

A STUDY OF REACTIONS OF TRICHLORO-TERT-BUTYL-ALCOHOL  
WITH A HALOBENZENE, HYDROXYBENZENE, AND AN  
AMINO BENZENE

by

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TABLE OF CONTENTS

INTRODUCTION .....	1
EXPERIMENTAL .....	6
Apparatus Used .....	6
Procedure .....	6
Preparation of Para-tert-butyl Phenol (IV) .....	6
Synthesis of $\beta, \beta, \beta$ -Trichloro-tert-butyl Phenyl Ether (V) .....	8
Synthesis of 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI) .....	9
Preparation of $\alpha$ -phenoxyisobutyric Acid (VII) .....	10
Synthesis of the Postulated 1-Chloro-2-methyl-5-hydroxy-indene (VIII) .....	12
Rearrangement of $\beta, \beta, \beta$ -Trichloro-tert-butyl Phenyl Ether to the Postulated Product, (VIII) ..	14
Other Attempted Rearrangements of $\beta, \beta, \beta$ -Trichloro-tert-butyl Phenyl Ether .....	15
Reaction of $\beta, \beta, \beta$ -Trichloro-tert-butyl Alcohol with N-N-Dimethyl Aniline .....	20
Reaction of $\beta, \beta, \beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Zinc Chloride as Condensing Agent .....	21
Reaction of $\beta, \beta, \beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Aluminum Chloride as Condensing Agent .....	22
Other Reactions of $\beta, \beta, \beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Aluminum Chloride as Condensing Agent .....	25
Reaction of $\beta, \beta, \beta$ -Trichloro-tert-butyl Chloride and Chlorobenzene Using Aluminum Chloride as Condensing Agent .....	25

DISCUSSION .....	26
SUMMARY .....	40
ACKNOWLEDGMENTS .....	42
LITERATURE CITED .....	43

## INTRODUCTION

An intensive search for new synthetic organic insecticides has been under way extensively for the past decade, and is necessarily continuing. The discovery of D. D. T. gave great impetus to this search.

The library and laboratory investigations that were recorded for this thesis were undertaken for the purpose of obtaining and studying:

(a) the electronic effects of three chlorines on one carbon in  $\beta, \beta, \beta$ -trichloro-tert-butyl alcohol (I) as compared to tert-butyl alcohol in its reactions with phenol, the halobenzenes, and the anilines,

(b) the actual compounds produced from reactions of trichloro-tert-butyl alcohol (I) with phenol, chlorobenzene, and N-dimethyl aniline,

(c) provision of the new compounds formed for testing as insecticides, fungicides, and pesticidal agents.

The question in each case was whether the reaction would take place between the hydroxyl group of (I) and a hydrogen extracted from the aromatic compound in a dehydration type reaction, or whether one of the chlorines on (I) would react with the aromatic compound in a Friedel-Crafts reaction, or whether some hitherto unheard of type of reaction would occur. Since a concentration of three chlorines on one carbon tends to make the chlorines relatively inert, the first mechanism appeared to be a

possibility likely to occur. Other reaction-paths, however, were not excluded. If the reaction went according to the mechanism postulated, the products obtained would be analogous to the products obtained by the reaction of tert-butyl alcohol with the same aromatic compounds.

It is well known that para-tert-butyl phenol has insecticidal and other toxic qualities. Thus it seemed likely that  $\beta,\beta,\beta$ -trichloro-tert-butyl phenol with an added high concentration of bunched chlorine atoms therein, but with otherwise the same essential type of structure, would have even more potentialities for many of the purposes for which para-tert-butyl phenol is used.

In the writer's exhaustive search and reported survey of the literature (12), it was found that reactions of (I) with phenol, the halobenzenes, and the anilines had never been reported previously. On the other hand, several methods had been used successfully for the arylation of tert-butyl alcohol (II) where, in the process, the alcoholic hydroxyl had been eliminated in the form of water and a carbon-to-carbon link established with the aryl ring. It was felt that one or more of these methods might be utilized for similar arylations of (I). From the writer's written survey of the literature (12), it was made evident that the tert-butyl group was introduced into the aryl compounds by a variety of methods. It was introduced by means of tert-butyl alcohol, isobutyl alcohol, isobutylene, or by rearrangement of a mixed aryl-alkyl ether. A list of the condensation catalysts

used would include: ferric chloride, aluminum chloride, zinc chloride, sulfuric acid, phosphoric acid, hydrogen fluoride, boric acid, oxalic acid, perchloric acid, chlorosulfonic acid, potassium hydroxide, and hydrogen chloride. A few reactions using heat and pressure without a catalyst have also been reported (12).

After a critical evaluation of all the methods reported in the syntheses of para-tert-butyl phenol (III), aluminum chloride and zinc chloride were chosen as the most promising condensation-agents for causing synthesis of para ( $\beta$ ,  $\beta$ ,  $\beta$ -trichloro-tert-butyl) phenol from the corresponding tertiary alcohol and phenol. Natelson (8) reported a yield of 90 percent of para-tert-butyl phenol (III) using sulfuric acid as a condensing agent, but later experiments by Ipatieff, Pines, and Friedman (6) showed that Natelson had misinterpreted his results and that practically none of (III) was formed by this method. Simons and Hart (10) obtained a 90 percent yield using hydrogen chloride under moderate temperature and pressure, but the inherent difficulties of working under pressure, and the lengthy reaction time more than offset the advantages of the high yield. Tsukervanik and Nazarova (16) reported 75 percent yield when phenol and (II) were condensed via aluminum chloride as catalyst in petroleum ether. When isobutyl alcohol was used (17), the yield was increased to 82 percent. Huston and Hsieh (5) at about the same time in the United States developed a method which gave 45-60 percent yields of III. This method was very similar to the one developed by

Tsukervanik and Nazarova. Smith (11) prepared isobutyl phenyl ether and tert-butyl phenyl ether (IV) by the Williamson synthesis and subsequently rearranged these ethers by the use of aluminum chloride to III. Yields were always in excess of 50 percent. McGreal and Niederl (7), using the Liebmann method of condensing alcohols with phenols in the presence of zinc chloride obtained 40-80 percent yields of III. They also applied this method with success to aromatic alcohols.

Due to the large concentration of chlorine and the nature of the structure in I, it has in part a tendency toward aromatic properties. This indicates that it, too, might react along the lines of the aromatic alcohols as indicated above.

Condensations of halobenzenes with tert-butyl alcohol have been less extensively investigated than the corresponding condensation of II with phenol. This situation exists for two reasons: (a) para-tert-butyl phenol has extensive commercial values, while para-tert-butyl phenyl halide has no practical commercial value at present and is primarily of research interest, and (b), the hydroxyl group confers much more activation on the benzene ring than does a halogen such as chlorine or bromine. Therefore, the probability of a successful reaction giving a high yield is much greater with phenol.

In 1906, Boedther (2) claimed that para-bromo-tert-butyl benzene would never be synthesized in any appreciable yield because his investigations indicated that bromine in the nucleus interfered with straight alkylation. Tsukervanik (14), in his

investigations of the condensations of halobenzenes showed that Boedther's conclusions were in error. Bromobenzene and chlorobenzene gave substantially the same yields (30 percent) of the para-tert-butyl phenyl halide when phosphoric acid was used as a condensing agent (15). Tsukervanik also investigated the use of aluminum chloride (14), and zinc chloride (13) as condensing agents for this reaction. He found that both gave approximately the same yields (65 percent).

During World War II, the Chemical Warfare Service found that chlorosulfonic acid was a good condensing agent in the synthesis of D. D. T. Rueggberg, Cushing, and Cook (9) adopted the procedure for the preparation of para-tert-butyl phenyl chloride, but found that they could not obtain any yields higher than 25 percent.

These experiments indicated that aluminum chloride or zinc chloride would probably be best for the condensation of I with chlorobenzene.

The reaction of  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol (I) with dimethyl aniline was also contemplated. A survey of the literature (12) showed that isobutyl alcohol and aniline had been condensed to give para-tert-butyl aniline. While there was considerable doubt whether the reaction could be accomplished without protecting the amino group by acetylation, it was decided that the analogous reaction with N-dimethyl aniline and trichloro-tert-butyl alcohol was worthy of investigation.

The condensations of trichloro-tert-butyl alcohol, as indi-

cated above, with phenol, with chlorobenzene, and with N-dimethyl aniline, respectively, appeared to be of interest to chemists for the contributions which reaction-studies thereon would make to fundamental organic chemistry, and for the possibility that successful synthesis of these compounds or unexpected other new products might serve as a basis for further investigation of the kind of reactions discovered, or established by analogy.

## EXPERIMENTAL

### Apparatus Used

The apparatus used in the reactions recorded here consisted essentially of a 500 ml three-necked flask fitted with a mechanical stirrer, an air condenser to which was attached a calcium chloride drying tube and a water trap for hydrogen chloride fumes, and a thermometer that was extended into the reaction mixture. Additionally, the third neck was fitted with a large rubber tube attached to an Erlenmeyer flask which contained a desired solid catalyst for gradual addition of this solid. A Glascol heating jacket served as a source of heat for those reactions which were carried out above room temperature.

### Procedure

Preparation of Para-tert-butyl Phenol.(III). The principal conditions and molar relationships employed, were:

Phenol .....	0.5 mole
Tert-butyl alcohol .....	0.5 mole

Anhyd. aluminum chloride .....	0.25 mole
Petroleum ether (B. p. 70°) (Skelly-Solve-B) .....	200 ml
Time .....	1.5 hours
Temperature .....	25-30°C.

To a solution of 47 g of phenol, 37 g of tert-butyl alcohol and 200 ml of said petroleum ether in the reaction flask, there was added 55.4 g of anhydrous aluminum chloride over a period of one hour with constant stirring. Upon initial addition of the aluminum chloride, hydrogen chloride was evolved. With the addition of more aluminum chloride, a dark-red, pasty mass formed at the bottom of the reaction vessel together with an increase in temperature and more evolution of hydrogen chloride. The temperature was controlled by the use of an ice bath. After all the aluminum chloride had been added, the stirring was continued for another 30 minutes, and the reaction mixture allowed to stand overnight at room temperature. The red-pasty mass and entire contents were removed from the reaction vessel, and decomposed by transferring gradually with stirring into a mixture of 300 g of ice and 25 ml of concentrated aqueous hydrogen chloride. A reddish-orange crystalline product settled out and was extracted with three portions of ether (100 ml each). The ether extractions were combined, and dried overnight over 25-30 g of anhydrous potassium carbonate. The ether solution of the product was filtered and then the ether was removed by distillation on a steam bath. The residue was distilled at reduced pressure through a Vigreux column (30 cm in length, two cm in diameter).

There was obtained 26.7 g (36.4 percent of theoretical) of a golden yellow oil, boiling point 136-138° at 25 mm of Hg, which crystallized in the receiver. The product, melting point 93-94°, was recrystallized from petroleum ether and then had a melting point of 97-98°. This confirmed the work of Huston and Hsieh (5).

Synthesis of  $\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether (V).

The principal conditions and molar relationships employed, were:

Phenol .....	0.5 mole
$\beta,\beta$ -Trichloro-tert-butyl alcohol ..	0.5 mole
Anhyd. aluminum chloride .....	0.25 mole
Petroleum ether (B. p. 70°C.) .....	200 ml
Time .....	1.5 hours
Temperature .....	25-30°C.

To a solution of 47 g of phenol, 83.8 g of trichloro-tert-butyl alcohol and 200 ml of petroleum ether in the reaction flask, there was added 33.4 g of anhydrous aluminum chloride over a period of one hour with constant stirring. Upon initial addition of the aluminum chloride, the reaction mixture turned milky white and hydrogen chloride was evolved. After about four-fifths of the aluminum chloride had been added, the reaction mixture, which had been a faint peach color, gave a yellow oil. This separated to the bottom of the flask. Hydrogen chloride was evolved throughout the reaction. After all the aluminum chloride was added, the stirring was continued for another 30 minutes and the reaction mixture allowed to stand overnight at

room temperature. The reaction products were decomposed by pouring the reaction mixture slowly with stirring into a mixture of 400 g of ice and 25 ml of concentrated aqueous hydrogen chloride. A white crystalline product was precipitated. The organic products were extracted with three portions of ether (100 ml each). The ether extracts were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution was filtered, and then ether was removed by distillation on a steam bath. The light yellow liquid residue was distilled at reduced pressure through a Vigreux column (30 cm in length, two cm in diameter). There was obtained 119.1 g (94.1 percent) of a colorless oil, boiling point 75-78° at 15 mm of Hg. This oil solidified on standing, melting at 34.5-35.5°, b. p. 173-174° at atmospheric pressure. This synthesis was repeated three times and gave yields of 87.7, 93.9, and 94.5 percent. The product gave a negative alcoholic silver nitrate test for halogens and a negative permanganate test for unsaturation.

This new product was split with hydrogen iodide giving a brown oil which was not characterized and a derivative identified as phenol, melting point 38.5-39.5°. The brown oil had an odor strongly reminiscent of iodoform.

Analysis: Calculated for  $C_{10}H_{11}OCl_3$  ( $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V): Cl, 42.0. Found: Cl, 40.3, 40.5.

Synthesis of 1,1-dichloro-2-methyl-3-phenoxy-propene-1 (VI).

When attempts were made to purify the several samples of V by distillation, it was noted that it was impossible to obtain the total reduction in pressure that the tested apparatus was capable

of when connected to the water pump. The system acted as if a gas was being evolved. During each distillation of a sample of V, after a time the gas ceased being evolved, the vacuum pressure then went down to the water pump pressure, and there then distilled a new product having the constant narrow boiling-point ranges under pressures as follows:

boiling point 81-82° at 18 mm of Hg,

boiling point 74-77° at 12 mm of Hg,

boiling point 76-82° at 16 mm of Hg.

Three successive fractionations of V through a six-inch glass-helices packed column to obtain an analytically pure sample resulted in obtaining apparently analytically pure 1,1-dichloro-2-methyl-3-phenoxy-propene-1 (VI). The analytical sample boiled at 76-78°C. at 15 mm of Hg, and also had a boiling point 173-174°C. at atmospheric pressure. The density ( $D_4^{20}$ ) was 1.270 and the refractive index ( $n^{40}$ ) was 1.5126.

Analysis: Calculated for  $C_{10}H_{10}OCl_2$ ; Cl, 32.8. Found; Cl, 32.8.

Preparation of Alpha-phenoxy Isobutyric Acid (VII). The principal conditions and molar relationships were as follows:

Mixture of V and VI .....	0.039 mole
Potassium hydroxide .....	0.277 mole
Diethylene glycol .....	125 ml
Time .....	18 hours
Temperature .....	134-137°C.

A mixture of 125 ml of diethylene glycol and 10 g of a prod-

uet mixture consisting of  $\beta,\beta,\beta$ -trichloro-tert-butyl-phenyl ether (V) and 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI) obtained by two distillations of a preparation of V, was placed in a 300 ml three-necked flask fitted with a mechanical stirrer, reflux condenser, and a thermometer. To the mixture was added a solution of 16.1 g of potassium hydroxide in 8.8 ml of water. The mixture was stirred and refluxed for 18 hours at such a rate that the temperature was maintained at 134-137°. The mixture was allowed to cool with vigorous stirring and then was poured into 250 ml of cold water. The filtrate from the latter mixture was then boiled gently for five minutes with 0.3 g of Norite, the carbon was removed, the filtrate was acidified to litmus with 20 percent sulfuric acid and then an additional five ml of acid added. Three-quarters of the water was evaporated off under reduced pressure, and the remainder was made basic to litmus with sodium hydroxide. The diethylene glycol was extracted with ether, and the remainder of the solution was acidified with 20 percent sulfuric acid. The acidified solution was extracted with five portions of ether (75 ml each), and the ether was removed by distillation on a steam bath. The resultant oil was taken up with 15 ml of boiling 95 percent alcohol and filtered. Water was added to the filtrate until it just became turbid. The solution was cooled to 0°, and a light brown crystalline compound (0.270 g, 3.25 percent) (VII) was removed by suction filtration. The melting point was 93-95°.

After recrystallization from alcohol and water, the melting point was 95-97°. Bergellini (1) reported a melting point of 98-99° for  $\alpha$ -phenoxyisobutyric acid. The neutralization equivalent calculated for  $\alpha$ -phenoxyisobutyric acid ( $C_{10}H_{12}O_3$ ) was 180; that found was 183.5.

Synthesis of the Postulated 1-Chloro-2-methyl-5-hydroxyindene (VIII). The principal conditions and molar relationships were as follows:

Phenol .....	0.5 mole
$\beta,\beta,\beta$ -Trichloro-tert-butyl alcohol..	0.5 mole
Aluminum chloride .....	0.75 mole
Petroleum ether (B. p. 70°) .....	200 ml
Time .....	7 hours
Temperature .....	25-30°C.

A mixture of 47 g of phenol and 88.8 g of  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol was dissolved in 200 ml of petroleum ether in the reaction flask and then 100.2 g of aluminum chloride were added to the reaction mixture over a period of two hours with constant mechanical stirring. Approximately one-third of the aluminum chloride was added in the first hour and the remainder was added in the second hour. After all the aluminum chloride had been added, the reaction mixture was a golden yellow color. After five hours of further stirring, with increased evolution of hydrogen chloride, the reaction mixture was dark red. After standing overnight at room temperature, the reaction products were decomposed by transferring the reaction mixture slowly with stir-

ring into a mixture of 500 g of ice and 50 ml of concentrated aqueous hydrogen chloride. The organic matter was extracted with four portions of ether (100 ml each). The ether extracts were combined, and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution was filtered, the ether removed by heating on a steam bath, and the residue distilled at reduced pressure. Thereupon, 30.4 g of a colorless oil was obtained over a 30 degree temperature range with fluctuating pressure due to evolution of a gas, and a second fraction consisting of a cherry-red, viscous material was obtained with increasing decomposition and rise in temperature. Redistillation of the first fraction gave about 15 g (7 percent) of 1,1-dichloro-2-methyl-3-phenoxypropene-1, and 15.3 g (12.9 percent of theoretical) of VIII, a colorless oil, boiling point 93-96° at one mm. The boiling point was 225° at atmospheric pressure, the density ( $D_4^{20}$ ) was 1.169, and the refractive index ( $n_D^{20}$ ) was 1.5139. The compound gave: (a) a positive ferric chloride test characteristic of a phenolic hydroxyl, (b) a delayed, weakly positive alcoholic silver nitrate test for halogens, (c) a negative bromine in carbon tetrachloride test for unsaturation, and (d) a negative permanganate test for unsaturation in the cold. Warming slightly gave a positive permanganate test characteristic of a phenol type ring. In (b) it was particularly noted that only a turbidity due to silver chloride was obtained even after about a minute of reaction with saturated alcoholic silver nitrate. When the compound (VIII) was oxidized with fuming nitric acid, the

phenolic ring portion was broken up and additionally a compound believed to be acetone was obtained. This compound gave a strong positive iodoform test. The compound (VIII) gave a turbid solution in 5 percent sodium hydroxide and a white precipitate in 30 percent sodium hydroxide.

The mechanism postulated (see Discussion section) indicated the compound was 1-chloro-2-methyl-5-hydroxy indene (VIII). An alternative, based only on quantitative chlorine content and some of the characterization tests, but not on a plausible mechanism, indicated that the structure of 1,1-dimethyl-2-chloro-2-para-hydroxyphenyl ethylene was a possibility.

Analysis calculated for  $C_{10}H_{11}OCl$  (1,1-dimethyl-2-chloro-2-para-hydroxyphenyl ethylene): Cl, 19.5. Found: Cl, 19.58.

Analysis calculated for the postulated  $C_{10}H_9OCl$  (1-chloro-2-methyl-5-hydroxy indene)(VIII): Cl, 19.66. Found: Cl, 19.58.

Rearrangement of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether to the Postulated Product (VIII). The principal conditions and molar relationships were as follows:

$\beta,\beta,\beta$ -Trichloro-tert-butyl phenyl ether <sup>1</sup> .....	0.214 mole
Anhyd. aluminum chloride .....	0.204 mole
Time .....	2.5 hours
Temperature .....	60-70°C.

To 54.5 g of said  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether placed

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<sup>1</sup> Nearly pure as obtained in the earlier experiment.

in the reaction flask, 27.3 g of aluminum chloride were added over a period of one hour with constant mechanical stirring. When all the aluminum chloride had been added, the reaction mixture was reddish-orange. After one and one-half hours of further stirring, the reaction mixture was dark red. Hydrogen chloride was evolved throughout the course of the reaction. The reaction-products were then decomposed by transferring the reaction mixture slowly with stirring into a mixture of 200 g of ice and 20 ml of concentrated aqueous hydrogen chloride. The organic material was extracted with three portions of ether (100 ml each). The ether extracts were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution was filtered, the ether removed by distillation on a steam bath, and the residual liquid was distilled at reduced pressure. 1,1-Dichloro-2-methyl-3-phenoxy propene-1 (10.7 g, 19.7 percent of theoretical) was obtained along with a colorless, oily compound (six g, 11 percent of theoretical) boiling at 102-105° at two mm and giving a positive ferric chloride test characteristic of a phenolic hydroxyl. This compound was identical with the compound prepared in the one-step synthesis (boiling at 93-96° at one mm) and therefore was believed to be 1-chloro-2-methyl-5-hydroxyindene (VIII).

Other Attempted Rearrangements of  $\alpha,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether:

a.  $\alpha,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether Refluxed at Atmospheric Pressure.  $\alpha,\beta,\beta$ -Trichloro-tert-butyl phenyl ether

(V)(25 g) was refluxed for 24 hours. The gas given off during reflux was hydrogen chloride and was passed into a solution of silver nitrate. An immediate precipitate of silver chloride was obtained, proving the gas to be hydrogen chloride. The boiling point at atmospheric pressure of the rearranged product after the refluxing was substantially the same as for the initial starting material. The product was cooled and distilled at reduced pressure. The material recovered was believed to be 1,1-dichloro-2-methyl-3-phenoxypropene-1 since it had a boiling point of  $77-82^{\circ}$  at 14 mm of Hg. The two g residue was insufficient for distillation and characterization.

b.  $\beta,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether Treated with an Equal Weight of Aluminum Chloride. The principal conditions and molar relationships employed were:

$\beta,\beta,\beta$ -Trichloro-tert-butyl phenyl ether .....	0.105 mole
Anhyd. aluminum chloride .....	0.185 mole
Time .....	2 hours
Temperature .....	$25-30^{\circ}$ (Initial)

To 25 g of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether in the reaction vessel, there was added 25 g of anhydrous aluminum chloride over a period of one hour with external cooling and constant stirring. Upon the addition of aluminum chloride, hydrogen chloride was evolved. When all the aluminum chloride had been added, the reaction mixture was dark red. The stirring was continued for one hour, with the reaction vessel immersed in an ice-salt bath. The reaction mixture was immediately decomposed by transferring the

reaction mixture gradually with stirring into a mixture of 300 g of ice and 30 ml of concentrated hydrogen chloride immersed in an ice-salt bath. More ice was added as the heat of decomposition dissolved the ice. A large amount of hydrogen chloride fumes were evolved as the reaction mixture was decomposed. The product of the decomposition was dark red and crystalline in appearance. This product was extracted with three portions of ether (100 ml each). The ether extractions were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution of the product was filtered, and the ether removed by distillation on a steam bath. The resulting dark red, heavy, viscous material was distilled at reduced pressure through an electrically heated column (16 cm long and 1.5 cm in diameter) packed with glass helices. There was obtained 6.4 g of a colorless oil, boiling point 103-107° at 56 mm. This compound was believed to be 1,1-dichloro-2-methyl-3-phenoxypropene-1. The second fraction was 4.6 g of a cherry-red, viscous material obtained with increasing decomposition and rise in temperature. A residue (10 g) remained in the distilling flask after the distillation.

c.  $\beta,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether (V) Treated with Aluminum Chloride in Petroleum Ether. The principal conditions and molar relationships employed were:

$\beta,\beta,\beta$ -Trichloro-tert-butyl phenyl ether .....	0.16 mole
Anhyd. aluminum chloride .....	0.25 mole
Petroleum ether (B. p. 70°) (Skelly-Solv-B) .....	125 ml

Time ..... 17 hours

Temperature ..... 25-30°C.

To a solution of 40.5 g of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether and 125 ml of petroleum ether, there was added 33.4 g of anhydrous aluminum chloride over a period of one-half hour with constant stirring. After all the aluminum chloride was added, the stirring was continued for 17 hours. The color of the reaction mixture at this time was deep orange. The reaction products were decomposed by transferring the reaction mixture gradually with stirring into a mixture of 300 g of ice and 30 ml of concentrated aqueous hydrogen chloride. A red, crystalline product was precipitated and extracted with three portions of ether (100 ml each). The ether extractions were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution of the product was filtered, and the ether removed by distillation on a steam bath. The residue was distilled at reduced pressure through an electrically heated column (16 cm long and 1.5 cm in diameter) containing glass helices. There was obtained 30.9 g of a colorless oil, boiling point 75-79° at 14 mm of Hg, which was believed to be 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI) in view of all other data. A residue (5.5 g) was left in the distilling flask. During the course of the reaction, 4.1 g of material was lost. If all the hydrogen chloride were accounted for, 5.8 g of material would have been lost. Thus, the amount lost accounts for 71 percent of the hydrogen chloride theoretically lost in the reaction.

d.  $\beta,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether and Aluminum Chloride at 100°C. The principal conditions and molar relationships employed were:

$\beta,\beta,\beta$ -Trichloro-tert-butyl phenyl ether .....	0.19 mole
Anhyd. aluminum chloride .....	0.16 mole
Time .....	2 hours
Temperature .....	100°C.

To 47 g of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether in the reaction vessel at 55°, there was added 21.4 g of anhydrous aluminum chloride over a period of one hour with constant stirring. When all the aluminum chloride had been added, the color of the reaction mixture was deep orange. After stirring for another hour, the color had changed to reddish-orange. The temperature of the reaction mixture was raised to 100°. Hydrogen chloride was violently evolved, and the reaction mixture was quickly converted to a hard tar-like material which could not be decomposed by a mixture of ice and hydrogen chloride.

e.  $\beta,\beta,\beta$ -Trichloro-tert-butyl Phenyl Ether and Aluminum Chloride at 55°. The principal conditions and molar relationships employed were:

$\beta,\beta,\beta$ -Trichloro-tert-butyl phenyl ether .....	0.437 mole
Anhyd. aluminum chloride .....	0.385 mole
Time .....	2 hours
Temperature .....	55°

To 110.6 g of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether in the re-

action vessel, there was added 51.3 g of anhydrous aluminum chloride over a period of one hour with constant stirring. The color of the reaction mixture at this time was deep orange. The stirring was continued for another hour and the reaction products then were decomposed by transferring the reaction mixture slowly with stirring to a mixture of 300 g of ice and 30 ml of concentrated hydrogen chloride. The organic precipitate was extracted with three portions of ether (100 ml each). The ether extractions were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution of the product was filtered, and the ether removed by distillation on a steam bath. The residue was distilled at reduced pressure through an electrically heated column (16 cm long, and 1.5 cm in diameter) containing glass helices. There was obtained 52 g (42 percent) of a colorless oil, boiling at 58-60° at 0.5 mm, and 13.9 g of a colorless oil, boiling at 62-90° at 0.5 mm. The major fraction, according to boiling point, was 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI), and was logical in view of all of the experiments.

Reaction of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Alcohol with N,N-Dimethyl Aniline. The principal conditions and molar relationships were as follows:

$\beta,\beta,\beta$ -Trichloro-tert-butyl alcohol .....	0.5 mole
N,N-Dimethyl aniline .....	0.5 mole
Anhyd. aluminum chloride .....	0.25 mole
Petroleum ether (B. p. 70°) .....	300 ml

Time ..... 2 hours

Temperature ..... 25-30°C.

To a solution of 60.6 g of dimethyl aniline (boiling point 190-193°C.) and 88.8 g of trichloro-tert-butyl alcohol in 200 ml of petroleum ether, there was added 33.4 g of aluminum chloride over a period of one hour, with constant mechanical stirring. After all the aluminum chloride had been added, the stirring was continued for another hour, and the reaction mixture was allowed to stand overnight at room temperature. The reaction products were decomposed by introducing the reaction mixture slowly with stirring into 300 g of ice and 30 ml of concentrated aqueous hydrogen chloride. The organic products were extracted with three portions of ether (100 ml each). The ether extracts were combined and dried over 25-30 g of anhydrous magnesium sulfate for 30 minutes. The ether solution was filtered, the ether removed on a steam bath, and the oily residue distilled at reduced pressure. The trichloro-tert-butyl alcohol (73.4 g, 82.5 percent) was recovered in the distillation. No products were found in the ether extract. After the ether extraction, the aqueous solution was made basic to litmus. A yellow, oily layer formed on top, which was separated and identified as the unreacted dimethyl aniline.

Reaction of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Zinc Chloride as Condensing Agent. The principal conditions and molar relationships were as follows:

$\beta,\beta,\beta$ -Trichloro-tert-butyl alcohol .....	0.075 mole
Chlorobenzene .....	0.075 mole
Zinc chloride (anhyd.) .....	0.05 mole
Time .....	3 hours

A solution of 8.4 g of chlorobenzene and 12.3 g of trichloro-tert-butyl alcohol was refluxed over 6.8 g of anhydrous, powdered zinc chloride for three hours. A small amount of hydrogen chloride was given off during the reaction. The reaction mixture was allowed to cool and stand overnight at room temperature. The reaction products were decomposed by introducing the reaction mixture into 300 ml of water and 30 ml of concentrated hydrogen chloride. The insoluble organic products were separated and dissolved in 200 ml of ether. The ether solution was dried over 25-30 g of anhydrous potassium carbonate, filtered, and the ether removed by distillation on a steam bath. The oily residue was distilled. Three fractions were obtained. The first fraction (boiling point 130-140°) was practically all chlorobenzene. The second fraction (boiling point 140-150°) was a mixture of chlorobenzene and trichloro-tert-butyl alcohol. The third fraction (boiling point 160-182°) was mainly trichloro-tert-butyl alcohol. There probably was a small amount of reaction product in the third fraction, but it was so small that it could not be isolated.

Reaction of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Aluminum Chloride as Condensing Agent. The principal conditions and molar relationships were as follows:

$\beta,\beta,\beta$ -Trichloro-tert-butyl alcohol .....	1.5 moles
Chlorobenzene .....	2.66 moles
Anhyd. aluminum chloride .....	0.53 mole
Time .....	2 hours
Temperature .....	100°C.

Trichloro-tert-butyl alcohol (266.5 g) was dissolved in 309.4 g of chlorobenzene, the excess chlorobenzene acting as a solvent. Then 70.7 g of anhydrous aluminum chloride were added to the reaction mixture over a period of one hour with constant stirring while heating in a boiling water bath. After all the aluminum chloride had been added, the color of the reaction mixture was reddish-orange. The stirring was then continued for another hour, the reaction mixture cooled, and allowed to stand overnight at room temperature. The reaction products were then decomposed by pouring the reaction mixture slowly with stirring into a mixture of 300 g of ice and 25 ml of concentrated hydrogen chloride. The organic products were extracted with three portions of ether (100 ml each). The ether extracts were combined and dried over 25-30 g of anhydrous magnesium sulfate. The ether solution was filtered, the ether removed on a steam bath, and the oily residue distilled at reduced pressure. The excess chlorobenzene was distilled and amounted to 175.6 g, boiling point 85-87° at 143 mm. A second fraction, 11.6 g, boiling point 90-95° at 143 mm gave a positive permanganate test for unsaturation. The remainder of the reaction mixture was then distilled, giving 59.3 g (20.4 percent based on chlorobenzene used) of a new product as a

colorless oil, boiling point  $72-74^{\circ}$  at 1.5 mm, which solidified on standing. The melting point was  $30^{\circ}$ , the boiling point  $181^{\circ}$  at atmospheric pressure, the density ( $D_4^{20}$ ) 1.209 and the refractive index ( $n_D^{40}$ ) 1.4319. On the new product, the alcoholic silver nitrate test was positive, bromine in carbon tetrachloride and the permanganate tests were negative. The compound was insoluble in 5 percent sodium hydroxide solution. The compound, although insoluble in Lucas reagent, gave a turbid lower layer, indicating that a tertiary hydroxyl group might be present. A mechanism was postulated that the compound was 2-hydroxy-2-methyl-3,3-dichloro-dihydroindene (IX). A higher boiling product, 56.4 g (12.6 percent based on chlorobenzene used) of a colorless oil, boiling point  $120-124^{\circ}$  at 1.5 mm was also isolated. The boiling point was  $217^{\circ}$  with decomposition at atmospheric pressure. The density was 1.330 ( $D_4^{20}$ ), and the refractive index ( $n_D^{20}$ ) was 1.5600. On the latter, the alcoholic silver nitrate test was positive, bromine in carbon tetrachloride and permanganate tests were negative. The compound was insoluble in 5 percent sodium hydroxide. A mechanism was postulated that the compound was 2-hydroxy-2-methyl-3,3-dichloro-5(1,1-dichloro-2-hydroxy-2-methyl propyl)dihydro indene (X).

Analysis calculated for  $C_{10}H_{10}OCl_2$  (IX): Cl, 32.8. Found: Cl, 33.6, 33.75.

Analysis calculated for  $C_{14}H_{16}O_2Cl_4$  (X): Cl, 44.2. Found: Cl, 44.5, 44.6.

Other Reactions of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Alcohol and Chlorobenzene Using Aluminum Chloride as Condensing Agent.

1. The conditions and molar relationships used, were the same as for the reaction between trichloro-tert-butyl alcohol and chlorobenzene at  $100^{\circ}$  except that the temperature was reduced to  $50^{\circ}\text{C}$ . The color of the reaction mixture after the reaction was completed was yellowish-orange instead of the dark, reddish-orange obtained when the reaction was run at  $100^{\circ}$ . Upon distillation, only the starting products were recovered.

2. The conditions and molar relationships used were the same as for the reaction between trichloro-tert-butyl alcohol and chlorobenzene at  $100^{\circ}$  except that the temperature was reduced to  $85^{\circ}$ . Distillation through a six inch, electrically heated column packed with glass helices gave 14.8 g (5.04 percent) of a colorless oil, boiling point  $69-75^{\circ}$  at one mm, and 9.2 g (2.06 percent) of a colorless oil, boiling point  $119-120^{\circ}$  at one mm. An intermediate fraction (4.0 g) was believed to be a mixture of the two. The boiling points of these two products checked with those of the products in the previously reported experiments and were believed to be compounds IX and X respectively.

Reaction of  $\beta,\beta,\beta$ -Trichloro-tert-butyl Chloride and Chlorobenzene Using Aluminum Chloride as Condensing Agent. The principal conditions and molar relationships employed were:

$\beta,\beta,\beta$ -Trichloro-tert-butyl alcohol .....	0.5 mole
Chlorobenzene .....	0.5 mole
Anhyd. aluminum chloride .....	0.25 mole

Time ..... 1 hour

Temperature ..... 145-155°C.

A stream of dry hydrogen chloride was passed into a mixture of 88.8 g of trichloro-tert-butyl alcohol and 66.3 g of chlorobenzene for two hours at 145-155°C. After the trichloro-tert-butyl alcohol was converted to the corresponding chloride, 33.4 g of anhydrous aluminum chloride was added to the reaction mixture over a period of one hour. The reaction mixture was allowed to cool; the only noticeable product was a black tarry residue which could not be decomposed by ice and hydrogen chloride as was done in the previous experiments.

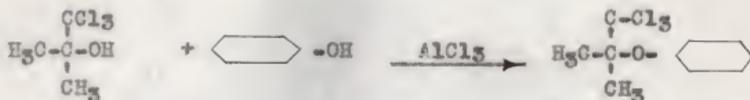
#### DISCUSSION

When para-tert-butyl phenol was prepared according to the method outlined by Ruston and Hsieh (5), substantially the same yield (36.4 percent of the theoretical) was obtained as they reported. On the basis of this experiment, it appeared likely that B,B,B-trichloro-tert-butyl alcohol would condense with phenol to give the analogous para-trichloro-tert-butyl phenol. It was postulated that the condensation would proceed by the trichloro-tert-butyl alcohol reacting with the phenol to split out water under the influence of anhydrous aluminum chloride. The aluminum chloride would react as an intermolecular dehydrating catalyst to effect the condensation.

Theoretically, it was figured on the basis of electronic inductive effects that the yield of product from  $\beta,\beta,\beta$ -trichloro-

tert-butyl alcohol and phenol would be considerably lower than analogous product from tert-butyl alcohol. This was believed on the basis that the three chlorines attached to the  $\beta$ -carbon would inductively have a tendency to deactivate the hydroxyl group and therefore increase the activation energy necessary to cause a reaction. However, in actual practice, there was no evidence that increase in activation energy was required; instead, the opposite effect was observed -- since very mild conditions (25-30°C.) produced practically 100 percent yield of products. On the other hand, there was always a possibility that the hydroxyl would be deactivated sufficiently so that the reaction would take place with one of the chlorines on the  $\beta$ -carbon in preference to the hydroxyl group.

The results obtained when trichloro-tert-butyl alcohol was condensed with phenol showed a remarkable difference in the isolatable position attacked by each of the cited tertiary alcohols in their overall effects. The reactions of these two tertiary alcohols were compared under the same set of standardized conditions. Tertiary-butyl alcohol, from an analysis of the end-product obtained, appeared to attack the para hydrogen in phenol and gave the corresponding alkylated phenol in about 50 percent yield. Trichloro-tert-butyl alcohol attacked the hydrogen on the hydroxyl group in phenol and gave  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V) in approximately 95 percent yield.

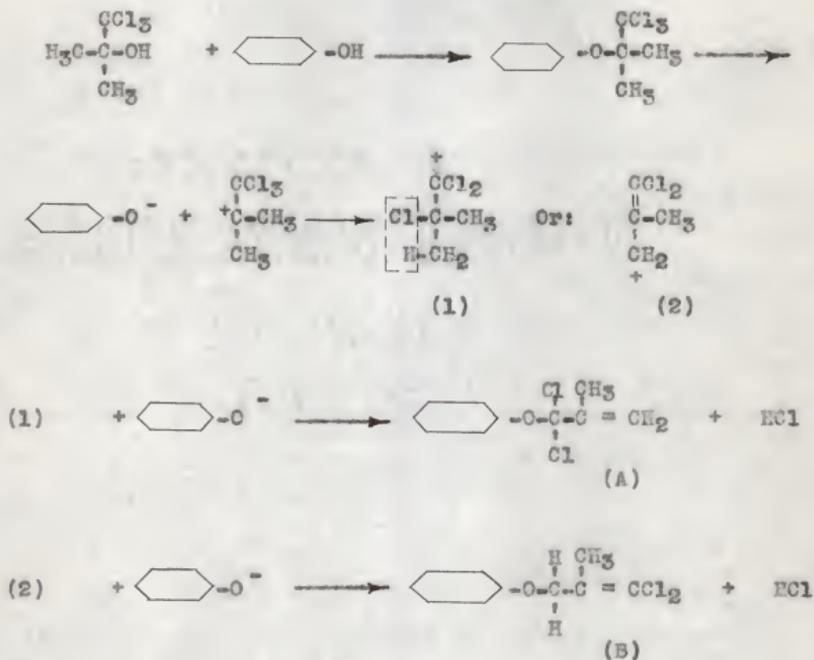


The same high yield was reproduced within 1 percent in four different preparations of the compound (V). The 6 percent necessary to make the reaction completely quantitative was probably lost in the various stages of the preparation and in the normal hold up in the column during the distillation of the compound.

Tert-butyl phenyl ether (IV) has not been synthesized by the route for V achieved in this thesis. Attempts to prepare IV by the present method failed. Smith (11) found it necessary to prepare tertiary-butyl phenyl ether by the Williamson Synthesis, but obtained poor yields because said ether rearranged for the most part to para-tertiary-butyl phenol. The tertiary butyl phenyl ether rearranged entirely to the aforementioned phenol on a few hours of refluxing. On the other hand, it was found that trichloro-tert-butyl phenyl ether could be synthesized provided that it was not repeatedly subjected to temperatures above about 100°C. during distillations for purification. Thus this ether (V) was also unstable to heat. But there the similarity between the two ethers ends. While tertiary-butyl phenyl ether rearranges to para-tertiary-butyl phenol (III),



trichloro-tertiary-butyl phenyl ether rearranges to 1,1-dichloro-2-methyl-3-phenoxypropene-1. This rearrangement is postulated as occurring by means of a Whitmore rearrangement.



Compounds (A) and (B) would both have the same percent chlorine present in the molecule; but compound (A), due to the chlorines being in the allyl position to the double bond, would give a very strong silver nitrate test for chlorines. Compound (B), having vinyl chlorines, would give a negative silver nitrate test. Additionally, compound (A) would give a positive permanganate test for unsaturation, while in compound (B), the

double bond would be sterically hindered by the two chlorines, and consequently would give a negative permanganate test. The chlorine content found, 32.8 percent corresponded exactly to  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether minus one molecule of hydrogen chloride. The alcoholic silver nitrate and permanganate tests indicated that the product isolated was compound (B) and not compound (A). Additionally, hydrogen iodide cleavage of compound (B) gave phenol as a characteristic derivative -- this would not be expected of the type of structure in compound (A).

When  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V) is prepared, some hydrogen chloride gas is evolved in the initial distillation because of rearrangement of a small percentage of V to 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI). This explains why the chlorine content found, 40.3, 40.5 percent is lower than the chlorine content calculated for V, 42 percent. Redistillation of V, gives an increasing amount of VI. This is shown by the fact that compound V redistilled twice gives almost 100 percent of compound VI. Experimental evidence seems to indicate that V and VI have identical boiling points, or boiling points so nearly identical, that they could not be separated with the apparatus used.

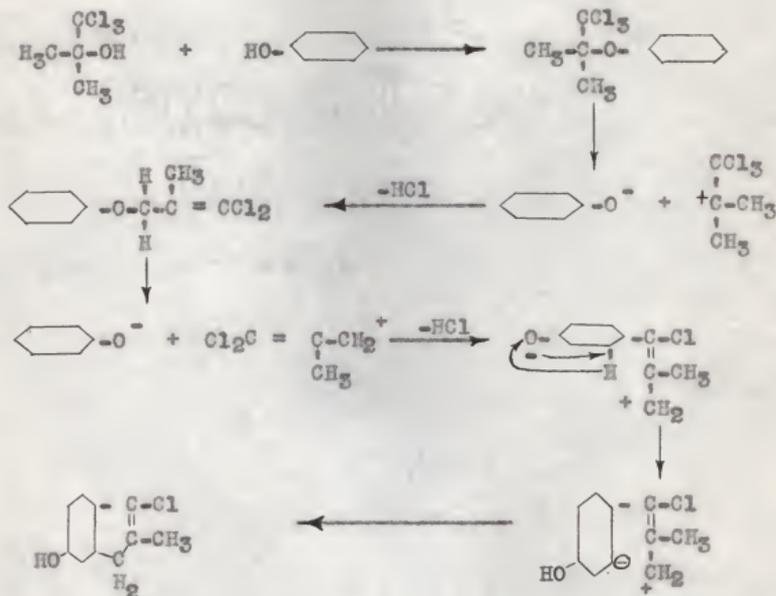
Choice of drying agents was shown to have a large effect on the yield of V. When anhydrous potassium carbonate was used, it was necessary to leave the drying agent in contact with the ether solution of the product overnight. When anhydrous magnesium sulfate was used, it was only necessary to leave the drying agent

in contact with the ether solution for 30 minutes. Drying the ether solution overnight, gave the product time to become occluded on the drying agent and gave about a 20 percent lower yield, than when magnesium sulfate was used.

Grummit and Buck (4) converted D.D.T. to di-(p-chlorophenyl)-acetic acid by treating D.D.T. with potassium hydroxide. This suggested that  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether could be similarly treated with potassium hydroxide to give  $\alpha$ -phenoxyisobutyric acid (VII). The carbon-chlorine linkages in D.D.T. were activated by the two para-chloro phenyl groups. The phenoxy group in V also activated the carbon-chlorine linkages. Guido Bergellini (1) prepared  $\alpha$ -phenoxyisobutyric acid by heating a mixture of phenol, acetone, and chloroform with sodium hydroxide. The preparation of VII from  $\beta,\beta,\beta$ -trichloro-tert-butyl-phenyl ether, marks the first time that this compound was ever prepared by any other method. The low yield obtained can be explained in two ways. First, the  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V) used in the reaction was redistilled to obtain a pure product. Subsequent experimental data showed that most of V, when redistilled, is rearranged to 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI). Thus the compound used in the reaction was probably a mixture of a considerable amount of VI, and a small amount of V. Since VI would not react with potassium hydroxide, that would explain the low yield obtained. Second, there are competing reactions taking place at the temperature employed in the reaction. While V reacted with the potassium

hydroxide, at the same time it was rearranging to form VI. However, the reaction of V with potassium hydroxide was exothermic, forming a potassium salt almost immediately. Therefore the amount of V rearranging to VI was probably very little.

Since tert-butyl phenyl ether rearranged to para-tert-butyl phenol by heat alone, it was believed possible to rearrange the more stable  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether to the corresponding phenol by increasing the activation in the reaction. Three times as much aluminum chloride was introduced into the reaction mixture in the preparation of the ether (V). It was thought that after the ether was formed, the large excess of aluminum chloride, and the increased reaction time would be sufficient activation to induce the rearrangement to the phenol. The compound isolated had a very high boiling point and was totally unexpected in that it contained only one chlorine. A mechanism was postulated, which had  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol reacting with phenol to give  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V). This compound then rearranged by means of the Whitmore rearrangement to give 1,1-dichloro-2-methyl-3-phenoxypropene-1. This rearrangement product then underwent an intramolecular Friedel-Craft reaction with a tautomeric shift and subsequent ring closure to give 1-chloro-2-methyl-5-hydroxy-indene (VIII).



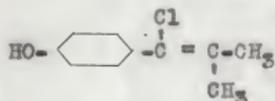
## VIII

While an intramolecular Friedel-Craft reaction of this type has never been postulated before to the writer's knowledge, no other explanation can be seen for the high boiling compound that contains one chlorine as obtained from the reactions. An examination of the literature for substituted indenenes of similar structure showed that the boiling point obtained for the indene postulated was quite possible.

In the light of the indene structure, the phenolic hydroxyl would still give a positive ferric chloride test, and the very

weak alcoholic silver nitrate test is understood in view of the modified vinyl position of the chlorine. At the same time, the chlorine is partially activated by the para phenolic hydroxyl. The negative permanganate test in the cold, and the positive permanganate test when slightly heated, can be interpreted as follows: The chlorine and methyl groups on the double bond sterically hinder the permanganate from reaching the double bond. Applied heat provides sufficient activation to overcome the blocking effect of these groups and also probably causes attack of permanganate on the phenolic ring of the indene (VIII).

An alternative compound to the 1-chloro-2-methyl-5-hydroxyindene, based only on a quantitative chlorine content and some of the characterization tests, indicated that the structure of 1,1-dimethyl-2-chloro-2-para-hydroxy phenyl ethylene (XI) was a possibility.



XI

This compound would also have to be formed through an intramolecular Friedel-Craft reaction. However, it is difficult to see how this compound could have been formed, since it would have been necessary to abstract two hydrogens from some unknown source during the reaction. This cannot be accounted for in

terms of any weight-balanced reactions.

The mechanism postulated for the preparation of VIII has as an intermediate step the preparation of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V). If compound V was an intermediate in the rearrangement, then the preparation of VIII by rearranging V was theoretically possible. The reaction was tried, and the theory was substantiated. The rearrangement product (VIII) was obtained by using practically equimolar amounts of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether and aluminum chloride at 60-70°C. Attempts were made to increase the yield of the aforesaid indene by varying the reaction conditions. Reactions attempted at 55° and at 100° showed that a temperature of 55° was insufficient to activate the rearrangement. A temperature of 100° on the other hand, gave practically all tar formation. Therefore a temperature of about 70° appears to be ideal for the rearrangement with the molar relationships used. From an analysis of the data obtained, it now appears probable that a longer reaction time would be advantageous in increasing the yield.

The color of the reaction mixture at the end of the reaction gave a good indication as to what extent the rearrangement had occurred. A golden yellow reaction mixture was always obtained in the preparation of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V). The various rearrangements attempted gave other colors such as orange, reddish-orange, pink, and dark red. In no case was the rearrangement product ever obtained in any but the dark red reaction mixtures.

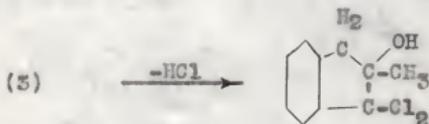
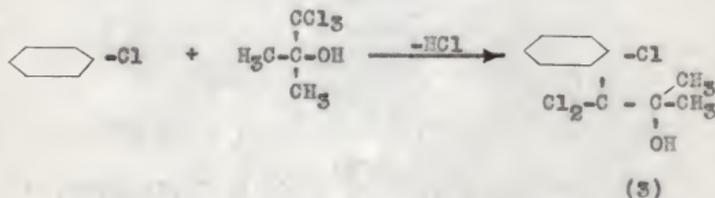
In view of a report in the literature by Wilgorodt (18) that isobutyl alcohol and aniline had been condensed in the presence of zinc chloride, the condensation of  $\beta,\beta,\alpha$ -trichloro-tert-butyl alcohol and N-dimethyl aniline was attempted. The N-dialkylated aniline was used in order to avoid any possible reaction with active hydrogens attached to nitrogen. As expected, the condensation was unsuccessful. The aluminum chloride acted as a Lewis acid and reacted with N-dimethyl aniline to form a salt. In this way, the activating electronic structure of the dimethyl aniline was tied up. This prevented it from reacting with the trichloro-tert-butyl alcohol, because the para and ortho hydrogens on the ring were not activated sufficiently. If acetanilide or N-methyl acetanilide had been used, the condensation would probably have been effected because the electrons would have been drawn away from the nitrogen by the acetyl group. This would have made it impossible for the electrons on the nitrogen to form a salt with the aluminum chloride.

When Tsukervanik (14) condensed tert-butyl alcohol and chlorobenzene using aluminum chloride as condensing agent, there was obtained 65 percent of isomeric tert-butyl phenyl chlorides and a mixture of polyalkyl chlorides. This suggested that trichloro-tert-butyl alcohol could be condensed with chlorobenzene in a similar manner. It was expected however, that the yield of trichloro-tert-butyl phenyl chloride would be considerably lower than the yield of the analogous tert-butyl phenyl chloride for the same reason mentioned previously -- i.e. the inductive effect

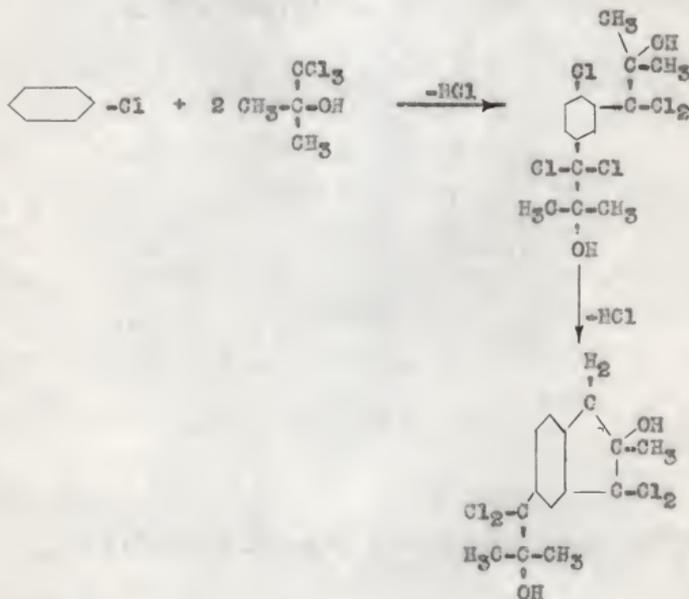
of the three chlorines attached to the  $\beta$ -carbon on the lability of the hydroxyl group. However, with trichloro-tert-butyl alcohol, one or more of the chlorines therein could undergo a Friedel-Crafts reaction with the aromatic compound, and this was postulated.

When the reaction was attempted, the results were far different from those originally postulated as the final obtainable products. Two new compounds were isolated. Chlorine analyses of these compounds on the basis of 1:1 and 2:1 addition of the trichloro-tert-butyl alcohol to chlorobenzene indicated that two molecules of hydrogen chloride must have been lost in the first product, and that three molecules of hydrogen chloride were lost in the second higher-boiling product.

The mechanism postulated to account for the compounds obtained, involves a Friedel-Craft reaction with subsequent ring closure by an intramolecular elimination of hydrogen chloride.



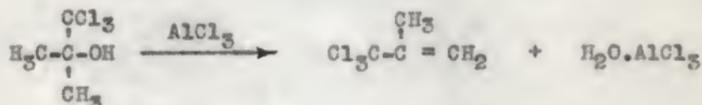
At present it appears that this novel ring closure can only be explained by the ortho  $-C(Cl_2)-$  group having an activating effect on the aromatic chlorine coupled with a possible activating effect of the hydroxyl group on the hydrogens of the methyl group involved. The readiness with which 5-membered rings form, is also an important factor. No other compound of the various compounds postulated, came anywhere close to the quantitative chlorine analyses repeatedly substantiated.



The postulated 2-hydroxy-2-methyl-3,3-dichloro-dihydro indene (IX) was obtained in 20.4 percent conversion of the starting materials. The 2:1 addition product, 2-hydroxy-2-methyl-3,3-

dichloro-5 (1,1-dichloro-2-hydroxy-2-methyl-propyl) dihydroindene (X) was obtained in 12.6 percent conversion of the chlorobenzene.

A fraction boiling slightly higher than chlorobenzene was recovered in the distillation. This fraction, 11 g, gave a positive permanganate test for unsaturation. Froman (3), reported the boiling point of 1,1,1-trichloro-2-methyl-propene-2 as 150-137°. The boiling point of chlorobenzene is 132°. Thus, the aluminum chloride must have acted as a dehydrating agent,



and the 1,1,1-trichloro-2-methyl-propene-2 was mixed in with the chlorobenzene in said 11 g fraction. This finding helped explain why the yield of the reaction products were not as high as might otherwise have been. The tarry residue in the flask after distillation accounted for the remainder of the starting products. This was typical of a Friedel-Craft reaction. Attempts to prove the presence of tertiary hydroxyl groups in products IX and X were inconclusive due to the insolubility of the compounds in the Lucas reagent.

The reaction of trichloro-tert-butyl alcohol and chlorobenzene at 50° gave back the starting products. There was no trace of compounds IX and X. The same reaction at 85° gave a greatly reduced yield of compounds IX and X. These experiments

indicate that a temperature of 100° is the minimum necessary for good yields of IX and X. Whether a temperature above 100° would increase the yield is unknown, but it is probable that an increased yield at a higher temperature would result in an increased proportion of polyalkylated products.

Experimental evidence obtained so far appears to indicate that the compounds prepared in the condensation of trichloro-tert-butyl alcohol and chlorobenzene are substituted dihydroindenes, but there is no definite final proof as yet. More experimental evidence must be obtained before the structure of the postulated compounds can be established. A quantitative analysis for carbon and hydrogen will definitely be required. A suggested experiment for future work involves the condensation of trichloro-tert-butyl alcohol and bromobenzene. If the postulated mechanism is correct, hydrogen bromide should be evolved in the reaction. Then, the final products should contain no bromine, and should be identical with the compounds synthesized in the analogous reaction with chlorobenzene, i. e. compounds IX and X.

#### SUMMARY

Reaction of phenol and  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol by admixture in petroleum ether and addition of anhydrous aluminum chloride at 30-35° resulted repeatedly in reproducible syntheses of  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V) in yields of about 94 percent. This product was mixed with a little of 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI). The

latter product (VI) resulted from heating during distillation. Upon further heating of V, it lost hydrogen chloride quantitatively and rearranged completely to 1,1-dichloro-2-methyl-3-phenoxypropene-1 (VI). The latter was obtained analytically pure. This conversion of V to VI is a new example of the Whitmore rearrangement.

Alpha-phenoxyisobutyric acid (VII), was prepared by a new method; viz., treating  $\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether (V) with potassium hydroxide.

$\beta,\beta,\beta$ -trichloro-tert-butyl alcohol and phenol when reacted with excess aluminum chloride, gave a new compound postulated as 1-chloro-2-methyl-3-hydroxy indene (VIII). Considerable evidence was adduced for this compound.

$\beta,\beta,\beta$ -trichloro-tert-butyl phenyl ether reacted with excess aluminum chloride, gave the same compound (VIII).

The attempted reaction of  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol and dimethyl aniline using aluminum chloride as a condensing agent was unsuccessful.

The reaction of chlorobenzene and  $\beta,\beta,\beta$ -trichloro-tert-butyl alcohol using aluminum chloride as condensing agent gave two new compounds postulated as 2-hydroxy-2-methyl-3,3-dichloro-dihydro indene (IX), and 2-hydroxy-2-methyl-3,3-dichloro-5(1,1-dichloro-2-hydroxy-2-methyl propyl) dihydro indene (X). Considerable evidence was obtained for these postulates.

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