THE CONDENSATION OF SOME TERTIARY DIMETHYL AMYL CARBINOLS WITH PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE

A DISSERTATION

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by

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Introduction

As a contribution from this laboratory in 1936 Huston and Hsieh (1) reported the condensation of tertiary butyl, tertiary anyl, and the three possible tertiary hexyl alcohols with phenol in the presence of aluainum chloride.

In 1937 Huston and Hedrick (2) published results on the condensation of the tertiary heptyl alcohols with phenol using aluminum chloride as the condensing agent.

Extension of this work to the tertiary octyl alcohols by Huston and Anderson (3) covered the action of methyl ethyl n-butyl and methyl ethyl tertiary butyl carbinol with phenol under the same conditions.

To continue further investigation in this field the dimethyl tertiary octyl alcohols were prepared and condensed with phenol in the presence of aluminum chloride.

Historical

Preparation of the alkyl phenols to which class the principal products described in this thesis belong is accomplished by three general methods. First the direct alkylation of phenols using alkyl halides, acyl halides, alcohols and alkenes in the presence of various catalysts. Second the replacement of a variety of groups by a hydroxyl in alkyl benzene derivatives. And third by rearrangement of the alkyl phenyl ethers.

Primary synthesis of all alkyl phenols reported herein is by the first general method and synthesis for proof of structure by the second.

Since this work is concerned with the use of alcohols as alkylating agents under the catalytic influence of aluminum chloride only those papers dealing with condensations of alcohols and benzene nuclei in the presence of aluminum chloride will be included in this review. However, two facts should be mentioned in passing. First that as early as 1884 Auer (4) reported condensation between alcohols and phenols using as a catalyst a mixture of zinc and zinc chloride and second that from that time to the present alcohols and phenols have been condensed under the influence of a great variety of catalysts some of which are phosphoric acid, zinc chloride, magnesium chloride, alkali bisulfates, concentrated sulfuric acid, and perchloric acid.

In 1897 Nef (5) mentioned the formation of diphenyl methane from benzyl alcohol and benzene in the presence of aluminum chloride. Repeating this work Huston and Friedmann (6) reported this reaction to give a 30 percent yield of diphenyl methane. A little later Huston

and Friedmann (7) continuing their previous work condensed successfully mixed aliphatic aromatic secondary alcohols and true aromatic secondary alcohols with benzene.

In 1924 Huston (8) extended this reaction of benzyl alcohol using phenol, anisole, and phenetole in a similar manner to benzene. He reported yields of the alkylated products as 45, 45 and 50 percent respectively. Huston and Sager (9) 1926 attempted to condense various primary alcohols with benzene. Negative results were obtained for methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, isoamyl, phenyl ethyl and phenyl propyl alcohols. However, allyl alcohol gave a 16 percent yield of a condensed product - allyl benzene. Huston and Newmann (10) followed this work by condensation of allyl alcohol and phenol. This led to the conclusion that only those alcohols in which the alpha carbon atom was a member of a benzene ring or was double bonded would condense under the action of aluminum chloride.

Later Huston, Lewis and Grotemut (11) reported condensation between phenol and benzhydrol, methyl phenyl carbinol and ethyl phenyl carbinol. Benzhydrol giving a much larger yield of alkylated product then benzyl alcohol they stated that here was additional evidence of the effect of unsaturation of the alpha carbon atom on condensation for both the alpha carbon atoms in benzhydrol are members of an aromatic unsaturated benzene ring.

Huston and Davis (12) found that the tertiary alcohol triphenyl carbinol reacted with benzene to give triphenyl methane and not tetraphenyl methane. The reaction between triphenyl carbinol and phenol has not been reported. Other papers by Huston and co-workers (13) condensing benzyl or halogenated benzyl alcohols with phenol or halogenated phenols, cresols or halogenated cresols followed. Mono and di substituted derivatives were the products.

Further to investigate the effect of unsaturation of the alpha atom on condensation Huston and Goodemoot (14) compared the reactivity of cyclohexyl, cyclopentyl, and cyclobutyl carbinols with benzene. They showed a progressive increase in activity as the number of carbon atoms of the ring was reduced from six to four.

Work with various diaryl-alkyl and dialkyl-aryl carbinols by Huston and Wilsey (15), Huston and Hradel (16), and Huston and MacComber (17) showed that they did not condense but dehydration of the alcohol occurred.

All these experiments indicated that unsaturation of the alpha carbon atom, whether it was double bonded or a member of the benzene ring favored condensation reactions of aliphatic and aromatic alcohols with aromatic hydrocarbons and phenols in the presence of aluminum chloride.

With the work of Huston and Hsieh (1) the field of condensation reactions of saturated alighatic alcohols with phenol and with benzene in the presence of aluminum chloride was discovered. In reacting isopropyl alcohol with benzene they obtained a fair yield of cumene (9) and following this lead using simple alighatic primary, secondary, and tertiary alcohols discovered that primary alcohols did not condense with either phenol or benzene, secondary alcohols condensed with benzene (or its homologues) and tertiary alcohols with phenol under the influence of aluminum chloride as a catalyst. Huston and Fox (18) using the simple tertiary alcohols already condensed with phenol by Hsieh namely tertiary butyl, amyl and hexyl alcohols found that they condensed also with benzene. Tzukervanik (19) reported the condensation of some simple secondary and tertiary alcohols with benzene and toluene obtaining results similar to those of Huston and Hsieh and Huston and Fox but explained them by a different mechanism.

Since tertiary aliphatic alcohols condensed readily with both benzene and phenol an extension of this work to higher homologues of that type of compound seemed logical. Hence Huston and Binder (20) condensed the tertiary heptyl alcohols with benzene and Huston and Hedrick (2) condensed these same alcohols with phenol.

Soon afterwards work was started in this laboratory upon the condensation of the tertiary octyl alcohols with phenol and benzene. Huston and Sculati (21) condensed tertiary dimethyl n-amyl, isoamyl, active amyl and secondary amyl carbinols with benzene. Huston and Anderson (3) investigated the reaction between methyl ethyl n-butyl and methyl ethyl tertiary butyl carbinol and phenol. Huston and Breining (22) described the condensation of diethyl n-propyl and diethyl isopropyl carbinols with benzene.

This present work is a continuation of the investigation on the condensation of tertiary aliphatic octyl alcohols under the influence of aluminum chloride with phenols and benzene. In specific it deals primarily with the condensation between phenol and the various dimethyl anyl carbinols.

The only one of the substituted phenols prepared as principal products of this reaction and reported herein that has been, to the writer's

knowledge, prepared and identified in the literature is 2, 4, 4-trimethyl-2-p-hydroxyphenyl methane. It is the subject of a patent by Hester (23) who prepared it from phenol and diisobutylene under the action of H_2SO_4 . It was also prepared and reported by Natelson (24).

Theoretical

In all cases of condensations between alcohols and aromatic hydrocarbons in the presence of aluminum chloride it has been shown by Huston and co-workers that the alpha carbon atom of the alcohol must be under strain such that the hydroxyl group is activated. This activation is present where the bond between carbon and the oxygen of the hydroxyl is relatively unstable. Thus benzyl and allyl alcohols both of which condense readily can be represented by the following formula.

The electron pair (a) forming the bond between C and the O of the hydroxyl is attracted strongly by both the -OH and the C atom resulting in a bond such as found in a molecule of chlorine : Cl : Cl : which is unstable and hence reactive.

When we consider various primary, secondary and tertiary alcohols the existant conditions may be represented as follows.



Relatively then the electron pair (b) is closer to the hydroxyl group in tertiary alcohols than in secondary or primary and closer to the hydroxyl in secondary alcohols than in primary. In tertiary alcohols the bond between G and G approaches more nearly the type of bond in a molecule of hydrogen chloride H : Gl : which we know is a highly reactive compound. Therefore, we have an activated hydroxyl in tertiary Alcohols and we would expect condensation. Similarly less condensation would be expected with secondary alcohols and still less with primary ones. Experimental results are found to support this view for in general tertiary aliphatic alcohols condense more readily and with higher yields than secondary aliphatic alcohols while condensation of primary aliphatic alcohols takes place only under much more drastic conditions.

That the carbon and oxygen bond in tertiary aliphatic alcohols is reactive is also supported by the case of dehydration of such alcohols and the case of replacement of this hydroxyl group by halogen of a halogen acid.

Since condensation first was observed between tertiary aliphatic alcohols and aromatic hydrocarbons there have been several mechanisms advanced to explain the course of the reaction, none of which have been conclusively established. Due to the use of different catalysts, temperatures and solvents the results are not always strictly comparable, but there have been evolved three possible mechanisms that merit attention. These mechanisms for convenience will be designated as follows:

1. Alkyl halide formation plus Friedel-Crafts Reaction

2. Alkene formation plus condensation

5. Ether formation plus rearrangement

and will be discussed briefly, confining the presentation to that applicable to tertiary alighatic alcohols with the understanding that the mechanism for primary and secondary alcohol condensation may or may not be similar to those given for tertiary alcohols.

Each of these mechanisms is an attempt to explain the path by which condensation can take place with the net result of water being split off between the hydroxyl group of the alcohol and the para hydrogen of the aromatic ring as

I. $R_3COH + HC_6H_4OH \xrightarrow{AlCl_3} R_3C-C_6H_4OH + H_2O$

While AlCl₃ is a good dehydrating agent this simple conception of intermolecular cleavage of water as represented above does not account for all the phenomena of the reaction nor does it suggest how the elimination of water is actually accomplished.

1. Alkyl Halide Formation plus Friedel-Crafts Reaction

This mechanism was proposed by Tzukervanik and Nazarova (25) who observed that after the first phase of the condensation between tertiary aliphatic alcohols and benzene there were present all the components, such as an alkyl halide, olefin, an excess of AlCl₃ and HCl required for the Friedel-Crafts reaction and the condensation of olefines with aromatic hydrocarbons. From this they outlined a scheme of reaction applicable to any tertiary alcohol and benzene. Illustrated with tertiary butyl alcohol it was

II. $(CH_3)_3COH + AlCl_3 \longrightarrow AlCl_2OC(CH_3)_3 + HCl$

 $\begin{array}{c} \operatorname{CH}_{3} \\ \operatorname{III. Alcl_{2}OC(CH_{3})_{3}} \longrightarrow \operatorname{CH}_{3}C=\operatorname{CH}_{2} + \operatorname{Alcl_{2}OH} \\ \\ \operatorname{CH}_{3} \\ \operatorname{IV. CH}_{3}C=\operatorname{CH}_{2} + \operatorname{Hcl} \longrightarrow (\operatorname{CH}_{3})_{3}C-\operatorname{Cl} \end{array}$

v. $(CH_3)_3C-Cl + C_6H_6 \longrightarrow (CH_3)_3C-C_6H_5 + HCl$

However, this mechanism is not completely satisfactory for it seems unlikely that an aluminate can form as in equation II. in view of the fact that it is not easy to replace the hydroxyl hydrogen of a tertiary alcohol. Further, Hedrick (26) in this laboratory attempting to test the validity of Tzukervanik's conception added a tertiary alcohol to aluminum chloride suspended in an inert solvent and observed almost instantaneous evolution of hydrogen chloride and heat. This evolution of hydrogen chloride would not be expected to occur if the alkyl halide formation was an intermediate step. It is significant also that an addition of a solution of phenol in petroleum ether to the same mixture did without evidence of further reaction, give 18 percent of the alkyl phenol expected which was a much smaller yield than that obtained under ordinary condensations between the same alcohol and phenol.

2. Alkene Formation plus Condensation

The mechanism of alkene formation was offered by McKenna and Sowa (27) for the alkylation of benzene using alcohols and boron trifluoride as a catalyst and is applicable to either primary, secondary or tertiary alcohols. Shown for normal butyl alcohol it is

VI.
$$CH_3CH_2CH_2CH_2OH \xrightarrow{BF_3} CH_3CH_2C=CH_2 + H_2O$$

VII. $CH_3CH_2CH=CH_2 + C_6H_6 \xrightarrow{BF_3} CH_3CH_2-C=C_6H_5$
H

That normal and secondary alcohols give identical products as do iso and tertiary alcohols is evidence of this mechanism.

McGreal and Niederal (28) have suggested a like mechanism for the use of ZnCl₂ as a catalyst and Welsh and Drake (29) believe this path is probable in the condensation of aryl substituted carbinols with phenol in the presence of aluminum chloride. Where the alcohol employed is incapable of dehydration eg. benzyl alcohol, benzhydrol, and triphenyl carbinol they suggest the reaction may proceed in effect by elimination of water from the hydroxyl group and nuclear hydrogen a procedure which they use to account for the reaction between triphenyl carbinol and phenol at elevated temperatures without a catelyst.

Certainly unsaturated hydrocarbons do condense with aromatic hydrocarbons using aluminum chloride as a catalyst as shown by numerous workers (30).

Evidence against such a mechanism is slight but it should be mentioned that McKenna and Sowa used a catalyst other than aluminum chloride and a much higher temperature than employed in the Huston method and consequently obtained condensations between primary alcohols and benzene. In contrast Huston and Sager (9) have shown that primary alcohols will not react with benzene in the presence of aluminum chloride under ordinary conditions.

Olefin formation and alkyl halide formation as intermediates are not mutually independent in all cases, for according to Grosse and Ipatieff (31) the presence of a hydrogen halide is often necessary for reaction. In which case they assume its action to consist in the addition to the olefin to form an alkyl halide which then reacts with the aromatic hydrocarbon whose C to H bond is activated by the metal halide.

3. Ether Formation plus Rearrangement

Briefly this mechanism consists in the formation of an ether of phenol and then its rearrangement into the substituted phenol itself. It seems probable that if alkyl ethers were formed as intermediates they

might rearrange into alkyl phenols for Smith (32) has reported the rearrangement of m-cresyl isopropyl ether, tertiary butyl -, isobutyl -, secondary butyl -, isopropyl phenyl ethers and p-cresyl isobutyl ethers when treated in the cold with aluminum chloride. He prepared the ethere by treating an alkali salt of the phenol with an alkyl halide.

VIII. $C_6H_5ONa + RC1 \longrightarrow C_6H_5OR + NaCl$ Rearrangement was effected by the addition of an equal molecular amount of aluminum chloride. Similar works are numerous (33).

However, the formation of alkylphenyl ethers as intermediates is questionable. Merz and Weith (34) did report a yield of 10 to 12 percent of diphenyl ether from aluminum chloride and phenol at reflux temperature. Niewland (35) using boron fluoride with phenol and methyl, ethyl, and isopropyl alcohols obtained ethers and substituted ethers. Dehydration was given as the first step in the progress of this reaction.

Clasien (36) has pointed out that in alkylating the alkali salt of phenol with a halide of an unsaturated alkene the ether is not a necessary intermediate for phenylalkyl ethers under the conditions of formation do not rearrange to alkyl phenols. Thus allyl bromide and sodium phenolate in a medium of alcohol gives a 90 percent yield of the allyl ether but in benzene medium there is only a 30 percent yield of the ether and a 70 percent yield of ortho allyl phenol.

It is significant also that Huston has reported good yields of the alkylated hydrocarbon in the condensation of tertiary alcohols and benzene, anisole and m-cresylmethyl ether (1) and the condensation of benzyl alcohol with anisole and phenetole (8) in which reactions there is no possibility of ether formation. Also no alkylphenyl ethers have been isolated even in traces in this laboratory from aluminum chloride condensations between tertiary aliphatic alcohols and phenol (1, 2, 3).

In general no mechanism yet reported seems completely satisfactory. In this laboratory (26) some work has been done in an attempt to explain the color phenomena observed in condensations between phenol and tertiary aliphatic alcohols as due to the formation of a complex ion or molecule much as phenol forms with ferric chloride, but such an explanation is supported by very little evidence. A similar mechanism with the formation of addition compounds and ionization has been suggested by Daugherty (57) for the Friedel-Crafts reaction.That the path of condensation between tertiary aliphatic alcohols and phenol and those same alcohols and benzene is different seems highly probable based on the observation of reaction progress. The color formation noted in condensations with phenol has not been observed in condensations with benzene nor has the splitting of long branched alkyl chains been demonstrated in condensations with phenol.

At present in this laboratory (38) a mechanism based on addition products between aluminum chloride, alcohol, and phenol fellowed by rearrangement is being considered. The idea is new only to this particular field for addition products with AlCl₃ have been reported (39) and their existance and formation postulated as an explanation of the catalytic action of several catalysts (40). In brief this theory is; that a catalyst unites with the substance catalyzed through some of the electrons of the outer shell of one of the atoms of the molecule.

The new arrangement of electrons and atoms in the "polymolecule" is not stable at the temperature of reaction, and rearrangement of atoms as well as electrons then take place to form systems which are more stable. The theory as applied in this particular field is promising and timely.

Experimental Data

Materials

Normal anyl, isoamyl, secondary anyl, and active anyl bromides were prepared from the corresponding alcohols (Eastman technical) by the action of sulfuric acid and hydrobromic acid (41).

The bromides of diethyl carbinol and methyl isopropyl carbinol were prepared by treating the carbinols with phosphorous tribromide. Diethyl carbinol was Eastman technical (B. P. 110 - 117° C) and the methyl isopropyl carbinol was prepared by a Grignard Reaction between isopropyl bromide and freshly prepared acetaldehyde (42).

Tertiary anyl chloride was obtained from tertiary anyl alcohol (Eastman B. P. 100 - 102° C) by treatment with concentrated hydrochloric acid (43) or by passing dry hydrogen chloride gas into the alcohol (44).

Tertiary butyl alcohol Eastman M. P. 25 - 25° C was used without distillation to prepare diisobutylene.

Acetone used was of C. P. grade dried over sodium sulfate and twice redistilled.

Magnesium turnings especially prepared for Grignard reactions were used after being dried for several days over CaCl₂.

Benzene was thiophene free, C. P. grade.

Petroleum ether. B. P. 30 - 65° C.

Ether for Grignard reactions was anhydrous.

Each of the last three chemicals was dried over freshly cut sodium before use.

Methyl iodide and acetyl chloride were both Eastman's and used without further purification.

Phenol was twice redistilled and a one degree fraction used. Aluminum chloride was Merk's Reagent anhydrous sublimed.

Alcohols condensed were:

- A. 2-methyl heptanol-2
- B. 2, 3-dimethyl hexanol-2
- C. 2, 4-dimethyl hexanol⁻²
- D. 2, 5-dimethyl hexanol-2
- E. 2-methyl-3-ethyl pentanol-2
- F. 2, 4, 4-trimethyl pentanol-2
- G. 2, 3, 4-trimethyl pentanol-2
- H. 2, 3, 3-trimethyl pentanol-2

A. 2-methyl heptanol-2

$$GH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

This alcohol was prepared by use of the Grignard reaction using the Whitmore method (44) for preparing the Grignard Reagent and the Edgar procedure (45) for the reaction of this reagent with a ketone and subsequent hydrolysis of the resulting compound. As this procedure was used with slight modifications for the preparation of several alcohols it is described in detail.

In a * dry three-liter three-necked round bottom flask fitted with an efficient stirrer, reflux condenser, and dropping funnel are placed

*Extreme care must be taken to insure dry apparatus and reagents. Also the reaction must be protected from the carbon dioxide and water vapor of the air. first a few small crystals of iodine and then 98 gms (4 moles) of fresh magnesium turnings (dried over $CaCl_2$). The bottom of the flask is heated with a small flame until the iodine commences to vaporize and is then allowed to cool while the normal amyl bromide is weighed out. Thirty cc of a mixture of four moles of the halide and 500 cc of anhydrous diethyl ether is then added directly to the dry magnesium. After the reaction has started and progressed for a few minutes 200 ec of dry ether is added directly to the reaction mixture. Then, 475 cc of the above halide ether solution is placed in the dropping funnel and added with stirring at the rate of a drop every second.

The remainder of the halide ether solution is diluted with 300 cc of dry ether and added at the same rate. Ether refluxes slightly during the halide-ether addition no external cooling being applied. It is unnecessary to heat the mixture after the ether-halide solution has been added but stirring is continued four hours and then the mixture let stand overnight before proceeding.

After the solution has stood overnight to it is added at the rate of a drop a second four moles of very pure acetone in an equal volume of anhydrous ether. It is again let stand overnight and the next day decomposed by pouring on water and ice. The precipitated magnesium compounds are dissolved by adding 10 percent HCl, (keep cool with ice during the addition). The ether layer is separated, washed with dilute sodium carbonate, followed by distilled water and dried finally over anhydrous sodium sulfate. Fractionated under reduced pressure ** a four mole run yielded 194 gms (37 percent) of a product B. P. 78 - 80° C at 30 mm. Checked as to physical constants this corresponded to the carbinol as described in the literature (46) and as prepared and reported in this laboratory by Huston and Sculati (21).

$$CH_3 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3$$

Using the above described method for 2-methyl heptanol-2 the bromide of methylpropyl carbinol (secondary amyl alcohol) was substituted for normal amyl bromide. Yield from a four mole preparation 60 gms (15 percent of theoretical) boiling at 68° C at 15 mm. This product checked as to physical constants with that prepared by Clark (47) and prepared also in this laboratory by Huston and Sculati (21).

$$\begin{array}{c} \mathbf{H} & \mathbf{\ddot{\phi}} \\ \mathbf{CH}_{3} - \mathbf{CH}_{2} - \mathbf{\dot{c}} - \mathbf{CH}_{2} - \mathbf{\dot{c}} - \mathbf{CH}_{3} \\ \mathbf{CH}_{3} & \mathbf{CH}_{3} \end{array}$$

Prepared according to the method used for 2-methyl heptanol-2 substituting the bromide of secondary butyl carbinol (active amyl alcohol)

**These tertiary alcohols dehydrate to some extent when distilled under atmospheric pressure. for normal anyl bromide. Yield from 4 moles was 72 gms (14 percent) of a product boiling between $153 - 156^{\circ}$ C at 748 mm. The physical constants of this product checked with those of the same carbinol prepared in this laboratory (21) and reported in the literature (48).

D. 2. 5-dimethyl hexanol-2

$$\begin{array}{c} H & H \\ H & \Theta \\ CH_3 - \dot{C} - CH_2 - CH_2 - \dot{C} - CH_3 \\ \dot{C}H_3 & \dot{C}H_3 \end{array}$$

Prepared according to the already described method. Isoamyl bromide used in place of normal amyl bromide. A four mole run yielded 268 (53 percent) of a product B. P. 68 - 70° C at 12 mm. This was the 2, 5-dimethyl hexanol-2 as its physical constants checked with those obtained in this laboratory by Huston and Sculati (21) and reported in the literature (49).

> E. <u>2-methyl-3-ethyl pentanol-2</u> H $H_3 - CH_2 - C - C - CH_3$ $CH_2 - CH_2 - C - CH_3$ $CH_2 - CH_3$

Prepared according to the already described method, using 3-bromopentane in place of normal anyl bromide. Yield 7 percent of a product B. P. 60 - 64° C at 13 mm. This was used as the carbinol as it corresponded to that prepared in this laboratory by other workers and reported in the literature (50).



This alcohol was prepared by the method of Butlerow (51) with slight modifications.

Two parts by volume of a quantity of like volumes of sulfuric acid and water were mixed with one part by volume of tertiary butyl alcohol and the mixture placed in a round-bottomed flask fitted with reflux condenser and heated for twenty-four hours on a steam bath. Two layers appeared. The layers were separated by means of a separatory funnel and the top oily layer was saved. After being washed with water it was dried over anhydrous calcium chloride. It was then further dried by use of phosphoric acid anhydride followed by refluxing over freshly cut metallic sodium. The product was fractionally distilled and that portion boiling $102 - 104^{\circ}$ C at 756 mm was saved as diisobutylene.

Into the diisobutylene at 10° C was passed gaseous hydrogen iodide, generated by allowing water to drop on a mixture of red phosphorus, iodine and sand, until the diisobutylene was completely saturated with hydrogen iodide. The resulting iodide was washed with water until all unused hydrogen iodide had been removed. Then to the iodide was added the calculated amount of moist silver oxide. This was added in small quantities with vigorous stirring at 0° C. The resulting mixture was allowed to warm up to room temperature and all the liquid removed from the precipitated silver iodide by vacuum distillation. This distillate consisted of two layers which were separated. The water layer was extracted three times with ether and this extract was added to the oily layer which, after being dried with anhydrous sodium sulfate, was freed of ether at ordinary pressure and then fractionally distilled. From eight moles of tertiary butyl alcohol was obtained 164 gms (31 percent) of a product B. P. 51° C at 15 mm or 144° C at 738 mm.

This fraction was used as 2, 4, 4-trimethyl pentanol-2 as it corresponded to the literature reported carbinol (51) and the carbinol as prepared by other workers in this laboratory.

G. 2. 3. 4-trimethyl pentanol-2

This alcohol to the writer's knowledge has not been reported in the literature so several methods were tried. Of these the preparation of 3, 4-dimethyl pentanone-2 and its reaction with methylmagnesium iodide was the most satisfactory and will be described in detail.

1. Preparation of 3, 4-dimethyl pentanone-2.

A Grignard reagent was prepared in the usual fashion (44) using 790 gms of 2-methyl-3-bromobutane. The yield of Grignard was determined by the Gilman method (52) of titrating a hydrolyzed aliquoit, to be 412.8 gms or a 45 percent yield. Using a modification of the Whitmore-Bradertscher procedure for preparing ketones (44) the Grignard reagent was added to 230.3 gms (2.95 moles) of acetyl chloride dissolved in 708 cc of dry ether contained in a five-liter three-necked round-bottomed flask fitted with reflux condenser, separatory funnel, and mechanical stirrer. This addition was at such a rate that the ether refluxed and after three-fourths of the reagent was added, an additional 50 cc of acetyl chloride was placed in the reaction flask to insure its presence in excess. A white precipitate formed which turned yellowish later in the reaction. The solution upon completion of addition of the reagent was allowed to stir for four hours and then stand overnight.

The precipitate and filtrate were then poured on ice, the ether layer separated and the water layer extracted three times with ether and added to the ether layer. The combined extracts were washed with onefourth of their volume of saturated aqueous potassium carbonate solution. The solution was dried with anhydrous potassium carbonate and the ether was then removed at ordinary pressure. The remaining residue was steam distilled with aqueous potassium carbonate solution and the ketone was salted out of the distillate with NaCl, separated from the water and dried overnight with anhydrous sodium sulfate at zero degrees. It was then fractionally distilled collecting the fraction $135 - 140^\circ$ C at 744 mm. This fraction weighing 55 gms was a yield of 3.3 percent based on 1-methyl-2-bromobutane.

2. Preparation of 2, 3, 4-trimethyl pentanol-2.

Methylmagnesium iodide was prepared in the usual fashion by allowing a dry ether solution of methyl iodide to react with magnesium. In

this case 0.7 of a mole of methyl iodide was used.

To the Grignard reagent in a two-liter three-necked round-bottom flask fitted with a separatory funnel, reflux condenser and mercurysealed mechanical stirrer was added the 55 gms of ketone obtained above dissolved in an equal volume of anhydrous ether. After the addition which was made not faster than one drop of the mixture a second, the solution was allowed to stand overnight. The next day it was hydrolyzed in the usual manner by being poured on ice and the basic magnesium compound removed with 15 percent sulfuric acid. The ether layer was separated from the water layer which was extracted three times with ether. The combined ether extracts were shaken with solid sodium carbonate until basic. The sodium carbonate was then removed by washing with distilled water and the other and the other solution dried over enhydrous sodium sulfate. Ether was removed from the product and it was fractionally distilled at 13 mm. A thirty-six gram yield was obtained, boiling point 45 - 50° C. This was 58.1 percent based on the ketone. Physical constants were determined upon this fraction.

> Boiling Point - - 151 - 153° C at 732 mm Refractive Index $\frac{p^{13^{\circ}}}{20^{\circ}}$ - 1.4400 Specific Gravity $\frac{20^{\circ}}{20^{\circ}}$ - .8332 Surface Tension $\frac{20^{\circ}}{20^{\circ}}$ -28.1 dynes

H. <u>2.3, 3-trimethyl pentanol-2</u> H. <u>CH3</u> $\overset{\text{H}}{\overset{\text{CH3}}{_{3}}}$ CH₃ - CH₂ - CH₂ - CH₃ $\overset{\text{H}}{\overset{\text{CH3}}{_{3}}}$

This alcohol was prepared in two ways; first by treating tertiary amyl magnesium chloride with acetone (see preparation of 2-methyl heptanol-2); and second by synthesizing the ketone 3, 3-dimethyl pentanone-2 and reacting that with methyl magnesium iodide (see preparation 2, 3, 4-trimethyl pentanol-2). However, due to the difficulty encountered in obtaining tertiary Grignard reagents very small yields of the alcohol were obtained (2 - 5 percent based on tertiary anyl chloride). The alcohol thus obtained, however, was in accord with that prepared by other workers (53). 12335132331

Table A which follows gives several physical constants on the various alcohols used in condensations as determined in this laboratory.

		:				1	Refractive	:	Speci	F10
A1	cohol	1	Boilin	g Po	<u>int</u>		Index	1	Gravi	ty
		:	Temperature ^o C	:Pr	essure	ma:	D	;		-050
2-methyl	heptanol-2	\$	159.5	1	746	:	1.4255 17.5	*	.81666	250
2,3-dime	thyl hexanol-2	\$.	155.5-156.5	\$	75 6	:	1.4 33 ²⁰⁰	:	.8390	200 200
2,4-dime	thyl hexenol-2	1	152 - 155	:	750		1.4221 200	ŧ	.81235	250 250
2,5-dime	thyl hexanol-2	:	154.5	:	746	:	1.4242 17.50	:	.81826	250 250
2-methyl-	-3-ethyl pentanol-2	2	151 - 153	:	738	1	1.430140		,8362 .90864	250 250
2,4,4-tr	methyl pentanol-2	:	144	:	746	:	1.4291180	:	.82063	250 250
2,3,4-tri	methyl pentanol-2	1	151 - 153	1	732		1.4359 ^{18.5°}	:	.8332	25° 25°
2,3,5-tri	imethyl pentanol-2	\$	157	T	746	. 1	1.4409 ^{20°}	2	.8136	250 250

TABLE A

Condensations with Phenol

The alcohols were prepared as described and condensed with phenol using a method of condensation as to relative quantities, temperature, and addition of reagents which has been determined by a series of workers in this laboratory to produce the best results and be most convenient when applied to the condensations between tertiary aliphatic alcohols and phenol with aluminum chloride as a catalyst.

In as much as all the condensations were carried out in a similar manner except for slight variations in temperature only a typical run is described.

Thirty-two grams (0.25 mole) of the octyl alcohol and 28 grams (0.3 mole) of phenol dissolved in 100 cc of petroleum ether was added dropwise with stirring over a period of two hours to 17 gms (0.125 moles) of aluminum chloride suspended in 150 cc of petroleum ether in a 500 cc round-bottomed three-necked flask equipped with a condenser, dropping funnel, and stirrer. The temperature was controlled between $25 - 30^{\circ}$ C by immersing the flask in a water bath and the reaction mixture was protected from the moisture in the air by means of a CaCl₂ tube on the reflux condenser. Hydrogen chloride was given off all during the course of the reaction, and a deep reddish color developed in the solution. After standing overnight the mixture was hydrolyzed by pouring it into ice and hydrochloric acid 1 : 1 mixture. Two layers resulted and were separated. The water layer was extracted three times with ether and this extract combined with the petroleum ether layer. The combined extract was dried over anhydrous sodium sulfate and the ether removed under ordinary pressures. The residue was then fractionated in a modified Claisen flask

with an 18 to 24 inch column at 4 mm.

There were always three main fractions. A small amount below 70° which was uncondensed alcohol, traces of its chloride and unsaturated compounds obtained from the alcohol; a second fraction between $70 - 100^{\circ}$ C consisting chiefly of phenol; and a higher fraction $100 - 150^{\circ}$ C the desired alkyl phenol. Tarry residues or the fraction above 150° C were from 2 - 6 grams.

The fraction 100 - 130° C at 4 mm in cases where it failed to crystallize was fractionated repeatedly until a cohorless liquid was obtained boiling over a 2 to 5 degree range. Those phenols that crystallized, after the removal of any oily impurities by use of a porous plate and pressing between filter paper, were recrystallized from a 50 percent mixture of alcohol and petroleum ether until a constant sharp melting point was obtained.

Table B shows the yields obtained of the principal products resulting from condensations between tertiary alcohols and phenol.

								IADUE D									
Alcohol	++ +=	Moles	** **	Moles Phenol	P.F.	oles LC1 5	en 10	Product	H.	emper-: ture ^o C:	Con	d	iverage: Yield :	A D Mo	** **	B. P.	•
2-methyl heptanol-2	** **	• 25	+* **	£ •	•	L25	ાં અવ્ય હ	-methyl-2-p-hydroxy- phenyl heptane		28-30 :	ભ	• •	69.5 :	1	11.	14-1170 at 2 mm	1
2,5-dimethyl hexanol-2	476 ⁻ ##	.17	63 8 9	04 •	*	æ	or a 	"S-dimethyl-2-p- ydroxyphenyl hexane	, m	28-30 : elow : 10 ⁰	1-1 08		35.5 9.5	ł	FT 40) FT 44 48	11-114° it 2 mm	
2,4-dimethyl hezenol-2	66. 87	\$£	₽\$ € 3	* KQ	* #* #*	125	N H	,4-dimethyl-2-p- ydroxyphenyl hexane	** **	28-30 :	6 2	88 89	58 . 53	ł		.5-1160 tt 2 mm	
2,5-dimethyl hexanol-2	44	52	44 #3	ю •	** **	125	ରୀ ମି •• ••	,5-dimethyl-2-p- ydroxyphenyl hexane	48 84	28-30 :	Q2	** **	64.6 *	ł	*10 * a	15-107 ⁰ It 2 mm	
2-methyl-2-ethyl pentanol-2	** **	53 *	#9 # 5	دی •	*** #*	125	े <u>व</u>	-methyl-3-ethyl-2-p- ydroxyphenyl pentane	** **	25-30	ы	7 7 22	28 . 58.	ł	a 10 8 8	8-110 ⁰ t 2 m	
2,3,3-trimethyl pentanol-2	** **	ส	¥8 49	- 26	1 # ## ##	4	र्भ म	, 5, 5-trimethyl-2-p- ydroxyphenyl pentane	40 +4	25-30 :	r-1	44 24	2. 1. 2.	160	** **	1	
2,3,4-trimethyl Pentanol-2	43 85	10 2	FE 14	1Q	·	125	<u>ल</u> म	, 3, 4-trimethyl-2-p- ydroxyphenyl pentane	49 64	25-30 :	64	** **	23 .1 .	74	40 14	ţ	
2,4,4-trimethyl pentanol-2		• 25	** **	ю •	· · · · · ·	125	द्ध स्व •	,4,4-trimethyl-2-p- ydroxyphenyl pentane		25-30 :	ભ	** •4	64.6 ; ;	83	•• ••	8	

Physical constants and analysis of these p-hydroxyphenyl derivatives are tabulated in Table I.

TARLE R

Derivatives

A. Benzoyl Esters

Of seven of the alkyl phenols were prepared by a method described by Shriner and Fuson (55). The procedure consisted in dissolving three grams of the phenol in 4 cc of pyridine and adding 5 cc of benzoyl chloride. After the initial reaction the mixture was warmed over a low flame, refluxed for one hour, cooled, poured on ice, and the oily material extracted with ether. The ether extract was washed with cold dilute sulfuric to remove pyridine and then cold dilute sodium carbonate solution to remove excess acid. After removal of the ether the ester was distilled under reduced pressure from a small modified Clasien flask. Usually upon cooling in the refrigerator the ester crystallized out. It was then removed from contaminating oily material by absorbing such impurities on a porous plate. And finally it was recrystallized several times from 85 percent alcohol until further recrystellization caused no changes in melting point. Table II gives the data on these esters.

B. Alpha-napthylurethanes

These were prepared by the following method (56). One gram of the tertiary octyl phenol was placed in a large test tube and 1.5 cc of alpha-mapthyl isocyanate was added the reaction being catalyzed by two drops of a dilute anhydrous ether solution of trimethyl amine. The tube was protected from moisture by being fitted with a CaCl₂ tube and thus stoppered, the reaction was heated on a steam bath for half an hour. Upon cooling the reaction contents became solid. This solid was ex-

material filtered out. In the clear filtrate the alpha-napthylurethane crystallized out on cooling. It was filtered off and recrystallized from hot ligroin until a constant melting point was obtained. Results on these urethanes are given in Table III.

No derivatives were prepared of the supposedly 2, 3, 3-trimethyl-2-p-hydroxyphenyl pentane as it was obtained in a quantity of less than 0.7 gram upon recrystallization to a constant melting point.

Proof of Structure

This was accomplished by synthesis of the octyl phenols by another method; namely that of preparation of the octyl benzenes, their nitration, reduction to the p-nitro derivative formed to the corresponding p-amino compound, followed by diazotization and hydrolysis of the diazonium salt to yield the phenol. A description of this process in detail follows.

A. Preparation of the Alkyl Benzenes

Four of these compounds had already been prepared in this laboratory and their physical constants determined (21). However it was necessary to obtain them in larger quantities and to prepare the others of the series. Since their preparations were carried out in a similar manner a typical synthesis is given.

In 97 grams (1.25 moles) of benzene in a 500 cc three-necked round-bottom flask fitted with dropping funnel, condenser, mercury-sealed stirrer, and thermometer, was suspended 17 grams (0.125 mole) of aluminum chloride by rapid stirring. To this suspension was added drop by drop 32 grams (0.25 mole) of the octyl alcohol the temperature being maintained

below 30° C by immersing the reaction flask in a mater bath if necessary. During the addition of the octyl alcohol the mixture first became yellow in color and the AlCl_g seemed to go into solution. Then upon further addition a dark brown viscous layer appeared which separated out on the bottom of the flask and the whole mixture became dark brownish in color.

After complete addition of the octyl alcohol the mixture was allowed to stir four additional hours and then to stand overnight. The next day the reaction mixture was poured on ice and hydrochloric acid 1 : 1 to cause decomposition. Two layers resulted which were separated. The water layer was extracted three times with ether and this ether extract added to the benzene layer. The combined ether and benzene extract was washed with dilute sodium carbonate solution and dried over anhydrous sodium sulfate. The ether and benzene were removed at ordinary pressures and then the remainder fractionated under reduced pressures to obtain the alkyl benzene.

This procedure was found adequate for the preparation of 2-methyl-2-phenyl heptane, the hexanes 2, 3; 2, 4; and 2, 5-dimethyl-2-phenyl and 2-methyl-3-ethyl-2-phenyl pentane but applied to the prepration of 2, 4, 4-trimethyl-2-phenyl pentane and 2, 3, 4-trimethyl-2-phenyl pentane splitting of the long alkyl side chains occurred giving products of lower molecular weights. In these cases a modification of the originally described method was tried with apparently better results. It consisted of carrying out the reaction at a lower temperature; but, since benzene solidifies at 5° G, it was necessary to use a solvent that would permit the reaction mixture to remain a liquid at sub-zero temperatures. Such a solvent was petroleum ether and the 97 (1.25) moles of benzene was dissolved in 150 cc of petroleum ether in

which was suspended 17 grams (0.125 moles) of aluminum chloride and the octyl alcohol added as usual. The temperature was maintained between -5 and -10° C by use of a bath of ice and HCl or solid carbon dioxide (dry ice) in which the reaction flask was immersed. The remainder of the preparation was as already described.

Due to the limited supply of these alcohols and the late discovery of this modified procedure to prevent in part splitting of the alkyl chain, the data presented is based upon only two condensations and hence is only suggestive of a promising possibility. That the 2, 4, 4-trimethyl pentanol-2 splits in condensation in such a way that tertiary butyl benzene is formed has been definitely established by isolation of this compound, nitration of it, reduction of the nitrocompound, diazotization of the formed amine, and hydrolysis of the diazonium compound with isolation of tertiary butyl phenol (M. P. 35 - 96° C). The benzoyl ester of this phenol when prepared (M. P. 81 - 82° C) was mixed with known benzoyl ester of tertiary butyl phenol and gave no melting point change to the known ester.

The 2, 5, 4-trimethyl pentanol-2 in a similar condensation gave as the principal product an alkyl benzene B. P. $160 - 170^{\circ}$ C at 756 mm which converted to a phenol by a similar series of reactions as those used to convert tertiary butyl benzene to p-tertiary butyl phenol melted at 95 - 96° C. Its benzoyl ester melted at 86 - 87° C.

No attempt to prepare 2, 3, 3-trimethyl-2-phenyl pentane was made as the alcohol 2, 3, 3-trimethyl pentanol-2 could not be obtained in sufficient quantities.

Table C summarizes the condensations carried out to prepare the octyl benzenes as to yields and products.

								TABLE C								
Alcohol		Moles	48 FA	Moles Benzene	44 44	doles AlCl ₃		Product	\$** • 1	Tempe ature	* * * 0	No Cond	** **	verage: Yield	Boil	ing Point o C
E-methyl heptanol-2	24 ##	ъ •	 	2*2	** **	55	20 20 00	2-methyl-2-phenyl heptane	** **	જ		н	** **	35.7 :	116 at	- 118 16 mm
2, 3-dimethyl hexanol-2	48 94	ୟ *	** **	8° 5	44 43	52	પ્પર પ્રત્ય સરક સ્થ	2, 3-dimethyl-2- Shenyl hexane		10	42 -4	4	48° 44	19.5	105 at	- 107 14 mm
2, 4-dimethyl hexanol-2	49 - 48	e L	48 48	ា ខ្ល	** **	52	** **	2 , 4-dimethyl- 2- bhenyl hexane		1 33	•• •• 93	02	80 ap	35.7 :	112 at	- 115 17 mm
2, 5-dimethyl hexanol+2	**	.	58 94	रू ब	** **	25	99 99 99 99	2, 5-dimethyl-2- shenyl hexane	** **	1 22	••••	64	39 48	57 . 5 :	113 at	- 116 19 Aun
2-methyl-3-ethyl pentanol-2	4 6 63	80°. *	49 99	1.75	44 47	.175	44 44 44	2-methyl-3-ethyl-2- bhenyl pentane		10	28 93	83	50 5 8	17.5 :	10 3 et	- 106 12 mm
2, 4, 4-trimethyl pentamol-2	## # \$	ς γ		2°2		25		2,4,4-trimethyl- 2-phenyl pentane tertiary butyl phenol	** ** ••	10		જ્ય જા		9.4 42.0 22.0 17.5	a to at to	-96 -15 mm - 58 12 mm
2, 3, 4-trimethyl pentanol-2		ଅ ୧	**	1.75	**	.175	••	Products at lower Melecular weight tha the expected 2, 3, 1-trimethyl-2-phenyl Mentane	• g	ର୍	••	-1	**	••		

The alkyl benzenes thus prepared were nitrated.

B. Nitration of the Tertiary Octyl Benzenes

Malherbe's procedure (56) was used. It consisted of treating the hydrocarbon with an equal weight of fuming nitric acid (1.52) and cooling during the addition. After the reaction had subsided the mixture was warmed to 90° C in a water bath for one hour. It was then poured on ice and the resulting solution extracted three times with ether. These ether extracts were dried over CaCl₂ and after removal of the ether the remaining p-nitro tertiary alkyl benzenes which were liquids were fractionally distilled under reduced pressure. Boiling points and analyses of these compounds are recorded in Table IV.

C. Oxidation of Para Nitro Tertiary Alkyl Benzenes

In order to establish the position taken by the nitro group in reference to the alkyl side chain a portion of the nitro tertiary alkyl benzene was oxidized by a method adapted from Malherbe (56). One gram of the nitro compound and 20 cc of 6 N nitric acid was placed in a Carius tube, sealed and heated in a Carius furnace for six days at 130° C. By this time crystals had formed in the tube which were removed and collected. They were washed with hot petroleum ether to remove oily material and then recrystallized several times from alcohol. In each case the crystals melted at $238 - 240^{\circ}$ C and mixed melting points with p-nitro benzoic acid showed no depression indicating a para nitro tertiary alkyl benzene as the original compound.

D. Reduction of the Para Nitro Tertiary Alkyl Benzenes This reduction to yield the p-amino tertiary alkyl benzenes was accomplished as follows. Thirty grams of tin were placed in a 500 cc round-bottomed flask fitted with an air condenser. From 10 - 15 grams of the p-nitro tertiary alkyl benzene was added and then 100 cc of concentrated hydrochloric acid in two portions. After the initial reaction had subsided the mixture was placed on a steam bath and left for four hours. At the end of this time it was treated with a large amount of water (200 - 300 cc) cooled and made alkaline with 40 percent sodium hydroxide. This alkaline solution was then steam distilled. The amine was extracted from the distillate with ether and the ether solution of the amine was dried over solid potassium hydroxide. After removal of the ether the residue was fractionally distilled from a 10 cc Glasien flask with a 12 inch column. Results as to boiling points and percent nitrogen of these amines are summarized in Table V.

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E. Phonols from the Para Amino Tertiary Alkyl Benzenes

These amines were diazotized and then the diazonium sult hydrolyzed to form the phenol. A typical procedure is as follows. The amine was treated with concentrated sulfuric acid 1.5 cc in 10 cc of water for each 2 grams of the amine. The solid salt thus formed was quite insoluble in water but it was suspended by vigorous stirring in 10 times the volume of the mixture of water, amine, and sulfuric acid. After cooling to about 5° C a 25 percent solution of sodium nitrite was added dropwise with continued stirring over a five hour period until the calculated amount to act with the amine had been reached. Stirring was then continued for two hours more and finally the diszotized solution was warmed on a steam bath for an hour. This reaction mixture was then subjected to steam distillation. The phenol was extracted from the distillate with

ether and after drying the ether extract with anhydrous potassium sulfate it was fractionated under reduced pressure to obtain the pure phenol.

F. Derivatives

The alpha-napthylurethanes were prepared using 0.5 grams of the phenol obtained and their melting points determined. In all cases these melting points were identical with those of alpha-napthylurethanes prepared from phenols from the aluminum chloride condensations of alcohol and phenols already described. Mixed melting points showed no depressions and hence the phenols as synthesized by the two different methods were identical. Absolute proof in this fashion was established for 2-methyl-2-p-hydroxyphenyl heptane; 2, 3-dimethyl, 2, 4-dimethyl and 2, 5-dimethyl-2-p-hydroxyphenyl hexane; and 2-methyl-3-ethyl and 2, 4,

Further proof of the structure of 2, 4, 4-trimethyl-2-p-hydroxyphenyl pentane was obtained by synthesizing it as described by Natelson (24) as follows;

G. Synthesis of 2, 4, 4-trimethyl-2-p-hydroxyphenyl pentane. A mixture of one mole of powdered potassium hydroxide and one mole of phenol was heated at 65 - 100° C in a 500 cc round-bottom flask immersed in an oil bath until solution was complete. Then a mole of diisobutylene chloride was added drop by drop at a temperature of 75° C until the reaction was complete. Potassium chloride separated out. The temperature of the bath was raised to 125° C, kept there for three to four hours and then raised to 180° C where it was kept for one hour. After cooling the potassium chloride was dissolved in water and the separated crystalline product was purified by pressing out oily impurities and recrystallization from petroleum ether. This product according to Natelson is 2, 4, 4-trimethyl-2-p-hydroxyphenyl pentane or diisobutylphenol, M. P. 34° C.

Bensoyl ester and alpha-napthylurethane derivatives had melting points corresponding to those derivatives prepared from the 2, 4, 4trimethyl-2-p-hydroxyphenyl pentane obtained as a product from the condensation of 2, 4, 4-trimethyl pentanol-2 and phenol with aluminum chloride as a catalyst. Wixed melting point determination showed these phenols and corresponding derivatives to be identical.

No absolute proof is offered of the structures of 2, 3, 4-trimethyl or 2, 3, 3-trimethyl-2-p-hydroxyphenyl pentanes due to the difficulty in obtaining the alcohols 2, 3, 4-trimethyl pentanol-2 and 2, 3, 5-trimethyl pentanol-2. In the former case splitting of the alkyl chain upon condensation with benzene prevented preparation of the alkyl benzene in sufficient quantities and in the latter all the alcohol prepared was used in condensations with phenol. TABLES

Phenol		Do °d"	-	Boili	gu	Point		: Ref	fractive n ^D 16	lndex	+ Su	urface 2	fension a	<u>85</u>	act fic avity 200 200	* Ar	alysi	в Fo	*pun
				(41 m	**												5	*	
k-metuyi-k-p-nydroxy- heptane	**	ł	••	293.5	**	114-11	2		1.51	.02	**	22	a		95055	8	.16	10.	74
2,5-dimethyl-2-p- hydroxyphenyl hexane	**	Ŧ		295	••	11-11	4		1.51	IC.	**	33.	74	-	96836	80 **	* 76*1	10.1	89
2,4-dimethyl-2-p- hydroxyphenyl hexane		ł	**	290.5	**	11-211	ပ	-	1.51	ត	••	52.(•	*	95427	8	• 00 •	10.	46
2,5-dimethyl-2-p- hydroxyphenyl hexane	**	1	**	288	44 .	105.10	2	*#	1.51	01	**	51.(•• 8	*	95183	8 0	• 79	10.	8
2-methyl-5-ethyl-2-p- hydroxyphenyl pentane	**	1	**	293		109-11	Ч		1.51	90		35.6	÷	*	36 845	44 44	0,90;	10,6	14
2,4,4-trimethyl-2-p- hydroxyphenyl pentane	48	83	**	583	••	# #	4	•4	* * *	i	**	* * *		1	1	90 #	* 50 *	10,4	6
2,5,4-trimethyl-2-p- hydroxyphenyl pentane	**	74	54	258	**	1 1 1			t t	j	44	1 1 1	••	1	1 1 1	800 800	• 81 •	10.6	25
2,3,3-trimethyl-2-p- hydroxyphenyl pentane	••	160	D.	32 5 ∋comp.	-	5 F		**	1 	l	**	8		1	1 1 1	8 0	• 88 •	10.6	8
* Calc. for $C_{1_4H_2,2}^{H_2,2}$		8 11 12	1.46	38		H = 10	. 75	74											

TABLE I

Benzoyl Ester of	\$	y.	P.	o c	1	Analy	sis	Found*
					\$	% C	1	%H
2-methyl-2-p-hydroxyphenyl heptane	\$	22		23	1	80.55	3	8.27
2,3-dimethyl-2-p-hydroxyphenyl hexane	:	54.	2-	55.	21	81.22	ţ	8.53
2,4-dimethyl-2-p-hydroxyphenyl hexane	\$	37		38	;	81.28	Ŧ	8.41
2,5-dimethy1-2-p-hydroxyphenyl hexane	ŧ	46	-	47	1	81.1 8	\$	8.26
2-methyl-3-ethyl-2-p-hydroxyphenyl pentane	t	69	-	70	1	81.19	ł	8.39
2,4,4-trimethy1-2-p-hydroxyphenyl pentane	1	7 3	-	74	t	80. 66	1	8.22
2,3,4-trimethyl-2-p-hydroxyphenyl pentane	\$	47		48	ŧ	80.45	#	8.18

TABLE II BENZOYL ESTERS

* Calcd. for $C_{20}H_{26}O_2$ C = 81.23% H= 8.45%

ALPHA-NAPTHYLURETH	IANES	
Alpha-napthylurethanes of	: M. P.ºC : Analys	is Found* % N
2-methyl-2-p-hydroxyphenyl heptane	: 120-121 :	3.69
2,3-dimethyl-2-p-hydroxyphenyl hexane	:105-105.5:	3.7 5
2,4-dimethyl-2-p-hydroxyphenyl hexane	:119.5-120.5:	3.72
2,5-dimethyl-2-p-hydroxy phenyl hexane	:132.5-133.5:	3.70
2-methyl-3-ethyl-2-p-hydroxyphenyl pentane	:109.5-110.5:	3.70
2,4,4-trimethy1-2-p-hydroxyphenyl pentane	: 102-103 :	3 . 69
2,3,4-trimethy1-2-p-hydroxyphenyl pentane	:114.5-115.5:	3.68

TABLE III ALPHA-NAPTHYLURETHANES

* Calcd. for $C_{26}H_{29}O_2N$ N= 3.73 %

Substance	t Boiling	Point	:An	alysis Found
	*Temp. ^o C :P	ressui MA	'e:	Z N
2-methy1-2-p-nitrophenyl heptane	: 148-150:	2	1	6 .01
2,3-dimethyl-2-p-nitrophenyl hexane	: 133-135:	2	t	5.99
2,4-dimethy1-2-p-nitropheny1 hexane	: 135-137:	2	1	5.98
2,5-dimethyl-2-p-nitrophenyl hexane	: 129-131:	2	90 #	6.09
2-methyl-3-ethyl-2-p-nitrophenyl pentane	: 127-130:	4	t	6.09
2,4,4-trimethyl-2-p-nitrophenyl pentane	: 108-110:	4	:	6.05

TABLE IV PARA NITEO TERTIARY OCTYL BENZENES

*Calcd. for C₁₄H₂₁O₂N N= 5.95%

TABLE V PARA AMINO TERTIARY OCTYL BENZENES

Substance	: Boiling	g Po	int	:A:	nalysis Found*
	;Temp.ºC	:Pr	essur mm	e: :	% N
Z-methyl-2-p-aminophenyl heptane	: 108-111	2	2	\$	6.77
2,3-dimethy1-2-p-aminophenyl hexane	: 115-119	t	4	ĩ	6.58
2,4-dimethy1-2-p-aminophenyl hexane	: 99-101	:	2	\$	6.87
2,5-dimethyl-2-p-aminophenyl hexane	: 99-102	1	2	;	6.92
2-methyl-3-ethyl-2-p-aminophenyl pentane	: 103-106	:	2	:	6 .8 6
2,4,4-trimethyl-2-p-aminophenyl pentane	: 112-115	1	5	\$	6.73

*Calcd. for $C_{14}H_{25}N$ N = 6.82 %

Discussion

The general procedure employed in preparing the tertiary octyl phenols described in this work consisted of the preparation of the various dimethyl anyl tertiary carbinols followed by their condensation with phenol in the presence of aluminum chloride as a catalyst.

$$\begin{array}{c} H \\ H \\ H \\ C \\ H \\ IX. \\ R \\ - \\ C \\ - \\ OH \\ H \\ C \\ H \\ H \end{array} + C_6 H_5 OH \\ \underbrace{AlCl_3}_{R} \\ - \\ C \\ - \\ C \\ - \\ C \\ - \\ C \\ - \\ C_6 H_5 OH \\ + \\ H_2 O \\ H \\ C \\ H \\ H \end{array}$$

The carbinols thus condensed were

- A. 2-methyl heptanol-2
- B. 2, 3-dimethyl hexanol-2
- C. 2, 4-dimethyl hexanol-2
- D. 2, 5-dimethyl hexanol-2
- E. 2-methyl-3-ethyl pentanol-2
- F. 2, 4, 4-trimethyl pentanol-2
- G. 2, 3, 4-trimethyl pentanol-2
- H. 2, 5, 3-trimethyl pentanol-2

Of these,all have been reported in the literature except 2, 3, 4-trimethyl pentanol-2. This alcohol as well as the others were prepared and a detailed description of their preparation along with their physical constants as determined in this laboratory has been given in the Experimental portion of this thesis. In general, good yields were obtained of the simpler compounds by using direct methods of synthesis eg. the reaction between anyl magnesium bromides and acetone. However, as the amyl bromide involved became more complex the yield of the alcohol diminished. For this reason, complex ketones were prepared in several cases so that a simple bromide might be used. Yields, however, of 2, 3, 4-trimethyl and 2, 5, 5-trimethyl pentanols-2 remained small.

The alkyl phenols were prepared by suspending a one-half molecular equivalent of AlCl₃ in stirred petroleum ether at $20 - 30^{\circ}$ C 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 phenol. A deep red color developed and hydrogen chloride was evolved during the reaction. The mixture was stirred for four hours let stand overnight and then decomposed with ice and hydrochloric acid. From this was isolated the alkyl phenols.

$$CH_3$$

I. CH_3 - CH_2 - $CH_$

 $\begin{array}{cccccccc} \mathsf{CH}_{5} & \mathsf{CH}_{5} & \mathsf{CH}_{5} \\ \texttt{III. CH}_{3}-\mathsf{CH}_{2}-\mathsf{C}-\mathsf{CH}_{2}-\mathsf{C}-\mathsf{CH}_{2}-\mathsf{C}-\mathsf{CH}_{2}-\mathsf{C}-\mathsf{C}_{6}\mathsf{H}_{4}\mathsf{O}\mathsf{H} & + \mathsf{N}_{2}\mathsf{O} \\ \texttt{H} & \mathsf{CH}_{3} & \mathsf{CH}_{3} & \mathsf{CH}_{3}-\mathsf{CH}_{2}-\mathsf{C}-\mathsf{C}_{6}\mathsf{H}_{4}\mathsf{O}\mathsf{H} & + \mathsf{N}_{2}\mathsf{O} \\ \texttt{H} & \mathsf{CH}_{3} & \mathsf{H} & \mathsf{CH}_{3} \end{array}$

$$\begin{array}{cccccccc} & & & & & & \\ CH_3 & & & & & \\ KIII. CH_5 - C - CH_2 - CH_2 - C - OH & + & C_6H_5OH & - & - & \\ H & & & CH_5 & & & CH_3 - C - CH_2 - CH_2 - C - C_6H_4OH & + & H_2OH_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 - C_6H_2 - C_6H_2 - C_6H_4OH_2 & + & H_2OH_2 & + & H_2$$

Good yields resulted when the condensations were carried out at $25 - 30^{\circ}$ C; lower temperatures 10° C were observed to decrease the amount of alkyl phenol. Of the phenols prepared five were liquids and did not crystallize even when subjected to ice box temperature. However, they were very viscous requiring several distillations to obtain pure fractions. The alkyl phenols after purification were analyzed for C and H. Their physical constants were determined and derivatives were made.

The benzoyl esters and alpha-napthylurethenes were prepared for means of identification of all the phenols except 2, 3, 5-trimethyl-2p-hydroxyphenyl pentane. Since these derivatives were all solids their melting points were determined and they were analyzed; the benzoyl esters for percent C and H and the alpha-napthylurethanes for percent nitrogen. Data on these phenols and derivatives is contained in the tables accompanying this thesis.

Absolute proof of the structure of these alkyl phenols was accomplished by synthesizing them from the corresponding alkyl benzenes prepared by condensations between the already listed carbinols and benzene in the presence of aluminum chloride. In this procedure it was

noted that highly branched alighatic chains often undergo splitting resulting in products of lower molecular weight. This was especially true in the case of 2, 4, 4-trimethyl pentanol-2 and 2, 3, 4-trimethyl pentanol-2. Temperature appeared to affect this splitting; et lower temperatures -10° C it occurred to a lesser degree than at 25 - 30° C.

These alkyl benzenes when purified were nitrated with fuming nitric acid giving the para-nitro derivative. That substitution of the MO_2 group into the benzene ring took place para to the alkyl chain was proven by exidation of a portion of the nitro derivative with dilute nitric acid in a Carius furnace to give in every case p-nitro benzoic acid.

The para-nitro derivative was then reduced with tin and concentrated hydrochloric to the p-tertiary octylphenyl amine which upon diazotization and subsequent hydrolysis of the diazonium salt yielded an alkyl phenol. These phenols were then identified by their alpha-mapthylurethanes mixed melting point determinations indicating that they were identical with the urethanes made from the phenols obtained by direct condensation of phenol with the various carbinols under the action of aluminum chloride.

Am - anyl groupings -

 $\begin{array}{c} CH_{3} & CH_{3} \\ XVIII. An - C - C_{6}H_{5} & + HNO_{2} \longrightarrow An - C - C_{6}H_{4}NO_{2} \\ CH_{3} & CH_{3} \end{array}$

XIX. Am - C - C₆H₄NO₂ $\xrightarrow{\text{Oxidised}}$ Ho - C - C₆H₄NO₂ CH₃

XX. Am -
$$C - C_6H_4NO_2 \xrightarrow{\text{Reduced}} Am - C - C_6H_4NH_2$$

CH₃
CH₃
CH₃
CH₃
CH₃
CH₃
CH₃

XXI. Am
$$-C - C_6H_4NH_2 \xrightarrow{\text{Diazotized HNO}_2 \text{ in Acid}}_{\text{Hydrolyzed with HOH}} Am - C - C_6H_5OH CH_3$$

In this fashion was established the structure of six of the alkyl phenols namely, 2-methyl-2-p-hydroxyphenyl heptane; 2, 3-dimethyl-2-phydroxyphenyl hexane; 2, 4-dimethyl-2-p-hydroxyphenyl hexane; 2, 5-dimethyl-2-p-hydroxyphenyl hexane; 2-methyl-3-ethyl-2-p-hydroxyphenyl pentane and 2, 4, 4-trimethyl-2-p-hydroxyphenyl pentane.

No absolute proof of the structure of 2, 3, 4-trimethyl-2-p-hydroxyphenyl pentane and 2, 3, 5-trimethyl-2-p-hydroxyphenyl pentane was possible due to the difficulties encountered in preparing 2, 5, 4-trimethyl-2phenyl pentane and 2, 3, 5-trimethyl-2-phenyl pentane. However, since the preparation of these alkyl phenols was similar to that used to prepare those whose structures have been definitely established in six separate cases the writer feels that they are undoubtedly the compounds as designated.

Summary

1. Some tertiery dimethyl anyl carbinols have been condensed with phenol in the presence of aluminum chloride to yield p-tertiery octyl phenols.

2. 2-methyl-2-p-hydroxyphenyl heptane; 2, 3-dimethyl-2-p-hydroxyphenyl hexane; 2, 4-dimethyl-2-p-hydroxyphenyl hexane; 2, 5-dimethyl-2p-hydroxyphenyl hexane; 2-methyl-3-ethyl-2-p-hydroxyphenyl pentane; 2, 4, 4-trimethyl-2-p-hydroxyphenyl pentane; 2, 3, 4-trimethyl-2-phydroxyphenyl pentane; and 2, 3, 3-trimethyl-2-p-hydroxyphenyl pentane have been prepared in this way.

5. Benzoyl ester and alpha-napthylurethenes have been prepared of all the alkyl phenols except 2, 3, 5-trimethyl-2-p-hydroxyphenyl pentane.

4. Proof of structure has been advanced for the phenols excluding the 2, 3, 3-trimethyl and 2, 3, 4-trimethyl-2-p-hydroxyphenyl pentanes by synthesizing them in another way. Bibliography

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