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

OCTYL ALCOHOLS AND BENZENE

Thesis for the Degree of M. S.
MICHIGAN STATE COLLEGE
E. Robert Breining
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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

E. Robert Breining

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HISTORICAL

Condensations

A history of condensation reactions brought about by such catalysts as sulfuric acid (1), zinc chloride (2), phosphoroic anhydride (3), phosphoric acid, phosphorous pentachloride, acetic acid (4), sulfuric and acetic acid mixture (5), magnesium chloride (6), stannic chloride (7), hydrochloric acid (8) and aluminum chloride (9) have been covered by former workers in this laboratory. However it was felt necessary to include a brief summary of research work carried out in this laboratory involving the reactions between alcohols and benzene in the presence of aluminum chloride as a catalytic agent.

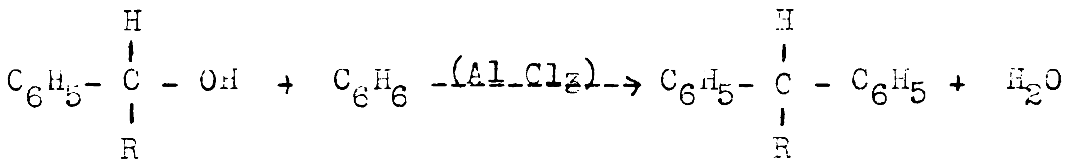
The first work in this field was stated by Huston and Friedemann (10) who found out that primary aromatic alcohols react with benzene in the presence of aluminum chloride. Benzyl alcohol reacted with benzene to give di-phenyl methane according to the equation:

$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{(Al\ Cl_3)} C_6H_5CH_2C_6H_5 + H_2O$$

When equimolecular amounts of the reacting substances are used the yields of di-phenyl methane are not large (about 30%) and the yields of secondary products p-o-di-benzyl benzene, anthracene and tar are quite large.

If an excess of benzene (5 moles) is used the yield of diphenyl methane is increased, the yield of the secondary products is decreased.

Later Huston and Friedemann (11) showed that secondary aromatic alcohols condense with benzene under the dehydrating influence of anhydrous aluminum chloride according to the general equation:



$$C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-OH + C_6H_6 \xrightarrow{(Al\ Cl_3)} C_6H_5-\overset{\displaystyle H}{\underset{\displaystyle R}{\overset{|}{\underset{|}{C}}}}-C_6H_5 + H_2O$$

When R is the phenyl group the reaction is smoother and a larger yield of condensation product is obtained than when R is a methyl of ethyl group. The ethyl group has a greater retarding effect than the methyl group.

An excess of aluminum chloride tends to eliminate a phenyl or an alkyl radical from the product especially if the temperature is not kept low.

Huston (12) found that triphenyl carbinol did not condense with benzene to form tetra-phenyl methane as expected, instead the product formed was tri-phenyl methane which can be expressed by the equation:

$$(C_6H_5)_3COH + C_6H_6 \xrightarrow{(Al\ Cl_3)} (C_6H_5)_3H + \text{---------}$$

Apparently, the oxygen is removed from the carbinol and its

its disappearance or migration has not been determined.

Huston and Sager (13) reported that saturated aliphatic alcohols (methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, amyl, iso-amyl) do not condense with benzene.

Unsaturated allyl alcohol condenses with benzene according to the equation:

$$H_2C{=}CHCH_2OH \quad + \quad C_6H_6 \xrightarrow{(AlCl_3)} CH_2CHCH_2C_6H_5 \quad + \quad H_2O$$

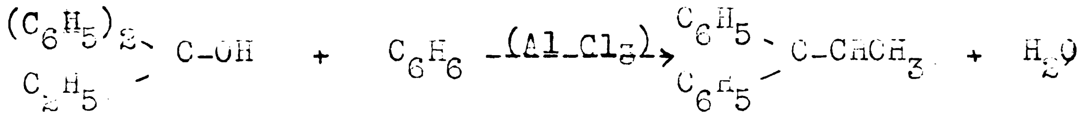
The yield of the allyl benzene was 16%.

Huston and Sagar reported in the same journal that of the alcoholic derivatives of aromatic hydrocarbons, only those in which the hydroxyl group is on the carbon adjacent to the ring condense with benzene in the presence of anydrous aluminum chloride.

Unsaturation on the carbon adjacent to the hydroxyl group increases the reactivity of the hydroxyl group toward the dehydrating effect of aluminum chloride.

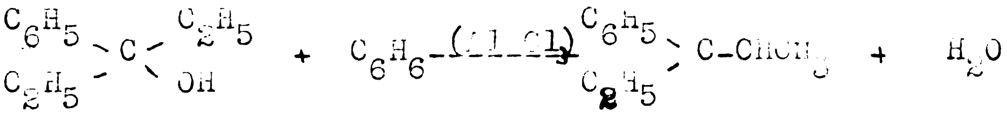
Huston and Goodemoot (14) condensed cyclo alkyl carbinols with benzene in the presence of aluminum chloride and found a progressive increase in activity as the number of carbon atoms of the ring is reduced from six to four.

Huston, Wilsey, and Hradel (15) found that di-aryl alkyl carbinols do not condense with benzene in the presence of a luminum chloride, instead dehydration occurs, as expressed by the equation:



$$\begin{matrix}(C_6H_5)_2\\ C_2H_5\end{matrix}\!>C-OH \quad + \quad C_6H_6 \xrightarrow{(Al\,Cl_3)} \begin{matrix}C_6H_5\\ C_6H_5\end{matrix}\!>C-CHCH_3 \quad + \quad H_2O$$

Later Huston and Macomber (16) showed the same effect in working with dialkyl aryl carbinols:



$$\begin{matrix}C_6H_5\\ C_2H_5\end{matrix}\!>C<\!\begin{matrix}C_2H_5\\ OH\end{matrix} \quad + \quad C_6H_6 \xrightarrow{(Al\,Cl_3)} \begin{matrix}C_6H_5\\ C_2H_5\end{matrix}\!>C-CHCH_3 \quad + \quad H_2O$$

Huston and Hsieh (17) with slight modifications in the normal procedure for condensations were able to condense alephatic alcohols with benzene and benzene derivatives.

Huston and Fox (18) condensed tertiary butyl alcohol, tertiary amyl alcohol, dimethyl n-propyl carbinol and dimethyl iso-propyl carbinol with benzene to form tertiary butyl benzene, tertiary amyl benzene, dimethyl n-propyl phenyl methan and dimethyl iso-propyl phenyl methane in good yields.

Huston and Binder (19) condensed dimethyl n-butyl carbinol, dimethyl iso-butyl carbinol, dimethyl secondary butyl carbinol, methyl ethyl n-propyl carbinol, methyl ethyl iso-propyl carbinol and tri-ethyl carbinol with benzene to obtain in good yield di-methyl normal butyl phenyl methane, di-methyl iso-butyl phenyl methane, di-methyl secondary butyl phenyl methane, methyl ethyl n-propyl phenyl methane, methyl ethyl iso-propyl phenyl methane and tri-ethyl phenyl methane.

Huston and Sculati (20) condensed dimethyl amyl carbinols (n-amyl, iso-amyl, active amyl and secondary amyl) with benzene in the presence of aluminum chloride to form the alkyl benzene and also found that the branched chain carbinols showed decreasing readiness to condense with benzene as the branching approached the carbinol group.

Branching of the tertiary aliphatic atoms inhibited condensation with benzene especially if the branching occurred near the tertiary group.

Summary

1. Primary aliphatic alcohols do not condense with benzene in the presence of aluminum chloride under the given experimental conditions.

2. Secondary and tertiary aliphatic alcohols condense with benzene in the presence of aluminum chloride to give the corresponding alkyl benzene. The tertiary alcohols reach more readily and five higher yields of the alkyl benzene than the secondary alcohols.

3. Primary and secondary aromatic alcohols condense with benzene in the presence of aluminum chloride to form benzene derivatives. Tertiary aromatic alcohols do not condense with benzene.

4. Mixed tertiary aliphatic-aromatic alcohols do not condense but the dehydration occurs.

5. Unsaturated primary alcohols with the double bond adjacent to the carbon containing the hydroxyl group condense with benzene.

6. Branching of the tertiary aliphatic atoms inhibit condensation with benzene, particularly if the branching occurred near the tertiary group.

Other Methods of Preparing Alkyl Benzenes

There are many ways of preparing alkyl benzenes recorded in literature. The polymerization of alkyl acetylenes (21), the reduction of phenols or ketones by zinc dust (22), the use of zinc alkyls and benzyl chlorides (23), and the dry distillation of an aromatic acid with soda lime (24) have been successfully used.

The most frequently used methods are the Fittig Synthesis discovered in 1934 (25) and the Friedel and Craft reaction discovered in 1877 (26).

The Gringnard reaction can be frequently employed as in the preparation of normal propyl benzene from the reaction of benzyl magnesium chloride and di-ethyl sulfate (27).

Alkyene benzene derivative prepared from Grignards can be reduced to alkyl benzenes (28).

EXPERIMENTAL

Materials

1. n-Butyric Acid

   This substance was obtained from the store room; having a boiling point of 162° to 163° C.

2. iso-Butyric acid

   C.P. iso-Butyric acid was obtained from the Central Scientific Co. at Chicago, Ill. Boiling point - 151.5° to 154° C.

3. n-Butyryl Chloride was prepared by the reaction of phosphorous tri-chloride on butyric acid (29) according to the equation:

   $$3CH_3CH_2CH_2COOH \ + \ PCL_3 \ --- \ 3CH_3CH_2CH_2COCL \ + \ P(OH)_3$$

   Boiling Point 100° to 101° C.

4. iso-Butyryl Chloride was prepared from iso-Butyric acid and phosphorous tri-chloride. Boiling point 90° to 91° C.

5. Ethyl bromide (C.P.) was obtained from the store room and was a product of the Eastman Kodak Co., Rochester, N.Y. Boiling point 38.0° C.

6. Magnesium. Fresh Magnesium turnings were obtained from the store room and allowed to remain in a vacum dessicator, using $CaCl_2$ as the dehydrating agent, until ready for use.

7. Anhydrous diethyl ether (C.P.) was obtained from the store room and was allowed to stand over sodium, and as it was needed the ether was distilled on a water bath. Boiling Point 34.5° C.
8. Ethyl Magnesium Bromide was prepared as described under Grignard Reagents.
9. Diethyl n-propyl carbinol was prepared by hydrolyzing the product formed when two moles of ethyl magnesium bromide reacted with one mole of **butyryl** chloride.
10. Diethyl iso-propyl carbinol was prepared by hydrolyzing the product formed from the interaction of one mole of iso-butyryl chloride and two moles of ethyl magnesium bromide.
11. Benzene (C.P.) trio-phene-free was obtained from the store room and allowed to stand over sodium and before using the benzene was distilled from a Wurtz flask on a water bath. Boiling point. 79.6° C.
12. Anhydrous aluminum chloride (tech.) was obtained from the store room.

Preparation of Grignard Reagent (30)

In a three liter three -necked flask fitted with an efficient stirrer, reflux condenser and dropping funnel is placed four moles (98 grams) of fresh Magnesium turnings.

Thirty ml. of a mixture of four moles of the halide and 500 ml. of dry anhydrous ether is added directly to the dry magnesium. After the reaction has started and progressed a few minutes, 200 ml. of dry ether is added directly to the reaction flask or mixture. 475 ml. of the above halide-ether solution is placed in a separatory funnel and added with stirring at the rate of one drop per second or less. The remainder of the ether-halide solution is diluted with 300 ml. of ether and added at the same rate. The mixture is allowed to reflux during the addition with no external cooling being applied. After all the ethereal-halide solution is added the stirring is continued for four hours and allowed to stand over night.

Preparation of Octyl Alcohols (31)

In general the preparation of the tertiary alcohols, di-ethyl n-propyl carbinol (3-ethyl hexanol-3) and di-ethyl iso-propyl carbinol (2-methyl-3-ethyl pentanol-3) moles of ethyl magnesium bromide with two moles of the proper acid-chloride in ether solution or in other words, two moles of ethyl magnesium bromide with one mole of the proper acid chloride in ether solution.

Two moles of the acid chloride was dissolved in five volumes of dry ether. The addition of the ethereal-acid-halide solution to the four moles of ethyl magnesium bromide was accomplished by means of a dropping funnel at the rate of a drop per second. The high rate of dilution and the slow rate of addition was necessary to control the reaction. Also rapid and vigorous stirring (mercury sealed mechanical stirred) proved very helpful. After the last acid-halid-ether mixture was added the mixture was allowed to stir for four hours.

After standing overnight the mixture was hydrolyzed by pouring the contents of the flash on ice and treating the resulting product with concentrated hydrochloric acid until the mixture becomes clear.

The ether-water layers were separated by the use of a separatory funnel and the remaining water solution was extracted three times with ether. The ether extracts were combined and the ether distilled off on a water bath.

The product was subjected to distillation under reduced pressure.

Di-ethyl n-propyl carbinol was collected between 46° and 48° C. at 6mm. pressure. Boiling point at 748mm. was 153° to 155° C. The following constants were recorded in literature as follows:

$B.P._{756mm.}$ 155° to 159° C.

$B.P._{760mm.}$ 158° to 159° C. (160.5)

$D^{22°}_{4°}$ 0.8365

$N^{13°}_{D}$ 1.43216

Di-ethyl iso-propyl carbinol was collected between 54° and 56° C. at 5mm. pressure. Boiling point at 748mm. was 156°-157°

The following constants were recorded in litereature as follows:

$B.P._{750mm.}$ 159.5° to 161°C

$D^{20°}_{20°}$ 84635

$N^{20°}_{D}$ 1.4341

Condensations

General Procedure

A 500 ml. three-necked round bottom flask was provided with a mercury sealed mechanical stirrer, a tube to remove hydrochloric acid fumes, a thermometer, and a separatory funnel. Benzene (five equivalents) was placed in a flask and the stirrer started. The entire amount of aluminum chloride (one-half equivalent) was added to the benzene and uniformly suspended in the benzene. The carbinol (one equivalent) was added by means of a dropping funnel and at a rate of a drop every five seconds. Considerable amount of hydrochloric acid was evolved during the addition of the carbinol. The temperature was maintained between 25 and 30 C. No external cooling was necessary. After all the carbinol was added the mixture was stirred an additional four hours. During the addition of the carbinol, the mixture changed from a yellow to a dark red color. The mixture was allowed to stand over night and then decomposed with ice and concentrated hydrochloric acid. The benzene layer was separated and the aqueous portion extracted several times with small portion of ether. In the ether extraction hydrochloric acid was added to destroy the ether-water emulsion. The ether and benzene extracts were washed with dilute sodium carbonate solution to remove the excess hydrochloric acid and allowed to dry over calcium chloride. The ether and benzene was distilled in a fractionating column on a water bath, then the remaining mixture was subjected to reduced pressure.

Di-ethyl n-propyl carbinol, benzene and aluminum chloride

Following the procedure above, but using one-sixth mole of the carbinol, no fractions were obtained which consisted of the desired hydrocarbon so a larger quanity of carbinol was used:

	Grams	Equivalents	Moles
Carbinol	32.5	1	1/4
Benzene	97.5	5	1 1/4
Aluminum chloride	8.4	1/2	1/8

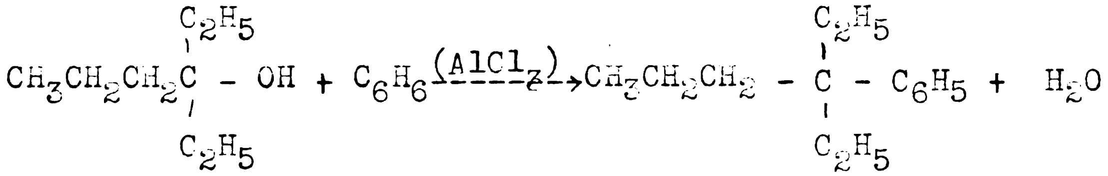
The following fractions were obtained at 15mm. pressure

1. 46° - 115° C. 7.0 grams
2. 115° - 118° C. 12.1 grams
3. above 118° C. 3.0 grams

The second fraction, after many distillations had a constant boiling point between 116° and 117° C. at 15mm. and is di-ethyl n-propyl phenyl methane yield. Boiling point at 745mm. was 237°-238° C. Yield = 25.5%

The fraction between 46° - 115° C. yielded two other fractions 47° - 50° C. @ 15mm. and 63° - 67° C. @ 15mm. the former consisting largely of unsaturated product (3-ethyl hexene-2) and the latter faction contained 3-chloro-3-ethyl hexane and some unsaturated compound.

Equation of reaction



$$CH_3CH_2CH_2\overset{C_2H_5}{\underset{C_2H_5}{C}} - OH + C_6H_6 \xrightarrow{(AlCl_3)} CH_3CH_2CH_2 - \overset{C_2H_5}{\underset{C_2H_5}{C}} - C_6H_5 + H_2O$$

Analysis of fraction

Wt. of sample	Wt. of Carbon-dioxide	Wt.of water	%C.	%H.
.2160	.6986	.2249	88.20	11.65
.2070	.6691	.2153	88.15	11.64

Molecular wt. determination

Wt. of Benzene	Wt. of sample	Temp. diff.	Mol. Wt.
17.560	.6301	.935°	188.1
17.560	.5250	.778°	188.3
Calculated for $C_{14}H_{22}$	....	....	190.18

Di-ethyl iso-propyl carbinol, Benzene and Aluminum Chloride.

The procedure, as outlined above, was followed aga in, being unsuccessful in isolating any fractions containing the desired hydrocarbon when one-sixth mole of the carbinol was used. Therefore the latter procedure used one-fourth mole of the carbinol;

	Grams	Equivalents	Moles
Carbinol	32.5	1	1/4
Benzene	97.5	5	1 1/4
Aluminum Chloride	8.4	1/2	1/8

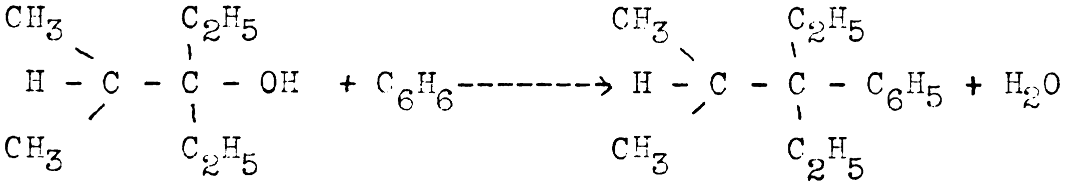
The following fractions were obtained at 14mm. pressure:

1.	46° - 112° C.	8.0 grams
2.	112° - 115° C.	11.7 "
3.	above 115° C.	5.0 "

The fraction having boiling point between 112° - 115° C. was distilled several times and a liquid having a boiling point between 113° - 114° C. at 14mm. was obtained. This liquid is di-ethyl iso-propyl phenyl methane having a boiling point between 238° - 239° C. at 745mm. pressure. The yield of di-ethyl iso-propyl phenyl methane was 24.6%.

The fraction between 46° - 112° C. yielded two other fractions 47° - 50° C. @ 15mm. and 77-81° C. @ 15mm., the former consisted largely of unsaturated product, the latter fraction contained 3-chloro-2-methyl-3-ethyl pentane and some unsaturated product.

Equation of Reaction



Analysis of Fraction

Wt.of sample	Wt.of carbon-dioxide	Wt.of water	%c.	%H.
.2001	.6469	.2080	88.16	11.63
.2020	.6545	.2101	88.11	11.64
Calculated for $C_{14}H_{22}$........................			88.30	11.69

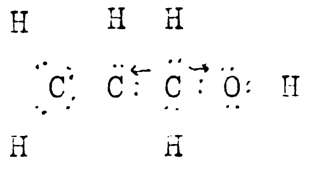
Molecular Wt. determination

Wt.of Benzene	Wt.of sample	Temp.diff.	Mol. Wt.
17.560	.5331	.789°	188.6
17.560	.5621	.833°	188.3
Calculated for $C_{14}H_{22}$			190.18

THEORETICAL

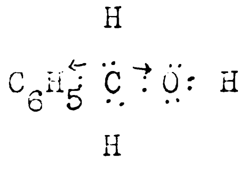
Theory of Condensations

For condensations of alcohol, whether aliphatic or aromatic alcohols with benzene or aromatic hydorcarbons in the presence of anhydrous aluminum chloride the alpha carbon must be under strain. If we examine the electronic structure of such a system as for example allyl alcohol (I) or benzyl alcohol (II) and a tertiary alcohol (III) we can see why tertiary alcohols are able to condense.



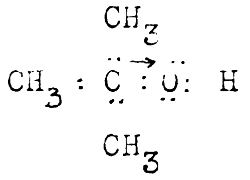
$\underset{H}{\overset{H}{\dot{C}}}\;\overset{H}{C}\overset{\leftarrow}{:}\underset{H}{\overset{H}{C}}\overset{\rightarrow}{:}\ddot{O}{:}\,H$

I.



$C_6H_5\overset{\leftarrow}{:}\underset{H}{\overset{H}{C}}\overset{\rightarrow}{:}\ddot{O}{:}\,H$

II.



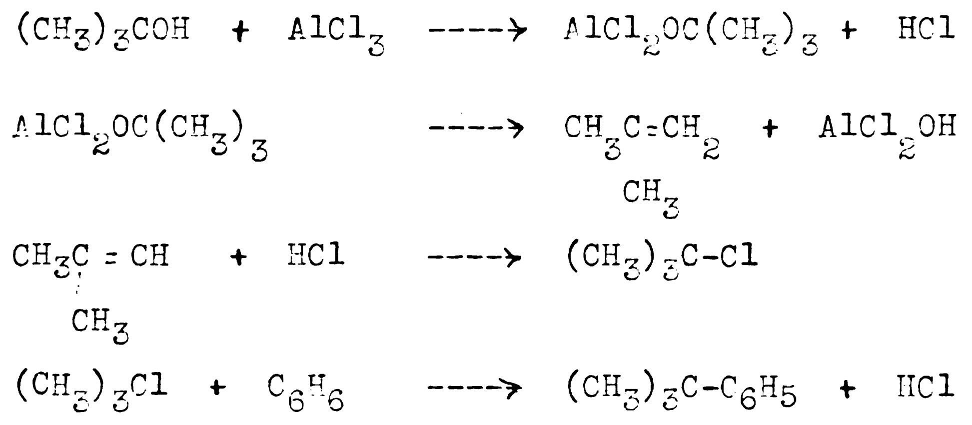
$CH_3{:}\underset{CH_3}{\overset{CH_3}{C}}\overset{\rightarrow}{:}\ddot{O}{:}\,H$

III.

The Carbon to oxygen bond is relatively unstable. This is experimentally proved by the ease with which the -OH can be replaced by a halogen from a halogen acid and also by the ease of dehydration.

The electronic pair between the carbon and oxygen in I. and II. is strongly attracted by the carbon and also by the -OH group and in III. the carbon has a weak attraction but the -OH a strong attraction. The result in either case is an unstable system.

Tzukervanik (32) reported the alkalation of benzene a nd toluene by use of secondary and tertiary alcohols in the presence of anhydrous aluminum chloride as a catalyst. He offered as a mechanism the formation of aluminum alcoholate which decomposed to form an alkene which in turn added hydrogen chloride to form the alkyl halide and the latter reacted with the hydrocarbon to give the alkylated hydro-carbon. This can be shown in the following steps using tertiary buyl alcohol, benzene and aluminum chloride.



1. $(CH_3)_3COH + AlCl_3 \dashrightarrow AlCl_2OC(CH_3)_3 + HCl$

2. $AlCl_2OC(CH_3)_3 \dashrightarrow CH_3\underset{CH_3}{C}{=}CH_2 + AlCl_2OH$

3. $CH_3\underset{CH_3}{C} = CH + HCl \dashrightarrow (CH_3)_3C-Cl$

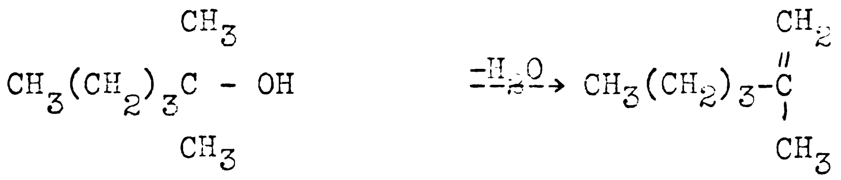
4. $(CH_3)_3Cl + C_6H_6 \dashrightarrow (CH_3)_3C-C_6H_5 + HCl$

If the above conception is correct the addition of a tertiary alcohol to a mixture of aluminum chloride suspended in an inert solvent should go throught the first three steps to the formation of the alkyl chloride.

Hedrick (33) investigated the validity of the mechanism by adding normal-butyl di-methyl carbinol in petroleum ether to a suspension of Aluminum Chloride in petroleum ether. Almost instantly hydrogen chloride and heat were evolved. The mixture at first turned yellow than a deep red color. After the reaction subsided a solution of phenol in petroleum ether was added. There was no further change in color nor any evidence of reaction. After purification an 18% yield of n-butyl di-methyl p-hydroxy phenyl methane was obtained.

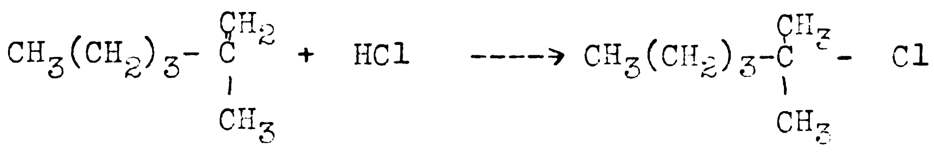
It was noted that in the above reaction when alcohol and aluminum chloride reacted, hydrogen chloride was evolved, but by Tzukervanik's conception no hydrogen chloride would be expected to be give off until the hydrocarbon was added.

A plausible explanation for the formation of hydrogen chloride in this reaction is the dehydration of the alcohol, forming the alkene, and then the water reacting with the aluminum chloride forming hydrogen chloride and the latter reacted with the alkene to form the alkyl halide which would react with the aromatic compound to form the alkyl benzene and can be expressed by:

1. 

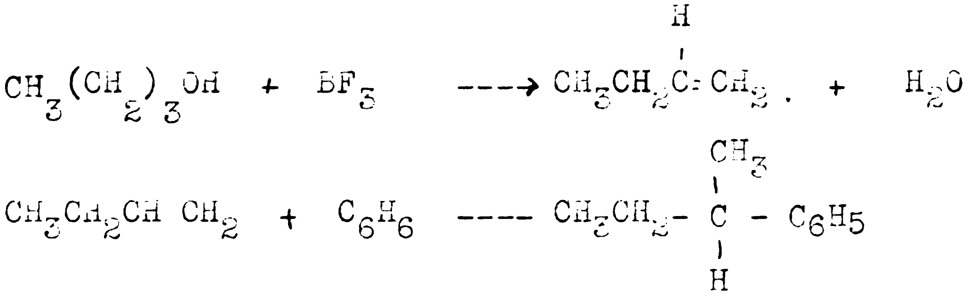
$$CH_3(CH_2)_3\overset{CH_3}{\underset{CH_3}{C}} - OH \xrightarrow{-H_2O} CH_3(CH_2)_3-\overset{CH_2}{\underset{CH_3}{\overset{\|}{\underset{|}{C}}}}$$

2. $AlCl_3 + H_2O \dashrightarrow AlCl_2OH + HCl$

3. 

$$CH_3(CH_2)_3-\overset{CH_2}{\underset{CH_3}{\underset{|}{C}}} + HCl \dashrightarrow CH_3(CH_2)_3-\overset{CH_3}{\underset{CH_3}{\underset{|}{C}}} - Cl$$

Another mechanism is offered by McKenna and Sowa (34) who have shown that when benzene is alkylated with alcohols using boron fluoride as a catalyst the alcohol is first dehydrated and the alkene condenses with benzene according to the following scheme:



$$CH_3(CH_2)_3OH + BF_3 \text{ ---}\rightarrow CH_3CH_2\overset{H}{\overset{|}{C}}=CH_2 . + H_2O$$

$$CH_3CH_2CH\ CH_2 + C_6H_6 \text{ ----- } CH_3CH_2-\overset{CH_3}{\underset{H}{C}}-C_6H_5$$

As further proof they state that normal and secondary alcohols give identical products and iso- and tertiary alcohols give identical products.

McGreal and Niederl (35) also supports this mechanism.

More evidence in favor of such a mechanism is in the condensation of unsaturated hydrocarbons with aromatic hydrocarbons, using aluminum chloride as a catalyst. Berry and Reid (36) have shown that ethylene and benzene condense using aluminum chloride as a catalyst. Other works similar to this are numerous.

Evidence against such a mechanism is slight. It must be noted that McKenna, Sowa and Niederl used a catalyst other than aluminum chloride and a much higher temperature than is employed in the Huston method. Also Huston and Sager (38) have shown that primary alcohols will not condense with benzene in the presence of aluminum chloride.

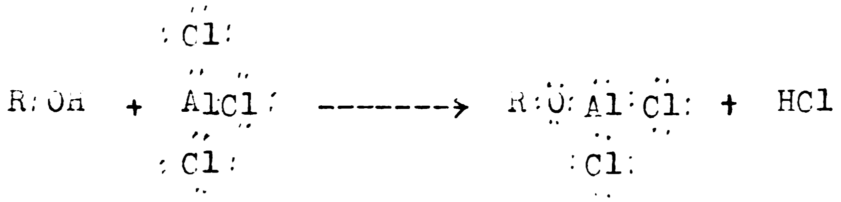
In the condensation of tertiary alcohols with benzene there is no possibility of ether formation that may take place but a good yield of alkylated hydrocarbon is obtained.

Huston has given as a possible mechanism the clevage of water, the hydroxyl of the alcohol and the hydrogen of the aromatic hydrocarbon combined as represented by:

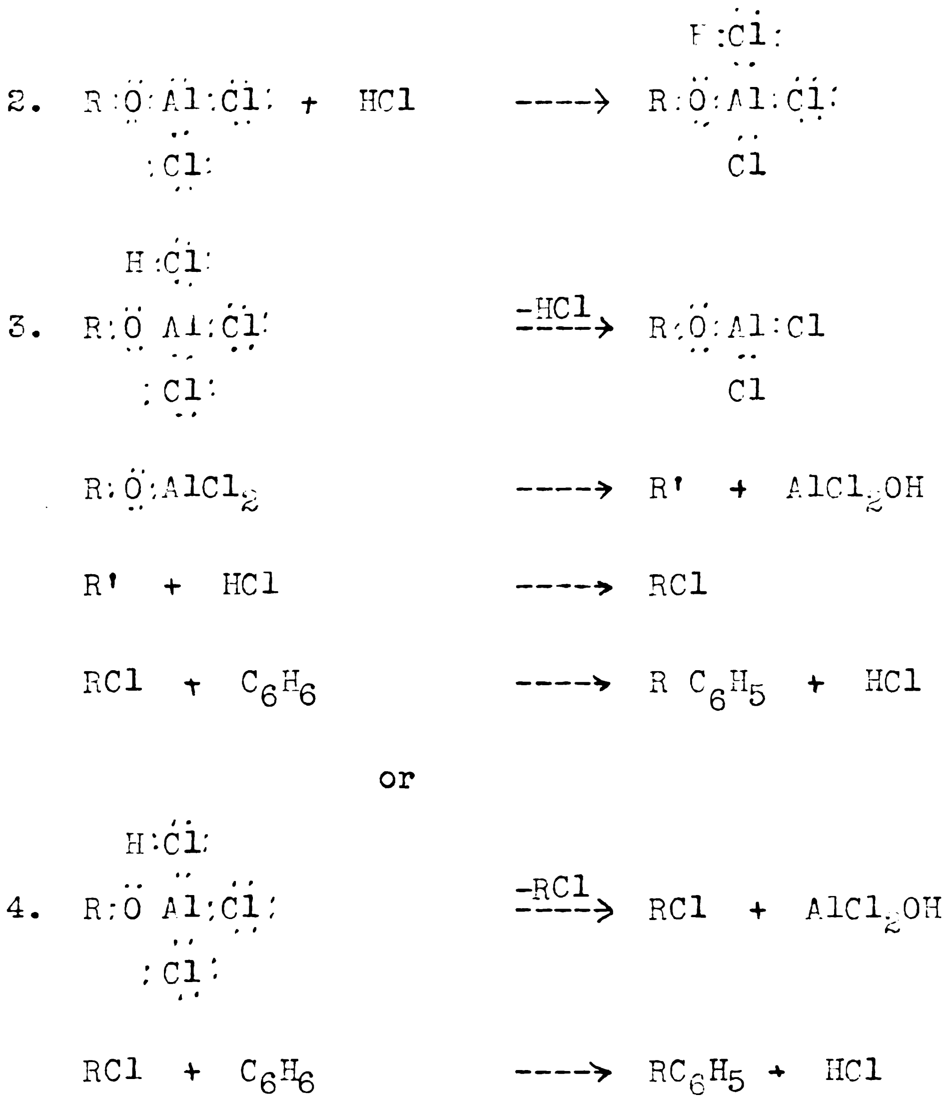
$$R_3COH + HC_6H_5 \xrightarrow{(AlCl_3)} R_3C - C_6H_5 + H_2O$$

This scheme does not account for the highly colored complex which accompanies the condensations.

A plausible scheme offered for condensation of tertiary alcohols with benzene in the presence of aluminum chloride is the formation of aluminum alcoholate which adds hydrogen chloride and then splits off either hydrogen chloride or alkyl halide and then the reaction proceeds as in Tzubervanicks conception:

1. 

$$R{:}OH + \overset{:\ddot{Cl}:}{\underset{:\ddot{Cl}:}{Al\ddot{Cl}:}} \dashrightarrow R{:}\ddot{O}{:}\underset{:\ddot{Cl}:}{\ddot{Al}}{:}\ddot{Cl}: + HCl$$



2. $\mathrm{R:\ddot{O}:\underset{:\ddot{Cl}:}{Al}:\ddot{Cl}: + HCl \longrightarrow R:\ddot{O}:\overset{H:\ddot{Cl}:}{\underset{Cl}{Al}}:\ddot{Cl}:}$

3. $\mathrm{R:\ddot{O}\ \overset{H:\ddot{Cl}:}{\underset{:Cl:}{Al}}:\ddot{Cl}: \xrightarrow{-HCl} R:\ddot{O}:\underset{Cl}{Al}:Cl}$

$\mathrm{R:\ddot{O}:AlCl_2 \longrightarrow R' + AlCl_2OH}$

$\mathrm{R' + HCl \longrightarrow RCl}$

$\mathrm{RCl + C_6H_6 \longrightarrow R\ C_6H_5 + HCl}$

or

4. $\mathrm{R:\ddot{O}\ \overset{H:\ddot{Cl}:}{\underset{:Cl:}{Al}}:\ddot{Cl}: \xrightarrow{-RCl} RCl + AlCl_2OH}$

$\mathrm{RCl + C_6H_6 \longrightarrow RC_6H_5 + HCl}$

R represents the tertiary alkyl group

R' represents unsaturated hydrocarbon

Determination of Physical Constants

Density measurements were made by means of a small picnometer. 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 Du Nouy Tensionmeter Method.

For the drop weight method, surface tension was calculated from the expression:

$$\gamma = \frac{mg}{R} F$$

where surface tension in dynes/cm

m = mass of drop in grams

g = pull of gravity (981)

R = radius of tip (.27130 cm.)

F = a constant obtained from a table corresponding to V/R^3

V = volume of drop (m/d)

The Du Nouy Tensionmeter is a direct reading instrument. There is a correction factor necessary and that factor is given by,

$$\frac{\text{wt. of Cu. Wire} \times 981}{2 \times 4 \times \text{dial reading}}$$

The Theoretical molecular volume was calculated by the formula,

$$V_m = 16.27\,n - 7.02$$

where n = number of carbon atoms

or $V_m = 16.27\, n - 16.03 - 74.57$

where n = number of carbon atoms in aliphatic side-chain

16.03 = effect of one hydrogen

74.57 = effect of phenyl ring

The molecular refractions were calculated by the Lorenz-Lorentz formula,

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

M_D = molecular refraction

M = molecular weight

d = density

n = index of refraction

The theoretical molecular refraction was calculated from the following atomic refractions: (Zeitschrift Physicalische Chemie, V.7, 140 L891)

C - H = 1.705
C - C = 1.209
C - C = 4.151
C = 2.148
H = 1.100
double bond = 1.733

The observed parachor was calculated by the formula,

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

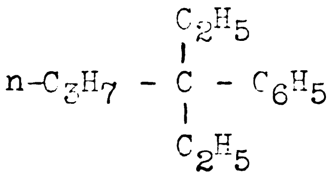
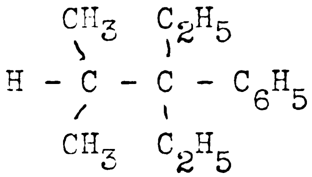
P = parachor of compound

M = molecular weight

d = density

γ = surface tension

Boiling Points, Density and Molecular Volumes

Substance	Boiling Point	$d\frac{20^\circ}{4^\circ}$
1.  $n\text{-}C_3H_7-\overset{C_2H_5}{\underset{C_2H_5}{C}}-C_6H_5$	237°-238° @ 745mm. 116°-117° @ 15mm.	.8788
2.  $H-\overset{CH_3}{\underset{CH_3}{C}}-\overset{C_2H_5}{\underset{C_2H_5}{C}}-C_6H_5$	238°-239° @ 745mm. 113°-114° @ 14mm.	.8816

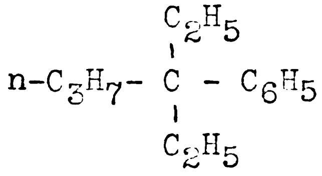
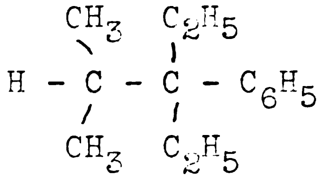
V_m

	Theoretical	Observed
1.	220.76	216.4
2.	220.76	215.7

The molecular volumes as determined experimentally are lower than the teoretical value. The formulae used for the calculation of molecular volume only hold for straight chain compounds, therefore the theoretical value would be the value for n-octyl benzene. The difference between the theoretical and observed molecular volume must be due to the effect of chain branching.

According to Kauffman a decrease in molecular volume is due to the heaping of eurogens on adjacent carbon atoms. Kauffmann states that the carbon atom in the benzene ring, to which is attached an aliphatic side chain, acts as a heaping center and in compounds where heaping of groups is on a carbon atom adjacent to a carbon in the benzene ring, the difference in molecular volume must be due to the groups present. Heaping of eurogens on adjacent carbon atoms decrease the molecular volume, therefore, the iso-compoud should possess the lower molecular volume because in the iso-compound we have a closer packing of atoms within the molecule and therefore an effective contraction in molecular volume.

Index of Refraction and Molecular Refraction

Substance	$N_D^{20°}$	$M_D^{20°}$ Calculated	Observed
1.  $n\text{-}C_3H_7-C(C_2H_5)_2-C_6H_5$	1.4968	63.25	63.30
2. 	1.4981	63.25	63.24

From the above data we observed and calculated values of molecular refraction agree very closely. The index of refraction of the iso-compound would be expected to be higher due to the effect of heaping eurogens on adjacent carbon atoms.

Surface Tension and Parachors
of the above substances

	Surface Tension		Parachors			
	Drop-Wt.	DuNouy	Sugdens	Calc.	Harkins	DuNouy
1.	30.24	32.47	519.1	516.4	506.6	516.6
2.	30.04	32.16	519.1	513.4	505.9	513.7

Sugden (39) states that for iso-merides 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 structural constants, he did not consider chain-branching and therefore the parachor calculated by his atomic and structural constants are decidedly off. The values given by Sugden are:

C = 4.8
H = 17.1
CH_2 = 39.0

Double bond = 23.2
Effect of six membered ring = 6.1

Mumford and Phillips (40) have evaluated another series of constants in which he considered the branched chain and its lessening effect on the parachor. These constants are as follows:

H = 15.4
C = 9.2
O = 20.0
CH_2 = 40.0

Double bond = 19.0
six-membered ring = 0.8

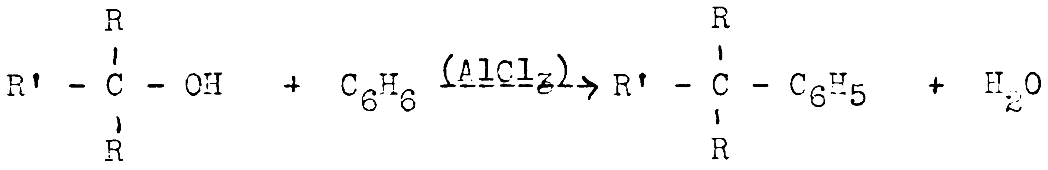
The parachor, when calculated from these constants is larger than the observed parachor. This difference may be due to chain branching. Mumford and Phillips state that "chain branching in aliphatic hydro-carbons and their derivatives is accompanied by a slight but definite diminution of the parachor. The decrement varies according to the position and length of the side chain, but within the limits of experimental error a mean value of - 3.0 appears to be applicable to all branched groups of the type - CHR_2 and - 6.0 for - CR_3 radicals and double branched compounds of the type CHR_2.........CHR_2

When these decrements are used the calculated parachor checks more closely with the observed parachor. A closer check is obtained if a decrement of - 3.0 is used for branching on a phenyl ring. The calculated value of parachor in the above table includes this decrement. It is shown in this table that the calculated parachor now checks very clsoely 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. Therefore, the Drop-Weight parachors are lower than the DuNouy parachors. This seems to suggest that a new set of constants must be introduced for the Drop-Weight method for this series of compounds.

SUMMARY

1. Tertiary octyl aliphatic carbinols condense with benzene in the presence of aluminum chloride, according to the equation:



$$R' - \underset{R}{\overset{R}{C}} - OH + C_6H_6 \xrightarrow{(AlCl_3)} R' - \underset{R}{\overset{R}{C}} - C_6H_5 + H_2O$$

Where R' is n-propyl or iso-propyl group and R represents the ethyl group.

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

3. The relationship between structure andphysical properties is shown.

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