CONDENSATION OF TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE II. HEPTYL ALCOHOLS AND BENZENE

THESIS FOR THE DEGREE OF M. S.

Marvin Norman Binder

1935

R. C. Mustain
5/6/35

CONDENSATION OF TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE

II. HEPTYL ALCOHOLS AND BENZENE

CONDENSATION OF TERTIARY ALIPHATIC CARBINOLS WITH AROMATIC COMPOUNDS IN THE PRESENCE OF ALUMINUM CHLORIDE II. HEPTYL ALCOHOLS AND BENZENE

A Thesis

Submitted to the Faculty of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the Master of Science Degree

By

Marvin Norman Binder

June 1935

ACKNOWLEDGEMENT

The author takes this opportunity to acknowledge his indebtedness to Dr. R.C.Huston for his friendly advice and helpful suggestions during the performance of this work.

CONTENTS

HISTORICAL

A history of condensation reactions, brought about by such catalysts as H_2SO_4, P_2O_5, H_3PO_4, $MgCl_2$, $ZnCl_2$, PCl_5, $AlCl_3$, etc. has been amply covered by former workers in this laboratory. This material is already available in good form, however, it was felt necessary to include a brief resume of research carried out in this laboratory involving the reactions of alcohols with benzene in the presence of aluminum chloride as a catalyst. The alcohols include aromatics, aliphatics, and mixed aromatic aliphatics.

The first work in this field was started by Huston and Friedmann (J. Am. Chem. Soc., 38, 2527, 1916). They found that primary aromatic alcohols react with benzene in the presence of aluminum chloride. Benzyl alcohol and benzene react to give diphenylmethane as the principal product.

$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + H_2O$$

Later work by Huston and Friedmann (J. Am. Chem. Soc., 40, 785, 1918), shows that secondary aromatic alcohols condense with benzene according to the reaction:

$$\begin{matrix} C_6H_5 \\ R \end{matrix}\!\!\diagdown\!\!\diagup CHOH + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} C_6H_5 \\ R \end{matrix}\!\!\diagdown\!\!\diagup CHC_6H_5 + H_2O$$

R may be methyl, ethyl, or phenyl. A better yield is obtained when R is phenyl.

Reactions with tertiary aromatic alcohols and benzene:

Huston* found that triphenyl carbinol will not condense with benzene to form tetraphenyl methane as expected. In-

* unpublished

stead, the product is triphenyl methane.

$$(C_6H_5)_3COH + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH + ---$$

Apparently, the oxygen is removed from the carbinol. Where this oxygen goes to, has yet to be determined.

Huston, Wilsey, and Hradel (Master's Theses)* found that diaryl-alkyl carbinols do not condense with benzene; instead, dehydration occurs.

$$\begin{matrix}(C_6H_5)_2\\ C_2H_5\end{matrix}\!\!>\!COH + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!\!>\!C{=}CHCH_3 + H_2O$$

Huston and Macomber*, in working with dialkyl-aryl carbinols, observed no condensation but dehydration instead.

$$\begin{matrix}C_6H_5\\ C_2H_5\end{matrix}\!\!>\!C\!<\!\begin{matrix}C_2H_5\\ OH\end{matrix} + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix}C_6H_5\\ C_2H_5\end{matrix}\!\!>\!C{=}CHCH_3 + H_2O$$

Condensation of aliphatic carbinols with benzene in the presence of aluminum chloride:

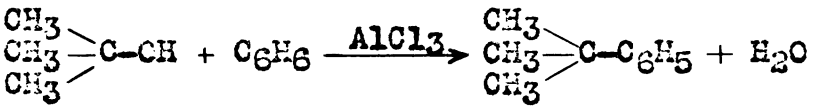
Huston and Sager (J. Am. Chem. Soc., 43, 1955, 1926) report that saturated aliphatic alcohols do not condense with benzene. Among these are methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, and iso-amyl. However, they found that the unsaturated alcohol, allyl alcohol, will condense with benzene.

$$CH_2{=}CHCH_2OH + C_6H_6 \xrightarrow{AlCl_3} CH_2{=}CHCH_2C_6H_5 + H_2O$$

Huston and Hsieh (Doctor's Thesis)*, with slight

* unpublished

modifications in procedure, were able to condense aliphatic alcohols with benzene and benzene derivatives. Primary alcohols do not react at all; secondary alcohols react very slightly; tertiary alcohols react very readily to form the corresponding alkyl benzene.



Huston and Fox (Master's Thesis)* condensed tert-butyl alcohol, tert-amyl alcohol, dimethyl n-propyl and dimethyl iso-propyl carbinol with benzene to obtain tert-butyl benzene, tert-amyl benzene, dimethyl n-propyl phenyl methane, and dimethyl iso-propyl phenyl methane in good yields.

Summary-

1. Primary and secondary aromatic alcohols condense with benzene in the presence of aluminum chloride to form the corresponding benzene derivative.

2. Mixed tertiary aliphatic-aromatic alcohols do not condense with benzene. Dehydration of the carbinol occurs to form the corresponding unsaturated hydrocarbon.

3. Unsaturated aliphatic (primary) alcohols, with the double bond adjacent to the hydroxyl carbon, condense with benzene.

4. Tertiary aliphatic alcohols condense readily with benzene, secondary alcohols react only slightly, while primary alcohols do not react at all.

* unpublished

Other Methods for Preparing the tert-Alkyl Benzenes

Dimethyl iso-butyl phenyl methane-

From 2-chlor-2,4-dimethyl pentane and benzene in the presence of aluminum chloride (Schreiner, J. pr. [2], 82, 294). B.P. 218°; d_4^{15} - 0.8741; $n_D^{16.5}$ - 1.4938.

Methyl ethyl n-propyl phenyl methane-

From 3-chlor-3-methyl hexane and benzene in the presence of aluminum chloride (Halse, J. pr. [2], 89, 452). B.P. 110-112°/15 mm.; d_4^{20} - 0.8819; n_D^{15} - 1.4995.

Triethyl phenyl methane-

From triethyl chloromethane and benzene in the presence of aluminum chloride (Schreiner, J. pr. [2], 82, 296). B.P. 220-222°; d_4^{25} - 0.8656; n_D^{25} - 1.4921.

EXPERIMENTAL

MATERIALS

The butyl bromides were obtained from Eastman Kodak Laboratories. It was also necessary to prepare some of the bromides from the corresponding alcohol because the supply on hand was not sufficient to carry on satisfactory research. The alcohols were also obtained from Eastman.

Tert-butyl chloride was prepared from tert-butyl alcohol.

Methyl ethyl ketone and ethyl carbonate were obtained from Eastman.

Ethyl bromide was prepared from commercial (95%) ethyl alcohol.

Acetone was C.P. grade.

n-Propyl bromide and iso-propyl bromide were prepared from the corresponding alcohols.

Magnesium (turnings), especially prepared for Grignard reactions, was used.

C.P. thiophene-free benzene was used in all condensations.

Aluminum chloride was a high grade commercial product.

Preparation of Carbinols

Dimethyl n-butyl carbinol or 2-methyl hexanol-2,

From n-butyl magnesium bromide and acetone (Whitmore & Church, J. Am. Chem. Soc., 55, 1113-24, 1933).

B.P. 139-142°

59-61° (25 mm)

n_D^{20} - 1.4179, 1.4176

Approximate yield obtained - 60%

Dimethyl iso-butyl carbinol or 2,4-dimethyl pentanol-2,

From iso-butyl magnesium bromide and acetone (Edgar, Calingaert, and Marker, J. Am. Chem. Soc., 51, 1483-91, 1929)

B.P. 137-139°

50-52° (20 mm)

n_D^{20} - 1.4172

Approximate yield obtained - 30%

Dimethyl sec-butyl carbinol or 2,3-dimethyl pentanol-2,

From sec-butyl magnesium bromide and acetone (Edgar, Calingaert, & Marker, J. Am. Chem. Soc., 51, 1483-91, 1929)

B.P. 128-130.5°

52-53.5° (20 mm)

n_D^{20} - 1.4370

Approximate yield obtained - 25%

Dimethyl tert-butyl carbinol or 2,2,3-trimethyl butanol-3,

From tert-butyl magnesium chloride and acetone (Whitmore, J. Am. Chem. Soc., 55, 1559-67, 1933; Edgar, Calingaert, & Marker, ibid., 51, 1483-91, 1929). Better yields

are obtained when tert-butyl chloride is used instead of tert-butyl bromide.

B.P. 130° M.P. 17°

The carbinol is very hygroscopic and forms a hydrate with melting point around 80-83°. When it is distilled in small amounts and without special precautions, only the hydrate is obtained. When larger quantities are handled, the distillate is a mixture of the liquid carbinol and acicular crystals of its hydrate. The hydrate loses its water readily when kept in a dessicator over barium oxide (E., C., & M.).

Approximate yield obtained - 15 to 20%

Methyl ethyl n-propyl carbinol,

From n-propyl magnesium bromide and methyl ethyl ketone (Whitmore & Badertscher, J. Am. Chem. Soc., 55, 1559-67, 1933).

B.P. 139-141°

56° (20 mm)

n_D^{20} - 1.4231

Approximate yield obtained - 61%

Methyl ethyl iso-propyl carbinol,

From iso-propyl magnesium bromide and methyl ethyl ketone (Whitmore & Evers, J. Am. Chem. Soc., 55, 812-16, 1933).

B.P. 138-140° (750 mm)

49-50° (20 mm)

n_D^{20} - 1.4287, 1.4280

Approximate yield obtained - 26%

Triethyl carbinol.

From ethyl magnesium bromide and diethyl carbonate (Moyer & Marvel, Organic Synthesis XI, 98-100, 1931).

B.P. 140-142°

72-73° (53 mm)

n_D^{20} - 1.4294

Approximate yield obtained - 83%

CONDENSATIONS

A. Dimethyl n-butyl carbinol, benzene, and $AlCl_3$,

Trial I.

Carbinol - 1 eq. - 20 g.

Benzene - 5 " - 67 g.

$AlCl_3$ - ½ " - 11.5 g.

A 500 ml. three-necked round-bottom flask was provided with a mercury sealed mechanical stirrer, a tube to remove HCl fumes, a thermometer, and a separatory funnel. Benzene was placed in the flask and the stirrer started. The entire amount of $AlCl_3$ was then added to the benzene. The $AlCl_3$ is thus uniformly suspended in the benzene. By this procedure, the temperature may easily be controlled by the rate of addition of the carbinol. The carbinol was then added drop by drop (about a drop every five seconds). Three hours elapsed during the addition. Considerable HCl was evolved during the reaction. The temperature was easily maintained between 25 and 30° C. and not allowed to go above 30°. No external cooling was necessary. The entire mixture was stirred for an additional two hours. During the addition of the carbinol, the mixture changes from a yellow to a dark red color, forming a coagulate which breaks up after more of the carbinol is added and later turning a dark red-brown. Mixture was allowed to stand overnight (about 18-20 hours); then decomposed with ice and hydrochloric acid. The benzene layer was separated and the aqueous portion extracted several times with ether. In the

ether extraction, it was necessary to add HCl to destroy the ether-water emulsion which formed. The ether and benzene extracts should be washed with dilute sodium carbonate to remove any remaining HCl. It is then dried over anhydrous calcium chloride. The ether and benzene are distilled off and the residue distilled in a fractionating column at reduced pressure. The following fractions were obtained at 20 mm.

I. (30 - 106°) - 2 g.

II. (106 - 109°) - 12 g.

III. Above 109° - 6 g.

The fraction boiling at 106-109° is dimethyl n-butyl phenyl methane.

Equation of Reaction:

$$CH_3CH_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-CH + C_6H_6 \xrightarrow{AlCl_3} CH_3CH_2CH_2CH_2\overset{CH_3}{\underset{CH_3}{C}}-C_6H_5 + H_2O$$

Trial II.

The same quantities, procedure, and conditions were used as in trial I. Fractions at 20 mm.:

I. (30 - 106°) - 2 g.

II. (106 - 109°) - 12 g.

III. Above 109° - 6 g.

Trial III.

The same procedure was followed as in trial I & II.

Carbinol - 1 eq. - 20 g.

Benzene - 4 " - 54 g.

$AlCl_3$ - ½ " - 11.5 g.

The following fractions were obtained at 20 mm.:

I. (30 - 106°) - 1½ g.

II. (106 - 109°) - 11 g.

III. Above 109° - 6 g.

An increase in the amount of $AlCl_3$ seems to lower the yield of alkyl benzene.

Trial IV.

Carbinol - 1 eq. - 20 g.

Benzene - 6 " - 81 g.

$AlCl_3$ - ½ " - 11.5 g.

The following fractions were obtained at 20 mm.:

I. (30 - 106°) - 3 g.

II. (106 - 109°) - 12 g.

III. Above 109° - 5 g.

Trial V.

Carbinol - 1 eq. - 20 g.

Benzene - 7 " - 94 g.

$AlCl_3$ - ½ " - 11.5 g.

The following fractions were obtained at 20 mm.:

I. (30 - 106°) - 1½ g.

II. (106 - 109°) - 13 g.

III. Above 109° - 5 g.

So far, in all trial runs only one-sixth of a mole of the carbinol was used. It was thought that if larger quantities are used a better yield of alkyl benzene is obtained. In the next trial one-half mole of the carbinol is used.

Trial VI.

Carbinol - 1 eq. - 58 g.

Benzene - 5 " - 195 g.

$AlCl_3$ - ½ " - 33.4 g.

Upon fractionation at 20 mm. obtained

I. (106 - 109°) - 39 g.

Analysis of Fractions

Fraction (30-106°) contains a small amount of 2-chlor-2-methyl hexane, B.P. 132°; 39-40°/20 mm.; n_D^{20} - 1.4210.

As a check, the chloride was prepared from the corresponding carbinol by saturating with dry HCl gas. The product boiled at 39-40°/20 mm.; n_D^{20} - 1.4208.

The boiling point of the chloride, as recorded in the literature, is 130-135°.

Fraction (106-109°) is the condensation product, dimethyl n-butyl phenyl methane. After several fractionations, it boiled at 107-107.5°/20 mm. This compound is not recorded in the literature.

Carbon-Hydrogen Determination:

Wt. sample	wt. CO_2	% C	wt. H_2O	% H_2
.2002	.6504	88.61	.2047	11.44
.2149	.6982	88.35	.2203	11.47
Calculated for $C_{13}H_{20}$		88.63		11.36

Molecular Weight Determination:

Wt. sample	Temp. diff.	Wt. benzene	Mol. wt.
1.0136	.335	43.4442	169
Calculated for $C_{13}H_{20}$			176

The following table shows the yields of dimethyl n-butyl phenyl methane obtained from the various trials.

Table of Results

Reactants						Products		
Carbinol		Benzene		$AlCl_3$		Act.Yld.	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
20	1	67	5	11.5	½	13	30.3	39
20	1	67	5	11.5	½	13	30.3	39
20	1	54	4	11.5	½	11	30.3	36
20	1	81	6	11.5	½	12	30.3	39
20	1	94	7	11.5	½	13	30.3	43
58	1	195	5	33.4	½	39	88.0	44

Only a light increase in yield is observed when larger quantities are used.

Fraction boiling above 109°/20 mm. was fractionated to yield a heavy yellow-colored oil boiling at 135-160°/20 mm. Probably a polymer; it may also contain some dialkyl benzene. It was allowed to stand in the ice-box for several months but no crystallization was noted.

B. Dimethyl iso-butyl carbinol, benzene, and $AlCl_3$, Trial I.

Carbinol - 1 eq. - 10 g.

Benzene - 5 " - 34 g.

$AlCl_3$ - ½ " - 6 g.

The same procedure used in previous condensations was followed. The carbinol was added, drop by drop, to a suspension of $AlCl_3$ in benzene. HCl was evolved. The temperature was kept between 25 and 30°. After about half of the carbinol had been added, a black coagulate formed which broke up as more carbinol was added. The mixture turned dark red-brown. Three hours elapsed during the addition of the carbinol. Stirring was continued for two more hours. Allowed to stand overnight. Decomposed with HCl and ice-water, etc. Distilled and fractionated.

Recovered benzene - 24 g.

Fractions at 20 mm.:

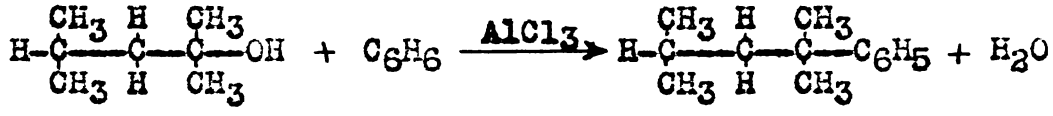
I. (33 - 40°) - 4 g.

II. (40 - 99°) - ½ g.

III. (99 - 103°) - 3 g.

IV. Above 103° - 4 g.

Equation of Reaction:



The fraction boiling at 99-103° is the condensation product, dimethyl iso-butyl phenyl methane.

Trial II.

Carbinol - 1 eq. - 30 g.

Benzene - 5 " - 67 g.

$AlCl_3$ - $\frac{1}{2}$ " - 11.5 g.

The following fractions were obtained at 20 mm.:

I. (33 - 40°) - 5 g.

II. (40 - 93°) - $\frac{1}{2}$ g.

III. (93 - 103°) - 6 g.

IV. Above 103° - 6 g.

Analysis of Fractions

Fraction (33-40°) when fractionated yielded a liquid boiling at 33-34°/20 mm. It is saturated and contains halide. Probably the chloro compound of the carbinol, 2-chlor-2,4-dimethyl pentane. n_D^{20} - 1.4339.

This compound is recorded in the literature with the following properties: B.P. 135-136°; n_D^{17} - 1.4202.

As a check, the chloro compound was prepared by saturating dimethyl iso-butyl carbinol with dry HCl gas. The product had the following properties:

B.P. 32-33°/20 mm. n_D^{20} - 1.4335

Determination of its boiling point at atmospheric pressure was difficult. The substance decomposes, liberating HCl.

The crude fraction (33-40°/20 mm) also contains some unsaturated products as shown by the bromine test.

The fraction (40-99°) is a mixture of the chloride and condensation product.

Fraction (99-103°) is the condensation product, dimethyl iso-butyl phenyl methane. When fractionated several times it yielded a fraction with the properties:

B.P. 216-217° (745.6 mm)

100-102° (20 mm)

$n_D^{16.5} - 1.4940$

This corresponds to the properties of dimethyl iso-butyl phenyl methane as recorded in the literature.

B.P. 213° $n_D^{16.5} - 1.4938$

The following table shows the yields obtained from the various condensations, dimethyl iso-butyl phenyl methane being the product.

Table of Results

Reactants						Product		
Carbinol		Benzene		$AlCl_3$		Act.Yld.	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
10	1	34	5	6	½	3	15.5	19.4
20	1	67	5	11.5	½	6	30.3	19.8
20	1	81	6	11.5	½	5	30.3	16.5
23.2	1	103	7	13.7	½	5	35.2	14.2
30	1	98	5	16.7	½	8	44.0	18.4

C. Dimethyl sec-butyl carbinol, benzene, and $AlCl_3$, Trial I.

Carbinol - 1 eq. - 23.2 g.

Benzene - 5 " - 78 g.

$AlCl_3$ - ½ " - 13.7 g.

The same procedure used in previous condensations was followed. The carbinol was added to a suspension of $AlCl_3$ in benzene with constant stirring. The temperature was kept at 25°. Addition of the carbinol required three hours. HCl was evolved freely. Stirring was continued for two more hours and the mixture allowed to stand overnight. It was decomposed, extracted, etc. The extracts were distilled and fractionated.

Recovered benzene - 65 g.

The following fractions were obtained at 20 mm.:

I. (33 - 43°) - 6 g.

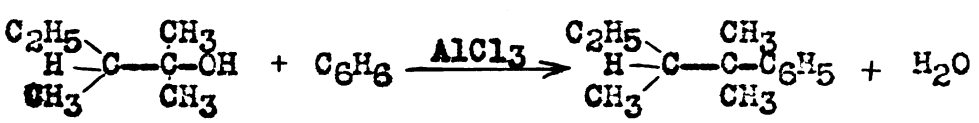
II. (43 - 102°) - 1 g.

III. (102 -108°) - 5 g. (10 g. recovered)

IV. Above 108° - 8 g.

The fraction boiling at 102-108° contains the condensation product, dimethyl sec-butyl phenyl methane.

Equation of Reaction:



Analysis of Fractions

Fraction (33-43°) contains halogen and is unsaturated.

A fraction was isolated boiling at 38-39°/20 mm. This fraction contains halogen but shows no unsaturation.

$$n_D^{20} - 1.4264$$

This corresponds very closely to the chloro compound, 2-chlor-2,3-dimethyl pentane. It has been previously shown that the fraction obtained in the dimethyl iso-butyl condensation is the chloro compound. Since these compounds are isomeric, their boiling points are closely related.

Fraction (43-102°) is a mixture of the chloride, condensation product, and unsaturated products.

Fraction (102-108°) was repeatedly fractionated to yield a liquid boiling at 105-107°/20 mm. It is saturated and does not contain halide. It was assumed to be the alkyl benzene.

Dimethyl sec-butyl phenyl methane is not recorded in the literature.

Carbon-Hydrogen Determination:

Wt. sample	wt. CO_2	% C	Wt. H_2O	% H_2
.2063	.6359	83.03	.2089	11.33
Calculated for $C_{13}H_{20}$		88.63		11.36

Molecular Weight Determination:

Wt. sample.	Temp. diff.	Wt. benzene	Mol. wt.
1.0623	.351	44.000	167
Calculated for $C_{13}H_{20}$			176

The following table shows the yields obtained from various condensation trials, the product being dimethyl

iso-butyl phenyl methane.

Table of Results

Reactants						Products		
Carbinol		Benzene		$AlCl_3$		Act.Yld.	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
23.2	1	78	5	13.7	½	5	35.2	14.2
"	1	"	5	"	½	4½	"	12.8
"	1	"	5	"	½	5	"	14.2
30	1	98	5	17	½	6½	44.0	15.0

D. Dimethyl tert-butyl carbinol, benzene, and $AlCl_3$, Trial I.

Carbinol - 1 eq. - 23.2 g.

Benzene - 5 " - 78 g.

$AlCl_3$ - ½ " - 13.7 g.

The carbinol was mixed with about one-half of the quantity of benzene and then added from a dropping funnel to the benzene-aluminum chloride suspension. Since the carbinol is very hygroscopic and crystallizes, it was necessary to mix it with some benzene to prevent crystallization. A calcium chloride tube was attached to the funnel to exclude all moisture. The reaction proceeded in the usual manner. Upon distillation and fractionation, obtained the following:

Recovered benzene - 70 g.

Recovered carbinol - 12 g.

Fractionation at 20 mm. yielded,

I. (104 - 109°) - 1 to 1½ g.

II. Above 109° - 2 g.

The fraction boiling at 104-109° has the characteristic odor of the other butyl hydrocarbons, does not contain halogen, but shows unsaturation. The boiling point corresponds to the boiling point of the other hydrocarbons. Probably it is the hydrocarbon with a little of unsaturated material.

Due to the difficulty involved in working with the carbinol, that is, purification and dehydration, work was discontinued.

E. Methyl ethyl n-propyl carbinol, benzene, and $AlCl_3$, Trial I.

Carbinol - 1 eq. - 23.2 g.

Benzene - 5 " - 78 g.

$AlCl_3$ - ½ " - 13.7 g.

The same procedure used in previous condensations was followed. Distillation and fractionation yielded:

Recovered benzene - 63 g.

Fractions at 15 mm.:

I. (35 - 98°) - 1½ g.

II. (98 - 101°) - 12.5 g.

III. Above 101° - 4 g.

Equation of Reaction:

$$\begin{matrix} CH_3 \\ C_2H_5 \\ C_3H_7 \end{matrix}\!\!>\!C\!-\!OH + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} CH_3 \\ C_2H_5 \\ C_3H_7 \end{matrix}\!\!>\!C\!-\!C_6H_5 + H_2O$$

The fraction boiling at 98-101°/15 mm. is methyl ethyl

n-propyl phenyl methane.

Trial II.

Carbinol - 1 eq. - 32 g.

Benzene - 5 " - 130 g.

$AlCl_3$ - ½ " - 22 g.

Distillation and fractionation yielded the following fractions.

Recovered benzene - 107 g.

Fractions at 15 mm.

I. (35 - 99°) - 3 g.

II. (99 - 102°) - 24 g.

III. Above 102° - 9 g.

Analysis of Fractions

Fraction (35-99°) when fractionated, yielded a liquid boiling at 40-42°/20 mm. This fraction is saturated and contains halogen. It corresponds to the chloro compound, methyl ethyl n-propyl chloromethane. The chloro compound was prepared from the corresponding carbinol by saturating with dry HCl gas. Its properties are

B.P. 41°/20 mm. n_D^{20} - 1.4383

As recorded in the literature, its properties are

B.P. 39-40°/15 mm. n_D^{15} - 1.4271

Only a very small amount of the chloride was obtained from the condensation reaction; about two to three grams from both condensations.

Fraction (99-102°) when fractionated several times

yielded a liquid boiling at 100°/15 mm. and 106.5-107°/ 20 mm. It is assumed to be the condensation product, methyl ethyl n-propyl phenyl methane. Its properties are

$$n_D^{20} = 1.4964 \qquad n_D^{15} = 1.4935$$

It is recorded in the literature with the following properties:

$$\text{B.P. } 110\text{-}112^{\circ}/15 \text{ mm.} \qquad n_D^{15} = 1.4935$$

The boiling points do not check very closely.

Carbon-Hydrogen Determination:

Wt. sample	wt. CO_2	% C	wt. H_2O	% H_2
.2020	.6535	88.23	.2065	11.44
Calculated for $C_{13}H_{20}$		88.63		11.36

The following table shows the yields of methyl ethyl n-propyl phenyl methane obtained from various trials.

Table of Results

Reactants						Products		
Carbinol		Benzene		$AlCl_3$		Act. Yld.	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
23.2	1	78	5	13.7	½	12.5	35.2	35
39	1	130	5	22	½	24	59	40

F. Triethyl carbinol, benzene, and $AlCl_3$,

Trial I.

Carbinol - 1 eq. - 23.2 g.

Benzene - 5 " - 78 g.

$AlCl_3$ - ½ " - 13.7 g.

The same procedure used in previous condensations was followed.

Recovered benzene - 64 g.

Fractions at 20 mm.:

I. (33 - 105°) - 1 g.

II. (105 - 108°) - 13 g.

III. Above 108° - 5½ g.

The fraction boiling at 105-108° is triethyl phenyl methane.

Equation of Reaction:

$$(C_2H_5)_3C\text{-}CH + C_6H_6 \xrightarrow{AlCl_3} (C_2H_5)_3C\text{-}C_6H_5 + H_2O$$

Trial II.

Carbinol - 1 eq. - 39 g.

Benzene - 5 " - 130 g.

$AlCl_3$ - ½ " - 22 g.

Fractions at 20 mm.:

I. (33 - 105°) - 3 g.

II. (105 - 108°) - 24 g.

III. Above 108° - 7 g.

Analysis of Fractions

Fraction (33-105°) when fractionated yielded a liquid boiling at 42-43°/20 mm. It is assumed to be the chloride of the carbinol. As a check, triethyl chloromethane was made from triethyl carbinol and dry HCl gas.

B.P. 43°/20 mm. n_D^{20} - 1.4320

It is recorded in the literature with the following properties:

B.P. 143-144° n_D^{25} - 1.4328

Very little of the chloro compound was obtained; about one gram from both trials.

Fraction (105-108°) was fractionated several times to yield a fraction boiling at 107-108°/20 mm. It is assumed to be the condensation product, triethyl phenyl methane.

B.P. 107.5°/20 mm.

225-226°/745.6 mm.

n_D^{20} - 1.4975 n_D^{25} - 1.4953

The following properties are recorded in the literature:

B.P. 220-222° n_D^{25} - 1.4981

Carbon-Hydrogen Determination:

Wt. sample	wt. CO_2	% C	wt. H_2O	% H_2
.2031	.6581	88.37	.2071	11.41
Calculated for $C_{13}H_{20}$		88.63		11.36

The following table shows the yields of triethyl phenyl methane obtained from various trials.

Table of Results

Reactants						Products		
Carbinol		Benzene		$AlCl_3$		Act.Yld.	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
23.2	1	78	5	13.7	½	13	35.2	36
39	1	130	5	22	½	24	59	40

G. Methyl ethyl iso-propyl carbinol, benzene, and $AlCl_3$, Trial I.

Carbinol - 1 eq. - 23.2 g.

Benzene - 5 " - 78 g.

$AlCl_3$ - ½ " - 13.7 g.

The same procedure used in previous condensations was followed. Distilled and fractionated, at 20 mm.

Recovered benzene - 64 g.

I. (35 - 45°) - 4 g.

II. (45 - 103°) - 5 g.

III. (103 -108°) - 5 g. (12 g Hvanick)

IV. Above 108° - 5 g.

Four more trials were made using the same quantities as above. The same results were obtained in each case.

Analysis of Fractions

Fraction (35-45°) was fractionated to yield a liquid boiling at 41-43°/20 mm. This was found to be the chloro compound, 3-chlor-3,4-dimethyl pentane.

Fraction (45-103°) probably is a mixture of the chloro compound, unsaturated products, and some rearrangement pro-

ducts. No definite boiling fractions could be separated.

Fraction (103-108°) when fractionated several times yielded a liquid boiling at 105-107°/20 mm. This must be the condensation product, methyl ethyl iso-propyl phenyl methane which is not recorded in the literature.

Carbon-Hydrogen Determination:

Wt. sample	wt. CO_2	% C	wt. H_2O	% H_2
.2113	.6838	88.26	.2153	11.42
Calculated for $C_{13}H_{30}$		88.63		11.36

Molecular Weight Determination:

Wt. sample	Temp. diff.	wt. benzene	Mol. wt.
1.0623	.352	44.00	166
Calculated for $C_{13}H_{20}$			176

The following table shows the yield of methyl ethyl iso-propyl phenyl methane obtained.

Table of Results

Reactants						Products		
Carbinol		Benzene		$AlCl_3$		Act.Yld	Theo.	Yld.
g.	eq.	g.	eq.	g.	eq.	g.	g.	%
23.2	1	78	5	13.7	½	4	35.2	11.4

The higher boiling fractions of each group of condensations have not been separated. No definite boiling fractions could be isolated.

Determination of Physical Constants

Density determinations were made by means of a small picnometer devised by the author. All determinations were made at 20° C. compared to water at 4° C.

Index of refraction measurements were made with the Abbe' refractometer.

Surface tension measurements were made by means of the Harkins' Drop-Weight method and by the DuNouy Tensiometer method.

For the drop-weight method, surface tension was calculated by the formula,

$$\gamma = \frac{m\,g}{R} F$$

where

γ - surface tension in dynes/cm.

m - mass of drop in grams

v - volume of drop $(\frac{m}{d})$

g - pull of gravity (981)

R - radius of tip (.27158 cm)

F - a constant, obtained from table corresponding to $\frac{v}{R^3}$

The DuNouy Tensiometer is a direct reading instrument, that is, values for surface tension are read directly on a dial.

The observed molecular volume was calculated by dividing the molecular weight of the compound by its density.

The observed parachor was calculated by the formula,

$$P = \frac{M}{d} \cdot \gamma^{1/4}$$

where P - parachor of compound
M - molecular weight
d - density
γ - surface tension

Molecular refractions were calculated by the formula,

$$M_D = \frac{M}{d} \cdot \frac{n^2 - 1}{n^2 + 2}$$

where M_D - molecular refraction
M - molecular weight
d - density
n - index of refraction

Theoretical molecular volumes were calculated by the formula,

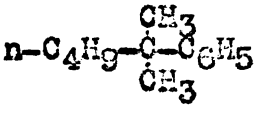
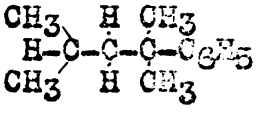
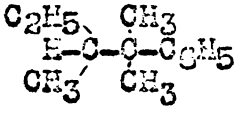
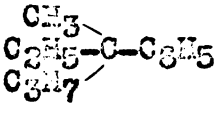
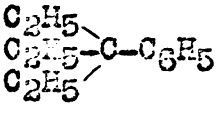
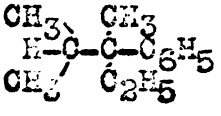
$$V_m = 16.27\ n - 7.02$$

n - number of carbon atoms

or $$V_m = 16.27\ n + 16.03 + 74.57$$

n - number of carbon atoms in aliphatic side chain
16.03 - effect of one hydrogen
74.57 - effect of phenyl ring

Index of Refraction and Molecular Refractions

Substance	n_D^{20}	M_D^{20}	
		Calc.	Found
	1.4942	58.65	58.68
	1.4928	58.65	58.67
	1.4966	58.65	58.48
	1.4964	58.65	58.53
	1.4975	58.65	58.53
	1.4974	58.65	58.54

From this table, the conclusion may be made that heaping of eurogens on adjacent carbon atoms increases the index of refraction. Index of refraction is lowest when eurogens are heaped, but not on adjacent carbon atoms.

Boiling Points, Density, and Molecular Volumes

Substance	B.P.	$d_{\frac{20^\circ}{4^\circ}}$	V_m Calc.	V_m Found
$n\text{-}C_4H_9\text{-}C(CH_3)_2\text{-}C_6H_5$	223.5-224.5° 745.6 mm. 107-107.5° 20 mm.	.8737	204.49	201.44
$CH_3\text{-}CH(CH_3)\text{-}C(CH_3)_2\text{-}C_6H_5$	216-217° 745.7 mm. 101-102° 20 mm.	.8724	204.49	201.74
$CH_3\text{-}CH(CH_3)\text{-}C(CH_3)(C_2H_5)\text{-}C_6H_5$	219-221° 740 mm. 105-107° 20 mm. (222-223° 744 mm.)	.8801	204.49	199.97
$C_3H_7\text{-}C(CH_3)(C_2H_5)\text{-}C_6H_5$	224-226° 745.6 mm. 100° 15 mm.	.8786	204.49	200.32
$(C_2H_5)_3\text{-}C\text{-}C_6H_5$	225-226° 745.6 mm. 107.5° 20 mm.	.8807	204.49	199.83
$CH_3\text{-}CH(CH_3)\text{-}C(CH_3)(C_2H_5)\text{-}C_6H_5$	221-222° 740.1 mm. 105-107° 20 mm. (222, 224° 744 mm.)	.8803	204.49	199.93

Molecular volumes as determined experimentally are lower than the calculated value. The formulae developed for calculation of molecular volumes only hold for straight chain compounds. Therefore, the calculated molecular volume would be the value for n-heptyl benzene. The difference between the calculated and the observed molecular volume must be the effect due to chain branching.

According to Kauffmann, a decrease in molecular volume is due to heaping of eurogens on adjacent carbon atoms. As shown in the table, dimethyl sec-butyl phenyl methane and methyl ethyl iso-propyl phenyl methane have a low molecular volume.

According to Kauffmann, the carbon atom in the benzene ring, to which is attached an aliphatic side chain, may act as a heaping center. In compounds were heaping of groups is on a carbon atom adjacent to a carbon in a benzene ring, the difference in molecular volume must be due to the groups present. Of the three isomers having straight chain branching, dimethyl n-butyl phenyl methane has the highest molecular volume; methyl ethyl n-propyl phenyl methane is slightly lower, while triethyl phenyl methane is still lower. It becomes apparent that heaping of like groups on an adjacent carbon atom causes a greater lowering of molecular volume than do unlike groups.

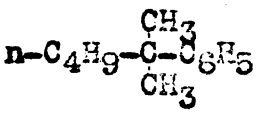
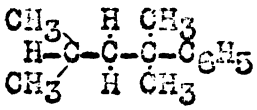
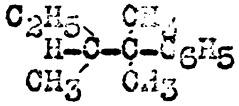
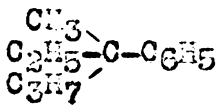
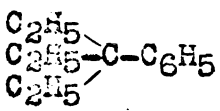
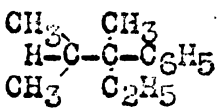
In triethyl phenyl methane, the three groups are exactly alike and the molecular volume is lowest. When the three groups are slightly different, as in methyl ethyl

n-propyl phenyl methane, molecular volume should be somewhat higher and it is. Dimethyl n-butyl phenyl methane when considered as the normal compound in the series should have the highest molecular volume and it has.

Dimethyl iso-butyl phenyl methane has the greatest molecular volume in the series. This increase in molecular volume occurs when eurogens are heaped on carbons not adjacent to each other. Kauffmann states that heaping of eurogens not on adjacent carbon atoms increases the molecular volume and decreases the boiling point.

It seems peculiar that dimethyl sec-butyl phenyl methane and methyl ethyl iso-propyl phenyl methane have such low boiling points. Heaping of eurogens on adjacent carbon atoms ordinarily increases the boiling point, however, this was not found to be the case. Maybe the ethyl group in the molecule has some influence on the boiling point. Also, there may be some doubt as to the purity of these compounds.

Surface Tension and Parachors

Substance	Surface Tension		Parachors		
	Drop-Wt.	DuNouy	Calc.	Drop-Wt.	DuNouy
	29.45	31.52	476.4	469.4	476.5
	28.63	30.80	473.4	466.6	475.3
	29.26	31.52	473.4	465.2	473.2
	29.60	31.93	476.4	466.6	476.1
	29.66	32.13	476.4	464.0	475.8
	29.47	31.83	473.4	465.8	474.8

Sugden (J. Chem. Soc., 125, 1177, 1924) states that "for isomerides of different structure only, parachors are identical within the limits of experimental error. Also, position isomerism seems to cause no change in the parachor."

In calculating atomic and structural constants, he did not consider chain branching. For this reason, Sugden's constants were not considered in this work.

In calculating parachors, the atomic and structural constants of Mumford and Phillips (J. Chem. Soc., 33, 2112, 1929) were used. These constants are as follows:

H = 15.4	Double bond = 19.0
C = 9.2	6-memb. ring = 0.8
O = 20.0	CH_2 = 40.0

The parachor, when calculated from these constants is larger than the observed parachor. This difference may be due to chain branching.

Mumford and Phillips state that "chain branching in aliphatic hydrocarbons and their derivatives is accompanied by a slight, but definite diminution of the parachor. The decrement varies somewhat according to the position and length of the side chain, but within the limits of experimental error a mean value of -3.0 would appear to be applicable to all branched groups of the type CHR_2• and double this value for CR_3• radicals and doubly-branched compounds CHR_2•——•CHR_2."

When these decrements are used, the calculated parachor checks more closely. If, however, a decrement of -3.0 is used for branching on a phenyl ring, a still closer check is obtained. It is shown in the table that the calculated parachor now checks very closely with the observed parachor calculated from surface tension values determined

by the DuNouy method.

Surface tension values determined by the Drop-Weight method are lower than those determined by the DuNouy method. Consequently, the parachors calculated from Drop-Weight surface tension values will be lower than those calculated from surface tension values determined by the DuNouy method. Sugden determined surface tension by the Bubble-Pressure method; also, Mumford and Phillips used the same method. Parachors calculated from DuNouy values check very closely with parachors calculated from the Mumford and Phillips constants. Apparently, the DuNouy method approximates very closely the Bubble-Pressure method. It appears, therefore, that a new set of constants must be introduced for the Drop-Weight method for this series of compounds.

Structure of Alkyl Benzenes

In these condensation reactions, there may be a possibility of rearrangement products to be formed. To determine whether the condensation products have the structures as expected, several reactions were carried in an attempt to prepare these products.

To prepare Dimethyl n-butyl phenyl methane:

I. By Wurtz-Fittig Synthesis:

$$n\text{-}C_4H_9\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}Cl + BrC_6H_5 \xrightarrow{2\ Na} n\text{-}C_4H_9\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}C_6H_5 + \text{---}$$

This reaction is very reliable, in preparing hydrocarbons from alkyl halides. However, no dimethyl n-butyl phenyl methane was obtained. Some diphenyl is formed.

The formation of diphenyl may be due to the reactivity of the two reactants, bromobenzene being more reactive than dimethyl n-butyl chloromethane. In place of bromobenzene, chlorobenzene was used. Unfortunately, the same results were observed. It appears, therefore, that the aromatic halides are more reactive than aliphatic halides, because in each case diphenyl is formed.

II. By the Grignard Reaction:

$$C_6H_5Br + Mg \longrightarrow C_6H_5MgBr$$

$$C_6H_5MgBr + Cl\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}C_4H_9 \longrightarrow C_6H_5\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}C_4H_9 + \text{-----}$$

The reaction did not proceed in this manner. The original chloride was recovered and diphenyl was formed. Chlorobenzene would not react with magnesium to form the Grignard reagent.

III. By Friedel-Crafts Synthesis:

$$n\text{-}C_4H_9\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}Cl + C_6H_6 \xrightarrow{AlCl_3} n\text{-}C_4H_9\text{-}\overset{CH_3}{\underset{CH_3}{C}}\text{-}C_6H_5 + \text{---}$$

A fraction boiling at 108-109°/20 mm. was isolated. It is very unsaturated but does not contain halogen. It is not the expected product, dimethyl n-butyl phenyl methane.

No other reaction was found by which these condensation products could be prepared.

It is shown that the physical constants for each compound is different. If rearrangement takes place, two of these compounds should be exactly alike. Since each compound has decidedly different physical constants, it is safe to say that the hydrocarbons have the structure as expected.

SUMMARY-

1. Tertiary heptyl aliphatic alcohols condense with benzene in the presence of aluminum chloride according to the reaction:

$$\begin{matrix} R' \\ R-C-CH \\ R' \end{matrix} + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} R' \\ R-C-C_6H_5 \\ R' \end{matrix} + H_2O$$

where R' is methyl and R is n-butyl, iso-butyl, or secondary butyl. When the groups are all different, the reaction is as follows:

$$\begin{matrix} R'' \\ R-C-CH \\ R' \end{matrix} + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} R'' \\ R-C-C_6H_5 \\ R' \end{matrix} + H_2O$$

2. The straight chain carbinols, as dimethyl n-butyl carbinol, methyl ethyl n-propyl carbinol, and triethyl carbinol condense very readily with benzene to give good yields of the corresponding hydrocarbon.

3. The branched chain carbinols, as dimethyl iso-butyl carbinol, dimethyl sec.-butyl carbinol, and methyl ethyl iso-propyl carbinol do not condense so readily with benzene as do the straight chain carbinols. The yields of hydrocarbons is small. Considerable amounts of the halogen derivative of the carbinol are formed.

4. Physical constants, as boiling points, densities, index of refraction, molecular refractions, molecular volumes, surface tension, parachors, were determined for each compound.

5. The relationship between structure and physical properties is shown.