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TITLE A Study of The Fragmentation of Some Tertiary Carbinols When Condensed With Benzene In The Presence of Aluminum Chloride

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A STUDY OF THE FRAGMENTATION OF SOME TERTIARY CARBINOLS WHEN CONDENSED WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Henry Lewis Van Dyke, Thesis (Ph. D.)
Michigan State College, 1944

Condensations were carried out at 40-45° C. using reactants in the ratio of one mole of alcohol, one-third mole of aluminum chloride and five moles of benzene. Gaseous products were collected by means of a suitably designed train and liquid products were separated by fractionation.

2, 3-Dimethylbutanol-2

The yield of 2,3-dimethyl-2-phenylbutane from 2,3-dimethylbutanol-2 was good (40%). The chloride, 2-chloro-2,3-dimethylbutane and the unsaturated hydrocarbon, 2,3-dimethylbutene-1, were formed in about equal amount (20%). The isomer, 2,3-dimethylbutene-2, was not found. Isolation of a small amount of 2-methyl-2-phenylpropane (less than 1 %) was the only evidence of fragmentation.

2,3-Dimethylpentanol-2

The condensation of 2,3-dimethylpentanol-2 with benzene gave, as the main product, 2,3-dimethyl-2-phenylpentane (22%). A smaller amount (14%) of 2-chloro-2,3-dimethylpentane was isolated. The unsaturated fraction C_7H_{14} (10%) showed physical constants near those of 2,3-dimethylpentene-1. Fragmentation, as evidenced by the isolation of 2-methyl-2-phenylpropane, was about one percent.

2,3,3-Trimethylbutanol-2

It was found that in the condensation of 2,3,3-trimethylbutanol-2, as was the case in other alcohols where a tertiary group was attached to the carbinol carbon, that demethylation occured as well as fragmentation of the same type found in the first two alcohols.

The yield of 2,3,3-trimethyl-2-phenylbutane was only nine percent while that of 2-methyl-2-phenylpropane was more than four percent. Small amounts of 2-chloro-2,3,3-trimethylbutane (2%) and 2,3,3-trimethylbutene-1 (5%) were recovered, together with about seven percent of unchanged 2,3,3-trimethylbutanol-2. The recovery of 2-chloropropane and propene gave evidence of fragmentation of the original alcohol into <u>iso</u> butene and propene. The formation of saturated gaseous hydrocarbons, probably methane and ethane, together with ethylene gave evidence of demethylation. Further evidence of demethylation was found in the isolation of 2-methyl-3-phenylbutene-2 and a mixture of hydrocarbons ($C_{11}H_{16}$) which contained 2-methyl-2-phenylbutane. This was identified by nitration, reduction and diazotization to 2-methyl-2-p-hydroxyphenylbutane.

2,2,3-Trimethylpentanol-3

In the case of 2,2,3-trimethylpentanol-3, the yield (10%) of the product of direct condensation, 2,2,3-trimethyl-3-phenylpentane, was about the same as for the preceding alcohol. The yield of 2-methyl-2-phenylpropane was slightly lower (3%). Attempts to isolate n-butene or butylchloride were not successful. No unchanged alcohol was isolated but evidence of its transformation into 3-chloro-2,2,3-trimethylpentane was found in the isolation of more than fifty percent of this compound, together with an unsaturated fraction C_8H_{16}. This fraction boiled at at 100°-103°. Analysis and molecular refraction showed it to be an octene but its density and refractive index do not check with the constants for 2,4,4-trimethylpentene-2. It was thought to be a mixture containing 2,4,4-trimethylpentene-2 and 3,3-dimethyl-2-ethylbutene-1. An eight percent yield of a second unsaturated hydrocarbon fraction was obtained which boiled at 74°-77° (15 mm). Analysis and molecular refraction showed the molecular formula to be $C_{12}H_{16}$. Oxidation gave as the main product, phenylethylketone, indicating the presence of 2-methyl-3-phenylpentene-2 in the mixture.

A saturated fraction which boiled at 85°-88° (15 mm) was obtained in five percent yield. Analysis and molecular refraction gave $C_{12}H_{18}$ as the molecular formula. Nitration, reduction and diazotization gave a mixture of phenols which by anaolgy would contain 3-methyl-3-p-hydroxyphenylpentane. A sharp melting derivative was not obtained.

2,3,3-Trimethylpentanol-2

Condensation of 2,3,3-trimethylpentanol-2, with benzene, gave 2,3,3-trimethyl-2-phenylpentane as the direct product in yields of about ten percent. The yield of 2-methyl-2-phenylpropane was two and one-half percent and, as in the preceeding case, where the yield of t-butylbenzene was small, butenes were not isolated. No unchanged alcohol was found but the yield of the stable 2-chloro-2,3,3-trimethylpentane averaged 35 percent. The unsaturated compound formed in the condensation and by decomposition of the chloride was proved by its boiling point, density and molecular refraction to be 2,3,3-trimethylpentene-1. The evoluation of hydrocarbons which did not liquify at -80° C. and the isolation of methyl chloride (5 %) indicated demethylation. Products of demethylation consisted, as before, of unsaturated and saturated compounds. The unsaturated fraction (2-3%) boiled at 78°-83° (15 mm). Analysis and molecular refraction gave $C_{12}H_{16}$ as the molecular formula and oxidation gave acetophenone as the main product. 2-Phenyl-3-methylpentene-2 was present in the mixture. The saturated fraction (3%) was, as shown by analysis and molecular refraction a mixture of hexylbenzene which boiled at 95°-99° (15 mm) and which, by analogy, shoud contain 3-methyl-3-phenylpentane. Nitration, reduction and diazotization gave a mixture of phenols from which a sharp melting derivative could not be prepared.

There is presented a theoretical discussion of the mechanisms of condensation, rearrangement and fragmentation.

A STUDY OF THE FRAGMENTATION OF SOME TERTIARY CARBINOLS CONDENSED WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

by

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CONTENTS

INTRODUCTION

The reaction of saturated aliphatic tertiary alcohols with benzene and phenol in the presence of aluminum chloride has been investigated in this laboratory by Professor Huston and coworkers through the octyl alcohols. The yield of the expected condensation product has been found to be, in general, better with phenol than with benzene.

Beginning with the work of Huston and Friedemann (1) in 1916, all workers have reported fragmentation to some degree. This fragmentation has been greater with highly branched alcohols, with a resulting low yield of the expected tertiary alkylbenzene.

In recent years, an extensive study of the products formed during fragmentation has been made. Huston and Awuapara (2) studied the formation of unsaturated compounds and of chloride complexes during the condensation of di-isopropylmethyl and di-isopropylethyl carbinols with benzene in the presence of aluminum chloride. Huston and Barrett (3) constructed a fractionating column with special properties in order to better separate and study the compounds formed during the condensation of dimethyl tertiary butyl carbinol with benzene in the presence of aluminum chloride.

It was the purpose of this investigation to study further the fragmentation occurring when tertiary alcohols, with a varying degree of branching on the carbon atom adjacent to the hydroxyl carbon, were condensed with benzene in the presence of aluminum chloride.

HISTORICAL

Alkylbenzenes may be prepared by numerous methods. Kaye (4) and other workers in this laboratory have given an excellent review of these methods. Calloway (5) also has reviewed the entire field of the Friedel and Crafts reaction and those related to it. It is the purpose of this brief review to recall the general methods as they were developed historically and to point out those cases where workers particularly observed side reactions, especially when compounds with a 'strained' alpha carbon, such as tertiary compounds, compounds with branching at the alpha carbon, or unsaturated compounds, were condensed with an aromatic nucleus.

Gerhardt and Cahours (6) prepared cumene by the distillation of para cumic acid with calcium or barium oxide. Cumene was also prepared by Liebmann (7) from benzal dichloride and dimethyl zinc, while Sabatier and coworkers (8-9) prepared it by passing the vapors of terpenes with hydrogen over nickel at 350-360 degrees centigrade.

The decarboxylation reaction was used by Pulvermacher (10) to prepare 2-phenylpentane by distilling a mixture of alpha, alpha diethylhomophthalic acid anhydride, calcium oxide and sodium hydroxide.

The Wurtz reaction was used by Schramm (11) to prepare secondary butylbenzene from ethyl iodide and alpha bromoethyl benzene. The Grignard reaction was used by Spath (12) to prepare 3-phenyl pentane from ethylmagnesiumbromide and 1-bromo-1-phenyl propane.

The alkylbenzenes have been prepared by the reduction of their halogen substituted derivatives with sodium (13), and by the reduction of ketones, acids, and ketoacids with hydrogen in the presence of nickel (14).

It is interesting to note in passing, that one of the reactions during the initial observations of Friedel and Crafts (15) was the formation of long chain alkyl halides and hydrocarbons when amyl chloride was treated with thin aluminum strips. This first reaction was aliphatic and remained undeveloped for fifty years while the concept prevailed that the Friedel and Crafts reaction was confined to aromatically bound hydrogen.

Of the various methods stated above, the Grignard reaction is one of the few methods that gives a pure alkylbenzene in good yields. This method has been used by Klages to prepare many of the alkylbenzenes (16). Levene and Marker also made use of the Grignard reaction to obtain compounds with optical activity (17).

Perhaps the most widely used and more direct method is the condensation reaction wherein an alkyl halide, alcohol, ether, ester, olefin, or naphthene is combined with an aromatic nucleus in the presence of some catalytic agent. The condensation agents include zinc chloride, sulphuric acid, hydrogen fluoride, boron fluoride, hydrogen chloride, and aluminum chloride. Although this method has the advantage of being rapid and in most cases will give a good yield, it often has the dissadvantage of giving other products which form mixtures difficult to separate from the main product.

Professor Huston and coworkers of this laboratory have focused their attention on the condensation of various alcohols with aromatic nuclei in the presence of aluminum chloride, and the greater part of the work in this field has been accomplished by them. This reaction was used first by Nef (18) in 1897 to prepare diphenylmethane from benzyl alcohol and benzene, and was repeated by Huston and Friedemann (1) in 1916. These workers reported other products formed during the reaction. Similar reactions have given di- and tri-substituted benzenes as well as phenyl alkanes probably formed by a splitting process.

In 1933 Huston and Davis (19) noted that the tertiary alcohol, triphenyl carbinol, gave triphenylmethane when condensed with benzene rather than the expected tetraphenylmethane.

The work of Huston and Fox (20) with tertiary butyl, tertiary amyl, and some tertiary hexyl alcohols condensed with benzene, and the work of Tzukervanik (21) with tertiary alcohols condensed with benzene and toluene gave results which agreed both as to the main reaction and the side reactions.

The work of Huston and Guile (22) with tertiary alcohols as well as the work of Huston and Wasson (23) indicated that fragmentation took place when highly branched members were condensed. The work of Awuapara (2) and that of Barrett (3) has been mentioned. These workers found that condensations at higher temperatures gave greater yields of by-products and lower yields of the expected compound of the condensation.

They also noted that aluminum chloride as a condensation agent did not follow the mass action law above a certain concentration.

It was the purpose of this investigation to continue the work begun by these workers, using selected tertiary alcohols that have an increasing methyl grouping on the alpha carbon, and to condense them with benzene in the presence of aluminum chloride, in order to compare the properties of the resulting compounds formed due to fragmentation.

THEORETICAL

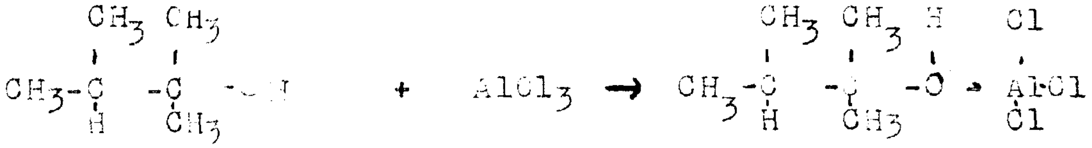
No mechanism yet suggested for the condensation reaction of an aliphatic alcohol and benzene seems completely satisfactory.

Any theory, however, must be related to the alkylation with alkenes and alkyl halides, since they also give good yields of the alkylbenzenes.

It is the purpose here to list the evidence that points to the most common mechanism and supports the facts brought to light by this laboratory where most of the work has been done.

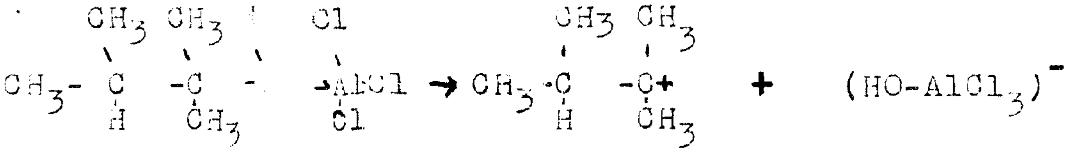
Huston and coworkers have shown that, during the condensation of alcohols and aromatic hydrocarbons, the hydroxyl group of the alcohol was activated and the alpha carbon of the alcohol was under strain.

First, the cationoid theory as reviewed by Price (24) explains the formation of a positive ion. In this theory an ionic complex between aluminum chloride and the alcohol is formed first,



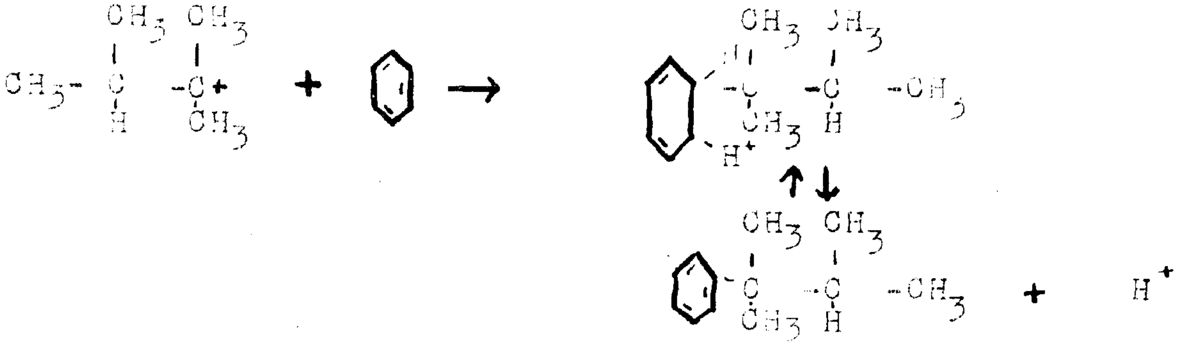
$$CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OH + AlCl_3 \rightarrow CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\overset{H}{O} \rightarrow \underset{Cl}{\overset{Cl}{Al}}Cl$$

which dissociates into an electron-deficient carbonium ion.

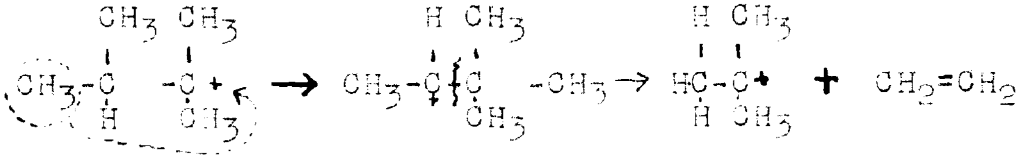


$$CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\overset{H}{O} \rightarrow \underset{Cl}{\overset{Cl}{Al}}Cl \rightarrow CH_3\text{-}\underset{H}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}+ \;+\; (HO\text{-}AlCl_3)^-$$

The carbonium ion then may react with benzene due to the aromatic properties of benzene.

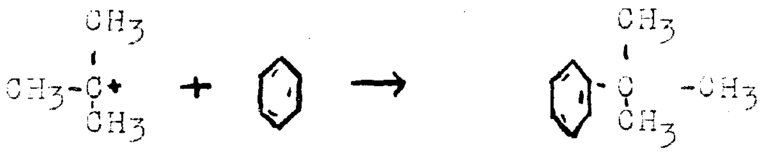


Since tertiary butylbenzene often has been isolated from the condensation products of tertiary alcohols with benzene in the presence of aluminum chloride in this laboratory, a side reaction must be added to the above mechanism. That is, a shift of an alkyl group to the positive carbon with a shift in 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:



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}{}^{+} \rightarrow CH_3-\overset{H}{C}\{\underset{CH_3}{\overset{CH_3}{C}}-CH_3 \rightarrow \underset{H}{\overset{H}{HC}}-\underset{CH_3}{\overset{CH_3}{C}}{}^{+} + CH_2=CH_2$$

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

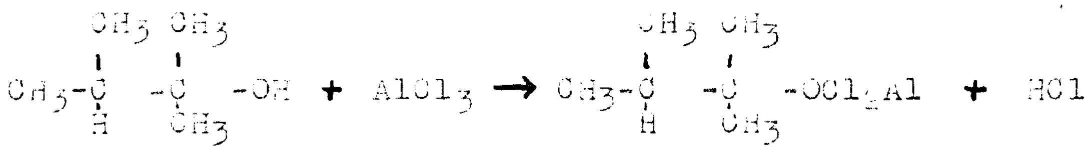


The theory of splitting and recombination of groups has support from the work of Radziewanowski (25) and from the work of Huston and Friedeman (1) who found anthracene as one of the products in the formation of diphenylmethane.

Huston and Goodemoot (26) also have shown that aluminum chloride alkylates by means of an alcohol only where there is a strained carbon attached to the hydroxyl group.

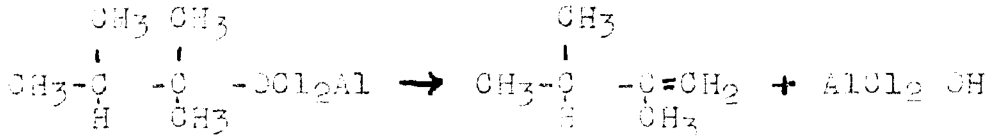
The work of Nenitzescu, Isacescu, and Ionescu (27) emphasizes that the alkylation by metal halides is essentially an activation reaction occurring when suitable activity of the nuclear hydrogen and the aliphatic halogen are realized, in their case an elevated temperature <u>without a catalyst</u>.

This lends support to the mechanism suggested by Tzukervanik and Nazaranova (28) in which the chloride of the alcohol is formed in the following manner:



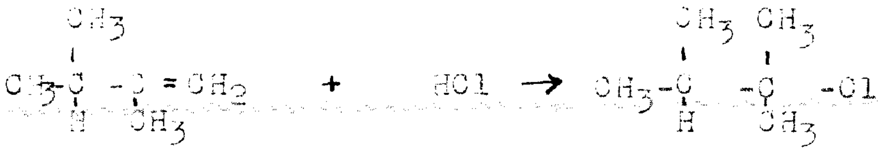
$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OH + AlCl_3 \rightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OCl_2Al + HCl$$

The complex thus formed breaks down into an olefin,



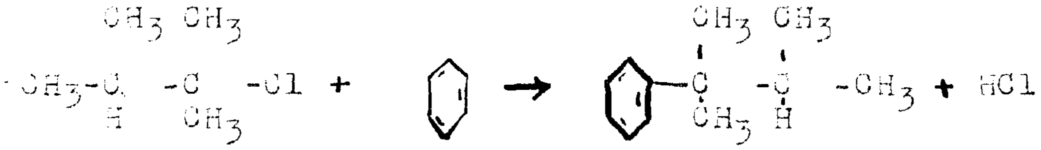
$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OCl_2Al \rightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{C}=CH_2 + AlCl_2\ OH$$

which adds hydrochloric acid.



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{C}=CH_2 + HCl \rightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-Cl$$

The chloride then may react with the activated nucleus.



Addition products between aluminum chloride, the alcohol, and benzene followed by rearrangement may well be the basis for the condensation reaction since addition products with aluminum chloride have been reported (29).

The effects of activation by catalysts have been shown upon the rearrangement of methyl groups from one nucleus to another by Anschutz and Immendorf (30), while Boedtker and Halse (31) found that the same law affected the movement of alkyl groups.

Further, unsaturated compounds have been reported in activated condensation reactions by Varet and Vienne (32) in the form of styrene and polymers of styrene in their reaction of acetylene and benzene to give unsymmetrical diphenylethane as the main product.

Since the facts observed in this laboratory may be explained by various steps of the above proposals but not all of the facts by any one of the suggested mechanisms, it is possible that at the higher temperatures a combination of the above reactions may take place by different routes. The mechanism for the reactions and facts observed in this work will be suggested under the section for the discussion of the results.

EXPERIMENTAL

I. Chemicals

The description of commercial chemicals used for the preparation of starting compounds, for drying purposes, for solvents, and for the condensation procedures, are listed here, while other purchased chemicals are described in Section II under the preparation of alcohols.

Acetone was that of Merck's C.P. grade twice re-distilled and dried over anhydrous sodium sulfate.

Acetyl chloride was Baker's (C.P. grade, specific gravity 1.10-1.12), re-distilled and that fraction boiling from 50-51 degrees centigrade at 747 mm. was used.

Aluminum chloride was Baker's reagent anhydrous sublimed.

Tertiary amyl alcohol from Eastman was re-distilled and that fraction boiling from 100-101 degrees centigrade at 750 mm. was used.

Benzene from Merck was treated with concentrated sulfuric acid, washed with water, re-distilled, and dried over sodium.

Bromine was Dow's C.P. grade re-distilled and the fraction boiling from 58-59 degrees centigrade at 746 mm. was used.

Calcium chloride was Dow's C.P. anhydrous grade.

Carbon dioxide (solid) was dried with concentrated sulfuric acid at the time of use.

Carbon tetrachloride from Merck was redistilled and the fraction boiling from 76-77 degrees centigrade at 760 mm. was used.

Ether was Merck's Reagent Absolute dried over sodium.

Ethyl bromide from Eastman was redistilled and the fraction boiling from 37-39 degrees at 760 mm. was used.

Hydrochloric acid was Baker's C.P. grade.

Magnesium turnings were specially prepared for Grignard reactions by Dow and oven dried.

Methyl alcohol was Merck's C.P. Absolute grade.

Mercuric chloride was Baker's C.P. grade oven dried before use.

Phosphoric anhydride was Baker's chloride free grade.

Red phosphorus was Baker's C.P. grade and oven dried before use.

Potassium carbonate was Baker's C.P. anhydrous grade.

Potassium hydroxide was Baker's C.P. grade.

Sodium was from Baker and freshly cut before use.

Sodium carbonate was Baker and Adamson's C.P. grade.

Sodium bicarbonate was Baker and Adamson's C.P. grade.

Sodium bisulphite was Baker's C.P. grade.

Sodium bromide was Baker's C.P. grade.

Sodium sulphate was Baker's C. P. grade, free of chloride.

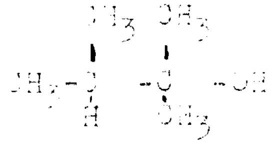
Sulfuric acid was Grasselli's C. P. grade.

II. Preparation of the Alcohols

The following alcohols were selected for preparation on the basis of increasing the length and complexity of the carbon chain attached to the hydroxyl carbon by the theoretical addition of methyl groups. Four were selected on the basis of the original group having two methyl groups in addition to the alkyl branch chain (1) and a methyl and ethyl group for comparative purposes:

A. 2,3-Dimethylbutanol-2
B. 2,3-Dimethylpentanol-2
C. 2,3,3- Trimethylbutanol-2
D. 2,2,3-Trimethylpentanol-3
E. 2,3,3-Trimethylpentanol-2

Part A. 2,3-Dimethylbutanol-2



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

This alcohol was prepared by the use of the Grignard reaction, by adding methyl isopropyl ketone to methylmagnesium bromide followed by hydrolysis of the resulting addition product. The ketone was prepared according to Organic Syntheses (33) as follows: In a five liter flask containing a dropping funnel, reflux condenser, stirrer, and thermometer, were placed 176 grams (2 moles) of tertiary amyl alcohol. The flask was placed on a water bath and the temperature of the alcohol held between 10-15 degrees centigrade.

with stirring, 320 grams of bromine were added slowly over a period of two hours. The stirring was continued until the orange color disappeared, and then 540 ml. of water were added and refluxed with stirring five hours. After this period, the reflux condenser was replaced for distillation and the ketone distilled with stirring until the temperature rose and oil drops stopped coming over. To the distillate (yellow oil with small lower layer of water), was added ten grams of powdered sodium carbonate with shaking until the water layer was alkaline. The layers were separated and the oil refluxed with 20 grams of powdered potassium carbonate and 5 ml. of water for sixteen hours in order to remove the bromides. The oil layer was again separated and dried over ten grams of anhydrous potassium carbonate. The ketone was distilled through a column. The fraction boiling from 91-93 degrees centigrade at 733mm. was used. The yield ranged from [illegible]-65 per cent. The Grignard reagent was prepared with some modifications in the following manner (3): A three liter three-neck flask was used as a generator for methyl bromide. In the flask were placed 1030 grams of sodium bromide, 320 grams of methyl alcohol, and 70 ml. of water. Then with a washing train connected between the generator and the reaction flask, 950 grams of concentrated sulphuric acid were added by means of a dropping funnel connected to one of the three necks of the generator. This gave enough gas to prepare five moles of the Grignard reagent. Toward the end of the reaction, the generator was heated by means of a sand bath. The train consisted of nine, 500 ml. wide mouth bottles connected with delivery tubes. The first bottle was empty, serving as a trap, followed by three bottles half full of 40 per cent sodium hydroxide, followed by another trap bottle, and this followed by three bottles half full of concentrated sulphuric acid, and finally another empty trap bottle with a delivery tube leading to the reaction flask. This delivery tube was fitted with a three-way stop-cock to better control the rate of flow of gas into the reaction flask especially at the beginning of the reaction, since ether absorbed a great deal of gas before the reaction started and then would need cooling before more gas was admitted. The reaction flask consisted of a two liter three-neck flask (for one to two moles), fitted with a mechanical glycerine stirrer and a reflux condenser. The condenser was closed with a calcium chloride tube(1). When the magnesium had disappeared, the reagent was stirred at least one hour longer, allowed to stand another hour, and titrated for percentage of Grignard reagent (34).

The calculated amount of ketone was then added with an equal volume of ether at the rate of one drop per second with stirring. After stirring at least one hour from the time the addition had been completed, the product was hydrolyzed with ice and enough concentrated hydrochloric acid (usually 200 ml. per mole) to dissolve the basic salts. The

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(1) All materials and apparatus were dried and protected from the moisture and carbon dioxide of the air.

ether layer was separated and the water layer extracted at least three times with ether. The combined ether layers were washed with 5 per cent sodium carbonate until basic to litmus and then with distilled water. The product was dried over anhydrous sodium sulfate for four hours or longer. The ether was removed through a column and the alcohol distilled at reduced pressure.

Yield : [illegible] (1)

B_{760} : 117-120°C.

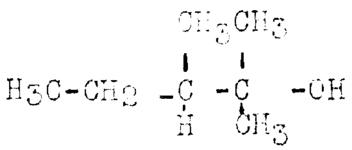
B_{20} : 52-54°C.

D_4^{20} : 0.8115

n_D^{20} : 1.4141

This alcohol has been prepared by Henry (35) and Edgar (36). Fox (20) working in his laboratory also prepared the alcohol. The above constants checked with those of these workers.

Part [illegible]. 2,3-Dimethylpentanol-2



$$H_3C-CH_2-\underset{H}{C}(CH_3)-\underset{CH_3}{C}(CH_3)-OH$$

This alcohol was prepared by the use of the Grignard reaction by adding acetone to secondary butyl magnesium bromide. The procedure for the preparation of the Grignard reagent was the same as that employed by Doctor H.L. Cuike of this laboratory (22). The remaining procedure for the

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(1) Based upon the Grignard reagent [illegible]
[illegible] per cent.

preparation of this alcohol was the same as the reaction in Part A. This alcohol was prepared by Binder (37) working in this laboratory. The following constants checked closely with those obtained by him:

Yield: 55-60%(1)

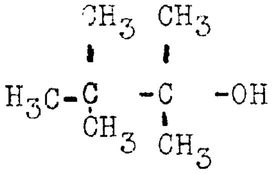
B_{25} : 56-57°C.

B_{750} : 129-131°C.

D_4^{20} : 0.8055

n_D^{20} : 1.4275

Part C. 2,3,3-Trimethylbutanol-2



$H_3C-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-OH$

This alcohol was prepared by adding pinacolone to methylmagnesiumbromide according to the above methods of adding ketones to Grignard reagents.

Pinacolone was prepared according to the method given in Organic Syntheses (38) as follows: A five liter three-neck flask was fitted with a separatory funnel and a long reflux condenser (with a 12-15 mm. inner tube) closed at the top with a calcium chloride tube. Eighty grams of magnesium and 800 ml. of dry benzene were placed in the flask. A mixture of 90 grams of mercuric chloride and 505 ml. of acetone were placed in the separatory funnel. About one-half of this

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(1) Based upon the Grignard reagent.

mixture was added and the reaction allowed to start(2). The reaction was vigorous and the flask was cooled with an ice water bath. After all of the acetone and mercuric chloride had been added, a mixture of 252 ml. of acetone and 200 ml. of benzene was added before the reaction stopped. When no further reaction was visible the flask was heated on a water bath until no further reaction took place. Magnesium pinacolate swelled and nearly filled the flask. The flask was removed from the condenser and shaken until the mass was well broken up. The condenser was attached again and heating continued one hour. Then two hundred ml. of water were added through the separatory funnel and the mixture heated another hour. The mixture was then cooled to 50 degrees centigrade and filtered. The solid was returned to the flask and heated 10 minutes with a fresh 500 ml. portion of benzene. This second mixture was filtered, and the combined filtrates were distilled to one-half their original volume. The remaining benzene solution was treated with 300 ml. of water and cooled to 10 degrees centigrade. The pinacol hydrate was filtered after [illegible] minutes by suction, washed with benzene, and air dried at room temperature. This pinacol hydrate was treated with 750 grams of 6 N sulphuric acid for every 250 grams of the hydrate and distilled until no more pinacolone came over with the water. The distillate was separated from the water and dried over calcium chloride, filtered, and fractionally distilled. The fraction boiling

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(2) A 30 minute induction period was required unless heated. Heating was not desirable because of the rapid reaction once started.

from 103-105 degrees centigrade at 749 mm. was used. The yield was usually 25-30 per cent based on the magnesium.

The Grignard reagent was prepared as in Part A. The alcohol formed a solid hydrate if special care was not used. The addition product, formed during the preparation of the alcohol, was hydrolyzed, the ether layer separated, and the water layer extracted three times with ether. Then the combined ether layers were washed with 5 per cent sodium carbonate but <u>not</u> followed by water washing. The ether solution was dried over sodium, the ether removed through a column, and the alcohol distilled over sodium at reduced pressure. A short column and a short condenser, <u>carefully dried</u>, were used. The containers of alcohol, after distillation, were sealed air tight. The alcohol was distilled thereafter at atmospheric pressure over sodium(1).

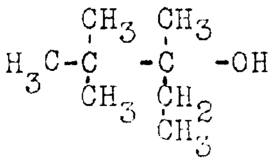
Yield: 75-80%(2)

B_{744} : 129-131°C.

B_{20} : 49-52°C.

The alcohol was prepared in this laboratory by Binder (37) and by Barrett (3). It was prepared first by Butlerow (39) in 1875. Edgar (36) also has prepared it.

Part D. 2,2,3-Trimethylpentanol-3



$$\begin{array}{l} \qquad\quad CH_3 \;\; CH_3 \\ H_3C-\overset{|}{C}\;\;-\overset{|}{C}\;\;-OH \\ \qquad\quad CH_3 \;\; \underset{|}{CH_2} \\ \qquad\qquad\quad\; CH_3 \end{array}$$

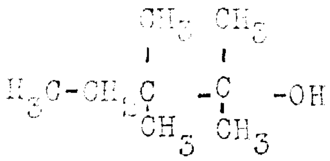
---

(1) When used for condensations, benzene was added immediately upon breaking the seal of the containers.

(2) Based upon the Grignard reagent.

This alcohol was prepared by the use of the Grignard reaction, adding pinacolone to ethylmagnesiumbromide. The pinacolone and the Grignard reagent were prepared according to the above procedures, and the reaction for the alcohol was carried out as before. B_{742}:148-149 C. Yield:35-40%(1).

Part E. 2,3,3-Trimethylpentanol-2



$$H_3C-CH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OH$$

The best method for the preparation of this alcohol was found to be the addition of methyl tertiary amyl ketone to methylmagnesiumbromide. The ketone was prepared by adding tertiary amyl magnesium bromide drop-wise to acetyl chloride according to the Whitmore procedure (40). Then the alcohol was prepared by the addition of the ketone to methylmagnesiumbromide according to the Edgar procedure (41), and was similar to the reactions for the alcohols prepared above. The product was hydrolyzed and dried as usual. The methyl Grignard was prepared as in Part A. The Whitmore and Edgar procedures were used by Doctor R.L. Guile (22) of this laboratory and described by him in detail.

Due to the difficulty of preparing tertiary Grignards in good yields, the procedure for tertiary amyl magnesium bromide is described here in detail.

Phosphorous tribromide was prepared by the following method; this is a modification of the procedure found in Organic Syntheses (42): Thirty-seven grams (1.2 gram atoms)

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(1) It has been prepared by Clarke and Jones(37).

of dried red phosphorous were suspended in 250 ml. of redistilled carbon tetrachloride in a dry one liter three-neck flask equipped with a condenser sealed with a calcium chloride tube, a glycerine stirrer, and a dropping funnel. The flask was cooled with a mixture of ice and salt, and 342 grams (4.2 moles) of bromine were added drop-wise with stirring. The carbon tetrachloride and excess bromine were distilled from the mixture with the aid of a short air condenser. The tribromide was distilled from the remaining mixture into a Claisen distilling flask. The crude phosphorous tribromide was redistilled, and the fraction distilling from 168-172 degrees centigrade a 750 mm. was used. The yield was from 60-70 per cent. During each of the steps, the system was protected from the moisture of the air with a calcium chloride tube.

Then, tertiary amyl bromide was prepared by placing 232 grams (0.87 moles) of the phosphorous tribromide in a dry one liter three-neck flask equipped as in the preparation of the tribromide and cooled with a mixture of ice and salt. Then, 230 grams (2.61 moles) of redistilled tertiary amyl alcohol (boiling from 101-102 degrees centigrade at 750 mm.) was added drop-wise over a period of three hours. The mixture was washed with five ml. of saturated sodium bisulfite solution, the water layer separated, and the product was washed twice with cold concentrated sulphuric acid. The layers were separated and the crude bromide washed with water, and then with 25 ml. of saturated sodium bicarbonate solution. The layers were separated again and the bromide washed with water, dried over anhydrous calcium chloride, and distilled. The fraction boiling from 106-109 degrees centigrade at 746.2 mm. was used. The yield was usually from 70-80 per cent.

The tertiary amyl bromide thus prepared was used immediately to prepare the Grignard reagent, since it was necessary that the bromide be pure and free from decomposition products that formed on standing.

The bromide was diluted with an equal volume of ether and added drop-wise to one mole of pure dry magnesium(1) suspended in 400 ml. of anhydrous ether. Larger or smaller runs were made with satisfactory results. The ether and tertiary amyl bromide mixture was added very slowly, one drop per two to three seconds, during the entire reaction, and a large excess of the bromide was avoided at first before the reaction started. The yield was 50-60 per cent.

The alcohol has been prepared by Norton (43) and also by Guile (22). The physical constants corresponded to those determined by these workers for the alcohol.

Yield: 45-60%

B_{745} : 155-157°C.

B_{20} : 59-61°C.

n_D^{20} : 1.4397

D_4^{20} : 0.8520

---

(1) Alloy magnesium was found to be unsatisfactory. Finely divided magnesium gave improved yields, but it was necessary to add the bromide more slowly.

III. The Condensation Apparatus

The following photograph and figure 1 show the condensation apparatus as it was developed and used in the last of the condensations and as it was employed in repeating some of the earlier condensations.

The purpose and size of each part will be described here while the general use in condensations will be given in the Section IV under the general procedures for the condensation of the alcohols with benzene.

A--A three-neck reaction flask, the size of which varied according to the number of moles of alcohol condensed.

B--An electric motor for stirring.

C--The glass stirrer and glycerine seal. (A mercury seal was not used because of the back pressure created).

D--The alcohol addition tube with inner sealed tube and connections for the purpose of equalization of pressure. The size of this tube also varied according to the number of moles of alcohol condensed.

E--The carbon dioxide generator (for solid carbon dioxide) of 125 ml. capacity.

F--Drying trap for the carbon dioxide containing concentrated sulphuric acid, with a T-tube connecting it to the addition tube in order to allow an opening to the air. This trap was of 100 ml. capacity.

G--Safety valve to the air.

H--The thermometer suspended inside the condenser.

I--Water condenser.

J--Ice salt cooled trap used to condense and hold benzene and alcohol vapors. This tube was 8 x 1.5 inches.

K--Carbon dioxide-acetone cooled trap used to condense and hold any substance that did not boil lower than -80°C. This tube was the same size as trap (J).

L--Two-way stop-cock used to direct the gases through trap (K) or directly to the nitrometer from trap (J).

M--One-way stop-cock operated in conjunction with stop-cock (L) from trap (K). This stop-cock was closed when stop-cock (L) was opened to allow gases to go past trap (K), and opened when stop-cock (L) forced gases through trap (K).

N--Mercury well connected to stop-cocks (L) and (M) by means of the Y-connecting tube and 90 ml. of vertical 1 mm. capillary tubing. The well was of 100 ml. capacity and contained mercury to a height of 4 mm. The capillary dipped 3 mm. into the mercury. This capillary had the equivalence of 760 mm. of mercury.

O--Empty trap of 100 ml. capacity to hold liquids from container (P) in case the mercury failed to hold.

P--Container for a 5 per cent solution of bromine in carbon tetrachloride. This container was tapered at the end in order to concentrate the amount of liquid having gases passed through it. It contained 10 ml.

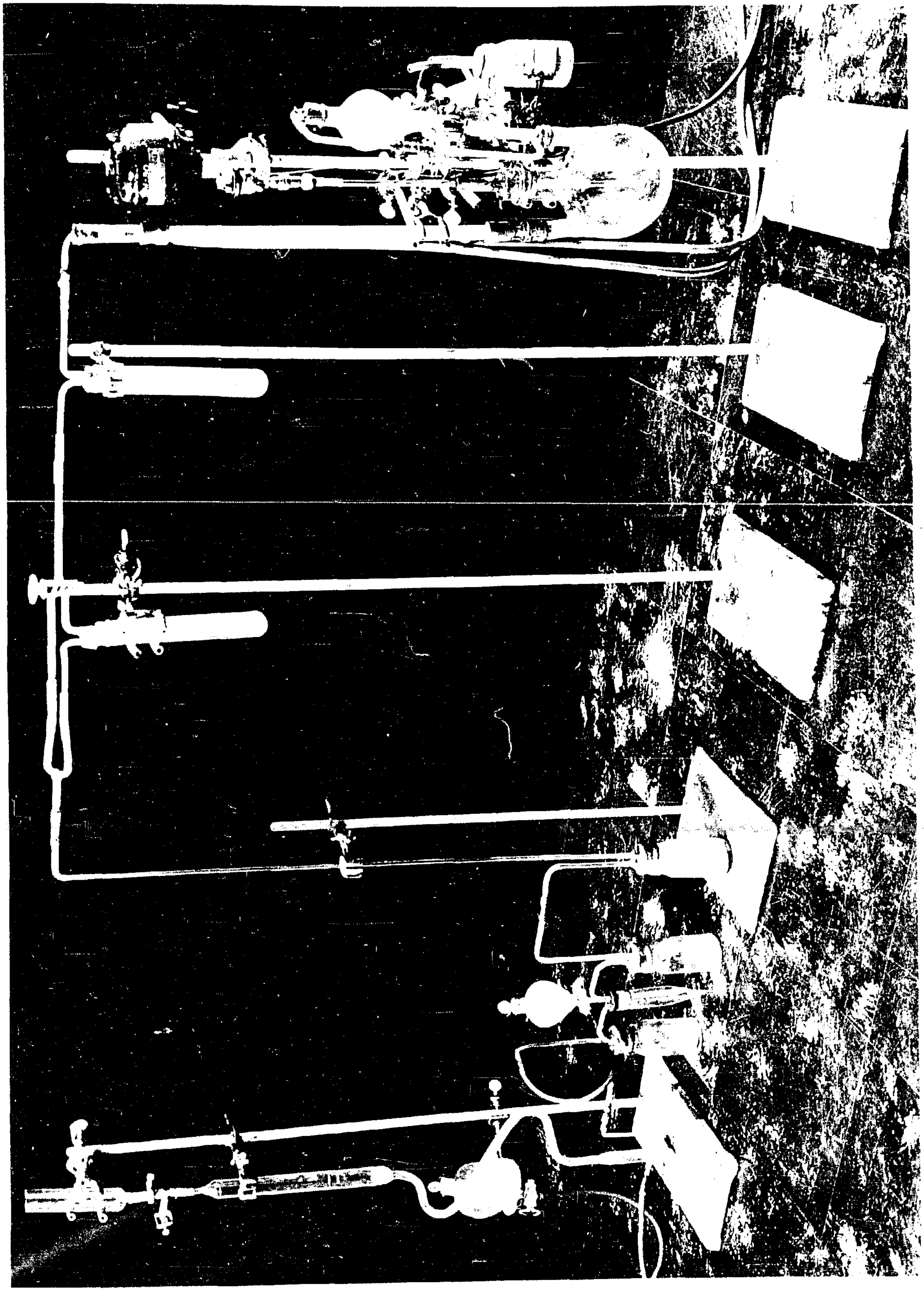
when half full.

R--Dropping funnel of 25 ml. capacity, used to hold pure bromine until needed.

Q--The nitrometer was of 300 ml. capacity with a diameter of 25 mm. in the vertical sections and 10 mm. in the curved section, and had its head above the level of the traps (K) and (J). Mercury was placed in the bottom of the nitrometer to seal it from trap (O) and 50 per cent potassium hydroxide filled the remaining space of the nitrometer.

U--Nitrometer leveling bulb of 250 ml. capacity.

The Dewar flasks used to hold the bath solutions and maintain the traps (J) and (K) at their desired temperatures are not shown.



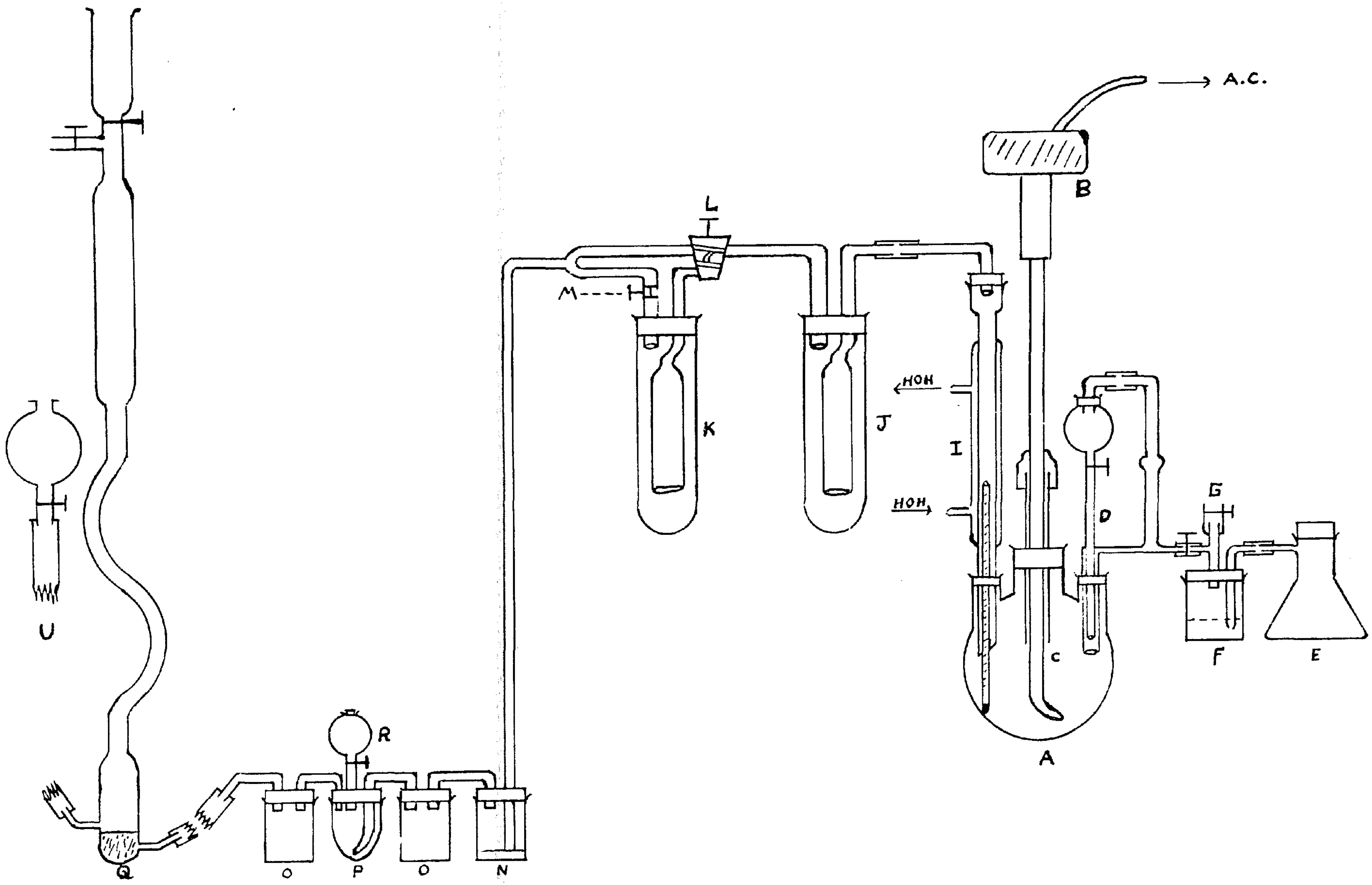


FIGURE 1

IV. The General Procedure for the Condensation of the Alcohols with Benzene

The alcohols prepared were condensed with benzene in the presence of anhydrous aluminum chloride according to the general methods by Kaye (4), and other workers in this laboratory, for the first few condensations, and for the most part at a temperature between 40-45 degrees centigrade in order to obtain the maximum amount of fragmentation as determined by Barrett (3).

It was noticed early in the study of the condensation products, that gases and low boiling materials were obtained during the reaction. This was noticed, especially when the products were hydrolyzed without standing, by the solubility of these gases and low boiling products in the solvents. It was necessary to modify the original procedures of condensation in order to determine if these gases were saturated or unsaturated or both, and their amounts.

For comparison purposes the original and modified methods are described in detail.

The first few condensations were carried out in a three-neck flask fitted with a glycerine stirrer, a dropping funnel with a calcium chloride tube, and a water condenser fitted with a calcium chloride tube. All of the reactions were carried out in a molecular ratio of one mole of alcohol, one-third mole of aluminum chloride, and five moles of benzene. The benzene and the aluminum chloride were suspended by stirring one hour or longer, and the alcohol added dropwise in such a manner that the temperature was maintained between 40-45 degrees centigrade. The rate varied with the alcohols, but after the initial reaction, it usually was necessary to control the rate at one drop per second. After all the alcohol was added the reaction product was stirred one hour or longer and hydrolyzed on ice with stirring. Concentrated hydrochloric acid (200 ml. per mole) was added to dissolve the basic salts of aluminum. It was later discovered that the acid was not necessary for the alcohols used. The benzene layer was separated and the water layer extracted at least three times with benzene, ether, or hexane depending upon the boiling point of suspected low boiling fractions in the condensation product. Both layers were then dried over anhydrous sodium sulfate.

The majority of the condensations were run with the modified equipment (see figure 1)(1). The following description of the condensation procedure was general for all the alcohols discussed and varied only slightly in detail which will be discussed under the separation, analysis, and identification of the fractions.

The aluminum chloride was suspended in the benzene and heated to reflux temperature for one hour to drive off large amounts of air dissolved in the benzene. Hydrogen chloride was evolved in large amounts and the aluminum chloride finally went into solution with a change in color similar to that found in condensations. When the aluminum chloride was added after the benzene was heated and cooled, there seemed to have

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(1) The improvements and glass blowing for the condensation apparatus were made by Doctor G.L. Goerner of this laboratory.

been no change in the condensation products. During this time the nitrometer was not connected to the system, container (P) figure 1 contained no bromine, and the traps (K) and (J) were not cooled, but the system was washed out with carbon dioxide by placing solid carbon dioxide in the generator (E). The carbon dioxide was allowed to pass until the benzene was cooled to room temperature, then the alcohol was measured into the dropping funnel (D) and marked at each one-third portion. The container (P) was half filled with a 5 per cent solution of bromine in carbon tetrachloride and then pure bromine was left in the funnel (R) in case that more bromine was needed. The nitrometer was connected and gases allowed to flow through the system until the bubbles in the nitrometer became micro-bubbles. Trap (J) was cooled with a salt-ice mixture and trap (K) with solid carbon dioxide-acetone mixture. The stop-cocks (L) and (M) were adjusted so that the gases passed into the trap (K), and the addition of the alcohol was started. The reaction began with the first drop with a change in color of the reaction mixture and a rise in temperature. A temperature of 45°C. was reached in about fifteen minutes and remained at about that temperature for the rate of alcohol addition (about one drop per second). Hydrogen chloride was evolved during the first one-third addition of the alcohol. When one-half of the alcohol was added, back pressure was created in the system and mercury from the trap (N) rose as much as 200-300 mm. in the capillary. The evolution of gases began to decrease when one-third of the alcohol was added.

After two-thirds of the alcohol was added, rapid addition of the remaining one-third did not increase the temperature of the reaction, and both the temperature and the back pressure decreased until the reaction mixture reached room temperature. Then the system was washed out with carbon dioxide until micro-bubbles were obtained. The liquid condensed in trap (K) was transferred to the nitrometer by allowing it to warm up from the temperature of the carbon dioxide-acetone mixture (-80°C.), or was kept cold and analyzed separate from any other low boiling substances that escaped as gases through this trap into the nitrometer. Three pounds of 'dry ice' were sufficient to work with for twenty-four hours and took care of the needs of one condensation. One-half to one mole of the alcohol was used for the majority of the condensations. Dewar flasks, packed on the outside for protection, were used to maintain the low temperature baths for cooling the traps (K) and (J). Hempel's gas analysis apparatus was used for the analysis of the gases except the purified fractions isolated which will be described under analysis of fractions.

V. The Separation, Identification, and Analysis of Products

The general procedure for the condensation of the alcohols was discussed in Section IV. The products were stirred in all cases one hour after the reaction was completed as shown by the decrease of temperature to room temperature. In some cases the stirring was continued several hours and the reaction products allowed to stand over night before they were hydrolyzed. Both procedures were used several times with each alcohol. No difference in the products isolated was observed except in the amount of gas dissolved in the solvent. Several moles of each of the alcohols were condensed until the amounts of the high boiling fractions of the condensation products were large enough for fractionation. This was especially true in the case of 2,2,3-trimethylpentanol-3 and 2,3,3-trimethylpentanol-2 because of the small yield of the higher fractions. While the condensation products were drying, the gases collected in the nitrometer (figure 1) and in the traps (K) and (J) were analyzed. The gases which could not be liquified by the trap (K) were analyzed with Hempel's gas analysis apparatus. The gases gave an average value of 13-19 per cent oxygen when one-half to three-fourths of a mole of alcohol was condensed. This was interpreted to mean that air entered the system through the glycerine stirrer after the back pressure from the reaction had subsided.

Methane, hydrogen, and ethane were suspected as being present in the gases since they burned with a faint blue flame. But if present, they were in too small concentrations to be detected and separated with the apparatus. However, the gases partly reduced cupric oxide in the case of 2,3,3-trimethylbutanol-2 condensation. In another case, the cupric oxide was charred to a carbon-like mass. Since these gases were small in amount and could not be liquified under the conditions(1), no further work was attempted with them. One to two grams of benzene and small amounts of alcohol were collected in trap (J) in each condensation. Methyl chloride was liquified in trap (K) when 2,2,3-trimethylpentanol-3 and 2,3,3-trimethylpentanol-2 were condensed. In the case of 2,3-dimethylbutanol-2, 2,3-dimethylpentanol-2, and 2,3,3-trimethylbutanol-2 no liquid was detected in trap (K) but the gases from the nitrometer burned weakly with a blue flame and a yellow to greenish fringe.

After drying, the solvents for the liquid fractions of the condensation products were distilled at atmospheric pressure with a modified Claisen flask having a fourteen inch column (44). The distillations were continued for most of the condensations from this point with the special column built by Barrett (3) until it was necessary for distillation at reduced pressure for an extended period with small amounts of material. The spinning band could not be used for long periods and the spiral gave too large a hold-up. The fractions were distilled from this point with small modified Claisen flasks with columns of various lengths according to

---

(1) The concentration of gases was small because of the entrance of air after the back pressure. This mixture of air and hydrocarbons could not be satisfactorily analyzed with the Hempel apparatus.

the size of fractions. Fairly good separations were made with flasks holding 5 ml. of solution with six inch columns.

Distillation difficulties were greatly reduced by removing the alkyl chloride before distillation was continued beyond the low boiling fractions. This was accomplished by refluxing with stirring, the combined high fractions (those boiling above 115-130 degrees centigrade) from two to four hours with an equal volume of fifty per cent alcoholic potassium hydroxide(1). The layers were separated without adding water and the organic layer was washed several times with water. The remaining emulsion was washed with water, the organic layer separated and washed several times with water. The combined organic layers were dried with anhydrous potassium carbonate. Upon distillation the material was found free from chloride as a rule. Sometimes it was necessary to repeat the procedure. Even a small amount of the alkyl chloride made separation difficult with resulting high values for the constants of each fraction. The above treatment and careful distillation for fractions less than twenty grams gave fractions sufficiently pure for the preparation of derivatives after constants and qualitative tests had indicated the class of compound involved, although some fractions were more or less mixtures after final distillation. A small tarry residue remained in each condensation.

---

(1) The alcoholic potassium hydroxide was made by adding directly to the reaction flask 50 grams of potassium hydroxide and 50 grams of alcohol for each 100 grams of organic material. No water was used at this point.

Sometimes fractions boiling higher than the expected product were obtained in appreciable quantities and were suspected of being di- and tri-substituted alkylbenzenes.

Part A --The condensation of 2,3-dimethylbutanol-2 with benzene in the presence of anhydrous aluminum chloride.

Fraction I 2,3-Dimethylbutene-1

Three to five grams of this material per mole of alcohol condensed was isolated when the solvent was removed. It gave an unsaturated test with a 5 per cent solution of bromine in carbon tetrachloride and was free from chloride. Larger amounts were isolated after the alcoholic potassium hydroxide treatment, and both portions were identified as 2,3-dimethylbutene-1 by preparing 2-chloro-2,3-dimethylbutane from the alcohol(1) according to the method given by Shriner and Fuson (45) and treating this chloride with alcoholic potassium hydroxide. The product obtained was identical with that obtained from the condensation. The constants checked with those reported in the literature (51). The yield(2) and constants were determined as follows:

---

(1) See Part G on proof of structure.

(2) All yields for the condensations were based directly upon the alcohol unless otherwise indicated. Identified fractions were calculated in terms of per cent, while unidentified fractions and residues were reported in grams.

Yield: 15%(1)

B_{745} : 55-59°C.

n_D^{20} : 1.3915

D_4^{20} : 0.6874

M_R* : Calc. 29.33 Obs. 29.33

Fraction II 2-Chloro-2,3-dimethylbutane

This fraction distilled without difficulty after the solvent was removed. It gave a heavy chloride test with alcoholic silver nitrate, and the same constants as the compound prepared from the alcohol for the purposes of Fraction I. The constants checked with those reported in the literature (59). It gave the following yield and constants:

Yield: 18%

B_{741} : 106-109°C.

n_D^{20} : 1.4298

D_4^{20} : 0.8772

M_R : Calc. 34.67 Obs. 35.40

Fraction III 2-Methyl-2-phenylpropane

This fraction was isolated in small amounts when one mole or more of the alcohol was condensed. It was identified by means of the acetamino derivative(2) (46) which

---

(1) Two-thirds of this yield came from the decomposition of the chloro-compound by alcoholic potassium hydroxide.

* Molecular refraction data for all the calculations were taken from Swietoslawski (58).

(2) See Part F for the preparation of derivatives.

required many recrystallizations for purification. The physical constants agreed with those reported by Hennion and Auspos (52). The following constants, except the derivative, were obtained after combining several of these fractions from several condensations in order to purify the fraction:

Yield: 0.9%
B_{741} : 165-168°C.
B_{10} : 52-54 C.
n_D^{20} : 1.4910
D_4^{20} : 0.8632
M_R : Calc. 44.85 Obs. 43.95
M Pt.: 2-Methyl-2-p-acetaminophenyl propane
168-171°C.

<u>Fraction IV</u> 2,3-Dimethyl-2-phenylbutane

This fraction was the expected condensation product and was obtained in good yields. It was distilled with the special column using the spiral coil (3). Its identity was verified by the acetamino derivative[1] and the constants checked closely with those found by other workers in this laboratory (47).

The following yield and constants were determined:

---

[1] See Part F for the preparation of derivatives.

Yield: 40%

B_{741} : 203-205°C.

B_{25} : 99-101°C.

n_D^{20} : 1.4988

D_4^{20} : 0.8814

M_R : Calc. 54.05 Obs. 54.07
M.Pt.: 2,3-Dimethyl-2-p-acetaminophenyl butane 118-119 C.

Fraction V Tarry residue

Yield: 1 gram

Part B --The condensation of 2,3-dimethylpentanol-2 with benzene in the presence of anhydrous aluminum chloride.

Fraction I 2,3-Dimethylpentene-1

This fraction was separated from the benzene in small amounts with difficulty. It was difficult to determine the total amount that was formed during the condensation for this reason. It was identified by comparison with the compound prepared from 2-chloro-2,3-dimethylpentane according to the procedures used in Part A, Fraction 1. The physical constants checked with those reported in the literature (53). The following yield and constants were determined:

Yield: 10%(1)

B_{744} : 82-84°C

n_D^{20} : 1.4025

D_4^{20} : 0.7055

M_R : Calc. 34.98 Obs. 34.28

---

(1) Four-fifths of this yield was obtained from Fraction II of this condensation by the alcoholic potassium hydroxide treatment.

Fraction II 2-Chloro-2,3-dimethylpentane

This fraction decomposed on attempts to distill it at atmospheric pressure. It gave a heavy chloride test and was compared with the chloride prepared from the alcohol as in Part A, Fraction I. The constants proved that the compounds were identical and they agreed with constants determined by Binder (37). The following constants were determined:

Yield:	14%		
B_{18} :	39-42°C		
n_D^{20} :	1.4355		
D_4^{20} :	0.8788		
M_R :	Calc. 39.27	Obs. 39.95	
Cl :	Calc. 26.37%	Found 26.99%(1)	

Fraction III 2-Methyl-2-phenylpropane

This fraction was not separated easily until one or more moles of the alcohol was condensed. The acetamino derivative(2) for one condensation was purified with difficulty. It gave the same constants as Fraction III, Part A. Fractions from several condensations were saved and purified in order to determine the following constants:

---

(1) The analysis for the chlorine was by Pregl's microtechnique.

(2) See Part F for the preparation of derivatives.

Yield: 1%

B_{740} : 165-168°C.

B_{15} : 57-59°C.

n_4^{20} : 1.4912

D_4^{20} : 0.8631

M_R : Calc. 44.85 Obs. 43.95

M. Pt: 2-Methyl-2-p-acetaminophenyl propane
168-171°C.

Fraction IV 2,3-Dimethyl-2-phenylpentane

This fraction was the expected condensation product and was easily purified from the alkyl chloride. It was verified by the acetamino derivative, and the constants checked with those previously determined for this compound in this laboratory (47). The following yield and constants were determined:

Yield: 22%

B_{740} : 219-221°C.

B_{25} : 105-107°C.

n_D^{20} : 1.4966

D_4^{20} : 0.8801

M_R : Calc. 58.65 Obs. 58.43

M. Pt: 2,3-Dimethyl-2-p-acetaminophenyl pentane
85-86°C.

Fraction V Tarry residue

Yield: 2 grams

Part C --The condensation of 2,3,3-trimethylbutanol-2 with benzene in the presence of anhydrous aluminum chloride[1].

Fraction I 2-Chloro-propane

This fraction was very small and small amounts of the derivative were isolated. The anilide was prepared in the manner described by Shriner and Fuson (45). Small amounts of the purified derivative were obtained. The ether solution gave a strong chloride test after careful washing with 10 per cent sodium carbonate solution. This indicated that the chloride was not due to dissolved hydrogen chloride. The alkyl chloride was concentrated by carefully fractionating the ether solution from the condensation extraction with the special column (3). The fraction could not be completely separated from the ether because of the close range of the boiling points of the two compounds. The ether mixture boiling from 35-36 degrees centigrade at 750 mm. was used for the preparation of the derivative . Since the isopropyl chloride was not completely separated and the pure anilide obtained in small amounts, no yield was calculated.

---

(1) This alcohol was investigated in detail by Barrett (3) and was selected here in order to compare the gases and unsaturated compounds with the alcohols in this series under the same conditions and with the same techniques. This alcohol was particularly difficult to handle and condense. The alcohol formed a solid hydrate and a solide chloride. They distilled together and were separated by fractional crystallization.

M.Pt.: 2-Methyl-propionanilide(1)

105-108°C.

Fraction II 1,2-Dibromo-ethane

This fraction was obtained in one to two gram yields by means of the bromine trap (P) figure 1, when three-fourths of a mole or more of the alcohol was condensed. The excess bromine was destroyed with aqueous sodium bisulphite. The mixture was extracted with ether, dried over anhydrous sodium sulphate, filtered, and distilled in a small modified Claisen flask. The compound was sufficiently pure to be recognized by its odor and its constants corresponded to those listed in chemistry handbooks. The following constants were determined:

Yield: 0.87%

B_{744}: 130-132°C.

M.Pt.: 9.8°C.

$n_D^{16.5}$: 1.5404

Fraction III 1,2-Dibromo-propane

This fraction was obtained in small yield when one mole of the alcohol was condensed. It was collected during the distillation of Fraction II above and its boiling point determined at that time. The purified portion was analyzed for halogen by the Carius procedure (49). The following data were obtained:

---

(1) This derivative has been reported by Underwood and Gale (60).

Yield: 0.5%

B_{744} : 138-145°C.

Br : Calc. 79.15% Found 78.37%

Fraction IV 2,3,3-Trimethylbutene-1

Small amounts of this fraction were obtained when the solvent was removed, but the greater portion came from the decomposition of the chloro-compound with 50 per cent alcoholic potassium hydroxide. It was identified by its preparation from 2-chloro-2,3,3-trimethyl butane which was prepared from the alcohol as in Part A, Fraction I. The constants corresponded to those reported in the literature (54). The following yield and constants were obtained:

Yield: 5%(1)

B_{743} : 74-76°C.

n_D^{20} : 1.4023

D_4^{20} : 0.7029

M_R : Calc. 33.93 Obs. 33.48

Fraction V 2-Chloro-2,3,3-trimethylbutane

This fraction was a solid chloride and distilled over with the solid hydrate of the alcohol. It was necessary to separate them from the higher fractions and then determine the amount of chlorine(1) from a mixture of the two. The chlorine content was 8.38%. The alkyl chloride was identified by means of its preparation from the alcohol as stated

---

(1) Based on the alkyl chloride from the condensation, which in turn was calculated from a mixture of the hydrate of the alcohol by a Carius analysis (49).

in Fraction IV above. The freezing point and boiling point checked with those obtained by Barrett (3). The following constants were determined:

Yield: 2%[1]

B_{745} : 129-131°C.

M.Pt.: 123°C.

Fraction VI Hydrate of 2,3,3-trimethylbutanol-2

This compound was the alcohol with one molecule of water which formed a solid as discussed in Fraction IV. It was identified by exposing the alcohol (2,3,3-trimethylbutanol-2 to moist air. The crystals were separated and dried. This compound was identified by Binder (37). The yield and the constants were determined as follows:

Yield: 7%[1]

B_{740} : 120-124°C.

M.Pt.: 80-82°C.

Fraction VII 2-Methyl-2-phenylpropane

This compound was obtained after the solids were cleared from the condensation products and identified as in Part A and B. The following yield and constants were obtained:

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(1) Based upon the mixture from the condensation. (See footnote page 40).

Yield: 4%

B_{740} : 166-169°C.

B_{11} : 53°C.

n_D^{20} : 1.4910

D_4^{20} : 0.8632

M_R : Calc. 44.85 Obs. 43.95

M.Pt.: 2-Methyl-2-p-acetaminophenyl propane 168-170°C.

Fraction VIII 2-Methyl-2-phenylbutane

This compound was identified by its acetamino derivative(1) and the constants given by Fox (20). The constants also corresponded to those given for the fraction isolated by Barrett (3). The following yield and constants were determined:

Yield: 2%

B_{741} : 189-192°C.

B_{11} : 69-70°C.

n_D^{20} : 1.4931

D_4^{20} : 0.8735

M_R : Calc. 49.45 Obs. 49.11

M.Pt.: 2-Methyl-2-p-acetaminophenyl butane 139-142°C.

Fraction IX 2-Methyl-3-phenylbutene-2

This fraction corresponded to the fraction isolated and identified by Barrett (3) as trimethyl styrene and was ob-

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(1) See Part F for the preparation of derivatives.

tained in one to two gram yields per mole of alcohol condensed. The following constants were determined:

Yield: 1.3%

B_{727} : 188-193°C.

B_{11} : 88-93 C.

n_D^{20} : 1.5185

D_4^{20} : 0.8921

M_R : Calc. 49.05 Obs. 49.60

Fraction X 2,3,3-Trimethyl-2-phenylbutane

This was the expected alkyl benzene and was identified by its acetamino derivative(1). The constants were determined as follows and corresponded to those obtained by Barrett (3):

Yield: 9%

B_{11} : 100-103°C.

n_D^{20} : 1.5014

D_4^{20} : 0.8665

M_R : Calc. 58.65 Obs. 59.77

M.Pt.: 2,3,3-Trimethyl-2-p-acetaminophenyl butane 142-143°C.

Fraction XI Tarry residue

Yield: 3 grams

Part D --The condensation of 2,2,3-trimethylpentanol-3 with benzene in the presence of anhydrous aluminum chloride.

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(1) See Part F for the preparation of derivatives

Fraction I Methyl chloride

This fraction was isolated as a liquid in trap (K), figure 1. It was identifies by distilling from the container in which it was collected into another tube the same size. The two containers were connected with a delivery tube. A low temperature toluene thermometer was placed in the distilling tube by means of a two hole rubber stopper. The other hole was used for the delivery tube. The receiving tube was left free to the air. Both tubes were placed in baths of solid carbon dioxide and acetone. The temperature was controlled by gradually lifting and lowering the distilling tube in the bath. The liquid was distilled and separated from small amounts of benzene that formed a solid in this trap(1). Then the methyl chloride was collected in a small sample tube having two side arms with stop-cocks and one of the side arms was an inner sealed tube running to the bottom of the sample tube. This allowed for the methyl chloride to be retained as a gas and to be forced out slowly by liquids in order to burn it. The gas burned with a deep yellow flame with a green fringe. Known methyl chloride was treated in the same manner and gave the same properties and constants. This left no doubt as to its identity.

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(1) This small amount of material resulted from the vapor left on the tube when the benzene was heated to drive out all air, and was not the result of the inefficiency of the trap (J) figure 1.

Yield: 4%

B_{745} : -24 to -22°C.

Fraction II 3,4,4-Trimethylpentene-2

This fraction corresponded to 3,4,4-trimethylpentene-2 as reported in the literature (55-56). However, the presence of 2-ethyl-3,3-dimethylbutene-1 was not excluded, since the constants reported (57) for the latter also closely agreed with the constants of this fraction. This compound was compared with that obtained from the alcoholic potassium hydroxide treatment of the chloride prepared from the alcohol as in Part A, Fraction I. The constants obtained from the two compounds were in close agreement. The carbon and hydrogen were determined by Pregl's micro-technique. The yield and following constants were determined:

Yield:	45%(1)			
B_{745} :	106-108°C.			
n_D^{20} :	1.4211			
D_4^{20} :	0.7282			
M_R :	Calc.	39.24	Obs.	39.58
C :	Calc.	85.61%	Found	85.55%
H :	Calc.	14.38%	Found	13.91%

Fraction III 3-Chloro-2,2,3-trimethylpentane

This compound was identified by its preparation from the alcohol as stated above for Fraction I and by the analysis of the chlorine content by Pregl's micro-method. This

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(1) Based entirely upon the chloro-compound in Fraction III.

chloride was very stable. It could be distilled at atmospheric pressure and it was necessary to repeat the alcoholic treatment in order to completely convert the compound into the unsaturated component. The constants for this compound were not found in the literature. The following yield and constants were determined:

Yield: 50%
B_{745} : 158-160°C.
B_{16} : 57-58 C.
n^{20}_{D} : 1.4609
D^{20}_{4} : 0.8840
M_{R} : Calc. 43.87 Obs. 44.09
Cl : Calc. 23.86% Found 23.63%

<u>Fraction IV</u> 2-Methyl-2-phenylpropane

This fraction which appeared in all the condensations, was identified, as in Part A, Fraction III, by its acetamino derivative. The constants were determined as follows:

Yield: 3%
B_{14} : 57-59°C.
B_{750} : 166-169 C.
n^{20}_{D} : 1.4910
D^{20}_{4} : 0.8632
M_{R} : Calc. 44.85 Obs. 43.95
M.Pt.: 2-Methyl-2-p-acetaminophenyl propane
168-170°C.

Fraction V 2-Methyl-3-phenylpentene-2

This compound was aromatic in nature and highly unsaturated. The analysis and comparison of the physical constants with the literature (61) indicated that it was a styrene derivative. Oxidation with potassium permangnate gave degradation products(1) which further supported the evidence that this compound was 2-methyl-3-phenyl-pentene-2. The following yield and constants were obtained:

Yield: 8%

B_{15} : 74-77°C.

n_D^{20} : 1.4980

D_4^{20} : 0.8738

M_R : Calc. 53.66 Obs. 53.86

C : Calc. 89.92% Found 88.99%

H : Calc. 10.07% Found 10.54%

Fraction VI 3-Methyl-3-phenylpentane

An attempt was made to prove the structure of this compound by its conversion into the benzoyl ester,(1) but due to the small yield of material which was difficult to purify, no satisfactory derivative was obtained. However, on the basis of the demethylation that occurred in this condensation, and on the basis of the physical constants (47) and analysis obtained, the evidence was strongly in favor of 3-methyl-3-phenylpentane for this fraction. The following yield and constants were obtained:

---

(1) See Part G on proof of structure.

Yield: 5%

B_{15} : 85-88°C.

n_D^{20} : 1.5015

D_4^{20} : 0.8873

M_R : Calc. 54.05 Obs. 53.77

C : Calc. 88.81% Found 88.75%

H : Calc. 11.19% Found 11.64%

<u>Fraction VII</u> 2,2,3-Trimethyl-3-phenylpentane

This fraction was the expected alkyl benzene and was analyzed for carbon and hydrogen by the Pregl micro-technique. The constants determined agreed with those determined by other workers in this laboratory (48). The yield and constants were determined as follows:

Yield: 10%

B_{15} : 107-110°C.

n_D^{20} : 1.5031

D_4^{20} : 0.8901

M_R : Calc. 63.26 Obs. 63.10

C : Calc. 88.34% Found 88.29%

H : Calc. 11.66% Found 11.73%

<u>Fraction VIII</u> Tarry residue

Yield: 4 grams

Part E --The condensation of 2,3,3-trimethylpentanol-2 with benzene in the presence of anhydrous aluminum chloride.

Fraction I Methyl Chloride

This fraction was isolated in trap (K), figure 1, as a liquid as described in Part D, Fraction I, and identified in the same way.

Yield: 5%

B_{740} : -24 to -22°C.

Fraction II 2,3,3-Trimethylpentene-1

This fraction was identified in the same way as the similar fraction in Part D, Fraction II. The constants agreed with those given by Egloff (61). The following yield and constants were obtained:

Yield: 50%(1)

B_{744} : 106-109 C.

n_D^{20} : 1.4205

D_4^{20} : 0.7366

M_R : Calc. 38.53 Obs. 38.11

Fraction III 2-Chloro-2,2,3-trimethylpentane

This compound was identified by its preparation from the alcohol by the procedure described in Part A, Fraction I (45). The chloride formed in the condensation was analyzed for chlorine by Pregl's micro-analysis. The chloride was found to be just as stable as 3-chloro-2,3,3-trimethylpentane. The following yield, analysis, and constants were obtained:

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(1) Based entirely upon the chloro-compound from Fraction III.

Yield: 55%

B_{740} : 156-159°C.

B_{15} : 55-57 C.

n_D^{20} : 1.4629

D_4^{20} : 0.8845

M_R : Calc. 43.87 Obs. 44.91

Cl : Calc. 23.86% Found 23.70%

Fraction IV 2-Methyl-2-phenylpropane

This fraction, as in the case of Part D, Fraction IV, was formed in the condensation in sufficient quantity to be easily purified. It was identified by the acetamino derivative and the following yield and constants were determined:

Yield: 2.5%

B_{740} : 166-168°C.

B_{15} : 60-63 C.

n_D^{20} : 1.4909

D_4^{20} : 0.8587

M_R : Calc. 44.85 Obs. 44.05

M.Pt.: 2-Methyl-2-p-acetaminophenyl propane 168-169°C.

Fraction V 2-Phenyl-3-methylpentene-2

This compound was aromatic in nature and gave a positive test for unsaturation with 5 per cent bromine in carbon tetrachloride. The physical constants corresponded with the suspected compound and oxidation with potassium permangnate gave a degradation product(1) which supported the evidence

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(1) See Part G on proof of structure.

for this compound as being 2-phenyl-3-methylpentene-2. This compound has been reported by Doss (60). The following yield and constants were determined:

Yield: 2.8%

B_{15} : 78-83°C.

n_D^{20} : 1.4921

D_4^{20} : 0.8723

M_R : Calc. 53.65 Obs. 53.25

Fraction VI 2-Methyl-2-phenylpentane

This compound was saturated and aromatic in nature. Since demethylation also occurred in the condensation from which this fraction was isolated and since the physical constants (62) indicated that this compound was 2-methyl-2-phenylpentane, an attempt was made to convert it into the alpha naphthylurethane derivative (1). The derivative was obtained in small amounts, very impure, and no absolute proof of the structure was offered. However, all evidence pointed to the fact that this fraction was a mixture containing mostly 2-methyl-2-phenylpentane. The following yield and constants were determined:

Yield: 3.1%

B_{15} : 95-99°C.

n_D^{20} : 1.4989

D_4^{20} : 0.8825

M_R : Calc. 54.07 Obs. 54.01

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(1) See Part G on proof of structure.

Fraction VII 2,3,3-Trimethyl-2-phenylpentane

This fraction was the expected condensation product and its constants corresponded to the product as prepared by workers in this laboratory (50). The acetamino derivative was prepared for verification. The following constants and yield were obtained:

Yield: 10%

B_{740} : 230-233°C.

B_{13} : 109-111 C.

n_D^{20} : 1.5011

D_4^{20} : 0.8868

M_R : Calc. 63.26 Obs. 63.12

M.Pt.: 2,3,3-trimethyl-2-p-acetaminophenyl pentane 90-92°C.

Fraction VIII

This fraction was not identified but was suspected of being a mixture of di- and tri-substituted alkyl benzenes. It distilled above 129 degrees centigrade at 13 mm. but over a wide range.

Yield: 3 grams

Fraction IX Tarry residue

Yield : 2 grams

Part F The Preparation of Derivatives

1. Acetamino derivatives

These compounds were prepared according to the method of Ipatieff and Schmerling (46) in the following manner: A mixture of one to two ml. of the aromatic hydrocarbon and 5 ml. of a nitrating mixture was shaken until the reaction no longer evolved heat and had cooled nearly to room temperature. The nitrating mixture consisted of equal volumes of concentrated nitric and concentrated sulfuric acids. The resulting mononitro-compound was poured upon cracked ice and extracted three times with ether. The ether solution was washed twice with water, and the ether evaporated on a steam bath. The oil was dissolved in alcohol and 5 grams of granular tin and 5 ml. of concentrated hydrochloric acid added. The mixture was shaken until no turbidity was observed when a few drops were added to water. Then the mixture was allowed to stand thirty minutes in order to assure complete reduction. Sometimes it was necessary to heat on the steam bath. The liquid was decanted from the excess tin into 20 ml. of water, extracted with ether, and 40 per cent sodium hydroxide added in order to free the amine. The alkali was added until the precipitate of tin hydroxide, which first formed, was redissolved. The mixture was extracted with ether, washed with water, and dried with anhydrous potassium carbonate. The ether solution was filtered from the drying agent, the ether evaporated, and one to two ml. of acetic anhydride added to the residue. Sometimes, at this point the derivative crystallized. The excess anhydride was hydrolyzed by warming with 5 ml. of water, the solution evaporated nearly to dryness, cooled, and filtered. The impure derivative was washed free of acetic acid and recrystallized from 50 per cent alcohol. Hexane or isopropyl alcohol diluted with water was used satisfactorily for recrystallization.

2. Alpha naphthylurethanes

These compounds were prepared according to Malherbe's procedure (63) which was used with some modifications by Guile (64) and also by Kaye (4).

(a) Preparation of the mononitro-alkylbenzenes:

Twenty-four ml. of a mixture of concentrated nitric and sulfuric acids in equal parts by volume were added drop-wise to one-tenth of a mole of the alkylbenzene with shaking. The temperature was not allowed to exceed 50 degrees centigrade. When the addition of the nitrating mixture was complete, the reaction mixture was heated on a water bath for two hours. Then it was poured upon ice and extracted with ether. The ether solution was washed three times with a saturated salt solution and the ether removed on a steam bath. The residue was distilled under reduced pressure.

(b) The Reduction of the nitro-compound:

The nitrated alkylbenzene was converted into the amine by catalytic hydrogenation, using platinum oxide as the catalyst, according to the procedure given in Gilman (65).

The apparatus was calibrated with a known compound at room temperature. The compound to be reduced was placed in the shaking bottle with 100 ml. of alcohol and 0.1 gram of catalyst for each 15 grams of the nitro-compound. The bottle containing the mixture was exhausted of air, and hydrogen under 5-10 atmospheres of pressure was admitted until the pressure ceased to fall. The mixture was filtered from the platinum compound, the alcohol distilled from the amine, and the amine distilled at 1-2 mm. of pressure. The catalyst was prepared by Bailey (66) according to the method given by Voorhees and Adams (67): Chloroplatinic acid was fused with an excess of sodium nitrate at 550 degrees centigrade. The melt was allowed to cool, dissolved in water, and the hydrated platinum dioxide was removed by suction. It was washed with a solution of 1 per cent sodium nitrate, dried, and used in that form.

(c) Conversion of the amine into the phenol:

A hot solution of 11 ml. of concentrated sulfuric acid dissolved in 50 ml. of water was added to each one-tenth mole of amine in a beaker. The solution was stirred and placed in an ice-salt bath. The mixture was maintained at zero degrees centigrade while a saturated aqueous solution of eight grams of sodium nitrite was added slowly with stirring. The solution was stirred after the addition until all the suspended amine sulfate dissolved. Then two grams of urea, dissolved in a minimum of water, was added slowly for each one-tenth mole of the amine. The solution was allowed to stand for ten to fifteen minutes and then poured into a four liter beaker containing two liters of water and heated on the steam bath two hours. The solution was extracted with ether and placed in a Claisen flask. The ether was removed and water added to the residue. Then the mixture was steam distilled, the distillate extracted with ether, and dried over anhydrous sodium sulfate. The ether solution was filtered, the ether removed, and the phenol distilled at reduced pressure.

(d) Preparation of the alpha naphthylurethane:

The phenol was treated with half its volume of alpha naphthylisocyanate, and catalyzed by the addition of a few drops of an anhydrous ether solution of trimethyl amine(1). The mixture was shaken, stopped with a cork having a calcium chloride drying tube and warmed five to fifteen minutes on a steam bath. The derivative crystallized on cooling and was recrystallized from ligroin.

3. 2,4-Dinitrophenylhydrazones

These compounds were prepared according to the procedure given by Shriner and Fuson (68) in the following manner: The unsaturated hydrocarbons were oxidized to a ketone(2) and two ml. of the ketone mixed with 1.5 grams of 2,4-dinitrophenylhydrazine and 100 ml. of alcohol. This mixture was brought to boiling on a steam bath and 2 ml. of concentrated hydrochloric acid added. The mixture was heated

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(1) Kept anhydrous over anhydrous sodium sulfate.

(2) See Part G on proof of structure.

until all material was in solution (usually two to five minutes), and allowed to cool. The precipitate was filtered and washed with cold alcohol. The derivative was recrystallized from hot alcohol, ethyl acetate, or chloroform.

4. Oximes

These compounds were prepared according to the procedure of Shriner and Fuson (69) in the following manner: The unsaturated hydrocarbons were oxidized to ketones(1), and 0.2 gram of the ketone mixed with 2 ml. of 10 per cent sodium hydroxide. Sometimes alcohol was added to give a clear solution. Then 0.5 gram of hydroxylamine hydrochloride in 3 ml. of water was added to the ketone mixture, warmed 10 minutes on a steam bath, and cooled in ice. Crystallization was induced by scratching the walls of the container or adding a small amount of water. The oxime was recrystallized from water or dilute alcohol. It was necessary to add a minimum of solvent because of the solubility of the oximes.

Part G Proof of Structure

1. 2,3-Dimethylbutene-1 and 2-chloro-2,3-dimethylbutane(2)

(a) In order to prove the structure of 2,3-dimethylbutene-1 the structure of 2-chloro-2-3-dimethylbutane was

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(1) See Part G on proof of structure.

(2) Similar compounds were formed in each comdensation and their structure proved as with these compounds. All constants were listed under each fraction.

proven first by its preparation from 2,3-dimethylbutanol-2 according to Shriner and Fuson (45) as follows: For each 1 ml. of alcohol, 10 ml. of a reagent consisting of hydrochloric acid, and zinc chloride, was added drop-wise with stirring. The reagent was prepared by dissolving 136 grams (1 mole) of anhydrous zinc chloride in 105 grams (1 mole) of concentrated hydrochloric acid. The mixture was cooled during the addition. Concentrated hydrochloric acid may be used with the tertiary alcohols without this reagent but with reduced yields of the chloride. The layers formed after this addition were separated and the chloride layer dried with anhydrous sodium sulfate. The chloride was filtered and distilled at reduced pressure. The constants were compared with those found in the literature and with those obtained from the compound coming from the condensation. If the literature did not give all the constants desired, then the compound was converted into the unsaturated compound (b) and the constants of the latter compared with the literature. Chlorine analysis was made also on the compound coming from the condensation when sufficient constants were not given.

(b) The structure of the compound 2,3-dimethylbutene-1 was proved by refluxing 2-chloro-2,3-dimethylbutane with its volume of 50 per cent alcoholic potassium hydroxide for a period of two hours. Then the compound was isolated and purified as described on page 31. The procedure was repeated until a complete conversion was obtained. Usually one treatment for the least branched compounds and two treatments for the more highly branched compounds sufficed. If the conversion was complete and the constants of the chloro-compound agreed with the literature as well as with the chloro-compound from the condensation, then the structure of the unsaturated compound was considered to be proven. If any substance remained after the alkali treatment, the unsaturated compound was treated with dry hydrogen chloride and the resulting compound compared with the prepared chloro-compound as to constants.

2. 2-Methyl-3-phenylpentene on page 47

This compound was synthesized by Bailey (66) using Klages' procedure (70). Potassium dichromate and acetic acid were tried first as an oxidizing mixture in oxidizing this compound to the ketone. Thirteen grams of the compound were refluxed two hours with 36 grams of potassium dichromate and 30 grams of acetic acid. The reaction mixture was poured upon ice and water and extracted with ether. The ether solution was washed with water and dried with anhydrous sodium sulfate. The ether was removed from the filtered solution and the residue distilled under reduced pressure. Most of the original 2-methyl-3-phenylpentene-2 was recovered and the residue gave no satisfactory derivative. The oxidation was repeated using the method of Barrett (3) which was a modification from Shriner and Fuson (71). Ten grams of the known 2-methyl-3-phenylpentene-2 were refluxed with 22 grams of potassium permangnate and 33 grams of concentrated sulfuric acid diluted in water. The reaction was cooled in an ice bath until the reaction subsided and then was gently refluxed on a water bath one hour. The refluxed mixture was treated as above in the case of the dichromate oxidation and the distillation products were used to prepare the 2,4-dinitrophenylhydrazone derivative. Propiophenone was one of the expected degradation products. It was synthesized from propionyl chloride and benzene using the Friedel and Crafts reaction (72). Then seven grams of the suspected 2-methyl-3-phenylpentene-2 from the condensation was treated with 16 grams of potassium permangnate and 24 grams of concentrated sulfuric acid diluted with water and the product purified as in the case with the known compounds above. The hydrazone was prepared as before. These products gave the following data:

M.Pt. of the derivative from known propiophenone: 195-197°C.

M. Pt. of derivative from oxidation products of synthesized 2-methyl-3-phenylpentene-2 : 196-197°C.

M.Pt. of derivative from oxidation products of the suspected 2-methyl-3-phenylpentene-2 : 196-198°C.

M.Pt. of mixed derivatives from synthesized propiophenone and the derivative from the oxidation of the suspected 2-methyl-3-phenylpentene-2 : 195-198°C.

M.Pt. of mixture of 2,4-dinitrophenylhydrazine and the hydrazone of the known propiophenone : 172-180°C.

M.Pt. of the oxime of the known propiophenone : 52-54°C. The derivatives from the oxidation product coming from the condensation were purified with difficulty by using mixed solvents of alcohol, benzene, and ether. An unidentified derivative was isolated which melted from 202-204°C. The above data combined with the constants on page 47 gave good assurance that the compound was 2-methyl-3phenylpentene-2.

3. 3-Methyl-3-phenylpentane on page 47

This fraction was converted into the phenol as described in Part F, 2. The yield of the phenol was too small to purify by fractionation. An attempt to prepare the benzoyl ester resulted in an oily mass that would not crystallize. A few impure crystals were isolated that melted from 110-115°C. Although no absolute proof for this fraction was given; from the constants determined for the fraction and from the fact that a phenolic compound was obtained, the writer was certain that the compound was 3-methyl-3phenylpentane.

4. 2-Phenyl-3-methylpentene-2 on page 50

This fraction was oxidized by treating 2.7 grams of the substance with 6.2 grams of potassium permangnate and 9.3 grams of concentrated sulfuric acid diluted with water in the same manner as with 2-methyl-3-phenylpentene-2. Acetophenone was one of the suspected degradation products. The 2,4-dinitrophenylhydrazone of known acetophenone was prepared. The following data were obtained:

M.Pt. of derivative from known acetophenone : 249-250°C.

M.Pt. of derivative from oxidation products of suspected 2-phenyl-3-methylpentene-2 : 248-251°C.

M.Pt. of mixed derivatives : 251-253°C.

The above data combined with the facts from the constants proved that the fraction was 2-phenyl-3-methylpentene-2.

5. 2-Methyl-2-phenylpentane on page 51

This fraction also was converted into the phenol as described in Part F, 2. The yield was very small and a pure fraction was not obtained. An attempt to form the alpha naphthylurethane porduced an oil that would not crystallize. No rigorous proof of structure was offered. However, a phenolic compound was formed from this fraction. Demethylation occurred in the condensation from which this fraction was isolated and the physical constants corresponded to the suspected compound in spite of the fact that the fraction was known to be a mixture. It was certain, therefore, that the majority of this fraction contained 2-methyl-2-phenylpentane.

DISCUSSION

The amount of fragmentation, resulting from the action of aluminum chloride used in this investigation, was in accord with other workers (3) who found that condensation at higher temperatures produced more fragmentation than at lower temperatures, and that the yield of these fragments was greater at the higher temperatures. The comparison of the selected carbinols showed further that more of these fragments formed and in the greater yield as the branching on the hydroxyl carbon was increased. The yield of the expected alkylbenzene was decreased as the number and yield of fragments increased. Therefore the condensations at the higher temperatures gave the best opportunity to study a mechanism for the condensation of tertiary carbinols in the presence of anhydrous aluminum chloride.

Other workers have observed that catalysts of the type of aluminum chloride have caused products to rearrange (73) and to break the molecules (31). Whether the molecule was cleaved, rearranged, or demethylated by various catalysts seemed to be dependent largely upon the varying conditions of temperature, pressure, and electronic configuration as well as the catalyst itself.

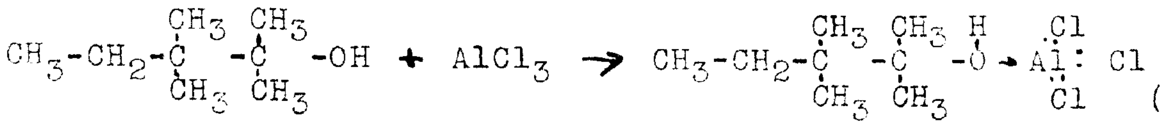
In this investigation one would expect the same type of catalytic action of aluminum chloride on 2,3,3-trimethylbutanol-2, 2,2,3-trimethylpentanol-3, and 2,3,3-trimethylpentanol-2. For the most part this was true. However, in the case of 2,3,3-trimethylbutanol-2, small amounts of ethylene and propylene were obtained and demethylation was detected. While in the case of 2,2,3-trimethylpentanol-3 and 2,3,3-trimethylpentanol-2, relatively large amounts of methyl chloride were obtained and no unsaturated compounds comparable to ethylene or propylene were isolated.

Common to all the condensations, however, was the rearranged product 2-methyl-2-phenylpropane. The yield of this product became larger as the branching of the alcohol was increased. The formation of the alkyl chloride was also common to all the condensations. The chloride proved to be more stable in the case of the highly branched carbinols where it was formed in large amounts. Here, the speed of reaction seemed greater between the cation of the carbinol and the chloride ion than between the carbinol cation and the activated benzene nucleus. The stability of the alkyl chloride was shown in the case of the more branched carbinols where the corresponding alkene was not isolated from the reaction products, but was isolated in the less branched carbinol condensations.

In the case of the more highly branched carbinols, demethylation was definite, with methyl chloride isolated in two cases, and with ethylene and propylene isolated in one other case. The low boiling hydrocarbons that came over as gases below -80°C. indicated in all cases a loss of alkyl groups. The amounts were smaller in the less branched carbinols as would be expected. It seemed important to note that the greater the yield of methyl chloride, the smaller the yield of ethylene and related products, and the greater the yield of ethylene and related products, the smaller the yield of methyl chloride. Where the amounts of products resulting from the loss of alkyl groups were large, the higher fractions of the condensation products gave two types of compounds that verified this loss of alkyl groups. One type was the styrene derivative which was found in three cases. The type was the lower boiling saturated alkylbenzene found in the same three cases.

In light of the theory upon which this investigation was based, a low boiling alkyl chloride was expected. For 2,3,3-trimethylpentanol-2, secondary butyl chloride was expected as one of the products after the rearrangement in which the tertiary butyl cation was formed. Although some of the condensations were run at low temperatures in order to investigate this fraction, it was not found. This expected fraction was found in one case (2,3,3-trimethylbutanol-2) in the form of isopropyl chloride in small amounts. The following equations illustrate the proposed mechanism for all the condensations, using 2,3,3-trimethylpentanol-2 as the illustrative example:

The carbonium ion was believed to have been formed according to Price (24) in the follwing manner:



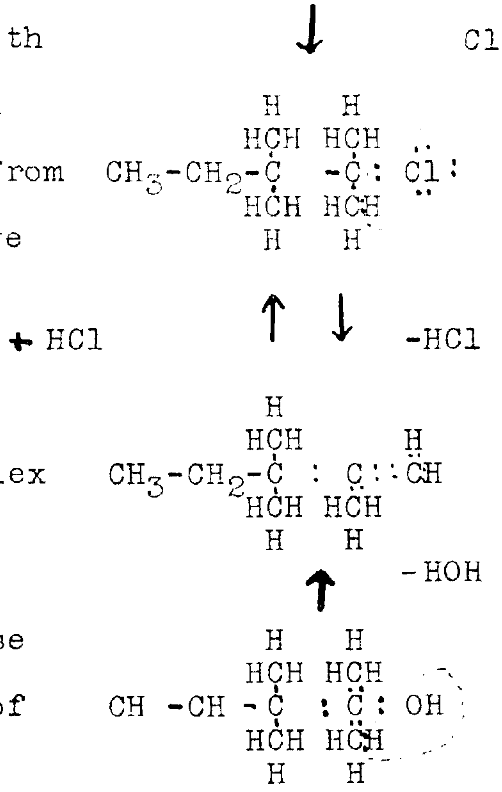
$$CH_3\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}OH + AlCl_3 \rightarrow CH_3\text{-}CH_2\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\underset{CH_3}{\overset{CH_3}{C}}\text{-}\overset{H}{O}\rightarrow \underset{Cl}{\overset{Cl}{Al}}:Cl \qquad (1)$$

$$(HOAlCl_3)^- \quad + \quad CH_3\text{-}CH_2\text{-}\underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}} : \underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}}+ \qquad (2)$$

This cation then reacted with a chloride ion from the HCl formed in the reaction or from the aluminum complex to give the alkyl chloride.

The alkyl chloride then lost HCl to the AlCl$_3$ complex to form the Alkene, or

the alcohol lost HOH because of the dehydrating action of AlCl$_3$



$$\downarrow \quad Cl^-$$

$$CH_3\text{-}CH_2\text{-}\underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}}\text{-}\underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}}:\ddot{C}l: \qquad (3)$$

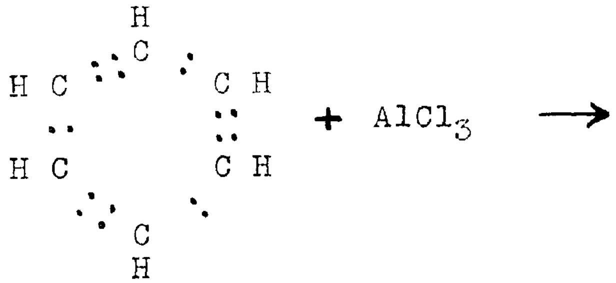
$$+HCl \quad \uparrow \downarrow \quad -HCl$$

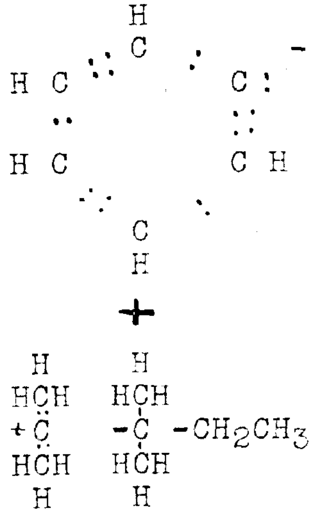
$$CH_3\text{-}CH_2\text{-}\underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}} : \underset{\underset{H}{HCH}}{C}::\overset{H}{CH} \qquad (4)$$

$$\uparrow \quad -HOH$$

$$CH\ \text{-}CH\ \text{-}\underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}} : \underset{\underset{H}{HCH}}{\overset{\overset{H}{HCH}}{C}} : OH \qquad (5)$$

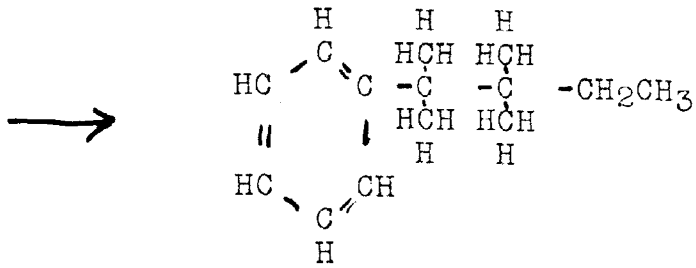
The benzene was activated by the AlCl$_3$,





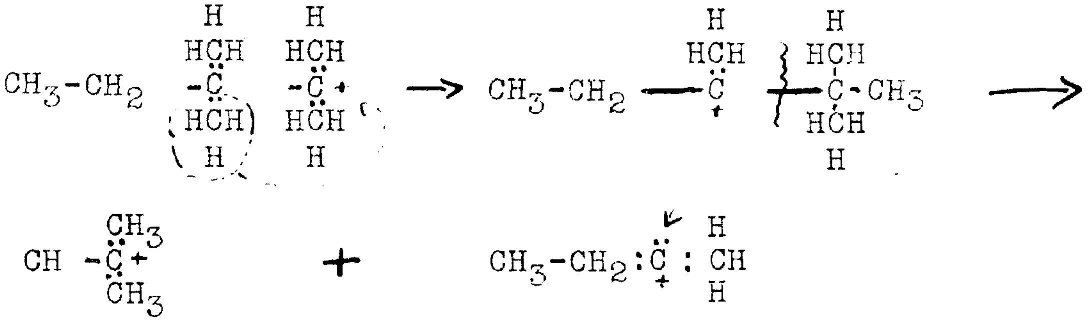
(6)

and the carbonium ion from step two reacted.



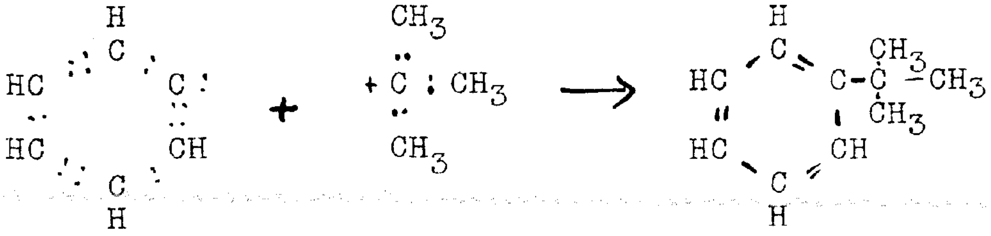
(7)

Parallel with these reactions was the rearrangement of the carbonium ion.

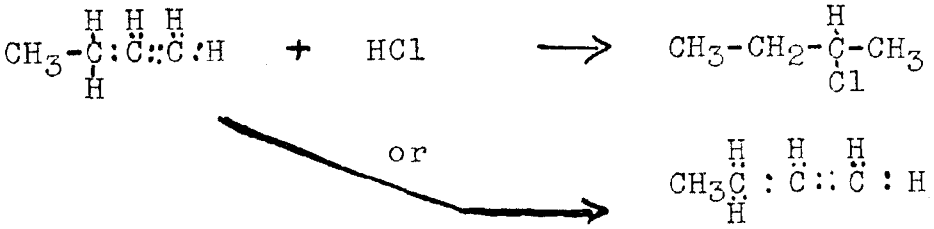


(8)

The rearranged fragments reacted with the activated benzene nucleus and the liberated chloride ion of the reaction or one product formed an alkene.



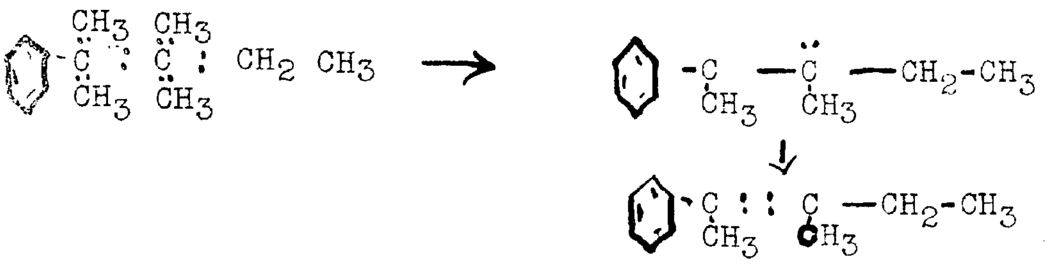
(9)



$CH_3-\underset{H}{\overset{H}{C}}:\overset{H}{C}::\overset{H}{C}:H + HCl \longrightarrow CH_3-CH_2-\underset{Cl}{\overset{H}{C}}-CH_3$ (10)

$CH_3\underset{H}{\overset{H}{C}}:\overset{H}{C}::\overset{H}{C}:H$ (11)

When demethylation took place, the reaction may have followed two paths, one in which the electrons formed a double bond,

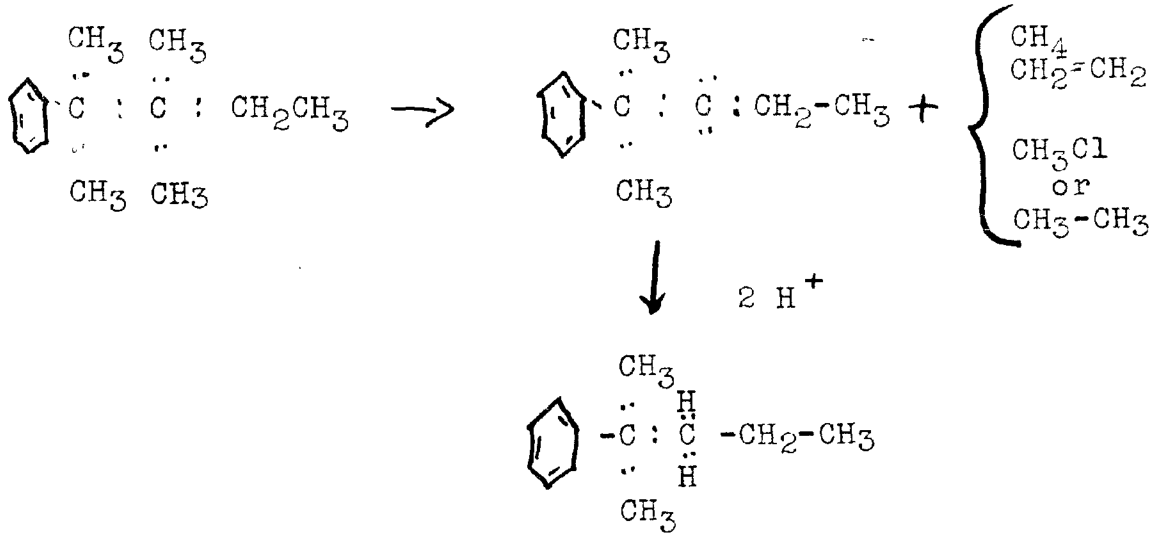


(12)

or one in which a proton from the reaction

$$HCl + {}^{+}CH_3 \longrightarrow CH_3Cl + H^{+}$$

reacted with the demethylated compound



(14)

SUMMARY

1. The method of condensation of carbinols with benzene in the presence of aluminum chloride has been modified in such a manner that the nature of all reaction products could be investigated.

2. Five tertiary carbinols with increased branching on the hydroxyl carbon have been condensed with benzene in the presence of anhydrous aluminum chloride and the reaction products studied.

3. Demethylation was found to be pronounced in the more highly branched alcohols, and was evident in other cases.

4. Fragmentary products were isolated and identified which verified the demethylation process.

5. A procedure has been suggested for the removal of alkyl chlorides which have prevented the separation of fractions.

6. A mechanism for the condensation of tertiary carbinols with benzene in the presence of anhydrous aluminum chloride at elevated temperatures has been proposed.

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