was investigated. A series
of runs with slightly over a 2:1 excess of acetic acid to
\( \alpha \)-pinene were made (Table VIII). The reaction, as shown
below, involves a rearrangement which is common in the bi-
cyclic terpene series. The pinene type structure rearranges
to the bornyl type structure. (The simplified mechanism in-
volving the initial proton was used here to save space.)
This type of rearrangement is analogous to the rearrangement involved in the addition of hydrobromic acid to t-butyl ethylene, as shown below.

\[
\text{CH}_3\text{C-CH-CH}_2 \rightleftharpoons \text{CH}_3\text{C}^+\text{H-CH-CH}_3
\]

\[
\text{CH}_3\text{C-CH-CH}_2 \rightleftharpoons \text{CH}_3\text{Br}^+\text{H-CH-CH}_3
\]

Notice that in both of the examples, the rearrangement involves the formation of the more stable carbonium ion.

The yields of bornyl acetate were low in general. Very little unreacted pinene was recovered, as it either reacted with the acetic acid or polymerized. In general, the reactions carried out by heating on a steam bath led to better yields of ester per unit time than those heated to reflux. The best yield using an excess of acid was 19.1%, which was obtained in a short one hour reaction on a steam bath. Longer heating and higher catalyst concentrations led to increased polymerization and a decreased yield of bornyl acetate. In one reaction using a 2:1 excess of \(\alpha\)-pinene to acetic acid and small amount of catalyst, a 29.3% yield of bornyl acetate was obtained by heating the mixture for an hour and a half on the steam bath.

In all cases the initial reaction was violent, due probably to the exothermic rearrangement from the pinene to bornyl type structure. It is thought that the addition re-
TABLE VIII

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recvd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>39.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.94 M</td>
<td>0.02</td>
<td>18.7%</td>
<td>7&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.02 M&lt;sup&gt;c&lt;/sup&gt;</td>
</tr>
<tr>
<td>40.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.94 M</td>
<td>0.01</td>
<td>6.3%</td>
<td>3&lt;sup&gt;a&lt;/sup&gt;</td>
<td>0.01 M&lt;sup&gt;d&lt;/sup&gt;</td>
</tr>
<tr>
<td>41.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.94 M</td>
<td>0.01</td>
<td>17.9%</td>
<td>3&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.06 M&lt;sup&gt;e&lt;/sup&gt;</td>
</tr>
<tr>
<td>42.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.94 M</td>
<td>0.01</td>
<td>19.1%</td>
<td>1&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.09 M&lt;sup&gt;f&lt;/sup&gt;</td>
</tr>
<tr>
<td>43.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.94 M</td>
<td>0.10</td>
<td>6.3%</td>
<td>6&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.04 M&lt;sup&gt;g&lt;/sup&gt;</td>
</tr>
<tr>
<td>44.</td>
<td>α-pinene 0.40 M</td>
<td>Acetic 0.20 M</td>
<td>0.01</td>
<td>29.3%</td>
<td>1.5&lt;sup&gt;b&lt;/sup&gt;</td>
<td>0.03 M&lt;sup&gt;h&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

a. Heated reaction mixture to boiling (120°-130°).
b. Reaction mixtures were heated on a steam bath.
c. 38.0 gms. of pinene polymer B.P. above 90° @ 3mm.
d. 26 gms. of pinene polymer B.P. above 90° @ 3mm.
e. 31.0 gms. of pinene polymer B.P. above 90° @ 3mm.
f. 18.0 gms. of pinene polymer B.P. 144°-146° @ 3mm; 11.0 gms. of pinene polymer B.P. above 155° @ 3mm. g. 9.0 gms. of pinene polymer B.P. 137°-139° @ 2mm; 28.0 pinene polymer B.P. above 150° @ 2mm. h. 31.0 gms. of pinene polymer B.P. above 90° @ 4mm.
action is rapid in the first few minutes, but on longer heating the polymerization reaction becomes foremost.

The reaction of acetic acid with 2-pentene was also investigated. The results are given in Table IX. The reaction is shown below using the simplified mechanism involving the assumption of an available proton.

\[
\begin{align*}
\text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3 + \text{H}^+ &\rightleftharpoons \text{CH}_3\text{CH}_2\text{CHCH}_2\text{CH}_3^+ \\
\text{H}^+ + \text{CH}_3\text{CH}_2\text{COO}^- &\rightleftharpoons \text{CH}_3\text{CH}_2\text{HCOO}^-
\end{align*}
\]

In these runs as usual, a 2:1 excess of olefin to acid was maintained. The reactions were run at room temperature and reflux temperature (36°C - 38°C), both with and without stirring. Even in a one hundred hour reaction at reflux temperature, the yield of diethyl carbinol acetate was only 23.3%. A similar reaction with twice the amount of catalyst, in a sealed tube over which steam was passed for one hundred hours, gave a 71.4% of the ester.

The reaction with 2-pentene and acetic acid is presumably a rate-limited process at reflux temperature. In the sealed tube run, the pressure increase leading to a greater concentration of the olefin in the liquid phase would increase the rate. The increased reaction temperature would appear to increase the rate also. Doubling the catalyst con-
### TABLE IX

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles Yield</th>
<th>Time Hrs.</th>
<th>Recvd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>45.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04 9.3%f</td>
<td>24a</td>
<td>0.50 Me</td>
</tr>
<tr>
<td>46.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04 11.6%f</td>
<td>24b</td>
<td>0.50 Me</td>
</tr>
<tr>
<td>47.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04 19.6%f</td>
<td>6c</td>
<td>0.43 Me</td>
</tr>
<tr>
<td>48.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04 24.0%f</td>
<td>12c</td>
<td>0.45 Me</td>
</tr>
<tr>
<td>49.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04 23.3%f</td>
<td>100c</td>
<td>0.48 Me</td>
</tr>
<tr>
<td>50.</td>
<td>2-pentene 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.08 71.4%f</td>
<td>100d</td>
<td>0.38 Me</td>
</tr>
</tbody>
</table>

a. Room temperature.  b. Room temperature with stirring.  
c. Reflux conditions. (36°-38°)  d. Reaction carried out in a sealed tube over which steam was passed.  
e. Residue was less than 1 cc.  f. Diethyl carbinol acetate sole product.
centration also should double the rate. Thus in the sealed-tube reaction, a better approach to equilibrium conditions must have been attained.

In order to discover further limitations of the reaction, a variety of different types of unsaturated molecules were used. The results are given in Table XI.

A sample of styrene was prepared in order to determine whether it was possible to add acetic or chloroacetic acid to the ethylenic double bond in the molecule. Acetic acid and styrene in equivalent amounts, when heated for six hours on a steam bath in the presence of boron trifluoride, led to an almost clear, viscous liquid which solidified on standing. Another sample of styrene was heated with a 4:1 excess of chloroacetic acid, using toluene as a solvent media. The product, obtained along with polymer, was a clear liquid boiling at 125°-130° at 2mm. The product contained chlorine and gave a neutral equivalent of 975. This may be said to correspond to partial addition of the chloroacetic acid, one mole of the acid to every eight or nine polymer units.

With allyl bromide, acetic acid did not react under reflux conditions (71°). However, in a sealed tube reaction in which a 2:1 excess of the bromide was used, acetic acid reacted to give a 13.4% of β-bromo isopropyl acetate when heated for 100 hours.

\[
\text{Catalyst} \quad \begin{align*}
\text{CH}_2\text{C-CH}_2\text{Br} + \text{CH}_3\text{COOH} & \rightarrow \text{BrCH}_2\text{CH} = \text{CHCOCH}_3 \\
\end{align*}
\]
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Unsaturate and Conc.</th>
<th>Acid and Conc.</th>
<th>Cat. Moles</th>
<th>Ester Yield</th>
<th>Time Hrs.</th>
<th>Recv'd Unsaturate</th>
</tr>
</thead>
<tbody>
<tr>
<td>78.</td>
<td>Styrene 0.40 M</td>
<td>Acetic 0.40 M</td>
<td>0.02</td>
<td>-0-</td>
<td>6</td>
<td>----a</td>
</tr>
<tr>
<td>79. b</td>
<td>Styrene 0.18 M</td>
<td>Chloroacetic 0.72 M</td>
<td>0.02</td>
<td>---c</td>
<td>6</td>
<td>----d</td>
</tr>
<tr>
<td>80.</td>
<td>Allyl bromide 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>-0-</td>
<td>6</td>
<td>0.74 M</td>
</tr>
<tr>
<td>81.</td>
<td>Allyl bromide 0.76 M</td>
<td>Acetic 0.38 M</td>
<td>0.08</td>
<td>13.4%e</td>
<td>100f</td>
<td>0.67 M</td>
</tr>
<tr>
<td>82.</td>
<td>Allyl acetate 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>0.04</td>
<td>-0-</td>
<td>5g</td>
<td>0.42 Mh</td>
</tr>
<tr>
<td>83.</td>
<td>Methyl crotonate 0.35 M</td>
<td>Chloroacetic 0.35 M</td>
<td>0.03</td>
<td>-0-</td>
<td>6</td>
<td>0.14 Ml</td>
</tr>
<tr>
<td>84. k</td>
<td>Methyl acrylate 0.40 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.02</td>
<td>-0-</td>
<td>5j</td>
<td>0.31 M</td>
</tr>
<tr>
<td>85. k</td>
<td>Methyl acrylate 0.40 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.02</td>
<td>-0-</td>
<td>100</td>
<td>0.30 Mf</td>
</tr>
<tr>
<td>86. k</td>
<td>Methyl acrylate 0.40 M</td>
<td>Trichloroacetic</td>
<td>0.02</td>
<td>-0-</td>
<td>6j</td>
<td>----</td>
</tr>
<tr>
<td>87.</td>
<td>Methyl acrylate 0.40 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.02</td>
<td>-0-</td>
<td>5m</td>
<td>----</td>
</tr>
<tr>
<td>88. k</td>
<td>Methyl acrylate 0.40 M</td>
<td>Chloroacetic 0.40 M</td>
<td>0.06</td>
<td>-0-</td>
<td>6j</td>
<td>0.73 M</td>
</tr>
<tr>
<td>89.</td>
<td>Vinyl ethyl ether 0.30 M</td>
<td>Acetic 0.30 M</td>
<td>0.01n</td>
<td>----o</td>
<td>3</td>
<td>----</td>
</tr>
<tr>
<td>90.</td>
<td>Vinyl ethyl ether 0.30 M</td>
<td>Acetic (2-drops.)</td>
<td>(2-drops.)</td>
<td>----o</td>
<td>4p</td>
<td>----</td>
</tr>
<tr>
<td>91.</td>
<td>Vinyl isopropyl ether 0.80 M</td>
<td>Acetic 0.40 M</td>
<td>(0.2 cc)</td>
<td>----o</td>
<td>2q</td>
<td>----</td>
</tr>
<tr>
<td>92.</td>
<td>Vinyl isopropyl ether 0.40 M</td>
<td>Acetic (1-drop.)</td>
<td>(1-drop.)</td>
<td>----o</td>
<td>4r</td>
<td>----</td>
</tr>
</tbody>
</table>

(See next page for footnotes)
Footnotes for TABLE XI:

a. Residue contained 38 gms. of a semi-solid which solidified on standing.  
b. Toluene (1.73 M) was added as a solvent.  
c. Obtained product containing chlorine B.P. 125°-130° @ 2mm.  
d. 14.0 gms. of polymer obtained in the distillation residue.  
e. 2-bromo 1-methyl ethyl acetate was obtained (2-bromo isopropyl acetate).  
f. The reaction was carried out in a sealed tube over which steam was passed.  
g. Reaction temperature was 100°-105°.  
h. 7.0 gms. of allyl alcohol identified as the phenylurethane.  
i. 2.0 gms. of methyl alcohol obtained also.  
j. At reflux temperature.  
k. The reaction mixture was distilled directly without removal of the unreacted acid.  
l. Added 2.5 gms. mercuric oxide along with BF₃-etherate.  
m. With stirring on a steam bath.  
n. Violent reaction on catalyst addition.  
o. Products unidentified.  
p. At room temperature.  
q. The vinyl isopropyl ether was added dropwise for one hour to the acid-catalyst mixture at room temperature.  
Followed by one hour of standing at room temperature.  
r. The vinyl isopropyl ether was added dropwise for one hour to the acid-catalyst mixture at room temperature.  
Followed by three hours of standing at room temperature.
Allyl acetate, methyl crotonate, and methyl acrylate did not react with organic acids to give the desired addition products.

Reppe (43) reported that vinyl ethers add organic acids easily to give alkoxy or aryloxyethylidene esters. The conditions for this reaction were not mentioned.

\[
\text{ROCH=CH}_2 + R'\text{COOH} \xrightarrow{\text{Catalyst}} \text{RO-CH-CH}_3
\]

With vinyl ethyl and vinyl isopropyl ethers and acetic acid in the presence of a few drops of boron trifluoride-etherate, no identifiable addition product was isolated.

From the reaction of acetic and chloroacetic acids with 1-methyl cyclohexene-1 at 120°, no product was isolated except for polymer. However, 8% of 1-methyl cyclohexyl acetate was obtained in a six hour reaction of a 2:1 excess of 1-methyl cyclohexene-1 over acetic acid. A 4% yield of this ester was obtained in another reaction wherein a 2:1 excess of acid to olefin was used. In both these reactions a fair amount of high boiling unsaturate was found.

A run with 3-methyl cyclohexene-1 and acetic acid, using a 2:1 excess of olefin, gave 22.4% of product, B.P. 58.5°-59.5°
### TABLE XII

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Olefin</th>
<th>Acid</th>
<th>Moles</th>
<th>Yield</th>
<th>Time Hrs.</th>
<th>Recov'd Olefin</th>
</tr>
</thead>
<tbody>
<tr>
<td>93</td>
<td>1-methyl cyclohexene-1</td>
<td>Acetic 0.20 M</td>
<td>0.04</td>
<td>-0-</td>
<td>6^a</td>
<td>0.05 M^b</td>
</tr>
<tr>
<td>94</td>
<td>1-methyl cyclohexene-1</td>
<td>Chloro-acetic 0.32 M</td>
<td>0.01</td>
<td>-0-</td>
<td>6^a</td>
<td>0.04 M^c</td>
</tr>
<tr>
<td>95</td>
<td>1-methyl cyclohexene-1</td>
<td>Acetic 0.20 M</td>
<td>0.02</td>
<td>8.0%</td>
<td>6^d</td>
<td>0.17 M^e</td>
</tr>
<tr>
<td>96</td>
<td>1-methyl cyclohexene-1</td>
<td>Acetic 0.80 M</td>
<td>0.01</td>
<td>4.0%</td>
<td>6^d</td>
<td>0.29 M^f</td>
</tr>
<tr>
<td>97</td>
<td>3-methyl cyclohexene-1</td>
<td>Acetic 0.31 M</td>
<td>0.04</td>
<td>22.4%</td>
<td>6^d</td>
<td>0.13 M^g</td>
</tr>
</tbody>
</table>

^a. Heated at 120°.  ^b. 8.8 gms. product B.P. 103°-105° @ 3.4mm d^25 - 0.903, also 21.5 gms. orange polymer B.P. above 110° @ 4mm.  ^c. 1.0 gms. product B.P. 102°-104° @ 4mm, 20.0 gms. of polymer.  ^d. Heated at 90°.  ^e. 7.5 gms. product B.P. 102°-104° @ 3mm d^25 - 0.904; 4.0 gms. of polymer.  ^f. 1.5 gms. of polymer B.P. above 110° @ 4mm.  ^g. 16.5 gms. of product B.P. 100°-101° @ 3mm, d^25 - 0.913, n^D - 1.4911; 11.7 gms. of polymer B.P. above 115° @ 4mm.
at 3mm which when hydrolyzed gave an alcohol having properties similar to those of the 2 and 3-methyl cyclohexanols.

Since oleic acid has an isolated double bond, it was thought oleic acid might condense with an acid as cyclohexene does.

\[
\begin{align*}
\text{CH}_3(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH} & \quad \rightarrow \quad \text{CH}_3\text{COOH} \\
\text{CH}_3(\text{CH}_2)_8\text{CH}=(\text{CH}_2)_7\text{COOH} & \quad \text{or} \quad \text{CH}_3(\text{CH}_2)_7\text{CH}=(\text{CH}_2)_8\text{COOH} \\
& \quad \text{Catalyst}
\end{align*}
\]

Accordingly, 0.40 moles of oleic acid were heated to reflux for six hours with 0.40 moles of acetic acid in the presence of 0.04 moles of boron trifluoride. A product, which boiled at \(200^\circ-203^\circ\) @ 5-6mm, was isolated; and a large amount of residue, which boiled above \(300^\circ\) @ 5-6mm, remained.

The results of neutral equivalents obtained on the product, and hydrolyzed product; together with the data from cooling curves run on the original oleic acid, the product obtained, and the hydrolyzed product; and the determination of the per cent of hydroxy groups in the hydrolyzed product, all indicate that acetic acid did add to the oleic acid. From these observations, it was impossible to decide whether the 9 or 10-acetoxy derivative was obtained.

In all probability a mixture of both products is obtained thus accounting for the low value of \(28^\circ-30^\circ\) obtained
for the solidification point of the hydrolyzed product. Tomecko and Adams (44) give the melting point of 9-hydroxy stearic acid as 74°-75° and 10-hydroxy stearic acid as 81°-82°. A mixture of these acids would in all probability have a lower melting point than either pure isomer.

Although the esters of α,β unsaturated acids did not react with organic acids, it seemed possible that a β,γ unsaturated acid might react. According to Gilman (45) the rate of addition of bromine to β,γ unsaturated acids is over ten thousand times as fast as addition to the corresponding α,β unsaturated acids.

Accordingly, a sample of "hydrosor bonic acid" or 3,4 hexenoic acid was prepared according to the method of Sudborough and Thomas (46) by the reduction of sorbic acid with sodium amalgam. This acid together with acetic acid in equivalent amount was heated in the presence of boron trifluoride-etherate. The product isolated was later proven to be the γ-lactone of hexanoic acid (B.P. 80°-81° @ 5-6mm). The yield of lactone was 56% in the six hour reaction.

\[
\text{CH}_3\text{CH}_2\text{CH} = \text{CH} - \text{CH}_2\text{COOH} \xrightarrow{\text{Catalyst}} \text{CH}_3\text{CH}_2\text{CCH}_2\text{CH}_2\text{C} = \text{O}
\]

The formation of the γ-lactone is not surprising in view of the fact that the reaction is of the same type as the addition of an acid to an olefin. The reaction is favored, for cyclization always occurs with more ease than an intra-molecular reaction.
A thorough check of the literature disclosed that what
Sudborough and Thomas thought was the pure $\mathbf{p, 7}$ unsaturated
acid was a mixture of the $\mathbf{p, 7}$ and $\mathbf{7, 8}$ unsaturated acid.
Evans and Farmer (47) estimated the amount of $\mathbf{7, 8}$ impurity
to be about 35%. Eccott and Linstead (48) confirmed the
findings of Evans and Farmer.

Boxer and Linstead (49) showed conclusively that pure
3,4 hexenoic acid can be prepared by the reaction of n-
butyraldehyde with malonic acid in the presence of trieth-
olamine, followed by decarboxylation. A sample of this
acid was prepared by their method.

Equivalent amounts of 3,4 hexenoic acid and chloroacetic
acid together with boron trifluoride-etherate were heated
on a steam bath for five hours. The product isolated
(B.P. 86\textdegree-88\textdegree @ 6mm), unlike the lactone obtained with
acetic acid, was acidic and insoluble in water. It also had
a much higher density and contained chlorine. The neutral
equivalent obtained was 248 as compared to a calculated
value of 208.7 for chloroacetoxy-hexanoic acid. The neutral
equivalent of 3,4 hexenoic acid is 114.1. The high value
for the neutral equivalent can be explained by contamination
with a small amount of the lactone. The yield was 45.5%
of the theoretical value (assuming a pure product).

Hydrolysis of the product gave a material which was
proven to be the $\mathbf{7}$-lactone of hexanoic acid. The supposed
reaction sequence is given below.
CH₃CH₂CH=CHCH₂COOH + ClCH₂COOH $\xrightarrow{\text{Catalyst}}$ CH₃CH₂CCH₂CH₂COOH

A further reaction with an excess of chloroacetic acid gave nothing but the lactone. Since the reaction mixture was distilled directly instead of being treated with water initially, it is possible that the addition product decomposed.

With oxalic acid, the 3,4 hexenoic acid gave only the result of internal esterification or the β-lactone. The yield was 79.5%. Here again, direct distillation of the reaction mixture may have decomposed the addition product.

**THE EFFECT OF SOLVENTS:**

In all previous runs, no solvents or diluents had been added to the reaction mixture. In order to ascertain the effect of various solvents, a series of runs were made with acetic and benzoic acids using benzene, carbon tetrachloride, chloroform, nitrobenzene, and isoamyl ether as solvents. The results obtained in these reactions are tabulated in Table X. In all runs the reaction time was six hours, and 0.04 moles of catalyst were added.

In the reactions of acetic acid (0.40 moles) with cyclohexene (0.08 moles) in the presence of 0.40 moles of benzene, carbon tetrachloride, and chloroform, the yields of cyclohexyl acetate were 46.8%, 45.8% and 37.3% respectively. The
yields of ester may be correlated with the reflux temperatures of the various mixtures. The boiling points of benzene (80°) and carbon tetrachloride (76°-77°) are close together, so that the reflux temperature of mixtures containing them are little different. On the other hand the boiling point of chloroform is 61°, so that the reflux temperature of a mixture containing this material is much lower. Assuming that in all three of these runs equilibrium was not reached, the amount of ester produced in the six hour reaction period would be greatly influenced by the boiling points of the respective solvents used.

Benzoic acid was made to react with cyclohexene with the addition of various solvents. In all these runs, catalyst addition was at a temperature just below the reflux temperature of the reaction mixture.

With benzene, carbon tetrachloride, and chloroform as solvents, the yields were 75.3%, 76.6% and 76.4% in six hour reactions. Hence the dilution effect of the solvents leading to slower reaction rates did not prevent the reactions from reaching equilibrium in six hours (see Figure II). A modification in the method of isolation of the ester gave similar results with these solvents, only with slightly lower yields (see footnotes to Table X). In these runs as in the previous runs where this method of catalyst introduction was employed, the dimer of cyclohexene was isolated. Benzene seemed to facilitate the production of the dimer more than chloroform or carbon tetrachloride.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Acid</th>
<th>Moles Acid</th>
<th>Solvent Added</th>
<th>Moles Solvent</th>
<th>Cat. Moles</th>
<th>Time Hrs.</th>
<th>Yield Ester</th>
</tr>
</thead>
<tbody>
<tr>
<td>58.</td>
<td>Acetic</td>
<td>0.40</td>
<td>Benzene</td>
<td>0.40</td>
<td>0.04</td>
<td>6</td>
<td>46.8%</td>
</tr>
<tr>
<td>59.</td>
<td>Acetic</td>
<td>0.40</td>
<td>CCl₄</td>
<td>0.40</td>
<td>0.04</td>
<td>6</td>
<td>45.8%</td>
</tr>
<tr>
<td>60.</td>
<td>Acetic</td>
<td>0.40</td>
<td>HCCl₃</td>
<td>0.40</td>
<td>0.04</td>
<td>6</td>
<td>37.3%</td>
</tr>
<tr>
<td>66.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>Nitro-benzene</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>71.5%ᵇ</td>
</tr>
<tr>
<td>67.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>Isoamyl ether</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>9.2%</td>
</tr>
<tr>
<td>68.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>C₂H₅OH</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>26.1%ᶜ</td>
</tr>
<tr>
<td>69.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>CCl₄</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>76.6%ᵈ</td>
</tr>
<tr>
<td>70.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>HCCl₃</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>76.4%ᵈ</td>
</tr>
<tr>
<td>71.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>Benzene</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>75.3%ᵈ</td>
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<tr>
<td>72.</td>
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<td>0.40</td>
<td>CCl₄</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>73.2%ᵈ</td>
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<tr>
<td>73.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>HCCl₃</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>72.3%ᵈ</td>
</tr>
<tr>
<td>74.</td>
<td>Benzoic</td>
<td>0.40</td>
<td>Benzene</td>
<td>0.40</td>
<td>0.04ᵃ</td>
<td>6</td>
<td>72.9%ᵈ</td>
</tr>
</tbody>
</table>

The amount of cyclohexene used in all reactions was 0.80 moles.
All reaction mixtures were heated on a steam bath.

a. The catalyst was added to the olefin-acid mixture at a temperature just below the reflux temperature.
b. The ester had a yellow color which could not be removed.
c. Ethyl benzoate was the sole product.
d. Dilute acid wash used after 5% KOH treatment; followed by usual water wash.
e. Dimer of cyclohexene B.P. 82⁰-83⁰ @ 2mm, 92⁰-94⁰ @ 7mm, 96⁰-98⁰ @ 8-9mm. Quantities: #69 - 9.5 gms., #70 - 6.0 gms., #71 - 12.3 gms., #72 - 6.0 gms., #73 - 6.5 gms., #74 - 7.5 gms. g. The solvent was removed.
f. Two washings with 5% KOH were used in order to extract the unreacted acid, followed by the usual water wash.
Nitrobenzene (0.40 moles), when added as a solvent to a mixture of 0.40 moles of benzoic acid and 0.40 moles of cyclohexene, led to a 71.5% yield of cyclohexyl benzoate after four distillations to remove the yellow color in the product.

With isoamyl ether as a solvent, the yield of ester fell to 9.2%. The competition in equilibrium between the various boron trifluoride complexes seems to be the logical explanation for the low yield of cyclohexyl benzoate. The equilibrium may be shifted due to the stability of the isoamyl ether complex with boron trifluoride at the reaction temperature (85°-90°).

A reaction (wherein 0.40 moles of ethyl alcohol was added to a mixture of 0.80 moles of cyclohexene, 0.40 moles of benzoic acid, and 0.04 moles of catalyst) was run in order to see whether a mixture of ethyl and cyclohexyl benzoate would be obtained. However, the only product obtained was ethyl benzoate in 26.1% yield.

**DETERMINATION OF THE EQUILIBRIUM CONSTANT AND REACTION RATE:**

In order to investigate more fully the addition of organic acids to olefins using boron trifluoride-etherate, quantitative measurements were made in order to obtain the data on the equilibrium constant and the reaction rate. The reaction between chloroacetic and cyclohexene, using benzene as a solvent media, was chosen.

For the determination of the equilibrium constant, two techniques were used: isolation of the equilibrium amount
of cyclohexyl chloroacetate, and quantitative bromination of an aliquot sample of the reaction mixture to determine the amount of cyclohexene present at equilibrium.

The equilibrium constant for the catalytic esterification of organic acids with olefins may be expressed as follows:

\[ K_{eq} = \frac{\text{conc. of ester}}{\text{conc. of acid} \times \text{conc. of olefin}} \]

for the reaction

\[ \text{Acid + Olefin } \xrightarrow{k_1} \xleftarrow{k_2} \text{ Ester} \]

A summary of the data on the equilibrium constants is tabulated in the experimental section.

Since a constant temperature bath was not immediately available, the initial runs (1-6) were thermostatted very crudely at 85°c by means of a Glascol heating mantle. In all these runs, the equilibrium constant was calculated from the isolation of the ester after equilibrium had been attained. A correction was calculated from the average percent loss found in the isolation of known amounts of ester, and added to the values obtained. The value for the equilibrium constant varies from 21.2 to 5.6, depending on the ratio of chloroacetic acid to cyclohexene. For the runs using equivalent concentrations of olefin and acid, the values 21.2 and 19.1 were obtained. For the runs where a 2:1 excess of acid to olefin was used, the values obtained for the equilibrium constant were 10.6 and 12.9.
In runs #7 and #8 the equilibrium concentration of olefin of an aliquot portion, as well as the determination of the equilibrium concentration of ester from the remaining solution was used to calculate the equilibrium constant. The values obtained check fairly well. In run #7 where the initial concentration of olefin and acid was zero, the equilibrium constant is quite high. In run #8 where 0.820 moles of ester and 0.410 moles of acid were present initially, the equilibrium constant obtained is approximately the same as that previously obtained using a 2:1 excess of olefin to acid.

Runs #9 and #10 involve the use of a sealed tube technique, wherein aliquot portions of a known starting mixture were put into small constricted tubes and sealed off. Here the ratio of olefin to acid was almost unity, and the equilibrium constant obtained was very high.

In all the succeeding runs (11-#17), the reaction temperature was maintained at 50°C±0.2 in a bath. In runs #11 and #12 a comparison of sealed tube technique versus the pipetting of samples at intervals was made. The values of the equilibrium constant check well, but are again high.

The high values obtained with a low ratio of acid to olefin can be explained by the fact that, under these conditions, the polymerization side-reaction is appreciable and causes a large error in the determination of the equilibrium concentration of olefin.
In runs #13 and #14, where the acid to olefin ratio was maintained at 2.5:1 and only the catalyst concentration changed, consistent results were obtained. The values 11.7 and 11.3 obtained for the equilibrium constant are in good agreement.

However in runs #15, #16, and #17, lowering the acid to olefin ratio led to a big increase, and raising the ratio led to a big decrease in the value of the equilibrium constant. The low values obtained in runs where a large excess of olefin acid to olefin was used can be explained in part, by the fact that the equilibrium concentration of olefin was very low. The accuracy of the method is poorer at low concentrations of olefin. In all fairness, the results are far from consistent with a true equilibrium process.

In Figure III, the per cent yield of cyclohexyl chloroacetate is plotted against the reaction time for runs #13, #14, and #15.

The reversible catalytic esterification of chloroacetic acid with cyclohexene is given below. Assuming a true catalyst action, the forward reaction is pseudo second order; and the reverse reaction is pseudo first order. The rate of formation of the ester may then be expressed as

\[
\frac{dx}{dt} = k_1(a-x)(b-x) - k_2(x)
\]

where \(x\) is the amount of ester formed at time \(t\), \(a\) is the
Figure III

A - Run #14
- Cyclohexene 0.200 m/liter
- Chloroacetic Acid 0.502 m/liter
- Catalyst 0.320 m/liter

B - Run #15
- Cyclohexene 0.200 m/liter
- Chloroacetic Acid 0.320 m/liter
- Catalyst 0.358 m/liter

C - Run #13
- Cyclohexene 0.160 m/liter
- Chloroacetic Acid 0.502 m/liter
- Catalyst 0.160 m/liter

% Yield of Ester vs. Time in Minutes
initial concentration of olefin, b is the initial concentration of acid, \( k_1 \) is the reaction rate for the forward reaction, and \( k_2 \) is the reaction rate for the reverse reaction.

Equating the forward and reverse rates at equilibrium, and substituting the value of \( k_2 \) in terms of \( k_1 \), the expression becomes

\[
\frac{dx}{dt} = k_1(a-x)(b-x) - k_1 \frac{(a-x_e)(b-x_e)(x)}{x_e}
\]

where \( x_e \) is the amount of ester formed at equilibrium. This expression when integrated gives

\[
k_1 t - \text{constant} = \frac{x_e}{ab-x_e^2} \ln \frac{x \cdot x_e - ab}{x \cdot x_e - x_e^2}
\]

A plot of \( \log \frac{x \cdot x_e - ab}{x \cdot x_e - x_e^2} \) against \( t \) should then give a straight line.

The data obtained in runs \#13, \#14, and \#15 was introduced into this expression and the \( \log \frac{x \cdot x_e - ab}{x \cdot x_e - x_e^2} \) values calculated. Figure IV gives the plot of the above log expression against time. From the best straight line through the plotted points a value of \( k_1 \) was calculated for each run.

The value of \( k_1 \) calculated from Figure IV for runs \#13, \#14, and \#15 is 31.1, 14.7, and 27.0 liters/mole·hour respectively.

When the product of the catalyst concentration and \( k_1 \) is calculated for runs \#13 and \#14 which differed only in catalyst concentration the values of 5.0 and 4.7 are obtained. Thus the product of the rate times the catalyst concen-
tration is roughly a constant. The value obtained for run \#15, where a high value of the equilibrium constant was obtained, is 8.6 however.

Other runs were not calculated and plotted due to the poor data obtained on the constancy of the equilibrium constant with varying proportions of reactants.

In general, the results are not too inconsistent with the view that the reaction is a pseudo second order forward reaction in competition with a pseudo first order reversal.

With reference to the two possible mechanisms discussed previously, the results of this investigation have by no means distinguished between them. However, the mechanism involving formation of the acid-boron trifluoride complex is preferred, for it alone implies the effect of the acid strength in the reaction.
EXPERIMENTAL
REAGENTS AND SOLUTIONS

ACETIC ACID -- Baker's C.P. glacial acetic acid was distilled with acetic anhydride to remove any water.

BENZOIC ACID -- The C.P. acid was dried in a vacuum desiccator over calcium chloride.

OXALIC ACID -- C.P. oxalic acid containing two moles of hydrated water per mole of oxalic acid was put in a desiccator over concentrated sulfuric acid and heated in an oven at 60° C. for eight hours according to the method recommended by Koltzoff and Sandell (51). The resulting anhydrous acid was then kept in a desiccator under vacuum until used.

CHLORACETIC ACID -- The commercial acid was dried in a vacuum desiccator over calcium chloride.

TRICHLOROACETIC ACID -- The Eastman Kodak product was cooled and only the crystalline material was used. The solid acid was dried in a vacuum desiccator over calcium chloride.

CYCLOHEXENE -- Initially, cyclohexene was prepared by dehydrating cyclohexanol according to the method of Coleman and Johnstone (52). The product after distillation was dried over sodium. The product boiled at 82°-83°, d^2₀₄ = 0.810, n^D₂₀ = 1.456.

Since so much time was spent in preparing cyclohexene as needed, it finally was decided to obtain this material from Eastman Kodak Company. The commercial material was
found to need no further purification other than drying over sodium for ordinary runs.

For use in the study of the kinetics of the reaction, the Eastman Kodak product was distilled at a reflux ratio of 15:1 in a 6' column with solenoid-operated take off. The refractive index of the Eastman Kodak product as taken on the Pulfrich refractometer was 1.4471 at 20° as against Egloff's (53) quoted value of 1.4465 at 20° was found.

After distillation, the value of 1.4467 at 20° was obtained on the main sample (95%) which is within two ten thousands of the quoted value. The cyclohexene (B.P. 82.7°-83.3° @ 759mm) was dried over sodium.

**BORON TRIFLUORIDE - ETHERATE: CATALYST** -- This material was obtained from the General Chemical Company in pound bottles. The material was brownish colored, and darkened on standing. Distillation under reduced pressure gave a colorless material. Both the colored commercial product and the distilled product gave identical results in check runs however. (B.P. 125°-126° @ 760 mm, Density 1.15)

Since the commercial product was satisfactory for our purposes, it was used directly in most runs.

**α-PINENE** -- The technical grade material was distilled. The α-pinene collected had the following physical constants: B.P. 154°-155° @ 760mm, d²₀⁴ - 0.887, n²₀⁴ - 1.4661.

**2-PENTENE** -- This material was prepared according to the method of Norris (54). The product was distilled through a twenty-five inch column packed with 3/16" glass helices.
The fraction boiling at 36°-37° was collected. \( d_{20}^{20} = 0.650, n_{D}^{20} = 1.3832 \).

**STYRENE** -- Styrene was prepared by the method of Abbott and Johnson (55). The decarboxylation of cinnamic acid proceeded smoothly. The styrene was collected over 0.5 gms. of hydroquinone. Final distillation gave a 49.7% yield of product B.P. 45°-46° @ 40mm.

**ALLYL BROMIDE** -- Allyl bromide was prepared from allyl alcohol according to the method of Kamm and Marvel (56). A 90% yield of allyl bromide boiling at 70°-71° @ 757mm was obtained.

**METHYL CROTONATE** -- Eastman Kodak's crotonic acid was esterified by refluxing with methyl alcohol and sulfuric acid. A 70% yield of methyl crotonate (B.P. 120°-121° @ 759mm) was obtained.

**METHYL ACRYLATE** -- This material was obtained from the Eastman Kodak Co. and used without further purification.

**VINYL ETHERS** -- The vinyl ethers used were research samples donated by Carbide and Carbon Chemicals Inc.

**1-METHYL CYCLOHEXENE-1** -- Dehydration of the available 0-methyl cyclohexanol was used in order to prepare this material, although as expected a mixture of 1-methyl cyclohexene and 3-methyl cyclohexene results which is difficult to separate.

Into a one liter 2-necked flask fitted with a dropping funnel, thermometer, and fractionating tube leading to a condenser, 100 gms. of 85% phosphoric acid were introduced.
The flask was heated in an oil bath kept at 170°, and the methyl cyclohexanol was added dropwise to the hot acid. The temperature top of the fractionating tube rose to 85°, and the olefin began to distill off. 500 gms. of the alcohol (5.05 moles) were added over a period of six hours. The bath temperature was maintained below 185°, and the distillation temperature was kept below 90°.

The material was collected in an ice-cooled receiver, and the water layer was removed. The product was dried with anhydrous magnesium sulfate and distilled using a Vigreux column (8'). The material boiling at 106°-109° was the major fraction. One to two cc. of material came over at 101°-105° and the last few cc. at 109°-111°. The density of the combined material was 0.803 at 20°. The yield of olefin was 78.1%.

In order to separate the 1-methyl cyclohexene-1 from any 3-methyl cyclohexene-1, a 24" column packed with 1/4" glass helices was used. 1-methyl cyclohexene-1 has the following physical constants: B.P. 109.5° @ 760mm., d_4^20 = 0.812, n_20^D = 1.4505. 3-methyl cyclohexene-1 has the following physical constants: B.P. 104.4° @ 760mm, d_4^20 = 0.802, n_20^D = 1.4424. Thus only a five degree difference in boiling points exists. Egloff reported the above constants (62).

After three passes of the crude mixture through the column in the usual manner. The following results were obtained: Cut #1 -- 98°-103.5°, 19 gms., d_4^25 = 0.795; Cut #2 104°-106°, 62 gms., d_4^25 = 0.798, n_32^D = 1.4382; Cut #3 --
106°-109°, 48 gms., d^{25}_4 - 0.803, n^{32}_D - 1.4423; Cut #4 -- 109°-110°, 151 gms., d^{25}_4 - 0.804, n^{32}_D - 1.4438; Cut #5 -- above 110°, 39 gms. d^{25}_4 - 0.845. The total weight of product was 319 gms. Cut #2 would appear to be predominantly 3-methyl cyclohexene-1; whereas Cut #4 is apparently 1-methyl cyclohexene-1 for the most part. Cut #3 appears to be a mixture of both isomers and from the density and index of refraction comparison there is more 1-methyl cyclohexene-1 than 3-methyl cyclohexene-1 present.

Of the total weight of product 47.4% appeared to be the 1-methyl product and 19.4% the 3-methyl compound.

**BENZENE** -- In order to remove all water from the J.P. benzene, the benzene was distilled. Only the middle cut was taken (80%). This fraction boiled at 80.0°-80.2°. This material was also dried over sodium.

**SOLUTIONS OF CYCLOHEXENE AND CHLOROACETIC ACID IN BENZENE:** A 2.000 M solution of cyclohexene and a 1.004 M solution of chloroacetic acid in benzene were prepared.
GENERAL METHOD FOR REACTION OF CARBOXYLIC ACIDS WITH OLEFINS

The appropriate acid was mixed with the olefin in a 500 cc. round bottom flask fitted with a reflux condenser to which was attached a calcium chloride tube. (If the acid did not dissolve at room temperature, the mixture was warmed on a steam bath until solution was accomplished.) The catalyst, boron trifluoride etherate, was then added slowly to the solution, cooling if heating was necessary to 30°-40° C. The mixture was then heated with reflux on a steam bath, usually for six hours.

At the end of this time, the dark solution was cooled in ice water and treated with cold water, cold 10% sodium bicarbonate, or 5% potassium hydroxide solution to remove any unreacted acid. (The solubility of the acid in water and the ease of hydrolysis of the ester determined the method of removal of unreacted acid.)

The ester-unsaturate layer was then separated from the aqueous layer. The organic solution was then washed with water and dried over calcium chloride or magnesium sulfate.

The dry material was then distilled under atmospheric conditions to remove any unreacted olefin. No particular emphasis was placed on recovery of the unreacted olefin, however. The residue was then distilled under vacuum (2-10mm) using a modified Claisen flask.

The ester was then redistilled under vacuum. In each reaction, a certain small amount of residue remained - dark
viscous material giving a positive test with bromine in carbon tetrachloride and with 2% potassium permanganate.

Both the olefin and ester were dried and weighed.
## Properties of Esters

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ester</th>
<th>Boiling point</th>
<th>$d_1$</th>
<th>$n_D$</th>
<th>Saponif. Equiv.</th>
<th>Calc'd.</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cyclohexyl acetate</td>
<td>$40^\circ-51^\circ@2\text{mm}$ $17^\circ-175^\circ@760\text{mm}$</td>
<td>0.971 @ 21$^\circ$</td>
<td>1.4416 @ 20$^\circ$</td>
<td>14.2 2</td>
<td>141</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Cyclohexyl acetate</td>
<td>$65^\circ-67^\circ@9\text{mm}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Cyclohexyl acetate</td>
<td>$54^\circ-56^\circ@4\text{mm}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Cyclohexyl acetate</td>
<td>$54^\circ-56^\circ@4\text{mm}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Cyclohexyl acetate</td>
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<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>Cyclohexyl acetate</td>
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<td></td>
<td></td>
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<tr>
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<td>14</td>
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<td></td>
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<td>15</td>
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<td>$64^\circ-66^\circ@7-8\text{mm}$</td>
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<td></td>
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<tr>
<td>16</td>
<td>Cyclohexyl acetate</td>
<td>$66^\circ-70^\circ@8-10\text{mm}$</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Cyclohexyl acetate</td>
<td>$55^\circ-56^\circ@5\text{mm}$</td>
<td>0.974 @ 20$^\circ$</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td>18</td>
<td>Cyclohexyl acetate</td>
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<td></td>
<td></td>
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<tr>
<td>19</td>
<td>Cyclohexyl acetate</td>
<td>$52^\circ-54^\circ@3-4\text{mm}$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
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</tr>
</tbody>
</table>
**PROPERTIES OF ESTERS (Continued)**

| Run No. | Ester               | Boiling point   | $d_4$   | $n_D$   | Saponif. Equiv.  
<table>
<thead>
<tr>
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<th></th>
</tr>
</thead>
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<td>29.</td>
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<td>--------</td>
<td>--------</td>
<td>142.2</td>
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<tr>
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<td>Cyclohexyl acetate</td>
<td>45°-47° @ 1mm</td>
<td>--------</td>
<td>--------</td>
<td>141</td>
</tr>
<tr>
<td>31.</td>
<td>Cyclohexyl acetate</td>
<td>50°-53° @ 2-3mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>51.</td>
<td>Cyclohexyl acetate</td>
<td>56°-58° @ 6mm</td>
<td>0.970 @ 20°</td>
<td>1.4417 @ 20°</td>
<td>140.5</td>
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<tr>
<td>52.</td>
<td>Cyclohexyl acetate</td>
<td>53°-55° @ 4mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>53.</td>
<td>Cyclohexyl acetate</td>
<td>52°-54° @ 3-4mm</td>
<td>--------</td>
<td>--------</td>
<td>140.5</td>
</tr>
<tr>
<td>54.</td>
<td>Cyclohexyl acetate</td>
<td>52°-54° @ 3-4mm</td>
<td>--------</td>
<td>--------</td>
<td>140.5</td>
</tr>
<tr>
<td>55.</td>
<td>Cyclohexyl acetate</td>
<td>53°-55° @ 4mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>56.</td>
<td>Cyclohexyl acetate</td>
<td>53°-55° @ 4mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>57.</td>
<td>Cyclohexyl acetate</td>
<td>50°-53° @ 2-3mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>58.</td>
<td>Cyclohexyl acetate</td>
<td>55°-57° @ 4-5mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>59.</td>
<td>Cyclohexyl acetate</td>
<td>53°-55° @ 3-4mm</td>
<td>0.975 @ 25°</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>60.</td>
<td>Cyclohexyl acetate</td>
<td>57°-59° @ 6mm</td>
<td>0.974 @ 20°</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>75.</td>
<td>Cyclohexyl acetate</td>
<td>55°-57° @ 4-5mm</td>
<td>--------</td>
<td>--------</td>
<td>142.2</td>
</tr>
<tr>
<td>Ester</td>
<td>Boiling point</td>
<td>d_40</td>
<td>n_D</td>
<td>Sapon.</td>
<td>E.D.</td>
</tr>
<tr>
<td>-------</td>
<td>--------------</td>
<td>------</td>
<td>-----</td>
<td>--------</td>
<td>------</td>
</tr>
<tr>
<td>2. Cyclohexyl benzoate</td>
<td>134°-137° @ 5-6mm</td>
<td>1.055 @ 200</td>
<td>1.054 @ 200</td>
<td>202</td>
<td>1.521 @ 200</td>
</tr>
<tr>
<td>27. Cyclohexyl benzoate</td>
<td>128°-132° @ 3-4mm</td>
<td>2.204 @ 200</td>
<td>1.057 @ 200</td>
<td>202</td>
<td>1.525 @ 200</td>
</tr>
<tr>
<td>32. Cyclohexyl benzoate</td>
<td>126°-128° @ 2mm</td>
<td>2.304 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>33. Cyclohexyl benzoate</td>
<td>127°-130° @ 2-3mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>61. Cyclohexyl benzoate</td>
<td>126°-126° @ 2mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>62. Cyclohexyl benzoate</td>
<td>124°-126° @ 2mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>63. Cyclohexyl benzoate</td>
<td>120°-127° @ 3mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>64. Cyclohexyl benzoate</td>
<td>120°-128° @ 3mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>65. Cyclohexyl benzoate</td>
<td>126°-130° @ 5-6mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>66. Cyclohexyl benzoate</td>
<td>120°-130° @ 5-6mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>67. Ethyl benzoate</td>
<td>760°-78° @ 3mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>68. Ethyl benzoate</td>
<td>123°-129° @ 2mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>70. Cyclohexyl benzoate</td>
<td>123°-125° @ 2mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
<tr>
<td>71. Cyclohexyl benzoate</td>
<td>130°-132° @ 4mm</td>
<td>2.307 @ 200</td>
<td>1.045 @ 200</td>
<td>202</td>
<td>1.517 @ 200</td>
</tr>
</tbody>
</table>
### Properties of Esters (Continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ester</th>
<th>Boiling point</th>
<th>d&lt;sub&gt;4&lt;/sub&gt; @ 25°</th>
<th>n&lt;sub&gt;D&lt;/sub&gt;</th>
<th>Saponif. Equiv. Calc'd</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td>72.</td>
<td>Cyclohexyl benzoate</td>
<td>129°-131° @ 5mm</td>
<td>1.048</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>73.</td>
<td>Cyclohexyl benzoate</td>
<td>130°-132° @ 5mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>74.</td>
<td>Cyclohexyl benzoate</td>
<td>127°-129° @ 14mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>3.</td>
<td>Cyclohexyl oxalate&lt;sup&gt;e&lt;/sup&gt;</td>
<td>145°-148° @ 3mm (M.P. 42°-43°)</td>
<td>------</td>
<td>------</td>
<td>127.7</td>
<td>127</td>
</tr>
<tr>
<td>4.</td>
<td>Cyclohexyl oxalate</td>
<td>145°-146° @ 2mm (M.P. 41.5°-42°)</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>21.</td>
<td>Cyclohexyl oxalate</td>
<td>145°-148° @ 3mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>28.</td>
<td>Cyclohexyl oxalate</td>
<td>143°-146° @ 2-3mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>35.</td>
<td>Cyclohexyl oxalate</td>
<td>146°-148° @ 3mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>36.</td>
<td>Cyclohexyl oxalate</td>
<td>140°-143° @ 1-2mm</td>
<td>------</td>
<td>------</td>
<td>127.7</td>
<td>129</td>
</tr>
<tr>
<td>37.</td>
<td>Cyclohexyl oxalate</td>
<td>140°-142° @ 1-2mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>6.</td>
<td>Cyclohexyl Trichloroacetate&lt;sup&gt;f&lt;/sup&gt;</td>
<td>97.5°-98.5° @ 3mm</td>
<td>1.2509 @ 20° 1.4804 @ 20°</td>
<td>245.5</td>
<td>243</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>105°-106° @ 6mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>111°-112° @ 9mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td></td>
<td>119°-120° @ 12-13mm</td>
<td>------</td>
<td>------</td>
<td>----</td>
<td>---</td>
</tr>
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</table>
### PROPERTIES OF ESTERS (Continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ester</th>
<th>Boiling point</th>
<th>( d_4 ) @ 20(^\circ)</th>
<th>( n_D ) @ 20(^\circ)</th>
<th>Saponif. Equiv. Calc'd.</th>
<th>Founda</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.</td>
<td>Cyclohexyl trichloroacetate</td>
<td>97.5(^\circ)-98.5(^\circ) @ 3mm</td>
<td>1.2510</td>
<td>1.4805</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>25.</td>
<td>Cyclohexyl trichloroacetate</td>
<td>97(^\circ)-99(^\circ) @ 3mm</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>27.</td>
<td>Cyclohexyl trichloroacetate</td>
<td>100(^\circ)-103(^\circ) @ 4-5mm</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>5.</td>
<td>Cyclohexyl chloroacetate</td>
<td>72(^\circ)-75(^\circ) @ 1-2mm</td>
<td>1.100</td>
<td>1.4705</td>
<td>88.3</td>
<td>87</td>
</tr>
<tr>
<td>23.</td>
<td>Cyclohexyl chloroacetate</td>
<td>84(^\circ)-86(^\circ) @ 5mm</td>
<td>1.083</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>24.</td>
<td>Cyclohexyl chloroacetate</td>
<td>80(^\circ)-82(^\circ) @ 3-4mm</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>29.</td>
<td>Cyclohexyl chloroacetate</td>
<td>74(^\circ)-76(^\circ) @ 2-3mm</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>30.</td>
<td>Cyclohexyl chloroacetate</td>
<td>76(^\circ)-78(^\circ) @ 2-3mm</td>
<td>---</td>
<td>---</td>
<td>88.3</td>
<td>89</td>
</tr>
<tr>
<td>31.</td>
<td>Cyclohexyl chloroacetate</td>
<td>77(^\circ)-81(^\circ) @ 2-4mm</td>
<td>---</td>
<td>---</td>
<td>----</td>
<td>---</td>
</tr>
<tr>
<td>Run No.</td>
<td>Ester</td>
<td>Boiling point</td>
<td>$d_1^+$</td>
<td>$n_D$</td>
<td>Saponif. Equiv. Calcd. Founda</td>
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<td>-----------</td>
<td>--------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>Cyclohexyl chloroacetate</td>
<td>83°-88° @ 5-6mm</td>
<td>---------</td>
<td>-------</td>
<td>----------------------------</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>Cyclohexyl chloroacetate</td>
<td>80°-83° @ 3mm</td>
<td>---------</td>
<td>-------</td>
<td>88.3 86</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>Cyclohexyl chloroacetate</td>
<td>79°-83° @ 3-4mm</td>
<td>---------</td>
<td>-------</td>
<td>88.3 87</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>Cyclohexyl chloroacetate</td>
<td>82°-85° @ 4-5mm</td>
<td>---------</td>
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<tr>
<td>37</td>
<td>Cyclohexyl chloroacetate</td>
<td>79°-82° @ 3-4mm</td>
<td>---------</td>
<td>-------</td>
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<tr>
<td>38</td>
<td>Cyclohexyl chloroacetate</td>
<td>77°-83° @ 3-4mm</td>
<td>---------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Bornyl acetate</td>
<td>76°-78° @ 4mm</td>
<td>0.9845 @ 20° 1.4633 @ 20°</td>
<td>88.3 86</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>Bornyl acetate</td>
<td>74°-77° @ 3-4mm</td>
<td>---------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>Bornyl acetate</td>
<td>75°-77° @ 3mm</td>
<td>---------</td>
<td>-------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Run No.</td>
<td>Ester</td>
<td>Boiling point</td>
<td>d_4</td>
<td>n_D</td>
<td>Saponif. Equiv.</td>
<td></td>
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<tr>
<td>--------</td>
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<td>--------------</td>
<td>--------------</td>
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<td></td>
<td></td>
<td></td>
<td>Cac'd. Found</td>
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</tr>
<tr>
<td>42.</td>
<td>Bornyl acetate</td>
<td>75⁰-78⁰ @ 3mm</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>43.</td>
<td>Bornyl acetate</td>
<td>72⁰-74⁰ @ 2mm</td>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>45.</td>
<td>Diethyl carbinol acetate</td>
<td>132⁰-134⁰ @ 759mm</td>
<td>0.8912 @ 15⁰</td>
<td>1.408 @ 15⁰</td>
<td>130.2</td>
<td>129</td>
</tr>
<tr>
<td>46.</td>
<td>Diethyl carbinol acetate</td>
<td>131.5⁰-133.5⁰ @ 758mm</td>
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<td></td>
<td></td>
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</tr>
<tr>
<td>47.</td>
<td>Diethyl carbinol acetate</td>
<td>132⁰-134⁰ @ 761mm</td>
<td></td>
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<tr>
<td>48.</td>
<td>Diethyl carbinol acetate</td>
<td>132⁰-133⁰ @ 760mm</td>
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<tr>
<td>49.</td>
<td>Diethyl carbinol acetate</td>
<td>131.5⁰-133⁰ @ 756mm</td>
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<tr>
<td>50.</td>
<td>Diethyl carbinol acetate</td>
<td>132⁰-134⁰ @ 762mm</td>
<td></td>
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<tr>
<td>81.</td>
<td>p-bromo isopropyl acetate</td>
<td>48⁰-49⁰ @ 4mm</td>
<td>1.411 @ 20⁰</td>
<td>1.450 @ 20⁰</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
## PROPERTIES OF ESTERS (Continued)

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ester</th>
<th>Boiling point</th>
<th>(d_4)</th>
<th>(n_D)</th>
<th>Saponif. Equiv. Calc'd. Founda</th>
</tr>
</thead>
<tbody>
<tr>
<td>95.</td>
<td>1-methyl cyclohexyl acetate</td>
<td>52°-53° @ 3mm</td>
<td>0.945 @ 25°</td>
<td>1.4367 @ 30°</td>
<td>156.2 155</td>
</tr>
<tr>
<td>96.</td>
<td>1-methyl cyclohexyl acetate</td>
<td>53°-55° @ 3-4mm</td>
<td>0.947 @ 25°</td>
<td>1.4366 @ 30°</td>
<td>---- ---</td>
</tr>
<tr>
<td>97.</td>
<td>3-methyl cyclohexyl acetate (?)</td>
<td>58.5°-59.5° @ 3mm</td>
<td>0.941 @ 25°</td>
<td>1.4360 @ 30°</td>
<td>156.2 154</td>
</tr>
</tbody>
</table>

a. All esters were saponified using NaOH in 90% methyl alcohol. b. Zavgorodnii, (see bibliography #36) gives B.P. 173°-175°, \(d_{15}^0\) - 0.9760, \(n_{11.5}^0\) - 1.4428.

c. Zaki, J. Chem. Soc., 1932, 1184. gives B.P. 160° @ 18mm, no density or refractive index is given.
d. Hodgman, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Company, Cleveland, Ohio, 24th Ed., (1940) p. 664, gives the following: B.P. 212.6°, \(d_{15}^0\) - 1.0509, \(n_{17.3}^0\) - 1.5068.
e. Wistatter and Hatt, Ber., 45, 1464 (1912) gives M.P. 142; Schmidt, Eichler, and Seydel, U.S. Patent 1,600,700, (1926), gives M.P. 47°, B.P. 171°-172° @ 11mm.
f. Zavgorodnii, (see bibliography #36), gives B.P. 105°-107° @ 3mm, \(d_{15}^0\) - 1.2864, \(n_{15}^0\) - 1.4840.
g. Peet, U.S. Patent 1,816,441, (1932), is the only reference to the compound and no data is given.
i. Hodgman, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Company, Cleveland, Ohio, 28 Ed., p. 662, (1944), gives B.P. 114° @ 22mm, \(d_{14}^0\) - 0.985, \(n_{20}^0\) - 1.4630.
j. Zavgorodnii, (see bibliography #35) gives B.P. 137°-138.8° @ 758mm, \(d_{12}^0\) - 0.8919, \(n_{16}^0\) - 1.410.
l. The ester could not be found in the literature.
m. The ester could not be found in the literature.
## Ester Derivatives Prepared

<table>
<thead>
<tr>
<th>Run No.</th>
<th>Ester</th>
<th>Acid Fragment</th>
<th>Alcohol Fragment</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.</td>
<td>Cyclohexyl benzoate</td>
<td>(Took M.P. of acid) M.P. Found-M.P. Lit\textsuperscript{a} 120°-122° 121°</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{b} 111°-112° 112°</td>
</tr>
<tr>
<td>3.</td>
<td>Dicyclohexyl oxalate</td>
<td>(Took M.P. of acid) M.P. Found-M.P. Lit\textsuperscript{a} 100°-101° 100°</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{b} 110°-112° 112°</td>
</tr>
<tr>
<td>5.</td>
<td>Cyclohexyl chloroacetate</td>
<td>Amide M.P. Found-M.P. Lit\textsuperscript{a} 118°-120° 120°</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{b} 111°-112° 112°</td>
</tr>
<tr>
<td>6.</td>
<td>Cyclohexyl trichloroacetate</td>
<td>p-nitrobenzyl ester M.P. Found-M.P. Lit\textsuperscript{a} 78°-80° 80°</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{b} 111°-112° 112°</td>
</tr>
<tr>
<td>68.</td>
<td>Ethyl benzoate</td>
<td>N-benzylamide M.P. Found-M.P. Lit\textsuperscript{a} 104°-106° 105°-105.5°</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{a} 92°-93° 93°</td>
</tr>
<tr>
<td>39.</td>
<td>Bornyl acetate</td>
<td>--------</td>
<td>Phenyl urethane M.P. Found-M.P. Lit\textsuperscript{b} 136°-138° 138° (Mixed M.P. with phenyl urethane of an authentic borneol sample gave 137.5° to 139°)</td>
</tr>
<tr>
<td>45.</td>
<td>Diethylcarbinol acetate</td>
<td>--------</td>
<td>3,5 Dinitrobenzoate M.P. Found-M.P. Lit\textsuperscript{a} 96°-98° 97°</td>
</tr>
<tr>
<td>81.</td>
<td>p-bromo isopropyl acetate</td>
<td>Trimethyl Amine Derivative M.P. Found 147°-149°</td>
<td>M.P. Lit\textsuperscript{a} 148°-149°</td>
</tr>
<tr>
<td>95.</td>
<td>1-methyl cyclohexyl acetate</td>
<td>--------</td>
<td>Phenyl urethane M.P. Found-M.P. Lit\textsuperscript{k} 104°-106° 105°</td>
</tr>
</tbody>
</table>

(See next page for footnotes.)
Footnotes for ESTER DERIVATIVES PREPARED

IDENTIFICATION OF THE HIGH BOILING UNSATURATE FORMED IN ALL RUNS WHERE THE CATALYST WAS ADDED NEAR REFLUX TEMPERATURE TO THE CYCLOHEXENE - ACID MIXTURE

The combined material from all runs was redistilled and the following physical constants were obtained: B.P. 92°-94° @ 7mm, d²⁰₄ = 0.918.

The material decolorized bromine in carbon tetrachloride with the evolution of hydrobromic acid. It dissolved in cold concentrated sulfuric acid, but reacted very slowly with 2% permanganate in acetone. On refluxing with 50% potassium hydroxide for seven hours, the material was recovered and redistilled. (B.P. 98°-99° @ 8mm, d²⁰₄ = 0.911, n²⁰₅ = 1.4926) Truffaut (57) gives the following physical constants for 1-cyclohexyl cyclohexene: B.P. 103°-105° @ 12mm, d²⁰₄ = 0.904, n²⁰₅ = 1.493.

The attempt to make the tribromo-derivative, reported by Truffaut to melt at 127°, led to a compound melting at 102°-104°. Wallach (58) gives 68°-69° for the melting point of the 1,1'-dibromo-derivative. The material, when shaken reacted with amyl nitrite and concentrated hydrochloric acid, gave a nitroso-derivative melting at 138°-140°. Truffaut gave 140° as the melting point of the nitroso-derivative of 1-cyclohexyl cyclohexene.
THE REACTION OF OLEIC ACID WITH ACETIC ACID:

A mixture of 113.0 gms. (0.40 moles) of oleic acid, 24.0 gms. (0.40 moles) of glacial acetic acid, and 5 cc. (0.04 moles) of boron trifluoride-etherate was refluxed for six hours. The unreacted acetic acid was removed by several washings with water. The residual material was then dried and distilled.

As the material was distilled under vacuum, a noticeable quantity of white vapor came before the boiling point was reached. 56.5 gms. of product, boiling at 200°-203° @ 5-6 mm., were obtained. The residue, boiling above 300° @ 5-6 mm., weighed 43.4 gms.

The product, boiling at 200°-203° @ 5-6 mm., did not react with 2% potassium permanganate in acetone. The neutral equivalent, as obtained using a standard solution of sodium hydroxide in 90% methyl alcohol, was 332. The theoretical value for 9 or 10-acetoxystearic acid is 342.5.

A sample of the product was refluxed for two hours with a large excess of sodium hydroxide in 90% methyl alcohol. Most of the methyl alcohol was then distilled off.

An oily liquid was obtained on acidification of the residue with phosphoric acid. This material was separated, heated on a steam bath to remove any residual methyl alcohol, and dried in a vacuum dessicator over phosphorus pentoxide.

Rough cooling curves were run on the original U.S.P. grade oleic acid used in the reaction, the product obtained
boiling at \(200^\circ\text{C}-203^\circ\text{C}\) @ 5-6mm, and the hydrolysis product. The flat portion of the plot of temperature versus time occurred at \(65^\circ\text{C}-70^\circ\text{C}\) for the oleic acid, \(18.5^\circ\text{C}-19.0^\circ\text{C}\) for the reaction product, and \(28^\circ\text{C}-30^\circ\text{C}\) for the hydrolyzed reaction product.

The neutral equivalent run as before gave a value of 307 for the hydrolyzed material. The theoretical value of the neutral equivalent of 9 or 10-hydroxy oleic acid is 300.6.

A determination of the per cent of hydroxy groups in the hydrolyzed material by the method of Ogg, Porter and Willets (59) using acetic anhydride in pyridine as the acetylating reagent led to a value of 4.88%. The theoretical per cent of hydroxy groups in 9 or 10-hydroxystearic acid is 5.69%.

The densities of the various materials at \(20^\circ\text{C}\) were as follows: oleic acid - 0.849, the reaction product - 0.889, and the hydrolyzed reaction product - 0.920.
REACTIONS WITH 3,4 HEXENOIC ACID

PREPARATION OF "HYDROSORBIC ACID" OR 3,4 HEXENOIC ACID:

According to Sudborough and Thomas (46), this acid can be prepared by treating a sodium hydroxide solution of sorbic acid with sodium amalgam. Therefore following their method, 30.0 gms. of sorbic acid were treated with 425 gms. of 3½ sodium amalgam. The reaction was carried out in a separatory funnel which was maintained at 25°-35°. The reduction product was converted to the acid (after removal of the mercury) by acidifying with dilute hydrochloric acid. The acid was extracted with ether, and the ether evaporated. Distillation gave 16.8 gms. of material B.P. 90°-91° @ 5mm, d²⁰₄ - 0.968. Sudborough and Thomas gave 103° @ 9-10 mm as the boiling point of their so-called "hydrosorbic acid" or 3,4 hexenoic acid. The yield in this reaction was 45½; whereas they obtained a 51½ yield.

REACTION OF "HYDROSORBIC ACID" WITH ACETIC ACID:

17.0 gms. (0.148 moles) of the "hydrosorbic acid", prepared by reduction with sodium amalgam, together with 8.9 gms. (0.148 moles) of acetic acid were heated on a steam bath for six hours. Two and one-half cc. of boron trifluoride-etherate (0.02 moles) were added to the mixture before heating. The mixture was added to 50 cc. of cold water. The material went into solution, so ether extraction of the material was necessary.
Distillation of the dried product gave 2.5 gms. of acidic material, boiling at 115°-125° under atmospheric conditions. (This cut undoubtedly was predominantly acetic acid.) Under vacuum 9.5 gms. of material, boiling at 80°-81° @ 5-6mm, was obtained.

The product (B.P. 80°-81° @ 5-6mm) did not decolorize bromine in carbon tetrachloride and was neutral to litmus. 5.0 gms. of this material was refluxed for three hours with 50 cc. of 1.8 normal sodium hydroxide in 90% methyl alcohol. The methyl alcohol was distilled off; the mixture was acidified; and the residue (3-4 cc.) was taken off, dried and distilled. 2.5 cc. of material was obtained which boiled at 78°-80° @ 5mm, d₂₀/₄ - 1.027. Approximately 1-2 cc. of water distilled over initially. The material was soluble in water, did not decolorize bromine in carbon tetrachloride, and did not react with 2% potassium permanganate solution. To litmus, the water solution was slightly acidic. The neutral equivalent obtained for this material was 2730.

The physical constants of the product from this reaction (B.P. 80°-81° @ 5-6mm, d₂₀/₄ - 1.024), together with the facts that it was not unsaturated and was a neutral compound, suggested the α-lactone of hexanoic acid. Linck (61) gives the following physical constants for the α-lactone: B.P. 86° @ 10mm, d₂₀/₄ - 1.0261, n₀°D - 1.4387. According to him, the α-hydroxyamide derivative has a melting point of 74°-75°. Therefore, 2 cc. of concentrated ammonium hydroxide, cooled to 0°, were added to a 2.0 gm. sample of
the supposed lactone at 0°. The mixture was left standing for one hour as Linstead directed. The solution which was not homogeneous was then put in an open dish and left in a vacuum dessicator for a day over concentrated sulfuric acid. The same reaction was tried again with the following variation. Instead of letting the mixture of supposed lactone and ammonium hydroxide stand for one hour, it was left overnight. A completely homogeneous solution resulted, which on being subjected to vacuum conditions over concentrated sulfuric acid, deposited 1.6 gms. of a white crystalline substance. The melting point observed was 66°-71°. Washing several times with ether, gave a product which melted at 73°-75°. Thus the product of the original reaction was the γ-lactone of hexanoic acid wherein the acid added internally instead of reacting with acetic acid.

**PREPARATION OF PURE 3,4 HEXENOIC ACID BY THE METHOD OF BOXER AND LINSTEAD:**

Boxer and Linstead's method (49) of treating malonic acid with n-butyraldehyde in the presence of triethanolamine to give an adduct which on decarboxylation gives 3,4 hexenoic acid was used to obtain the pure acid rather than a mixture of isomers.

In order to prepare malonic acid, 480.2 gms. (3.00 moles) of diethyl malonate were refluxed with 1350 cc. of aqueous 50% potassium hydroxide solution for five hours. The alcohol layer was distilled off and the residue was neutralized with hydrochloric acid. The potassium chloride which precipitat-
ed was filtered off. 1.50 moles of calcium chloride were added and the acid precipitated as the calcium salt. The calcium malonate was filtered off, dried and weighed (546 gms.). The amount of oxalic acid needed to remove the calcium as the very insoluble calcium oxalate was calculated. 2.55 moles of oxalic acid dihydrate was found to be sufficient.

The calcium malonate was suspended in 500 cc. of water warmed to 35° and the oxalic acid was added slowly with stirring. The insoluble calcium oxalate was filtered off, and the filtrate was concentrated by boiling to a volume of 50-60 cc. The material was then put in a vacuum dessicator over potassium hydroxide and evaporated to dryness under vacuum. 213 gms. of malonic acid was obtained. The yield was rather low, only 68.2%. The acid, when heated, decomposed at 133°-134° which is in agreement with the decomposition point quoted by Shriner and Fuson (60) of 133°.

The malonic acid (213.0 gms., 2.05 moles) was added slowly to the ice cooled triethanol amine (80.0 gms.) with stirring. The n-butyraldehyde (181.0 cc., 2.05 moles) was then added slowly, stirring constantly. The mixture was then allowed to stand for three hours at room temperature. For fifteen hours the mixture was heated to 100°. The carbon dioxide came off rapidly at first, but the reaction slowed down considerably after five or six hours. The mixture was made definitely acid with 50% sulfuric acid and steam distilled. Approximately three liters of distillate were col-
lected. The distillate was then made basic with sodium bicarbonate solution and extracted with ether (300 cc.). The distillate was then acidified and extracted with ether (200 cc.). The latter ether extract was dried and heated on a steam bath to remove the ether. Distillation under vacuum conditions gave 81.0 gms. of light yellow product (B.P. 82°-85° @ 5-6mm). A viscous residue remained (approx. 3 gms.). Redistillation of the product led to 77.2 gms. of product (B.P. 89.5°-90.5° @ 5mm, d²⁰₄ - 0.957, n²⁰₀ - 1.4405). According to Boxer and Linstead, 3,4 hexenoic acid has the following physical constants: B.P. 109° @ 15mm, d¹⁷₄ - 0.960, and n²⁰₀ - 1.4402. The yield was 32.6% as compared to 37.5% obtained by Boxer and Linstead.

**REACTION OF 3,4 HEXENOIC ACID WITH CHLOROACETIC ACID:**

A mixture, 17.0 gms. (0.15 moles) of the 3,4 hexenoic acid, together with 14.0 gms. (0.15 moles) of chloroacetic acid and 0.02 moles (2.5 cc.) of boron trifluoride-etherate, was heated on a steam bath for five hours. The reaction mixture was then poured into 100 cc. of cold water to eliminate the unreacted chloroacetic acid. Unlike the similar reaction involving acetic acid and "hydrosorobic acid", the reaction mixture did not all dissolve in the water. The insoluble layer was removed and dried. Distillation of the product gave 14.1 gms. of colorless liquid (B.P. 86°-88° @ 6mm, d²⁸₄ - 1.137).

This product was slightly acidic to litmus and contained chlorine. The calculated neutral equivalent was 248.
The theoretical neutral equivalent for chloroacetoxyhexanoic acid is 208.7.

Saponification of a 5 gm. sample of the product with excess sodium hydroxide in 90% methyl alcohol, followed by acidification and extraction with ether, led to a product (B.P. 77⁰-79⁰ @ 5mm, d²⁴⁴ - 1.023). No evidence of chloroacetic acid was found in the ether extract.

Since the hydrolysis product had physical constants suggesting the lactone, it was treated with cold, concentrated ammonia. Approximately one gram of derivative was obtained from a two gram sample. The hydroxyamide melted at 74⁰-76⁰, which shows that the γ-lactone was obtained on hydrolysis.

**REACTION OF CHLOROACETIC ACID WITH 3,4 HEXENOIC ACID:**

A 2:1 ratio of chloroacetic acid to 3,4 hexenoic acid was used in this reaction, so that external addition would be favored rather than internal addition or lactone formation. 20.0 gms. (0.174 moles) of the unsaturated acid, 32.8 gms. (0.348 moles) of chloroacetic acid, and 2.5 cc. (0.02 moles) of boron trifluoride-etherate were heated for four hours on a steam bath. The reaction mixture was distilled directly, instead of being treated with water as in the previous reaction.

Distillation led to 30.8 gms. of chloroacetic acid (B.P. 74⁰-76⁰ @ 5mm) and 17.0 gms. of product (B.P. 83⁰-84⁰ @ 5mm, d²⁶⁴ - 1.021.) The residue amounted to 2 cc. of dark, viscous liquid. The product is undoubtedly the γ-lactone, for the
boiling point and density check, and the compound is soluble in water.

**REACTION OF 3,4 HEXENOIC ACID WITH OXALIC ACID:**

This reaction was attempted in hopes of obtaining an addition product that was a solid, and thus could be characterized with more ease. 20.0 gms. (0.174 moles) of the unsaturated acid, 7.83 gms. (0.087 moles) of oxalic acid, and 2.5 cc. (0.02 moles) of boron trifluoride-etherate were heated on a steam bath for six hours. The unreacted oxalic acid was removed with sodium bicarbonate solution, and the organic layer was dried and distilled. Distillation gave 15.9 gms. of product (B.P. 80°-81.5° @ 5-6mm, d₄³₀ - 1.012). The product was soluble in water and neutral to litmus as the lactone. The percent yield of the γ-lactone was 79.5.
QUANTITATIVE MEASUREMENTS

DETERMINATION OF THE ESTER CONCENTRATION BY ISOLATION:

In the isolation of the ester, after sufficient time had elapsed for equilibrium to be obtained, the usual technique was employed. The mixture was treated with 5% potassium hydroxide solution to remove the unreacted chloroacetic acid and then washed several times with water. After drying, the benzene used as solvent was removed by distillation. Initially a modified Claisen flask was used, but a two foot column packed with 1/4" glass helices proved more effective and was used in later runs. The residue was distilled under vacuum conditions from a 125 cc. Vigreux column, taking off the cyclohexyl chloroacetate fraction. This material was then redistilled.

Experiments involving the isolation of ester from solutions of known concentration showed that on the average the amount isolated by this method was 9% low. Hence, all equilibrium constants obtained by ester isolation were calculated with this correction factor figured in.

DETERMINATION OF THE OLEFIN CONCENTRATION:

The sample containing the olefin (usually 5 cc.) was added to a 250 cc. iodine flask containing 25 cc. of 6 normal hydrochloric acid and 10 cc. of C.P. carbon tetrachloride. After the mixture was shaken thoroughly, a moderate excess of standard bromide-bromate solution was added from a burette. The mixture was allowed to stand in the dark for five to ten
minutes. Then 5 cc. of potassium iodide solution (30 gms./200 cc.) was added and the mixture shaken. The stopper and lip were rinsed with distilled water and approximately 100 cc. of water added. The dark mixture was then titrated with standard thiosulfate solution with swirling until a pale yellow color appears. One or two cc. of fresh 1% starch solution was then added, and more thiosulfate was added until the color was gone.

This procedure is the standard method used in determining the amount of unsaturates in hydrocarbon fractions, except that hydrochloric acid was substituted for acetic acid.

An investigation of the effect of the catalyst and acid in known olefin solution showed no interference. The amount of carbon tetrachloride used is not critical. However, the use of excessive amounts led to lengthy titrations, due to the necessity for increased shaking. The amount of time elapsed before titrating with thiosulfate, after the addition of potassium iodide solution, is critical. Five to fifteen minutes is alright, but long periods lead to considerable error.

The results on tests of known solutions were within 1% of the given molarity in all cases.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>Initial Conc. of Olefin</th>
<th>Initial Conc. of Acid</th>
<th>Initial Conc. of Ester</th>
<th>Catalyst Conc.</th>
<th>Temp.</th>
<th>Equilib. Conc. of Olefin</th>
<th>Equilib. Conc. of Ester</th>
<th>K&lt;sub&gt;eq&lt;/sub&gt; by Isolation</th>
<th>K&lt;sub&gt;eq&lt;/sub&gt; by Titration</th>
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<td>0.881</td>
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<td>0.053</td>
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SUMMARY OF REACTION CONDITIONS

RUNS #1, #2 and #3:

In these runs the acid and olefin were weighed out and dissolved in a given volume of benzene. The mixture was heated on a Glascol heating unit and kept at 85°C. The unreacted acid was removed by 5% potassium hydroxide treatment, and the benzene by distillation, using a modified Claisen flask. A correction was made in the amount of ester found, as results using known solutions indicated 9% ester was lost in the isolation stage on the average.

RUNS #4, #5, and #6:

These runs are identical with #1 through #3 except that a two foot column packed with 1/4" glass helices was used to distill off the benzene. The temperature was maintained at 85°C using a Glascol heating unit.

RUNS #7 and #8:

In these runs the bromide bromate technique for determination of the equilibrium concentration of olefin was used as well as determination of the equilibrium constant by the isolation of ester technique. The temperature was again maintained at 85°C using a Glascol heating unit.

RUNS #9 and #10:

In these runs the sealed tube technique was employed. Aliquot portions of a known solution of acid, olefin, and catalyst at 15°C were pipetted into small constructed tubes and then sealed immediately. These were thermostatted at
78.3° by introducing them into the vapor of boiling ethanol. The equilibrium value of olefin was determined by the bromide-bromate method.

**RUNS #11 through #17:**

In these runs, the initial mixture was made up to a given volume from previously prepared solutions of the acid and olefin in benzene. In #11 the sealed tube technique was employed, but in all others the initial mixture was placed directly in a bath at 50°±0.2. The equilibrium value of the olefin concentration was determined by pipetting samples from the reaction mixture and immediately titrating the amount of olefin.
RUN #13 -- DATA FOR PLOTTED GRAPHS:

\[ a = 0.200 \text{ m/l} \] initial concentration of cyclohexene
\[ b = 0.502 \text{ m/l} \] initial concentration of chloroacetic acid
\[ 0.160 \text{ m/l} \] concentration of BF$_3$-etherate
\[ x_e = 0.805 \]
\[ x^2 = 0.0259 \]
\[ ab = 0.1004 \]

<table>
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<tr>
<th>Time in minutes</th>
<th>Olefin Conc. in m/l</th>
<th>% Ester Calc'd.</th>
<th>Am't. of Olefin Re-acted in m/l</th>
<th>( \log \frac{x.x_e-ab}{x.x_e-x^2} )</th>
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<td>73.3</td>
<td>0.1466</td>
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RUN #14 -- DATA FOR PLOTTED GRAPHS:

\[ a = 0.200 \text{ m/l} \] initial concentration of cyclohexene  
\[ b = 0.502 \text{ m/l} \] initial concentration of chloroacetic acid  
\[ 0.320 \text{ m/l} \] concentration of BF₃-etherate  
\[ x_e = 0.1585 \quad x_e^2 = 0.0251 \quad ab = 0.1004 \]

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Olefin Conc. in m/l</th>
<th>% Ester Calc'd.</th>
<th>Am't. of Olefin Re-</th>
<th>( \log \frac{x \cdot x_e - ab}{x \cdot x_e - x_e^2} )</th>
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<td>56.5</td>
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<td>65.7</td>
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<tr>
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<td>66.8</td>
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<td>78.5</td>
<td>0.1570</td>
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<tr>
<td>428</td>
<td>0.043</td>
<td>78.7</td>
<td>0.1585</td>
<td>2.599</td>
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</table>
RUN #15 -- DATA FOR PLOTTED GRAPHS:

\[ a = 0.200 \text{ m/l} \] initial concentration of cyclohexene
\[ b = 0.358 \text{ m/l} \] initial concentration of chloroacetic acid
\[ 0.320 \text{ m/l} \] concentration of BF$_3$-etherate
\[ x_e = 0.1530 \]
\[ x_e^2 = 0.0234 \]
\[ ab = 0.0716 \]

<table>
<thead>
<tr>
<th>Time in minutes</th>
<th>Olefin Conc. in m/l</th>
<th>% Ester Calc'd.</th>
<th>Am't. of Olefin Reacted in m/l</th>
<th>( \log \frac{x \cdot x_e - ab}{x \cdot x_e - x_e^2} )</th>
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ACKNOWLEDGEMENTS

I wish to express my gratitude to Dr. George H. Richter, whose help and encouragement in connection with this problem were invaluable. Thanks are also due Dr. Edward S. Lewis, for his kind assistance with the kinetics work.

Wallace J. Hay
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PART II

THE PREPARATION OF SOME STEREOCHEMICALLY INTERESTING POLYCYCLIC COMPOUNDS
INTRODUCTION
In this investigation, it was proposed to prepare the Diels-Alder adducts of 9-substituted anthracene and quinones, to aromatize them, and to convert the resulting hydroquinones to the parent bridge-head substituted hydrocarbons. This was to be done in order to ascertain whether or not steric hindrance involving the original 9-substituent and the adjacent atoms would lead to an asymmetric molecule. The following diagram is an attempt to show the type of molecule that theoretically should exhibit this phenomenon.

The substituent (the aminomethyl group in the example) must be an angular group, for a linear substituent would lead to a symmetrical molecule with no possibility for optical isomerism. A model of the molecule shown above demonstrates that the steric hindrance involving the angular aminomethyl group compares favorably with the hindrance observed in models of compounds known to be resolvable. Thus there can exist a meso structure having a plane of symmetry as shown above, a d-form, and an l-form. The following diagram using lines to represent a top view of the molecule may assist in the visualization of these forms.
The racemization of an optically active form would occur with difficulty because of the high activation energy that would be needed.

With any angular substituent, there is a possibility of optical isomerism. However the energy required for interconversion of the various spatial configurations would be different for different groups. Another possible substituent is the methoxy group. A model of the compound with this substituent shows more freedom of movement for this group than the previously mentioned aminomethyl group due to less interference of the hydrogen atoms. Interconversion among the different possible spatial configurations that the methoxy or aminomethyl substituted compound may assume, might be effected through a combination of bending and stretching of various bond angles and bonds involved.

At this point it might be well to state that the material with which the substituted anthracene is condensed must either contain more than one ring or else have some substituent to distinguish it from the other benzene rings
resulting from the original anthracene compound. Otherwise, the three possible spatial configurations discussed above become identical.

In the reaction of the 9-substituted anthracene with naphthoquinone for example, the meso form seems to be the most logical product of the reaction, since the meso form is less hindered in the addition product. Thus, in order to demonstrate the existence of optical isomers, it would first be necessary to convert the meso form to the racemic mixture. If both the meso form and the racemic mixture were formed in the reaction, a separation by fractional crystallization would be necessary.

Assuming one has the meso form and the racemic mixture, the work can proceed in one of two ways. First, the usual technique of the formation of suitable diastereoisomeric derivatives might be attempted. In the case of the amino-methyl substituent this would be easier than in case of the methoxy substituent; in the former, one has a handle with which to work, whereas the methoxy compound would have to be condensed with some material that would lead to a product with a reactive group.

Secondly, x-ray diffraction patterns of single crystals of the meso form and the racemate might be taken. Since the number of molecules of the d and l forms must be equal in the racemate, the number of molecules in the unit cell must be even for the crystal formed from the racemate. This evolves from the fact that the unit cell is defined as
the smallest spatial unit of a crystal which when reproduced will give the structure of the crystal. However, the number of molecules of the meso form in the unit cell can be either even or odd. If the value calculated is odd, the meso form is clearly indicated. To repeat, if the calculated number of molecules in the cell for the supposed meso form is odd, the presence of optical activity can be shown by comparison with the even number that must be obtained for the racemate. If however, the calculated number of molecules in the unit cell for the meso form is even, then the x-ray method is much more difficult.

In order to demonstrate the existence of the type of optical isomerism discussed above, it is first necessary to prepare the compounds needed, however. The Diels-Alder reaction is a convenient tool to use in this connection.

In general, the Diels-Alder reaction is the reaction of a diene component containing at least two multiple bonds with a dienophile containing at least one multiple bond. The reaction involves the addition of the dienophile to the 1,4-positions of the conjugated diene with the formation of a six membered carbon ring. The following examples are typical.

\[
\begin{align*}
(1) & & \\
& & \\
(2) & & 
\end{align*}
\]
The versatility of this reaction was recognized primarily by Diels and Alder, whose series of papers began to appear in 1928 (1). In recognition of their research, the reaction bears their names. A discussion of the literature concerning this reaction would occupy a volume, but fortunately several excellent reviews of the work done on this reaction are available. Kloetzel (2) has evaluated the work on the Diels-Alder reaction using maleic anhydride. Holmes has prepared an excellent review of the literature involving ethylenic and acetylenic dienophiles. The Diels-Alder reactions with quinones and other cyclanones as the dienophile were reviewed recently by Butz and Rytina (4). A comprehensive summary by Alder is also available (5).

However, very few investigators used anthracene or 9-substituted anthracene as the diene component of the reaction. Clar (6) reported the addition of anthracene to p-benzoquinone in 93% yield. Bartlett and Lewis (7,9) were able to condense 9-anthraldehyde and 9-bromo anthracene with p-benzoquinone, and also aromatized the resulting adducts. Also the bromo adduct was converted to the parent bridge-head bromo-substituted hydrocarbon, bromotriptycene, without too much difficulty. All of the above mentioned reactions were run with benzene as a solvent.
DISCUSSION OF EXPERIMENTAL WORK
Since very few examples of the Diels-Alder reaction with anthracene or 9-substituted anthracene have been reported, the preparation of the quinone adducts served a two-fold purpose - the preparation of new compounds, and a step in the synthesis of compounds which should exhibit optical isomerism of the type discussed above.

The initial condensations were made with p-benzoquinone while waiting for the arrival of a supply of 1,4 naphthoquinone. Condensation of 9-cyanoanthracene with an appropriate quinone is the logical method to obtain the amino-methyl bridge-head substituent desired. Thus the synthesis of 9-cyanoanthracene by way of 9-anthraldehyde and the oxime was carried out using the method of Fieser and Hartwell (8).

The 9-anthraldehyde was obtained in 60% yield from anthracene and N-methyl formanilide. The product, recrystallized from glacial acetic acid, melted at approximately the reported temperature, but had a brown-yellow color instead of the bright yellow color described. Several recrystallizations from methyl alcohol led to a constant melting point of 84°-86°. The product reported by Fieser and Hartwell melted at 98.5°-99.5° or 104.5°-105.5°, depending on whether the stable or unstable form was obtained.

The supposed aldehyde, when heated with hydroxylamine, gave 93% of an oxime which had the reported melting point. The oxime in turn, when heated with acetic anhydride, gave a 97% yield of 9-cyanoanthracene which also melted at the reported temperature.
It was thought at this point that the low melting point of the aldehyde obtained might be correct and might indicate a different crystalline form. Fieser and Hartwell report that two modifications exist: an unstable material melting at 98.5\(^\circ\)-99.5\(^\circ\), and a stable material melting at 104.5\(^\circ\)-105.5\(^\circ\). Since the aldehyde before recrystallization from methanol melted at 97\(^\circ\)-99\(^\circ\), it seemed reasonable to assume that the low melting product was indeed the aldehyde.

The low melting aldehyde was condensed with p-benzoquinone by the method of Bartlett and Lewis (9) in order to ascertain whether the melting point of the adduct would also be low. The product obtained in 60\% yield melted sharply at 168\(^\circ\)-169\(^\circ\), whereas the reported melting point for this compound is 183\(^\circ\)-189\(^\circ\). The adduct was aromatized by the method of Bartlett and Lewis to give a 75\% yield of a product melting at 300\(^\circ\)-302\(^\circ\) with partial decomposition. This value agrees with the reported melting point of 300.5\(^\circ\)-302\(^\circ\).

A possible explanation for the low melting point of the aldehyde and its adduct with p-benzoquinone is the presence of the acetal formed with methanol during the recrystallization of the aldehyde. The aldehyde when recrystallized from methyl alcohol still contained some acetic acid in all probability. Since acids are catalysts for the formation of acetals, the probability of some acetal formation is high. The low melting point of the adduct which was formed in benzene solution and recrystallized from
chloroform and petroleum ether can also be explained in this way. The aromatization reaction, which was carried out in hot glacial acetic acid solution, would regenerate the aldehyde. Also the final recrystallization of this material was made from acetic acid, so that there was no opportunity for reformation of the acetal. Thus the aromatized material should give the reported melting point.

All attempts to condense 9-cyanoanthracene with p-benzoquinone failed. The reaction was run in boiling ether, benzene, and xylene. In all cases, 60-80% of pure cyano-compound were recovered from the reaction mixture.

Since the 9-cyanoanthracene did not undergo the Diels-Alder reaction, it was decided to reduce the cyano group to the aminomethyl group and attempt to condense it with p-benzoquinone and naphthoquinone.

The reduction was carried out according to the method of Nystrom and Brown (10) using lithium aluminum hydride as the reducing agent. An ether solution of the cyano-compound was added to an ether solution of the lithium aluminum hydride. The reaction mixture gave nothing but unreacted 9-cyanoanthracene, however.

The oxime of 9-anthraldehyde was boiled with an equivalent amount of 1,4 naphthoquinone in xylene. The green-yellow adduct (A in Figure I) obtained, melted at 157°-158° after final recrystallization form chloroform and petroleum ether. The yield however, was only 12.3%. A by-product of this reaction was isolated melting with decomposition at 208°-210°.
The melting point, solubility in alkali, and positive test for nitrogen, indicated the product was the dioxime of 1,4 naphthoquinone. However, a last minute micro-combustion analysis showed that this was not 1,4 naphthoquinone.

Since the attempts to prepare the desired aminomethyl compound by way of the cyano-compound were unsuccessful, it was decided to prepare 9-methoxyanthracene and find out whether it would undergo the Diels-Alder reaction with quinones.

In this connection, it was necessary to prepare anthrone. This material was prepared in 64% yield by the method of Meyer (11). Methylation of the anthrone, by the addition of dimethyl sulfate to a mixture of anthrone in 20% sodium hydroxide at 100°, failed to give the methoxy compound. The insolubility of the sodium enolate in water is a plausible explanation. Apparently, the dimethyl sulfate hydrolyzed as fast as it was added.

Another sample of anthrone was methylated by the use of methyl p-toluene sulfonate using the method Barnett and Hewitt (12) employed to methylate 1,3 dimethyl anthrone. The 9-methoxyanthracene was obtained in 41.8% yield as white flakes melting at 97°-98°. The reported melting point is 97°-98° (13).

A mixture of 9-methoxyanthracene and an excess of p-benzoquinone in benzene, when refluxed for six hours, gave a 77% yield of the pale yellow adduct (B in Figure I), melting at 139°-140°. A glacial acetic acid solution of the adduct,
when heated on a steam bath in the presence of a small amount of concentrated hydrochloric acid, gave a 67\% yield of crude yellow-white hydroquinone (C, Figure II), melting at 215°-220° with decomposition. Purification by the extraction of the impurities with hot methyl alcohol gave only 6-7\% of product, melting at 234°-235° with decomposition.

In a similar reaction, 9-methoxyanthracene with 1,4-naphthoquinone in xylene led to a 41\% yield of the tan colored adduct (D in Figure II). The pure material melted at 157°-158°. Aromatization of the adduct by the method previously used gave a 77\% yield of the pale yellow hydroquinone (E in Figure II). The material melted at 223°-224°.

Since the Diels-Alder adduct of anthracene and 1,4-naphthoquinone has not been reported in the literature, it also was prepared. The addition reaction was run in boiling xylene. A 41\% yield of the pure adduct (F in Figure III) was obtained. The white product melted at 193°-195°. Aromatization was effected by boiling for thirty minutes a glacial acetic acid solution of the adduct, to which had been added 4 or 5 drops of 40\% hydrobromic acid solution. The hydroquinone obtained (G in Figure III) melted at 274°-276°. As in the case with the aromatized adduct of 9-methoxyanthracene and 1,4-naphthoquinone, this compound had a yellow color. The yield was 80\% of the theoretical amount.
Figure I

```
\[ \text{CH}_3\text{C}=\text{O} \]
\[ \text{H} = \text{C}=\text{NOH} \]
\[ \text{H}_2\text{NOH} \]
\[ \text{H} = \text{C}=\text{NOH} \]
\[ \text{93\%} \]
\[ \text{12.3\%} \]
\[ \text{xylene} \]
\[ \text{A} \]
\[ \text{CH}_3\text{SO}_3\text{K} \]
\[ \text{KOH} \]
\[ \text{41.8\%} \]
\[ \text{B} \]
\[ \phi\text{H} \]
\[ \text{66\% and 77\%} \]
\[ \text{C} \]
```
Figure II

B \rightarrow \text{CH}_3\text{COOH} \rightarrow \text{HCl} \rightarrow 67\% \rightarrow C

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{B} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{C} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{D} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{E} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{41\%} & \quad \text{xylene} \\
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

\[
\begin{align*}
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{77\%} & \quad \text{CH}_3\text{COOH} + \text{HCl} \\
\text{O-CH}_3 \\
\text{H} & \quad \text{H} \\
\text{O} & \quad \text{O} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]
Figure III

[Diagram showing chemical structures and reactions]

F

41% xylene

G

80% CH₃COOH + 40% HBr
EXPERIMENTAL
PREPARATION OF 9-ANTHRALDEHYDE:

The method of Fieser and Hartwell (8) in which anthracene reacts with N-methyl formanimide in the presence of phosphorus oxychloride was used. As no N-methyl formanimide was available, the first step was the preparation of this compound. The N-methyl formanimide was prepared in 75% yield by the method of Fieser and Jones (15).

A mixture of 64 gms. (0.48 moles) of N-methyl formanimide, 41.3 gms. (0.34 moles) of anthracene, and 64 gms. (0.43 moles) of phosphorous oxychloride together with 37 cc. of o-dichlorobenzene as a solvent was stirred under reflux conditions for one hour. The hydrochloric acid evolved was removed by a sodium hydroxide trap.

At the end of the heating period 455 cc. of crystalline sodium acetate solution containing 254 gms. was added to the cooled solution in order to decompose the N-methyl aniline-phosphorus oxychloride complex. The mixture was then steam distilled to remove the N-methyl aniline and o-dichlorobenzene. The residue solidified on cooling. The solid mass was broken up, and the solution decanted. The solid was washed with 750 cc. of dilute hydrochloric acid in 100 cc. portions to remove any residual amine present. Recrystallization of the crude brown solid was effected from hot glacial acetic acid. On cooling, the solid was filtered and washed with 50 cc. of methyl alcohol. The melting point of the dried product was 97°-99°. The product still had a

a. All melting points are uncorrected.
brown-yellow color however, instead of the bright yellow described.

In order to purify the product it was recrystallized three times from hot methyl alcohol solution. 26 gms. of bright yellow needles (M.P. 84°-86°) were obtained. From the filtrate 3 gms. of additional product were obtained (M.P. 83°-85°). The yield of recrystallized purified material was 60% of the theoretical. Further recrystallization from methyl alcohol did not change the melting point. Fieser and Hartwell reported a melting point of 104.5° - 105.5° for the stable form and 98.5° - 99.5° for the unstable form.

PREPARATION OF THE OXIME OF 9-ANTHRALDEHYDE:

The oxime was prepared according to the method of Fieser and Hartwell (8). From 15 gms. of the supposed aldehyde and 5.5 gms. of a solution of the hydroxyl amine hydrochloride in 50 cc. of water (neutralized by sodium bicarbonate), 15 gms. of the oxime as yellow needles were obtained, corresponding to a 93% yield. The melting point was 151°-154°. The solid was extracted with 5% KOH reprecipitated with acid and recrystallized from hot ethanol. The melting point obtained was 164°-165°. Fieser and Hartwell reported a melting point of 165°-165.5°.

PREPARATION OF 9-CYANOANTHRACENE:

Two grams of the oxime when heated in acetic anhydride
under reflux according to the method of Fieser and Hartwell (8) gave 1.8 gms. of lemon-yellow needles melting at 175°-177°. The yield was 97% of the theoretical. Recrystallization from glacial acetic acid led to a melting point of 176°-178°. Fieser and Hartwell reported a melting point of 177.5°-179°.

PREPARATION OF THE DIELS-ALDER ADDUCT OF 9-ANTHRALDEHYDE AND p-BENZOQUINONE:

The Diels-Alder adduct of the previously prepared 9-anthraldehyde and p-benzoquinone was prepared according to the method of Bartlett and Lewis (9). 6.8 gms. (0.033 moles) of the aldehyde together with 11.8 gms. (0.109 moles) of p-benzoquinone in 60 cc. of benzene were refluxed for six hours. The solvent was removed by distillation, and the mixture cooled and filtered. The crude product was washed with approximately two liters of hot water to remove the excess quinone. The crude solid (9.8 gms.) was dried and dissolved in a minimum quantity of hot chloroform. Petroleum ether was added to precipitate the solid. The tan-yellow solid was obtained in two crops. Repeated recrystallization of this material from chloroform and petroleum ether gave a light-yellow product which melted at 168°-169° giving a red melt. Recrystallization did not effect the melting point. The yield was 60%. Lewis gives a melting point of 188°-189° for the adduct.
AROMATIZATION OF THE DIELS-ALDER ADDUCT OF 9-ANTHRALDEHYDE 
AND p-BENZOQUINONE

Two grams of the adduct in 75 cc. of glacial acetic acid were heated on a steam bath with stirring. One-half cc. of concentrated hydrochloric acid was added to the mixture, as recommended by Bartlett and Lewis (9). The adduct dissolved within a few minutes, and the heating was continued for three hours. The solution was cooled slowly, but no crystals formed. Water was added to precipitate the solid. A mass of light-yellow solid came out of solution. This material was dried and recrystallized from methyl alcohol and chloroform. The product obtained decomposed on heating at 285°-290°. Final recrystallization from 15 cc. of glacial acetic acid gave an almost white solid which melted with slight decomposition at 300°-302°. The yield of pure product was 1.5 gms. which is equivalent to a 75% yield. The melting point as given by Bartlett and Lewis is 300°-305.5°.

THE ATTEMPTED PREPARATION OF THE DIELS-ALDER ADDUCT OF CYANO-
ANTHRACENE AND p-BENZOQUINONE

Another batch of the 9-cyanoanthracene was prepared from the aldehyde as previously described. Portions of this material were refluxed for several hours with excess p-benzoquinone in benzene, xylene and ether in an attempt to prepare the adduct. In all cases, the material obtained after washing with hot water to remove the quinone, and recry-
stallization from chloroform and petroleum ether led to the recovery of the cyano-compound. Approximately 60-80% of the original amount of 9-cyanoanthracene was recovered from the reaction mixtures.

THE ATTEMPTED REDUCTION OF THE 9-CYANOANTHRACENE TO THE CORRESPONDING AMINOMETHYL COMPOUND:

A solution of lithium aluminum hydride in ether was prepared by refluxing 200 cc. of anhydrous ether with approximately 10 gms. of lithium aluminum hydride for four hours. The solution was prepared according to the procedure recommended by Finholt, Bond, and Schlesinger (16). At the end of the heating period, the solution was transferred to a bottle by forcing the solution out with nitrogen pressure. A fair amount of powdery white insoluble material remained.

The attempted reduction of the cyanide was carried out according to the method of Nystrom and Brown (10). 2.0 gms. (0.010 moles) of the cyanide were dissolved in 300 cc. of anhydrous ether and added dropwise to 50 cc. (.025 moles) of the prepared lithium aluminum hydride solution in a three-necked flask equipped with reflux condenser, mercury sealed stirrer, and dropping funnel. After the addition, which took one hour, the excess of the hydride was decomposed by the slow addition of water. Very rapid evolution of hydrogen was observed as a large amount of white solid precipitated. The mixture was transferred to a two liter beaker, and 100 cc.
of a 20% solution of sodium potassium tartrate was added. The mixture at this point contained three layers; ether, water, and solid, respectively. The basic solution, after filtering off the solid material, was extracted with 1500 cc. of ether in 150-200 cc. portions. Approximately 0.5 gms. of orange-yellow solid were obtained on removal of the ether. This material on heating darkened at 150°-155° and melted with decomposition around 165°. Recrystallization from methyl alcohol led to 0.3 gms. of yellow flocks, melting point 174°-176° which indicated the cyanide.

The basic aqueous solution which remained after ether extraction was discarded, but the white precipitate was removed and investigated. An excess of sodium hydroxide appeared to dissolve part of this material. The mixture was then extracted with 500 cc. of ether. Evaporation of the solvent led to nothing.

PREPARATION OF THE DIELS-ALDER ADDUCT OF THE OXIME OF 9-
ANTHRALDEHYDE AND 1,4 NAPHTHOQUINONE:

A mixture of 2.0 gms. (0.008 moles) of the oxime and 1.25 gms. (0.008 moles) of 1,4 naphthoquinone was refluxed for two hours in 75 cc. of xylene. The mixture became quite dark. Cooling in an ice bath led to approximately one gram of brown needles, which were filtered off. The filtrate was evaporated to dryness and two grams of brown solid remained. The combined solid was treated with 100 cc.
of hot 5% potassium hydroxide solution. The insoluble material was filtered off. This material was dried and then dissolved in 50 cc. of chloroform. The insoluble material was filtered off (0.4 gms.). This material, when heated, darkened at 175° and charred badly at 210°. The chloroform solution was heated with a small amount of Norite and filtered while hot. Petroleum ether was added to the hot solution till it became cloudy, and on cooling a flocculent precipitate formed. This material was tan in color and on heating decomposed at 207°-209°. The filtrate was concentrated and petroleum ether again added. A yellow solid, which melted at 155°-156° with decomposition, was obtained on cooling (0.2 gms.).

The crude product, which was soluble in 5% potassium hydroxide solution, was precipitated by the addition of dilute hydrochloric acid, filtered, and dried. This material was then put into 120 cc. of ethyl alcohol, heated with Norite, and filtered. The filtrate was concentrated to a volume of 20 cc. Water was added dropwise to the hot alcohol solution, and on cooling a green-brown solid crystallized. This material weighed 0.4 gms. On heating, the material melted with decomposition at 155°-157°.

The combined material, with a melting point of 155°-157° (0.5 gms.), was recrystallized from chloroform and petroleum ether. A crop of green-yellow crystals was obtained from the fluorescent solution. The melting point of this material was 157°-158° without decomposition. The melt was red-
brown. The yield of purified product was 0.5 gms., corresponding to only a 12.3% yield.

A sample of the purified material was dried under vacuum in a drying pistol over phosphorus pentoxide at the temperature of boiling acetone (56°C). The dried sample was subjected to micro-combustion analysis for carbon and hydrogen.

Analysis:

Calculated for C25H16O3N: C - 79.35% H - 4.26%

Found:

The material melting at 207°C-209°C with decomposition, obtained from that part of the crude product which was soluble in 5% potassium hydroxide, was recrystallized from chloroform and petroleum ether. A pale yellow-green solid was obtained (0.2 gms.), which melts with decomposition at 208°C-210°C. This material was fused with sodium, and the water solution of the fusion product gave a faint but positive test for nitrogen. Thus the compound has the characteristics of the dioxime of 1,4 naphthoquinone.

Analysis:

Calculated for C10H8O2N2: C - 64.35% H - 4.29%

Found: C - 80.48% H - 4.97%

From the analysis however, the only thing certain is that the product is not the dioxime of 1,4 naphthoquinone.

a. The results of the analysis did not arrive in time for inclusion.
PREPARATION OF 9-METHOXYANTHRACENE:

It was decided to prepare this compound by methylation of anthrone using dimethyl sulfate as a methylating agent in basic solution.

Since anthrone was not available, it was prepared by the reduction of anthraquinone by the method of Meyer (11). 100 gms. (.48 moles) of anthraquinone together with 100 gms. of tin were put into 750 cc. of glacial acetic acid in a two liter round bottom flask fitted with a reflux condenser. The mixture was heated to boiling and 250 cc. of concentrated hydrochloric acid were added in 10 cc. portions until all the anthraquinone dissolved.

The solution was then filtered through a Gooch crucible with a fixed porous plate, and 100 cc. of water were added. On cooling in an ice bath, the anthrone crystallized and was filtered off. The crude product was dried and recrystallized from a mixture of 690 cc. of benzene and 230 cc. of petroleum ether. The yield was 62 gms., or 64% of the theoretical amount. The anthrone melted at 154°-155°.

An attempt was made to methylate the anthrone by the method commonly employed for the methylation of phenols. 60 gms. (0.31 moles) of anthrone were added to 180 cc. of a 20% solution of sodium hydroxide, and 20.2 gms. (0.16 moles) of dimethyl sulfate were added dropwise to the mixture maintained at 100°. The reaction was vigorous and produced a great quantity of white vapor. After addition of
the dimethyl sulfate the mixture was cooled, and 300 cc. of water were added. The color was a weak orange. Extraction of the solution with ether gave nothing.

A check of the literature revealed that Barnett and Hewitt (12) methylated 1,3 dimethyl anthrone with methyl p-toluene sulfonate in boiling alcohol solution. Thus their method was used.

31.0 gms. of anthrone (0.10 moles) were dissolved in 400 cc. of boiling ethyl alcohol giving a clear pale yellow solution. A three-necked 500 cc. flask was used, fitted with two dropping funnels and a reflux condenser. Alternately in small amounts, 50% potassium hydroxide solution and methyl p-toluene sulfonate were added to the mixture until the color of the solution was orange in neutral and alkaline solution. The basic solution of anthrone is deep red and the dimethyl sulfate in excess gives a bright orange. A pale orange color was obtained at the completion of the addition which remained the same in neutral and alkaline solution. The excess of methyl p-toluene sulfonate was destroyed by the addition of excess 50% potassium hydroxide and boiling for 10-15 minutes.

The basic solution was steam distilled, and the six liters of distillate when extracted with ether and recrystallized from methyl alcohol gave 7.0 gms. of white flakes, M.P. 97°-98°. The residue when extracted with ether and recrystallized from methyl alcohol gave 8.0 gms. of pale yellow-white material which melted at 95°-97°. The combined
mother liquor gave 3.1 gms. of dirty yellow needles which melted at 88°-90°. The reported melting point is 97°-98°.(13)

The combined yield of product was 18.1 gms., or 41.8% of the theoretical amount.

PREPARATION OF THE DIELS-ALDER ADDUCT OF 9-METHOXYANTHRACENE AND p-BENZOQUINONE

A mixture of 6.0 gms. (0.029 moles) of 9-methoxyanthracene and 12.0 gms. (0.111 moles) of p-benzoquinone in 60 cc. of benzene was refluxed for six hours. The solvent was evaporated and the product was washed with five 100 cc. portions of hot water to remove the excess quinone. The tan colored crude product weighed 10 gms. The material was recrystallized from chloroform and petroleum ether. Pale yellow crystals were obtained. The material melted at 139°-140° to give a red melt. The yield of purified product was 6.0 gms. corresponding to 66% of the theoretical value.

Analysis:

Calculated for C_{21}H_{16}O_3:  C - 79.73%  H - 5.10%

Found:  C - 79.59%  H - 5.04%

In another experiment a 77% yield of the adduct was obtained melting again at 139°-140°.

AROMATIZATION OF THE DIELS-ALDER ADDUCT OF 9-METHOXYANTHRACENE AND p-BENZOQUINONE

Three grams of the adduct along with 100 cc. of glacial acetic acid to which was added 1 cc. of concentrated hydro-
chloric acid were heated with stirring on a steam bath. The adduct dissolved in fifteen minutes, and the solution was heated for four hours. Nothing but charred material was isolated however.

A 1.5 gm. sample of the adduct in 50 cc. of glacial acetic acid, to which was added 0.5 cc. of concentrated hydrochloric acid, when heated in the same manner for two hours did not char however. Water was added dropwise to the mixture, and on cooling a tan solid crystallized out. The material was put into 15 cc. of methyl alcohol and heated on a steam bath. The insoluble material was filtered off. The filtrate on cooling gave a tan solid contaminated by a red oil which could not be removed. The material insoluble in methyl alcohol (0.2 gms.) was almost white. It melted with decomposition at 234°-235°.

In a subsequent run 3.0 gms. of the adduct in 60 cc. of glacial acetic acid, to which 1.0 cc. of concentrated hydrochloric acid was added, were heated on a steam bath for three hours with stirring. On long standing, 2.0 gms. of dirty white crystals were obtained from the acetic acid solution. This material melted with decomposition at 215°-220°. Purification by leeching with 100 cc. of hot methyl alcohol left only 0.2 gms. of light tan solid, which melted with decomposition at 234°-235°. The filtrate, when concentrated and cooled, gave up 1.5 gms. of yellow white material which decomposed at 216°-220°. The yield of crude product here was 67%, but as in the previous experiment only a very
small amount of pure material was obtained.

Analysis:

Calculated for $C_{21}H_{16}O_3$ : C - 79.73%  H - 5.10%
Found : C - 79.16%  H - 5.11%

PREPARATION OF THE DIELS-ALDER ADDUCT OF 9-METHOXYPHTHALENES AND 1,4 NAPHTHOQUINONE:

A solution of 3 gms. (.014 moles) of 9-methoxyanthra-
cene and 4.75 gms. (.030 moles) of 1,4 naphthoquinone was
boiled under reflux for seven hours. The solvent was evap-
orated and a dark red solid remained. This material was
treated with 200 cc. of hot petroleum ether in order to ex-
tract the excess 1,4 naphthoquinone. The insoluble material
weighed 4.0 gms.

The petroleum ether, when allowed to evaporate, gave two
types of crystals: small dark red crystals and red-yellow
fan shaped leaflets. The former melted at 113°-116° giving
a dark red melt, and the latter at 90°-94° giving a light
red melt. The lower melting material was apparently im-
pure 9-methoxyanthracene, and the higher melting material
indicates impure 1,4 naphthoquinone. This material was
discarded.

The material insoluble in petroleum ether was then ex-
tracted with 100 cc. of hot methyl alcohol. The insoluble
material (1.5 gms.) was filtered from the dark red solution.
This material was reddish-brown in color and melted at 155°-
157°.
The methyl alcohol solution was treated with a small amount of Norite and filtered while hot. The solution was concentrated to a volume of 35 cc., and a light tan solid crystallized. This material (0.7 gms.) gave a red melt at 157°-158°.

Thus 2.2 gms. of the adduct (41% of the theoretical amount) were obtained. Further recrystallization of a sample of this material from a mixture of methyl alcohol and chloroform gave small white crystals which melted at 157.3°-157.7°.

Analysis:

Calculated for C_{25}H_{18}O_{3} : C - 81.97% H - 4.95%

Found : C - 81.39% H - 4.79%

Non-alkaline ash - 0.53%

AROMATIZATION OF THE ADDUCT OF 9-METHOXYANTHREATACENE AND 1,4 NAPHTHOQUINONE:

A mixture of 1.3 gms. of the adduct and 50 cc. of glacial acetic acid containing 0.3 cc. of concentrated hydrochloric acid was heated with stirring on a steam bath for three hours. To the dark solution obtained, water was added dropwise while cooling. An almost black solid precipitated. This material was filtered off, dried, and dissolved in methyl alcohol and treated with Norite. The yellow-brown filtrate on standing overnight gave a fluffy bright yellow solid. This material weighed 0.6 gms. and melted at 217°-220° to give an orange-red melt. The remaining solution
was treated with Norite again and concentrated. The bright yellow solution gave 0.4 gms. of yellow flocks. This material (0.4 gms.) melted at 222°-224° to give a tan-yellow melt. The total amount of the hydroquinone obtained (1.0 gms.) was equivalent to 77% of the theoretical yield.

A small sample of this material was recrystallized from methyl alcohol giving a product which melted sharply at 223°-224°.

Analysis:

Calculated for \( C_{25}H_{18}O_3 \): C - 81.97%  H - 4.95%

Found : C - 81.28%  H - 4.59%

PREPARATION OF THE DIELS-ALDER ADDUCT OF ANTHRACENE AND 1,4 NAPHTHOQUINONE:

A solution of 2.0 gms. (0.011 moles) of anthracene and 5.0 gms. (0.032 moles) of 1,4 naphthoquinone in 75 cc. of xylene was refluxed for one hour. Concentration of the solution, followed by cooling, led to the precipitation of 5.0 gms. of dark material. The product was dissolved in chloroform. The resulting solution was treated with Norite, filtered, and concentrated. Addition of petroleum ether led to the precipitation of 4.5 gms. of brown solid, which melted at 182°-185° with decomposition.

This material was then added to 100 cc. of boiling methyl alcohol. After heating on a steam bath for a few minutes, the solution was filtered. 1.5 gms. of light tan
material was obtained which melted at 192°-194° with decomposition. Concentration of the methyl alcohol solution and cooling led to 1.2 gms. of a brown solid which decomposed on heating below 155°. The low melting material was then boiled with 50 cc. of ethyl alcohol and the solution filtered. The light red-brown soluble material (0.2 gms.) when heated darkened at 285°-290° and gradually decomposed as the temperature was raised.

A sample of the material melting at 192°-194° was re-crystallized from chloroform and petroleum ether. The small crystals obtained were almost white and melted with decomposition at 193°-195°. The yield of adduct was 41% of the theoretical amount.

Analysis:

Calculated for C_{24}H_{16}O_{2} : C - 35.59% H - 4.79%

Found : C - 35.58% H - 4.90%

AROMATIZATION OF THE DIELS-ALDER ADDUCT OF ANTHRACENE AND 1,4 NAPHTHOQUINONE:

A mixture of one gram of the adduct in 50 cc. of glacial acetic acid to which was added 4 drops of 40% hydrobromic acid was refluxed for thirty minutes according to the method used by Bartlett and Cohen (14) for the aromatization of the anthracenequinone adduct. The solution obtained was red-brown in color. On cooling, a dark, blue-black solid precipitated and was filtered off. This material, when
dry, weighed 0.5 gms. and melted at 255°-260° with decomposition. The filtrate was heated on a steam bath and a small amount of water added. Cooling led to precipitation of a tan solid (0.5 gms.).

This material was recrystallized from hot ethyl alcohol. 0.4 gms. of small yellow crystals were obtained which melted at 274°-276° giving a light brown melt.

The dark product melting at 255°-260° with decomposition was added to 30 cc. of hot chloroform. The solution was filtered to remove any insoluble material. Petroleum ether was added cautiously to the hot solution before cooling. 0.4 gms. of yellow crystals with a slight orange tinge were obtained. On heating, this material melted at 268°-270°.

The yield on the basis of the combined material was 80% of the theoretical value.

Analysis:

Calculated for C_{24}H_{16}O_{2} : C - 85.69% H - 4.79%

Found : C - 84.88% H - 4.27%
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Wallace S. Hay
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