

THE CONDENSATION OF THE TERTIARY HEPTYL ALCOHOLS WITH  
PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE  
AS A CATALYST

A Dissertation

submitted to the faculty of Michigan State College of  
Agriculture and Applied Science in partial fulfillment  
of the requirements for the degree of Doctor of Philosophy.

by

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June, 1937

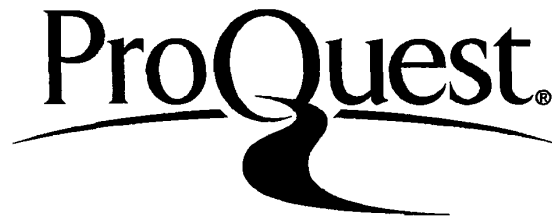
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## INTRODUCTION

In the year 1916 Huston and Friedemann (1) discovered that aromatic alcohols condense with aromatic hydrocarbons in the presence of aluminum chloride as a catalyst. Since that time much work of this type has been done in this laboratory.

In 1936 Huston and Hsieh (2) reported the condensation of some simple tertiary aliphatic alcohols with phenol. To investigate further the scope of the reaction, the tertiary heptyl alcohols were prepared and condensed with phenol using aluminum chloride as a catalyst.

## HISTORICAL

Many papers have been written concerning the alkylation of phenols. There are two general methods for preparing alkyl phenols. They are, the alkylation of phenols using alkyl halides, acyl chlorides, alcohols, and alkenes in the presence of a variety of catalysts, and the preparation of phenols by the replacement of a variety of groups by a hydroxyl in alkyl benzene derivatives. Alkyl phenols are also prepared by the rearrangement of alkyl phenyl ethers.

Only those papers dealing with the condensation of alcohols with aromatic hydrocarbons using aluminum chloride as a catalyst are mentioned in this review.

As far back as 1884 Auer (3) and Dermstedt (4), reported the interaction of simple aliphatic alcohols and phenols to give alkyl phenols using as a catalyst a mixture of zinc and zinc chloride. A little later Nef (5) mentioned the formation of diphenylmethane from benzyl alcohol and benzene in the presence of aluminum chloride.

In 1916 Huston and Friedemann (1) repeated the work of Nef's and reported that aromatic alcohols such as benzyl alcohol reacted with benzene in the presence of aluminum chloride to give a 30 per cent yield of diphenylmethane.

A few years later (1924), Huston (6) condensed benzyl alcohol with phenol in a similar manner as with benzene and obtained p-benzylphenol in a 45 per cent yield.

This led to a further investigation concerning the scope of the reaction. Different types of alcohols were used, as well as different aromatic hydrocarbons. Huston (6) reported the condensation of benzyl alcohol with anisole and phenetole in a 45 and 50 per cent yield respectively.

In 1926 Huston and Sager (7) attempted to condense phenylethyl- and phenylpropyl alcohols with benzene. The results were negative. They concluded that of the aromatic alcohols, only those in which the hydroxyl group was on the carbon atom adjacent to a ring condense. They tried methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl and isoamyl alcohols, none of which condensed. They then tried allyl alcohol which condensed to give a 16 per cent yield. From this they concluded that only those alcohols in which the alpha carbon atom was a member of a benzene ring or is double-bonded, condense with benzene. Huston and Newmann (8) followed this work by the condensation of allyl alcohol and phenol.

Later Huston and co-workers (9) reported the interaction of benzhydrol, methylphenyl and ethylphenyl carbinols with phenol to give good yields of the condensation products. They pointed out that the experiments gave

additional evidence of the effect of unsaturation of the alpha carbon atom on the reactivity of the alcoholic hydroxyl group for benzhydrol, in which both alpha carbons are members of an unsaturated benzene ring, gave a much larger yield than did benzyl alcohol.

The condensation of an aromatic tertiary alcohol as triphenyl carbinol and phenol in the presence of aluminum chloride has not yet been reported. Although Davis (10) found that triphenyl carbinol reacted with benzene to give triphenylmethane and not tetraphenylmethane.

Later Huston (11) reported the condensation of benzyl alcohol with o-cresol, p-cresol, and m-cresol to give two monosubstituted derivatives and one disubstituted derivative for each.

Huston and Goodemoot (12) in 1933 carried out some experiments to show the effect of strain in cycloalkyl carbinols on their reactivity with benzene in which they condensed cyclohexyl, cyclopentyl, and cyclobutyl carbinol with benzene. They were able to show that the carbinols show a progressive increase in activity as the number of carbon atoms of the ring is reduced from six to four.

Huston and Wilsey (13) found that 1, 1 - diphenylethyl carbinol did not condense with benzene, but instead dehydration occurred producing 1, 1 - diphenyl - 1 - propene. Huston and Hradel (14) and Huston and MacComber (15) in



some similar work concluded that neither diaryl-alkyl carbinols nor dialkyl-aryl carbinols condense to give the desired product. Only dehydration of the alcohol occurred.

All these experiments indicated that unsaturation or strain on the alpha carbon atom, whether it be double-bonded or a member of a benzene ring favors condensation reactions of aliphatic and aromatic alcohols with aromatic hydrocarbons and phenols or their ethers in the presence of aluminum chloride.

Very recently Huston and co-workers have directed their efforts toward the condensation of some saturated aliphatic alcohols. In 1933 Huston and Hsieh (2) were interested in preparing some p-isopropylphenol. In their work they added isopropyl alcohol to a stirred mixture of aluminum chloride in an excess of benzene and it gave a fair yield of cumene. This was followed by more condensations reported by Huston and Fox (16) using some of the simpler tertiary alcohols and benzene. Huston and Hsieh (2) were successful in condensing some tertiary alcohols with phenol, toluene, m-xylene, m-cresylmethyl ether and anisole. They also condensed isopropyl and sec-butyl alcohols, methyl n-propyl carbinol, and methyl isopropyl carbinol with benzene. Huston and Binder (17) condensed the tertiary heptyl alcohols with benzene, Huston and

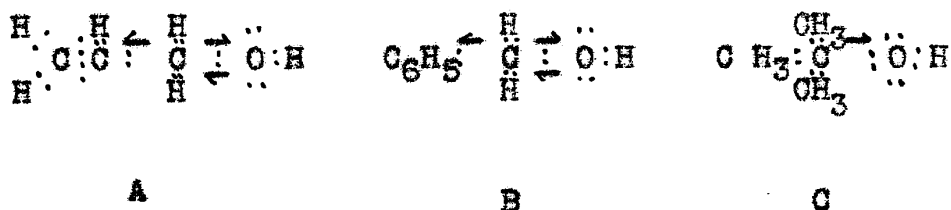
Soulati (18), and Huston and Anderson (19) condensed some tertiary octyl alcohols with benzene and phenol.

Tzuber<sup>K</sup>vanik (20) recently reported the condensation of some simple secondary and tertiary alcohols with benzene and toluene obtaining the same results as Huston and Hsieh (2) but offered a different mechanism which is to be discussed later.

The only account of the condensation of heptyl alcohol with phenol is covered by a patent taken out by McKesson and Robbins (21), and McGreal and Niederl (22) who condensed n-butyl dimethyl carbinol with phenol in the presence of zinc chloride to give p-tertiary heptyl phenol.

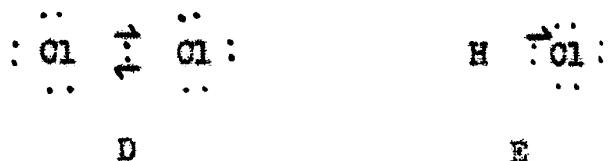
## THEORETICAL

From previous works Huston and co-workers have shown that for the condensations of alcohols, whether aromatic or aliphatic with aromatic hydrocarbons in the presence of aluminum chloride the alpha carbon atom must be understrain. If we examine the electronic structure of such a system, as for example allyl alcohol (A) or benzyl alcohol (B) and compare it with the electronic structure of a tertiary alcohol, as tertiary butyl alcohol (C) we will see why either are capable of condensation. In all three cases we have a carbon - oxygen bond that is relatively



unstable. This is borne out experimentally by the ease of replacement of the hydroxyl group by the halogen of a halogen acid and also by the ease of dehydration. By virtue of the groups present the electron pair forming the carbon to oxygen bond of the first two is attracted strongly by the carbon atom and also by the hydroxyl group, and in the third the carbon has a weak attraction but the

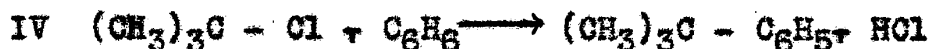
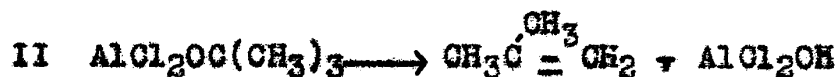
hydroxyl has a strong attraction. The result in either case leads to an unstable system which for comparison are like the bonds in a molecule of chlorine (D) and a molecule of hydrogen chloride (E) respectively. With this in



view it is obvious that tertiary alcohols should condense with aromatic hydrocarbons the same as benzyl, allyl, benzhydrol, and the other alcohols that have been shown to react.

There have been four possible mechanisms advanced to explain the course of the reaction, none of which have been conclusively established. In many cases the different workers have used different catalysts, temperatures, and solvents thus leading to incongruous results.

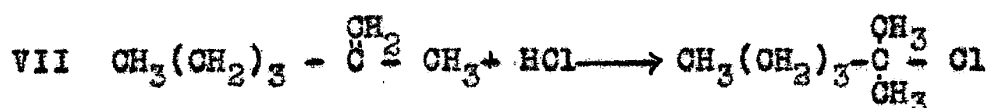
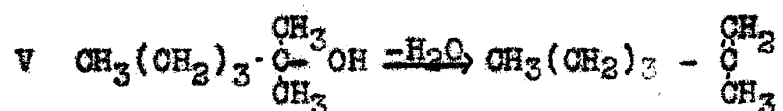
Tzukurvanik (20) reported the alkylation of benzene and toluene by use of secondary and tertiary alcohols in the presence of anhydrous aluminum chloride as a catalyst. He offered as a mechanism the formation of hydrogen chloride and an aluminum alcoholate (I) which decomposed to form an alkene (II). The alkene then took up the hydrogen chloride to form the alkyl halide (III). This in turn reacted with the hydrocarbon to give the alkylated hydrocarbon IV. This is represented by equations using tertiary butyl alcohol, benzene, and aluminum chloride.



If Tzumervanik's conception is correct the addition of a tertiary alcohol to a mixture of aluminum chloride suspended in an inert solvent should go through the first three steps to the formation of the alkyl chloride. Then the addition of phenol should lead to an alkyl phenol. To investigate the speciousity of the mechanism this was done. Normal butyl dimethyl carbinol in petroleum ether was added dropwise to aluminum chloride suspended in petroleum ether. Almost instantly hydrogen chloride was evolved and heat liberated. The mixture turned at first yellow then a deep red color. After the reaction had subsided, a solution of phenol in petroleum ether was added dropwise. There was no further change in color nor any evidence of a reaction. After the usual procedure of decomposition and purification to be described later an 18% yield of n-butyl dimethyl-p-hydroxyphenylmethane was obtained. This is a much smaller yield than was obtained with this alcohol in an ordinary run using the same molecular proportions.

It should be noted that in the reaction of the

alcohol and aluminum chloride, hydrogen chloride was given off. This cannot be interpreted as following the mechanism offered by TzuKervanik because in that hydrogen chloride was not given off until the hydrocarbon was added. A plausible explanation for the formation of hydrogen chloride in this reaction is in the dehydration of the alcohol, and the water then reacting with the aluminum chloride according to the equations (V) and VI). At the same time some of the hydrogen chloride might react with the alkene (VII). In view of this it must have been the

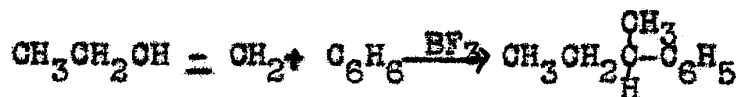
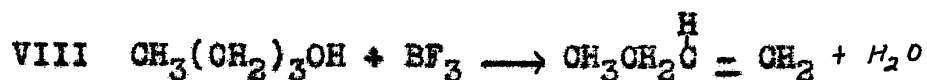


alkyl halide that reacted with the phenol to give the alkyl phenol.

In addition it seems unlikely that the formation of an aluminate I is possible in view of the fact that it is not easy to replace the hydroxyl hydrogen of a tertiary alcohol. All this seems to indicate that the hypothesis set up by TzuKervanik is not probable.

Another mechanism is offered by McKenna and Sowa (23). They have shown that when benzene is alkylated with alcohols using boron fluoride as a catalyst, the alcohol is

first dehydrated and then the alkene condenses with benzene according to the following scheme (VIII).



They state as evidence that normal and secondary alcohols give identical products and iso- and tertiary alcohols also give identical products.

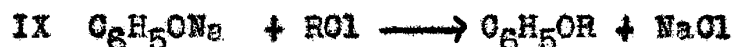
Likewise Niederl (23) has shown that dehydration of the alcohol is the first step in the reaction for when phenylethyl alcohol and phenol are treated with zinc chloride 4 - hydroxy 1, 1 - diphenyl ethane is the chief product.

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 (24) have shown that ethylene condenses with benzene using this catalyst. Other workers similar to this are numerous (25).

Evidence against such a mechanism is slight. It must be noted that McKenna and Sowa, and Niederl used a catalyst other than aluminum chloride and a much higher temperature than is employed in the Huston method. Huston and Sager (7) have shown that primary alcohols will not

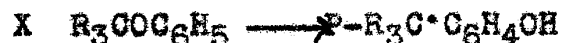
react with benzene in the presence of aluminum chloride.

The idea of ether formation followed by rearrangement to the substituted phenol presents itself as a possible mechanism. Much has been reported on the rearrangement of mixed aromatic ethers. The ether was formed in most cases by the alkali salt of the phenol and an alkyl halide (1X).



Most of the workers have used agents other than aluminum chloride.

R. A. Smith (24) reports the rearrangement of *m*-cresyl-isopropyl-ether, tertiary butyl-, isobutyl-, secondary butyl-, and isopropyl-phenyl ethers, and *p*-cresyliso butyl ethers when treated in the cold with aluminum chloride (X). He made the ethers by the above method (IX) and



effected rearrangement by the addition of an equal molecular amount of aluminum chloride. He stated that the ethers could not be distilled even in vacuo without rearrangement. Other works similar to this are numerous (26).

In view of this it seems probable that if the alkyl ethers were formed as an intermediate they might rearrange to the alkyl phenols. The only accounts recorded in the literature of the formation of an ether by a catalyst

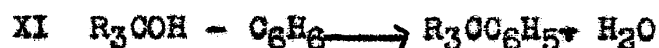


similar to aluminum chloride are those of Merz and Weith (27), and Newland (28). The former in 1881 found that aluminum chloride reacted with phenol to give a 10 to 12 per cent yield of diphenyl ether at a reflux temperature. The former treated phenol in the presence of boron fluoride with methyl, ethyl and isopropyl alcohols. The ethers and substituted ethers were obtained. Isopropyl alcohol and phenol gave 2, 4-isopropylphenylisopropyl ether and 4-isopropylphenol. They found that dehydration was the first step in the progress of the reaction.

Claisen (29) pointed out that in alkylating the alkali salt of phenol with a halide of an unsaturated alkyl the ether is not a necessary intermediate for phenyl alkyl ethers under the conditions of formation do not rearrange to the alkyl phenols. He noticed that alkyl phenols were always present with the ethers. He states further that carbon-alkylation is still further increased if alkylphenols are used, that the solvent medium is most important, and that phenols with a vacant ortho position alkylate in that position. Thus allyl bromide and sodium phenolate in an alcohol medium give a 90 per cent yield of the allyl ether but in a medium of benzene there is only a 30 per cent yield of the ether and a 70 per cent yield of o-allylphenol.

This work of Claisen's is in agreement with that of

Huston's for he has reported the condensation of tertiary alcohols with benzene (XI), anisole (XII), and m-cresyl-methyl ether (2) and the condensation of benzyl alcohol with anisole and phenetole (4).



In these, there is no possibility of ether formation however the reaction takes place giving a good yield of the alkylated hydrocarbon.

To investigate the possibility of ether formation that might take place according to the reaction represented by equation XIII) the following was done. After the



reaction of a condensation was completed the mixture was decomposed with water, acid and ice, and extracted with ether. The ether layer was then washed three times with an excess of an alcoholic potassium hydroxide solution to remove the phenols. Care was taken to keep the mixture cold. The ether layer was then dried and the ether evaporated off. No phenyl alkyl ethers were present. This would indicate that an ether was not formed even as an intermediate.

Huston has given as a possible mechanism the cleavage of water, the hydroxyl group of the alcohol and the para hydrogen of the aromatic ring being split off as is represented in equation (XIV). Aluminum chloride then appears to be merely a dehydrating agent. This scheme is

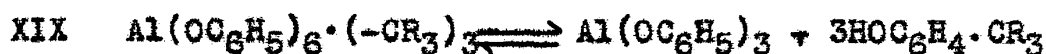
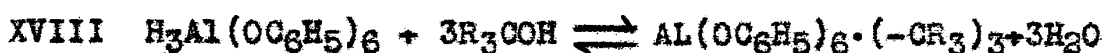
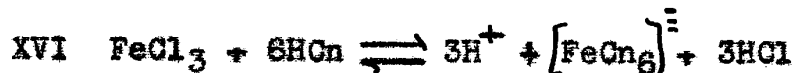
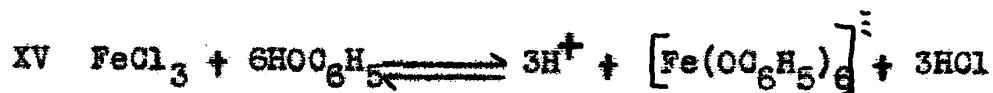


unlikely for it cannot explain the fact that a highly colored complex always accompanies the reaction.

The proof of the mechanism for this reaction is beyond the scope of this thesis, but another mechanism that seems reasonable suggests itself. There is little, but some evidence for it. It is known that ferric chloride forms colored compounds with phenol. Such a reaction may be represented by equation (XV). It will seem more obvious when it is compared with the reaction for the formation of the ferric cyanide ion or its acid as in equation (XVI). If we substitute aluminum chloride for ferric chloride an hydro-aluminum phenolic acid would result as in equation (XVII).

The hydro-aluminumphenolic acid then reacts with the alcohol (XVIII), to form an intermediate addition complex which rearranges (XIX) to give the substituted phenol and aluminum phenolate. The water formed in the step (XVIII) then would react with the aluminum phenolate to produce

ordinary phenol and aluminum hydroxide (XX). No theory is



offered for the rearrangement in the step represented by the equation (XIX) although it might be by the formation of the ether (XXI). The ether then rearranges quantitative-



ly to the phenol as is represented by equation (XI). It is difficult to visualize what would go on in a molecule so complex. The above scheme seems unwarranted but experimental evidence gives some support to such a mechanism.

Huston (6), to throw some light on the mode of condensation of phenol with benzyl alcohol, added aluminum chloride to a petroleum ether solution of phenol in the molecular ratio of 1 to 2. They obtained a colorless, viscous mass which solidified on standing. After decomposition with water and hydrochloric acid the phenol was recovered. The reaction can be represented by XXII in

which aluminum phenolate would be formed leaving an excess



of aluminum chloride.

This work was repeated using the same relative quantities. The evolution of hydrogen chloride was quite vigorous and some heat was liberated. Instead of decomposing the reaction mixture at this point, a quantity of alcohol stoichiometrically equivalent to the phenol was added dropwise. This represented the relative quantities of the ingredients in an ordinary condensation. After all of the alcohol was added there was no color, nor any perceptible evidence of a reaction. After decomposition and purification a 17 per cent yield of the alkylphenol was obtained. This would indicate that the alcohol had reacted with aluminum phenolate in the presence of an excess of aluminum chloride. However, this does not eliminate the possibility of the alcohol reacting with the aluminum hexo-phenolate for it might exist in a relatively small quantity. ✓

This was followed by allowing phenol and aluminum chloride to react in a 6 to 1 molecular ratio as is represented by equation XVII. The chloride was added to the phenol as above. A little heat and much hydrogen chloride was evolved but there was no color. Toward the

end the petroleum ether layer was clear and below it was a thick viscous mass that did not solidify. It did not resemble the aluminum phenolate above in any way. After the reaction had subsided, as evidenced by no perceptible evolution of hydrocarbon chloride, alcohol was added to the mixture in the ratio of 2 to 1 compared with the chloride or 1 to 3 compared with the phenol. Again there was no evidence of a reaction nor any color. However, after decomposition a 51 per cent yield of the alkyl phenol was obtained which agrees with the yields obtained with this alcohol in an ordinary condensation.

From the above it is evident that using the constituents in the ratio as is represented in the equations (XV) to (XX) inclusive favors condensation. It seems logical to suggest that the mechanism in an ordinary condensation follows a scheme similar to that presented above.

## DISCUSSION

The general procedure employed in preparing the tert-heptyl phenols consisted of the preparation of the tertiary heptyl alcohols followed by their condensation with phenol in the presence of aluminum chloride as a catalyst (XXIII).



The alcohols that were thus condensed consisted of the following:

- 1 - N-butyl dimethyl carbinol.
- 2 - Isobutyl dimethyl carbinol.
- 3 - Sec.-butyl dimethyl carbinol.
- 4 - Tert-butyl dimethyl carbinol.
- 5 - N-propyl dimethyl carbinol.
- 6 - Isopropyl dimethyl carbinol.
- 7 - Triethyl carbinol.

These all have been prepared and reported in the literature. Likewise Binder (17) prepared them and reported them. N-butyl dimethyl carbinol has been prepared by Whitmore (30) by condensing n-butyilmagnesium bromide and acetone. Isobutyl dimethyl carbinol has been prepared by Edgar and co-workers (31) from isobutyilmagnesium bromide

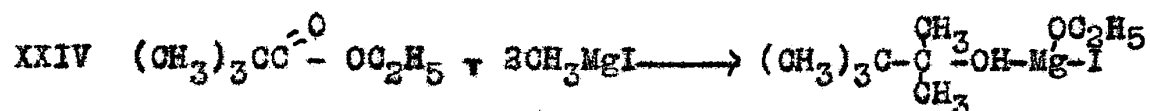
and acetone. Secondary butyl dimethyl carbinol has been prepared by Edgar (31) from secondary butylmagnesium bromide and acetone. Methyl ethyl-n-propyl carbinol has been prepared by Whitmore (32) from n-propylmagnesium bromide and methyl ethyl ketone. Whitmore (32) and Edgar (31) prepared tert-butyl dimethyl carbinol from tert-butylmagnesium chloride and acetone. Tri-ethyl carbinol was prepared from ethylmagnesium bromide and diethyl carbonate. Isopropyl methyl ethyl carbinol has been prepared from isopropyl bromide and methyl ethyl ketone by Whitmore and Evers (34). The above methods were used to prepare the alcohols for condensing purposes.

The halides were made from the corresponding alcohols and phosphorous tribromide (35) in all cases, with the exception of ethyl bromide and tert-butyl chloride. Ethyl bromide was purchased and tert-butyl chloride was prepared from tert-butyl alcohol and concentrated hydrochloric acid. (36) The halides were then treated with magnesium and the ketone following generally the procedure of Whitmore (32).

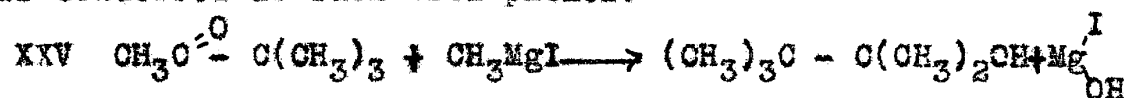
Good yields were obtained in all cases with the exception of tert-butyl dimethyl carbinol and isopropyl methyl ethyl carbinol. It was apparent that as the bromide used became more complex the yield of the alcohol diminished tremendously. For this reason a more complex ketone was sought so that a simple bromide might be used.



Tert-butyl dimethyl carbinol was prepared by treating the ethyl ester of trimethyl acetic acid (37) with methylmagnesium iodide. (XXIV). A good yield of the alcohol was obtained. However, this involved using two moles of methylmagnesium iodide so an attempt was made to condense



pinacolone with methylmagnesium iodide (XXV). The alcohol, which consisted of a hydrate described by Whitmore (31), was obtained in a 70 per cent yield. The solid hydrate was condensed as such with phenol.



~~dimethyl~~  
~~Methyl-ethyl~~ isopropyl carbinol was prepared in a 50 per cent yield from methyl isopropyl ketone (38) and ethylmagnesium iodide (XXVI).



The alkyl phenols were prepared by suspending a one-half molecular equivalent of aluminum chloride in stirred petroleum ether (20-30°) to which was added dropwise a petroleum ether solution of a molecular equivalent of the alcohol and a one and two tenths molecular equivalent of the phenol. The addition was added during a period of about two hours. During this time a deep red color developed accompanied by the evolution of hydrogen chloride.

The mixture was stirred for four to six hours longer, then allowed to stand over night.

In the case of the isopropyl, secondary butyl and tertiary butyl derivatives, the condensations were carried out using an ice bath. If they were run at 20-30° a lower yield was obtained which was accompanied by a large amount of a tarry residue. This is probably because these alcohols by virtue of their structure are dehydrated more easily than the other alcohols. The effect of the secondary or tertiary group attached to the hydroxyl carbon atom weakens the carbon to oxygen bond making dehydration easier.

After standing over night the deep red brown mixture was decomposed by pouring on to a mixture of ice, water and hydrochloric acid. The petroleum ether was separated and the aqueous layer was extracted three times with ordinary ether. After drying the combined petroleum ether and ether solutions with anhydrous potassium sulfate, the ether was evaporated on a steam bath. The resulting oil was then submitted to fractional distillation. There were three fractions, a low boiling fraction which consisted of alcohol, its chloride and unsaturated derivative, another of ordinary phenol and the last consisted of the alkyl phenol.

Thus, n-butyl dimethyl-p-hydroxyphenylmethane was prepared from n-butyl dimethyl carbinol and phenol (XXVII);



The only one reported in the literature is n-butyl dimethyl-p-hydroxyphenylmethane prepared by McGreal and Niederl (22). They report a boiling point for this phenol of  $280^\circ$  at 760 mm. which agrees with the boiling point found,  $277^\circ$  at 748.5 mm. The boiling points of the phenols were taken at atmospheric pressure using the micro method. (39)

Of the above phenols prepared all of them solidified with the exception of the n-propyl methyl ethyl derivative when they were cooled in the ice box. The lower melting ones were pressed between filter papers to remove the oil and kept in an ice box until the crystals were crisp. The n-butyl derivative could not be recrystallized. The other solid phenols were recrystallized from a 50 per cent alcohol, petroleum ether mixture. The results are tabulated in table 1.

The following derivatives were prepared for purpose of identification -- the benzoyl and o-chlorobenzoyl esters and the  $\alpha$ -naphthyl urethanes. The benzoyl and o-chlorobenzoyl esters were prepared according to the method described by Shriner and Fuson (40). After isolation of the esters they were recrystallized twice from an 85 per cent alcohol water solution and finally from an 85 per cent

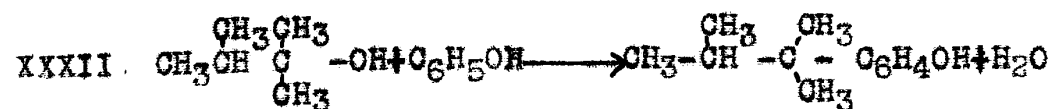
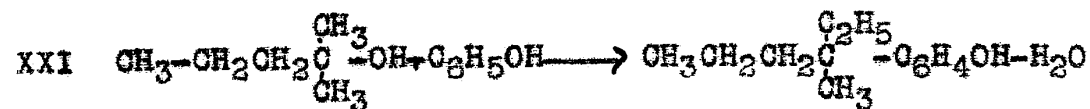
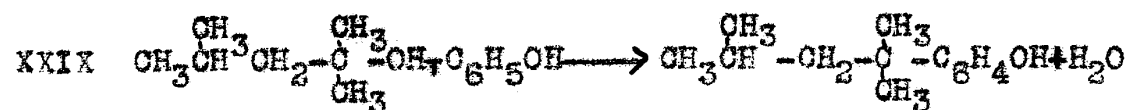
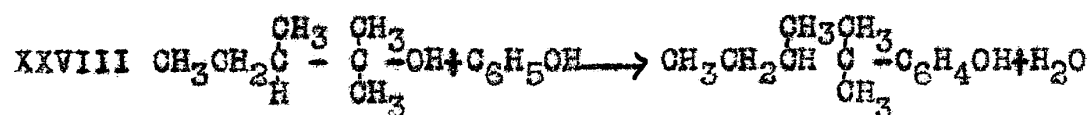
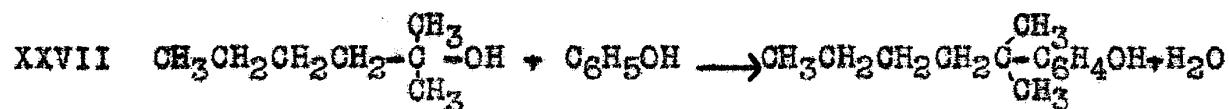
acetic acid water solution. The results are tabulated in table II and III.

The  $\alpha$ -naphthyl urethanes were also prepared according to Shriner and Fuson (41). The urethanes thus prepared were all solids and were readily recrystallizable from ligroin with the exception of the tertiary butyl derivative which was only slightly soluble in this solvent. For this reason it was not purified. The results are summarized in table IV.

By observing the properties listed in the tables I, II, III, and IV, it is obvious that of the seven phenols prepared they are all different. This indicates that the alkyl group of the alcohol combines with the benzene nucleus of the phenol without rearrangement. More evidence of this is shown in their melting points. It is known that the heaping of eurygens on adjacent carbon atoms of a compound causes an increase in the melting point of the compound. This fact is in support of the structure of these phenols for as the heaping increases there is a decided increase in the melting point.

The absolute proof of the structure was established by synthesizing the phenols by another method. Binder (17) prepared and definitely established the structure of the seven alkyl benzenes corresponding to the phenols reported in this thesis by use of the parachor, molecular refraction, and molecular volume measurements. In all cases

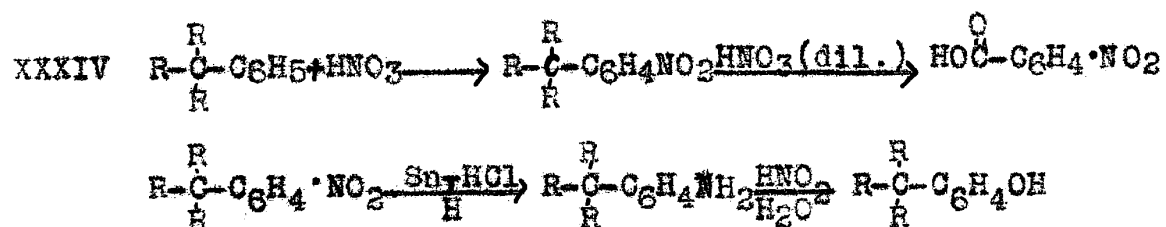
sec-butyl dimethyl-p-hydroxyphenylmethane was prepared from sec-butyl dimethyl carbinol and phenol (XXVIII); isobutyl dimethyl-p-hydroxyphenylmethane was prepared from isobutyl dimethyl carbinol and phenol (XXIX); tert-butyl dimethyl-p-hydroxyphenylmethane was prepared from tert-butyl dimethyl carbinol and phenol (XXX); n-propyl methyl ethyl-p-hydroxyphenylmethane was prepared from n-propyl methyl ethyl carbinol and phenol (XXXI); isopropyl methyl ethyl-p-hydroxyphenyl methane was prepared from isopropyl ~~dimethyl~~ methyl ethyl carbinol and phenol (XXXII); and triethyl-p-hydroxyphenylmethane was prepared from triethyl carbinol and phenol (XXXIII).



the observed values agree with the calculated values.

The phenols were prepared from these alkyl benzenes by the method of Senkowski (42) and Malherbe (43). The alkyl benzenes were nitrated with fuming nitric acid giving in the para nitro derivative. The position was established by oxidation of a portion of the nitro derivative with dilute nitric acid in a Carius furnace (41). This lead, in every case, to p-nitro benzoic acid. The more complex alkyl groups, as the tert-butyl dimethyl group, were very difficult to oxidize.

The nitro groups were then reduced with tin and concentrated hydrochloric acid. This gave the p-tert-heptyl phenyl amines which were diazotized and hydrolyzed to the desired alkyl phenols. The general procedure is represented in the series of equations (XXIV). The results are summarized in tables V and VI.



Tert-butyl dimethyl-p-hydroxyphenylmethane was recrystallized and identified by its melting point and a mixed melting point. The other phenols were identified by their  $\alpha$ -naphthyl urethanes. Mixed melting points indicated that they were identical with the urethanes made from

the phenols obtained in the condensations.

Thus the structure of each of the seven phenols n-butyl dimethyl, isobutyl dimethyl, sec-butyl dimethyl, tert-butyl dimethyl, n-propyl methyl ethyl, isopropyl methyl ethyl-, and triethyl-p-hydroxyphenylmethane was established.

## EXPERIMENTAL

Isopropyl methyl ethyl carbinol.

Thirty-six grams (1.5 moles) of dry magnesium turnings and 200 cc. of anhydrous ether were placed in a one-liter 3 necked flask equipped with a mercury-sealed stirrer, a reflux condenser and a dropping funnel. To this 153.5 g (1.5 moles) of dry, redistilled ethyl bromide was added with stirring through the dropping funnel at a rate fast enough to keep the mixture refluxing gently. After the addition was complete the stirring was continued for one hour at room temperature. Then 130 g (1.5 moles) of isopropyl methyl ketone, in 200 cc. of ether was added dropwise. The ketone was prepared from tert-amyl carbinol (38).

After the ketone was all added stirring was continued for two hours at room temperature then the mixture was cooled in an ice bath and poured on to ice in a large beaker. Dilute hydrochloric acid was added to dissolve the magnesium hydroxide. The ether layer was separated and dried for several hours over anhydrous sodium carbonate. The ether was distilled on a steam bath and the resulting alcohol was submitted to fractional distillation



using a Claisen flask with an 18 inch fractionating column.

Eighty-seven grams of the alcohol, boiling at  $50^{\circ} - 52^{\circ}$  (20mm.),  $n_D^{20}$  1.4283, was obtained which was 50 per cent of the theoretical yield based on the ketone.

Tert-butyl dimethyl carbinol.

1 - From pinacolone (44).

Twenty-two grams (.8 mole) of magnesium turnings in 100 cc. of dry ether was placed in a 500 cc. round bottomed, 3-necked flask equipped with a mercury-sealed stirrer, reflux condenser and a dropping funnel. A mixture of 128 g (.9 mole) of pinacolone in 100 cc. of anhydrous ether in a 500 cc. round bottomed 3-necked flask equipped as above. When the Grignard reagent was all added stirring was continued for one hour, after which the mixture was decomposed and purified as in the case of isopropyl methyl ethyl carbinol above.

Seventy-five grams of the alcohol, 71 per cent of the theoretical yield based on pinacolone, boiling at  $48^{\circ} - 51^{\circ}$  (20mm.), was obtained. This consisted of a mixture of colorless crystals (M.P.  $80^{\circ}$ ) and a liquid which solidified when cooled in ice. This corresponds to the carbinol described by Whitmore (32). The alcohol was used without further purification for the condensation with phenol.

2 - From the ethyl ester of trimethyl acetic acid.

The general procedure is the same as above. Ninety-nine and six tenths grams (.6 moles) of methylmagnesium iodide in 150 cc. of ether was added dropwise to a stirred mixture of 35 g. (.3 mole) of the ester in 100 cc. of ether. After the complex was hydrolyzed and purified 28 g. of alcohol, 40 per cent of the theoretical yield, was obtained which had the same physical properties as that prepared from pinacolone.

Condensations:

The alcohols were prepared as described and condensed with phenols. In as much as all the condensations were carried out in a similar manner only a typical run is described here. It should be noted that preliminary runs were made to determine the best procedure and the best relative quantities to use. Thus, for example, the aluminum chloride was added to a mixture of the alcohol and phenol, or a solution of the alcohol and phenol was added to a suspension of aluminum chloride in petroleum ether. There was no difference in the yields obtained from either method and since the latter method was more convenient it was employed. A slight excess of phenol was used in every case.

Twenty-nine grams (.25 mole) of n-butyl dimethyl carbinol and 28 g. (.3 mole) of phenol dissolved in 100 cc.

of petroleum ether was added dropwise with stirring over a period of two hours to 17 g. of aluminum chloride (.125 moles) suspended in 150 cc. of petroleum ether in a 500 cc. round bottomed flask equipped with a mercury-sealed stirrer, condenser and a dropping funnel. The addition was carried out at room temperature ( $20^{\circ}$ - $30^{\circ}$ ). A water bath was employed to insure that the temperature would not rise above ( $20^{\circ}$ - $30^{\circ}$ ). After the addition was complete the bath was removed and stirring was continued for 4 to 6 hours. During all this time hydrogen chloride was given off and a deep red brown color developed. After allowing the mixture to stand over night it was treated with ice and hydrochloric acid. The hydrolyzed product was then extracted three times with ether and dried with anhydrous potassium sulfate. The ether was removed by distillation and the residue was fractionated by a modified Claisen flask using reduced pressure and an 18 inch fractionating column. There were three fractions, usually a small amount boiling from  $40^{\circ}$ - $70^{\circ}$  at 20mm. was obtained which consisted of a mixture of the uncondensed alcohol, its chloride, and unsaturated compounds obtained from the alcohol; the next fraction consists chiefly of phenol boiling from  $70^{\circ}$ - $110^{\circ}$  at 4mm.; and the last fraction was the desired alkyl phenol boiling from  $110^{\circ}$ - $130^{\circ}$  at 4mm. The last fraction was distilled repeatedly yielding a colorless liquid which solidified after cooling. Thirty-

one grams of the phenol or a 64.6 per cent of the theoretical yield based on the alcohol was obtained which melted at  $16^{\circ}$  and boiled at  $123-5^{\circ}$  (4mm.),  $157^{\circ}-60^{\circ}$  (17mm.), and  $277^{\circ}$  (748.5mm.).

This particular phenol was not recrystallized. Instead the solid was pressed between filter paper to remove the oil. The other phenols, except the n-propyl derivative, were recrystallized from a 50 per cent mixture of alcohol and petroleum ether after they were distilled. The results are tabulated in table 1.

For a study concerning the mechanism the following was done - all the reactions were run at room temperature.

A. Twenty-three grams (.25 mole) of phenol was suspended in 100 cc. of petroleum ether in a set-up like the above and 17 g. (.125 moles) of aluminum chloride was added in small portions. The mixture warmed up slightly and hydrogen chloride was given off. After a while the mixture turned to a white solid. To this 29 g. (.35 moles) of n-butyl dimethyl carbinol in 100 cc. of petroleum ether was added dropwise. There was no evidence of a reaction. The reaction mixture remained a white solid. This mixture after standing over night was decomposed and treated as in the general directions for decomposition and purification. The following fractions were obtained.

(fractions on next page)

10 g. B.P. 40-60° (20 mm.) alcohol, chloride, alkenes.  
 15 g. " 80-110° (4 " ) phenol.  
 10 g. " 120-30° " " n-butyl dimethyl-p-hydroxy-phenylmethane.

The yield was 25.6 per cent of the theoretical based on the alcohol.

B. Thirty-five and two tenths (.37 mole) of phenol was suspended in 100 cc. of petroleum ether as in the above and 8.2 g. (.062 moles) of aluminum chloride was added in small portions. Hydrogen chloride was given off vigorously. Toward the end of the addition the mixture was clear and almost colorless. After standing a few minutes two layers appeared. The bottom layer was viscous possessing a light yellow color. To this mixture 14.5 grams (.124 moles) of n-butyl dimethyl carbinol in 100 cc. of petroleum ether was added dropwise. No color, nor any evidence of a reaction developed, but toward the end the lower viscous layer became more viscous. This was allowed to stand overnight and then decomposed. The following fractions were obtained. The yield was 51.3 per cent of the theoretical based on the alcohol.

1 g. B.P. 40-60° (20mm.)  
 27 g. " 80-110° (4mm.) phenol  
 15 g. " 120-30° " n-butyl dimethyl-p-hydroxy-phenylmethane.

C. Twenty-nine grams (.25 mole) of n-butyl dimethyl

carbinol in 50 cc. of petroleum ether was added dropwise to 17 g. (.125 moles) of aluminum chloride suspended in 100 cc. of petroleum ether in a set-up like the one above. Hydrogen chloride was evolved at the start and a yellow color followed by a deep red color developed. After the addition was complete and the evolution of hydrogen chloride stopped, 28 g. (.3 mole) of phenol in 200 cc. petroleum ether was added slowly. There was little evidence of a reaction. The color did not change. After decomposition and purification 11 g. or an 18.9 per cent of the theoretical yield based on the alcohol was obtained. The following fractions were obtained.

7½ g.	B.P.	40-60°	(20mm.)	alcohol, chloride and alkene.
19.5 g.	"	80-110°	(4 " )	phenol.
11 g.	"	120-30°	" "	n-butyl dimethyl-p-hydroxyphenylmethane.

#### Preparation of derivatives:

A. Benzoyl and o-chlorobenzoyl esters of the seven phenols were prepared by the method described by Shriner and Fuson (40). A typical run is as follows:

Three grams of the phenol was dissolved in a 4 cc. of pyridine and 3 cc. of the acid chloride was added. After the initial reaction the mixture was warmed over a low flame, refluxed for one hour, cooled, poured on to ice with stirring, and extracted with ether. The ether extract was washed with acid to remove the pyridine, then

with sodium carbonate solution. After the removal of the ether the ester was distilled under reduced pressure and cooled in the ice box. The crystals thus obtained were recrystallized from 85 per cent alcohol and finally from 85-90 per cent acetic acid.

The results are in tables II and III.

#### B. $\alpha$ -Naphthyl Urethanes (41):

One half gram of the tertiary heptyl phenol was placed in a 50 cc. dry Erlenmeyer flask with a pinch of anhydrous potassium carbonate and 1 cc. of  $\alpha$ -naphthyl isocyanate was added. A calcium chloride tube was placed in the flask and the mixture was heated on the steam bath for a few minutes. After cooling, 20 cc. of ligroin (80-90°) was added to extract the urethane. It was warmed to boiling, filtered hot and a fine white crystalline product separated by cooling. The urethane was recrystallized from petroleum ether.

The results are tabulated in table IV.

#### Nitration of the tertiary heptyl benzenes.(17)

The nitration was carried out according to Malherbe's (43) procedure by treating the hydrocarbon with an equal weight of fuming nitric acid (1.52). After the reaction subsided the mixture was warmed to 90° on a steam bath for one hour, then poured on to ice. The nitro derivative thus prepared was extracted with ether then fractionally

distilled. The tertiary butyl dimethyl derivative was a solid which was recrystallized from alcohol. All the others were liquids.

The results are tabulated in table V.

Reduction of the para-nitro tertiary alkyl benzenes.

The reduction of the seven p-nitro tertiary alkyl benzenes above to the corresponding p-amino tertiary alkyl benzenes was accomplished by means of tin and hydrochloric acid. A typical run is as follows.

Thirty grams of tin was placed in a 300 cc. round bottomed flask fitted with an air condenser. From 10 to 15 grams of p-nitro tertiary alkyl benzene was added, then 100 cc. of concentrated hydrochloric acid was added in two portions. This mixture was placed on the steam bath after the initial reaction subsided and left there several hours. The amine floated on the surface as an oil which solidified by cooling. This was probably a salt of tin described by Ipatieff (45).

This was treated with a large amount of water (200 cc.) and made alkaline with 40 per cent sodium hydroxide, then steam distilled from a liter flask. The amine was extracted with ether, dried with solid potassium hydroxide and finally fractionally distilled using a small flask under reduced pressure. From 2 to 5 grams of the amine was thus obtained.

The results are summarized in table VI.



Phenols from para amino tertiary alkyl benzenes (2).

A typical diazotization is as follows. The amine (2 g.) obtained above was treated with 1.5 cc. of concentrated sulfuric acid in 10 cc. of water. The solid salt formed was then suspended in 100 to 150 cc. of water. After cooling it down to about 5°, a 25 per cent solution of sodium nitrite was added dropwise from a dropping funnel with vigorous stirring until a positive test for nitrous acid was obtained with starch potassium iodide paper. The diazotized solution was then warmed on a steam bath and subjected to steam distillation. The phenol was extracted with ether, dried with anhydrous potassium sulfate and distilled in vacuo. After isolation in this way the  $\alpha$ -naphthyl urethane was prepared using half of the phenol obtained. The melting points were the same as those prepared from the phenols prepared by the previously described method. Mixed melting point determinations gave no decrease in the melting points indicating that the phenols were identical with the other phenols.

Oxidation of para-nitro tertiary alkyl benzenes.

The oxidation method was adapted from Malherbe (43). One gram of the nitro compound and 20 cc. of dilute nitric acid (6 N.) was placed in a Carius tube, sealed and placed in the Carius combustion furnace. It was heated up to 130° for two to six days. By that time crystals formed in the

tube after it was cooled. The tube was opened, its contents cooled in ice and collected on a filter. The white solid was washed with ether and recrystallized several times from alcohol. In each case the crystals had a melting point of 238-240°. A mixed melting point determination with p-nitro benzoic acid showed no depression.

Table I

ALCOHOL	MOLES PHENOL	MOLES ALCl <sub>3</sub>	P-hydroxyphenyl methanes	% YIELD	M. P.	B. P.	% C	% H
								Found.*
N-propyl methyl ethyl carbinol	.25	.3	.125	30.7	---	124.5° (4mm.) 278.5° (748.5)	80.75	10.45
N-butyl dimethyl carbinol	.25	.3	.125	64.6	16-17°	123-50° (4mm.) 277° (748.5)	80.56	10.35
Isobutyl dimethyl carbinol	.25	.3	.125	44.4	31-32°	115-17° (4mm.) 273° (748.5)	80.88	10.47
Isopropyl methyl ethyl carbinol	.33	.4	.16	40.6	42-43°	125-7° (4mm.) 278° (748.5)	80.66	10.24
Sec.-butyl dimethyl carbinol	.25	.3	.125	27.3	49-50.5°	117-19° (4mm.) 281° (748.5)	80.81	10.44
Triethyl Carbinol	.33	.4	.16	30.0	75.5° - 76.5	120-2° (4mm.) 275° (748.5)	81.11	10.49
Tert.-butyl dimethyl carbinol	.25	.3	.125	25.8	133-134°	287° (748.5) **(4mm.)	80.82	10.34

\*B. P. not found at 4mm.

\*Calc. for C<sub>13</sub>H<sub>20</sub>O: C, 81.16%; H, 10.49

Table II  
Benzoyl esters

Substance	M. P.	Composition found.*	
		% C	% H
P-Hydroxy-phenylmethanes			
N-propyl methyl ethyl	38-39°	80.40	8.16
N-butyl dimethyl	36-37°	80.91	8.10
Isobutyl dimethyl	71-72°	80.42	8.12
Isopropyl methyl ethyl	40-41°	80.61	8.28
Sec-butyl dimethyl	44-45°	80.39	8.00
Triethyl	74-75°	81.09	8.19
Tert.-butyl dimethyl	84-84.5°	81.01	8.15

\*Calc. for  $C_{19}H_{24}O_2$ : C, 81.03%; H, 8.16%

Table III  
O-chlorobenzoyl esters.

Substance	M. P.	B. P.	% Cl Found*
P-Hydroxy-phenylmethanes			
N-propyl methyl ethyl	25-26°		10.68
N-butyl dimethyl		177-9° (2mm.)	10.71
Isobutyl dimethyl	51-52°		10.63
Isopropyl methyl ethyl	42-43°		10.59
Sec-butyl dimethyl		175-8° (2mm.)	10.64
Triethyl	67-68°		10.81
Tert. butyl dimethyl	83-85°		10.62

\*Calc. for  $C_{19}H_{23}O_2Cl$ : Cl, 10.73%

Table IV  
Naphthyl Urethanes.

P-hydroxyphenylmethanes	M. P.	% N Found.*
N-propyl methyl ethyl	82-83°	3.84
N-butyl dimethyl	110-11°	3.87
Isobutyl dimethyl	114-115°	3.78
Isopropyl methyl ethyl	112-113°	3.92
Sec-butyl dimethyl	122-23 °	3.79
Triethyl	133-35°	3.91
Tert.-butyl dimethyl	---	---

\*Calc. for  $C_{19}H_{24}O_2N$ : N, 3.87%

Table V and VI  
P-nitro and p-amino tert.-heptyl benzenes

P-hydroxyphenylmethanes	P-nitro tert.-heptyl benzenes.			P-amino tert.-heptyl benzenes.	
	M.P.	B.P. (741)	% N Found*	B.P.	% N Found**
N-propyl methyl ethyl		292	6.31	117-18° (5mm.)	6.98
N-butyl dimethyl		291	6.31	145-6° (10mm.)	7.22
Isobutyl dimethyl		284	6.25	124-5° (5mm.)	7.06
Isopropyl methyl ethyl		285	6.24	146-8° (11mm.)	7.01
Sec-butyl dimethyl		277	6.29	120-1° (5mm.)	6.87
Triethyl		282	6.30	123-31° (5mm.)	7.21
Tert.-butyl dimethyl	108°	---	6.33	M.P. 55-56°	6.9

\*Calc. for  $C_{13}H_{19}O_2N$ : N, 6.32%

\*\*Calc. for  $C_{13}H_{21}N$ :  
N, 7.17%

### SUMMARY

1. The aliphatic tertiary heptyl alcohols have been condensed with phenol in the presence of aluminum chloride to give good yields of the p-tertiary heptyl phenols.

2. N-butyl dimethyl-p-hydroxyphenylmethane, isobutyl dimethyl-p-hydroxyphenylmethane, sec-butyl dimethyl-p-hydroxyphenylmethane, tert-butyl dimethyl-p-hydroxyphenylmethane, n-propyl methyl ethyl-p-hydroxyphenylmethane, isopropyl methyl ethyl-p-hydroxyphenylmethane and triethyl-p-hydroxyphenylmethane have been prepared in this way.

3. The benzoyl, o-chlorobenzoyl esters and the  $\alpha$ -naphthyl urethanes have been prepared.

4. The structures have been established by synthesis.

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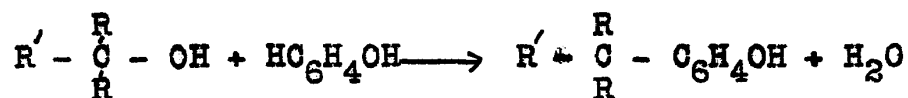


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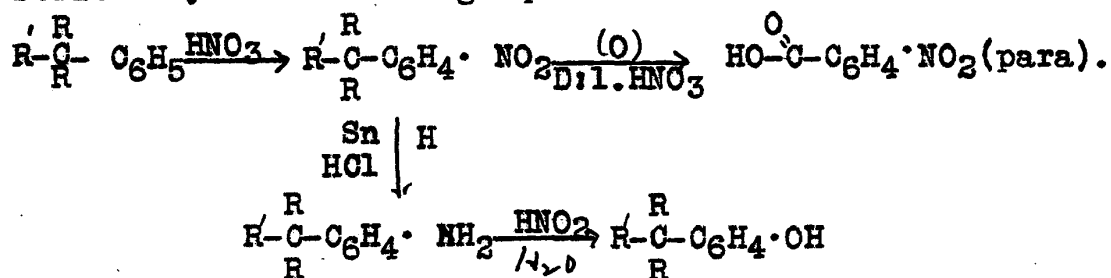
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THE CONDENSATION OF THE TERTIARY HEPTYL ALCOHOLS WITH  
PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE  
AS A CATALYST

The alcohols were prepared using an alkyl magnesium halide and a ketone. These alcohols were condensed with phenol using  $\text{AlCl}_3$  as a catalyst. The quantities of the alcohol, phenol and  $\text{AlCl}_3$  used were in the ratio of 1 : 1.2 : 0.5 respectively. Equation:



The proof of the structure of the phenols consisted of preparing the phenol by another method which is illustrated by the following equations:



Benzoyl, O-chlorobenzoyl esters and  $\alpha$ -naphthyl urethanes were prepared of the seven phenols.