SOME HYDROXY DERIVATIVES OF CHLORODIPHENYLMETHANE

THESIS FOR THE DEGREE OF M. S.

Philip Stanley Chen

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CHLORODIPHENYLMETHANE

A Thesis

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Philip Stanley Chen

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I. Introduction

In this thesis, two methods of condensing phenols with ortho chlorobenzyl chloride are described. By the Claisen method, the phenols were first made to form a sodium salt which was suspended in a suitable medium and then treated with the benzyl chloride. According to former investigations, this method gives only the ortho substituted carbon compounds or the ethers, depending upon the nature of the medium used.

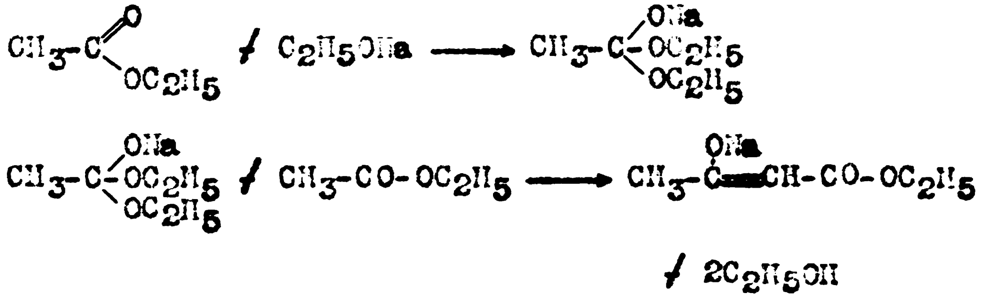
By the Huston method, the condensation was effected by the catalytic action of anhydrous aluminum chloride. The products formed were generally the para substituted compounds, a small per cent of the ortho derivatives being also formed in some cases.

Both these methods are discussed in detail in the historical part of this thesis.

II. Historical

1. The work of Claisen

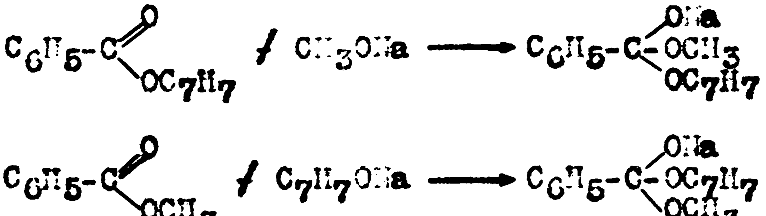
Claisen (Ber., 20,646) in 1887 published his first serious contribution to the theory of the acetoacetic ester synthesis. He explained the methanism of the process as follows:



$$CH_3-C(=O)-OC_2H_5 + C_2H_5ONa \longrightarrow CH_3-C(ONa)(OC_2H_5)(OC_2H_5)$$

$$CH_3-C(ONa)(OC_2H_5)(OC_2H_5) + CH_3-CO-OC_2H_5 \longrightarrow CH_3-C(ONa)=CH-CO-OC_2H_5 + 2C_2H_5OH$$

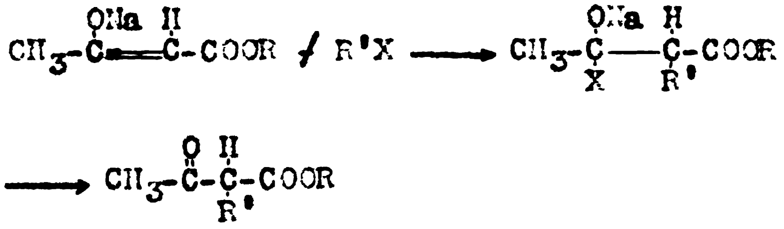
The formation of an addition product as indicated above was proved by the fact that benzyl benzoate unites with sodium methylate and methyl benzoate with sodium benzylate to form the same addition product which can be isolated.



$$C_6H_5-C(=O)-OC_7H_7 + CH_3ONa \longrightarrow C_6H_5-C(ONa)(OCH_3)(OC_7H_7)$$

$$C_6H_5-C(=O)-OCH_3 + C_7H_7ONa \longrightarrow C_6H_5-C(ONa)(OC_7H_7)(OCH_3)$$

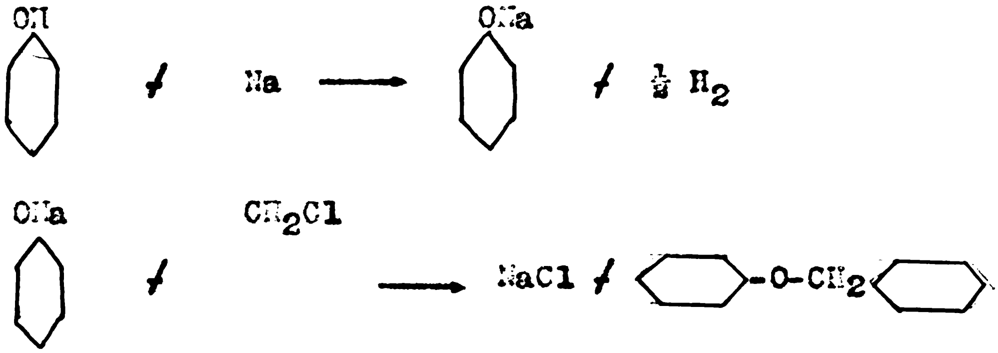
When sodioacetoacetic ester is allowed to react with alkyl halides, the alkyl radical of the latter replaces the metal in the ester. An intermediate addition product is formed previous to the elimination of sodium halide. The methanism of the substitution is represented by the following equation:



$$CH_3-\overset{ONa}{C}=\overset{H}{C}-COOR + R'X \longrightarrow CH_3-\underset{X}{\overset{ONa}{C}}-\underset{R'}{\overset{H}{C}}-COOR \longrightarrow CH_3-\overset{O}{C}-\underset{R'}{\overset{H}{C}}-COOR$$

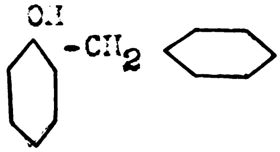
That the substituent alkyl radical attaches to the carbon instead of to the oxygen was explained by the theory on enol-keto tautomerism. As soon as the sodium is removed from the sodioacetoacetic ester by acidifying the derivative, acetoacetic ester is liberated in the enol form, but it rapidly changes until 90 per cent of the enol is changed to the keto form. The equilibrium between the two forms, however, may be disturbed and one form may be changed to the other according to the nature of the reagent used. If a reagent is used that acts only with the enol form, the keto form is gradually changed to the enol by the shifting of the hydrogen atom from carbon to oxygen. On the other hand, if a reagent that removes the keto is added, the shift occurs in the opposite direction. There are other factors besides the nature of the reagent, that determine the shift from one form to the other.

The enol-keto tautomerism was also found in many other organic compounds and reactions. For instance, when benzyl chloride is condensed with phenol, the resulting product may be phenyl benzyl ether, benzyl phenol, or both, depending upon various factors as will be discussed in later sections.



Phenyl benzyl ether

or



Benzyl phenol

Claisen states that while the ether is the product one would expect to be formed, the benzyl phenol formed is the result of "anomalous metal substitution", or, as he otherwise expresses it, the result of ring alkylation.

To explain the formation of the carbon deivative, three different views have been advanced and were discussed by K. Von Auwers, G. Wegener, and Th. Bahr (Chem. Zentr., I, 2347-8, 1920), namely:

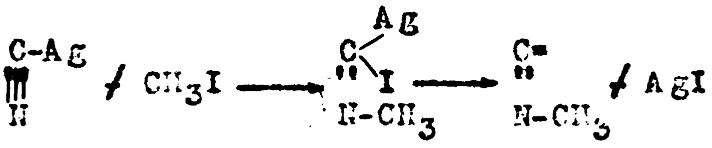
(1) "The initial formation of addition products with subsequent splitting.

(2) "The initial formation of normal oxygen derivatives with rearrangement of these into carbon derivatives.

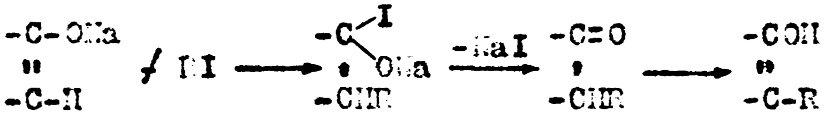
(3) "The separation of the metal as metalic halide, formation of free alkyl and enol radicals,

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

The first hypothesis was based on Michael's theory of the reaction between silver cyanide and methyl iodide (J. pr. 37, 486; 46, 189) which may be represented by the following scheme:



It can be seen that the methyl readical of CH_3I attaches to the nitrogen, instead of to the carbon as we might expect. As applied to the reaction of sodium phenolate and an alkyl halide, the mechanism may be illustrated as follows:



Thus, by the formation of an addition, a shift of bonds takes place which makes possible the final formation of a compound with the alkyl radical attached to a carbon in the ring, instead of to the oxygen atom, the carbon having the position ortho to the oxygen. Thus, when alkyl or benzyl phenols are condensed by using Claisen's method, the resulting product is of the ortho type, that is, in the new compound thus formed, the OH group and the new substituant occupy positions adjacent to each other in the ring.

The second hypothesis, that of the rearrangement from the initial O-derivatives to the final C-derivatives, is inadequate, for it is incomprehensible why an O-derivative should be transformed into a C-derivative in benzene more easily than in ether.

The third hypothesis was proposed by Wislicenus. According to this hypothesis, O-derivatives should be formed with allyl or benzyl radicals because of their great reactivity, but this is not the case, as shown by the experiment of Claisen (Ann., 442, 210-45, 1925) on the alkylation of phenols. But rather the opposite view is more probable. Since allyl and benzyl radicals are distinguished by their slight valence requirements and therefore hold oxygen only loosely, they show a preference for combining with carbon to form a stable combination. Nevertheless the formation of radicals and the isomerization of enol to keto radicals is necessary to explain the reactions of this kind.

It was found that the formation of O- or C-derivative depends upon a number of factors among which the following ones are most important.

1. <u>The nature of the alkylization agent</u>---K. Von Auwers and Th. Bahr (Ber., 61B, 408-16, 1928) state that the halides of such radicals as are characterized by a small affinity consumption, such as allyl and benzyl, yield chiefly C-derivatives; while true alkyls like ethyl and propyl, favor the formation of O-derivatives. This is also a question of saturation. Claisen states that the looser the bond between the halogen and the alkyl radical the more smoothly the reaction progresses. We know that unsatuation in the alkyl radicle on the carbon atom adjacent to that one bearing the halogen

results in a comparatively loosely held halogen.

M. Busch (Z. Angew. Chem. 38, 1145-6, 1925) states that the tendency of benzyl radicals toward C-alkylation of phenols increases with the increasing substitution of the hydrogen of methane carbon with aryl group. While it is possible to obtain ethers with $C_6H_5CH_2Cl$ in non-dissociating media, $(C_6H_5)_2CHCl$ yields only the carbon derivatives.

2. <u>The nature of the solvent or the medium in which the reaction occurs</u>---Solvents such as water, alcohol, and other oxygen compounds, that are characterized by a tendency to dissociate, are called dissociating media and, when employed, give O-derivatives as the condensation products. On the other hand, if a non-dissociating medium, such as benzene, toluene, or other substances which contain no oxygen, is used, C-derivatives will be formed.

Claisen and Tietze (Ber., 58B, 275, 1925) found that when alkali phenolates were treated in non-dissociating media with unsaturated alkyl halides, there was obtained almost entirely carbon derivatives.

Claisen, Kremers, Roth, and Tietze (Ann., 442, 210-45, 1925) found that allyl bromide and sodium p-cresolate in methyl alcohol gave 90 % of p-cresol allyl ether, while in benzene there resulted 30 % O-allyl derivatives and 60 % C-allyl derivatives.

While it is not easy to explain why dissociating media yield O-derivatives and non-dissociating media yield C-derivatives, it is probably true that reaction media such as toluene exert a loosening effect on the valence bonds between the alkyl or benzyl radical and the halogen, thus producing the carbon substitution.

According to Michael (Ber., 41, 1080-1091, 1908), there is an interaction between the molecules of the solvent and of the solute and this involves a constant interchange between the free and bound molecules of the solvent. Thus, for example, if the transformation of the complexes

$$(\text{Keto} + \text{solvent}) \rightleftharpoons (\text{Enol} + \text{solvent})$$

is accomplished by an increase in entropy, the solution in this particular solvent will result in isomerization, the degree of isomerization depending upon the relative increase in entropy in any given case. But this in turn depends collectively upon the total change suffered by the various physical and chemical forces taking a part in the transformation. It is, therefore, extremely hard to establish any simple relationship between any given physical constant of a solvent and its power of isomerization.

2. Aluminum Chloride as Condensing Agent

Since the discovery of the Friedel-Crafts reaction in 1877 (Comp. rend., 84, 1392-95; Ber., 10, 1180), aluminum chloride has found wide application in organic synthesis. It is used in almost every type of change which involves the elimination of hydrogen chloride, bromide, or iodide. Its nature in effecting condensations has not been definitely known. It is probable that its action may be explained by one or a combination of the following theories:

(1) Intermediate compounds.

(2) Catalytic action.

(3) Dehydration.

The first view was held by Boeseken (Rec. trav. Chim., 19, 19-28, 1900; 20, 102-106, 1901; 22, 301-314, 1903; 23, 98, 1904; 30, 148-150, 1911) who represented the action of aluminum chloride by the following scheme:

$$RCOCl + AlCl_3 \longrightarrow RCOCl,AlCl_3$$

$$RCOCl,AlCl_3 + R'H \longrightarrow RCOR',AlCl_3 + HCl$$

$$RCOR',AlCl_3 + xH_2O \longrightarrow RCOR' + AlCl_3 + xH_2O$$

where R'H represents an aromatic hydrocarbon or one of its derivatives.

The catalytic action of aluminum chloride was advocated by Friedel and Crafts and supported by Gustavson and Steel. Friedel and Crafts assumed the formation of an intermediate compound which unites with the halogen compound, regenerating aluminum chloride, as shown below:

$$C_6H_6 + Al_2Cl_6 \longrightarrow C_6H_5Al_2Cl_5 + HCl$$

$$C_6H_5Al_2Cl_5 + RCl \text{ —— } C_6H_5R + Al_2Cl_6$$

This theory was for sometime doubted since it was found that the amount of product increased when a large qu quantity of aluminum chloride was used, which showed that aluminum chloride could not be a true catalyst. Gustavson (Ber., 11, 2151, 1878) isolated a number of stable compounds formed by the union of aluminum chloride with hydrocarbons and having the formulas Al_2Cl_6,C_6H_6 and $Al_2Cl_6,6C_6H_6$, which accounts for the nesessity of using large quantities. From this, Steele (Trans. Chem. Soc., 1470, 1903) concludes that aluminum chloride is a true catalyst, differing from other catalysts only in its tendency to become inactive through the formation of stable compounds with certain substances produced duting the reaction.

Norris (Ind. Eng. Chem., 16, 184, 1924) also studied the catalytic action of aluminum chloride. Triphenyl methyl chloride, ethyl ether and similar compounds were used in the condensation.

The dehydrating action of aluminum chloride is illustrated by the work of Merz and Weith, and also by that of Jaubert. Merz and Weith (Ber., 14, 187, 1881) treated phenol with aluminum chloride and obtained diphenyl ether. Jaubert (Comt. rend. 132, 184, 1901) prepared aniline and p-toluidine from hydroxyl amine-hydrochloride and benzene.

3. Benzylation of Phenols

The work of Kollaritz and Mertz from 1871-1873 (Ztschr. Chem., 1871, 705; Ber., 5, 447; 6, 446) marked some of the earliest work done on benzylation of phenols. They prepared diphenyl ketone, using phosphoric anhydride as dehydrating agent.

In 1872 Paterno (Gazz. Chem. ital., I, 589; II, 1-6) synthesized benzyl phenol and benzyl anisol respectively by the action of benzyl chloride on phenol and anisol in the presence of zinc turnings. In 1875 Paterno, in connection with Filetti (ibid., 5, 381), used a mixture of acetic and sulfuric acids instead of zinc, as the catalytic agent. In the preperation of benzylated anisol three years later, zinc was again used by Paterno and Mazzara (Gazz., 8, 303).

In 1881 Liebmann (Ber., 15, 152) used zinc chloride in the condensation of benzyl phenol, while zinc was used in Paterno's experiment in 1872. Incidently Liebmann raised the question as to whether the zinc or the zinc chloride was the active catalyst, as in Paterno's experiment zinc c chloride could be easily formed from the zinc and the free HCl found in benzyl chloride. He also showed from his own observations that a very small quantity of zinc chloride could catalyze the reaction.

Perkins and Hodgkenson (J. C.S., 37, 721, 1880) prepared benzyl phenyl acetate by treating benzyl chloride with phenyl acetate in the presence of aluminum chloride.

The work on condensations of aromatic alcohols with aromatic compounds using aluminum chloride as a dehydrating agent was not known before 1916 when Huston and his helpers began their research along this line, which shall be taken up in detail in the next section. They obtained fairly good results although Friedel and Crafts (J. Chem. Soc., 41, 116, 1882) stated that their reaction is usually impossible in the presence of compounds containing the group OH or OR.

4. The work of Huston

In 1916 Huston and Friedemann (J. A. Chem. Soc., 38, 2527) condensed benzyl alcohol and benzene by the use of anhydrous aluminum chloride as a dehydrating agent. They obtained diphenylmethane as the principal condensation product besides a certain amount of ortho and para dibenzylbenzenes and other hydrocatbons among which was anthracene.

Two years later Huston and Friedemann (J. A. Chem. Soc., 40, 785) applied the same reaction to the secondary aromatic alcohols, tertiary hydrocarbons being the principal products. With benzene the reaction is as follows:

$$C_6H_5CH(OH)R + C_6H_6 \xrightarrow{AlCl_3} C_6H_5CHRC_6H_5 + H_2O$$

They found that the yield could be increased by using a larger quantity of benzene and at low temperature. They also stated that the yield is better when R is an aryl group then when it is a alkyl group such as methyl or ethyl, the latter being more depressing.

In 1920 Huston (Science, 52, 206-7) prepared p-benzyl phenol by condensing aromatic alcohols with phenols in the presence of aluminum chloride at low temperature. As before noted, benzylphenol had previously been prepared by Paterno and his helpers, and also by Libbmann, although amuminum chloride was not used by these investigators.

In 1924 Huston (J. A. Chem. Soc., 46, 2775) applied the same reaction to the condensation of benzyl alcohol with phenol, anisol and phenetol, and concluded that the phenolic hydroxyl group does not interfere with the substitution of the benzyl group in the benzene ring.

Two years later Huston and Sager (J. A. Chem. Soc., 48, 1955) applied this reaction to saturated and unsaturated aliphatic and aromatic alcohols with benzene and found that, of the alcoholic derivatives of the aromatic hydrocarbons, only those in which the hydroxyl is on the carbon atom adjacent to the ring react, that unsaturated aliphatic alcohols, and saturated aliphatic alcohols up to and including amyl alcohol do not react, and that unsaturation onthe carbon atom, adjacent to the alcoholic group, increased the reactivity of the hydroxyl toward the dehydrating effect of aluminum chloride.

In the same year (1926) Huston and Bartlett prepared P-hydroxyl-1,1-diphenyl pentane from phenyl butyl carbinol and phenol in the presence of aluminum chloride.

By the same method Huston and Strickler in 1927 condensed propyl phenyl carbinol with phenol and obtained P-hydroxyl-1,1-diphenyl butane.

Huston, Lewis and Grotemut (J. A. Chem. Soc., 49, 1365, 1927) used phenol this time instead of benzene in the condensation od secondary alcohols. They found that the yield of ethylphenyl carbinol and phenol was 30-35 % while benzhydrol and phenol gave a 40 % yield. This gives further evidence that unsaturation on the alpha carbon atom increases the reactivity of the hydroxyl group, and consequently the yield.

In the same year Huston and Swartout carried out the benzylation of O-cresol by the use of aluminum chloride on O-cresol and benzyl alcohol and obtained 2-methyl-4-benzyl phenol along with a small amount of 2-methyl-6-benzyl phenol.

The yield of 2-methyl-4, 6-dibenzyl phenol was about 19 % of the theory. In order to distinguish between the two isomeric mono-benzyl derivatives, the investigators benzylated O-cresol by the method of Claisen.

In 1928 Huston and Houk benzylated meta cresol by the same method. Since in this phenol both ortho positions are open as well as the para, there is a greater possibility for substitution. Three compounds were obtained from the condensation: 3-methyl-4-benzyl phenol and 3-methyl-4,6-dibenzyl phenol, and 3-methyl-6-benzyl phenol.

Work on the condensation of para cresol was next carried out by Huston and Lewis in the same year. Both aluminum chloride and Claisen's methods were used in their investigation. Since in the para cresol only the ortho positions to the hydroxyl are open, both methods should give a mono- and a di-benzylated product. This was borne out by the production of 2-benzyl-4-methyl phenol and 2,6-dibenzyl-4-methyl phenol. It was found that using the phenol and alcohol in the molecular ratio of three to one increased the yield.

In 1929 Huston and Maxfield studied the effect of varying proportions of phenol and $AlCl_3$ on the yields of O- and P-benzyl phenol. They found that the yield of the latter was increased by increasing the amount of phenol, but not by increasing the $AlCl_3$. One mol of $AlCl_3$ did not give higher yields than half a mol.

In 1930 Huston and Eldridge obtained the ether as well as the benzylated phenol from the condensation of 2,6-dichlor phenol and benzyl alcohol. The ether was identified to be 2, 6

2,6-dichlor phenyl benzyl ether. It might be mentioned that this was the first time that the ether had been identified in any of the previous $AlCl_3$ condensations.

III. The Problem Defined

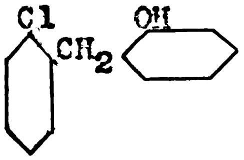
The object of this problem can be stated as follows:

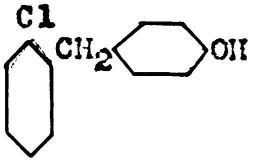
1. To prepare, identify, and study the properties of some hydroxy derivatives of chlorodiphenylmethane.

2. To prepara also benzoyl derivatives of the above compounds.

3. To establish definitely that O-substitution accompanies the P-substitution in condensations with Aluminum ~~cl~~ chloride.

4. To determine the positions of chlorine entering into the following groups upon direct chlorination:





IV. Experimental

A. Condensation by the Claisen Method

1. Preparation of 2-hydroxy-2'-chlorodiphenylmethane

The chlorobenzyl chloride used in these experiments was prepared by first making ortho chlorototuene according to the method of Marvel and Mc. Elvain (Org. Syn. Vol. 3, pp. 33-35, 1923). This was then chlorinated according to the procedure used by Erdmann (A. 272, 151, 1892). The product, a colorless oil, distilled over at 213-214°.

The condensation of chlorobezyl chloride and phenol by the Claisen method was carried out in the following manner. 29.2 g. of phenol was first dissolved in 100 cc. of totuene, to which 7 g. of finely cut sodium was then added. The mixture was allowed to stand over night under a refrex condenser. A white cheesy mass was formed. This was sodium phenylate according to the following reaction:

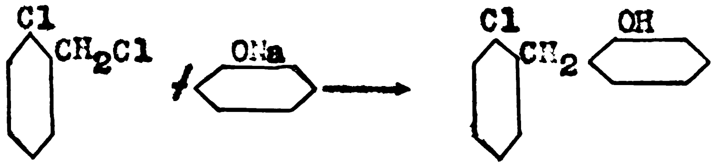
$$C_6H_5OH + Na \longrightarrow C_6H_5ONa + \frac{1}{2} H_2$$

To this was added 50 g. of vhlorobenzyl chloride and the resultant mixture heated at 150° for eight hours while connected to a reflex condenser. This product was shaken out with two portions of water to remove the salt. Difficulty to separate the aqueous salt solution from the oil product was sometimes encountered due to the nearly equal densities of the two. It was found that if a small quantity of water was taken for the first portion and a rather large quantity for the second portion, the difficulty could be easily overcome. After the salt had been removed from the oily product, the totuene was then distilled off and the residue treated with Claisen's alcoholic potash (A. 442, 244, 1925) which dissolves any free hydroxyl groups. This mixture was shaken out with petroleum ether to remove any possible ethers and the extract was saved for further investigation. The remainder was acidified. The dark red oil which separated out was extracted with ether and this was dried over anhydrous potassium carbonate over night. The ether was then distilled off and the residue fractionated.

Third fractionation

Below 95°	15 mm.	Phenol	8.5 g.
95-140°	3 mm.		4.5 g.
140-150°	" "		11.0 g.
150-220°	" "		4.0 g.
Residue			10.0 g.

The fraction 140-150°, boiling at 146-151 (3mm.) was a light green oil. It turned to deep pink on long standing. From its method of preparation this compound must be 2-hydroxy-2'-chlorodiphenylmethane:

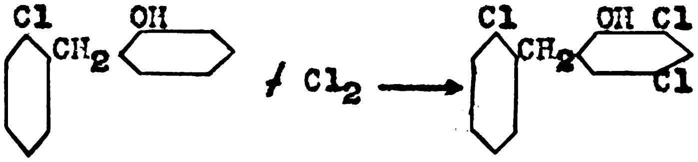


A Parr Bomb determination for chlorine (J. A. Chem. Soc., 39, 2069, 1917) carried out on this compound gave the following results:

Sample	% Cl detn.	% Cl calc.	cc 0.1N AgNO3
.4882 g.	16.69	16.22	22.95
.5256	16.66	16.22	24.67

The theoretical percentage of chlorine was calculated for one atom of chlorine and the experimental result verifies this statement.

5 g. of the 2-hydroxy-2'-chlorodiphenylmethane was weighed out and chlorinated according to the method given by Houben (Die Methoden Der Org. Chem., Vol. III, 799), using chloroform as solvent. A ten per cent excess of the theoretical amount of chlorine required to form the compound 2-hydroxy-3,5,2'-trichlorodiphenylmethane



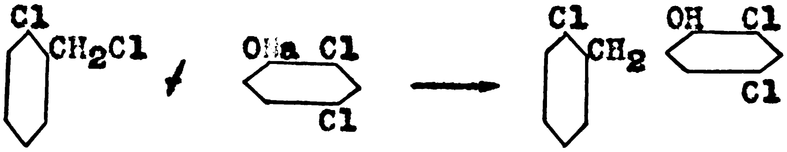
was used. The product did not solidify before it was seeded by 2-hydroxy-3,5,2'-trichlorodiphenylmethane crystals obtained from condensation of chlorobenzyl chloride and 2,4-dichlorophenol as described below. The solidified product was pressed between filter papers and recrystallized from alcohol. It melted at 59.5-60.5°.

A Parr Bomb determination for chlorine was calculated for three atoms of chlorine and the experimental data confirms this statement as shown by the following results:

Sample	% Cl detn.	% Cl calc.	cc 0.1N AgNO3
.1717 g.	36.64	37.01	17.72
.1876	36.86	37.01	19.47

2. Preparation of 2-hydroxy-3,5,2'-trichlorophenylmethane

The same procedure previously employed in the preparation of 2-hydroxy-2'-chlorophenylmethane was used in the condensation of 2,4-dichlorophenol and chlorobenzyl chloride. The fraction 147-155° (2mm.) solidified to a light grey mass during a few weeks' standing. This was pressed between filter papers and recrystallized in alcohol into clusters of fine needles in the form of rosette. The compound has a melting point of 59.5-60.5°. From its method of preparation this compound must be 2-hydroxy-3,5,2'-trichlorodiphenylmethane:



The compound upon quantitative analysis gave the following results for its chlorine content:

Sample	% Cl detn.	% Cl calc.	cc 0.1 N $AgNO_3$
.2172 g.	35.91	37.01	21.98
.1813	36.18	37.01	18.47

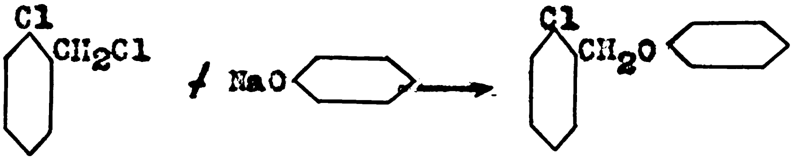
The theoretical per cent of chlorine was calculated for three atoms of chlorine and the experimental results bear out this statement.

It is seen that this compound checks exactly with 2-hydroxy-3,5,2'-trichlorodiphenylmethane obtained by chlorinating 2-hydroxy-2'-chlorodiphenylmethane. This is a further evidence that the substitution derivatives formed by

Claisen's condensation of phenol and ortho chlorobenzyl chloride is 2-hydroxy-2'-chlorodiphenylmethane.

3. Preparation of 2-chlorobenzylphenylether

This ether was prepared by condensing chlorobenzyl chloride with phenol in a dissociating medium of methyl alcohol instead of in non-dissociating medium of toluene. The method used was almost identical with the procedures employed in the previous experiments except that the condensed product was fractionated right after the removal of the salt. After two fractionations a clear light green oil distilled over at 140-145° (2.5 mm.). This compound according to the method of preparation must be 2-chlorobenzylphenylether:



That the molecule contains one atom of chlorine was proved by the Parr Bomb determination as follows:

Sample	% Cl detn.	% Cl calc.	cc 0.1N $AgNO_3$
.3257 g.	15.45	16.22	14.17
.2832	15.57	16.22	12.42

The petroleum ether extract from the preparation of 2-hydroxy-2'-chlorodiphenylmethane was first distilled to remove the petroleum ether and finally fractionated. An oil of the same color and same boiling point was obtained. A Parr Bomb determination proved the compoind to contain also one atom of chlorine:

Sample	% Cl detn.	% Cl calc.	c.c. 0.1N $AgNO_3$
.4003	16.21	16.22	18.27
.2006	16.87	16.22	9.53

Therefore both ethers are identical, although the ether formed in the non-dissociating medium was only a small fraction of the condensation product, whereas the ether formed in methyl alcohol was exclusively.

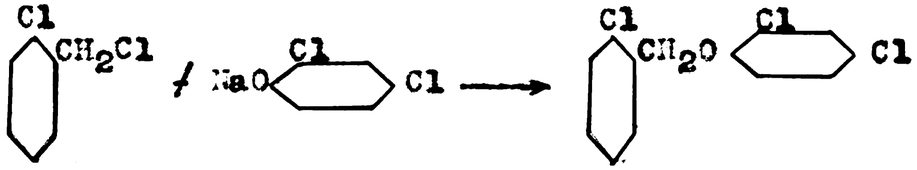
4. Preparation of 2-chlorobenzyl-2,4-dichlorophenylether

In the preparation of this ether the following amounts were used:

2,4 dichlorophenol	25 g.
chlorobenzyl chloride	25 g.
Soidum	6 g.
Methyl alcohol	100 cc.

After eight hours' reflexing, the salt in the condensation mixture was shaken out with two portions of water. The oil solidified instantly. It was fractionated at 2 mm. The fraction between 150-175° is pressed between filter papers and recrystallized in alcohol. 19 g. of pure white needles was obtained; m.p. 61-62°. The yield was 43 %.

The compound according to the method of preparation must be 2-chlorobenzyl-2,4-dichlorophenylether.



A Parr Bomb determination for chlorine gave the following results:

Sample	% Cl detn.	% Cl calc.	cc 0.1 N $AgNO_3$
.2091	36.80	37.01	21.67
.2385	36.63	37.01	24.54

The theoretical per cent of chlorine was calculated for three atoms of chlorine and the experimental result verifies this assumption.

The same ether was obtained by fractionating the petroleum ether extract from the preparation of 2-hydroxy-3,5,2'-trichlorodiphenylmethane. It has the same crystalline form and also melted at 61-62°. A parr Bomb determination also showed the three chlorine atoms in the molecule:

Sample	% Cl detn.	% Cl calc.	c c 0.1 N $AgNO_3$
.1975 g.	36.84	37.01	20.49
.1971	36.72	37.01	20.38

B. Condensation by the Huston Method

1. Preparation of 4-hydroxy-2'-chlorodiphenylmethane

The procedure used in this experiment was similar to that previously employed by Huston in the preparation of benzyl phenol (J. A. Chem. Soc., 46, 2775). 50 g. of chlorobenzyl chloride and 87 g. of phenol were placed in a glass cylinder which contained 200 cc. of petroleum ether. The mixture was vigorously stirred by means of a mechanical stirrer. 21 g. of freshly ground anhydrous aluminum chloride was added in small portions. The reaction was not as violent as in other experiments of this type. The temperature did not rise above 27°. Stirring was continued for half an hour after all the aluminum chloride had been added. The reaction mixture was allowed to stand until all the hydrochloric gas had been given off. Two layers were formed with petroleum ether on top and a pinkish grey oil at the bottom. The whole mass was decomposed by pouring on cracked ice to which some hydrochloric acid (1:1) had been added. The petroleum ether layer was separated out and distilled. The water and oil portion was extracted with ether. To this extract was added the residue obtained from distilling off the petroleum ether. The whole was dried over potassium carbonate and allowed to stand overnight. The ether was then distilled off and the remained fractionated at 3mm.

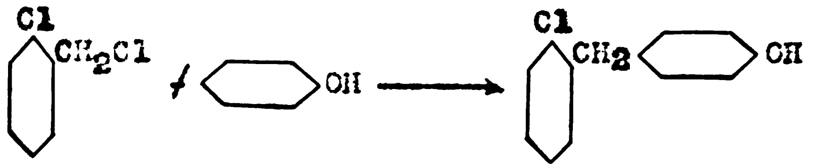
Third fractionation

Below 75° (phenol)	48.5 g.
75-140°	6.0 g.
140-150°	10.0 "
150-170°	16.0 "
170-220°	6.0 "
Residue	3.0 "

The fraction 150-170° solidified after several hours standing. It was pressed between filter papers and recrystallized from ligroin. 10 g. of clusters of white short needles was obtained; m. p. 68-69°. A Parr Bomb determination showed that there is one chlorine atom in the molecule:

Sample	% Cl detn.	% Cl calc.	cc 0.1 N $AgNO_3$
.2170	15.85	16.22	9.64
.2216	16.04	16.22	10.01

The filter papers were extracted with ether, from which 4 g. of oil boiling at 140-150° was obtained. This was combined with the original 140-150° fraction and refractionated, giving 13 g. of a purer product which resembled the ortho compound prepared by the Claisen method. The above crystallized compound, therefore, must be the para compound, 4-hydroxy-2'-chlorodiphenylmethane:



A bigger yield of the para than the ortho compound was observed in subsequent condensations when larger quantities were used. Much resinous material boiling between 170-220° (3mm.) was also obtained from the condensation product.

To prove whether or not the 140-150° (3mm.) fraction was the ortho compound, a Parr Bomb determination was run. It gave the following results, showing the compound to contain one chlorine atom in the molecule:

Sample	% Cl detn.	% Cl calc.	0.1N AgNO$_3$
.2026	16.14	16.22	10.51
.3540	16.40	16.22	16.35

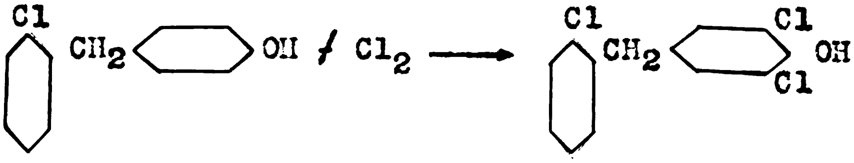
For further evidence, 5 g. of the product was chlorinated and the melting point determined. It melted at 59.5-60.5° which checked exactly with that of 2-hydroxy-3,5,2'-trichlorodiphenylmethane.

The structure of the para compound was proved by the same method. The following were the results of the chlorine determination, calculated for one atom of chlorine in the molecule:

Sample	% Cl detn.	% Cl calc.
.2170	15.85	16.22
.2216	16.04	16.22

Then 5 g. of the compound was chlorinated. The pure crystals melted at 86.5-87.5°, which checks with the melting point of the product prepared by condensing 2,6-dichlorophenol with chlorobenzyl chloride, as described below. Therefore, the chlorinated product must be 4-hydroxy-3,5,2'-tri-

chlorodiphenylmethane:



2. Preparation of 4-hydroxy-3,5,2'-trichlorodiphenylmethane

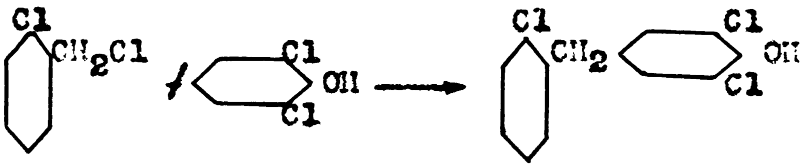
The procedure used was similar to the one described above. The following amounts were used:

Chlorobenzyl chloride	50 g.
2,6-dichlorophenol	154 g.
Aluminum chloride	21 g.
Petroleum ether	200 cc.

Second fractionation gave the following results at 3 mm.

Below 110°	Phenol	51 g.
110-160°	Mostly phenol	19 "
160-200°		27 "
200-220°		3.5 "
Residue		51 "

The fraction 160-200° was pressed between filter papers and recrystallized from ligroin. 15 g. of white needles melting at 86.5-87.5° was obtained. From the method of preparation this compound must be 4-hydroxy-3,5,2'-trichlorophenylmethane:



A Parr Bomb determination for chlorine gave the following results:

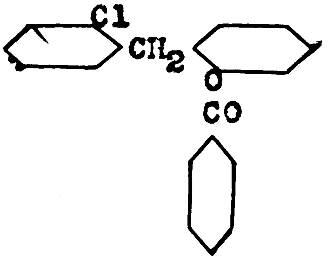
Sample	% Cl detn.	% Cl calc.	cc 0.1 N $AgNO_3$
.2025	36.77	37.01	20.97
.2072	36.84	37.01	21.50

The theoretical per cent of chlorine was calculated for three atoms of chlorine and the experimental result bears out this statement.

C. Esterification

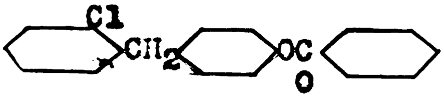
The benzoyl derivatives of (1) 2-hydroxy-2'-chlorodiphenylmethane, (2) 4-hydroxy-2'-chlorodiphenylmethane, (3) 2-hydroxy-3,5,2'-trichlorodiphenylmethane, and (4) 4-hydroxy-3,5,2'-trichlorodiphenylmethane were prepared by dissolving 2 g. of the phenols in 5 cc. of pyridine and adding calculated amount of benzoyl chloride. The following esters indicate the compounds respectively formed:

(1)



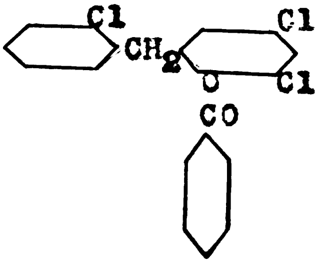
b. p. 173-176°
at 2.5 mm.

(2)



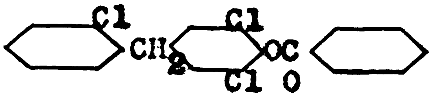
m. p. 64.5-65.5°

(3)



m. p. 81-82°

(4)



m. p. 86-87°

V. Summary

1. The following compounds were prepared and identified:

   a. 2-hydroxy-2'-chlorodiphenylmethane.

   b. 4-hydroxy-2'-chlorodiphenylmethane.

   c. 2-hydroxy-3,5,2'-trichlorodiphenylmethane.

   d. 4-hydroxy-3,5,2'-trichlorodiphenylmethane.

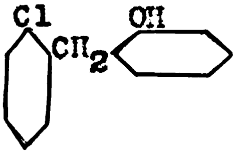
   e. Benzoyl derivatives of the above compounds.

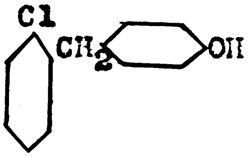
   f. 2-chlorobenzylphenylether.

   g. 2-chlorobenzyl-2,4-dichlorophenylether.

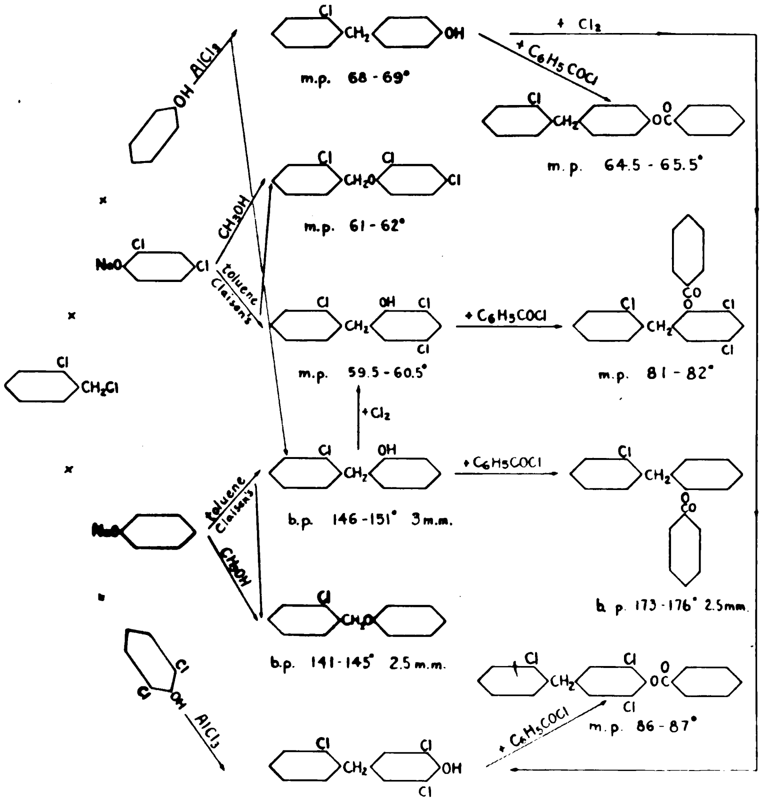
2. In the aluminum chloride condensations both the ortho and the para compounds were formed, the bulk of which was the para.

3. When the following compounds were chlorinated, chlorine was found to take the 3,5 (meta) position to the connecting carbon in the ring containing the hydroxyl:





Some Hydroxy Derivatives of Chloro Diphenyl Methane



By
Philip S. Chen

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SUPPLEMENTARY
MATERIAL