ACTION OF TERTIARY DIALKYL ARYL CARBINOLS WITH BENZENE IN THE PRESENCE OF ALUMINUM CHLORIDE

Thesis for the Degree of M. S.

Richard Allen Macomber

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R.C. Huston
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In Partial Fulfillment of the
Requirements for the Degree
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-by-
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ORGANIC SYNTHESIS BY CONDENSATION

Condensation when applied to organic chemistry has been defined as "the union of two or more molecules or parts of the same molecule with or without the elimination of a molecule of water or inorganic acid in which the new molecule is effected between carbon atoms". The union referred to may be accompanied by unsaturation with these unsaturated groups tending to saturate themselves. According to this condensation may be divided into two parts: those effected by the separation of the elements and those effected by addition. In the scope of this present work both processes may take place, but the former being the main reaction involved.

Condensation by the separation of the elements may be divided still further into catalytic and dehydrative reactions. However, these may be united again when the reagent used may serve both purposes in the same reaction. The work involved here deals mainly with the elimination of water, thus, the review of previous work will be limited to condensations by dehydration.

HISTORICAL

HISTORICAL

Dehydrating Agents

1-Sulfuric acid

Becker (Ber. 15, 2090) condensed m-nitrobenzyl alcohol and benzene to give m-nitrodiphenylmethane. Noelting (Ber. 24, 3126) formed tetramethyltriaminodiphenyltolylmethane from tetramethyldiaminobenzhydrol and p-toluidine. Gattermann and Koppert (Ber. 26, 2810) prepared dinitrobenzyltoluene using sulfuric acid. Bistrzycki, Flateau, and Simonis (Ber. 28, 989; 31, 2812) prepared hydroxydiphenyl acetic lactone and α- hydroxydiphenyl acetolactone. Other workers using sulfuric acid are Meyer and Wurster (Ber. 6, 964) and Fritsch (Ber. 29, 2300).

2-Zinc chloride

Fischer and Roser (Ber. 13, 674) condensed benzhydrol and aniline hydrochloride to yield aminotriphenylmethane. Liebermann (Ber. 14, 1842) prepared butylphenol, amylphenol, and benzylphenol using butyl alcohol, amyl alcohol, and benzyl alcohol with phenol respectively. Merz and Werth (Ber. 14, 187) prepared diphenylether from phenol. Auer (Ber. 17, 669) condensed ethyl alcohol and phenol to give ethyl phenol. Kippenberg (Ber. 30, 1140) also worked with zinc chloride condensation.

3-Phosphorous pentoxide

Hemilian (Ber. 16, 2360) prepared diphenyl p- xylymethane from benzhydrol and p-xylene. Micheal and Jeanpretre (Ber. 25, 1615) condensed phenyl-hydroxy acetonitrile and benzene to yield diphenyl-acetonitrile.

4-Acetic acid

Khotinski and Patzewitch (Ber. 24, 3104) found that triphenyl cerbinols condensed with pyrrole. Szeki (Acta. R. 2, 5) condensed benzhydrol with di and trimethoxybenzenes in glacial acetic acid solution by passing hydrogen chloride through the solution.

5-Sulfuric and Acetic acid mixture

Meyer and Wurster (Ber. 6, 963) condensed benzyl alcohol and benzene to give diphenylmethane. Paterno and Fileti (Gazz. Chim. ital. 5, 381) condensed benzyl alcohol and phenol. Pistrzycki and Cyr (Ber. 37, 655) condensed diphenyl p-tolylcarbinol with phenol. Mohlau and Klopfer (Ber. 32, 2147) condensed benzhydrol and p-quinone in sulfuric acetic acid or in absolute alcohol.

6-Magnesium chloride

Mazzara (Gazz. Chim. ital. 12, 505) prepared propyl m-cresol from propyl alcohol and m-cresol.

7-Stannic chloride

Micheal and Jeanpretre (Ber. 25, 1615) condensed phenylhydroxy acetonitrile and mesitylene to give phenyltrimethylphenylacetonitrile. Bistrzycki (Ber. 37, 659) prepared diphenyl p-tolylmethane from benzhydrol and toluene.

8-Hydrogen chloride

Noelting (Ber. 24, 553) prepared p-nitrodimethyldraminodiphenyltolylmethane using hydrogen chloride as a dehydrating agent. Suais (Bull. 1, 517) also used hydrogen chloride as a condensing agent.

9-Aluminum chloride

Aluminum chloride came into use as a catalyst in condensation reactions with the work of Fridel and Craft (Comp. Rend. 84, 1392). Their work was entirely in the aliphatic series; they went so far as to say it would not hold for the aromatic series, this, however, was disproven by by later work. Merz and Weith (Ber. 14, 187) condensed phenol with itself using aluminum chloride to form diphenyl ether. Wass (Ber. 15, 1123) obtained triphenyl ethane by condensing dichlorethyloxide. It is shown here that aluminum chloride acts not only as a catalyst but also as a dehydrating agent. Graebe (Ber. 34, 1778) obtained aniline in small yields by condensing benzene and hydroxylamine with the elimination of water.

It was reported by Frankforter (J. Am. Chem. Soc. 36, 1511; 37, 385) that he and his coworkers had obtained condensation products from chloral, chloral hydrate, and trioxymethylene with the elimination of water by using aluminum chloride, but could not obtain all of the same final products by the Baeyer or sulfuric acid reaction. Thus he maintained that aluminum chloride acts primarily as a catalyst and only secondary as a dehydrating agent.

It was not until Prins in 1927 (Chem. Weekblad 24, 615) that some light was thrown on the mechanism of aluminum chloride condensation. He stated that benzene under the influence of aluminum chloride acted as if it had a mobile hydrogen and was comparable at this time to an alcohol. With aluminum chloride a carbon to hydrogen linkage corresponds to an oxygen to hydrogen linkage. The former linkage apparently has undergone ionization under the influence of aluminum chloride's strong positive ion. Dougherty (J. Am. Chem. Soc. 51, 576) agreed mainly with Prins but more generally believed in an addition compound between benzene and aluminum chloride with the hydrogen only lightly held. Wohl and Werlzporoch (Ber. 64, 1357) were of the same opinion. The dehydrative power of aluminum chloride should not be lost sight of whatever its catalytic action is toward aromatic compounds.

Huston and Friedmann (J. Am. Chem. Soc. 33, 2527) were the first to apply aluminum chloride condensation to the aromatic alcohols. They obtained diphenylmethane as the principle product when treating benzyl alcohol with benzene in the presence of aluminum chloride.

$$C_6H_5CH_2OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_5 + H_2O$$

The amounts of reagents and temperature of the reaction controlled the yields of the final product

and by-products. When equimolecular quantities are used, the yield of diphenylmethane was much smaller than when a large excess of benzene was used, while the secondary products were correspondingly decreased. They extended the work (J. Am. Chem. Soc. 40, 785) to the secondary alcohols, methyl phenyl, ethyl phenyl carbinols, and benzhydrol obtaining on condensation with benzene in the presence of aluminum chloride diphenylethane, diphenylpropane, and triphenylmethane respectively. The reaction can best be represented by the following equation:

$$C_6H_5\underset{R}{C}HOH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\underset{R}{C}HC_6H_5 + H_2O$$

The best yields were obtained when the R was a phenyl group. When the R was methyl the results showed better yields than when it was ethyl. It was thus concluded that the ethyl group had a greater retarding effect than the methyl group.

This work was extended by Huston (J. Am. Chem. Soc. 46, 2775) to the condensation of benzyl alcohol and phenol to give p-benzylphenol.

$$C_6H_5CH_2OH + C_6H_5OH \xrightarrow{AlCl_3} C_6H_5CH_2C_6H_4OH(p) + H_2O$$

The methyl and ethyl ethers were formed when anisole and phenetole were used. Thus the phenolic hydroxyl group presented no hinderance with the introduction of a benzyl group into the benzene ring when using aluminum chloride as a dehydrating agent.

Attention was then turned to the aliphatic alcohols by Huston and Sager (J. Am. Chem. Soc. 48, 1955), who reported at that time that methyl, ethyl, propyl, iso-propyl, butyl, iso-butyl, and iso-amyl alcohols would not condense with benzene in the presence of aluminum chloride. Since that time, the field has been again opened by Hsieh (Doctor's Thesis 1935) who modified the former procedure and condensed iso-propyl, iso-butyl, and iso-amyl alcohols(but not the normal alcohols) with benzene.

$$\begin{matrix}CH_3\\CHOH\\CH_3\end{matrix} + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\begin{matrix}CH_3\\CH\\CH_3\end{matrix} + H_2O$$

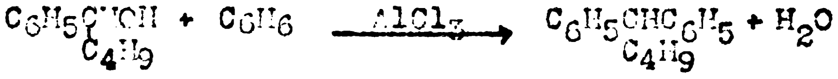
It will be well to note at this time the change in procedure. Heretofore the anhydrous aluminum chloride was added to the misture of benzene and alcohol in small amounts, while the mixture was stirred vigorously. The modified procedure is to add the alcohol dropwise to the stirred suspension of aluminum chloride in benzene. Fox (Master's Thesis 1931) obtained corresponding hydrocarbons with tertiary butyl, tertiary amyl alcohol, dimethyl n-propyl, and dimethyl iso-propyl carbinols with benzene in the presence of aluminum chloride using this modified procedure. Binder (Master's Thesis 1935) prepared several heptyl benzenes with this method.

The unsaturated alcohol, allyl alcohol did give in small yield the allyl benzene when it was condensed with benzene.

$$CH_2{=}CHCH_2OH + C_6H_6 \xrightarrow{AlCl_3} CH_2{=}CHCH_2C_6H_5 + H_2O$$

It was therefore advanced that the presence of unsaturation when adjacent to the carbinol carbon increased the activity of the alcoholic hydroxyl group.

Huston and Bartlet (Master's Thesis 1926) condensed phenyl butyl carbinol and phenol to give p-hydroxy 1, 1 diphenylpentane. The large yield of p-hydroxytriphenylmethane confirms the hypothesis that unsaturation of carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group.

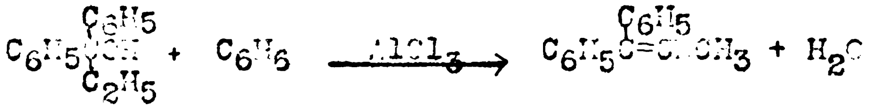


$$C_6H_5\underset{\displaystyle C_4H_9}{C}HOH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\underset{\displaystyle C_4H_9}{C}HC_6H_5 + H_2O$$

Huston, Lewis, and Grotemut (J. Am. Chem. Soc. 49, 1365) obtained p-hydroxy 1, 1 diphenylpropane, and p-hydroxytriphenylmethane by condensation. p-Hydroxy

1, 1 diphenylbutane was later added to this list by Huston and Stickler (J. Am. Chem. Soc. 55, 4317). The large yield of p-hydroxytriphenylmethane confirms the hypothesis that unsaturation of carbon atoms adjacent to the alcoholic group increases the reactivity of the hydroxyl group.

Hradel (Master's Thesis 1934) reported to have had no condensation of diphenylethyl or diphenylpropyl carbinol with benzene in the presence of aluminum chloride. Instead there was noted marked pulling out of a molecule of water from the carbinol itself to form an unsaturated hydrocarbon.



$$C_6H_5\overset{C_6H_5}{\underset{C_2H_5}{C}}OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\overset{C_6H_5}{C}=CH \cdot CH_3 + H_2O$$

This unsaturated product is believed to polymerize to a cyclo butane derivative. Fox (Bachelor's Thesis 1933) reported no condensation of diethylphenyl carbinol. The inability of these latter carbinols to condense is explained by the fact that the OH group is drawn closely to the carbon atom, thereby inhibiting it from being split off.

Summary of Alcoholic Condensations Using Aluminum Chloride

1-Of the aromatic alcohols (primary and

secondary only) only those having the hydroxyl group on the carbon adjacent to the benzene ring will condense with benzene in the presence of aluminum chloride.

2-Of the mixed tertiary alcohols no condensation has been reported instead dehydration took place.

3-In the saturated aliphatic series the tertiary carbinols show the greatest condensation with benzene in the presence of aluminum chloride; secondary carbinols next, but the normal carbinols do not condense at all.

4-In the unsaturated aliphatic series only those with the unsaturation adjacent to the carbon having the hydroxyl group show aluminum chloride condensation with benzene.

Other Methods for Preparing Diphenyl Propane, Butane, and Pentane.

ββ-Diphenylpropane has been prepared by Sabatier and Murat (Com. Rend. 155, 308). It was obtained by the condensation of ββ-dichloropropane and benzene in the presence of aluminum chloride.

The product had the following physical constants: M. P. 29°; B. P. 282°-283°; $D^{25°}$ .9958; $n_D^{25°}$ 1.570.

$\beta\beta$-Diphenylbutane has been prepared by Zincke and Thorner (Ber. 11, 1990). It was prepared by the reduction of α-methyl,α,α-diphenylacetone with hydrogen iodide and phosphorous, and has the following property: Platelets, M. P. 127.5°-128.5°.

γ,γ-Diphenylpentane has not been reported in the literature.

EXPERIMENTAL

EXPERIMENTAL

Materials

Ethyl bromide was prepared in the laboratory from sodium bromide, ethyl alcohol, and sulfuric acid. The crude product distilled carefully, and the fraction boiling 38° was collected and saved.

Ethyl benzoate was prepared from benzoyl chloride and ethyl alcohol. The crude product was refluxed with sodium hydroxide to get rid of excess benzoyl chloride. This product was then carefully distilled in a fractionating column; the ethyl benzoate obtained came over at 212°-213°.

Bromobenzene, acetone, methylethyl ketone, ether over sodium, and magnesium turnings were of good commercial grade. Refractionated or dried over anhydrous potassium carbonate when necessary.

Diethylphenyl carbinol was prepared by the Grignard reaction using ethyl benzoate and ethyl bromide. The product collected was that defined by Klages (Ber. 36, 3692) 125°-127°/10 mm.

Dimethylphenyl and methylethylphenyl carbinols were obtained from the Grignard reactions using acetone and methylethyl ketone respectively with bromobenzene. Dimethyl carbinol collected at 93°-95°/10mm. and the methylethyl carbinol at 102°-105°/14mm.

Thiophene-free benzene was used in all condensations. The anhydrous aluminum chloride was of good commercial grade.

Condensations

A.

Dimethylphenyl Carbinol, Benzene, and Aluminum Chloride I.

17 g. - 1/8 mole - 1 eq. Carbinol

78 g. - 1 " - 8 eq. Benzene

13 g. - 1/10 " - 4/5 eq. $AlCl_3$

The benzene was placed in a 500 ml-3 neck flask fitted with a stirring apparatus. The aluminum chloride was added to the benzene which was being stirred quite vigorously. The carbinol was placed in a small dropping funnel, the stem of which had been constructed to allow the carbinol to be added dropwise. The addition was completed in 2-1/2 hours. The temperature ranged from 25° to 30°; a water bath being used when the temperature reached 30°. The reddish mixture was stirred for an additional period of 3 hours and then allowed to stand over night. HCl gas was given off right from the start with the last traces being noticed the following morning when the stirrer was again started for a few moments. The mixture was then decomposed with ice in a dilute hydrochloric acid solution. The benzene and aqueous layer were separated, and the aqueous layer extracted three times with ether. The benzene and ether layers were united, washed with water and placed in a flask to dry over anhydrous potassium carbonate. The ether and benzene was distilled off over a steam bath, and the residue fractionated under vacuum of 2 mm.

- 110° - 1 g.
110° - 115° - 6 g. ββ-Diphenylpropane
115° - 120° - 3 g. Product "A"
120° - 125° - 2 g. Dimer of β-phenylpropene
Above 125° - 2 g. Tar

Equation for the formation of ββ-diphenylpropane:

$$C_6H_5\underset{CH_3}{\overset{CH_3}{C}}OH + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\underset{CH_3}{\overset{CH_3}{C}}C_6H_5 + H_2O$$

Dimethylphenyl Carbinol, Benzene, and Aluminum Chloride II

34 g. - 1/4 mole - 1 eq. Carbinol
98 g. - 5/4 " - 5 eq. Benzene
22 g. - 1/6 " - 2/3 eq. $AlCl_3$

Same procedure used as in I above. The time for addition of carbinol was increased to 3-1/2 hours with two additional hours of stirring after the final addition. After refractioning:

- 110° - 2-1/2 g.
110° - 115° - 4 g. ββ-Diphenylpropane
115° - 120° - 6 g. Product "A"
120° - 125° - 15 g. Dimer of β-Phenylpropene
Above 125° - 2-1/2 g. Tar

Dimethylphenyl Carbinol, Benzene, and Aluminum Chloride III.

The previous result seemed to show that too much aluminum chloride was used, so the amount was cut down in the following procedure:

34 g. - 1/2 mole - 1 eq. Carbinol = 1/4 mole
98 g. - 5/4 " - 5 eq. Benzene
17 g. - 1/8 " - 1/2 eq. $AlCl_3$

The same procedure as in II above was used giving the following fractions under 2 mm. vacuum:

- 110° - 2 g.
110° - 115° - 15 g. ββDiphenylpropane

115° - 120° - 3 g. Product "A"

120° - 125° - 2 g. Dimer of β-Phenylpropene

Above 125° - 2 g. Tar

The fraction 115°-120° crystallized into prisms of a melting point of 54°-55° when recrystallized into needles which after recrystallizations from alcohol gave a melting point of ~~133°-135°~~ 51° ??

?!
!!
higher

The percentage yields of ββ-diphenylpropane from three condensations were as follows:

I	6	grams yield	or 24 %	of theorectical
II	4	" "	or 8 %	of "
III	15	" "	or 31 %	of "

B.

Methylethylphenyl Carbinol, Benzene, and Aluminum Chloride I.

38 g. - 1/4 mole - 1 eq. Carbinol

98 g. - 5/4 " - 5 eq. Benzene

17 g. - 1/8 " - 1/2 eq. $AlCl_3$

The alcohol was added dropwise in 3 hours time to the stirred mixture of benzene and aluminum chloride. Stirred additional 2 hours and allowed to stand over night. A good evolution of HCl throughout the reaction. Decomposed, extracted, and dried over

anhydrous potassium carbonate. Fractions after fractionating three times under a 2 mm. vacuum:

37° - 38° - 4 g. β-Phenylbutane

38° - 117° - 4 g. Mostly unchanged Carbinol

117° - 122° - 15 g. ββ-Diphenylbutane

122° - 150° - 2 g. Polymers of β-Phenylbutene

Above 150° - 2 g. Tar

The fraction 117°-120° crystallized out into platelets from ethyl alcohol melting 127°-128°. It will be noted here that there does not seem to be the tendency of the unsaturated compound polymerizing into a dimer as in the other condensations.

Equation of reaction,

$$C_6H_5C(CH_3)(OH)(C_2H_5) + C_6H_6 \xrightarrow{AlCl_3} C_6H_5C(CH_3)(C_6H_5)(C_2H_5) + H_2O$$

Yield,

15 grams or 29% of theoretical.

C.

Diethylphenyl Carbinol, Benzene, and Aluminum Chloride I.

41 g. - 1/4 mole - 1 eq. Carbinol

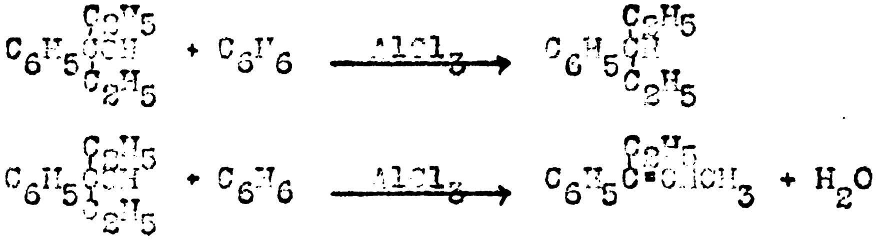
98 g. - 5/4 " - 5 eq. Benzene

17 g. - 1/8 " - 1/2 eq. $AlCl_3$

The procedure the same as above. Time of addition of the carbinol through a constricted funnel was 3-1/2 hours with 2 additional hours of stirring. The temperature of the reaction mixture was 22°. During the reaction there was no HCl gas given off, however, the solution darkened considerably. It was allowed to stand over night and decomposed with ice and hydrochloric acid, separated, extracted, and dried over anhydrous potassium carbonate. Fractionation three times under 2 mm. vacuum gave:

42° - 44° - 14 g. γ-Phenylpentane
44° - 130° - 10 g. γ-Phenylpentene
130° - 135° - 11 g. Dimer of γ-Phenylpentene
Above 135° - 3 g. Tar

Reactions:



$$C_6H_5\overset{C_2H_5}{\underset{C_2H_5}{COH}} + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\overset{C_2H_5}{\underset{C_2H_5}{CH}}$$

$$C_6H_5\overset{C_2H_5}{\underset{C_2H_5}{COH}} + C_6H_6 \xrightarrow{AlCl_3} C_6H_5\overset{C_2H_5}{C}=CHCH_3 + H_2O$$

Diethylphenyl Carbinol, Benzene, and Aluminum Chloride II.

Same procedure and amounts as used in I

above, but here the temperature of the reaction was kept between 3°-6°. The fractions were under a 2 mm. vacuum:

42° - 44° - 5 g. γ-Phenylpentane
44° - 130° - 5 g. Mostly γ-Phenylβpentene
130° - 135° - 18 g. Dimer of γ-Phenylβpentene
Above 135 - 4 g. Tar

Diethylphenyl Carbinol, Petroleum Ether, and Aluminum Chloride III.

Same procedure and amounts as used in I above, 100 grams of Petroleum ether instead of 98 grams of benzene. Fractionating under 2 mm. vacuum gave:

- 68° - 2 g.
68° - 72° - 26 g. γ-Phenylβpentene
72° - 135° - 2 g. Unchanged Carbinol
Above 135° - 2 g. Tar

It will be noted above that at room temperature the product mainly formed was γ-phenylpentane, while at lower temperature the dimer of the unsaturated γ-phenylβpentene was the main product. In a petroleum ether solution dehydration of the carbinol was the main reaction, and it did not polymerize to any great extent in this medium.

Analysis

1-The fraction 110°-115°/2 mm. from the dimethylphenyl carbinol condensation thought to be $\beta\beta$-diphenylpropane gave the following analysis:

Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.2095	.7045	91.71	.1571	8.35
Calc. $\beta\beta$-diphenylpropane		91.83		8.17

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.5387	.405	43.16	200.5
Calc. $\beta\beta$-diphenylpropane			196

The index of refraction by the Abbé refractometer was $1.569_D^{25°}$; reported $1.570_D^{25°}$.

This analysis checks very favorably to that reported in Comp. Rend. 155, 388 for $\beta\beta$-diphenylpropane.

2-The product marked "A" from the dimethylphenyl carbinol condensation gave the following analysis:

Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.2059	.6894	91.31	.1597	8.67
mine		91.46		8.59

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.4956	.274	43.16	266.5 236,16

Actual identification of the compound could not be reached.

3-The product melting 132-133° from dimethylphenyl carbinol condensation gave on analysis:

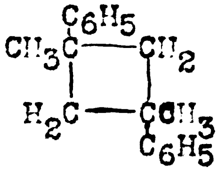
Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.2040	.6836	91.41	.1524	8.35
Calc. $(C_9H_{10})_2$		91.52		8.48

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.4062	.255	43.16	240.2
Calc. $(C_9H_{10})_2$			236

This compound was found to compare favorably to what Hradel (Master's Thesis 1934) would call a substituted cyclo butane, namely, 1 methyl 1 phenyl 3 methyl 3 phenyl cyclobutane.



4-The fraction coming over 37°-38°/2 mm. from the condensation of methylethylphenyl carbinol gave the following analysis:

Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.2047	.6710	89.40	.1886	10.31
Calc. β-phenylbutane		89.55		10.45

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.5206	.596	43.16	131.7
Calc. β-phenylbutane			134

The product compares favorably with that β-phenylbutane described by Klages (Ber. 35, 3509). Boiling at atmospheric pressure at 172°-173°. This compound might be expected since Huston and Freidmann (J. Am. Chem. Soc. 40, 785) noted the elimination of an aryl group from methane by the action of aluminum chloride.

5-The solid product melting 127°-128° from the condensation of methylethylphenyl carbinol gave upon analysis:

Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.1881	.6303	91.37	.1439	8.57
Calc. $\beta\beta$-diphenylbutane		91.42		8.58

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.4247	.318	43.16	201.4
Calc. ββ-diphenylbutane			210

The product compares closely to that described by Zincke and Thorner (Ber. 11, 1990) having the same melting point 127.5°-128.5°.

6-The first fraction, 42°-44°/2 mm. from the aluminum chloride reaction on diethylphenyl carbinol gave the following analysis:

Carbon and Hydrogen

Wt. of Sample	Wt. CO_2	% C	Wt. H_2O	% H
.2353	.7699	89.17	.2242	10.65
Calc. γ-phenylpentane		89.18		10.82

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.5462	.563	43.16	145
Calc. γ-phenylpentane			148

This compound compares favorably to that γ-phenylpentane described by Klages (Ber. 36, 693) having an atmospheric boiling point of 178° and an index of refraction of $1.4988_D^{25°}$.

3[illegible] ([illegible])

7-The next fraction, 130°-135°/2 mm. ,in the condensation of diethylphenyl carbinol gave on analysis:

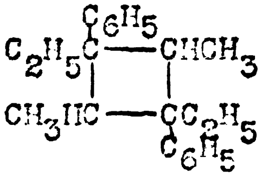
Carbon and Hydrogen

Wt, of Sample	Wt, CO_2	% C	Wt. H_2O	% H
.2704	.8949	90.21	.2268	9.33
Calc. $(C_{11}H_{14})_2$				9.57

Molecular Weight

Wt. of Sample	Temp. Diff.	Wt. Benzene	Mol. Wt.
.5486	.285	43.16	287.1
Calc. $(C_{11}H_{14})_2$			292.74 Cond 224

The dimer is thought to be 1 ethyl 1 phenyl 2 methyl 3 ethyl 3 phenyl 4 methyl cyclo butene, naming it according to Hradel (Master's Thesis 1934).



Summary

1-Dimethylphenyl and methylethylphenyl carbinols condense with benzene in the presence of aluminum chloride to form the corresponding hydrocarbons. The -diphenylpropane being formed in larger yields than the -diphenylbutane as would be expected since an ethyl group has a more retarding effect than methyl group.

2-Diethylphenyl carbinol does not condense with benzene.

3-All of these mixed tertiary aryl dialkyl carbinol condensation reactions are accompanied with dehydration to form the unsaturated hydrocarbon.

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