CONDENSATION OF TERTIARY DI-METHYL AMYL CARBINOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Thesis for the Degree of M. S.

John J. Sculati

1936

THESIS

R. C. Huston.
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CONDENSATION OF TERTIARY
DI-METHYL AMYL CARBINOLS
WITH BENZENE IN THE
PRESENCE OF ALUMINUM CHLORIDE

CONDENSATION OF TERTIARY
DI-METHYL ALKYL CARBINOLS
WITH BENZENE IN THE
PRESENCE OF ALUMINUM CHLORIDE

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

John Joseph Sculati

June 1936

6-27-58
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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.

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HISTORICAL:

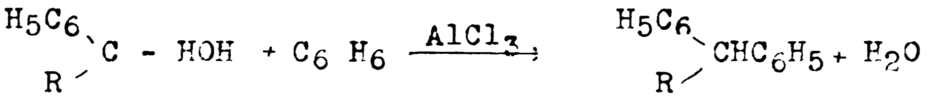
This paper deals with condensations with aluminum chloride. Numerous condensation reactions have been brought about by such reagents as sulphuric acid, phosphorous pentoxide, dilute or concentrated hydrochloric acid, acetic acid, absolute alcohol, phosphoric acid, zinc chloride, phosphorous pentachloride and aluminum chloride.

Huston and Friedmann (J. Am. Chem. Soc., 38, 2527, 1916) first reported work in connection with the dehydrating action of aluminum chloride on aromatic alcohols and aromatic compounds. Diphenylmethane was found to be the principal product of the reaction between benzyl alcohol and benzene in the presence of aluminum chloride.

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

It may be noted here that if equi-molecular amounts of the reacting substances are used, about 30% of the yield is diphenylmethane and the remainder secondary products. However, if the benzene is used in excess (5:1) the yield of diphenylmethane is greatly increased whereas the yield of secondary products is diminished.

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



$$\begin{matrix} H_5C_6 \\ R \end{matrix}\!\!>C-HOH + C_6H_6 \xrightarrow{AlCl_3} \begin{matrix} H_5C_6 \\ R \end{matrix}\!\!>CHC_6H_5 + H_2O$$

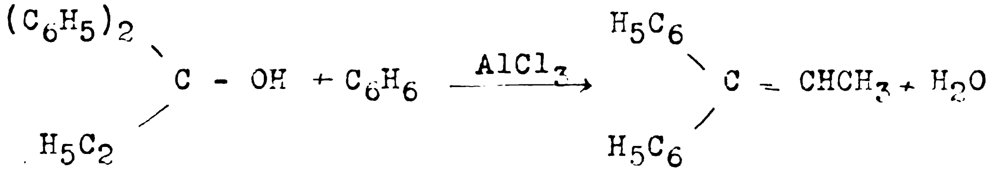
with R being a methyl, ethyl, or phenyl. When R is a phenyl group, the reaction is smoother and a larger yield of condensation product is obtained.

Huston found that triphenyl carbinol will not condense with benzene to form the expected tetraphenyl methane. Rather, triphenyl methane is obtained. The reaction is:

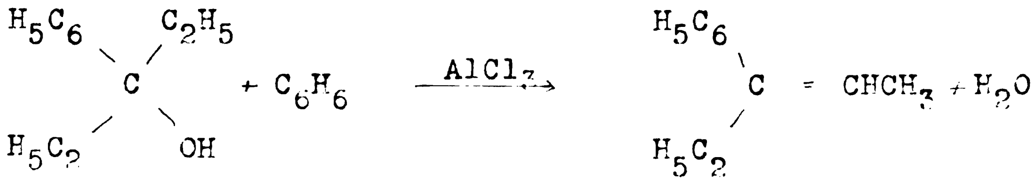
$$(C_6H_5)_3COH + C_6H_6 \xrightarrow{AlCl_3} (C_6H_5)_3CH + \_\_ \ \_\_$$

Seemingly, the oxygen is pulled out of the carbinol but what happens to it is not known.

Huston, Wilsey and Hradel found that diarylalkyl carbinols undergo dehydration rather than condensation with benzene.



Later Huston and Macomber showed the same effect in working with di-alkyl-aryl carbinols.



Huston and Sager (*J. Am. Chem. Soc.*, 48, 1955, 1926) reported that the saturated aliphatic alcohols (methyl, ethyl, propyl, iso propyl, butyl, isobutyl, and iso amyl) do not condense with benzene. However, they found that unsaturated alcohol (allyl alcohol) will condense with benzene.

$$H_2C = CHCH_2OH + C_6H_6 \xrightarrow{AlCl_3} CH_2 = CHCH_2C_6H_5 + H_2O$$

With a slight change in procedure, Huston and Hsieh (Doctor's thesis) were able to condense aliphatic alcohols with benzene. It was found that primary alcohols do not react at all; secondary alcohols react very slightly and tertiary alcohols react very readily

to form the corresponding alkyl benzene.

$$(H_3C)_3C-OH + C_6H_6 \xrightarrow{AlCl_3} (H_3C)_3C-C_6H_5 + H_2O$$

Huston and Fox (Master's thesis) condensed tert-butyl alcohol and tert-amyl alcohol with benzene to obtain tert-butyl benzene and tert-amyl benzene.

Dimethyl-n butyl carbinol, dimethyl iso-butyl carbinol and dimethyl secondary butyl carbinol were successfully condensed with benzene to obtain the corresponding alkyl benzene (Huston and Binder.) The yield produced by condensing dimethyl tert-butyl carbinol with benzene was discouraging on the first run and no further condensations were attempted.

<u>Summary</u>:--

1. Primary and secondary aromatic alcohols condensed with benzene in the presence of aluminum chloride.

2. Mixed tertiary aliphatic-aromatic alcohols did not condense with benzene. Dehydration resulted.

3. Unsaturated primary alcohols, with the double bond adjacent to the hydroxyl carbon, condensed with benzene.

4. The primary aliphatic alcohols did not condense with benzene; the secondary reacted only slightly, while the tertiary reacted readily.

5. Branching of the tertiary aliphatic alcohols inhibited condensation with benzene. Especially was this true as the branching occurred near the tertiary group.

EXPERIMENTAL

MATERIALS

Amyl bromide and secondary-amyl bromide and active amyl bromide were prepared by treating the respective alcohols with phosphorous tribromide.

Phosphorous tribromide was obtained by treating red phosphorous with bromine.

Iso amyl bromide was obtained from the stockroom supply.

Tertiary amyl chloride was prepared by treating the respective alcohols with concentrated hydrochloric acid.

Acetone was C. P. grade.

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

The benzene was C. P. thiophene-free.

The aluminum chloride was a high grade commercial product.

Preparation of Carbinols

Dimethyl n-amyl carbinol.

From n-amyl bromide and acetone. Grignard's reaction (Whitmore and Church) J. Am. Chem. Soc., V. 55, pt. 1, p. 1561.

B. P. 65° to 66° / 15 mm.

n_D^{20} 1.4235

Approximate yield -- 40%

Dimethyl isoamyl carbinol.

From iso amyl bromide and acetone. Grignard's reaction:

B. P. 154° - 155°

Compt. rendu 1913, 156, 1624.

Approximate yield -- 15%

Dimethyl active amyl carbinol.

From active amyl bromide and acetone. Grignard's reaction.

B. P. 150°; 64°/ 20 mm.

J. Bio. Chem, 1931, 91, 405.

Dimethyl-secondary amyl carbinol.

From secondary amyl bromide and acetone. Grignard's reaction.

B. P. 150° - 151°

J. Clarke, J. Am. Chem. Soc., 1911, 33, 529.

Yield -- 15%

Dimethyl tert-amyl carbinol.

From tert-amyl chloride and acetone. Grignard's reaction.

B. P. 150° - 151°

Not found in literature.

Yield -- about 5%.

CONDENSATIONS

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

Trial I:

Carbinol - 1 eq. - 32 gm. - 1/4 mol.
Benzene - 5 eq. - 97 gm. - 5/4 mol.
$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

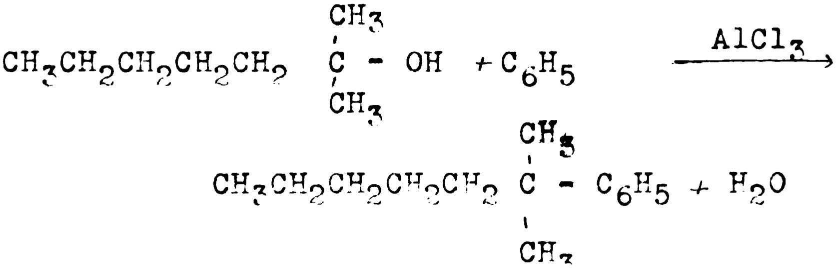
A 500 ml. three-necked flask was provided with a mechanical mercury-sealed stirrer, a dropping funnel and a condenser. A thermometer was introduced into the flask from the condenser and was suspended from the latter with a copper wire. A drying tube was placed at the top of the condenser.

The benzene was introduced into the flask, and the stirrer started. The entire amount of $AlCl_3$ was added to the benzene. The carbinol was then added drop by drop (about a drop every three seconds). This procedure required about three hours. The temperature was easily maintained below 30° C. and cooling with water was hardly necessary. The mixture was stirred for an additional two hours. During the addition of the carbinol, the mixture changed from a yellow to a dark red. All of the $AlCl_3$ seemed to disappear but later a coagulate appeared which was dark brown in appearance. The mixture was allowed to stand for twentyfour hours: then decomposed with ice and hydrochloric acid. The benzene layer was separated and the aqueous portion extracted several times with ether. A little HCl was added in extracting with ether, to break up the water-ether emulsion that formed. The combined ether and benzene extracts were washed with dilute sodium carbonate solution to remove any remaining HCl. The mixture was dried and the ether distilled off. The following fractions were obtained from the residue at 15 mm.:

1. 40° - 120° - 4 gm.
2. 120° - 122° -10 gm.
3. Above 122° - 5 gm.

The fraction boiling from 120° - 122° was dimethyl-n-amyl phenyl methane.

Equation of the Reaction:



$$CH_3CH_2CH_2CH_2CH_2\underset{CH_3}{\overset{CH_3}{C}} - OH + C_6H_5 \xrightarrow{AlCl_3}$$

$$CH_3CH_2CH_2CH_2CH_2\underset{CH_3}{\overset{CH_3}{C}} - C_6H_5 + H_2O$$

Trial II:

The same procedure was followed as in Trial I.

Carbinol - 1 eq. - 64 gm. -$\frac{1}{2}$ mol.

Benzene - 5 eq. - 194 gm. -2$\frac{1}{2}$ mol.

$AlCl_3$ - $\frac{1}{2}$ eq. - 34 gm. - $\frac{1}{4}$ mol.

The following fractions were obtained at 15 mm.:

1. 40° - 120° - 7
2. 120° - 122° - 21
3. Above 122° - 10

Trial III:

The same amounts and procedure were used as in Trial I. The following fractions were obtained at 15 mm.:

1. 40° - 120° - 4
2. 120° - 122° - 9
3. Above 122° - 5

Analysis of Fractions

The fraction 40° - 120° / 15 mm. was found to contain a small amount of chloride. Further fractionation yielded an unsaturated product between 40° - 49°. A saturated chloride was obtained between 49° - 52° and is believed to be 2 chlor-2 methyl heptane.

The fraction between 120° - 122° is dimethyl-n-amyl phenyl methane and its boiling point was found to be 242.5° at 740 mm. This compound was not recorded in the literature.

Carbon-Hydrogen Determination:

Wt. Sample	Wt. CO_2	% C	Wt. H_2O	% H_2
.1330	.4302	88.21	.1372	11.56
.1713	.5545	88.27	.1774	11.59
Calculated for $C_{14}H_{22}$		88.35		11.65

Molecular Weight Determination:

Wt. Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.3461	.266	35.16	185
Calculated for $C_{14}H_{22}$			190

B. Dimethyl isoamyl carbinol, benzene and $AlCl_3$

Trial I:

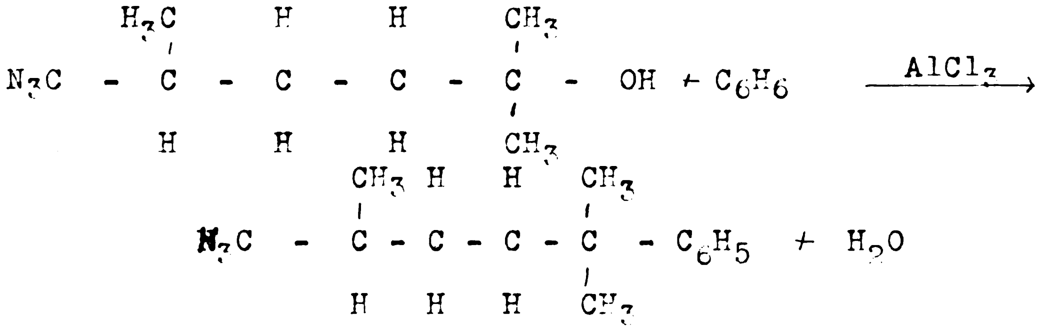
Carbinol - 1 eq. - 32 gm. - 1/4 mol.
Benzene - 5 eq. - 97 gm. - 5/4 mol.
$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

The same procedure used in the previous condensations was followed. The carbinol was slowly added to the suspension of $AlCl_3$ in benzene while the temperature was kept between 25° and 30°. The procedure took about three hours. Stirring was continued for an additional two hours. The mixture was allowed to stand over night and was decomposed with HCl and ice water.

Fractions at 15 mm.:

I. 40° - 110° - 3 gm.
II. 110° - 114° - 6 gm.
III. Above 114° - 4 gm.

Equation of Reaction:



$$H_3C - \underset{H}{\overset{H_3C}{C}} - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{CH_3}{C}} - OH + C_6H_6 \xrightarrow{AlCl_3}$$

$$H_3C - \underset{H}{\overset{CH_3}{C}} - \underset{H}{\overset{H}{C}} - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{CH_3}{C}} - C_6H_5 + H_2O$$

The fraction boiling at 110 - 114° was the condensation product dimethyl-iso-amyl phenyl methane.

Trial II.

Carbinol - 1 eq. - 64 gm. - ½ mol.
Benzene - 5 eq. - 194 gm. - 2½ mol.
$AlCl_3$ - ½ eq. - 34 gm. - ¼ mol.

The following fractions were obtained at 15 mm.:

I. 40°- 110° - 5 gm.
II. 110°- 114° - 11 gm.
III. Above 114° - 7 gm.

Trial III:

Carbinol - 1 eq. - 32 gm. - 1/4 mol.
Benzene - 5 eq. - 97 gm. - 5/4 mol.
$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

The following fractions were obtained at 15 mm.:

I. 40° - 110° - 3 gm.
II. 110° - 114° - 7 gm.
III. Above 114° - 4 gm.

Analysis of Fractions

Refractionation of the fraction between 40° - 110° yielded a product which condensed between 49° - 53°. It was saturated and contained a chloride and was believed to be 2 chlor, 2-5 di-methyl hexane. This compound is not recorded in the literature and no check was made on the condensation product.

The fraction between 110° - 114° contained the dimethyl iso amyl phenyl methane and after repeated refractionation was found to boil at 233° at 740 mm. This compound is not recorded in the literature.

Carbon-Hydrogen Determination:

Wt. Sample	Wt. CO_2	% C	Wt. H_2O	% H_2
.1895	.6132	88.24	.1960	11.57
.1818	.5882	88.23	.1872	11.55
Calculated for $C_{14}H_{22}$		88.35		11.65

Molecular Weight Determination:

Wt. Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.7994	0.621	35.16	183
Calculated for $C_{14}H_{22}$			190

C. Dimethyl Active Amyl Carbinol, Benzene, and $AlCl_3$.

Trial I:

Carbinol - 1 eq. - 32 gm. - 1/4 mol.
Benzene - 5 eq. - 97 gm. - 5/4 mol.
$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

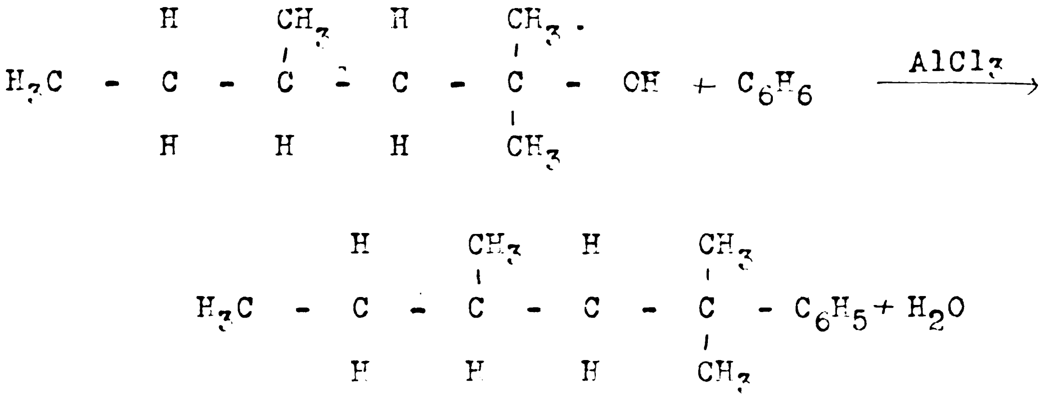
The same procedure used in previous condensations was followed. The carbinol was added to a suspension of $AlCl_3$ in benzene. The temperature was kept between 25 - 30°. Addition of the carbinol required three hours. HCl gas was evolved freely. Stirring was continued for two hours, and the mixture allowed to stand over night. It was decomposed and extracted. The extracts were fractionated.

The following fractions were obtained at 15 mm.:

I. 40 - 108° - 5 gm.
II. 108 - 111° - 7 gm.
III. Above 111° - 4 gm.

The fraction boiling at 108 - 111° contains the condensation product dimethyl active amyl phenyl methane.

Equation of reaction:



$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-OH+C_6H_6\xrightarrow{AlCl_3}$$

$$H_3C-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{CH_3}{C}}-\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5+H_2O$$

Trial II:

Carbinol - 1 eq. - 32 gm. - 1/4 mol.

Benzene - 5 eq. - 97 gm. - 5/4 mol.

$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

The following fractions were obtained at 15 mm.:

I. 40 - 108° - 5 gm.

II. 108 - 111° - 6 gm.

III. Above 111° - 4 gm.

Analysis of Fractions.

The fraction between 108 - 111° was refractionated several times and yielded a product which boiled at 109.2° at 15 mm. and at 220.5 at 740 mm. The product was the expected di methyl active amyl phenyl methane.

Carbon-Hydrogen Determination:

Wt. Sample	Wt CO_2	% C	Wt. H_2O	% H_2
.1615	.5229	88.30	.1691	11.71
.1827	.5911	88.25	.1896	11.61
Calculated for $C_{14}H_{22}$		88.35		11.65

D. Dimethyl secondary amyl carbinol, benzene, and $AlCl_3$.

Trial I:

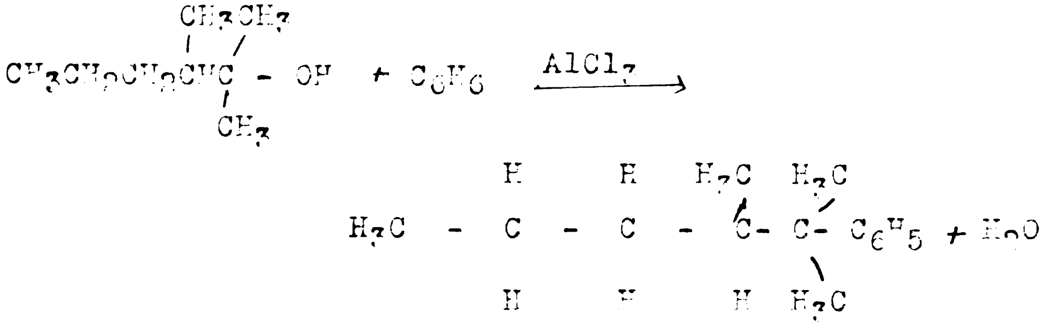
Carbinol - 1 eq. - 32 gm. - 1/4 mol.
Benzene - 5 eq. - 97 gm. - 5/4 mol.
$AlCl_3$ - ½ eq. - 17 gm. - 1/8 mol.

The same procedure used in the previous condensations was followed. The carbinol was slowly added to the stirred suspension of $AlCl_3$ in benzene while the temperature was kept between 25 and 30°. The procedure required about three hours. Stirring was continued for an additional two hours. The mixture was allowed to stand over night, decomposed with HCl and ice water.

Fractions at 15 mm.:

I. 40 - 111° - 2
II. 111 - 114° - 3
III. Above 114° - ?

Equation of reaction:



$$CH_3CH_2CH_2CH(CH_3)C(CH_3)_2-OH + C_6H_6 \xrightarrow{AlCl_3} H_3C-CH_2-CH_2-CH(CH_3)-C(CH_3)_2-C_6H_5 + H_2O$$

The fraction boiling between 111 - 114° is the condensation product di methyl secondary amyl phenyl methane.

Trial II:

Carbinol - 1 eq. - 64 gm. ½ mol.
Benzene - 5 eq. - 194 gm. 2½ mol.
$AlCl_3$ - ¼ eq. - 34 gm. ¼ mol.

The following fractions were obtained at 15 mm.:

I. 40 - 111° - 5 gm.
II. 111 - 114° - 6 gm.
III. Above 114° - 4 gm.

Analysis of Fractions.

Refractionation of the fraction between 40 - 111° yielded a product which condensed between 50 - 54°. It was saturated and contained chlorine. It was believed to be 2 chlor, 2-3 di-methyl hexane. This compound is not recorded in the literature and no check was made on the condensation product.

The fraction between 111 - 114° contained the dimethyl secondary amyl phenyl methane and after refractionation was found to boil at 275° at 740 mm. However, due to the small yield of the product and in view of the deviations of the physical constants from the expected constants, the product was believed to contain slight impurities. This compound is not recorded in the literature.

Carbon-Hydrogen Determinations:

Wt. Sample	Wt. CO_2	% C	Wt. H_2O	% H_2
.1687	.5461	88.37	.1741	11.54
.1941	.6281	88.34	.1997	11.51
Calculated for $C_{14}H_{22}$		88.75		11.65

Molecular Weight Determination:

Wt. Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.5711	0.426	75.16	181.4
Calculated for $C_{14}H_{22}$			190.3

E. Dimethyl tert. amyl carbinol, benzene and AlCl$_3$.

Trials I and II:

Carbinol - 1 eq. - 32 gm. 1/4 mol.
Benzene - 5 eq. - 97 gm. 5/4 mol.
AlCl$_3$ - $\frac{1}{2}$ eq. - 17 gm. 1/8 mol.

The same procedure used in the previous condensations was adhered to. The carbinol was slowly added to the stirred suspension of AlCl$_3$ in benzene while the temperature was kept between 25 - 30°. The procedure required about three hours. Stirring was continued for an additional two hours. The mixture was allowed to stand over night and then hydrolyzed with ice water.

The ether was distilled off and the residue fractionated, but no condensation product was obtained. The mixture gave evidence that a small amount might be present but never was there any constant boiling product.

Determination of Physical Constants.

Density determinations were made at 20° C. compared to water at 4° C.

Index of refraction measurements were made with the Abbe refractometer.

Surface tension was determined with the DuNouy tensiometer and by the Harkins' drop-weight method.

The DuNouy tensiometer gives a dial reading which must be multiplied by the standard of the apparatus in order to obtain the surface tension.

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

$$\gamma = \frac{mg}{2\pi r f\left(\frac{r}{V^{1/3}}\right)}$$

in which: $V = \frac{m}{d}$

V = Volume

m = mass of drop

d = density

γ = surface tension

r = radius of tip

g = gravity

$f\left(\frac{r}{V^{1/3}}\right)$ = fraction of ideal drop which falls

The observed parachor was calculated by the formula:

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

in which: P = parachor of compound

M = molecular weight

d = density

γ = surface tension

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

Theoretical molecular volumes were calculated by the formula:

$$V_m = 16.27_n - 7.02$$

where: n = number of carbon atoms

Molecular refractions were calculated by the formula:

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

in which M_D = molecular refraction

M = molecular weight

d = density

n = index of refraction

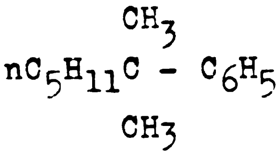
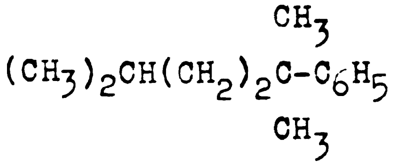
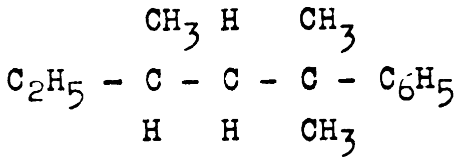
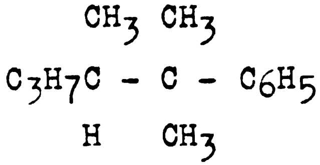
Theoretical molecular refractions were found by using the values:

C = 2.418

H = 1.100

and: 1.733 for a double bond.

Index of Refraction and Molecular Refractions

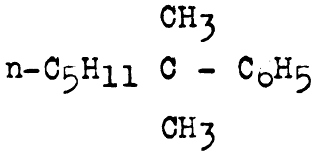
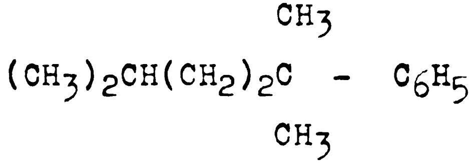
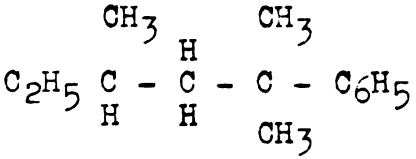
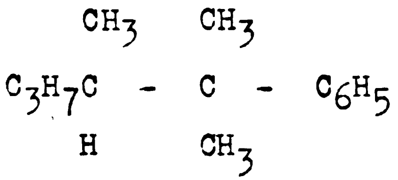
Substance	n_D^{20}	M_D^{20}	
		Calc.	Found
 $nC_5H_{11}\underset{CH_3}{\overset{CH_3}{C}} - C_6H_5$	1.4951	63.25	63.36
 $(CH_3)_2CH(CH_2)_2\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5$	1.4939	63.25	63.21
 $C_2H_5 - \underset{H}{\overset{CH_3}{C}} - \underset{H}{\overset{H}{C}} - \underset{CH_3}{\overset{CH_3}{C}} - C_6H_5$	1.4920	63.25	63.10
 $C_3H_7\underset{H}{\overset{CH_3}{C}} - \underset{CH_3}{\overset{CH_3}{C}} - C_6H_5$	1.4961	63.25	62.71

Index of Refraction and Molecular Refractions.

(See table on preceding page.)

With the exception of the fourth compound it may be noticed that the index of refraction decreased as the eurogens were heaped. The purity of the last compound was exceedingly doubtful and may be disregarded. However, it has been noticed that the index of refraction increases when eurogens are heaped on to adjacent carbon atoms and decreases when heaped but not on adjacent carbon atoms. This holds true as is shown on the table.

Boiling Points, Densities, and Molecular Volumes

Substance	B. P.		d	Vm	
	740 mm.	15 mm.	$\frac{20^\circ}{4^\circ}$	Calc.	Found
 $n\text{-}C_5H_{11}\,\overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	242.5°	120-1°	.87546	220.76	216.78
 $(CH_3)_2CH(CH_2)_2\overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	233.0	110-111	.87493	220.76	217.16
 $C_2H_5\,\overset{CH_3}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	220.5	109.2	.87204	220.76	217.65
 $C_3H_7\overset{CH_3}{\underset{H}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	235.0	111-112	.8861	220.76	214.55

Boiling Points, Densities and Molecular Volumes

(See table of computation on preceding page.)

The difference between the calculated and found molecular volume was probably due to chain branching. The formula for calculating Vm held only for straight chain compounds, so that the calculated value would be, in this case, that of n-octyl benzene. It will be noticed that the Vm increased as the eurogens were heaped except in the case of the di-methyl secondary amyl phenyl methane where the Vm decreased. This may be due to the heaping of eurogens on adjacent carbon atoms.

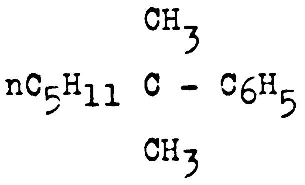
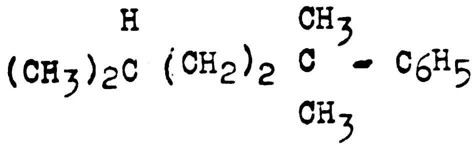
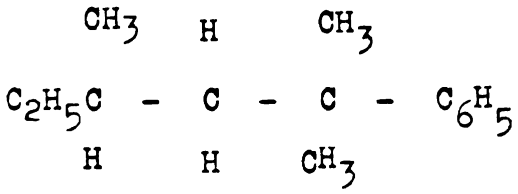
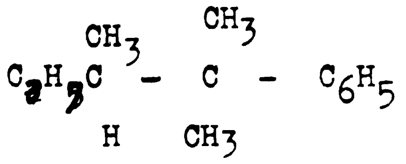
Kauffmann states that a decrease of molecular volume is effected by the heaping of eurogens on adjacent carbon atoms. This accounts for the difference between the calculated and found molecular volume and also explains the decrease of the molecular volume as noticed in the case of dimethyl secondary-amyl phenyl methane.

Kauffmann goes on to say that heaping of eurogens on other than adjacent carbon atoms increases the molecular volume and decreases the boiling point. The experimental evidence above entirely agrees with this

statement. The molecular volumes of di-methyl n-amyl phenyl methane, dimethyl iso amyl phenyl methane and dimethyl active amyl phenyl methane gradually increased while their boiling points decreased.

It would be expected that the boiling point of di methyl secondary amyl phenyl methane would be higher than the others since it has a greater density. This did not hold in all cases as the di-methyl n-amyl phenyl methane was found to boil higher but this may be due to the impurity of the dimethyl secondary amyl phenyl methane.

Surface Tension and Parachors

Substance	Surface Tension Drop-wt.	Surface Tension DuNouy	Parachors Drop-wt.	Parachors DuNouy	Calc.
 $nC_5H_{11}\overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	29.68	32.13	506.5	516.7	516.4
 $(CH_3)_2\overset{H}{C}(CH_2)_2\overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	29.61	31.19	506.2	513.2	513.4
 $C_2H_5\overset{CH_3}{\underset{H}{C}} - \overset{H}{\underset{H}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	28.88	31.01	504.4	513.6	513.4
 $C_2H_5\overset{CH_3}{\underset{H}{C}} - \overset{CH_3}{\underset{CH_3}{C}} - C_6H_5$	29.64	32.99	497.0	513.9	513.4

Surface Tension and Parachors

(See table on preceding page.)

The parachors were calculated by using the atomic and structural constants of Mumford and Phillips (J. Chem. Soc. 1929 - 2112). These constants were:

C	9.2
H	15.4
Double bond	19.0
6 memb. ring	0.8
Chain branching	—3
Branching on phenyl ring	—3

The surface tension values determined by the drop-weight differed from those determined by the DuNuoy method. The parachors, as a result, also differed. The parachor, as determined by the DuNuoy method, check with the parachors as calculated using the values of Mumford and Phillips. A new set of constants must be calculated for the drop-weight method in order that the two methods agree on this series of compounds.

Summary: --

1. The tertiary di methyl amyl carbinols (n-amyl, iso amyl, active amyl and secondary amyl) were condensed with benzene in the presence of aluminum chloride.

2. The di methyl tert-amyl carbinol showed little tendence to condense with benzene in the presence of aluminum chloride.

3. The branched chain carbinols showed decreasing readiness to condense with the benzene as the branching approached the carbinol group.

4. The physical constants, such as boiling points, densities, indices of refraction, molecular refractions, molecular volumes, surface tension, and parachors, were determined for each compound.

5. The relation between structure and physical properties was shown.

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