# SOME CHLORINE DERIVATIVES OF
# P & O - BENZYL PHENOL

THESIS FOR THE DEGREE OF M. S.

EDWARD FRANKLIN ELDRIDGE

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# p & o-BENZYL PHENOL

A

Thesis

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## Foreword

A large amount of work has been done in this laboratory on the condensation products of phenols and cresols and their derivatives. Consequently the literature on this subject has been reviewed and discussed to a considerable extent in the various theses. For this reason, it was not thought necessary to repeat this review, but to confine the historical portion of this thesis principally to a discussion of the literature dealing directly with the benzyl phenols and their halogen derivatives.

### 1. Early work on the preparation of benzyl phenol.

The preparation of benzyl phenol was first reported by Paterno (Gass chem. ital. 2, 1-6, 1872). Benzyl chloride and phenol were condensed in the presence of zinc. The resulting compound had a boiling point of 175-180° at 4-5 mm. This same compound was also prepared by benzylating anisole and treating the mixture with HI.

In a later paper (Gass. chem. ital. 5, 381, 1875) Paterna and Filete report the use of a mixture of sulphuric and acetic acids as a dehydrating agent in the condensation of benzyl alcohol and phenol. This time crystals and an oil were obtained. The crystals were said to be the benzyl phenol and the oil an isomer.

Perkins and Hodglinson (J.C.S. 724, 1880) report the isolation of the benzyl phenol from the KOH solution of a mixture of phenyl acetate and benzyl chloride. M.p. 80-81° and b.p. 320-322°.

Leibmann (Ber. 15, 152, 1882) used zinc chloride as the catalyst in the condensation of benzyl alcohol and phenol. The resulting product had a m.p. of 84° and b.p. 325-330°.

### 2. The Friedel and Crafts Reaction.

Aluminum chloride has been found to have remarkable condensation powers. These were first discovered by Friedel and Crafts (Compt. rend. 84, 1392-95, 1876) while investigating the condensation of alkyl halides and aromatic hydrocarbons. This reaction has been given the name of the Friedel Crafts reaction and has received wide spread application in the condensation of both aliphatic and aromatic compounds. We are proncipally concerned with it here in the preparation of the benzyl phenols and their derivatives.

$$C_6H_5CH_2Cl + C_6H_5OH \quad \underline{AlCl_3} \quad C_6H_5CH_2C_6H_4OH + HCl$$

There have been many theories advanced as to the action of $AlCl_3$ in these condensations. Boeseken (Rec. trav. chim. 29, 85-112, 1910) believes that the catalyst does not react thru the production of intermediate products, but rather that the reaction is a result of the change in the affinity of one atom for another. This change may result either in an entire elimination of the atom or group from the rest of the molecule and a reacting as such, or an activation without separation from the rest of the molecule. He gives as evidence of this assumption, the (1) reaction of $SO_2CL_2$ with PhCl in the presence of $AlCl_3$ when no dichlor diphenyl sulphone was obtained, only polychloro benzene and (2) the action of BzCL and $C_6H_6$ where BzPh was obtained.

Later, the same author (Rec. trav. chim. 30, 381, 1911) shows that dissociated chlorides like $SO_2CL_2$, $C_2HCl_5$ and $CCl_3CHO$ act in the presence of $AlCl_3$ like non-dissociated molecules with activated chlorine atoms. The reaction of $C_6H_6$, $SO_2CL_2$ and $AlCl_3$ gave much $PhSO_2H$ and PhCl, but also $PhSO_2Cl$ and $Ph_2SO_2$. This is to be expected from the theory as a catalyst displaces the equilibrium $SO_2CL_2 = SO_2 + Cl_2$ considerably to the right.

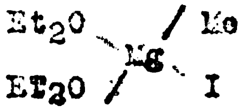
Boeseken finally explains the reaction (Rec. trav. chim. 30, 148-50, 1911) by stating that "in order to secure condensation, an unsaturated compound and one which can be so activated that it can combine with the unsaturated compound, must be brought together in the presence of the catalyst, the reaction being made possible by the loss of free energy". The fàllowing reactions were given in explaination:

$$RCOCl + AlCl_3 = RCOCl.AlCl_3$$

$$RCOCl.AlCl_3 + R'H = RCOR'.AlCl_3 + HCl$$

$RCOR'AlCl_3$ decomposed with $H_2O$ = $RCOR'$ + $AlCl_3$

Meisenheimer and Casper (Ber. 54B, 1655-65, 1921) liken the reaction of $AlCl_3$ to that of Grignard reagents in that the aluminum compounds are formed with the Al functioning as the controling atom with a coordination number of 4, similar to Mg in the compound



Weiland and Bettag (Ber. 55B, 2246-55, 1922) believe that the $AlCl_3$ forms complexes with double bonds such as that with acyl chloride $AlCl_3$..(CR:O).Cl which result in a loosening of the union between the Cl and C, thus enabling both to add. They state that an aliphatic double bond and those of the benzene ring differ only as a matter of degree.

Schaarschmidt (Z. Angew. Chem. 37, 286-8, 1924) affers much the same explaination. He states that the $AlCl_3$ activates the aromatic hydrocarbon, which activation is accompanied by a loosening of the bonds of the organic halide. A complex is formed between the three compounds in which the $AlCl_3$ is held by auxilary valences and the addition compound by ordinary valences. The stability of the complex depends upon the division of the inner valences. If these are neutralized, the "molecular course" is followed and the $AlCl_3$ is not regenerated. This calls for molecular quantities of the metallic chloride. If a splitting out occurs in the complex at the point where the addition takes place, the $AlCl_3$ is regenerated and can be used again. This involves the "catalytic course" and much smaller quantities of $AlCl_3$ are required. Secondary reactions or substituents in the ring may decompose or use up the metallic chloride, thus calling for larger amounts.

Aluminum chloride as a dehydrating agent.

Huston (J.A.C.S. 38, 2527-33, 1916) and Friedeman report the use of $AlCl_3$ in the condensation of benzyl alcohol and benzene, giving large yields of diphenyl methane.

$$C_6H_5CH_2OH + C_6H_6 \overset{AlCl_3}{=} C_6H_5CH_2C_6H_5 + H_2O$$

In this and in subsequent work on the condensation of secondary alcohols, phenols and cresols (J.A.C.S. 40, 785-93, 1918; Ibid 48, 1955-9, 1926; Ibid 49, 1365-8, 1927) the reactions are dehydrating rather than catalytic, altho the line between the two classes is difficult to determine.

Huston (Sci. 52, 206, 1920 and J.A.C.S. 46, 2775-9, 1924) reports the preparation of p-benzyl phenol by the condensation of phenol and benzyl alcohol in the presence of $AlCl_3$. The reaction was carried out in petroleum ether suspension at a temperature below 30° in which case the phenol and $AlCl_3$ did not react to give diphenyl ether as reported by Merz and Weith. One half mol of $AlCl_3$ was found to be sufficient for the best yields. Omitting the petroleum ether lessened the yield.

The methyl and ethyl esters of p-benzyl phenol were also prepared by the $AlCl_3$ condensation, anisole and phenetole respectively being used. In all of the preparations the temperature was a controlling factor, as at the higher temperatures (40° and above) a vigprous reaction takes place giving a variety of products.

Benzyl chloride and phenol were also condensed in the preparation of p-benzyl phenol, thus making use of the catalytic action of the metallic chloride. With either the benzyl alcohol or benzyl chloride, the same intermediate complexes seemed to be produced and HCl was evolved in large amounts.

M.N.Maxfield, in a thesis written 1929 at the Michigan State College, studied the effect of varying proportions of phenol and $AlCl_3$ on the yield of o and p-benzyl phenol. He found that by increasing the amount of phenol the proportion of the o-benzyl phenol to the para compound increased. One mol of $AlCl_3$ did not give higher yields than ½ mol.

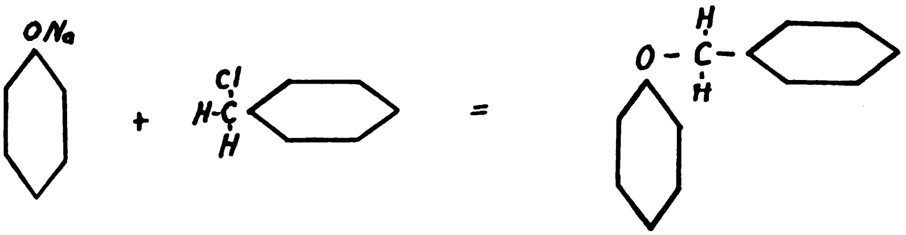
Claisen reaction and Alkylation of phenols.

The Claisen reaction is important in the preparation of the benzyl phenols because it makes possible the production of the ortho derivative in almost quantitative amounts. The action of sodium, sodium ethoxide and sodamide in effecting the condensation between carboxylic esters and ketones or other carboxylic esters as given by Clasien (Ber. 20, 646-650, 1877) was later applied by the same author to carbon alkylation of phenols (Z. angew. chem. 36, 478-9, 1923; Ber. 58B, 275-81, 1925; Ann. 442, 210-45, 1925).

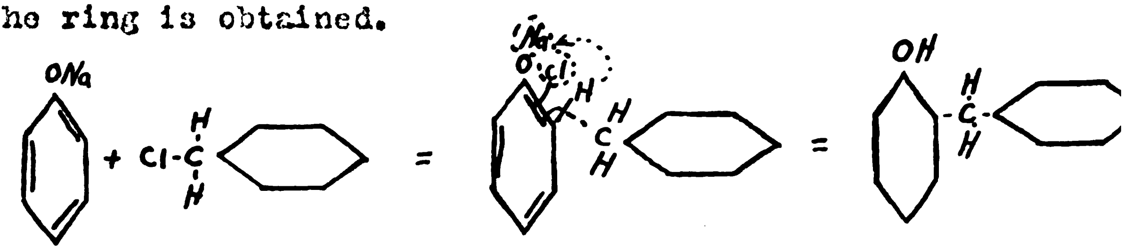
$$C_6H_5ONa + C_6H_5CH_2Cl = C_6H_4OHC_6H_5CH_2 + NaCl$$

In this preparation, the phenol was treated with sodium in a non-dissociating medium such as toluole and the benzyl chloride added. The result was a mixture of mono and di benzyl phenols and an ether. The ether was removed by first dissolving the red liquid in alcoholic KOH and then extracting with petroleum ether. The potassium salt of the phenol is not soluble in petroleum ether and is not removed by the extraction. The ether produced by the reaction was identified as the same compound as is obtained when the condensation is carried out in a dissociating medium such as ethyl alcohol.

The benzyl phenol is the result of ring alkalation, the medium being the most important factor in the reaction. With the dissociating medium the benzyl group substitutes on the hydroxide of the phenol.

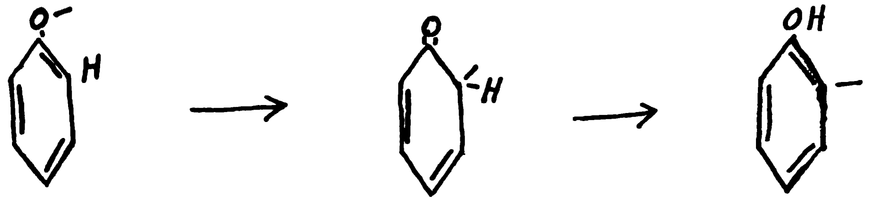


In the non-dissociating medium, ortho substitution in the ring is obtained.



Clasien, von Auwers, Busch and others have offered explanations for the carbon alkylation (in the ring) of phenols. The first author (Z. angew. chem. 36, 478-9 1923) finds that the formation of the alkyl phenols must be by direct carbon alkylation as the ethers do not rearrange to produce them. The alkylation is affected by the unsaturation of the alkyls. The tendency is still further increased by the use of alkaline phenols. Para substitution, where the ortho position is taken, has not been demonstrated. The ortho benzyl phenol, prepared by the author, had a m.p. of 21° and a b.p. of 312°. In 1925, however, he reports the ortho derivative to exist in two forms, the unstable form melting at 21° and the stable at 52°. Subsequent attempts to produce the latter have failed.

K. von Auwers and associates (Chem. Zentr. I, 2347-8, 1926) advanced three possible explanations for the carbon alkylation. First, the formation of addition products with the subsequent splitting as given by C;aisen. Second, the formation of normal oxygen derivatives followed by rearrangement. Third, the separation of the metal as a metallic halide with the formation of the free alkyl and enol radicals. With the rearrangement of the enol to the keto and finally the union of the radicals, we have this reaction:



The character of the keto-enol and the alkylation agent as well as the medium, directs the alkylization to the oxygen or carbon. Saturated halides promote the formation of the oxygen derivatives while allyl and benzyl halides favor the carbon. In dissociating media the exchange between ions is stronger and for that reason the oxygen is favored.

K. von Auwers (Ber. 61B, 408-16, 1928) studied the effect of different halides on the direction of the alkylation. From these studies it appears that iodides yield more carbon derivatives than bromides. Also the methyl halides favor the carbon, while the ethyl favors the oxygen. No explanation is given for these results.

Busch (Z. angew chem. 38, 1145-6, 1925) and Busch and Knoll (ber. 60B, 2243-57, 1927) state that carbon alkylation of phenols increases with the increasing substitution of the methane carbon atom. While it is possible to obtain ethers with benzyl chloride in non-dissociating media, di-benzyl chloride yields only carbon derivatives. The introduction of electronegative groups favors ether formation. Alkyl groups on the phenol nucleus diminishes ether formation.

W. F. Short (J. Chem. Soc. 528, 1928) reports the rearrangement of benzyl phenyl ether by heating to 225° with $ZnCl_2$ or to 180° in a stream of HCl. A mixture of phenol, o-benzyl phenol and p-benzyl phenol was obtained.

The preparation of halogen compounds.

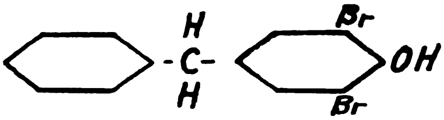
There has been very little work reported on the halogenation of benzylated phenols. E. Paterno and M. Filete (Gazz. Chem. ital. 3, 121-129; 251-254, 1874) prepared a dibrom derivative by treating the benzyl phenol in $CS_2$ with an excess of bromine. An amorphous substance was obtained which was soluble in $CHCl_3$ and $CS_2$, but not in ethyl alcohol or ether. M.p. 175°.

Sintenis (Ann 161, 345 ) reports the preparation of benzyl chlorophenyl ether and benzyl bromophenyl ether. These were made by passing chlorine or bromine into an alcoholic solution of the ether to which some $H_2O$ had been added as a catalyst.

Peratoner and Vitali (Gazz. chim. ital. 28, 197-240, 1898) report a chlor benzyl phenol made by treating benzyl phenol with sulphuryl chloride. The expla~~i~~nation given for this reaction is that the chlorine adds on, followed by an elimination of HCl. The chlorine supposedly enters the phenol ring in the ortho position.

Auvers (Ann 357, 85-94, 1907) prepared tri-brom phenyl benzyl ether, tri-chlor phenyl benzyl ether and two di-brom derivatives. In these experiments the tri-chlor or tri-brom phenol was dissolved in alcohol and treated with benzyl phenol and sodium ethoxide.

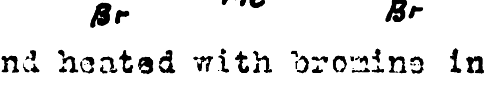
L. Zincke and W. Walter (Ann 334, 367-385, 1909) studied the bromine substitution in p-benzyl phenol. The reaction gave two types of crystals, one which was unstable and melted at 44° and which changed to a rhombic form with a m.p. of 57°. The formula given was



The tri brom and penta brom derivatives were also reported.

The same author (Ann 350, 269-87; Ann 363, 246-84) states that mono, di and tri brom o-cresol can be prepared by direct bromination with or without a catalyst. The mono derivative is reported as 5 brom o-cresol and the di as 3-5 di brom o-cresol. The tri is probably 3-4-5- tri brom o-cresol. Pseudo bromides were obtained if the reaction was carried out at high temperatures.

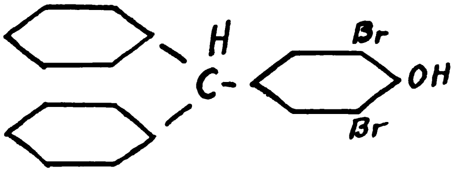
Zinche has done a great deal of work on the halogenation of phenol and cresol derivatives. Diphenol methyl methane with bromine in acetic acid gave



m.p. 140-1°

This compound heated with bromine in a sealed tube at 100° gave the hexa brom derivative. M.p. 169-170°. The hepta brom compound was also prepared.

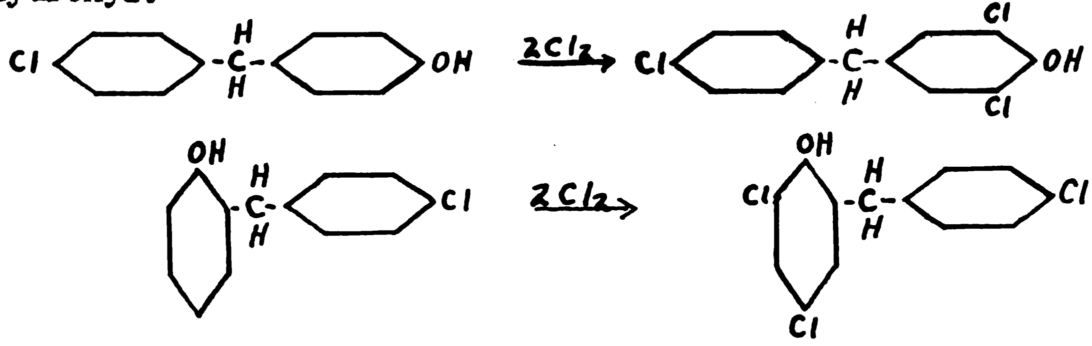
Van Alphen (Rec. trav. chem. 46, 799-812, 1921) reports the bromination of 4 hydroxy tri phenyl methane giving the di-brom derivative.



Barv (Quant. J. Indian Chem. Soc. 3, 101-4, 1926) prepared benzyl o-chlor phenyl ether, the meta and para derivatives of the same ether and benzyl 2-4 dichlor phenyl ether. All of these were prepared by means of the leucotrope.

Maxfield of this laboratory in a thesis written in 1929 reports definately that bromination of benzyl phenol takes place in the phenol ring rather than in the benzyl radical. He found the same change in the melting point and crystal form of dibrom p-benzyl phenol as reported by Zincke and Walter. The stable form has a m.p. of 56-7°.

Headley (Master's thesis, Michigan State College, 1928) studied the effect of the introduction of a chlorine atom upon the activity of the benzyl group. He found that the activity was greatly increased. He also established the fact that chlorine enters the following groups by first substituting in the ring containing the hydroxyl.



The theory of the substitution of the halogen.

The directing influence of various groups attached to the benzene ring on entering groups or atoms, has been the subject of considerable study. Holleman (Ber. 44, 725, 2504, 3556, 1911; J.A.C.S. 36, 2495, 1914; and Chem. Rev. 1, 187, 1924) explains that this influence is indicated by the velocities of the reactions of the groups already in the ring. That is, when a third substituent C is to enter a di substituted benzene compound $C_6H_4AB$, the reaction can be predicted by a study of the speed of the reactions:

$$C_6H_5A + C = C_6H_4AC$$
$$C_6H_5B + C = C_6H_4BC$$

The groups which influence the ortho-para substitution in such a reaction are in diminishing series as follows:

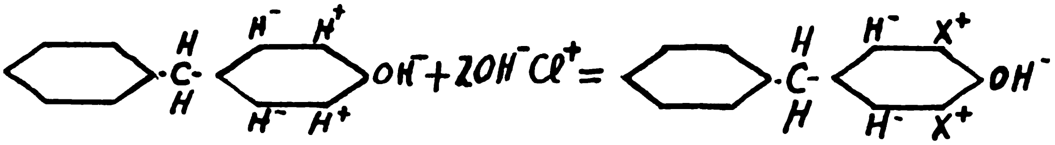
$$OH \quad NH_2 \quad I \quad Br \quad Cl \quad CH_3$$

and the meta position:

$$COOH \quad SO_2OH \quad NO_2$$

Korner (Gazz. chem. ital. 4, 305, 446, 1874) states that acid groups direct a new atom or radical to the meta position. The halogens, OH and basic groups direct to the ortho and para.

Fry (J.A.C.S. 36, 1035, 1914) suggests an electronic explanation for the substitution, in which he assumes that the hydrogens on the benzene ring are alternately positive and negative. Substituents of the same polarity as the group already in the ring are directed to the meta position, while those of opposite polarity will take the ortho or para. According to this explanation the halogens in the presence of a very small amount of moisture or some other halogen carrier, produces positive X by splitting of the $X_2$ molecule, giving the compound $HO^-X^+$. The halogenation of the benzyl phenol would be explained according to the following equation:



Fry gives as proof of the positive halogen, the fact that it cannot be directly replaced by an $OH^-$. The para position in the above equation being occupied, limits the substitution to the ortho position.

While the idea of positive and negative hydrogen and probably halogen has been seriously questioned and largely dropped from the theory, yet the effect of the polarity tendency of the groups in the ring is still held. Pfeiffer (Ann. 461, 132-54, 1928) explains the substitution of the bromine in the benzene nucleus by assuming that such groups as OH, $NH_2$ etc. confer polar properties on the attached carbon atom. This causes polar rearrangement or shifting thru the rest of the ring which is the factor governing the substitution of other atoms or radicals. Those of like polarity go to the meta position which is the farthest from the effecting group. Unlike groups substitute in the ortho and para.

Substitution would be explained in a similar manner by the Lewis-Langmuir electronic theory of valence (Valence and the Structure of the Atom and Molecules, A. C. S. Monograph 1923). This theory assumes that the chemical bond is produced by a pair of electrons shared by the two atoms. The position of these electrons with reference to the positive nucleus of the atoms depends upon the comparative strength of these nucleae. With similar atoms, such as the carbons of ethane, the pair assumes a position midway between the centers. The other extreme is illustrated by the Na and Cl of NaCl in which the strong positive character of the Cl nucleus entirely removes the electron pair from the field of the Na atom.

In the combination of three or more atoms, the position of the pair of electrons between any two is effected by the other atoms depending upon their strength and position in the molecule. Thus in benzyl phenol, the position of the electrons between carbon and carbon or carbon and hydrogen is effected by the presence of the hydroxide group. This group having a strong attraction for electrons will pull the electron pair nearer to the oxygen atom. This pulling effect is relayed thru the carbon to the carbon-carbon bond and also to the carbon-hydrogen bond of the ortho position. As the pairs of electrons of this position are pulled toward the carbon, the carbon-hydrogen bond is weakened, directing substitution to that position. Thus in the preparation of the chlorine derivatives of para benzyl phenol, the chlorine will substitute in the ortho position.

# STATEMENT OF THE PROBLEM

The object of this problem can be divided into three parts as follows:

1. To prepare, identify and study the properties of the chlorine derivatives of ortho and para benzyl phenol.

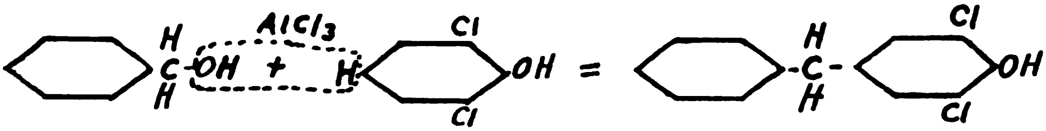
2. To prepare some of the derivatives of these chlor benzyl phenols.

3. To determine to what extent chlorine is substituted in the benzyl phenol by direct chlorination and the position taken by the entering chlorine atoms.

## EXPERIMENTAL

A. The preparation of 3-5 dichlor 4 hydroxy diphenyl methane.

1. By the $AlCl_3$ condensation of 2-6 dichlor phenol and benzyl alcohol.



Fifty grams of benzyl alcohol and 225 grams of 2-6 dichlor phenol were suspended in about 250 cc of petroleum ether. The suspension was mechanically stirred while 30 grams of $AlCl_3$ was added at intervals over a period of 1 hour. The phenol is only slightly soluble in the ether. Stirring was continued 30 minutes after the addition of the $AlCl_3$ and the mixture allowed to stand over night. At no time during the reaction did the temperature go above 32 degrees.

The suspension was decomposed with ice and HCl and the petroleum ether withdrawn. The water mixture was extracted with ethyl ether and both solution dried over potassium carbonate. After drying, the solvents were distilled and the residues combined. The residue from the petroleum ether was an oil while that from the ethyl ether solidified on cooling. The combined residues were fractionated by distillation.

1st. Fractionation.

1. 100 to 122° at 15 mm --- A small amount of oil, mostly benzyl alcohol.

2. 132 to 155°--- A large fraction which solidified in the receiver. Mostly 2-6 dichlor phenol.
3. 155 to 204°--- A smaller fraction which only partially solidified.
4. Above 204° --- A large amount of charred material.

The fraction between 155 and 204° was refractionated. A small amount of 2-6 dichlor phenol was obtained between 155 and 195°. The larger portion distilled between 195 and 205°. From this portion, 23 grams of a yellow oil was isolated.

This condensation was repeated using the same materials and procedure as before except that $CS_2$ was substituted for petroleum ether as a solvent. Upon fractionation of the residues obtained after drying and removing the solvents, a large amount of charred material was obtained and only 15 grams of product.

In order to obtain a better yield, a study was made of the charred material left in the flask after distillation. It was found to contain a large amount of potassium undoubtedly as a result of the drying with $K_2CO_3$. In subsequent preparations, therefore, the drying was omitted. By this method, the charring was avoided, but the yield was not greatly increased.

The yellow oil from six preparations was combined and purified by distillation. The boiling point after three fractionations was 194-196° at 15 mm.

A determination of the chlorine content of the oil was made by the Parr bomb method (J.A.C.S. 39, 2069).

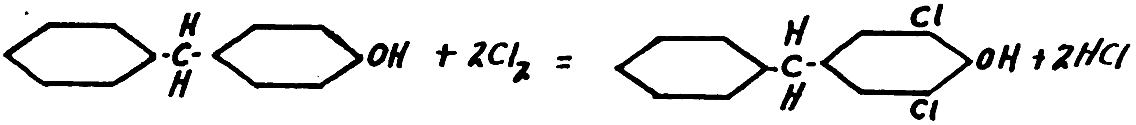
Results of the Chlorine analysis

| | 1 | 2 |
|---|---|---|
| Weight of oil used | .1840 | .1889 |
| Vol. of .1N $AgNO_3$ | 14.35 cc | 14.95 cc |
| Wt. of Cl in sample | .050968 | .05293 |
| Percent Cl in sample | 27.7 | 28.1 |

Theoretical % Cl in the dichlor benzyl phenol-- 28.0.

Since the method of preparation of the oil and the analysis, checked with the theoretical, it was at first supposed that the compound was 3-5 dichlor 4 hydroxy diphenyl methane. Subsequent results, however, showed that this was not entirely true, as will be seen later.

2. By the chlorination of p-benzyl phenol.



Para benxyl phenol was first prepared by the $AlCl_3$ condensation method previously described. 30 grams of phenol, 50 grams of benzyl alcohol and 30 grams of $AlCl_3$ were used. Petroleum ether was the solvent. After fractionation and recrystallization from petroleum ether, 11 grams of pure product was obtained.

The para benxyl phenol was chlorinated according to the method outlined in "Methods of Organic Chemistry", Houben Vol. 2, p 799. Ten grams of the phenol was suspended in chloroform in a flask connected with a chlorine generator and wash bottle of sulphuric acid. The generator consisted of an Erlenmeyer flask and separatory funnel. The calculated amount of $KMnO_4$ (7 grams) was placed in the flask and 42 to 45 cc of HCl in the funnel. After all of the chlorine had been swept thru the chloroform solution, the solvent was distilled and a yellow oil obtained. The oil solidified on cooling, but was fractionated by distillation. All but a very small amount came over at 190 to 205° at 15 mm. The distillate solidified and was separated from an oily substance by pressing between filter papers. The crystalline product was then recrystallized until pure. M.p. 58.-58.5°. B.p. 195-196° at 15 mm.

The crystalline compound was analyzed for chlorine.

Results of the chlorine analysis.

| | 1. | 2. |
|---|---|---|
| Weight of sample | .1843 | .2137 |
| Vol. of .1N $AgNO_3$ used | 14.3 cc | 16.8 cc |
| Wt. of Cl in sample | .050765 | .05964 |
| Percent Cl in sample | 27.6 | 28.1 |
| Theoretical % Cl in dichlor benzyl phenol | | 28.0 |

Again the analysis and method of preparation indicated 3-5 dichlor 4 hydroxy diphenyl methane, but a very different compound was obtained by the previous method. Crystals of this compound seeded in the oil prepared by the $AlCl_3$ condensation, dissolved.

The benzoyl derivative of each of these compounds were prepared, using the Schotte and Bauman reaction. Two grams of each were dissolved in 10 cc of pyridine and 1.2 grams of benzoyl chloride added. The mixture was poured into water in which a small amount of KOH was dissolved. The KOH prevented the extraction of benzoic acid by the ether which was next used to remove the product of the reaction. The ether was evaporated and the solid which remained pressed between filter papers and recrystallized. The product obtained from the oil was in appearance and melting point (98.5-99.0°) identical with that from the crystalline compound obtained by direct chlorination.

Further studies were made in an effort to determine which of these apparently pure compounds was the product desired. Previous to the chlorine analysis, it was thought that the crystalline compound was the tri chlor derivative reported by Headley. The melting point of his compound was 55.0 to 57.5°, which was very near that of the crystals prepared here. The chlorine analysis, however, showed only two chlorines.

During the course of these studies, the solubilities of the compounds in alkalae was tested and it was found that, whereas all of the crystalline compound dissolved in the KOH, only a part of the oil was soluble. Following this indication, 10 grams of the oil was treated with KOH. The insoluble portion was separated and the KOH solution acidified with HCl. A crystalline compound was obtained which when recrystallized gave a melting point of 58.0-59.0° and was identical with the crystals obtained by direct chlorination of p-benzyl phenol. The information was sufficient to prove that the crystals from both of these reactions, meaning the $AlCl_3$ condensation and the direct chlorination, was 3-5 dichlor 4 hydroxy diphenyl methane.

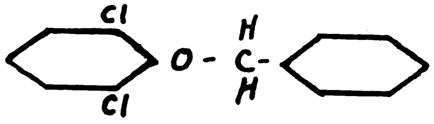
Finding the crystalline compound in the mixture of oil, accounted for the benzoyl derivatives being the same, but did not account for the similarity in boiling point and chlorine content. Apparently the crystals are soluble in the oil, thus preventing their isolation. The oil, however, must have the same molecular formula as the crystals, but can not be a phenol, as it is not soluble in alkalae.

The oil left after the treatment with KOH and separation, was redistilled until practically pure. B.p. 195-196° at 15 mm. It was then analyzed for chlorine.

Results of the chlorine analysis

| | | |
|---|---|---|
| Weight of oil used | .2413 | .1930 |
| Vol. of .1N $AgNO_3$ used | 19.00 cc | 15.05 cc |
| Wt. of Cl in sample | .06746 | .05346 |
| Percent Cl in sample | 27.9 | 27.7 |

The analysis indicates a compound having two chlorines and the same molecular weight as that of the dichlor benzyl phenol. The most likely compound, not a phenol, with this molecular formula is 2-6 dichlor phenyl benzyl ether.



### B. The preparation of 2-6 dichlor phenyl benzyl ether.

The ether was prepared by treating 2-6 dichlor phenol and benzyl chloride with sodium in methyl alcohol according to the Claisen method before described. 6.5 grams of sodium was allowed to react with 100 cc of methyl alcohol. The solution was cooled and 45 grams of 2-6 dichlor phenol added. This mixture was heated on the oil bath at 150° for 30 minutes, cooled and 35 grams of benzyl chloride added. The entire mixture was allowed to stand over night and then heated on the oil bath for five hours. After cooling, the oil was extracted with petroleum ether, the ether removed and the residue distilled.

A very small amount of benzyl chloride was obtained between 90 and 170° at 15 mm. The second fraction all distilled between 180 and 196°. This was purified by further distillation. The resulting compound was a yellow oil, having a boiling point of 194 to 195° at 15 mm, insoluble in KOH and with an odor similar to the oil obtained along with the benzyl phenol derivative in the first $AlCl_3$ condensation.

Thus in the condensation of 2-6 dichlor phenol and benzyl alcohol, a mixture is obtained which has been shown to contain the benzylated chlor phenol and the ether.

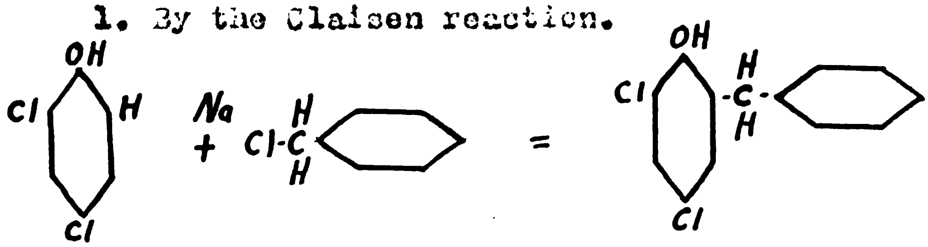
### C. Attempt to introduce three chlorines in p-benzyl phenol.

3-5-4' tri chlor 4 hydroxy diphenyl methane had been previously prepared by Headley (thesis before mentioned) by the $AlCl_3$ condensation of 2-6 dichlor phenol and p-chlor benxyl phenol. An attempt was here made to introduce the three chlorines into p-benzyl phenol by direct chlorination.

Ten grams of the phenol were treated with the equivalent of three chlorines by the permanganate method. The product obtained in two trials gave a m.p. of 58.0 to 58.5° and was identical with that from the previous chlorination when two chlorines were introduced. A large excess of chlorine was then used, but again only the dichlor derivative was obtained.

### D. Preparation of 3-5 dichlor 2 hydroxy diphenyl methane.

#### 1. By the Claisen reaction.



Sodium (11.5 grams) was suspended in 130 cc of toluene and 81.5 grams of 2-4 dichlor phenol added. This mixture was heated on the oil bath at 150° for 30 minutes during which time the white sodium salt was produced. The mixture was cooled and 63.3 grams of benzyl chloride added. After standing over night, it was heated for 5 hours on the oil bath, cooled and treated with 250 cc of methyl alcoholic KOH. The solution was then extracted with petroleum ether to remove the ether produced by the reaction. The petroleum ether solution was set aside for a later isolation of the etherial compound. The methyl alcoholic solution was neutralized with HCl to again liberate the phenol and extracted with ethyl ether. After removing the ether, the residue was fractionated by distillation.

### 1st. Fractionation

1. 90 to 140° at 15 mm--- A light oil which proved to be mostly unchanged benzyl chloride and 2-4 dichlor phenol.

2. 140 to 210° at 15 mm ---35 grams of material which solidified in the receiver and which proved to be almost entirely the dichlor benzyl phenol.

3. 210 to 220° at 15 mm ---A heavy red oil.

4. Above 220° --- A tarry product from which no material would distill.

The fraction 140 to 210° was recrystallized several times from high test gasoline and gave about 30 grams of product melting at 77.0 to 77.5°. The chlorine analysis gave the following results:

Results of the chlorine analysis.

| | | |
|---|---|---|
| Weight of sample | .2000 | .1895 |
| Vol. of .1N $AgNO_3$ used | 15.0 cc | 14.8 cc |
| Wt. of Cl in sample | .055025 | .05254 |
| Percent Cl in sample | 27.5 | 27.7 |

Theoretical Cl in the dichlor derivative--- 28.0%.

2. By the direct chlorination of o-benzyl phenol.

Ortho benzyl phenol was prepared by the Claisen reaction using 1 mol. each of sodium, phenol and benzyl chloride suspended in toluene. 33 grams of pure product was obtained.

The chlorination was carried out in the same manner as before using the weight of $KMnO_4$ calculated to furnish two equivalents of chlorine. The dark colored oil obtained was fractionated and the portion boiling between 190 and 200° at 15 mm was purified by recrystallization from high test gasoline. The crystals were identical with those from the reaction of 2-4 dichlor phenol and benzyl chloride. M.p. 77.5 to 78.5°. This compound was analyzed for chlorine.

Results of the chlorine analysis

| | | |
|---|---|---|
| Weight of sample | .2216 | .2364 |
| Vol. of .1N $AgNO_3$ used | 17.0 cc | 18.4 cc |
| Wt. of Cl in sample | .06035 | .0650 |
| Percent Cl in sample | 27.64 | 27.6 |

Theoretical Cl in the dichlor derivative--- 28.0%.

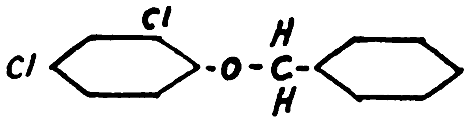
The benzoyl derivative of each of the two products was prepared. The resulting compounds were recrystallized from alcohol to which water had been added. Needle shaped crystals developed in each case. M.p. 66.0-67.0°.

As the product of each of these reactions was the same, the compound must be 3-5 dichlor 2 hydroxy diphenyl methane.

E. Attempt to introduce three chlorines in o-benzyl phenol.

o-Benzyl phenol was subjected to three equivalents of chlorine and finally super-chlorination, but as in the case of the para compound, no evidence of further chlorination was obtained.

F. Preparation of 2-4 dichlor phenyl benzyl ether.



11.5 grams of sodium was allowed to react with 200 cc of methyl alcohol. 83.5 grams of 2-4 dichlor phenol was added and the mixture heated for 30 minutes on the oil bath. Then 63.3 grams of benzyl chloride was added and the whole let stand over night. It was then heated for 5 hours and extracted with petroleum ether. After the ether was removed, the residue was distilled. A small amount of benzyl chloride came over between 90 and 150° but the major portion of the oil distilled between 190 and 192° at 15 mm. The distillate solidified in the receiver and was recrystallized from petroleum ether. The purified crystals were prisms having a melting point of 59.0 to 59.5°. Almost a quantitative yield was obtained.

In order to identify the petroleum ether extract set aside from the preparation of 3-5 dichlor 2 hydroxy diphenyl methane, the residue from this extraction was distilled. Most of the material came over between 191 and 193° at 15 mm. The distillate was purified by recrystallization and gave the same prismatic crystals as prepared above. M.p. 59.5-60.0°.

## SUMMARY OF EXPERIMENTAL WORK

1. The following compounds were prepared, identified and some of their properties determined: (See flow sheet)

    3-5 dichlor 4 hydroxy diphenyl methane.

    Its benzoyl derivative.

    2-6 dichlor phenyl benzyl ether.

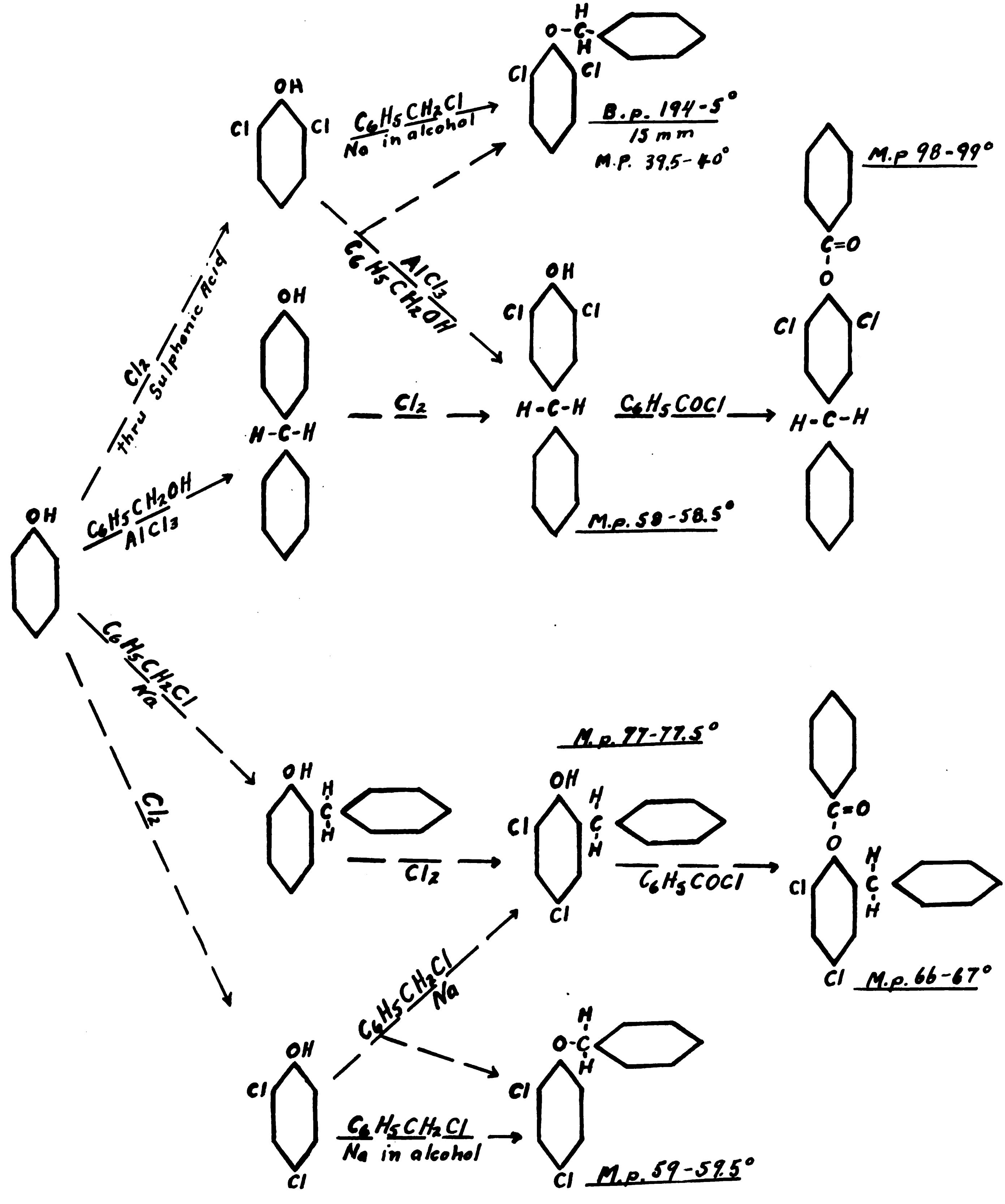
3-5 dichlor 2 hydroxy diphenyl methane

Its benzoyl derivative.

2-4 dichlor phenyl benzyl ether.

2. No evidence was obtained of the substitution by direct chlorination of more than two chlorines in either para or ortho benzyl phenol.

3. The $AlCl_3$ condensation of 2-6 dichlor phenol and benzyl alcohol gave the ether as well as the benzylated phenol. This is the first time that the ether has been identified in any of these $AlCl_3$ condensations. It is possible that it is formed in all of them and that it was only because of the difficulties encountered in the purification of the phenol that it was identified in this case. It may be that the ether is formed in all $AlCl_3$ condensations, and that this is followed by a rearrangement to the phenol. In the case of the condensation here reported, the presence of the chlorine atoms strengthens the ether bond and the rearrangement may have been retarded. This, of coarse, will require further study.



SOME CHLORINE DERIVATIVES OF

o & p-BENZYL PHENOL