

A STUDY OF REACTIONS OF CHLORITONE

by

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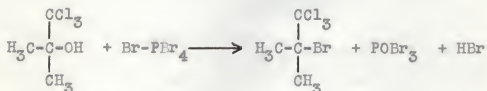
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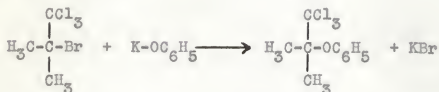
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INTRODUCTION

Willgerodt and Durr (1) published a paper in 1889 which stated that 1,1,1-trichloro-tert.-butyl bromide was prepared by the action of phosphorus pentabromide on chloretone.



In the light of our research on projects at Kansas State College, it seemed desirable to obtain the 1,1,1-trichloro-tert.-butyl bromide so that a Williamson synthesis could be carried out with it and potassium phenoxide to give 1,1,1-trichloro-tert.-butyl phenyl ether.



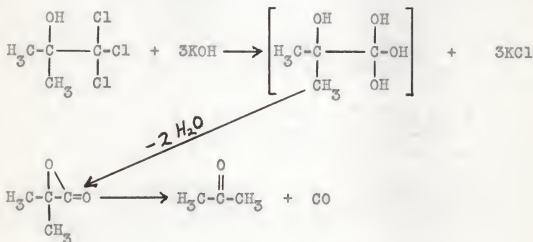
The major portion of this investigation dealt with (a) studies of the chemistry of chloretone in its reaction with phosphorus pentabromide, (b) identification of the products, and (c) the preparation of derivatives of these products.

A portion of the investigation dealt with attempts to prepare 1,1,1-trichloro-tert.-butyl phenyl ether, both by the method reported by Stoloff (2) and by the Williamson synthesis.

The paper by Willgerodt and Durr (1) was a very loosely

written and incomplete paper. Yields, the weights of materials used and the weights of the products obtained were not given. In fact, no essential details were reported. In an earlier paper by Willgerodt and Durr (3) the statement that the reaction of chloretone with phosphorus pentachloride yielded a di-1,1,1-trichloro-tert.-butyl ether was disputed in 1915 by Wolfenstein, Loewy and Bachstetz (4).

Bressanin and Serge (5) found that when chloretone was treated with 10 percent aqueous potassium hydroxide, it was broken down into carbon monoxide and acetone.



This typical decomposition could be used for identification of chloretone through the characterization of its derivatives.

According to Stoloff (2), the 1,1,1-trichloro-tert.-butyl phenyl ether could be synthesized from chloretone and phenol by action of anhydrous aluminum chloride through modifying a process used by Huston and Hsieh (6). In the process of Huston and Hsieh, tert. butyl alcohol was reacted with phenol under the influence of aluminum chloride, and yielded p-tertiary butyl

phenol. Theoretically, and by reference to other experimental data (11), the tertiary butyl phenyl ether was first formed in this process but immediately rearranged to the p-tertiary butyl phenol under the reaction conditions. Therefore, in Stoloff's work (2), either the 1,1,1-trichloro-tert.-butyl phenyl ether or the 1,1,1-trichloro-tert.-butyl phenol was a desired objective.

One of the fundamental objects of this investigation was to find out if either 1,1,1-trichloro-tert.-butyl phenyl ether or 1,1,1-trichloro-tert.-butyl phenol could be produced. Also, whether the three chlorines in the 1,1,1-trichloro-tert.-butyl phenyl ether had a sufficiently strong stabilizing influence to permit isolation of this ether.

DISCUSSION OF RESULTS

A vigorous reaction between phosphorus pentabromide and anhydrous chloretone was found to take place. According to Willgerodt and Durr (1) only one product, 1,1,1-trichloro-tert.-butyl bromide was formed from such a reaction. However, the present worker ultimately found that instead of only the expected 1,1,1-trichloro-tert.-butyl bromide being produced, 1,1,1-trichloro-tert.-butyl phosphate, Product I, was isolated in yields up to 26 percent.

When the attempts to produce the bromide failed, it was thought at first that perhaps Willgerodt and Durr (1) had been

mistaken; however, it was found that they were partly in error, judging by their literal report. Thus, in later attempts some of the bromide was also isolated, but only up to a 5 percent yield.

The reaction that obtained Product I in 26 percent yield was not difficult to perform after the essential details and critical factors were discovered. The successful reaction comprised mixing equimolar portions of chloretone and phosphorus pentabromide. After these two components formed a homogeneous liquid, either by standing at room temperature for about five days or heating to 100^o C. for eight hours, the solution was treated with an equal volume of diethyl ether. Next, a volume of distilled water equal to approximately one-fourth the volume of the reaction mixture was added. It was found that when more than this relative amount was mixed in, then none of the Product I would ever crystallize out. It was found also that no material would crystallize out if the reaction mixture was kept in a closed container. It was found necessary to allow the reaction mixture to stand for at least 1.5 days in contact with the atmosphere before the original reaction mixture separated into two layers. Further, it was found necessary to have these two layers stand for an additional 3.5 to 8.5 days to obtain separation of the crystalline products, 1,1,1-trichloro-tert.-butyl phosphate (I) and 1,1,1-trichloro-tert.-butyl bromide (II).

Isolation of Product I

It was found necessary to filter the above crystals upon a sintered glass filter. In one case, carbon tetrachloride washings of these crystals gave only 1,1,1-trichloro-tert.-butyl bromide (II). In other cases none of II was found in the carbon tetrachloride washings of the original crystalline product. In all cases, however, Product I was produced and found to be insoluble in carbon tetrachloride. A comparison of the yields of Product I and of the 1,1,1-trichloro-tert.-butyl bromide, Product II, is given in Table 1. It was noted that when there was no bromide (II) produced, the yield of Product I was about twice as high.

Table 1. Comparison of yields¹ of Product I and 1,1,1-trichloro-tert.-butyl bromide (Product II).

Trial number	I	II
Weight of Product I	45.8 gm	57.2 gm
Weight of Product II	none	21.1 gm
Yield of Product I	25.6 percent	12.2 percent
Yield of Product II	-	4.8 percent
Moles of Product I	0.1781	0.2223
Moles of Product II	-	0.0874

¹ Yields represent overall conversions

In one case it was found impossible to filter the crystals from the reaction mixture because the fineness and type of crystals completely blocked the filter. These crystals were

separated by use of a centrifuge. The centrifugation was successful. The crystals so obtained were white and rather fine. They were found to be slightly soluble in cold water but very soluble in hot. It seemed, therefore, that water would be a good solvent for recrystallization.

In recrystallizing Product I from water, it was necessary sometimes to seed the solution, because Product I seemed to form easily supersaturated solutions. Crystallization usually could be induced by other conventional methods also. Two recrystallizations were performed to find the amount of Product I recoverable by the technique used. The results are to be found in Table 2.

Table 2. Recoveries on recrystallization¹ of Product I.

Weight of Product I dissolved	Weight of Product recovered	Percent of re- covery
3.23 gm	2.05	63.46
6.22 gm	4.31	69.30

¹ Recrystallizations from distilled water.

Identification of Product I

When some of Product I was ignited, a small residue was left which was soluble in water. The most likely material in Product I was some form of phosphorus. The residue was therefore

tested with ammonium phosphomolybdate. This test gave a very heavy precipitate of the characteristic yellow solid and proved the presence of phosphate ion in aqueous solution. Since phosphorus was present in product I, it could not be 1,1,1-trichloro-tert.-butyl bromide. A melting point of the initial Product I material was attempted, but this material decomposed at 103° - 129° C. After one recrystallization, the decomposition was in a range of 159° - 163° C. After several recrystallizations, the decomposition point rose to a final 184.5° - 185.5° C. The latter range could not be changed by additional recrystallizations.

After a pure sample of Product I was obtained in this manner, the percent of phosphorus was determined. Two different methods for the determinations of phosphorus were used. The first determination was according to the method of Fales and Kenny (9). This method involved the precipitation of the phosphorus as ammonium phosphomolybdate trihydrate. The ammonium phosphomolybdate trihydrate was redissolved and the phosphorus was precipitated as magnesium ammonium phosphate hexahydrate. This latter precipitation was repeated to eliminate any error that could be introduced if molybdc oxide were precipitated in the ammonium phosphomolybdate trihydrate. The average amount of phosphorus found in pure Product I was 12.02 percent.

The second method was according to the method of Shriner (10). The phosphorus was determined directly as ammonium

phosphomolybdate trihydrate. Here the average amount of phosphorus was found to be 12.26 percent.

In the first method Product I was oxidized by placing it in a Carius tube with fuming nitric acid at a temperature of 330° C. for twenty-four hours. In the second method Product I was oxidized by boiling with concentrated sulfuric and nitric acids until no more brown fumes were evident. The results of the phosphorus analyses are found in Table 3.

Table 3. Physical and chemical properties of Product I.

Property	Observed	Calculated (Compound "B")
Physical property		
Melting point	184.5-185.5 (decomposes)	-
Molecular weight	259.12 ^a	257.45
Percent chlorine	41.71	41.33 ^b
	41.07	
Percent phosphorus	11.96 ^c	12.03 ^b
	12.08 ^c	
	12.16 ^d	
	12.13 ^d	
	12.20 ^d	
Tests with		
Aq. AgNO ₃	positive ^e	positive ^e
(NH ₄) ₂ MoO ₃	negative	negative
Congo red	acid	acid

^a By neutral equivalent. Titrated with standard sodium bicarbonate.

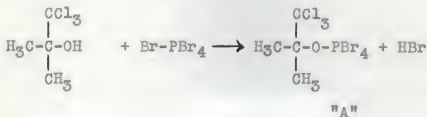
^b Based on a molecular weight of 257.46. Individual values for neutral equivalents were 256.06 and 261.81.

^c Weighed as MgNH₄PO₄·6H₂O (8).

^d Weighed as (NH₄)₃P₃O₄·12MoO₃·3H₂O (9).

^e Definite colorless crystalline product believed to be silver salt of the substituted phosphoric acid.

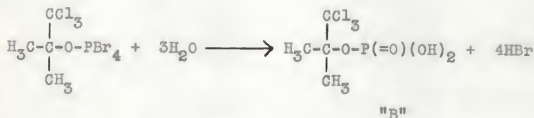
Since phosphorus was found in Product I, it was thought that the following reaction took place between the chloretone and the phosphorus pentabromide in a first step to produce intermediate "A" below.



This kind of reaction appeared logical. According to Kuntz (12), the following reaction takes place.



Phenol and chloretone have tightly bound oxygen with relatively labile hydrogen, and so both should have certain similarities. By analogy then, the compound "A" should undergo a similar hydrolysis.



The compound "B" would have a molecular weight of 257.46. The calculated phosphorus and chlorine contents of compound B are listed in Table 3. These values agree within acceptable experimental limits with the analytical values for phosphorus and

chlorine found on Product I.

The Carius analyses for the chlorine content in Product I were made by the techniques described by Fisher (13). Samples were heated for about five hours at 330° C., each in a sealed tube with forty drops of fuming nitric acid and 0.5 gm silver nitrate. The chlorine was weighed as silver chloride. The average of the observed values was 41.34 percent, Table 3. The calculated value was 41.33 percent.

A determination of the molecular weight by the Rast method, as described by McElvain (14), gave values ranging from 285.5 to 430.5. These erratic values were believed to be due to the decomposition of Product I.

Neutral equivalent determinations were made to obtain the molecular weight of Product I and to identify also its characteristic acid properties. In this connection Product I was found acid enough to liberate carbon dioxide from sodium bicarbonate. Also, a 0.001 molar solution of Product I had a pH of 3.15 as determined by Beckman pH meter. According to Fales and Kenny (9), when phosphoric acid is titrated and methyl orange is used as the indicator, the end point indicated is the titration of only one of the replaceable hydrogens. Since Product I was believed at this point to be a substituted phosphoric acid having the structure of "B" as shown, it was titrated according to Fales and Kenny (9). Since the titration employed sodium bicarbonate and methyl orange indicator, the neutral equivalent and the molecular weight were identical. The

average of the observed values was 259.12 or the very small difference of 1.66 from the calculated value of 257.46 based on the molecular weight of compound "B". Individual neutralization equivalents observed for Product I are presented in Table 3.

In order to consider Product I identical with compound "B", it was necessary to perform more characterization work. Since compound "B" is an ester of phosphoric acid, it should have been possible to saponify it with aqueous potassium hydroxide. If this were true, and the concentration of the hydroxide were high enough, then the chloretone that was formed would be characteristically degraded to carbon monoxide and acetone (5). This characterization was tried and met with success. Some of Product I was placed in an aqueous solution of about 60 percent potassium hydroxide, and the aqueous alkali-insoluble gas which was evolved was identified as carbon monoxide. That acetone was also present was shown by its yielding a strongly positive iodoform test. The 2,4-dinitrophenylhydrazone derivative of acetone was also isolated from this characterization reaction.

In order to establish that Product I was quite acid, a test was made on its pH. A solution was made up which contained 0.2575 gm per liter or a molarity of 0.001 M, based on the formula of compound "B". The pH of this solution was 3.15 as determined by a Beckman pH meter. This value compares favorably with the pH of 0.01 N benzoic acid.

In the light of the above analyses, molecular weight determinations and characterizations, it appeared reasonable to conclude that the formula for Product I and compound "B" was the same, namely:



In order that future work might be simplified, it was thought that tests of the solubility of Product I in various solvents would be valuable. Results of these solubility tests are shown in Table 4.

Table 4. Solubilities of 1,1,1-trichloro-tert.-butyl phosphate.

Solvent	:	Result
Benzene	:	insoluble
o-Xylene	:	insoluble
Petroleum ether	:	insoluble
Carbon tetrachloride	:	insoluble
Ethyl alcohol	:	soluble
Acetone	:	soluble
Ethyl acetate	:	soluble
Glacial acetic acid	:	soluble
Diethyl ether	:	soluble
1,4-Dioxane	:	soluble
Water	:	very soluble, hot sparingly soluble, cold
H ₂ SO ₄ (conc.)	:	soluble
NaHCO ₃ (5 percent aqueous)	:	soluble ^a

^a - liberates CO₂ gas.

Isolation of 1,1,1-Trichloro-tertiary
Butyl Bromide (II)

Some of the 1,1,1-trichloro-tert.-butyl bromide in yields of about 5 percent was produced in only one experiment. The carbon tetrachloride washes of the crystals of Product I were evaporated to detect any Product II which might have been present. The amount of Product II isolated was obtained in this manner. It displayed the general characteristics as set forth by Willgerodt and Durr (1). Characteristics of II not noted by them were decomposition at its melting point range, lachrymatory quality of the crystals, and solubilities. The solubilities are presented in Table 5.

Table 5. Solubility of 1,1,1-trichloro-tert.-butyl bromide (II).

Solvent	:	Result
Carbon tetrachloride		soluble
Petroleum ether		soluble
Benzene		soluble
o-Xylene		soluble
1,4-Dioxane		soluble
Diethyl ether		soluble
Ethyl acetate		soluble
Ethyl alcohol		soluble
Acetone		soluble
Glacial acetic acid		soluble
Water		insoluble
NaHCO ₃ (5 percent aqueous)		insoluble
H ₂ SO ₄ (conc.)		insoluble

These newly determined solubilities agree with the standard solubility tests which should be characteristic of such a structure as II.

Products from Reaction of Potassium Phenoxide and
1,1,1-Trichloro-tert. Butyl Bromide (II)

It was hoped that 1,1,1-trichloro-tert.-butyl phenyl ether could be made by a Williamson synthesis using 1,1,1-trichloro-tert.-butyl bromide (II) and potassium phenoxide. When these reagents were brought together, it was definitely evident that a reaction took place. A water soluble precipitate formed, and the reaction mixture changed color. When the reaction was apparently complete, the precipitate was filtered and weighed. A portion of the dioxane solution was washed with water to remove the solvent. Dilution with water in this way gave a water-insoluble precipitate.

A Carius analysis on this precipitate revealed that it could not possibly be 1,1,1-trichloro-tert.-butyl phenyl ether. The precipitate had a chlorine content of 63.8 percent when the gravimetric factor was used for the conversion of silver chloride to chlorine. The calculated chlorine content for the ether was 42 percent. However, when a gravimetric factor that had a ratio of three silver chloride and one silver bromide was used, then a halogen content value of about 77.9 percent was obtained (the same ratio that was used to calculate the halogen

content of the 1,1,1-trichloro-tert.-butyl bromide (II)). This value compared sufficiently close with the value obtained by Carius analysis on the bromide (II). It analyzed for about 77.5 percent chlorine. Therefore, it was thought that this precipitate was some of the starting material (II).

Since a reaction did take place, it was thought that the precipitate that was filtered from the reaction mixture might give the answer as to the extent of reaction. According to the syntheses postulated, this precipitate should have been potassium bromide. A halogen analysis, according to Scott (15), showed that the precipitate contained about 80 percent potassium bromide and about 17 percent potassium chloride. The remaining 3 percent was assumed to be occluded organic material.

These findings indicated that the formation of the 1,1,1-trichloro-tert.-butyl phenyl ether did not exceed 5 percent. It was speculated that the possible reason this ether was not found was due to the fact that it would easily rearrange to the 1,1,1-trichloro-tert.-butyl phenol. Its detection in the manner attempted would not be realized. Time did not permit further investigation of this synthesis.

The potassium chloride which was produced must have been formed by a reaction between the trichloro methyl group of the bromide (II) and the potassium phenoxide. This side reaction would give rise to mono-, di- and tri-phenoxy methyl products.

Products from the Reaction of Chloretone with
Phenol in the Presence of Aluminum Chloride

Since the synthesis of the 1,1,1-trichloro-tert.-butyl phenyl ether had been reported by Stoloff (2), it was of interest to reproduce this preparation. The performance of this synthesis was the same as Stoloff's, but the findings were different.

When the water layer was tested for phenol, after the usual decomposition of the Friedel-Crafts reaction mixture and separation of the water layer from the ether solution, the test was negative. However, it was found that with the hydrochloric acid that was present under the circumstances, ferric chloride did not give a color with phenol. When some of the product was washed until sufficiently free of hydrochloric acid, and then a subsequent water wash of the product tested with ferric chloride, the test was strongly positive. The same behavior was noted and checked in a control experiment on a known sample of phenol to which hydrochloric acid was added.

During the first half of the vacuum distillation of the product, the temperature in the air condenser was allowed to drop to almost body temperature. Crystals then appeared in the condenser. The same procedure was used during the second half of the distillation, but no crystals formed. There also appeared in the receiver a marked "shlieren" when it was moved, indicating that a single compound was not being obtained.

When some of the product was shaken with water, a crystalline precipitate was formed. This precipitate was identified as chloretone both by decomposition into acetone and carbon monoxide and by the melting point (mixed and pure).

According to these findings, the product produced by Stoloff and reproduced by the author was not the 1,1,1-trichloro-tert.-butyl phenyl ether, but mainly a mixture of chloretone and phenol in equimolar ratio.

The formation of the crystals in the condenser during the first half of the distillation and not during the second half could have been explained in the following manner. During the first half of the distillation the chloretone could have distilled out of the mixture, since its boiling point is lower than that of phenol. Upon cooling the condenser, the chloretone solidified. However, during the second half of the distillation, when the phenol was being distilled, no crystals formed because of its comparatively low melting point.

It was thought that if the product named as 1,1,1-trichloro-tert.-butyl phenyl ether by Stoloff was an equimolar mixture of chloretone and phenol, the same characteristics should have been displayed by a mixture of chloretone and phenol. Therefore, equimolar quantities of chloretone and phenol were placed in the same flask and allowed to stand at room temperature overnight. The mixture became liquid. It displayed a melting point, both mixed and pure, identical with Stoloff's "ether". When the

mixture was distilled, it naturally showed the same characteristics when the condenser was allowed to cool during the first and second half of the distillation. It also gave the same reaction to water; a white crystalline precipitate of chlore-tone, and a strong phenol test in the water.

After attempting the Williamson synthesis of the 1,1,1-trichloro-tert.-butyl phenyl ether, and also after attempting to produce the ether in the same manner as Stoloff and having received none of the product in either case, it was thought that the stabilizing influence of the trichloro methyl group was not strong enough to stabilize the ether. Although there may have been some of the 1,1,1-trichloro-tert.-butyl phenol produced by rearrangement, after the Williamson synthesis, time did not permit further investigation of this possibility.

EXPERIMENTAL

Starting Materials

Chlore-tone. U.S.P. grade chlorbutanol manufactured by Givaudan Delawanna, was ground and placed in a desiccator over anhydrous calcium chloride immediately after it was removed from the container.

Phosphorus Tribromide. Eastman phosphorus tribromide, 1354, white label grade, was employed.

Bromine. Baker and Adamson, 1473, was used.

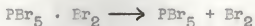
Phenol. Mallinckrodt analytical reagent grade, 0028, was kept in the refrigerator at 4° C. until used.

Potassium Hydroxide. Baker and Adamson reagent grade, 2118, pellet form was used. A correction was applied for its 85 percent content of potassium hydroxide; the remaining 15 percent being potassium carbonate and water.

Preparation of Phosphorus Pentabromide (7,8)

The phosphorus pentabromide was prepared in a 500 ml round bottom side arm distilling flask. The flask was fitted with a rubber stopper bearing a 60 ml dropping funnel. A calcium chloride drying tube was attached to the side arm.

Phosphorus tribromide (492 gm or 1.817 mole) was placed in the flask. The stopper with the dropping funnel was re-fitted to the flask and 290 gm (1.817 mole) liquid bromine were placed in the funnel. This amount of bromine was allowed to drop into the phosphorus tribromide at a rate that required one and a half hours for its addition. The temperature was maintained at about 20° C. with a water bath. The flask was rocked to prevent build up of solid phosphorus pentabromide under the funnel tip. After the addition was complete, the temperature of the reaction mixture was raised until it became liquid (99°-100° C.). At this temperature any phosphorus heptabromide that was formed by local high concentrations of bromine broke down as follows (8):



The liberated bromine then reacted with the remaining phosphorus tribromide to form the desired phosphorus pentabromide.

Preparation of Potassium Phenoxide

Phenol, 155.2 gm (1.65 mole), was dissolved in 50 ml dry methyl alcohol in a 500 ml Erlenmeyer. Then 108.9 gm (1.65 mole) of the 85 percent potassium hydroxide were dissolved in 300 ml of dry methyl alcohol in a second 500 ml Erlenmeyer. The flask containing the potassium hydroxide was placed in a water bath maintained at a temperature of 13° C. by running tap water. The solution of phenol was then poured slowly into the potassium hydroxide solution with rapid stirring. The solution was stirred for several minutes, stoppered, and allowed to stand overnight.

The alcoholic solution of potassium phenoxide was poured into four liters of distilled dry benzene with stirring. This mixture was cooled to 14° C. in a running water bath. When the precipitation of the crystals of potassium phenoxide was complete, the mixture was filtered by suction on a Buchner funnel. The filter cakes were broken up and spread out to allow the benzene to evaporate. The crystals were then placed in a vacuum desiccator, at 20 mm pressure, over anhydrous calcium chloride for eighteen hours. The crystals were weighed at the

end of this period. Their weight was 209 gm (1.58 mole). This amount was 95.8 percent of the calculated theoretical yield.

Reaction of Chloretone
with Phosphorus Pentabromide (1)

CAUTION: When performing the experiment involving the reaction of phosphorus pentabromide with chloretone, it is strongly advised that the operator wear rubber gloves and apron. When handling the products of the reaction after they have become liquid for the first time (after mixing phosphorus pentabromide and chloretone), the operator should in addition to the above precautions, wear a gas mask and carry out the work in the hood.

Some of the products have extremely persistent lachrymatory and irritating effects. The nose stops up, sinuses experience a pressure sensation, eyes sting and water profusely. A headache develops also, and the blood vessels in the eyes become very much dilated.

The reaction was carried out in a 500 ml side arm distilling flask which contained 783 gm (1.817 mole) phosphorus pentabromide. To this was added 323 gm (1.817 mole) of anhydrous chloretone. The flask was stoppered and the side arm was fitted with a calcium chloride drying tube. Evolution of fumes was noted from the drying tube. This drying tube was

connected to a piece of glass tubing that led to just below the neck of a 2.5 liter bottle. The bottle contained water to within about 20 mm of the end of the tube and acted as a hydrogen bromide trap.

The reaction flask was heated at 100° C. on a water bath for about eight hours. There was considerable evolution of hydrogen bromide. The mixture became completely liquid, homogeneous and dark amber in color. It then was allowed to stand for about two weeks.

At the end of this period the mixture was poured into a two liter beaker and 430 ml of diethyl ether added. Then, while stirring the mixture, 100 ml of distilled water were added, about 5 ml at a time. Much heat was evolved and caused the ether to boil. Boiling continued for about an hour after the water was added. The beaker was covered with a watch glass and allowed to stand in the hood for three days. The beaker was then uncovered and after about three days of standing, the mixture separated into two layers, but showed no crystals. Seven days later, two types of crystals appeared. One type, which was predominant in the top layer and in the upper surface of the lower layer, appeared as tiny plates. The other type, which appeared to exist only in the lower layer, resembled fern fronds or feathers. On account of mechanical difficulties the two types of crystals could not be separated from within the two-layered mixture. All of the crystals were filtered from the mixture upon a sintered glass filtering

funnel by suction. When the crystals were sucked as dry as possible, they were washed with ten 10 ml portions of carbon tetrachloride. The carbon tetrachloride wash was stored in a glass stoppered bottle. The crystals were dried and placed in a vacuum desiccator at 20 mm pressure over anhydrous calcium chloride for about fourteen hours. These crystals were almost pure white and were termed Product I. This product was not pure but was purified according to the data presented along with discussion and tables in the Discussion section.

In one case it was found necessary to separate the crystals from the reaction mixture by an alternative method. In this method the crystals and liquid (a slurry) were placed in 50 ml pyrex centrifuge tubes and centrifuged at 2500 R.P.M. for 3 hours. (The rotor diameter was 12 inches.) The liquid was decanted off and the crystals were mixed with carbon tetrachloride and centrifuged an additional 0.5 hour at 2500 R.P.M. The carbon tetrachloride was decanted from each tube and the crystals were sucked as dry as possible on the filter. They were then washed with portions of carbon tetrachloride and dried.

Next, the carbon tetrachloride wash was placed in a 250 ml flask fitted with an air condenser, 400 mm x 16 mm, arranged for downward distillation. The receiver was a 250 ml three necked flask with one neck stoppered, and one neck was used for evacuation. The third neck was connected to the condenser. The receiver was cooled by running water, and the still flask was

heated by boiling water. When the carbon tetrachloride ceased to distil, the pressure was lowered to 23 mm. The upper portion of the distilling flask and the interior of the air condenser were immediately covered with a mass of sublimed material. The pressure was returned to atmospheric and the apparatus was allowed to cool.

The apparatus was dissembled and the remaining few drops of liquid in the distilling flask were removed with a pipette. The crystalline sublimate was removed from the apparatus and recrystallized from ether. This crystalline sublimate (the carbon tetrachloride soluble product) was termed Product II. The yields from this experiment are given in Table 1, column II.

Reaction of Product I with Potassium Hydroxide

About 0.25 gm of Product I was added to 10 ml of 60 percent potassium hydroxide in water solution in a 50 ml side arm distilling flask. A Saf-CO-Meter indicator tube was placed in the neck of the flask with the tip extending to within 5 mm of the liquid surface.¹ The gases from the interior of the flask were drawn through this indicator tube for about one minute at a

¹ Saf-Co-Meter indicator tube No. Co-100 made by U.S. Safety Service Company, Kansas City, Missouri.

rate of about 100 ml per minute. The indicating band changed from yellow to green, thus showing the presence of carbon monoxide gas. The tube was withdrawn and 15 ml of distilled water were added along with three pyrex glass beads. The flask was then stoppered and a condenser was attached to the side arm. The flask was heated and about 15 ml of the condensate was collected while distillation proceeded at a rate of about 40-50 drops per minute.

The condensate was divided into two portions. One portion was treated with 10 percent sodium hydroxide aqueous solution and then with potassium iodide-iodine solution. A fairly heavy precipitate of iodoform (m.p. 118.5° - 119.5° C.) was obtained. The second portion was treated with 2,4-dinitrophenylhydrazine dissolved in concentrated hydrochloric acid. A precipitate formed that had a melting point of 127.5° - 128° C., which is the melting point of the 2,4-dinitrophenylhydrazone of acetone. These derivatives identify acetone present in the condensate.

Reaction of 1,1,1-Trichloro-tertiary Butyl Bromide with Potassium Phenoxide

A three necked 100 ml flask was fitted with a prepared Hirschberg stirrer. A reflux condenser was attached and also a dropping funnel. Ten gm (0.0416 mole) 1,1,1-trichloro-tert.-butyl bromide dissolved in 20 ml dry 1,4-dioxane was placed in

the flask. A solution of 5.49 gm (0.0416 mole) potassium phenoxide, in a mixture of 45 ml pre-dried 1,4-dioxane and 4 ml pre-dried ethyl alcohol, were placed in the dropping funnel and added to the bromide over a period of twenty minutes. The mixture was stirred constantly and the temperature remained at 28.5° C. throughout the addition.

The temperature was raised to 85° C. by a Glas-Col heating mantle, and held at about 85° for 3.75 hours. A fine white precipitate formed slowly. The color of the reaction mixture gradually changed from colorless to amber. The reaction mixture was returned to room temperature, and the mixture was then stirred for an additional 15 hours. The precipitate was reddish brown and gummy in appearance. The liquid portion of the reaction mixture was amber colored.

The liquid was decanted from the precipitate and placed in a stoppered flask. The precipitate was in the form of pellets and was washed with a few ml of dry 1,4-dioxane. This dioxane was added to the reaction mixture liquid.

The precipitate was placed in a sintered glass filtering crucible. Residual precipitate adhering to the reaction flask was washed into the crucible with small amounts of dry methyl alcohol. The precipitate was then washed on the filter with fresh dry methanol until successive filtrates were no longer colored. The filtrate and methanol washings (reddish brown) were placed in a stoppered bottle. The precipitate, after drying, had a constant weight of 0.2785 gm.

Next, 10 ml of the liquid reaction mixture were placed in a separatory funnel and shaken with 20 ml distilled water. A precipitate formed that was slightly yellow. The washing was repeated four times. Then, 15 ml diethyl ether was added to dissolve the precipitate. The ether solution was dried over one gm of anhydrous magnesium sulfate for twenty minutes. The magnesium sulfate was filtered off and the ether solution was evaporated. Cream colored crystals formed. The weight of these crystals was 0.2068 gm. They were placed in a desiccator over anhydrous calcium chloride for ten hours.

Halogen analyses, by the Carius method, gave a value of 77.88 percent of total halogen when the gravimetric factor for Ag_4Cl_3Br was used. (Bromine was shown present by prior qualitative analysis.) This value checked sufficiently close to the 77.49 percent of total halogen obtained by the present worker on a sample of known 1,1,1-trichloro-tert.-butyl bromide.

Reaction of Chlorethane with Phenol in Presence of Anhydrous Aluminum Chloride

The essential details of this experiment were the same as those given by Stoloff (2).

Chlorethane, 88.75 gm or 0.5 mole, was treated with 47 gm of phenol in the presence of 33.4 gm (0.25 mole) anhydrous aluminum chloride, using petroleum ether as a solvent. The reaction mixture was decomposed with a mixture of crushed ice

and concentrated hydrochloric acid. After the decomposition was complete, the product was dissolved in diethyl ether and separated from the water and hydrochloric acid.

The diethyl ether and the petroleum ether were removed by distillation, after drying the solution over anhydrous magnesium sulfate for twenty minutes. The product was distilled at reduced pressure. The yield, based upon hypothetical figures and calculated in the same manner as Stoloff's, was 95.5 percent.

SUMMARY

Chloretone and phosphorus pentabromide were found to produce a new compound. This compound was identified as 1,1,1-trichloro-tert.-butyl phosphate by analyses for halogen, and for phosphorus, by neutralization equivalent, and by characterization of the degradation products from alkaline cleavage of the compound.

It was obtained in crude form (fairly pure) in yields of about 26 percent. It was recrystallized, and a yield of about 69 percent analytically pure 1,1,1-trichloro-tert.-butyl phosphate was obtained. To obtain this new compound, the first phosphate ester of a tertiary alcohol to be produced and isolated, required sensitive and critical crystallizing conditions in the original reaction mixture, and also a particular

technique of slow hydrolysis of the intermediate oxyphospho-bromo compound, $(\text{CH}_3)_2\text{C}(\text{CCl}_3)\text{-O-PBr}_4$, over to the desired 1,1,1-trichloro-tert.-butyl phosphate.

In one case, out of several trials, it was possible to isolate 1,1,1-trichloro-tert.-butyl bromide in about 5 percent yield. Obtaining this bromide was found to be a matter of critical and sensitive crystallizing conditions of the reaction mixture.

An attempted Williamson synthesis between potassium phenoxide and the obtained 1,1,1-trichloro-tert.-butyl bromide did not yield any isolated 1,1,1-trichloro-tert-butyl phenyl ether, but there was a reaction evidenced by the formation of some potassium bromide. If the ether was formed, it seemed to have rearranged to the p-(1,1,1-trichloro-tert.-butyl) phenol.

Attempts to reproduce the synthesis of 1,1,1-trichloro-tert.-butyl phenyl ether as reported by Stoloff (2), indicated that he had not obtained it. The product from these attempted syntheses was found to have the same behavior with regard to melting point, solubility, and distillation characteristics as did an independently prepared equimolar mixture of chloretone and phenol. It was thought, therefore, that the product called 1,1,1-trichloro-tert.-butyl phenyl ether by Stoloff was identical with such a mixture.

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A STUDY OF REACTIONS OF CHLOROTONE

by

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B. S., Wagner College,
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The studies of the chemistry of chloretone in its reaction with phosphorus pentabromide, the identification of the products, and the preparation of derivatives of these products formed the major portion of this investigation.

Chloretone and phosphorus pentabromide were found to react to yield a new compound. This compound was identified as 1,1,1-trichloro-tert. butyl phosphate. It was obtained in crude form (fairly pure) in yields of about 26 percent. It was recrystallized from water with a yield of about 69 percent analytically pure product. This phosphate ester of a tertiary alcohol was the first to be reported. It was designated as Product I.

The postulated structure for Product I, obtained from the reaction of phosphorus pentabromide and chloretone, was shown by chemical and physical data to be:

1,1,1-trichloro-tert. butyl phosphate, m. p. 184.5-185.5° C. (decomposes), calculated percent chlorine 41.38, found as the average of two analyses 41.34, calculated percent phosphorus 12.03, found as the average of three analyses 12.02, calculated molecular weight 257.45, found as the average of two neutral equivalent determinations 259.12.

Alkaline cleavage of Product I yielded acetone and carbon monoxide. The acetone was identified as the 2,4-dinitrophenylhydrazone derivative and the carbon monoxide was identified by a Saf-CO-Meter indicating tube.¹ A test of the solubility of Product I was made in thirteen different solvents.

¹ Saf-CO-Meter indicator tube contains silico-molybdic acid.

Obtaining this new compound required sensitive and critical crystallizing conditions in the original reaction mixture, and a particular technique of slow hydrolysis of the intermediate oxy-phospho-bromo compound, $(\text{CH}_3)_2\text{C}(\text{CCl}_3)\text{-O-PBr}_4$, over to the desired 1,1,1-trichloro-tert. butyl phosphate.

In one case, out of several trials, it was possible to isolate 1,1,1-trichloro-tert. butyl bromide in about a 5 percent yield. Obtaining this bromide was also found to be a matter of critical and sensitive crystallizing conditions of the reaction mixture. A test of the solubility of the bromide was made in thirteen solvents.

It was desired that 1,1,1-trichloro-tert. butyl phenyl ether be synthesized from potassium phenoxide and 1,1,1-trichloro-tert. butyl bromide by way of the Williamson synthesis. However, when this synthesis was attempted, none of the ether was isolated. A reaction was evidenced by the formation of some potassium bromide. If some of the ether was formed, it seemed to have rearranged to the corresponding p-(1,1,1-trichloro-tert. butyl) phenol. The trichloro-methyl group was affected in this synthesis since some potassium chloride was also formed. This part of the reaction would lead to the formation of phenoxy-methyl compounds in place of the trichloro compounds.

Attempts to reproduce the synthesis of 1,1,1-trichloro-tert. butyl phenyl ether after the method reported by Alfred Stoloff, indicated that he had not isolated the ether. Stoloff's "ether", the product prepared by the author, and an equimolar

mixture of chloretone and phenol exhibited the same behavior with regard to melting point, alkaline breakdown, solubility, and distillation characteristics. It was thought, therefore, that the product called 1,1,1-trichloro-tert. butyl phenyl ether by Stoloff was identical with such a mixture of chloretone and phenol.

Within the scope of this investigation neither the 1,1,1-trichloro-tert. butyl phenyl ether nor the p-(1,1,1-trichloro-tert. butyl) phenol were isolated.