SYNTHESIS OF SOME POLYMERS FROM BENZYL ALCOHOL OR ITS DERIVATIVES

by

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This Thesis

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(Signature of Research Adviser)

This thesis is dedicated to Professor William B. Martin. His technical assistance and vast experience enabled me to stay on the right path. Equally as important was his pleasant friendly manner which made working on this project much easier.

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PREFACE

It should be noted that in the following text, the use of "Reaction (Roman Numeral)" refers to the experimental reactions in their chrononological sequence. On the other hand, "Reaction (Arabic Numeral)" refers to reactions listed in the discussion on pages 20 and 21.

INTRODUCTION

The orininal project was concerned with the production of ortho-nitro-para-[ω-(β-naphthyl)]-ethyl-benzyl alcohol or its alkyl-ether. This was to be accomplished by following a five step synthesis, the first step of which was a Friedel Crafts acylation of methyl-benzyl ether according to reaction (1).

In working up the product, it became apparent that a moderate degree of polymerization had taken place. Altering the reactants only added to the degree of polmerization and the apparent molecular weight. For this reason, it was decided that it would be more interesting to investigate the polymers that were being formed, and their various properties. Therefore, the problem was formulated as follows: What is the nature of the polymers that are formed when methyl-benzyl ether and benzyl alcohol are acylated?

These studies were carried out by running various related reactions and analyzing the products with infra-red and attenuated-total-reflectance spectrophotometry.

These reactions were carried out using anhydrous aluminum chloride catalyst. Aluminum chloride is one of a class of substance called Lewis acids (ie. electron pair acceptors).

Only one literature reference to such a polymerization of benzyl systems (benzyl chloride, ethers, alcohols or esters) with Lewis acids was found, although the literature search carried out on this aspect was not an exhaustive one. Noller (5) mentions polymerization of benzyl alcohol with Lewis acids or sulfuric acid to give polymers.

EXPERIMENTAL

REACTION I

The solvent used for this reaction was tetrachloroethane (Eastman Chemical Company). Approximately 200 ml. of solvent was added to a round bottom flask. To this, 16.24 grams of acetic anhydride (Fisher Chemical Company) and 21.04 grams of methyl-benzyl ether (K and K Laboratories) were added. The aluminum chloride (50.18 grams) (Fisher Chemical Company) was added slowly. A violent reaction occured evolving much heat. An ice bath was used to slow the reaction. Hydrogen chloride was given off rapidly. The reaction quickly took on a dull red color characteristic of aluminum chloride complexes. Upon completion, the reaction was terminated with ice chips. This was followed by rapid evolution of hydrogen chloride and heat. The color turned green as the sample was extracted with water. After decanting off the water, the sample was extracted with ether and the solvent was allowed to evaporate. The result was a light green solution that showed no characteristic carbonyl absorbtion in the rather poor infra-red spectrum. The aromatic C-H absorbtion at 3.32 μ was weak but stronger than the 3.46 μ aliphatic C-H stretch. The aliphatic C-C stretch at 6.9 μ was moderately weak. Strong absorbtion at 7.85 μ indicated CH_2OH of $AlCl_3$-catalysed hydrolysis of The ether. Broad absorbtion at 12-14 microns could be interpeted as due to 1,2-and 1,4-substitution, and to rocking of a phenyl-methyl low molecular weight polymer chain. Other unexplained bands are 8.08 microns (medium), 8.88 microns (strong) and 9.89 microns (strong).

REACTION II

In this reaction, carbon disulfide was used as a solvent. Approximately 250ml. of solvent was placed in a round-bottom flask. To this, 20ml. of methyl-benzyl ether and 13.2ml. of acetyl bromide (Eastman Chemical Company) was added. Fifty grams of aluminum chloride (Fisher Chemical Company) and 25 grams of sodium carbonate were added slowly to the reaction.

As in the first case, the reaction was exothermic in nature. The hydrogen chloride gas was given off at a much reduced rate. This was due to the neutralizing effect of the sodium carbonate. The reaction color was again a dull red.

Upon completion of the reaction, ice was added and the product was extracted with water. The result was a dark yellow gummy material floating on the water. This tacky substance was heated under partial vacuum and the resulting clear liquid, approximately 2ml., was separated. A 2,4-dinitro-phenylhydrazine derrivative was prepared, (M.P. 178). This indicated the carbonyl nature of the product. Because of the nature of the reactants, the carbonyl must have been a ketone.

REACTION III

The solvent was again carbon disulfide. Approximately 200ml. of solvent was placed in a round bottom flask. To this was added 11.70 grams of methyl-benzyl ether (K and K Laboratories). Slowly, 49.20 grams of aluminum chloride (Fisher Chemical Company) was added and, along with this, 20 grams of sodium carbonate. This reaction was treated in a similar manner to the others. The reaction was found to be quite exothermic in nature and some hydrogen chloride was evolved. Upon the completion of the reaction, the water extraction was carried out. The water and the product were allowed to stand in an open dish. The result was a water layer covered with a thick yellow gummy material. The water was poured off and the solid was found to be soluable in ether. The product was analysed by infra-red spectrophotometry and the results are discussed later in this report in discussion section.

REACTION IV

In this reaction as in the others, carbon disulfide was used as the solvent. In this case, 40 grams of benzyl alcohol (Fisher Chemical Company) and 27 grams of acetyl chloride were added. For this case, a vast excess of aluminum chloride (Fisher Chemical Company) was slowly added. The reaction was treated in the same way as before and the product was a large amount of light yellow polymeric substance. This was boiled in ether but was found to be insoluable. It was then heated with trituration in hydrochloric acid, but this had no effect. Finally, the solid was dried throughly and suspended in hydrochloric acid for twelve hours. An ash content was taken on this solid after treatment and was found to be 1.84 percent. The softening point of this pliable material was 145-150° C.

SOLUBILITY OF THE POLYMER MADE FROM BENZYL ALCOHOL-ACETYL CHLORIDE

Water	insoluable
Ethanol	insoluable
Benzene	insoluable
Methanol	insoluable
Toluene	slightly soluable
Dimethylformamide	slightly soluable
Dimethylacetamide	slightly soluable
Dimethyl-Sulfoxide	slightly soluable
Meta-para-Cresol	slightly soluable
Methyl-ethyl-ketone	slightly soluable
Camphor	insoluable

REACTION V

This reaction was carried out exactly the same as number (IV), with only the temperature changed. Carbon disulfide was the solvent. Forty grams of benzyl alcohol (Fisher Chemical Company) and 27 grams of acetyl chloride were added. The flask was then immersed in a trough containing a dry ice-acetone bath (-73° C). Only 92.54 grams of aluminum chloride were added because the complexes had completely tied up the reaction in a gravel-like matrix with that amount. The reaction took place, however, and the product formed was somewhat similar to that formed in reaction (IV). This polymeric substance was stickier in nature and was partially soluable in ether.

REACTION VI

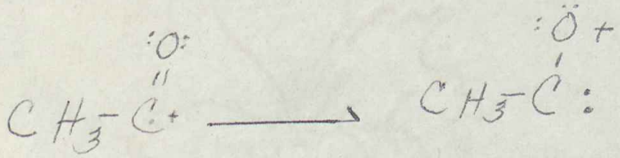
Reaction (VI) was an attempt to polymerize benzyl alcohol by itself using aluminum chloride as a catalyst in carbon disulfide. Twenty-five grams of benzyl alcohol (Fisher Chemical Company) was added to the solvent and 52.5 grams of aluminum chloride (Fisher Chemical Company) was added slowly. As in the other cases, the reaction was kept under control by use of an ice bath. After the standard treatment, the product was found to be a reddish black solid that was soluable in toluene. The softening point of this product was found to be 85-90° C.; this time the material became fluid more readily than in earlier products.

REACTION VII

Benzyl acetate was produced by reacting benzyl alcohol with acetic anhydride. For this reaction, 54.43 grams of acetic anhydride and 51 grams of acedic ahhydride were refluxed. The unreacted benzyl alcohol was distilled off (b.p. 205°C.) and the resulting benzyl acetate was reacted with 86.1 grams of aluminum chloride (Fisher Chemical Company). The resulting product, after treating the reaction mixture with ice and water in the usual manner, was very similar in appearance to the product formed in reaction (VI).

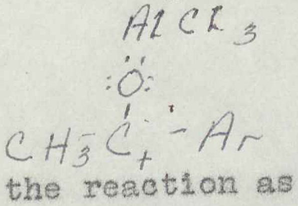
DISCUSSION

The original reaction was an attempted acylation of methyl-benzyl ether with aluminum chloride catalyst. The reaction was intended to proceed as shown in reaction (1). This reaction can be grouped with the general class known as Friedel-Crafts reactionS. The aluminum chloride reacts with the acetyl chloride to form a carbonium ion. The ion is stabilized by the pi bond system, and perhaps somewhat by hyperconjugation.



$$\mathrm{CH_3{-}\overset{\overset{:O:}{\|}}{C}{}^{+}} \longrightarrow \mathrm{CH_3{-}\overset{\overset{:\ddot{O}+}{|}}{C}:}$$

The Friedel-Crafts acylations are found to require more than a mole-for-mole amount of an electrophilic catalyst. The product of an acylation is a ketone which is in itself basic and may inhibit the reaction by tying up the catalyst as shown below:

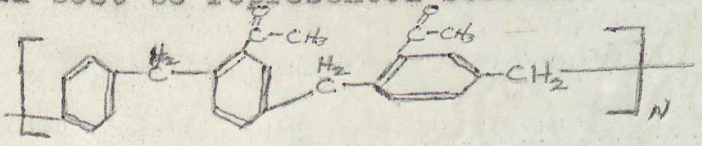


$$\mathrm{CH_3{-}\overset{\overset{\overset{\bar{Al}Cl_3}{\cdot\cdot}}{:\ddot{O}:}}{\underset{+}{C}}{-}Ar}$$

This of course will retard the reaction as well as limiting the effectiveness of aluminum chloride.

The overall reaction would ideally progress as in reaction (2). This was not the case however; the final product was a gummy, polymer-like substance that Was soluable in ether. The solid, when dried, still retained its plyability. For this reason, it was necessary to look further for a possible explanation. It is conceivable that the acetyl chloride polymerized with itself to some extent as shown in reaction (3). It is more likely, since the acetyl chloride was added slowly, that the acetyl chloride collided with the methyl benzyl ether as given in reaction (4).

The ether would be cleaved by the catalyst forming the carbonium ion (reaction 5) and the polymer formed probably would best be represented somewhat as follows:



This mechanism could be used to explain the apparently low molecular weight of the products as suggested by its ether solubility. The ether cleavage should be the rate determining step and this could easily slow the reaction. This would increase the probability of termination because this is a stepwise reaction and dependent upon the concentration of carbonium ion for each step.

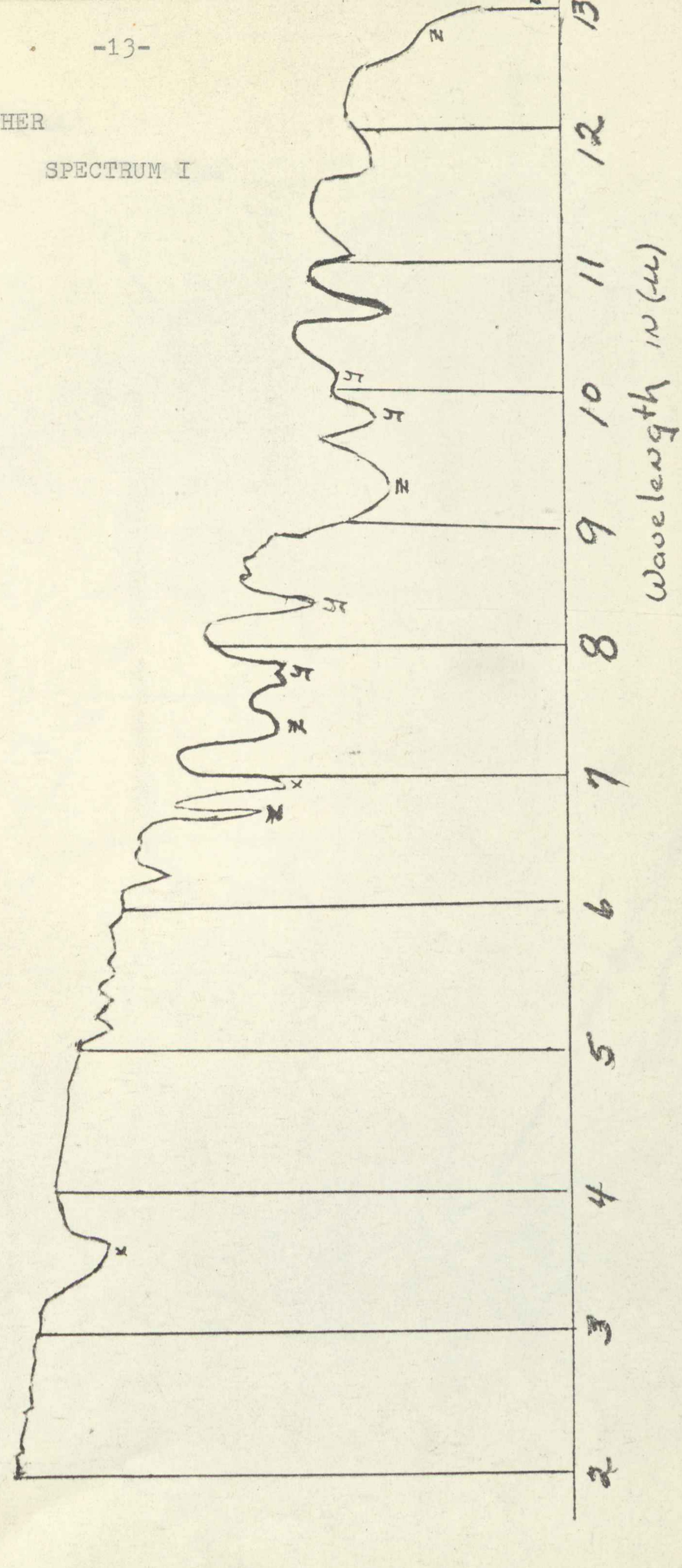
In all, three different reactions were run with methyl benzyl ether. Reaction (I), involving acetic anhydride, was covered earlier in the experimental section. By analysis of the infra-red spectrum it was possible to conclude that the acetic anhydride did not enter into this reaction. The weak CH_2 at about 3.5µ stretch and the weak C-C stretch at about 6.9µ suggested a phenyl-methyl-phenyl structure. The fact that the product was a non-viscous liquid indicated the formation of some dimer, trimer, and/or some low degree of polymerization. The acetyl bromide reaction (II) was very similar to reaction (III) in regard to physical properties of the product. Therefore, for this reason, reaction (II) could be explained by the medhanism already discussed.

Infra-red spectra were taken on many of the products of the experimental reaction of methyl-benzyl ether and were compared with the methyl-benzyl ether spectrum (I). Absorbtions labeled X are those caused by methyl groups.. The Y peaks denote the C-O stretch (ether linkages) and the Z peaks are probably those caused by ring structure. The small peaks between five and six microns are caused by mono-substitution of the aromatic ring. Spectrum number (II) is that of the product of reaction (III). Absorbtions, similar to those of spectrum (I), are labeled in the same code. The largest difference occured near six microns (c). This was due to the carboxyl absorbtion of the acetyl group. Peaks at 6.2 and 6.7 microns were caused by aromatic ortho-di-substitution or unsymetrical-di-substitution (o). This supported the structure previously given for the polymer chain.

METHYL-BENZYL ETHER

SPECTRUM I

SAMPLE I
METHYL-
BENZYL ETHER



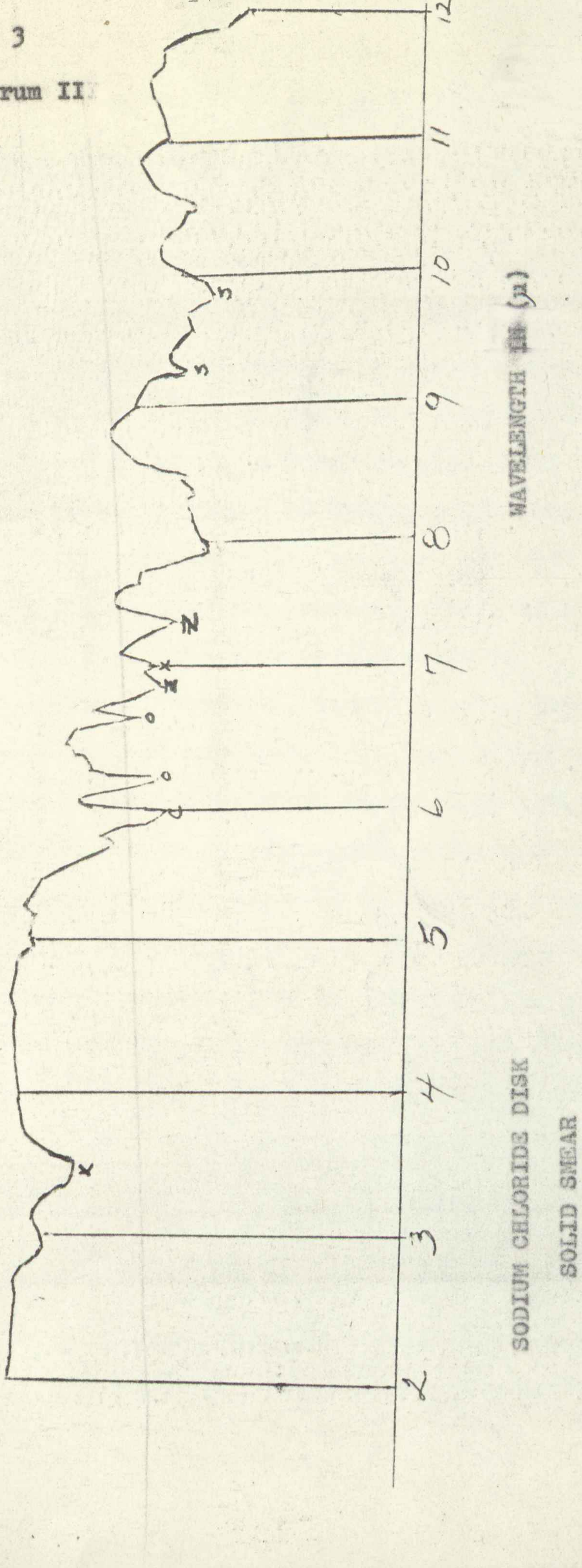
SODIUM CHLORIDE
SOLID SMEAR

SAMPLE NO. 3

Spectrum II

II

SAMPLE NO. 3



When benzyl alcohol was used in place of the methylbenzyl ether, the apparent molecular weight of the resulting polymer seemed to increase. This could be explained by examining the difference between the two chemicals. As stated before, the ether was cleaved by the aluminum chloride. In the case of benzyl alcohol, the aluminum chloride picked up the (O-H) group as in reaction (6). This was followed by the rapid evolution of hydrogen chloride gas. This reaction should proceed quite rapidly, and with the acetyl chloride acetylating the aromatic rings, it should form a moderately high molecular weight polymer.

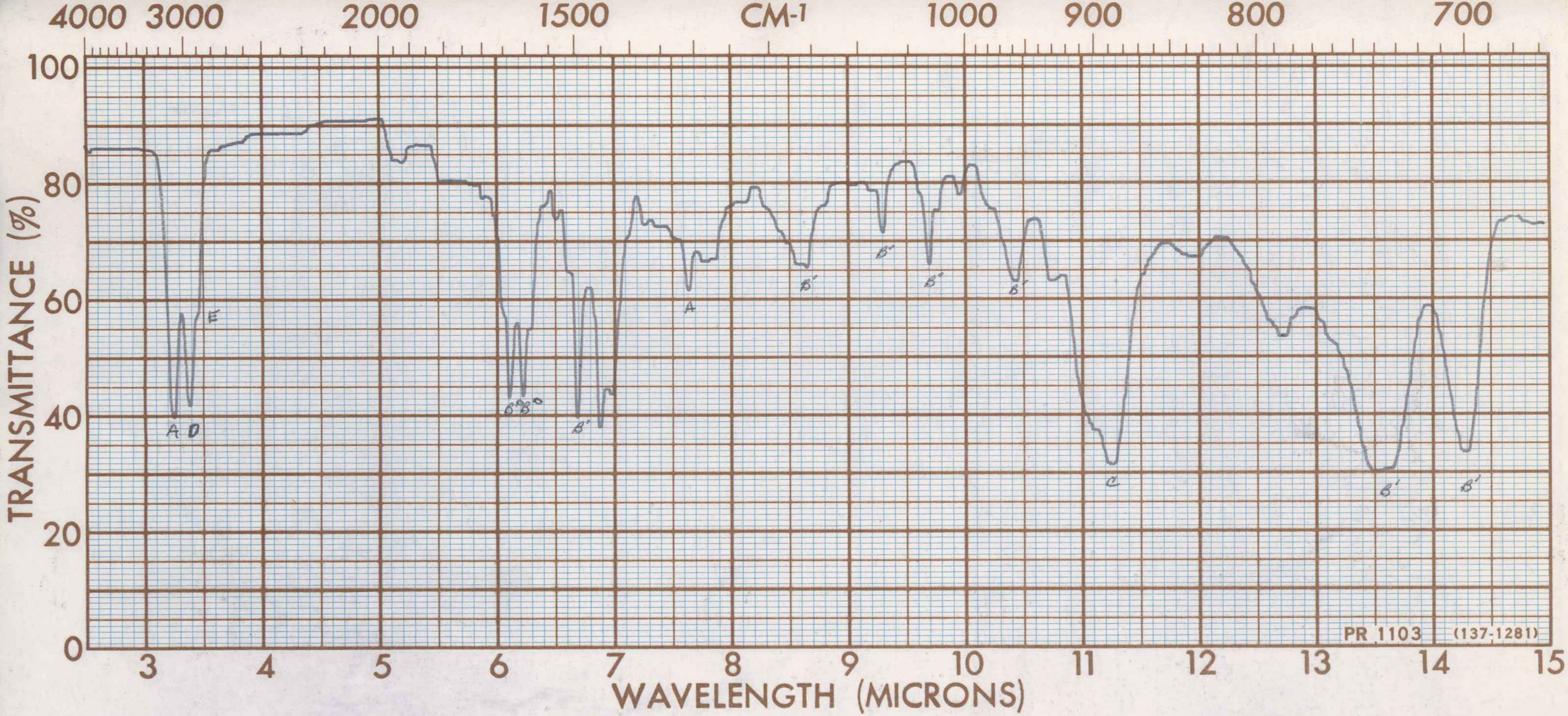
According to the literature, benzyl alcohol self-polymerizes with an acid catalyst. (5) This high molecular weight polymer is produced as shown in reaction number (7). The product is the result of ortho-para self-condensation. Condensation polymerization proceeds by stepwise intermolecular condensing of functional groups. This particular reaction was initiated as indicated in reaction (8). The carbonium ion is stabilized by resonance and the structures are shown as "reaction (9)". Because of this stabilization, the carbonium ion can retain its identity long enough to collide with another benzyl alcohol molecule, thus causing the polymerization.

The spectra of the benzyl alcohol self-polymerization product and the polymer formed from benzyl alcohol and acetyl chloride are included in the following pages.

Spectrum III, (the benzyl alcohol polymer) was interpreted as follows: A= alcohol (this could be terminal CH_2OH groups); B°= ring structure; B'= ortho and unsymetrical-disubstitution of the ring; C= C-C stretch; D= aromatic hydrogen; and E= hindered CH_2 absorbtion. The latter could be attributed to the fact that the methyl groups are spaced between large, bulky benzene rings.

Spectrum IV, the product of reaction (IV), (benzyl alcohol and acetyl chloride) shows a similar abosrbtion to that of Spectrum III between 3 and 3.5 microns. This however, is not very well resolved possibly due to absorbtion caused by moisture in the sample. The most significant difference is the absorbtion at approximately 5.99 microns (X). This is significant in that it shows that the acetyl chloride does enter into the polymerization as postulated earlier. The peak labled F is most likely due to aliphatic ketone. This would tend to back up the idea that acetyl chloride polymerizes with itself to some extent. It should be pointed out that spectrum IV is an A.T.R. (attenuated-total-reflectance) curve. There is no significant difference is the way a particular peak is shown between this method and transmittance methods. The remainder of the peaks are labeled using the same code as stated for spectrum III.

SPECTRUM NO. III
SAMPLE



SPECTRUM NO. III

SAMPLE Benzyl alcohol polymer

Product of reaction VI

ORIGIN

PURITY

PHASE Solid

THICKNESS .1 %

LEGEND

1.

2.

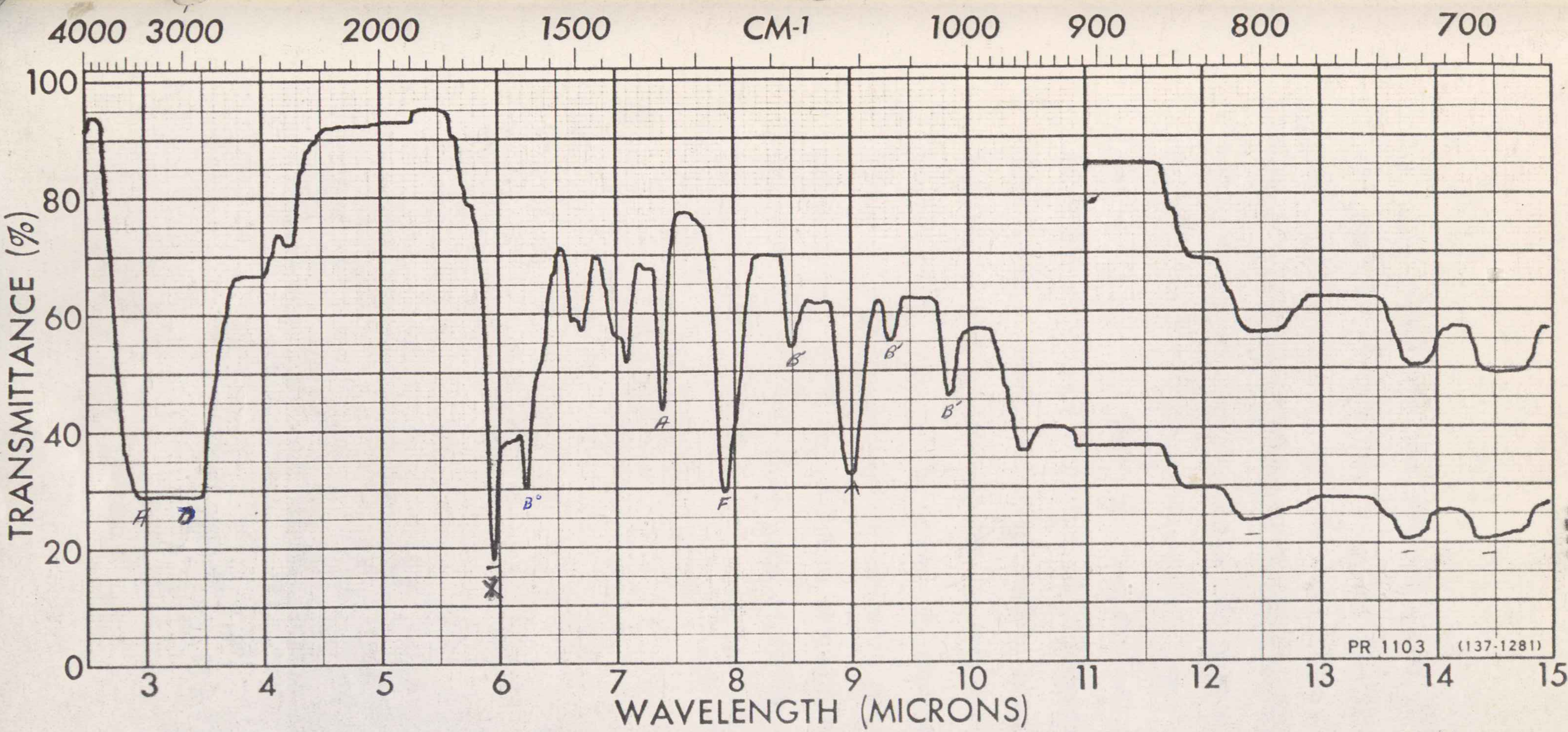
DATE 4/22/64

OPERATOR J. R.

REMARKS ~~KBr 200 mg.~~

Sample 2 mg. pressed at 1200 lbs. per square inch.

SPECTRUM NO. IV
SAMPLE



SPECTRUM NO. IV	ORIGIN	LEGEND	REMARKS Spectrum
SAMPLE Polymer		1.	was repeated from 11-
formed from Benzyl	PURITY	2.	15 microns for better
Alcohol and acetyl	PHASE Solid	DATE 2/25/64	resolution
chloride	THICKNESS A.T.R.	OPERATOR J. R.	

RECORDING CHARTS
GRAPHIC CONTROLS CORPORATION
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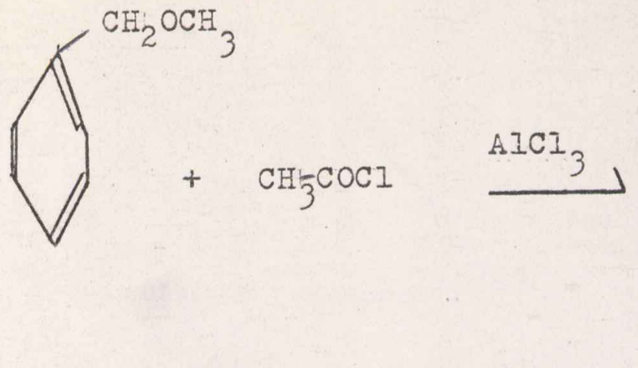
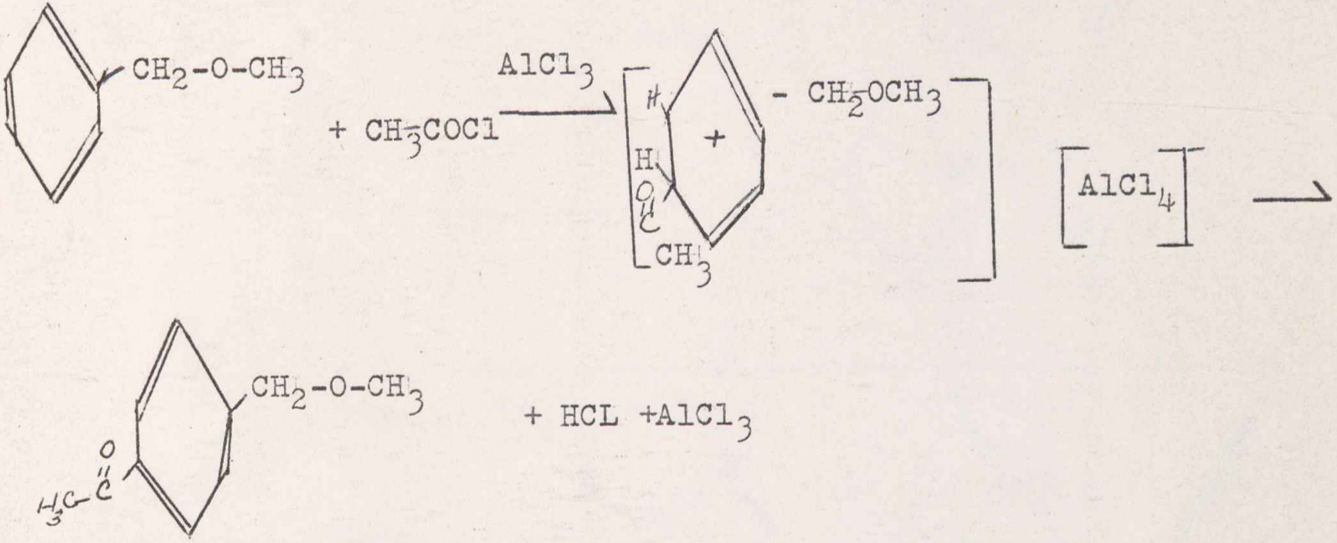
The fact that the polymer produced in reaction (IV) was so hard to put into solution indicated a moderately high molecular weight. This was also a reason that no effective molecular weight determination was accomplished since freezing point depression (Rast method) and viscosity determinations were unsuccessful. One of the projected means of analysis that was not carried out due to a lack of time was to submit the product of reaction (IV) to the iodoform test. Using sodium hydroxide and iodine (iodine-potassium iodide solution) the acetyl groups could have been converted to carboxylic ions. Titration would then have given an average number of carbonyl groups per known amount of polymer. This information coupled with a carbon oxygen analysis would have shed some light on the actual structure of the chain.

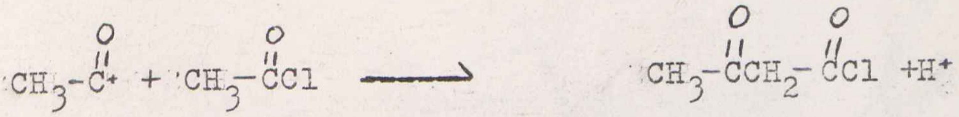
REACTION (1)



REACTION (2)

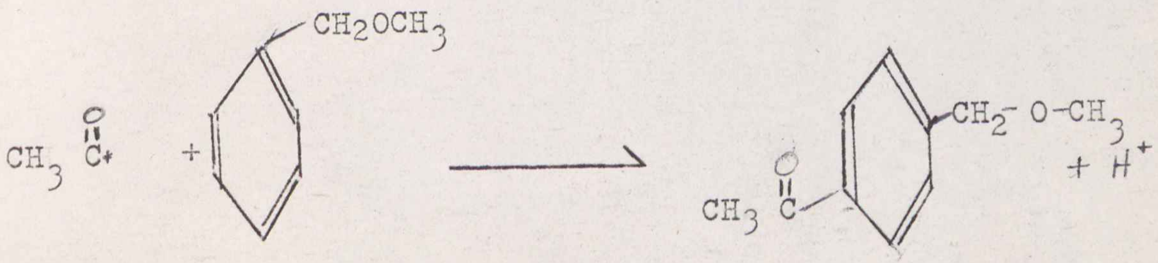


REACTION (3)

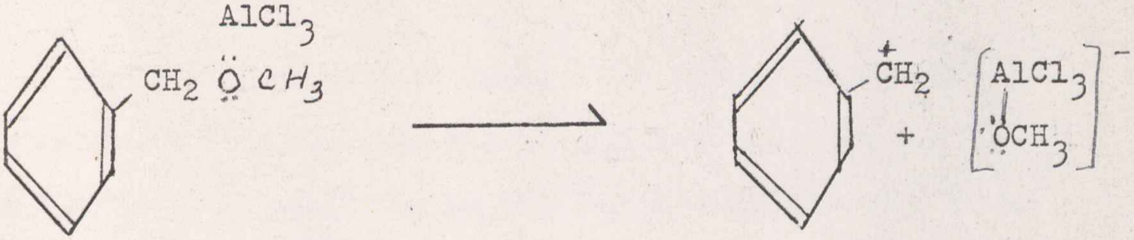


$$CH_3-\overset{O}{\overset{\|}{C}}{}^{+} + CH_3-\overset{O}{\overset{\|}{C}}Cl \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}CH_2-\overset{O}{\overset{\|}{C}}Cl + H^+$$

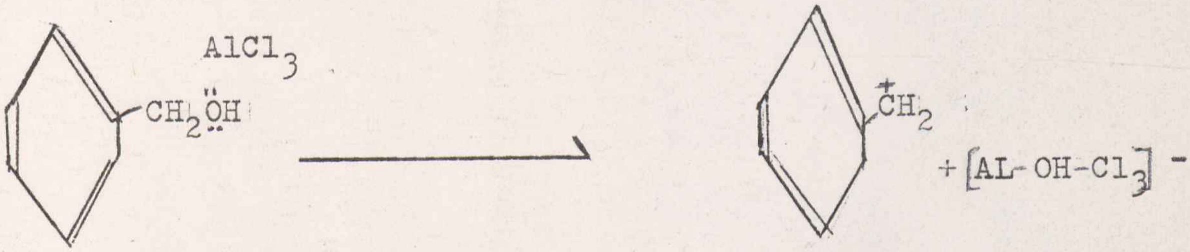
REACTION (4)



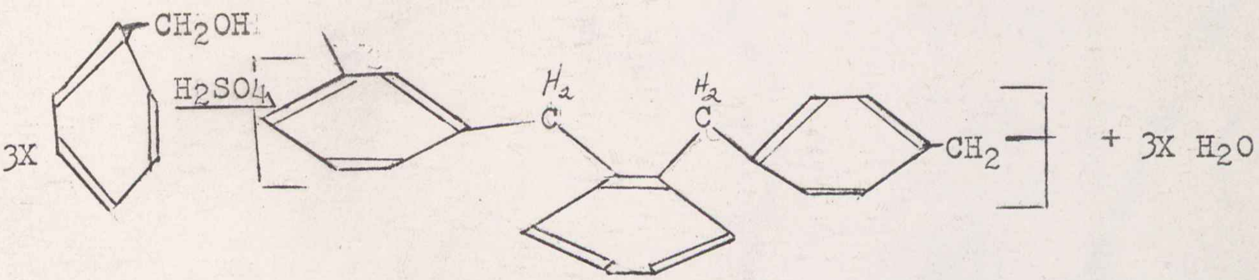
REACTION (5)



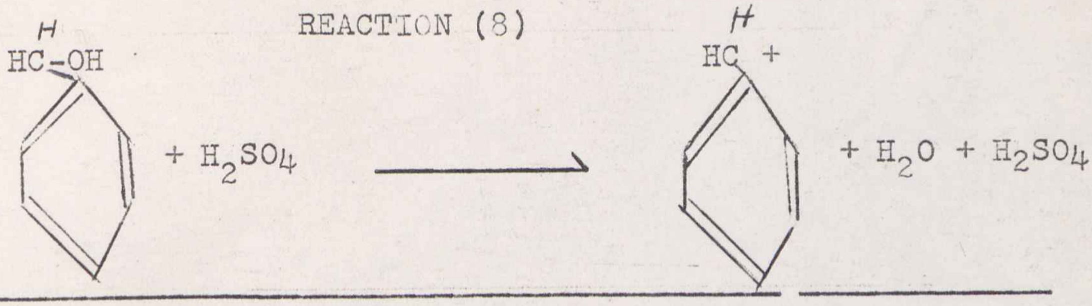
REACTION (6)



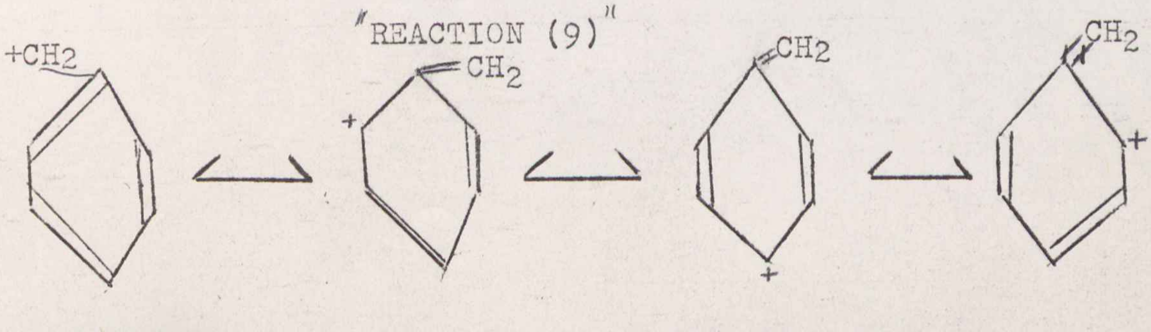
REACTION (7)



REACTION (8)



"REACTION (9)"



SUMMARY

The polymers formed during the acylation of both methyl-benzyl ether and benzyl alcohol were the result of carbonium ion formation in the Friedel-Crafts reaction. These polymers contained both the acyl and the benzyl groups in undetermined relative amounts.

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