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Report

of

Committee on Examination

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This is to certify that we the undersigned, as a committee of the Graduate School, have given Arthur Hubert Kohlhase final oral examination for the degree of Master of Science . We recommend that the degree of Master of Science be conferred upon the candidate.

Minneapolis, Minnesota

June 2 1921

J. H. Hunter
Chairman

M. C. Sneed

F. H. MacDougal

W. J. Larson

THE UNIVERSITY OF MINNESOTA

GRADUATE SCHOOL

Report
of
Committee on Thesis

The undersigned, acting as a Committee of the Graduate School, have read the accompanying thesis submitted by Arthur Hubert Kohlhasse for the degree of Master of Science.

They approve it as a thesis meeting the requirements 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.

J. H. Hunter
Chairman

M. C. Sneed

F. H. MacDougall

A. P. Janson

June 2 ¹⁹²¹ ~~1918~~

THE ACTION OF IODINE AND ALKYL IODIDES
UPON THE SILVER SALT
OF
TRIBROMTHIOPHENOL.

A Thesis

Submitted to the Graduate Faculty

of the

University of Minnesota

by

Arthur Hubert Kohlhasse

In partial fulfillment of the requirements

for the

degree of

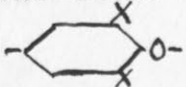
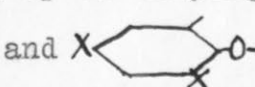
Master of Science.

June

1921.

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THEORETICAL PART.

During the course of work published by Torrey and Hunter¹ in 1911, it was noticed that the salts of tribromophenol reacted in a very unusual manner with dry, undiluted ethyl iodide. In an article appearing in 1916, it was shown² that the product of the reaction was a substance of very large molecular weight. It was named poly-dibromophenylene oxide and assigned the formula $(C_6H_2Br_2O)_n$, in accordance with what appeared to be the mechanism of the reaction. It was further demonstrated that the ethyl iodide reacted catalytically and that a like catalytic effect was shown by free iodine, bromine, propyl bromide, and even warm benzene in some cases. In a second article on the subject,³ it was shown by W.H.Hunter and F.E.Joyce that the halogen going out with the metal from the salt came from the ring and from either the ortho or para positions. Later, it was shown by Hunter and G.H.Woollett⁴ that tribromophenol bromide acted in a very similar manner and the same authors showed also⁵ that, in addition to the usual colorless, amorphous poly-dibromophenylene oxide made up of varying numbers of residues of the formulae  and , there could be obtained a reddish-purple substance giving the same analysis and showing the same properties of solubility. The latter substance was obtained in by the action of iodine in water. Investigation indicated that this colored form contained .3 - .4 o/o

¹ Jour. Am. Chem. Soc. 33, 204 (1911)

² Jour. Am. Chem. Soc. 38, 1761 (1916)

³ Jour. Am. Chem. Soc. 39, 2640 (1917)

⁴ Jour. Am. Chem. Soc. 42, 131 (1921)

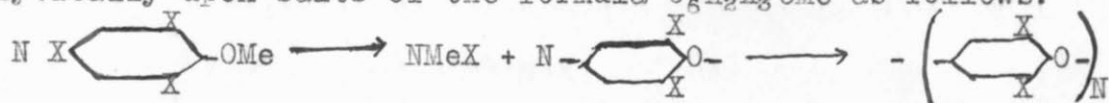
⁵ W.H.Hunter and Lillian M.Seyfried, J. Am. Ch. Soc. 43, 135 (1921)

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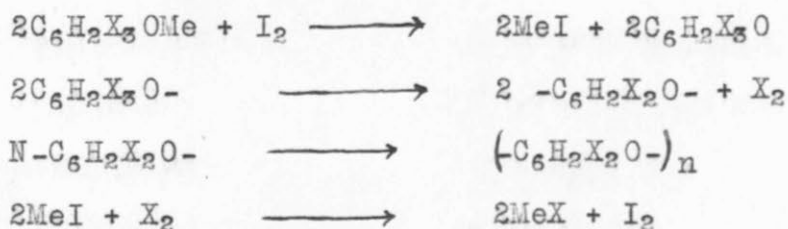
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of quinoid oxygen.

Thus far the research done upon the subject had shown that benzene, the halides and certain of their derivatives acted catalytically upon salts of the formula $C_6H_2X_3OMe$ as follows:



An attempt was made⁵ in 1921 to determine the mechanism of the reactions involved in the formation of these substances. The information gained was not complete but seemed sufficient to show that, in the cases at least where free iodine was used to bring about the decomposition into poly-dihalogenphenylene oxide, the reaction can be expressed as follows:



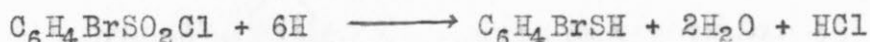
But it has **not** yet been demonstrated that the mechanism is the same with all the tri-halogen phenol salts or with all the catalysts used; it seems quite possible that it might not be the same.

To aid in throwing more light upon this subject of the mechanism of these reactions, it seemed advisable to investigate the analogous thiophenols. Sulphur seemed sufficiently like oxygen to show in general the same reactions. However, it is known that sulphur more readily forms compounds with the halogens and that those compounds are fairly stable. Thus it seemed possible that any intermediate compounds might be isolated or the reaction stopped before reaching the poly-phenylene stage. If such should

⁵ W.H. Hunter and Lillian M. Seyfried, Jour. Am. Chem. Soc. 43, 135 (1921)

be the case, the problem in hand would be very nearly solved. If, on the other hand, the reaction should take another course, a study of the reaction-products should still be enlightening in that it would necessitate an explanation of the course of the reaction being different and would thus point to the probable intermediate steps. In any case, the probable behavior of the sulphur compounds seemed of sufficient interest and importance to merit investigation.

Apparently, none of the trihalogen substituted thiophenols had ever been prepared; so it was necessary to first work out a method for their preparation. Hübner and Alsberg¹ had prepared p-bromthiophenol by the reduction of p-brombenzenesulphonyl chloride with tin and concentrated HCl:



Reinke² had prepared the tribrombenzenesulphonyl chloride by treating the potassium salt of tribrombenzenesulphonic acid with PCl_5 . By reduction of this compound according to the method of Hübner and Alsberg, small yields of s-tribromthiophenol were obtained. However, the yields were small, the process was laborious, starting from tribromaniline, and PCl_5 was exceedingly disagreeable to work with. Furthermore, there was the danger of contaminating the final product with mono or dibromthiophenol by side reactions.

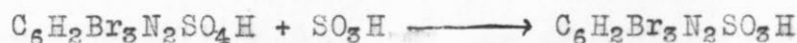
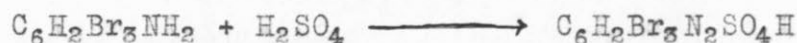
A second method tried was one due to Gattermann.³ The first step in this method is to prepare the diazonium compound, $\text{C}_6\text{H}_2\text{Br}_3\text{N}_2\text{SO}_4\text{H}$. However, because of the insolubility of both the

¹Annalen 156, 327

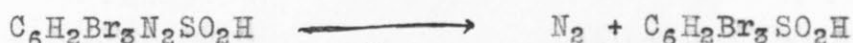
²Annalen 186, 271 (1877)

³Berichte 32, 1136 (1899)

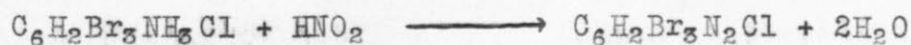
hydrochloride and hydrosulphate of tribromaniline, I found it impossible to prepare the diazonium compound. I succeeded in overcoming this difficulty later, as will be described in the experimental part of this paper, but because of the necessity of using a reduction in the final step to the thiophenol, this method seemed open also to the objection that reduction products would contaminate the final product. While no thiophenol was prepared by this method, I believe it could be made to give good yields since the same objections as were raised against this manner of preparation, with the exception of the contamination in reduction, also appeared and were overcome in the method finally used. The reactions involved in this Gattermann process are as follows:



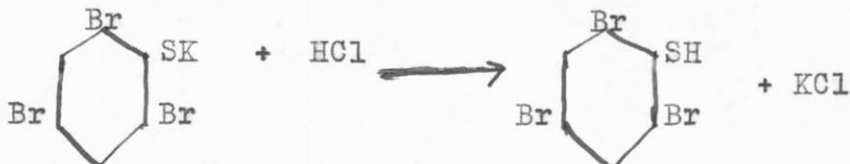
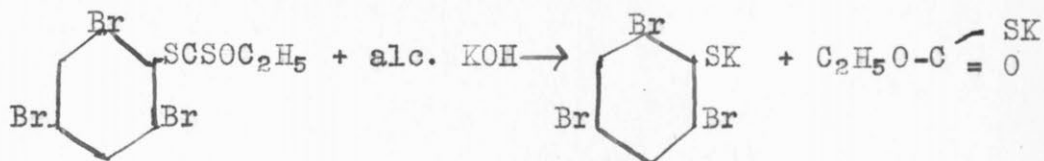
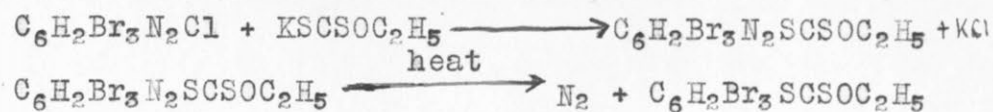
In the presence of finely divided copper this reacts:



The method finally used for the preparation of the s-tribromthiophenol used in the greater part of the experimental work described in this paper was adapted from Leuckardt.¹ The exact procedure followed in the preparation of the thiophenol as well as the various derivatives made from it, will be fully described in the experimental part. In outline, the method is as indicated below:



¹ Jour. fur Prak. Chemie, Neue folge 41, 179-224.



In addition to the intermediate xanthogenic ester indicated above, the following derivatives were prepared, analyzed and their solubility, melting-points, etc. determined: silver tribromthiophenylate, the ethyl and methyl ethers of the thiophenol, tribromthiophenyl acetate and hexabrom-diphenyldisulfide. Another compound was isolated from the xanthogenic ester which by analysis seemed to be identical with the methyl-tribromphenylthioether but showed different solubility and melting point. Its exact constitution has not yet been determined.

The silver salt of the tribromthiophenol was readily prepared from the sodium salt.

This silver salt is the starting point of our investigation. The work to be discussed in this thesis is concerned with a comparison of its reactions with the corresponding ones of the silver salt of *s*-tribromophenol. A secondary but very important topic which will be considered is certain preliminary evidence for dissociation of the hexabrom-diphenyl-disulfide. The results obtained will be briefly stated under A and B immediately following, and then discussed in some detail.

A. THE REACTIONS OF THE SILVER SALT OF TRIBROMTHIOPHENOL.

I. With Iodine.

When treated with one-half molecular equivalent of iodine in dry benzene, almost quantitative yields of hexabrom-diphenyl-disulphide were obtained. There was a small amount of oily product, 2-3 o/o, but nothing which corresponded to the poly-dibromophenylene oxides which always resulted from the reaction of the silver salt of the oxygen analogue with iodine under similar conditions. This immediately showed a very distinct difference between the oxygen phenol and the thiophenol.

On using one-tenth grain atom equivalent of iodine, a quantitative yield of disulfide was found, calculated from the iodine used. The rest of the silver salt was unchanged in direct contrast to the action with salts of tribromophenol.

II. With Ethyl Iodide.

Upon treating the silver salt with cold ethyl iodide for about two days, the product again failed to show the presence of any substance corresponding to the poly-phenylene oxides. Instead, quantitative yields of the ethyl ether were obtained. As the silver salt of the oxygen compound had given some phenetol derivative¹ with cold ethyl iodide, it was thought that by varying the conditions, especially by raising the temperature, the silver salt of the sulfur compound might form a poly-phenylene type of substance, also, though the results with iodine did not make this probable.

¹ Journ. Am. Chem. Soc. 39, 2645.

A sample of the silver salt was accordingly warmed to about 80° and then refluxed with ethyl iodide for a short time. The only effect of the increased temperature seemed to be that the speed of the reaction was much increased. The product again gave the analysis of pure tribromthiophenetol and no other products were detected.

To further test the possibility of forming poly-phenylene sulfides, some of the silver salt was heated to 110°-115° and then hot ethyl iodide was poured upon it. Again the thiophenetol was the only substance produced in detectable amounts.

III. With Methyl Iodide.

A final reaction was carried out with cold methyl iodide upon the dry, silver salt. With this reagent there was produced a very small amount of a reddish oily substance in addition to the methyl-tribromphenyl thioether. The oily product was not analyzed as it apparently amounted to not more than 1 0/0 of the total product. Here again, then, the yield of thioether was practically quantitative and no poly-phenylene sulfide was formed in identifiable amount.

Under all the conditions thus far studied, the products resulting from the treatment of the silver salt with iodine and alkyl iodides failed to give the analogue of the poly-phenylene oxides. In order to throw some light upon the reaction and discover, if possible, some explanation for the difference in the course of the reactions of the oxygen phenylate and the thiophenylate, the products of the reaction of the latter were more fully investigated. The hexabrom-diphenyldisulfide was especially studied.

B. SIGNIFICANT PROPERTIES OF HEXABROM-DIPHENYLDISULFIDE.

The hexabrom-diphenyldisulfide, when dissolved in boiling benzene changes from pale-yellow to a light reddish-brown. Upon cooling and recrystallizing, it again becomes pale-yellow. Considerations as to the manner of formation of the disulfide and the different product formed from the salt of the tribromophenol, suggested that the disulfide was dissociated¹ after the manner of hexaphenylethane.

Accordingly the molecular weight of the disulfide in solution was determined. The cryoscopic method was used with ethylene dibromide as the solvent. Benzene was found unsuitable because of the very limited solubility in this solvent at the freezing temperature. Even ethylene dibromide will dissolve only about .35 gm. in 20 cc. at 10° but this was found sufficient for molecular weight determinations. The following data will indicate the extent of dissociation at three different concentrations.

In a solution .00324 molar, M.W. = 572

In a solution .01806 molar, M.W. = 614

In a solution .0201 molar, M.W. = 626

Calculated from formula, M.W. = 691.7

These figures indicate that for the various concentrations, if

α = o/o of dissociation, for

.00324 molar, α = 20.9 \pm 2.1 o/o

.01806 molar, α = 12.6 o/o

.0201 molar, α = 10.5 o/o

¹ See F. Henrich, Theorien der Organischen Chemie, Vierte Auflage, Chap. XIII.

The figures for .00324 molar solution are subject to the indicated correction of ± 2.1 o/o because the depression obtained at this concentration amounted to only .021°. If we allow for an error of .002° in the thermometer readings, this amounts to about 10 o/o of the total depression. Therefore the value found for α is also in error to the extent of about 10 o/o of the value given, or 2.1 o/o.

If the disulfide is truly dissociated, it should obey the law of mass action:

$$\frac{I^2}{U} = k$$

where I represents the concentration of the ion of either kind and U the concentration of the undissociated molecules. The agreement found was not very close. For the various concentrations, the values found for k were as follows:

.0201 molar, $k = .00025$

.01806 molar, $k = .00033$

.00324 molar, $k = .00023$ ($\alpha = 23$ o/o)

.00324 molar, $k = .00018$ ($\alpha = 20.9$ o/o)

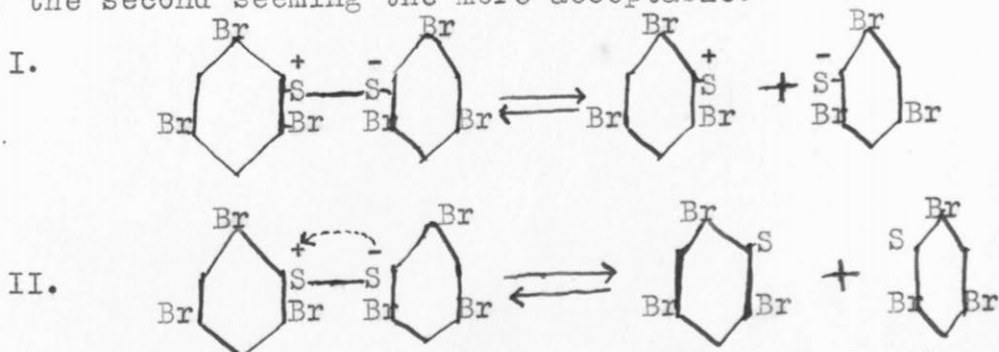
Since the cryoscopic method of determining dissociation is not very accurate and the depressions in freezing point found were small, it is not surprising that the agreement in values of k is not better. The agreement seems sufficiently close to show that there is real dissociation in dilute solutions of the disulfide. Further work upon this point will be done with this and other solvents and also by the ebullioscopic method. To determine whether the phenomenon is due to actual free radicals or is a case of ionization, its conductivity will also have to be determined.

As indicated in the experimental part, the compound appears to be quite stable in the air, even when heated to not over 150°. Of

some significance here also is the fact that it is quite readily reducible by hydrogen to tribromthiophenol.

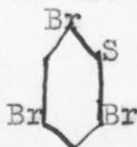
C. DISCUSSION AND CONCLUSIONS.

If, as seems quite certain, the disulfide dissociates, the dissociation may be one of two kinds: there may be ordinary ionization or we may have present "free radicals." In a compound of this structure, ionization seems very unlikely as the ionic condition is characteristic only of those compounds having a part of strongly negative character in combination with one of positive character, or of a strongly positive part with a negative part. In this disulfide, the radicals which may be reasonably supposed to exist are identical in structure and composition. The possible dissociation may therefore be represented by one of the following equations, the second seeming the more acceptable:



This view accounts for the color of the solution, for the abnormal and varying molecular weight found and for the ease of reduction by hydrogen.

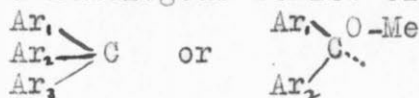
We have in this compound then a sulfur atom existing as a monovalent element and forming the basis for the ability of the group



to exist as a free radical. This is the first

instance of the preparation and detection of such a sulfur radical.

The only other known analogues are a homologous series of carbon compounds of the general formula



and a series of nitrogen compounds of the general type



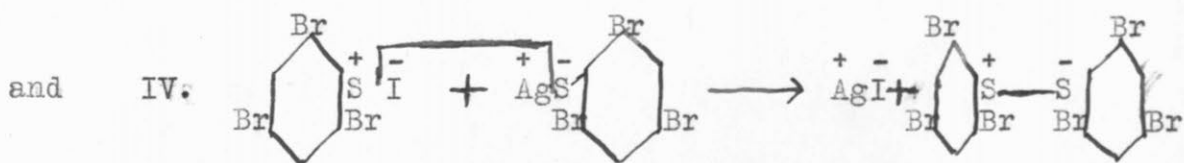
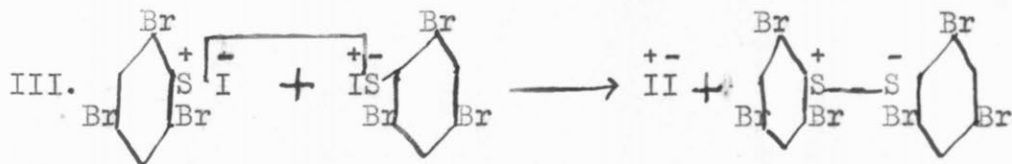
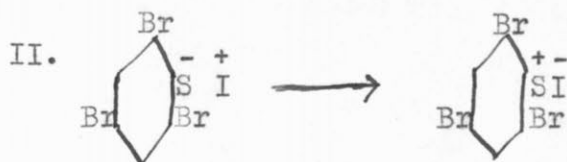
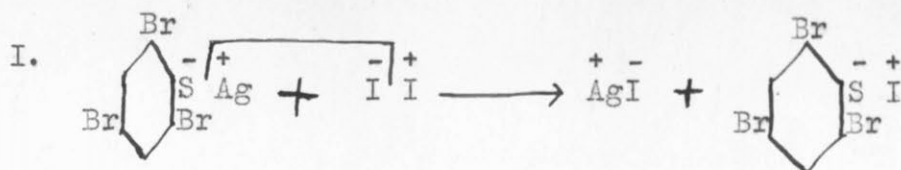
the nitrogen being bivalent and the carbon trivalent. The possibility of the existence of free radicals containing sulfur as the characteristic element was suggested in 1915 by Hans Lecher.¹ He investigated p-dimethylanilino-disulfide,

$(\text{CH}_3)_2\text{NC}_6\text{H}_4\text{S} - \text{SC}_6\text{H}_4\text{N}(\text{CH}_3)_2$, and diphenyldisulfide but failed to obtain any evidence of a dissociation into radicals.

The next question is how is the disulfide formed and to what extent does the mechanism arrived at apply to the oxygen analogues? In answering this question, it is well to recall the following facts: sulfur quite readily forms fairly stable compounds such as S_2Cl_2 , SCL_2 , SCL_4 , S_2Br_2 , SCL_7I , etc. Oxygen, on the other hand, forms them with difficulty and they are readily decomposed. Again, sulfur forms such linkages as R-S-SR₂, for example, cystine, a product of the hydrolysis of certain proteins existing in nature, of the formula $\text{HOOC} \cdot \text{CHNH}_2 \cdot \text{CH}_2 \cdot \text{S} - \text{SCH}_2 \cdot \text{CHNH}_2 \cdot \text{COOH}$. The analogous linking of oxygen atoms to peroxides is much more unstable. In the light of these facts, we may explain the formation of the products obtained from the silver tribromthiophenylate as shown by the following equations:

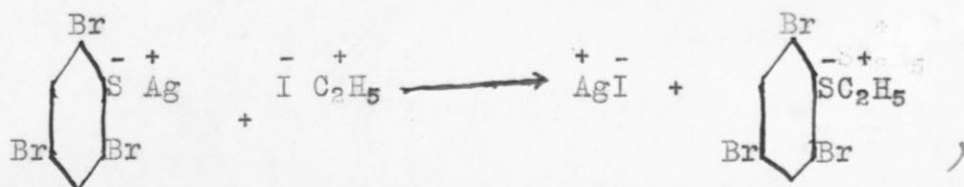
¹Berichte, 48, 524.

See Henrich, Theorien der Organischen Chemie (Vierte Auflage) Ch. XIII.

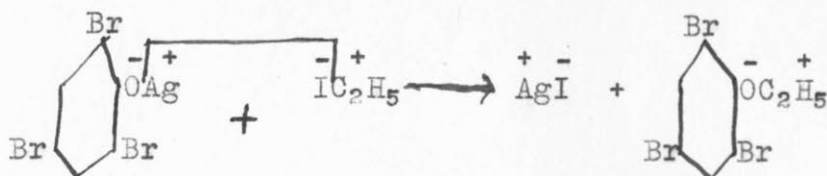


Equation IV is probably preferable to III. Considering equation II, and also further reactions to be discussed in connection with the oxygen compounds, it is well to remember that the following elements may be arranged, in order of decreasing "negative" nature, as follows: $\text{Cl} > \text{Br} > \text{I} > \text{O} > \text{S}$. As a result of the reaction represented by I, the iodine is positively charged while the S is negative. This is therefore an unstable condition and the transfer of electrons represented in II takes place. This transfer of charges seems natural and establishes the conditions necessary for reactions III and IV.

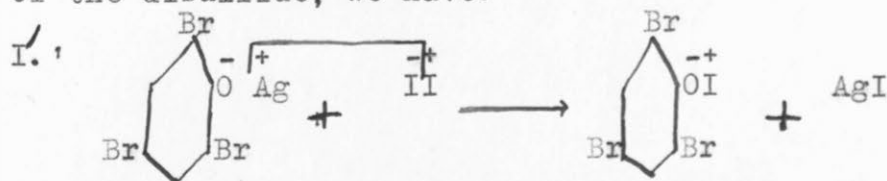
The mechanism for the reaction between ethyl iodide and the silver salt is apparently that of a simple double decomposition:



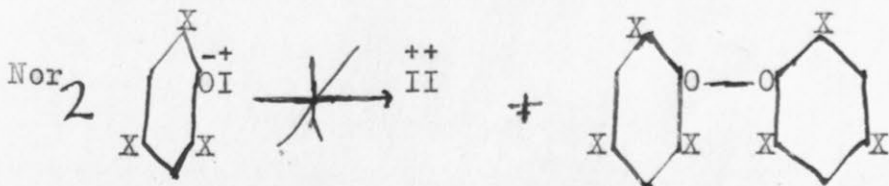
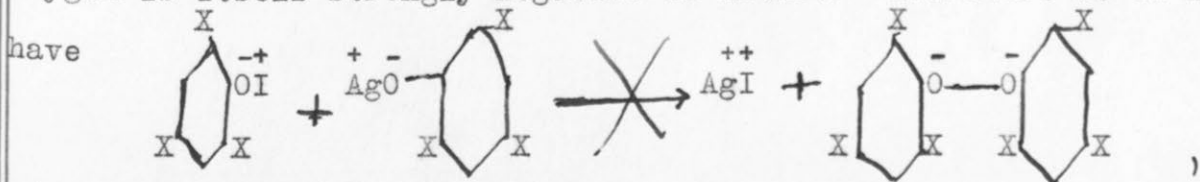
all the atoms and groups retaining their original charges. The reaction of the silver salt of tribromophenol with ethyl iodide, producing the phenetol derivative,¹ is perfectly analogous:



The abnormal reaction of the oxygen compounds, however, producing the poly-dihalogenphenylene oxides, was the real question to be solved and may now be regarded in the light of what has gone before. First of all, it seems impossible that a peroxide forms in the given conditions and, if supposed to be formed, must exist in a completely dissociated state or nearly so. The following considerations will amplify the above statements, Applying the principle of the mechanism postulated in explanation of the formation of the disulfide, we have:



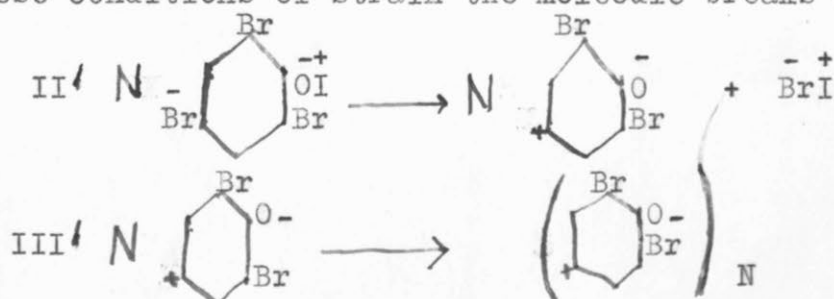
Here, now, we have a compound containing a positive iodine atom held by a negative oxygen. In this case, however, the iodine does not acquire an electron from the oxygen, as it does from the sulfur atom in equation II of the preceding series considered, because oxygen is itself strongly negative in nature. Therefore we do not



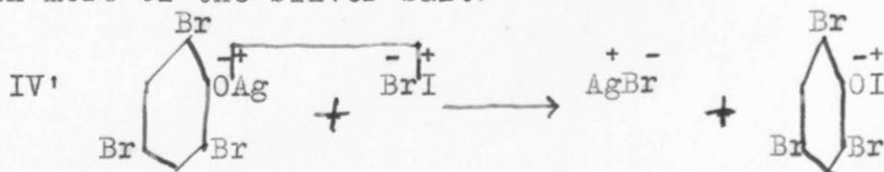
¹ Jour. Am. Chem. Soc. 39, 2644-45; 38, 1768-9.

At least, it is exceedingly unlikely that under the ordinary conditions of these experiments, any appreciable amount of the peroxide should be formed. This is in accordance with the reaction observed with tribromophenol bromide and silver tribromophenolate by Hunter and Woollett.¹ The tribromophenol bromide was unchanged by the silver derivative, only the latter being catalytically decomposed.

The compound which is temporarily formed in the first step of the reaction, then, exists in a state of intramolecular strain, an atom of iodine with a strong tendency to assume the negatively charged state being attached to a negative oxygen. In the ortho and para positions are bromine atoms negatively charged. Under these conditions of strain the molecule breaks down as follows:



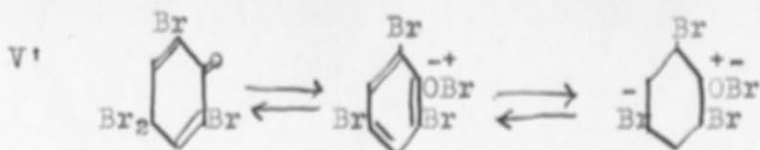
In the compound BrI the bromine atom is the negative one as well as the most reactive in the free state. Therefore it reacts further with more of the silver salt:



and the cycle is repeated, only silver bromide being produced.

It may here be asked, if the reaction indicated in II^{\dagger} can and does take place, how is it possible for tribromophenol bromide to exist? Here we may suppose an equilibrium of the following sort to become established:

¹ Jour. Am. Chem. Soc. 42, 123.



The failure of the tribromophenol bromide to react with silver tribromophenolate mentioned above is a very good indication that the reaction indicated in V' above is ~~not~~ displaced very far to the left, very little negative bromine being in combination with oxygen. Here again the reluctance of oxygen to assume a positive form is manifested, even the distinctly more negative bromine being unable to remove the electron. Although the positive bromine does not appear spontaneously to leave with one of the bromines from the ring, this does happen without the use of reagents when the compound is dissolved in carbon disulfide¹ and placed in sunlight. Work is now being done on this question in this laboratory.

The formation of the polyphenylene oxides from silver salt and ethyl iodide is not so readily explained. To account for the poly-oxides upon the same general theory as was used to explain the reactions forming the disulfide and oxides with free iodine as the catalyst, necessitates the assumption that a phenetol is formed and decomposed as follows:



The molecule is here again in a state of strain due to the heavily halogenated condition of the nucleus and the fact that the positive silver is replaced by the much less positive ethyl radical. At the

¹ Am. Chem. Jour. 27, 21-52.

proper temperature or due to the operation of some disturbing influence, ethyl bromide is eliminated in the same way as two atoms of halogen were supposed to be. The residue then polymerizes in the usual way and the ethyl bromide reacts with the AgI as fast as formed to form AgBr and ethyl iodide. Thus the ethyl iodide is regenerated as fast as used up. This explanation is dependent upon the assumption that, in such a medium as ethyl iodide, the AgBr is as insoluble or more so than AgI, the determining factor being the more negative nature of bromine which enables it to displace the iodine from AgI in the same way as it does from KI for example.

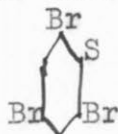
SUMMARY.

The conclusions reached in the course of the work described in this paper may be summarized as follows:

1. The silver salt of tribromthiophenol reacts with alkyl iodides at all temperatures between room temperature and 115° in a perfectly normal manner to form the corresponding alkyl-tribromphenylthioether in practically quantitative amount.
2. The silver salt of the thiophenol reacts with free iodine in benzene to form hexabromdiphenyldisulfide in almost quantitative amount.
3. Under no conditions does the silver salt of tribromthiophenol give any poly-dibromophenylene sulfide corresponding to the oxide obtained from the silver salt of tribromphenol.

4. The products obtained are the result primarily of the ability of the sulfur atom to assume a positive character toward halides.

5. The hexabromdiphenyldisulfide is dissociated in solution into free radicals of the formula



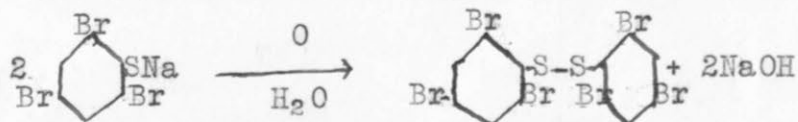
, containing monovalent sulfur. These radicals are the first known instance of the preparation of a sulfur compound which exists in a form analogous to triphenylmethyl, tetraphenylhydrazine and a few others.

6. The salts of tribromphenol fail to give a peroxide analogous to the disulfide for the reasons set forth in the discussion in the body of this paper.

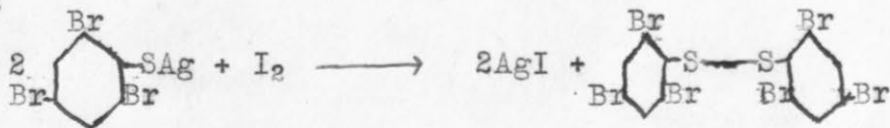
EXPERIMENTAL PART.

A. SILVER TRIBROMTHIOPHENOLATE + 1/10 EQUIVALENT OF I₂ IN BENZENE.

The iodine was dissolved in benzene and then the finely pulverized silver salt was added and the mixture shaken from time to time during the course of several hours. The complete disappearance of the iodine color indicated that the reaction was not a catalytic one but that the iodine was being used up in the formation of some product or other. Upon filtering off the precipitate formed and the unchanged silver salt the filtrate deposited, on partial evaporation and cooling, the usual light yellow crystals of hexabrom-diphenyldisulphide. These crystals were identified by taking their melting point, which checked with that found for the disulfide prepared by the oxidation of the sodium salt of tribromthiophenol in the air as follows:



Both the product formed by the action of iodine on the silver salt and the one formed by the atmospheric oxidation of the sodium salt were analyzed for bromine and sulfur content and found to check well with the theoretical. We may most simply express the reaction as follows:



B. SILVER TRIBROMTHIOPHENOLATE + EQUIVALENT OF IODINE IN DRY BENZENE

Pure, dry silver tribromthiophenolate was pulverized and added to the calculated amount of iodine dissolved in dry benzene. The mixture was shaken up occasionally and gradually lost the color of iodine. In about three days'time the change was considered complete and the benzene was filtered from the precipitate of AgI. After washing the flask and AgI precipitate with warm benzene and combining the filtrates, the latter was evaporated to small volume and the crystals removed and weighed. The yield was found to be 92 o/o of the theoretical amount but since there was some chance for loss in manipulation and the disulfide is somewhat soluble in cold benzene, the small amount of mother liquor was considered to account for most of the missing product. In addition to the disulfide there was separated from the benzene solution remaining after crystallization of the disulfide, a small amount of greenish-red oil which amounted to 2.5 - 3 o/o of the theoretical amount of disulfide. This was analyzed to determine whether or not it was the sulfur analogue of the poly-dibromphenylene oxides which had been described by earlier investigators from this laboratory.

Analysis gave Br = 50.12 o/o; S = 4.77 o/o
Calc: for $(C_6H_2Br_2S)_n = 60.10$ o/o; S = 12.05 o/o

Calculations from the experimental percent of Br and S failed to give any molecular weight which could be made to check with the formula of any possible reaction product which we could reasonably assume. It was therefore decided that this reddish product must be a mixture of substances resulting either from impurities in the benzene or else from some side reaction undergone by one of the

reacting substances. Such very small amounts of it were obtained that it seemed unnecessary as well as impracticable to investigate it further.

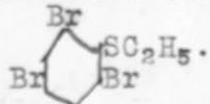
Amount of silver tribromthiophenolate;	7.4764 gm.
Iodine,	2.091 gm.
Theoretical amount of disulfide,	5.6989 gm.
Found,	5.243 gm.
Yield =	92+ o/o

Amount of oily product found, .1375 gm.

Oily product equals 2.4 o/o of theoretical amount of disulfide.

C. SILVER TRIBROMTHIOPHENOLATE + ETHYL IODIDE IN COLD.

Finely pulverized silver tribromthiophenolate was placed in a dry flask and colorless ethyl iodide was added, in amount sufficient to cover the silver salt to a depth of about seven millimeters. After two days the silver salt seemed to be completely transformed, so the ethyl iodide was poured off and filtered and evaporated spontaneously. A viscous light-yellow oil was left. After washing the silver iodide and utensils thoroly to recover all of the oily product, the latter was freed of solvent, dried, weighed and analyzed. The analysis indicated that the product was pure ethyl-tribromphenyl thioether,



Assuming this as the reaction product, the yield was calculated and found to be 100.3 o/o of the theoretical.

Analysis(Carius' method)

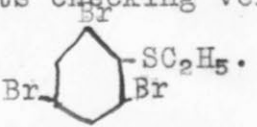
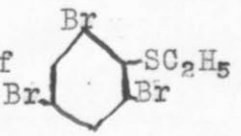
- Weight of silver salt taken = 1.9944 gm.
- Weight of thioether found(dry) = 1.6545 gm.
- Calculated amount of thioether = 1.6489 gm.

Yield = 100.3 o/o

Analysis.

Wt. ethyl-tribromphenyl thioether	.1885 gm.,	.2020 gm.
Wt. AgBr	.2852 gm.,	.3039 gm.
Wt. BaSO ₄	.1219 gm.,	.1330 gm.
o/o Br	64.387 o/o,	64.023 o/o
o/o S	8.88 o/o,	9.04 o/o
Theoretical o/o Br = 63.95; o/o S = 8.55 o/o		

D. SILVER TRIBROMTHIOPHENOLATE + BOILING ETHYL IODIDE.

Finely pulverized silver tribromthiophenolate was placed in a flask connected with a reflux condenser and warmed a few minutes on a steambath. Then ethyl iodide was poured in through the condenser and the mixture refluxed for about fifteen minutes. On filtering off the ethyl iodide and evaporating, there was left a light-yellow oil identical in appearance, consistency, etc. with the product obtained with cold ethyl iodide. Analysis of the product by the method of Carius gave results checking very closely with the theoretical percent of S and Br in . The percentage of yield of  formed in the reaction was not calculated but there seemed to be no evidence of side products.

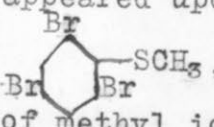
Analysis.

Wt. of product taken for analysis	.2107 gm.
Wt. AgBr	.3181 gm.
Wt. BaSO ₄	.1360 gm.
Found for Br, 64.25 o/o; for S, 8.86 o/o	
Calculated, for Br, 63.95 o/o; for S, 8.55 o/o	

E. SILVER TRIBROMTHIOPHENOLATE AT 110°-115° + hot C₂H₅I.

We desired to investigate further the effect of heat upon the reaction between the silver salt and ethyl iodide. Accordingly about 2 grams of the silver salt was heated to 110° in a test-tube immersed in an oil-bath, ethyl iodide was first heated to boiling and then poured on to the amount of about 2 cc. After allowing sufficient time for the silver salt to again reach the temperature of 110°, about 2 cc. more of ethyl iodide was added. The resulting product was extracted with warm benzene and also with chloroform. The product was again a light-yellow, viscous oil identical in all its properties with the product obtained under C and D. It was thought unnecessary to analyze it to establish its identity. There were no detectable side products.

F: SILVER TRIBROMTHIOPHENOLATE + COLD METHYL IODIDE. PROPERTIES OF METHYL-TRIBROMPHENYL THIOETHER AND AN ISOMERIC(?) SUBSTANCE.

It seemed unlikely that methyl iodide would react upon the silver salt in any way different from the ethyl iodide but a product formed during the course of the preparation of the free tribromthiophenol and isolated from the xanthogenic ester of the latter, appeared upon analysis to be the methyl-tribromphenyl thioether, , and, accordingly, it was decided to try the reaction of methyl iodide upon the silver tribromthiophenolate in the expectation that the ether would be formed, as in the reaction with ethyl iodide. This would give a convenient way of identifying the substance formed in the same reaction with the xanthogenic ester.

Cold, redistilled and dried methyl iodide was accordingly poured upon finely pulverized silver salt and allowed to stand two or three days. Upon filtering off the methyl iodide and washing the silver iodide with benzene, the filtrates, upon evaporation, deposited long colorless needles, together with a very small smear of reddish oil which was not investigated. Upon analysis the product gave the following results:

Wt. of product analyzed .1995 gm.

Wt. of Ag Br .3122 gm.

Wt. of BaSO₄ .1324 gm.

Found, for Br, 66.59 o/o; for S, 9.115 o/o

Calculated, for Br 66.43 o/o; for S, 8.88 o/o

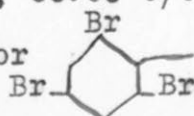
Analysis of supposed iso-methyl tribromthio-phenolate.

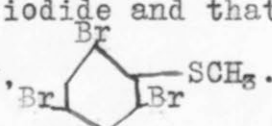
Wt. of substance analyzed, .2089 gm., .1938 gm.

Wt. of Ag Br, .3286 gm., .3044 gm.

Wt. of BaSO₄, .1434 gm., .1317 gm.

Found for Br, 66.65 o/o, 66.84 o/o; for S, 9.38 o/o, 9.33 o/o

Calculated for SCH₃, Br 66.43 o/o; for S, 8.88 o/o

It therefore seemed evident that the reaction was again the same as that found for ethyl iodide and that the substance must be methyl-tribromphenyl thioether, .

Judging from analyses therefore, the two appear to be the same. However, after careful purification, the melting point of the methyl-tribromphenyl thioether prepared from the silver salt was found to be 59.6° - 60.5°, 59.7° - 60.4°. The melting point of the other, which we may name iso-methyl tribromthiophenylate,

was found to be 194.2° - 194.7° . The solubilities of the two also, while much the same in various solvents, showed unmistakable differences.

Properties

Methyl-tribromphenyl thioether Isomeric (?) substance

Solubility

in CS_2 , very soluble	Very soluble
$(\text{CH}_3)_2\text{CO}$, very soluble	Very soluble
CHCl_3 , very soluble	Very soluble
warm ligroin	Fairly soluble
$(\text{C}_2\text{H}_5)_2\text{O}$, slightly soluble	Fairly soluble
CH_3COOH , fairly soluble	Slightly soluble
$\text{C}_2\text{H}_5\text{OH}$, slightly soluble	Less soluble

Crystalline form.

Long, fairly broad, flat	Long, very thin, silky
needles, colorless, glistening	needles, colorless

Melting-point.

59.6° - 60.5° ; 59.7° - 60.4°	194.5° - 195.5° ; 194.2° - 194.7°
---	--

Further work is being done to establish the exact composition and constitution of this second substance which appeared in an apparently inexplicable manner in the xanthogenic ester preparations. It is suspected that it arises from probable methyl alcohol in the ethyl alcohol used to prepare the potassium xanthogenate.

The solvent used was ethylene dibromide ($K = 118$)

Freezing point of pure solvent 3.470° ; 3.470° ; 3.470°

Amount of solvent, 1st determination = 43.091 gm.

Amount of disulfide, 1st determination = .0439 gm.

= .00324 molar

Freezing point 3.449° ; 3.449° ; 3.450° ; 3.448° ; 3.448°

$\Delta = .021^{\circ} \pm .002^{\circ}$

Calculated molecular wt. = 572

Theoretical M.W. from formula = 692

α (dissociation) = 20.9 o/o \pm 2.2 o/o

Second Concentration

Total amount of disulfide added = .0439 + .2285 gm

= .2724 gm.

= .0201 molar.

Freezing point 3.352° ; 3.351° ; 3.351° ; 3.351°

$\Delta = .119^{\circ}$

Calculated molecular wt. = 626

$\alpha = 10.5$ o/o

Third Concentration

Total amount of solvent = 47.962 gm.

Amount of disulfide = .2724 gm.

= .01806 molar.

Freezing point 3.359° ; 3.361° ; 3.361° ; 3.361°

$\Delta = .109^{\circ}$

Calculated molecular wt. = 614

$\alpha = 12.6$ o/o

By the law of mass action $\frac{(i)^2}{(u)} = k.$

where i = concentration of ions and u = conc. of unionized part.

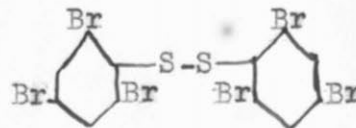
For solution .0201 molar, $k = .00025$

.01806 " , $k = .00023$

.00324 " , $k = .00018$ ($\alpha = 20.9$ o/o)

.00324 " , $k = .00023$ ($\alpha = 23.1$ o/o)

H. PROPERTIES OF THE HEXABROMDIPHENYLDISULFIDE



This substance crystallizes from benzene in rhombic prisms. During crystallization, marked surface-tension and concentration effects appear which cause the crystals to group themselves into closely packed clusters so that they rarely develop with any large part of the crystal in perfect form. They are fairly short and thick and all samples prepared showed a very pale-yellow color.

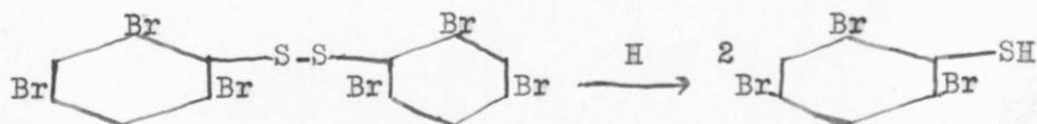
The substance is quite readily soluble in hot benzene dissolving to the amount of about 25 parts in 100 of the hot solvent and about 1.85 parts in 100 at 16°. It is much more soluble in hot and cold ethylene dibromide and in hot or cold bromoform. The latter dissolves about 13 grams of the substance in 100 cc. at 17°. Chloroform dissolves it in smaller amounts but carbon disulfide dissolves it quite readily and in fairly large amounts. Ethyl alcohol dissolves very small amounts while ether dissolves it only slightly. It appears to be almost entirely insoluble in acetone, warm or cold.

The odor is not very strong, It bears some resemblance to that of acetone but is more mildly disagreeable.

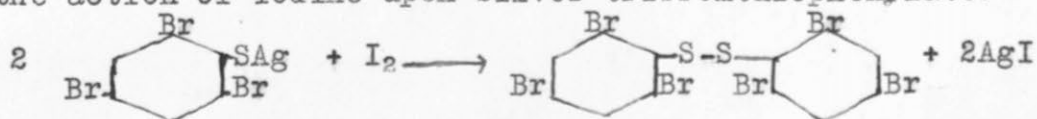
The melting-point of samples purified by crystallizing from benzene several times was found to be 219.2° - 219.8° . In order to obtain a sharp melting-point, the heating bath must be warmed to about 205° before inserting the sample as the prolonged heating from room temperature to the melting-point seems to cause some decomposition. On the other hand, analyses by the Carius method failed to give accurate or concordant results unless the tubes were heated to 290° - 315° for about three hours.

As shown by the data under G and as discussed in the theoretical part, the compound appears to be dissociated.

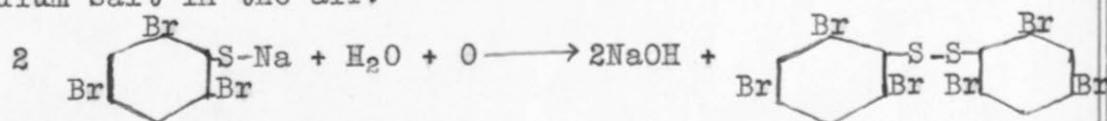
In benzene containing a small amount of alcohol, it can be reduced by the hydrogen generated from the action of metallic sodium to tribromthiophenol:



As discussed under part B of the experimental part, the hexabromdiphenyldisulfide is readily formed in almost quantitative yield by the action of iodine upon silver tribromthiophenylate:



It is also formed in a very pure state by the oxidation of the sodium salt in the air:



Likewise the uncrystallized thiophenol itself is slowly oxidized in the air to the disulfide and water. The sodium salt also, when acidified with HNO_3 , gives a quite large amount of disulfide in addition to the free tribromthiophenol.

Analyses are given under B of the experimental part of this thesis; so they will not be repeated here.

I. PROPERTIES OF ETHYL TRIBROMTHIOPHENETOL (ETHYL-TRIBROMPHENYL THIOETHER).

The preparation and analysis of this compound is given under C of the experimental section. It is a quite viscous oil of a pale reddish-yellow color. All efforts to crystallize it failed. No attempt was made to obtain its specific gravity accurately but it was found to be about 2.1. It possessed but little odor, which was somewhat ethereal but was more characteristic of the thiophenols. It showed no evidence of decomposition after weeks of standing and could be heated to about 100° without evidence of any breaking down.

The compound is very readily soluble in chloroform, benzene, ether, ethyl iodide; it is quite soluble in acetone and but slightly soluble in absolute alcohol.

J. PREPARATION AND PROPERTIES OF THE TRIBROMPHENYL ESTER OF ETHYL XANTHOGENIC ACID (TRIBROMPHENYL ETHYLXANTHOGENATE).

This preparation was merely a step in the preparation of the tribromthiophenol. The method is due to Leuckardt¹ and the starting material is tribromaniline.

This method of preparation involves a diazotization and it was this step which presented the chief difficulty. The hydrochloride and acid sulfate of tribromaniline are either extremely insoluble in water or are hydrolyzed upon dilution; at any rate, I found it impossible to dissolve them in water. The tribrom-aniline is freely and readily soluble in 95 o/o sulfuric acid but precipitates out as soon as the solution is diluted to

¹ Jour. für Praktische Chemie, Neue Folge 41, 179-224

about 75 o/o. Diazotization in alcohol was tried but the reaction failed to give an appreciable yield and the method was abandoned because of the limited solubility of tribromaniline in alcohol at low temperatures. The following procedure was finally worked out and gave very gratifying yields and was found to be very satisfactory also from the standpoint of convenience and directness.

Thirty-eight grams of pure tribromaniline was dissolved in about 75 cc. of 95 o/o sulfuric acid, stirring and shaking to hasten the solution. When all had completely dissolved, giving a light gray-green solution, the mixture was poured in a thin stream with stirring into about 800 cc. of ice-cold water. This throws down the tribromaniline in a very finely-divided condition. The mixture was then neutralized with sodium hydroxide but overheating was avoided. The whole was then filtered by suction and washed once with water on the filter. Now the tribromaniline was transferred to a three-liter beaker and 200 cc. of conc. HCl added and left stand about twenty minutes. This was to insure the formation of the hydrochloride before dilution.

At the end of this time about 1400 cc. of cold water was added and enough cracked ice to bring the volume up to about 2400 cc. This would cool the mixture usually to -5° C. or lower and during the entire process of diazotization and subsequent esterification the temperature was kept below 5° C.

A mechanical stirrer was now placed in the mixture so that the impeller was below and clear of the floating ice and while maintaining thoro and continuous stirring about 15 cc. of a solution of 9.46 grams of sodium nitrite in 100 cc. of cold water were added. After about 15 minutes, another 15 cc. portion was

added and the remainder in equal amounts at about half-hour intervals. Thoro stirring was maintained during all this time and after about two hours the solution gradually grew clearer. About four or five hours from the beginning of the diazotization, not more than two or three o/o of the original material remained undissolved. Stirring was now discontinued and about 10 cc. of a 20 o/o solution of urea was added to destroy the excess HNO_2 .

Before esterification the large excess of HCl present must be destroyed. This was accomplished by adding, as rapidly at first as practicable, a thin paste of sodium bicarbonate and water. Sodium carbonate is entirely unsuitable. When the slow evolution of CO_2 indicated that the solution was nearly neutral, a solution of the bicarbonate was used and the addition discontinued when the mixture was still slightly acid.

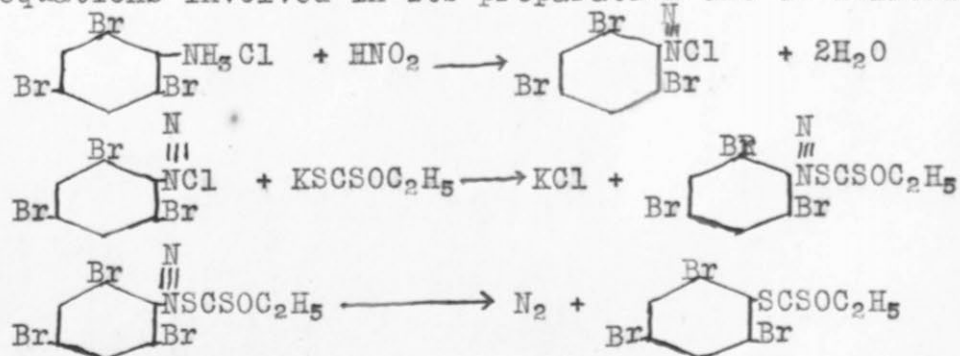
Now the mixture was filtered by suction thru a Buechner funnel containing a few pieces of ice; a little ice was also placed in the filter flask itself. This filtration was necessary to remove any unchanged tribromaniline and any precipitate thrown down during the neutralization.

At this stage, the solution had become diluted to about 2600 cc. and before esterifying it was found best to transfer to a fairly broad vessel. This obviated the danger from the ester clotting in large explosive lumps during the subsequent liberation of N_2 . A solution of 19 grams of potassium xanthogenate in about 75 cc. of water was then poured in with thoro mixing. This caused the separation of a very finely-divided, bright yellow oil which changed to an orange color in about ten minutes and then began to

become a reddish-brown as N_2 began to be evolved. The mixture was set aside and allowed to slowly warm to room temperature. Subsequent heating on a steam-bath at 70° for 1 1/2 hours completed the liberation of the N_2 and the xanthogenic ester settled to the bottom as a deep reddish-brown oil.

Upon cooling, the water was shaken with ether if any of the oily substance remained suspended in the form of droplets. The usual extraction was unnecessary as the ester is quite insoluble in water. The vessel was then washed out with ether in which the ester is exceedingly soluble. Solution of the ester in ether caused the separation of a white, macrocrystalline substance which constituted very nearly 10 o/o of the total product. This substance is described in detail under F in connection with the methyl tribromthiophenetol. The ether solution of the ester was shaken thoroly with 5 o/o NaOH solution to remove any possibly formed phenols, then with dilute H_2SO_4 and then washed with water. Upon allowing the ether solution to evaporate, and drying the residue in a vacuum desiccator, the tribromphenyl ester of ethyl xanthogenic acid was left as a clear red-brown oil.

The equations involved in its preparation are as follows:



Theoretical yield = 50.09 grams.

Actual yield = 40.6 grams

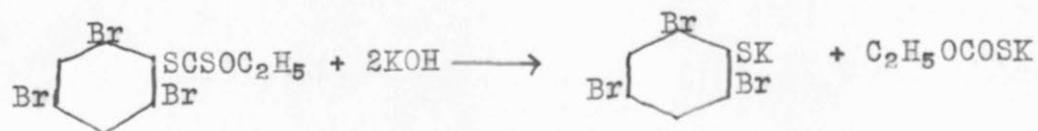
= 81 + o/o

A rough analysis was made by the Carius method.

Calculated for Br, 55.12 o/o; for S, 14.74 o/o

Found for Br 53.3; for S, 17.5 o/o; 17.8 o/o.

This compound is a heavy, viscous, red-brown oil of a not unpleasant odor. It is apparently miscible with ether in all proportions but is difficultly soluble in cold alcohol, dissolving to the extent of about 1 part in 100 in the latter. It is somewhat more soluble in hot alcohol. It dissolves more readily in methyl alcohol and very easily in benzene. In water it is insoluble. When boiled with alcoholic KOH it is hydrolyzed as follows:



K. PREPARATION AND PROPERTIES OF TRIBROMTHIOPHENOL

As indicated above, the potassium salt of tribromthiophenol results upon hydrolysis of the tribromphenyl ethylxanthogenate by boiling with alcoholic KOH.

The xanthogenate was nearly dissolved in boiling methyl alcohol in a flask and reflux condenser. About 4-8 o/o excess of alcoholic KOH was then added and the whole refluxed for about 1/2 hour. A small sample of about .5 cc. was removed from time to time and added to water. When the hydrolysis is complete, little or no precipitate is formed. Too long boiling with excess caustic must be avoided as it seems to cause decomposition, probably causing reaction with the bromine in the ring. When the test indicated approximately complete hydrolysis, most of the alcohol was distilled off and a solution of NaOH, about 3 o/o, was poured

into the mixture. This causes the separation of any unchanged xanthogenic ester and of possible side products. After thoro stirring and the addition of bone-black, the mixture was filtered. The sodium and potassium salts of tribromthiophenol appeared in the filtrate, which was colored a reddish brown. Upon acidifying the solution with 15 o/o acetic acid, the free tribromthiophenol was precipitated as a very finely-divided, pale-yellow to pure white amorphous substance. When the presence of color indicated the presence of impurities, the thiophenol was redissolved in dilute NaOH, shaken thoroly with bone-black, refiltered and again precipitated with acetic acid. During filtration and washing of the precipitate, it was kept in an atmosphere of CO₂. It was then dried in a vacuum desiccator which had been previously filled with CO₂ and which was again evacuated after the thiophenol had been placed therein. When thoroly dry, the thiophenol was dissolved in the minimum amount of boiling alcohol, the solution being kept under CO₂ all the while. The flask was stoppered and kept full of CO₂ while cooling and crystallization was taking place and an atmosphere of CO₂ was kept over the crystals while being filtered off and dried. Drying in CO₂ in a vacuum desiccator completed the purification. When crystallized and thoroly dry, the substance shows little tendency to be oxidized.

40.6 grams of xanthogenic ester hydrolyzed

1500 cc. methyl alcohol as solvent

12.56 gm. KOH in alcohol

Calculated yield (theoretical) = 32.38 gm.

Actual yield = 25.97 gm.

o/o yield = 80.2 o/o

The tribromthiophenol crystallizes from alcohol in rather long, glittering, very nearly colorless needles, slightly yellow. It has the characteristic thiophenol odor but is not nearly so odorous or disagreeable as most of its analogues.

It dissolves in the following solvents, arranged in order of decreasing solubility: carbon disulfide, chloroform, ether, benzene, acetone, glacial acetic acid, (there is probably combination in hot glacial acetic acid, forming the acetyl derivative) methyl alcohol, ethyl alcohol. The ethyl alcohol dissolves about 1 part in 100. It dissolves also with great readiness in aqueous sodium or potassium hydroxide, forming the salts.

Because of its tendency to oxidize to the disulfide, it is necessary to use great pains in its purification for the purpose of obtaining a sample which will melt sharply. I found the melting point to be 115.5° - 115.9° .

Analysis (Carius method 275°)

Weight of sample = .1509 gm.

Wt. of AgBr = .2452 gm.

Wt. of BaSO₄ = .1096 gm.

Calculated for Br, 69.12 o/o; for S, 9.24 o/o

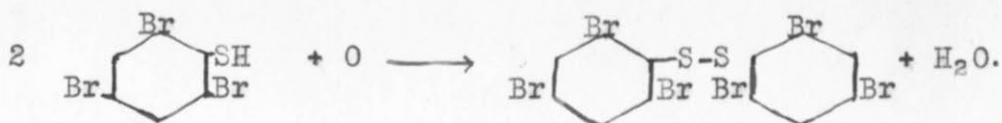
Found, Br, 69.15 o/o; for S, 9.97 o/o

Found for other samples, S, 9.80 o/o, 9.85 o/o.

It was found necessary to use temperatures of 275° - 300° in heating the tubes in order to secure concordant results.

Reactions.

The thiophenol slowly oxidizes in the air, forming the disulfide:



As stated above, it readily forms the sodium salt.

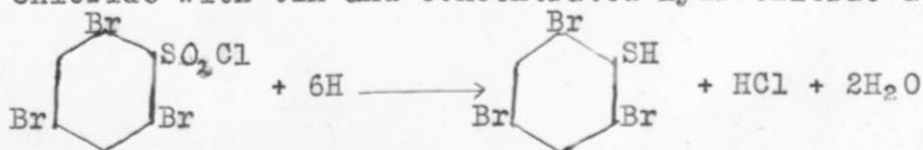


The acetyl derivative is readily formed by boiling in acetic anhydride for about twenty minutes then pouring the solution into a solution of sodium hydroxide which dissolves any unchanged thiophenol. On filtering off the precipitate of the acetyl compound and crystallizing from hot alcohol it is obtained quite pure. It may be further purified by boiling in a minimum amount of alcohol, filtering off the undissolved residue while hot and cooling, whereupon pure crystals are formed with a sharp melting point. M. P. 102.1° - 102.7°.

The substance is quite readily soluble in hot alcohol, glacial acetic acid, benzene. It crystallizes in long, glittering, colorless needles.

Alternative Method of Preparation of Thiophenol.

As stated in the beginning of the theoretical part, the thiophenol was also successfully prepared by the reduction of the sulfonyl chloride with tin and concentrated hydrochloric acid:



The process, however, was long and slow and yields were poor; so it was abandoned.

L. PREPARATION AND PROPERTIES OF THE SILVER SALT OF TRIBROM-
THIOPHENOL.

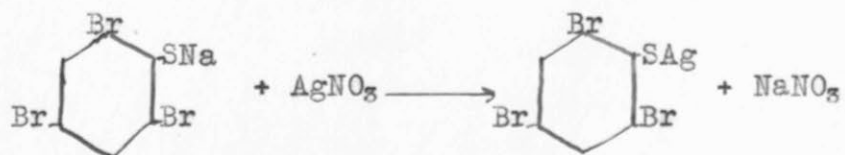
The silver salt was prepared from the thiophenol through the sodium salt as an intermediate step.

Free tribromthiophenol, carefully purified by crystallization from alcohol in an atmosphere of CO_2 , was dissolved in excess of 10 o/o NaOH (halogen-free). Acetic acid, 20 o/o, was then added until near the neutral point when 4 o/o acid was used. When nearly neutral, the mixture was stirred up with animal charcoal and filtered. This is necessary as the addition of acid causes the precipitation of free thiophenol which does not entirely redissolve in the excess alkali, apparently forming the disulfide instead; the solution thus becomes badly clouded and makes it very difficult to detect the neutral point. When the neutral point, indicated by the permanence of the precipitate, was reached, about 3 drops of 3 o/o AgNO_3 was added to throw down any halogen present. The whole was then thoroly shaken up with bone-black, filtered and a slight excess of AgNO_3 was added. This causes the precipitation of gelatinous silver tribromthiophenylate. From this point, it was found best to work in a dark-room as the silver salt appears to be sensitive to light.

The precipitate was then washed repeatedly by stirring up in water, heated to not over 60° , and filtering through a pleated filter paper on a Witt filter-plate, from which the silver salt was again washed by means of a stream of water from a wash-bottle and thoroly stirred. This was continued until the filtrate gave only a very slight opalescence upon addition of HCl, thus indicating that the AgNO_3 had been quite completely removed.

The precipitate was then allowed to drain as completely as possible on the filter and then spread out upon the paper to dry in the air in a dark-room for about 30 hours. It was then placed in a vacuum desiccator containing CaCl_2 and left for about a week.

At the end of this time, the substance had dried into light-gray, very hard and brittle lumps which, when crushed in a mortar, reminded one strongly of broken lumps of soft brick. When first thrown down, the silver salt is nearly white and very gelatinous. Heating to $75 - 85^\circ$ in water causes it to darken, apparently as the result of some decomposition. No melting-point was taken as heat causes decomposition. It is insoluble in ordinary solvents. It was not analyzed but the analyses and yields of the products formed in parts B, C, D and F indicated that it was pure and formed according to the equation:



Its reactions with iodine, $\text{C}_2\text{H}_5\text{I}$ and CH_3I are described under B, C, D, E, and F.

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