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SOME CHLORO DERIVATIVES OF PARA AND
ORTHO BENZYL PHENOLS IN REFERENCE TO
CONDENSATION OF META CHLORO BENZYL
CHLORIDE WITH PHENOL 2, 4 DICHLORO
PHENOL AND 2, 6 DICHLORO PHENOL

THESIS FOR THE DEGREE OF M. S.

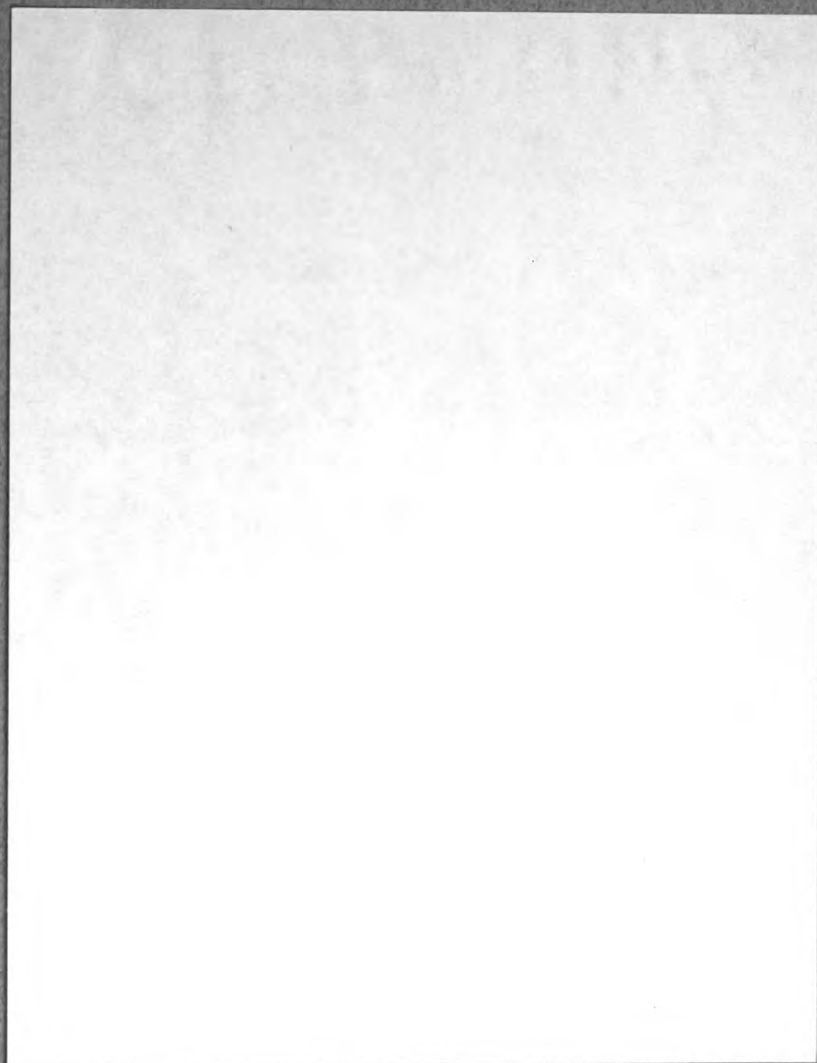
Ralph Lawrence Guile

1933

R.C. Huston

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IN REFERENCE TO
CONDENSATION OF META CHLORO BENZYL CHLORIDE WITH PHENOL
2, 4 DICHLORO PHENOL AND 2, 6 DICHLORO PHENOL

A THESIS

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of
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Ralph Lawrence Guile

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Introduction

This thesis describes two methods of condensing phenols with meta chlorobenzyl chloride.

The Clasien method in which the phenols were converted to a sodium salt which was suspended in a suitable medium and then treated with the benzyl chloride. Former investigators showed that this method gave only the ortho substituted phenols or the corresponding ethers, the yields of each depending on the nature of the medium used.

The Huston method in which the condensation was effected by the catalytic action of anhydrous aluminum chloride. The products being para substituted phenols and a small per cent of the ortho derivatives in some cases.

The above methods will be discussed in detail in Section II (Historical) of this thesis.

Historical Data

I. Early Benzoylation of Phenol

The earliest work on benzoylation of phenols might be considered to be by Kollarits and Merts from 1871 - 1873 (Aschr. Chem. 1871, 705; Br., 5, 447; 6, 446) when they prepared diphenyl ketone, using phosphoric acid as a dehydrating agent.

About this same time E. Paterno (Gazz. Chim. ital., 2, 1 - 6; 1872) prepared benzyl phenol by gently heating a mixture of phenol and benzyl chloride in the presence of zinc dust. The compound had a melting point of 84° C., crystallized in silky white needles and was soluble in ethyl ether, alcohol, benzene, chloroform, or in alkaline solutions. Substitution products were formed with nitric acid and a sulphonic acid was prepared on treatment with sulphuric acid. This same benzyl phenol was prepared by benzylating anisole and treating the mixture with HI.

Three years later (1875) Paterno and Fileti (Gazz. chim. ital., 5, 381) published an article describing the condensation of phenol and benzyl alcohol using a mixture of sulphuric and acetic acids as a dehydrating agent. This time crystals and an oil were obtained. These crystals were said to be the benzyl phenol and the oil an isomer probably an isomeric benzyl phenol.

Perkins and Hodgkinson (J. Chem. Soc. 1880, 724; 1880) reported the isolation of benzyl phenol. They heated a mixture of phenyl acetate and benzyl chloride obtaining a compound which showed by analysis to possess the formula $C_{25}H_{24}O_3$ and upon treatment with alcoholic KOH yielded an oil which when purified gave crystals (m. p. 39° C) analysing to have the formula $C_{10}H_{10}O$. Acidification and purification of the alkaline solution

yielded a crystalline compound (m. p. 80 - 81°C) which had the formula $C_{13}H_{12}O$. Although there was a difference in melting point of 3° they assumed their compound was the same benzyl phenol as prepared by Paterno and the lower melting point was due to impurities.

Besides the above work the same two men prepared benzyl phenyl acetate by treating benzyl chloride with phenyl acetate in the presence of aluminum chloride (J. Chem. Soc., 57, 721, 1880). This is the first work with aluminum chloride in condensations as a dehydrating agent. Its use in this connection will be discussed later in this thesis.

In 1881 Liebmam (Br., 15, 152) used molten $ZnCl_2$ as a dehydrating agent in the condensation of benzyl alcohol and phenol and obtained a crystalline product M.P. 80 - 81° C and B.P. 320 - 322° C.

Rennie in 1882 (J. Chem. Soc., 53, 220) showed that the compound melting at 84° C obtained by Paterno and Fileti was parabenzyl phenol and the oil was ortho benzyl phenol.

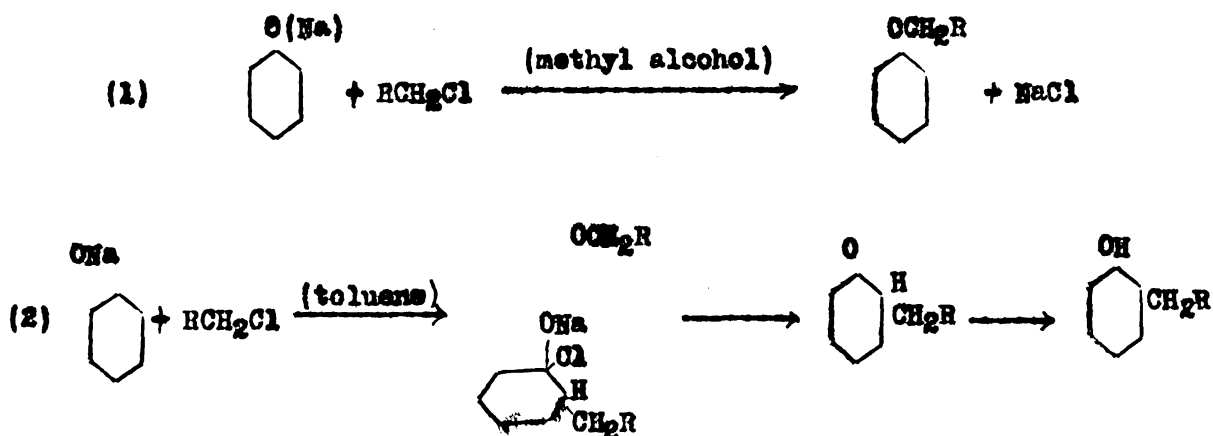
By use of sulphuric acid at boiling temperatures J. V. Braun (Be., 43, 1550; 1910) prepared benzyl methyl ether, benzylethyl ether, oxyl ethyl ether and benzyl allyl ether by condensation of the corresponding aromatic bromine derivatives and the respective alcohols.

Johnson and Hodges (J. Am. Chem. Soc., 35, 1014; 1913) prepared substituted phenols and ethers (by reduction with Zn amalgam and HCl) of mixed ketones containing hydroxyl or ether radicals in the benzene nucleus. Example: preparation of methyl ether of 4 ethyl phenol by reduction of p - acetyl anisole.

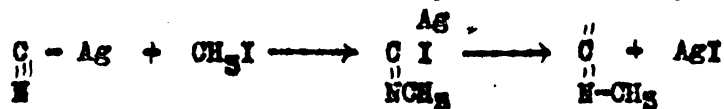
II. The Work of Claisen

In 1923, L. Claisen (Z. Angew. Chem., 36, 478) published his first article on the carbon alkylation of phenols. The results of his investigation showed definitely that when the sodium derivative of monohydric phenols was heated with an alkyl halide in a "non dissociating" medium such as toluene, carbon alkylation took place mainly in the position ortho to the hydroxyl group while in a "dissociating" medium as methyl alcohol the alkylation took place on the oxygen, forming the corresponding ether.

Claisen gave the following reactions:



This mechanism was built on Michael's theory (J. pr., 37, 486; 46, 189) for the reaction between silver cyanide and methyl iodide.

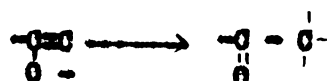


To explain the formation of the carbon derivative three different views have been advanced and were discussed by K. von Auwers, G. Wegener, and Th. Bahr (Chem. Ventr.; I, 2347 - 8, 1926) namely:

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

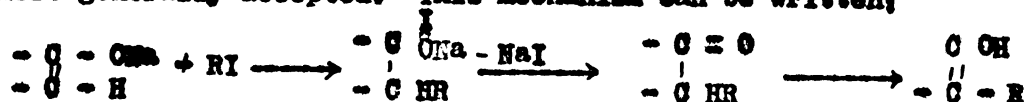
(b) The initial formation of normal oxygen derivatives with subsequent rearrangement into the carbon derivatives.

(c) The separation of the metal as metallic halides, forming free alkyl and enol radicals



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

Of the above the first was formulated originally by Claisen and is most generally accepted. This mechanism can be written;



in which after addition a shift of bonds takes place making possible the final formation of a compound with the alkyl radical attached to the ortho position of the ring instead of the oxygen atom.

Claisen listed the factors which effect the reaction as follows;

1. The kind of phenol: Condensations of complex phenols were carried out with greater difficulty than the more simple ones.
2. The kind of radical attached to halogen: Unsaturated, saturated, aliphatic or aromatic. It was found that saturated alkyl halides promoted the formation of oxygen-derivatives, while unsaturated alkyl halides promoted the formation of carbon-derivatives.
3. The kind of halogen.
4. The kind of metal in the metal phenolate.
5. The temperature
6. The reaction medium: Dissociating media such as water and alcohol give oxygen-derivatives as condensation products but in non-dissociating media such as benzene, toluene and substances lacking in oxygen then carbon-derivatives will be formed.

Related somewhat to the work of Claisen was the rearrangement of phenyl benzyl ether to give a benzylated phenol, J. Von Alphen (Rec. trav. chim. Vol 44, 799; 1927). He heated benzyl phenyl ether with SnCl_4 at 160°C for one hour and found that it yielded 4 hydroxy diphenyl methane and a dyestuff.

III. Aluminum Chloride as Condensing Agent

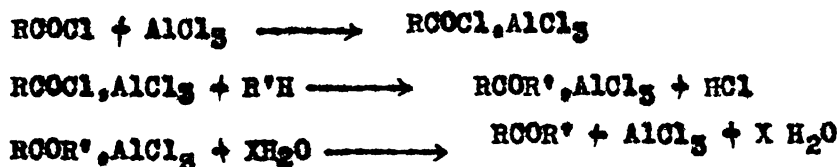
(a) Early work

In 1878 Friedel and Crafts condensed amyl alcohol and various hydrocarbons (Compt. rend., 84, 1592 - 95; Bes., 10, 1180). They worked only with aliphatic compounds but aluminum chloride has found a far wider use in organic chemistry in that it may be utilized in almost any case where the elimination of hydrogen chloride, bromide or iodide is to be accomplished.

The action is not well explained but three theories have been evolved;

- (1) Intermediate compounds.
- (2) Catalytic action
- (3) Dehydration

Theory (1) was supported by Boeseken (Rec. trav. chim., 19, 19 - 26, 1900; 20, 102 - 106, 1901; 22, 301 - 314, 1903; 23, 98, 1904; 30, 148 - 150, 1911) and the reaction represented as;



Gustavson (Ber., 13, 157; 1880) and Büttgenbach (J. Prakt. Chem., 150, 355; 1923) supported somewhat the same idea of instable aluminum-organic compounds.

Since Gustavson (Ber., 11, 2151, 1878) isolated several stable compounds of aluminum chloride with hydrocarbons formulas $\text{Al}_2\text{Cl}_6\text{-C}_6\text{H}_6$ and $\text{Al}_2\text{Cl}_6\text{-6C}_6\text{H}_6$ which might account for the large amounts of AlCl_3 used. Steele (Trans. Chem. Soc., 1470, 1903) formulated the theory that aluminum chloride was a true catalyst differing from other catalysts only in its tendency to become inactive due to the formation of stable compounds with certain substances produced during the reaction.

The dehydration theory was upheld by the work of Hers and Weith (Ber., 14, 187, 1881) in treating phenol with aluminum chloride and obtaining diphenyl ether and later by Jaubert (Compt. rend., 132, 841; 1901) in the preparation of aniline and p-tolindine. The action of $\text{H}_2\text{NOH.HCl}$ with the hydrocarbon in the presence of AlCl_3 apparently indicates a dehydration reaction.

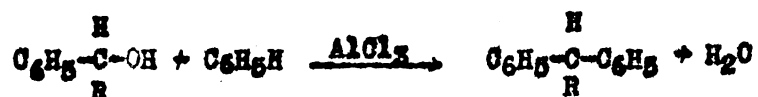
(b) The work of Huston

Using aluminum chloride the condensation of benzene and benzyl alcohol was carried out by Huston and Friedeman (J. Am. Chem. Soc., 38, 2527; 1916). The products were diphenyl methane, some p-benzyl benzene and anthracene. However, at low temperatures and in a large excess of benzene the yield of diphenyl methane was high and that of the by-product lower.

Later in 1918 the same investigators extended their work to various secondary alcohols (J. Am. Chem. Soc., 40, 785; 1918). Good yields were obtained using diphenyl carbinol but much lower yields when ethyl phenyl carbinol and methyl phenyl carbinol were used although the retarding

effect of the ethyl group appeared to be greater than that of the methyl.

The mechanism was given as:



and the AlCl_3 was assumed to be a catalyst.

Huston (Sci., 52, 206; 1920) condensed benzyl alcohol and phenol in the presence of AlCl_3 and obtained p-benzyl phenol. Later he extended his work using phenyl methyl ether, phenyl ethyl ether and benzyl chloride instead of benzyl alcohol (J. Am. Chem. Soc., 46, 2775; 1924) and from the respective yields proved that benzyl alcohol was not converted into benzyl chloride before the reaction took place.

Two years later Huston and Sager (J. A. Chem. Soc. 48, 1926) applying the AlCl_3 reaction to saturated and unsaturated aliphatic and aromatic alcohols with benzene found that, in aromatic alcoholic derivatives only those with the hydroxyl on the carbon atom adjacent to the ring react, that unsaturated aliphatic alcohols up to and including amyl do not react, and that unsaturation on the carbon atom adjacent to the alcoholic group increased the reactivity.

In the same year Huston and Bartlett obtained p-hydroxyl-1, 1 - diphenyl pentane by condensing phenol and phenyl butyl carbinol and in 1927 Huston and Strickler prepared p-hydroxy - 1, 1 - diphenyl butane in the same manner by use of propyl phenyl carbinol and phenol.

Huston, Lewis and Grotemut (J. A. Chem. Soc., 49, 1365, 1927) condensed secondary alcohols and phenol concluding that unsaturation on the alpha carbon atom increased the reactivity of the hydroxyl group.

About this time the benzylation of cresols was attempted and accomplished by means of the AlCl_3 condensation. Huston and Swartout worked on the benzylation of o-cresol, Huston and Hank on the benzylation of

m-cresol and Huston and Lewis on a similar benzylation of p-cresol. This work is contained in Masters theses as is much of the following.

In 1929 Huston and Maxfield studied the effect of varying proportions of phenol and AlCl_3 on the yields of o- and p- benzyl phenols. Yields were increased by increasing the amount of phenol but not the amount of AlCl_3 .

Huston and Eldridge (J. Am. Chem. Soc. 53, 2260, 1931) condensed 2, 6-dichlorophenol and benzyl alcohol by the AlCl_3 method isolating for the first time an ether produced along with the substituted phenol in an aluminum chloride condensation.

Closely related to the investigation to be outlined in this thesis is the work done in this laboratory by Chen (Master's Thesis, 1930) and Headley (Master's Thesis, 1929).

Chen carried out the condensation of o-chlorobenzyl chloride and phenol by both the AlCl_3 and the Claisen methods. Using AlCl_3 he prepared and identified 4 hydroxy-2'-chlorodiphenyl methane and showed that some 2 hydroxy 2' chlorodiphenyl methane was also formed. With Claisens he prepared 2 hydroxy 2' chlorodiphenyl methane and identified it. Chlorination of either 4 hydroxy 2' chlorodiphenyl methane or 2 hydroxy 2' chlorodiphenyl methane he found to take place only in the unoccupied ortho and para positions of the phenolic ring.

Headley working with p-chlorobenzyl chloride and phenol in a similar manner as described for the work of Chen drew practically the same conclusions and prepared analogous compounds with the chlorine in the 4' position. However, no ortho substitution was demonstrated to accompany para substitution in AlCl_3 condensations.

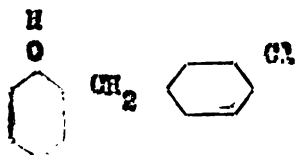
Statement of the Problem

The object of this problem is as follows:

1. To prepare, identify, and study the properties of some hydroxy derivatives of chlorodiphenyl methane.
 - a) 2 hydroxy 3° dichloro diphenyl methane
 - b) 4 hydroxy 3° dichloro diphenyl methane
 - c) 2 hydroxy 3, 5, 3' trichloro diphenyl methane
 - d) 4 hydroxy 3, 5, 3' trichloro diphenyl methane
2. To increase the yields of the above compounds.
3. To prepare their ester derivatives
4. To determine the positions chlorine will take on entering the groups



and



Source, Preparation and Purification of Materials

I. *m*-chlorobenzoyl chloride

(a) Preparation of meta-chlorotoluene

m-chlorotoluene was prepared by a method analogous to that described for ortho and para chlorotoluene page 163, volume I of Organic Syntheses - Gilman, starting with meta toluidine instead of ortho or para-toluidine. A fraction boiling at 161 to 165° was considered to be pure *m*-chlorotoluene and was used in the following preparation.

(b) Chlorination of *m*-chlorotoluene

A weighed amount of *m*-chlorotoluene usually about 100 grams was placed in a round bottomed three necked flask fitted with a reflux condenser and a tube for the introduction of chlorine. Chlorine washed with sulphuric acid was passed at the rate of a bubble per second into the liquid, a small piece of phosphorus pentachloride was added as a catalyst and a reaction temperature of 155° was maintained by use of an oil bath.

The flask plus the *m*-chlorotoluene was weighed at the beginning of the chlorination and at intervals through out the process until about 90% of the theoretical amount of chlorine had been added. Then the contents of the flask were fractionally distilled. The fraction distilling over between 214° - 217° was the *m*-chlorobenzoyl chloride used in the following condensations. Lower fractions were returned to the flask with fresh *m*-chlorotoluene and further chlorinated while higher fractions undoubtedly a dichloro-product were discarded.

II. Phenol

Ordinary phenol was used without repurification.

III. 2, 4 dichlorophenol

The technical 2, 4 dichlorophenol was twice redistilled under reduced pressure until a nearly white crystalline product was obtained. Melting point of repurified product was 44.5° to 45° C.

IV. 2, 6 dichlorophenol

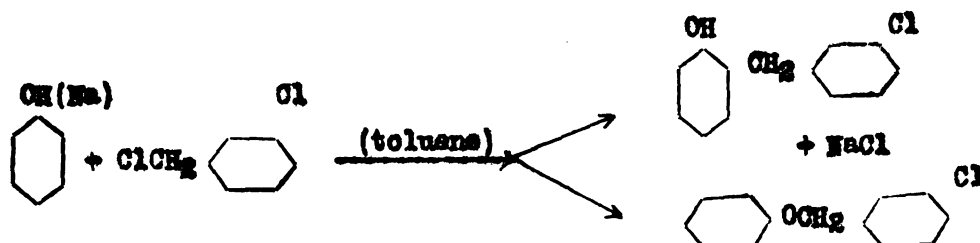
It was prepared by the method of M. Tanaka and K. Kutani (C. A., 21, 2255) but the yields were very low so variations in the method were made and many trials were run in which time of reaction, amount of sulphuric acid, amount of sodium hydroxide, and procedure were changed. However, no more than seven grams could be obtained for each mole of phenol used and so the 2, 6 dichlorophenol used in the condensations represents the combined product of many reactions. In general the procedure was as follows; 1.5 moles of phenol was treated with 220 grams of concentrated sulphuric acid in a 3 necked 5 liter flask equipped with a mechanical stirrer and a tube for the introduction of chlorine.

The mixture was heated for four hours on a boiling water bath to insure complete sulphonation and then made alkaline with 40% sodium hydroxide. The resulting solid was entirely dissolved by 500 cc of water and when the mixture had cooled the theoretical amount of washed chlorine was added by weighing the flask and reaction mixture before bubbling chlorine into it and then weighing at intervals until the proper amount of chlorine as calculated had been taken up by the reaction. The mixture was then divided into two portions and steam distilled to remove the trichlorophenol which had been formed to some extent. After it stopped coming over the mixture was evaporated to dryness, 500 cc of concentrated sulphuric acid added and steam distillation continued, the flask being heated to 200° - 210° C on

an oil bath. The 2, 6 dichlorophenol came over as an oil which solidified and was redistilled under reduced pressure. The purified product had a melting point of $67 - 67.2^{\circ} \text{C}$.

Experimental Data

I. Preparation of 2 hydroxy 3' chlorodiphenyl methane and 3 chlorobenzyl phenyl ether by Claisen condensation



One-half mole of fresh sodium was suspended in 150 - 200 cc of toluene in a three necked one liter round bottomed flask, equipped with a reflux condenser and a mercury sealed stirrer. The contents of the flask was heated until the toluene boiled and the sodium melted rising to the surface of the liquid. Then the stirrer was started and the sodium reduced to bird shot size by stirring. All flames were removed from the vicinity of the reacting mixture and one half mole of phenol in toluene was added. A vigorous reaction occurred with the evolution of hydrogen and the formation of a white mass of sodium phenolate.

The reaction was brought to completion by heating the flask on an oil bath at 100° for about four hours stirring continually. To the hot solution one half mole of m-chlorobenzyl chloride and in these condensations described a definite amount of 3 chlorobenzyl phenyl ether was added. Previous work on a Master's Thesis by L. S. Baur and work by myself had given very poor yields of 2 hydroxy 3' chlorodiphenyl methane ranging from 2.4 to 6 grams where no 3 chlorobenzyl phenyl ether was added. Following the work of Arthur Hecley "Some Bromo Derivatives of Ortho and Para Benzophenols", Master's Thesis, an equilibrium was assumed to exist between the formation of 2 hydroxy 3' chlorodiphenyl methane and 3

chloro benzyl phenyl ether and it was thought the addition of 3 chlorobenzyl phenyl ether would result in an increased yield of 2 hydroxy 3' chlorodiphenyl methane.

The condensation after the addition of the m-chloro benzyl chloride and 3 chlorobenzyl phenyl ether was carried out by heating the flask for eight to ten hours on an oil bath at a temperature of 150° - 155° C stirring continually. After the specified time the mixture was cooled, washed twice with water to remove the NaCl and distilled under atmospheric pressure to 125° C to remove the toluene and traces of water. The resulting oil was treated with 300 cc of Clasien's reagent (350 grams of KOH dissolved in 400 cc of water and made up to one liter with methyl alcohol) to form the potassium salt of the phenol derivative which is insoluble in petroleum ether. The mixture was then extracted with three 100 cc portions of petroleum ether to remove the 3 chlorobenzyl phenyl ether and the residue was made acid with concentrated HCl and ice 1 : 1 after which it was extracted with three separate 100 cc portions of diethyl ether. The solvents were distilled off in the case of both the petroleum ether and diethyl ether extracts and the oils that resulted from both extractions were fractionated under reduced pressure. The results were as follows:

First Condensation (15 grams 3 chlorobenzyl phenyl ether)

Etlyl ether extract

10.1 grams (mostly phenol)	Upto 180° C at 14/mm
11.6 grams, 2 hydroxy 3' chloro di phenyl methane	180° - 210° at 14/mm
3.2 grams, tar	Above 210° at 14/mm

Petroleum ether extract

34.7 grams (Mostly m-chloro benzyl chloride)	Up to 155° at 14/mm
15-22 grams 3 chlorobenzyl phenyl ether	155°-190° at 14/mm
1.6 grams tar	Above 190° at 14/mm

Second Condensation (20 grams 3 chlorobenzyl phenyl ether)**Ethyl ether extract**

5.3 grams mostly phenol	Up to 180°C at 14/mm
10.7 grams 2 hydroxy 3' chlorodiphenyl methane	180°-210° C at 14/mm
7.5 grams tar	Above 210°C at 14/mm

Petroleum ether extract

42.5 grams mostly m-chlorobenzyl chloride	Up to 155°C at 14/mm
20-10.3 grams 3 chlorobenzyl phenyl ether	155°-190° C at 14/mm
4.2 grams Tar	Above 190°C at 14/mm

Third Condensation (30.0 grams 3 chlorobenzyl phenyl ether)**Ethyl ether extract**

7 grams most phenol	Up to 180°C at 14/mm
22.5 grams 2 hydroxy 3' chlorodiphenyl methane	180°-210° C at 14/mm
2.3 grams tar	Above 210°C at 14/mm

Petroleum ether extract

16 grams mostly m-chlorobenzyl chloride	Up to 155°C at 14/mm
30-10.9 grams 3 chlorobenzyl phenyl ether	155°-190° C at 14/mm
2.1 grams Tar	Above 190°C at 14/mm

Fourth Condensation (47 grams 3 chlorobenzyl phenyl ether)**Ethyl ether extract**

5.4 grams mostly phenol	Up to 180°C at 14/mm
23.2 grams 2 hydroxy 3' chlorodiphenyl methane	180°-210° C at 14/mm
2.5 grams tar	Above 210 C at 14/mm

Petroleum ether extract

56.6 grams mostly m-chlorobenzyl chloride	Up to 155°C at 14/mm
47-15.2 grams 3 chlorobenzyl phenyl ether	155°-190° C at 14/mm
6.5 grams tar	Above 190°C at 14/mm

Fifth Condensation (60 grams 3 chlorobenzyl phenyl ether)**Ethyl ether extract**

5.5 grams mostly phenol	Up to 180°C at 14/mm
10.1 grams 2 hydroxy 3' chlorodiphenyl methane	180°-210° C at 14/mm
4.5 grams tar	Above 210°C at 14/mm

Petroleum ether extract

42.5 grams mostly m-chlorobenzyl chloride	Up to 155°C at 14/mm
60-15.6 grams 3 chlorobenzyl phenyl ether	155°-190° C at 14/mm
2.1 grams tar	Above 190°C at 14/mm

From these condensations assuming the average yield of 2 hydroxy 3 chloro diphenyl methane where no 3 chloro benzyl phenyl ether is added at the beginning of the reaction to be 4.2 grams, the average of the yields 2.4 to 6 grams already mentioned, it can be seen that adding 15 grams of 3 chlorobenzyl phenyl ether increases the yield of 2 hydroxy 3' chloro diphenyl methane about 3 times, 30 grams increasing it about 5 times, 47 grams about 5 times and 60 grams a little more than twice.

These facts seem to indicate that there is some sort of an equilibrium established between the substituted phenol and the corresponding ether formed as a result of the reaction and they also point to the fact that perhaps too much ether if present may interfere with the production of the substituted phenol. Further work would be necessary to demonstrate this and find the equilibrium point.

The five $180^{\circ} - 210^{\circ} \text{ C}$ fractions of 2 hydroxy 3- chloro diphenyl methane were combined and re-fractionated twice at 14 mm pressure, coming over quite constantly at $192^{\circ} - 194^{\circ} \text{ C}$ as a straw colored oil. A total yield of 42.5 grams of the purified product was obtained for the five condensations. This represents an average yield of 7.78% based on the amount of phenol used.

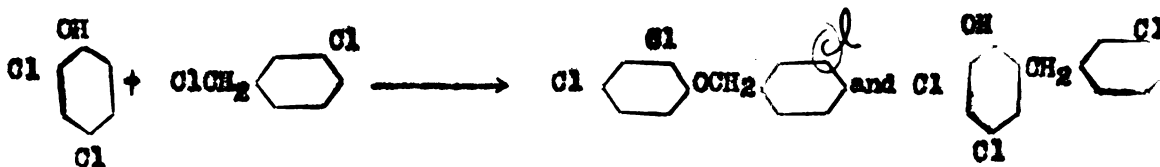
The 3 chlorobenzyl phenyl ether fractions on re-distillation came over at a constant temperature of $179^{\circ} - 180^{\circ} \text{ C}$ at 14 mm pressure yielding 59.5 grams of the purified ether. It crystallized on standing and after re-crystallization several times from alcohol formed in translucent plates having a constant melting point of $56^{\circ} - 56.4^{\circ} \text{ C}$. The average yield of ether based on the amount of phenol used was 10.89%.

II. Proof of structure of 2 hydroxy 3,5 dichloro diphenyl methane.

This proof depends upon the preparation of 3,5,3' trichloro diphenyl methane by condensing 2,4 dichloro phenol and 3 chloro benzyl chloride and checking the compound thus prepared with the 3,5,3' trichloro diphenyl methane formed by direct chlorination of 2 hydroxy 3,5 dichloro diphenyl methane.

(a) Preparation of 2 hydroxy 3,5,3' trichloro diphenyl methane and 3 chlorobenzyl 2,4 dichloro phenyl ether.

Glasien condensations similar to the ones already outlined except for the adding of excess ether were carried out with 3 chloro benzyl chloride and 2,4 dichloro phenol. The reaction was considered to take place as follows:



One-half mole quantities were used and the following results were obtained;

First Condensation

Ethyl ether extract

18.5 grams 2,4 dichlorophenol	Up to 100°C at 14/mm
12 grams 2 hydroxy 3,5 3' trichloro diphenyl methane	220°-225° at 14/mm
4 grams tar	Above 225°C at 14/mm

Petroleum ether extract

51.5 grams 3 chlorobenzyl chloride	Up to 110°C at 14/mm
2.5 grams 3 chlorobenzyl 2,4 dichloro phenyl ether	214°-220° C at 14/mm
5.6 grams tar	Above 220°C at 14/mm

Second Condensation**Ethyl Ether Extract**

26.3 grams 2, 4 dichlorophenol	Up to 100°C at 14/mm
7.2 grams 2 hydroxy 3,5 3' trichloro diphenyl methane	220°- 225°C at 14/mm
4.1 grams tar	Above 225°C at 14/mm

Petroleum ether extract

36.1 grams 3 chlorobenzyl chloride	Up to 110°C at 14/mm
2.1 grams 3 chlorobenzyl 2, 4 dichloro phenyl ether	214°-220° C at 14/mm
4.1 grams tar	Above 220°C at 14/mm

Third Condensation**Ethyl ether extract**

19.2 grams 2, 4 dichlorophenol	Up to 100°C at 14/mm
11.9 grams 2 hydroxy 3 5 3' trichloro diphenyl methane	220°- 225°C at 14/mm
2 grams tar	Above 225°C at 14/mm

Petroleum ether extract

29.8 grams 3 chlorobenzyl chloride	Up to 110°C at 14/mm
3.5 grams 3 chlorobenzyl 2, 4 dichloro phenyl ether	214°- 220°C at 14/mm
1.2 grams tar	Above 220°C at 14/mm

Both the 2 hydroxy 3 5 3' trichloro diphenyl methane and the 3 chlorobenzyl 2, 4 dichlorophenyl ether being crystalline they were repurified by that method.

From the three condensations 19.7 grams of 2 hydroxy 3 5 3' trichloro diphenyl methane were obtained as small reddish yellow needles which upon

repeated recrystallisation from petroleum ether had a constant melting point of $59.4^{\circ} \sim 60^{\circ} \text{ C}$. Based on the amount of 2, 4 dichlorophenol used the average yield was 4.56% of the theoretical.

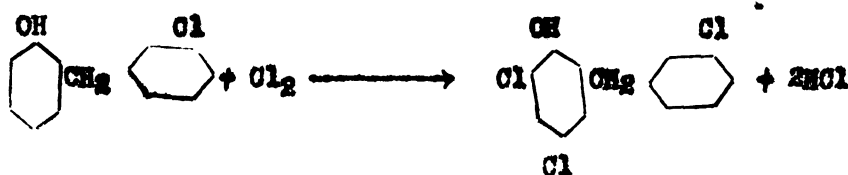
The 3 chlorobenzyl 2, 4 dichlorophenyl ether upon repeated recrystallisation from alcohol came down as long white needles with a constant melting point of $42^{\circ} \sim 42.5^{\circ} \text{ C}$. The total yield of 3 chlorobenzyl 2, 4 dichlorophenyl ether from the three condensations was 6.3 grams or an average yield of 1.46% based on the amount of phenol used.

(b) Direct chlorination of 2 hydroxy 3' chlorodiphenyl methane.

Ten grams of 2 hydroxy 3' chlorodiphenyl methane was dissolved in about 75 cc of chloroform in a 500 cc three necked round bottomed flask fitted with a mechanical stirrer and a delivery tube for the introduction of chlorine. The mixture was cooled in an ice and salt bath and gaseous chlorine added with stirring until the theoretical amount for substitution of two atoms of chlorine in the phenol had reacted as shown by the change in weight of the flask and its contents.

When this point was reached the reaction mixture was poured into a beaker and the chloroform evaporated off leaving an oil which crystallised on standing.

Since Chen, Warren and Headley had been unable to introduce chlorine in any positions but the ortho and para of the phenolic ring the reaction was considered to be;



The crystals were pressed between filter paper to remove the oil and recrystallized six times from petroleum ether. After which they had a melting point of $58.8^{\circ} - 59.2^{\circ} \text{ C}$.

(c) Comparison of substituted phenols from (a) and (b)

The 2 hydroxy 3 5 3' trichloro diphenyl methane prepared by the Claisen condensation of 2, 4 dichloro phenol and m-chloro benzyl chloride had a melting point of $59.4^{\circ} - 60^{\circ} \text{ C}$, analysed ~~36~~^{36.45}~~35~~% chlorine, yielded a benzoyl ester with melting point $62.5^{\circ} - 65^{\circ} \text{ C}$ analysis 27.17% chlorine, and crystallized in fine brownish tinged needles.

The compound prepared by the direct chlorination of the assumed 2 hydroxy 3' chloro diphenyl methane had a melting point of $58.8^{\circ} - 59.2^{\circ} \text{ C}$, analysed 36.72% chlorine, yielded a benzoyl ester with melting point $62.5^{\circ} - 65^{\circ} \text{ C}$, analysis 27.08% chlorine and crystallized in fine brownish needles.

From this data it was assumed that the compound prepared by direct chlorination of the supposed 2 hydroxy 3 chloro diphenyl methane was 2 hydroxy 3 5 3' tri chloro diphenyl methane and thus the substituted phenol from the Claisen condensation of phenol and m-chloro benzyl chloride was as expected 2 hydroxy 3' chloro diphenyl methane.

III. Proof of Structure of 3 chlorobenzyl phenyl ether.

Williamson's Syn.

A condensation of phenol and 3 chloro benzyl chloride was run in methyl alcohol in order to prove the structure of 3 chloro benzyl phenyl ether formed by the Claisen condensation (in toluene) of phenol and 3 chloro benzyl chloride.

To 75 cc of methyl alcohol in a 500 cc three necked flask fitted with a stirrer and condenser was added 2.76 grams of sodium. After the reaction had subsided 11.6 grams of phenol was added, the stirrer started and after eight hours of heating to 100° to 110° C on an oil bath with continual stirring the mixture was poured into a beaker and the alcohol evaporated off on a steam bath. Then the residual oil was washed with water to remove the NaCl formed and then extracted with 200 cc of ethyl ether in 50 cc portions. The ether was driven off and the remaining oil was vacuum distilled. 14 grams of 3 chloro benzyl phenyl ether was obtained coming over in the fraction 165° - 180° at 14/mm.

This fraction solidified and after repeated crystallisation melted at 36.2° - 36.8° C a melting point which corresponded closely to 36° - 36.4° C given by the supposed 3 chloro benzyl ether obtained in the Claisen (toluene) condensation of phenol and m-chloro benzyl chloride. Chlorine analyses of the two compounds checked very closely.

1. 3 chloro benzyl phenyl ether (Claisen) Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated .
1	.2176	9.87	16.08	16.23
2	.2060	9.88	<u>16.21</u>	
			16.20	

2. 3 chlore benzyl phenyl ether (Williamson's Syn)

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2594	10.97	16.25	16.23
2	.2698	12.3	$\frac{16.16}{16.21}$	

IV Proof of Structure of 3 chlore benzyl 2, 4 dichlore phenyl ether

A condensation in methyl alcohol (Williamson's Syn.) similar to the one described for the preparation of 3 chlore benzyl phenyl ether (above) was made using 2, 4 dichlore phenol and m-chlore benzyl chloride. A yield of 13.2 grams was obtained which upon recrystallization from alcohol melted at $42^{\circ} - 42.5^{\circ} \text{C}$ a melting point corresponding to that of 3 chlore benzyl 2, 4 dichlore phenyl ether obtained in the Clasien condensation of 2, 4 dichlore phenol and m-chlore benzyl chloride. Chlorine analyses of the two compounds are as follows;

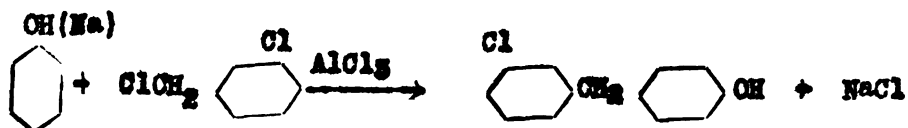
1. 3 chlore benzyl 2, 4 dichlore phenyl ether (Clasien) Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2656	27.86	37.2	37.01
2	.2640	27.69	$\frac{37.19}{37.2}$	
		Average		

2. 3 chlore benzyl 2, 4 dichlore phenyl ether (Williamson's Syn.) Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2310	24.01	36.86	37.01
2	.2120	22.1	$\frac{36.96}{36.91}$	

V Preparation of 4 hydroxy 3' chlore diphenyl methane



One and one half moles of phenol were suspended in 400 cc of petroleum ether in a condensation cylinder fitted with a mechanical stirrer and immersed in a water bath used to regulate the temperature of the reaction. To this solution of phenol one-half mole of 3 chloro benzyl chloride was added. The stirrer was started and when the desired temperature had been obtained by use of the water bath one-fourth mole of AlCl_3 was added with continual stirring over a period of one and a half to two hours. During the addition of AlCl_3 large amounts of HCl were evolved. The mixture was then stirred for two hours more and allowed to stand over night.

It was then decomposed by pouring it into ice and hydrochloric acid 1 : 1 and extracted three times with 75 cc portions of ethyl ether. After distilling off the ether the remaining oil was treated with 500 cc of Glasien's reagent and extracted three times with 75 cc portions of petroleum ether. The residue from this extraction was then neutralised with concentrated hydrochloric and ice 1 : 1 and extracted with diethyl ether until all the oil was removed leaving a clear solution.

The solvents were driven off from both the petroleum ether and the diethyl ether extracts and the remaining oils from each solvent were fractionally distilled.

Four condensations were carried out at different temperatures to determine the effect of temperature on the yield of 4 hydroxy 3' chlore diphenyl methane. The results were as follows.

First Condensation 8° - 10° C**Ethyl ether extract**

115.2 grams 2, 4 dichlorophenol	Up to 110°C at 14/mm
16 grams 4 hydroxy 3'chlorodiphenyl methane	199° -215°C at 14/mm
4.2 grams tar	Above 215°C at 14/mm

Second Condensation 10° - 12° C**Ethyl ether extract**

89.7 grams 2, 4 dichlorophenol	Up to 110°C at 14/mm
27 grams 4 hydroxy 3'chlorodiphenyl methane	199° -215°C at 14/mm
5.1 grams tar	Above 215°C at 14/mm

Third Condensation 15° - 18° C**Ethyl ether extract**

95.3 grams 2, 4 dichlorophenol	Up to 110°C at 14/mm
20 grams 4 hydroxy 3'chlorodiphenyl methane	199° -215°C at 14/mm
1.2 grams tar	Above 215°C at 14/mm

Fourth Condensation 22° - 24° C**Ethyl ether extract**

76 grams 2, 4 dichlorophenol	Up to 110°C at 14/mm
55.3 grams 4 hydroxy 3'chlorodiphenyl methane	199° - 215°C at 14/mm
6.2 grams tar	Above 215°C at 14/mm

The petroleum ether extracts did not yield any compound except unreacted 3 chloro benzyl chloride. The amounts recovered were, first

condensation 49.2 grams, second 54 grams, third 47.6 grams, and fourth 41.2 grams.

From previous work in this laboratory by Philip Stanley Chen on the aluminum chloride condensation of phenol with 2-chlorobenzyl chloride both the ortho and the para substituted phenols were formed. Arthur House Keeley reports also using analogous bromine compounds to the chlorine compounds used in this work that there is evidence of ortho substitution.

Following these ideas the fractions of the ethyl ether extracts between 110° and 199° C at 14/mm were combined and refractionated with the object of obtaining 2-hydroxy 3'-chlorodiphenyl methane boiling at 192°-194° C at 14/mm. Most of the oil came over between 194°-199° C at 14/mm showing it to be impure 4-hydroxy 3'-chlorodiphenyl methane. Its ester (benzoyl) melted at 55° C the melting point of the benzoyl ester prepared by use of pure 4-hydroxy 3'-chlorodiphenyl methane. Not enough substance was obtained between 192° - 194° C to prepare an ester and so no definite proof of ortho substitution was established although it might have occurred to a slight extent and was not detected.

The four 199° - 210° C at 14/mm fractions from the above condensations were combined and refractionated twice at 14/mm pressure, coming over quite constantly at 200° - 202° C as a straw colored oil. A total yield of 69.4 grams of the purified 4-hydroxy 3'-chlorodiphenyl methane was obtained. This represents an average yield of 15.84% based on the amount of 2-chlorobenzyl chloride used.

From the data it appears that a temperature of 22° - 24° C is preferable to lower temperatures for the production of 4-hydroxy 3'-chloro

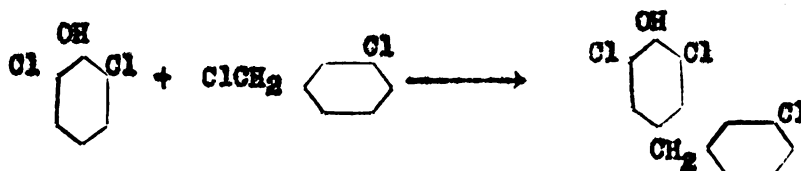
diphenyl methane. What would be the effect of even a higher temperature was not clearly determined, but from an earlier condensation at 25°-25°C the fraction 199°- 205°C at 14/mm yielded 6.3 grams and the fraction 205° - 250°C at 14/mm yielded 2.9 grams.

VI. Proof of Structure of 4 hydroxy 3, 5 chloro diphenyl methane

The method adapted for the proof was similar to that employed for the proof of the compound formed in the Claisen condensation of phenol and 3 chloro benzyl chloride. It consisted of preparing 4 hydroxy 3, 5 3' trichloro diphenyl methane by an AlCl_3 condensation of 2, 6 dichloro phenol and 3 chloro benzyl chloride and checking this substituted phenol with the compound produced by the direct chlorination of the supposed 4 hydroxy 3' chloro diphenyl methane.

(a) Preparation of 4 hydroxy 3, 5 3' trichloro diphenyl methane.

Two AlCl_3 condensations as already described in this thesis under the preparation of 2 hydroxy 3, 5 3' trichloro diphenyl methane were run using 20 grams of 2, 6 dichloro phenol, 20 grams of m-chloro benzyl chloride and grams of anhydrous AlCl_3 . The temperature of the first condensation was kept at $8^\circ - 10^\circ \text{C}$ and the second at $15^\circ - 18^\circ \text{C}$. A reaction was to take place according to the following equation.



However none of the 4 hydroxy 3, 5 3' trichloro diphenyl methane was formed but the original 2, 6 dichloro phenol and the 3 chloro benzyl chloride were returned almost quantitatively. Two more condensations were carried out at $25^\circ - 25^\circ \text{C}$; the first using 20 grams and the second 10 grams of 2, 6 dichloro phenol with the corresponding amounts of 3 chloro benzyl chloride and anhydrous AlCl_3 . The results were as follows;

First Condensation**Ethyl ether extract**

14.5 grams 2, 6 dichlorophenol	Up to 120°C at 14/mm
7.3 grams 4 hydroxy 3 5 3'trichlorodiphenyl methane	190° -220°C at 14/mm
13.2 grams tar	Above 220°C at 14/mm

Petroleum ether extract

No product isolated

Second Condensation**Ethyl ether extract**

4.1 grams 2, 6 dichlorophenol	Up to 120°C at 14/mm
2.8 grams 4 hydroxy 3 5 3'trichlorodiphenyl methane	190° -220°C at 14/mm
9.1 grams tar	Above 220°C at 14/mm

Petroleum ether extract

No product isolated

The fraction of the ethyl ether extract coming over at 190° - 220° C at 14/mm crystallized immediately. It formed white needle like crystals from petroleum ether and had after several recrystallizations a constant melting point of 79° - 80° C. The total yield of the purified product was 6.1 grams representing a 11.52% yield based on the amount of 2, 6 dichloro phenol used.

None of the corresponding ether was isolated in these condensations.

(b) Direct chlorination of 4 hydroxy 3' chlore diphenyl methane.

This chlorination was carried out as described for the chlorination of 2 hydroxy 3' chlore diphenyl methane using 10 grams of 4 hydroxy 3' chlore diphenyl methane. The reaction was supposed to take place according to the following equation.



When the chloroform was evaporated a substance crystallized out which was assumed to be 4 hydroxy 3 5 3' trichlore diphenyl methane. After pressing out the oil from the crystals with filter paper and recrystallizing some seven times from petroleum ether a melting point of $78.5^\circ - 79.2^\circ \text{ C}$ was obtained.

(c) Comparison of 4 hydroxy 3 5 3' trichlore diphenyl methane as prepared in (a) and in (b)

The 4 hydroxy 3 5 3' trichlore diphenyl methane as prepared by the AlCl_3 condensation of 2, 6 dichlore phenol and 3 chlore benzyl chloride had a melting point $79^\circ - 80^\circ \text{ C}$, analysed 56.95% chlorine, yielded a benzoyl ester with melting point $130^\circ - 130.4^\circ \text{ C}$, analysis 27.46% chlorine and crystallized in fine white needles from petroleum ether.

The compound prepared by the direct chlorination of 4 hydroxy 3'chlore diphenyl methane had a melting point $78.5^\circ - 79.5^\circ \text{ C}$, analysed 57.34% chlorine, yielded a benzoyl ester with melting point $129^\circ - 129.5^\circ \text{ C}$ analysis 27.28% chlorine and crystallized in fine white needles.

The above data apparently offered proof that the compound prepared by the direct chlorination of the assumed 4 hydroxy 3' chlore diphenyl was 4 hydroxy 3 5 3' trichlore diphenyl methane and hence the substituted phenol from the $AlCl_3$ condensation of phenol and 3 chlore benzyl chloride was the expected 4 hydroxy 3' chlore diphenyl methane.

V. Esterification

The benzoyl esters of the substituted phenols were prepared by the method of Einhorn and Holland (A., 301, 95; 1898) (Method of Organic Chem. Porter, Stewart, and Branch; page 181 - 182) as follows: 2 grams of the substance was dissolved in 5 grams of dry pyridine and a 10% excess of the calculated amount of benzoyl chloride was added. After standing over night an equal volume of water was slowly added and the mixture shaken until no odor of benzoyl chloride could be detected. The mixture was then poured into cold dilute sulphuric acid and extracted with ether. After being washed with cold dilute sodium carbonate the ether was distilled off and the ester allowed to crystallize. Recrystallization from alcohol was then resorted to until a constant melting point was obtained.

For the preparation of the para tolyl sulfonyl and the benzene sulfonyl esters, para tolyl sulfonyl chloride and benzene sulfonyl chloride were substituted respectively in place of the benzoyl chloride in the above procedure.

The benzoyl esters of 2 hydroxy 3'chloro diphenyl methane, 4 hydroxy 3' chloro diphenyl methane, 2 hydroxy 3 5 3' trichloro diphenyl methane and 4 hydroxy 3 5 3' trichloro diphenyl methane; the benzene sulfonyl ester of 2 hydroxy 3 5 3' trichloro diphenyl methane, and the para tolyl sulfonyl esters of 2 hydroxy 3 5 3' trichloro diphenyl methane and 4 hydroxy 3 5 3' tri chloro diphenyl methane were prepared.

The benzene sulfonyl esters and the para tolyl sulfonyl esters of 2 hydroxy 3' chloro and 4 hydroxy 3' chloro diphenyl methane failed to crystallize.

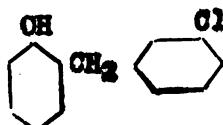
For further information regarding the melting points, chlorine analysis, crystalline structures and formulae of the above esters refer to the General Table of Compounds under the heading of Esters.

VI. General Table of Compounds

Phenols

1. 2 hydroxy 3' chloro diphenyl methane

Structural formula



Crystalline form; Straw colored liquid

Boiling point; 192° - 194° C at 14/mm

Yield; 7.78%

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2152	9.9	16.51	16.23
2	.2276	10.55	16.44	16.23
Average			16.58	

2. 4 hydroxy 3' chloro diphenyl methane

Structural formula



Crystalline form; Straw colored liquid

Boiling point; 200° - 202° C at 14/mm

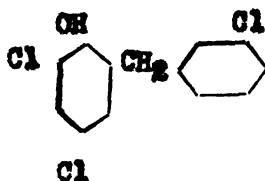
Yield; 15.84%

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2474	11.17	16.01	16.23
2	.2140	9.65	15.99	
Average			16.00	

3. 2 hydroxy 3, 5, 5' trichloro diphenyl methane (from Claisen condensation)

Structural formula



Crystalline form; Small needles from petroleum ether

Melting point : $59.4^{\circ} - 60^{\circ} \text{C}$

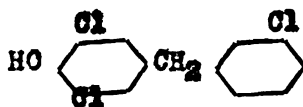
Yield : 4.56%

Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.1999	20.85	36.99	37.01
2	.2339	24.16	<u>36.89</u>	
Average			36.89	

4. 4 hydroxy 3, 5, 5' trichloro diphenyl methane

Structural formula



Crystalline form; White small needles from petroleum ether

Melting point : $79^{\circ} - 80^{\circ} \text{C}$

Yield : 11.52%

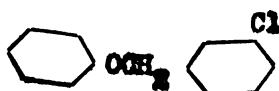
Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.2234	23.29	36.98	37.01
2	.1986	20.67	<u>36.91</u>	
Average			36.95	

Ethers

1. 3 chloro benzyl phenyl ether

Structural formula



Crystalline form;

Melting point : $36^{\circ} - 36.4^{\circ} \text{ C}$

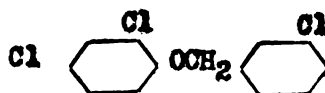
Yield : 10.89%

Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.2176	9.87	16.08	16.23
2	.2080	9.51	<u>16.21</u>	
Average			16.20	

2. 3 chloro benzyl 2, 4 dichloro phenyl ether

Structural formula



Crystalline form;

Melting point : $42^{\circ} - 42.5^{\circ} \text{ C}$

Yield : 1.46%

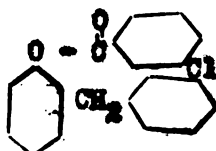
Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.2656	27.86	57.2	57.01
2	.2640	27.69	<u>57.19</u>	
Average			57.2	

Esters

1. Benzoyl ester of 2 hydroxy 3' chloro diphenyl methane

Structural formula



Crystalline form: white flakes from alcohol

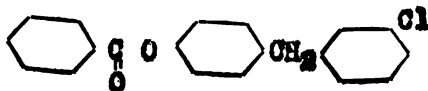
Melting point : $67^{\circ} - 67.4^{\circ} \text{C}$

Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.2234	7	11.17	10.99
2	.2046	6.4	<u>11.09</u>	
Average			11.13	

2. Benzoyl ester of 4 hydroxy 3' chloro diphenyl methane

Structural formula



Crystalline form : Fine white needles from alcohol

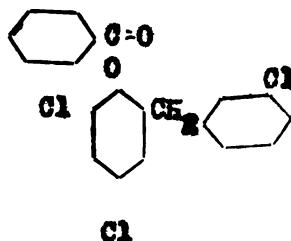
Melting point : $57.5^{\circ} - 58^{\circ} \text{C}$

Analysis

Sample	Weight	cc .1 N AgNO_3	% chlorine Found	% chlorine Calculated
1	.2018	6.28	11.03	10.99
2	.2086	6.41	<u>10.89</u>	
Average			10.96	

3. Benzoyl ester of 2 hydroxy 3, 5, 3' trichlore diphenyl methane

Structural formula



Crystalline form: Long white needles from alcohol

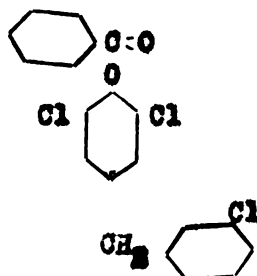
Melting point : 63.5° - 64° C

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2036	15.58	27.15	27.17
2	.1998	15.5	<u>27.16</u>	
Average			27.14	

4. Benzoyl ester of 4 hydroxy 3, 5, 3' trichlore diphenyl methane

Structural formula



Crystalline form: white small flakes from alcohol

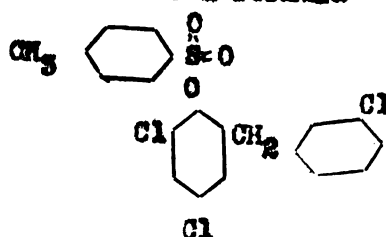
Melting point: 130° - 130.4° C

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2064	15.94	27.51	27.17
2	.2030	15.75	<u>27.38</u>	
Average			27.46	

5. Para tolyl sulfonyl ester of 2 hydroxy 3, 5, 3' trichloro diphenyl methane

Structural formula



Crystalline form: Broad white blunt needles from alcohol

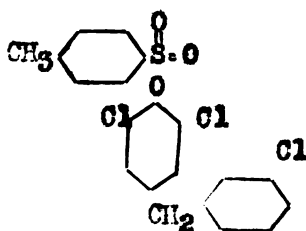
Melting point : 125.4° - 126° C

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2032	13.71	23.92	24.09
2	.2056	13.97	<u>24.09</u>	
Average			24.01	

6. Para tolyl sulfonyl ester of 4 hydroxy 3, 5, 3' trichloro diphenyl methane

Structural formula



Crystalline form: Long white needles from alcohol

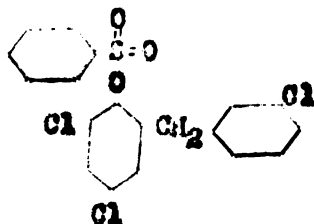
Melting point : 104.5° - 105° C

Analysis

Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2174	14.71	24.01	24.09
2	.2418	16.39	<u>24.00</u>	
Average			24.01	

7. Benzene sulfonyl ester of 2 hydroxy 3, 5, 5' trichloro diphenyl methane

Structural formula



Crystalline form: white translucent rectilinear crystals from alcohol

Melting point : 114.5° - 115° C

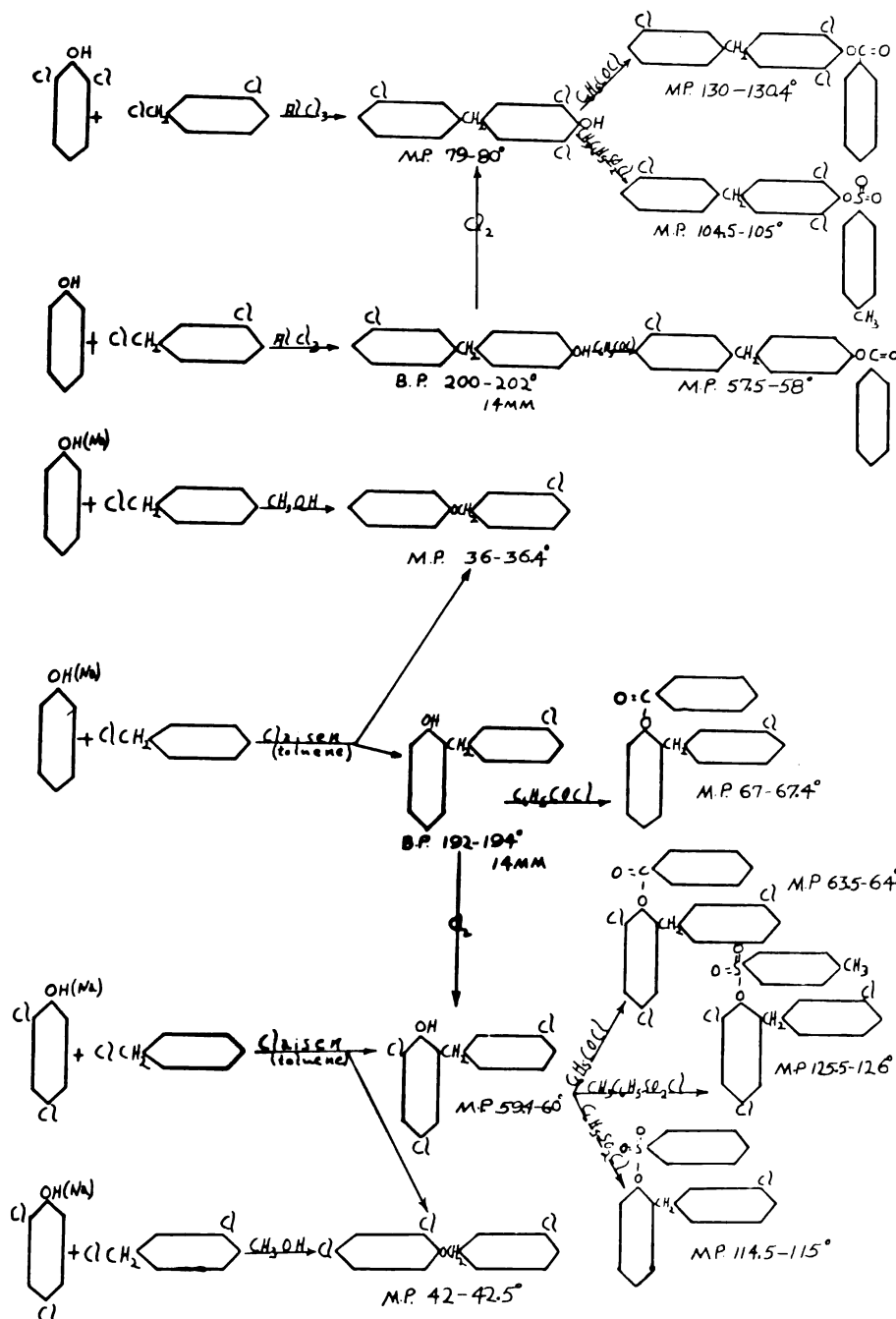
Analysis

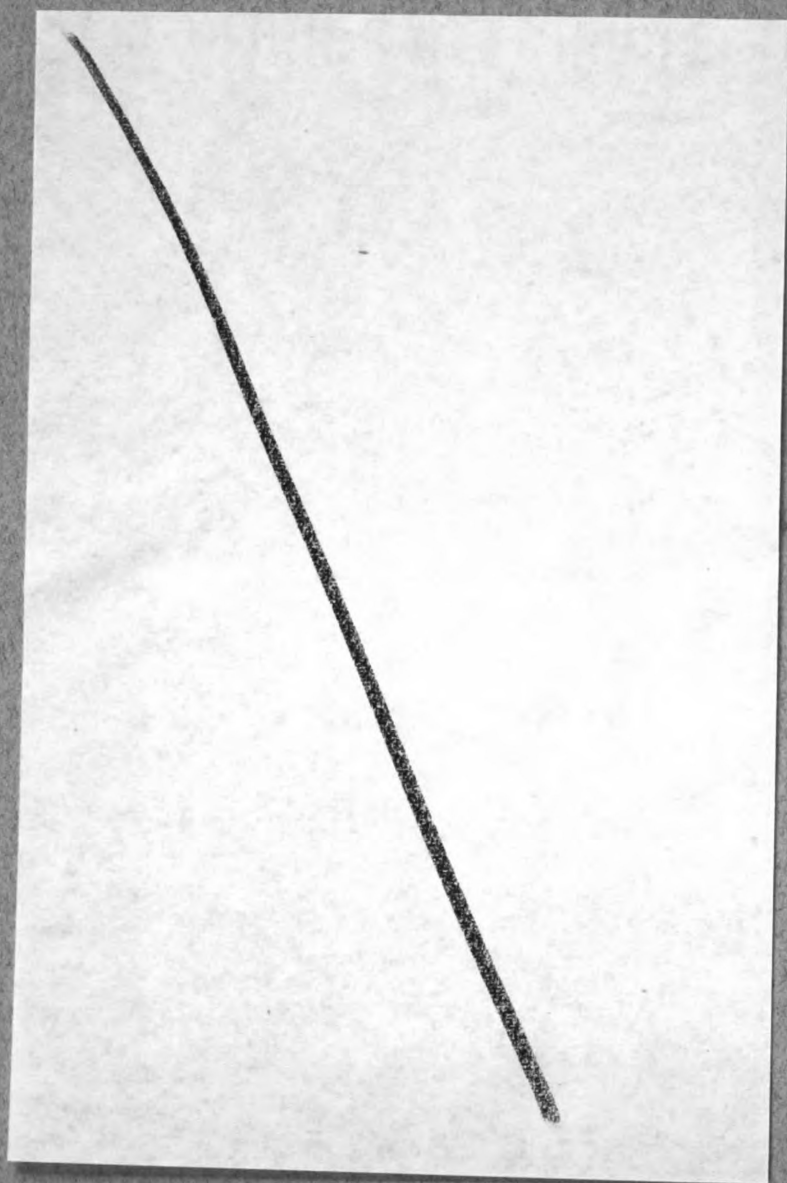
Sample	Weight	cc .1 N AgNO ₃	% chlorine Found	% chlorine Calculated
1	.2100	14.71	24.84	24.88
2	.2078	14.57	24.86	
Average			24.85	

VII. Summary

1. 2 hydroxy 3' chloro diphenyl methane and 4 hydroxy 3' chloro diphenyl methane and derivatives have been prepared and identified.
2. No evidence of ortho substitution in the aluminum chloride condensation of 3 chloro benzyl chloride and phenol was obtained.
3. Temperatures above 20° C were found to favor the formation of the phenol derivative by the aluminum chloride method.
4. Chlorine was found to enter the unoccupied ortho and para positions of the phenolic ring of 2 hydroxy 3' chloro diphenyl methane and 4 hydroxy 3' chloro diphenyl methane.
5. No ethers were isolated from any of the aluminum chloride condensations.
6. A relationship was demonstrated to exist between the formation of 2 hydroxy 3' chloro diphenyl methane and the amount of the 3 chloro benzyl phenyl ether present in the reaction mixture.

SCHEME OF CONDENSATION





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