

A STUDY OF THE REACTIONS OF CHLOROTONE AND ITS DERIVATIVES
WITH BENZENE AND SUBSTITUTED BENZENES

by

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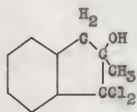
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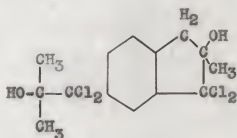
INTRODUCTION

Willgerodt and Gemesee (9) first studied the reaction of 1,1,1-trichloro-tert-butanol-2 (hereafter called chloretoe) with benzene, toluene, and p-xylene in the presence of anhydrous aluminum chloride. Their work indicated that the chlorines on chloretoe underwent condensation reactions analogous to chloroform and consequently, the mono-, di-, and tri-phenylated chloretones were obtained. However, studies made in this laboratory by Stoloff (7) indicated such compounds were not obtained when chlorobenzene was used in the place of benzene.

To account for the physical and chemical properties of the two major liquid products Stoloff isolated from the reaction of chloretoe with chlorobenzene in the presence of aluminum chloride, he postulated two substituted indanes, viz.:



(I)



(II)

Furthermore, he proposed that these indanes were formed by an intramolecular dehydrohalogenation of the nuclear chlorine and an aliphatic hydrogen liberating hydrogen chloride (7).

At the time the writer set about to verify Stoloff's work,

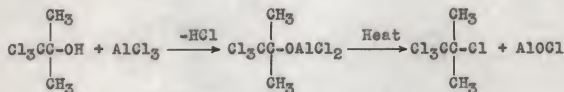
he was skeptical of such a reaction path and, as work progressed, it began to show that this type reaction had not occurred. Several of Stoloff's qualitative tests were found to be in error as well as some of the physical constants that he reported. Repeated syntheses have indicated these errors.

McElvain and Stevens (2) have shown that chloretone can be dehydrated using thionyl chloride to give 1,1,1-trichloroisobutene-2 which will undergo an allylic rearrangement to 1,1,3-trichloroisobutene-1 (III) under somewhat drastic conditions. The writer (4) found that this rearrangement could occur during dehydration under certain conditions which need not be discussed here.

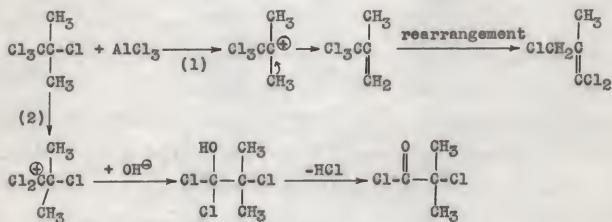
Therefore, chloretone might also dehydrate in the presence of anhydrous aluminum chloride to 1,1,1-trichloroisobutene-2 which then immediately rearranges to form (III). This allylic chloride could then undergo a normal Friedel-Crafts type condensation with the para-hydrogen of chlorobenzene yielding 3-(p-chlorophenyl)-1,1-dichloroisobutene-1 (V).

Chloretone might also undergo the reactions shown in the equations below with subsequent dehydrohalogenation to alpha-chloroisobutyryl chloride which would finally yield alpha-chlorisobutyric acid (IV) in the presence of water. These reactions would possibly occur at the same time. In proposing a mechanism for the path of reaction for arriving at these products, several factors have been considered: Work in this laboratory has shown that the oxygen-hydrogen bond in chloretone is weakened by the decrease in electron density about the oxygen atom. This effect

is probably due to the inductive effect of the three chlorines. Morris and Sturgis (3) have shown that ethyl alcohol forms a compound with aluminum chloride which is similar to that formed by phenol and the same reagent. Under the influence of heat, this breaks down into aluminum oxychloride and ethyl chloride. Chloroacetone should thus be expected to behave in an analogous way. The intermediate 1,1,1-trichloro-2,2-dimethyl ethyl chloride could then react with more aluminum chloride in the two ways shown. The following mechanisms are thus proposed, although they may be considerably more complex:





Then, (1) and (2) both occur;



These paths do not violate accepted electronic concepts of reaction mechanism and seem to give an explanation of the mechanisms of formation of the two kinds of products (IV and V and analogues

of V) obtained in all major reactions of this study.

The chlorine analyses on the products obtained by Stoloff did not check with the theoretical structures one would predict from the work of Willgerodt and Gemesee (9); i.e., Cl--CCL₂C(CH₃)₂OH and (Cl-)₂CCLC(CH₃)₂OH. On the other hand, the chlorine analyses checked for one of the structures postulated by Stoloff. If the type reaction proposed by Stoloff had occurred, then bromobenzene should give the same products as did chlorobenzene with hydrogen bromide being liberated in the reaction. If the structures predictable from Willgerodt's work were the products of this reaction, then two different products should be obtained using bromobenzene and chloretohe. Finally, if the reaction was like the one proposed by the writer, then one product should be the same and one different, with no hydrogen bromide liberated, when bromobenzene and chloretohe are reacted.

Furthermore, if the reaction proceeds as proposed by the writer, one would expect anisole and benzene to react in an analogous manner to chlorobenzene.

Thus, the scope of this investigation included: (a) the reaction of chloretohe using aluminum chloride as a catalyst for the purpose of obtaining the same products that Stoloff had obtained, (b) the determination of the structures of products isolated from the reactions of chlorobenzene, bromobenzene, anisole, and benzene with chloretohe, (c) a study of the path of reaction to the isolated products from these various combinations by whatever means that seemed necessary, (d) the isolation of new compounds

which might prove to be useful insecticides, or pesticides, (e) the synthesis of several homologs of a new type structure never before known which would be patentable.

DISCUSSION

This study has shown that chloretone in the presence of aluminum chloride does not remain intact and does not react with benzene, chlorobenzene, bromobenzene, or anisole in a way analogous to chloroform. In every case, chloretone reacts differently and forms two entirely different types of products. One of these products reacts with the aromatic compound, whereas the other does not. Whenever any one of the above-mentioned aromatic compounds and aluminum chloride are present, chloretone (1) rearranges to yield alpha-chloroisobutyryl chloride and (2) dehydrates with subsequent rearrangement to yield 1,1,3-trichloroisobutene-1 (III). The acid chloride was never isolated, although phenolic esters of it have been isolated by Wheeler (8) and by the writer. In every case, except when anisole was used, alpha-chloroisobutyric acid was isolated as a product of the reaction. A possible explanation for the acid chloride failing to condense with the aromatic molecule would be that the water that is present immediately reacts with this acid chloride to give the corresponding acid. However, whenever a phenol is present, there exists a competition between the active hydrogen of the phenol and the water for the acid chloride and both the ester and the acid are formed. Wheeler has obtained evidence to show that alpha-chloroisobutyric acid is one of the products of the reac-

tion between phenols and chloretone.

The other product of chloretone, compound (III), reacts with the previously mentioned benzenoid compounds to yield, in every case, dichlorovinyl benzenoid compounds which are unique in their physical and chemical properties. These compounds are all 1,1-dichloro-3-phenylated-2-methyl-propene-1's in which the phenyl group can be substituted with various substituents.

These compounds contain an isolated double bond which in conjunction with the two vinyl chlorines appears to weaken the carbon-hydrogen bond on the aliphatic carbon atom adjacent to the aromatic ring. Therefore, as would be expected, these compounds are found to react easily with sodium carbonate in a solution of diluted methanol yielding substituted alpha-methyl cinnamaldehydes. This reaction then offers a convenient path for the synthesis of nuclear substituted alpha-methyl cinnamaldehydes from either chloretone or its derivative, 1,1,3-trichloroisobutene-1 (III). The yield of aldehyde from the dichlorovinyl benzenoid compound can be expected to be in the vicinity of 80-90 per cent of the theoretical.

In addition to the above findings, a new synthesis of alpha-chloroisobutyric acid was found. This acid might be termed a by-product of the reaction. Formation in these reactions offers possibly the best means of preparing this compound. No other method as good was found in the literature. Further, it offers a means of preparing alpha-aminoisobutyric acid by a relatively cheap process. The copper complex salt of this amino acid was prepared

by the writer and it was found to crystallize in beautiful blue lath-shaped crystals which melted at 232.3-233.0° C. These crystals were insoluble in hot methanol, in water, and in acetone at room temperature. Time did not permit further study of this compound.

Detailed consideration of all the products isolated in this study will now be considered.

Products Resulting from the Reaction of Chlorotone
and Chlorobenzene using Aluminum Chloride as a Catalyst.
Synthesis of 3-(p-chlorophenyl)-1,1-dichloroisobutene-1 (V)

The purpose of this work was to substantiate the work of Stoloff (7) and, more particularly, to determine the structures of the two major products that were isolated.

The object of the first synthesis was to obtain the same two products that Stoloff first reported. His procedure was followed as closely as was possible. However, modifications were made in the apparatus used for fractionation at reduced pressure, and, consequently, the procedure of fractionation had to be somewhat altered. As a whole, his work was substantiated except that several of the physical and chemical properties of the two major products were found to be different from what he had reported. Some of these discrepancies can be attributed to the presence of impurities and errors in the apparatus used, while others are unexplainable.

Stoloff reported two major products: A low boiler, b.p. 72-74° C. at 1.5 mm and a high boiler, b.p. 120-124° C. at 1.5 mm of pressure. The writer also obtained two major products: A low

boiler, b.p. 55.5-58.0° C. at 0.9 to 1.0 mm of pressure and a high boiler, b.p. 95-99° C. at 0.8 mm of pressure. Redistillation of a portion of the writer's low boiler showed this liquid distills between 62-66° C. at 1.7 mm. Later, Allen (1) duplicated the writer's results and found the low boiler had a boiling point of 59-60° C. at 1.6 mm. The erroneous boiling point reported by Stoloff was perhaps due to a defective monometer or to superheating of the distilling vapors.

Additionally, Stoloff reported that the high boiler gave a positive alcoholic silver nitrate test and a negative permanganate test. Both the writer and Allen found that just the opposite was true when the high boiler was pure. Stoloff's values for the refractive index and density were slightly off, also, and these differences are attributed to impurities in his samples.

The evidence in support of the low boiler, product IV, being alpha-chloroisobutyric acid IV is given in Table 1. This acid based upon the chlorotone was isolated in yields of 33 to 36 per cent of the theoretical. Further evidence to prove that product IV was alpha-chloroisobutyric acid was obtained when the same compound was found to result during the course of reaction of chlorotone with bromobenzene. Furthermore, product IV was not obtained when 1,1,3-trichloroisobutene-1 (III) was reacted with chlorobenzene but a high boiling liquid was isolated which was the high boiler isolated when chlorotone was reacted with chlorobenzene.

Alpha-chloroisobutyric acid was found to react immediately with aniline and mono methyl aniline at room temperature. The crystalline products had the same melting points. Further, mix-

ing of the two showed no depression of the melting point which indicated that both might be the same compound. Quantitative chlorine analyses on the aniline derivative gave an average value of 16.61 per cent chlorine. The theoretical value for the per cent chlorine of the aniline, alpha-chloroisobutyric acid salt and the hydrochloride salt of the substituted aniline is 16.47 per cent. The neutral equivalent also checked for either one of these two compounds. This close agreement between the found and the theoretical was taken as evidence enough that the aniline derivative was one of the above-mentioned salts. Further data on these compounds will be found in Table 3.

The evidence proving that product V was 3-(p-chlorophenyl)-1, 1-dichloroisobutene-1 (V) is given in Table 4. The yields of this compound were 27 to 29 per cent of the theoretical (based upon the assumption that all chloretoe that was not rearranged to isolatable alpha-chloroisobutyric acid was available for production of the needed (III); see equations with mechanisms on page 3). Further evidence in support of structure (V) for product V was obtained when known (III) was reacted with chlorobenzene to give product V in a 58 per cent yield. These two products were shown to be identical by the fact that their boiling points, refractive indices, and densities were the same. Alkaline hydrolysis of product V to p-chloro-alpha-methyl cinnamaldehyde adds to the proof of product V being structure (V). This point will be discussed in detail later on.

Table 1. Physical and chemical properties of product IV, characterized as alpha-chloroisobutyric acid (IV).

Properties	Observed	Theoretical
Physical properties		
Boiling point	51-52.5° C. (1.0 mm)	
Boiling point	181-182.5° C. (atm.)	
Melting point	about 31° C.	31° C ^a
Refractive index (25° C.)	1.4315	
Density (25° C.)	1.182	
Molecular refraction	27.0	27.07
Per cent chlorine ^b	28.95	28.9
Chemical properties		
Neutral equivalent	122	122.5 or 61.25 ^f
Br ₂ /CCl ₄	negative	negative
Aq. KMnO ₄	positive	positive
Alc./AgNO ₃ (cold)	positive	positive
Lucas reagent	insoluble	insoluble
Acetyl chloride	negative	negative
Alkaline KMnO ₄	α-hydroxyiso- butyric acid	α-hydroxyiso- butyric acid
Solubilities		
Water	nearly completely	soluble
5% NaOH	soluble	soluble
Ether	soluble	soluble
Conc. H ₂ SO ₄	soluble	soluble
Conc. HCl	insoluble	insoluble
20% NaOH soln. (refluxed) ^c	α-hydroxyiso- butyric acid	α-hydroxyiso- butyric acid
Aniline in benzene ^d	Aniline salt of acid	Aniline salt of acid
Monomethylaniline in benzene ^d	unidentified	the acid salt
Sodium cyanide ^e	α-hydroxyisobutyric acid, m.p. 80- 82° C.	α-hydroxyisobutyric acid

a - Ostropiatow, P., Journ. Russ. Physc. Chem. Ges., 1, 47-56 (1896). See also: Beilstein, II, 295.

b - This is the average of the two values: 28.9 and 29.0.

c - See Table 2 for proof of the identity of this acid.

d - See Table 3 for the proof of the identity of these products.

e - Mixed melting point with an authentic sample of alpha-hydroxyisobutyric acid gave no depression of the melting point.

f - These two values are both possible because the alpha chlorine will also hydrolyze slowly during titration and the latter would be possible if time were given for the chlorine to hydrolyze.

Table 2. Identification of the acid from hydrolysis of product IV.

	: Acid obtained:	: Alpha-hydroxyisobutyric acid ^a
Melting point	78.6-80° d.	79° C.
Neutral equivalent	105.1	104
Anilide	135-136.5° C.	136° C.
Toluidide ^b	131.5-132.5° C.	133° C.
p-Bromophenacyl ester ^b	62.5-65.0° C.	Not listed in literature
Mixed melting point ^c	78-81° C.	-

a - Constants were taken from the literature.

b - These derivatives were prepared by Wheeler since he obtained the same acid as evidenced by mixed melting points.

c - This is the mixed melting point of the acid obtained by treatment with alkaline $KMnO_4$ and alkaline hydrolysis of product IV with 20 per cent NaOH solution.

Table 3. Identification of the products from the reaction of aniline and mono-methyl aniline in benzene with alpha-chloroisobutyric acid.

Properties	: Observed	: Theoretical
Aniline derivative		
Melting point	100-101° C.	-
Neutral equivalent	215.7 ^a	215.5 or 107.8
Per cent chlorine	16.61	16.47
Solubilities		
Water	soluble	soluble
Ether	soluble	insoluble
5% NaOH	insoluble ^b	insoluble
5% HCl	soluble	soluble
2% $AgNO_3$	precipitate ^c	precipitate
Methyl aniline derivative		
Melting point	98.5-99.3° C.	-
Neutral equivalent		229.5 or 114.8
Mixed melting point with aniline derivative	99-100° C.	depression

a - Proves it is the acetate salt of aniline.

b - Would be insoluble because aniline would be liberated as an insoluble oil.

c - Showed that chlorine was loosely held in the molecule.

Table 4. Physical and chemical properties of product V, characterized as 3-(p-chlorophenyl)-1,1-dichloroisobutene-1 (V).

Properties	Observed	Theoretical
Physical properties		
Boiling point	88° C. (0.5 mm)	-
Boiling point	92° C. (0.7 mm)	-
Boiling point (micro) ^a	226° C. (atm.)	-
Refractive index (25° C.)	1.5585	-
Refractive index (20° C.)	1.5577	-
Density (20°/4° C.)	1.283	-
Per cent chlorine ^b	44.35 (44.47) ^c	45.20
Per cent carbon ^c	50.85	50.99
Per cent hydrogen ^c	3.89	3.35
Molecular refraction	59.2	58.9
Empirical formula	C _{3.4} H _{3.04} Cl _{1.0}	
Chemical properties		
Br ₂ /CCl ₄	negative	slow addition
Aq. KMnO ₄	positive	positive
Alc./AgNO ₃ (cold)	negative	negative
" (hot)	negative	negative
Solubility		
Water	insoluble	insoluble
5% NaOH	insoluble	insoluble
5% HCl	insoluble	insoluble
Ether	soluble	soluble
Conc. H ₂ SO ₄	insoluble	insoluble
85% H ₃ PO ₄ ^d	insoluble	insoluble
Alkaline KMnO ₄ oxidation ^e	p-chlorobenzoic acid	p-chlorobenzoic acid

a - Decomposed as boiling point was approached at atmospheric pressure.

b - Average of three determinations.

c - Analyses by courtesy of Dow Chemical Company's laboratories.

d - Determined by J. Allen (Senior Problem Report).

e - See Table 5 for proof of identity of this acid.

Oxidation of product V with alkaline potassium permanganate resulted in a 35 per cent yield of p-chlorobenzoic acid. Proof for the identity of this acid will be found in Table 5. The low yield of this acid may be due to the possibility that product V

is actually a mixture of the ortho and para isomers. This seems unlikely, however, since the nuclear halogen exerts a steric hinderance to ortho substitution. However, if product V was a mixture of the two isomers, any ortho chlorobenzoic acid formed probably remained in the filtrate due to it being five times as soluble in water as the para acid.

The chlorine analyses for product V are not within the limits of experimental error and low values may be reasonably attributed to traces of impurities. Excellent values obtained from Carius analyses on all other compounds isolated, including the p-bromophenyl analogue were obtained.

Table 5. Identification of the acid from oxidation of product V.

Acid obtained		p-chlorobenzoic acid ^a
Melting point	235.5-237.0° C.	237.0-237.5° C.
Anilide	192-193.3° C.	194° C.
Mixed melting point with acid obtained from the Eastman Kodak Co.	235.5-236° C.	

a - Purchased from the Eastman Kodak Co.

In this reaction as well as all reactions involving chlore-tone, and those using 1,1,3-trichlorisobutene-1 (III), a small amount of crystals sublimed into the still-head at reduced pressure. These crystals have not been identified, but, since (III) was the only compound that was present in every synthesis, they must be a product resulting from the reaction of (III) with itself. They have been shown not to be chlore-tone, although they

resemble it in odor. They crystallize in octahedrons, whereas chloretone crystallizes in long needles or in multi-pointed stars. Evidence points to their being 1,3-di-(trichloromethyl)-1,3-dimethyl cyclobutane.

Products Resulting from the Reaction of Bromobenzene
and Chloretone using Aluminum Chloride as a Catalyst.
Synthesis of 3-(p-bromophenyl)-1,1-dichloroisobutene-1

This reaction was carried out to determine if hydrogen bromide would be evolved. Evolution of this gas would show that ring closure had occurred.

A low boiling liquid, product IV, was isolated which proved to be alpha-chloroisobutyric acid since it had the same boiling point and refractive index as this acid. The yield of this acid (based upon the chloretone used) was 24.3 per cent of the theoretical.

A high boiling liquid, product VII, was isolated also, and shown to be 3-(p-bromophenyl)-1,1-dichloroisobutene-1 (VII). Evidence in support of this structure is given in Table 6. The method used in determining the percentage bromine needs clarification. If product VII is assumed to be structure (VII), then the equation

$$\text{Per cent bromine} = \frac{(42.555)(\text{weight of ppt. obtained})}{(\text{weight of sample used})} - 44.14$$

can be derived for calculating the percentage bromine by the Carius method of halogen determination. It is, of course, necessary to use the theoretical value for the per cent chlorine in deriving the equation. This is permissible for the equation will give the

correct theoretical value only provided product VII was a compound having the correct ratios of carbon to hydrogen to chlorine to bromine.

It was felt that no further characterization, aside from that listed in Table 6, was necessary because bromobenzene should give a product analogous to that obtained with chlorobenzene. Analyses check with the theoretical.

Table 6. Physical properties of product VII, characterized as 3-(p-bromophenyl)-1,1-dichloroisobutene-1 (VII).

Properties	Observed	Theoretical
Physical properties		
Boiling point	110-111° C. (0.9 mm)	
Refractive index (25° C.)	1.5757	
Refractive index (20° C.)	1.5747	
Density (20/4° C.)	1.508	
Per cent bromine ^a	28.45 (28.45) ^b	28.54
Per cent carbon ^b	42.57	42.89
Per cent hydrogen ^b	3.30	3.24
Per cent chlorine ^b	25.4	25.33
Molecular refraction	61.33	61.76

a - Average of two determinations. A fraction, b.p. 110° (0.9 mm) and refractive index of 1.5777 at 25° C.; and the same fraction purified with concentrated sulfuric acid was used for these two determinations. They differed by 0.3 per cent in bromine content.

b - These determinations were made by the Dow Chemical Co. laboratories without cost. Empirical formula: $C_{10}H_9BrCl_2$.

Products Resulting from the Reaction of Anisole and Chloretone using Aluminum Chloride as a Catalyst. Synthesis of 3-(p-methoxyphenyl)-1,1-dichloroisobutene-1 (X)

The study of the reactions of chlorobenzene and of bromobenzene with chloretone gave an insight into what products might be expected from the condensation of anisole and chloretone. There-

fore, this condensation was run and small yields of two products resulted. The fractions collected are to be found in Table 16 in the EXPERIMENTAL section of this thesis. Fraction 7, product IX, is probably alpha-chloro-phenylisobutyrate (IX) and evidence supporting this supposition is given in Table 7. The yields of this product were too low to warrant further work with it. Fraction 10, product X, is evidently 3-(p-methoxyphenyl)-1,1-dichloroisobutene-1 (X). Evidence in support of this structure is given in Table 8.

To obtain further evidence in support of structure (X) for product X a condensation was run between anisole and (III). Only one major product was obtained, but a small amount of phenols were obtained also. However, no fraction corresponding to alpha-chloro-phenylisobutyrate was obtained. This result was further evidence that product IX is structure (IX). In other words, no alpha-chloroisobutyryl chloride was present in this reaction, and, consequently, no ester of the corresponding acid and phenol could be formed. Therefore, as expected, phenol was isolated and found in fraction 4.

The yield of pure product X, based upon the amount of compound (III), was found to be 43.2 per cent of the theoretical. The overall yield of product X was 53.3 per cent of the theoretical.

Table 7. Properties of product IX in support of the material being alpha-chlorophenylisobutyrate (IX).

Properties	:	Observed	:	Theoretical
		<u>Product IX</u>		<u>Wheeler's</u>
Physical properties				
Boiling point		70-75° (1.1 mm)		67-70° (0.3 mm)
Refractive index (25° C.)		1.5070		1.5023
Refractive index (20° C.)		1.5097		1.5023
Density (20/4° C.)		1.138		1.125
Molecular refraction		52.1		51.88
				51.66

a - Properties found by Wheeler for compound IX obtained from the reaction of phenol and chlorestone in the presence of aluminum chloride.

The yield of crude acid from the oxidation of product X was 61.7 per cent. The yield of pure acid was 37.9 per cent. The 40 per cent loss in recrystallization indicates that the crude acid might have been a mixture of the ortho and para acid. Further evidence for this supposition was shown by the fact that the crude acid melted approximately 24° C. lower than the recrystallized acid. If this were true, then product X was a mixture of the ortho and para isomers of structure (X).

Table 8. Properties of product X, characterized as 3-(p-methoxyphenyl)-1,1-dichloroisobutene-1 (X).

Properties	Observed	Theoretical
Physical properties		
Boiling point	105-105.5° C. (1.1 mm)	
Refractive index (20° C.)	1.5505	
Density (20° C.)	1.211	
Per cent chlorine ^a	30.70	30.68
Per cent carbon ^a	57.10	57.16
Per cent hydrogen ^a	5.26	5.23
Per cent oxygen	6.94 ^b	6.92
Molecular refraction	60.88	60.61
Empirical formula	C ₁₁ H ₁₂ OCl ₂	
Chemical properties		
Br ₂ /CCl ₄	Decol. with HBr lib.	Decol. with HBr lib.
Alkaline KMnO ₄ oxidation	p-methoxybenzoic acid ^c	p-methoxybenzoic acid
Solubility	only conc. H ₂ SO ₄	only conc. H ₂ SO ₄

a - Analyses by Dow Laboratories.

b - By difference from analyses.

c - See Table 9 for identity of this acid.

Table 9. Identification of the acid obtained by the oxidation of product X.

Properties	Acid obtained	p-methoxybenzoic acid ^a
Melting point	184-186.3° C.	183.8-185.3° C.
Mixed melting point	184-186-7° C.	
Neutral equivalent	152	152 (theoretical)

a - Purchased from the Eastman Kodak Co.

Products Resulting from the Reaction of Benzene
and Chlorotone using Aluminum Chloride as Catalyst

Mention was made of the work of Willgerodt and Gomese (9) on this reaction in the INTRODUCTION. They claimed to have ob-

tained 1,1-dichloro-1-phenyl-2-methyl propanol-2; 1-chloro-1, 1-diphenyl-2-methyl propanol-2; triphenyl-tert-butyl alcohol; and tetraphenyl iso-butane. They boiled at 217°, 239°, and above 260° respectively. The latter compound was never isolated but was assumed to remain in the tarry residue. Their paper gave no experimental details and no chemical evidence in support of the above-mentioned structures, although their results solely from chlorine, carbon, and hydrogen analyses are in fairly good agreement with the theoretical values. They make no mention of having found any products similar to those obtained in the present work from the reactions of chlorobenzene, bromobenzene, and anisole with chloreton.

Reaction of chloreton and benzene was run to determine if products analogous to those obtained with chlorobenzene would be obtained, or if the compounds reported by Willgerodt and Gemesee would be obtained.

Very little alpha-chloroisobutyric acid was found to result from this reaction unless it was in the intermediate fractions which were relatively large. A constant boiling liquid was obtained, b.p. 56.0-60.5° C. (0.3 to 0.5 mm), and appeared to be a mixture, mixture A, containing considerable alpha-chloroisobutyric acid. This was evidenced by the large variance in the refractive indices and densities of three successive cuts that had the same boiling points. Furthermore, the last cut was about 50 per cent soluble in concentrated sulfuric acid, which indicates a mixture of alpha-chloroisobutyric acid and 1,1-dichloro-3-phenylisobutene -1 (XI) based on previous determinations of the solubility of

substances having the latter kind of structure. Alkaline oxidation of a portion of the middle cut gave a 9.0 per cent yield of benzoic acid.

In order to gain some insight into the reasons for these unexpected results, benzene was reacted with compound (III) in the presence of aluminum chloride. Only one major product resulted, product XI, having a boiling point range of 67.0-68.5° C. at 0.25 mm of pressure. The total of product XI was taken off in three successive fractions. All three fractions had the same density and very nearly the same refractive index. To eliminate possible errors due to traces of impurities, these values were averaged and the average used in calculating the experimental molecular refraction. Evidence showing that product XI was pure compound (XI) is summarized in Table 10.

Oxidation of a portion of the middle cut resulted in a 71.2 per cent yield of benzoic acid. This acid was proven only by a mixed melting point with an authentic sample of benzoic acid.

The boiling point of mixture A is far too low to correspond to any of the products obtained by Willgerodt and Gemesee. Perhaps his conditions and molar ratios were different. It is doubtful that the components of mixture A can be resolved by fractionation since they appear to boil too close together.

Product of the Reaction of 1,1,1-Trichloro-tert-butylacetate (XII) with Anisole using Aluminum Chloride as Catalyst. Synthesis of p-methoxy acetophenone

Previous workers have shown that esters react in a Friedel-Crafts reaction principally as the corresponding alcohol. For

example, tert-butyl acetate and benzene using hydrogen flouride as catalyst gives a 72 per cent yield of tert-butyl benzene and some acetophenone (5). However, this work has shown that the chlorotone ester of acetic acid does not give analogous products in the same proportionate yields. A 45.5 per cent yield of p-methoxy acetophenone was obtained and no other products were isolated. This work indicates that the strong inductive effects of the chlorines in the alcohol part of the molecule of the ester, (XII), alter the course of the reaction that most esters undergo in a Friedel-Crafts reaction. Evidence that the product is p-methoxy acetophenone is summarized in Table 11.

Table 10. Properties of products resulting from the reaction of benzene and 1,1,3-trichloroisobutene-1 in the presence of aluminum chloride as a catalyst. Synthesis of 1,1-dichloro-3-phenylisobutene-1 (XI).

Property	Observed	Theoretical
Physical properties		
Boiling point	67.0-68.5° (0.25 mm)	
Refractive index (20° C.)	1.5467 ^a	
Density (20/4° C.)	1.174	
Molecular refraction	54.26	54.05
Per cent chlorine		35.32
Chemical properties		
Alkaline KMnO ₄ oxidation	benzoic acid	benzoic acid

a - Average of the three values: 1.5465, 1.5473, and 1.5462.

Table 11. Properties of the product from the reaction of anisole and 1,1,1-trichloro-tert-butyl acetate in the presence of aluminum chloride as a catalyst. Synthesis of p-methoxy acetophenone.

Property	Observed	Theoretical
Physical properties		
Boiling point	88-88.5° C. (0.5 mm)	
Boiling point (micro)	257.2° C. (atm.)	257° C.
Melting point	39-41° C.	38-39° C.
Chemical properties		
2,4-dinitrophenylhydrazones:		
Melting point	222-223° C.	220° C.
Oxime derivative		
Melting point	86.5-87.3° C.	87° C.

A list of the reactions run together with the kind of products and their yields obtained is stated in Table 13 below.

Product Resulting from the Alkaline Hydrolysis of 3-(p-chlorophenyl)-1,1-dichloroisobutene-1 in Aqueous Methyl Alcohol

To prove that product VIII was p-chloro-alpha-methyl-cinnamaldehyde, it was to be oxidized to the corresponding acid. A search of the literature revealed that this acid, p-chloro-alpha-methyl-cinnamic acid, had never been prepared. It was synthesized by a Perkin condensation between p-chlorobenzaldehyde and propionic anhydride in the presence of sodium propionate. The resulting acid had a melting point of 166.7-167.7° C. and was obtained in a 69.5 per cent yield.

Attempts to oxidize product VIII in an alkaline suspension of silver oxide at 80° C. for 20 hours was unsuccessful. Attempts to oxidize it with Tollens reagent resulted in a violent

explosion. Oxidation with Fehling's solution gave considerable red cuprous oxide but only a minute trace of an organic solid.

Reduction of an alpha-beta unsaturated acid to the alpha-beta unsaturated aldehyde by the method of Sonn and Müller (6) involves preparation of the iminochloride from the anilide of the acid. Although the reduction of the above acid was unsuccessful, the anilide was obtained as colorless needles, m.p. 115.5-116.0° C. The yield of crude brown needles was 92.0 per cent, and of pure colorless needles was 83.9 per cent of the theoretical.

The few properties of product VIII which were determined are listed in Table 12. Attempts to prepare the p-nitrophenyl hydrazone failed. The product gave a 2,4-dinitrophenylhydrazine test, but that derivative could not be obtained in 2 and 3 gram yields by the standard procedures. There is evidence to indicate that this aldehyde is contaminated with the corresponding acid. Its structure has not been proved to date.

Table 12. Properties of product VIII.

Property	Observed	Theoretical
Physical properties		
Boiling point	96.7-100° C. (0.9 mm)	
Boiling point	274.5-276.0° (atm.)	
Refractive index (20° C.)	1.5625	
Density (20/4° C.)	1.283	
Chemical properties		
2,4-dinitrophenylhydrazine	positive	positive
Fehling's reagent	positive	positive
Tollen's reagent	positive	positive
Shiff's reagent	positive	positive
Br ₂ /CCl ₄	decol., HBr lib.	decol., HBr lib.
Solubilities		
Water	insoluble	insoluble
Ether	soluble	soluble
5% NaOH	insoluble	insoluble
Conc., H ₂ SO ₄	soluble	soluble

Table 13. Summary of products obtained from reactions conducted.

Reactants	Structures found	Yields : per cent
Chlorobenzene and chloretoene	α -chloroisobutyric acid. 3-(p-chlorophenyl)-1,1- dichloroisobutene-1. (V).	33-36 27-29
Chlorobenzene and 1,1,3-trichloroisobutene-1	3-(p-chlorophenyl)-1,1- dichloroisobutene-1. (V).	57.9
Bromobenzene and chloretoene	α -chloroisobutyric acid. 3-(p-bromophenyl)-1,1- dichloroisobutene-1. (VII).	24.3 21.4
Anisole and chloretoene	α -chloro-phenylisobutyrate (IX). 3-(p-methoxyphenyl)-1,1- dichloroisobutene-1. (X).	4.05 4.1
Anisole and 1,1,3-trichloroisobutene-1	Phenol. 3-(p-methoxyphenyl)-1,1- dichloroisobutene-1 (X).	14.9 53.3
Benzene and chloretoene	α -chloroisobutyric acid. 3-phenyl-1,1-dichloroiso- butene-1 (XI).	19.4
Anisole and 1-1-1-tri- chloro-tert-butyl acetate	p-methoxy acetophenone	45.5
3-(p-chlorophenyl)-1,1- dichloroisobutene-1 and sodium carbonate.	p-chloro- α -methylcinna- maldehyde (VIII). ^a	83.3
p-Chlorobenzaldehyde and propionic anhydride with sodium propionate	p-chloro- α -methyl cinnamic acid	69.5
Benzene and 1,1,3-trichloroisobutene-1	3-phenyl-1,1-dichloroisobutene-1	25.01

a - Not proven.

EXPERIMENTAL

Preparation of Starting Materials

Chloretone (Trichlorobutanol) was purchased from the Givaudan-Delawanna Co., Inc. It was found to melt at 80-81.5° C. This showed that it contained one mole equivalent of water of hydration. The chloretone was used in this hydrated form.

Chlorobenzene was obtained from the Dow Chemical Co. as sample #8987, Ordinance #73748M. When redistilled, it gave a liquid distilling between 128-129.5° C. at atmospheric pressure.

Bromobenzene was obtained from the Dow Chemical Co. as Ordinance #73771M. When redistilled, it gave a liquid distilling at 152-153° C. at atmospheric pressure.

Anisole was purchased from the Eastman Kodak Co. as white label grade. This anisole was distilled at atmospheric pressure and the fraction distilling 150-151.5° C. was used.

Benzene was that supplied by our storeroom and was shown to contain thiophene. This impurity probably did not interfere seriously with the reaction for which the benzene was used.

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

Ether was Commercial U.S.P.

Sodium Propionate was purchased from the Fischer Scientific Co.-Eimer and Amend: C.P. S-388.

Para-chlorobenzaldehyde was a sample from the Heyden Chemical Co.

Apparatus Used

For Reactions. The apparatus in which these reactions were carried out was of two types: (1) Whenever chlore-tone was used as the alkylating agent, a three-neck flask of appropriate volume was used. To one side neck was attached a water condenser bearing a calcium chloride drying tube which led to a trap containing water for absorbing all water soluble gases liberated in the reaction. An Erlenmeyer flask containing the desired quantity of catalyst was attached to the other side neck by a rubber hose. A mercury sealed, motor driven stirrer was attached at the center neck. (2) When both reactants were liquids, the apparatus was the same except that a dropping funnel was substituted for the Erlenmeyer flask for the purpose of adding the liquid alkylating agent or a solution of the aromatic compound and dissolved chlore-tone. In such cases, the aluminum chloride was placed in the flask and covered with the aromatic compound.

For Fractionations. The apparatus consisted of a jacketed, 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 a total reflux-partial takeoff still head was attached and to the still head a fraction cutter was attached. A water aspirator was used for all pressures above 5 mm. For pressures below 5 mm, a Hy-Vac oil pump with a McLeod gauge was used. An oil bath was used as a source of heat in all fractionations.

The Reaction of Chlorobenzene and Chlorethane
in the Presence of Anhydrous Aluminum Chloride
as a Catalyst

Eight hundred eighty-eight grams (0.45 mole) of hydrated chlorethane and 1015 g (9.03 mole) of the specified chlorobenzene were added to the reaction flask. The flask and contents were then heated by an oil bath maintained at 99-103° C., stirred constantly, and 238.5 g (1.80 mole) of aluminum chloride was added slowly over a period of 2 hours and 35 minutes. After all aluminum chloride had been added, the reaction mixture was heated with stirring for one hour longer at 100° C. and then was allowed to stand undisturbed at room temperature for 16 hours.

The contents of the flask were then poured slowly with stirring into 1500 g of crushed ice containing 150 ml of concentrated hydrochloric acid. The resulting emulsion was extracted with 5000 ml of ether. However, Allen has since found that the use of such large amounts of ether for extraction can be reduced by adding more concentrated hydrochloric acid (1). After drying the ether extract over anhydrous magnesium sulfate for one hour, it was filtered and the ether removed by distillation from the steam cone. All remaining entrapped ether was next removed by subjecting the residual red liquid to a reduced pressure of a minimum of 25 mm.

This residual liquid weighing 1592 g was then divided into three portions. Only the treatment of the portion weighing 537 g will be reported herein since it is typical of the results obtained with the other two portions. The 537 g was placed in the

fractionation apparatus and subjected to reduced pressure. The flask was heated by an oil bath, and the fractions collected are listed in Table 14.

Table 14. Fractionation of the products from the reaction of chlorotone and chlorobenzene in the presence of aluminum chloride as a catalyst.

Fraction ^a :	Distilling temperature:	Pressure in Hg.:	Wt. in grams:	Identity
1	37-42	23 to 38	113.6	Crude chlorobenzene
-	61	10	4.2	Unidentified crystals ^b
5	51.7	1.0	4.1	Impure product IV ^o
6,7,8,9	51.0-51.7	1.0	32.2	Pure product IV ^d
10,11	50.3-50.5	0.8	14.7	Pure product IV ^e
12	50.5-51.0	0.8 to 1.0	6.4	Impure product V ^f
15	94.5-95.0	0.7 to 0.8	3.46	Impure product V ^g
16,17	87.5-92.0	0.5 to 0.7	20.05	Impure product V ^h
18 thru 23	88.0-92.0	0.5 to 0.7	53.45	Pure product V ⁱ
24	above 91	0.6	30.47	Unidentified tars.

- a - Intermediate fractions are not included in this table, but amounted to 148.0 grams.
- b - These crystals sublimed onto the still head. They were of such relatively small amount that they were not investigated further.
- c - The refractive index was 1.4315 at 25° C.
- d - The refractive indices of all the component cuts were the same, i.e., 1.4320 at 25° C.
- e - The refractive indices of the two cuts were 1.4321 and 1.4327 respectively at 25° C. Product IV was proven to be alpha-chloroisobutyric acid (IV).
- f - Refractive index was 1.4338 at 25° C.
- g - Refractive index was 1.5517 at 25° C.
- h - The refractive indices of the two component cuts were 1.5563 and 1.5567, respectively, at 25° C.
- i - The refractive indices of the six component cuts were 1.5578, 1.5578, 1.5580, 1.5581, 1.5581, and 1.5584, respectively, at 25° C. Product V was proven to be 3-(p-chlorophenyl)-1,1-dichloroisobutene-1 (V).

The Reaction of Chlorobenzene and 1,1,3-Trichloroisobutene-1
in the Presence of Aluminum Chloride as a Catalyst

The apparatus used for this reaction is described on page 27 under Apparatus Used for Reactions, type (1).

Forty-eight grams (0.3 mole) of 1,1,3-trichloroisobutene-1, b.p. 154-158° C. was added to 112 g (1.00 mole) of chlorobenzene contained in the reaction flask. The flask and its contents was then heated by an oil bath maintained at 100° C. The reaction mixture was constantly stirred while 48 g (0.3 mole) of aluminum chloride was added in small portions over a period of one-half hour (only 5 g or 0.037 mole was added because no more than this amount was necessary for reaction). At the end of this period, the reaction mixture was stirred and heated at 95-110° C. for one-half hour longer. The mixture was then allowed to stand undisturbed for 41 hours at room temperature.

The reaction mixture was decomposed in the usual manner, and the organic materials were extracted with ether. After removing the ether in the same way as in previous experiments, the liquid was subjected to fractionation at reduced pressure. The fractions collected are listed in Table 15 below.

The Reaction of Bromobenzene and Chlorotone in the Presence
of Aluminum Chloride as a Catalyst

The apparatus used for this reaction is described on page 27 under Apparatus Used for Reactions, type (1).

One-hundred seventy-eight grams (0.9 mole) of hydrated chlorotone and 284 g (1.81 mole) of distilled bromobenzene were added

to a 500 ml flask. The flask and its contents were then heated by an oil bath maintained at 99-102°. The reaction was stirred and 48 g (0.36 mole) of aluminum chloride was then added to the flask in small portions over a period of three hours. The reaction was then stirred and heated at 99-102° C. for one hour longer. The reaction mixture was then allowed to sit undisturbed for 19 hours at room temperature. It was then decomposed in the usual way. The organic materials were extracted with ether and the ether removed as previously described. The residual liquid was then fractionated at reduced pressure. The fractions collected are listed in Table 16.

Table 15. Fractionation of the products from the reaction of chlorobenzene and 1,1,3-trichloroisobutene-1 in the presence of aluminum chloride.

Fraction:	temperature: mm. Hg.:	Pressure:	Wt. in: grams:	Refractive index (20°):	Identity
1	55.5-59.0	65	65.77		chlorobenzene
3	crystals ^a	1.4	2.63		unidentified
6	91.5-93.5	0.65	34.16	1.5567 ^b	product V ^b
7	93.0-94.0	0.65	6.61	1.5577	product V ^c
Residue	above 94.0	0.65	6.1		unidentified tars

- a - These crystals sublimed onto the still head as noted in all other experiments also.
 b - The density was 1.180 at 20° C. as found on a Fischer Gravitometer.
 c - This product is crude.

The Reaction of Anisole and Chlorotone in the Presence of Aluminum Chloride as a Catalyst

The apparatus used in this reaction is described on page 27 under Apparatus Used for Reactions, type (1).

One hundred seventy-seven and one-half grams (0.9 mole) of hydrated chlorethane and 235 g (2.2 mole) of anisole were added to a 500 ml flask. The flask and its contents were heated by an oil bath maintained at 85-90° C. The mixture was stirred constantly and 66.3 g (0.5 mole) of aluminum chloride was then added to the flask in small portions over a period of one hour and ten minutes. The reaction mixture was stirred and heated at 83-85° C. for one hour longer.

The reaction mixture was then cooled with an ice bath, decomposed in the usual manner, and the organic materials extracted with ether. This ether extract was treated in the usual way; the ether was removed by distillation; and the residual liquid was fractionated at reduced pressure. The fractions collected are listed in Table 17.

The fraction in Table 17 having b.p. 63.5-65.0° C. (23 mm) was refractionated at atmospheric pressure through a Vigreux type bubble tower and the fractions collected are listed in Table 18. The fraction, b.p. 156-160° C. was probably 1,1,3-trichloroisobutene-1 contaminated with anisole.

Table 16. Fractionation of the products from the reaction of bromobenzene and chloretone in the presence of aluminum chloride as catalyst.

Fraction	Distilling temperature: mm. Hg.	Pressure: mm. Hg.	Wt. in: grams	Refractive index (25°):	Identity
4	34-64	3.0-3.5	2.7		Intermediate
5	61	3.3	2.32		Crystals
6,7	51.5-59.5	1.1-2.5	19.05	1.4325	Product IV
8	50.0	1.1	5.78	1.4328	Product IV
9	50.0	1.1	5.25	1.4340	Crude Product IV
11	109 - 110	1.1-1.2	7.74	1.5727	Crude Product VII
12	110	1.2	11.91	1.5770	Product VII ^a
13	110 - 110.5	1.2	13.57	1.5767	Product VII
14	110 - 111	0.9-1.0	16.40	1.5777	Product VII
Residue	above 111	0.9-1.0	21.13		Unidentified tars

a - Product VII was proven to be 3-(p-bromophenyl)-1,1-dichloro-*isobutene*-1 (VII).

Table 17. Fractionation of the products from the reaction of anisole and chlorotone in the presence of aluminum chloride as a catalyst.

Fraction	Distilling : temperature :	Pressure : mm. Hg. :	Wt. in : grams :	Refractive : index (20°) :	Identity
0	35-61	25	1.3	-	-
1	62.5-65.0	23-25	139.29	-	Anisole
2	65-72	25	26.11	-	Anisole
3	36.5-40	2.8	21.47	-	-
4 ^a	40-42	2.8	13.7	-	-
5 ^a	35-40	1.75-2.0	1.7	-	-
6	50-70	1.1	3.61	-	-
7	70-75	1.1	7.01	1.5095	Product IX ^c
8	75-81	1.1	2.52	-	-
9	81.5-108	1.1	3.35	-	-
10 ^b	110-114	1.1	9.53	1.5483	Product X ^d
11	-	-	8.87	-	-
Residue	above 114	1.1	30.95	-	-

a - White crystals sublimed and condensed in the still head and were removed with ether. The weight recorded is the weight of the liquid that distilled along with them, not weight of the crystals.

b - This is the trap liquid for the entire fractionation.

c - Product IX was proven to be alpha-chloro-phenylisobutyrate (IX).

d - Product X was proven to be 3-(p-methoxyphenyl)-1,1-dichloro-isobutene-1 (X), although quite impure.

Table 18. Refractionation of fraction 1, b.p. 62.5-65.0 (23-25 mm).

Fraction	Distilling : temperature :	Wt. in : grams :	Identity
1a	138-151	1.6	Forerun
1b	152-156	102.0	Anisole
1c	156-160	28.06	Impure (III) ^a
Residue	above 160	8.4	Hold up

a - This fraction was probably 1,1,3-trichloroisobutene-1 (III) which was contaminated with considerable anisole.

The Reaction of Anisole and 1,1,3-trichloroisobutene-1
in the Presence of Aluminum Chloride as a Catalyst

The apparatus used in this reaction is described on page 27 under Apparatus Used for Reactions, type (2).

Thirteen and four-tenths grams (0.1 mole) of aluminum chloride was added to 235 g (2.2 mole) of anisole, contained in the reaction flask. The flask and its contents were heated on an oil bath maintained at 95-105° C. and, with constant stirring, 80 g (0.5 mole) of 1,1,3-trichloroisobutene-1 (III) was added dropwise over a period of one hour and forty minutes. The reaction mixture was stirred and heated for thirty minutes at 100-103° C. The reaction mixture was then allowed to stand undisturbed for 16 hours at room temperature.

The products were decomposed in the usual manner, the organic layer drawn off, and the water layer was extracted with ether. The ether extract was combined with the organic layer and dried over anhydrous magnesium sulfate. A few days later the mixture was filtered and the ether removed by distillation. The residual liquid was then subjected to fractionation at reduced pressure. The fractions that were collected are listed in Table 19.

Table 19. Fractionation of products from reaction of 1,1,3-trichloroisobutene and anisole in the presence of aluminum chloride as a catalyst.

Fraction	:Distilling :temperature:	:Pressure: mm.	:Wt. in: Hg.:	:Refractive index (20°):	Identity
1	51-53.5	15	123.5	-	Anisole
2	50.0	15			
2	38-46	5.5-6.0	4.7	-	Intermed.
3	43.7	6.0			
3	36-38	1.3	9.85	-	Impure phenol
4	38-40	1.3	7.00	-	Pure phenol
5	61-99	1.3-1.1	4.80	-	Intermed.
6	99-105	1.1	11.16	1.5447	Crude product X ^a
7 ^b	105-105.5	1.1	21.44	1.5505	Product X
8 ^b	105-107	1.1-1.25	19.80	1.5512	Product X
9 ^b	108-110.6	1.25-1.4	8.57	1.5517	Product X ^c
10 ^b	108-108.5	1.2	9.60	1.5520	Product X ^c
Residue	Above 108.5	1.2	24.94	-	-

- a - Shown to be impure by the low value in the refractive index.
 b - The densities of these fractions at 20° C. are in order: 1.211, 1.214, 1.211, and 1.214. The densities were taken on a Fischer Gravitometer.
 c - These fractions contained traces of impurities. Product X was proven to be 3-(p-methoxyphenyl)-1,1-dichloroisobutene-1 (X).

Table 20. Refractionation of combined fractions 6, 8, 9, 10 and Residue.

Fraction	:Distilling :temperature:	:Pressure: mm.	:Wt. in: Hg.:	:Refractive index (20°):	Identity
a	72.2-80.0	0.25	2.83	-	Forerun
b	80.2-84.0	0.25	5.48	1.5490	Crude product X
c	84.5-85.0	0.25	13.41	1.5508	Product X
d	84.7-85.0	0.25	11.70	1.5510	Product X
e	85.0-88.0	0.25	3.43	1.5512	Product X
f	97.5-98.0 ^a	0.50	11.66	1.5525	Crude product X
g	95.5-130 ^a	0.45-1.6	3.20	-	Tailings
h	Above 130 ^a	1.6	13.1	-	Residue

- a - These fractions were taken using a free flame as a source of heat, in place of an oil bath as in all other cases.

The Reaction of Benzene and Chloretone in the Presence
of Aluminum Chloride as a Catalyst

The apparatus used in this reaction is described on page 27 under Apparatus Used for Reactions, type (2).

Fifty-three and six-tenths grams (0.4 mole) of aluminum chloride was added to a 500 ml flask. Then 177.5 g (0.9 mole) of hydrated chloretone was dissolved in 295 ml (259 g or 3.32 mole) of benzene. The flask was heated to 73° by an oil bath, the benzene-chloretone mixture was added slowly with constant stirring over a period of three hours and thirty minutes in a dropwise manner from a separatory funnel. The reaction mixture was next heated and stirred for one hour longer and then allowed to stand for 16 hours at room temperature.

The reaction mixture was decomposed after 16 hours by pouring it into 500 g of crushed ice containing 60 ml of concentrated hydrochloric acid. The organic layer was drawn off in a separatory funnel and the water layer was extracted with ether. The two were combined, the solution dried, filtered, and the ether removed by the standard procedure. The residual liquid was fractionated at reduced pressure and the fractions collected are listed in Table 21.

Table 21. Fractionation of products from reaction of benzene and chlorotone.

	Distilling temperature:	Pressure: mm. Hg.	Wt. in: grams	Refractive index (20°):	Identity	
3	75-76		21		Crystals	
5	59.5-60.0		0.5	11.44	1.5038	Mixture A
6	59.0-60.5		0.5	7.97	1.5173	Mixture A
7	56.0-60.0	0.3-0.5	19.57	1.5253	Mixture A	
Residue	Above 56.0		0.3	15.54		Unidentified tars

The Reaction of Benzene and 1,1,3-Trichloroisobutene-1 (III) in the Presence of Aluminum Chloride as a Catalyst

The apparatus used is described on page 27 under Apparatus Used for Reactions, type (2).

Six and five-tenths grams (0.04 mole) of aluminum chloride and 80 g of benzene were added to a 500 ml flask. This reaction mixture was stirred, and 69.8 g (0.44 mole) of (III) mixed with 33 g of benzene was added dropwise over a period of two hours. The total amount of benzene used was 1.45 mole. The oil bath was maintained at 80-85° C. After all reactants had been added, the reaction mixture was decomposed in the usual way. The organic layer was drawn off, and the water layer was extracted with ether. The two were combined, dried, filtered, and the ether and benzene removed. The residual liquid was fractionated at reduced pressure, and the fractions collected are listed in Table 22.

Table 22. Fractionation of products from reaction of benzene and (III).

Fraction:	Distilling temperature:	Pressure: mm. Hg.:	Wt. in: grams:	Refractive index (20°):	Identity
2	77-80	atm.	50.0		Benzene
3	47-80	0.5 -0.3	10.05		Intermediate
4	68-70	0.45-0.5	7.91	1.5465	Product XI ^a
5	67.0-68.5	0.25	10.87	1.5473	Product XI ^a
6	62.5	0.5	3.35	1.5462	Product XI ^b

a - These two fractions have the same density: 1.174, at 20/4° C.

b - This fraction had density of 1.175 at 20/4° C.

The Reaction of 1,1,1-Trichlor-tert-butyl Acetate and Anisole in the Presence of Aluminum Chloride as a Catalyst

The apparatus used in this reaction is described on Page 27 under Apparatus Used for Reactions, type (2).

Forty-six and seven-tenths grams (0.35 mole) of anhydrous aluminum chloride was placed in a 500 ml flask and covered with 100 ml of Skelly Solv B. Then 33 ml (0.3 mole) of anisole and 66 g (0.3 mole) of the ester of chlore-tone were mixed and diluted with 100 ml of Skelly Solv B. The oil bath was raised to 55-65° C. and the anisole-ester-Skelly Solv B mixture was added dropwise over a period of two hours. During this period the reaction mixture was stirred continuously. The water trap gained in weight by five grams and an insoluble oil, which had the odor of 1,1,1-trichloroisobutene-2, appeared upon the surface of the water in the trap. After all the reactants had been added, the reaction mixture was heated for one hour longer at room temperature. The

oil bath was then raised to 95° over a period of 15 minutes with stirring and then allowed to stand undisturbed at room temperature for 15 hours.

The reaction mixture was then decomposed in the usual manner and the organic materials were extracted with ether. After drying the ether extract over anhydrous magnesium sulfate and filtering, the ether and Skelly B were distilled off. The residual, red liquid was then fractionated at reduced pressure and the fractions collected are listed in Table 23.

Fraction 5 was refractionated through a micro Vigreux column. The fractions collected are listed in Table 24.

Table 23. Fractionation of the products from the reaction of anisole and the acetate ester of chloretono.

Fraction	Distilling temperature	Pressure mm. Hg.	Wt. in grams	Identity
1	Less than 26	2.0-2.75	18.97	Anisole
2	29-32	1.6-1.75	4.81	Ester of chloretono
3	36-37	0.75	9.57	Ester " "
4	35	0.45	19.48	Ester " "
5	71-75	0.3-0.6	20.42	Impure product ^a
6	Trap liq.	-	6.74	Anisole
Residue	Above 75	0.3	9.8	Tars

a - Impure p-methoxy acetophenone.

Table 24. Refractionation of fraction 5, b.p. 71-75° (0.3-0.6 mm).

Fraction	Distilling temperature	Pressure mm. Hg.	Wt. in grams	Identity
5-1	71-76	0.6	1.42	Forerun
5-2	83-88	0.50-0.76	4.23	Impure product ^a
5-3	88-88.5	0.5	11.24	Pure product ^b

a - This cut was probably impure p-methoxy acetophenone.

b - This cut was pure p-methoxy acetophenone and was used in proof of identity.

Alkaline Hydrolysis of 3-(p-chlorophenyl)-1,1-dichloro-isobutene-1 in an Aqueous Methanol Solution

A solution of 100 ml of water and 21.2 g (0.2 mole) of anhydrous sodium carbonate was added dropwise and with stirring to a flask containing 23.1 g (0.1 mole) of product V, b.p. 110-115° C. at 1.4 mm and 100 ml of methyl alcohol. During the addition of this solution the solution was refluxed. A white precipitate formed immediately, and carbon dioxide was liberated. The solution was refluxed 2 hours and 30 minutes after all the sodium carbonate solution had been added. The solution was then made basic to litmus and the inorganic salt filtered off. The white crystalline salt was washed with ether, the filtrate diluted with 300 ml of water and extracted with ether. The ether solution was dried, filtered, and the ether and methyl alcohol were removed by distillation. The yellow-orange liquid weighed 16.51 g and was fractionated at reduced pressure. A yellow liquid, b.p. 96.7-100° C. (0.9 mm) was obtained in 79.3 per cent yield. This

yellow liquid distilled at atmospheric pressure, b.p. 274.5-276.0° C. with no apparent decomposition, and gave no tars. Its refractive index remained constant (see Table 12, page 24).

Synthesis of p-Chloro-alpha-methyl Cinnamic Acid
from p-Chlorobenzaldehyde and Propionic Anhydride
in the Presence of Sodium Propionate as Catalyst

A 300 ml three-neck flask was set up with a condenser bearing a calcium chloride drying tube in one neck. A stirrer was placed in the center neck and a rubber stopper in the third neck. Then 42.2 g (0.3 mole) of p-chlorobenzaldehyde, 52 g (0.4 mole) of propionic anhydride, and 28.8 g (0.3 mole) of anhydrous sodium propionate were placed in the flask. After adding five drops of pyridine, the mixture was stirred constantly and heated for 41 hours by an oil bath maintained at 130-135° C.

The hot mixture was poured with stirring into 800 ml of water. The solution was neutralized with a solution of sodium carbonate and extracted with four 50 ml portions of ether to remove any unreacted aldehyde. The solution was boiled for 15 minutes with two grams of Norite and filtered while hot. The warm filtrate was added slowly, with stirring, to 1000 g of crushed ice containing 200 ml of concentrated hydrochloric acid. The white precipitate was filtered and partially dried in a vacuum desiccator for eight hours. The melting point of these crude crystals was 159.3-160.5° C. These crystals were recrystallized from alcohol and water. The acid was crystallized out in three successive crops. The melting points were:

First crop (pure white crystals, 16.7 g): m.p. 166.7-167.7° C.

Second crop (cream-colored crystals, 14.2 g): m.p. 167.0-167.7° C.

Third crop (cream-colored crystals, 10.1 g): m.p. 167-167.9° C.

The yield of pure acid based upon the p-chlorobenzaldehyde was 69.5 per cent.

Number of Experiments Carried Out

Besides the many degradations, characterization, and analytical experiments conducted in this investigation, the following synthesis experiments were carried out: Chlorobenzene with chloretone, five experiments; chlorobenzene with (III), one experiment; bromobenzene with chloretone, one experiment; anisole with chloretone, seven experiments; anisole with (III), one experiment; benzene with chloretone, one experiment; benzene with (III), two experiments; hydrolysis of product V, three experiments; para-chlorobenzaldehyde with propionic anhydride, one experiment.

SUMMARY

Table 13 contains the reactions run in this investigation along with the products and the yields resulting from the reactions.

Reaction of excess chlorobenzene with chloretone gave two compounds. One of these was also synthesized by reaction of chlorobenzene and 1,1,3-trichloroisobutene-1 (III). This compound, product V, was proved to be 3-(p-chlorophenyl)-1,1-dichloroiso-

butene-1 by carbon, hydrogen, and chlorine analyses; molecular refraction; degradation; and chemical tests. The other compound, product IV, was proved to be alpha-chloroisobutyric acid by chlorine analyses, molecular refraction, hydrolysis to alpha-hydroxyisobutyric acid, and chemical tests.

Reaction of excess bromobenzene with chloretone gave two compounds. One of these was a new compound, product VII, which was indicated to be 3-(p-bromophenyl)-1,1-dichloroisobutene-1 by carbon, hydrogen, chlorine, and bromine analyses, and by molecular refraction. The other compound was proved to be alpha-chloroisobutyric acid since it had the boiling point, refractive index, and density of this acid.

Reaction of excess anisole with chloretone gave three compounds. One of these was a new compound, product X, which was synthesized also by reaction of anisole and (III). Product X was proved to be 3-(p-methoxyphenyl)-1,1-dichloroisobutene-1 by carbon, hydrogen, and chlorine analyses; molecular refraction; degradation; and chemical tests. In addition to phenol, alpha-chloro-phenylisobutyrate was shown to result also from this reaction.

Reaction of excess benzene with chloretone gave what was believed to be a mixture of alpha-chloroisobutyric acid and 1,1-dichloro-3-phenylisobutene-1. There were no indications that the compounds which Willgerodt claimed to have isolated were present. Reaction of benzene with (III) gave a new compound, product XI, which was proved to be 1,1-dichloro-3-phenylisobutene-1 by molecular refraction and reasoning from results of the above men-

tioned reactions. Further work on mixture A will be necessary before one can state that benzene reacts with chloretone to give a new compound that is 1,1-dichloro-3-phenylisobutene-1.

Reaction of the chloretone ester of acetic acid with anisole gave p-methoxyacetophenone. This showed the three chlorines on the alcohol portion of the molecule weakens the normally difficult-to-break acyl oxygen linkage so that it breaks easier than the alcoholic oxygen linkage. Previous work (3) with esters has shown that the ease of breaking the acyl oxygen linkage preferable to the ethyl oxygen linkage in ethyl acetate depends upon the ratios of reactants to aluminum chloride used. Normally, the ethyl oxygen linkage breaks before the acyl oxygen linkage. The reverse is true when chlorines are in the alcoholic portion of the ester.

Hydrolysis of product V resulted in the formation of p-chloro-alpha-methyl cinnamaldehyde. The structure of this new compound, product VIII, was not definitely proved, but principles of organic chemistry do not indicate any other possibility. Further work will be necessary to prove the structure of this compound for it is not listed in the literature. The literature lists alpha-methyl cinnamaldehyde so that hydrolysis of product XI should give this aldehyde proving the structure of product VIII. The writer suggests that these aldehydes be tested for plant growth inhibitors.

The yields of dichlorovinyl benzenoid compounds could probably be increased by using a larger excess of aromatic compound. This would be, in effect, reducing the concentration of hydroxyl

ions that seem to be necessary for the formation of the acid. If one were to react chlorestone and aluminum chloride in a high boiling hydrocarbon such as octane, the postulated chloride isobutene should be obtained and help to substantiate the proposed mechanism.

This work indicates that a nuclear substituted chlorine, or methoxy group, activates rather than deactivates the ring to electrophilic substitution.

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A STUDY OF THE REACTIONS OF CHLORETONE AND ITS DERIVATIVES
WITH BENZENE AND SUBSTITUTED BENZENES

by

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A study of the reactions of chloretone with benzene and with substituted benzenes was undertaken (a) to investigate the manner in which chloretone reacts in a Friedel-Crafts type reaction and (b) to produce and to identify new chlorinated organic compounds which would possibly be useful insecticides. Previous workers had reported that chloretone reacted in a normal way with benzene, toluene, and p-xylene; but this investigation has given evidence to the contrary. It was shown that chloretone (1) rearranges to yield alpha-chloroisobutryl-chloride and (2) dehydrates with subsequent rearrangement to yield 1,1,3-tri-chloroisobutene-1 (III), when substituted benzenes containing a plus E or plus I group and when aluminum chloride were present. A mechanism was proposed to explain how these products were formed.

In most cases, tarry residues resulted from the fractionations of the reaction mixtures and they may possibly contain products that should result if a portion of the chloretone reacted normally. These tars might also contain polysubstituted products as well as polymerization products.

Several new compounds resulted from this work and a new synthesis of alpha-chloroisobutyric acid also resulted. This acid was found to be a by-product of all reactions that were studied involving chloretone and was obtained in conversion-yields of 33-36 per cent in the reactions between chloretone and chlorobenzene.

The new compound resulting from the reaction of chloretone and chlorobenzene in the presence of aluminum chloride was proved

to be 3(p-chlorophenyl)-1,1-dichloroisobutene-1 by carbon, hydrogen, and chlorine analyses; molecular refraction; degradation studies; and chemical tests. The compound was also synthesized by reaction of known 1,1,3-trichloroisobutene-1 with chlorobenzene in the presence of aluminum chloride.

The new compound resulting from the reaction of chlore-tone and bromobenzene in the presence of aluminum chloride was proved to be 3(p-bromophenyl)-1,1-dichloroisobutene-1 by quantitative carbon, hydrogen, chlorine, and bromine analyses; and by molecular refraction.

The new compound resulting from the reaction of anisole and chlore-tone in the presence of aluminum chloride was proved to be 3(p-methoxyphenyl)-1,1-dichloroisobutene-1 by carbon, hydrogen, and chlorine analyses; molecular refraction; degradation studies; and chemical tests. The compound was also synthesized by reaction of known 1,1,3-trichloroisobutene-1 with anisole in the presence of aluminum chloride.

The new compound resulting from the reaction of benzene and 1,1,3-trichloroisobutene-1 in the presence of aluminum chloride was assumed to be 1,1-dichloro-3-phenylisobutene-1 because the molecular refraction checked with the theoretical and because of previous results from the analogous reactions mentioned above. A mixture of what was believed to be alpha-chloroisobutyric acid and 1,1-dichloro-3-phenylisobutene-1 was obtained from the reaction of chlore-tone and benzene in the presence of aluminum chloride.

Hydrolysis of 3(p-chlorophenyl)-1,1-dichloroisobutene with base yielded an aldehyde believed to be p-chloro-alpha-methyl cinnamaldehyde. Thus a new method of synthesizing nuclear substituted alpha-methyl cinnamaldehydes was discovered.

The reaction of chloretone ester of acetic acid and anisole in the presence of aluminum chloride gave a 45.5 per cent conversion yield of p-methoxyacetophenone. This result showed that the acyl oxygen linkage breaks easily, which is not the case when a trichloromethyl group is absent in the alcoholic portion of an ester. This phenomenon can be attributed to the inductive effect of the chlorines which probably draw the oxygen closer to the adjacent carbon, thus lengthening the acyl oxygen linkage. This would weaken the acyl oxygen linkage and strengthen the alcoholic oxygen linkage.