THE CONDENSATION OF SOME SECONDARY ALIPHATIC ALCOHOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

by

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INTRODUCTION

The reaction of saturated aliphatic and mixed aliphaticaromatic alcohols with benzene and other aromatic compounds, using aluminum chloride as catalyst, has been the subject of an intensive investigation in this laboratory since 1916 when Huston and Friedemann (1) reported the condensation of benzyl alcohol with benzene.

In the case of the saturated aliphatic alcohols it has been shown that the tertiary alcohols, up to and including those containing eight carbon atoms, condense readily, and in good yield for the most part, with benzene to give the expected products.

The secondary alcohols in this series have not been studied as thoroughly. Isopropyl, secondary butyl, the secondary amyl and four of the secondary hexyl alcohols have been condensed with benzene by Huston and Hsieh (2), Thompson (3), and Applegate (4). However the yields of alkylbenzenes were rather poor and the nature of the products was not ascertained.

It is the purpose of the present investigation to further the work begun by these men with a view to improving their yields and determining the nature of the products.

HISTORICAL

Numerous methods have been used to prepare alkylbenzenes. As a rule these methods have been restricted to the preparation of the lower members, but in most cases they can, and in some cases have been, extended to the higher homologues.

The simplest secondary alkylbenzene, cumene, was first prepared by the distillation of para cumic acid with calcium or barium oxides (5-6). It was thought to be normal propylbenzene until Liebmann (7) showed it to have the secondary structure by preparing it from benzal dichloride and dimethyl zinc. Sabatier and coworkers (8-9) prepared it by passing the vapors of various terpenes with hydrogen over nickel at 350-360 degrees centigrade.

Decarboxylation by the distillation of an aromatic acid in the presence of a strong base has been used, too, to prepare a higher alkylbenzene. Pulvermacher (10) obtained 2-phenylpentane by distilling a mixture of alpha, alpha diethylhomophthalic acid anhydride, calcium oxide and sodium hydroxide.

Liebmann's method, involving the reaction of zinc alkyls with phenylmethyl halides, has been used to prepare other alkylbenzenes. Diethyl zinc and benzyl chloride have yielded n-propylbenzene (11-12) and 2-phenylpentane (13). The latter compound has also been prepared by the action of diethyl zinc on trichlorophenylmethane (14), though in poorer yield. Sec.-butylbenzene has been prepared by reacting diethyl zinc with alpha phenylethyl bromide (15).

The Wurtz reaction and some of its modifications have also been used. Cumene has been prepared by reacting sodium with a boiling ether or benzene solution of bromobenzene and isopropyl bromide (16). Sec.-butylbenzene has been prepared in similar fashion from ethyl iodide and alpha phenylethyl bromide (17). Sodium benzyl gave n-phenylhexane on treatment with n-amyl chloride (18). The Grignard reaction has been used similarly for the preparation of 3phenylpentane from ethylmagnesium bromide and 1-brom-1phenylpropane (19) as well as from phenyl magnesium bromide and 3-bromopentane (20).

Alkylbenzenes have been prepared by the reduction of their halogen substituted derivatives, sec.-butylbenzene being formed by reducing the 3-chloro or 3-bromo derivative with sodium (21), while n-phenylhexane and n-phenylheptane have been prepared similarly from their corresponding 6and 7-chloro derivatives (22).

Other compounds that have been reduced to alkylbenzenes are ketones, acids and ketoacids. Hydrogen, in the presence of nickel has been used to reduce n-amyl and n-hexylphenyl ketones to the corresponding hydrocarbons (23). This is an excellent method for the preparation of the normal alkylbenzenes since the ketones are easily prepared by condensing acyl halides (24) or acid anhydrides (25) with aromatic nuclei. In place of nickel and hydrogen, sodamide has effected the reduction of sec.-amylphenyl ketone (26) and 3-benzoylhexane (27). Phosphorus and hydriodic acid have been used to reduce 2-methyl-5-phenylpentanone-3 (28). The ethyl ester

of 2-phenylbutyric acid gave a fair yield of sec.-butylbenzene on reduction with a copper-chromium oxide catalyst (29). Electrolytic reduction has produced the hydrocarbon from the ethyl ester of methylbenzylacetoacetic acid (30).

Perhaps one of the best methods available for the preparation of a pure, unrearranged alkylbenzene is that involving the Grignard reagent. Normal propylbenzene can be prepared in excellent yield by the action of diethyl sulfate (31) or para ethyl toluene sulfonate with benzylmagnesium chloride (32). Propyl sulfate and phenylmagnesium bromide gave a ten per cent yield of cumene (33). The product formed by the reaction of phenylmagnesium bromide with n-heptaldehyde on reduction gave n-phenylheptane (34), while di-isopropyl ketone, treated in the same fashion, gave 2,4 dimethyl-3-phenylpentane (35).

Klages has prepared many alkydbenzenes by a synthesis involving the use of the Grignard reagent. He treated a ketone, as acetophenone, with the appropriate alkylmagnesium halide to form a tertiary alcohol which split out water easily to yield an unsaturated compound. The olefin, on reduction with sodium and absolute alcohol, gave the alkylbenzene in good yield. In this fashion were prepared n-propylbenzene (36), cumene (37), sec.-butylbenzene (38), the 2 and 3-phenylpentanes (37-39), 2-methyl-3-phenylbutane (39), 2-methyl-4-phenylpentane (40), 3-methyl-1-phenylpentane (41), and 2-methyl-5-phenylhexane (38).

In the course of their studies on the relationship between molecular structure and optical activity, Levene and Marker synthesized quite a few alkylbenzenes. Their syntheses usually consisted of the replacement of the hydroxyl group of a primery phenyl substituted alcohol by a carbinol group. This was accomplished by replacing the hydroxyl group first by bromine, forming the Grignard reagent of the halide and condensing it with formaldehyde to give an alcohol containing one more carbon atom than the original starting compound. This was then converted to the corresponding bromide, the Grignard reagent of this compound formed, and subsequently treated with a substance containing active hydrogen to yield the alkylbenzene. Using this procedure, they prepared 3-phenylpentane (42), the 2- and 3-phenylhexanes (43) and 3-phenylheptane (43).

More popular than any of the preceding reactions for the preparation of alkylbenzenes is the condensation reaction wherein an alkyl halide, ether, alcohol, ester, olefin or naphthene is combined directly with an aromatic nucleus in the presence of some catalytic agent. The latter is usually a strong dehydrating agent, as zinc chloride, sulfuric acid, aluminum chlorde, hydrogen fluoride or boron fluoride.

This method is far more direct and rapid and gives much better yields of alkylbenzenes. The chief disadvantage, however, lies in the fact that rearrangement frequently accompanies the reaction, giving an altogether different

product from that expected, or a mixture of several products, difficult to separate.

Normal propyl and isopropyl halides both give cumene on condensing with benzene (44,45,72). Condensing agents used in this reaction have been aluminum chloride (46), (72), aluminum bromide (47), aluminum turnings and hydrogen chloride gas (48), and hydrogen fluoride (45). Simons and Archer (45) reported that their product, when n-propyl chloride was condensed in the presence of hydrogen fluoride, consisted of the rearranged secondary product to the extent of eighty eight per cent. Ipatieff, using aluminum chloride (72), obtained a mixed product of similar composition.

Normal or secondary butyl chloride, in condensing with benzene in the presence of aluminum turnings and mercuric chloride (49), or aluminum chloride alone (50), gave only the secondary product. Konovalov and Jegorov (51) found that isoamyl and tertiary amylbenzenes are formed in addition to the secondary product when 2-methyl-3-chlorobutane was condensed with benzene in the presence of aluminum chloride. Curiously enough, no rearrangement was reported in the condensation of 1,1-dichloroheptane with benzene, aluminum chloride acting as catelyst. The product formed was normal phenylheptane (52-53). Tertiary alkyl halides and benzene give the expected product in the presence of aluminum chloride. In this manner were 3-methyl-3phenylhexane (54), 2,5-dimethyl-2-phenylhexane (55), and 3-ethyl-3-phenylpentane (55) prepared.

Olefins, too, have been condensed with benzene to form alkylbenzenes. The catalysts used have been aluminum chloride and hydrogen chloride gas (46), sulfuric acid, either alone (57,72) or in conjunction with phosphoric acid (56), hydrogen fluoride (58) and boron fluoride (59). Propene gave cumene (56,59), butene sec.-butylbenzene (57), isopropylethylene tert.-amylbenzene in the presence of sulfuric acid (60,72) and 3-methyl-2-phenylbutane in the presence of aluminum chloride (72), and hexene-1 gave 2-phenylhexane (61). Ipatieff (72) considers sulfuric acid a stronger isomerizing agent than aluminum chloride in the condensation of olefins.

Compounds other than clefins, which also exhibit strain, can be condensed. Some naphthenes, of which cyclopropane is the simplest, have been condensed with benzene. Ipatieff and coworkers (72) found that the aluminum chloride-catalyzed reaction, whether carried out at zero or seventy one degrees centigrade, gave the same product, normal propylbenzene. The use of sulfuric acid, on the contrary, results in the formation of cumene.

In similar fashion and with similar rearrangements have esters (62,101-102) and ethers (103) been condensed with benzene. In the case of the esters some anomalous results have been reported. Bowden (62) reported that n-propyl esters of formic, acetic and sulfuric acids gave normal propylbenzene when aluminum chloride was used as catalyst. The corresponding n-butyl esters gave sec.-butylbenzene

and the isobutyl esters tert.-butylbenzene. Contrast this with the work of McKenna and Sowa (63) who found that npropyl formate gave isopropylbenzene in the presence of boron fluoride.

More recently have the alcohols achieved prominence in this condensation reaction with benzene and other aromatic nuclei. Condensations in the presence of zinc chloride (64), sulfuric acid (65), aluminum chloride (66) (76, 100), boron fluoride (67), and hydrogen fluoride (68) have been reported. In general it has been found that tertiary alcohols give no rearrangement, though fragmentation has been found to occur with the higher highly branched members (69, 70). Toussaint and Hennion (71) found that primary alcohols gave the secondary alkylbenzene exclusively when boron fluoride was the catalyst. On the other hand, Ipatieff (72) reported that n-propyl alcohol gave n-propylbenzene exclusively in the presence of aluminum chloride. While seemingly in conflict, these results are in harmony with those of others using the corresponding esters. In keeping with the findings of Toussaint and Hennion, Meyer and Bernhauer (44) obtained sec.-butylbenzene from both normal and secondary butyl alcohols in the presence of sulfuric acid. Isopropyl alcohol has been found to give only the secondary alkylbenzene in the presence of aluminum chloride (73-74).

The Chemical laboratories of Michigan State College have witnessed considerable progress in the condensation of variousalcohols with aromatic nuclei in the presence of aluminum

chloride. This catalyst was first used in the condensation of alcohols with aromatic nuclei by Nef (75) who, in 1897, prepared diphenylmethane by allowing benzyl alcohol to react with benzene in its presence. This work was repeated in 1916 by Huston and Friedemann (1) and a thirty per cent yield of diphenylmethane was reported.

This was followed up by the condensation of mixed aliphatic-aromatic and true aromatic secondary alcohols with benzene (76). Huston (77) later used phenol and its methyl and ethyl ethers in place of benzene and found that benzyl alcohol gave yields of 45-50 per cent of alkylated products.

In 1926 Huston and Sager (78) investigated the reaction of primary alcohols with benzene but were unsucessful in condensing methyl, ethyl, propyl, isopropyl, n-butyl, isobutyl, isoamyl, phenylethyl and phenylpropyl alcohols. They did succeed in getting a 16 per cent yield of allylbenzene from allyl alcohol. This alcohol was later condensed with phenol by Huston and Newmann (79). The conclusion was then drawn that aluminum chloride favored condensation only when the alpha carbon of the alcohol was double bonded or the member of a benzene ring.

Confirmation of this theory was obtained in the work of Huston, Lewis and Grotemut (80) who condensed phenol with benzhydrol, methylphenylcarbinol and ethylphenylcarbinol. Benzhydrol, in which both carbon atoms adjacent the carbinol group are members of a benzene ring, gave a much larger

yield of alkylated product than benzyl alcohol under the same conditions. This was pointed out as definite evidence that aromatic unsaturation has a pronounced effect on the activity of the hydroxyl group.

In 1933 Huston and Davis (81) found that the tertiary alcohol, triphenyl carbinol, reacted with benzene to give triphenyl methane instead of the expected tetraphenylmethane.

Huston and coworkers (82-84) condensed benzyl and halogenated benzyl alcohols with phenol and halogenated phenols and with the cresols and their halogenated derivatives. In each case, two monosubstituted and one disubstituted derivatives were obtained.

To investigate the effect of unsaturation of the alpha carbon atom on condensation, Huston and Goodemoot (85) compared the reactivities of cyclohexyl, cyclopentyl and cyclobutyl carbinols with benzene. They found a progressive increase in activity as the number of carbon atoms of the ring was reduced from six to four.

Investigation of several diaryl-alkyl and dialkyl-aryl carbinols by Huston and Wilsey (86), Huston and Hradel (87), and Huston and MacComber (88) showed that they did not condense with benzene but were dehydrated yielding the corresponding unsaturated products.

All these experiments indicate that unsaturation of the alpha carbon atom, whether it be that of an ordinary double bond or that of a benzene ring, favors condensation reactions of aliphatic and aromatic alcohols with aromatic hydrocarbons and phenols in the presence of aluminum chloride.

The groundwork for the condensation of saturated aliphatic alcohols with benzene and phenol was laid by Huston and Hsieh (2) in 1936. They prepared cumene in fair yield by reacting isopropyl alcohol with benzene and followed up this work with the condensation of simple aliphatic primary, secondary, and tertiary alcohols with benzene and phenol. It was found that under the conditions of their experiment, primary alcohols would not condense with either phenol or benzene while secondary and tertiary alcohols reacted with both benzene and phenol. They also condensed some tertiary alcohols with toluene, meta cresyl methyl ether and anisole.

In 1934 Huston and Fox (89) condensed tertiary butyl, tertiary amyl and the three tertiary hexyl alcohols with benzene. These alcohols had already been condensed with phenol by Huston and Hsieh (2). Tsukervanik (73-74, 100) condensed some simple secondary and tertiary alcohols with benzene and toluene and obtained results similar to those of Huston and Hsieh (2) and Huston and Fox (89).

Since the tertiary aliphatic alcohols condensed readily with both benzene and phenol, the condensation of the higher tertiary aliphatic alcohols was studied. Huston and Binder (90) condensed the tertiary heptyl alcohols with benzene and Huston and Hedrick (91) condensed the same alcohols with phenol.

The condensation of the tertiary octyl alcohols with

benzene and phenol was investigated by several later workers. Huston and Anderson (92) condensed methylethyl-n-butyl and methylethyl-tert.-butylcarbinols with benzene and phenol. Huston and Sculati (93) reacted some of the dimethylamylcarbinols with benzene. Huston and Cline (94) and Huston and Breining (95) worked with the methyldipropyl and propyldiethyl carbinols respectively. In 1940 Huston and Wasson (69) condensed some dimethylamylcarbinols with benzene, and Huston and Guile (70) condensed the dimethylamylcarbinols with phenol. Fragmentation of the carbon chain was found to occur when the amyl radical was highly branched. As a result of this fragmentation, some alkylphenols of lower molecular weight were obtained.

In 1940 Huston and Jackson (96) reported the condensation of some diphenylalkylcarbinols with phenol and Huston and Hughes (97) continued the investigation of the reaction of dialkylarylcarbinols with phenol.

In the same year Huston and Esterdahl (98) condensed the secondary amyl alcohols with phenol and found that a mixture of products was formed as though a dehydration of the alcohol had occurred in the reaction followed by the condensation of the phenol with the olefin formed. Similar results were found by Huston and Curtis (99) the next year when they studied the reaction of the secondary hexyl alcohols with phenol, and by Tsukervanik and Nazaranova (100) who obtained a mixture of the 2- and 3-p-hydroxyphenylpentanes when methylpropylcarbinol was condensed with phenol in the presence of aluminum chloride.

This investigation is a continuation of the work begun in this laboratory on the condensation of the secondary alcohols. The propyl, butyl, amyl, hexyl, and some of the heptyl secondary alcohols were condensed with benzene under the influence of aluminum chloride and the nature of the products was studied.

THEORETICAL

It will be shown later that the results of this study, in agreement with those of other workers at this laboratory and elsewhere, would indicate that the condensation of a secondary aliphatic alcohol with benzene, in the presence of aluminum chloride, takes place with the splitting out of water and the condensation of the resulting olefin.

Tsukervanik and Nazaranova (100) have suggested as a mechanism for the condensation of the tertiary alcohols, the formation of an intermediate compound from the alcohol and the aluminum chloride, hydrogen chloride being eliminated simultaneously. An olefin is then thought to be formed by the scission of this compound. The olefin can then combine with the hydrogen chloride that has been eliminated to form an alkyl halide which then condenses with the aromatic nucleus in true Friedel-Crafts style. The reaction may be represented as follows:

- (1) $(CH_3)_3COH + AlCl_3 \longrightarrow AlCl_3OC(CH_3)_3 + HCl$
- (2) $Alcl_{g}OC(CH_{s})_{s} \longrightarrow (CH_{s})_{g}-C=CH_{g} + Alcl_{g}OH$
- (3) $(CH_a)_a C = CH_a + HC1 \longrightarrow (CH_a)_a C C1$
- (4) $(CH_3)_3$ -C-Cl + C₆H₆ \rightarrow $(CH_3)_3$ -C-C₆H₅ + HCl

However, it is difficult to conceive of the formation of the intermediate aluminate by the replacement of the hydrogen atom of the tertiary hydroxyl grouping. The theory, too, conflicts with work of Huston and Hedrick (91) who

found that hydrogen chloride is evolved when aluminum chloride is treated with a petroleum ether solution of a tertiary alcohol. According to the above mechanism, no hydrogen chloride should be evolved until the aromatic nucleus has been introduced and condensation taken place.

Tsukervanik's mechanism for the condensation of secondary alcohols with benzene (73) is supported by Ipatieff (72), but fails to explain the rearrangement obtained in this present study. The intermediate aluminum alkoxy compound is thought to react directly with benzene without prior splitting and formation of the olefin. Cumene may be pictured as being formed from isopropyl alcohol and benzene in the following fashion:

- (1) sec.-C₃H₇OH + AlCl₃ \longrightarrow sec.-C₃H₇OAlCl₃ + HCl
- (2) $\sec C_3 H_7 OAlCl_3 + C_6 H_6 \xrightarrow{AlCl_3} \sec C_3 H_7 C_6 H_6 + HOAlCl_8$

McKenna and Sowa (67) propose as a mechanism for the condensation of alcohols, with boron trifluoride as catalyst, the formation of an alkene by the dehydration of the alcohol. Sec.-butylbenzene may be formed from n-butyl alcohol in this manner.

(1)
$$CH_{s}-CH_{s}-CH_{s}-CH_{s}OH \xrightarrow{BF_{s}} CH_{s}-CH_{s}-CH_{s}-CH_{s}+H_{s}O$$

(2) $CH_{s}-CH_{s}-CH_{s}-CH_{s}+C_{s}H_{s} \longrightarrow CH_{s}CH_{s}-CH_{s}-CH_{s}H_{s}$
 $CH_{s}CH_{s}-CH_{s}-CH_{s}H_{s} \longrightarrow CH_{s}CH_{s}-CH_{s}H_{s}$

The condensation of unsaturated hydrocarbons with aluminum chloride as catalyst (72) gives support to this theory.

An excellent discussion of the catinoid theory of

condensation may be found in a review by Price (134). An ionic type of mechanism is postulated for all acylations with acid chlorides, anhydrides and esters, and alkylations with alkyl halides, alcohols, ethers, esters or olefins using such compounds as boron, aluminum or iron halides, as well as, sulfuric, phosphoric, or hydrofluoric acids as catalysts.

An ionic complex between aluminum chloride and the alcohol is first assumed to be formed.

$$\begin{array}{c} CH_{s}-CH_{s}-CH_{s}-CH_{s} \xrightarrow{+} AlCl_{s} \xrightarrow{-} CH_{s}-CH_{$$

In this complex the carbon-exygen bond is weakened, probably due to the greater attraction of aluminum for the electrons of the oxygen, and the compound dissociates into an electrondeficient carbonium ion and a negatively charged aluminum complex.

$$\begin{array}{ccc} CH_{s}-CH_{s}-CH_{c}CH_{s} & \longrightarrow (CH_{s}-CH_{s}-CH_{c}CH_{s}) & (HO-Al-Cl_{s})^{*} \\ & O-H & \downarrow \\ Cl-Al-Cl & \\ & Cl & \end{array}$$

The carbonium ion can then complete its octet of electrons by association with a pair of electrons from a double bond of the aromatic nucleus.

d-Sec.-butyl alcohol, in the presence of boron fluoride, was found to yield a sec.-butylbenzene product, 95 per cent of which was a racemic mixture, the remainder being the laevo form. This phenomenon was explained on the basis of the life period of the cation. If the asymmetric alkyl cation reacts almost simultaneously with the process of ionization, the only avenue of approach is at the face opposite that being vacated by the anion. Complete inversion of the configuration would then occur. The longer the life of the cation, however, the more extensive would be its racemization before subsequent reaction.

If the catinoid theory were correct, the results of this present investigation might indicate a further change occurring in the carbonium ion formed in the reaction, possibly a dynamic equilibrium involving the shift of a hydrogen from an adjacent atom to the carbon containing the positive charge. The result would be a shift of the positive charge, too, to the adjacent carbon atom.

$$\begin{pmatrix} H_{s}C-CH_{s}-CH_{s}-CH_{s}-CH_{s} \end{pmatrix} \text{ or } \begin{pmatrix} H_{s}C-CH_{s} : \overset{H}{C} : \overset{H}{C} : CH_{s} \end{pmatrix}^{+} \\ \begin{pmatrix} I \end{pmatrix} \end{pmatrix} \begin{pmatrix} H_{s}C-CH_{s} : \overset{H}{C} : CH_{s} + H^{+} \end{pmatrix}^{+} \\ \begin{pmatrix} H_{s}C-CH_{s} : \overset{H}{C} : CH_{s} + H^{+} \end{pmatrix}^{+} \rightleftharpoons \begin{pmatrix} H_{s}C-CH_{s}-\overset{H}{C}-CH_{s} \end{pmatrix} \\ \begin{pmatrix} H_{s}C-CH_{s} : CH_{s} + H^{+} \end{pmatrix}^{+} \rightleftharpoons \begin{pmatrix} H_{s}C-CH_{s}-\overset{H}{C}-CH_{s} \end{pmatrix} \\ \begin{pmatrix} II \end{pmatrix} \end{pmatrix}$$

A mixture of carbonium ions I and II would result which, on condensation with benzene, would give a mixture of the 2 and 3 phenylpentanes. In like fashion, the formation of a tert.-alkylbenzene from an alcohol having an adjacent branched methyl group might be explained.

$$\begin{pmatrix} CH_{s}-CH_{c}-CH_{s} \\ H \end{pmatrix} \longrightarrow \begin{pmatrix} CH_{s}-CH_{s}-CH_{s} \\ CH_{s}-CH_{s}-CH_{s} \end{pmatrix}$$

What the correct mechanism for the condensation of secondary alcohols with benzene is cannot be ventured to be said at present. Suffice it to say that the reaction <u>appears</u> to proceed with the elimination of water followed by the subsequent condensation of the olefin formed.

EXPERIMENTAL

I. Preliminary

The problem of condensing secondary aliphatic alcohols with benzene first necessitated an improvement in the yields of alkylated products obtained by previous workers in this laboratory. Their studies were quite extensive, involving condensations in petroleum ether solution using a slight excess of benzene and one-eighth to one-half mole of aluminum chloride.

In order to improve the yields, the preparation of cumene was studied. A much greater excess of benzene was used, petroleum ether was omitted, more aluminum chloride was employed and dry hydrogen chloride gas was bubbled through the reaction mixture in an attempt to remove the water formed in the reaction. All these factors, it was hoped, would make the reaction,

$$\begin{array}{c} H \\ H \\ R-C-R^{\dagger} + C_{g}H_{g} \\ OH \end{array} \xrightarrow{AlCl_{g}} R-C-R^{\dagger} + H_{g}O \\ C_{g}H_{g} \end{array}$$

go more to completion.

The first factor studied was the amount of aluminum chloride to be added. The proportions of reactants used are shown in Table I. It was found that poor yields resulted when much aluminum chloride was used, many side-reactions taking place. This is in accordance with the observation of Tsukervanik (100) who reported that an excess of aluminum

Isopropyl Alcohol		Benzene	AlCla	Yield of Cumene	
3 0	grams(0.5 mole)	450 ml.(5 moles)	100 grams	13.7	grams
30	grams	450 ml.	25 grams	0.0	grams
30	grams	450 ml.	50 grams	35.0	grams

Table I

chloride resulted in the formation of polyalkyl compounds. Too little catalyst gave no yield at all. Good results were obtained with 50 grams of aluminum chloride. It is to be noted that these reactions were carried out, unlike later experiments, at, or below, room temperature. It was found in later work, under conditions finally worked out, that the amount of catalyst could be reduced to 35 grams with no decrease in yield.

Smaller amounts of benzene were next tried but given up after a few attempts. Viscous gels were formed, when the aluminum chloride dissolved, which were difficult to stir and decreased the yields considerably. It was found that when a ratio of ten moles of benzene to one of alcohol was used, the aluminum chloride dissolved easily to give a clear, non-viscous, yellow, orange or brown solution.

Another factor studied was the influence of temperature upon the yield. It was found that the suspension of aluminum chloride in benzene should be kept cold when the alcohol was being introduced. This fact is borne out by a reaction carried out at two different temperatures. When the alcohol was added to the boiling suspension, a 36 per cent yield of cumene resulted. The yield rose to 53 per cent when the same experiment was repeated at zero degrees centigrade. Later experiments, using the higher homologues, diethyl, methyl isobutyl, methyl secondary butyl, methyl isoamyl, methyl tertiary and ethyl tertiary butyl carbinols, showed that the reaction could be carried out without external cooling with no decrease in yield. The alcohol was added, in these latter reactions, at such a rate that the temperature of the system was maintained at about 50 degrees centigrade. The nature of the products was shown to be identical with that carried out at the lower temperature. In fact, in almost all cases these higher alcohols gave slightly better yields of alkylbenzene at the higher temperature.

After the alcohol had been added, the reaction mixture was allowed to remain at room temperature for various periods of time. Standing for four or sixty four hours made little difference in the yield. A shorter period of time did reduce the yield considerably. Under final conditions, the reaction mixture was permitted to stand overnight, usually for a period of eight hours.

After standing a few hours, better yields were obtained if the reaction mixture was refluxed. In one experiment, the reaction mixture after standing forty eight hours, was divided into two equal parts. One was refluxed for three hours and the other allowed to stand at room temperature for the same length of time. The latter gave a fifty seven per cent yield while the other procedure gave a sixty six

per cent yield. The yields were even better when the reaction mixture was refluxed seven to eight hours. Under these conditions, the yield rose to seventy one per cent and was not improved by longer refluxing. This period of refluxing was later abandoned in the condensation of the branched chain alcohols, since yields were not improved and in some cases actually decreased.

The hydrogen chloride gas was found to have a beneficial effect upon the reaction for in one experiment where it was omitted the yield dropped from sixty six to sixty per cent. These conditions were used in all subsequent condensations with the higher alcohols: namely,

- (1) using fifty grams of aluminum chloride for a half mole run,
- (2) using a ratio of ten moles of benzene to one of alcohol,
- (3) adding the alcohol to a suspension of aluminum chloride in benzene kept in an ice bath with hydrogen chloride gas bubbling through the reaction mixture,
- (4) permitting the reaction mixture to stand at room temperature for about eight hours after the addition of the alcohol, and
- (5) refluxing the reaction mixture for eight hours
 longer while bubbling in hydrogen chloride gas
 (in the case of alcohols having no branching).

II. Preparation of Alcohols

In a dry, three liter, three neck, round bottom flask, fitted with a separatory funnel and soda-lime tube, reflux condenser and soda-lime tube, and mechanical stirrer with glycerol seal, were placed 49 grams of magnesium turnings, a few crystals of iodine and about 100 ml. of anhydrous ether. A few grams of the alkyl halide was added and the solution stirred. If necessary, the flask was warmed by means of a water bath to start the reaction. After the reaction began, the external heating was removed and the remainder of the two moles of alkyl halide, dissolved in an equal volume of anhydrous ether, was added with stirring. The addition was dropwise, at a rate just sufficient to cause mild refluxing. Stirring was continued for almost 15 minutes after the addition of the alkyl halide.

To the Grignard reagent was added dropwise, with cooling and stirring, two moles of the aldehyde dissolved in an equal volume of anhydrous ether. Acetaldehyde was prepared by the depolymerization of paraldehyde (104).

The reaction mixture was decomposed with ice and sufficient concentrated hydrochloric acid was added to barely dissolve the basic magnesium salts that were formed. The ether layer was then separated and the aqueous layer extracted twice with ether. The combined ether extracts were washed once with water, then with a dilute sodium bicarbonate solution and then dried over anhydrous sodium sulfate. The ether was removed on a steam bath and the alcohol distilled at atmospheric pressure. With the exception of methyl isopropyl carbinol, which was prepared by Mr. Wasson using the Grignard reaction, the following alcohols were obtained from Eastman Kodak Company and redistilled over sodium.

(1)	Propanol-2	B.Pt.	-	82-83°C.
(2)	Butano1-2	B.Pt.		99°C.
(3)	Pentano1-2	B.Pt.	=	117-118°C.
(4)	Pentano1-3	B.Pt.	=	115-116°C.
(5)	2-Methylbutanol-3	B.Pt.	Ħ	112-114°C.
(6)	Hexanol-2	B.Pt.		136-138°C.
(7)	2-Methylpentanol-4	B.Pt.	=	130-132°C.

(8) Hexanol-3 (105-107)

By the Grignard reaction using ethyl bromide (108) and n-butyraldehyde. Yield = 65 per cent $B_{762} = 133-135^{\circ}C.$ $D_{4}^{22} = 0.8227$

$$n_D^{14} = 1.4167$$

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Surface Tension at 25°C. = 27.30 dynes

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(9) 3-Methylpentanol-2 (109)
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By the Grignard reaction using sec.-butyl bromide (108)
and acetaldehyde (104).
Yield = 48 per cent
B_{755} = 133^{\circ}C.
D_{4}^{22} = 0.8305
n_{D}^{14} = 1.4213
```

Surface Tension at 25°C. = 28.60 dynes

(10) 2-Methylpentanol-3 (110)

By the Grignard reaction using isopropyl bromide (108) and propionaldehyde.

Yield = 42 per cent $B_{768} = 125-128^{\circ}C.$ $D_{4}^{36} = 0.8269$ $n_{D}^{16} = 1.4193$ Surface Tension at 25°C. = 28.60 dynes

```
(11) 2,2-Dimethylbutanol-3 (Pinacolyl Alcohol) (11)
```

```
By the Grignard reaction using tert. Butyl bromide) (108) and acetaldehyde.
```

Yield = 24 per cent

 $B_{782} = 120 - 124^{\circ}C_{\circ}$

```
(12) Heptanol-2 (112)
```

```
By the Grignard reaction using n-amyl bromide (108)
and acetaldehyde.
Yield = 75 per cent
B_{762} = 157-158^{\circ}C.
D_{4}^{21} = 0.8187
n_{D}^{14} = 1.4212
Surface Tension at 25°C. = 28.70 dynes
(13) Heptanol-3 (107)
```

```
By the Grignard reaction using n-butyl bromide (108)
```

and propionaldehyde.

Yield = 62 per cent $B_{768} = 154-156^{\circ}C.$

```
D_4^{21} = 0.8225
n_D^{14} = 1.4214
```

Surface Tension at 25°C. = 28.80 dynes

```
(14) Heptanol-4 (113-117)
```

```
By the Grignard reaction using n-propyl bromide (108)
and n-butyraldehyde.
Yield = 73 per cent
B_{762} = 154-155^{\circ}C.
D_{4}^{21} = 0.8192
n_{D}^{14} = 1.4209
Surface Tension at 25°C. = 27.80 dynes
(15) 2-Methylhexanol-3 (118-119)
```

```
By the Grignard reaction using isopropyl bromide (108)
and n-butyraldehyde.
Yield = 54 per cent
B_{768} = 146-147^{\circ}C.
D_{4}^{31} = 0.8234
n_{D}^{14} = 1.4216
Surface Tension at 25°C. = 27.40 dynes
```

```
(16) 3-Methylhexanol-4 (120)
```

```
By the Grignard reaction using sec.-butyl bromide (108) and propionaldehyde.
```

```
Yield = 42 per cent

B_{768} = 147-148^{\circ}C_{\circ}

D_{\bullet}^{21} = 0.8355

n_{D}^{14} = 1.4250
```

Surface Tension at 25°C. = 28.60 dynes

```
(17) 2-Methylhexanol-4 (121)
```

By the Grignard reaction using isobutyl bromide (108) and propionaldehyde.

Yield = 33 per cent $B_{762} = 144-146^{\circ}C.$ $D_{4}^{26} = 0.8164$ $n_{D}^{14} = 1.4167$ Surface Tension at 25°C. = 27.10 dynes

```
(18) 2-Methylhexanol-5 (122)
```

```
By the Grignard reaction using isoamyl bromide (108) and acetaldehyde.
```

```
Yield = 73 per cent

B_{762} = 150.5 - 152^{\circ}C.

D_{4}^{22} = 0.8156

n_{D}^{14} = 1.4200
```

Surface Tension at 25°C. = 27.00 dynes

```
(19) 3-Methylhexanol-2 (123)
```

```
By the Grignard reaction using 2-chloropentane (124)
```

```
and acetaldehyde.
```

```
Yield = 57 per cent

B_{755} = 150.5 - 151.5^{\circ}C.

D_{4}^{22} = 0.8291

n_{D}^{14} = 1.4266
```

Surface Tension at 25°C. = 28.50 dynes

(20) 2,2-Dimethylpentanol-3 (125)

By the Grignard reaction using tert.-butyl chloride (108)

and propionaldehyde.

Yield = 22 por cent

 $B_{762} = 135 - 138^{\circ}C_{\bullet}$

III. Condensation of the Secondary Aliphatic Alcohols with Benzene.

In a dry, one liter, three neck, flask equipped with a mercury sealed stirrer, dropping funnel and calcium chloride tube, and inlet tube were placed 50 grams of aluminum chloride (C.P. anhydrous) and 400 ml. of benzene (anhydrous, thiophene-free). The stirrer was set in motion and hydrogen chloride gas was bubbled through the reaction mixture at such a rate that the bubbles could just be counted. The reaction mixture was then surrounded by an ice bath and after 10-15 minutes, a solution of one-half mole of the alcohol in 50 ml. of benzene was added dropwise and with stirring over a period of about one and a half hours. Stirring was continued for about one hour longer and then the reaction mixture was permitted to stand for about eight hours. In the case of the straight-chain alcohols, the reaction mixture was then refluxed for eight hours more, the dropping funnel beingg replaced by a reflux condenser and calcium chloride tube. An oil bath was used in the heating and hydrogen chloride gas was kept bubbling through the reaction mixture.

The reaction mixture was then poured onto ice and concentrated hydrochloric acid was added to dissolve any basic aluminum salts that separated. The resulting mixture was shaken well in a separatory funnel, the aqueous layer

separated and extracted twice with small amounts of benzene or ether. The combined benzene or benzene-ether extracts were washed once with water, then with a dilute sodium bicarbonate solution and finally once more with water.

After drying over anhydrous sodium sulfate, the benzene and ether were removed by vacuum distillation. The residual liquid was distilled at atmospheric pressure using a short column.

(1) Condensation of Propanol-2 with benzene.

Yield of monoalkylbenzene = 71 per cent $B_{759} = 151^{\circ}C.$ $D_{4}^{25} = 0.8600$ $n_{D}^{14} = 1.4956, n_{D}^{25} = 1.4858$ Surface Tension at 25°C. = 27.78 dynes (Drop Weight) = 29.28 dynes (Du Nouy) Parachor = 320.6 (Drop Weight), calculated^x = 319.8 = 324.8 (Du Nouy)

XAll calculated values are those of the expected secondary monoalkylbenzene. The molecular volumes were calculated by the formulae developed by Kauffmann for unbranched homologues of benzene. Kauffmann, "Beziehungen Zwischen Physikalischen Eigenschaften und Chemisher Konstitution," Verlag F. Enke, Stuttgart, Germany, 1920, p. 98. Molecular volumes were corrected to 20°C. by subtracting 0.11 for each degree above this temperature.

Parachor values are calculated using the constants of Mumford and Phillips (J. Chem. Soc. 33, 2112 (1929)). Decrements of 3.0 for branched groups of the type -CHR_g and double this value for the group -CR₃ were subtracted. A similar decrement was used for the attachment of an alkyl group to a benzene ring.

Indices of refraction were observed using an Abbe[†] refractometer. Molecular refractions were calculated from the Lorentz-Lorenz formula. Molecular Refraction = 40.28, calculated = 40.24 Molecular Volume at 20°C. = 138.88, calculated = 139.41 Monoacetamino derivative, M.Pt. = 105°C. Diacetamino derivative, M.Pt. = 213-214°C.

Yield of monoalkylbenzene = 81 per cent $B_{759} = 171^{\circ}C.$ $D_4^{36} = 0.8597$ $n_D^{14} = 1.4936, n_D^{36} = 1.4878$ Surface Tension at 25°C. = 28.20 dynes (Drop Weight) = 29.40 dynes (Du Nouy) Parachor = 359.5 (Drop Weight), calculated = 359.4 = 363.2 (Du Nouy) Molecular Refraction = 44.93, calculated 44.85 Molecular Volume at 20°C. = 155.14, calculated = 155.68 Monoacetamino derivative, M.Pt. = 126°C. (3) Condensation of Pentanol-2 with benzene.

Yield of monoalkylbenzene = 83 per cent

 $B_{758} = 190°C.$

^aC = 88.89 per cent, H = 10.98 per cent

Das = 0.8599

 $n_D^{14} = 1.4921, n_D^{14} = 1.4867$

Surface Tension at 25°C. = 28.49 dynes (Drop Weight)

^acalculated, C = 89.12 per cent H = 10.88 per cent Parachor = 397.0 (Drop Weight), calculated = 399.4 = 402.2 (Du Nouy)

Molecular Refraction = 49.19, calculated = 49.45 Molecular Volume at 20°C. = 171.32, calculated = 171.95 Monoacetamino derivative, M.Pt. = 118-119°C.

Alpha naphthylurethane, M.Pt. = 99-99.5°C.

(4) Condensation of Pentanol-3 with benzene.

i.

Yield of monoalkylbenzene = 65 per cent $B_{757} = 189 - 190 \cdot 5^{\circ}C$. ⁸C = 88.97 per cent, H = 10.83 per cent $D_{4}^{35} = 0.8605$ $n_{D}^{16} = 1.4932, n_{D}^{25} = 1.4877$ Surface Tension at 25°C. = 28.51 dynes (Drop Weight) = 29.65 dynes (Du Nouy) Parachor = 397.4 (Drop Weight), calculated = 399.4 = 401.7 (Du Nouy) Molecular Refraction = 49.57, calculated = 49.45 Molecular Volume at 20°C. = 171.17, calculated = 171.95 Monoacetamino derivative, M.Pt. = 121-122°C. Alpha naphthylurethane, M.Pt. = 97.5-98.5°C. (5) Condensation of 2-Methylbutanol-3 with benzene. Yield of monoalkylbenzene = 54 per cent $B_{760} = 188.5 - 190^{\circ}C.$ ac = 89.23 per cent, H = 10.79 per cent

 $D_{*}^{25} = 0.8634$

 $n_D^{1*} = 1.4952, n_D^{2*} = 1.4908$

Surface Tension at 25°C. = 28.60 dynes (Drop Weight) = 29.92 dynes (Du Nouy) Parachor = 394.5 (Drop Weight), calculated = 396.4 = 399.1 (Du Nouy) Molecular Refraction = 49.38, calculated = 49.45 Molecular Volume = 171.95, calculated = 169.63 at 20°C. Monoacetamino derivative, M.Pt. = 137-138°C. Para hydroxy derivative, M.Pt. = 89-90°C. Alpha naphthylurethane, M.Pt. = 125-126°C. (6) Condensation of Hexanol-2 with benzene Yield of monoalkylbenzene = 72 per cent $B_{760} = 208 - 210^{\circ}C.$ ^bC = 88.86 per cent, H = 11.06 per cent $D_{A}^{23} = 0.8608$ $n_D^{14} = 1.4909, n_D^{28} = 1.4866$ Surface Tension at 25°C. = 28.79 dynes (Drop Weight) = 30.16 dynes (Du Nouy) Parachor = 436.3 (Drop Weight), calculated = 439.4 = 441.5 (Du Nouy) Molecular Refraction = 54.15, calculated = 54.05Molecular Volume at 20°C. = 187.33, calculated = 188.22 Alpha naphthylurethane, M.Pt. = 95-96.5°C. (7) Condensation of 2-Methylpentanol-4 with benzene.

^bcalculated, C = 88.82 per cent H = 11.18 per cent

Yield of monoalkylbenzene = 50 per cent $B_{760} = 205 - 206^{\circ}C_{\bullet}$ bC = 88.53 per cent, H = 11.31 per cent $D_4^{28} = 0.8754$ $n_D^{14} = 1.4988, n_D^{35} = 1.4932$ Surface Tension at 25°C. = 28.79 dynes (Drop Weight) = 29.84 dynes (Du Nouy) Parachor = 431.6 (Drop Weight), calculated = 436.4 = 432.9 (Du Nouy) Molecular Refraction = 53.85, calculated = 54.05 Molecular Volume at 20°C. = 184.20, calculated = 188.22 Alpha naphthylurethane, M.Pt. = 103-112°C. (8) Condensation of Hexanol-3 with benzene. Yield of monoalkylbenzone = 65 per cent $B_{760} = 209-211^{\circ}C_{\bullet}$ ^bC = 88.67 per cent, H = 11.11 per cent $D_{*}^{33} = 0.8580$ $n_D^{14} = 1.4894, n_D^{26} = 1.4845$ Surface Tension at 25°C. = 28.93 dynes (Drop Weight) = 29.84 dynes (Du Nouy) Parachor = 438.1 (Drop Weight), calculated = 439.4 = 441.7 (Du Nouy) Molecular Refraction = 54.11, calculated = 54.05 Molecular Volume at 20°C. = 187.93, calculated = 188.22 Alpha naphthylurethane, M.Pt. = 95-96°C. (9) Condensation of 3-Methylpentanol-2 with benzene Yield of monoalkylbenzene = 56 per cent
$B_{760} = 207 - 208^{\circ}C_{\circ}$ ^bC = 89.17 per cent, H = 10.94 per cent $D_{A}^{85} = 0.8760$ $n_D^{14} = 1.4990, n_D^{25} = 1.4951$ Surface Tension at 25°C. = 29.28 dynes (Drop Weight) = 30.55 dynes (Du Nouy) Parachor = 430.6 (Drop Weight), calculated = 436.4 = 435.1 (Du Nouy) Molecular Refraction = 53.99, calculated = 54.04Molecular Volume at 20°C. = 184.07. calculated = 188.22 Alpha naphthylurethane, M.Pt. = 103.5=105.5°C. (10) Condensation of 2-Methylpentanol-3 with benzene. Yield of monoalkylbenzene = 66 per cent $B_{760} = 208 - 209^{\circ}C_{\bullet}$ $b_{C} = 89.00 \text{ per cent}$, H = 11.04 per cent $D_{4}^{90} = 0.8702$ $n_D^{14} = 1.4947, n_D^{35} = 1.4900$ Surface Tension at 25°C. = 28.96 dynes (Drop Weight) = 29.78 dynes (Du Nouy) Parachor = 432.3 (Drop Weight), calculated = 436.4 = 435.3 (Du Nouy) Molecular Refraction = 53.88, calculated 54.05 Molecular Volume at 20°C. = 185.31, calculated = 188.22 Alpha naphthylurethane, M.Pt. = 123.5-125°C. (11) Condensation of 2,2-Dimethylbutanol-3 with benzene.

Yield of monoalkylbenzene = 62 per cent

 $B_{7ee} = 205 - 207^{\circ}C.$ ^bC= 88.96 per cent, H = 10.99 per cent $D_4^{25} = 0.8763$ $n_D^{14} = 1.4985, n_D^{25} = 1.4942$ Surface Tension at 25°C. = 28.92 dynes (Drop Weight) = 30.16 (Du Nouy) Parachor = 429.1 (Drop Weight), calculated = 433.4 = 433.6 (Du Nouy) Molecular Refraction = 53.89, calculated 54.05 Molecular Volume at 20°C. = 184.01, calculated = 188.22 Alpha naphthylurethane, M.Pt. = 109-110°C. (12) Condensation of Heptanol-2 with benzene. Yield of monoalkylbenzene = 72 per cent $B_{760} = 226 - 227^{\circ}C_{\bullet}$ ^CC = 88.47 per cent, H = 11.40 per cent $D_{4}^{25} = 0.8585$ $n_D^{14} = 1.4882, n_D^{40} = 1.4837$ Surface Tension at 25°C. = 28.94 dynes (Drop Weight) = 29.72 dynes (Du Nouy) Parachor = 475.9 (Drop Weight), calculated = 479.4 = 479.1 (Du Nouy) Molecular Refraction = 58.68, calculated = 58.66 Molecular Volume at 20°C. = 204.47, calculated = 204.49 Alpha naphthylurethane, M.Pt. = 94.5-96.5°C. ^Ccalculated, C = 88.56 per cent H = 11.44 per cent

(13) Condensation of Heptanol-3 with benzene Yield of monoalkylbenzene = 67 per cent $B_{762} = 227 - 228^{\circ}C_{\circ}$ $^{\circ}C = 88.55 \text{ per cent. H} = 11.59 \text{ per cent}$ $D_{A}^{35} = 0.8569$ $n_D^{14} = 1.4873, n_D^{35} = 1.4828$ Surface Tension at 25°C. = 28.73 dynes (Drop Weight) = 30.03 (Du Nouy) Parachor = 475.9 (Drop Weight), calculated = 479.4 = 481.2 (Du Nouy) Molecular Refraction = 58.69, calculated = 58.66Molecular Volume at 20°C. = 204.45, calculated = 204.49 Alpha naphthylurethane, M.Pt. = 95.5-97.5°C. (14) Condensation of Heptanol-4 with benzene. Yield of monoalkylbenzene = 63 per cent $B_{---} = 226 - 229^{\circ}C_{--}$ ^CC = 88.29 per cent, H = 11.62 per cent $D_4^{25} = 0.8613$ $n_D^{14} = 1.4899, n_D^{25} = 1.4847$ Surface Tension at 25°C. = 29.03 dynes (Drop Weight) = 29.78 dynes (Du Nouy) Parachor = 474.7 (Drop Weight), calculated = 479.4 = 477.8 (Du Nouy) Molecular Refraction = 58.59, calculated = 58.66 Molecular Volume at 20°C. = 203.38, calculated = 204.49 Alpha naphthylurethane, M.Pt. = 93.5-94°C.

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(15) Condensation of 2-Methylhexanol-3 with benzene.
       Yield of monoalkylbenzene = 62 per cent
       B_{7,62} = 225 - 226^{\circ}C_{\bullet}
      <sup>C</sup>C = 88.19 per cent. H = 11.56 per cent
       D_{\star}^{33} = 0.8688
       n_{\rm D}^{14} = 1.4935, n_{\rm D}^{25} = 1.4893
        Surface Tension at 25°C. = 29.08 dynes (Drop Weight)
                                    = 30.09 dynes (Du Nouy)
        Parachor = 470.9 (Drop Weight), calculated = 476.4
                  = 474.9 (Du Nouy)
        Molecular Refraction = 58.55, calculated = 58.65
       Molecular Volume at 25°C. = 201.65. calculated = 204.49
        Alpha naphthylurethane, M.Pt. = 125-127°C.
(16) Condensation of 3-Methylhexanol-4 with benzene.
        Yield of monoalkylbenzene = 60 per cent
        B_{7**} = 224 - 226^{\circ}C_{*}
      <sup>C</sup>C = 88.27 per cent, H = 11.63 per cent
       D_{*}^{36} = 0.8727
       n_D^{14} = 1.4952, n_D^{20} = 1.4913
       Surface Tension at 25°C. = 29.88 dynes (Drop Weight)
                                    = 30.91 dynes (Du Nouy)
        Parachor = 470.0 (Drop Weight), calculated = 476.4
                  = 476.0 (Du Nouy)
       Molecular Refraction = 58.49, calculated = 58.66
        Molecular Volume at 20°C. = 200.75, calculated = 204.49
        Alpha naphthylurethane, M.Pt. = 101-103°C.
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(17) Condensation of 2-Methylhexanol-4 with benzene.
       Yield of monoalkylbenzene = 54 per cent
       D_{7,62} = 224 - 225^{\circ}C_{\bullet}
      C = 88.13 per cent, H = 11.40 per cent
       D_{*}^{35} = 0.8654
       n_D^{10} = 1.4911, n_D^{20} = 1.4873
       Surface Tension at 25°C. = 28.74 dynes (Drop Weight)
                                   = 29.84 dynes (Du Nouy)
       Parachor = 471.3 (Drop Weight), calculated = 476.4
                 = 475.8 (Du Nouy)
       Molecular Refraction = 58.58, calculated = 58.66
       Molecular Volume at 20°C. = 202.45, calculated = 204.49
       Alpha naphthylurethane, M.Pt. = 119-121°C.
(18) Condensation of 2-Methylhexanol-5 with benzene
       Yield of monoalkylbenzene = 44 per cent
       B_{760} = 223 - 226^{\circ}C_{\bullet}
      <sup>C</sup>C = 88.43 per cent. H = 11.31 per cent
       D_{4}^{25} = 0.8777
       n_D^{14} = 1.4973, n_D^{26} = 1.4929
       Surface Tension at 25°C. = 29.06 dynes (Drop Weight)
                                   = 29.97 dynes (Du Nouy)
        Parachor = 466.0 (Drop Weight), calculated = 476.4
                  = 469.0 (Du Nouy)
       Molecular Refraction = 58.33, calculated = 58.66
       Molecular Volume at 20°C. = 199,59, calculated = 204.49
       Alpha naphthylurethane, M.Pt. = 119-121°C.
(19) Condensation of 3-Methylhexanol-2 with benzene.
```

Yield of monoalkylbenzene = 56 per cent $B_{768} = 224 - 225 \cdot 5^{\circ}G$. ^cC = 88.99 per cent, H = 11.52 per cent $D_{\perp}^{25} = 0.8767$ $n_{D}^{24} = 1.4976, n_{D}^{25} = 1.4939$ Surface Tension at 25°C. = 29.14 dynes (Drop Weight) = 30.09 dynes (Du Nouy) Parachor = 466.8 (Drop Weight), calculated = 476.4 = 470.6 (Du Nouy) Molecular Hefraction = 58.48, calculated = 58.66 Molecular Volume at $20^{\circ}C_{\bullet} = 199.82$, calculated = 204.49 Alpha naphthylurethane, M.Pt. = 106-108°C. (20) Condensation of 2,2-Dimethylpentanol-3 with benzene Yield of monoalkylbenzene = 58 per cent $B_{7*2} = 221 - 223^{\circ}C_{\bullet}$ ^CC = 88.63 per cent, H = 11.30 per cent $D_{4}^{25} = 0.8720$ $n_D^{14} = 1.4947, n_D^{25} = 1.4912$ Surface Tension at 25°C. = 28.67 dynes (Drop Weight) = 29.65 dynes (Du Nouy) Parachor = 467.5 (Drop Weight), calculated = 473.4 = 471.4 (Du Nouy) Molecular Refraction = 58.53, calculated = 58.66 Molecular Volume at 20°C. = 200.90, calculated = 204.49 Alpha naphthylurethane, M.Pt. = 114-115°C.

IV. Derivatives

(1) Acetamino Derivatives

These compounds were prepared by the method of Ipatieff and Schmerling (126-127).

(2) Alpha naphthylurethanes

These compounds were prepared by a modification of the methods given in Fisher's text (104) and is almost the same as Malherbe's procedure used by Guile (70).

(a) Preparation of the mononitro alkylbenzenes.

To one-tenth of a mole of alkylbenzene was added dropwise and with shaking, twenty four ml. of a mixture consisting of concentrated sulfuric and nitric acids in equal parts by volume. The temperature of the reaction mixture was kept below 50°C. by immersion in an ice bath when this temperature was approached. The reaction mixture was then placed in a water bath at 50°C. and kept there, with frequent shaking for one-half to two hours. It was then poured onto ice and extracted with ether. The ether layer was washed three times with a saturated salt solution and the ether removed on a steam bath. The residue was distilled in vacuo using a hyvac oil pump.

(b) Reduction of the nitro compound to the amine.

To the nitro compound, placed in a flask fitted with a reflux condenser was added 30 grams of mossy tin for each one-tenth mole of compound. Eighty ml. of concentrated hydrochloric acid (for each 1/10 mole of compound)

Note: The para position of the entering nitro group has been well established by previous workers in this laboratory (2,98). was added in small portions through the mouth of the condenser, the flask being shaken after each addition. After the vigorous reaction had subsided, the flask was heated on a steam bath for one-half hour.

Ice and sufficient concentrated sodium hydroxide to dissolve most of the tin hydroxide that precipitated were then added. The solution was then extracted three times with ether and the combined ether extracts washed til clear with a saturated salt solution. The ether was evaporated on a steam bath and the residue distilled under reduced pressure.

(c) Conversion of the amine to phenol.

For each one-tenth mole of amine, placed in a beaker, was added a hot solution of 11 ml. of concentrated sulfuric acid dissolved in 50 ml. of water. The solution was stirred well with a thermometer and placed in an ice-salt bath. Ice was added to the solution and when the temperature of the latter had dropped below zero degrees centigrade, a saturated aqueous solution of eight grams of sodium nitrite was added slowly and with stirring. The temperature was maintained at or below zero degrees centigrade during this addition. When all the sodium nitrite had been added, the solution was stirred until all the suspended solid amine sulfate dissolved. When all, or nearly all, the solid had dissolved, two grams of urea (for each 1/10 mole of compound), dissolved in a minimum of water, was slowly added. The solution was then permitted to stand for about ten minutes and then

steam-distilled by allowing it to drop slowly on a boiling, dilute, sulfuric acid solution through which steam was being passed. The reaction mixture was steam-distilled until no more phenol came over. The distillate was saturated with salt, cooled, and extracted twice with ether. The ether was evaporated on a steam bath and the residue distilled in vacuo.

(d) Preparation of the Alpha naphthylurethane of the phenol (128).

1-2 grams of the phenol was treated with half its volume of Alpha naphthylisocyanate. The reaction was catalyzed by the addition of a few drops of an anhydrous ether solution of trimethyl amine (kept anhydrous over sodium sulfate). The mixture was shaken well, stoppered with a cork to which was attached a drying tube, and placed on a steam bath for five to fifteen minutes. On cooling, the solution solidified completely and the solid was recrystallized to constant melting point from skellysolve (B.Pt. 60-70 degrees Centigrade)(a higher boiling petroleum ether portion) or ligroin.

Table II

Para Nitro Derivatives of the Monoalkylbenzenes

Alcohol Condensed with Benzene	B. Pt. of Nitro Compd.	At. Pressure
Pentanol-2	112-114°C.	2 mm.
Pentanol-3	111-117°C.	2 mm.
2-Methylbutanol-3	113-118°C.	2 mm.
Hexanol-2	133-141°C.	3 mm.
2-Methylpentanol-4	134-138°C.	3 mm.
Hexanol-3	122.5-124°C.	2 mm.
3-Methylpentanol-2	124-127°C.	2 mm.
2-Methylpentanol-3	123.5-127°C.	2 mm.
2,2-Dimethylbutanol-3 ^x	117-123°C.	2 mm.
Heptanol-2	154-156°C.	3 mm.
Heptanol-3	143-149°C.	3 mm.
Heptanol-4	146-150°C.	3 mm.
2-Methylhexanol-3	140-146°C.	3 mm.
3-Methylhexanol-4	143-148°C.	3 mm.
2-Methylhexanol-4	136-143°C.	3 mm.
2-Methylhexanol-5	139-142°C.	3 mm.
3-Methylhexanol-2	135-139°C.	3 mm.
2,2-Dimethylpentanol-3	139-141°C.	3 mm.

XAnal.	for	Nitrogen:	Found, $N =$	6.68	per d	cent	
			Calculated,	N =	6.73	per	cent

Table III

Para Amino Derivatives of the Monoalkylbenzenes

.

Alcohol Condensed with benzene	B. Pt. of Amine	Pressure
Pentanol-2	101-102°C.	2 mm.
Pentanol-3	103-105.5°C.	2 mm.
2-Methylbutanol-3	99-103°C.	2 mm.
Hexanol-3	111-114°C.	2 mm.
2-Methylpentanol-4	124°C.	3 mm.
Hexanol-3	121.5°C.	3 mm.
5-Methylpentano1-2	112-113°C.	2 mm.
2-Methylpentanol-3	111-113°C.	2 mm.
2,2-Dimethylbutanol-3 ^X	115-118°C.	2 mm.
Heptanol-2	124-127°C.	2 mm.
Heptanol-3	124-126°C.	2 mm.
Heptanol-4	129-130°C.	2 mm.
2-Methylhexanol-3	127-129°C.	2 mm.
3-Methylhexanol-4	124-126°C.	2 mm.
2-Methylhexanol-4	120-124°C.	2 mm.
2-Methylhexanol-5	123-127°C.	2 mm.
3-Methylhexanol-2	120-125°C.	2 mm.
2,2-Dimethylpentanol-3	120-126°C.	2

XAnel.	for	Nitrogen:	Found, N = 7.74 per cent	
		-	Calculated, N = 7.87 per cen	t

Table IV

Para Hydroxy Derivatives of the Monoalkylbenzenes

Alcohol Condensed with Benzene	B. Pt. of Phenol	Pressure	N.Pt.
Pentano1-2	100-104°C.	2 mm.	
Pentanol-3	100°C.	2 mm.	
2-Methylbutanol-3	110-111°C.	3 mm.	89 -90°C.
Hexano1-2	108-113°C.	2 mm.	
2-Methylpentanol-4	<u>115-119°</u> C.	3 mm.	
Hexanol-3	117-119°C.	3 mm.	
3-Methylpentanol-2	117-121°C.	3 mm.	
2-Methylpentanol-3	116-119°C.	3 mm.	
2,2-Dimethylbutanol-3X	115-118°C.	3 mm.	122°C.
Heptanol-2	120-122°C.	2 mm.	
Heptanol-3	125-127°C.	2 mm.	
Heptanol-4	117-121°C.	2 mm.	
2-Methylhexanol-3	123-127°C.	3 mm.	
3-Methylhexanol-4	128-131°C.	3 mm.	
2-Methylhexanol-4	122-129°C.	3 mm.	
2-Methylhexanol-5	123-126°C.	3 mm.	
3-Methylhexanol-2	121-125°C.	3 mm.	
2,2-Dimethylpentanol-3	131-133°C.	3 mm.	

XAnal. for C and H: Found, C = 80.63 per cent, H = 10.35 per cent Calculated, C = 80.85 per cent, H = 10.18 per cent

Table V

Alpha Naphthylurethanes from the Monoalkylbenzenes

Alcohol Condensed with Benzene	M. Pt. of Urethene	% N
Pentanol-2	99-99.5°C.	4.13 ⁸
Pentanol-3	97.5-99.5°C.	4.18 ⁸
2-Methylbutanol-3	125-126.5°C.	4.17 ⁸
Hexanol-2	95-96.5°C.	3.99 ^b
2-Methylpentanol-4	108-112°C.	3.970
Hezanol-3	95 -96*C .	4.03b
3-Methylpentanol-2	103-105.5°C.	3.99D
2-Methylpentanol-3	123.5-125°C.	4.00b
2,2-Dimethylbutanol-3	109-110°C.	3.98 ^b
Heptanol-2	94.5-96.5°C.	3.82 ⁰
Heptanol-3	95.5-97.5°C.	3. 86 ⁰
Heptanol-4	93.5-94°C.	3.82 ⁰
2-Methylhexanol-3	125-126°C.	3.83 ^e
3-Methylhexanol-4	101-103°C.	3.87°
2-Methylhexanol-4	119-121°C.	3.79°
2-Nethylhexanol-5	119-121°C.	3.86°
3-Methylhexanol-2	106-108°C.	3.83 ⁰
2,2-Dimethylpentanol-3	114-115°C.	3.790

Calculated: (a) N = 4.12 per cent (b) N = 4.03 per cent (c) N = 3.87 per cent

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V. Determination of the Nature of the Monoalkylbenzenes

The monoalkylbenzenes obtained in these condensations may be divided roughly into three classes:

- (a) pure monoalkylbenzenes obtained from the secondary alcohol without rearrangement,
- (b) tertiary alkylbenzenes, with the possibility of a small amount of secondary alkylbenzene as impurity, obtained from a secondary alcohol with branching adjacent the hydroxyl group,
- (c) mixtures of two or more alkylbenzenes obtained from secondary alcohols which may or may not have branching in their molecules.

Two members of the first class, cumene and sec.-butylbenzene, were shown to be formed without rearrangement from their corresponding secondary alcohols by comparison of the melting points of their monoacetamino derivatives with those in the literature (126-127).

The structure of the tertiary alkylbenzenes was proven by converting these compounds to their corresponding para hydroxy derivatives. Alpha naphthylurethanes were prepared from the latter and mixed melting points were taken with the alpha naphthylurethanes prepared from the tertiary alkylphenols obtained by previous workers in this laboratory by the condensation of tertiary alcohols with phenol in the presence of aluminum chloride. Curtis (99) prepared the alpha naphthylurethanes of the tertiary hexyl phenols condensed by Hsieh (2). The author prepared the alpha naphthylurethanes of Hsieh's para tert.-amylphenol and Hedrick's methylethyl-n-propyl-para-hydroxyphenylmethane, dimethyl-n-butyl-para-hydroxyphenylmethane and methylethylisopropyl-para-hydroxyphenylmethane. The last three derivatives were found to have higher melting points than those reported by Hedrick and are listed, together with the aforementioned data in Tables VI. and VIII.

To get some idea of the nature of those alkylbenzenes which were mixtures, the moncalkylbenzenes which would have been obtained from the secondary alcohols if no rearrangement occurred, were prepared by independent synthesis. This was done by a modification of the method of Klages (37) which consisted of treating an alkyl Grignard compound with asetophenone or its homologues, forming a tertiary alcohol. The alcohol was reduced to the hydrocarbon by first forming an olefin by splitting out water, and then reducing the unsaturated compound with sodium and absolute ethyl alcohol. This procedure (Procedure I) gave a pure alkylbenzene which was converted to the para hydroxy derivative by the procedure already outlined (see Section IV under Experimental). The alpha naphthylurethanes of these phenols were then prepared and compared with those obtained in the condensation, mixed melting points being performed wherever feasible. A more convenient method (Procedure II) for obtaining the alpha naphthylurethanes of the para hydroxyphenylalkanes consisted in using the para methoxy derivatives of acetophenone and

its homologues, propiophenone and butyrophenone. These compounds, when treated with the Grignard reagent, reduced and demethylated, gave the alkylphenol directly, avoiding the lenghthy nitration, reduction and diazotization scheme. Procedure I.

The Grignard reagent was prepared by the technique previously described (Section II under Experimental). The crude product was converted into the olefin, without isolating the tertiary alcohol formed, by refluxing, using a Dean and Stark moisture trap (129) until no more water collected. This usually took but a few minutes. The product was then distilled.

The unsaturated compound was reduced by dissolving 0.25 mole of olefin in 375 ml. of absolute ethyl alcohol and treating the boiling solution with 40 grams of sodium, added in several large pieces at intervals. The solution was refluxed gently on a steam bath, using anhydrous precautions, during the treatment with sodium. When all the sodium had dissolved, water was added in great excess, and the mixture extracted three times with ether. The ether layer was then washed free of alcohol repeatedly with a saturated salt solution until its volume remained constant. The ether was then removed on a steam bath and the residue, after cooling, shaken thoroughly with a saturated potassium permanganate solution. The excess permanganate was then reduced by the addition of solid sodium bisulfite and the alkylbenzene extracted with ether. After evaporation of the ether on a steam bath, the residue was distilled at atmospheric pressure. The alkylbenzene was then converted to the phenol by the procedure in Section IV under Experimental and the alpha naphthylurethane of the latter was prepared.

- (1) 3-Phenylpentane (39), B₇₄₁ = 189-191°C.
 Prepared from diethylphenylcarbinol (prepared by Hughes (97)).
 - (a) Intermediate unsaturated compound (39), $B_{741} = 199-201^{\circ}C$.
 - (b) Para Nitro derivative, B_g = 110-115°C.
 Found: Nitrogen = 7.18 per cent
 Calculated: Nitrogen = 7.25 per cent
 - (c) Para Amino derivative, B₈ = 107-116°C.
 Found: Nitrogen = 8.43 per cent
 Calculated: Nitrogen = 8.58 per cent
 - (d) Para Hydroxy derivative, B₄ = 108-117°C.
 M.Pt. = 75.5°C. This compound has been reported as melting at 79-80°C. (133).
 - (e) Monoacetamino derivative of the alkylbenzene
 M.Pt. = 144°C. Ipatieff and Schmerling (127) report
 a melting point of 145-146°C.
 - (f) Alpha naphthylurethane, M.Pt. = 114°C. Found: Nitrogen = 4.07 per cent Calculated: Nitrogen = 4.12 per cent
- (2) 2-Phenylpentane (37), B₇₆₂ = 191-193°C.
 Prepared from propyl bromide and acetophenone.
 - (a) Intermediate unsaturated compound (37)

 $B_{762} = 202 - 204°C.$

- (b) Para Nitro derivative, B₂ = 112-118°C.
 Found: Nitrogen = 7.21 per cent
 Calculated: Nitrogen = 7.25 per cent
- (c) Para Amino derivative, B₂ = 101-104°C.
 Found: Nitrogen = 8.49 per cent
 Calculated: Nitrogen = 8.58 per cent
- (d) Para Hydroxy derivative, B_B = 101°C.
 Found: C = 80.83 per cent, H = 10.33 per cent
 Calculated: C = 81.19 per cent, H = 10.48 per cent
- (e) Alpha naphthylurethane, M.Ft. = 100-101°C. Found: Nitrogen = 4.09 per cent Calculated: Nitrogen = 4.12 per cent
- (3) 2-Phenylhexane (43), B₇₃₇ = 210°C.
 Prepared from n-butyl bromide and acetophenone.
 - (a) Intermediate olefin, $B_{727} = 219-224^{\circ}C_{\bullet}$
 - (b) Para Nitro derivative, $B_2 = 120-128^{\circ}C$. Found: Nitrogen = 6.62 per cent Calculated: Nitrogen = 6.73 per cent
 - (c) Para Amino derivative, $B_{2} = 112-116$ °C. Found: Nitrogen = 7.78 per cent Calculated: Nitrogen = 7.82 per cent
 - (d) Para Hydroxy derivative (134), B₂ = 110-112°C.
 - (e) Alpha naphthylurethane, M.Pt. = 108-109°C.
 Found: Nitrogen = 3.98 per cent
 Calculated: Nitrogen = 4.03 per cent
- (4) 4-Phenylheptane, B₇₆₀ = 221-224°C.
 Prepared from n-propyl bromide and ethyl benzoate.

Found: C = 88.37 per cent, H = 11.51 per cent Calculated: C = 88.56 per cent, H = 11.44 per cent

- (a) Intermediate clefin, $B_{B} = 80-95^{\circ}C$.
- (b) Para Nitro derivative, B_R = 140-143°C.
 Found: Nitrogen = 6.29 per cent
 Calculated: Nitrogen = 6.33 per cent
- (c) Para Amino derivative, B₂ = 128-132°C.
 Found: Nitrogen = 7.25 per cent
 Calculated: Nitrogen = 7.32 per cent
- (d) Para Hydroxy derivative, $B_2 = 121-123^{\circ}C$. Found: C = 80.78 per cent, H = 10.27 per cent Calculated: C = 81.19 per cent, H = 10.48 per cent
- (e) Alpha naphthylurethane, M.Pt. = 104-105°C.
 Found: Nitrogen = 3.88 per cent
 Calculated: Nitrogen = 3.87 per cent
- (5) 2-Methyl-4-phenylpentane (40), B₇₈₅ = 197-198°C.
 Prepared from isobutyl bromide and acetophenone.
 - (a) Intermediate olefin (40), $B_{736} = 213-225^{\circ}C_{\bullet}$
 - (b) Para Nitro derivative, $B_2 = 132^{\circ}C$. Found: Nitrogen = 6.66 per cent Calculated: Nitrogen = 6.73 per cent
 - (c) Para Amino derivative, B₂ = 113-115°C.
 Found: Nitrogen = 7.83 per cent
 Calculated: Nitrogen = 7.87 per cent
 - (d) Para Hydroxy derivative, $B_{2} = 109-110^{\circ}C$. Found: C = 80.37 per cent, H = 10.18 per cent

Calculated: C = 80.85 per cent, H = 10.18 per cent
(e) Alpha naphthylurethane, M.Pt. = 107°C.
Found: Nitrogen = 3.96 per cent
Calculated: Nitrogen = 4.03 per cent

Procedure II.

The method was the same as the preceeding but instead of acetophenone, para methoxyacetophenone (25), para methoxypropiophenone (24,130), and para methoxybutyrophenone were used and the para hydroxyphenylalkanes prepared without preparing the intermediary products. After the reduction with sodium and alcohol, the product was demethylated without isolating the ether. In the hydrolysis of the ether, 10 grams of the product was refluxed with 50 grams of phenol and 100 ml. of 48 per cent hydrobromic acid for 4 hours (131). The mixture was then extracted with ether, the ethereal layer washed three times with water to remove any acid and the ether removed on a steam bath. The product was then vacuum-distilled, discarding the lower boiling phenol. The alpha naphthylurethane of the phenol was then prepared.

(1) 3-Para hydroxyphenylhexane, $B_4 = 133^{\circ}C_{\bullet}$

Prepared from n-propyl bromide and para methoxypropiophenone.

Found: C = 80.67 per cent, H = 10.11 per cent Calculated: C = 80.85 per cent, H = 10.18 per cent Alpha naphthylurethane, M.Pt. = 95-95.5°C. Found: Nitrogen = 3.99 per cent Calculated: Nitrogen = 4.03 per cent (2) 3-Para hydroxyphenylheptane, $B_2 = 117^{\circ}C$. Prepared from n-butyl bromide and para methoxypropio-

phenone.
Found: C = 81.07 per cent, H = 10.31 per cent
Calculated: C = 81.19 per cent, H = 10.48 per cent
Alpha naphthylurethane, M.Pt. = 100°C.
Found: Nitrogen = 3.79 per cent
Calculated: Nitrogen = 3.87 per cent

- (3) 2,2-Dimethyl-3-para hydroxyphenylpentane, B₂ = 108°C. Prepared from tert.-butyl chloride and para methoxypropiophenone.
 Found: C = 80.87 per cent, H = 10.64 per cent
 Calculated: C = 81.19 per cent, H = 10.48 per cent
 Alpha naphthylurothane, M.Pt. = 118-119°C.
 Found: Nitrogen = 3.82 per cent
 Calculated: Nitrogen = 3.87 per cent
- (4) 2-Methyl-4-para hydroxyphenylhexane, B₂ = 111°C.
 Prepared from isobutyl bromide and para methoxypropiophenone.
 Found: C = 81.49 per cent, H = 10.29 per cent
 Calculated: C = 81.19 per cent, H = 10.48 per cent
 Alpha naphthylurethane, M.Pt. = 117-117.5°C.

Found: Nitrogen = 3.81 per cent

Calculated: Nitrogen = 3.87 per cent

 (5) 3-Methyl-2-para hydroxyphenylpentane, B₃ = 120-123.5°C.
 Prepared from sec.-butyl bromide and para methoxyacetophenone. Found: C = 80.71 per cent, H = 9.99 per cent Calculated: C = 80.85 per cent, H = 10.18 per cent Alpha naphthylurethane, M.Pt. = 100-101°C. Found: Nitrogen = 3.95 per cent Calculated: Nitrogen = 4.03 per cent

(6) 2-Para hydroxyphenylheptane, B₄ = 140°C.
Prepared from n-amyl bromide and para methoxyacetophenone.
Found: C = 80.78 per cent, H = 10.53 per cent

Calculated: C = 81.19 per cent, H = 10.48 per cent Alpha naphthylurethane, M.Pt. = 115-116°C. Found: Nitrogen = 3.85 per cent Calculated: Nitrogen = 3.87 per cent

(7) 2-Methyl-5- para hydroxyphenylhexane, B₂ = 123.5°C. Prepared from isoamyl bromide and para methoxyacetophenone.
Found: C = 80.79 per cent, H = 10.20 per cent Calculated: C = 81.19 per cent, H = 10.48 per cent Alpha naphthylurethane, M.Pt. = 125°C.
Found: Nitrogen = 3.81 per cent

Calcula ted: Nitrogen = 3.87 per cent

(8) 3-Methyl-2-para hydroxyphenylhexane, $B_2 = 123-125^{\circ}C$. Prepared from sec.-amyl chloride and para methoxyacetophenone. Found: C = 80.77 per cent, H = 10.37 per cent

Calculated: C = 81.19 per cent, H = 10.48 per cent Alpha naphthylurethane, M.Pt. = 110-111°C. Found: Nitrogen = 3.82 per cent

Calculated: Nitrogen = 3.87 per cent

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(9) 2,2-Dimethyl-3-para hydroxyphenyl butane, B<sub>4</sub> = 123°C.
M.Pt. = 120-121°C.
Prepared from tertiary butyl chloride and para methoxy-
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acetophenone.

Found: C = 80.94 per cent, H = 10.64 per cent

Calculated: C = 81.19 per cent, H = 10.48 per cent

Alcohol Condensed with Benzene	M.Pt. of Mono- acetamino Derivative	M.Pt. of D1- acetamino Derivative	Fure Alkyl- benzene	Monoacetamino Derivative	Diacetamiro Derivative
Propanol-2	105°C.(126)	213-214°C. (126)	Cumene	106°C.(126)	216°C. (126)
Butanol-2	126°C.(126)		2-Fhenyl- butane	126°C+(126)	
	M.Pt. of para H phenyl Derivs	ydroxy- Phe tive	lou	M. Pt.	of Phenol
2,2-Dimethyl- butanol-3	128°C. (a) 2,2 hyd	-Dimethyl-3- roxyphenylbu	para 120-1 tane	(q) • 0 。1 81

(a) and (b), mixed M.Pt. showed no depression.

Table VI

Monoalkylbenzenes from Secondary Alcohols without Rearrangement

Alcohols	
Secondary	
from	
Monoalky lbenzenes	
Tertlary	

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M.Pt. of M.Pt. of Alpha Phenol Naphthyl Urethane	95°C.(60) 127°C.(b)	123.5-124.5°C.(d)	125 - 126°0.(f)	101-102.5°C. (h)
Fure Phenol	2-Methyl-2- para hydroxy- phenylbutane	2-Methyl-2- para hydroxy- phenylpentane	2-Methyl-2- para hydroxy- phenylhexane	3-Methyl-3- para hydroxy- phenylhexane
M.Pt. of Alpha Naphthyl Urethane	125-126.5°C.(a)	123.5-125°C.(c)	125-127°C.(•)	101-103°C.(g)
M.Pt. of para Hydroxy Derivative	89 - 90°C.			
Alcohol Condensed with Benzene	2-Methylbutanol-5	2-Methylpentanol-3	2-Methylhexanol-3	3-Methylhexanol-4

Mixed melting points of (a+b), (c+d), (e+f), fg+h), showed no depression (b) prepared by author from Hsieh's phenol (c) prepared by Curtis from Hsieh's phenol (f) and (h) prepared by author from Hedrick's phenols

	Mixtures of Alkylbense	nes from Secondary Alcohols	
Alcohol Condensed with Benzene	M.Pt. of Urethans Derivative	Synthetic Phenol	M. Pt. of Urethane Derivative
Pentanol-3	97.5-98.5°C.	3-para hydroxyphenyl- pentane	114°C.
Pentanol-2	9 9- 99 • 8°0 •	2-para hydroxyphenyl- pentane	100-101-6.
Hexanol-2	9 5-96.5°C .	2-para hydroxypheny1- hexane	108-109°C.
Hexanol-3	95-96°C.(a)	3-para hydroxypheny 1- heptane	95-95.5°C.(b)
Heptenol-2	94 •5 •96 • 5°C•	2-para hydroxyphenyl- heptane	115-116°C.
Heptanol-3	95.5 . 97.5°C.	3-para hydroxyphenyl- heptane	100°C.
Heptanol-4	93.5-94°C.	4-para hydroxypheny1- heptane	104-105°C.
3-Methylpentanol-2	103.5-105.5°C.	3-methy1-2-para hydroxy- phenylpentane	100-101-00
2-Methylpentenol-4	108-112°C.	2-methyl-4-para hydroxy- phenylpentane	107°C.

from

Table VIII

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(con. on next page)

Alcohol Condensed with Benzene	M.Pt. of Urethane Derivative	Synthetic Phenol	M.Pt. of Urethane Derivative
2-Methylhexanol-5	119-221°C. (c)	2-methyl-5-para hydroxy- phenylhexane	lesoc.
2-Methylhexanol-4	119-121°C. (d)	2-methyl-4-para hydroxy- phenylhexane	117-117.5°C.
2,2-Dimethylpentanol-3	114-115°G.	2,2-dimethyl-3-para hydroxyphenylpentane	118-119°C.
3-Methylhexanol-2	106-108°C.	3-methyl-2-para hydroxy- phenylhexane	110-111°C.

Mixtures of Alkylbenzenes from Secondary Alcohols

Table VIII (con.)

Mixed melting points: (a+b) = 91-92°C., (a+d) = 117.5-120°C.

DISCUSSION

The results of this investigation can be reconciled with the catinoid mechanism (134) of Fridel-Crafts condensations or the olefin mechanism of McKenna and Sowa (67). Either path would yield the same product, assuming the addition of the phenyl group to be in accordance with Markownikoff's rule.

This work is in direct contrast with the statement by Ipatieff (72) that a luminum chloride causes no rearrangement in the condensation of secondary alcohols with benzene. He based this conclusion on only one reaction, the formation of n-propylbenzene in the condensation of n-propyl alcohol with benzene. It is interesting, in this connection to point out once again the work of Bowden (62) who found that n-propyl esters formed n-propylbenzene while n-butyl esters gave sec.-butylbenzene. This work is in agreement with that of the Author's who used alcohols instead of esters.

In harmony with the present results is the work of Esterdahl (98) who condensed the secondary anyl alcohols with phenol in the presence of aluminum chloride. With either pentanol-2 or pentanol-3, he obtained a mixture of the 2- and 3-para hydroxyphenylpentanes. With 2-methylbutanol-3 he, too, obtained rearrangement to the tert.amylaryl compound.

Gurtis' (99) work, also is in agreement with this work. With hexanol-2 and hexanol-3, he obtained, in his condensations

with phenol in the presence of aluminum chloride, mixtures of the 2- and 3-para hydroxyphenylhexanes. With 2-methylpentanol-3, he obtained the tertiary phenol, 2-methyl-2para hydroxyphenylpentane. He, too, obtained a mixture in the condensation of 2-methylpentanol-4, though the composition of his mixture must be somewhat different from that of the Author's because the melting point of his alpha naphthylurethane is a few degrees higher. These results are in agreement with those presented here where benzene was used in place of phenol.

However, where Curtis got rearrangement to the tertiary phenol in the case of 3-methylpentanol-2, the present work yielded a mixture, probably of the secondary and tertiary alkylbenzenes. In addition, where Curtis got migration of a methyl group and formation of a tertiary phenol, using pinacolyl alcohol, the author obtained the sec.-alkylbenzene with no rearrangement.^X This discrepancy probably is due to the difference in reactivity of benzene and phenol in condensations, each reacting by a different mechanism.

Although the temperature in the condensations run by Curtis and Esterdahl was much higher than that in the present work, this factor is not responsible for the difference in results. This was shown by condensing pentanol-3, 3-methylpentanol-2, 3-methylhexanol-2, 4-methylpentanol-2, 3,3dimethyabutanol-2, and 2,2-dimethylpentanol-3 with benzene

XRepetition of this reaction of Curtis' by the author, using his conditions and reactants, gave the same product as he obtained. at 50°C. The alpha naphthylurethanes, prepared from the alkylbenzenes obtained in these condensations, melted at exactly the same temperatures as the urethanes from the products obtained at the lower temperature. This would seem to indicate that, under the conditions of this experiment, temperature plays no, or very little, role in determining the nature of the products.

Tsukervanik's (100) condensation of isoamyl alcohol with phenol to give tertiary anyl phenol among other products. would indicate that an olefin might be the intermediate in the condensation. In this case, however, the double bond, if it were formed, shifted to a new position in order to give the tertiary product. This migration of a double bond during a condensation reaction has been observed by Ipatieff (72), too, when sulfuric acid was the condensing agent. The migration may actually have occurred in some of the condensations described in this paper. Where branching occurs at a position remote from the carbinol group. some tert .- alkylbenzene may be admixed with the mixture of secondary alkylbenzenes. The great similarity in the physical and chemical properties of the alkylbenzenes renders remote the chances of separating the constituents of these mixtures.

Using a different condensing agent, boron fluoride, Toussaint and Hennion (71) came to the same conclusion when they alkylated benzene with primary alcohols. They obtained sec.-alkylbenzenes only and concluded, "While the reaction

mechanism is in doubt, the products are those which would be formed by dehydration of the alcohol to olefin and addition of benzene according to Markownikoff's rule."

Simons and Archer (58) dehydrated sec.-amyl alcohol to get a mixture of pentene-1 and pentene-2 which was condensed with benzene, hydrogen fluoride acting as catalyst. The monoacetamino derivative of the alkylbenzene mixture which they obtained melted at 119-120°C. In the present work, pentanol-2 gave a product whose monoacetamino derivative melted at 118-119°C., while the product from pentanol-3 had a monoacetamino derivative that melted at 121-122°C. The pure alkylbenzenes, 2- and 3-phenylpentanes have monoacetamino derivatives that melt at 107°C. and 145-146°C. respectively (127). Simons and Archer concluded then that their product was probably "a mixture of the beta and gamma phenylpentanes."

Ipatieff (72) has recently published an article which contains a temperature-composition graph. The melting points of various mixtures of the 2- and 3-phenylpentanes were plotted against the percentage composition of these two isomers in the mixture. The melting points of these mixtures were shown to lie between the values of the pure alkylbenzenes. This is in agreement with the work of Simons and Archer as well as with that of the author. According to this graph, the alkylbenzene mixture from pentanol-2 and benzene should consist of about 65 per cent of 2-phenylpentane and 35 per cent of 3-phenylpentane while the product

from pentanol-3 should be 55 per cent 2-phenylpentane and 45 per cent 3-phenylpentane.

Ipatieff and coworkers (60) have shown that when benzene is alkylated, in the presence of sulfuric acid, with an olefin having branching on one of the carbons in the double bond, the product is exclusively the tertiary alkylbenzene. This may not be so in the case of the alcohols having branching on the carbon adjacent the carbinol group: 3-methylpentanol-2 and 3-methylhexanol-2 gave mixtures of alkylbenzenes whose alpha naphthylurethanes had melting points intermediate with those of the corresponding secondary and tertiary compounds. That all the tert .- alkylbenzenes obtained by the author from secondary alcohols were admixed with a little sec .- alkylbenzene may be indicated by the repeated recrystallizations that were required before their alpha naphthylurethanes gave constant melting points. Furthermore, the tertiary amylbenzene, prepared from 2,2dimethylbutanol-3 gave a monoacetamino derivative (M.Pt. = 137-138°C.) that melted a few degrees lower than that reported in the literature (60) for the monoacetamino derivative of synthetic tert.-amylbenzene (M.Pt. = 141-142°C.). This was probably due to the presence of 3-methyl-2-phenyl butane in very small amounts. The latter's moncacetamino derivative, while possessing a higher melting point (M.Pt. = 147-148°C.), if present in small enough amounts, could act as an impurity and depress the melting point. Though the formation of this secondary product would not be in

accordance with Markownikoff's rule, it frequently happens in addition reactions that a small amount of product is formed in opposition to the rule. The same may hold true in the condensation reaction.

It has already been mentioned that in the case of alcohols having extreme branching on the carbon atom adjacent the carbinol group, as in pinacolyl alcohol, migration of a methyl group occurs in the condensation with phenol, and a tertiary alkylphenol results. This does not occur when benzene is used instead of phenol. The phenyl group replaces the hydroxy group. In the case of 2,2-dimethylpentanol-3, a similar situation occurs, only here olefin formation without any rearrangement of methyl groups is possible. The alpha naphthylurethane of the product has a melting point of 114-115°C. while that of the urethane of 2.3-dimethyl-3-para hydroxyphenylpentane melts at 124-125.5°C. and that of 2.3-dimethyl-2-para hydroxyphenylpentane melted at 122-123°C., according to Hedrick. It is possible that the product is a mixture of these rearranged alkylbenzenes, possibly admixed with one or both of the two possible sec .alkylbenzenes which could be formed without migration of a methyl group. In view of the fact that the lower homologue. pinacolyl alcohol, underwent no change in condensing with benzene, it seems more likely that the product consists of the sec.-alkylbenzenes formed from an intermediary olefin, namely 3- and 4-phenyl-2,2-dimethylpentanes. This may be summarized by the following equations:

$$\begin{array}{cccc} CH_{3} & CH_{3} & CH_{3} \\ CH_{3} - C - CH - CH_{3} + C_{3}H_{6} & \longrightarrow & CH_{3} - C - C - CH_{3} \\ CH_{3} & OH & & C_{3}H_{5} & H \end{array}$$

(2) Author's Work

(a)
$$CH_{s} - C - CH - CH_{s} + C_{s}H_{s} \xrightarrow{AlCl_{s}} CH_{s} - C - C - CH_{s}$$

 $CH_{s} OH \xrightarrow{CH_{s} H_{s}} CH_{s} - C - C - CH_{s}$

(b)
$$CH_{3} = C + CH_{3} + CH$$

SUMMARY

- (1) Conditions have been worked out for condensing isopropyl alcohol with benzene in the presence of aluminum chloride to give a good yield of cumene.
- (2) Using these conditions, the secondary butyl, amyl, hexyl and some secondary heptyl alcohols were condensed with benzene.
- (3) The alkylbenzenes obtained by these condensations were converted to the corresponding para hydroxy derivatives by nitration, reduction of the nitro group to amine, and diazotization. Alpha naphthylurethanes of the para hydroxy compounds were also prepared as well as some acetamino derivatives.
- (4) A number of pure sec.-alkylbenzenes and sec.-alkylphenols were prepared by synthesis and their alpha naphthylurethanes made.
- (5) By comparison of the melting points of the acetamino derivatives of the alkylbenzenes, of the phenols and of the alpha naphthylurethanes with those synthesized and with those of the prepared tertiary alkylphenols, the following facts have been established:
 - (a) Isopropyl alcohol, sec.-butyl alcohol and pinacolyl alcohol gave the corresponding secondary alkylbenzenes in pure form.
 - (b) 2-Methylbutanol-3, 2-methylpentanol-3, 2-methylhexanol-3 and 3-methylhexanol-4 gave tertiary

alkylbenzenes.

- (c) The straight chain carbinols, as well as those having a branched methyl group remote from the carbinol group, gave mixtures of the secondary alkylbenzenes.
- (d) 3-Methylpentanol-2 and 3-methylhexanol-2 gave mixtures consisting probably of the sec.- and tert.alkylbenzenes.
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