POLYMERIZATION OF CINNAMIC ACID I.

POLYMERIZATION OF CINNAMIC ACID AND p-METHYL CINNAMIC ACID IN CHLOROFORM BY MEANS OF ANHYDROUS ALUMINUM CHLORIDE

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ABSTRACT

Aluminum salts of cinnamic acid and p-methyl cinnamic acid have been polymerized in chloroform in presence of anhydrous aluminum chloride to yield some characterisable oligomers and insoluble high polymer.

INTRODUCTION

It is difficult to polymerize cinnamic acid because of delocalisation of ethylenic pi bond between benzene ring and carboxylic acid groups. This weakens its double bond character, for this reason little work have been appeared in the literature on this matter. Actually present work has been started to add some polyhalogene compounds to the double bond of cinnamic acid or its derivatives in presence of some electrophyllic reagents. However all these attempts have been failed in order to obtain some addition products, but always oligomers or polymers formed and isolated. This observation is novel, and found to be interesting to publish.

Early work of addition of benzene to the ethylenic double bond in presence of anhydrous aluminum chloride have been achieved by Balzohn (1879). After then addition of benzene or other aromatic compounds to variety of ethylenic compounds have widely been investigated by Eijkman (1907), Shith et al. (1947), Patieff et al. (1940), Dippy et al. (1952). Addition of benaene to cinnamic acid have been worked
by Wislicenous et al. (1917) and Fusen (1933). Use of chloroform and carbontetrachloride in Friedel–Crafts reaction to obtain Ar–CHCl₂ or Ar–CCl₃ type compounds of its hydrolized derivatives is widespread in the literature. Also several works of addition of chloroform or carbontetrachloride to the alkenes especially to the polychlorinated alkenes are in the literature. (Boesken et al. (1911), (1911a), (1914); Prince (1914), (1932), (1935), (1935a), (1937), (1937a), (1938), (1949)). However, addition of chloroform nor carbontetrachloride to the double bond is not found in the literature.

RESULTS AND DISCUSSION

In this work, aluminum cinnamate reacted with chloroform in presence of anhydrous aluminum chloride to give some oligomers of cinnamic acid. Oligomers having an aldehyde group, carboxylic acid groups and a double bond have been isolated, no chlorine is found. Also an insoluble high polymer was isolated (This is yet under investigation).

As a matter of fact, free cinnamic acid, its sodium, calcium, barium and aluminum salts have been tested for the reaction. Only aluminum salt gave satisfactory result. Also carbondisulfide which is a good solvent for the Friedel–Crafts reaction is not effective for this reaction. So, chloroform is used as solvents as well as reactant.

For a typical experiment, 50/3 mmoles of aluminum cinnamate, 100 mmoles of anhydrous aluminum chloride and 200 ml of chloroform heated for 5 hours. Reaction mixture poured in a ice–hydrochloric acid mixture and stirred for 1 hour for hydrolysing, then filtered off by suction and collected crude product dissolved in an aqueous sodium carbonate solution and filtered. Insoluble material is 40 %. Filtrate acidified by dilute HCl and filtered. Crude product is 60 %. This is unsoluble in aprotic solvent like chloroform carbontetrachloride, benzene and carbondisulfide and soluble in protic solvent like acetic acid, methanol, ethanol, triethylamine.

Recrystallization column and thin layer chromatography is unsuccessful for the seperation of this crude material. IR spectra and chemical tests have shown that there are carboxylic acid groups, carbonyl group and unsaturation (alkene). Afterwards the preparation of an easily crystallizable derivative has been decided, such as polynitroaromatic compounds (2, 4–dinitrophenylhydrozone of the crude material).
In fact, we were able to separate into three fractions of it simply by fractional crystallisation. IR spectra showed that, each fraction has COOH group(s), double bond, N–N bond and nitro groups in the derivative. Molecular weight determination by means of tree different methods was effected. 1. Perkin Elmer vapor pressure depression apparatus, 2. ICl addition of double bond and iodometric titration method, 3. Kjeldahl “N” determination method. The results are tabulated in Table I.

Table I. The Molecular Weight of the 2,4-Dinitrophenylhydrazon Derivatives of Oligomers of Cinnamic Acid

<table>
<thead>
<tr>
<th>Fractions</th>
<th>ICl addition and iodometric titration</th>
<th>Kjeldahl method</th>
<th>Vapour pressure method (Perkin-Elmer)</th>
<th>Theoretical mol. weight</th>
<th>n</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>916</td>
<td>939</td>
<td>945</td>
<td>948</td>
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<td>15</td>
</tr>
<tr>
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<td>50</td>
</tr>
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<td>1570</td>
<td></td>
<td>1560</td>
<td>7</td>
<td>35</td>
</tr>
</tbody>
</table>

The similar experiment was effected with 10/3 mmoles of aluminum p–methylcinnamate, 20 mmoles of anhydrous aluminum chloride and 30 ml of chloroform. The reaction mixture was worked up as before. In this reaction 10% of unreacted p–methylcinnamic acid was recovered. Oligomer fraction which is soluble in aqueous sodium carbonate solution, showed similar behaviour as cinnamic acid experiment. Functional group analysis and molecular weight determination was made as before and the data obtained are given in Table II.

Table II. The Molecular Weight of the 2,4-Dinitrophenylhydrazon Derivatives of Oligomers of p-Methylcinnamic Acid

<table>
<thead>
<tr>
<th>Fraction</th>
<th>ICl addition and iodometric titration</th>
<th>Kjeldahl method</th>
<th>Vapour pressure method (Perkin-Elmer)</th>
<th>Theoretical mol. weight</th>
<th>n</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
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<tr>
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<td>1165</td>
<td></td>
<td>1180</td>
<td>4</td>
<td>60</td>
</tr>
</tbody>
</table>

Inspection of the Tables show that, there are good accordance between experimental values and theoretical calculation.

According to these data we postulate the following molecular formula for the derivatives of the oligomers:
\[
\text{Ar} \quad \text{Ar} \quad \text{Ar} \\
\text{CH} = \text{C-}(\text{-CH-CH-})_n\text{-CH-CH-CH = N-N-H} \quad \text{NO}_2
\]

\[
\text{Ar} \quad \text{COOH} \quad \text{Ar} \quad \text{COOH} \quad \text{Ar} \quad \text{COOH}
\]

\(\text{Ar: phenyl for cinnamic acid}\)
\(\text{p-tolyl for p-methylcinnamic acid}\)

All attempts of acidic and basic hydrolysis of these derivatives to recover the oligomer have been failed.

**Reaction Mechanism**

Anhydrous aluminum chloride reacts to chloroform to give dichloromethyl carbocation. Also, anhydrous aluminum chloride being an electrophyl, weakens the double bond of cinnamic acid or p-methylcinnamic acid:

\[
\text{CHCl}_3 + \text{AlCl}_3 \rightleftharpoons +\text{CHCl}_3 + \text{AlCl}_4^-
\]
\[
\text{Ar-CH} = \text{CH-COOal} + \text{AlCl}_3 \rightleftharpoons \text{Ar-CH} = \text{CH-COOal}
\]

\(\text{AlCl}_3\)

\((\text{Ar, phenyl or p-tolyl}; \quad \text{al} = \text{Al}^{3+}/3)\)

Dichloromethyl carbocation adds to the double bond of cinnamic acid (or p-methyl cinnamic acid), resulting in a new carbocation whose positive charge is on the side of "Ar" group:

\[
\text{Ar-CH} = \text{CH-COOal} + +\text{CHCl}_3 \rightleftharpoons +\text{CH-CH-CHCl}_3
\]

\(\text{AlCl}_3\)

\(\text{COOal}\)

\((n + 1) \text{Ar-CH} = \text{CH-COOal} \) add successively as the same manner to give:

\[
\text{Ar} \quad \text{Ar} \quad \text{Ar} \\
+\text{CH-CH-}(-\text{-CH-CH-})_n\text{-CH-CH-CHCl}_3
\]

\[
\text{COOal} \quad \text{COOal} \quad \text{COOal}
\]

Hydrolysis of this carbocation in acidic media, proton, chloride and \("\text{al}\) elimination take place to give the oligomer:
\[
\begin{align*}
\text{Ar} & \quad \text{Ar} & \quad \text{Ar} \\
\text{CH} = C(-\text{CH-CH})_n\text{-CH-CH-CHO} & \\
\text{COOH} & \quad \text{COOH} & \quad \text{COOH}
\end{align*}
\]

However representation of aluminum cinnamate as \(\text{Ph-CH=CH-COO}\text{Al}\), may be deceive, because of real formula is \((\text{Ph-CH=CH-COO})_3\text{Al}\) and spatial arrangement of carboxylate ion oxygens around Al\(^{3+}\) cation has an octahedral arrangement:

![Spatial Arrangement of Aluminum Chloride](image)

Although the spatial arrangement of aluminum chloride is symmetrical, after interaction of one equimolar aluminum chloride, it becomes unsymmetrical so that, two cinnamate ions are equal, one is different. As a matter of fact, in all experiments always \(\frac{2}{3}\) of oligomers and \(\frac{1}{3}\) of high polymer are formed. This fact may be attributed to this spatial arrangement.

**EXPERIMENTAL**

All chemicals used are commercial and pure grade. Molecular Weight determination apparatus is Perkin–Elmer Coleman Model: 115. IR spectrophotometer is Perkin–Elmer Model: 377.

**Aluminum cinnamate**: 14.8 g (0.1 moles) of cinnamic acid dissolved in 14.3 g (0.05 moles) of \(\text{Na}_2\text{CO}_3\) 10\(\text{H}_2\text{O}\) in water to make 100 ml aqu-
euous solution by slightly heating in a water bath. A solution of 12.0 g (0.05 moles) of AlCl₃.6H₂O dissolved in 50 ml of water, this slowly added into the first solution while stirring. Formed precipitate filtered out by suction, dried in air and powdered, 13.6 g (87%). This is not soluble in water and other solvent and it has not a definite melting point.

Oligomers of Cinnamic Acid: In a round bottom flask, equipped with reflux condenser, introduced 7.8 g (0.05 / 3 moles) of aluminum cinnamate 15 g (0.1 moles) of anhydrous AlCl₃ and 200 ml of chloroform. Mixture heated under reflux for 5 hours. Cooled down and poured in a crouched ice containing enough amount of HCl, stirred for one hour for hydrolysing. Dark yellow precipitate filtered off by suction, washed twice with water and dried. Crude product 6.5 g. Melting point 120°C.

Crude product dissolved in a dilute solution of sodium carbonate. Insoluble material was filtered out and filtrate acidified with dilute hydrochloride solution. Precipitate filtered again washed twice with water and dried. 3.9 g, melting point 115–120°C. IR spectra showed unsaturation (alkene) (= 1600 cm⁻¹), carbonyl group (= 1710 cm⁻¹), carboxylic acid carbonyl (= 1710 and 1690 cm⁻¹). Chemical tests: Baeyer’s tests with KMnO₄ solution and bromin addition was positive showing the double bond, Tollen’s tests (silver mior tests) was positive showing an aldehyd group and solubility in NaHCO₃, indicating the presence of the –COOH group. Separation of this material into its components by fractional Crystallization colon and thin layer chromatography were unsuccessful.

2,4 - Dinitrophenylhydrzone Derivative: 0.3 g of above crude product dissolved in smallest amount of ethanol. In a sparette vessel containing 1 ml conc. HCl and 10 ml of ethanol, dissolved 0.2 g 2,4-dinitrophenyl-hydrzone by heating slowly. Two solution were mixed together and heated for 30 minutes. Formed precipitate filtered out, washed with small amount of ethanol and dried. 0.2 g, melting point 200°C (decomp.)

This 2,4- dinitrophenylhydrazine mixture was fractionally recrystallized from water-ethanol (50v/50v) mixture into three fraction. IR spectra, chemical tests indicated that each fraction has free carboxylic acid group and alkenic double bond. Molecular weight determined by three different method:
1- Vapour pressure depression method using Perkin–Elmer apparatus,

2- ICl addition to the double bond and iodometric titration method,

3- Kjehldahl “N” estimating method.

These are with accordance with each other, (Table 1.)

**Aluminum p - Methylcinnamate:** This is prepared as above using 7.7 g (0.08 moles) of p-methylcinnamic acid 11.44g (0.04 moles) of Na₂CO₃.10 H₂O and 10.8 g (0.04 moles) AlCl₃.6H₂O. 7.5 g (90 %).

**Oligomers of p - Methylcinnamic Acid:** Similar experiment as cinnamic acid oligomers, was effected with 1.71 g (10/3 mmoles) of aluminum salt of p-methylcinnamic acid, 3.0 g (20 mmoles) of anhydrous aluminumchloride and 30 ml of chloroform. The reaction mixture was worked up as cinnamic acid and 1.2 g crude product obtained. Sodium carbonate soluble fraction is 0.78 g (65 %), melting point 200°C (de-comp.). Insoluble high polimer is 0.42 g (35 %) in this case. Also approximately 0.3 g unreacted p-methylcinnamic acid recovered in this experiment. IR spectra, chemical tests gave similar results as cinnamic acid.

**2,4 - Dinitrophenylhydrazone Derivative:** 0.4 g of above crude product dissolved in a minimum amount of ethanol in a separate vessel, 0.2 g 2, 4-dinitrophenylhydrazine was dissolved in a small amount of HCl + methanol mixture. Two solution were mixed by stirring and heated, formed precipitate filtered and washed twice with small amount of methanol and dried. 0.31 g material was obtained. Solubility, IR spectra and chemical tests showed the similar properties. This mixture was Crystallized from ethanol + water (50v; 50v) mixture into two fraction. Experimental and theoretical molecular weight of these compounds are given in Table II.

**REFERENCES**


WISLICENOUS, W., EBLE, K., Ber., 50, 250, 1917.