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REPORT  
of  
Committee on Thesis

The undersigned, acting as a Committee of  
the Graduate School, have read the accompanying  
thesis submitted by G. H. Woollett  
for the degree of Master of Science  
They approve it as a thesis meeting the require-  
ments of the Graduate School of the University of  
Minnesota, and recommend that it be accepted in  
partial fulfillment of the requirements for the  
degree of Master of Science

R. H. Hunter  
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A Catalytic Decomposition of

Some Silver Salts.

A Thesis submitted to the

Faculty of the Graduate School of the

University of Minnesota.

By

G. H. Woollett

In partial fulfillment of the requirements

For the degree of

Master of Science.

June

1916.

Theoretical Part.

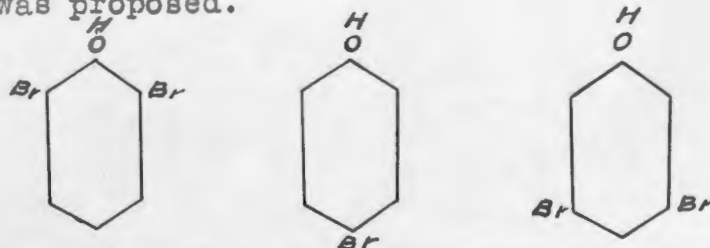
The abnormal reaction of the silver salt of symmetrical tri-bromophenol in undiluted ethyl iodide has been described by Torrey and Hunter! Either the red or the white form splits out silver bromide to form an amorphous white substance which is insoluble in alcohol and has the empirical formula  $(C_6H_2Br_2O)_n$ .

The reaction is accompanied by the appearance of a greenish blue color in the ethyl iodide, which soon fades. Almost all of reaction product consists of the above mentioned compound, tho a little of the normal ether is always formed.

This work has been continued by students in this laboratory, working with Dr. Hunter. They account for the occurrence of the two organic compounds by the assumption that two reactions with different velocities take place, the one leading to the amorphous substance being more rapid than that which yields the normal ether. They have also found that the same compound is formed on treating the silver salts of s-tri-halogenated phenols with boiling benzene and in the case of the silver salt of tri-bromresorcin mono-methyl ether on simple treatment with cold benzene.

One of the interesting questions suggested by this work is: which of the two possible positions does the reactive bromine atom occupy? It was the primary purpose of this research to answer that question.

In order to get at this point the study of the three following phenols was proposed.



The advantage of these phenols is that they each have bromine in only one position relative to the hydroxyl. In the case of the first two the positions in question are separated, being found in two different phenols so that if the bromine in the ortho position is different in reactivity from bromine in the para position this difference will be easily determined and fixed without doubt to the proper position.

It was deemed possible that no great difference would be found in the action of the two first silver salts and if such was the case it was desired to find out if the non-selective action would extend to bromine in the meta position. For this the obvious phenol was the 3:5 - di-bromo-phenol given third in the above list.

- Properties of the Phenols -

The silver salts of para-bromo-phenol and of 2:6 di-bromo-phenol were found to be colorless, attempts to prepare colored varieties were not successful. The para-bromo and 3:5 salts, as expected were found to be quite unstable but the 2:6 salt contrary to all expectations proved to be remarkably stable, more so even than that of 5- tri-bromo phenol.

The salt of 3:5 di-bromo phenol when freshly precipitated was distinctly yellow but changed rapidly to the colorless variety.

<sup>2</sup>  
Torrey and Hunter found several cases in which a red silver salt was first precipitated but changed to a white one before it could be isolated. In all of these cases three bromine atoms were present in the 2:4:6 positions to a hydroxyl.

<sup>3</sup>  
Hantzsch found one silver salt, that of di-bromo-para-cresol

which showed a red and a white form. This contains only two bromine atoms it is true but it has three substituents in the 2:4:6 positions to the hydroxyl, which he concludes are necessary for the existence of chromo isomers.

He also found that some of the colored salts of phenols which showed only the one form contained water. We were not able to isolate the colored variety of the 3:5 salt but the white salt which was isolated was distinctly crystalline and somewhat soluble in water. It does not seem probable that a hydrated form would be precipitated first and later change to an anhydrous crystalline form, but as the colored salt could not be isolated, it is not desired to lay any stress on this point.

- Reactions of the Salts. -

\* Ethyl Iodide -

With cold undiluted ethyl iodide the 2:6 salt gave the normal reaction only, and slowly. With hot ethyl iodide the velocity of the reaction was greater but the product was the same, 2:6 di-bromo-phenetole. No definite color changes were noticed.

The 3:5 salt gave the normal reaction instantly with cold ethyl iodide without any definite color changes.

The silver salt of para-bromo-phenol in cold ethyl iodide reacted much like the silver salt of tri-bromo-phenol, in that the reaction when it had started was quite vigorous and was accompanied by the appearance of a brilliant green color which faded in a few hours. An amorphous compound was isolated which in physical properties was like that obtained from the tri-bromo-phenol silver salt under like conditions.

From this it will be seen that the para-bromo-phenol was the only one which gave an "abnormal" reaction with ethyl iodide corresponding to the one given by the s-tri-bromo phenols.

#### Reactions in Benzene.

Since the silver salt of tri-bromoresorcin mono-methyl ether gave the decomposition smoothly in cold benzene while both it and other tri-halogenated phenolates gave the same decomposition in boiling benzene, the action of this substance was tried on our salts.

Cold benzene had no visible effect within a reasonable time on any but the para-bromo salt. This one blackened and gave off a small quantity of gas, an amorphous compound being also formed.

On boiling with the benzene each was found to decompose as did the salts of the symmetrically tri-substituted phenols, but the reaction proceeded with widely differing facility, and to our regret we found that both silver bromide and metallic silver were split out, indicating some decomposition of the molecule in other directions.

The salt of para-bromo-phenol reacted most easily as was expected from its behavior in cold benzene. The percentage of metallic silver eliminated, as calculated from the amount of bromine present in the amorphous compound in excess of that required by the assumption that Ag Br only was split out, we found to be 44.8% of the total silver present in the original silver salt. In this case the figures were checked up by separating the silver and silver bromide in the residues and weighing. The results were found to agree as well as could be expected.

The 3:5 salt reacted readily but split out metallic silver

to the extent of about 81% of the total silver present.

The 2:6 salt reacted with extreme reluctance but split out only about 32% of its silver as the metal. With the other two salts the decomposition was complete in a few minutes but with the 2:6 salt it was found necessary to boil the mixture from five to eight hours to get enough of the amorphous compound to analyze and in addition the substance was not white like the others but red, probably thru contamination.

The physical properties of these amorphous compounds were all like the one from tri-bromo-phenol.

As the corresponding free phenol always appeared in the reaction product and as a distinct loss in weight took place in the case of the para-bromo salt, we suspect that the metallic silver found, was reduced at the expense of hydrogen from other molecules of the salt which underwent a deep seated change.

Splitting out of metallic silver is a characteristic of unstable silver salts and can be taken as an inverse measure of the stability of the salt. It would be expected that the unstable para-bromo-phenol silver salt on being heated would split out some metallic silver with the silver bromide.

The 2:6 & 3:5 salts also split out silver as such in the inverse order of their stability but in them the bromine seems to be bound very firmly.

A carbon, hydrogen and halogen determination on the amorphous compound from para-bromo-phenol showed that no great amount of oxidation had taken place.

Undoubtedly, then, it may safely be assumed that these amorphous



substances are mixtures of compounds containing more or less of the amorphous oxide comparable to that obtained from tri-bromo-phenol, as the original silver salt is less or more stable.

This makes no difference in the conclusion which may be easily reached, which is that it is without doubt the para halogen atom which is responsible for the "abnormal" reaction and which leaves the molecule with the silver in the case of the symmetrically substituted tri-halogenated phenols.

Several other interesting deductions can be made from the action of these three salts.

Evidently the two ortho substituents have a retarding effect on the velocity of the normal reaction and have little effect on the "abnormal" one. The para substituent is responsible for, and takes part in, the "abnormal" reaction while it has not much effect on the normal one.

These two assumptions explain satisfactorily the action of the silver salt of symmetrical tri-bromo-phenol, in which the normal reaction is retarded while the abnormal one is favored, resulting in the large yield of amorphous compound.

The substituents in the meta positions evidently will not retard the normal reaction and do not take part in the abnormal one thus accounting for the great velocity of the normal ether formation with that salt.

It may be questioned whether or not this retardation is a case of ordinary steric hindrance as the atoms responsible for the hindrance are ones which would normally react with those they are "protecting." In such a case the influence would not seem to be

due simply to space filling.

Certainly the most clear cut examples of steric hindrance are to be found where ortho substituents come into play. It was the surprising influence of such substituents on the esterification of the benzoic acids which led V. Meyer to formulate his "Esterification law." He found all ortho substituted benzoic acids formed esters more reluctantly than unsubstituted benzoic acids, and that some di-ortho substituted ones, notably those containing  $\text{NO}_2$ , Br or I, refused entirely to form esters.

As both positive and negative substituents gave the same sort of effect differing only in degree, he concluded that the position and weight of the group was more important to the hindering effect than its nature. The effect was supposed to be due to a crowding of atoms around one end of the benzene ring so that the space around the reactive group was actually filled up and entrance to it blocked partially or entirely.

This view has been much modified both by V. Meyer and other investigators. It has been found that a larger alkyl group has no more effect than  $\text{C}_2\text{H}_5$ , and also in some cases that  $\text{NO}_2$  has a greater effect than the heavier Br or I.

Cases have also been found in which di-ortho substituted molecules are more reactive than the mother substance; notably in the well known case of picryl chloride.

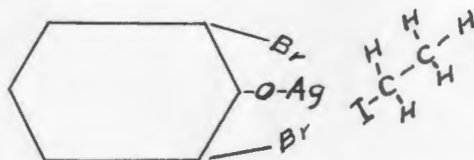
Other cases have been found like ours in which ortho substituents retard a reaction while meta and para substituents greatly accelerate it, as in the acetylation of substituted anilines.<sup>5</sup> A significant point in this connection is that this

<sup>4</sup> Kellas Zeit. Phys. Ch 24, 221, 1897. <sup>5</sup> Menshutkin C, 1, 551, '06.

reaction was also found by Menschutkin to be di-molecular in the absence of a catalyst but with the halogen salt of the amine as a catalyst the reaction was monomolecular, the hydriodide having the greatest accelerating effect.

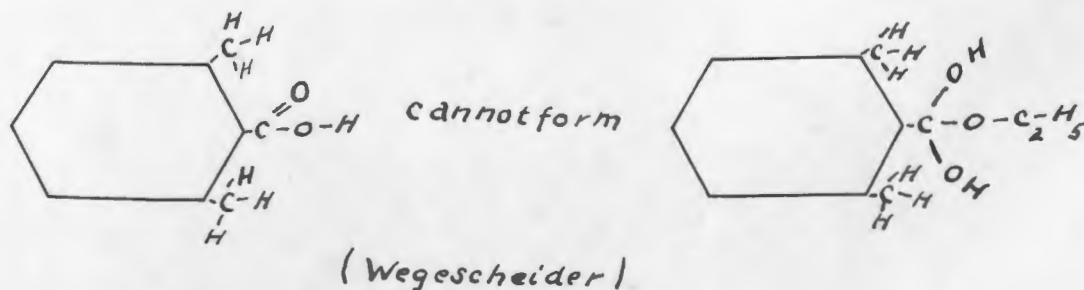
The idea of steric hindrance has gradually been extended to take account of the nature of the substituent, and the idea of actual crowding of atoms or space filling has in some instances become untenable. The influence of atoms far beyond their actual distance must be considered, and we believe the action of the 2:6 silver salt will add some evidence to this view.

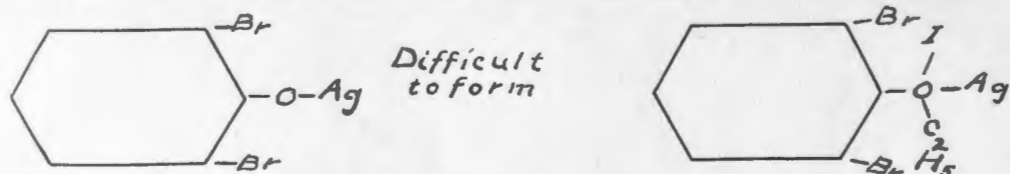
According to the old conception the action of this salt would be pictured as below:



It is hard to see how the silver and bromine on this assumption could be close enough to prevent the approach of the ethyl iodide without reacting with each other.

There is some reason to believe an addition compound may be formed prior to the formation of the ether, with silver phenolates.<sup>7</sup> This may be compared to the one assumed by Wegscheider to account for the hindrance in esterification mentioned above;

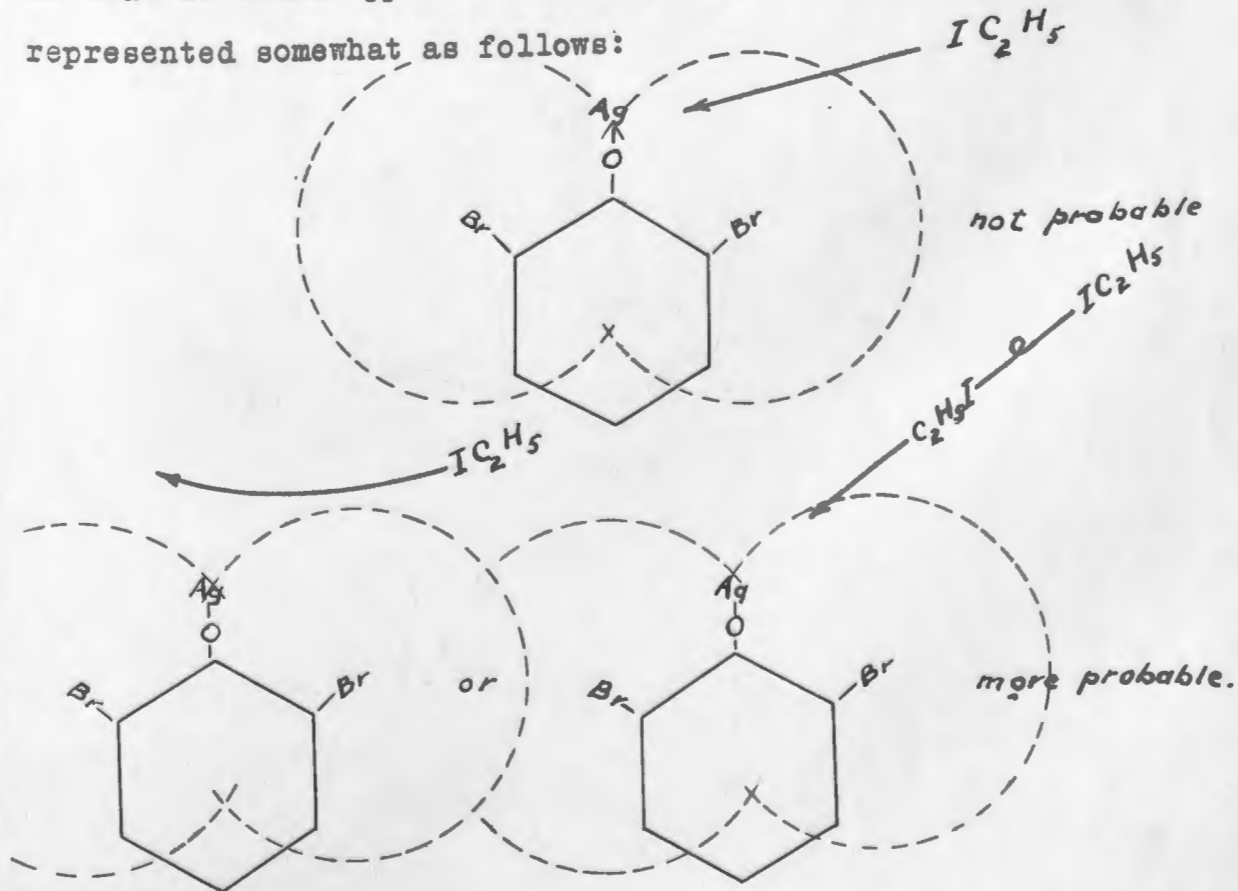




If such a compound is formed with phenolates not containing ortho substituents it is hard to believe that such a close relationship could exist between the Br, O, and Ag as to prevent the formation of such a compound in this case without the Br & Ag reacting with each other.

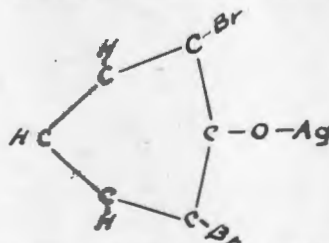
A better explanation of this case, at least, is based on the assumption of electronegative spheres of influence around the bromine atoms, which are very large compared with the actual size of the atom itself..

This force would act on an approaching molecule of ethyl iodide and cause it to shear off or at least to rotate enough so that it would approach with the alkyl end first. It may be represented somewhat as follows:



This sort of action would be in some measure comparable to the mechanism of the reflection of the alpha particles by heavy atoms as suggested by Rutherford.<sup>6</sup>

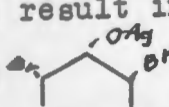
It may well be possible that the repulsion between these two bromine atoms would distort the benzene ring somewhat making the two last assumptions more plausible, as -

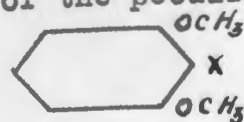


The stability of this salt toward other disintegrating influences may also be explained, as it is a well known fact that negative substituents in a chain of carbon atoms lend negative qualities to the neighboring substituents. This is true for instance of tri-chlor-acetic acid which is a much stronger acid than acetic acid.

This is exactly the case with the 2:6 salt, the two bromine atoms lend additional acidic properties to the hydroxyl making this phenol a stronger acid than the others considered and of course making its salts more stable.

The attraction between bromine and silver must also be taken into consideration.

In the 2:6 salt it could not result in any change other than the knitting together of the  group by a partition of valences, into a more or less stable structure. This has already been suggested as an explanation of the peculiar properties of compounds of the type



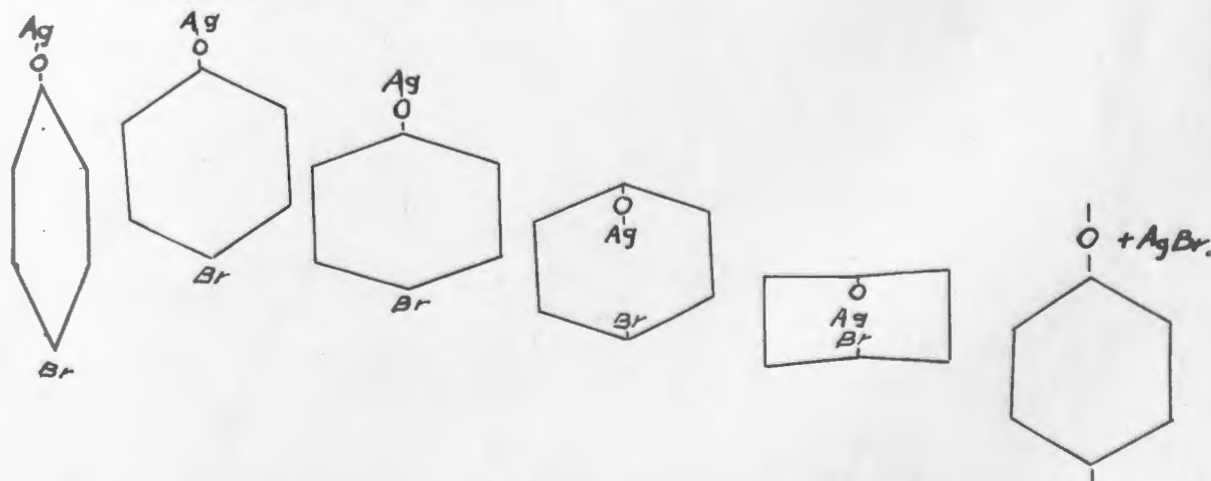
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Compounds of this type show the usual sluggish reactivity; the amine  $\text{C}_6\text{H}_4(\text{OCH}_3)_2\text{NH}_2$  diazotizes very slowly and gives a diazosulphate which is remarkably stable, being able to endure long boiling.

The attraction assumed here together with a certain degree of flexibility in the benzene ring would explain the reactivity of the para bromine atom very well indeed.

That the benzene ring vibrates as an elastic ring has long been one of the important theories of organic chemistry. In the course of its oscillation the para positions would be the ones which could approach each other most closely and it is only a small step further to imagine in our para substituted salts that the stress between the Ag and Br is sufficient to make them come close enough to react with each other.

The "abnormal" reaction may be represented as follows, using the idea of Baly & Stewart:



On the other hand two bromine atoms in the ortho position to the O Ag group would prevent the near approach of a third negative atom (iodine) from outside the molecule thus retarding

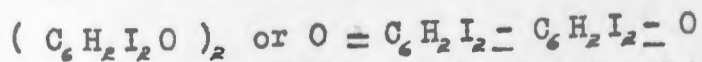
the normal ether formation in the S-tri-bromo silver salts.

Whether these speculations, which are based strictly on theories already presented by well known chemists, are well founded or not, it certainly is true that definite experimental evidence is at hand for the different activities of the bromine atoms in these salts. It is sure that the para atom is the one that reacts in the tri-bromo-phenol and the other symmetrically substituted phenols, and that is what we set out to find out.

Our attention was next turned to the silver salt of s-tri-phenol.

This salt which is light yellow in color was found to react with cold ethyl iodide slowly to give a small quantity of white amorphous compound but a much larger amount of the tri-iodo-phenetole.

This action is of the utmost importance for an understanding of the reaction, on account of the relation of the s-tri-iodo phenol to the red tetra-iodo-diphenylene quinone, to which is ascribed the formula.



This red compound is isomeric with the white amorphous compound which should be obtained from the silver salt by ethyl iodide, and it is represented as being formed by loss of the para iodine atom of tri-iodo-phenol.

It became necessary then, to study the decomposition of both the silver and the potassium salts of this phenol, the only the

silver salt will be considered at the present time.

It was desired to increase the yield of the white amorphous oxide over that of the tri-iodo-phenetole and proceeding from our conception of the reaction, as a decomposition, it was found that by simply warming the salt before mixing with the ethyl iodide a reaction can be made to occur which is very similar to that given by the silver salts of the tri-bromo- and para-bromo-phenols, even to the appearance of a quickly fading green color. This color was found to originate in the lumps of the salt and the presence of lumps was also found to greatly promote the "abnormal" reaction as well as the appearance of the color.

On long continued boiling with benzene the salt gave a white amorphous compound but one which was low in iodine content. The reaction proceeded more quickly in boiling xylene but that product was also low in iodine.

In most of the reactions described in connection with tri-iodo-phenol a little of the red tetra-iodo-diphenylene quinone was always found but not usually in quantity sufficient to cause difficulty in separating the white from it.

#### Summary.

In cold ethyl iodide the silver salts of phenols containing para bromine react in part "abnormally", those containing two ortho or meta bromine atoms only, react normally.

The velocity of the ether formation is least in the molecule containing two ortho bromine atoms and greatest in that containing two meta bromine atoms, the one containing para bromine only, being intermediate.

The boiling benzene each gives an amorphous compound, the



para-bromo salt giving one which resembles the compound given by it in ethyl iodide.

It is suggested that the reaction is due to a strain in the molecule caused by an attraction between silver and bromine attached to the same benzene ring.

The repulsion between bromine and iodine retards the ether formation when two ortho bromine atoms are present in the silver salt.

The silver salt of symmetrical tri-iodo-phenol can be made to react in ethyl iodide like the silver salt of the corresponding tri-bromo-phenol.

The resulting substance is a white amorphous compound having the formula  $(C_6H_2I_2O)_n$  entirely different from the red one obtained by Lauteman etc. from the potassium salt. This is obviously a most important relation for the study of the reaction.

Experimental Part.

- The Silver Salt of 2:6 di-bromo-phenol. -

The 2:6 di-bromo-phenol was made by the method of Pope and Wood<sup>9</sup> from 3:5 di-bromo-4-oxy-benzioic acid.

55.2 grams of para-oxy-benzoic acid were stirred into 1600 grams of 75% sulphuric acid and cooled to 0°. 128 grams of bromine in 128 grams of glacial acetic acid (also cooled) were added to the suspension of para-oxy-benzoic acid, drop by drop at first, with constant stirring. The temperature was kept low, not exceeding 5° to avoid the formation of tri-bromo-phenol.

The reaction proceeded slowly. After one half the bromine had been added the mixture became a thick paste, and the rest of the bromine was added more rapidly.

At this point Pope and Wood allowed the mixture to stand a week.

One batch of ours was allowed to stand over night only, a poor yield resulted (55 grams).

Another batch stood two days, after which the bromine color had disappeared, this gave 98 grns.

The reaction mixture after standing was poured into a large quantity (4 liters) of water, collected on a plaited filter, washed and transferred to a Büchner filter and sucked dry.

The cake was dissolved in a small excess of potassium hydroxide in 500 c. c. volume and carbon dioxide passed in to precipitate any tri-bromo-phenol present. When the precipitate so formed melted above 180° the process was stopped, the di-bromo-para-oxy-benzoic acid precipitated by dilute sulphuric acid, filtered off washed and dried.

The acid without further purification melted at 258°.

<sup>9</sup> Soc. 101, 1826, (1912).

The acid without further purification melted at  $258^{\circ}$ . Pope and Wood give for the pure acid  $268^{\circ}$ . It is colorless, quite soluble in alcohol and crystallizes as long needles.

The 2:6 di-bromo-phenol was made from this by heating under pressure with alkali.

30 grams of the acid were heated with 200 c. c. of normal sodium hydroxide solution for  $1\frac{1}{2}$  hours at  $165^{\circ}$  as recommended by Pope and Wood, who also say that they obtained a better yield by heating with water alone, but as they were heating in glass tubes the pressure developed by the C. O. usually burst the tubes.

We also found this to be the case but as we were using a copper digester the slight leakage of the apparatus evidently kept the pressure from mounting too high, as none was noticed on opening it.

After the first preparation only  $\frac{1}{8}$  of the quantity of alkali was used (25 c c to 30 grams).

The mixture after heating was acidified with sulphuric acid and distilled with steam.

The phenol passing over was dissolved in a slight excess of potassium hydroxide in 250 c. c. volume and precipitated by passing in  $\text{CO}_2$ . By filtering off the precipitated phenol in fractions the precipitation was expedited somewhat as when considerable precipitated phenol is in the mixture further precipitation seems to proceed very slowly.

One repetition of this process gave a product consisting of fine colorless needles which melted at  $55^{\circ} - 56^{\circ}$  (Pope & Wood give  $56^{\circ} - 57^{\circ}$ ). The product is very soluble in alcohol, slightly in water and has a very penetrating phenolic odor, not unpleasant when not strong.

The silver salt was made by dissolving 1-3 grams of the phenol in a slight excess of twice normal potassium hydroxide solution and making up to about 50 c. c. Dilute acetic acid (2%) was added till a slight permanent precipitate was formed then 1 - 2 drops of 10% silver nitrate solution were added to remove halogen, the mixture shaken to coagulate the precipitate and filtered. To the filtrate, made up of 500 c c, an excess of the silver nitrate solution was added.

The white precipitate of silver salt was washed several times by decantation then transferred to a plaited filter and washed till the washings were silver free. The salt was then transferred to a Buechuer filter and sucked dry. Drying was completed either on glass in the air (dark) and subsequently in the dessicator, or in a Gooch crucible thru which a slow current of dry air was being drawn. The latter method gave quicker results.

At first this preparation was carried on in subdued light but later as light was found not to affect the salt particularly it was made in the ordinary diffused light of the laboratory. It was also found that the salt could be washed with alcohol and ether without any apparent change. This was done to the last few samples as it made drying easier, tho in all cases drying was completed over Calcium chloride.

The silver salt is pure white, appears granular under the microscope and is remarkably stable. A sample left in an east window about three months was not changed noticeably. It can be prepared in alcohol or acetone without blackening if filtered off within a few hours. It is not decomposed at 100° but is at a considerably higher temperature.

All attempts to prepare a colored variety failed.

- Analysis of the Silver Salt -  
for Ag.

.2021 grams gave .1036 grams Ag. Br.  
or 29.45% Br. Calculated for  $C_6H_4Br_2O$  Ag. 30.07%. Nitric acid  
alone was added in this analysis as the salt contained two atoms  
of bromine to one of silver.

- Action of Ethyl Iodide -

A 1/2 gram sample was covered with pure dry ethyl iodide in a  
corked test tube and left 27 days. When examined the ethyl iodide  
had evaporated leaving a yellow solid having the appearance of silver  
iodide. This was extracted with ethyl iodide. No amorphous com-  
pound could be precipitated by alcohol but on evaporating the ethyl  
iodide - - alcohol solution a faintly yellow crystalline compound  
was found. This substance melted without purification at about  
35° had an ethereal odor and was volatile at ordinary temperatures -  
the whole disappearing when left over night. The compound was  
undoubtedly the normal ether, 2:6- di-bromo-phenetole described by  
Pope and Wood who give the melting point of the pure substance as  
40.6°.

On heating with ethyl iodide a reaction took place slowly, the  
silver salt fluffed up, completely filling the ethyl iodide; silver  
iodide gradually separated and settled out leaving a clear straw  
colored liquid. No very distinct color changes could be noticed.  
The yellow liquid contained a crystalline compound exactly like the  
one described above, but no amorphous compound.

- Action of Boiling Benzene. -

A .9 gram sample was boiled 5 hours with dry benzene under a reflux

condenser. The salt slowly blackened. The benzene which was colored red, was filtered from the black residue and an amorphous compound precipitated from it by alcohol. The amorphous compound was stained pink, probably thru contamination.

On evaporating the filtrate from this a quantity of the phenol was found mixed with a little of the amorphous compound which had not been precipitated by the alcohol. The amorphous compound appeared as a reddish varnish out of which crystals of the phenol were projecting.

The precipitated amorphous compound which was a pink powder was analysed for bromine. 0.944 grams gave .1191 grams Ag Br or 53.58% Br. Calculated for (C<sub>6</sub>H<sub>2</sub>Br<sub>2</sub>O)<sub>n</sub> - 63.97%.

Several other samples of the amorphous compound were made in the same way, none of them were white, the color varying from pink to brown. It was found impossible to get enough to analyse from a one gram sample of silver salt by boiling less than 5 hours, 5-8 hours gave good results. A silver mirror was always formed on the flask in which the operation was carried out.

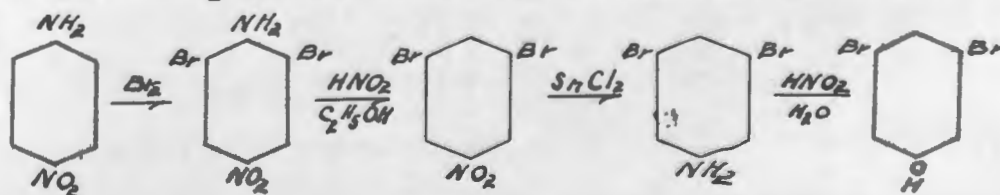
- Analysis of Amorphous Compound -

( Different sample )

.1163 grams gave .1474 grams of Ag Br. or 53.94% Br.

- The Silver Salt of 3:5 Di-bromo-phenol -

The phenol was made by a modification of the method used by Blankema,<sup>10</sup> according to the following series of reactions:



The di-bromo-para-nitraniline was prepared by the method given by Hollemann.<sup>17</sup> 69 grams of para-nitraniline were dissolved in 2.5 liters of water and 500 grams of crude sulphuric acid, in a 4 liter flask. The solution was cooled to 25°-30° and stirred by bubbling air thru it while 160 grams of bromine were dropped in from a dropping funnel. The reaction proceeded smoothly without attention and was complete in about two hours, the di-bromo-para-nitraniline separating out as yellow flocks. The product was filtered off, washed and dried. The yield was very good, varying from 94% to 100% of unpurified substance.

The 3:5 di-bromo-nitrobenzene was made from this by Hollemann's method.<sup>18</sup>

An attempt was made to prepare the 3:5 di-bromo-aniline by the same author's method<sup>1, 13</sup> but without good results. Hollemann reduced with iron in dilute sulphuric acid but we got much better results by using the following method.

A boiling solution of 20 grams. of the nitro compound in 75 c. c. of glacial acetic acid was poured into a solution of 96 grams of stannous chloride in 96 c. c. of concentrated hydrochloric acid, also boiling. The operation was carried out in the hood, with constant stirring of the reacting mixture. After boiling had stopped the clear solution was allowed to stand five minutes; it was then cooled by placing the vessel (casserole) in cold water. Crystals, presumably of the double compound .

$C_6H_3Br_2NH_2$   $SrCl_2 \cdot HCl$  separated out till the whole mass was set to a soft cake. This crystalline mass was transferred to a Buechner filter where the excess of acid was sucked out. The solid cake was covered with water in a casserole and treated with a 40%



potassium (or sodium) hydroxide solution till the tin hydroxides which first separated were dissolved.

In the bottom of the vessel a dark colored mud was found consisting of the amine sought, mixed with some metastannic acid. This mud was partially separated from the liquid by decantation and each portion extracted with benzene. These two portions must be extracted separately on account of their great tendency to emulsify with the benzene. On evaporating the benzene the amine appears as an oil which crystallizes on cooling. When heated much above 100 degrees it decomposes.

The amine crystallizes from dilute alcohol as colorless needles which melt at 56°.

It was found most convenient and economical of material to crystallize the amine as sulphate. For this the crude amine was covered with water and an excess of concentrated sulphuric acid poured on it. The sulphate formed at once and was dissolved in the smallest possible amount of boiling water, best by boiling with successive small portions. The hot solution was filtered and on cooling, white crystals of the amine sulphate separated. These were filtered off and dried. It does not melt but turns black at about 180°. Crystallizing the amine, this way separates all of the troublesome tarry matter.

To make the 3:5 di-bromo-phenol 5 grams of the amine or 7 grams of the sulphate were suspended in 100 c. c. of water containing 10 c. c. (9 c. c. for the sulphate) of concentrated sulphuric acid. The mixture was cooled with ice and the calculated amount (1.35) grams) of sodium nitrite added.

When diazotization was complete, which usually occurred in about 1/2 hour the cold mixture was filtered into two liters of water which was ~~just~~ below the boiling point, and was kept at that temperature until no more nitrogen was given off. This usually took about 1 1/2 hours. Blanksma recommends the use of 500 c. c. of 10% sulphuric acid here, but we failed to get any phenol by that method.

The mixture (2 liters) was filtered to remove the insoluble dye formed, cooled and the phenol extracted with ether, in which it is extremely soluble. Because of this great solubility, all of the ether must be driven off before attempting to purify the phenol. The yield of the crude product by this method was about 60%.

Purification was accomplished by the same method as used with the 2:6 di-bromo-phenol, using not more than 50 c. c. of water per gram of phenols. The stained portion of the phenol is precipitated first. When that is filtered off and the process continued the rest of the phenol comes down white.

On account of the considerable solubility of the phenol in water not all of it could not be precipitated. The mother liquor was extracted with ether to recover the dissolved part.

The pure 3:5 di-bromo-phenol crystallizes as colorless needles which melt at 81° and have a very disagreeable but not very strong odor.

A somewhat different method from the one given before was used in preparing the silver salt of this phenol, as the salt is soluble to some extent in water and cannot be precipitated if the solution is dilute.

One gram of the phenol was dissolved in a slight excess of twice normal potassium hydroxide and made up to 20 c. c. Acetic

acid (3%) was added till the slight permanent precipitate was formed and then one drop of 10% silver nitrate solution. The mixture was filtered into a small flask and made up to 50 c c. Two c. c. of this was diluted to 25 c. c. and set aside in another flask, to be used in washing.

An excess of silver nitrate was added to the larger bulk of phenolate solution whereupon a yellow precipitate formed which immediately turned white. The yellow color could best be noticed if the silver nitrate solution was added slowly, for after some of the precipitate had turned white it acted as a contrasting background against which the yellow color of the freshly precipitated salt showed up clearly.

The precipitate was filtered off on a small Buechner filter and washed with the diluted portion set aside for that purpose and lastly with about 20. c c of water. It was then sucked as dry as possible and dried in a Gooch crucible as described for the 2:6 silver salt or on glass in ~~vacuo~~ over calcium chloride. The salt after drying was kept over calcium chloride in the dark. None of the samples dried quite white, the fresh salt however is white, crystalline under the microscope (needles) and not very stable. It is decomposed below 100° and slowly blackens in the light.

#### Analysis of the Silver Salt.

For Ag. .2187 grams gave .1117 g Ag. Br, or 29.34% Br. For Br, .0856 grams gave .0912 grams Ag Br, 45.34%.

Calculated for  $C_6H_5Br_2O$  Ag, Br 44.57% Ag 30.07%.

The salt evidently contains some free phenol, probably carried down with it from the water solution.

- Action of Ethyl Iodide -

The silver salt reacts instantly with ethyl iodide whether the salt is wet or dry, and reacts violently even if the ethyl iodide is considerably diluted. Not much difference could be noticed in the reaction if the ethyl iodide was diluted with an equal volume of benzene or alcohol.

When a small quantity of the salt was dropped into the ethyl iodide it reacted with a hissing sound at the same time giving off a little cloud of vapor.

With iso-amyl iodide the reaction was less violent. No color changes could be noticed in either case which could not have been due to the silver iodide formed, which was always slightly dark and usually somewhat green.

No amorphous compound could be found in the reaction mixture when light colored samples of silver salt had been used altho a very little was found after using some very much blackened samples. This was no larger in amount than could be expected from previous decomposition.

A non-volatile brownish oil having an ethereal odor was found on evaporating the filtered reaction mixture. This product did not crystallize in a mixture of ice and salt. This corresponds to Mohlan and Oehmichen's <sup>14</sup> description of 3:5 -di-bromo-phenetole.

The oil was distilled and analysed for bromine.

.1957 gram gave .2621 g. Ag Br 57.00%

Calculated for  $C_6H_4Br_2O$   $C_2H_5$  57.11%

A small quantity of the silver salt was placed in a porcelain boat in a horizontal condenser thru the jacket of which steam was passed. The 3:5 salt decomposed with the evolution of a small puff

of vapor before the eight minutes had passed necessary to reach constant temperature. A second experiment was tried, 3:5 salt and 3:6 salt being placed in opposite ends of the same boat, ethyl iodide vapor mixed with air was drawn thru without waiting for constant temperature to be reached. The 3:5 salt decomposed in about the same time (2 or 3 minutes) while the 3:6 salt was not changed in ten minutes. The 3:6 salt gradually took on the appearance of silver iodide when a little of the liquid ethyl iodide was placed on it, while the residue left by the 3:5 salt was dark grey and appeared to have been fused.

- Action of Boiling Benzene. -

A sample about one gram in weight was boiled 20 minutes with 20 c. c. of dry benzene. It darkened rapidly while a silver mirror formed on the sides of the flask. The finely divided solid residue was difficult to filter from the benzene solution. After several filtrations a clear solution was obtained but no amorphous compound was precipitated by alcohol. On boiling off the benzene, adding alcohol from time to time, a solution was obtained from which a very small quantity of water caused a white amorphous compound to separate. This was washed dried and analysed for bromine.

.0502 grams gave .0795 grams Br. 61.30%.

A second sample of silver salt nearly two grams in weight was boiled with benzene as before but the benzene was evaporated off on the water bath. Crystals having the odor of 3:5- di-bromo- phenol appeared on the sides of the flask. Upon taking up the soluble matter in benzene and filtering a clear filtrate was obtained in one operation.

This filtrate was evaporated down to about 10 c. c. in which

volume 95% alcohol brought down the amorphous compound.

It was washed with alcohol and water as before, dried and analysed.

.0765 grams gave .1106 grams Ag Br  $\frac{61.53\%}{}$ .

Both of these samples were very white.

On evaporating the filtrate from the amorphous compound a soft yellow resinous substance was found, soluble in alcohol and alkalis. On standing crystals gradually formed in the mass, which was probably largely 3:5 di-bromo-phenol as it had the characteristic odor of that substance.

The ethyl iodide used in these experiments was purified in the usual way and had the boiling point  $70^{\circ}$ -  $72^{\circ}$ .

On account of the somewhat unexpected behavior of the silver salt of the 3:5 substituted phenol a question might arise as to whether the 3:5 and the 2:6 salts had not been confused.

Special preparations of each silver salt were carried thru from the beginning for the purpose of being able to say this point had been covered.

It may be said here that at no point in their preparation are these two phenols or their silver salts sufficiently alike in appearance to cause any real danger of confusion.

#### - The Silver Salt of Para-bromo-phenol. 15-

This silver salt was made from a sample of Kahlbaum's para-bromo phenol which melted at  $66^{\circ}$ -  $67^{\circ}$  and was used without further purification. The phenol is somewhat soluble in water and like ordinary unsubstituted phenol forms an oil with a small quantity of water, dissolving in a larger quantity. On this account considerable free para-bromo-phenol is present in the solution of potassium salt from which the silver salt is precipitated, if the former is

freed from excess of potassium hydroxide by adding dilute acid till a slight permanent precipitate is formed. Several samples were made in this way however, but while they were quite white and clean in appearance they did not keep.

Two of these samples decomposed spontaneously. One of them had been kept near the radiator but the other had not. The decomposition product was a dark grey gummy mass from which a white amorphous compound was extracted with chloroform and precipitated by alcohol. The silver bromide etc. was very finely divided and did not filter off easily, making it necessary to submit the mixture, (after evaporating off the solvent) to the action of a solution of potassium cyanide for about twenty four hours.

This treatment removed the finer particles of insoluble matter. The cyanide solution was filtered off, the precipitate washed with water, then with alcohol and finally the amorphous compound dissolved out with chloroform, from which it was precipitated by alcohol. The amorphous compound was re-dissolved in benzene precipitated by ligroin, filtered and washed with ligroin after which it was dried at about 60 °.

The compound consisted of small chalky white cakes.

- Analysis of this Compound. -

.0769 grams gave .0523 grams Ag Br.

or 28.93% Br.

Another scheme for preparing the silver salt was tried. The phenol was dissolved in a very slight excess of potassium hydroxide as usual and diluted to 200 - 300 c. c. volume (for 5 grams) then treated with successive small portions of silver nitrate solution, the mixture being shaken after each addition. When the addition

of a further small quantity produced a white precipitate, the mixture was filtered and an excess of silver nitrate added to the filtrate after which the procedure was the same as that given for the silver salt of 2:6 di-bromo-phenol. It was not possible to get washings from this silver salt absolutely silver free, probably due to the solubility of the salt.

A flash of darker color was always noticed at the spot where the silver nitrate solution entered the phenolate solution. The color always disappeared immediately and was supposed to be silver oxide formed due to hydrolysis of the phenolate.

No difference in action could be detected in the silver salts made by either of the above methods. The one case in which a sample made by the latter method was not used immediately after drying, we succeeded in keeping it somewhat more than a month, at which time it was used.

All samples of this salt were kept over calcium chloride in the dark, as light was found to blacken them. All samples other than the one mentioned were used within a week after preparation - none of them dried absolutely white, all were slightly grey.

- Analysis of the Silver Salt -

- For Silver -

.2343 grams gave .1545 grams Ag Br

or .37.87% Ag.

. . . . . Calculated for .

$C_6H_4Br_2O$  Ag. 38.58% Ag.

The salt evidently contained the free phenol as was shown later.

- Action of Ethyl Iodide -

Three grams of silver salt were covered with ethyl iodide in



a test tube. After a few seconds the action began and quickly became vigorous. The ethyl iodide boiled and the tube became uncomfortably hot. The reaction was accompanied by the appearance of a brilliant green color in the solution which persisted several hours.

The experiment was repeated with a like amount of silver iodide. The ethyl iodide was filtered off and the insoluble portion washed with chloroform. In the filtrate and washings was a white amorphous compound which was precipitated by alcohol. It was separated in the same way as the ones previously described, and analysed for bromine.

.0495 grams gave .0387 grams Ag Br

or

33.27% Br.

In the filtrate from the amorphous compound was found on evaporation a yellow oil which smelled strongly of anise and refused to crystallize at room temperature. This was undoubtedly the para-bromo-phenetole.

These two products are produced in approximately equal amounts, more of the ether being formed if of either.

- Action of Boiling Benzene -

5.78 grams of the silver salt were boiled with dry benzene 3/4 hours under a reflux condenser. The silver residue was filtered off washed with benzene, dried and reduced with zinc and dilute sulphuric acid. The silver reduced was ignited and weighed, giving 39.1% silver.

The amorphous compound present in the benzene filtrate was

precipitated by alcohol, washed with alcohol, dilute alkali and finally with water after which it was dried over Calcium Chloride and analysed for bromine.

.1782 grams gave .1095 grams Ag Br.

or 26.15% Br.

The amorphous compound made in these three ways had the same appearance.

The remainders of the three analysed samples were mixed, extracted with hot alcohol for about 1/4 hour, dried and analysed for bromine.

.1774 grams gave .1141 grams. Ag Br.

or 27.37% Br.

Calculated for a mixture of the following composition:

$(C_6H_4BrO - C_6H_4O)_n = 30.15\% \text{ Br.}$

This shows that approximately 1/2 of the bromine has remained in the compound.

On evaporating the benzene - alcohol filtrate after the precipitation of the amorphous compound (from 5.78 gm. Sample) a crystalline substance was found having the odor of para-bromophenol, which it undoubtedly was, altho its melting point was low. It melted at about 50° tho not sharply.

- Examination of Residues. -

Two small samples of silver salt were each boiled 1/2 hour with benzene. The insoluble residue was filtered off washed with benzene, dried and weighed; after which it was reduced with zinc and dilute sulphuric acid. The silver was ignited and weighed and the bromine determined in the filtrate as silver bromide.

The benzene filtrate containing the amorphous compound etc.

was evaporated to dryness and the soluble residue weighed.

Sample	.6161 grms.	100%	.6875 grms.	100%
Insol. residue	.3284 "	53.30%	.3845 "	55.93%
Total Ag. in residue)	.2283 "	37.06%	.2316 "	33.69%
Ag. in residue As Ag. Br.	.1136 "	18.44%	.1114 "	16.21%
Ag in residue As Ag. (by diff.)	.1147 "	18.62%	.1202 "	17.48%
Ag Br in residue	.2024 "	32.85%	.1940 "	28.22%
Soluble residue	.1906 "	30.94%	.1922 "	27.96%
Total residue	.5190 "	84.24%	.5767 "	83.88%
Loss	.0971 "	15.76%	.1108 "	16.21%

To test the loss a sample of silver salt was boiled in a small weighed glass dish with a small quantity of benzene on the water bath till the benzene was driven off.

Weight of sample	.2559 grms.
After benzene was driven off	.2276 "
Loss	.0283 "

or 11.1%

This does little more than show that some loss occurs during the process and that the silver in the residue is about equally divided between silver bromide and metallic silver.

Further experiments were made with silver salt made from para-bromo phenol prepared by the method of Hantzsch and Mai.<sup>16</sup>

The samples used had the melting point of 65°- 66°

A sample of silver salt about three grams in weight was prepared in the usual way and boiled 20 minutes with benzene.

A solution of the amorphous compound was obtained in the usual way but on adding alcohol this went over into a colloidal

state without precipitating. A small drop of hydrochloric acid caused the immediate coagulation of the amorphous substance, which was separated and dried at 80°.

A carbon, hydrogen and bromine determination was made on this compound principally to see how much oxidation had taken place.

.1519 grams gave .3249 grams  $C O_2$

and .0403 grams  $H_2 O$  or

58.28% C and 2.96% H.

.0775 grams gave .0503 grams Ag. Br.

or 27.52% Br.

Calculated for a mixture of equal parts  $(C_6H_4OBr)_n$  and  $(C_6H_5O)_n$ , C, 54.54%; H, 3.03%; Br, 30.30%; O, 12.13%.

Another sample of silver salt when put in the cold benzene began to react immediately turning dark and giving off bubbles of gas. The white amorphous compound was found in a small test sample taken from the cold mixture but the main bulk was boiled a few minutes to make sure the salt was all decomposed.

The mixture was filtered and the benzene driven off on the water bath, the resulting mixture was extracted with chloroform, the colloidal silver and silver bromide were coagulated with a small drop of HCl and filtered off. The amorphous compound was precipitated with alcohol filtered off washed with alcohol and dried at 80°. It was a little yellower than the previous sample.

A carbon, hydrogen and bromine determination was made on this sample also.


.1806 grams gave .3555 grams  $C O_2$  and


.0485 grams  $H_2 O$  C, 58.65% C and 2.80% H

.1028 grams gave .0764 grams Ag Br or 31.70 % Br.

It can be seen from the following table that no great amount of oxidation could have occurred.

	Found	Calc.	
Carbon	58.26%	53.65%	54.54%
Hydrogen	2.96%	2.60%	3.03%
Bromine	27.62	31.73	30.30%
Oxygen	<u>11.16</u>	<u>12.02</u>	<u>12.13%</u>
	100.00	100.00	100.00

The percentages required by the formula  are, C 78.26%, H, 4.35, O, 17.39%.

Those required by the formula  are C 41.87%, H, 2.33, O, 9.30, Br, 46.50.

The calculated percentages in the table are for an equimolecular mixture of these two, which seem to approximate roughly those found in the substance.

The Silver Salt of Tri-iodo-phenol.

This phenol was made by Korner's <sup>17.</sup> method and was purified by crystallization from dilute alcohol till it gave the melting point of 156°. The silver salt was made by the usual method, drying as rapidly as possible.

The salt is yellow and when dry quite stable. Bromine or Iodine converts it into the red tetra-iodo-diphenylene quinone, sunlight also does this but very slowly. A sample left where the sun reached it a few hours everyday was found to be deeply colored upon the surfaces exposed but the action had not proceeded beyond the surface appreciably.

<sup>17</sup> Korner A, 137, 213.

- Action of Ethyl Iodide-

A sample treated with cold ethyl iodide gave a very small quantity of white amorphous compound. While samples treated with hot ethyl iodide gave slightly more the yield was still small.

A sample about two grams in weight coarsely powdered was heated on the water bath in a small flask, ethyl iodide being added thru an empty reflux condenser after the salt was thoroughly heated. A reaction took place immediately, the ethyl iodide boiled and the mixture became intensely green. The green color faded in a few minutes leaving a dark residue and a pinkish yellow liquid, from which an amorphous compound was precipitated by alcohol. The amorphous compound was stained pink by the small amount of tetra-iodo-diphenylene quinone formed.

The dark residue remaining in the flask was extracted with bromoform and on adding alcohol to this extract gave a pure white amorphous compound which was dried at 100° and analysed for iodine.

.1394 grams gave ;1899 grams Ag I    73.60% I.

.1063 grams gave .1452 grams Ag. I    73.80% I

Calculated for  $(C_6H_2I_2O)_n$                     73.83% I

The experiment was repeated omitting the condenser and using a more finely pulverized sample of silver salt. The reaction was much more rapid, the color being obscured at first by darkening of the salt. After the dark mud had settled the green color was found to be persisting around several small lumps, spreading from them to the surrounding solution.

The experiment was repeated again using silver salt entirely in lumps about the size of rice. The reaction this time was much

slower giving a clear green color which proceeded from the lumps, with hardly any blackening.

White amorphous compound was found in both these experiments mixed with a very little of the red substance.

#### Action of Benzene Etc.

Several samples were boiled with benzene for varying lengths of time up to eight hours. Very little action took place, the salt slowly darkened and in some cases a pink color was noticed in about half an hour. Samples boiled from five to eight hours gave some white amorphous compound but this was found to be low in iodine content.

On boiling with ortho xylene the salt decomposed in from one half to one hour giving a good yield of amorphous compound which was also found to be low in iodine content.

.1929 grams gave .2258 grams Ag. I , 63.25% I

.0712 grams gave .0753 grams Ag I 57.17% I

At times a slight pinkish color was noticed while boiling with xylene but this never persisted thru a full hour's boiling.

A flow sheet to show the preparation of the amorphous compound from the silver salt of 3;5 di-bromo-phenol is appended.

