THE CONDENSATION OF SOME DIALKYL ARYL CARBINOLS WITH BENZENE AND PHENOL IN THE PRESENCE OF ALUMINUM CHLORIDE

by

FRANCIS ALOYSIUS HUGHES

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Introduction

In this laboratory, since 1916, Huston and co-workers have worked with the condensation of alcohols with benzene and phenol in the presence of aluminum chloride. They have investigated the primary, secondary, and tertiary aliphatic alcohols. In the aromatic series of alcohols, they have also included the primary, secondary, and tertiary.

In continuing the study of aluminum chloride condensations, the mixed aliphatic-aromatic alcohols are under investigation. Some dialkyl aryl alcohols were condensed with benzene and phenol in the presence of aluminum chloride.

Historical

Condensation reactions, in which alcohols and various compounds combine, have been known for quite some time. The reactions are brought about by the use of a catalyst. A great number of catalysts have been employed; namely, zinc chloride, sulfuric acid, magnesium chloride, acetic acid, phosphoric acid, perchloric acid, and aluminum chloride. Aluminum chloride is the catalyst with which this paper is concerned, and its history in relation to its influence on condensation reactions between alcohols and the benzene nuclei shall be considered.

In 1897, Nef (1) condensed benzyl alcohol and benzene in the presence of aluminum chloride and obtained diphenyl methane. The work was repeated by Huston and Friedmann (2) and a thirty per cent yield of diphenyl methane was reported.

Since Nef's first condensation, many have been reported. Of the primary saturated aliphatic alcohols Huston and Sager (3) tried to condense methyl, ethyl, propyl, n-butyl, iso-butyl, and iso-amyl alcohols with benzene using aluminum chloride as a catalyst; no condensation was noted. Huston and Hsieh (4) repeated and extended this work, in place of benzene they used phenol, but no condensation was noted in either case. In the unsaturated primary aliphatic series, allyl alcohol gave a sixteen per cent yield of the condensation product with benzene (3) and also condensed with phenol (5).

The aliphatic secondary alcohols condense with benzene giving yields of from twenty-five to thirty per cent. Huston and Hsieh (4) condensed isopropyl and secondary butyl alcohols as well as methyl

propyl and methyl isopropyl carbinols with benzene. Tzukervanik and co-workers (6) report the condensation of simple secondary alsohols with benzene and toluene. At the present time, the condensations of isopropyl, secondary butyl, the secondary amyls, and the secondary hexyl alcohols with phenol are being studied in this laboratory by Monroe, Esterdahl, and Curtis.

Tertiary aliphatic alcohols condense readily with both benzene (7) and phenol. Huston and Hsieh (4) condensed tertiary butyl, tertiary amyl, and tertiary hexyl alcohols with phenol, and Huston and Fox (8) extended this work to include benzene. Tzukervanik (6) reported the condensation of tertiary alcohols with benzene and toluene obtaining similar results. The tertiary heptyl alcohols were condensed with benzene by Huston and Einder (9) and with phenol by Huston and Hedrick (10). The condensation of tertiary octyl alcohols with benzene have been reported by various authors working under Huston; namely, Schulati (11), Anderson (12), and Breining (13). Huston and Guile have condensed some tertiary dimethyl amyl carbinols with phenol (14).

In the aromatic alcohols, Huston and Friedmann (2) condensed benzyl alcohol with benzene and later Huston (15) extended this work using phenol, anisole, and phenetole in a similar manner. Huston, Lewis, and Grotemut (16) condensed phenol with diphenyl carbinol. When the tertiary alcohol, triphenyl carbinol (17), was tried with benzene, only triphenyl methane was obtained.

The mixed aliphatic-aromatic alcohols have been investigated by various workers. In the secondary alcohols, methyl phenyl and ethyl phenyl carbinols have been condensed with benzene by Huston and Friedmann (18) and with phenol by Huston, Lewis, and Grotemut (16).

Of the tertiary dialkyl aryl carbinols, dimethyl phenyl, methyl ethyl phenyl, and diethyl phenyl carbinols have been investigated by Macomber (19), and Welsh and Drake (20) have reported the condensation of dimethyl phenyl carbinol with phenol. With the tertiary diaryl alkyl alcohols, ethyl diphenyl carbinol, Huston and Wilsey (21), propyl diphenyl and isopropyl diphenyl carbinols, Huston and Hradel (22), gave only unsaturated products of the alcohols when subject to condensation with benzene. Welsh and Drake (20) reported the condensation of methyl diphenyl carbinol with phenol. At the present time, the condensation of ethyl diphenyl, propyl diphenyl, isopropyl diphenyl, n-butyl diphenyl, isobutyl diphenyl, secondary butyl diphenyl, tertiary butyl diphenyl, and n-amyl carbinols with phenol is being investigated in this laboratory by Jackson.

Other alcohols have been condensed with different compounds. Huston and co-workers (23) reported condensation of halogenated benzyl alcohols with halogenated phenols, cresols, and halogenated cresols. Huston and Goodemoot (24) condensed cyclobutyl, cyclopentyl, and cyclohexyl alcohols with benzene.

Theoretical

Work done by Huston and co-workers indicates that in all condensations between alcohols and aromatic hydrocarbons in the presence of aluminum chloride, the alpha carbon atom must be under strain. Thus, the hydroxyl group is activated due to the unstable bond between the carbon and oxygen atom. This bond is present in allyl alcohol (A) and benzyl alcohol (B), both of which condense with ease.

A

The electron pair between carbon and oxygen is attracted strongly by both atoms, forming the same type of bond as does a molecule of chlorine : Cl;Cl; which is unstable and very reactive.

в

In the primary (C), secondary (D), and tertiary (E) alcohols, attention is riveted on the carbon to oxygen bond.

This bond is unstable in tertiary alcohols, less so in secondary, and fairly stable in primary alcohols. This fact is borne out in the ease of replacing the hydroxyl group by the halogen of a halogen acid and also the ease of dehydration. Thus, the carbon to oxygen bond of tertiary alcohols can be compared to that found in a molecule of hydrogen chloride H :C1: which is highly reactive. In view of this, tertiary alcohols should condense very readily due to the active hydroxyl group, while secondary alcohols should condense less readily, and primary ones only under drastic conditions. A review of the literature shows this view to be true.

To explain the path of reaction in condensations, several mechanisms have been advanced, but none conclusively established. The data accumulated is not always comparable, as different catalysts, temperatures, and solvents were used. In discussing the mechanism, a tertiary alcohol will be used with the view that the same mechanism may or may not be similar for primary and secondary alcohols.

Tzukervanik and Nazarova (25) suggested a Friedel-Craft reaction in which the alkyl halide formed from the alcohol and aluminum chloride condensed with the hydrocarbon by means of the excess aluminum chloride present. Their scheme of reaction was as follows: $I - (CH_3)_3COH + AlCl_3 \longrightarrow AlCl_2OC(CH_3)_3 + HCl$

II - AlCl₂OC(CH₃)₃ \longrightarrow CH₃- \dot{C} = CH₂ + AlCl₂OH CH₃- \dot{C} = CH₂ + HCl \longrightarrow (CH₃)₃C-Cl

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

In criticizing this course, note that the presence of an aluminate is highly improbable, as it is not easy to replace the hydroxyl hydrogen of a tertiary alcohol. In addition, Hedrick (10) added the tertiary alcohol, normal butyl dimethyl carbinol, to aluminum chloride suspended in petroleum ether and noted that hydrogen chloride was given off almost instantaneously with the generation of heat. Thus, if Tzukervanik's idea holds, no hydrogen chloride should be evolved and condensation should give a normal yield, but the yield also was found to be much smaller than in ordinary condensations.

The dehydration of the alcohol to form an alkene was offered by McKenna and Sowa (26) as the path taken in condensations using boron trifluoride as the catalyst. For normal butyl alcohol the path is: $V - CH_3CH_2CH_2CH_2OH \longrightarrow BF_2 \longrightarrow CH_3CH_2CH = CH_2 + H_2O$

$$VI - CH_3CH_2CH = CH_2 + C_6H_5 \xrightarrow{BF_3} CH_3CH_2 - CHC_6H_5$$

It can be seen that normal and secondary alcohols give identical products as do iso- and tertiary alcohols.

Zinc chloride is the catalyst used by McGreal and Niederal (27) who claim a like mechanism. Welsh and Drake (28) use this course to explain the condensation of aryl-substituted carbinols with phenol using aluminum chloride as a catalyst. Benzyl alcohol, benzhydrol, and triphenyl carbinol, which cannot dehydrate, split water off by loosing the hydroxyl group of the alcohol and a nuclear hydrogen of the phenol.

Many workers (29) have reported condensations of unsaturated hydrocarbons with aromatic hydrocarbons using aluminum chloride as a catalyst. The work done favors the alkene-formation idea.

In defeat of the alkene-formation course, there is little evidence. It should be noticed that different catalysts and temperatures were employed from that of Huston's, who has shown that primary alcohols will not react with benzene in the presence of aluminum chloride under ordinary conditions.

Another plausible mechanism is the formation of an ether of phenol followed by rearrangement into the substituted phenol. Smith (30) reported the rearrangement of m-cresyl isopropyl ether, tertiary butyl-, isobutyl-, secondary butyl-, isopropyl-phenyl ethers and pcresyl isobutyl ethers when treated in the cold with equal molecular amounts of aluminum chloride. Others (31) have reported ether rearrangements in a similar manner. Thus, if the ether was formed in the reaction, it might rearrange into alkyl phenols. Merz and Weith (32) did report a yield of 10 - 12 per cent of diphenyl ether from aluminum chloride and phenol at reflux temperature. Niewland (33) obtained ethers and substituted ethers, using boron fluoride with phenol and methyl, ethyl and isopropyl alcohols.

Claisen (34) 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 phenyl alkyl ethers, under the conditions of formation, do not rearrange to alkyl phenols. Furthermore, Huston has reported good yields in the condensation of tertiary alcohols and benzene, anisole, and m-cresyl methyl ether (4) and the condensation of benzyl alcohol with anisole and phenetole (15) in which reactions there is no possibility of ether formation.

In this laboratory (35) work was started on a mechanism for aluminum chloride condensations based on addition products between aluminum chloride, alcohol, and phenol. The idea is not new, as addition products with aluminum chloride (36) have been reported as well as with other catalysts (37). The theory is that a complex molecule is formed between the outer shells of electrons of aluminum chloride and the reacting substances. The compound formed is not stable and rearranges to give other compounds or its starting products according to the reacting compounds and the conditions under which the experiment takes place. The theory is still too vague to draw definite conclusions.

Experimental Data

Materials

Magnesium turnings especially prepared for Grignard reactions were used after drying in an oven at 40°C for several days.

Benzene was thiophene free, C.P. grade.

Petroleum ether, B.P. 30-65°C.

Acetone was dried over sodium sulfate and was of C.P. grade. Methyl ethyl ketone was dried over sodium sulfate and was of

C.P. grade.

Phenol was Mallinckrodt's (crystals).

Aluminum chloride was Merck's Reagent white anhydrous sublimed. Diethyl ether was anhydrous for Grignard reactions.

Bromobenzene was made from bromine and benzene, B.P. 153°C.

Diethyl ketone was prepared by the oxidation of Eastman's diethyl carbinol using potassium dichromate and sulfuric acid (25), B.P. 101-102°C.

P-bromo anisole was prepared by the bromination of anisole, B.P. 232-233°C.

Dimethylphenyl Carbinol

In a dry, three-liter, three-necked, round-bottom flask fitted with a rubber-sealed stirrer, a reflux condenser with calcium chloride tube attached, and dropping funnel were placed 50 grams (2 moles) of magnesium turnings, a crystal of iodine, 100 ml. of anhydrous diethyl ether, and 14 grams of bromobenzene. The reaction started automatically and was externally cooled if too violent.

After the reaction had subsided, the stirrer was started and a mixture of 300 grams of bromobenzene (Total-2 moles) and one liter of anhydrous ether was run in at such a rate that the reaction mixture refluxed gently. When the addition was completed (about 4 hours), the mixture was stirred for two hours. To the reacted mixture was added 120 grams (2 moles) of acetone dissolved in 200 ml. of anhydrous ether: it was added fast enough to cause gentle refluxing. The resulting solution was stirred for two hours and then poured on cracked ice. The precipitate was dissolved by the addition of dilute hydrochloric acid. The ether layer was separated and the water layer was extracted once with ether. The combined ether layers were washed twice with water and then dried with anhydrous sodium sulfate. The ether was removed under reduced pressure and the resulting liquid was fractionated (no column) using an oil bath. Yield: 220 grams (81%).

> B.P. 77 - 78°C/ 3 mm. bath 115°C 93 - 94°C/13 mm. bath 130°C 177 - 179°C/737 mm. decomposes

Checks were obtained on physical constants as recorded in the

literature.

This alcohol was previously prepared by Klages (38), Stephens (39), and Rotbart (40).

Methylethylphenyl Carbinol

The above method was used except that the acetone was replaced by 144 grams (2 moles) of methyl ethyl ketone. Yield: 250 grams (83%).

B.P. 83 - 84°C at 2 mm. bath 115°C 98 - 99°C at 13 mm. bath 135°C 198 - 199°C at 742 mm. decomposes

Klages (41), Tiffeneau (42), Inglis (43), and McKenzie and Ritchie (44) have prepared this alcohol.

Diethylphenyl Carbinol

This alcohol was prepared by the same method using 172 grams (2 moles) diethyl ketone in place of the acetone. Yield: 214 grams (65%).

B.P. 93 - 94°C at 2 mm. bath 140°C 103 - 104°C at 13 mm. bath 150°C 220 - 223°C at 738 mm. decomposes

This alcohol contains slight impurities of diphenyl. Other methods were tried, such as, ethyl benzoate with ethyl bromide, but this contained ethyl benzoate; benzoyl chloride with ethyl bromide gave benzoic acid as the impurity. Due to the fact that the alcohol splits off water readily (even on standing), no method was found to remove these slight impurities.

Many methods have been used to prepare this alcohol. The authors who reported the work are: Grignard (45); Bayer and Company (46); Kling (47); Klages (48); Schoringin (49), and Gilmaro (50).

Condensations

In view of the fact that all condensations were carried out in a similar manner, only a typical run is described.

A. Condensations with Benzene

In a 500 ml., three-necked, round-bottom flask fitted with a stirrer, calcium chloride tube, and a dropping funnel were placed 98 grams (1.25 moles) of benzene and 17.3 grams (0.13 moles) of anhydrous aluminum chloride. 34 grams (0.25 moles) of dimethylphenyl carbinol was added dropwise to the stirred suspension. The temperature was kept between 25-30°C, using a water bath when necessary. The color changed to a deep reddish-brown and generally hydrogen chloride was given off during the addition. The mixture was stirred for an additional three hours and then allowed to stand overnight. The mixture was then decomposed by means of a crushed ice-hydrochloric acid solution (1:1). After separating and washing the water layer twice with benzene, the benzene layers were united, washed once with water, dried over calcium chloride, and placed on a steam bath to remove the solvent. The residue was distilled under reduced pressure using a modified Claisen (12-inch column, 1/2-inch bore). In some cases no column was used for the higher fractions.

Condensations:

A. Dimethylphenyl Carbinol, Benzene, and Aluminum Chloride
34 grams - 0.25 moles - carbinol
98 grams - 1.25 moles - benzene
17 grams - 0.13 moles - aluminum chloride

Fractions:

	- 110°C/2 mm.	4 grams	Diphenyl (2 ml. undetermined liquid)
	110 - 115°C/2 mm.	4 grams	2, 2-diphenyl propane (8.2%)
	115 - 120°C/2 mm.	4 grams	l, l, 3-trimethyl-3-phenyl indan
	120 - 130°C/2 mm.	9 grams	1, 1, 3-trimethy1-3-phenyl indan
	130 - 135°C/2 mm.	4.5 grams	4-methy1-2, 4-dipheny1-2-pentene
	135 - 180°C/2 mm.	4 grams	4-methyl-2, 4-diphenyl-2-pentene
	Above 180°C/2 mm.	l gram	Tar
В.	Methylethylphenyl Car	binol, Benze	ene, and Aluminum Chloride
	38 grams - 0.25 mole	- carbinol	
	98 grams - 1.25 moles	s – benzene	
	17 grams - 0.13 mole	- aluminum	chloride
	Fractions:		
	37 - 38°C/2 mm.	4 grams	2-phenyl butane
	38 - 117°C/2 mm.	3 grams	Diphenyl (1 ml. undetermined liquid)
	117 - 122°C/2 mm.	6 grams	2, 2-diphenyl butane (11.3%)
	122 - 150°C/2 mm.	15 grams	1, 2, 3-trimethyl-l-ethyl-3-phenyl indan
	Above 150°C/2 mm.	5 grams	Tar
C.	Diethylphenyl Carbino	ol, Benzene,	and Aluminum Chloride
	41 grams - 0.25 mole	- carbinol	
	98 grams 1.25 moles	s – benzene	
	17 grams - 0.13 mole	- aluminum	chloride
	Fractions:		
	- 72°C/12 mm.	90 grams	Benzene
	72 - 80°C/12 mm.	4.5 grams	3-phenyl pentane
	80 - 110°C/12 mm.	3.5 grams	3-phenyl-2-pentene

110 - 160°C/12 mm. 3.0 grams 1, 1, 3-triethyl-2-methyl-3-phenyl indan(?)
160 - 190°C/12 mm. 4.0 grams 1, 1, 3-triethyl-2-methyl-3-phenyl indan(?)
190 - 210°C/12 mm. 12.0 grams 1, 1, 3-triethyl-2-methyl-3-phenyl indan(?)
Above 210°C/12 mm. 10.0 grams 1, 1, 3-triethyl-2-methyl-3-phenyl indan(?)

B. Condensations with Phenol

As with benzene the condensations here carried out are in the same manner, only the benzene was replaced by phenol dissolved in petroleum ether.

Condensations:

80 - 115°C/ 2 mm. 0.5 gram Diphenyi (1/5 mi. Undetermined Hquid) 115 - 125°C/ 2 mm. 4.0 grams 1, 1, 3-trimethyl-3-phenyl indan 125 - 140°C/ 2 mm. 0.0 grams 140 - 160°C/ 2 mm. 82.0 grams P-(<,,<-dimethyl benzyl)-phenol (77%) Above 160°C/ 2 mm. 2.0 grams Tar

B. Methylethylphenyl Carbinol, Phenol, and Aluminum Chloride

38 grams - 0.25 mole - carbinol
28 grams - 0.30 mole - phenol
9 grams - 0.068 mole - aluminum chloride
50 ml. - petroleum ether

	- 90°C/12 mm.	6.0 grams	Phenol
	58 - 65°C/2 mm.	1.0 gram	2-phenyl-2-butene
	65 - 90°C/2 mm.	2.0 grams	Diphenyl
	90 - 140°C/ 2 mm.	0.0 grams	
	140 - 170°C/ 2 mm.	4.5 grams	P-(~-methyl-«-ethyl benzyl)-phenol (79%)
	Above 170°C/ 2 mm.	3.0 grams	Tar
C.	Diethylphenyl Carbino	l, Phenol, a	nd Aluminum Chloride
	41 grams - 0.25 mol	e - carbinol	
	28 grams - 0.30 mol	e – phenol	
	17 grams - 0.125 mol	e - aluminum	chloride
	100 ml	petroleu	m ether
	Fractions:		
	- 70°C/12 mm.	3.0 grams	Phenol
	70 - 80°C/2 mm.	3.5 grams	3-phenyl pentane
	80 - 100°C/ 2 mm.	2.0 grams	3-pheny1-2-pentene
	100 - 150°C/ 2 mm. o	ccasionally	Diphenyl
	150 - 165°C/ 2 mm.	41.0 grams	P-(~,~-diethyl benzyl)-phenol (68%)
	165 - 195°C/ 2 mm.	0.0 grams	
	Above 195°C/ 2 mm.	4.0 grams	Tar

Identification

The liquids were distilled until at least a three-degree fraction was obtained. In almost all cases, this constituted about ninety per cent of the main fraction under observation.

The solids were subject to crystallization until a constant melting point was obtained from two different solvents.

Diphenyl

Found in the carbinols and in some condensations due to the reaction between bromobenzene and phenyl magnesium bromide.

M.P. $68 - 69^{\circ}C$ (Handbook: $69 - 70^{\circ}C$)

2-phenyl-butane

Prepared and recorded in the literature by Schramm (51), Estreicher (52), Klages (53), and Levene and Marker (54).

B.P. 37 - 38°C/ 2 mm./80°C 53 - 55°C/12 mm./100°C 165 - 166°C/740 mm.

 $D_4^{20} = 0.8640$ ($D_4^{21} = 0.8634 - K \text{lages}$)

 $n_D^{25} = 1.4880$ ($n_D^{25} = 1.4878 - Levene$)

Bromination using iron as a catalyst giving 2-(P-bromo phenyl)-butane.

2-phenyl-2-butene

B.P. 55 - 57°C/ 2 mm./95°C 72 - 74°C/12 mm./110°C 183 - 185°C/747 mm.

Reduced to 2-phenyl butane using sodium and ethyl alcohol.

B.P. 170 - 171°C/745 mm. - Klages (53)

Perrot (55) and Tiffeneau (42) also describe this compound.

3-phenyl-pentane

Described by Klages (48), Spath (56), Luginin (57), Dafert (58), and Levene (54).

Prepared by two different methods:

1. Friedel-Crafts Reaction:

Fifty grams of 3-bromopentane and 150 grams of benzene were placed in a three-necked, 500 ml., round-bottom flask fitted with a stirrer, reflux condenser, and calcium chloride tube. Ten grams of aluminum chloride were added slowly while stirring. After addition, it was allowed to stir for three hours and then decomposed by the usual method.

B.P. 50 - 53°C/2 mm. Yield: 20 grams (40%) 2. Grignard Reaction:

This was run on 157 grams of bromobenzene, 27 grams of magnesium, and one liter of benzene as the solvent. 151 grams of 3-bromopentane was added and the mixture refluxed five hours. It was decomposed in the usual manner.

B.P. 50 - 53°C/ 2 mm. Yield: 15 grams (10%)

All three compounds were brominated as follows:

Eight grams of the compound and a pinch of powdered iron was cooled in ice, 0.9 gram of bromine was added dropwise with shaking. After setting two days, the solution was taken up in ether, washed with water, and dilute sodium carbonate, dried, and distilled.

B.P. 116 - 118°C/72 mm. Yield: (42%) 240 - 242°C/738 mm.

% bromine from condensation fraction: 35.20 (found)

35.17 (calculated)

The compound is 3-(P-bromo phenyl)-pentane.

Proof:

One gram of the above compound and twenty ml. of 6 N nitric acid were sealed in a Carius tube and heated twenty hours at 180°C. A solid resulted having a M.P. of 249°C, which was P-bromobenzoic acid (M.P. 251 -253°C).

<u>3</u>	-pheny	1-2-pen	ntene	
B.P. 63	- 65°0	C/2 mm	1./1109	2C
82	- 84°(C/12 mm	1./1259	2 C
202	- 2049	°C/750	mm .	
Nitroso chloride,	M.P. 3	114°C	(M.P.	117°C - Klages)
% chlorine			16.60	(found)
			16.75	(calculated)

Reduced to 3-phenyl-pentane, B.P. 186 - 188°C/740 mm.

Found in the literature under Klages (48), Grignard (59), and Tiffeneau (42).

2, 2-diphenyl-propane

 $D_4^{25} = 0.9956$ ($D_4^{25} = 0.9958 - \text{Sabatier}$) $n_4^{25} = 1.568$ ($n_D^{25} = 1.570 - \text{Sabatier}$) $y^{25} = 29.12$

Compound did not solidify as stated by Sabatier (60), but reacted as stated by Silva (61).

2. 2-diphenyl-butane

B.P. 118 - 119°C/ 2 mm.

M.P. 127°C

As described by Zincke (62).

P-(~, ~-dimethyl benzyl)-phenol

B.P. 152 - 155°C/ 2 mm.

M.P. 73°C

Aryloxy acetic acid, M.P. 116°C (M.P. 117°C - Welsh). Synthesised in patents (63), (64), and synthesised and proven by Welsh and Drake (20).

4-methyl-2, 4-diphenyl-2-pentene

B.P. 168 - 169°C/12 mm./215°C

M.P. 130 - 131°C

Two and one-half grams of the compound, 6 grams of aluminum chloride, and 100 ml. of benzene were mixed together and shaken frequently during the course of four days. It was then decomposed by ice and dilute hydrochloric acid and the benzene layer evaporated.

A solid, M.P. 50 - 51°C, resulted, which is 1, 1, 3-trimethyl-3phenyl indan (see below) according to Bergmann (65). Bogert and Davidson also refer to this compound (66). 1, 1, 3-trimethyl-3-phenyl-indan

B.P. 163 - 165°C/24 mm.

305 - 306°C/734 mm.

M.P. 51 - 52°C

This data agrees with the compound described by Bergmann (65) and Bogert and Davidson (66) as well as that of Welsh and Drake (20).

Proof of Structure

P-(-methyl---ethyl benzyl)-Phenol

The chloride of methyl ethyl phenyl carbinol was prepared, according to Klages (48), with great difficulty. The carbinol was saturated with dry hydrogen chloride and allowed to stand in an ice box for one day, the water separated, and the saturated carbinol dried with calcium chloride; the process was repeated three times. The chloride was dried again by shaking it with anhydrous sodium carbonate for two minutes and the resulting solution was distilled under vacuum. The boiling point of the chloride was $78^{\circ}C/2$ mm.

Seven grams of magnesium turnings and 20 ml. of anhydrous ether were put in a three-necked, three-liter, round-bottom flask provided with a reflux condenser with calcium chloride tube attached, a stirrer, and a separatory funnel. Five grams of P-bromo-anisole was added and heat applied until the reaction started, when 45 grams of the P-bromoanisole, dissolved in 100 ml. of ether, was run in at such a rate that the solution refluxed. After addition, the solution was stirred for three hours: forty-six grams of the chloride of methyl ethyl phenyl carbinol dissolved in 100 ml. of ether was run in fast enough to cause refluxing. After the addition, the ether was removed by distillation, one liter of anhydrous benzene was added and the solution was refluxed one day on a water bath. It was then decomposed by dilute hydrochloric acid and ice, the benzene layer separated, washed with water, the solvent removed on a steam bath and the resulting solution distilled under The methyl ether of P-(~-methyl-~ethyl benzyl)-phenol thus vacuum.

prepared boiled at 140-142°C/ 2 mm. Yield: 15 grams (23%).

The 15 grams of methyl ether of P-(\ll -methyl- \approx -ethyl benzyl)-phenol were refluxed with 100 grams of phenol and 50 ml. of 48% hydrobromic acid for four hours. The solution was separated from the water layer, washed with water until neutral, and distilled. After the phenol was removed, the remaining P-(\ll -methyl- \ll -ethyl benzyl)-phenol came over at 147-148°C/ 2 mm. Yield: 8 grams (57%).

	Carbon and Hydros	gen	
Found	% Carbon 84.43	% Hydrogen 7.99	
Calculated	84.91	8.01	
Benzoyl ester	M.P.	55° C (benzene)	
Methyl ether	B.P.	. 140-142°C/ 2 mm./185°C	

Mixed melting points with the benzoyl ester of P-(<-methyl-<-ethyl benzyl)-phenol, obtained from the condensation of methyl ethyl phenyl carbinol with phenol, gave no depression of the melting point.

The methyl ether of P-(<-methyl-<-ethyl benzyl)-phenol, obtained from the condensation of methyl ethyl phenyl carbinol with phenol, boiled at 140-141°C/ 2 mm./185°C.

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Physical Constants of P-(~-methyl-~-ethyl benzyl)-Phenol
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B.P. 147-149°C/ 2 mm./215°C
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196-197°C/12 mm.

318°C/740 mm.

 $d_4^{25} = 1.062$

 $n_4^{25} = 1.5810$

 $y^{25} = 30.99$ Molecular Weight

Found		230.0	
Calculated		226.30	
Found Calculated	Carbon and Hydroge % Carbon 84.82 84.91	en % Hydrogen 7.99 8.01	
Benzoyl ester	M.P.	55–56°C	
Found	Carbon and ^H ydroge % Carbon 83.62	en % Hydrogen 5.95	
Calculated	83.60	6.71	
Methyl ether	B.P.	140-141°C/ 2 mm./185°C	

McGreal and Niederal (27) prepared this compound but gave no definite proof of its structure.

P-(~, ~-diethyl benzyl)-Phenol

The method used in the preparation of P-(\ll -methyl- \ll -ethyl benzyl)phenol was also used in the synthesis of this compound. Eleven grams of magnesium turnings, 85 grams of P-bromo-anisole and 83 grams of the chloride of diethyl phenyl carbinol were used to prepare the methyl ether of P-(\ll , \ll -diethyl benzyl)-phenol, which boiled at 135-138°C/ 2 mm. Yield: 20 grams (17.5%). In changing the methyl ether to the phenol, a yield of 12 grams (63.5%) was obtained. B.P. 142-143°C/ 2 mm.

		Carbon and Hy	<i>r</i> drogen	
		% Carbon	% Hydrogen	
	Found	84.92	8.49	
			0.50	
	Calculated	84,95	8.38	
Methy	l ether		B.P. 135-138°C/ 2 mm.	
Benzo	yl ester		M.P. 99.5-100°C (benzene)

Mixed melting points with the same derivatives of the phenol from the condensation of diethyl phenyl carbinol with phenol gave no depression of the melting point.

Physical Constants of $P-(\alpha, \alpha - diethyl benzyl)$ -Phenol

B.P. 142-143°C/ 2 mm./230°C

200-203°C/12 mm.

344°C/741 mm.

 $d_4^{25} = 1.068$

 $n_d^{25} = 1.5770$

 $\delta^{25} = 30.52$

Molecular Weight

Found

Calculated

240.33

242.0

	Carbon and Hydrogen			
	% Carbon	Ŕ	Hydrogen	
Found	85.16		8.45	
Calculated	84.95		8.38	

Benzoyl ester

M.P. 99.5-100°C

	Carbon and Hydro	ogen	
	% Carbon	% Hydrogen	
Found	83.63	6.63	
Calculated	83.68	7.02	
Methyl ether	B.P.	. 136-137°C/ 2 m	nm./210°C

Synthesis of 1, 2, 3-trimethyl-l-ethyl-3-phenyl Indan

Homomesitone was prepared (67) by saturating one liter of methyl ethyl ketone, at five degrees, with dry hydrogen chloride. The mixture was stoppered and allowed to stand in an ice box for ten days. It was then poured into water and the oily layer separated. This layer was dried with sodium sulfate and distilled. B.P. 159-162°C/740 mm., 150 grams yield.

The 150 grams of homomesitone and 400 ml. of benzene were stirred together in a three-liter, round-bottom flask fitted with a calcium chloride tube; 180 grams of aluminum chloride were added gradually so that at no time did the mixture reflux. After addition, the solution was stirred for four hours and allowed to stand for two days. The mixture was then decomposed with ice and hydrochloric acid. The benzene layer was distilled, collecting the fraction which boiled between 120-130°C at 2 mm. pressure. Yield: 63 grams. It is believed that the compound is 3, 4-dimethyl-4-phenyl-2-hexanone produced by the following reactions:

An ether solution of phenyl magnesium bromide was prepared from 10 grams of magnesium, 62 grams of bromobenzene, and 100 ml. of ether. The 3, 4-dimethyl-4-phenyl-2-hexanone prepared above was dissolved in 100 ml. of anhydrous ether and added to the phenyl magnesium bromide solution. The resulting solution was stirred for two hours, decomposed by ice and hydrochloric acid; the other layer was dried with sodium sulfate and distilled. The fraction boiling between 140-145°C at 2 mm. was collected. Yield: 30 grams. The fraction was believed to contain 3, 4-dimethyl-2, 4-diphenyl-2-hexanol synthesized by the

equation:

$$CH_{3}-CH_{2}-\overset{CH_{3}}{\overset{C}{\leftarrow}},\overset{CH_{3}}{\overset{C}{\leftarrow},\overset{CH_{3}}{\overset{C}{\leftarrow}},\overset{CH_{3}}{\overset{C}{\leftarrow},\overset{CH_{3}}{\overset{C}{\leftarrow},\overset{CH_{3}}{\overset{C}{\leftarrow}},\overset{CH_{3}}{\overset{C}{\leftarrow},\overset{$$

The 140-145°C fraction from the above preparation was dissolved in 50 ml. of dry benzene and 20 grams of aluminum chloride added. The suspension was allowed to stand for a week with frequent shaking, then it was decomposed with ice and hydrochloric acid, and distilled. B.P. 126-130°C/ 2 mm. Yield: 10 grams. This compound was thought to be 1, 2, 3-trimethyl-l-ethyl-3-phenyl indan:



it agreed in boiling point and stability towards oxidation with the dimer isolated in the methyl ethyl phenyl carbinol condensation with benzene, but differed in nitration and spectrographic behavior.

This compound when nitrated did not form a solid nitro derivative.

Physical Constants of the Dimer Isolated in the Methyl Ethyl Phenyl Carbinol Condensation with Benzene

B.P. 127-129°C/ 2 mm.

180-182°C/12 mm.

321°C/738 mm.

264

 $d_4^{25} = 0.996$

$$n_4^{25} = 1.5646$$

x 25 = 27.03

Molecular Weight

Found		

Calculated 264.39

Found	Carbon and Hydroge % Carbon 90.40	∍n %	Hydrogen 9.01
Calculated	90.85		9.14

Nitro derivatives M.P. 192.5-193°C, 232°C

Nitration of the dimer from the methyl ethyl phenyl carbinol condensation with benzene was brought about by mixing 3 grams of the compound with 7 ml. of concentrated nitric acid and 5 ml. of concentrated sulfuric acid and then heating for a half hour at 50°C while shaking. The mixture then was poured into water, filtered, and the solid recrystallized from ether. M.P. 192.5-193°C.

Nitration, using fuming nitric acid without the aid of sulfuric acid, gave a solid. M.P. 232°C.

Oxidation of the dimer with alkaline permanganate was attempted. Eight grams of the dimer, 70 grams of potassium permanganate, and 6 grams of potassium hydroxide were added to 100 ml. of water and the resulting solution was allowed to stand on the steam bath for one month, but the dimer was recovered unchanged.

Synthesis of 1, 1, 3-triethyl-2-methyl-3-phenyl indan

The ethyl ester of 3-hydroxy-2-methyl-3-ethyl pentanoic acid was prepared by means of a reaction by Reformatski according to Armond, Kon, and Leton's procedure (68). Two hundred grams of diethyl ketone, 370 grams of the ethyl ester of \sim -bromo propionic acid, 130 grams of zinc and 200 ml. of benzene were placed in a three-necked, three-liter, round-bottom flask fitted with a stirrer and reflux condenser with calcium chloride tube attached. The reaction was kept cool by the use of cold water on the outside of the flask. After the reaction had slowed down, the mixture was heated until almost all of the zinc had disappeared. It was then poured on cracked ice and decomposed with hydrochloric acid. The oily layer was washed three times with water, dried over calcium chloride, and distilled. B.P. 95-100°C/14 mm. Yield: 65 grams.

$$C_{2}H_{5}-C=0 + Br-\dot{C} - COOC_{2}H_{5} + Zn \xrightarrow{hydrolyzed} C_{2}H_{5}-\dot{C} - \dot{C} - COOC_{2}H_{5}$$

The ester was refluxed for an hour with 60 grams of acetic anhydride, separated from it, washed once with water, and poured into 300 ml. of 5% alcoholic potassium hydroxide. The resulting solution was refluxed two hours and then poured into 500 ml. of water. The water solution was made acid with hydrochloric acid and extracted three times with ether. The ether layer was then evaporated on the steam bath and distilled. B.P. 120-124°C/12 mm. Yield: 47 grams.

$$C_{2}H_{5}-C = C - COOC_{2}H_{5} + (CH_{3}CO)_{2}O \xrightarrow{C_{2}H_{5}-C} = C - COOC_{2}H_{5} + H_{2}OC_{2}H_{5} + H_{2}OC_{2}H_{5} + CH_{3}$$

$$C_{2}H_{5}-C = C - COOC_{2}H_{5} + alc. \text{ KOH } \xrightarrow{acidify} C_{2}H_{5}-C = C - COOH + C_{2}H_{5}OH + C_{2}H_$$

The 2-methyl-3-ethyl-2-pentenoic acid was converted to 4-methyl-5-ethyl-4-hepten-3-cole using the method described by Kon and Leton (68). Fifty grams of thionyl chloride was used to convert the acid to the chloride and the chloride was then run into an ether solution of ethyl magnesium bromide made from 9.5 grams of magnesium, 40 grams of ethyl bromide and 200 ml. of anhydrous ether. The Grignard was decomposed in the usual manner. B.P. 82-84°C/12 mm. Yield: 30 grams.

$$C_{2}H_{5}-C = C - COOH + SOCl_{2} \longrightarrow C_{2}H_{5}-C = C - COCl + SO_{2} + HCl$$

$$C_{2}H_{5} CH_{3}$$

$$C_{2}H_{5}-C = C - COCl + C_{2}H_{5} MgBr \xrightarrow{hydrolyzed} C_{2}H_{5}-C = C - COC_{2}H_{5}$$

$$C_{2}H_{5} CH_{3}$$

The unsaturated ketone was dissolved in 300 ml. of anhydrous benzene and, while stirring, 35 grams of aluminum chloride were added. The solution was stirred two hours and allowed to stand for a week. It was then decomposed in the usual manner and distilled. B.P. 110-120°C/ 2 mm. Yield: 37 grams.

$$C_{2}H_{5}-C = C - COC_{2}H_{5} + C_{6}H_{6} + AlCl_{3} \longrightarrow C_{2}H_{5}-C - COC_{2}H_{5}$$

$$C_{2}H_{5} CH_{3} CH_{3} COC_{2}H_{5} CH_{3}$$

The 4-methyl-5-ethyl-5-phenyl-3-heptanone from the above preparation was dissolved in 100 ml. of anhydrous ether and dropped into an ether solution of phenyl magnesium bromide prepared from 40 grams of phenyl bromide, 8 grams of magnesium, and 200 ml. of anhydrous ether. The reaction was decomposed with ice and hydrochloric acid and, after removal of the benzene, was distilled. B.P. 130-135°C/ 2 mm. Yield: 30 grams.

$$C_{2}H_{5}-\overset{C_{6}H_{5}}{\overset{H}{\underset{C_{2}H_{5}}{\leftarrow}}}\overset{H}{\underset{C_{2}}{\overset{H}{\underset{C_{2}}{\leftarrow}}}} \xrightarrow{COC_{2}H_{5}} + C_{6}H_{5}MgBr \xrightarrow{hydrolyzed} C_{2}H_{5}-\overset{C_{6}H_{5}}{\overset{H}{\underset{C_{2}}{\leftarrow}}}\overset{H}{\underset{C_{2}}{\overset{H}{\underset{C_{2}}{\leftarrow}}}} \xrightarrow{C_{6}H_{5}} \overset{H}{\underset{C_{2}}{\overset{C_{6}H_{5}}{\leftarrow}}} \xrightarrow{C_{6}H_{5}} C_{2}H_{5}$$

The above alcohol was dissolved in 50 ml. of benzene and 15 grams of aluminum chloride added. The mixture was shaken frequently during the course of a week; then decomposed by ice and hydrochloric acid, and distilled. B.P. 138-140°C/ 2 mm. Yield: 14 grams.



This compound showed the same boiling point and stability towards oxidation with the dimer isolated in the diethyl phenyl carbinol condensation with benzene, but did not behave the same toward nitric acid.

A different attempt was made to synthesize the dimer, using the same idea as before but following a different procedure.

A Reformatski Reaction was run on 290 grams of phenyl ethyl ketone, 370 grams of the ethyl ester of ~-bromo propionic acid, 130 grams of zinc, and 200 ml. of benzene, and the fraction between 130-140°C/12 mm. was collected. Yield: 70 grams.

The ethyl ester of 3-hydroxy-2-methyl-3-phenyl pentanoic acid from the Reformatski was run into an ether solution of ethyl magnesium bromide prepared from 20 grams of magnesium, 80 grams of ethyl bromide and 200 ml. of anhydrous ether. The Grignard was decomposed in the usual manner. The 120-125°C/ 2 mm. fraction was collected and weighed 15 grams.

The 3, 5-dihydroxy-4-methyl-3-ethyl-5-phenyl heptane so prepared was dissolved in 200 ml. of benzene and 30 grams of aluminum chloride added: the solution was allowed to stand for one week with frequent shaking. It was decomposed with ice and hydrochloric acid and after removal of the benzene layer, distilled. B.P. 137-141°C/ 2 mm. Yield: 8 grams.

$$C_{2}H_{5} \xrightarrow{C_{6}H_{5}} \stackrel{H}{\overset{C}{\leftarrow}} \xrightarrow{C_{2}H_{5}} \stackrel{H}{\overset{C}{\leftarrow}} \xrightarrow{C_{2}H_{5}} C_{2}H_{5} + C_{6}H_{6} + AlCl_{3} \xrightarrow{\longrightarrow} C_{2}H_{5} \xrightarrow{C_{6}H_{5}} \stackrel{H}{\overset{C}{\leftarrow}} \xrightarrow{C_{2}H_{5}} \stackrel{C_{2}H_{5}}{\overset{C}{\leftarrow}} \xrightarrow{C_{2}H_{5}} C_{2}H_{5} + H_{2}O$$



This compound was not the same as the dimer isolated from the diethyl phenyl carbinol condensation with benzene, but it was comparable to the compound described above.

Physical Constants of the Dimer Isolated from the

Diethyl Phenyl Carbinol Condensation with Benzene

B.P. 139-140°C/ 2 nm./220°C

195-197°C/12 mm.

338°C/740 mm.

 $d_4^{25} = 1.000$

 $n_d^{25} = 1.5670$

 $\delta^{25} = 27.03$

Molecular Weight

Found

291

292.44

Calculated

Carbo	n and	Hydrogen	L	
₹	Carbo	n	%	Hydrogen
Found	90.33			9,40
Calculated	90.35			9.65

Nitration of the dimer, using a mixture of nitric and sulfuric acids, as well as fuming nitric acid, did not give a solid compound.

Oxidation of the dimer with alkaline permanganate did not occur, for it was recovered unchanged as in the dimer from the methyl ethyl phenyl carbinol condensation with benzene.

Discussion

The procedure used in this work consisted of the preparation of dimethyl, methyl ethyl, and diethyl phenyl carbinols followed by their condensation with both benzene and phenol: all resulting products of the reactions were analyzed in order to identify them.

The alcohols thus used were prepared from phenyl magnesium bromide and the ketone corresponding to the carbinol. A detailed description of their preparation, along with their constants and a review of the literature, has been given in the "Experimental" portion of this thesis.

The condensations with benzene were carried out by mixing one equivalent of the carbinol with five equivalents of benzene, stirring, and gradually adding one-half equivalent of aluminum chloride; addition taking place in such a manner that the temperature was maintained between 25-30°C. The mixture was stirred for four hours, allowed to stand overnight, and then decomposed with ice and hydrochloric acid. The benzene layer was then fractionally distilled and all fractions collected.

The condensations with phenol were run in the same manner, but one and two-tenths equivalents of phenol were used in place of the benzene, and petroleum ether was used as a solvent.

At first, crude fractions with a wide range of boiling points were taken and these fractions then worked upon until fractions of a three to five degree range were obtained. In most cases, the last fraction contained ninety per cent of the original wide-range fraction. The distilling was done either at 2 mm. or 12 mm. pressure followed by boiling point determinations at atmospheric pressure.

The fractions contained reasonably pure compounds. They were identified, in most cases, by comparison with those already known. The comparison consisted of their physical constants and often certain derivatives were made. In four cases, the compounds had never been made: two of these four compounds were synthesized and their structures established during the course of this work, but the other two are as yet unidentified.

From the condensation of dimethyl phenyl carbinol with benzene was isolated the condensation product, 2, 2-diphenyl propane. Two other compounds were also isolated. These proved to be an unsaturated and a saturated dimer, namely, 4-methyl-2, 4-diphenyl-2-pentene and 1, 1, 3trimethyl-3-phenyl indan. The method of their synthesis probably was:



The methyl ethyl phenyl carbinol condensation with benzene gave 2-phenyl butane, 2, 2-diphenyl butane, the condensation product, and a dimer which was believed to be 1, 2, 3-trimethyl-l-ethyl-3-phenyl indan, whereas, the diethyl phenyl carbinol reaction gave 3-phenyl pentane, 3phenyl-2-pentene, and a dimer, but no condensation product.

In the phenol condensation series, dimethyl phenyl carbinol gave the saturated dimer 1, 1, 3-trimethyl-3-phenyl indan and the condensation product $P-(\prec, \prec-dimethyl-benzyl)$ -phenol. This reaction had already been run by Welsh and Drake (20) who used a different method. The condensation, using methyl ethyl phenyl carbinol, gave 2-phenyl-2-butene and $P-(\prec-methyl-\prec-ethyl benzyl)$ -phenol, the condensation. The unsaturated compound, 3-phenyl-2-pentene, was isolated in the diethyl phenyl carbinol condensation, along with the saturated compound 3-phenyl pentane. The condensation, $P-(\prec, \prec-diethyl benzyl)$ -phenol, was also obtained.

P-(~-methyl-~ethyl benzyl)-phenol was presumably prepared by McGreal and Niederal (27), but not a great deal of proof was offered. In the present work the proof of P-(~-methyl-~ethyl benzyl)-phenol was run according to Welsh and Drake's method (20). The chloride of methyl ethyl phenyl carbinol was made by saturating 2-phenyl-2-pentene with hydrogen chloride. The chloride was reacted with P-anisyl magnesium bromide in dry benzene. The resulting ether was decomposed by refluxing with phenol and hydrobromic acid, giving rise to P-(<-methyl-~ ethyl benzyl)-phenol. The equations for the reactions are:

$$CH_{3} - O - C_{6}H_{4} - MgBr + Cl - C_{6}H_{5} - C_{6}H_{5} - CH_{3} - O - C_{6}H_{4} - C_{6}H_{5} + MgClBr$$

$$CH_{3} - O - C_{6}H_{4} - C_{6}H_{5} + MgClBr$$

$$CH_{3}-O-C_{6}H_{4}-C_{6}H_{5}+HBr \longrightarrow HO-C_{6}H_{4}-C_{6}H_{5}+CH_{3}Br \xrightarrow{CH_{3}}{C_{2}H_{5}}$$

The $P-(\prec, \prec-\text{diethyl benzyl})$ -phenol was proven in the same way as $P-(\prec-\text{methyl}-\prec-\text{ethyl benzyl})$ -phenol, using the chloride of diethyl phenyl carbinol. This chloride was hard to obtain as it readily split off hydrogen chloride when distilled. It was used immediately without

distilling, after being dried with sodium sulfate for a short time.

Attempts were made to synthesize the compound in the 122-150°C fraction of the methyl ethyl phenyl carbinol condensation with benzene, as well as the 110-190°C fraction of diethyl phenyl carbinol condensation with benzene, but such attempts were futile. In view of the fact that an indan was identified in the dimethyl phenyl carbinol condensation with benzene along with 2-phenyl propene, it appeared reasonable that an indan should also be isolated in the other two cases. The formation of the indan should take place for the methyl ethyl phenyl carbinol condensation as follows:



Thus, the compound can be 1, 2, 3-trimethyl-l-ethyl-3-phenyl indan: its molecular weight, as well as its carbon and hydrogen analysis, agree with this dimer. The attempted synthesis followed along the lines of the procedure that Bergmann (65) used in synthesizing the dimethyl phenyl carbinol indan. Homomesitone reacted with benzene in the presence of aluminum chloride: the resulting ketone then reacted with phenyl magnesium bromide and, presumably, 3, 4-dimethyl-2, 4-diphenyl-2-hexanol was obtained. This compound was then treated with aluminum chloride to obtain the indan, but the resulting compound did not compare with the compound isolated from the condensations. The equations for the process are:



The compound from the diethyl phenyl carbinol condensation with benzene was believed to be 1, 1, 3-triethyl-2-methyl-3-phenyl indan. Its synthesis was attempted using the same method as that of the methyl ethyl phenyl carbinol condensation, but the polymerization product of diethyl ketone was used instead of methyl ethyl ketone. The ketone, 4-methyl-5-ethyl-4-hepten-3-one, was made according to Kon and Leton (68) and reacted with benzene in the presence of aluminum chloride: the resulting ketone then reacted with phenyl magnesium bromide and 4-methyl-5-ethyl-3, 5-diphenyl-3-heptanol was believed produced. This alcohol was treated with aluminum chloride to obtain the indan; however, the product obtained after synthesis was not the same as that from the diethyl phenyl carbinol condensation.

A different approach to the above synthesis was attempted by substituting phenyl ethyl ketone for diethyl ketone, along with other changes in the reactions. The procedure was:

Again no compound, comparable to the compound isolated from the diethyl phenyl carbinol condensation, was formed.

Oxidations of the dimers were tried, employed alkaline permanganate, but in both cases the dimer was recovered unchanged. It was interesting to note that the dimer from dimethyl phenyl carbinol did not oxidize under the same conditions. The dimers were nitrated, but only the one from methyl ethyl phenyl carbinol gave rise to a solid nitro derivative.

Summary

- 1. Dimethyl and methyl ethyl phenyl carbinols condense with both benzene and phenol in the presence of aluminum chloride.
- 2. Diethyl phenyl carbinol condenses with phenol using aluminum chloride as a catalyst, but it does not condense with benzene under similar conditions.
- 3. The dehydration product of the alcohol was obtained in the condensation of diethyl phenyl carbinol with both benzene and phenol, as well as in the case of methyl ethyl phenyl carbinol with phenol.
- 4. A saturated compound of the alcohol, in which the hydroxyl group has been replaced by a hydrogen, was identified in the condensation of diethyl phenyl carbinol with benzene as well as with phenol. A similar compound was obtained with methyl ethyl phenyl carbinol and benzene.
- 5. In the condensations with benzene, the carbinols, dimethyl, methyl ethyl, and diethyl phenyl, gave rise to dimers of the unsaturated compounds derived from the carbinols by means of the removal of water. A dimer was also identified in the phenol condensation with dimethyl phenyl carbinol.
- 6. The attempted synthesis of the dimers of methyl ethyl and diethyl phenyl carbinol condensations were not successful.
- 7. Proof of structure has been given for $P_{(\alpha-methyl-\alpha-ethyl benzyl)-}$ phenol and $P_{(\alpha, \alpha-diethyl benzyl)-phenol by synthesizing them in$ another manner.

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