ALUMINUM CHLORIDE-CATALYZED REACTIONS OF CHLORETONE WITH A VARIETY OF PHENOLS

by

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INTRODUCTION

The aluminum chloride-catalyzed reactions of 1,1,1-trichloro-2-methyl propanol-2, more commonly called chloretone, with benzene, toluene, and xylenes were first studied by Willgerodt and Geniesser (10). As a result of their investigation they believed that chloretone behaved like chloroform and formed various substituted aryl chloretones.

Investigations in this laboratory by Stoloff (8) indicated that when chlorobenzene and phenol were the aromatic reactants analogous reactions did not take place. When phenol was used, the primary product formed was assumed to be the 1,1,1-trichloro-tert-butyl phenyl ether. However, when this ether was treated with aluminum chloride, another compound was formed. The latter compound also was synthesized by a reaction between chloretone and phenol. The structure proposed for this product was that of a substituted indane. Further work in this laboratory showed that the 1,1,1-trichloro-tert-butyl phenyl ether was really a co-distilled mixture of chloretone and phenol.

In another investigation in this laboratory, Madison (3) obtained a product by reacting chloretone and phenol in the presence of aluminum chloride. This product was similar to that reported by Stoloff. These two products differed, however, in some of their physical and chemical characteristics.

The effects of various reagents upon chloretone have been studied by other workers. McElvain and Stevens (4) and also

Pledger (6) have shown that chloretone is dehydrated by thionyl chloride to give 1,1,1-trichloro-2-methyl propene-2. Under suitable conditions an allylic rearrangement occurs to give 1,1,3-trichloro-2-methyl propene-1. Jacob (2) has shown that when chloretone is heated with phosphoric acid anhydride 1,1,3-trichloro-2-methyl propene-1 is obtained in a 57 percent yield and a 15 percent yield of 1,1,1-trichloro-2-methyl propene-2 and some alpha-chloroisobutyric acid were formed.

Pledger (7), a co-worker of the writer, has shown that under the influence of aluminum chloride and in the presence of chlorobenzene, two products were formed from chloretone monohydrate. The lower boiling product was alpha-chloroisobutyric acid while the higher boiling product was 3-(p-chlorophenyl)-1,1-dichloro-2-methyl propene-1. This latter product arose from the condensation of 1,1,3-trichloro-2-methyl propene-1 and chlorobenzene. The aluminum chloride-catalyzed reactions of chloretone are therefore considerably more complex and fundamentally different from those of chloroform.

The scope of the present work included (a) the successful preparations and identifications of condensation products of chloretone and a variety of phenols, (b) purification of these products to a state of analytical purity, and (c) especially the synthesizing of new condensation products of chlorophenols since many other derivatives of chlorophenols exhibit insecticidal properties (1). Preliminary toxicity tests showed that the condensation product of phenol and chloretone possessed insecti-

cidal properties.

The insecticidal properties of the chlorophenols and their derivatives, suggests a particular interest in the condensation of chloretone and pentachlorophenol. Pentachlorophenol is quite toxic, and some of its derivatives exhibit marked insecticidal properties (1).

EXPERIMENTAL

Preparation of Starting Materials

Chloretone (Trichlorobutanol) was purchased from the Givaudon-Delawanna Co., Inc. It was found to melt at 80.0-81.5° C. This showed that it contained one mole equivalent of water of hydration. The hydrated chloretone was distilled and the portion boiling at 168.0-169.5° C. (m.p. 96.0-97.0° C.) was collected as the anhydrous chloretone.

Phenol was purchased from the Mallinckrodt Chemical Co. as analytical reagent grade. A sample was also obtained from Dow Chemical Co. as Ordinance #73749M.

p-Chlorophenol was obtained as a sample from Dow Chemical Co. The melting point of the sample was 41.0-43.0° C.

2,4-Dichlorophenol was obtained as a sample from Dow Chemical Co. The melting point of the sample was 43.5-45.0° C.

2,4,6-Trichlorophenol was purchased from the Eastman Kodak Co. code #1469. The material was white lable grade and had a melting point of 67.5-69.0° C.

o-Nitrophenol was purchased from the Eastman Kodak Co. code #191. The material was white lable grade and had a melting point of 44.0-45.5° C.

Pentachlorophenol was recovered from Dowicide 7 furnished by the Dow Chemical Co. A total of 566 gm of Dowicide 7 was dissolved in 1500 ml of hot chlorobenzene and 100 gm of activated charcoal was added. The solution was filtered, using a steam-heated hot-water funnel. The filtrate was stirred and allowed to cool. The crystals which formed were collected on a filter and washed with cold chlorobenzene. The crystals, dried over calcium chloride, melted at 189.0-191.5° C.

Aluminum Chloride was purchased from the General Chemical Co. (Baker and Adams), and was sublimed anhydrous material.

Anhydrous Magnesium Sulfate was purchased from the General Chemical Co. (Baker and Adams), and was dried powder.

Ether was commercial U.S.P.

Apparatus and General Procedure

Apparatus for Reactions. The apparatus consisted of a three-neck, round-bottom flask equipped with a mercury-sealed, motor-driven stirrer; a water condenser vented through a suitable hydrogen chloride absorber employing water; and an Erlenmeyer flask containing the catalyst and attached to a side arm by a large rubber tube. The reaction vessel was heated by an oil bath while the temperature of the reaction mixture was determined by a thermometer suspended through the condenser.

Apparatus for Ether Removal. The apparatus consisted of a suitable size round-bottom flask connected to a water cooled condenser leading to an ice-cooled receiver. The entire apparatus was made of glass with standard-taper connections to permit the removal of the last traces of ether at reduced pressure.

Apparatus for Fractionation. The apparatus consisted of a suitable size three-neck, round-bottom flask connected to a glass-helices packed column (120 mm in length and 20 mm in diameter) provided with an electrical heating element which could be used for adjusting the temperature of the column. To this column was attached a total-reflux variable-take-off still head and a suitable fraction cutter. A Hi-Vac oil pump with a McLeod gauge was used in all fractionations. An oil bath was used as a source of heat.

General Procedure. The desired amount of the phenol was placed in the reaction flask in the molten or solid state. To this was added the proper amount of anhydrous chloretone in the molten state. The mixture was stirred and heated to the desired temperature. The catalyst was placed in an Erlenmeyer flask attached to the reaction vessel. When the desired temperature was reached, the slow addition of the catalyst was started. The rate of addition was dependent upon the amount of hydrogen chloride gas evolved and the ability of the condenser and the gas absorber to handle the evolved gas. After the addition of the catalyst was completed, the reaction was allowed to continue until the amount of the hydrogen chloride gas evolved had decreased con-

siderably. The reaction was stopped by mixing the reaction mixture with crushed ice and concentrated hydrochloric acid. At this point the reaction was allowed to stand in some cases, or treated further directly. The organic materials were extracted from the water mixture by treatment with ether. The emulsion which usually formed at this point was broken by adding excess concentrated hydrochloric acid. This ether solution was then dried over anhydrous magnesium sulfate after being washed with water. The magnesium sulfate was removed by filtration and the dried ether solution placed in the apparatus for the removal of ether. The ether was distilled from the residual organic products. The final traces of ether were removed under reduced pressure maintained by a water aspirator. The residual organic liquid was placed in the apparatus previously described and separated into component fractions by vacuum fractionation.

The Aluminum Chloride-Catalyzed Reaction of Phenol and Anhydrous Chloretone

A mixture of 101 gm (0.6 mole) of anhydrous chloretone and 57 gm (0.6 mole) of phenol was heated in the reaction flask to 68° C. A total of 79 gm (0.59 mole) of aluminum chloride was added to the stirred reaction mixture over a period of one hour while the reaction temperature was 68-72° C. The reaction was allowed to continue at this temperature for two additional hours.

The reaction was stopped by pouring the reactants over a mixture of 600 gm of crushed ice and 60 ml of concentrated hydrochloric acid. A red water-insoluble oily layer was formed below

the acidic water solution. The organic material was extracted from the water mixture with two 200 ml and two 100 ml portions of ether. The combined ether solution was then washed with three 75 ml portions of water and dried over 30 gm of anhydrous magnesium sulfate for 18 hours. The magnesium sulfate was removed by filtration and the ether was removed by distillation. The residual oil separated by distillation with a Claisen flask and a water aspirator, into gross fractions as listed in Table 1.

Table 1. Preliminary fractionation of products resulting from the aluminum chloride-catalyzed reaction of phenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt. in grams	Identity
1	Up to 98	58-70	2.88	Ether, forerun of fraction 2
2	99-133	48	34.89	Phenol, chloretone, and product II[a]
3	137-147	49-50	40.22	Crude product IV[b]
4	Above 147		27.22	Unidentified tars

a - Product II is alpha-chloroisobutyric acid.
b - Product IV is phenyl alpha-chloroisobutyrate. The yield of IV was 34 percent.

The crude product IV (fraction 3, Table 1) was refractionated using the fractionation apparatus described on page 5 at 7 mm of mercury pressure. The semi-pure product boiled at 93-97° C. at this pressure and amounted to 24.13 gm (20 percent yield). Since this corresponded roughly with the boiling point reported by

Stoloff (Table 9) at a lower pressure, the material was again fractionated using a lower pressure. The fractions collected are listed in Table 2.

Table 2. The fractionation of the semi-pure product IV obtained from the aluminum chloride-catalyzed reaction of phenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt.in grams	Refractive index(20°C.)	Identity
1	67-69	0.3	4.27	--	Product IV[a]
2	67-68	0.3	5.04	1.5023	Pure Product IV
3	66-71	0.3	4.44	1.5023	Pure Product IV
4	76-85	0.5	4.91	1.5028	Pure Product IV
5	72-76	0.3	4.62	--	Product IV

a - Product IV is phenyl alpha-chloroisobutyrate.

The Aluminum Chloride-Catalyzed Reaction of Phenol and Chloretone Monohydrate

A mixture of 141 gm (1.5 moles) of phenol and 266 gm (1.37 moles) of chloretone monohydrate was placed in the reaction flask and heated to 70° C. Addition of 195 gm (1.46 moles) of catalyst was done in one and one-half hours while the stirred reaction mixture was held at 67-73° C. The reaction was allowed to continue at this temperature an additional three hours.

The dark viscous mass remaining was decomposed by pouring it over a mixture of 1300 gm of crushed ice and 130 ml of concentrated hydrochloric acid. The mixture was heated to 80° C. to

complete the hydrolysis of the hard mass of aluminum chloride complex which formed. The organic material was extracted from the water mixture by six 100 ml portions of ether. The combined ether solution was treated as in the previous experiment.

The forerun of product II, phenol and chloretone boiled at 94-131° C. (42 mm) and amounted to 73.7 gm. The crude product IV boiled at 129°-144° C. (40 mm) and amounted to 73.0 gm (27 percent) while 95.6 gm of unidentified tars were obtained. The crude product IV was separated into its component parts as listed in Table 3 by fractional distillation.

Table 3. Fractionation of the crude product IV obtained from the aluminum chloride-catalyzed reaction of phenol and chloretone monohydrate.

Fraction	Distilling temperature	Pressure in mm Hg	Wt.in grams	Refractive index(20°C.)	Identity
1	57.5-75.0	0.7	8.22	1.4993	Forerun
2	72.0-75.0	0.5	5.91	1.4980	Semipure Product IV[a]
3[b]	72.5-74.0	0.4	5.92	1.5021	Pure Product IV
4	71.0-73.0	0.5	9.07	1.5023	Pure Product IV
5	72.0-75.0	0.5	8.13	1.5020	Pure Product IV
6	73.0-78.0	0.6	9.07	1.5025	Pure Product IV
7	75.0-76.0	0.5	10.48	1.5039	Pure Product IV
8	73.0-79.0	0.5	6.56	1.5003	Semipure Product IV
9	90.0-100.0	0.5	5.91	1.5374	Crude Product IV
10			1.70		Residue

a - Product IV is phenyl alpha-chloroisobutyrate.
b - Fractions 3 through 6 combined with fractions 2 and 8, Table 2, had a density of 1.125 and a micro boiling point of 231.0-231.5° C. The other physical properties listed in Table 10 were determined using an analytically purified sample. Yield of total practical grade IV was 25 percent, yield of pure IV was 13 percent.

The Aluminum Chloride-Catalyzed Reaction of p-Chlorophenol and Anhydrous Chloretone

A mixture of 193 gm (1.5 moles) of p-chlorophenol and 266 gm (1.5 moles) of anhydrous chloretone was heated to 70° C. The addition of 200 gm (1.5 moles) of the catalyst was done in one and one-half hours. The reaction was allowed to continue for an additional one and one-half hours at 65-70° C.

The reaction was stopped by pouring the reaction mixture over 1000 gm of crushed ice and 100 ml of concentrated hydrochloric acid. The organic materials were extracted from the water mixture by successive portions of ether totalling 800 ml. It was necessary to add excess concentrated hydrochloric acid to break the emulsion which formed. The combined ether extractions were treated as before. The liquid was separated into the fractions listed in Table 4 by fractional distillation.

The Aluminum Chloride-Catalyzed Reaction of 2,4-Dichlorophenol and Anhydrous Chloretone

A mixture of 81.5 gm (0.5 mole) of 2,4-dichlorophenol and 88.75 gm (0.5 mole) of anhydrous chloretone was heated in the reaction flask to 70° C. The addition of the 66.8 gm (0.5 mole) of aluminum chloride catalyst required one-third of an hour. The stirred reaction was allowed to continue an additional one and one-sixth hours at 68-72° C.

Table 4. Fractionation of the products obtained from the aluminum chloride-catalyzed reaction of p-chlorophenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt. in grams	Refractive index (25°C.)	Identity
1	52.5- 60.0	0.5-0.6	34.7	1.4865	Crude Product II[a]
2	61.0- 72.0	0.3-0.7	42.0	1.5507	Crude p-chlorophenol
3	72.0- 85.0	0.3-0.4	21.0	1.5300	Intermediate
4-10	85.0- 87.0	0.3-0.4	162.7	1.5150-1.5130[b]	Pure Product V[c]
11	105.0-121.0	0.4-0.8	6.4	--	Crude Product V
12			55.4	--	Unidentified tars

a - Product II is alpha-chloroisobutyric acid.
b - The refractive indices of the 7 fractions were 1.5150, 1.5137, 1.5136, 1.5132, 1.5132, 1.5130, and 1.5130 at 25° C.
c - Product V is p-chlorophenyl alpha-chloroisobutyrate. The yield of pure product V was 46.5 percent.

The reaction was stopped by pouring the reactants over a mixture of 400 gm of crushed ice and 40 ml of concentrated hydrochloric acid. The organic materials were extracted from the water mixture by two 300 ml and three 100 ml portions of ether. Excess concentrated hydrochloric acid was added to break the emulsion which formed. The combined ether solutions were treated as before. The dark liquid remaining was separated into the components listed in Table 5 by fractional distillation.

Table 5. The fractionation of the products obtained from the aluminum chloride-catalyzed reaction of 2,4-dichlorophenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt.in grams	Refractive index(25° C.)	Identity
1	50.0- 74.0	0.8	12.32	1.5379	Product II[a] and the phenol
2	74.0-103.5	0.8	4.80	1.5458	Intermediate
3-5	105.0-107.0	0.7-1.0	78.55	1.5247-1.5242[b]	Product VI[c]
6	107.0-137.0	0.7	5.98	1.5356	Crude Product VI
7			10.90		Unidentified tars

a - Product II is alpha-chloroisobutyric acid.
b - The refractive indices of these fractions were 1.5247, 1.5242, and 1.5245 respectively at 25° C.
c - Product VI is 2,4-dichlorophenyl alpha-chloroisobutyrate. The yield of Product VI was 63 percent.

The Aluminum Chloride-Catalyzed Reactions of 2,4,6-Trichlorophenol and Anhydrous Chloretone

Procedure One. A total of 59.1 gm (0.3 mole) of 2,4,6-trichlorophenol was placed in the reaction flask and heated to 75° C. The liquid phenol was held at 70-80° C. while 37.0 gm (0.3 mole) of aluminum chloride was added slowly over a period of one and one-quarter hours. The mixture became quite viscous as the catalyst was added. An aliquot of the water present in the hydrogen chloride gas absorber was titrated with standard sodium hydroxide. The acidity found indicated that 0.123 mole of hydrogen chloride had been evolved.

A total of 53.1 gm (0.3 mole) of molten chloretone was added to the phenoxy aluminum chloride and aluminum chloride mixture. A violent reaction in which hydrogen chloride was evolved occurred. The reaction mixture was stirred at 70° C. another hour.

The reaction was stopped by pouring the reactants over a mixture of 240 gm of crushed ice and 24 ml of concentrated hydrochloric acid. The organic material was extracted from the water mixture by one 200-ml and two 100-ml portions of ether. The combined ether extracts were treated as before. The heavy residue was separated into the components listed in Table 6 by fractional distillation. Considerable difficulty was encountered in the distillation since the 2,4,6-trichlorophenol solidified in the still head and the fraction cutter of the distillation apparatus.

Procedure Two. A mixture of 296 gm (1.5 moles) of 2,4,6-trichlorophenol and 266 gm (1.5 moles) of anhydrous chloretone was heated in the reaction flask to 70° C. A total of 200.0 gm (1.5 moles) of aluminum chloride was added over a period of two and one-quarter hours to the reaction mixture at 70° C. The stirred reaction mixture was allowed to proceed one additional hour.

The reaction was stopped by pouring the reactants over a mixture of 1000 gm of crushed ice and 100 ml of concentrated hydrochloric acid. The organic materials were extracted from the water mixture by two 200 ml and two 250 ml portions of ether.

Table 6. The fractionation of the products resulting from an aluminum chloride-catalyzed reaction of 2,4,6-trichlorophenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt. in grams	Melting point	Identity
1	52.0- 70.0	0.65	4.24	About 27	Product II[a]
2	100.0-110.0	1.5-2.0	16.75	67.0-68.5	2,4,6-trichlorophenol
3	104.0-109.0	0.7	5.25	--	Intermediate
4-6	110.0-119.0	0.7-1.0	33.89	39.0-43.0[b]	Product VII[c]
7	--	--	10.38	--	Unidentified tars

a - Product II is alpha-chloroisobutyric acid.
b - The melting points of these fractions were 39.0-43.0, 42.0-43.0, and 39.0-41.0° C. respectively. After three recrystallizations of a portion of fraction 5 from dilute alcohol, the melting point of the product VII was 41.8-42.3° C.
c - Product VII is 2,4,6-trichlorophenol alpha-chloroisobutyrate. The yield of VII was 37 percent.

The combined ether extracts were washed five times with 500 ml portions of 2.5 percent potassium hydroxide to remove any unreacted phenol and any of product II, alpha-chloroisobutyrate, formed. The ether solution was then washed with three 500 ml portions of water followed by two 50 ml portions of 5 percent hydrochloric acid and two 50 ml portions of water. The ether was removed by distillation, leaving 189.0 gm of an oily crude liquid product VII, 2,4,6-trichlorophenyl alpha-chloroisobutyrate. A total of about 130 gm (29 percent yield) of purified product VII

was recovered from the crude liquid by eight crystallizations from dilute alcohol followed by charcoal decolorization and concentration of the mother liquor. The melting point of this solid was 41.0-42.5° C. A portion of this material was recrystallized seven times from dilute alcohol following a charcoal decolorization. The melting point of the resulting material was 42.1-42.9° C.

The Aluminum Chloride-Catalyzed Reaction of Pentachlorophenol and Anhydrous Chloretone

A mixture of 66.5 gm (0.25 mole) of pentachlorophenol and 94.0 gm (0.53 mole) of anhydrous chloretone was heated to 100° C. It had been determined that a mixture of this composition would be a liquid at 100° C.; smaller ratios of chloretone to the phenol were not. A total of 66.75 gm (0.5 mole) of aluminum chloride catalyst was added over a period of two hours to the reaction mixture while the temperature of the reaction was 97-100° C. The reaction was continued one additional hour at 100° C.

The reaction was stopped by pouring the reactants over a mixture of 400 gm of crushed ice and 40 ml of concentrated hydrochloric acid. The organic material was extracted from the water mixture by successive portions of ether totalling 1600 ml. A total of 45 gm of black solid tar was removed from the water and ether solutions by filtration. The combined ether solutions were dried over 40 gm of anhydrous magnesium sulfate.

The magnesium sulfate was removed by filtration and the ether by distillation. An attempt to distill the remaining mixture of

liquid and solid was unsuccessful in that only a small amount of liquid, probably product II, alpha-chloroisobutyric acid, was distillable using a large direct take-off distilling apparatus. The remaining solid was dissolved in ether and this solution was washed twice with 100 ml of aqueous 5 percent sodium hydroxide. The ether solution was evaporated to dryness leaving 36.6 gm (39 percent yield) of a brown solid. The solid was decolorized with charcoal in an alcohol solution and then allowed to crystallize. A total of 16.8 gm of a light brown solid was recovered having a melting point of 74.0-82.0° C. Further purification involving another charcoal decolorization and eight recrystallizations from dilute alcohol produced a white crystalline solid with a melting point of 117.3-117.9° C. Independent purification of another sample prepared in an analogous manner yielded a white solid with a melting point of 118.5-119.0° C. after twelve recrystallizations.

The Aluminum Chloride-Catalyzed Reaction of o-Nitrophenol and Anhydrous Chloretone

A mixture of 69.5 gm (0.5 mole) of o-nitrophenol and 83.75 gm (0.5 mole) of anhydrous chloretone was placed in the reaction flask and heated to 68° C. The addition of the 66.75 gm (0.5 mole) of aluminum chloride catalyst required two hours. The reaction temperature rose to 76° C. An ice bath was used to cool the reaction; however, just as the cooling started the reaction mixture solidified.

The reaction mixture was decomposed by adding a mixture of 500 gm of crushed ice and 50 ml of concentrated hydrochloric acid to the flask. The organic materials were extracted from the water mixture by one 400 ml, two 200 ml and one 100 ml portion of ether. The combined ether extracts were washed and dried as before. The heavy residual liquid was separated into the component parts listed in Table 7 by fractional distillation.

Table 7. Fractionation of the mixture resulting from the aluminum chloride-catalyzed reaction of o-nitrophenol and anhydrous chloretone.

Fraction	Distilling temperature	Pressure in mm Hg	Wt. in grams	Identity
1	58.0- 64.0	0.6-1.0	28.16	Product II[a], chloretone and the phenol
2	57.7- 59.5	1.0	32.47	o-Nitrophenol
3	55.0- 69.0	0.4	25.86	o-Nitrophenol
4	80.0-128.0	0.7-0.8	1.82	Unidentified
5			25.28	Unidentified tars

a - Product II is alpha-chloroisobutyric acid.

Number of Experiments Carried Out

Besides the many degradation and characterization reactions carried out, the following synthesis experiments were: Phenol and chloretone monohydrate, five experiments; phenol and anhydrous chloretone, five experiments; p-chlorophenol and anhydrous chloretone, two experiments; 2,4-dichlorophenol and anhy-

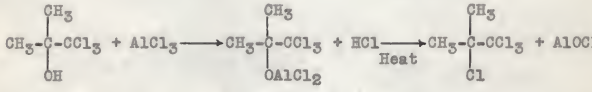
drous chloretone, two experiments; 2,4,6-trichlorophenol and anhydrous chloretone, two experiments; pentachlorophenol and chloretone monohydrate, two experiments; pentachlorophenol and anhydrous chloretone, four experiments; o-nitrophenol and anhydrous chloretone, two experiments. The total synthesis experiments were twenty-four.

DISCUSSION OF PRESENT EXPERIMENTAL RESULTS

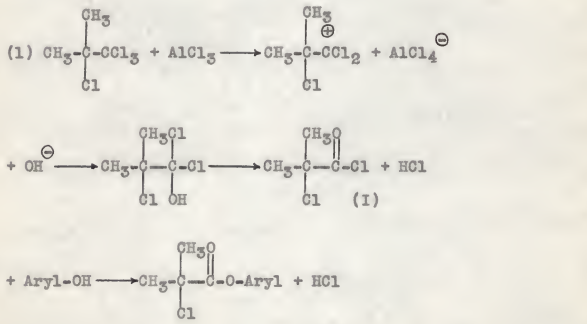
The formation of aryl alpha-chloroisobutyrate esters by the aluminum chloride catalyzed condensation of chloretone and a phenol is a reaction that is considerably more complex than the condensation of chloroform and an aromatic nucleus. The complexity of the reaction is caused by the adjacency of two different negative groups in chloretone. This situation permits the net overall effect of a Whitmore Rearrangement, the general pattern of which is well known.

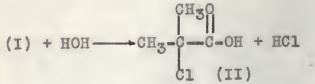
The alcoholic properties of chloretone resemble those of a primary alcohol since the trichloro group inductively decreases the electron density of the carbinol group and thus counterbalances the effect of the other two methyl groups attached to the carbinol group. Thus chloretone and ethyl alcohol would be expected to behave in an analogous manner when treated with aluminum chloride. Norris and Sturgis (5) have shown that aluminum chloride forms a complex with ethyl alcohol which under the influence of heat breaks down to ethyl chloride and aluminum oxychloride. Applying this reaction to chloretone it is possible

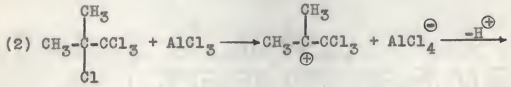
to propose a mechanism which leads to the observed products. The chloretone rearrangement follows two separate paths, (a) rearrangement and dehydrohalogenation leads to the formation of alpha-chloroisobutyryl chloride (I) which reacts with the phenol to form an aryl alpha-chloroisobutyrate ester, and (b) the dehydration leads to 1,1,1-trichloro-2-methyl propene-2 which then undergoes an allylic rearrangement to 1,1,3-trichloro-2-methyl propene-1 (III). Although, in the present work, neither of the last two compounds was isolated, Pledger (7) isolated a p-chlorophenyl derivative of the latter compound in good yield. The proposed mechanism is indicated in the following.

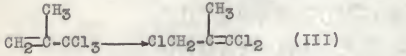


Then both (1) and (2) occur simultaneously.









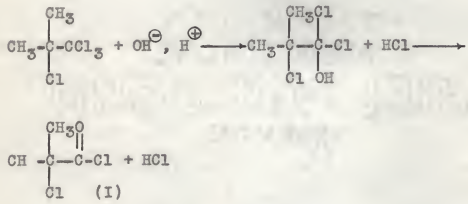
The mechanism is undoubtedly more complex than illustrated since both the phenoxy aluminum chloride and the aluminum oxychloride act similar to aluminum chloride as catalysts.

The water formed in the dehydration of the chloretone from union of the hydroxyl and hydrogen ions competes with the phenol for the acid chloride (I). Actually, the water would be present for only a fleeting instant in the presence of aluminum chloride. However, it is possible that the elements of water (H^+, OH^-) may be regenerated from the aluminum oxychloride under the influence of heat in the hydrogen chloride atmosphere provided there is the high affinity reactor for the OH^- as shown under (1) above.

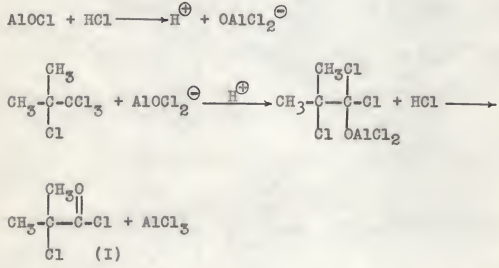
Another possible mechanism to explain the formation of the acid chloride (I) is indicated below. For the sake of comparison the reaction of the chloride of chloretone with a hydroxyl ion is given first. The basis of the mechanism is the same as

stated above. The chloride of chloretone is formed with the subsequent formation of aluminum oxychloride and hydrogen chloride (page 20). From this stage the two paths are indicated as follows.

Path (1):



Simultaneously, also path (2):



This mechanism has the possible advantage that it does not require the fleeting presence of hydroxyl ion for the formation of I. The latter mechanism depends upon the formation of $OAlCl_2$

anion and its attack on the trichloromethyl group that is similar to the attack of the hydroxyl ion as illustrated above. However, the actual mechanism is probably more complicated than indicated by either of these illustrations.

The 1,1,3-trichloro-2-methyl propene-1 (III) was not isolated as such. However, large amounts of a polymeric tar were always formed and may account for any of III which was formed. An attempt to form a derivative of III within the reaction by employing chlorobenzene was unsuccessful.

From a consideration of the proposed mechanism the factors which influence the course and yield of the reaction are (a) the acidic strength of the phenol, (b) the steric factors involved in the formation of the ester, (c) the amount of water present and, (d) the amount of catalyst present. The latter two factors appeared to be of lesser importance. The effect of the catalyst was not clear since wide variations in the amount present had little effect on the amount and kind of products formed. However, it was shown that at least a trace of the catalyst must be present even at high temperatures. The amount of water present should seriously affect the amount of aryl ester formed since the water would compete with the phenol for the acid chloride. Anhydrous reactants and precautions to prevent the introduction of any external water were used to give as large a yield of the aryl ester as possible. However, some acid II was always formed.

The influence of the phenol employed was much more profound than the other factors. This influence was due to two causes,

the acidic strength of the phenol and the steric hindrance of the substituted phenols. The weakness of the oxygen hydrogen bond of the phenol shifted the rearrangement of the chloretone to give a larger amount of the acid chloride (I). The acidic strength of the phenols which were used increased from the unsubstituted to the pentachlorophenol. However, the amount of aryl ester up to the trichlorophenyl ester increased proportionally to the acid strength of the phenol. At this point the steric hindrance of ortho substituents prevented to some extent the formation of the ester. Thus, although more acidic phenols than the 2,4-dichlorophenol were employed, the amount of aryl ester formed was at a maximum with this compound. A summary of the effect of these factors follows in Table 8. It is of interest to note that the amount of tar formed decreased as the yield of the aryl ester increased. Since it was assumed that the tar was formed by polymerized III, this is further proof that the rearrangement equilibrium was shifted due to the presence of a greater amount of a reactive acceptor for the acid chloride (I).

The Friedel-Crafts reaction of an acid chloride and an aromatic ring to form a ketone was not observed in any of the present reactions. Also, no Fries rearrangement of any of the present aryl esters was observed. This finding resulted from the unusual stability of the esters formed and also particularly from the low reaction temperature, which was too low for the Fries rearrangement. Although Pledger (7) obtained a condensation product of III and anisole, none was obtained when a phenol was employed.

Table 8. Summary of the acidic and steric nature of the phenol reacting with chloretone and the yield of aryl ester and tar.

Phenol	Dissoc. const. of the phenol X 10^{10} (9)	Reaction time in hours	Temperature in ° C.	Products and yields in percent	
Phenol	1.3	3	70	Product II	10
				Product IV[a]	20
				Tar	21*
p-Chlorophenol	210	2½	70	Product II	--
				Product V[b]	47
				Tar	12*
2,4-Dichlorophenol	310	1½	70	Product II	--
				Product VI[c]	63
				Tar	6*
2,4,6-Trichlorophenol	3900	1	70	Product II	--
				Product VII[d]	36
				Tar	9*
Pentachlorophenol	55000	3	100	Product II	--
				Product VIII[e]	39
				Tar	28*
o-Nitrophenol	750	1½	70	Tar	16*

a - Product IV is phenyl alpha-chloroisobutyrate.
b - Product V is p-chlorophenyl alpha-chloroisobutyrate.
c - Product VI is 2,4-dichlorophenyl alpha-chloroisobutyrate.
d - Product VII is 2,4,6-trichlorophenyl alpha-chloroisobutyrate.
e - Product VIII is pentachlorophenyl alpha-chloroisobutyrate.
* - These percentage yields are percent by weight of the total initial weight of the phenol and chloretone reactants.

Individual considerations of the syntheses and identifications of the aryl esters follow.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of Phenol and Chloretone. Synthesis of Phenyl Alpha-chloroisobutyrate (IV)

The purpose of this work was the formation of the product obtained from the condensation of chloretone monohydrate and phenol by Stoloff (8) and also by Madison (3). The second objective was identification of this product.

The procedure reported by Stoloff was essentially reproduced using equal molar amounts of phenol and chloretone monohydrate instead of the co-distilled anhydrous mixture of chloretone and phenol reported by Stoloff. The product which was isolated resembled that obtained by Madison very closely. It differed from that obtained by Stoloff in various physical and chemical properties. These differences are shown in Table 9.

Repeated syntheses and the identification of the product have shown that the data and proposed structure given by Stoloff were in error, probably because of the presence of impurities.

Table 9. Comparison of physical and chemical properties of the condensation product of chloretone and phenol obtained by D. D. Wheeler and A. Stoloff.

Properties	Observed by Wheeler	Observed by Stoloff (8)
Physical properties		
Boiling point	67.0-68.0° C.(0.3mm)	93-96° C.(1mm)
Boiling point	231.0-231.5° C.(atm)	225° C.(atm)
Refractive index	(20° C.)	
	1.5025	1.5139
Density (20°C.)	1.135	1.169
Percent chlorine	16.53 (16.17)*	19.58
Chemical properties		
$FeCl_3$	Negative	Positive
$Alc/AgNO_3$	Negative	Positive
Br_2/CCl_4	Negative	Negative
Alk. $KMNO_4$ (cold)	Negative	Negative
Alk. $KMNO_4$ (hot)	Positive	Positive
Solubility		
5% NaOH (cold)	Insoluble	--
5% NaOH (hot)	Soluble	Partially soluble

* - Analysis by courtesy of Dow Chemical Company.

In another experiment an attempt was made to determine the optimum reaction time for the components by analyzing aliquots withdrawn at various times during a reaction. These aliquots were analyzed for their chloretone content. Advantage was taken of the decomposition of chloretone into acetone and carbon monoxide when it is treated with 10 percent potassium hydroxide. The method was standardized by decomposing known mixtures of chloretone and phenol and collecting the gas formed over water. The results obtained from analyses of the reaction indicated that chloretone formed a product with aluminum chloride with about the

same stability as the product of phenol and aluminum chloride. No change in free chloretone was noted as the reaction proceeded.

In further studies the best general procedure was slow addition of the catalyst to an equal molar mixture of anhydrous chloretone and phenol in the molten state (70° C.). After decomposition of the reaction mixture the organic components were separated by fractional distillation under reduced pressure. By this method it was possible to obtain a yield of 20 percent of IV and 10 percent of II based on starting materials.

The evidence obtained characterized the product as phenyl alpha-chloroisobutyrate (IV), and is shown in Table 10.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of p-Chlorophenol and Chloretone. Synthesis of p-Chlorophenyl Alpha-chloroisobutyrate (V)

With p-chlorophenol, which is more acidic than phenol itself, and the procedure worked out in the case of phenol, a 47 percent yield of product V was obtained in a shorter reaction time.

In this case the more acidic nature of the phenol, unhindered by steric effects, made the higher yield possible. This situation combined with the fact that a smaller amount of tar was formed indicated that the rearrangement of chloretone had been shifted to favor formation of the acid chloride (I) at the expense of product III and subsequent tar.

Table 10. The physical and chemical properties of product IV, identified as phenyl alpha-chloroisobutyrate (IV).

Properties	Observed	Theoretical
Physical properties		
Boiling point	67.0-68.0°C.(0.3mm)	111.0-112.0°C. (10 mm)[c]
Boiling point	231.0-231.5°C.(atm)	
Refractive index(25°C.)	1.5020	
Refractive index(20°C.)	1.5025	1.4988[c]
Density (20°C.)	1.135	
Molecular refraction	51.69	51.29
Percent Carbon	61.39[a]	60.46
Percent Hydrogen	5.98[a]	5.58
Percent Chlorine	16.17[a]	17.85
Chemical properties		
Br_2/CCl_4	Negative	Negative
$Alc/AgNO_3$	Negative	Negative
$Alk/KMnO_4$ (cold)	Negative	Negative
$Alk/KMnO_4$ (warm)	Positive	Positive
2,4-Dinitrophenyl-hydrazine	Negative	Negative
$FeCl_3$	Negative	Negative
Plugge's Reagent	Negative	Negative
Acetyl chloride	Negative	Negative
Solubilities		
Water	Negative	Negative
5% HCl	Negative	Negative
Ether	Positive	Positive
Conc. H_2SO_4	Positive	Positive
5% NaOH (cold)	Negative	Negative
5% NaOH (hot)	Positive	Positive
10% KOH (refluxed)	Phenol and alpha-hydroxyisobutyric acid[b]	Phenol and alpha-hydroxyisobutyric acid
Derivatives of phenol prepared		
Tribromophenol m.p.	92.0-93.0°C.	95.0°C.
Aryloxyacetic acid m.p.	97.0-98.0°C.	99.0°C.

a - These analyses by courtesy of Dow Chemical Company differed from the theoretical to the extent stated because it was later found that the same sample contained traces of alpha-chloroisobutyric acid (II). A new sample free of II has been sent for analysis.
b - See Table 11 for identification of this acid.
c - Reported by McElvain and Stevens (4).

Table 11. Identification of product II as alpha-chloroisobutyric acid, and of the acid from hydrolysis of the esters as alpha-hydroxyisobutyric acid.

Properties	Observed	Theoretical
Alpha-chloroisobutyric acid		
Melting point	About 27° C.	31° C.
Alkaline hydrolysis	Alpha-hydroxy-isobutyric acid	See below[a]
Alpha-hydroxyisobutyric acid[a]		
Melting point	80.0-82.0° C.	79° C.
Neutral equivalent	106.3	104
p-Toluidide m.p.	131.5-132.5° C.	133° C.
p-Bromophenacyl ester m.p.	62.5-65.0° C.	Not reported
Anilide[b] m.p.	135.0-136.5° C.	136° C.

a - The hydrolysis product from product II and the acid fragment from hydrolysis of product IV were identical as shown by mixed melting point.
b - Prepared by Pledger as he obtained the same acid as shown by no depression in mixed melting point determinations.

The kind or class of chemical properties of the product V was identical with those of IV previously discussed. The physical and chemical properties that were used for the identification of V are given in Table 12.

Table 12. The physical and chemical properties and identification of V, characterized as p-chlorophenyl alpha-chloroisobutyrate.

Properties	Observed	Theoretical
Physical properties		
Boiling point	85.5-86.5°C.(0.3mm)	Not reported as it is a new compound
Refractive index (25° C.)	1.5132	
Refractive index (20° C.)	1.5142	
Density (20° C.)	1.245	
Molecular refraction	56.39	56.10
Percent carbon	51.54[a]	51.53
Percent hydrogen	4.48[a]	4.33
Percent chlorine	29.94[a]	30.42
Chemical properties		
Hydrolysis with 10 percent KOH (refluxed)	p-chlorophenol (91 percent) alpha-hydroxy-isobutyric acid (64 percent)	p-chlorophenol (100 percent) alpha-hydroxy-isobutyric acid (100 percent)
p-Chlorophenol		
Melting point	42.0-44.0° C.	43° C.
Mixed melting point	42.0-44.0° C.	43° C.
Alpha-hydroxyisobutyric acid		
Melting point	80.0-82.0° C.	79° C.
Mixed melting point	80.0-81.5° C.[c]	79° C.

a - Analyses by courtesy of Dow Chemical Company. A newly-purified sample has been sent for analysis.
b - The authentic sample of the phenol was the same as the starting material obtained from Dow Chemical Company.
c - Authentic sample was obtained from previous reaction. See Table 11 for the proof of its identity.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of 2,4-Dichlorophenol and Chloretone. Synthesis of 2,4-Dichlorophenyl Alpha-chloroisobutyrate (VI)

The ester (VI) was obtained in a yield of 63 percent, while only a small amount of tar (6 percent) was formed.

The intrinsically much higher acidic strength of the phenol correlated with the increased amount of ester (VI) that formed and the corresponding decreased tar formation. Reference to Table 8 shows the acid dissociation constants of the phenols employed. The increased yield of VI showed that any steric hindrance offered by the single ortho chloro group was greatly overshadowed by the increased ease of removal of the phenolic hydrogen.

The same procedure for the reaction was employed in this case as for synthesis of V. The maximum yield of this ester VI from the 2,4-dichlorophenol was obtained in the present case in a shorter time (Table 8) than that required for any of the other reactions. In general the chemical properties were the same as those of IV. The physical and chemical properties used for the identification of VI are given in Table 13.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of 2,4,6-Trichlorophenol and Chloretone. Synthesis of 2,4,6-Trichlorophenyl Alpha-chloroisobutyrate VII

Reaction of this phenol with chloretone proceeded smoothly and the ester (VII) was obtained in a yield of 36 percent. The tar formation was 9 percent.

Since the trichlorophenol is more acidic than any phenol previously discussed, the lower yield observed must have been caused by the steric hindrance offered by the two ortho chloro groups.

Table 13. The physical and chemical properties, and the identification of VI, characterized as 2,4-dichlorophenyl alpha-chloroisobutyrate (VI).

Properties	Observed	Theoretical
Physical properties		
Boiling point	105.5-106.5° C. (0.5mm)	Not reported as it is a new compound
Refractive index (25° C.)	1.5250	
Refractive index (20° C.)	1.5258	
Density (20° C.)	1.345	
Molecular refraction	61.03	60.91
Percent carbon[a]	44.88	44.89
Percent hydrogen[a]	3.52	3.39
Percent chlorine[a]	39.57	39.76
Chemical properties		
Hydrolysis with 10 percent KOH (refluxed)	2,4-dichlorophenol (93 percent) alpha-hydroxyisobutyric acid (77 percent)	2,4-dichlorophenol (100 percent) alpha-hydroxyisobutyric acid (100 percent)
2,4-Dichlorophenol		
Melting point	44.0-44.5° C.	45° C.
Mixed melting point	42.5-43.5° C.[b]	45° C.
Alpha-hydroxyisobutyric acid		
Melting point	81.0-82.0° C.	79° C.
Mixed melting point	80.0-82.0° C.[c]	79° C.

a - Analyses by courtesy of Dow Chemical Company.
b - Authentic sample was the same as the starting material obtained from Dow Chemical Company.
c - Authentic sample previously described. See Table 11.

Besides the general procedure previously discussed (page 28), a new method of synthesis was also used. The aluminum chloride catalyst was added to the molten phenol and upon completion of the addition it was found that not all of the phenol was tied up by the catalyst. Molten chloretone was then added, resulting in a vigorous reaction. The total reaction time in this different

procedure was one hour. Identical products and approximately equal yields were obtained by both procedures.

The chemical properties of the product were the same in type as those previously discussed for the new analogs, the esters IV, V, and VI. Table 14 gives a summary of the physical and chemical properties used for the identification of VII.

Table 14. The physical and chemical properties used for identification of VII, characterized as 2,4,6-trichlorophenyl alpha-chloroisobutyrate (VII).

Properties	Observed	Theoretical
Physical properties		
Melting point	42.1-42.9° C.	Not reported as it is a new compound
Percent carbon[a]	39.73	39.77
Percent hydrogen[a]	2.86	2.67
Percent chlorine[a]	46.55	46.96
Chemical properties		
Hydrolysis with 10 percent KOH (refluxed)	2,4,6-trichlorophenol(78 percent) alpha-hydroxyisobutyric acid (30 percent)	2,4,6-trichlorophenol (100 percent) alpha-hydroxyisobutyric acid (100 percent)
2,4,6-Trichlorophenol		
Melting point	67.0-68.5° C.	68° C.
Mixed melting point[b]	67.0-68.5° C.	68° C.
Alpha-hydroxyisobutyric acid		
Melting point	81.0-82.5° C.	79° C.
Mixed melting point[c]	81.5-82.5° C.	79° C.

a - Analyses by courtesy of Dow Chemical Company. A newly-prepared sample also has been sent for analysis.
b - Authentic sample was the same as the starting material obtained from Dow Chemical Company.
c - Authentic sample previously discussed. See Table 11.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of Pentachlorophenol and Chloretone. Synthesis of Pentachlorophenyl Alpha-chloroisobutyrate (VIII)

The high melting point of pentachlorophenol made it necessary to modify the procedure previously used. A ratio of two moles of chloretone to one mole of the chlorinated phenol was necessary to obtain a liquid mixture of the reactants at 100° C. The reaction time was three hours at this temperature, and resulted in a yield of 39 percent of the new ester (VIII). This yield was based on crude product since purification of the crude solid product (VIII) involved a long and wasteful process of chemical separation, and eight to twelve recrystallizations were found necessary to obtain analytically pure product.

Several other methods in the synthesis of VIII were tried but all were unsuccessful. They involved use of inert solvents and also high temperature reactions. No product was isolated from these attempts.

The pentachlorophenol was the most acidic phenol studied as shown in Table 8. Possibly, the yield of 39 percent of the characteristic ester (VIII) indicated that the steric effect of the two ortho chloro groups interferes with the smooth functioning of that very high acidity as was also observed in the case of the trichlorophenol (page 32). But it must be emphasized that the modified procedure found necessary for reaction with the pentachlorophenol did not permit a common basis for comparison.

An important point appears to be that pure pentachlorophenol

reacted with pure alpha-chloroisobutyryl chloride (I) without the aid of aluminum chloride could result in significantly higher yields of pentachlorophenyl alpha-chloroisobutyrate (VIII). This experiment to produce VIII by an independent synthesis will be tried in a later investigation.

Table 15 lists physical and chemical products of VIII which in general are similar to the preceding aryl esters.

Products Resulting from the Aluminum Chloride-Catalyzed Reaction of o-Nitrophenol and Chloretone

The general procedure was applied to the condensation of chloretone and o-nitrophenol but no ester product was obtained. This result was interpreted as being caused by chelation of the ortho nitro group with the phenolic hydroxyl. At the same time a considerable amount of tar was formed by rearrangement of chloretone to 1,1,1-trichloro-2-methyl propene-2 and its allylic rearrangement product, 1,1,3-trichloro-2-methyl propene-1 and their polymerization to tar by the effects of the aluminum chloride.

Table 15. The physical and chemical properties of VIII used for its identification as pentachlorophenyl alpha-chloroisobutyrate (VIII).

Properties	Observed	Theoretical
Physical properties		
Melting point	118.5-119.0° C.	Not reported as it is a new compound
Percent carbon[a]	32.65	32.38
Percent hydrogen[a]	1.95	1.63
Percent chlorine[a]	56.46	57.36
Chemical properties		
Hydrolysis with 10 percent KOH(refluxed)	Pentachlorophenol (99 percent) Alpha-hydroxyisobutyric acid (61 percent)	Pentachlorophenol (100 percent) Alpha-hydroxyisobutyric acid (100 percent)
Pentachlorophenol		
Melting point	187.5-189.5° C.	191° C.
Mixed melting point[b]	187.5-189.0° C.	191° C.
Alpha-hydroxyisobutyric acid		
Melting point	80.0-81.0° C.	79° C.
Mixed melting point[c]	80.5-81.5° C.	79° C.

a - Analyses by courtesy of Dow Chemical Company. A newly-prepared sample has been sent for analysis.
b - Authentic sample prepared from Dowicide G obtained from Dow Chemical Company.
c - Authentic sample previously prepared. See Table 11.

SUMMARY

Table 8 contains the reactions run in this investigation along with the products and the yields resulting from the reaction.

Reaction of chloretone (anhydrous or monohydrate) with phenol gave alpha-chloroisobutyric acid and phenyl-alpha-chloroisobutyrate.

Reaction of anhydrous chloretone and p-chlorophenol gave p-chlorophenyl alpha-chloroisobutyrate.

Reaction of anhydrous chloretone and 2,4-dichlorophenol gave 2,4-dichlorophenyl alpha-chloroisobutyrate.

Reaction of anhydrous chloretone and 2,4,6-trichlorophenol gave 2,4,6-trichlorophenyl alpha-chloroisobutyrate.

Reaction of anhydrous chloretone and pentachlorophenol gave pentachlorophenyl alpha-chloroisobutyrate.

Reaction of anhydrous chloretone and o-nitrophenol did not result in the formation of any aryl ester of alpha-chloroisobutyric acid.

In each of the reactions listed above, some alpha-chloroisobutyric acid probably was formed. Since the yield of this acid was small and since a better method of synthesizing this acid was known from work at Kansas State College, the isolation and identification of this acid was made only in the case of the reaction with phenol as described above. It is of interest that by saponification of Product VI, obtained in a 63 percent yield, there was obtained a high yield, 77 percent, of alpha-hydroxy-

isobutyric acid for formation of an amino acid or other useful products.

Probably the yield of each of the aryl esters could be increased by reacting each appropriate phenol with pure alpha-chloroisobutyryl chloride. In this way there should be reductions in amounts of tar formed because of aluminum chloride being absent. However, in the new syntheses described in this thesis, aluminum chloride was necessary for forming the alpha-chloroisobutyryl chloride in situ from chloretone.

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ALUMINUM CHLORIDE-CATALYZED REACTIONS OF CHLORETONE WITH A VARIETY OF PHENOLS

by

DONALD DEAN WHEELER

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AN ABSTRACT OF A THESIS

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A study of aluminum chloride-catalyzed reactions of chloretone with a variety of phenols was undertaken (a) to investigate the manner in which chloretone reacts in a Friedel-Crafts type reaction and (b) to produce and identify new chlorinated organic compounds which would possibly be useful insecticides. A search of the literature showed that reaction between chloretone and a phenol had not been reported.

The writer and co-workers have shown that chloretone (1) rearranges to yield alpha-chloroisobutyryl chloride and (2) dehydrates with subsequent rearrangement to yield 1,1,3-trichloro-2-methyl propene-1 when a variety of substituted benzenes and phenols and when aluminum chloride were present. A mechanism was proposed to explain the formation of these products.

In the present work large amounts of polymeric tar were formed and were assumed to be composed mainly of polymerized 1,1,1-trichloro-2-methyl propene-2 and 1,1,3-trichloro-2-methyl propene-1 since none of these compounds were isolated.

Several new compounds resulted from this work and new syntheses of alpha-hydroxyisobutyric acid (49 percent yield) and phenyl alpha-chloroisobutyric acid (10 percent or less) was a by-product of all the reactions that were studied involving chloretone.

The compound resulting from the aluminum chloride-catalyzed reaction of chloretone and phenol was phenyl alpha-chloroisobuty-

rate (20 percent yield), identified by analytical results for carbon, hydrogen, and chlorine; molecular refraction, saponification and identification of the fragments so produced; and by characterization tests.

The new compound resulting from the aluminum chloride-catalyzed reaction of chloretone and p-chlorophenol was p-chlorophenyl alpha-chloroisobutyrate (47 percent yield), identified by analytical results for carbon, hydrogen, and chlorine; molecular refraction; saponification and identification of the fragments so produced.

The new compound resulting from the aluminum chloride-catalyzed reaction of chloretone and 2,4-dichlorophenol was 2,4-dichlorophenyl alpha-chloroisobutyrate (63 percent yield), identified by analytical results for carbon, hydrogen, and chlorine; molecular refraction; saponification and identification of the fragments so produced.

The new compound resulting from the aluminum chloride-catalyzed reaction of chloretone and 2,4,6-trichlorophenol was 2,4,6-trichlorophenyl alpha-chloroisobutyrate (36 percent yield), identified by analytical results for carbon, hydrogen, and chlorine; saponification and characterization of the fragments so produced.

The new compound resulting from the aluminum chloride-catalyzed reaction of chloretone and pentachlorophenol was pentachlorophenyl alpha-chloroisobutyrate (39 percent yield), identified by analytical results for carbon, hydrogen, and chlorine; saponifi-

cation and characterization of the fragments so produced.

The aluminum chloride-catalyzed reaction of chloretone and o-nitrophenol did not result in the formation of the corresponding aryl alpha-chloroisobutyrate ester.

The relationship between the yields of aryl alpha-chloroisobutyrate esters obtained and the acidic and steric characteristics of the phenols used was noted.