

## THESIS 3.METHYL-4.HYDROXY DIPHENYLMETHANE

Gladys Kidder Wardwell 1924



3-Methyl-4-Hydroxy Diphenylmethane

Thesis

Submitted to the Faculty of

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by

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## 1. Aluminum Chloride as Dehydrating & Condensing Agent. (Mechanism)

The two chief methods for organic condensations, the Friedel-Craft and Baeyer's reactions, were hitherto considered as distinct and entirely separate in mechanism; Friedel-Craft being purely catalytic, the aluminum chloride hence not entering into the reaction at all, and Baeyer's being dehydrolytic with consequent elimination of water. Frankforter and kritchevsky (Jr. Am. Chem. Soc., 36,1511, 1914) have shown that the mechanism of these two reactions is in reality very similar, inasmuch as aluminum chloride often acts like sulphuric in breaking off water.

In a very few cases aluminum chloride was found to act as a dehydrating agent alone, but in most cases it acts as both dehydrating and catalytic agent in spite of the fact that some of it is changed to the oxide.

As to how the reaction with aluminum chloride takes place was for a long time and for that matter still is a matter of speculation. Flayfair was the first to show the catalytic properties of aluminum. He observed that when a piece of cotton was dropped into indigo and then in nitric acid, no change took place until a very small amount of some aluminum salt was added, when the color disappeared.

Friedel-Craft found that when small quantities of aluminum chloride was added to amyl alcohol a vigorous

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reaction took place with evolution of hydrogen chloride and formation of a hydrocarbon which did not absorb bromine. If this reaction was made to take place in the presence of a hydrocarbon, a compound consisting of the hydrocarbon and the amyl radical was formed. (Compt. Rend., 84,1292, 1876). No explanation was given for this reaction for some time.

Gustavson (Bull. Soc. Chem., 42,325, 1884; Ber., 13,157, 1880) said an organic aluminum compound of unstable nature, which readily broke down to the condensed hydrocarbon and reformed aluminum chloride, was formed. Recently Scheichen and Buttgenbach (Jr. Prakt. Chem., 105,355, 1923) have confirmed Gustavson's idea.

Sholl and Seer (Monatsh., 33,1, 1912) observed that free hydrogen is sometimes given off and explained it as follows;

 $C_{b}H_{12} + Al_{2}Cl_{6} \longrightarrow C_{5}H_{11}Al_{2}Cl_{5} + HCl$ 

 $C_5H_{11}A1_2C1_5 + HC1 \longrightarrow C_5H_{10} + A1_2C1_6 + H_2$ 

Boeseken (Chem. Zentr., 1,897, 1912) condensed benzene with chloral in the presence of aluminum chloride and explains the reaction by assuming that diphenylmethane and chloroform are formed. He does not conclusively prove this however.

Dienesmann (Compt. Rend., 141,201, 1905) obtained the aldol reaction, due probably to a large excess of benzene and a higher temperature.

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Fage (Ann., 225,196) has recently shown that aluminum chloride possesses the power of transporting free chlorine to certain organic compounds.

Frankforter and Kritchevsky (Jr. Am. Chem. Soc., 36,1511, 1914) believed the reaction to take place something like this:

 $C_6H_6 + Al_2Cl_6 \longrightarrow Al_2Cl_5 - C_6H_5 + HCl$  or

 $C_6H_6 + Al_2Cl_6 \longrightarrow Al_2(C_6H_5)_6 + 6HCl$ 

Up to this point the reaction is purely catalytic and then through the catalytic action of the hydrogen ions the second part takes place.

 $Al_2(c_6H_5)_6 + 3ccl_3cho + 6hcl \longrightarrow$ 

 $3CC1_3CH(C_6H_5)_2 + A1_2C1_6 + 3H_2O$ 

The same authors show by the following equations the relationsnip between the Grignard, Eriedel-Craft, Baeyer, and their own reaction (as they believed it took place). (Jr. Am. Chem. Soc. 36,1516, 1914).

### Grignard

 $C_{6}H_{6} + CCH - CCl_{3} + Mg + I_{2} \longrightarrow C_{6}H_{5}CH(OH)CCl_{3} + MgI_{2}$   $\xrightarrow{\text{Friedel-Craft}} C_{6}H_{6} + CCH - CCl_{3} + Al_{2}Cl_{6} \longrightarrow C_{6}H_{5} - CH(OH)CCl_{3} + Al_{2}Cl_{6}$   $\xrightarrow{\text{Baeyer}} 2C_{6}H_{6} + OCH - CCl_{3} + H_{2}SO_{4} \longrightarrow (C_{6}H_{5})_{2}CH - CCl_{3} + H_{2}O + H_{2}SO_{4}$   $\xrightarrow{\text{Frankforter \& Kritchevsky}} 2C_{6}H_{6} + OCH - CCl_{3} + Al_{2}Cl_{6} \longrightarrow (C_{6}H_{5})_{2}CH - CCl_{3} + H_{2}O + Al_{2}Cl_{6}$ 

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· · · ·  2. Aluminum Chloride as a Dehydrating Agent in Organic

### Chemistry.

Many investigators used aluminum chloride as a dehydrating agent: Merz and Weith in 1881 (Ber., 14,189) prepared diphenylmethane by the action of aluminum chloride on phenol. Waas in 1872 (Ber., 15,1128) prepared di and triphenylmethane by the action of aluminum chloride on dichlorethyl oxide and benzene. believing that the aluminum chloride first converts the oxide into monochloraldehyde, which reacts with benzene to form monochlordiphenylmethane and finally triphenylethane. Graebe in 1901 (Ber., 34,1778: Chem. Ztg., 25,268) produced an aromatic amine by the action of hydroxylamine on the hydrochloride in the presence of eluminum chloride end ferric cnloride. Zinc chloride would not react. About the sime time Jeubert (Compt. Rend., 132,841, 1901) similarly prepared the hydrochloride of the amine using hydroxylamine hydrocnloride in place of the hydroxylamine. The per cent yield in both cases was very low. Sholl and Seer (1912) succeeded in uniting aromatic nuclei, especially in the case of aromatic ketones (Ann., 394, 119). For instance from orthotolyl-a-naphyl ketone he prepared 5-metnyl-1:9 benzanthrone. In this case aluminum chloride takes out free hydrogen in place of water.

Kritchevsky and Foppe (Jr. Am. Soc., 36,1511, 1914) showed the dehydrating properties of aluminum chloride when

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tney condensed pinene and chloral in the presence of aluminum chloride with consequent elimination of water. Later similar experiments with anisol and phenetol gave similar results.

Frankforter and kritchevsky (same reference) developed the following general method. "Mix reacting substances and cool to zero or below. Add aluminum chloride in small portions and allow to stand in a freezing mixture for some time (24-72 hrs.). Wash with water and distill with steam to remove any unchanged components. Extract with ether from which the condensation product will usually crystallize. Sometimes it is necessary to distill in vacuum". The above experimenters applied this method to aliphactic hydrocarbons, aromatic hydrocarbons, and also to the condensation of phenols, phenol ethers, alcohols, and ketones with chloral hydrate, the reaction taking place according to the general equation,

 $2RH + OCH-CCl_3 + Al_2Cl_6 \longrightarrow R_2CH-CCl_3 + H_2O+Al_2Cl_6$ They note that temperature plays a very important part in the reaction.

Frankforter and Kokatnur (Jr. Am. Chem. Soc., 36,1529, 1914) carried on experiments with trioxymethylene, benzene, and aluminum chloride, obtaining in each case the same general condensation products, anthracene and diphenylmethane. Toluene, xylene, and mesitylene in similar experiments were substituted for benzene.

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3. Action of Some Other Dehydrating Agents on Aromatic

Alcohols & Aromatic Compounds.

Several other dehydrating agents besides aluminum chloride have been used in Organic Chemistry. Meyer and Wurster (Ber., 6,964, 1873) prepared diphenylmethane from benzene and benzyl alcohol in the presence of concentrated sulphuric acid. Becker (Ber. 7,1203, 1874) prepared metanitro diphenylmethane in a similar manner. Noelting (Ber., 15,2091, 1882) has prepared by this same method dyes of the triphenylmethane group as. for example: tetramethyltriamidodiphenyltolylmethane was prepared from tetramethyldiamidobenzhydrol and para-toluidine in the presence of concentrated sulphuric acid. Gatterman and Koppert (Ber., 26,2811, 1893) prepared dinitrobenzyltoluene from paranitrobenzylic alcohol and paranitrotoluene. Bistrzycki and Flateau (Ber., 28,989, 1895) condensed mandelic acid with phenol to give hydroxydi, henylacetic lactone. Bistrzycki and Simonis (Ber., 31,2812, 1898) have prepared a-hydroxydiphenylacetolactone from mandelonitile and phenol using concentrated sulphuric acid.

Michael and Jeanpretre (Ber., 25,1615, 1892) prepared aromatic nitriles with phosphorus pentoxide as the dehydrating agent.

Fischer and Roser (Ber., 13,674, 1879), Liebmann (Ber., 15,152, 1882), and Kippenberg (Ber., 30,1140, 1897) have

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used zinc chloride as a dehydrating agent, preparing aminotriphenylmethane, some higher homologues of phenols, and some aromatic amino alcohols and their derivatives respectively.

Suais (Bull., (3)17,517, 1897) and Noelting Ber., 24, 1127 and 553, 1891) have used hydrochloric acid as the dehydrating agent while Faterno and Filetti (Gazz., 5,381, 1875) and Mohlau and Klopfer (Ber., 32,2147-2149, 1899) have used a mixture of concentrated sulphuric and acetic acids in the preparatins of benzylated phenols and the condensation products of benzhydrol and paraquinone respectively. Mohlau and Klopfer (Ber., 32,2150,2153, 1899) also used absolute alcohol as dehydrating agent in the preparation of the above compounds.

Khotinski and Fatzewitch (Ber., 42,3104, 1909) condensed aromatic carbinols with pyrrole in the presence of acetic acid.

## 4. Aluminum Chloride as Dehydrating Agent on Aromatic Alcohols and Aromatic Compounds.

Thus far it has been shown that a number of dehydrating agents such as sulphuric acid, phosphorus pentoxide, zinc chloride, dilute or concentrated hydrochloric acid, a mixture of concentrated sulphuric and acetic acids, absolute alcohol, acetic acid have been used in the condensation of arometic

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alcohols and aromatic compounds; also that aluminum chloride has been used in Organic Chemistry as a dehydrating agent by various investigators.

Aluminum chloride, however, was not used in the condensation of aromatic electhols with aromatic compounds until about 1916 when Euston and Friedemann (Jr. Am. Chem. Soc., 38,2527, 1916) prepared diphenylmethane and anthracene (as a by-product to the extent of about 20% of the theoretical yield) from benzene and benzyl alcohol in the presence of aluminum chloride and found that the amounts of reagents used, and the temperature at which the reaction took place greatly influenced the final yield.

In a later paper (Jr. Am. Chem. Soc., 40, 1918) the same experimenters extended their experiments to secondary alcohols, benzene and aluminum chloride (as a dehydrating agent) using methyl phenyl carbinol, ethyl phenyl carbinol (both mixed aliphactic aromatic alcohols), and benzhydrol (a true secondary aromatic alcohol), obtaining diphenylmethane, diphenylpropane, and triphenylmethane respectively. They concluded that methyl and ethyl groups interfere with condensation of aromatic alcohols and benzene, the latter having the greatest retarding effect, and that a second phenyl group does not interfere with the second condensation.

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5. Benzyleted Thenols; Dehydreting Agents Other

Than Aluminum Chloride.

Several investigators have benzylated phenols using dehydrating agents other than aluminum chloride. Taterno (Gazz. 2.20, 1872) prepared benzylated pnenol by treating both benzyl chloride and benzyl elcohol with zinc turnings. He also bonzylated anisole in the same way. Paterno and Filetti (Gazz., 5.381, 1875) prepared the same compound using a mixture of acetic and sulphuric acids as the dehydrating agent. Liebmann (Ber., 14,1844, 1881; Ber., 15,152, 1882) carries out this same reaction using zinc chloride and states that Paterno's reaction in which he uses zinc is not aue to the metallic zinc, but to the zinc chloride formed from the zinc and hydrochloric acid in the benzyl chloride. Faterno and Mazzara (Gazz., 8,303) extended this reaction to the benzylation of substituted pnenols using cresol, benzyl chloride, and zinc turnings. Venturi (Gazz., 31,1,469, 1901) benzylated cervacrol and meta-cresol using zine chloride.

Still other investigators have by this method condensed phenols with alcohols other than benzyl alsohol. Auer (Ber., 17,669, 1884) prepared ethyl phenol from phenol, ebsolute alcohol and zinc chloride. Dennstedt (Ber., 23, 2569, 1890) successfully prepared the same compound by passing absolute alcohol and phenol over heated zinc dust.

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Senkowski (Ber., 24,2974, 1891) in the same way prepared the nigher nomologues of phenols by the action of zinc / chloride and states that they invariably belong to the para series. Hauer (Her., 1614, 1894) condensed cresol and **iso**- / butyl alcohol with zinc enloride.

These and similar benzylated and alkyl phenols have been prepared by the reduction of ketones by zinc amalgam and hydriodic acid. (Clemmensen Ber., 47,55, 1914; Claus, Jr. Prakt. Chem., 45,377; Graebe, Ber., 7,1624; Borgelline and Milacene, Centrablt., 2,948.)

Darzens successfully reduced ketones by a specially prepared nickel at a temperature of 190-195 degrees. (Compt. Rend., 139,868). Voswinkel (Ber., 42,165) showed that aromatic hydroxy ketones can be reduced to alkyl phenols. Johnson and Hodge (Jr. Am. Chem. Soc., 35,1014) smoothly reduced mixed ketones containing ether or hydroxy redicals by the zinc amalgam method to alkyl derivatives. Herzig and Wenzel (Monatsz., 27,781) introduced methyl groups into the ring of certain phenols with methyl iodode in alkaline solution.

# 6. Benzylation of Phenols in the Presence of Aluminum Chloride.

There seems however to have been no attempt made to prepare the benzylated or alkyl phenol using aluminum

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chloride as a dehydrating agent. Dr. Huston has successfully condensed phenol, anisol and phenetol with benzyl alcohol in the presence of aluminum chloride.

It was found that when a mixture of ortho-cresol and benzyl alcohol in petroleum ether was mechanically stirred during the slow addition of anhydrous aluminum chloride, much hydrochloric acid gas was driven off and after some time a semi-solid granular precipitate settled out. On decomposing with ice, extracting with ether, and distilling in vacuum the residue left after distilling off the ether, a good yield of a yellow crystalline substance, boiling at 155-160 at a pressure of five millimeters was obtained. On recrystallization from petroleum ether long white needles melting at 49-49.5 degrees were obtained. This was thought to have the structure of 3-methyl-4-hydroxy diphenglmethane. That this is correct will be shown under the experimental part of this thesis.

#### Experimental

1. Metnod.

One hundred grams of benzyl alconol, one hundred and twenty grams ortho-cresol, and two hundred grams of petroleum ether were mixed and stirred constantly with a motor. Aluminum chloride was adaed in small portions until a total of sixty grams had been added. The reaction started Very slowly, it being necessary to warm the mixture to

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about 35 degrees. This temperature was maintained thoughout the experiment. After about an hour hydrochloric acid gas began to come ofr, slowly at first and then more rapidly. If the aluminum chloride is added too fast the mixture will foam a great deal and probably overflow. (This is prevented by againg from time to time, when necessary. more petroleum ether). Two layers formed and a semi-solid, granular precipitate settled out. After practically no more hyperogen chloride came off the motor was turned off. more petroleum ether saded if necessary and the mixture allowed to stand overnight. It was then poured onto ice to decompose it, extracted with ether and the ether extract dried over anhydrous potassium carbonate. After distilling off the ether, the residue was fractionally distilled in vacuum at a pressure of five millimeters.

1.	Up to	14040.0	grs.
	150-1	• 5554.0	Π
	155-1	8.6	n
	180-2	4035.1	Π
	Resid	ue24.1	17

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The fraction from 155-180° came over as a thin, light yellow oil which on standing a short time crystallized out in long needles. The fraction from 180-240° was a thick readish brown syrup which did not crystallize. The residue on cooling was a very thick dark brown tar.

Distillation in each case was repeated from four to eight times until the final product (fraction boiling between 155 & 180) seemed sufficiently pure for recrystallization. Two more batches were made up and this time the first fraction (up to 140) was distilled under atmospheric pressure.

- 4. 188-195 (atmos. pressure)-----27.70 grs. 155-160-----46.00 " 180-250------54.50 "
  - Residue-----14.10 "

The corresponding fractions from each of these four lots were combined and redistilled, giving the following results.

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220-225-----(mostly 224)----113.5 grs. 225-250-----(mostly 227)-----14.5 " Residue------13.00 "

(Note; All except the first fraction were distilled at five millimeters pressure.)

The principal fraction from 155-160 was recrystallized from petroleum etner to constant melting point (49-49.5). The fraction from 160-180 after standing somewhat over a wook also crystallized out and was recrystallized as above. After the greater part of the fraction has crystallized from petroleum ether and had been filtered off, quite a little came down, not as crystals, but as an oil. The ether was allowed to evaporate off. After standing in a cool place for a couple of weeks the oil crystallized out. The crystals were pressed between filter papers to remove any oil and recrystallized as before.

The substance is insoluble in water, very soluble in chloroform, ether, alcohol, and alkali. It crystallizes in fine long needles from petroleum ether. It boils between 155 & 160, 5 mm. pressure and melts from 49 to 49.5.

Analysis (Huston)

.1515 Ers. substance gave .0970 Ers. 190 &

.474 grs. CO

.1523 Ers. substance gave .0971 Ers. H.O &

.4746 grs. CO

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Found 7.13% and 7.17% hydrosen. \* 55.01% \* 85.31% carbon. Calculated 7.12% hydrogen 85.80% carbon.

So far as is known in condensation of this type, the CH<sub>2</sub> group boes into the position para to the hydroxyl group; for instance, Senkowski prepared para-tertiary butyl phenol from butyl alcohol, phenol and zine chloride (Ber., 24,2974); Anschutz and Beckerhoff prepared paratertiary amyl phenol from iso-amyl or tertiary amyl alcohol, phenol, and a mixture of acetic and sulphuric acids (Ber., 28,407); Oscar Döbner prepared para-dioxytriphenyl carbinol from benzotrichloride and phenol (Ann., 217,223); and para-benzyl phenol may be prepared from benzyl chloride, phenol and zine chloride or from benzyl alcohol, phenol and concentrated sulphuric acid (Richter-Smith Creanic Chem., Vol., 2,343).

Therefore the structure of this condensation product of benzyl alconol and ortho-cresol was thought to be 3-methyl-4-hydroxy dipnenylmethane.

СН20Н AlCl<sub>3</sub> CH2

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2. Freparation of the Amine.

The first step in an attempt to prove this was to replace the phenolic hydroxy group with the amino group. (Die Methoden der Organischen Chemie. Besonderer Teil, Abl., 2,1218, Weyl). Twenty grams of the substance were mixed thoroughly in a mortar with forty grams of zine ammonia chloride and four grams of ammonium chloride. The mixture was placed in pressure tubes, care being taken not to fill each tube more than one quarter full. After heating in a bomb furnace for twenty hours at a temperature of 330 degrees, the contents of the tube (a dark oily substance) were loosened with warm hydrochloric acid (one part of concentrated hydrochloric acid to one of water), and shakened vigorously for sometime. The oil which came to the top was allowed to stand in contact with the acid over night. It was then extracted with ether to remove the unchanged phenol. The acid solution was just neutralized with concentrated ammonium hydroxide and the amine precipitated with reagent sodium hydroxide. After standing over night the amine was filtered off and allowed to dry. No solvent was found from which the amine could be recrystallized.

From twenty grams of the original phenol, two grams of the amine were obtained. The yield is slightly increased by evaporating the ether off from the ether extract and again shaking the residue with more hydrocaloric acid. • •

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The zinc ammonia chloride used was prepared as follows; (Treatise on Chem. Roscoe and Schlorlemmer, Vol., 2,652) Ammonia was added to a solution of zinc chloride until the precipitete first formed redissolved. The solution was evaporated elmost to dryness and heated on a send bath to 149 degrees, during constant stirring.

ZnCl<sub>2</sub>+ NH<sub>4</sub>OH ---- ZnCl<sub>2</sub>4NH<sub>3</sub>H<sub>2</sub>O

 $2nCl_24NH_3H_2O \longrightarrow 2nCl_22NH_3$ 

Two hundred grams of zinc chloride gave a theoretical yield of two hundred and eighty grams of zinc ammonia chloride.

3. Preparation of the Hydrocerbon.

The next step in the proof of the structure of the condensation product was reduction of the amine to the hydrocarbon. (Gatterman. Laboratory Manual of Organic Chemistry, 207) Five grams of the amine were discolved in a mixture of fifteen grams of concentrated hydrochloric acid and thirty c.c. of water until free nitrous acid was recognized with steron potessium iodide paper. The diazobenzene chloride solution thus prepared was allowed to flow carefully into a solution of ten grams of caustic soda in thirty c.c. of water contained in a four hundred c.c. flask, well cooled with ice water. Further, twenty grams stennous chloride were dissolved in fifty c.c. water and treated with a concentrated solution of sodium hydroxide (two parts sodium hydroxide to three of water) until the precipitate first formed was redissolved in an excess of alkali. The alkeline diszobenzene solution, well cooled with ice water, was gradually treated with small portions of the sodium stannous oxide solution, previously well cooled, waiting after each addition until the lively evolution of nitrogen had ceased before adding more.



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It was immediately warmed on the water bath to drive off nitrous oxide gas, extracted with ether, and dried over anhydrous calcium chloride. The ether was distilled off and the hydrocarbon distilled, using a weighed test tube as a receiver. .530 grams of a hydrocarbon boiling at 274-276 were obtained, giving a yield of about thirty per cent. This boiling point corresponds exactly with that of benzyyl-



toluol, the hydrocarbon one would expect to get from the amine, providing the assumed structure is correct. This is in itself sufficient proof that the condensation

product is 3-methyl-4-hydroxy diphenylmethane (page 13).

4. Preparation of the Acid.

To further substantiate the proof of the above structure an attempt was made to oxidize the hydrocarbon to an acid expecting to get benzoylbenzoic acid; M.P. 140-144 (Senff, Ann., 220-237)

Starting with .530 grams of hydrocarbon, proportional amounts of sulphuric acid and potassium dichromete were used according to the following method; ten grams of hydrocerbon, sixty grams of potassium dichromate, ninety grams of concentrated sulphuric acid and two hundred grams of water were boiled under reflux condenser for two or three days. On cooling a hard cake of unoxidizable hydrocarbon,

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ketone, and enromoxide was formed. Oxidation was evidenced by the enange in color of the mixture from a red to a cark green. The mixture was digested on the water bath with dilute sodium hydroxide, filtered and washed with water. The filtrate was more than neutralized with hydrochloric acid and the precipitated acid dissolved in ammonia, decolorized with snimal enarcoal and reprecipitated and recrystallized from alcohol.

A few crystels were obtained in the bottom of the beaker, but they were not abundant enough to filter and obtain the melting point as the filter paper absorbed them. Eack of time and more of the hydrocarbon prevented the repetition of this experiment.

5. Preparation of the Esters.

Either of two isomeric phenols (condensation products of ortho-cresol and benzyl alcohol) might give benzyltoluol on reduction to the corresponding hydrocarbon.



Thus far it has been proven that the benzyl alcohol, ortno-cresol condensation product has the structure of either compound one or two above. I should esterify very readily. II would not, due to the position of the hydroxy group.

I. Schotten-Baumm Method (Meyer and Jacobsen II pt. I 546.)

One gram of the substance to be esterified was dissolved in reagent solur hydroxide and about twice the calculated amount of penzoyi chloride added to it. After a very little shaking the mixture became quite not and on further shaking the ester separated out as a solid, while the excess benzoyi chloride went into solution as sodium benzoate. The liquid was poured off and the solid ester pressed between filter papers, until the oil was entirely gone. This fast step was necessary in order to prevent the ester coming down as an oil on recrystallization. After the oil was entirely removed from the ester it was recrystallized from dilute alcohol to constant melting point; 114.5-115 degrees. The yield is excellent, being almost theoretical.



The ester is soluble in dilute alconol, ether, chloroform, silently soluble in petroleum ether, and insoluble in alkali and water.

A similar ester was made with toluoi sulphone chioride according to the above method. In this case the reaction takes place much more slowly, it being necessary to neat on the water bath for about three quarters of an nour. Even then it is impossible to crystallize the greater part of the ester. Most of it remains as an oil, the boiling point of which it was impossible to obtain due to the

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and not melt below Sou desrees.



The ester is only slightly soluble in chlorolorm and ether, is soluble in water, and insoluble in alkali.

II. Reverain Methoa (Ber., 35,1443)

The same esters were prepared by the Reverain method. One gram of the substance to be esterilied was dissolved in a small amount of pyridine. About twice the calculated amount of benzoyl chloride was added and the mixture shaken vigorously for sometime. On cooling it was poured into water when the ester separated out as a solid and the pyridine dissolved in the water. The ester was initered off, washed in a very small amount of cold alcohol and pressed between filter papers until the oil was all out. It was then recrystallized from allute alcohol to constant meiting point; 114.5-lib degrees.

A similar ester was made with toluoi sulphone chicride, it being necessary to near on the water path as perore. As in the Schotten-Baum method the ester came down as Bh oil and did not crystallize. No polling point was obtained.

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Summary.

1. Fnenois may be benzylated in the presence of aluminum chioriae with good results.

2. The condensation product of ortho-cresol and penzyl alcohol was isolated and described.

3. By replacement of the phenolic hydroxy group with the smino group and consequent reduction of the amine to the hydrocarbon the condensation product was shown to have the structure of 3-methyl-4-hydroxy diphenylmethane. Analysis substantiated this formula.

4. Ease of esterilication confirms the above structure.

1. General References.

1. Ador and Rillet. Ber., 12,2000 (10/9)

2. Vincent & Roux. Bull., (2) 40,103 (1003)

3. 0. Fischer. Ann., 206,113 (1000)

4. Enotlusky & Patzewitch. Ber., 42,3104 (1909)

5. Kollaritz & Merz. Zschr. Chem., (1071), 705

Ber., 0,441 (1012)

Ber., 0,440,000 (1073)

6. Oscar Döuner. Ann., 217,223

7. Richter Smith. Organic Chem. Vol. II, p.343.

2. General; Action of Aromatic Alconols on Aromatic Compounds

i. E. & A. Fischer. Ber., ii,197 (1070)

2. Hemilian. Ber., 10,2000

5. E. & A. Fischer. Ann., 194,213

4. Hemilian. Ber., 19,3061 (1006)

υ. Ειυμ., Jr. Pr. Chem., (Δ) 35,476,404,400, (1007)

6. Suoll, Holderman, & Manield. Ber., 40,1654 (1907)

7. Scaremm. Ber., 26,1700 (1093)

0. Radzie wa nowski. Ber., 27,3237 (1094)

9. Verley Bull., (3) 14,914 (1097)

10. Meyer. Jr. Prakt. Chem. (2) 82,538 (1910)

il. Dienesmann. Compt. Rend., 141,201 (1905)

3. Aluminum Culoride as Denyarching Agent in Organic Cuemistry

L. Merz & Weith. Ber., Loy (1001)

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2. SHOLL & SEET. ADD., 394,194 (1914) 5. Wars. Bei., iu, 1120 4. Graeue. Chem. Ztg., 20,200 (1901) Ber., 34,1770 (1901) 5. Jaubert. Compt. Rena., 152,41 (1901) 6. Frankiorter & Kritunevsky Jr. Am. Chem. Soc., 36,1611 (1914)Jr. Am. Cuem. Soc., 37,300 (1910) 7. Flankister & Kokathur Jr. Am. Chem. Soc. 30,1629 (1914) 4. Suiphuric Acia as a Demyarating Agent 1. Myer & Wurster, Ber., 0,904 (1075) 2. Becker. Ber., 10,2091 (1002) 5. Nuelting. Ber., 24,3127,3130 (1091) 4. Gatterman & Koppert. Ber., 20,2011 (1093) U. BISTRZYCKI & FLETCER. BOR., 20,909 (190) 6. Fritson. Ber., 29,2000 (1090) 7. Bistrzycki & Simonis. Ber., Si, Zoik (1090) 5. Phosphorous Fentoxius as Denyarating Agent 1. Michael & Jeanpretre. Ber., 20,1015 (1092) 6. Zino Caloriae as Denyarating Agent 1. Fischer & Roser. Ber., 15,014 (1013) Ann., 200,110,105 (1000) 2. Lieumann. Ber., 10,102 (1002) 5. Kippenberg Ber., 50,005 (losi) 7. Dilute or Concentratea Hydrochloric Acia

1. Sualo Bull., (3) 17,017 (1097); D. R. P. 27002

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L. NOBITING. BOI., 24,0127 (1091)

Ber., £4.663 (1091)

o. Sulphurio & Acetic Acias (mixeu)

1. Paterno & Filetti Gazz., 5,801 (1075)

2. Moniau & Klopfer. Ber., 32,2147,2149 (1099)

y. Absolute Alconol.

l. Monlau & Klopfer Ber., 52,2100, 2105 (1099) 10. Stannio Culoriúe

1. Bistrzycki. Ber., 37,009 (1904)

11. Acetic Aciú.

1. Knotinaki & Patzewitca Ber., 42,3104 (1909) 12. Benzylation of Paenols.

1. Paterno Gazz., 2,2 (1072); 3,121 (1073)

2. Meyer & Wurster Ber., 6,964, (1873)

5. Paterno & Filetti Gazz., 0,301 (1075)

4. Paterno & Mazzara Gazz., 303

5. Liebmann Ber., 14,1044 (1001)

6. Becher Bel., 10,2091(1002)

7. Liebmann Ber., 15,152 (1002)

5. Venturi £822., 31 91, 469

13. Almyl Puenols.

Auer. Ber., 17,669 (1804)
 Dennatedt Ber., 20,2009 (1890)
 Senkowski Ber., 24,2974 (1891)
 Bauer Ber., 27,1014 (1894)

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- 5. Anschutz & Beckerholl Ber., 20,407 (1095)
- 6. Herzig & Wenzel Monston. 37,101 (Aus. L 3212)
- 7. Степшензен Вег., 41,00 (тэі4)
- 6. Johnson & Hoase Jr. Am. Chem. Soc. 56,1014
- 9. Johnson & Komman Jr. Am. Chem. Soc. 36.1259
- 14. Experimentar
  - 1. Weyl, "Die Methoden der Organischen Chemie" Pt.2.1210
  - 2. Roscoe & Schlorlenner "Tractice on Chemistry" Vol., 2.602.
  - 5. Gatterman "Laboratory Hanuar of Organic Chemistry" P. 207.
  - 4. Зенії. Анн., 220,201
  - 5. Meyer & Jacobsen Vor. 2, pt. 1., 540.
  - 6. Reverain & Crepieux Ber., 85.1443



