A STUDY OF THE REACTION OF DIMETHYL TERTIARY BUTYL CARBINOL WITH BENZENE AND ALUMINUM CHLORIDE

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R. C. Hutton

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by

WAYNE THOMAS BARRETT

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INTRODUCTION

The condensation of tertiary alcohols with benzene in the presence of aluminum chloride has been extensively studied in this laboratory. In the case of highly branched alcohols, the yields of the expected tertiary alkyl benzene have been low, many other products being formed. The object of this investigation is to separate and identify some of these products. In order to accomplish this, a fractionating column with some special properties was essential, so that more or less precise separations of the variety of compounds formed, could be made.

THE FRACTIONATING COLUMN

The design of any laboratory fractionating column must necessarily depend upon the particular type of separation to be accomplished. Of course, it is desireable in any column to have as high a separating power, that is plate value, as possible. Thus with high plate values, a mixture of two closely boiling liquids can be separated quite completely by one distillation. However, the type of distillation, the character of the liquids to be separated, the amounts, and other practical considerations greatly affect the type of column to be chosen.

From previous work it was known that the liquid to be distilled consisted of a mixture of hydrocarbons, some unsaturated, and halogen containing compounds. The amount of liquid to be distilled varied from ten to one hundred milliliters. The boiling temperature ranged from 35 to well over 200 degrees. Vacuum fractionation was necessary since there was a good possibility that some of the compounds decomposed when distilled at atmospheric pressure.

From the above characteristics it was seen that the column should be built for batch distillation, that is the whole amount of the liquid mixture to be distilled was placed in the still pot at one time, the mixture slowly changing composition as the more volatile componets were removed.

This is in contrast to the type column used industrially in which a mixture of definite composition is slowly fed into the column. It must be built for vacuum distillation and designed so that there will be no heat loss from the column. Since semiquantitative separations on small amounts of liquid are to be made, the column should have an overall low holdup. The term holdup is defined as the number of cc of liquid retained in the column and head during distillation. Finally the column should have a fairly high plate value.

Before entering into a discussion of the more common type laboratory fractionating columns, some of the terms generally used will be defined.

The term "plate value" is frequently used in describing the ability of a column to separate two liquids by means of their differences in vapor pressure. It is derived from a consideration of a column which is composed of a series of theoretical plates each acting as a center of equilibrium distillation, the vapors passing from any plate to the plate above to be partially revaporized. This continuous redistillation and recondensation, termed rectification, results in the concentration of the more volatile liquid in the upper portion of the column. Thus a theoretical plate is a hypothetical apparatus which fulfills the requirement that the vapor rising from a plate is in equilibrium with the liquid leaving the plate. These considerations make it necessary that there be no heat loss.

Many laboratory fractionating columns are not composed of actual distinct plates. The column may be packed with glass rings, spirals, ect., or it may be a bubble cap type, or unpacked, e.g. the Vigereux column. All of these devices serve as plates and the efficiency of the column is therefore described in terms of the number of theoretical plates it contains.

The expression H.E.T.P. is commonly used to indicate the relationship of the number of plates to the height of the column, the height equivalent for a theoretical plate. The lower this value the more efficient is the type of packing.

A factor greatly affecting the separating power of any is the reflux ratio. This is defined as the moles of liquid returned to the column over the moles of liquid removed as product. With high reflux ratios the number of theoretical plates apparently increases but the time required to collect a definite quantity of liquid increases.

A large number of laboratory fractionating columns have been described in the literature. The bubble cap and gauze plate type columns have extremely low H.E.T.P. but the holdup of this type culumn is very considerable and they are not suited for vacuum fractionation.

Of the packed columns, the Podbielniak packing, a close spiral extending the length of the column, is by far the best. The holdup on this type packing is not great. It has been criticised for vacuum work because of its tendency to from slugs of liquid in the column.

The Vigereux type column has a low holdup and, if properly constructed, does not tend to slug. However, the H. E.T.P. is rather high. It is ideal for micro-work.

The column chosen for this work was of the spinning band type, similiar to that described by Lesesne and Lochte (1). Baker, Barkenbus and Roswell (2) have also described a column of this type. The column consists of a steel band spinning rapidly in an insulated glass tube. The holdup per plate is the lowest of any of the above types and the H.E.T.P. is also low, comparing favorably with the bubble cap type.

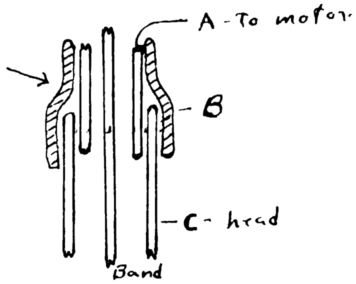
For this work, the head designed by Whitmore (3) appeared to be the most satisfactory of the types that could be constructed with facility. The Whitmore head was modified to allow for the extension of the band through it. This type head contains a stopcock by which the reflux ratio can be regulated.

The insulation of the column is quite as important as the packing. For vapor temperatures below 100 a silvered vacuum jacket is quite sufficient. For higher temperatures ordinary pipe covering is used to supplement the vacuum jacket. However, for best results, it was found necessary to install a controlled electrical heating element the length of the column. The heating element is controlled by a small transformer.

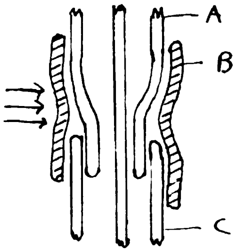
Because of the extreme fragility of the head of the column, the take-off tube is supported by a metal connection to the upper part of the column proper (not shown in the diagram). The head is wrapped extensively with asbestos cord to a point two cm above the entrance of the thermometer well, to insure accurate thermometer readings. Anschutz thermometers are used

The two stopcocks through which the organic liquids pass are lubricated with a hydrocarbon insoluble stopcock grease.

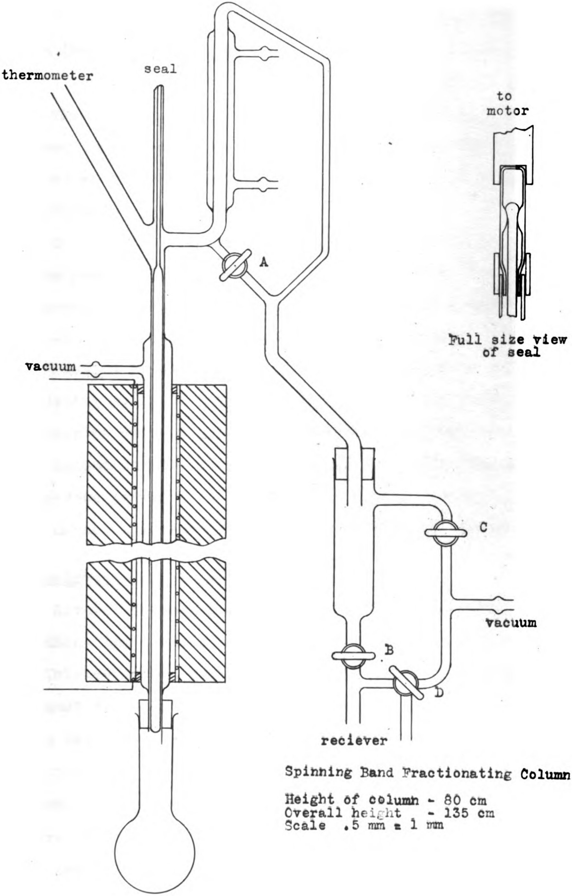
The glass bearing at the top of the head through which the end of the band was constructed very carefully, so as to allow the band to be driven and at the same time maintaining a vacuum. With an ordinary glass bearing (A)



the rubber tube (B) which completes the vacuum seal is soon worn through because of the high external pressure. However if the glass tube (A) is tapered to the external diameter of the glass tube from the head (C)



the rubber lasts many times as long. The rubber to glass moving joint is lubricated with very small amounts of a graphite suspension in glycerine.



Spinning Band Fractionating Column

Height of column - 80 cm
Overall height - 135 cm
Scale .5 mm = 1 mm

The spinning band is made of stainless steel and is 95 cm long and 7 mm wide. It is tapered to 3 mm at its upper end.

The distillation pot is filled with glass wool to prevent bumping. It is heated by a hot plate, the temperature of which is accurately controlled by a 5 amp. transformer.

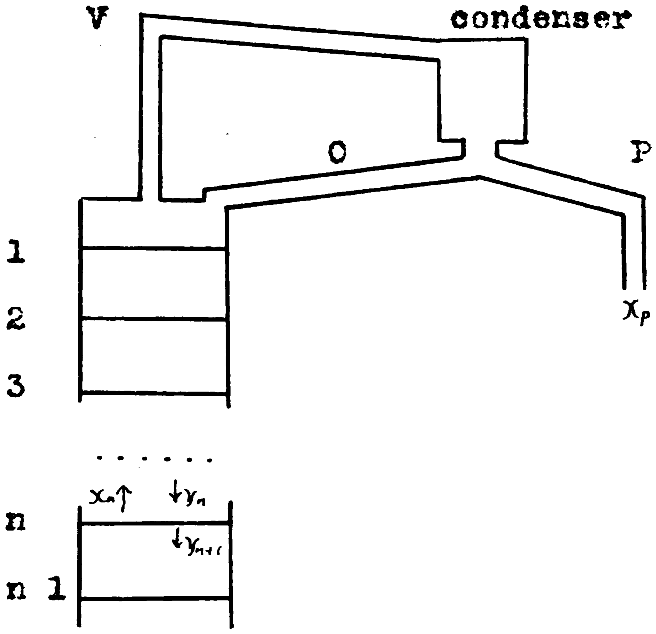
The fraction cutter is designed so that the reciever can be removed and replaced by another without disturbing the vacuum of the system. To accomplish this the system is evacuated with stopcocks C and D open and A and B closed. The fraction is collected and allowed to run into the reciever by opening B. With B closed air is allowed to enter the reciever by adjusting D. The reciever is replaced with another. C is closed and the reciever evacuated by adjusting D, until the proper pressure is attained. C is then opened and in this manner the distillation proceeds without interruption.

Determination of Plate Value.

Several methods for determining the plate value of fractionating columns have been described in the literature. The Thiele-McCabe graphical method is one of the simplest and most commonly used. This method was derived for columns which are actually made up of a series of plates but it can be applied to columns of the spinning band type if we view the column as a series of segments each of which can be considered as a plate.

Certain assumptions and conditions of distillation are necessary for the application of this method. First, the vapor passing up the column (V) on reaching the condenser must be all condensed, one portion returned to the column as reflux or overflow (O) and the rest being collected as product (P). The letters V, O, and P refer to moles per unit time. The column must be assumed to act adiabatically. We must also assume constant vaporization and constant overflow from any plate to the next. The column must operate at constant rate of distillation and constant reflux ratio. The composition of the material in the still pot and that of the product must remain constant. This assumption is only approached if the amounts of product are very small as compared with the amount of residue.

A diagram of a theoretical column is shown below:



The column is composed of plates 1,2, 3, n, and (n+1); a condenser and reflux return. The term x refers to the mole fraction of the more volatile componet in the <u>liquid</u> under consideration; and, the term y refers to the mole fraction of the more volatile componet in the vapor under consideration. x_p is the composition of the product.

For any plate the material leaving will equal that entering it

(1) $$V = O + P$$

In terms of the more volatile componet, for plate n

(2) $$V\, y_{n+1} = O\, x_n + P\, x_p$$

Eliminating V

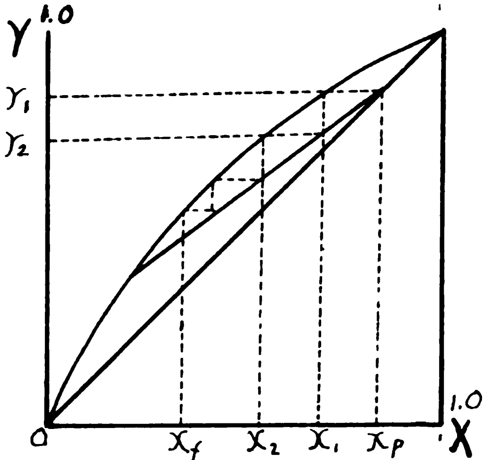
(3) $$y_{n+1} = \left(\frac{O}{O+P}\right) x_n + \left(\frac{P}{O+P}\right) x_p$$

and in terms of reflux ratio, R = O/P

(4) $$y_{n+1} = \left(\frac{R}{R+1}\right) x_n + \left(\frac{1}{R\ 1}\right) x_p$$

x_n and y_{n+1} are the only variables and so the equation (4) represents a straight line of slope (R/R+1), this line being called the operating line. Since the slope can be obtained from the reflux ratio the line can be determined by establishing a point on the line.

The x - y equilibrium curve can be plotted from experimental data.



The composition of the reflux coming to the first plate is the same as that of the product, $x_0 = x_p$. The vapor rising from this plate has the composition y. Therefore

$$(5) \qquad y_1 = \left(\frac{R}{R+1}\right) x_0 + \left(\frac{1}{R+1}\right) x_p = x_p$$

Since from this equation $y_1 = x_p$ the operating line must intersect the $x = y$ line at (x_p, y_1). The operating line DC, is thus established.

Since y_1 is known, x_1 can be calculated from the equation of the operating line, and from this we can obtain y_2, and from this x_2 ect. This procedure may be accomplished graphically by merely drawing a series of horizontal and vertical lines between the operating line and the x-y equilibrium curve, starting at x_p.

Each of these steps represents one perfect distillation and so the total number of steps represents the number of perfect plates in the column.

Thus, for the determination of plate value it is necessary to know the reflux ratio, the composition of the product and the composition of the residue.

For this work, the binary system benzene-carbon tetrachloride was used. The composition of these mixtures is readily established by determining the refractive index. The data for the x-y equilibrium curve and the refractive index-composition curve was that given by Zawidzki (4).

The liquids used were Baker's C. P., dried and carefully redistilled, a .1 degree fraction being used. The refractive indices were determined by means of an Abbe' refractometer at 25.2 C. The values determined on known mixtures checked well with the values given by Zawidzki.

The x_f values in the table following refer to the composition of the residue. Samples of residue were removed during distillation by means of a capillary extending into the still pot. About .2 cc were collected as product.

The minimum reflux ratio was calculated from the slope of the line intersecting the $x = y$ line at x_p , and the x-y equilibrium curve at x_f. The actual reflux ratio was determined by comparing the rate at which the drops of product came off the take-off tube and the bottom of the column. The graph for the first determination is shown.

Table I

Trial	1	2
Ref. $Ind._f$	1.4930	1.4901
x_f	.115	.187
Ref. $Ind._p$	1.4719	1.4682
x_p	.642	.734
R	24:1	18:1
min R	19:1	12:1
Plate Value	25	24
H.E.T.P.	3.1	3.1

The holdup was determined by the method given by Tongberg, Fenske, and Quiggle (5). A known volume of a solution of stearic acid in benzene of known concentration was refluxed in the still. A sample was withdrawn from the still pot and its composition determined. From the change in concentration the volume of benzene in the column and head could be calculated. The stearic acid was assumed to be nonvolatile at 80 C. The concentration was determined by

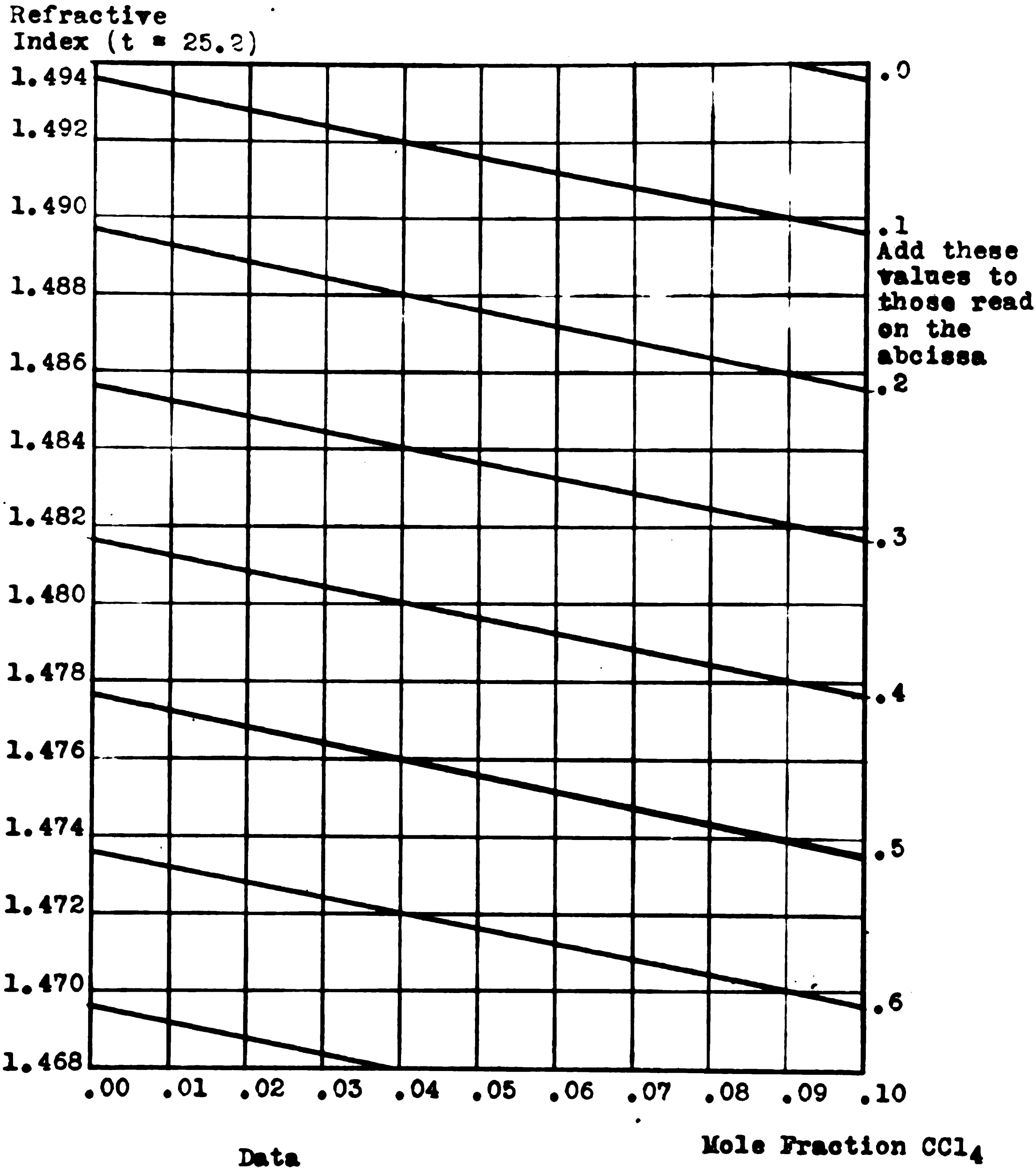
pipetting a two cc sample, evaporating off the benzene and weighing the residual stearic acid.

Table II

	Before reflux	After reflux	After draining
Weight stearic acid in 2 cc	.0605 .0604	.0667 .0664	.0618 .0620
concentration	.0302	.0332	.0310
volume of liquid in still pot	23.0	20.6	22.6
Holdup		2.4 cc	.5
Holdup/plate		.1 cc	

The values found for holdup per plate agree well with those found by Lesesne and Lochte. The H.E.T.P., however is somewhat higher, probably because of the different type head used.

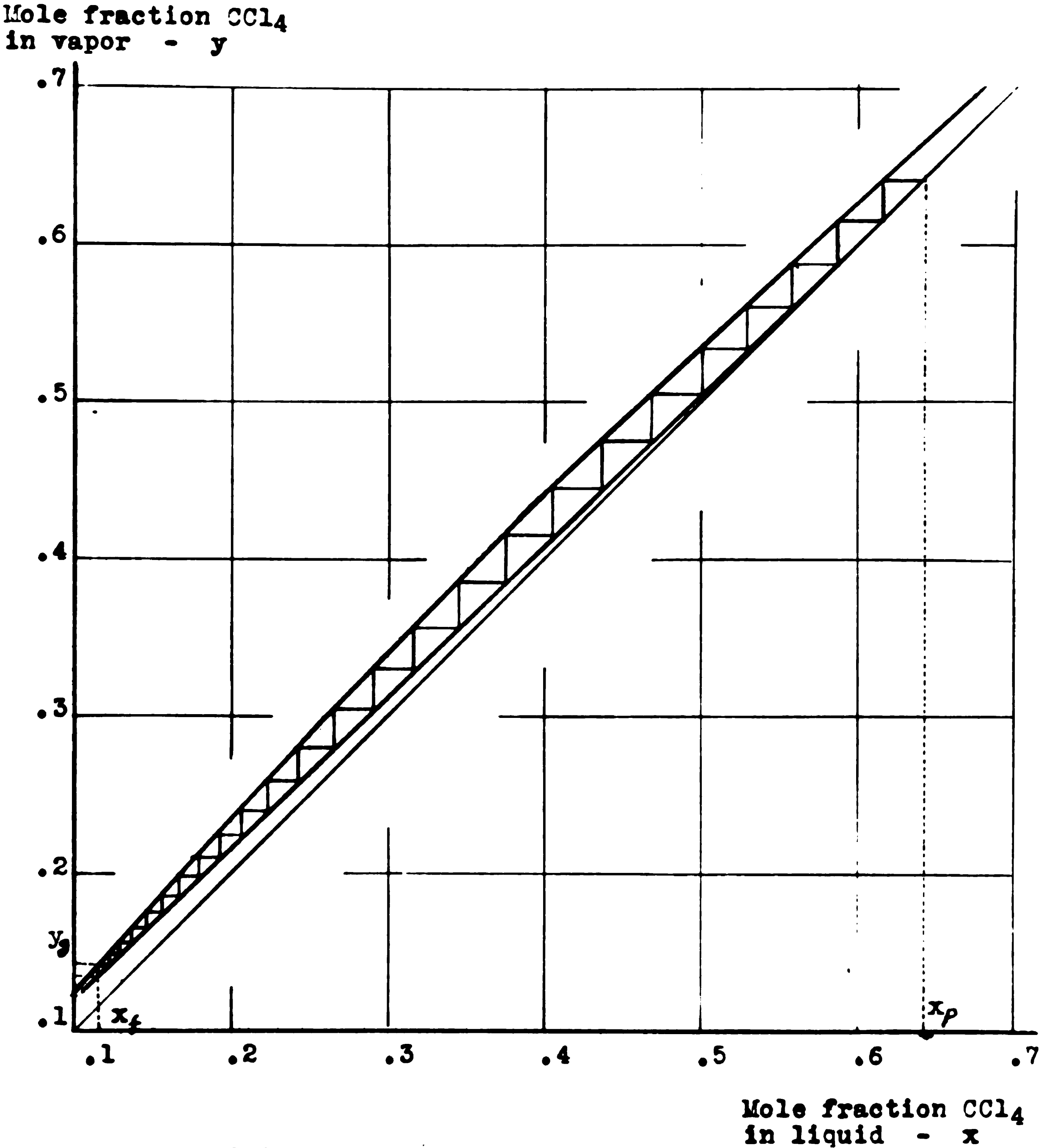
DETERMINATION OF COMPOSITION FROM REFRACTIVE INDEX
(Benzene and CCl_4)



Data

.0390	1.4936
.1579	1.4913
.2133	1.4891
.3061	1.4854
.4203	1.4808
.5131	1.4771
.6000	1.4736
.6831	1.4703
.7709	1.4667

DETERMINATION OF PLATE VALUE



Data for Equilibrium Curve
(Benzene and CCl_4)

x	y
.051	.069
.117	.146
.175	.211
.253	.292
.295	.337
.396	.439
.560	.586
.674	.693
.765	.779

Data for Operating Line

Reflux ratio - 24:1
Slope - .963
x_p .642
x_f .115

Number of Plates - 25

Historical

The alkylation of aromatic compounds with alcohols has been accomplished by various condensing agents. A short review of the use of aluminum chloride for this purpose will follow.

The greater portion of the work i n this field has been done by Huston and co-workers.

Huston and Friedmann condensed benzyl alcohol (6), methyl, phenyl carbinol, ethyl, phenyl carbinol and benzhydrol with benzene. In addition to the expected substituted benzene they found di- and tri-substituted benzenes and in the case of aryl-alkyl carbinols they found phenyl alkanes which were assumed to form by the splitting off of one of the phenyl groups of the main condensation product, the 1,1-diphenyl alkanes. They also found that the ratio of one mole alcohol, five moles benzene and one-half mole of aluminum chloride was optimum for the production of the main condensation product. Increasing the amounts of aluminum chloride did not increase the yields. Higher temperatures gave more of the by-products.

Huston and Hager (7) attempted to condense some primary alcohols at room temperature and with one-half mole aluminum chloride to one mole of alcohol. Under these

conditions, methyl, ethyl, propyl, isopropyl, butyl, isobutyl, and isoamyl alcohols did not give the alkyl benzenes. Allyl alcohol did give the allyl benzene. Huston and Goodemoot (8) condensed three cycloalkyl carbinols (-hexyl, -pentyl, -butyl) and showed that the ease of condensation was related to the strain in the ring: the greater strain being more conducive to condensation.

Huston and others (9) have condensed tert.-butyl, tert.-amyl, the three tert.-hexyl, the seven tert.-heptyl and all of the tert.-octyl carbinols with benzene.

From these condensations it has been found that the ratio of one mole of alcohol to one-half mole of aluminum chloride is optimum for the production of the corresponding mono-alkyl benzene. As branching on the α carbon increases the yields of the expected alkyl benzene decrease and unsaturated compounds, halides and lower alkyl benzenes form. Condensation at lower temperatures decreases the amount of these side-products formed. For example the condensation of dimethyl n-butyl carbinol gave a 45 % yield of 2-methyl, 2-phenyl-hexane while condensation of dimethyl tert.-butyl carbinol gave only a 7 % yield of 2,3,3-trimethyl, 2-phenyl butane.

Condensation of dimethyl tert.-amyl carbinol gave, in addition to the expected alkyl benzene, a 9 % yield of tert.-butyl benzene. Dimethyl neo-amyl carbinol at 10 gave a 42 % yield of tert.-butyl benzene.

Most of above alcohols have also been condensed with phenol (10). The reaction, in general, appears to proceed analogously. However two differences are to be noted. The condensation, itself, proceeds with the formation of more intense colors, and the yields of alkyl phenols are much higher. In no case, has there been reported the formation of lower molecular weight alkyl phenols.

Huston and Jackson (11) condensed several alkyl-diphenyl carbinols with phenol. The primary alkyl-diphenyl carbinols gave the expected products, the secondary alkyl diphenyl carbinols gave p-benzyl phenol and secondary alkyl benzenes in addition to the expected products. Tert.-butyl diphenyl carbinol condensed to give the rearranged product; 3,p-hydroxyphenyl 2,2-diphenyl, 3-methyl butane.

Hughes, (12) condensing some dialkyl-aryl carbinols with benzene reported the formation of dimers of the corresponding unsaturated products of the alcohols, in addition to the expected diphenyl alkanes.

Kaye, and others, (13) have condensed many of the secondary alcohols with benzene. The conditions used for the condensation were somewhat different from those mentioned above. Fifty grams (0.3 mole) of aluminum chloride were needed for one-half mole of alcohol. More aluminum chloride decreased the yields of mono-alkyl benzene. The addition of dry HCl throughout the addition of alcohol increased the yields. The alcohol was added

to the suspension of aluminum chloride and benzene in an ice bath. The mixture, in some cases was refluxed for several hours. In many cases rearranged alkyl benzenes were formed.

Several condensations of alcohols with other aromatic substances have been reported from this laboratory (14).

Tsukervanik (Tzoukerwanik) and co-workers (15) have reported the condensation of some of the lower primary, secondary and tertiary alcohols with benzene and phenol.

The ratio of aluminum chloride to alcohol used by these workers has varied. In general, 1.5 to 2 moles aluminum chloride per mole of primary alcohol; one mole aluminum chloride per mole of secondary alcohol; and, one-half mole aluminum chloride per mole tertiary alcohol has been used. The mixtures after the addition of the aluminum chloride have been refluxed several hours before hydrolysis. Alkenes and alkyl halides have been isolated as byproducts in the condensation of tertiary alcohols with benzene. Secondary alcohols gave no alkenes or alkyl halides.

Several cyclic alcohols have also been condensed with benzene by Tsukervanik and co-workers (16). The alkenes and alkyl halides were again isolated as byproducts.

Welsh and Drake (17) have condensed some tertiary-aryl carbinols with benzene. They, also, report the formation of the corresponding alkene of the carbinols and their saturated dimers.

Norris and co-workers (18) have condensed several primary alcohols under conditions similiar to those used by Tsukervanik. They report the formation of symmetrical tri-alkyl benzenes.

Ipatief and co-workers (19) have reported the condensation of n-propyl alcohol with several condensing agents. With aluminum chloride the unrearranged product, n-propyl benzene, was obtained. Neo-pentyl alcohol also gave the unrearranged alkyl benzene.

THEORETICAL

The discussion of the theoretical aspects of the alkylation of benzene with alcohols must be closely related to its alkylation with alkenes and alkyl halides, since all act in a similiar manner to give the alkyl benzene. The alkylation reaction by any of the three above alkylating agents has been proposed to have a common ionic intermediate. Or, the reaction of alcohols has been proposed to involve alkenes and/or alkyl halides as intermediates. Aluminum chloride complexes with either the aromatic substance or the alkylating agent have also been proposed as intermediates.

The great activity of aluminum chloride with a wide variety of substances has given data to support all of the above types of mechanisms.

The direct removal of water from the alcohol and benzene by the dehydrating agent, aluminum chloride, does not explain the reaction characteristics, color, ect., and the rearranged products obtained.

The formation of alkenes as intermediates has been assumed to explain the rearrangement of the alkyl groups of certain alcohols. Thus primary alcohols have given secondary alkyl benzenes, and some iso-alcohols give tertiary alkyl benzenes, e.g. isobutyl alcohol gives tert.-butyl benzene. The work of Kaye (13) with secondary alcohols, in this laboratory has shown, that in every case where unsaturation of the alcohol and subsequent addition of HCl or benzene would, by the Markonikow rule, lead to rearranged products or mixtures of rearranged products, such products have been found. Thus, butanol-2 gives the expected 2-phenyl butane, while 2-methyl butanol-3 gave the tertiary alkyl benzene, 2-methyl, 2-phenyl butane. Heptanol-3 gave mixtures of the two secondary heptyl benzenes predicted by the above concept.

McKenna and Sowa, using boron triflouride as a catalyst have proposed such a mechanism on the basis of the above type rearrangements and the isolation of small amounts of the alkenes and their polymers from the products of the reaction (20).

$$R\text{-}CH_2\text{-}CH_2OH \xrightarrow{BF_3} R\text{-}CH = CH_2$$

$$R\text{-}CH = CH_2 + C_6H_6 \longrightarrow R\text{-}CH(C_6H_5)\text{-}CH_3$$

Welsh and Drake (17) condensing tert.-aryl carbinols with phenol and benzene in the presence of alumunim chloride have found analogous results. They have proposed a mechanism similiar to that above. Hughes (12), in this laboratory, has condensed some dialkylaryl carbinols with benzene and phenol and found, in addition to the expected diphenyl alkanes, dimers of the corresponding alkene of the alcohol. The reduction product of the alcohol, 3-phenyl pentane in the case of diethylphenyl carbinol was also obtained.

Jackson (11), in this laboratory, condensing diaryl-

alkyl carbinols has also noted the formation of the reduction product with some alcohols. These reduction products might be explained by the addition of hydrogen to the alkene formed from the alcohol.

Tsukervanik (Tzoukerwanik)(15) has proposed a mechanism of the following type for tertiary alcohols.

$$t\text{-}C_5H_{11}OH + AlCl_3 \longrightarrow t\text{-}C_5H_{11}OAlCl_2 + HCl$$

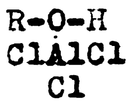
$$t\text{-}C_5H_{11}OAlCl_2 \longrightarrow C_5H_{10} + AlCl_2OH$$

$$C_5H_{10} + HCl \longrightarrow t\text{-}C_5H_{11}Cl$$

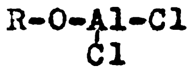
$$t\text{-}C_5H_{11}Cl + C_6H_6 \xrightarrow{AlCl_3} t\text{-}C_5H_{11}C_6H_5 + HCl$$

The experimental evidence offered has been the isolation of alkenes and alkyl halides as byproducts. Tsukervanik suggests that the aluminum alcoholate is formed through the preliminary addition of aluminum chloride to the alcohol with the subsequent elimination of HCl.

Complex formation of alcohols and aluminum chloride has been investigated by several workers. Perrier and Pouget (21) have proposed two types of solid complexes between primary alcohols and aluminum chloride. The first, the "addition product" is formed at lower temperatures with an excess of alcohol. The other, the "substitution product", is formed at higher temperatures with an excess of aluminum chloride and the elimination of HCl



$$\begin{array}{c} R\text{-}O\text{-}H \\ ClAlCl \\ Cl \end{array}$$

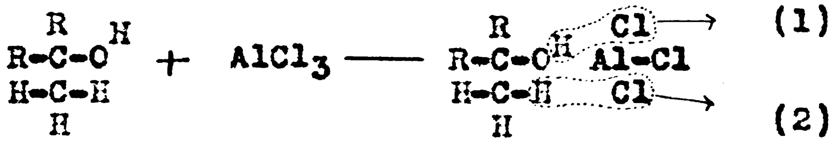


$$R\text{-}O\text{-}\underset{Cl}{Al}\text{-}Cl$$

addition product   substitution product

This work has been repeated and extended by Mpetse (22) who arrived at the same conclusions. The analytical data has shown that usually several molecules of alcohol are associated with one molecule of aluminum chloride.

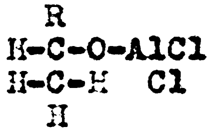
The ease of formation of an alcoholate would be predicted to be primary ⟩ secondary ⟩ tertiary, since the ease of replacement of the H of the alcoholic hydroxyl group is in this order. This is, of course, in the reverse order of the ease of condensation of alcohols. This criticism is only valid if it is assumed (1), that the alcoholate formation is the rate determining step in the overall reaction and (2), that it is the O - H bond which is broken in the formation of the aluminate. That this, in the case of tertiary alcohols, may not be so is illustrated below:



$$\begin{array}{c}R\\R{-}C{-}O^{H}\\H{-}C{-}H\\H\end{array} + AlCl_3 \longrightarrow \begin{array}{l}\;\;R \qquad Cl \rightarrow\\ R{-}C{-}O^{H}\ Al{-}Cl\\ H{-}C{-}H \quad Cl \rightarrow\\ \;\;H\end{array}$$

addition complex

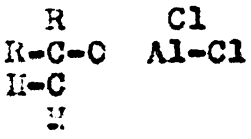
(1)



$$\begin{array}{l}\;\;R\\ H{-}C{-}O{-}AlCl\\ H{-}C{-}H \quad Cl\\ \;\;H\end{array}$$

stable aluminate of primary or secondary alcohol

(2)



$$\begin{array}{l}\;\;R \qquad Cl\\ R{-}C{-}C \quad Al{-}Cl\\ H{-}C\\ \;\;H\end{array}$$

unstable aluminate of tertiary alcohol

The known stability of the complexes of tertiary alcohols as compared with those of primary alcohols agrees well with this hypothesis.

The decomposition of prepared aluminates gives varied products. With primary alcohols the decomposition takes place at high temperatures giving the chloride. Ethers also have been reported as forming (22). Aluminates of tertiary alcohols decompose at room temperature or slightly above giving alkenes (23).

The addition of HCl to olefins, catalyzed by aluminum chloride is well known. It takes place rapidly even at very low temperatures (24). At this point, all of the substances necessary for an ordinary Friedel-Crafts reaction are present.

Tsukervanik (15) again proposes an aluminate as the intermediate in the condensation of secondary alcohols with benzene.

$$\text{sec-ROH} + AlCl_3 \longrightarrow ROAlCl_2 + HCl$$

$$ROAlCl_2 + C_6H_6 \xrightarrow{AlCl_3} R\text{-}C_6H_5 + HOAlCl_2$$

He found no chlorides or alkenes as byproducts. This mechanism would not explain the rearranged products found by Kaye.

Tsukervanik (16) proposes the following mechanism for cyclic alcohols, on the basic of the isolation of the olefins and halides as byproducts, e.g. cyclohexanol

$$C_6H_{11}OH + AlCl_3 \longrightarrow C_6H_{10} + AlCl_2OH + HCl$$

$$C_6H_{10} + HCl \longrightarrow C_6H_{11}Cl$$

$$C_6H_{10} + C_6H_6 \longrightarrow C_6H_{11}C_6H_5$$

$$C_6H_{11}Cl + C_6H_6 \xrightarrow{AlCl_3} C_6H_{11}C_6H_5 + HCl$$

Gustavson (25) has prepared crystalline ternary complexes at low temperatures, some containing a molecule of HCl.

These probably do not enter into the Friedel-Crafts reaction sinse they do not appear to form at higher temperatures.

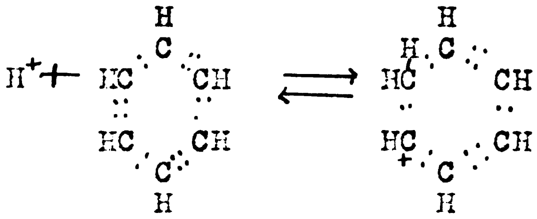
Several ionic mechanisms have been suggested. The three to be discussed all involve a catanoid attack on the benzene ring. Dougherty (26) suggests that the active agents are polarized or ionized addition compounds between the halide and aluminum chloride and the benzene and aluminum chloride which exist in small amounts with the ordinary molecules.

$$C_6H_6 + AlCl_3 \rightleftarrows C_6H_6AlCl_3 \rightleftarrows (C_6H_5AlCl_3)^- - H^+$$
$$RX + AlCl_3 \rightleftarrows AXAlCl_3 \rightleftarrows R^+ - (XAlCl_3)^-$$
$$(C_6H_5AlCl_3)^- - H^+ + R^+ - (XAlCl_3)^- \rightleftarrows (C_6H_5AlCl_3)^- - R^+ + H^+ - (XAlCl_3)^-$$
$$(C_6H_5AlCl_3)^- - R^+ \rightleftarrows C_6H_5RAlCl_3 \rightleftarrows C_6H_5R + AlCl_3$$
$$H^+ - (XAlCl_3)^- \rightleftarrows HXAlCl_3 \rightleftarrows HX + AlCl_3$$

This theory is supported by the work of Prins (27) which indicates that benzene ionizes to give phenyl and hydrogen ions under the influence of aluminum chloride. On the basis of the above mechanism Dougherty predicted and demonstrated the transference of halogen from one halide to another, e.g. the formation of ethylene chlorobromide from ethylene bromide and ethylene chloride under the action of aluminum chloride.

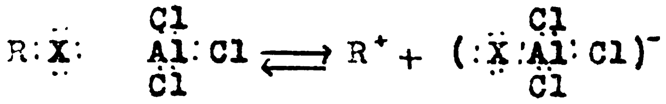
Thomas (28) suggests a proton theory in which the proton attacks the benzene.

$$HCl + AlCl_3 \rightleftarrows HAlCl_4$$
$$HAlCl_4 \rightleftarrows H^+ + AlCl_4^-$$

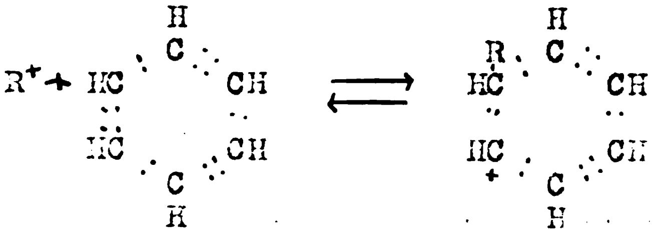


The hydrogenated benzene is now susceptible to substitution by any compound having an unshared pair of electrons (olefin, halide, alcohol). Addition of the proton to the alcohol or halide with subsequent shifting to a more stable state is proposed to account for the isomerization of the alkylating agent. This proton theory will explain the action of aluminum chloride in effecting cracking of paraffins, dehydrogenation, isomerization,polymerization and alkylation.

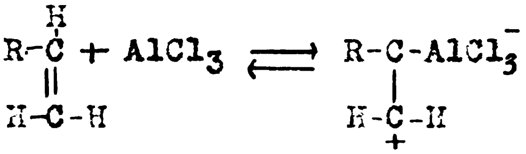
The last mechanism to be discussed is the catenoid theory proposed by Price (29). The reversibility of the alkylation of benzene is well known. Dialkyl benzenes are readily converted to monoalkyl benzenes by refluxing them with benzene and aluminum chloride. Ulich and Heyne (30) have found that the rate of alkylation of benzene was directly proportional to the concentration of the catalyst-aklyl halide complex shown below. Wertyporoch (31) has shown that this complex is ionic.



$$R{:}\ddot{\underset{..}{X}}{:}\ \ \overset{Cl}{\underset{Cl}{Al}}{:}Cl \rightleftarrows R^{+} + (:\underset{..}{\ddot{X}}:\overset{Cl}{\underset{Cl}{Al}}:Cl)^{-}$$

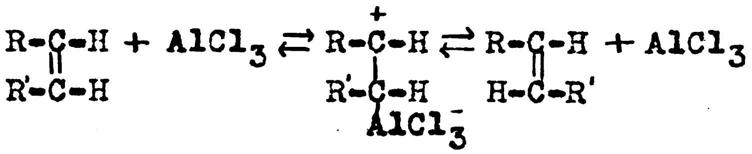


Alcohols would react analogously. Olefins would associate with aluminum chloride to give a slightly different tpye cation.



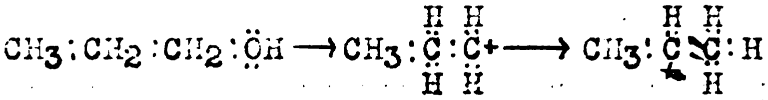
$$\begin{array}{c} H \\ R\text{-}C \\ \| \\ H\text{-}C\text{-}H \end{array} + AlCl_3 \rightleftarrows \begin{array}{c} R\text{-}C\text{-}AlCl_3^{-} \\ | \\ H\text{-}\underset{+}{C}\text{-}H \end{array}$$

The cis-trans isomerization of olefins by aluminum chloride is easily explained by this type complex



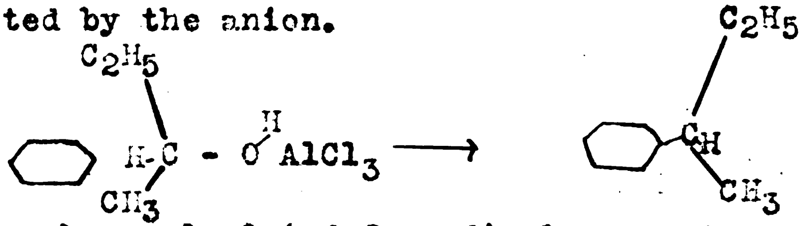
$$\begin{matrix}R-C-H\\ \|\\ R'-C-H\end{matrix} + AlCl_3 \rightleftarrows \begin{matrix}\overset{+}{R-C-H}\\ |\\ R'-C-H\\ AlCl_3^-\end{matrix} \rightleftarrows \begin{matrix}R-C-H\\ \|\\ H-C-R'\end{matrix} + AlCl_3$$

The rearrangement of alkyl groups during alkylation, primary to secondary, ect., is then due to the electron deficient carbon atom in the cation. This is in accordance with the views expressed by Whitmore in his article on molecular rearrangements (32)



$$CH_3:CH_2:CH_2:\ddot{O}H \longrightarrow CH_3:\overset{H}{\underset{H}{\ddot{C}}}:\overset{H}{\underset{H}{\ddot{C}}}+ \longrightarrow CH_3:\overset{H}{\ddot{C}}:\overset{H}{\underset{H}{\ddot{C}}}:H$$

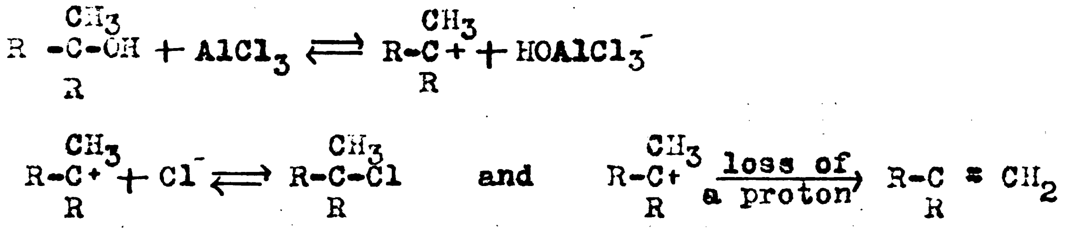
The rearrangements observed by Kaye can be easily explained in the above manner. In the case of boron trifluoride as a catalyst, the alkylation with alcohols must be so rapid, in some cases that isomerization does not occur. For example, d-sec.-butyl alcohol gives small amounts of l-sec.-butyl benzene in addition to the d,l-sec.-butyl benzene. The asymmetric alkyl cation must have reacted simultaneously with the process of its formation so that racemization was not complete. The inversion was due to the approach of the ring at the face of the asymmetric carbon opposite that being vacated by the anion.



Price has calculated from dipole moments and interatomic

distances the charge on the α atom of various substituent groups on the benzene ring. From these he has calculated the polarizing force on the double bond of the ring. And from this he obtains the degree of meta orientation of the entering group on the basis of his catenoid theory. The calculated values agree very well with the observed meta orientation.

The formation of olefins and halides, therefore, in the condensation of alcohols with benzene is a side reaction.



$$R-\underset{R}{\overset{CH_3}{C}}-OH + AlCl_3 \rightleftharpoons R-\underset{R}{\overset{CH_3}{C}}^{+} + HOAlCl_3^{-}$$

$$R-\underset{R}{\overset{CH_3}{C}}^{+} + Cl^{-} \rightleftharpoons R-\underset{R}{\overset{CH_3}{C}}-Cl \quad \text{and} \quad R-\underset{R}{\overset{CH_3}{C}}^{+} \xrightarrow[\text{a proton}]{\text{loss of}} R-\underset{R}{C} = CH_2$$

In an earlier article Price (33) has shown that with BF_3 as a catalyst, the conditions for the alkylation of naphthalene with cyclohexanol are much less vigerous than those for the formation of cyclohexene from the alcohol by the action of BF_3.

In summary, and mechanism to be considered should be consistent with the observations made by Huston and co-workers that condensation is aided greatly by strain on the α carbon atom of the entering group. In the case of saturated aliphatic alcohols the amount of strain is in direct relationship with the ease of dehydration. However, in considering other types of alcohols, it becomes apparent that some condense readily which cannot dehydrate easily, e.g. benzyl alcohol, benzhydrol, and cyclybutyl carbinol. The relation-

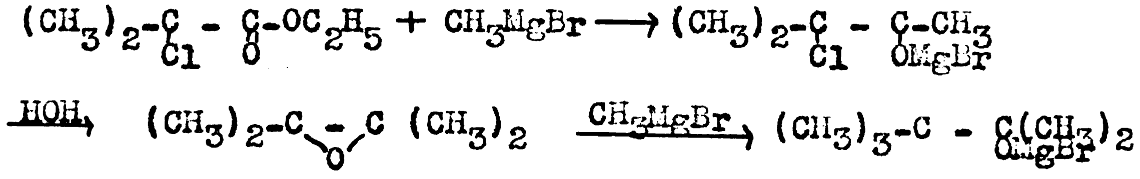
ship of this strain to the formation of carbonium ions is not well established.

Preparation of Dimethyl Tert.-butyl Carbinol.

Butlerow first reported the synthesis of dimethyl tert.-butyl carbinol in 1875 (34). He prepared it by the laborious reaction of zinc dimethyl on trimethyl acetyl chloride. He noted the striking property of the ease of formation of a solid hydrate and showed by analysis that it contained two molecules of carbinol per molecule of water. He prepared the corresponding chloride, iodide, and alkene from the alcohol by the usual methods.

The carbinol was prepared in 1881, with difficulty, by the action of zinc dimethyl on the acid chloride of trichlor-acetic acid (35). In the same year it was prepared by Kaschirsky from α bromo isobutyryl bromide and zinc dimethyl.(36)

Henry (37) isolated the carbinol as the main product in the attempt to make the monochlorhydrin of pinacol by the action of methyl magnesium bromide on ethyl chloro-isobutyrate. Henry suggested that the carbinol was formed in the following manner (38):



$$(CH_3)_2\text{-}\underset{Cl}{C}\text{-}\underset{O}{\overset{}{C}}\text{-}OC_2H_5 + CH_3MgBr \longrightarrow (CH_3)_2\text{-}\underset{Cl}{C}\text{-}\underset{OMgBr}{C}\text{-}CH_3$$

$$\xrightarrow{HOH} (CH_3)_2\text{-}C\underset{O}{-}C\,(CH_3)_2 \xrightarrow{CH_3MgBr} (CH_3)_3\text{-}C\text{-}\underset{OMgBr}{C}(CH_3)_2$$

Henry (39) prepared the intermediates by separate synthesis and showed that both were converted into the carbinol on treatment with CH_3MgBr. He also prepared the carbinol from acetone and tert.-butyl magnesium chloride (40). He obtained very good yields of the carbinol by the action of methyl magnesium bromide on pinacolone (41).

Several other methods, very similiar to the above, have been described.

All of the above mentioned workers have described the peculiar ease with which the carbinol combines with water to form a solid hydrate. Edgar (42) and Whitmore (43) have also described this property.

While several other aliphatic alcohols form hydrates (tert.-butyl, isopropyl, ect.) the melting point of the hydrate in all cases, is lower than that of the pure alcohol. Dry dimethyl tert.-butyl carbinol forms a hydrate instantly on contact with water or even moist air, which has a melting point sisty-five degrees higher than the carbinol itself. In this laboratory, all of the possible tert.- amyl, hexyl, heptyl and octyl and some of the higher secondary alcohols have been prepared. All are liquids at room temperature and with the above exception none form solid hydrates (none has been reported as forming a liquid hydrate). This unique case of the formation of a white crystalline hydrate by dimethyl tert.-butyl carbinol alone has not been satisfactorily explained.

Butlerow and Edgar reported that the hydrated water could be removed by allowing the crystals to stand over

barium oxide. This worker, however, found that the anhydrous form was not obtained by this method even after standing a dessicator over barium oxide for several months. The alcohol was readily dried by allowing an ether solution to stand several days in the presence of metallic sodium, the latter at reduced pressure.

The carbinol, itself, melts at 17 and boils at 128-30. It has a camphor-like odor characteristic of the tertiary heptyl and octyl alcohols. The hydrate melts at 80 sublimes readily at room temperature, and distills over as the solid at about 120-5.

Edgar (42) and Whitmore (43) have prepared the carbinol by the action of tert.-butyl magnesium chloride on specially purified acetone. In this laboratory Binder (44) prepared the carbinol by the procedure of Whitmore obtaining yields o f 15-20 %. Hedrick (45) also in this laboratory prepared the carbinol from pinacolone and methyl magnesium bromide obtaining 70 % yields based on the pinacolone.

Several methods were used by this worker. The preparation from pinacolone proved to be the most successful. Pinacolone was prepared by the reduction of acetone with magnesium and rearrangement of the resulting pinacol by means of the procedure given in Organic Synthesis (46).

The carbinol was also prepared by the action of two moles of methyl magnesium bromide on trimethyl acetyl-chloride. The latter was prepared from the acid by

means of thionyl chloride. Trimethyl acetic acid was prepared from tert.-butyl magnesium chloride and carbon dioxide.

Another method of preparation was again by use of methyl magnesium bromide, this time five moles reacting with one mole of the ethyl ester of tricholo-acetic acid. The ester was prepared from the acid chloride, the latter being prepared from the acid by means of phosphorous pentachloride.

Experimental

Preparation of Pinacolone

Pinacol hydrate was prepared from acetone and magnesium by the procedure given in Organic Synthesis (46). The pinacol hydrate was converted into pinacolone by distilling from 6 N sulfuric acid (Org. Syn.). The pinacolone was dried and fractionated. The fraction boiling at 103-7 was collected. Yields, based on magnesium, are from 30-35 %. In all about 1800 grams (20 runs) were prepared.

Preparation of Methyl Magnesium Bromide

The Grignard reagent was made by passing gaseous methyl bromide into magnesium turnings suspended in ether in a three-necked flask fitted with a reflux condenser, motor stirrer, and inlet tube for the gas. Enough methyl bromide for five moles of Grignard reagent was generated by heating (sand bath) 320 g methyl alcohol, 750 g conc.

sulfuric acid, 50 cc water, and 1030 g sodium bromide in a three liter round-bottomed flask. The methyl bromide was passed through a wash train consisting of three bottles of 40 % NaOH and three bottles of conc. sulfuric acid with three saftey bottles. Five and one half moles of magnesium and three liters of anhydrous ether were used in a five liter three necked flask. The methyl bromide was passed in until the magnesium had all disappeared.

Reaction of Methyl Grignard Reagent.

The pinacolone, or trimethyl acetyl chloride (see below), was slowly dropped in, substituting the inlet tube with a dropping funnel, and the mixture stirred for several hours after the carbonyl compound had been added. Sometimes, it was necessary to add more anhydrous ether.

The mixture was hydrolized on ice and enough hydrochloric acid to dissolve the magnesium hydroxide. The ether layer was separated and the water layer extracted five or six times, with ether, to remove the hydrate, which is fairly soluble in water. The ether extracts were washed with water and dried first with anhydrous sodium sulfate and then with metallic sodium for several days. The alcohol was distilled from the sodium under reduced pressure, the fraction boiling at 48-51 (20 mm) was collected. About ten moles of carbinol were prepared

from pinacolone by this method, the yields being 70-75 %.

Preparation of Trimethyl Acetyl Chloride.

Tert.-butyl magnesium chloride was prepared according to the excellent procedure given by Whitmore (43). Details will not be given here.

Carbon dioxide was passed into 2.5 moles of the Grignard reagent according to the directions given in Organic Synthesis (47). Trimethyl acetic acid (B P 164, M P 35) was obtained in 33 % yield.

The acid chloride was obtained by adding 60 g thionyl chloride to the acid in a 250 cc Vigereux column. The mixture was slowly distilled, HCl, SO_2 and excess thionyl chloride coming off first. The acid chloride was collected at 116, 80 g were obtained (69 % yield).

Preparation of Ethyl Ester of Trichlor-Acetic Acid.

One hundred and eighty grams of PCl_5 were slowly added to 200 g trichlor-acetic acid (commercial product) in a 500 cc Vigereux column. The acid chloride, along with some phosphorous oxychloride were slowly distilled off (B P 115-20). The distillate was immediately placed in a 500 cc round-bottomed flask fitted with a reflux condenser. To the mixture was added 100 cc absolute ethyl alcohol with cooling. The mixture was then refluxed for two hours until the evolution of HCl ceased. The ester was then distilled (B P 168) and 170 g were obtained. The percent yield of ester, based on the acid was 73 %.

This ester was added dropwise with stirring to five moles of methyl magnesium bromide, prepared as above. When the reaction had subsided the ether had evaporated off and two liters of anhydrous toluene added. The mixture was refluxed for eight hours and allowed to stand over night. It was then hydrolized, extracted, dried, and distilled in the manner described above. Twenty-three g of alcohol were obtained (20 % yield).

EXPERIMENTAL

Several preliminary condensations were run to determine the conditions and amount of $AlCl_3$ to be used. The following procedure was used with slight modifications for all condensations.

The reaction was carried out in a three-necked flask fitted with a mechanical, glycerine stirrer, a reflux condenser and a dropping funnel. Thiophene free benzene, dried over sodium was used. The aluminum chloride was Baker's C. P. anhydrous resublimed. The aluminum chloride was added to the benzene, the mixture stirred for two or three hours, and the alcohol slowly added dropwise with stirring. After all the alcohol was added the mixture was stirred several hours more and then allowed to stand overnight. The mixture was hydrolized on ice and small amounts of hydrochloric acid. The benzene layer was separated and the water layer extracted several times with ether. The combined layers were washed with dilute sodium carbonate and then dried with anhydrous sodium sulfate. The ether and benzene were distilled off and the residue fractionated under reduced pressure. For the first five condensations a Vigereux column was used. The products of the remaining condensations were fractionated with the spinning band column.

Condensation I

Alcohol	½ mole	(61 g)
$AlCl_3$	1/3 "	(44 g)
Benzene	2½ "	(270 cc)

The hydrated form of the carbinol was used. Slightly larger amounts of $AlCl_3$ were used to take up the water. The alcohol was dissolved in half of the benzene and the solution added dropwise to the mixture. The reaction temperature was 0. Only small amounts of product were formed.

Condensation II

Alcohol	1 mole	(125 g)
$AlCl_3$	½ "	(70 g)
Benzene	5 "	(390 g)

The anhydrous alcohol was added to the mixture of benzene and aluminum chloride. The reaction temperature was 0. The following fractions were obtained. The weights listed are not to be taken as those of pure fractions since no precise separation could be made.

1	48-51	20 mm	-	25 g
2	60-71	20 mm	-	1 g
3	71-74	20 mm	-	4 g
4	75-104	20 mm	-	3 g
5	104-109	20 mm	-	25 g
6	115-130	20 mm	-	5 g
7	above 130	20 mm	-	4 g

Fraction 1 consisted mostly of the alcohol, as solid hydrate. Fraction 3 was identified as tert.-butyl benzene.*

Condensation III

Alcohol	1 mole	(115 g)
$AlCl_3$	½ "	(68 g)
Benzene	5 "	(390 g)

The anhydrous alcohol was used. The temperature was

40-45. The reaction mixture turned very dark. The following fractions were obtained. Again the separations are not very accurate.

1	43-55	20 mm	-	7 g
2	55-70	20 mm	-	2 g
3	70-78	20 mm	-	6 g
4	78-83	20 mm	-	1 g
5	83-93	20 mm	-	1 g
6	93-102	20 mm	-	2 g
7	102-108	20 mm	-	20 g
8	108-130	20 mm	-	7 g
9	108-155	11 mm	-	4 g
10	above 155	11 mm	-	6 g

Fraction 1 consisted mostly of the alcohol. Fractions 3 and 7 were identified as tert.-butyl and tert.-heptyl benzenes, respectively.*

Condensation IV

Alcohol	1 mole	(130 g)
$AlCl_3$	1 "	(133 g)
Benzene	5 "	(390 g)

The reaction temperature was 10-15. The mixture turned very dark. The fractions were:

1	43-50	20 mm	-	10 g
2	50-62	20 mm	-	3 g
3	64-70	20 mm	-	12 g
4	70-78	20 mm	-	4 g
5	78-83	20 mm	-	2 g
6	83-93	20 mm	-	1 g
7	93-102	20 mm	-	7 g
8	103-107	20 mm	-	8 g
9	107-111	20 mm	-	11 g
10	111-130	20 mm	-	6 g
11	108-140	11 mm	-	9 g
12	above 140	11 mm	-	4 g

Fractions 3 and 4 were identified as tert.-butyl benzene.

Fraction 8 was identified as tert.-heptyl benzene.

Table III

Condensation	recovered alcohol	t.-butyl benzene	intermediate Mol. Wt. 150	t.-heptyl benzene
I	30 %	1 %	1 %	1
II	20 %	4 %	2 %	14
III	5 %	5 %	4 %	12
IV	7 %	8 %	7 %	6

From the results above it can be seen that the hydrated form of the alcohol is not very active in condensations. Low temperatures give relatively higher amounts of the tert.-heptyl benzene while higher temperatures give more of the lower alkyl benzenes and also more of the very high boiling compounds. Larger quantities of aluminum chloride at about room temperatures appear to have little efect on the products.

Accordingly a larger amount of the alcohol was condensed at 10-15 using one mole of alcohol per half mole of aluminum chloride.

<u>Condensation</u> V

Alcohol	4 moles	(460 g)
$AlCl_3$	2 "	(264 g)
Benzene	20 "	(1500 cc)

The reaction temperature was 10-15. An 18 inch Vigereux column was used for the first fractionation. Large quantities of HCl were given off during the first part of the distillation. The fractions below were subject to careful refractionation using the special column built for this purpose.

1	80-110	760 mm	-	88 g	(HCl off)
2	110-130	760 mm	-	93 g	(HCl off)
3	50-64	20 mm	-	9 g	
4	64-69	20 mm	-	17 g	
5	69-83	20 mm	-	32 g	
6	83-93	20 mm	-	7 g	
7	93-102	20 mm	-	40 g	
8	103-106	20 mm	-	14 g	
9	106-111	20 mm	-	45 g	
10	111-130	20 mm	-	6 g	
11	121-180	8 mm	-	60 g	
12	above 180	8 mm	-	30 g	

Fractionation

Fractions 1, 2, and 3 consisted of a mixture of benzene, the solid hydrate and other compounds. This mixture could not be fractionated with the spinning band column because of the solids. Accordingly a vacuum jacketed 20 inch Vigereux column with a large bore sidearm (10 mm) was used. An ordinary Wurtz flask was used as a reciever. It was cooled with a stream of water. By this method of fractionation three compounds were isolated. One, boiling at 70-74 was identified as 2,3,3-trimethyl butene-1. Another was the benzene, boiling at 80-82. The third, boiling at 110-130 was the solid hydrate of the alcohol. The hydrated form of the alcohol, even when carefully purified, does not boil sharply, small crystals first appearing on the sides of the reciever at about 110. The majority of this third fraction boiled at 124-128. Small amounts of chloride were found mixed with it.

Fractions 4, 5, and 6 were fractionated under reduced pressure with the spinning band column. Small amounts of the lower boiling compounds, above, were found. The greatest portion boiled constantly at 52-52.5 (11 mm). This portion was identified as tert.-butyl benzene. The residue was mixed with fractions 7, 8, and 9.

The separation of the compounds mixed in 7, 8, and 9 was accomplished only by carefull adjustment of the different variables of the column. With the column set at total reflux, the temperature of the heater for the still pot was adjusted so as to allow very gentle reflux. The jacket temperature was adjusted to the temperature of the refluxing vapor(Anschutz readings). Too slow refluxing caused the vapor temperature to fluctuate and be markedly low. Too rapid refluxing again caused too low temperature readings and also caused slugs of liquid to pass up and down the column. The large volume of vapor rising into the reflux condenser gave rise to appreciable amounts of cold liquid which were returned to the column. This relatively cold liquid lowered the temperature readings and, in addition, condensed more of the vapor - which is at equilibrium temperature. This formed a mass of liquid in the upper portion of the column completely upsetting the equilibrium conditions.

After the lowest, constant, temperature readings, with refluxing, were obtained, the stopcock A was partially opened to allow the distillate to collect. The reflux ratio was set at about 10:1 or 15:1. If the temperature varied more than one-half degree, the stopcock was closed and the column was operated at reflux until the temperature came back to normal. The distillate was then collected as before.

When most of the lower boiling compound had been removed the temperature readings were not constant. For example, in the separation of tert.-butyl benzene from the next higher boiling compound, tert.-amyl benzene (B. P. 69 - 11 mm), when only small amounts of tert.-butyl benzene were left the temperature would drop. The heat input at the bottom of the column, which was just sufficient to drive the tert.-butyl benzene vapor to the head of the column, was not quite sufficient to drive the tert.-amyl benzene vapor to the head in sufficient quantities to give accurate temperature readings. This difficulty was remedied by increasing slightly the heat input at the bottom of the column.

As the amount of tert.-butyl benzene in the vapor became very small the temperature readings rose rapidly. The column was then operated at total reflux until the temperature readings dropped to the boiling point of tert.-butyl benzene (53 - 11 mm). The stopcock was then opened and distillate collected, at a high reflux ratio, until the readings again rose. By using this procedure repeatedly a rather precise separation could be made. Only a few drops were collected between the boiling ranges of tert.-butyl and tert.-amyl benzenes.

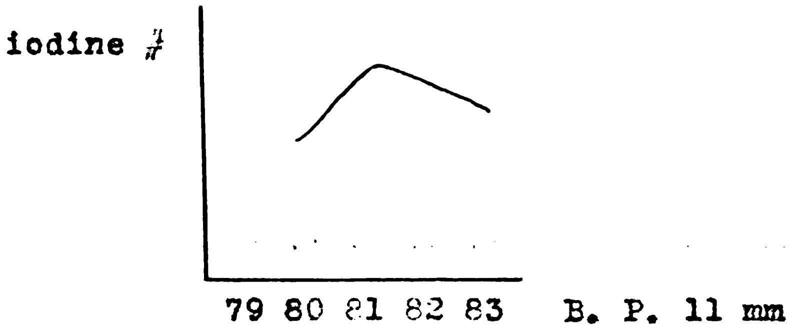
The tert.-amyl benzene was separated from the higher boiling compounds by this same procedure.

The separation of highly boiling compounds by fractionation under reduced pressure becomes more difficult as the boiling point increases. With the above compounds the boiling points of the pure compounds under reduced pressure were very simply determined. However, the distillation of fractions 7, 8 and 9 gave no sharp boiling temperatures, ranging from 75 to 95 (11 mm) depending upon the conditions of distillation. These variations in vapor temperatures were due to; first, the inherent difficulties found in fractionating high boiling compounds and; second, the fact that three or more rather closely boiling compounds were present in the vapor.

The boiling point of the first was known, 69 (11 mm) - the tert.-amyl benzene. The highest boiling compound was the tert.-heptyl benzene. Its boiling range was approximately known, 103 (12 mm).

The boiling point of the compound comprising the middle portion of this fraction was, of course, unknown. For a good separation it was, however, necessary to know its boiling point.

This intermediate compound showed positive tests for unsaturation. A series of fractions of this intermediate compound differing in boiling point by about one degree were cut. Micro-iodine numbers were run on each. The fraction having the highest iodine number was assumed to have the boiling point of the pure unsaturated compound. The results are shown in the graph below. They indicate that 81 (11 mm) is the boiling point of this compound.



Continued fractionation gave a fairly large portion boiling at 80-83 (11 mm). This unsaturated fraction probably still contained some amounts of tert.-amyl and tert.-heptyl benzene. However, it was sufficiently pure for identification.

Since relatively large amounts of tert.-heptyl benzene were formed its boiling point was readily determined. The separation of the tert.-heptyl benzene was attended with no special difficulties. Its boiling range was 103-106 (11mm).

The rather large amount of material boiling above the tert.-heptyl benzene was not redistilled. The distillation with the Vigereux column had indicated no sharp fractions, the temperature readings rising steadily as the distillation proceeded.

Identification of Fractions

The fractionation of the lower boiling portions of later condensations has shown the existence of three more byproducts in addition to those mentioned above. The proof of structure of these compounds will be discussed here.

Isopropyl Chloride. The identification of this compound is based on the following facts:

Boiling point	35-6
Very strong Beilstein test	
Melting point of the anilide	107-8

The only possible halogen present is chloride. The isopropyl chloride was mixed with the ether (used in the extraction) from which it is very difficult to separate. The difference in boiling point is two degrees. The spinning band column was used to obtain the chloride in sufficient concentration so that identification was possible. The anilide was made by the procedure given in Shriner and Fuson (48) except that no more ether was needed as a solvent.

2,3,3-Trimethyl Butene-1. This compound was identified by passing in dry HCl which converted it to the chloride of dimethyl tert.-butyl carbinol. This chloride has a characteristic odor and melting point.

Boiling point	77-8
Melting point of derivative	125-7
Melting point of known	126-7
Mixed melting point	124-7

Details for the preparation of the known are given on page

The phenomenon observed during the distillation of this portion of the condensation products would indicate that this unsaturated compound had arisen from the chloride. During the distillation of the benzene (used in excess in the condensation) no HCl is given off. When the boiling point reaches about 82, instead of rising further, it suddenly drops to about 67. During the collection of this portion of the distillate the temperature ranges between 67 and 70 and large quantities of HCl are evolved. This portion, when washed with dilute sodium carbonate solution, dried and distilled, boils at 77°. These facts are interpreted to mean that after the benzene is removed, the chloride - the next higher boiling compound - is decomposing and coming over as the alkene and HCl, the mixture of which boils lower than the alkene alone.

2.3.3-Trimethyl 2Chloro-butane. This compound was identified by means of its melting point, 125-6. Only small amounts are left from the distillation at atmospheric pressure, above. The solid chloride and the hydrate of the alcohol distill over together. The mixture can be separated by recrystallization from warm 70 % alcohol. The chloride sublimes very readily.

Tert.-Butyl Benzene. This compound was identified by its acetamino derivative.

Boiling point	165-6 (740 mm) 54 (11 mm)
Melting point of derivative	169-70
Melting point of known	169-70
Mixed melting point	169-70

The acetamino derivatives were also used for the identification of the other alkyl benzenes found as byproducts. The method used for their preparation was that given by Ipatieff and Schmerling (49) with slight modifications.

The nitro compound was prepared bycarefully treating 3-5 cc of the alkyl benzene with 5-10 cc of a 1:1 mixture of concentrated sulfuric and nitric acids. When the reaction mixture had cooled down it was poured onto cracked ice and extracted several times with ether. The extracts were washed

with water and the ether evaporated.

The nitro compound was dissolved in a few cc of alcohol and 5 grams mossy tin added. About 5 cc concentrated HCl was added dropwise, with shaking. The reaction mixture was allowed to stand 15-30 minutes. The liquid was decanted on to water and the tin hydrochloride complex salt of the amine extracted with ether. The ether was evaporated off and 40 % sodium hydroxide was added to free the amine. With larger amounts the amine was steam distilled at this point. Otherwise it was extracted with ether. It was sometimes necessary to centrifuge to break the emulsions of ether and sodium hrdroxide solution. The ether extracts were washed and dried with potassium carbonate.

After the ether was evaporated off the acetyl derivative was made by adding two cc of acetic anhydride to the amino compound. The excess anhydride was then hydrolized by warming with 30 cc water. The solution was then cooled and the impure solid filtered off and washed free of acetic acid. It was then recrystallized from 30-50 % alcohol.

Tert.-Amyl Benzene. This compound was identified by means of its acetamino derivative.

Boiling point	190 (740 mm)
	79-80 (11 mm)
Melting point of derivative	137-8
Melting point of known	138-9
Mixed melting point	137-9

Tert.-amyl benzene was synthesized by condensing tert.-amyl chloride with benzene in the presence of aluminum chloride.

About 80 % yields were obtained. The acetamino derivatives were prepared by the method described above.

Trimethyl Styrene. The identification was made by means of the acetamino derivative of the hydrogenated compound.

Boiling point	88-90 (11 mm)
Melting point of derivative	139-40
Melting point of known	140-41
Mixed melting point	139-41

The oxidation of the unsaturated alkyl benzene gives acetophenone, identified by its semicarbazone.

Boiling point (oxidized product)	200-215
Melting point of semicarbazone	192-4
Melting point of known	193-4
Mixed melting point	192-4

The semicarbazone was made by the procedure given in Shriner and Fuson (50). It was purified only with repeated recrystallization. The fact that oxidation gave acetophenone very strongly indicated that the unsaturation was on the carbon of the alkyl benzene.

Trimethyl styrene was made by Grignard synthesis. Phenyl magnesium bromide was treated with methyl,isopropyl ketone to give, on hydrolysis, methyl,isopropyl,phenyl carbinol. This alcohol was distilled from anhydrous oxalic acid to form the alkene, B. P. 75-8 (12 mm).

Another unsaturated alkyl benzene which might form in the condensation, and which gives acetophenone on oxidation is αtert.-butyl styrene (51). This compound was synthesized in a manner similiar to that above except that pinacolone was used as the ketone, B. P. 88-92 (15 mm)

The two above known compounds along with the unknown fraction were hydrogenated using the procedure given by Kaye (13). The resulting alkyl benzenes (secondary isoamyl benzene, pinacolyl benzene and the unknown) were converted to the acetamino derivatives. The derivative of pinacolyl benzene came down as an oil, the other two as crystalline plates.

Procedure:

Onehalf mole bromobenzene was added dropwise to 12 g magnesium turnings in 200 cc anhydrous ether in a three-necked flask. The reaction mixture was stirred and the halide added at such a rate as to reflux the mixture gently. The was added slowly to the Grignard reagent with stirring. The mixture was hydrolized, extracted and dried in the usual manner. The ether was distilled off and the carbinol placed in a small Vigereux column. About 10 g anhydrous oxalic acid was added and the mixture distilled under reduced pressure. The alkene was then redistilled. The yields were 20-30 %.

The alkenes were dissolved in 60 cc absolute ethyl alcohol and pieces of sodium added at intervals. About 12 grams was used for each. The mixture was kept at gentle reflux for five hours. The alcohol solutions were then poured on a large volume of water and extracted several times with ether. The ether extracts were washed free of alcohol with concentrated $CaCl_2$ solution. The ether was then evaporated off and the resulting product shaken with cold

saturated $KMnO_4$ solution to remove the unreduced alkenes. The excess $KMnO_4$ was destroyed with sodium bisulfite and the mixture again ether extracted. After the ether has been extracted the resulting alkyl benzenes were used without further purification for the preparation of the acetamino derivatives.

The acetamino derivative of the unknown was purified only with great difficulty.

The range in atmospheric boiling point (190-9) and the necessity for repeated recrystallization show the lack of purity of this fraction. The atmospheric boiling points recorded in Beilstein's handbook are only slightly above those given for tert.-amyl benzene. Any fraction containing the former compound must also contain some of the latter. The tert.-amyl benzene fraction fraction, however, did not show a positive test for unsaturation.

The fact that the unsaturated fraction boils much higher than the tert.-amyl benzene fraction (at reduced pressure) certainly indicates that it must contain compounds boiling higher than trimethyl styrene. This again indicates the presence of another unsaturated compound e.g. α tert.-butyl styrene. This compound which has raised the boiling point of the trimethyl styrene fraction must also be unsaturated, it cannot be the tert.-heptyl benzene alone, since the boiling point was determined by determining the maximum unsaturation.

2.3.3.-Trimethyl.2Phenyl Butane. This is the expected condensation product of the alcohol and benzene. It was identified by means of its nitro compound which has been previously prepared by Hedrick (45). Of the pure para-nitro alkyl benzenes which have been prepared in this laboratory, which includes all of the tert.-aliphatic benzenes up to the octyl group, this is the only one that is solid at room temperature.

Boiling point	103-5 (12 mm) 220-5
Melting point of derivative	108

This compound has only been synthesided by Friedel-Crafts or related reactions. However, dimethyl tert.-butyl carbinol, its chloride and its unsaturated derivative all gave this same product. This alkyl benzene converted to the p-hydroxy compound is identical with the compound obtained by the condensation of the above carbinol with phenol. These facts leave little doubt as to its identity.

Thr reaction characteristics of a typical condensation are described below. The temperature of the condensation has a marked effect.

Aluminum chloride in benzene has a pale yellow color, if refluxed or allowed to stand several days it becomes darker yellow. The addition of the alcohol immediately gives a orange compound. During the addition of the first half of the alcohol (ratio of alcohol to aluminum chloride is 2;1) HCl is given off and more of this colored compound is formed. This compound at -10 is solid and becomes dark red. At 25-30 it is liquid and is also dark red, three layers are therefore present; benzene, unreacted aluminum chloride, and

the above compound.

During the addition of the second half of the alcohol at -10 there is no more HCl evolved, and more of the tarry red solid forms, making stirring difficult. Petroleum ether is added to keep the benzene from freezing. At 30-40 HCl is evolved throughout the addition of the alcohol. At the end of the condensation (at 35) two layers are present, the lower layer having formed at the expense of the $AlCl_3$ layer.

Discussion.

The reaction characteristics agree well with the mechanism proposed by Tsukervanik. The large quantities of HCl evolved during the addition of the first half of the alcohol would be due to the formation of the alcoholate which is stable at -10. During the addition of the last half of the alcohol, the alcoholate, for some reason, is broken down and the resulting alkene takes up the HCl as fast as it is formed by the addition of more alcohol. Therefore, at low temperatures, no HCl is evolved during the latter portion of the reaction. At higher temperatures, the alcoholate is decomposed as soon as it is formed, the series of reactions proceeding to the formation of the alkyl benzene and, consequently HCl is liberated throughout the addition of the alcohol.

The Tsukervanik mechanism, of course, does not explain the mechanism of the actual formation of the alkyl benzene from the halide.

EXPERIMENTAL - PART II

Some further condensations were run to investigate the possibilities of the Tsukervanik mechanism and to attempt to explain the origin of the byproducts formed.

The alcohol was condensed at -10 and at 40. The alkene formed by the dehydration of the alcohol was condensed with and without the presence of large quantities of HCl. The chloride of the alcohol was also condensed. Some aluminum chloride complexes of tert.-butyl alcohol were also investigated. The results of these condensations are listed below.

<u>Condensation</u> VI

Alcohol	$\frac{1}{2}$ mole	(58 g)
$AlCl_3$	$\frac{1}{4}$ "	(33 g)
Benzene	1 "	(80 g)
Temperature	-10	
Pet. ether	65 g	

The reaction flask and contents were weighed before and after the condensation. The loss in weight was 11 g. About .15 moles HCl (5.5 g) were evolved during the reaction. Another gas was given off which decolorized 5 % bromine in carbon tetrachlroide.

A dark red, tarry mass formed in the flask. The liquid and solid portions of the condensation products were hydrolized and distilled separately.

The liquid portion gave:

1	35-40	740 mm	-	5 g
2	60-80	740 mm	-	60 g
3	125-30	740 mm	-	.5 g
4	above 130	740 mm	-	7 g
		740 mm		

The solid portion gave:

5	35-43	740 mm	-	5 g
6	67-70	740 mm	-	2.5 g
7	125-30	740 mm	-	19 g

The higher boiling portions were combined and fractionation gave:

8	51	11 mm	-	2 g
9	69	11 mm	-	1 g
10	88-93	11 mm	-	4 g
11	98-103	11 mm	-	10 g
12	above 103	11 mm	-	7 g

<u>Condensation</u> VII

Alcohol	½ mole	(59 g)
$AlCl_3$	¼ "	(35 g)
Benzene	1 "	(79 g)
Temperature	40	

The reaction flask and contents were weighed before and after condensation. The loss in weight was 12 g. Again a gas that decolorized bromine was evolved. At the end of the reaction two layers were apparent. Hydrolysis and fractionation gave:

1	35-40	740 mm	-	10 g
2	67-70	740 mm	-	16 g
3	125-30	740 mm	-	8 g
4	53	11 mm	-	2 g
5	69	11 mm	-	1 g
6	88-91	11 mm	-	1.5 g
7	98-103	11 mm	-	8 g
8	above 103	11 mm	-	10 g

Condensation VIII

Alkene	½ mole	(39 g)
$AlCl_3$	¼ "	(34 g)
Benzene	1 "	(80 g)
Temperature	25-30	

2,3,3-trimethyl butene-1 was prepared by the method used by Edgar (42). Fifty-five g of the alcohol and 1 g iodine were placed in a Vigereux column and the mixture distilled slowly, the temperature of the vapor being maintained at 68-70. The distillate was washed with $Na_2S_2O_3$ solution, water, and dried over $CaCl_2$. The product was distilled, the major portion coming over 77-79. Yield - 39 g (80 %). The fractions obtained from the condensation.

1	35-40	740 mm	-	5 g
2	53	11 mm	-	2 g
3	70	11 mm	-	.5 g
4	80	11 mm	-	2 g
5	94-97	11 mm	-	1 g
6	100-103	11 mm	-	2.5 g
7	above 103		-	5 g

Condensation IX

Alkene	1/3 mole	(34 g)
$AlCl_3$	1/6 "	(24 g)
Benzene	2/3 "	(52 g)
HCl	½ "	
Temperature	25-30	

The alkene was prepared as above. The dry hydrogen chloride was made from sulfuric acid and hydrochloric acid and was passed in slowly throughout the addition of the alkene.

1	35-40	740 mm	-	5 g
2	53	11 mm	-	.5 g
3	69	11 mm	-	3 g
4	87-90	11 mm	-	1 g
5	100-103	11 mm	-	2.5 g
6	above 103	11 mm	-	8 g

Condensation X

Chloride	¼ mole	(30 g)
$AlCl_3$	1/6 "	(23 g)
Benzene	1 "	(80 g)
Temperature	25-30	

2,3,3-trimethyl,2-chloro butane was prepared from the alcohol by treating with thionyl chloride and distilling. It was also prepared by passing dry HCl into the alkene. The chloride prepared by each method was a solid. It was dissolved in half the benzene for this condensation. The fractions were:

1	35-40	740 mm	-	5 g
2	53	11 mm	-	.5 g
3	90-92	11 mm	-	4.5 g
4	100-103	11 mm	-	7 g
5	above 103	11 mm	-	5 g

Condensation XI

Tert.-heptyl benzene	¼ mole	(42 g)
$AlCl_3$	1/8 "	(15 g)
Benzene	1 "	(80 g)
Temperature	25	

The tert.-heptyl benzene obtained from previous condensations was added in the usual manner to the benzene and aluminum chloride. The mixture turned dark. The fractions were:

1	35-40	740 mm	-	5 g
2	48-50	11 mm	-	1 g
3	87-90	11 mm	-	3 g
4	100-103	11 mm	-	34 g
5	above 103	11 mm		3 g

Condensation XII

Complex of tert.-butyl alcohol and $AlCl_3$	30 g
Benzene	80 g
Temperature	25-30

Both the addition and the substitution complexes as reported by Perrier and Pouget (21) were prepared. Each was mixed with benzene and stirred several hours. A dark red tarry mass formed, in each case, which on hydrolysis gave high boiling aliphatic compounds. The substitution complex was also added to benzene while passing in HCl. However, in no case was there any tert.-butyl benzene found as a product.

The addition complex was prepared by adding 24 g $AlCl_3$ slowly to 30 g tert.-butyl alcohol in 100 cc CS_2. Little HCl was evolved. A red tarry mass separated and the carbon disulfide was decanted off and the complex dried in a vacuum desiccator. It was then ground to a red powder.

The substitution complex was prepared in the same manner except that 36 g $AlCl_3$ were used for 20 g alcohol and the mixture refluxed. Large quantities of HCl were given off.

The results of these condensations are summarized in table IV. It must be kept in mind that the results are quantitative in only a rough sense. The per cent yields are calculated on the assumption that one mole alcohol theoretically forms one mole of the product. No figures are given for isopropyl chloride and 2,3,3-trimethyl butene-1 since these compounds boil so near to ether and benzene, respectively.

Where the alkene is listed as being formed it may be taken that 2,3,3-trimethyl 2-chloro butane was also formed.

The per cent yields of tert.-butyl benzene and tert.-heptyl benzene are lower than the values reported in the preliminary condensations due to the fact that more of these substances are lost during the fractionation.

Table IV

Fraction	35-40	67-70	53 (11mm)	69 (11mm)	87-90 (11mm)	100-3 (11mm)	above 103 (11mm)
Identified as	isopropyl chloride	2,2,3,tri methyl butene-1	tert.- butyl benzene	tert.- amyl benzene	trimethyl styrene	tert.- heptyl benzene	uniden- tified
			Per cent Yields				
Condensation							
VI alcohol **(-10)**	found	found	3	1.5	5.5	11.5	7
VII alcohol **(40)**	found	found	3	1.5	1	9	10
VIII alkene	found	none	3	.5	.5	3	5
IX alkene **(HCl)**	found	none	4.5	6	5	4.5	12.5
X chloride	found	none	3	none	12	16	10
XI t.-heptyl benzene	found	none	6	none	8	78	
XII complex with t.-butyl alcohol	-----	----	none	----	----	----	----

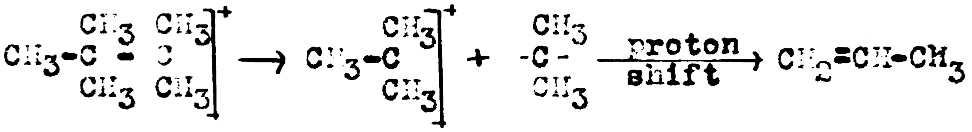
DISCUSSION

The condensation of dimethyl tert.-butyl carbinol at at higher temperatures leads to larger quantities of split products than at lower temperatures, as is to be expected.

The condensation of the dehydration product of this alcohol is greatly aided by the presence of large quantities of HCl. However, condensation of the alkene does not give the chloride of the alcohol as a product isolated at the end of the reaction, as is the case with the condensation of the alcohol itself. This would indicate that the mechanism suggested by Tsukervanik is not correct. His mechanism is based on the formation of the chloride (and alkene) as byproducts in the condensation of the alcohol and would, of course, predict the isolation of the chloride in the condensation of the alkene. The fact that aluminum chloride complexes with tert.-butyl alcohol give no tert.-butyl benzene when mixed with benzene is another criticism of this mechanism.

The formation of the split products by mixing tert.-heptyl benzene with aluminum chloride indicates the reversibility of the alkylation reaction. This reversibility of alkylation, especially with tertiary alkyl groups has been demonstrated by other workers (52). This is strong evidence in favor of an ionic mechanism. This reversibility would not be expected if an unsaturation mechanism is to be taken as correct.

On the basis of the Price theory it would appear that the carbonium ion is formed either from the alcohol, the chloride, the alkene, or the tert.-heptyl benzene. This cation partially fragmentates as a result of the weakening of the C-C bonds.



$$\left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}\right]^+ \longrightarrow \left[CH_3-\overset{CH_3}{\underset{CH_3}{C}}\right]^+ + -\overset{CH_3}{\underset{CH_3}{C}}- \xrightarrow[\text{shift}]{\text{proton}} CH_2=CH-CH_3$$

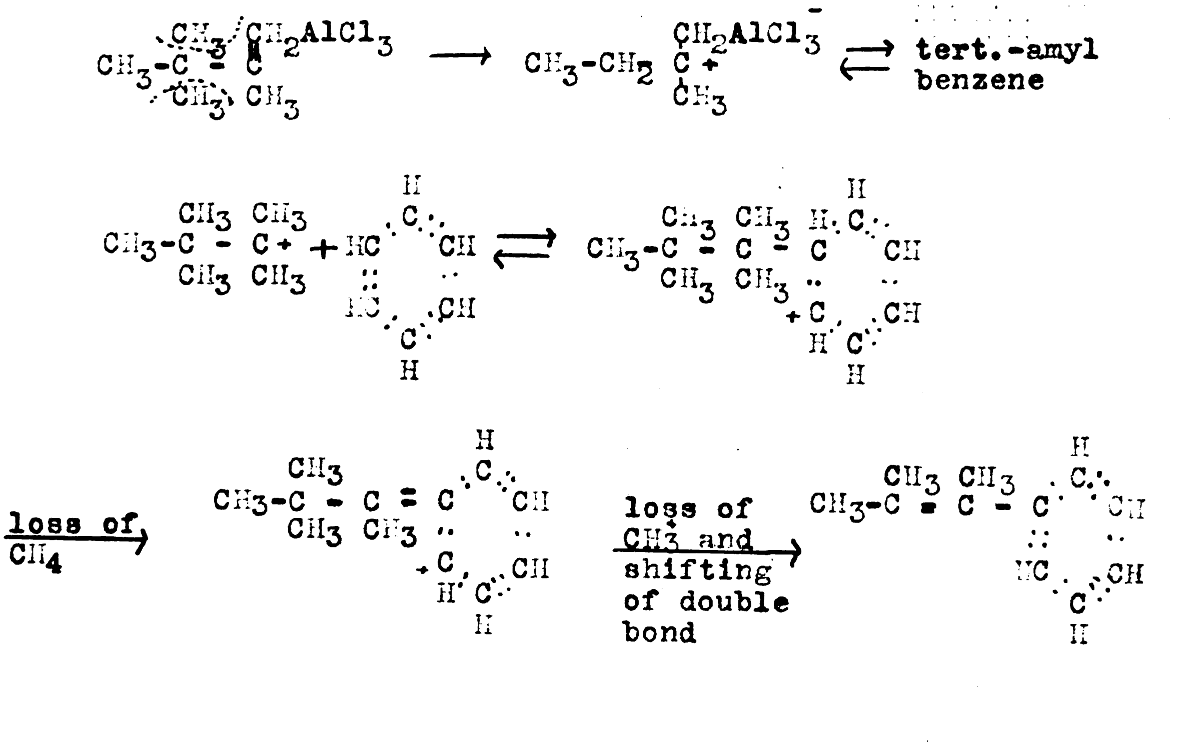
The tert.-butyl cation then attacks benzene to form tert.-butyl benzene. The propene adds on HCl to form isopropyl chloride. The reason why the isopropyl chloride does not form cumene in the presence of benzene is not clear. Generally, however, secondary groups require more aluminum chloride than tertiary for the alkylation of benzene.

The results of table IV would also indicate that the tert.-amyl group is formed from the tert.-heptyl cation of the alkene, which is somewhat different from that formed directly from the alcohol, the chloride or the alkyl benzene. Since the alcohol gives small quantities of the tert.-amyl group it might be assumed that the alcohol has partially dehydrated to give the intermediate alkene which subsequently forms the ionic substance with aluminum chloride.

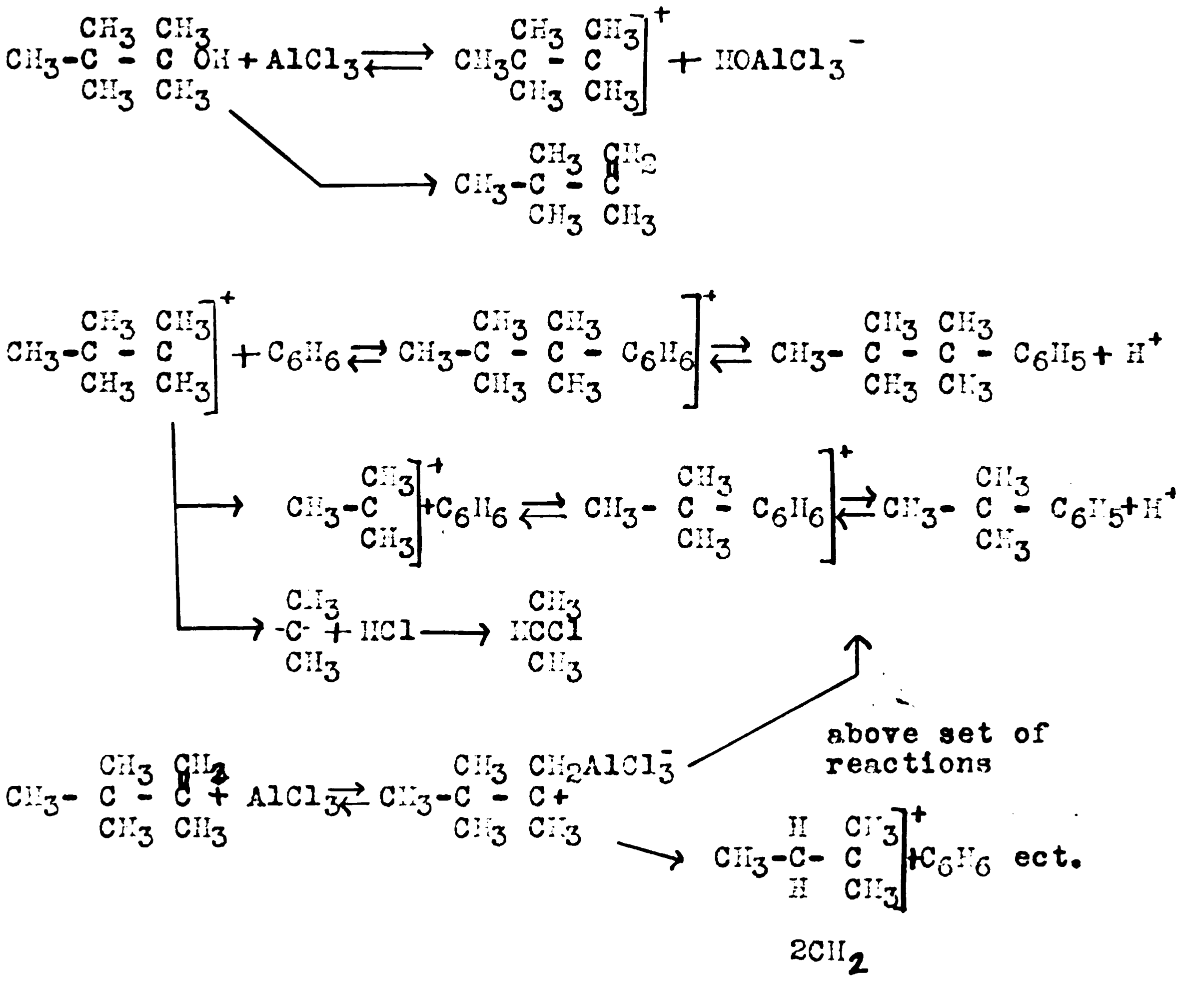
It would appear that the trimethyl styrene (found in all condensations) is formed non-ionically from the tert.-heptyl benzene. The loss of an alkyl group from the carbon

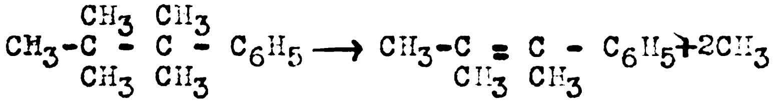
atom of highly branched alkyl benzenes has been observed by other workers (6). There is no reason to suppose that α-tert.-butyl styrene could not and did not form. Its formation would be accounted for by the loss of only one methyl group from the alkyl benzene.

The formation of trimethyl styrene and tert.-amyl benzene can only be accounted for by the rupture of the $-\beta-\gamma$ C-C bond of the alkyl group. Schmidt (53) has shown that the enzymatic decomposition of carbohydrates and the cracking of hydrocarbons is probably preceeded by the formation of a double bond which so weakens the $\beta-\gamma$ bond as to cause the splitting at that point. If his double bond rule can be applied here, the formation of these compounds could be readily explained.



On the basis of the Price theory, an overall mechanism for the reaction of the alcohol is suggested





$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{CH_3}{C}}-C_6H_5 \longrightarrow CH_3-\underset{CH_3}{C}=\underset{CH_3}{C}-C_6H_5+2CH_3$$

The chloride of the alcohol then arises from the action of Cl on the tert.-heptyl cation. The unsaturated gasses evolved during the reaction may come from the methylene groups liberated, the propene, or isobutene.

An explanation of the facts on the basis of the theories of Thomas or Dougherty would be similiar to that suggested above since in both the alkyl group is converted into a positive ion.

The system of equations above was evolved to explain the facts observed. Its only value lies in its ability to accomplish this end.

SUMMARY

1. A spinning band fractionating column designed for vacuum distillation has been constructed
2. The plate value of this column has been determined to be 25, and the holdup per plate to be .1 cc.
3. Dimethyl tert.-butyl carbinol has been prepared and condensed with benzene.
4. The products which have been isolated and identified from this condensation are: isopropyl chloride; 2,2,3-trimethyl butene-1; 2,2,3-trimethyl 2-chloro butane; tert.-butyl benzene; tert.-amyl benzene; trimethyl styrene; and 2,2,3-trimethyl 2-phenyl butane.
5. All of these products and their derivatives have been synthesized.
6. The dehydration product and the chloride of the above alcohol have been condensed and some of the products identified.
7. Dimethyl tert.-butyl phenyl methane has been mixed with benzene and aluminum chloride to give some of the products also isolated in the condensation of the alcohol.

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