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A STUDY OF THE REACTION OF
METHYL ETHYL ISOPROPYL
CARBINOL WITH BENZENE AND
ALUMINUM CHLORIDE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
William S. Thurber
1948

THESIS

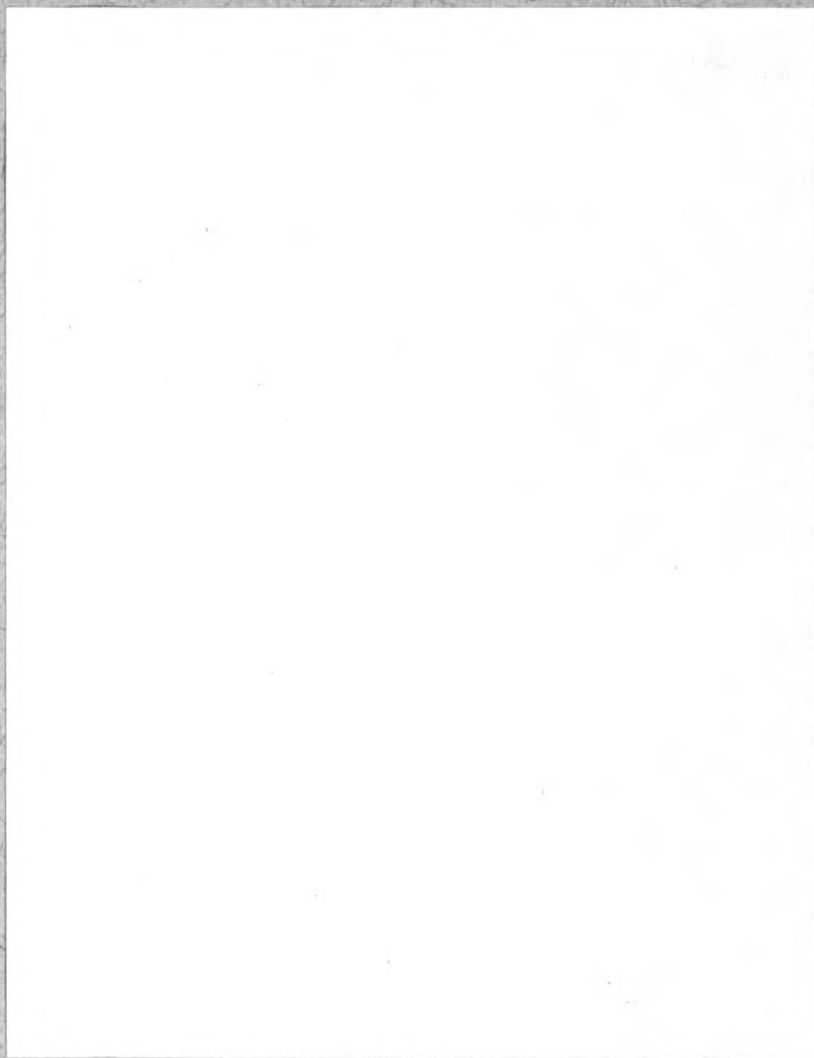
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**A STUDY OF THE REACTION OF
METHYL ETHYL ISOPROPYL CARBINOL WITH BENZENE
AND ALUMINUM CHLORIDE**

by

WILLIAM S. THURBER

A THESIS

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CONTENTS

	Page
Introduction.....	1
Historical.....	3
Theoretical.....	6
Experimental.....	10
I. Preparation of Methyl Ethyl Isopropyl Carbinol.....	10
II. The Condensation Apparatus.....	11
III. Condensation, Separation and Fraction- ation.....	13
IV. Identification of Fractions.....	17
Discussion.....	23
Summary.....	28
Bibliography.....	29

INTRODUCTION

The condensation of aliphatic tertiary alcohols with benzene or phenol in the presence of anhydrous aluminum chloride has been studied extensively by Huston and co-workers in this laboratory.

In the early work, beginning with that of Huston and Friedemann (1) in 1916, the studies were primarily concerned with the formation of the direct condensation product. However, all workers have reported fragmentation to some degree. This fragmentation being greater with highly branched alcohols, with a subsequent lowering of yields in the expected tertiary alkylbenzenes.

Recent studies (2) (3) (4) (5) have been concerned with the products of fragmentation and rearrangement when reactive conditions and molar quantities of the reactants were varied and when branching on the carbon atom adjacent to the hydroxy carbon was increased.

Huston and Binder (6) have condensed the heptyl alcohols with benzene and obtained good yields of the corresponding hydrocarbon from the straight chain carbinols. With the branched chain alcohols, the hydrocarbon was obtained in small yield with considerable amounts of the halogen derivative of the carbinol being formed. No other products were definitely isolated.

It is the purpose of this investigation to continue the study of the reaction of methyl ethyl isopropyl carbinol with benzene in the presence of anhydrous aluminum

chloride in an effort to determine what products of fragmentation and rearrangement are produced.

HISTORICAL

The studies of the condensations of alcohols with benzene in the presence of anhydrous aluminum chloride were begun in this laboratory in 1916, when Huston and Friedemann, repeating the work of Nef (7), condensed benzyl alcohol with benzene in the presence of aluminum chloride. In addition to diphenylmethane obtained by Nef, these workers reported the formation of di- and tri-substituted benzenes.

Several primary alcohols, methyl, ethyl, propyl, isopropyl, butyl, isobutyl and the isoamyl alcohols, were condensed by Huston and Sager (8), using one-half mole of aluminum chloride to one mole of alcohol. The expected alkylbenzene was not obtained.

In 1933 Huston and Davis (9) condensed triphenyl carbinol with benzene and obtained triphenylmethane rather than the expected tetraphenylmethane. Huston and Goode-moot (10) have condensed three cycloalkyl carbinols to show that the ease of condensation was related to the strain in the ring, a greater strain being more conducive to condensation. Tzukurvanik (11) found that saturated primary aliphatic alcohols do not condense, simple secondary alcohols give a 25-30 per cent yield of the secondary alkylbenzene and tertiary butyl alcohol gives a 60-70 per cent yield of trimethylphenylmethane.

Huston and others (12) have condensed tertiary butyl, tertiary amyl, the three tertiary hexyl, seven

tertiary heptyl and all of the tertiary octyl carbinols with benzene. From these condensations it has been found that the mole ratio of alcohol to aluminum chloride is one to one-half respectively for the optimum production of the corresponding mono alkyl benzene. An increase in branching on the alpha carbon decreases the yields of the expected alkyl benzene and increases the formation of unsaturated compounds, halides and lower alkyl benzenes. Condensations at lower temperatures decreases the amounts of these side products.

Huston and Hughes (13) condensing some dialkyl-aryl carbinols with benzene have reported formation of dimers of the corresponding unsaturated products of the alcohols, as well as the expected diphenyl alkanes.

Kaye and others (14) have condensed a number of secondary alcohols with benzene and found that in general, more than .3 moles of aluminum chloride per one-half mole of alcohol decreases the yields of the mono-alkylbenzenes. The addition of dry HCl throughout the addition of alcohol increases the yields. Welsh and Drake (15) have condensed several tertiary aryl carbinols with benzene and have reported the formation of the corresponding alkene of the carbinol, as well as their saturated dimers.

Norris and co-workers (16) have reported the formation of symmetrical tri-alkylbenzenes from the condensation of primary alcohols.

Huston and Barrett (2) have studied the condensation of the dehydration product of tertiary butyl carbinol and have shown that the reaction is greatly aided by the addition of HCl. The condensation of the alkene however did not give the chloride of the alcohol as does the condensation of the alcohol itself. By mixing tertiary heptylbenzene with aluminum chloride they obtained split products indicating the reversibility of the alkylation reaction.

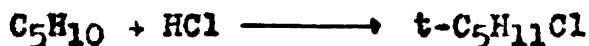
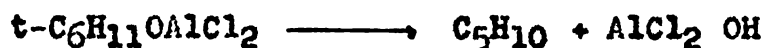
Huston and Van Dyke (17) have found a pronounced demethylation in the condensation of several more highly branched alcohols.

In recent studies by Huston and Smith (3) it was found that by increasing the proportion of anhydrous aluminum chloride from one-third to one-half mole per mole of alcohol in the condensation of 4-methyl-4-heptanol the alkylbenzene fraction was increased approximately fifty per cent. They have also shown that reduction may take place during the condensation reaction and cite as evidence the isolation of the paraffin hydrocarbon fraction from the condensation of non-branched alcohols and isobutane from 2,4,4 trimethyl-2-pentanol.

THEORETICAL

The isolation of alkenes and alkyl halides from the condensation of aliphatic alcohols with benzene in the presence of anhydrous aluminum chloride show that alkylation of benzene with alcohol must be closely related to the alkylation of benzene with alkenes and alkyl halides. Good yields of the alkylbenzene in both cases is additional evidence of this relationship.

Tzukervanik (11) has proposed a mechanism for the alkylation of benzene with aliphatic tertiary alcohols using as a basis the formation of the alkyl halide as an intermediate.



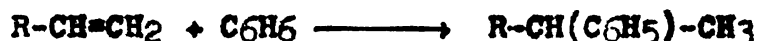
The isolation of alkenes and alkyl halides as by-products has been offered as experimental evidence to support such a mechanism. Tzukervanik suggests that the evolution of HCl was due to the formation of the aluminum chloride - alcohol complex with a subsequent elimination of the gas.

This same mechanism has again been proposed by Tzukervanik to explain the condensation of secondary alcohols with benzene. However, no chlorides or alkenes were

found as by-products from these condensations. This type of mechanism has failed to explain the rearranged products found by Kaye (14), in condensing some secondary alcohols with benzene in the presence of anhydrous aluminum chloride.

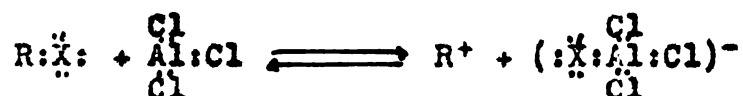
Norris and Sturgis (16) have proposed a similar mechanism with essentially the same steps involved.

McKenna and Sowa (18) have proposed a mechanism whereby a rearrangement of the alkyl groups takes place on certain primary and secondary alcohols. This is based on the formation of alkenes during the reaction. Using Boron tri-fluoride as a catalyst they have isolated small amounts of the alkenes and their polymers.



By this mechanism the condensation of a primary alcohol leads to a secondary alkylbenzene.

Price (19) has proposed an ionic mechanism involving a catanoid attack on the ring. Conductance studies by Wertyporoch and Firla (20) have shown the existence of an ionic complex between aluminum chloride and an alkyl halide.



Ulich and Heyne (21) in studying the equilibrium for the formation of certain catalyst-alkyl halide complexes

postulated by Wertyporouch found that the rate of alkylation is directly proportional to the concentration of the catalyst-alkyl halide complex. This same type of complex may be shown using alcohols or other oxygen containing compounds such as ethers or esters.



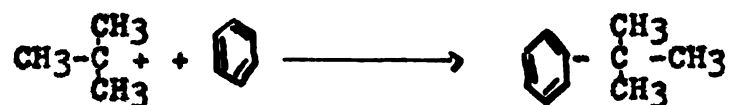
According to Price, the electron deficient carbonium ion formed above may replace a hydrogen atom in benzenoid compounds by association with a pair of electrons from a double bond of the aromatic nucleus to complete its octet.



This reaction becomes more complex in the more highly branched tertiary alcohols. The isolation of such products as tertiarybutyl benzene is an indication that fragmentation and rearrangement must take place as a side reaction. This side reaction may be explained by a shift of an alkyl group to the positive carbon with a shift in the electron arrangement of the molecule so that the carbon adjacent to the original positive carbon now becomes positive with a resulting scission of the chain.



This rearrangement and cleavage allows the activated benzene nucleus to react to form tertiary butyl benzene in the case selected.



This explanation is in accordance with Whitmore's (22) views on molecular rearrangements and will easily explain the rearrangements observed by Kaye (14) in this laboratory.

EXPERIMENTAL

I. Preparation of Methyl Ethyl Isopropyl Carbinol

This alcohol was prepared by use of the Grignard reaction, by the addition of methyl isopropyl ketone to ethyl magnesium bromide, followed by hydrolysis of the resulting addition compound. The procedure followed was that used by G. W. Hedrick (23) in this laboratory.

The Grignard reagent was prepared by placing 36 g. (1.5 moles) of dry magnesium turnings and 200 cc. of anhydrous ether in a one-liter, three-necked flask equipped with reflux condenser, dropping funnel and a mercury seal mechanical stirrer. To this mixture was added 153.5 g. (1.5 moles) of dry, redistilled ethyl bromide in 100 ml. of anhydrous ether. The mixture was stirred during addition and the ethyl bromide and ether added at a rate just fast enough to keep the mixture refluxing gently. After addition was complete, stirring was continued for one hour at room temperature. At the end of this time the Grignard reagent was titrated according to the method developed by Gilman, Wilkinson, Fischel, and Meyers (24). The calculated amount of Grignard was 1.4 moles or a 94 per cent yield. On the basis of this yield, 122 g. (1.4 moles) of redistilled methyl isopropyl ketone in 200 cc. of anhydrous ether was added dropwise and stirring was continued for two hours at room temperature. The mixture was cooled in an ice bath and then poured into a large beaker of ice. Dilute hydrochloric

acid was added to dissolve the magnesium hydroxide. The ether layer was separated and the water layer extracted three times with ether. The combined ether layers were then washed with a ten per cent solution of sodium carbonate until neutral to litmus and then dried for several hours over anhydrous sodium carbonate.

The ether was removed through a packed column and the remaining alcohol was distilled and collected over a two-degree range at reduced pressure.

Yield: 51%

BP₁₈ : 48-49°C

BP₇₅₀: 138-140°C

n_D^{20} : 1.4292

This alcohol has been prepared by Whitmore and Evers (25) and by Hedrick (23). Physical constants obtained check with those Whitmore and Evers obtained by preparing the alcohol from the reaction of methyl ethyl ketone and isopropyl magnesium bromide.

II. The Condensation Apparatus

The condensation apparatus is essentially the same as that developed by Van Dyke (17), variations of which have been used extensively in this laboratory. Figure 1 shows a diagram of the apparatus and the essential parts are listed below:

A. A one liter, three-necked, round bottom flask.

B. Dropping funnel with inner sealed tube and

connections for equalizing the pressure to form an air-tight system.

- C. Mechanical stirrer consisting of an electric motor and glycerine sealed glass stirrer.
- D. Carbon dioxide generator system consisting of a vacuum bottle for solid carbon dioxide connected to a wash bottle consisting of concentrated sulfuric acid and a mercury safety valve.
- E. A side arm delivery tube to which is attached a thermometer and reflux condenser.
- F. A two-way stopcock used to by-pass the ice-salt cooled trap.
- G. Ice-salt cooled trap to condense the vapors of the more volatile liquids, such as benzene and alcohol.
- H. A two-way stopcock used to by-pass the carbon dioxide - acetone cooled trap.
- I. Carbon dioxide - acetone cooled trap to condense any substance that did not boil lower than -80°C .
- J. One-way stopcock operated in conjunction with stopcocks F and H. This was closed when L was adjusted to by-pass the trap.
- K. Mercury trap to prevent back pressure due to the cooling down of the system toward the end of the reaction.
- L. Safety bottle.
- M. Gas nitrometer containing 50 per cent C.P. potassium hydroxide for dissolving the carbon dioxide.

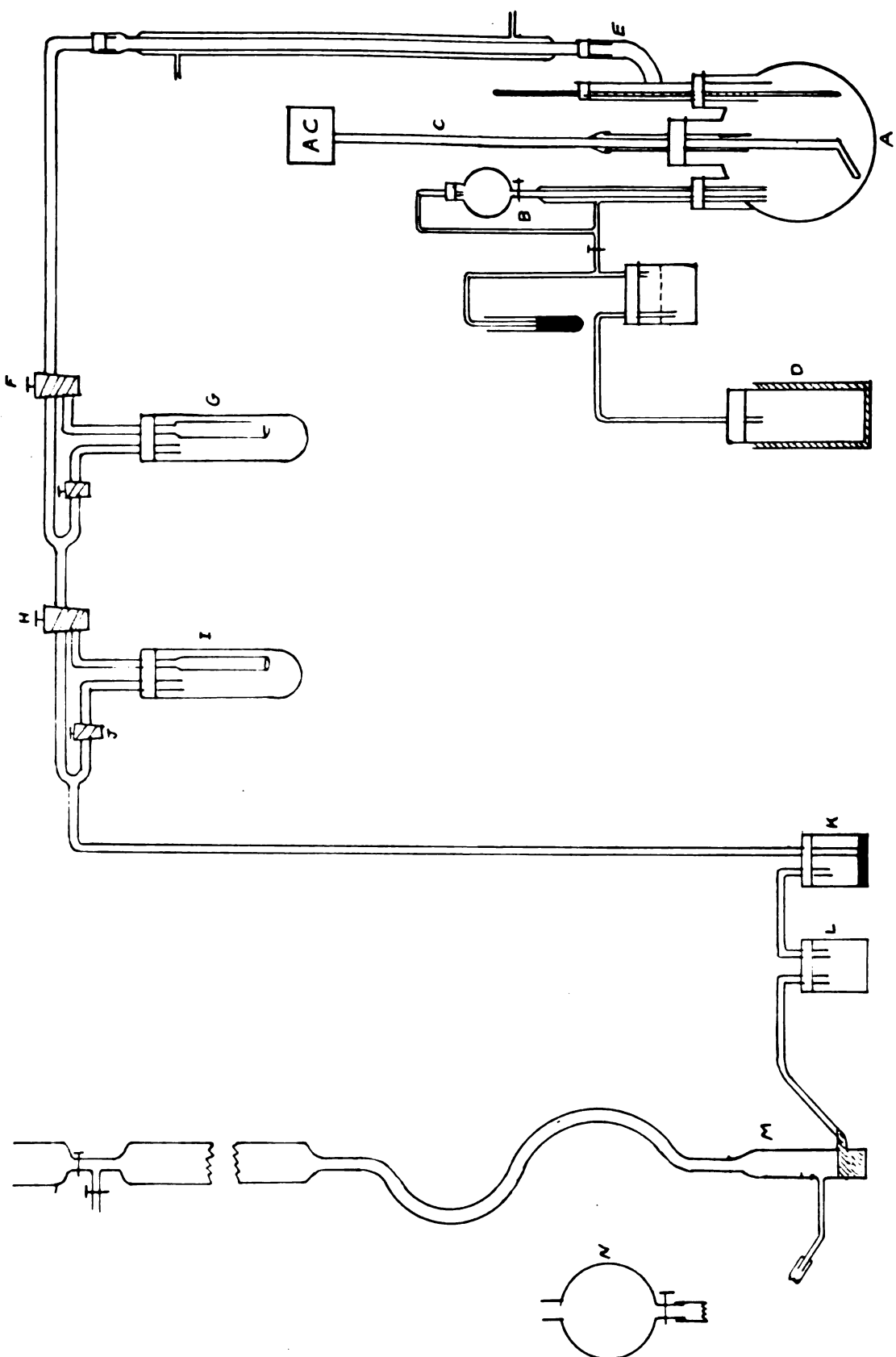


FIGURE 1

The nitrometer was of 300 ml. capacity with a diameter of 25 mm. in the vertical section and 10 mm. in the curved section. Mercury was placed in the base to seal the potassium hydroxide from trap L.

N. Nitrometer leveling bulb consisting of a 250 ml. separatory funnel.

Dewar flasks used to hold the bath solutions and to maintain the traps G and I at their desired temperature are not shown.

III. Condensation, Separation and Fractionation

Two moles of methyl ethyl isopropyl carbinol were condensed with benzene in the presence of anhydrous aluminum chloride. The general procedure followed was that developed by Huston and several earlier workers in this laboratory.

It has been established by Huston and Friedemann (1) that the proportion of benzene to alcohol should be about five moles to one mole respectively. Huston and Barrett (2) and Huston and Smith (3) have found that the proportion of aluminum chloride to alcohol should be one-half mole to one mole respectively in order to obtain the maximum yield of the expected alkylbenzene condensation product. Two condensations were carried out using these proportions. A typical condensation will be described below in detail.

Sixty-six and eight-tenths grams ($\frac{1}{2}$ mole) of C.P. anhydrous aluminum chloride was placed in the reaction flask with 390 g. (5 moles) of anhydrous, thiophene free benzene. This mixture was heated to reflux with stirring to drive off large amounts of air dissolved in the benzene. Hydrogen chloride was evolved in quantity and the aluminum chloride suspension took on a reddish color. The solution was then allowed to cool to room temperature. At this time the system was swept out with CO_2 . The nitrometer was connected and the flow of gas adjusted until microbubbles appeared in the nitrometer. The ice-salt trap and dry ice-acetone trap were connected and the alcohol was added with stirring at a rate just fast enough to maintain the temperature between 30° and 35° C. After addition of approximately one-half mole of the alcohol, considerable back pressure was noticed. This may have been due to a decrease in the gaseous products being formed and a subsiding of the heat of reaction. When the addition was complete, the product was stirred for one hour and then allowed to stand overnight. At this time any gas which formed in the nitrometer was transferred to gas burettes and analyzed. Volatile liquids found in the traps were purified by distillation, their boiling points determined and then sealed. During these condensations only a very small amount of liquid was found in the gas traps. In an effort to determine the boiling point, a time-temperature curve was run revealing a depression of the curve over an approximate ten degree range close to

-23° C. and again at about -10° C. These depressions are in the boiling point range of methyl chloride and isobutane respectively. Theory would predict these compounds as being present. The small quantity of liquid made separation of these liquids and determination of physical constants an impossibility.

Gas caught in the nitrometer was transferred to gas burettes and tested for condensibility by passing it back and forth through a tube immersed in a dry ice - acetone bath. Only a very small amount condensed so that positive identification was still not possible. The gas did, however, burn with a blue to bright yellow flame, giving additional evidence of the presence of methyl chloride.

The reaction product was hydrolyzed by the addition of cracked ice and stirring. The temperature was maintained below 35° C. until addition of a small amount of ice caused no rise in temperature. Then 100 ml. of water was added. The organic layer was separated from the aqueous layer and the latter extracted three times with 25 ml. portions of benzene. The combined extracts and organic layer was dried over anhydrous sodium sulfate.

Distillations were carried out with a 60 cm. helice packed column. The head on the column was designed for distillation under reduced pressure with a take-off for permitting reflux. The condensation products were combined and the solvent distilled off at atmospheric pressure. A carbon dioxide - acetone trap was connected

to the head of the column at this time to condense any low boiling liquids dissolved in the solvent. The amount of liquid caught in this manner was not sufficient for further investigation.

Previous workers in this laboratory (17) (3) have found it necessary to remove the alkyl chloride fraction in order to prevent contamination of the higher boiling fractions. Since Binder (6) had previously isolated and identified this fraction in quantity and had difficulty in making any further separation of the high boiling fractions, no attempt was made to isolate this product. It was removed by refluxing the combined fractions with an equal volume of fifty per cent alcoholic potassium hydroxide for a period of four hours. The organic layer was then separated from the water layer and the former washed with small portions of water. The organic layer was then dried over anhydrous potassium carbonate.

On subsequent distillation the high boiling fractions were found to be free of chloride. Due to the large hold-up in a 60 cm. column, it was found necessary to purify each fraction using a smaller column of the same type. Upon two or three repeated distillations, fractions were obtained sufficiently pure for the preparation of derivatives after the class of compound had been determined. An appreciable quantity of material boiled higher than the expected heptyl benzene and is suspected of being

di- and tri-substituted alkylbenzenes. A small tarry residue remained from the distillations.

IV. Identification of Fractions

Fraction I: This fraction was isolated as a liquid in the dry ice - acetone trap. An attempt was made to determine its boiling point as described in the section on condensation, separation and fractionation. No definite boiling compounds were isolated. The mixture boiled over a range of from -30° to 10° C. Since this is over the boiling range of both methyl chloride and isobutane, they are suspected of being present in this fraction. Gases condensed and isolated in this manner burned with a blue to bright yellow flame, giving additional evidence of the presence of methyl chloride.

Fraction II: Tertiary Butyl Benzene. Three grams of the hydrocarbon per mole of alcohol condensed was isolated. This compound was identified by means of its acetamino derivative. Physical constants of the hydrocarbon are recorded below:

Yield: 3%
BP₇₅₀: 169° C.
BP₁₁ : 53° C.
 n_D^{20} : 1.4926

Melting point of acetamino derivative: $168.5-169.5^{\circ}$ C. Physical constants checked with the literature

(27) and the melting point of the derivative checked with the work of Ipatieff and Schmerling (26) and with Barrett (2).

The method of preparation was that given by Ipatieff and Schmerling (26). The nitro compound was prepared by treating 1-2 cc. of the alkyl benzene with 5 cc. of a 1:1 mixture of concentrated nitric and sulfuric acids. When the reaction of mixture had cooled down, it was poured onto cracked ice and extracted several times with ether. The extracts were washed with water and the ether evaporated.

The nitro compound was dissolved in a few cc. of alcohol and 5 g. of granular tin were added. About 5 cc. of concentrated HCl were added dropwise with shaking. The mixture was shaken until a few drops tested in water showed no marked turbidity. The mixture was then allowed to stand 30 minutes to insure complete reduction. The mixture was decanted into 20 cc. of water and the tin hydrochloride complex salt of the amine extracted with ether; and 40% sodium hydroxide was added to free the amine. The amine was extracted with ether, washed with water, and dried over anhydrous potassium carbonate.

The ether solution was filtered from the drying agent and the ether evaporated. The acetyl derivative was made by adding 1-2 cc. of acetic anhydride to the amino compound. The excess anhydride was then hydrolyzed by warming with 5 ml. of water and the solution evaporated nearly to dryness. The impure solid was filtered off

and washed free of acetic acid. It was then recrystallized from 50% alcohol.

Fraction III: Tertiary Amyl Benzene. A total of seven grams of this compound were isolated and were identified by means of the acetamino derivative. The following physical constants were determined:

Yield: 2.4g

BP₇₄₈: 190° C.

BP₁₅ : 88° C.

n_D^{20} : 1.4917

Melting point of acetamino derivative: 137-138° C.

The acetamino derivative was prepared in the manner previously described. The melting point of the derivative checked with the work of Ipatieff and Schmerling and with Barrett. The physical constants of the tertiary amyl benzene checked with those found in the literature (27).

Fraction IV: 3-Methyl-3-phenylpentane. The physical constants were found to be as follows:

Yield: 5 grams

BP₇₅₀: 215-218° C.

BP₁₃ : 86-88° C.

n_D^{20} : 1.4945

An attempt was made to prove the structure of this compound by means of its acetamino derivative.

However, the small yield of material and the large amount of contamination from the heptyl benzene fraction just above it and the unsaturated fraction just below made purification impossible, and no satisfactory derivative was obtained.

It was interesting to note that in the small fraction immediately before this, there occurred a very sharp decrease in refractive index. The decrease was from 1.4945 to 1.4910. This is a very strong indication of the presence of unsaturated aliphatic compounds. When tested with a 5% solution of Br_2 in CCl_4 , this small fraction gave a very positive test for unsaturation. The B.P. of this fraction is in the range of $\text{C}_{13}\text{H}_{26}$, and our theory would predict the presence of both 3-methyl-3-phenylpentane and these unsaturated compounds. The mechanism of their formation will be taken up more fully in the Discussion. It is felt, however, that the evidence points strongly to the presence of these compounds in this fraction.

Fraction V: Methyl ethyl isopropyl phenyl methane. This fraction was the expected condensation product, but a poor yield was obtained. The compound was isolated in a very pure form, however, and the physical constants reported below are in very close agreement with those recorded in the literature (28) (23).

Yield: 9%
 BP₇₄₈: 220.5° C.
 BP₁₄ : 99° C.
 n_D^{20} : 1.5012
 D_4^{20} : .8886
 20 : 31.24 dynes (Du Nou y)
 29.02 dynes (Drop wt.)

A carbon and hydrogen analysis of this compound has been run by Binder (28), and Hedrick (23) has prepared a derivative of it by converting it to the phenol. Since all physical constants were in excellent agreement with the work of these investigators, it was felt that these additional checks were unnecessary, and that there is no doubt as to the identity of the compound.

Fraction VI: An attempt was made to purify this fraction, but no definite separation could be made. It is suspected of being a mixture of di- and tri-substituted alkyl benzenes. It distilled above 123° C. @ 3 mm. and over a very wide range.

Yield: 31 grams

Fraction VII: Tarry residue

Yield: 5 grams

TABLE I

Fraction Identified	B.P.°C.	n_D^{20}		Lit.	Derivative or means of Identification	Yield (gms.)
		Obs.				
Tertiary butyl benzene	169 (750 mm.)	1.4926	1.4926	(27)	p-acetamino deriv. m.p. 168.5 - 169.5°	3
Tertiary amyl benzene	190 (748 mm.)	1.4917	1.4715	(27)	p-acetamino deriv. m.p. 137 - 138°	7
3-Methyl-3-phenyl- pentane	215-218 (750 mm.)	1.4945	1.4955	(27)	not identified	
Methyl ethyl isopropyl phenyl methane	220.5 (748 mm.)	1.5012	1.4974	(6)	Physical Constant	31

DISCUSSION

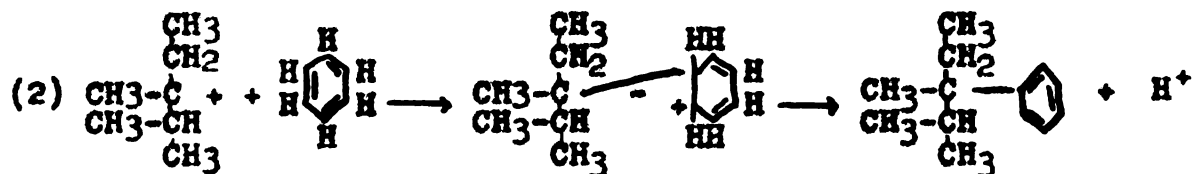
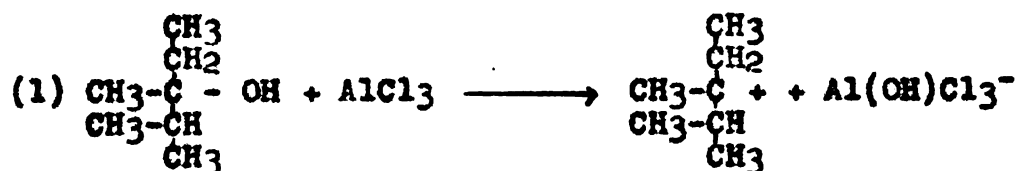
In condensing methyl ethyl isopropyl carbinol with benzene, in the presence of anhydrous aluminum chloride, Binder (6) found that the yield of the expected heptyl benzene condensation product was very low. This was apparently due to considerable fragmentation and rearrangement of the alcohol during the course of the reaction. The purpose of this investigation was to separate and identify these products of fragmentation and rearrangement.

It has been shown by previous investigators in this laboratory (2) (3) (17) that fragmentation takes place to a much greater extent with the highly branched alcohols than with the non-branched alcohols. The large amount of fragmentation found in this study is consistent with these facts.

Whitmore (22) has found that aluminum chloride can cause molecules to rearrange by methyl group migration. Boedtker and Halse (28) have observed a rupture of the molecule with aluminum chloride as catalyst. Both rearrangement and chain rupture are evident in the study of this alcohol.

At the present time, the most generally accepted theory for the condensation mechanism is that of Price (19), as mentioned in the theoretical part of this thesis. On the basis of this theory, the carbonium ion may be formed from the alcohol, the chloride, the alkene or the alkyl benzene. The electron deficient cation then receives its

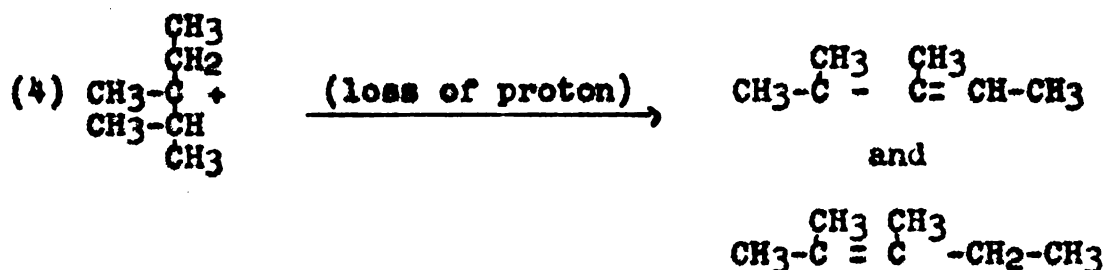
pair from the double bond of the benzene ring. The formation of the condensation product proceeds in the following manner:



The formation of the carbonium ion in equation (1) may now lead to a number of possible side reactions. Combination with the chloride ion present in large quantities would occur as in equation (3). This compound has previously been isolated from the condensation of this alcohol by Binder (6) and no attempt was made to isolate it in this study.

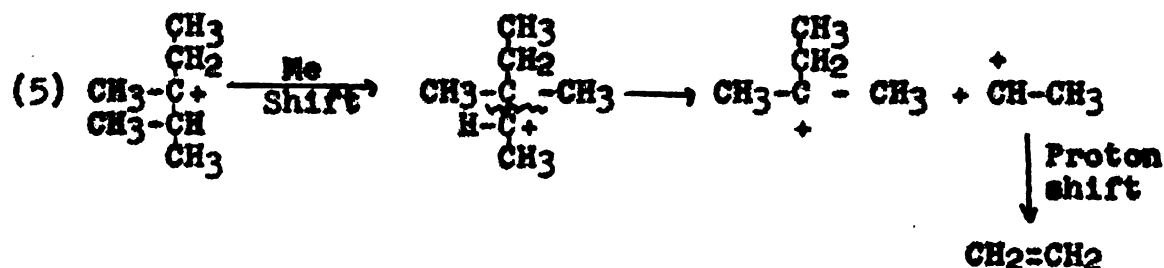


Loss of a proton from the carbonium ion would lead to the formation of an olefin.

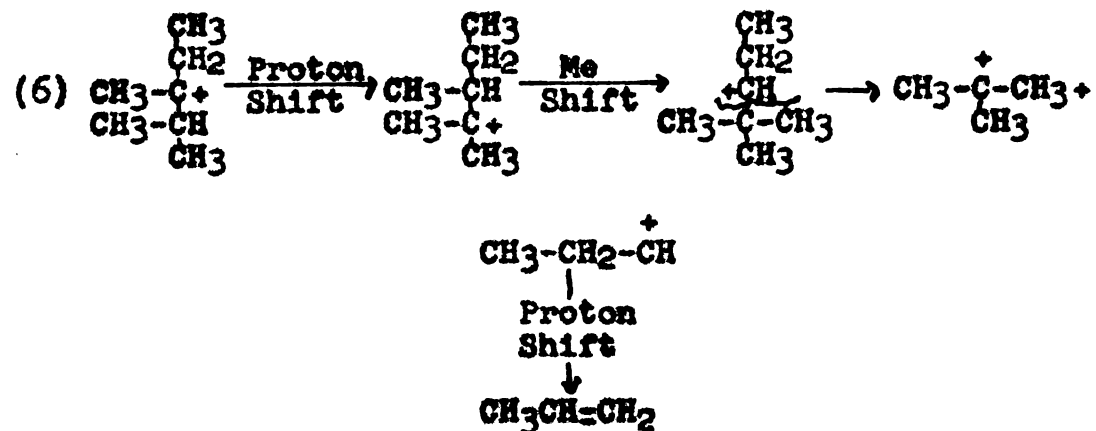


Neither of the two alkenes predicted by equation (4) were isolated in this condensation. However, the solvent removed from the condensation products gave a positive test for unsaturation on treatment with a 5% solution of Br_2 in CCl_4 . The boiling point and refractive index of the solvent were also significantly lowered. On treatment with bromine the benzene was separated from the contaminant but the residue was not large enough to enable a satisfactory separation of the resulting mixture. Since the boiling points of these two alkenes are 86° and 97° C. respectively, it is quite feasible that they may have been present in small amounts.

The formation of t-butyl benzene and t-amyl benzene and the resulting low yield of the condensation product, may be attributed to the tendency of the cation to undergo rearrangement with a resulting rupture of the chain.

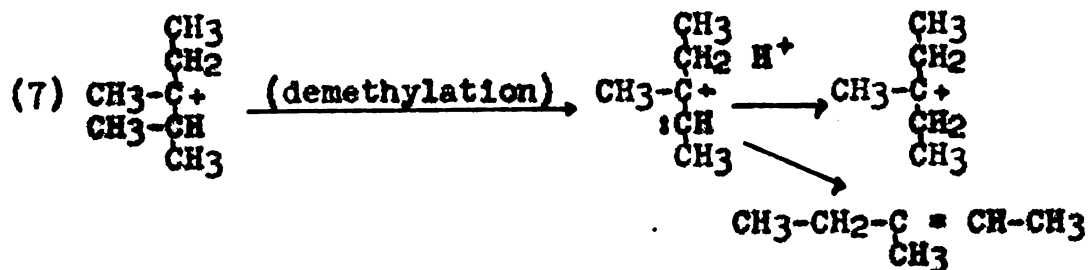


The t-amyl carbonium ion immediately hooks up with the benzene nucleus to form the alkyl benzene. In a similar manner we can account for the formation of t-butyl benzene.

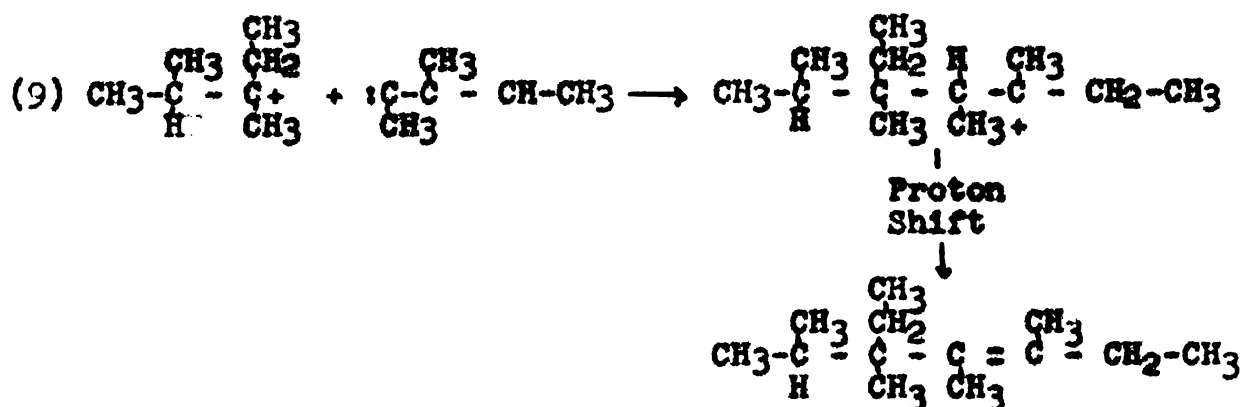


The t-butyl cation may then react with the benzene nucleus to give the alkyl benzene or a proton shift may take place to form isobutene. It appears from previous work in this laboratory (3) (5) that isobutene may condense with benzene or be immediately reduced to isobutane although the mechanism of this reduction is not yet clear. This possibility would account for the isobutane suspected of being present in the gas traps.

If the cation in equation (5) were to undergo demethylation during the methyl shift, we can account for the formation of such products as methyl chloride and 3-methyl-3-phenyl pentane, both of which are strongly indicated as being present among the condensation products. Evidence of such demethylation has been presented by Van Dyke (17) and Barrett (2) in earlier investigations in this laboratory. The mechanism might be as follows:



The tertiary hexyl cation formed could then hook up with a benzene nucleus to form the alkyl benzene. It is quite possible that a demethylated heptyl cation, formed in equation (7) might attack another heptyl cation as follows:



Such a mechanism as the one postulated above would account for the formation of an unsaturated $\text{C}_{13}\text{H}_{26}$ fraction such as is thought to be present in fraction III. Evidence of the formation of such compounds has been presented by Krantz (5) in an earlier investigation in this laboratory.

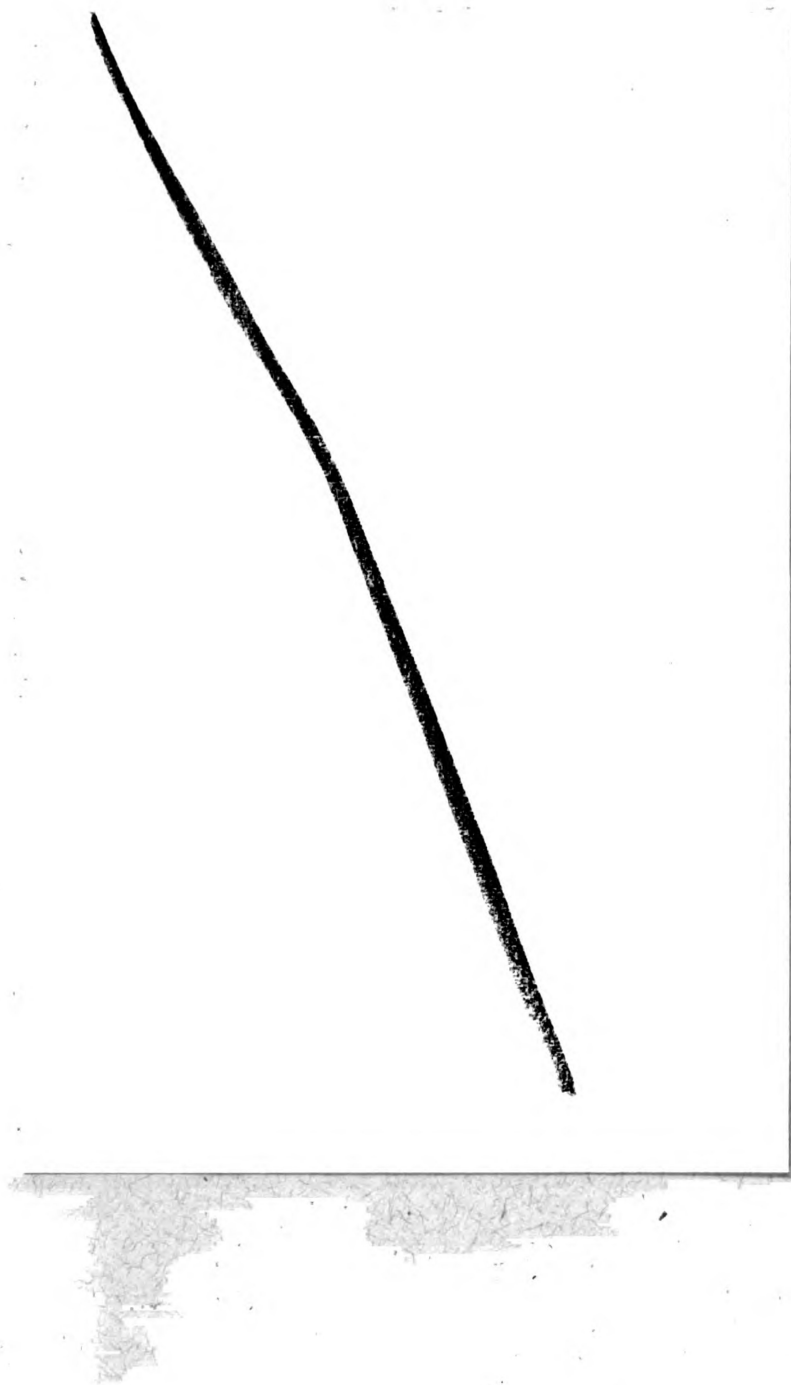
SUMMARY

1. Methyl ethyl isopropyl carbinol was condensed with benzene in the presence of anhydrous aluminum chloride. Only 9% of the expected methyl ethyl isopropyl phenyl methane was obtained.
2. Tertiary butyl benzene and tertiary amyl benzene have been isolated and their structures proven by means of their acetamino derivatives.
3. Several other fragmentary products were isolated but their structures were not definitely proven.
4. Mechanisms have been suggested for the formation of all products.

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