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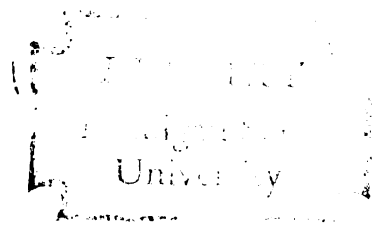
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A STUDY OF P- AND O-BENZYL-PHENOL
AND SOME OF THEIR DERIVATIVES
THESIS FOR DEGREE OF M. S.
FRANK HIRSH MAXFIELD

1929

THESIS

N. G. Houston



**A Study of
P-and O-Benzyl Phenol
and
Some of Their Derivatives**

Thesis

**Submitted to the Faculty of
Michigan State College as partial fulfillment
of the requirements of the Degree of
Master of Science.**

**By
Frank Hiram Maxfield**

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Appreciation

The writer wishes to express his appreciation to Dr. R. C. Huston for the assistance and timely advice given throughout this work, without which the work would not have been possible.

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In 1872, L. Paterno (Gazz. chim. ital. 2, 1-6) heated gently a mixture of benzyl chloride and phenol in the presence of Zn. HCl was given off, and the liquid entered into ebullition. Later, a brown liquid was separated from the Zn, and distilled. The uncombined benzyl chloride and phenol were distilled off below 260°. The remaining mass was distilled at 6 mm., and the main fraction thus distilling at 180-190°. This solidified to a mass of small needles, contaminated with an oil, which was pressed out and discarded, while the needles were recrystallized from alcohol. This benzylated phenol crystallized in white silky needles (M. 84) which were soluble in alcohol, ether, benzene and chloroform. The pure phenol boiled at 175-180 at 4-5 mm. It was soluble in alkaline solutions, but was precipitated by acids. It was insoluble in NH_3 . HNO_3 formed substitution products. H_2SO_4 gave a sulfonic acid with the phenol, the barium salt of which was soluble in H_2O .

Benzylated anisole treated ^{with} HI, and boiled for eight hours at 170° gave CH_3I , and the same benzyl phenol as just described.

In 1874, E. Paterno and M. Filletti (Gazz. chim. ital. 3 121-129, 251-254) published an article in which they describe more derivatives of benzyl phenol. Benzyl phenol with acetyl chloride gave benzyl phenol acetate in the cold. This compound could not be crystallized but remained a pale yellow liquid, B.P. 517°, density 1.1043 at 16°. It was very

easily hydrolyzed, absorbing sufficient moisture from the air to decompose the ester, benzyl phenol crystallizing out.

Benzyl phenol and benzoyl chloride gave benzyl phenol benzoate. This was very soluble in C_6H_6 , and crystallized from C_6H_6 in friable crystals of the triclinic system. It crystallized from alcohol in glistening needles, M.P. 86° . This compound was not decomposed by alcohol, H_2O or aqueous potassium hydroxide.

The same authors describe a di-brom derivative prepared by adding excess Br_2 to a solution of benzyl phenol in CS_2 . This compound melted at 175° and remained an amorphous substance, soluble in $CHCl_3$ and CS_2 , but insoluble in alcohol and ether. Later workers have questioned this compound. (Zincke and Walter. Ann. 334, 367-385, (1904)).

In 1875, Paterno and Fioleti (Gazz. chim. ital. 5, 381) again published an article in which they describe the preparation of benzyl phenol by a different method. Benzyl alcohol and phenol were condensed, using a mixture of H_2SO_4 and acetic acids to eliminate a molecule of HOH . They obtained a mass of crystals, which on purification proved to be benzylated phenol. A fluorescent oil was also obtained in considerable quantity which did not crystallize, but appeared to be an isomeric benzyl phenol.

In 1880, Perkin and Hodgkinson (Journ. Chem. Soc. 1880, P 724) boiled phenyl acetate with benzyl chloride. A beautiful fluorescent liquid was obtained, B. P. $310-320^\circ$. Analysis showed a composition of $C_{25}H_{24}O_2$. This was readily

saponified with alcoholic KOH. An oil rose to the surface. This oil on purification, yielded crystals, M.P. 39° . Analysis indicated formula of $C_{10}H_{10}O$. This may be cinnamyl methyl ketone, $C_6H_5-CH=CH-CO-CH_3$. The alkaline solution from the above saponification was acidified, and an oil separated out. On purification it melted at $80-81^{\circ}$ and boiled at $320-322^{\circ}$. Analysis indicated formula of $C_{13}H_{12}O$. They concluded that this compound was identical to the benzyl phenol prepared by Paterno by the action of benzyl chloride on phenol in the presence of Zn dust. The difference in melting point was thought due to impurities in their compound.

Liebmann (Ber. 15, P. 152, 1882) (Ber. 14, 1842, 1881) prepared benzyl phenol from benzyl alcohol and phenol in the presence of molten $ZnCl_2$. Propyl and amyl phenols were prepared by the same method. The benzyl phenol thus prepared had a M.P. 84° and boiled at $325-330^{\circ}$.

In 1882, Rennie made a rather extensive study of benzyl phenol, and its derivatives. (J. Chem. Soc. 1882, P 33). He prepared his benzyl phenol in the same manner as Paterno, i.e. benzyl chloride and phenol in the presence of Zn dust. He prepared and described the mono sulfonic acid and its salts with barium and potassium, potassium bromo-benzyl sulfonate, tri nitro benzyl phenol and the methyl ether of benzyl phenol. After a study of these derivatives, he states that benzyl phenol resembles p-cresol in its action with H_2SO_4 , HNO_3 or Br_2 .

Later in the same year Rennie (J. Chem. Soc. 1882 P 220) reports a further study of benzyl phenol derivatives. This time he includes benzyl phenol-sulfonic acid, mono nitro benzyl phenol, amido benzyl phenol, di nitro benzyl phenol, tri nitro benzyl phenol oxidation products, nitro brom benzyl phenol and its reaction with HNO_3 . Di nitro benzyl phenol oxidized gave benzoic acid, indicating that these two nitro groups were in the original phenol ring. Tri nitro benzyl phenol, upon oxidation, gave p-nitro benzoic acid, hence indicating that the third nitro group went into benzyl group, rather than in the original phenol ring.

After studying these compounds, all derivatives of benzyl phenol, Rennie concludes that the benzyl group must be in the para position in the phenol ring. This view is substantiated by the fact that the same nitro-brom derivative is obtained, whether HNO_3 acts on the mono brom derivative or Br_2 acts on the mono nitro derivative. Hence, the nitro brom derivative, and consequently the nitro sulphonate, and the brom sulfonate must be symmetrical. The only possible way to explain this fact, is to assume that the benzyl group is in the para position of the phenol ring. Also nitro brom benzyl phenol, with HNO_3 , gave ortho-brom-alpha-dinitrophenol, the second NO_2 group taking the position left by the benzyl group.

Although the above reasoning seemingly makes it certain, that the benzyl group is in the para position, other

facts served to add an element of uncertainty to Rennie's theory. First, the melting points of the mono and di-nitro derivatives differed by only 130, while the corresponding derivatives of para cresol differed by 40°. Secondly, the yield of di nitro benzyl phenol was always small, regardless of the method of preparation. Still more important, however, was the fact that the potassium salt was of an abnormal color for such di-nitro compounds. This salt gives orange needles in contrast to the depth and beauty of the crystals of di-ortho-nitro derivatives of other phenols. The fact, that addition of nitric acid to the di-nitro-benzyl phenol gave tri-nitro phenol instead of tri-nitro benzyl phenol, was also puzzling. Tri nitro benzyl phenol is formed by direct nitration of di nitro benzyl phenol. Its constitution will depend on that of the di nitro derivative. One NO₂ group must be in the benzyl group; p-to the CH₂, however, since it yields p-nitro benzoic acid on oxidation, and a second one must be in the position ortho to the OH group. The position of the third must be regarded as somewhat doubtful.

Rennie published again in 1886 (J. Chem. Soc. 49, 405) reporting some further examination of di nitro para benzyl phenol, and also a study of the oil which always occurs with the crystals of p-benzyl phenol. This oil was pressed out, extracted with alcohol and studied. It was first sulfonated and the barium salt formed. The Ba salt of the p-benzyl phenol crystallized out, but the remainder did not promise to crystallize well, so the barium was replaced with

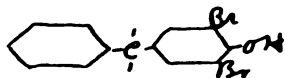
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potassium, whereupon good crystals were obtained with 2 1/2 molecules of H₂O of crystallization. The nitro sulfonate formed pale yellow rosettes, M. 81-82. The sulfonate treated with bromine, gave some brom sulfonate but also some white flakes, which on recrystallizing from alcohol and water, formed minute white crystals melting at 91°. This compound was soluble in alcohol, ether, acetic acid or alkali. He remarks that this is probably a di brom derivative, but he makes no further study of it. (This will be shown later in this paper, to be 2, 4, di brom 6 benzyl phenol, as Rennie suspected but had no definite proof).

M. Backunin studied the condensation of benzyl chloride and phenol in the presence of zinc (Gazzetta 33 1, 495-496 (1903), *ibid*, 33 11, 454-460 (1903)) with the idea of determining the best conditions of condensation. He concludes that a neutral solvent is the best to use, since it gives a finer division of the substances reacting, and hence more chance for contact and reaction. He prepared benzyl phenol benzoate (M.P. 86-87) by heating benzyl phenol with benzoic acid, in the presence of phosphoric oxide in benzene solution.

L. Zincke and W. Walter (Ann. 334, 367-385, (1909)) published some work on bromine substitution in phenols, especially in the case of *p*-benzyl phenol. They prepared the benzyl phenol by condensing benzyl chloride and phenol with zinc, as Paterno had done before. (*loc. cit*). He describes

the benzoyl derivative, as needles melting at 87° . p-benzyl phenol treated with 2Br_2 in a solution of chloroform, gave a product having two crystalline forms, one being colorless needles melting at 44° , but which was unstable and readily passed to the more stable form on standing, the stable form being rhombic crystals M. 57° . The acetyl derivative of this di brom benzyl phenol formed mono-clinic prisms, M.P. 53° . He concludes that the formula of this compound is



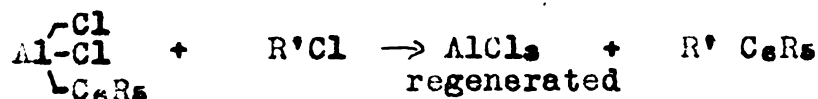
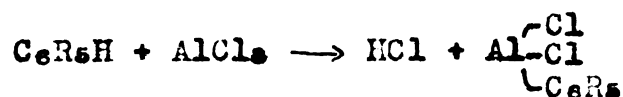
because when it is treated with NaNO_2 , a bromine atom is readily replaced with a NO_2 as is the case when ordinary brom phenols are treated with NaNO_2 , under the same conditions. Zincke and Walter also describe tri-brom and penta brom-derivatives of p-benzyl phenol. It is to be noted, that the di brom derivative of o-benzyl phenol, announced by Paterno and Fileti (Gazz. chim. ital. 3, 121-129, 251-254) M.P. 175° , does not agree with any compound prepared by Zincke and Walter.

The action of AlCl_3 , as a catalyst, in condensing various substances has been studied extensively since 1876, when Friedel and Crafts worked with amyl alcohol and hydrocarbons. (Compt. rend. 84, 1392) At this time they worked only with aliphatic compounds, and even state that AlCl_3 will not condense aromatic compounds. Gustavson (Ber. 13, 157, 1880) (Bull. Soc. Chem. 42, 325, 1884) believed that an unstable organic aluminum compound was formed, which broke down giving AlCl_3 . In 1881, Merz and Weith, (Ber. 17, 187), report having

prepared di phenyl ether from the action of AlCl_3 on phenol.

This would point to a dehydrating action of the AlCl_3 .

Friedel and Crafts (Ann. Chim. Phys. 1, 489, 1884), advanced the following theory of the action of an aromatic compound on an alkyl halide in the presence of AlCl_3 , giving an alkylated benzene ring.



In 1901, Jaubert, (Comp. Rend. 132, 841) prepared aniline and p-toluidine from the action of $\text{H}_2\text{NOH.HCl}$ with the hydrocarbon in the presence of AlCl_3 , or ZnCl_2 . This action must be strictly a dehydration reaction.

Buttgenbach (J. Prakt. chem. 105, 355 (1923)), believes that an unstable Al-organic compound is first produced, which breaks up, giving AlCl_3 and the final condensed product.

In 1916, (Huston and Friedeman, J. A. C.S. 38, 2527) published the results of some work with AlCl_3 as a catalyst in the condensation of benzene and benzyl alcohol. They obtained di phenyl methane, some p-dibenzyl benzene, a trace of the corresponding ortho isomer, and anthracene as a by-product. There appeared to be a dehydrating action of the AlCl_3 in this reaction. The proportion of reagents used, and the temperature, affected the yields of different products.

Huston published a brief report, (Sci. 52, 206-1920), of the condensation of benzyl alcohol and phenol in the presence of AlCl_3 , obtaining p-benzyl phenol as a product.

In 1918, Huston and Friedeman, (J. A.C.S. 40, 785-93) published work on the condensation of benzene with secondary alcohols. They used phenyl methyl carbinol, phenyl ethyl carbinol and di phenyl carbinol in this study. They found that the methyl and ethyl group seemed to hinder the condensation, the ethyl having the greatest retarding effect, while the presence of the phenyl group did not hinder the condensation.

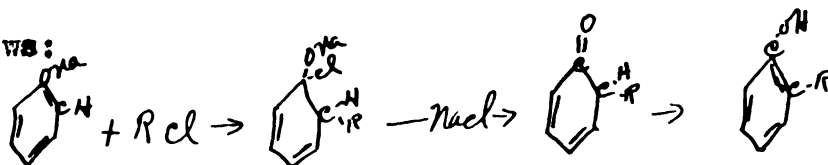
Huston, (J. A. C.S. 46, 2775-9, (1924) studied the action of AlCl_3 in the condensing of phenol and benzyl alcohol, to give p-benzyl phenol. Phenol + AlCl_3 in petroleum ether gave a viscous mass, probably Al phenolate, from which the phenol was quantitatively recovered on addition of HCl. With phenol and benzyl alcohol in petroleum ether, with 0.5 mol. of AlCl_3 at 20-30°, he obtained 43-5% p-benzyl phenol. The yield was not increased by the addition of larger amounts of AlCl_3 . Similarly, phenyl methyl ether gave 46% p-benzyl phenyl methyl ether, and phenyl ethyl ether gave 57% of p-benzyl phenyl ethyl ether. Benzyl chloride and phenol in the presence of AlCl_3 , gave 36% of p-benzyl phenol. This would bar the possibility that the action of benzyl alcohol and phenol with AlCl_3 is a reaction in which the benzyl alcohol is first converted to benzyl chloride, and then the reaction being merely an example of Friedel and Crafts reaction.

This is further barred by the fact, that when benzyl alcohol and AlCl_3 react below 35° , 96% of the benzyl alcohol is recovered, while if the reaction occurs above 40° , 25-30% of benzyl chloride is recovered after a vigorous reaction. It will be noted that the above condensation was carried on between $20-30^\circ$, which eliminates the possibility of the formation of benzyl chloride in appreciable amounts.

In 1923, L. Claisen (Z. Angew. Chem. 36, 478-9) published some work on the carbon-alkylation of phenols in which he gives a method of preparing the ortho alkylated phenol, to the practical exclusion of the para isomer. This is done by treating the Na phenolate with the alkyl halide, in the presence of a non-dissociating medium, such as C_6H_6 , or toluene, which gives almost entirely the ortho alkylated phenol, instead of the ether, as obtained with the use of alcohol or other dissociating medium, as a solvent. He characterizes several ortho alkyl phenols, among them being ortho benzyl phenol, M. 21° , B 312° , which he reports is accompanied by p-benzyl phenol, M. 84, B $320-2^\circ$. In an article published by Claisen, Kremers, Roth and Lietze, (Ann. 442, 210-45, 1925), ortho benzyl phenol is reported to exist in two forms, - the labile form M.21 and the stable form, M 52° . Other ortho alkylated phenols are also described. Claisen's work is also reported by Claisen & Tietzke (Ber. 58B, 275 (1925)). In this article, they show that when the reaction between the sodium phenolate and benzyl chloride takes place in a non-dissociating medium,

such as benzene or toluene, that ortho alkylation takes place, to the almost entire exclusion of the ether.

Claisen explains this reaction, on the basis of Michael's theory (J. pr. 37, 486; 216,189) of the reaction between silver cyanide and methyl iodide. According to this theory, Claisen's reaction takes place as follows:

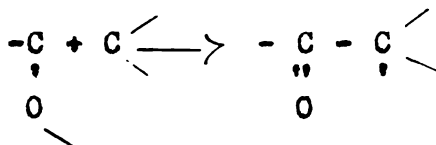


K. von Auwers, Wegener and Bohr (Chem. Zentr. 1926, I, 2347) carried on experiments to explain the reaction of salts of keto-enols and alkyl halide. They sum up three possibilities:

1. "The initial formation of addition products with subsequent splitting" (Michael).

2. "The initial formation of normal O-derivatives with rearrangement into the C-derivative".

3. "Separation of metal as metallic halide, formation of free keto and enol radicals,



and, with the slight reactivity of the alkyl group, partial or complete rearrangement of the enol to keto radical, and finally union of the radicals". (Wislicenus).

The course of the alkylation depends on the nature of the enol-keto, and also the alkylation agent, as well

as on the type of medium used. Saturated alkyl halides promote the formation of O-derivatives, while unsaturated alkyl halides such as allyl and benzyl halides promote the formation of C-derivatives. These facts are best explained by the first hypothesis, which it will be noted agrees with Claisen's idea. It is hard to see why an ether should be rearranged to a C-derivative in benzene, more readily than in alcohol, as the second hypothesis would indicate. According to the hypothesis, it would seem that allyl and benzyl halides should form ethers because of their greater reactivity, but this is not the case. Allyl and benzyl radicals hold oxygen only loosely, whereas they form stable compounds with carbon because of their slight valence requirements.

Some work has been carried out on the rearrangement of phenyl benzyl ether to give benzylated phenols. J. Von Alphen (*Rec. trav. chim.* 46, 799-812, 1927) heated benzyl phenyl ether with ZnCl_2 to 160° for one hour, and found that it was converted to 4-hydroxydiphenylmethane, M. 84° and also a dyestuff. The above named compound was also obtained when 10 g. phenol, 14 g. of benzyl chloride and a small piece of ZnCl_2 , were heated together at 100° .

W. F. Short, (*J. Chem. Soc.* 1928, 528) also reports a small note on the rearrangement of benzyl phenyl ether. The ether was heated with ZnCl_2 to 225° or to 180° in a stream of HCl and he obtained a mixture of phenol, O-benzyl phenol, p-benzyl phenol and high boiling products. He remarks that the rearrangement follows a course similar to the Hofmann rearrangement of alkyl anilines. The p-OH diphenyl

methane so obtained melted at $84^{\circ} - 84.5^{\circ}$, and was later oxidized to p-methoxy benzo phenone M. $61-62^{\circ}$. The O-hydroxy diphenyl methane reported melted at 54° and no proof of structure is given. No further details are given in this note.

There is also in existence a patent (U. S. 1, 580, 053), issued to W. Kropp, W. Schremz and W. Schulerman in which they prepare an O-benzyl phenol, M. 52° , by treating the phenol with benzyl chloride and later treating the resulting mixture with $\text{Ba}(\text{OH})_2$ and heating. The cooled liquid is filtered, and the O-benzyl phenol liberated from the filtrate by acidulation. Inquiry has failed to produce any of this product to be checked with the O-benzyl phenol, later reported in this paper.

Experimental

This work was undertaken with two objects in mind; -

1. To study the condensation of phenol and benzyl alcohol in the presence of anhydrous AlCl_3 , with emphasis on the effect of varying proportions of phenol and AlCl_3 , on the yield of the various products produced.

2. To determine definitely, whether substitution in benzylated phenols took place in the phenol ring, or in the ring of the benzyl radical.

Part I

Duplicate determinations were made with the following proportions of phenol, benzyl alcohol and AlCl_3 :

1.	1 mol.	phenol;	1 mol.	benzyl alcohol;	1/2 mol	AlCl_3		
2.	2	"	"	1	"	"	1/2	" "
3.	3	"	"	1	"	"	1/2	" "
4.	1	"	"	1	"	"	1	" "
5.	2	"	"	1	"	"	1	" "
6.	3	"	"	1	"	"	1	" "

The phenol, 52 g., and benzyl alcohol, 55 g., were suspended in 100 cc. of petroleum ether in a bottle which had three openings in the top. In one opening was fitted a reflux condenser to return all evaporating petroleum ether during the course of the reaction. In the second and center opening was fitted a mechanical stirrer so arranged with a mercury seal that no gasses could escape around the stirring rod during the process. This stirring rod was hooked up with an electric

motor in such a way that a steady flow of power was assured. The third hole of the bottle was kept corked, except when AlCl_3 was added through it from time to time. 33 g. AlCl_3 , finely pulverized, were added in small portions over the course of about an hour, until the entire amount had been added. When the AlCl_3 is added, some heat is evolved, and if added too fast, the temperature rises too high. The temperature should be maintained below $30^\circ - 35^\circ$, as Huston has shown that at this temperature very little benzyl alcohol is converted to benzyl chloride by AlCl_3 . At higher temperatures, - above 40° , however, 25-30% of the alcohol is converted to the chloride, and the reaction then becomes a Friedel and Crafts reaction rather than one of dehydration. (J. Am. Chem. Soc. 46, 2775-9, 1924). A thermometer may be inserted in the cork if desired, but it is difficult to read, since the mass soon becomes amber colored, and smears the thermometer. After one or two runs, the operator can tell quite definitely, should the temperature rise above 30° . A cooling bath is unnecessary if the AlCl_3 is added slowly, because the evaporation of the petroleum ether will carry off all excess heat generated.

After all the AlCl_3 has been added, the mass is stirred for another hour, at which time it is quite viscous and cloudy amber in color. It is allowed to stand for at least twenty-four hours, and then the jelly-like mass is decomposed with ice, acidified with HCl , and extracted with ether.

The ether is distilled from the ether extract, and the residue heated at atmospheric pressure to about 220° , to remove all phenol and benzyl alcohol remaining in the mixture.

It is then distilled in vacuo at 3-4 mm. and the fraction collected from 130° to 175°. Also a fraction is collected from 175° to 220° at 3-4 mm. This is a viscous oil, probably a di benzyl phenol which seldom crystallizes, although one sample has crystallized some on long standing. Above 220° at 3-4 mm. no distillate is obtained, the residue being a thick tarry mass, which will coke on continued heating. This residue has not been investigated. All condensations as above outlined were carried out in the same apparatus as described above, and in essentially the same manner, save for the varying amounts of ingredients.

The weights of the fractions from 130-175° at 3-4 mm. follow. 1/2 mol. wts. were used in the ratios given below:

						1/2 mol. AlCl ₃	1 mol. AlCl ₃
1 mol.	Benzyl alcohol;	1 mol.	Phenol			27 g.	23 g.
1 "	"	"	2 "	"	"	45 "	45 "
1 "	"	"	3 "	"	"	49 "	55 "

It will be noticed at once that the increased amount of AlCl₃ causes little or no increase in the fraction from 130-175°, but that the increased proportion of phenol does cause a decided increase, especially the increase from 1 to 2 mols of phenol per mol of benzyl alcohol.

These samples crystallized partially, and developed a reddish quinone color on standing, as any phenol does. Closer fractionation indicated that there were two compounds present, whose boiling points were rather close together. These two compounds are ortho benzyl phenol and para benzyl phenol. 0-

benzyl phenol did not crystallize, whereas the p-benzyl phenol did largely crystallize out. These fractions were then filtered by suction, and a heavy oil thus obtained in the filtrate was fractionated a number of times, and the major part of it proved to be ortho benzyl phenol, b.p. 138-90°C, 3 mm. The crystals remaining were redistilled and then recrystallized and proved to be p-benzyl phenol, b.p. 153-4° at 3 mm., m.p. 84°. The purified p-benzyl phenol does not color on standing, but remains as a white crystalline compound. The ortho benzyl phenol does develop the characteristic red color on standing.

It is impossible, by any known method, to quantitatively separate a mixture of ortho and para benzyl phenol. Accordingly the exact amounts of each isomer obtained in each case are not known, but approximate amounts are of interest. These figures are as accurate as can be obtained by filtration, and subsequent close fractionation of the isomers, but at best are only approximate. The approximate figures follow:

						1/2 mol. AlCl ₃		1 mol. AlCl ₃	
						Wt.	%O- %P-	Wt.	%O- %P-
1 mol. Benzyl alcohol; 1 mol phenol						27 g.	30% 70%	23 g.	40% 60%
1	"	"	"	2	"	45 "	40% 60%	45 "	40% 60%
1	"	"	"	3	"	49 "	55% 45%	53 "	50% 50%

These figures show merely that the amount of the ortho isomer produced is greatly increased, as the amount of phenol is increased. With 3 mols of phenol to 1 of benzyl alcohol, the amount of ortho isomer produced is practically equal to

the amount of para isomer.

The ortho benzyl phenol spoken above proved identical with that obtained by Claisen's method of producing ortho alkylated phenols. Claisen's ortho compound is prepared by preparing sodium phenolate in toluene solution, and later adding molecular quantities of benzyl chloride and refluxing on an oil bath for about five hours at 160° and allowing to stand for about twelve hours. In a typical preparation, forty-seven grams of phenol were dissolved in 150 cc. of toluene, and 11.5 g. of Na added in small pieces. This mass was refluxed on an oil bath for about four to five hours, with occasional addition of more toluene as it was needed to cover the reacting mass. A total of 100 cc. were added in all. 63.6 grams of Benzyl chloride were then added, and allowed to stand for one hour. The reaction mass was then refluxed on an oil bath, at 150° to 160°, for about five hours. The mass was then extracted with 20% NaOH solution, the lower dark red layer being reserved. This extract was then acidified with HCl, and extracted with ether. On the third fractionation, 16 grams of ortho-benzyl phenol, b.p. 134-140° at 2-3 mm. were obtained. This is about 17% of the theoretical. Such a yield was obtained twice, while attempting to duplicate a previous yield of 48%, apparently under the same conditions. This yield, however, could not be duplicated.

The ortho-benzyl phenol, so prepared, is a liquid at ordinary temperatures, b.p. 138-90° at 3 mm. It will solidify if kept in a freezing mixture for some time, but readily melts

on being brought to room temperature, 20°-21°C. Claisen describes this form as the labile form which changes on standing to a stable form with m.p. 52°. I have samples that were prepared a year ago and which have not changed at all. It seems rather doubtful that they will change. I have not obtained any sample, as yet, with a m.p. of 52°. U. S. Pat. 1,580,053 describes this product obtained from treating phenol with benzyl chloride. However, I have not tried this particular method for the preparation, and the owners of the patent are apparently unable to supply me with any of this material.

The ortho benzyl phenol, so prepared by Claisen's method, gives a di brom derivative, which crystallizes from alcohol and water in ~~five~~ white silky crystals, m.p. 90°-91°. The ortho isomer from the AlCl₃ condensation, gives the same di brom derivative. Analysis for bromine gave the following results:

Calculated for C₆H₅.CH₂.C₆H₄Br₂OH- 46.75% Br.

Found	46.82%	46.80%
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Av.	46.81% Br.
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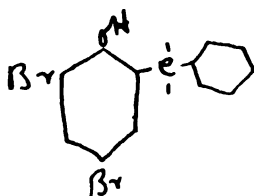
Part II

As previously stated, this part of the work was designed to determine definitely where bromine substitution took place in benzylated phenols, in the phenol ring or in the benzyl ring. Zincke and Walter, (Ann. 334, 367-385 (1904)), assumed that this substitution took place in the phenol ring because of the ease with which NaNO_2 would react with the compound, substituting NO_2 for Br, as was also the case with simple brom phenols. Other than this assumption, they produced no positive evidence.

To study this question, two experiments were carried on:

1. The ortho benzyl phenol prepared in Part I by both Claisen's method, which produces ortho alkylated compounds, and the ortho isomer from the AlCl_3 condensation, were brominated. A di-brom derivative formed very readily, but further bromination was difficult. This would be expected if the two bromine atoms went in the 2,4 positions of the phenol ring.

2. The next step was to take 2, 4 di-brom phenol, M. 35-36°, (Eastman) and convert it to the sodium salt, and condense the resulting compound with benzyl chloride, according to Claisen's method. The resulting compound proved to be identical in every way with the compound resulting from the direct bromination of the ortho benzyl phenol. In this case the benzyl group must be in the ortho or 6 position and the structure must be as follows:



M.P. 91°

B.P. 174-5° @ 2 mm.

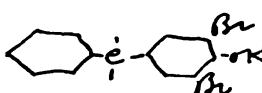
Since the product of the bromination of ortho benzyl phenol is identical with the above compound, bromination in benzyl phenols takes place in the phenol ring, rather than in the benzyl group attached.

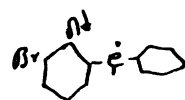
The di brom derivative of p-benzyl phenol is likewise easily formed, but further bromination is difficult. This compound was easily purified by distillation but was crystallized with difficulty, until material was available for seeding. After eight days the thick liquid did crystallize, and on first crystallization, the crystals melted at 42-30. These same crystals, after standing for three days were melted again, and melted at 56-70. These crystals had not been touched or treated in any way, but apparently a change took place as described by Zincke and Walter. (loc. cit.). Since this time, the only form that has been obtained, is the apparently stable form, M. 56-70. It is possible that this is true, because all samples have crystallized as a result of seeding with the stable form. The compound crystallizes in prismatic needles, M. 56-70.

The same product is produced on bromination of p-benzyl phenol, whether CHCl_3 or CS_2 is used as a solvent, thereby confirming Zincke and Walter's statement, that Paterno and Fileti (Gazz. chim. ital. 3, 121-129, 251-254) reported erroneous work, when they stated that bromination in CS_2 solution, produced an amorphous substance, M. 1750. It is indeed "difficult to know what they may have had in hand".

The above compounds were analyzed for bromine content, by the Parr Bomb method, as reported by J. F. Zemp and

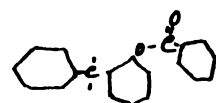
H. J. Broderson, (J. Am. Chem. Soc. 39, 2069).

Theory for  46.75% Bromine.
 Found I 46.28% II 46.6% Av. 46.44% Bromine.

Theory for  46.75% Bromine
 Found I 46.84% II 46.80% Av. 46.82% Bromine

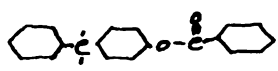
The benzoates of ortho and para benzyl phenol, were prepared and analyzed. The benzyl phenol in either case was dissolved in 5% KOH, and equimolecular quantities of benzoyl chloride added with stirring.

The benzoate of ortho-benzyl phenol has never crystallized. The compound boils at 201-202 at 2 mm. Analysis gave the following results.

Theory for  83.29% C 5.59% H

Found	I	II	Average
C	83.36%	82.95%	83.15%
H	5.58%	5.55%	5.565%

The benzoate of para-benzyl phenol crystallized well, M.P. 84-5°. Analysis gave the following results:

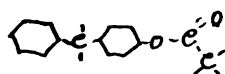
Theory for  83.29% C 5.59% H

Found	I	II	Average
C	83.25%	83.40%	83.33%
H	5.595%	5.62%	5.61%

An attempt was made to prepare the acetates of both para and ortho benzyl phenol. 10 grams of benzyl phenol were added to 17 cc. of acetic anhydride and 4.5 g. of sodium acetate added. The molecular ratios are 1 : 3 : 1 respectively. The mixture was then refluxed eight hours, although later it was found that the same result was obtained with two hours of refluxing. The mass was neutralized with Na_2CO_3 and extracted with ether. When purified by redistillation the para benzyl phenol product boiled at 151-2° at 2 mm. This compound crystallized in the ice box and the crystals melt at 31-2°. The corresponding ortho benzyl phenol compound boiled at 140-141° at 2 mm., and has never crystallized. On analysis, these compounds, both isomeric, gave the following result:

	I	II	III	IV	V	VI	Av.
C	77.96%	78.31%	77.76%	77.61%	78.13%	78.01%	77.96%
H	6.08%	5.98%	6.01%	5.93%	6.02%	6.07%	6.004%

Theory for



C - 79.6%

H - 6.24%

It is evident that the products obtained above are not the acetates of para or ortho benzyl phenol. The compounds are very stable to moisture of the air. Paterno and Fileti (Gazz. chim. ital. 3, 121-129, 251-254) report the acetate of para benzyl phenol as being a pale yellow liquid, which is easily hydrolyzed by moisture of the air, and which never crystallized. Their compound boiled at 317°, density at 16°, -1.1043. The compound which I prepared with acetic anhydride acting on para benzyl phenol, was a colorless liquid, crystalliz-

ed in the ice box to icy appearing crystals, M 31-2^o, and is very stable to atmospheric moisture.

Time has not permitted complete investigation of these compounds, but the work is being continued, and it is hoped that a report in the future will be possible.

Summary

The work reported in this thesis may be summarized as follows:

1. The condensation of benzyl alcohol and phenol, in the presence of AlCl_3 , has been studied with reference to the varying proportions of phenol and AlCl_3 added to the benzyl-alcohol. In this particular condensation at least, the increase in amount of phenol, increases the proportion of the ortho benzyl phenol produced with the para benzyl phenol. 1 mol. of AlCl_3 does not give higher yields than $1/2$ mol. of AlCl_3 used as a catalyst.

2. It has been definitely shown, that bromination of ortho benzyl phenol, takes place in the phenol ring rather than in the benzyl radical.

3. 2-benzyl, 4-6-di brom phenol has been prepared and described for the first time. It was prepared by Rennie, (Jour. Chem. Soc. 49, 406) as a by-product of the study of para benzyl phenol, but its structure was not determined.

4. The benzoate of ortho benzyl phenol has been prepared and described.

5. Benzyl phenols have been treated with acetic anhydride, and products obtained which apparently are not acetates, but the exact nature of the compounds has not yet been determined. This work is being continued, in the hope of being able to make a later report.

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